

Electronic Supplementary Material

Structure-properties relationships in a series of diglycerol tetraether model lipids and their lyotropic assemblies: Effect of branching topology and chirality

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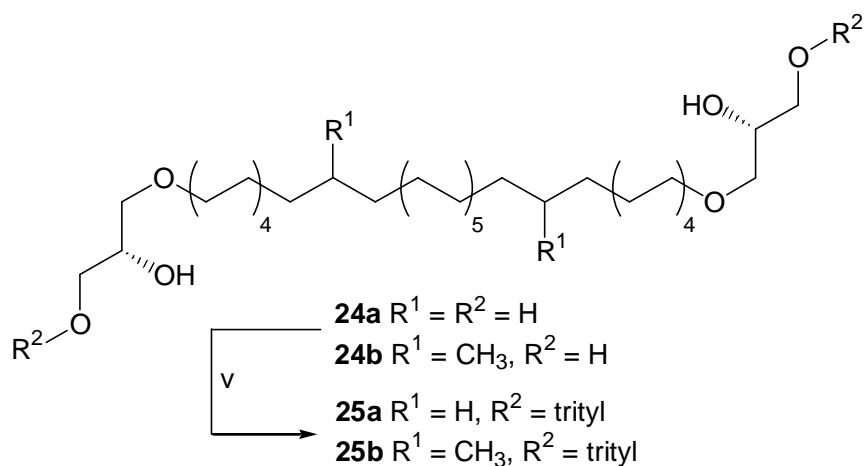
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1. Multiple tritylation reaction on 3,3'-O,O-(alkane-1,32-diyl)bis(*sn*-glycerol)s (24)

Reaction scheme:



Reaction of **24a**:

main product with 2 trityl moieties (compound **25a**): $C_{76}H_{106}O_6$ MW = 1,115.65 g mol⁻¹

side-product with 3 trityl moieties:
 $C_{95}H_{120}O_6$ MW = 1,357.96 g mol⁻¹
 $C_{95}H_{119}O_6Na$ MW = 1,379.94 g mol⁻¹

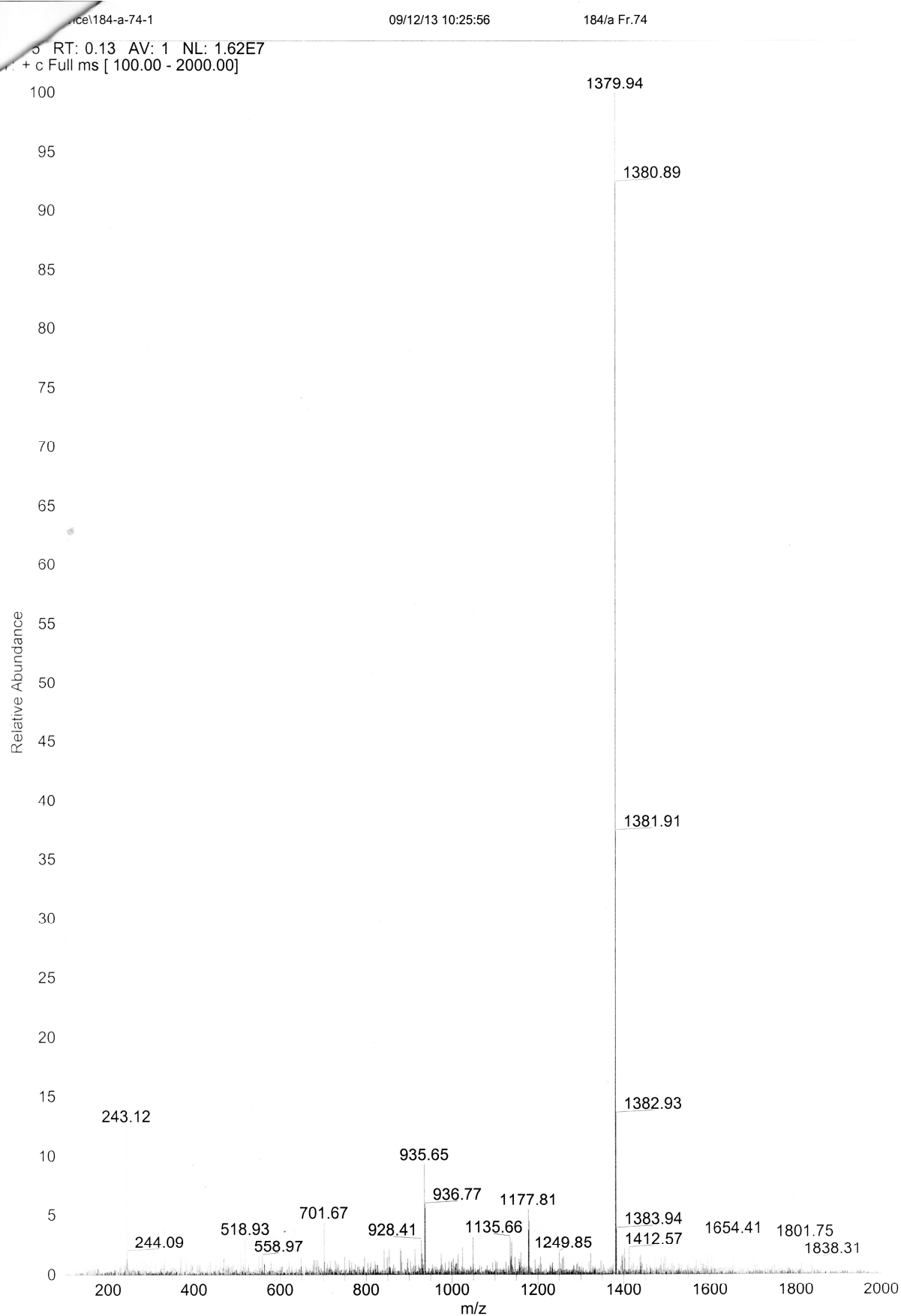
side product with 4 trityl moieties:
 $C_{114}H_{134}O_6$ MW = 1,600.27 g mol⁻¹
 $C_{114}H_{134}O_6Na$ MW = 1,623.26 g mol⁻¹

Reaction of **24b**:

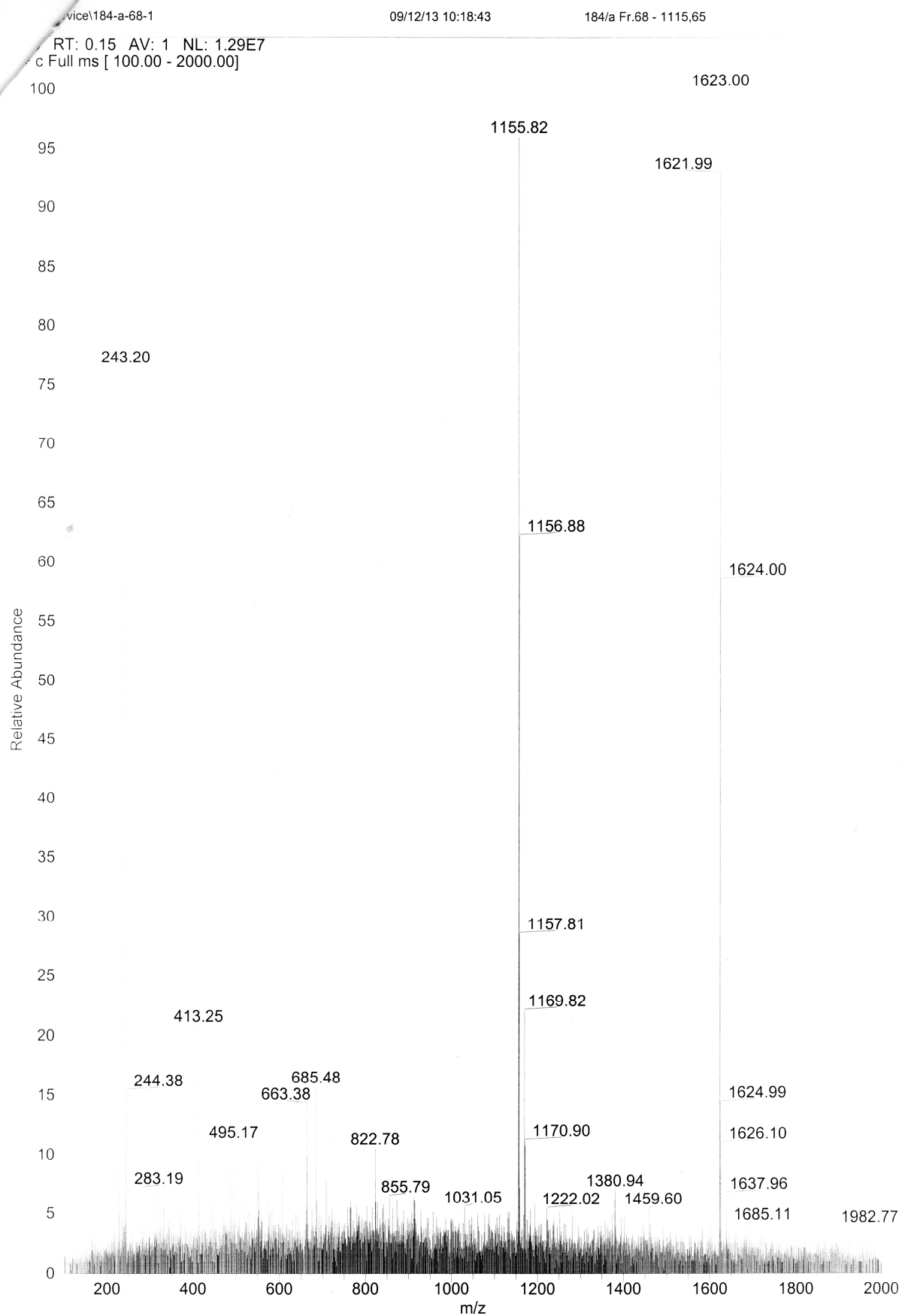
main product with 2 trityl moieties (compound **25b**): $C_{78}H_{110}O_6$ MW = 1,143.70 g mol⁻¹

side-product with 3 trityl moieties:
 $C_{97}H_{124}O_6$ MW = 1,386.01 g mol⁻¹
 $C_{97}H_{123}O_6Na$ MW = 1,408.00 g mol⁻¹

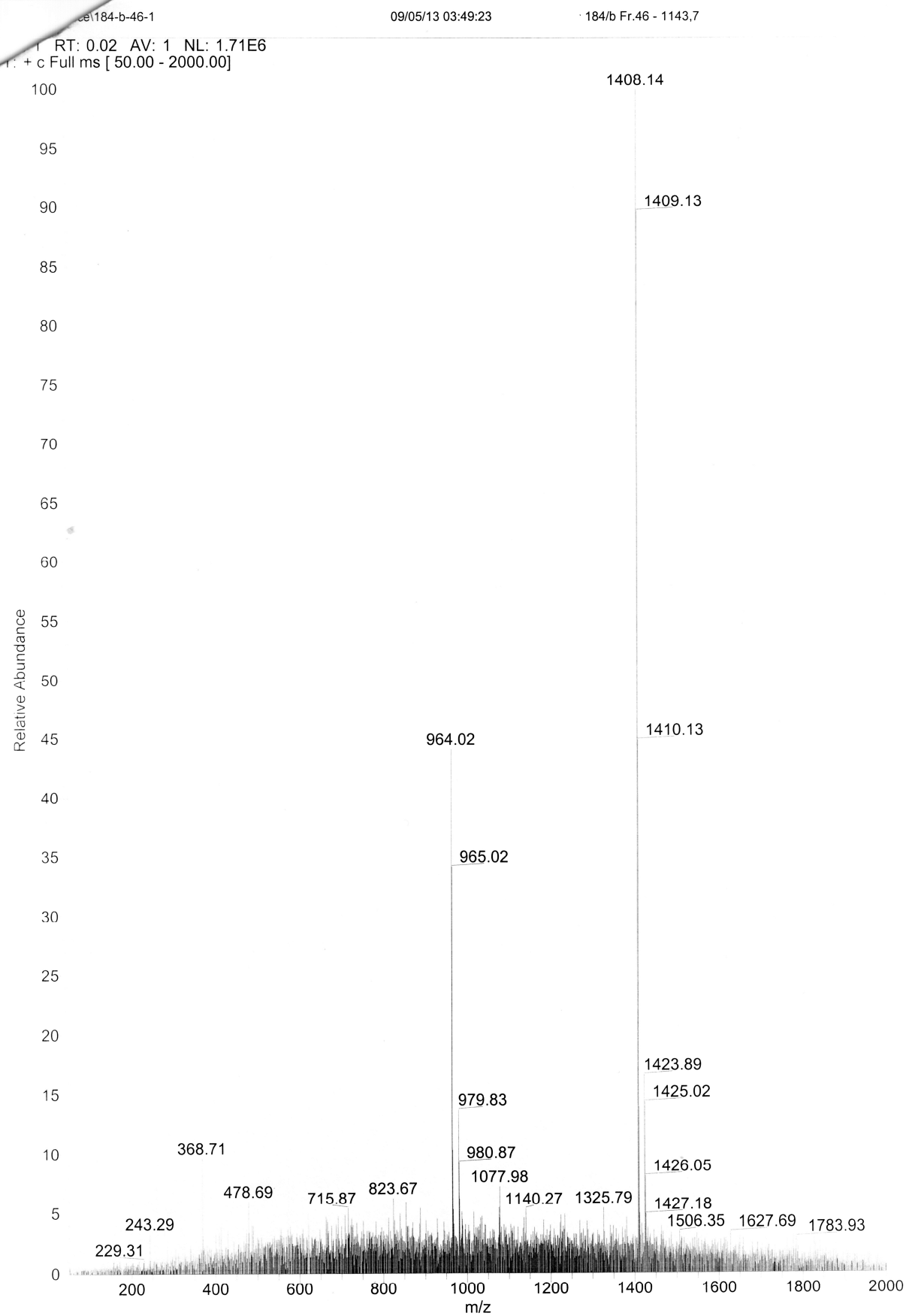
ESI-MS, positive mode side-product of **25a** with 3 trityl moieties



ESI-MS, positive mode side-product of **25a** with 4 trityl moieties



ESI-MS, positive mode side-product of 25b with 3 trityl moieties



2. DLS measurements

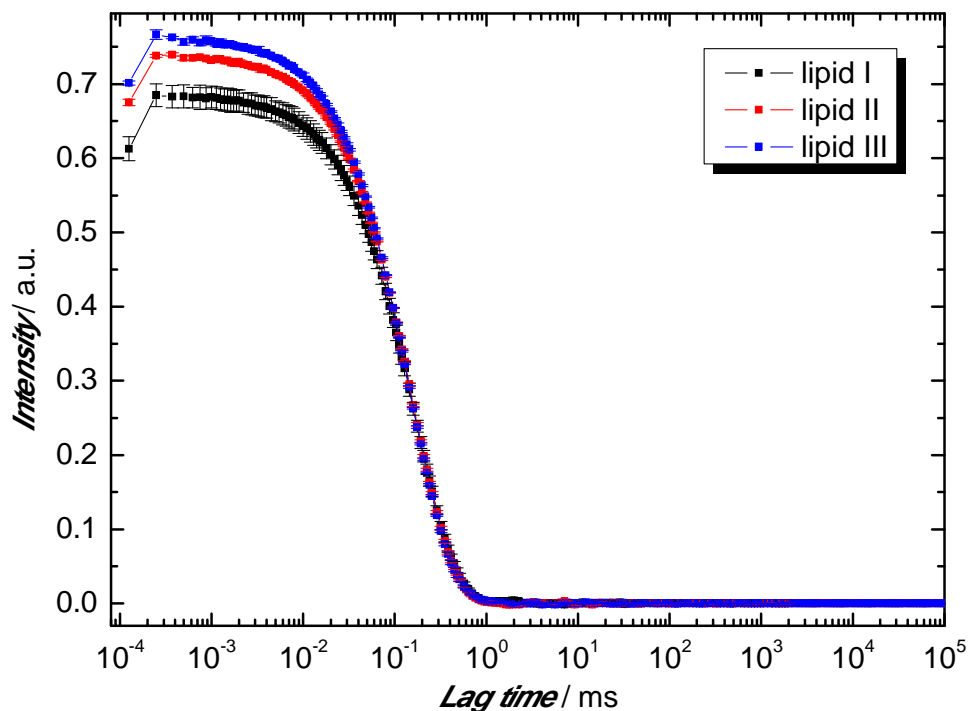


Figure S1: Intensity correlation function of liposomes prepared from aqueous lipid suspensions ($c = 1 \text{ mg mL}^{-1}$) using the technique described by Bangham et al.¹ ($n = 3$). DLS measurements were performed directly after preparation.

Correlation data were fitted using ALV-Regularized Fit (model: *DLS-Exponential* ($g_2(t)$), lag time = 1 – 512 μs , min decay time = 0.001 ms, max decay time = 1000 ms)

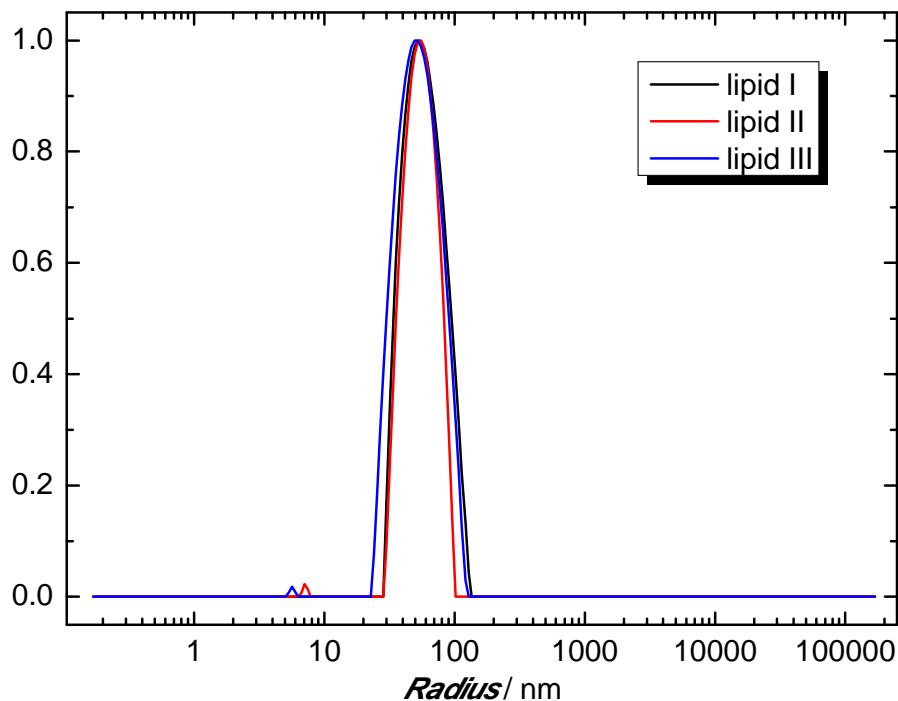


Figure S2: Unweighted (logarithmic) size distribution of liposomes prepared from aqueous lipid suspensions ($c = 1 \text{ mg mL}^{-1}$) using the technique described by Bangham et al.¹ ($n = 3$).

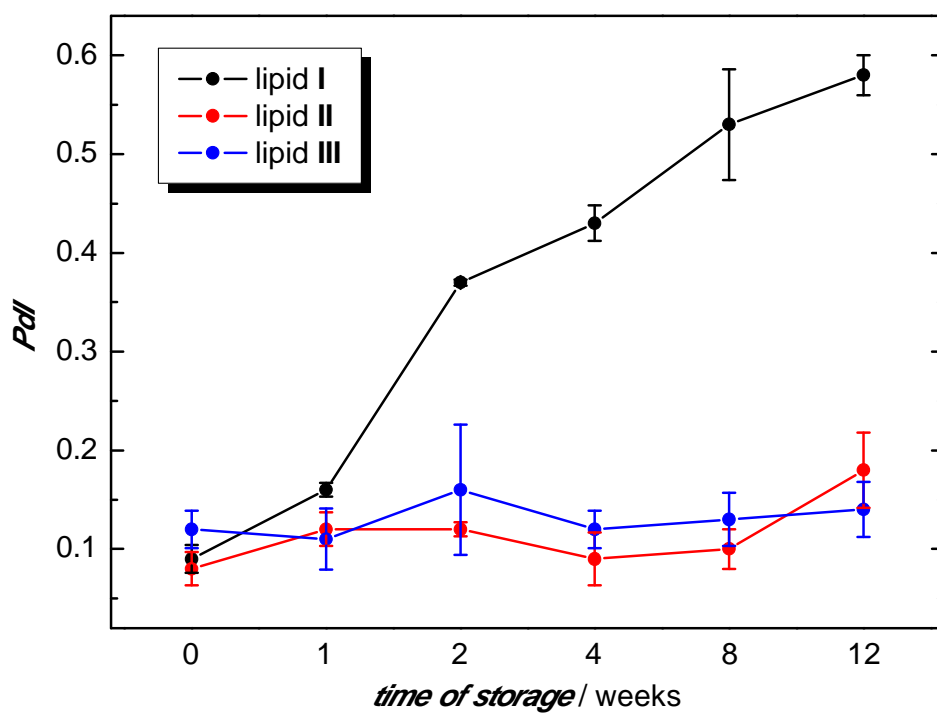


Figure S3: PdI values of liposomes prepared from aqueous lipid suspensions ($c = 1 \text{ mg mL}^{-1}$) using the technique described by Bangham et al.¹ after different time of storage ($n = 3$).

3. Syntheses of compounds

Synthesis of methyl-branched bromoalkanes – the malonic ester pathway

Hexyl(methyl)malonic acid diethyl ester (2a). To a suspension of NaH (60%, 12.0 g, 0.3 mol) in dry toluene (300 mL) was added a solution of methyl malonic acid diethyl ester (**1**; 52.3 g, 0.3 mol) in dry toluene (50 mL). After the salt formation was complete 1-bromohexane (57.8 g, 0.35 mol) was added and the mixture was stirred under reflux for 8 h. After common work up the crude hexyl(methyl)malonic acid diethyl ester (**2a**) was purified by vacuum distillation yielding a colourless liquid (64.3 g, 83%). K.p. (0.5 kPa) 93–95 °C; C₁₄H₂₆O₄ requires C, 65.08; H, 10.15; found: C, 65.03; H, 10.23%; ¹H NMR (400 MHz; CDCl₃) δ 0.85 (t, *J* = 6.9 Hz, 3 H, (CH₂)₅CH₃), 1.15–1.35 (m, 14 H, CH₂, OCH₂CH₃), 1.40 (s, 3 H, CCH₃), 1.80–1.85 (m, 2 H, H₃C(CH₂)₄CH₂), 4.15–4.21 (m, 4 H, OCH₂CH₃); EI-MS *m/z* 213 (18%, M – OC₂H₅), 185 (20, M – COOC₂H₅), 174 (100, M – C₆H₁₂). The data are in agreement with published values.²

Hexyl(methyl)malonic acid (3a). Compound **2a** (46.6 g, 0.2 mol) and potassium hydroxide (33.0 g, 0.6 mol) were dissolved in water (145 mL) and EtOH (300 mL), and were heated under reflux for 6 h. The alcoholic portion was removed mainly in vacuum. The residue was mixed with water (150 mL), extracted two times with Et₂O (50 mL) and acidified with ice-cold aqueous HCl to a final pH value of 2. The precipitate was collected and recrystallised from heptane yielding a white solid substance (32.4 g, 80%). M.p. 133–134 °C; C₁₀H₁₈O₄ requires C, 59.38; H, 8.97; found: C, 59.61; H, 8.73%; ¹H NMR (400 MHz; CDCl₃) δ 0.88 (t, *J* = 6.9 Hz, 3 H, CH₂CH₃), 1.10–1.50 (m, 8 H, CH₂) 1.54 (s, 3 H, CCH₃), 1.87–1.94 (m, 2 H, H₃C(CH₂)₄CH₂). The data are in agreement with published values.³

(2RS)-2-Methyloctanoic acid (4a). The hexyl(methyl)malonic acid (**3a**; 30.3 g, 0.15 mol) was heated up to 180 °C within 2 h. When the CO₂ evolution was finished the crude acid was distilled in vacuum yielding colourless oil (23.0 g, 97%). Kp (0.4 kPa) 94 °C; C₉H₁₈O₂ requires C, 68.31; H, 11.46; found: C, 68.56; H, 11.37%; ¹H NMR (400 MHz; CDCl₃) δ 0.88 (t, *J* = 6.4 Hz, 3 H, CH₂CH₃), 1.17 (d, *J* = 6.9 Hz, 3 H, CHCH₃), 1.21–1.40 (m, 8 H, CH₂), 1.39–1.46 and 1.64–1.71 (2 m, 2 H, CH₂CH), 2.41–2.48 (m, 1 H, CHCH₃); EI-MS *m/z* 158 (28%, M), 129 (68, M – C₂H₅). The data are in agreement with published values.⁴

(2RS)-2-Methyloctan-1-ol (5a). 2-Methyloctanoic acid (**4a**; 25.0 g, 0.158 mol) were heated with MeOH (130 mL, 4 mol) and conc. H₂SO₄ (5 mL, 28 mmol) for 2 h under reflux. The mixture was evaporated to the half of the original volume. Water (100 mL) was added and the mixture was extracted two times with Et₂O (100 mL). The combined ethereal extracts were washed with conc. sodium acetate solution (50 mL) and water (100 mL). After drying over Na₂SO₄ the solvent was removed in vacuum. The crude methyl ester was reduced to 2-methyloctanol (**5a**) without further purification. Therefore, the ester was dissolved in dry Et₂O (100 mL) and dropped into a stirred mixture of lithium aluminium hydride (7.12 g, 0.188 mol) in dry Et₂O (150 mL). The mixture was heated for 2 h under reflux. After the generally work up procedure with water, acidification,

separation and drying, the solvent was evaporated and the residue was purified by chromatography yielding colourless liquid (18.0 g, 79%); $C_9H_{20}O$ requires C, 74.93; H, 3.98; found: C, 74.70; H, 13.96%; 1H NMR (400 MHz; $CDCl_3$) δ 0.84–0.90 (m, 6 H, $2 \times CH_3$), 1.05–1.10 (m, 2 H, CH_2), 1.17–1.40 (m, 8 H, CH_2), 1.54–1.62 (m, 1 H, CH), 3.37–3.50 (m, 2 H, CH_2OH); EI-MS m/z 144 (M), 143 (M – H), 129 (M – CH_3). The data are in agreement with published values.⁵

(2*RS*)-1-Bromo-2-methyloctane (6a). 2-Methyloctan-1-ol (**5a**; 17.31 g, 0.12 mol) and TEA (13.2 g, 0.13 mol) were dissolved in dry $CHCl_3$ (150 mL). Methansulphonic acid chloride (14.89 g, 0.13 mol) diluted in dry $CHCl_3$ (50 mL) was added drop wise at 0 °C. The mixture was stirred for 1 h at that temperature and then at r.t. overnight. The solution was poured into ice (200 mL) and the organic layer was separated. The water phase was extracted two times with $CHCl_3$ (100 mL) and the collected organic layers were dried over Na_2SO_4 . The solvent was removed under reduced pressure and residue was taken up in dry acetone (100 mL). LiBr (18 g, 0.2 mol) was added in one portion and the mixture was stirred for 6–8 h (TLC control) under reflux. Afterwards, the mixture was concentrated to 50 mL, ice water (150 mL) was added and the mixture was extracted three times with petrol ether (50 mL). After drying the organic layers with Na_2SO_4 , the solvent was removed and the residue was purified by column chromatography using heptane/ Et_2O as eluent and gradient technique yielding colourless oil (16.9 g, 68%). $C_9H_{19}Br$ requires C, 52.18; H, 9.25; found: C, 52.26; H, 9.38%; 1H NMR (400 MHz; $CDCl_3$) δ 0.80 (t, J = 6.9 Hz, 3 H, CH_2CH_3), 0.94 (d, J = 6.5 Hz, 2 H, $CHCH_3$), 1.10–1.45 (m, 10 H, CH_2), 1.65–1.78 (m, 1 H, CH), 3.20–3.35 (m, 2 H, $BrCH_2$); EI-MS m/z 206/208 (3.5%, M). The data are in agreement with published values.³

Synthesis of methyl-branched bromoalkanes – the citronellyl bromide pathway

(4*RS*)-6-Bromo-4-methylhexan-1-ol (9). Compound **9** was synthesised from (*RS*)-citronellyl bromide (**8**) according to the procedure described previously.⁶ The crude alcohol **9** was used for the subsequently performed blocking of the hydroxyl moiety.

2-[[*(4RS)*-6-Bromo-4-methylhexyl]oxy]tetrahydro-2*H*-pyran (10). Compound **9** (7.8 g, 40 mmol) was dissolved in CH_2Cl_2 (50 mL), 3,4-dihydro-2*H*-pyran (5.04 g, 60 mmol) and PPTS (0.1 g) were added and the mixture was stirred for 18 h at r.t. Afterwards, the solution was washed with water (50 mL), dried with Na_2SO_4 , evaporated and the residue was purified by column chromatography using heptane/ Et_2O as eluent yielding **10** (10.6 g, 95%), colourless liquid. $C_{12}H_{23}O_2Br$ requires C, 51.62; H, 8.30; found: C, 51.56; H, 8.28%; 1H NMR (400 MHz; $CDCl_3$) δ 0.88 (d, J = 5.8 Hz, 3 H, CH_3), 1.14–1.25 (m, 1 H, $CH_2CH(CH_2)_2Br$), 1.32–1.43 (m, 1 H, $CH_2CH(CH_2)_2Br$), 1.47–1.72 (m, 9 H, $2 \times CH_2CH_2O$, CH_2CH_2CHO , $CHCH_3$), 1.76–1.91 (m, 2 H, CH_2CH_2Br), 3.32–3.50 (m, 4 H, CH_2Br , $2 \times CHOCHH$), 3.66–3.73 (m, 1 H, $CHOCHH$), 3.81–3.87 (m, 1 H, $CHOCHH$), 4.53–4.55 (m, 1 H, $OCHO$); EI-MS m/z 277/279 (5%, M).

2-[[*(4RS)*-4-Methylundec-10-en-1-yl]oxy]tetrahydro-2*H*-pyran (11). Bromopent-1-ene (16.4 g, 0.11 mol), dissolved in dry Et_2O (70 mL), was slowly added to Mg turnings (3.2 g, 0.132 mol). The mixture was stirred for 2 h at reflux. The Grignard solution was decanted from excess Mg under a stream of argon. After removing the Et_2O *in vacuo* the oily residue was diluted in dry THF and

cooled to $-5\text{ }^{\circ}\text{C}$. Afterwards, compound **10** (21.5 g, 77 mmol), dissolved in dry THF (10 mL), was added in one portion followed by a freshly prepared Li_2CuCl_4 solution (10 mL, 0.1 m). The mixture was stirred for 2–3 h at -5 to $0\text{ }^{\circ}\text{C}$. Then, the mixture was poured into an ice-cold saturated solution of NH_4Cl . The organic layer was separated and the aqueous phase was extracted with Et_2O . The combined ethereal phases were washed with water and brine, dried with Na_2SO_4 and evaporated. The oily residues were purified by column chromatography yielding **11** (14.3 g, 69%) as colourless oil. $\text{C}_{17}\text{H}_{32}\text{O}_2$ requires C, 76.06; H, 12.02; found: C, 76.06; H, 12.17%; ^1H NMR (400 MHz; CDCl_3) δ 0.85 (d, $J = 6.4$ Hz, 3 H, CH_3), 1.07–1.40 (m, 11 H, $\text{CH}_2\text{CH}(\text{CH}_2)_4$), 1.47–1.62 (m, 6 H, $2\times\text{CH}_2\text{CH}_2\text{O}$, $\text{CH}_2\text{CH}_2\text{CHO}$), 1.67–1.73 (m, 1 H, CH_2CHO), 1.79–1.83 (m, 1 H, CH_2CHO), 1.99–2.04 (m, 2 H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.32–3.38 (m, 1 H, CHOCH_2), 3.45–3.51 (m, 1 H, CHOCH_2), 3.66–3.73 (m, 1 H, CHOCH_2), 3.83–3.88 (m, 1 H, CHOCH_2), 4.55–4.56 (m, 1 H, OCHO), 4.89–5.00 (m, 2 H, $\text{CH}=\text{CH}_2$), 5.74–5.84 (m, 1 H, $\text{CH}=\text{CH}_2$); EI-MS m/z 367 (1%, $\text{M} - \text{H}$).

(8*RS*)-11-Bromo-8-methylundec-1-ene (12). Triphenylphosphane (21.5 g, 82 mmol) was dissolved in dry CH_2Cl_2 (200 mL) and Br_2 (13.1 g, 82 mmol) diluted in CH_2Cl_2 (50 mL), was added dropwise into the solution whilst stirring at $0\text{ }^{\circ}\text{C}$. Compound **11** (13.68 g, 51 mmol) was added and the mixture was stirred overnight at r.t. The organic layer was washed with water and the crude bromide **12** was purified by column chromatography with heptane as eluent yielding **12** (10.46 g, 83%) as colourless oil. $\text{C}_{12}\text{H}_{23}\text{Br}$ requires C, 58.30; H, 9.38; found: C, 58.36; H, 9.55%; ^1H NMR (400 MHz; CDCl_3) δ 0.85 (d, $J = 6.4$ Hz, 3 H, CH_3), 1.07–1.45 (m, 11 H, $\text{CH}_2\text{CH}(\text{CH}_2)_4$), 1.75–1.92 (m, 2 H, BrCH_2CH_2), 2.00–2.05 (m, 2 H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.37 (t, $J = 7.0$ Hz, 2 H, BrCH_2), 4.90–5.00 (m, 2 H, $\text{CH}=\text{CH}_2$), 5.74–5.84 (m, 1 H, $\text{CH}=\text{CH}_2$); EI-MS m/z 246/248 (1%, M).

General procedure for the synthesis of 2-[(10-Methylalk-1-yl)oxy]tetrahydro-2*H*-pyrans **13a** and **13b**

Method A.

Mg (2.19 g, 90 mmol) was poured into an argon-secured flask. Then compounds **6a,b** (75 mmol) dissolved in dry Et_2O (50 mL) were added dropwise whilst stirring. The mixture was heated for 3 h under reflux. Afterwards, the Et_2O was removed under reduced pressure and dry THF (80 mL) was added at $0\text{ }^{\circ}\text{C}$. A solution of 2-[(8-bromooctyl)oxy]tetrahydro-2*H*-pyran (**7a**; 17.6 g, 60 mmol) in dry THF (10 mL) was added in one portion whereas the temperature should be below $0\text{ }^{\circ}\text{C}$. At a temperature of -3 to $0\text{ }^{\circ}\text{C}$, a Li_2CuCl_4 solution in THF (0.1m, 5 mL) was added and the mixture was stirred at that temperature for 3 h. For work up, saturated NH_4Cl solution (100 mL) and Et_2O (100 mL) were added and the organic layer was separated. The water phase was extracted with Et_2O (50 mL) and the collected organic layers were dried over Na_2SO_4 followed by evaporation of the solvent. The purification of the compounds **13** were realised using column chromatography with heptane/ Et_2O and gradient technique.

Method B.

The Grignard reagent was prepared from Mg (1.46 g, 60 mmol) and 2-[(6-bromohexyl)oxy]tetrahydro-2*H*-pyran (**7b**; 13.25 g, 50 mmol) in dry THF (100 mL) according to the procedure described above. The resulting Grignard solution was coupled with compound **12** (34 mmol) under catalytic conditions with Li_2CuCl_4 (0.1m, 3.5 mL) at $0\text{ }^{\circ}\text{C}$. After work-up as described above, the crude product was purified by column chromatography with heptane/ Et_2O and gradient technique.

2-[[*(10R)*-10-Methylhexadecyl]oxy]tetrahydro-2H-pyran (13a). Following the general procedure method A, **6a** (15.54 g) gave **13a** (16.3 g, 80%), colourless oil. C₂₂H₄₄O₂ requires C, 71.64; H, 12.21; found: C, 72.64; H, 12.94%; ¹H NMR (400 MHz, CDCl₃) δ 0.81 (d, *J* = 6.5 Hz, 3 H, CHCH₃), 0.88 (t, *J* = 6.9 Hz, 3 H, CH₂CH₃), 1.18–1.29 (m, 25 H, CH₂, CHCH₃), 1.45–1.88 (m, 8 H, 2× CH₂CH₂O, CH₂CH₂CHO), 3.32–3.40 (m, 1 H, CHOCH₂), 3.45–3.51 (m, 1 H, CHOCH₂), 3.68–3.75 (m, 1 H, CHOCH₂), 3.83–3.89 (m, 1 H, CHOCH₂), 4.55–4.57 (m, 1 H, OCHO); ESI-MS *m/z* 363.3 (M + Na).

