Supplementary Material (ESI) for Chemical Communications

Supporting Information For:

Cu(II)-Mediated Oxidative Intermolecular *ortho* C-H Functionalisation Using Tetrahydropyrimidine as the Directing Group

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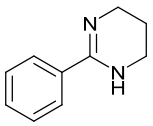
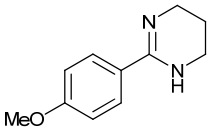
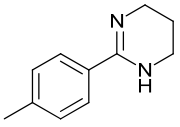


General Procedure for Preparation of the Substrates.[1] **Synthesis of 2-Phenyl-1,4,5,6-tetrahydropyrimidine (1a):** To a solution of benzaldehyde (5.00 g, 47.1 mmol) in *t*-BuOH (470 mL) was added propylenediamine (3.84 g, 51.8 mmol). The mixture was stirred at 70 °C for 30 min, and then K_2CO_3 (19.53 g, 141.3 mmol) and I_2 (14.95 g, 58.8 mmol) were added. After stirring at this temperature for 3 h, the mixture was quenched with sat. Na_2SO_3 until the iodine color almost disappeared. The organic layer was separated and concentrated in vacuo. The resulting solid was recrystallised from MeOH–Et_2O to give 2-phenyl-1,4,5,6-tetrahydropyrimidine hydroiodide. The resulting crystal was dissolved with H_2O, and then pH was adjusted to 12–14 with 2N NaOH. The whole was extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The filtrate was concentrated in vacuo, and the resulting solid was recrystallised from $CHCl_3$–*n*-hexane to give the compound **1a** as colorless crystals (6.62 g, 82%): mp 88–89 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1618 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.83-1.85 (m, 2H, CH_2), 3.49 (t, J = 5.9 Hz, 4H, 2 × CH_2), 5.02 (br s, 1H, NH), 7.34-7.38 (m, 3H, Ar), 7.63-7.66 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 42.3 (2C), 126.0 (2C), 128.2 (2C), 129.6, 137.3, 154.5. *Anal.* calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found; C, 74.79; H, 7.53; N, 17.43.

[1] M. Ishihara and H. Togo, *Tetrahedron*, 2007, **63**, 1474.

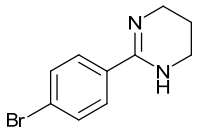


2-(4-Methoxyphenyl)-1,4,5,6-tetrahydropyrimidine (1b): *p*-Methoxybenzaldehyde (1.36 g, 10 mmol) was subjected to general procedure as described above. Colorless crystals (1.40 g, 74%): mp 132–134 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1611 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.81-1.87 (m, 2H, CH_2), 3.49 (t, J = 5.7 Hz, 4H, 2 × CH_2), 3.81 (s, 3H, OCH_3), 4.87 (br s, 1H, NH), 6.86 (d, J = 9.4 Hz, 2H, Ar), 7.60 (d, J = 9.4 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 42.4 (2C), 55.2, 113.5 (2C), 127.2 (2C), 130.0, 153.9, 160.6. *Anal.* calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.18; H, 7.46; N, 14.58.

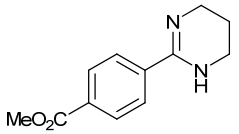


2-(4-Tolyl)-1,4,5,6-tetrahydropyrimidine (1c): *p*-Tolualdehyde (1.20 g, 10 mmol) was subjected to general procedure as described above. Colorless crystals (1.03 g, 59%): mp 120–121 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1615 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.82-1.85 (m, 2H, CH_2), 2.35 (s, 3H, CH_3), 3.49 (t, J = 5.7 Hz, 4H, 2 × CH_2), 4.90 (br s, 1H, NH), 7.15 (d, J = 8.3 Hz, 2H, Ar), 7.54 (d, J = 8.3 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.2, 42.3 (2C), 125.8 (2C), 128.9 (2C), 134.5, 139.5, 154.3. *Anal.* calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.76; H, 8.01; N,

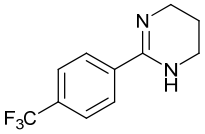
15.91.



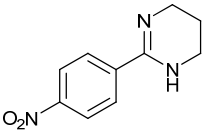
2-(4-Bromophenyl)-1,4,5,6-tetrahydropyrimidine (1d): *p*-Bromobenzaldehyde (1.85 g, 10 mmol) was subjected to general procedure as described above. Colorless crystals (1.82 g, 76%): mp 174–175 °C (from $CHCl_3$–*n*-hexane); IR cm^{-1}: 1619 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.81-1.88 (m, 2H, CH_2), 3.49 (t, J = 5.7 Hz, 4H, 2 × CH_2), 4.81 (br s, 1H, NH), 7.48 (d, J = 8.8 Hz, 2H, Ar), 7.53 (d, J = 8.8 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 42.4 (2C), 123.8, 127.6 (2C), 131.4 (2C), 136.3, 153.5. *Anal.* calcd for $C_{10}H_{11}BrN_2$: C, 50.23; H, 4.64; N, 11.72. Found: C, 50.20; H, 4.51; N, 11.66.



Methyl 4-(1,4,5,6-Tetrahydropyrimidin-2-yl)benzoate (1e): Methyl 4-formylbenzoate (1.00 g, 6.09 mmol) was subjected to general procedure as described above. Colorless crystals (1.63 g, 80%): mp 152–153 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1721 (C=O), 1620 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.83-1.89 (m, 2H, CH_2), 3.52 (t, J = 5.7 Hz, 4H, 2 × CH_2), 3.92 (s, 3H, OCH_3), 5.04 (br s, 1H, NH), 7.72 (d, J = 8.5 Hz, 2H, Ar), 8.02 (d, J = 8.5 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 42.3 (2C), 52.1, 126.0 (2C), 129.5 (2C), 130.8, 141.5, 153.6, 166.6. *Anal.* calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.84. Found: C, 65.76; H, 6.28; N, 12.69.

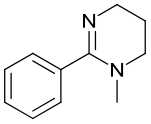


2-[4-(Trifluoromethyl)phenyl]-1,4,5,6-tetrahydropyrimidine (1f): *p*-(Trifluolomethyl)benzaldehyde (1.74 g, 10 mmol) was subjected to general procedure as described above. Colorless crystals (1.71 g, 75%). mp 176–177 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1620 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.83-1.89 (m, 2H, CH_2), 3.51 (t, J = 5.7 Hz, 4H, 2 × CH_2), 4.92 (br s, 1H, NH), 7.61 (d, J = 8.3 Hz, 2H, Ar), 7.76 (d, J = 8.3 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 42.4 (2C), 122.6, 125.2 (q, J = 3.7 Hz, 2C), 126.4 (2C), 131.4 (d, J = 32.3 Hz), 140.7, 153.3; ^{19}F NMR (500 MHz, $CDCl_3$) δ –62.6. *Anal.* calcd for $C_{11}H_{11}F_3N_2$: C, 57.89; H, 4.86; N, 12.28. Found: C, 57.89; H, 4.82; N, 12.29.

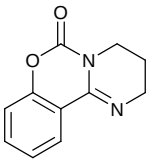


2-(4-Nitrophenyl)-1,4,5,6-tetrahydropyrimidine (1g): *p*-Nitrobenzaldehyde (1.51 g, 10 mmol) was subjected to general procedure as described above. Yellow crystals (1.63 g, 80%): mp 169–171 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1623 (C=N), 1519 (NO_2), 1339 (NO_2); ^1H NMR (400 MHz, $CDCl_3$) δ

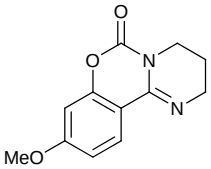
1.85-1.90 (m, 2H, CH_2), 3.54 (t, J = 5.6 Hz, 4H, 2 × CH_2), 5.08 (br s, 1H, NH), 7.83 (d, J = 9.1 Hz, 2H, Ar), 8.20 (d, J = 9.1 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 42.3 (2C), 123.4 (2C), 127.0 (2C), 143.2, 148.3, 152.7. *Anal.* calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.61; H, 5.45; N, 20.48.



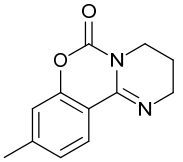
1-Methyl-2-phenyl-1,4,5,6-tetrahydropyrimidine (4): Benzaldehyde (1.06 g, 10 mmol) and *N*-methyl propandiamine (0.97 g, 11 mmol) was subjected to general procedure as described above (without further purification after demineralisation). Yellow oil (1.49 g, 85%); IR (neat) cm^{-1}: 1600 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92-1.98 (m, 2H, CH_2), 2.74 (s, 3H, NCH_3), 3.27 (t, J = 5.6 Hz, 2H, CH_2), 3.51 (t, J = 5.2 Hz, 2H, CH_2), 7.32-7.40 (m, 5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 40.3, 45.0, 49.0, 127.9 (2C), 128.0 (2C), 128.4, 138.1, 159.1; HRMS (EI): *m/z* calcd for $C_{11}H_{13}N_2$ $[M - 1]^-$ 173.1084; found: 173.1082.



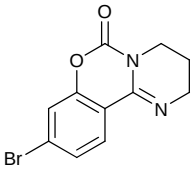
General Procedure for the C-H Hydroxylation (Table 1, entry 10). Synthesis of 2,3-Dihydro-*1H*-9-oxa-4,10a-diazaphenanthren-10-one (3a): DMF (0.83 mL) and water (4.5 μL, 0.25 mmol) were added to a flask containing 2-phenyltetrahydropyrimidine (40.1 mg, 0.25 mmol) and $Cu(OAc)_2$ (45.4 mg, 0.25 mmol) under O_2 atmosphere. After stirring at 130 °C for 20 min, TMEDA (*N,N,N',N'*-tetramethylethylenediamine) (150 μL, 1 mmol) was added, and the mixture was stirred for 1 min at the same temperature. The reaction mixture was concentrated in vacuo. To a stirring solution of this residue and TMEDA (150 μL, 1 mmol) in CH_2Cl_2 (16.6 mL) was added dropwise a solution of triphosgene (77.9 mg, 0.26 mmol) in CH_2Cl_2 (1.7 mL) at 0 °C. After stirring at room temperature for 1h, the mixture was quenched with sat. NH_4Cl, and CH_2Cl_2 was removed in vacuo. The resulting mixture was made basic with 28% NH_4OH. The whole was extracted with EtOAc. The extract was washed with sat. NH_4Cl-28% NH_4OH, brine, and dried over $MgSO_4$. The filtrate was concentrated in vacuo. The residue was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (1:1) to give **3a** as colorless crystals (35.2 mg, 70%): mp 146–147 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1730 (C=O), 1647 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98-2.04 (m, 2H, CH_2), 3.68 (t, J = 5.6 Hz, 2H, CH_2), 3.95 (t, J = 6.0 Hz, 2H, CH_2), 7.14 (d, J = 8.3 Hz, 1H, Ar), 7.23-7.30 (m, 1H, Ar), 7.48-7.51 (m, 1H, Ar), 8.02 (d, J = 7.8 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 42.5, 44.1, 116.2, 125.0, 125.5, 127.8, 129.0, 132.9, 147.5, 150.4; HRMS (FAB): *m/z* calcd for $C_{11}H_{11}N_2O_2$ $[M + H]^+$ 203.0821; found: 203.0813.



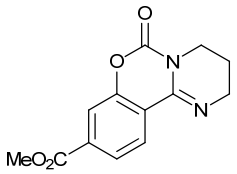
7-Methoxy-2,3-dihydro-*1H*-9-oxa-4,10a-diazaphenanthren-10-one (3b): 2-(4-Methoxyphenyl)-1,4,5,6-tetrahydropyrimidine (47.6 mg, 0.25 mmol) was subjected to general procedure as described above. Pale yellow solid (37.3 mg, 64%): mp 160–161 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1731 (C=O), 1650 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ 1.97-2.02 (m, 2H, CH_2), 3.64 (t, J = 5.7 Hz, 2H, CH_2), 3.85 (s, 3H, OCH_3), 3.92 (t, J = 6.0 Hz, 2H, CH_2), 6.59 (d, J = 2.3 Hz, 1H, Ar), 6.79 (dd, J = 8.6, 2.3 Hz, 1H, Ar), 7.90 (d, J = 8.6 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 42.5, 44.0, 55.7, 100.0, 108.8, 112.6, 126.6, 142.7, 147.8, 151.7, 163.3; HRMS (FAB): *m/z* calcd for $C_{12}H_{13}N_2O_3$ $[M + H]^+$ 233.0926; found: 233.0921.



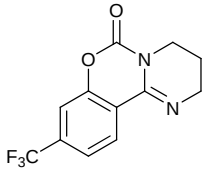
7-Methyl-2,3-dihydro-*1H*-4,10a-diaza-9-oxaphenanthren-10-one (3c): 2-(4-Tolyl)-1,4,5,6-tetrahydropyrimidine (43.6 mg, 0.25 mmol) was subjected to general procedure as described above. Yellow crystals (32.8 mg, 61%): mp 153–154 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1736 (C=O), 1650 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ 1.98-2.02 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 3.66 (t, J = 5.4 Hz, 2H, CH_2), 3.93 (t, J = 6.0 Hz, 2H), 6.93 (s, 1H, Ar), 7.05 (d, J = 8.0 Hz, 1H, Ar), 7.88 (d, J = 8.0 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.4, 21.5, 42.5, 44.1, 113.4, 116.2, 125.2, 126.2, 143.0, 144.0, 148.0, 150.4; HRMS (FAB): *m/z* calcd for $C_{12}H_{13}N_2O_2$ $[M + H]^+$ 217.0977; found: 217.0979.



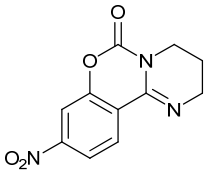
7-Bromo-2,3-dihydro-*1H*-4,10a-diaza-9-oxaphenanthren-10-one (3d): 2-(4-Bromophenyl)-1,4,5,6-tetrahydropyrimidine (59.8 mg, 0.25 mmol) was subjected to general procedure as described above. Pale yellow crystals (31.3 mg, 45%): mp 206–207 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1729 (C=O), 1651 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ 1.98-2.03 (m, 2H, CH_2), 3.65 (t, J = 5.7 Hz, 2H, CH_2), 3.93 (t, J = 6.0 Hz, 2H, CH_2), 7.31 (d, J = 1.7 Hz, 1H, Ar), 7.37 (dd, J = 8.6, 1.7 Hz, 1H, Ar), 7.87 (d, J = 8.6 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.3, 42.6, 44.2, 115.2, 119.4, 126.4, 126.8, 128.4, 142.1, 147.0, 150.7; HRMS (FAB): *m/z* calcd for $C_{11}H_{10}BrN_2O_2$ $[M + H, {}^{79}Br]^+$ 280.9926; found: 280.9922.



