Biomimetic studies towards the cardinalins: Synthesis of (+)-ventiloquinone L and an unusual dimerisation.

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SUPPLEMENTARY INFORMATION

Experimental

General

All reactions were carried out in oven-dried or flame-dried glassware under a nitrogen atmosphere unless otherwise stated. Analytical thin layer chromatography was performed using 0.2 mm Kieselgel F254 (Merck) silica plates and compounds were visualised under 365 nm ultraviolet irradiation followed by staining with either alkaline permanganate or ethanolic vanillin solution. Infrared spectra were obtained using a Perkin Elmer spectrum One Fourier Transform Infrared spectrometer as thin films between sodium chloride plates. Absorption maxima are expressed in wavenumbers (cm^{-1}). Optical rotations were measured using a Perkin-Elmer 341 polarimeter at λ = 598 nm and are given in 10^{-1} deg cm^2 g^{-1}. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded as indicated on either a Bruker DRX-400 spectrometer operating at 400 MHz for ^1H nuclei and 100 MHz for ^{13}C nuclei or on a Bruker Avance 300 spectrometer operating at 300 MHz and 75 MHz for ^1H and ^{13}C nuclei, respectively. Chemical shifts are reported in parts per million (ppm) relative to the tetramethylsilane peak recorded as δ 0.00 ppm in $CDCl_3$/ TMS solvent, or the residual chloroform peak at δ 7.25 ppm. The ^{13}C NMR values were referenced to the residual chloroform peak at δ 77.0 ppm. ^{13}C NMR values are reported as chemical shift δ, multiplicity and assignment. ^1H NMR shift values are reported as chemical shift δ, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (*J* in Hz) and assignment. Assignments are made with the aid of DEPT 135, COSY, NOESY and HSQC experiments. High resolution mass spectra were recorded on a VG-70SE mass spectrometer at a nominal accelerating voltage of 70 eV. For all microwave-assisted reactions the CEM Discover system with a circular single mode and

focused waves was used, resulting in formation of a homogeneous field pattern surrounding the sample.

4,6-Dimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-carbonitrile 3

Prepared from 2,4-dimethoxybenzoic acid[1]

(*S*,*E*)-6-(*tert*-butyldiphenylsilyloxy)hept-3-en-2-one 4

Prepared from (*S*)-ethyl 3-hydroxybutanoate[2]

(*S*)-1-(3-(2-(*tert*-butyldiphenylsilyloxy)propyl)-1,4,6,8-tetramethoxynaphthalen-2-yl)ethanone 5

To a solution of potassium *tert*-butoxide (35 mg, 0.31 mmol) in distilled DMSO (0.7 mL) was added a solution of 4,6-dimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-carbonitrile **3** (58 mg, 0.26 mmol) in distilled DMSO (0.7 mL) followed by a solution of (*S*,*E*)-6-(*tert*-butyldiphenylsilyloxy)hept-3-en-2-one **4** (87 mg, 0.24 mmol) in distilled DMSO (1.1 mL). The reaction mixture was stirred for 4 min then diluted with diethyl ether (7 mL) and quenched upon addition of a saturated aqueous solution of ammonium chloride (7 mL). The resulting mixture was partitioned between diethyl ether and ammonium chloride and the aqueous layer extracted with diethyl ether (3 x 15 mL). The combined organic extracts were washed with water (3 x 10 mL), dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The resulting residue was taken up in THF (4 mL) and water (1.5 mL) and tetrabutylammonium bromide (8 mg, 0.025 mmol) was added. The reaction vessel was evacuated and filled with hydrogen repeatedly. A solution of sodium dithionite (270 mg, 1.55 mmol) in water (1.5 mL) was then added and the reaction mixture was stirred for 1 h under an atmosphere of hydrogen. A solution of sodium hydroxide (215 mg, 5.38 mmol) in water (2.2 mL) was added followed by dimethylsulfate (0.50 mL, 667 mg, 5.28 mmol). The reaction mixture was stirred at r.t. for 3 h under an atmosphere of hydrogen. Water (4 mL) and ethyl acetate (15 mL) were added and the layers separated. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The resulting residue was purified by flash chromatography eluting with hexanes-ethyl acetate (95:5) to afford the *title compound* **5** (72 mg, 0.12 mmol, 52%) as a yellow oil; $[\alpha]_D^{25}$ +5.6 (*c* 0.41, CH_2Cl_2); υ_{max} (oil)/cm^{-1} 3378, 2931, 2855, 1693, 1618, 1580, 1464, 1427, 1407, 1380,

1338, 1245, 1208, 1153, 1105; δ_H (300 MHz, $CDCl_3$) 0.99 (9 H, s, $C(Me)_3$), 1.05 (3 H, d, *J* 3.6, Me), 2.42 (3 H, s, Me), 2.79 (1 H, dd, *J* 7.7 and 13.5, C*H*H), 3.02 (1 H, dd. *J* 6.6 and 13.5, CH*H*), 3.68 (3 H, s, OMe), 3.70 (3 H, s, OMe), 3.92 (3 H, s, OMe), 3.97 (3 H, s, OMe), 4.26 (1 H, m, CH), 6.53 (1 H, d, *J* 2.1, Ar-H), 6.91 (1 H, d, *J* 2.1, Ar-H), 7.27 (2 H, m, Ar-H), 7.29 (4 H, m, Ar-H), 7.56 (2 H, dd, *J* 1.4 and 8.0, Ar-H), 7.65 (2 H, m, Ar-H); δ_C (75 MHz, $CDCl_3$) 19.1 (C-Si), 23.3 (CH*Me*), 27.0 ($C(Me)_3$), 33.1 (C(O)*Me*), 37.2 (CH_2), 55.4 (OMe), 56.1 (OMe), 60.7 (OMe), 63.7 (OMe), 69.5 (CH), 93.3 (CH), 99.1 (CH), 115.2 (C), 125.5 (C), 127.4 (4 x CH), 129.4 (2 x CH), 132.2 (C), 132.9 (C), 134.4 (2 x C), 135.86 (2 x CH), 135.92 (2 x CH), 149.5 (C), 150.3 (C), 157.7 (C), 159.1 (C), 205.8 (C=O); *m/z* (EI+) 586 (12%, M^+) 529 (100), 514 (32), 512 (15), 330 (10), 313 (30), 282 (19), 199 (75), 197 (34), 181 (12), 135 (90), 77 (13), 57 (21); HRMS (EI+, M^+) found 586.2742, calc. for $C_{35}H_{42}O_6Si$ 586.2751.

(1*R*,3*S*)-7,9,10-trimethoxy-1,3-dimethyl-3,4-dihydro-1*H*-benzo[g]isochromen-5-ol 7

(*S*)-1-(3-(2-(*tert*-butyldiphenylsilyloxy)propyl)-1,4,6,8-tetramethoxynaphthalen-2-yl)ethanone **5** (150 mg, 0.26 mmol) was taken up in distilled THF (9 mL) and tetra-*n*-butylammonium fluoride (1 M in pentane, 2.5 mL, 2.5 mmol) was added. The reaction mixture was stirred for 4 days at r.t. under an atmosphere of nitrogen. The solvents were removed *in vacuo*, and the residue flushed through a plug of silica eluting with hexanes-ethyl acetate (2:3) and the filtrate concentrated *in vacuo*. The resulting lactol **6** was taken up in distilled dichloromethane (9 mL) and cooled to –78 °C. Trifluoroacetic acid (0.12 mL, 180 mg, 1.58 mmol) was added and the reaction mixture stirred for 15 min before the addition of triethylsilane (0.24 mL, 173 mg, 1.49 mmol). The reaction mixture was then allowed to reach r.t. over 20 h. Water (40 mL) was added and the aqueous layer was extracted with ethyl acetate (40 mL x 3). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, concentrated *in vacuo* and the resulting residue was purified by flash chromatography eluting with hexanes-ethyl acetate (4:1) to give the *title compound* **7** as a cream coloured solid (55 mg, 0.17 mmol, 65%); m.p. 75–76 °C; $[\alpha]_D^{25}$ +65.6 (*c* 0.44, CH_2Cl_2); υ_{max} (neat)/cm^{-1} 3364, 2967, 2930, 2837, 1735, 1620, 1598, 1580, 1449, 1409, 1380, 1336, 1258, 1203, 1155; δ_H (300 MHz, $CDCl_3$) 1.41 (3 H, d, *J* 6.0, CH_2CHMe), 1.66 (3 H, d, *J* 6.3, Me), 2.58 (1 H, dd, *J* 11.0 and 15.9, $CH_{ax}H$), 3.04 (1 H, dd, *J* 2.0 and 15.9, CHH_{eq}), 3.69 (1 H, m, H-3), 3.75 (3 H, s, OMe), 3.87 (3 H, s, OMe), 3.93 (3 H, s, OMe), 3.97 (3 H, s, OMe), 5.22 (1 H, q, *J* 6.3, H-1), 6.51 (1 H, d, *J* 2.3, Ar-H), 6.97 (1

H, d, *J* 2.3, Ar-H); δ_C (75 MHz, $CDCl_3$) 21.8 (Me), 23.2 (Me), 32.0 (CH_2), 55.3 (CH), 56.1 (CH), 60.6 (OMe), 61.5 (OMe), 69.4 (OMe), 71.2 (OMe), 92.4 (CH), 98.7 (CH), 115.3 (C), 126.5 (C), 127.7 (C),130.4 (C), 147.8 (C), 149.3 (C), 157.4 (C), 158.1 (C); *m/z* (EI+) 332 (64%, M^+), 317 (100), 287 (20), 273 (27); HRMS (EI+, M^+) found 332.1622, calc. for $C_{19}H_{24}O_5$ 332.1624.

