Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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An *N*,*N*′-Dioxide-In(OTf)$_3$ Catalyst for the Asymmetric Hetero-Diels-Alder Reaction Between Danishefsky's Dienes and Aldehydes: Application in the Total Synthesis of Triketide

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Supporting Information

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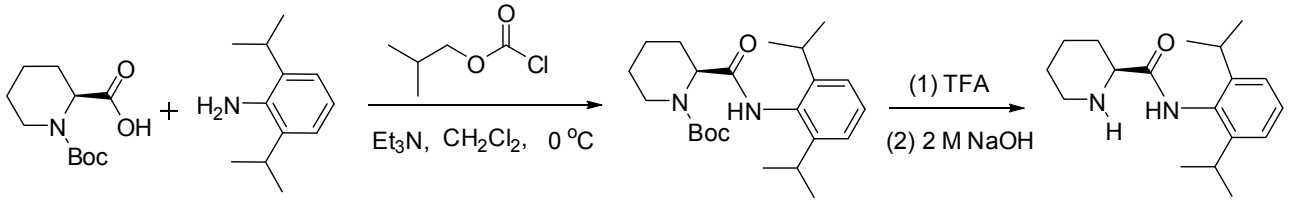
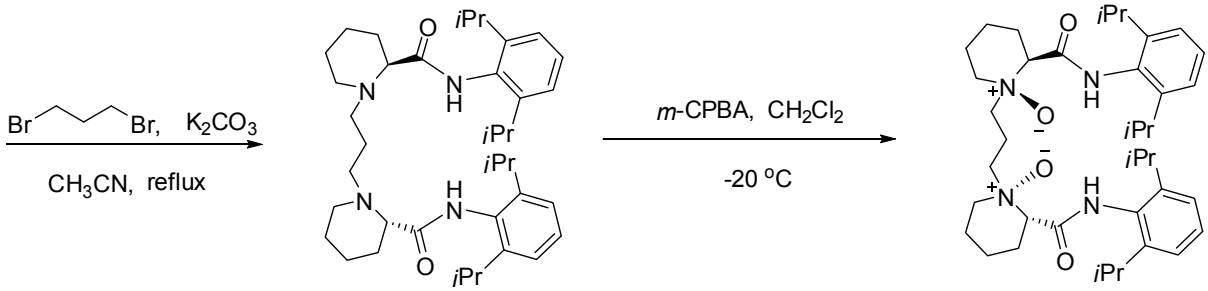
1. General Remarks

Reactions were carried out using commercial available reagents in over-dried apparatus. Toluene, Et_2O, *t*-BuOMe and THF were dried and distilled from sodium benzophenone under nitrogen just before use. CH_2Cl_2 was dried over powdered CaH_2 and distilled under nitrogen just before use. Anisole was dried over powdered CaH_2 and distilled under vacuum. Melting points (m.p.) were measured on electrothermal digital melting point apparatus and were uncorrected. Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral column as stated in the experimental procedures at 23 ˚C with UV detector at 254 nm or GC. Optical rotations were reported as follows: $[\alpha]^{25}_{D}$ (c g/100 mL, in solvent). ^{1}H NMR spectra were recorded on commercial instruments (300, 400 or 600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (75, 100 or 150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). HRMS was recorded on a commercial apparatus (ESI Source).

Dienes **1** and **4** were prepared according to the reported procedure.[1] The *N*,*N*'-dioxide ligands were prepared according to the methods mentioned in catalyst preparation section.[2] 4 Å MS was purchased from Acros powdered <50 μm, it was activated at 200 ^{o}C for 2 h and stored under nitrogen. All aldehydes were commercially purchased and distilled or recrystallized just before use. Racemic samples of **3a-3ah, 5a-5h** were prepared with 20% anhydrous $BF_3\cdot Et_2O$ as the catalyst and Et_2O as solvent.

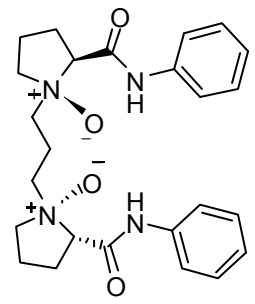
2. Typical Procedure for *N,N*'-Dioxide Ligand Preparation[2]



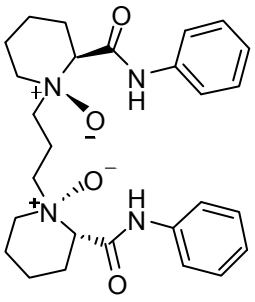


To a solution of (*S*)-1-*N*-Boc-piperidine-2-carboxylic acid (2200 mg, 10 mmol) in CH_2Cl_2 (20 mL) was added Et_3N (1.55 mL, 11 mmol), isobutyl chloroformate (1503 mg, 11 mmol) at 0 °C under stirring. After 55 min, 2,6-diisopropylaniline (2215 mg, 12.5 mmol) was added. The reaction was allowed to warm to room temperature and detected by TLC. After 24 h, the mixture was washed with 1 M $KHSO_4$, saturated $NaHCO_3$, brine, dried over anhydrous $MgSO_4$ and concentrated and purified through flash chromatograph (Et_2O : *n*-hexane = 1:8, R_f 0.2, 1787 mg, 46% isolate yield). The white solid **PPL8** in CH_2Cl_2 (8 mL) was added TFA (2 mL) and stirred until the reaction was finished (10 h). Then, the solvent was evaporated, and H_2O (10 mL) was added. The pH value of the mixture was brought into the range of 10 - 12 by the addition of 2 M NaOH. The aqueous phase was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic phase was washed with brine, dried over anhydrous $MgSO_4$ and evaporated in vacuo. The residue was directly used for next step without further purification. To a solution of (*S*)-*N*-(2,6-diisopropylphenyl)-piperidine-2-carboxamide (1153 mg, 4 mmol) in CH_3CN (6 mL) was added K_2CO_3 (1126 mg, 8.8 mmol) and 1,3-dibromopropane (204 μL, 2 mmol) under stirring. It was kept at 80 °C, and monitored by TLC. Then, K_2CO_3 was removed by filtration and washed by CH_2Cl_2. The filtrate was concentrated and purified by silica gel column chromatography (EtOAc : *n*-hexane = 1:1, R_f 0.2) to give (2*S*,2'*S*)-1,1'-(propane-1,3-diyl)bis(*N*-(2,6-diisopropylphenyl)piperidine-2-carboxamide) 1.048 g (85% isolate yield). The *N*,*N*'-dioxide was prepared through oxidation of **PL8** (797 mg, 1.29 mmol) by *m*-CPBA in CH_2Cl_2 (20 mL) at -20 °C for 1 h and purified through flash chromatograph (MeOH : EtOAc =

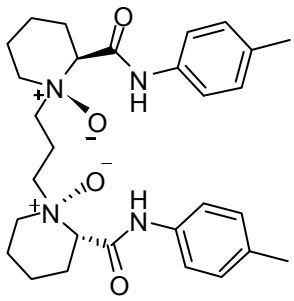
1:2, R_f 0.2). Finally a white foam solid obtained, then it was dissolved in CH_2Cl_2 and filtration through Celite to remove the silicon gel, concentrate to get a kind white foam **L8** (470 mg, 56% isolated yield). For other ligand, the synthesis method could be find in reference.[2]



L1: white solid; m.p. 102-104 ^oC; $[\alpha]^{25}_D$ = -72.4 (c = 0.170, in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 13.32 (s, 2H), 7.55-7.59 (m, 4H), 7.26-7.31 (m, 4H), 7.08 (m, 2H), 3.63-3.69 (m, 4H), 3.47-3.56 (m, 4H), 3.29-3.37 (m, 2H), 2.44-2.76 (m, 8H), 2.06-2.09 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 165.2, 137.7, 128.9, 124.2, 120.1, 68.1, 64.7, 27.6, 22.6, 20.3, 14.1 ppm; ESI-HRMS: calcd for $C_{25}H_{33}N_4O_4$ $[M+H^+]$ 453.2502, found 453.2498.

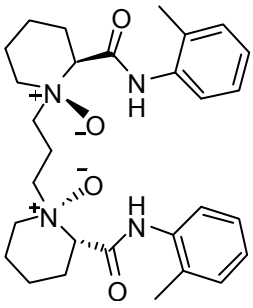


L2: white solid; m.p. 93-95 ^oC; $[\alpha]^{25}_D$ = -87.5 (c = 0.352, in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 12.78 (s, 2H), 7.47-7.50 (m, 4H), 7.23-7.28 (m, 4H), 7.03-7.07 (m, 2H), 3.35-3.51 (m, 8H), 2.85-2.94 (m, 2H), 2.47-2.61 (m, 2H), 2.28-2.43 (m, 6H), 1.99-2.04 (d, 2H), 1.84-1.88 (d, 2H), 1.62-1.67 (d, 2H), 1.32-1.46 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 166.3, 137.5, 128.9, 124.1, 119.9, 76.5, 66.8, 64.6, 26.2, 22.2, 20.1, 16.3 ppm; ESI-HRMS: calcd for $C_{27}H_{37}N_4O_4$ $[M+H^+]$ 481.6071, found 481.6077.

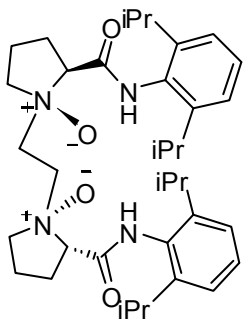


L3: white solid; m.p. 96-98 ^oC; $[\alpha]^{25}_D$ = -93.9 (c = 0.266, in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 12.63 (s, 2H), 7.37-7.39 (m, 4H), 7.05-7.07 (m, 4H), 3.39-3.50 (m, 8H), 2.87-2.90 (m, 2H), 2.30-2.61 (m, 12H), 1.86-2.05(m, 4H), 1.19-1.42 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 166.2, 135.0, 129.5, 120.0, 68.1, 64.7, 31.6, 22.7, 20.9, 20.2, 14.1 ppm; ESI-HRMS: calcd for $C_{29}H_{41}N_4O_4$

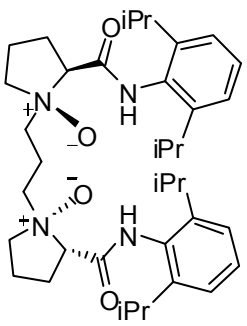
[M+H$^+$] 509.3128, found 509.3147.



L4: white solid; m.p. 91-93 ^{o}C; $[\alpha]^{25}_D$ = -74.6 (c = 0.122, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 12.66 (s, 2H), 7.97-7.99 (m, 2H), 7.10-7.16 (m, 4H), 7.00-7.01 (m, 2H), 3.45-3.55 (m, 8H), 2.89-2.96 (m, 2H,), 2.62-2.66 (m, 2H), 2.44-2.51 (m, 2H), 2.36-2.40 (m, 2H), 2.25-2.28 (m, 6H), 2.06-2.09 (m, 2H), 1.87-1.90 (m, 2H), 1.67-1.87 (m, 2H), 1.41-1.46 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 166.4, 136.2, 130.4, 128.2, 126.6, 124.4, 121.2, 66.8, 64.6, 31.6, 26.6, 22.7, 20.2, 18.4 ppm; ESI-HRMS: calcd for $C_{29}H_{41}N_4O_4$ [M+H$^+$] 509.3128, found 509.3147.

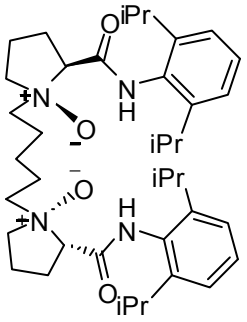


L5 : white solid; $[\alpha]^{25}_D$ = -31.2 (c = 0.404, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.51 (s, NH, 2 H), 7.26-7.11 (m, ArH, 6 H), 3.91 (dd, *J* = 10.8, 8.4 Hz, 2 H), 3.85-3.72 (m, 4 H), 3.52 (m, 2 H), 3.07 (m, 4 H), 2.76-2.51 (m, 6 H), 2.14 (m, 2 H), 1.92 (s, 2 H), 1.25-1.09 (m, 24 H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ = 166.03, 145.12, 130.75, 127.82, 123.19, 76.57, 70.05, 61.53, 29.00, 27.41, 23.53, 23.33, 20.54 ppm; ESI-HRMS: calcd for $C_{36}H_{55}N_4O_4$ [M+H$^+$] 607.4218, found 607.4214.

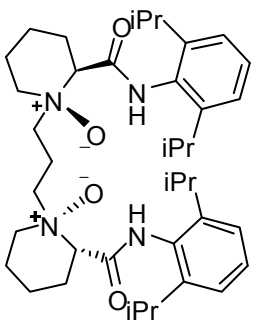


L6 : white solid; m.p. 111-112 ^{o}C; $[\alpha]^{25}_D$ = -50.4 (c = 0.274, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.47 (s, NH, 2 H), 7.29-7.17 (m, ArH, 6 H), 3.84 (dd, *J* = 11.2, 7.6 Hz, 2 H), 3.77 (m, 2 H), 3.71-3.64 (m, 2 H), 3.55 (m, 2 H), 3.42 (m, 2 H), 3.06 (m, 4 H), 2.87 (m, 2 H), 2.72-2.49 (m, 6 H), 2.12 (m, 2 H), 1.21 (dd, *J* = 20.8, 7.2 Hz 24 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.35, 144.91, 130.91, 127.87, 123.32, 77.00, 68.06, 64.05,

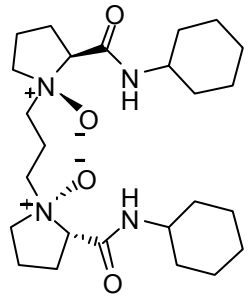
28.34, 27.55, 23.86, 23.21, 20.26, 19.79 ppm; ESI-HRMS: calcd for $C_{37}H_{57}N_4O_4$ [M+H$^+$] 621.4374, found 621.4368.



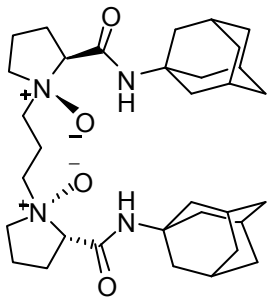
L7 : white solid; $[\alpha]^{25}_D$ = -38.6 (c = 0.264, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.64 (s, NH, 2 H), 7.29-7.17 (m, ArH, 6 H), 3.81 (dd, *J* = 11.2, 8.0 Hz, 2 H), 3.63 (m, 4 H), 3.31 (m, 4 H), 3.08 (m, 4 H), 2.71-2.39 (m, 8 H), 2.09 (m, 2 H), 1.88 (m, 2 H), 1.49 (m, 2 H), 1.21 (m, 24 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.64, 131.10, 127.76, 123.25, 76.37, 67.72, 66.69, 28.89, 27.48, 24.90, 24.12, 20.35 ppm; ESI-HRMS: calcd for $C_{39}H_{61}N_4O_4$ [M+H$^+$] 649.4687, found 649.4681.



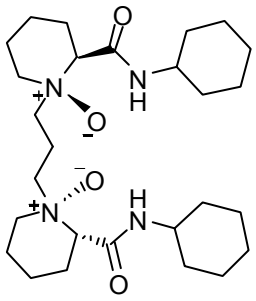
L8 : white solid; m.p. 96-98 ^{o}C; $[\alpha]^{25}_D$ = -54.0 (c = 0.576, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.86 (s, NH, 2 H), 7.30-7.17 (m, ArH, 6 H), 3.62 (m, 4 H), 3.36 (m, 2 H), 3.07-2.96 (m, 6 H), 2.79-2.71 (m, 4 H), 2.65 (m, 2 H), 2.40 (m, 2 H), 2.15 (d, *J* = 13.6 Hz, 2 H), 1.94 (d, *J* = 13.2 Hz, 2 H), 1.69 (d, *J* = 13.6 Hz, 2 H), 1.46 (m, 2 H), 1.23-1.16 (m, 24 H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ = 167.73, 145.03, 13.64, 127.95, 123.35, 76.16, 65.97, 64.77, 28.88, 28.44, 26.40, 23.53, 22.20, 20.11, 16.11 ppm; ESI-HRMS: calcd for $C_{39}H_{61}N_4O_4$ [M+H$^+$] 649.4687, found 649.4685.



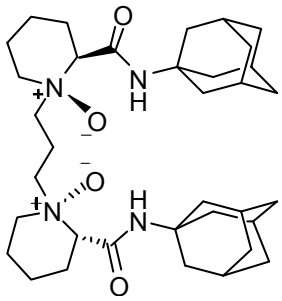
L9 : white solid; $[\alpha]^{25}_D$ = -31.8 (c = 0.500, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.59 (d, *J* = 6.8 Hz, NH, 2 H), 3.77 (m, 2 H), 3.62 (m, 2 H), 3.32-3.60 (m, 8 H), 2.39-2.64 (m, 8 H), 1.57-2.03 (m, 12 H), 1.27-1.35 (m, 10 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 76.5, 67.6, 64.7, 47.3, 32.7, 32.3, 27.4, 25.3, 24.4, 19.7 ppm; ESI-HRMS: calcd for $C_{25}H_{44}N_4O_4$ [M$^+$] 464.3363, found 464.3428.



L10 : white solid; $[\alpha]^{25}_{D}$ = -35.1 (c = 0.450, in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, NH, 2 H), 3.56-3.26 (m, 10 H), 2.94 (s, 2 H), 2.66-2.62 (m, 2 H), 2.47-2.35 (m, 6 H), 2.05-1.98 (m, 18 H), 1.71-1.68 (m, 12 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 76.7, 67.6, 64.8, 51.3, 41.5, 36.2, 29.3, 27.5, 19.9, 19.7 ppm; ESI-HRMS: calcd for $C_{33}H_{53}N_4O_4$ $[M+H^+]$ 569.4061, found 569.4061.



L11 : white solid; $[\alpha]^{25}_{D}$ = -50.8 (c = 0.634, in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 10.32 (d, *J* = 7.2 Hz, NH, 2 H), 3.77 (m, 2 H), 3.62 (m, 2 H), 3.32-3.60 (m, 8 H), 2.39-2.64 (m, 8 H), 1.57-2.03 (m, 12 H), 1.27-1.35 (m, 12 H) ppm; ESI-HRMS: calcd for $C_{27}H_{49}N_4O_4$ $[M+H^+]$ 493.3748, found 493.3748.



L12: white power; m.p. 88-90 ^oC; $[\alpha]^{25}_{D}$ = -88.20 (c = 0.500, in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 9.90 (s, 2H, NH), 3.20-3.40 (m, 10H), 2.78-2.86 (m, 2H), 2.31-2.40 (m, 2H), 2.18-2.16 (m, 4H), 1.83-1.96 (m, 22H), 1.70-1.74 (m, 2H), 1.50-1.64 (m, 10H), 1.26-1.35 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 167.1, 76.2, 66.3, 64.5, 51.2, 41.3, 36.1, 29.2, 26.1, 22.1, 20.0, 16.6 ppm; ESI-HRMS: calcd for $C_{35}H_{56}N_4O_4$ $[M^+]$ 596.4302, found 596.4292.

PPL8: white power; m.p. 148-150 ^oC; $[\alpha]^{23}_{D}$ = -79.86 (c = 0.452, in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 7.52 (s, 1H, NH), 7.29-7.16 (m, 3H), 4.97 (s, 1H), 4.34-4.10 (m, 1H), 3.10-2.99 (m, 2H), 2.96 (m, 1H), 2.50-2.38 (m, 1H), 1.63-1.45 (m, 5H), 1.51 (s, 9H), 1.20 (d, *J* = 6.8 Hz, 12H) ppm.

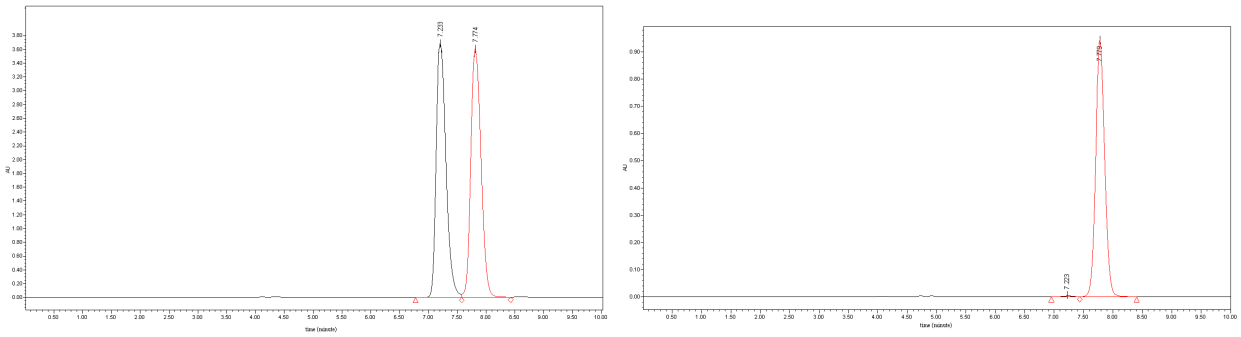
PL8: white power; m.p. 182-185 °C; $[\alpha]^{25}_{D}$ = -85.70 (c = 0.858, in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.01 (s, NH, 2 H), 7.32-7.17 (m, ArH, 6 H), 3.24-3.22 (m, 2 H), 3.08-3.01 (m, 4 H), 2.93-2.78 (m, 4 H), 2.38-2.22 (m, 2 H), 2.12-2.06 (m, 4 H), 1.90 (m, 2 H), 1.80-1.69 (m, 6 H), 1.55 (m, 2 H), 1.37 (m, 2 H), 1.24-1.18 (m, 24 H) ppm.

3. Typical Procedure for the Synthesis of 3,5-Dimethyl-dihydropyrones and 5-Methyl-dihydropyrones[4]

3,5-dimethyl-2-phenyl-2,3-dihydro-4*H*-pyran-4-one (**3a**). A nitrogen protected mixture of *N,N*'-dioxide **L8** (8.2 mg, 0.0125 mmol), $In(OTf)_3$ (7.0 mg, 0.0125 mmol) and 4 Å MS (25 mg) in THF (100 μL) was stirred at room temperature for 20 min. The mixture was evaporated under vacuum and refilled with nitrogen by three times, and anisole (2 mL) was added. After the mixture was cooled to 0 °C for 10 min, benzaldehyde (26 μL, 0.25 mmol), diene **1** (100 μL, 0.375 mmol) was added. The contents were stirred at 0 °C for 48 h, and then TFA (0.1 mL) was added to this solution. After the mixture was stirred for 10 min to afford the final product (monitored by TLC), saturated $NaHCO_3$ (10 mL) was added, and then the solution was stirred for 5 min. After diluted with 10 mL Et_2O, the mixture was filtered through a plug of Celite. The layers were separated. The acquired aqueous layer was extracted with Et_2O (3 × 10 mL), and then the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$ and concentrated. The crude oil was purified by flash chromatography (petroleum : Et_2O = 10 : 1) to afford the products of both isomers respectively. *cis* Isomer (2*S*,3*S*), a colourless viscous liquid (petroleum : Et_2O = 3 : 1, R_f 0.5, 48.5 mg, 96% isolated yield, 98% ee). $[\alpha]^{23}_{D}$ = -6.6 (c = 0.36, 99% ee, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45-7.39 (m, 5H), 7.34 (s, 1H), 5.47 (d, *J* = 3.2 Hz, 1H), 2.59 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.74 (s, 3H), 0.89 (d, *J* = 7.4 Hz, 3H) ppm. The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (minor) = 7.22 min, t_r (major) = 7.77 min. *trans* Isomer, a colourless solid (petroleum : Et_2O = 3 : 1, R_f 0.58, 1.5 mg, 3% isolated yield, 81% ee) The ee was determined by HPLC analysis using a chiralcel OD-H column,

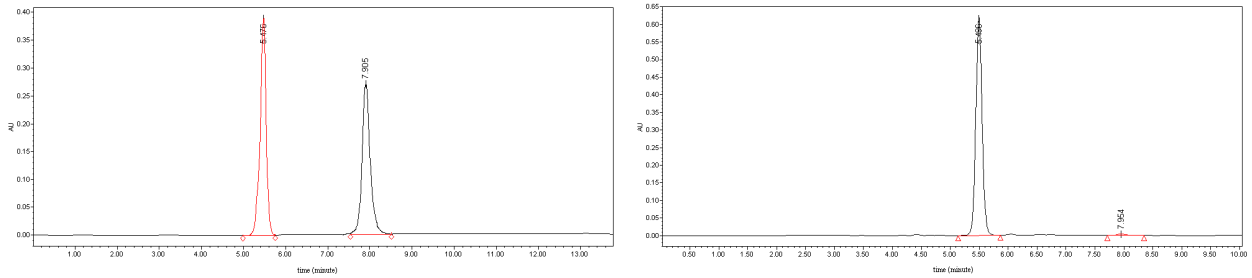
hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 7.50 min, t_r (minor) = 8.23 min.

HPLC of *cis*-**3a**



2-(*p*-chlorophenyl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3b**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless viscous liquid (53.0 mg, 89% isolated yield, 98% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (minor) = 7.9 min, t_r (major) = 5.4 min). $[\alpha]^{25}_D$ = -17.9 (c = 0.630, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 5H), 5.42 (d, *J* = 2.6 Hz, 1H), 2.55 (dq, *J* = 7.3, 3.2 Hz, 1H), 1.72 (s, 3H), 0.87 (d, *J* = 7.4 Hz, 3H) ppm. *trans* Isomer, a colourless solid (2.3 mg, 4% isolated yield, 89% ee) The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 6.2 min, t_r (minor) = 6.5 min.

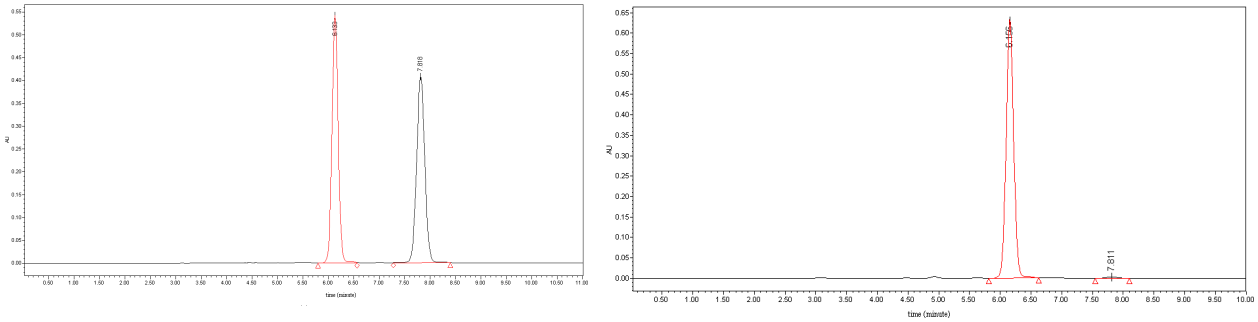
HPLC of *cis*-**3b**



2-(*m*-chlorophenyl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3c**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless viscous liquid (58.2 mg, 98% isolated yield, 99% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 7.8 min, t_r (major) = 6.2min). $[\alpha]^{25}_D$ = -12.5 (c = 0.480, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 5H), 5.42 (d, *J* = 2.6 Hz, 1H), 2.55 (dq, *J* = 7.3, 3.2 Hz, 1H), 1.72 (s, 3H), 0.87 (d, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75

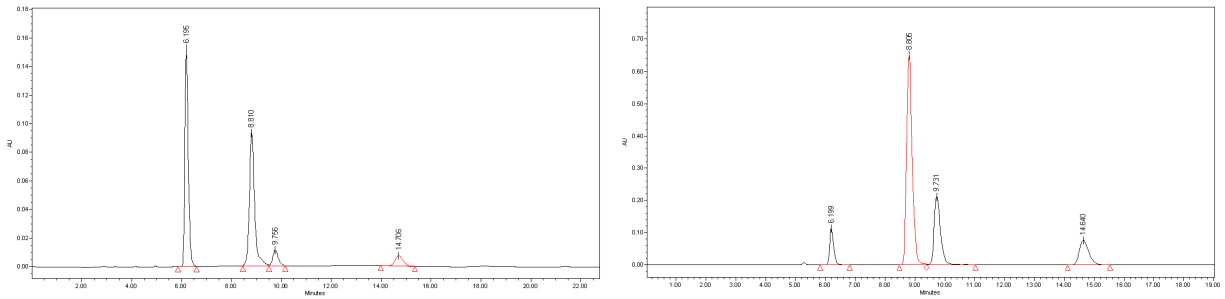
MHz, $CDCl_3$): δ = 9.89, 10.57, 45.44, 82.02, 112.69, 123.42, 125.68, 128.09, 129.81, 134.60, 138.85, 158.35, 197.09 ppm. *trans* Isomer, a colourless solid (1.2 mg, 2% isolated yield, 89% ee) The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 6.2 min, t_r (minor) = 6.5 min. HRMS (ESI): calcd for $C_{13}H_{14}ClO_2$ [M+H$^+$] 237.0677, found 237.0681.

HPLC of *cis*-**3c**



2-(*o*-chlorophenyl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3d**) Purified by flash chromatography (petroleum : Et_2O = 10 : 1, R_f 0.3) to afford a colourless liquid, mixed product of both *cis* and *trans* (56.2 mg, >99% yield, 78% ee of *cis*, 31% ee of *trans*). The ee was determined by HPLC analysis using a chiralcel OJ-H column (*cis*: hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 6.2 min, t_r (major) = 8.8 min, *trans*: t_r (major) = 9.7 min, t_r (minor) = 14.6 min). *cis*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.29 (m, 5H), 5.78 (d, *J* = 2.8 Hz, 1H), 5.85 (dq, *J* = 7.2, 2.8 Hz, 1H), 1.75 (s, 3H), 0.89 (d, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.46, 158.76, 134.28, 130.87, 129.63, 129.23, 128.20, 126.74, 112.71, 80.53, 42.40, 10.68, 10.35 ppm. HRMS (ESI): calcd for $C_{13}H_{14}ClO_2$ [M+H$^+$] 237.0677, found 237.0680.

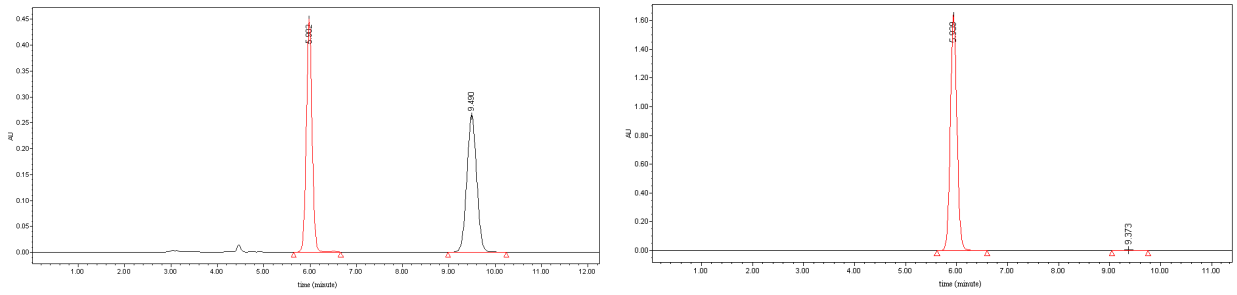
HPLC of *cis*-**3d**



2-(3,4-dichlorophenyl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3e**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 8 : 1, R_f 0.3) to afford a colourless liquid (62.7 mg, 93%

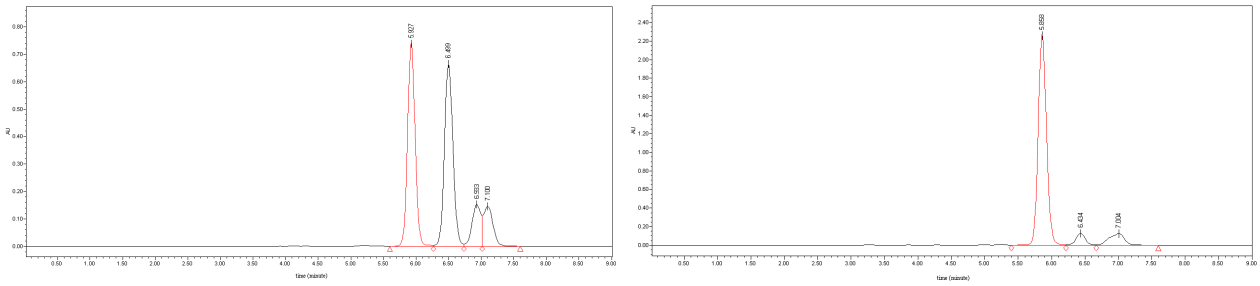
isolated yield, 99% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 9.4 min, t_r (major) = 5.9 min). $[\alpha]^{25}_D$ = -8.09 (c = 0.408, in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.14 (m, 4H), 5.41 (d, *J* = 2.0 Hz, 1H), 2.58 (dq, *J* = 7.2, 2.8 Hz, 1H), 1.74 (s, 3H), 0.89 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.90, 10.61, 81.48, 112.87, 124.65, 127.67, 130.58, 132.02, 132.92, 137.04, 158.20, 196.87 ppm. *trans* Isomer, a colourless solid (3.8 mg, 5.6% isolated yield, 91% ee). The ee was determined by HPLC analysis using a chiral OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 6.66 min, t_r (minor) = 7.34 min. HRMS (ESI): calcd for $C_{13}H_{12}Cl_2NaO_2$ $[M+Na^+]$ 293.0107, found 293.0106.

HPLC of *cis*-**3e**



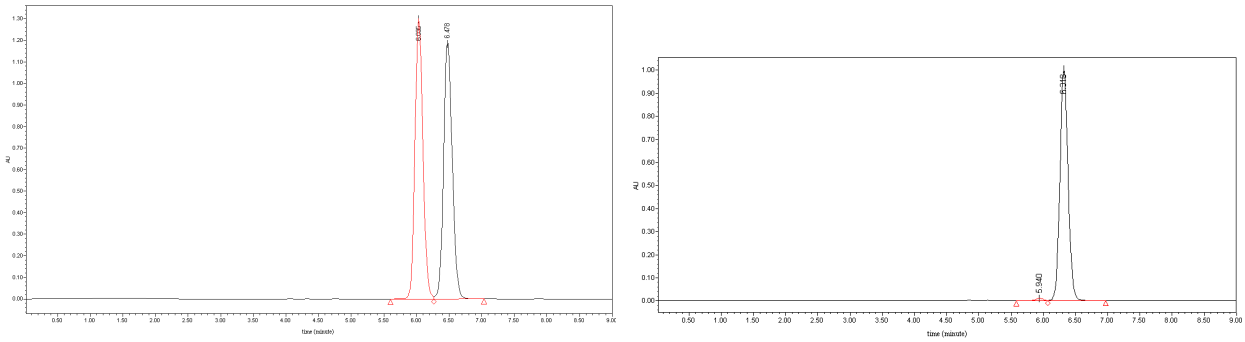
2-(2,4-dichlorophenyl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3f**) Purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless liquid, mixed product of both *cis* and *trans* (60.8 mg, 90% yield, 90% ee of *cis*, <60% ee of *trans*). The ee was determined by HPLC analysis using a chiralcel OD-H column (*cis*: hexane/2-propanol 98:2, 1.0 mL/min, t_r (minor) = 6.4 min, t_r (major) = 5.1 min, *trans*: t_r (major) = 7.1 min, t_r (minor) = 6.9 min). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.27 (m, 4H), 5.71 (d, *J* = 2.4 Hz, 1H), 2.82 (dq, *J* = 4.8, 4.0 Hz, 1H), 1.75 (s, 3H), 0.89 (d, *J* = 2.8 Hz, 3H) ppm. HRMS (ESI): calcd for $C_{13}H_{13}O_2$ $[M+H^+]$ 271.0287, found 271.0290.

HPLC of*cis*-**3f**



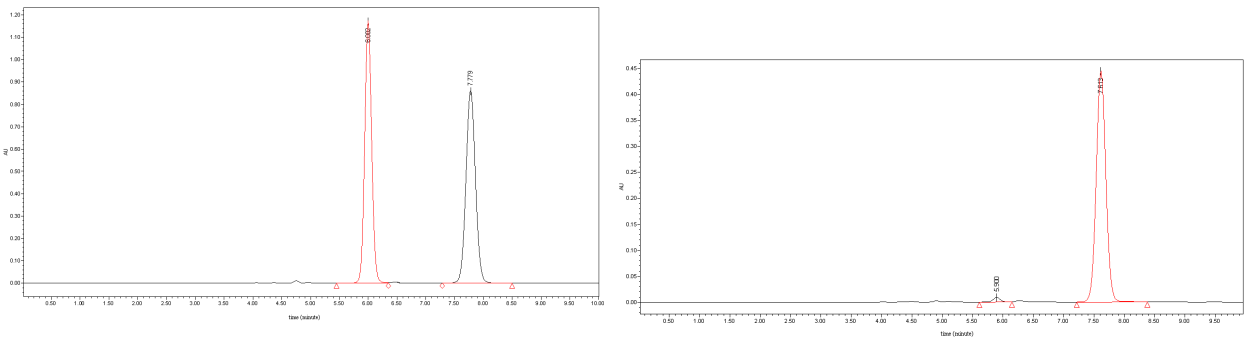
3,5-dimethyl-2-(*p*-tolyl)-2,3-dihydro-4*H*-pyran-4-one (**3g**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 4 : 1, R_f 0.4) to afford a colourless liquid (51.8 mg, 96% isolated yield, 98% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 5.9 min, t_r (major) = 6.3 min). $[\alpha]^{25}_D$ = -13.6 (c = 0.302, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.18 (m, 5H), 5.43 (d, *J* = 7.4 Hz 3.3 Hz, 1H), 2.56 (dq, *J* = 7.4, 3.2 Hz, 1H), 2.36 (s, 3H), 1.73 (d, *J* = 1.2Hz, 3H), 0.90 (d, 3H, *J* = 7.4 Hz) ppm. *trans* Isomer, a colourless liquid (1.7 mg, 3.2% isolated yield, 79% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 6.1 min, t_r (minor) = 5.7 min.

HPLC of *cis*-**3g**



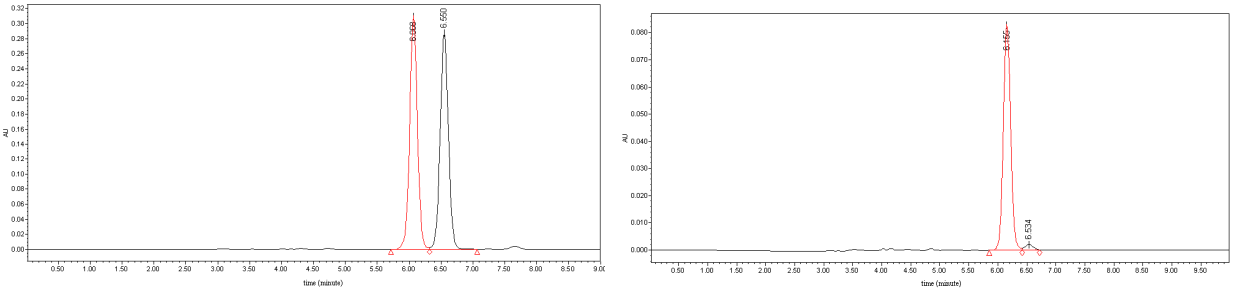
3,5-dimethyl-2-(*m*-tolyl)-2,3-dihydro-4*H*-pyran-4-one (**3h**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 4 : 1, R_f 0.4) to afford a colourless liquid (52.5 mg, 97% isolated yield, 97% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 5.9 min, t_r (major) = 7.6 min). $[\alpha]^{25}_D$ = -25.09 (c = 0.273, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3-7.11 (m, 5H), 5.42 (d, *J* = 3.2 Hz, 1H), 3.83 (s, 3H), 2.59 (dq, *J* = 7.4, 3.2 Hz, 1H), 2.37 (s, 3H), 1.73 (d, *J* = 1.1Hz, 3H), 0.90 (d, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.90, 158.88, 138.15, 136.68, 128.63, 128.34, 126.04, 122.47, 112.38, 82.95, 45.62, 21.45, 10.60, 9.94 ppm. *trans* Isomer, a colourless liquid (1.7 mg, 3.2% isolated yield, 81% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 98:2, flow rate = 1.0 mL/min, t_r (major) = 9.2 min, t_r (minor) = 10.6 min. HRMS (ESI): calcd for $C_{14}H_{17}O_2$ [M+H$^+$] 217.1223, found 217.1226.

HPLC of *cis*-**3h**



3,5-dimethyl-2-(*o*-tolyl)-2,3-dihydro-4*H*-pyran-4-one (**3i**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 10 : 1, R_f 0.4) to afford a colourless viscous liquid (18.0 mg, 33% isolated yield, 93% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 6.5 min, t_r (major) = 6.2 min); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.17 (m, 5H), 5.63 (d, *J* = 7.6, 3.2 Hz, 1H), 2.55 (dq, *J* = 4.4 Hz, 1H), 2.27 (s, 3H), 1.75 (s, 3H), 0.93 (d, *J* = 7.2 Hz, 3H) ppm. *trans* Isomer, almost undetectable. HRMS (ESI): calcd for $C_{14}H_{17}O_2$ [M+H$^+$] 217.1223, found 217.1219.

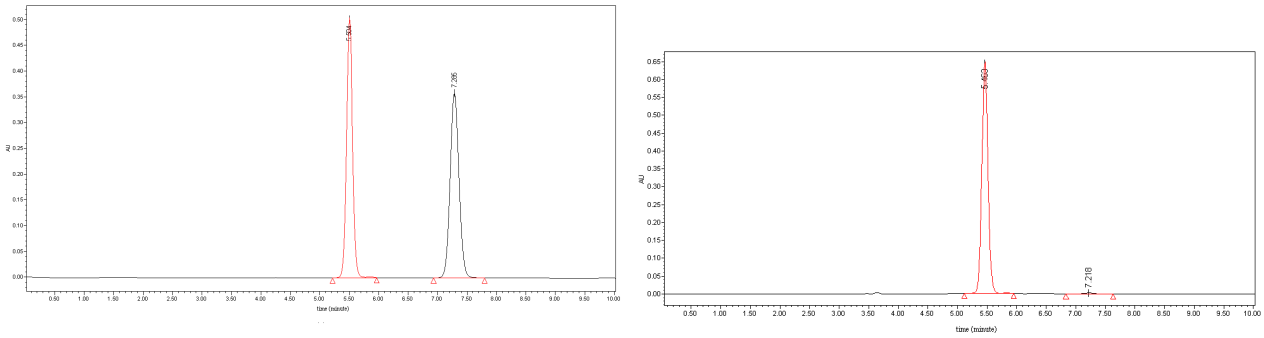
HPLC of *cis*-**3i**



3,5-dimethyl-2-(*p*-fluorophenyl)-2,3-dihydro-4*H*-pyran-4-one (**3j**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless liquid (53.1 mg, 96% isolated yield, 99% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 7.2 min, t_r (major) = 5.5 min). $[\alpha]^{25}_D$ = -20.3 (c = 0.236, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.07 (m, 5H), 5.45 (s, 1H), 2.56 (dq, *J* = 7.2, 3.2 Hz, 1H), 1.74 (s, 3H), 0.89 (d, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 158.64, 127.21, 127.13, 115.57, 115.35, 112.6, 82.33, 45.65, 10.64, 9.86 ppm. *trans* Isomer, a colourless liquid (1.8 mg, 3.2% isolated yield, 88% ee) The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 8.2

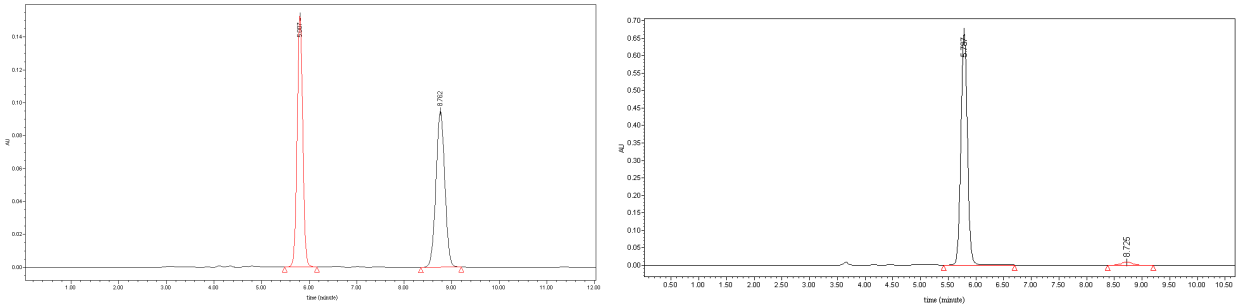
min, t_r (minor) = 8.7 min. HRMS (ESI): calcd for $C_{13}H_{14}FO_2$ [M+H$^+$] 221.0972, found 221.0972.

HPLC of *cis*-**3j**



2-(*p*-bromophenyl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3k**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless liquid (62.9 mg, 90% isolated yield, 96% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 8.7 min, t_r (major) = 5.8 min). $[\alpha]^{25}_D$ = +4.59 (c = 0.676, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53-7.19 (m, 5H), 5.40 (d, *J* = 3.1 Hz, 1H), 2.56 (dq, *J* =7.4, 3.2 Hz, 1H), 1.72 (d, *J* = 0.96 Hz, 3H), 0.88 (d, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.23, 158.47, 135.81, 131.65, 127.12, 112.65, 82.24, 45.43, 10.59, 9.83 ppm. *trans* Isomer, a colourless liquid (3.8 mg, 5.4% isolated yield, 80% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 98:2, flow rate = 1.0 mL/min, t_r (major) = 9.5 min, t_r (minor) = 10.2 min. HRMS (ESI): calcd for $C_{13}H_{14}BrO_2$ [M+H$^+$] 281.0172, found 281.0174.

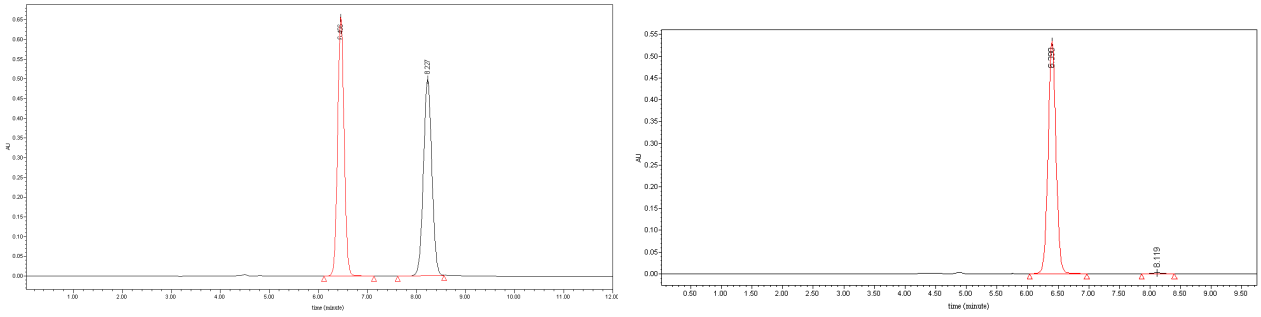
HPLC of *cis*-**3k**



2-(*m*-bromophenyl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3l**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless liquid (67.2 mg, 96%

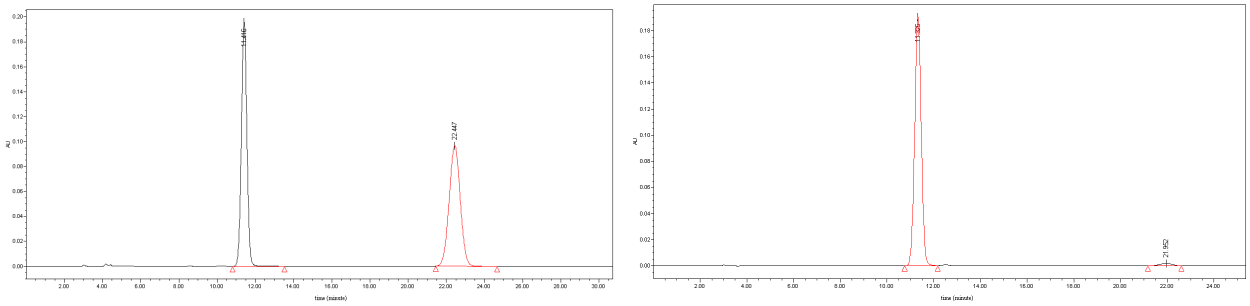
isolated yield, 97% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 8.1 min, t_r (major) = 6.4 min). $[\alpha]^{25}_D$ = -10.2 (c = 0.830, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.18 (m, 5H), 5.40 (d, *J* = 3.1 Hz, 1H), 2.57 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.72 (d, *J* = 0.90 Hz, 3H), 0.87 (d, 3H, *J* = 7.4 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.08, 158.34, 139.06, 131.02, 130.07, 128.56, 123.88, 122.72, 112.68, 81.92, 45.42, 10.57, 9.89 ppm. *trans* Isomer, a colourless liquid (2.5 mg, 3.6% isolated yield, 74% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 6.4 min, t_r (minor) = 8.2 min. HRMS (ESI): calcd for $C_{13}H_{14}BrO_2$ [M+H$^+$] 281.0172, found 281.0179.

HPLC of *cis*-**3l**



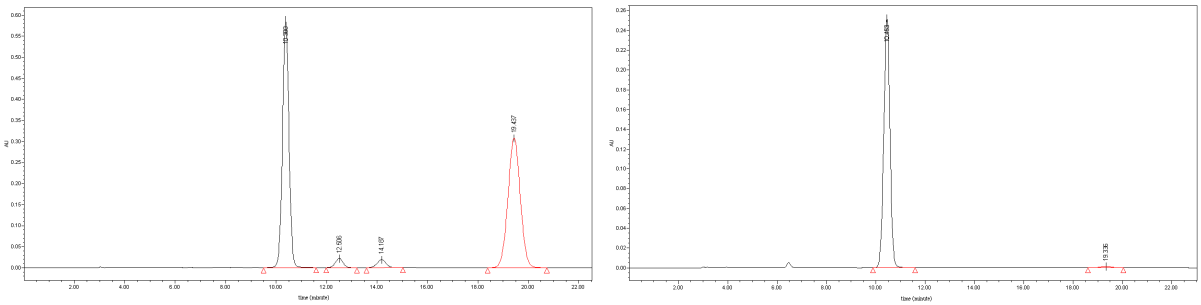
3,5-dimethyl-2-(*p*-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (**3m**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 4 : 1, R_f 0.2) to afford a colourless solid (51.3 mg, 83% isolated yield, 95% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 21.9 min, t_r (major) = 11.3 min). $[\alpha]^{25}_D$ = -26.5 (c = 0.232, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28-7.38 (m, 5H), 5.54 (d, *J* = 3.1 Hz, 1H), 2.63 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.73 (s, 3H), 0.85 (d, *J* = 7.1 Hz, 3H) ppm. *trans* Isomer, a colourless solid (4.8 mg, 7.0% isolated yield, 80% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 13.2 min, t_r (minor) = 15.2 min.

HPLC of *cis*-**3m**



3,5-dimethyl-2-(*m*-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (**3n**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 4 : 1, R_f 0.2) to afford a colourless solid (55.7 mg, 90% isolated yield, 97% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 19.3 min, t_r (major) = 10.5 min). $[\alpha]^{25}_D$ = -26.5 (c = 0.170, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26-7.39 (m, 5H), 5.54 (d, *J* = 3.2 Hz, 1H), 2.64 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.73 (s, 3H), 0.86 (d, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.49, 158.05, 148.41, 131.24, 129.63, 122.94, 120.61, 112.99, 81.50, 45.19, 10.53, 9.82 ppm. *trans* Isomer, a colourless solid (2.8 mg, 4.5% isolated yield, 84% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 12.8 min, t_r (minor) = 14.6 min. HRMS (ESI): calcd for $C_{13}H_{14}NO_4$ $[M+H^+]$ 248.0917, found 248.0920.

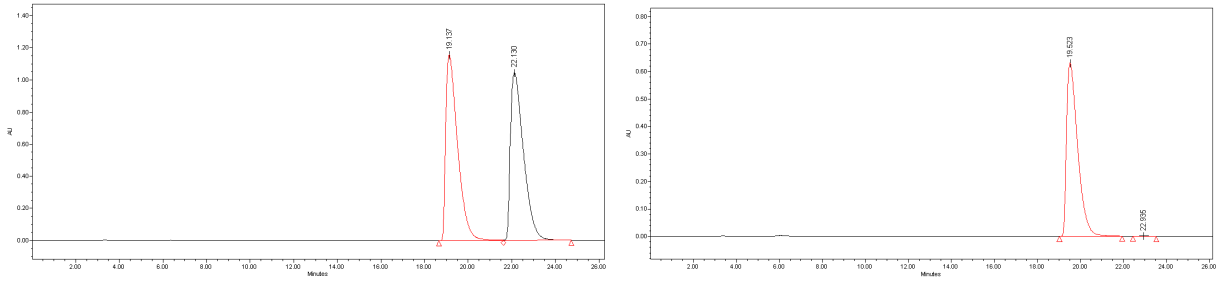
HPLC of *cis*-**3n**



2-(benzo[*d*][1,3]dioxol-5-yl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3o**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 5 : 1, R_f 0.2) to afford a colourless solid (51.0 mg, 83% isolated yield, 98% ee). The ee was determined by HPLC analysis using a chiralcel OJ-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 22.9 min, t_r (major) = 19.5 min). $[\alpha]^{25}_D$ = +6.7 (c = 0.344, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77-7.36 (m, 4H), 5.99 (s, 2H),

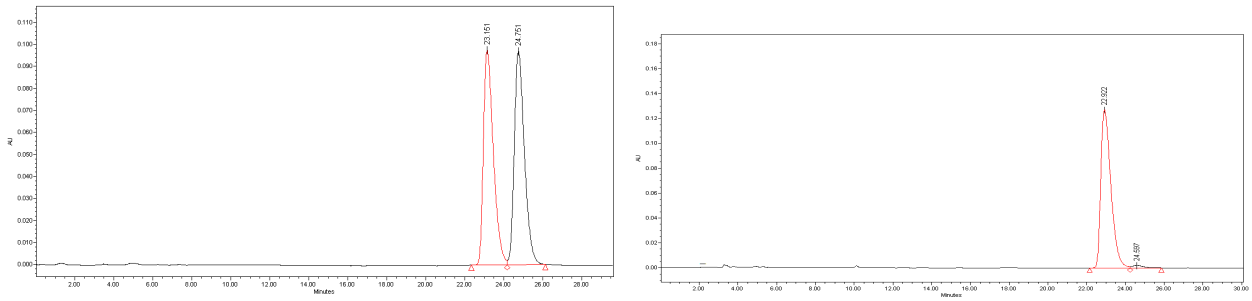
5.37 (d, J = 2.8 Hz, 1H), 2.53 (dq, J = 7.2, 2.8 Hz, 1H), 1.73 (s, 3H), 0.92 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.76, 158.75, 147.80, 147.17, 130.61, 118.84, 112.44, 108.27, 106.27, 101.17, 82.74, 45.87, 10.64, 9.97 ppm. *trans* Isomer, a colourless liquid (2.8 mg, 4.5% isolated yield, 88% ee). The ee was determined by HPLC analysis using a chiralcel OJ-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 31.2 min, t_r (minor) = 32.9 min. HRMS (ESI): calcd for $C_{14}H_{15}O_4$ [M+H$^+$] 247.0965, found 247.0969.

HPLC of *cis*-**3o**



3,5-dimethyl-2-(*p*-methoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (**3p**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 5 : 1, R_f 0.2) to afford a colourless solid (38.1 mg, 66% isolated yield, 92% ee). The ee was determined by HPLC analysis using a chiralcel OJ-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 22.9 min, t_r (major) = 19.5 min). $[\alpha]^{25}_D$ = +21.6 (c = 0.296, in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-6.90 (m, 5H), 5.42 (d, J = 3.2 Hz, 1H), 3.82 (s, 3H), 2.55 (dq, J = 7.4, 3.2 Hz, 1H), 1.73 (s, 3H), 0.92 (d, J = 7.4 Hz, 3H) ppm. HRMS (ESI): calcd for $C_{14}H_{17}O_3$ [M+H$^+$] 233.1172, found 233.1175.

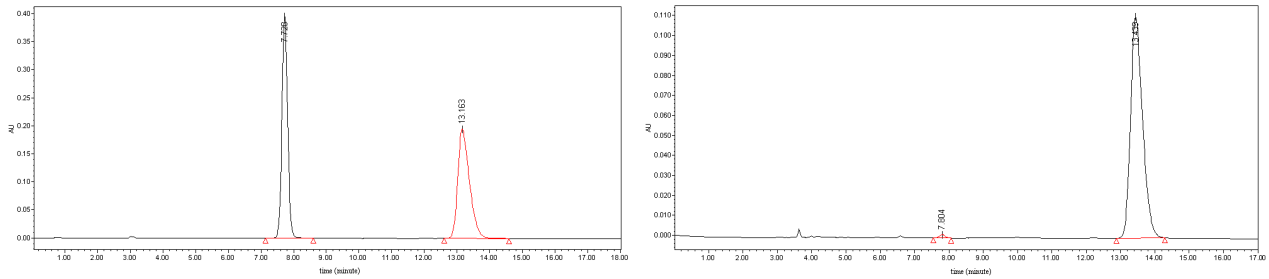
HPLC of *cis*-**3p**



3,5-dimethyl-2-(1-naphthalenyl)-2,3-dihydro-4*H*-pyran-4-one (**3q**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless liquid (50.2 mg, 80%

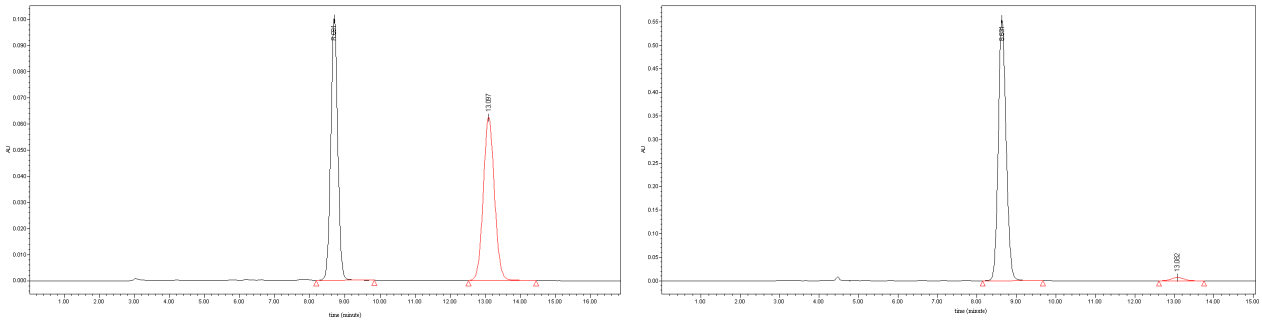
isolated yield, 98% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 7.8 min, t_r (major) = 13.4 min). $[\alpha]^{25}_D$ = -296.6 (c = 0.626, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.49 (m, 8H), 6.2 (d, *J* = 3.2 Hz, 1H), 2.85 (dq, *J* = 7.6, 3.2 Hz, 1H), 1.80 (s, 3H), 0.88 (d, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.86, 159.22, 133.55, 131.88, 129.11, 129.02, 128.56, 126.55, 125.81, 125.13, 124.14, 122.00, 112.57, 80.64, 44.42, 10.76, 10.54 ppm. HRMS (ESI): calcd for $C_{17}H_{17}O_2$ $[M+H^+]$ 253.1223, found 253.1218.

HPLC of *cis*-**3q**



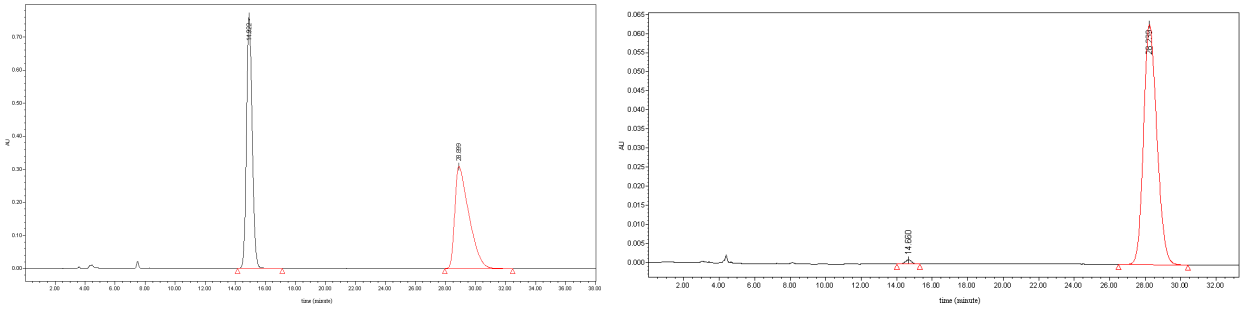
3,5-dimethyl-2-(2-naphthalenyl)-2,3-dihydro-4H-pyran-4-one (**3r**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless solid (57.6 mg, 91% isolated yield, 96% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 13.1 min, t_r (major) = 8.5 min). $[\alpha]^{25}_D$ = -13.5 (c = 0.244, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.36 (m, 8H), 5.63 (d, *J* = 2.8 Hz, 1H), 2.71 (dq, *J* = 7.2, 2.8 Hz, 1H), 1.77 (s, 3H), 0.92 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.75, 158.79, 134.18, 133.06, 132.88, 128.32, 128.00, 127.71, 126.43, 126.22, 124.54, 123.05, 112.54, 82.94, 45.61, 10.69, 10.05 ppm. *trans* Isomer, a colourless liquid(2.4 mg, 3.8% isolated yield, 80% ee). The ee was determined by HPLC analysis using a chiralcel OJ-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 23.9 min, t_r (minor) = 25.7 min. HRMS (ESI): calcd for $C_{17}H_{16}NaO_2$ $[M+Na^+]$ 275.1043, found 275.1047.

HPLC of *cis*-**3r**



3,5-dimethyl-2-(*m*-phenoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (**3s**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless solid (70.1 mg, 95% isolated yield, 98% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 15.3 min, t_r (major) = 29.7 min). $[\alpha]^{25}_D$ = +6.6 (c = 0.152, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-6.95 (m, 10H), 5.43 (d, *J* = 2.8 Hz, 1H), 2.57 (dq, *J* = 7.6, 2.8 Hz, 1H), 1.72 (s, 3H), 0.91 (d, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.53, 158.63, 157.52, 156.82, 138.82, 129.87, 129.80, 123.49, 120.01, 118.92, 118.10, 115.89, 112.50, 82.40, 45.52, 10.61, 9.97 ppm. *trans* Isomer, a colourless liquid (3.0 mg, 4% isolated yield, 83% ee) The ee was determined by HPLC analysis using a chiralcel OJ-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 11.7 min, t_r (minor) = 21.2 min. HRMS (ESI): calcd for $C_{19}H_{18}NaO_3$ [M+Na^+] 317.1148, found 317.1148.

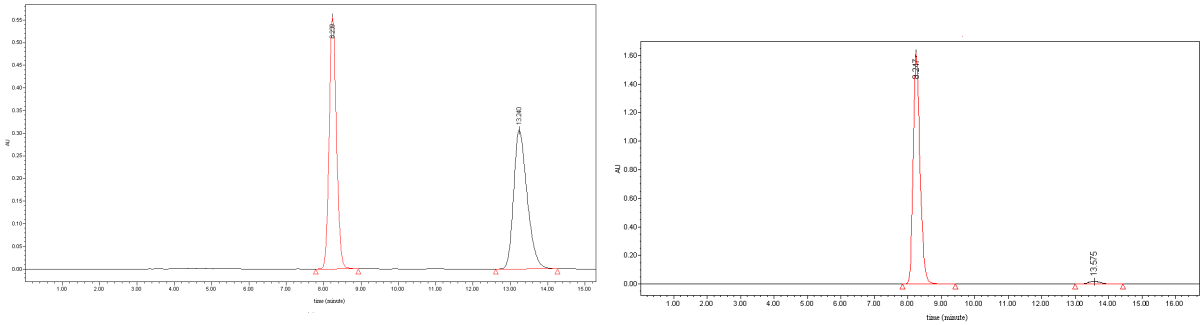
HPLC of *cis*-**3s**



2-(biphenyl-4-yl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3t**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless solid (56.2 mg, 81% isolated yield, 97% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 13.6 min, t_r (major) = 8.2 min). $[\alpha]^{25}_D$ = +15.04 (c = 0.266, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.34 (m, 10H), 5.51 (d, *J* = 2.8 Hz,

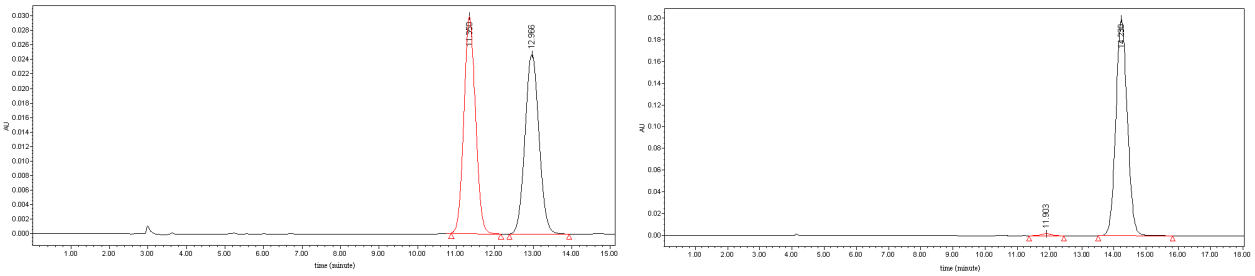
1H), 2.63 (dq, J = 7.6, 3.2 Hz, 1H), 1.76 (s, 3H), 0.95 (d, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.71, 158.80, 140.83, 140.45, 135.73, 128.80, 127.45, 127.17, 127.03, 125.89, 112.48, 82.76, 45.62, 10.67, 10.00 ppm. *trans* Isomer, a colourless solid (3.2 mg, 4.6% isolated yield, 83% ee). The ee was determined by HPLC analysis using a chiralcel OJ-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (major) = 8.0 min, t_r (minor) = 8.6 min. HRMS (ESI): calcd for $C_{19}H_{19}O_2$ [M+H$^+$] 279.1380, found 279.1385.

