Electronic Supplementary Information

for

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

Jeremy Robertson,* Praful T. Chovatia, Thomas G. Fowler, Jonathan M. Withey and Daniel J. Woollaston

Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford, UK OX1 3TA.

* jeremy.robertson@chem.ox.ac.uk

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

(2) ^{1}H NMR expansion for spirocycle **13**

(3) ^{1}H NMR spectra for experiments in Schemes 7 and 8 and ^{13}C 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* **6**[1]

To a stirred solution of dimethyl methylphosphonate (1.38 mL, 12.7 mmol) in THF (20 mL) at –78 °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 °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 °C for 2 h then quenched with saturated NH_4Cl solution (20 mL). The mixture was extracted with ether (3 × 25 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, $Si(CH_3)_2$), 0.89 (9 H, s, *t*-BuSi), 3.18 (2 H, d, $^2J_{PH}$ 22.5, CH_2PO), 3.76 (6 H, d, $^3J_{PH}$ 11.3, $P(OMe)_2$), 4.22 (2 H, s, CH_2OSi); δ_C ($CDCl_3$, 100 MHz) –5.6, 18.2, 25.7, 36.2 (d, $^1J_{PC}$ 129), 53.0 (d, $^2J_{PC}$ 7.0), 69.4 (d, $^3J_{PC}$ 2.0), 201.8 (d, $^2J_{PC}$ 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 °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 °C for 2 h before being poured into saturated NH_4Cl solution and extracted with ether (3 × 10 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, $Si(CH_3)_2$), 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 × 1 H, 2 × d, *J* 15.8, CH=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; $C_{14}H_{23}O_3Si$ (MH^+) requires 267.1411.

*(3*S*, 4*S*)-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 Na_2SO_3 (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 $MgSO_4$ 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); $[\alpha]_D^{25}$ –268 (*c* 0.15, $CHCl_3$); ν_{max} (thin film)/$^{-1}$ 3440br, 2931s, 2887s, 1731s, 1257s, 1101s, 839s; δ_H ($CDCl_3$, 400 MHz) 0.10 and 0.11 (2 × 3 H, 2 × s, $Si(CH_3)_2$), 0.92 (9 H, s, *t*-BuSi), 2.71 (1 H, br s, FuCHO*H*), 3.64 (1 H, br s, CHO*H*CO), 4.41 and 4.50 (2 × 1 H, 2 × d, *J* 17.8, CH_2OSi), 4.89 (1 H, s, C*H*(OH)CO), 5.26 (1 H, s, FuC*H*OH), 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 ($CDCl_3$, 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; $C_{14}H_{24}O_5NaSi$ (MNa^+) requires 323.1285.

*(3*S*,4*S*)-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 $NaHCO_3$ solution (10 mL), extracted with dichloromethane (3 × 10 mL) and the combined extracts washed with hydrochloric acid (1 M, 10 mL), dried over $MgSO_4$ 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); $[\alpha]_D^{25}$ +29 (*c* 0.5, $CHCl_3$); ν_{max} (thin film)$^{-1}$ 2930s, 1789s, 1726s, 1601m, 1452m, 1255s, 838m, 706s; δ_H ($CDCl_3$, 400 MHz) 0.11 and 0.12 (2 × 3 H, 2 × s, $Si(CH_3)_2$), 0.93 (9 H, s, *t*-BuSi), 4.44 and 4.53 (2 × 1 H, 2 × d, *J* 18.0, CH_2OSi), 6.20 (1 H, d, *J* 4.1, C*H*(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, FuC*H*OBz), 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 ($CDCl_3$, 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, $M{\cdot}CH_3CN{\cdot}NH_4^+$); HRMS found 531.1804; $C_{28}H_{32}O_7NaSi$ (MNa^+) requires 531.1810.

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

To a stirred solution of ketone **9** (540 mg, 1.06 mmol) in dichloromethane (50 mL) at –25 °C was added $Zn(BH_4)_2$ (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 NH_4Cl

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 $MgSO_4$, 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); $[\alpha]_D^{25}$ –4.3 (*c* 0.11, $CHCl_3$); 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, $Si(CH_3)_2$), 0.91 (9 H, s, *t*-BuSi), 3.66 and 3.81 (2 × 1 H, 2 × dd, *J* 10.4, 5.5, CH_2OSi), 3.97–4.05 (1 H, m, C*H*OH), 4.47 (1 H, d, *J* 6.2, CHO*H*), 5.96 (1 H, app. t, *J* 5.8, C*H*(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, FuC*H*OBz), 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 ($M{\cdot}CH_3CN{\cdot}NH_4^+$), 533 (35); HRMS ($ESI^+$) found 533.1986; $C_{28}H_{34}NaO_7Si$ requires 533.1966. Also obtained was *(2*R*,3*R*,4*S*)-1-(tert-butyldimethylsilyloxy)-3,4-dibenzoyloxy-4-(furan-2-yl)butan-2-ol* **10β**, as a colourless oil (263 mg, 49%). R_f 0.22 (petrol/ether, 1:1); $[\alpha]_D^{25}$ –51 (*c* 2.0, $CHCl_3$); 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, $Si(CH_3)_2$), 0.90 (9 H, s, *t*-BuSi), 3.14–3.20 (3 H, m, C*H*(OH)C*H*$_2$OSi), 4.38 (1 H, d, *J* 6.7, CHO*H*), 6.19 (1 H, d, *J* 9.6, C*H*(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, FuC*H*OBz), 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 ($M{\cdot}CH_3CN{\cdot}NH_4^+$), 533 (35); HRMS ($ESI^+$) found 533.1983; $C_{28}H_{34}NaO_7Si$ requires 533.1966.

*(2*S*,3*R*,4*S*)-1-(tert-Butyldimethylsilyloxy)-2,3,4-tribenzoyloxy-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 $NaHCO_3$ solution, dried over MgSO, 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); $[\alpha]_D^{25}$ –350 (*c* 0.2, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 2986s, 1727s; δ_H ($CDCl_3$, 400 MHz) 0.00 and 0.01 (2 × 3 H, 2 × s, $Si(CH_3)_2$), 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, CH_2OSi), 5.20–5.25 (1 H, m, C*H*(OBz)CH_2OSi),

6.42–6.45 (1 H, m, furan), 6.41 (1 H, dd, *J* 8.2, 3.0, FuCH(OBz)C*H*OBz), 6.42–6.45 (1 H, m, furan), 6.48 (1 H, d, *J* 8.2, FuC*H*OBz), 7.31–7.62 (10 H, m) and 7.93–8.22 (6 H, 3 × 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%, $M{\cdot}CH_3CN{\cdot}NH_4^+$), 637 (14), 632 (12, MNH_4^+), 285 (18); HRMS (ESI^+) found 632.2670; $C_{35}H_{42}NO_8Si$ (MNH_4^+) requires 632.2674.

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

Method 2 (from **10β**): To a stirred solution of alcohol **10β** (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 × 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.

*(2*S*,3*R*,4*S*)-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 × 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 °C; R_f 0.14 (petrol/ether, 1:1); $[\alpha]_D^{25}$ –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, C*H*(OBz)CH_2OH), 6.29 (1 H, ddd, *J* 8.8, 2.4, 1.2, FuCH(OBz)C*H*OBz), 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, FuC*H*(OBz)), 7.14–7.62 (10 H, m) and 7.91–8.11 (6 H, m, 3 × 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, $M{\cdot}CH_3CN{\cdot}NH_4^+$), 518 (19, MNH_4^+); HRMS (ESI^+) found 518.1807; $C_{29}H_{28}O_8N$ (MNH_4^+) requires 518.1809.

*(5*S*,8*S*,9*R*,10*S*)-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 Na_2SO_3 (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 $NaHCO_3$ solution (20 mL) and brine (20 mL), then dried over $MgSO_4$, 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); $[\alpha]_D^{25}$ –165 (*c* 0.01, CHCl3); δ_H ($CDCl_3$, 400 MHz) 4.16 (1 H, t, *J* 10.8) and 4.40 (1 H, dd, 10.8, 5.6, CH_2), 5.56 (1 H, app. td, *J* 10.4, 5.6, CH_2CHOBz), 5.70 (1 H, d, *J* 10.4, C*H*(OBz)-spiro), 6.15 (1 H, d, *J* 5.2, =CHCO), 6.26 (1 H, t, *J* 10.4, C*H*(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 ($CDCl_3$, 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, $M{\cdot}CH_3CN{\cdot}NH_4^+$), 449 (19), 337 (12); HRMS (ESI^+) found 537.1161; $C_{29}H_{22}O_9Na$ (MNa^+) requires 537.1156.

N-*2-(Hydroxyethyl)crotonamide*[3]

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} ($CHCl_3$)/cm^{-1} 3325m, 1673s, 1633s, 1522s, 1222s, 1071m, 964m, 784s; δ_H (200 MHz, $CDCl_3$) 1.82 (3 H, dd, *J* 7.0, 1.5, CH_3), 3.42 (2 H, app. q, *J* 5.5, CH_2NH), 3.67 (2 H, t, *J* 5.5, CH_2OH), 4.34 (1 H, br s, OH), 5.87 (1 H, dq, *J* 15.0, 1.5, =C*H*CO), 6.79 (1 H, dq, *J* 15.0, 7.0, CH_3CH=), 7.08 (1 H, br s, NH); δ_C (50.3 MHz, $CDCl_3$) 18.0, 42.6, 61.5, 125.4, 140.1, 167.7; *m/z* (CI) 130 (MH^+, 42%), 112 (100), 104 (18).