Ventiloquinone L methyl ether 8

To a solution of naphthopyran **7** (110 mg, 0.331 mmol) in acetonitrile (5 mL) and water (2 mL) was added phenyliodine bis(trifluoroacetate) (PIFA, 213 mg, 0.496 mmol) portionwise over 5 min. The resulting solution was stirred for 2 h and the whole partitioned between diethyl ether (30 mL) and water (30 mL). The aqueous layer was removed and extracted with diethyl ether (x 2) and the combined organic extracts washed with water, brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography eluting with hexanes-ethyl acetate (3:1) gave the *title compound* **8** (81 mg, 0.27 mmol, 81%) as a bright yellow solid, m.p. 147–149 °C (Lit[3] 153-154 °C); $[\alpha]_D^{20}$ +344.4 (*c* 0.5, CH_2Cl_2) [Lit[3] $[\alpha]_D^{24}$ +265 (*c* 0.16, CH_2Cl_2)]; υ_{max} (neat)/cm^{-1} 2973, 2937, 1649, 1594, 1566, 1456, 1346, 1320, 1271, 1199, 1158, 827; δ_H (300 MHz, $CDCl_3$) 1.35 (3 H, d, *J* 8.0, CH_2CH*Me*), 1.53 (3 H, d, *J* 8.0, Me), 2.13-2.24 (1 H, ddd, *J* 18.0, 10.2 and 3.6, H_{ax}H), 2.75 (1 H, dt, *J* 2.4 and 18.0, HH_{eq}), 3.59-3.60 (1 H, m, H-3), 3.94 (3 H, s, OMe), 3.96 (3 H, s, OMe), 4.81-4.86 (1 H, m, H-1), 6.70 (1 H, d, *J* 3.2, Ar-H), 7.23 (1 H, d, *J* 3.2, Ar-H); δ_C (75 MHz, $CDCl_3$) 21.0 (Me), 21.2 (Me), 30.0 (CH_2), 55.9 (OMe), 56.4 (OMe), 68.7 (CH), 70.3 (CH), 102.9 (CH), 104.2 (CH), 114.8 (C), 135.7 (C), 139.4 (C), 148.8 (C), 161.6 (C), 164.4 (C), 182.5 (C=O), 184.1 (C=O); *m/z* (EI+) 302 (100%, $[M]^+$), 287 (76), 273 (77), 269 (20), 259 (22), 244 (14), 229 (10), 165 (10), 128 (12), 115 (13), 106 (14), 43 (36); HRMS (EI+, M^+) found 302.1157, calc. for $C_{17}H_{18}O_5$ 302.1154. Data consistent with literature[3]

Ventiloquinone L 2

A solution of ventiloquinone L methyl ether **8** (50 mg, 0.17 mmol) in dichloromethane (10 mL) was cooled to -78 °C. Boron trichloride (0.33 mmol, 0.33 mL of a 1M solution in dichloromethane) was added dropwise over 5 min. The resulting dark red solution was stirred at -78 °C for 15 min then warmed to r.t and stirred for 1 h. The reaction mixture was poured into water (30 mL) and extracted with dichloromethane (3 x 15 mL). The combined organic extracts washed with water, brine, dried ($MgSO_4$), filtered and concentrated *in*

vacuo. Flash chromatography eluting with hexanes-ethyl acetate (5:1) gave the *title compound* (41 mg, 0.14 mmol, 84 %) as a bright yellow solid m.p. 120–122 °C (Lit[4] 126 °C); $[\alpha]_D^{20}$ +435.2 (*c* 0.01, $CHCl_3$) (Lit isolation[4] $[\alpha]_D^{30}$ +387.1 (*c* 0.01, $CHCl_3$)); υ_{max} (neat)/cm^{-1} 2973, 2938, 2848, 1664, 1631, 1596, 1487, 1445, 1386, 1367, 1297, 1273, 1208, 1152, 1128, 1100, 990, 829, 779; δ_H (400 MHz, $CDCl_3$) 1.35 (3 H, d, *J* 6.4, CH_2CHMe), 1.57 (3 H, d, *J* 6.4, Me), 2.17-2.25 (1 H, ddd, *J* 4.0, 10.8 and 18.4, $H_{ax}H$), 2.69-2.75 (1 H, dt, *J* 2.8 and 18.4, HH_{eq}), 3.54-3.58 (1 H, ddq, *J* 2.8, 6.0 and 9.6, H-3), 3.88 (3 H, s, OMe), 4.81 (1 H, ddq, *J* 2.8, 3.9 and 6.0, H-1), 6.58 (1 H, d, *J* 2.4, Ar-H), 7.12 (1 H, d, *J* 2.4, Ar-H), 12.22 (1 H, s, OH); δ_C (100 MHz, $CDCl_3$) 21.2 (2 x Me), 30.6 (CH_2), 56.0 (OMe), 68.6 (CH), 69.8 (CH), 106.11 (CH), 107.6 (CH), 109.5 (C), 133.2 (C), 143.2 (C), 146.7 (C), 164.2 (C), 165.7 (C),183.0 (C=O), 187.4 (C=O); *m/z* (EI+) 288 (100%, $[M]^+$), 273 (42), 259 (30), 244 (28), 151 (11), 43 (16); HRMS (EI+, M^+) found 288.1001, calc. for $C_{16}H_{16}O_5$ 288.0998. Data consistent with literature[4,5]

(1*R*,1'*R*,3*S*,3'*S*,6*R*)-7,7',9,9'-tetramethoxy-1,1',3,3'-tetramethyl-3,3',4,4'-tetrahydro-1*H*,1'*H*-6,6'-bibenzo[*g*]isochromene-5,5',10,10'-tetraone (10a) and (1*R*,1'*R*,3*S*,3'*S*,6*S*)-7,7',9,9'-tetramethoxy-1,1',3,3'-tetramethyl-3,3',4,4'-tetrahydro-1*H*,1'*H*-6,6'-bibenzo[*g*]isochromene-5,5',10,10'-tetraone (10b)

Naphthopyran **7** (48 mg, 0.14 mmol) was taken up in acetonitrile (4 mL) and a solution of cerium(IV) ammonium nitrate (245 mg, 0.45 mmol) in distilled water (2 mL) was added. The reaction mixture stirred for 30 min at r.t. and water (12 mL) was then added. The aqueous layer was extracted with ethyl acetate (3 x 30 mL) and the combined organic layers dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The resulting residue was purified by flash chromatography eluting with hexanes-ethyl acetate (1:3 then 100% ethyl acetate) to give the *title compound* as an orange solid and a 1:1 mixture of atropisomers; (30.7 mg, 0.051 mmol, 71%). Purification of this mixture by further flash chromatography eluting with hexanes-ethyl acetate (1:1 then 2:3) gave pure (*R*)-atropisomer **10a** (R_f 0.42, ethyl acetate) as a yellow solid (14.1 mg, 0.023 mmol, 34%) and pure (*S*)-atropisomer **10b** (R_f 0.35, ethyl acetate) as a yellow solid (15.1 mg, 0.025 mmol, 36%).

10a m.p. 270–272 °C; $[\alpha]_D^{24}$ +852.9 (*c* 0.13, CH_2Cl_2); υ_{max} (neat)/cm^{-1} 2928, 2851, 1737, 1649, 1634, 1582, 1551, 1456, 1433, 1341, 1300, 1253, 1211, 1149; δ_H (300 MHz, $CDCl_3$) 1.27 (6 H, d, *J* 6.3, 2 x CH_2CH*Me*), 1.56 (6 H, d, *J* 6.6, 2 x Me), 1.97 (2 H, ddd, *J* 3.8, 10.2 and 18.2, 2 x CH_{ax}H), 2.50 (2 H, dt, *J* 2.6 and 18.2, 2 x CHH_{eq}), 3.48 (2 H, m, 2 x H-3), 3.74 (6 H, s, 2 x OMe), 4.05 (6 H, s, 2 x OMe), 4.81 (2 H, m, 2 x H-1), 6.757 (2 H, s, 2 x Ar-H); δ_C (75 MHz, $CDCl_3$) 20.7 (2 x Me), 21.2 (2 x Me), 29.9 (2 x CH_2), 56.1 (2 x OMe), 56.3 (2 x OMe), 68.8 (2 x CH), 70.3 (2 x CH), 99.6 (2 x CH), 114.8 (2 x C), 120.9 (2 x C), 132.3 (2 x C), 139.8 (2 x C), 148.0 (2 x C), 161.3 (2 x C), 161.6 (2 x C), 182.7 (2 x C=O), 184.8 (2 x C=O); *m/z* (EI+) 602 (100%, M^+), 587 (10), 260 (10), 43 (80); HRMS (EI+, M^+) found 602.2150, calc for $C_{34}H_{34}O_{10}$ 602.2152.

10b m.p. 127–129 °C; $[\alpha]_D^{24}$ +108.1 (*c* 0.16, CH_2Cl_2); υ_{max} (neat)/cm^{-1} 2928, 2851, 1737, 1649, 1634, 1582, 1551, 1456, 1433, 1341, 1300, 1253, 1211, 1149; δ_H (300 MHz, $CDCl_3$) 1.26 (6 H, d, *J* 6.0, 2 x CH_2CH*Me*), 1.53 (6 H, d, *J* 6.6, 2 x Me), 1.94 (2 H, ddd, *J* 3.8, 10.3 and 18.1, 2 x CH_{ax}H), 2.50 (2 H, t, *J* 2.6 and 18.1, 2 x CHH_{eq}), 3.49 (2 H, m, 2 x H-3), 3.73 (6 H, s, 2 x OMe), 4.05 (6 H, s, 2 x OMe), 4.82 (2 H, m, 2 x H-1), 6.76 (2 H, s, 2 x Ar-H); δ_C (75 MHz, $CDCl_3$) 20.6 (2 x Me), 21.2 (2 x Me), 29.8 (2 x CH_2), 56.1 (2 x OMe), 56.3 (2 x OMe), 68.8 (2 x CH), 70.3 (2 x CH), 99.4 (2 x CH), 114.9 (2 x C), 121.4 (2 x C), 131.3 (2 x C), 139.6 (2 x C), 148.2 (2 x C), 161.3 (2 x C), 162.6 (2 x C), 183.1 (2 x C=O), 184.8 (2 x C=O); *m/z* (EI+) 602 (100%, M^+), 587 (10), 260 (10), 43 (80); HRMS (EI+, M^+) found 602.2150, calc for $C_{34}H_{34}O_{10}$ 602.2152.

