# The Synthetic and Biological Studies of Discorhabdins and Related Compounds

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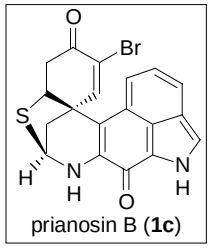
**Contents**

Syntheses of *N*,*O*-acetal intermediate (**51b**) were followed by ref 37.

**Total synthesis of prianosin B (1c)**

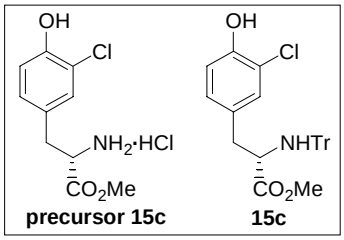


prianosin B (**1c**)

$NaN_3$ (1.1 mg, 0.0175 mmol) was added to a solution of compound **51b** (99.7 mg, 0.175 mmol) in DMF (0.3 mL) at rt under $N_2$. The mixture was allowed to warm to 70 °C and stirred for 1 h. The reaction mixture was quenched by $H_2O$ and extracted by AcOEt. Organic phase was washed by $H_2O$ (×3) and brine (×1). Organic phase was dried over $Na_2SO_4$. and evaporated *in vacuo*. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 20/1) to give prianosin B (**1c**) (35.1 mg, 48%) as red solid; m.p. 253-255 °C; $[\alpha]^{23.0}_D$ +362 (c 0.405, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ: 2.87-2.94 (3H, m), 2.98 (1H, dd, *J* = 16.5, 4.0 Hz), 4.80 (1H, dd, *J* = 12.0, 6.5 Hz), 5.49-5.58 (1H, m), 6.30 (1H, br s), 7.54 (1H, d, *J* = 5.5 Hz), 7.78 (1H, s), 8.03 (1H, s), 8.49 (1H, d, *J* = 5.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 40.0, 45.6, 50.8, 56.5, 61.7, 113.7, 118.2, 119.6, 120.2, 125.3, 129.0 (2C), 143.0, 143.6, 146.1, 155.7, 167.6, 188.3; IR (KBr): 3057, 2924, 2853, 1682, 1645, 1595, 1472, 1303 $cm^{-1}$; HRMS (FAB) calcd for $C_{18}H_{13}BrN_3O_2S$ $[M+H]^+$: 413.9912, found 413.9920.

Syntheses of **15a**, **b**, **16b**, **17b**, **18b**, **38b**, **49b, 49'b**, **50b, 50'b** and **54b, 54'b** were followed by ref 37.

**Methyl-3-(3chloro-4-hydroxyphenyl)-2-(tritylamino)propionate (15c)**

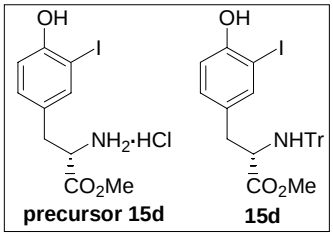



$SO_2Cl_2$ (0.38 mL, 4.74 mmol) was added to a solution of **11** (1.0 g, 4.32 mmol) in AcOH (7.7 mL) and $Et_2O$ (0.86 mL) at 0 ºC under $N_2$. The resulting solution was warmed to rt under stirring. Then the solution was filtered through Celite pad, and washed with $Et_2O$. The filtrate was concentrated *in vacuo* to give **precursor 15c** (910 mg, 79%) as colorless solid; m.p. 191-192 °C; $^1$H NMR (500 MHz, $CD_3OD$) δ: 3.06 (1H, dd, *J* = 14.4, 7.5 Hz), 3.16 (1H, dd, *J* = 14.4, 6.0 Hz), 3.81 (3H, s), 4.26 (1H, dd, *J* = 7.5, 6.0 Hz), 6.90 (1H, d, *J* = 8.4 Hz), 7.01 (1H, dd, *J* = 8.4, 2.1 Hz), 7.22 (1H, d, *J* = 2.1 Hz); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ: 34.5, 52.6, 53.2, 116.7, 119.5, 126.0, 129.0, 130.8, 152.4, 169.4; IR (KBr): 3100, 1743, 1613, 1580, 1510 $cm^{-1}$; HRMS (FAB) calcd for $C_{10}H_{13}ClNO_3$ $[M+H]^+$: 230.0584, found 230.0565 (as free base).

$Et_3N$ (103 μL, 0.750 mmol) was added to a solution of **precursor 15c** (100.0 mg, 0.375 mmol) in DMF (1.8 mL) at rt under $N_2$. After being stirred for 10 min, tritylchloride (TrCl) (104.5 mg, 0.375 mmol) was added to the resulting solution. The mixture was stirred at rt for 3 h. The reaction was quenched with $H_2O$ and extracted with AcOEt. The organic layer was washed with $H_2O$ and brine, dried over $Na_2SO_4$, and evaporated

in vacuo. The residue was purified by $SiO_2$ column chromatography using hexane/AcOEt (3/1) as the eluent to give **15c** (123 mg, 69%) as colorless oil: $^1$H NMR (300 MHz, $CDCl_3$) δ: 2.60 (1H, br s), 2.85 (2H, d, *J* = 6.6 Hz), 3.05 (3H, s), 3.47-3.55 (1H, m), 5.64 (1H, s), 6.91 (1H, d, *J* = 8.2 Hz), 6.99 (1H, d, *J* = 8.2 Hz), 7.09-7.23 (10H, m), 7.40 (6H, d, *J* = 7.2 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 41.0, 51.4, 58.0, 70.9, 115.9, 126.3, 127.7, 128.7, 129.7, 130.1, 130.5, 145.7, 150.2, 174.8; IR (KBr): 3533, 3342, 1730, 1595, 1500 cm$^{-1}$; HRMS (FAB) calcd for $C_{29}H_{27}ClNO_3$ $[M+H]^+$: 472.1679, found 472.1686.

**Methyl-3-(3-iodo-4-hydroxyphenyl)-2-(tritylamino)propionate (15d)**



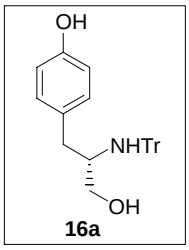

$SOCl_2$ (0.52 mL, 7.16 mmol) was added dropwise to a solution of 3-iodo-*L*-tyrosine (**12**) (2.00 g, 6.51 mmol) in MeOH (13.0 mL). The suspension was heated at a reflux for 3 h. The mixture was evaporated in vacuo to give **precursor 15d** (2.30 g, 99%) as colorless solid; m.p. 201-202 °C; $^1$H NMR (300 MHz, $CD_3OD$) δ: 3.03 (1H, dd, *J* = 14.4, 7.5 Hz), 3.14 (1H, dd, *J* = 14.4, 6.0 Hz), 3.81 (3H, s), 4.24 (1H, dd, *J* = 7.5, 6.0 Hz), 6.82 (1H, d, *J* = 8.4 Hz), 7.07 (1H, dd, *J* = 8.4, 1.8 Hz), 7.22 (1H, d, *J* = 1.8 Hz); $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 34.3, 52.6, 53.2, 84.8, 115.0, 126.8, 130.5, 139.5, 156.0, 169.4; IR (KBr): 3200, 1741, 1600, 1570, 1502 cm$^{-1}$; HRMS (FAB) calcd for $C_{10}H_{13}INO_3$ $[M+H]^+$: 321.9940, found 321.9941 (as free base).

$Et_3N$ (1.78 mL, 13.02 mmol) was added to a solution of **precursor 15d** (2.3 g, 6.51 mmol) in DMF (32 mL) at rt under $N_2$. After being stirred for 10 min, TrCl (1.8 g, 6.51 mmol) was added to the resulting solution. The mixture was stirred at rt for 3 h. The reaction was quenched with $H_2O$ and extracted with AcOEt. The organic layer was washed with $H_2O$ and brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography using hexane/AcOEt (3/1) as the eluent to give **15d** (3.62 g, quant.) as colorless solid; m.p. 95-98 °C; $[\alpha]^{26.7}_D$ +15.2 (c 2.95, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ: 2.55 (1H, br s), 2.84 (2H, dd, *J* = 6.5, 2.6 Hz), 3.06 (3H, s), 3.50-3.55 (1H, m), 5.32 (1H, s), 6.92 (1H, d, *J* = 8.1 Hz), 7.07 (1H, dd, *J* = 8.1, 1.6 Hz), 7.17-7.24 (9H, m), 7.39 (6H, d, *J* = 7.2 Hz), 7.55 (1H, d, *J* = 1.6 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 40.6, 51.4, 57.9, 70.9, 85.2, 114.6, 126.4, 127.8, 128.7, 131.5, 131.6, 139.3, 145.7, 153.6, 174.7; IR (KBr): 3340, 3057, 3030, 2949, 2925, 2848, 1726, 1597, 1574, 1489, 1467, 1417 cm$^{-1}$; HRMS (FAB) calcd for $C_{29}H_{27}INO_3$ $[M+H]^+$: 564.1036, found 564.1043.

**General Procedure for the Syntheses of 17a,c,d from 15a,c,d.**

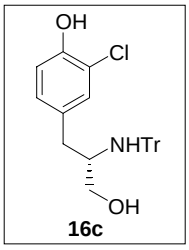
Diisobutylaluminium hydride (DIBAL) (0.94 M solution in hexane, 3.23 equiv) was added dropwise to a solution of **15** (1.0 equiv) in dry $CH_2Cl_2$ (0.053 M solution) at -78

ºC under $N_2$. The resulting solution was warmed to rt and stirred for 5 h. The mixture was cooled to 0 ºC and quenched with $H_2O$. The precipitate was filtered through Celite pad and the filtrate was evaporated in vacuo. The residue was dissolved in $CH_2Cl_2$ and the mixture was washed with sat. *aq*. $NaHCO_3$ and brine, then dried over $Na_2SO_4$ and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography to give **16.**



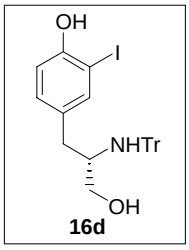
**16a**

**16a** (5.6 g, 95%) was obtained from **15a** (6.3 g, 14.4 mmol), DIBAL (50.5 mL, 47.5 mmol) and dry $CH_2Cl_2$ (280 mL). Eluent: hexane/AcOEt (2/1). **16a**: Colorless oil: $^1$H NMR ($CDCl_3$): δ = 2.17 (dd, 1H, *J* = 13.2, 4.6 Hz), 2.42 (dd, 1H, *J* = 13.2, 9.5 Hz), 2.72-2.75 (m, 1H), 2.92 (dd, 1H, *J* = 10.8, 3.8 Hz), 3.11 (dd, 1H, *J* = 10.8, 2.2 Hz), 4.92 (br s, 1H), 6.62 (d, 2H, *J* = 8.4 Hz), 6.76 (d, 2H, *J* = 8.4 Hz), 7.17-7.31 (m, 9H), 7.53 (d, 6H, *J* = 7.3 Hz).



**16c**

**16c** (3.9 g, 51%) was obtained from **15c** (8.15 g, 17.3 mmol), DIBAL (64.0 mL, 60.5 mmol) and dry $CH_2Cl_2$ (86 mL). Eluent: hexane/AcOEt (2/1). **16c**: Colorless oil: $^1$H NMR (300 MHz, $CDCl_3$) δ: 2.14 (1H, dd, *J* = 13.2, 9.6 Hz), 2.41 (1H, dd, *J* = 13.2, 9.6 Hz), 2.64-2.80 (1H, m), 2.97 (1H, dd, *J* = 10.8, 3.9 Hz), 3.10 (1H, dd, *J* = 10.8, 2.5 Hz), 6.71 (1H, dd, *J* = 8.1, 1.5 Hz), 6.80 (1H, d, *J* = 8.1 Hz), 6.83 (1H, d, *J* = 1.5 Hz), 7.16-7.30 (9H, m), 7.55 (6H, d, *J* = 7.5 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 37.8, 55.2, 67.9, 71.3, 115.9, 119.5, 126.5, 127.9, 128.6, 129.3, 129.7, 132.1, 146.4, 149.7; IR (KBr): 3247, 1700, 1590, 1575, 1500 cm$^{-1}$; HRMS (FAB) calcd for $C_{28}H_{27}ClNO_2$ [*M*+H]$^+$: 444.1730, found 444.1721.

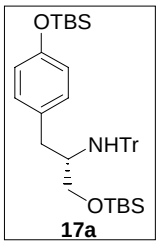


**16d**

**16d** (680 mg, 90%) was obtained from **15d** (792 g, 1.40 mmol), DIBAL (4.46 mL, 4.20 mmol) and dry $CH_2Cl_2$ (7.0 mL). Eluent: hexane-AcOEt (2/1). **16d**: Colorless solid: $^1$H NMR (300 MHz, $CDCl_3$) δ: 2.12 (1H, dd, *J* = 13.2, 4.5 Hz), 2.40 (1H, dd, *J* = 13.2, 9.5 Hz), 2.72-2.73 (1H, m), 2.98 (1H, dd, *J* = 10.9, 3.9 Hz), 3.10 (1H, dd, *J* = 10.9, 2.0 Hz), 6.73 (1H, d, *J* = 8.3 Hz), 6.78 (1H, dd, *J* = 8.3, 1.2 Hz), 7.22-7.34 (10H, m), 7.54 (6H, d, *J* = 7.5 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 37.5, 55.2, 67.9, 71.3, 85.3, 114.6, 126.6, 127.9, 128.6, 131.0, 132.9, 138.9, 146.4, 153.3; IR (KBr): 3500, 3315, 3057, 3030, 2937, 2889, 1703, 1597, 1574, 1487, 1446 cm$^{-1}$; HRMS (FAB) calcd for $C_{28}H_{27}INO_2$ [*M*+H]$^+$: 536.1087, found 536.1082.

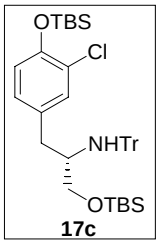
*tert*-Butyldimetylsilyl chloride (TBSCl) (3.0 equiv) was added to a solution of **16** (1.0 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (5.0 equiv) in dry $CH_2Cl_2$ (0.13 M solution) at 0 ºC under $N_2$. The mixture was stirred at the same temperature for 2.5 h.

The reaction was quenched with sat. *aq.* $NaHCO_3$ and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $Na_2SO_4$ and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography to give **17.**



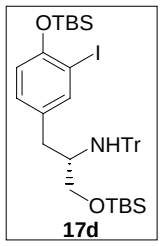
**17a**

**17a** (7.3 g, 84%) was obtained from **16a** (5.6 g, 13.6 mmol), TBSCl (6.2 g, 40.8 mmol), DBU (10.2 mL, 68.0 mmol) and dry $CH_2Cl_2$ (90 mL). Eluent: hexane/AcOEt (20/1). **17a**: Colorless solid: $^1$H NMR (300 MHz, $CDCl_3$): δ = -0.30 (s, 3H), -0.27 (s, 3H), 0.10 (s, 6H), 0.69 (s, 9H), 0.81 (s, 9H), 2.10 (br s, 1H), 2.36 (dd, 1H, *J* = 9.0, 3.0 Hz), 2.45-2.50 (m, 1H), 2.51 (m, 1H), 2.80 (dd, 1H, *J* = 9.6, 3.0 Hz), 6.52 (d, 2H, *J* = 8.1 Hz), 6.7 (d, 2H, *J* = 8.1 Hz), 7.00-7.14 (m, 9H), 7.43 (d, 6H, *J* = 8.4 Hz); $^{13}$C NMR ($CDCl_3$): δ = -5.6 (2C), -4.6, 18.0 (2C), 25.5, 25.7, 37.9, 55.3, 62.3, 70.9, 119.5, 126.0, 127.6, 128.6, 130.3, 132.2, 147.1, 153.5; IR (KBr): 2953, 2928, 1606, 1508, 1488, 1471 cm$^{-1}$;HRMS (FAB) calcd for $C_{40}H_{56}NO_2Si_2$ ($M$+H$^+$) 638.3850. found 638.3834.



**17c**

**17c** (4.9 g, 83%) was obtained from **16c** (3.9 g, 8.78 mmol), TBSCl (3.9 g, 26.3 mmol), DBU (3.9 mL, 26.3 mmol) and dry $CH_2Cl_2$ (44 mL). Eluent: hexane/AcOEt (20/1). **17c**: Colorless oil: $^1$H NMR (300 MHz, $CDCl_3$) δ: -0.31 (3H, s), -0.29 (3H, s), 0.00 (6H, s), 0.67 (9H, s), 0.83 (9H, s), 1.99 (1H, br s), 2.31-2.39 (3H, m), 2.48-2.50 (1H, m), 2.73 (1H, d, *J* = 9.3 Hz), 6.52 (1H, d, *J* = 8.5 Hz), 6.57 (1H, d, *J* = 8.5 Hz), 6.81 (1H, s), 6.95-7.09 (9H, m), 7.38 (6H, d, *J* = 7.5 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: -5.5, -5.4, -4.3, 18.1, 18.3, 25.7, 25.9, 37.8, 55.2, 62.3, 71.1, 120.2, 124.9, 126.3, 127.8, 128.6, 128.7, 131.2, 133.6, 147.2, 149.5; IR (KBr): 3327, 1596, 1494, 1471, 1462, 1448 cm$^{-1}$; HRMS (FAB) calcd for $C_{40}H_{55}ClNO_2Si_2$ [$M$+H]$^+$: 672.3460, found 672.3453.



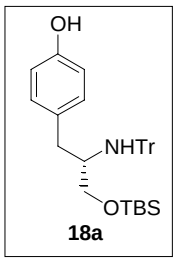
**17d**

**17d** (883 mg, 91%) was obtained from **16d** (680 mg, 1.27 mmol), TBSCl (564 mg, 3.81 mmol), DBU (0.564 mL, 3.81 mmol) and dry $CH_2Cl_2$ (12.7 mL). Eluent: hexane-AcOEt (20/1). **17d**: Colorless oil: $^1$H NMR (300 MHz, $CDCl_3$) δ: -0.35 (3H, s), -0.33 (3H, s), 0.00 (6H, s), 0.61 (9H, s), 0.80 (9H, s), 2.26-2.34 (3H, m), 2.44-2.45 (1H, m), 2.66 (1H, dd, *J* = 9.6, 3.3 Hz), 6.42 (1H, d, *J* = 8.3 Hz), 6.61 (1H, dd, *J* = 8.3, 2.1 Hz), 6.90-7.04 (9H, m), 7.21 (1H, d, *J* = 2.1 Hz), 7.33 (6H, d, *J* = 6.9 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: -5.4, -4.0, 18.1, 18.3, 25.8, 25.9, 34.6, 37.4, 55.2, 62.3, 71.1, 90.1, 117.8, 126.3, 127.8, 128.7, 130.3, 134.2, 140.5, 147.2, 153.2; IR (KBr): 3327, 1712, 1682, 1595, 1487, 1471, 1446 cm$^{-1}$; HRMS (FAB) calcd for $C_{40}H_{54}INNaO_2Si_2$ [$M$+Na]$^+$: 786.2662, found 786.2635.

**General Procedure for the Syntheses of 38a,c,d from 17a,c,d.**

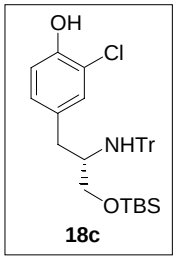
TBAF (1.0 M solution in THF, 1.0 equiv) was added to a solution of **17** (1.0 equiv) in

dry THF (0.063 M solution) at 0 ºC under $N_2$. The mixture was stirred at the same temperature for 0.5 h. The reaction was quenched with sat. *aq.* $NH_4Cl$ and extracted with AcOEt. The organic layer was washed with brine, dried over $Na_2SO_4$ and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography to give **18.**



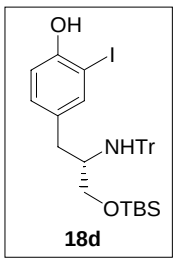
**18a**

**18a** (818 mg, 95%) was obtained from **17a** (1.05 g, 1.64 mmol), TBAF (1.64 mL, 1.64 mmol) and dry THF (26 mL). Eluent: hexane/AcOEt (10/1). **18a**: Colorless oil: $^1$H NMR (500 MHz, $CDCl_3$) δ: -0.25 (3H, s), -0.22 (3H, s), 0.74 (9H, s), 2.12 (1H, br s), 2.37 (1H, dd, *J* = 9.6, 4.6 Hz), 2.44-2.52 (3H, m), 2.83 (1H, dd, *J* = 9.6, 3.1 Hz), 6.65 (2H, d, *J* = 8.4 Hz), 6.77 (2H, d, *J* = 8.4 Hz), 7.06-7.20 (9H, m), 7.46 (6H, d, *J* = 7.5 Hz).



**18c**

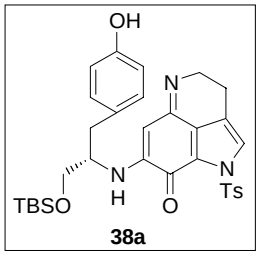
**18c** (2.75 g, 99%) was obtained from **17c** (3.35 g, 4.98 mmol), TBAF (4.98 mL, 4.98 mmol) and dry THF (79 mL). Eluent: hexane/AcOEt (10/1). **18c**: Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$) δ: -0.02 (3H, s), -0.01 (3H, s), 0.98 (9H, s), 2.23 (1H, br s), 2.60-2.68 (3H, m), 2.80-2.82 (1H, m), 3.00 (1H, dd, *J* = 9.3, 3.0 Hz), 6.91-6.97 (2H, m), 7.08 (1H, s), 7.26-7.40 (9H, m), 7.66 (6H, d, *J* = 7.5 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: -5.4, 18.1, 25.9, 37.7, 55.1, 62.3, 71.1, 115.6, 119.3, 126.3, 127.8, 128.7, 129.6, 129.9, 132.9, 147.1, 149.4; IR (KBr): 3541, 3327, 3057, 3030, 2927, 2854, 1595, 1498, 1470, 1448 $cm^{-1}$.



**18d**

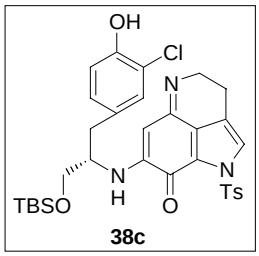
**18d** (2.82 g, 99%) was obtained from **17d** (3.35 g, 4.39 mmol), TBAF (4.39 mL, 4.39 mmol) and dry THF (70 mL). Eluent: hexane-AcOEt (10/1). **18d:** Colorless oil: $^1$H NMR (300 MHz, $CDCl_3$) δ: -0.02 (3H, s), -0.01 (3H, s), 0.98 (9H, s), 2.47-2.56 (3H, m), 2.80 (1H, m), 3.00 (1H, dd, *J* = 9.3, 3.0 Hz), 6.91-6.97 (2H, m), 7.08 (1H, s), 7.27-7.41 (9H, m), 7.66 (6H, d, *J* = 7.5 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: -5.4, 18.1, 25.9, 37.4, 55.1, 62.2, 71.1, 85.3, 114.4, 126.3, 127.8, 128.7, 131.3, 133.8, 139.1, 147.1, 152.9; IR (KBr): 3541, 3327, 3057, 3030, 2927, 2854, 1595, 1498, 1470, 1448 $cm^{-1}$; HRMS (FAB) calcd for $C_{34}H_{41}INO_2Si$ $[M+Na]^+$: 650.1951, found 650.1964.

A solution of **18** (1.2 equiv) in 0.1 M HCl/MeOH (1.44 equiv) was stirred at rt for 0.5 h under $N_2$. This solution was added dropwise to a solution of **32** (1.0 equiv) in MeOH (0.345 M solution). The mixture was stirred at rt for 16 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography to give **38**.



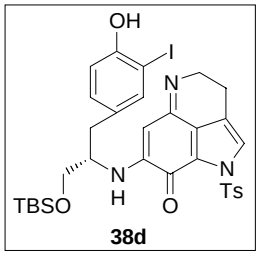
**38a**

**38a** (228 mg, 83%) was obtained from **18a** (446 mg, 0.851 mmol), 0.1 M HCl/MeOH (9.3 mL), **32** (260 mg, 0.709 mmol) and MeOH (1.6 mL). Eluent: $CH_2Cl_2$/MeOH/$Et_3N$ (100/5/0.1). **38a**: Red solid: $^1$H NMR (300 MHz, $CDCl_3$) δ: 0.00 (3H, s), 0.01 (3H, s), 0.92 (9H, s), 2.44 (3H, s), 2.61 (2H, d, *J* = 6.9 Hz), 2.80 (2H, t, *J* = 7.2 Hz), 3.30-3.32 (1H, m), 3.47 (2H, d, *J* = 3.0 Hz), 4.14 (2H, t, *J* = 7.2 Hz), 5.63 (1H, s), 5.95 (1H, br s), 6.74 (2H, d, *J* = 8.4 Hz), 6.84 (2H, d, *J* = 8.4 Hz), 7.34 (2H, d, *J* = 8.4 Hz), 7.54 (1H, s), 8.06 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR (75 MHz, $CD_3OD$) δ: -5.5, -5.4, 17.9, 18.2, 21.7, 25.8, 34.2, 48.3, 54.9, 61.4, 94.6, 116.0, 118.0, 122.8, 125.9, 126.3, 128.3, 128.8, 129.7, 130.1, 134.4, 145.2, 145.8, 155.7, 156.1, 169.4; IR (KBr): 3375, 1666, 1614, 1579, 1531, 1514, 1494, 1462, 1380 cm$^{-1}$; HRMS (FAB) calcd for $C_{32}H_{40}N_3O_5SSi$ $[M+H]^+$: 606.2458, found 606.2465.



**38c**

**38c** (128.1 mg, 58%) was obtained from **18c** (231.2 mg, 0.414 mmol), 0.1 M HCl/MeOH (4.97 mL), **32** (122.9 mg, 0.345 mmol) and MeOH (1.0 mL). Eluent: $CH_2Cl_2$-MeOH-$Et_3N$ (100/5/0.1). **38c**: Red solid: $^1$H NMR (270 MHz, $CD_3OD$) δ: 0.00 (6H, s), 0.91 (9H, s), 2.42 (3H, s), 2.61 (2H, d, *J* = 6.6 Hz), 2.77 (2H, t, *J* = 8.0 Hz), 3.33-3.36 (1H, m), 3.64-3.67 (2H, m), 4.11-4.12 (2H, m), 5.57 (1H, s), 6.75 (1H, d, *J* = 9.0 Hz), 6.82 (1H, d, *J* = 9.0 Hz), 7.03 (1H, s), 7.32 (2H, d, *J* = 8.9 Hz), 7.51 (1H, s), 8.03 (2H, d, *J* = 8.9 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: -5.6, -5.5, 17.9, 18.2, 21.7, 25.8, 34.0, 48.1, 54.7, 61.3, 74.0, 86.1, 94.4, 107.4, 117.0, 117.9, 120.8, 122.7, 126.0, 126.3, 128.5, 128.8, 129.7, 130.0, 134.2, 145.9, 151.4, 156.0, 162.6, 166.8; IR (KBr): 3375, 3018, 2928, 2856, 1666, 1614, 1580, 1537, 1495, 1462, 1445, 1379 cm$^{-1}$; HRMS (FAB) calcd for $C_{42}H_{43}ClN_3O_5SSi$ $[M+H]^+$: 640.2068, found 640.2095.



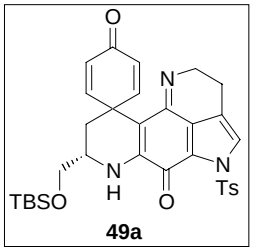
**38d**

**38d** (71.7 mg, 49%) was obtained from **18d** (171.3 mg, 0.264 mmol), 0.1 M HCl/MeOH (3.17 mL), **32** (78.4 mg, 0.200 mmol) and MeOH (0.5 mL). Eluent: $CH_2Cl_2$/MeOH/$Et_3N$ (100/5/0.1). 3**8d**: Red solid: $^1$H NMR (500 MHz, $CDCl_3$) δ: 0.01 (3H, s), 0.13 (3H, s), 0.85 (9H, s), 2.32 (3H, s), 2.63 (2H, d, *J* = 6.3 Hz), 2.77 (2H, t, *J* = 8.1 Hz), 3.37-3.40 (1H, m), 3.48-3.54 (2H, m), 4.03 (2H, t, *J* = 8.1 Hz), 5.48 (1H, s), 6.79 (1H, d, *J* = 7.8 Hz), 6.89 (1H, d, *J* = 7.8 Hz), 7.28 (1H, s), 7.30 (2H, d, *J* = 9.0 Hz), 7.34 (1H, s), 8.00 (2H, d, *J* = 9.0 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: -5.5, -5.4, 18.0, 18.2, 18.8, 21.8, 23.9, 25.9, 45.4, 45.6, 53.7, 56.4, 62.0,

97.1, 107.6, 117.2, 118.0, 119.3, 126.5, 128.7, 128.9, 129.8, 130.6, 131.0, 135.4, 137.0, 139.2, 158.1, 164.5, 175.7, 186.2; IR (KBr): 3368, 2953, 2928, 2856, 1709, 1666, 1616, 1578, 1558, 1534, 1491, 1464, 1443, 1379 $cm^{-1}$; HRMS (FAB) calcd for $C_{42}H_{43}IN_3O_5SSi$ $[M+H]^+$: 732.1424, found 732.1416.

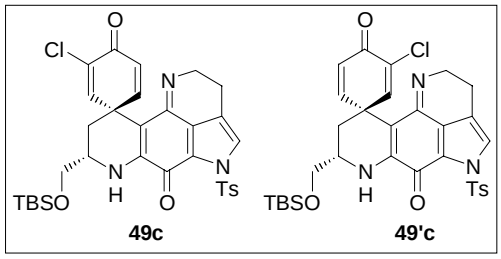
**General Procedure for the Syntheses of 49a, c-d, 49'c-d from 38a,c,d**

PIFA (1.2 equiv) and montmorillonite K10 (1/4 mg of **38** (mg)) was added to a solution of **38** (1.0 equiv) in $CF_3CH_2OH$ (0.03 M solution) at rt under $N_2$. The mixture was stirred at rt for 0.5 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography to give **49**.



**49a**

**49a** (66.0 mg, 57%) was obtained from **38a** (115 mg, 0.190 mmol), PIFA (98 mg, 0.228 mmol), and $CF_3CH_2OH$(6.3 ml). Eluent: hexane/AcOEt/$Et_3N$ (100/50/0.1). **49a**: Red solid: $^1H$ NMR (300 MHz, $CDCl_3$) δ: -0.02 (3H, s), 0.02 (3H, s), 0.84 (9H, s), 1.41 (1H, d, *J* = 13.2 Hz), 1.61 (1H, d, *J* = 13.2 Hz), 2.33 (3H, s), 2.52 (2H, t, *J* = 7.2 Hz), 3.43-3.45 (2H, m), 3.63-3.75 (3H, m), 3.99 (1H, t, *J* = 7.2 Hz), 5.99 (1H, br s), 6.12 (1H, dd, *J* = 9.9, 3.0 Hz), 6.13 (1H, dd, *J* = 9.9, 3.0 Hz), 6.80 (1H, dd, *J* = 9.9, 3.0 Hz), 6.89 (1H, dd, *J* = 9.9, 3.0 Hz), 7.23 (2H, d, *J* = 8.4 Hz), 7.35 (1H, s), 7.95 (2H, d, *J* = 8.4 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: -5.4, -5.3, 17.5, 18.3, 21.7, 25.7, 37.5, 40.8, 49.5, 66.3, 105.5, 118.5, 121.9, 125.8, 126.4, 127.5, 128.6, 129.7, 134.6, 141.9, 145.7, 152.9, 157.3, 168.7, 186.1; IR (KBr): 3394, 1660, 1620, 1595, 1574, 1524, 1460, 1435, 1379 $cm^{-1}$; HRMS (FAB) calcd for $C_{32}H_{38}N_3O_5SSi$ $[M+H]^+$: 604.2301, found 604.2323.

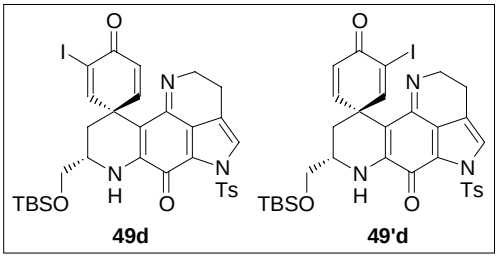


**49c** **49'c**

**49c** (24.7 mg, 24%) and **49'c** (18.2 mg, 17%) were obtained from **38c** (105.6 mg, 0.165 mmol), PIFA (85.1 mg, 0.198 mmol), and $CF_3CH_2OH$ (5.5 ml). Eluent: hexane/AcOEt/$Et_3N$ (100/50/0.1). **49c:** Red solid: m.p. > 300 °C; $[\alpha]^{26.3}_D$ +225 (c 1.84, MeOH); $^1H$ NMR (300 MHz, $CDCl_3$) δ: 0.01 (3H, s), 0.02 (3H, s), 0.84 (9H, s), 1.46-1.65 (2H, m), 2.33 (3H, s), 2.52 (2H, t, *J* = 7.3 Hz), 3.38-3.45 (2H, m), 3.64-3.76 (2H, m), 3.97-4.04 (1H, m), 6.19 (1H, d, *J* = 9.9 Hz), 6.88 (1H, dd, *J* = 9.9, 2.7 Hz), 6.93 (1H, d, *J* = 2.7 Hz), 7.22 (2H, d, *J* = 8.4 Hz), 7.36 (1H, s), 7.72 (1H, d, *J* = 8.4 Hz), 7.94 (1H, d, *J* = 8.4 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: -5.4, 17.5, 18.3, 21.7, 25.9, 36.6, 41.8, 42.9, 48.1, 49.5, 53.4, 66.1, 118.5, 121.8, 125.4, 126.1, 126.3, 128.6, 129.7, 130.2, 134.5, 145.8, 152.5, 153.2, 168.4, 179.3; IR (KBr): 3387, 3153, 2928, 1798, 1660, 1597, 1574, 1528, 1460, 1379 $cm^{-1}$; HRMS

(FAB) calcd for $C_{32}H_{37}ClN_3O_5SSi$ $[M+H]^+$: 638.1912, found 638.1909.

**49'c**: Red solid: $^1$H NMR (300 MHz, $CDCl_3$) δ: 0.00 (3H, s), 0.02 (3H, s), 0.84 (9H, s), 1.45-1.62 (2H, m), 2.33 (3H, s), 2.52 (2H, t, *J* = 7.5 Hz), 3.40-3.46 (2H, m), 3.64-3.73 (2H, m), 3.94-3.41 (1H, m), 5.27 (1H, br s), 6.24 (1H, d, *J* = 9.6 Hz), 6.82 (1H, d, *J* = 9.6 Hz), 7.06 (1H, s), 7.23 (2H, d, *J* = 7.8 Hz), 7.36 (1H, s), 7.93 (2H, d, *J* = 7.8 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: -5.4, -5.4, 17.5, 18.3, 21.7, 25.9, 36.9, 43.0, 49.4 53.4, 66.1, 77.2, 125.4, 126.4, 128.6, 129.6, 129.7, 133.0, 134.6, 142.1, 143.5, 145.8, 148.2, 157.2, 179.2; IR (KBr): 3393, 3153, 2955, 2930, 2856, 1661, 1595, 1574, 1529, 1462, 1379 cm$^{-1}$; HRMS (FAB) calcd for $C_{32}H_{37}ClN_3O_5SSi$ $[M+H]^+$: 638.1912, found 638.1926.

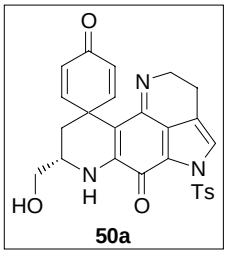



**49d** (21.8 mg, 25%) and **49'd** (10.8 mg, 12%) were obtained from **38d** (88.4 mg, 0.121 mmol), PIFA (63.3 mg, 0.145 mmol), and $CF_3CH_2OH$ (4.0 ml). Eluent: hexane/AcOEt/$Et_3N$ (100/50/0.1). **49d**: Red solid: $[\alpha]^{27.4}_D$ -164 (c 4.50, MeOH); $^1$H NMR (500 MHz, $CDCl_3$) δ: -0.23 (3H, s), 0.21 (3H, s), 0.84 (9H, s), 1.36-1.68 (2H, m), 2.33 (3H, s), 2.53 (2H, t, *J* = 7.1 Hz), 3.38-3.49 (2H, m), 3.63-3.82 (2H, m), 3.94-4.04 (1H, m), 5.99 (1H, br s), 6.19 (1H, d, *J* = 9.7 Hz), 6.90 (1H, dd, *J* = 9.7, 2.6 Hz), 7.23 (2H, d, *J* = 7.4 Hz), 7.36 (1H, s), 7.49 (1H, d, *J* = 2.6 Hz), 7.94 (2H, d, *J* = 7.4 Hz); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ: -5.3, -5.2, 17.6, 18.4, 21.6, 21.8, 24.7, 25.9, 29.7, 36.7, 45.1, 49.6, 66.1, 104.0, 118.5, 121.7, 123.2, 124.1, 125.5, 126.0, 126.3, 128.5, 129.5, 129.6, 129.7, 134.4, 139.0, 143.3, 145.6, 152.7, 157.2, 160.1, 168.1, 179.5; IR (KBr): 3395, 2928, 2856, 1659, 1574, 1529, 1461 cm$^{-1}$; HRMS (FAB) calcd for $C_{32}H_{37}IN_3O_5SSi$ $[M+H]^+$: 730.1268, found 730.1266.

**49'd**: Red solid: $^1$H NMR (270 MHz, $CDCl_3$) δ: 0.03 (3H, s), 0.06 (3H, s), 0.88 (9H, s), 1.60-1.65 (2H, m), 2.38 (3H, s), 2.55 (2H, t, *J* = 7.5 Hz), 3.43-3.46 (2H, m), 3.66-3.77 (2H, m), 3.97-4.04 (1H, m), 6.05 (1H, br s), 6.26 (1H, d, *J* = 9.6 Hz), 6.87 (1H, dd, *J* = 9.6, 2.5 Hz), 7.25 (2H, d, *J* = 8.4 Hz), 7.38 (1H, s), 7.69 (1H, d, *J* = 2.5 Hz), 7.96 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ: -5.2 (2C), 17.7, 18.4, 21.8, 24.7, 26.0, 29.8, 36.7, 45.1, 49.4, 49.6, 66.1, 104.1, 118.5, 121.8, 123.3, 125.5, 126.0, 126.3, 128.6, 129.2, 129.6, 129.8, 134.4, 143.4, 145.7, 152.7, 157.1, 160.0, 168.1, 179.5; IR (KBr): 3391, 3153, 2928, 2856, 1794, 1655, 1575, 1528, 1462, 1382 cm$^{-1}$; HRMS (FAB) calcd for $C_{32}H_{37}IN_3O_5SSi$ $[M+H]^+$: 730.1268, found 730.1284.

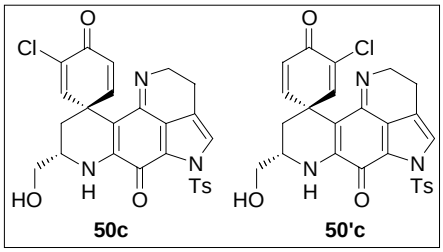
**General Procedure for the Syntheses of 50a, c-d, 50'c-d from 49a, c-d, 49'c-d**

$BF_3{\cdot}Et_2O$ (9.4 equiv) was added to a solution of **49** (1.0 equiv) in dry $CH_2Cl_2$ (0.055 M solution) at 0 °C under $N_2$. The mixture was allowed to warm to rt for 7 h. The reaction was quenched with $NaHCO_3$ powder, filtered and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography to give **50**.



**50a**

**50a** (35.3 mg, 87%) was obtained from **49a** (50.1 mg, 0.0829 mmol), $BF_3{\cdot}Et_2O$ (0.10 mL, 0.78 mmol), and dry $CH_2Cl_2$ (1.5 mL). Eluent: $CH_2Cl_2$/MeOH/$Et_3N$ (100/5/0.1). **50a**: Red solid: $^1$H NMR (270 MHz, $(CD_3)_2CO$) δ: 1.53 (1H, d, *J* = 12.0 Hz), 1.81 (1H, t, *J* = 12.0 Hz), 2.64 (3H, s), 2.83 (2H, m), 3.57-3.82 (4H, m), 4.32 (1H, m), 6.06 (2H, dd, *J* = 10.2, 2.2 Hz), 6.96 (1H, dd, *J* = 10.2, 2.2 Hz), 7.47 (2H, d, *J* = 8.4 Hz), 7.63 (1H, s), 8.06 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR (75 MHz, $(CD_3)_2CO$) δ: 18.0, 21.5, 38.4, 41.6, 50.4, 65.5, 111.9, 119.6, 122.5, 126.8, 127.3, 127.8, 129.4, 130.7, 135.6, 140.0, 147.0, 153.8, 158.0, 169.4, 185.6; IR (KBr): 3305, 1659, 1614, 1595, 1573, 1525, 1487, 1461, 1375 cm$^{-1}$; HRMS (FAB) calcd for $C_{26}H_{24}N_3O_5S$ [*M*+H]$^+$: 490.1437, found 490.1429.

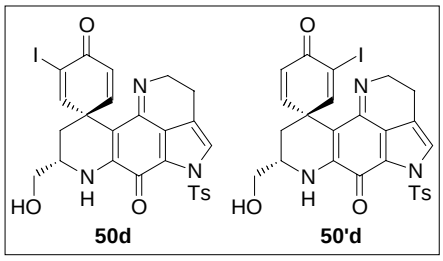


**50c** **50'c**

**50c** (9.0 mg, 65%) was obtained from **49c** (16.7 mg, 0.0262 mmol), $BF_3{\cdot}Et_2O$ (35 μL, 0.276 mmol), and dry $CH_2Cl_2$ (1.4 mL). Eluent: $CH_2Cl_2$/MeOH/$Et_3N$ (100/5/0.1). **50c**: Red solid: $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.55 (1H, d, *J* = 12.0 Hz), 1.79 (1H, d, *J* = 12.0 Hz), 2.36 (3H, s), 2.57-2.62 (2H, m), 3.54-3.56 (2H, m), 3.78-3.83 (2H, m), 4.00-4.03 (1H, m), 6.03 (1H, br s), 6.22 (1H, d, *J* = 9.9 Hz), 6.92 (1H, dd, *J* = 9.9, 2.4 Hz), 6.98 (1H, d, *J* = 2.4 Hz), 7.27 (2H, d, *J* = 8.4 Hz), 7.40 (1H, s), 7.95 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ: 17.8, 21.7, 28.9, 29.6, 38.6, 44.2, 49.4, 59.6, 68.1, 77.2, 80.1, 118.6, 122.0, 123.3, 125.4, 126.0, 128.5, 129.8, 134.5, 145.9, 152.5, 157.4, 168.3, 191.2; IR (KBr): 3389, 2930, 1713, 1661, 1595, 1573, 1529, 1485, 1462, 1377 cm$^{-1}$; HRMS (FAB) calcd for $C_{26}H_{23}ClN_3O_3S$ [*M*+H]$^+$: 524.1047, found 524.1066.

**50'c** (5.5 mg, 65%) was obtained from **49'c** (11.9 mg, 0.0160 mmol), $BF_3{\cdot}Et_2O$ (21.4 μL, 0.169 mmol), and dry $CH_2Cl_2$ (0.86 mL). Eluent: $CH_2Cl_2$/MeOH/$Et_3N$ (100/5/0.1). **50'c**: Red solid: $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.56-1.57 (1H, m), 1.80-1.84 (1H, m), 2.37 (3H, s), 2.57-2.62 (2H, m), 3.54-3.59 (2H, m), 3.79-3.85 (2H, m), 3.98-4.01 (1H, m), 4.72 (1H, br s), 6.29 (1H, d, *J* = 9.9 Hz), 6.86 (1H, d, *J* = 9.9 Hz), 7.10 (1H, s), 7.27 (2H, d, *J* = 7.8 Hz), 7.41 (1H, s), 7.95 (1H, d, *J* = 7.8 Hz); $^{13}$C NMR (75 MHz,

$(CD_3)_2CO$) δ: 18.0, 21.5, 37.6, 39.8, 42.4, 44.0, 47.9, 50.2, 65.2, 119.6, 125.8, 127.4, 129.4, 130.7, 131.7, 135.6, 147.0, 150.0, 158.7, 169.3, 178.9; IR (KBr): 3385, 3130, 1660, 1650, 1595, 1575, 1525, 1485, 1460, 1375 $cm^{-1}$; HRMS (FAB) calcd for $C_{26}H_{23}ClN_3O_3S$ $[M+H]^+$: 524.1047, found 524.1060.

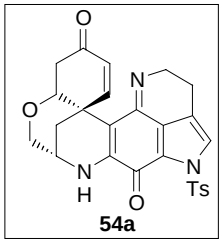



**50d** (14.9 mg, 81%) was obtained from **49d** (22.1 mg, 0.030 mmol), $BF_3{\cdot}Et_2O$ (39.3 μL, 0.303 mmol), and dry $CH_2Cl_2$ (1.5 mL). Eluent: $CH_2Cl_2$/MeOH/$Et_3N$ (100/5/0.1). **50d**: Red solid: $^1H$ NMR (300 MHz, $CDCl_3$) δ: 1.65 (1H, d, *J* = 12.0 Hz), 1.78 (1H, d, *J* = 12.0 Hz), 2.36 (3H, s), 2.58 (2H, t, *J* = 7.2 Hz), 3.54-3.57 (2H, m), 3.79-3.85 (2H, m), 4.00-4.05 (1H, m), 6.23 (1H, d, *J* = 9.7 Hz), 6.94 (1H, dd, *J* = 9.7, 2.6 Hz), 7.27 (1H, d, *J* = 8.4 Hz), 7.41 (1H, s), 7.53 (1H, d, *J* = 2.6 Hz), 7.96 (2H, d, *J* = 8.4 Hz); $^{13}C$ NMR (125 MHz, $(CD_3)_2CO$) δ: 18.0, 21.6, 37.1, 45.9, 50.0, 50.4, 65.4, 65.5, 119.6, 122.6, 124.3, 126.2, 127.4, 129.4, 130.2, 130.7, 135.6, 147.0, 153.8, 154.2, 166.4, 169.2, 179.7; IR (KBr): 3387, 2925, 2853, 1794, 1655, 1572, 1528, 1460, 1379 $cm^{-1}$; HRMS (FAB) calcd for $C_{26}H_{23}ClN_3O_3S$ $[M+H]^+$: 616.0403, found 616.0403.

**50'd** (6.3 mg, 68%) was obtained from **49'd** (10.6 mg, 0.015 mmol), $BF_3{\cdot}Et_2O$ (16.7 μL, 0.145 mmol), and dry $CH_2Cl_2$ (0.7 mL). Eluent: $CH_2Cl_2$/MeOH/$Et_3N$ (100/5/0.1). **50'd**: Red solid: $^1H$ NMR (300 MHz, $CDCl_3$) δ: 1.93-1.98 (1H, m), 2.15-2.22 (1H, m), 2.36 (3H, s), 2.53-2.62 (2H, m), 3.51-3.55 (3H, m), 3.79-3.84 (2H, m), 6.30 (1H, d, *J* = 9.8 Hz), 6.90 (1H, d, *J* = 9.8 Hz), 7.23 (1H, s), 7.28 (2H, d, *J* = 7.5 Hz), 7.71 (1H, s), 7.95 (2H, d, *J* = 7.5 Hz); $^{13}C$ NMR (125 MHz, $(CD_3)_2CO$) δ: 18.0, 21.6, 37.6, 46.2, 46.7, 50.3, 50.4, 65.3, 104.2, 119.6, 123.5, 127.4, 128.3, 129.4, 130.2, 130.7, 131.3, 147.0, 153.9, 158.9, 162.1, 169.3; IR (KBr): 3370, 2924, 1655, 1574, 1528, 1458, 1377 $cm^{-1}$; HRMS (FAB) calcd for $C_{26}H_{23}ClN_3O_3S$ $[M+H]^+$: 616.0403, found 616.0413.

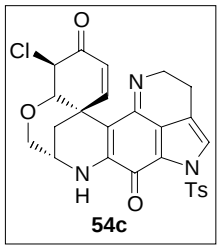
**General Procedure for the Synthesis of 54a, c-d, 54'c-d from 50a, c-d, 50'c-d**

30% HBr-AcOH (0.75 mL/1.0 mmol of **50**) was added to a solution of **50** (1 equiv) in dry $CH_2Cl_2$ (0.02 M solution) at 0 ºC under $N_2$. The mixture was stirred warming to rt for 36 h. The reaction was quenched with sat. *aq.* $NaHCO_3$ and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $Na_2SO_4$ and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography to give **54**.



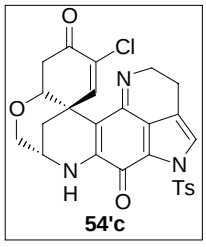
**54a**

**54a** (23.5 mg, 66%) was obtained from **50a** (35.3 mg, 0.0721 mmol), 30% HBr-AcOH (67 μL), and dry $CH_2Cl_2$ (3.6 mL). Eluent: hexane/AcOEt (1/1). **54a**: Red solid: m.p. > 300 °C; $[\alpha]^{26.5}_D$ +956 (c 0.541, MeOH); $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.69 (1H, d, *J* = 12.9 Hz), 1.92 (1H, d, *J* = 12.9 Hz), 2.34 (3H, s), 2.53-2.58 (3H, m), 2.84 (1H, dd, *J* = 16.8, 12.9 Hz), 3.55 (1H, s), 3.73-3.79 (2H, m), 4.15 (1H, dd, *J* = 16.8, 6.0 Hz), 4.28 (1H, dd, *J* = 9.6, 6.0 Hz), 5.85 (1H, s), 5.89 (1H, d, *J* = 10.2 Hz), 7.03 (1H, d, *J* = 10.2 Hz), 7.25 (2H, d, *J* = 8.4 Hz), 7.40 (1H, s), 7.95 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 17.8, 21.7, 27.9, 36.5, 37.5, 44.0, 44.5, 49.5, 53.4, 68.0, 75.0, 118.6, 122.1, 124.8, 125.5, 126.7, 128.6, 129.7, 134.6, 145.8, 148.3, 152.7, 157.6, 168.5, 174.9, 197.5; IR (KBr): 3392, 2941, 2842, 1660, 1595, 1569, 1523, 1488, 1458 cm$^{-1}$; HRMS (FAB) calcd for $C_{26}H_{24}N_3O_5S$ [*M*+H]$^+$: 490.1437, found 490.1439.



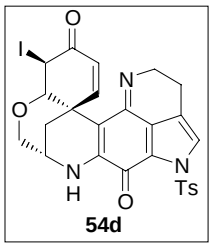
**54c**

**54c** (3.5 mg, 71%) was obtained from **50c** (4.9 mg, 0.00935 mmol), 30% HBr-AcOH (7 μL), and dry $CH_2Cl_2$ (0.47 mL). Eluent: hexane/AcOEt (1/1). **54c**: Red solid: $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.91 (1H, d, *J* = 12.9 Hz), 2.34 (1H, dd, *J* = 12.9, 2.1 Hz), 2.44 (3H, s), 2.85-2.99 (2H, m), 3.67-4.15 (7H, m), 5.48 (1H, br s), 6.36 (1H, d, *J* = 10.6 Hz), 7.06 (1H, d, *J* = 10.6 Hz), 7.45 (2H, d, *J* = 8.4 Hz), 7.91 (1H, s), 8.09 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 17.8, 21.7, 28.9, 29.6, 38.6, 44.2, 49.4, 59.6, 68.1, 77.2, 80.1, 118.6, 122.0, 123.3, 125.4, 126.0, 129.8, 134.5, 145.9, 152.5, 157.4, 168.3, 191.2; IR (KBr): 3395, 2928, 2853, 1682, 1658, 1574, 1526, 1487, 1462, 1379 cm$^{-1}$; HRMS (FAB) calcd for $C_{26}H_{23}ClN_3O_3S$ [*M*+H]$^+$: 524.1047, found 524.1057.



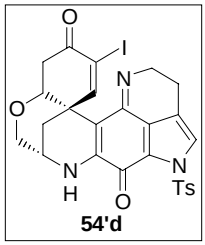
**54'c**

**54'c** (2.4 mg, 57%) was obtained from **50'c** (4.2 mg, 0.00801 mmol), 30% HBr-AcOH (6 μL), and dry $CH_2Cl_2$ (0.40 mL). Eluent: hexane/AcOEt (1/1). **54'c**: Red solid: $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.87 (1H, d, *J* = 13.5 Hz), 2.38 (1H, dd, *J* = 13.5, 2.1 Hz), 2.44 (3H, s), 2.78 (1H, dd, *J* = 16.8, 4.8 Hz), 2.93-2.99 (2H, m), 3.36 (1H, dd, *J* = 16.8, 13.2 Hz), 3.65-4.02 (5H, m), 4.32 (1H, dd, *J* = 13.2, 5.3 Hz), 7.22 (1H, s), 7.45 (2H, d, *J* = 8.7 Hz), 7.91 (1H, s), 8.09 (2H, d, *J* = 8.7 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 17.8, 21.7, 27.5, 29.7, 30.9, 37.7, 38.2, 44.3, 49.7, 68.2, 74.5, 118.6, 122.0, 125.9, 128.6, 129.8, 134.5, 140.8, 145.9, 152.4, 153.7, 174.9, 190.2; IR (KBr): 3400, 2928, 2853, 1682, 1659, 1595, 1574, 1526, 1489, 1462, 1377 cm$^{-1}$; HRMS (FAB) calcd for $C_{26}H_{23}ClN_3O_3S$ [*M*+H]$^+$: 524.1047, found 524.1071.



**54d**

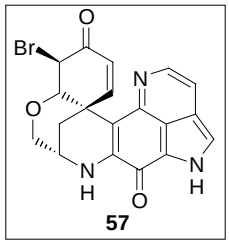
**54d** (2.8 mg, 76%) was obtained from **50d** (3.7 mg, 0.00601 mmol), 30% HBr-AcOH (9 μL), and dry $CH_2Cl_2$ (0.30 mL). Eluent: hexane/AcOEt (1/1). **54d:** Red solid: $[\alpha]^{21.0}_D$ +96.8 (c 0.322, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ: 1.78 (1H, d, *J* = 13.0 Hz), 2.00 (1H, d, *J* = 13.0 Hz), 2.43 (3H, s), 2.61-2.70 (2H, m), 2.92 (1H, dd, *J* = 16.8, 13.0 Hz), 3.61 (1H, s), 3.73 (1H, d, *J* = 12.5 Hz), 3.80-3.84 (1H, m), 3.88 (1H, d, *J* = 12.5 Hz), 4.23 (1H, dt, *J* = 17.5, 6.0 Hz), 4.36 (1H, dd, *J* = 13.0, 5.5 Hz), 5.89 (1H, br s), 5.97 (1H, d, *J* = 10.0 Hz), 7.11 (1H, d, *J* = 10.0 Hz), 7.33 (2H, d, *J* = 8.0 Hz), 7.48 (1H, s), 8.03 (2H, d, *J* = 8.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 17.9, 21.7, 28.1, 36.6, 37.6, 44.5, 49.6, 68.1, 75.1, 109.4, 118.6, 122.2, 124.9, 125.5, 125.7, 128.7, 129.8, 134.7, 143.5, 145.8, 152.8, 157.6, 168.6, 198.5; IR (KBr): 2928, 2853, 2359, 2341, 2253, 1659, 1570, 1523, 1489, 1458; HRMS (FAB) calcd for $C_{26}H_{23}ClN_3O_3S$ $[M+H]^+$: 524.1047, found 524.1071.



**54'd**

**54'd** (1.4 mg, 67%) was obtained from **50'd** (2.1 mg, 0.0341 mmol), 30% HBr-AcOH (3 μL), and dry $CH_2Cl_2$ (0.17 mL). Eluent: hexane/AcOEt (1/1). **54'd**: Red solid: m.p. > 300 °C; $[\alpha]^{22.0}_D$ -76.0 (c 0.626, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ: 1.79 (1H, d, *J* = 12.8 Hz), 2.04 (1H, d, *J* = 12.8 Hz), 2.41 (3H, s), 2.67 (2H, t, *J* = 7.5 Hz), 2.88 (1H, dd, *J* = 16.5, 6.0 Hz), 3.01 (1H, dd, *J* = 16.8, 13.0 Hz), 3.61 (1H, s), 3.72 (1H, d, *J* = 12.4 Hz), 3.82-3.99 (2H, m), 4.25 (1H, dt, *J* = 18.0, 6.5 Hz), 4.31 (1H, dd, *J* = 12.5, 5.0 Hz), 5.85 (1H, br s), 7.32 (2H, d, *J* = 8.3 Hz), 7.47 (1H, s), 7.74 (1H, s), 8.01 (2H, d, *J* = 8.3 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 17.8, 21.7, 27.1, 29.7, 36.3, 44.4, 49.8, 63.4, 68.2, 74.8, 98.4, 102.1, 118.5, 124.4, 125.9, 128.7, 129.8, 129.8, 145.8, 152.3, 154.1, 154.3, 165.5, 168.4, 185.0, 191.4; IR (KBr): 3018, 1710, 1659, 1526, 1487, 1460; HRMS (FAB) calcd for $C_{26}H_{23}ClN_3O_3S$ $[M+H]^+$: 524.1047, found 524.1071.

**Discorhabdin oxa-aromatic analogue (57)**

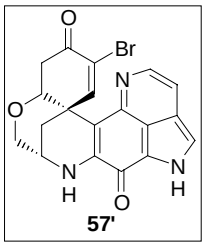


**57**

$NaN_3$ (0.248 mg, 0.00382 mmol) was added to a solution of **54b** (20.8 mg, 0.0366 mmol) in DMF (0.063 mL) at rt under $N_2$. The mixture was allowed to warm to 70 °C and stirred for 1 h. The reaction mixture was quenched by $H_2O$ and extracted by AcOEt. Organic phase was washed by $H_2O$ (×3) and brine (×1), dried over $Na_2SO_4$ and evaporated *in vacuo*. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 20/1) to give **57** (8.15 mg, 54%) as red solid.; $^1$H NMR (300 MHz, $CDCl_3$) δ: 2.10 (1H, d, *J* = 11.7 Hz), 2.29 (1H, d, *J* = 11.7 Hz), 2.79-2.82 (2H, m), 4.01-4.06 (1H, m), 4.14 (1H, d, *J* = 10.4 Hz), 4.57 (1H, d, *J* = 10.4 Hz), 5.97 (1H, s), 6.56 (1H, d, *J* = 9.7 Hz), 6.57 (1H, br s), 7.04 (1H, d, *J* = 9.7 Hz), 7.34 (1H, d, *J* = 5.8 Hz), 7.90 (1H, s), 8.31 (1H, d, *J* = 5.8 Hz); $^{13}$C NMR (125 MHz,

DMSO-$d_6$) δ: 26.0, 30.0, 35.5, 42.7, 57.7, 72.8, 80.6, 101.9, 114.9, 117.2, 117.3, 117.7, 119.3, 124.2, 132.5, 170.7, 178.1, 190.6, 191.8; IR (KBr): 2924, 1651, 1601, 1531, 1548, 1454 $cm^{-1}$.

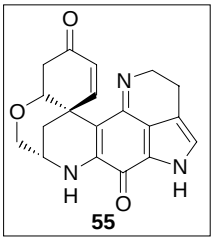
**Discorhabdin oxa-aromatic analogue (57')**



**57'**

$NaN_3$ (0.205 mg, 0.00315 mmol) was added to a solution of **54'b** (14.0 mg, 0.0246 mmol) in DMF (0.042 mL) at r.t. under $N_2$ atmosphere. The mixture was allowed to warm to 70 $^oC$. and stirred for 1 h. The reaction mixture was quenched by $H_2O$ and extracted by AcOEt. Organic phase was washed by $H_2O$ (×3) and brine (×1). Organic phase was dried over $Na_2SO_4$. and evaporated in vacuo. Residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 20/1) to give **57'** (5.07 mg, 50%) as red solid.; m.p. >300 °C; $^1H$ NMR (300 MHz, $CDCl_3$) δ: 2.10 (1H, d, *J* = 12.8 Hz), 2.25 (1H, d, *J* = 12.8 Hz), 2.97-3.00 (1H, m), 3.15-3.23 (1H, m), 3.86-4.05 (2H, m), 4.45-4.59 (1H, m), 5.23-5.30 (1H, m), 6.32 (1H, br s), 7.26-7.49 (2H, m), 7.87-7.94 (2H, m), 8.41 (1H, d, *J* = 5.9 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ: 27.4, 29.1, 39.7, 40.0, 52.4, 80.8, 110.6, 112.3, 118.0, 123.6, 125.0, 129.2, 142.9, 143.3, 146.2, 158.6, 165.3, 190.5, 191.0; IR (KBr): 3057, 2930, 2856, 1682, 1645, 1599, 1535, 1504, 1485, 1461 $cm^{-1}$; HRMS (FAB) calcd for $C_{19}H_{15}BrN_3O_3$ $[M+H]^+$: 412.0297, found 412.0293.

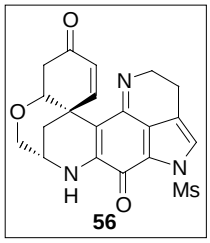
**Discorhabdin oxa analogue (55)**



**55**

5 M NaOMe in MeOH (9.60 μl, 0.0480 mmol) was added to a solution of **54a** in dry THF (1.6 ml) at 0 °C under $N_2$. The mixture was stirred at 0 °C for 0.5 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 5/1) to give **55** (10.3 mg, 64%) as green solid: $^1H$ NMR (300 MHz, $CD_3OD$) δ: 2.09 (1H, d, *J* = 12.3 Hz), 2.44 (1H, d, *J* = 12.3 Hz), 2.63-2.66 (3H, m), 3.04-3.14 (1H, m), 3.60-3.66 (4H, m), 3.88 (1H, d, *J* = 10.8 Hz), 4.23 (1H, d, *J* = 8.4 Hz), 5.94 (1H, d, *J* = 9.6 Hz), 6.70 (1H, s), 7.08 (1H, d, *J* = 9.6 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 19.4, 28.9, 37.7, 38.8, 46.6, 63.7, 67.7, 76.2, 103.2, 120.3, 124.1, 124.3, 124.8, 125.9, 128.5, 155.5, 156.7, 169.4, 200.5; IR (KBr): 3350, 2931, 2852, 1651, 1602, 1556, 1537, 1523, 1488, 1434 $cm^{-1}$; HRMS (FAB) calcd for $C_{19}H_{18}N_3O_3$ $[M+H]^+$: 336.1348, found 336.1370.

**Discorhabdin oxa analogue (56)**

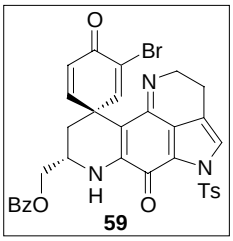


**56**

NaH (0.902 mg, 0.0228 mmol) was added to a solution of **55** (5.10 mg, 0.0152 mmol) in dry THF (0.75 ml) at 0 °C under $N_2$. The mixture was stirred at 0 °C for 10 min and MsCl (1.40 μl, 0.0182 mmol) was added to the mixture. The mixture was stirred at 0 °C for 30 min and evaporated in vacuo. The residue was purified by $SiO_2$

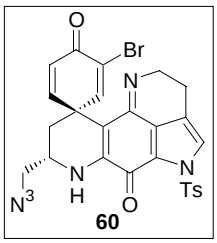
column chromatography ($CH_2Cl_2$/MeOH = 20/1) to give **56** (3.40 mg, 54%) as red solid; $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.78 (1H, d, *J* = 12.6 Hz), 1.99 (1H, d, *J* = 12.6 Hz), 2.61-2.66 (3H, m), 2.89 (1H, m), 3.57 (3H, s), 3.58-3.58 (2H, m), 3.71-3.89 (2H, m), 4.20 (1H,m), 4.35 (1H, dd, *J* = 12.9, 5.1 Hz), 5.89-5.92 (1H, br s), 5.94 (1H, d, *J* = 10.2 Hz), 7.08 (1H, d, *J* = 10.2 Hz), 7.26 (1H, s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 17.7, 28.0, 31.8, 36.7, 37.6, 42.3, 44.6, 49.7, 68.1, 74.2, 109.8, 118.4, 122.1, 124.9, 125.5, 145.9, 152.8, 157.5, 159.4, 165.4, 198.5; IR (KBr): 3400, 2933, 2849, 1651, 1614, 1568, 1523, 1494, 1462 cm$^{-1}$; HRMS (FAB) calcd for $C_{20}H_{20}N_3O_5S$ [*M*+H]$^+$: 414.1124, found 414.1138.