2-[[*(10R)*-10-Methylheptadec-16-en-1-yl]oxy]tetrahydro-2H-pyran (13b). Following the general procedure method A, **6b** (16.44 g) gave **13b** (16.5 g, 78%). Following the general procedure method B, **12** (8.35 g) gave **13b** (8.75 g, 73%), colourless oil. C₂₃H₄₄O₂ requires C, 78.35; H, 12.58; found: C, 78.07; H, 12.92%; ¹H NMR (400 MHz; CDCl₃) δ 0.82 (d, *J* = 6.6 Hz, 3 H, CH₃), 1.05–1.38 (m, 23 H, CH₂, CHCH₃), 1.47–1.61 (m, 6 H, 2× CH₂CH₂O, CH₂CH₂CHO), 1.67–1.73 (m, 1 H, CH₂CHO), 1.78–1.83 (m, 1 H, CH₂CHO), 2.00–2.05 (m, 2 H, CH₂CH=CH₂), 3.34–3.39 (m, 1 H, CHOCH₂), 3.45–3.50 (m, 1 H, CHOCH₂), 3.68–3.74 (m, 1 H, CHOCH₂), 3.83–3.88 (m, 1 H, CHOCH₂), 4.55–4.57 (m, 1 H, OCHO), 4.89–5.00 (m, 2 H, CH=CH₂), 5.74–5.85 (m, 1 H, CH=CH₂); EI-MS *m/z* 351 (0.7%, M – H).

Methyl-branched bromoalkanes **14a** and **14b**.

The bromides **14a,b** were prepared from triphenylphosphorane diyl dibromide and compounds **13a,b** according to the method described above for compound **12**.

(10R)-1-Bromo-10-methylhexadecane (14a). Following the general procedure, triphenylphosphane (13.0 g, 51 mmol), Br₂ (8.15 g, 51 mmol), and **13a** (7.83 g, 23 mmol) gave **14a** (7.12 g, 97%), colourless oil. C₁₇H₃₅Br requires C, 63.93; H, 11.05; found: C, 64.13; H, 11.18%; ¹H NMR (400 MHz; CDCl₃) δ 0.81–0.88 (m, 6 H, 2× CH₃), 1.03–1.42 (m, 25 H, (CH₂)₇CH(CH₂)₅), 1.84 (quint, *J* = 7.0 Hz, 2 H, BrCH₂CH₂), 3.37–3.41 (m, 2 H, BrCH₂); EI-MS *m/z* 318/320 (1%, M).

(8R)-17-Bromo-8-methylheptadec-1-ene (14b). Following the general procedure, triphenylphosphane (13.0 g, 51 mmol), Br₂ (8.15 g, 51 mmol), and **13b** (8.11 g, 23 mmol) gave **14b** (7.09 g, 93%), colourless oil. C₁₈H₃₅Br requires C, 65.24; H 10.65; found: C, 64.91; H, 10.76%. ¹H NMR (400 MHz; CDCl₃) δ 0.82 (d, *J* = 6.6 Hz, 3 H, CH₃), 1.03–1.43 (m, 23 H, (CH₂)₇CH(CH₂)₄), 1.84 (quint, *J* = 7.0 Hz, 2 H, BrCH₂CH₂), 2.00–2.05 (m, 2 H, CH₂CH=CH₂), 3.39 (t, *J* = 7.0 Hz, 2 H, BrCH₂), 4.90–5.00 (m, 2 H, CH=CH₂), 5.75–5.85 (m, 1 H, CH=CH₂); EI-MS *m/z* 330/332 (2.4%, M).

Synthesis of diglycerol tetraethers – reaction pathway I

General procedure of *O*-alkylation of 1,2-*O*-isopropylidene-*sn*-glycerols 16.

Suspension of KH (22.5 mmol, 30%) was freed from paraffin oil by washing with dry toluene under argon. The residue of KH was suspended in dry toluene (8 mL). A solution of 1,2-*O*-isopropylidene-*sn*-glycerol (**15**; 2.61 g, 22.5 mmol) in dry toluene (20 mL) was dropped into the slurry whilst stirring. The mixture was stirred for a further 18 h at r.t. until the K-salt formation was completed. Afterwards, compounds **14** (17 mmol), dissolved in dry toluene (10 mL), were added and the mixture was heated for 10 h under reflux. After cooling to r.t., water (30 mL) was added and the mixture was stirred for 30 min. The organic layer was separated and the water phase was extracted two times with CHCl₃ (20 mL). The combined organic layers were dried over Na₂SO₄, evaporated and purified using column chromatography and heptane/Et₂O as eluent and gradient technique.

1,2-*O*-isopropylidene-3-*O*-(heptadec-16-en-1-yl)-*sn*-glycerol (16a). Following the general procedure, **14a** (5.4 g) gave **16a** (4.51 g, 73%), colourless oil. $[\alpha]_D^{22} +12.82$ (*c* 0.86 g/mL, pure); C₂₃H₄₄O₃ requires C, 74.95; H, 12.03; found: C, 75.07; H, 12.24%; ¹H NMR (400 MHz; CDCl₃) δ 1.23–1.32 (m, 24 H, (CH₂)₁₂), 1.34 (s, 3 H, CH₃), 1.40 (s, 3 H, CH₃), 1.55 (quint, *J* = 7.0 Hz, 2 H, CH₂CH₂O), 1.99–2.04 (m, 2 H, CH₂CH=CH₂), 3.37–3.51 (m, 4 H, 2× CH₂O), 3.68–3.72 (m, 1 H, CHHOC(CH₃)₂O), 4.01–4.05 (m, 1 H, CHHOC(CH₃)₂O), 4.23 (quint, *J* = 6.0 Hz, 1 H, CHO), 4.88–4.99 (m, 2 H, CH=CH₂), 5.74–5.84 (m, 1 H, CH=CH₂); ¹³C NMR (100 MHz; CDCl₃) δ 25.89, 26.22, 26.94, 29.10, 29.30, 29.60–29.80, 33.94, 67.07, 71.91, 71.96, 74.85, 109.32, 114.0, 139.18; EI-MS *m/z* 368 (8.6%, M).

1,2-*O*-isopropylidene-3-*O*-[(10*RS*)-10-methylheptadec-16-en-1-yl]-*sn*-glycerol (16b). Following the general procedure, **14b** (5.6 g) gave **16b** (4.42 g, 68%), colourless oil. C₂₄H₄₆O₃ requires C, 75.34; H, 12.12; found: C, 75.27; H 12.24%; ¹H NMR (400 MHz; CDCl₃) δ 0.82 (d, *J* = 6.6 Hz, 3 H, CHCH₃), 1.05–1.36 (m, 23 H, (CH₂)₇CH(CH₂)₄), 1.34 (s, 3 H, CCH₃), 1.40 (s, 3 H, CCH₃), 1.50–1.59 (m, 2 H, CH₂CH₂O), 1.99–2.05 (m, 2 H, CH₂CH=CH₂), 3.38–3.52 (m, 4 H, 2× CH₂O), 3.69–3.73 (m, 1 H, CHHOC(CH₃)₂O), 4.02–4.05 (m, 1 H, CHHOC(CH₃)₂O), 4.21–4.27 (m, 1 H, CHO), 4.89–5.00 (m, 2 H, CH=CH₂), 5.74–5.85 (m, 1 H, CH=CH₂); ¹³C NMR (100 MHz; CDCl₃) δ 19.76, 25.49, 26.12, 26.83, 26.96, 27.12, 29.04, 29.52–29.69, 30.05, 32.79, 33.86, 37.07, 37.12, 67.01, 71.86, 71.91, 74.81, 109.32, 114.06, 139.19; EI-MS *m/z* 382 (4.3%, M).

General procedure of the synthesis of 3-*O*-alkyl-*sn*-glycerols 17.

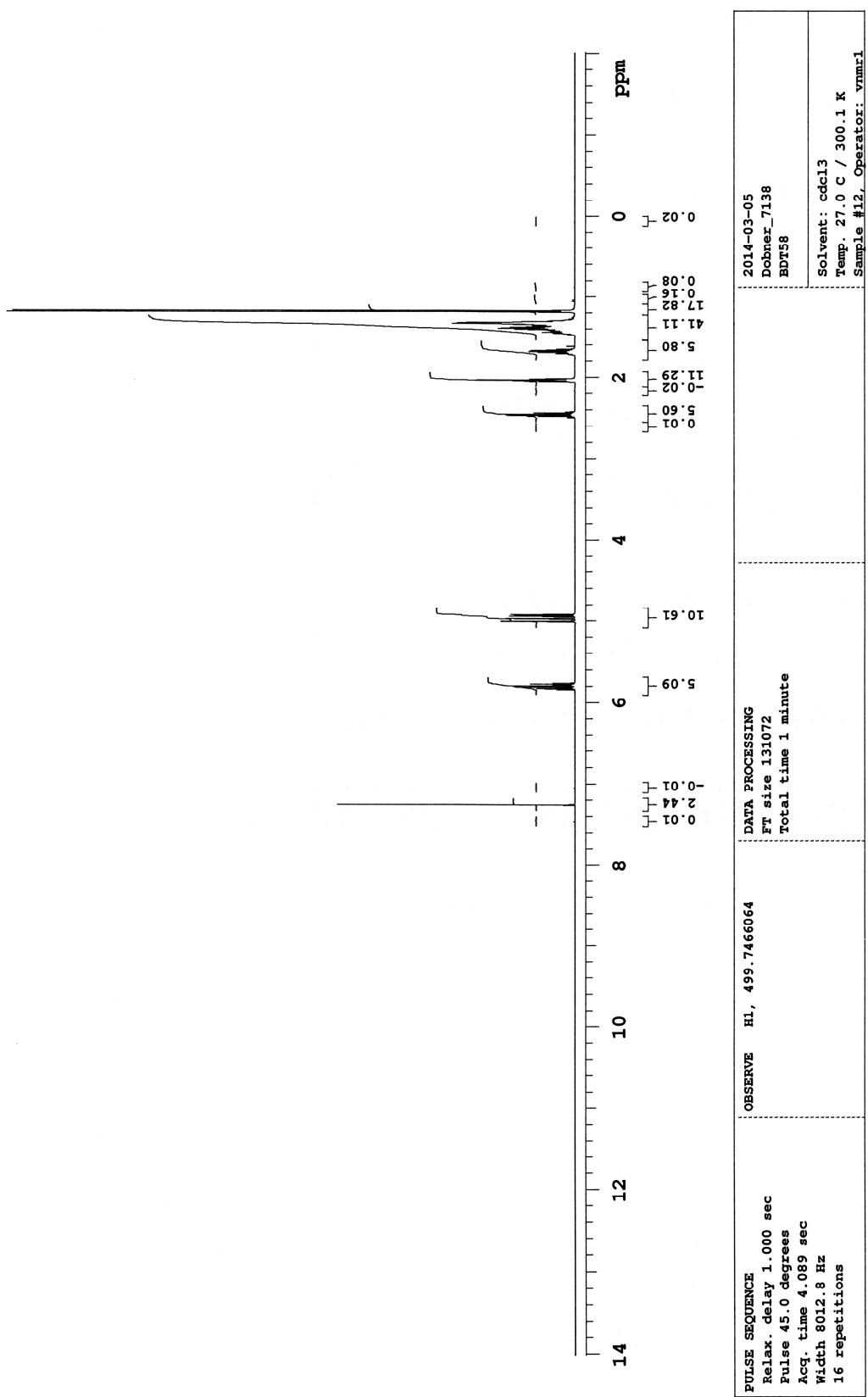
Compounds **16a** or **16b** (12 mmol) and PPTS (50 mg) were suspended in dry MeOH (40 mL) and heated for 10 h at reflux. Then, the solvent was removed, the residue was dissolved in CHCl₃ (70 mL) and washed with water (70 mL). The water layer was extracted two times with a CHCl₃/MeOH mixture (70 mL; 9/1, v/v) and the combined organic layers were dried over Na₂SO₄ and evaporated. The crude products were purified by column chromatography using CHCl₃/Et₂O as eluent and gradient technique.

3-*O*-(Heptadec-16-en-1-yl)-*sn*-glycerol (17a). Following the general procedure, **16a** (4.42 g) gave **17a** (3.35 g, 85%), white solid substance. M.p. 56 °C; $[\alpha]_{22}^D -0.6$ (*c* 0.1 g/mL, CHCl₃); C₂₀H₄₀O₃

requires C, 73.12; H, 12.27; found: C, 73.28; H, 11.94%; ^1H NMR (400 MHz; CDCl_3) δ 1.19–1.37 (m, 24 H, $(\text{CH}_2)_{12}$), 1.52–1.59 (m, 2 H, $\text{CH}_2\text{CH}_2\text{O}$), 1.99–2.04 (m, 2 H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.29 (bs, 2 H, $2\times \text{OH}$), 3.42–3.53 (m, 4 H, $2\times \text{CH}_2\text{O}$), 3.61–3.72 (m, 2 H, CH_2OH), 3.81–3.86 (m, 1 H, CHOH), 4.89–5.00 (m, 2 H, $\text{CH}=\text{CH}_2$), 5.74–5.84 (m, 1 H, $\text{CH}=\text{CH}_2$); ^{13}C NMR (100 MHz; CDCl_3) δ 26.14, 29.01, 29.21, 29.52–29.71, 33.85, 64.27, 70.59, 71.88, 72.46, 114.05, 139.20; EI-MS m/z 328 (8.9%, M).

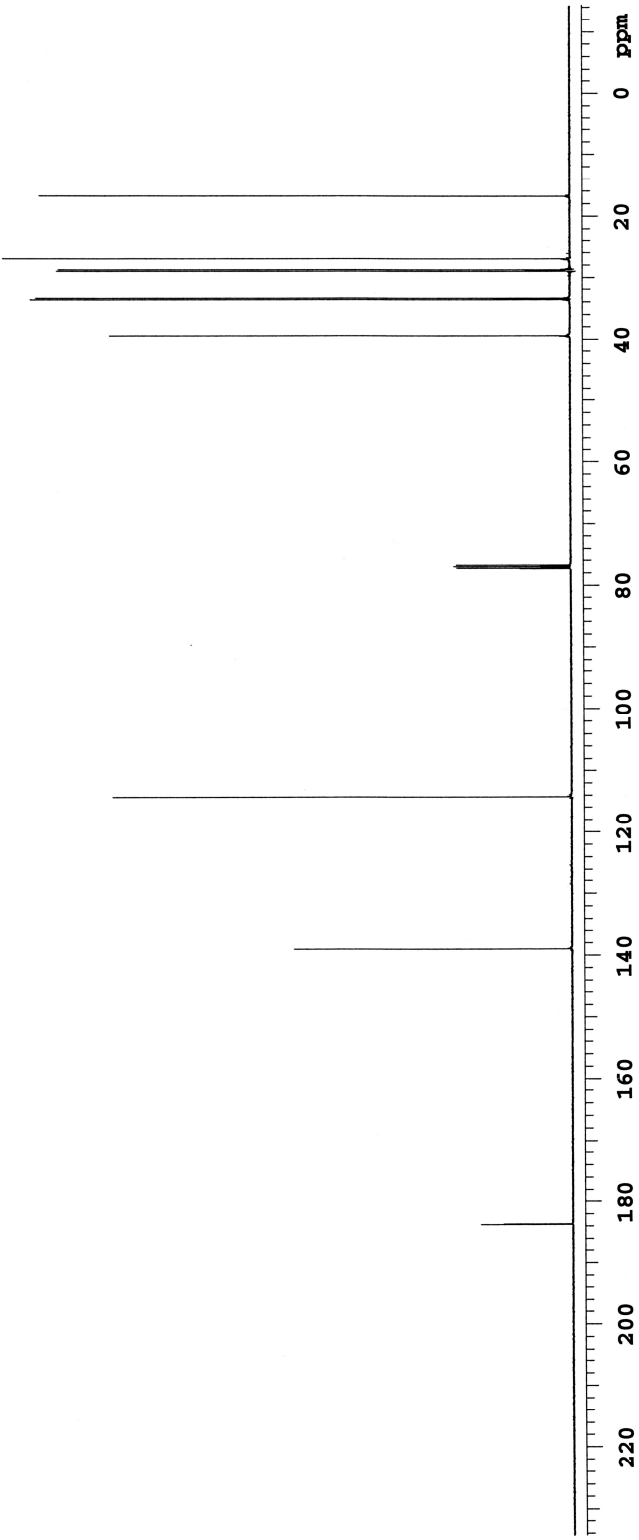
3-*O*-[(10*RS*)-10-methylheptadec-16-en-1-yl]-*sn*-glycerol (17b). Following the general procedure, **16b** (4.59 g) gave **17b** (3.74 g, 91%), colourless oil. $\text{C}_{21}\text{H}_{42}\text{O}_3$ requires C, 73.63; H, 12.36; found: C, 73.27; H, 12.35%; ^1H NMR (400 MHz; CDCl_3) δ 0.81 (d, $J = 6.6$ Hz, 3 H, CH_3), 1.04–1.37 (m, 23 H, $(\text{CH}_2)_7\text{CH}(\text{CH}_2)_4$), 1.51–1.58 (m, 2 H, $\text{CH}_2\text{CH}_2\text{O}$), 1.99–2.04 (m, 2 H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.52 (bs, 2 H, $2\times \text{OH}$), 3.39–3.54 (m, 4 H, $2\times \text{CH}_2\text{O}$), 3.59–3.70 (m, 2 H, CH_2OH), 3.81–3.85 (m, 1 H, CHOH), 4.88–4.99 (m, 2 H, $\text{CH}=\text{CH}_2$), 5.75–5.84 (m, 1 H, $\text{CH}=\text{CH}_2$); ^{13}C NMR (100 MHz; CDCl_3) δ 19.76, 26.14, 26.96, 27.12, 29.04, 29.52–29.70, 30.05, 32.79, 33.86, 37.07, 37.13, 64.31, 70.52, 71.89, 72.51, 114.06, 139.21; ESI-MS m/z 365.4 (M + Na).

4. Characterisation of products – MS, ¹H NMR, ¹³C NMR spectra
Compound 4b: ¹H-NMR



File: Dobner_7138_2014-03-05_01/Dobner_7138_PROTON_01

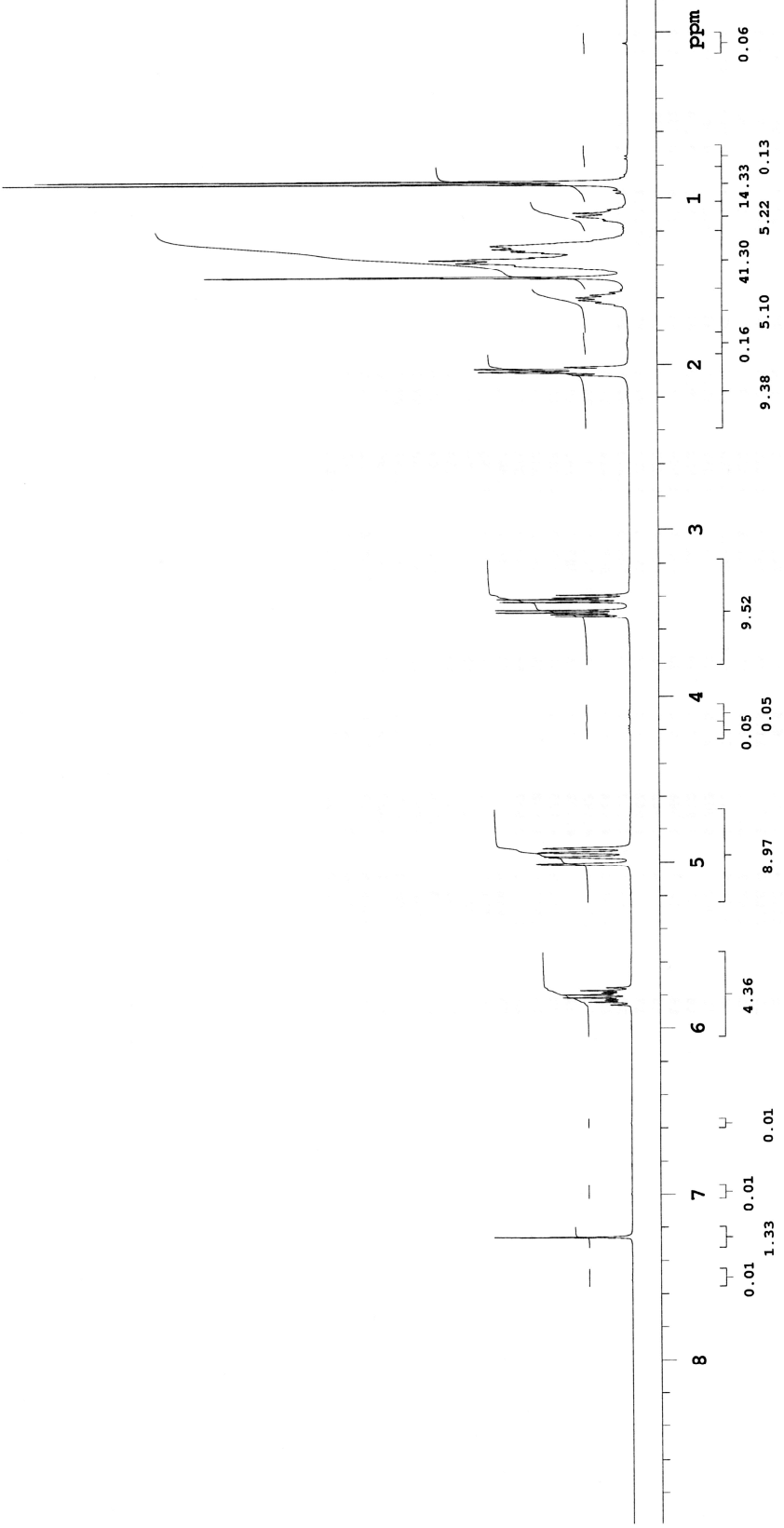
Compound **4b**: ^{13}C -NMR



PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 1000 repetitions	OBSERVE C13, 125.6613841 DECOUPLE H1, 499.7491051 Power 40 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 131072 Total time 34 minutes	2014-03-05 Dobner_7139 BDT58 Solvent: cdcl3 Temp. 27.0 C / 300.1 K Sample #1, Operator: vnmr1
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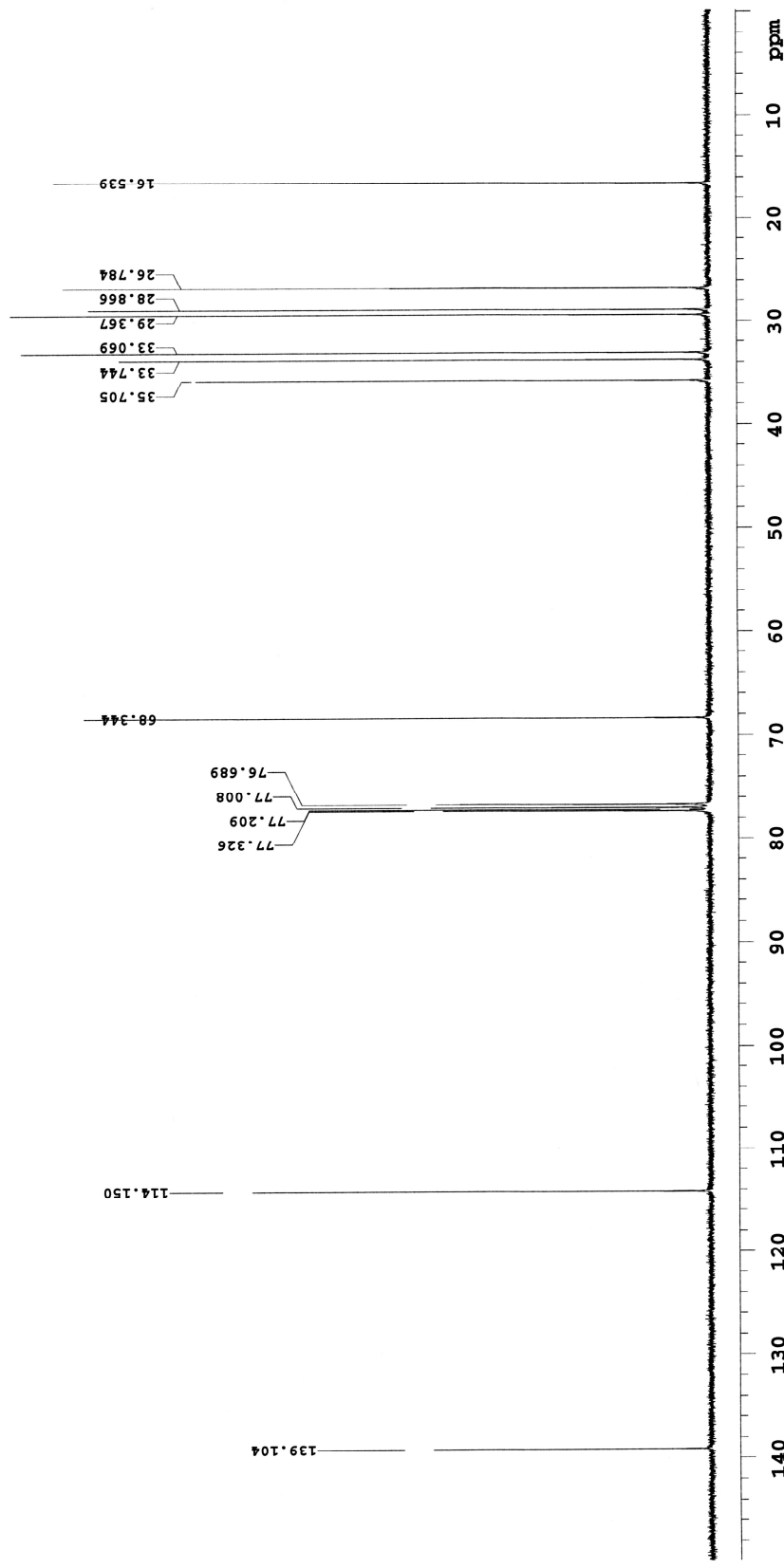
File: Dobner_7139_2014-03-05_01/Dobner_7139_CARBON_01

Compound 5b: ¹H-NMR



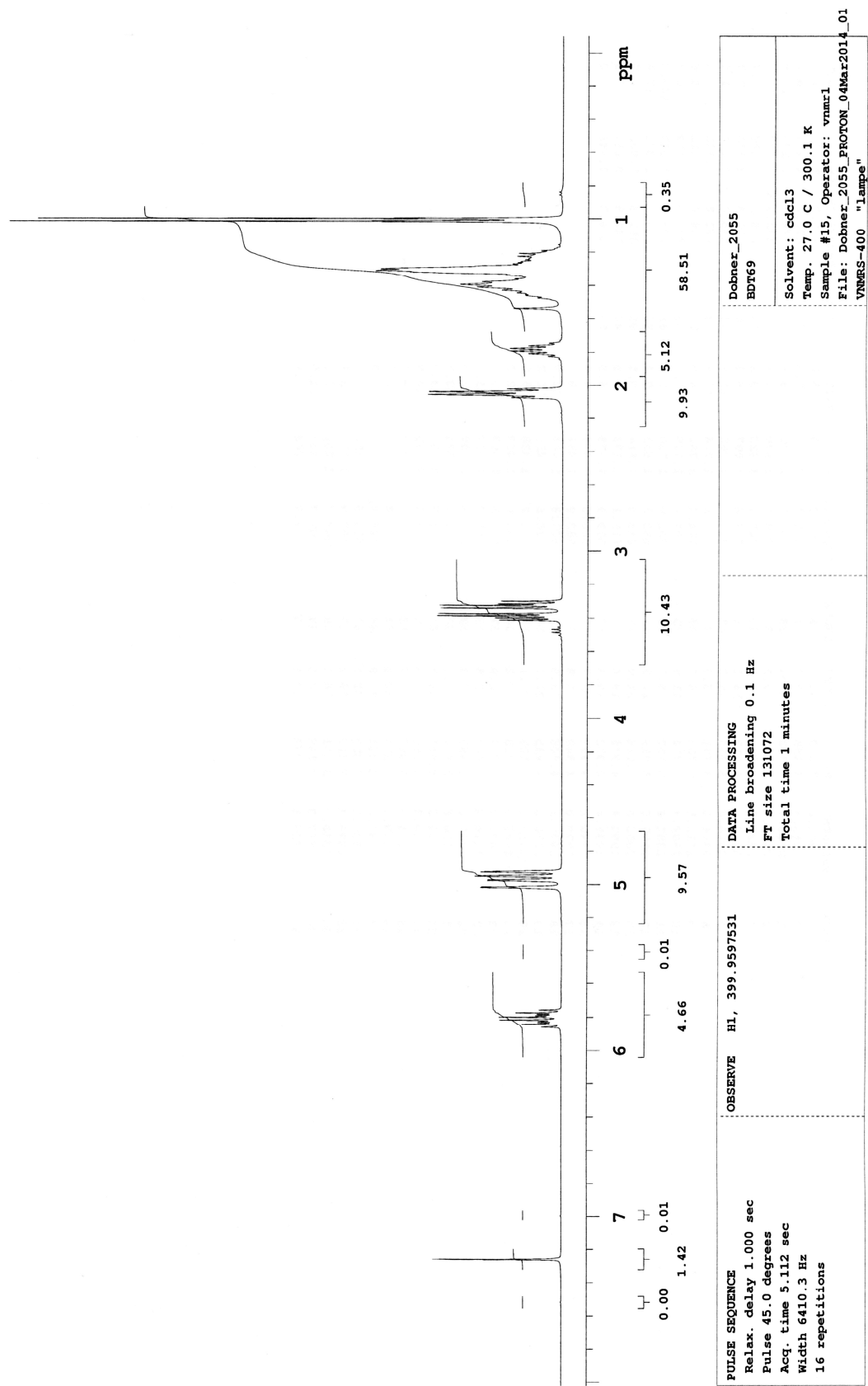
<p>PULSE SEQUENCE</p> <p>Relax. delay 1.000 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 5.112 sec</p> <p>Width 6410.3 Hz</p> <p>16 repetitions</p>	<p>OBSERVE H1, 399.9597531</p>	<p>DATA PROCESSING</p> <p>Line broadening 0.1 Hz</p> <p>FT size 131072</p> <p>Total time 1 minutes</p>	<p>Dobner_2059</p> <p>BD763/2</p> <p>Solvent: cdcl3</p> <p>Temp. 27.0 C / 300.1 K</p> <p>Operator: vnmr1</p> <p>VNMRS-400 "lampe"</p>
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Compound 5b: ¹³C-NMR

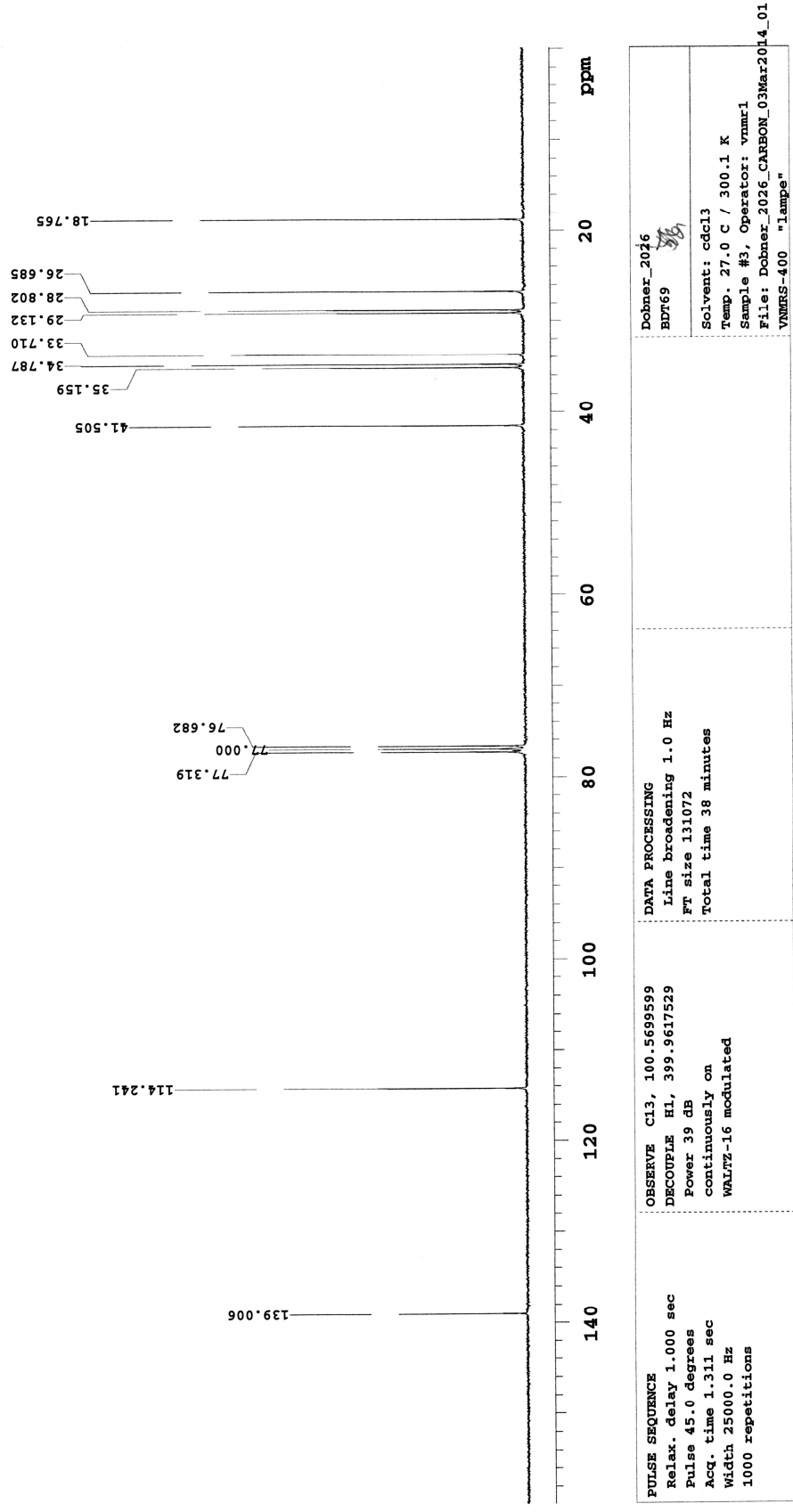


<p>PULSE SEQUENCE</p> <p>Relax. delay 1.000 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 1.311 sec</p> <p>Width 25000.0 Hz</p> <p>1000 repetitions</p>	<p>OBSERVE C13, 100.569599</p> <p>DECOUPLE H1, 399.9617529</p> <p>Power 39 dB</p> <p>continuously on</p> <p>WALTZ-16 modulated</p>	<p>DATA PROCESSING</p> <p>Line broadening 0.5 Hz</p> <p>FT size 131072</p> <p>Total time 38 minutes</p>	<p>Dobner_2060</p> <p>BDT62/2 = 63/2</p> <p>Solvent: cdcl3</p> <p>Temp. 27.0 C / 300.1 K</p> <p>Operator: vnmr1</p> <p>VNMRS-400 "lampe"</p>
--	--	---	--