(1*R*,1'*R*,3*S*,3'*S*,6*R*)-9,9'-dihydroxy-7,7'-dimethoxy-1,1',3,3'-tetramethyl-3,3',4,4'-tetrahydro-1*H*,1'*H*-6,6'-bibenzo[*g*]isochromene-5,5',10,10'-tetraone (12a) and (1*R*,1'*R*,3*S*,3'*S*,6*S*)-9,9'-dihydroxy-7,7'-dimethoxy-1,1',3,3'-tetramethyl-3,3',4,4'-tetrahydro-1*H*,1'*H*-6,6'-bibenzo[*g*]isochromene-5,5',10,10'-tetraone (12b)

A solution of **10a** and **10b** (1:1, 11 mg, 0.0183 mmol) in dichloromethane (5 mL) was cooled to -78 °C. Boron trichloride (0.11 mmol, 0.11 mL of a 1 M solution in dichloromethane) was added dropwise and the reaction mixture was warmed to 0 °C. After 3 h a solution of 1 M HCl was added (20 mL) and the mixture extracted with dichloromethane (x 3). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by preparative TLC (ethyl acetate-hexanes, 1:4) gave

the *title compounds* **12a** and **12b** (7 mg, 0.012 mmol, 68%) as an orange solid and an inseparable 1:1 mixture of atropisomers, m.p. >270 °C ; $[\alpha]_D^{24}$ + 22.4 (*c* 0.53, CH_2Cl_2); υ_{max} (neat)/cm^{-1} 2920, 2852, 1638, 1388, 1284, 1207, 904; δ_H (400 MHz, $CDCl_3$) 1.25-1.43 (24 H, m, 4 x CH_2CHMe + 4 x Me), 1.99 (4 H, m, 4 x $CH_{ax}H$), 2.44 (2 H, dt, *J* 2.6 and 18.6, 2 x CH_{eq} atropisomer a), 2.52 (2 H, dt, *J* 2.7 and 18.7, 2 x CH_{eq} atropisomer b), 3.50 (4 H, m, 4 x H-3), 3.71 and 3.72 (4 H, 2 x s, 4 x Me), 4.80 (4 H, m, 4 x H-1), 6.69 and 6.70 (4 H, 4 x s, 4 x Ar-H), 13.09 (4 H, br s, 4 x OH); δ_H (100 MHz, $CDCl_3$) 21.06 and 21.11 (2 x Me and 2 x Me'), 22.6 (2 x Me), 28.88 and 28.91 (2 x CH_2 and 2 x CH_2'), 56.4 (2 x OMe and 2 x OMe'), 69.7 (2 x CH and 2 x CH'), 70.2 (2 x CH and 2 x CH'), 103.83 and 103.87 (2 x CH and 2 x CH'), 116.72 and 116.75 (2 x C and 2 x C'), 118.1 (2 x C and 2 x C'), 129.8 (2 x C and 2 x C'), 130.9 (2 x C and 2 x C'), 162.2 (2 x C and 2 x C'), 168.9 (2 x C and 2 x C'), 182.1 (2 x C=O), 186.6 and 186.7 (2 x C=O and 2 x C'=O) 1 x C not observed; *m/z* (EI+) 575 (12%, MH^+), 360 (15), 267 (12), 202 (31), 172 (41); HRMS (EI+, MH^+) found 575.1908, calc for $C_{32}H_{30}O_{10}$ + H 575.1912.

References

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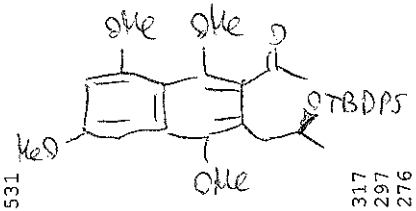

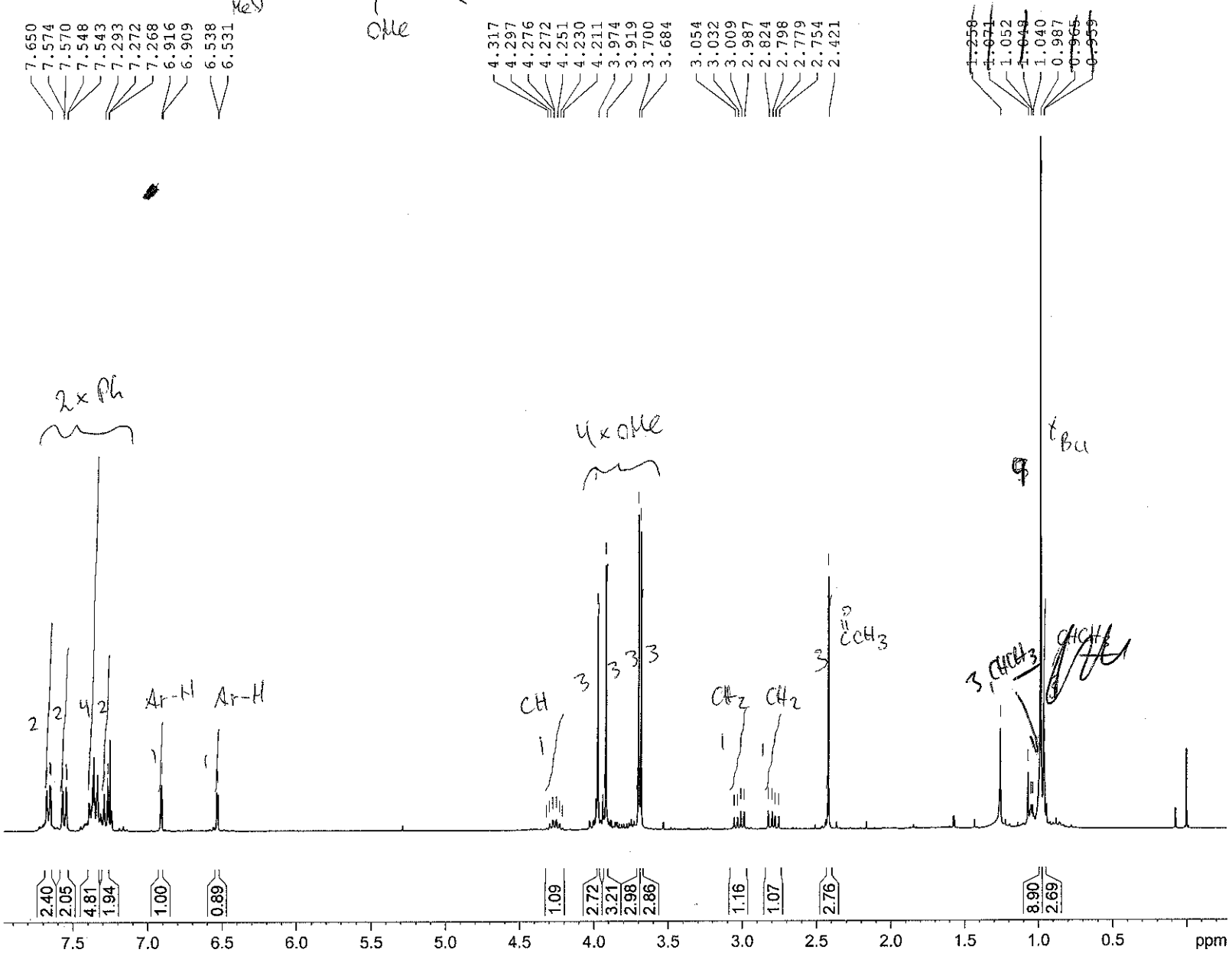


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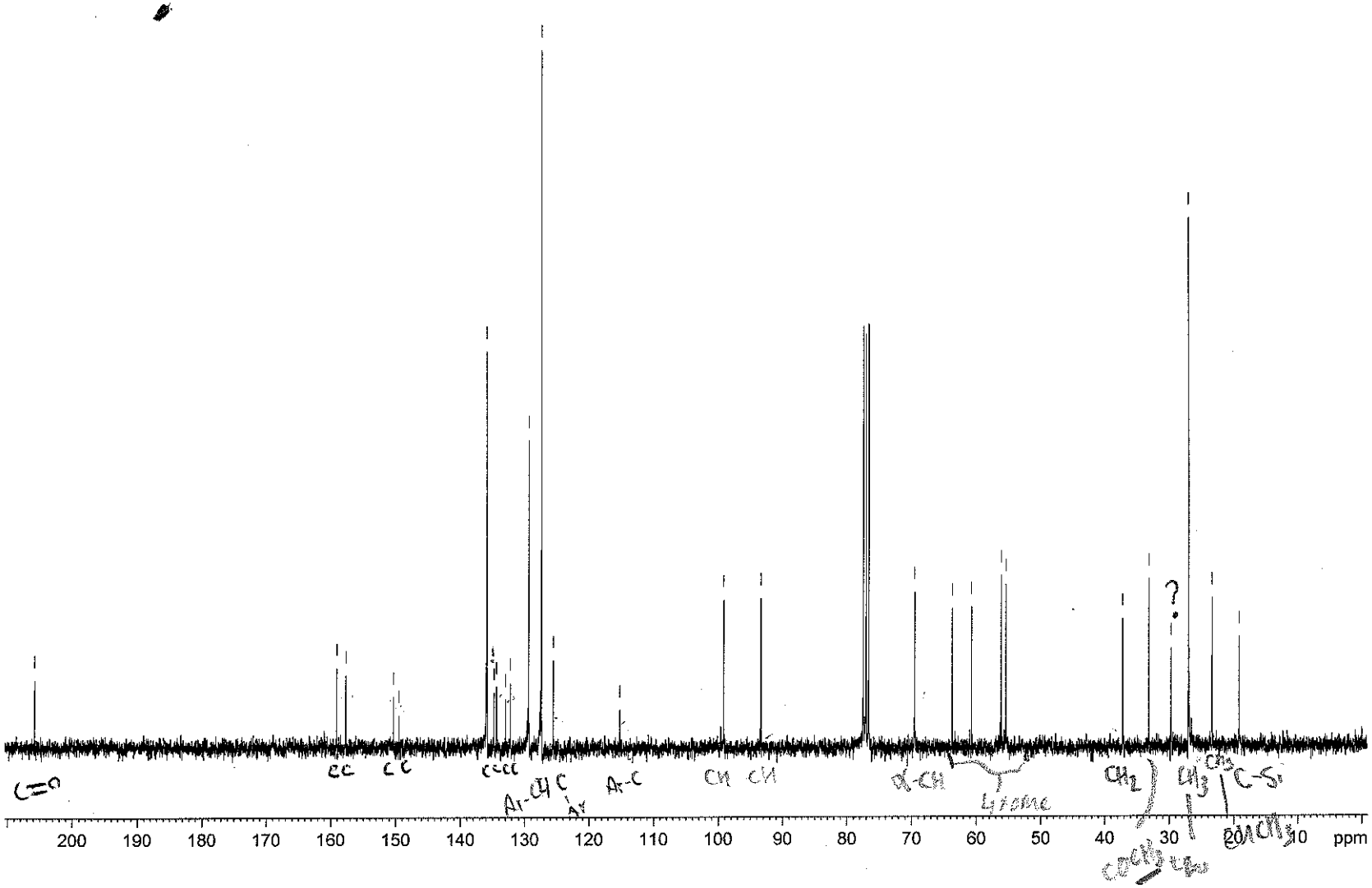

