Tetrakis(trifluoromethanesulfonyl)propane: Highly Effective Brønsted Acid Catalyst for Vinylogous Mukaiyama-Michael Reaction of α,β-Enones with Silyloxyfurans

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Supporting Information

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1. General and materials

All reactions were carried out under argon atmosphere. ^{1}H and ^{13}C NMR spectra were taken on Varian Mercury300 or Brucker DPX400 spectrometers, and chemical shifts were reported in parts per million (ppm) using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^{1}H NMR, and $CDCl_3$ (77.01 ppm) for ^{13}C NMR as an internal standard, respectively. Infrared (IR) spectra were recorded on JASCO FT/IR-620 or JASCO FT/IR-4100 infrared spectrophotometers. Mass spectra (MS) were obtained on a Micromass LCT (ESI-TOF) or a Micromass Auto Spec (EI). Medium pressure liquid chromatography (MPLC) was performed using prepacked column (KUSANO Prepacked column Si-10, 40 x 300 mm I. D., silica gel, 50 μm) with RI detector.

2. Preparation of 1,1,3,3-tetrakis(trifluoromethanesulfonyl)propane (1)

This compound was prepared by the reported procedure.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.46 (2H, t, J = 7.0 Hz), 5.83 (2H, t, J = 7.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.8, 72.5, 119.3 (q, $J_{C\text{-}F}$ = 329.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -9.5 (12F, s). Structure was confirmed by X-ray crystallographic analysis (CCDC 674990). Crystal data. $C_7H_4F_{12}O_8S_4$, M = 572.34, monoclinic, a = 9.9367(9), b = 16.5820(15), c = 10.9892(10) Å, *Volume* = 1760.0(3), T = 100 K, space group P 21/c, Z = 4.

3. Preparation of α,β-unsaturated ketones (2)

4-Methylpent-3-en-2-one **2a** and but-3-en-2-one **2c** are available commercially. 1-Cyclohexylideneacetone **2b**,[2] 1-phenylprop-2-en-1-one **2d**[3] and 1-(4-bromophenyl)prop-2-en-1-one **2e**[4] were prepared by the reported procedure.

4. Preparation of 2-silyloxyfurans

tert-Butyl(2-furyloxy)dimethylsilane, [5] *tert*-butyl(dimethyl)[(3-methyl-2-furyl)oxy]silane, [6] and *tert*-butyl(dimethyl)[(4-methyl-2-furyl)oxy]silane[6] were prepared by the reported procedure.

***tert*-Butyl(dimethyl)[(5-methyl-2-furyl)oxy]silane.** To a solution of 5-methylfuran-2(3*H*)-one (0.9 mL, 10 mmol) in CH_2Cl_2 (2 mL), *tert*-butyl(dimethyl)silyl trifluoromethanesulfonate (2.1 mL, 10 mmol) and Et_3N (2.1 mL 15 mmol) were added at 0 °C. After being stirred at room temperature for 2 h, extractive work-up and purification by silica gel column chromatography (hexane) gave *tert*-butyl(dimethyl)[(5-methyl-2-furyl)oxy]silane (1.27 g, 6.0 mmol, 60% yield) as colorless oil. IR (neat) 1628, 1592 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.27 (6H, s), 1.01 (9H, s), 2.19 (3H, s), 4.99 (1H, d, J = 3.0 Hz), 5.75-5.80 (1H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ -4.9, 13.5, 18.1, 25.6, 83.7, 106.1, 141.3, 155.3; MS (EI) *m/z* 212 $[M]^+$. Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49. Found: C, 61.97; H, 9.25.

5. Vinylogous Mukaiyama-Michael reaction of α,β-enones (2) with silyloxyfurans catalyzed by carbon acid

5-(1,1-Dimethyl-3-oxobutyl)furan-2(5*H*)-one (3a). To a solution of **1** in CH_2Cl_2 (0.25 mM solution, 1.0 mL, 0.25 μmol), a solution of **2a** (49 mg, 0.50 mmol) and *tert*-butyl(2-furyloxy)dimethylsilane (109 mg, 0.55 mmol) in CH_2Cl_2 (1 mL) were added at -78 °C over 10 min. After being stirred for 2 h at -24 °C, reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution and extracted with EtOAc (20 mL x 3). The organic layer was dried over $MgSO_4$, then it was concentrated under reduced pressure. The resulting residue was treated by 1 M HCl (10 mL) in THF (10 mL) for 30 min at room temperature. The reaction mixture was diluted with H_2O (10 mL), extracted with EtOAc (20 mL x 3), dried over $MgSO_4$ and evaporated. Purification of the resulting residue by column chromatography on silica gel (hexane / EtOAc = 2 : 1) gave **3a** (80.1 mg, 0.44 mmol, 88% yield) as colorless oil. IR (neat) 1754, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (3H, s), 1.17 (3H, s), 2.14 (3H, s), 2.40 (1H, d, J = 17.1 Hz), 2.69 (1H, d, J = 17.1 Hz), 5.26-5.28 (1H, m), 6.15 (1H, dd, J = 5.8, 2.1 Hz), 7.47 (1H, dd, J = 5.8, 1.5 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.3, 22.9, 31.7, 36.7, 50.2, 88.1, 122.3, 154.3, 172.8, 207.3; MS (ESI-TOF) *m/z* ; 183 $[M+H]^+$; HRMS calcd for $C_{10}H_{15}O_3$ $[M+H]^+$, 183.1021; found, 183.1012. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.74; H, 7.70.

5-[1-(2-Oxopropyl)cyclohexyl]furan-2(5*H*)-one (3b). According to the synthesis of **3a**, **3b** was obtained in 90% yield (100.0 mg, 0.45 mmol) by the reaction of (*tert*-buthyldimethylsilyloxy)furan (109 mg, 0.55 mmol) and **2b** (69 mg, 0.50 mmol) in the presence of **1a** (0.74 mg, 1.3 μmol) at -24 °C for 3 h. Colorless oil. IR (neat) 1757, 1713 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) δ 1.10-1.45 (5H, m), 1.45-1.63 (4H, m), 1.74-1.82 (1H, m), 2.12 (3H, s), 2.54

(1H, d, J = 17.4 Hz), 2.67 (1H, d, J = 17.4 Hz), 5.34-5.37 (1H, m), 6.07 (1H, dd, J = 5.8, 2.1 Hz), 7.51 (1H, dd, J = 5.8, 1.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.0, 21.1, 25.6, 30.5, 30.6, 32.1, 40.3, 43.6, 87.7, 121.9, 154.7, 172.9, 208.2; MS (ESI-TOF) m/z 223 $[M+H]^+$; HRMS calcd for $C_{13}H_{19}O_3$ $[M+H]^+$, 223.1334; found, 223.1320. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.45; H, 8.12.

5-(3-Oxobutyl)furan-2(5*H*)-one (3c). According to the synthesis of **3a,** the reaction of **2c** (35 mg, 0.50 mmol) and *tert*-butyl(2-furyloxy)dimethylsilane (109 mg**,** 0.55 mmol) in the presence of **1** (0.14 mg 0.25 μmol) for 2 h at -78 °C give 1,4-adduct **3c** (63.1 mg, 0.41 mmol, 82% yield). The structure was confirmed by comparison of spectrum data with those reported in the literature.[7]

5-(3-Oxo-3-phenylpropyl)furan-2(5*H*)-one (3d). To a solution of *tert*-butyl(2-furyloxy)dimethylsilane (109 mg**,** 0.55 mmol) in CH_2Cl_2 (1 mL), a solution of **1** (1.5 mM in CH_2Cl_2, 2.0 mL, 0.50 μmol) and **2d** (66 mg, 0.50 mmol) in CH_2Cl_2 (0.8 mL) were added at -78 °C over 10 min. After being stirred for 1 h at -78 °C, reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution and extracted with EtOAc (20 mL x 3). The organic layer was dried over $MgSO_4$, then it was concentrated under reduced pressure. The resulting residue was treated by TfOH (150 mg, 1.0 mmol) in CH_2Cl_2 (100 mL) for 1h at -78 °C. The reaction mixture was diluted with H_2O (50 mL), extracted with CH_2Cl_2 (40 mL), dried over $MgSO_4$ and evaporated. Purification of the resulting residue by column chromatography on silica gel (hexane/EtOAc = 3 : 1) gave **3d** (96.2 mg, 0.45 mmol, 89% yield) as white solid. Mp. 91.1-91.5 °C. IR (KBr) 1769, 1682 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.97-2.03 (1H, m), 2.37-2.48 (1H, m), 3.08-3.28 (2H, m), 5.17-5.27 (1H, m), 6.11 (1H, dd, J = 5.7, 2.0 Hz), 7.44-7.52 (3H, m), 7.55-7.61 (1H, m), 7.93-7.98 (2H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.1, 33.2, 82.3, 121.6, 127.9, 128.6, 133.3, 136.4, 156.2, 172.8, 198.5; MS (ESI-TOF) m/z 239 $[M+Na]^+$; HRMS calcd for $C_{13}H_{12}NaO_3$ $[M+Na]^+$, 239.0684; found, 239.0671.

5-[3-(4-Bromophenyl)-3-oxopropyl]furan-2(5*H*)-one (3e). According to the synthesis of **3d**, **3e** was obtained in 88% yield (129.9 mg, 0.44 mmol) by the reaction of **2e** (106 mg, 0.50 mmol) and *tert*-butyl(2-furyloxy)dimethylsilane (109 mg**,** 0.55 mmol) in the presence of **1** (0.14 mg 0.25 μmol) for 1 h at -78 °C. White solid. Mp. 84.3-84.9 °C. IR (KBr) 1746, 1687 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.88-1.99 (1H, m), 2.40 (1H, dtd, J = 14.5, 7.3, 3.8 Hz), 3.03-3.23 (2H, m), 5.16-5.22 (1H, m), 6.12 (1H, dd, J = 5.7, 2.0 Hz), 7.49 (1H, dd, J = 5.7, 1.5 Hz), 7.58-7.63 (2H, m), 7.78-7.83 (2H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.1, 33.3, 82.1, 121.8, 128.7, 129.5, 132.0, 135.2, 156.0, 172.7, 197.5; MS (ESI-TOF) m/z 295 $[M+H]^+$; HRMS calcd for $C_{13}H_{12}BrO_3$ $[M+H]^+$, 294.9970; found, 294.9966. Anal. Calcd for $C_{13}H_{11}BrO_3$: C, 52.91; H, 3.76. Found: C, 52.61; H, 4.00.

5-(1,1-Dimethyl-3-oxobutyl)-3-methylfuran-2(5*H*)-one (3f) and
5-(1-{[*tert*-butyl(dimethyl)silyl]oxy}-1,3-dimethylbut-2-enyl)-3-methylfuran-2(5*H*)-one (4f). According to the synthesis of **3a**, the reaction of **2a** (49 mg, 0.50 mmol) and *tert*-butyl(dimethyl) [(3-methyl-2-furyl)oxy]silane (117 mg**,** 0.55 mmol) in the presence of **1** (0.71 mg 1.3 μmol) for 2 h at -78 °C give 1,4-adduct **3f** (82.3 mg, 0.42 mmol, 84% yield) and two diastereomers of 1,2-adduct **4f** (major isomer, 2.1 mg, 0.007 mmol 1.3% yield; miner isomer, 2.0

mg 0.006 mmol, 1.3% yield).

3f Colorless oil. IR (neat) 1756, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, s), 1.14 (3H, s), 1.92-1.94 (3H, m), 2.14 (3H, s), 2.38 (1H, d, J = 16.9 Hz), 2.65 (1H, d, J = 16.9 Hz), 5.03-5.08 (1H, m), 7.04 (1H, t, J = 1.5 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.8, 22.4, 23.3, 32.0, 37.1, 50.5, 86.1, 131.2, 146.4, 174.2, 207.7; MS (ESI-TOF) m/z 197 $[M+H]^+$; HRMS calcd for $C_{11}H_{17}O_3$ $[M+H]^+$, 197.1178; found, 197.1186. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.30; H, 8.24.

4f For major isomer: colorless oil. IR (neat) 1767 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.11 (6H, s), 0.96 (9H, s), 1.26 (3H, s), 1.52 (3H, d, J = 1.3 Hz), 1.64 (3H, t, J = 1.8 Hz), 1.69 (3H, d, J = 1.3 Hz), 4.47-4.51 (1H, m), 4.92-4.96 (1H, m) 6.42-6.46 (1H, m); ^{13}C NMR (100.6 MHz, C_6D_6) δ -2.3, -1.9, 10.6, 18.5, 19.4, 26.1, 26.1, 27.6, 77.2, 86.8, 127.6, 131.4, 136.4, 145.6, 173.2; MS (ESI-TOF) m/z 333 $[M+Na]^+$; HRMS calcd for $C_{17}H_{30}NaO_3Si$ $[M+Na]^+$, 333.1862; found, 333.1877. For miner isomer: colorless oil. IR (neat) 1767 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.06 (3H, s), 0.09 (3H, s), 0.91 (9H, s), 1.26 (3H, s), 1.55 (3H, d, J = 1.3 Hz), 1.58 (3H, d, J = 1.3 Hz), 1.69 (3H, t, J = 1.7 Hz), 4.46-4.50 (1H, m), 5.09-5.14 (1H, m), 6.48-6.52 (1H, m); ^{13}C NMR (100.6 MHz, C_6D_6) δ -2.3, -1.9, 10.7, 18.4, 19.5, 25.5, 26.1, 27.5, 76.3, 85.9, 129.7, 131.5, 135.4, 145.8, 173.4; MS (ESI-TOF) m/z 333 $[M+Na]^+$; HRMS calcd for $C_{17}H_{30}NaO_3Si$ $[M+Na]^+$, 333.1862; found, 333.1880.

5-(1,1-Dimethyl-3-oxobutyl)-4-methylfuran-2(5*H*)-one (3g) and
5-(1-{[*tert*-butyl(dimethyl)silyl]oxy}-1,3-dimethylbut-2-enyl)-4-methylfuran-2(5*H*)-one (4g). According to the synthesis of **3a**, the reaction of **2a** (49 mg, 0.50 mmol) and *tert*-butyl [(1-ethoxyvinyl)oxy]dimethylsilane (159 mg, 0.75 mmol) in the presence of **1** (0.71 mg 1.3 μmol) for 2 h at -78 °C give 1,4-adduct **3g** (72.0 mg, 0.39 mmol, 78% yield) and two diastereomers of 1,2-adduct **4g** (major isomer, 9.4 mg, 0.03 mmol 6.3% yield; miner isomer, 2.6 mg 0.009 mmol, 1.8% yield).

3g colorless oil. IR (neat) 1763, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (3H, s), 1.18 (3H, s), 2.09 (3H, s), 2.13-2.15 (3H, m), 2.64 (1H, d, J = 17.4 Hz), 2.74 (1H, d, J = 17.4 Hz), 5.15 (1H, brs), 5.78 (1H, quin, J = 1.5 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.5, 22.4, 23.6, 31.5, 36.9, 51.7, 88.8, 119.1, 167.6, 172.6, 207.5; MS (ESI-TOF) m/z 219 $[M+Na]^+$; HRMS calcd for $C_{11}H_{16}NaO_3$ $[M+Na]^+$, 219,0997; found, 219.0977. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.31; H, 8.21.

4g For major isomer: colorless oil. IR (neat) 1767 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.03 (3H, s), 0.06 (3H, s), 0.89 (9H, s), 1.21 (3H, s), 1.52 (3H, s), 1.53 (3H, s), 1.67-1.70 (3H, m), 5.17 (1H, s), 5.28 (1H, s), 5.51 (1H, m); ^{13}C NMR (100.6 MHz, C_6D_6) δ -2.3, -1.8, 16.0, 18.4, 19.4, 24.9, 26.2, 27.4, 76.5, 88.4, 119.5, 131.1, 134.4, 166.5, 171.9; MS (ESI-TOF) m/z 333 $[M+Na]^+$; HRMS calcd for $C_{17}H_{30}NaO_3Si$ $[M+Na]^+$, 333.1862; found, 333.1881. For miner isomer: colorless oil. IR (neat) 1769 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.09 (3H, s), 0.11 (3H, s), 0.93 (9H, s), 1.40 (3H, s), 1.50 (3H, d, J = 1.4), 1.52-1.56 (3H, m), 1.70 (3H, d, J = 1.4 Hz), 4.31 (1H, brs), 4.88 (1H, brs), 5.43-5.46 (1H, m); ^{13}C NMR (100.6 MHz, C_6D_6) δ -2.1, -2.0, 16.1, 18.4, 19.2, 26.2, 26.7, 27.8, 77.9, 89.5, 119.3, 126.9, 136.7, 166.2, 171.5; MS (ESI-TOF) m/z 333 $[M+Na]^+$; HRMS calcd for $C_{17}H_{30}NaO_3Si$ $[M+Na]^+$, 333.1862; found, 333.1854.

