

Electronic Supplementary Information

for

Oxidative spirocyclisation routes towards the sawaranospirolides. Synthesis of *ent*-sawaranospirolide C and D

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- (1) Experimental procedures and characterisation data for experiments in Schemes 3, 4 and 6
- (2) ¹H NMR expansion for spirocycle **13**
- (3) ¹H NMR spectra for experiments in Schemes 7 and 8 and ¹³C NMR spectra for **30** and **43**

[n.b. all spectra are the machine-generated original PDFs, except that the spectra for **30** and **43** (weak samples) were processed in MestReNova for Mac OS X]

(1) Experimental procedures and characterisation data for experiments in Schemes 3, 4 and 6

Dimethyl 3-(tert-butyldimethylsilyloxy)-2-oxopropylphosphonate 6¹

To a stirred solution of dimethyl methylphosphonate (1.38 mL, 12.7 mmol) in THF (20 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-butyllithium (7.9 mL of a 1.6 M solution in hexanes, 12.6 mmol) and the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h. A solution of *tert*-butyldimethylsilyl (*tert*-butyldimethylsilyloxy)acetate (**5**)² (2.0 g, 6.58 mmol) in THF (20 mL) was added to the lithiated phosphonate and the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 2 h then quenched with saturated NH_4Cl solution (20 mL). The mixture was extracted with ether ($3 \times 25\text{ mL}$) then the combined organic layers were washed with brine, dried over MgSO_4 , and concentrated *in vacuo*. Column chromatography (ethyl acetate/petrol, 1:1) yielded phosphonate **6** as a colourless oil (1.23 g, 63%). R_f 0.22 (ethyl acetate/petrol, 1:1); ν_{max} (thin film)/ cm^{-1} 2956s, 2858s, 1735s, 1258s, 1033s; δ_{H} (CDCl_3 , 400 MHz) 0.06 (6 H, s, $\text{Si}(\text{CH}_3)_2$), 0.89 (9 H, s, *t*-BuSi), 3.18 (2 H, d, $^2J_{\text{PH}}$ 22.5, CH_2PO), 3.76 (6 H, d, $^3J_{\text{PH}}$ 11.3, $\text{P}(\text{OMe})_2$), 4.22 (2 H, s, CH_2OSi); δ_{C} (CDCl_3 , 100 MHz) -5.6 , 18.2 , 25.7 , 36.2 (d, $^1J_{\text{PC}}$ 129), 53.0 (d, $^2J_{\text{PC}}$ 7.0), 69.4 (d, $^3J_{\text{PC}}$ 2.0), 201.8 (d, $^2J_{\text{PC}}$ 7.0).

(E)-1-(tert-Butyldimethylsilyloxy)-4-(furan-2-yl)but-3-en-2-one 7

To a stirred suspension of NaH (48 mg, 60% by weight in mineral oil, 1.2 mmol) in THF (5 mL) at $0\text{ }^{\circ}\text{C}$ was added a solution of phosphonate **6** (350 mg, 1.18 mmol) in THF (5 mL) followed, after 10 min, by furfuraldehyde (0.1 mL, 1.2 mmol). The mixture was stirred at $0\text{ }^{\circ}\text{C}$ for 2 h before being poured into saturated NH_4Cl solution and extracted with ether ($3 \times 10\text{ mL}$). The combined organic extracts were washed with brine, dried over MgSO_4 and concentrated *in vacuo*. Column chromatography (petrol/ether, 20:1) afforded *enone* **7** as a colourless oil (204 mg, 88%). R_f 0.33 (petrol/ether, 9:1); ν_{max} (thin film)/ cm^{-1} 2930s, 1686s, 1607s, 1554m, 1304s, 1018m, 839s; δ_{H} (CDCl_3 , 400 MHz) 0.11 (6 H, s, $\text{Si}(\text{CH}_3)_2$), 0.95 (9 H, s, *t*-BuSi), 4.36 (2 H, s, CH_2OSi), 6.49 (1 H, dd, J 3.4, 1.7, furan), 6.68 (1 H, d, J 3.4, furan), 6.95 and 7.45 ($2 \times 1\text{ H}$, $2 \times \text{d}$, J 15.8, $\text{CH}=\text{CH}$), 7.49 (1 H, d, J 1.7, furan); δ_{C} (CDCl_3 , 100 MHz) -5.4 , 18.4 , 25.8 , 69.1 , 112.6 , 116.2 , 118.4 , 129.3 , 145.0 , 151.3 , 198.7 ; m/z (CI) 267 (MH^+ , 26%), 209 (19), 137 (100), 136 (23), 121 (22), 92 (11); HRMS (CI) found 267.1425; $\text{C}_{14}\text{H}_{23}\text{O}_3\text{Si}$ (MH^+) requires 267.1411.

(3S, 4S)-1-(tert-Butyldimethylsilyloxy)-3,4-dihydroxy-4-(furan-2-yl)butan-2-one 8

A mixture of AD-mix- β (11.8 g), methyl sulfonamide (400 mg, 4.21 mmol), water (21 mL) and *t*-butanol (21 mL) was stirred at RT for 10 min. *Enone* **7** (1.0 g, 3.76 mmol) was added and the

mixture was allowed to stir at RT for 16 h. Solid Na₂SO₃ (12.6 g) was added and, after 1 h, the mixture was poured into water (50 mL) and extracted with ethyl acetate (5 × 50 mL). The combined organic extracts were washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Column chromatography (petrol/ether, 2:1) afforded enone **7** (302 mg, 30%) and diol **8** (481 mg, 43%; 61% based on recovered enone **7**). R_f 0.23 (petrol/ether, 1:1); [α]_D²⁵ -268 (*c* 0.15, CHCl₃); ν_{max} (thin film)⁻¹ 3440br, 2931s, 2887s, 1731s, 1257s, 1101s, 839s; δ_H (CDCl₃, 400 MHz) 0.10 and 0.11 (2 × 3 H, 2 × s, Si(CH₃)₂), 0.92 (9 H, s, *t*-BuSi), 2.71 (1 H, br s, FuCHOH), 3.64 (1 H, br s, CHOHCO), 4.41 and 4.50 (2 × 1 H, 2 × d, *J* 17.8, CH₂OSi), 4.89 (1 H, s, CH(OH)CO), 5.26 (1 H, s, FuCHOH), 6.34 (1 H, dd, *J* 3.2, 1.8), 6.40 (1 H, d, *J* 3.2, 0.8) and 7.39 (1 H, d, *J* 1.8, 0.8, furan); δ_C (CDCl₃, 100 MHz) -5.6, 18.1, 25.6, 67.7, 67.9, 76.4, 107.5, 110.4, 142.4, 153.3, 209.2; *m/z* (ESI⁺) 323 (MNa⁺, 100), 318 (44); HRMS (ESI⁺) found 323.1299; C₁₄H₂₄O₅NaSi (MNa⁺) requires 323.1285.

(3S,4S)-1-(*tert*-Butyldimethylsilyloxy)-3,4-dibenzoyloxy-4-(furan-2-yl)butan-2-one **9**

To a stirred solution of diol **8** (481 mg, 1.60 mmol) in dichloromethane (10 mL) at RT was added benzoyl chloride (0.41 mL, 3.20 mmol), pyridine (0.43 mL, 4.80 mmol) and a crystal of DMAP. The mixture was stirred at RT for 16 h then poured into saturated NaHCO₃ solution (10 mL), extracted with dichloromethane (3 × 10 mL) and the combined extracts washed with hydrochloric acid (1 M, 10 mL), dried over MgSO₄ and concentrated *in vacuo*. Column chromatography (petrol/ether, 4:1) afforded the diester (**9**) as a colourless oil (716 mg, 88%). R_f 0.26 (petrol/ether, 4:1); [α]_D²⁵ +29 (*c* 0.5, CHCl₃); ν_{max} (thin film)⁻¹ 2930s, 1789s, 1726s, 1601m, 1452m, 1255s, 838m, 706s; δ_H (CDCl₃, 400 MHz) 0.11 and 0.12 (2 × 3 H, 2 × s, Si(CH₃)₂), 0.93 (9 H, s, *t*-BuSi), 4.44 and 4.53 (2 × 1 H, 2 × d, *J* 18.0, CH₂OSi), 6.20 (1 H, d, *J* 4.1, CH(OBz)CO), 6.36 (1 H, dd, *J* 3.4, 2.0) and 6.51 (1 H, dd, *J* 3.4, 0.8, furan), 6.91 (1 H, d, *J* 4.1, FuCHOBz), 7.42 (1 H, dd, *J* 2.0, 0.8, furan), 7.43–7.70 (6 H, m) and 8.05–8.18 (4 H, m, 2 × Ph); δ_C (CDCl₃, 100 MHz) -5.6 (2 peaks), 18.3, 25.7, 67.2, 68.5, 75.8, 109.9, 110.6, 128.5 (2 peaks), 129.0, 129.2, 129.9, 123.0, 133.5, 134.5, 143.2, 148.5, 162.4, 165.5, 202.5; *m/z* (ESI⁺) 569 (30%), 567 (100, M·CH₃CN·NH₄⁺); HRMS found 531.1804; C₂₈H₃₂O₇NaSi (MNa⁺) requires 531.1810.

(2S,3R,4S)-1-(*tert*-Butyldimethylsilyloxy)-3,4-dibenzoyloxy-4-(furan-2-yl)butan-2-ol **10a**

To a stirred solution of ketone **9** (540 mg, 1.06 mmol) in dichloromethane (50 mL) at -25 °C was added Zn(BH₄)₂ (11.0 mL, 0.2 M solution in ether, 2.2 mmol). The mixture was maintained at -25 °C and stirred for 2 h and then quenched by the dropwise addition of saturated NH₄Cl

solution (10 mL). The mixture was allowed to warm to RT and then extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. Column chromatography (petrol/ether, 2:1) yielded *alcohol 10α* as a colourless oil (217 mg, 40%). R_f 0.44 (petrol/ether, 1:1); [α]_D²⁵ –4.3 (*c* 0.11, CHCl₃); ν_{max} (thin film)/cm⁻¹ 3510br, 2930m, 1727s, 1261s; δ_H (*d*₆-acetone, 400 MHz) 0.04 and 0.06 (2 × 3 H, 2 × s, Si(CH₃)₂), 0.91 (9 H, s, *t*-BuSi), 3.66 and 3.81 (2 × 1 H, 2 × dd, *J* 10.4, 5.5, CH₂OSi), 3.97–4.05 (1 H, m, CHOH), 4.47 (1 H, d, *J* 6.2, CHOH), 5.96 (1 H, app. t, *J* 5.8, CH(OBz)CHOH), 6.40 (1 H, dd, *J* 3.3, 1.8) and 6.49 (1 H, d, *J* 3.3, furan), 6.72 (1 H, d, *J* 6.5, FuCHOBz), 7.44–7.67 (7 H, m) and 8.02–8.11 (4 H, m, 2 × Ph and furan); δ_C (*d*₆-acetone, 100 MHz) –5.8 (2 peaks), 18.4, 25.8, 64.4, 68.1, 70.9, 74.1, 109.9, 110.9, 128.9, 129.0, 129.9 (2 peaks), 130.0, 130.6, 133.5, 133.7, 143.5, 150.6, 165.2, 165.2; *m/z* (ESI⁺) 570 (20%), 569 (M·CH₃CN·NH₄⁺), 533 (35); HRMS (ESI⁺) found 533.1986; C₂₈H₃₄NaO₇Si requires 533.1966. Also obtained was (2*R*,3*R*,4*S*)-1-(*tert*-butyldimethylsilyloxy)-3,4-dibenzoxyloxy-4-(*furan*-2-yl)butan-2-ol **10β**, as a colourless oil (263 mg, 49%). R_f 0.22 (petrol/ether, 1:1); [α]_D²⁵ –51 (*c* 2.0, CHCl₃); ν_{max} (thin film)/cm⁻¹ 3500br, 2930m, 2858m, 1729s, 1277s; δ_H (*d*₆-acetone, 400 MHz) –0.02 and –0.01 (2 × 3 H, 2 × s, Si(CH₃)₂), 0.90 (9 H, s, *t*-BuSi), 3.14–3.20 (3 H, m, CH(OH)CH₂OSi), 4.38 (1 H, d, *J* 6.7, CHOH), 6.19 (1 H, d, *J* 9.6, CH(OBz)CHOH), 6.49 (1 H, dd, *J* 3.3, 1.8) and 6.67 (1 H, d, *J* 3.3, furan), 6.70 (1 H, d, *J* 9.6, FuCHOBz), 7.63 (1 H, d, *J* 1.8, furan), 7.44–7.55 (6 H, m) and 7.88–8.06 (4 H, m, 2 × Ph); δ_C (*d*₆-acetone, 100 MHz) –5.9, –5.7, 18.3, 25.8, 63.9, 68.9, 70.4, 72.4, 111.0, 111.2, 128.8 (2 peaks), 129.8, 129.9, 130.1, 130.6, 133.4, 133.6, 144.0, 150.0, 165.3, 165.8; *m/z* (ESI⁺) 570 (20%), 569 (M·CH₃CN·NH₄⁺), 533 (35); HRMS (ESI⁺) found 533.1983; C₂₈H₃₄NaO₇Si requires 533.1966.