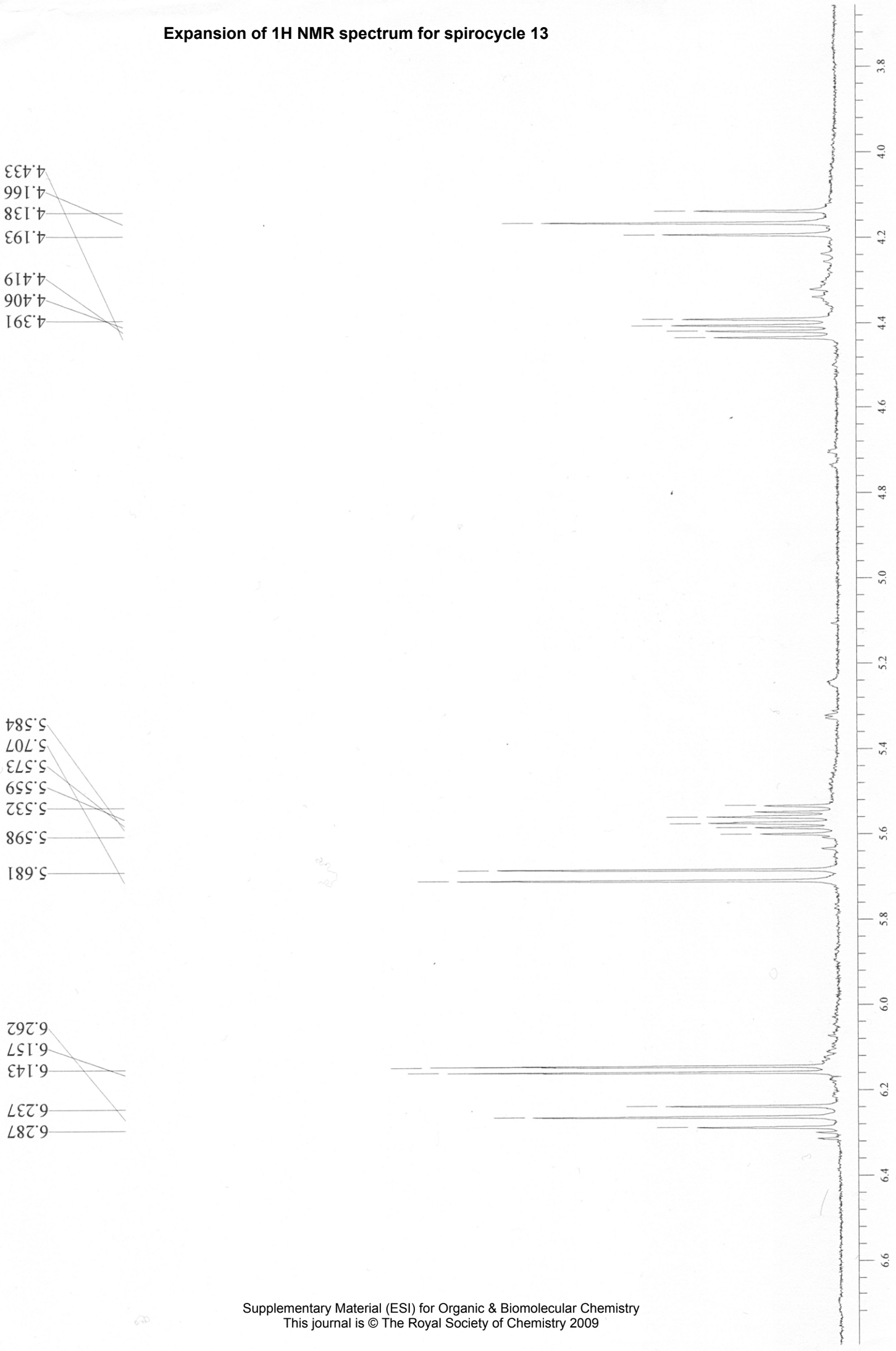
*2-[(*E*)-Propen-1-yl]-1,3-oxazoline* **22**[4]

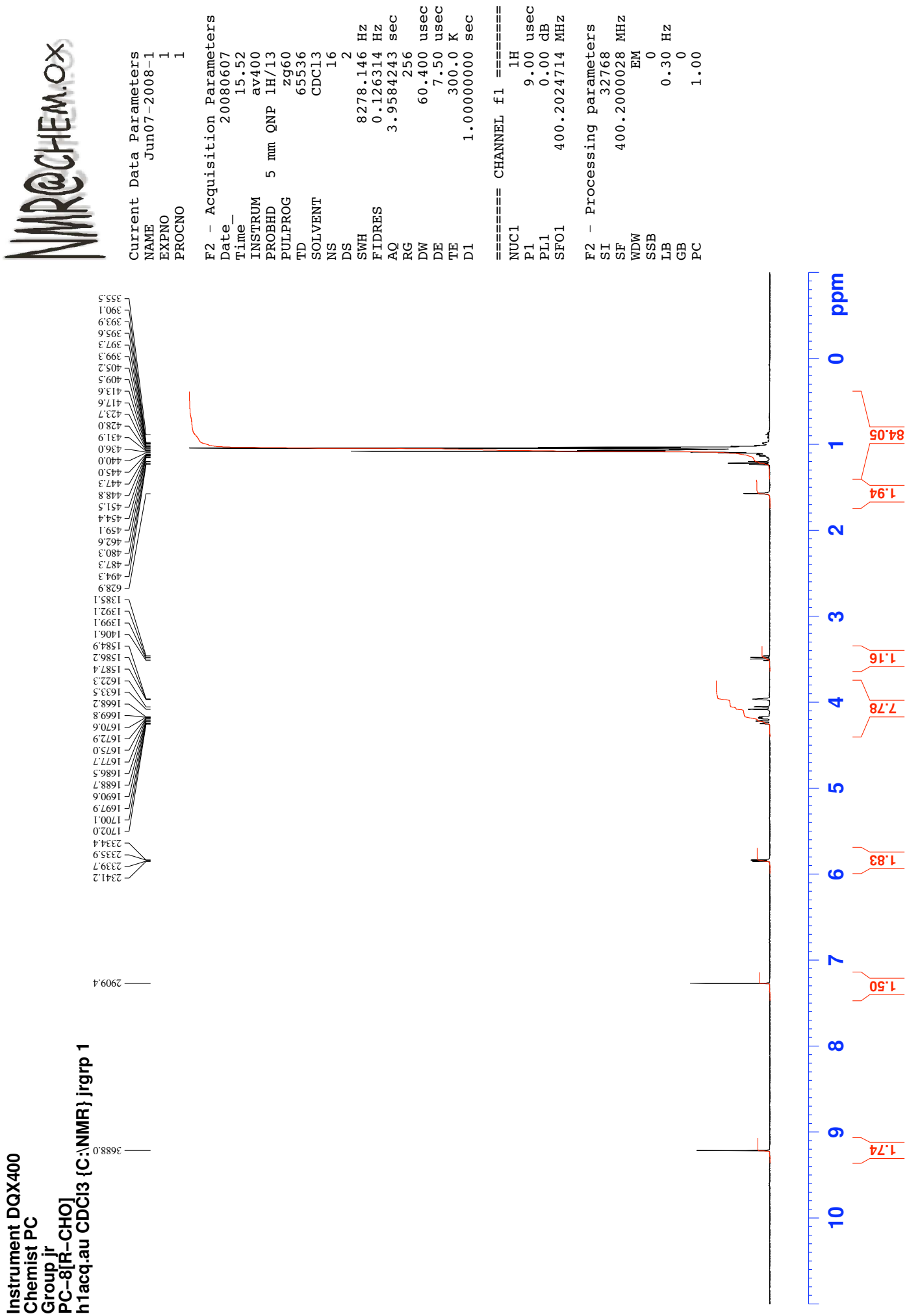
To a solution of *N*-2-(hydroxyethyl)crotonamide (3.95 g, 30.6 mmol) and triphenylphosphine (10.03 g, 38.2 mmol) in THF (5 mL) at 0 °C was added dropwise DIAD (7.53 mL, 38.2 mmol).