Compound **6b**: ^1H -NMR



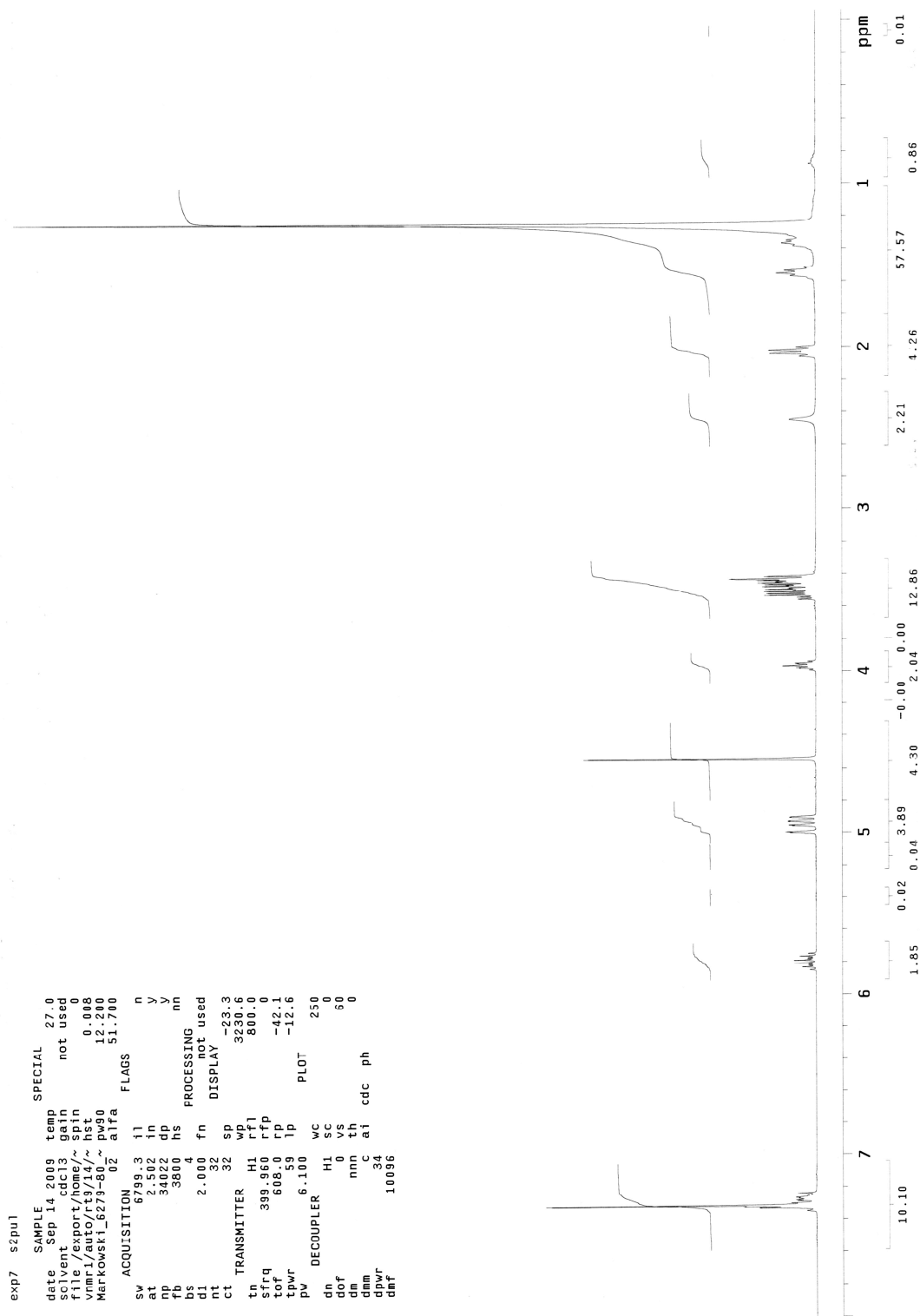
Compound **6b**: ^{13}C -NMR



```

markowski_6279~80_ IM-GR-13
exp7 szpul SAMPLE SPECIAL
date sep 14 2009 temp 27.0 y
solvent cdc13 gain not used
file export/home/~ spin 0
vnmr1/auto/r3/14/~ hst 0.008
Markowski_6279~80_ pw90 12.200
Markowski_6279~80_ pw90 12.200
02 alfa 51.700
FLAGS
ACQUISITION
sw 6799.3 il n y
at 2.502 in y y
np 34022 ds n y
pr 3800 hp n y
ds 4 n y
bs 2.000 fn not used
ct 32 sp
ct TRANSMITTER H1 wf1
tp 399.960 rfp 800.0
sfreq 608.0 rfp -42.1
tof 608.0 rfp -12.6
tpwr 59 lp PLOT
pv 6.100 wc 250
DECOUPLER H1 SC 0
dn do 0
dn do 0
dn nn th 60
dm c ai 0
dm c ai
dwr 34
dwr 10096
dwr ph
dwr def

```

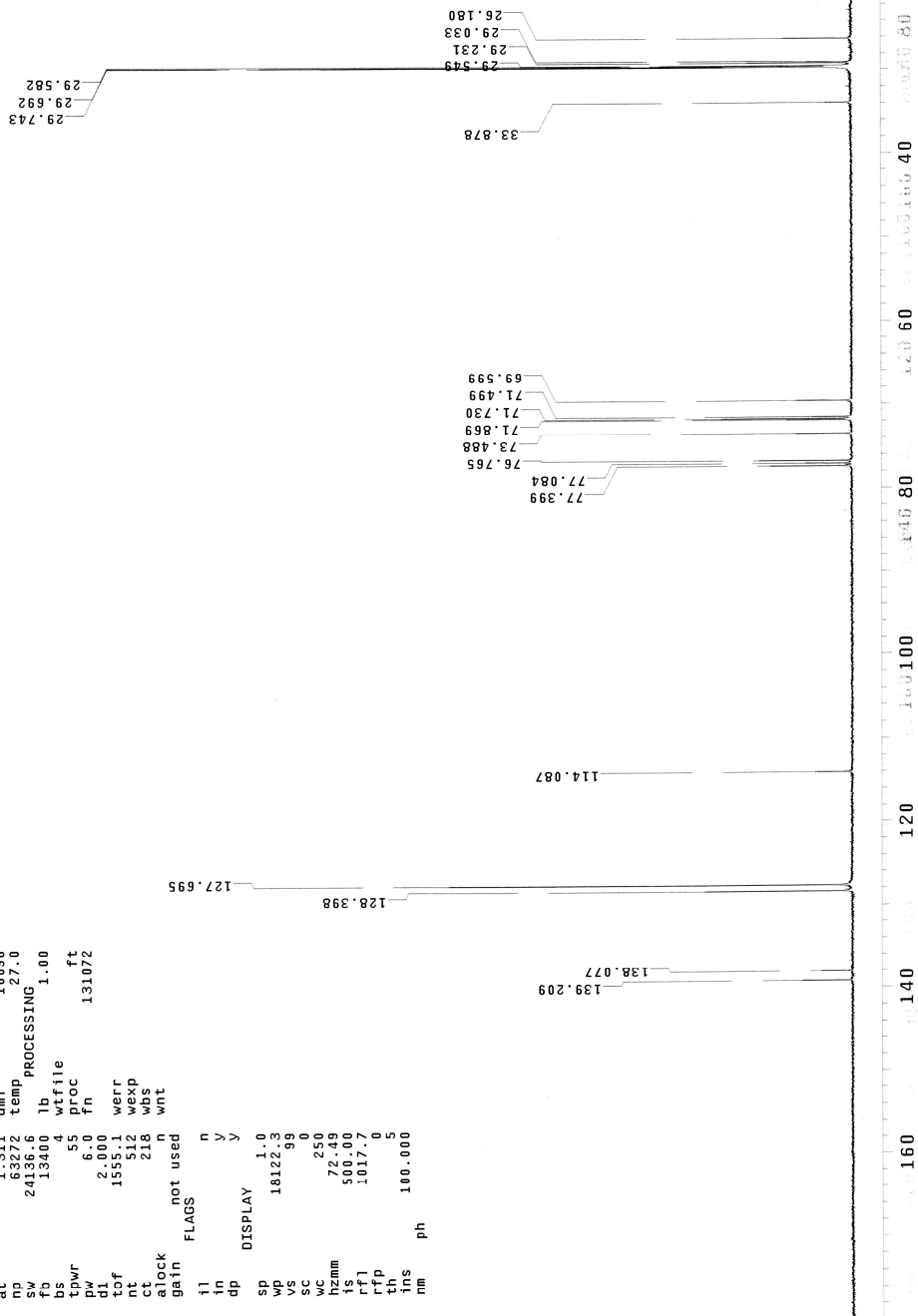


Compound 18a: ¹³C-NMR

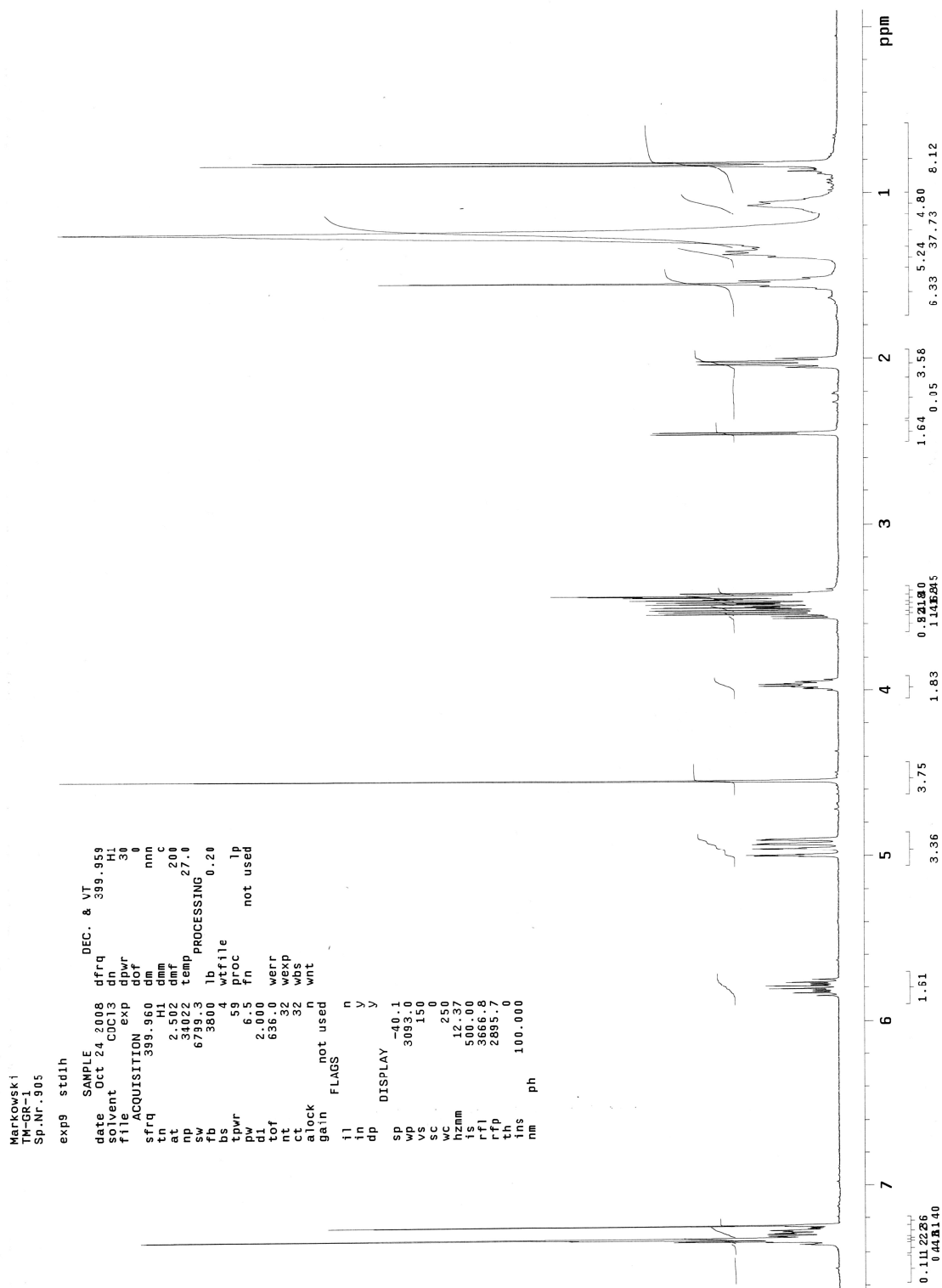
Markowski
TM-GR-13
Nr. 6283

expl std13c

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date Sep 15 2009 dfrq 399.959
solvent CDCl3 dn H1
file ACQUISITION exp 34
sfrq 100.580 dm 0
tn 1.013 dmm wvy
at 1.013 dmm 1009W
np 63272 dmm 1009W
sq 24136.6 temp 27.0
fo 13400 lb PROCESSING 1.00
bs 4 wfile
tpwr 55 proc ft
pw 6.0 fn 131072
d1 2.000
tof 1555.1 werr
nt 512 wexp
ct 218 wps
a1ock n
gain not used
flags n
f1 n
in n
dp DISPLAY y
sp 1.0
wp 18122.3
vs 99
sc 0
wc 250
hzmm 72.43
ss 50.00
rf1 1017.0
rfd 0
th 5
ins 100.000
nm ph

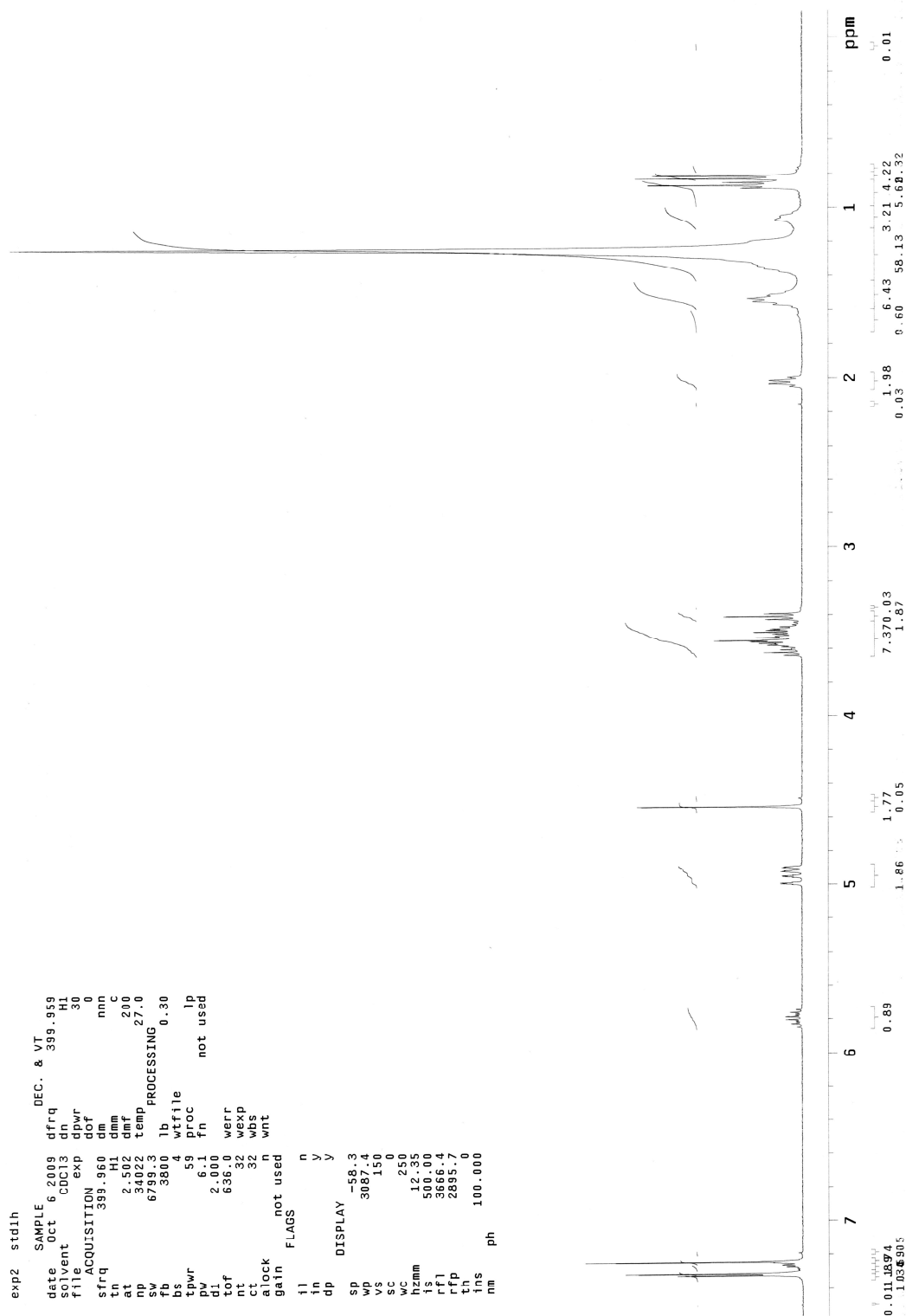


Compound 18b: ^1H -NMR



[illegible]

MARKOVSKI
TM-CR-114
SF-NR 6589



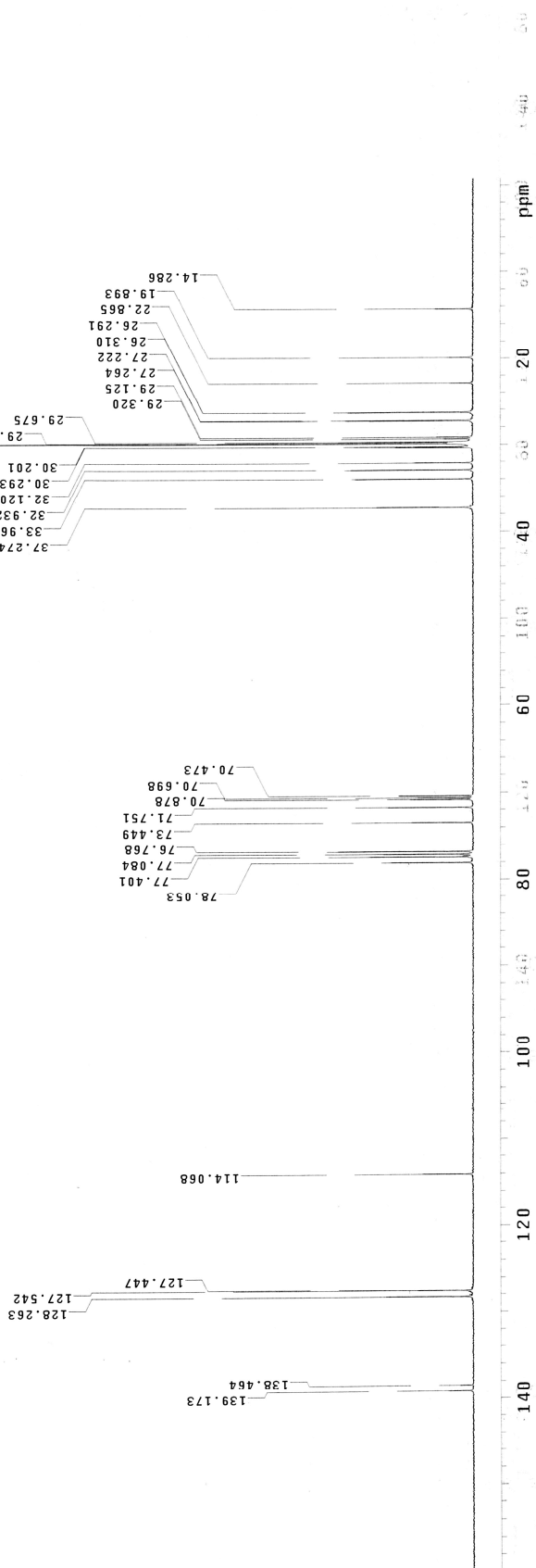
Compound 19a: ^{13}C -NMR

Markowski_6811_TM-GR-14

```

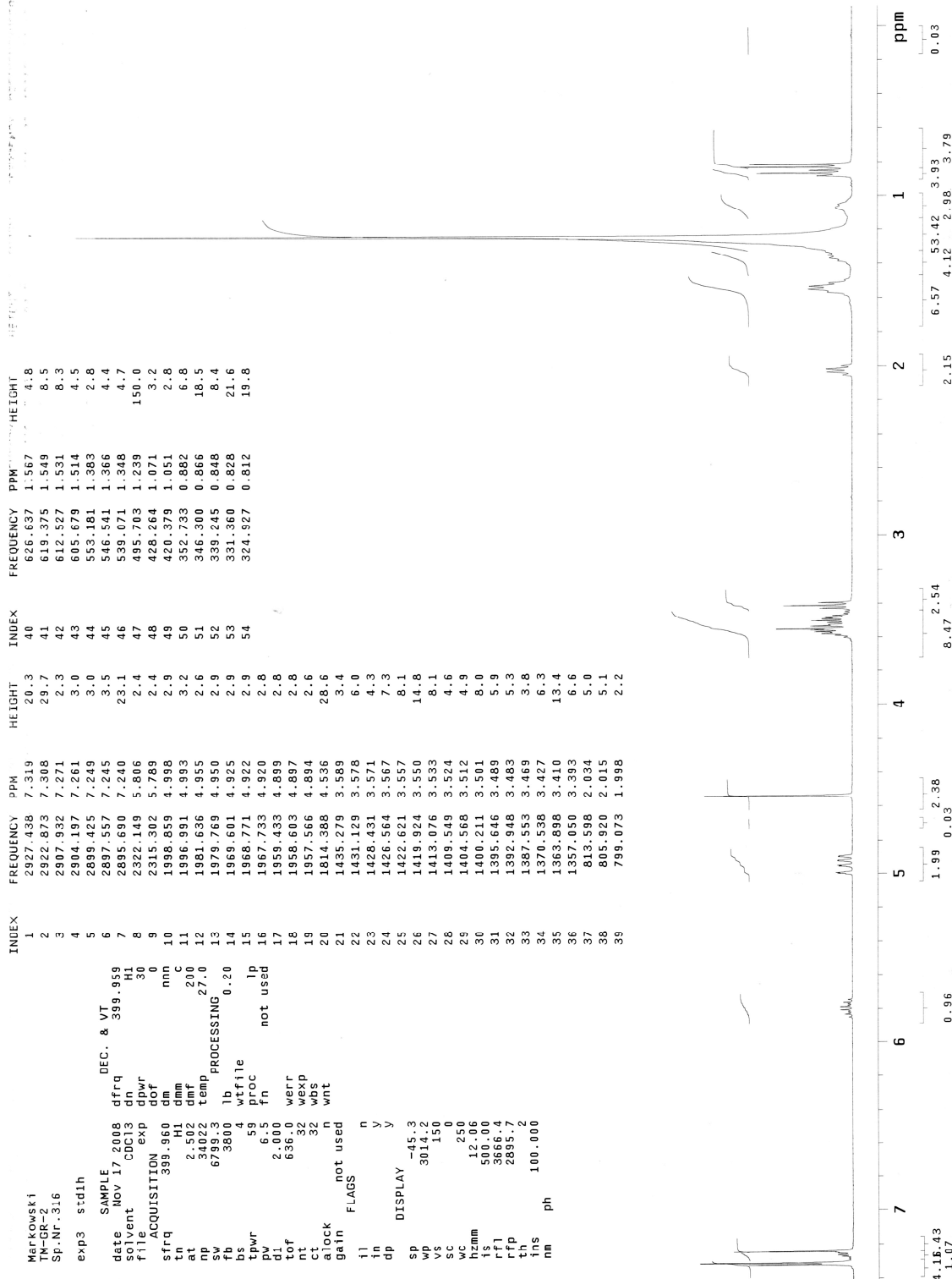
exp1 s2pul1
SAMPLE
date Oct 19 2009 temp 27.0
solvent cdcl3 gain not used
file /export/home/~spin 20
nmr1/autort10/19~hst 0.008
a/Markowski_6811_0~pw90 9.400
ACQUISITION I alfa 20.000
SW 25142.3 il n
at 1.311 in v
pp 65908 dp v
fb 13800 hs
bs 16
di 2.000 lb 1.00
nt 2048 fn 131072
ct 2048 ct DISPLAY -79.8
TRANSMITTER C13 wp 16170.7
sfreq 100.590 rfl 1508.5
cof 156751 rfp 21.1
tpwr 4.700 lp -217.1
PLOT
pv DECOUPLER H1 wc 250
dn 0 SC 36
dof 0 SC 36
dm vvy vs
dmm w th
dpwr 34 ai
dnf 10096
ph

```



Markowski
TM-GR-2
Sp. Nr. 316

Markowski		SAMPLE		DEC. & VT	
TM-GR-2		date Nov 17 2008		H1 399.959	
Sp.Nr.316		file		CO13	
exp3 stdh		ACQUISITION		exp	
sfrq	399.960	dm	0	nmn	0
at	2.502	dm	0	nmn	0
sw	3402	temp	27.0	nmn	0
fb	6799.3	PROCESSING	0.20	nmn	0
bw	3800	lb	0	nmn	0
bs	4	wfile	0	nmn	0
tpwr	59	fn	0	nmn	0
pv	6.5	fn	0	nmn	0
dd	2.000	werr	0	nmn	0
tofof	636.0	wexp	0	nmn	0
ct	32	wss	0	nmn	0
clock	n	wnt	0	nmn	0
magain	not used			nmn	0
flags				nmn	0
il	n			nmn	0
in	y			nmn	0
dp	y			nmn	0
DISPLAY				nmn	0
sp	-45.3			nmn	0
wp	3014.2			nmn	0
vs	150			nmn	0
sc	0			nmn	0
h	250			nmn	0
hmm	12.06			nmn	0
is	500.00			nmn	0
rfl	3666.4			nmn	0
rpf	2895.7			nmn	0
th	2			nmn	0
ins	100.000			nmn	0
ph				nmn	0