(2*S*,3*R*,4*S*)-1-(*tert*-Butyldimethylsilyloxy)-2,3,4-tribenzoxyloxy-4-(*furan*-2-yl)butane **11**

Method 1 (from **10α**): To a stirred solution of alcohol **10α** (162 mg, 0.318 mmol) in dichloromethane (10 mL) at RT was added pyridine (0.05 mL, 0.6 mmol), benzoyl chloride (0.07 mL, 0.6 mmol) and a crystal of DMAP. After 48 h the mixture was poured onto hydrochloric acid (1 M, 10 mL) and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 20 mL) and the combined organic layers were washed with saturated NaHCO₃ solution, dried over MgSO₄, filtered and concentrated *in vacuo*. Column chromatography (petrol/ether, 2:1) yielded *tribenzoate 11* as a colourless oil (171 mg, 88%). R_f 0.38 (petrol/ether, 2:1); [α]_D²⁵ –350 (*c* 0.2, CHCl₃); ν_{max} (thin film)/cm⁻¹ 2986s, 1727s; δ_H (CDCl₃, 400 MHz) 0.00 and 0.01 (2 × 3 H, 2 × s, Si(CH₃)₂), 0.88 (9 H, s, *t*-BuSi), 3.70 (1 H, dd, *J* 10.4, 6.8) and 3.88 (1 H, dd, *J* 10.4, 5.4, CH₂OSi), 5.20–5.25 (1 H, m, CH(OBz)CH₂OSi),

6.42–6.45 (1 H, m, furan), 6.41 (1 H, dd, J 8.2, 3.0, $\text{FuCH}(\text{OBz})\text{CHOBz}$), 6.42–6.45 (1 H, m, furan), 6.48 (1 H, d, J 8.2, FuCHOBz), 7.31–7.62 (10 H, m) and 7.93–8.22 (6 H, 3 \times Ph and furan); δ_{C} (CDCl_3 , 100 MHz) (one resonance obscured) –5.6, 25.7, 60.8, 68.3, 70.8, 72.4, 110.6 (2 peaks), 128.3, 128.4, 128.5, 129.0, 129.4, 129.6, 129.7, 129.8 (2 peaks), 133.1 (2 peaks), 133.3, 143.4, 150.8, 162.4, 165.4, 165.5; m/z (ESI^+) 674 (100%, $\text{M}\cdot\text{CH}_3\text{CN}\cdot\text{NH}_4^+$), 637 (14), 632 (12, MNH_4^+), 285 (18); HRMS (ESI^+) found 632.2670; $\text{C}_{35}\text{H}_{42}\text{NO}_8\text{Si}$ (MNH_4^+) requires 632.2674.

(2S,3R,4S)-1-(tert-Butyldimethylsilyloxy)-2,3,4-tribenzoyloxy-4-(furan-2-yl)butane 11

Method 2 (from **10 β**): To a stirred solution of alcohol **10 β** (217 mg, 0.425 mmol) in benzene (10 mL) at RT was added benzoic acid (78 mg, 0.64 mmol), triphenylphosphine (168 mg, 0.64 mmol) and DEAD (0.1 mL, 0.64 mmol). After 48 h the mixture was poured onto hydrochloric acid (1 M, 10 mL) and the mixture was extracted with dichloromethane (3 \times 20 mL). The combined organic layers were washed with saturated NaHCO_3 solution, dried over MgSO_4 , filtered and concentrated *in vacuo*. Column chromatography (petrol/ether, 5:1) gave *tribenzoate 11* as a colourless oil (149 mg, 57%). Spectroscopic data as above.

(2S,3R,4S)-2,3,4-Tribenzoyloxy-4-(furan-2-yl)butan-1-ol 12

To a stirred solution of silyl ether **11** (22 mg, 0.035 mmol) in acetonitrile (1 mL) at RT was added fluorosilicic acid (4 μL , 25% by weight solution in water, 0.007 mmol). The mixture was allowed to stir for 5 min and was then diluted with water (2 mL) and extracted with ether (3 \times 5 mL). The combined organic extracts were washed with saturated NaHCO_3 solution (5 mL), dried over MgSO_4 and concentrated *in vacuo*. Column chromatography (petrol/ether, 3:2) gave *alcohol 12* as a white solid (13 mg, 72%). Mp 98–100 $^\circ\text{C}$; R_f 0.14 (petrol/ether, 1:1); $[\alpha]_{\text{D}}^{25}$ –292 (c 0.012, CHCl_3); ν_{max} (CHCl_3)/ cm^{-1} 3424 br, 3080m, 1725s, 1522m; δ_{H} (CDCl_3 , 400 MHz) 2.76 (1 H, br s, CH_2OH), 3.71 (1 H, dd, J 11.7, 7.0) and 3.88 (1 H, dd, J 11.7, 6.0, CH_2OH), 5.15 (1 H, app. tdd, J 6.4, 2.4, 1.2, $\text{CH}(\text{OBz})\text{CH}_2\text{OH}$), 6.29 (1 H, ddd, J 8.8, 2.4, 1.2, $\text{FuCH}(\text{OBz})\text{CHOBz}$), 6.32 (1 H, dd, J 3.2, 1.6) and 6.43 (1 H, d, J 3.2, furan), 6.60 (1 H, dd, J 8.8, 1.2, $\text{FuCH}(\text{OBz})$), 7.14–7.62 (10 H, m) and 7.91–8.11 (6 H, m, 3 \times Ph and furan); δ_{C} (CDCl_3 , 100 MHz) (one resonance obscured) 60.5, 67.9, 71.9, 72.7, 110.7, 111.3, 128.3, 128.5, 128.6, 128.7, 128.9, 129.2 (2 peaks), 129.7, 129.8, 133.3, 133.5, 133.7, 143.8, 165.5, 165.7, 166.9; m/z (ESI^+) 559 (100, $\text{M}\cdot\text{CH}_3\text{CN}\cdot\text{NH}_4^+$), 518 (19, MNH_4^+); HRMS (ESI^+) found 518.1807; $\text{C}_{29}\text{H}_{28}\text{O}_8\text{N}$ (MNH_4^+) requires 518.1809.

(5S,8S,9R,10S)-8,9,10-Tribenzyloxy-2-oxo-1,6-dioxaspiro[4.5]dec-3-ene 13

To a stirred solution of alcohol **12** (160 mg, 0.32 mmol) in dichloromethane (5 mL) at 0 °C was added MCPBA acid (136 mg, *ca.* 70% by weight, 0.55 mmol). The mixture was warmed to RT and allowed to stir for 18 h. Solid Na₂SO₃ (75 mg, 0.60 mmol) was added and the mixture was allowed to stir for a further 1 h and then poured onto water (20 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed sequentially with saturated NaHCO₃ solution (20 mL) and brine (20 mL), then dried over MgSO₄, filtered and concentrated *in vacuo*. The crude mixture was immediately dissolved in dichloromethane (5 mL) and NMO (52 mg, 0.45 mmol) and TPAP (1.5 mg, 4.27 μmol) added. After 18 h the mixture was diluted with ether (50 mL), filtered through a short plug of silica and concentrated *in vacuo*. Column chromatography (petrol/ether, 2:1) yielded *butenolide 13* as a white solid (128 mg, 78%). Mp 114–115 °C; R_f 0.11 (petrol/ether, 1:1); [α]_D²⁵ –165 (*c* 0.01, CHCl₃); δ_H (CDCl₃, 400 MHz) 4.16 (1 H, t, *J* 10.8) and 4.40 (1 H, dd, 10.8, 5.6, CH₂), 5.56 (1 H, app. td, *J* 10.4, 5.6, CH₂CHOBz), 5.70 (1 H, d, *J* 10.4, CH(OBz)-spiro), 6.15 (1 H, d, *J* 5.2, =CHCO), 6.26 (1 H, t, *J* 10.4, CH(OBz)CH(OBz)-spiro), 7.24–7.53 (10 H, m) and 7.89–8.03 (6 H, m, 3 × Ph and =CH-spiro); δ_C (CDCl₃, 100 MHz) 67.4, 72.5, 73.2, 74.4, 115.1, 126.1, 158.8, 128.6 (2 peaks), 128.9 (3 peaks), 129.2, 129.4, 129.8, 130.1, 133.2, 133.5, 133.8, 165.7, 165.7, 166.9, 170.1; *m/z* (ESI⁺) 574 (37%), 573 (100, M·CH₃CN·NH₄⁺), 449 (19), 337 (12); HRMS (ESI⁺) found 537.1161; C₂₉H₂₂O₉Na (MNa⁺) requires 537.1156.

N-2-(Hydroxyethyl)crotonamide³

To a stirred solution of 2-aminoethanol (6.0 mL, 100 mmol) in chloroform (6 mL) at 0 °C was added dropwise a solution of crotonyl chloride (4.79 mL, 50 mmol) in chloroform (6 mL). Precipitated 2-aminoethanol hydrochloride was filtered off and washed with chloroform (2 × 10 mL). The filtrate was concentrated *in vacuo* to give a yellow oil that was distilled under reduced pressure to yield the title amide (5.29 g, 82%) as a viscous, pale yellow oil. Bp 150–155 °C, 1.5 mmHg (lit.,²⁵ bp 165 °C, 2.0 mmHg). R_f 0.30 (dichloromethane/methanol, 9:1); ν_{max} (CHCl₃)/cm⁻¹ 3325m, 1673s, 1633s, 1522s, 1222s, 1071m, 964m, 784s; δ_H (200 MHz, CDCl₃) 1.82 (3 H, dd, *J* 7.0, 1.5, CH₃), 3.42 (2 H, app. q, *J* 5.5, CH₂NH), 3.67 (2 H, t, *J* 5.5, CH₂OH), 4.34 (1 H, br s, OH), 5.87 (1 H, dq, *J* 15.0, 1.5, =CHCO), 6.79 (1 H, dq, *J* 15.0, 7.0, CH₃CH=), 7.08 (1 H, br s, NH); δ_C (50.3 MHz, CDCl₃) 18.0, 42.6, 61.5, 125.4, 140.1, 167.7; *m/z* (CI) 130 (MH⁺, 42%), 112 (100), 104 (18).

2-[(*E*)-Propen-1-yl]-1,3-oxazoline **22**⁴

To a solution of *N*-2-(hydroxyethyl)crotonamide (3.95 g, 30.6 mmol) and triphenylphosphine (10.03 g, 38.2 mmol) in THF (5 mL) at 0 °C was added dropwise DIAD (7.53 mL, 38.2 mmol).

The mixture was stirred for 30 min at 0 °C and for 4 h at room temperature. The solvent was removed *in vacuo*, replaced with ether (10 mL) and the reaction mixture left to stand for 16 h. Precipitated triphenylphosphine oxide was filtered off, washed with ether (2 × 10 mL) and the filtrate dried (Na₂SO₄). Concentration *in vacuo* and distillation of the crude product under reduced pressure afforded oxazoline **22** (2.35 g, 69%) as a pale yellow oil. Bp 20–25°C, 0.5 mmHg (lit.,⁴ 28–29 °C, 1.0 mmHg); R_f 0.47 (dichloromethane/methanol, 9:1); ν_{max} (thin film)/cm⁻¹ 3054w, 2973m, 2939m, 1674s, 1646m, 1614s, 1364s, 1252s, 997s, 908m, 731s; δ_H (200 MHz, CDCl₃) 1.81 (3 H, dd, *J* 7.0, 1.5, CH₃), 3.84 (2 H, t, *J* 9.5, CH₂N), 4.20 (2 H, t, *J* 9.5, CH₂O), 5.95 (1 H, dq, *J* 16.0, 1.5, CH₃CH=CH), 6.53 (1 H, dq, *J* 16.0, 7.0, CH₃CH=); δ_C (50.3 MHz, CDCl₃) 18.7, 54.9, 67.4, 119.4, 139.3, 164.3; *m/z* (CI) 112 (MH⁺, 100%).