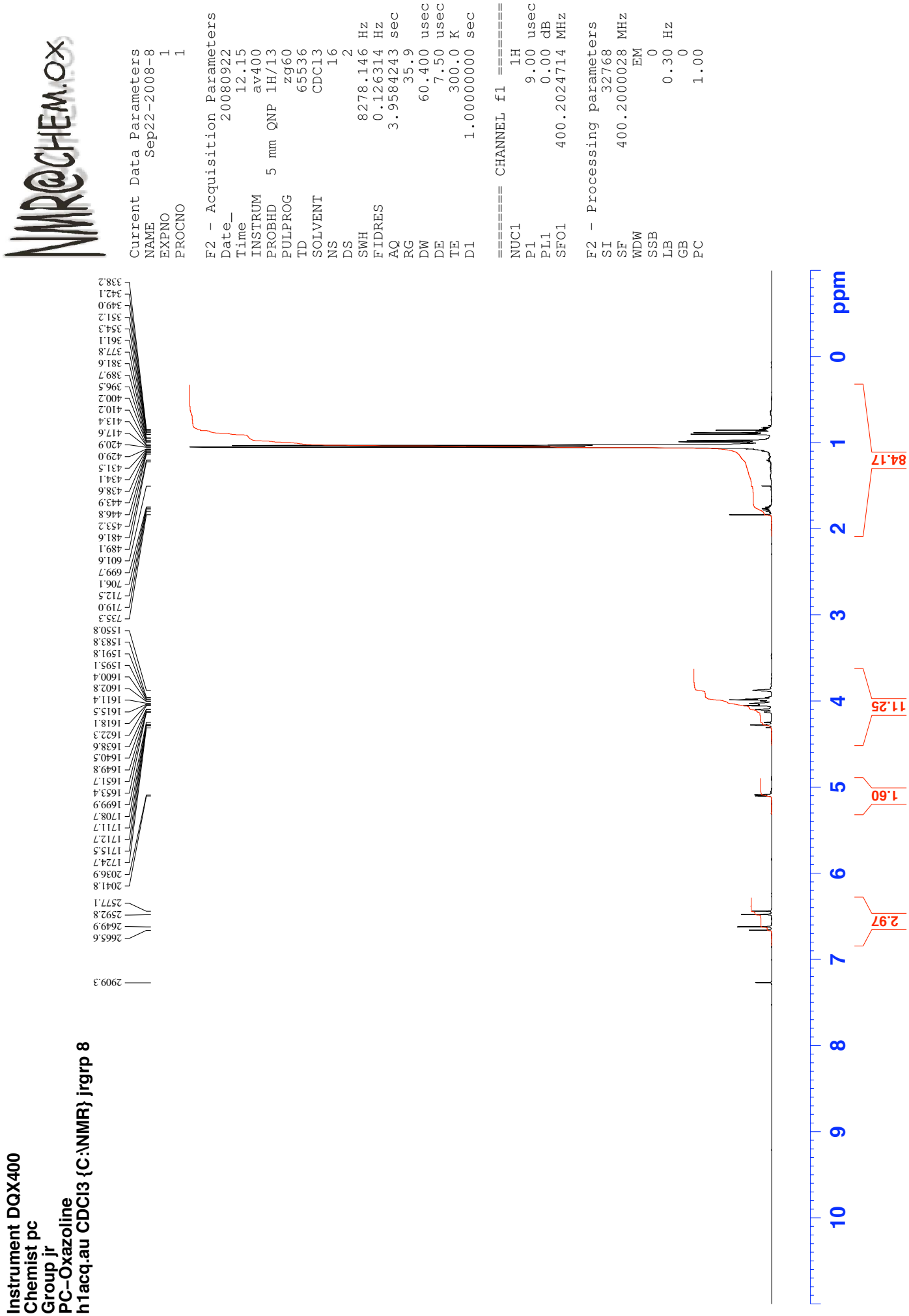
The mixture was stirred for 30 min at 0 °C and for 4 h at room temperature. The solvent was removed *in vacuo*, replaced with ether (10 mL) and the reaction mixture left to stand for 16 h. Precipitated triphenylphosphine oxide was filtered off, washed with ether (2 × 10 mL) and the filtrate dried (Na_2SO_4). 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, $CDCl_3$) 1.81 (3 H, dd, *J* 7.0, 1.5, CH_3), 3.84 (2 H, t, *J* 9.5, CH_2N), 4.20 (2 H, t, *J* 9.5, CH_2O), 5.95 (1 H, dq, *J* 16.0, 1.5, $CH_3CH{=}CH$), 6.53 (1 H, dq, *J* 16.0, 7.0, $CH_3CH{=}$); δ_C (50.3 MHz, $CDCl_3$) 18.7, 54.9, 67.4, 119.4, 139.3, 164.3; *m/z* (CI) 112 (MH^+, 100%).

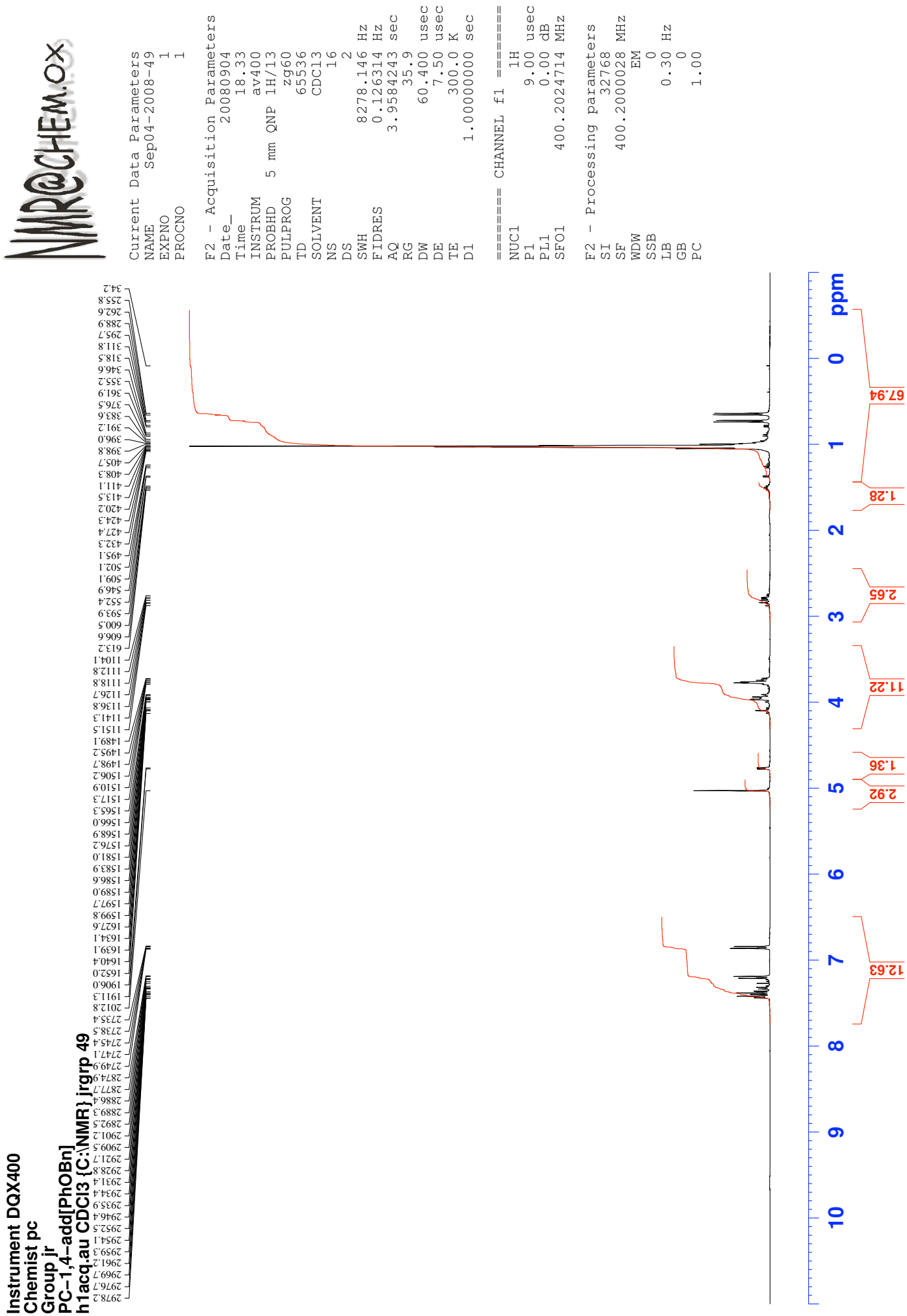
1) Angehrn, P.; Hebeisen, P.; Heinze-Krauss, I.; Page, M. *Eur. Pat. Appl.* **1998**, EP0831093 (A1) 1998-03-25.
2) Wissner, A.; Grudzinskas, C. V. *J. Org. Chem.* **1978**, *43,* 3972–3974.
3) Ushakov, S. N.; Aleev, K. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1962**, 693–4.
4) Woo, H. G. *Ind. J. Chem.* **1982**, *21B,* 1114.