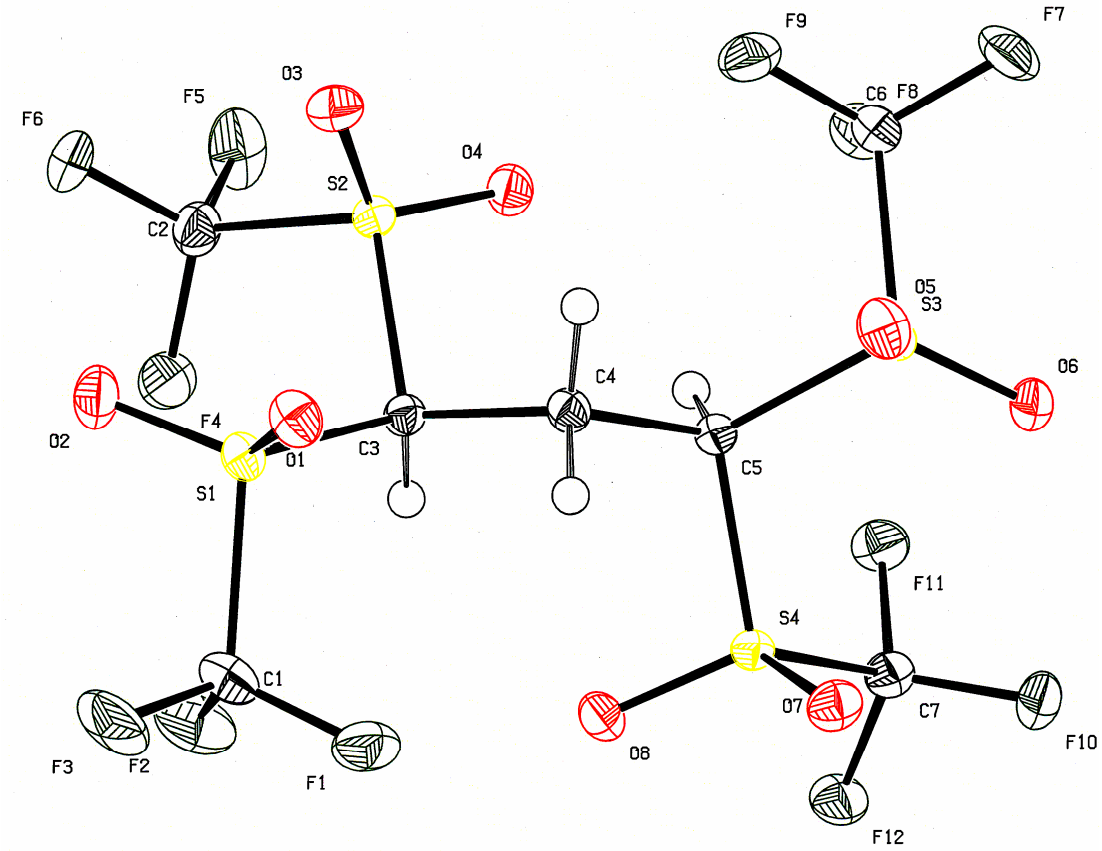
5-(1,1-Dimethyl-3-oxobutyl)-5-methylfuran-2(5*H*)-one (3h) and

3-(1,1-dimethyl-3-oxobutyl)-5-methylfuran-2(3*H*)-one (5). According to the synthesis of **3a**, the reaction of **2a** (49 mg, 0.50 mmol) and *tert*-butyl(dimethyl) [(5-methyl-2-furyl)oxy]silane (159 mg, 0.75 mmol) in the presence of **1** (0.71 mg 1.3 μmol) for 2 h at -78 °C, then 2h at –24 °C gave **3h** (51.0 mg, 0.28 mmol, 55% yield) and **5** (27.0 mg, 0.15 mmol 29% yield).

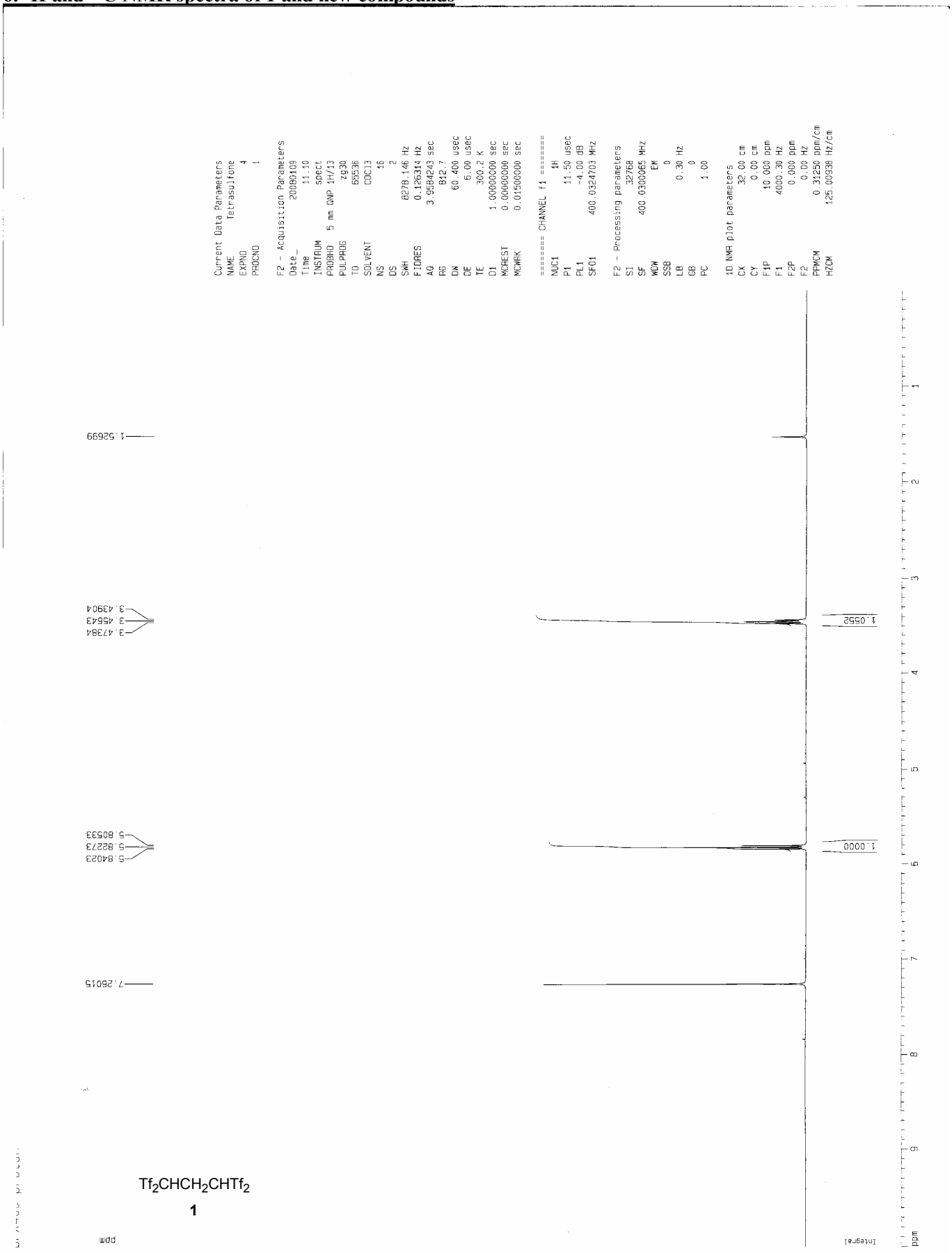
3h white solid. Mp. 55.5 °C. IR (KBr) 1752, 1705 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) δ 1.04 (3H, s), 1.13 (3H, s), 1.39 (3H, s), 2.09 (3H, s), 2.40 (1H, d, J = 15.5 Hz), 2.46 (1H, d, J = 15.5 Hz), 6.00 (1H, d, J = 5.8 Hz), 7.46 (1H, d, J = 5.8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.8, 22.0, 22.5, 32.7, 39.6, 48.5, 93.5, 121.0, 159.5, 172.5, 207.7; MS (ESI-TOF) *m/z* 197 $[M+H]^+$; HRMS calcd for $C_{11}H_{17}O_3$ $[M+H]^+$, 197.1178; found, 197.1177. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.33; H, 8.17.

5 colorless oil. IR (neat) 1789, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (3H, s), 1.12 (3H, s), 1.97-2.02 (3H, m), 2.15 (3H, s), 2.44 (1H, d, J = 17.2 Hz), 2.91 (1H, d, J = 17.2 Hz), 3.68 (1H, quin, J = 2.4 Hz), 5.08-5.12 (1H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 24.5, 25.6, 31.8, 35.7, 50.9, 52.2, 101.6, 152.5, 177.8, 208.0; MS (ESI-TOF) *m/z* 197 $[M+H]^+$; HRMS calcd for $C_{11}H_{17}O_3$ $[M+H]^+$, 197.1178; found, 197.1183. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.52; H, 8.32.

5. X-ray structure of 1,1,3,3-tetrakis(trifluoromethanesulfonyl)propane (1)



6. ^{1}H and ^{13}C NMR spectra of 1 and new compounds



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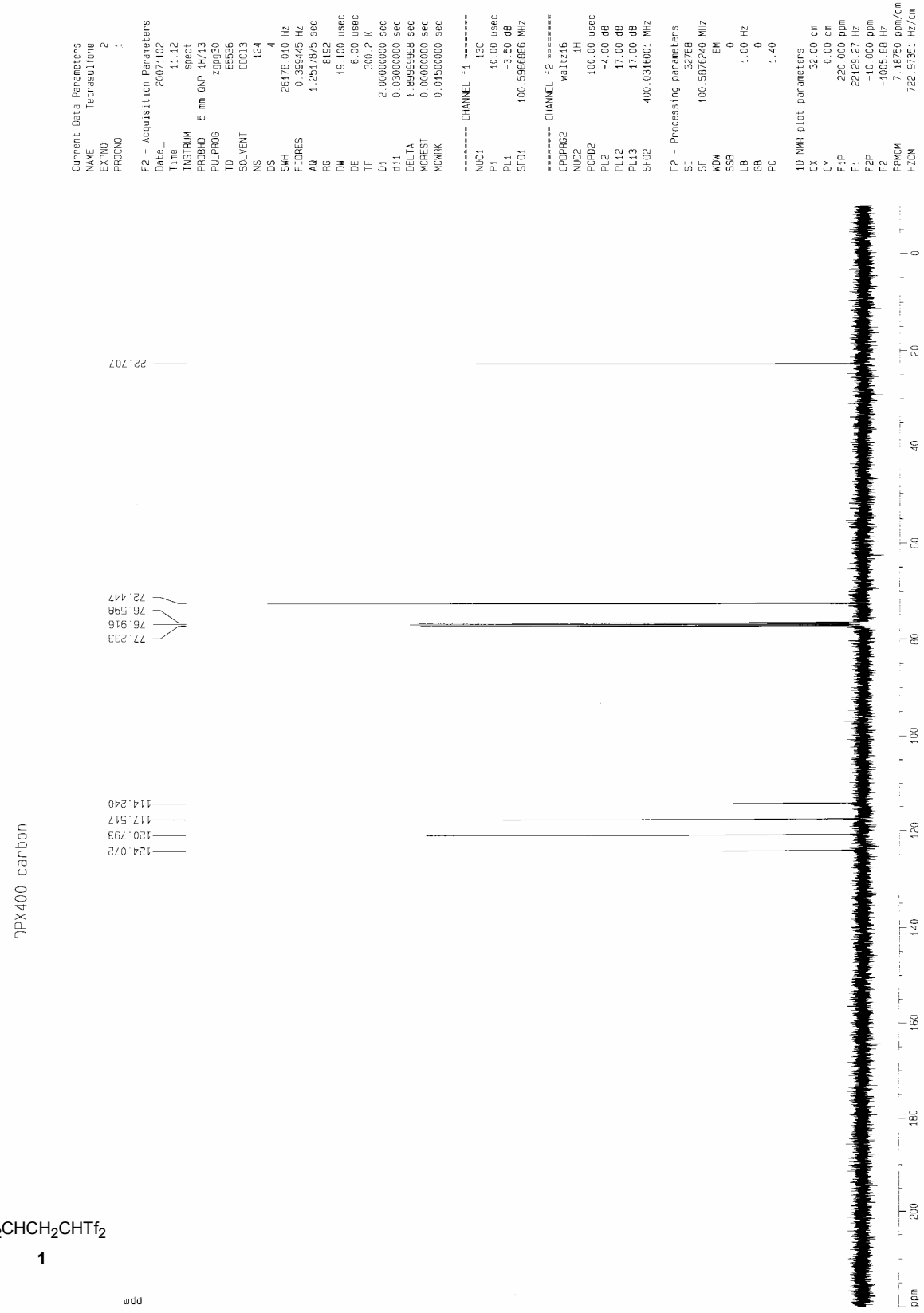