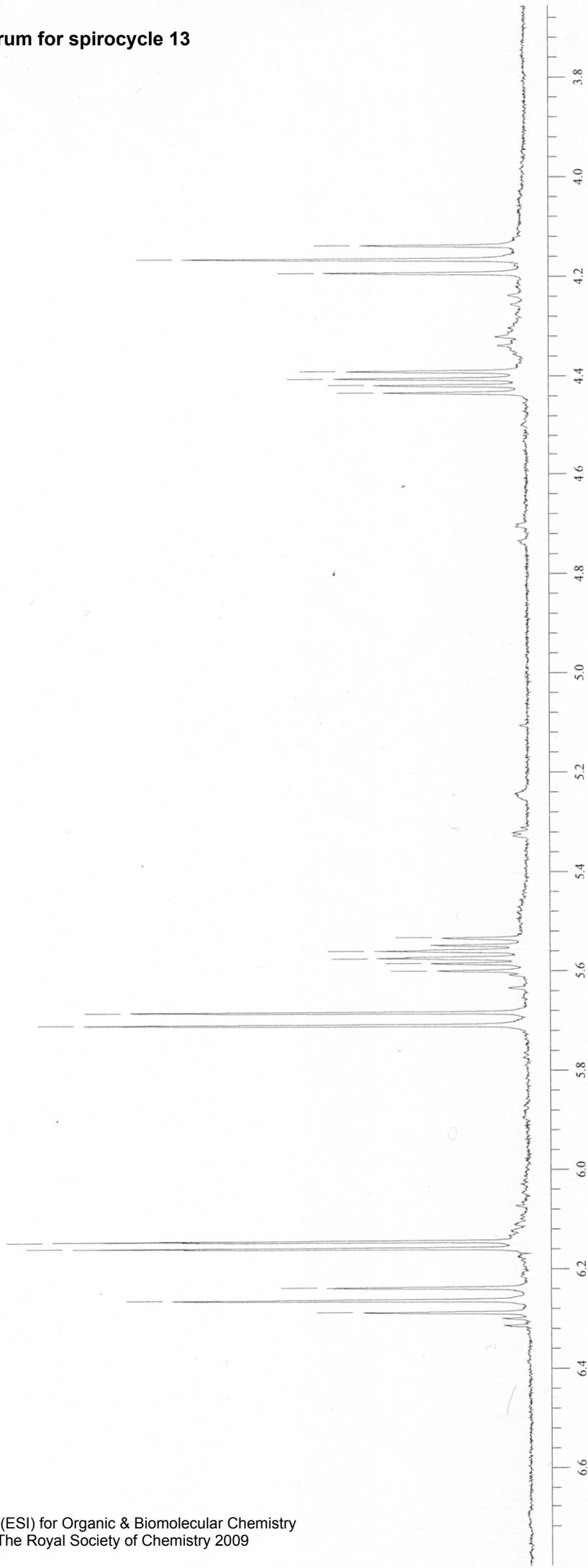
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Expansion of ¹H NMR spectrum for spirocycle 13

4.433
4.166
4.138
4.193
4.419
4.406
4.391

5.584
5.707
5.573
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5.532
5.598
5.681

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6.157
6.143
6.237
6.287



NMR@CHEM.OX

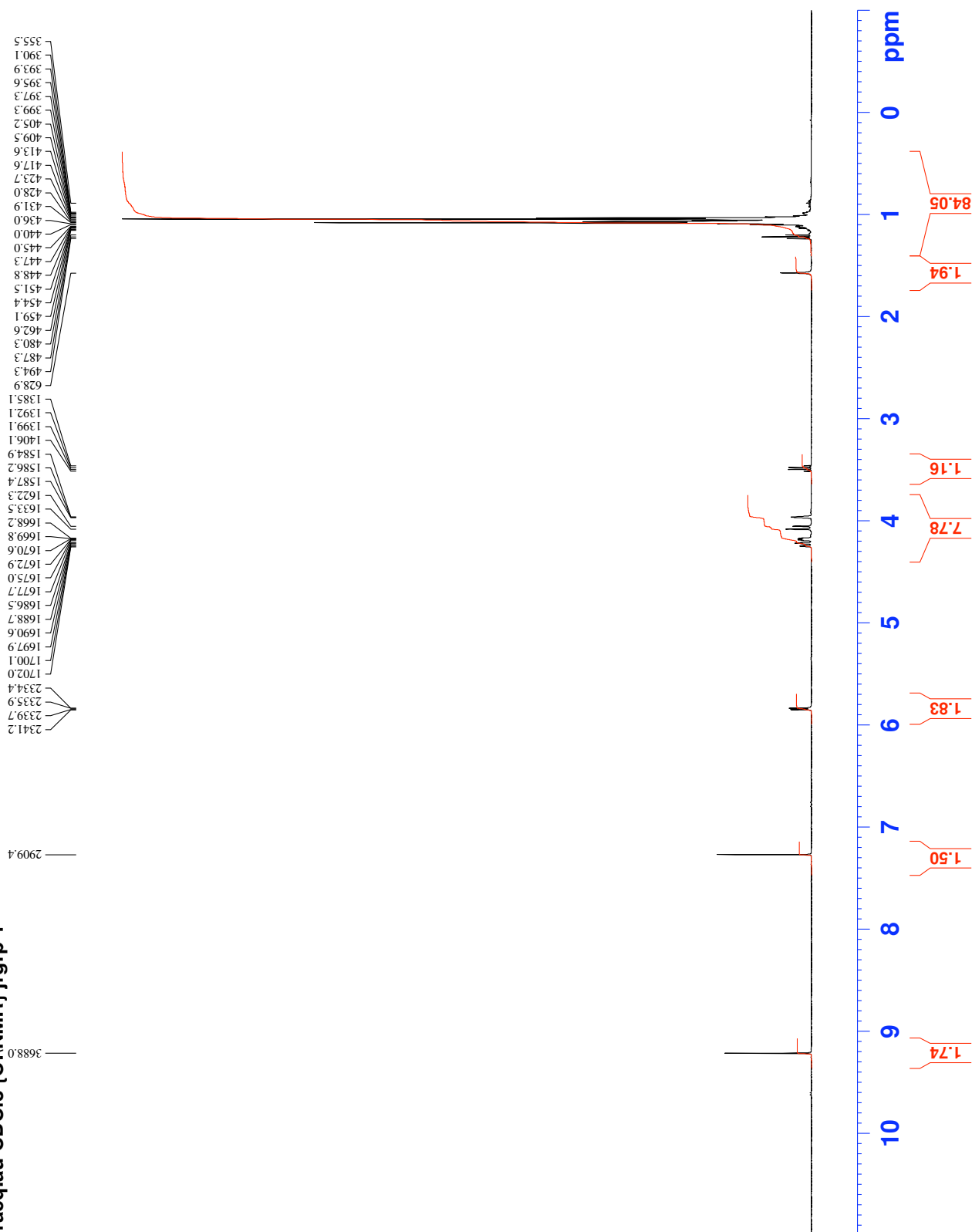
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Current Data Parameters
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 DE 7.50 usec
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 PL1 0.00 dB
 SFO1 400.2024714 MHz

F2 - Processing parameters
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 LB 0.30 Hz
 GB 0
 PC 1.00



NMR@CHEM.OX

Instrument DQX400
 Chemist pc
 Group jr
 PC--Oxazoline
 h1acq.au CDCI3 {C:\NMR} jrgrp 8

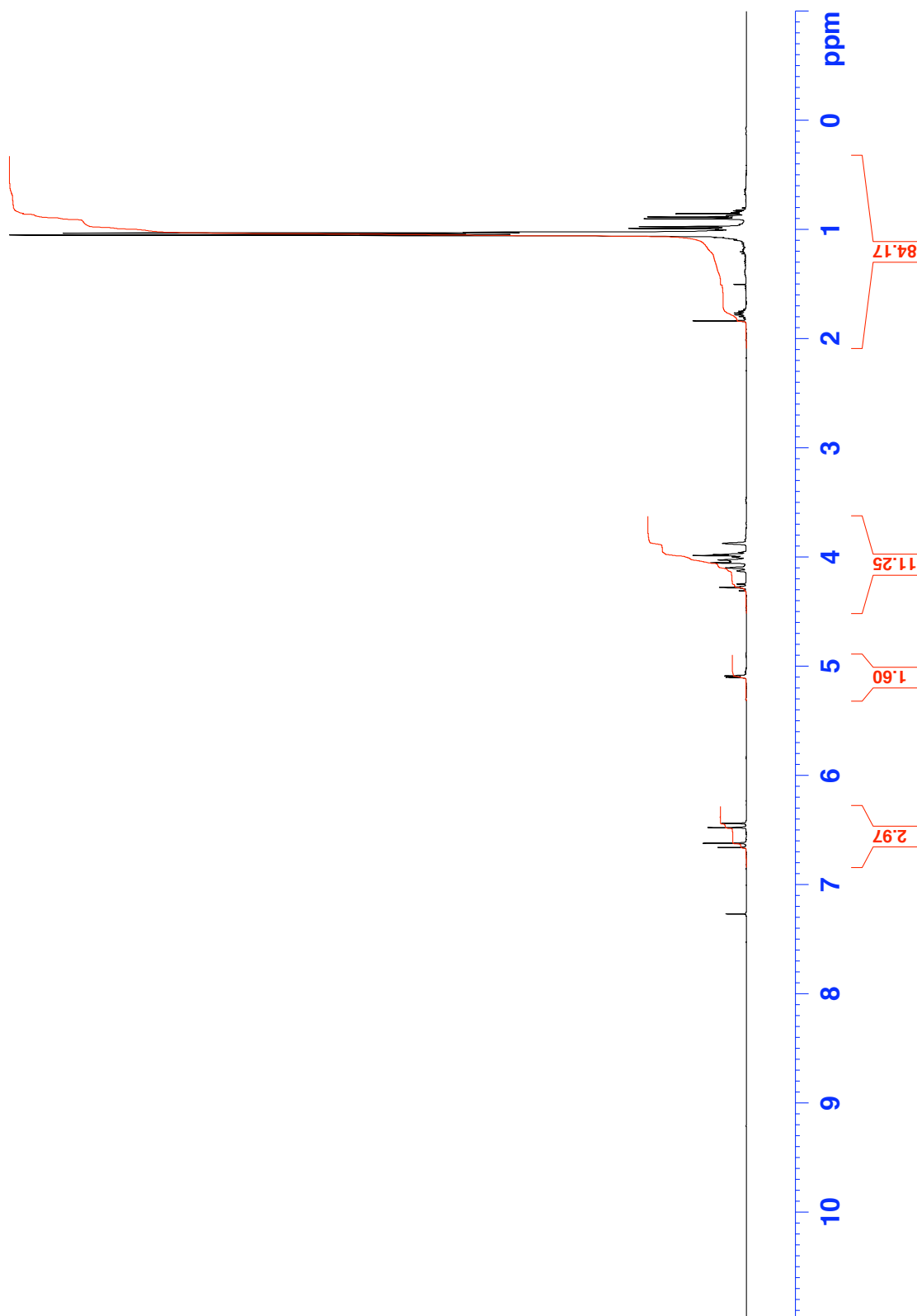
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361.1
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389.7
396.5
400.2
410.2
413.4
417.6
420.9
429.0
431.5
434.1
438.6
443.9
446.8
453.2
481.6
489.1
601.6
699.7
706.1
712.5
719.0
735.3
1550.8
1583.8
1591.8
1595.1
1600.4
1602.8
1611.4
1615.5
1618.1
1622.3
1638.6
1640.5
1649.8
1651.7
1653.4
1699.9
1708.7
1711.7
1712.7
1715.5
1724.7
2036.9
2041.8
2577.1
2592.8
2649.9
2665.6
2909.3

Current Data Parameters
 NAME Sep22-2008-8
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080922
 Time 12.15
 INSTRUM av400
 PROBHD 5 mm QNP 1H/13
 PULPROG zg60
 TD 65536
 SOLVENT CDCI3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 35.9
 DW 60.400 usec
 DE 7.50 usec
 TE 300.0 K
 D1 1.0000000 sec

==== CHANNEL f1 =====
 NUC1 1H
 P1 9.00 usec
 PL1 0.00 dB
 SFO1 400.2024714 MHz

F2 - Processing parameters
 SI 32768
 SF 400.2000028 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NMR@CHEM.OX

Instrument DQX400
 Chemist pc
 Group jr
 PC-1,4-add[PhOBn]
 h1acq.au CDC13 {C:\NMR}\jirgp 49