**59**




BzCl (5.00 μl, 0.0450 mmol) was added to a solution of **50b** (17.0 mg, 0.0300 mmol) and $Et_3N$ (6.30 μl, 0.0450 mmol) in dry $CH_2Cl_2$ (1.0 ml) at 0 ºC under $N_2$. The resulting solution was warmed to rt for 3.0 h. The reaction was quenched with $H_2O$ and extracted with AcOEt. The organic layer was washed with brine, dried over $Na_2SO_4$ and evaporated in vacuo. The residue was purified by NH column chromatography (*n*-hexane/AcOEt = 2/1) to give **59** (11.5 mg, 57%) as red solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.00-2.07 (2H, m), 2.42 (3H, s), 2.66 (2H, t, *J* = 8.0 Hz), 3.63-3.66 (2H, m), 4.01 (2H, t, *J* = 8.0 Hz), 4.15-4.17 (1H, m), 6.12 (1H, d, *J* = 10.4 Hz), 7.14 (1H, dd, *J* = 10.4, 2.8 Hz), 7.32 (2H, d, *J* = 8.4 Hz), 7.38 (1H, s), 7.47-7.56 (3H, m), 7.61 (1H, d, *J* = 7.2 Hz), 8.03 (2H, d, *J* = 8.4 Hz), 8.08 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ: 15.4, 22.3, 25.9, 29.7, 52.6, 72.5, 76.2, 93.4, 98.7, 102.0, 115.5, 117.6, 123.7, 129.3, 145.4, 145.8, 147.2, 147.8, 147.9, 148.3, 155.7, 157.9, 158.3, 163.7, 165.5, 169.3, 180.0, 191.7, 198.3; IR (KBr): 2963, 2924, 1719, 1655, 1595, 1481, 1458 cm$^{-1}$; HRMS (FAB) calcd for $C_{33}H_{26}BrN_3O_6S$ [*M*]$^+$: 671.0726, found 671.0690.

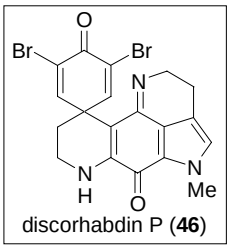
**60**




$PPh_3$ (19.4 mg, 0.0740 mmol), DEAD (33.6 μl, 0.0740 mmol) and DPPA (16.0 μl, 0.0740 mmol) were added to a solution of **50b** (28.0 mg, 0.0490 mmol) in toluene (1.0 ml) at 0 ºC under $N_2$. The resulting solution was warmed to rt for 7.0 h and evaporated in vacuo. The residue was purified by NH column chromatography ($CH_2Cl_2$/MeOH = 20/1) to give **60** (13.1 mg, 45%) as red solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 1.88 (1H, d, *J* = 12.8 Hz), 1.94 (1H, d, *J* = 12.8 Hz), 2.43 (3H, s), 2.66 (2H, t, *J* = 7.2 Hz), 3.67-3.85 (3H, m), 4.11-4.23 (2H, m), 5.07 (1H, d, J = 12.4 Hz), 5.94 (1H, br s), 6.01 (1H, d, *J* = 10.4 Hz), 7.14 (1H, d, *J* = 10.4 Hz), 7.33 (2H, d, *J* = 8.4 Hz), 7.49 (1H, s), 8.01 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR (DMSO-$d_6$) δ: 17.3, 21.2, 43.6, 49.2, 55.1, 67.5, 80.2, 100.1, 100.7, 111.0, 121.9, 126.2, 126.8, 128.0, 130.0, 143.9, 146.0, 152.0,

155.5, 157.2, 158.9, 168.1, 189.3, 195.0; IR (KBr): 1659, 1575, 1525, 1493, 1462, 1369 $cm^{-1}$.

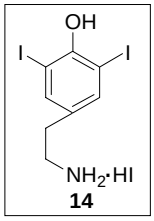
**Discorhabdin P (46)**



discorhabdin P (**46**)

$K_2CO_3$ (16.3 mg, 0.118 mmol) and MeI (3.70 μl, 0.0593 mmol) was added to a solution of discorhabdin C (**3**) (5.50 mg, 0.0118 mmol) in dry acetone (0.50 ml). The mixture was stirred at 40 °C for 12 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 10/1) to give discorhabdin P (3.60 mg, 64%) as red solid; m.p. > 300 °C; $^1$H NMR (300 MHz, $CD_3OD$) δ: 1.87-1.89 (2H, m), 2.51 (2H, t, *J* = 7.5 Hz), 3.43-3.47 (2H, m), 3.73 (2H, t, *J* = 7.5 Hz), 3.82 (3H, s), 6.79 (1H, s), 7.56 (2H, s); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 18.0, 35.4, 37.6, 43.1, 45.9, 71.1, 97.1, 99.2, 106.3, 128.2, 133.1, 141.2, 149.9, 155.3, 168.0, 186.0, 193.2; UV/Vis (MeOH) λmax = 488 (log ε 0.18), 341 (1.60), 246 (3.29), 211 (3.41) nm; IR (KBr): 3387, 2926, 2503, 1649, 1566, 1523, 1493 $cm^{-1}$; HRMS (FAB) calcd for $C_{19}H_{18}Br_2N_3O_2$ $[M+H]^+$: 477.9766, found 477.9581.

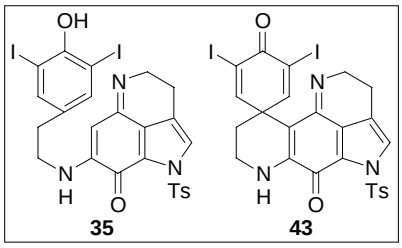
**14**



**14**

$I_2$ (8.20 g, 32.3 mmol) and 30% $H_2O_2$ (7.20 ml) were added to a solution of tyramine (**10**) (4.00 g, 29.2 mmol) in $H_2O$ (140 ml). The resulting solution was warmed to 55 °C for 3.0 h. The reaction mixture was quenched by sat. *aq.* $Na_2S_2O_3$ and sat *aq.* $NaHCO_3$. The solid was filtered and washed with $H_2O$ dried in vacuo to give **14** (10.8 g, 99%) as brown solid; m.p. 208-212 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 2.68 (2H, t, *J* = 7.8 Hz), 2.98 (2H, t, *J* = 7.8 Hz), 3.32 (1H, br s), 7.59 (2H, s), 8.01 (2H, br s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ: 30.9, 40.0, 87.7, 132.7, 139.3, 154.8; IR (KBr): 3349, 3127, 2997, 1589, 1471, 1454, 1300 $cm^{-1}$; HRMS (FAB) calcd for $C_8H_{10}I_3NNaO$ $[M+Na]^+$: 539.7794, found 539.7800.

**43**



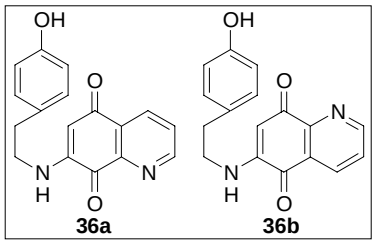
**35** **43**

$Et_3N$ (64.3 μl, 0.464 mmol) was added to a solution of **14** (240 mg, 0.464 mmol) in MeOH (5.5 ml) at rt for 10 min under $N_2$. This solution was added dropwise to a solution of **32** (138 mg, 0.387 mmol). The mixture was stirred at rt for 16 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH/$Et_3N$ = 100/5/0.1) to give **35** (76.6 mg, 23%) as red solid; $^1$H NMR (270 MHz, $CD_3OD$) δ: 2.42 (3H, s), 2.88 (2H, t, *J* = 7.0 Hz), 3.04 (2H, d, *J* = 7.0 Hz), 3.09 (2H, d, *J* = 7.0 Hz), 3.62 (2H, t, *J* = 7.0 Hz), 5.48 (1H, s), 7.41 (2H, d, *J* = 8.6 Hz), 7.48 (2H, s), 7.72 (1H, s), 8.05 (2H, d, *J* = 8.6 Hz); $^{13}$C NMR (100 MHz, $CD_3OD$) δ:

19.7, 21.7, 42.5, 47.2, 54.9, 94.6, 115.0, 119.4, 125.5, 128.3, 128.7, 130.0, 130.7, 131.0, 135.2, 135.8, 146.1, 148.1, 150.1, 156.6, 170.8; IR (KBr): 3262, 3053, 2101, 1681, 1614, 1566, 1556, 1531, 1525, 1494, 1469, 1446 $cm^{-1}$.

PIFA (55.0 mg, 0.129 mmol) was added to a solution of **35** (1.0 equiv) in $CF_3CH_2OH$ (4.0 ml) at rt under $N_2$. The mixture was stirred at rt for 3.0 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH/$Et_3N$ = 100/1/0.1) to give **43** (20.6 mg, 27 %) as red solid; $^1H$ NMR (500 MHz, $CDCl_3$) δ: 1.92-1.95 (2H, m), 2.43 (3H, s), 2.64 (2H, t, *J* = 7.5 Hz), 3.48-3.54 (2H, m), 3.99 (2H, t, *J* = 7.5 Hz), 5.81 (1H, br s), 7.33 (2H, d, *J* = 8.0 Hz), 7.48 (1H, s), 7.71 (2H, s), 8.01 (2H, d, *J* = 8.0 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 21.8, 29.7, 32.8, 37.5, 48.5, 49.8, 96.4, 102.2, 111.3, 118.6, 121.7, 125.6, 126.4, 126.5, 127.2, 128.6, 129.8, 134.6, 142.1, 145.9, 162.6, 168.4, 174.1; IR (KBr): 3391, 2926, 2853, 1659, 1574, 1528, 1495, 1460, 1435 $cm^{-1}$; HRMS (FAB) calcd for $C_{25}H_{20}I_2N_3O_4S$ $[M+H]^+$: 711.9264, found 711.9258.

**36a, 36b**



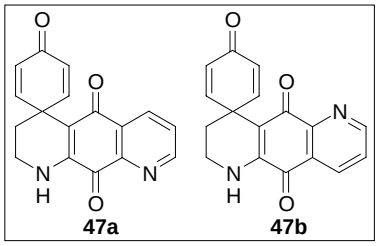
**36a** **36b**

Quinoline-5,8-dione (**20**) (25.1 mg, 0.158 mmol) was added to a solution of tyramine (**10**) (26.0 mg, 0.189 mmol) in MeOH (2.0 ml) at rt under $N_2$. The mixture was stirred at rt for 16 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 20/1) to give **36a** and **36b** (less polar; (13.3 mg, 24%), polar (27.3 mg, 49%)).

**36b** (less polar): brown solid: $^1H$ NMR (300 MHz, $CDCl_3$) δ: 2.92 (2H, t, *J* = 7.5 Hz), 3.46 (2H, t, *J* = 7.5 Hz), 5.83 (1H, s), 6.80 (2H, d, *J* = 8.4 Hz), 7.07 (2H, d, *J* = 8.4 Hz), 7.72 (1H, dd, *J* = 7.8, 4.5 Hz), 8.44 (1H, dd, *J* = 7.8, 1.8 Hz), 8.87 (1H, dd, *J* = 4.5, 1.8 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 32.2, 43.5, 98.5, 114.9, 128.2, 128.6, 129.4, 130.0, 133.1, 146.3, 148.6, 152.3, 155.5, 179.4, 180.1; IR (KBr): 3297, 2982, 2947, 1769, 1759, 1703, 1605, 1581, 1564, 1514, 1454 $cm^{-1}$; HRMS (FAB) calcd for $C_{17}H_{15}N_2O_3$ $[M+H]^+$: 295.1083, found 295.1079.

**36a** (polar): brown solid: $^1H$ NMR (300 MHz, $CDCl_3$) δ: 2.90 (2H, t, *J* = 6.9 Hz), 3.44 (2H, t, *J* = 6.9 Hz), 5.94 (1H, s), 6.11 (1H, br s), 6.80 (2H, d, *J* = 8.4, 2.1 Hz), 7.05 (2H, d, *J* = 8.4 Hz), 7.58 (1H, dd, *J* = 7.8, 4.8 Hz), 8.34 (1H, dd, *J* = 7.8, 1.8 Hz), 8.99 (1H, dd, *J* = 4.8, 1.8 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ: 33.5, 43.9, 101.7, 115.8, 126.4, 127.4, 128.6, 129.7, 134.3, 147.6, 149.2, 155.0, 155.7, 181.3, 181.4; IR (KBr): 3556, 2986, 2086, 1757, 1606, 1568 $cm^{-1}$; HRMS (FAB) calcd for $C_{17}H_{15}N_2O_3$ $[M+H]^+$: 295.1083, found 295.1089.

**47a, 47b**

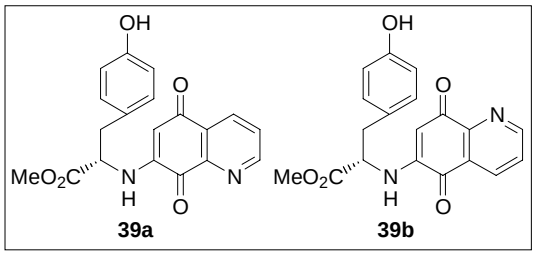



PIFA (74.3 mg, 0.173 mmol) was added to a solution of **36a**, **36b** (42.4 mg, 0.144 mmol) in $CF_3CH_2OH$ (7.2 ml) at rt under $N_2$. The mixture was stirred at rt for 1.0 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 15/1) to give **47a, 47b** (lesspolar: 9.80 mg, 23%. polar: 20.1mg, 48 %).

**47b** (less polar): brown solid; m.p. 246-249 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.99 (2H, t, *J* = 5.7 Hz), 3.65 (2H, t, *J* = 5.7 Hz), 6.42 (2H, d, *J* = 9.9 Hz), 6.57 (1H, br s), 6.96 (2H, d, *J* = 9.9 Hz), 7.64 (1H, dd, *J* = 7.8, 4.5 Hz), 8.35 (1H, dd, *J* = 7.8, 1.8 Hz), 8.91 (1H, dd, *J* = 4.5, 1.8 Hz); $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ: 32.8, 37.0, 48.6, 107.0, 126.8, 128.6, 130.6, 133.6, 146.1, 146.7, 152.4, 154.7, 176.9, 179.0, 185.1; IR (KBr): 3242, 2928, 1693, 1659, 1595, 1556, 1514, 1437, 1404 cm$^{-1}$; HRMS (FAB) calcd for $C_{17}H_{13}N_2O_3$ [*M*+H]$^+$: 293.0926, found 293.0932.

**47a** (polar): brown solid: $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.98 (2H, t, *J* = 5.7 Hz), 3.62 (2H, t, *J* = 5.7 Hz), 6.39 (2H, d, *J* = 9.9 Hz), 7.00 (2H, d, *J* = 9.9 Hz), 7.59 (1H, dd, *J* = 7.8, 4.8 Hz), 8.35 (1H, dd, *J* = 7.8, 1.8 Hz), 8.93 (1H, dd, *J* = 4.8, 1.8 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 33.3, 37.3, 39.7, 126.3, 126.6, 127.9, 130.1, 133.9, 137.3, 148.7, 153.2, 155.0, 177.2, 180.2, 186.2; IR (KBr): 3265, 2927, 2860, 2359, 2341, 2248, 2067, 1655, 1618, 1593, 1566, 1517, 1434 cm$^{-1}$; HRMS (FAB) calcd for $C_{17}H_{12}N_2NaO_3$ [*M*+Na]$^+$: 315.0746, found 315.0735.

**39a**, **39b**



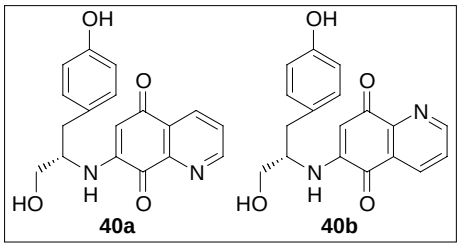

$Et_3N$ (0.200 ml, 1.47 mmol) was added to a solution of **11** (340 mg, 1.47 mmol) in MeOH (7.5 ml) at rt for 10 min under $N_2$. This solution was added dropwise to a solution of quinoline-5,8-dione (**20**) (213 mg, 1.33 mmol) in MeOH (7.5 ml). The mixture was stirred at rt for 16 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 10/1) to give **39a** and **39b** (less polar; (140 mg, 27%), polar (223 mg, 43%)).

**39b** (less polar): brown solid; $^1$H NMR (300 MHz, $CDCl_3$) δ: 3.10 (1H, dd, *J* = 13.8, 6.6 Hz), 3.21 (1H, dd, *J* = 13.8, 5.4 Hz), 3.77 (3H, s), 4.29 (1H, dd, *J* = 13.8, 5.7 Hz), 5.74 (1H, s), 6.46 (1H, d, *J* = 7.8 Hz), 6.82 (2H, d, *J* = 8.4 Hz), 7.00 (2H, d, *J* = 8.4 Hz), 7.17 (1H, br s), 7.67 (1H, dd, *J* = 7.5, 4.5 Hz), 8.43 (1H, dd, *J* = 7.8, 1.8Hz), 8.90 (1H, dd, *J* = 4.5, 1.5 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 36.6, 52.9, 56.4, 101.5, 116.0, 126.0, 128.6, 130.3, 130.4, 134.6, 146.3, 147.0, 153.0, 155.9, 170.5, 179.3, 181.9; IR (KBr): 3306, 3015, 2926, 2853, 1742, 1693, 1607, 1566, 1514, 1443 cm$^{-1}$; HRMS (FAB) calcd

for $C_{19}H_{17}N_2O_5$ [*M*+H]$^+$: 353.1137, found 353.1146.

**39a** (polar): brown solid; $^1$H NMR (500 MHz, $CDCl_3$) δ: 3.07 (1H, dd, *J* = 14.0, 7.0 Hz), 3.17 (1H, d, *J* = 14 Hz), 3.76 (3H, s), 4.28 (1H, dd, *J* = 14.0, 7.0 Hz), 5.82 (1H, s), 6.35 (1H, d, *J* = 8.0 Hz), 6.79 (2H, d, *J* = 8.0 Hz), 6.95 (2H, d, *J* = 8.0 Hz), 7.57 (1H, dd, *J* = 7.5, 4.5 Hz), 8.32 (1H, dd, *J* = 7.5, 1.5 Hz), 8.95 (1H, dd, *J* = 4.5, 1.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 37.5, 53.6, 57.0, 103.5, 116.8, 126.7, 127.3, 128.0, 130.9, 135.2, 147.1, 149.4, 155.6, 156.6, 171.4, 181.4, 182.3; IR (KBr): 3252, 2953, 1741, 1682, 1607, 1572, 1514, 1443 cm$^{-1}$; HRMS (FAB) calcd for $C_{19}H_{17}N_2O_5$ [*M*+H]$^+$: 353.1137, found 353.1138.

**40a, 40b**

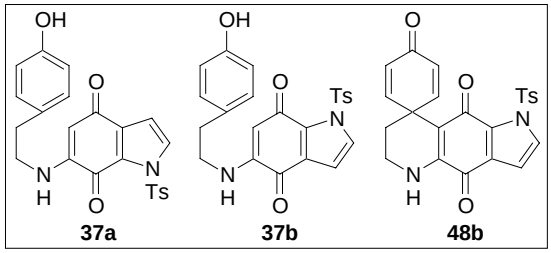



$Et_3N$ (0.120 ml, 0.893 mmol) was added to a solution of tyrosinol (182 mg, 0.893 mmol) in MeOH (4.5 ml) at rt for 10 min under $N_2$. This solution was added dropwise to a solution of quinoline-5,8-dione (**20**) (129 mg, 0.812 mmol) in MeOH (4.5 ml). The mixture was stirred at rt for 3.0 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/MeOH = 15/1) to give **40a** and **40b** (less polar; (63.7 mg, 22%), polar (116 mg, 40%))

**40b** (less polar): brown solid; $^1$H NMR (500 MHz, $CD_3OD$) δ: 2.80 (1H, dd, *J* = 14.0, 8.0 Hz), 2.91 (1H, dd, *J* = 14.0, 6.0 Hz), 3.63-3.75 (3H, m), 5.76 (1H, s), 6.67 (2H, d, *J* = 8.5 Hz), 7.08 (2H, d, *J* = 8.5 Hz), 7.77 (1H, dd, *J* = 8.0, 5.0 Hz), 8.39 (1H, dd, *J* = 7.5, 1.5 Hz), 8.81 (1H, dd, *J* = 5.0, 1.5 Hz); $^{13}$C NMR (125 MHz, $CD_3OD$) δ: 36.8, 57.9, 63.5, 100.4, 102.0, 116.3, 126.6, 129.8, 130.0, 131.4, 135.5, 150.6, 153.5, 175.2, 179.6, 183.1; IR (KBr): 3287, 2922, 2853, 1730, 1693, 1605, 1566, 1556, 1514, 1462 cm$^{-1}$; HRMS (FAB) calcd for $C_{18}H_{17}N_2O_4$ [*M*+H]$^+$: 325.1188, found 325.1173.

**40a** (polar): brown solid; $^1$H NMR (400 MHz, $CD_3OD$) δ: 2.70 (1H, dd, *J* = 13.6, 6.0 Hz), 2.81 (1H, dd, *J* = 13.6, 6.0 Hz), 3.53-3.65 (3H, m), 5.74 (1H, s), 6.57 (2H, d, *J* = 8.0 Hz), 6.97 (2H, d, *J* = 8.0 Hz), 7.56 (1H, dd, *J* = 7.2, 4.4 Hz), 8.28 (1H, d, *J* = 7.2 Hz), 8.76 (1H, d, *J* = 3.6 Hz); $^{13}$C NMR (100 MHz, $CD_3OD$) δ: 36.8, 57.8, 63.4, 101.4, 116.2, 116.3, 128.0, 129.7, 131.4, 135.8, 150.1, 150.3, 155.3, 157.2, 182.0, 182.6; IR (KBr): 3336, 2924, 2853, 1732, 1685, 1600, 1568, 1514, 1462 cm$^{-1}$; HRMS (FAB) calcd for $C_{18}H_{16}N_2NaO_4$ [*M*+Na]$^+$: 347.1008, found 347.1008.

**48b**

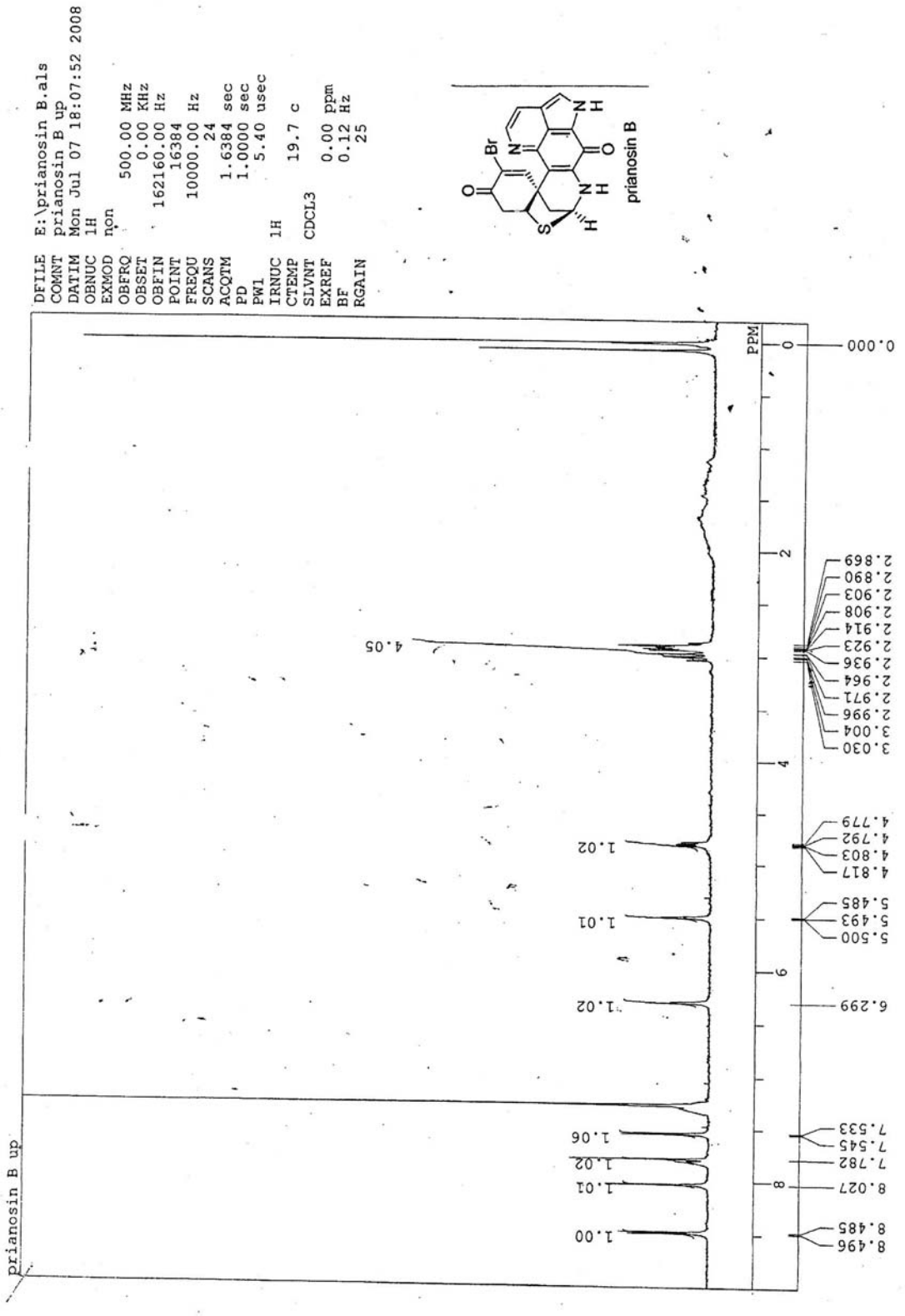


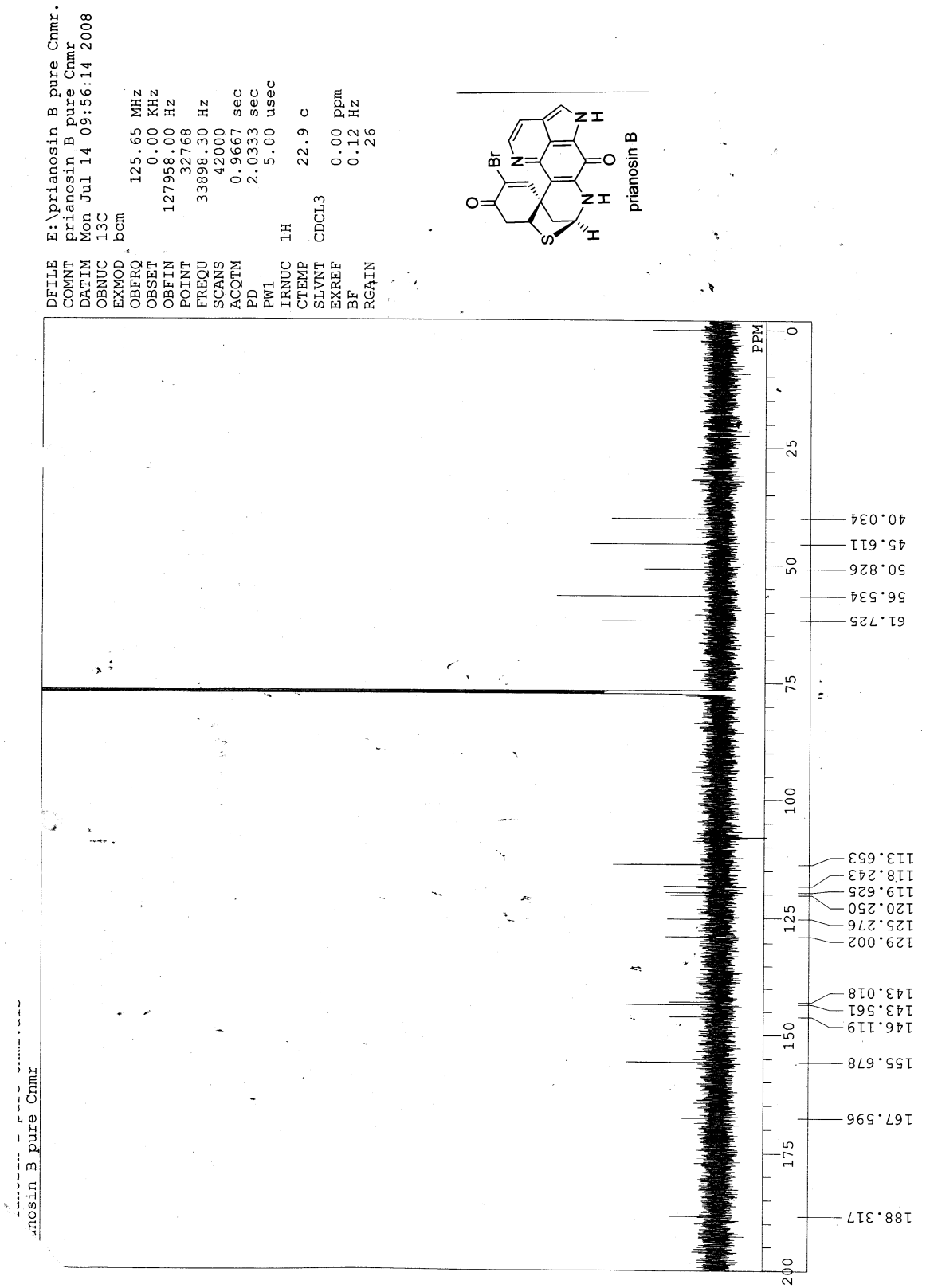

1-(toluene-4-sulfonyl)-1H-indole-4,7-dione (**23**) (228 mg, 0.755 mmol) was added to a solution of tyramine (**10**) (114 mg, 0.831 mmol) in MeOH (8.3 ml) at rt under $N_2$. The mixture was stirred at rt for 18 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography (*n*-hexane/AcOEt = 3/1) to give **37a** (polar: 116 mg, 32%), **37b** (less polar: 60.7 mg, 17%).

PIFA (65.8 mg, 0.153 mmol) was added to a solution of **37b** (60.7 mg, 0.139 mmol) in $CF_3CH_2OH$ (7.0 ml) at rt under $N_2$. The mixture was stirred at rt for 1.0 h and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography (*n*-hexane/AcOEt = 3/1) to give **48b** (28.3 mg, 47%) as brown solid.

$^1$H NMR (400 MHz, $CDCl_3$) δ: 1.82 (2H, t, *J* = 6.0 Hz), 2.42 (3H, s), 3.46-3.50 (2H, m), 6.07 (1H, br s), 6.28 (2H, dd, *J* = 8.4, 1.6 Hz), 6.62 (1H, d, *J* = 4.0 Hz), 6.76 (2H, d, *J* = 8.4, 1.6 Hz), 7.27 (2H, d, *J* = 8.4 Hz), 7.63 (1H, d, *J* = 3.2 Hz), 7.95 (2H, dd, *J* = 8.4, 1.6 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 21.8, 34.0, 37.6, 39.4, 105.8, 106.7, 126.0, 127.8, 127.9, 129.3, 129.6, 132.7, 133.8, 143.8, 145.9, 153.2, 171.4, 177.8, 185.9; IR (KBr): 3372, 2359, 2341, 1658, 1620, 1589, 1541, 1510, 1462 cm$^{-1}$; HRMS (FAB) calcd for $C_{23}H_{19}N_2O_5S$ $[M+H]^+$ 435.1015, found 435.1021.

## $^{1}$H NMR and $^{13}$C NMR spectra

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BF 0.12 Hz
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56.534
61.725
113.653
118.243
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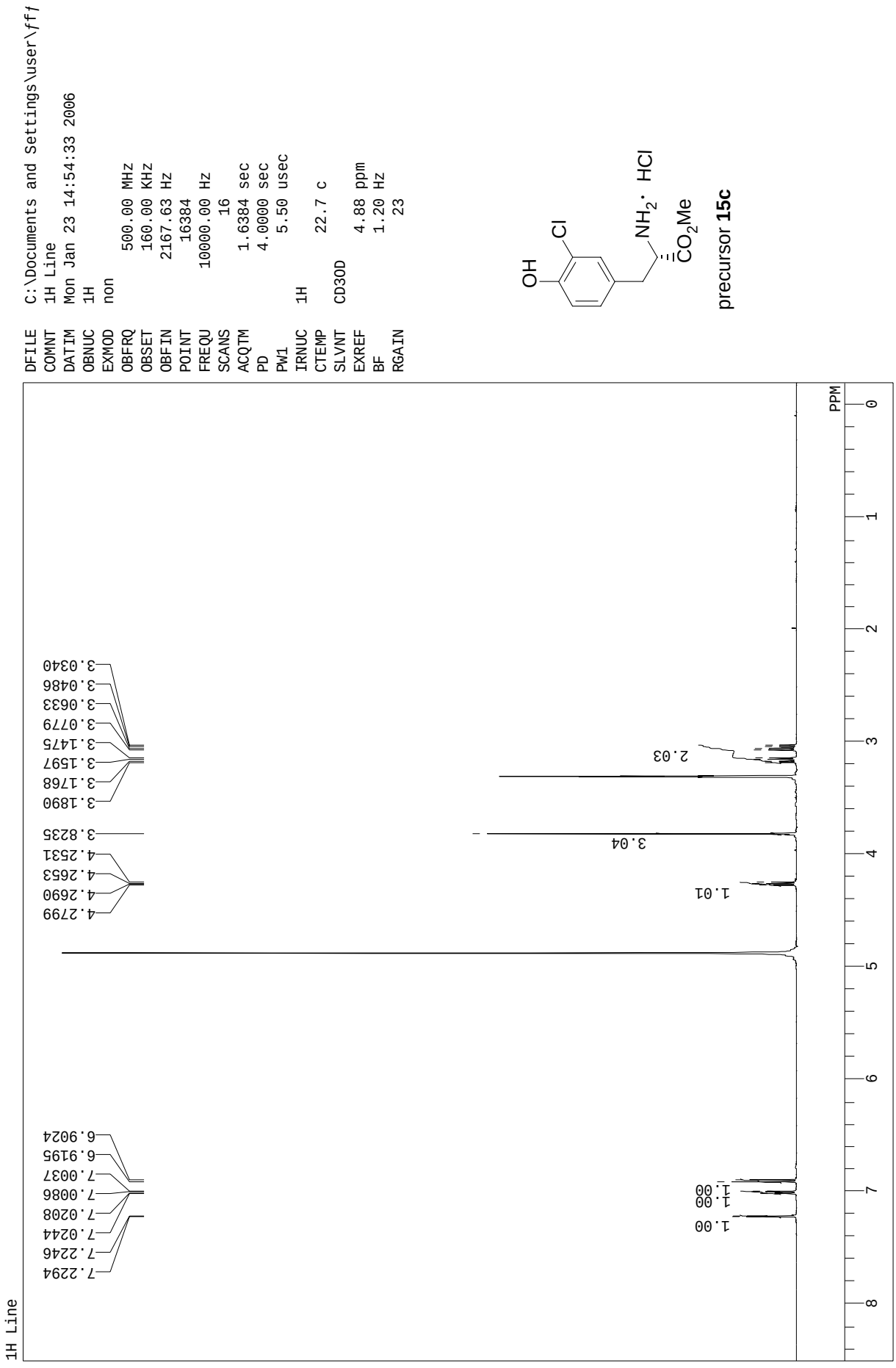
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2.03

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PD         2.0000 sec
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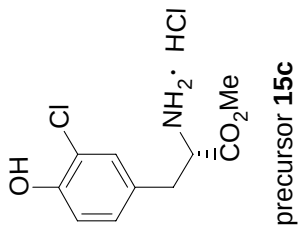
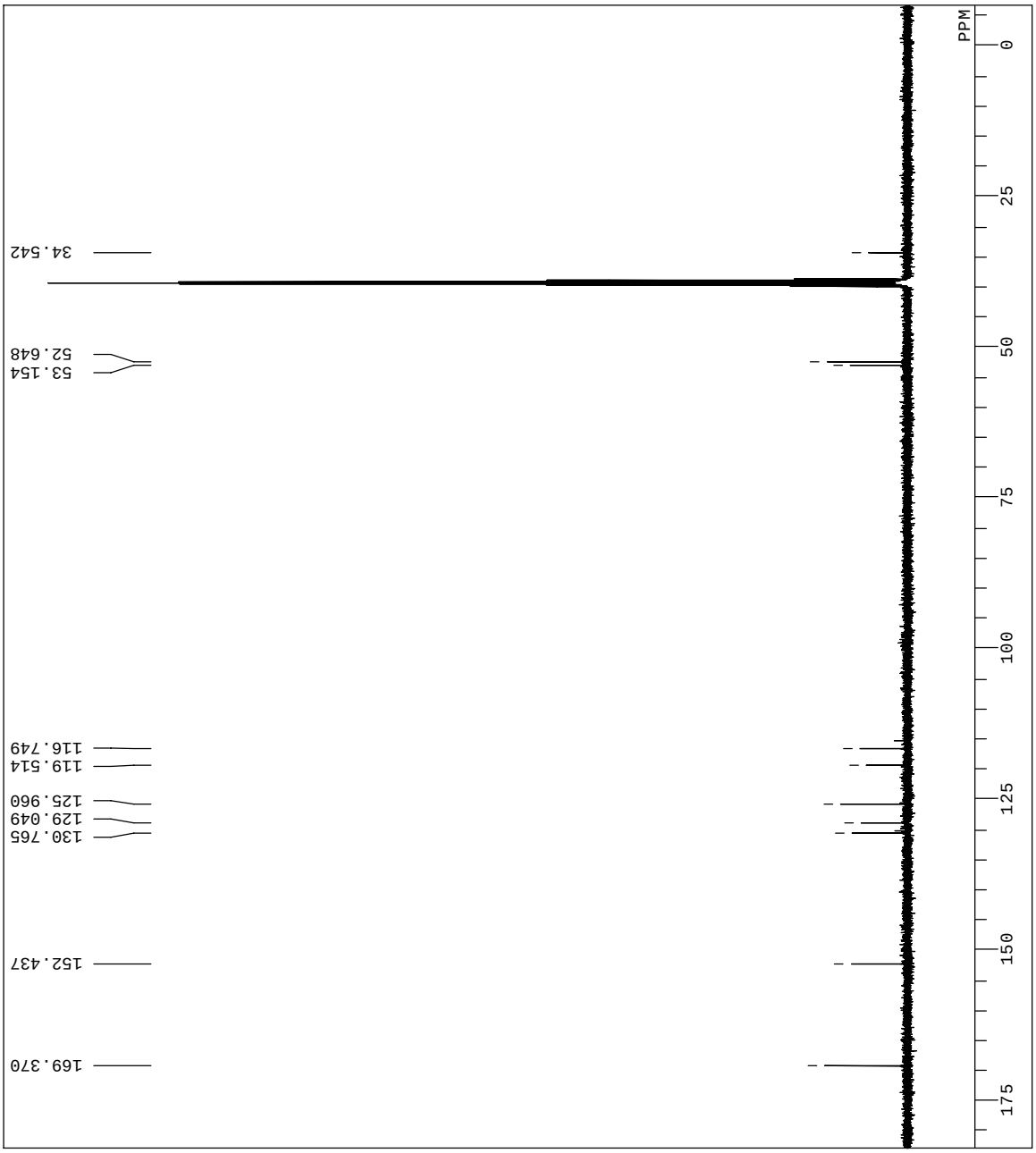
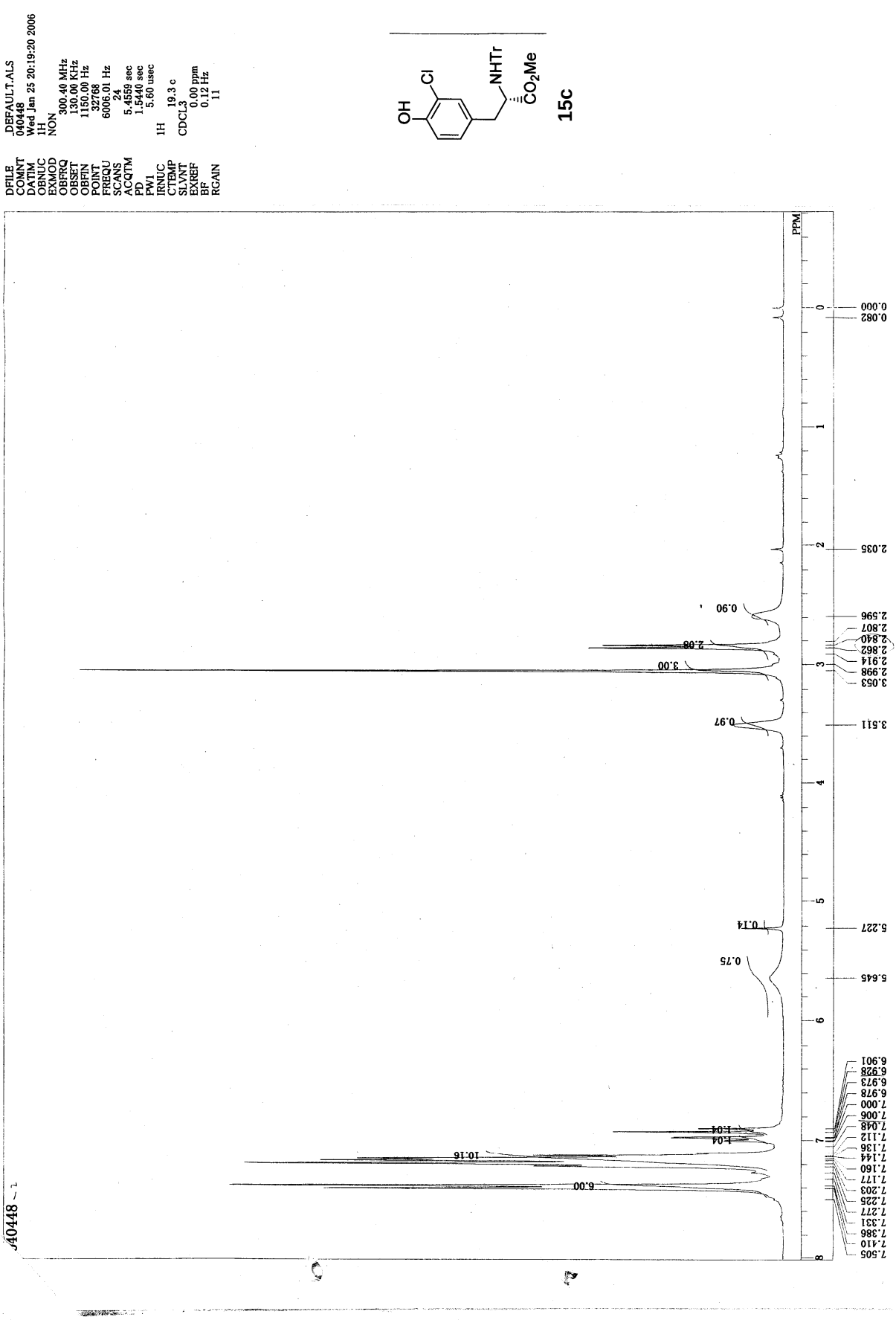



precursor **15c**

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1H
19.3 c
CDCL3
0.00 ppm
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EXMOD
OBFRQ
OBSET
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POINT
FREQU
SCANS
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PD
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6.928
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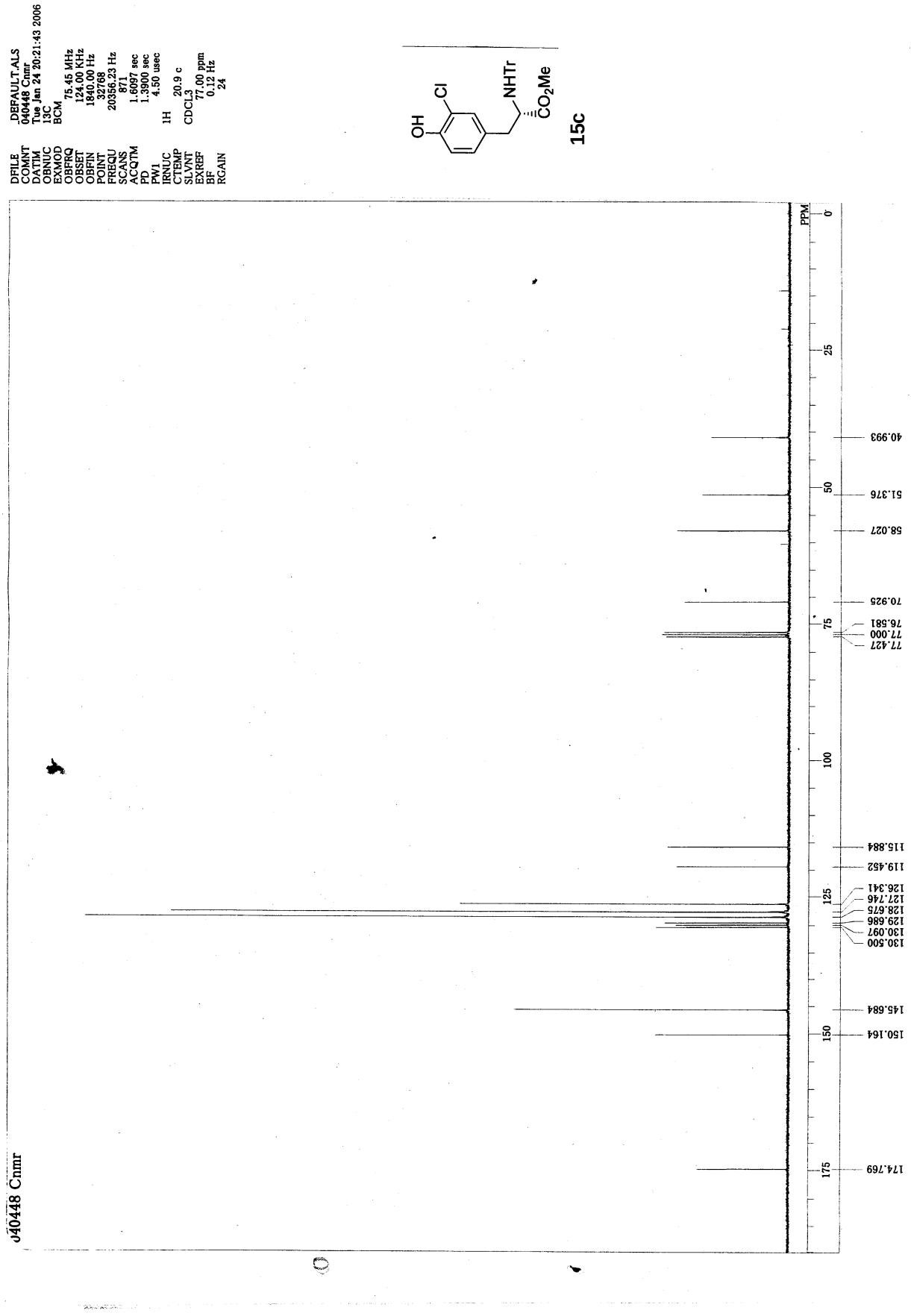
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0.12 Hz
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COMNT
DATTIM
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EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
OH
Cl
NHTr
CO2Me
15c
PPM
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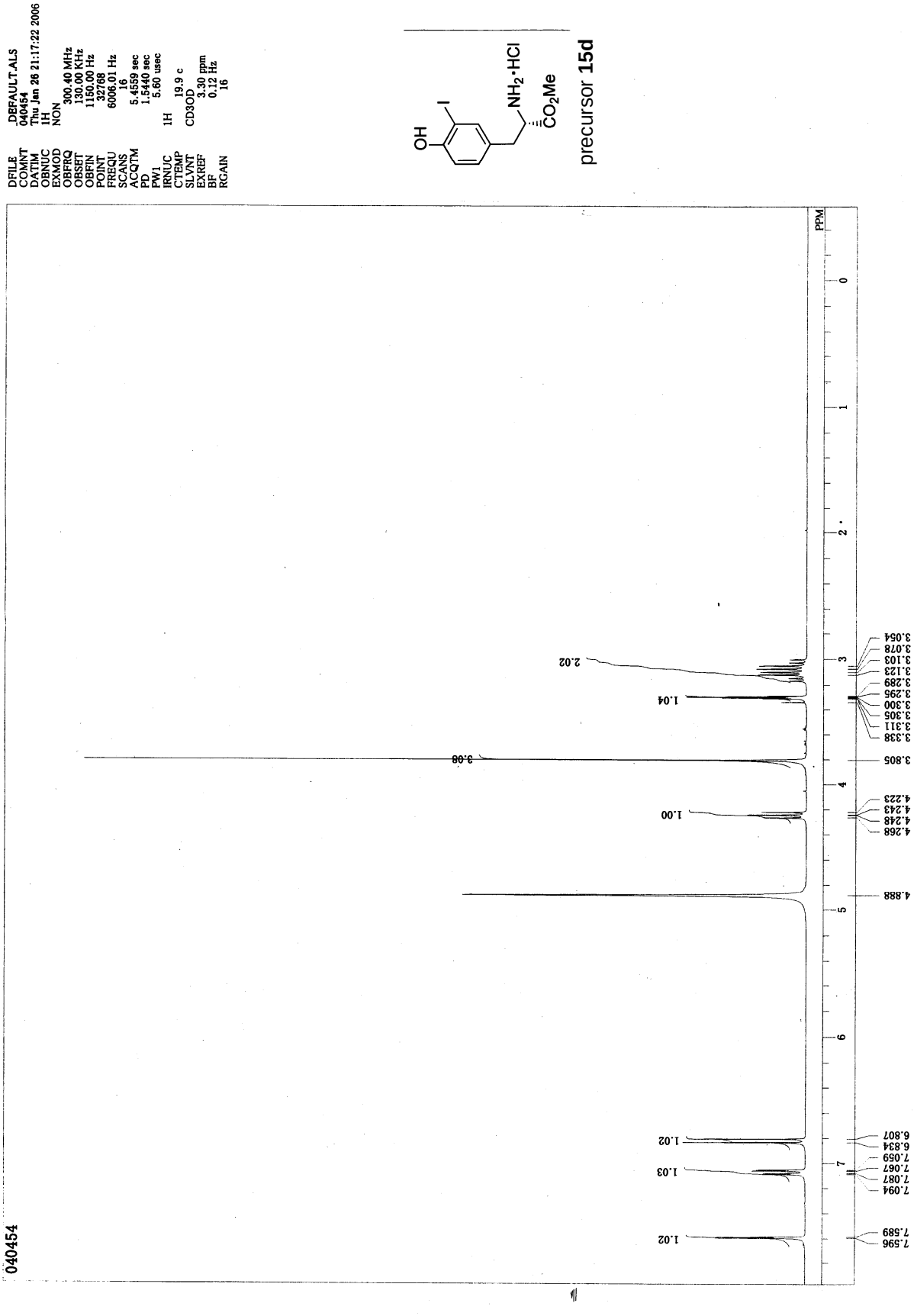
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precursor 15d
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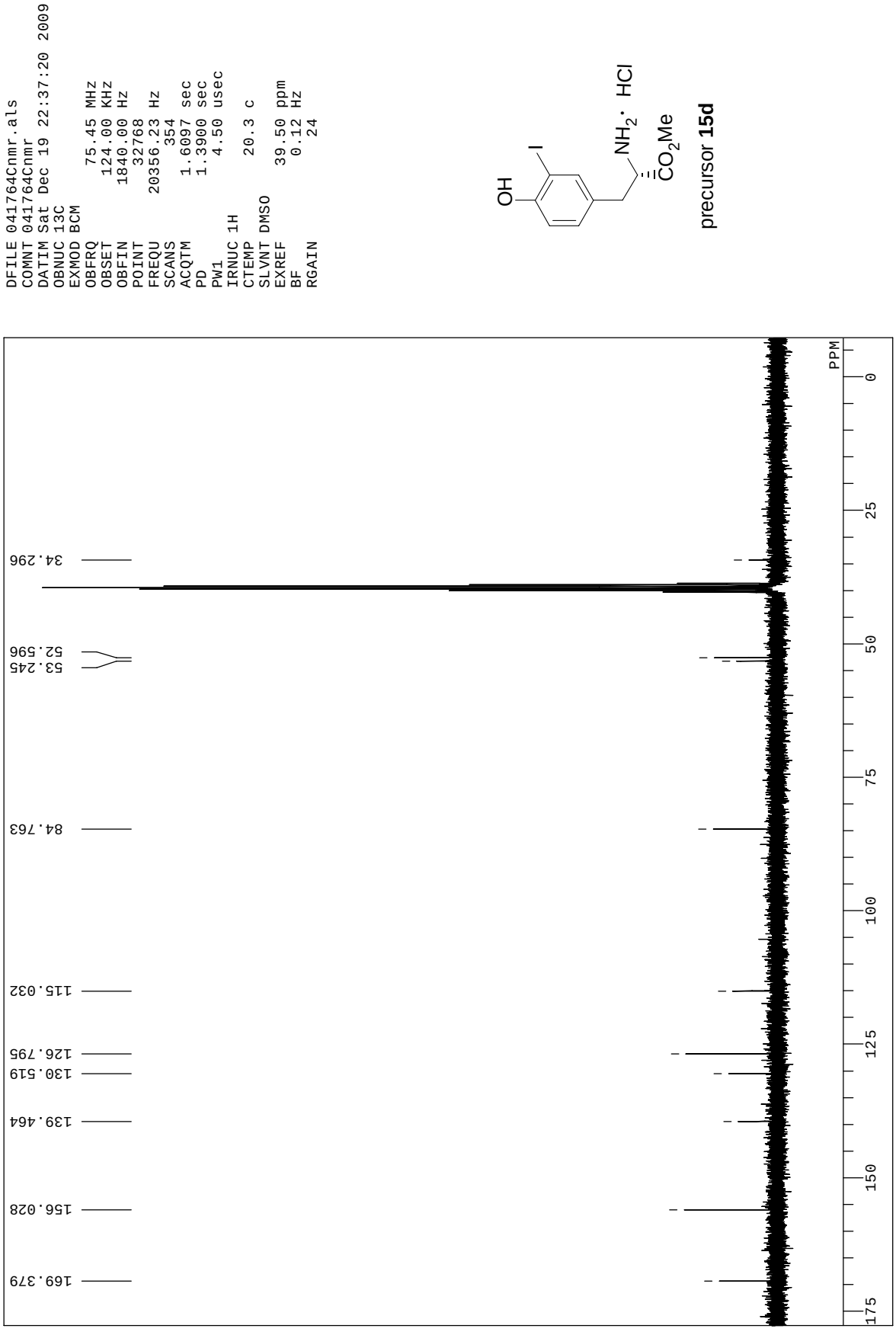
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PW1 4.50 usec
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CTEMP 20.3 c
SLVNT DMSO
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BF 0.12 Hz
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NH2· HCl
CO2Me
precursor 15d
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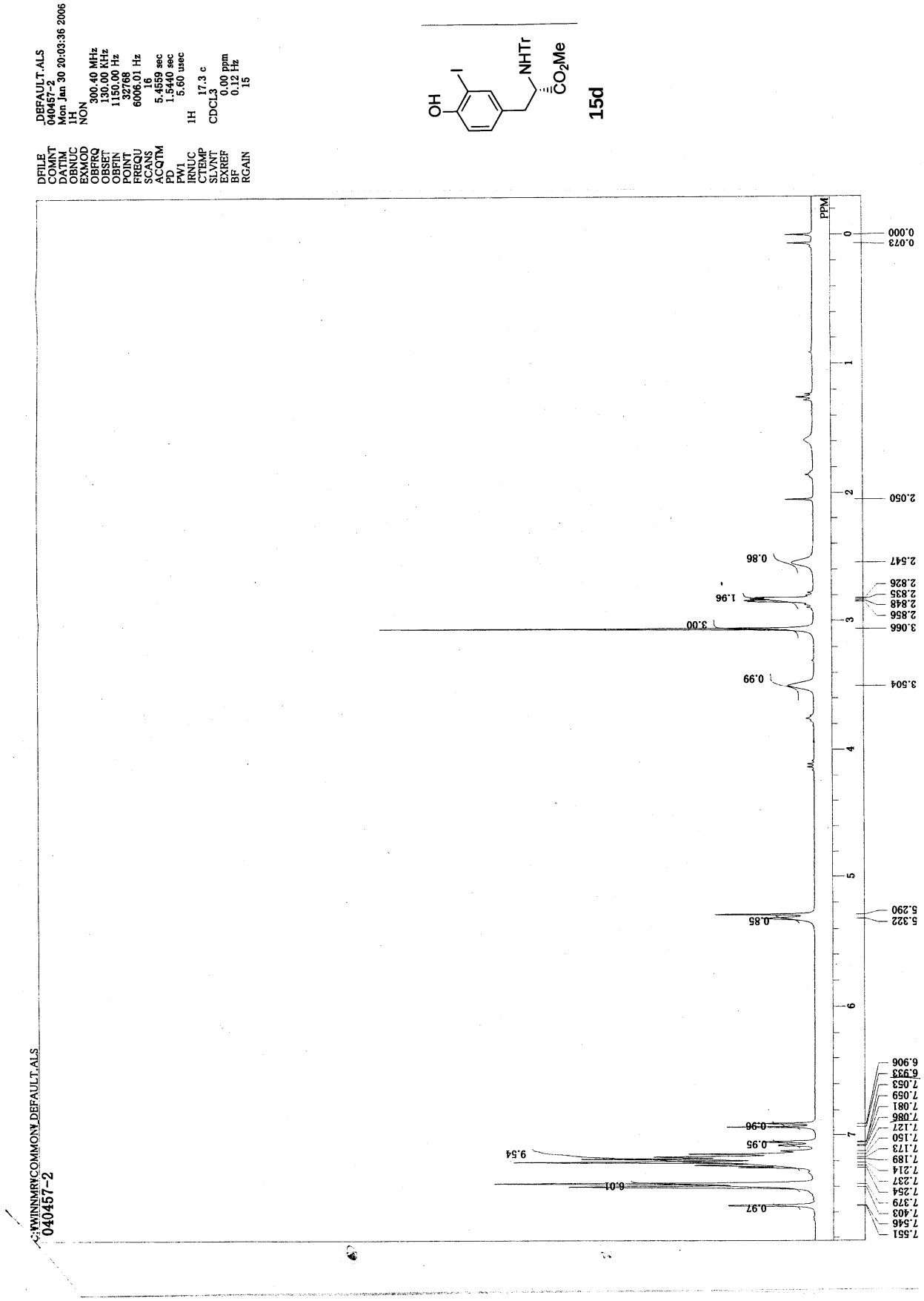
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POINT 32768
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PW1 5.60 usec
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NHTr
CO2Me
15d
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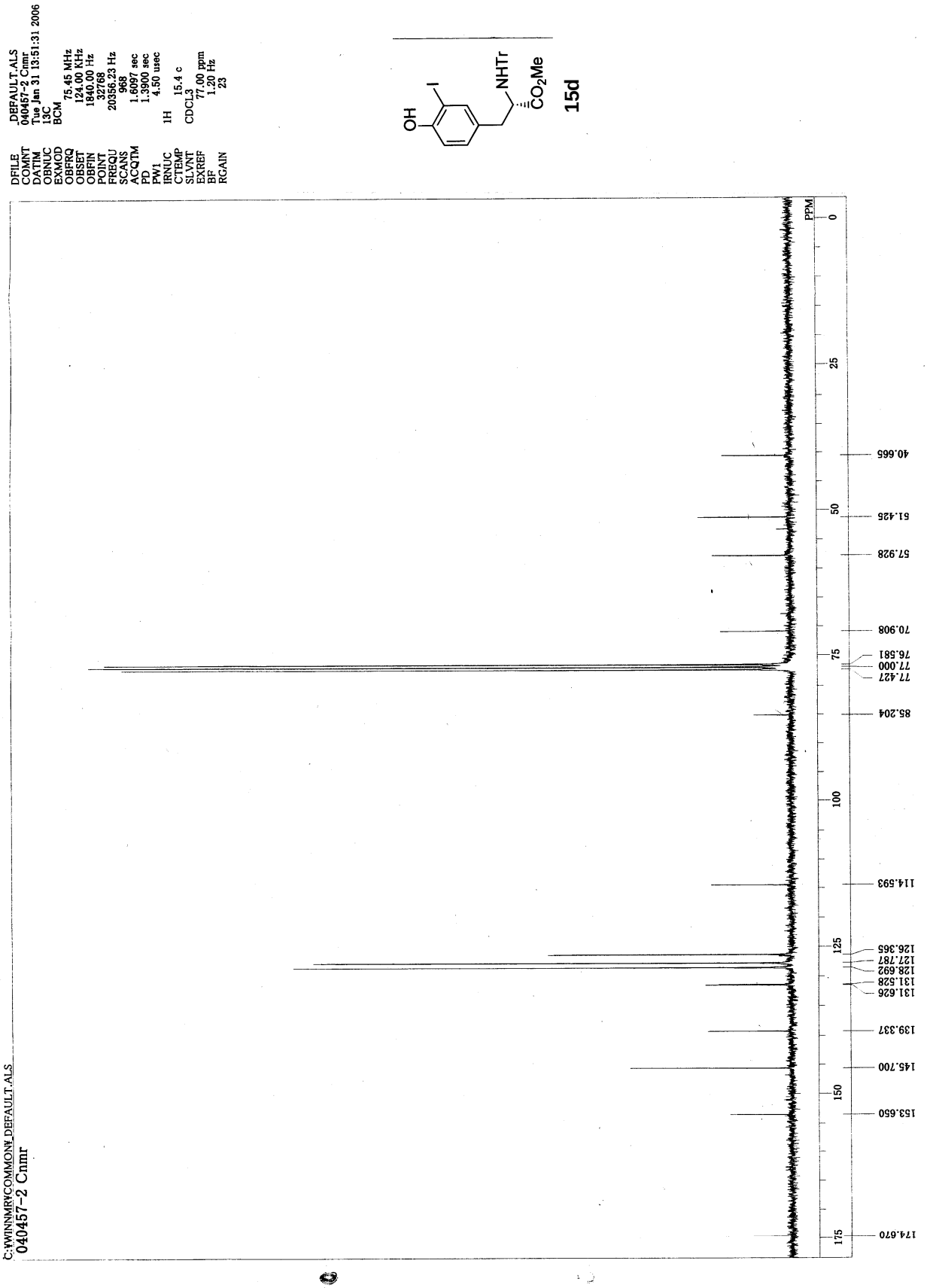
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IRNUC 1H
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NHTr
CO2Me
15d
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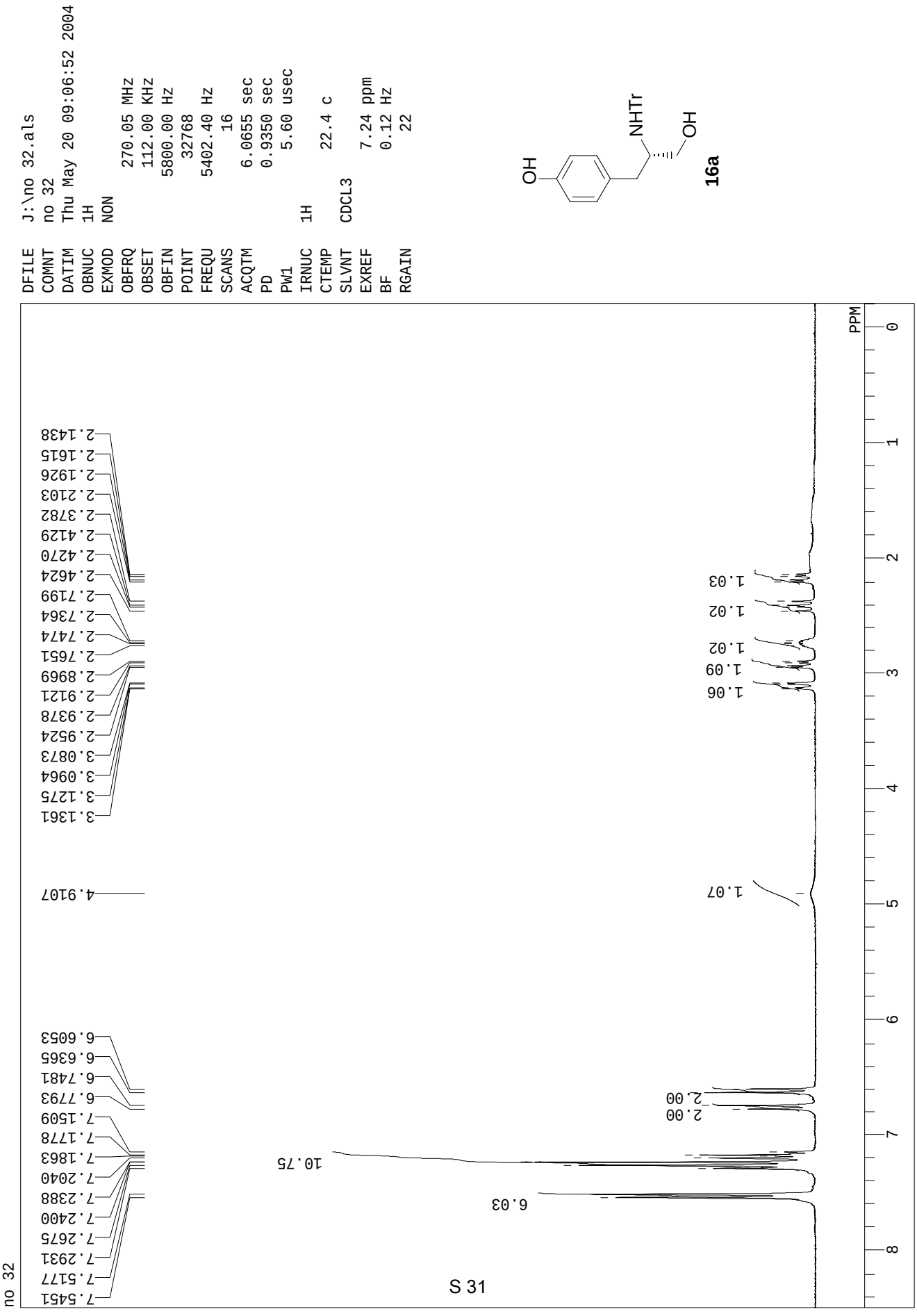
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NHTr
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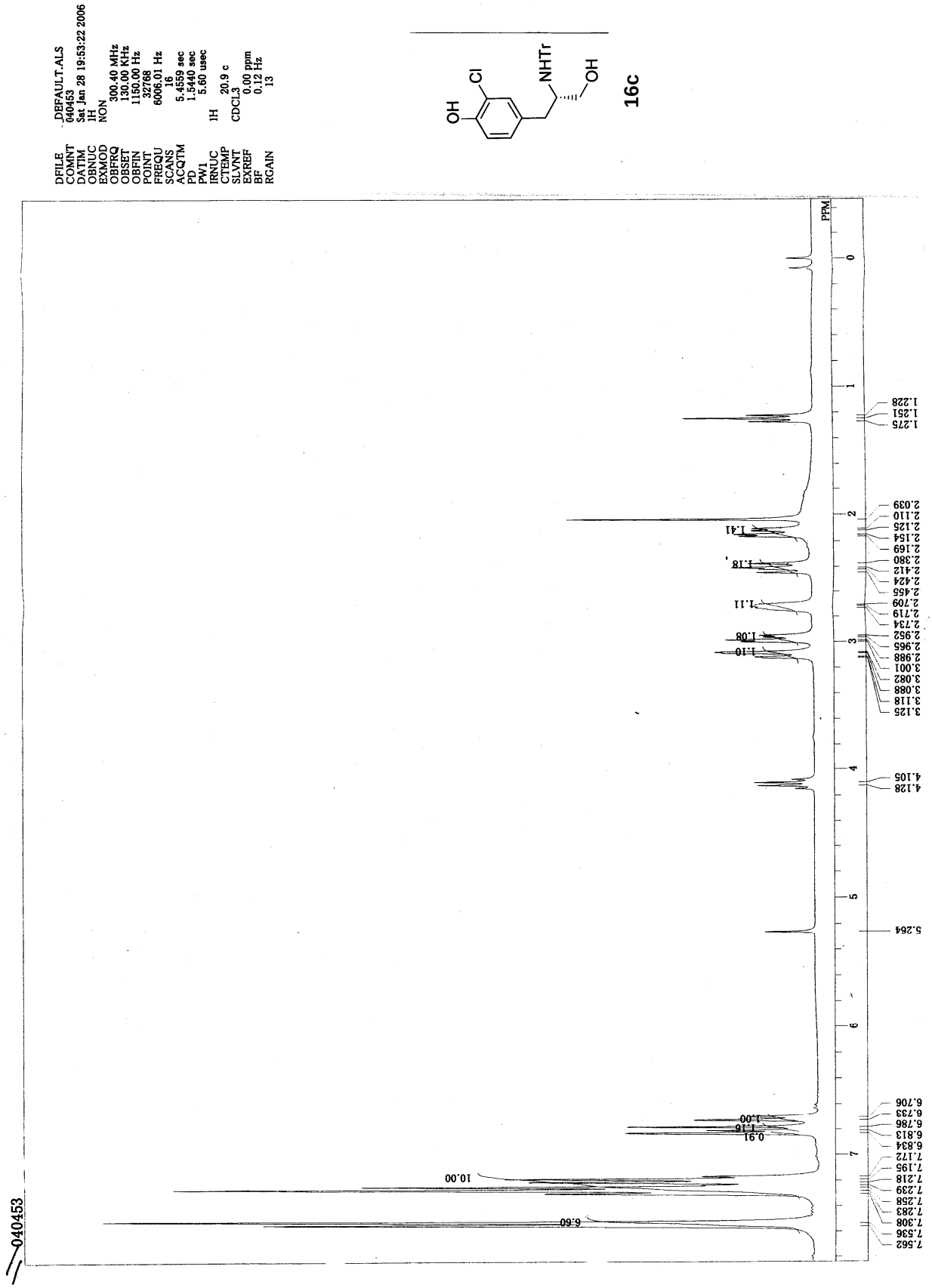
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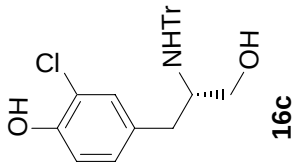
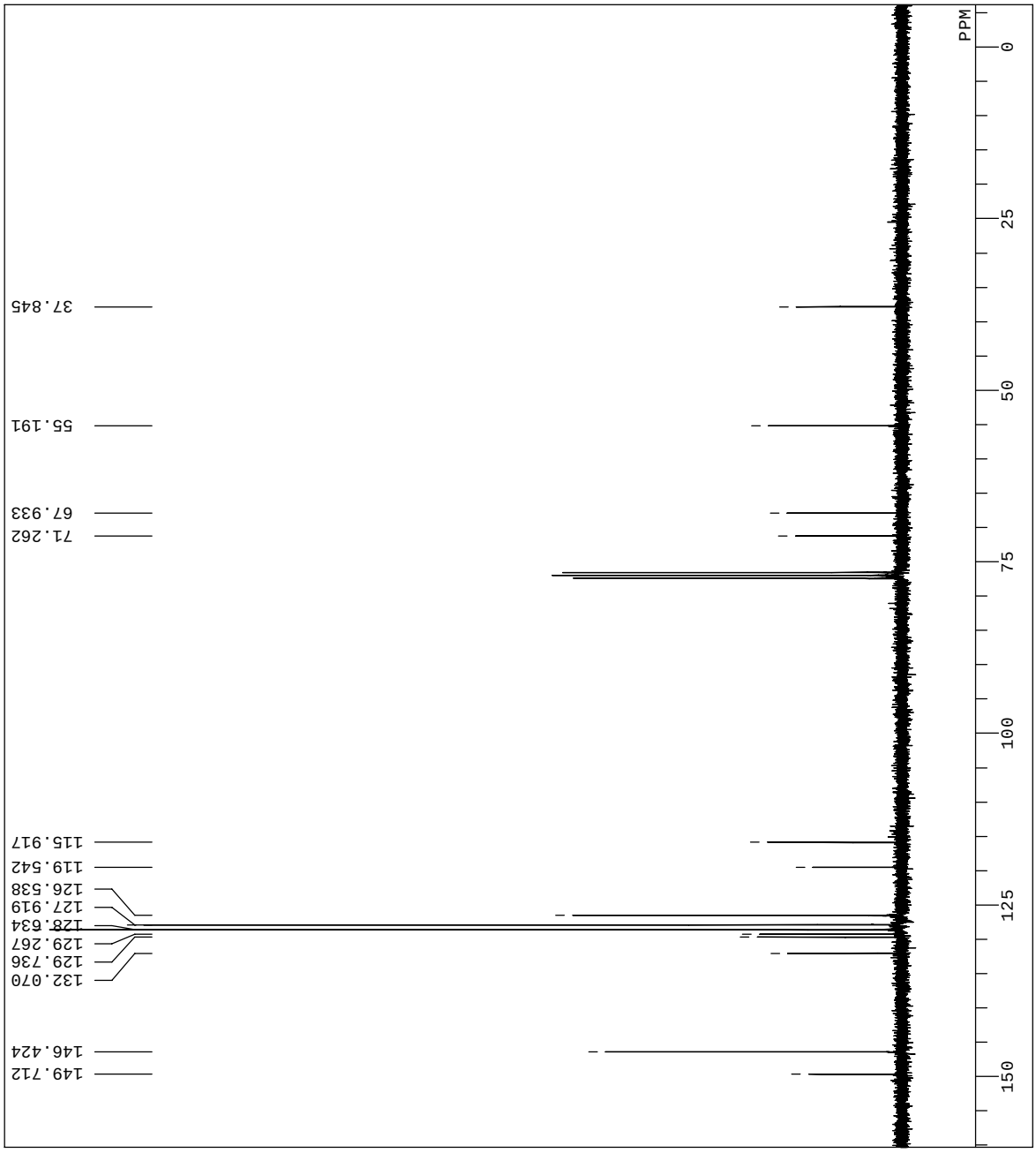
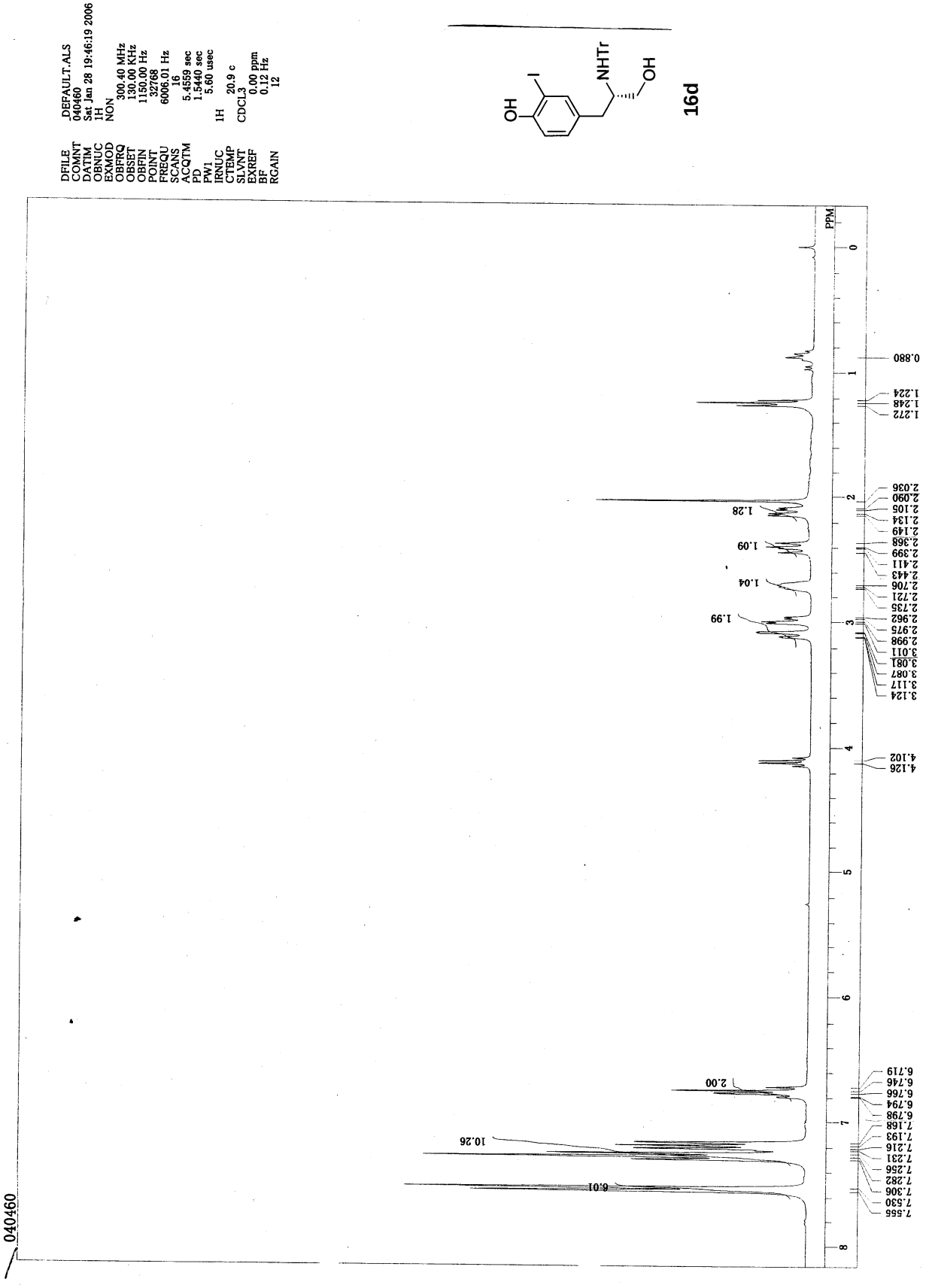