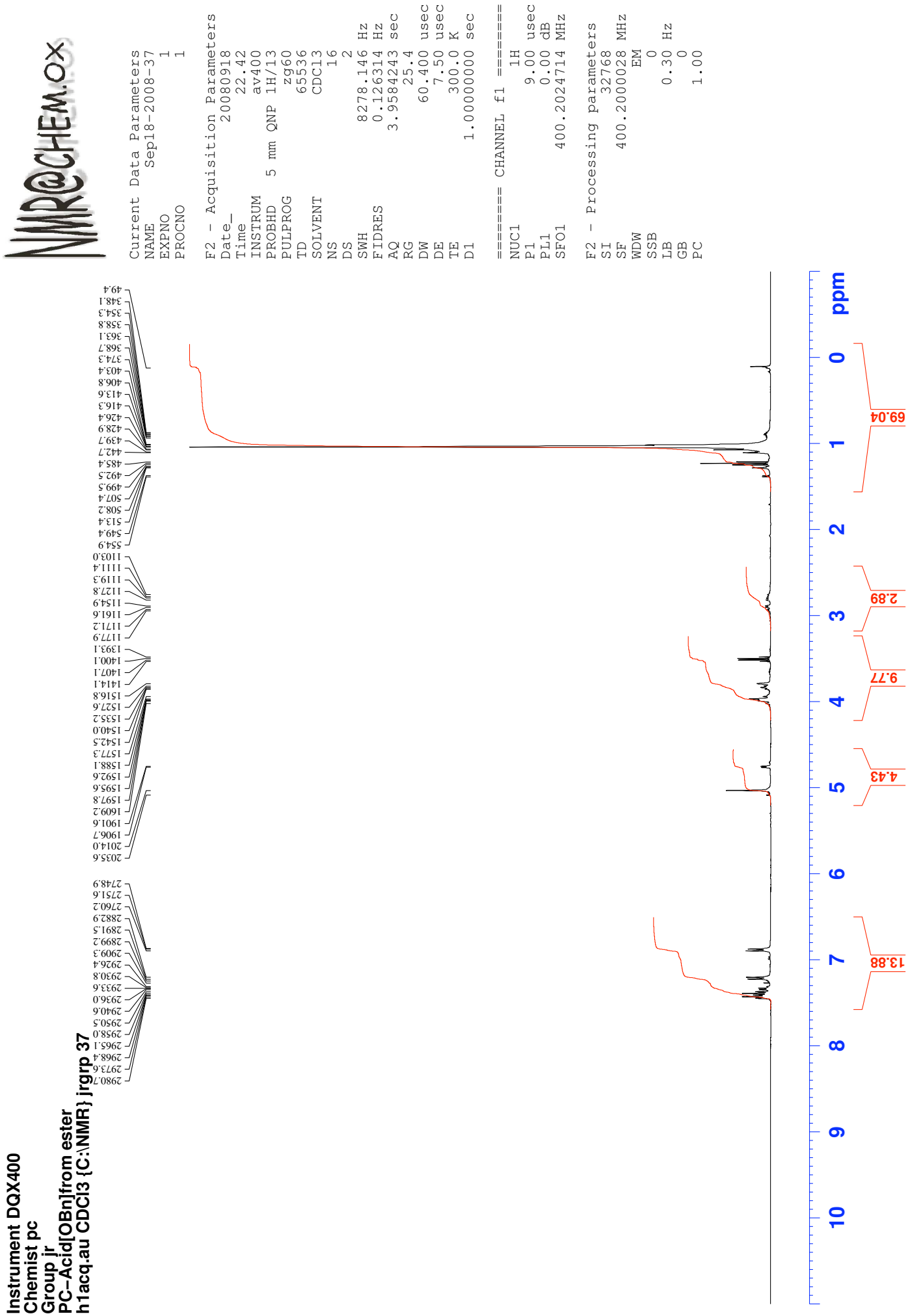
Expansion of 1H NMR spectrum for spirocycle 13