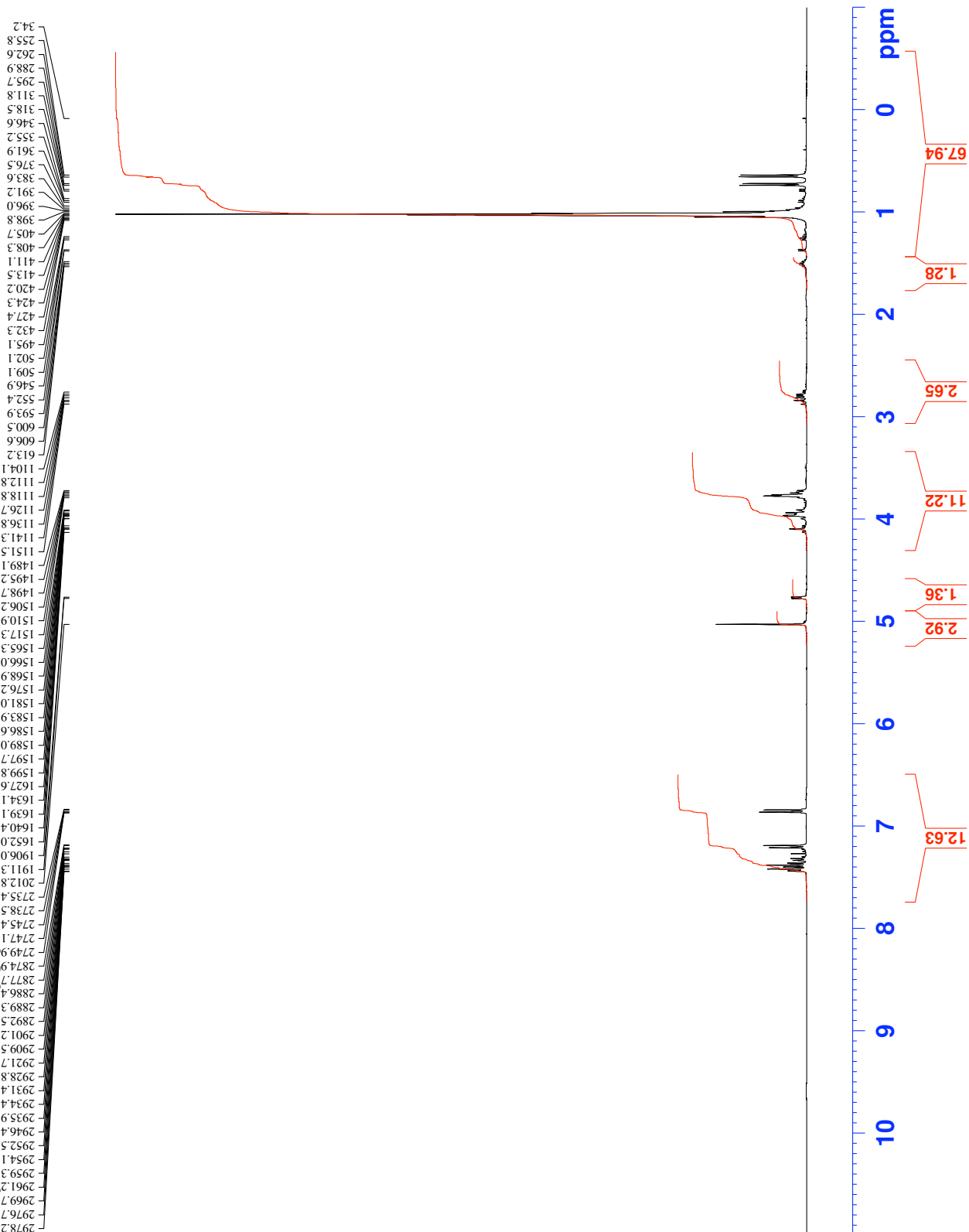
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Current Data Parameters
NAME      Sep04-2008-49
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20080904
Time     18.33
INSTRUM av400
PROBHD   5 mm QNP 1H/13
PULPROG zg60
TD        65536
SOLVENT  CDC13
NS        16
DS        2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9584243 sec
RG        35.9
DW        60.400 usec
DE        7.50 usec
TE        300.0 K
D1        1.0000000 sec

===== CHANNEL f1 =====
NUC1      1H
P1        9.00 usec
PL1       0.00 dB
SFO1      400.2024714 MHz

F2 - Processing parameters
SI        32768
SF        400.2000028 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
```



NMR@CHEM.OX

Instrument DQX400
 Chemist pc
 Group jr
 PC--Acid[OBn]from ester
 h1acq.au CDCl3 {C:NMR} jirgp 37

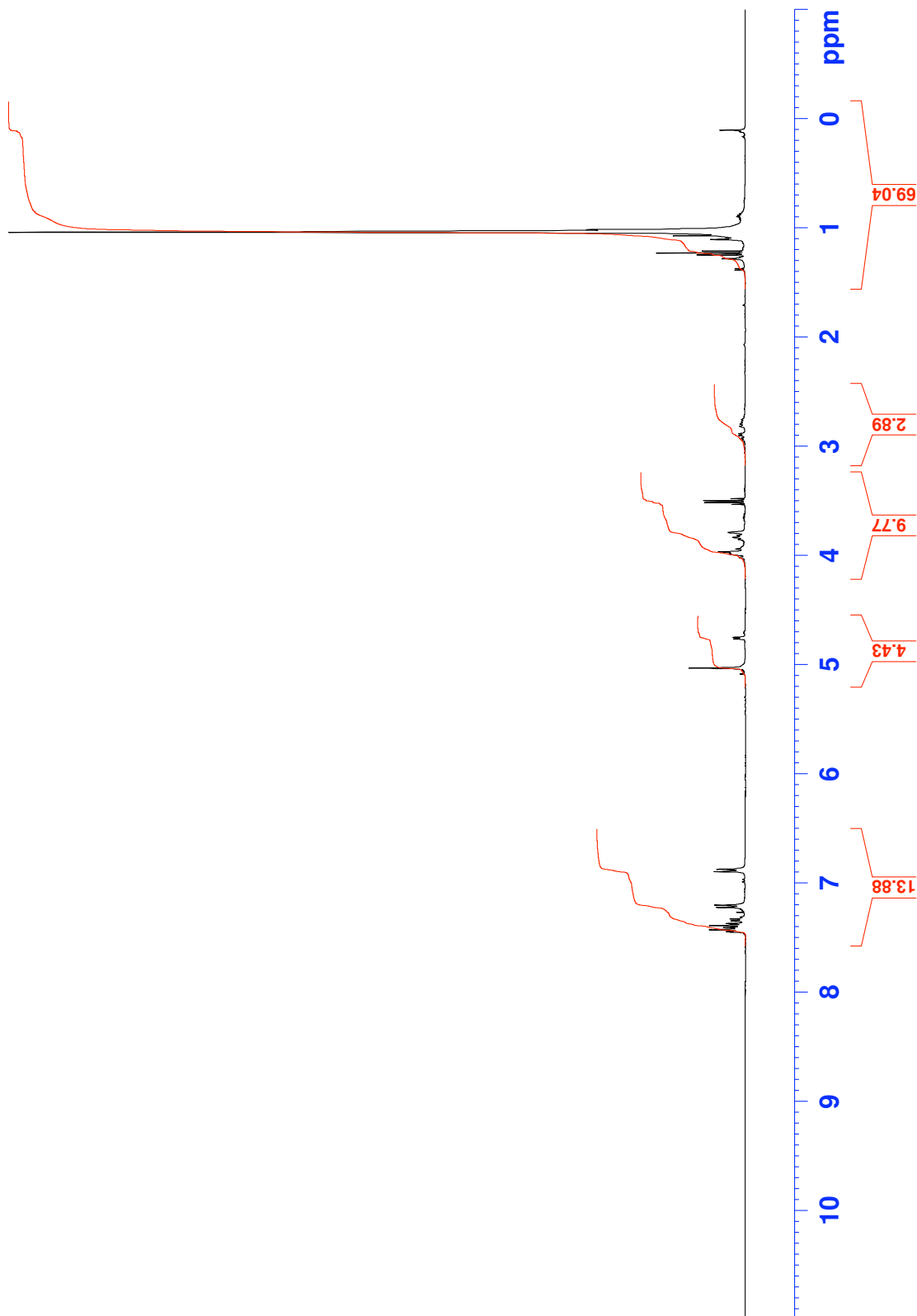
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2973.6
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2958.0
2950.5
2940.6
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2933.6
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2926.4
2909.3
2899.2
2891.5
2882.9
2760.2
2751.6
2748.9
2035.6
2014.0
1906.7
1901.6
1699.2
1597.8
1595.6
1592.6
1588.1
1577.3
1542.5
1540.0
1535.2
1527.6
1516.8
1414.1
1407.1
1400.1
1393.1
1179.9
1171.2
1161.6
1154.9
1127.8
1119.3
1111.4
1103.0
554.9
549.4
513.4
508.2
507.4
499.5
492.5
485.4
442.7
439.7
428.9
426.4
416.3
406.8
403.4
374.3
368.7
363.1
358.8
354.3
348.1
49.4

Current Data Parameters
 NAME Sep18-2008-37
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080918
 Time 22.42
 INSTRUM av400
 PROBHD 5 mm QNP 1H/13
 PULPROG zg60
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 25.4
 DW 60.400 usec
 DE 7.50 usec
 TE 300.0 K
 D1 1.0000000 sec

==== CHANNEL f1 =====
 NUC1 1H
 P1 9.00 usec
 PL1 0.00 dB
 SFO1 400.2024714 MHz

F2 - Processing parameters
 SI 32768
 SF 400.2000028 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NMR@CHEM.OX

Instrument DQX400
 Chemist pc
 Group jr
 PC-Spiro[OBn]82mg
 h1acq.au CDCl3 {C:\NMR}\jirgp 28

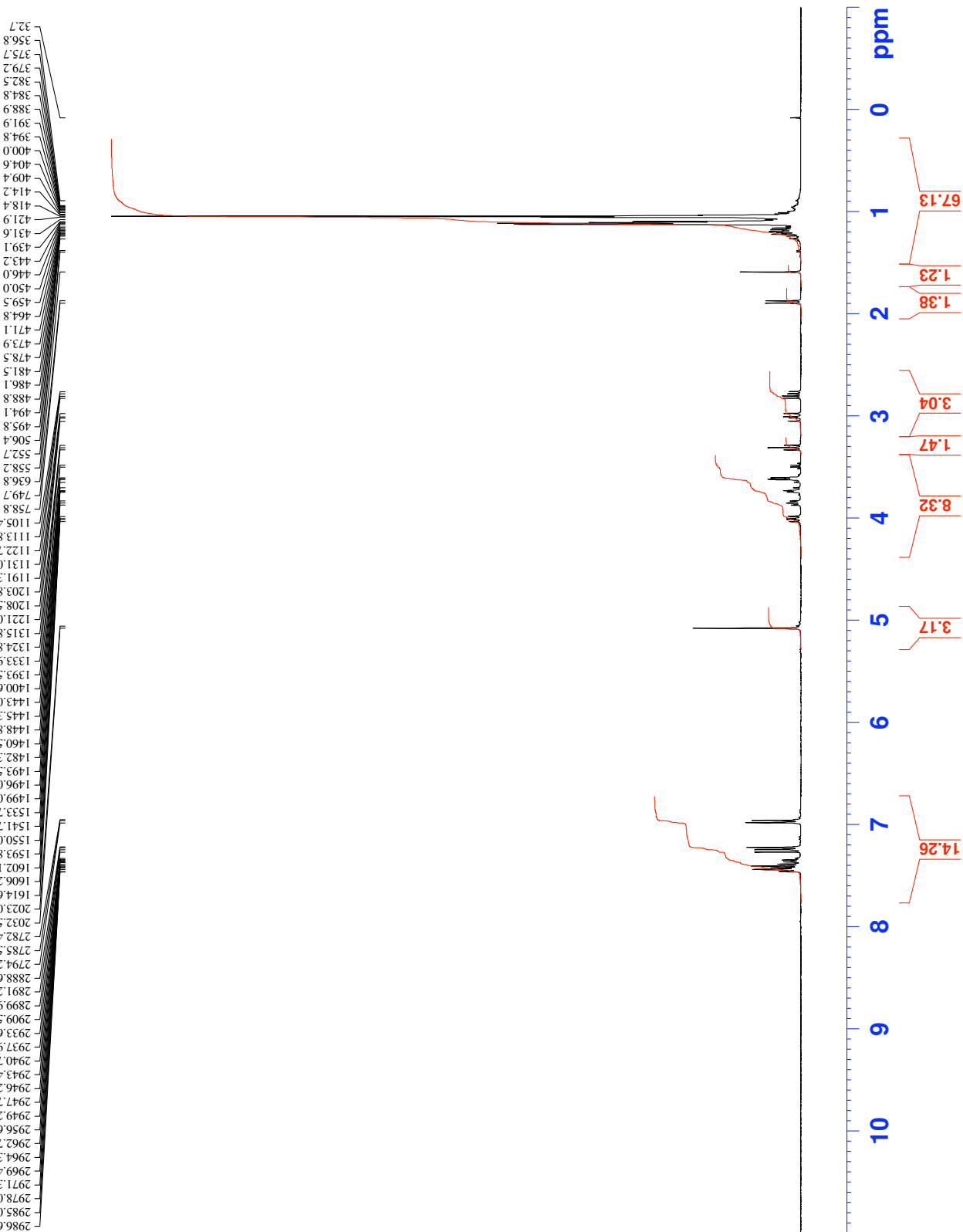
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Current Data Parameters
NAME      Sep15-2008-28
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20080915
Time     17.21
INSTRUM av400
PROBHD   5 mm QNP 1H/13
PULPROG zg60
TD        65536
SOLVENT  CDC13
NS        16
DS        2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9584243 sec
RG        90.5
DW        60.400 usec
DE        7.50 usec
TE        300.0 K
D1        1.0000000 sec

===== CHANNEL f1 =====
NUC1      1H
P1        9.00 usec
PL1       0.00 dB
SFO1      400.2024714 MHz

F2 - Processing parameters
SI        32768
SF        400.2000028 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
```