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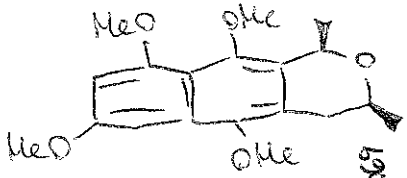
GB 0
PC 1.00

JS-52



Current Data Parameters

NAME	jsej52
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

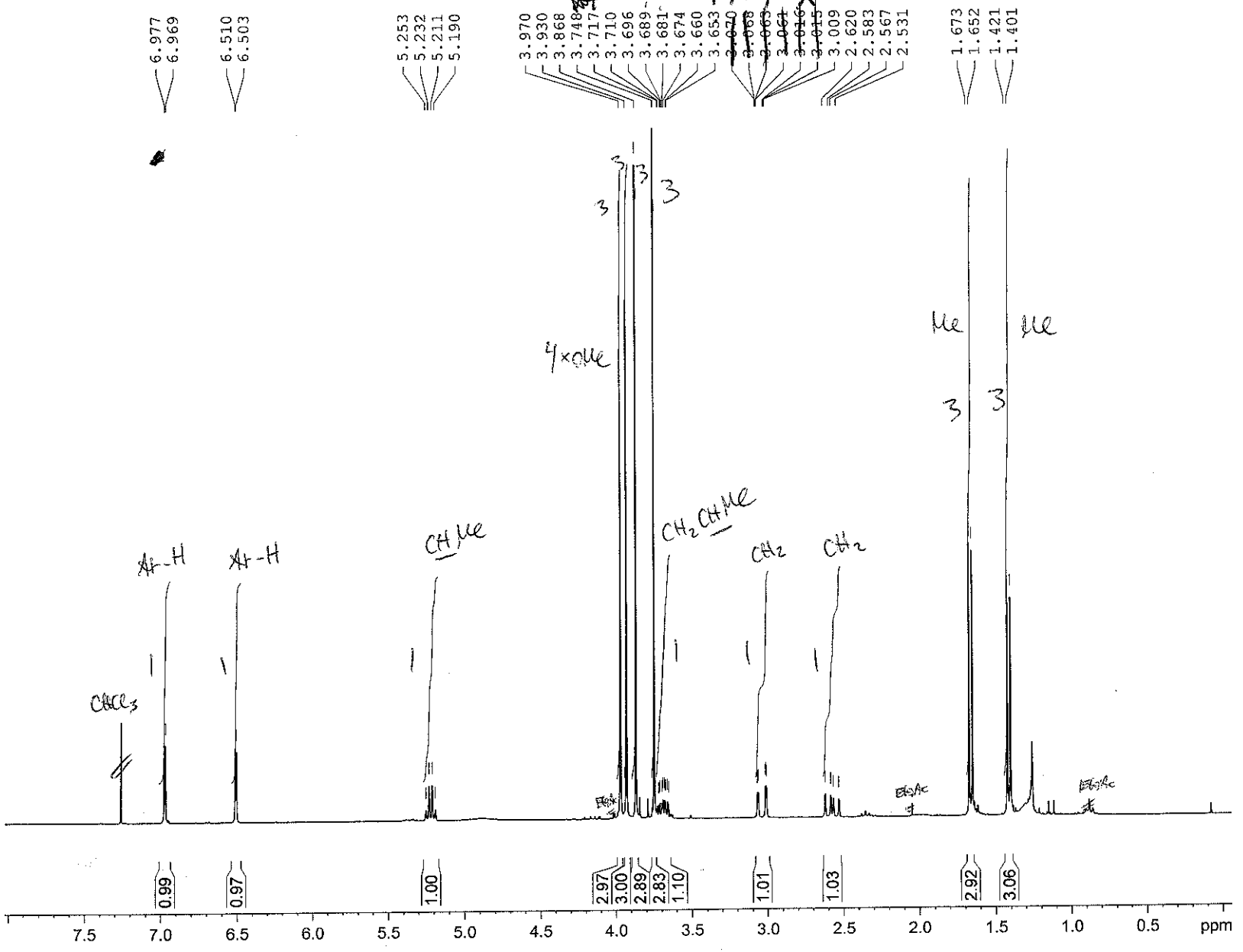
Date_	20080213
Time	16.10
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	
NS	64
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	256
DW	83.400 usec
DE	6.00 usec
TE	300.2 K
D1	0.10000000 sec
TD0	1

======== CHANNEL f1 ========

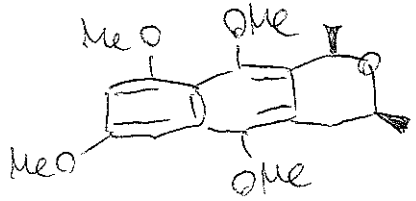
NUC1	1H
P1	11.90 usec
PL1	1.90 dB
SFO1	300.1315006 MHz

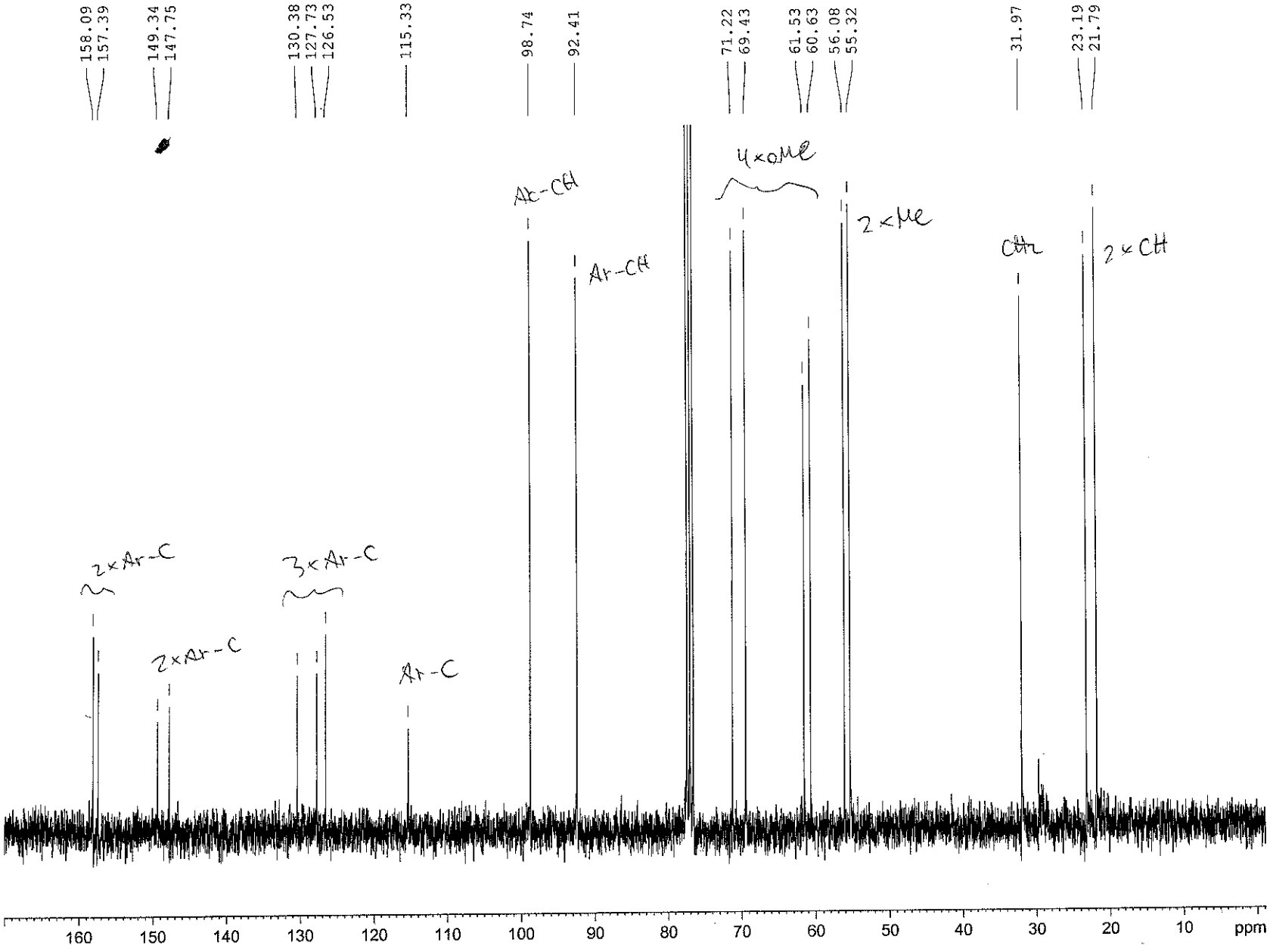
F2 - Processing parameters

SI	16384
SF	300.1300057 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	0.80