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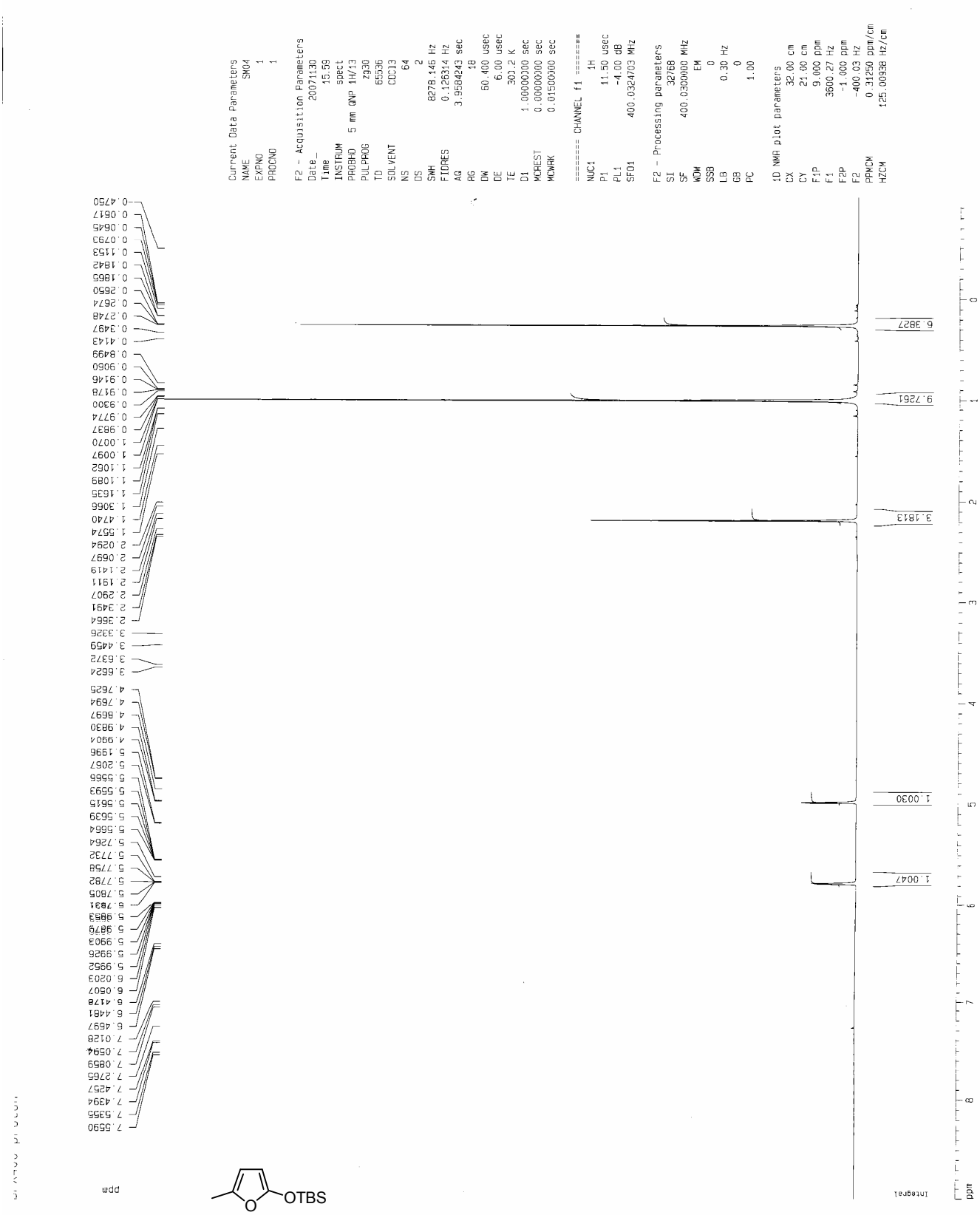
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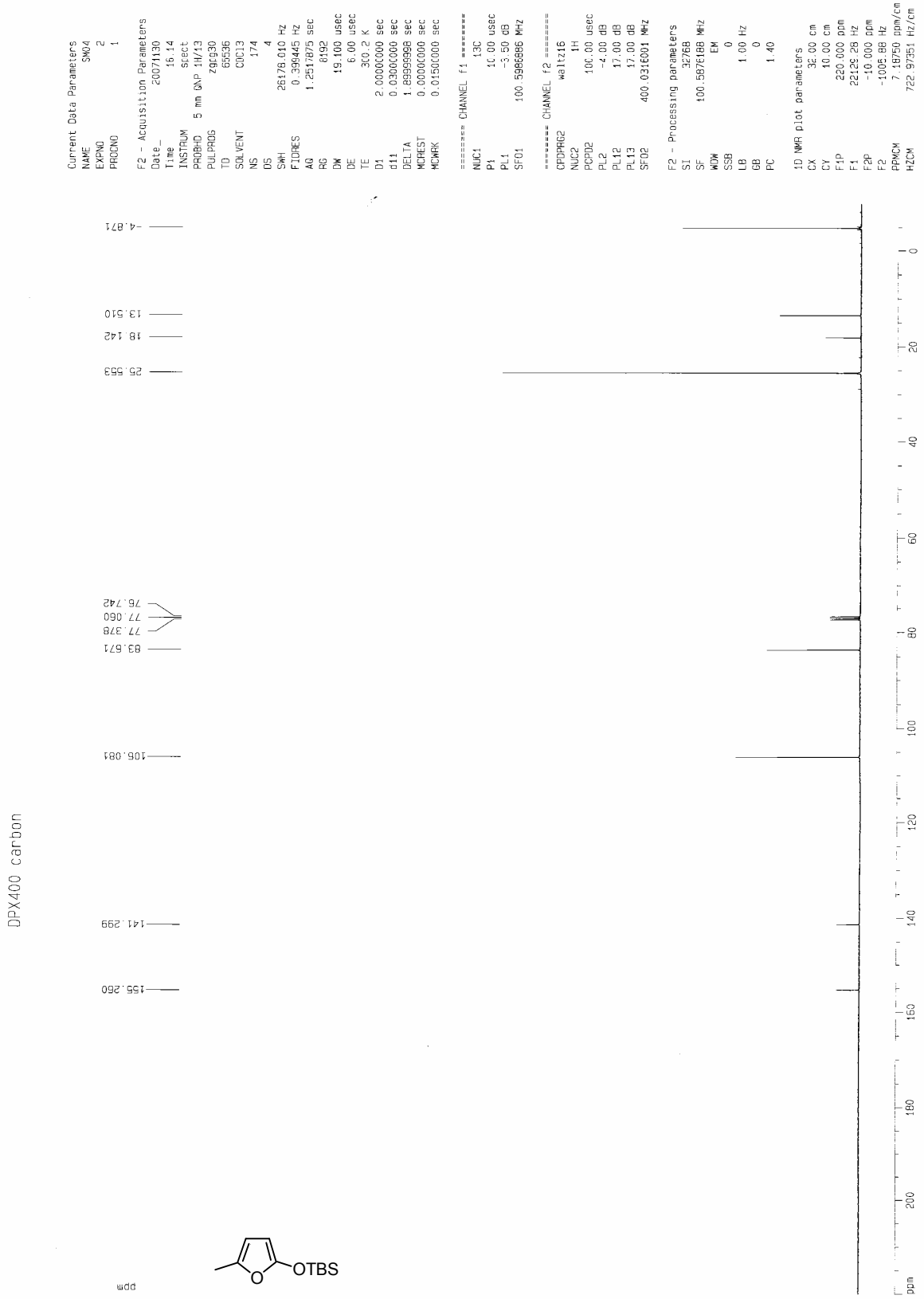
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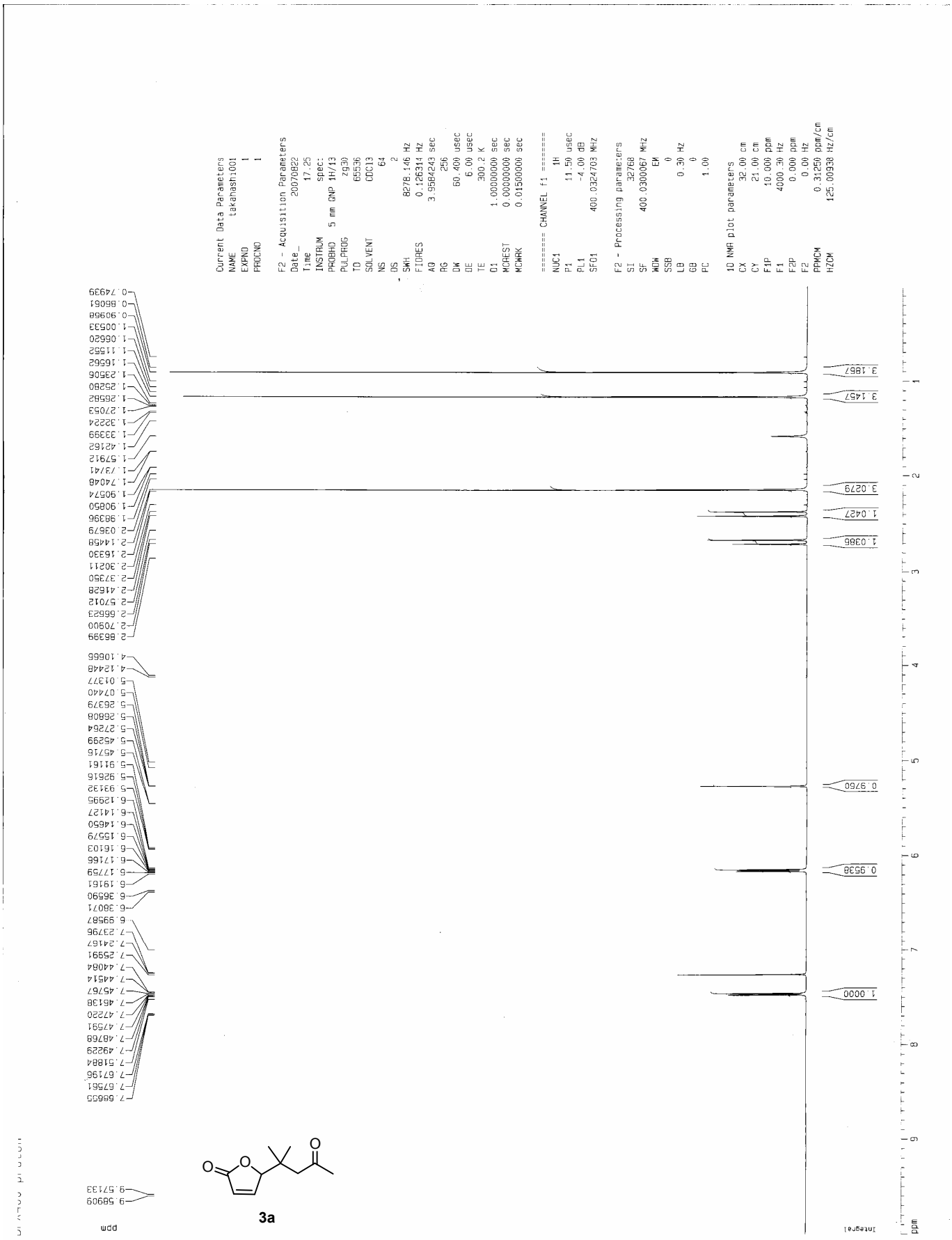
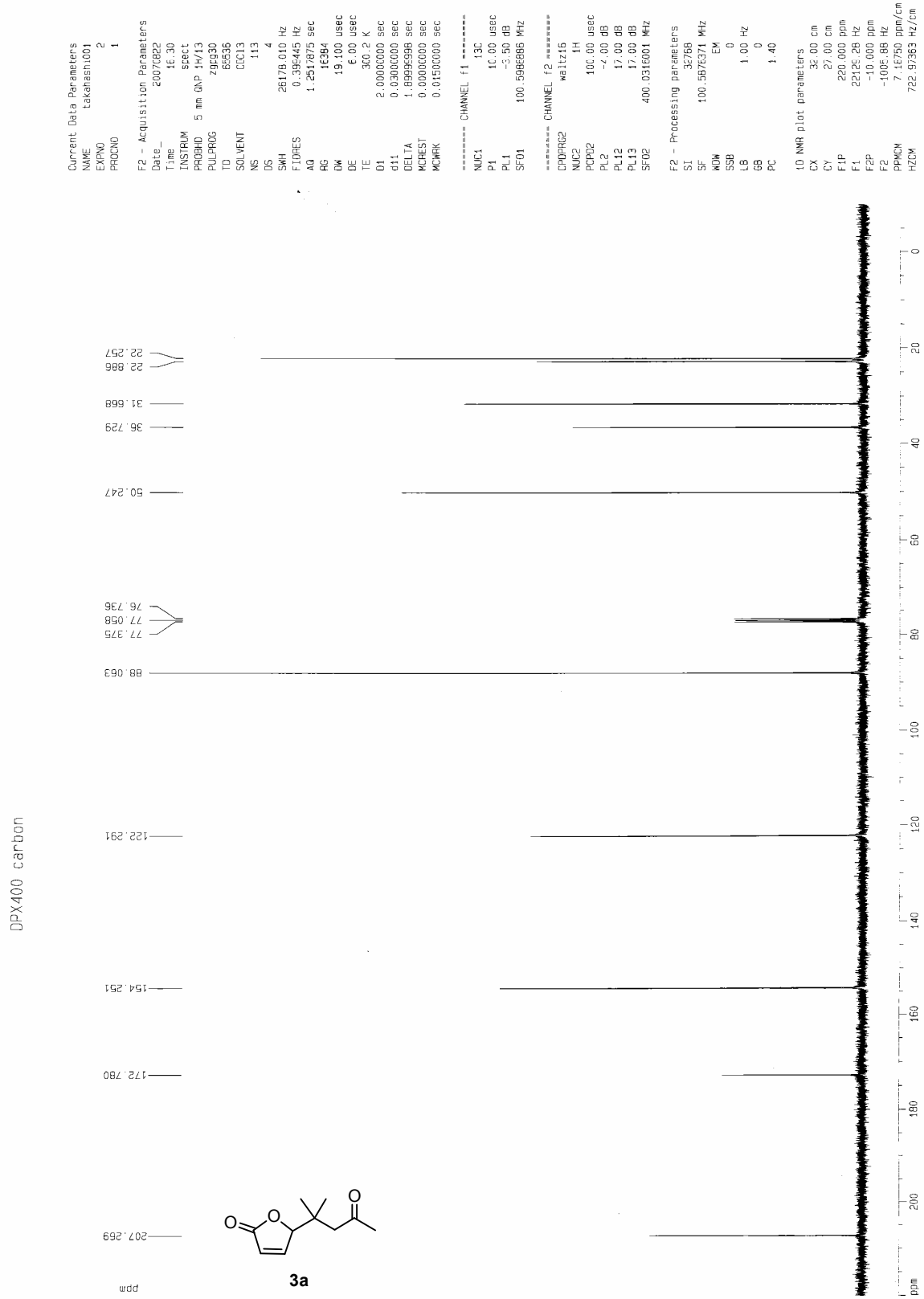
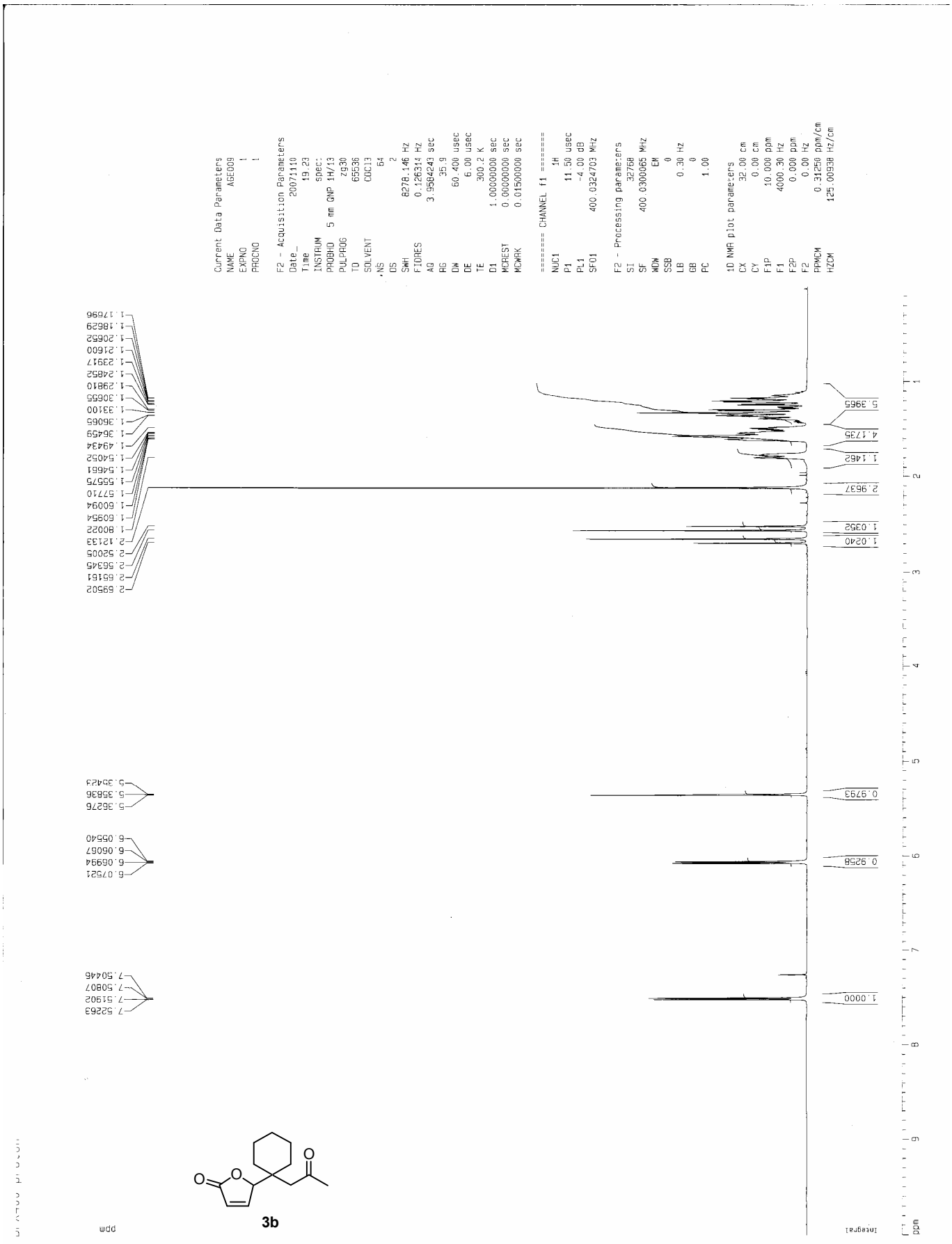
76.742
77.060
77.378
83.571
106.084
141.299
155.260
DPX400 carbon
ppm
OTBS


Current Data Parameters
NAME takahashi001
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070822
Time 17.25
INSTRUM spec
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 21.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00938 Hz/cm
3.1867
3.1457
3.0279
1.0427
1.0386
0.9760
0.9538
1.0000
Integral
ppm
O
O
O
3a


Current Data Parameters
NAME takahashi001
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070822
Time 16.30
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 113
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5988886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876371 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 36.00 cm
CY 27.00 cm
F1P 220.000 ppm
F1 22126.28 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.16750 ppm/cm
HZCM 722.97363 Hz/cm
22.257
22.886
31.668
36.729
50.247
76.736
77.058
77.375
88.063
122.291
154.251
172.780
207.269
DPX400 carbon
ppm
0
20
40
60
80
100
120
140
160
180
200
ppm