**16c**

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CTEMP 20.9 c
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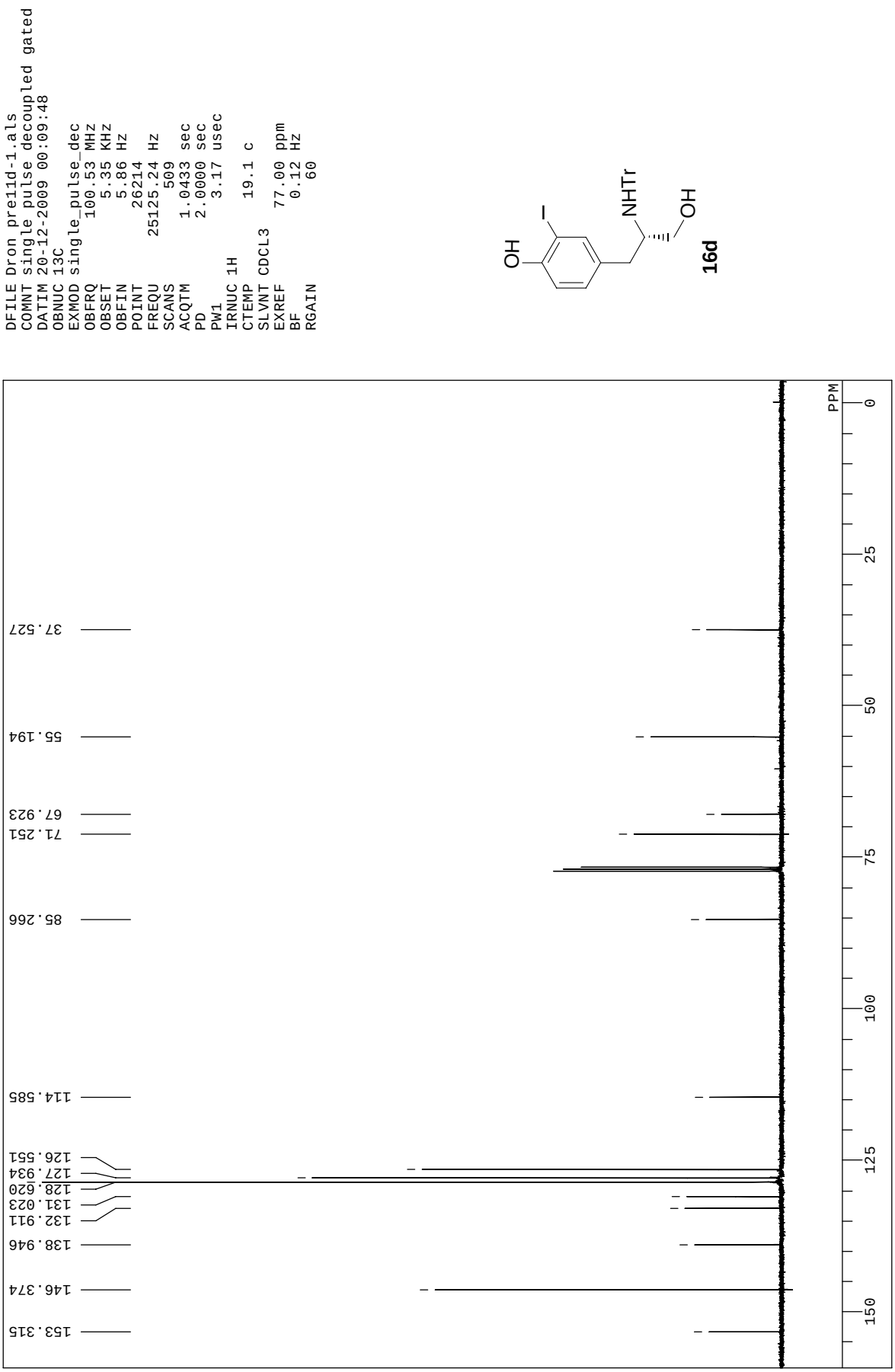
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PW1 3.17 usec
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PPM
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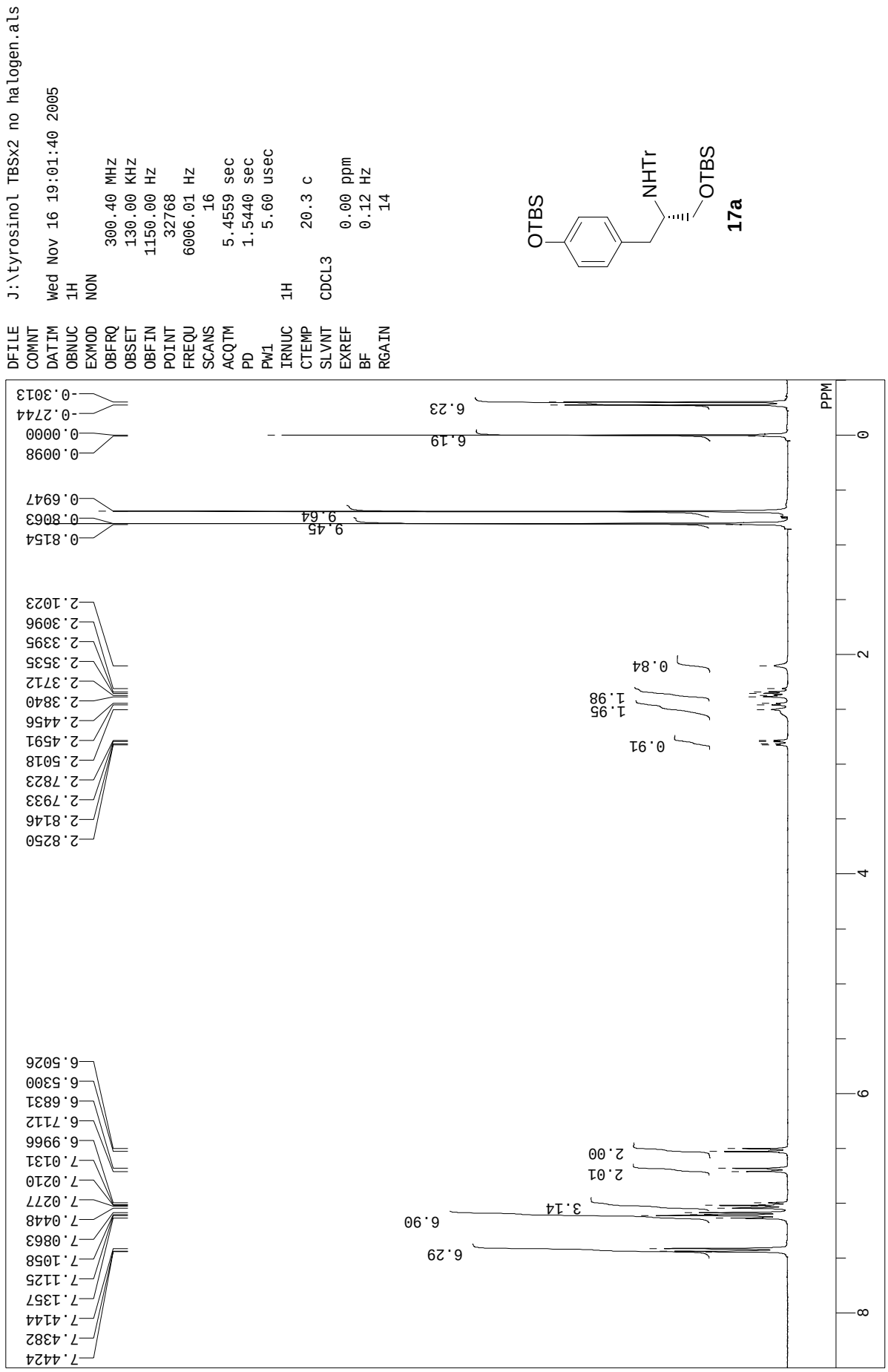
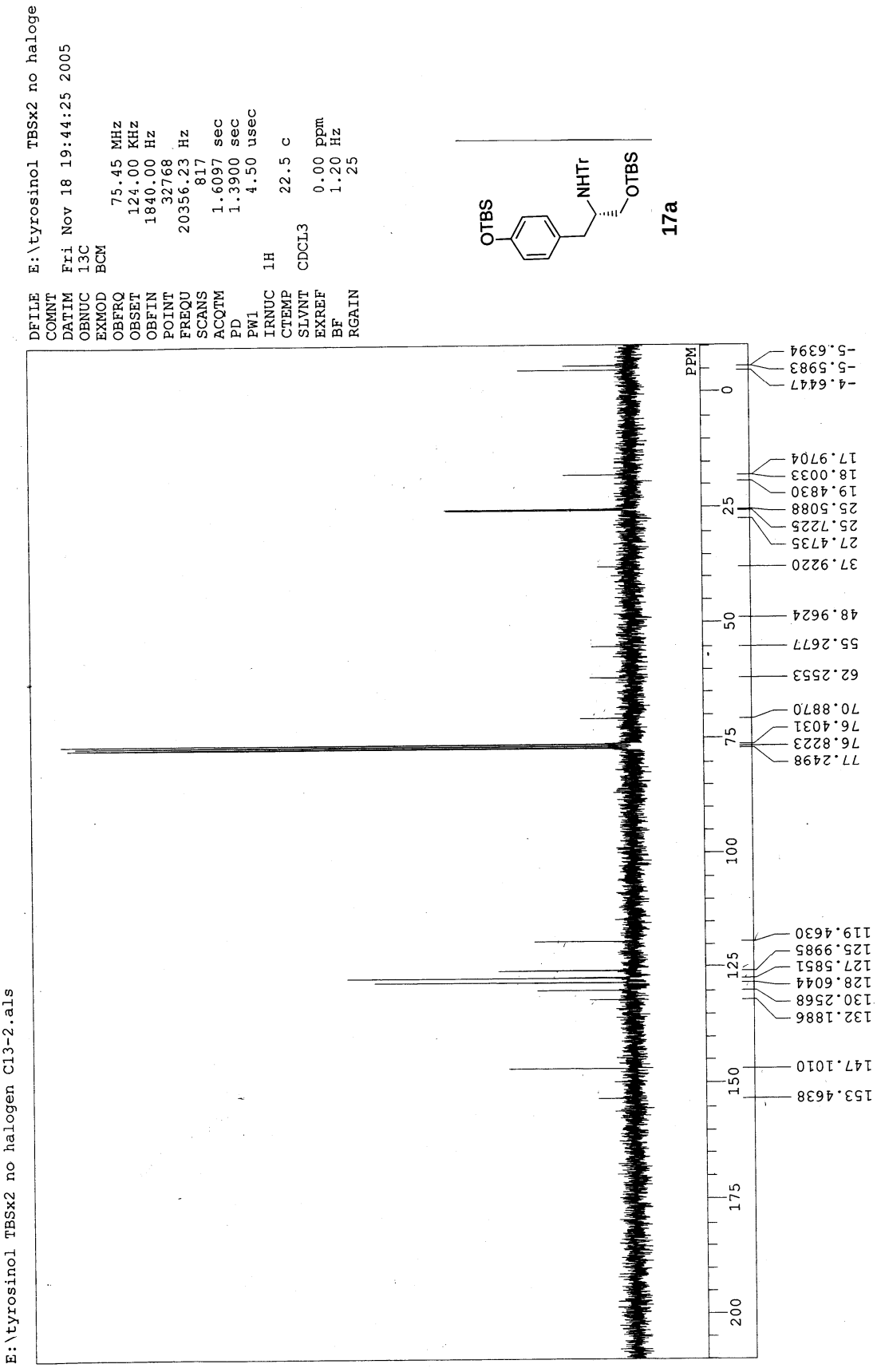
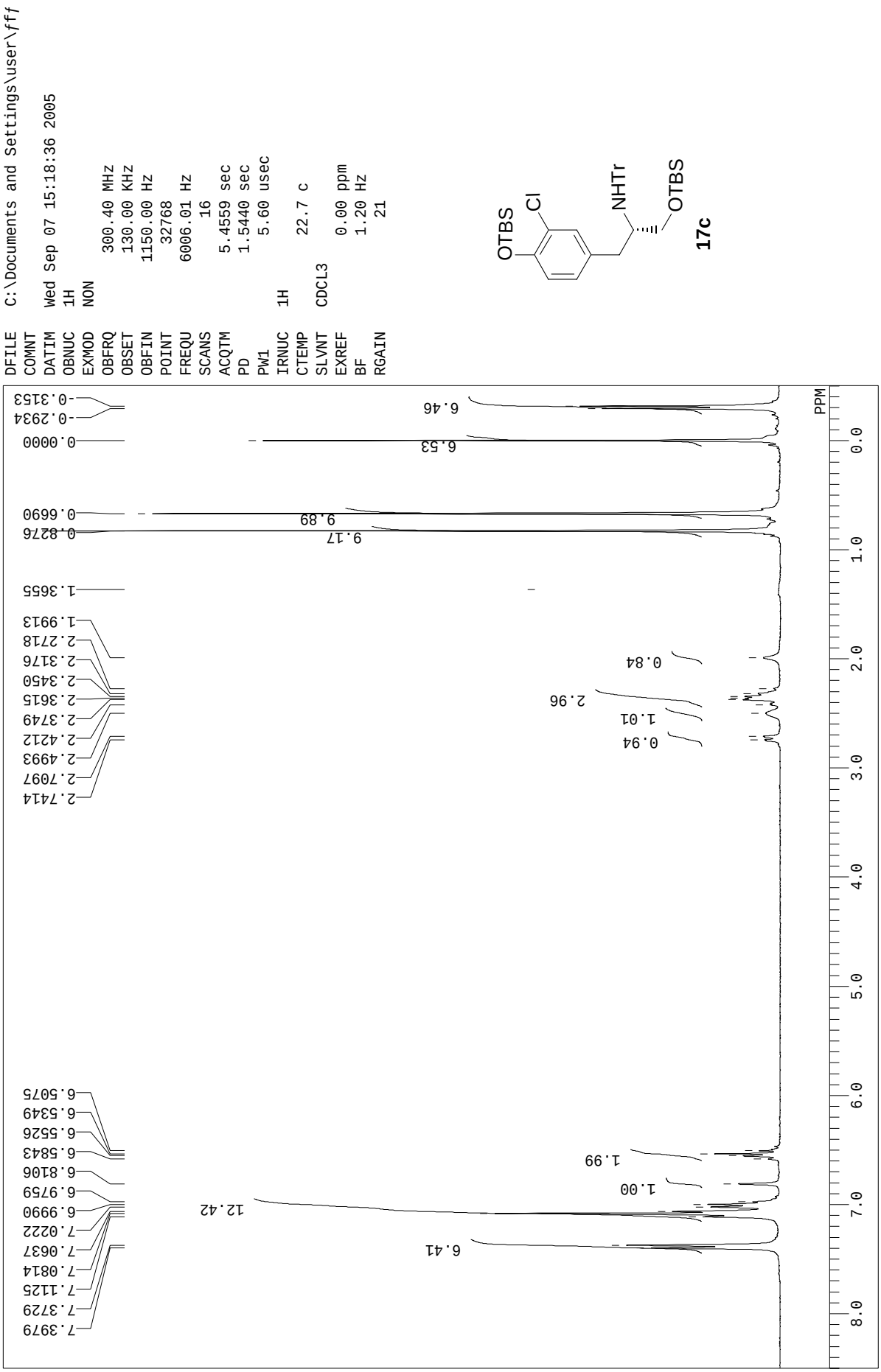
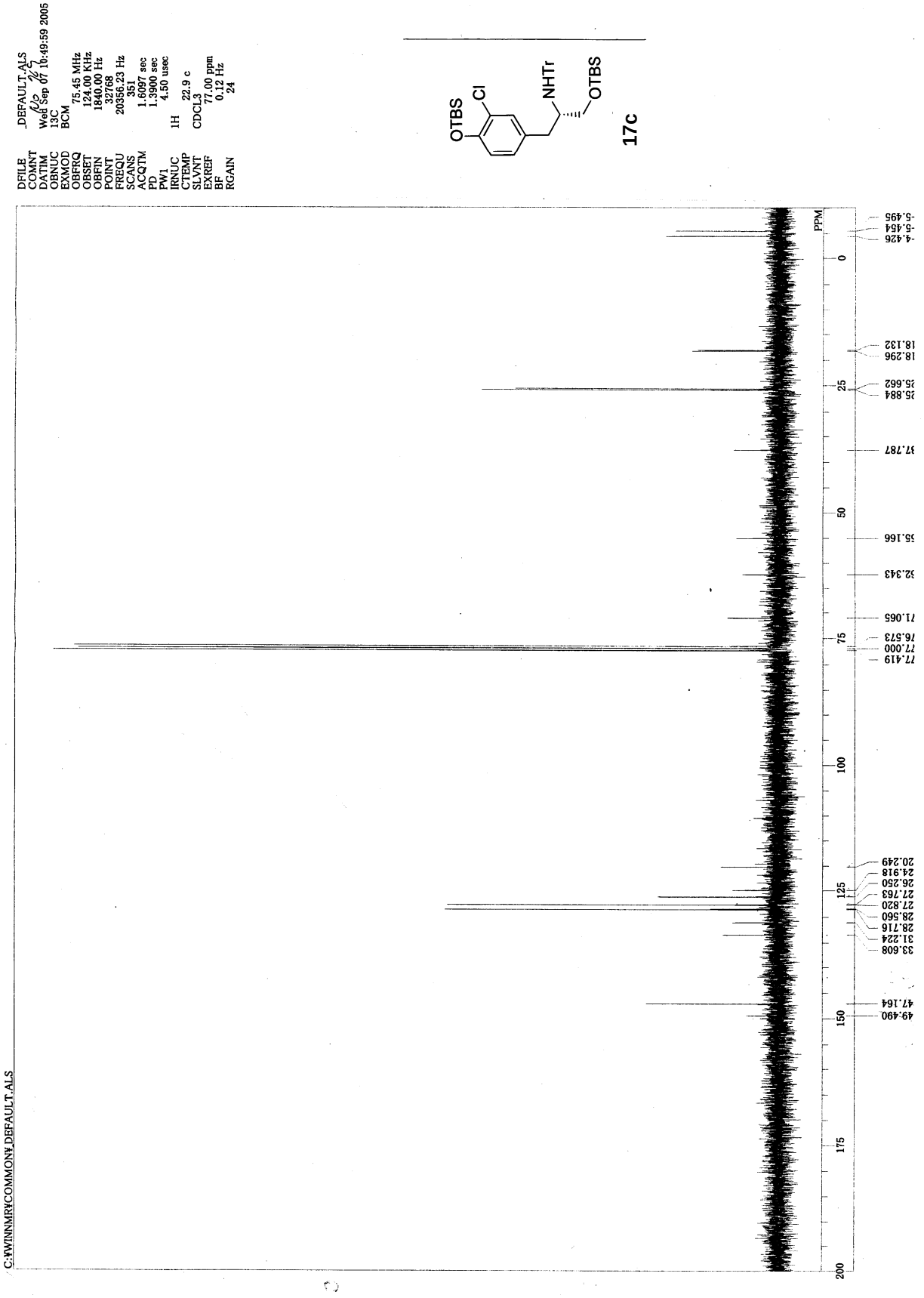
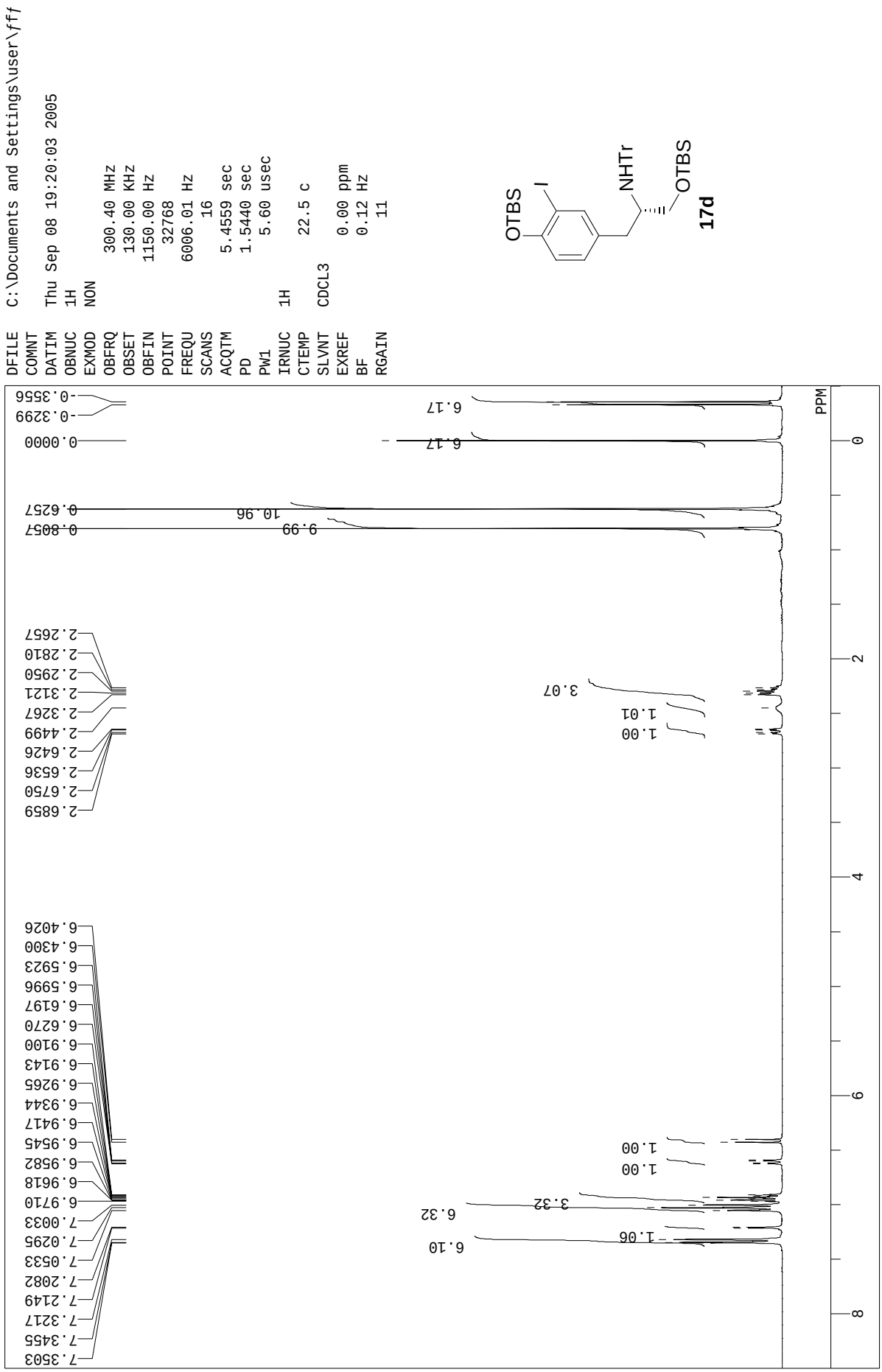
75
100
125
150

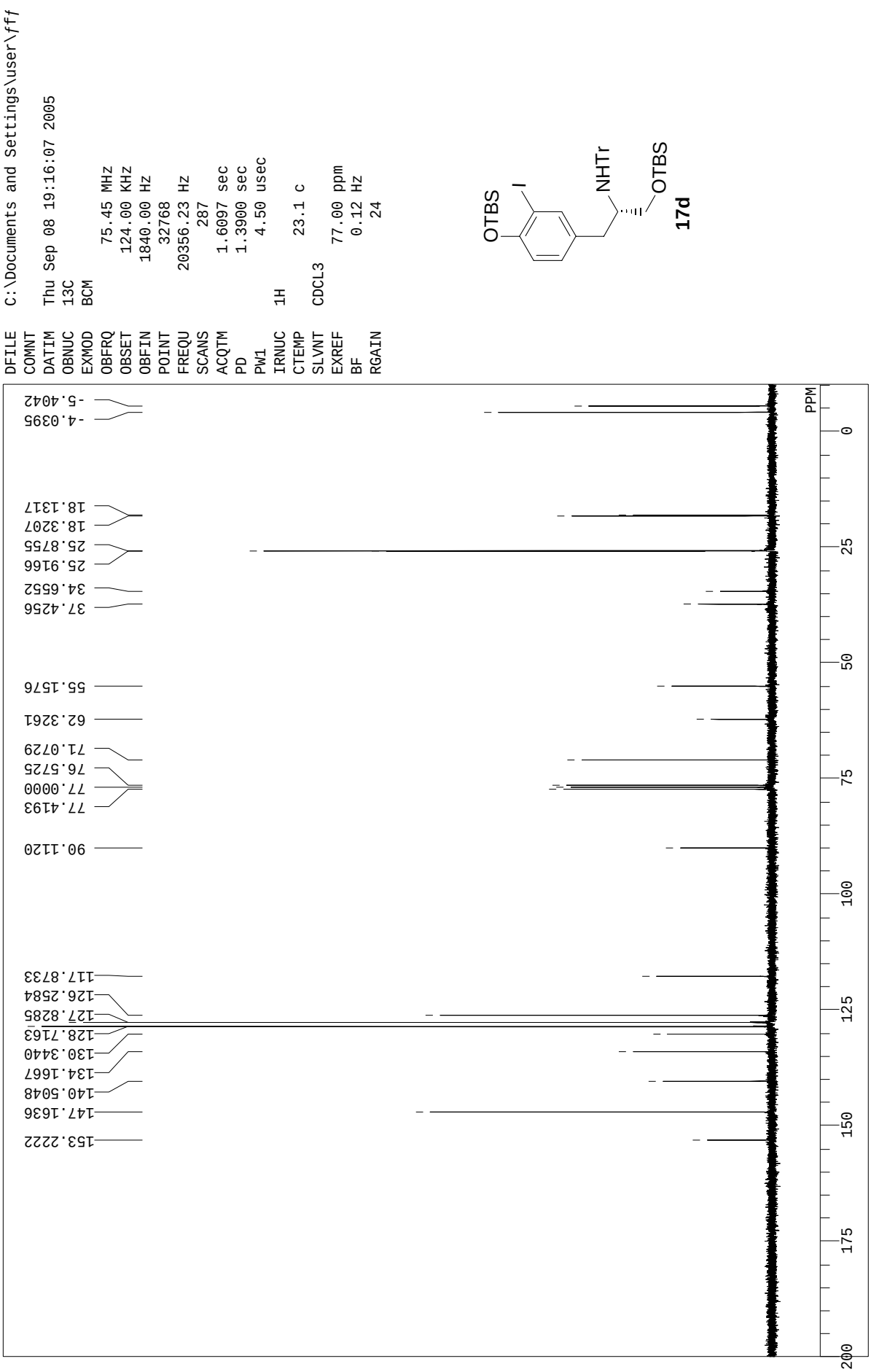

J:\tyrosinol TBSx2 no halogen.als
DFILE
COMNT
DATIM Wed Nov 16 19:01:40 2005
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14
OTBS
NHTr
OTBS
17a
PPM

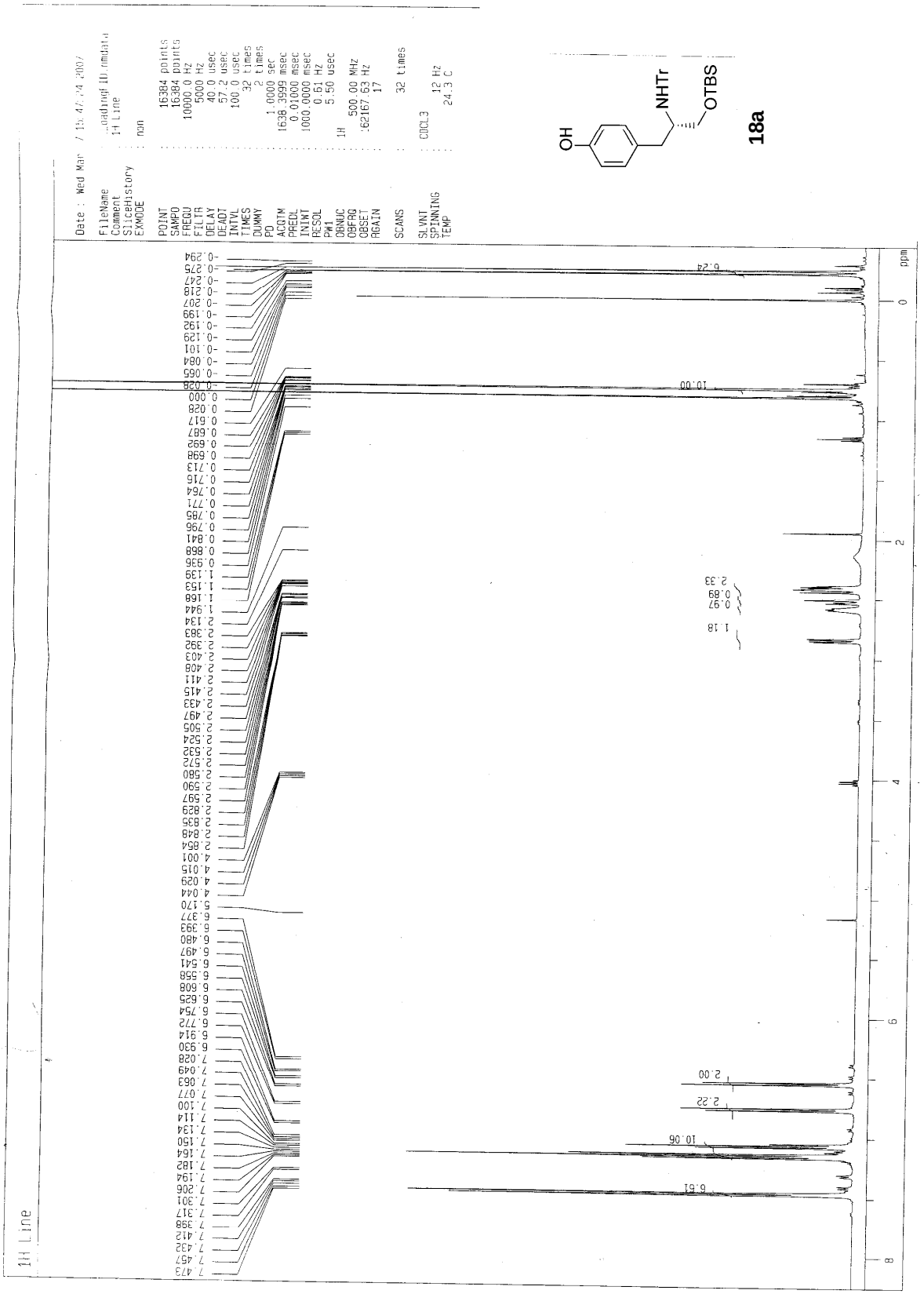

E:\tyrosinol TBSx2 no halogen C13-2.als
DFILE E:\tyrosinol TBSx2 no haloge
COMNT
DATIM Fri Nov 18 19:44:25 2005
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 817
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 25
OTBS
NHTr
OTBS
17a
PPM
-5.6394
-5.5983
-4.6447
17.9704
18.0033
19.4830
25.5088
25.7225
27.4735
37.9220
48.9624
55.2677
62.2553
70.8870
76.4031
76.8223
77.2498
119.4630
125.9985
127.5851
128.6044
130.2568
132.1886
147.1010
153.4638

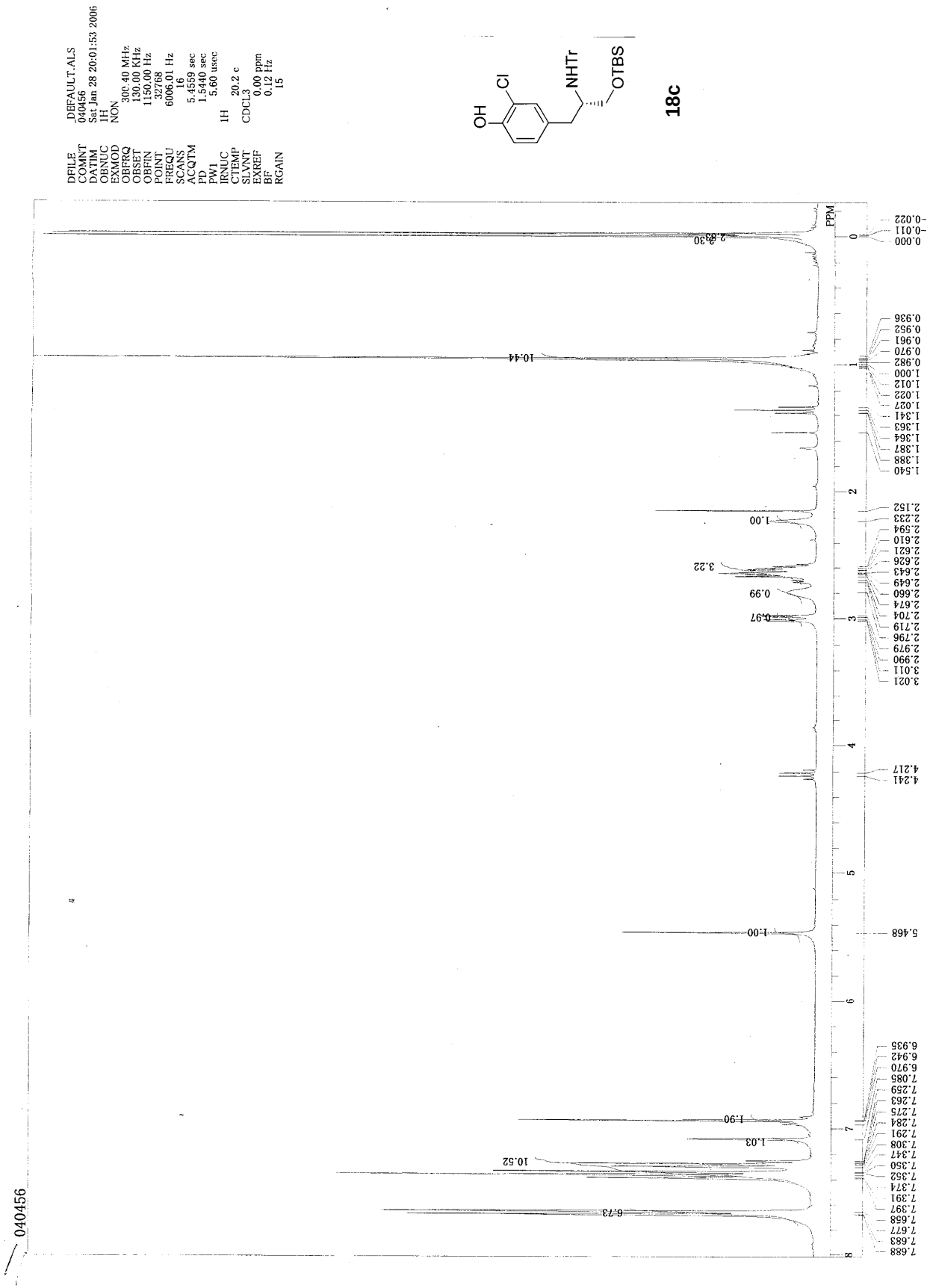

DFILE C:\Documents and Settings\user\fff
COMNT
DATIM Wed Sep 07 15:18:36 2005
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 21
OTBS
Cl
NHTr
OTBS
17c
PPM

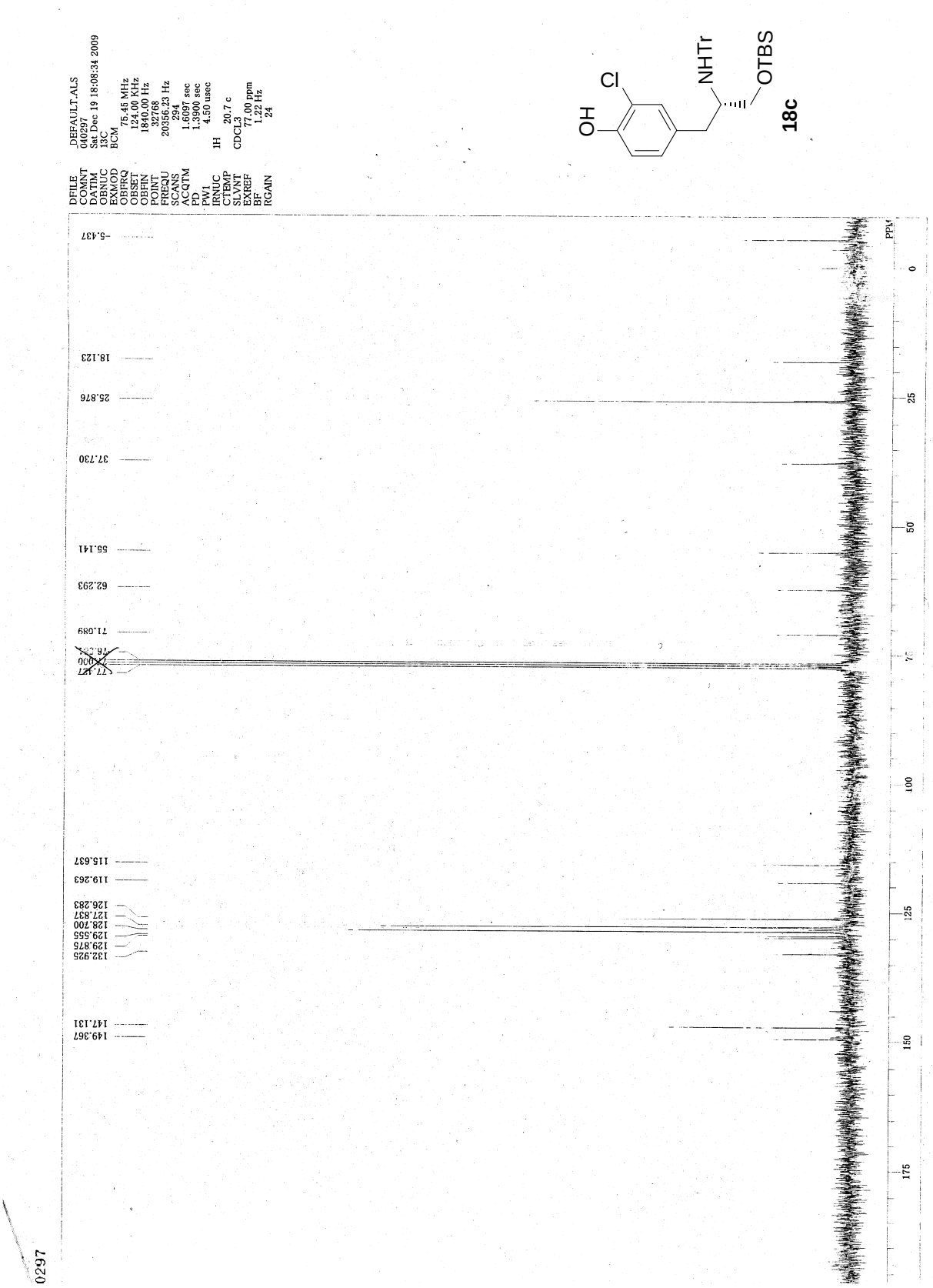

DEFAULT.ALS
Wed Sep 07 10:49:59 2005
13C
BCM
75.45 MHz
124.00 KHz
1840.00 Hz
32768
20356.23 Hz
351
1.6097 sec
1.3900 sec
4.50 usec
1H
22.9 c
CDCL3
77.00 ppm
0.12 Hz
24
OTBS
Cl
NHTr
OTBS
17c
PPM
C:\WINNMR\COMMON\DEFAULT.ALS

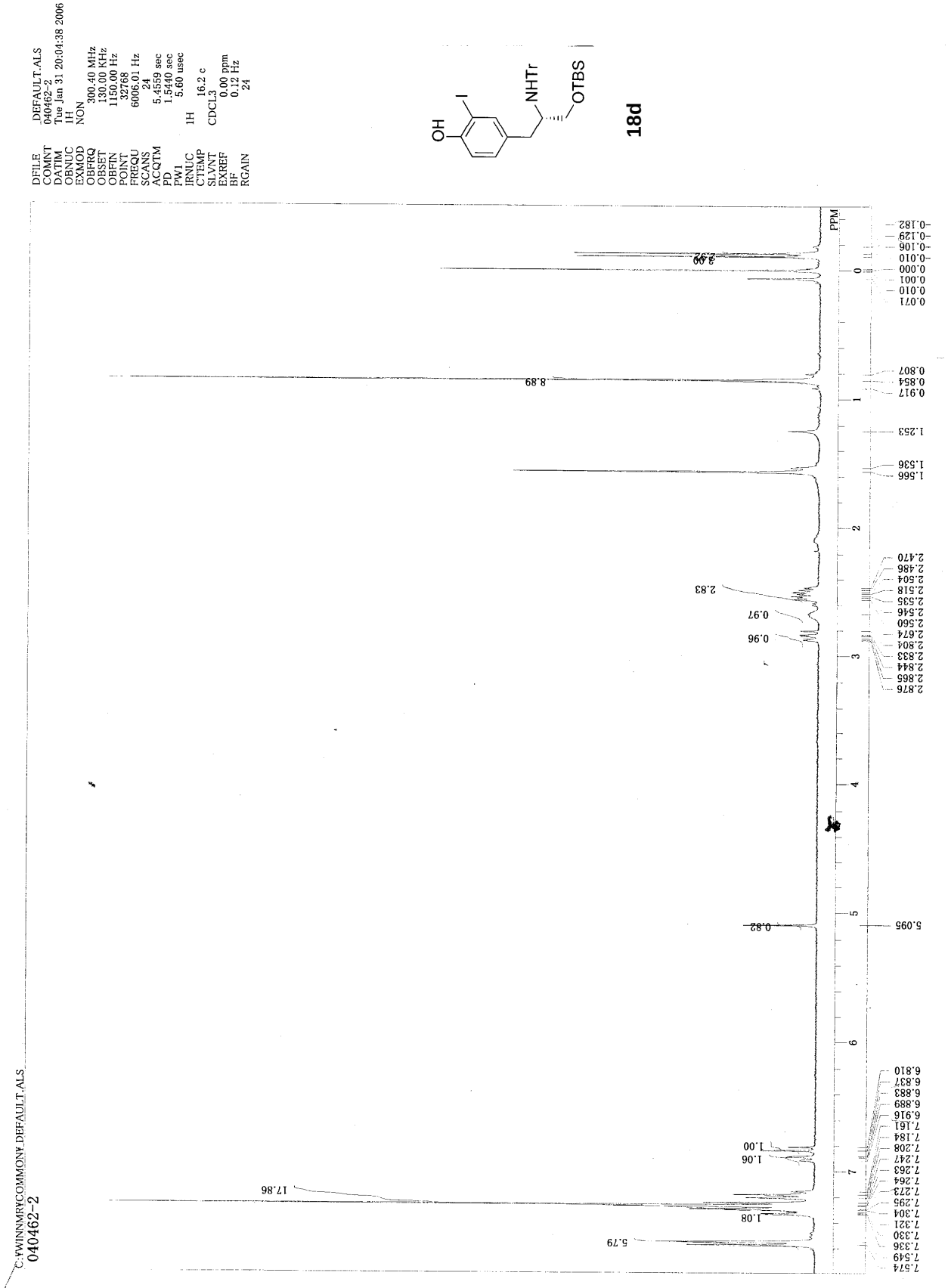

C:\Documents and Settings\user\fff
DFILE
COMNT
DATIM Thu Sep 08 19:20:03 2005
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 11
OTBS
I
NHTr
OTBS
17d
PPM

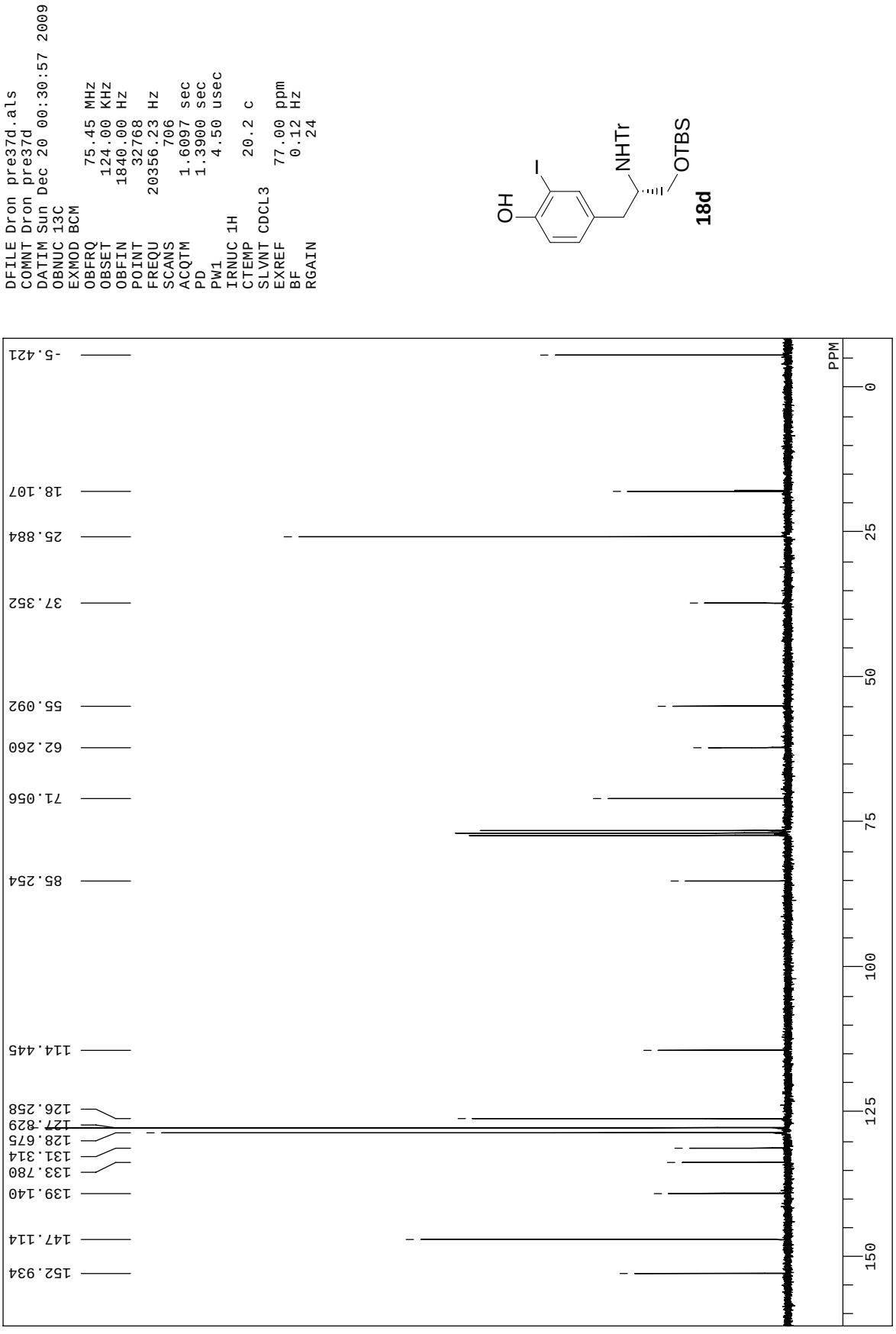

DFILE C:\Documents and Settings\user\fff
COMNT
DATIM Thu Sep 08 19:16:07 2005
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 287
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
OTBS
I
NHTr
OTBS
17d
-5.4042
-4.0395
18.1317
18.3207
25.8755
25.9166
34.6552
37.4256
55.1576
62.3261
71.0729
76.5725
77.0000
77.4193
90.1120
117.8733
126.2584
127.8285
128.7163
130.3440
134.1667
140.5048
147.1636
153.2222
PPM
0
25
50
75
100
125
150
175
200