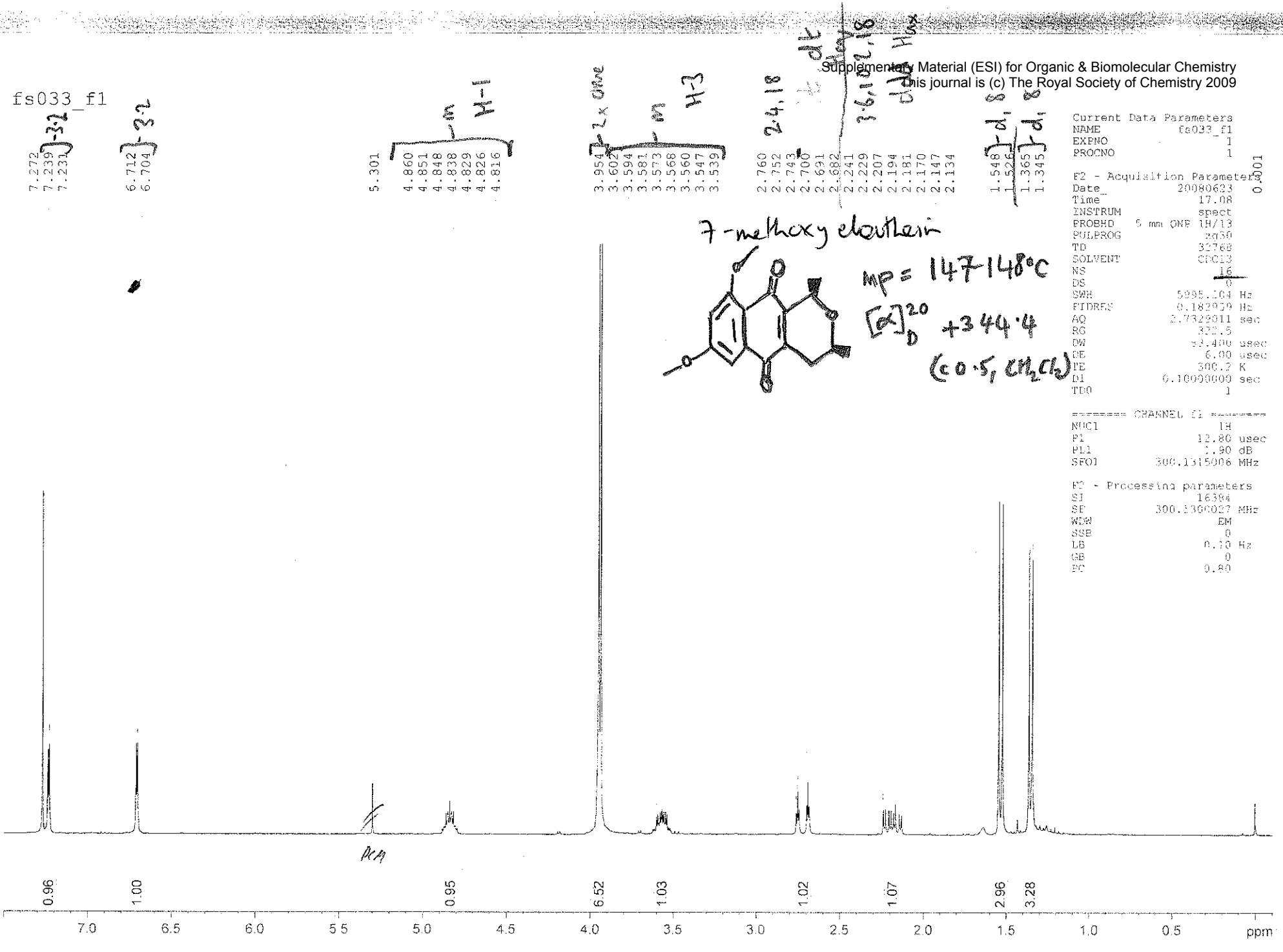


JS-S2



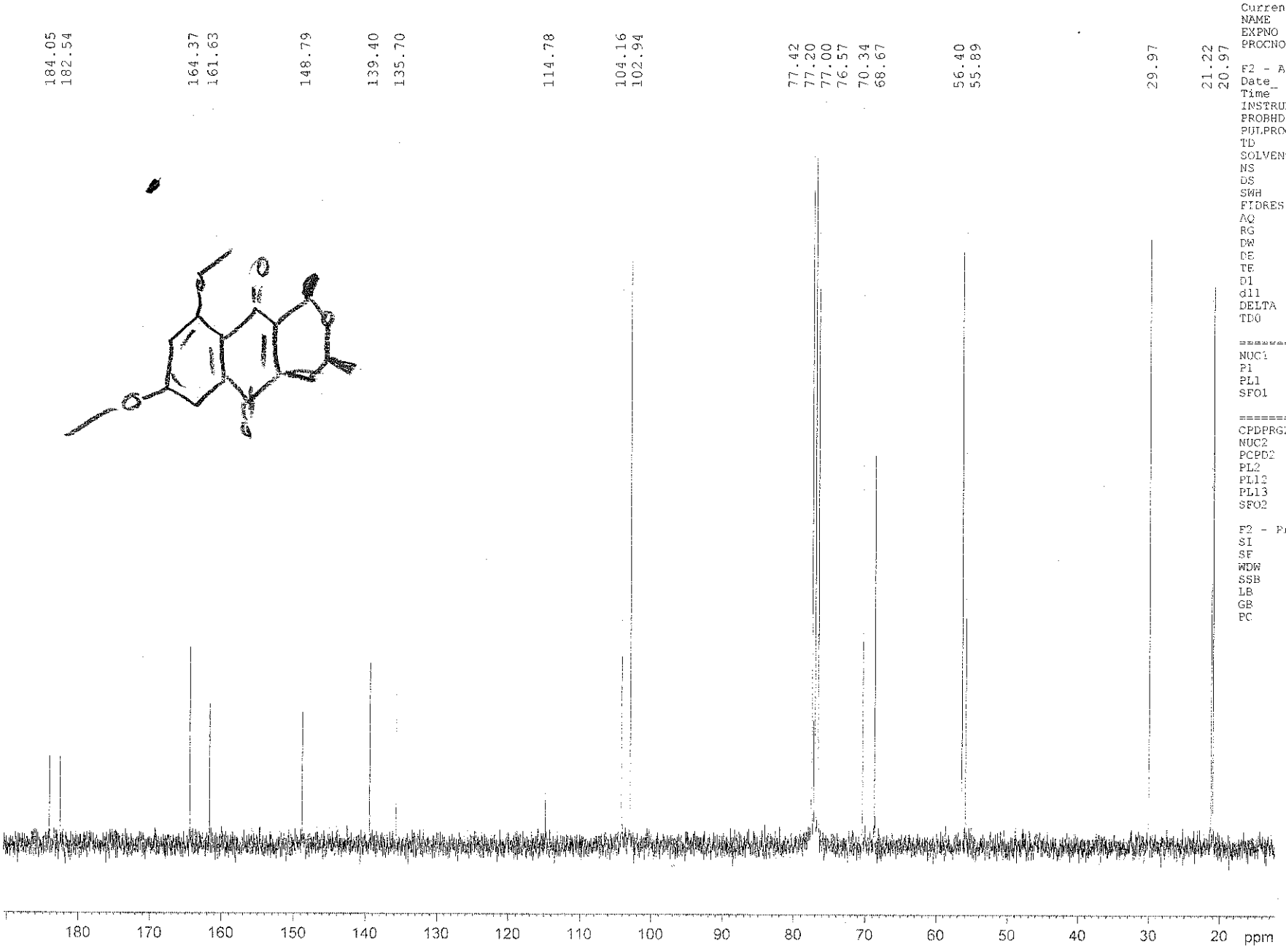



```
Current Data Parameters
NAME                  jsej52
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20080213
Time                  16.25
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG               zgpg
TD                   65536
SOLVENT
NS                     434
DS                       0
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                     16384
DW                 27.800 usec
DE                 20.00 usec
TE                   300.2 K
D1                0.17593171 sec
d11               0.03000000 sec
DELTA             0.07593171 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                  5.44 usec
PL1                 4.00 dB
SFO1          75.4760973 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2              100.00 usec
PL2                 1.90 dB
PL12                20.80 dB
PL13                26.40 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF            75.4677500 MHz
WDW                      EM
SSB                       0
LB                  1.00 Hz
GB                        0
PC                  1.00
```

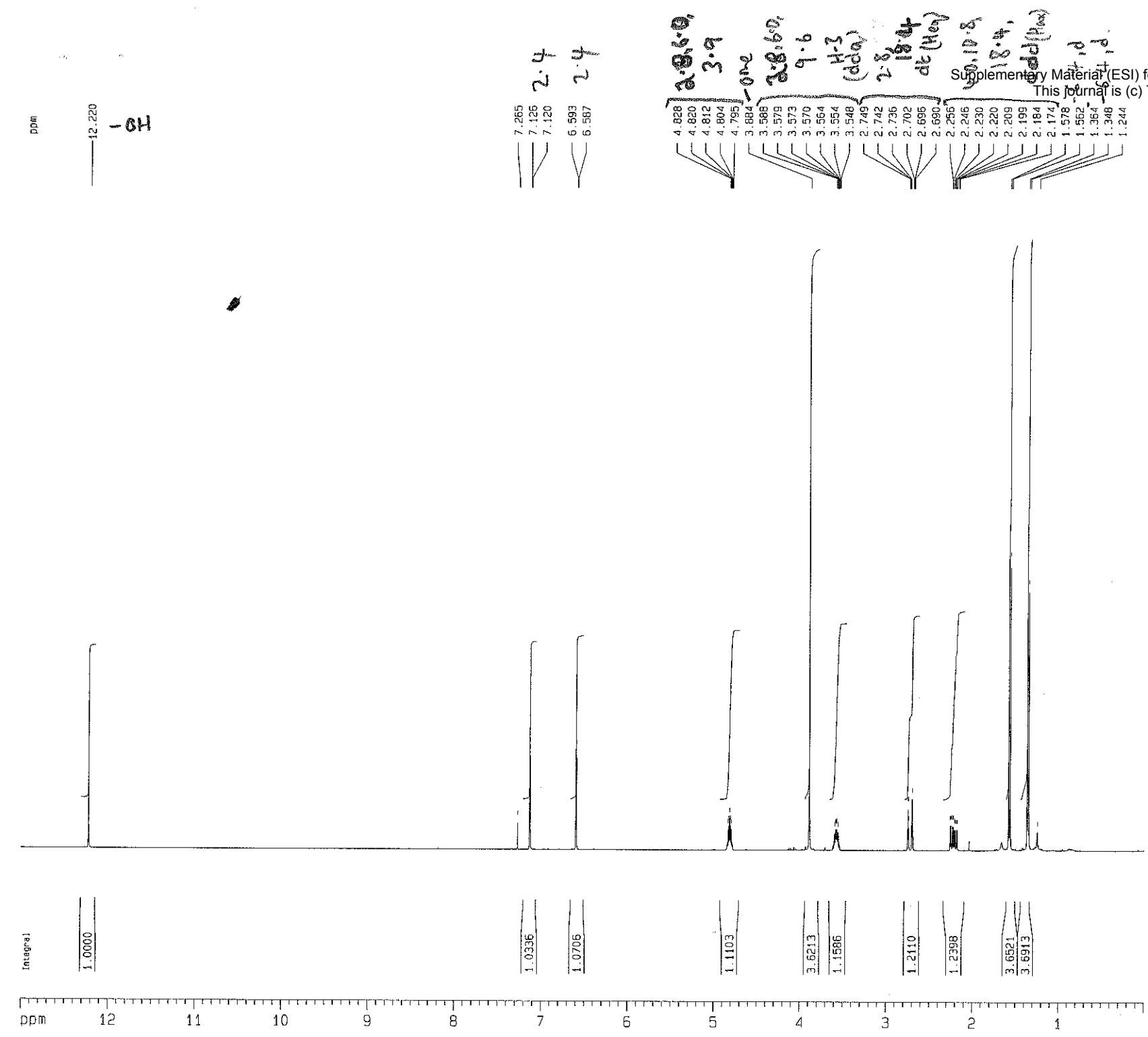



```
Current Data Parameters
NAME                  fs033_f1
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20080623
Time                   17.08
INSTRUM                spect
PROBHD    5 mm ONE 1H/13
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH               5995.204 Hz
FIDRES            0.182959 Hz
AQ                2.7328011 sec
RG                    322.5
DW                   83.400 usec
DE                    6.00 usec
TE                   300.2 K
D1                0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.80 usec
PL1                    1.90 dB
SFO1          300.1315006 MHz

F2 - Processing parameters
SI                       16384
SF            300.1300027 MHz
WDW                         EM
SSB                          0
LB                        0.10 Hz
GB                           0
PC                        0.80
```