3a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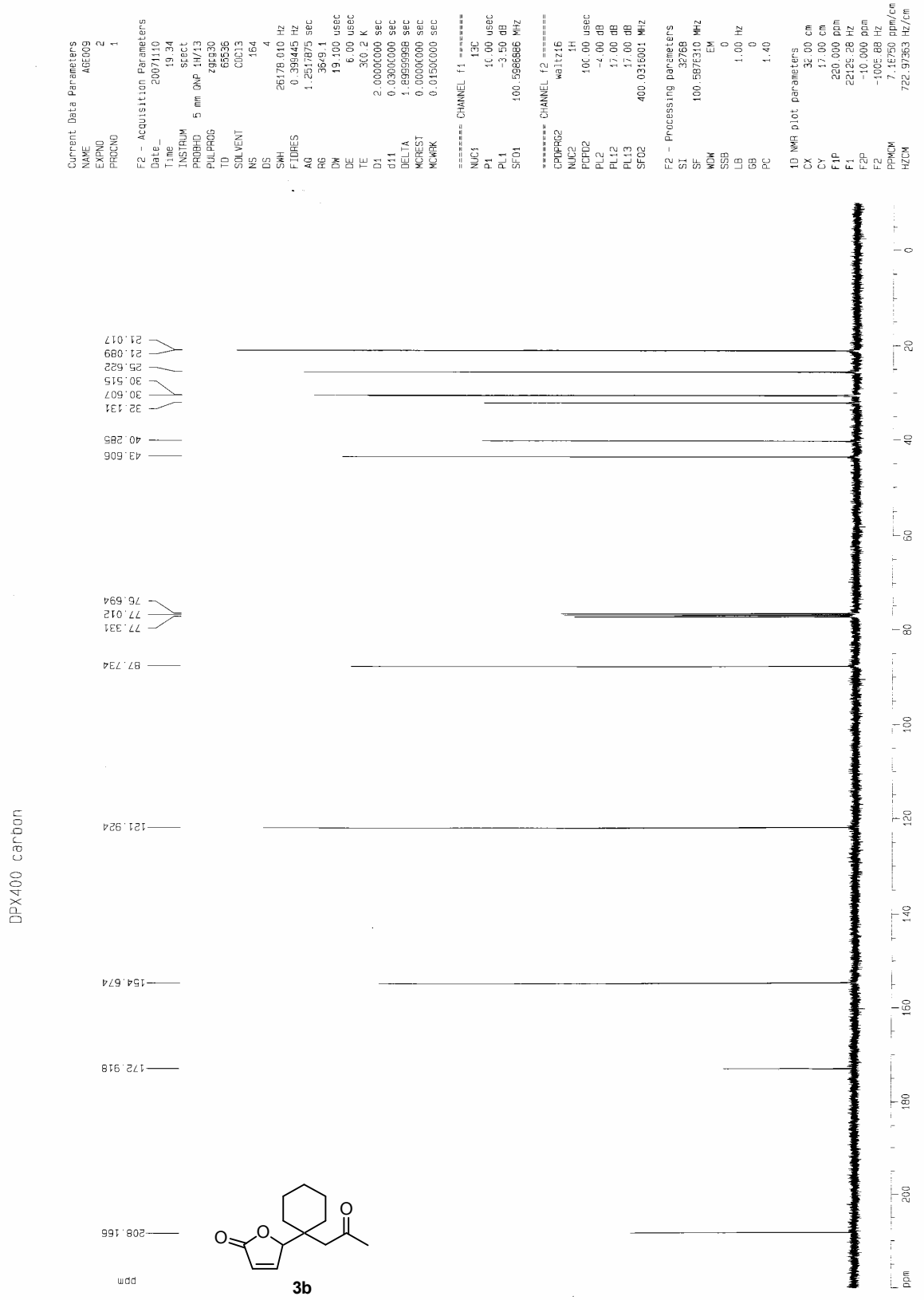
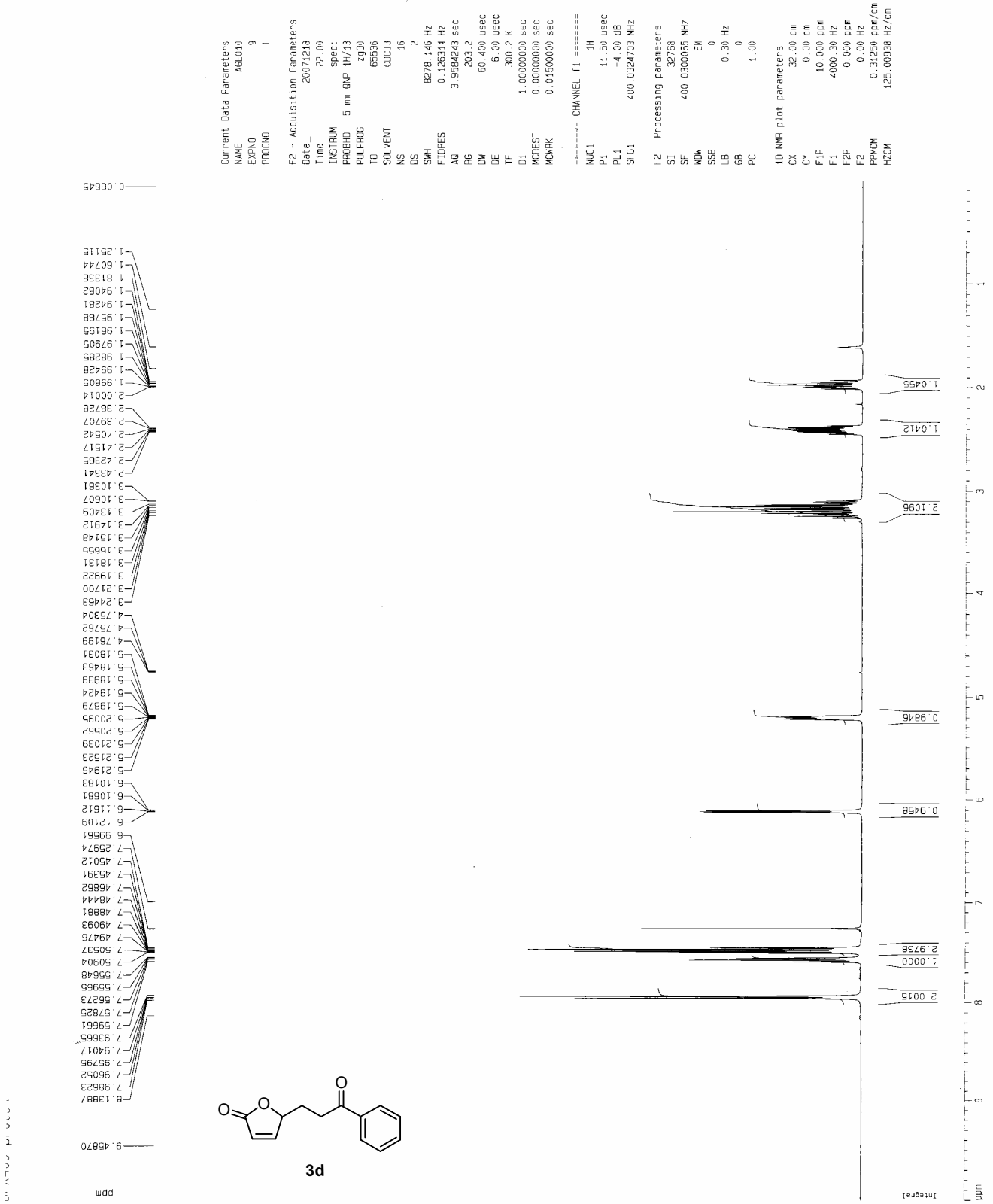
NAME AGE009
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071110
Time 19.23
INSTRUM spec
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300065 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 0.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00938 Hz/cm
1.17696
1.18629
1.20652
1.21600
1.23917
1.24852
1.29810
1.30655
1.33100
1.36065
1.36459
1.49434
1.54052
1.54661
1.55575
1.57710
1.60094
1.60954
1.80022
2.12133
2.52005
2.53645
2.55161
2.59502
5.35423
5.35836
5.36276
6.05540
6.06067
6.06994
6.07521
7.50446
7.50807
7.51902
7.52563
5.3965
4.1735
1.1462
2.9637
1.0352
1.0240
0.9793
0.9258
1.0000
ppm
Integral

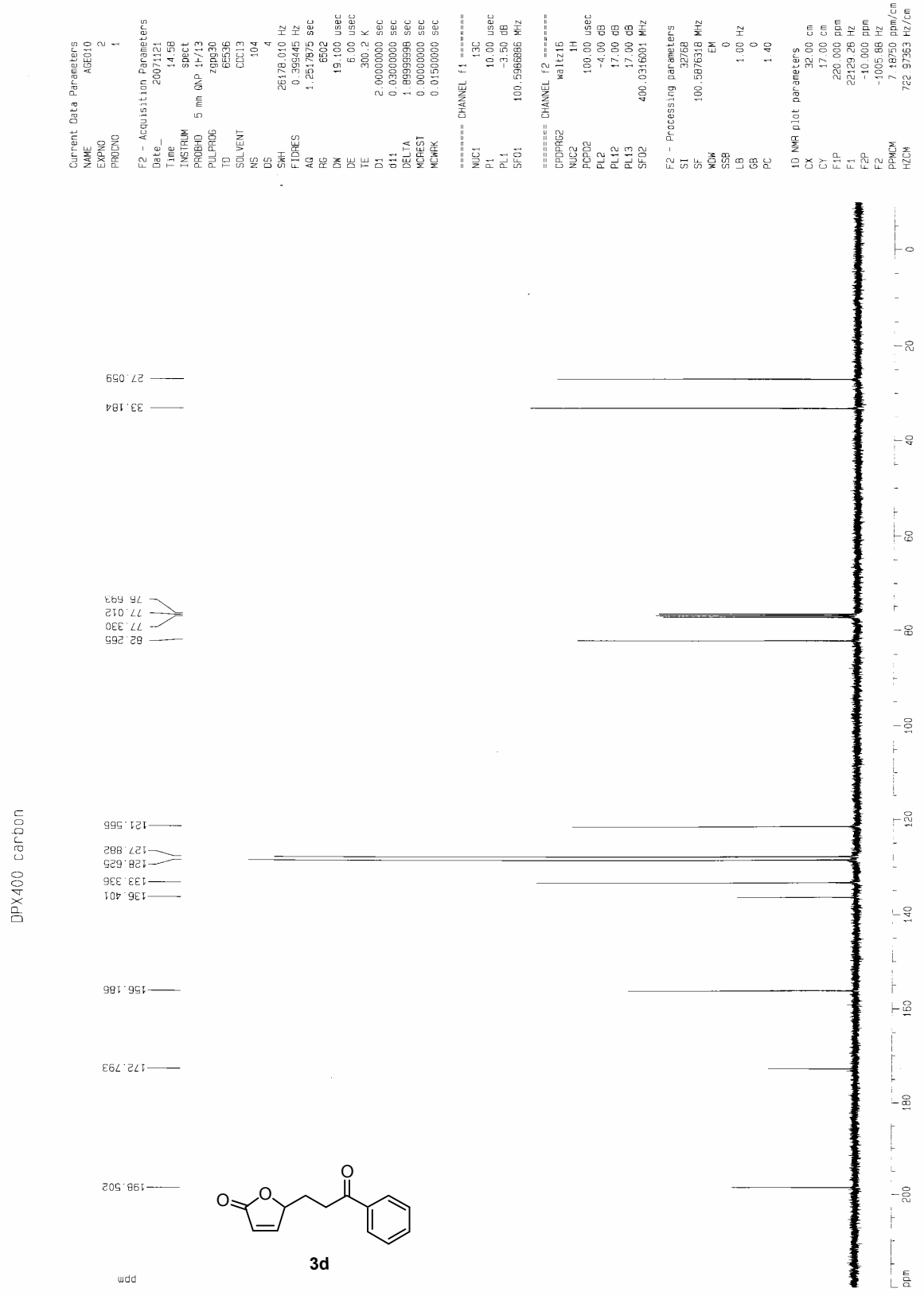
3b


Current Data Parameters
NAME AGE009
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071110
Time 19.34
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 164
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 3649.1
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5986866 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5877310 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 30.00 cm
CY 17.00 cm
F1P 220.000 ppm
F1 22125.28 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.16750 ppm/cm
HZCM 722.97363 Hz/cm
DPX400 carbon
21.017
21.089
25.622
30.515
30.607
32.131
40.285
43.606
76.694
77.012
77.331
87.734
121.924
154.674
172.918
208.166
ppm
0
20
40
60
80
100
120
140
160
180
200
ppm
O
O
O

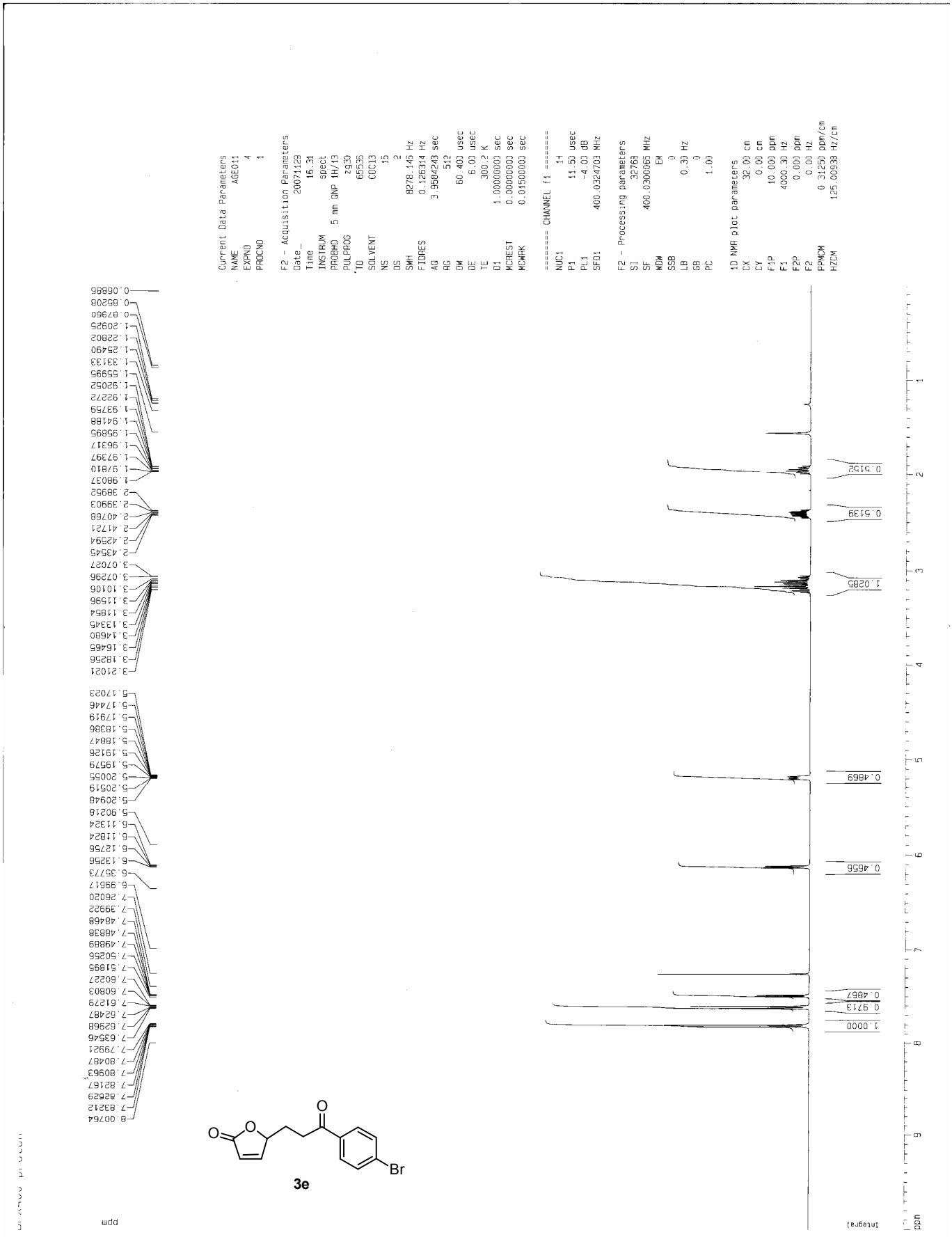
3b

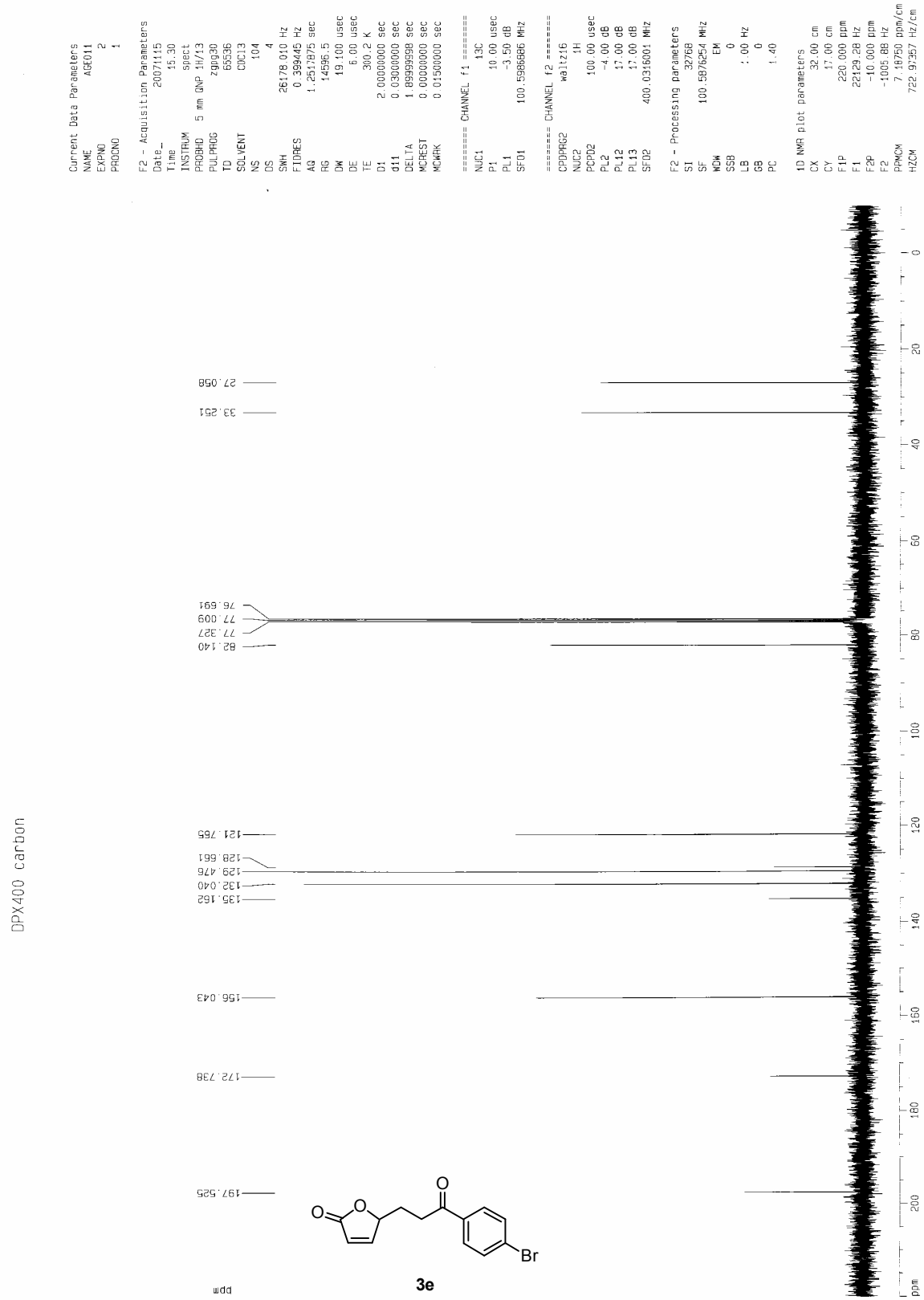

Current Data Parameters
NAME AGE01
EXPNO 9
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071218
Time 22.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 203.2
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SF01 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300065 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 0.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00938 Hz/cm
1.0455
1.0412
2.1096
0.9846
0.9458
2.9738
1.0000
2.0015
Integral
ppm