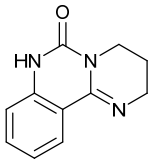
7-(Methoxycarbonyl)-2,3-dihydro-*1H*-4,10a-diaza-9-oxaphenanthren-10-one (3e): 2-[(4-Methoxycarbonyl)phenyl]-1,4,5,6-tetrahydropyrimidine (54.6 mg, 0.25 mmol) was subjected to general procedure as described above. Pale yellow crystals (30.2 mg, 46%): mp 136–137 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1741 (C=O), 1718 (C=O), 1644 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ 2.00-2.05 (m, 2H, CH_2), 3.70 (t, J = 5.4 Hz, 2H, CH_2), 3.94-3.96 (m, 5H, CH_2,OMe), 7.78 (d, J = 1.4 Hz, 1H, Ar), 7.88 (dd, J = 8.6, 1.4 Hz, 1H, Ar), 8.09 (d, J = 8.6 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 42.5, 44.4, 52.6, 117.6, 119.7, 125.6, 125.8, 134.3, 142.2, 147.1, 150.2, 165.4; HRMS (FAB): *m/z* calcd for $C_{13}H_{13}N_2O_4$ $[M + H]^+$ 261.0875; found: 261.0874.



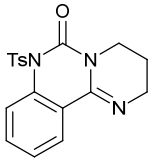
7-(Trifuluoromethyl)-2,3-dihydro-*1H*-4,10a-diaza-9-oxaphenanthren-10-one (3f): 2-[4-(Trifuluoromethyl)phenyl]-1,4,5,6-tetrahydropyrimidine (57.1 mg, 0.25 mmol) was subjected to general procedure as described above. Yellow solid (28.8 mg, 43%): mp 141–142 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1739 (C=O), 1650 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ 2.00-2.05 (m, 2H, CH_3), 3.70 (t, J = 5.7 Hz, 2H, CH_2), 3.95 (t, J = 6.0 Hz, 2H, CH_2), 7.40 (d, J = 1.1 Hz, 1H, Ar), 7.49 (dd, J = 8.0, 1.1 Hz, 1H, Ar), 8.15 (d, J = 8.0 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 42.7, 44.5, 113.9 (q, J = 4.1 Hz), 119.3, 121.6 (q, J = 3.6 Hz), 124.5, 126.7, 134.7 (q, J = 33.7 Hz), 141.8, 146.9, 150.4; ^{19}F NMR (500 MHz, $CDCl_3$) δ –63.0; HRMS (FAB): *m/z* calcd for $C_{12}H_{10}F_3N_2O_2$ $[M + H]^+$ 271.0694; found: 271.0692.



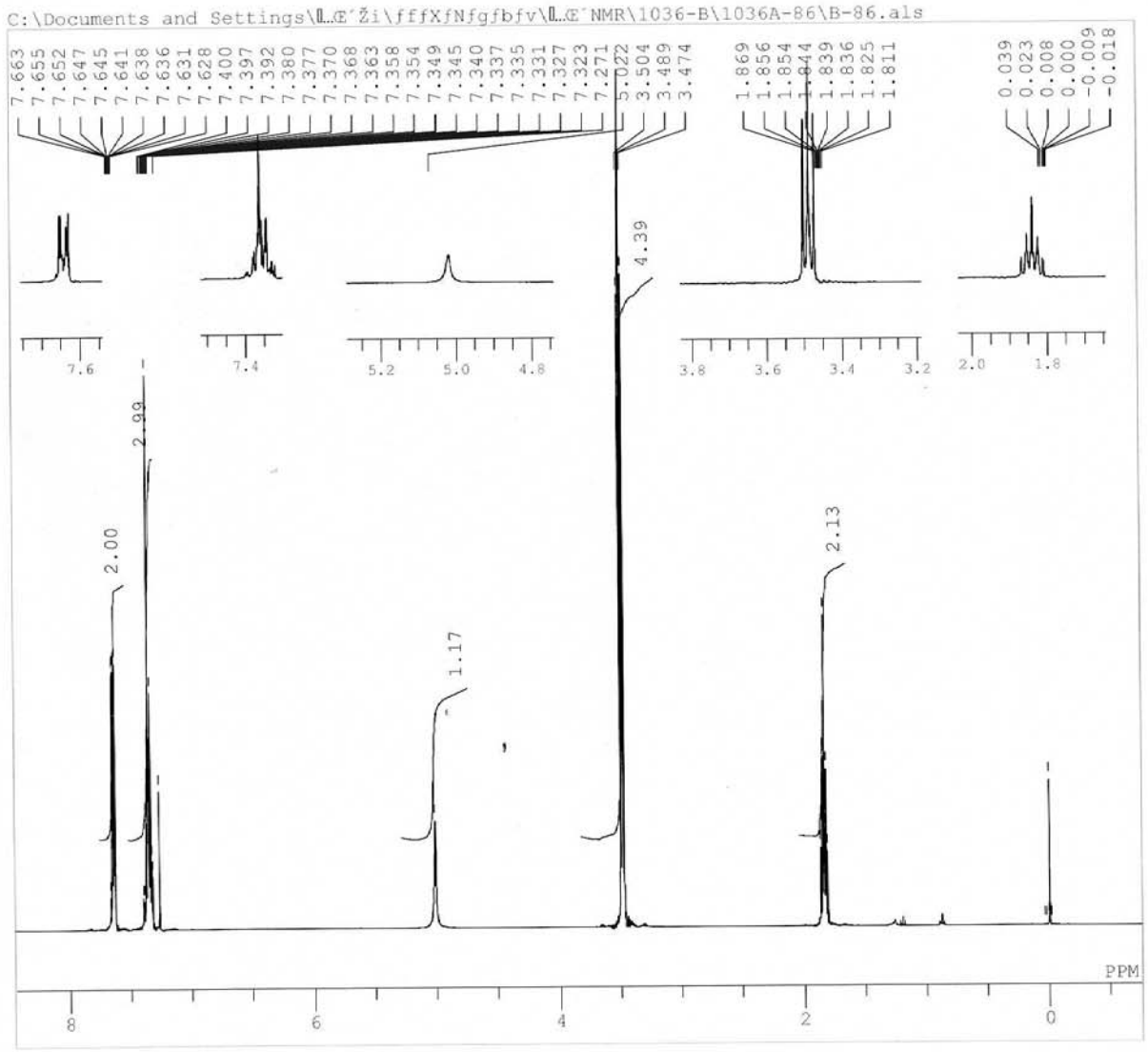
7-Nitro-2,3-dihydro-*1H*-4,10a-diaza-9-oxaphenanthren-10-one (3g): 2-(4-Nitrophenyl)-1,4,5,6-tetrahydropyrimidine (51.3 mg, 0.25 mmol) was subjected to general procedure as described above. Yellow crystals (11.9 mg, 19%): mp 235–236 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1732 (C=O), 1641 (C=N), 1531 (NO_2), 1349 (NO_2). ^1H NMR (400 MHz, $CDCl_3$) δ 2.01-2.07 (m, 2H, CH_2), 3.72 (t, J = 5.6 Hz, 2H, CH_2), 3.96 (t, J = 6.0 Hz, 2H, CH_2), 8.00 (d, J = 2.2 Hz, 2H, Ar), 8.08 (dd, J = 8.8, 2.2 Hz, 1H, Ar), 8.22 (d, J = 8.8 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 42.6, 44.5, 112.2, 119.4, 121.4, 127.1, 141.3, 146.4, 150.3, 150.5; HRMS (FAB): *m/z* calcd for $C_{11}H_{10}N_3O_4$ $[M + H]^+$ 248.0671; found: 248.0670.



C-H Amidation with $BocNH_2$. Synthesis of 3,4-Dihydro-*2H*-pyrimido[1,2-*c*]quinazolin-6(*7H*)-one (7a): DMF (0.83 mL) was added to a flask containing 2-phenyltetrahydropyrimidine (40.1 mg, 0.25 mmol), $Cu(OAc)_2$ (45.4 mg, 0.25 mmol) and *tert*-butyl carbamate (87.9 mg, 0.75 mmol) under O_2 atmosphere. After stirring at 100 °C for 40 min, the mixture was concentrated in vacuo. The residue was purified by flash chromatography over aluminium oxide with $CHCl_3$ [gradationally to $CHCl_3$–MeOH (99:1)] to give **7a** as a white solid (26.5 mg, 53%): mp 250–251 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1682 (C=O), 1616 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.95-2.00 (m, 2H, CH_2), 3.67 (t, J = 5.6 Hz, 2H, CH_2), 3.94 (t, J = 6.0 Hz, 2H, CH_2), 6.86 (d, J = 8.0 Hz, 1H, Ar), 7.09-7.13 (m, 1H, Ar), 7.38-7.42 (m, 1H, Ar), 8.07 (d, J = 8.0 Hz, 1H, Ar), 8.30 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 40.8, 44.5, 114.6, 116.5, 123.0, 125.8, 132.0, 136.5, 145.7, 151.2; HRMS (FAB): *m/z* calcd for $C_{11}H_{12}N_3O$ $[M + H]^+$ 202.0980; found: 202.0988.



C-H Amidation with $TsNH_2$. Synthesis of 7-Tosyl-3,4-dihydro-*2H*-pyrimido[1,2-*c*]quinazolin-6(*7H*)-one (7b): DMF (0.83 mL) was added to a flask containing 2-phenyltetrahydropyrimidine (40.1 mg, 0.25 mmol), $Cu(OAc)_2$ (45.4 mg, 0.25 mmol) and *p*-toluene sulfonamide (85.6 mg, 0.5 mmol) under O_2 atmosphere. After stirring at 130 °C for 20 min, the mixture was concentrated in vacuo followed by flash chromatography over aluminium oxide with $CHCl_3$–MeOH (95:5) to give *ortho*-amidated compound as a crude material. To a stirring solution of the *ortho*-amidated compound and Et_3N (145 μL, 1.0 mmol) in CH_2Cl_2 (16.6 mL) was added dropwise a solution of triphosgene (77.9 mg, 0.26 mmol) in CH_2Cl_2 (1.7 mL) at 0 °C. After stirring at room temperature for 1h, the mixture was quenched with sat. $NaHCO_3$, and CH_2Cl_2 was removed in vacuo. The whole was extracted with EtOAc. The extract was washed with sat. $NaHCO_3$, brine, and dried over $MgSO_4$. The filtrate was concentrated in vacuo. The residue was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (1:1) to give **7b** as colorless crystals (42.2 mg, 47%): mp 159–161 °C (from $CHCl_3$–*n*-hexane); IR (neat) cm^{-1}: 1695 (C=O), 1644 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.85-1.91 (m, 2H, CH_2), 2.46 (s, 3H, CH_3), 3.63 (t, J = 5.7 Hz, 2H, CH_2), 3.75 (t, J = 6.2 Hz, 2H, CH_2), 7.27-7.31 (m, 1H, Ar), 7.37 (d, J = 8.3 Hz, 2H, Ar), 7.48-7.53 (m, 1H, Ar), 7.87 (d, J = 8.5 Hz, 1H, Ar), 8.03 (d, J = 8.3 Hz, 2H, Ar), 8.07 (dd, J = 8.0, 1.7 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.8, 41.8, 44.6, 120.3, 121.0, 125.7, 126.4, 128.4 (2C), 129.8 (2C), 131.3, 134.6, 136.7, 144.5, 145.4, 148.3; HRMS (FAB): *m/z* calcd for $C_{18}H_{18}N_3O_3S$ $[M + H]^+$ 356.1069; found: 356.1074.

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PW1               5.50 usec
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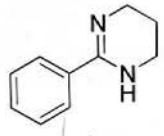

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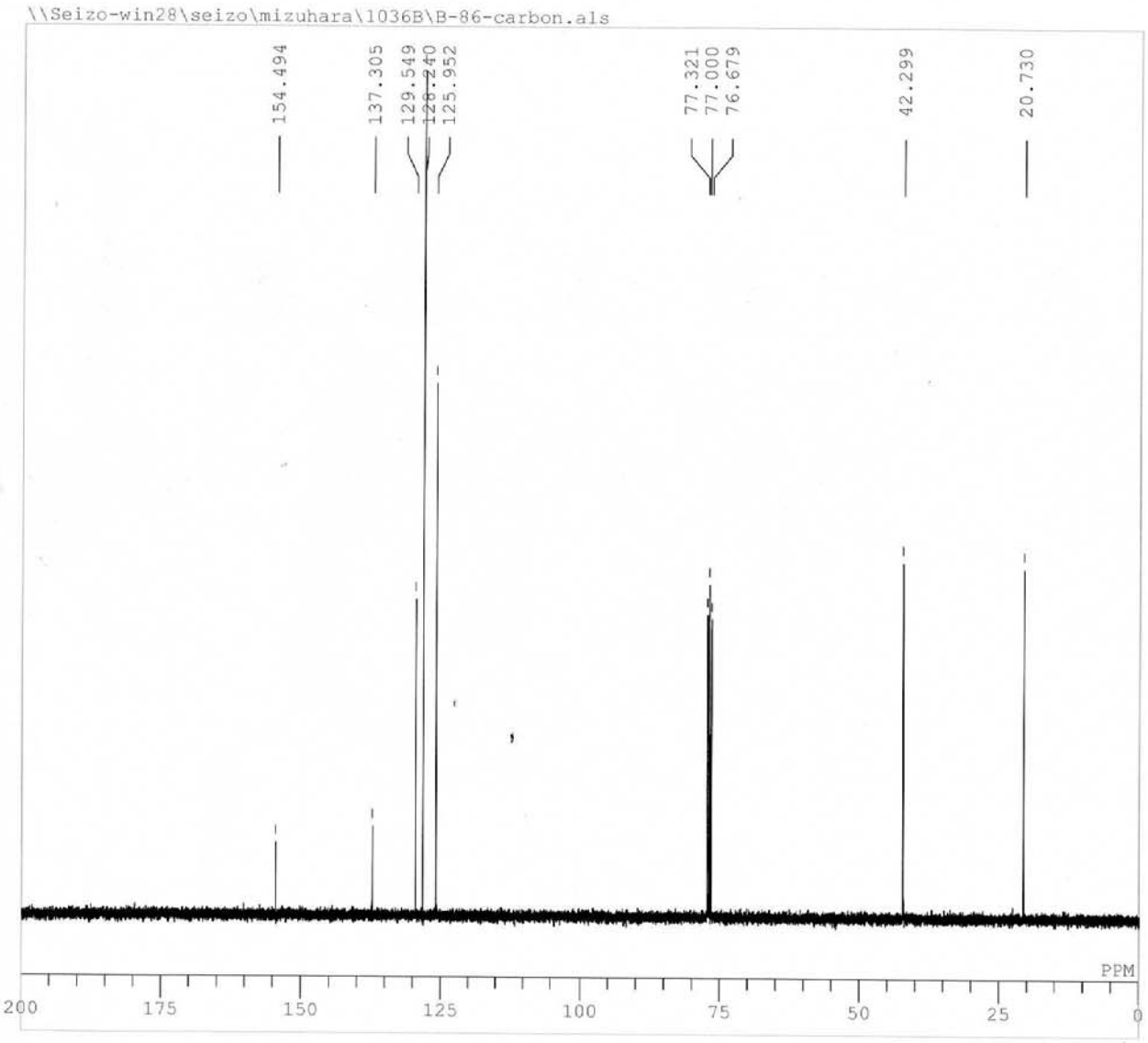