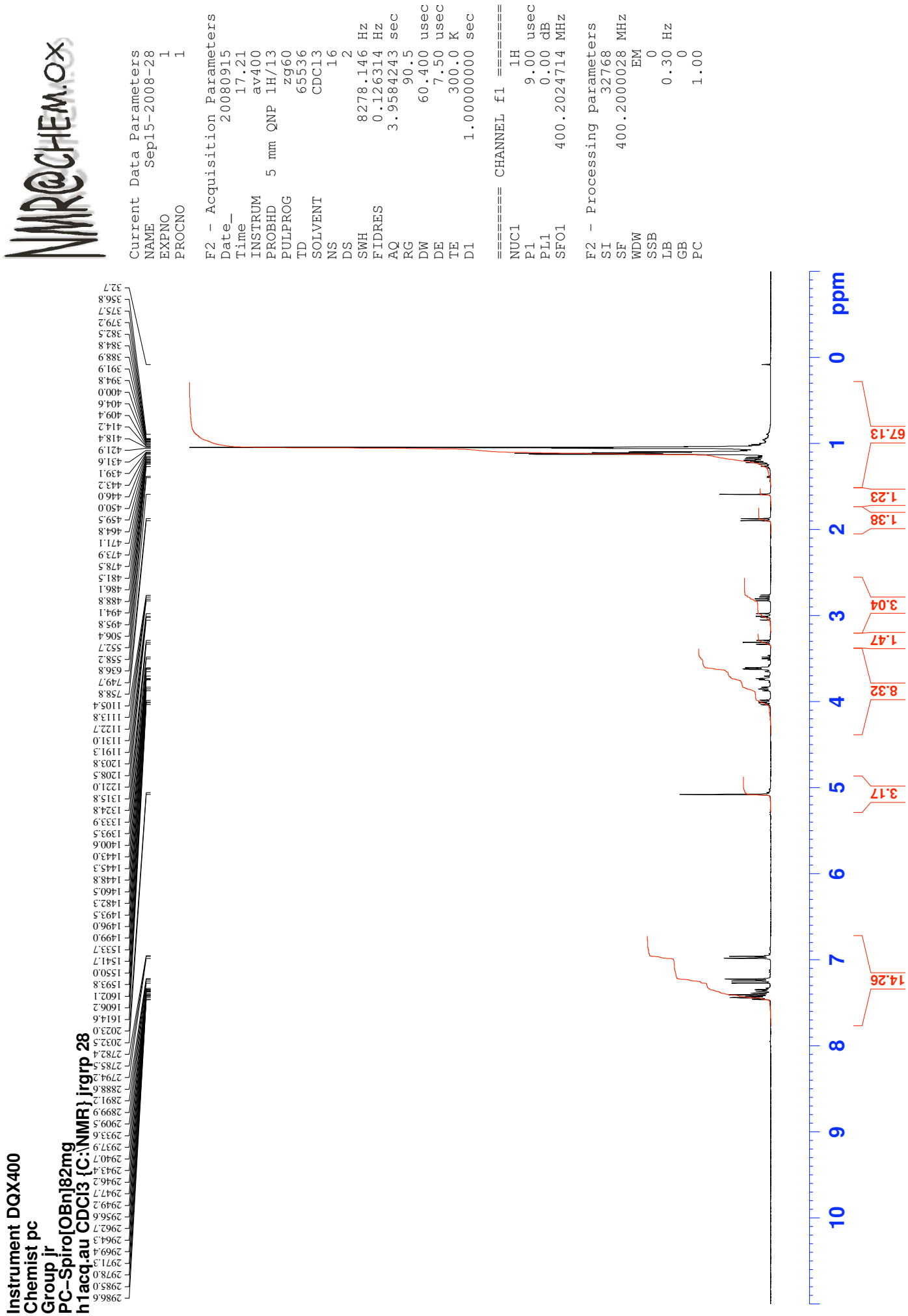


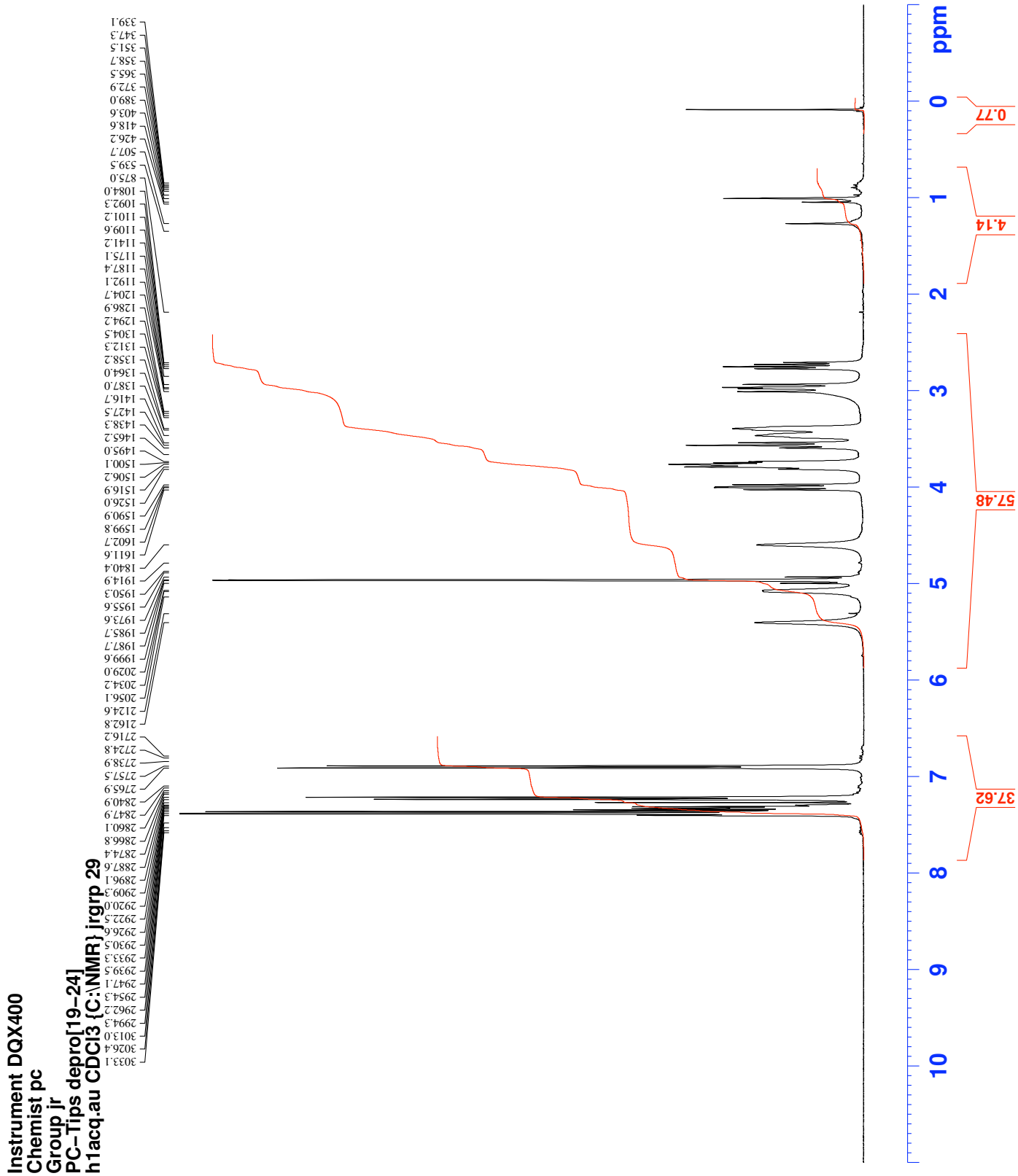




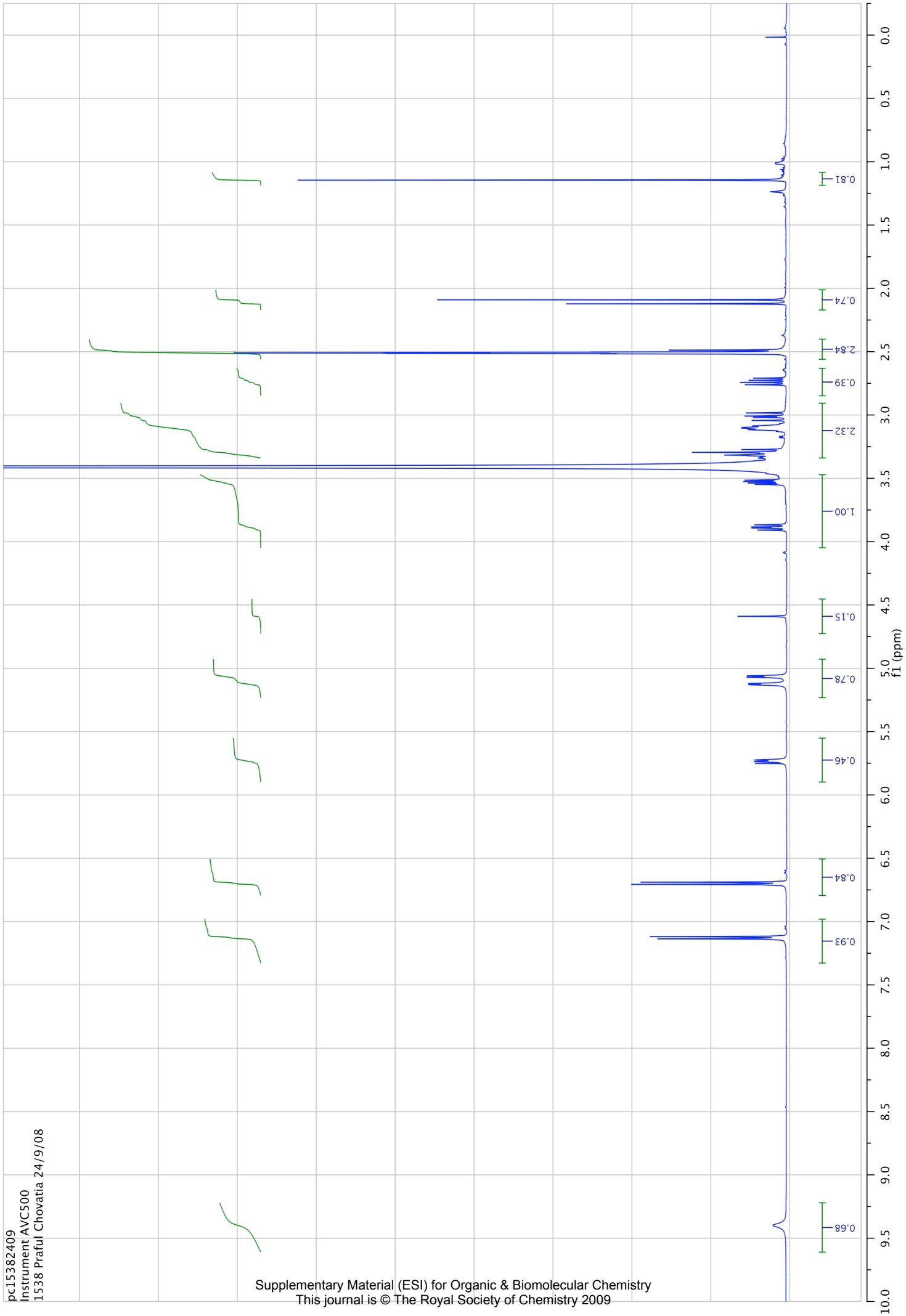




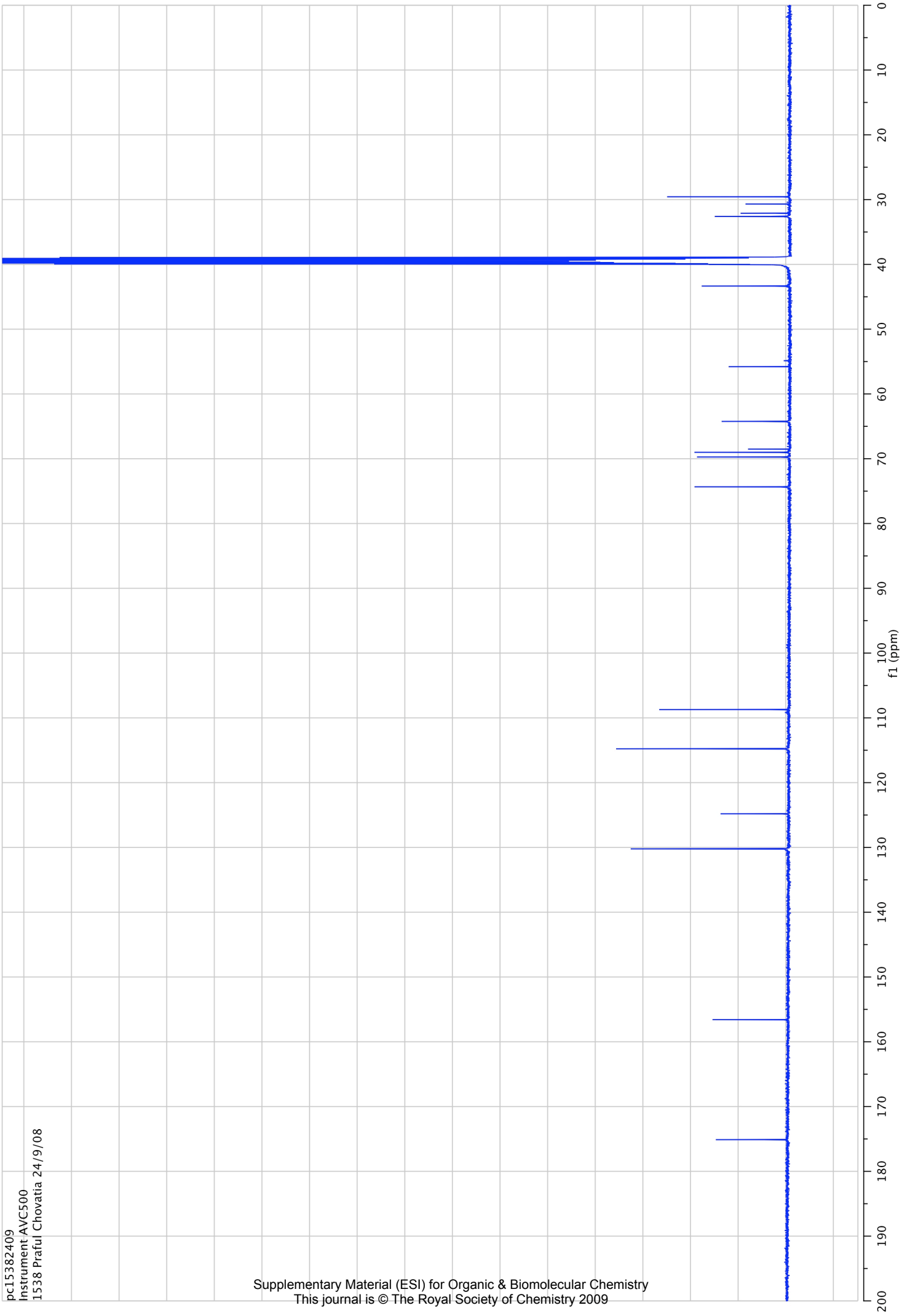