NMR@CHEM.OX

Instrument DQX400
 Chemist pc
 Group jr
 PC-Tips deprol[19-24]
 h1acq.au CDCl3 {C:[NMR]} jrgp 29

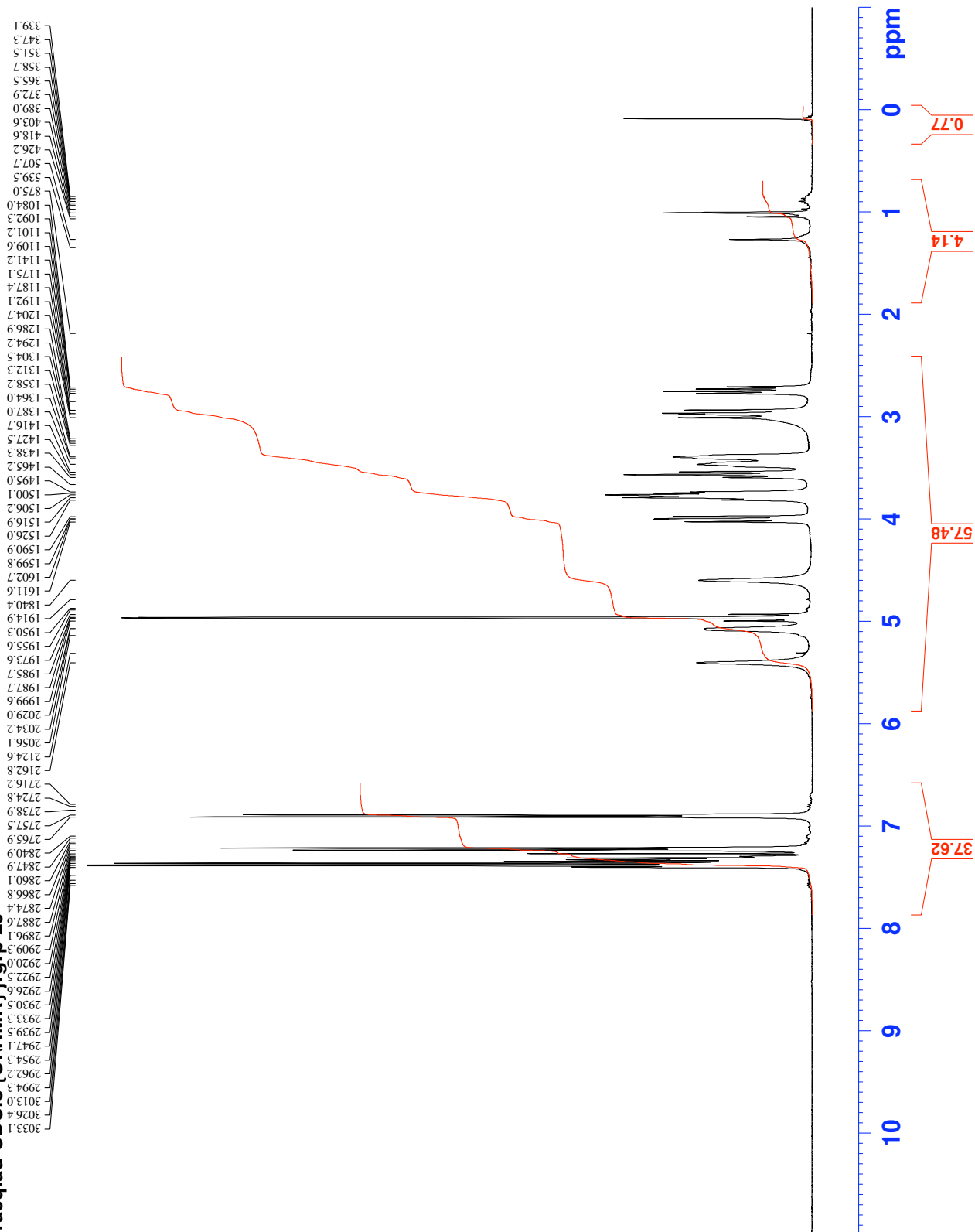
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Current Data Parameters
NAME      Sep18-2008-29
EXPNO    1
PROCNO   1

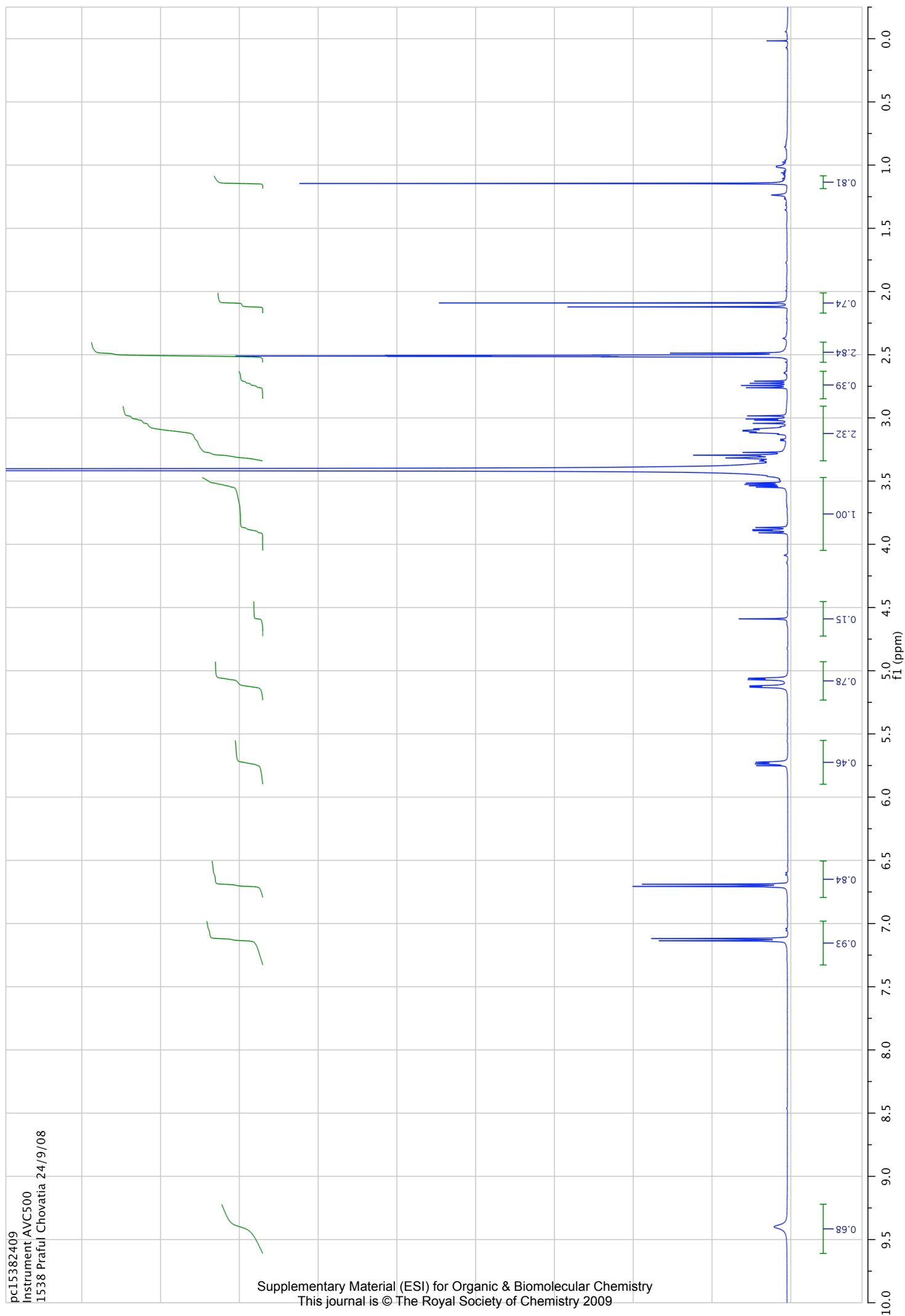
F2 - Acquisition Parameters
Date_    20080918
Time     20.08
INSTRUM  av400
PROBHD   5 mm QNP 1H/13
PULPROG  zg60
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9584243 sec
RG        128
DW        60.400 usec
DE        7.50 usec
TE        300.0 K
D1        1.0000000 sec

===== CHANNEL f1 =====
NUC1      1H
P1        9.00 usec
PL1       0.00 dB
SFO1      400.2024714 MHz