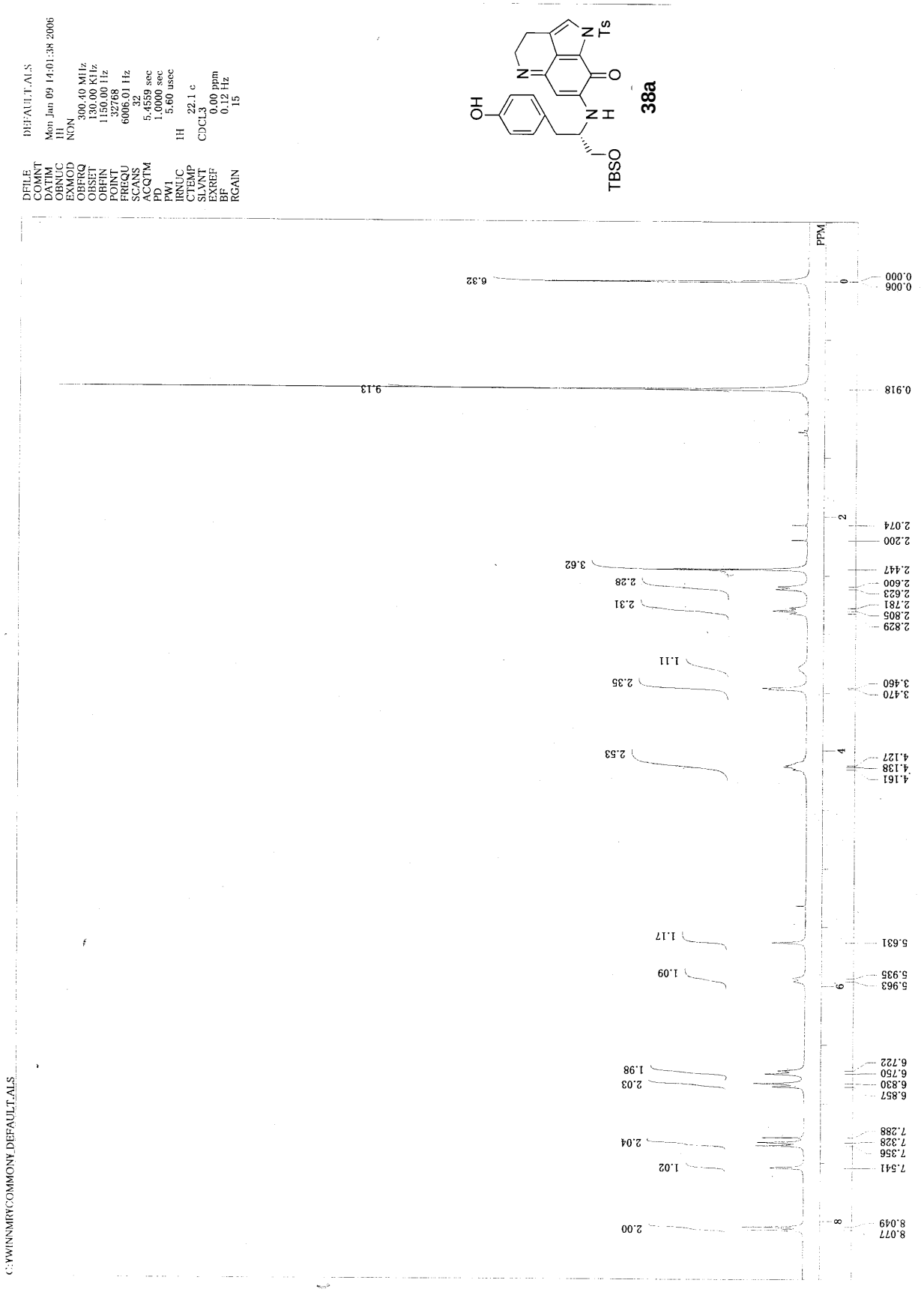

Date : Wed Mar
FileName
Comment
SliceHistory
EXMODE
POINT 16384 points
SAMPO 16384 points
FREQU 10000.0 Hz
FILTR 5000 Hz
DELAY 40.0 usec
DEADT 57.2 usec
INTVL 100.0 usec
TIMES 32 times
DUMMY 2 times
PD 1.0000 sec
ACQTM 1638.3999 msec
PREDL 0.01000 msec
1NINT 1000.0000 msec
RESOL 0.61 Hz
PW1 5.50 usec
1H
OBNUC
OBFRQ 500.00 MHz
OBSET 162167.63 Hz
REGAIN 17
SCANS 32 times
SLVNT CDCL3
SPINNING 12 Hz
TEMP 24.3 C
OH
NHTr
OTBS
18a
1H Line
ppm
6.24
10.00
2.33
0.97
0.89
1.18
2.00
2.22
10.06
6.61

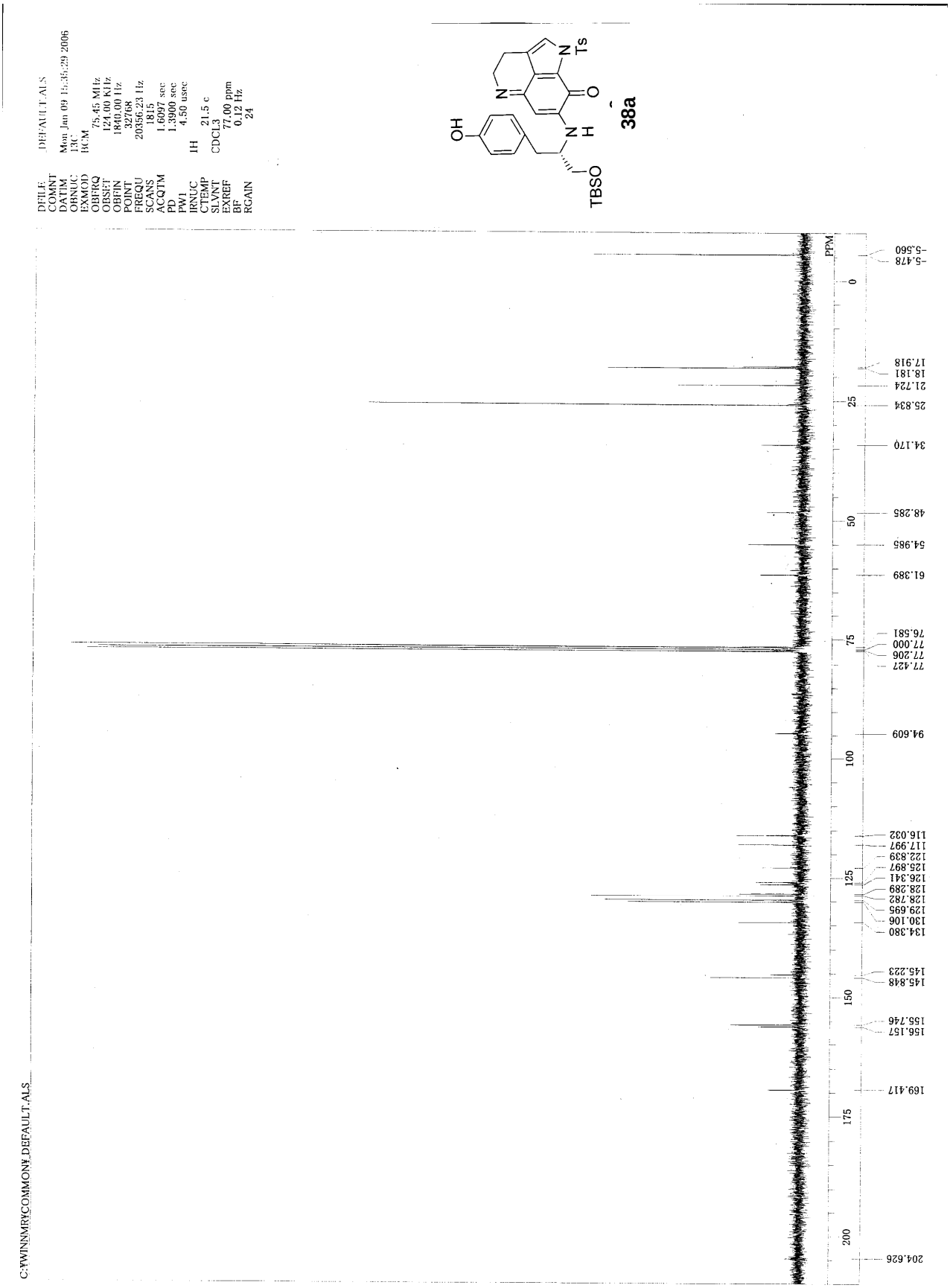

DEFAULT.ALS
040456
Sat Jan 28 20:01:53 2006
1H1
NON
300.40 MHz
130.00 KHz
1150.00 Hz
32768
6006.01 Hz
16
5.4559 sec
1.5440 sec
5.60 usec
1H
20.2 c
CDCL3
0.00 ppm
0.12 Hz
15
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
OH
Cl
NHTr
OTBS
18c
PPM
040456

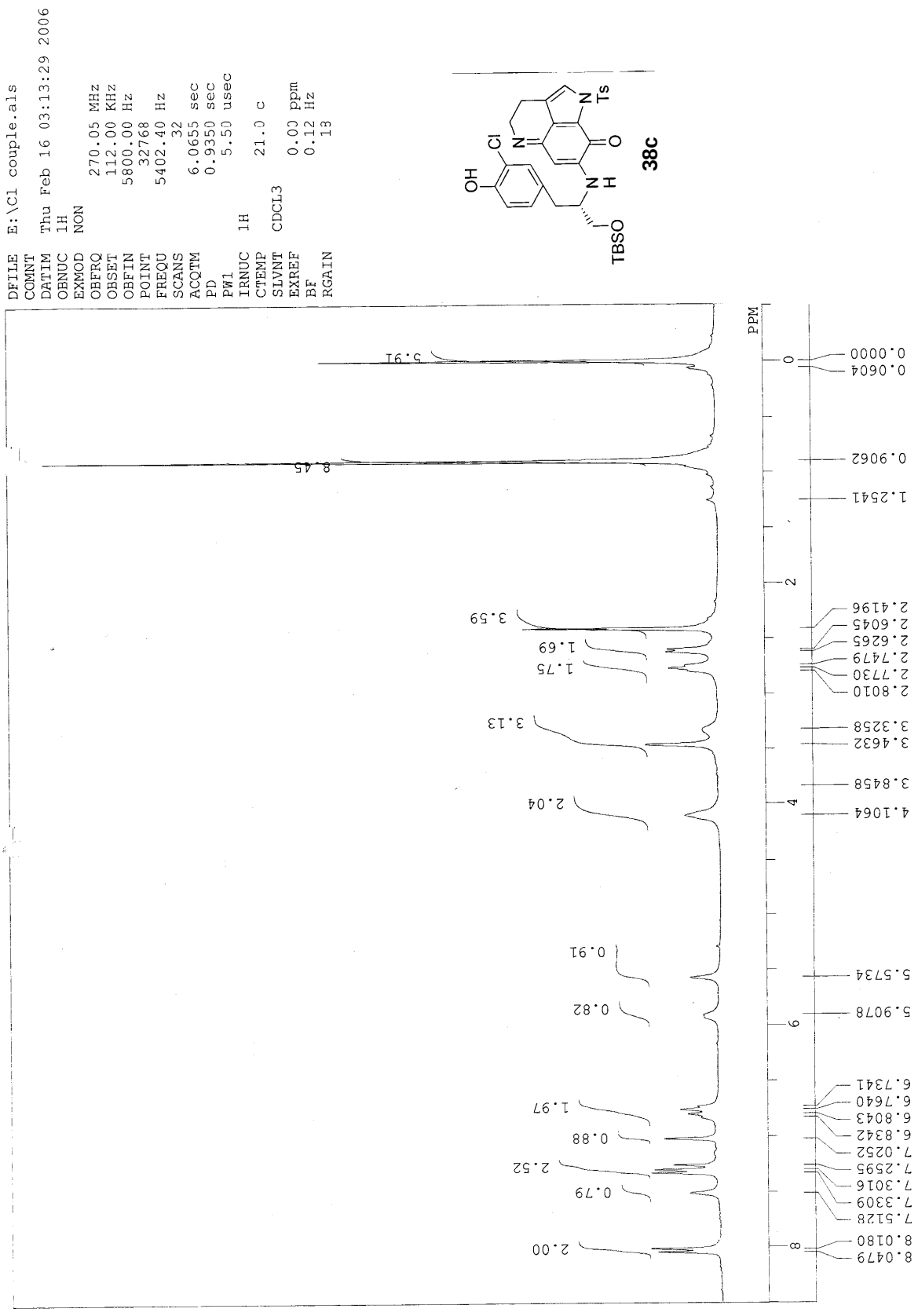

DEFAULT.ALS
040297
Sat Dec 19 18:08:34 2009
I3C
BCM
75.45 MHz
124.00 KHz
18432.00 Hz
32768
20356.23 Hz
294
1.6097 sec
1.3900 sec
4.50 usec
1H
20.7 c
CDCL3
77.00 ppm
1.22 Hz
24
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
Cl
NHTr
OTBS
OH
18c
-5.437
18.123
25.876
37.730
55.141
62.293
71.089
77.127
77.000
76.873
115.637
119.263
126.283
127.837
128.700
129.565
129.876
132.925
147.131
149.367
PPM
0
25
50
75
100
125
150
175
0297

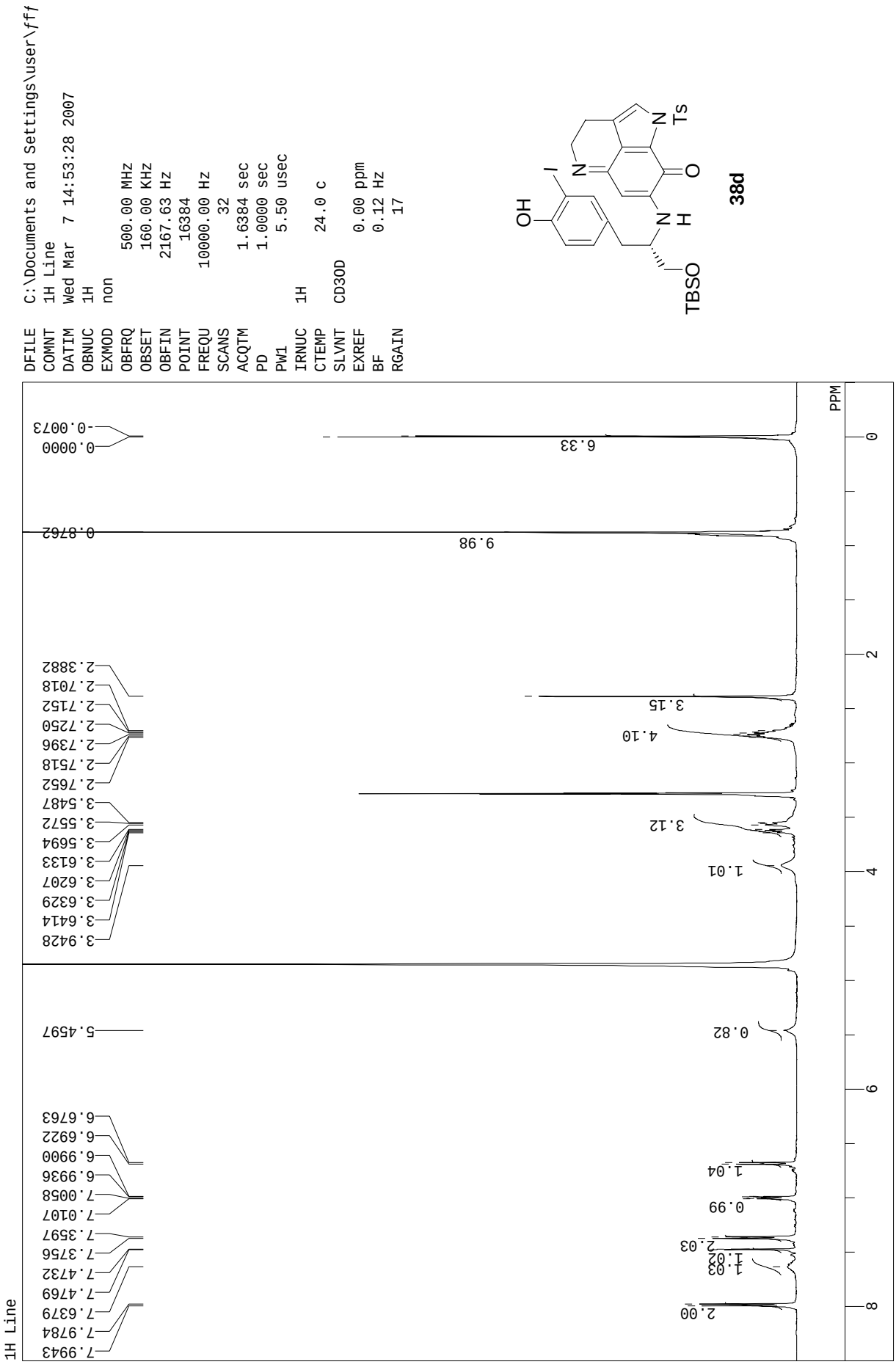

DEFAULT.ALS
040462-2
Tue Jan 31 20:04:38 2006
1H
NON
300.40 MHz
130.00 KHz
1150.00 Hz
32768
6006.01 Hz
24
5.4559 sec
1.5440 sec
5.60 usec
1H
16.2 c
CDCL3
0.00 ppm
0.12 Hz
24
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
OH
I
NHTr
OTBS
18d
PPM
C:\WINNMR\COMMON\DEFAULT.ALS
040462-2

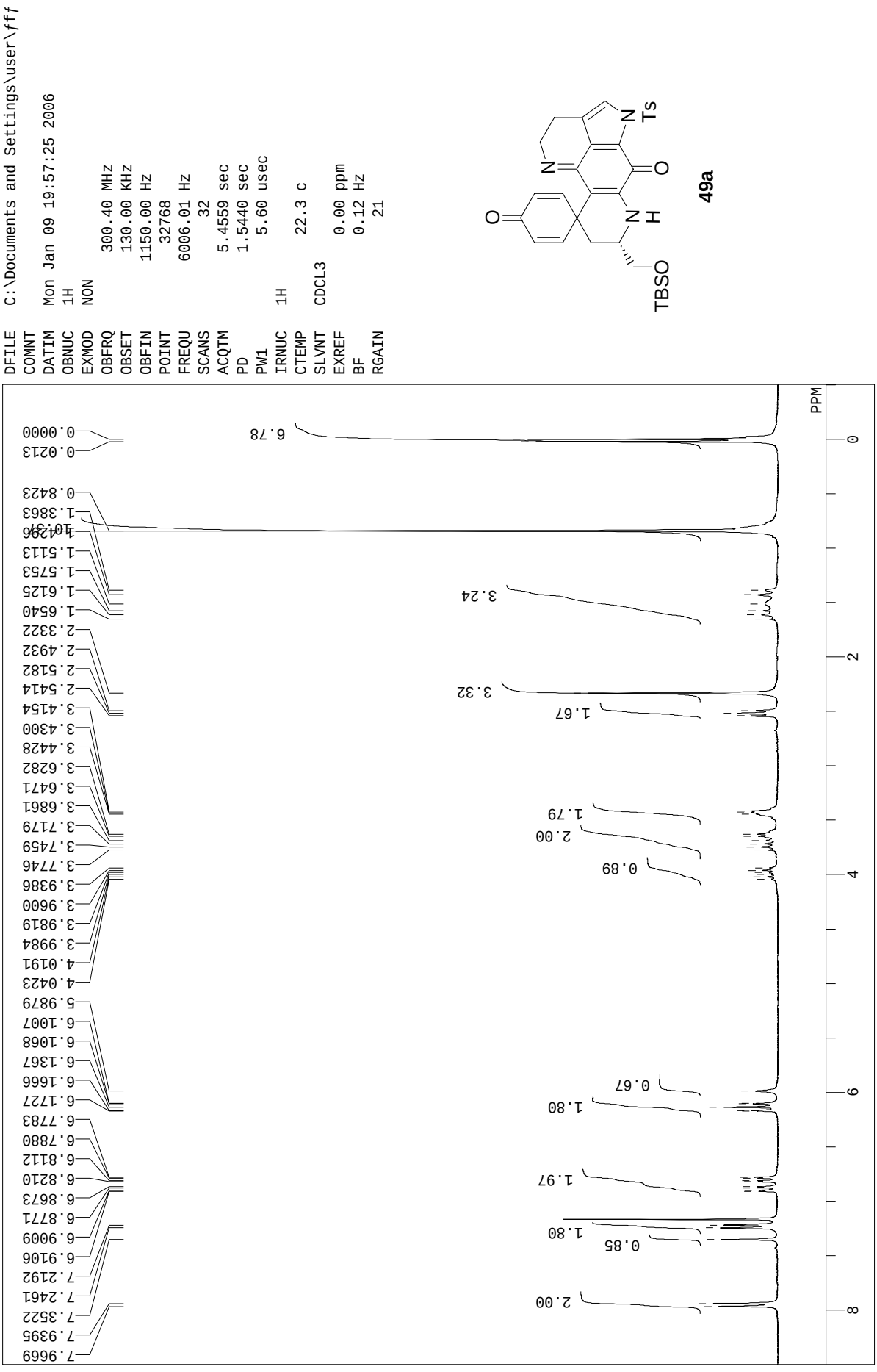

DFILE Dron pre37d.als
COMNT Dron pre37d
DATIM Sun Dec 20 00:30:57 2009
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 706
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
OH
I
NHTr
OTBS
18d
-5.421
18.107
25.884
37.352
55.092
62.260
71.056
85.254
114.445
126.258
127.829
128.675
131.314
133.780
139.140
147.114
152.934
PPM
0
25
50
75
100
125
150

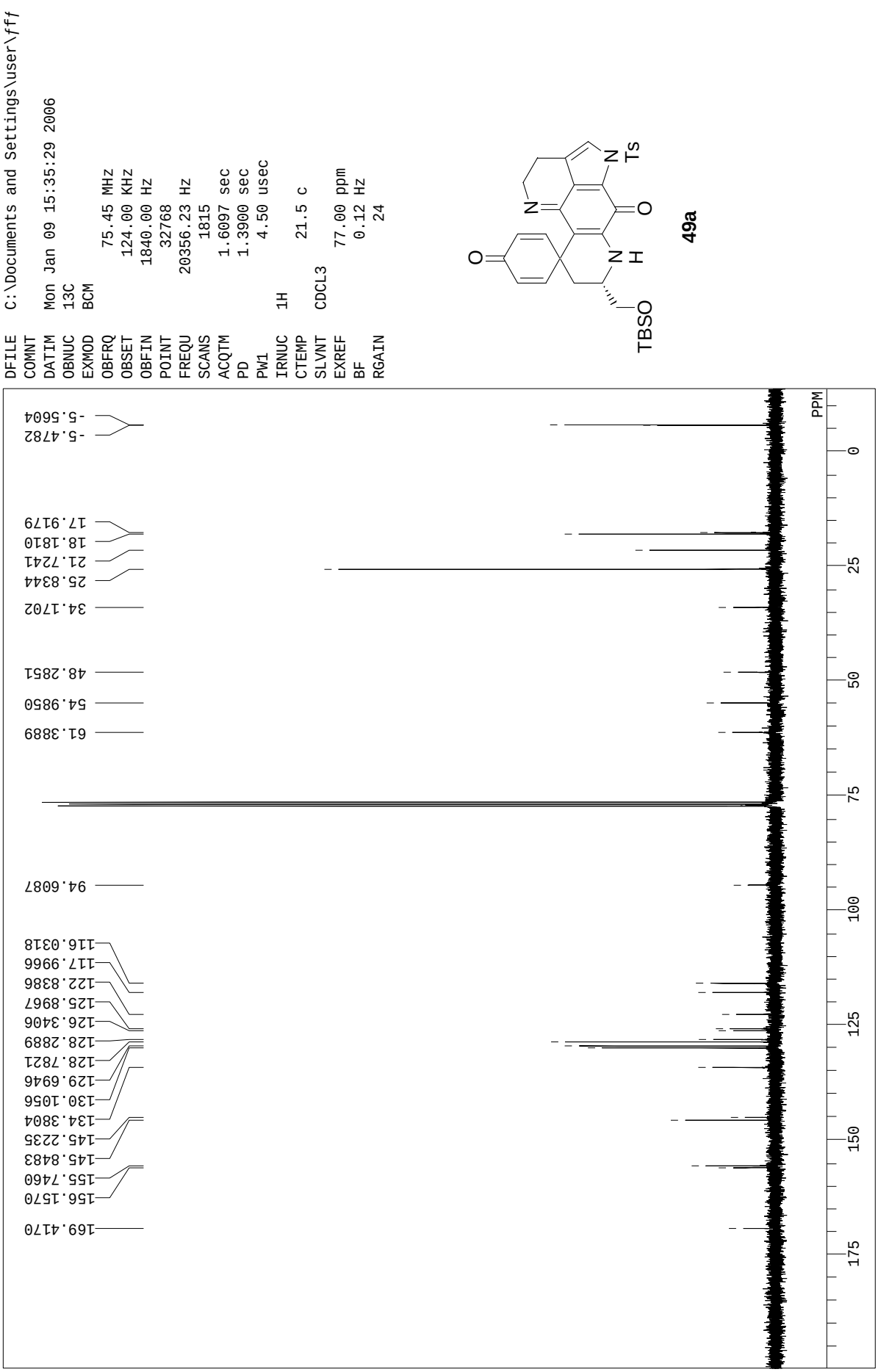

DEFILE DEFAULT.ALS
COMNT
DATIM Mon Jan 09 14:01:38 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 11150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 32
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15
OH
N
Ts
O
H
TBSO
38a
PPM
C:\WINNMR\COMMON\DEFAULT.ALS

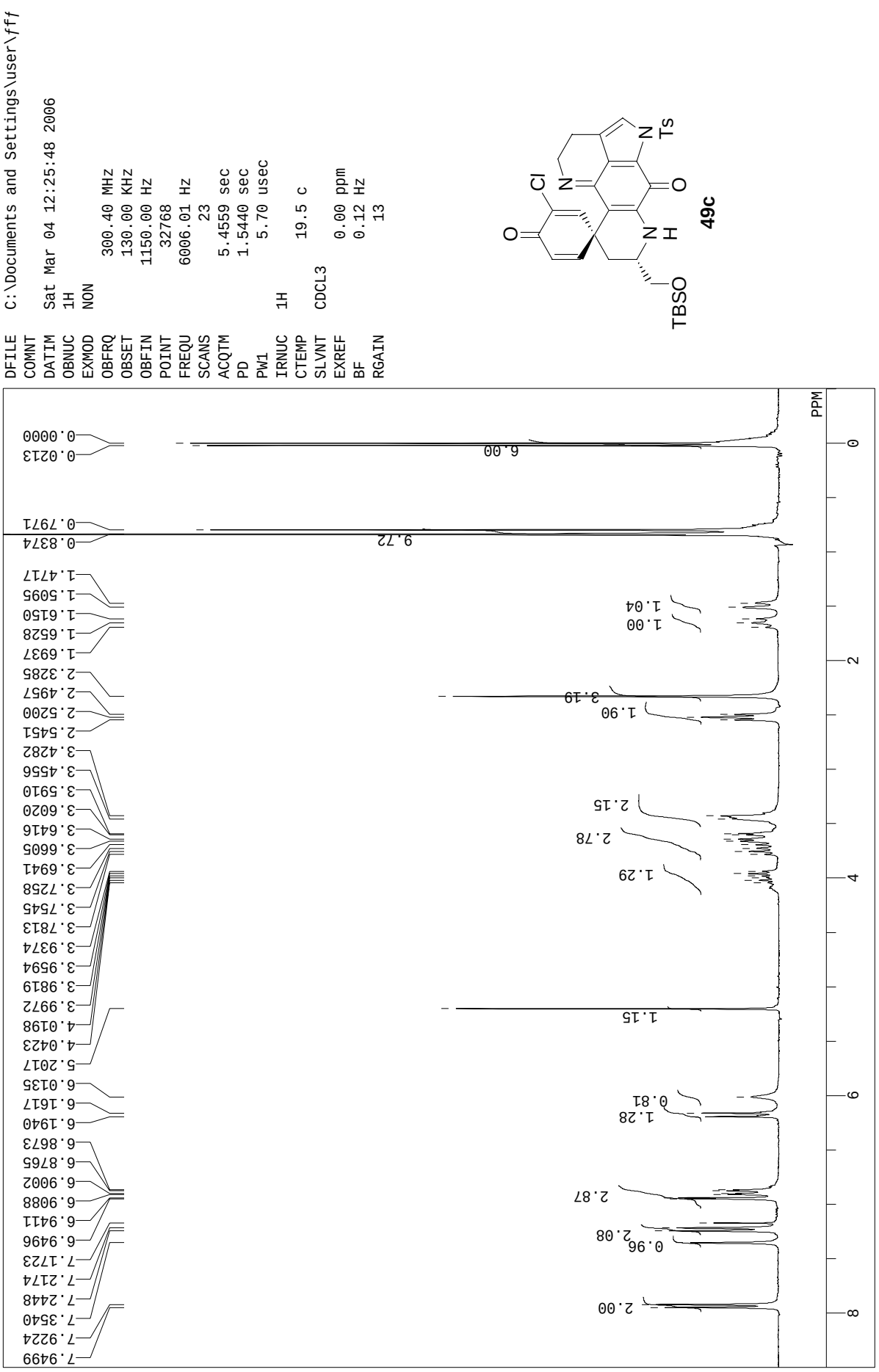

DEFAULT.ALS
Mon Jan 09 13:35:29 2006
13C
HCM
75.45 MHz
124.00 KHz
1840.00 Hz
32768
20356.23 Hz
1815
1.6097 sec
1.3900 sec
4.50 usec
1H
21.5 c
CDCL3
77.00 ppm
0.12 Hz
24
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
TBSO
OH
Ts
38a
PPM
-5.560
-5.478
17.918
18.181
21.724
25.834
34.170
48.285
54.985
61.389
76.581
77.000
77.206
77.427
94.609
116.032
117.997
122.839
125.897
126.341
128.289
128.782
129.695
130.106
134.380
145.223
145.848
155.746
156.157
169.417
204.626
C:\WINNMR\COMMON\DEFAULT.ALS

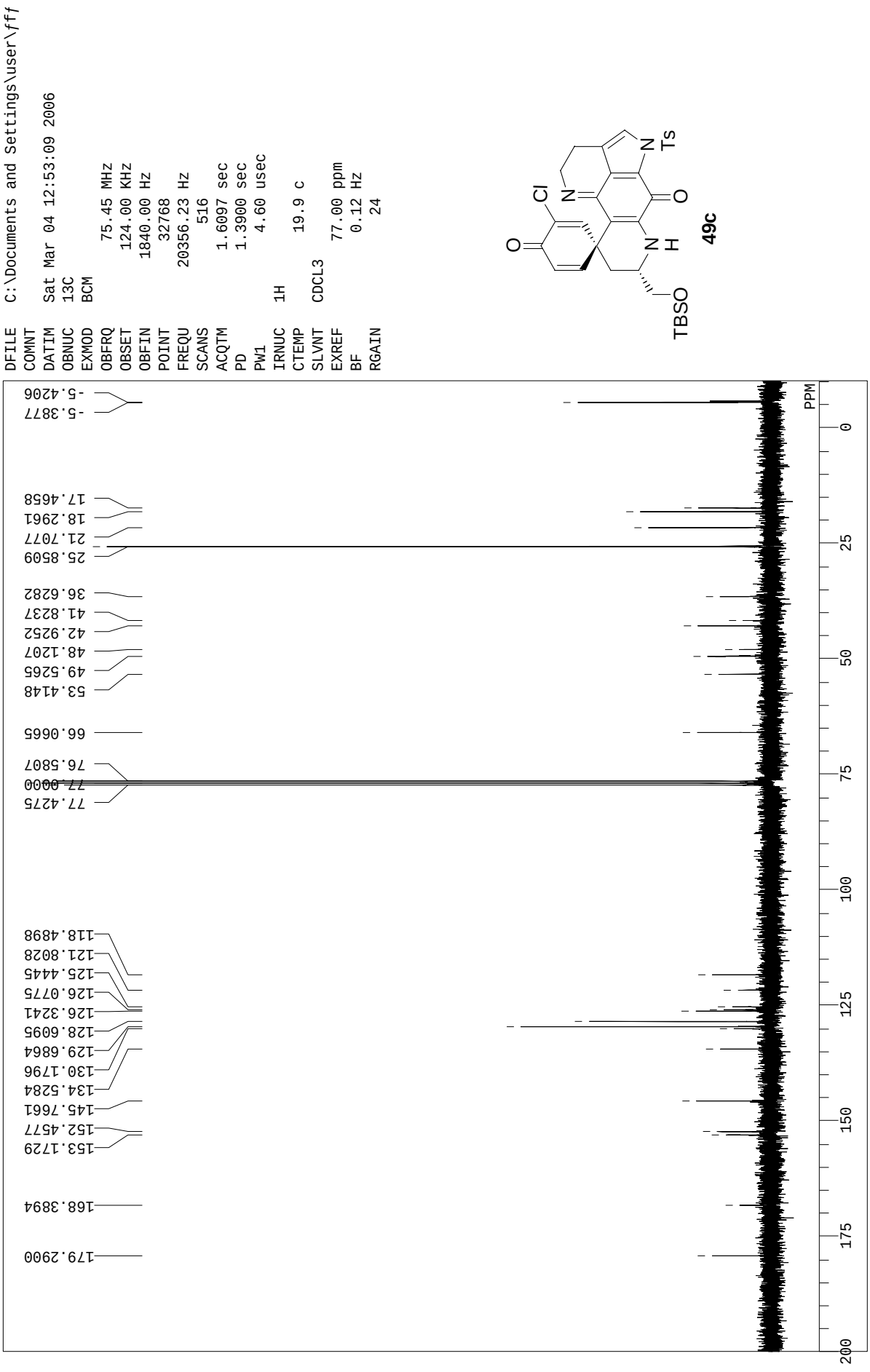

DFILE E:\Cl couple.als
COMNT
DATIM Thu Feb 16 03:13:29 2006
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 32768
FREQU 5402.40 Hz
SCANS 32
ACQTM 6.0655 sec
PD 0.9350 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13
38c
PPM
0.0000
0.0604
0.9062
1.2541
2.4196
2.6045
2.6265
2.7479
2.7730
2.8010
3.3258
3.4632
3.8458
4.1064
5.5734
5.9078
6.7341
6.7640
6.8043
6.8342
7.0252
7.2595
7.3016
7.3309
7.5128
8.0180
8.0479

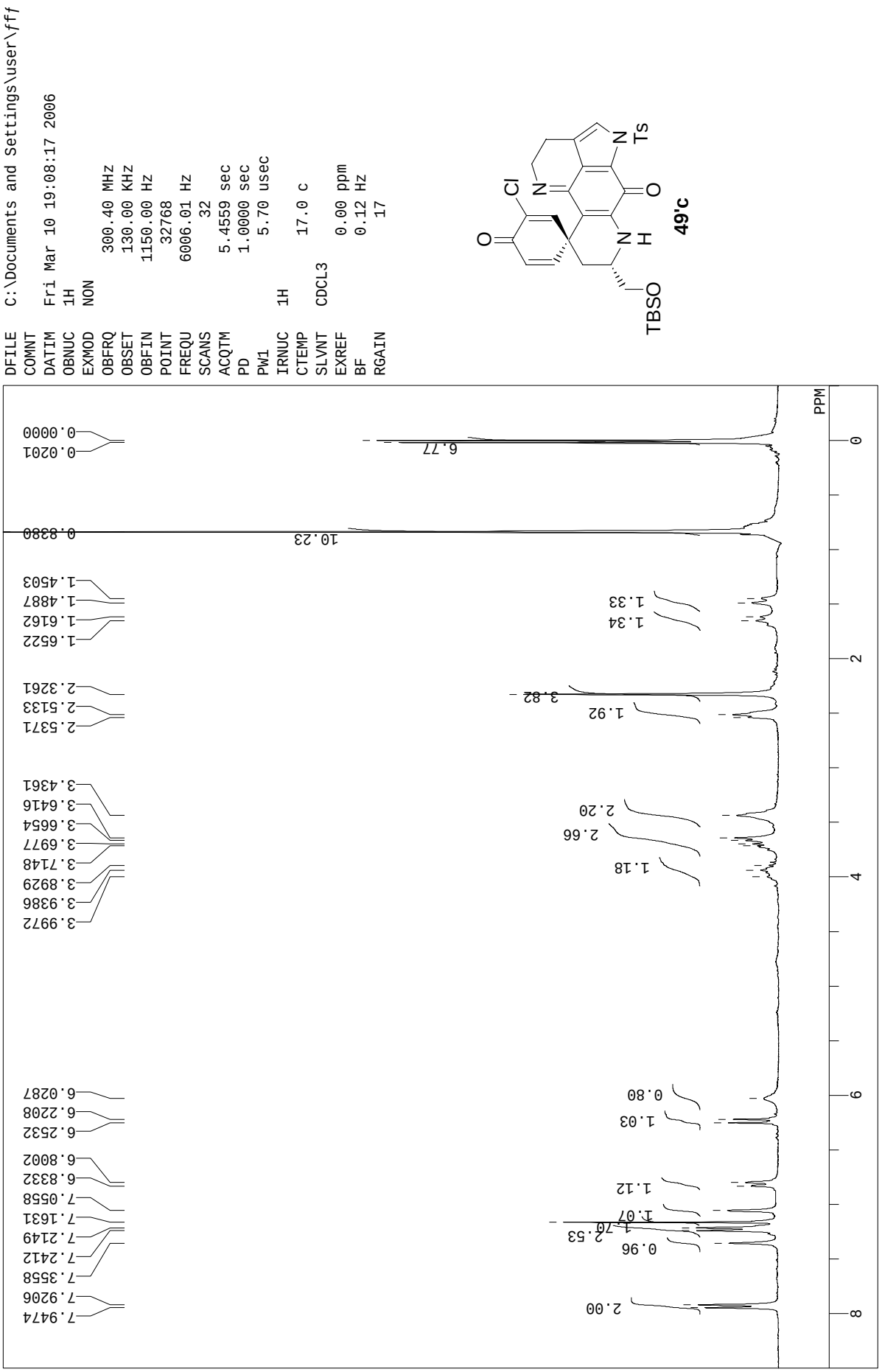

DFILE C:\Documents and Settings\user\fff
COMNT 1H Line
DATIM Wed Mar 7 14:53:28 2007
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2167.63 Hz
POINT 16384
FREQU 10000.00 Hz
SCANS 32
ACQTM 1.6384 sec
PD 1.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT CD3OD
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17
OH
I
N
N
Ts
O
N
H
TBSO
38d
1H Line
PPM
7.9943
7.9784
7.6379
7.4769
7.4732
7.3756
7.3597
7.0107
7.0058
6.9936
6.9900
6.9222
6.6763
5.4597
3.9428
3.6414
3.6329
3.6207
3.6133
3.5694
3.5572
3.5487
2.7652
2.7518
2.7396
2.7250
2.7152
2.7018
2.3882
0.8762
0.0000
-0.0073
6.33
9.98
3.15
4.10
3.12
1.01
0.82
2.00
1.03
1.02
2.03
0.99
1.04

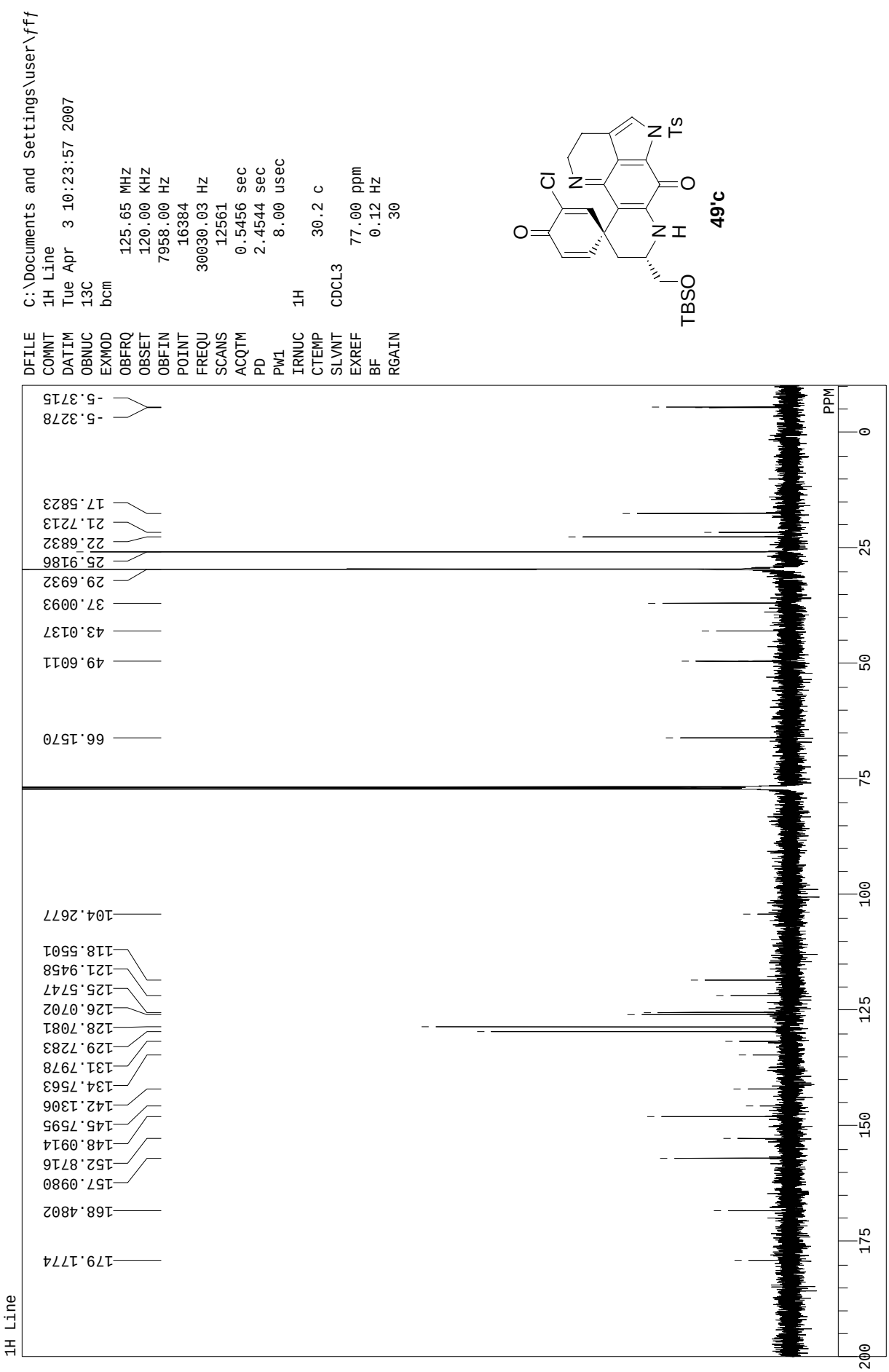

C:\Documents and Settings\user\fff
DFILE
COMNT
DATIM Mon Jan 09 19:57:25 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 32
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21
TBSO
N
H
O
N
Ts
O
49a
PPM
0
2
4
6
8
6.78
3.24
3.32
1.67
1.79
2.00
0.89
0.67
1.80
1.97
1.80
0.85
2.00

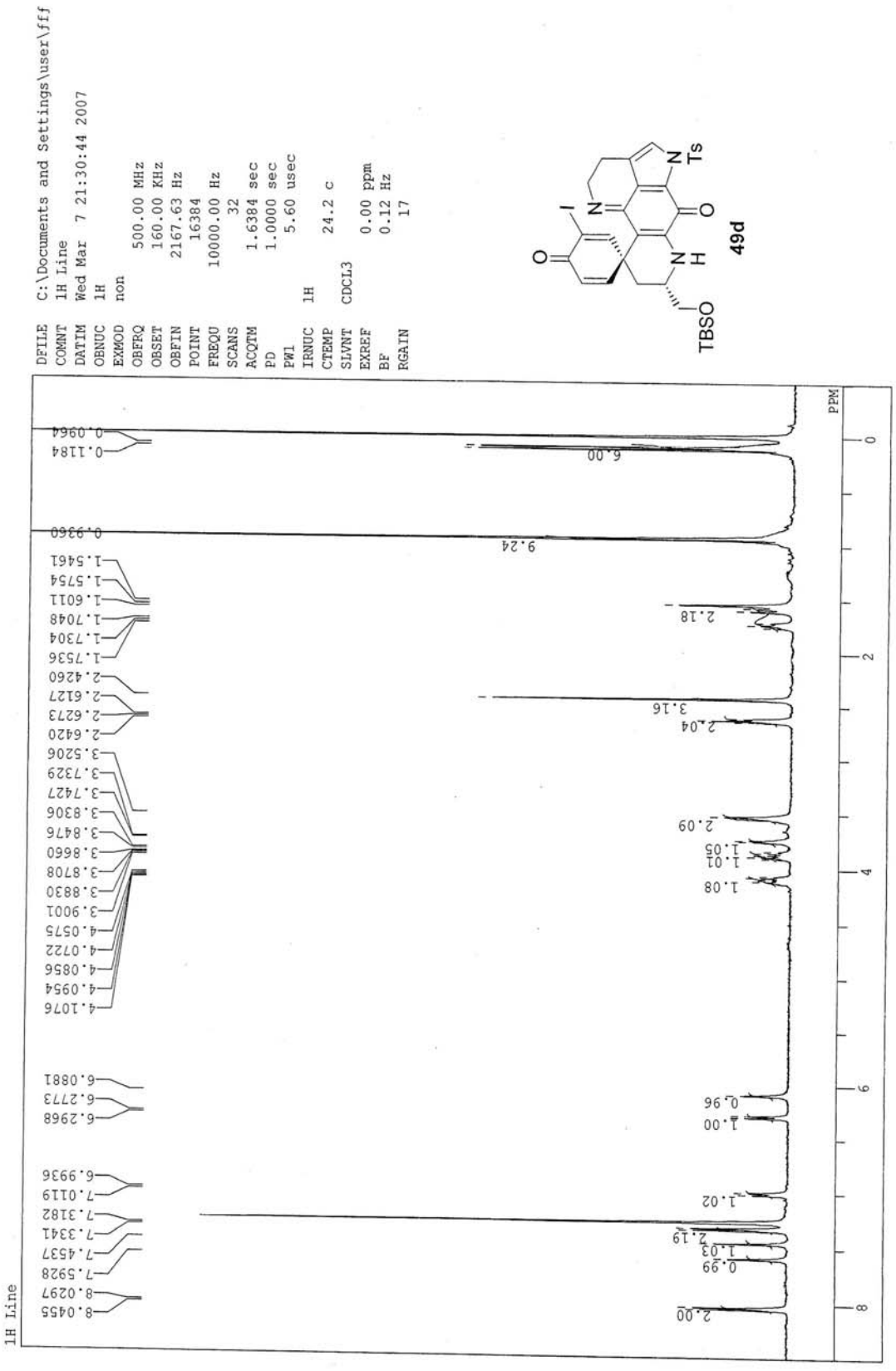

DFILE C:\Documents and Settings\user\fff
COMNT
DATIM Mon Jan 09 15:35:29 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 1815
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
TBSO
O
N
H
N
O
N
Ts
49a
-5.5604
-5.4782
17.9179
18.1810
21.7241
25.8344
34.1702
48.2851
54.9850
61.3889
94.6087
116.0318
117.9966
122.8386
125.8967
126.3406
128.2889
128.7821
129.6946
130.1056
134.3804
145.2235
145.8483
155.7460
156.1570
169.4170
PPM
0
25
50
75
100
125
150
175

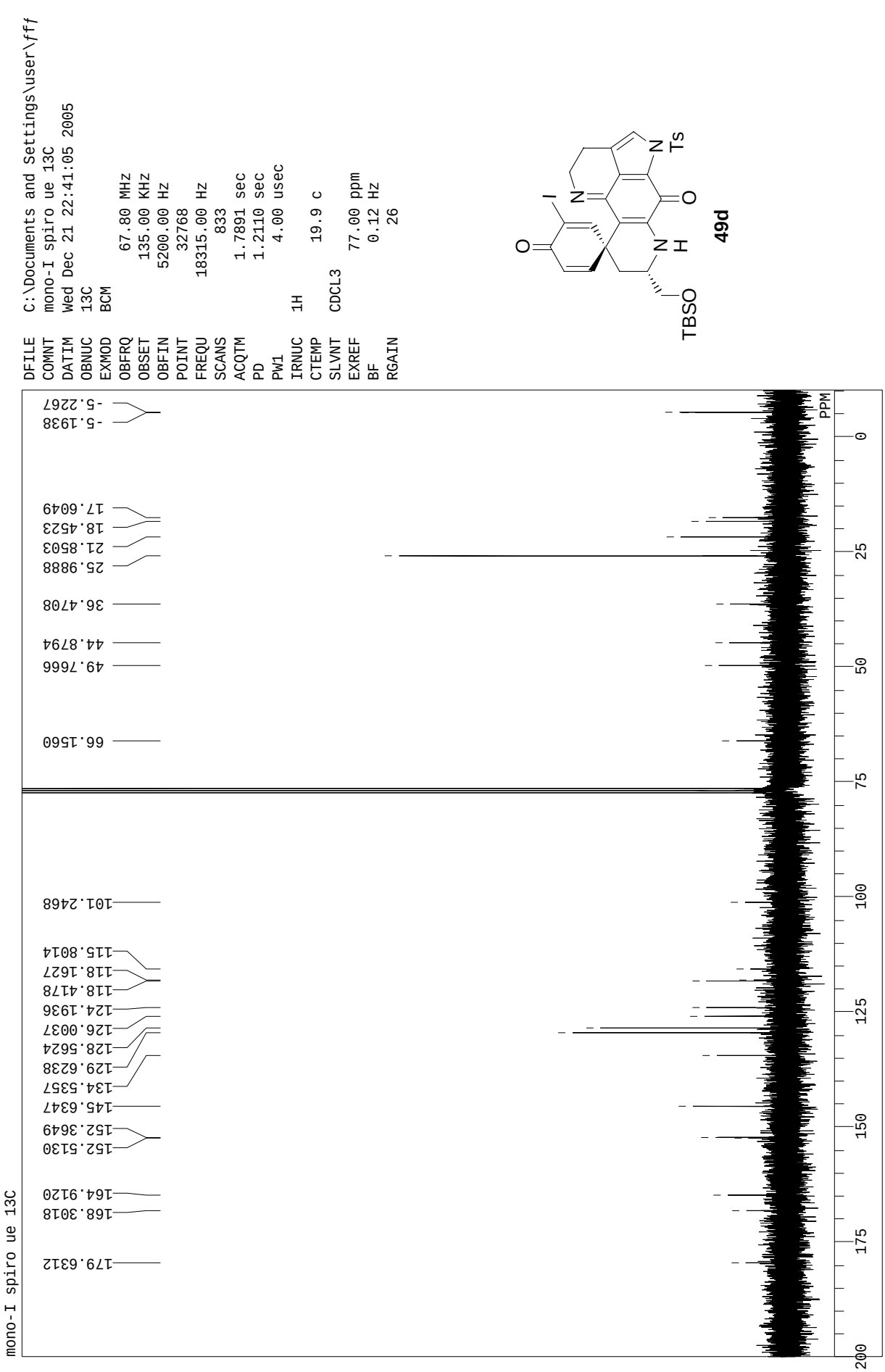

DFILE C:\Documents and Settings\user\fff
COMNT
DATIM Sat Mar 04 12:25:48 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 23
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.70 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13
Cl
N
Ts
O
O
N
H
TBSO
49c
PPM
0
2
4
6
8
6.00
9.72
1.04
1.00
3.19
1.90
2.15
2.78
1.29
1.15
0.81
1.28
2.87
0.96
2.08
2.00

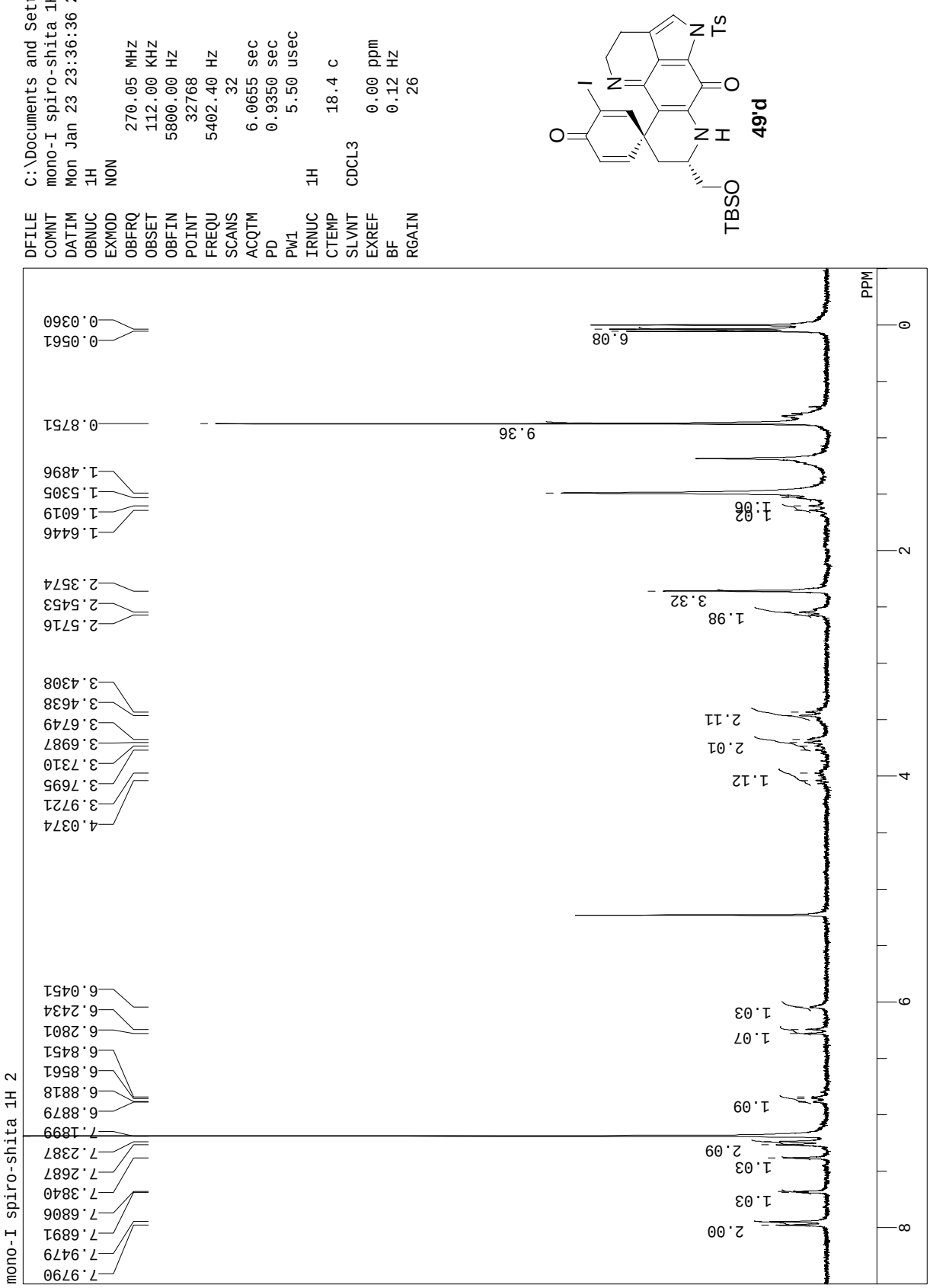

C:\Documents and Settings\user\fff
DFILE
COMNT Sat Mar 04 12:53:09 2006
DATIM
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 516
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.60 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
Cl
N
Ts
O
O
N
H
TBSO
49c
-5.4206
-5.3877
17.4658
18.2961
21.7077
25.8509
36.6282
41.8237
42.9252
48.1207
49.5265
53.4148
66.0665
76.5807
77.0000
77.4275
118.4898
121.8028
125.4445
126.0775
126.3241
128.6095
129.6864
130.1796
134.5284
145.7661
152.4577
153.1729
168.3894
179.2900
PPM
0
25
50
75
100
125
150
175
200

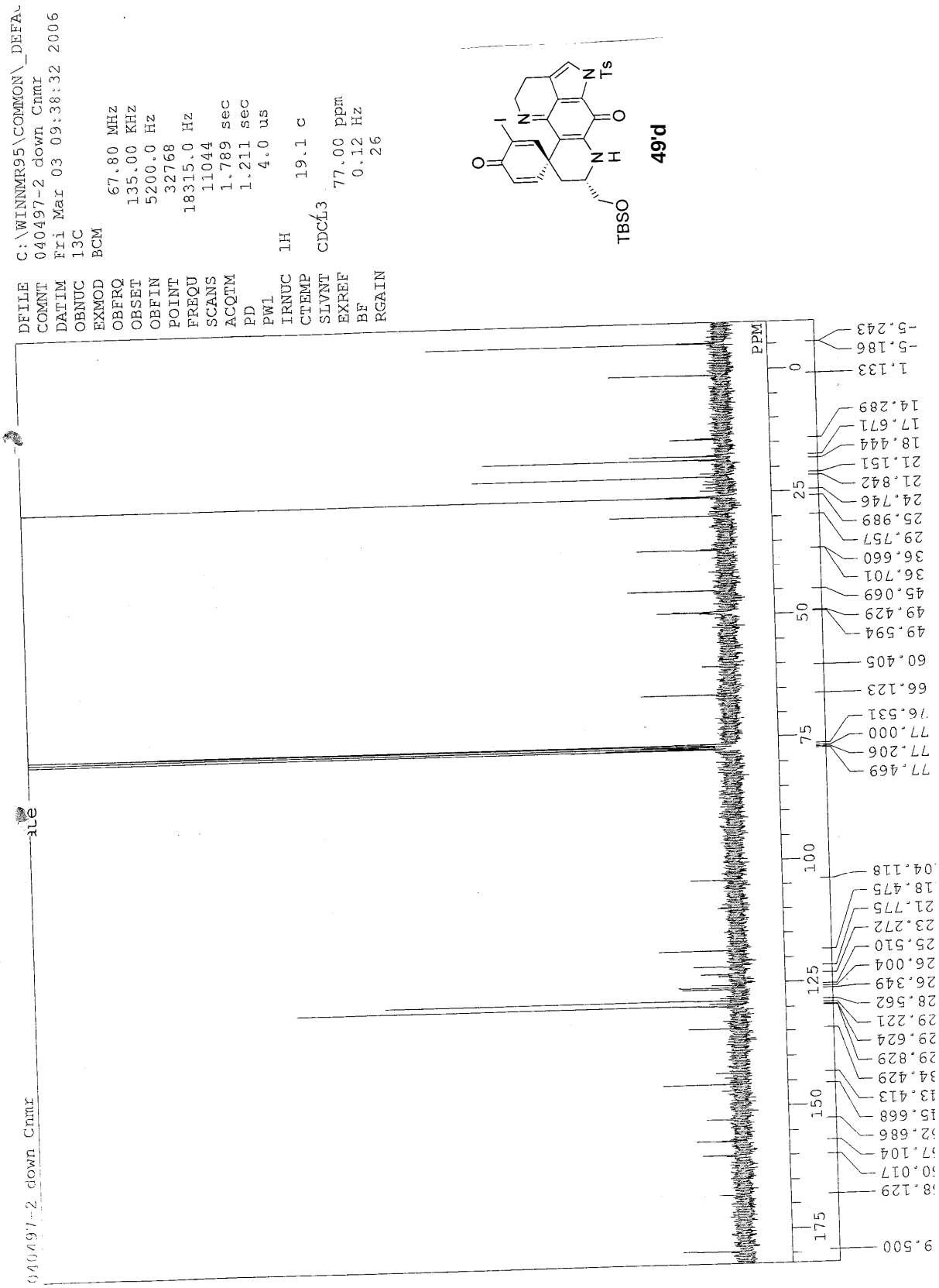

DFILE C:\Documents and Settings\user\fff
COMNT
DATIM Fri Mar 10 19:08:17 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 32
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.70 usec
IRNUC 1H
CTEMP 17.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17
TBSO
Cl
Ts
49'c
PPM

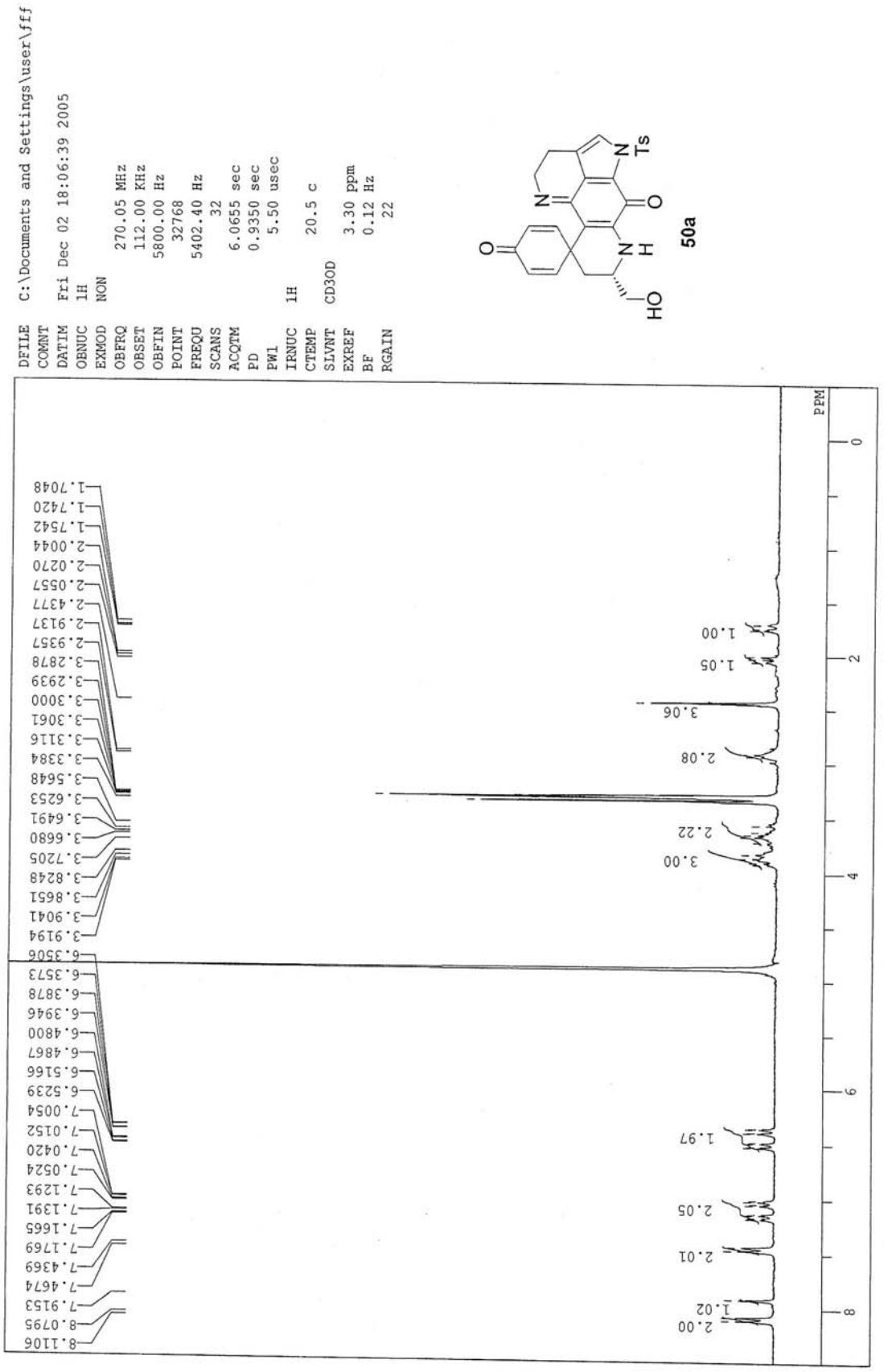

DFILE C:\Documents and Settings\user\fff
COMNT 1H Line
DATIM Tue Apr 3 10:23:57 2007
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 16384
FREQU 30030.03 Hz
SCANS 12561
ACQTM 0.5456 sec
PD 2.4544 sec
PW1 8.00 usec
IRNUC 1H
CTEMP 30.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 30
Cl
N
Ts
O
O
N
H
TBSO
49'c
1H Line
PPM
-5.3715
-5.3278
17.5823
21.7213
22.6832
25.9186
29.6932
37.0093
43.0137
49.6011
66.1570
104.2677
118.5501
121.9458
125.5747
126.0702
128.7081
129.7283
131.7978
134.7563
142.1306
145.7595
148.0914
152.8716
157.0980
168.4802
179.1774