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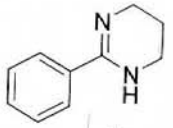

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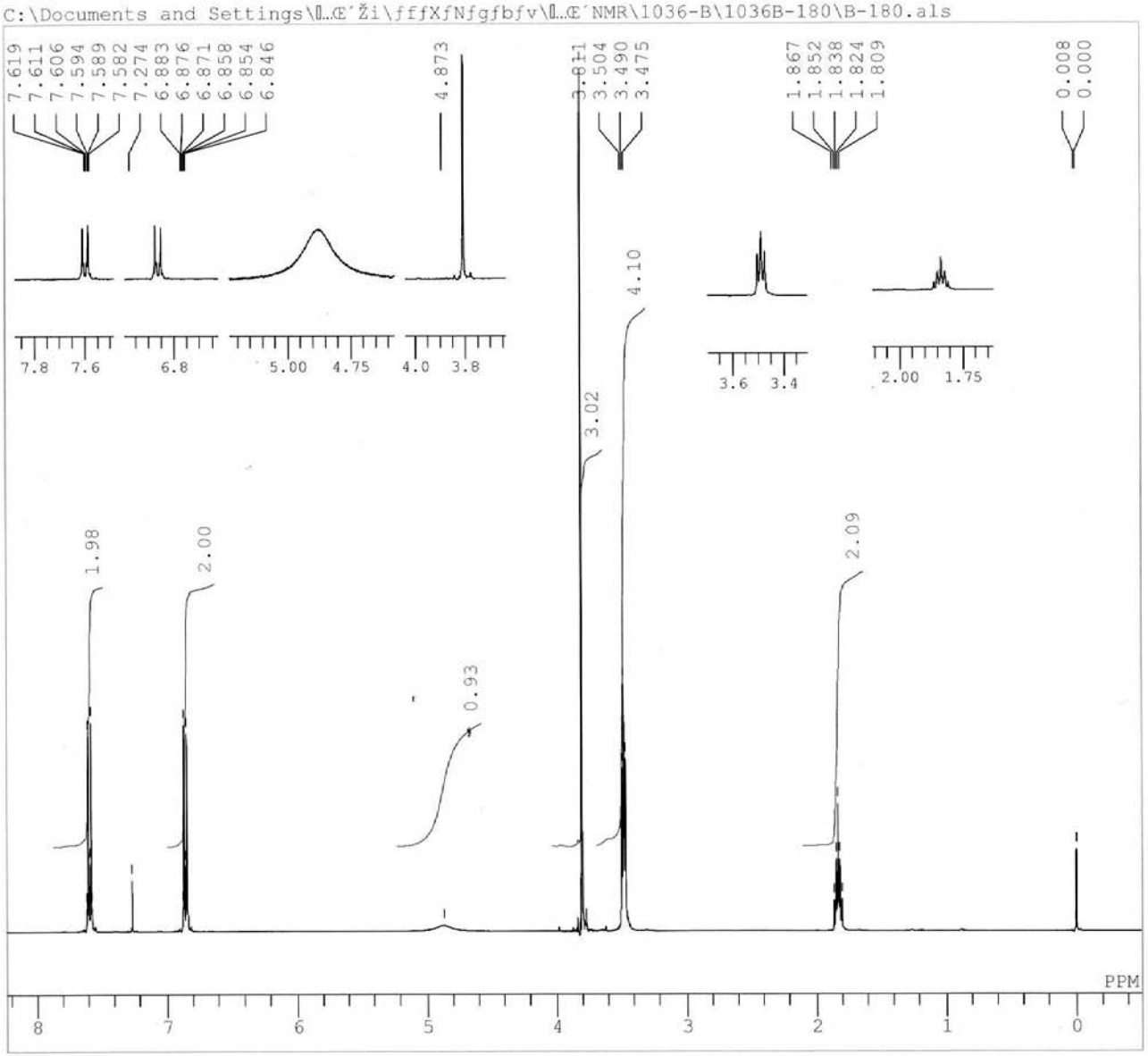

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EXREF 0.00 ppm
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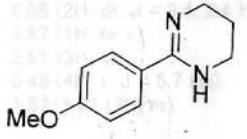
RGAIN 14



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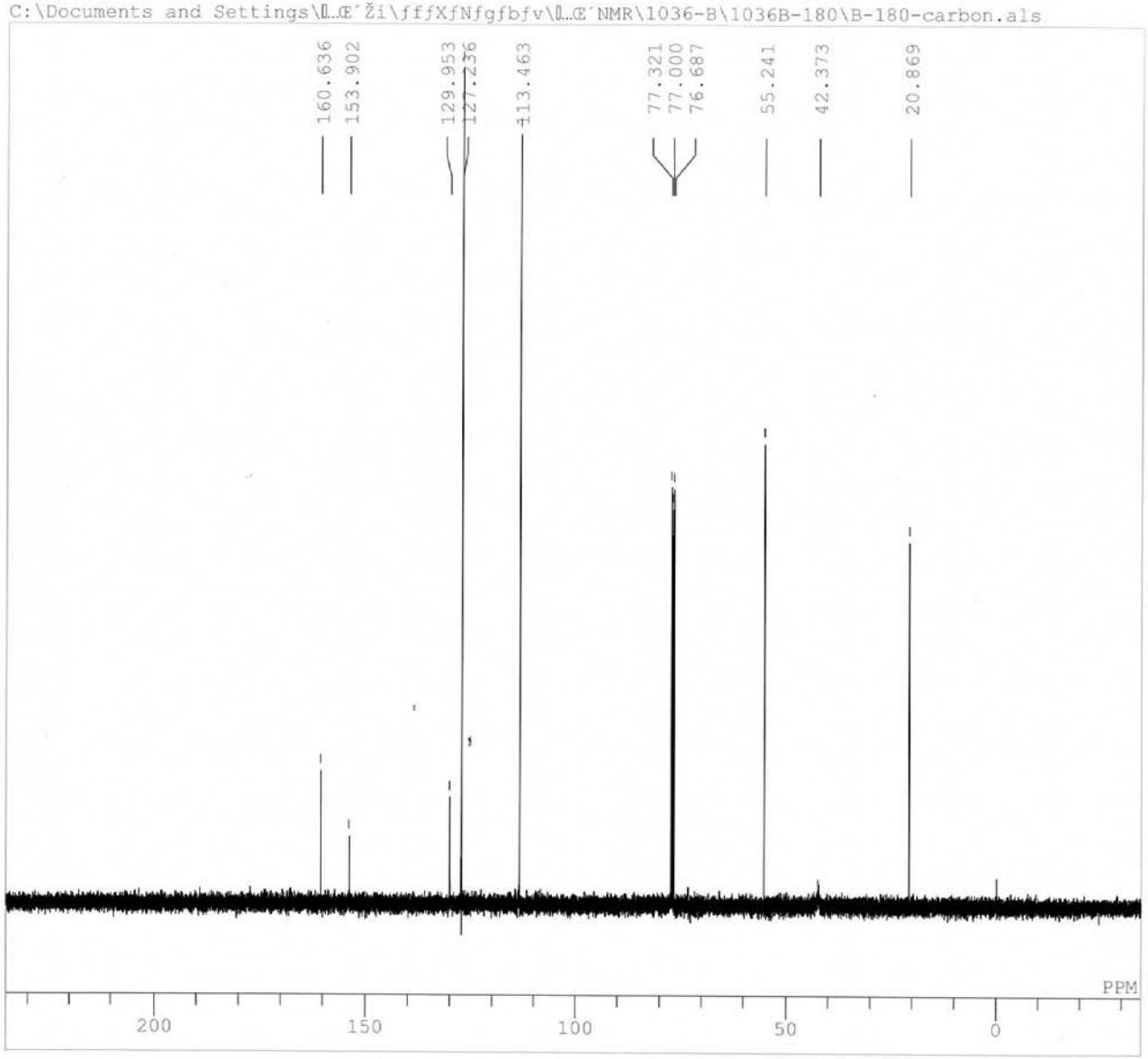


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SLVNT  CDCL3
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RGAIN              25
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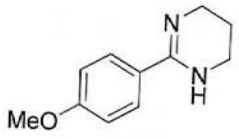

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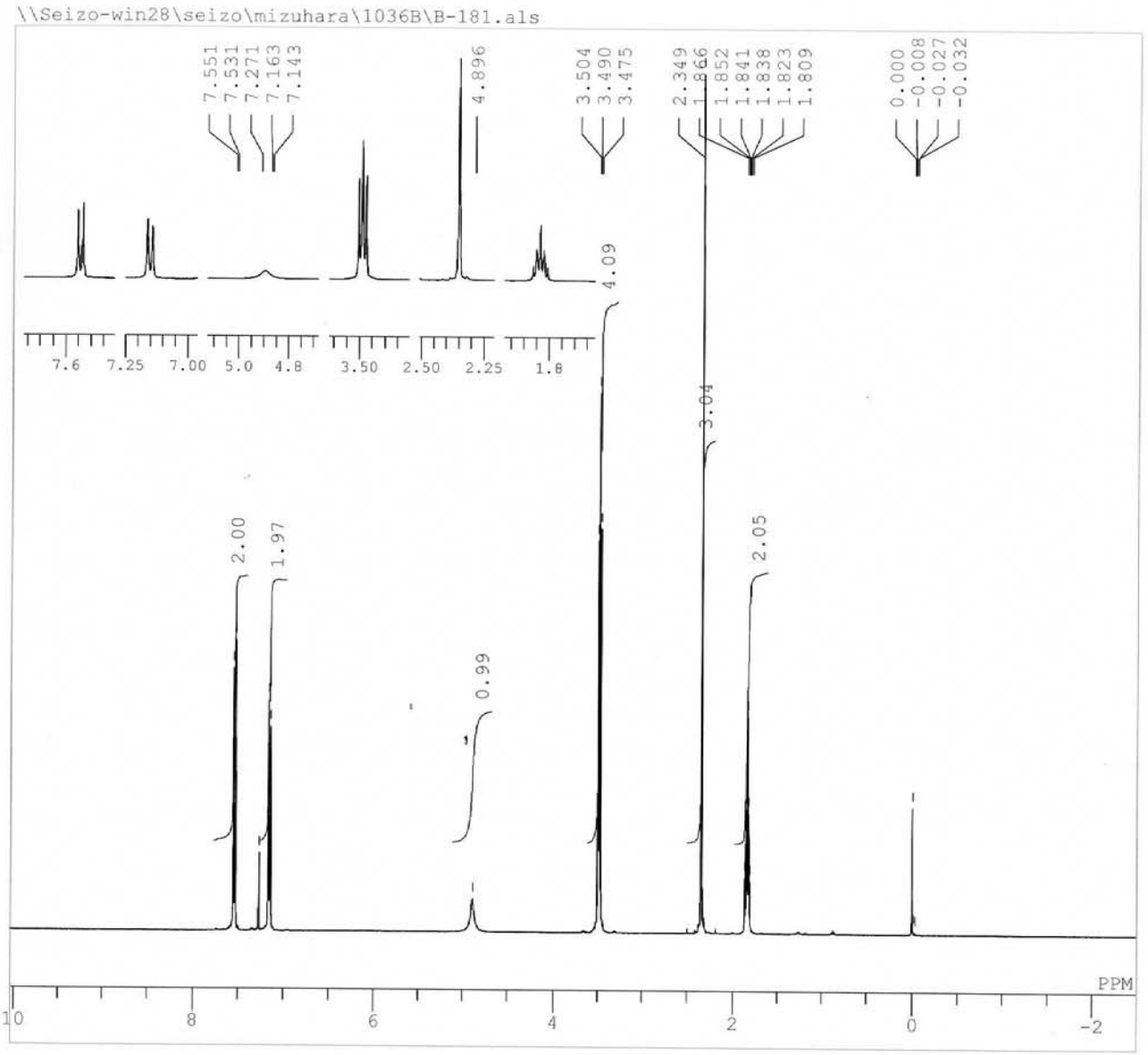

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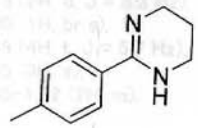
BF 0.12 Hz
RGAIN 14