HPLC of *cis*-**3t**



2-(*p*-benzylphenyl)-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3u**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless solid (40.1 mg, 55% isolated yield, 98% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 11.9 min, t_r (major) = 14.2 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-6.99 (m, 10H), 5.42 (d, J = 2.8 Hz, 1H), 5.09 (s, 2H), 2.56 (dq, J = 7.6, 2.8 Hz, 1H), 1.73 (s, 3H), 0.92 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.92, 158.92, 158.44, 136.76, 129.09, 128.60, 128.03, 127.47, 126.82, 114.77, 112.35, 82.77, 70.03, 45.75, 10.67, 9.95 ppm.

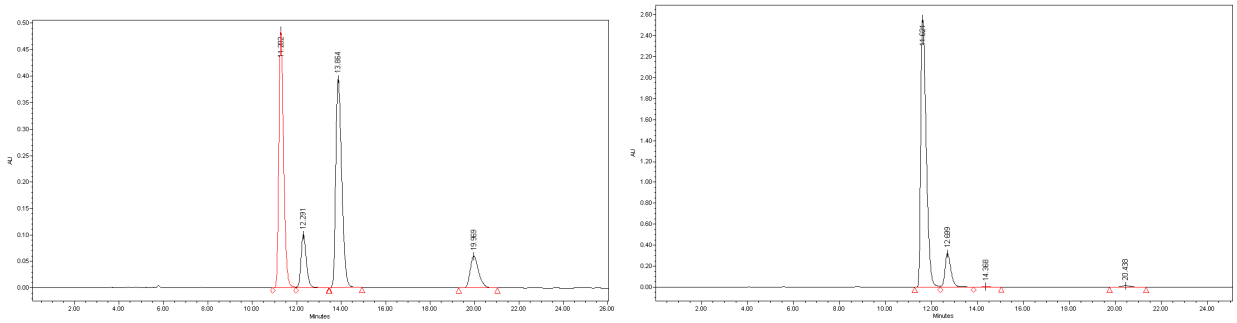
HPLC of *cis*-**3u**



3,5-dimethyl-2-(2-furanyl)-2,3-dihydro-4*H*-pyran-4-one (**3v**) Purified by flash chromatography (petroleum : Et_2O = 7 : 1, R_f 0.2) to afford a colourless liquid, mixed product of both *cis* and *trans*

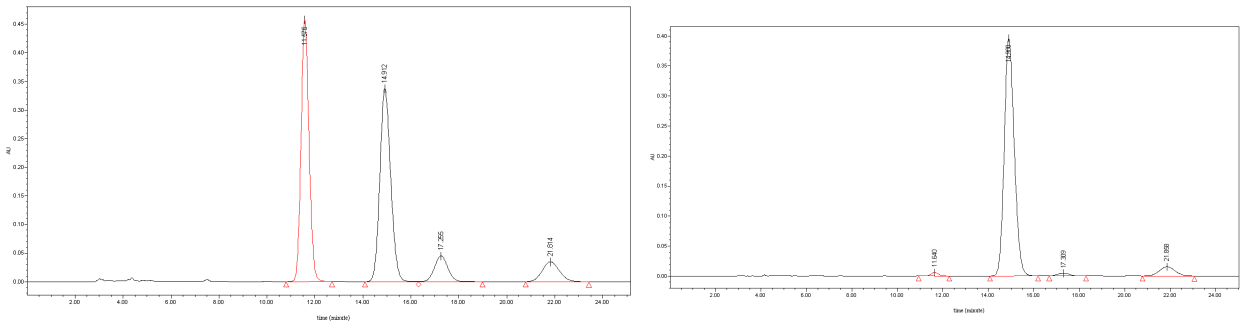
(48 mg, >99% yield, 99% ee of *cis*, 90% ee of *trans*). The ee was determined by HPLC analysis using a chiralcel OJ-H column (*cis*: hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 14.4 min, t_r (major) = 11.6 min, *trans*: t_r (major) = 12.7 min, t_r (minor) = 20.4 min). $[\alpha]^{25}_D$ = +282.35 (c = 0.204, in $CHCl_3$); *cis*: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45-7.39 (m, 1H), 7.18-7.17 (m, 1H), 6.37-6.32 (m, 2H), 5.43 (d, *J* = 4.4 Hz, 1H), 2.87 (dq, *J* = 7.2, 4.4 Hz, 1H), 1.68 (s, 3H), 1.08 (d, *J* = 7.2 Hz, 3H) ppm.

HPLC of *cis*-**3v**



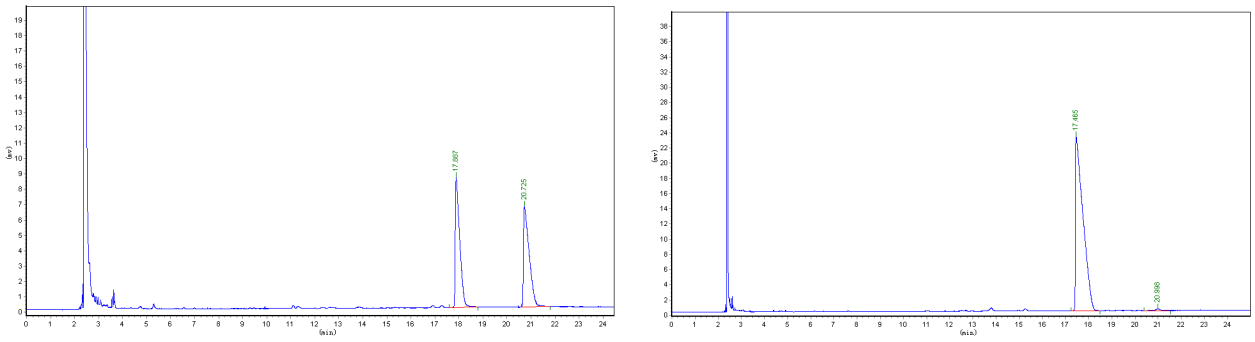
3,5-dimethyl-2-(*m*-hydoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (**3w**) Purified by flash chromatography (petroleum : Et_2O = 4 : 1, R_f 0.2) to afford a colourless solid, mixed product of both *cis* and *trans* (54.4 mg, >99% yield, 96% ee of *cis*, 64% ee of *trans*). The ee was determined by HPLC analysis using a chiralcel OD-H column (*cis*: hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 11.6 min, t_r (major) = 14.9 min, *trans*: t_r (major) = 21.9 min, t_r (minor) = 17.3 min). $[\alpha]^{25}_D$ = +9.2 (c = 0.434, in $CHCl_3$); *cis*: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-6.81 (m, 4H), 6.28 (s, 1H), 5.42 (d, *J* = 3.2 Hz, 1H), 2.59 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.73 (d, *J* = 1.1 Hz, 3H), 0.90 (d, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.59, 159.44, 156.17, 138.33, 129.80, 122.15, 117.40, 115.02, 112.50, 82.62, 45.53, 10.70, 10.05 ppm. HRMS (ESI): calcd for $C_{13}H_{15}O_3$ $[M+H^+]$ 219.1016, found 219.1019.

HPLC of *cis*-**3w**



2-ethyl-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3aa**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless liquid (27.3 mg, 71% isolated yield, 98% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 115 °C; detection temp. = 250 °C; t_r (major) = 17.5 min, t_r (minor) = 20.9 min). $[\alpha]^{25}_D$ = +156.3 (c = 0.490, in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (s, 1H), 4.19 (m, 1H), 2.36 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.80 (m, 1H), 1.65 (d, *J* = 1.1 Hz, 3H), 1.57 (m, 1H), 1.04 (d, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.90, 159.03, 111.99, 83.29, 42.98, 23.41, 10.52, 9.63, 9.42 ppm. *trans* Isomer, a colourless liquid (3.0 mg, 7.8% isolated yield, 60% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 115 °C; detection temp. = 250 °C; t_r (minor) = 16.6 min, t_r (major) =17.0 min). HRMS (ESI): calcd for $C_9H_{15}O_2$ [M+H$^+$] 155.1067, found 155.1069.

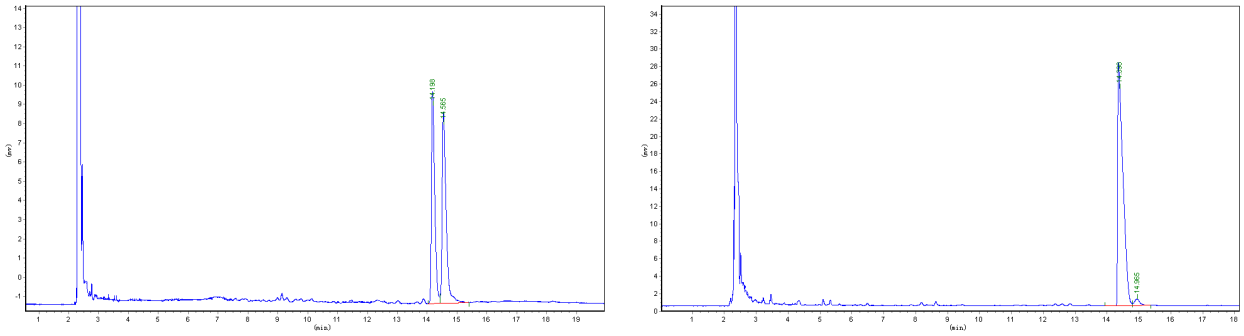
GC of *cis*-**3aa**



3,5-dimethyl-2-isopropyl-2,3-dihydro-4*H*-pyran-4-one (**3ab**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 11 : 1, R_f 0.3) to afford a colourless liquid (8.2 mg, 20% isolated yield, 96% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 115 °C; detection temp. = 250 °C; t_r (major) = 14.5 min, t_r (minor) = 14.9 min). $[\alpha]^{25}_D$ = +30.4 (c = 0.204, in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (t, 1H), 3.76 (dd, *J* = 10.1, 2.7 Hz, 1H), 2.43 (dq, *J* = 7.4, 2.8 Hz, 1H), 1.99 (m, 1H), 1.64 (d, *J* = 1.1 Hz, 3H), 1.03 (dd, *J* = 9.6, 6.5 Hz, 6H), 0.85 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.29, 159.48, 111.79, 87.20, 41.59, 28.42, 19.30, 17.66, 10.46, 9.42 ppm. *trans* Isomer, almost undetectable. HRMS (ESI): calcd for $C_{10}H_{17}O_2$ [M+H$^+$] 169.1223,

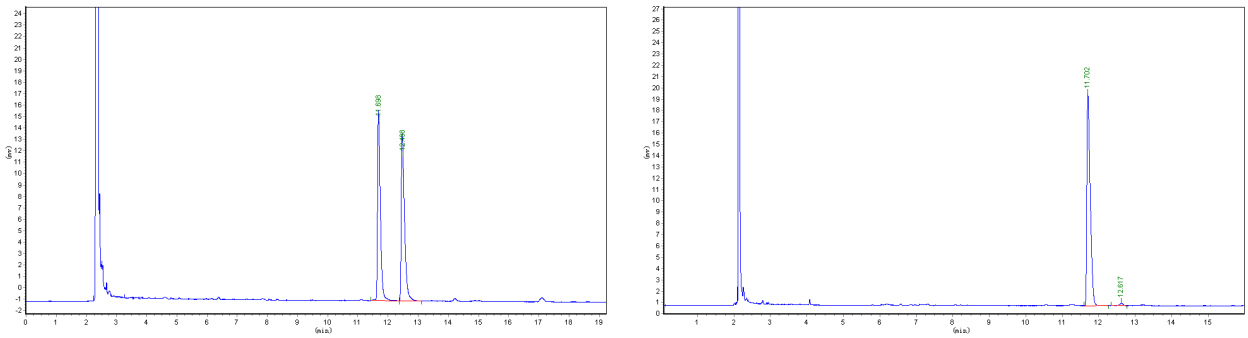
found 169.1226.

GC of *cis*-**3ab**



3,5-dimethyl-2-propyl-2,3-dihydro-4*H*-pyran-4-one (**3ac**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 11 : 1, R_f 0.3) to afford a colourless liquid (21.7 mg, 52% isolated yield, 98% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 125 °C; detection temp. = 250 °C; t_r (major) = 11.7 min, t_r (minor) = 12.6 min). $[\alpha]^{25}_D$ = +122.7 (c = 0.154, in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.20 (s, 1H), 4.29 (m, 1H), 2.34 (m, 1H), 1.65 (d, *J* = 1.05 Hz, 3H), 1.85-1.36 (m, 4H), 1.04 (d, *J* = 7.3 Hz, 3H), 0.93 (m, 3H) ppm. *trans* Isomer, a colourless liquid (2.1 mg, 4.9% isolated yield, 54% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 125 °C; detection temp. = 250 °C; t_r (minor) = 10.7min, t_r (major) = 10.8 min). HRMS (ESI): calcd for $C_{10}H_{17}O_2$ $[M+H^+]$ 169.1223, found 169.1224

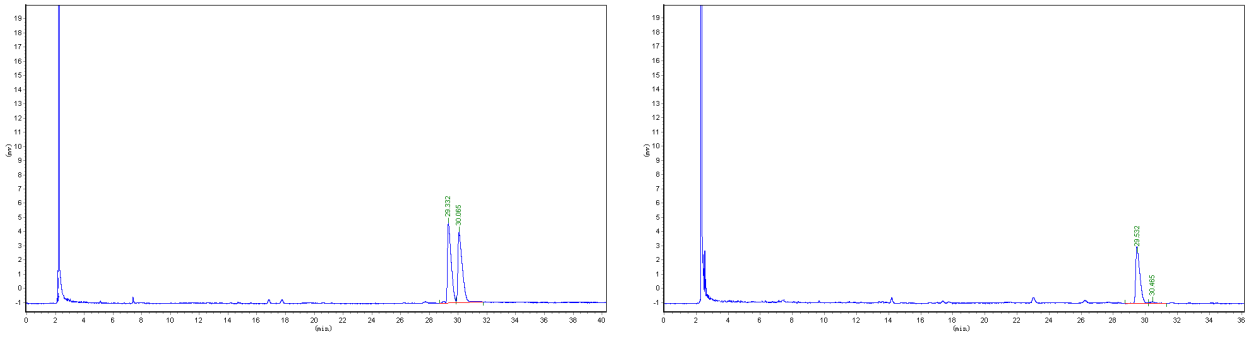
GC of *cis*-**3ac**



(*E*)-3,5-dimethyl-2-(prop-1-enyl)-2,3-dihydro-4*H*-pyran-4-one (**3ad**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.4) to afford a colourless liquid (24.2 mg, 58%

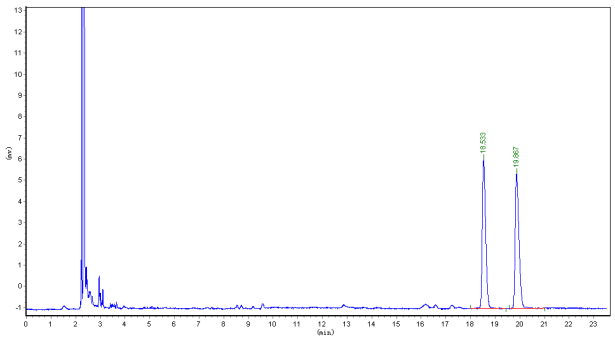
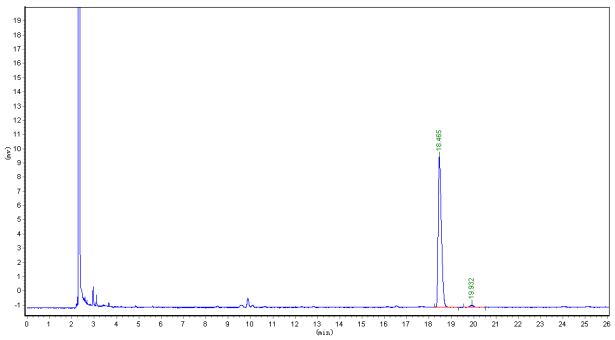
isolated yield, 98% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 105 °C; detection temp. = 250 °C; t_r (major) = 29.5 min, t_r (minor) = 30.4 min). $[\alpha]^{25}_D$ = +147.8 (c = 0.586, in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.19 (s, 1H), 5.83 (m, 1H), 5.59 (m, 1H), 4.75 (dd, *J* = 7.0, 3.6 Hz, 1H), 2.45 (dq, *J* = 7.3, 3.7 Hz, 1H), 1.75 (dd, *J* = 6.5, 0.6 Hz, 3H), 1.65 (d, *J* = 0.8 Hz, 3H), 1.05 (d, *J* = 7.3 Hz, 3H) ppm. *trans* Isomer, a colourless liquid (2.4 mg, 6.0% isolated yield, 62% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 105 °C; detection temp. = 250 °C; t_r (minor) = 32.2min, t_r (major) =34.5 min). HRMS (ESI): calcd for $C_{10}H_{15}O_2$ $[M+H^+]$ 167.1067, found 167.1071.

GC of *cis*-**3ad**



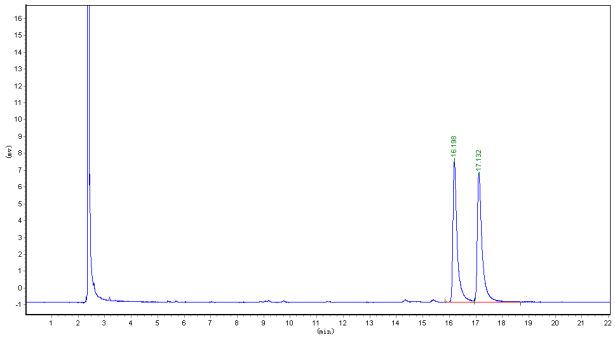
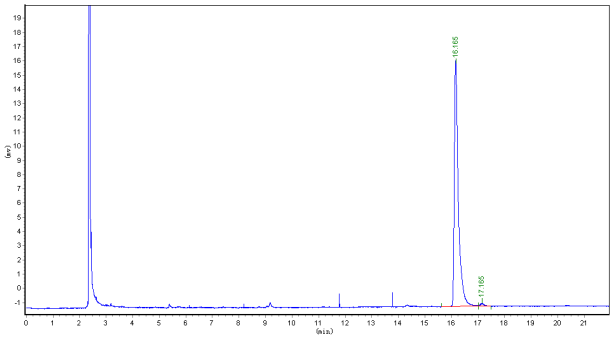
2-butyl-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3ae**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 12 : 1, R_f 0.3) to afford a colourless liquid (23.7 mg, 52% isolated yield, 97% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 125 °C; detection temp. = 250 °C; t_r (major) = 18.5 min, t_r (minor) =19.9 min). $[\alpha]^{25}_D$ = +143.0 (c = 0.140, in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.18 (s, 1H), 4.25 (m, 1H), 2.32 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.80-1.22 (m, 6H), 1.63 (d, *J* = 1.1 Hz, 3H), 1.02 (d, *J* = 7.4 Hz, 3H), 0.90 (m, 3H) ppm. *trans* Isomer, a colourless liquid (2.1 mg, 4.6% isolated yield, 63% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 115 °C; detection temp. = 250 °C; t_r (minor) = 19.8 min, t_r (major) =20.1 min).

GC of *cis*-**3ae**

3,5-dimethyl-2-pentyl-2,3-dihydro-4*H*-pyran-4-one (**3af**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 12 : 1, R_f 0.3) to afford a colourless liquid (25.5 mg, 52% isolated yield, 98% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 140 °C; detection temp. = 250 °C; t_r (major) = 16.2min, t_r (minor) =17.2 min). $[\alpha]^{25}_D$ = +102.5 (c = 0.289, in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (s, 1H), 4.25 (m, 1H), 2.32 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.80-1.16 (m, 8H), 1.63 (s, 3H), 1.02 (d, *J* = 7.4 Hz, 3H), 0.87 (m, 3H) ppm. *trans* Isomer, a colourless liquid (2.1 mg, 4.3% isolated yield, 71% ee). The ee was determined by GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), (injection temp. = 250 °C; column temp. = 115 °C; detection temp. = 250 °C; t_r (minor) = 17.4 min, t_r (major) =17.7 min).

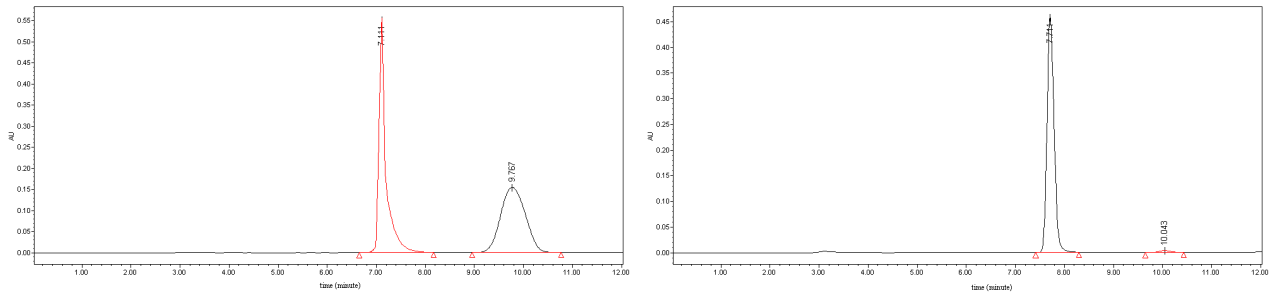
GC of *cis*-**3af**

2-cyclohexyl-3,5-dimethyl-2,3-dihydro-4*H*-pyran-4-one (**3ag**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 12 : 1, R_f 0.4) to afford a colourless solid (17.2 mg, 33% isolated yield, 98% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 99:1, 1.0 mL/min, t_r (minor) = 10.04 min, t_r (major) = 7.11 min). $[\alpha]^{25}_D$ = +3.6 (c = 0.274, in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (s, 1H), 2.88 (dd, *J* = 12.0, 4.0 Hz,

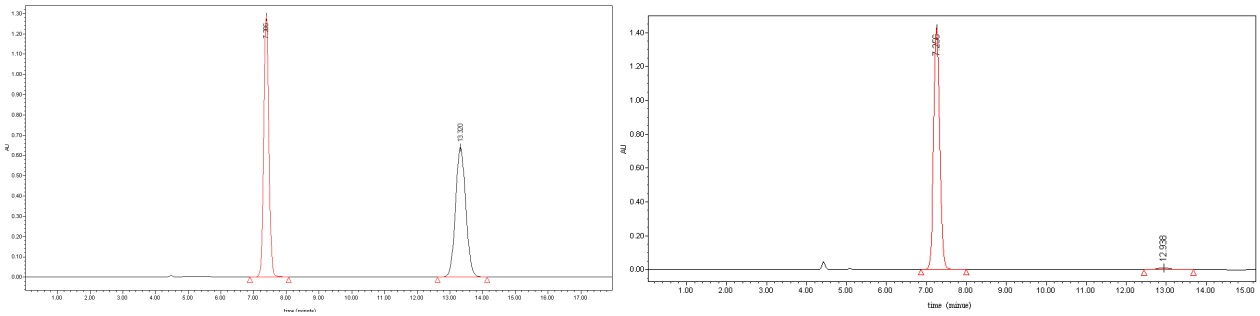
1H), 2.43 (dq, J = 8.0, 4.0 Hz, 1H), 2.13 (d, J = 12.0 Hz, 3H), 1.78-1.58 (m, 11H), 1.03 (d, J = 8.0 Hz, 3H), 1.32-0.84 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 159.6, 111.8, 85.9, 41.1, 37.5, 29.5, 27.5, 26.2, 25.6, 25.4, 10.6, 9.6 ppm. *trans* Isomer, N.D.

HPLC of *cis*-**3ag**



(*E*)-3,5-dimethyl-2-styryl-2,3-dihydro-4*H*-pyran-4-one (**3ah**) *cis* Isomer, purified by flash chromatography (petroleum : Et_2O = 9 : 1, R_f 0.3) to afford a colourless solid (52.3 mg, 92% isolated yield, 98% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 12.9 min, t_r (major) = 7.3 min). $[\alpha]^{25}_D$ = +165 (c = 0.270, in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.27 (m, 6H), 6.76 (d, J = 16 Hz, 1H), 6.25 (dd, J = 16, 6.4 Hz, 1H), 5.01 (m, 1H), 2.58 (dq, J = 7.2, 3.6 Hz, 1H), 1.71 (d, J = 0.8 Hz, 3H), 1.12 (d, J = 7.6 Hz, 3H), 0.87 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 158.43, 133.73, 128.67, 128.29, 126.64, 123.16, 112.43, 82.36, 44.16, 29.68, 10.67, 10.13 ppm. *trans* Isomer, a colourless solid (3.1 mg, 5.4% isolated yield, 86% ee). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, t_r (minor) = 9.9 min, t_r (major) = 11.1 min).

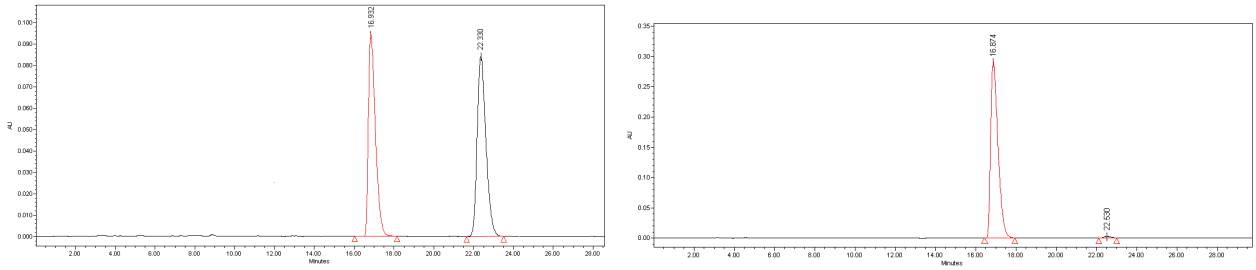
HPLC of *cis*-**3ah**



5-methyl-2-phenyl-2,3-dihydro-4*H*-pyran-4-one (5a). Purified by flash chromatography on silica gel (petroleum : Et_2O = 5:1, R_f 0.2) to afford the title compound as white solid (m.p. = 46-48

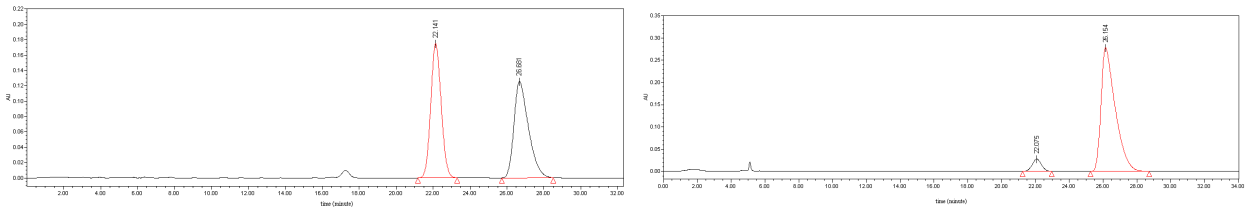
°C) 46.5 mg in 99% yield with 98% ee determined by HPLC analysis using a Chiralcel OJ-H column (hexane/2-propanol 90:10, 1.0 mL/min^{-1}, t_r (major) = 16.87 min, t_r (minor) = 22.53 min). $[\alpha]^{25}_D$ = +92 (c = 0.160, in CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46-7.40 (m, 5H), 7.39 (s, 1H), 5.41 (dd, *J* = 14.6, 3.2 Hz, 1H), 2.94-2.88 (m, 1H), 2.73-2.69 (m, 1H), 1.76 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.59, 159.49, 138.27, 128.80, 128.78, 126.05, 114.14, 80.99, 43.21, 10.51 ppm. HRMS (ESI): calcd for $C_{12}H_{13}O_2$ [M+H$^+$] 189.0910, found 189.0911.

HPLC of **5a**



5-methyl-2-(naphthalen-1-yl)-2,3-dihydro-4*H*-pyran-4-one (5b). Purified by flash chromatography on silica gel (petroleum : Et_2O = 3 : 1, R_f 0.3) to afford the title compound as white solid 55.1 mg (m.p. = 99-100 °C) in 92% yield with 88% ee determined by HPLC analysis using a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min^{-1}, t_r (minor) = 22.08 min, t_r (major) = 26.15 min). $[\alpha]^{25}_D$ = +20.0 (c = 0.350, in CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.00-7.98 (m, 1H), 7.93-7.88 (m, 2H), 7.68-7.66 (m, 1H), 7.58-7.52 (m, 3H), 7.47 (s, 1H), 6.14 (dd, *J* = 14.5, 3.2 Hz, 1H), 3.10-3.04 (m, 1H), 2.92-2.88 (m, 1H), 1.80 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.83, 159.72, 133.84, 133.71, 130.13, 129.40, 129.10, 126.70, 126.58, 126.00, 125.32, 123.80, 122.70, 78.37, 42.58, 10.60 ppm. HRMS (ESI): calcd for $C_{16}H_{15}O_2$ [M+H$^+$] 239.1067, found 239.1066.

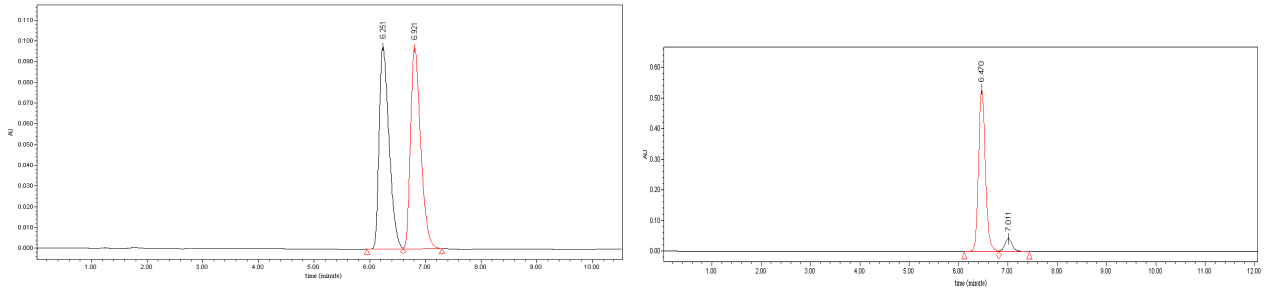
HPLC of **5b**



5-methyl-2-(*o*-chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (5c). Purified by flash

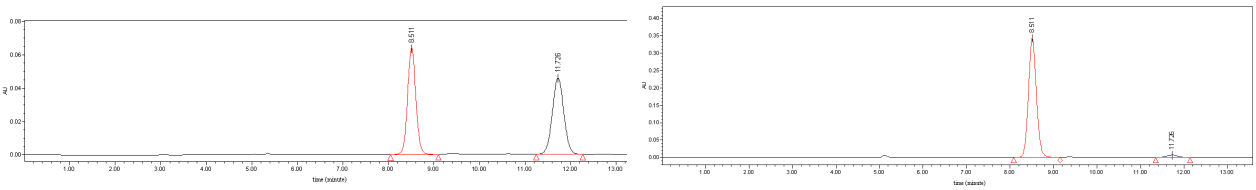
chromatography on silica gel (petroleum : Et_2O = 3:1, R_f 0.3) to afford the product 54.0 mg as light yellow solid (m.p. = 42-44 °C) in 97% yield with 84% ee determined by HPLC analysis using a Chiralcel OJ column (hexane/2-propanol 90:10, 1.0 mL/min^{-1}, t_r (major) = 6.47 min, t_r (minor) = 7.01 min); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.59 (m, 1H), 7.40 (s, 1H), 7.38-7.28 (m, 3H), 5.77 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.85-2.80 (m, 1H) 2.72-2.64 (m, 1H), 1.75 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.18, 159.36, 136.20, 131.58, 129.69, 129.60, 127.34, 127.06, 114.32, 77.92, 41.94, 10.53 ppm. HRMS (ESI): calcd for $C_{12}H_{12}ClO_2$ [M+H$^+$] 223.0520, found 223.0518.

HPLC of **5c**



5-methyl-2-(*m*-chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (5d). Purified by flash chromatography on silica gel (petroleum : Et_2O = 3:1, R_f 0.3) to afford the title compound as oil 55.1 mg in 99% yield with 95% ee determined by HPLC analysis using a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min^{-1}, t_r (major) = 6.51 min, t_r (minor) = 11.73 min). $[\alpha]^{25}_D$ = -20 (c = 0.330, in CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (s, 1H), 7.36-7.26 (m, 4H), 5.36 (dd, *J* = 14.5, 3.3 Hz, 1H), 2.86-2.81 (m, 1H), 2.71-2.68 (m, 1H), 1.74 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.94, 159.11, 140.33, 134.74, 130.10, 128.84, 126.21, 124.04, 114.37, 80.05, 43.14, 10.47 ppm. HRMS (ESI): calcd for $C_{12}H_{12}ClO_2$ [M+H$^+$] 223.0520, found 223.0522.

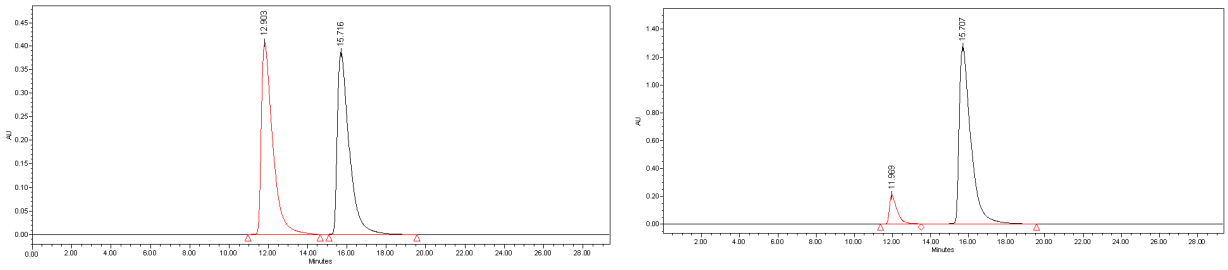
HPLC of **5d**



2-ethyl-5-methyl-2,3-dihydro-4*H*-pyran-4-one (5e). Purified by flash chromatography on silica gel (petroleum : Et_2O = 6:1, R_f 0.3) to afford the title compound as oil 28.7 mg in 82% yield with 80% ee determined by HPLC analysis using a Chiralpak AD-H column (hexane/2-propanol 99:1,

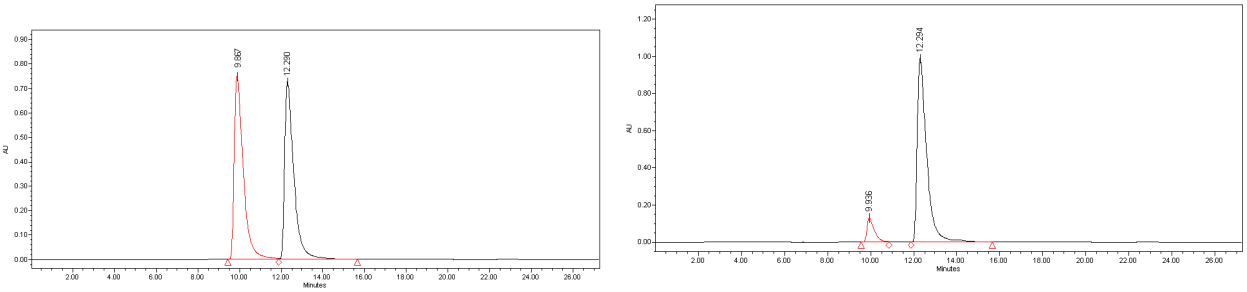
1.0 mL/min^{-1}, t_r (minor) = 11.97 min, t_r (major) = 15.71 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (s, 1H), 4.27 (m, 1H), 5.48 (m, 2H), 1.84-1.75 (m, 1H), 1.75-1.64 (m, 1H), 1.66 (s, 3H), 1.00 (t, *J* = 7.6 Hz, 3H) ppm.

HPLC of **5e**



2-butyl-5-methyl-2,3-dihydro-4*H*-pyran-4-one (5f). Purified by flash chromatography on silica gel (petroleum : Et_2O = 10:1, R_f 0.3) to afford the title compound as as oil 31.9 mg in 76% yield with 81% ee determined by HPLC analysis using a Chiralpak AD-H column (hexane/2-propanol 99:1, 1.0 mL/min^{-1}, t_r (minor) = 9.94 min, t_r (major) = 12.29 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (s, 1H), 4.32 (m, 1H), 2.45 (m, 2H), 1.80-1.75 (m, 1H), 1.65 (s, 3H), 1.65-1.59 (m, 1H), 1.41-1.31 (m , 4H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm.

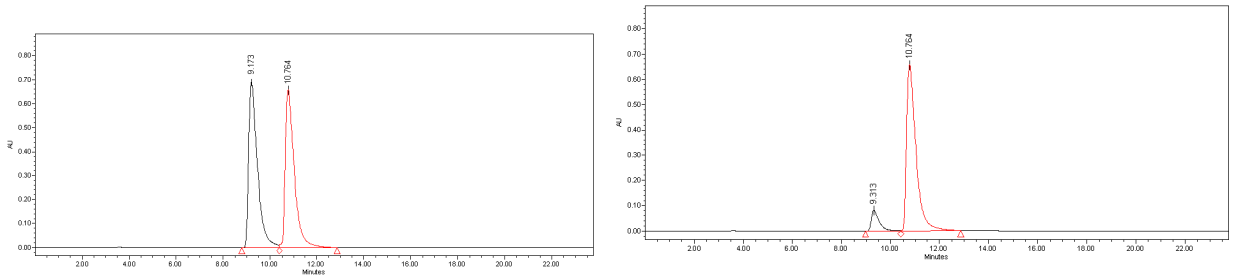
HPLC of **5f**



5-methyl-2-pentyl-2,3-dihydro-4*H*-pyran-4-one (5g). Purified by flash chromatography on silica gel (petroleum : Et_2O = 9:1, R_f 0.3) to afford the title compound as oil 43.3 mg in 95% yield with 81% ee determined by HPLC analysis using a Chiralpak AD-H column (hexane/2-propanol 99:1, 1.0 mL/min^{-1}, t_r (minor) = 14.110 min, t_r (major) = 19.627 min). $[\alpha]^{25}_D$ = +82 (c = 0.400, in CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 (s, 1H), 4.36-4.31 (m, 1H), 2.51-2.47 (m, 1H), 2.45-2.42 (m, 1H), 1.81-1.25 (m, 14H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.29, 159.76, 113.57, 79.46, 41.67, 34.48, 31.50, 24.46, 22.50, 13.96, 10.48 ppm. HRMS (ESI): calcd for

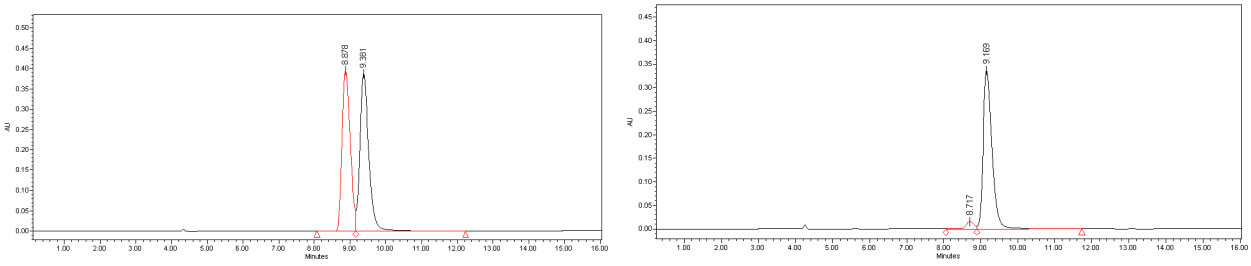
$C_{11}H_{19}O_2$ [M+H$^+$] 183.1380, found 183.1380.

HPLC of **5g**



2-cyclohexyl-5-methyl-2,3-dihydro-4*H*-pyran-4-one (5h). Purified by flash chromatography on silica gel (petroleum : Et_2O = 10:1, R_f 0.4) to afford the title compound as white solid 40.0 mg in 82% yield with 92% ee determined by HPLC analysis using a Chiralpak OB-H column (hexane/2-propanol 99:1, 1.0 mL/min^{-1}, t_r (minor) = 8.72 min, t_r (major) = 9.17 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.256 (s, 1H), 6.70 (d, *J* = 16 Hz, 1H), 4.10 (ddd, *J* = 14.8, 6, 4 Hz, 1H,), 2.56-2.24 (m, 2H), 1.90-1.60 (m, 7H), 1.67 (s, 3H), 1.33-0.99 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.53, 159.88, 113.30, 83.35, 41.34, 38.78, 28.07, 28.00, 26.16, 25.78, 25.72, 10.34 ppm.

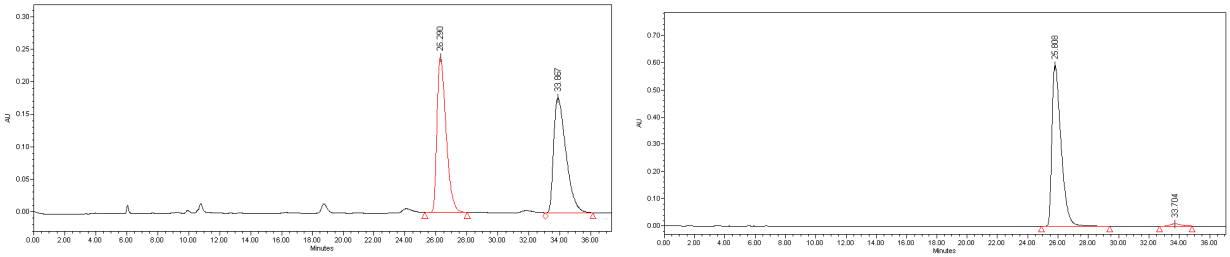
HPLC of **5h**



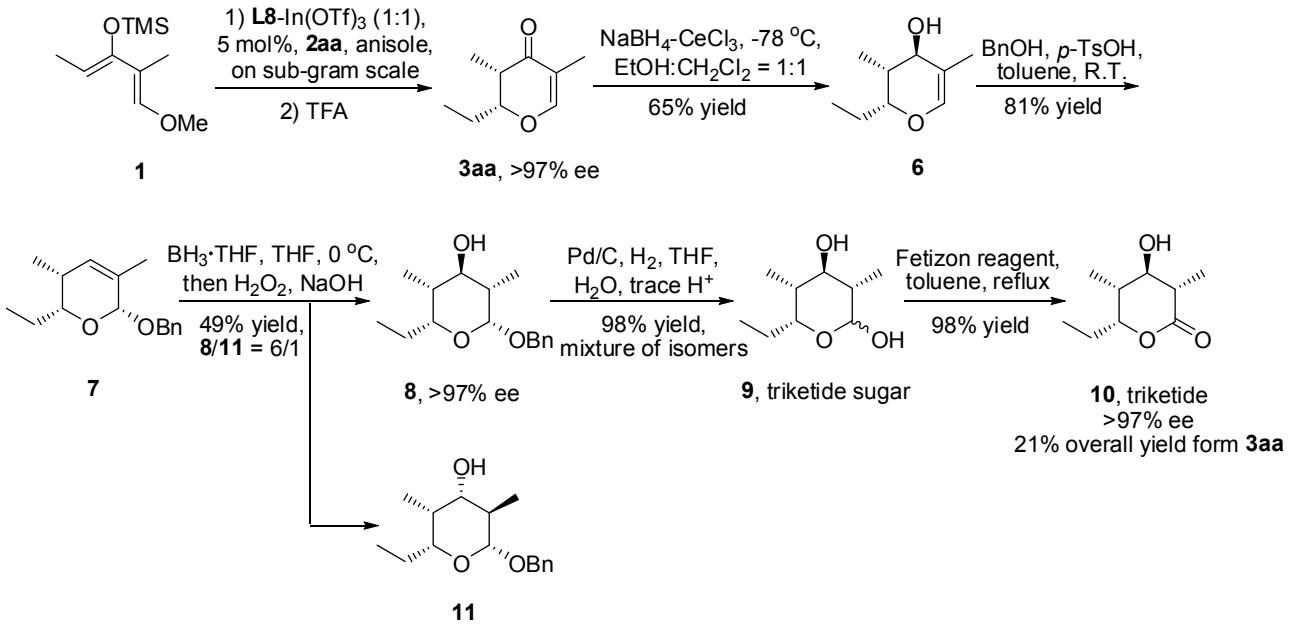
(*E*)-5-methyl-2-styryl-2,3-dihydro-4*H*-pyran-4-one (5i). Purified by flash chromatography on silica gel (petroleum : Et_2O = 5:1, R_f 0.2) to afford the title compound as white solid 53.0 mg (m.p. = 75-77 °C) in 99% yield with 97% ee determined by HPLC analysis using a Chiralcel OJ-H column (hexane/2-propanol 90:10, 1.0 mL/min^{-1}, t_r (major) = 25.81 min, t_r (minor) = 37.80 min). $[\alpha]^{25}_D$ = +145.1 (c = 0.220, in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.26 (m, 6H), 6.70 (d, *J* = 16 Hz, 1H), 6.30 (dd, *J* = 16, 6.4 Hz, 1H), 5.02 (m, 1H), 2.76-2.60 (m, 2H), 1.71 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.43, 159.30, 135.63, 133.38, 128.67, 128.42, 126.71, 125.45, 114.02, 79.56, 41.72, 10.55 ppm. HRMS (ESI): calcd for $C_{14}H_{15}O_2$ [M+H$^+$] 215.1067,

found 215.1064.

HPLC of **5i**



4. Asymmetric Synthesis of (3*S*,4*R*,5*R*,6*R*)-Triketide



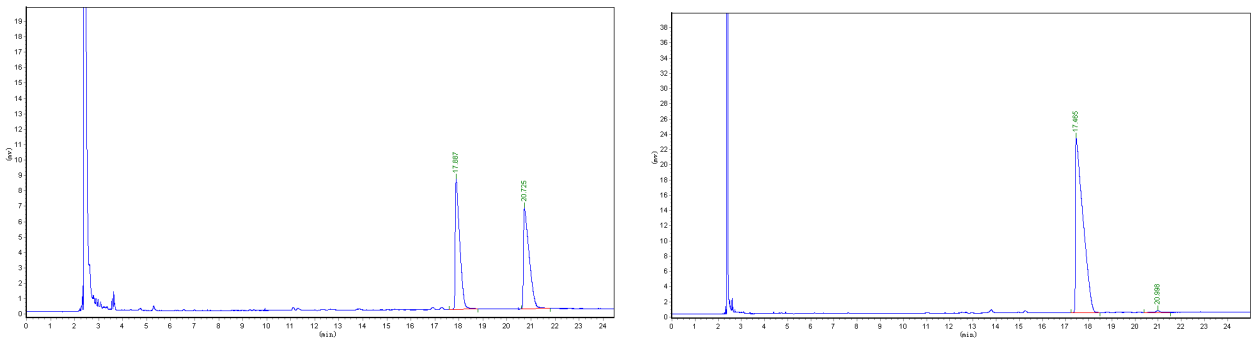
Preparation of catalyst: A nitrogen protected mixture of *N,N'*-dioxide **L8** (363.4 mg, 0.560 mmol), $In(OTf)_3$ (310.8 mg, 0.553 mmol) and 4 Å MS (1120.2 mg) in THF (1.0 mL) was stirred at room temperature for 30 min. The mixture was evaporated under vacuum for 2 h and refilled with nitrogen twice. A white powder was obtained. The catalyst powder was stored in brown bottle flushed with nitrogen at 23 °C. Standard reaction was carried out after more than half a year, and the same result was obtained as mentioned above.

(2*R*,3*S*)-2-ethyl-3,5-dimethyl-2*H*-pyran-4(*3H*)-one (**3aa**): A nitrogen protected 50 mL round

bottom flask was filled with catalyst powder 400.5 mg, and anisole (20 mL) was added. After the mixture was stirred at 0 °C for 30 min, diene **1** (1 mL, 3.75 mmol), and propionaldehyde (180 μL, 2.5 mmol) was added. The contents were stirred at 0 °C for 48 h, then TFA (0.3 mL) was added to this solution. After the mixture was stirred for 10 min to afford the final product (monitored by TLC), saturated $NaHCO_3$ (50 mL) was added, and then the solution was stirred for 5 min. After diluted with 20 mL Et_2O, the mixture was filtered through a plug of Celite. The layers were separated. The acquired aqueous layer was extracted with Et_2O (3 × 30 mL), and then the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$ and concentrated. The crude oil was purified by flash chromatography (petroleum : Et_2O = 10 : 1) to afford the products of both isomers respectively. *cis* Isomer, a colourless oil (petroleum : Et_2O = 3 : 1, R_f 0.51, 273.0 mg, 71% isolated yield, 97% ee on GC), *trans* isomer, a colourless oil liquid (petroleum : Et_2O = 3 : 1, R_f 0.59, 45.0 mg, 12% isolated yield, 50% ee on GC).

cis-**3aa**: $[\alpha]^{25}_D$ = +156 (c = 0.500, in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (s, 1H), 4.19 (m, 1H), 2.36 (dq, *J* = 7.4, 3.2 Hz, 1H), 1.80 (m, 1H), 1.65 (d, *J* = 1.1 Hz, 3H), 1.57 (m, 1H), 1.04 (d, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.90, 159.03, 111.99, 83.29, 42.98, 23.41, 10.52, 9.63, 9.42 ppm.

GC of *cis*-**3aa**



(2*R*,3*R*,4*R*)-2-ethyl-3,5-dimethyl-3,4-dihydro-2*H*-pyran-4-ol (**6**): To a solution of *cis*-**3aa** (600 mg, 3.89 mmol) in EtOH (20 mL) and CH_2Cl_2 (50 mL), was added $CeCl_3 \cdot 7H_2O$ (from Acros) (1886 mg, 5.07 mmol) in EtOH (10 mL) at -78 °C, and then sodium borohydride (250 mg, 6.6 mmol) in EtOH (10 mL) was added. The whole was stirred for 5 h at the same temperature and allowed to warm to 20 °C slowly in 2 h. Then, saturated aqueous $NaHCO_3$ (50 mL) was added to quench the reaction, and the mixture was filtered to remove insoluble solid. The organic layer was

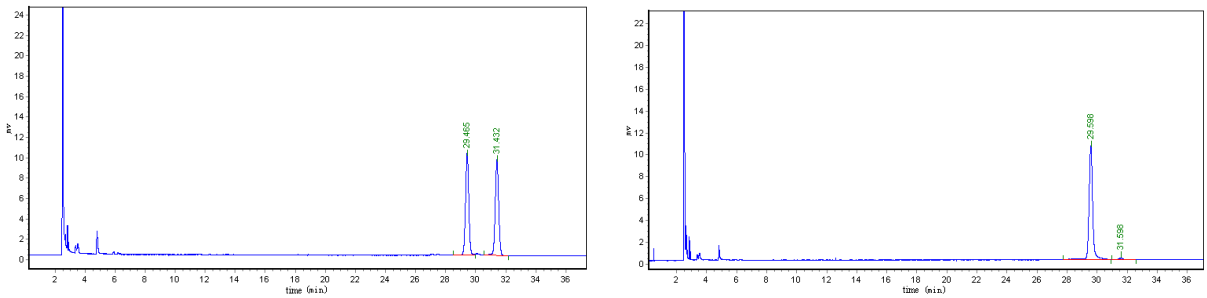
separated, and the aqueous layer was extracted with CH_2Cl_2 in four times. The CH_2Cl_2 layers were combined and dried over Na_2SO_4. After filtration and concentration under reduced pressure, the crude was crystalized to get a kind of colorless solid 395.0 mg (65% yield). The product was used for next step without further purification.

6: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.10 (s, 1H), 4.33 (d, *J* = 4.7 Hz, 1H), 3.75 (ddd, *J* = 8.0, 5.5, 2.0 Hz, 1H), 2.05 (m, 1H), 1.71 (m, 1H), 1.59 (s, 3H), 1.54-1.35 (m, 2H), 0.96-0.90 (m, 6H) ppm.

(2*R*,3*R*,6*R*)-6-(benzyloxy)-2-ethyl-3,5-dimethyl-3,6-dihydro-2*H*-pyran (**7**): The alcohol **6** (385.0 mg, 1.56 mmol) obtained was dissolved in 20 mL of toluene and treated with 770 μL (7.41 mmol) of benzyl alcohol and 10 mg of *p*-TsOH at 0 °C. After 2 h the reaction was poured into 10 mL of saturated aqueous $NaHCO_3$, and the layers were separated. The aqueous phase was extracted with three additional 20 mL x 3 of CH_2Cl_2, and the combined organic layers were dried ($MgSO_4$) and concentrated at reduced pressure. The residue was chromatographed on silica gel to give 493.1 mg (81% yield) of Ferrier product **7** as a colorless oil (petroleum : CH_2Cl_2 = 3 : 1, R_f 0.3).

7: 97% ee on GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), injection temp. = 250 °C; column temp. = 150 °C; detection temp. = 250 °C; t_r (minor) = 31.60 min, t_r (major) = 29.60 min. $[\alpha]^{25}_D$ = -50.0 (c = 0.334, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.25 (m, 5H), 5.67 (d, *J* = 5.2 Hz, 1H), 4.84-4.57 (m, 2H), 4.81 (s, 1H), 3.87 (ddd, *J* = 8.4, 5.2, 3.2 Hz, 1H), 1.96 (m, 1H), 1.71 (s, 3H), 1.62-1.41 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H) ppm. HRMS (ESI): calcd for $C_{16}H_{22}NaO_2$ [M + Na^+] 269.1517, found 269.1518.

GC of **7**

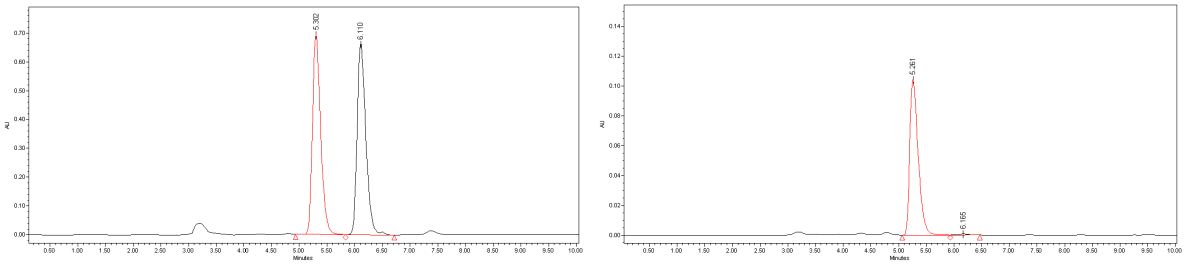


(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(benzyloxy)-6-ethyl-3,5-dimethyltetrahydro-2*H*-pyran-4-ol (**8**): A

solution of olefin **7** (280.0 mg, 1.14 mmol) in 20 mL THF was cooled to -20 °C and treated with 2.275 mL 1 M BH_3·THF. The reaction mixture was allowed to warm to room temperature over 8 h at which time 5 mL 1 M NaOH was added followed by 1 mL 30% H_2O_2. After being stirred at room temperature for 1 h, the reaction was diluted with 20 mL H_2O and extracted with 4 x 10 mL CH_2C1_2. The organic layers were combined and dried ($MgSO_4$), and the solvent was removed in vacuo. Chromatography of the residue (petroleum : Et_2O = 2:1) gave 125.1 mg (petroleum : Et_2O = 2 : 1, R_f 0.3, 42% yield) of alcohol **8** as a solid, m.p. 84-85 °C and alcohol **11**, 20 mg (petroleum : Et_2O = 3 : 1, R_f 0.36, 7% yield), as a white solid, m.p. 79-80 °C.

8: 98% ee on HPLC analysis using a chiralcel OJ-H column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, t_r (minor) = 6.17 min, t_r (major) = 5.26 min, $[\alpha]^{25}_D$ = +123.2 (c = 0.220, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.32 (m, 5H), 4.83-4.51 (m, 2H), 4.62 (d, *J* = 3.2 Hz, 1H), 4.05 (m, 1H), 3.44 (m, 1H), 3.10-2.70 (br, 1H), 1.96-1.89 (m, 1H), 1.88-1.80 (m, 1H), 1.65-1.42 (m, 2H), 1.11 (d, *J* = 7.2 Hz, 3H), 1.06-0.92 (m, 6H) ppm. HRMS (ESI): calcd for $C_{16}H_{24}NaO_3$ [M + Na^+] 287.1623, found 287.1624.

HPLC of **8**



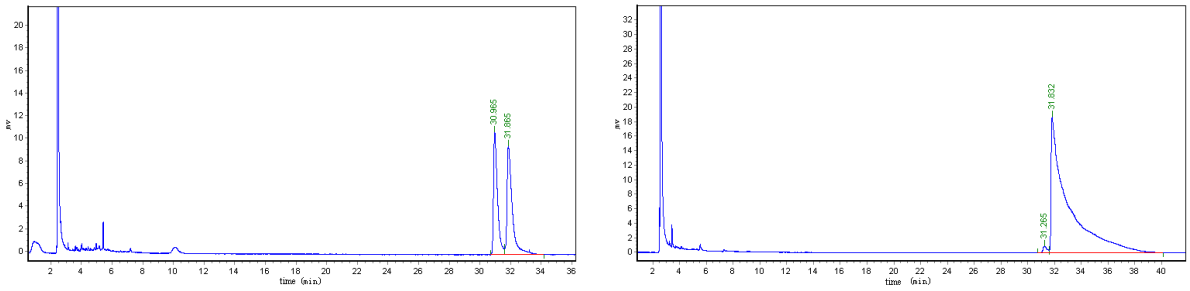
(3*S*,4*R*,5*R*,6*R*)-6-ethyl-3,5-dimethyltetrahydro-2*H*-pyran-2,4-diol (**9**): A solution of alcohol **8** (57 mg, 0.216 mmol) in 3 mL THF, 1 mL H_2O and 1μL 1 M HCl was protected with nitrogen at 20 °C. 10 mg Pd/C (10% unreduced on active carbon) was added and stirred at 20 °C, then 1 atm of H_2 stream was flush through the solution. After the disapperence of material by detecting via TLC, the solution was filtered on a pad of Celite to remove the active carbon. The filtrate was concentrated and chromatographed on silica gel to give 37.3 mg (petroleum : EtOAc = 1 : 1, R_f 0.25, 98% yield) of deprotected product **9** as a diastereomer mixture. The mixture was applied in next step without futher purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.78 (t, *J* = 5.2 Hz, 1H,) 4.04 (pentet, *J* = 4.8 Hz, 1H), 3.45 (s, 1H), 3.43 (bs, 1H), 2.26 (bs, 1H), 1.85-1.81(m, 1H), 1.76-1.70 (m, 1H), 1.58-1.41

(m, 2H), 1.11 (d, J = 7.2 Hz, 3H), 0.94 (m, 6H) ppm.

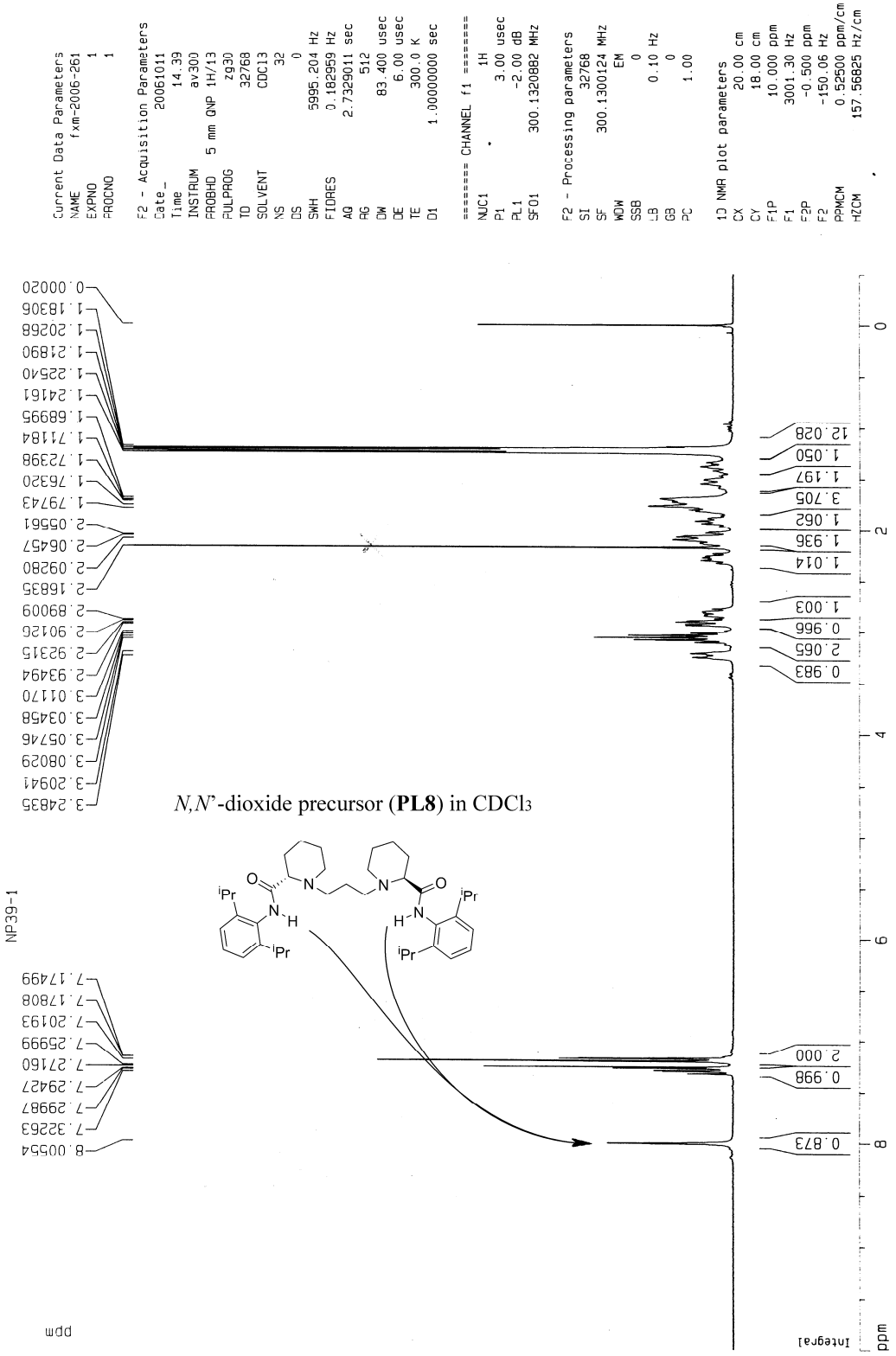
(3*S*,4*R*,5*R*,6*R*)-6-ethyl-4-hydroxy-3,5-dimethyltetrahydro-2*H*-pyran-2-one (**10**): a solution of **9** (30.2 mg, 0.173 mmol) and Fetizon reagent (Ag_2CO_3/Celite (1.5 mmol/g), 150 mg, 0.225 mmol) in toluene was heated to reflux for 3 h. The whole was cooled to room temperature and filtered to remove precipitate, and the precipitate was washed well with EtOAc. The organic filtrate were combined and concentrated under reduced pressure, the crude product obtained was purified by column chromatography (silica gel, ethyl acetate : *n*-hexane = 3:2, R_f 0.35) to afford **(3*S*,4*R*,5*R*,6*R*)- triketide, 10** as a yellow oil 29.3 mg (98% yield).