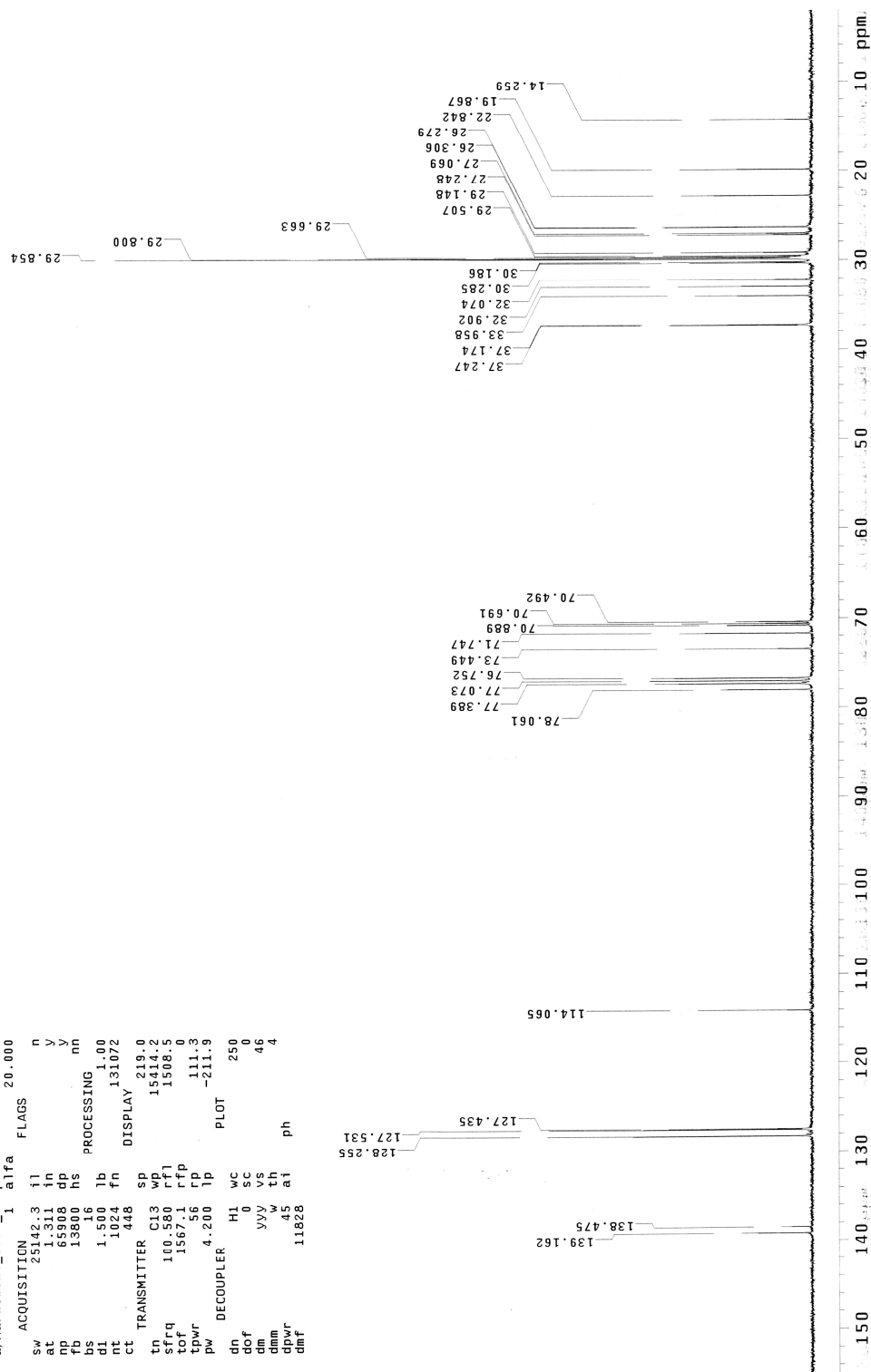


Compound 19b: ^{13}C -NMR

Markowski_1030_TH-OR-2

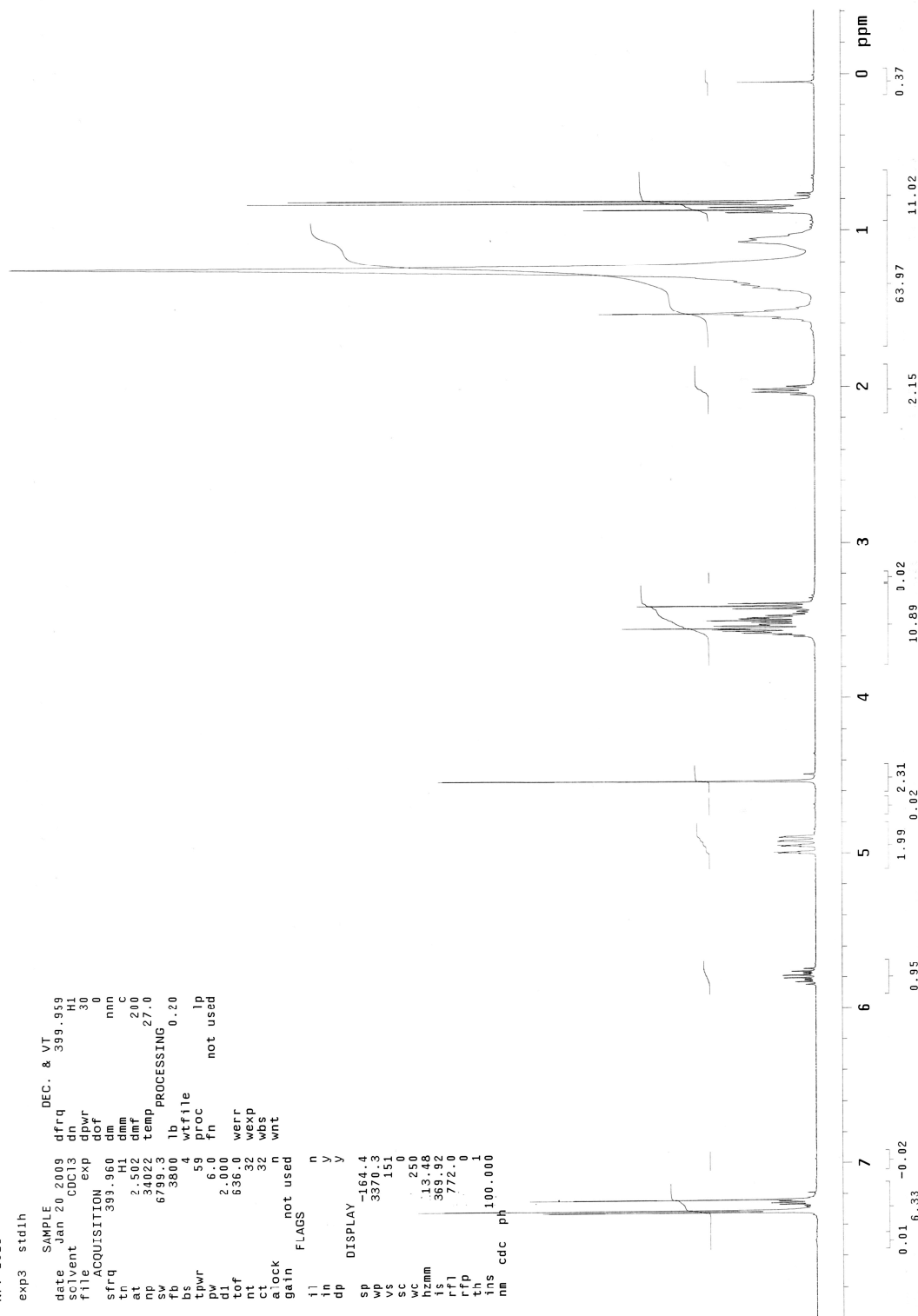
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date Dec 11 2008 temp 27.0
solvent cdcl3 gain not used
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nmr1/auto/rt12/11~het 0.008
a/Markowski_1030_0~pw90 8.400
ACQUISITION 1 alfa 20.000
  sw 25142.3 il n
  at 11311 in v
  pd 65908 dp v
  fd 13800 hs nn
  bs 16 PROCESSING
  d1 1.500 lb 1.00
  nt 1024 fn 131072
  ct 448 DISPLAY
TRANSMITTER C13 sp
tn sfrq 100.580 rfn 15414.2
tofr 15671 rfp 1508.5
tpwr 4.200 lp 111.3
pw DECOUPLER H1 wc 250
dn 0 sc 0
dm vvy vs 46
dmm w th 4
dpwr 45 ai ph
dmf 11828
  
```



Markowski
TM-GR3
Nr. 1521

exp3	stdlh	SAMPLE	DEC. & VT
date	Jan 20 2009	dfrq	399.959
solvent	COC13	dn	H1
file	exp	dprw	30
ACQUISITION		dof	0
nsfrq	399.960	dm	nnn
atn	H1	dmm	200
trn	2.502	dmr	c
np	34022	temp	27.0
sw	67380	lb	PROCESSING
ba	3800	lb	0.20
tw	4	wfile	
tpwr	59	fn	lp
pdv	6.0	fn	not used
d1	2.000	werr	
tof	636.0	wexp	
nt	32	wps	
ct	32	wnt	
aack	n		
gain	not used		
FLAGS			
il	n		
dp	y		
dp	y		
DISPLAY			
sp	-164.4		
wp	3370.3		
vs	151		
sc	0		
wc	250		
hzmm			
ls	13.48		
rs	36932		
rf	772.0		
rr	0		
rt	1		
ins	100.000		
nm	cdc		
ph			

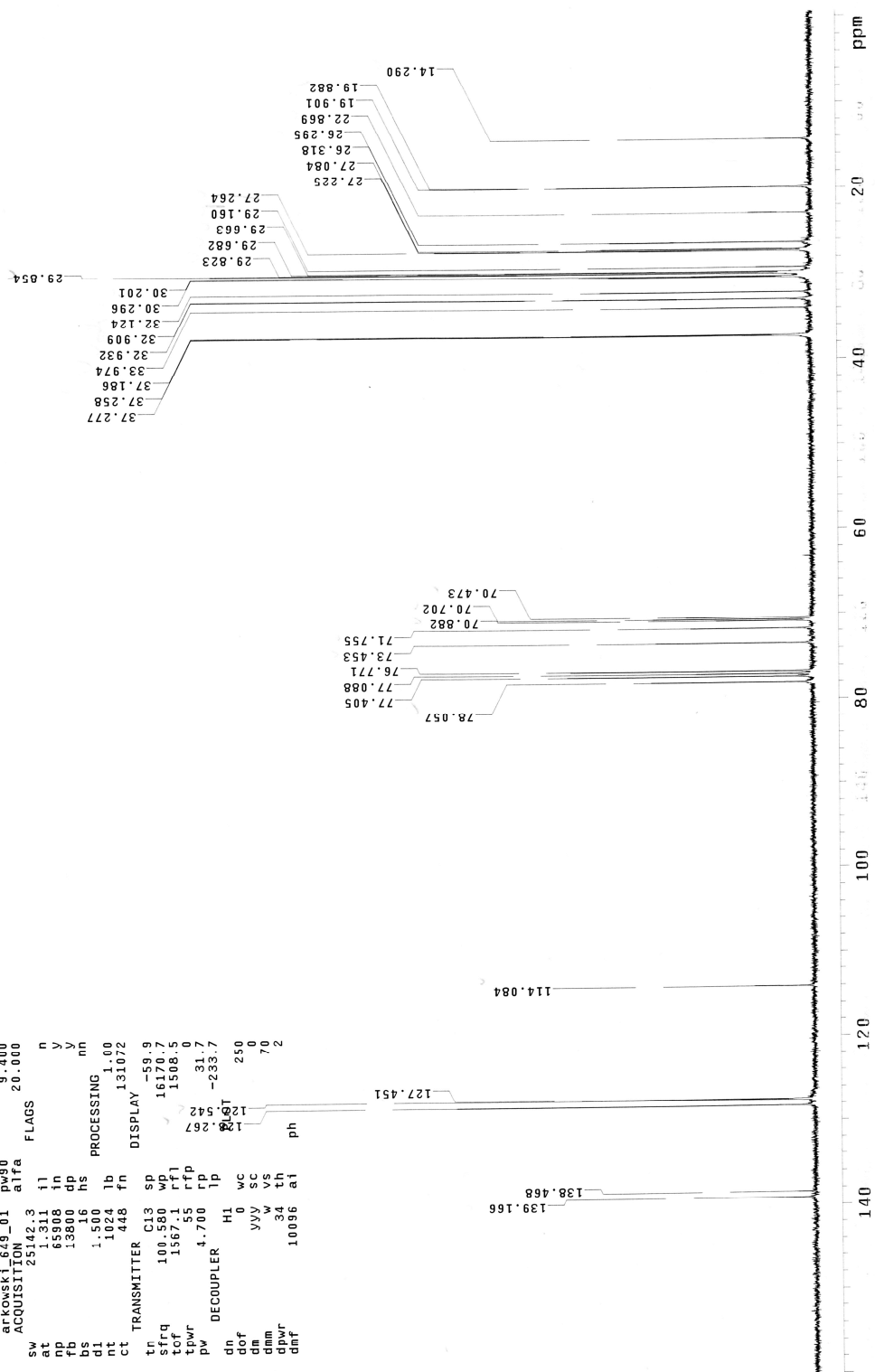


Compound 19c: ¹³C-NMR

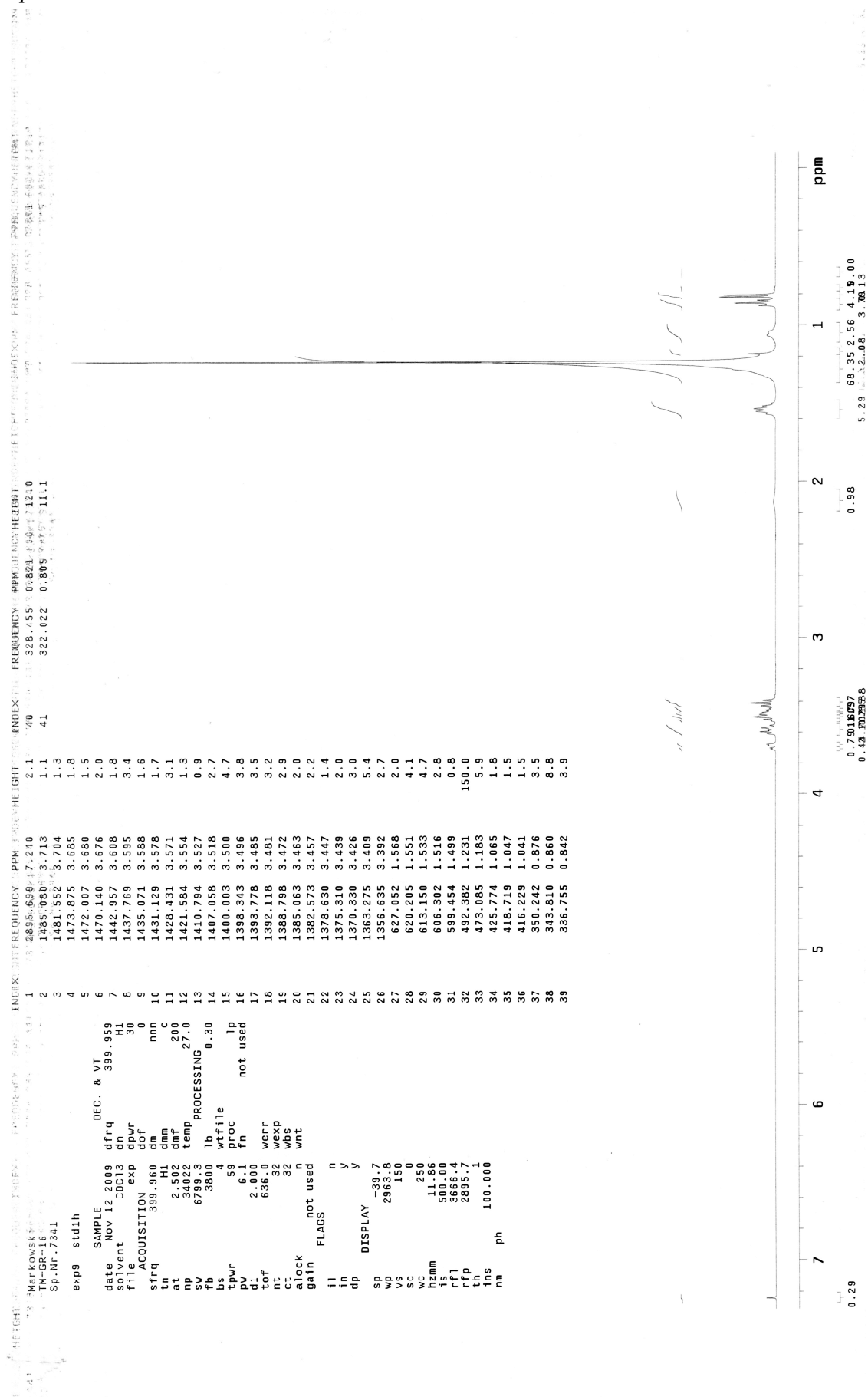
exp7 s2pu1

Markowski_649_TM-GR-3

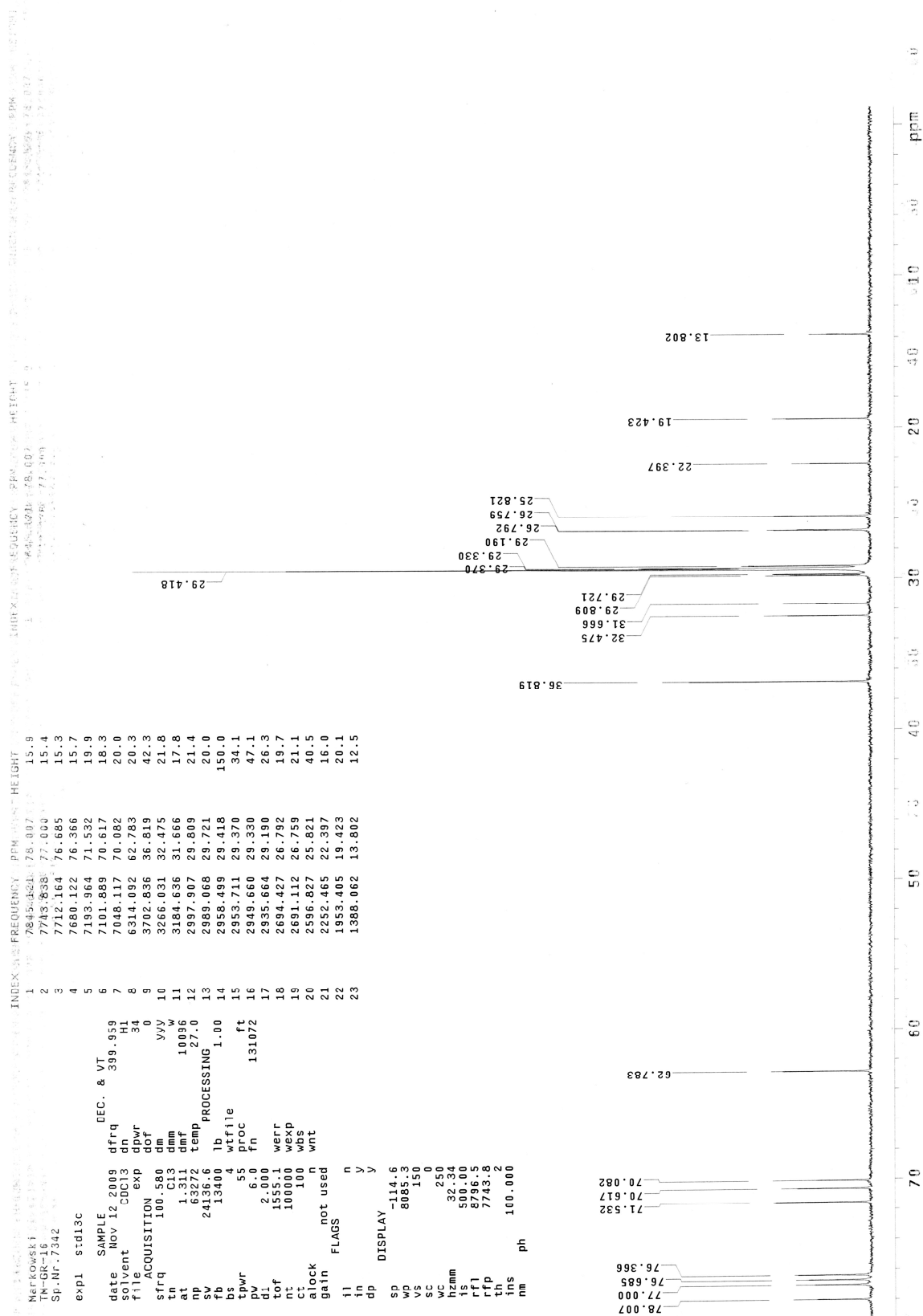
SAMPLE SPECIAL 27.0
 date Sep 3 2009 temp not used
 solvent cdcl3 gain 20
 file /export/home/~spin 0.008
 vmr1/auto/rts/2/M~bst 9.400
 arkowski_649_01 pw90 20.000
 ACQUISITION alfa
 sw 25142.3
 at 1.311 fl
 np 65908 in
 fb 13800 dp
 bs 16 hs
 dl 1.504
 ct 1024 lb
 ct 448 fn
 TRANSMITTER C13 SP
 tn -59.9
 sfrq 100.580 wp
 tof 16170.7
 tpwr 1567.1 rfl
 pw 55 rfp
 pv 4.700 lp
 DECOUPLER H1
 dn 0 wc
 dof 0 vs
 dm yy
 dm 34 th
 dmr 10056 ai
 dmf 2
 ph



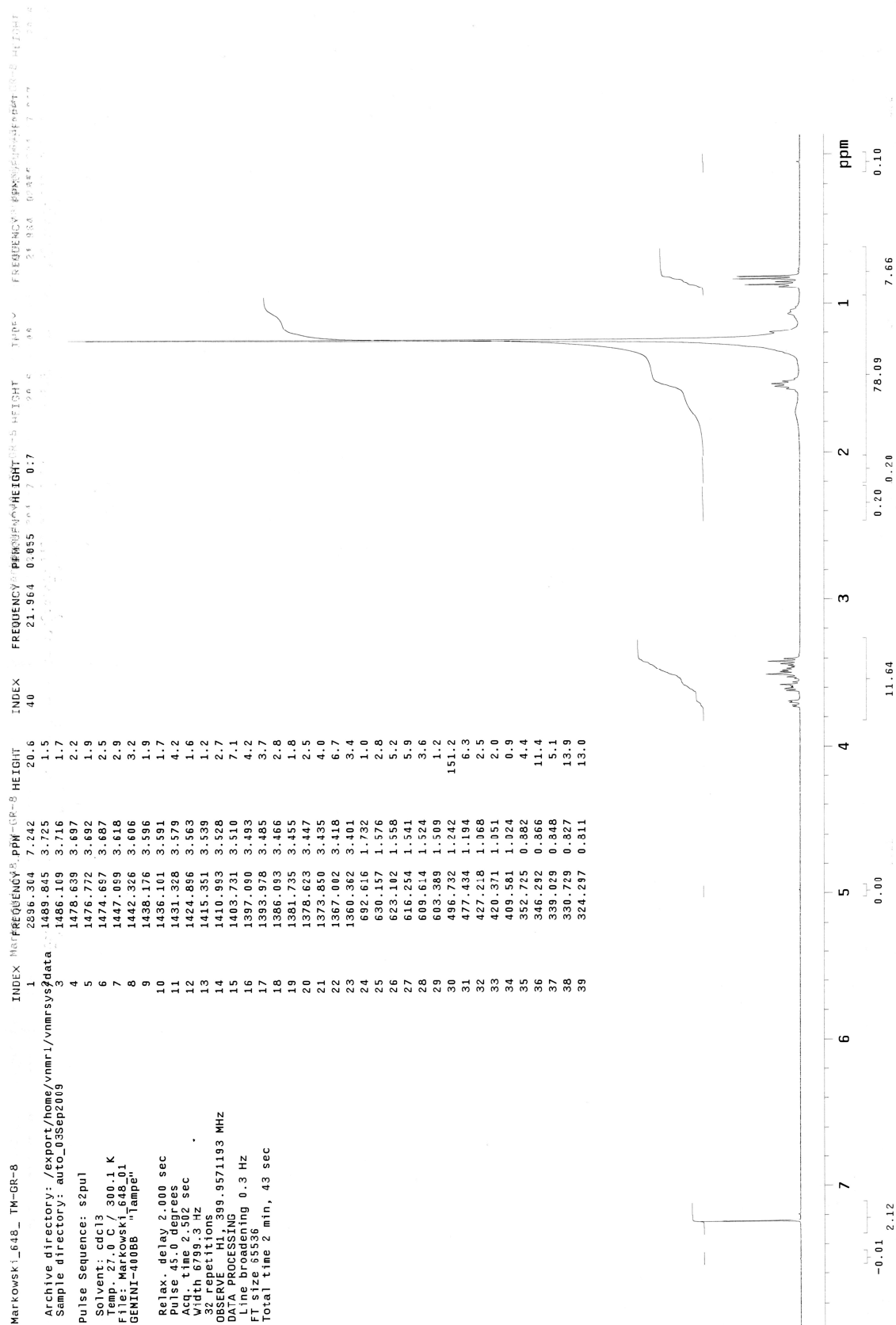
Compound 20a: ^1H NMR



Compound 20a: ^{13}C NMR



Compound 20b: ¹H NMR

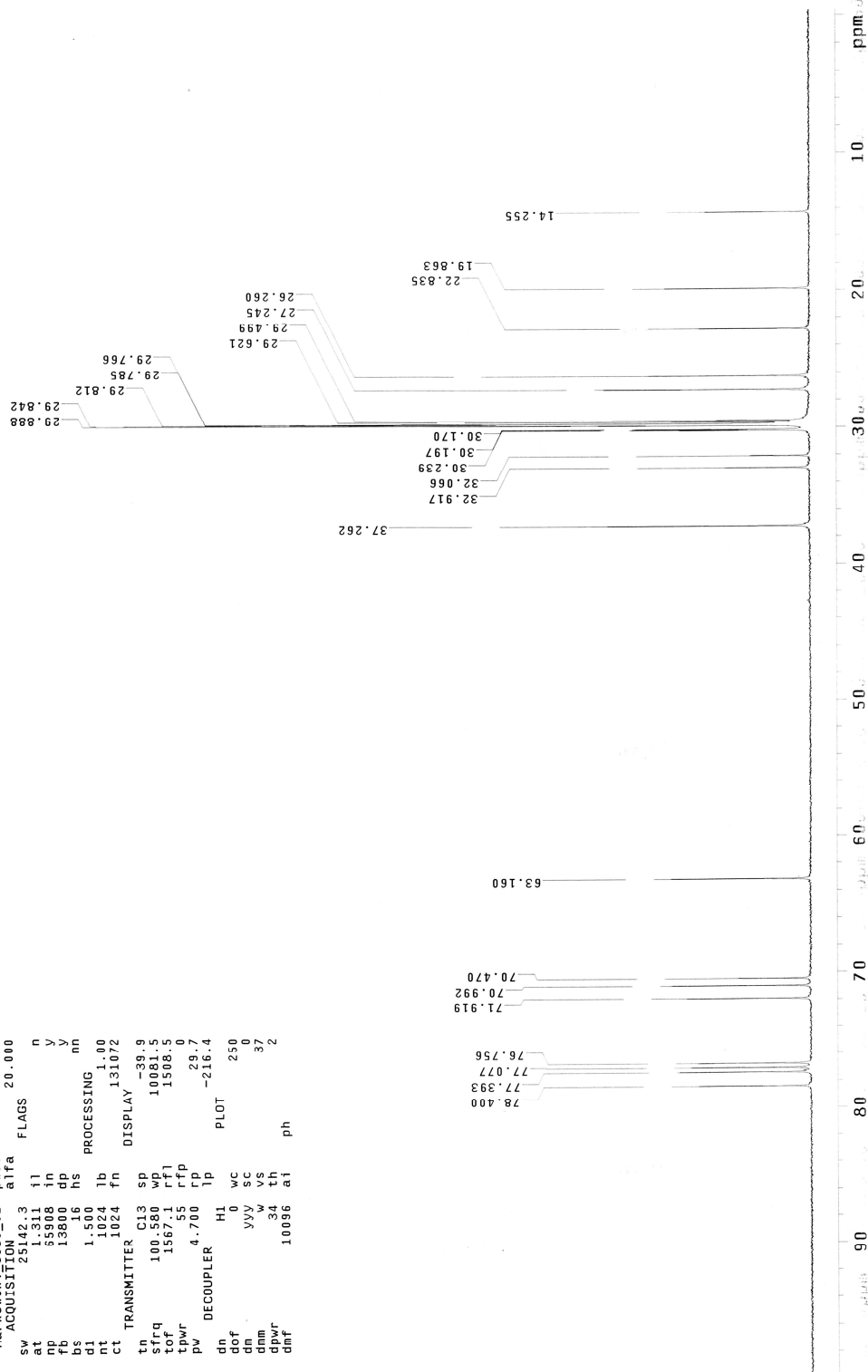


Compound 20b: ^{13}C NMR

Markowski_3980_TM-GR-8

```

exp1 szpul1
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date May 15 2009 temp 27.0
solvent not used
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vmr1/autos/15/~
Markowski_3980_01 hst 0.008
sv ACQUISIT 20.000
alifa 20.000
FLAGS
at 1.311 il n
np 55908 in y
fb 13800 dp y
bs 16 hs nn
d1 1.500 PROCESSING
nt 1024 lb 1.00
ct 1024 fn DISPLAY 131072
tn C13 SP -39.9
sfreq 100.580 wf 10081.5
cor 156745 fl 1508.5
tpwr 4.700 rfp 29.7
pv DECOUPLER lp -216.4
dn H1 PLOT
dof 0 wc 250
dn yyv sc 0
dnn w vs 37
dpwr 34 th 2
dmf 10096 ai ph
  
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Compound 20c: ¹H NMR

Markowski
TM-CR-5a
Nr. 2180

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 27.0 C / 300.1 K

GEMINI-400BB "1ampe"

Relax. delay 2.000 sec

Pulse 45.0 degrees

Acq. time 2.502 sec

Width 6799.3 Hz

32 repetitions

OBSERVE H1, 399.9571193 MHz

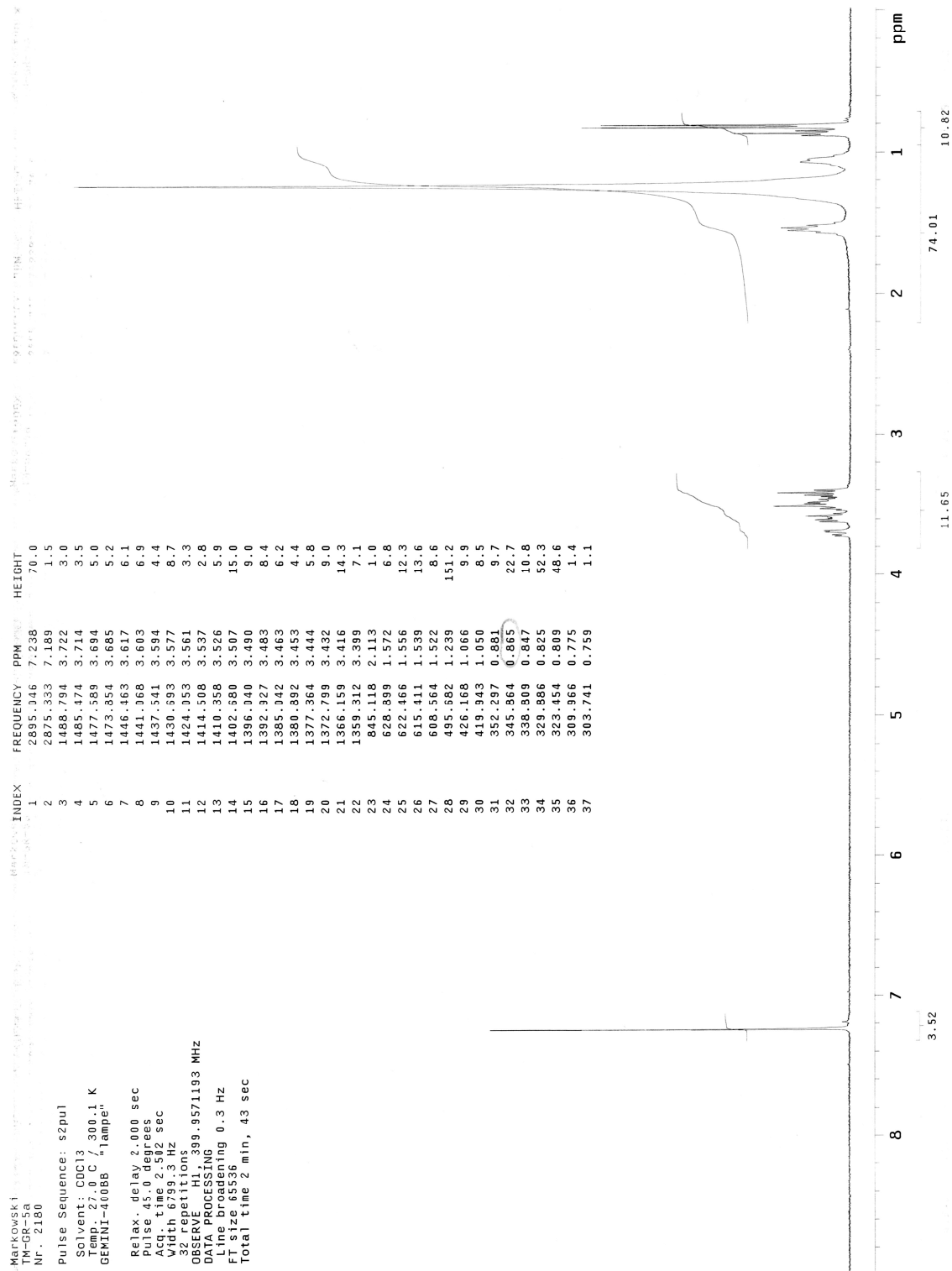
DATA PROCESSING

Line broadening 0.3 Hz

FT size 83396

Total time 2 min, 43 sec

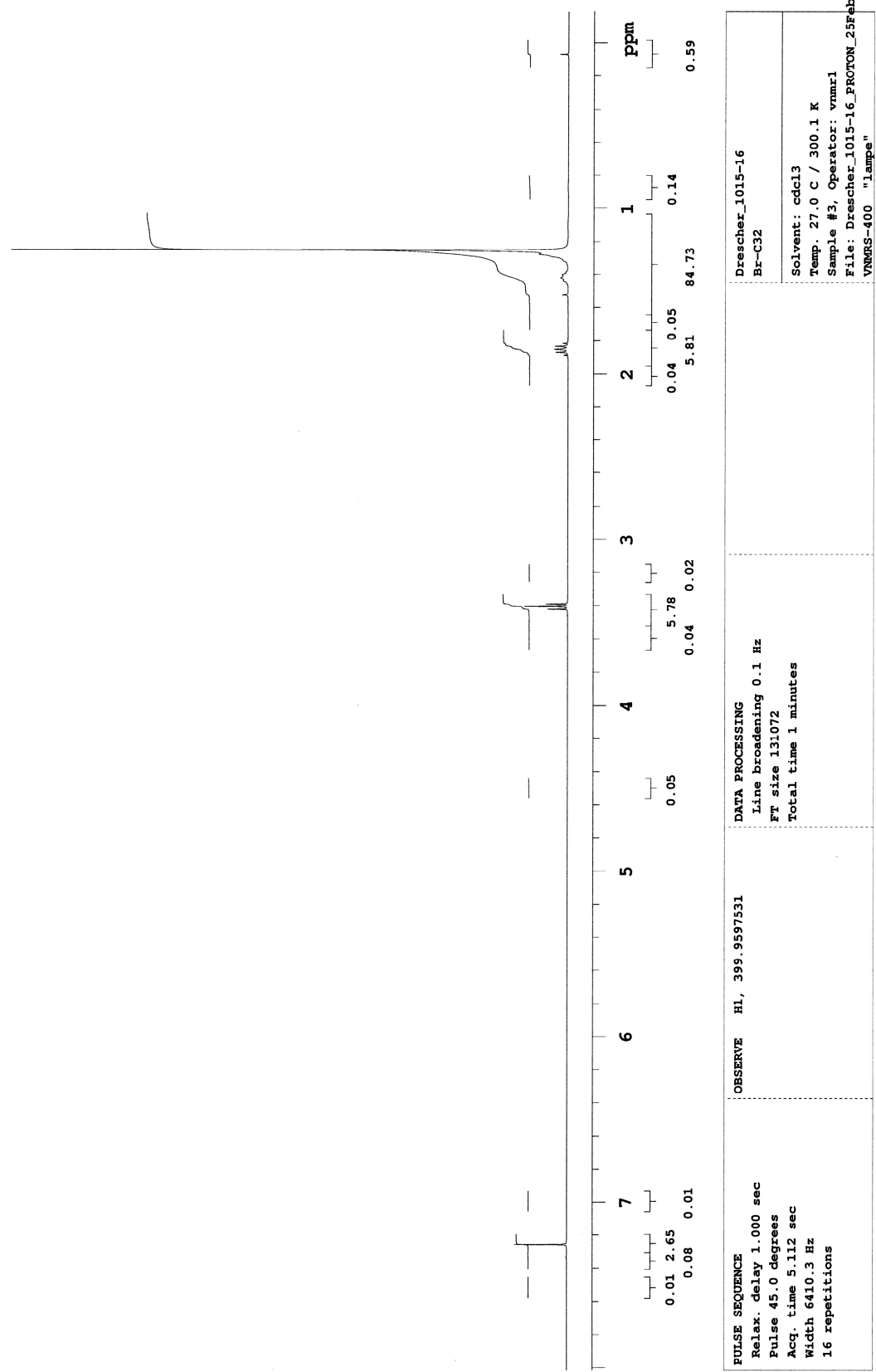
INDEX	FREQUENCY - PPM	HEIGHT
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2	2875.333 7.189	1.5
3	1488.794 3.722	3.0
4	1485.474 3.714	3.5
5	1477.589 3.694	5.0
6	1473.854 3.685	5.2
7	1446.463 3.617	6.1
8	1441.368 3.603	6.9
9	1437.541 3.594	4.4
10	1430.593 3.577	8.7
11	1424.053 3.561	3.3
12	1414.508 3.537	2.8
13	1410.358 3.526	5.9
14	1402.580 3.507	15.0
15	1396.040 3.490	9.0
16	1392.327 3.483	8.4
17	1385.042 3.463	6.2
18	1380.892 3.453	4.4
19	1377.364 3.444	5.8
20	1372.799 3.432	9.0
21	1366.159 3.416	14.3
22	1359.312 3.399	7.1
23	845.118 2.113	1.0
24	628.899 1.572	6.8
25	622.466 1.556	12.3
26	615.411 1.539	13.6
27	608.564 1.522	8.6
28	495.582 1.239	151.2
29	426.168 1.066	9.9
30	419.943 1.050	8.5
31	352.297 0.881	9.7
32	345.864 0.865	22.7
33	338.809 0.847	10.8
34	329.586 0.825	52.3
35	323.454 0.809	48.6
36	309.966 0.775	1.4
37	303.741 0.759	1.1