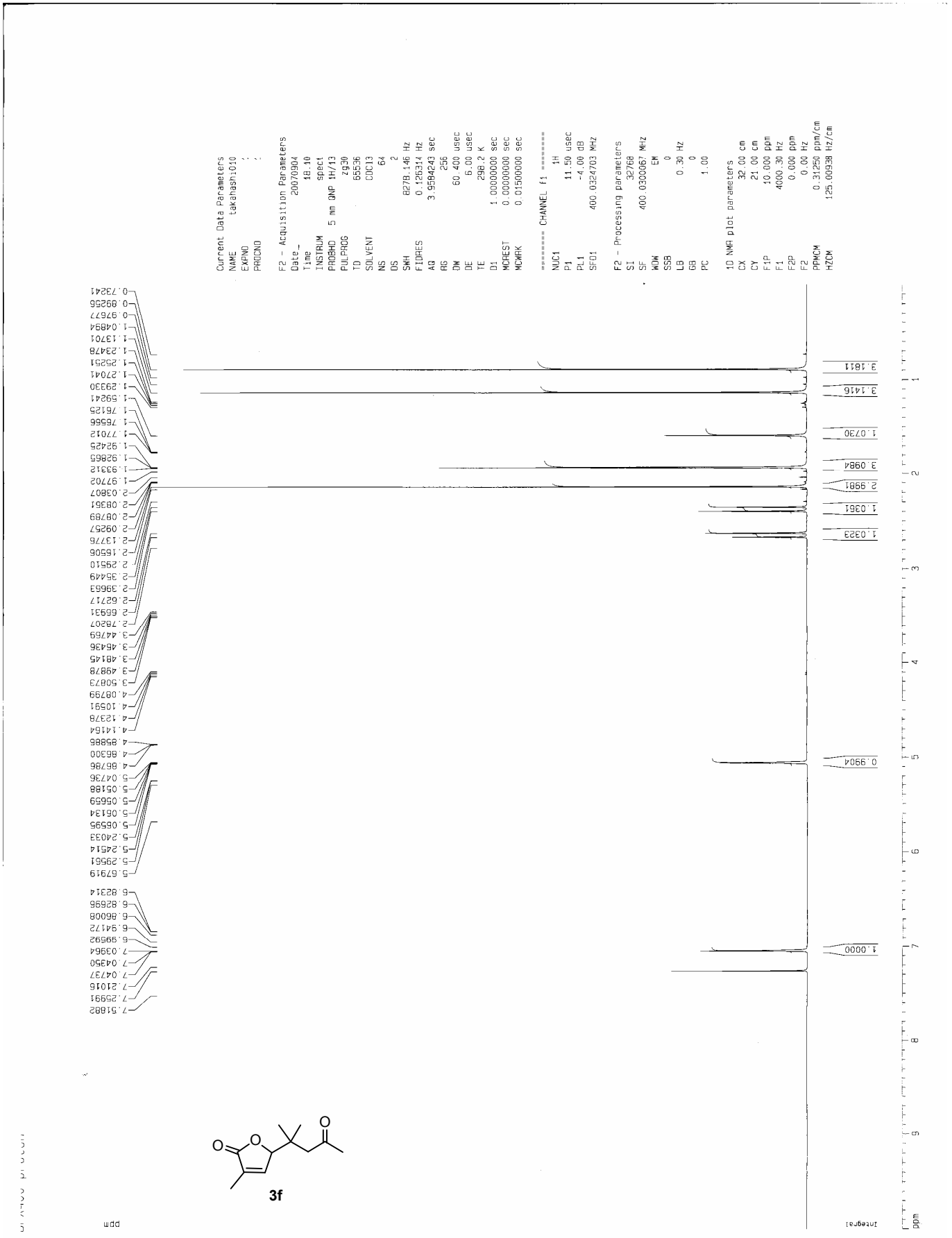
3d


Current Data Parameters
NAME AGE010
EXPNO 2
PRODNO 1
F2 - Acquisition Parameters
Date_ 20071121
Time 14.58
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 104
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 6502
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SF01 100.5966886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SF02 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876318 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 17.00 cm
F1P 220.000 ppm
F1 22129.26 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.18750 ppm/cm
HZCM 722.97363 Hz/cm
DPX400 carbon
27.059
33.184
76.693
77.012
77.330
82.265
121.565
127.882
128.625
133.336
136.401
156.186
172.793
198.502
ppm
0
20
40
60
80
100
120
140
160
180
200
O
O
O

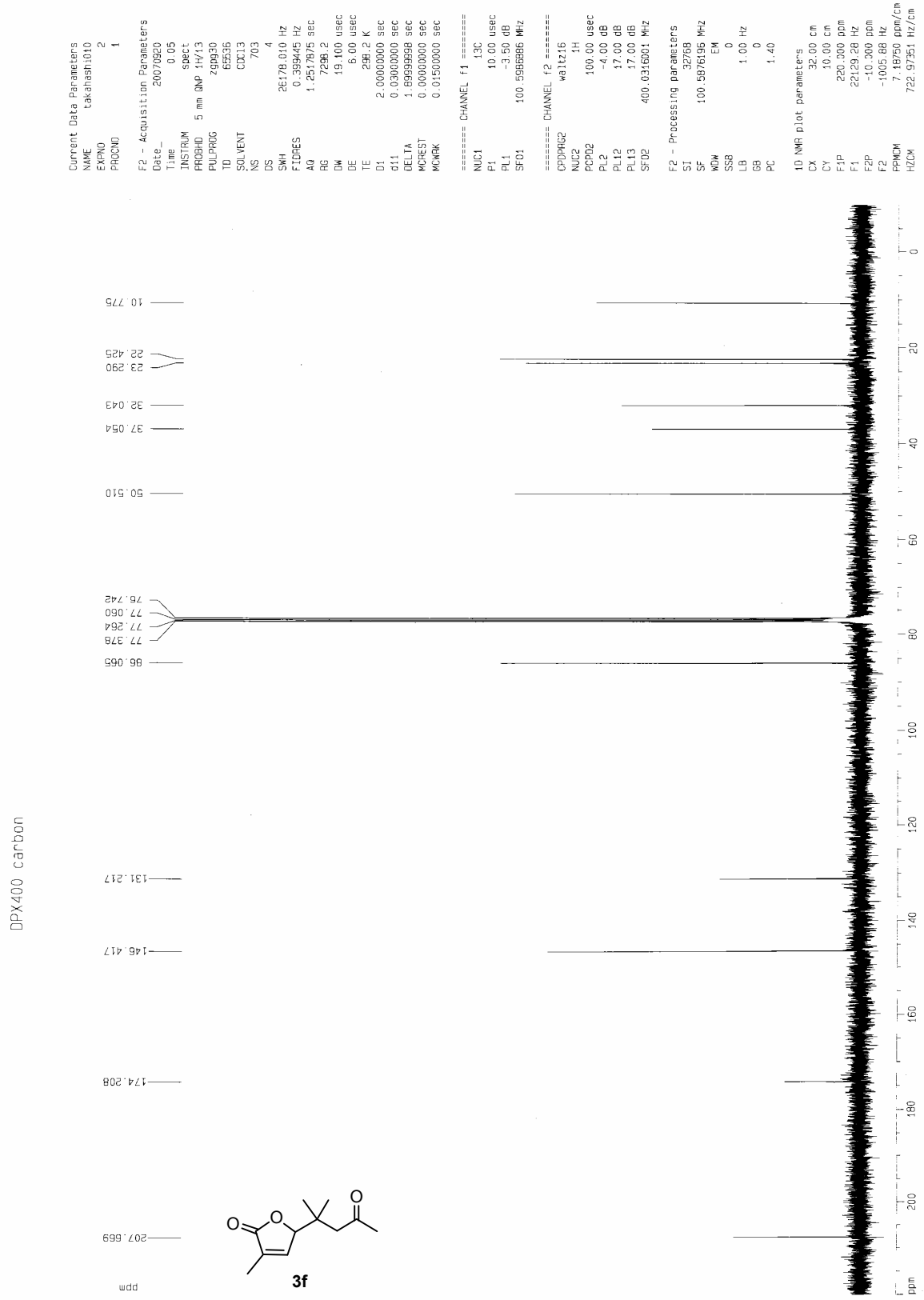
3d

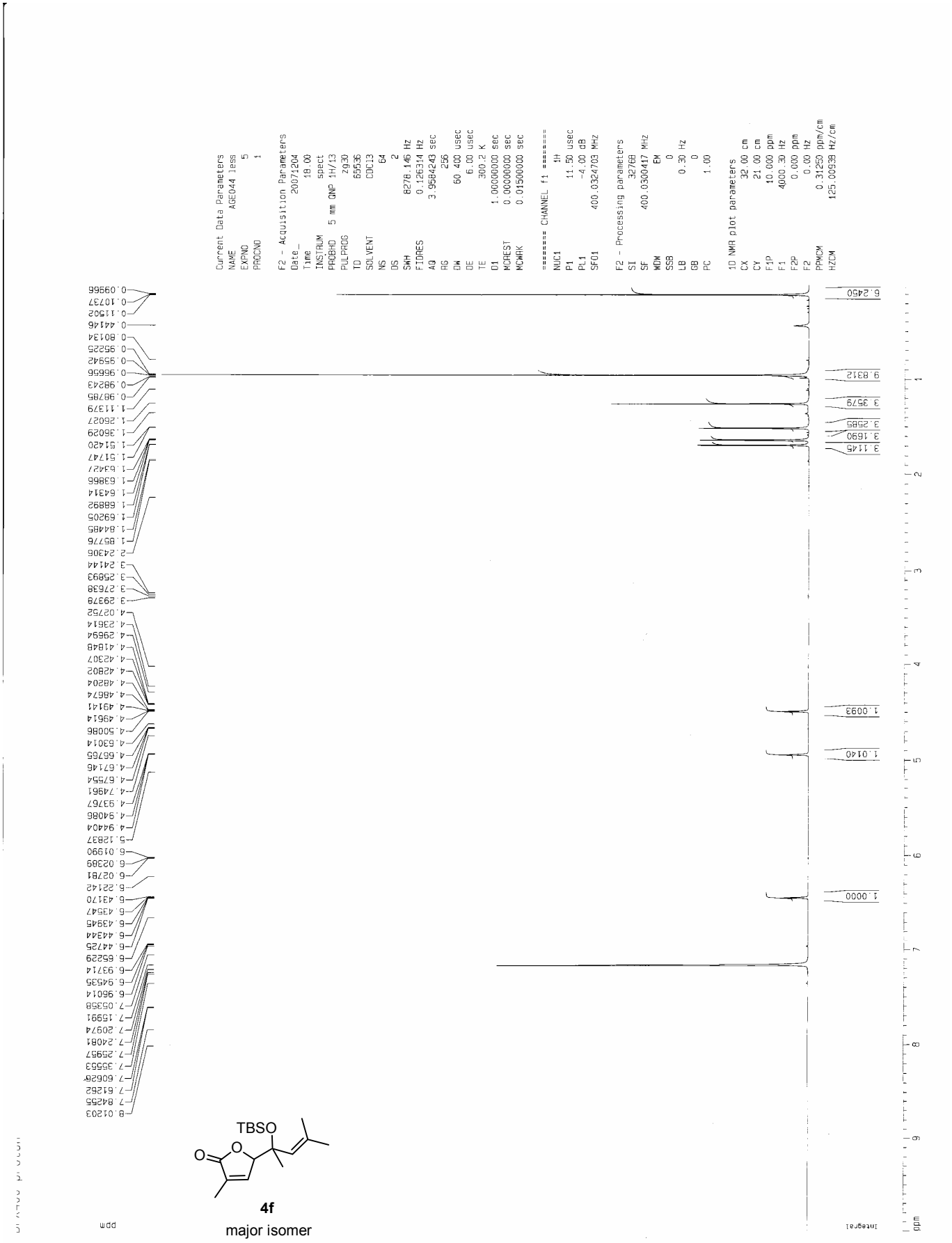

Current Data Parameters
NAME AGE011
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071129
Time 16.31
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 15
DS 2
SWH 8278.145 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 512
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300065 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 0.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00938 Hz/cm
0.5152
0.5139
1.0288
0.4869
0.4656
0.4867
0.9713
1.0000
Integral
ppm
O
O
O
Br
3e

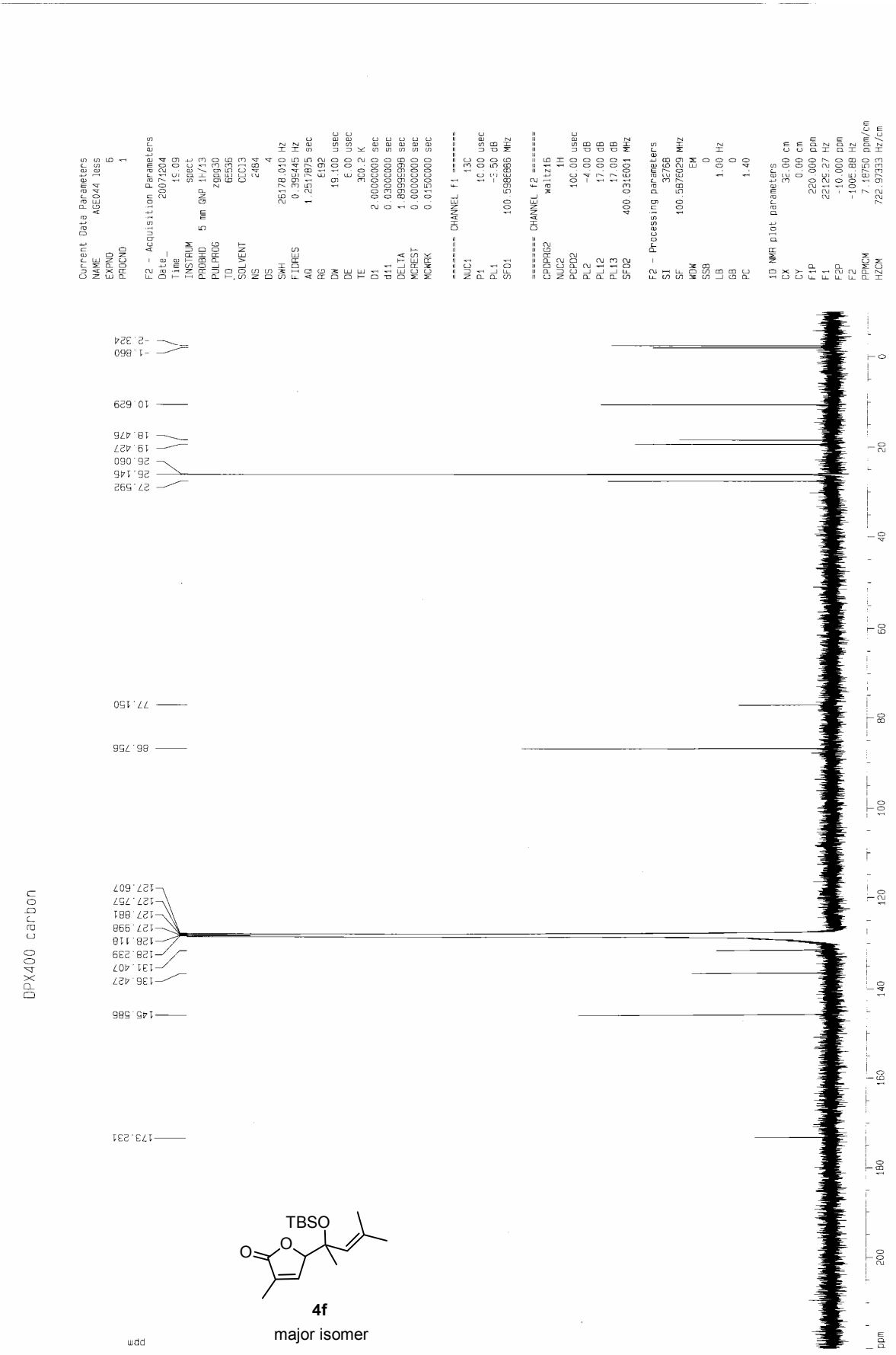

Current Data Parameters
NAME AGE011
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071115
Time 15.30
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 104
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 14596.5
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5986686 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876254 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 17.00 cm
F1P 220.000 ppm
F1 22129.28 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.16750 ppm/cm
HZCM 722.97357 Hz/cm
27.058
33.251
76.691
77.009
77.327
82.140
121.765
128.661
129.476
132.040
135.162
156.043
172.738
197.525
ppm
0
20
40
60
80
100
120
140
160
180
200
O
O
O
Br
3e
DPX400 carbon