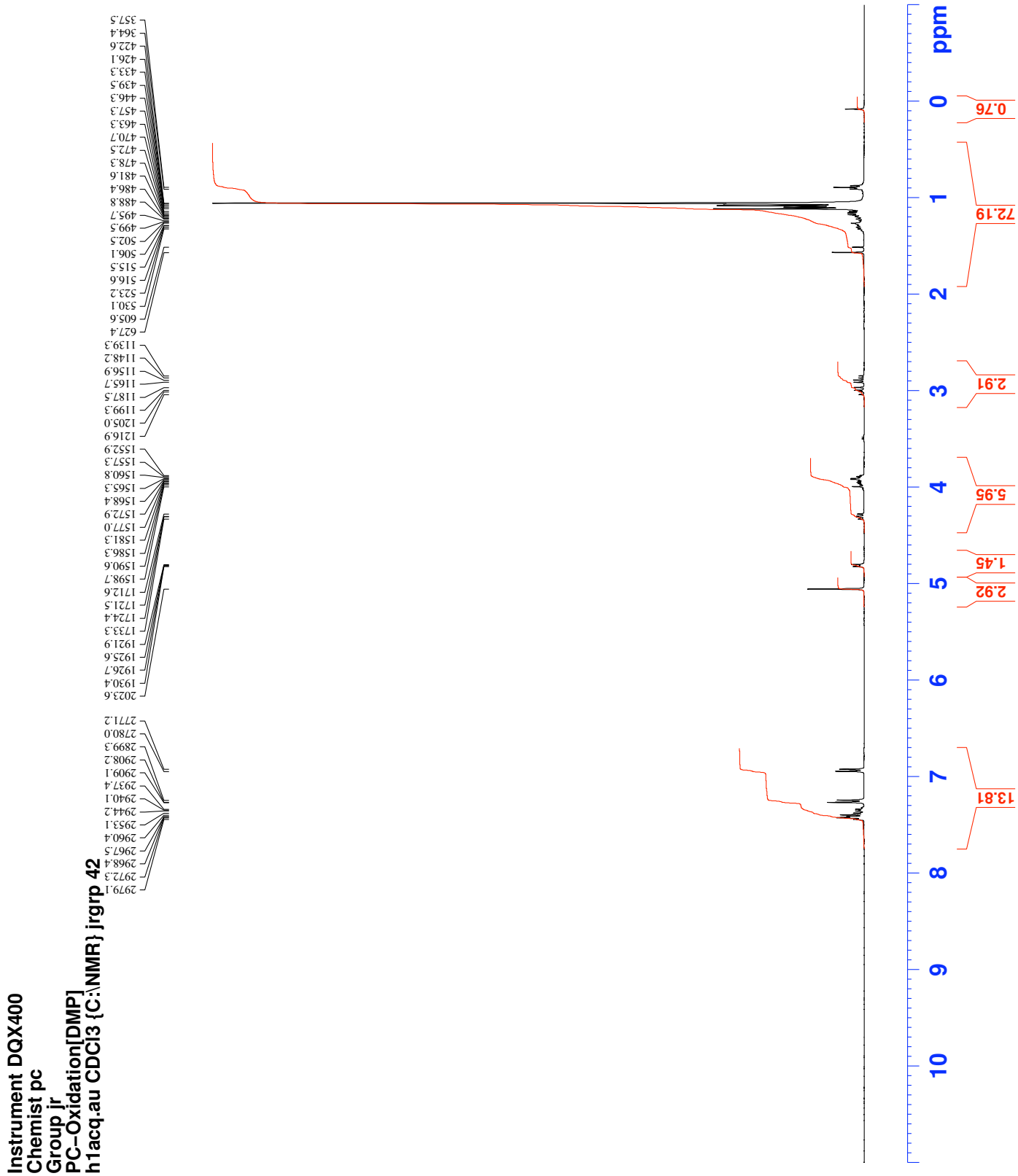


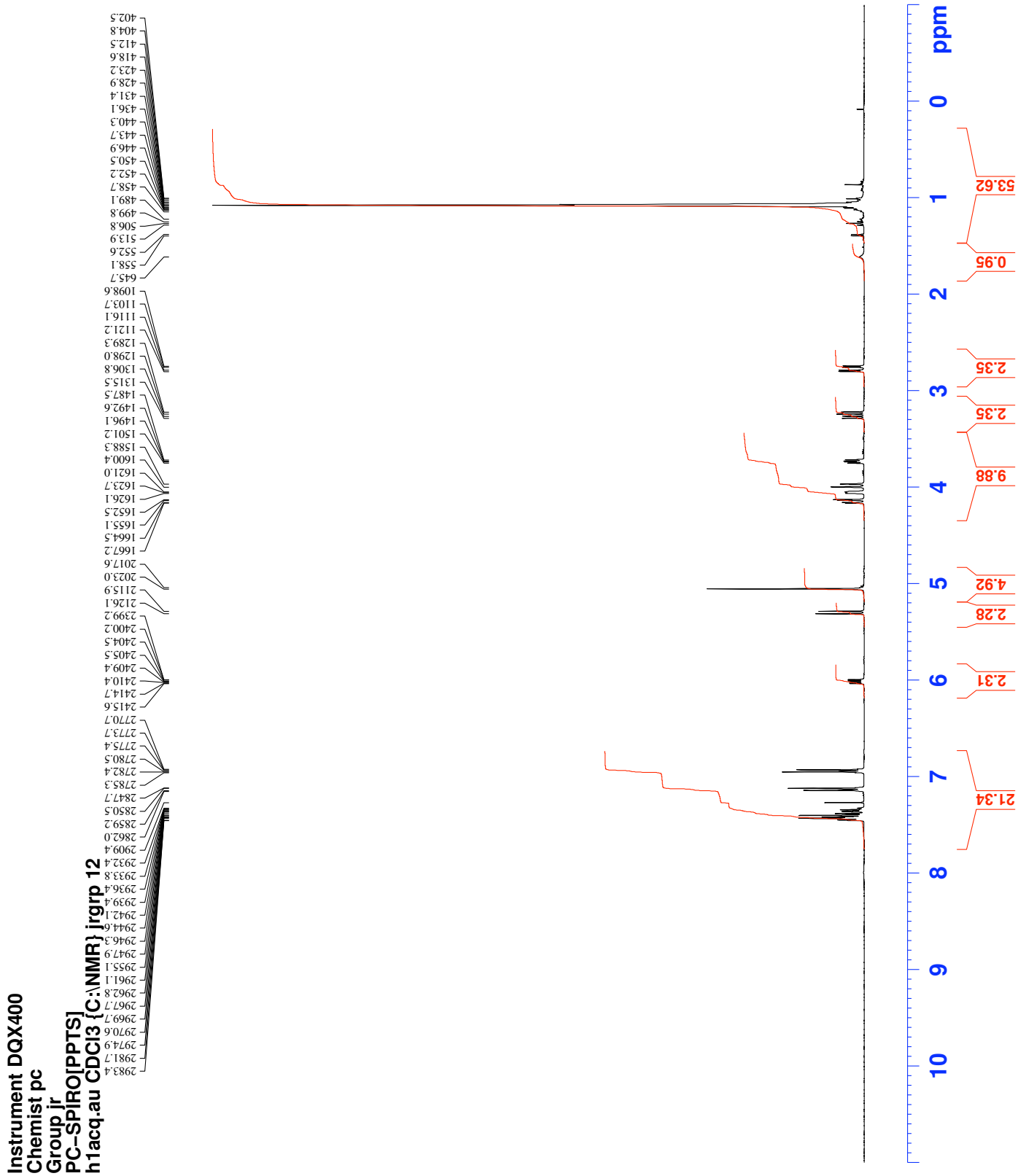
1H NMR spectrum for (30) [ent-sawaranospirolide C]