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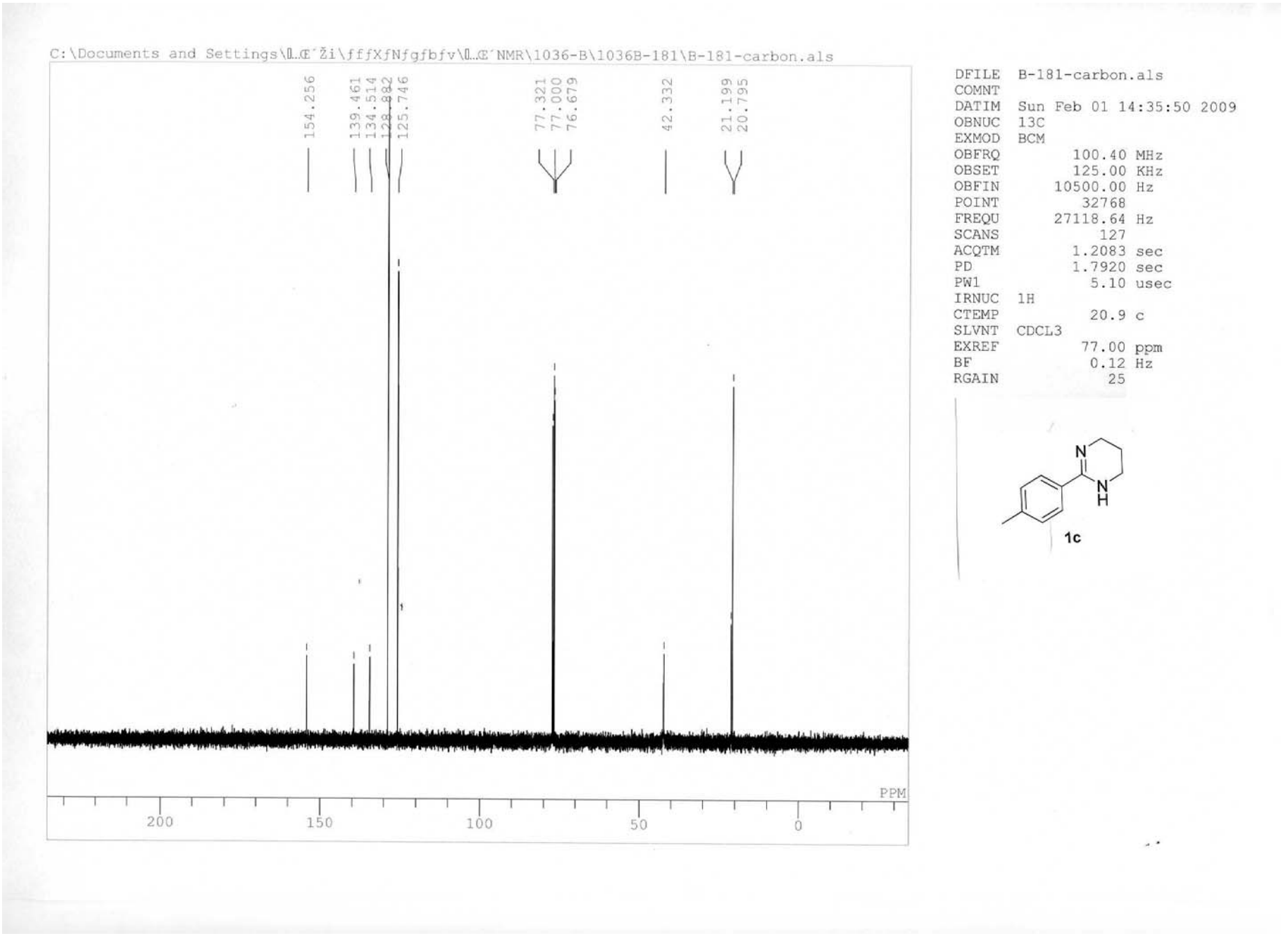
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134.514
128.882
125.746
77.321
77.000
76.679
42.332
21.199
20.795
PPM
200
150
100
50
0
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OBSET 125.00 KHz
OBFIN 10500.00 Hz
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FREQU 27118.64 Hz
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PD 1.7920 sec
PW1 5.10 usec
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SLVNT CDCL3
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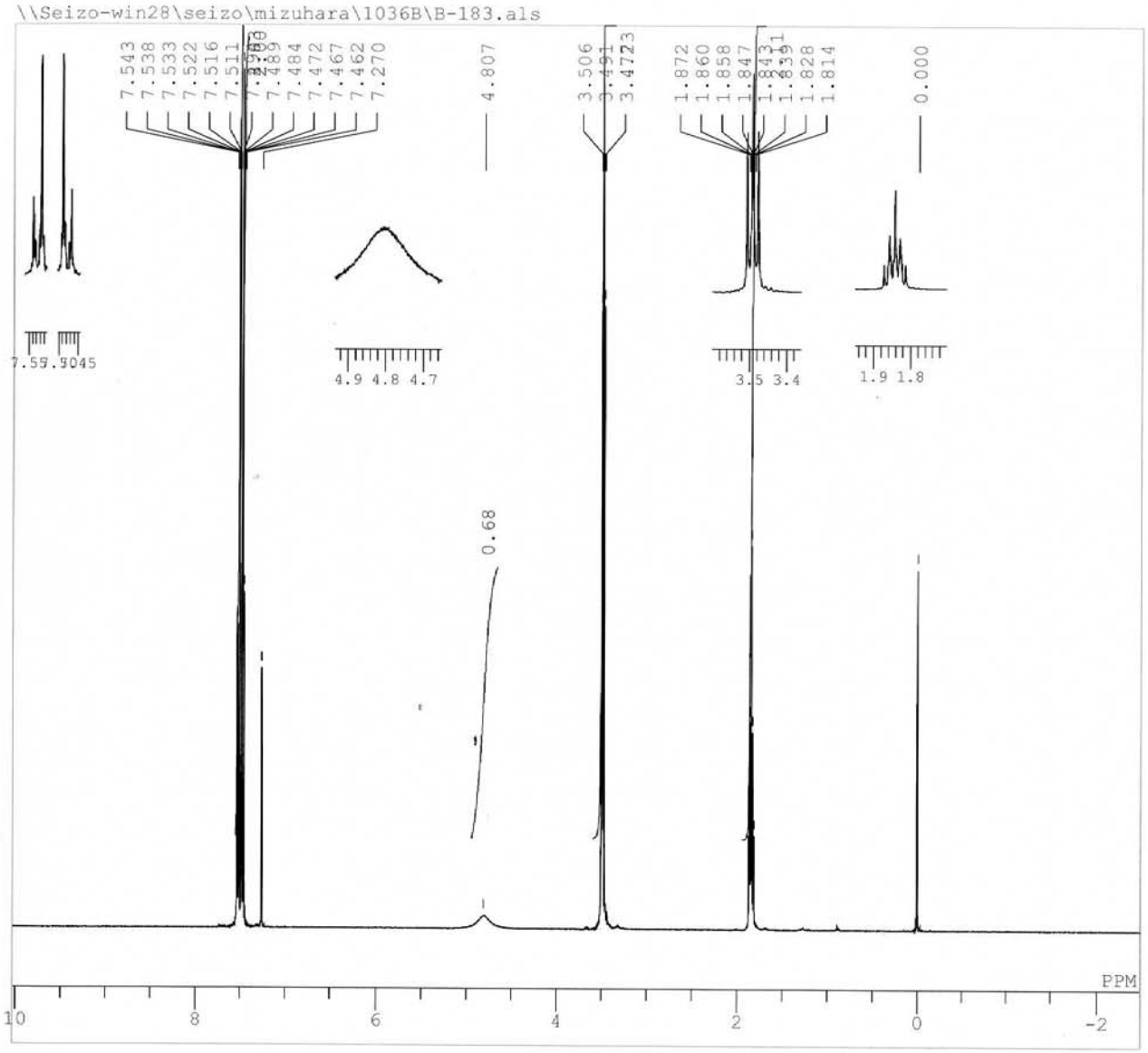
BF 0.12 Hz
RGAIN 25
N
N
H
1c



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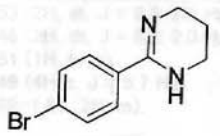
RGAIN 16



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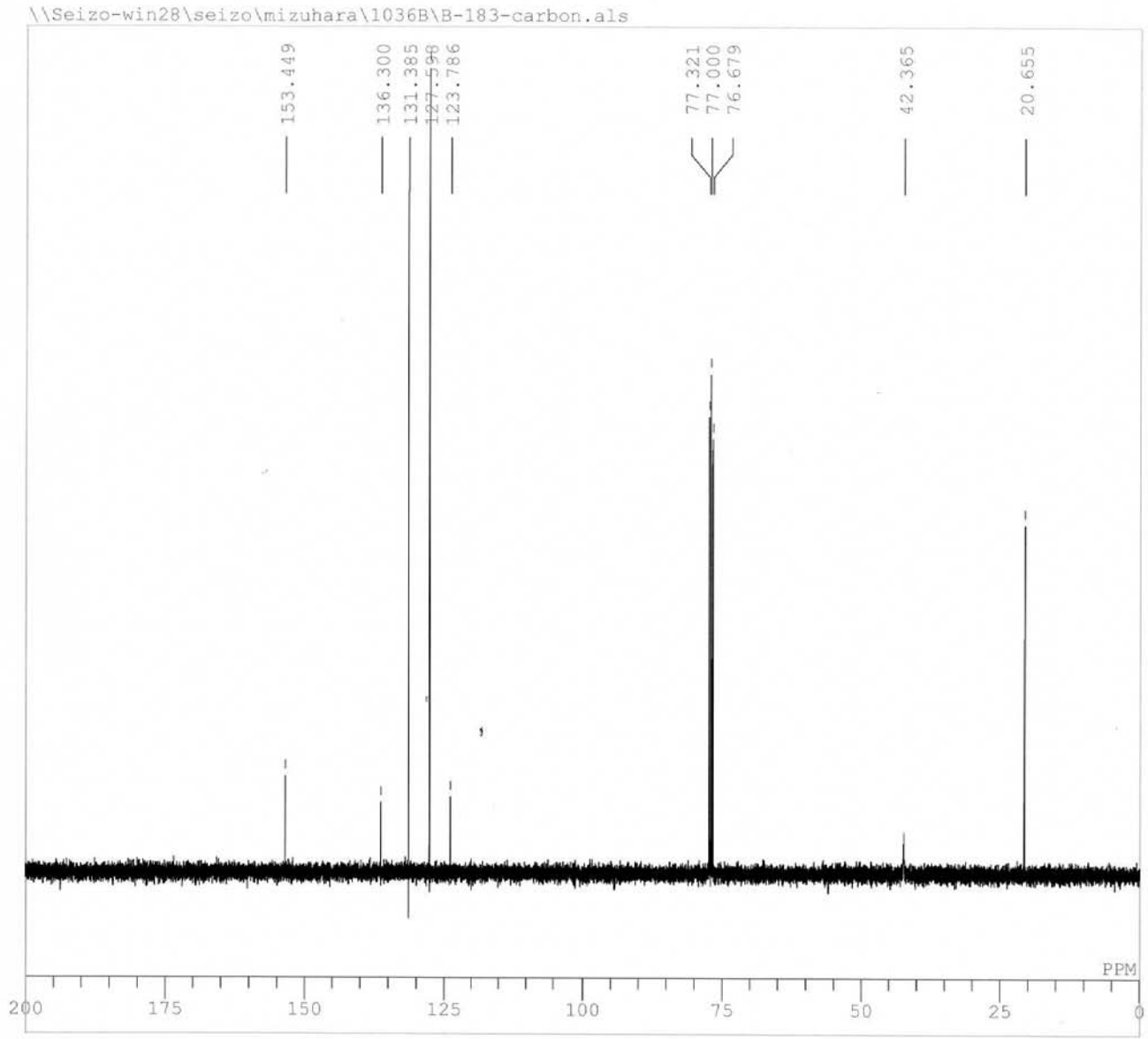


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FREQU       27118.64 Hz
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PD             1.7920 sec
PW1             5.10 usec
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BF               0.12 Hz
RGAIN              25
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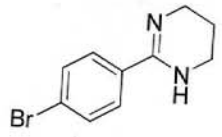

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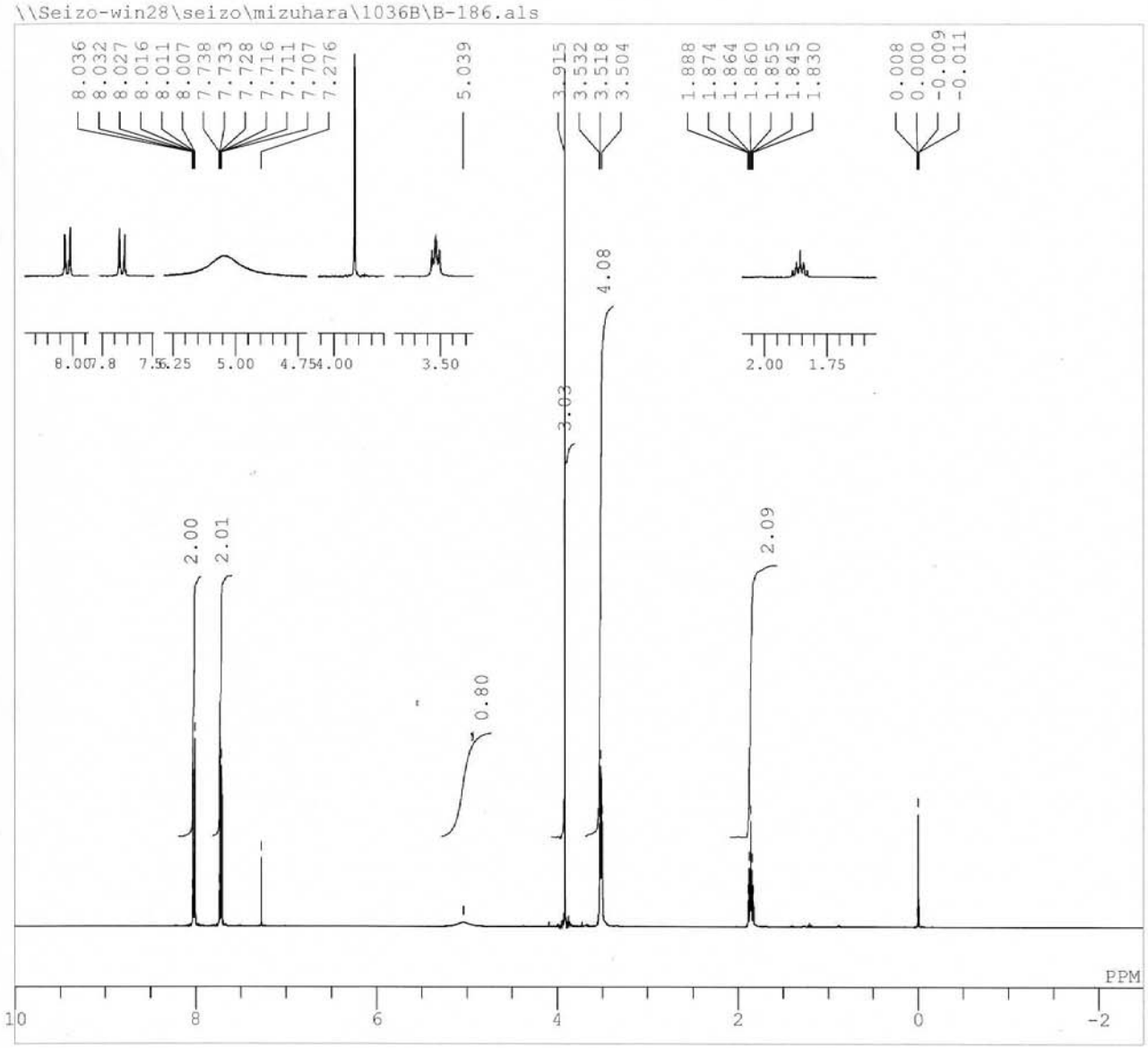