Current Data Parameters
NAME takahashi010
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070904
Time 18.10
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126311 Hz
AQ 3.9568243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 21.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00938 Hz/cm
3.1811
3.1416
1.0730
3.0984
2.9981
1.0361
1.0323
0.9904
1.0000
integral
ppm

3f

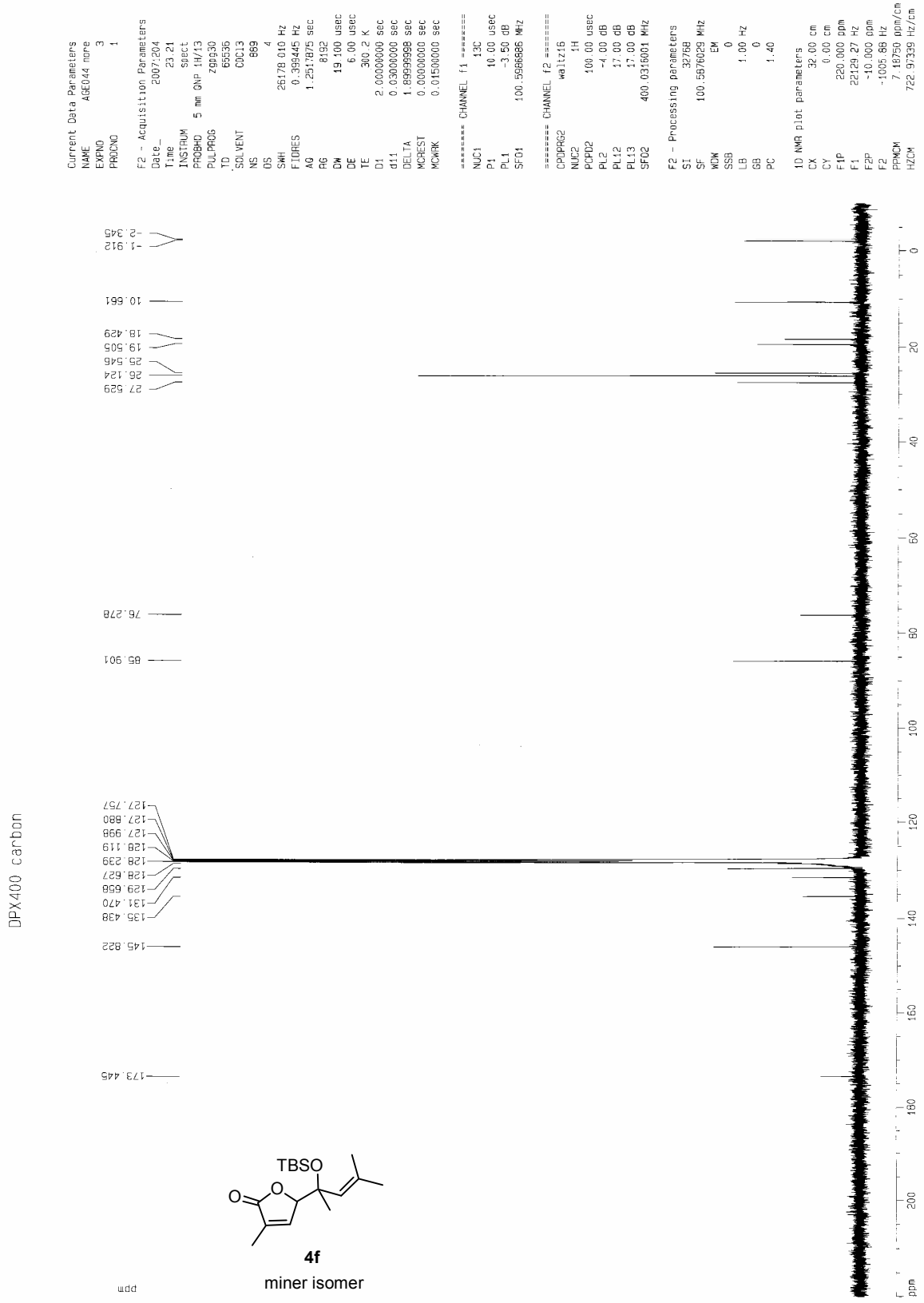

Current Data Parameters
NAME takahashi010
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070920
Time 0.05
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 703
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517675 sec
RG 7298.2
DW 19.100 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5966886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876196 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 10.00 cm
F1P 220.000 ppm
F1 22129.28 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.18750 ppm/cm
HZCM 722.97351 Hz/cm
10.775
22.425
23.290
32.043
37.054
50.510
76.742
77.060
77.264
77.378
86.065
131.217
146.417
174.208
207.669
DPX400 carbon
ppm
3f

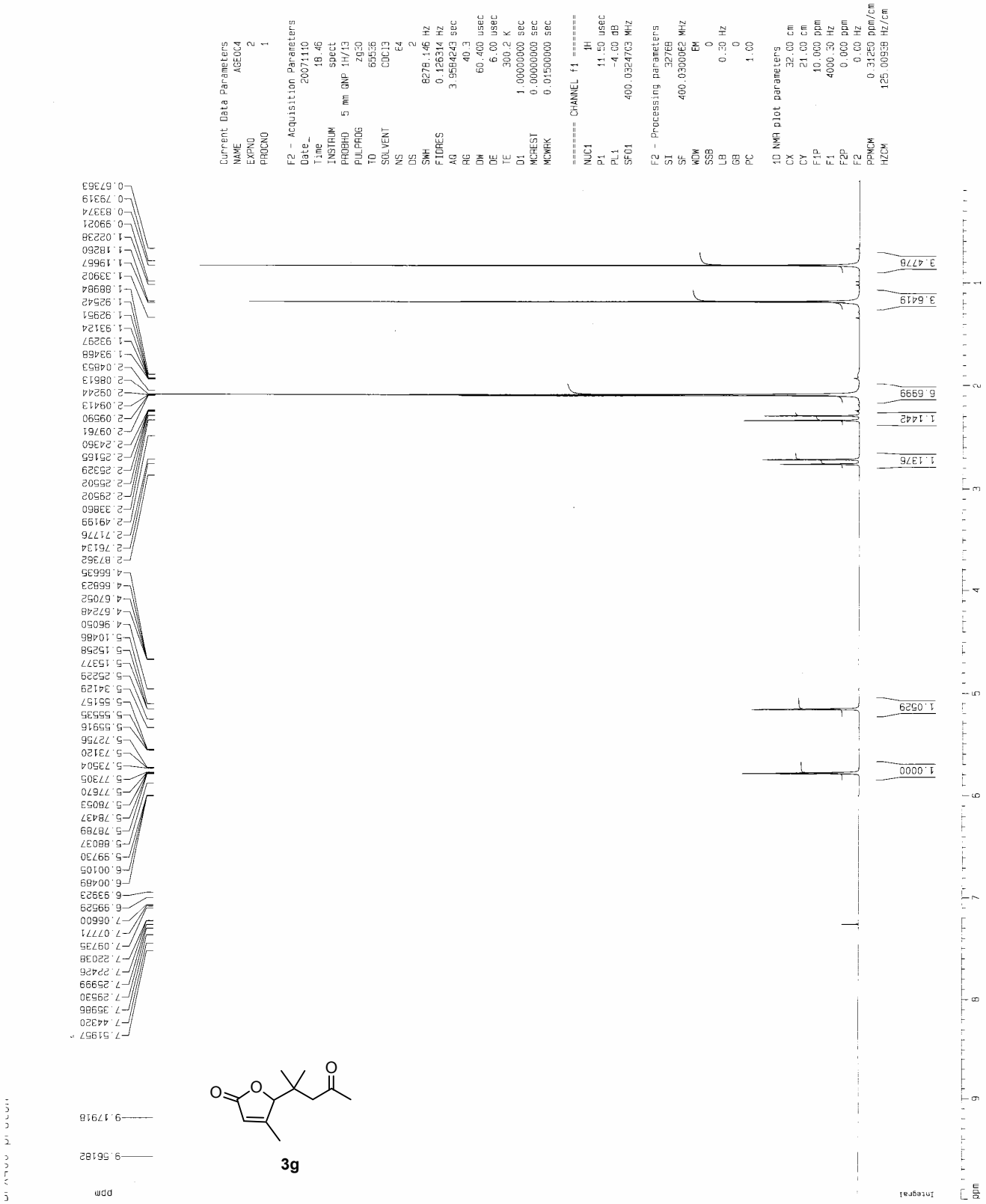

TBSO
O
O
4f
major isomer



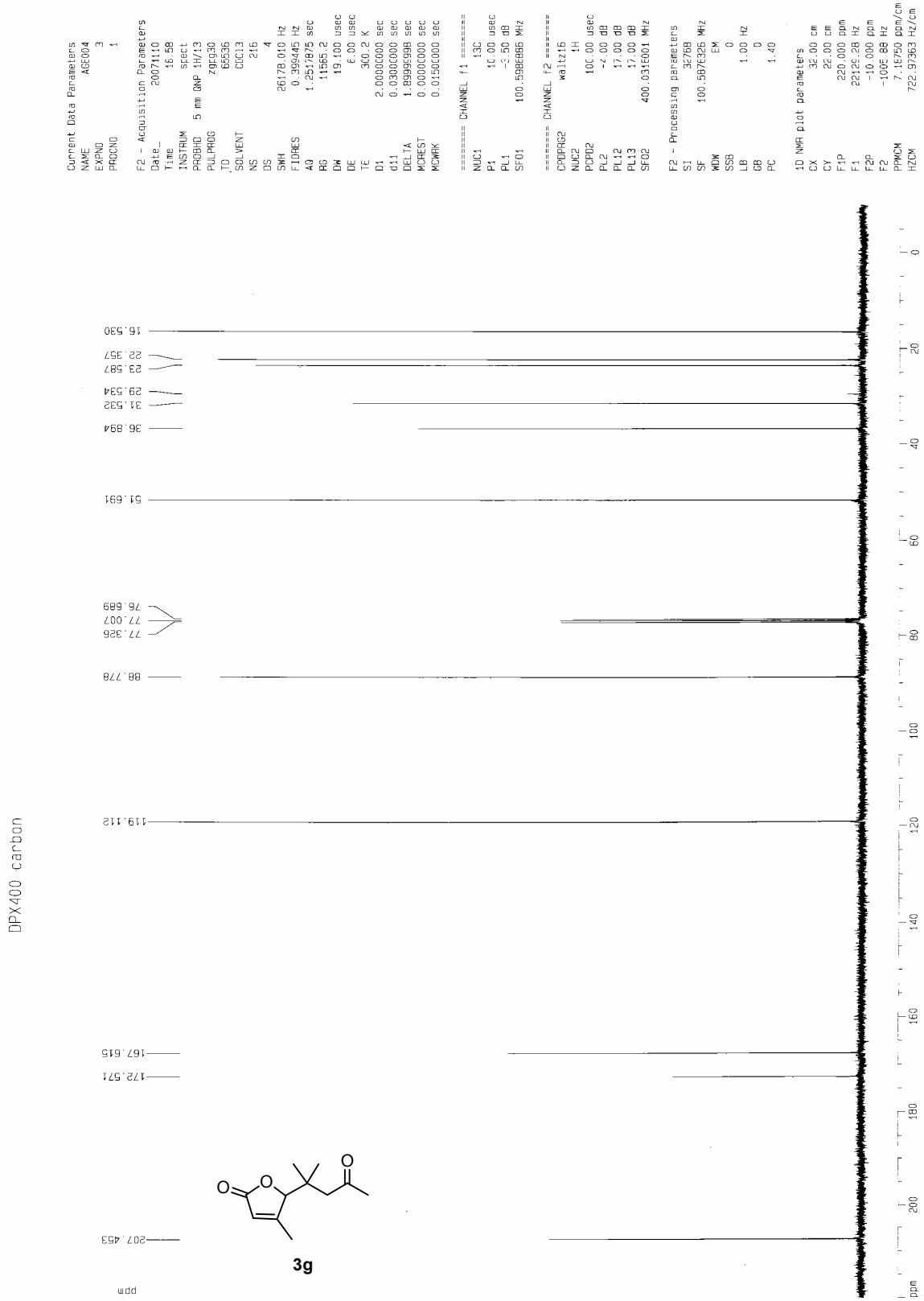
4f
major isomer


Current Data Parameters
NAME AGE044 more
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071204
Time 22.33
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300417 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 27.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00938 Hz/cm
0.05774
0.09313
0.90217
0.90925
1.25777
1.54591
1.54924
1.57436
1.57742
1.68869
1.69304
1.69743
7.15988
6.3080
9.5479
3.3935
3.3253
3.0424
3.1342
1.0092
1.0106
1.0000
TBSO
O
O
4f
miner isomer
ppm
Integral


Current Data Parameters
NAME AGE044 nore
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20072004
Time 23.21
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 889
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 8192
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5986886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876029 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 0.00 cm
F1P 220.000 ppm
F1 22129.27 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.18750 ppm/cm
HZCM 722.97339 Hz/cm
-2.345
-1.912
10.661
18.429
19.505
25.545
26.124
27.529
76.278
85.901
127.757
127.880
127.998
128.119
128.239
128.627
129.658
131.470
135.438
145.822
173.445
DPX400 carbon
ppm
TBSO
O
O
4f
miner isomer


Current Data Parameters
NAME AGE004
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071110
Time 18.46
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 40.3
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCHEST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300062 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 21.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00938 Hz/cm
3.4778
3.6419
6.6999
1.1442
1.1376
1.0529
1.0000
ppm
Integral