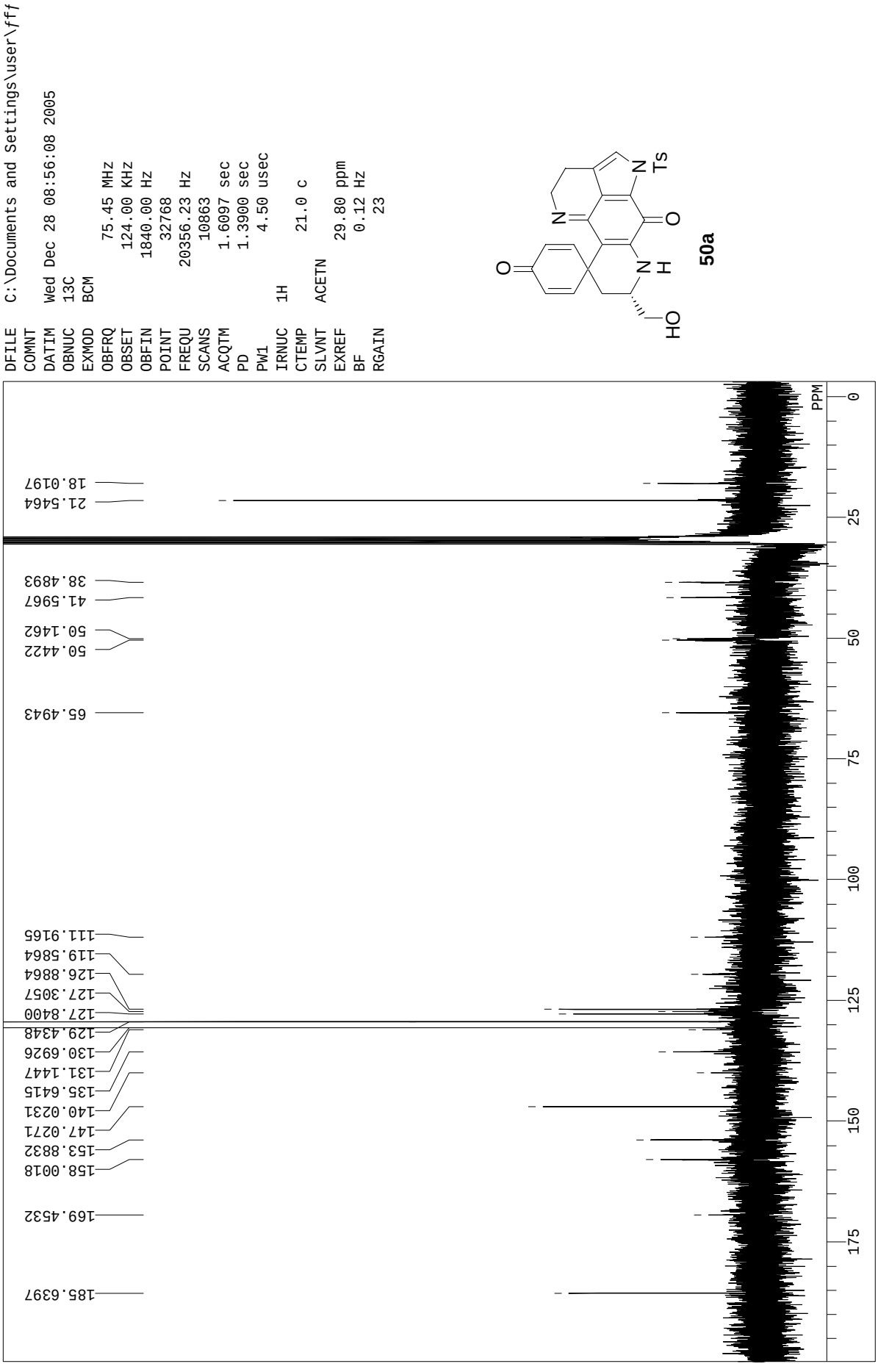

DFILE C:\Documents and Settings\user\fff
COMNT 1H Line
DATIM Wed Mar 7 21:30:44 2007
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2167.63 Hz
POINT 16384
FREQU 10000.00 Hz
SCANS 32
ACQTM 1.6384 sec
PD 1.0000 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17
TBSO
Ts
49d
1H Line
PPM

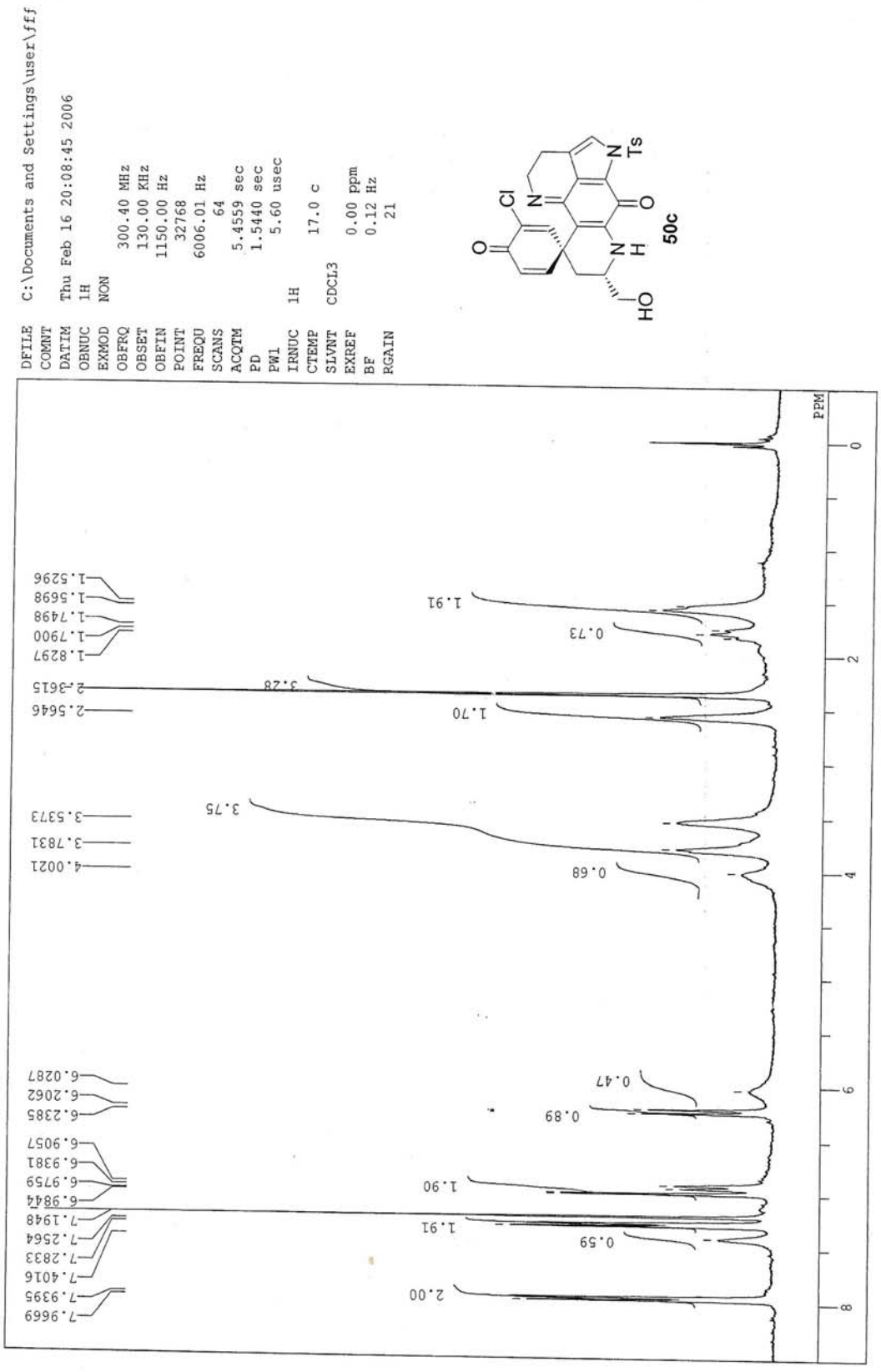

DFILE C:\Documents and Settings\user\fff
COMNT mono-I spiro ue 13C
DATIM Wed Dec 21 22:41:05 2005
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18315.00 Hz
SCANS 833
ACQTM 1.7891 sec
PD 1.2110 sec
PW1 4.00 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 26
TBSO
O
I
N
O
N
H
N
Ts
49d
mono-I spiro ue 13C
-5.2267
-5.1938
17.6049
18.4523
21.8503
25.9888
36.4708
44.8794
49.7666
66.1560
101.2468
115.8014
118.1627
118.4178
124.1936
126.0037
128.5624
129.6238
134.5357
145.6347
152.3649
152.5130
164.9120
168.3018
179.6312
PPM
0
25
50
75
100
125
150
175
200

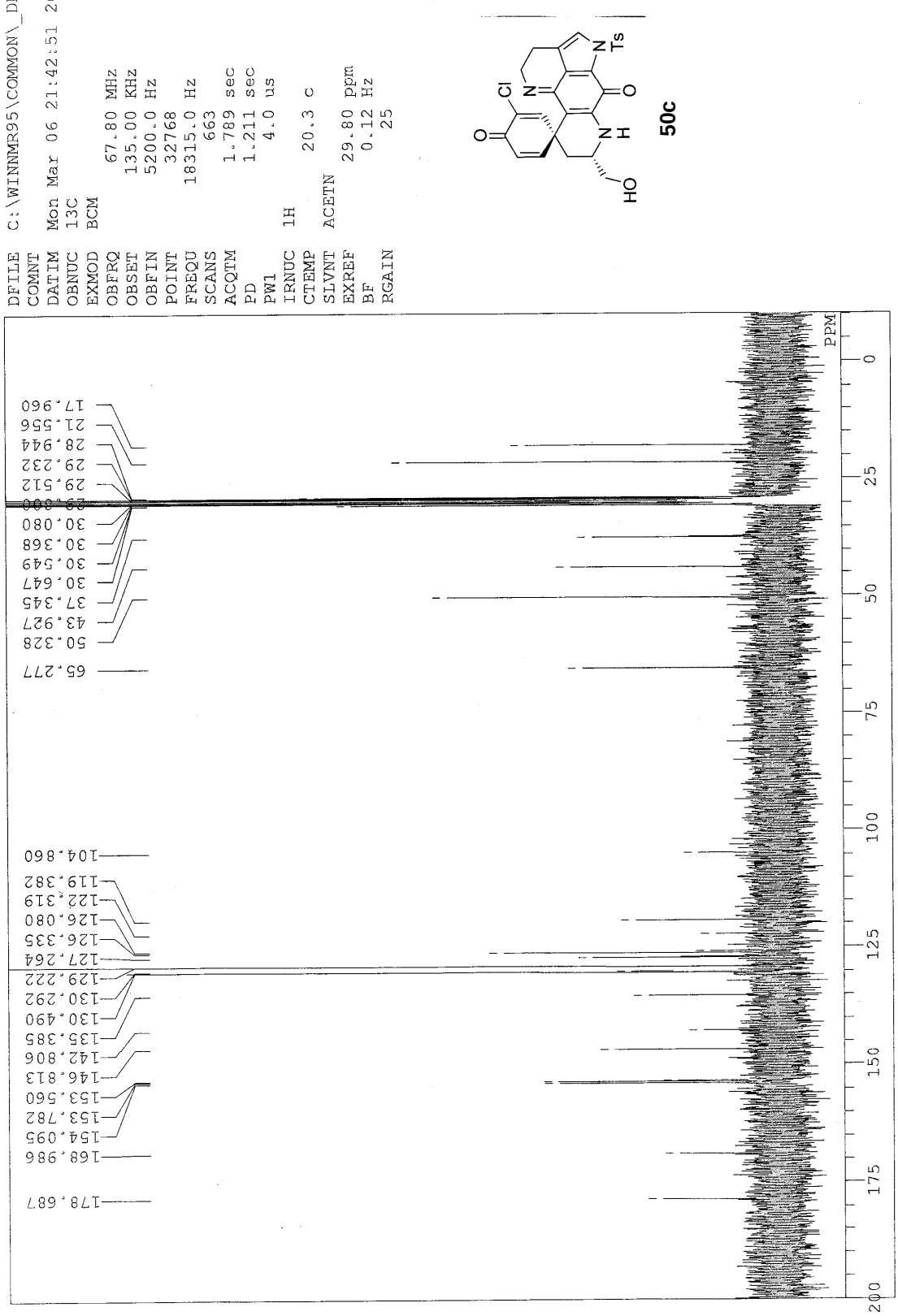

DFILE C:\Documents and Settings\user\fff
COMNT mono-I spiro-shita 1H 2
DATIM Mon Jan 23 23:36:36 2006
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 32768
FREQU 5402.40 Hz
SCANS 32
ACQTM 6.0655 sec
PD 0.9350 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 18.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26
TBSO
Ts
49'd
mono-I spiro-shita 1H 2
PPM
0
2
4
6
8
0.0360
0.0561
0.8751
1.4896
1.5305
1.6019
1.6446
2.3574
2.5453
2.5716
3.4308
3.4638
3.6749
3.6987
3.7310
3.7695
3.9721
4.0374
6.0451
6.2434
6.2801
6.8451
6.8561
6.8818
6.8879
7.1899
7.2387
7.2687
7.3840
7.6806
7.6891
7.9479
7.9790
6.08
9.36
1.06
1.02
3.32
1.98
2.11
2.01
1.12
1.03
1.07
1.09
2.09
1.03
1.03
2.00

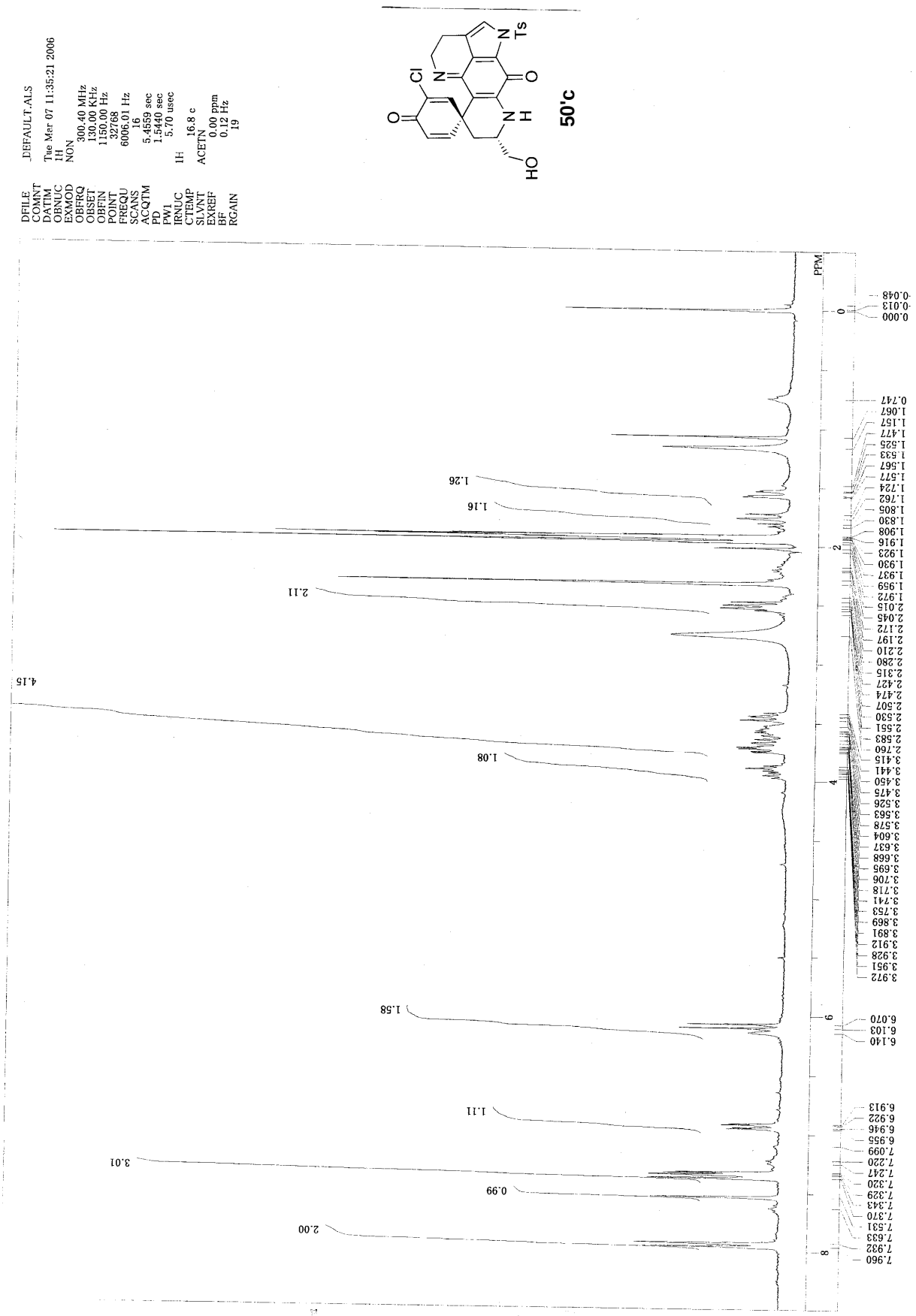

49'd
TBSO
Ts
N
H
O
DFILE C:\WINNMR95\COMMON_DEFA
COMNT 040497-2 down Cnmr
DATIM Fri Mar 03 09:38:32 2006
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 11044
ACQTM 1.789 sec
PD 1.211 sec
PW1 4.0 us
IRNUC 1H
CTEMP 19.1 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 26
040497-2 down Cnmr
PPM
-5.243
-5.186
1.133
14.289
17.671
18.444
21.151
21.842
24.746
25.989
29.757
36.660
36.701
45.069
49.429
49.594
60.405
66.123
76.531
77.000
77.206
77.469
104.118
18.475
21.775
23.272
25.510
26.004
26.349
28.562
29.221
29.624
29.829
34.429
13.413
15.668
52.686
57.104
50.017
58.129
9.500

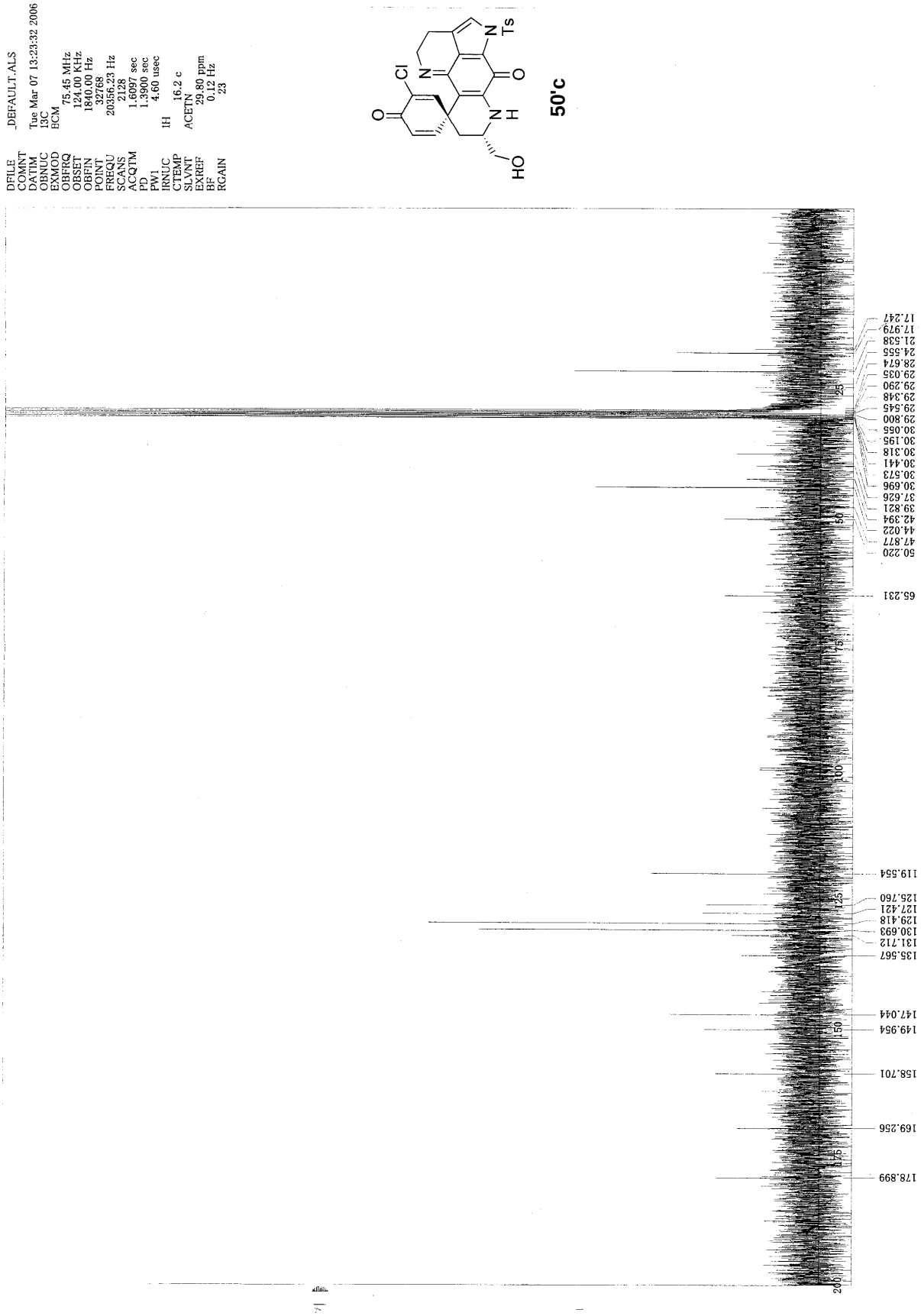

DFILE C:\Documents and Settings\user\fff
COMNT
DATIM Fri Dec 02 18:06:39 2005
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 32768
FREQU 5402.40 Hz
SCANS 32
ACQTM 6.0655 sec
PD 0.9350 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CD3OD
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 22
50a
Ts
HO
PPM

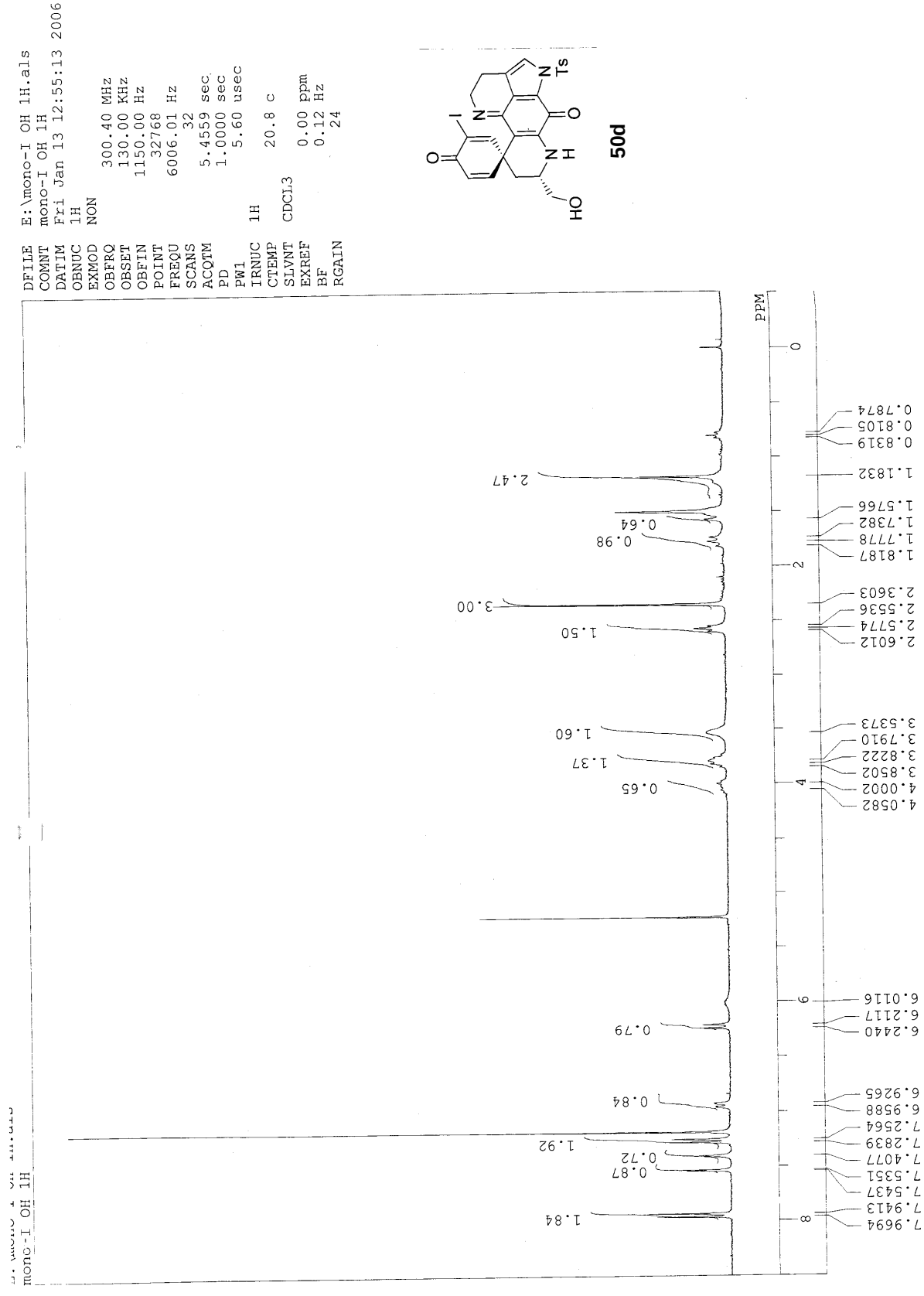

DFILE C:\Documents and Settings\user\fff
COMNT
DATIM Wed Dec 28 08:56:08 2005
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 10863
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT ACETN
EXREF 29.80 ppm
BF 0.12 Hz
RGAIN 23
50a
PPM
0
25
50
75
100
125
150
175
18.0197
21.5464
38.4893
41.5967
50.1462
50.4422
65.4943
111.9165
119.5864
126.8864
127.3057
127.8400
129.4348
130.6926
131.1447
135.6415
140.0231
147.0271
153.8832
158.0018
169.4532
185.6397

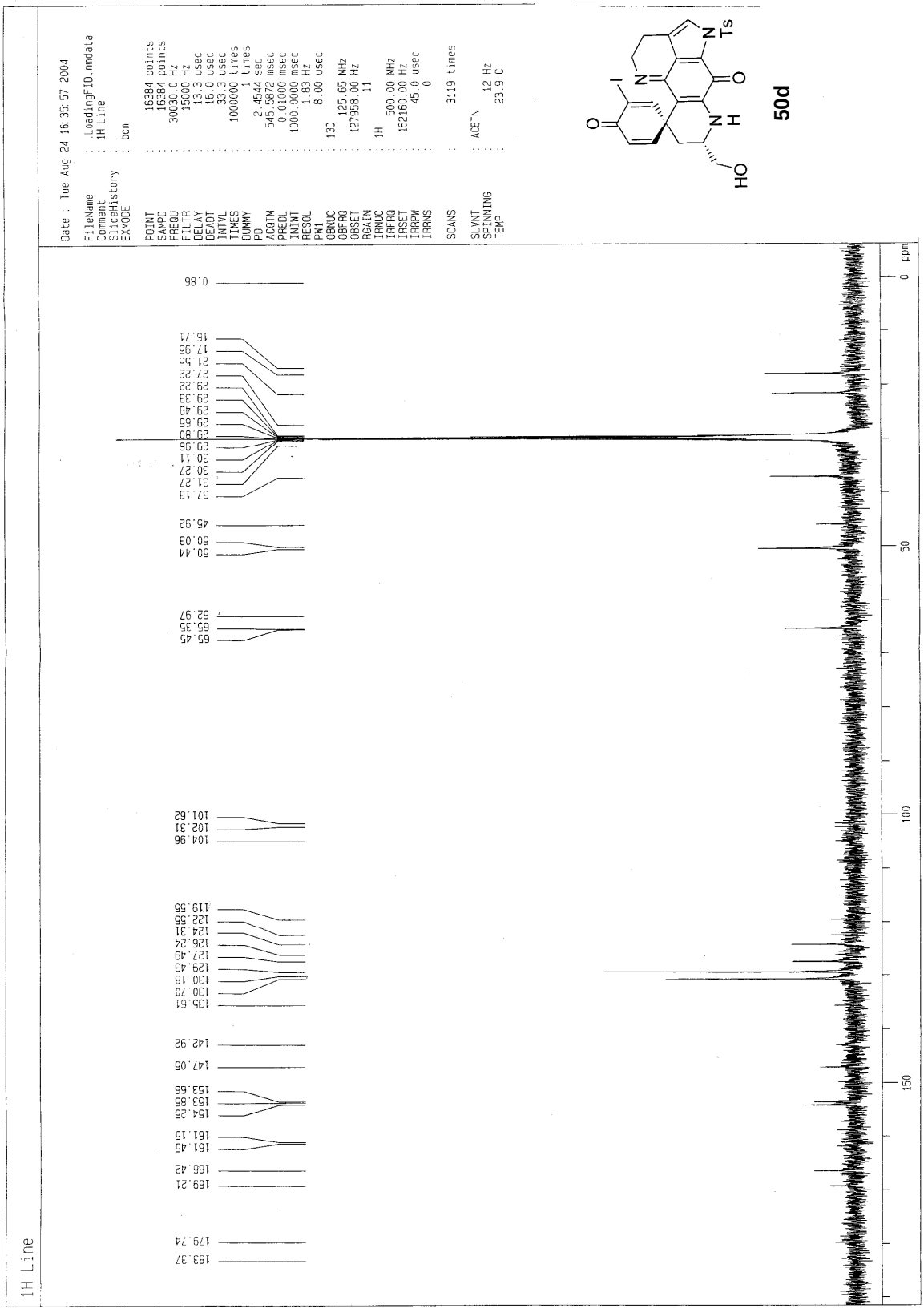

DFILE C:\Documents and Settings\user\fff
COMNT
DATIM Thu Feb 16 20:08:45 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 64
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 17.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21
Cl
N
Ts
O
N
O
N
H
HO
50c
PPM
0
2
4
6
8
1.5296
1.5698
1.7498
1.7900
1.8297
2.3615
2.5646
3.5373
3.7831
4.0021
6.0287
6.2062
6.2385
6.9057
6.9381
6.9759
6.9844
7.1948
7.2564
7.2833
7.4016
7.9395
7.9669
1.91
0.73
3.28
1.70
3.75
0.68
0.47
0.89
1.90
1.91
0.59
2.00

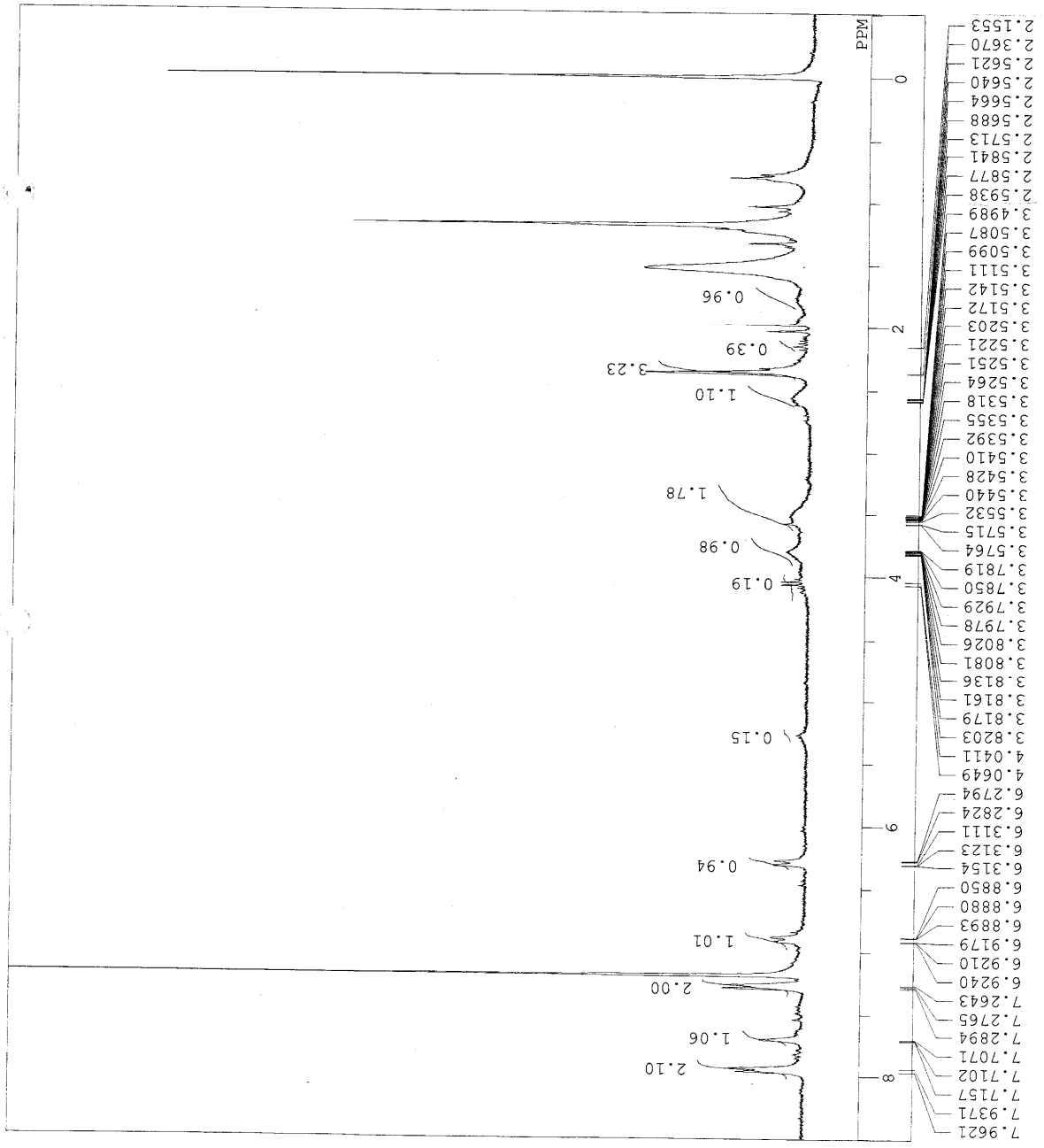

DFILE C:\WINNMR95\COMMON_DEFAULT
COMNT
DATIM Mon Mar 06 21:42:51 2006
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 663
ACQTM 1.789 sec
PD 1.211 sec
PW1 4.0 us
IRNUC 1H
CTEMP 20.3 c
SLVNT ACETN
EXREF 29.80 ppm
BF 0.12 Hz
RGAIN 25
17.960
21.556
28.944
29.232
29.512
30.080
30.368
30.549
30.647
37.345
43.927
50.328
65.277
104.860
119.382
122.319
126.080
126.335
127.264
129.222
130.292
130.490
135.385
142.806
146.813
153.560
153.782
154.095
168.986
178.687
PPM
0
25
50
75
100
125
150
175
200
Cl
N
O
N
Ts
O
N
H
HO
50c

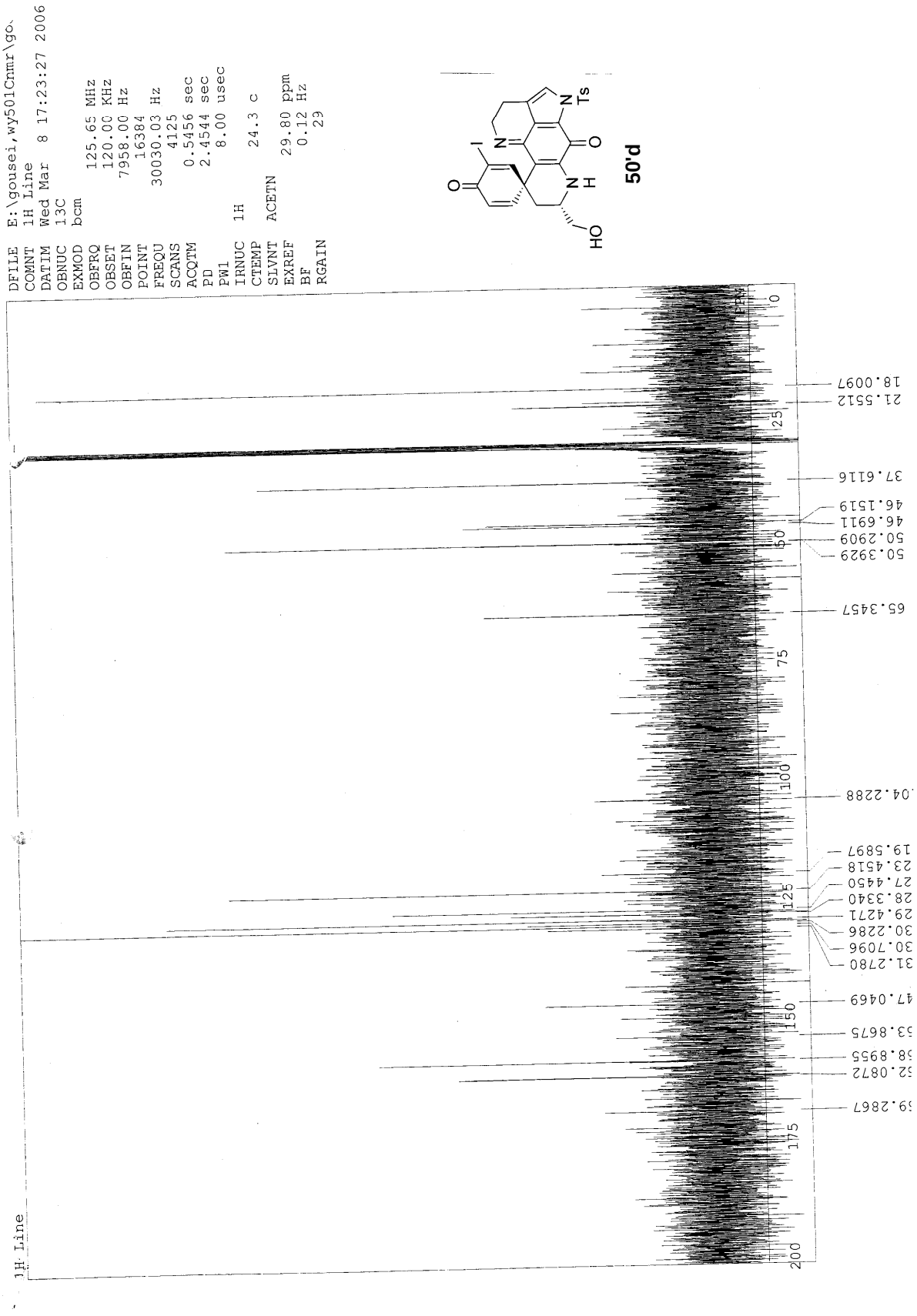

50'c
DEFAULT.ALS
DFILE
COMNT
DATIM Tue Mer 07 11:35:21 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4659 sec
PD 1.5440 sec
PW1 5.70 usec
IRNUC 1H
CTEMP 16.8 c
SLVNT ACETN
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19
PPM
4.15
2.11
1.58
1.26
1.16
1.08
1.11
3.01
0.99
2.00

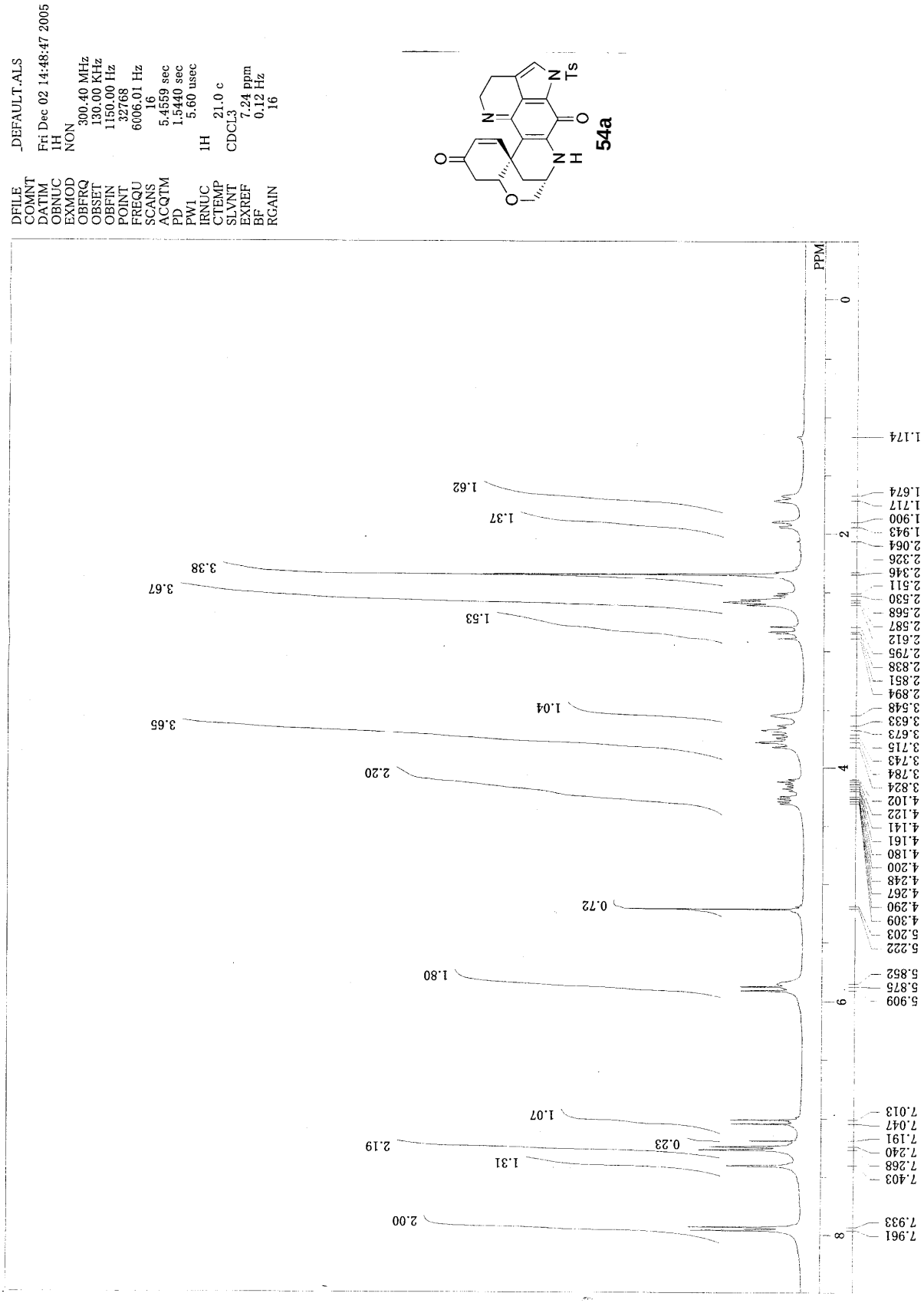

DFILE _DEFAULT.ALS
COMNT
DATIM Tue Mar 07 13:23:32 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 2128
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.60 usec
IRNUC 1H
CTEMP 16.2 c
SLVNT ACETN
EXREF 29.80 ppm
BF 0.12 Hz
RGAIN 23
50'c
17.247
17.979
21.538
24.555
28.674
29.035
29.290
29.348
29.545
29.800
30.055
30.195
30.318
30.441
30.573
30.696
37.626
39.821
42.394
44.022
47.877
50.220
65.231
119.554
125.760
127.421
129.418
130.693
131.712
135.567
147.044
149.954
158.701
169.256
178.899

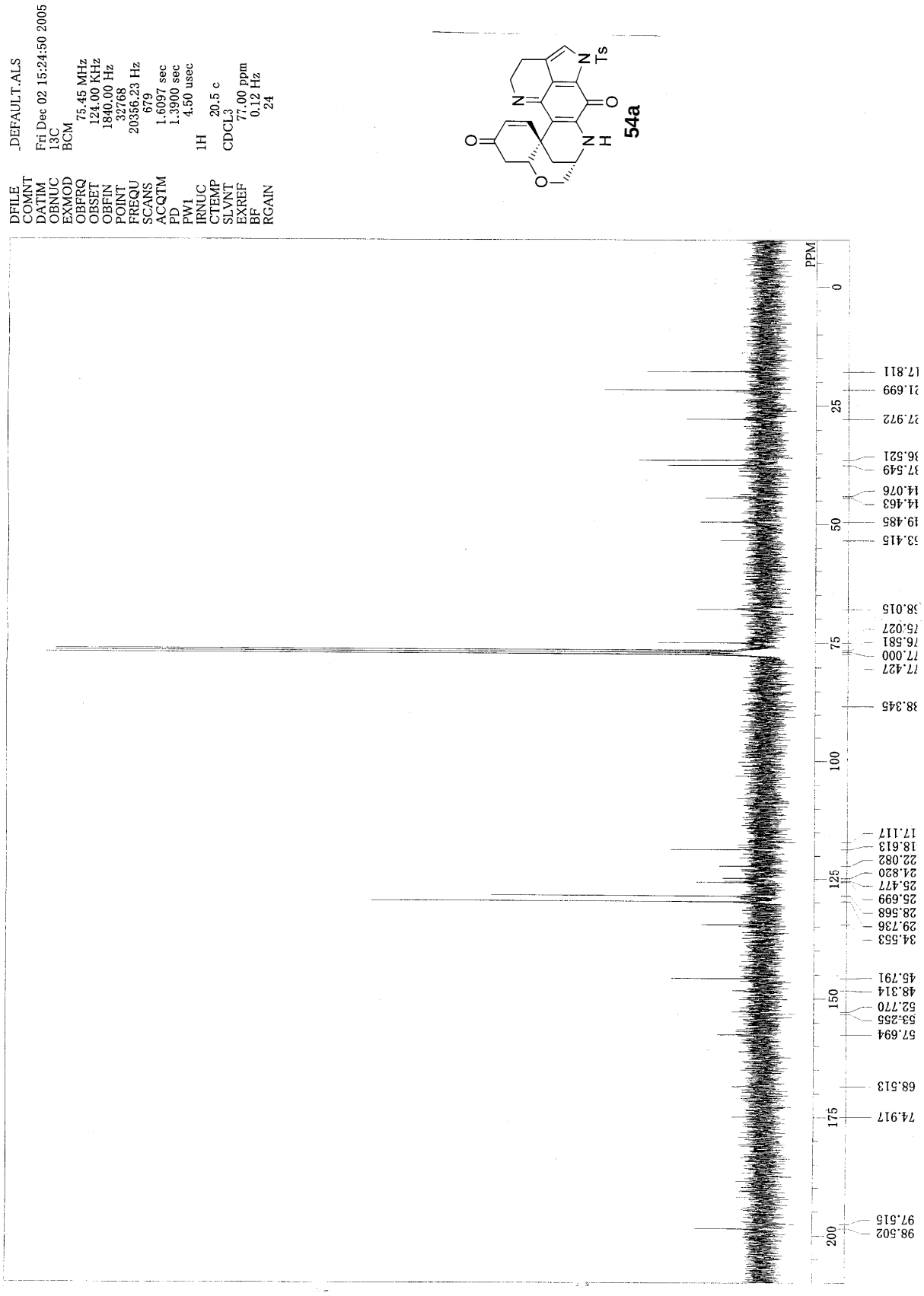

DFILE E:\mono-I OH 1H.als
COMNT mono-I OH 1H
DATIM Fri Jan 13 12:55:13 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 32
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24
50d
PPM
mono-I OH 1H

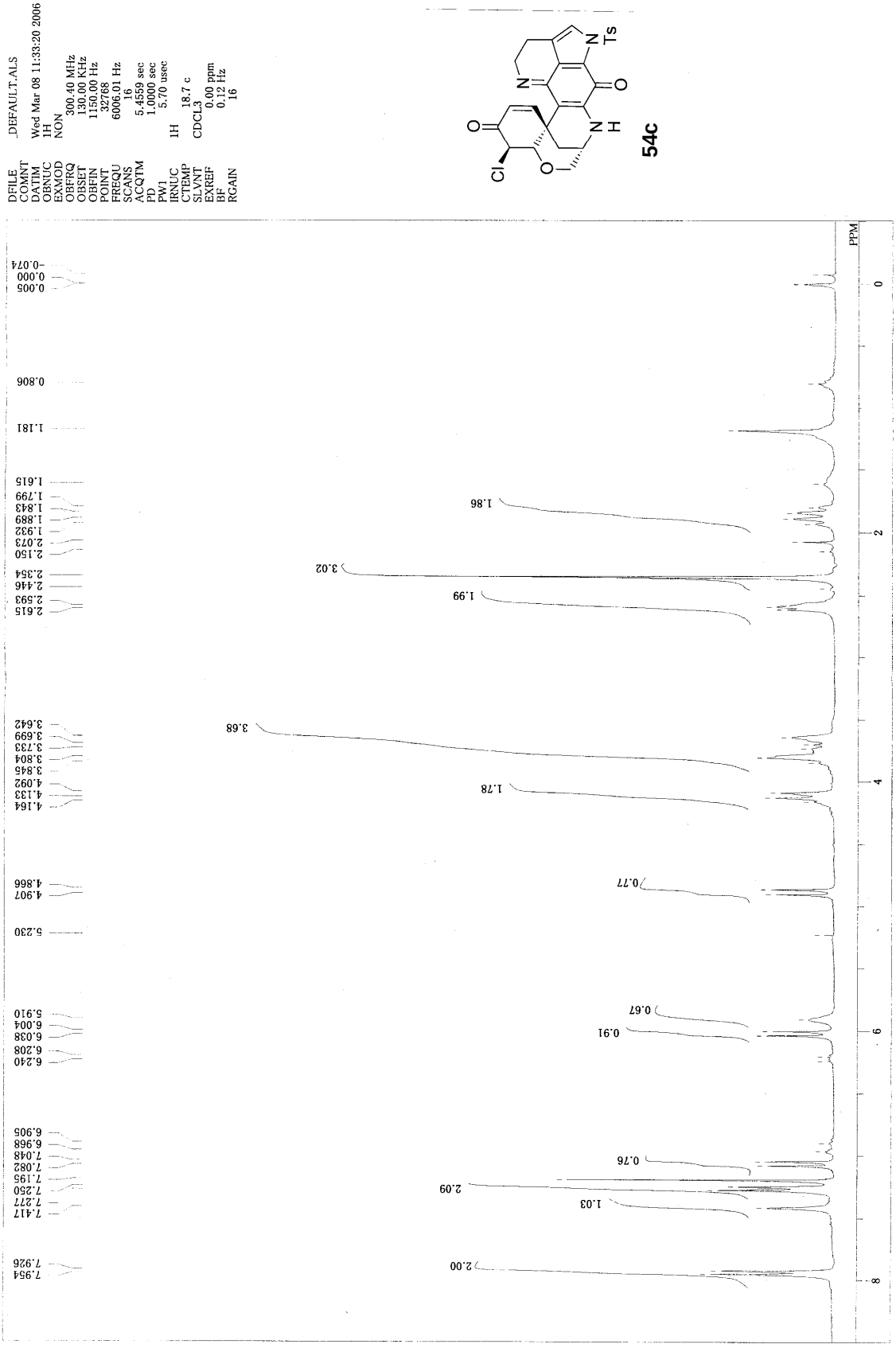

Date : Tue Aug 24 16:35:57 2004
FileName : LoadingFID.nmrdata
Comment : 1H Line
SliceHistory :
EXMODE : bcm
POINT 16384 points
SAMPD 16384 points
FREQU 30030.0 Hz
FILTR 15000 Hz
DELAY 13.3 usec
DEADT 16.0 usec
INTVL 33.3 usec
TIMES 1000000 times
DUMMY 1 times
PD 2.4544 sec
ACQTM 545.5872 msec
PREDL 0.01000 msec
INTWT 1000.0000 msec
RESOL 1.83 Hz
PW1 8.00 usec
OBNUC 13C 125.65 MHz
OBFRQ 127958.00 Hz
OBSET 11
AGAIN
IRNUC 1H 500.00 MHz
IRFRQ 132160.00 Hz
IRSET 45.0 usec
IRPWR 0
IRNS
SCANS 3119 times
SLVNT ACETN 12 Hz
SPINNING 23.9 C
TEMP
50d
1H Line
0.86
16.71
17.95
21.55
27.22
28.22
29.33
29.49
29.65
29.80
29.96
30.11
30.27
31.27
37.13
45.92
50.03
50.44
62.97
65.35
65.45
101.62
102.31
104.96
119.55
122.55
124.31
126.24
127.49
129.43
130.18
130.70
135.61
142.92
147.05
153.66
153.85
154.25
161.15
161.45
166.42
169.21
179.74
183.37
0 ppm
50
100
150

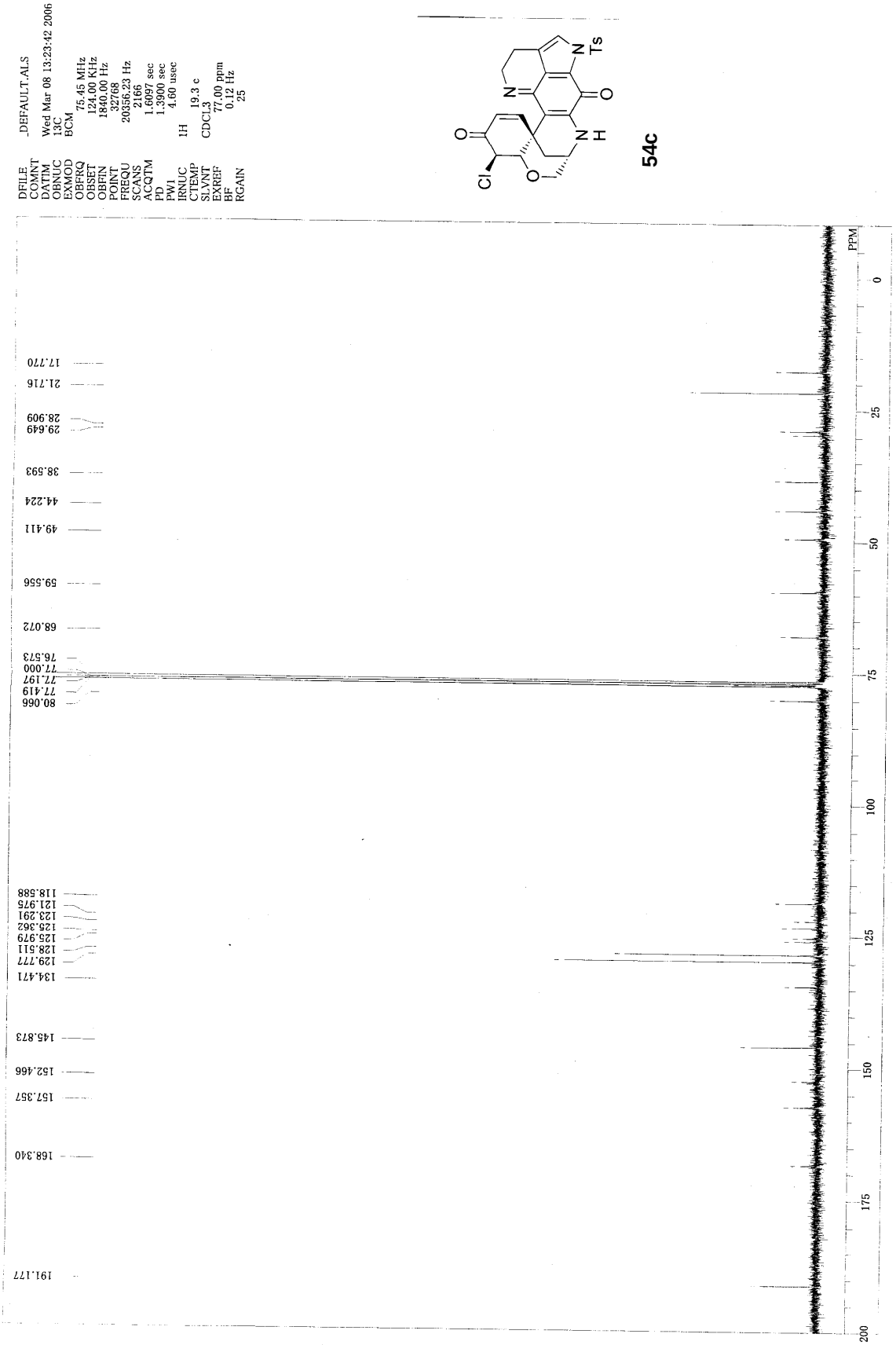

DFILE E:\I shita OH 1H.als
COMNT
DATIM Thu Feb 16 19:19:01 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 50
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 16.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24
50'd
Ts
HO
PPM
0.96
0.39
3.23
1.10
1.78
0.98
0.19
0.15
0.94
1.01
2.00
1.06
2.10

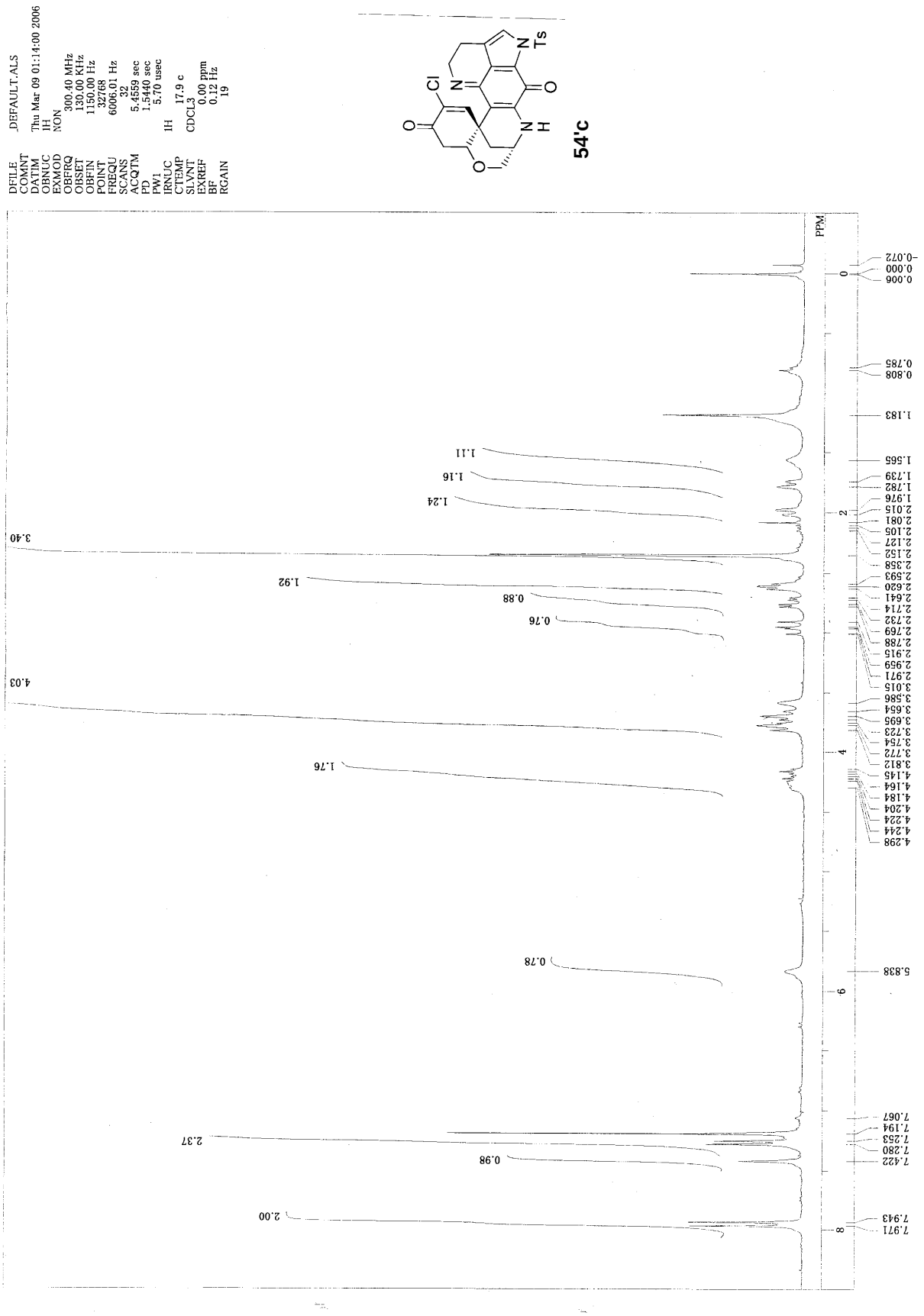

DFILE E:\gousei,wy501Cnmr\go
COMNT 1H Line
DATIM Wed Mar 8 17:23:27 2006
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 16384
FREQU 30030.03 Hz
SCANS 4125
ACQTM 0.5456 sec
PD 2.4544 sec
PW1 8.00 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT ACETN
EXREF 29.80 ppm
BF 0.12 Hz
RGAIN 29
50'd
1H Line
18.0097
21.5512
37.6116
46.1519
46.6911
50.2909
50.3929
65.3457
104.2288
119.5897
123.4518
127.4450
128.3340
129.4271
130.2286
130.7096
131.2780
147.0469
153.8675
158.8955
162.0872
169.2867

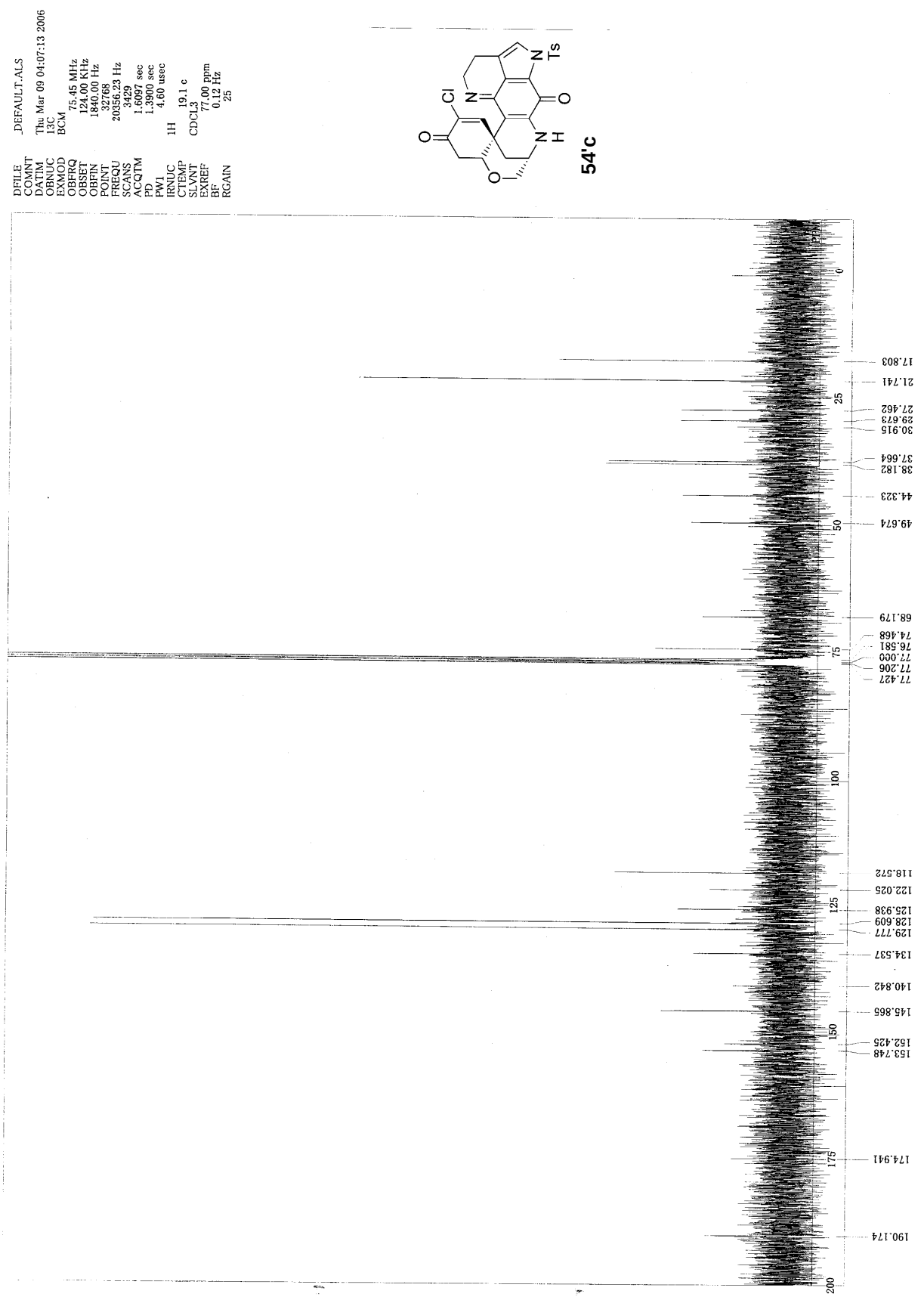

DFILE _DEFAULT.ALS
COMNT
DATIM Fri Dec 02 14:48:47 2005
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 16
Ts
N
O
N
H
O
O
54a
PPM
0
2
4
6
8
1.174
1.62
1.37
3.38
3.67
1.53
1.04
3.65
2.20
0.72
1.80
1.07
2.19
0.23
1.31
2.00
1.674
1.717
1.900
1.943
2.064
2.326
2.346
2.511
2.530
2.568
2.587
2.612
2.795
2.838
2.851
2.894
3.548
3.633
3.673
3.715
3.743
3.784
3.824
4.102
4.122
4.141
4.161
4.180
4.200
4.248
4.267
4.290
4.309
5.203
5.222
5.852
5.875
5.909
7.013
7.047
7.191
7.240
7.268
7.403
7.933
7.961