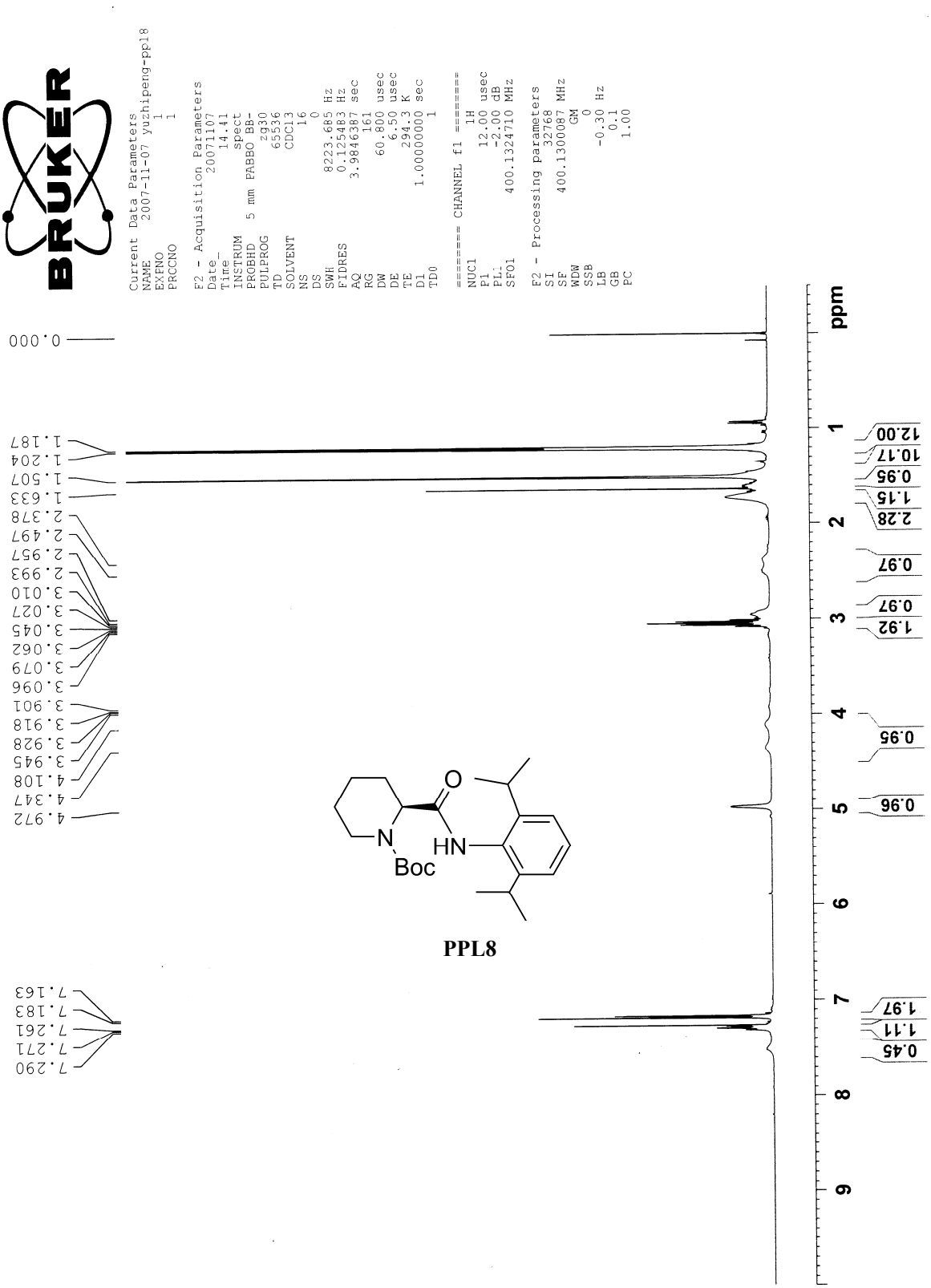
10: 97% ee on GC analysis using a Varian Chirasil DEX-CB column (0.25 mm x 25 m), injection temp. = 250 °C; column temp. = 145 °C; detection temp. = 250 °C; t_r (minor) = 31.27min, t_r (major) = 31.83 min. $[\alpha]^{25}_D$ = +86.7 (c = 0.468, in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.41 (ddd, J = 8.4, 5.2, 2.8 Hz, 1H,) 3.40 (dd, J = 7.6, 2.4 Hz, 1H), 2.55 (pentet, J = 6.8 Hz, 1H), 1.99 (qt, J = 7.2, 2.7Hz, 1H), 2.3-1.7 (br, 1H), 1.34 (d, J = 6.8Hz, 3H), 1.02 (t, J = 7.6 Hz, 3H), 0.94 (d, J = 7.2 Hz, 3H) ppm. HRMS (ESI): calcd for $C_9H_{16}NaO_3$ [M + Na^+] 195.0997, found 195.0997.

GC of **10**



5. Copy of NMR Spectra for *N,N*'-Dioxide Ligand.

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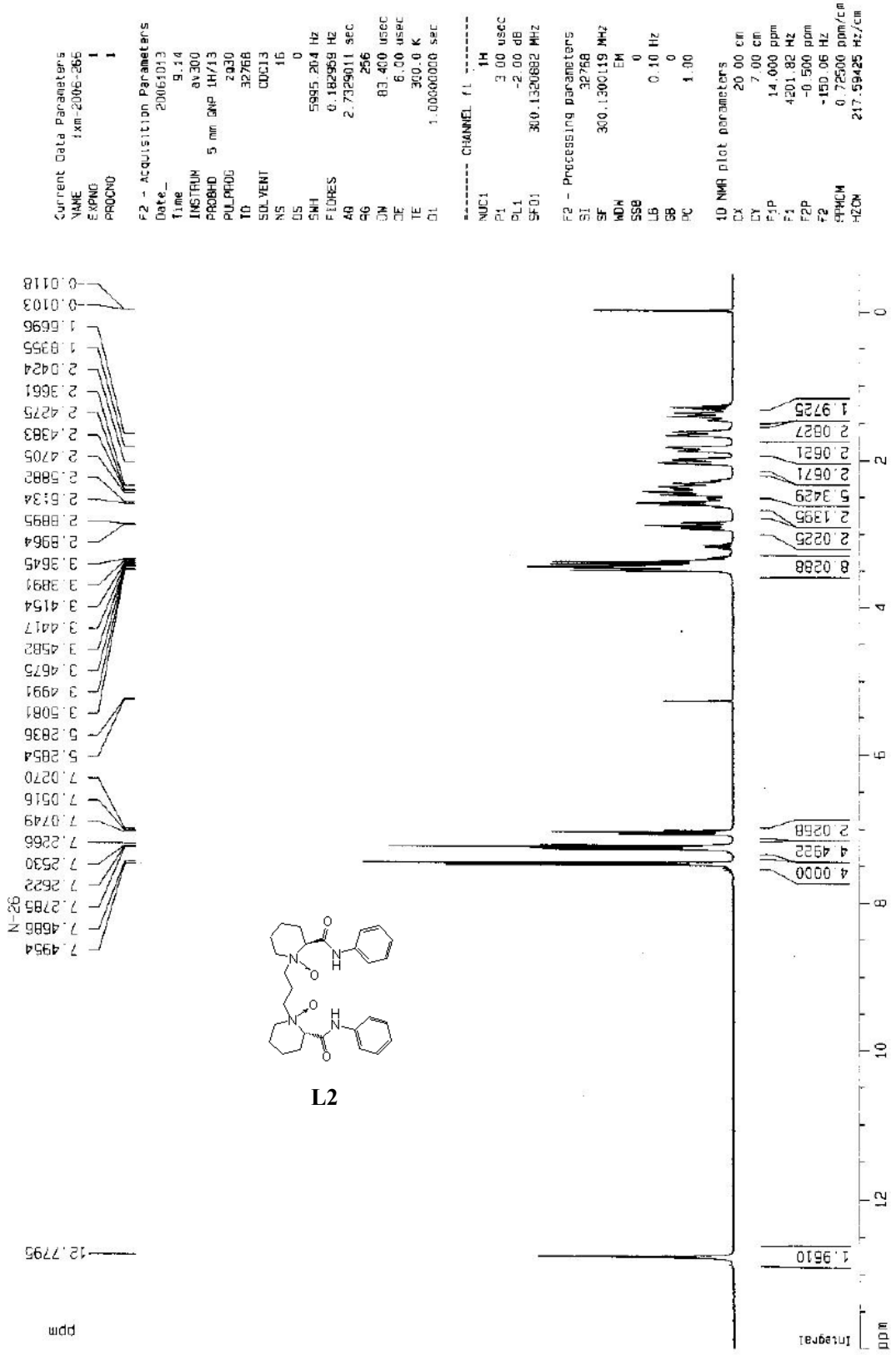
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ppm

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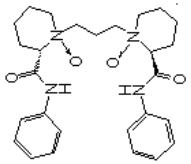

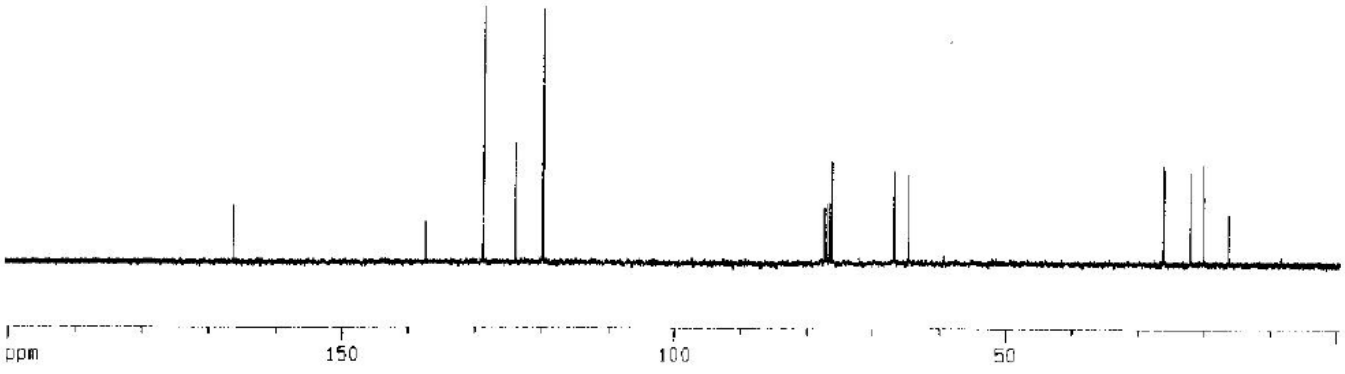


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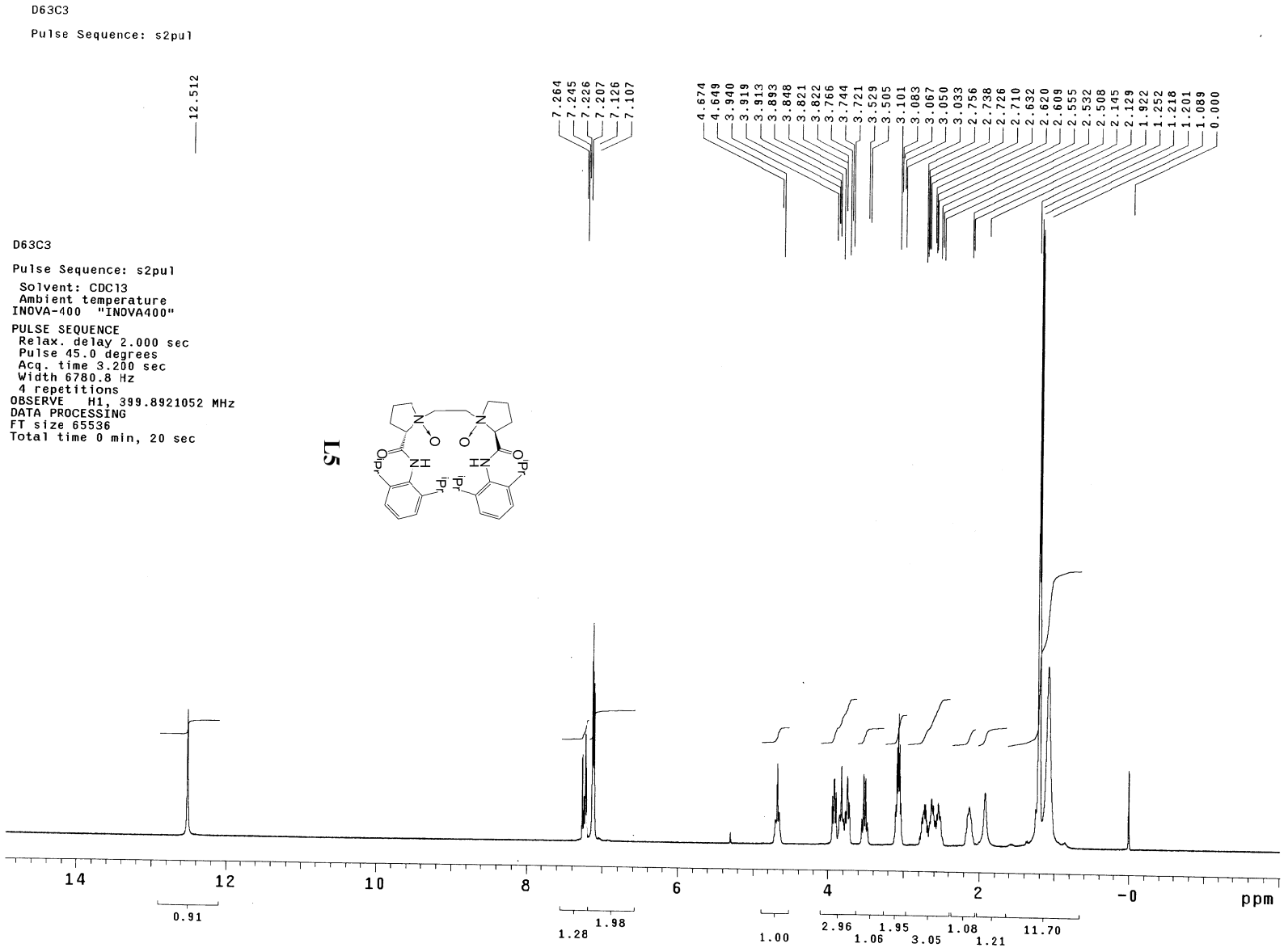
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Solvent: CDCl3
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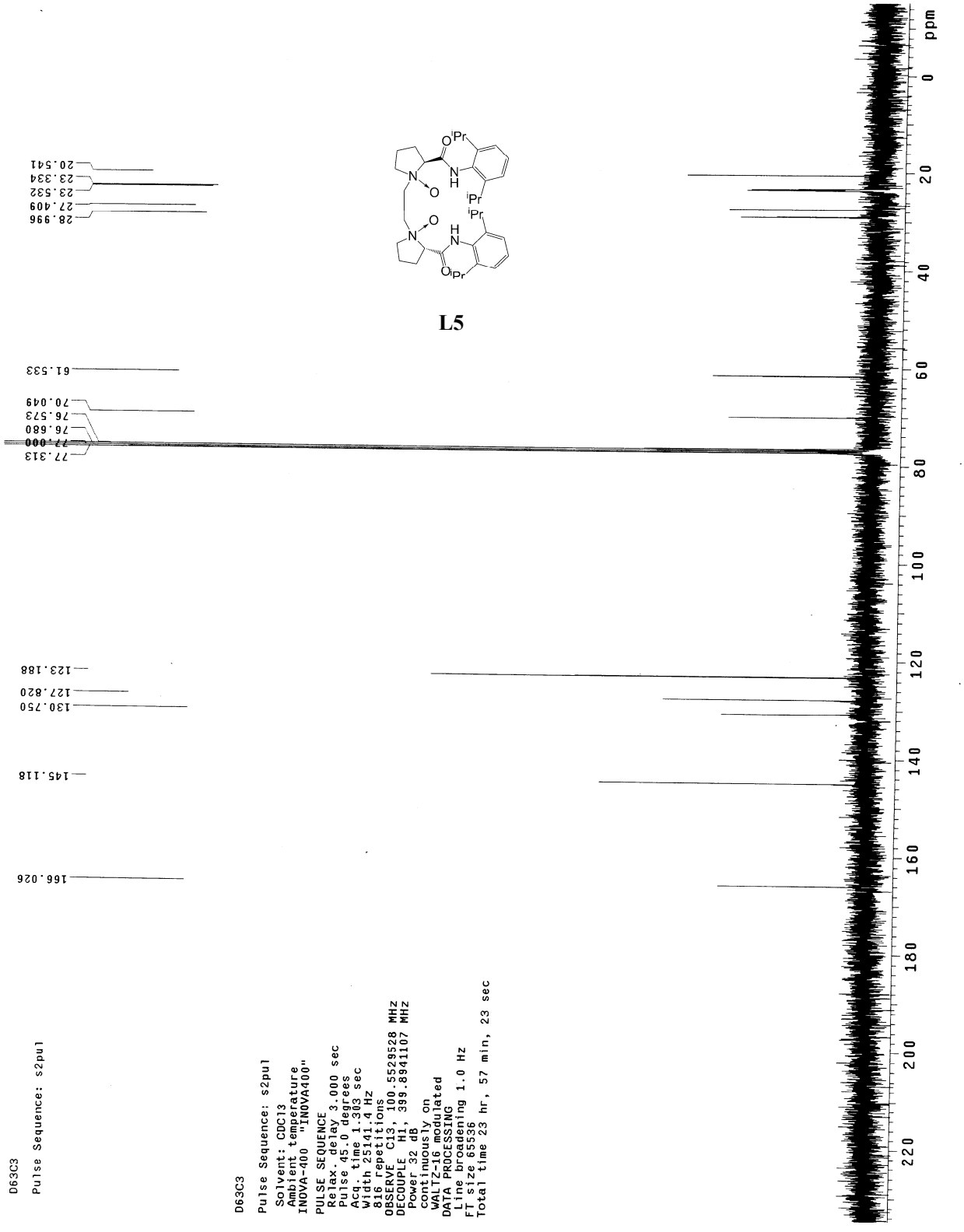
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continuously on
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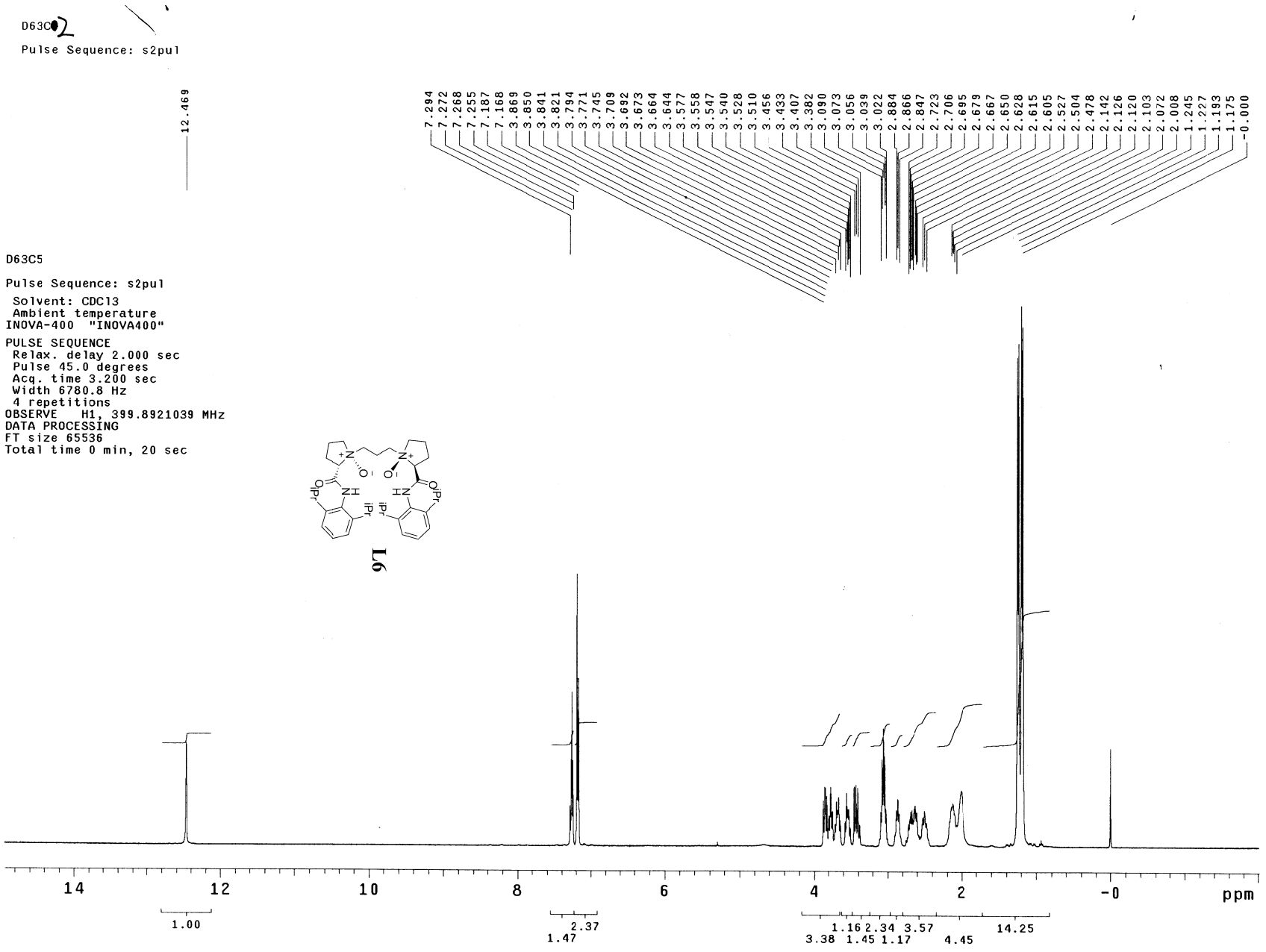
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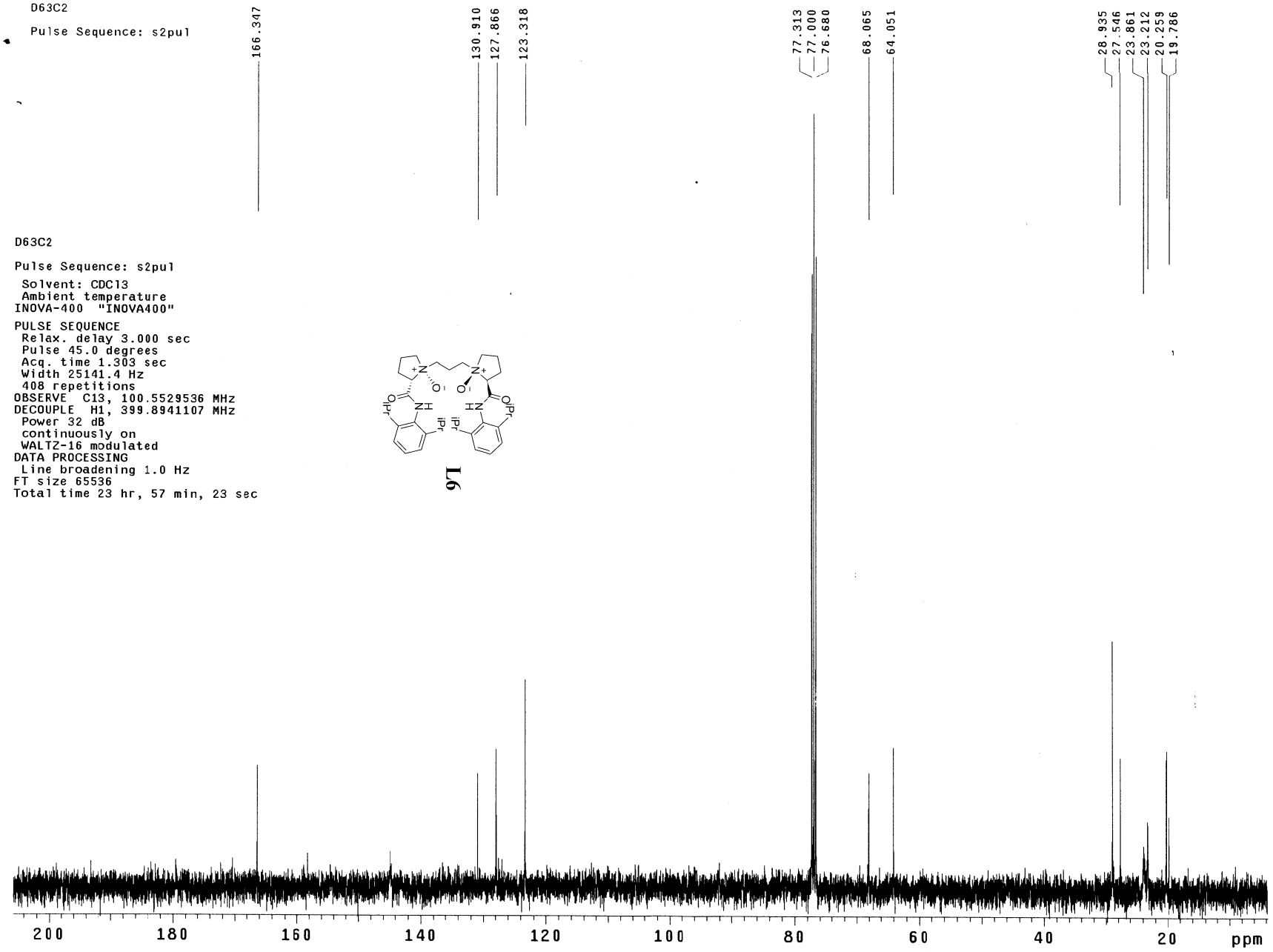
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D63C2
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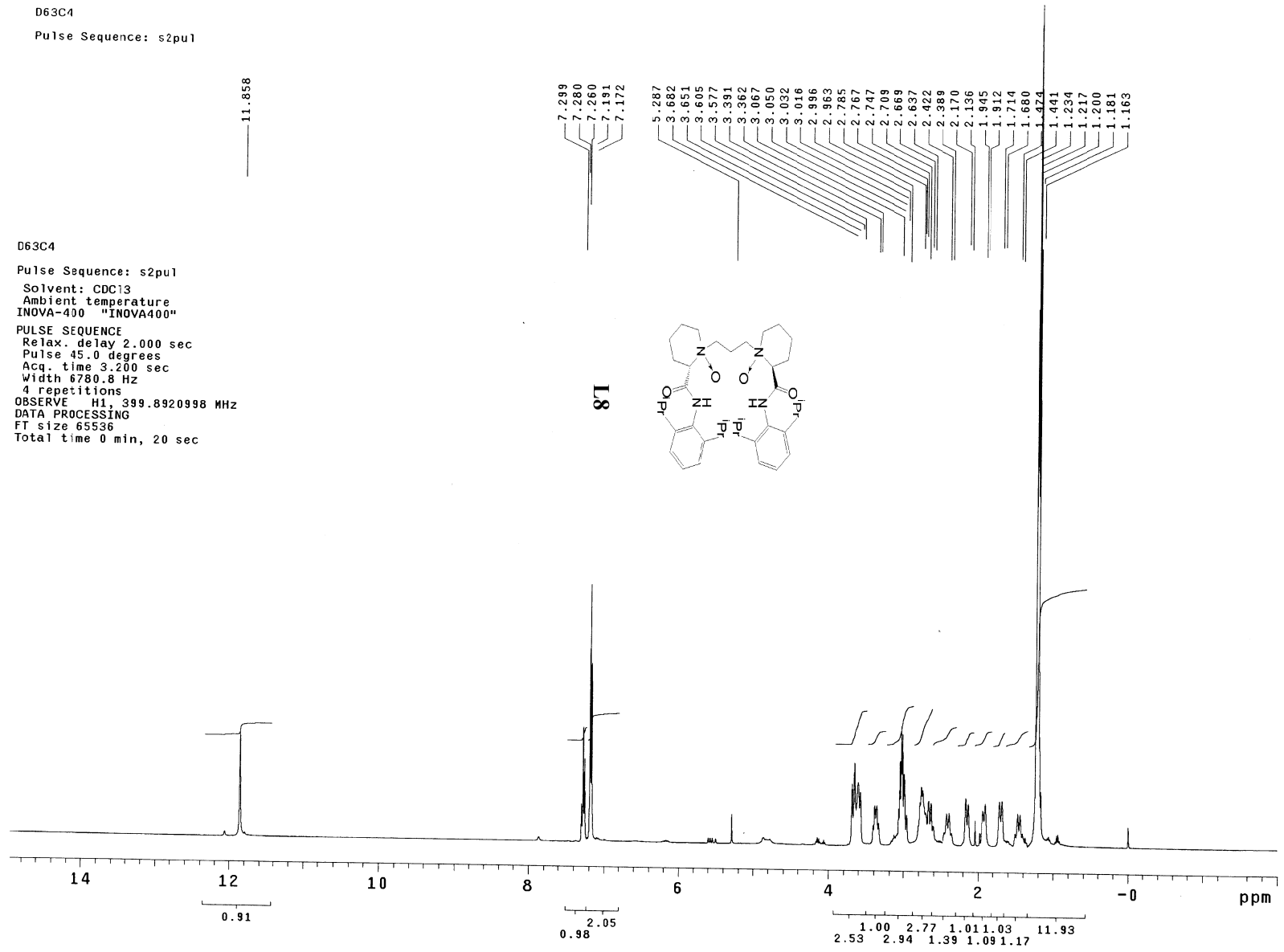
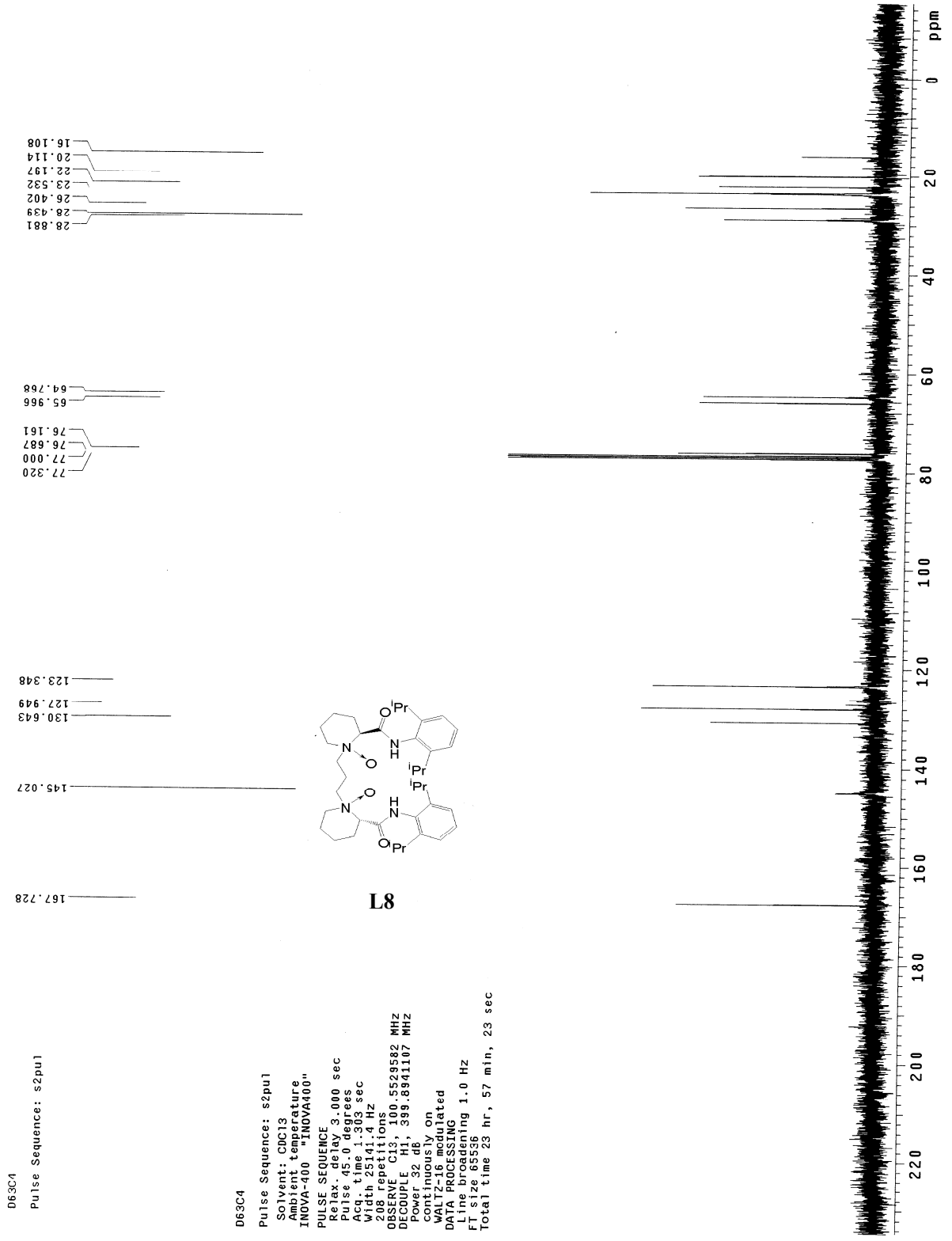
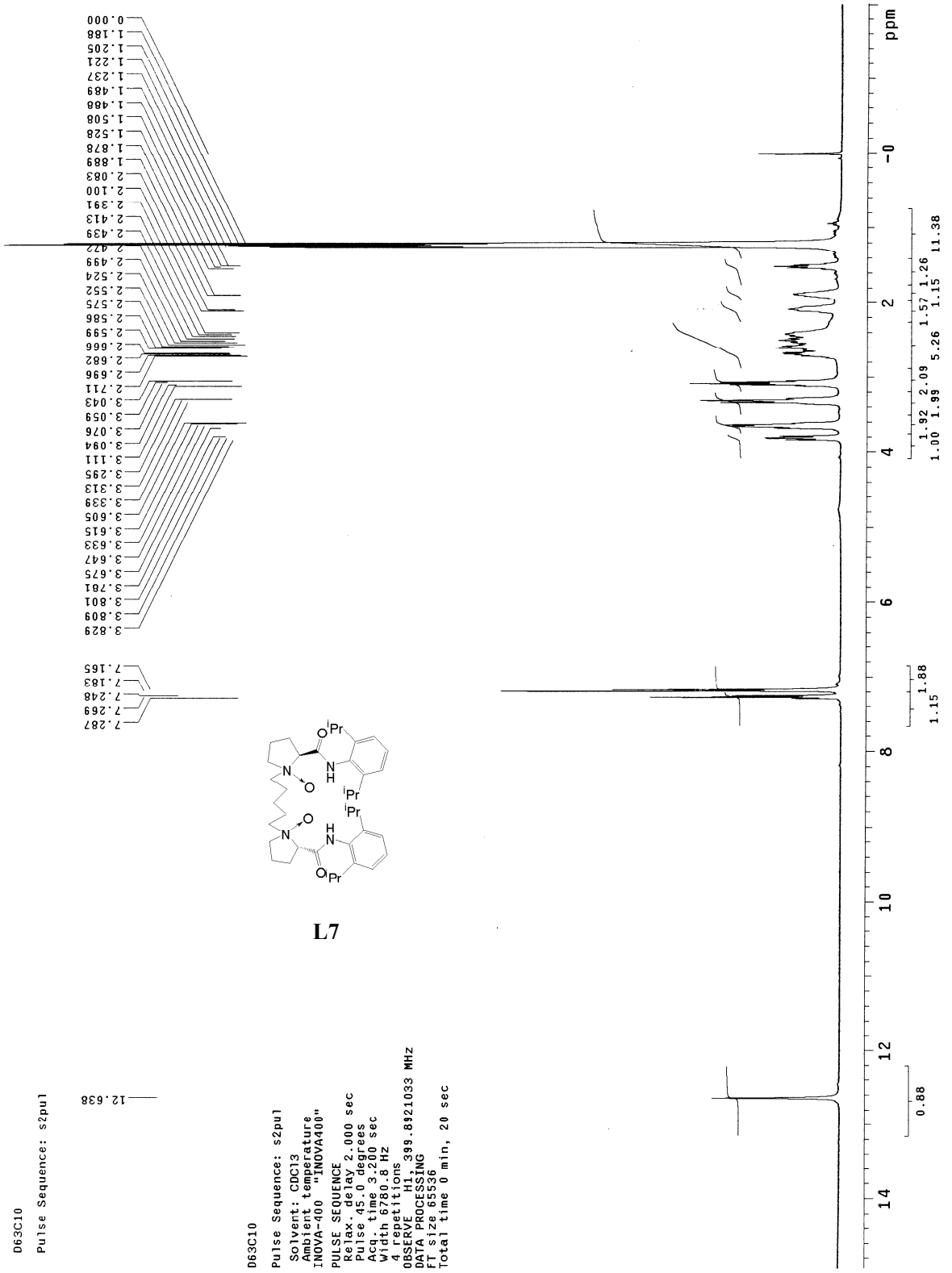
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
408 repetitions
OBSERVE C13, 100.5529536 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 23 hr, 57 min, 23 sec
L6
200
180
160
140
120
100
80
60
40
20
ppm

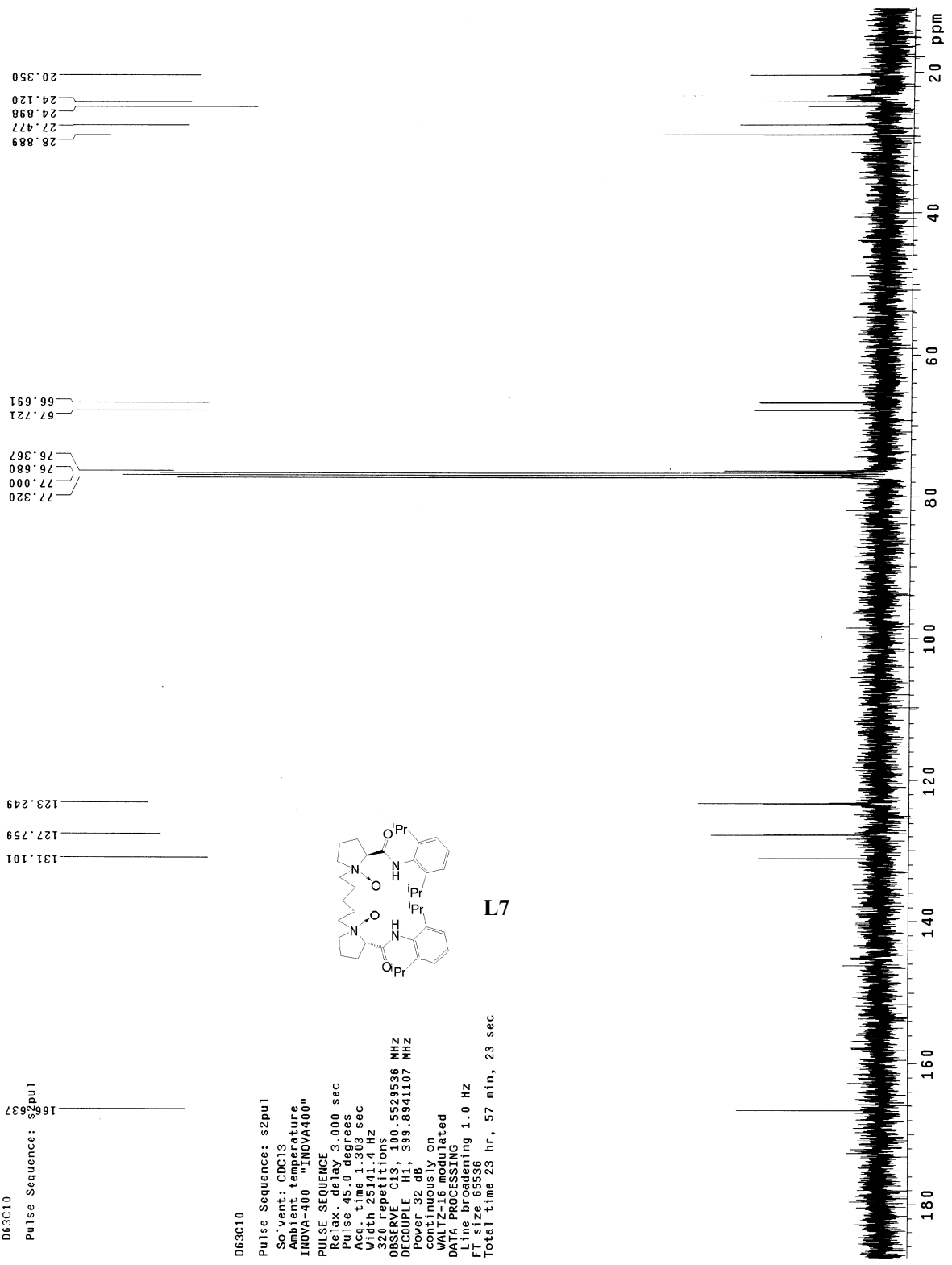

D63C4
Pulse Sequence: s2pul
11.858
7.299
7.280
7.260
7.191
7.172
5.287
3.682
3.651
3.605
3.577
3.391
3.362
3.067
3.050
3.032
3.016
2.996
2.963
2.785
2.767
2.747
2.709
2.669
2.637
2.422
2.389
2.170
2.136
1.945
1.912
1.714
1.680
1.424
1.441
1.234
1.217
1.200
1.181
1.163
D63C4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 6780.8 Hz
4 repetitions
OBSERVE H1, 399.8920998 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 20 sec
L8
14
12
10
8
6
4
2
-0
ppm
0.91
2.05
0.98
1.00
2.77
1.01
1.03
11.93
2.53
2.94
1.39
1.09
1.17


D63C4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
208 repetitions
OBSERVE C13, 100.5529582 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 23 hr, 57 min, 23 sec
167.728
145.027
130.643
127.949
123.348
77.320
77.000
76.687
76.161
65.966
64.768
28.881
28.439
26.402
23.532
22.197
20.114
16.108
ppm

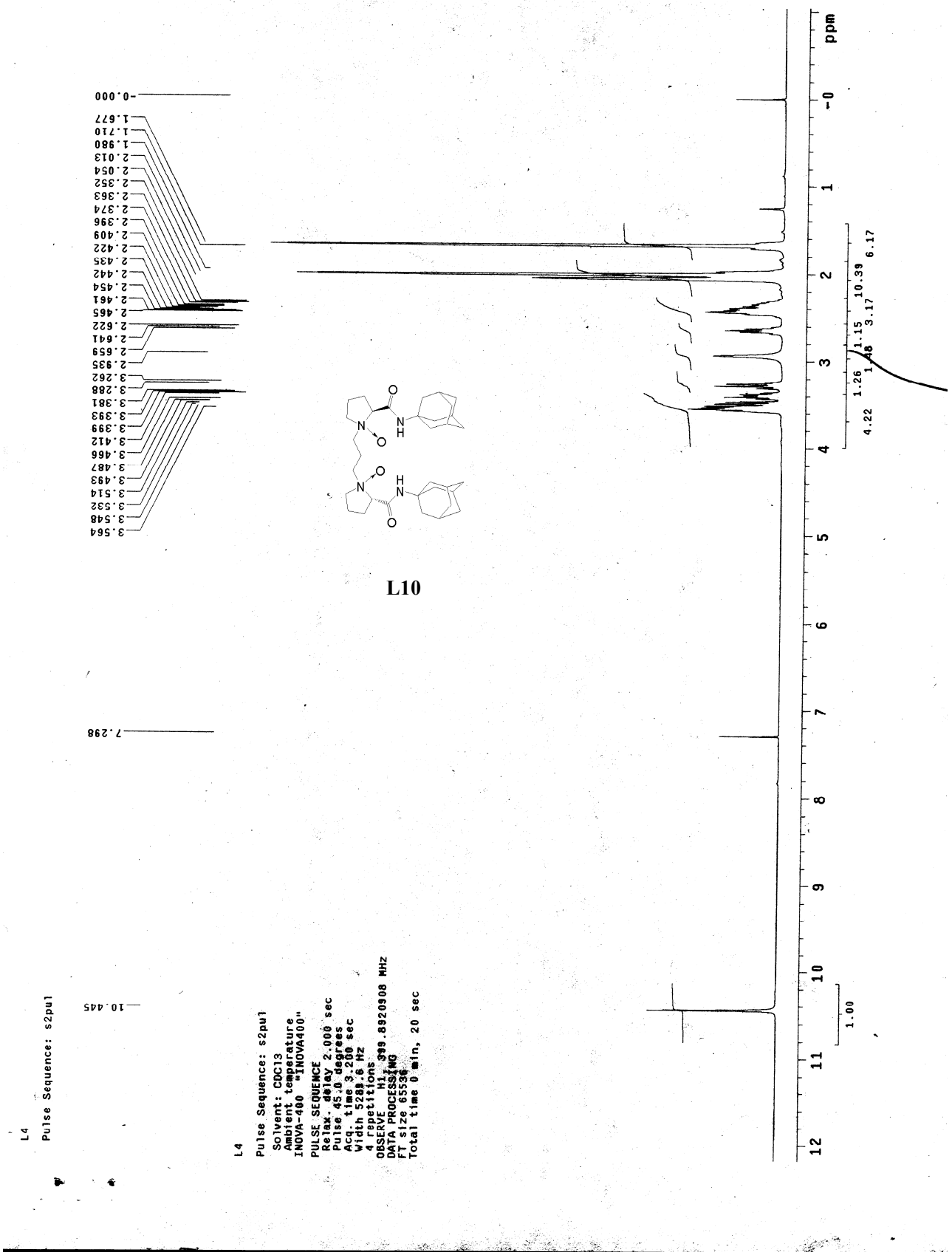
L8


D63C10
Pulse Sequence: s2pul
12.638
D63C10
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 6780.8 Hz
4 repetitions
OBSERVE H1, 399.8921033 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 20 sec
ppm

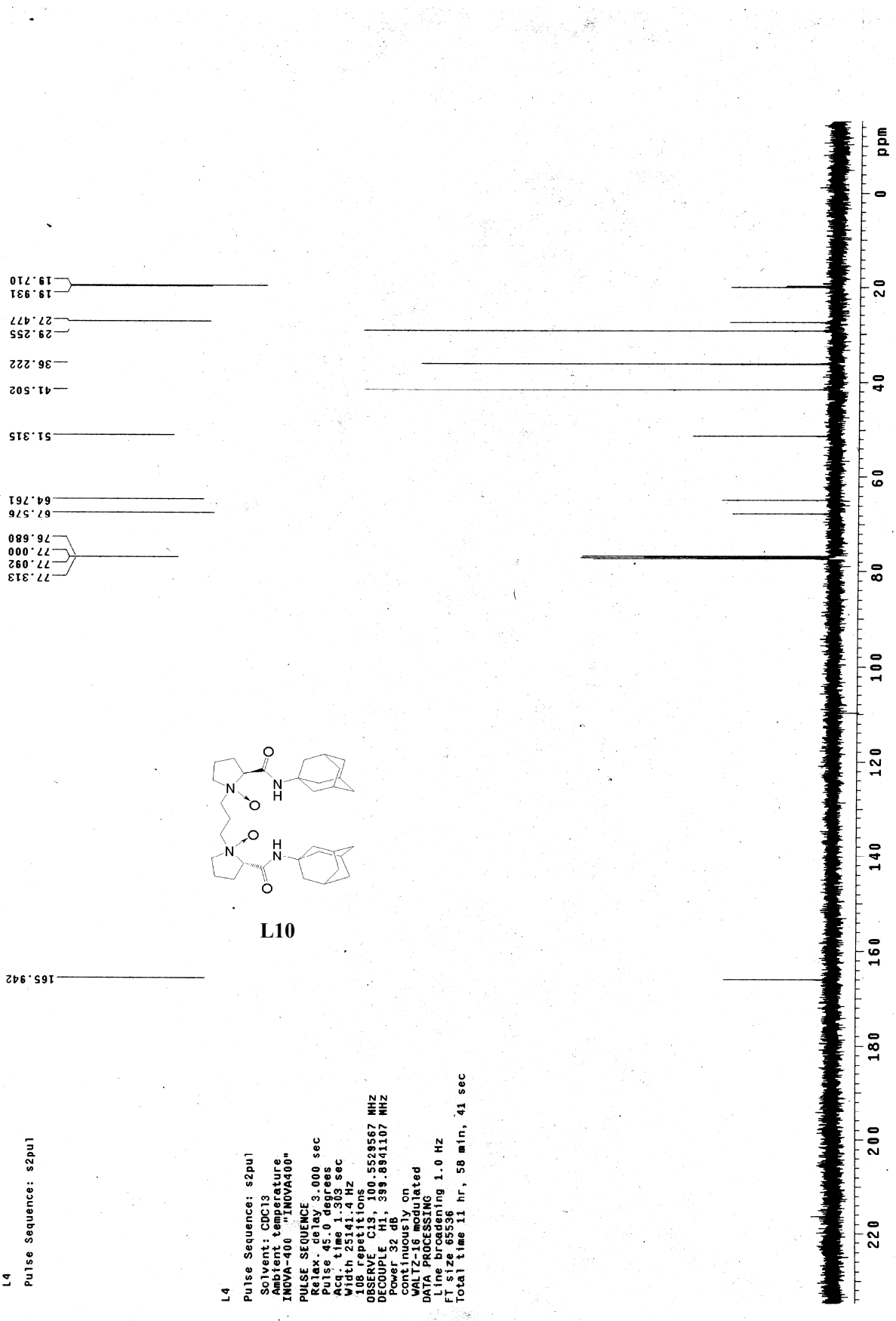
L7


D63C10
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
320 repetitions
OBSERVE C13, 100.5529536 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 23 hr, 57 min, 23 sec
D63C10
Pulse Sequence: s2pul
165.637
131.101
127.759
123.249
77.320
77.000
76.680
76.367
67.721
66.691
28.889
27.477
24.898
24.120
20.350
ppm
20
40
60
80
100
120
140
160
180

L7

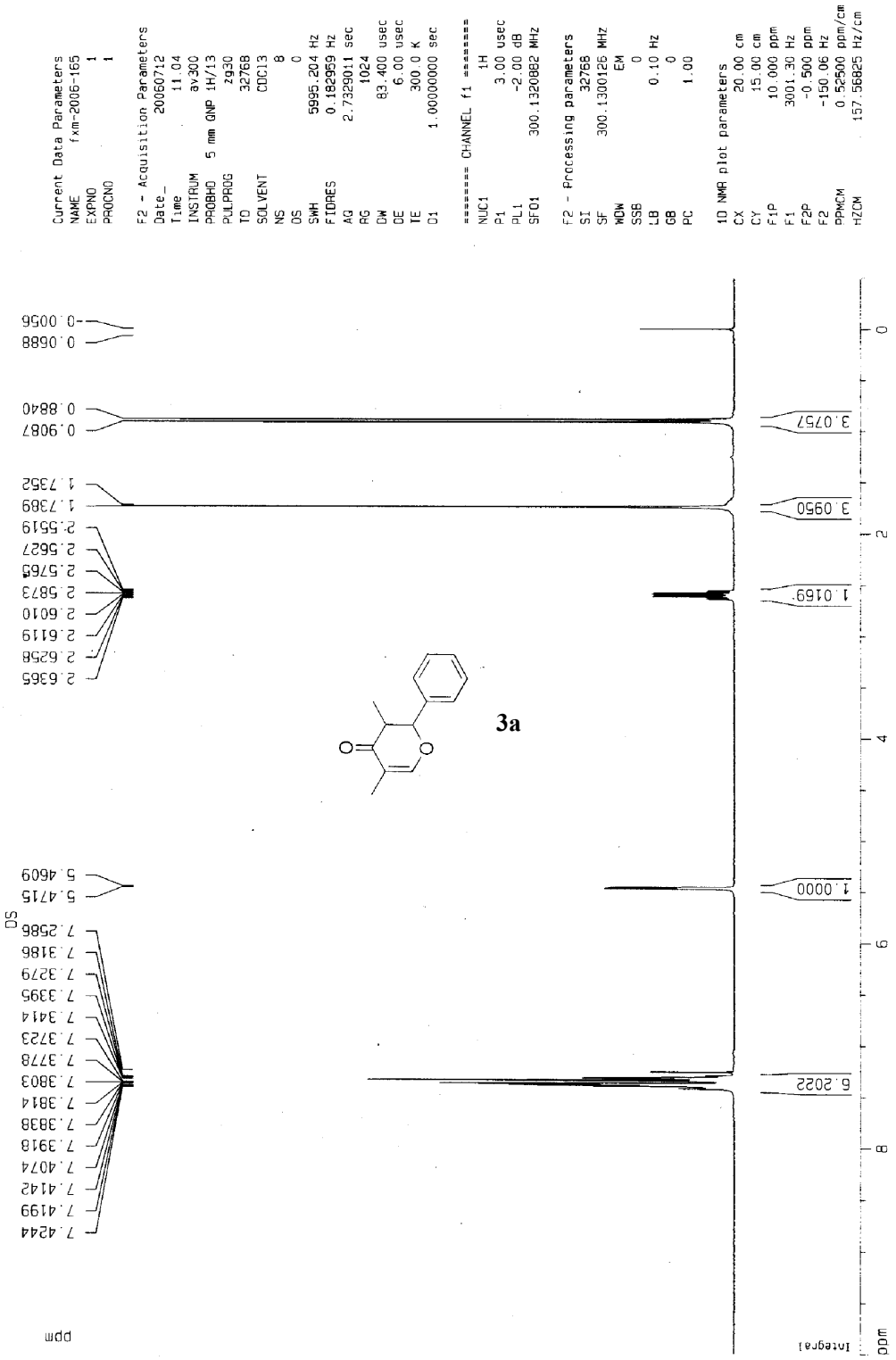

L4
Pulse Sequence: s2pul
10.445
7.298
3.564
3.548
3.532
3.514
3.493
3.487
3.466
3.412
3.399
3.393
3.381
3.288
3.262
2.935
2.659
2.641
2.622
2.465
2.461
2.454
2.442
2.435
2.422
2.409
2.396
2.374
2.363
2.352
2.054
2.013
1.980
1.710
1.677
-0.000
L4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5288.6 Hz
4 repetitions
OBSERVE H1, 399.8820908 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 20 sec
ppm
1.00
4.22
1.26
1.48
1.15
3.17
10.39
6.17

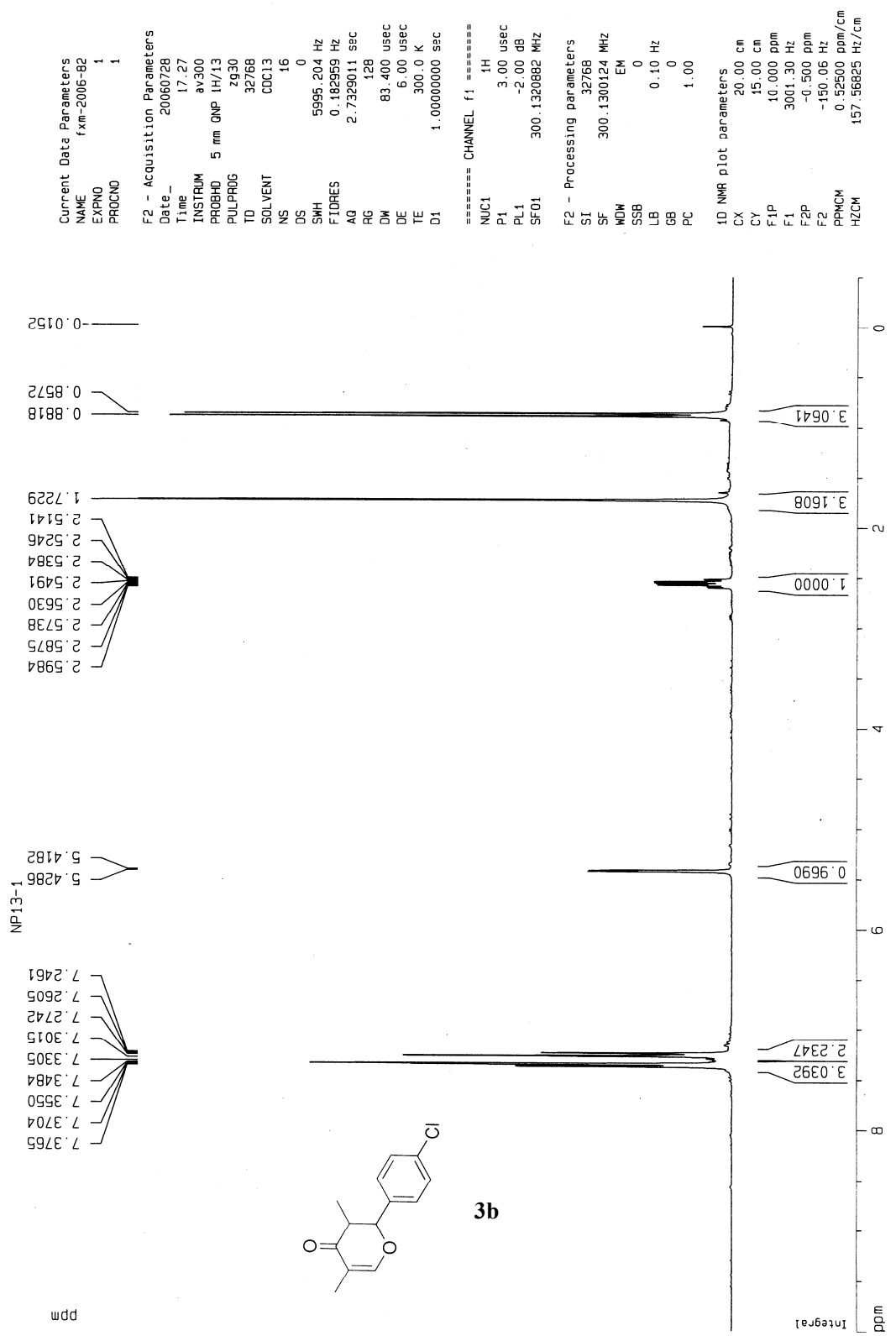
L10

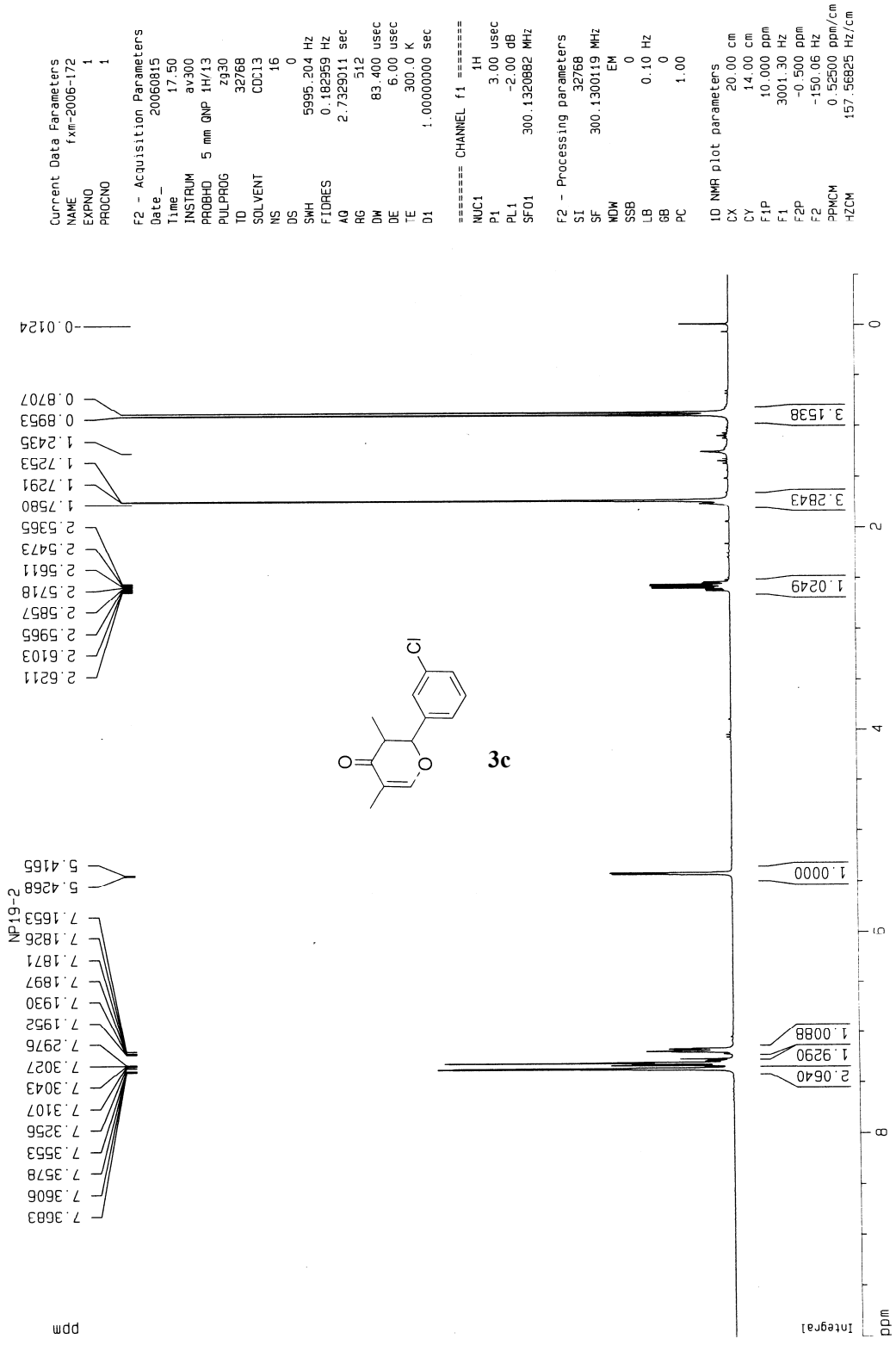

L4
Pulse Sequence: s2pul
L4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
108 repetitions
OBSERVE C13, 100.5529567 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 58 min, 41 sec
165.942
77.313
77.092
77.000
76.680
67.576
64.761
51.315
41.502
36.222
29.255
27.477
19.931
19.710
ppm

L10

6. Copy of NMR Spectra for Dihydropyranones



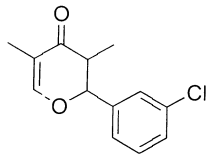

Current Data Parameters
NAME fxm-2006-82
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060728
Time 17.27
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
NP13-1
-0.0152
0.8572
0.8818
1.7229
2.5141
2.5246
2.5384
2.5491
2.5630
2.5738
2.5875
2.5984
5.4182
5.4286
7.2461
7.2605
7.2742
7.3015
7.3305
7.3484
7.3550
7.3704
7.3765
3.0641
3.1608
1.0000
0.9690
3.0392
2.2347
Cl
O
O
3b
ppm
Integral
ppm


Current Data Parameters
NAME fxm-2006-172
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060815
Time 17.50
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329911 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300119 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 14.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
NP19-2
0.0124
0.8707
0.8953
1.2435
1.7253
1.7291
1.7580
2.5365
2.5473
2.5611
2.5718
2.5857
2.5965
2.6103
2.6211
5.4165
5.4268
7.3683
7.3606
7.3578
7.3553
7.3256
7.3107
7.3043
7.3027
7.2976
7.1952
7.1930
7.1897
7.1871
7.1826
7.1653
3.1538
3.2843
1.0249
1.0000
1.0088
1.9290
2.0640
3c
Cl
O
O
ppm
Integral
ppm

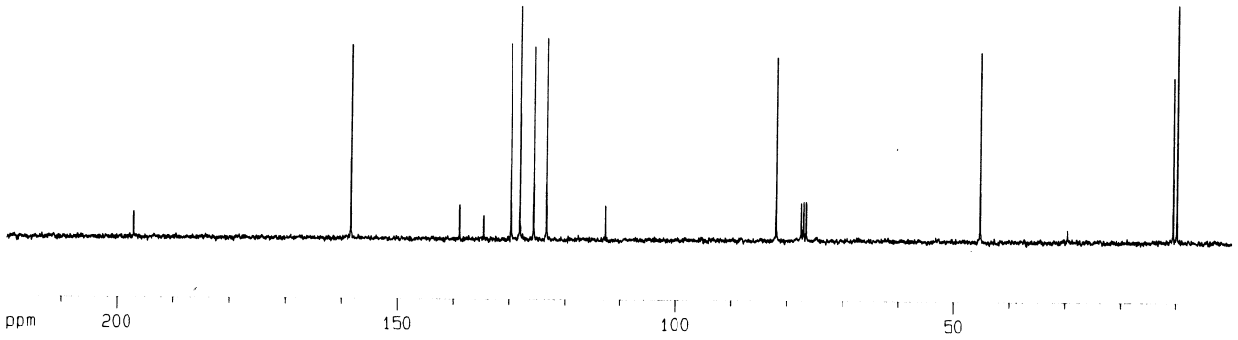
NP19-2

ppm

197.093
158.345
138.851
134.597
129.808
128.086
125.680
123.419
112.694
82.020
77.425
77.000
76.577
45.436
10.574
9.892