3g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EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071110
Time 16.58
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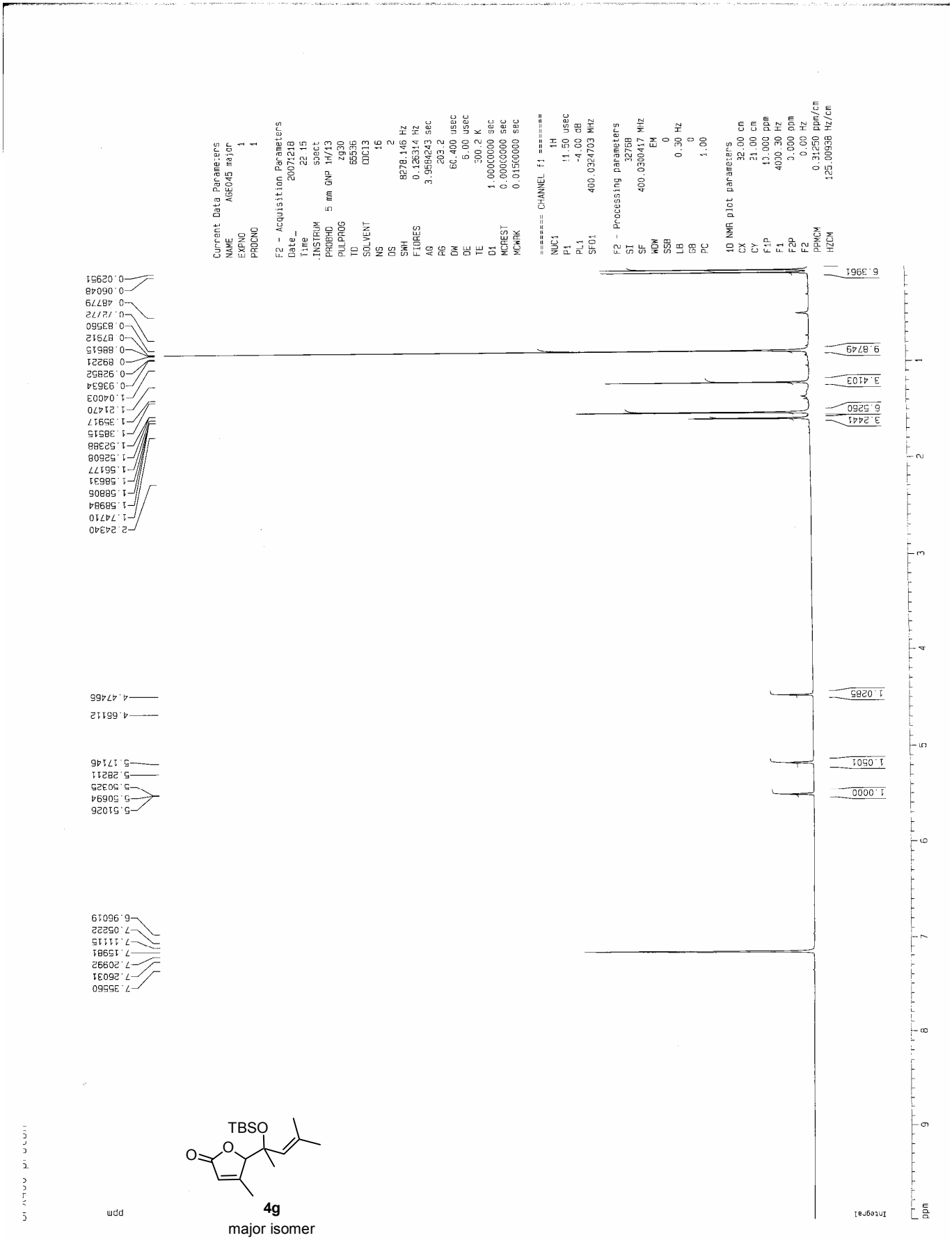
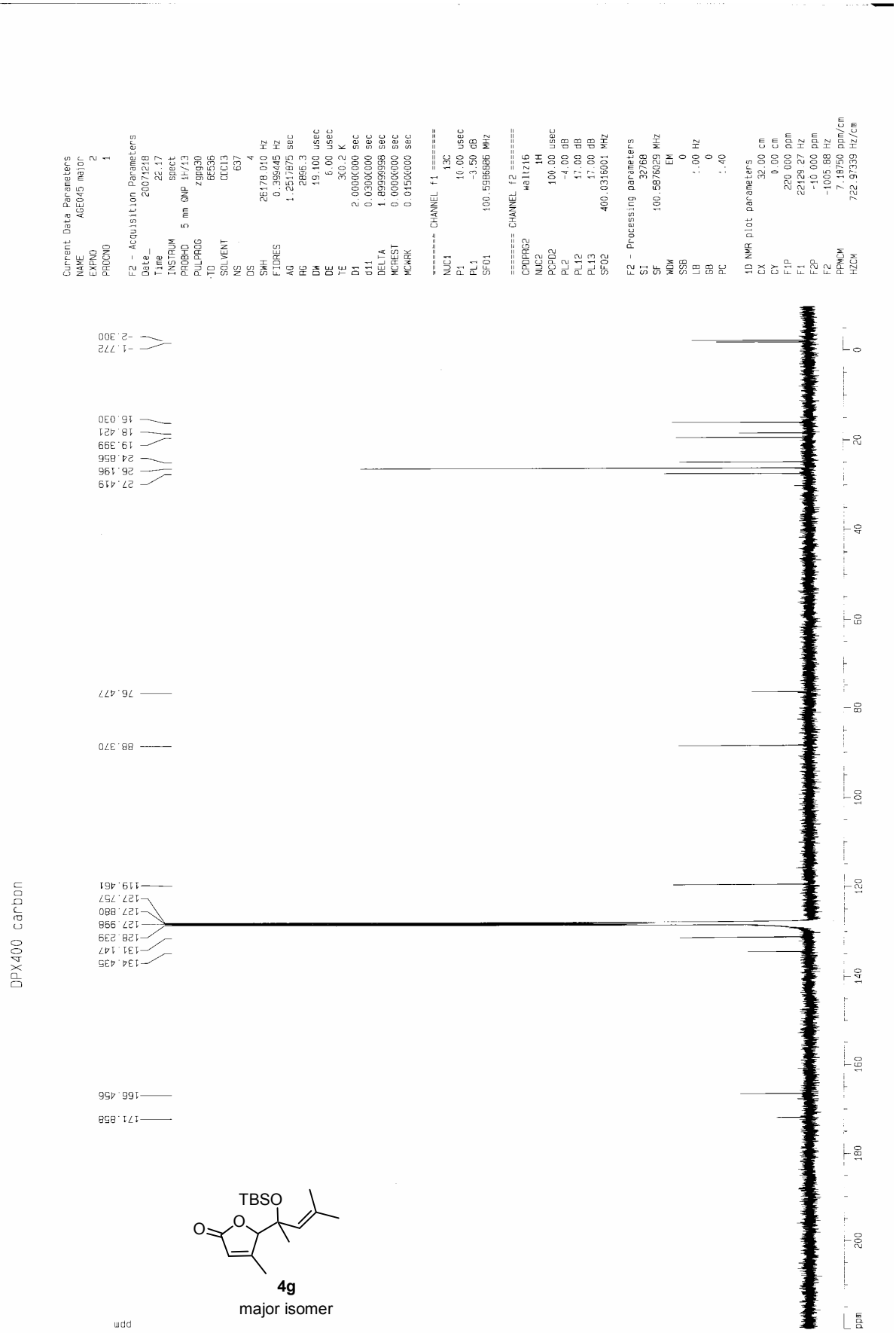
PROBHD 5 mm DNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 216
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 11585.2
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89995998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5988886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5875326 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 22.00 cm
F1P 220.000 ppm
F1 22125.28 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.16750 ppm/cm
HZCM 722.97363 Hz/cm
DPX400 carbon
16.530
22.357
23.587
29.534
31.532
36.894
51.691
76.689
77.007
77.326
88.778
119.112
167.615
172.571
207.453
ppm
O
O
O
3g


TBSO
O
O
4g
major isomer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NAME AGE045 major
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071218
Time 22.17
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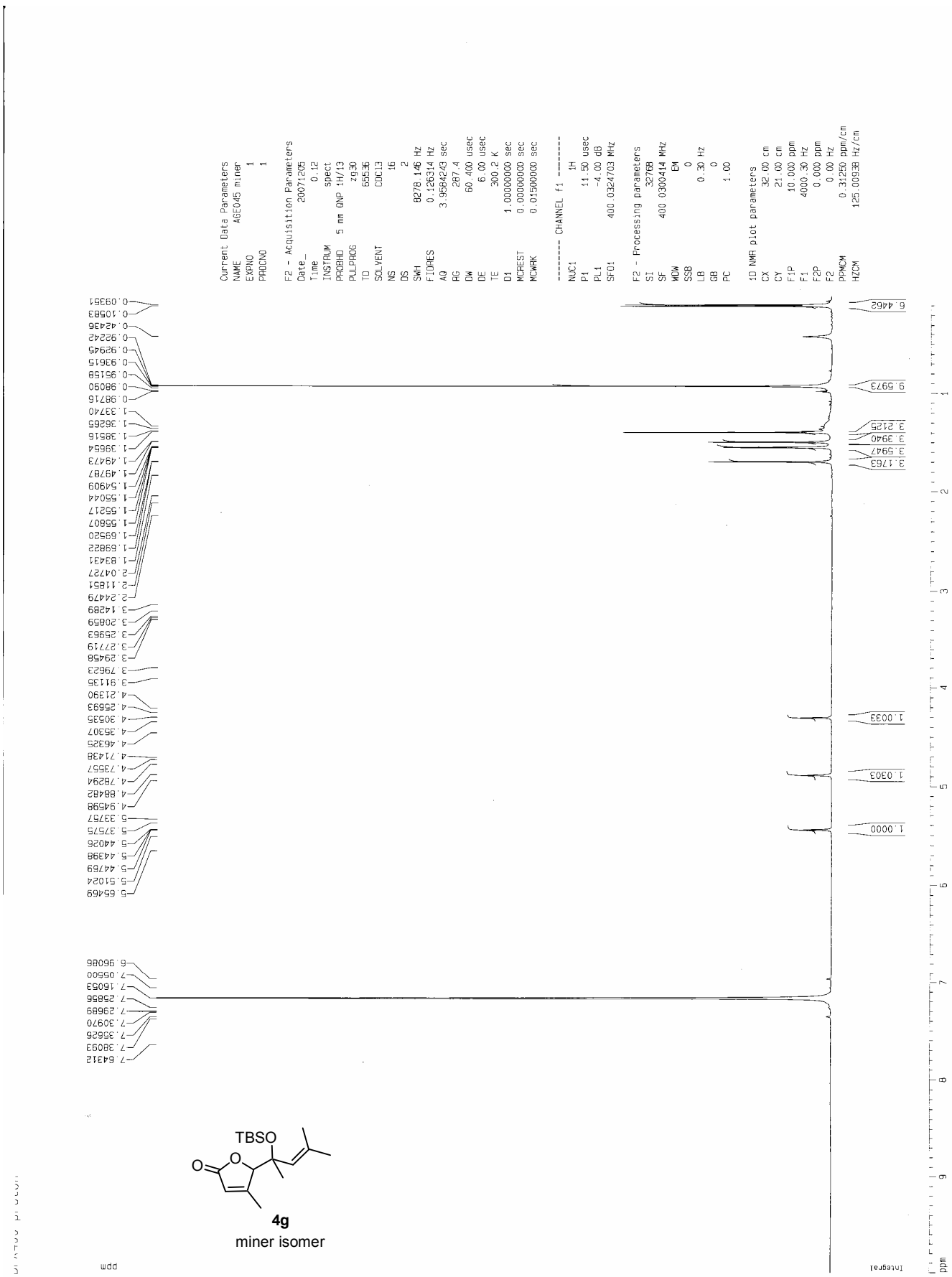
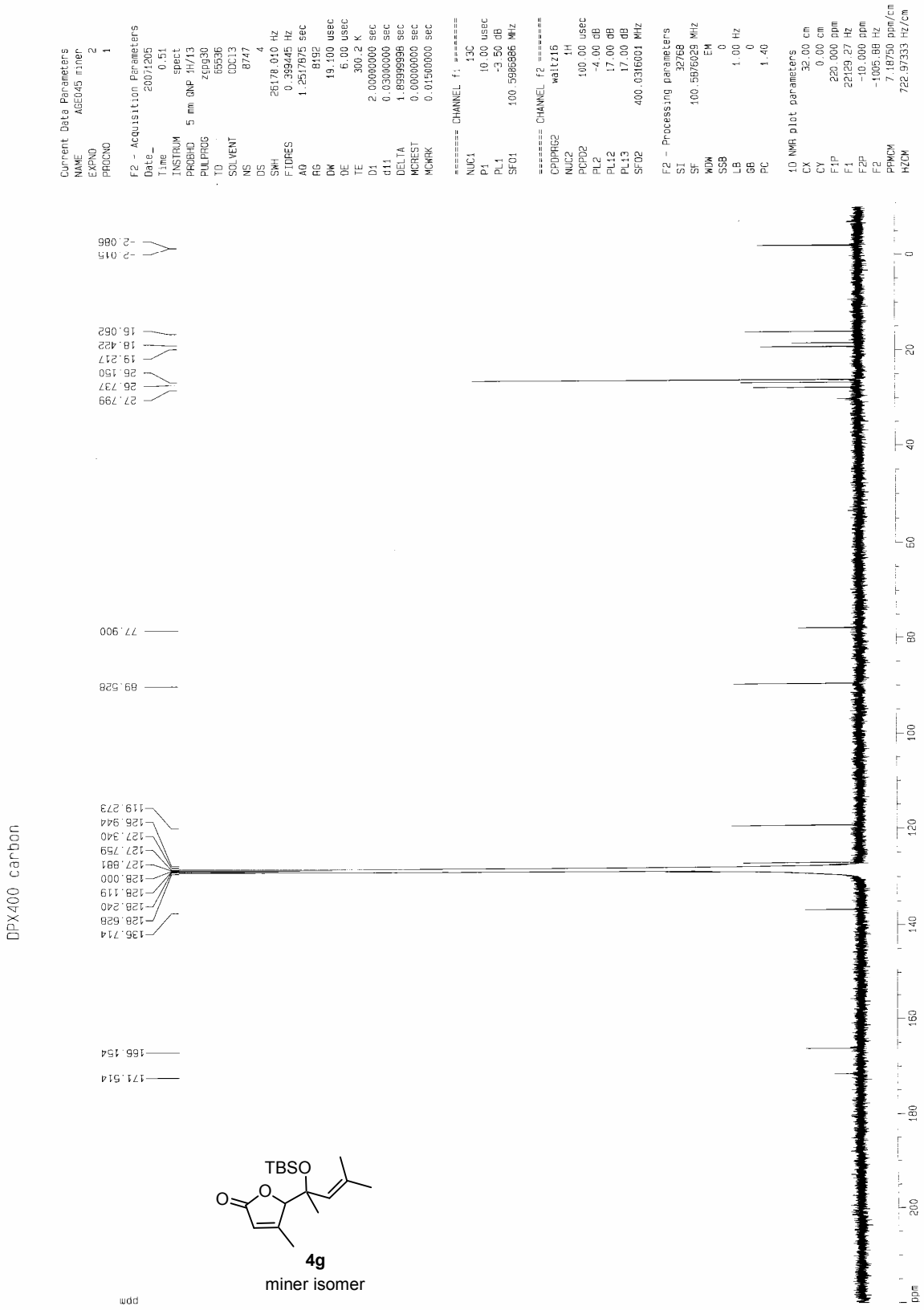
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 2896.3
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SF01 100.5988886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SF02 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876029 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 30.00 cm
CY 0.00 cm
F1P 220.000 ppm
F1 22129.27 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.19750 ppm/cm
HZCM 722.97339 Hz/cm
-2.300
-1.772
16.030
18.421
19.399
24.856
26.196
27.419
76.477
88.370
119.461
127.757
127.880
127.998
128.239
131.147
134.435
166.456
171.858
DPX400 carbon
ppm
TBSO
O
O
4g
major isomer