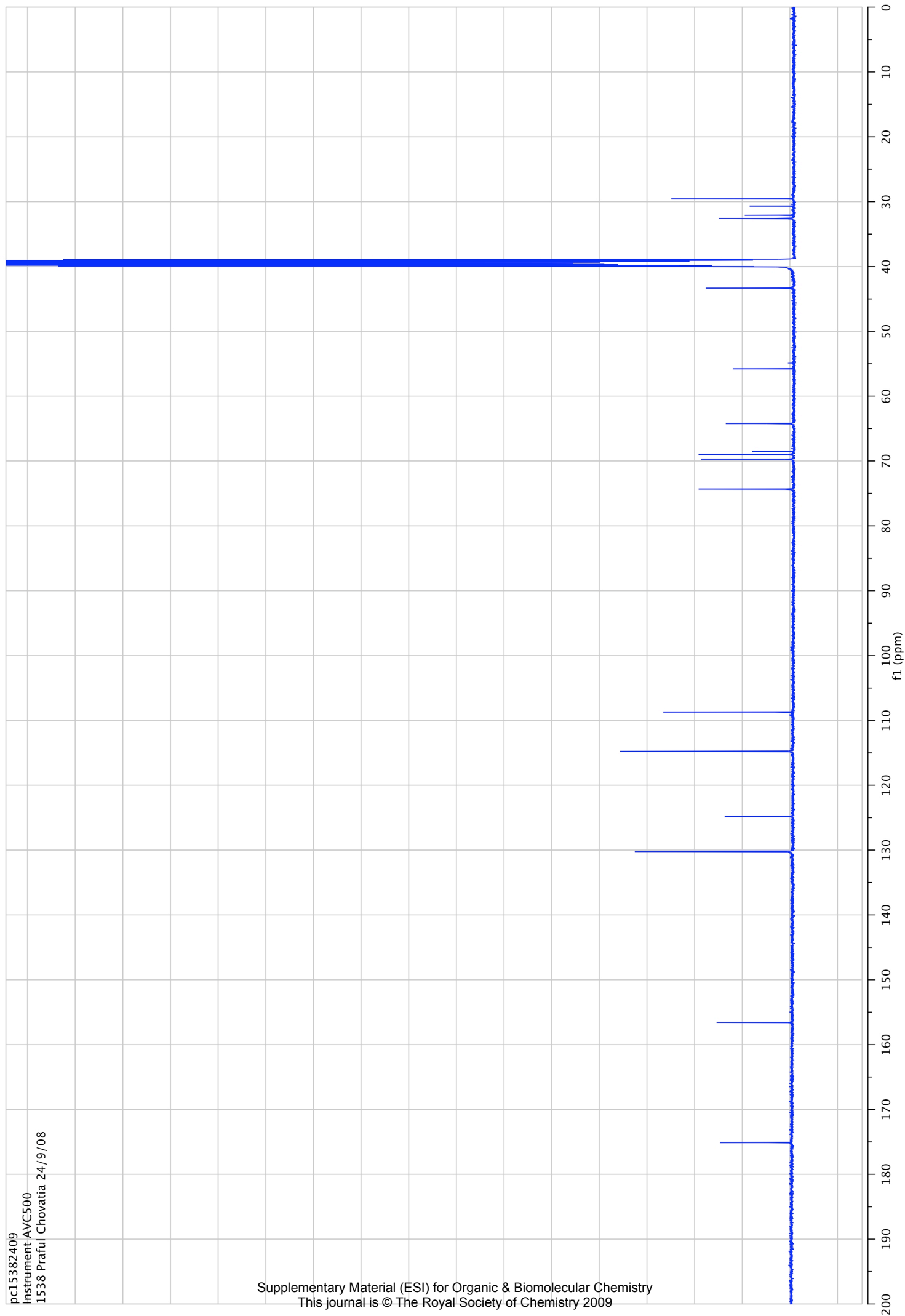
F2 - Processing parameters
SI        32768
SF        400.2000028 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
```



1H NMR spectrum for (30) [ent-sawaranospirolide C]



pc15382409
Instrument AVC500
1538 Pratul Chovatia 24/9/08



pc15382409
Instrument AVC500
1538 Pratul Chovatia 24/9/08

NMR@CHEM.OX

Instrument DQX400
 Chemist pc
 Group jr
 PC--Oxidation[DMP]
 h1acq.au CDCl3 {C:\NMR} jrgpr 42

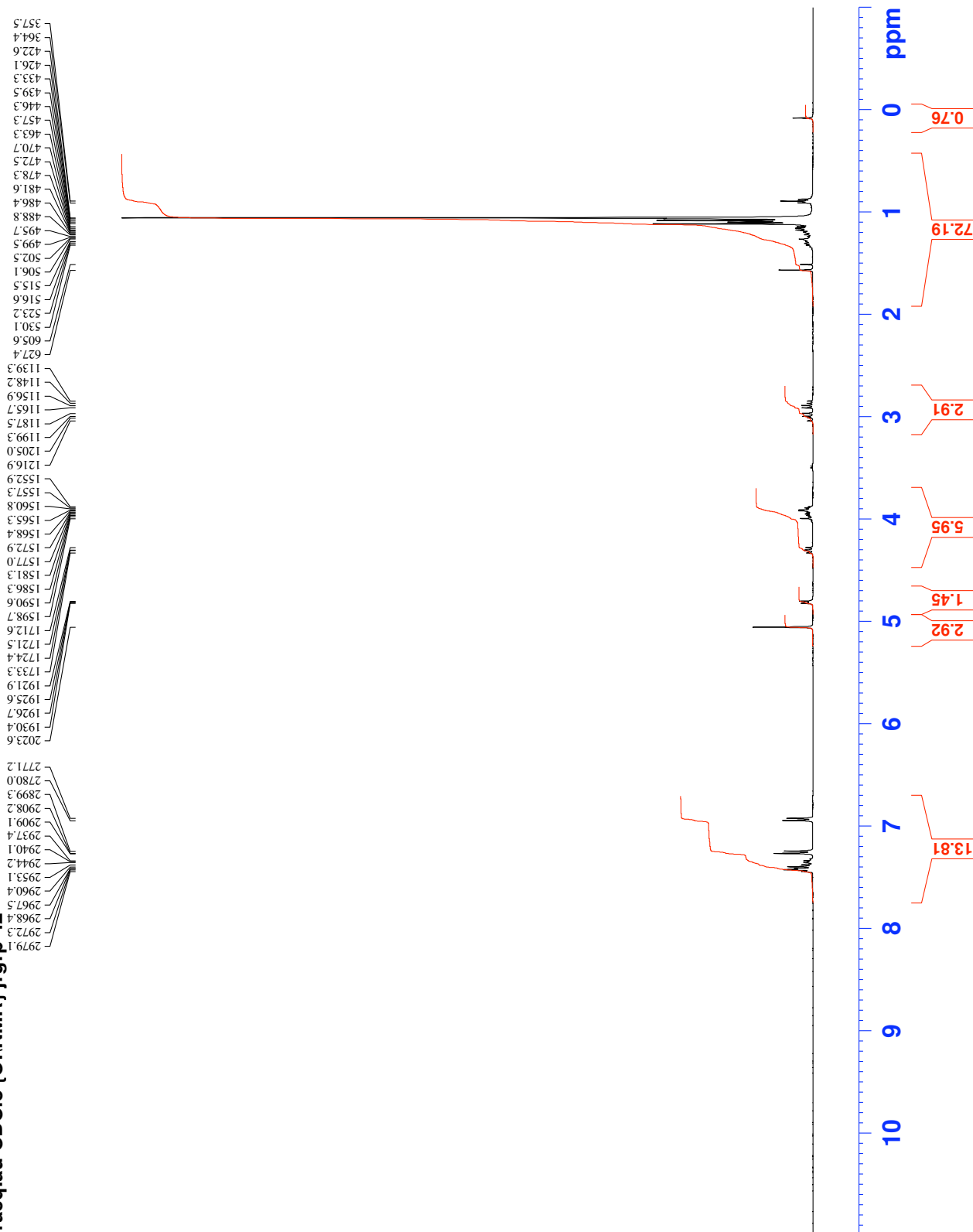
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Current Data Parameters
NAME      Nov11-2008-42
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20081111
Time     14.53
INSTRUM av400
PROBHD   5 mm QNP 1H/13
PULPROG zg60
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      8278.146 Hz
FIDRES   0.126314 Hz
AQ       3.9584243 sec
RG       90.5
DW       60.400 usec
DE       7.50 usec
TE       300.0 K
D1       1.0000000 sec

===== CHANNEL f1 =====
NUC1     1H
P1       9.00 usec
PL1      0.00 dB
SFO1     400.2024714 MHz

F2 - Processing parameters
SI       32768
SF       400.2000028 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
    
```



Instrument DQX400
 Chemist pc
 Group jr
 PC-SPIRO[PPTS]
 h1acq.au CDCI3 {C:\NMR} jgrp_12

NMR@CHEM.OX

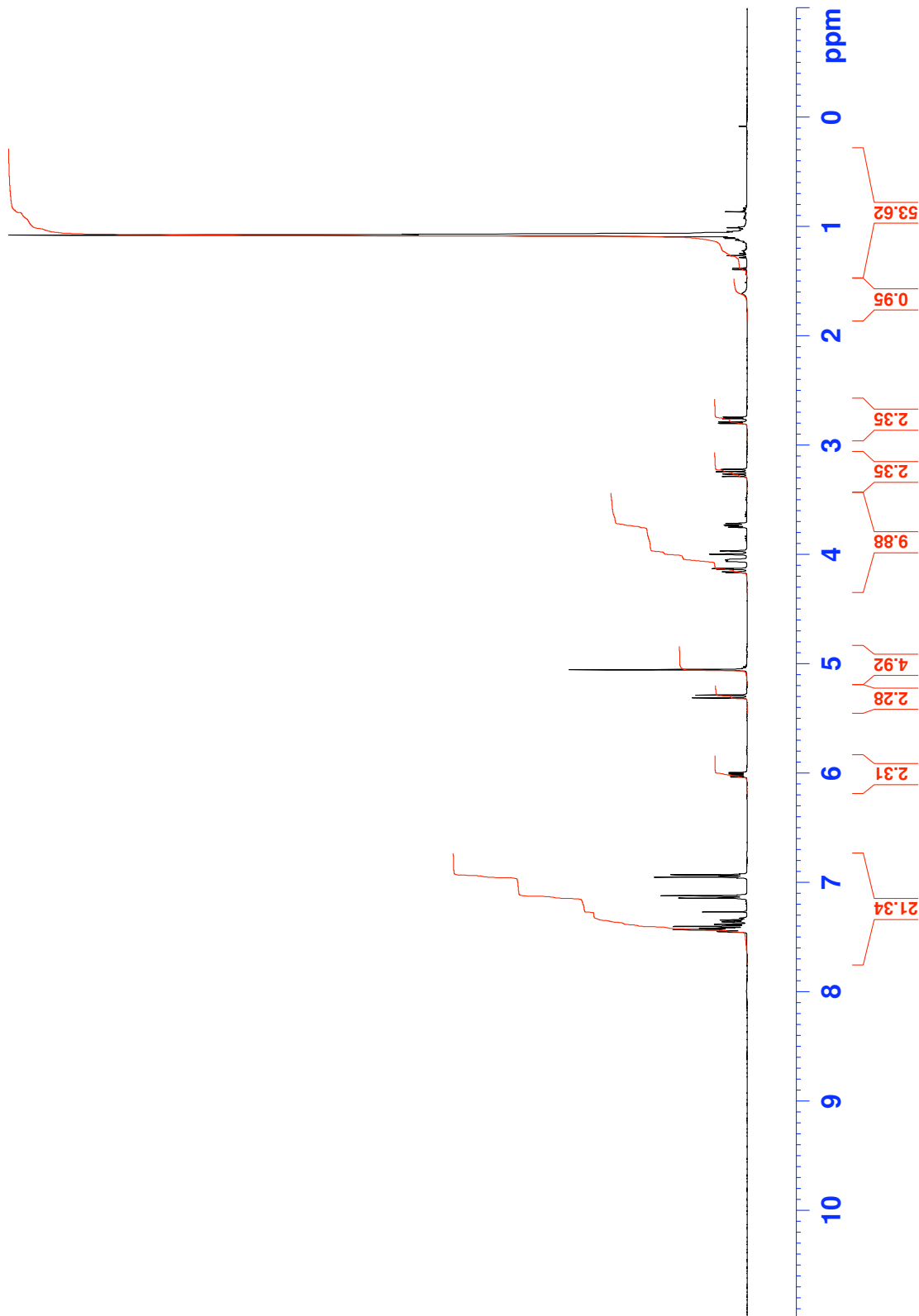
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2981.7
2974.9
2970.6
2969.7
2967.7
2962.8
2961.1
2955.1
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2946.3
2944.6
2942.1
2939.4
2936.4
2933.8
2932.4
2909.4
2882.0
2859.2
2850.5
2847.7
2785.3
2782.4
2780.5
2775.4
2773.7
2770.7
2415.6
2414.7
2410.4
2409.4
2405.5
2404.5
2400.2
2399.2
2126.1
2023.0
2017.6
1667.2
1664.5
1655.1
1652.5
1626.1
1623.7
1621.0
1600.4
1588.3
1501.2
1496.1
1492.6
1487.5
1315.5
1306.8
1298.0
1289.3
1121.2
1116.1
1103.7
1098.6
645.7
558.1
552.6
513.9
506.8
499.8
489.1
458.7
452.2
450.5
446.9
443.7
440.3
436.1
431.4
428.9
423.2
418.6
412.5
404.8

Current Data Parameters
 NAME Sep30-2008-12
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080930
 Time 10.06
 INSTRUM av400
 PROBHD 5 mm QNP 1H/13
 PULPROG zg60
 TD 65536
 SOLVENT CDCI3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 90.5
 DW 60.400 usec
 DE 7.50 usec
 TE 293.1 K
 D1 1.0000000 sec

==== CHANNEL f1 =====
 NUC1 1H
 P1 9.00 usec
 PL1 0.00 dB
 SFO1 400.2024714 MHz

F2 - Processing parameters
 SI 32768
 SF 400.2000028 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NMR@CHEM.OX

Instrument DQX400
 Chemist pc
 Group jr
 PC-SPIRO[CSA]-2nd spot
 h1acq.au CDCl3 {C:NMR} jrgpr 37