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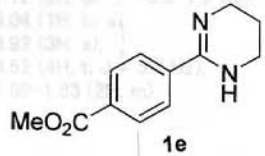
BF 0.12 Hz
RGAIN 15



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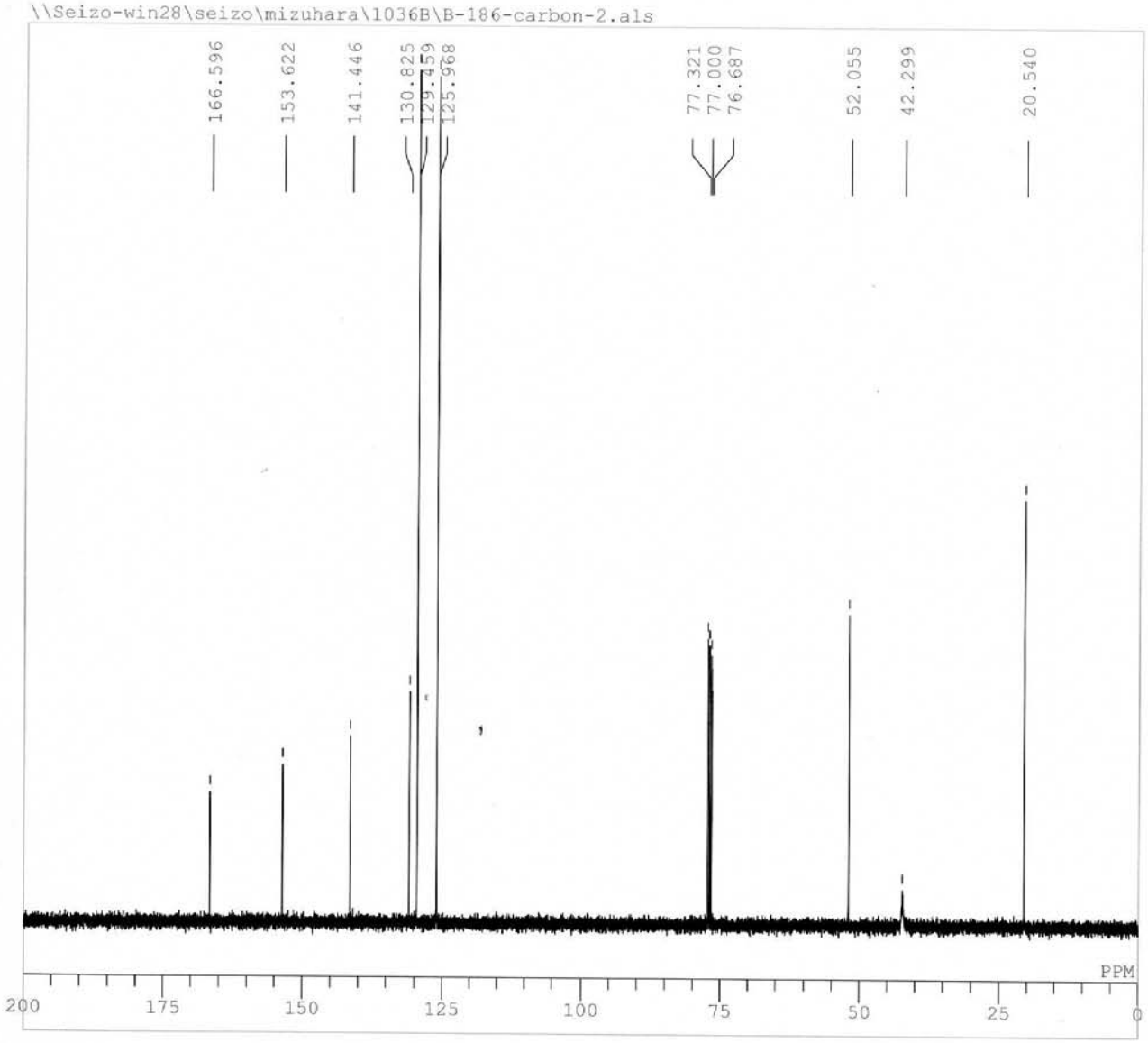


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POINT          32768
FREQU       27118.64 Hz
SCANS             89
ACQTM          1.2083 sec
PD             1.7920 sec
PW1               5.10 usec
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RGAIN              26
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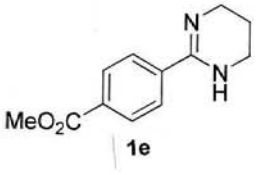

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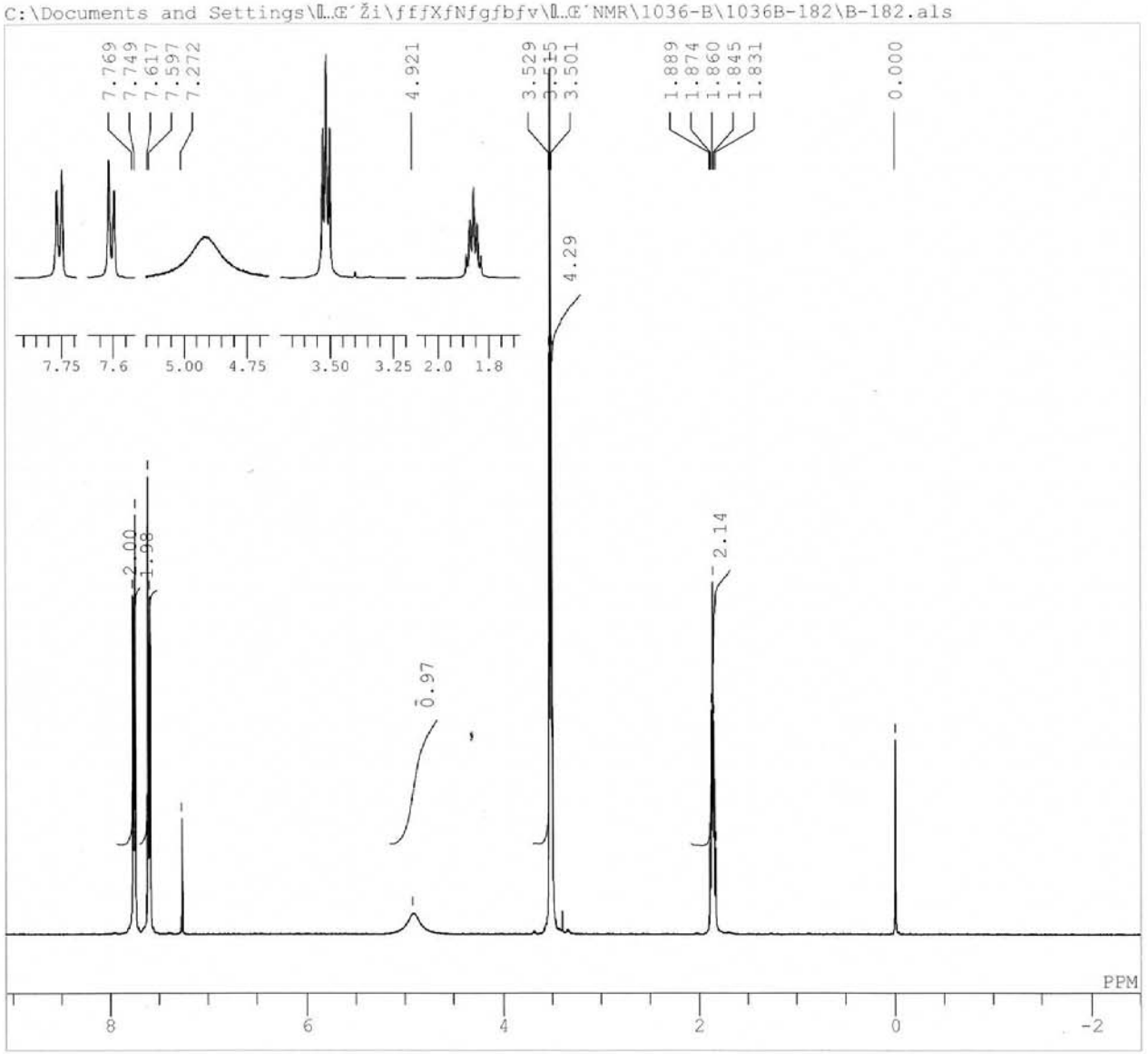

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POINT 32768
FREQU 7992.01 Hz
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ACQTM 4.1001 sec
PD 2.9000 sec
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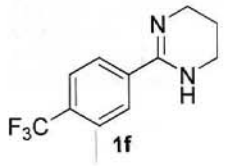
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15



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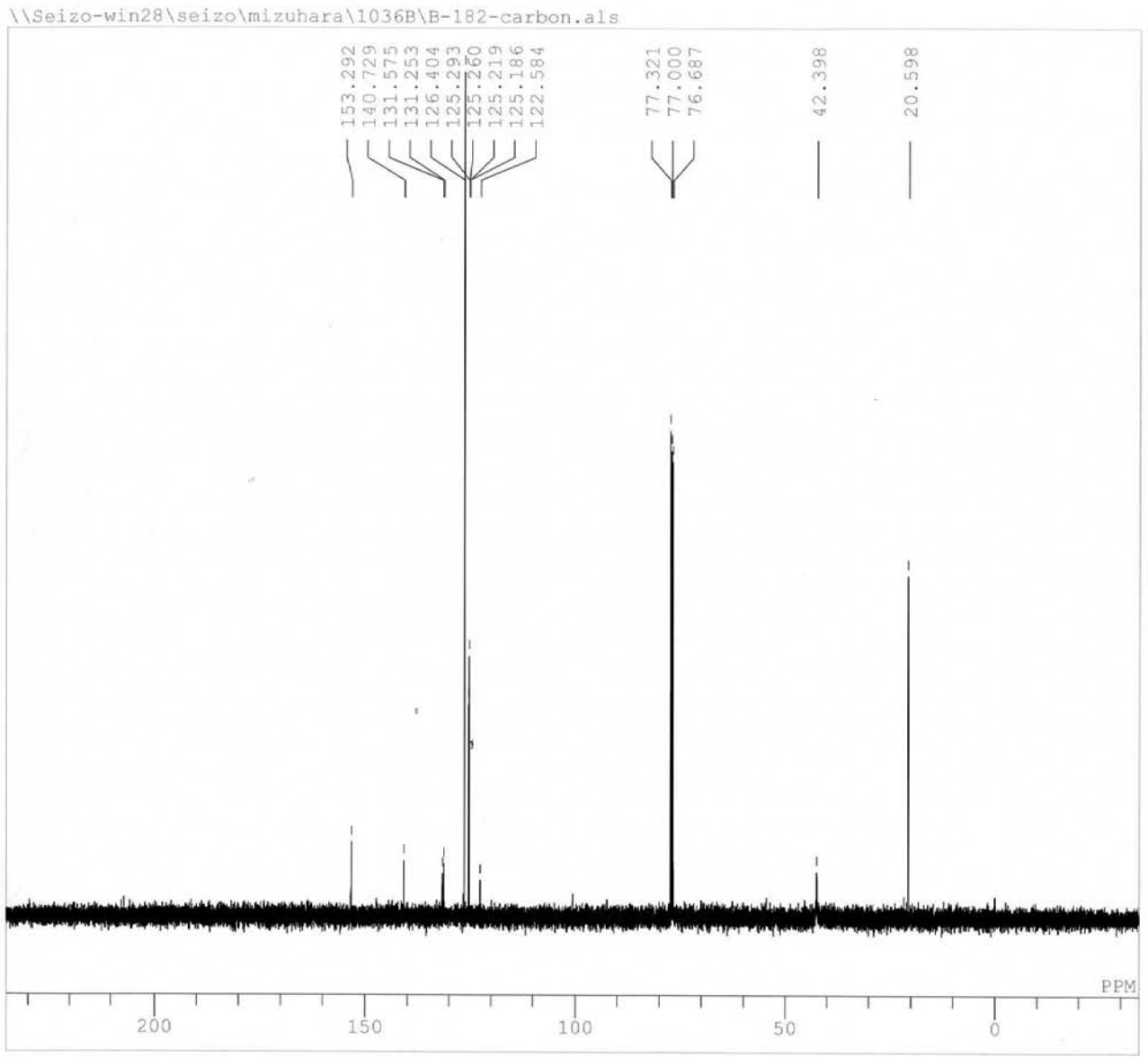


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SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             25
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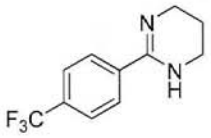

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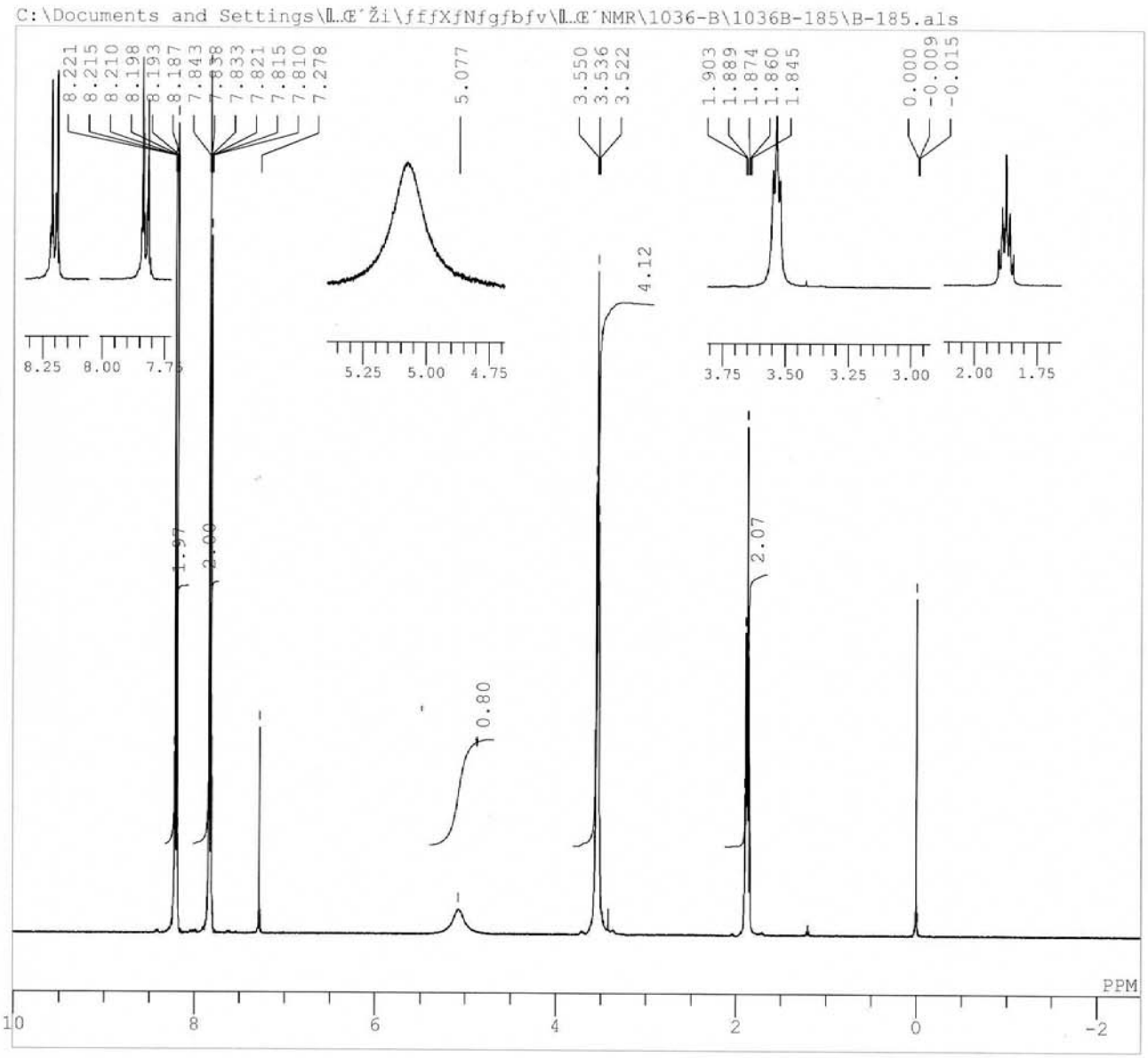