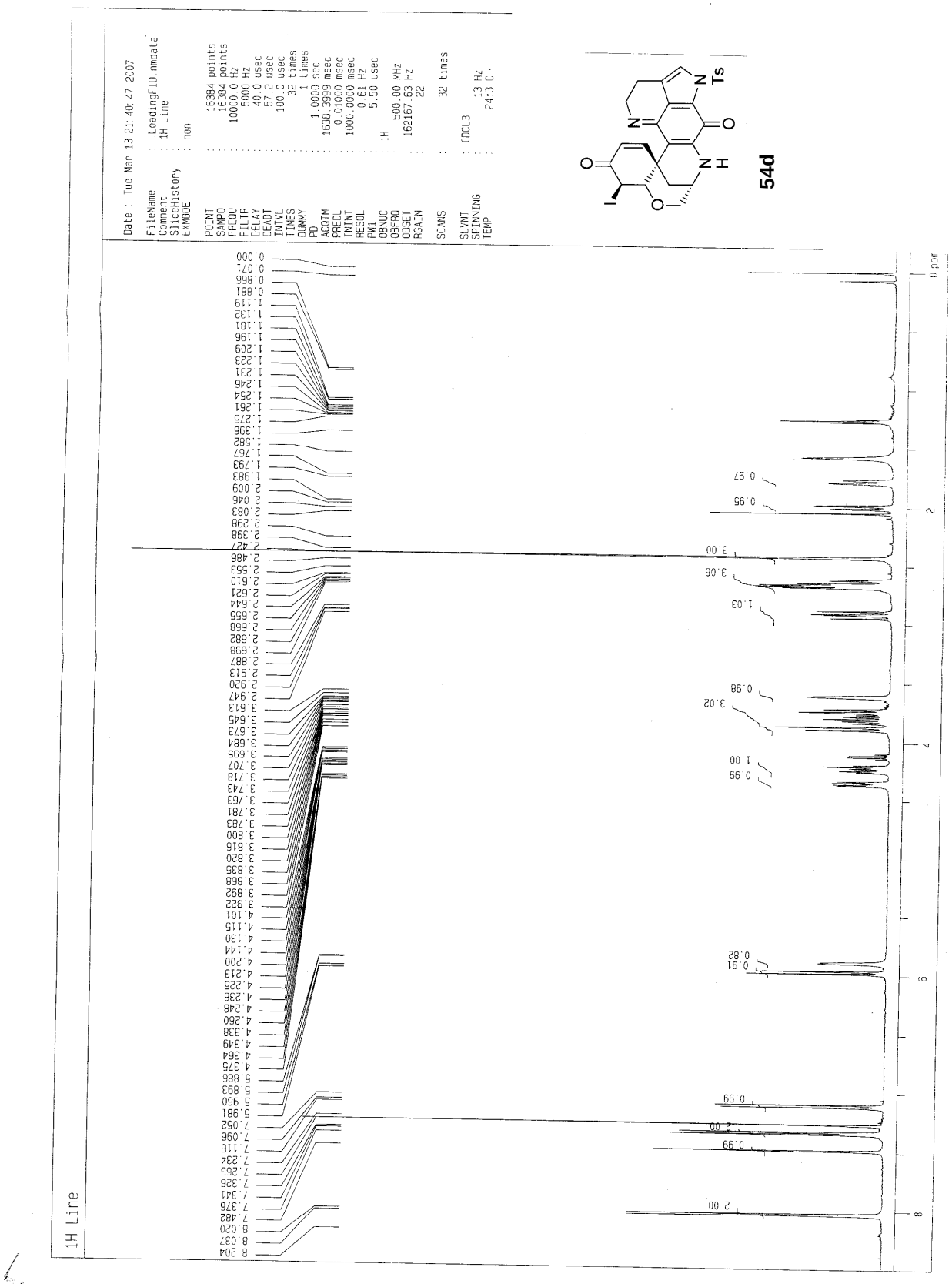

54a
Ts
N
O
H
DFILE _DEFAULT.ALS
COMNT
DATIM Fri Dec 02 15:24:50 2005
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 679
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
PPM
0
25
50
75
100
125
150
175
200
17.811
21.699
27.972
36.521
37.549
14.076
14.463
19.485
53.415
58.015
75.027
76.581
77.000
77.427
38.345
17.117
18.613
22.082
24.820
25.477
25.699
28.568
29.736
34.553
45.791
48.314
52.770
53.255
57.694
68.513
74.917
97.515
98.502

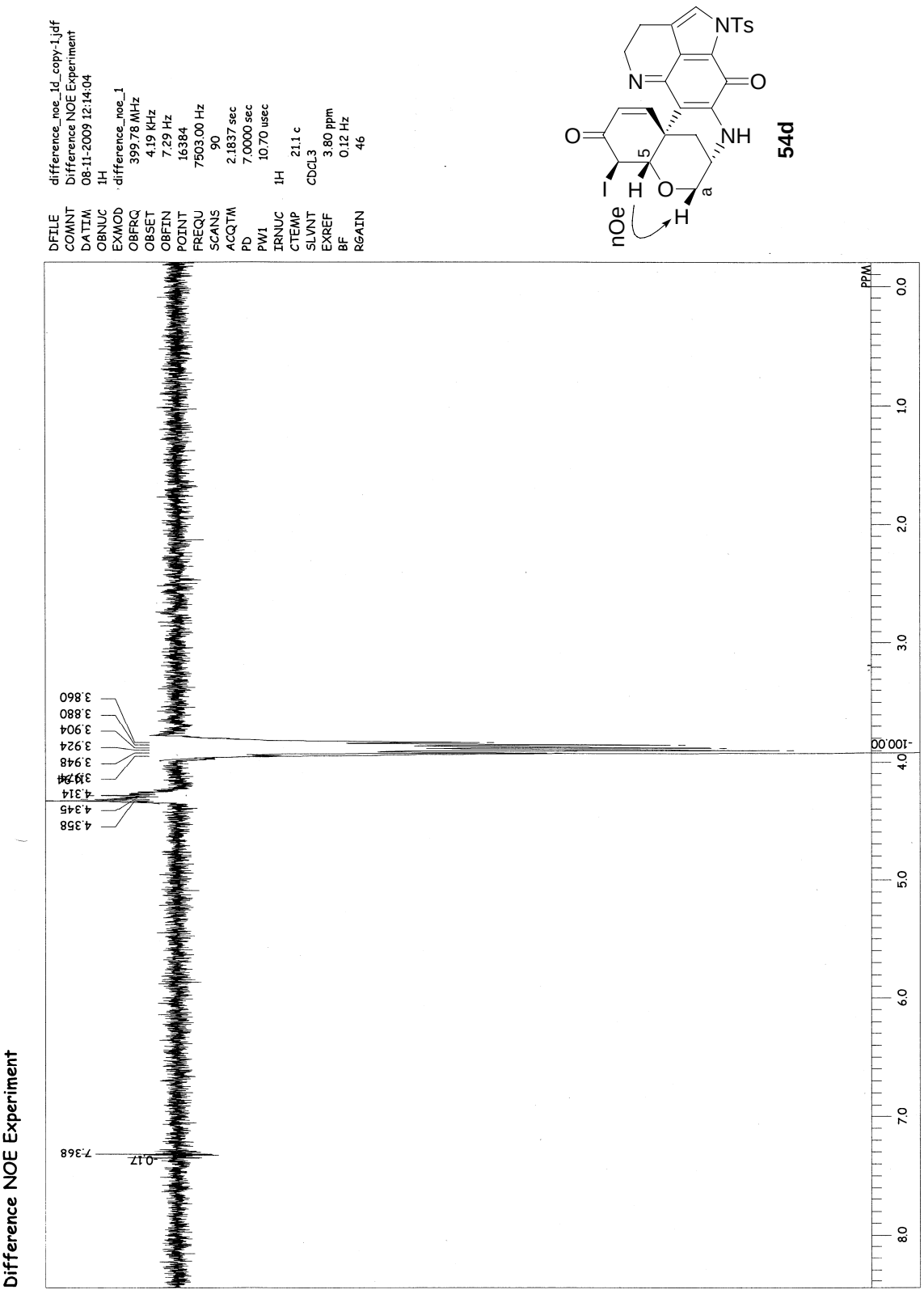

DFILE DEFAULT.ALS
COMNT
DATIM Wed Mar 08 11:33:20 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.70 usec
IRNUC 1H
CTEMP 18.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 16
54c
PPM
0.005
0.000
-0.074
0.806
1.181
1.615
1.799
1.843
1.889
1.932
2.073
2.150
2.354
2.446
2.593
2.615
3.642
3.699
3.733
3.804
3.846
4.092
4.133
4.164
4.907
4.866
5.230
5.910
6.004
6.038
6.208
6.240
6.905
6.968
7.048
7.082
7.195
7.250
7.277
7.417
7.926
7.954
1.86
3.02
1.99
3.68
1.78
0.77
0.67
0.91
0.76
2.09
1.03
2.00

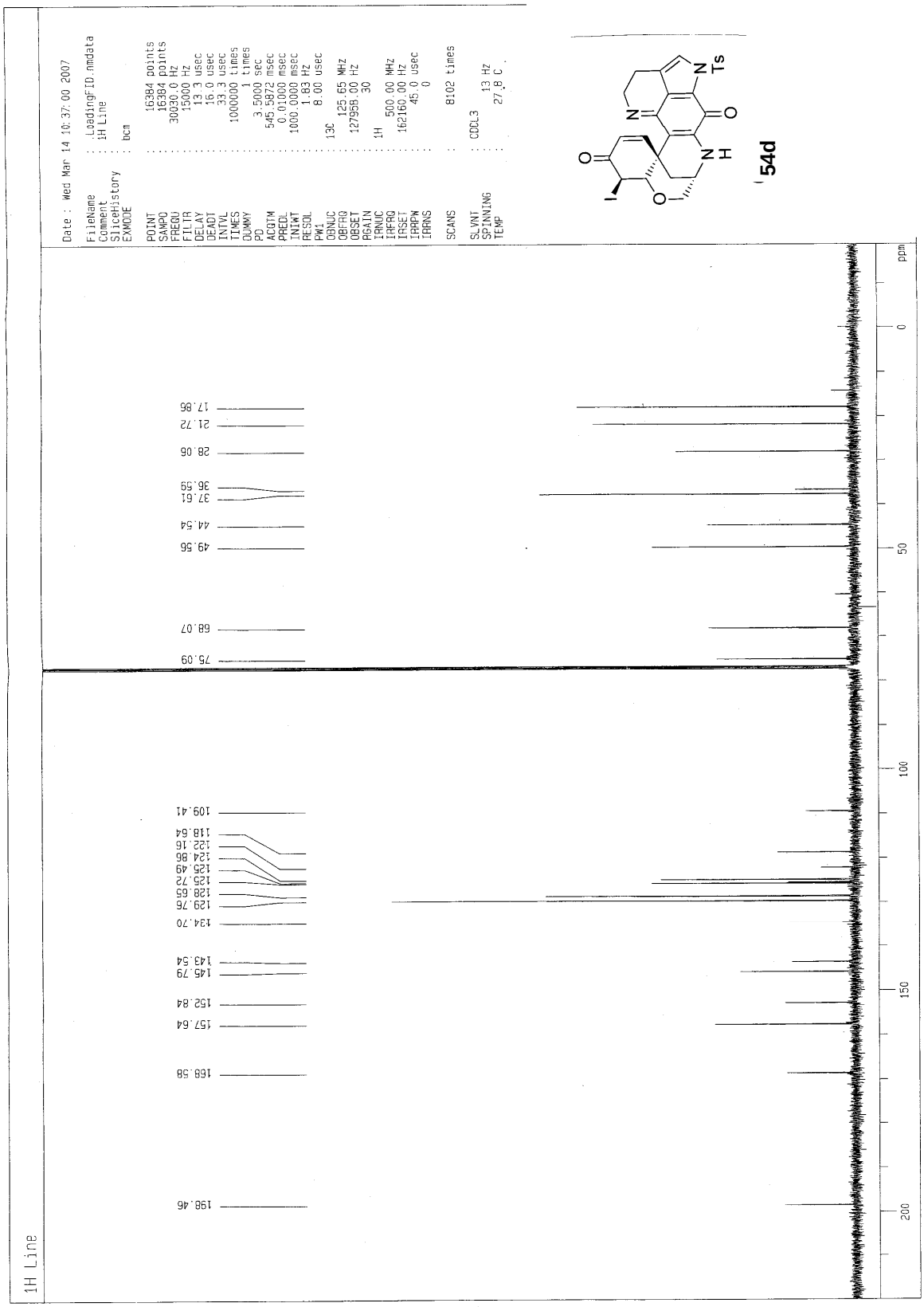

DFILE _DEFAULT.ALS
COMNT
DATIM Wed Mar 08 13:23:42 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 2166
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.60 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25
Ts
N
O
H
Cl
54c
PPM
0
25
50
75
100
125
150
175
200
17.770
21.716
28.909
29.649
38.593
44.224
49.411
59.556
68.072
76.573
77.000
77.197
77.419
80.066
118.588
121.975
123.291
126.362
126.979
128.511
129.777
134.471
145.873
152.466
157.357
168.340
191.177

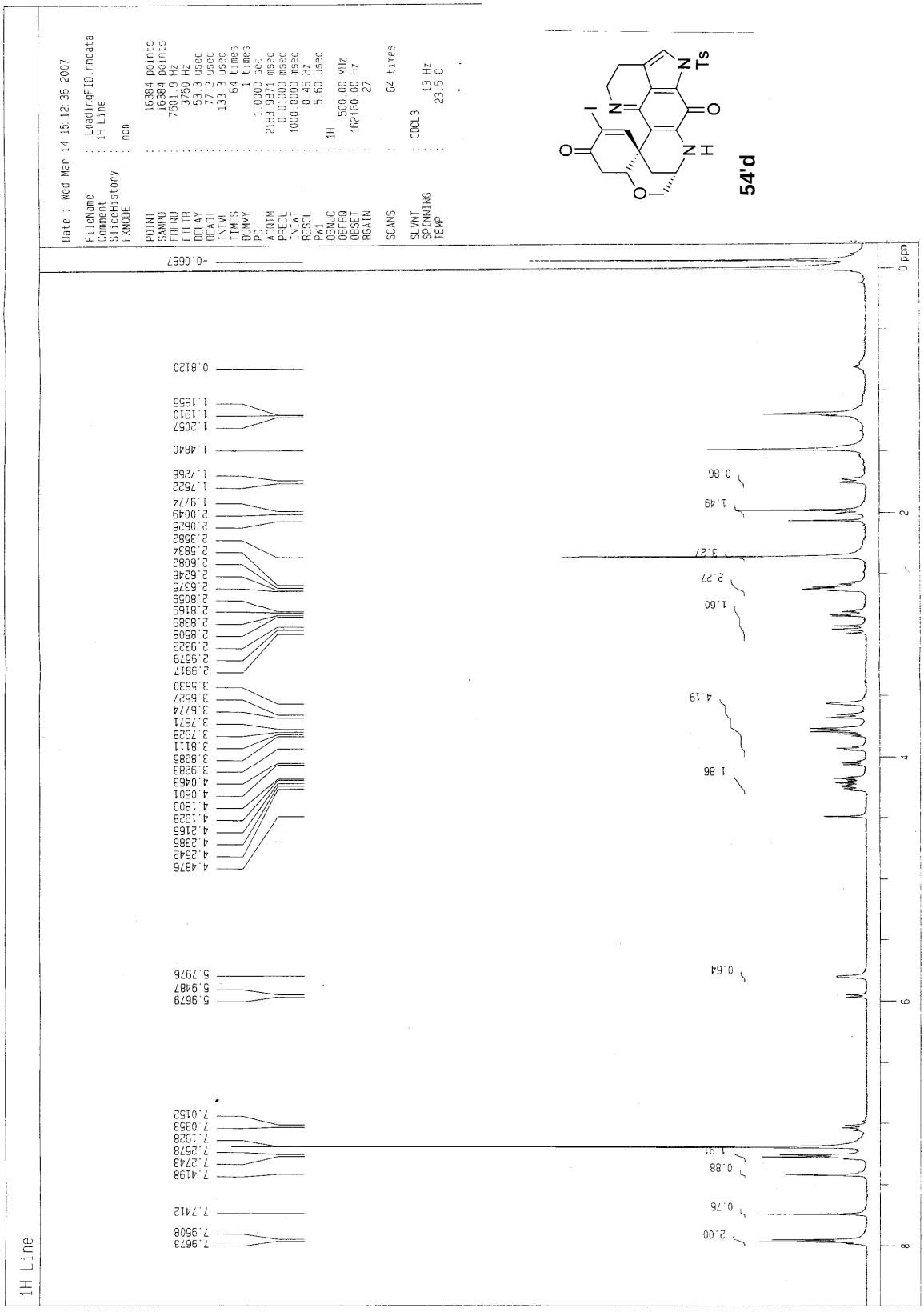

DEFILE DEFAULT.ALS
COMNT
DATIM Thu Mar 09 01:14:00 2006
OBNUC 1H
EXMOD NON
OBFRQ 900.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 32
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.70 usec
IRNUC 1H
CTEMP 17.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19
Cl
N
Ts
O
N
H
O
O
54'c
PPM
0.006
0.000
-0.072
0.808
0.785
1.183
1.565
1.739
1.782
1.976
2.015
2.081
2.105
2.127
2.152
2.358
2.593
2.620
2.641
2.714
2.732
2.769
2.788
2.915
2.959
2.971
3.015
3.586
3.654
3.695
3.723
3.754
3.772
3.812
4.145
4.164
4.184
4.204
4.224
4.244
4.298
5.838
7.067
7.194
7.253
7.280
7.422
7.943
7.971
1.11
1.16
1.24
3.40
1.92
0.88
0.76
4.03
1.76
0.78
2.37
0.98
2.00

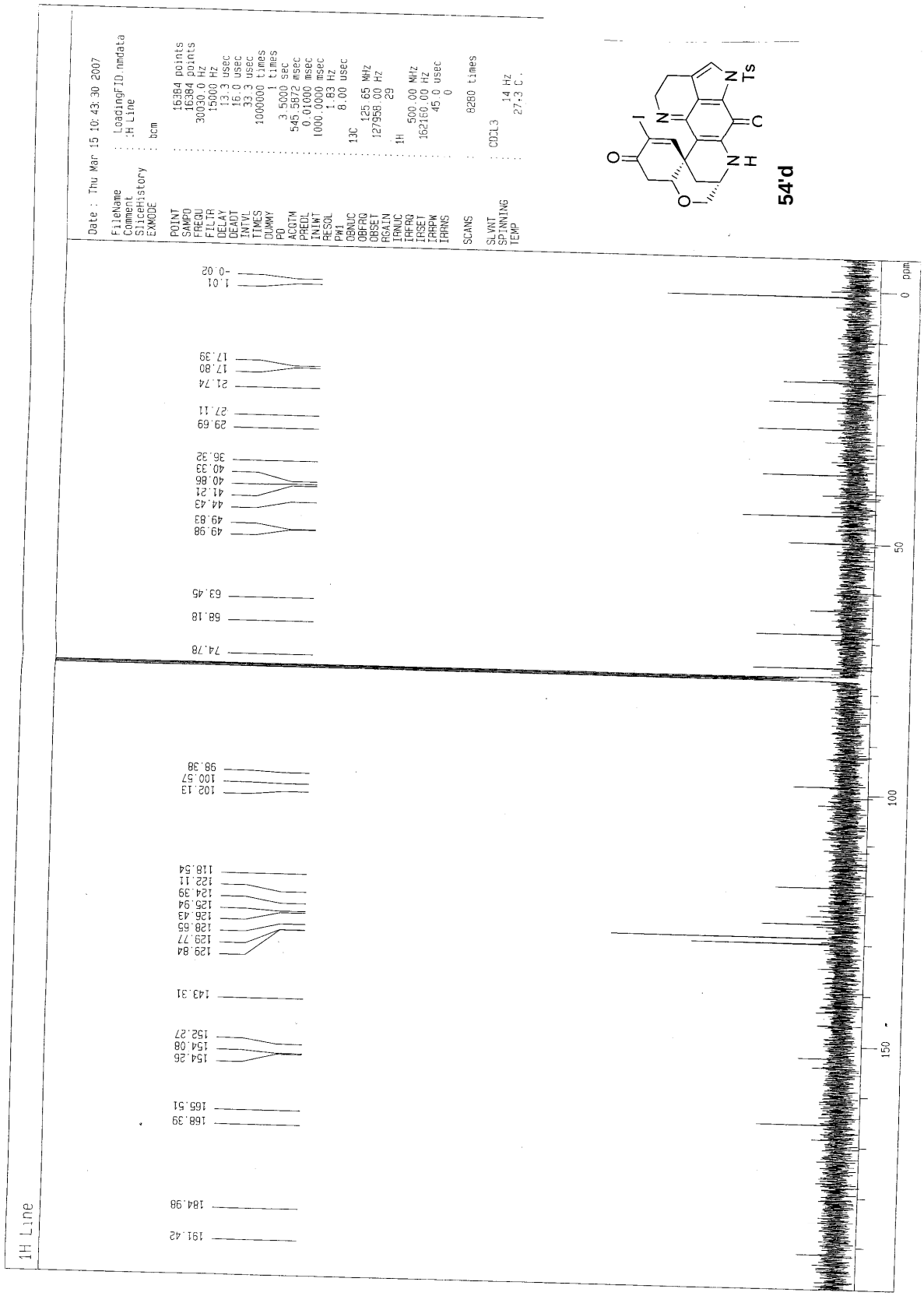

DFILE _DEFAULT.ALS
COMNT
DATIM Thu Mar 09 04:07:13 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 3429
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.60 usec
IRNUC 1H
CTEMP 19.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25
Cl
N
Ts
O
N
H
O
O
54'c
17.803
21.741
27.462
29.673
30.915
37.664
38.182
44.323
49.674
68.179
74.468
76.581
77.000
77.206
77.427
118.572
122.025
125.938
128.609
129.777
134.537
140.842
145.865
152.425
153.748
174.941
190.174

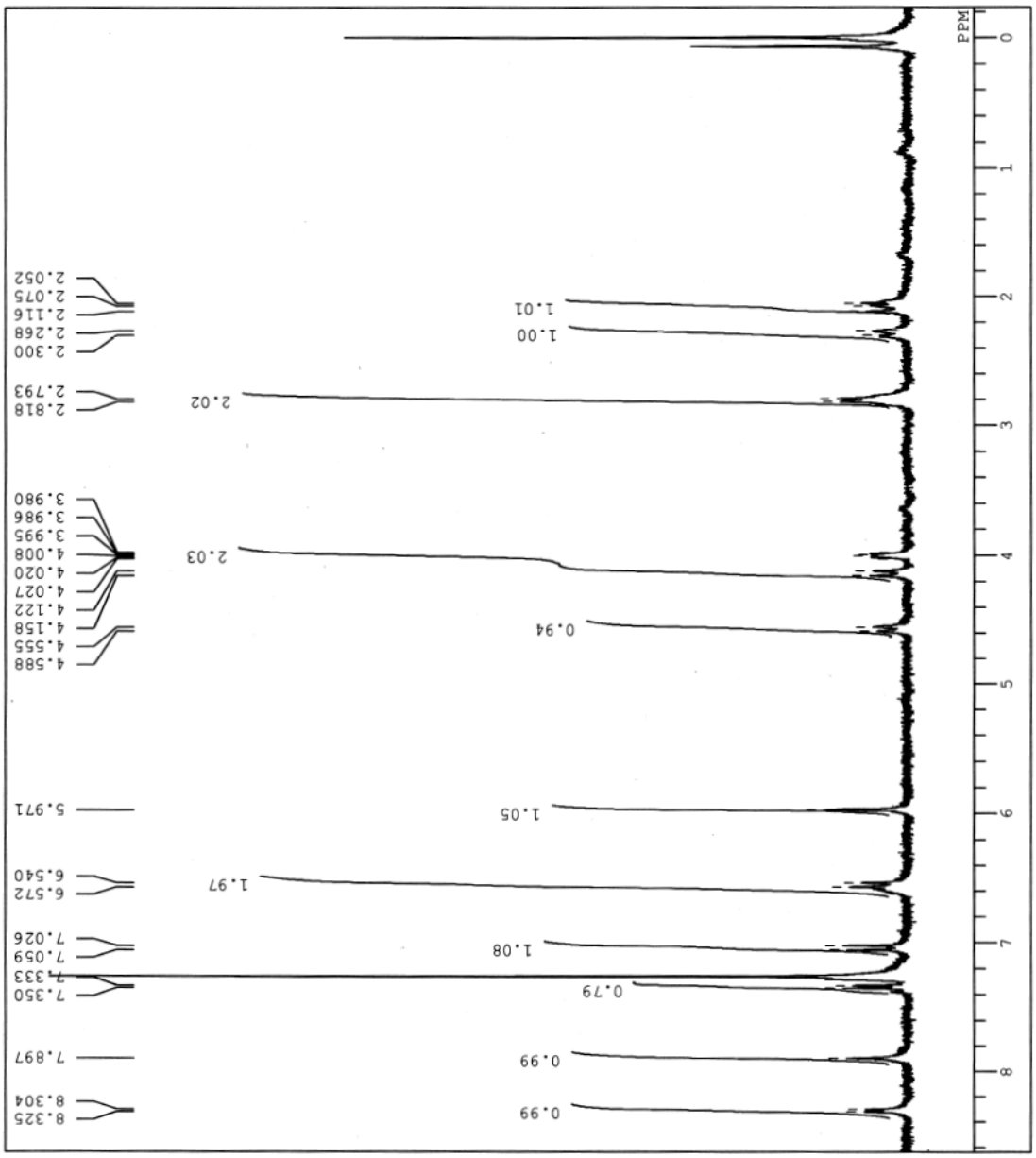

Date : Tue Mar 13 21:40:47 2007
FileName : LoadingFID nmdata
Comment : 1H Line
SliceHistory :
EXMODE : non
POINT 16384 points
SAMPO 16384 points
FREQU 10000.0 Hz
FILTR 5000 Hz
DELAY 40.0 usec
DEADT 57.2 usec
INTVL 100.0 usec
TIMES 32 times
DUMMY 1 times
PD 1.0000 sec
ACQTM 1638.3999 msec
PREDL 0.01000 msec
INIWT 1000.0000 msec
RESOL 0.61 Hz
PW1 5.50 usec
OBNUC 1H 500.00 MHz
OBFRQ 162167.63 Hz
OBSET 22
AGAIN
SCANS 32 times
SLVNT CDCL3
SPINNING 13 Hz
TEMP 24.3 C.
54d
1H Line
0.ppm
0.97
0.96
3.00
3.06
1.03
0.98
3.02
1.00
0.99
0.91
0.82
0.99
2.00
0.99
2.00

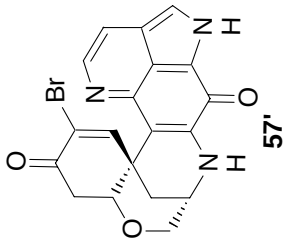

Difference NOE Experiment
DFILE difference_noe_1d_copy-1.jdf
COMNT Difference NOE Experiment
DATIM 08-11-2009 12:14:04
OBNUC 1H
EXMOD difference_noe_1
OBFRQ 399.78 MHz
OBSET 4.19 kHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 90
ACQTM 2.1837 sec
PD 7.0000 sec
PW1 10.70 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCl3
EXREF 3.80 ppm
BF 0.12 Hz
RGAIN 46
3.860
3.880
3.904
3.924
3.948
4.314
4.345
4.358
7.368
0.17
-100.00
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
NTs
N
O
O
NH
5
I
H
O
a
nOe
H
54d


Date : Wed Mar 14 10:37:00 2007
FileName : LoadingFID.nmdata
Comment : 1H Line
SliceHistory :
EXMODE : bcm
POINT : 16384 points
SAMPO : 16384 points
FREQU : 30030.0 Hz
FILTR : 15000 Hz
DELAY : 13.3 usec
DEADT : 16.0 usec
INTVL : 33.3 usec
TIMES : 1000000 times
DUMMY : 1 times
PD : 3.5000 sec
ACQTM : 545.5872 msec
PREDL : 0.01000 msec
INIWT : 1000.0000 msec
RESOL : 1.83 Hz
PW1 : 8.00 usec
OBNUC : 13C 125.65 MHz
OBFRQ : 12795B.00 Hz
OBSET : 30
OBSAIN :
IRNUC : 1H 500.00 MHz
IRFRQ : 162160.00 Hz
IRSET : 45.0 usec
IRPPW : 0
IRNNS :
SCANS : 8102 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 27.8 C
54d
1H Line
ppm
17.86
21.72
28.06
36.59
37.61
44.54
49.56
68.07
75.09
109.41
118.64
122.16
124.86
126.49
127.72
128.65
129.76
134.70
143.54
145.79
152.84
157.64
168.58
198.46

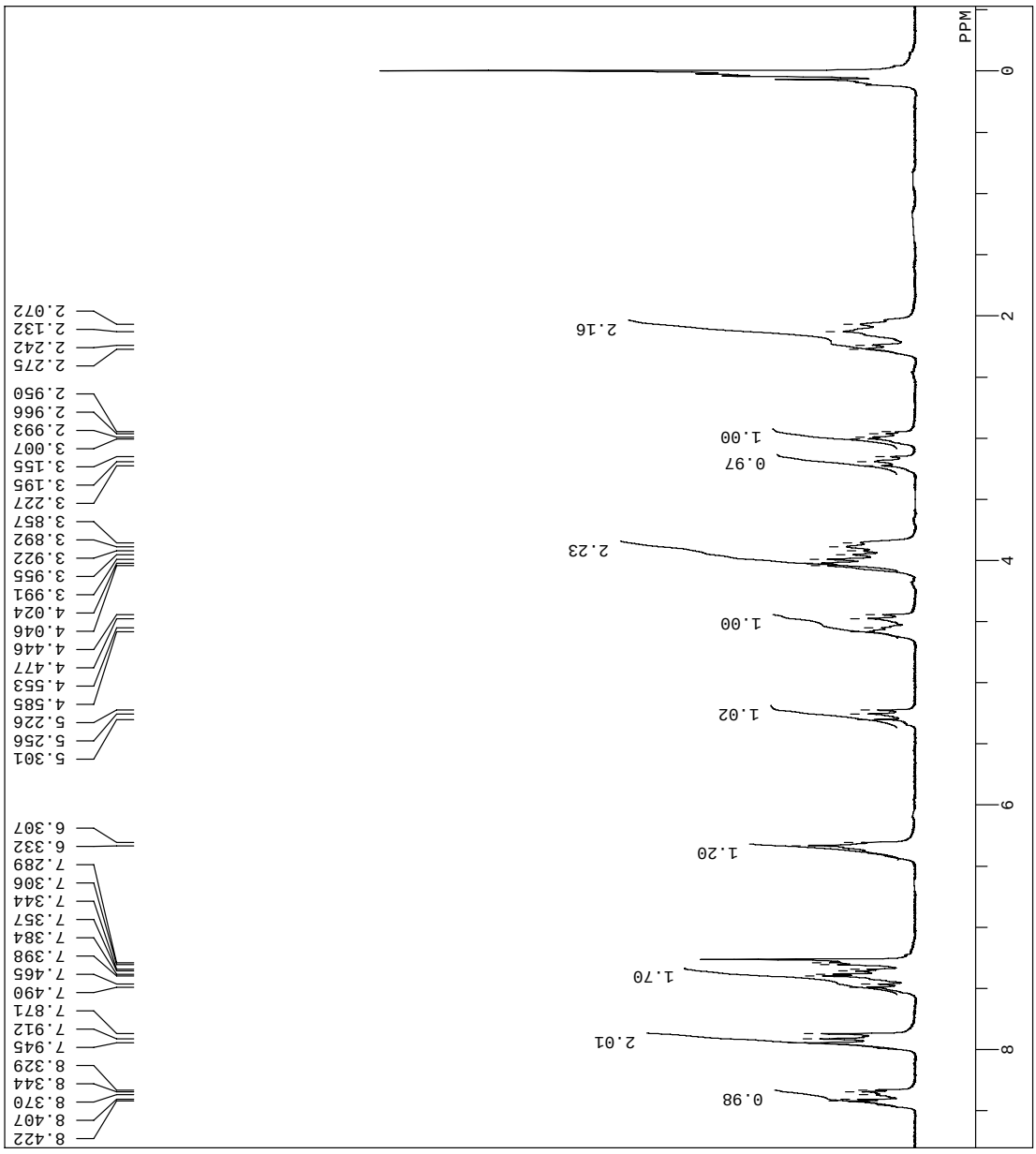

54'd
1H Line
0 ppm


Date : Thu Mar 15 10:43:30 2007
FileName : LoadingFID.nmrdata
Comment : 1H Line
SiliceHistory :
EXMODE : bcm
POINT 16384 points
SAMPO 16384 points
FREQU 30030.0 Hz
FILTR 15000 Hz
DELAY 13.3 usec
DEADT 16.0 usec
INTVL 33.3 usec
TIMES 10000000 times
DUMMY 1 times
PD 3.5000 sec
ACQTM 545.5872 msec
PREDL 0.01000 msec
1N1WT 1000.0000 msec
RESOL 1.83 Hz
PW1 8.00 usec
13C
OBNUC
OBFRQ 125.65 MHz
OBSET 127958.00 Hz
AGAIN 29
1H
IANUC 500.00 MHz
IAFRQ 162150.00 Hz
IASET 45.0 usec
IAPPM 0
IAMNS
SCANS 8260 times
SLVNT CDCl3
SPINNING 14 Hz
TEMP 27.3 C.
54'd
1H Line
ppm

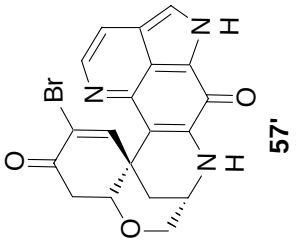

DFILE 041569down.als
COMNT 041569down
DATIM Thu Apr 30 00:19:04 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 3.80 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26
57
PPM



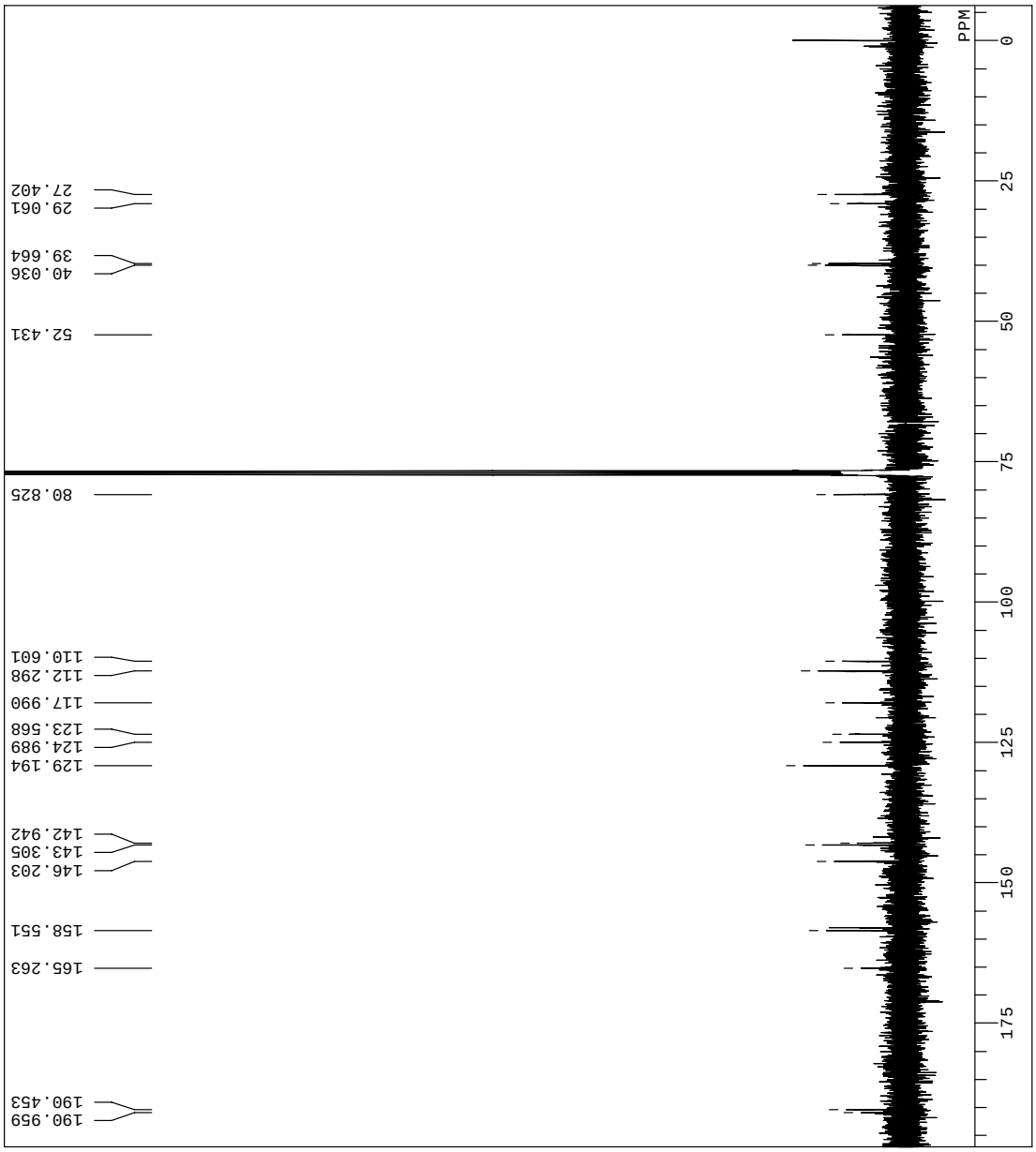

```
DFILE 041569uppure-1.als
COMNT single_pulse
DATIM 30-04-2009 14:41:02
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ    399.78 MHz
OBSET      4.19 KHz
OBFIN      7.29 Hz
POINT     13107
FREQU   6002.31 Hz
SCANS       24
ACQTM     2.1837 sec
PD        5.0000 sec
PW1          5.35 usec
IRNUC 1H
CTEMP     20.9 c
SLVNT CDCL3
EXREF     0.00 ppm
BF        0.12 Hz
RGAIN       48
```

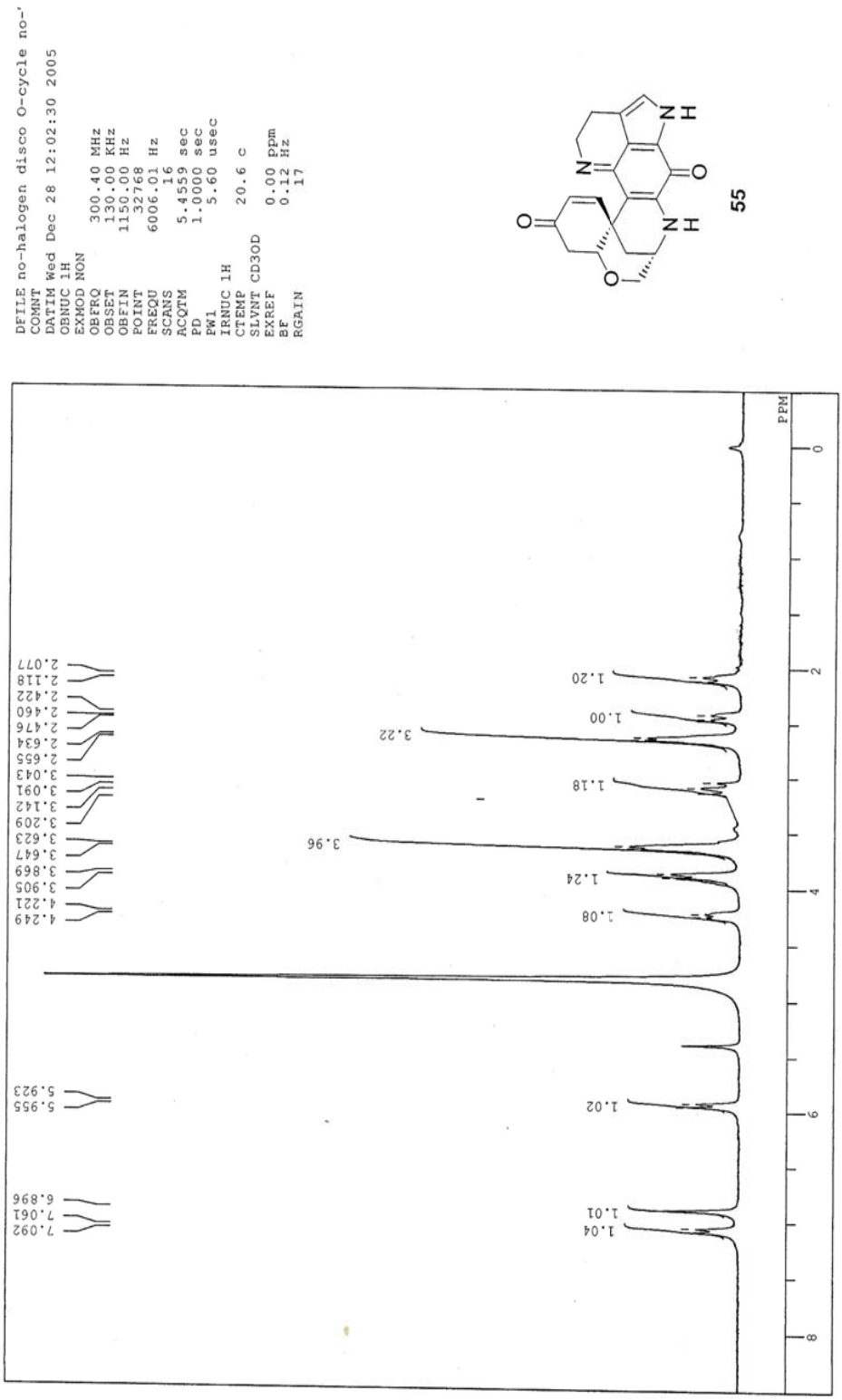


```
DFILE 041569uppurecnmr-1.als
COMNT single pulse decoupled gated
DATIM 01-05-2009 08:40:24
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ      100.53 MHz
OBSET        5.35 KHz
OBFIN        5.86 Hz
POINT       26214
FREQU    25125.24 Hz
SCANS       10302
ACQTM       1.0433 sec
PD          2.0000 sec
PW1            3.17 usec
IRNUC 1H
CTEMP       21.5 c
SLVNT CDCL3
EXREF       0.00 ppm
BF          0.12 Hz
RGAIN         60
```

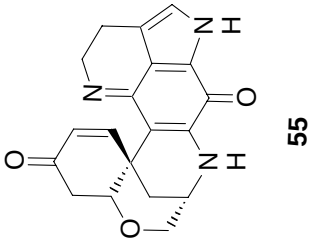



**57'**

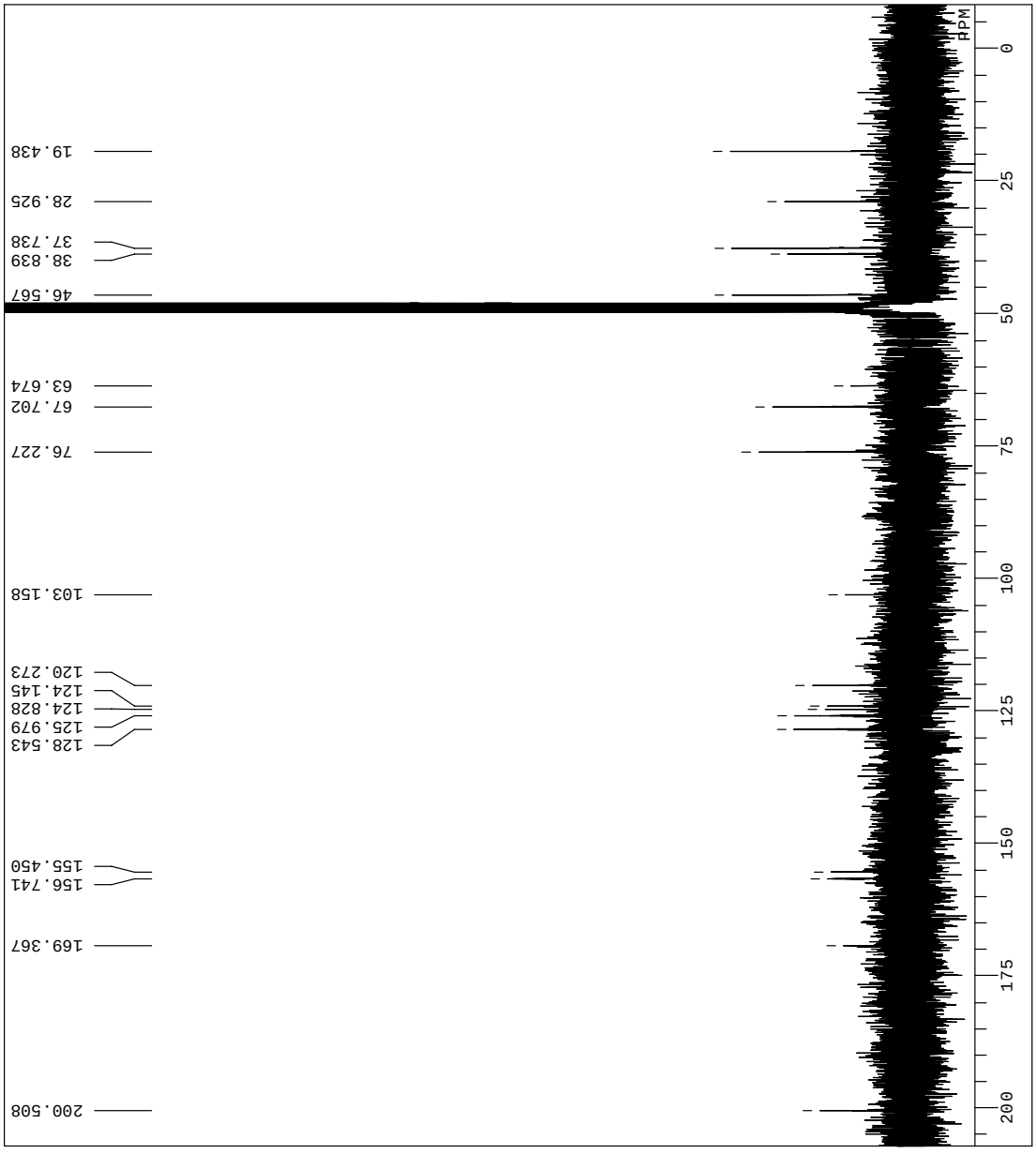



DFILE no-halogen disco O-cycle no-'
COMNT
DATIM Wed Dec 28 12:02:30 2005
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CD3OD
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17
55
PPM
0
2
4
6
8
1.20
1.00
3.22
1.18
3.96
1.24
1.08
1.02
1.04
1.01
7.092
7.061
6.896
5.955
5.923
4.249
4.221
3.905
3.869
3.647
3.623
3.209
3.142
3.091
3.043
2.655
2.634
2.476
2.460
2.422
2.118
2.077

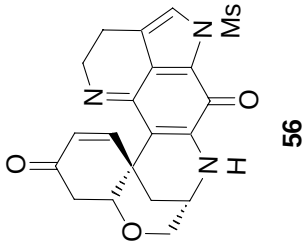
```
DFILE no-halogen disco O-cycle no-
COMNT
DATIM Thu Dec 29 08:52:02 2005
OBNUC 13C
EXMOD BCM
OBFRQ          75.45 MHz
OBSET         124.00 KHz
OBFIN        1840.00 Hz
POINT          32768
FREQU       20356.23 Hz
SCANS          11823
ACQTM          1.6097 sec
PD             1.3900 sec
PW1               4.50 usec
IRNUC 1H
CTEMP             20.7 c
SLVNT CD3OD
EXREF          49.00 ppm
BF              0.12 Hz
RGAIN             25
```



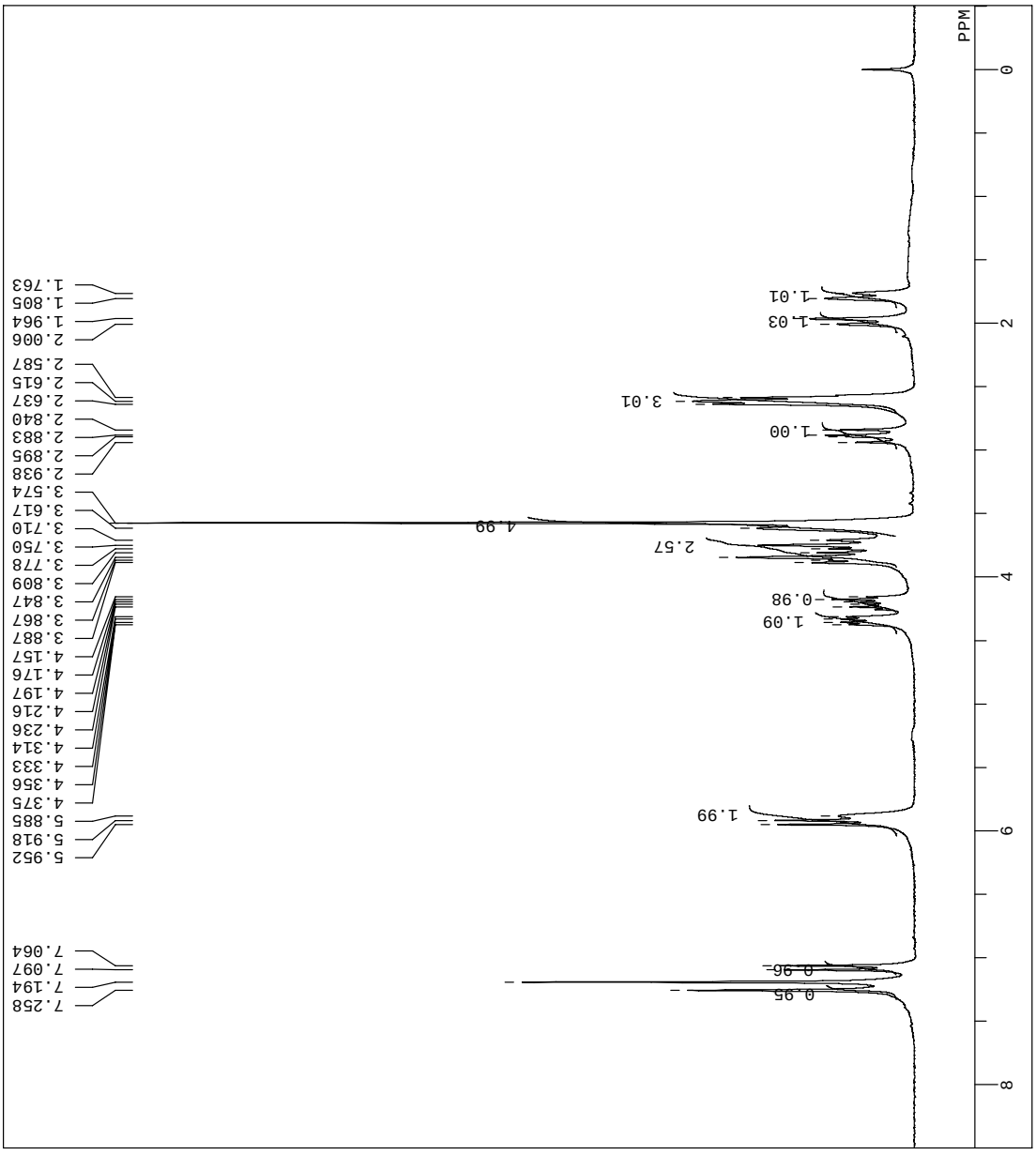
**55**

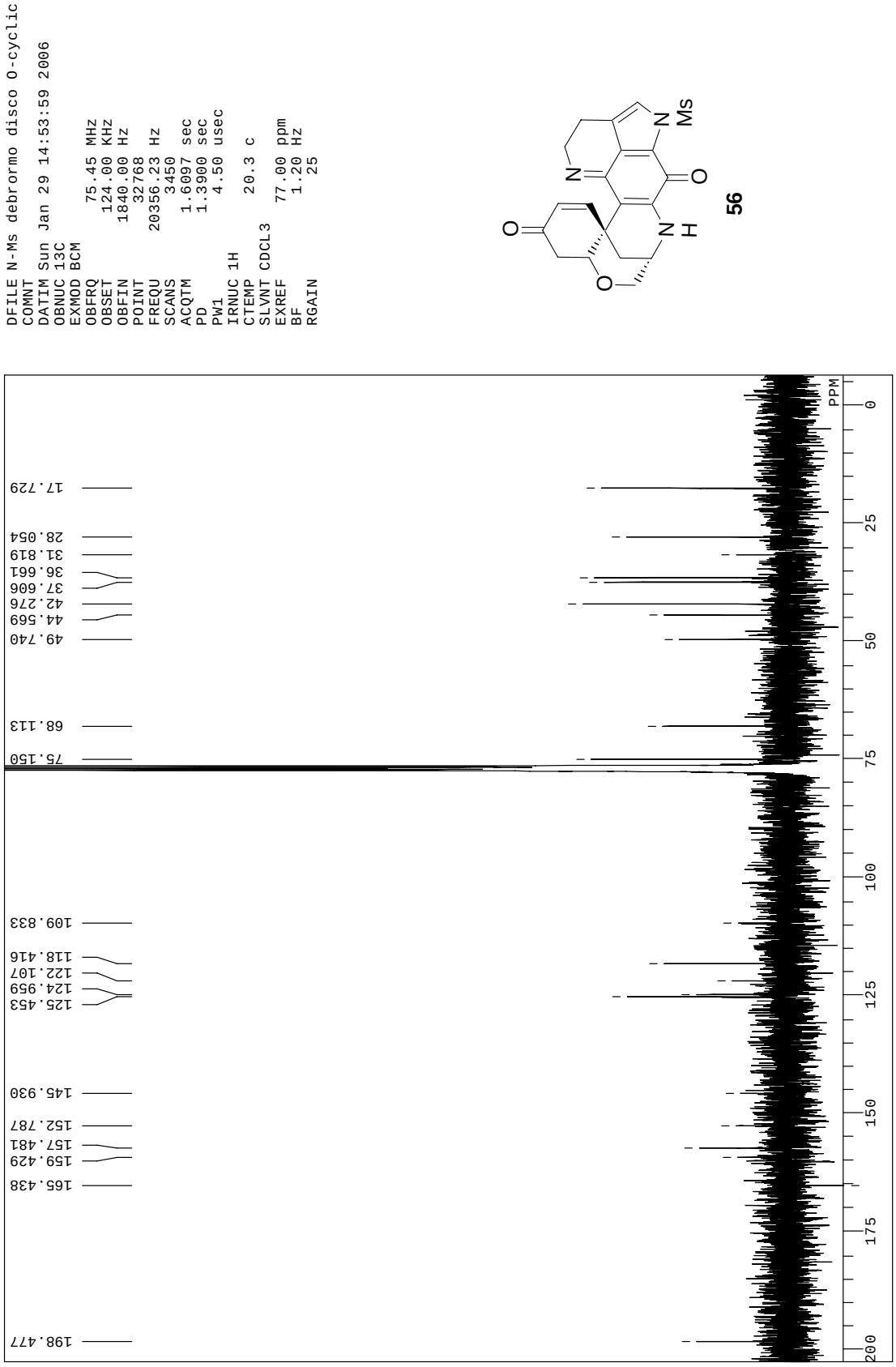


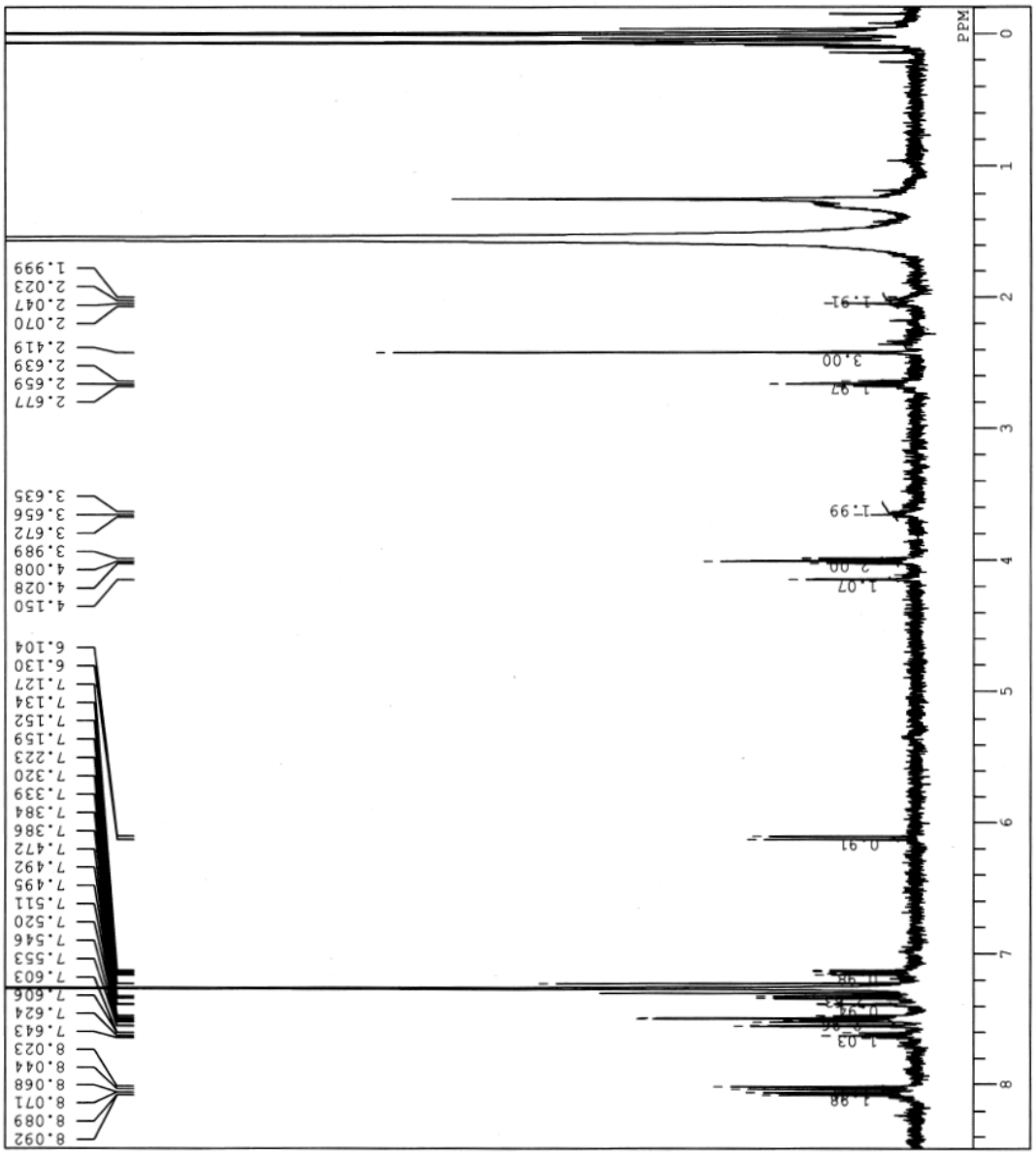
```
DFILE N-Ms debrormo disco O-cyclic
COMNT
DATIM Sun Jan 29 11:58:59 2006
OBNUC 1H
EXMOD NON
OBFRQ     300.40 MHz
OBSET     130.00 KHz
OBFIN    1150.00 Hz
POINT      32768
FREQU    6006.01 Hz
SCANS         32
ACQTM      5.4559 sec
PD         1.5440 sec
PW1           5.60 usec
IRNUC 1H
CTEMP     21.5 c
SLVNT CDCL3
EXREF      0.00 ppm
BF         1.20 Hz
RGAIN        22
```

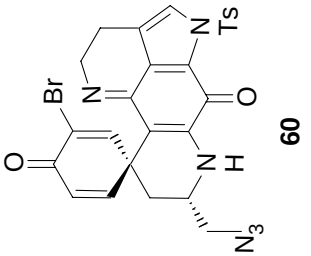



**56**



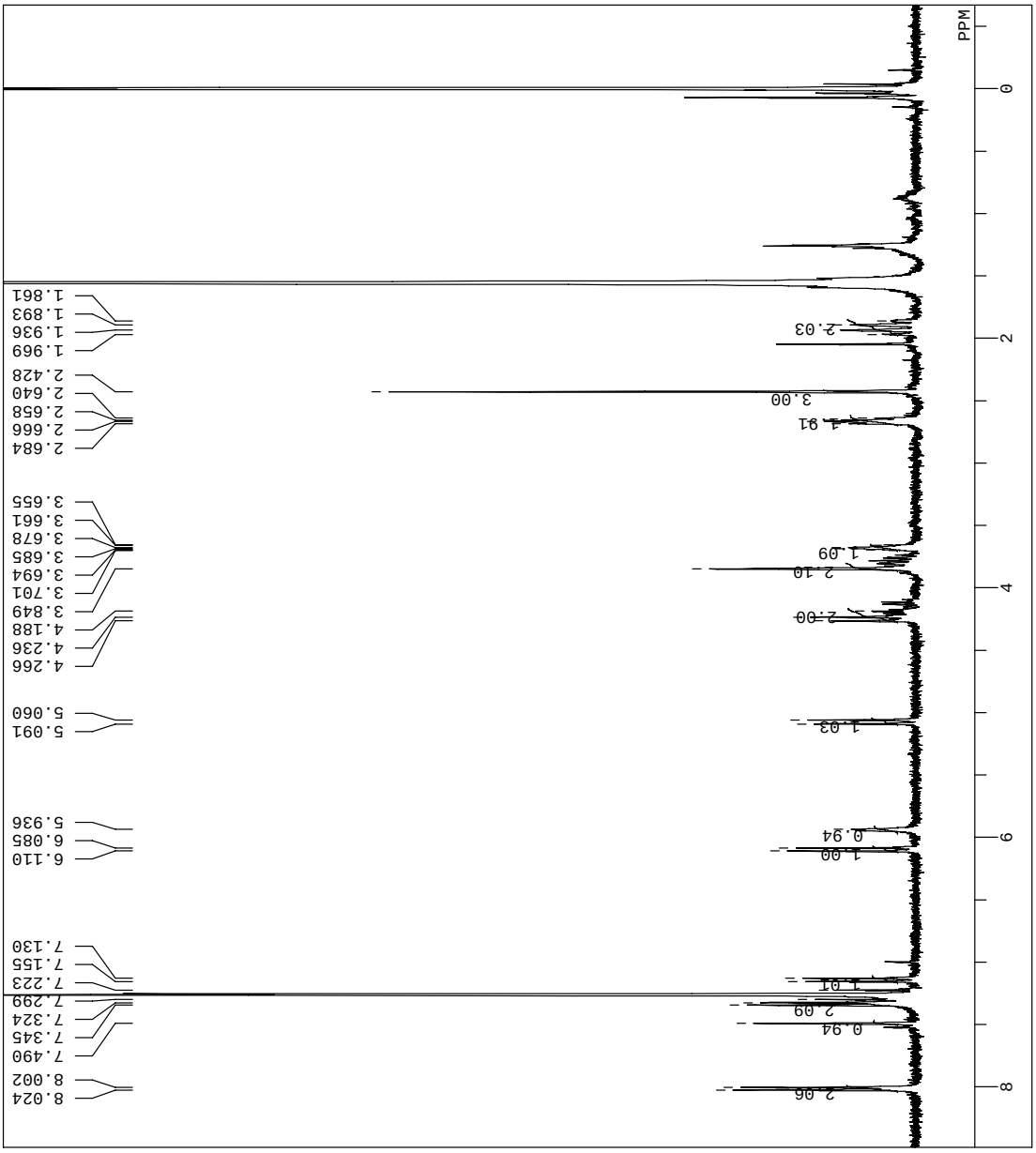

DFILE N-Ms debromo disco O-cyclic
COMNT
DATIM Sun Jan 29 14:53:59 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 3450
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25
N
Ms
O
N
O
N
H
O
56
17.729
28.054
31.819
36.661
37.606
42.276
44.569
49.740
68.113
75.150
109.833
118.416
122.107
124.959
125.453
145.930
152.787
157.481
159.429
165.438
198.477
PPM
0
25
50
75
100
125
150
175
200