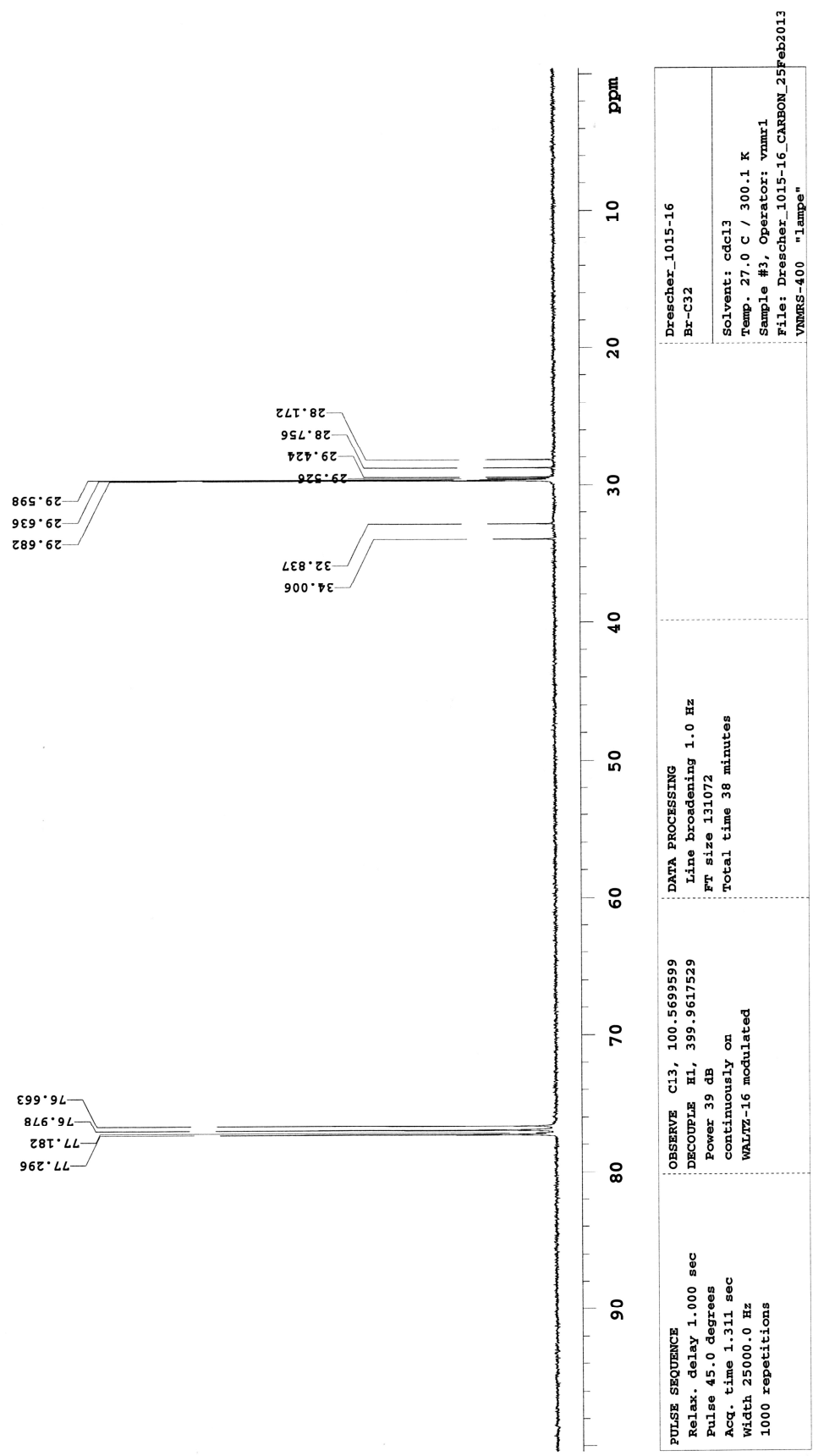
2000



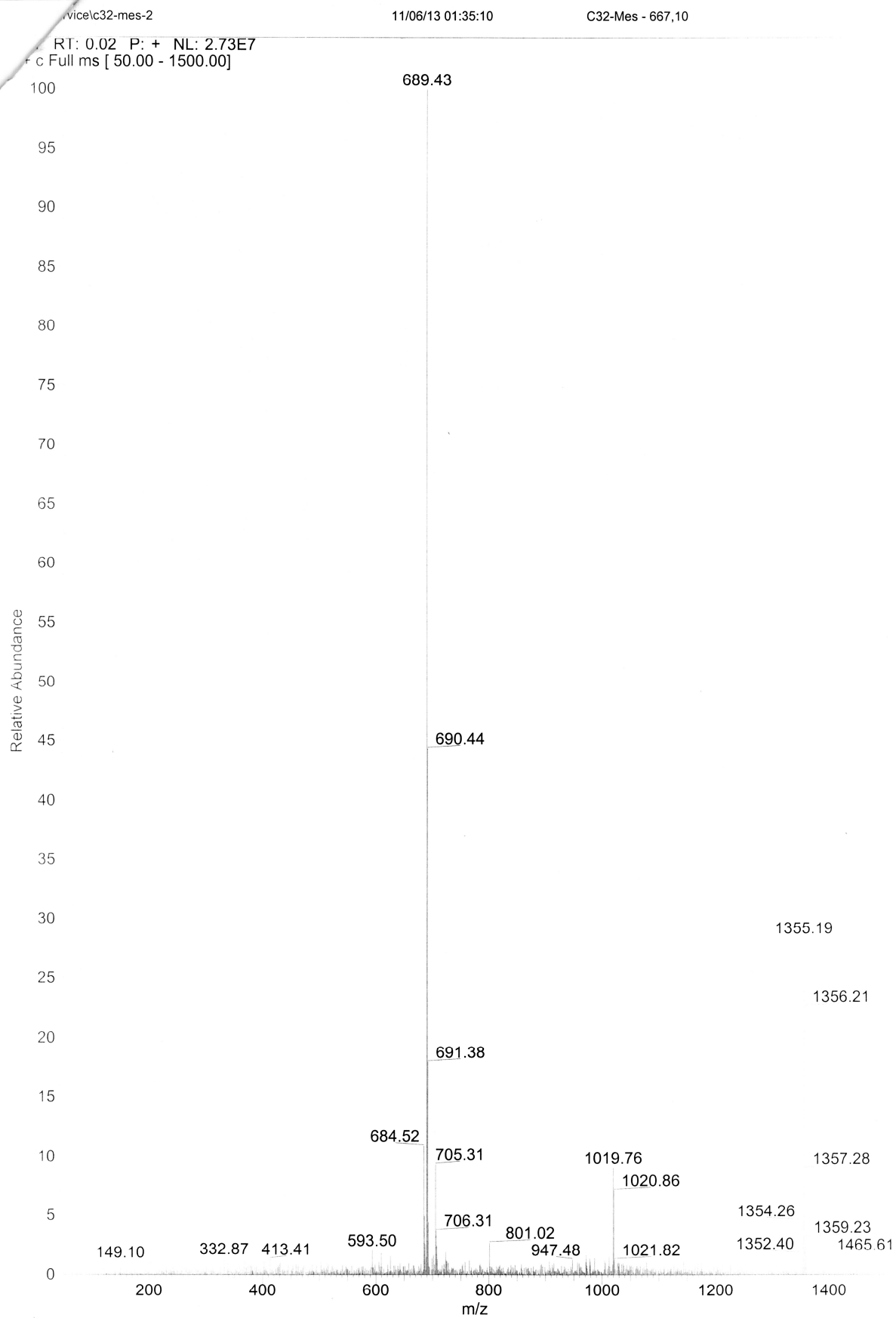
Compound 22a: ¹H NMR



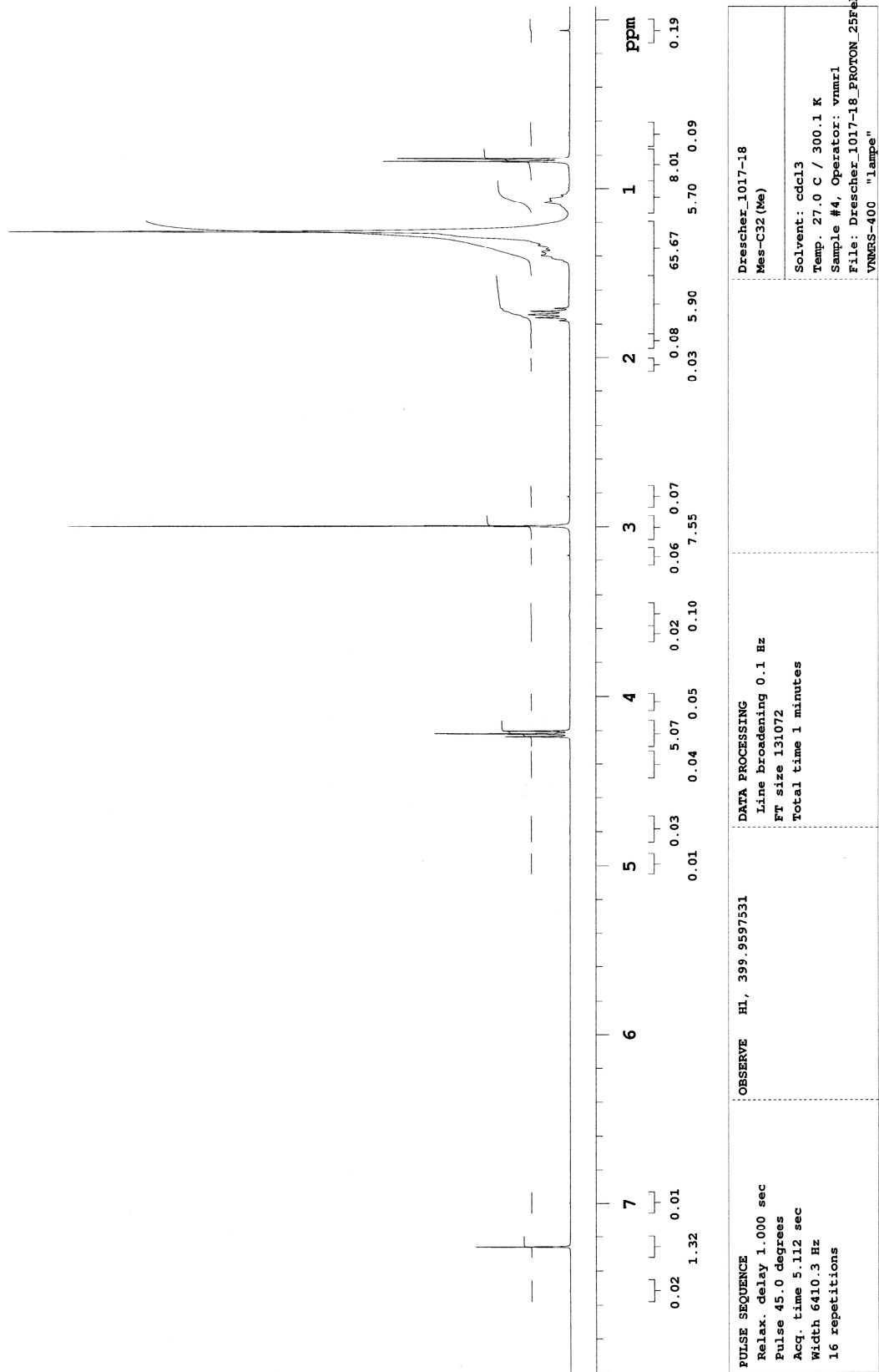
Compound 22a: ¹³C NMR



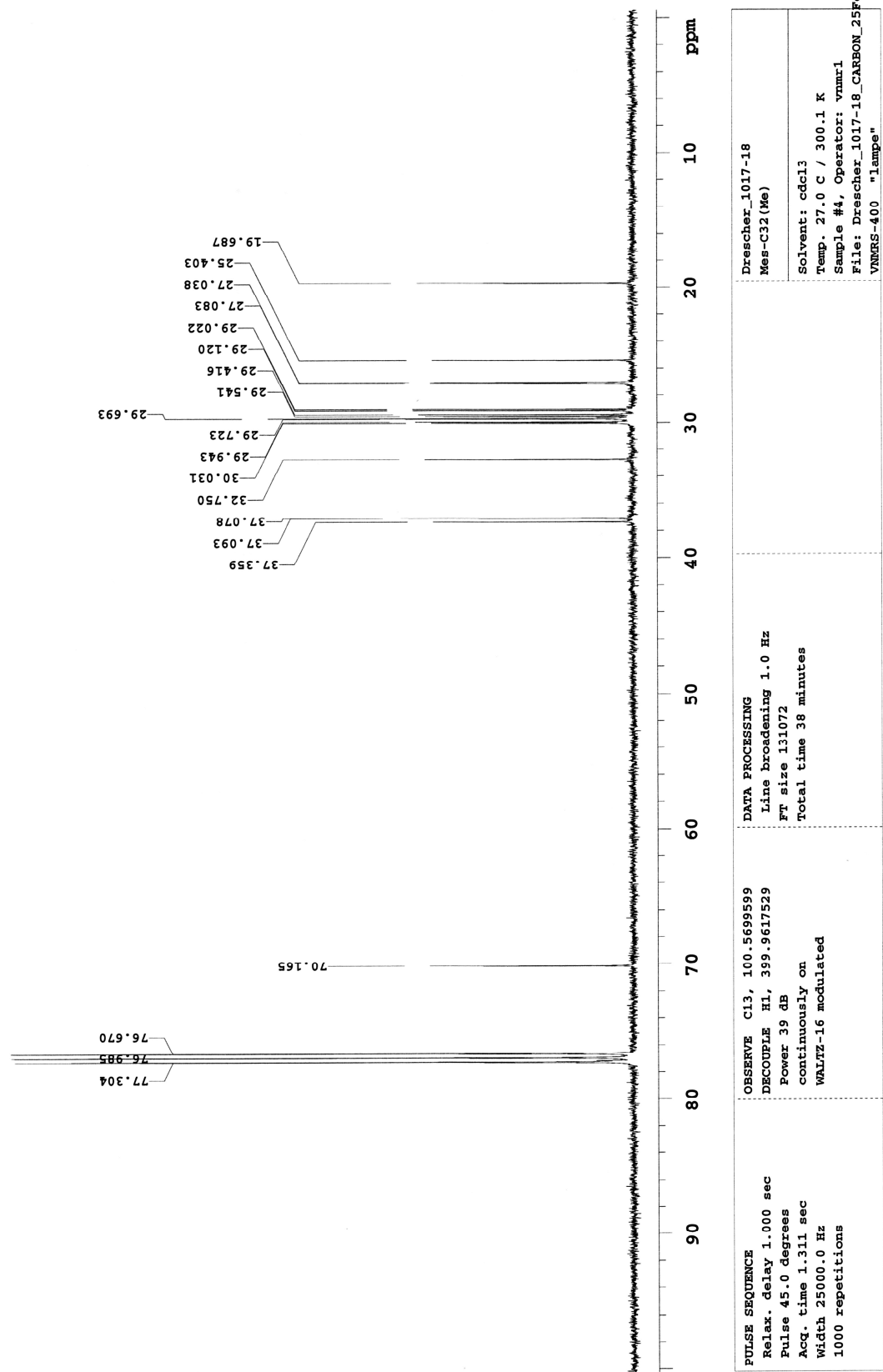
Compound 22b: ESI-MS, positive mode



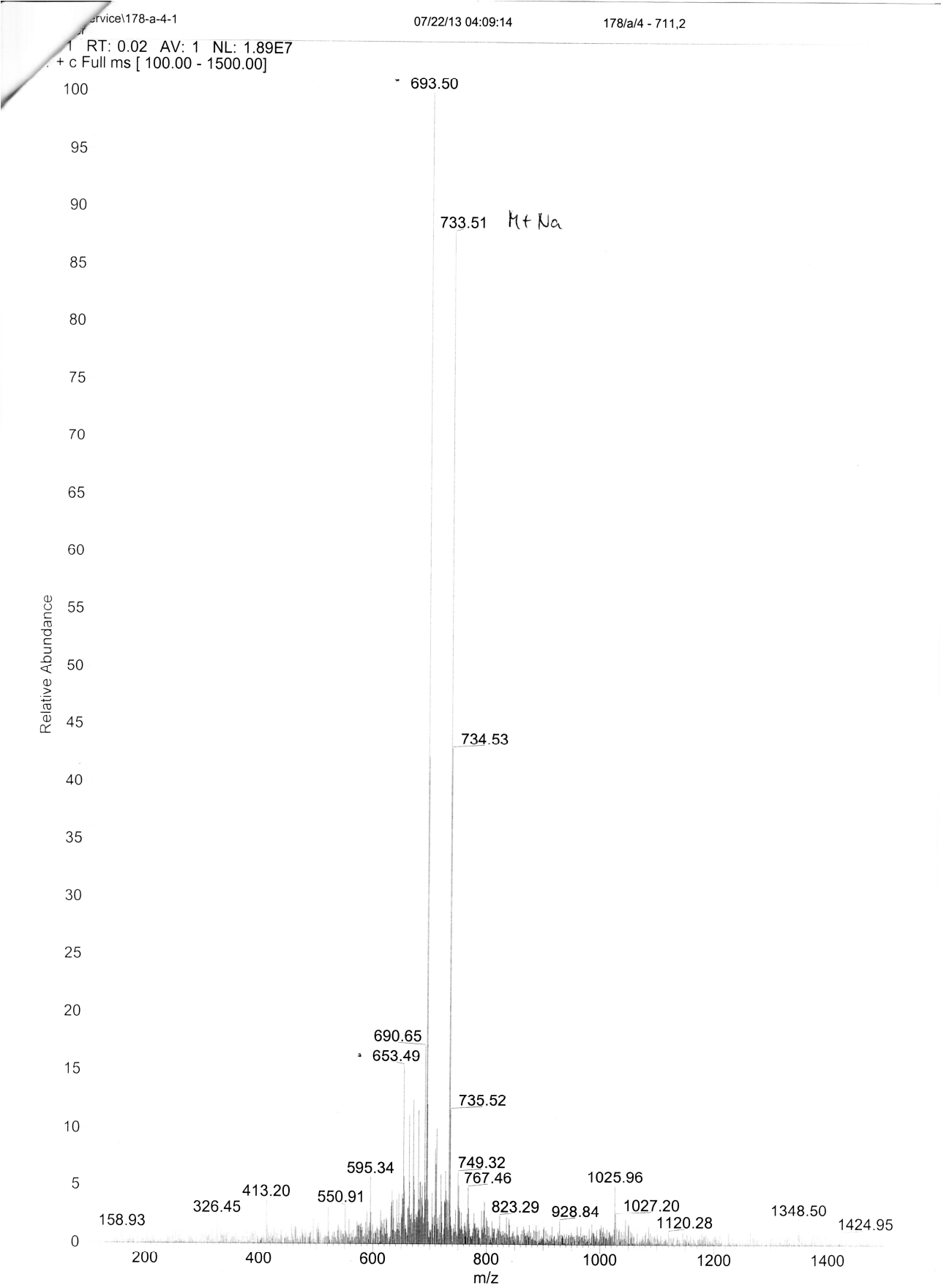
Compound 22b: ¹H NMR



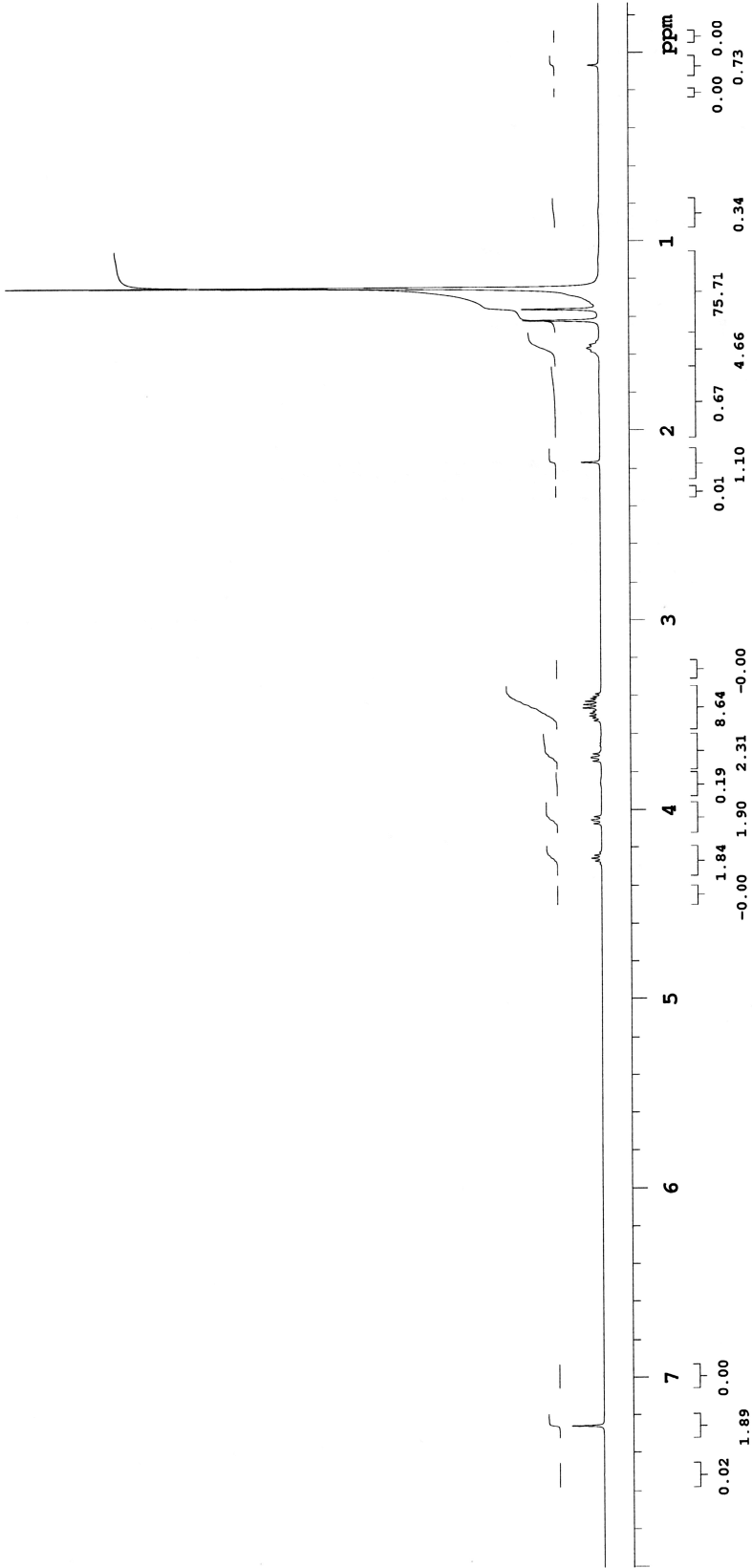
Compound 22b: ¹³C NMR



Compound **23a**: ESI-MS, positive mode

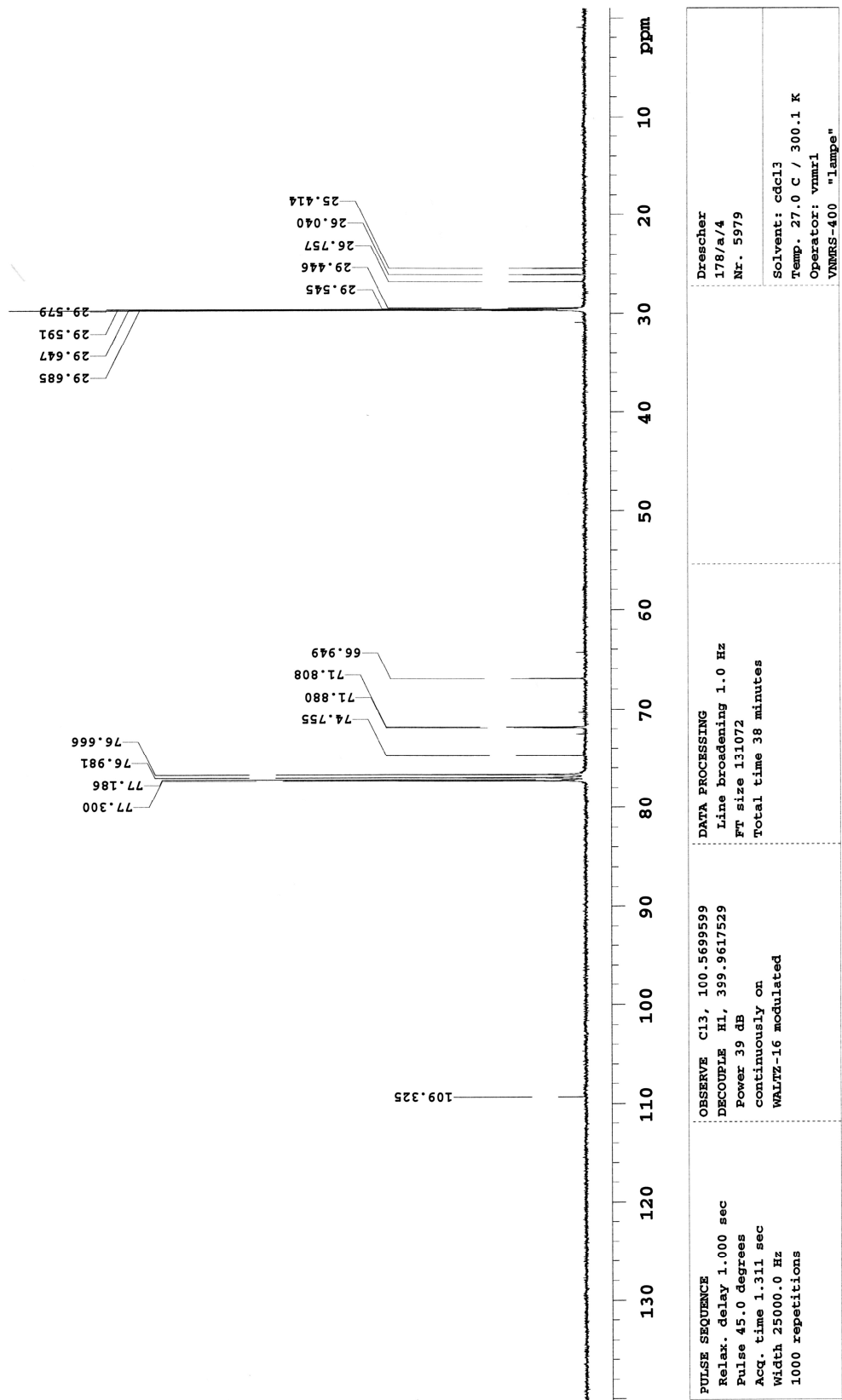


Compound 23a: ¹H NMR

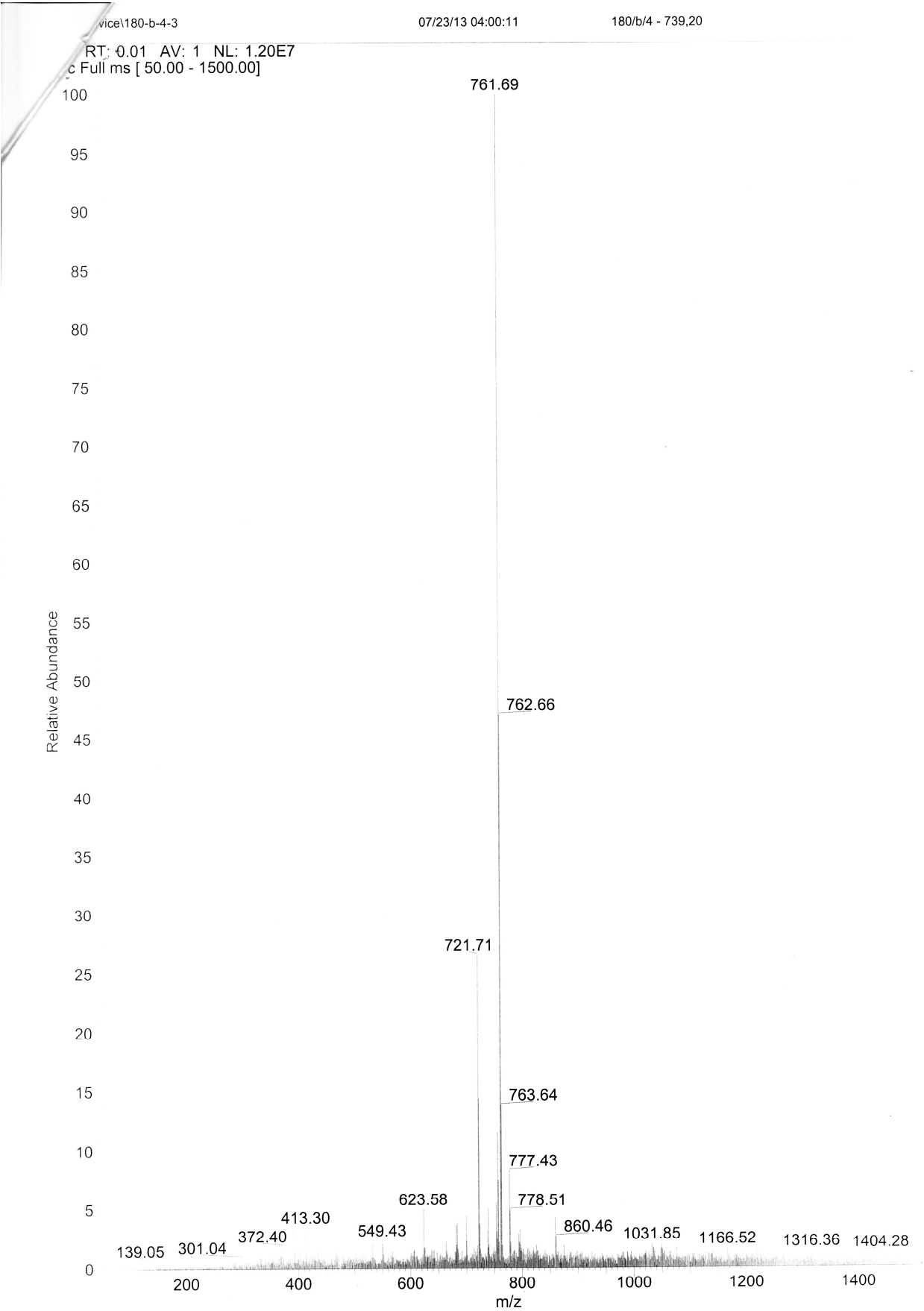


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 5.112 sec Width 6410.3 Hz 16 repetitions	OBSERVE H1, 399.9597531	DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 1 minutes	Drescher 178/a/4 Nr. 5978 Solvent: cdcl3 Temp. 27.0 C / 300.1 K Operator: vnmr1 VNMRS-400 "lampe"
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Compound 23a: ¹³C NMR



Compound **23b**: ESI-MS, positive mode

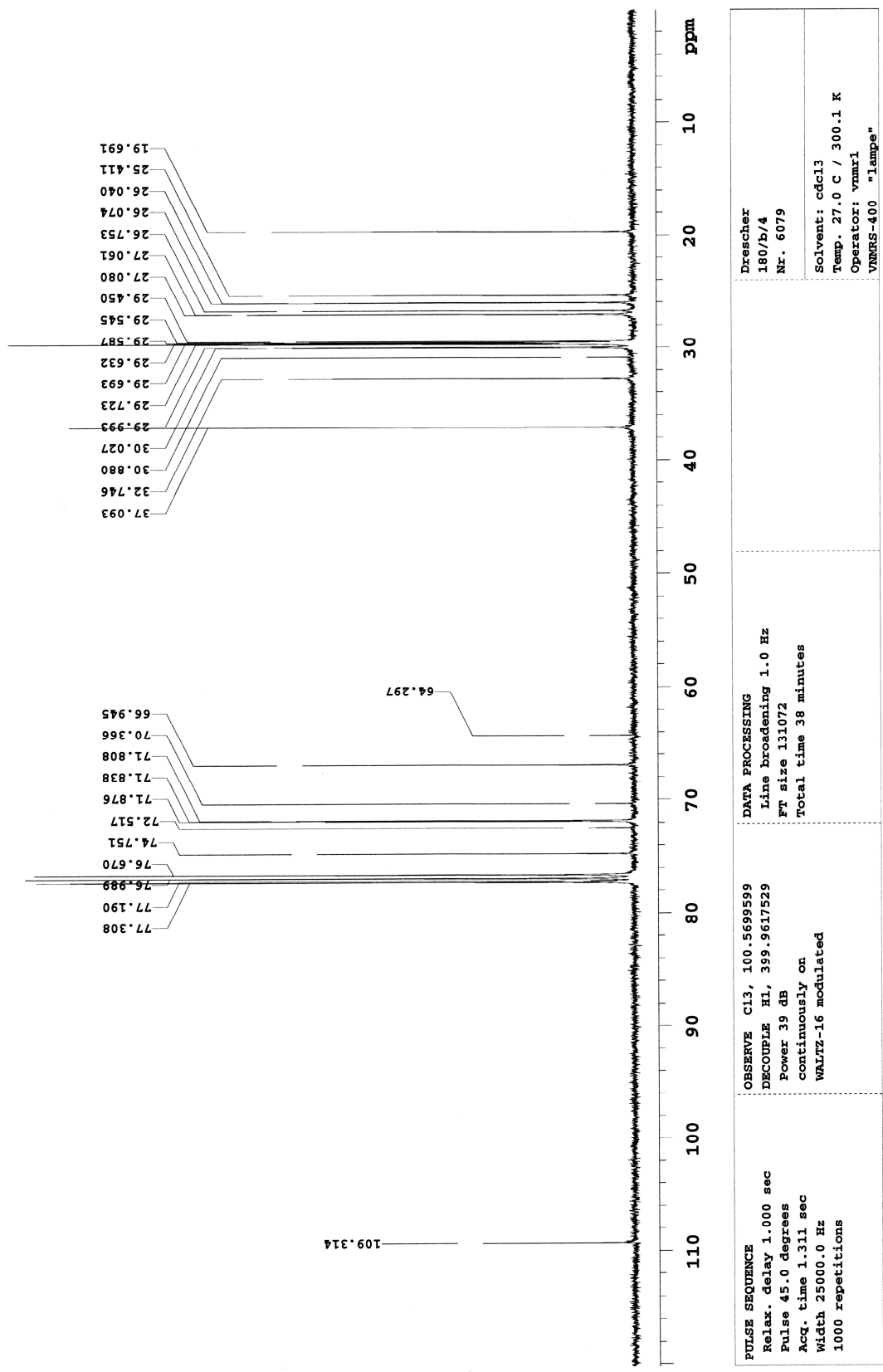


Compound 23b: ¹H NMR

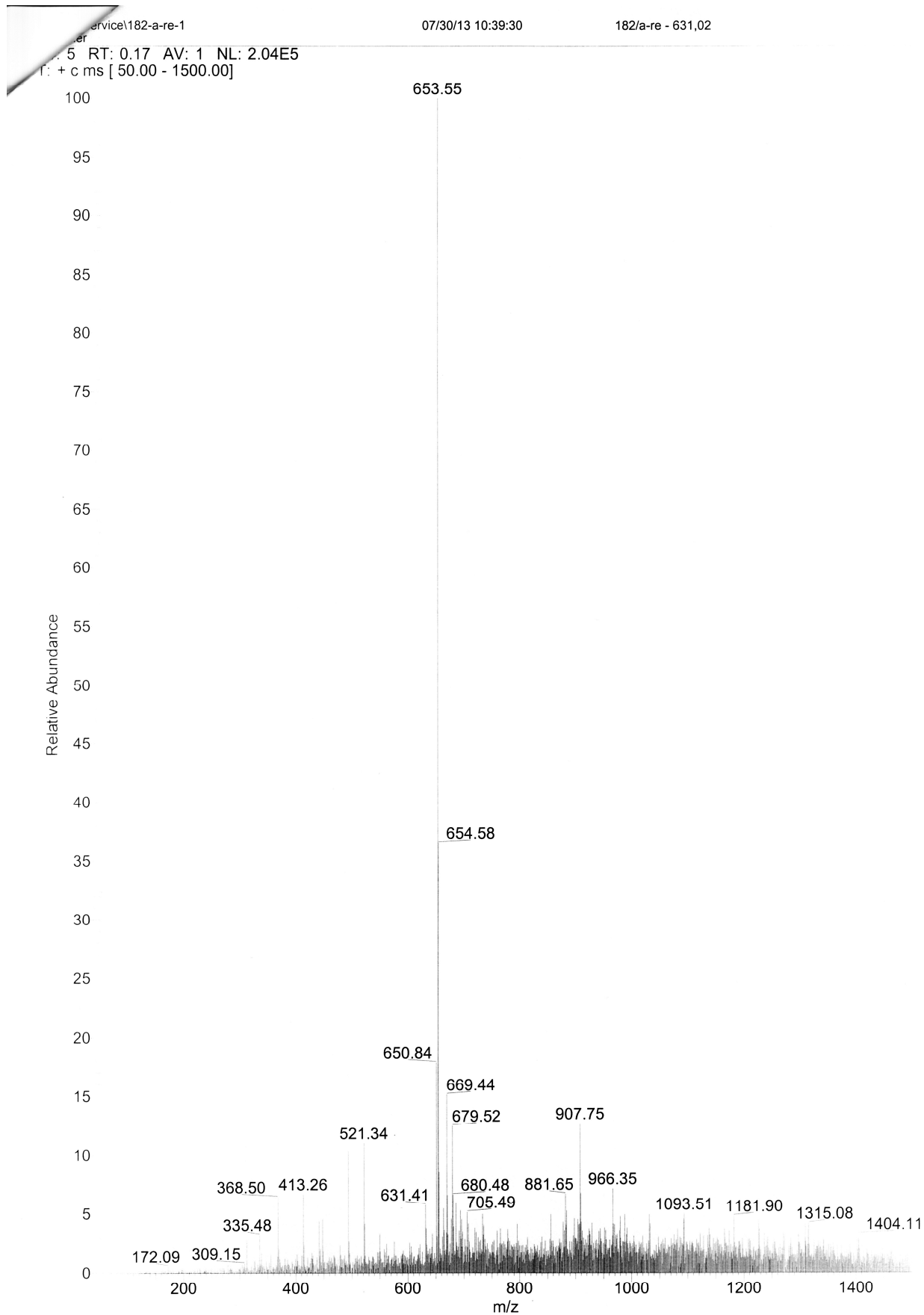


<div>PULSE SEQUENCE</div> <div>Relax. delay 1.000 sec</div> <div>Pulse 45.0 degrees</div> <div>Acq. time 5.112 sec</div> <div>Width 6410.3 Hz</div> <div>16 repetitions</div>	<div>OBSERVE</div> <div>H1, 399.9597531</div>	<div>DATA PROCESSING</div> <div>Line broadening 1.0 Hz</div> <div>FT size 131072</div> <div>Total time 1 minutes</div>	<div>Drescher</div> <div>180/b/4</div> <div>Nr. 6078</div> <div>Solvent: cdcl3</div> <div>Temp. 27.0 C / 300.1 K</div> <div>Operator: vnmr1</div> <div>VNMRS-400 "lampe"</div>
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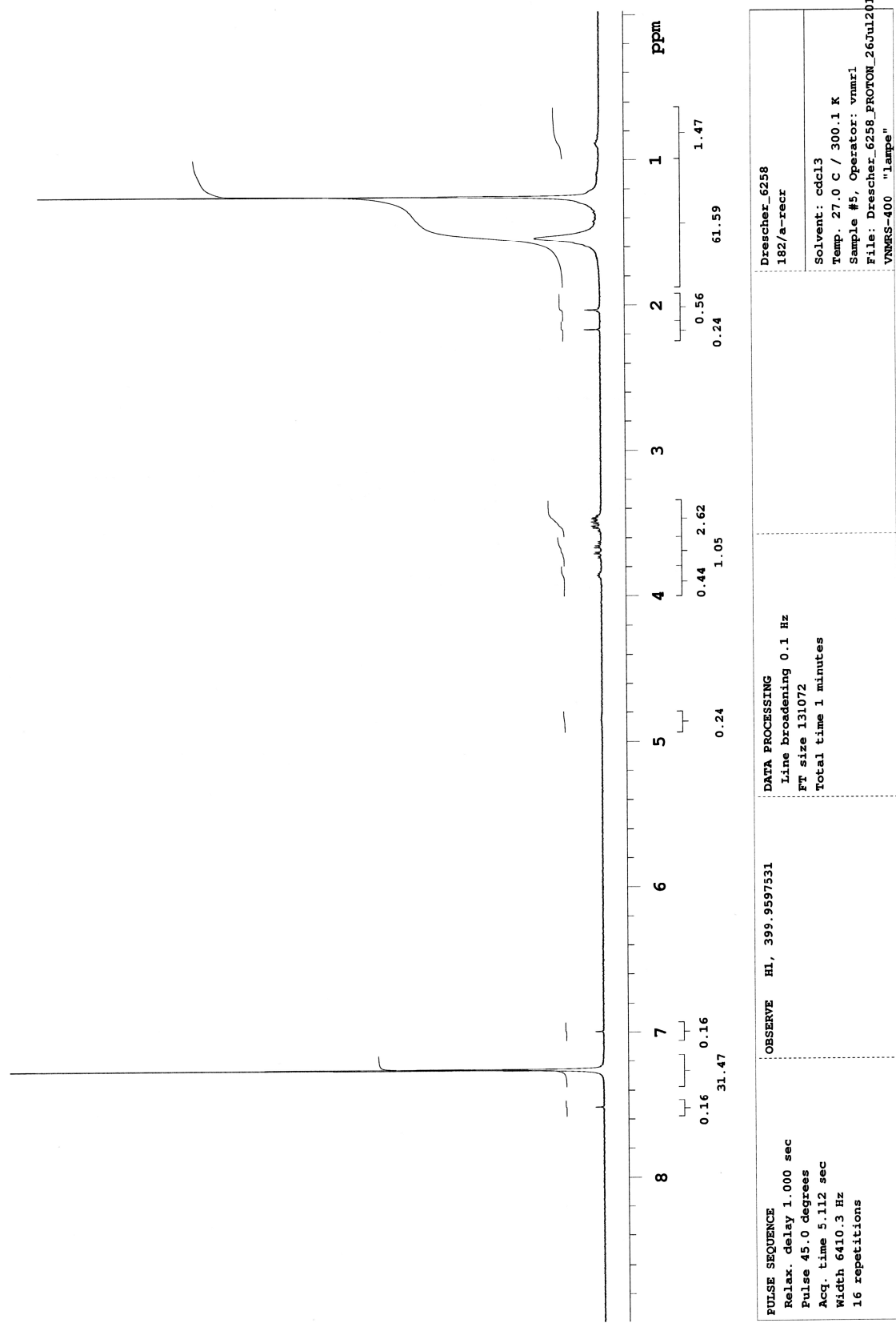
Compound 23b: ¹³C NMR