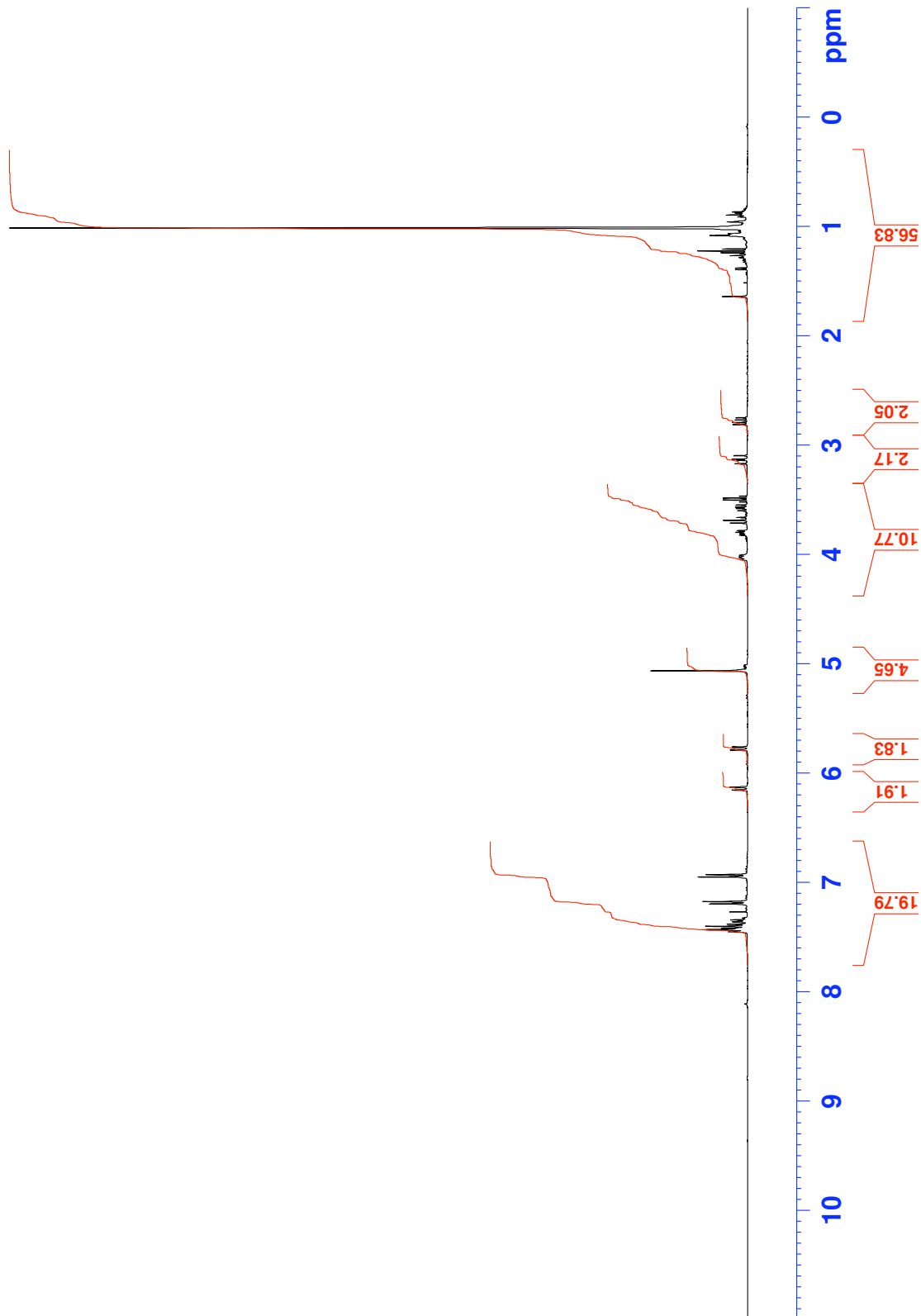
405.7
410.6
417.5
420.8
426.8
429.1
433.1
445.1
448.6
489.6
496.6
499.9
507.0
510.0
514.0
516.3
523.9
530.7
552.4
557.8
657.0
1100.8
1108.7
1117.6
1125.6
1239.2
1252.1
1256.1
1269.0
1387.6
1394.7
1401.7
1408.7
1420.2
1428.2
1433.1
1441.0
1465.8
1476.1
1486.2
1514.4
1520.1
1524.7
1530.4
1604.1
1610.0
1612.0
1614.0
1619.8
2008.7
2023.2
2026.9
2305.4
2307.3
2315.6
2317.5
2453.2
2463.4
2770.4
2773.1
2781.8
2869.2
2871.8
2880.5
2883.3
2909.5
2932.0
2936.2
2939.1
2941.8
2946.0
2954.6
2962.3
2969.4
2975.0
2982.0

Current Data Parameters
 NAME Oct14-2008-37
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20081014
 Time 15.46
 INSTRUM av400
 PROBHD 5 mm QNP 1H/13
 PULPROG zg60
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 90.5
 DW 60.400 usec
 DE 7.50 usec
 TE 300.0 K
 D1 1.0000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.00 usec
 PL1 0.00 dB
 SFO1 400.2024714 MHz

F2 - Processing parameters
 SI 32768
 SF 400.2000028 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NMR@CHEM.OX

Instrument DQX400
 Chemist pc
 Group JR
 PC-dihydroxylation
 h1acq.au CDCl3 {C:NMR} jrgp 23

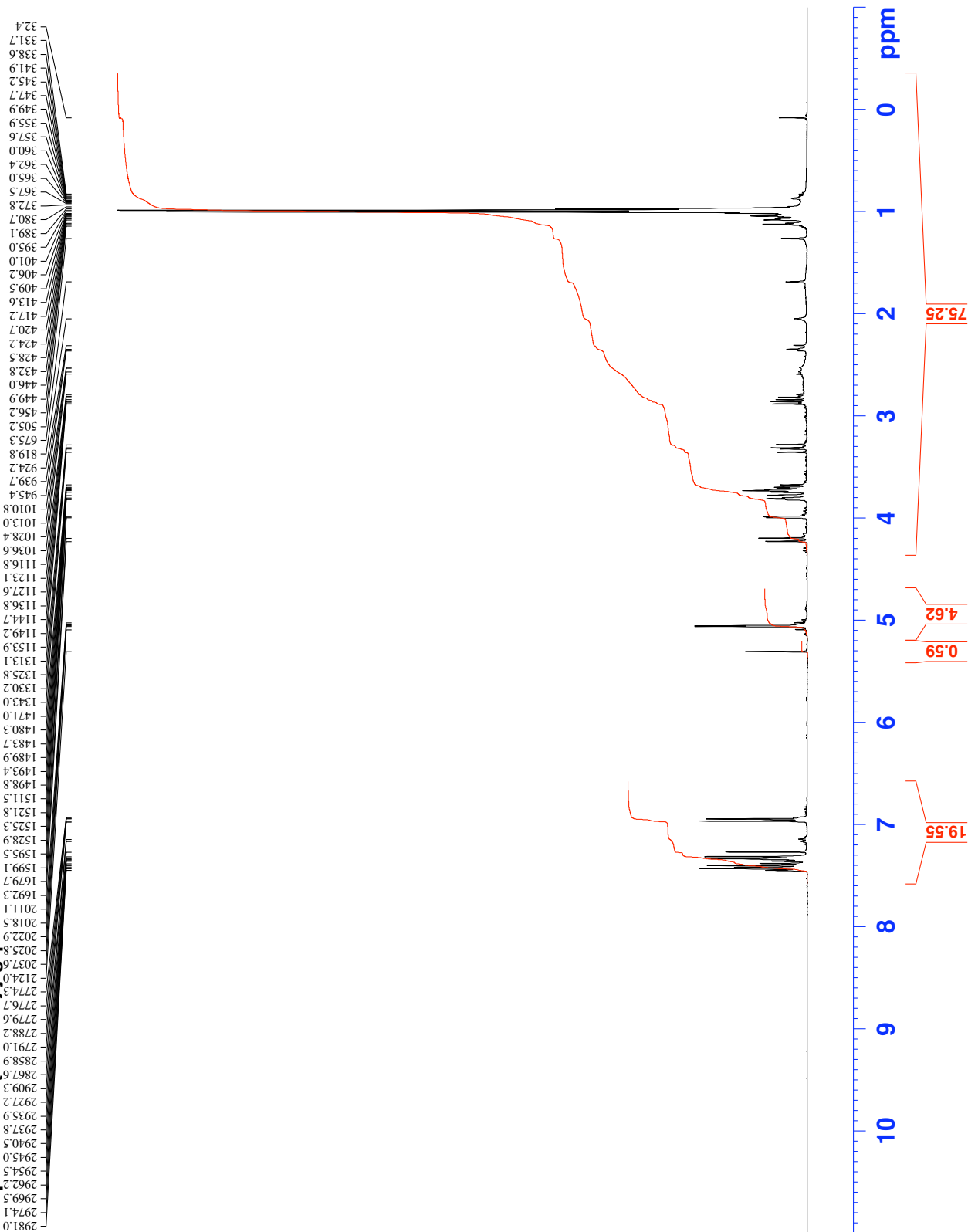
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Current Data Parameters
NAME      Oct06-2008-23
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20081006
Time     13.35
INSTRUM  av400
PROBHD   5 mm QNP 1H/13
PULPROG  zg60
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9584243 sec
RG        90.5
DW        60.400 usec
DE        7.50 usec
TE        300.0 K
D1        1.00000000 sec

===== CHANNEL f1 =====
NUC1      1H
P1        9.00 usec
PL1       0.00 dB
SFO1      400.2024714 MHz

F2 - Processing parameters
SI        32768
SF        400.2000028 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
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NMR@CHEM.OX

Instrument DQX400
Chemist pc
Group jr
PC-Dihydroxylation
h1acq.au CDCl3 {C:NMR} jirgrp 10

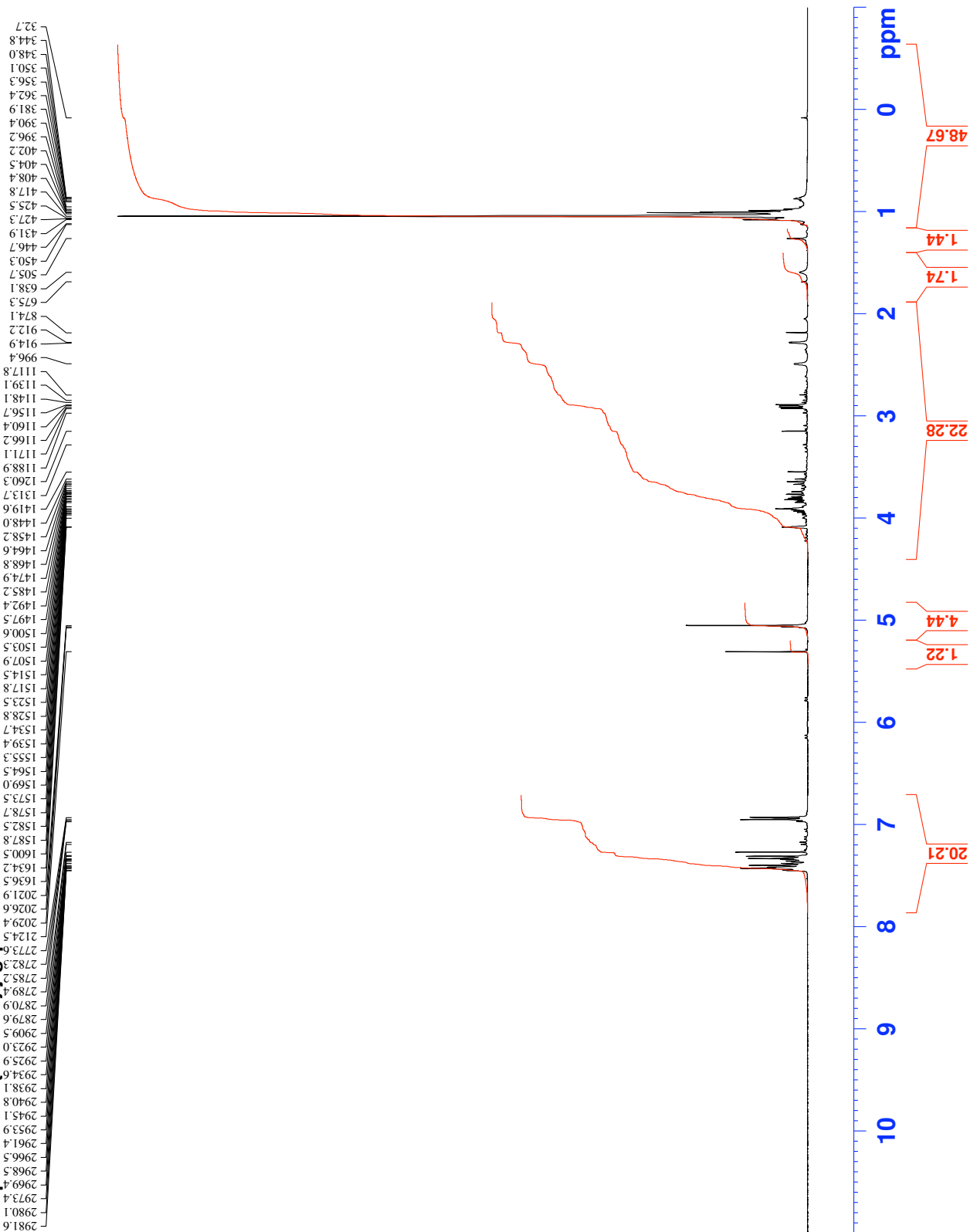
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Current Data Parameters
NAME      Oct28-2008-10
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20081028
Time     12.28
INSTRUM av400
PROBHD   5 mm QNP 1H/13
PULPROG zg60
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      8278.146 Hz
FIDRES   0.126314 Hz
AQ       3.9584243 sec
RG       161.3
DW       60.400 usec
DE       7.50 usec
TE       300.0 K
D1       1.0000000 sec