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PD	2.9000 sec
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CTEMP	21.1 c
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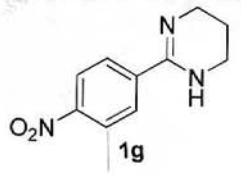
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	15



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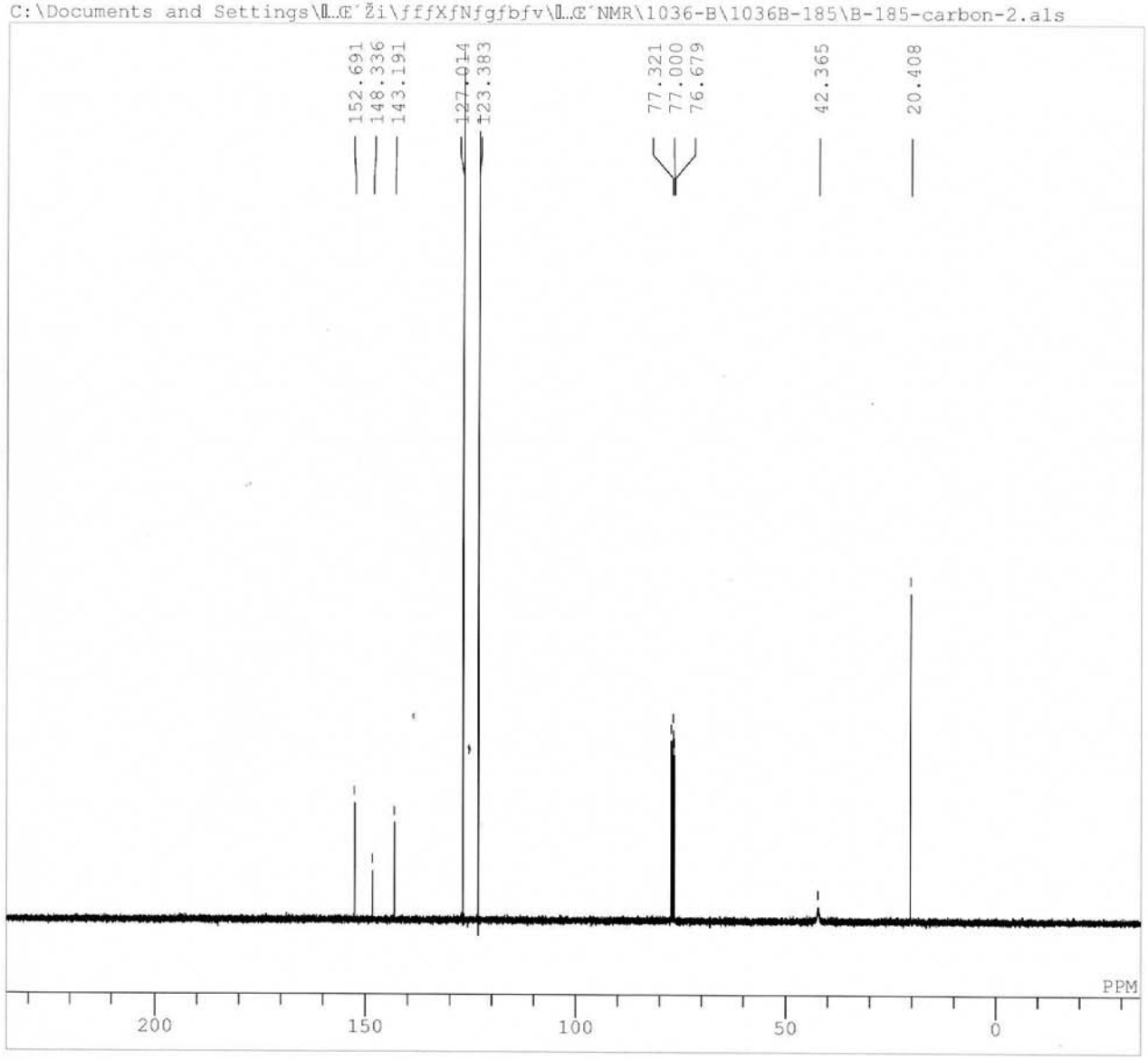

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POINT 32768
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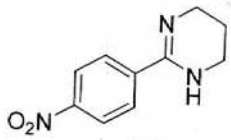
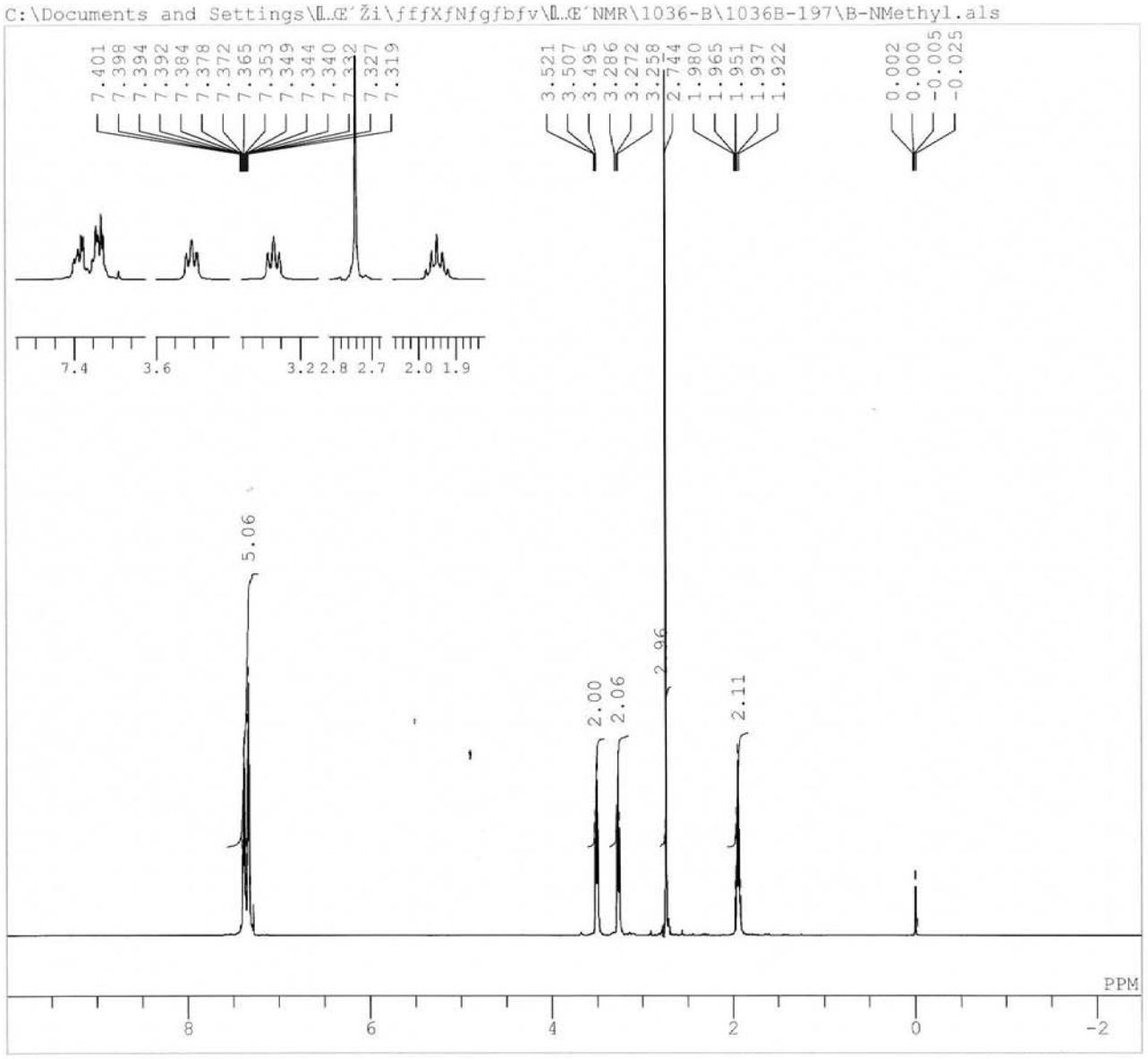
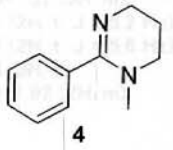
PW1 5.10 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25



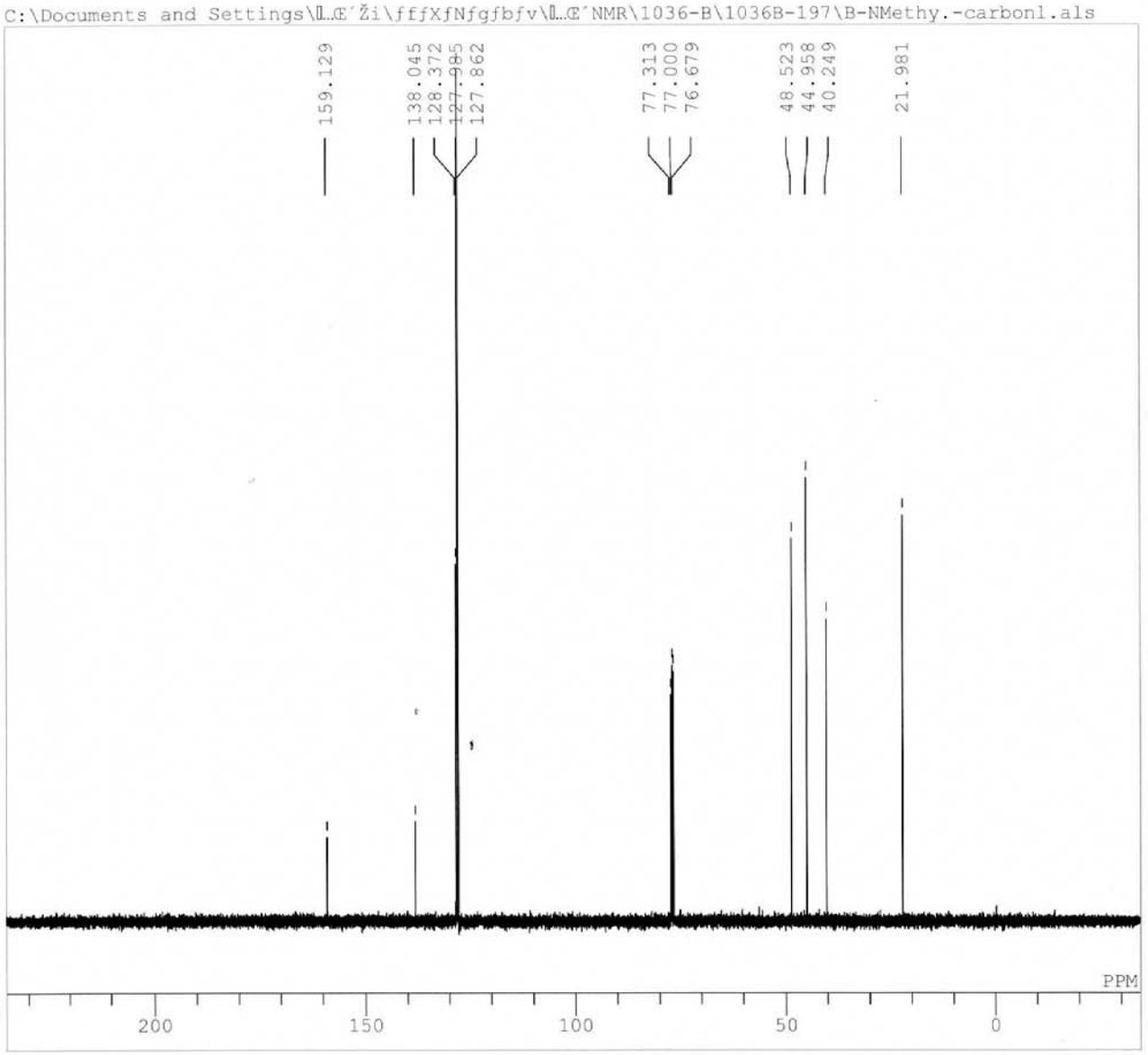
1g



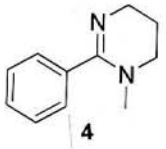

```
DFILE   B-NMethyl.als
COMNT
DATIM   Wed Feb 04 22:45:03 2009
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.00 Hz
POINT          32768
FREQU        7992.01 Hz
SCANS             2
ACQTM          4.1001 sec
PD             2.9000 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            19.9 c
SLVNT   CDCL3
EXREF             0.00 ppm
BF                0.12 Hz
RGAIN               12
```