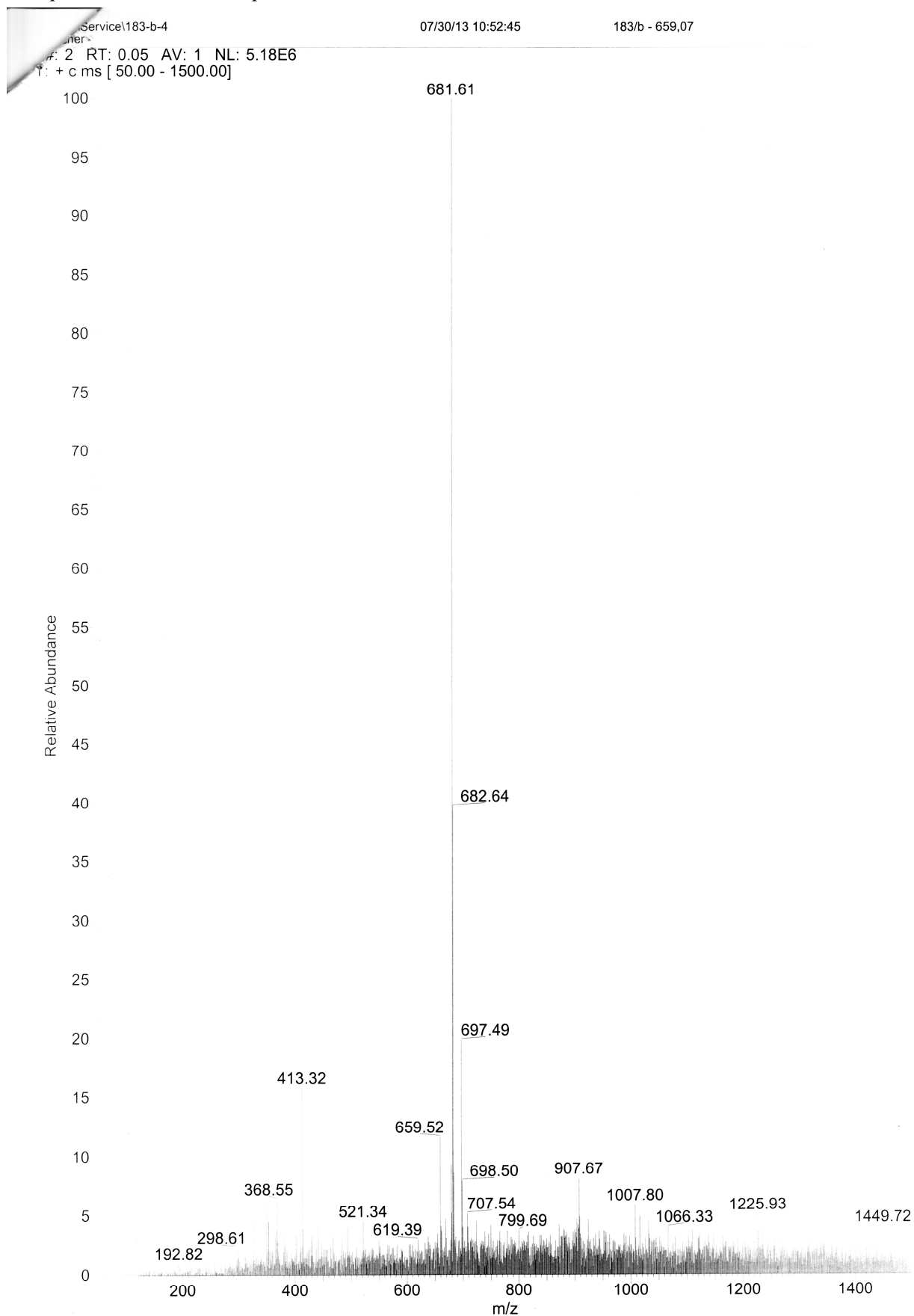
Compound **24a**: ESI-MS, positive mode



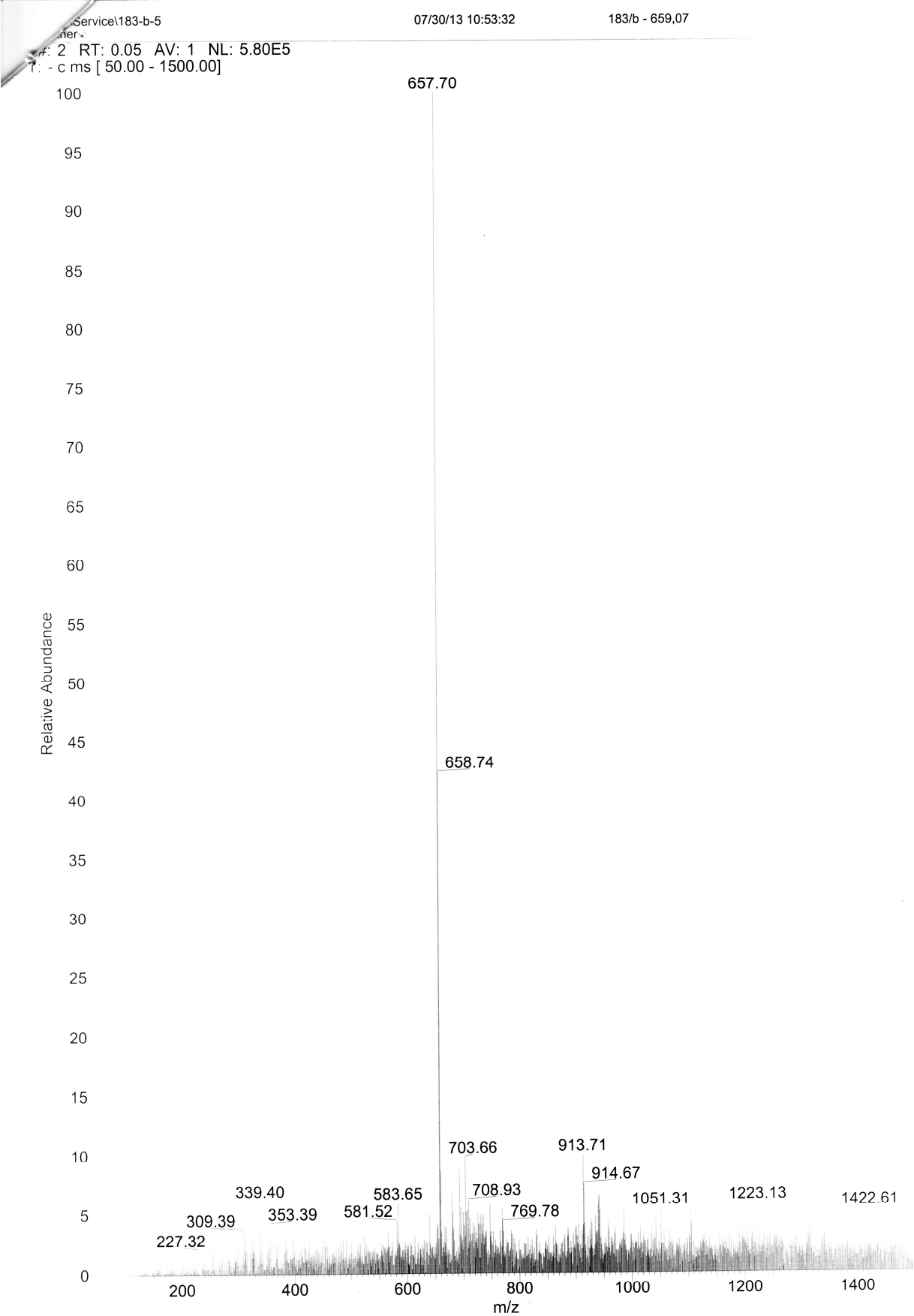
Compound 24a: ¹H NMR



Compound 24b: ESI-MS, positive mode

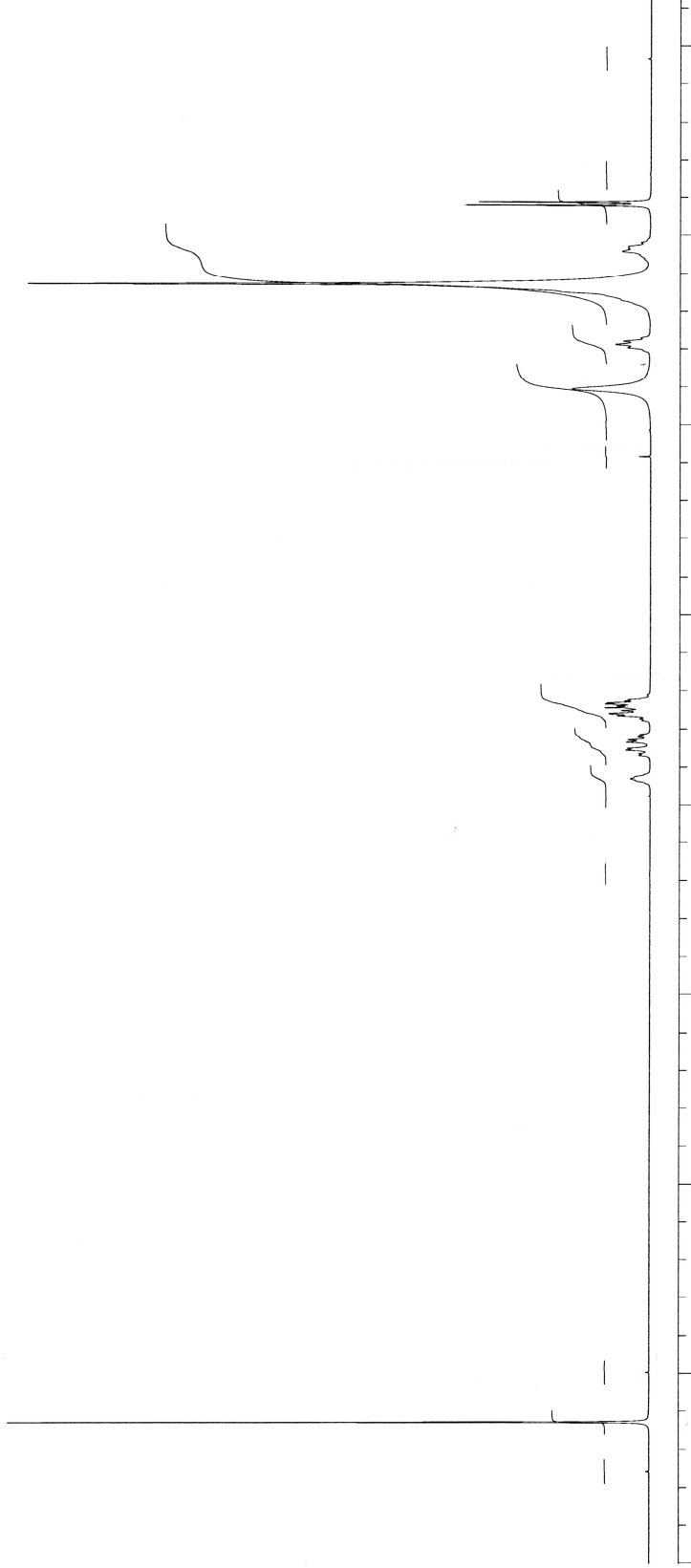


Compound **24b**: ESI-MS, negative mode



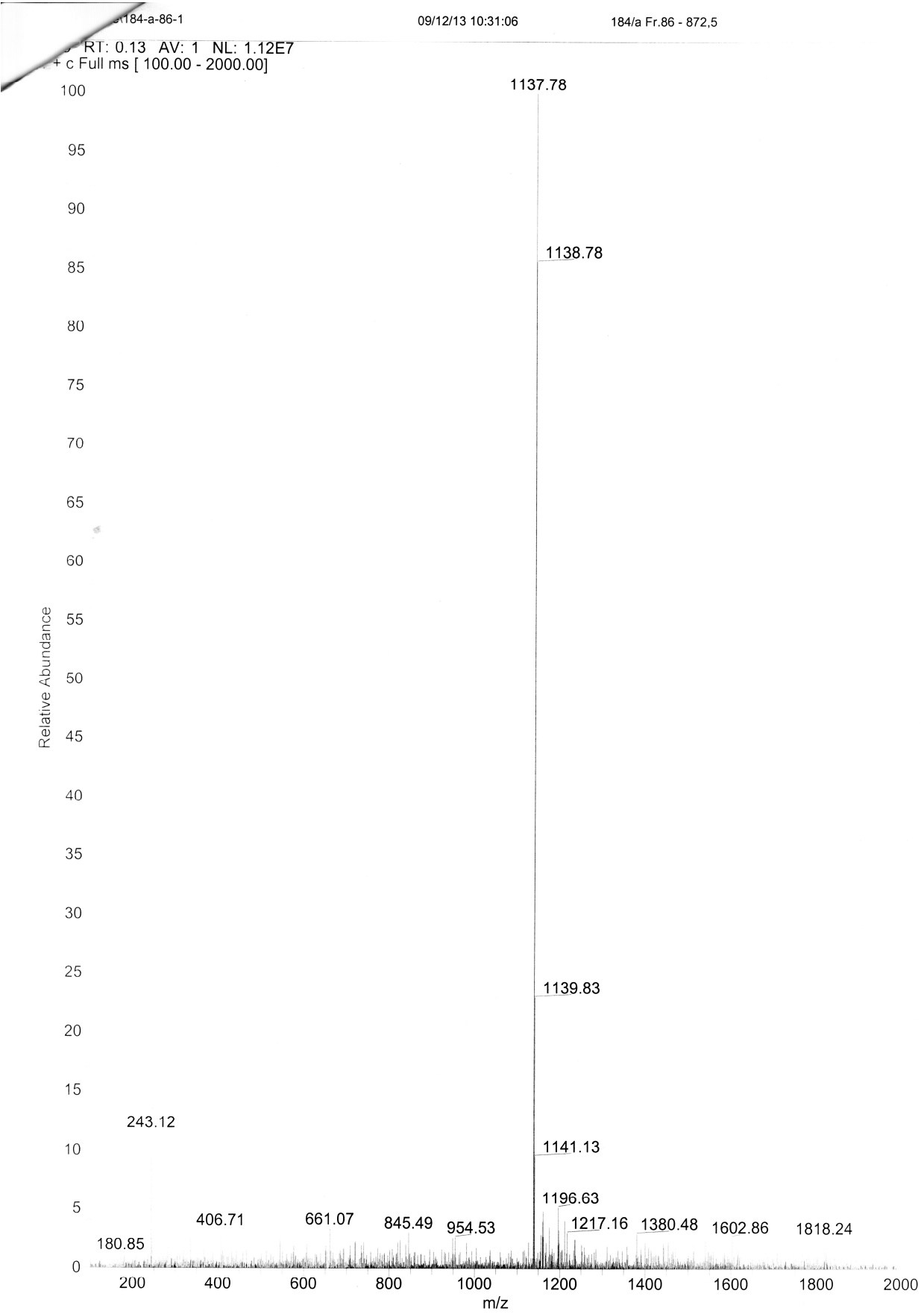
Compound 24b: ¹H NMR

Vorstufe
Netzgeräts

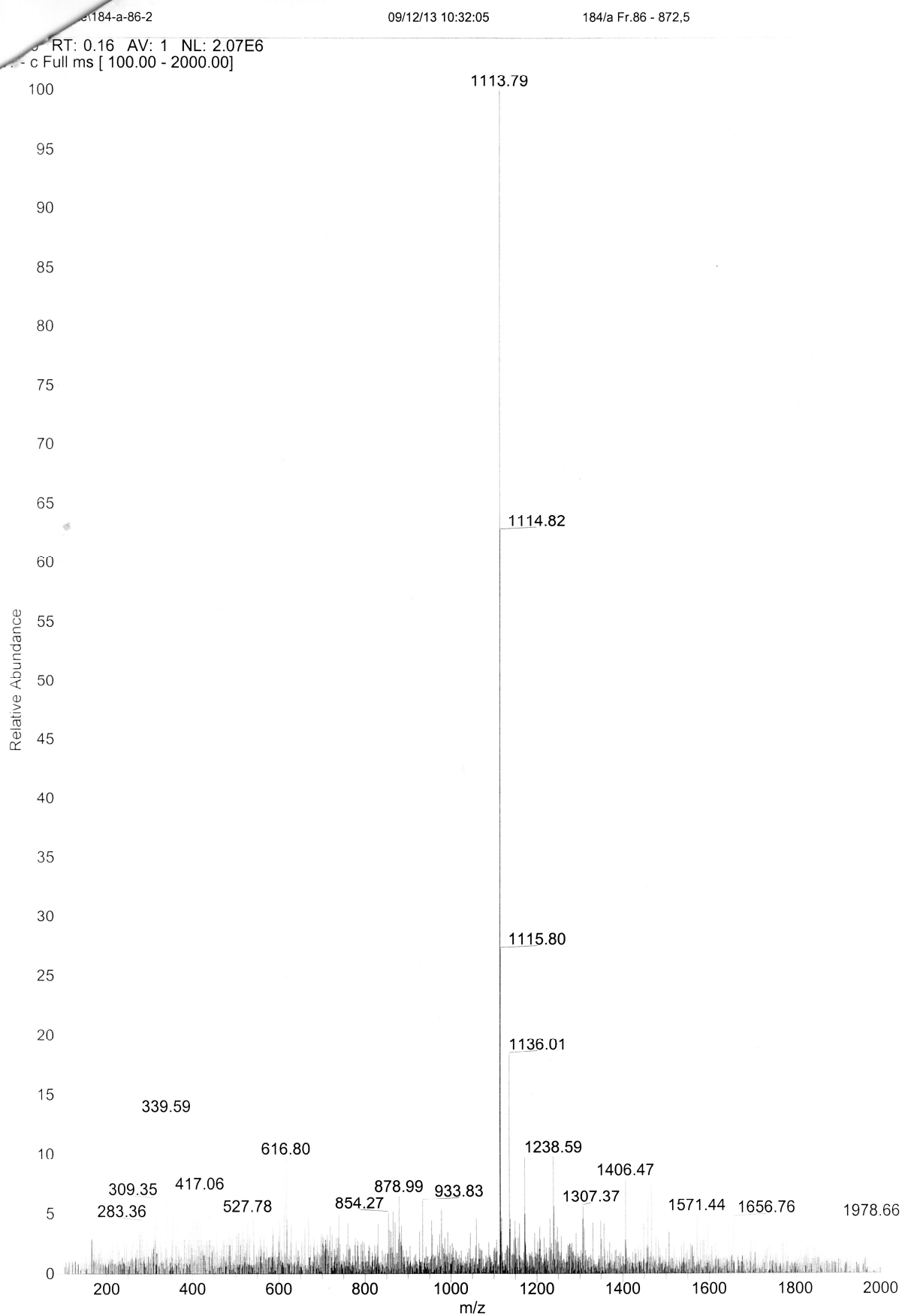


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 5.112 sec Width 6410.3 Hz 16 repetitions	OBSERVE H1, 399.9597531	DATA PROCESSING Line broadening 0.1 Hz FT size 131072 Total time 1 minutes	Drescher_6259 183/b Solvent: cdcl3 Temp. 27.0 C / 300.1 K Sample #6, Operator: vnmr1 File: Drescher_6259_PROTON_26Jul2013_01 VNMR5-400 "lampe"
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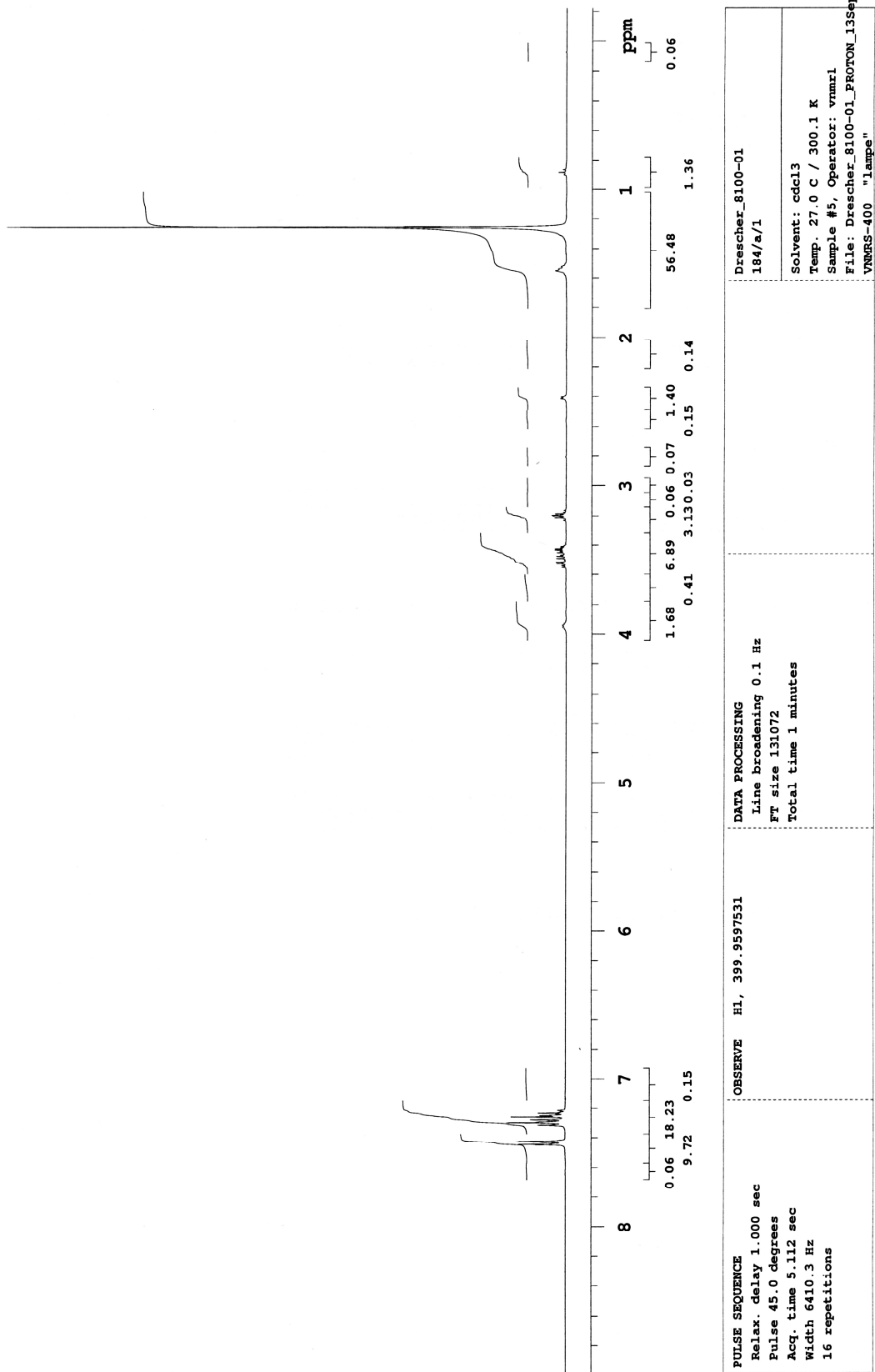
Compound 25a: ESI-MS, positive mode



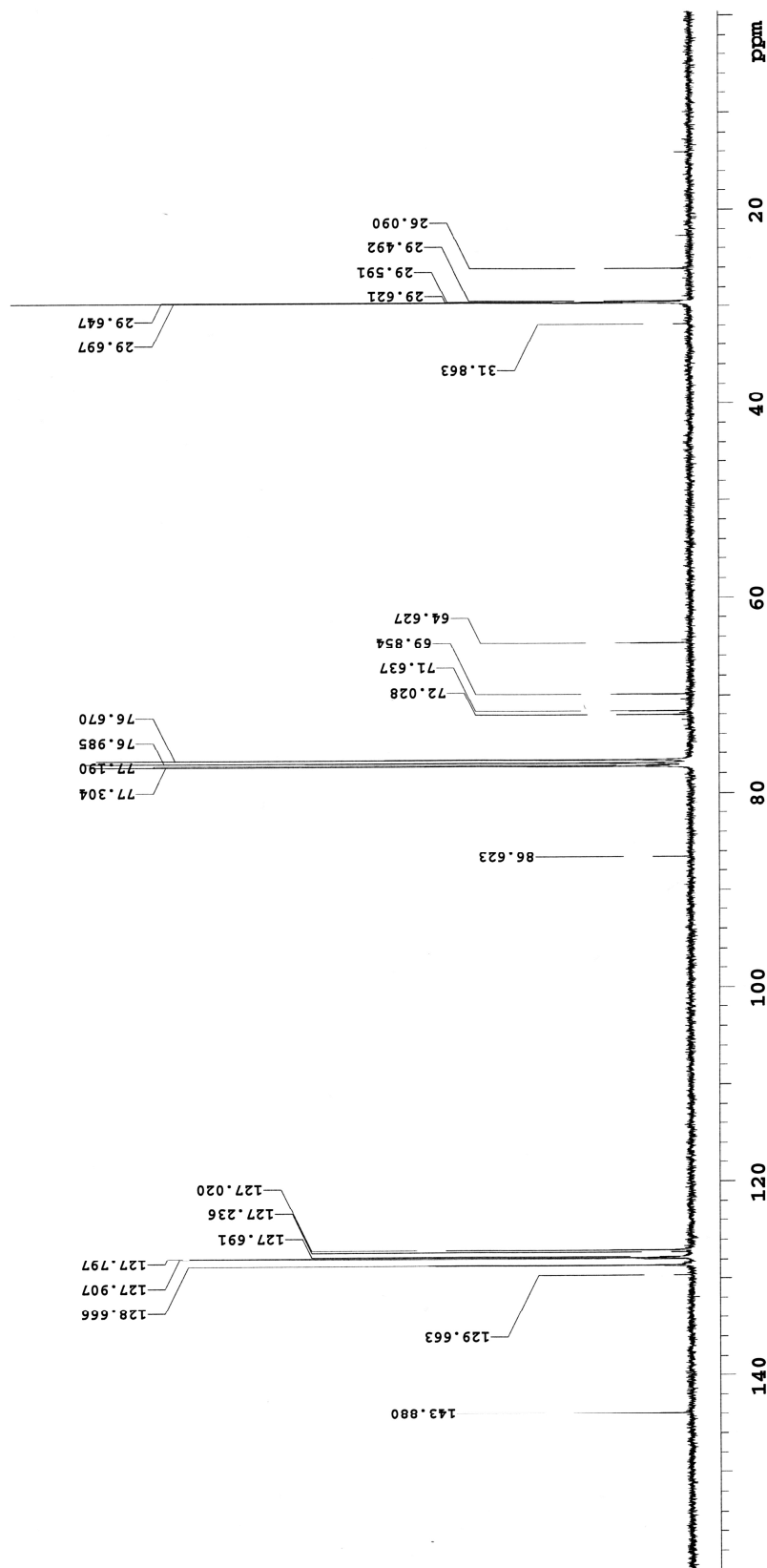
Compound 25a: ESI-MS, negative mode



Compound 25a: ¹H NMR

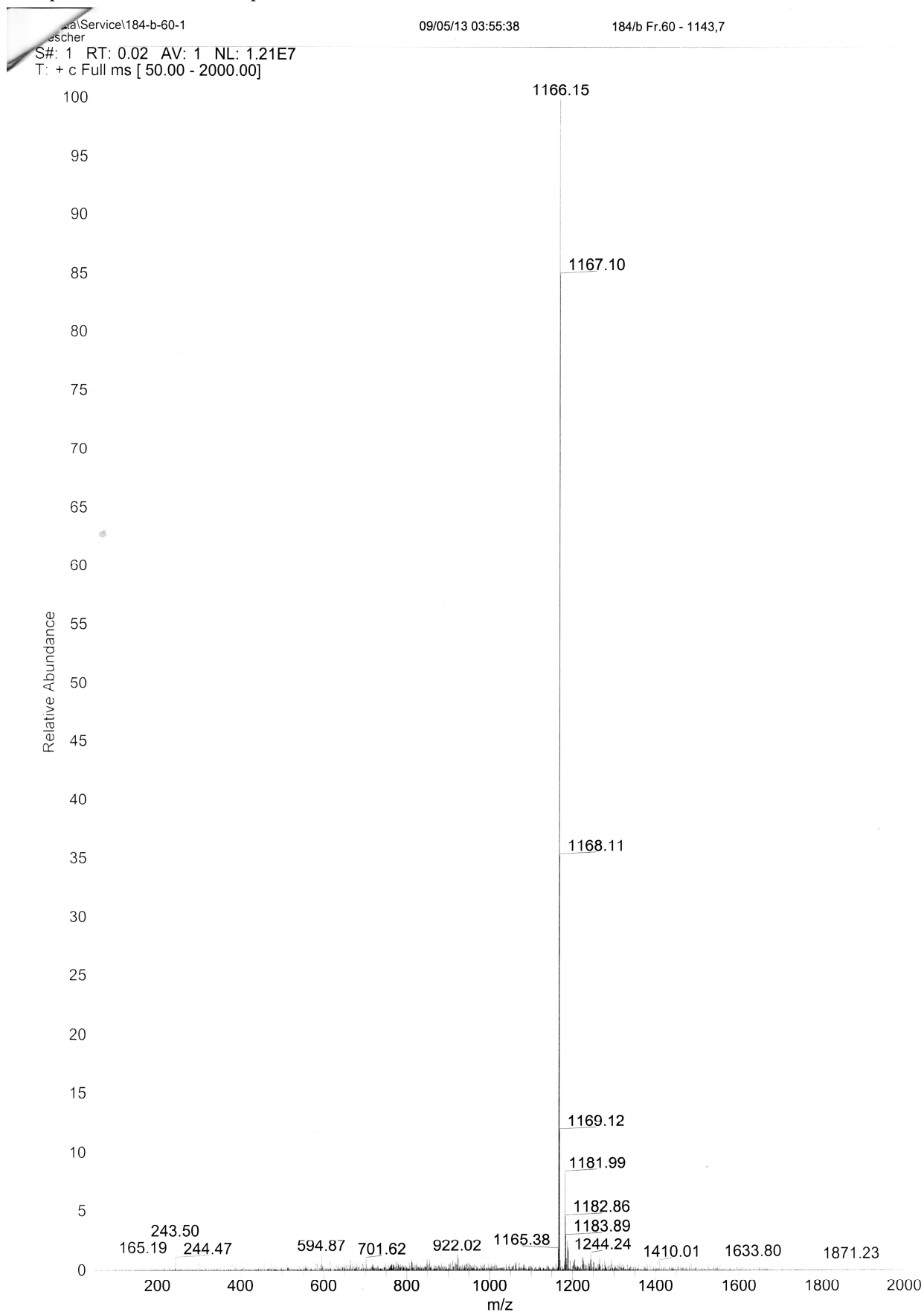


Compound 25a: ^{13}C NMR

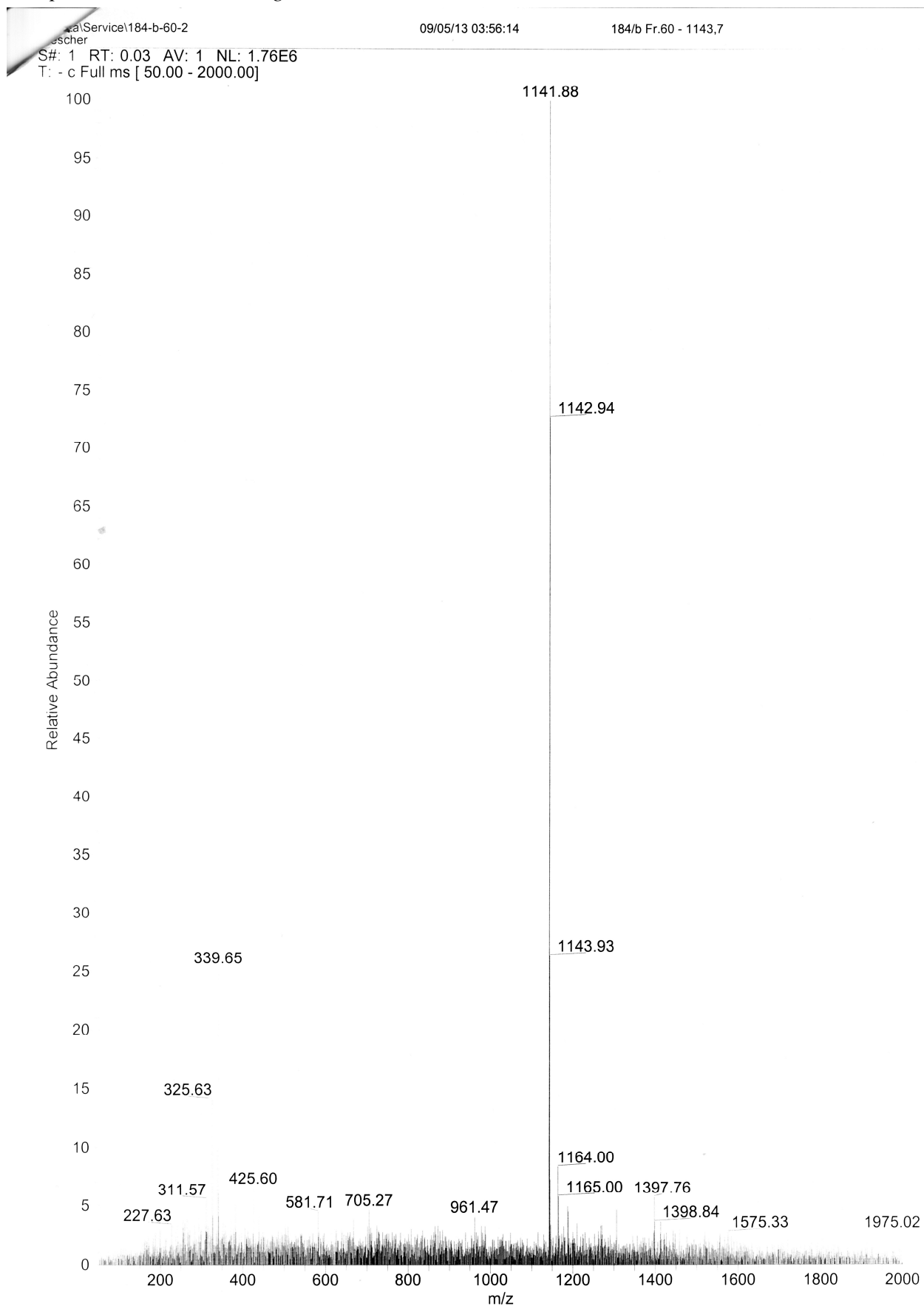


<p>PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.311 sec Width 25000.0 Hz 1000 repetitions</p>	<p>OBSERVE C13, 100.5699599 DECOUPLE H1, 399.9617529 Power 39 dB continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 1.0 Hz Ft size 131072 Total time 38 minutes</p>	<p>Drescher_8100-01 184/a/1 Solvent: cdcl3 Temp. 27.0 C / 300.1 K Sample #5, Operator: vnmr1 File: Drescher_8100-01_CARBON_13Sep2013 VNMR5-400 "lampe"</p>
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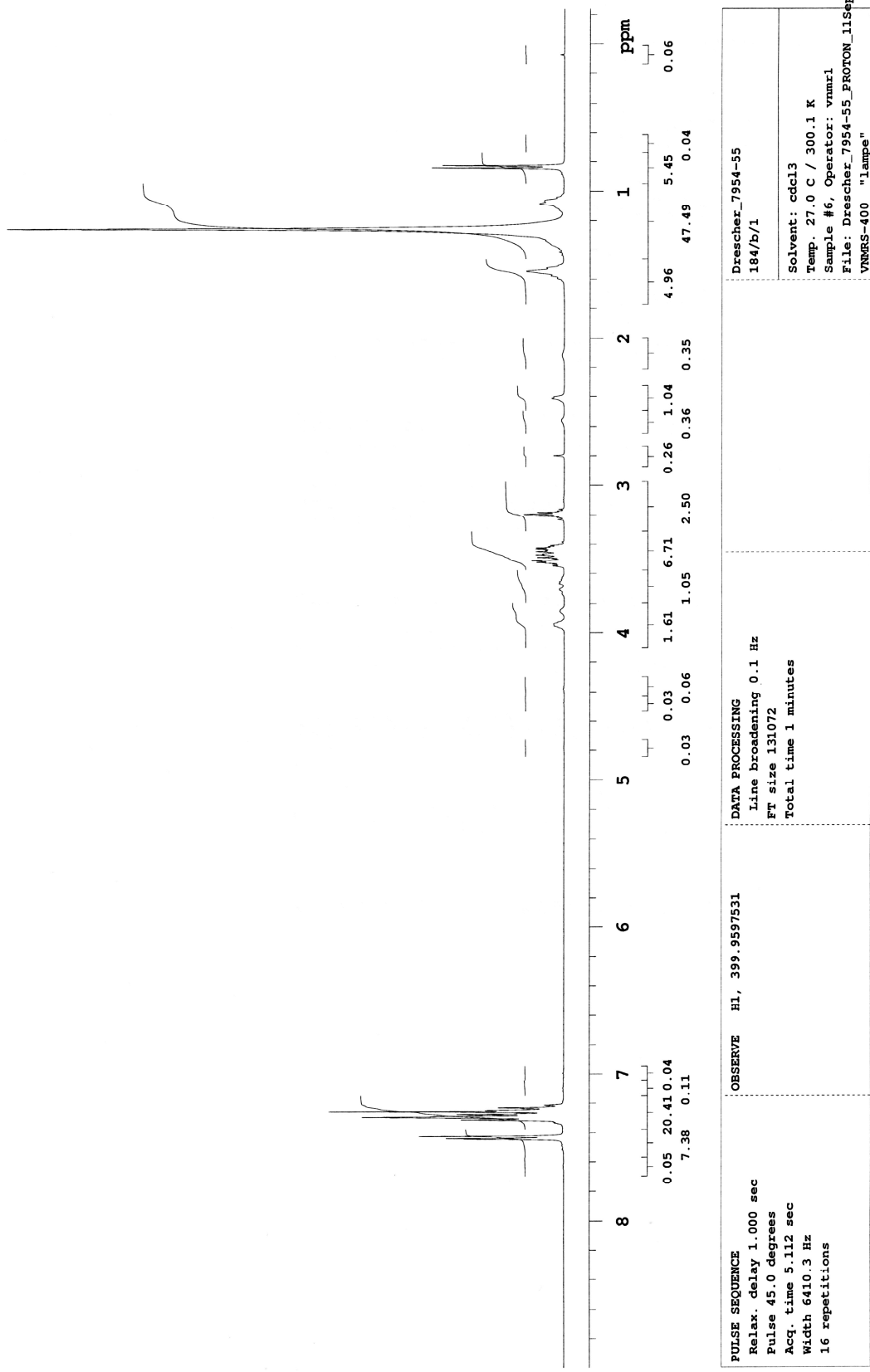
Compound **25b**: ESI-MS, positive mode