3c



Current Data Parameters

NAME	fxm-2006-170
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060817
Time	9.18
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg
TD	65536
SOLVENT	DMSO
NS	196
DS	4
SWH	22675.736 Hz
FIDRES	0.346004 Hz
AQ	1.4451188 sec
RG	8192
DW	22.050 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

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

NUC1	13C
P1	5.50 usec
PL1	-6.00 dB
SFO1	75.4775598 MHz

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

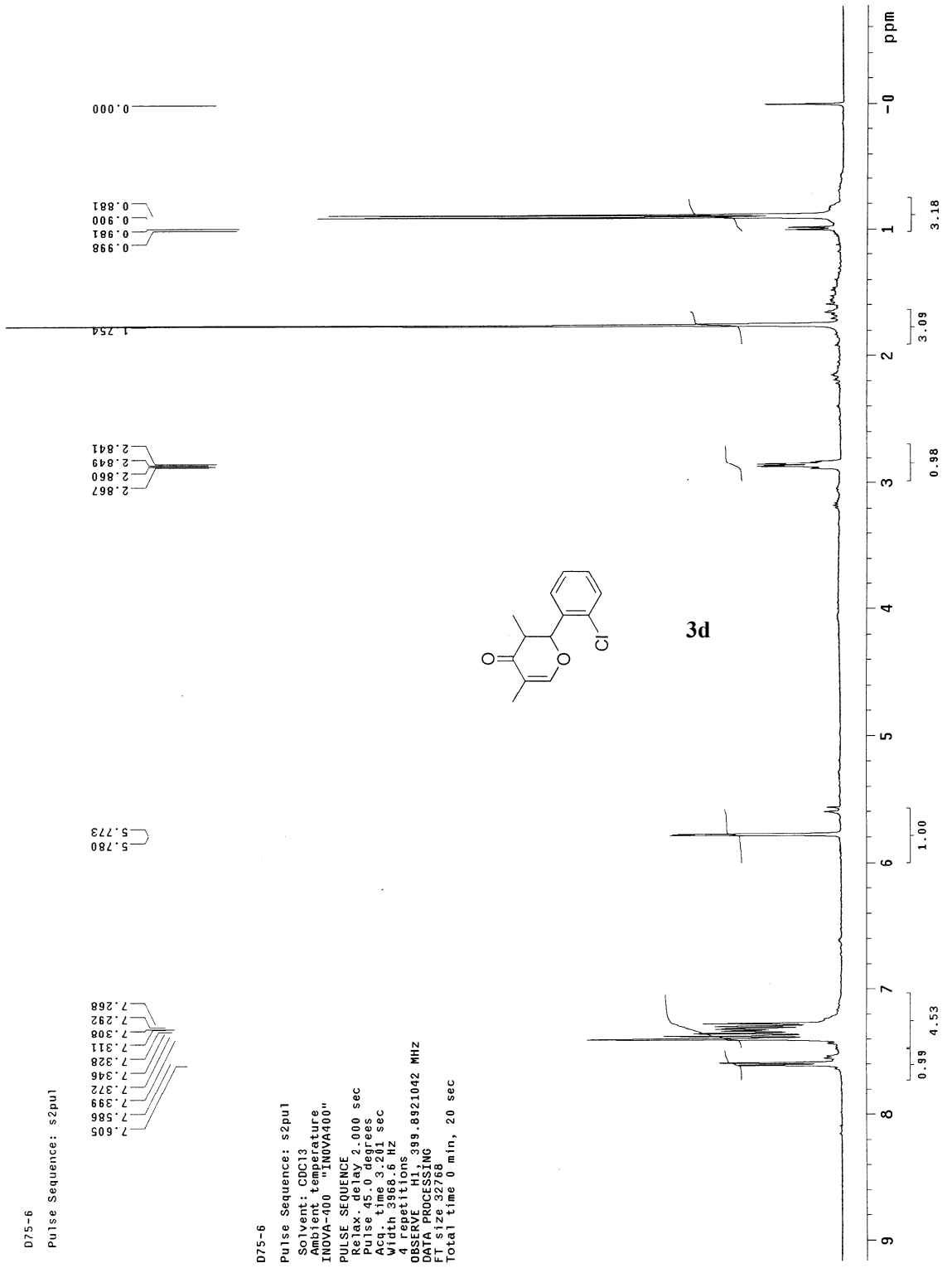
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	17.70 dB
PL13	17.71 dB
SFO2	300.1312005 MHz

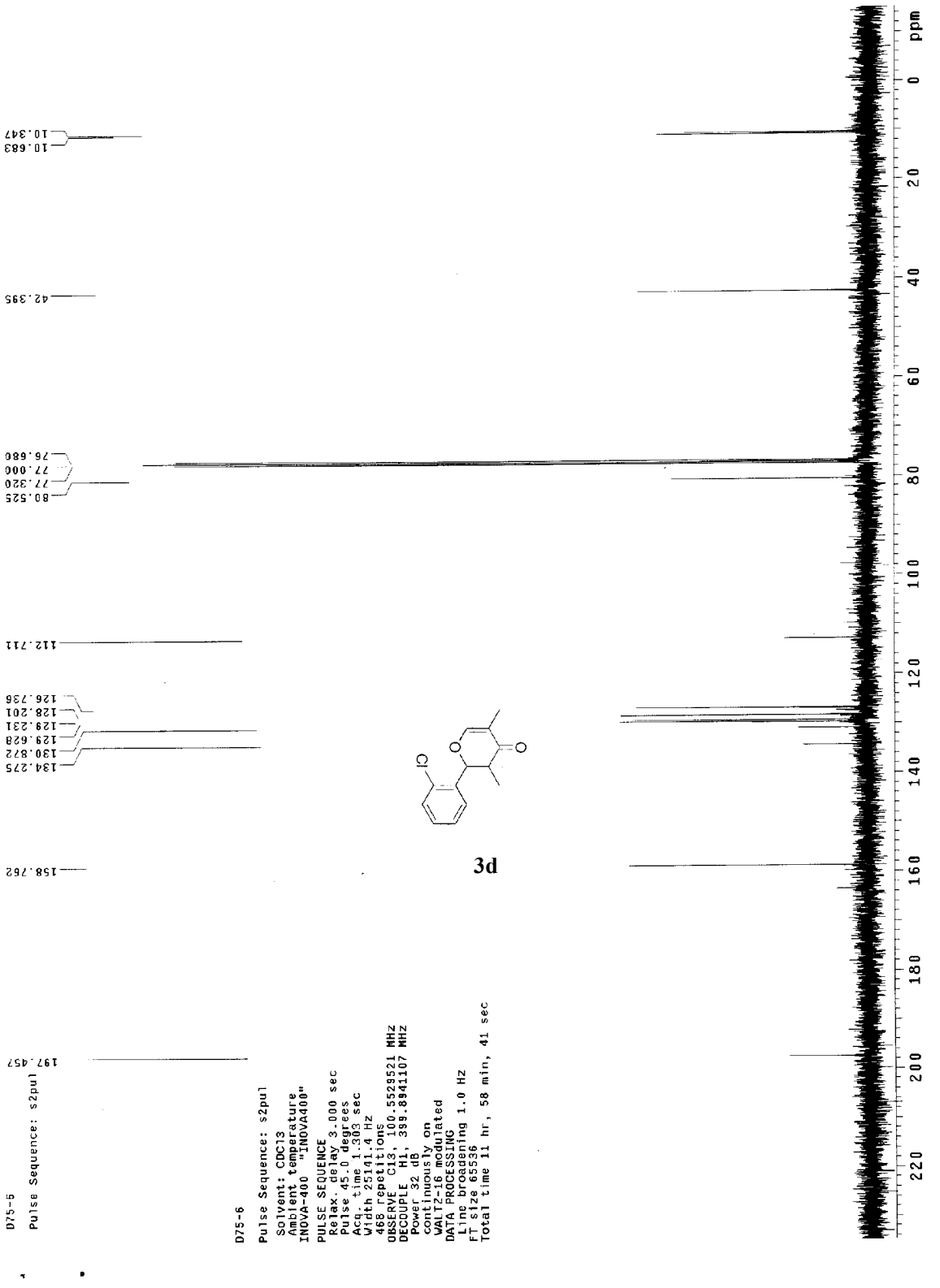
F2 - Processing parameters

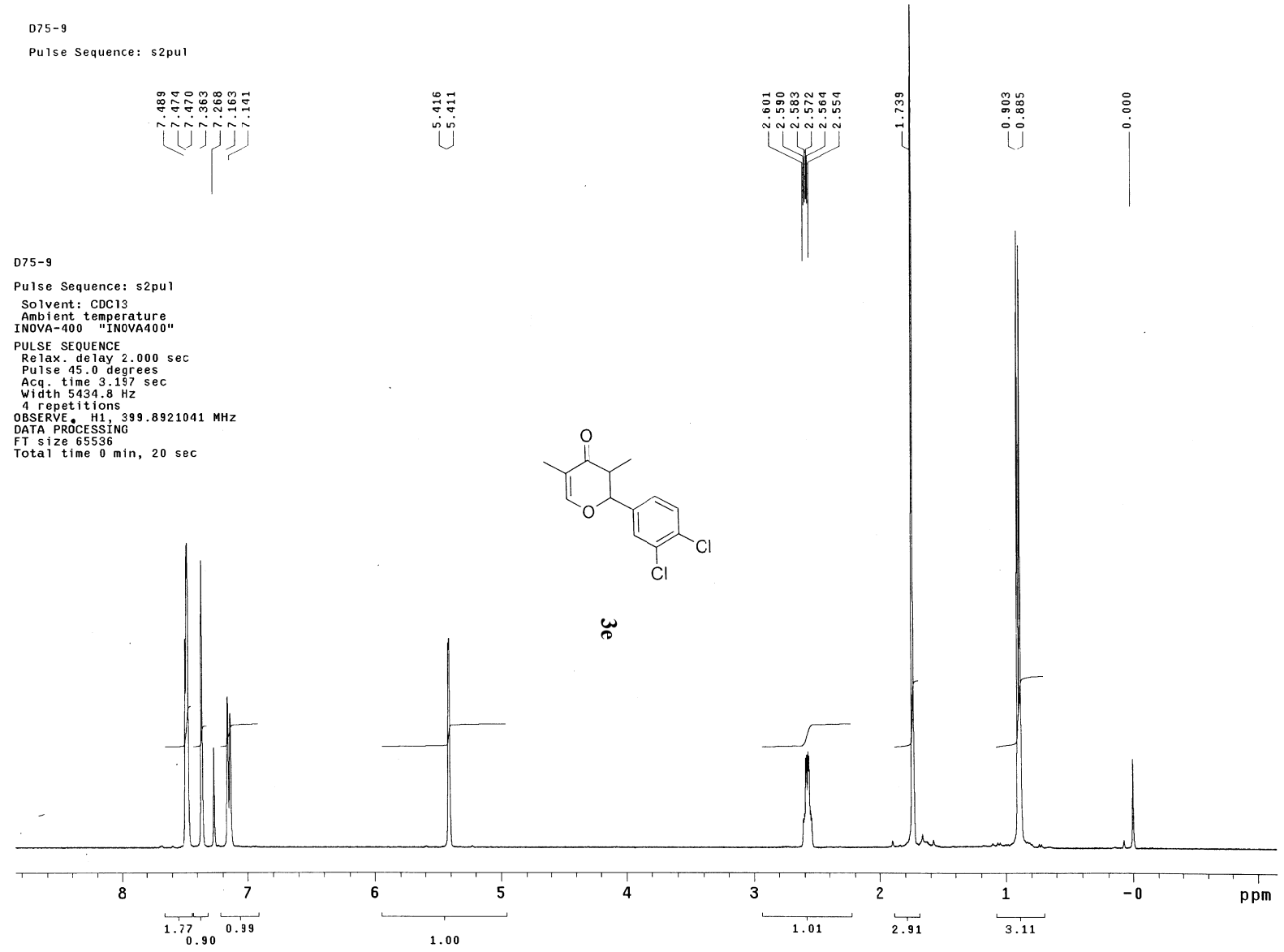
SI	32768
SF	75.4677538 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

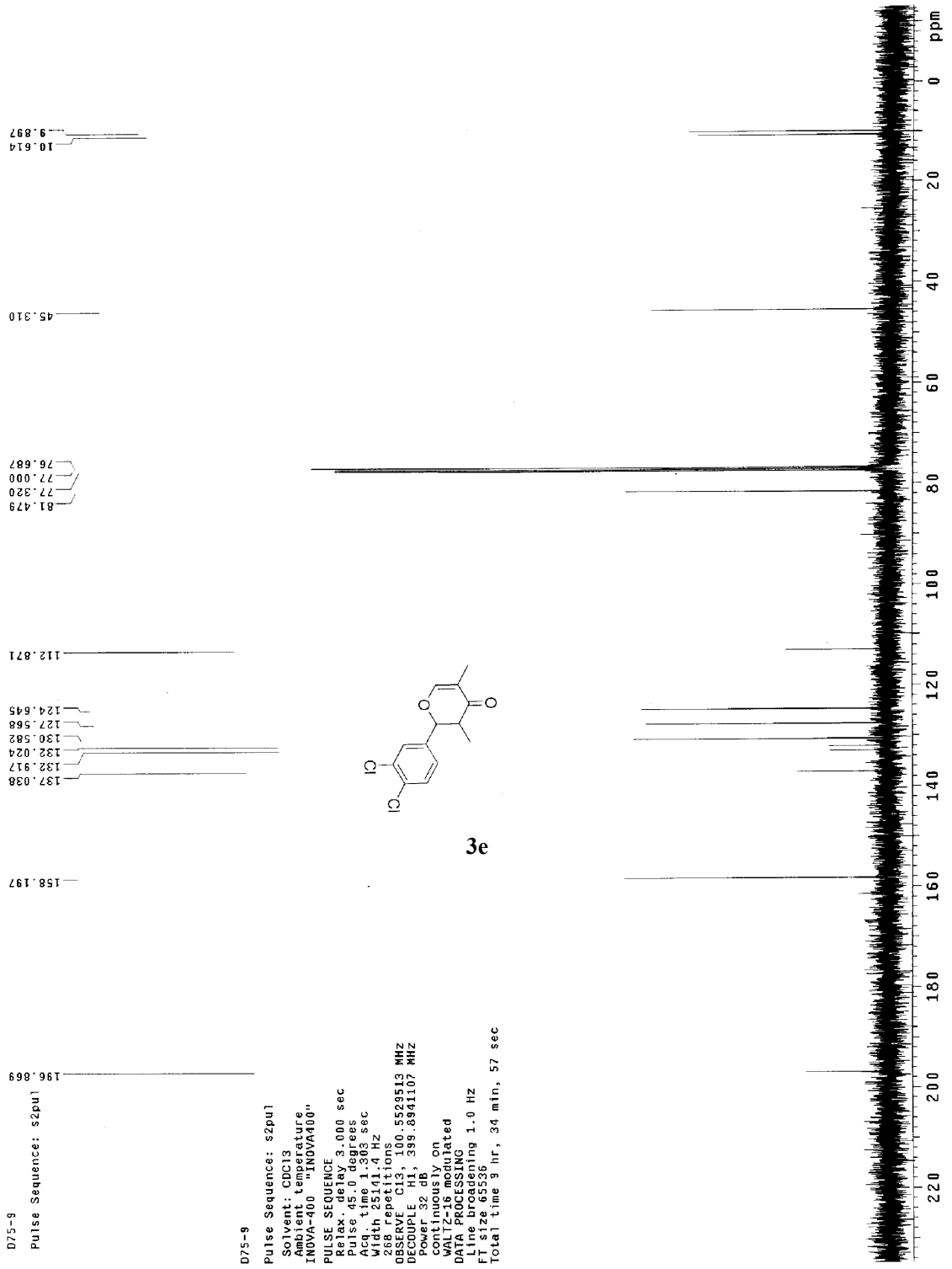
1D NMR plot parameters

CX	20.00 cm
CY	4.00 cm
F1P	220.000 ppm
F1	16602.91 Hz
F2P	-0.005 ppm
F2	-0.38 Hz
PPMCM	11.00025 ppm/cm
HZCM	830.16412 Hz/cm

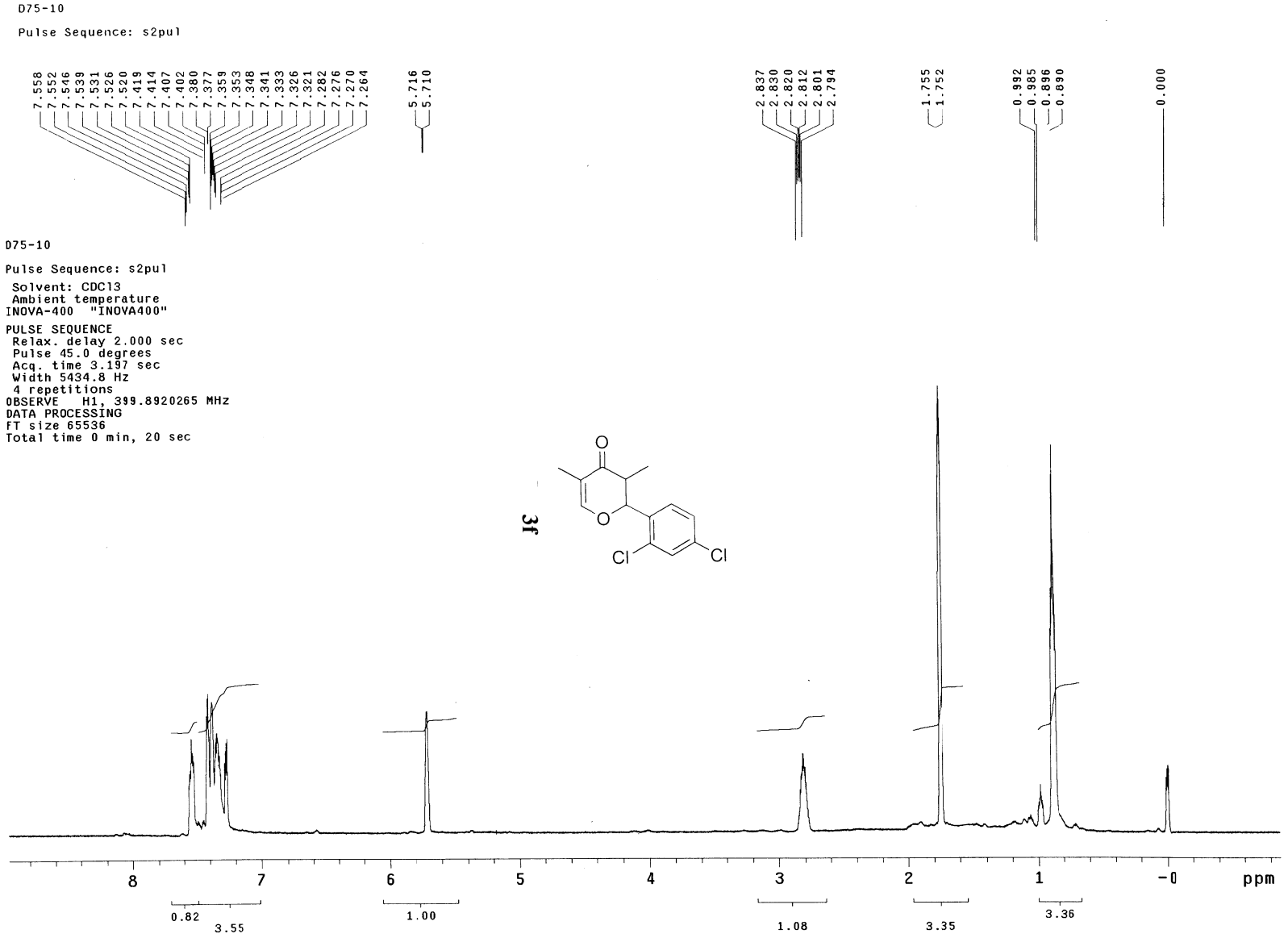

D75-6
Pulse Sequence: s2pul
7.605
7.586
7.399
7.372
7.346
7.328
7.311
7.308
7.292
7.268
5.780
5.773
2.867
2.860
2.849
2.841
1.754
0.998
0.981
0.900
0.881
0.000
ppm
3d
Cl
O
O
D75-6
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.201 sec
Width 3968.6 Hz
4 repetitions
OBSERVE H1, 399.8921042 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 20 sec

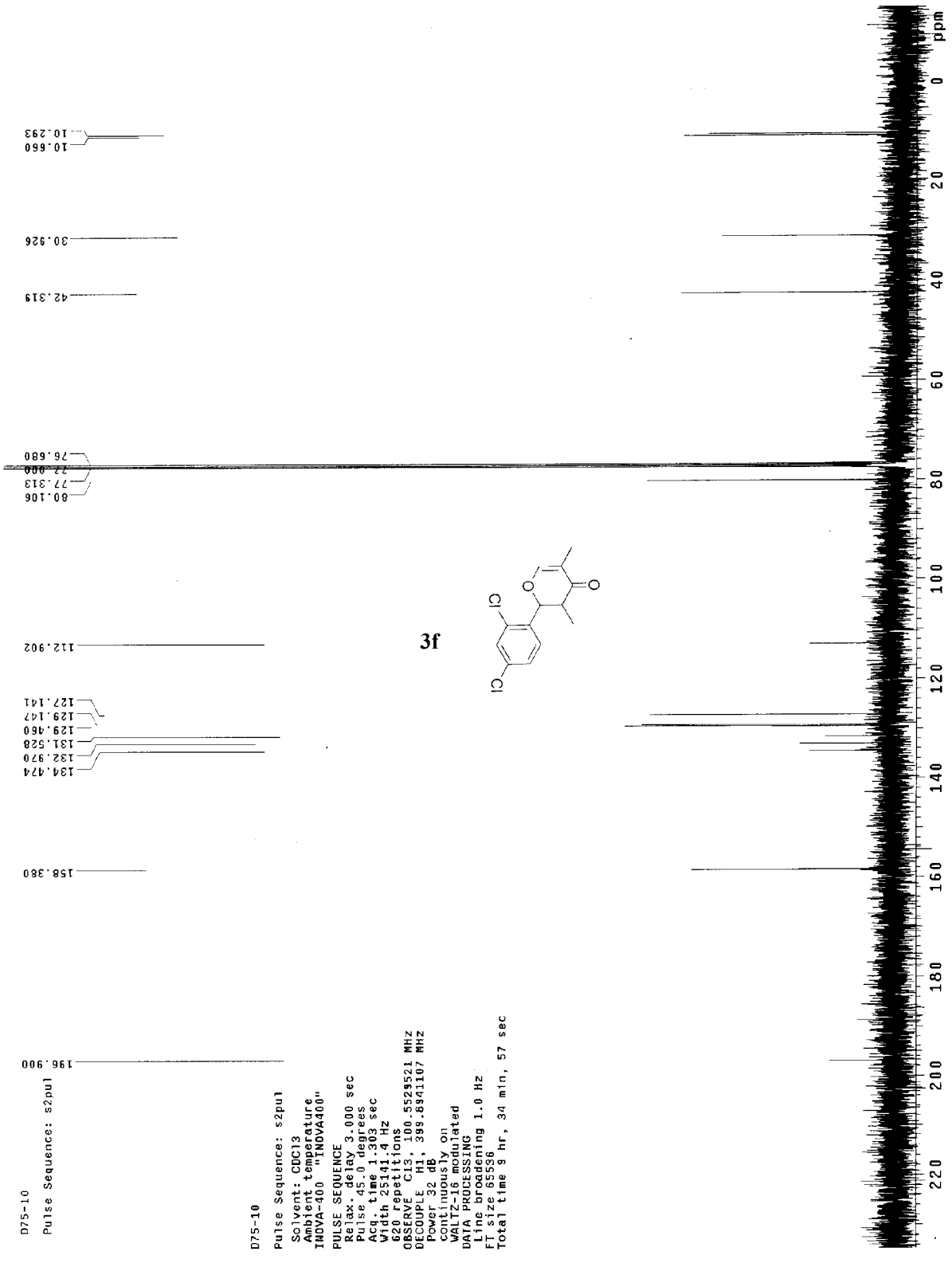

10.347
10.683
42.395
76.680
77.000
77.320
80.525
112.711
126.736
128.201
129.231
129.628
130.872
134.275
158.762
197.457
ppm
0
20
40
60
80
100
120
140
160
180
200
220
O
O
O
Cl
3d
D75-5
Pulse Sequence: s2pul
D75-6
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
468 repetitions
OBSERVE C13, 100.5529521 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 58 min, 41 sec

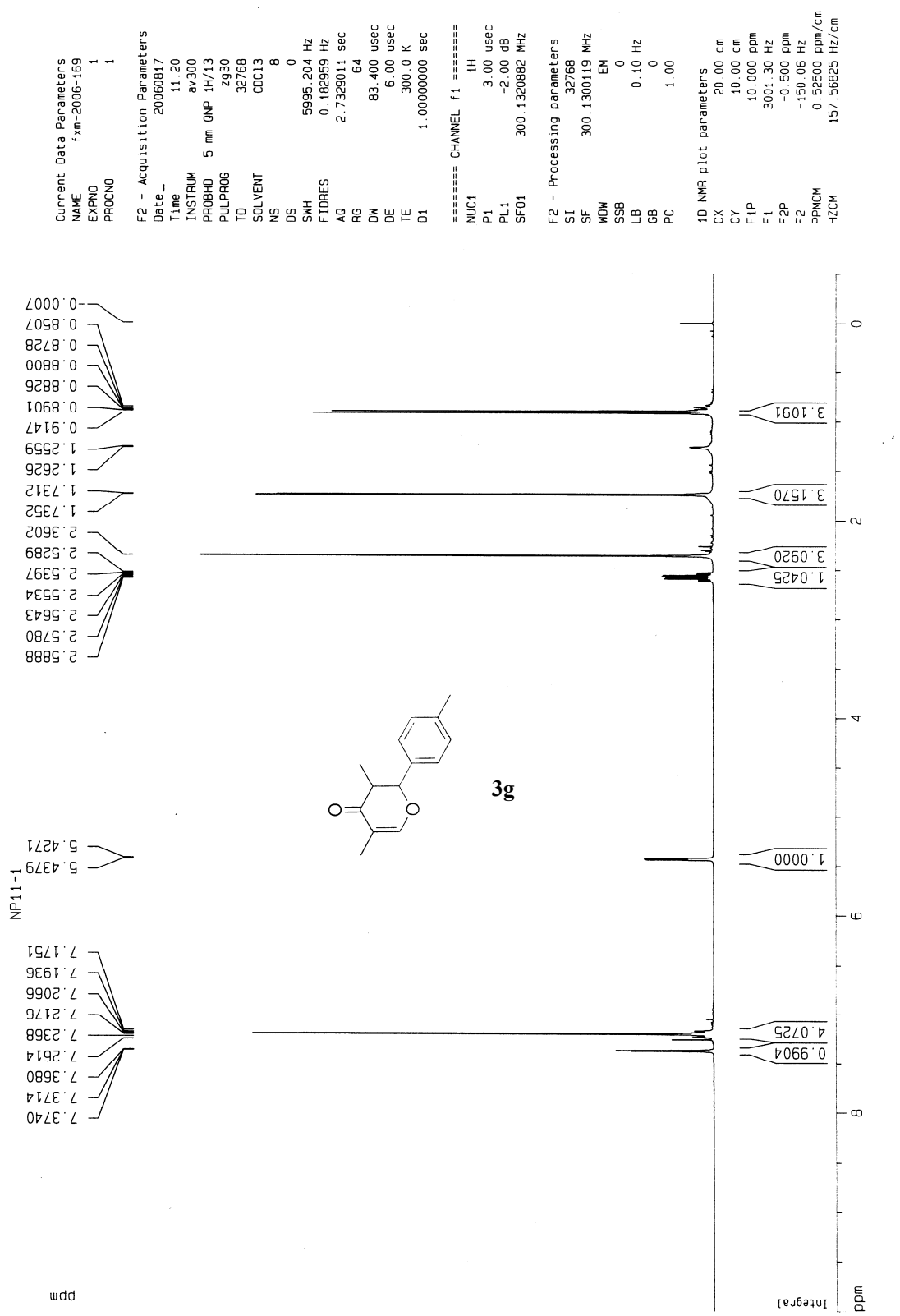

D75-9
Pulse Sequence: s2pul
7.489
7.474
7.470
7.363
7.268
7.163
7.141
5.416
5.411
2.601
2.590
2.583
2.572
2.564
2.554
1.739
0.903
0.885
0.000
D75-9
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.197 sec
Width 5434.8 Hz
4 repetitions
OBSERVE H1, 399.8921041 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 20 sec
O
O
Cl
Cl
3e
8
7
6
5
4
3
2
1
-0
ppm
1.77
0.90
0.99
1.00
1.01
2.91
3.11

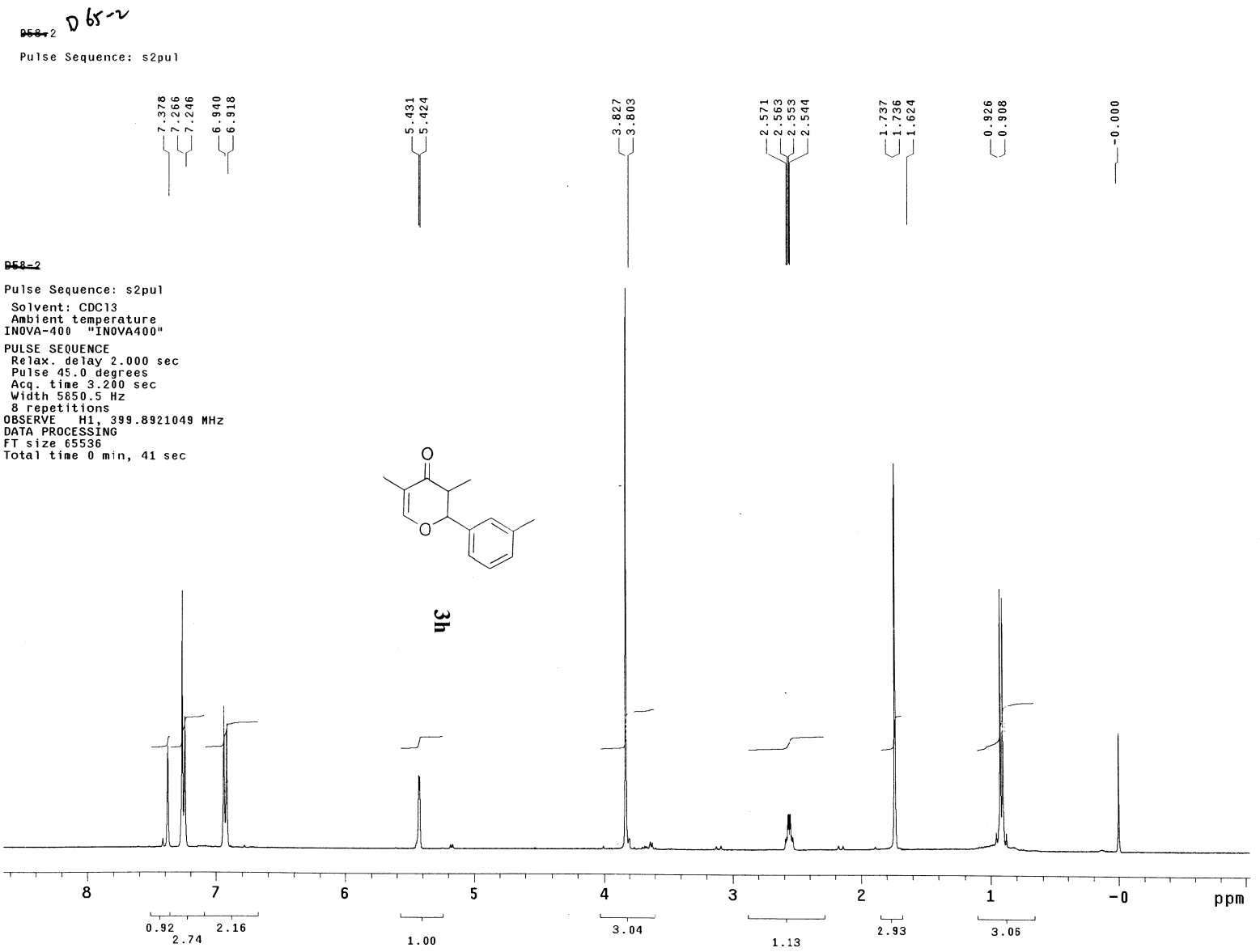

D75-9
Pulse Sequence: s2pul
196.869
158.197
137.038
132.917
132.024
130.582
127.568
124.645
112.871
81.479
77.320
77.000
76.687
45.310
10.614
9.897
ppm
0
20
40
60
80
100
120
140
160
180
200
220
D75-9
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
268 repetitions
OBSERVE C13, 100.5529513 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 9 hr, 34 min, 57 sec
O
O
Cl
Cl

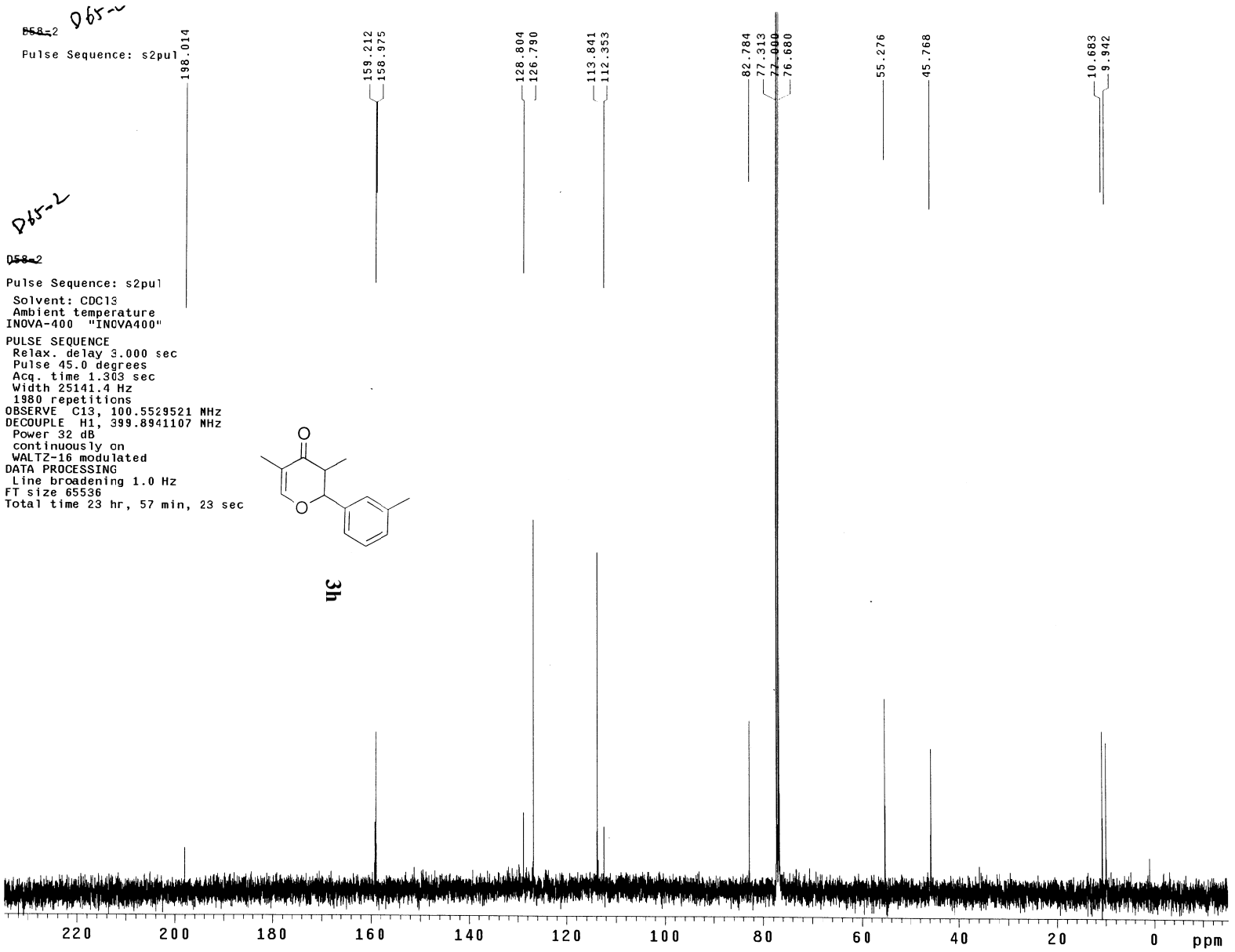
3e

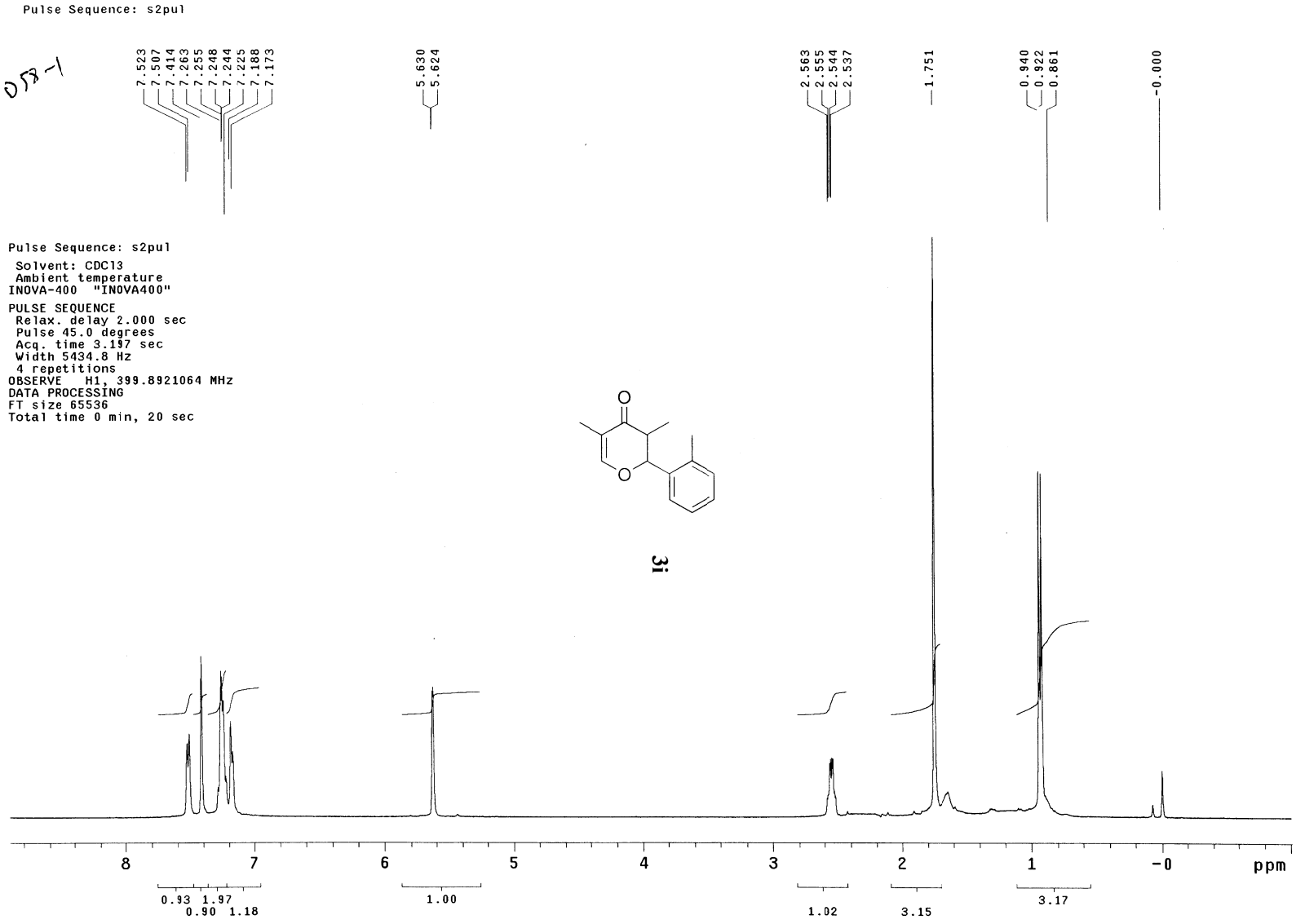

D75-10
Pulse Sequence: s2pul
7.558
7.552
7.546
7.539
7.531
7.526
7.520
7.419
7.414
7.407
7.402
7.380
7.377
7.359
7.353
7.348
7.341
7.333
7.326
7.321
7.282
7.276
7.270
7.264
5.716
5.710
2.837
2.830
2.820
2.812
2.801
2.794
1.755
1.752
0.992
0.985
0.896
0.890
0.000
D75-10
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.197 sec
Width 5434.8 Hz
4 repetitions
OBSERVE H1, 399.8920265 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 20 sec
O
O
Cl
Cl
3f
8
7
6
5
4
3
2
1
-0
ppm
0.82
3.55
1.00
1.08
3.35
3.36


10.293
10.660
30.926
42.319
76.680
77.000
77.313
80.106
112.902
127.141
129.147
129.460
131.528
132.970
134.474
158.380
196.900
3f
Cl
Cl
O
O
ppm
0
20
40
60
80
100
120
140
160
180
200
220
D75-10
Pulse Sequence: s2pul
D75-10
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
620 repetitions
OBSERVE C13, 100.5529521 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 9 hr, 34 min, 57 sec

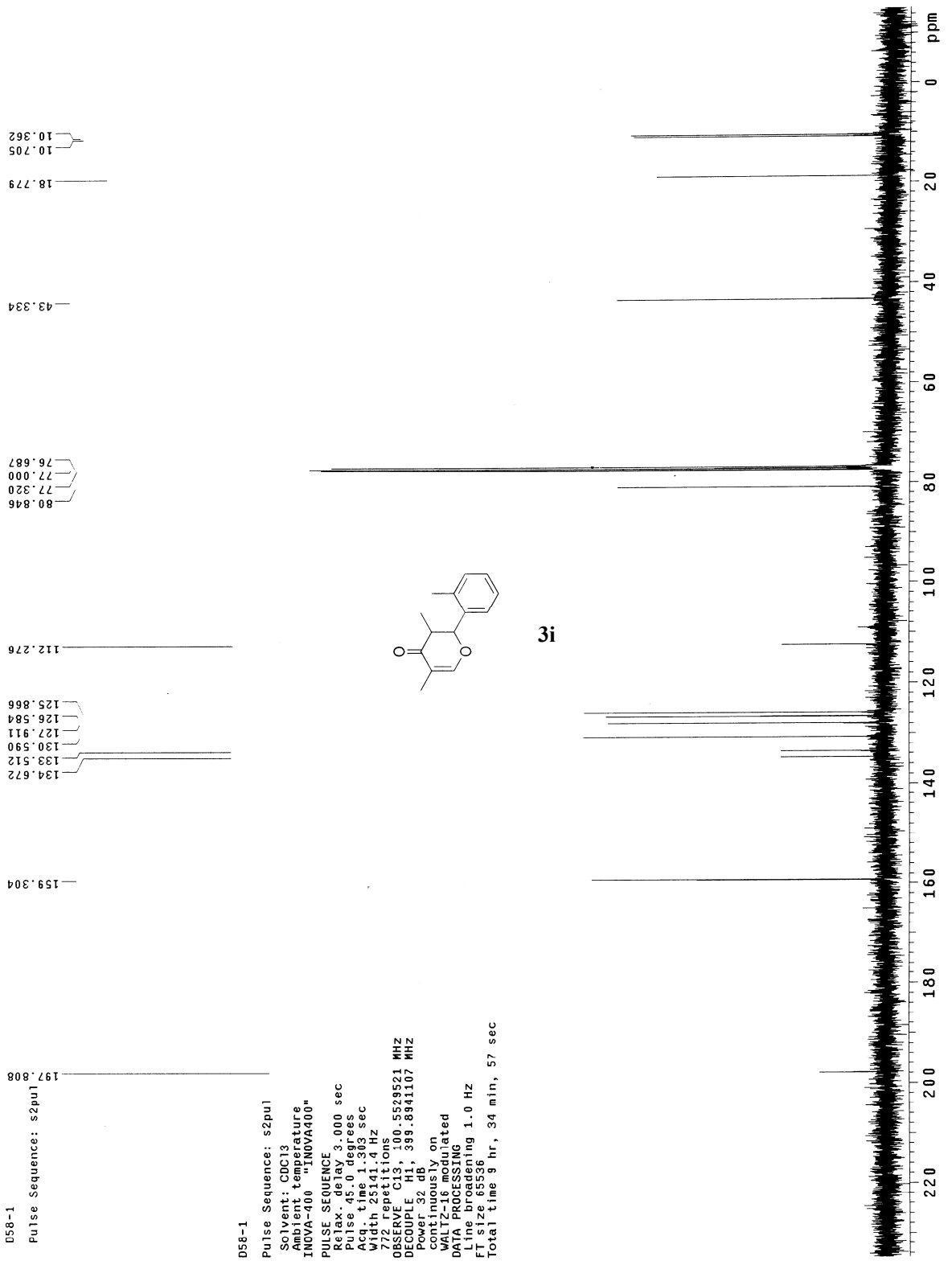

Current Data Parameters
NAME fxm-2006-169
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060817
Time 11.20
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 64
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300119 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
NP11-1
7.3740
7.3714
7.3680
7.2614
7.2368
7.2176
7.2066
7.1936
7.1751
5.4379
5.4271
2.5888
2.5780
2.5643
2.5534
2.5397
2.5289
2.3602
1.7352
1.7312
1.2626
1.2559
0.9147
0.8901
0.8826
0.8800
0.8728
0.8507
0.0007
3g
4.0725
0.9904
1.0000
1.0425
3.0920
3.1570
3.1091
Integral
ppm

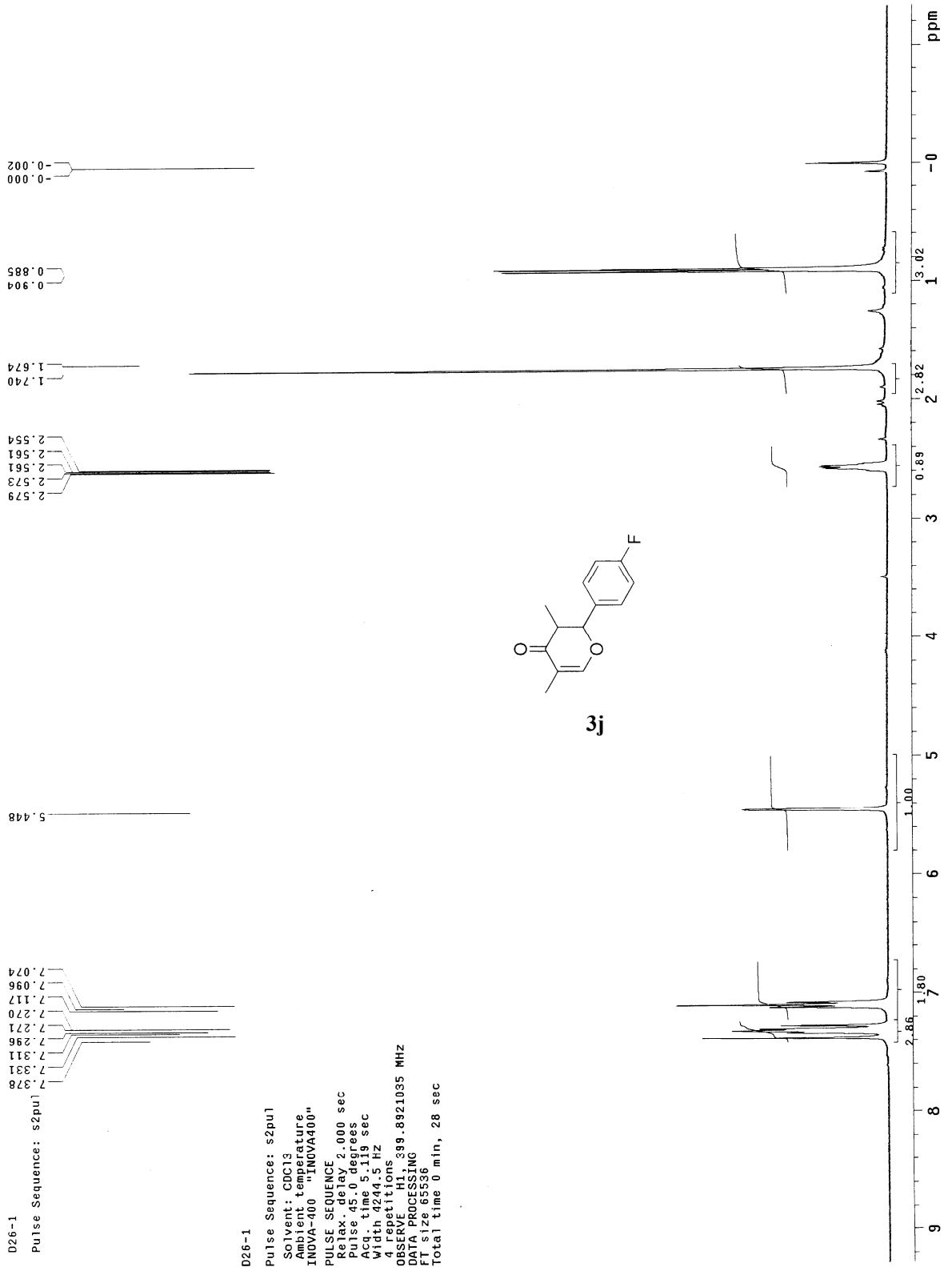

D58-2 D65-2
Pulse Sequence: s2pul
7.378
7.266
7.246
6.940
6.918
5.431
5.424
3.827
3.803
2.571
2.563
2.553
2.544
1.737
1.736
1.624
0.926
0.908
-0.000
D58-2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5850.5 Hz
8 repetitions
OBSERVE H1, 399.8921049 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 41 sec
O
O
3h
8
7
6
5
4
3
2
1
-0
ppm
0.92
2.16
2.74
1.00
3.04
1.13
2.93
3.05

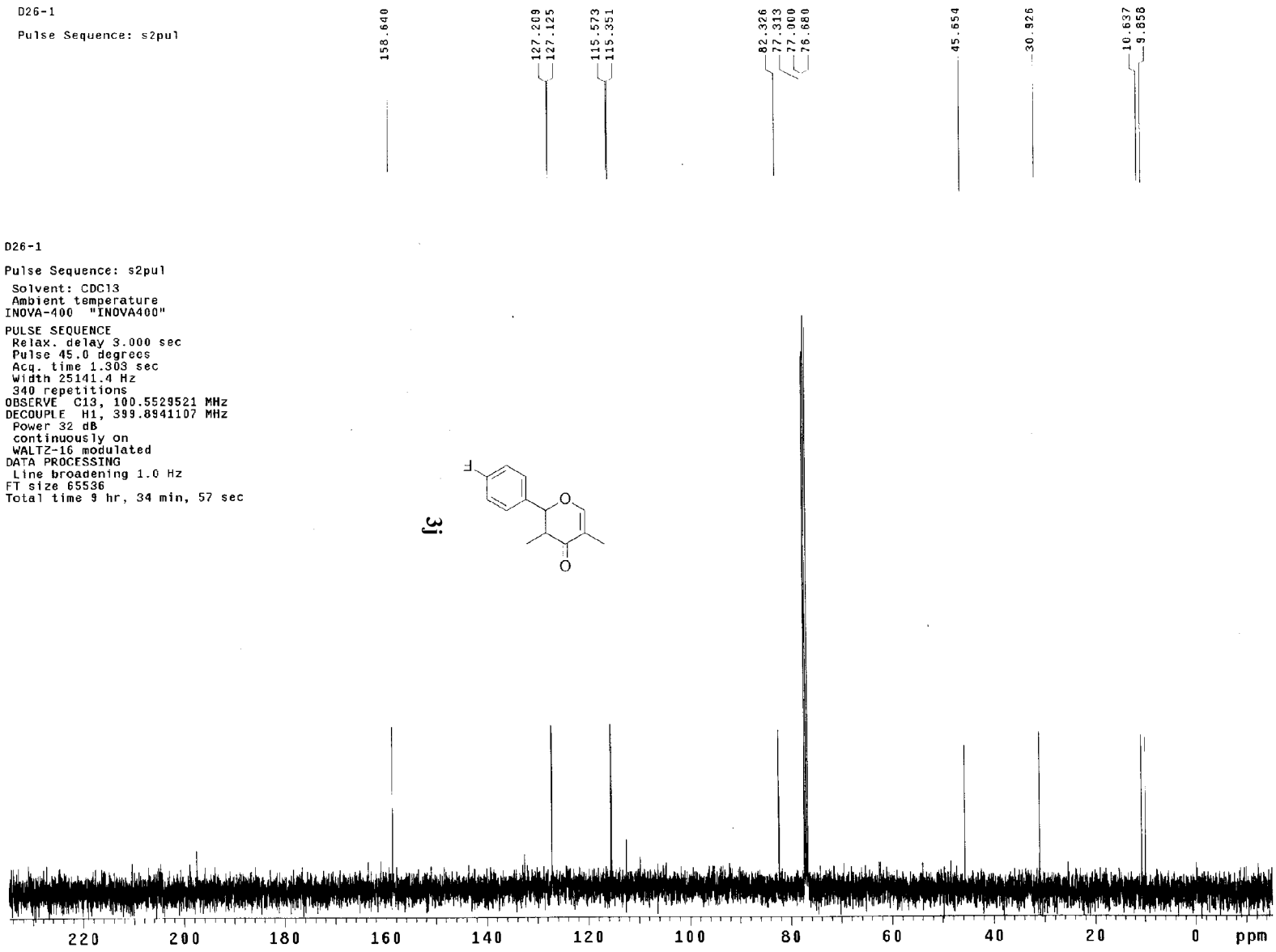

D65-2
~~D58-2~~
Pulse Sequence: s2pul
198.014
159.212
158.975
128.804
126.790
113.841
112.353
82.784
77.313
77.000
76.680
55.276
45.768
10.683
9.942
D65-2
~~D58-2~~
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
1980 repetitions
OBSERVE C13, 100.5529521 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 23 hr, 57 min, 23 sec
O
O
3h
220
200
180
160
140
120
100
80
60
40
20
0
ppm

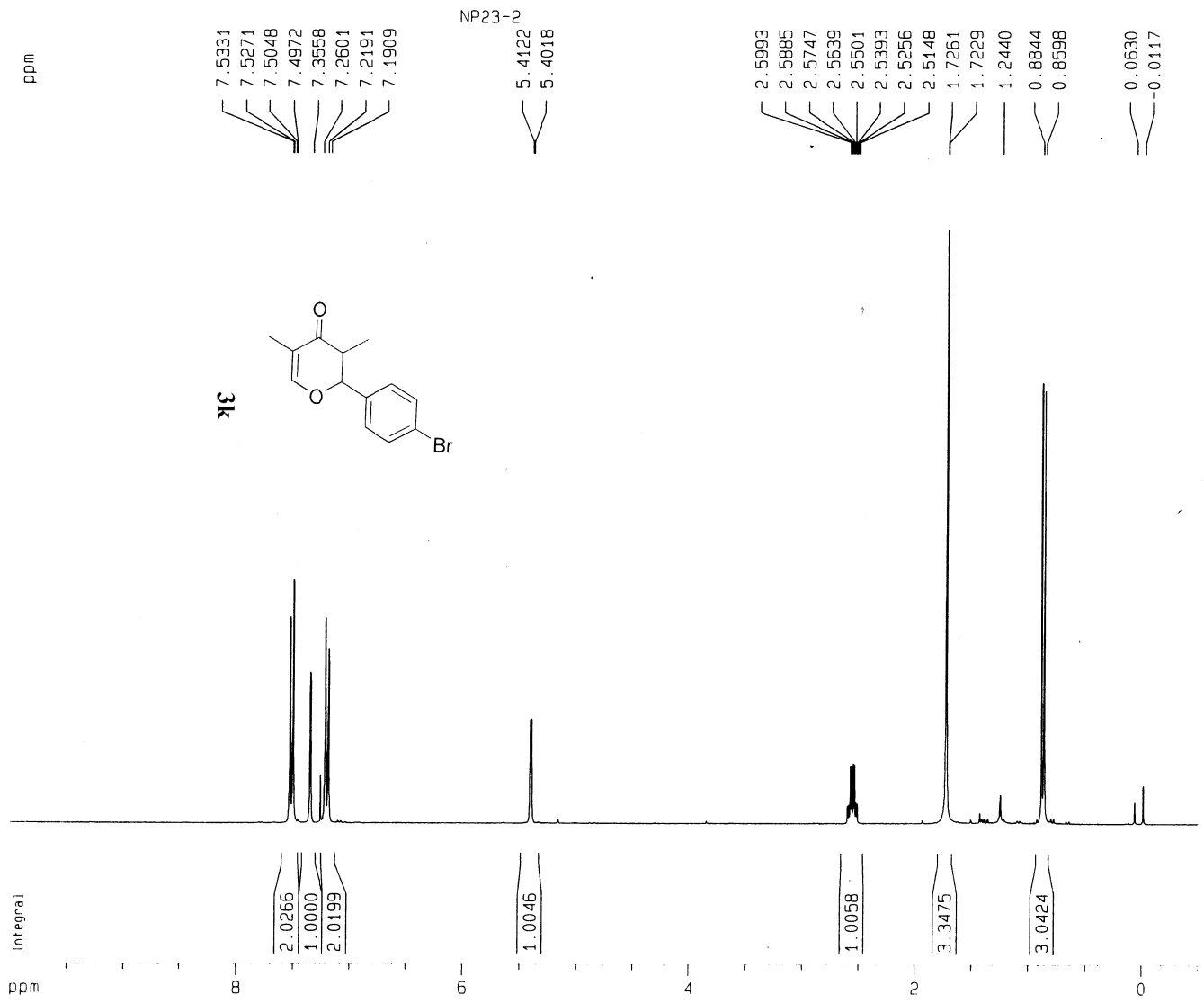

Pulse Sequence: s2pul
7.523
7.507
7.414
7.263
7.255
7.248
7.244
7.225
7.188
7.173
5.630
5.624
2.563
2.555
2.544
2.537
1.751
0.940
0.922
0.861
-0.000
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.197 sec
Width 5434.8 Hz
4 repetitions
OBSERVE H1, 399.8921064 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 20 sec
O
O
8
7
6
5
4
3
2
1
-0
ppm
0.93
1.97
0.90
1.18
1.00
1.02
3.15
3.17

3i


D58-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.383 sec
Width 25141.4 Hz
772 repetitions
OBSERVE C13, 100.5529521 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 9 hr, 34 min, 57 sec
197.808
159.304
134.672
133.512
130.590
127.911
126.584
125.866
112.276
80.846
77.320
77.000
76.687
43.334
18.779
10.705
10.362
ppm
3i


D26-1
Pulse Sequence: s2pul
7.378
7.331
7.311
7.296
7.271
7.270
7.117
7.096
7.074
5.448
2.579
2.573
2.561
2.561
2.554
1.740
1.674
0.904
0.885
-0.000
-0.002
D26-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 5.119 sec
Width 4244.5 Hz
4 repetitions
OBSERVE H1, 399.8921035 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 28 sec
F
O
O
3j
1.00
0.89
2.82
3.02
1.80
2.86
ppm


D26-1
Pulse Sequence: s2pul
158.640
127.209
127.125
115.573
115.351
82.326
77.313
77.000
76.680
45.654
30.826
10.637
9.858
D26-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
340 repetitions
OBSERVE C13, 100.5529521 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 9 hr, 34 min, 57 sec
3j
F
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm



Current Data Parameters

NAME	fxm-2006-191
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20060830
Time	16.28
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
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	300.0 K
D1	1.00000000 sec

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

NUC1	1H
P1	3.00 usec
PL1	-2.00 dB
SFO1	300.1320882 MHz

F2 - Processing parameters

SI	32768
SF	300.1300124 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters

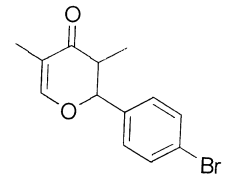
CX	20.00 cm
CY	10.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.52500 ppm/cm
HZCM	157.56825 Hz/cm

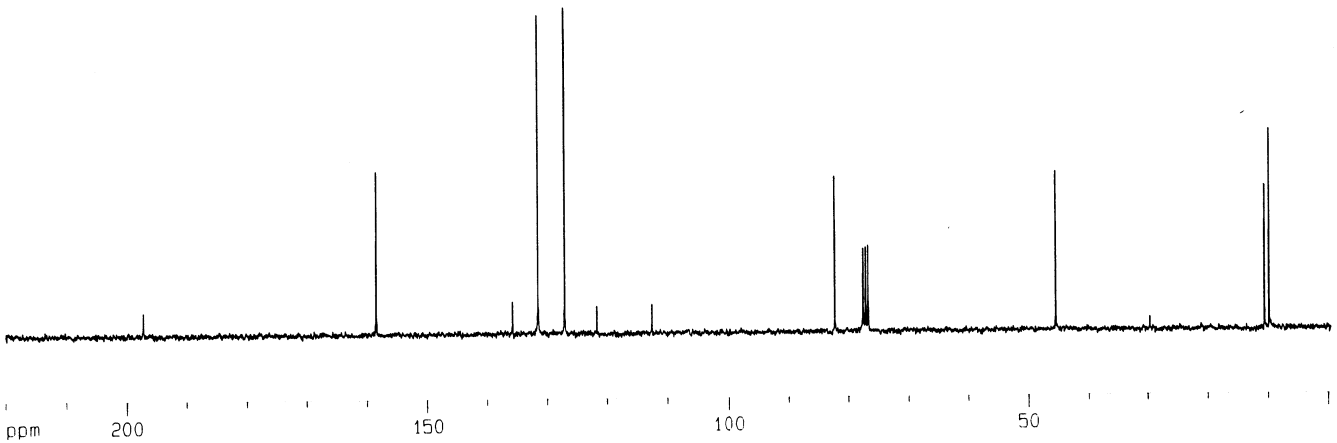
NP23-2

ppm

197.226
158.465
135.811
131.651
127.123
121.839
112.652
82.237
77.424
77.000
76.577
45.431
10.585
9.833

3k





Current Data Parameters
NAME fxm-2006-191
EXPNO 2
PROCNO 1

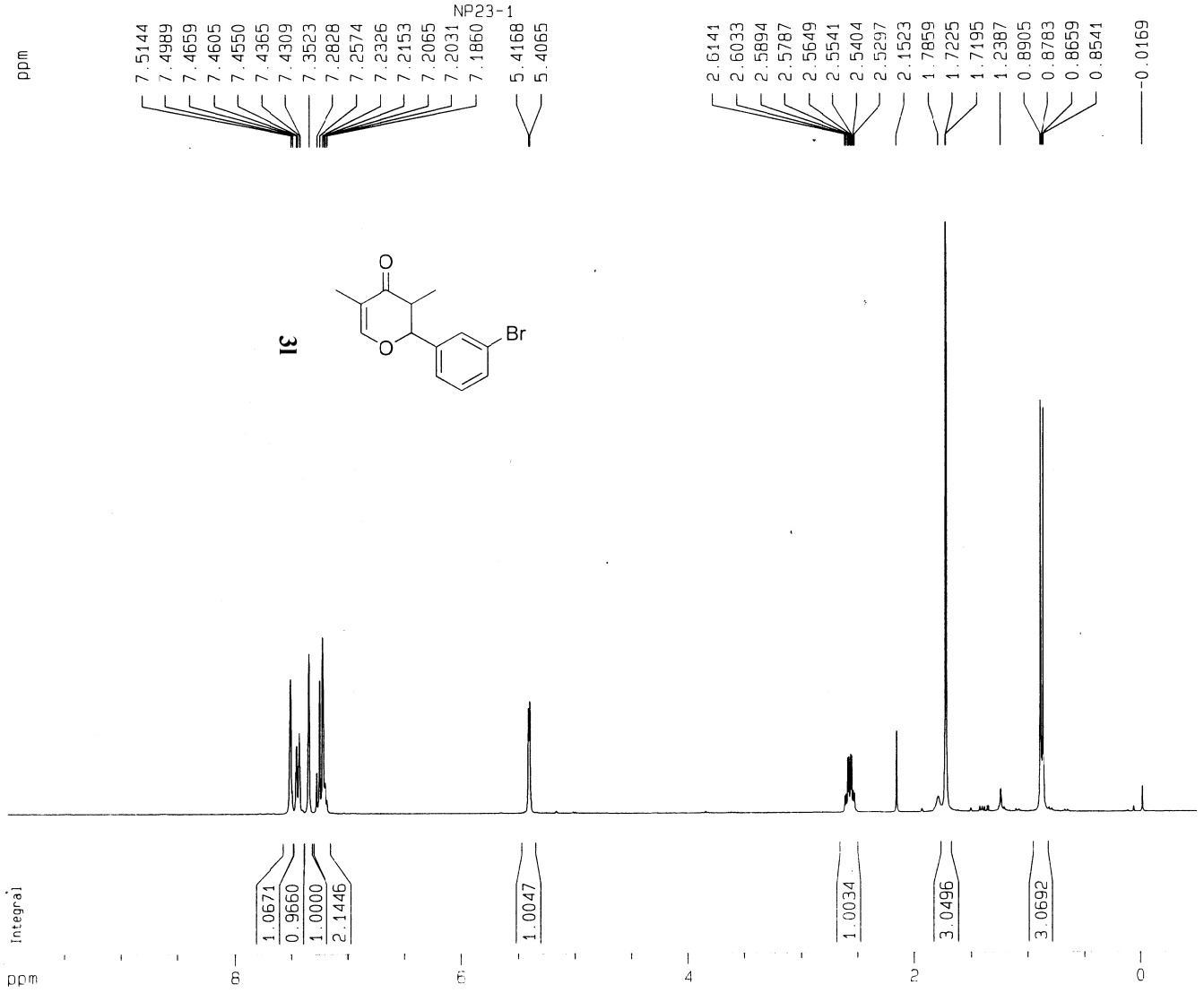
F2 - Acquisition Parameters
Date_ 20060830
Time 16.29
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT DMSO
NS 278
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677535 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 220.050 ppm
F1 16606.68 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCM 11.02750 ppm/cm
HZCM 832.22058 Hz/cm