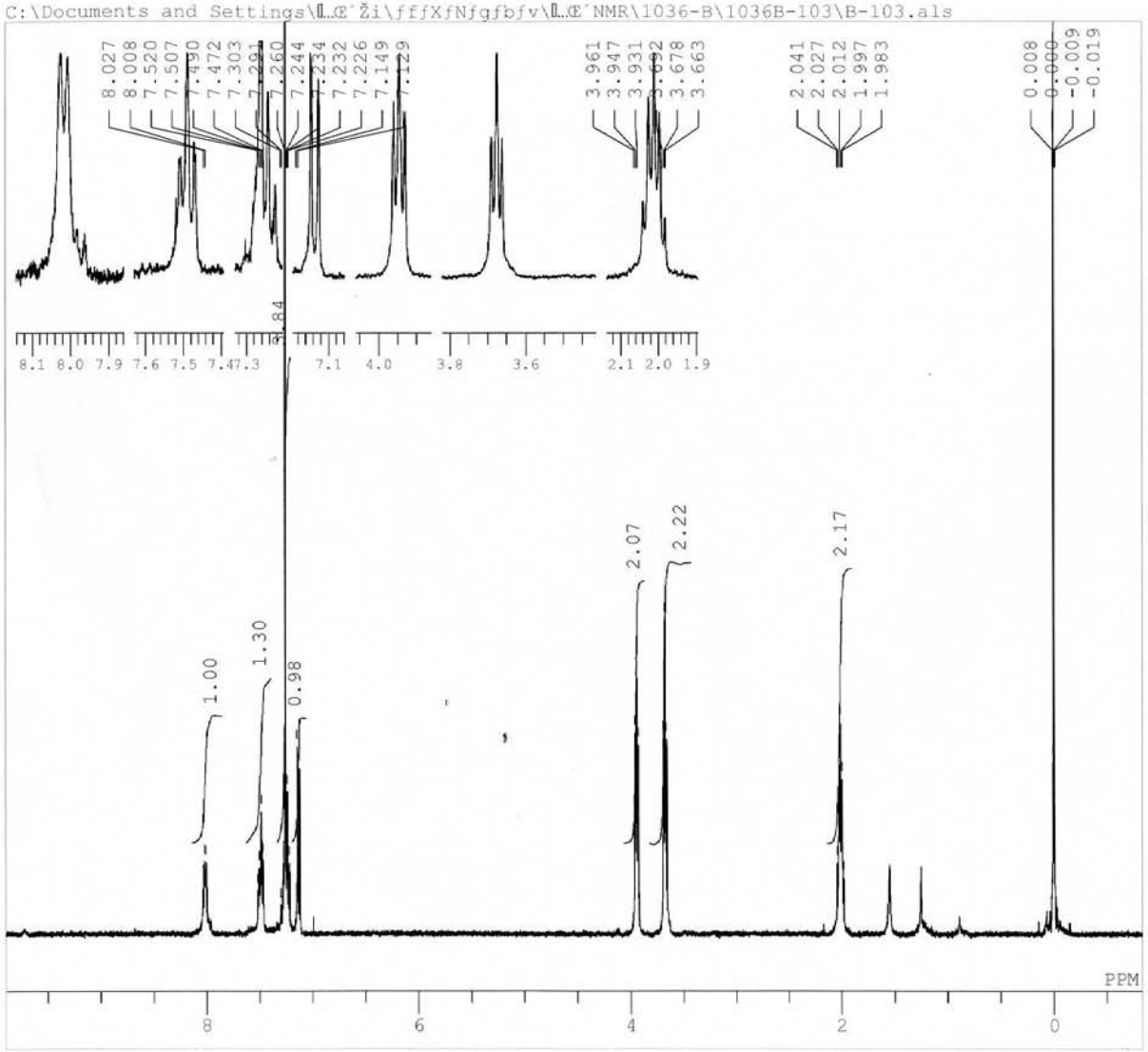
4



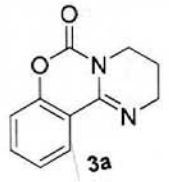

```
DFILE   B-NMethy.-carbonl.als
COMNT
DATIM   Wed Feb 04 22:52:19 2009
OBNUC   13C
EXMOD   BCM
OBFRQ         100.40 MHz
OBSET         125.00 KHz
OBFIN       10500.00 Hz
POINT         32768
FREQU       27118.64 Hz
SCANS           125
ACQTM         1.2083 sec
PD            1.7920 sec
PW1             5.10 usec
IRNUC   1H
CTEMP           21.2 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              25
```



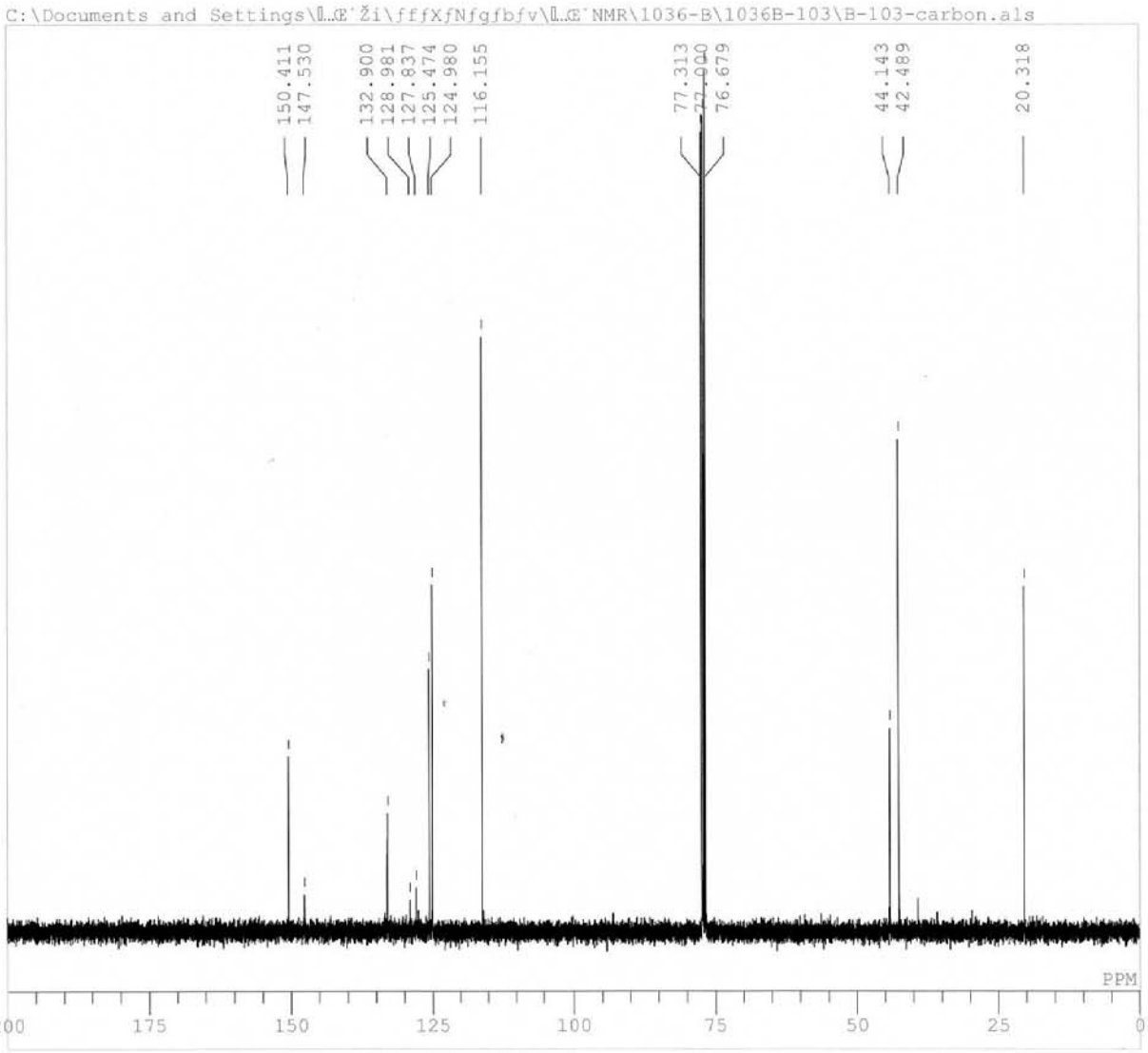
4



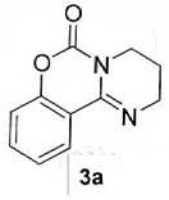

```
DFILE   B-103.als
COMNT
DATIM   Sat Dec 13 19:41:13 2008
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.00 Hz
POINT         32768
FREQU         7992.01 Hz
SCANS             8
ACQTM         4.1001 sec
PD            2.9000 sec
PW1             5.50 usec
IRNUC   1H
CTEMP           23.1 c
SLVNT   CDCL3
EXREF             0.00 ppm
BF                0.12 Hz
RGAIN               23
```



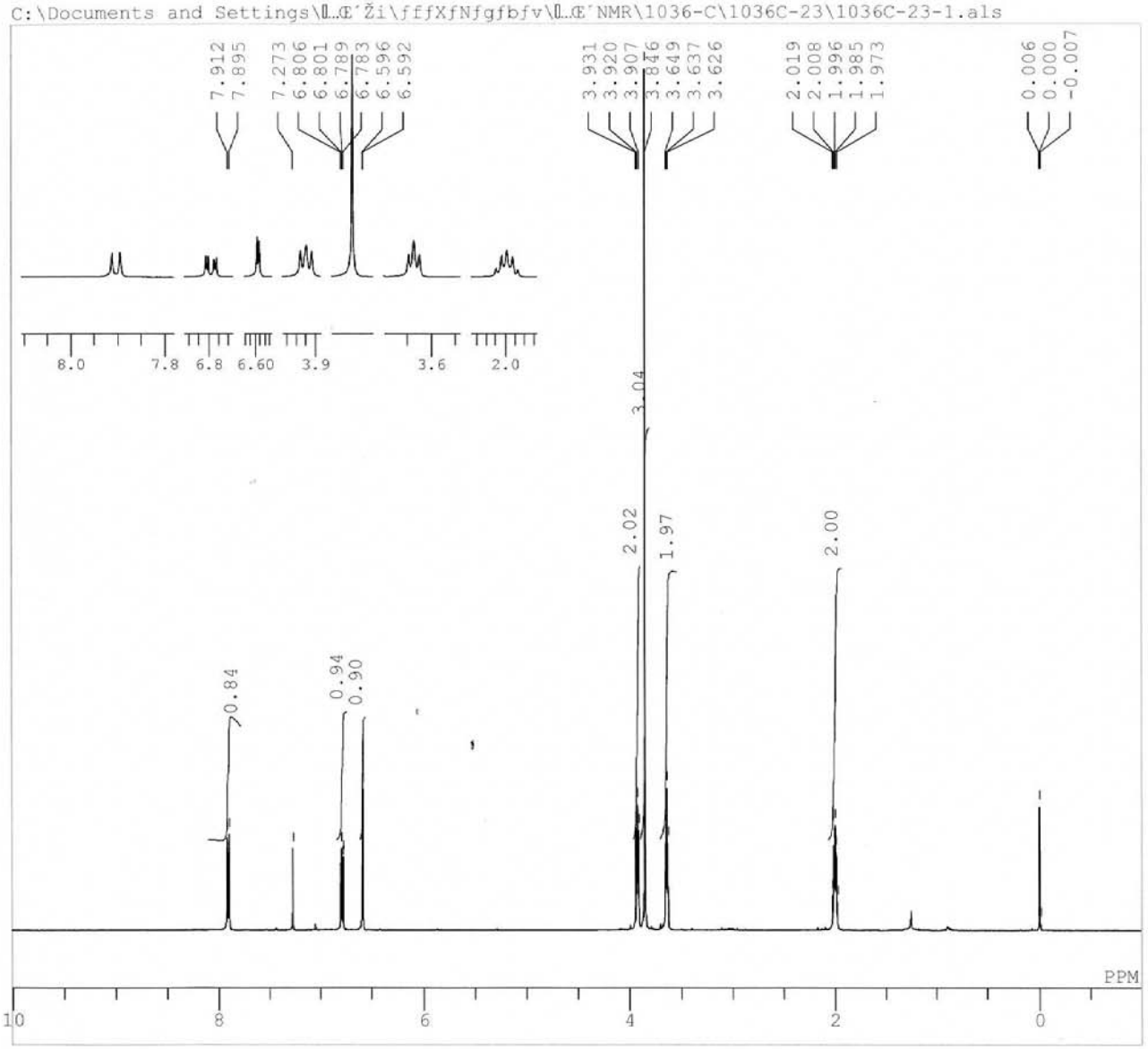
3a



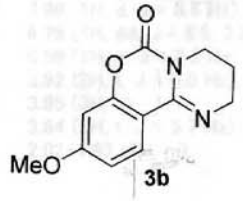

```
DFILE   B-103-carbon.als
COMNT
DATIM   Mon Dec 15 11:56:07 2008
OBNUC   13C
EXMOD   BCM
OBFRQ         100.40 MHz
OBSET         125.00 KHz
OBFIN       10500.00 Hz
POINT          32768
FREQU       27118.64 Hz
SCANS            467
ACQTM          1.2083 sec
PD             1.7920 sec
PW1             5.10 usec
IRNUC   1H
CTEMP            22.2 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              25
```