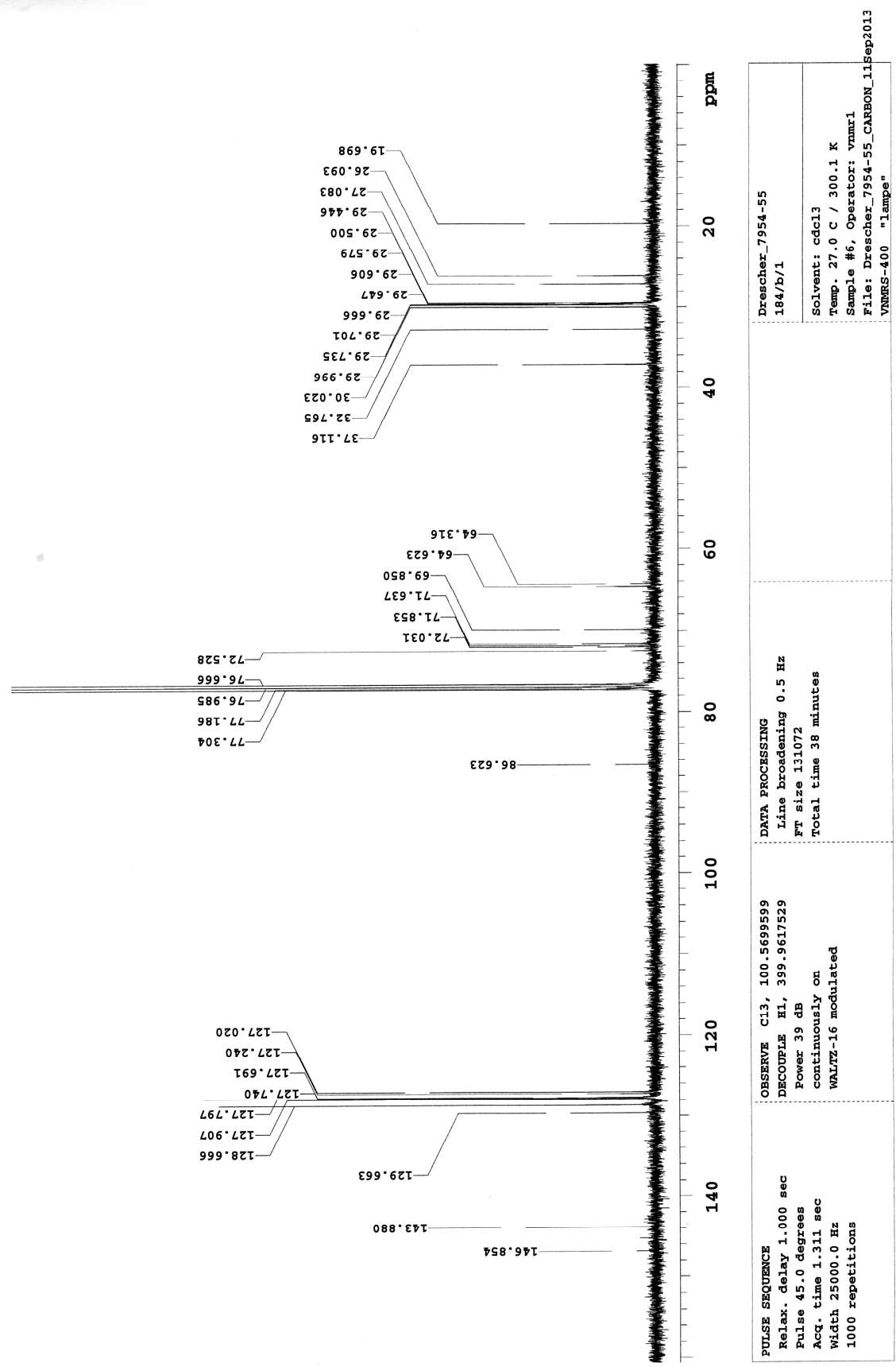
Compound **25b**: ESI-MS, negative mode



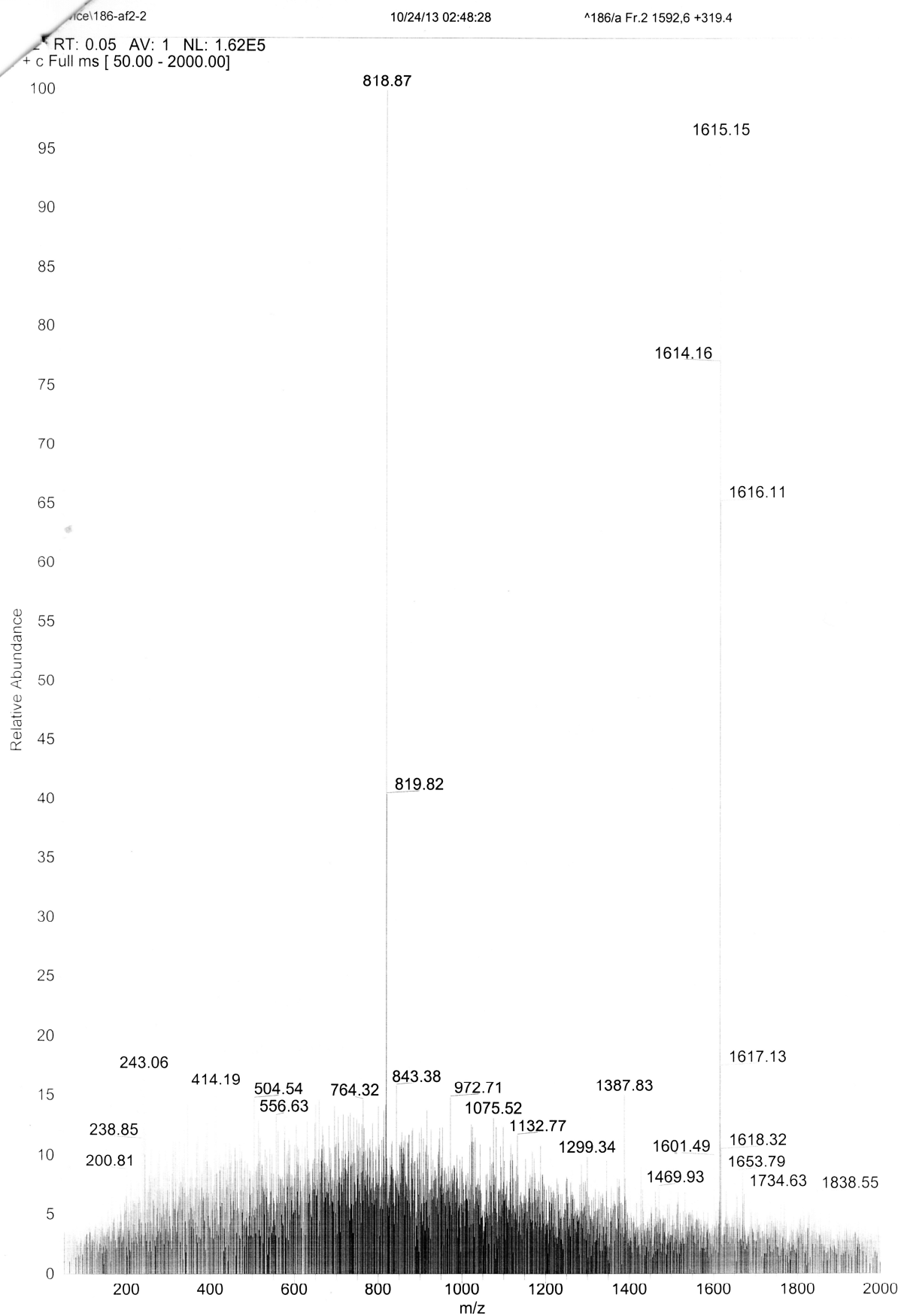
Compound 25b: ¹H NMR



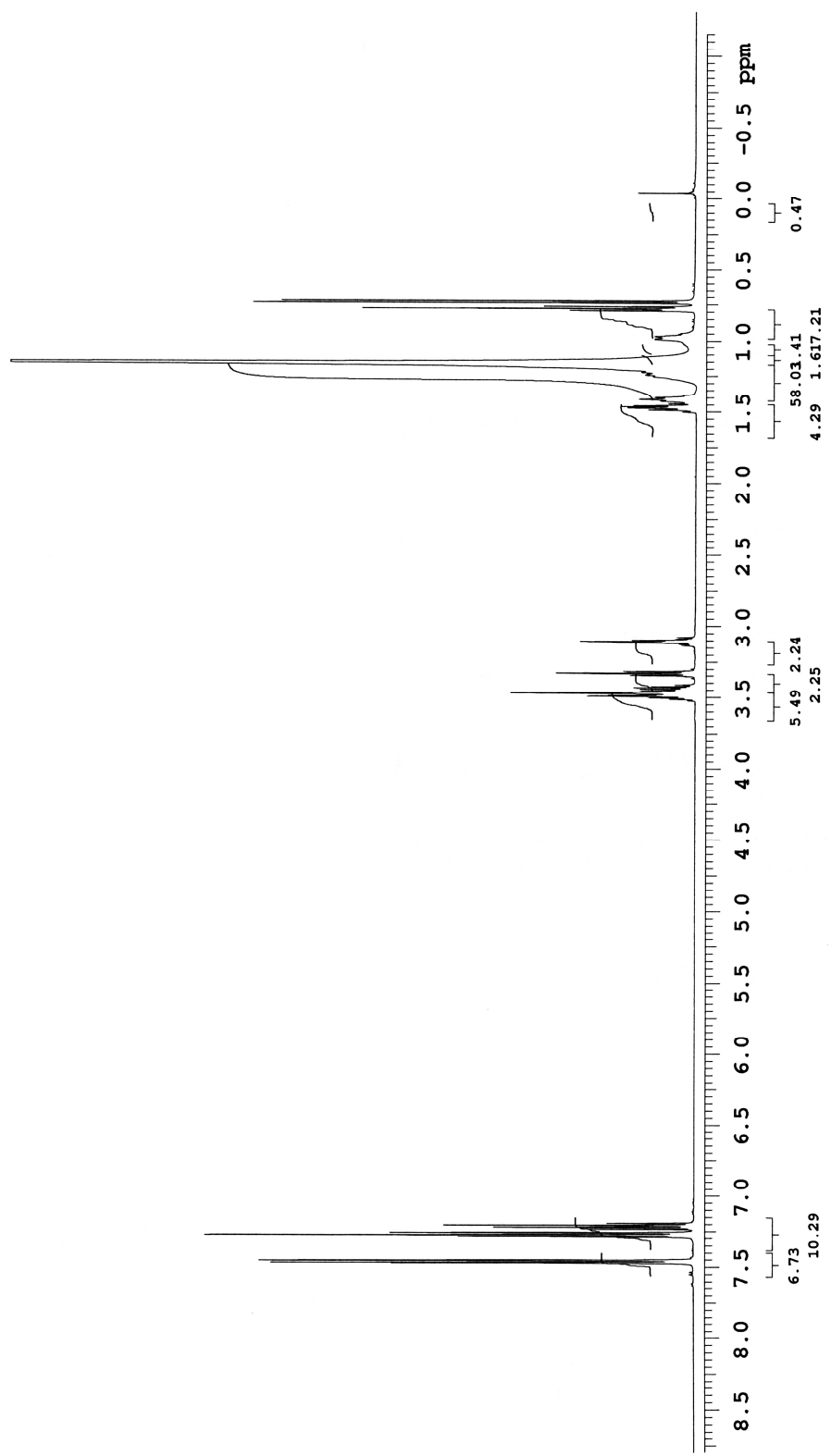
Compound 25b: ¹³C NMR



Compound **26a**: ESI-MS, positive mode



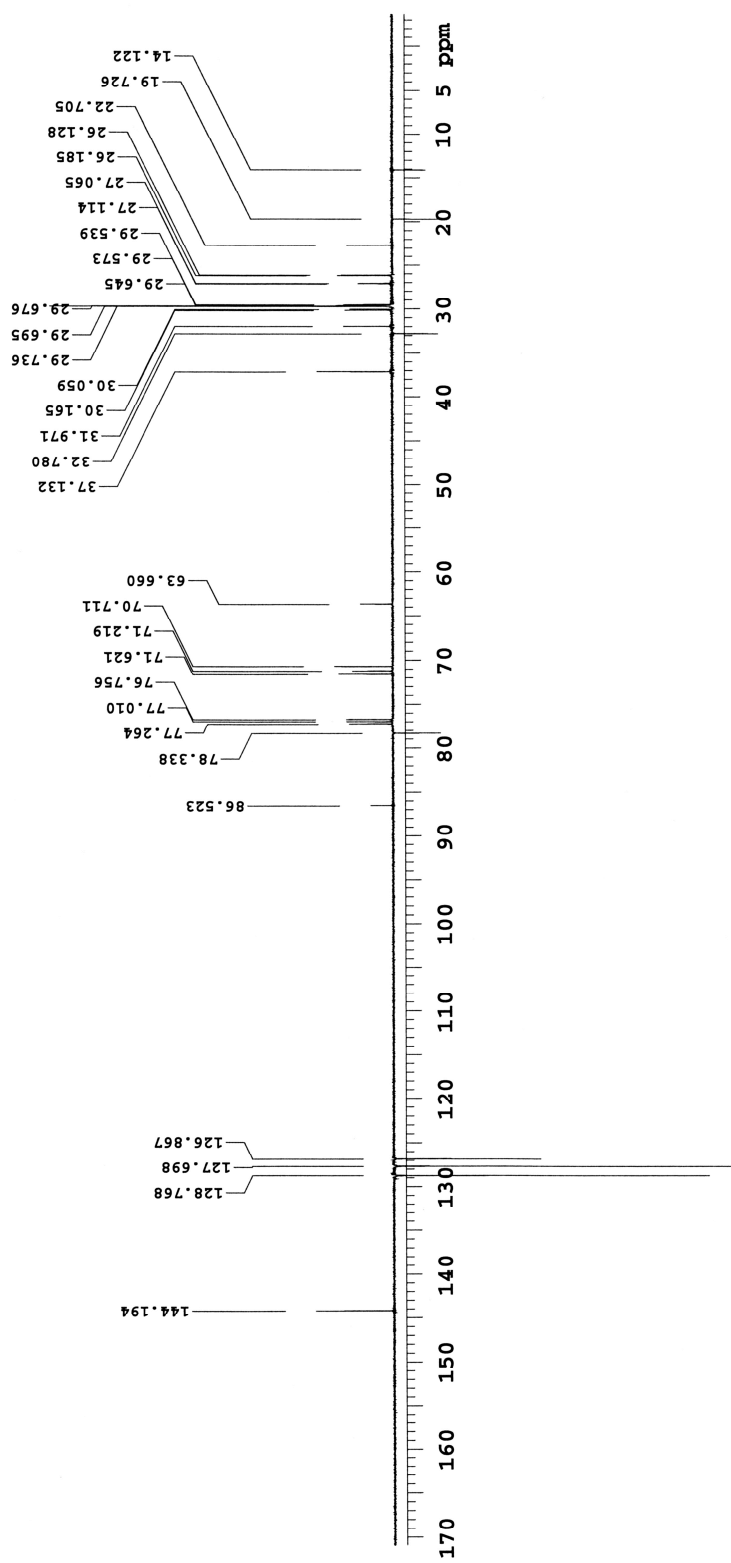
Compound 26a: ¹H NMR



PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 4.089 sec Width 8012.8 Hz 32 repetitions	OBSERVE H1, 499.7466064	DATA PROCESSING Ft size 131072 Total time 2 minutes	2013-10-25 Drescher_5376-77 186/a/1 Solvent: cdcl3 Temp. 27.0 C / 300.1 K Sample #6, Operator: vnmr1
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File: Drescher_5376-77_2013-10-25_01/Drescher_5376-77_PROTON_01

Compound 26a: ¹³C NMR, APT mode



<p>PULSE SEQUENCE: APT Relax. delay 1.000 sec 1st pulse 90.0 degrees 2nd pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 5000 repetitions</p>	<p>OBSERVE C13, 125.6613841 DECOUPLE H1, 499.7491051 Power 40 dB on during acquisition WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 0.5 Hz FT size 131072 Total time 2.8 hours</p>	<p>2013-10-25 Drescher_5376-77 186/a/1 Solvent: cdcl3 Temp. 27.0 C / 300.1 K Sample #6, Operator: vnmr1</p>
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File: Drescher_5376-77_2013-10-25_01/Drescher_5376-77_APT_01

Compound 26a – monoalkylate side-product: ESI-MS, positive mode

$\text{C}_{93}\text{H}_{140}\text{O}_6\text{Na}$ $[\text{M} + \text{Na}]^+$ – 1376.05 g mol^{-1}

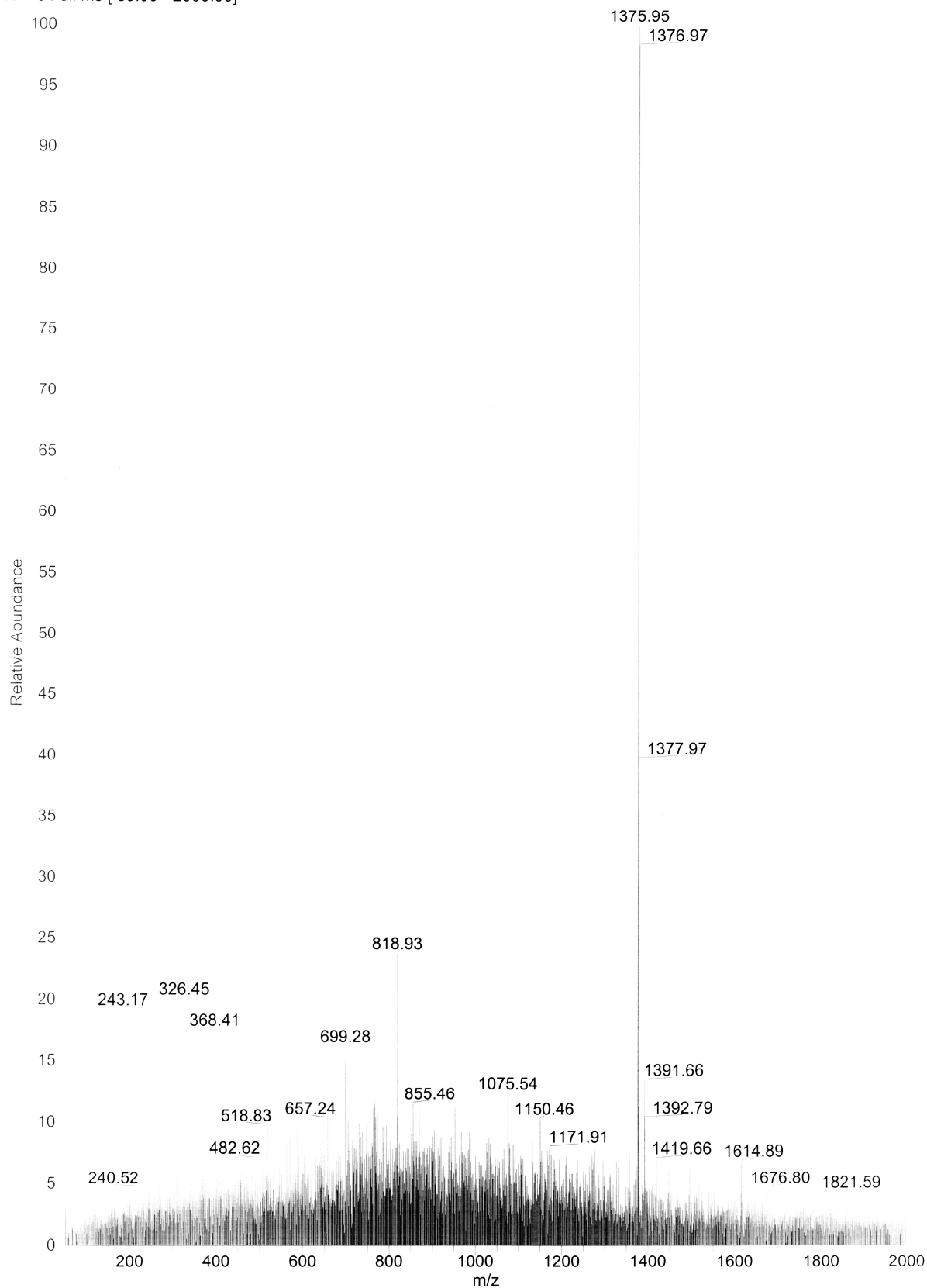
Service\186-af12-1

10/24/13 02:54:47

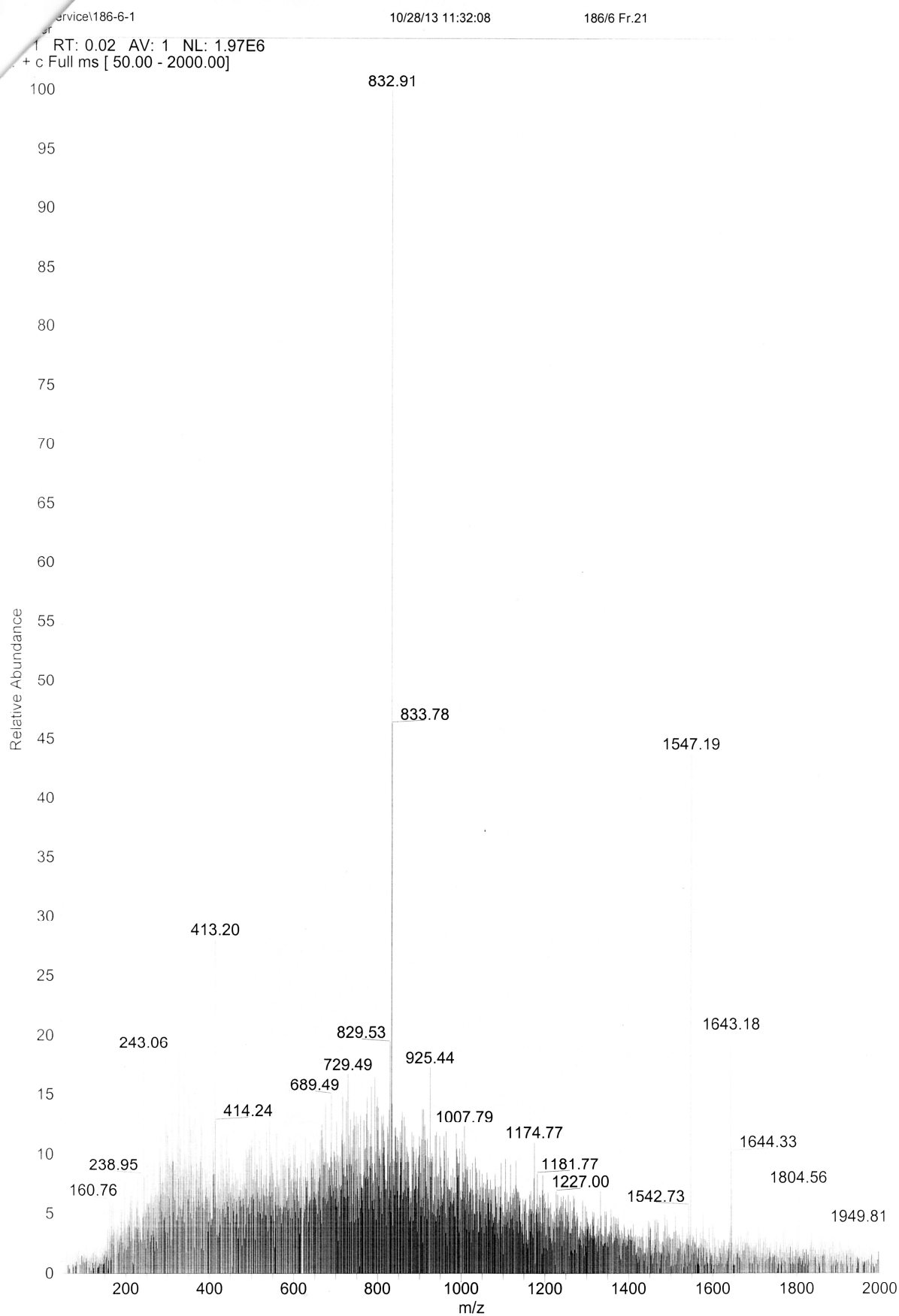
186/a Fr.12 1354,1

2 RT: 0.06 AV: 1 NL: 3.19E5

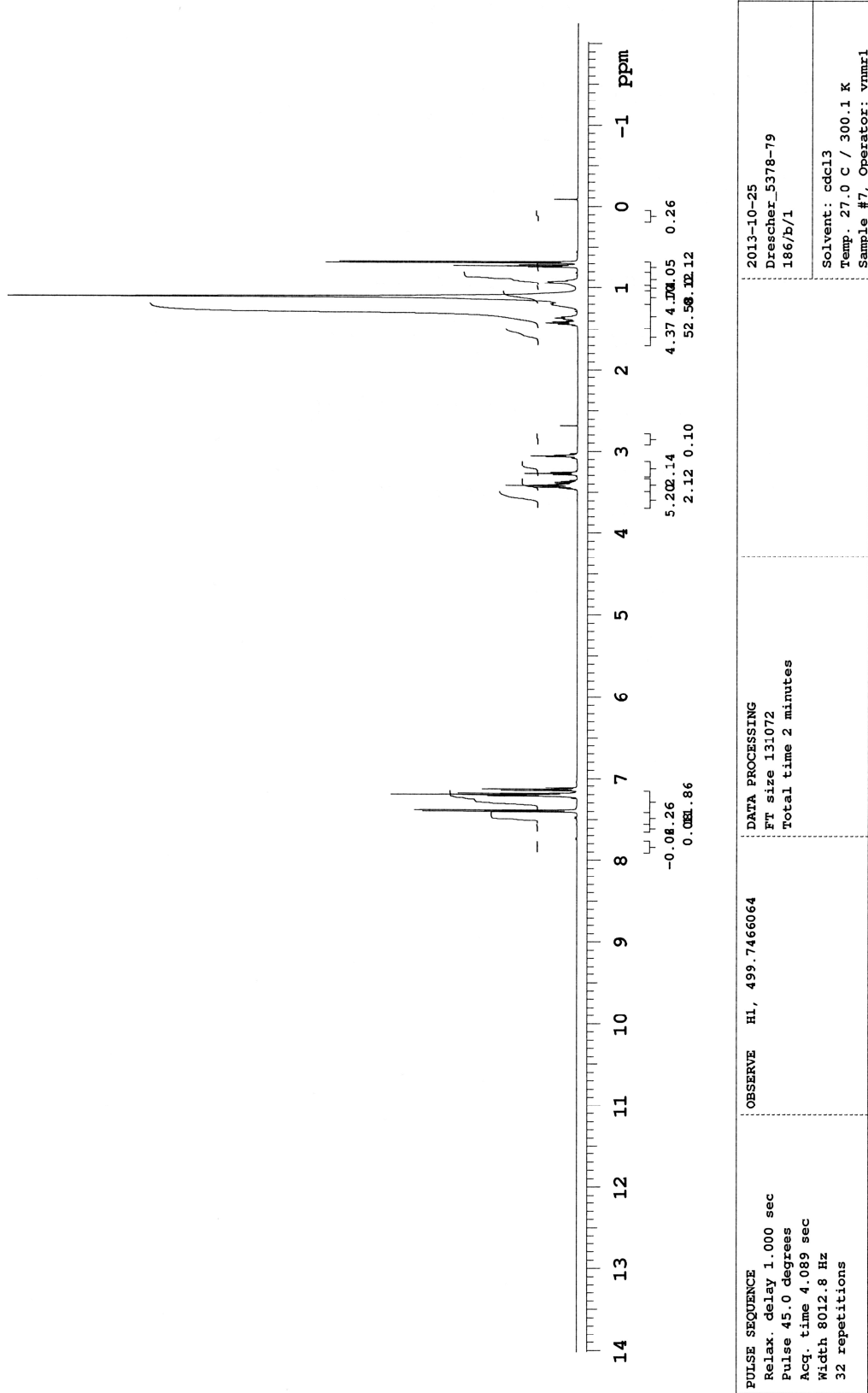
T: + c Full ms [50.00 - 2000.00]



Compound 26b: ESI-MS, positive mode

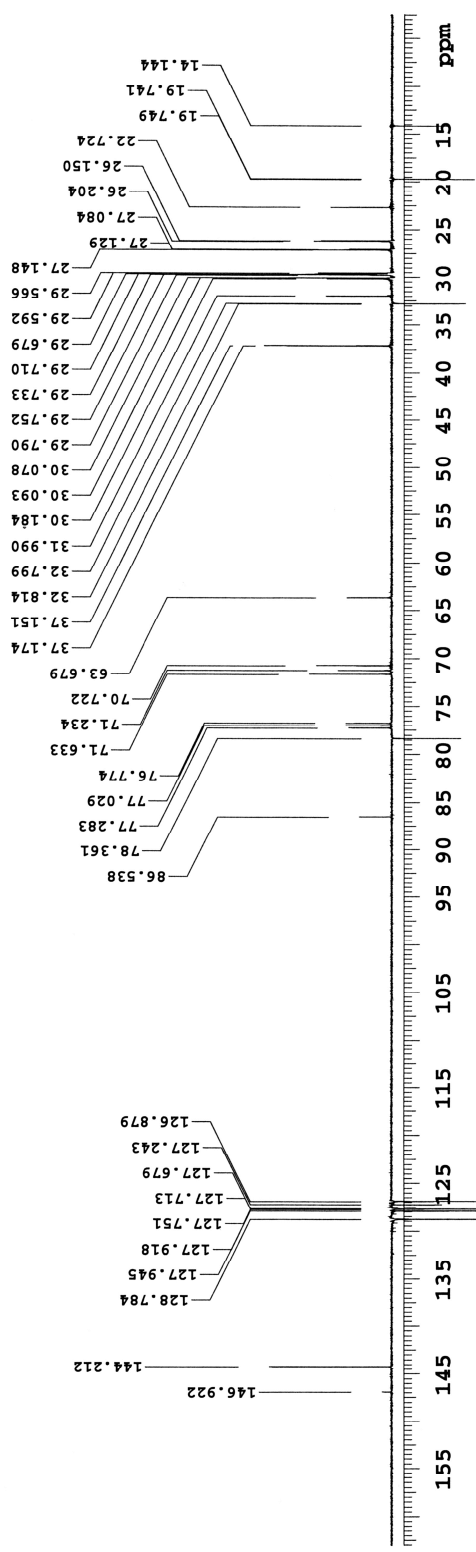


Compound 26b: ¹H NMR



File: Drescher_5378-79_2013-10-25_01/Drescher_5378-79_PROTON_01

Compound 26b: ¹³C NMR, APT mode



PULSE SEQUENCE: APT Relax. delay 1.000 sec 1st pulse 90.0 degrees 2nd pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 5000 repetitions	OBSERVE C13, 125.6613841 DECOUPLE H1, 499.7491051 Power 40 dB on during acquisition WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 131072 Total time 2.8 hours	2013-10-25 Drescher_5378-79 186/b/1 Solvent: cdcl3 Temp. 27.0 C / 300.1 K Sample #7, Operator: vnmr1
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File: Drescher_5378-79_2013-10-25_01/Drescher_5378-79_APT_01

$$\text{C}_{95}\text{H}_{144}\text{O}_6\text{Na} [\text{M} + \text{Na}]^+ - 1404.08 \text{ g mol}^{-1}$$


Lipid I: ¹H NMR

Markowski
TM-OR-D
Nr. 583

Pulse Sequence: zgpg30

Solvent: CDCl₃

Temp: 40.0 C / 313.1 K

QNP-135 "Jamps"

Relax. delay 2.000 sec

Pulse 52.2 degrees

Acc. time 2.502 sec

Width 6789.3 Hz

32 repetitions

OBSERVE F1: 399.9571183 MHz

DATA PROCESSING

FT: 812.1359611

Total time 2 min, 43 sec

HEIGHT INDEX FREQUENCY PPM HEIGHT

INDEX	FREQUENCY	PPM	HEIGHT
1	2894.218	7.236	13.3
2	1586.545	4.217	2.2
3	1542.122	3.855	2.6
4	1536.520	3.842	4.8
5	1530.917	3.828	2.8
6	1438.123	3.621	2.9
7	1433.551	3.609	3.1
8	1432.993	3.598	2.8
9	1427.373	3.569	1.2
10	1423.015	3.558	1.7
11	1418.035	3.545	2.2
12	1408.905	3.523	3.6
13	1401.850	3.505	3.5
14	1386.247	3.491	2.8
15	1382.305	3.481	2.7
16	1372.582	3.432	2.2
17	1356.863	3.418	2.0
18	1352.217	3.405	1.4
19	1356.614	3.392	2.8
20	1350.182	3.376	3.4
21	1348.106	3.371	3.4
22	1343.334	3.359	4.8
23	1341.259	3.354	2.1
24	1338.551	3.347	1.4
25	1281.705	3.205	53.5
26	843.458	2.108	8.7
27	593.641	1.489	2.8
28	593.258	1.483	4.2
29	586.583	1.463	3.2
30	483.231	1.268	151.2
31	464.141	1.180	2.5
32	446.371	1.121	3.5
33	415.170	1.058	1.8
34	408.115	1.050	1.4
35	355.186	0.946	3.2
36	331.754	0.829	7.8
37	324.689	0.812	8.5
38	317.421	0.793	11.0
39	310.381	0.775	16.1