Current Data Parameters

NAME	fxm-2006-190
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20060830
Time	15.22
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
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	300.0 K
D1	1.00000000 sec

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

NUC1	1H
P1	3.00 usec
PL1	-2.00 dB
SFO1	300.1320882 MHz

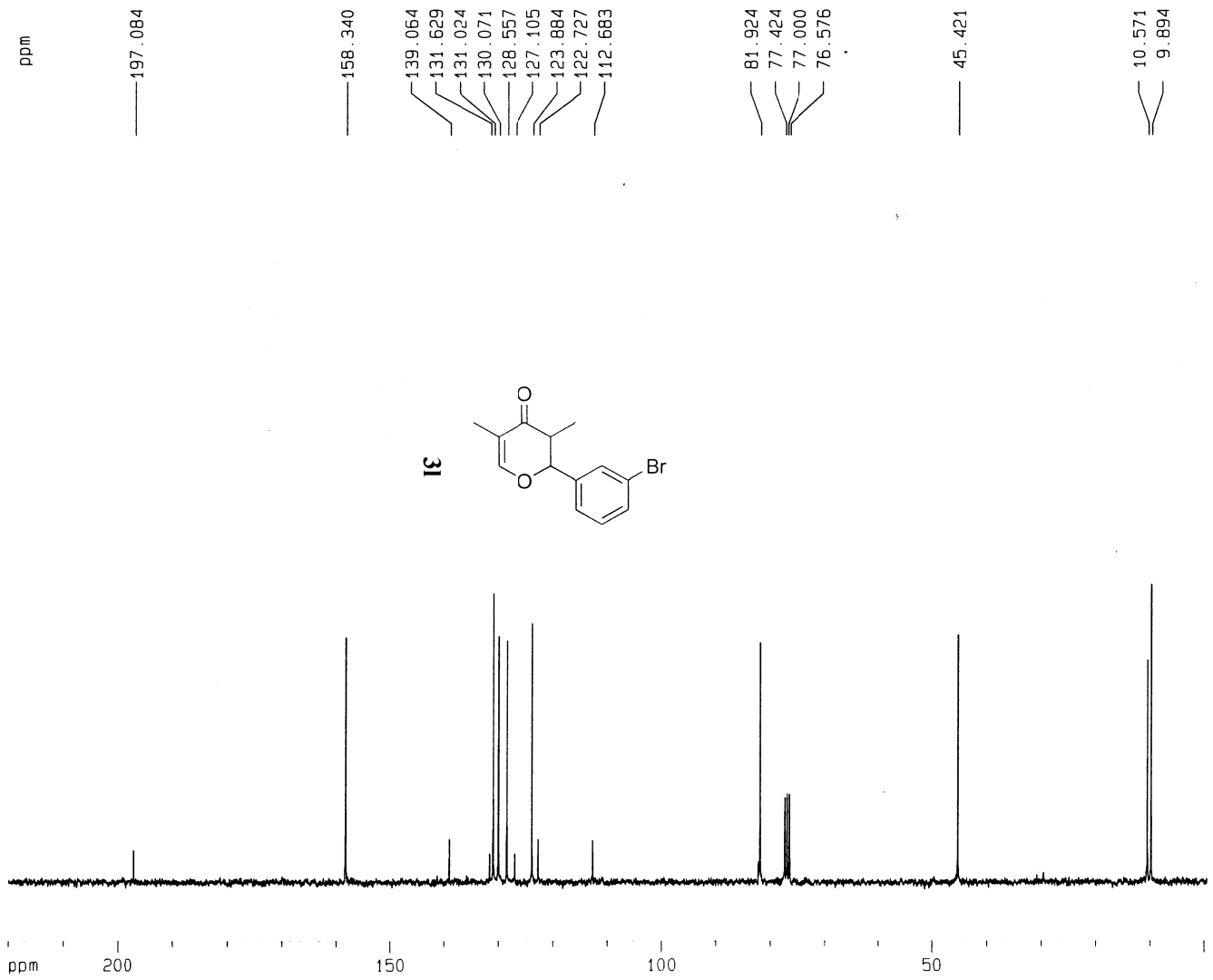
F2 - Processing parameters

SI	32768
SF	300.1300124 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

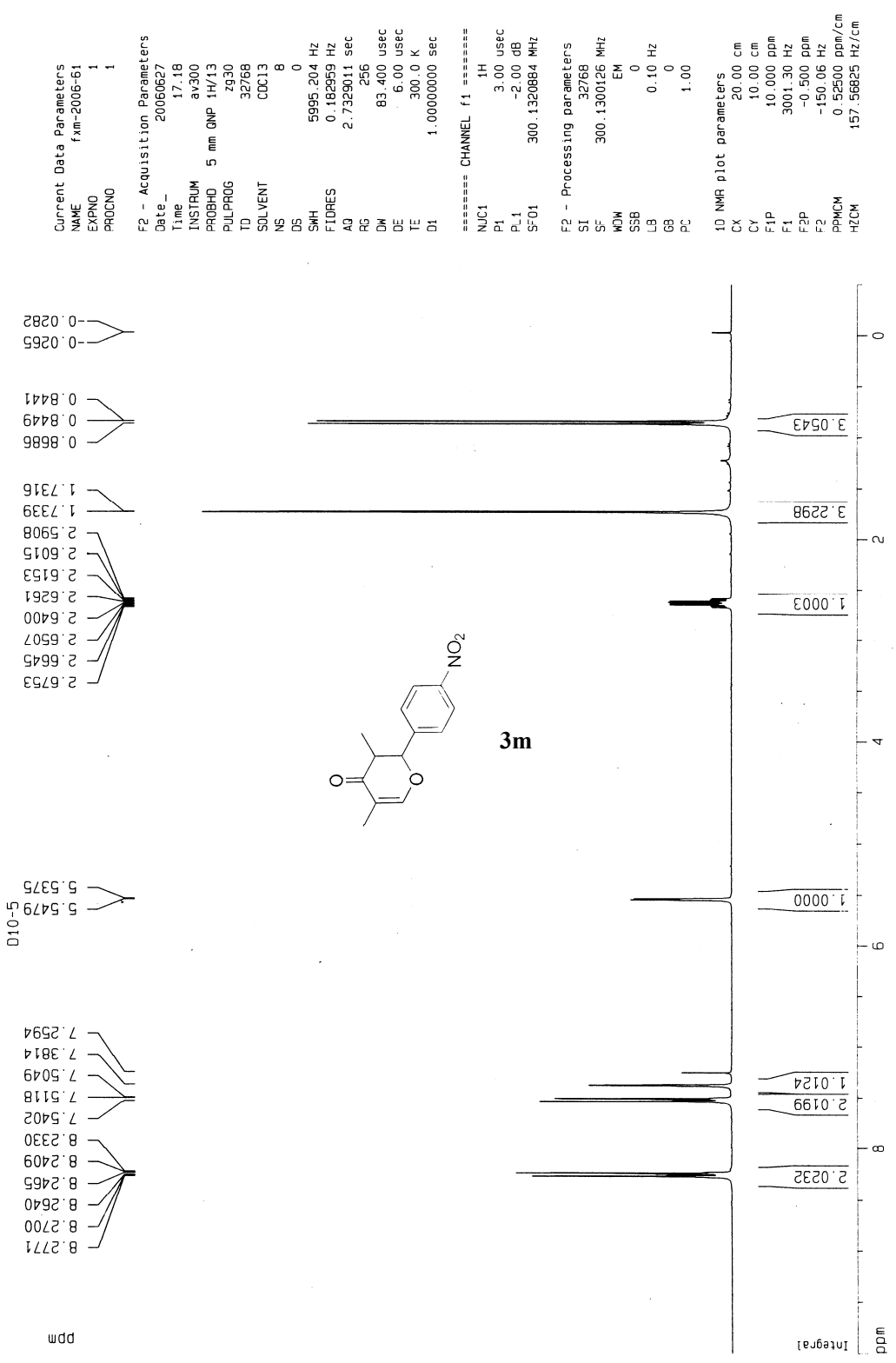
1D NMR plot parameters

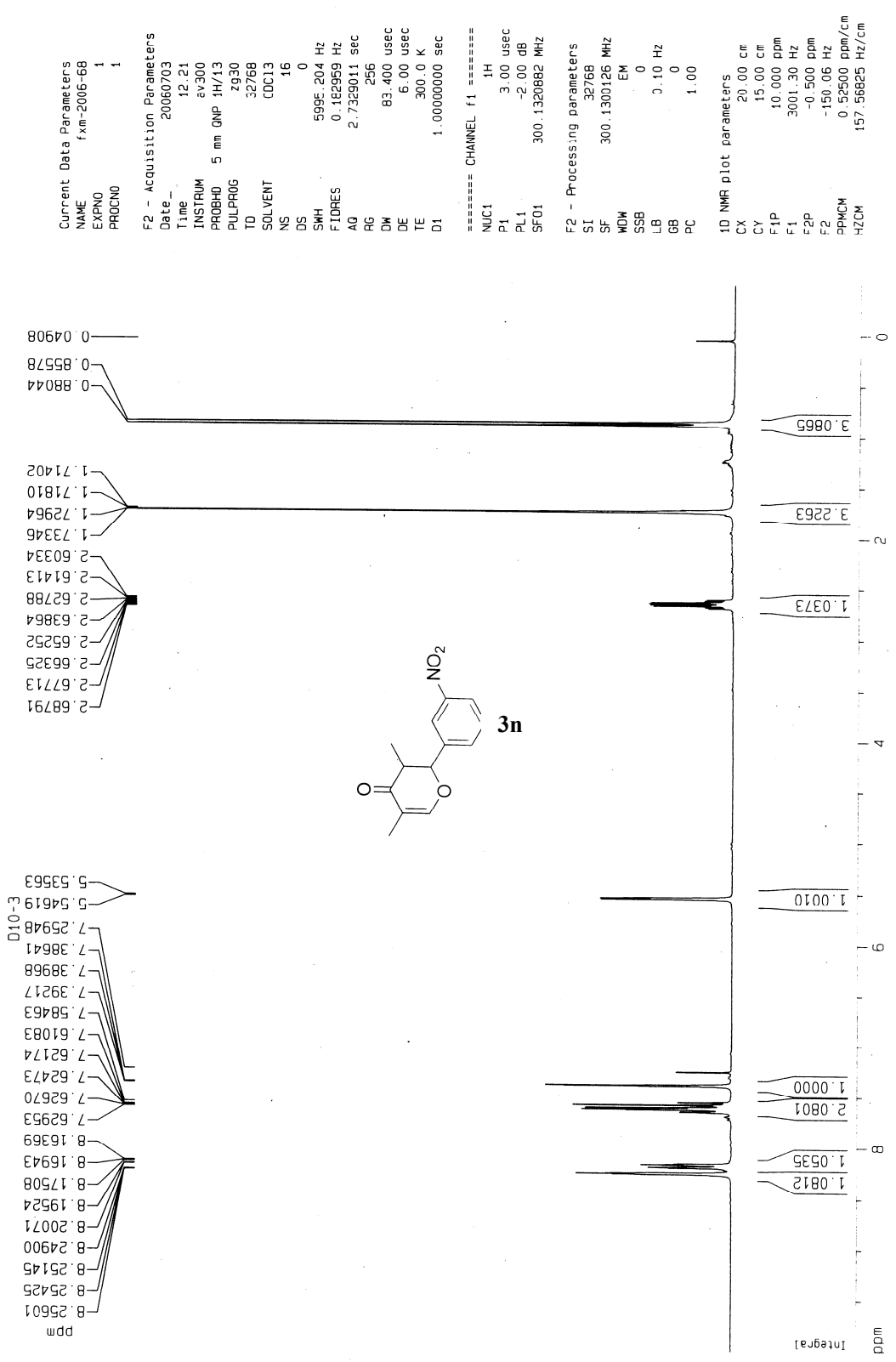
CX	20.00 cm
CY	10.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.52500 ppm/cm
HZCM	157.56825 Hz/cm

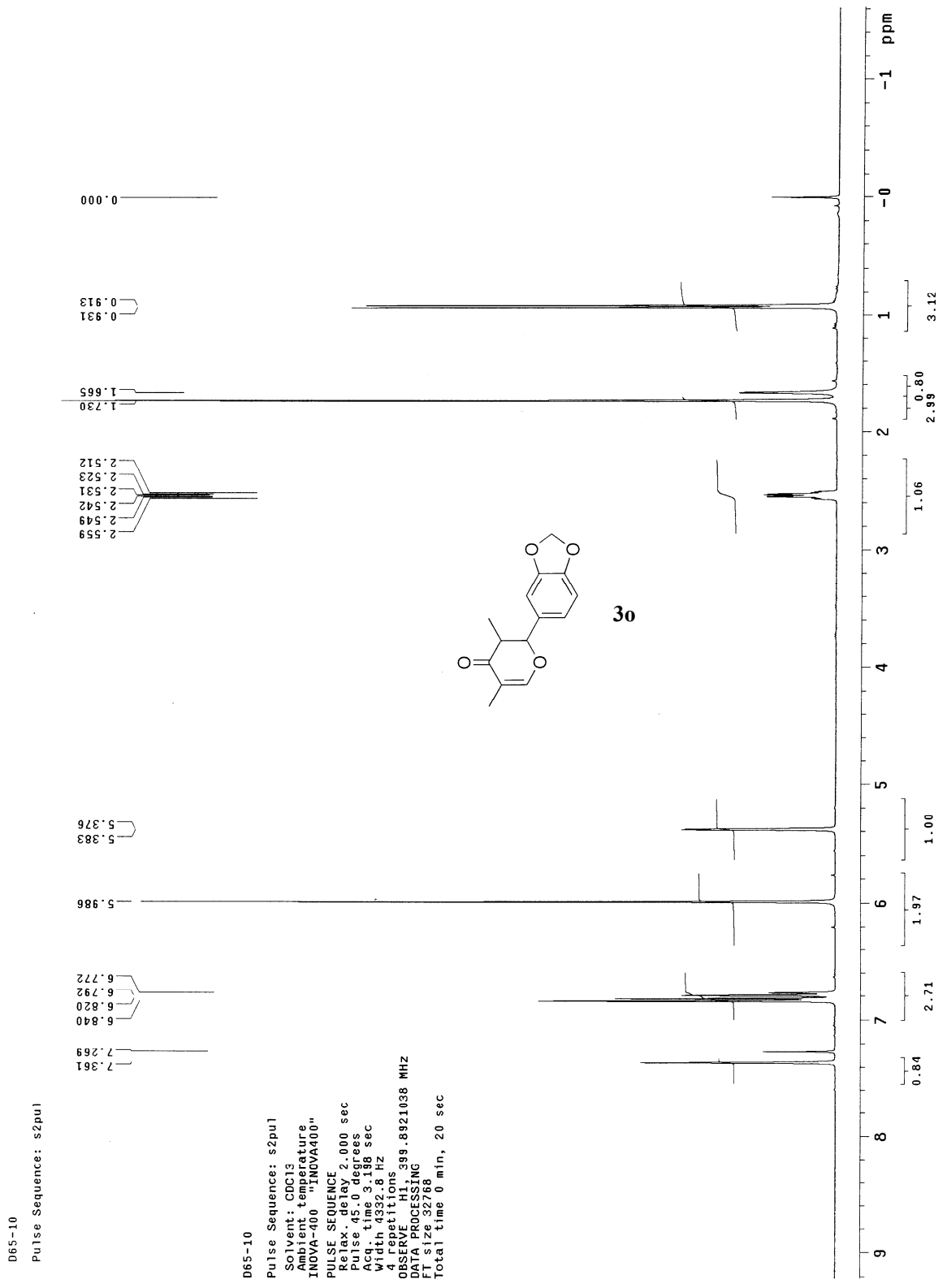
NP23-1

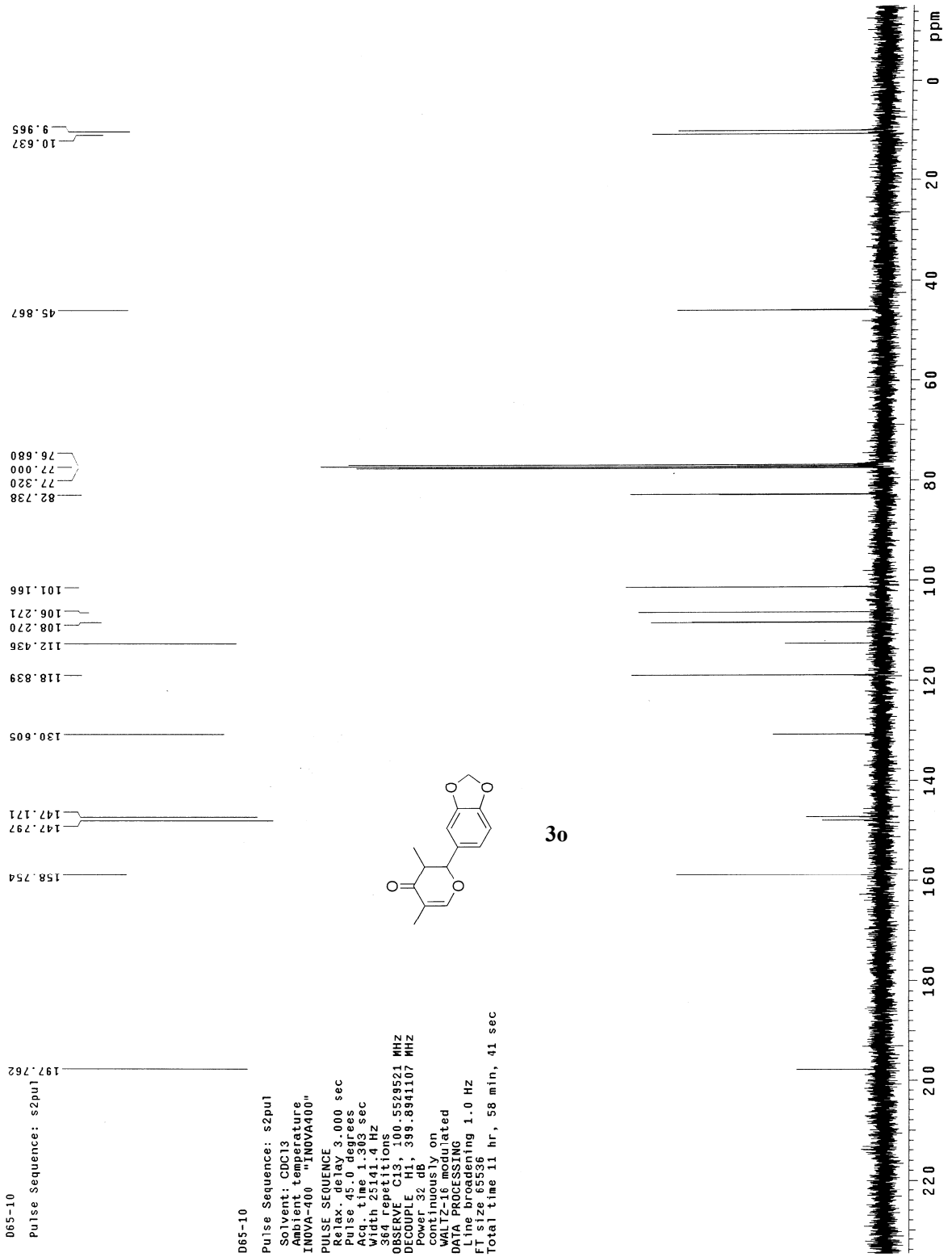



```
Current Data Parameters
NAME        fxm-2006-190
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060830
Time               15.23
INSTRUM            av300
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg
TD                 65536
SOLVENT             DMSO
NS                   240
DS                     4
SWH          22675.736 Hz
FIDRES        0.346004 Hz
AQ            1.4451188 sec
RG                  8192
DW               22.050 usec
DE                6.00 usec
TE               300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                5.50 usec
PL1              -6.00 dB
SFO1         75.4775598 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            80.00 usec
PL2              -2.00 dB
PL12             17.70 dB
PL13             17.71 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF          75.4677547 MHz
WDW                    EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                  5.00 cm
F1P              220.050 ppm
F1              16606.68 Hz
F2P               -0.500 ppm
F2               -37.73 Hz
PPMCM          11.02750 ppm/cm
HZCM          832.22070 Hz/cm
```

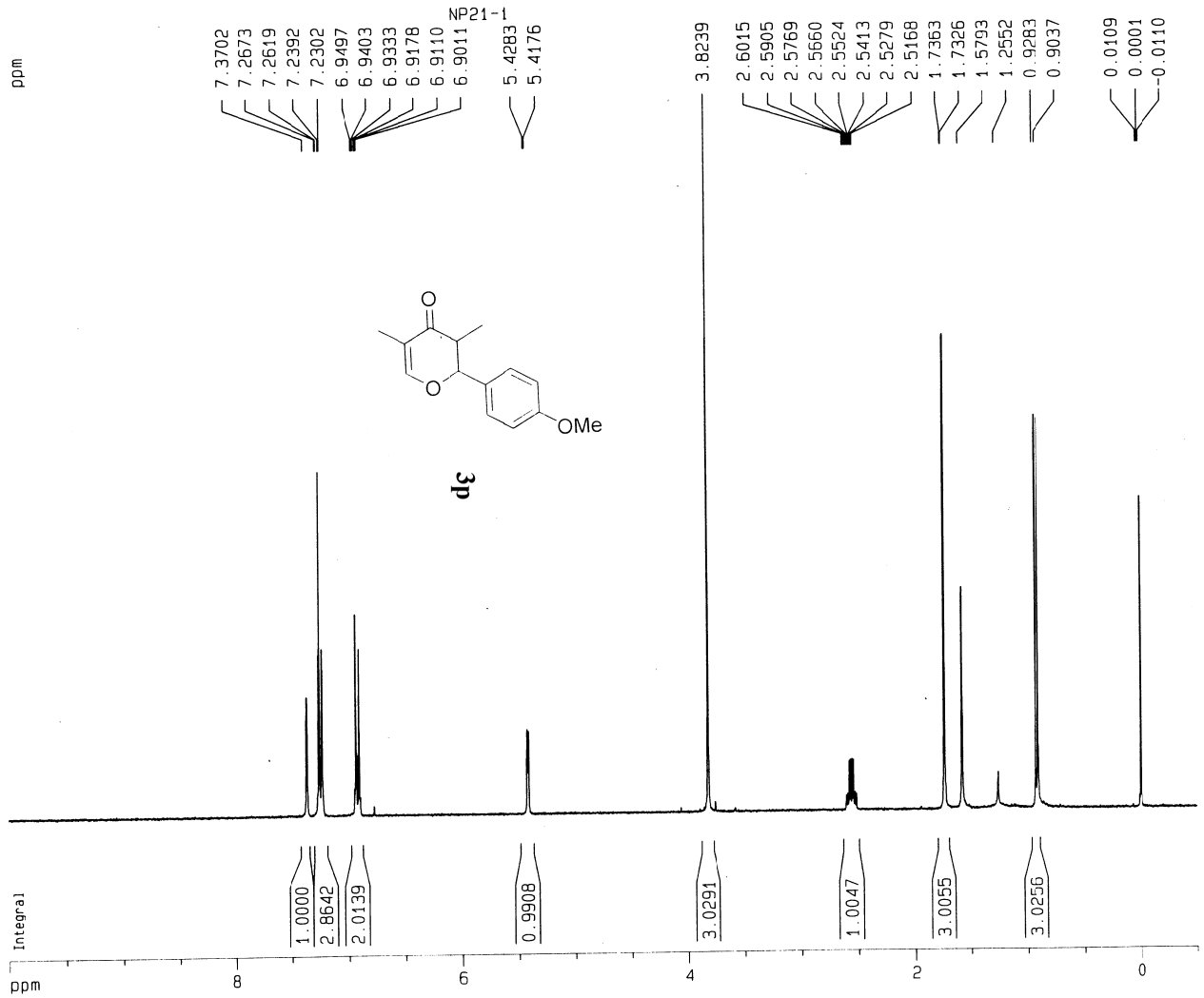

Current Data Parameters
NAME fxm-2006-61
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060627
Time 17.18
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 256
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320884 MHz
F2 - Processing parameters
SI 32768
SF 300.1300126 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
8.2771
8.2700
8.2640
8.2465
8.2409
8.2330
7.5402
7.5118
7.5049
7.3814
7.2594
5.5479
5.5375
D10-5
2.6753
2.6645
2.6507
2.6400
2.6261
2.6153
2.6015
2.5908
1.7339
1.7316
0.8686
0.8449
0.8441
0.0282
0.0265
NO2
O
O
3m
2.0232
2.0199
1.0124
1.0000
1.0003
3.2298
3.0543
ppm
Integral


Current Data Parameters
NAME fxm-2006-68
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060703
Time 12.21
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
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 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300126 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
0.04908
0.85578
0.88044
1.71402
1.71810
1.72964
1.73346
2.60334
2.61413
2.62788
2.63864
2.65252
2.66325
2.67713
2.68791
5.53563
5.54619
7.25948
7.38641
7.38968
7.39217
7.58463
7.61083
7.62174
7.62473
7.62670
7.62953
8.16369
8.16943
8.17508
8.19524
8.20071
8.24900
8.25145
8.25425
8.25601
D10-3
3n
3.0865
3.2263
1.0373
1.0010
1.0000
2.0801
1.0535
1.0812
Integral
ppm


D65-10
Pulse Sequence: s2pul
D65-10
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.198 sec
Width 4332.8 Hz
4 repetitions
OBSERVE H1, 399.8921038 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 20 sec
7.361
7.269
6.840
6.820
6.792
6.772
5.986
5.383
5.376
2.559
2.549
2.542
2.531
2.523
2.512
1.730
1.665
0.931
0.913
0.000
0.84
2.71
1.97
1.00
1.06
2.99
0.80
3.12
ppm
3o


D65-10
Pulse Sequence: s2pul
197.762
158.754
147.797
147.171
130.605
118.839
112.436
108.270
106.271
101.166
82.738
77.320
77.000
76.680
45.867
10.637
9.965
ppm
0
20
40
60
80
100
120
140
160
180
200
220
D65-10
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
364 repetitions
OBSERVE C13, 100.5529521 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 58 min, 41 sec

3o



Current Data Parameters

NAME	fxm-2006-171
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20060815
Time	17.29
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	512
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

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

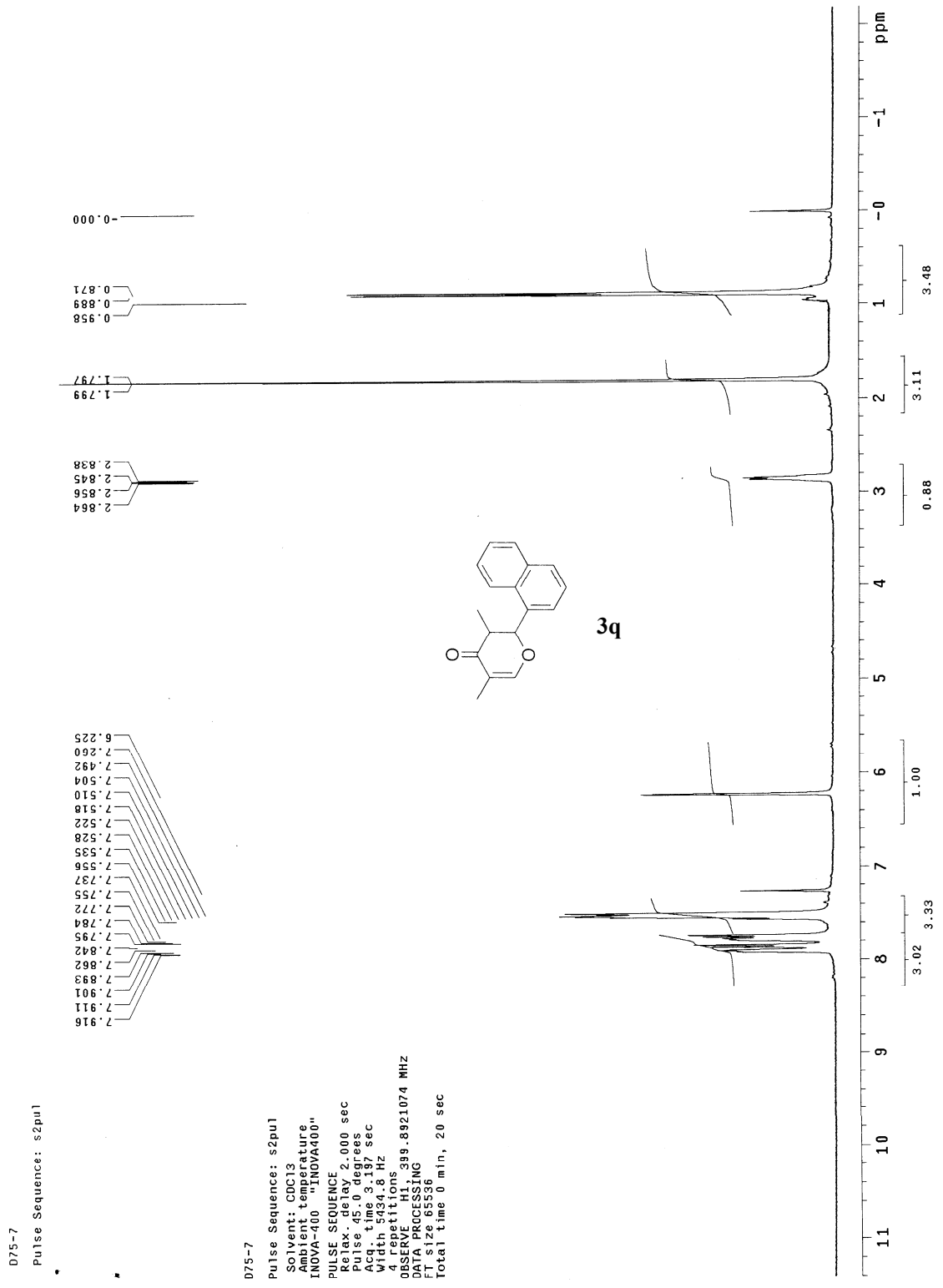
NUC1	1H
P1	3.00 usec
PL1	-2.00 dB
SFO1	300.1320882 MHz

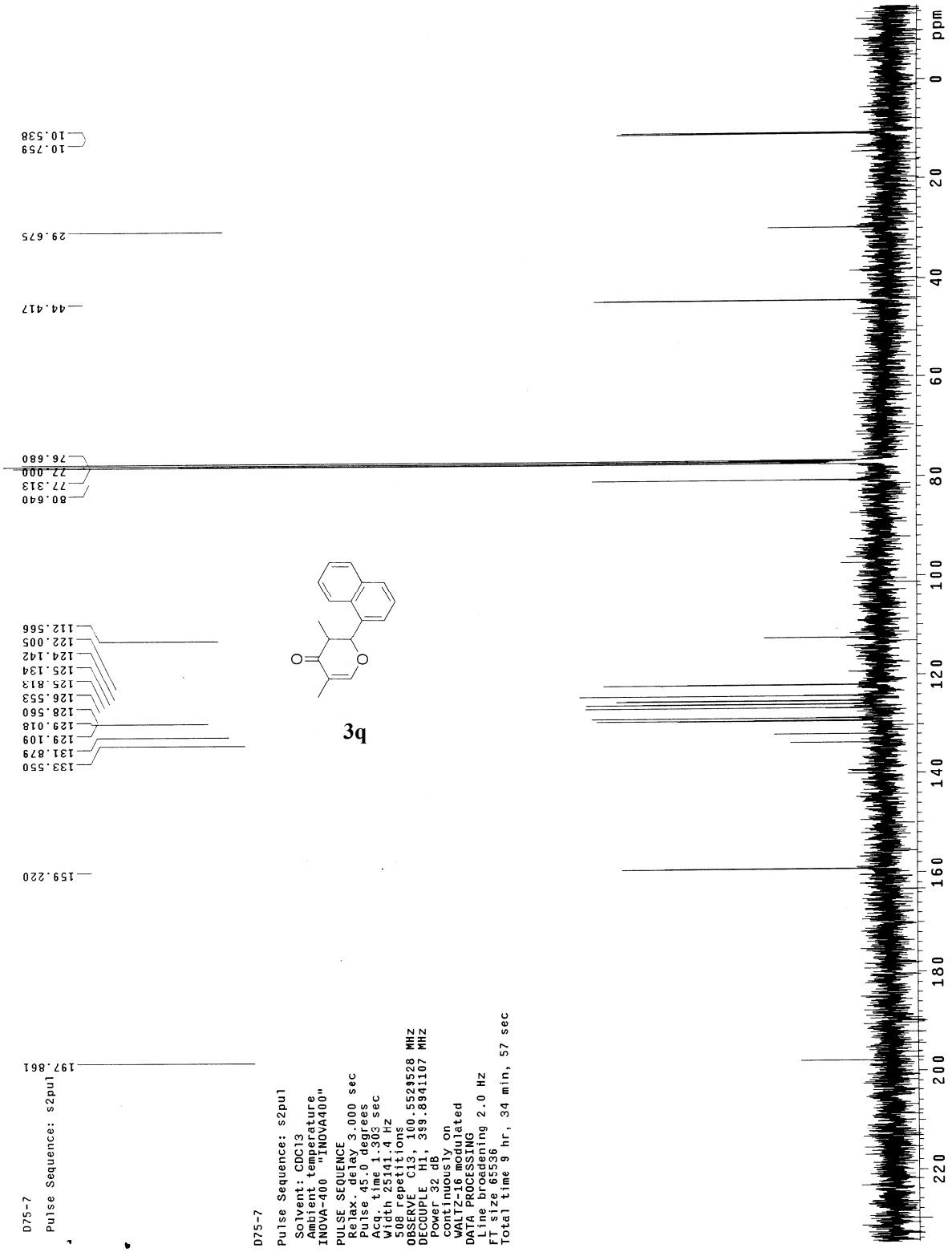
F2 - Processing parameters

SI	32768
SF	300.1300119 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

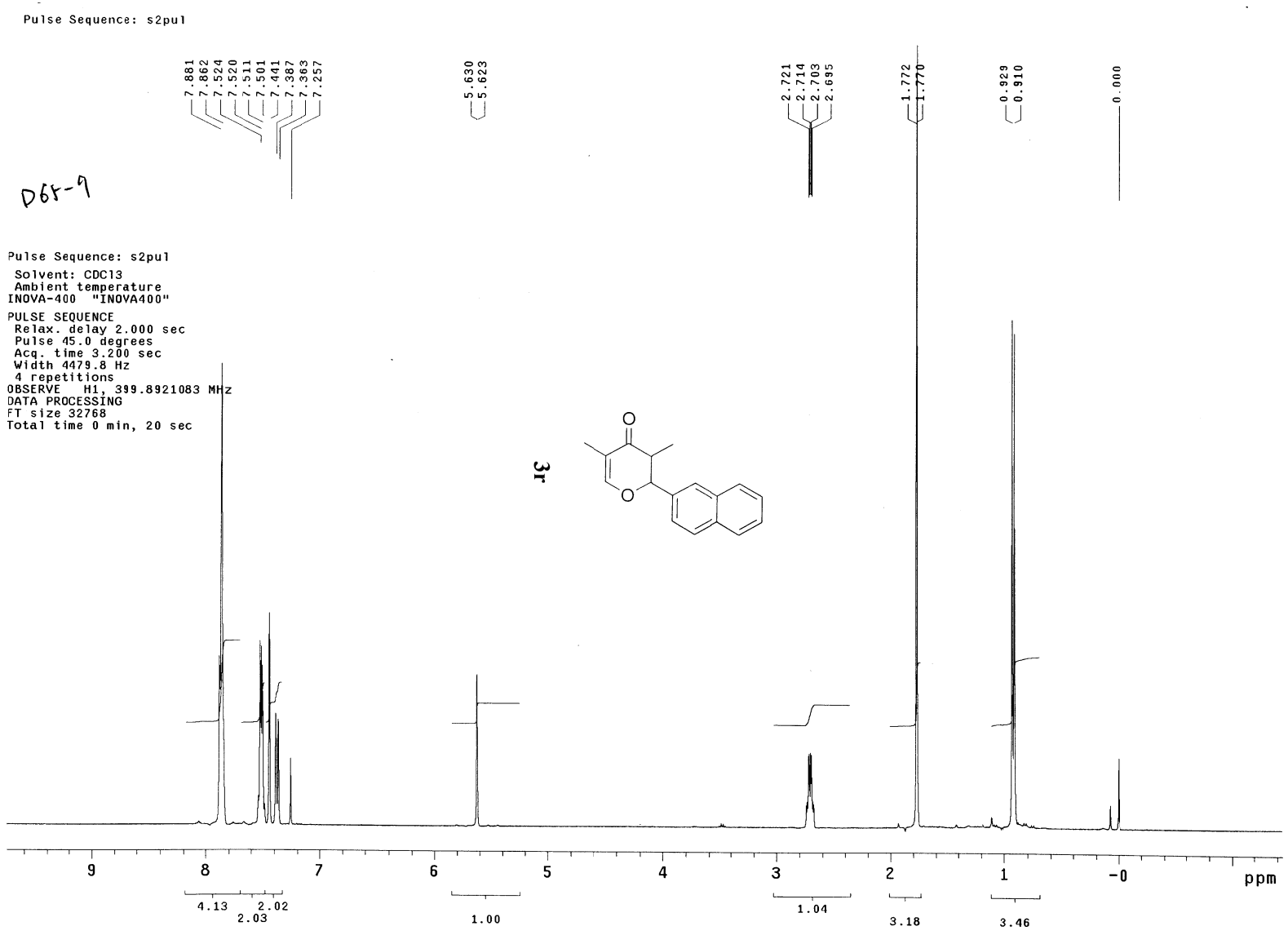
1D NMR plot parameters

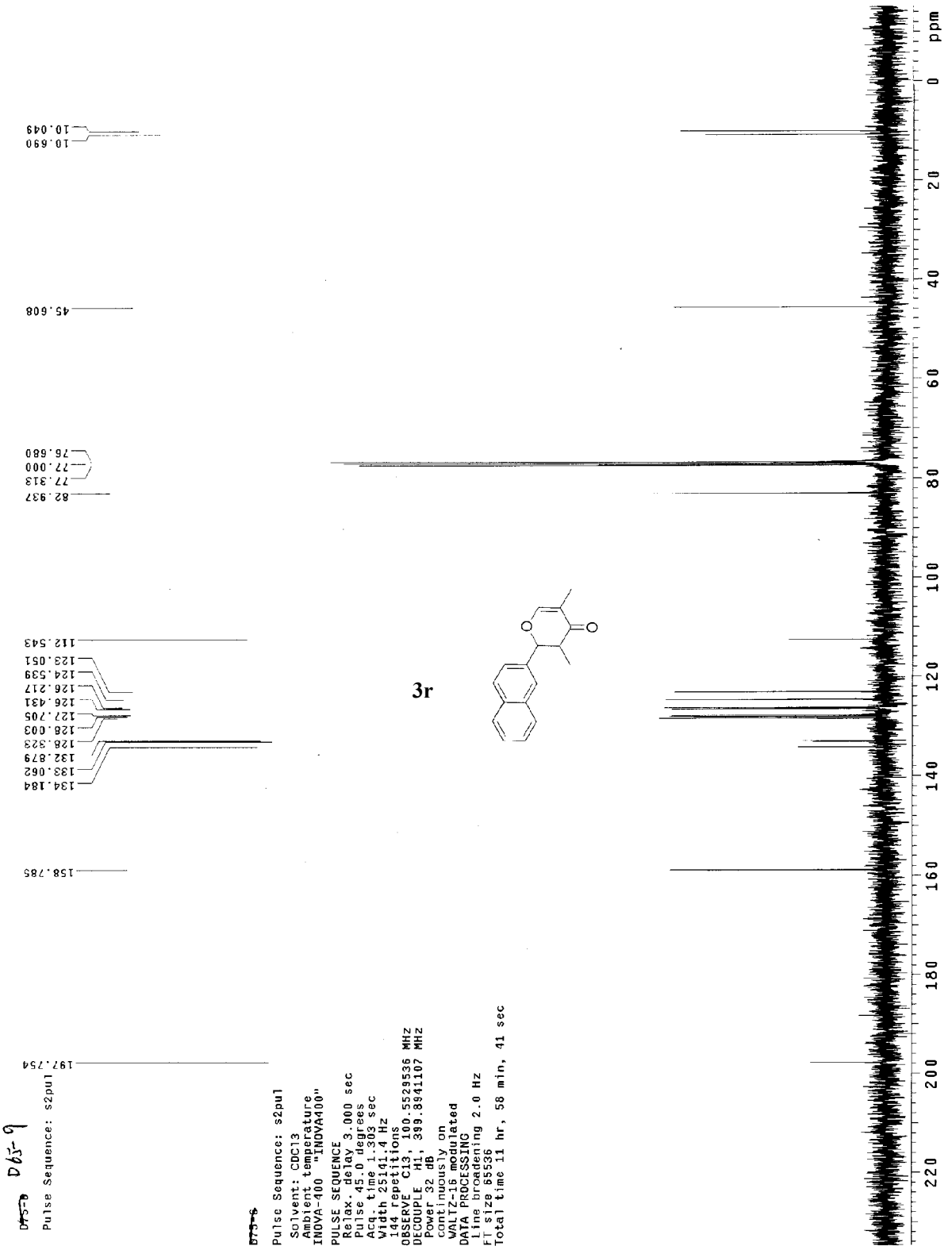
CX	20.00 cm
CY	15.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.52500 ppm/cm
HZCM	157.56825 Hz/cm

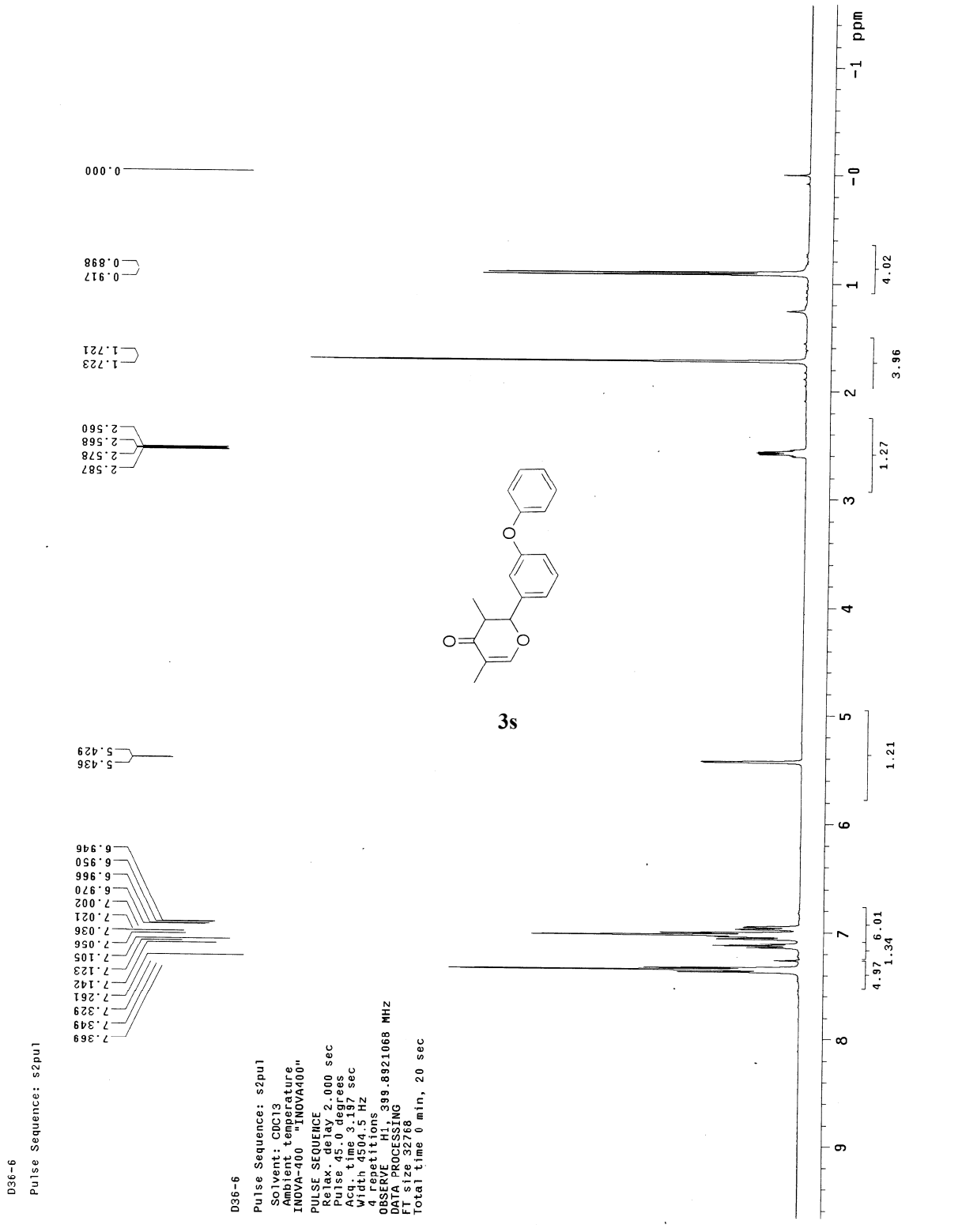

D75-7
Pulse Sequence: s2pul
D75-7
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.197 sec
Width 5434.8 Hz
4 repetitions
OBSERVE H1, 399.8921074 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 20 sec
7.916
7.911
7.901
7.893
7.862
7.842
7.795
7.784
7.772
7.755
7.737
7.556
7.535
7.528
7.522
7.518
7.510
7.504
7.492
7.260
6.225
2.864
2.856
2.845
2.838
1.799
1.797
0.958
0.889
0.871
-0.000
3q
ppm
3.02
3.33
1.00
0.88
3.11
3.48

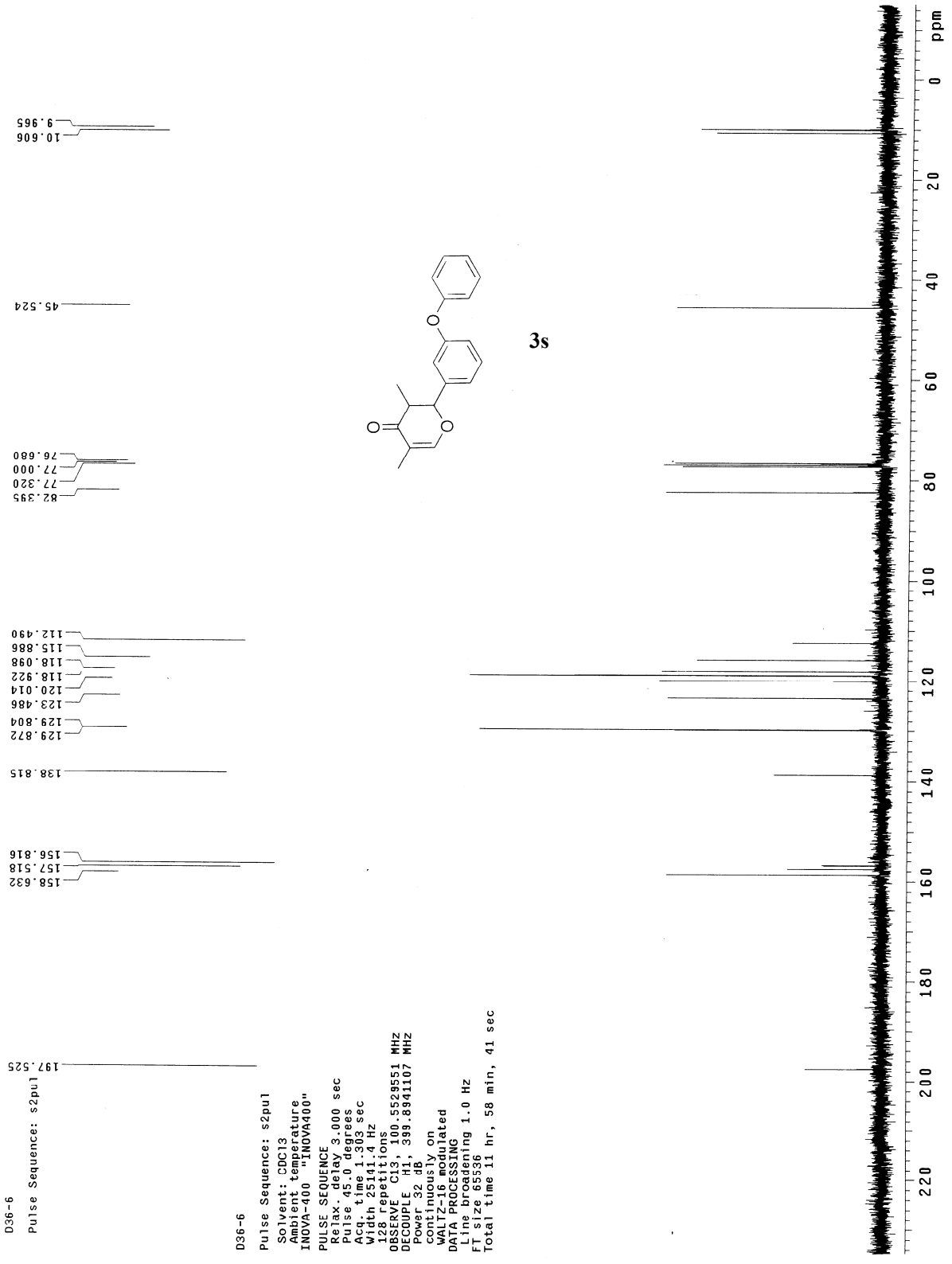

10.538
10.759
29.675
44.417
76.680
77.000
77.313
80.640
112.566
122.005
124.142
125.134
125.813
126.553
128.560
129.018
129.109
131.879
133.550
159.220
197.861
ppm
0
20
40
60
80
100
120
140
160
180
200
220
D75-7
Pulse Sequence: s2pul
D75-7
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
508 repetitions
OBSERVE C13, 100.5523528 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 hr, 34 min, 57 sec

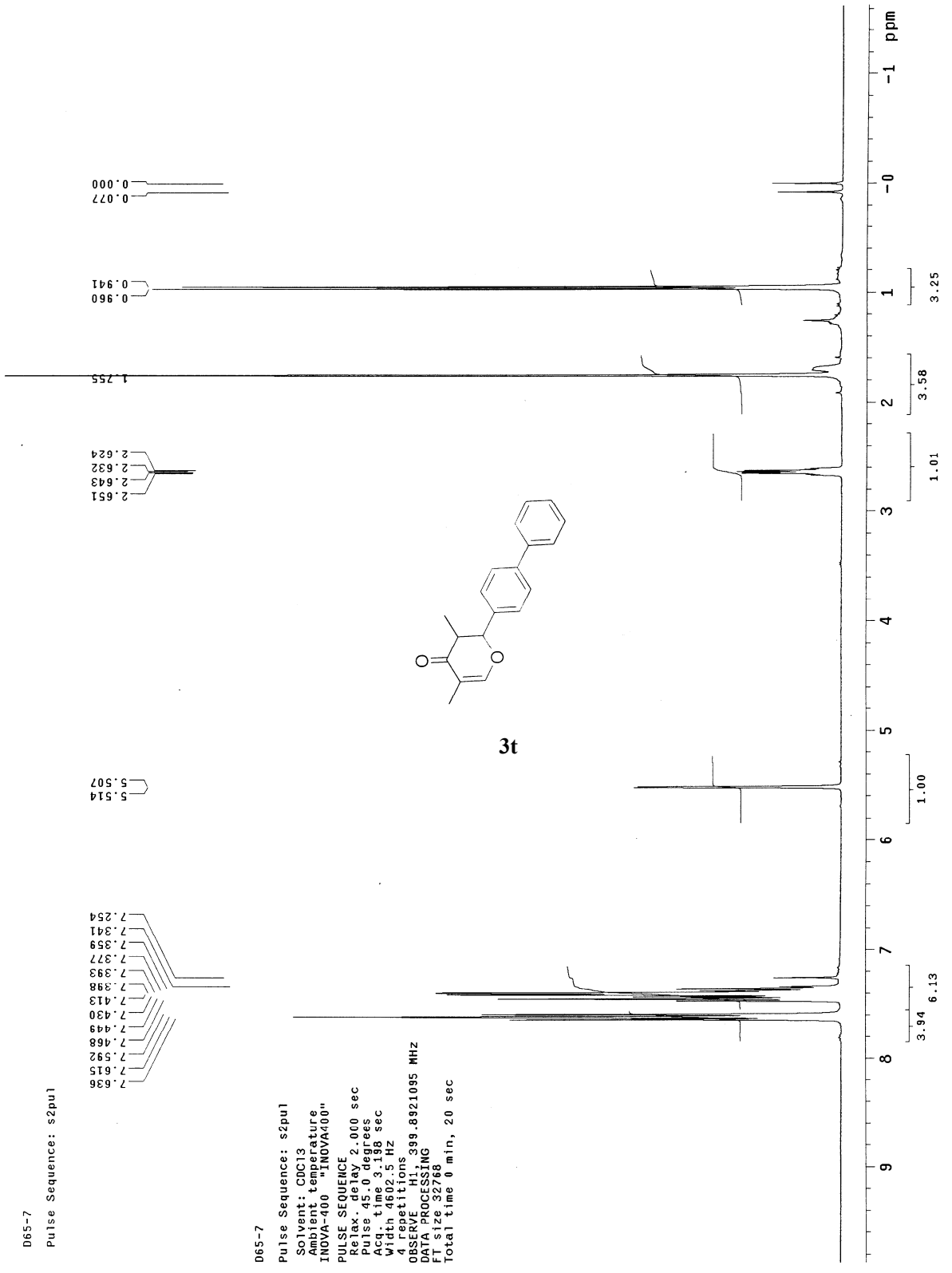
3q


Pulse Sequence: s2pul
7.881
7.862
7.524
7.520
7.511
7.501
7.441
7.387
7.363
7.257
5.630
5.623
2.721
2.714
2.703
2.695
1.772
1.770
0.929
0.910
0.000
D65-9
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 4479.8 Hz
4 repetitions
OBSERVE H1, 399.8921083 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 20 sec
3r
O
O
9
8
7
6
5
4
3
2
1
-0
ppm
4.13
2.02
2.03
1.00
1.04
3.18
3.46

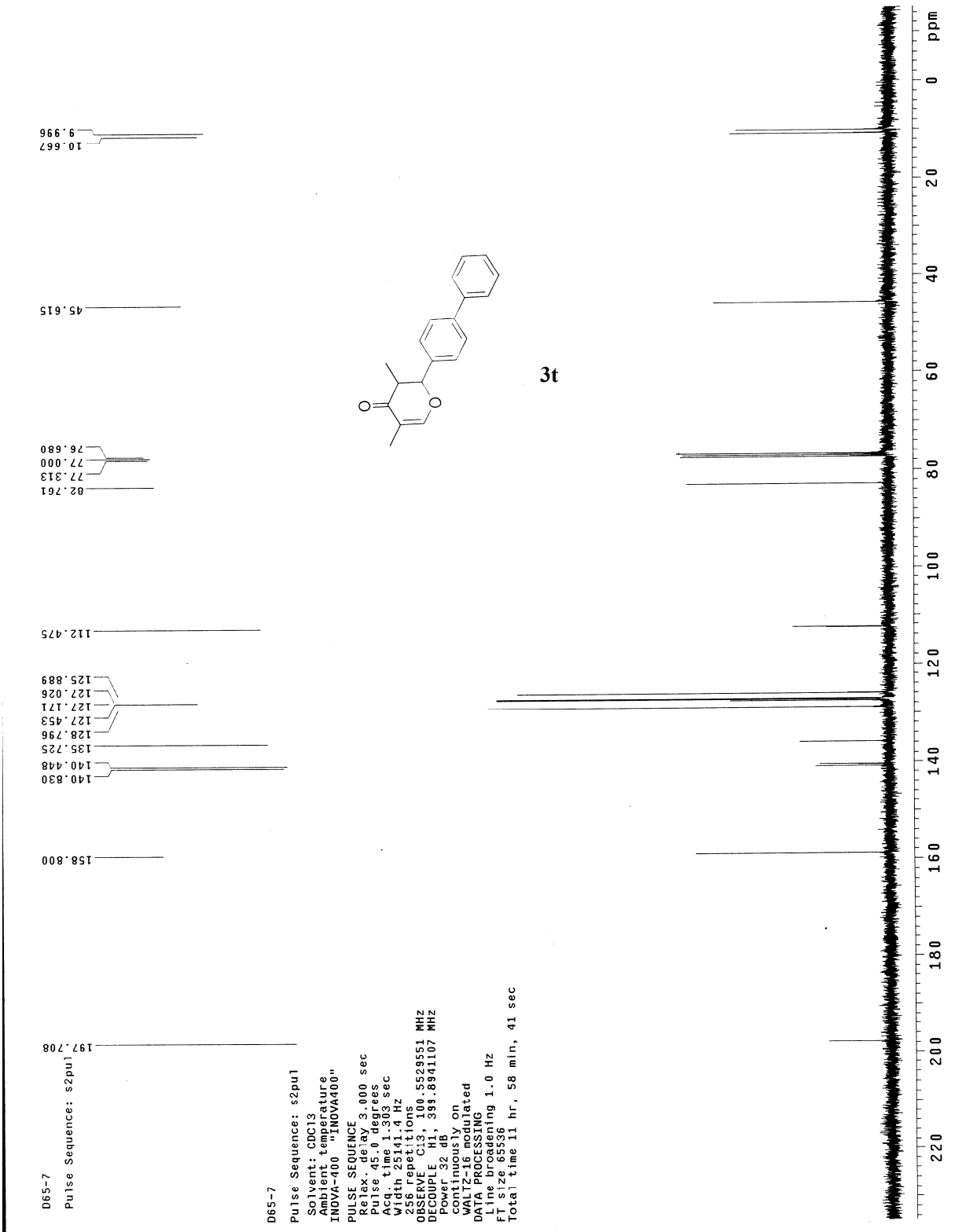

3r
197.754
158.785
134.184
133.062
132.879
128.323
128.003
127.705
126.431
126.217
124.539
123.051
112.543
82.937
77.313
77.000
76.680
45.608
10.690
10.049
ppm

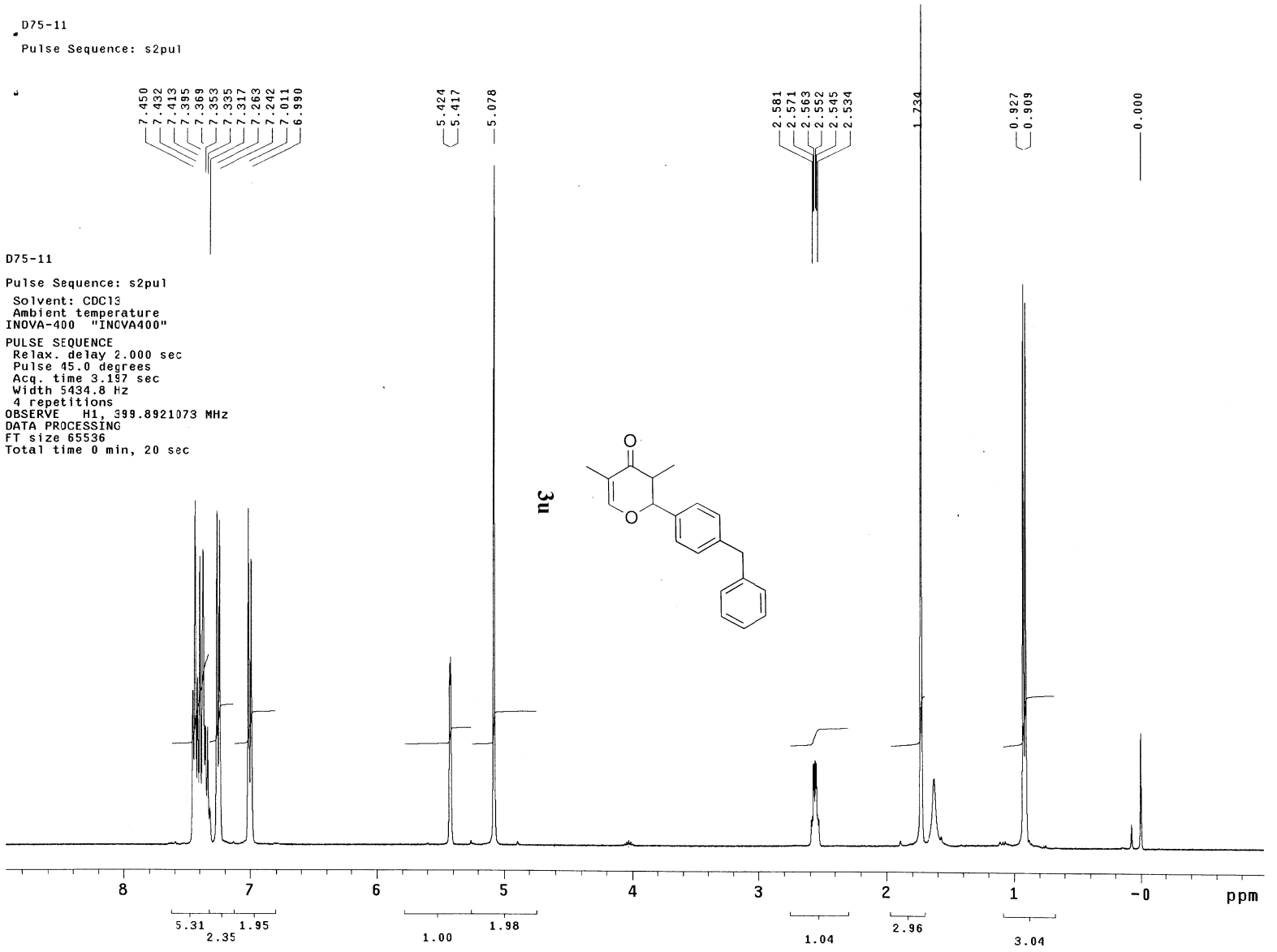

D36-6
Pulse Sequence: s2pul
D36-6
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.197 sec
Width 4504.5 Hz
4 repetitions
OBSERVE H1, 399.8921068 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 20 sec
0.000
0.898
0.917
1.721
1.723
2.560
2.568
2.578
2.587
5.429
5.436
6.946
6.950
6.966
6.970
7.002
7.021
7.036
7.056
7.105
7.123
7.142
7.261
7.329
7.349
7.369
4.97
1.34
6.01
1.21
1.27
3.96
4.02
ppm
3s