fs033_f1




```
Current Data Parameters
NAME                  fs033_f1
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20080623
Time                   17.30
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                zgpg
TD                     65536
SOLVENT                CDCl3
NS                      1000
DS                         0
SWH                17985.611 Hz
FIDRES                0.274439 Hz
AQ                 1.8219508 sec
RG                     16384
DW                    27.800 usec
DE                    20.00 usec
TE                    300.2 K
D1                 0.17593171 sec
d11                0.03000000 sec
DELTA              0.07593171 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                       5.14 usec
PL1                      4.00 dB
SFO1               75.4760973 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                      1.90 dB
PL12                    19.76 dB
PL13                    25.76 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                         32768
SF                 75.4677503 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                        1.00
```



Current Data Parameters

NAME	fs034f1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20080625
Time	6.29
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	8169.935 Hz
FIDRES	0.249327 Hz
AQ	2.0054517 sec
RG	128
DW	61.200 usec
DE	6.50 usec
TE	300.0 K
D1	0.10000000 sec

======== CHANNEL f1 ========

NUC1	1H
P1	14.40 usec
PL1	2.20 dB
SFO1	400.1321007 MHz

F2 - Processing parameters

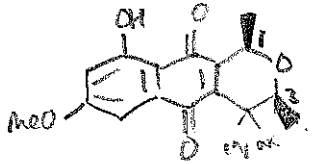
SI	16384
SF	400.1300113 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	0.80

1D NMR plot parameters

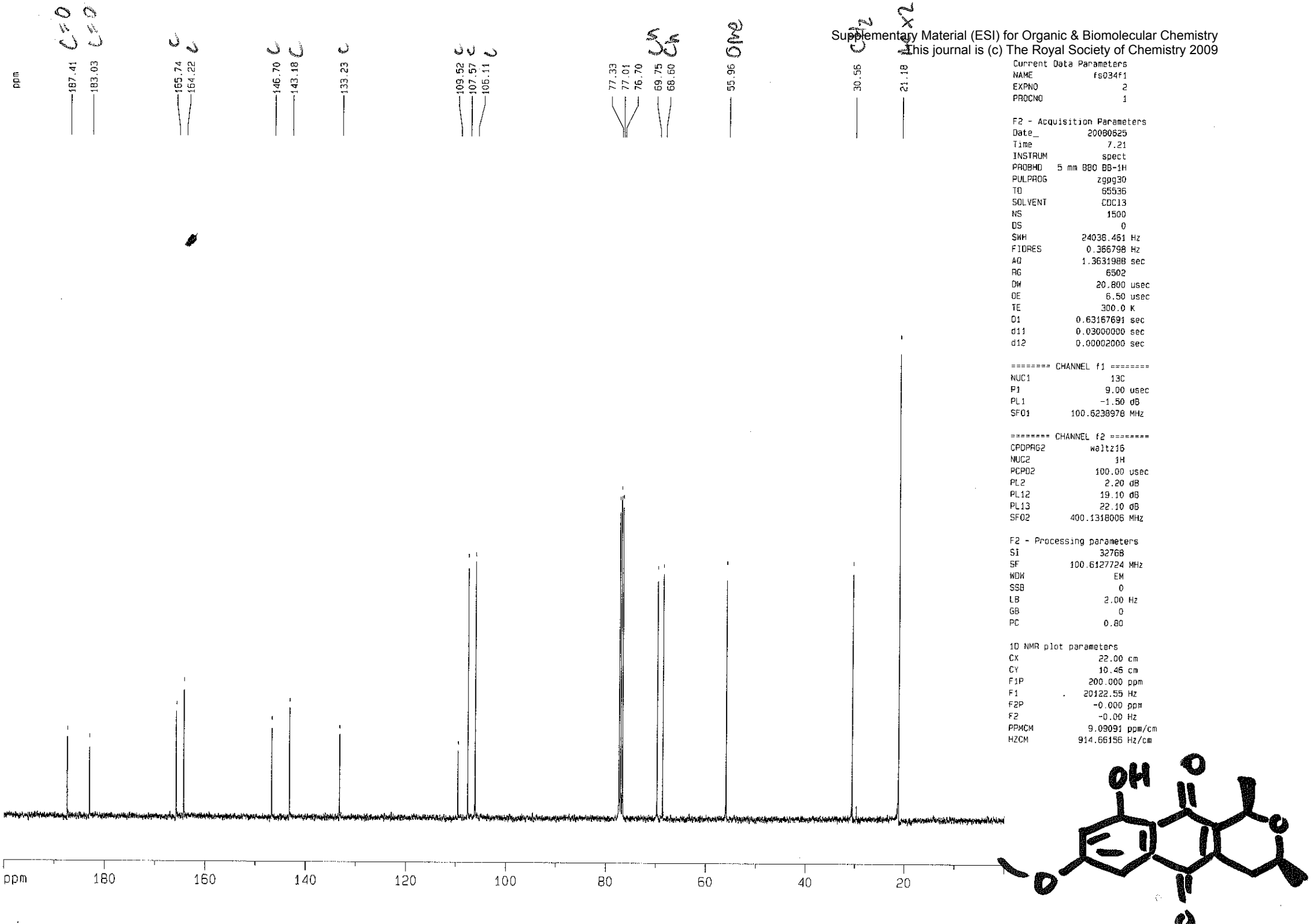
CX	22.00 cm
CY	11.04 cm
F1P	13.000 ppm
F1	5201.69 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.59091 ppm/cm
HZCM	236.44046 Hz/cm

mp-120-122°C

$[\alpha]_D^{20}$ (c, 0·011, $CHCl_3$) = +435·2



Ventiloquinone L



Current Data Parameters

NAME	fs034f1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20080625
Time	7.21
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1500
DS	0
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	6502
DW	20.800 usec
DE	6.50 usec
TE	300.0 K
D1	0.63167691 sec
d11	0.03000000 sec
d12	0.00002000 sec

======== CHANNEL f1 ========

NUC1	13C
P1	9.00 usec
PL1	-1.50 dB
SFO1	100.6238978 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	2.20 dB
PL12	19.10 dB
PL13	22.10 dB
SFO2	400.1318006 MHz

F2 - Processing parameters

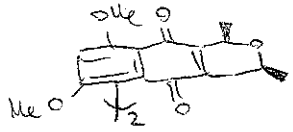
SI	32768
SF	100.6127724 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	0.80

1D NMR plot parameters

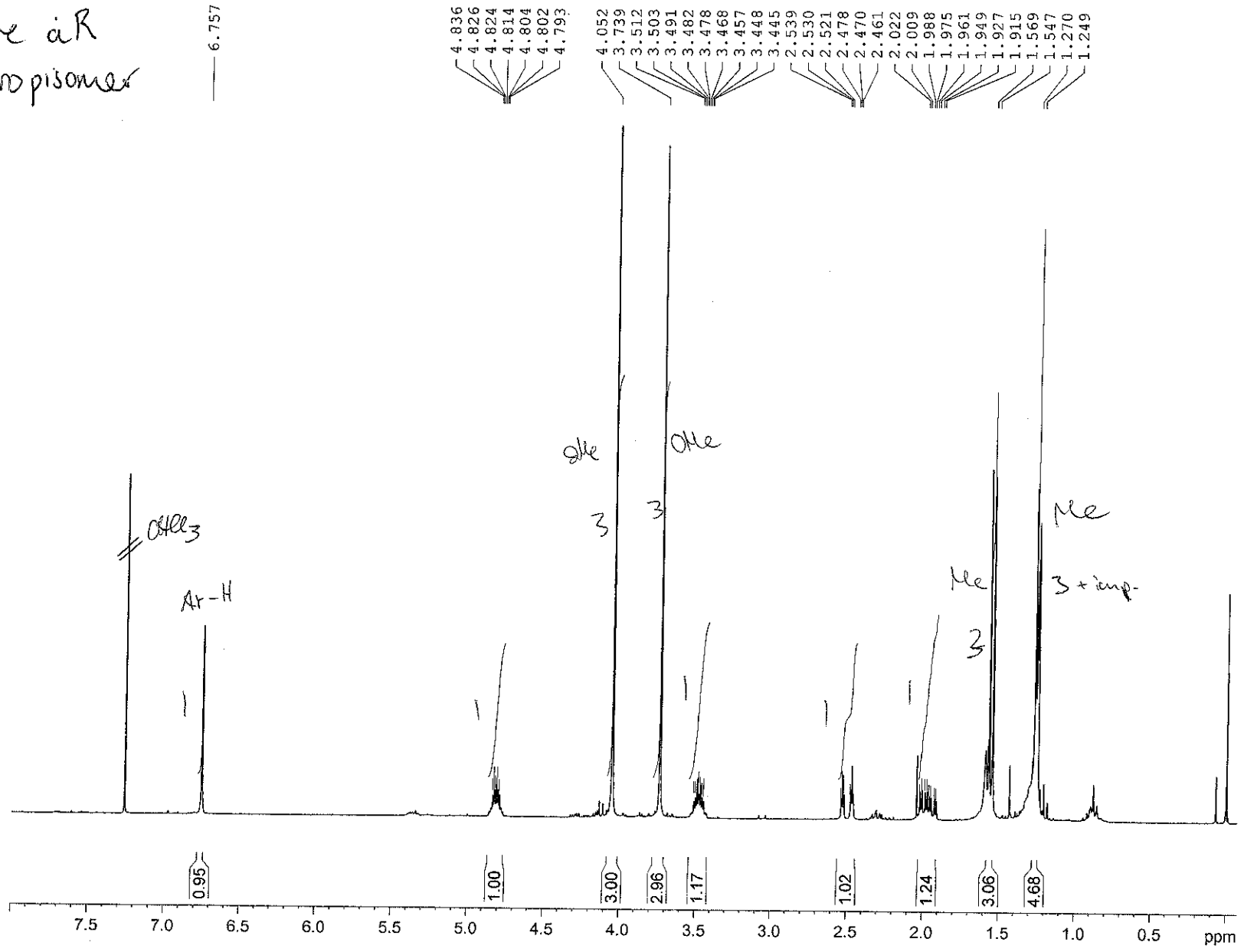
CX	22.00 cm
CY	10.46 cm
F1P	200.000 ppm
F1	20122.55 Hz
F2P	-0.000 ppm
F2	-0.00 Hz
PPMCM	9.09091 ppm/cm
HZCM	914.66156 Hz/cm