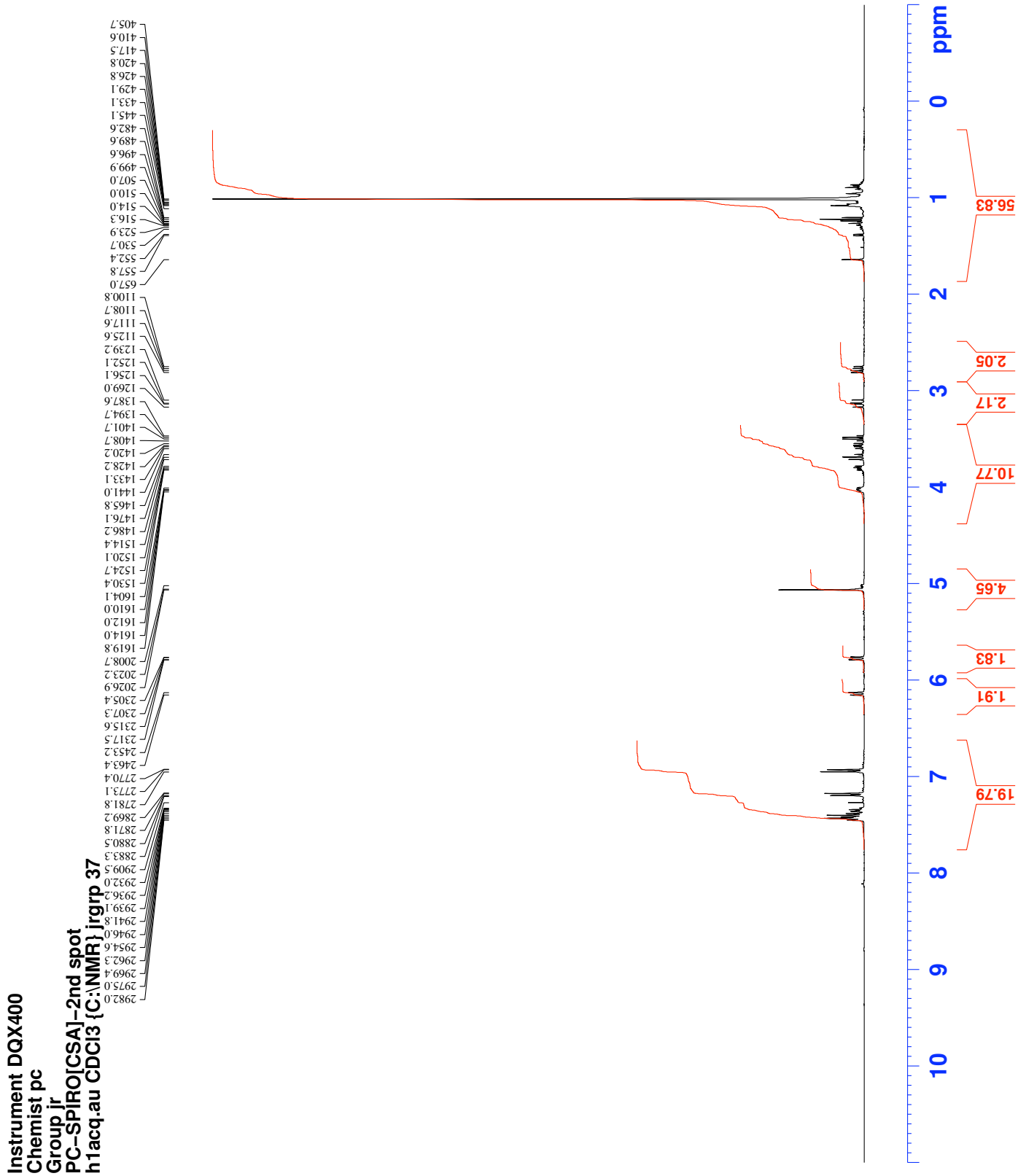


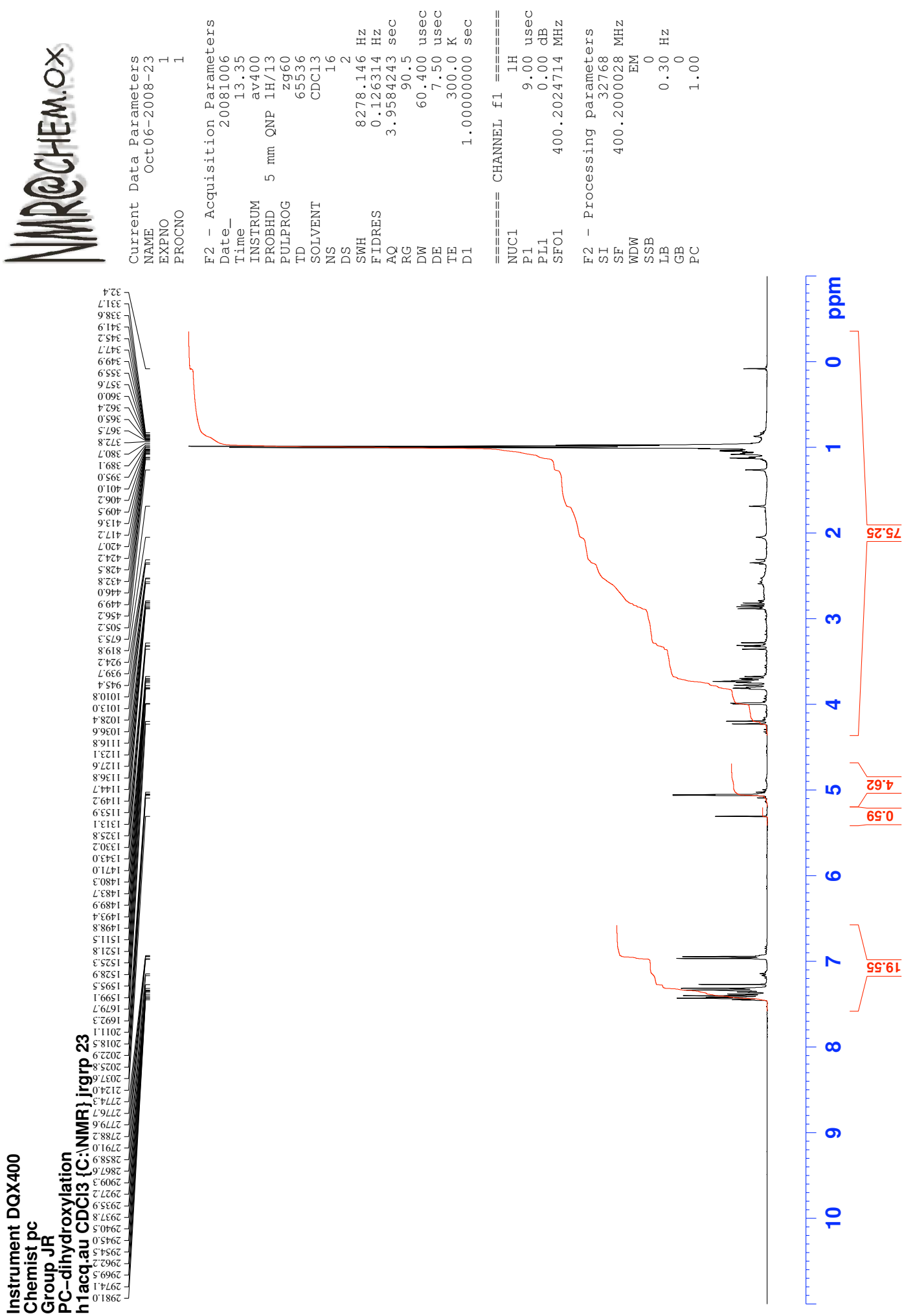
13C NMR spectrum for (30) [ent-sawaranospirolide C]