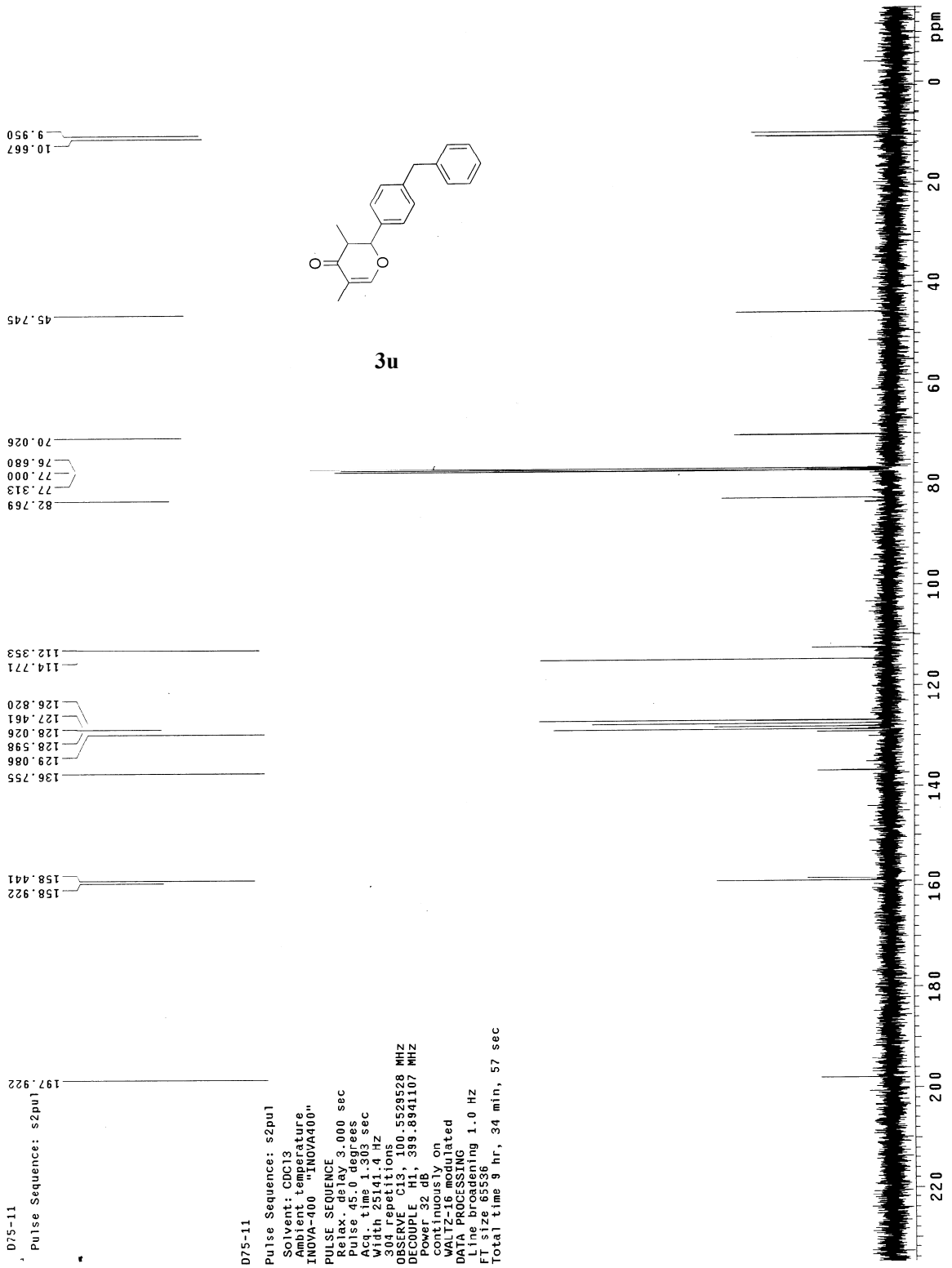

3s
D36-6
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
128 repetitions
OBSERVE C13, 100.5529551 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 58 min, 41 sec
197.525
158.632
157.518
156.816
138.815
129.872
129.804
123.486
120.014
118.922
118.098
115.886
112.490
82.395
77.320
77.000
76.680
45.524
10.606
9.965
ppm

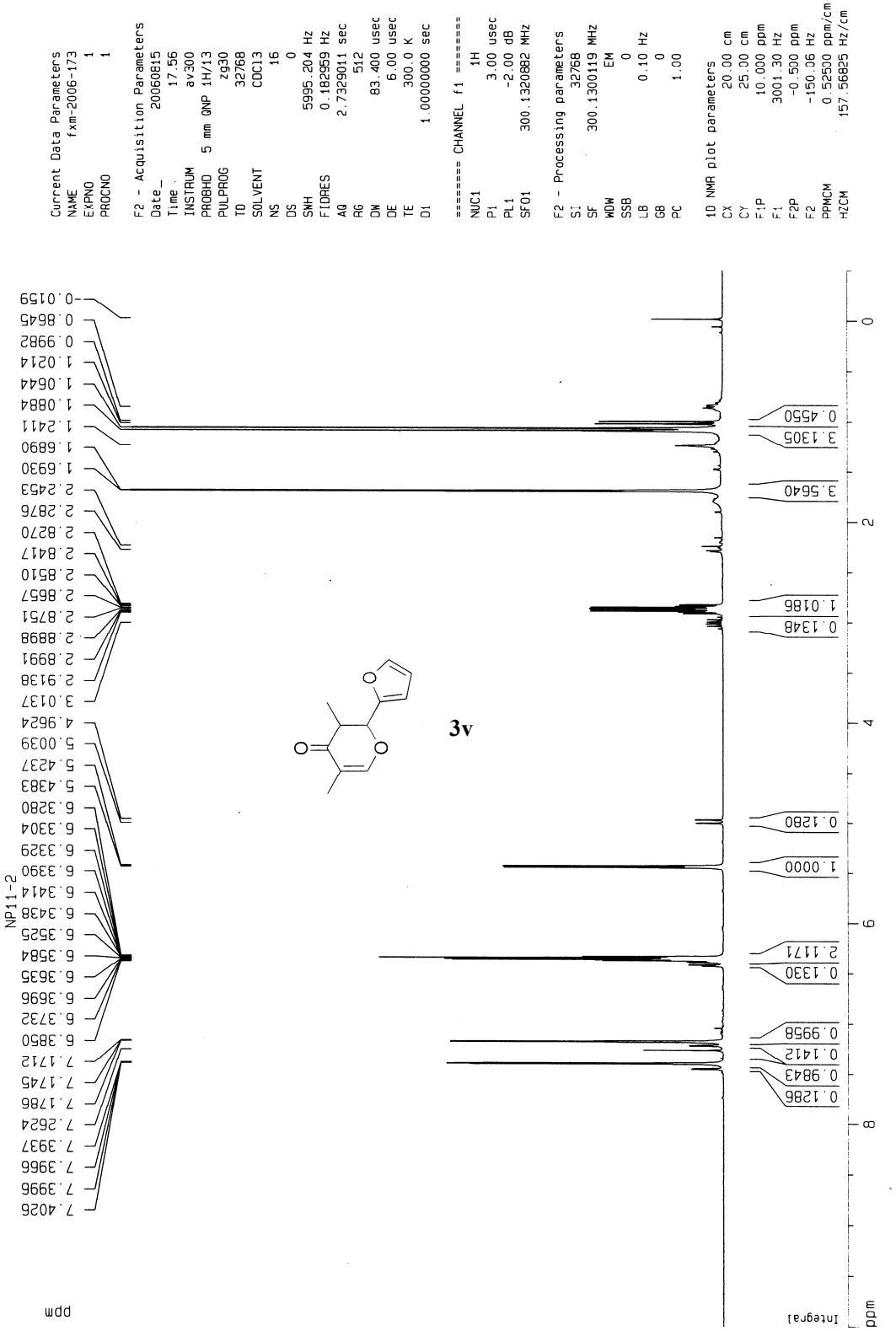

D65-7
Pulse Sequence: s2pul
7.636
7.615
7.592
7.468
7.449
7.430
7.413
7.398
7.393
7.377
7.359
7.341
7.254
5.514
5.507
2.651
2.643
2.632
2.624
1.755
0.960
0.941
0.077
0.000
3.94
6.13
1.00
1.01
3.58
3.25
ppm
D65-7
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.198 sec
Width 4602.5 Hz
4 repetitions
OBSERVE H1, 399.8921095 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 20 sec

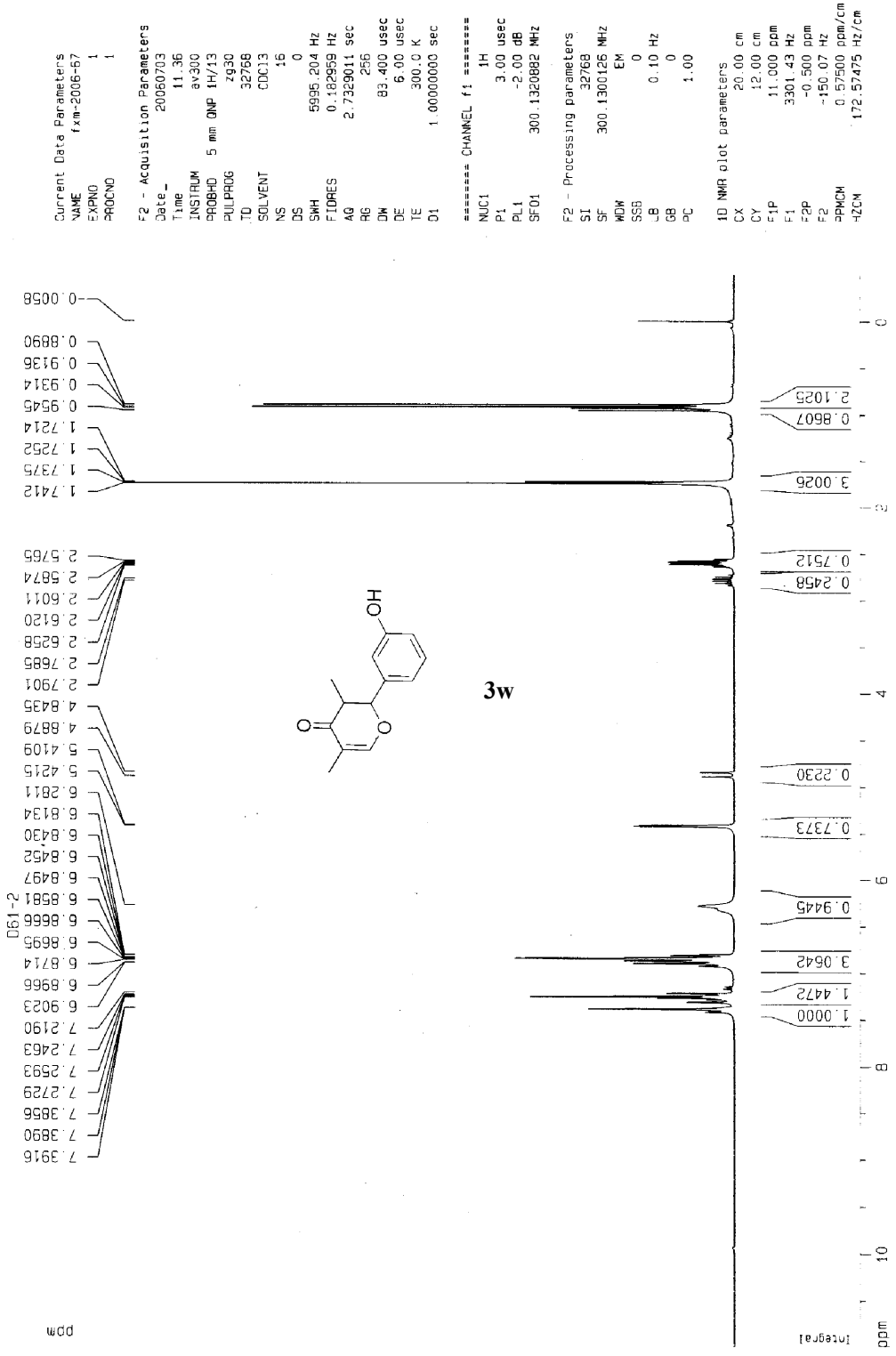
3t


D65-7
Pulse Sequence: s2pul
197.708
158.800
140.830
140.448
135.725
128.796
127.453
127.171
127.026
125.889
112.475
82.761
77.313
77.000
76.680
45.615
10.667
9.996
3t
ppm

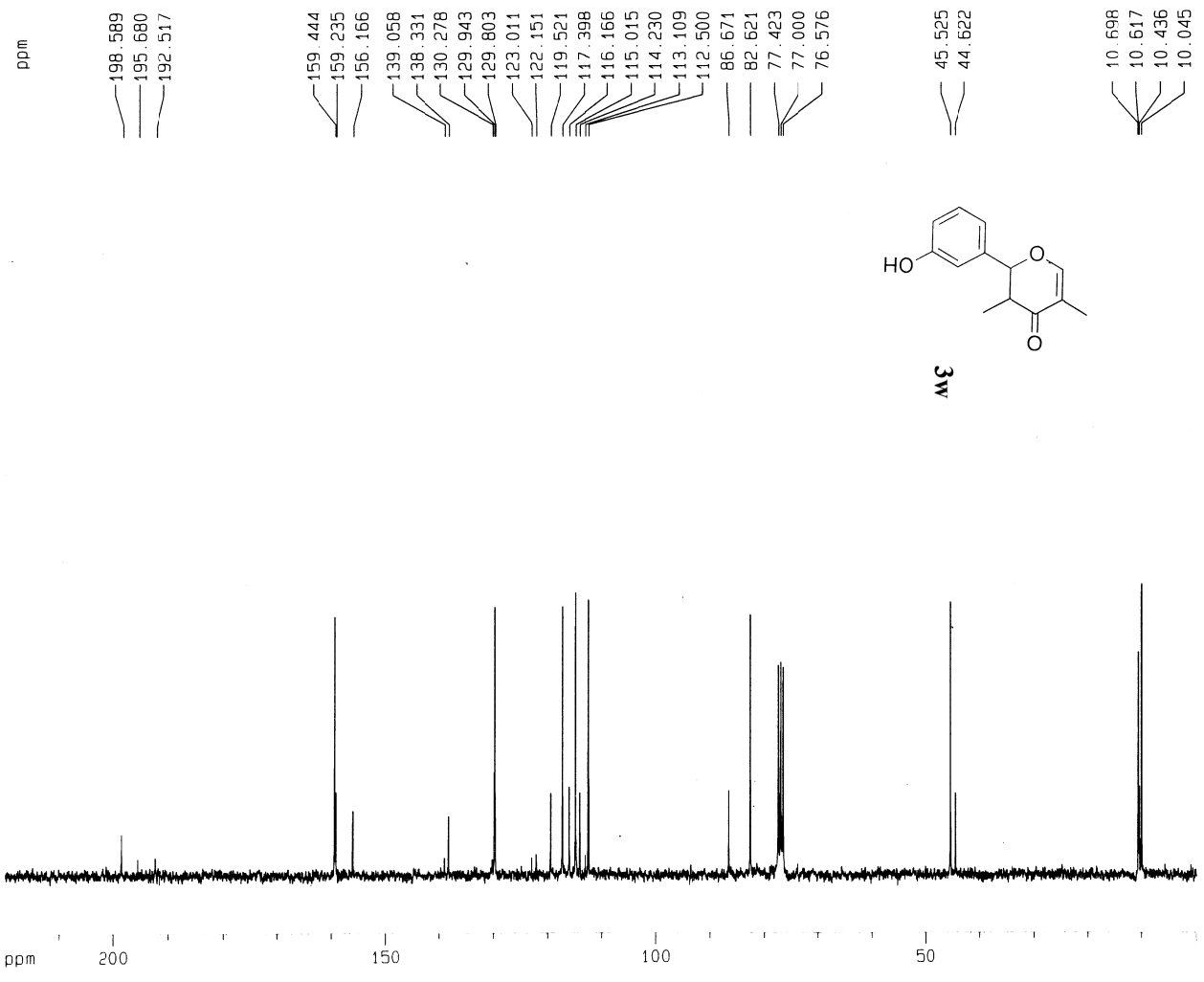

D75-11
Pulse Sequence: s2pul
7.450
7.432
7.413
7.395
7.369
7.353
7.335
7.317
7.263
7.242
7.011
6.990
5.424
5.417
5.078
2.581
2.571
2.563
2.552
2.545
2.534
1.734
0.927
0.909
0.000
D75-11
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.197 sec
Width 5434.8 Hz
4 repetitions
OBSERVE H1, 399.8921073 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 20 sec
3u
O
O
8
7
6
5
4
3
2
1
-0
ppm
5.31
1.95
2.35
1.00
1.98
1.04
2.96
3.04


9.950
10.667
45.745
70.026
76.680
77.000
77.313
82.769
112.353
114.771
126.820
127.461
128.026
128.598
129.086
136.755
158.441
158.922
197.922
ppm
0
20
40
60
80
100
120
140
160
180
200
220
O
O
3u
D75-11
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
304 repetitions
OBSERVE C13, 100.5528528 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 9 hr, 34 min, 57 sec

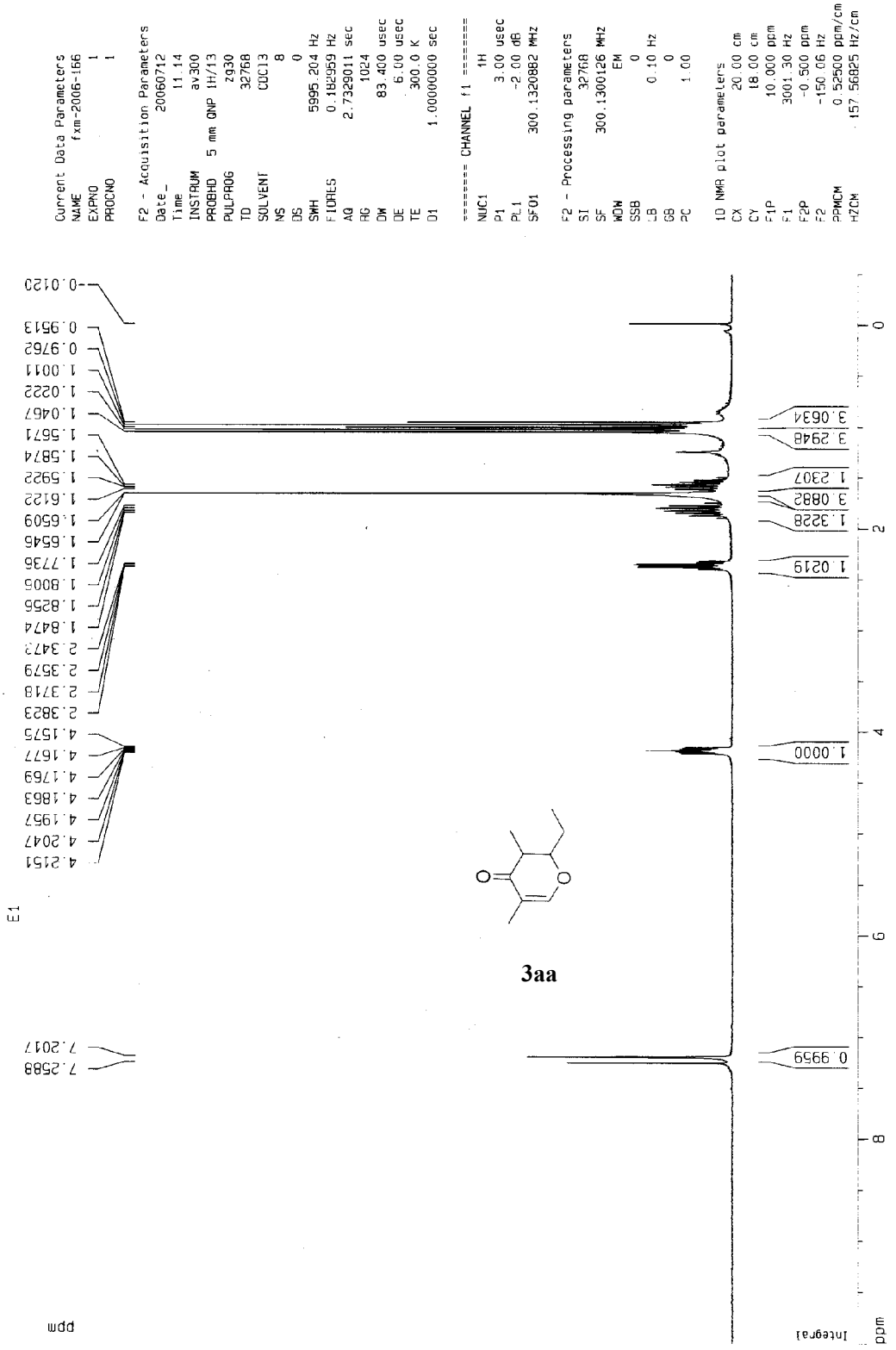

Current Data Parameters
NAME fxm-2006-173
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060815
Time 17.56
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300119 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 25.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
NP11-2
ppm
Integral
3v


Current Data Parameters
NAME fxm-2006-67
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060703
Time 11.36
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
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 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320082 MHz
F2 - Processing parameters
SI 32768
SF 300.1300126 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 11.000 ppm
F1 3301.43 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.57500 ppm/cm
HZCM 172.57475 Hz/cm
0.0058
0.8890
0.9136
0.9314
0.9545
1.7214
1.7252
1.7375
1.7412
2.5765
2.5874
2.6011
2.6120
2.6258
2.7685
2.7901
4.8435
4.8879
5.4109
5.4215
6.2811
6.8134
6.8430
6.8452
6.8497
6.8581
6.8666
6.8695
6.8714
6.8966
6.9023
7.2190
7.2463
7.2593
7.2729
7.3856
7.3890
7.3916
OH
O
O
3w
0.8607
2.1025
3.0026
0.7512
0.2458
0.2230
0.7373
0.9445
3.0542
1.4472
1.0000
ppm
Integral

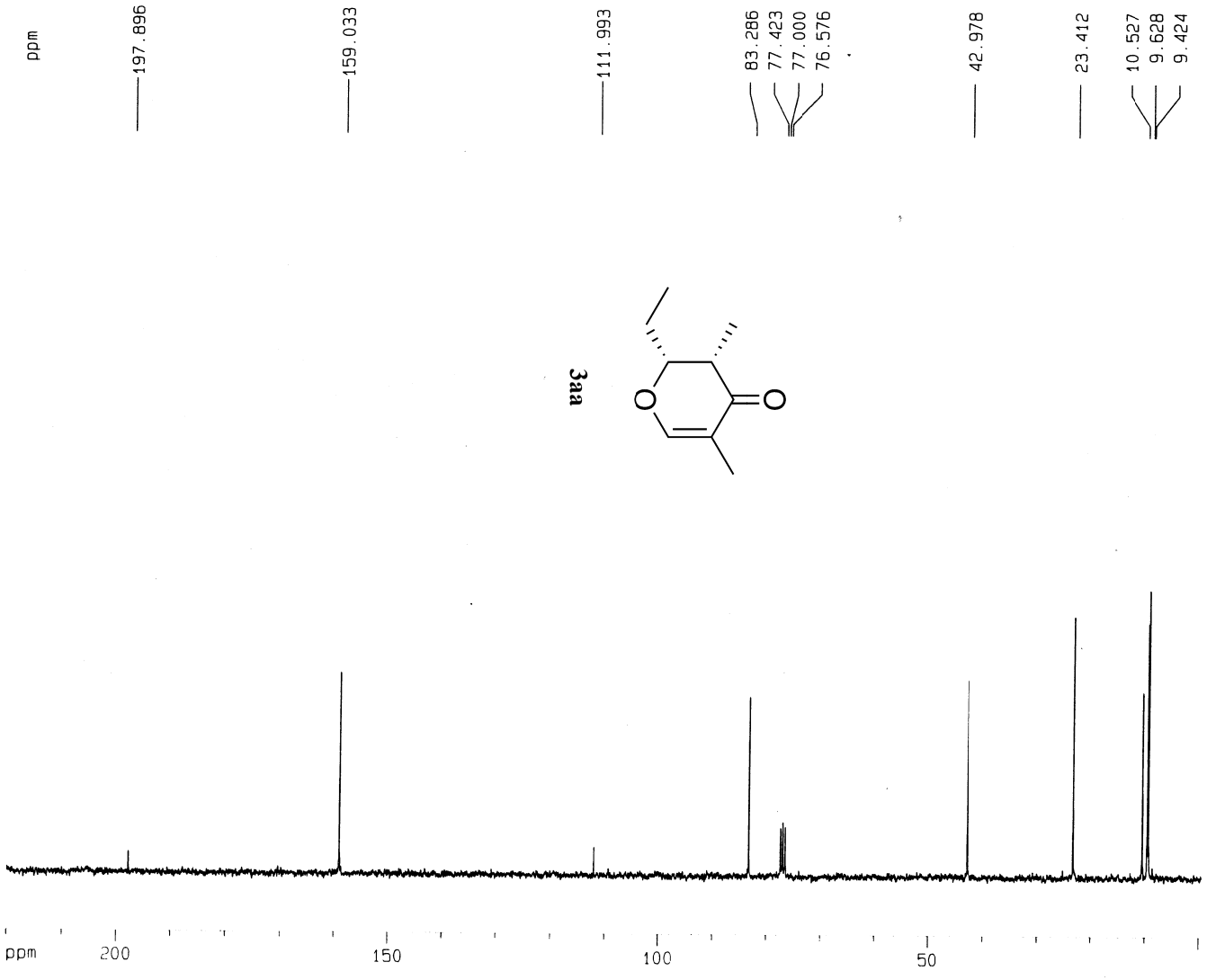
D61-2




```
Current Data Parameters
NAME          fxm-2006-67
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060703
Time                11.40
INSTRUM             av300
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg
TD                  65536
SOLVENT             CDCl3
NS                    680
DS                      4
SWH           22675.736 Hz
FIDRES         0.346004 Hz
AQ            1.4451188 sec
RG                   8192
DW                22.050 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 5.50 usec
PL1                -6.00 dB
SFO1          75.4775598 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              17.70 dB
PL13              17.71 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677533 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                  5.00 cm
F1P              220.005 ppm
F1             16603.28 Hz
F2P               -0.005 ppm
F2                -0.38 Hz
PPMCM          11.00050 ppm/cm
HZCM          830.18298 Hz/cm
```

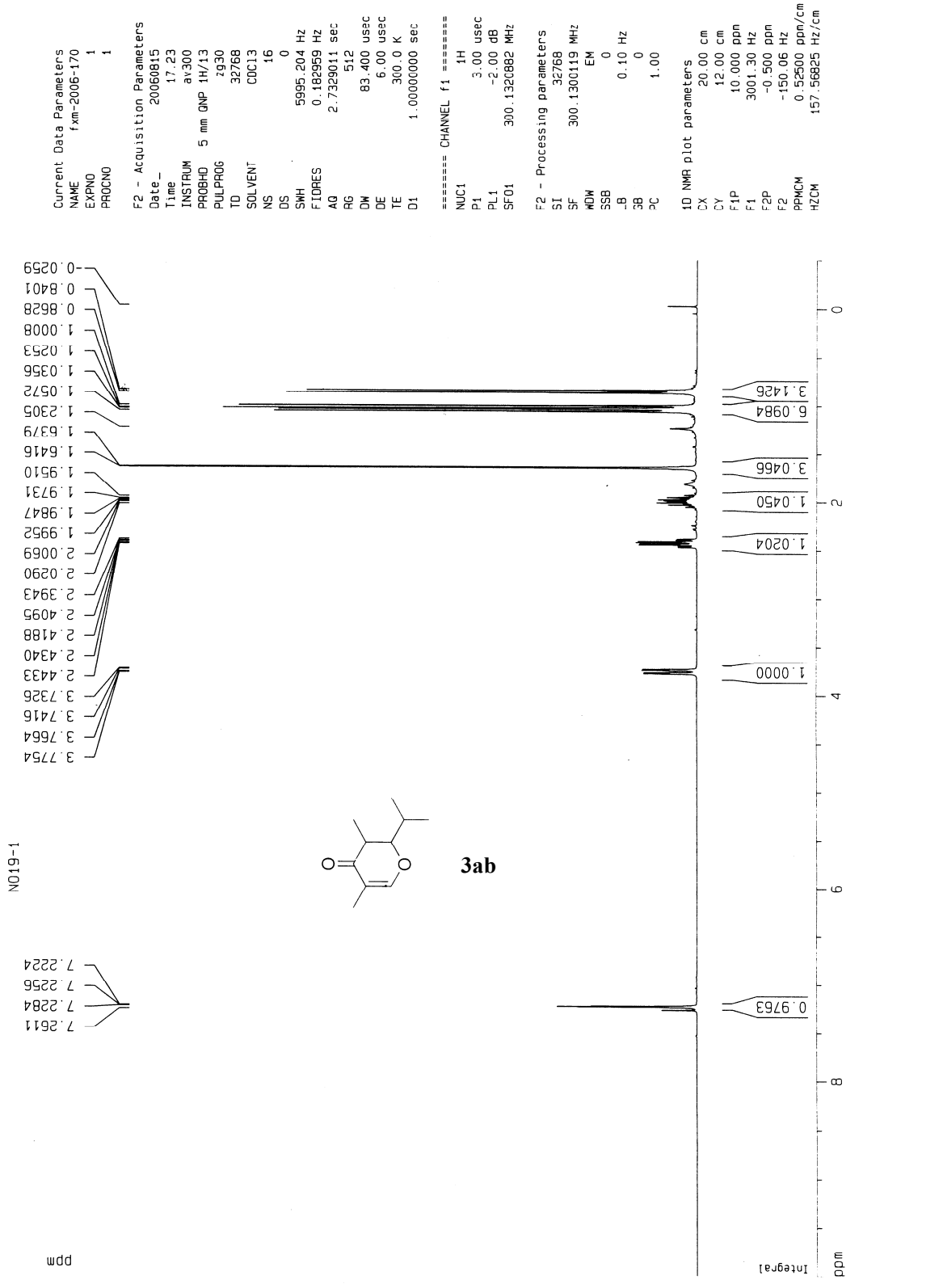

Current Data Parameters
NAME fxm-2006-166
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060712
Time 11.14
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 1024
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300126 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 18.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
0.0120
0.9513
0.9762
1.0011
1.0222
1.0467
1.5671
1.5874
1.5922
1.6122
1.6509
1.6546
1.7736
1.8005
1.8255
1.8474
2.3472
2.3579
2.3718
2.3823
4.1575
4.1677
4.1769
4.1863
4.1957
4.2047
4.2151
7.2588
7.2017
E1
3.0634
3.2948
1.2307
3.0882
1.3228
1.0219
1.0000
0.9959
Integral
ppm
3aa

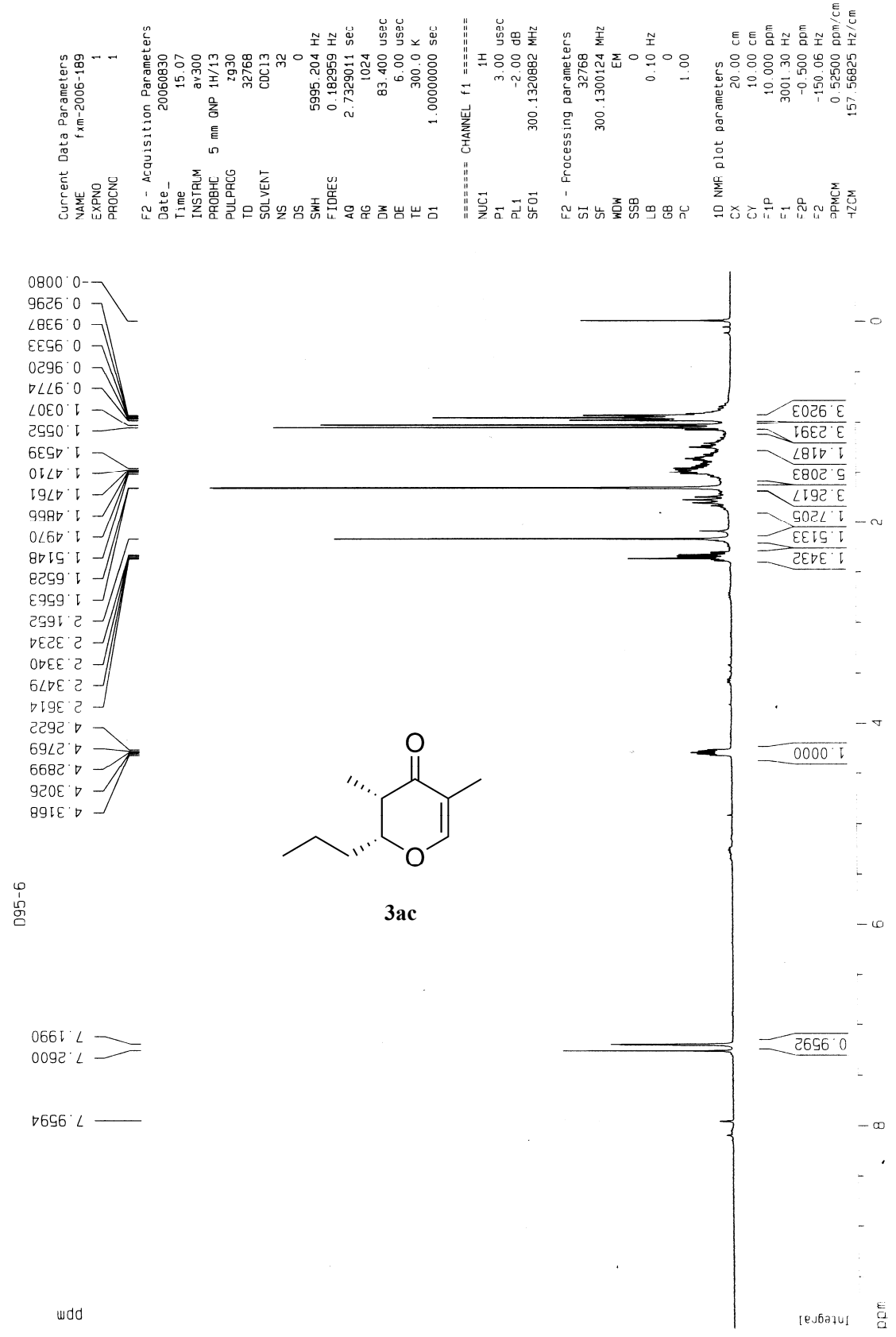
D95-4

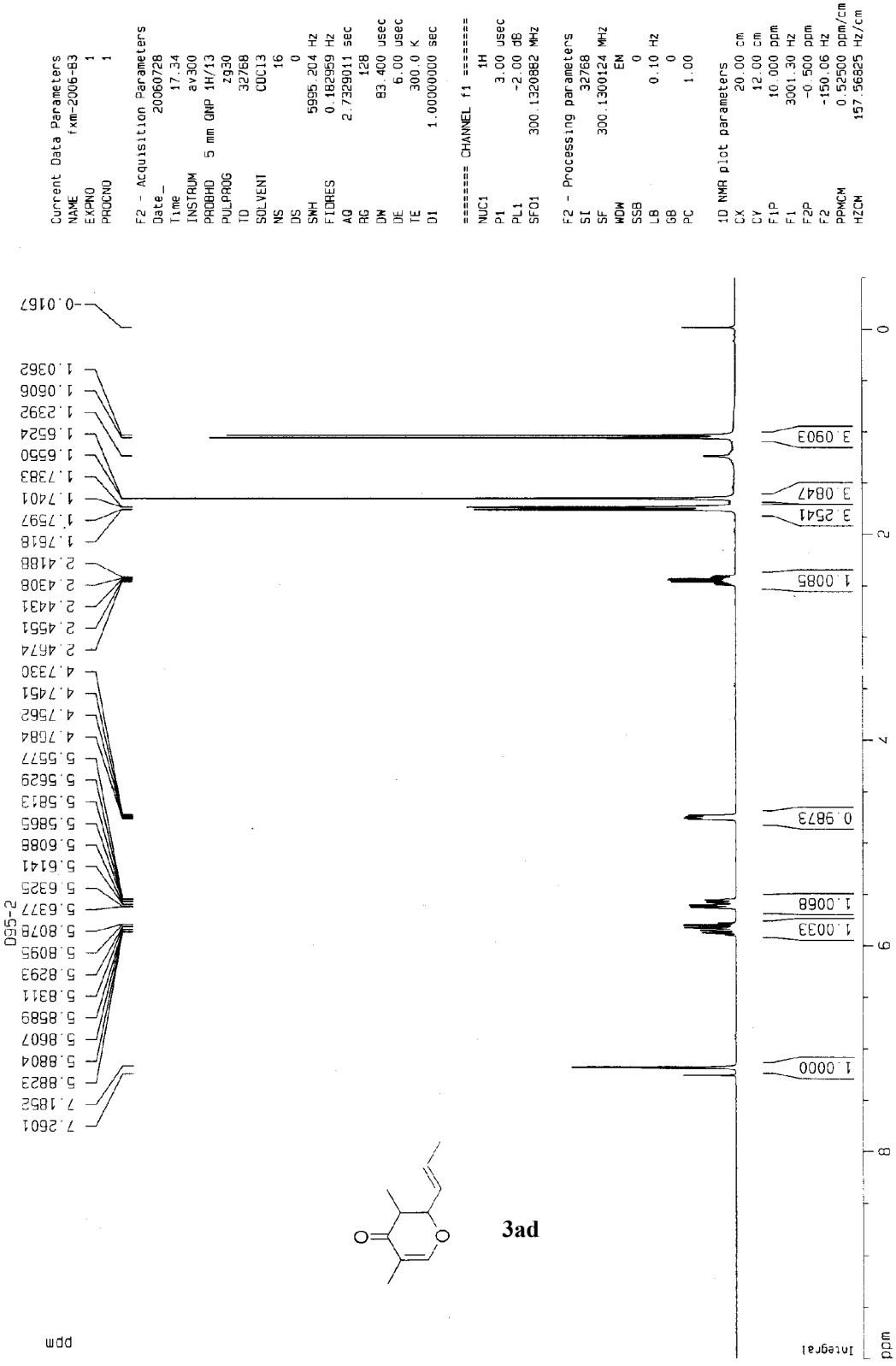


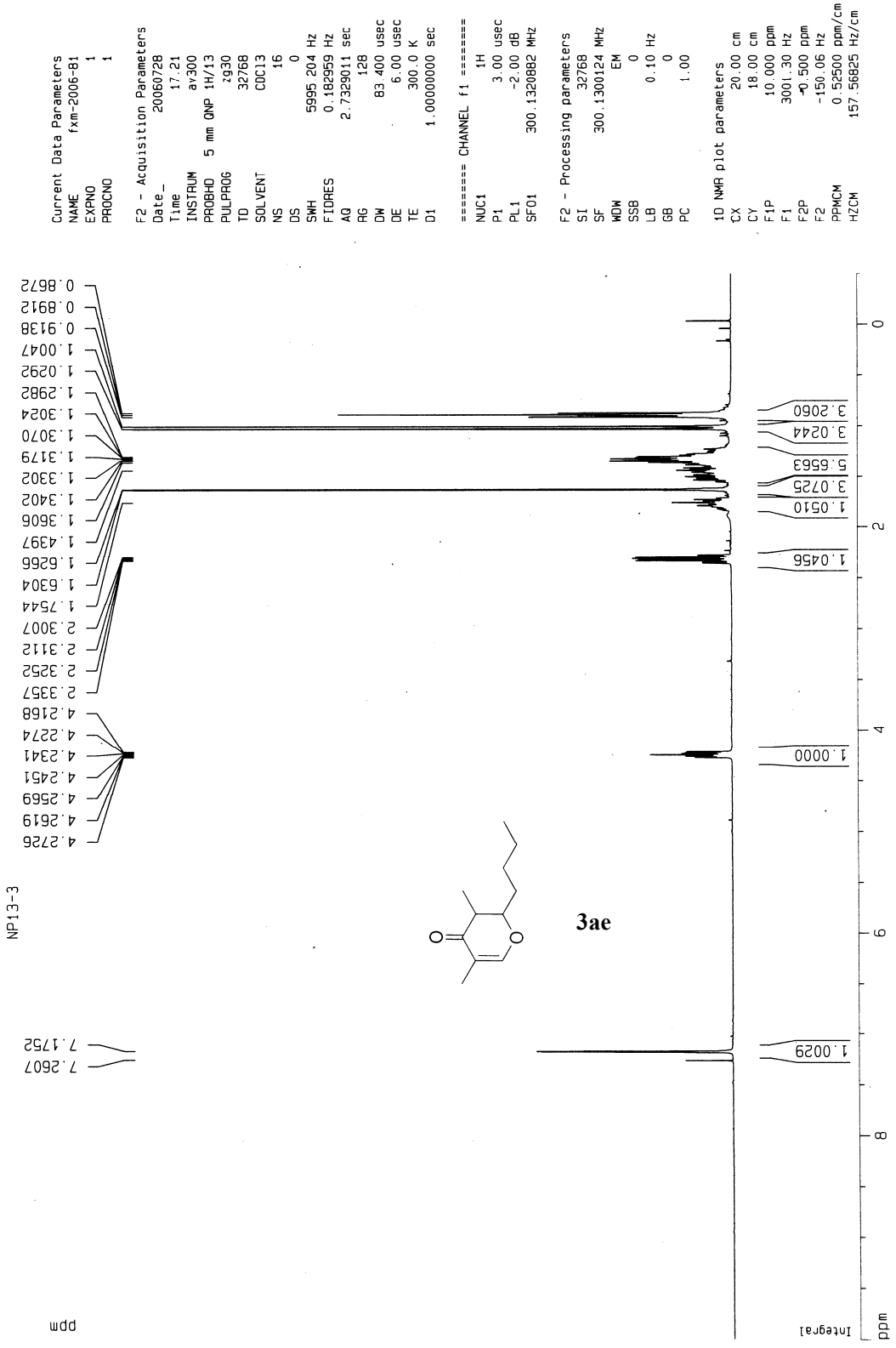
3aa

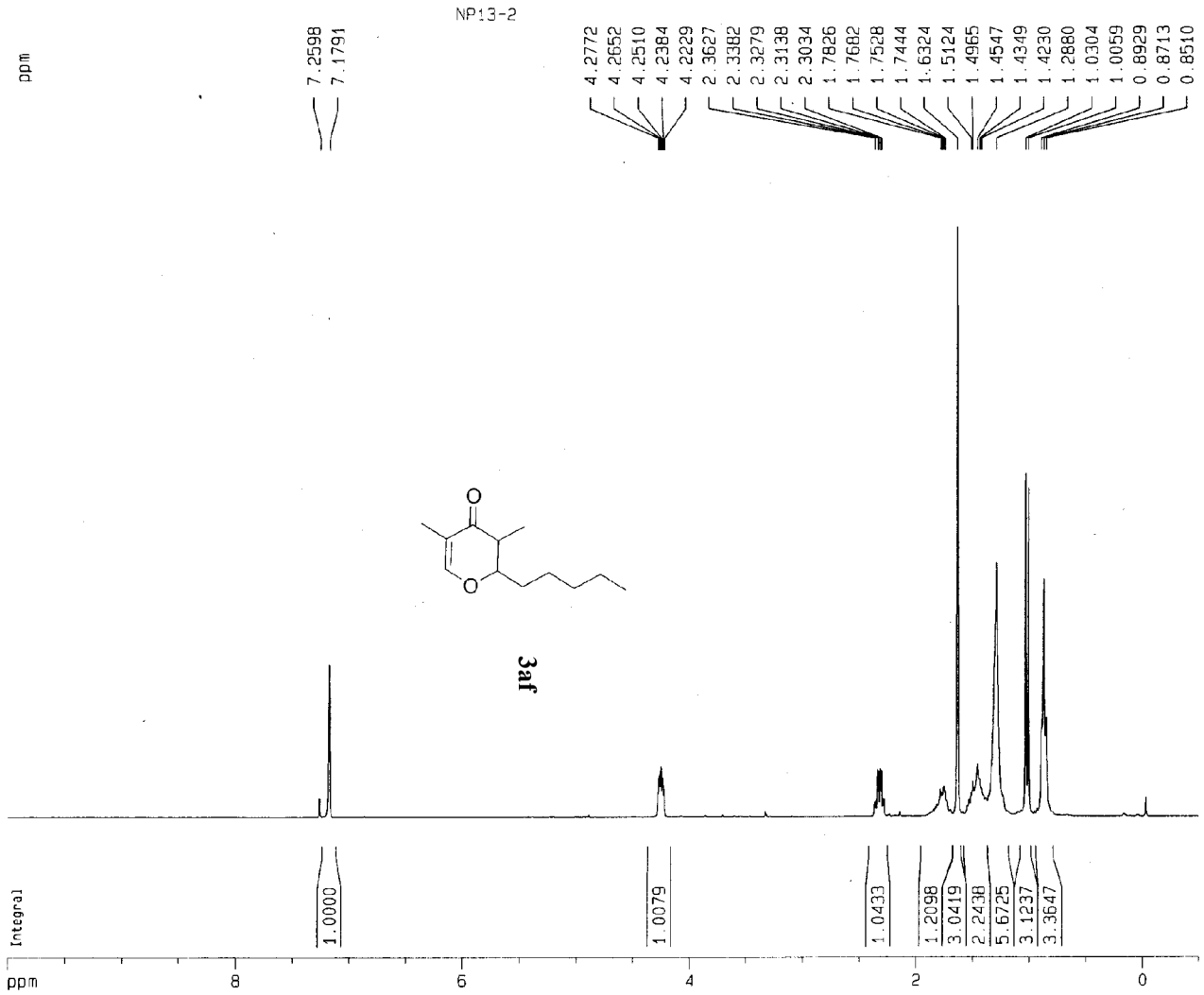

```
Current Data Parameters
NAME        fxm-2006-193
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_          20060830
Time              17.47
INSTRUM           av300
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg
TD               65536
SOLVENT           DMSO
NS                 282
DS                   4
SWH          22675.736 Hz
FIDRES        0.346004 Hz
AQ            1.4451188 sec
RG                8192
DW              22.050 usec
DE               6.00 usec
TE              300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1               13C
P1               5.50 usec
PL1              -6.00 dB
SFO1        75.4775598 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           80.00 usec
PL2              -2.00 dB
PL12             17.70 dB
PL13             17.71 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                32768
SF          75.4677525 MHz
WDW                EM
SSB                0
LB              3.00 Hz
GB                 0
PC              1.40

1D NMR plot parameters
CX             20.00 cm
CY              5.00 cm
F1P           220.050 ppm
F1          16606.68 Hz
F2P            -0.500 ppm
F2           -37.73 Hz
PPMCM        11.02750 ppm/cm
HZCM        832.22058 Hz/cm
```


Current Data Parameters
NAME fxm-2006-170
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060815
Time 17.23
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300119 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
NO19-1
3ab
0.9763
1.0000
1.0204
1.0450
3.0466
6.0984
3.1426
7.2611
7.2284
7.2256
7.2224
3.7754
3.7664
3.7416
3.7326
2.4433
2.4340
2.4188
2.4095
2.3943
2.0290
2.0069
1.9952
1.9847
1.9731
1.9510
1.6416
1.6379
1.2305
1.0572
1.0356
1.0253
1.0008
0.8628
0.8401
0.0259
ppm
Integral


Current Data Parameters
NAME fxm-2006-189
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060830
Time 15.07
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 1024
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
D95-6
ppm
Integral
ppm
3ac

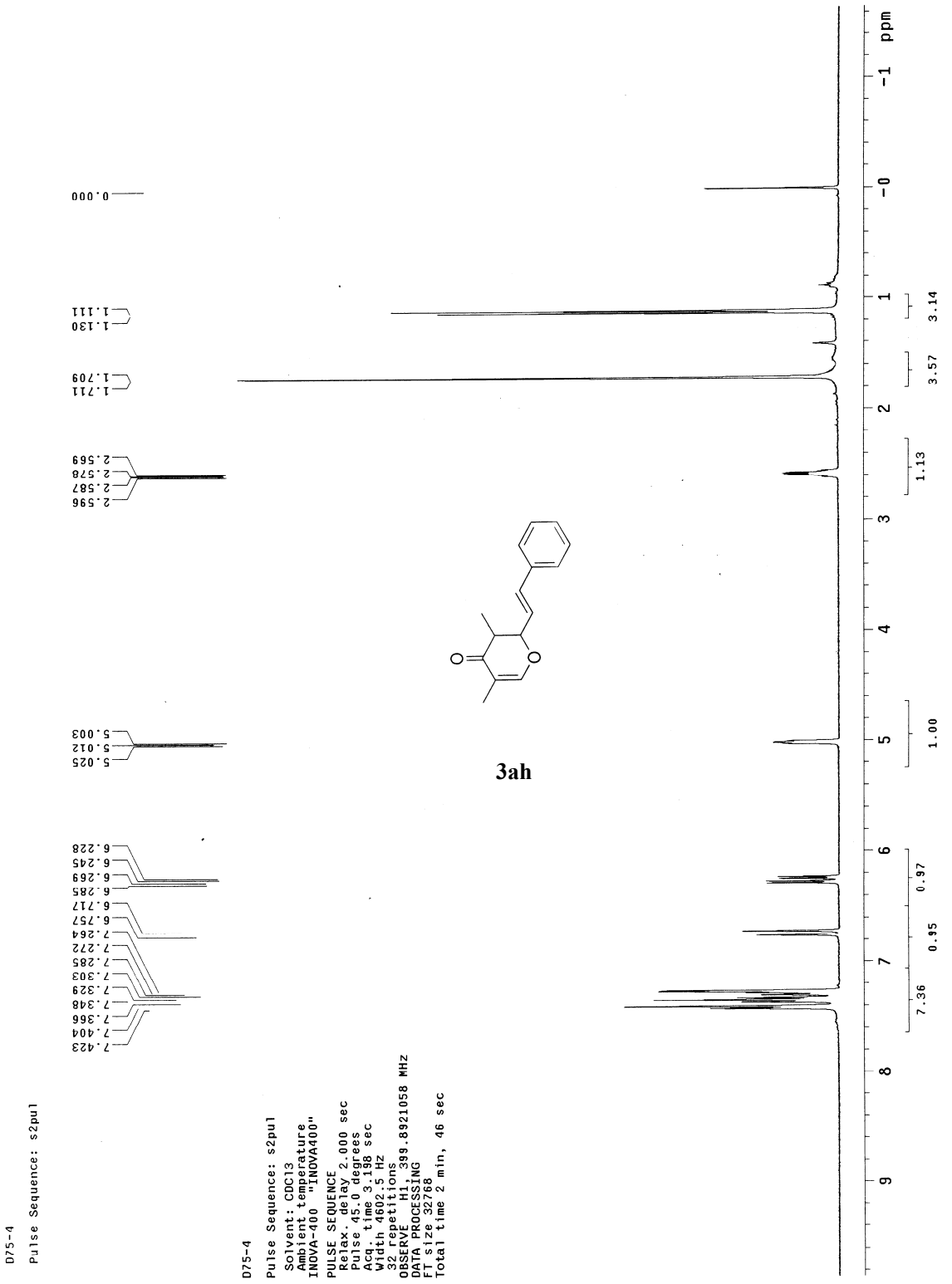

Current Data Parameters
NAME fxm-2006-83
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060728
Time 17.34
INSTRUM av300
PROBHD 5 mm GNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
-0.0167
1.0362
1.0606
1.2392
1.6524
1.6550
1.7383
1.7401
1.7597
1.7618
2.4188
2.4308
2.4431
2.4551
2.4674
4.7330
4.7451
4.7562
4.7684
5.5577
5.5629
5.5813
5.5865
5.6088
5.6141
5.6325
5.6377
5.8078
5.8095
5.8293
5.8311
5.8589
5.8607
5.8804
5.8823
7.1852
7.2601
D95-2
3.0903
3.0847
3.2541
1.0085
0.9873
1.0068
1.0033
1.0000
ppm
Integral
3ad


Current Data Parameters
NAME fxm-2006-81
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060728
Time 17.21
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 18.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
NP13-3
0.8672
0.8912
0.9138
1.0047
1.0292
1.2982
1.3024
1.3070
1.3179
1.3302
1.3402
1.3606
1.4397
1.6266
1.6304
1.7544
2.3007
2.3112
2.3252
2.3357
4.2168
4.2274
4.2341
4.2451
4.2569
4.2619
4.2726
7.2607
7.1752
1.0029
1.0000
1.0456
1.0510
3.0725
5.6563
3.0244
3.2060
3ae
ppm
Integral

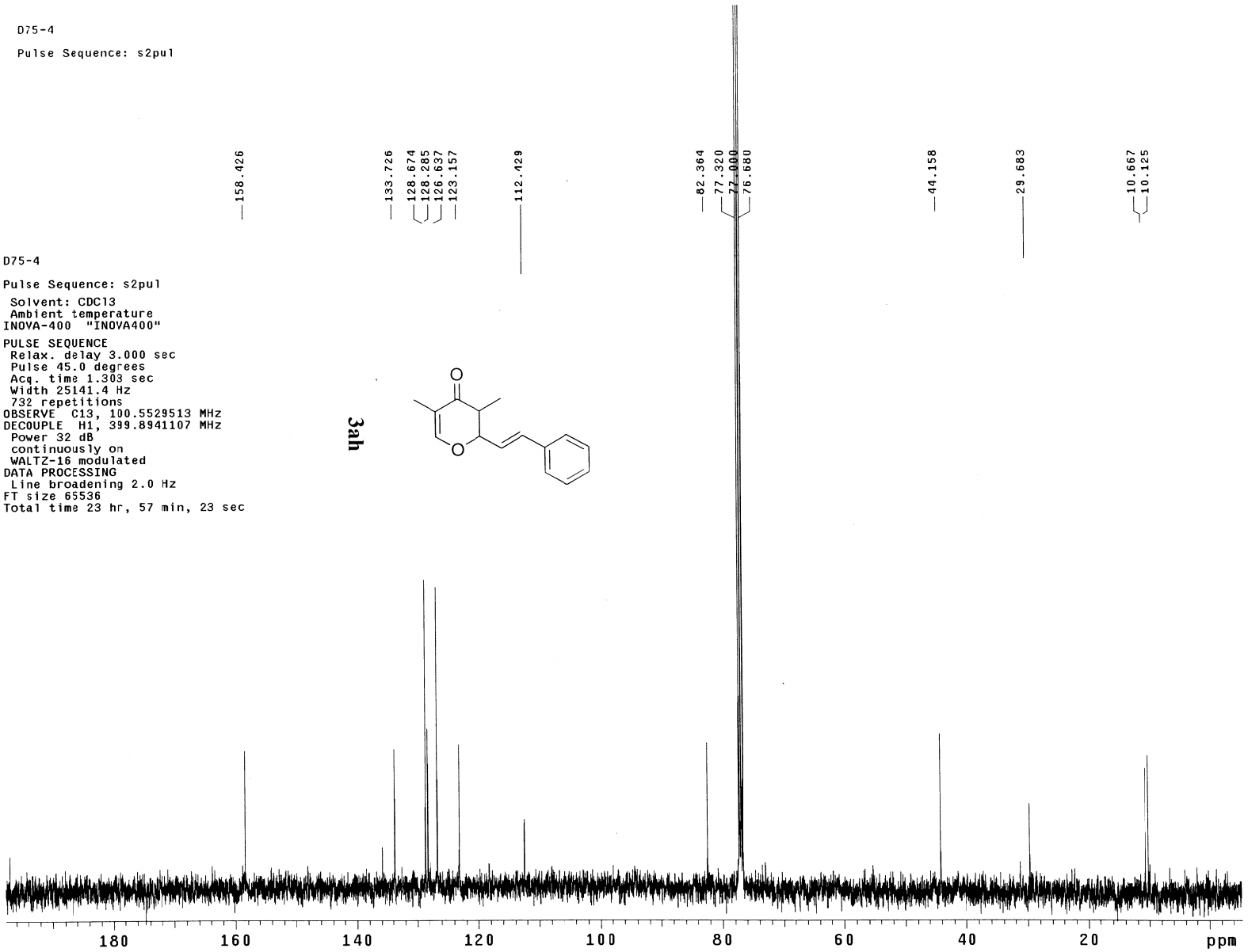


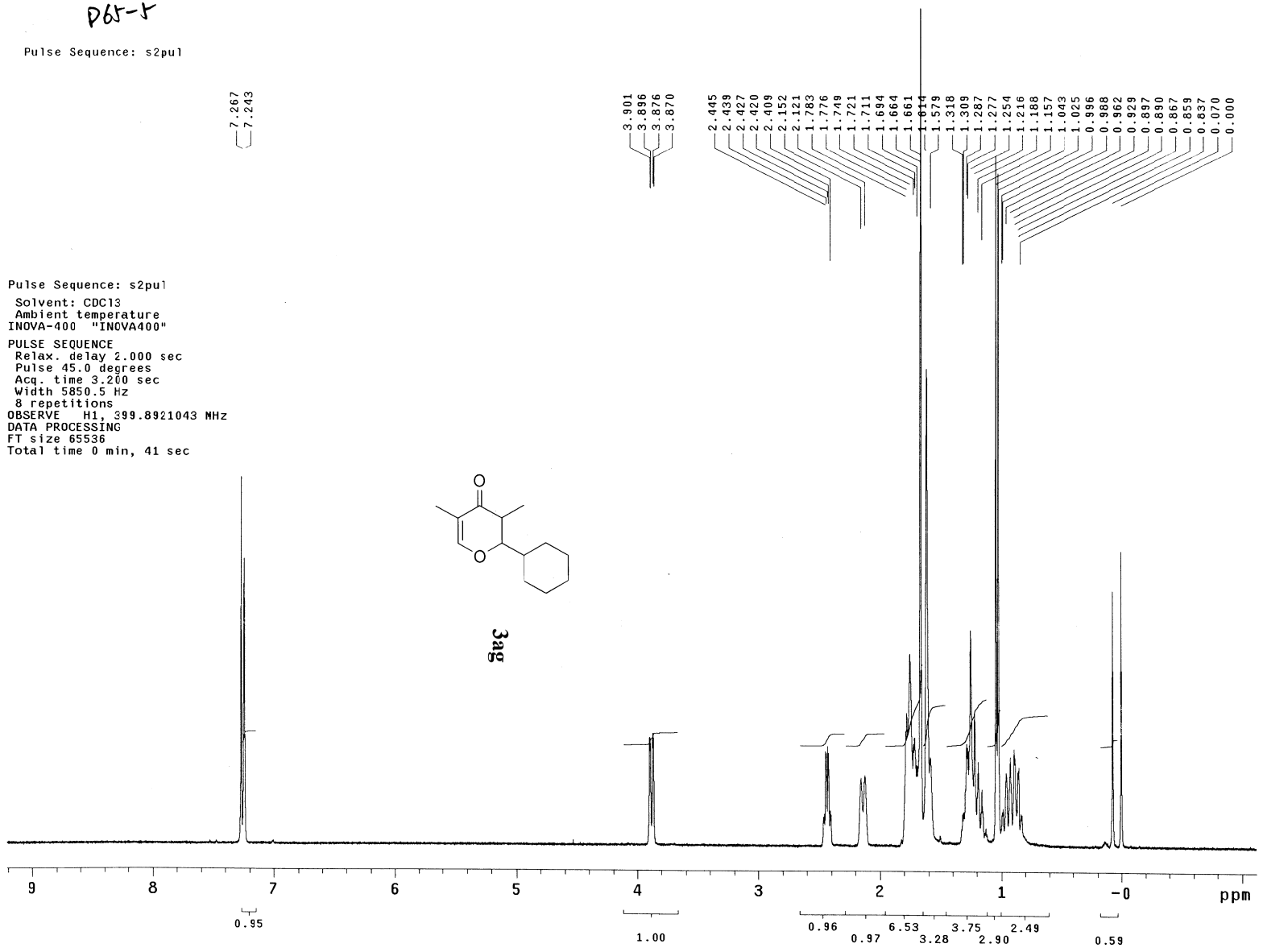
3af

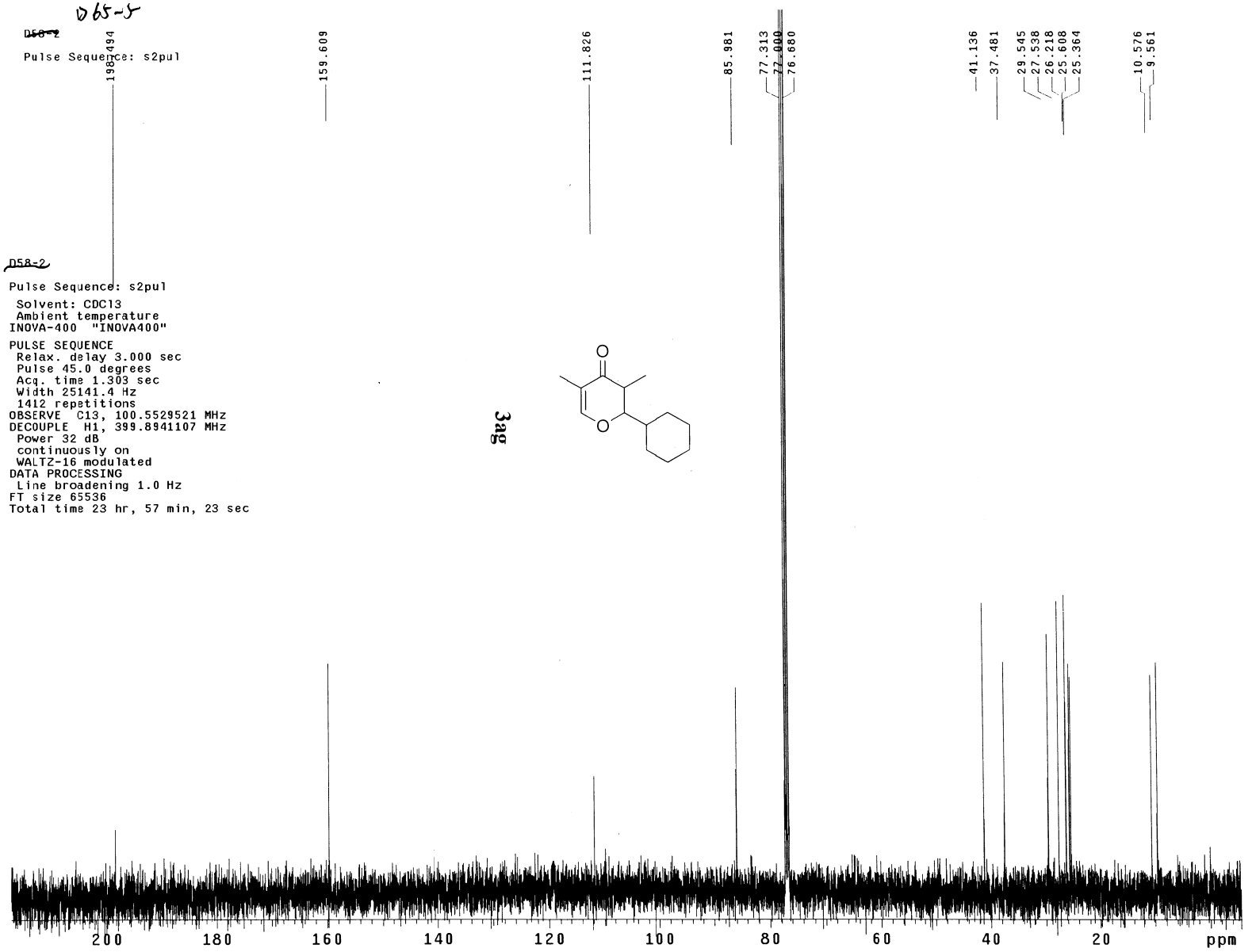
```
Current Data Parameters
NAME          fxm-2006-80
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060728
Time                17.15
INSTRUM             av300
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
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                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  3.00 usec
PL1                -2.00 dB
SFO1         300.1320882 MHz

F2 - Processing parameters
SI                  32768
SF           300.1300124 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
CY                  10.00 cm
F1P                10.000 ppm
F1                3001.30 Hz
F2P                -0.500 ppm
F2                -150.06 Hz
PPMCM             0.52500 ppm/cm
HZCM            157.56825 Hz/cm
```