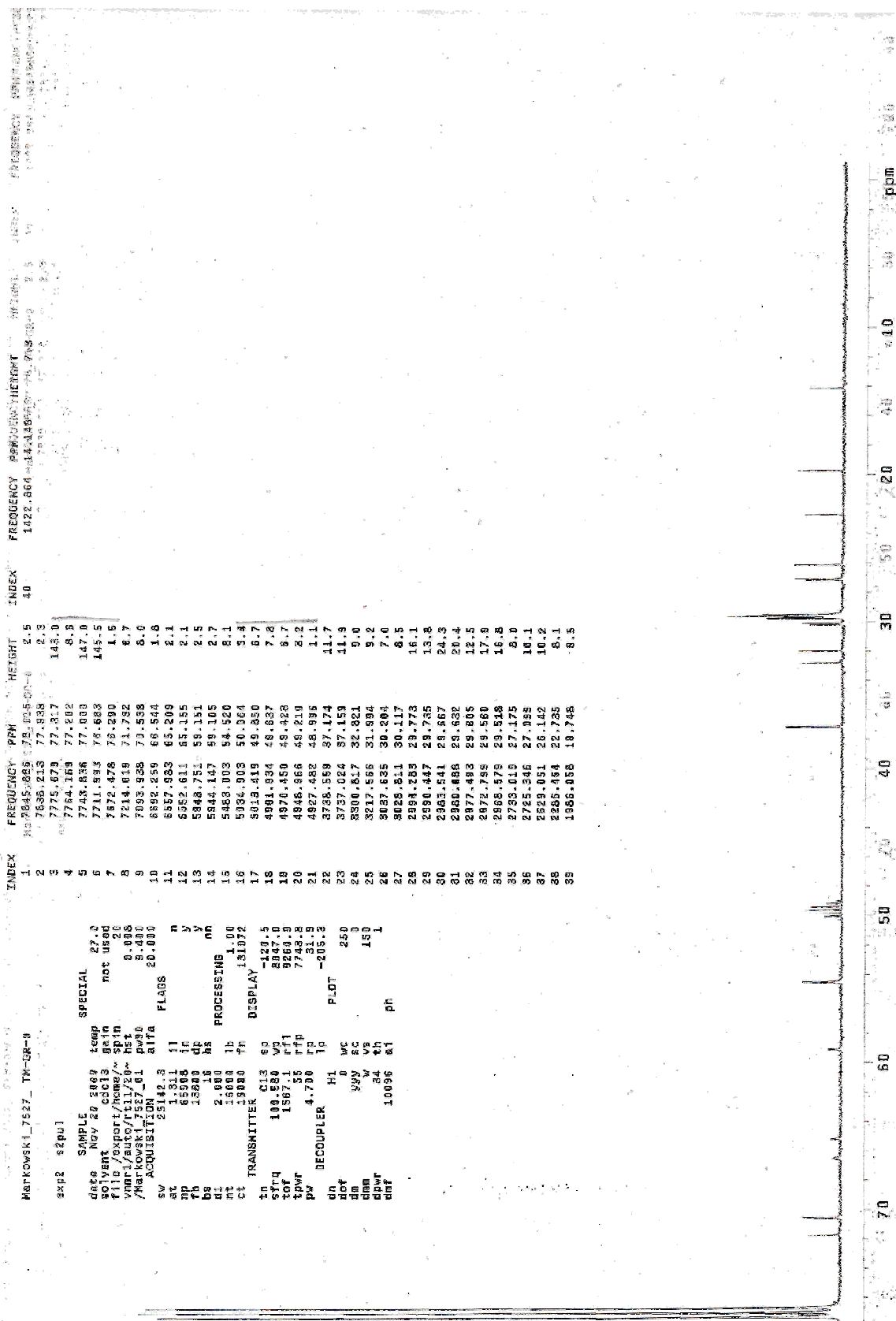
ppm

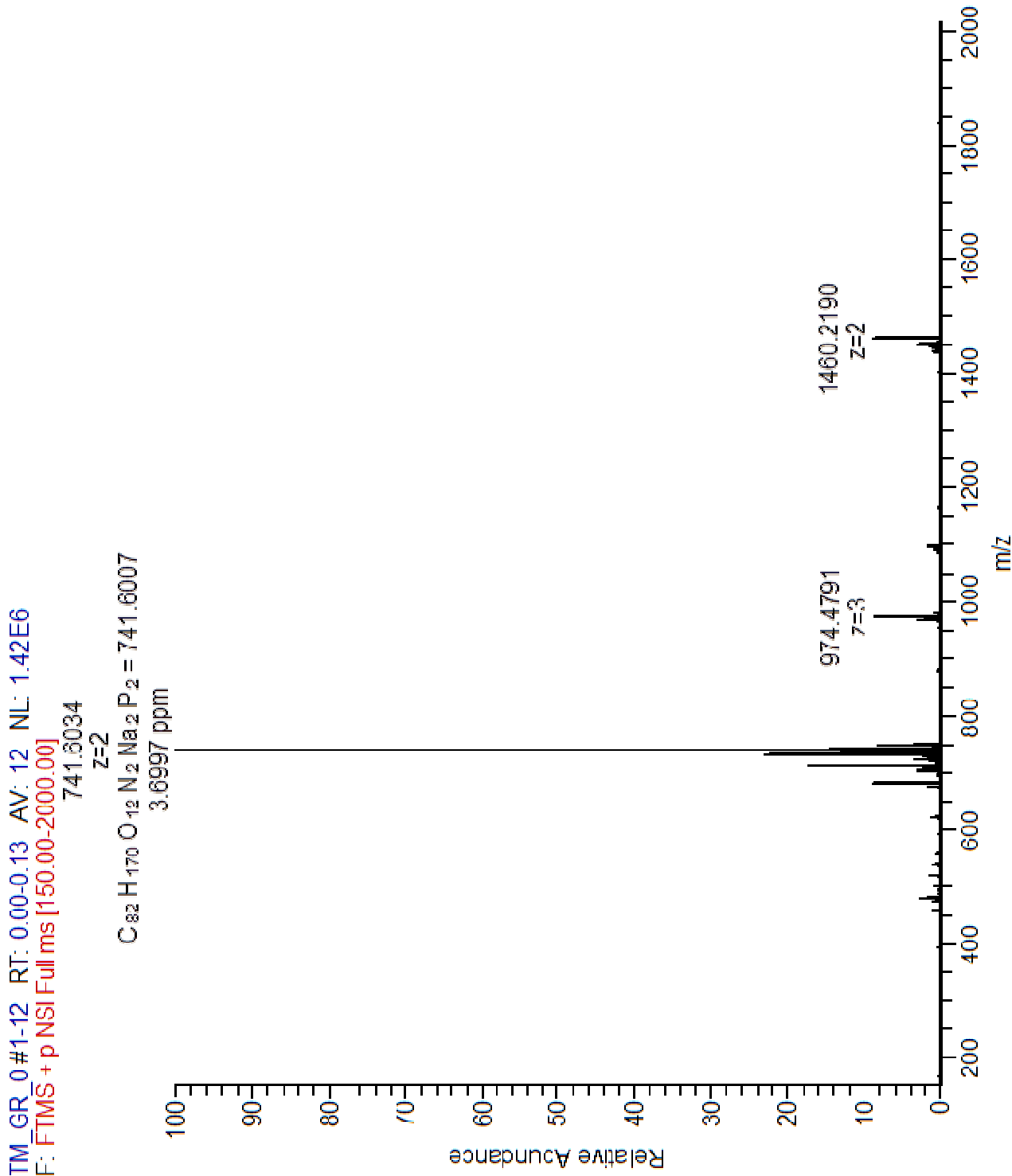
1.68

2

1

Lipid I: ¹³C NMR





Lipid II: ¹H NMR

MacKowski_7262_17-08-9

INDEX: 2594.758 7.127 132.7

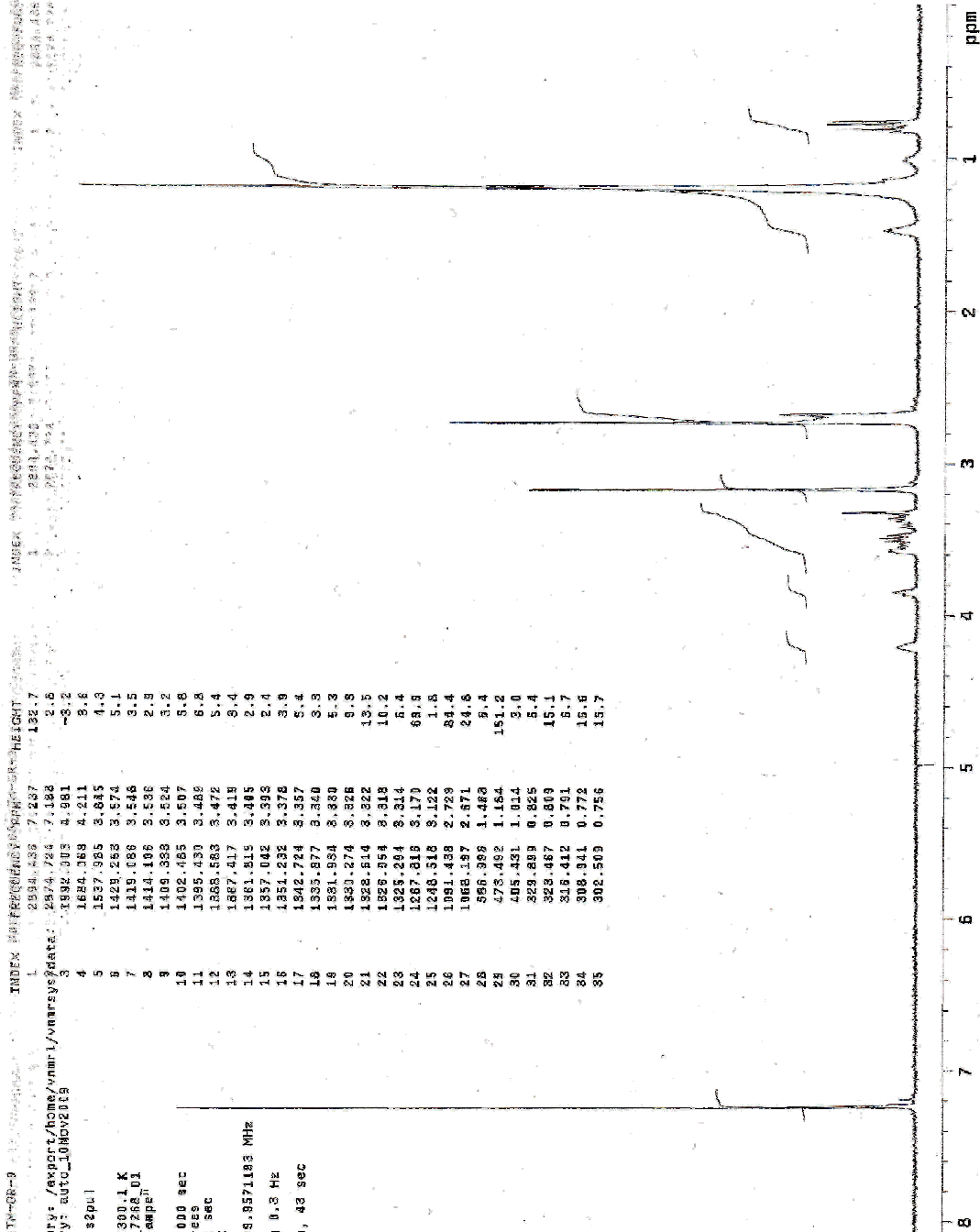
Archive directory: /export/home/vnmr1/vnmrsvs/data: 2594.754 7.128 2.6
Sample directory: auto_10Mv2019 3 1992.303 4.981 -3.2

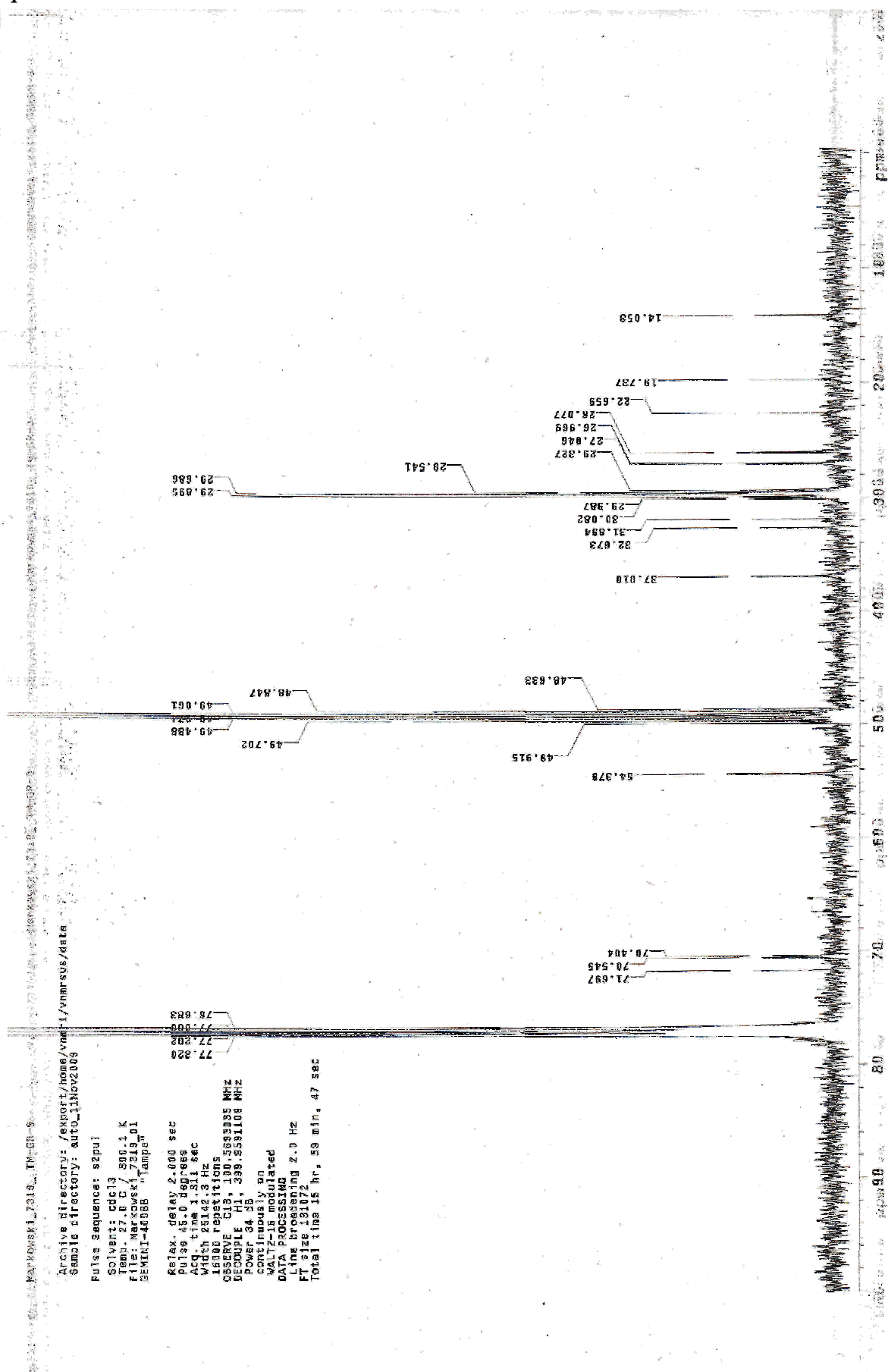
Pulse Sequence: s2pu1

Solvent: cdcl3
Temp: 27.3 C / 300.1 K
File: MacKowski_7262_01
GEMINI-300EB 17ampm

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.682 sec
Width 6789.3 Hz
256 repetitions
OBS. FREQ 300.13571183 MHz
NUC1: 1H
Line broadening 0.3 Hz
FT size 65536
Total time 2 min, 43 sec

4	1654.368	4.211	9.8
5	1637.965	3.845	4.3
6	1428.253	3.574	5.1
7	1419.086	3.546	3.5
8	1414.186	3.536	2.9
9	1409.383	3.524	3.2
10	1402.485	3.507	3.8
11	1395.430	3.488	6.8
12	1368.583	3.472	5.4
13	1367.417	3.418	3.4
14	1361.515	3.485	2.9
15	1357.042	3.393	2.4
16	1351.232	3.378	3.9
17	1342.724	3.357	5.4
18	1335.877	3.340	3.3
19	1331.934	3.330	5.3
20	1329.274	3.326	9.3
21	1328.514	3.322	13.5
22	1326.554	3.318	10.2
23	1325.294	3.314	5.4
24	1317.819	3.170	84.9
25	1248.518	3.132	1.8
26	1091.438	2.739	34.4
27	1068.157	2.671	24.6
28	956.959	1.483	9.4
29	478.482	1.164	151.2
30	405.431	1.014	3.0
31	323.889	0.825	5.4
32	323.467	0.809	15.1
33	316.412	0.791	6.7
34	308.341	0.772	15.6
35	302.509	0.756	13.7





Lipid II: ESI-MS, positive mode

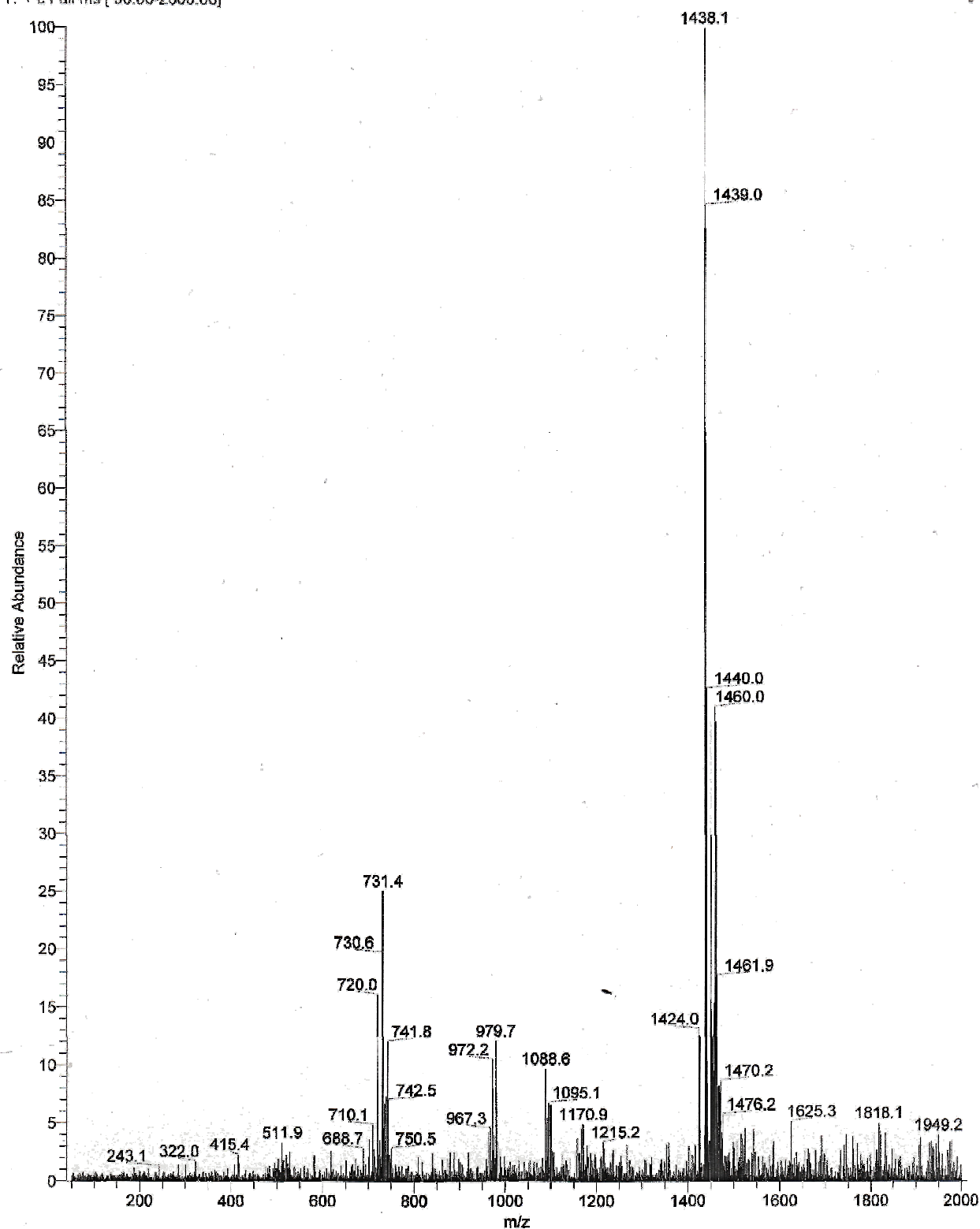
D:\Daten\service\lm-gr-9-1
Markowski

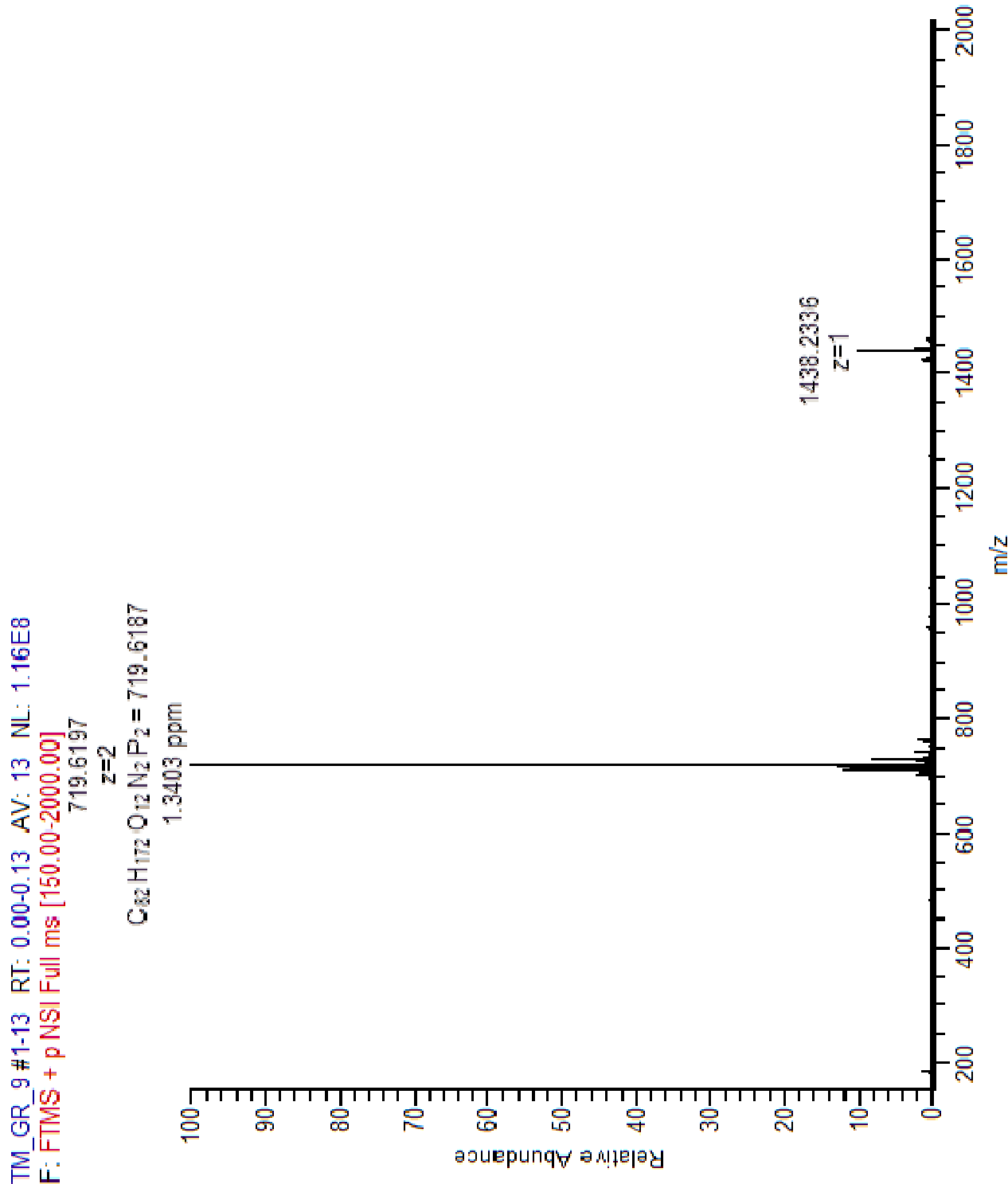
11/26/09 10:32:55

TM-GR-9 - 1438.18

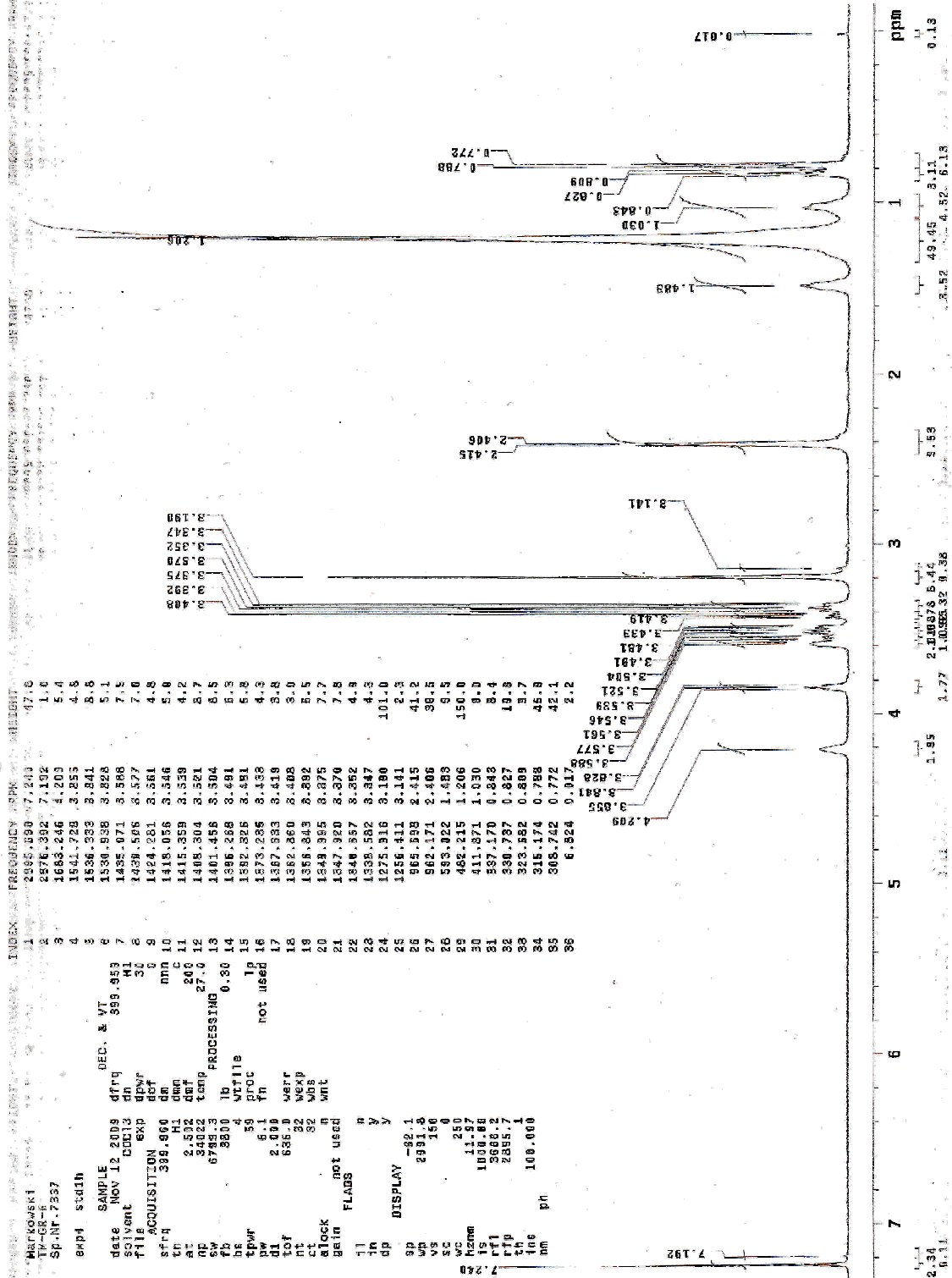
lm-gr-9-1#1 RT: 0.01 AV: 1 NL: 1.64E7

T: + c Full ms [50.00-2000.00]

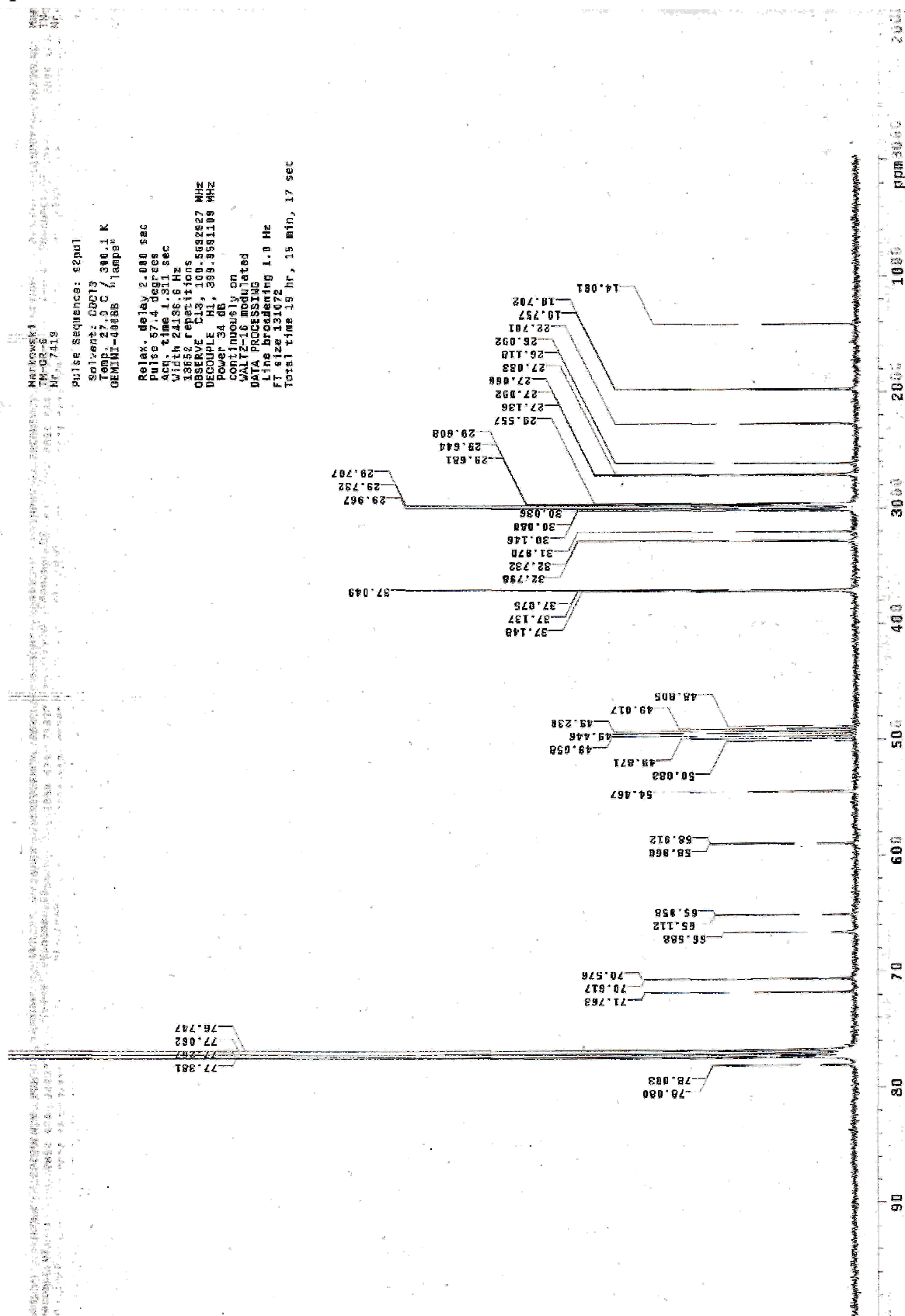




Lipid III: ^1H NMR



Lipid III: ^{13}C NMR



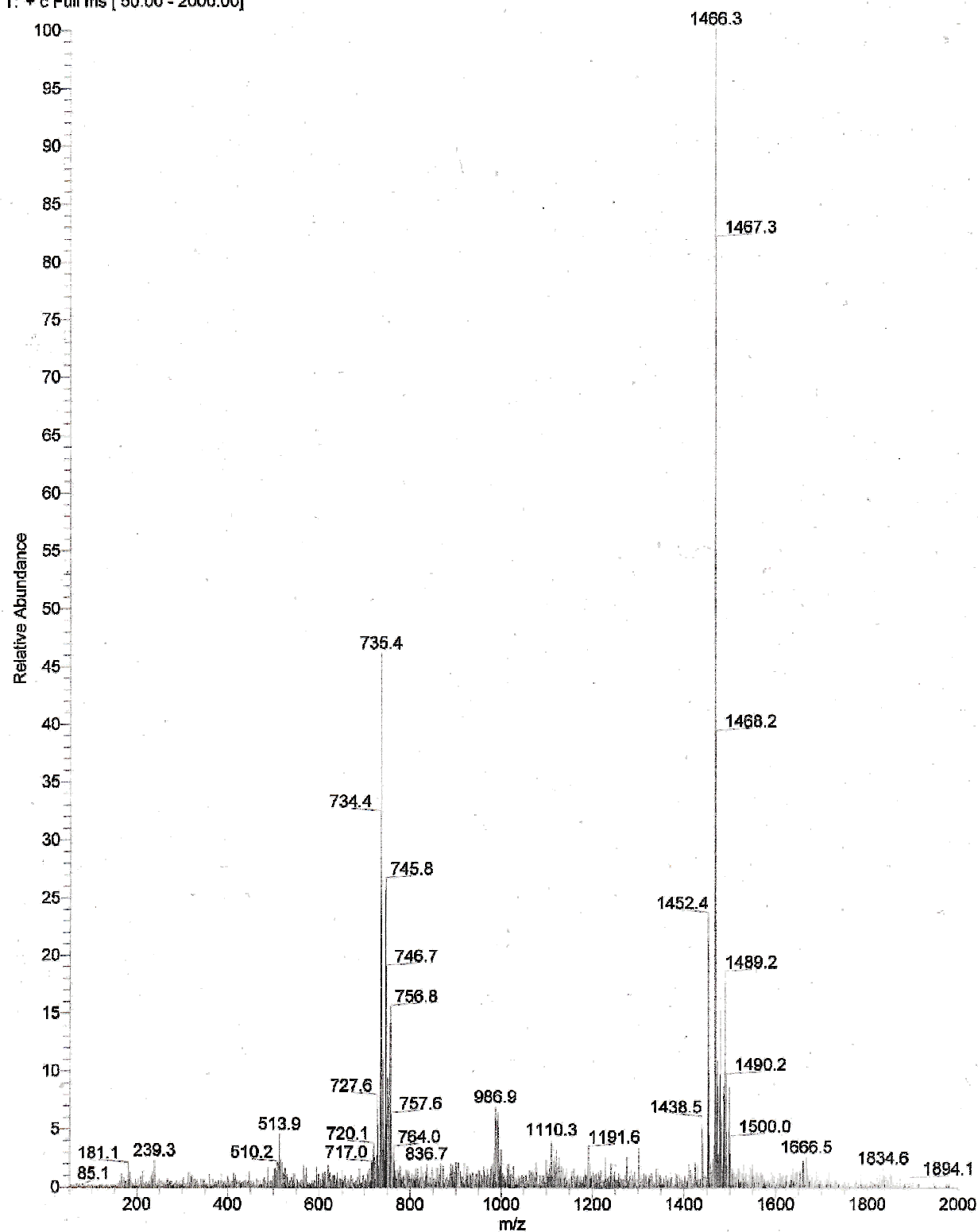
Lipid III: ESI-MS, positive mode

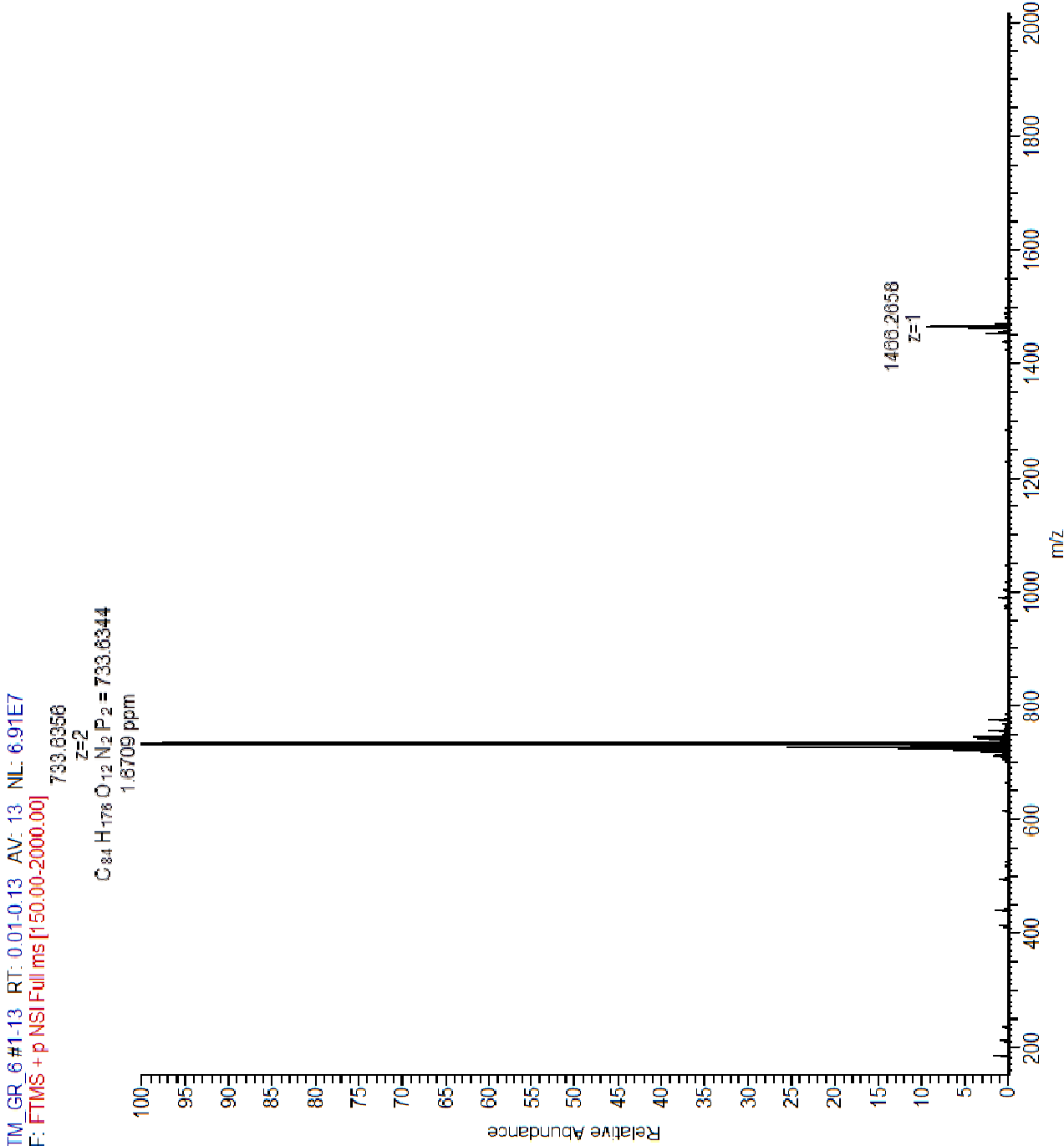
D:\Data\Service\m-gr-6-1
Markowski

08/18/09 02:07:47 PM

TM-GR-6 - 1466.2

S#: 1 RT: 0.03 AV: 1 NL: 1.61E7
T: + c Full ms [50.00 - 2000.00]





5. References

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2. J. Cason, K. L. Rinehart Jr. and S. D. Thornton Jr., *J. Org. Chem.*, 1953, **18**, 1594-1600.
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