TBSO
O
O
4g
miner isomer
ppm
Integral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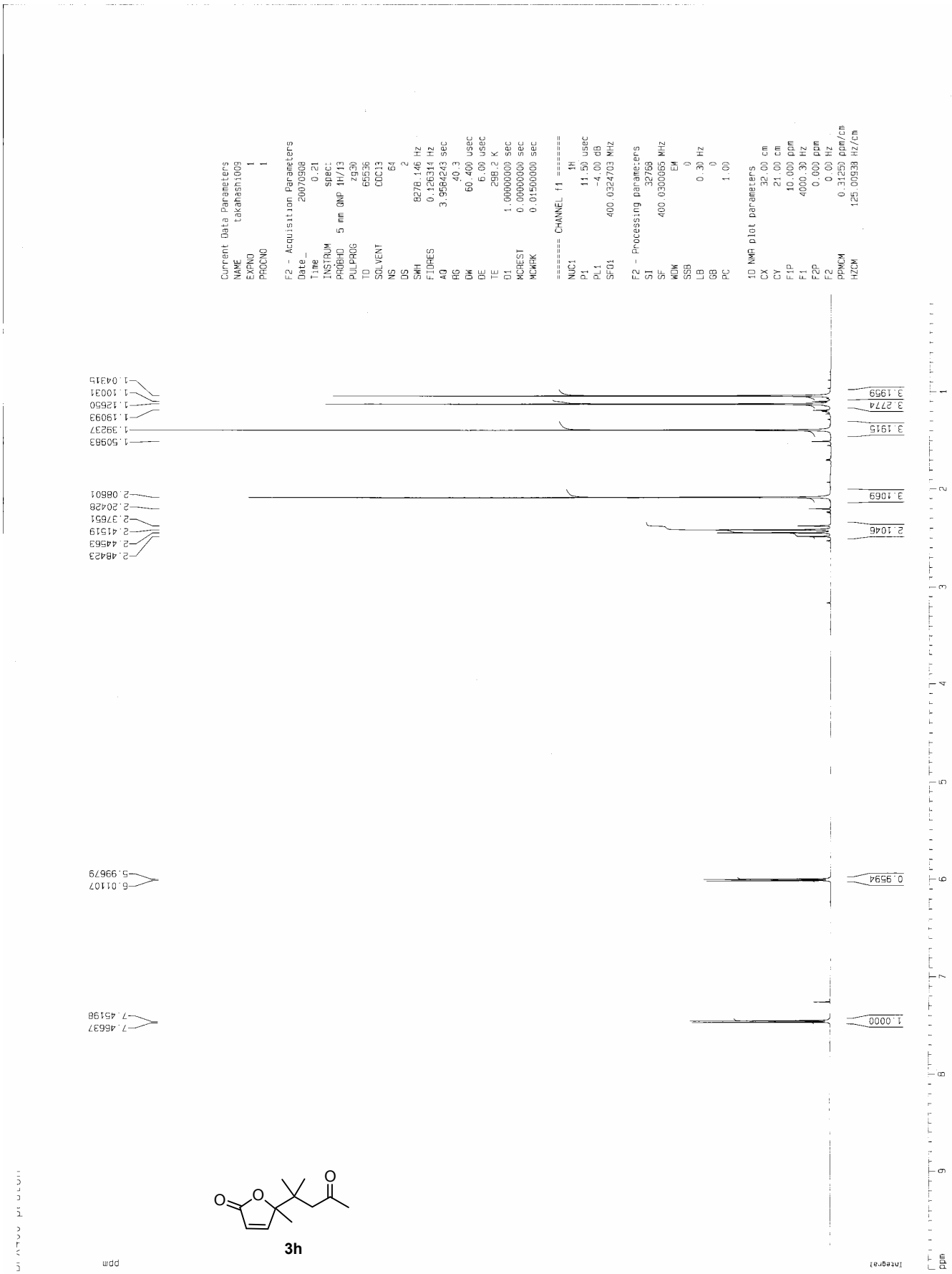
NAME AGE045 miner
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071205
Time 0.51
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8747
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517675 sec
RG 8192
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5985886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876029 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 0.00 cm
F1P 220.000 ppm
F1 22129.27 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.18750 ppm/cm
HZCM 722.97333 Hz/cm
-2.086
-2.015
16.062
18.422
19.217
26.150
26.737
27.799
77.900
89.528
119.273
126.944
127.340
127.759
127.881
128.000
128.119
128.240
128.628
136.714
166.154
171.514
DPX400 carbon
ppm
TBSO
O
O
4g
miner isomer


Current Data Parameters
NAME takahashi009
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070908
Time 0.21
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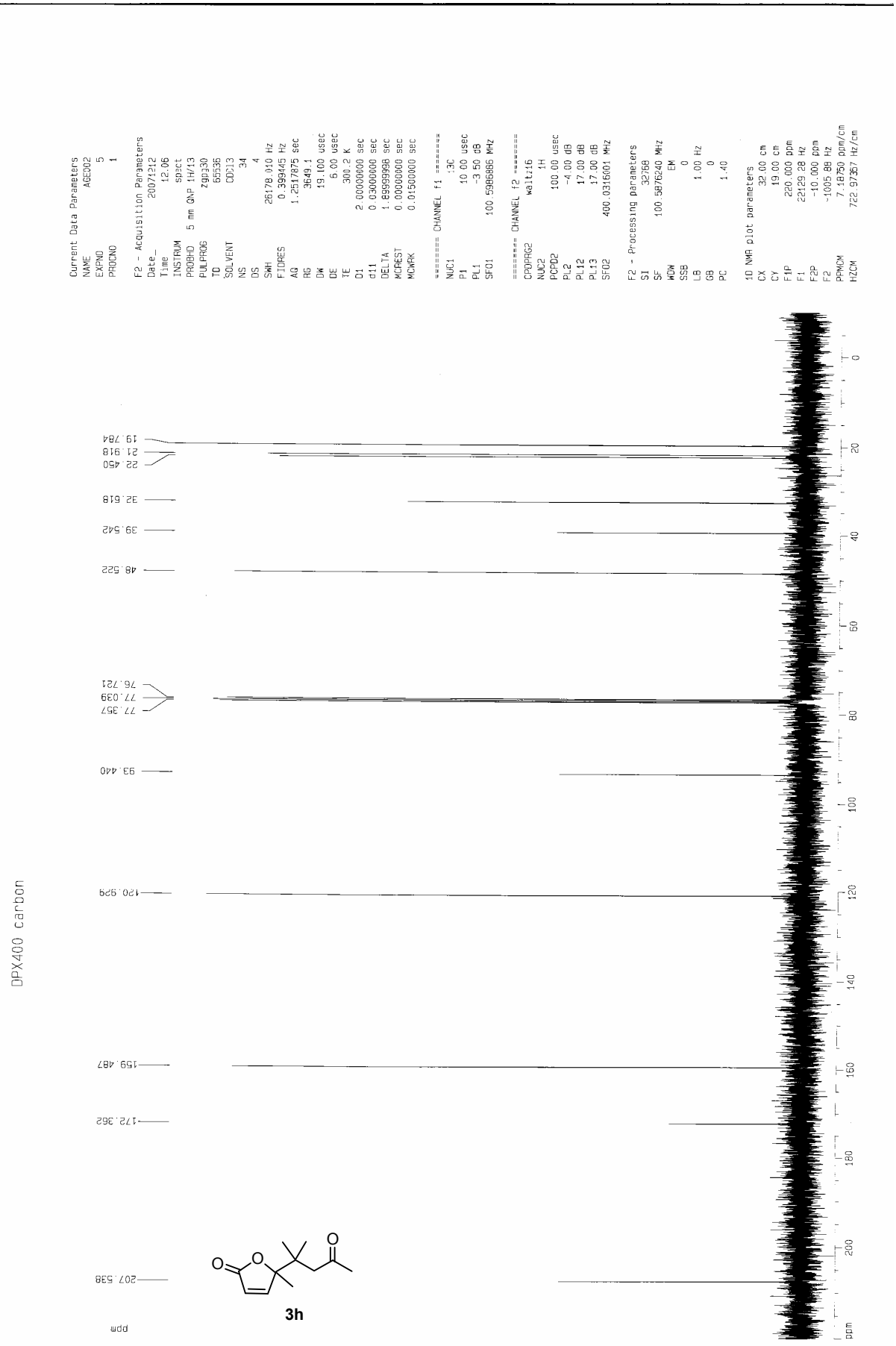
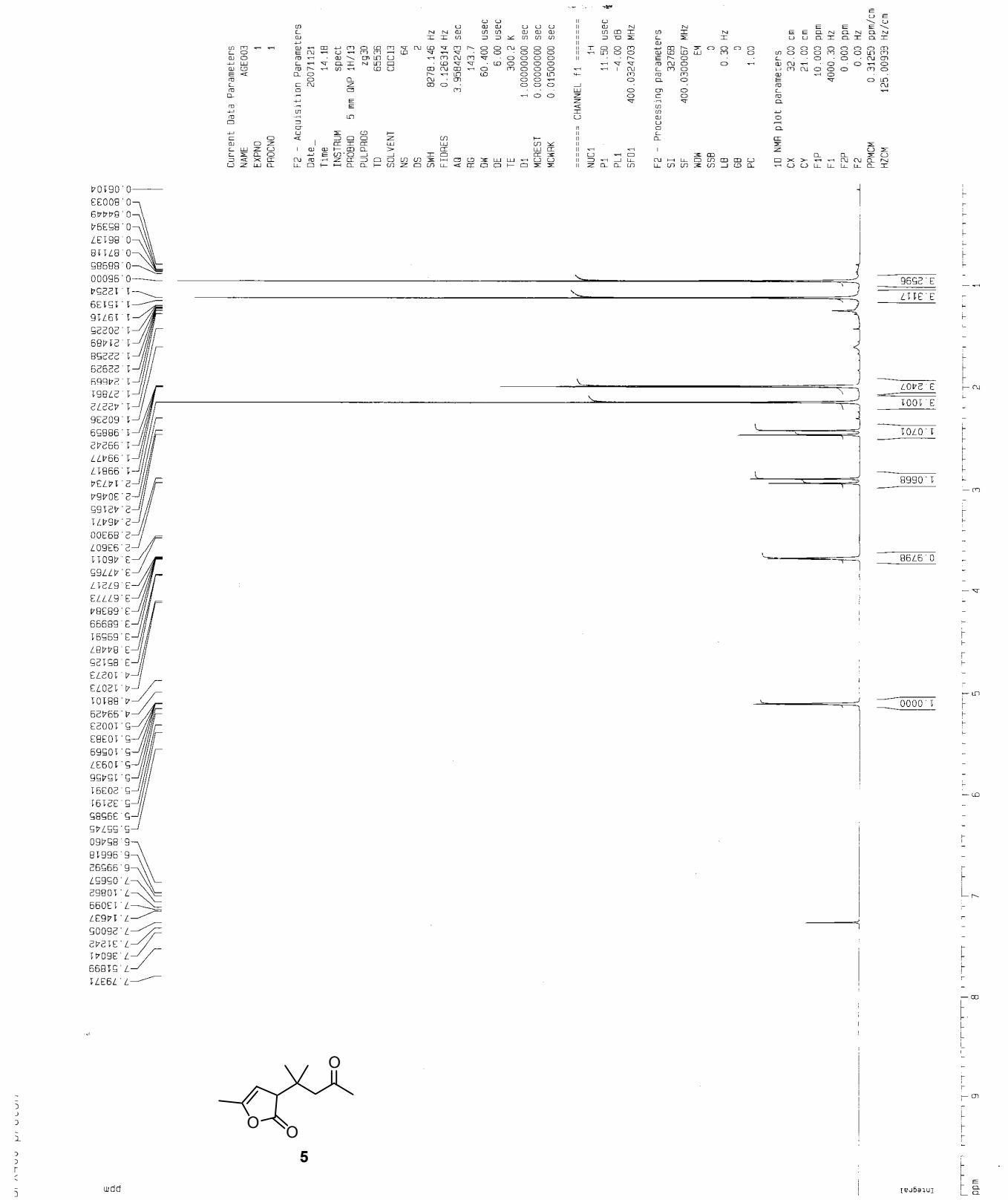
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9564243 sec
RG 40.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SF01 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300065 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 21.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00938 Hz/cm
1.04315
1.10031
1.12650
1.18093
1.39237
1.50983
2.08601
2.20428
2.37651
2.41519
2.44563
2.48423
5.99679
6.01107
7.45637
7.45198
3.1959
3.2774
3.1915
3.1069
2.1046
0.9594
1.0000
ppm
Integral

3h


Current Data Parameters
NAME AGE002
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071212
Time 12.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 34
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 3649.1
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5986886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876240 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 19.00 cm
F1P 220.000 ppm
F1 22129.28 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.18750 ppm/cm
HZCM 722.97357 Hz/cm
DPX400 carbon
19.784
21.918
22.450
32.618
39.542
48.522
76.721
77.039
77.357
93.440
120.929
159.487
172.362
207.538
ppm
3h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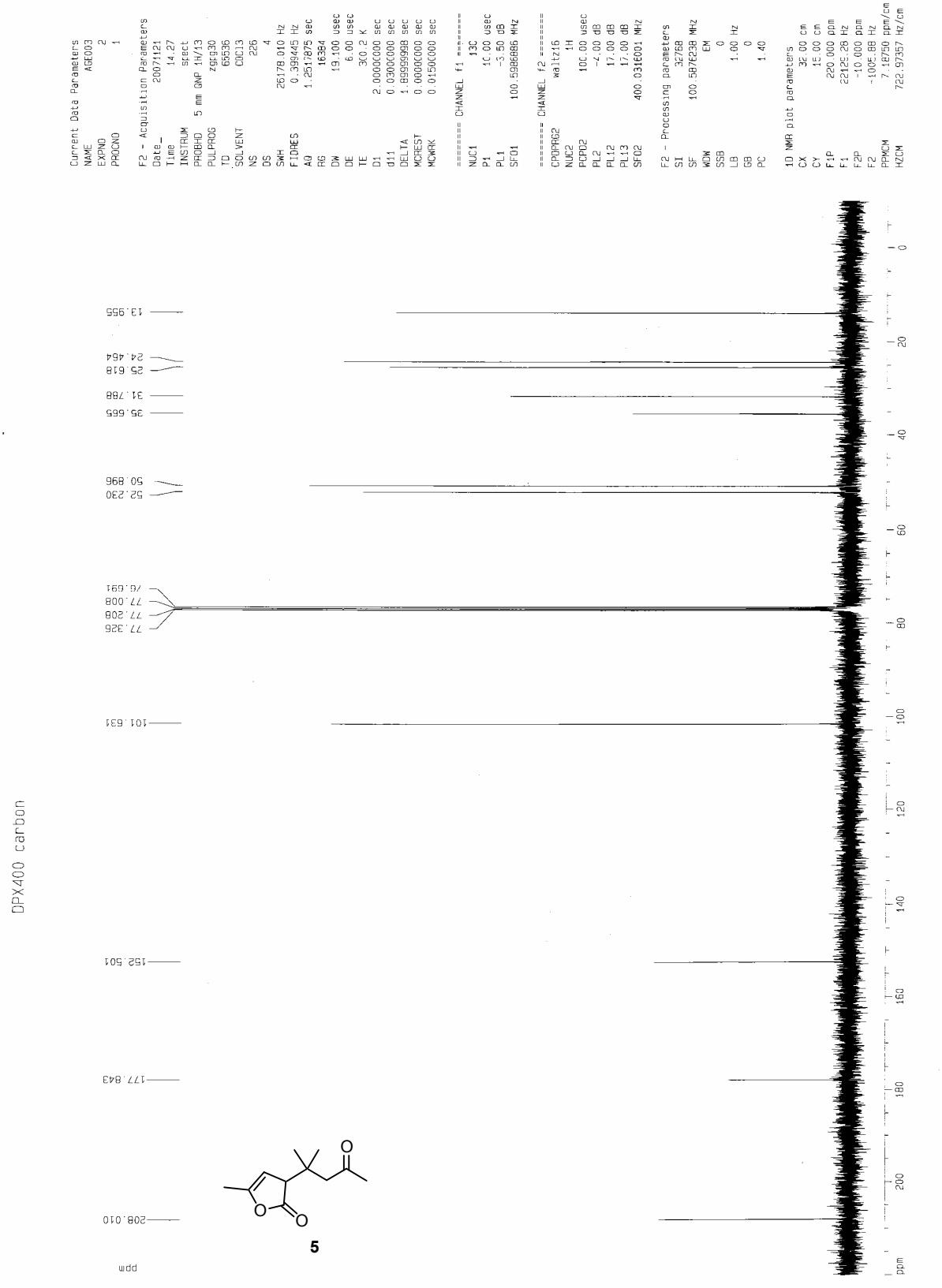
NAME AGE003
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071121
Time 14.18
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9568243 sec
RG 143.7
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 21.00 cm
F1P 10.000 ppm
F1 4000.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.31250 ppm/cm
HZCM 125.00939 Hz/cm
3.2596
3.3117
3.2407
3.1001
1.0701
1.0668
0.9798
1.0000
ppm
Integral

5


Current Data Parameters
NAME AGE003
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071121
Time 14.27
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 226
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2511875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5986886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876238 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 35.00 cm
CY 15.00 cm
F1P 220.000 ppm
F1 22125.28 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 7.18750 ppm/cm
HZCM 722.97357 Hz/cm
13.955
24.464
25.618
31.788
35.665
50.896
52.230
76.691
77.008
77.208
77.326
101.631
152.501
177.843
208.010
DPX400 carbon
ppm
0
20
40
60
80
100
120
140
160
180
200
O
O
O

5

7. References

1. Koshar, R. J.; Barber, L. L. *United States Patent* **1977**, 4053519.
2. Taniguchi, M.; Kim, H.; Ra, D.; Schwartz, J. K.; Kirmaier, C.; Hindin, E.; Diers, J. R.; Prathapan, S.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem*. **2002**, *67*, 7329-7342.
3. Bentley, K. W.; Ball, J. C. *J. Org. Chem.* **1958**, *23*, 1720-1725.
4. Pavlynchenko, A. I.; Purvaneckas, G.; Smirnova, N.I.; Titov, V. V. *Zh. Organiche. Khim*. **1986**, *22*, 1524-1529.
5. Rassu, G.; Zanardi, F.; Battistini, L.; Gaetani, E.; Casiraghi, G. *J. Med. Chem.* **1997**, *40,* 168-180.
6. Abe, M.; Torii, E.; Nojima, M. *J. Org. Chem*. **2000**, *65*, 3426-3431.
7. Asaoka, M.; Yanagida, N.; Sugimura, N.; Takei, H. *Bull. Chem. Soc. Jpn*. **1980,** *53*, 1061-1064.