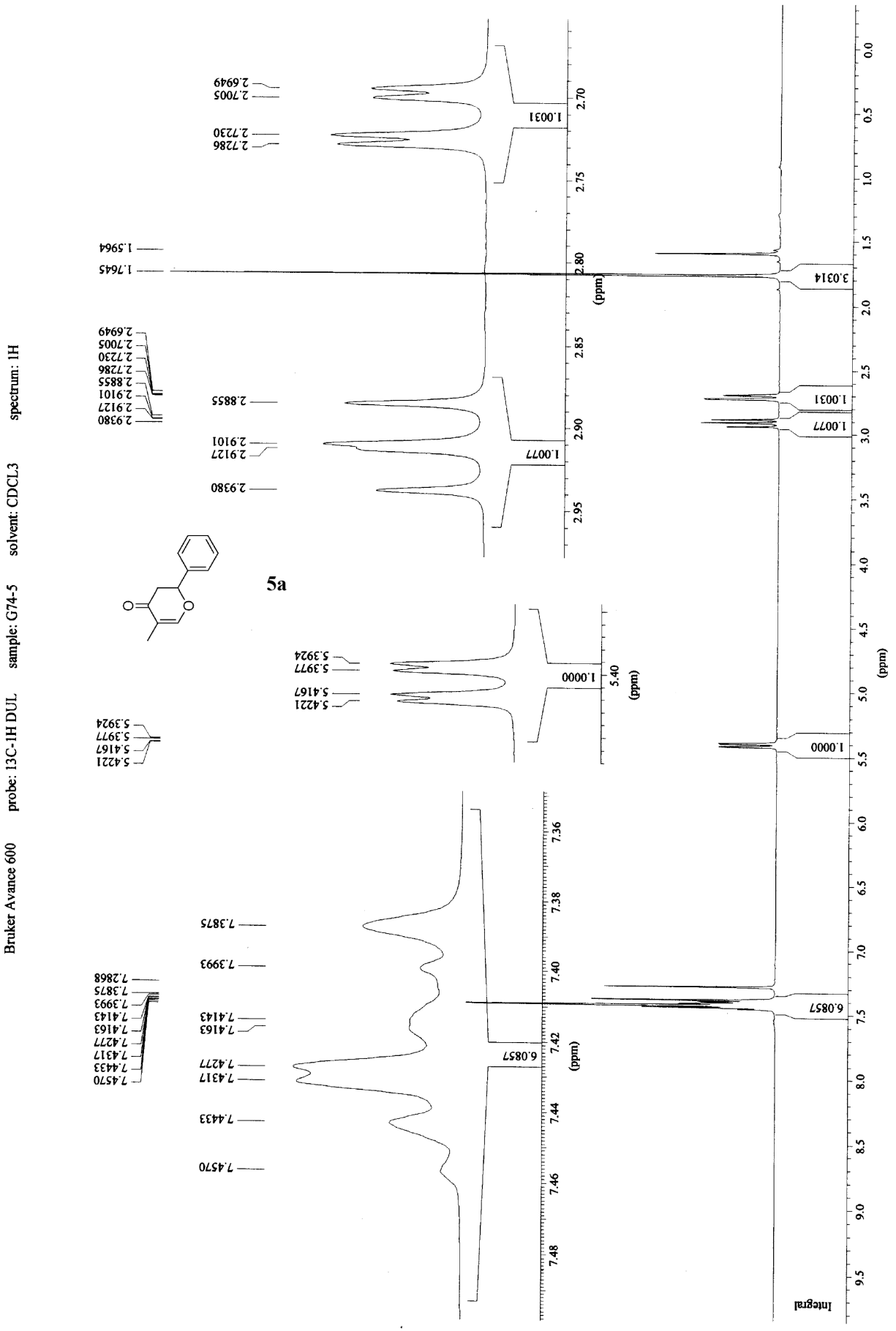

D75-4
Pulse Sequence: s2pul
7.423
7.404
7.366
7.348
7.329
7.303
7.285
7.272
7.264
6.757
6.717
6.285
6.269
6.245
6.228
5.025
5.012
5.003
2.596
2.587
2.578
2.569
1.711
1.709
1.130
1.111
0.000
7.36
0.95
0.97
1.00
1.13
3.57
3.14
ppm
D75-4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.198 sec
Width 4602.5 Hz
32 repetitions
OBSERVE H1, 399.8921058 MHz
DATA PROCESSING
FT size 32768
Total time 2 min, 46 sec

3ah

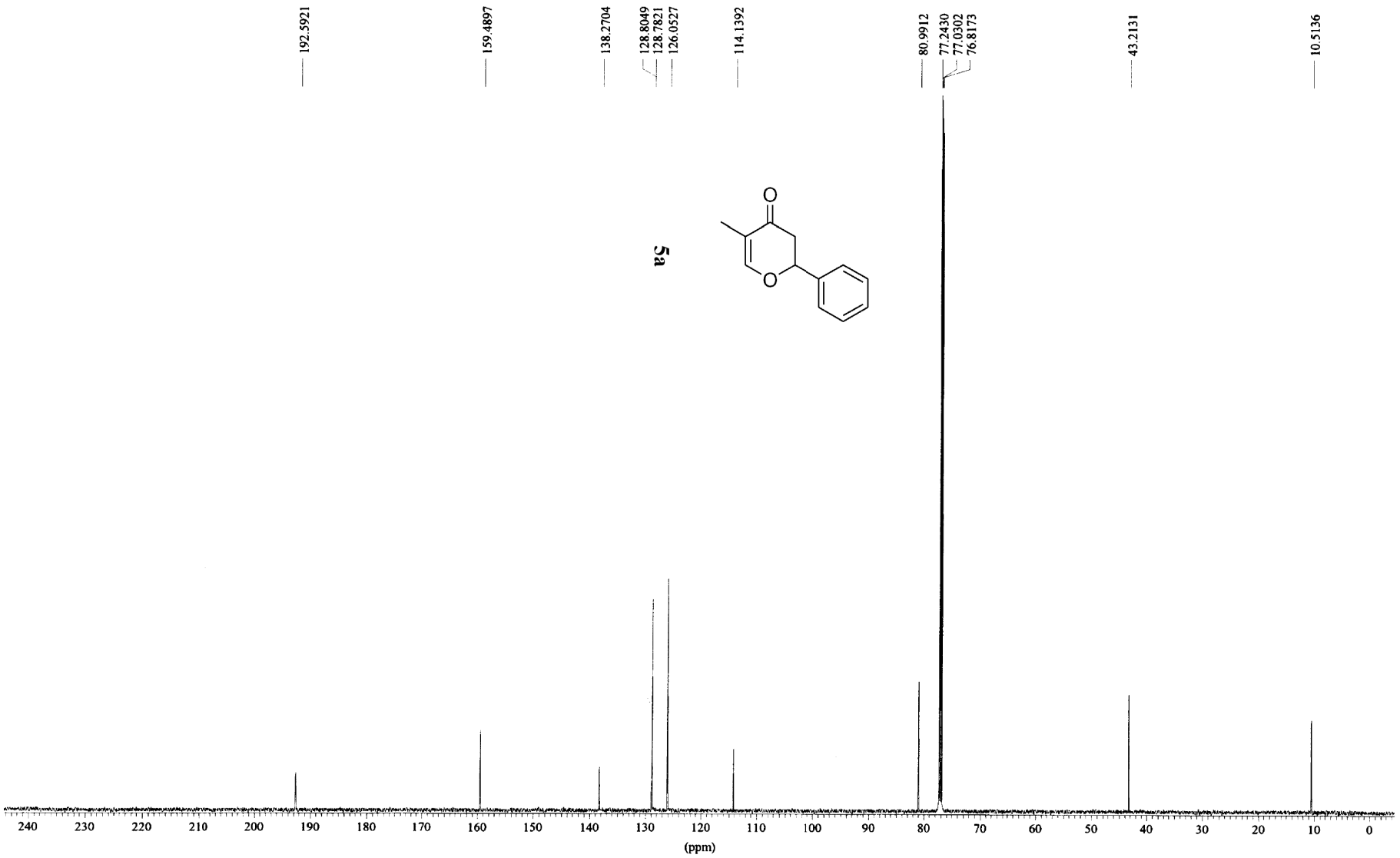

D75-4
Pulse Sequence: s2pul
158.426
133.726
128.674
128.285
126.637
123.157
112.429
82.364
77.320
77.000
76.680
44.158
29.683
10.667
10.125
D75-4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
732 repetitions
OBSERVE C13, 100.5529513 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 23 hr, 57 min, 23 sec
3ah
O
O
180
160
140
120
100
80
60
40
20
ppm

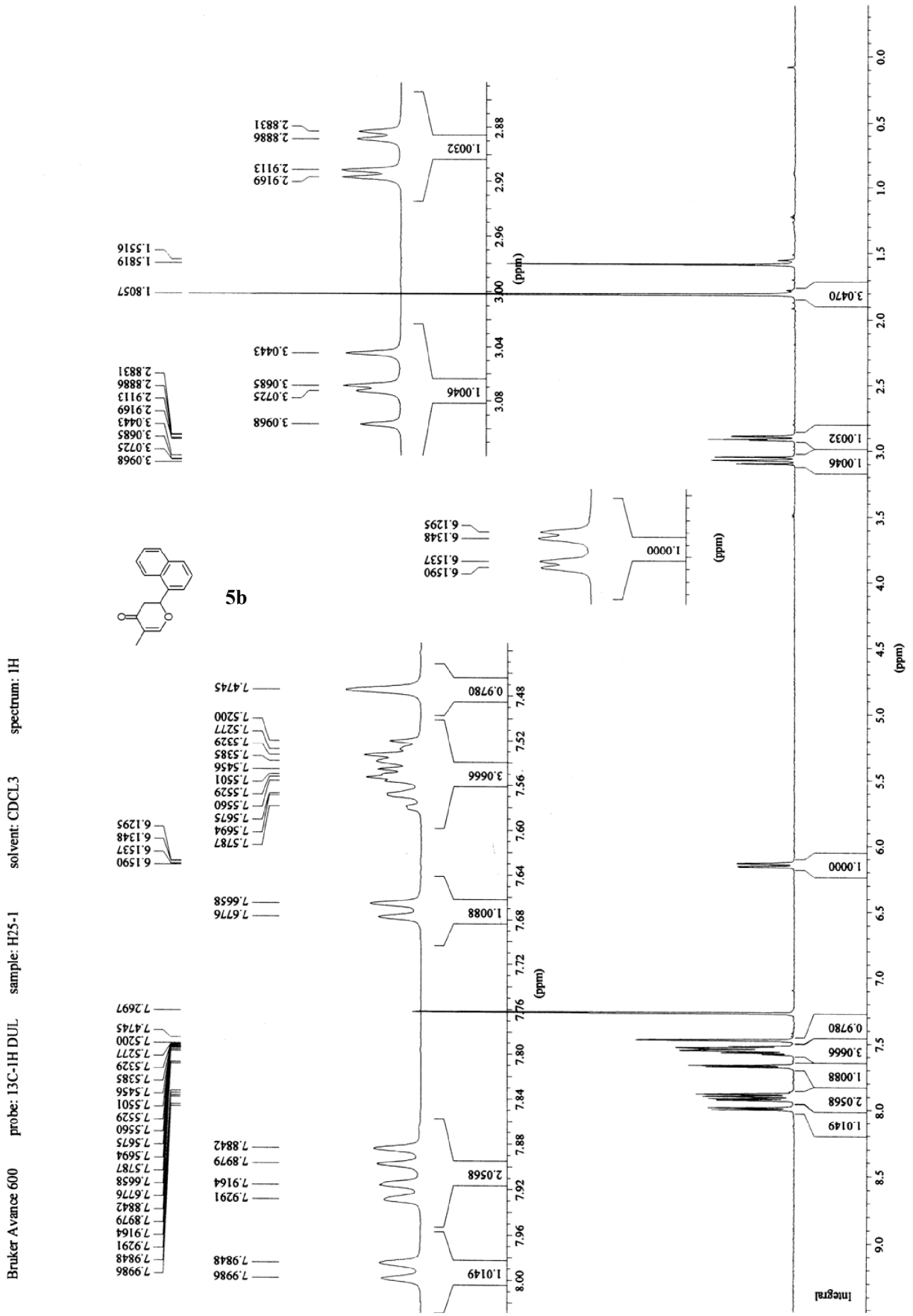

P65-5
Pulse Sequence: s2pul
7.267
7.243
3.901
3.896
3.876
3.870
2.445
2.439
2.427
2.420
2.409
2.152
2.121
1.783
1.776
1.749
1.721
1.711
1.694
1.664
1.661
1.614
1.579
1.318
1.309
1.287
1.277
1.254
1.216
1.188
1.157
1.043
1.025
0.996
0.988
0.962
0.929
0.897
0.890
0.867
0.853
0.837
0.070
0.000
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5850.5 Hz
8 repetitions
OBSERVE H1, 399.8921043 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 41 sec
O
O
3ag
9
8
7
6
5
4
3
2
1
-0
ppm
0.95
1.00
0.96
0.97
6.53
3.28
3.75
2.90
2.49
0.59

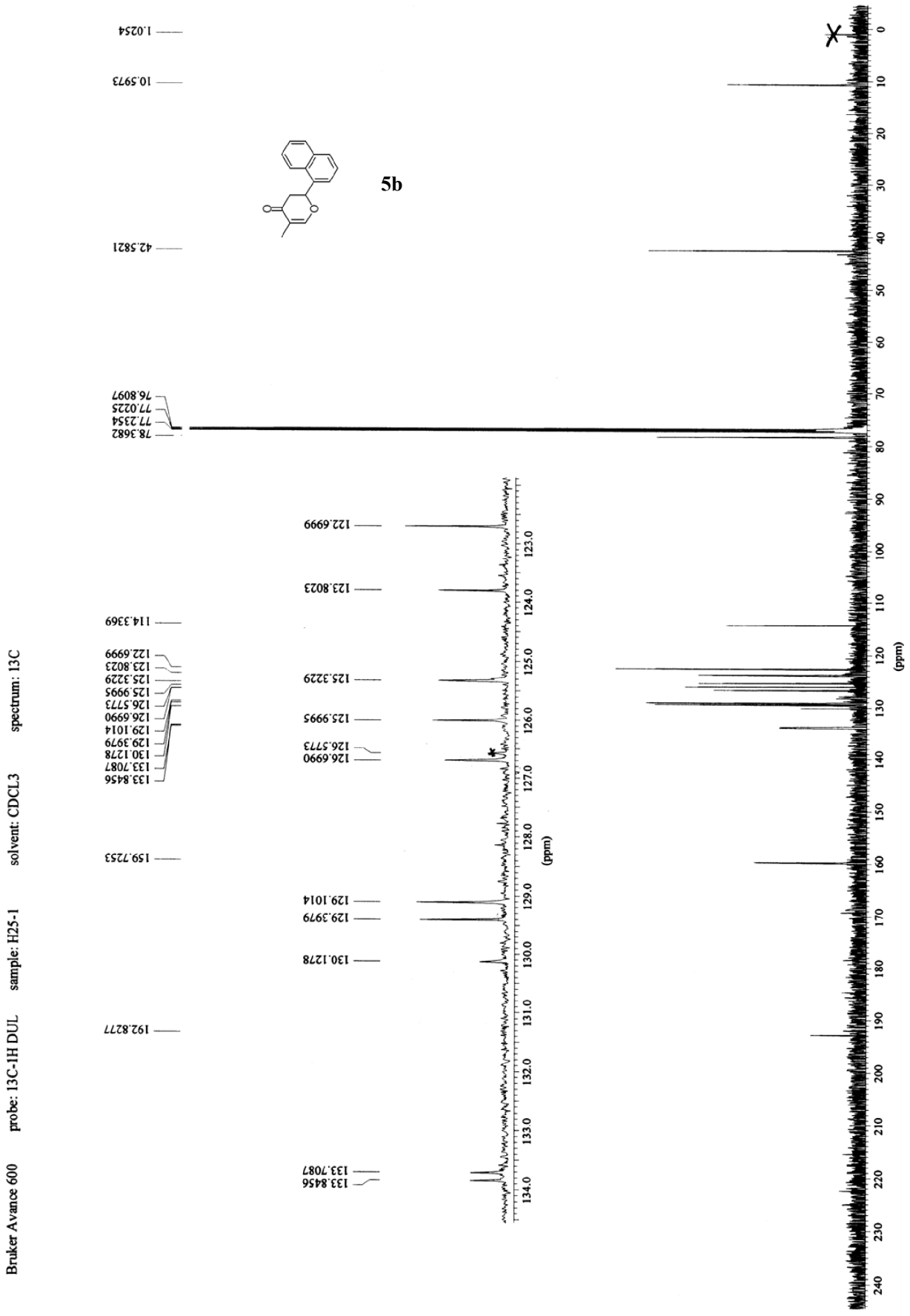

D65-5
D58-2
Pulse Sequence: s2pul
198.494
159.609
111.826
85.981
77.313
77.000
76.680
41.136
37.481
29.545
27.538
26.218
25.608
25.364
10.576
9.561
D58-2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
1412 repetitions
OBSERVE C13, 100.5529521 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 23 hr, 57 min, 23 sec
3ag
O
O
200
180
160
140
120
100
80
60
40
20
ppm

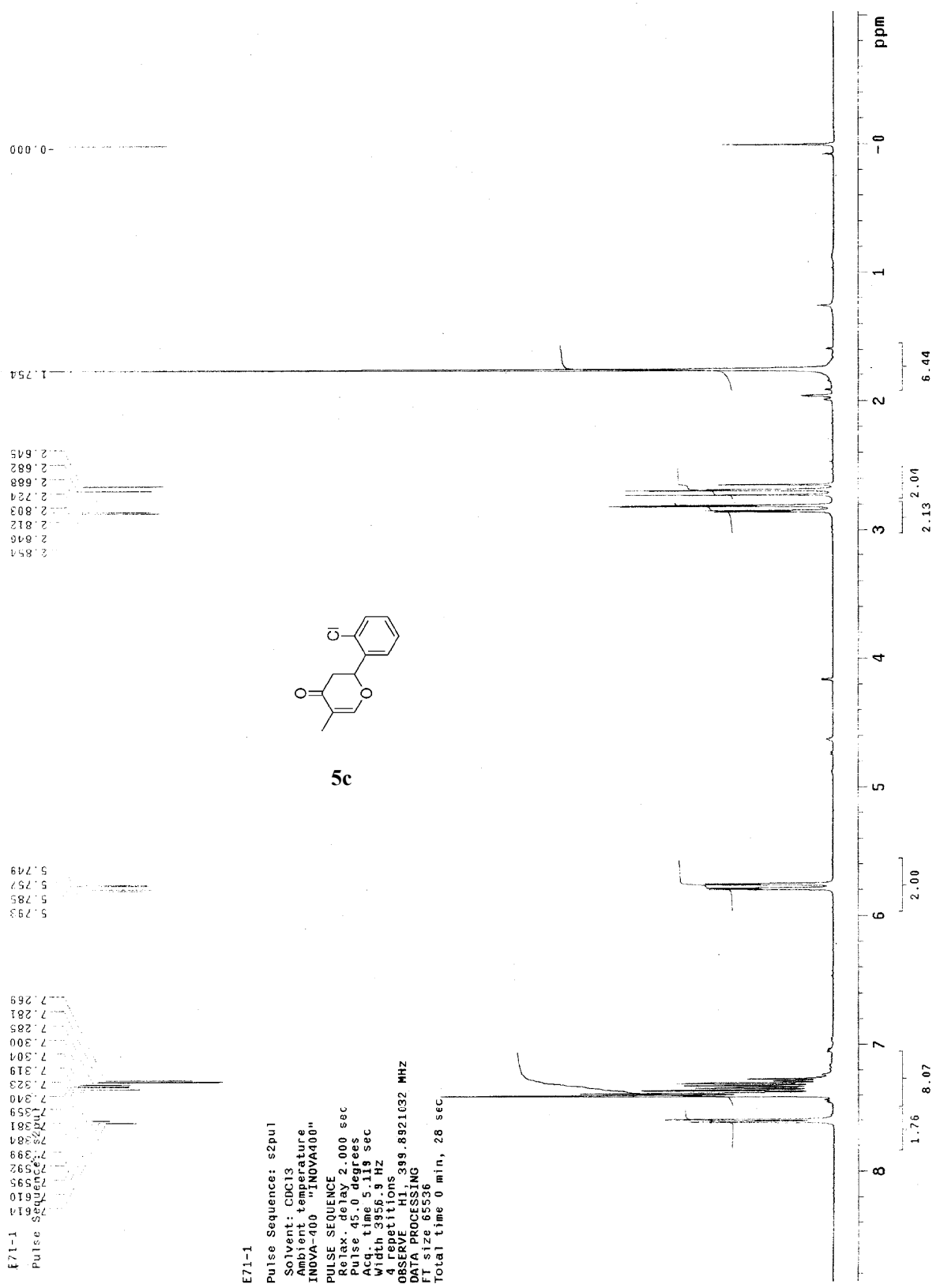

Bruker Avance 600 probe: 13C-1H DUL sample: G74-5 solvent: CDCL3 spectrum: 1H
5a
Integral
(ppm)

Bruker Avance 600 probe: 13C-1H DUL sample: G74-5 solvent: CDCL3 spectrum: 13C

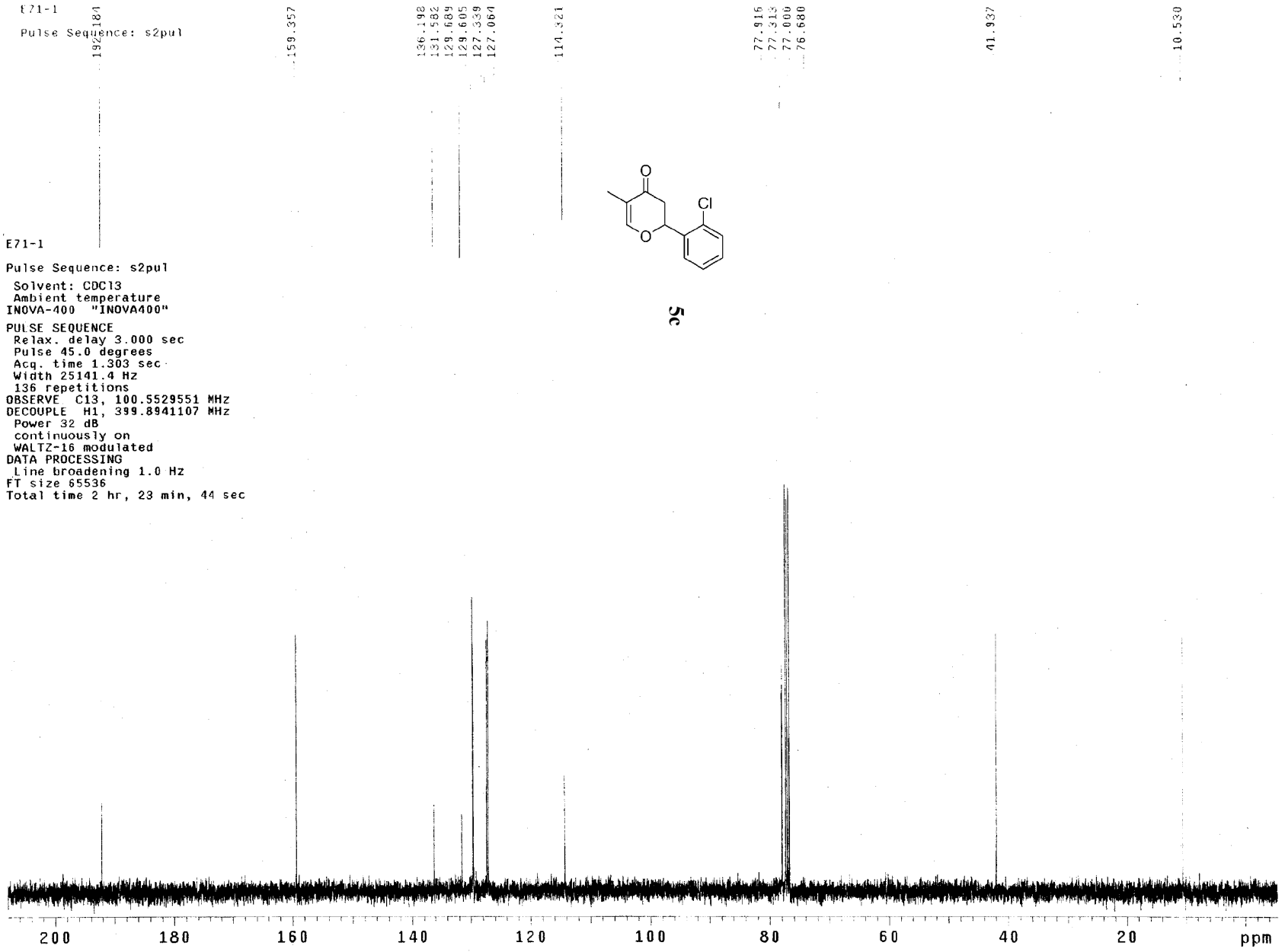


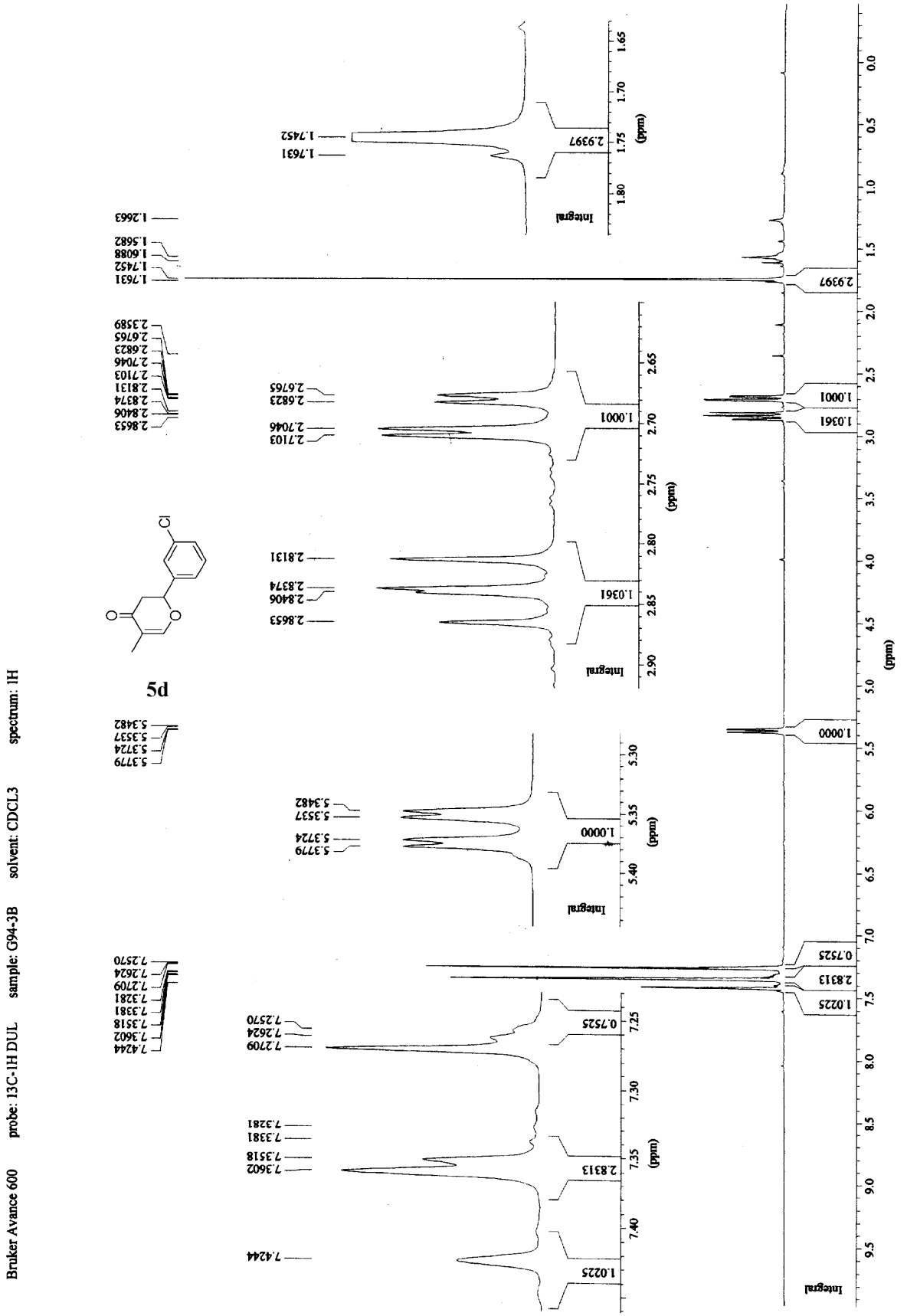

Bruker Avance 600 probe: 13C-1H DUL sample: H25-1 solvent: CDCL3 spectrum: 1H
5b
Integral
(ppm)


Bruker Avance 600
probe: 13C-1H DUL
sample: H25-1
solvent: CDCL3
spectrum: 13C
5b
1.0254
10.5973
42.5821
76.8097
77.0225
77.2354
78.3682
114.3369
122.6999
123.8023
125.3229
125.9995
126.5773
126.6990
129.1014
129.3979
130.1278
133.7087
133.8456
159.7253
192.8277
(ppm)

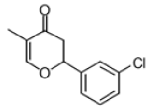

E71-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 5.119 sec
Width 3956.9 Hz
4 repetitions
OBSERVE H1, 399.8921032 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 28 sec
ppm
Cl
O
O

5c


E71-1
Pulse Sequence: s2pul
192.184
159.357
136.198
131.582
129.689
129.605
127.339
127.064
114.321
77.916
77.313
77.000
76.680
41.937
10.530
E71-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
136 repetitions
OBSERVE C13, 100.5529551 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 2 hr, 23 min, 44 sec
O
Cl
O
5c
200
180
160
140
120
100
80
60
40
20
ppm

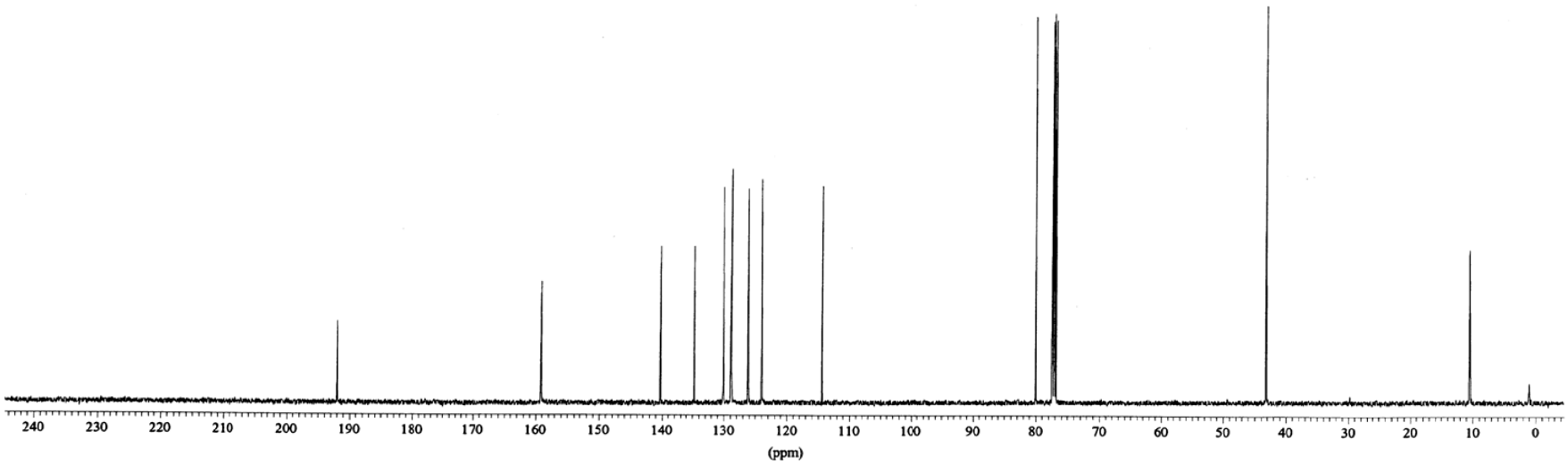

Bruker Avance 600 probe: 13C-1H DUL sample: G94-3B solvent: CDCL3 spectrum: 1H
5d
Cl
O
O
(ppm)
Integral

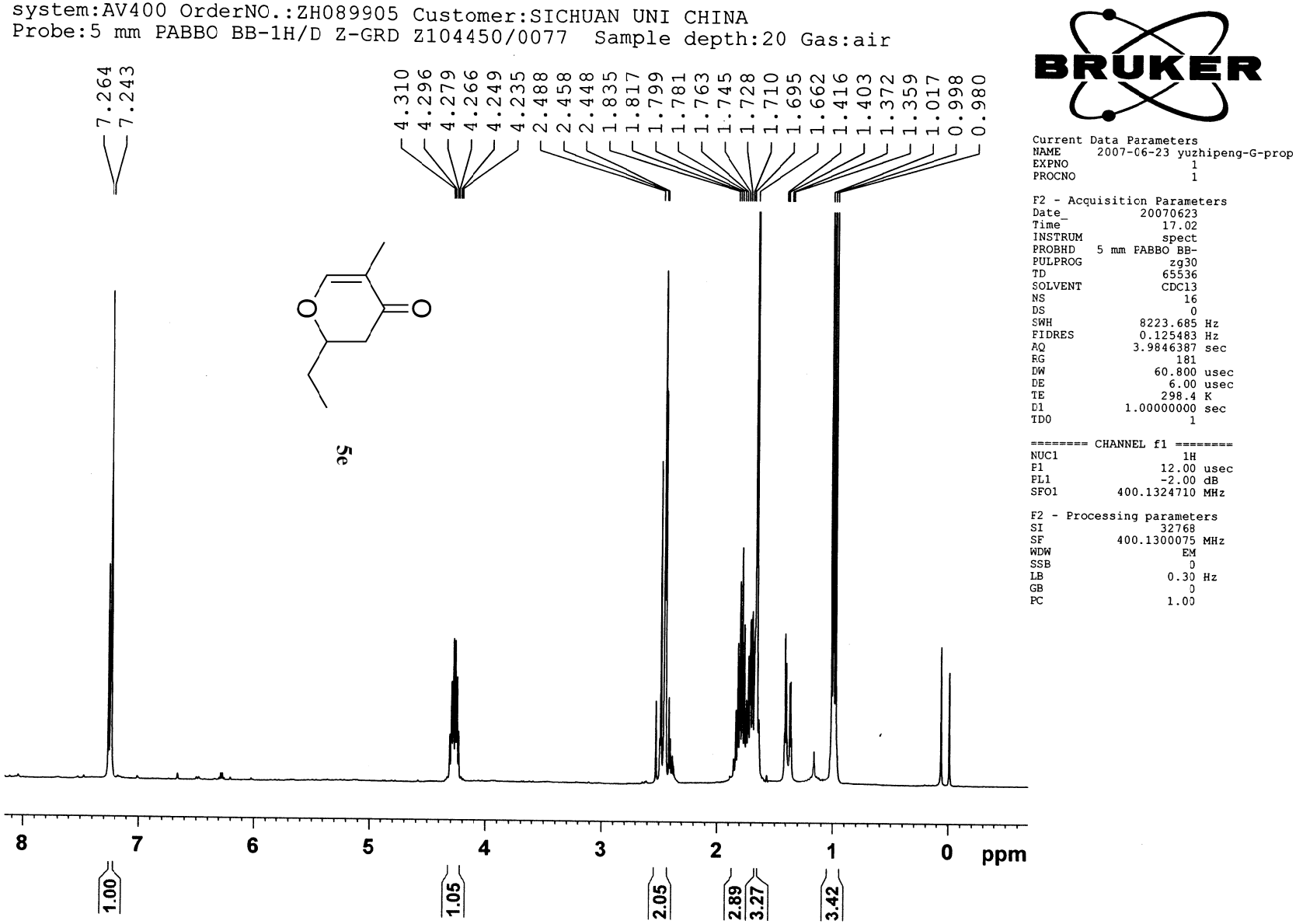
Bruker Avance 600 probe: 13C-1H DUL sample: H7H solvent: CDCL3 spectrum: 13C

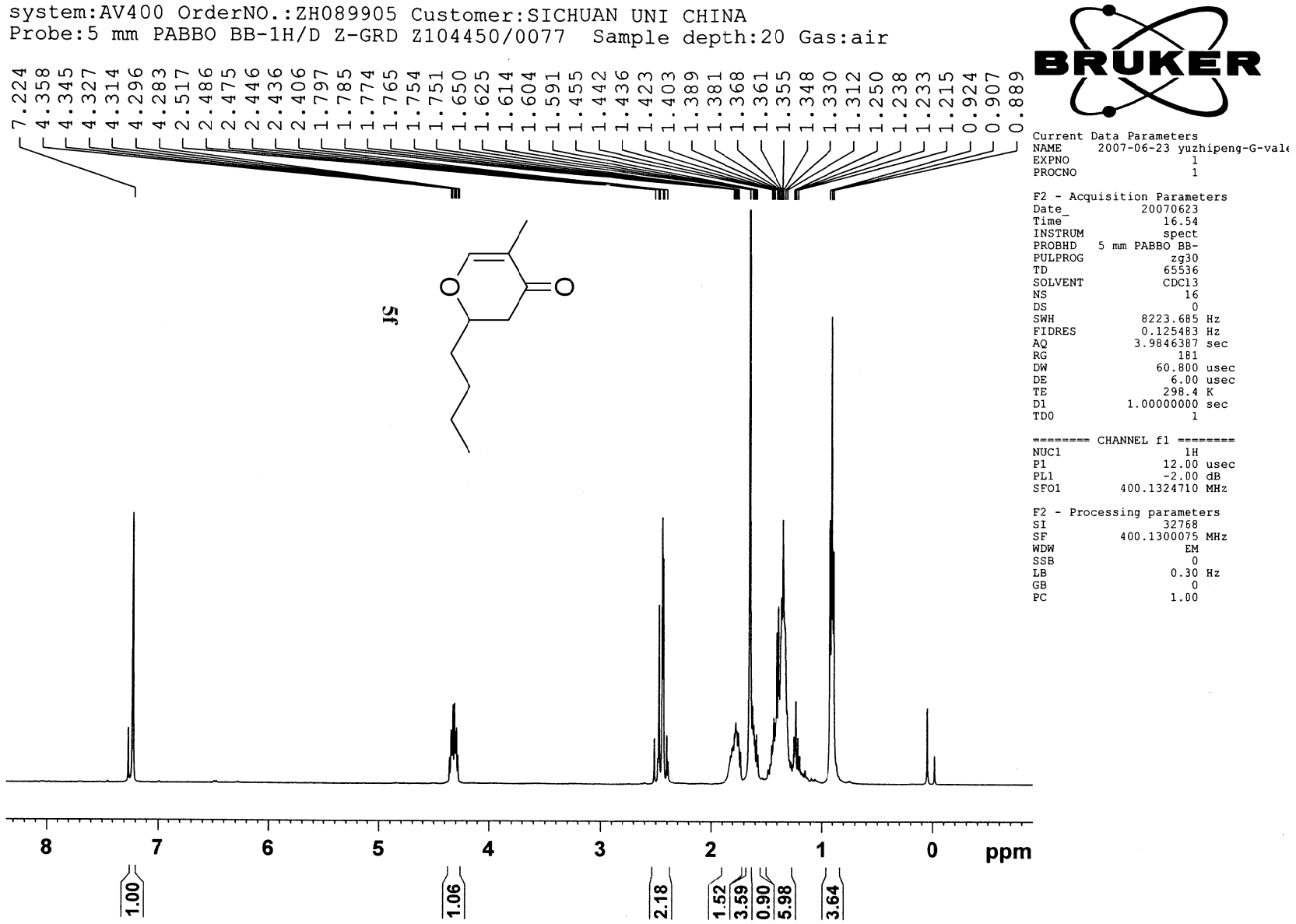


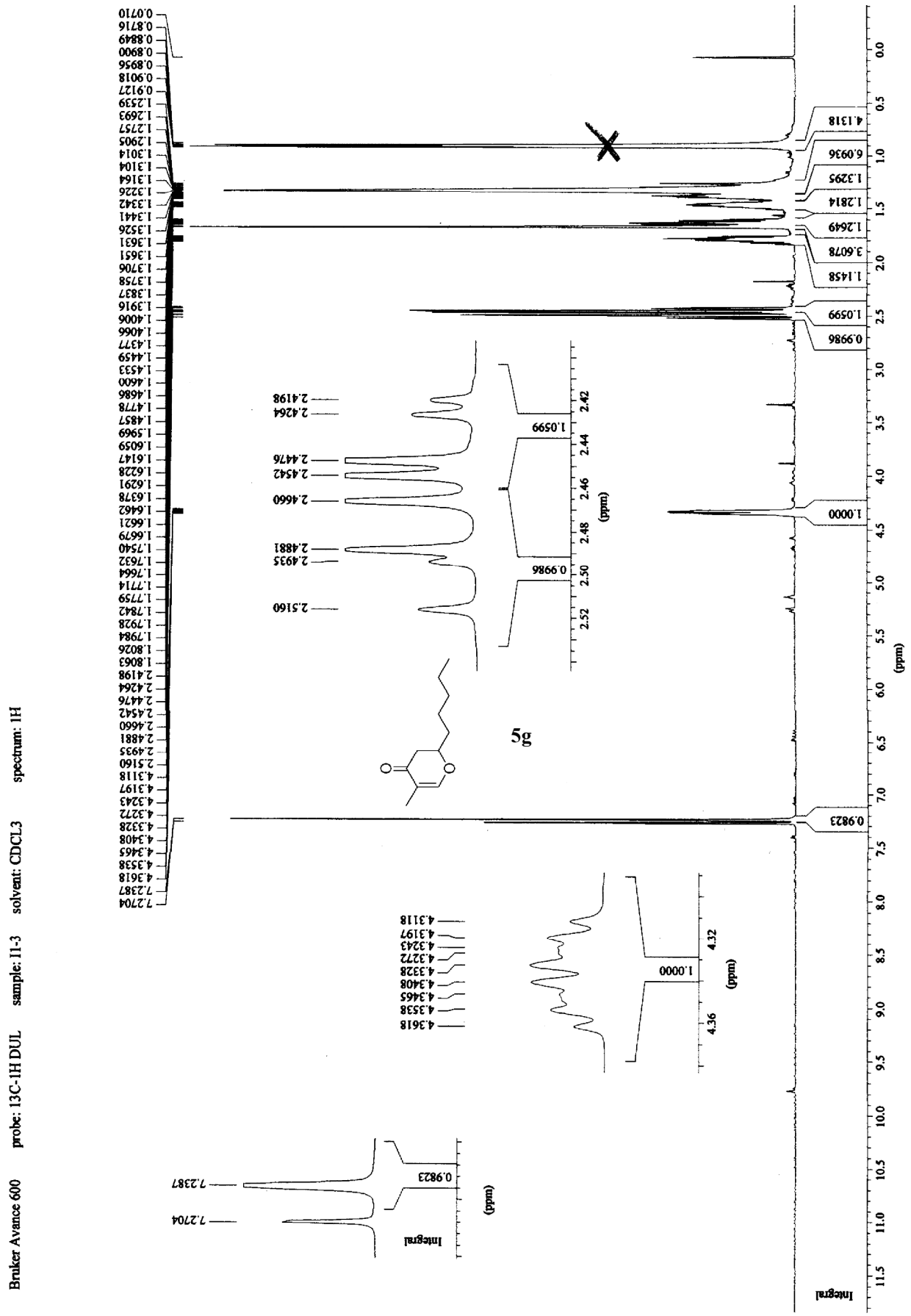
5d

191.9458
159.1095
140.3307
134.7427
130.0974
128.8353
126.2124
124.0456
114.3749
80.0484
77.3039
77.0910
76.8781
43.1447
10.4680
1.0178

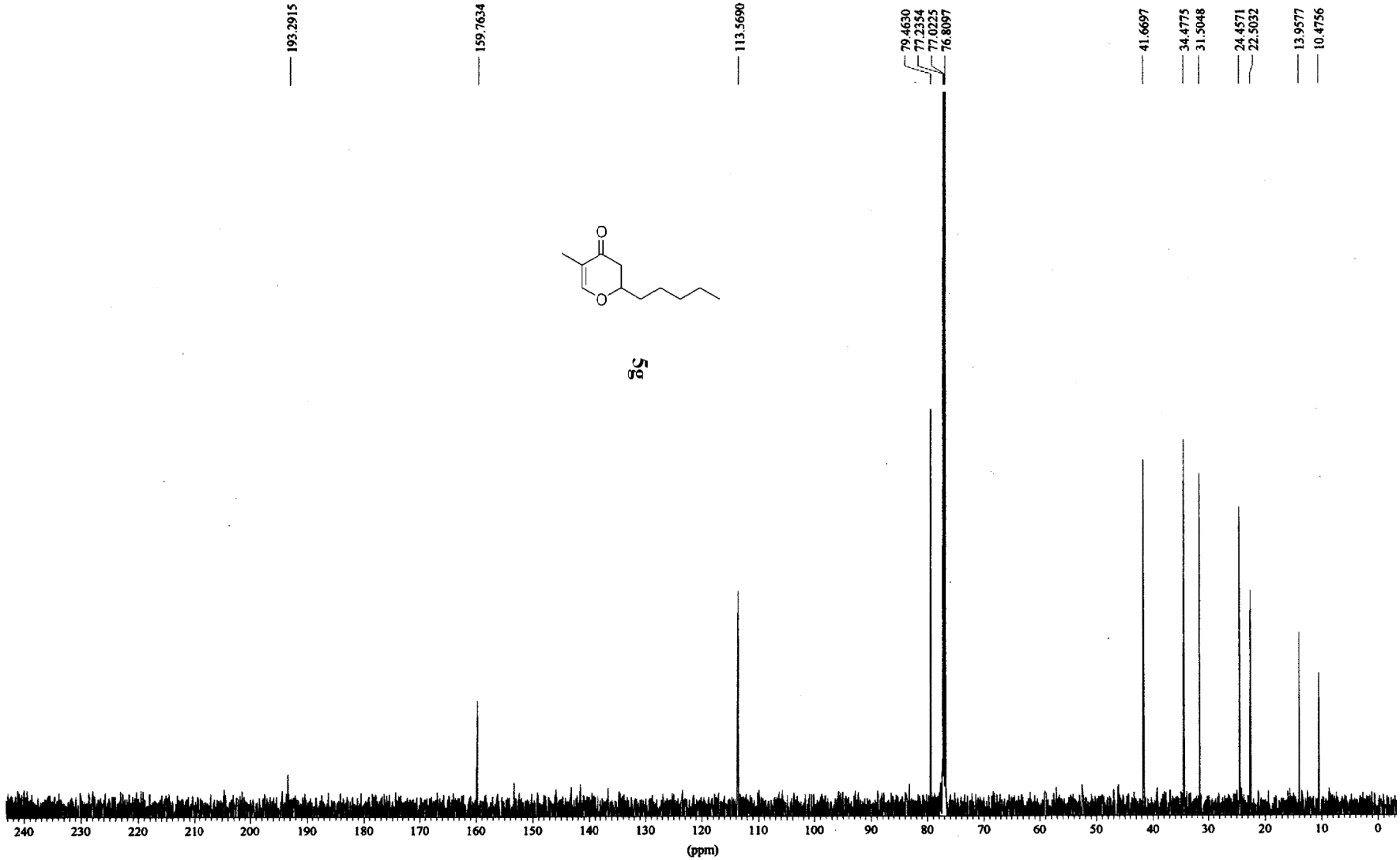


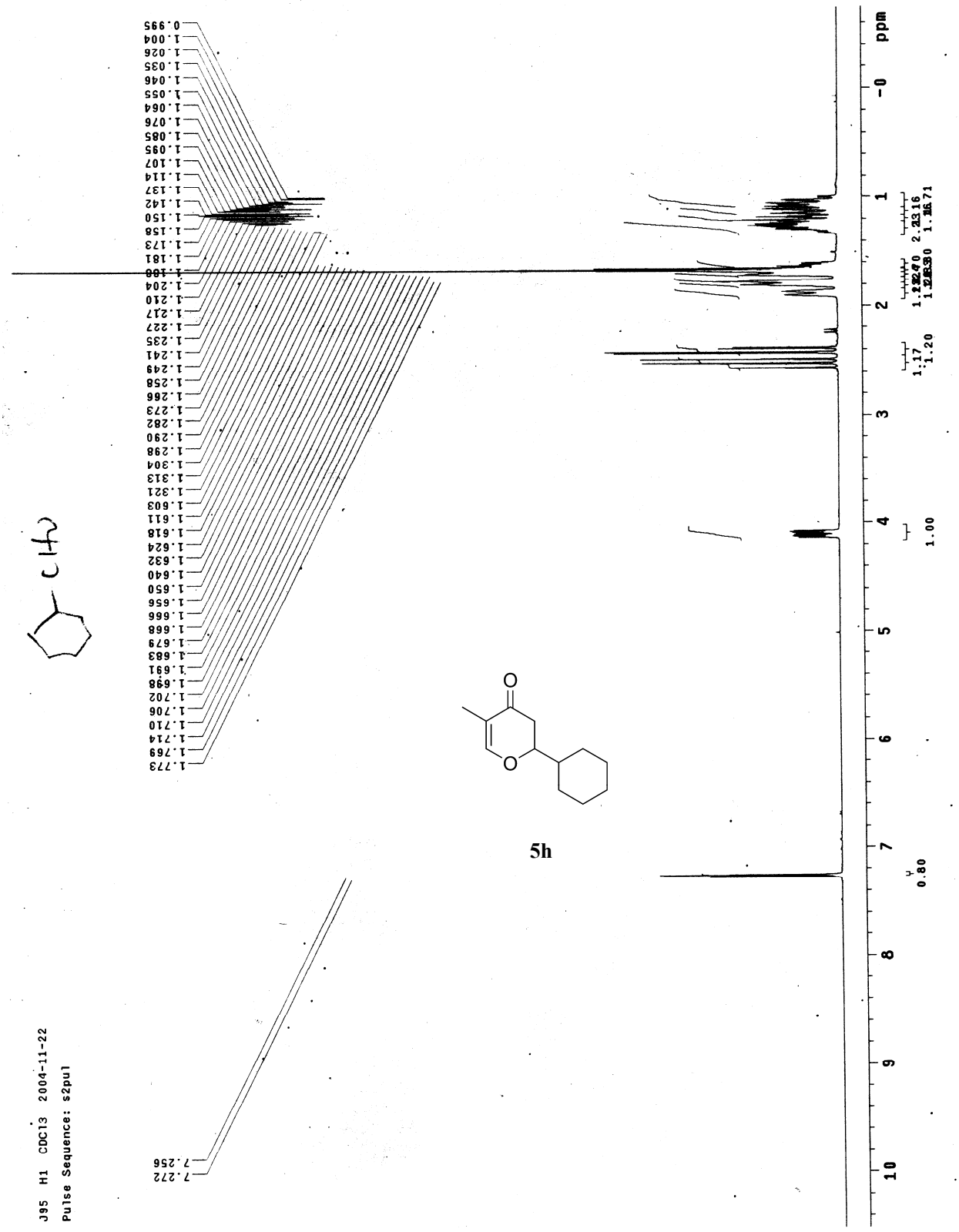

system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air
7.264
7.243
4.310
4.296
4.279
4.266
4.249
4.235
2.488
2.458
2.448
1.835
1.817
1.799
1.781
1.763
1.745
1.728
1.710
1.695
1.662
1.416
1.403
1.372
1.359
1.017
0.998
0.980
5e
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
2.05
2.89
3.27
3.42
BRUKER
Current Data Parameters
NAME 2007-06-23 yuzhipeng-G-prop
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070623
Time 17.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.00 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

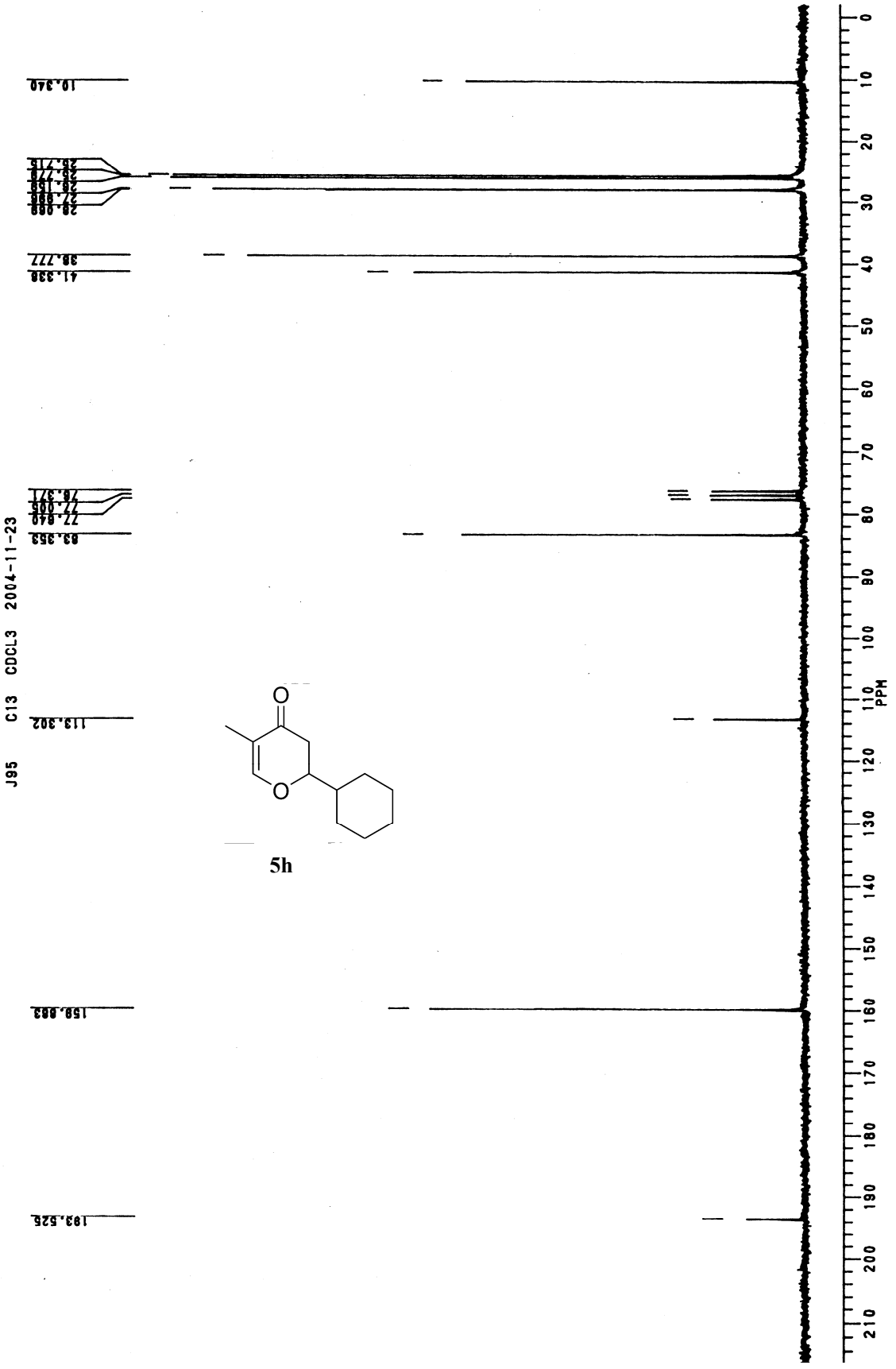

system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air
7.224 4.358 4.345 4.327 4.314 4.296 4.283 2.517 2.486 2.475 2.446 2.436 2.406 1.797 1.785 1.774 1.765 1.754 1.751 1.650 1.625 1.614 1.604 1.591 1.455 1.442 1.436 1.423 1.403 1.389 1.381 1.368 1.361 1.355 1.348 1.330 1.312 1.250 1.238 1.233 1.215 0.924 0.907 0.889
5f
8 7 6 5 4 3 2 1 0 ppm
1.00 1.06 2.18 1.52 3.59 0.90 5.98 3.64
BRUKER
Current Data Parameters
NAME 2007-06-23 yuzhipeng-G-vale
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070623
Time 16.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.00 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


Bruker Avance 600
probe: 13C-1H DUL
sample: I1-3
solvent: CDCL3
spectrum: 1H
5g
Integral
(ppm)

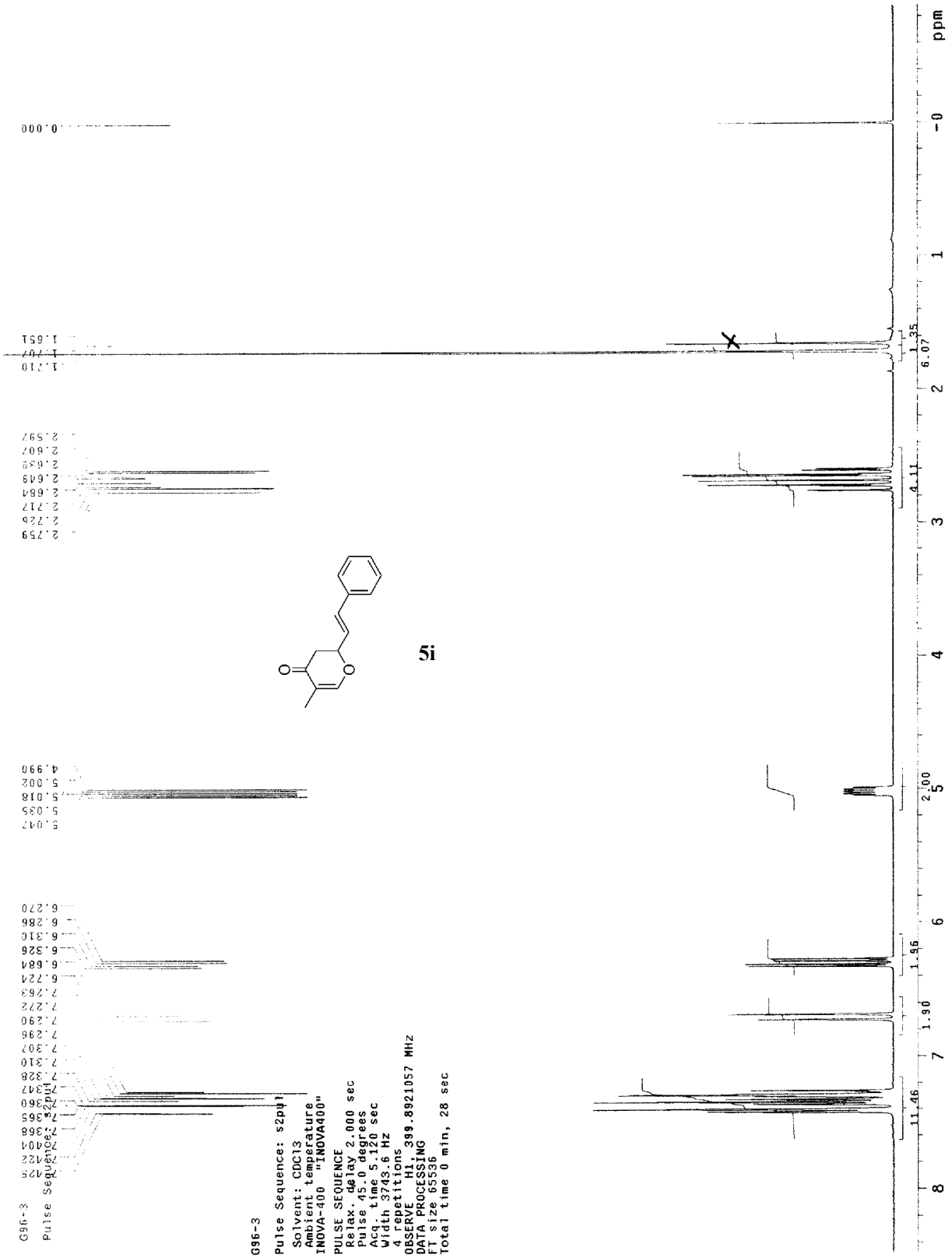
Bruker Avance 600 probe: 13C-1H DUL sample: I1-3 solvent: CDCL3 spectrum: 13C

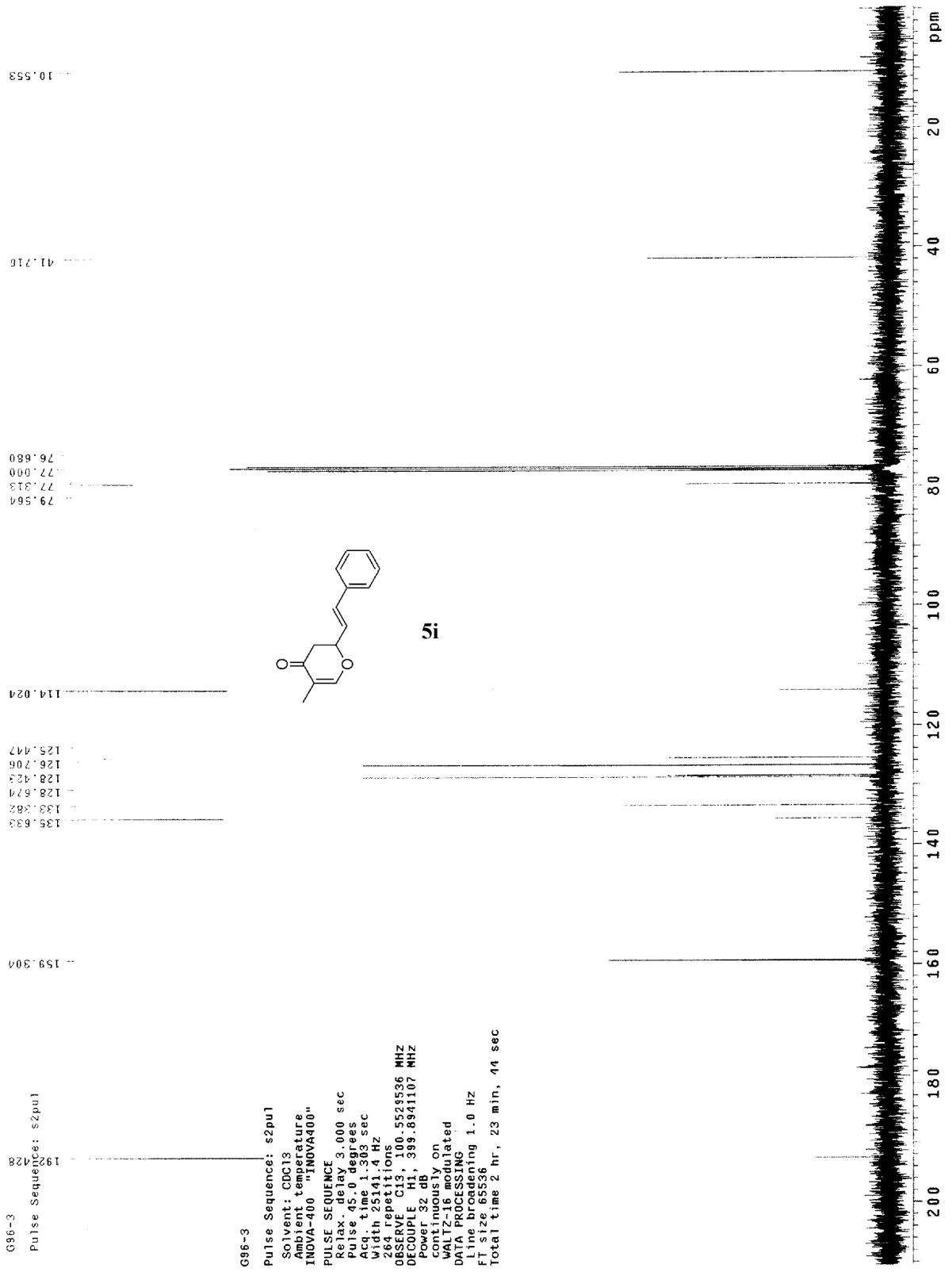



J95 H1 CDCl3 2004-11-22
Pulse Sequence: s2pul
ppm
5h



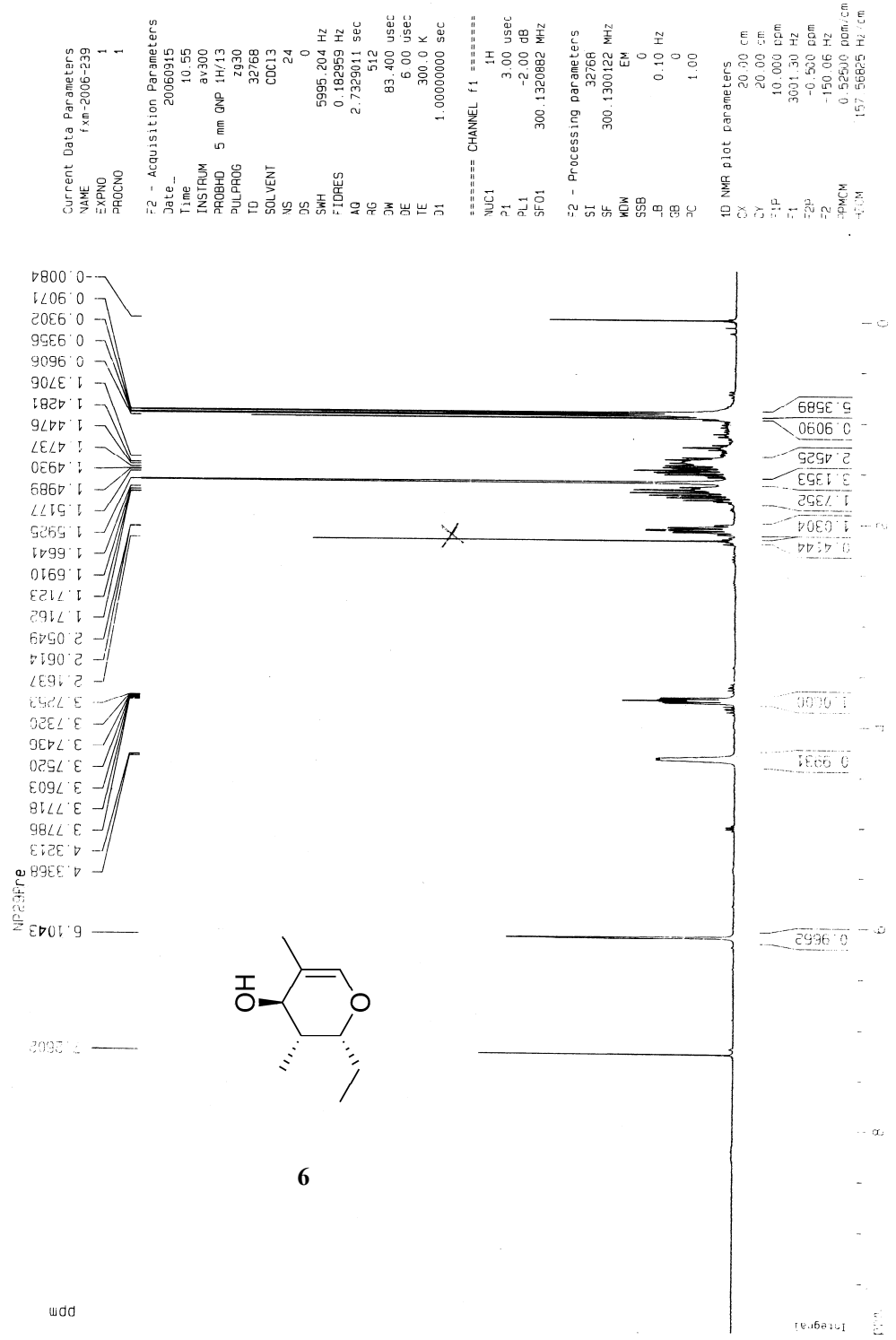
5h


5i
G96-3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 5.120 sec
Width 3743.6 Hz
4 repetitions
OBSERVE H1, 399.8921057 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 28 sec
ppm