JS-53 f11-18

(R_f 0.42, ~~EtOAc~~)



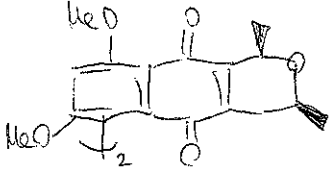
Pure aR atropisomer

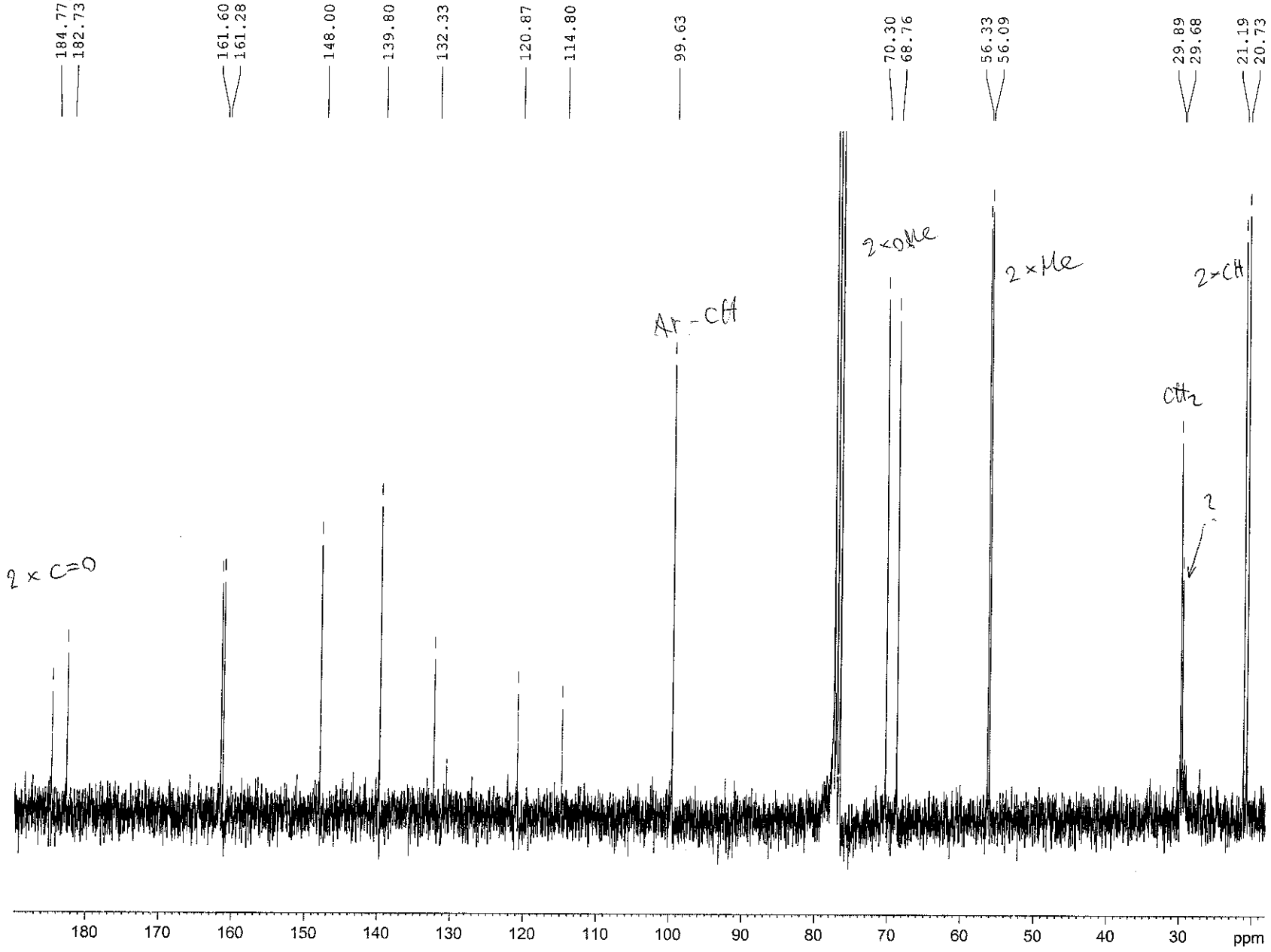



```
Current Data Parameters
NAME       jsej53_f11-18
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20080217
Time              15.17
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           zg30
TD               32768
SOLVENT
NS                   64
DS                    0
SWH            5995.204 Hz
FIDRES        0.182959 Hz
AQ            2.7329011 sec
RG                456.1
DW               83.400 usec
DE                6.00 usec
TE               300.2 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1               11.90 usec
PL1               1.90 dB
SFO1       300.1315006 MHz

F2 - Processing parameters
SI                16384
SF        300.1300057 MHz
WDW                  EM
SSB                   0
LB                 0.10 Hz
GB                    0
PC                 0.80
```

JS-53 f11-18

PURE aR atropisomer






```
Current Data Parameters
NAME        jsej53_f11-18
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080217
Time                15.51
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg
TD                 65536
SOLVENT
NS                  1500
DS                     0
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ           1.8219508 sec
RG                 16384
DW            27.800 usec
DE            20.00 usec
TE             300.2 K
D1           0.17593171 sec
d11          0.03000000 sec
DELTA        0.07593171 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1               5.44 usec
PL1               4.00 dB
SFO1        75.4760973 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2          100.00 usec
PL2               1.90 dB
PL12             20.80 dB
PL13             26.40 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677496 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.00
```

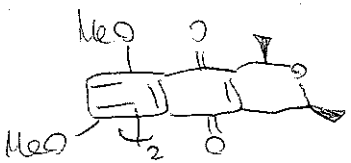
JS-53 f28-46

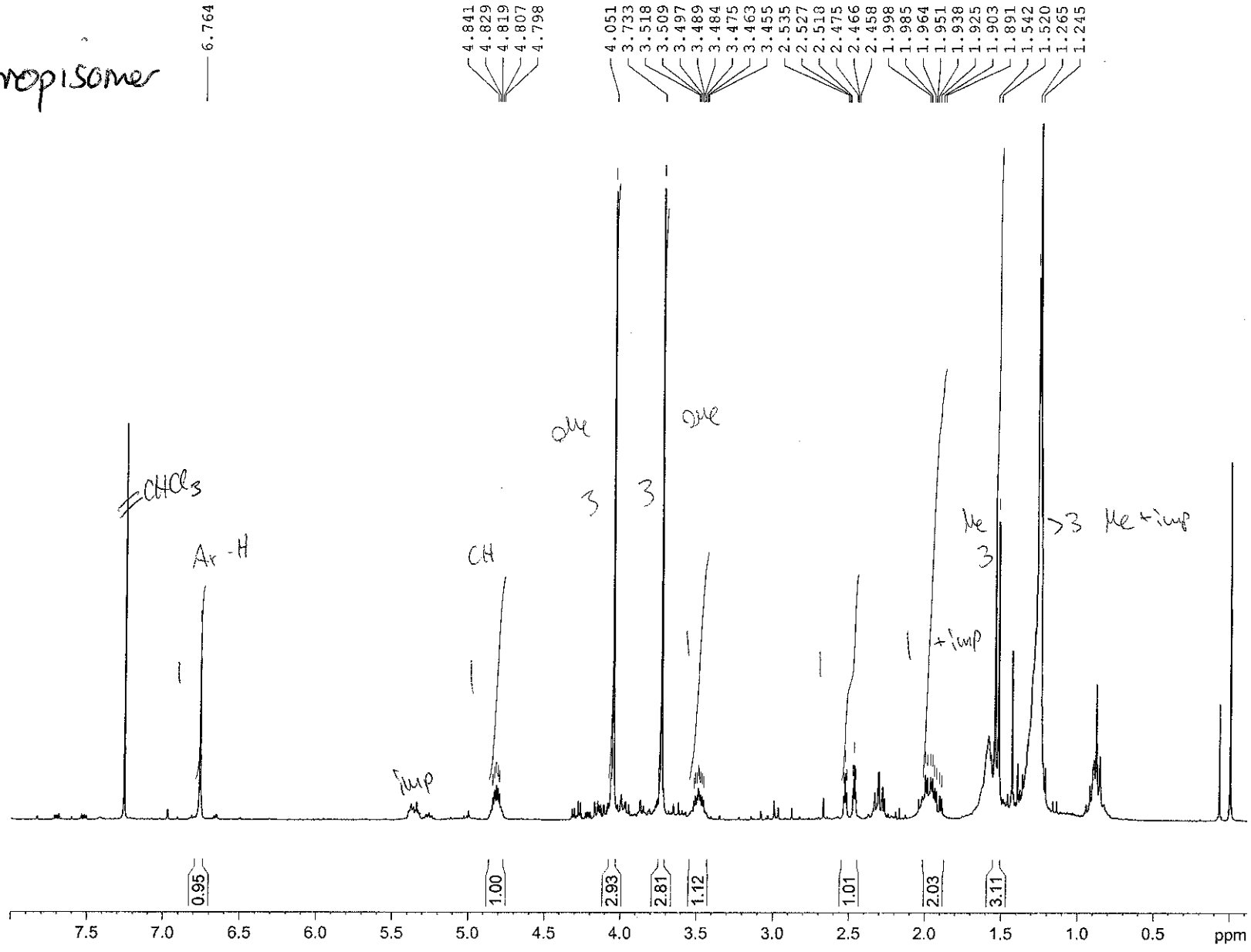
(R_f 0.35, EtOAc)