===== CHANNEL f1 =====
NUC1     1H
P1       9.00 usec
PL1      0.00 dB
SFO1     400.2024714 MHz

F2 - Processing parameters
SI       32768
SF       400.2000028 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
    
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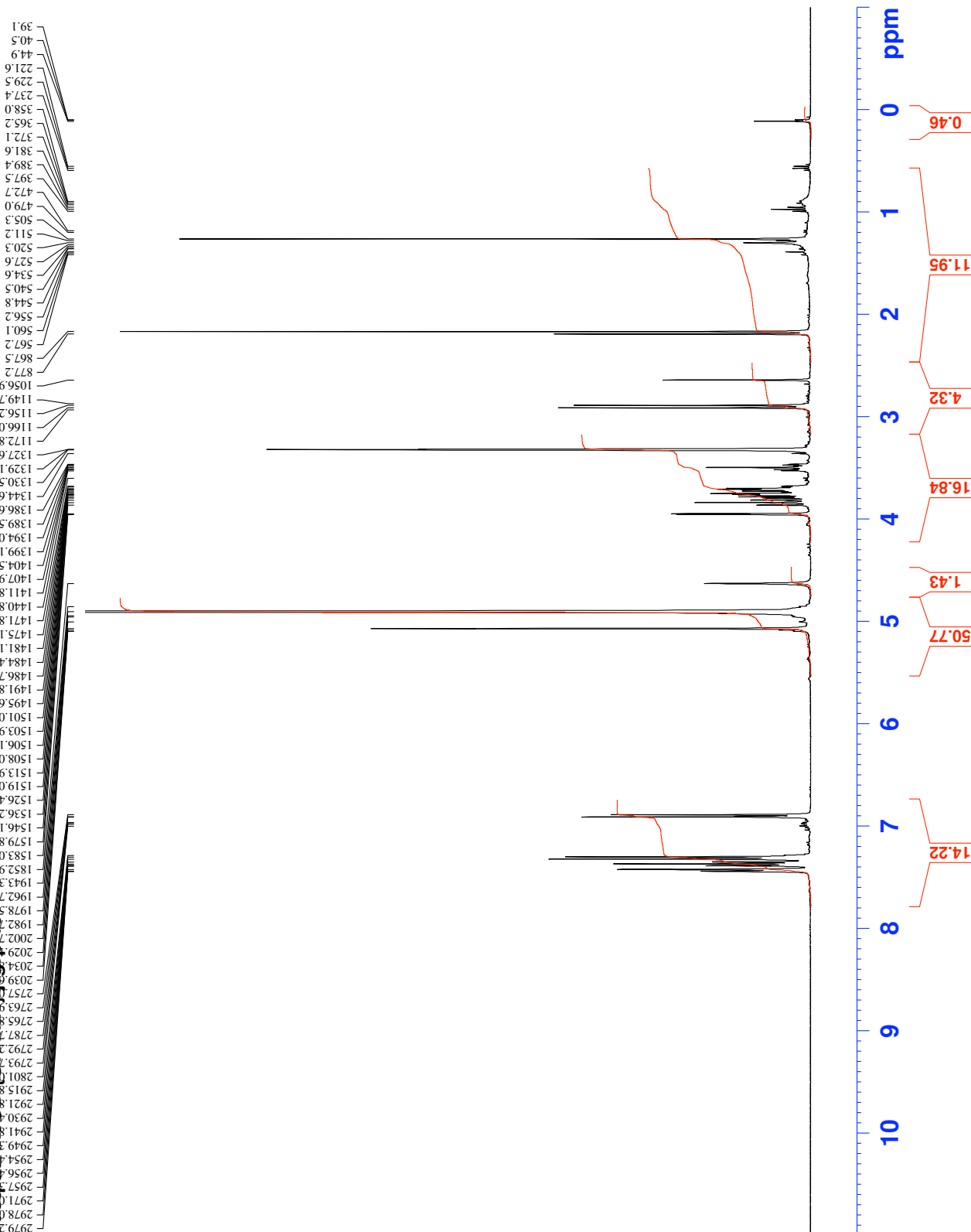


NMR@CHEM.OX

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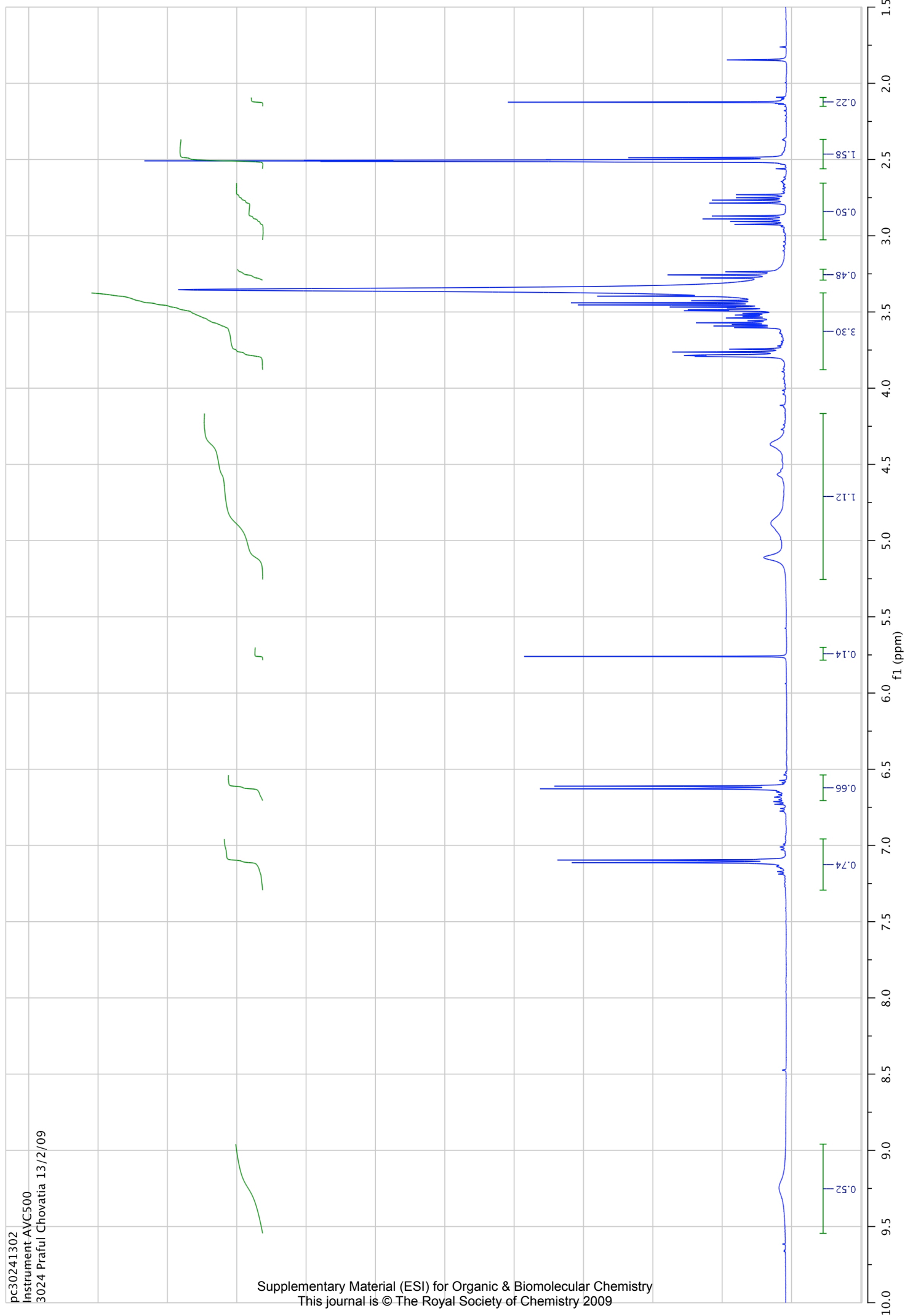
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EXPNO         1
PROCNO        1
Date_         20090210
Time          8.38
INSTRUM       av400
PROBHD        5 mm QNP 1H/13
PULPROG       zg60
TD            65536
SOLVENT       MeOD
NS            16
DS            2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG            128
DW            60.400 usec
DE            7.50 usec
TE            294.8 K
D1            1.0000000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            9.00 usec
PL1           0.00 dB
SF01          400.2024714 MHz
SI            32768
SF            400.2000000 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
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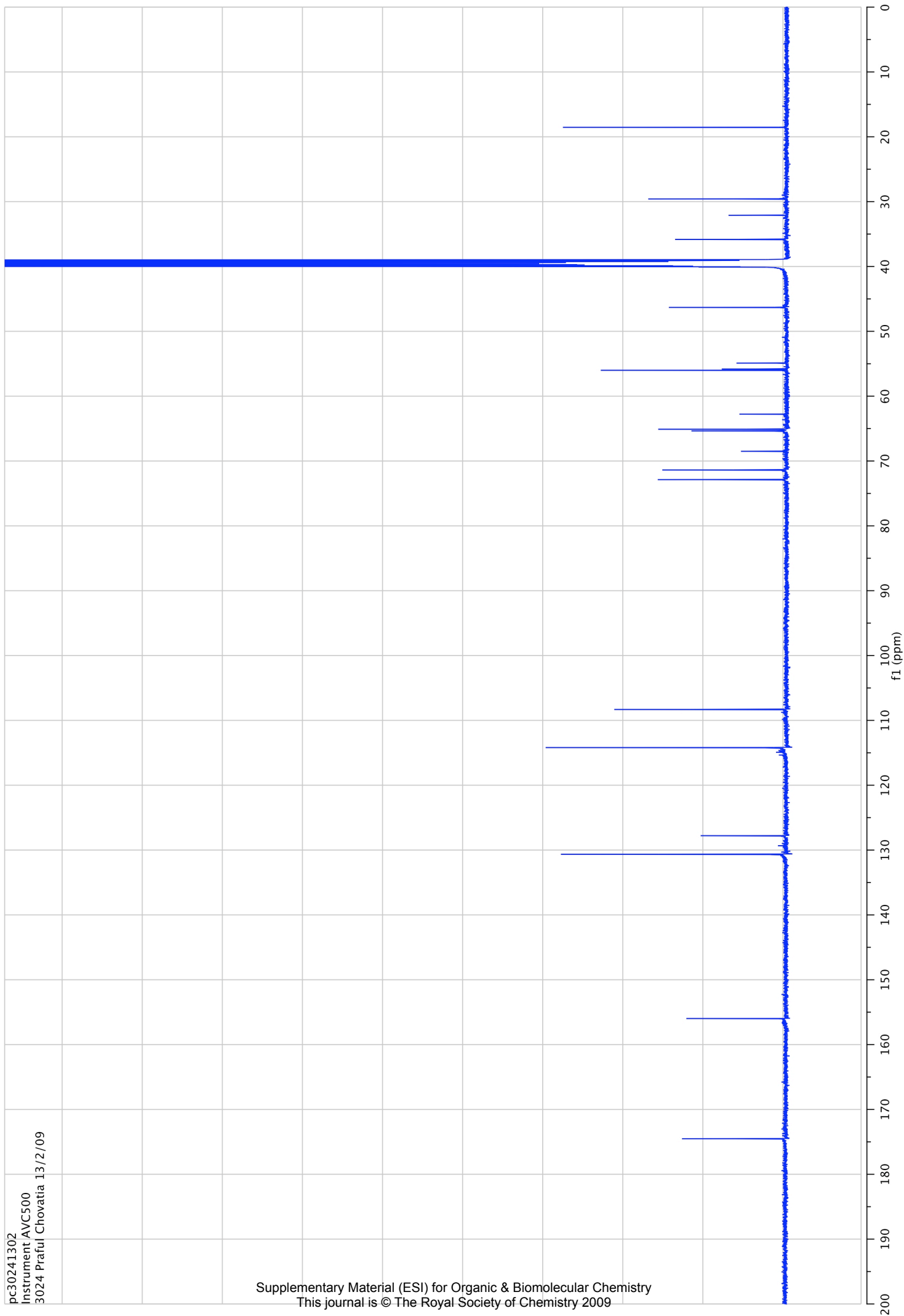


Instrument DQX400
 Chemist pc
 Group jr
 PC-Tips deproIV
 h1 acq. au MeOD (C: NMR) jrgp 10

1H NMR spectrum for (43) [ent-sawaranospirolide D]



pc30241302
Instrument-AVC500
3024 Praful Chovatia 13/2/09



pc30241302
Instrument AVC500
3024 Praful Chovatia 13/2/09