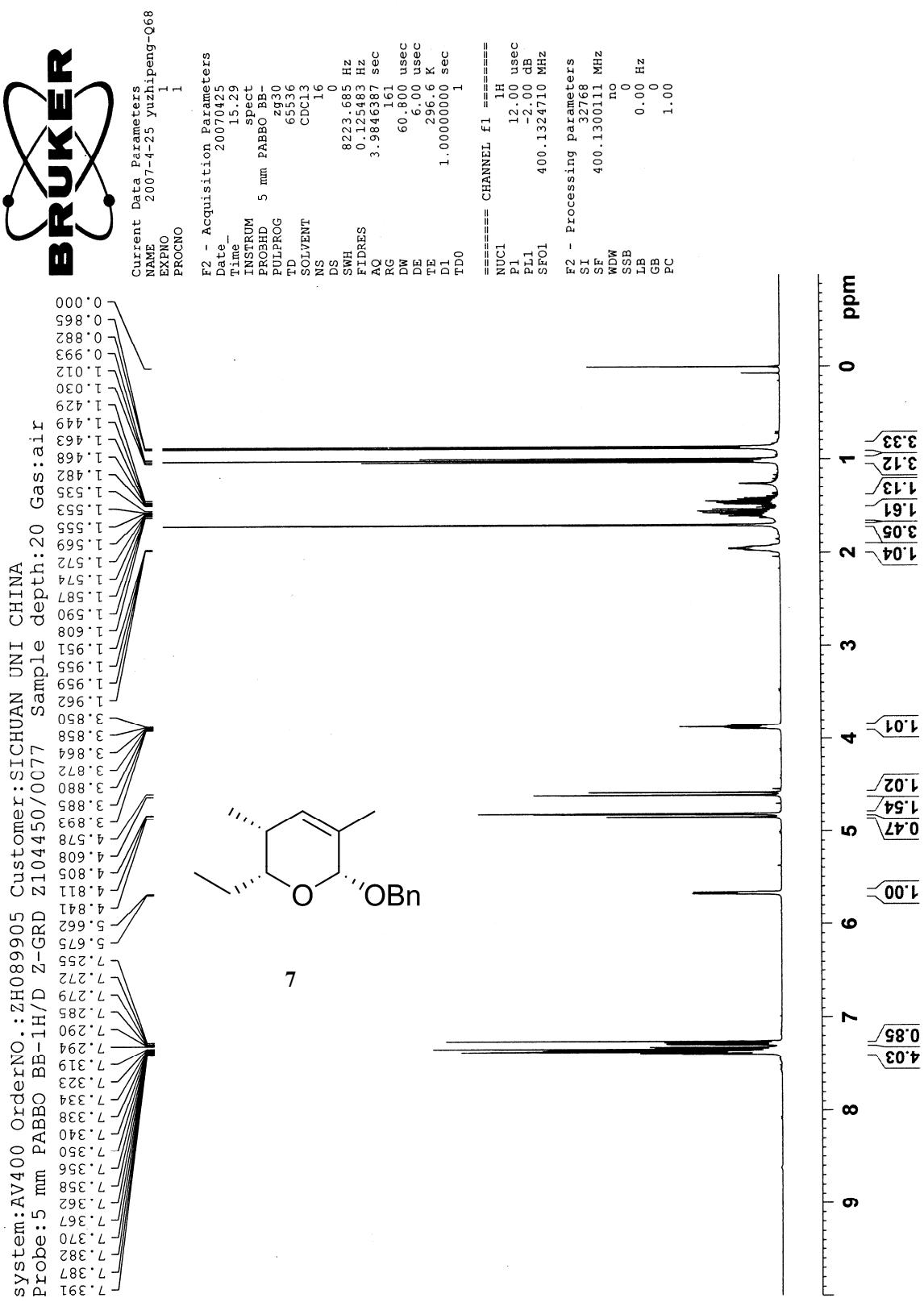

G96-3
Pulse Sequence: s2pul
192.428
159.304
135.833
133.382
128.674
128.423
126.706
125.447
114.024
79.564
77.313
77.000
76.680
41.716
10.553
ppm
G96-3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "INOVA400"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
264 repetitions
OBSERVE C13, 100.5529536 MHz
DECOUPLE H1, 399.8941107 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 2 hr, 23 min, 44 sec

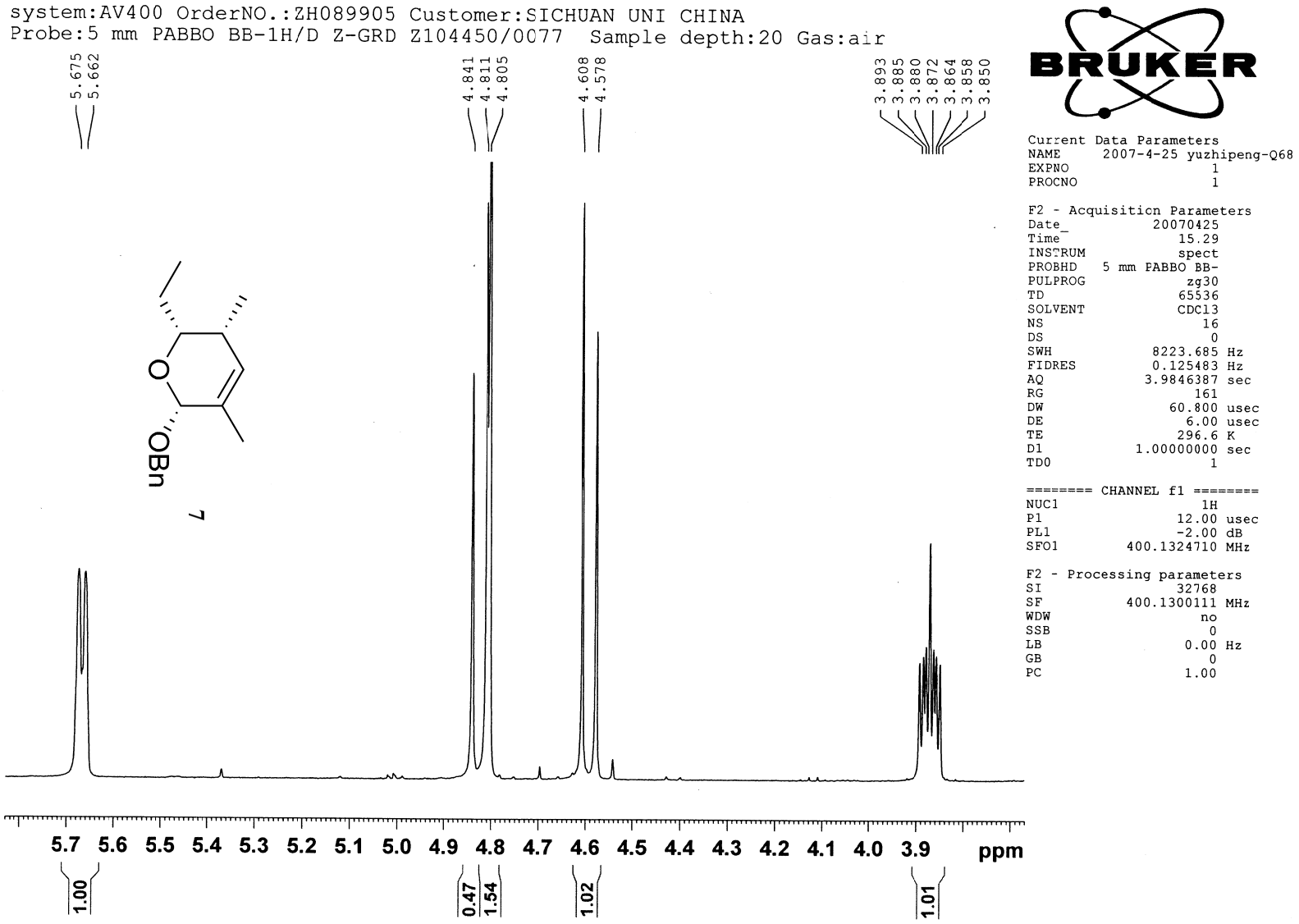
5i

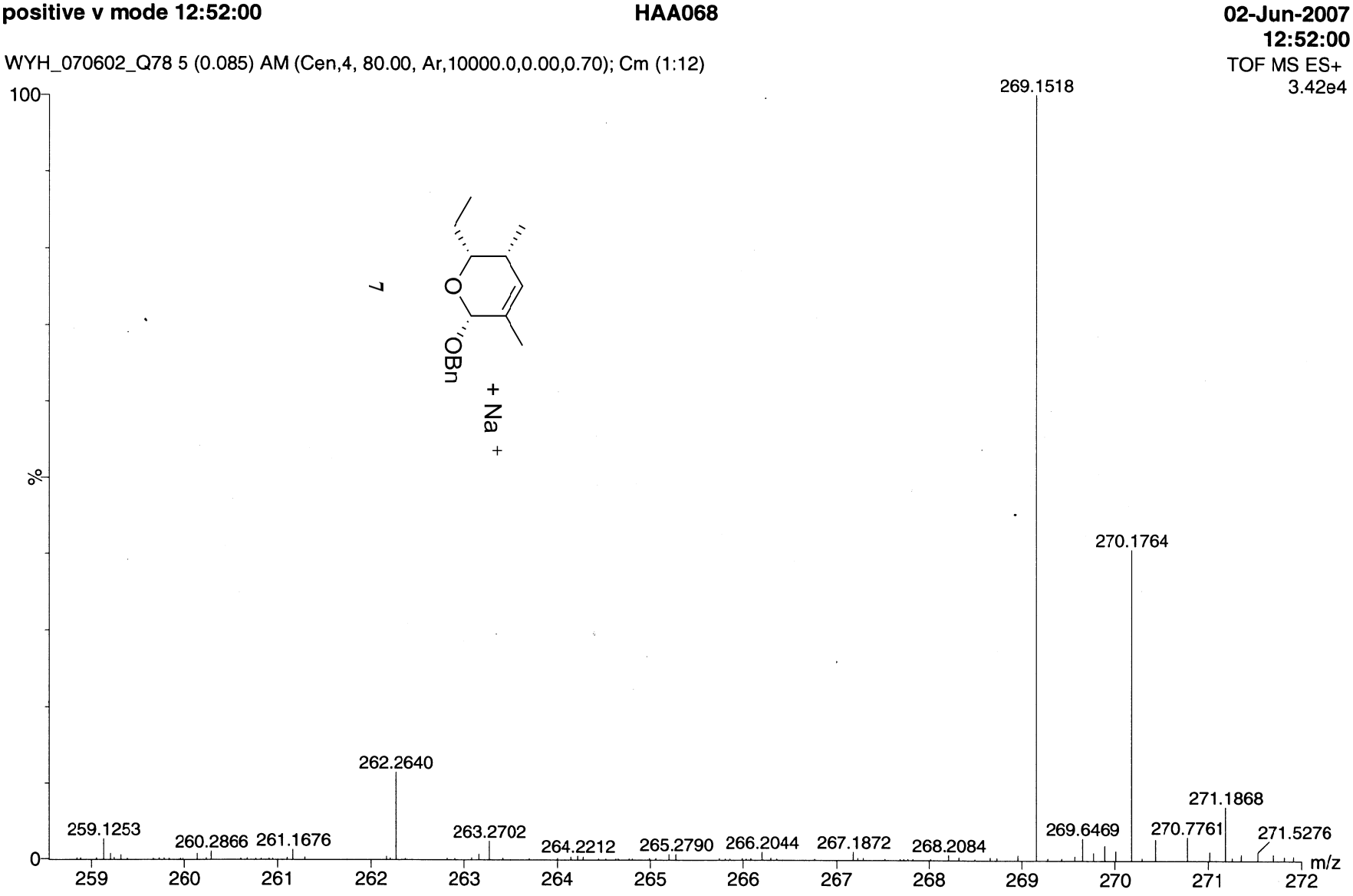
7. Copy of NMR and HRMS Spectra for Triketide Synthesis

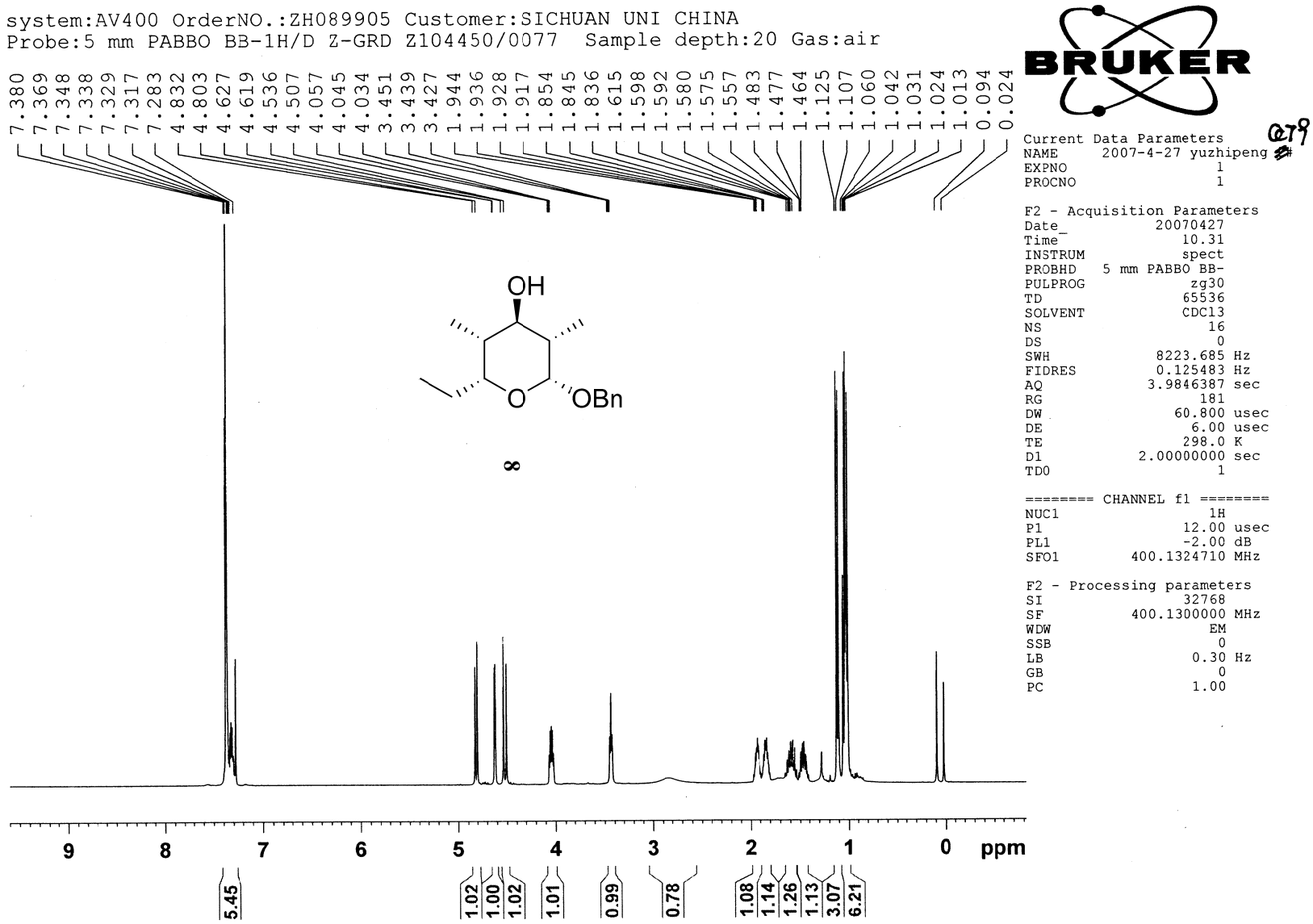


6


system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air
Current Data Parameters
NAME 2007-4-25 yuzhipeng-Q68
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070425
Time_ 15.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 161
DW 60.800 usec
DE 6.00 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300111 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
OBn
7
ppm
4.03
0.85
1.00
0.47
1.54
1.02
1.01
1.04
3.05
1.61
1.13
3.12
3.33


system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air
5.675
5.662
4.841
4.811
4.805
4.608
4.578
3.893
3.885
3.880
3.872
3.864
3.858
3.850
OBn
7
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9
ppm
1.00
0.47
1.54
1.02
1.01
BRUKER
Current Data Parameters
NAME 2007-4-25 yuzhipeng-Q68
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070425
Time 15.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 161
DW 60.800 usec
DE 6.00 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300111 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

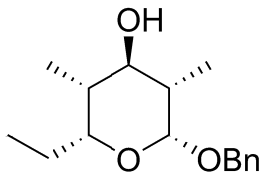

positive v mode 12:52:00
HAA068
02-Jun-2007
12:52:00
WYH_070602_Q78 5 (0.085) AM (Cen,4, 80.00, Ar,10000.0,0.00,0.70); Cm (1:12)
TOF MS ES+
3.42e4
100
%
0
7
OBn
+ Na +
269.1518
270.1764
262.2640
271.1868
259.1253
260.2866
261.1676
263.2702
264.2212
265.2790
266.2044
267.1872
268.2084
269.6469
270.7761
271.5276
m/z
259
260
261
262
263
264
265
266
267
268
269
270
271
272


system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air
7.380 7.369 7.348 7.338 7.329 7.317 7.283 4.832 4.803 4.627 4.619 4.536 4.507 4.057 4.045 4.034 3.451 3.439 3.427 1.944 1.936 1.928 1.917 1.854 1.845 1.836 1.615 1.598 1.592 1.580 1.575 1.557 1.483 1.477 1.464 1.125 1.107 1.060 1.042 1.031 1.024 1.013 0.094 0.024
OH
O
OBn
8
9 8 7 6 5 4 3 2 1 0 ppm
5.45 1.02 1.00 1.02 1.01 0.99 0.78 1.08 1.14 1.26 1.13 3.07 6.21
BRUKER
Current Data Parameters
NAME 2007-4-27 yuzhipeng
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070427
Time 10.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air

5.010 4.981 4.832 4.803 4.776 4.750 4.741 4.723 4.711 4.697 4.681 4.627 4.619 4.536 4.507 4.466 4.436 4.420 4.411 4.357 4.328 4.068 4.057 4.045 4.034 4.023 3.925 3.913 3.897 3.885 3.865 3.853 3.838 3.832 3.817 3.803 3.749 3.729 3.713 3.668 3.619 3.607 3.527 3.511

8



5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 ppm

1.02 1.00 1.02 1.01

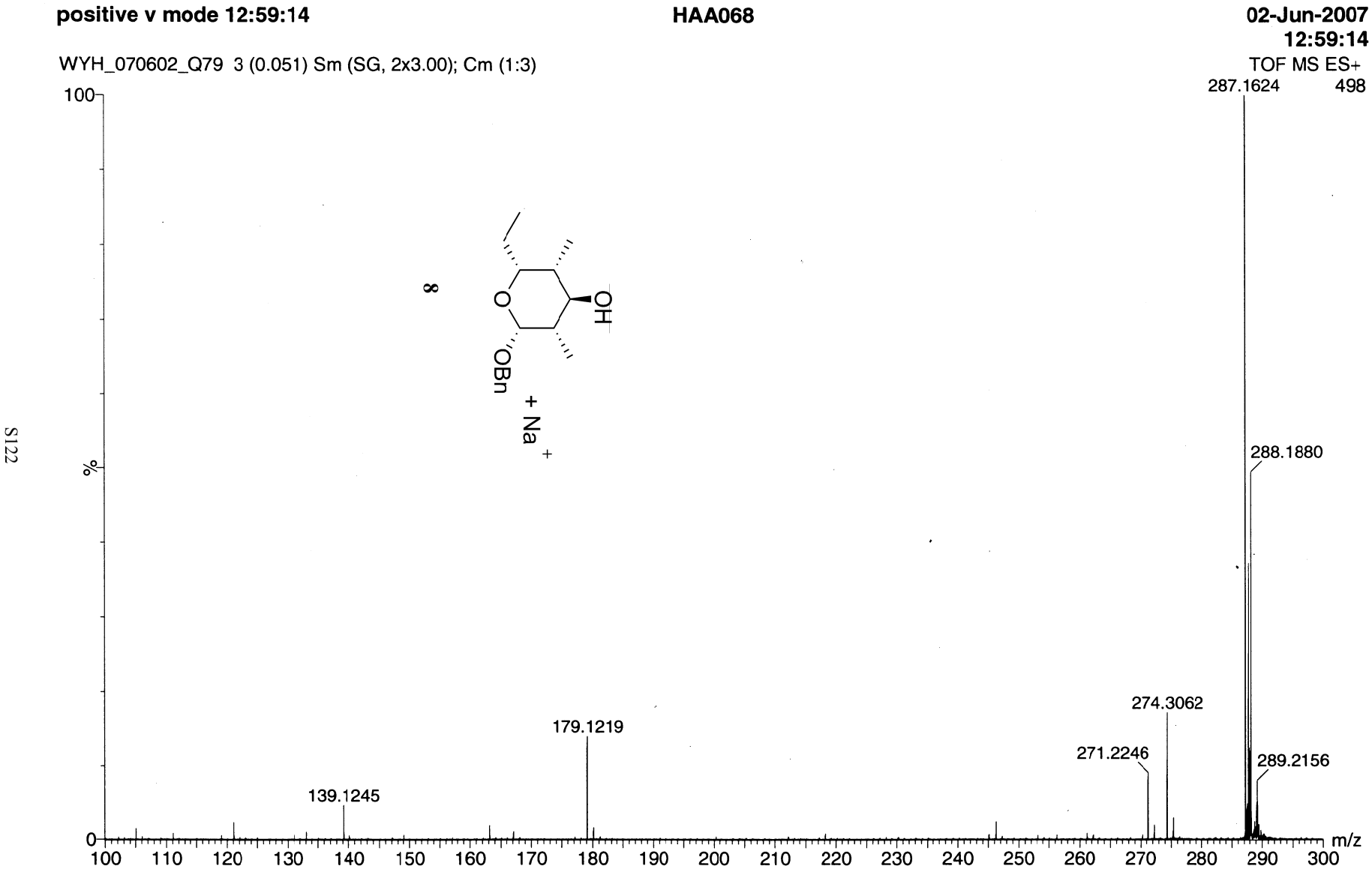
BRUKER

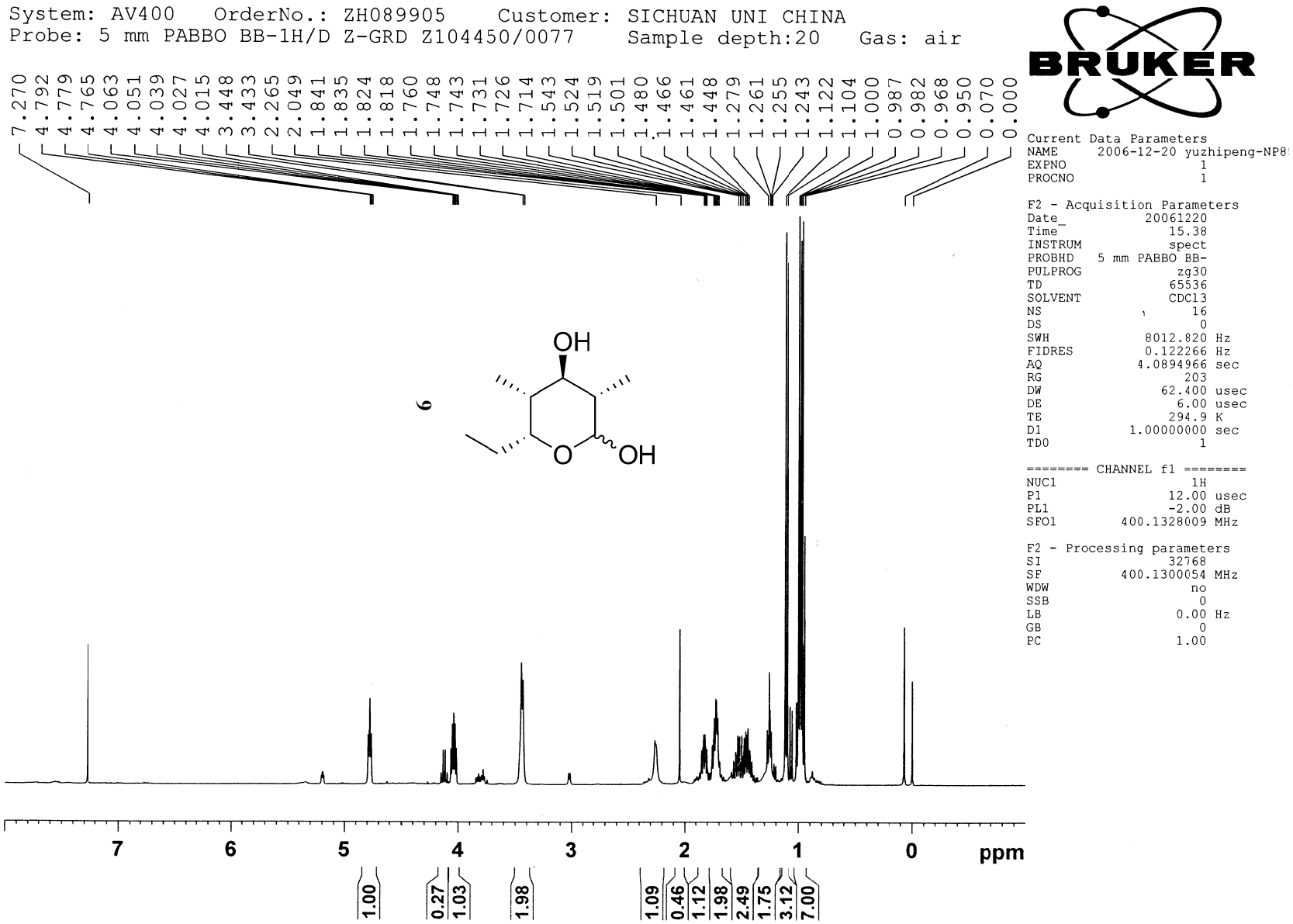
Current Data Parameters
NAME 2007-4-27 yuzhipeng #07
EXPNO 1
PROCNO 1

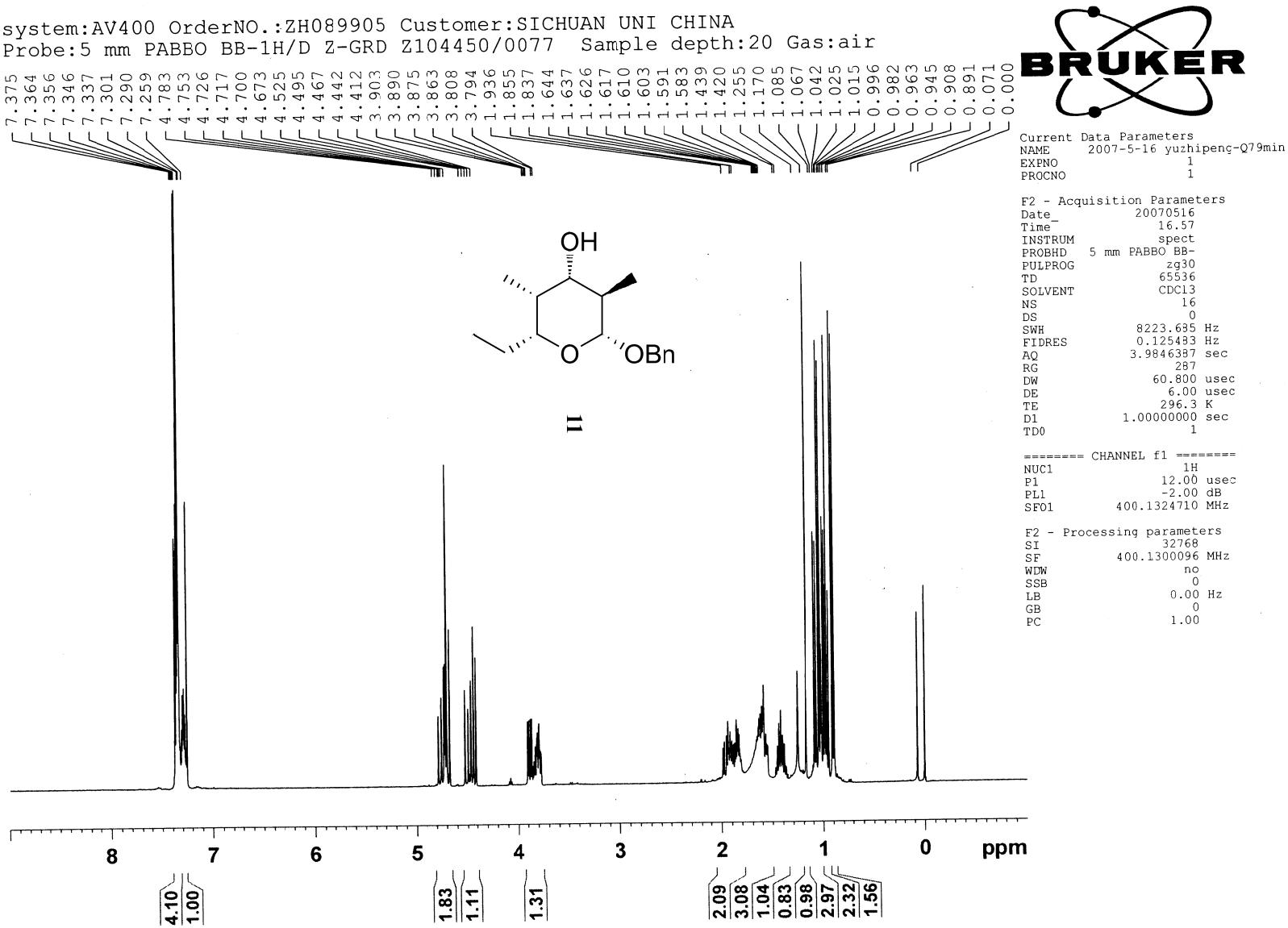
F2 - Acquisition Parameters
Date_ 20070427
Time 10.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1

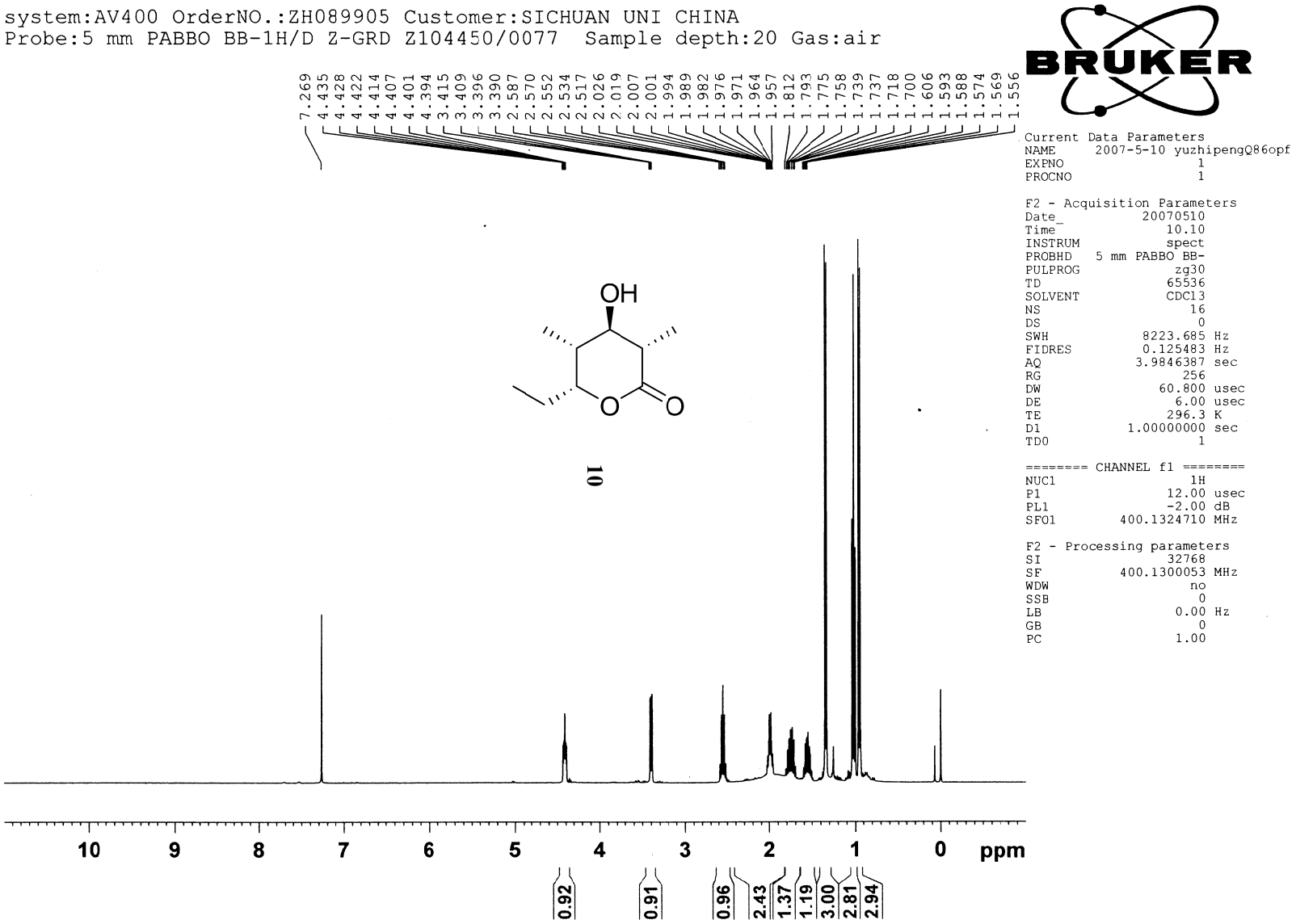
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz

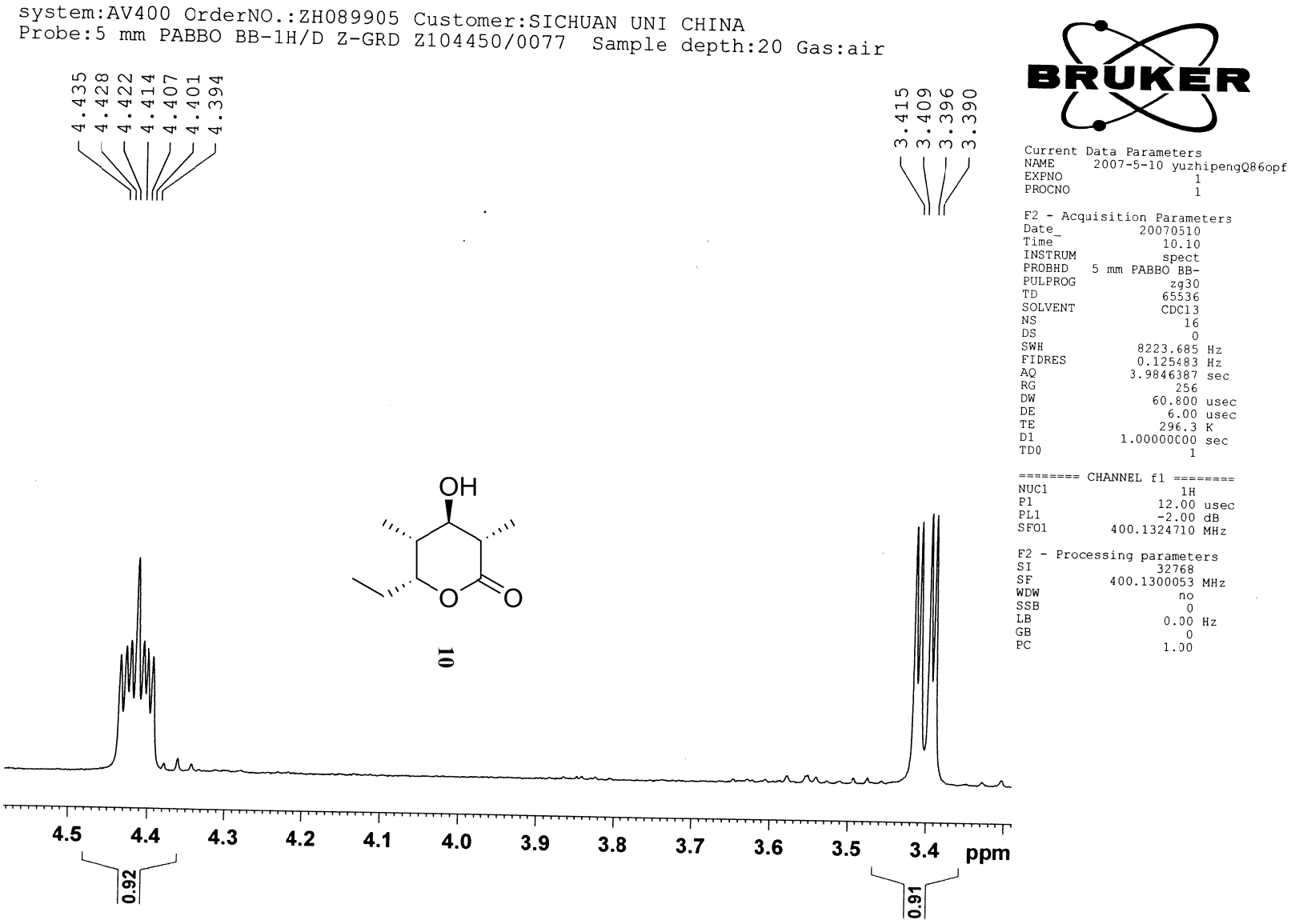
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

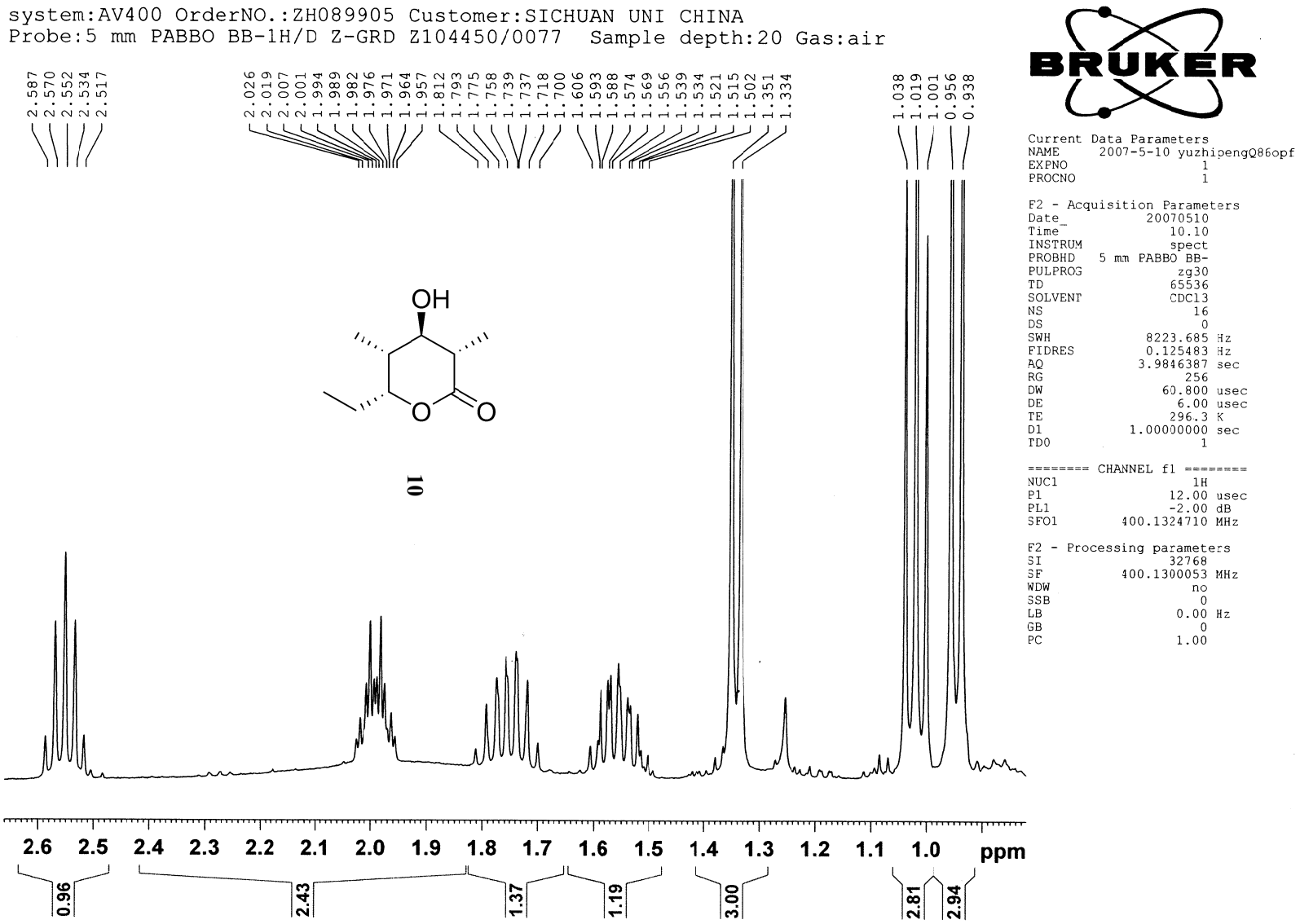

positive v mode 12:59:14
HAA068
02-Jun-2007
12:59:14
WYH_070602_Q79 3 (0.051) Sm (SG, 2x3.00); Cm (1:3)
TOF MS ES+
287.1624
498
288.1880
274.3062
179.1219
271.2246
289.2156
139.1245
100
%
0
m/z
100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300
8
OH
OBn
+ Na+


System: AV400 OrderNo.: ZH089905 Customer: SICHUAN UNI CHINA
Probe: 5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas: air
7.270 4.792 4.779 4.765 4.063 4.051 4.039 4.027 4.015 3.448 3.433 2.265 2.049 1.841 1.835 1.824 1.818 1.760 1.748 1.743 1.731 1.726 1.714 1.543 1.524 1.519 1.501 1.480 1.466 1.461 1.448 1.279 1.261 1.255 1.243 1.122 1.104 1.000 0.987 0.982 0.968 0.950 0.070 0.000
OH
O
OH
9
7 6 5 4 3 2 1 0 ppm
1.00 0.27 1.03 1.98 1.09 0.46 1.12 1.98 2.49 1.75 3.12 7.00
BRUKER
Current Data Parameters
NAME 2006-12-20 yuzhipeng-NP8
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20061220
Time 15.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 203
DW 62.400 usec
DE 6.00 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300054 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air
7.375 7.364 7.356 7.346 7.337 7.301 7.290 7.259 4.783 4.753 4.726 4.717 4.700 4.673 4.525 4.495 4.467 4.442 4.412 3.903 3.890 3.875 3.863 3.808 3.794 1.936 1.855 1.837 1.644 1.637 1.626 1.617 1.610 1.603 1.591 1.583 1.439 1.420 1.255 1.170 1.085 1.067 1.042 1.025 1.015 0.996 0.982 0.963 0.945 0.908 0.891 0.071 0.000
OH
O
OBn
11
8 7 6 5 4 3 2 1 0 ppm
4.10 1.00 1.83 1.11 1.31 2.09 3.08 1.04 0.83 0.98 2.97 2.32 1.56
BRUKER
Current Data Parameters
NAME 2007-5-16 yuzhipenç-Q79min
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070516
Time 16.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 287
DW 60.800 usec
DE 6.00 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300096 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air
BRUKER
7.269 4.435 4.428 4.422 4.414 4.407 4.401 4.394 3.415 3.409 3.396 3.390 2.587 2.570 2.552 2.534 2.517 2.026 2.019 2.007 2.001 1.994 1.989 1.982 1.976 1.971 1.964 1.957 1.812 1.793 1.775 1.758 1.739 1.737 1.718 1.700 1.606 1.593 1.588 1.574 1.569 1.556
OH
O
O
10
Current Data Parameters
NAME 2007-5-10 yuzhipengQ86opf
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070510
Time 10.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 256
DW 60.800 usec
DE 6.00 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300053 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
0.92 0.91 0.96 2.43 1.37 1.19 3.00 2.81 2.94


system:AV400 OrderNO.:ZH089905 Customer:SICHUAN UNI CHINA
Probe:5 mm PABBO BB-1H/D Z-GRD Z104450/0077 Sample depth:20 Gas:air
4.435
4.428
4.422
4.414
4.407
4.401
4.394
3.415
3.409
3.396
3.390
BRUKER
Current Data Parameters
NAME 2007-5-10 yuzhipengQ86opf
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070510
Time 10.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 256
DW 60.800 usec
DE 6.00 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300053 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
OH
O
O
10
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
ppm
0.92
0.91



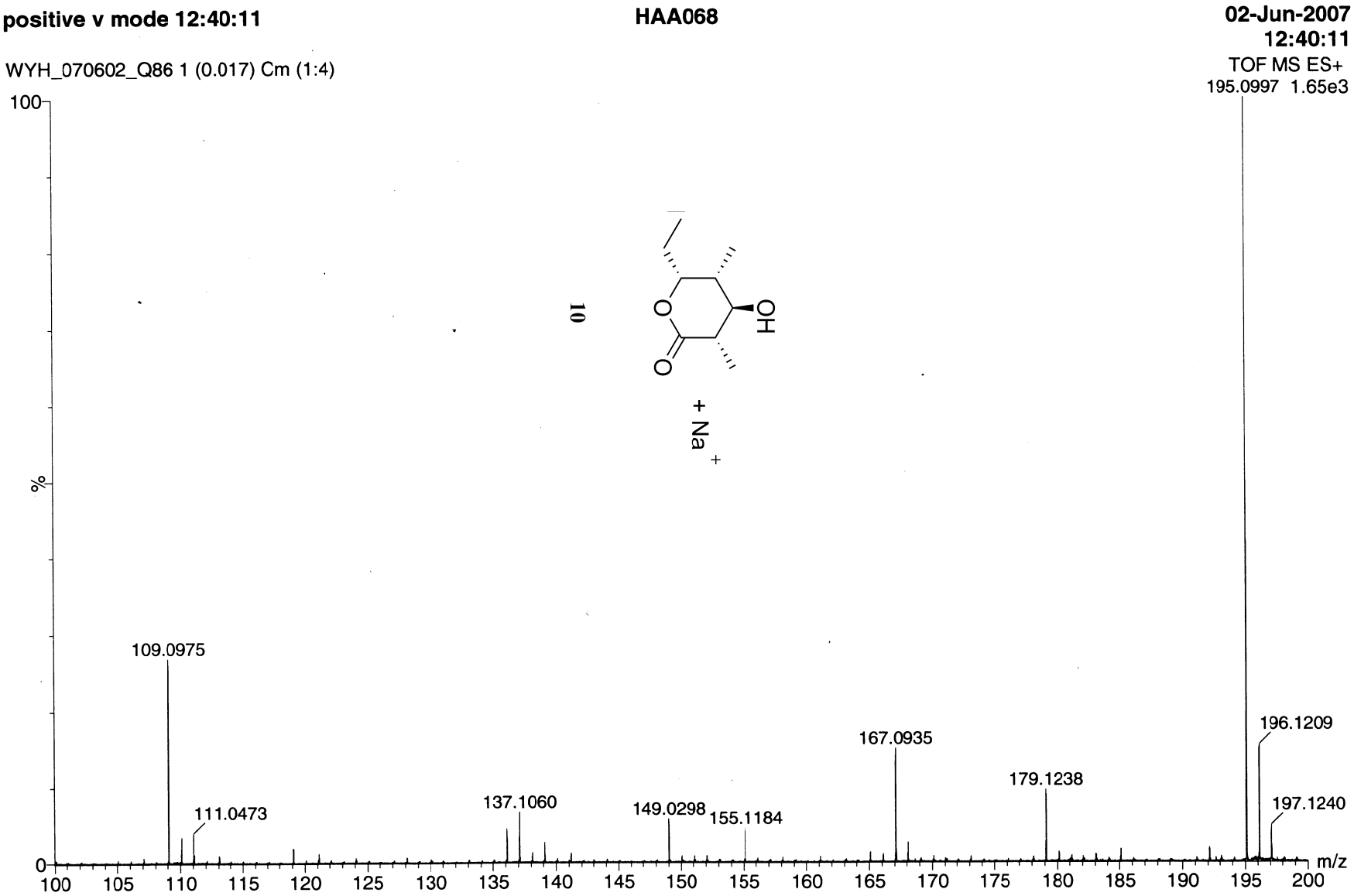
BRUKER

Current Data Parameters
NAME 2007-5-10 yuzhipengQ86opf
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070510
Time 10.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 256
DW 60.800 usec
DE 6.00 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1

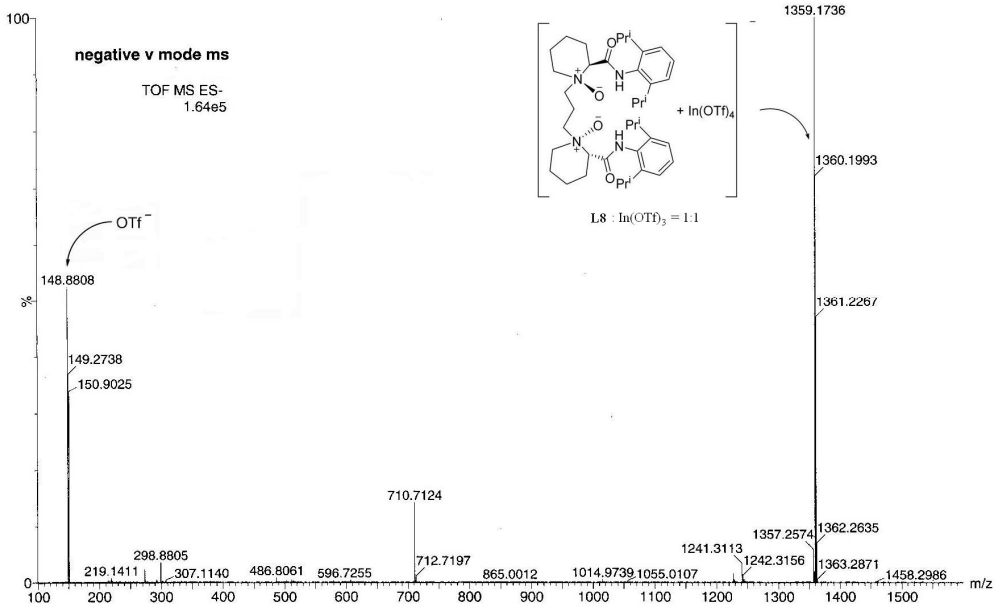
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300053 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


positive v mode 12:40:11
HAA068
02-Jun-2007
12:40:11
TOF MS ES+
195.0997 1.65e3
WYH_070602_Q86 1 (0.017) Cm (1:4)
100
%
0
109.0975
111.0473
137.1060
149.0298
155.1184
167.0935
179.1238
196.1209
197.1240
m/z
100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200
10
O
O
OH
+ Na +

8. Extra Optimizations and Preliminary Mechanism Research.

From data in electrospray ionization mass spectrometry (ESI-HRMS) measurement of the catalyst complex (the complex was prepared in THF) in a 1:1 ratio of **L8** to $In(OTf)_3$ (**Figure 2**), dominant peak cluster at 1359.1736 m/z position was found in negative mode, and resolved as the **L8**-$In(OTf)_4^-$ anion with calculated m/z 1359.1734. On the other hand, in positive mode, peak cluster at 1061.8617 m/z was found and analyzed as **L8**-$In(OTf)_2^+$ (**CA1**) cation, and peak cluster at 911.8349 m/z was assigned to the cation (**CA2**) of **CA1** losing a molecule of HOTf. The hydrogen of HOTf was most likely obtained from the amide moiety. Obviously, it was the relatively high stability of the anion of **L8**-$In(OTf)_4^-$ that indicated the high possibility of equivalent coordinating ratio of ligand to metal in the complex.



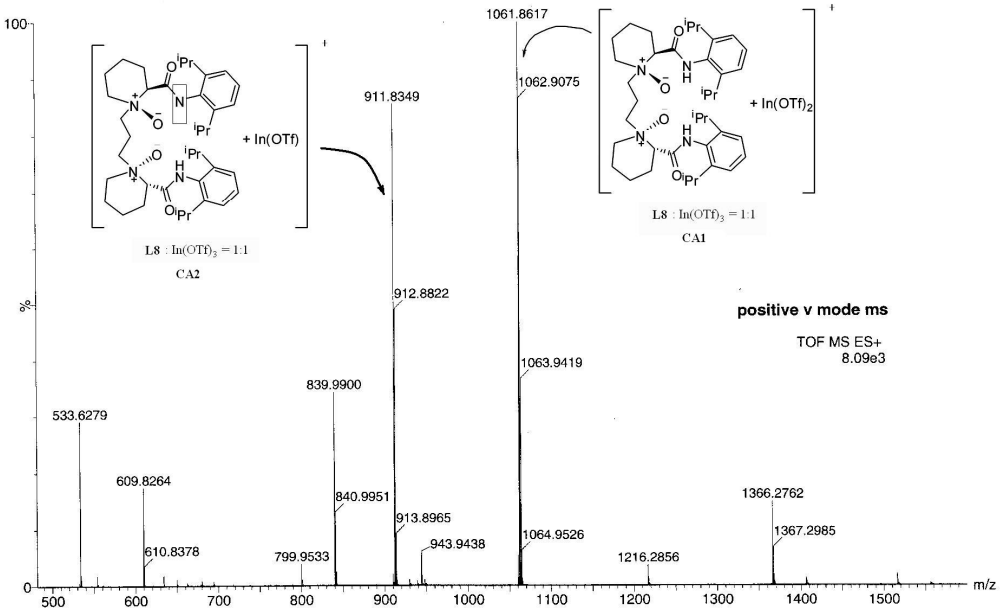
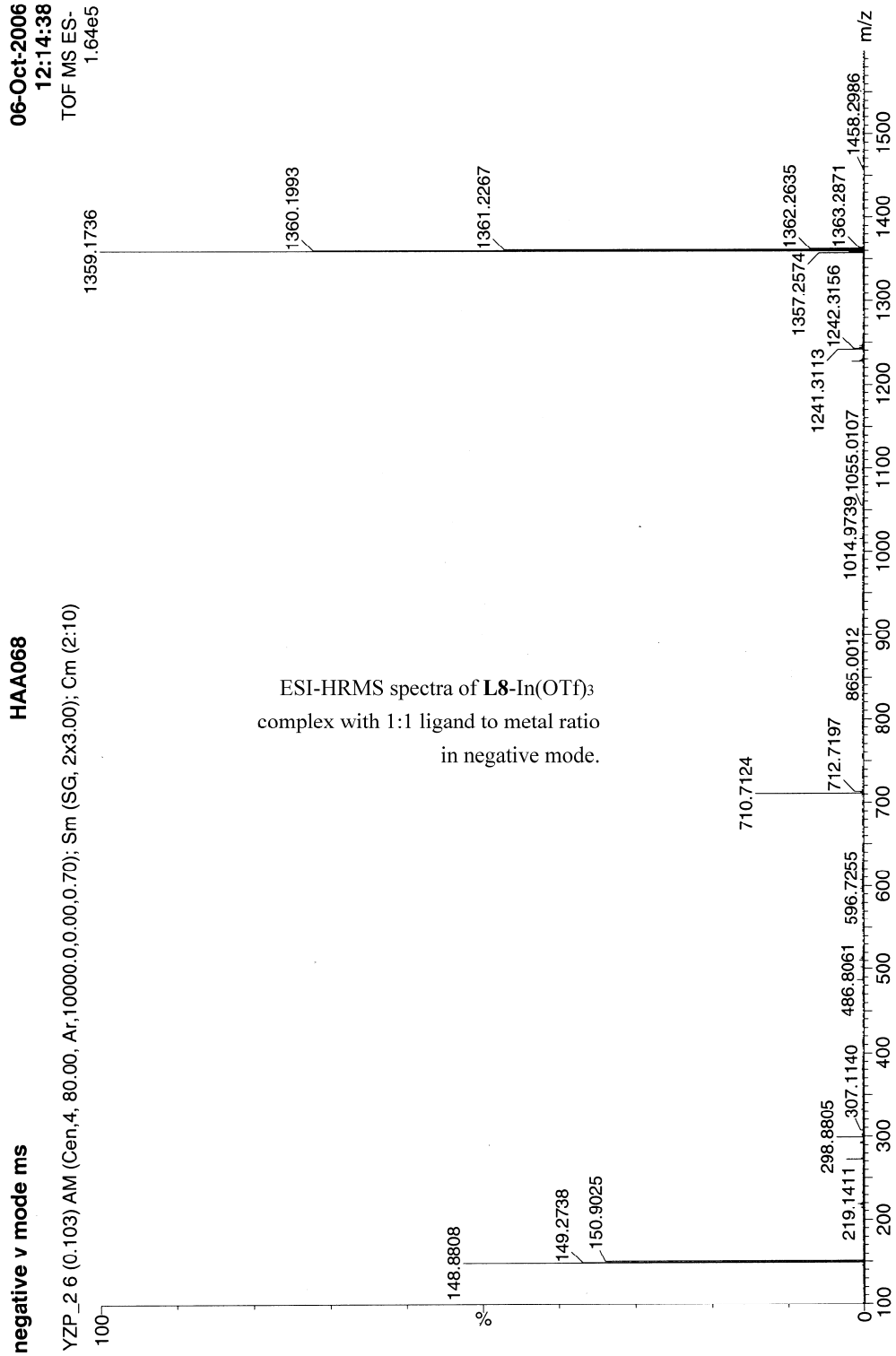


Figure. Negative Mode and Positive Mode ESI-HRMS Spectra of **L8**-$In(OTf)_3$ Complex (1:1).

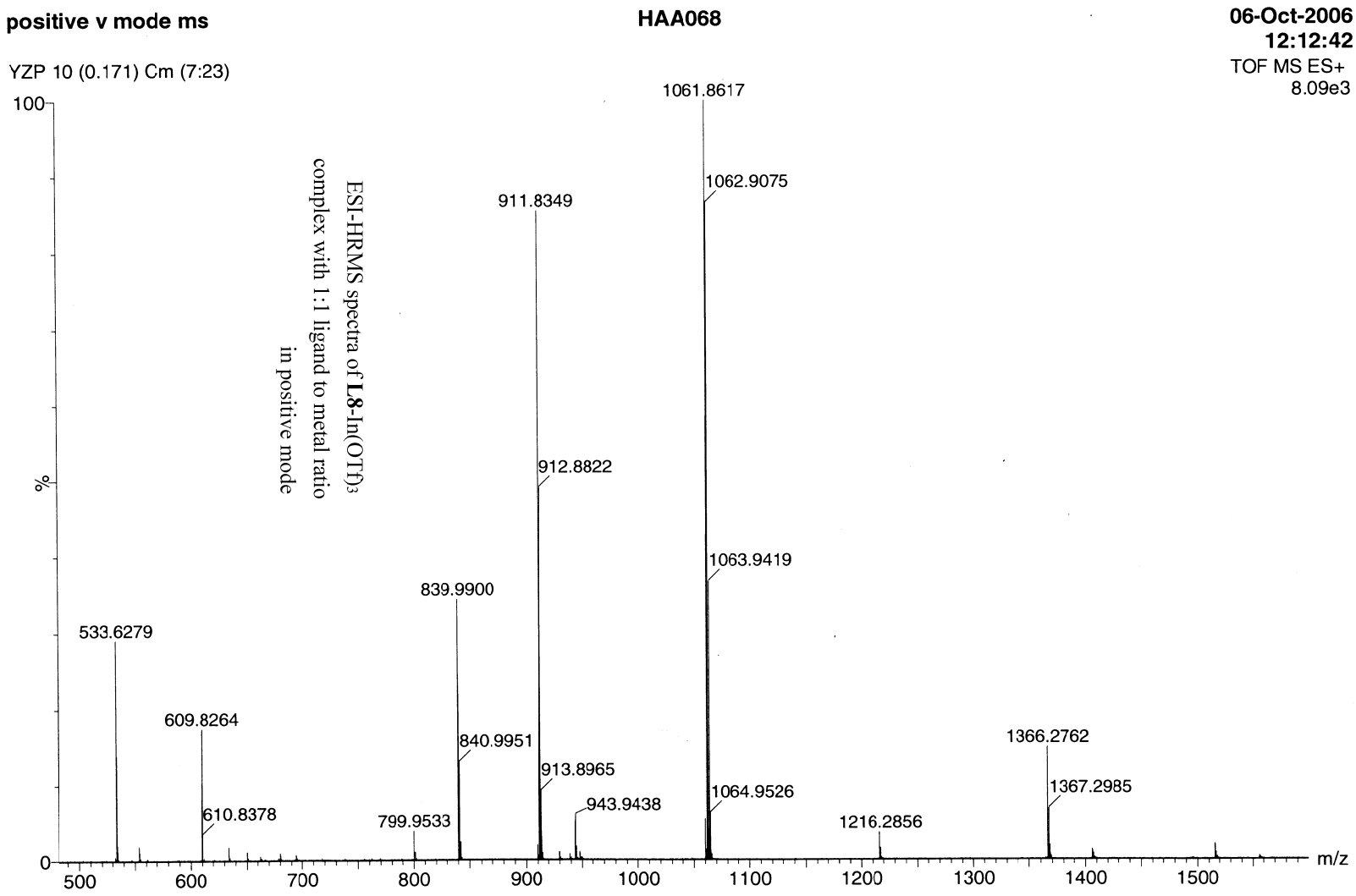
Table. Effect of Solvent and Concentration of Benzaldehyde on the Enantioselective HDA Reaction of Diene **1** using 5 mol% **L8**-$In(OTf)_3$ Complex (1:1).

Entry[a]	Solvent	Benzaldehyde conc. [M]	Yield [%][b]	*trans*/*cis*	*ee* (%)[c] of *cis*
1	Toluene	0.25	86	1/8.6	94
2	CH_2Cl_2	0.25	64	1/1.9	87
3	Et_2O	0.25	82	1/5	95
4	*n*-Hexane	0.25	52	1/5.8	84
5	^{t}BuOMe	0.25	85	1/6	96
6	*m*-Xylene	0.125	86	<1/20	84
7	Isopropyl ether	0.125	15	1/1	80
8	PhOEt	0.125	86	1/20	95

[a] Unless noted, reactions were carried out with aldehyde (0.25 mmol), diene **1** (1.5 equiv.) at 0 ^oC, 48 h. The catalyst was pre-prepared. [b] Isolated yield of *cis* isomer. [c] Determined by HPLC, configuration of *cis* isomer was (*2S*,*3S*).



ESI-HRMS spectra of **L8**-In(OTf)3 complex with 1:1 ligand to metal ratio in negative mode.


positive v mode ms
HAA068
06-Oct-2006
12:12:42
TOF MS ES+
8.09e3
YZP 10 (0.171) Cm (7:23)
ESI-HRMS spectra of L8-In(OTf)3
complex with 1:1 ligand to metal ratio
in positive mode
100
%
0
1061.8617
1062.9075
911.8349
912.8822
1063.9419
839.9900
533.6279
609.8264
840.9951
913.8965
1064.9526
943.9438
610.8378
799.9533
1216.2856
1366.2762
1367.2985
500
600
700
800
900
1000
1100
1200
1300
1400
1500
m/z

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