atropisomer B

as

atropisomer

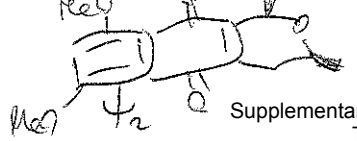


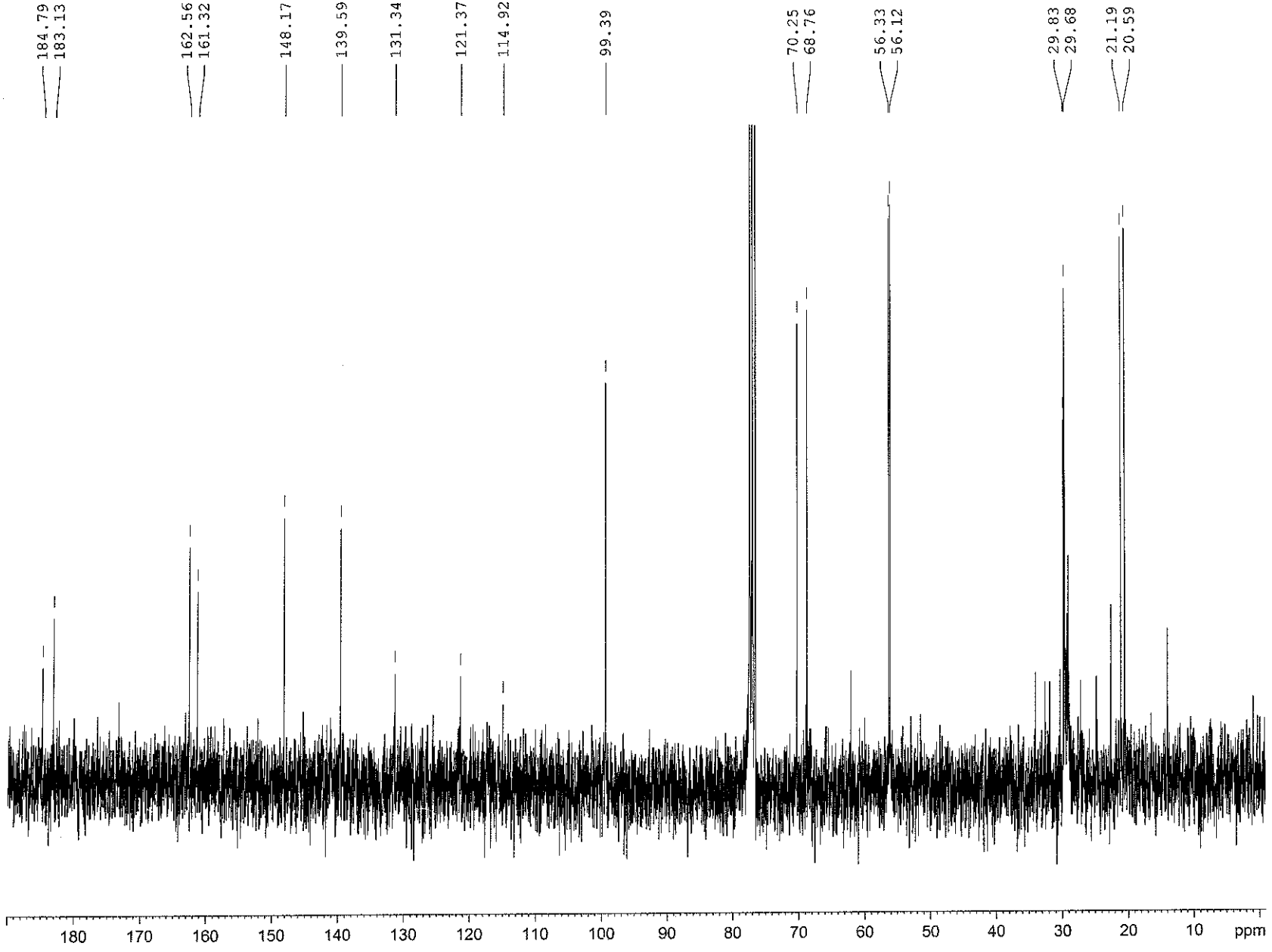



```
Current Data Parameters
NAME       jsej53_f28-46
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080217
Time               16.35
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 32768
SOLVENT
NS                    64
DS                     0
SWH             5995.204 Hz
FIDRES          0.182959 Hz
AQ              2.7329011 sec
RG                 406.4
DW                83.400 usec
DE                 6.00 usec
TE                300.2 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.90 usec
PL1                1.90 dB
SFO1        300.1315006 MHz

F2 - Processing parameters
SI                 16384
SF          300.1300057 MHz
WDW                   EM
SSB                    0
LB                 0.10 Hz
GB                     0
PC                 0.80
```

JS-53 f28-46

aS atropisomer



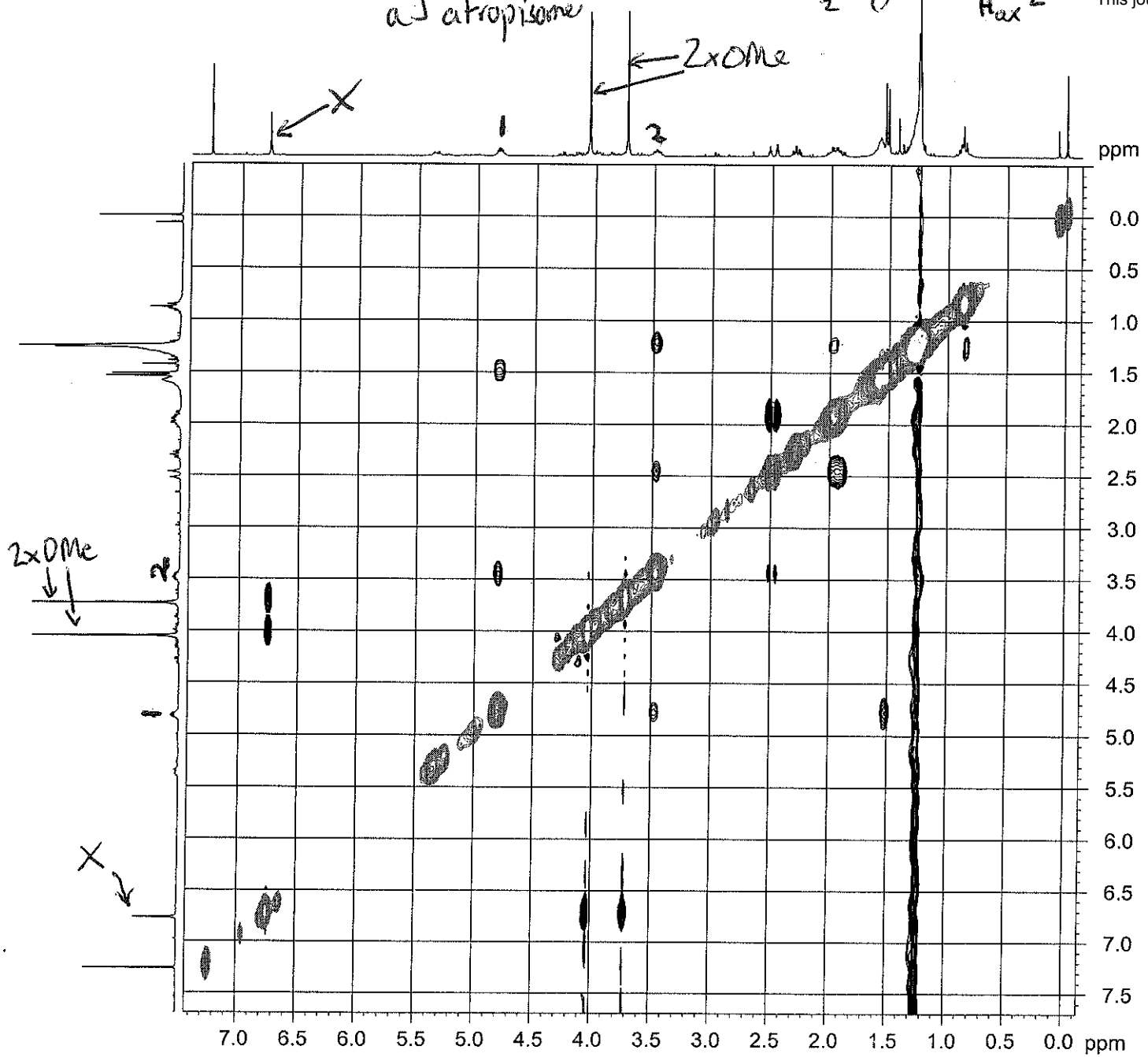



```
Current Data Parameters
NAME       jsej53_f28-46
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20080217
Time               17.10
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg
TD                65536
SOLVENT
NS                 1500
DS                    0
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                16384
DW               27.800 usec
DE               20.00 usec
TE               300.2 K
D1            0.17593171 sec
d11           0.03000000 sec
DELTA         0.07593171 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                5.44 usec
PL1               4.00 dB
SFO1         75.4760973 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2               1.90 dB
PL12             20.80 dB
PL13             26.40 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF          75.4677493 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.00
```

JS53 f28-46 (atropisomer B)

NOESY Tmix = 800 ms

a/ atropisome




```
Current Data Parameters
NAME       jsej53_f28-46
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080219
Time               14.20
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG  noesygpphpp.rak
TD                 2048
SOLVENT
NS                    5
DS                   16
SWH            5995.204 Hz
FIDRES         2.927346 Hz
AQ             0.1708532 sec
RG                   57
DW              83.400 usec
DE               6.00 usec
TE              300.2 K
d0             0.00006825 sec
D1             1.00000000 sec
D8             0.80000001 sec
D11            0.03000000 sec
d12            0.00002000 sec
d30            0.79895002 sec
IN0            0.00016680 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                11.90 usec
P17             2500.00 usec
PL1                1.90 dB
PL10               9.90 dB
SFO1        300.1315007 MHz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPZ1              17.00 %
P16             1000.00 usec

F1 - Acquisition parameters
ND0                   1
TD                  235
SFO1        300.1315 MHz
FIDRES      25.511505 Hz
SW             19.975 ppm
FnMODE            TPPI

F2 - Processing parameters
SI                 1024
SF          300.1300069 MHz
WDW               QSINE
SSB                   2
LB                 0.00 Hz
GB                    0
PC                 0.80

F1 - Processing parameters
SI                  256
MC2                TPPI
SF          300.1300069 MHz
WDW               QSINE
SSB                   2
LB                 0.00 Hz
GB                    0
```