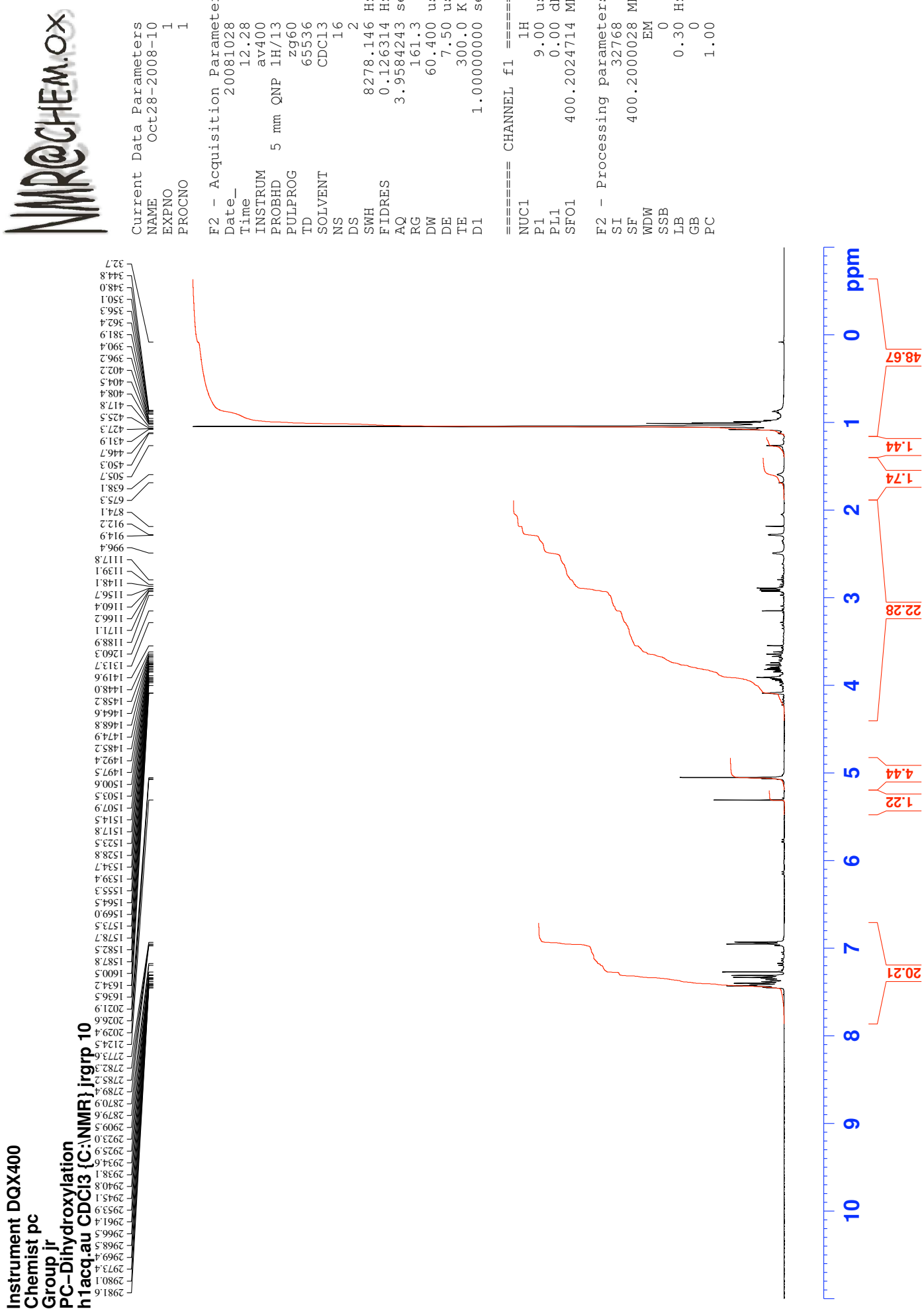


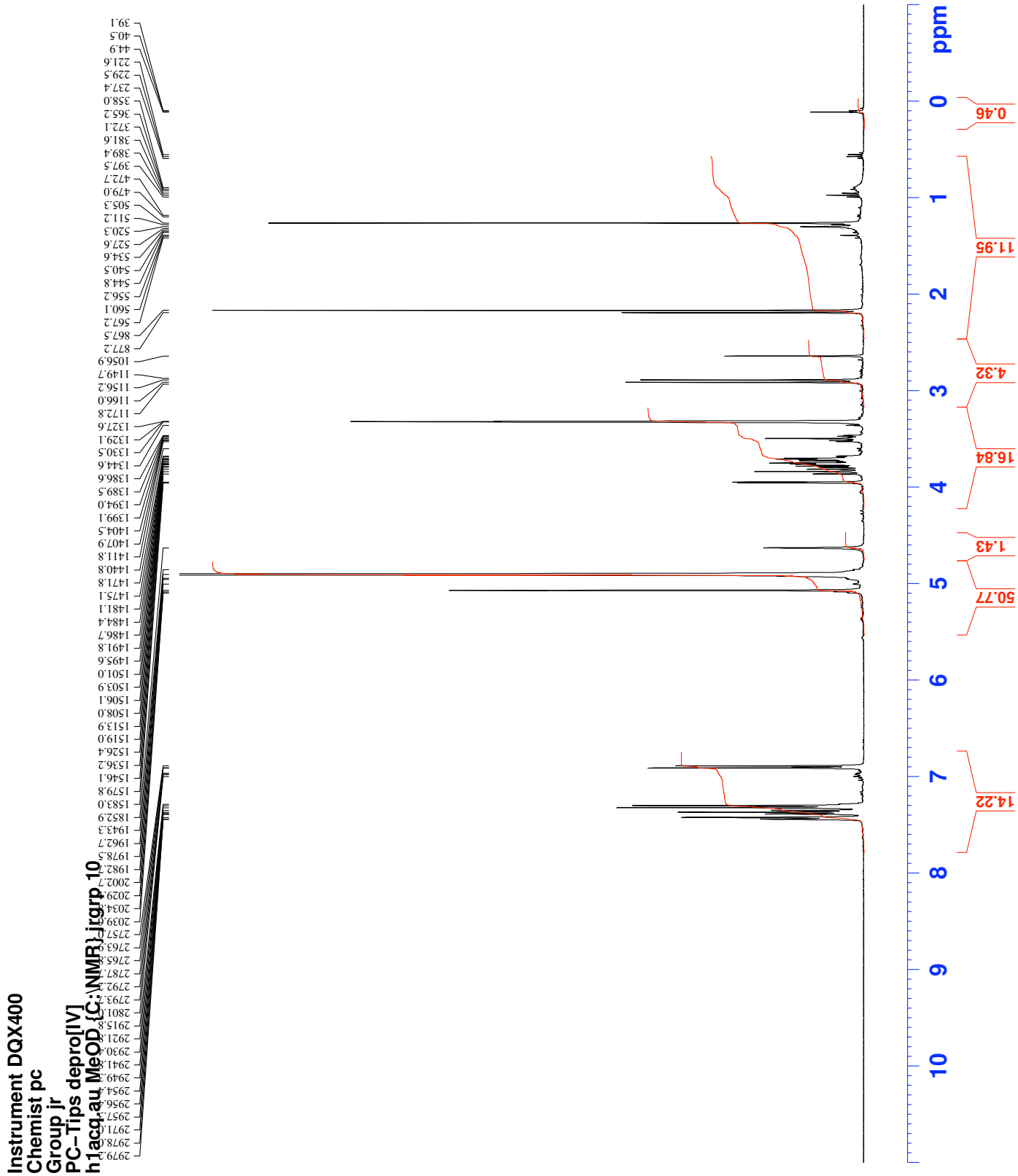




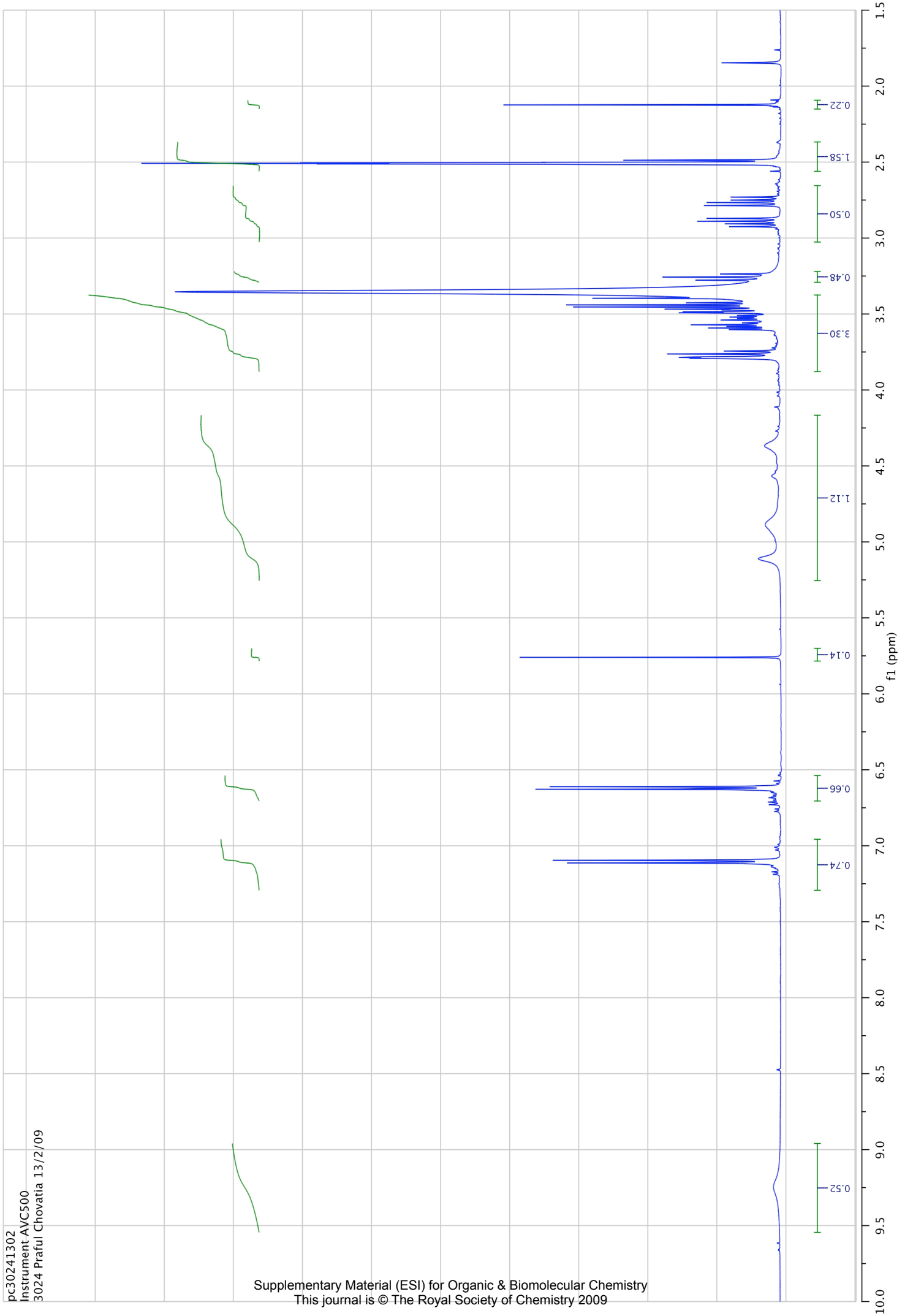








1H NMR spectrum for (43) [ent-sawaranospirolide D]



pc30241302
Instrument AVC500
3024 Praful Chovatia 13/2/09

13C NMR spectrum for (43) [ent-sawaranospirolide D]