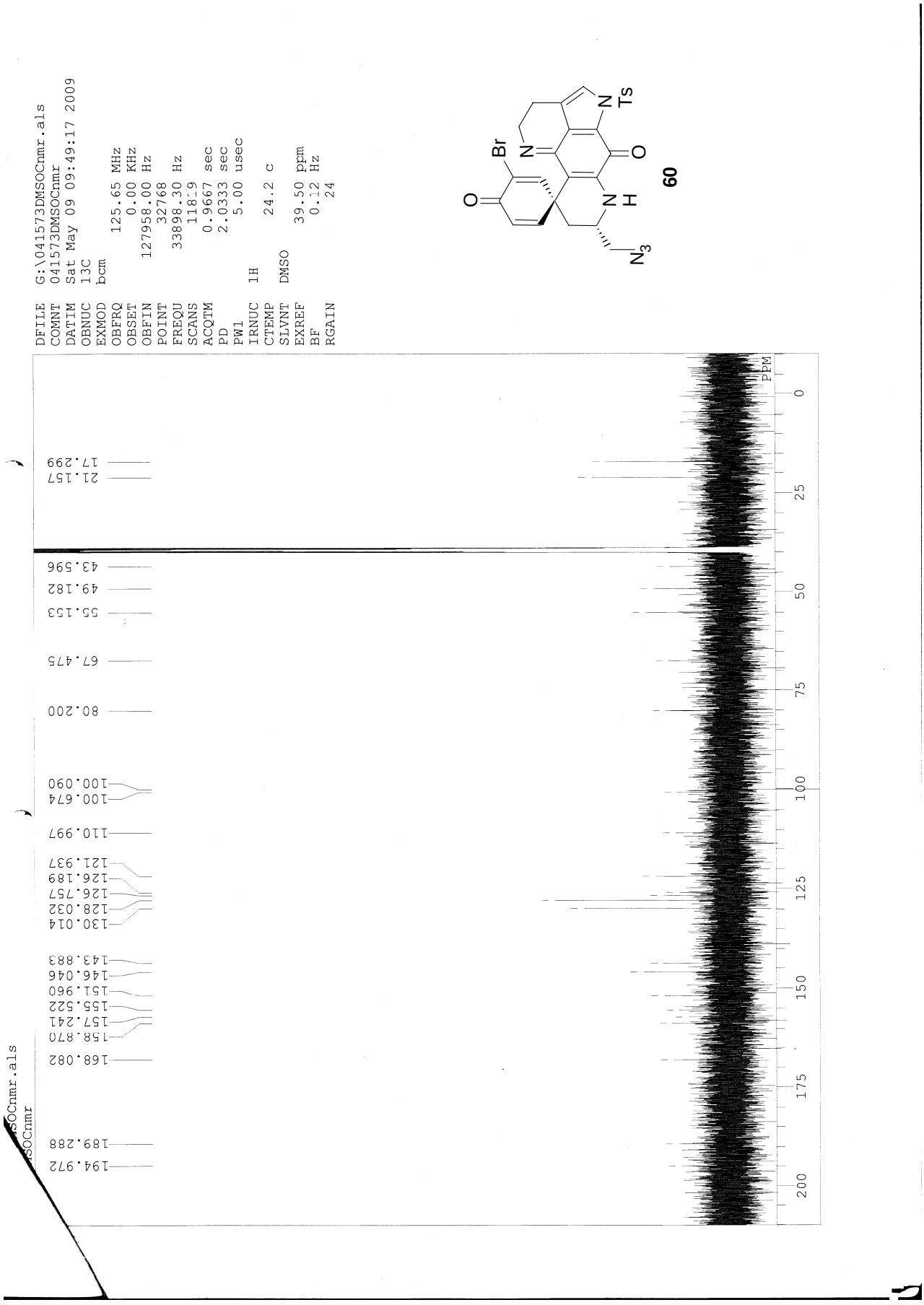

DFILE 041572up-2-1.als
COMNT single_pulse
DATIM 08-05-2009 09:15:35
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 24
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.35 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 56
Br
N
Ts
O
O
N
H
BzO
59
PPM

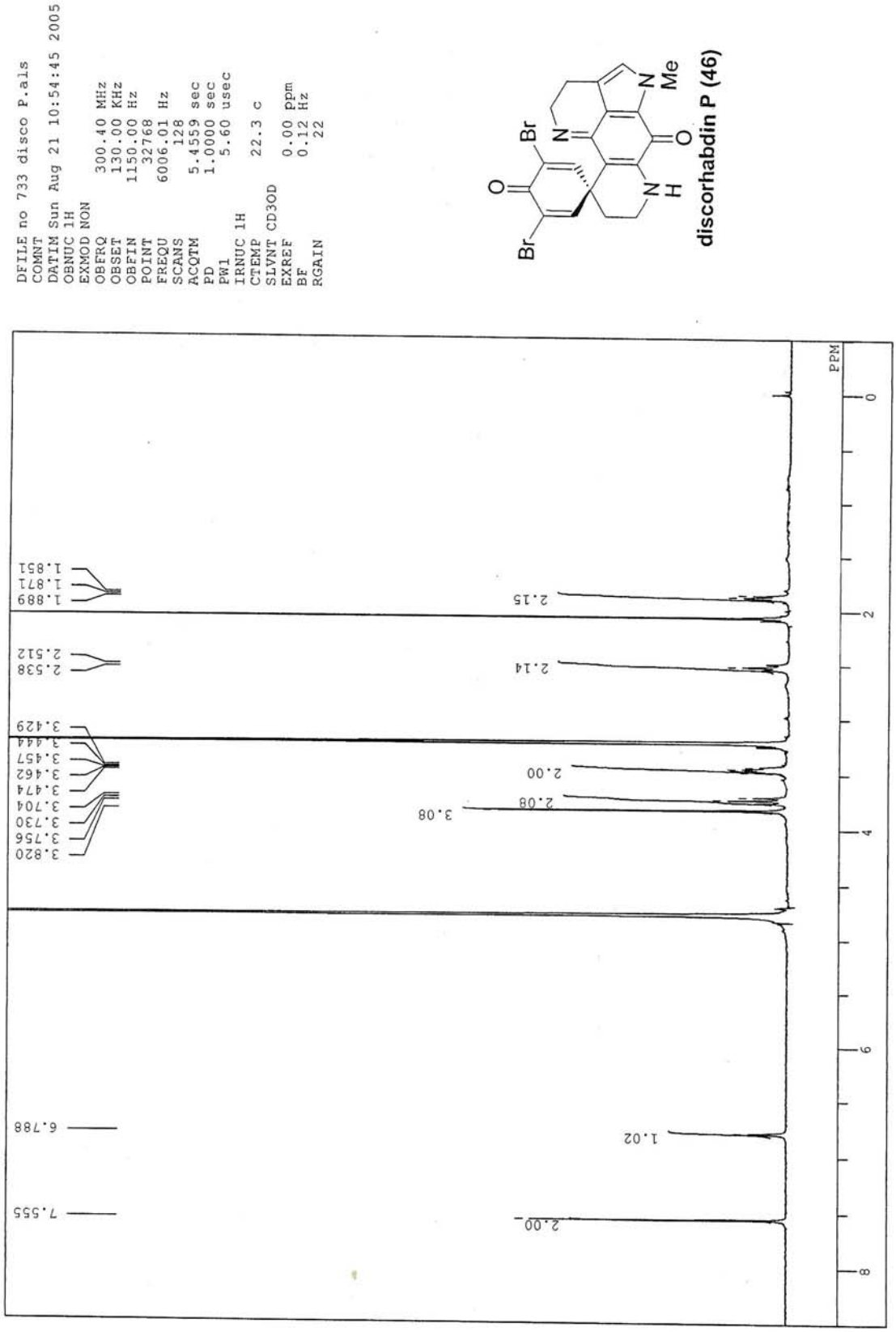


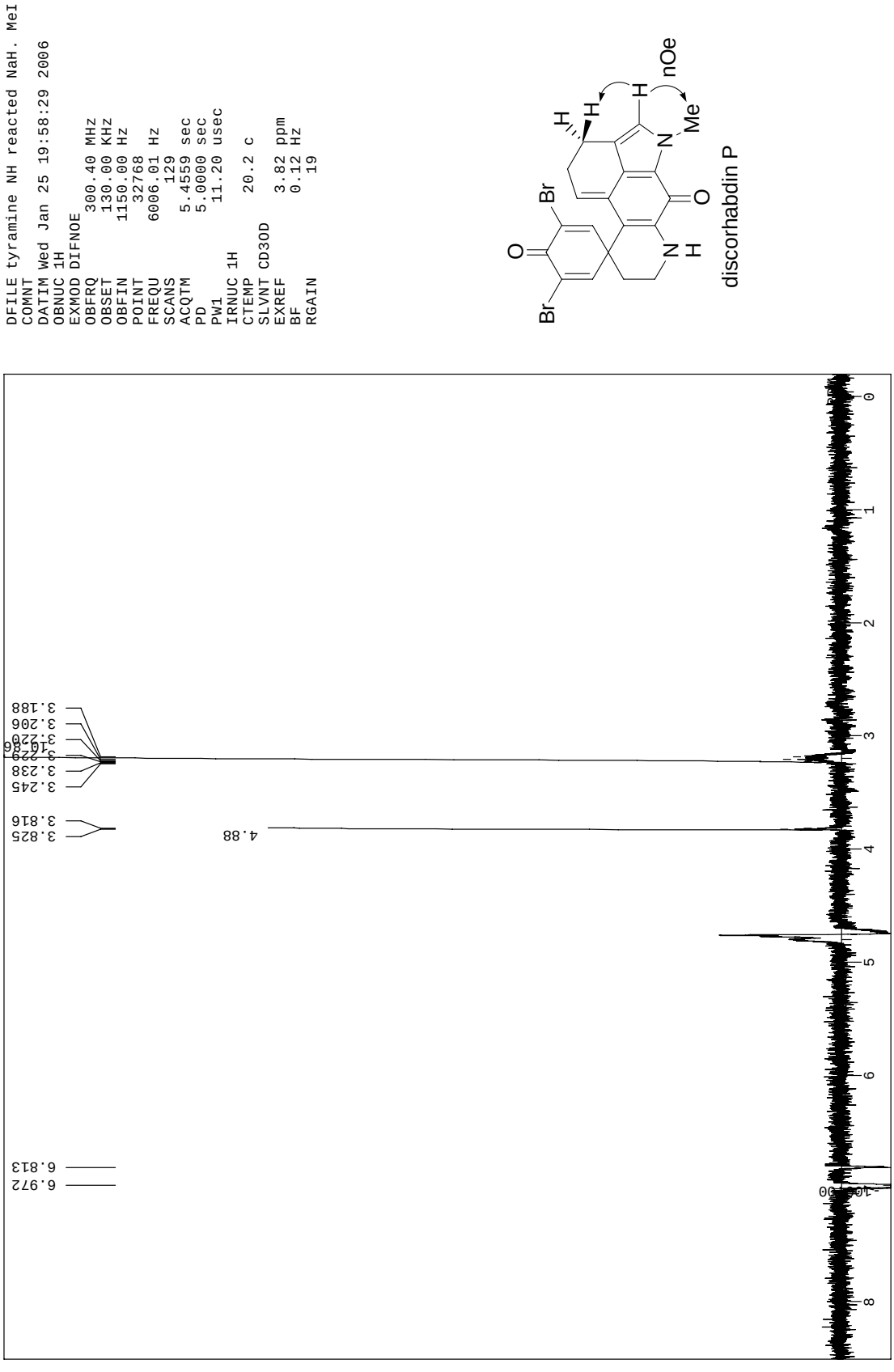

**60**

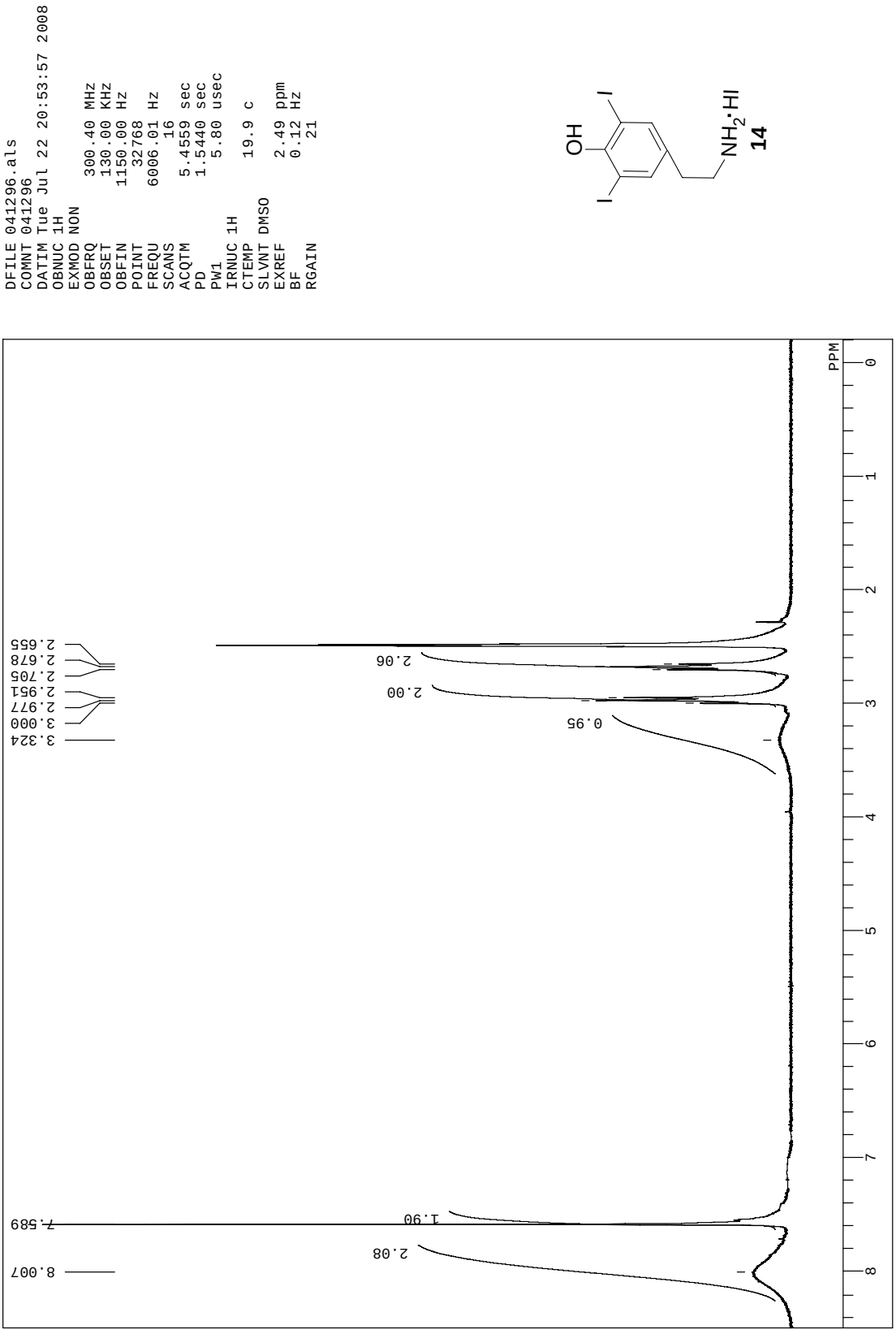
```
DFILE 041573-2-1.als
COMNT single_pulse
DATIM 08-05-2009 09:06:57
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ     399.78 MHz
OBSET       4.19 KHz
OBFIN       7.29 Hz
POINT      13107
FREQU    6002.31 Hz
SCANS         16
ACQTM      2.1837 sec
PD         5.0000 sec
PW1           5.35 usec
IRNUC 1H
CTEMP      21.1 c
SLVNT CDCL3
EXREF      0.00 ppm
BF         0.12 Hz
RGAIN        54
```

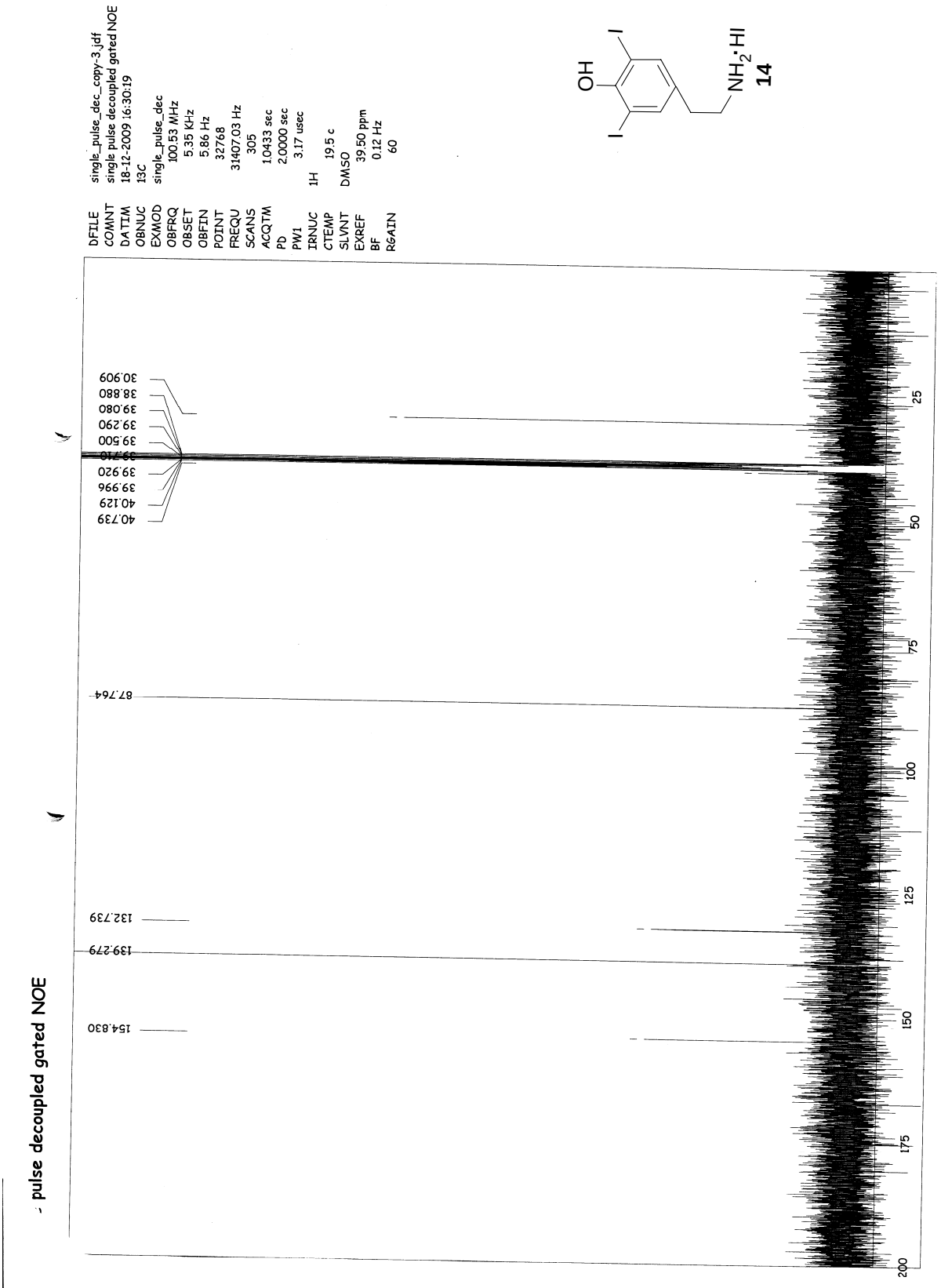


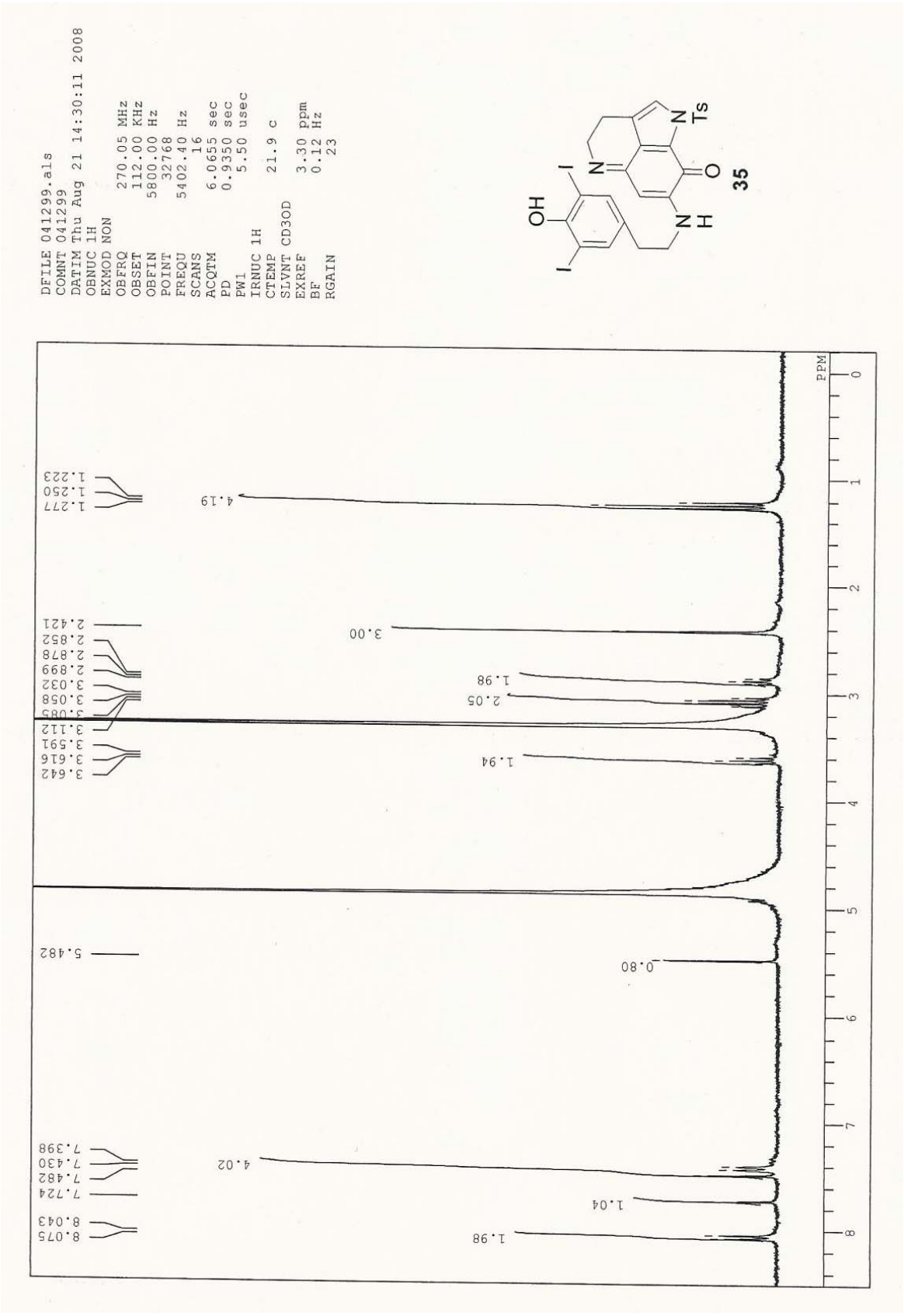

DFILE G:\041573DMSOCnmr.als
COMNT 041573DMSOCnmr
DATIM Sat May 09 09:49:17 2009
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 118.9
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.12 Hz
RGAIN 24
Br
N
Ts
O
N
H
O
$N_3$
60
21.157
17.299
43.596
49.182
55.153
67.475
80.200
100.674
100.090
110.997
121.937
126.189
126.757
128.032
130.014
143.883
146.046
151.960
155.522
157.241
158.870
168.082
189.288
194.972
PPM
0
25
50
75
100
125
150
175
200

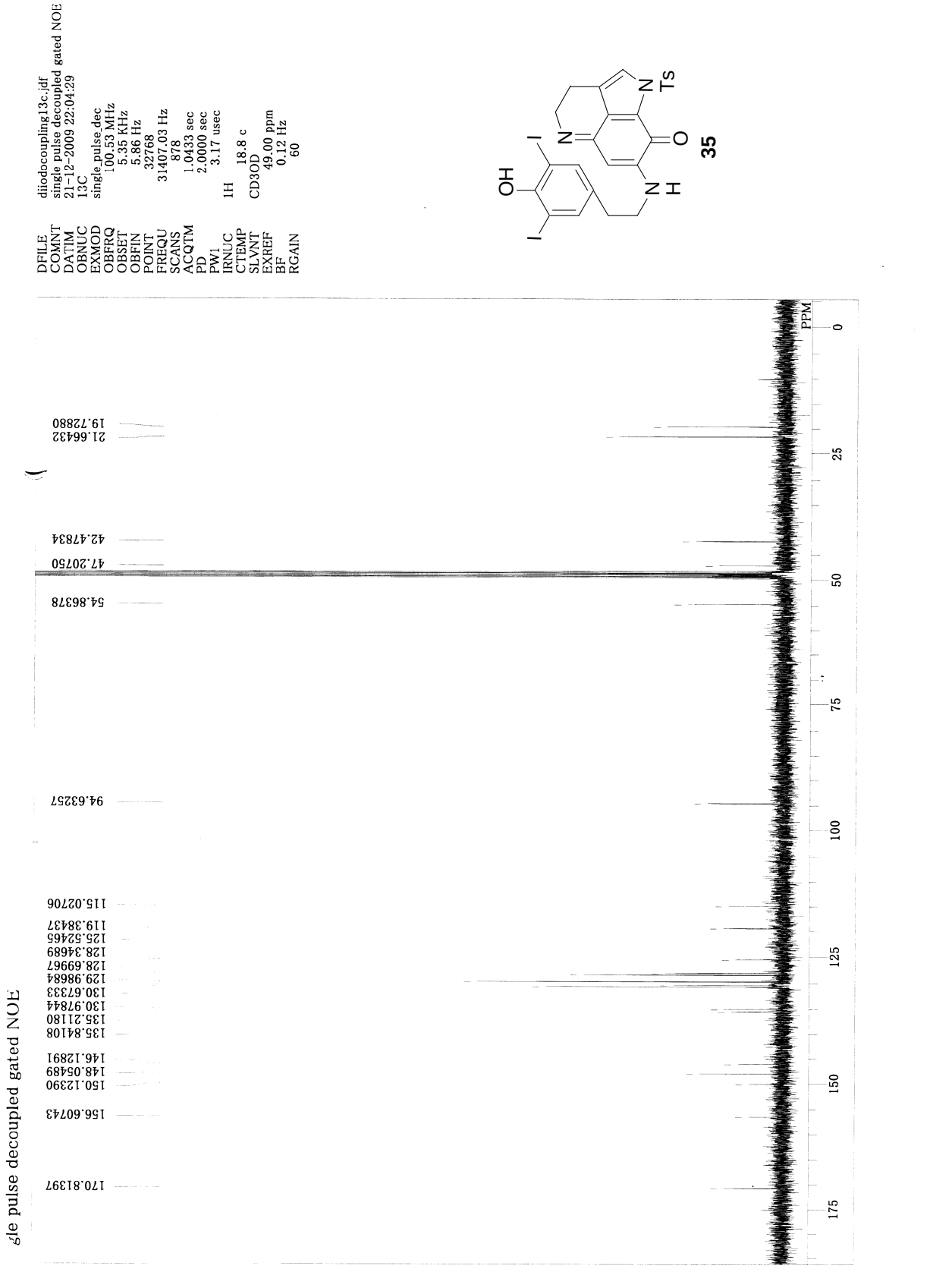

DFILE no 733 disco P.als
COMNT
DATIM Sun Aug 21 10:54:45 2005
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 128
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CD3OD
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 22
Br
O
N
H
N
Me
O
Br
discorhabdin P (46)
PPM
0
2
4
6
8
1.889
1.871
1.851
2.538
2.512
3.429
3.444
3.457
3.462
3.474
3.704
3.730
3.756
3.820
6.788
7.555
2.15
2.14
2.00
2.08
3.08
1.02
2.00

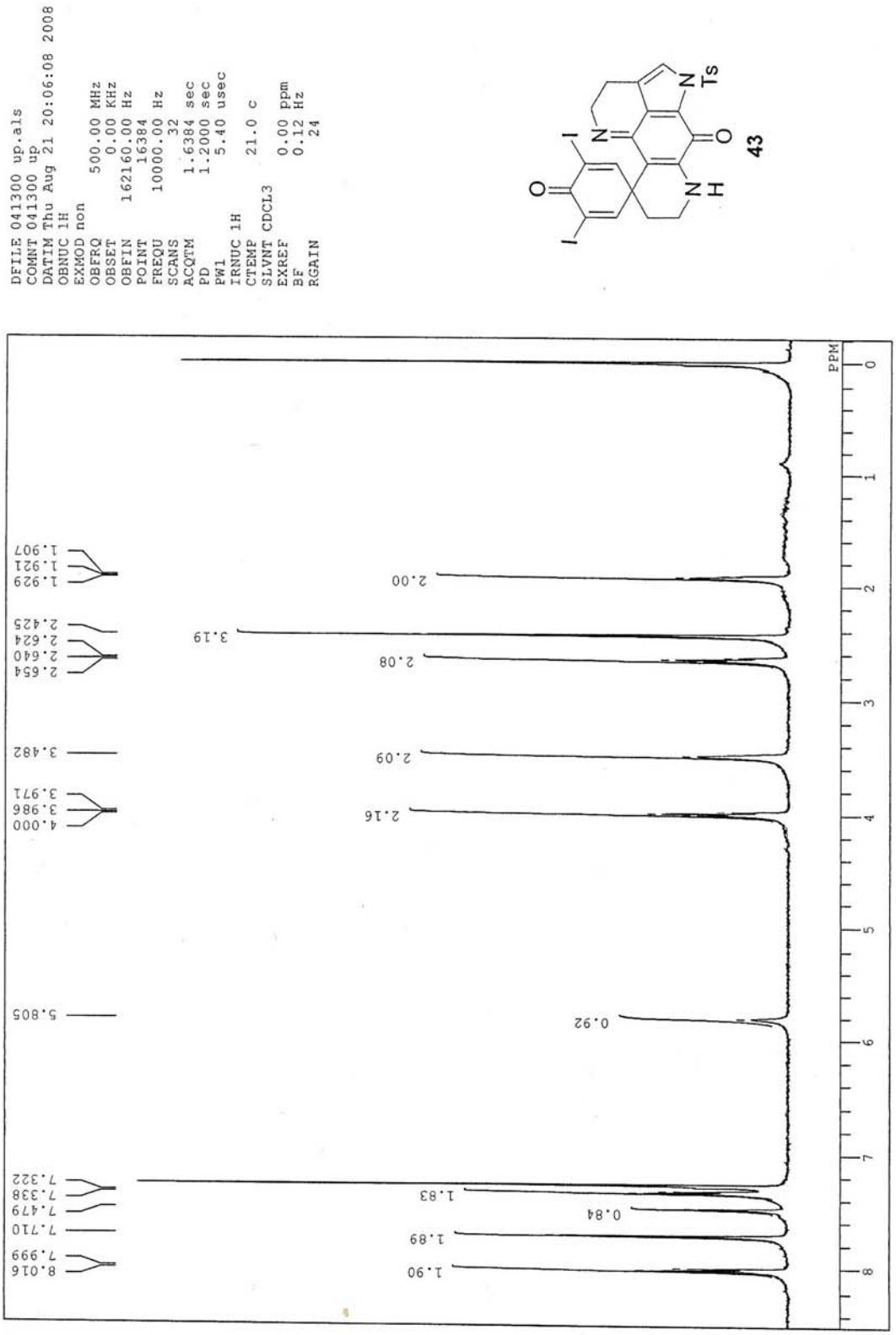

DFILE tyramine NH reacted NaH. MeI
COMNT
DATIM Wed Jan 25 19:58:29 2006
OBNUC 1H
EXMOD DIFNOE
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 129
ACQTM 5.4559 sec
PD 5.0000 sec
PW1 11.20 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CD3OD
EXREF 3.82 ppm
BF 0.12 Hz
RGAIN 19
nOe
Me
Br
O
N
H
discorhabdin P
6.972
6.813
3.825
3.816
4.88
3.245
3.238
3.229
3.220
3.206
3.188

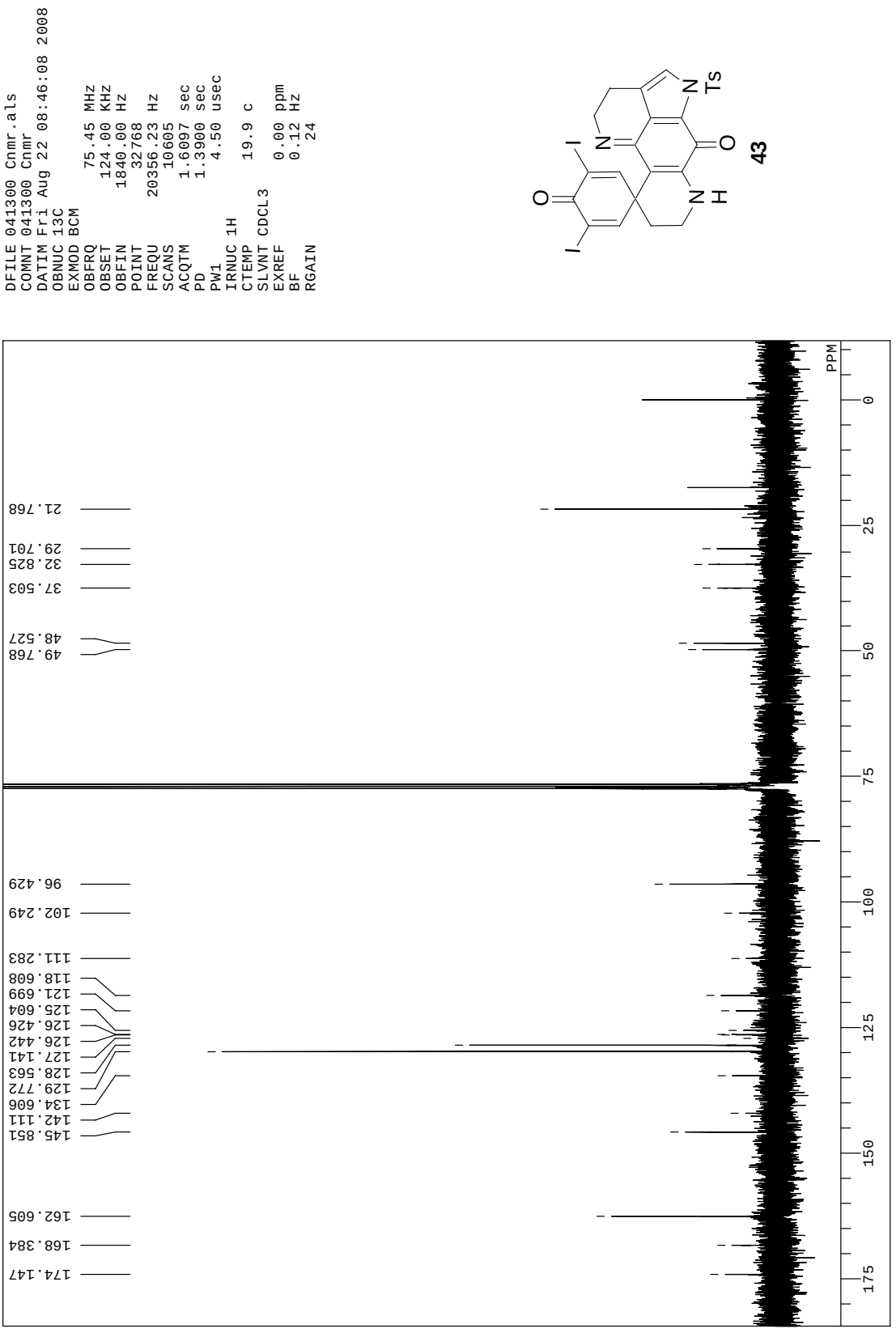

DFILE 041296.als
COMNT 041296
DATIM Tue Jul 22 20:53:57 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.12 Hz
RGAIN 21
OH
I
I
NH2·HI
14
PPM
0
1
2
3
4
5
6
7
8
8.007
7.589
3.324
3.000
2.977
2.951
2.705
2.678
2.655
2.08
1.90
2.06
2.00
0.95

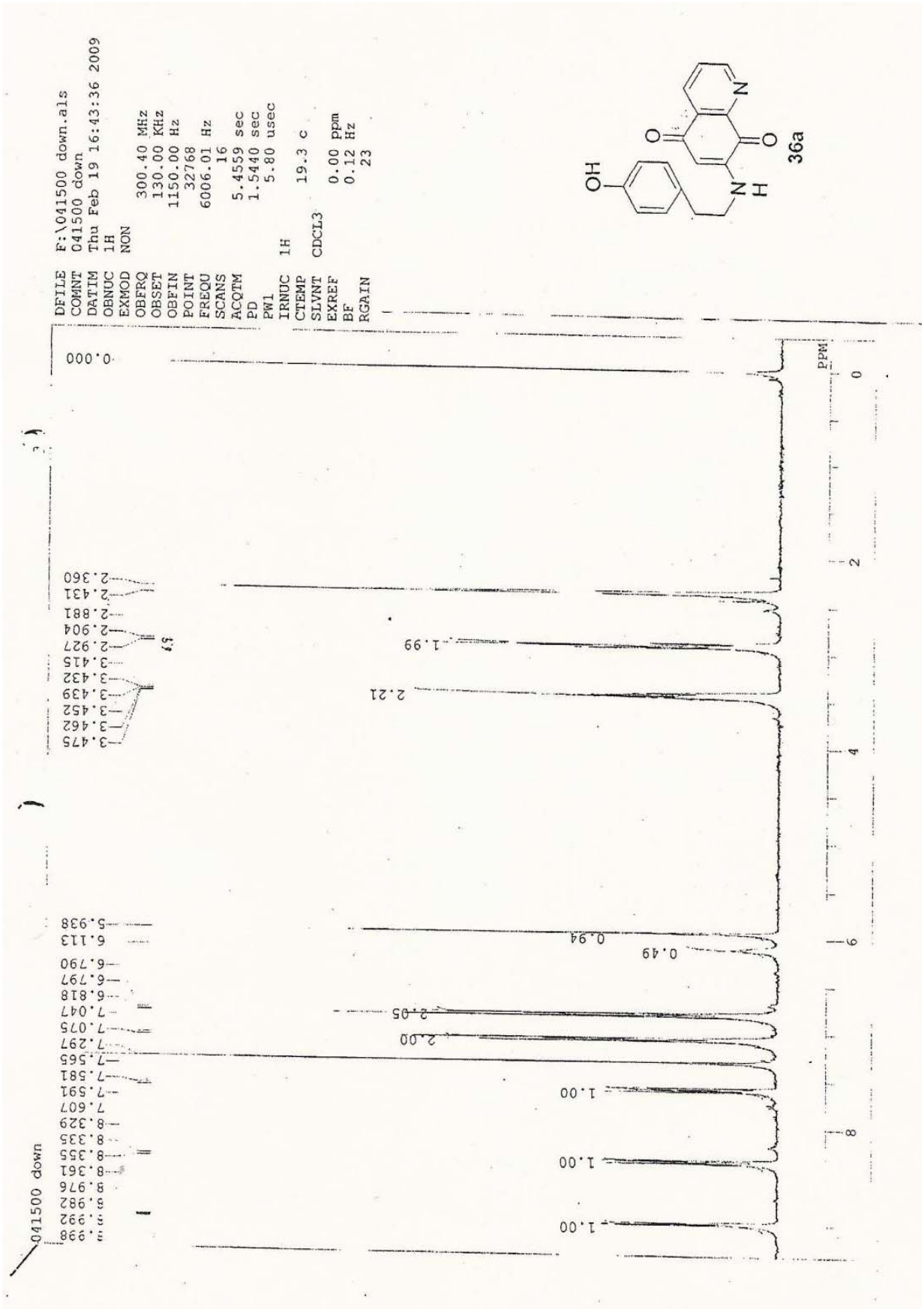

DFILE single_pulse_dec_copy-3.jdf
COMNT single pulse decoupled gated NOE
DATIM 18-12-2009 16:30:19
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.03 Hz
SCANS 305
ACQTM 10433 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.12 Hz
RGAIN 60
OH
I
I
NH2·HI
14
- pulse decoupled gated NOE
30.909
38.880
39.080
39.290
39.500
39.710
39.920
39.996
40.129
40.739
87.764
132.739
139.279
154.830
25
50
75
100
125
150
175
200

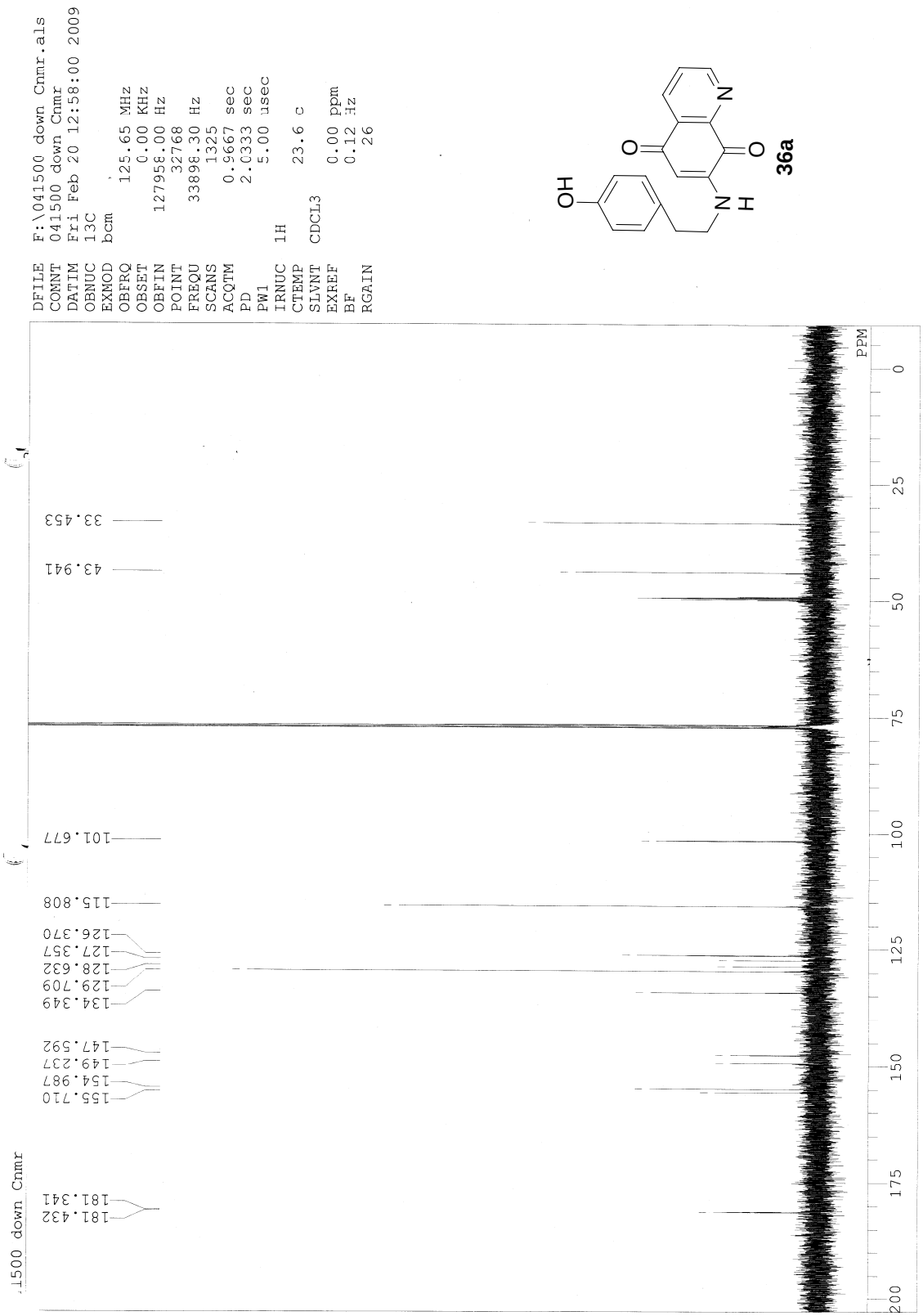

DFILE 041299.als
COMNT 041299
DATIM Thu Aug 21 14:30:11 2008
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 32768
FREQU 5402.40 Hz
SCANS 16
ACQTM 6.0655 sec
PD 0.9350 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CD3OD
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 23
35
PPM

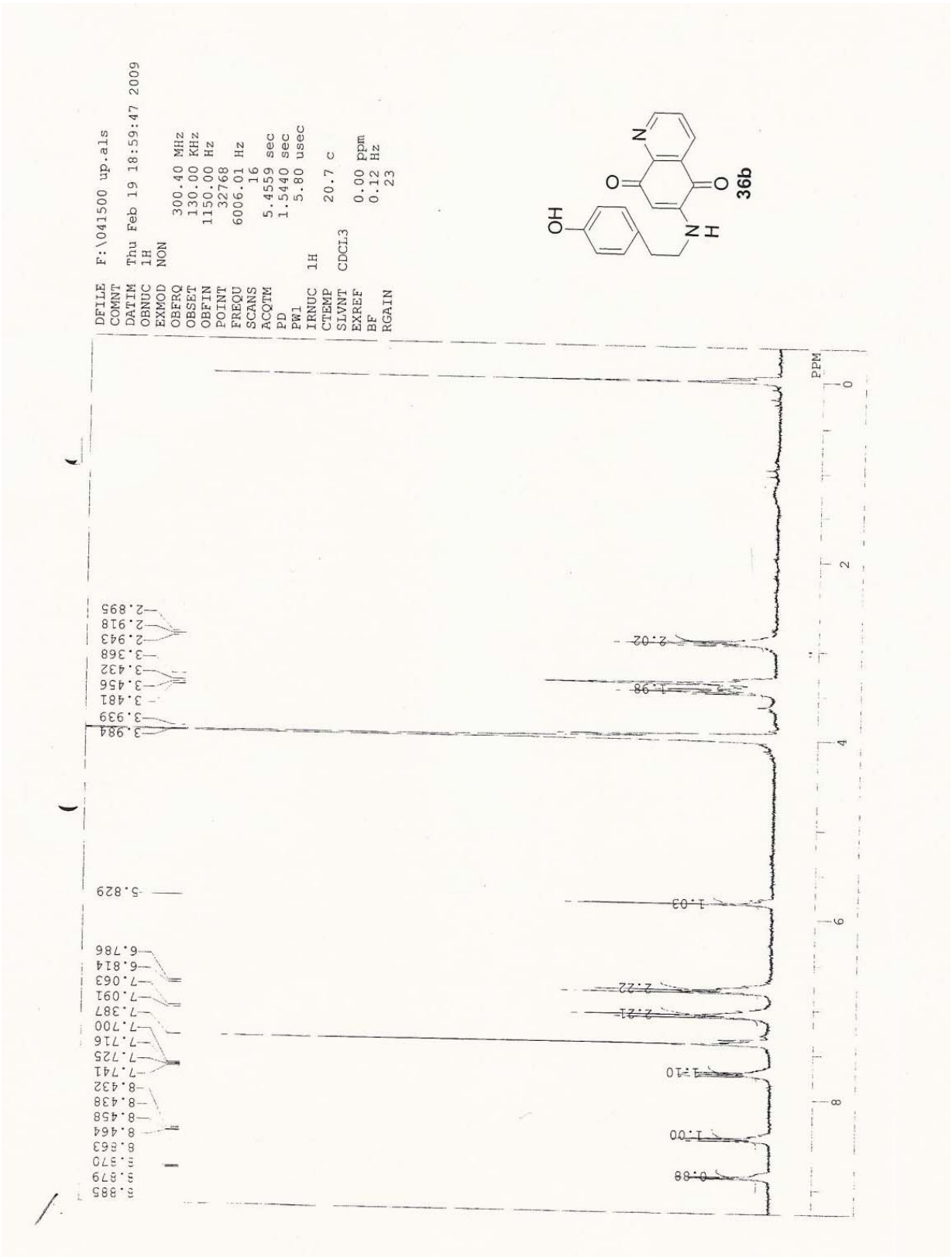

DFILE diiodocoupling13c.jdf
COMNT single pulse decoupled gated NOE
DATIM 21-12-2009 22:04:29
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.03 Hz
SCANS 878
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 18.8 c
SLVNT CD3OD
EXREF 49.00 ppm
BF 0.12 Hz
RGAIN 60
35
PPM
0
25
50
75
100
125
150
175
19.72880
21.66432
42.47834
47.20750
54.86378
94.63257
115.02706
119.38437
125.52465
128.34689
128.69967
129.98684
130.67333
130.97844
135.21180
135.84108
146.12891
148.05489
150.12390
156.60743
170.81397
gle pulse decoupled gated NOE

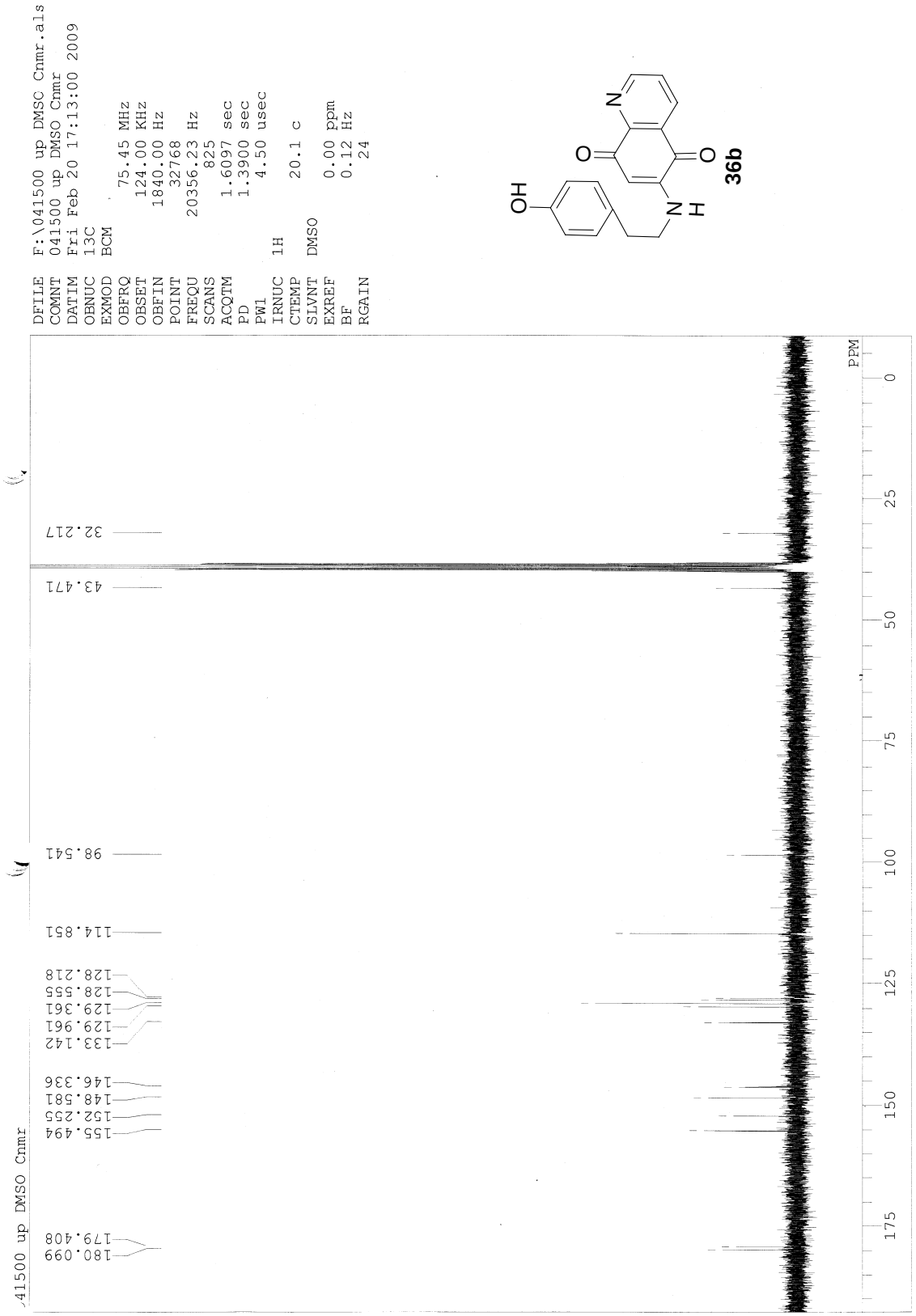

DFILE 041300 up.als
COMNT 041300 up
DATIM Thu Aug 21 20:06:08 2008
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.00 Hz
POINT 16384
FREQU 10000.00 Hz
SCANS 32
ACQTM 1.6384 sec
PD 1.2000 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24
Ts
43
PPM
1.907
1.921
1.929
2.425
2.624
2.640
2.654
3.482
3.971
3.986
4.000
5.805
7.322
7.338
7.479
7.710
7.999
8.016
2.00
3.19
2.08
2.09
2.16
0.92
1.83
0.84
1.89
1.90

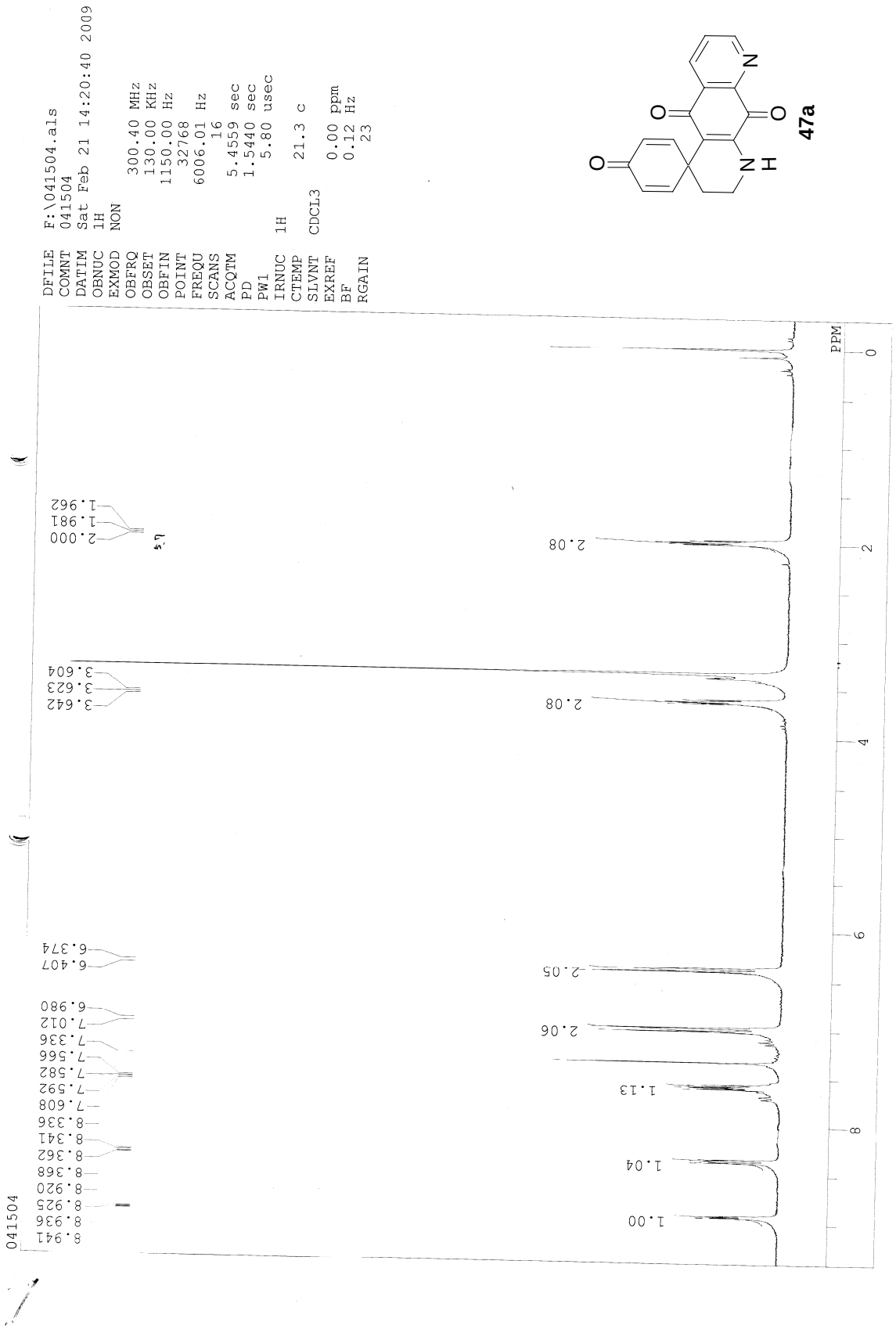

DFILE 041300 Cnmr.als
COMNT 041300 Cnmr
DATIM Fri Aug 22 08:46:08 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 10605
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24
Ts
43
21.768
29.701
32.825
37.503
48.527
49.768
96.429
102.249
111.283
118.608
121.699
125.604
126.426
126.442
127.141
128.563
129.772
134.606
142.111
145.851
162.605
168.384
174.147
PPM
0
25
50
75
100
125
150
175

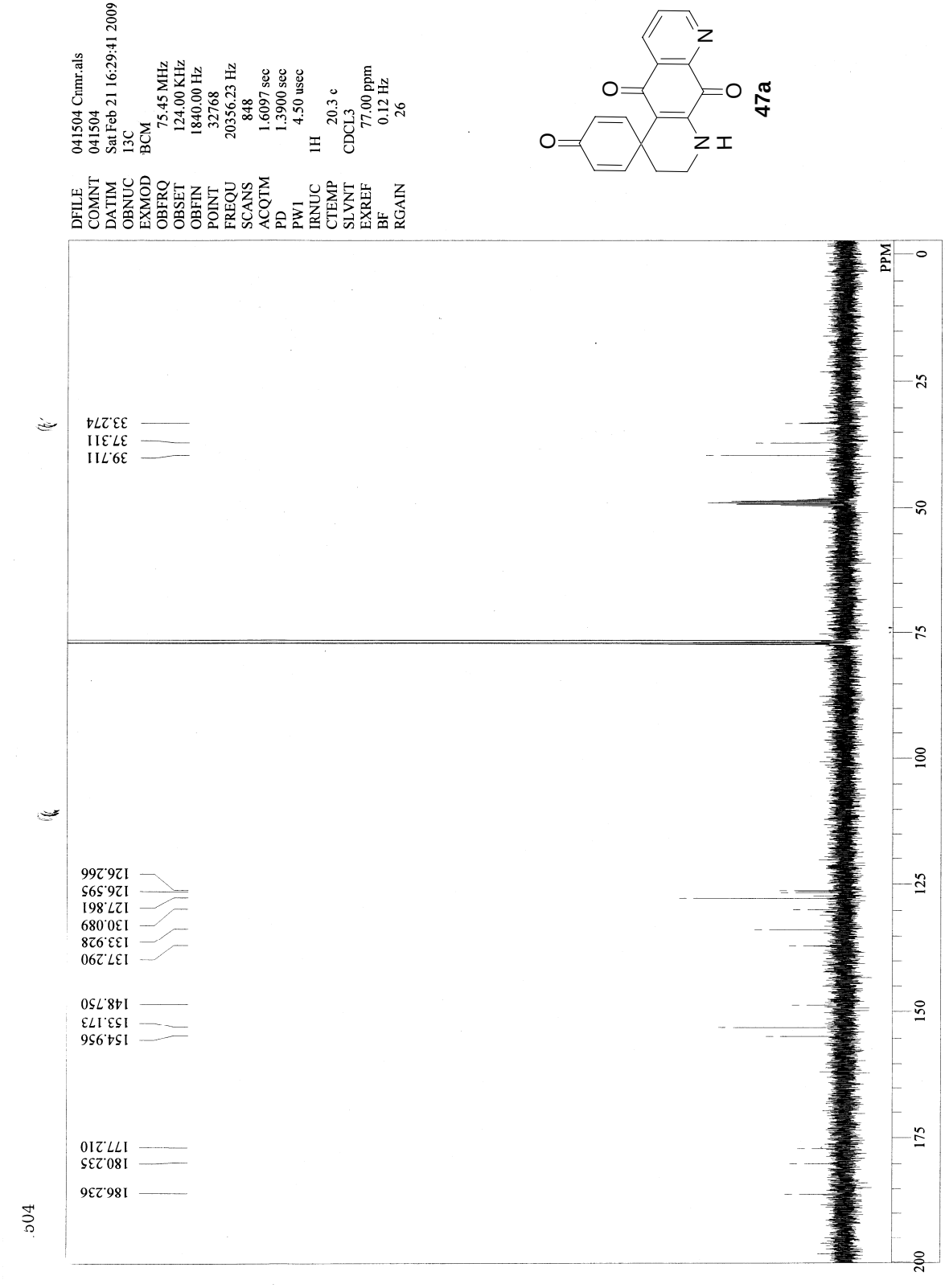

DFILE F:\041500 down.als
COMNT 041500 down
DATIM Thu Feb 19 16:43:36 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23
OH
O
N
H
O
36a
041500 down
PPM

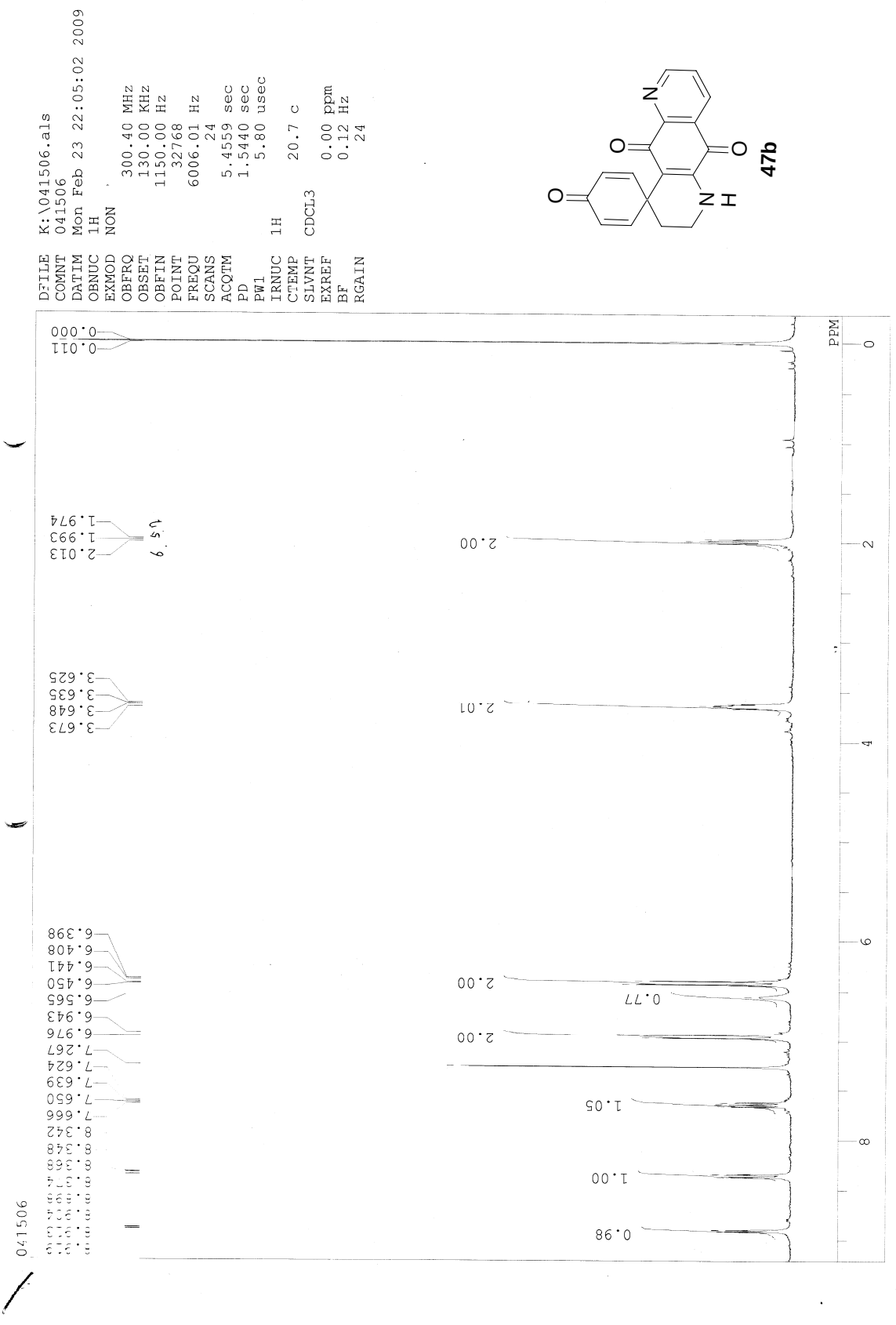

DFILE F:\041500 down Cnmr.als
COMNT 041500 down Cnmr
DATIM Fri Feb 20 12:58:00 2009
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 1325
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26
OH
O
O
N
N
H
36a
33.453
43.941
101.677
115.808
126.370
127.357
128.632
129.709
134.349
147.592
149.237
154.987
155.710
181.432
181.341
1500 down Cnmr
PPM
0
25
50
75
100
125
150
175
200

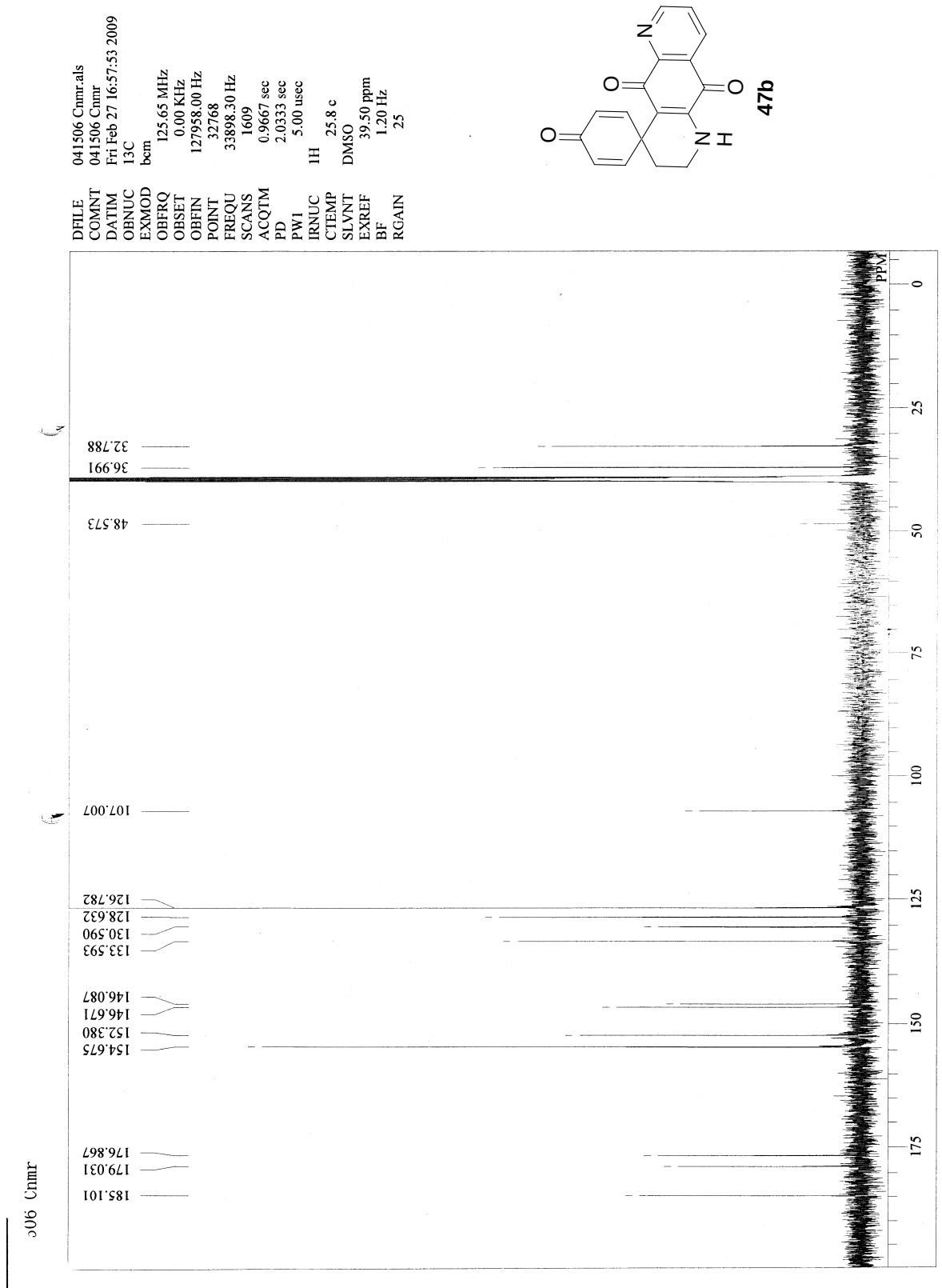

DFILE F:\041500 up.als
COMNT
DATIM Thu Feb 19 18:59:47 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23
OH
O
O
N
H
N
36b
PPM
0
2
4
6
8
2.02
1.98
1.03
2.22
2.21
1.10
1.00
0.88
2.885
2.879
2.870
8.863
8.464
8.458
8.438
8.432
7.741
7.725
7.716
7.700
7.387
7.091
7.063
6.814
6.786
5.829
3.984
3.939
3.481
3.456
3.432
3.368
2.943
2.918
2.895

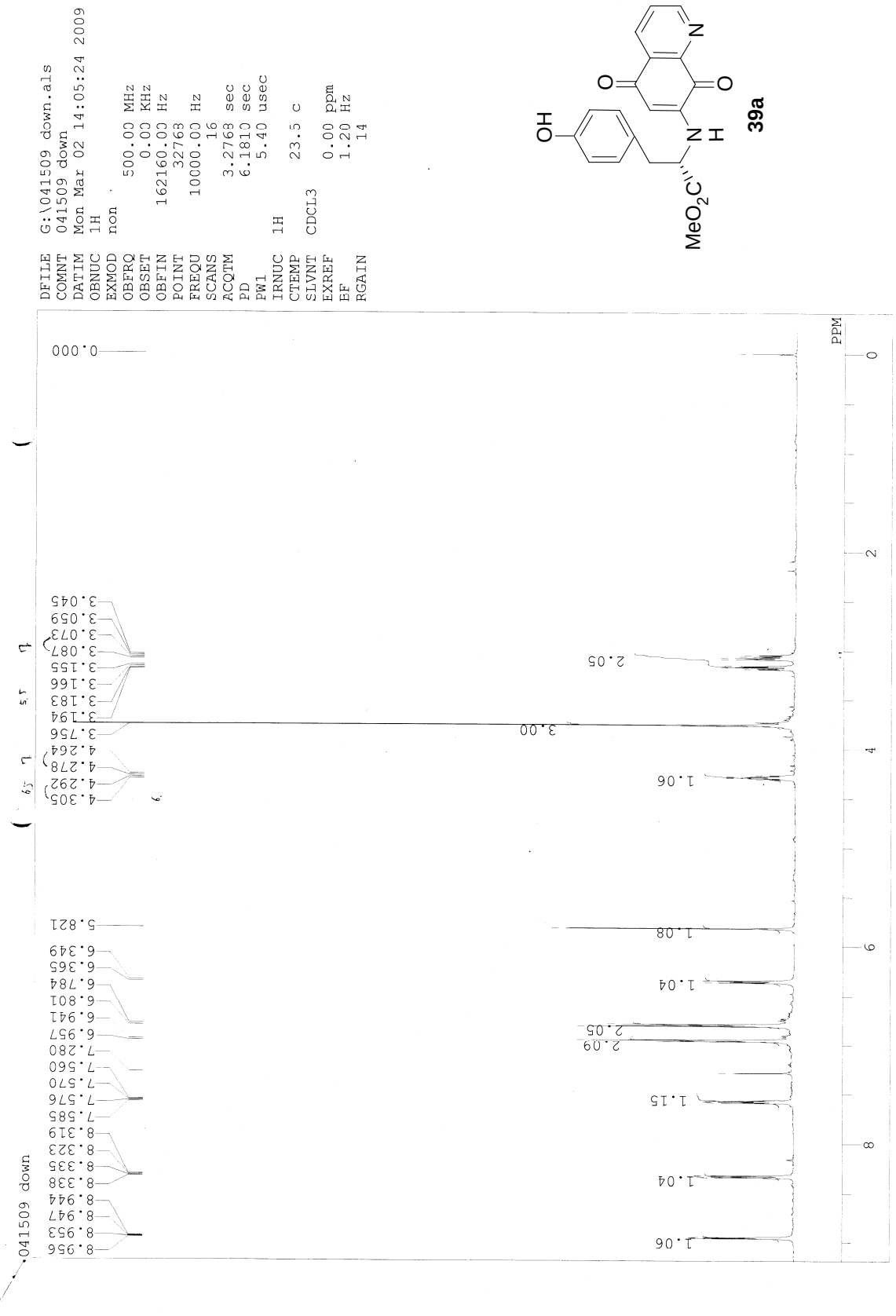

DFILE F:\041500 up DMSC Cnmr.als
COMNT 041500 up DMSO Cnmr
DATIM Fri Feb 20 17:13:00 2009
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 825
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24
36b
OH
O
O
N
H
N
041500 up DMSO Cnmr
32.217
43.471
98.541
114.851
128.218
128.555
129.361
129.961
133.142
146.336
148.581
152.255
155.494
179.408
180.099
PPM
0
25
50
75
100
125
150
175

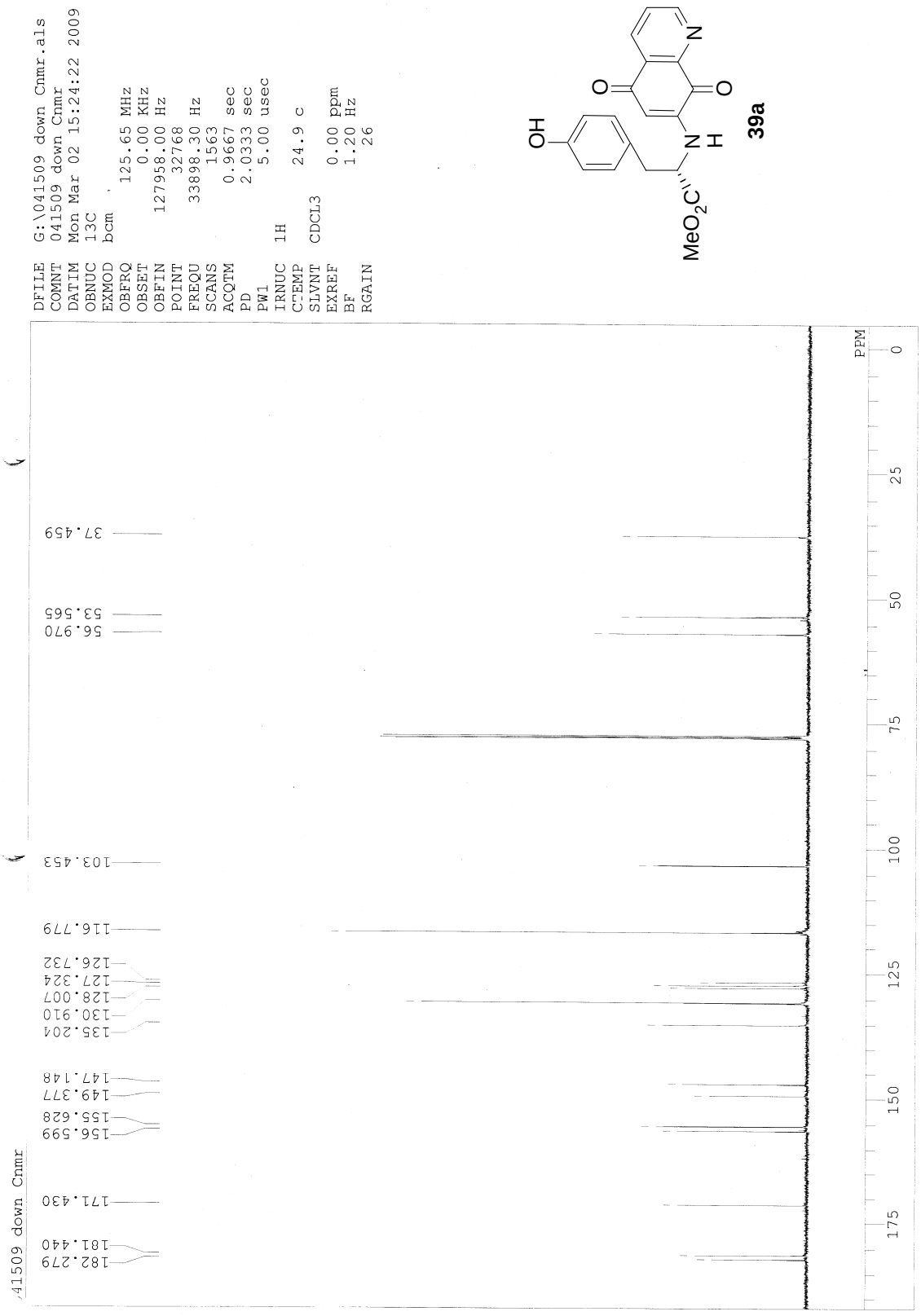

DFILE F:\041504.als
COMNT 041504
DATIM Sat Feb 21 14:20:40 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23
041504
PPM
47a

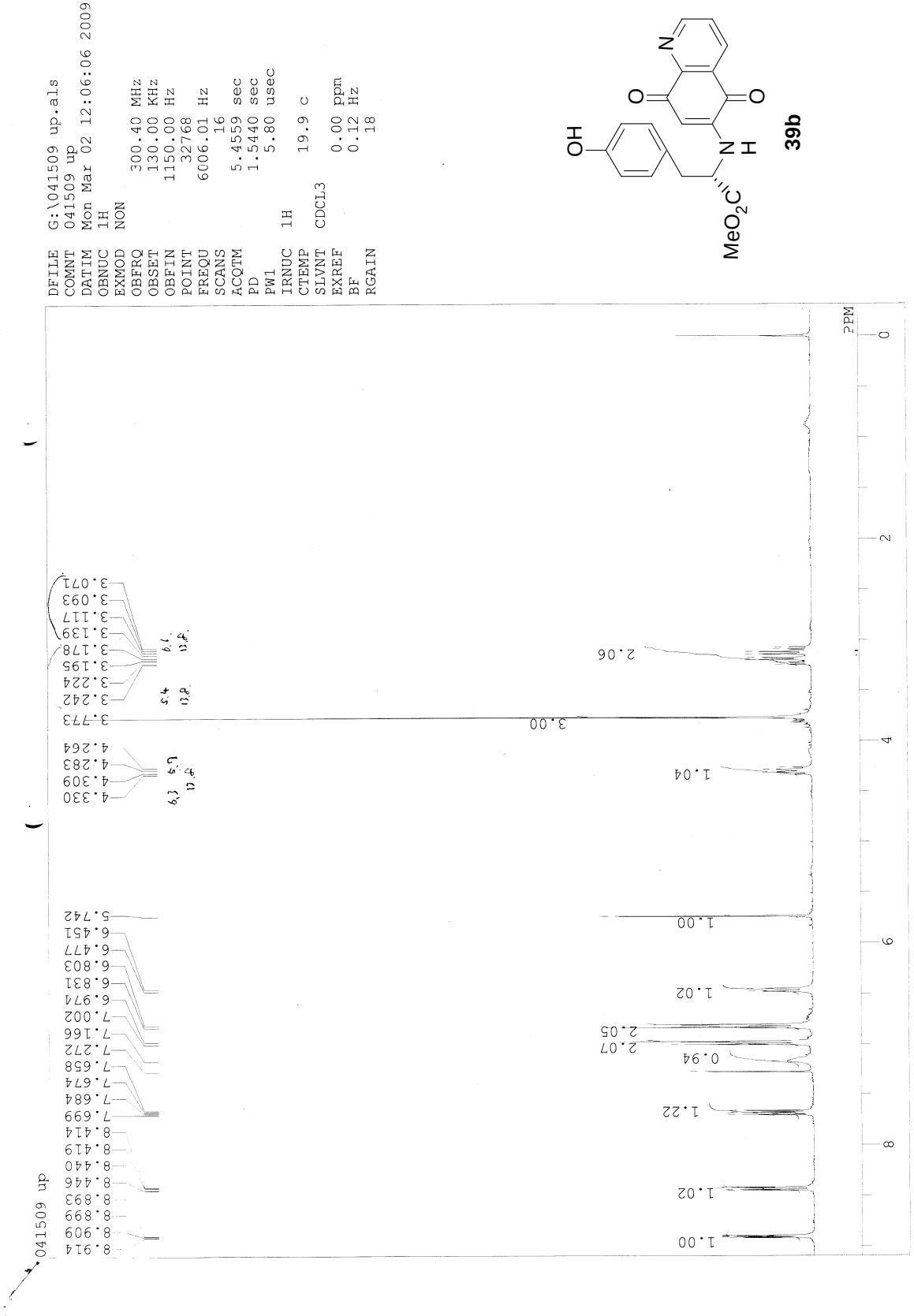

DFILE 041504 Cnmr.als
COMNT 041504
DATIM Sat Feb 21 16:29:41 2009
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 848
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 26
47a
PPM
0
25
50
75
100
125
150
175
200
39.711
37.311
33.274
126.266
126.595
127.861
130.089
133.928
137.290
148.750
153.173
154.956
177.210
180.235
186.236

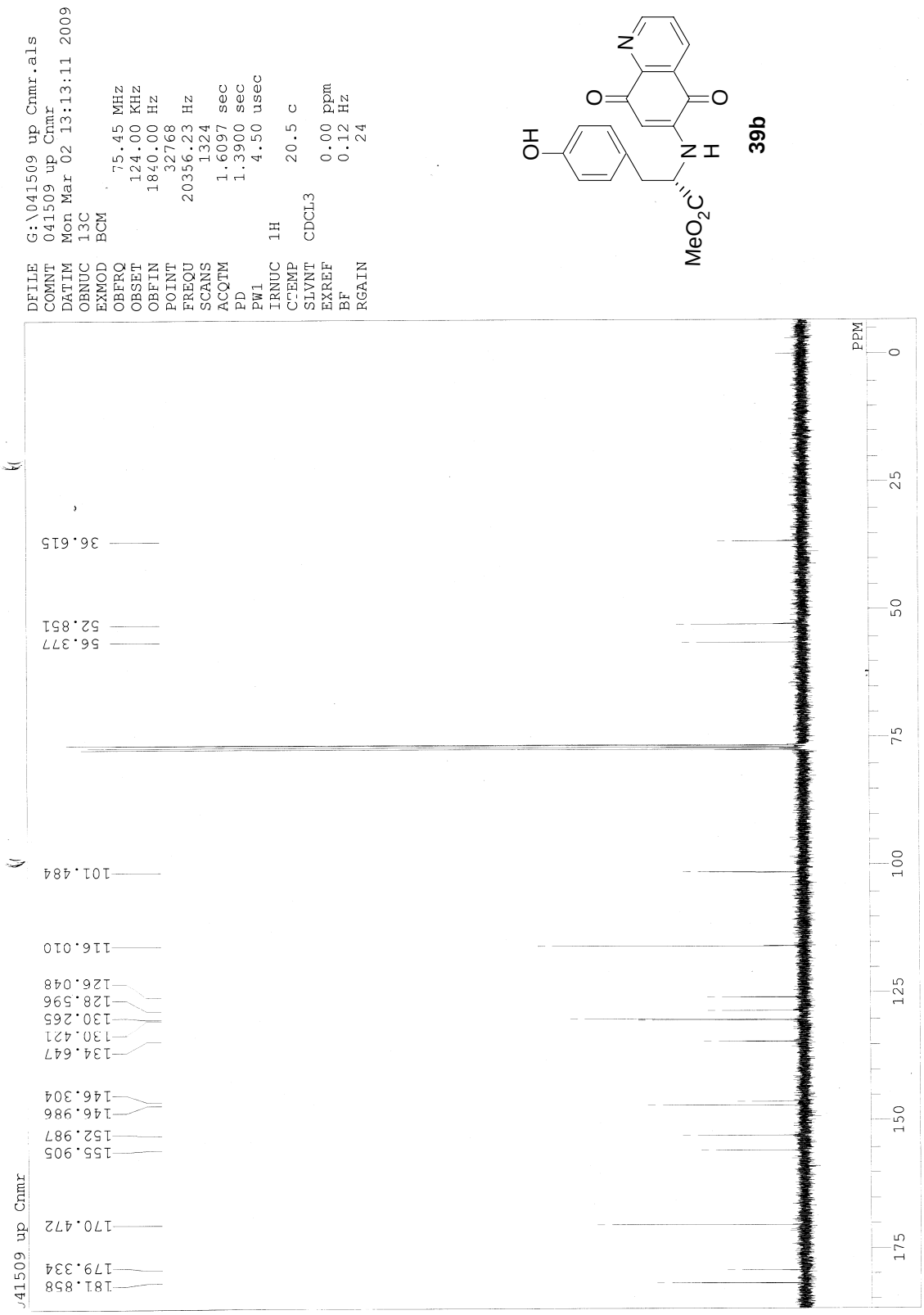

DATA K:\041506.als
COMNT 041506
DATIM Mon Feb 23 22:05:02 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 24
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24
47b
PPM
041506

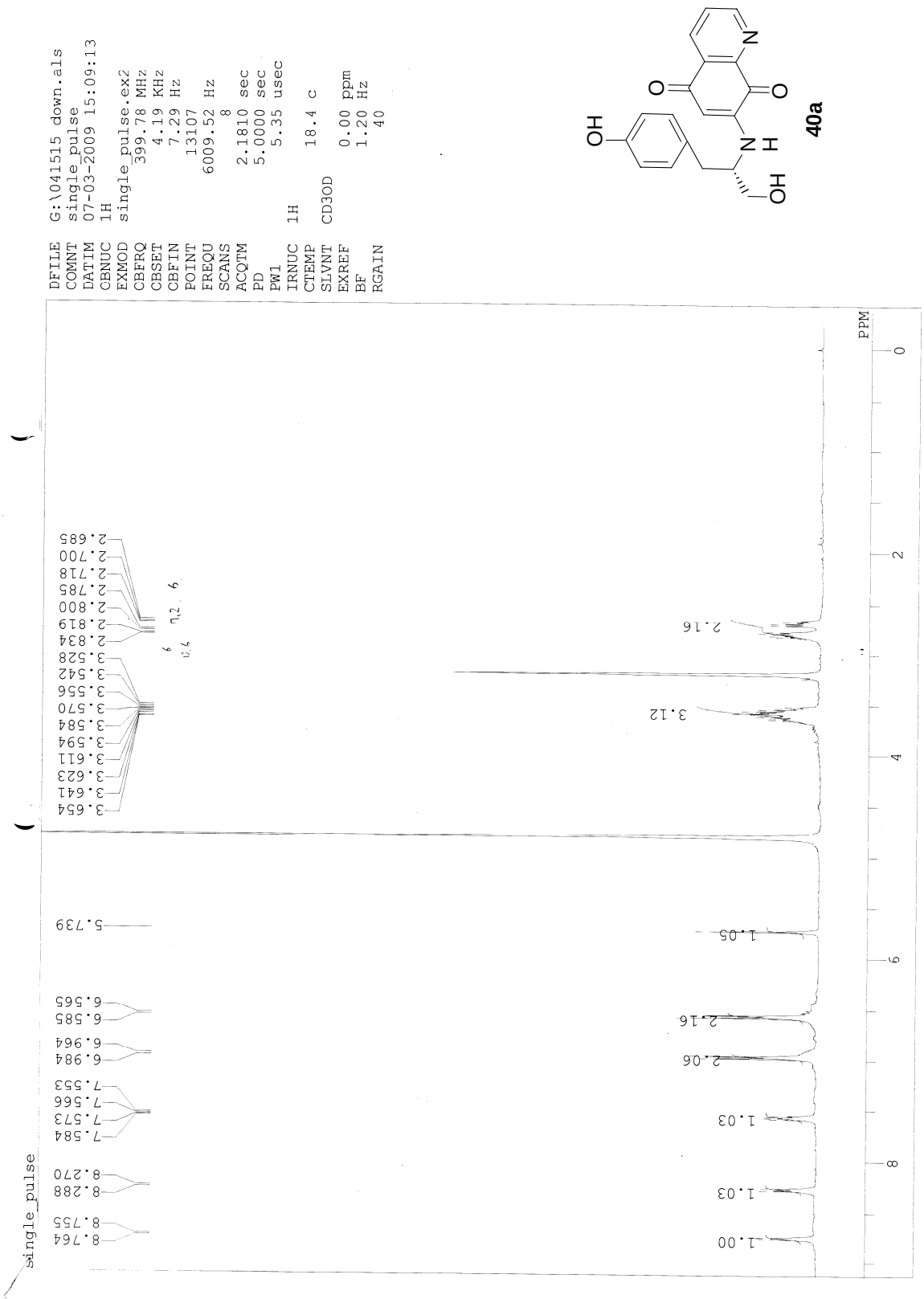

DFILE 041506 Cnmr.als
COMNT 041506 Cnmr
DATIM Fri Feb 27 16:57:53 2009
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 1609
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT DMSO
EXREF 39.50 ppm
BF 1.20 Hz
RGAIN 25
47b
32.788
36.991
48.573
107.007
126.782
128.632
130.590
133.593
146.087
146.671
152.380
154.675
176.867
179.031
185.101
PPM
0
25
50
75
100
125
150
175
306 Cnmr

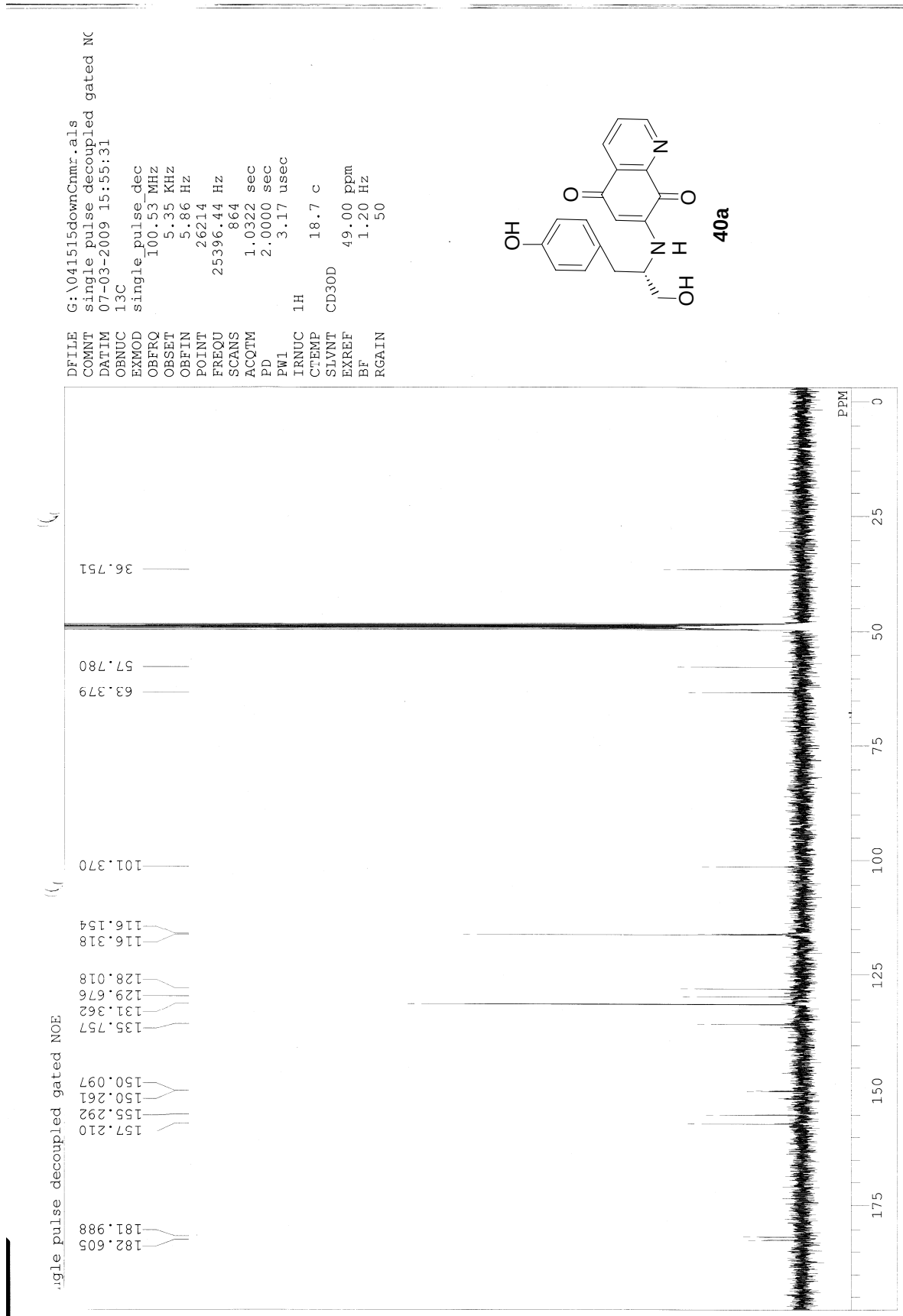

DFILE G:\041509 down.als
COMNT 041509 down
DATIM Mon Mar 02 14:05:24 2009
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.00 Hz
POINT 32763
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2763 sec
PD 6.1810 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 0.00 ppm
EF 1.20 Hz
RGAIN 14
OH
O
O
N
H
N
MeO2C
39a
041509 down
PPM

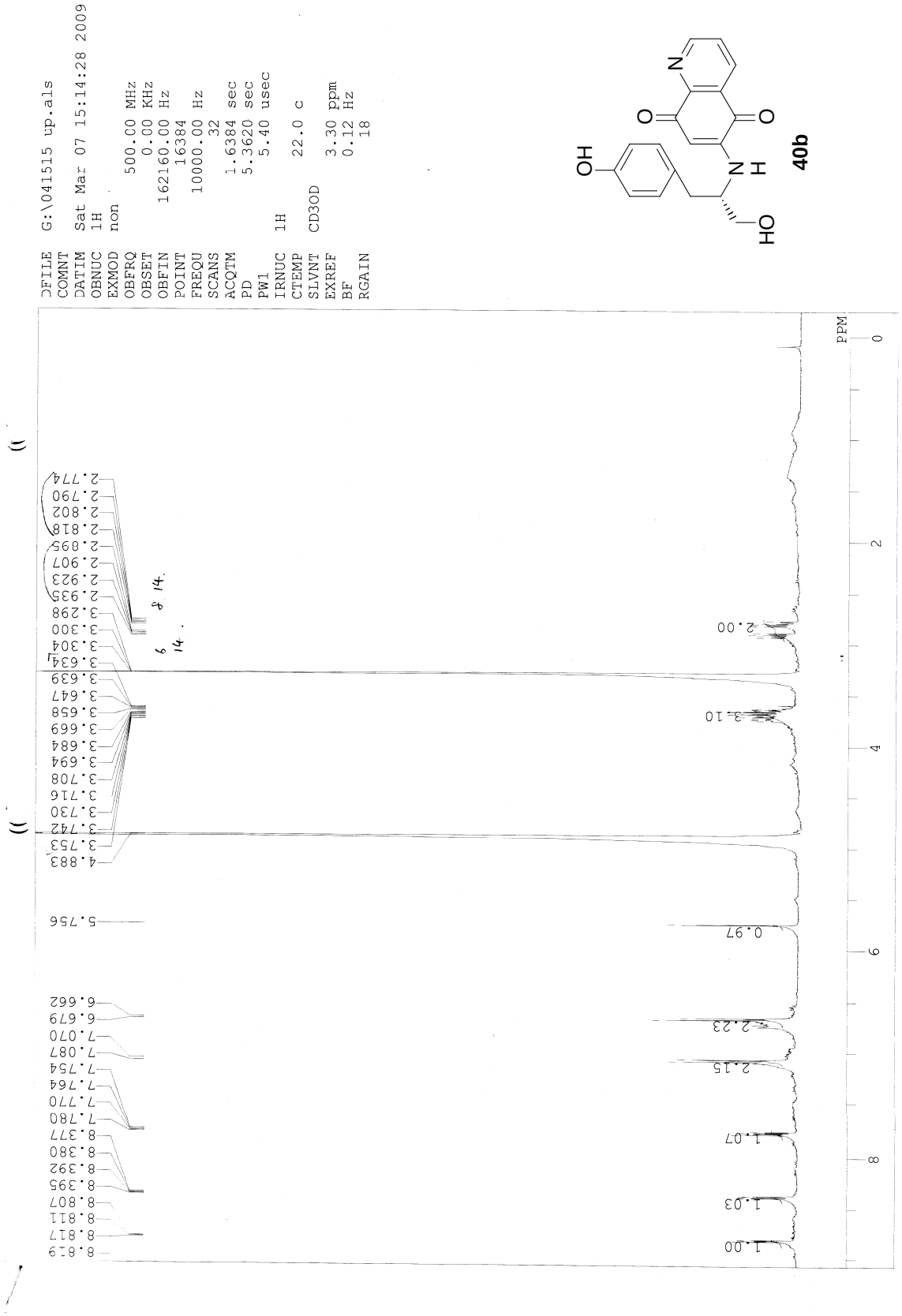

DFILE G:\041509 down Cnmr.als
COMNT 041509 down Cnmr
DATIM Mon Mar 02 15:24:22 2009
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 1563
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 24.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 26
OH
O
O
N
H
N
MeO2C
39a
041509 down Cnmr
182.279
181.440
171.430
156.599
155.628
149.377
147.148
135.204
130.910
128.007
127.324
126.732
116.779
103.453
56.970
53.565
37.459
PPM
0
25
50
75
100
125
150
175

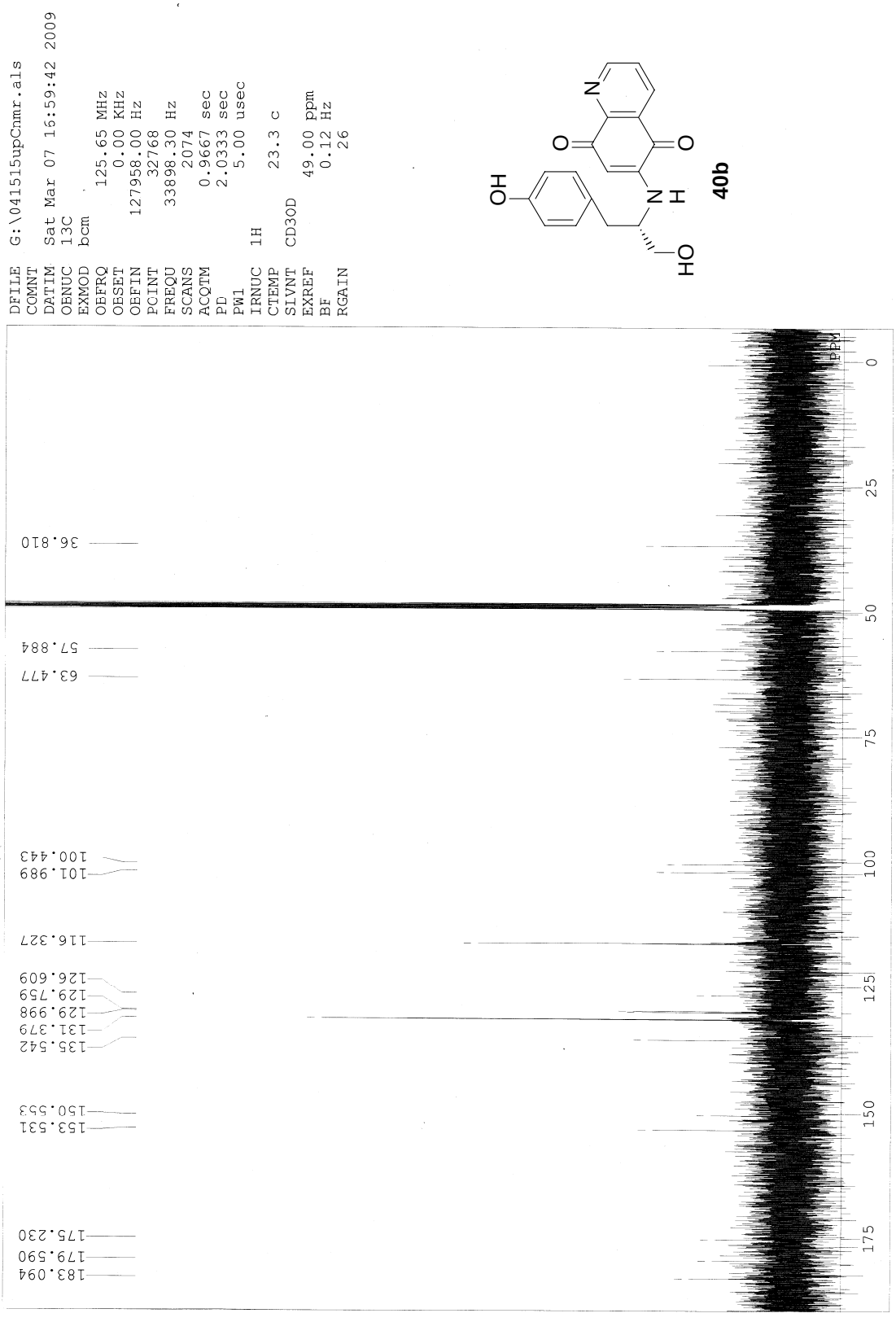

DFILE G:\041509 up.als
COMNT 041509 up
DATIM Mon Mar 02 12:06:06 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 18
041509 up
PPM
0
2
4
6
8
1.00
1.02
1.22
0.94
2.07
2.05
1.02
1.00
1.04
3.00
2.06
1.00
39b

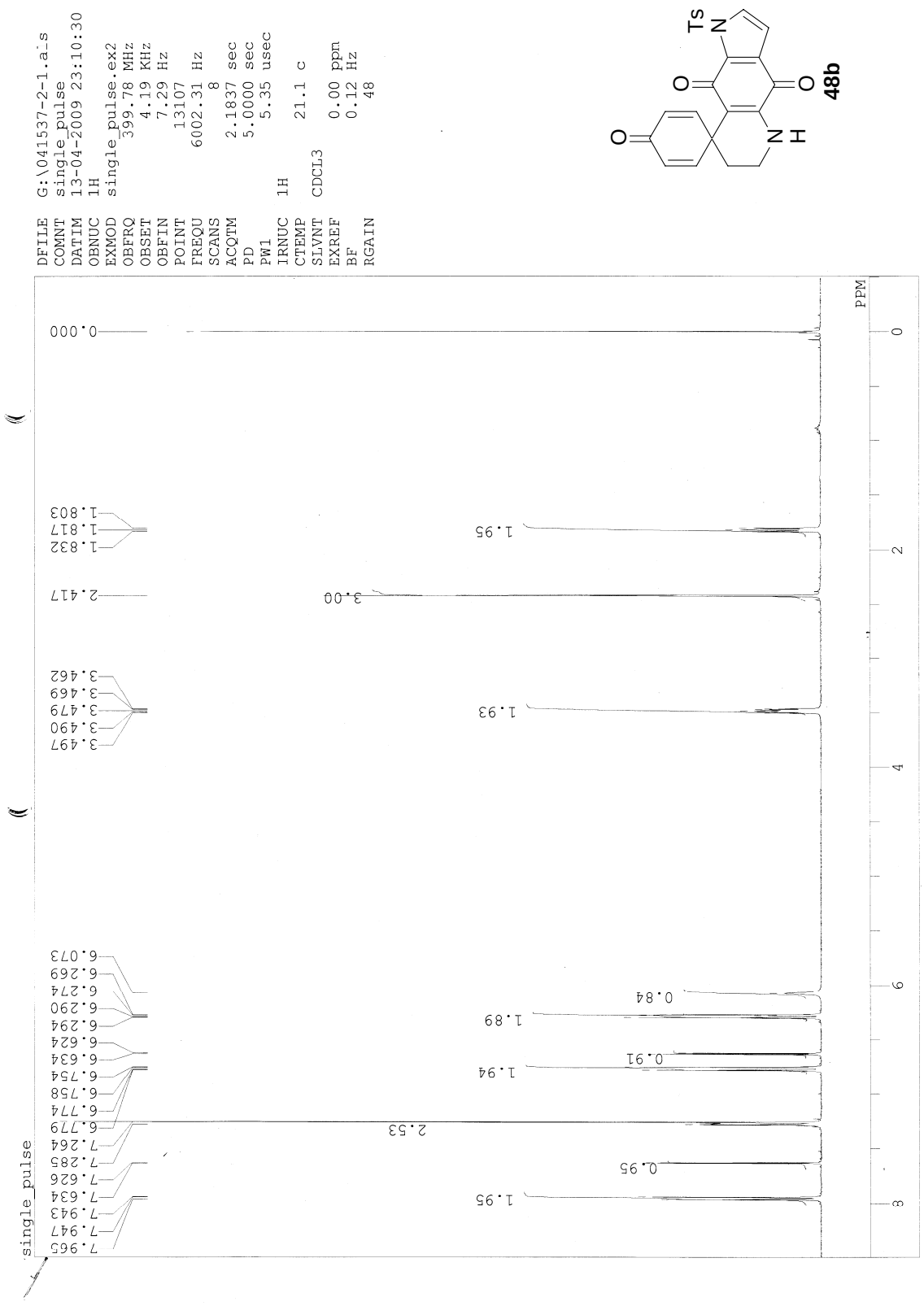

DFILE G:\041509 up Cnmr.als
COMNT 041509 up Cnmr
DATIM Mon Mar 02 13:13:11 2009
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 1324
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24
OH
O
N
O
N
H
MeO2C
39b
041509 up Cnmr
36.615
52.851
56.377
101.484
116.010
126.048
128.596
130.265
130.421
134.647
146.304
146.986
152.987
155.905
170.472
179.334
181.858
PPM
0
25
50
75
100
125
150
175

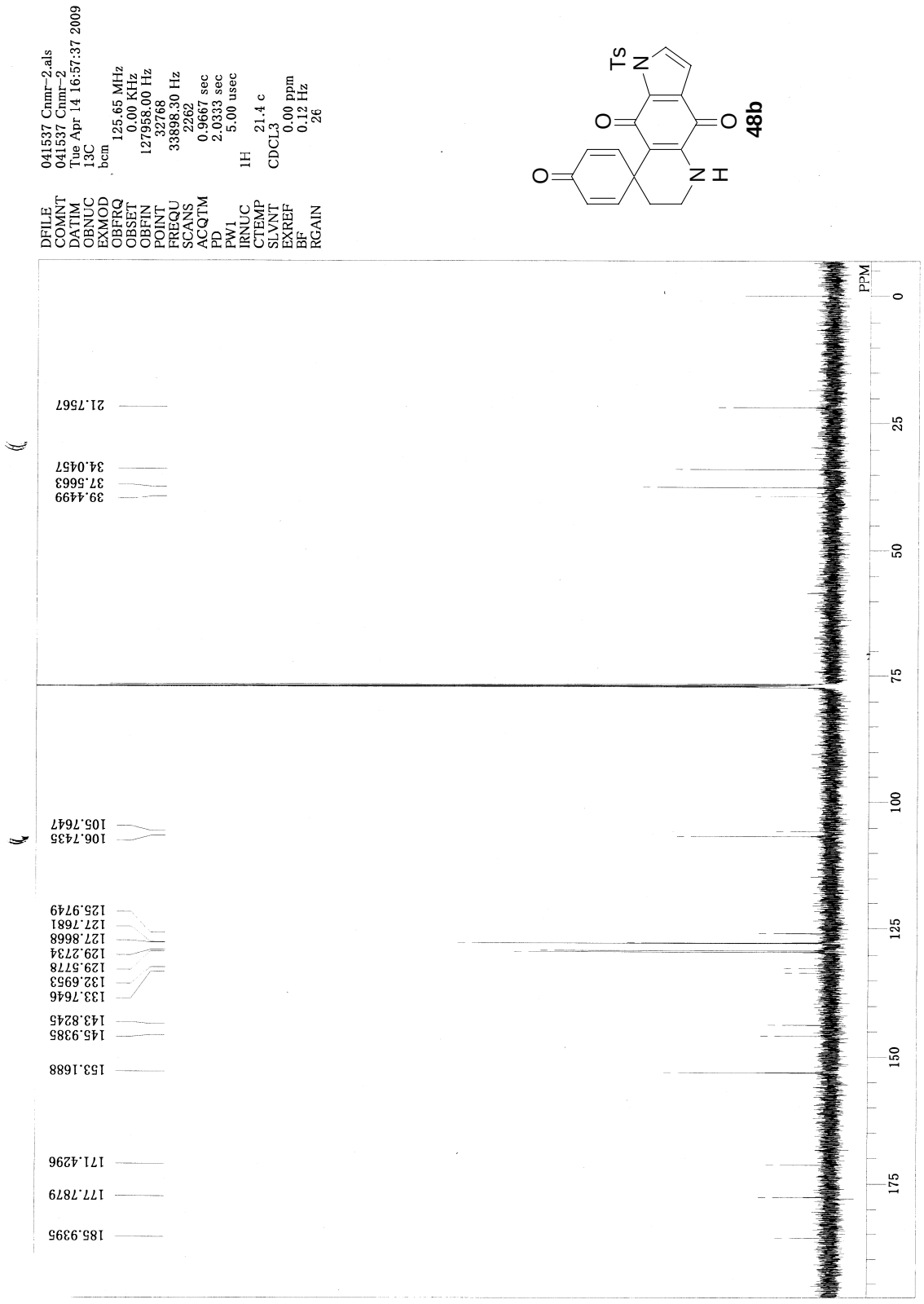

DFILE G:\041515 down.als
COMNT single_pulse
DATIM 07-03-2009 15:09:13
CBNUC 1H
EXMOD single_pulse.ex2
CBFRQ 399.78 MHz
CBSET 4.19 KHz
CBFIN 7.29 Hz
POINT 13107
FREQU 6009.52 Hz
SCANS 8
ACQTM 2.1810 sec
PD 5.0000 sec
PW1 5.35 usec
IRNUC 1H
CTEMP 18.4 c
SLVNT CD3OD
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 40
single_pulse
PPM
40a


DFILE G:\041515downCnmr.als
COMNT single_pulse_decoupled_gated_NC
DATIM 07-03-2009 15:55:31
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25396.44 Hz
SCANS 864
ACQTM 1.0322 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 18.7 c
SLVNT CD3OD
EXREF 49.00 ppm
BF 1.20 Hz
RGAIN 50
40a
36.751
57.780
63.379
101.370
116.154
116.318
128.018
129.676
131.362
135.757
150.097
150.261
155.292
157.210
181.988
182.605
PPM
0
25
50
75
100
125
150
175


DFILE G:\041515 up.als
COMNT
DATIM Sat Mar 07 15:14:28 2009
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.00 Hz
POINT 16384
FREQU 10000.00 Hz
SCANS 32
ACQTM 1.6384 sec
PD 5.3620 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CD3OD
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 18
40b
PPM
2.00
3.10
0.97
2.23
2.15
1.07
1.03
1.00


DFILE G:\041515upCnmr.als
COMNT
DATIM Sat Mar 07 16:59:42 2009
OENUC 13C
EXMOD bcm
OEFRQ 125.65 MHz
OESET 0.00 KHz
OEFIN 127958.00 Hz
PCINT 32768
FREQU 33898.30 Hz
SCANS 2074
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 23.3 c
SIVNT CD3OD 49.00 ppm
EXREF 0.12 Hz
BF 26
RGAIN
36.810
57.884
63.477
100.443
101.989
116.327
126.609
129.759
129.998
131.379
135.542
150.553
153.531
175.230
179.590
183.094
PPM
0
25
50
75
100
125
150
175
40b

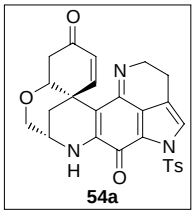

DFILE G:\041537-2-1.a1s
COMNT single_pulse
DATIM 13-04-2009 23:10:30
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.35 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48
Ts
N
O
O
O
N
H
48b
PPM
single_pulse
0.000
1.803
1.817
1.832
2.417
3.462
3.469
3.479
3.490
3.497
6.073
6.269
6.274
6.290
6.294
6.624
6.634
6.754
6.758
6.774
6.779
7.264
7.285
7.626
7.634
7.943
7.947
7.965
3.00
1.95
1.93
2.53
1.95
0.95
1.94
0.91
1.89
0.84


DFILE 041537 Cnmr-2.als
COMNT 041537 Cnmr-2
DATIM Tue Apr 14 16:57:37 2009
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 2262
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26
Ts
N
O
O
O
N
H
48b
21.7567
34.0457
37.5663
39.4499
105.7647
106.7435
125.9749
127.7681
127.8668
129.2734
129.5778
132.6953
133.7646
143.8245
145.9385
153.1688
171.4296
177.7879
185.9395
PPM
0
25
50
75
100
125
150
175

***in vivo* assay**

*Drug efficacy test*

1) oxa analogue (**54a**)



**54a**

Tumor volume ($mm_3$) (average/SE)

| Grouping | 7 | 10 | 14 | 17 | 21 | 24 |
|---|---|---|---|---|---|---|
| 1. control | 183 | 342 | 595 | 844 | 1141 | 1341 |
| | ±14 | ±49 | ±37 | ±57 | ±96 | ±134 |
| 2. **54a** 40 mg/kg | 193 | 354 | 631 | 901 | 1213 | 1518 |
| | ±10 | ±27 | ±52 | ±60 | ±83 | ±103 |
| 3. **54a** 20 mg/kg | 179 | 310 | 497 | 774 | 1071 | 1381 |
| | ±13 | ±37 | ±37 | ±59 | ±85 | ±116 |
| 4. **54a** 10 mg/kg | 185 | 315 | 517 | 770 | 1013 | 1288 |
| | ±12 | ±38 | ±58 | ±92 | ±108 | ±127 |

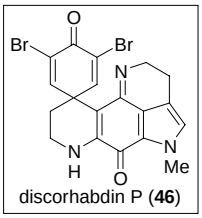
Tumor volume ($mm_3$) (% inhibition)

| Grouping | 7 | 10 | 14 | 17 | 21 | 24 |
|---|---|---|---|---|---|---|
| 2. **54a** 40 mg/kg | -5 | -4 | -6 | -7 | -6 | -13 |
| 3. **54a** 20 mg/kg | 2 | 9 | 16 | 8 | 6 | -3 |
| 4. **54a** 10 mg/kg | -1 | 8 | 13 | 9 | 11 | 4 |

Body weight (g) (average/SE)

| Grouping | 7 | 9 | 10 | 11 | 14 | 17 | 21 | 24 |
|---|---|---|---|---|---|---|---|---|
| 1. control | 20.8 | 20.7 | 21.3 | 20.6 | 21.2 | 20.9 | 20.6 | 20.7 |
| | ±0.5 | ±0.4 | ±0.5 | ±0.5 | ±0.6 | ±0.7 | ±0.8 | ±0.8 |
| 2. **54a** 40 mg/kg | 21 | 20.5 | 21.2 | 20.4 | 21.2 | 20.9 | 21 | 21.3 |
| | ±0.5 | ±0.3 | ±0.4 | ±0.4 | ±0.5 | ±0.6 | ±0.6 | ±0.7 |
| 3. **54a** 20 mg/kg | 21.8 | 21.7 | 22.2 | 21.5 | 22 | 21.8 | 22.1 | 22.1 |
| | ±0.3 | ±0.2 | ±0.2 | ±0.2 | ±0.3 | ±0.3 | ±0.6 | ±0.5 |
| 4. **54a** 10 mg/kg | 19.9 | 20 | 20.2 | 19.6 | 20.1 | 20.4 | 20.5 | 20.5 |
| | ±0.6 | ±0.7 | ±0.7 | ±0.7 | ±0.7 | ±0.6 | ±0.7 | ±0.8 |

2) discorhabdin P (**46**)



discorhabdin P (**46**)

Tumor volume ($mm_3$) (average)

| Grouping | 7 | 10 | 14 | 17 | 21 | 25 |
|---|---|---|---|---|---|---|
| control | 169 | 341 | 703 | 970 | 1275 | 1557 |
| **46** 20 mg/kg | 175 | 225 | 487 | 880 | 924 | 1772 |
| **46** 10 mg/kg | 167 | 195 | 362 | 603 | 1054 | 1521 |
| **46** 5 mg/kg (3times/w×2w) | 167 | 301 | 643 | 823 | 1348 | 1647 |
| **46** 2 mg/kg (3times/w×2w) | 166 | 310 | 567 | 809 | 1259 | 1792 |
| **46** 1 mg/kg (3times/w×2w) | 172 | 294 | 590 | 871 | 1283 | 1786 |

Tumor volume ($mm_3$) (% inhibition)

| Grouping | 7 | 10 | 14 | 17 | 21 | 25 |
|---|---|---|---|---|---|---|
| **46** 5 mg/kg (3times/w×2w) | 1 | 12 | 9 | 15 | -6 | -6 |
| **46** 2 mg/kg (3times/w×2w) | 2 | 9 | 19 | 17 | 1 | -15 |
| **46** 1 mg/kg (3times/w×2w) | -2 | 14 | 16 | 10 | -1 | -15 |

Body weight change (g) (average/SE)

| Grouping | 7 | 8 | 9 | 10 | 11 | 14 | 15 |
|---|---|---|---|---|---|---|---|
| control | 0 | 0.2 | -0.3 | -0.2 | -0.4 | -0.2 | -0.4 |
| **46** 20 mg/kg | 0 | -1.1 | -3 | -2.8 | -1.7 | -0.9 | -1.2 |
| **46** 10 mg/kg | 0 | -2 | -4 | -5.1 | -5.8 | -4.5 | -4.2 |
| **46** 5 mg/kg (3times/w×2w) | 0 | -0.3 | -1.2 | -1.5 | -1.5 | -0.9 | -1.3 |
| **46** 2 mg/kg (3times/w×2w) | 0 | -0.2 | -0.6 | -0.4 | -0.1 | -0.6 | -1 |
| **46** 1 mg/kg (3times/w×2w) | 0 | 0.2 | 0 | -0.3 | -0.2 | -0.5 | -1 |
| Grouping | 16 | 17 | 18 | 21 | 22 | 23 | 25 |
| control | 0 | 0.3 | -0.2 | -1.8 | -1.9 | -1.5 | -0.8 |
| **46** 20 mg/kg | -1 | -0.4 | -0.3 | 0 | 0.4 | 0.2 | 0.3 |
| **46** 10 mg/kg | -3 | -2.4 | -2.1 | -1.1 | -1.1 | -1.2 | 0.3 |
| **46** 5 mg/kg (3times/w×2w) | -1 | -0.3 | -0.5 | -0.3 | -0.5 | -0.7 | -0.7 |
| **46** 2 mg/kg (3times/w×2w) | -1 | -1.1 | -1.4 | -1.4 | -1.5 | -1.4 | -1.1 |
| **46** 1 mg/kg (3times/w×2w) | -1 | -0.4 | -0.7 | -1.1 | -1.5 | -1.3 | -0.7 |

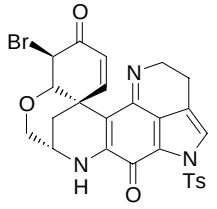
## HCC panel assay

[83 drugs]
4-Hydroperoxycyclophosphamide
6-Mercaptopurine
6-Thioguanine
Aclarubicin
Actinomycin-D
Amsacrine
aragusterol A
Bleomycin hydrochloride
Busulfan
Camptothecin
Carboplatin
Carboquone
Carmofur
Cisplatin
Clofarabine
CNDAC
Colchicine
Cytarabine
Dacarbazine
Daunorubicin hydrochloride
DMDC dihydrate
Docetaxel
Dolastatin 10
Doxifluridine
Doxorubicin hydrochloride
E7010
Edatrexate
Ellipticine
Enocitabine
Epirubicin
Estramustine phosphate sodium
Etoposide
FK317
FK973
Fluorouracil
FUdR
FUR
Gemcitabine monoHCl
Genistein
ICRF-154
ICRF-193
Indisulam
Interferon-α
Interferon-β
Interferon-γ
Irinotecan hydrochloride
KRN5500
KW2170
KW2331
L-Asparaginase
Melphalan
Methotrexate
Mitomycin-C
Mitoxantrone dihydrochloride
Navelbine
NC-190
Nedaplatin
Neocarzinostatin
Nimustine hydrochloride
Nitrogen mustard N-oxide hydrochloride
NK109 hydrogensulfate
NK611 hydrochloride
Oxaliplatin (l-OHP)
paclitaxel
Peplomycin
Pirarubicin
PSC833
Ranimustine
SM-5887
SM-5887-13-OH
SN-38
Soblidotin
SU5416
TAC-101
Tamoxifen citrate
TAS-103
Tegafur
Thiotepa
TNP-470
Toremifene citrate
Vinblastine sulfate
Vincristine sulfate
Vindesine sulfate

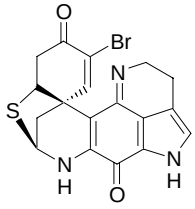
## The result of HCC panel assay

| | | oxa analogue (**54b**) | | | discorhabdin A (**1a**) | | |
|---|---|---|---|---|---|---|---|
| | | log $GI_{50}$ | log TGI | log $LC_{50}$ | log $GI_{50}$ | log TGI | log $LC_{50}$ |
| Br | HBC-4 | -6.67 | -6.30 | -5.84 | -5.66 | -5.26 | -4.72 |
| | BSY-1 | -6.73 | -6.31 | -5.79 | -5.82 | -5.45 | -5.08 |
| | HBC-5 | -7.25 | -6.72 | -6.32 | -5.79 | -5.49 | -5.19 |
| | MCF-7 | -6.69 | -6.35 | -6.01 | -5.67 | -5.31 | -4.00 |
| | MDA-MB-23 | -6.53 | -6.10 | -5.17 | -5.56 | -5.08 | -4.14 |
| CNS | U251 | -5.72 | -5.46 | -5.19 | -5.45 | -4.87 | -4.22 |
| | SF-268 | -6.38 | -5.85 | -5.30 | -5.53 | -5.01 | -4.23 |
| | SF-295 | -5.66 | -5.42 | -5.19 | -4.98 | -4.57 | -4.16 |
| | SF-539 | -6.36 | -5.93 | -5.36 | -5.61 | -5.29 | -4.88 |
| | SNB-75 | -5.57 | -5.33 | -5.09 | -4.79 | -4.45 | -4.10 |
| | SNB-78 | -6.20 | -5.73 | -5.30 | -5.57 | -5.01 | -4.36 |
| Co | HCC2998 | -6.60 | -6.13 | -5.24 | -5.62 | -5.20 | -4.54 |
| | KM-12 | -5.69 | -5.25 | -4.50 | -4.84 | -4.49 | -4.13 |
| | HT-29 | -7.41 | -5.95 | -5.31 | -5.49 | -4.96 | -4.39 |
| | HCT-15 | -6.64 | -6.37 | -6.10 | -5.47 | -4.91 | -4.20 |
| | HCT-116 | -6.94 | -6.42 | -5.36 | -5.62 | -5.20 | -4.36 |
| Lu | NCI-H23 | -6.39 | -5.75 | -5.14 | -5.25 | -4.59 | -4.00 |
| | NCI-H226 | -5.67 | -5.38 | -5.10 | -4.58 | -4.18 | -4.00 |
| | NCI-H522 | -6.76 | -6.45 | -6.13 | -5.73 | -5.37 | -5.01 |
| | NCI-H460 | -5.96 | -5.53 | -5.10 | -5.14 | -4.61 | -4.14 |
| | A549 | -5.69 | -5.29 | -4.74 | -4.89 | -4.49 | -4.08 |
| | DMS273 | -6.60 | -6.18 | -5.55 | -5.63 | -5.20 | -4.42 |
| | DMS114 | -6.79 | -6.45 | -6.11 | -5.73 | -5.42 | -5.11 |
| Me | LOX-IMVI | -6.55 | -6.14 | -5.10 | -5.72 | -5.29 | -4.00 |
| Ov | OVCAR-3 | -7.51 | -6.90 | -5.51 | -5.49 | -5.04 | -4.13 |
| | OVCAR-4 | -6.75 | -6.47 | -6.19 | -5.50 | -5.02 | -4.47 |
| | OVCAR-5 | -6.70 | -6.43 | -6.16 | -5.61 | -5.24 | -4.73 |
| | OVCAR-8 | -6.46 | -5.54 | -4.00 | -5.47 | -4.45 | -4.00 |
| | SK-OV-3 | -5.58 | -5.13 | -4.56 | -4.82 | -4.51 | -4.20 |
| Re | RXF-631L | -5.74 | -5.41 | -5.08 | -4.96 | -4.60 | -4.25 |
| | ACHN | -6.40 | -5.80 | -4.97 | -5.50 | -5.02 | -4.00 |
| St | St-4 | -5.50 | -5.13 | -4.30 | -4.89 | -4.37 | -4.00 |
| | MKN1 | -6.52 | -5.87 | -5.19 | -5.51 | -4.98 | -4.24 |
| | MKN7 | -6.69 | -6.25 | -5.51 | -5.51 | -5.16 | -4.20 |
| | MKN28 | -6.62 | -6.16 | -5.19 | -5.53 | -5.01 | -4.00 |
| | MKN45 | -6.61 | -6.28 | -5.81 | -5.51 | -4.93 | -4.35 |
| | MKN74 | -6.76 | -6.32 | -5.42 | -5.58 | -5.21 | -4.19 |
| xPg | DU-145 | -5.87 | -5.56 | -5.24 | -4.86 | -4.51 | -4.16 |
| | PC-3 | -6.25 | -5.50 | -4.69 | -5.37 | -4.71 | -4.00 |

COMPARE program of compounds **54b** and **1a**




**54b**




**1a**

| discorhabdin oxa analogue (**54b**) | | | |
|---|---|---|---|
| Rank | compounds | r | Molecular Targets/Drug Type |
| 1 | Vincristine | 0.433 | tubulin |
| 2 | Actinomycin-D | 0.430 | anti-neoplastic antibiotic. inhibits RNA polymerase and is a potent inducer of apoptosis |
| 3 | Vinblastine | 0.392 | tubulin |

| discorhabdin A (**1a**) | | | |
|---|---|---|---|
| Rank | compounds | r | Molecular Targets/Drug Type |
| 1 | Nitrogen mustard | 0.421 | DNA alkylating agent |
| 2 | Vincristine | 0.413 | tubulin |
| 3 | Vinblastine | 0.390 | tubulin |

Peason correlation coefficient were calculated using the following formula:

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}\sqrt{\sum_{i=1}^{n}(y_i - \bar{y})^2}}$$

Where $x_i$ and $y_i$ are log $GI_{50}$ of drug A and drug B, respectively, against each cell line, and $\bar{x}$ and $\bar{y}$ are the mean values of $x_i$ and $y_i$ respectively.