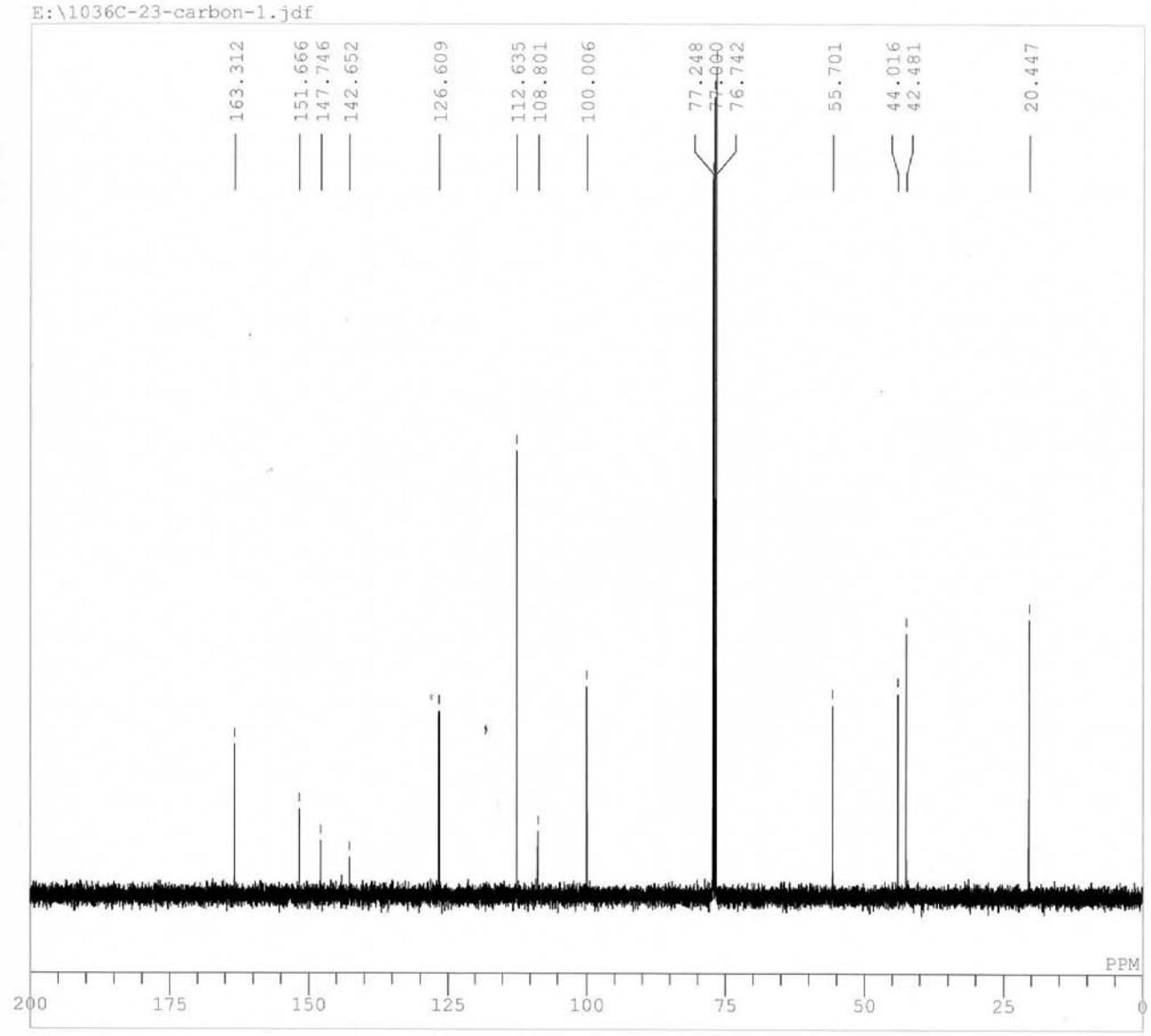
3a



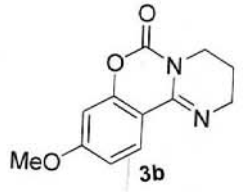
DFILE 1036C-23-1.als
COMNT single_pulse
DATIM 13-02-2009 22:02:20
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 4
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42



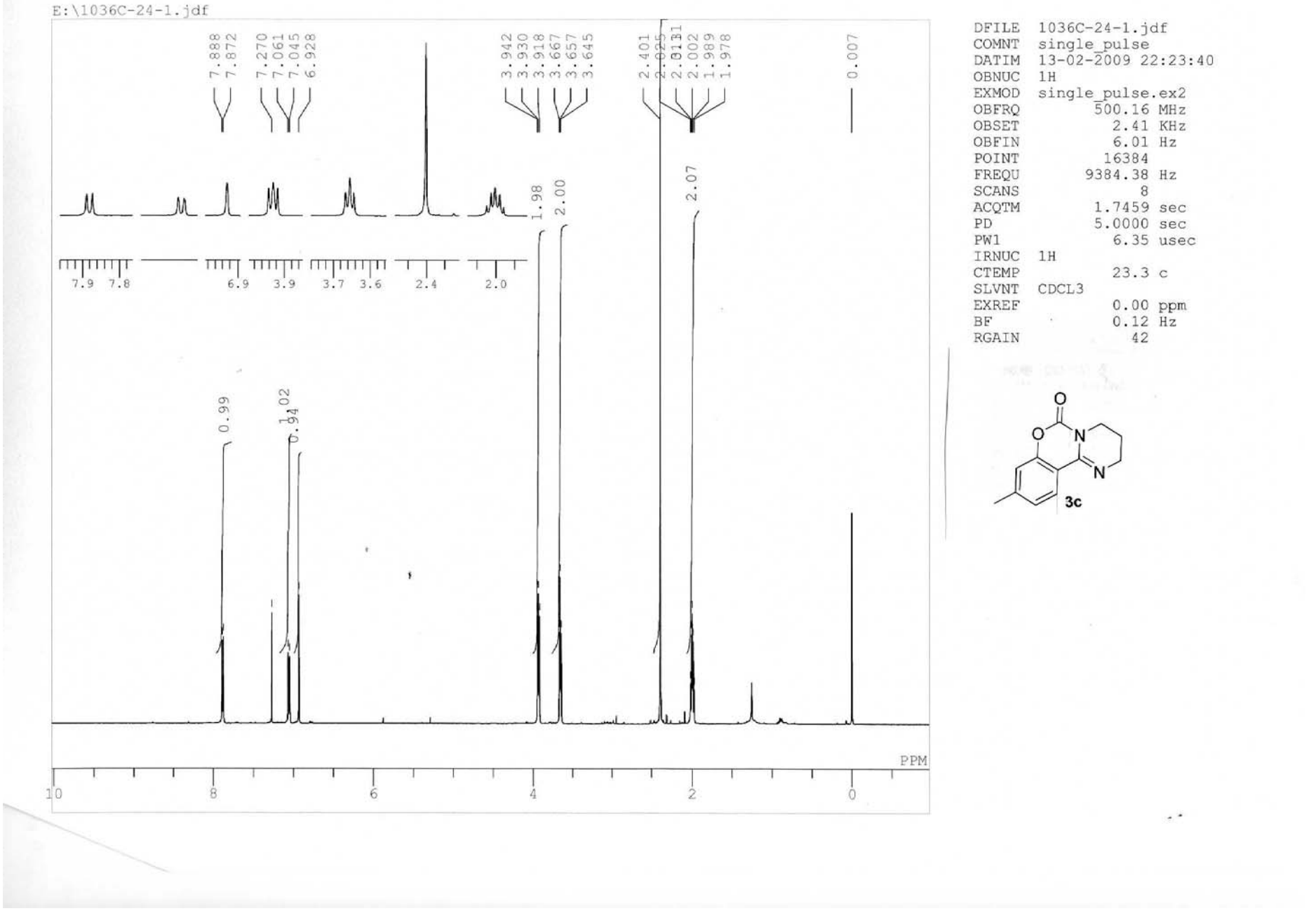
3b

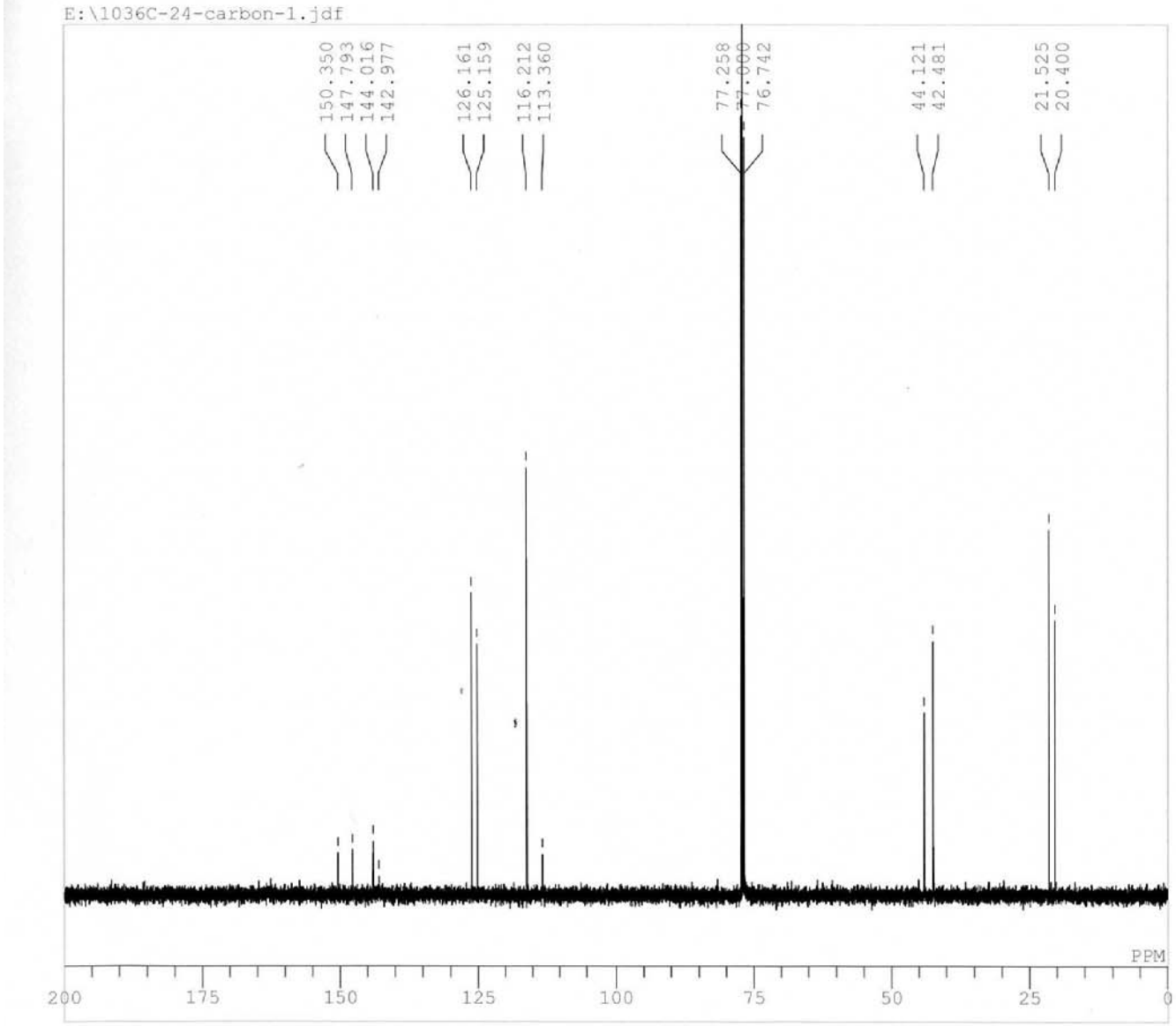



```
DFILE   1036C-23-carbon-1.jdf
COMNT   single pulse decoupled ga
DATIM   13-02-2009 22:19:19
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       39308.18 Hz
SCANS            336
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.50 usec
IRNUC   1H
CTEMP           23.7 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             60
```

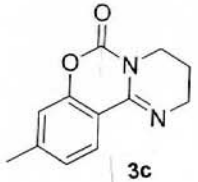


3b

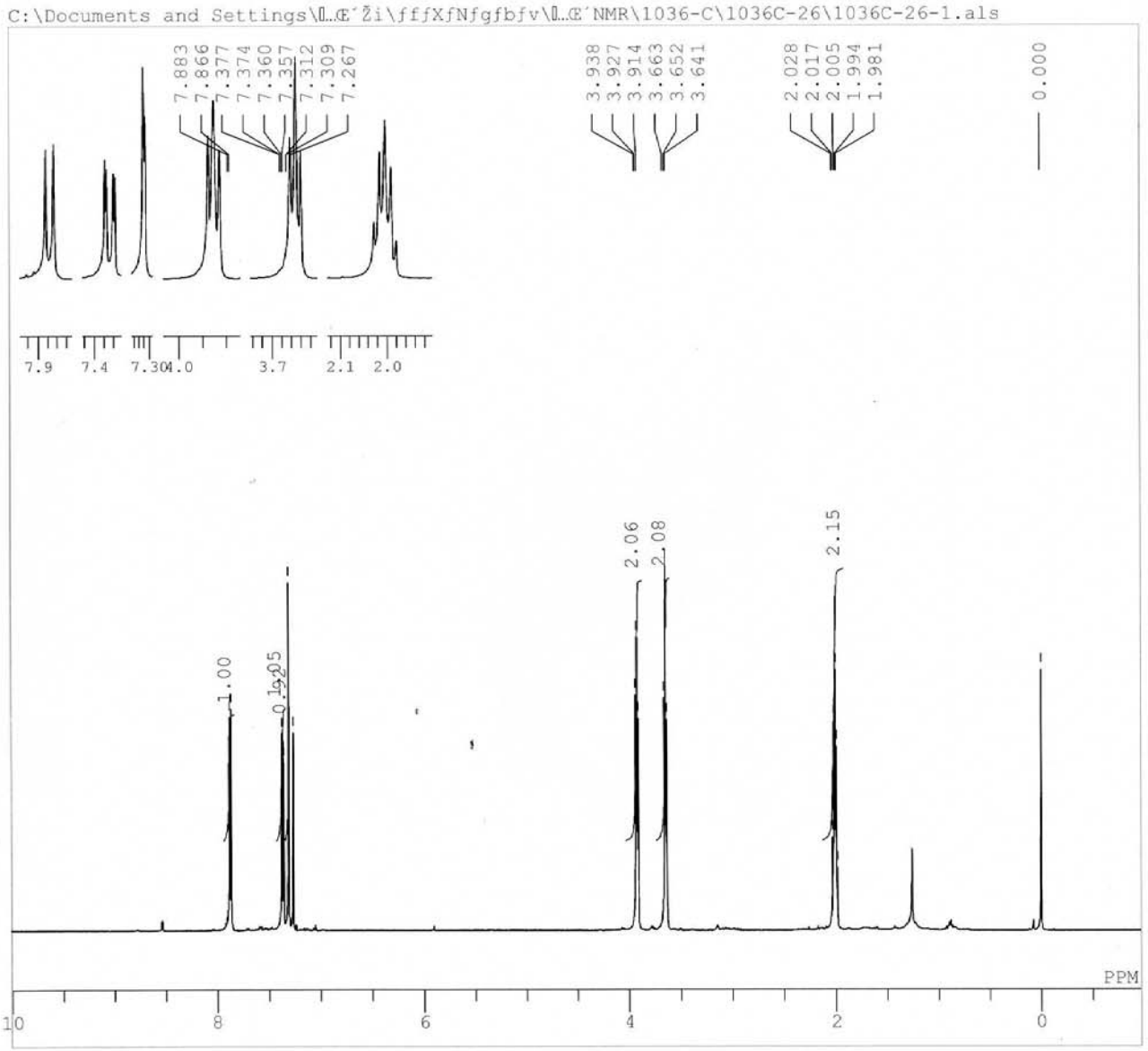

E:\1036C-24-1.jdf
7.888
7.872
7.270
7.061
7.045
6.928
3.942
3.930
3.918
3.667
3.657
3.645
2.401
2.025
2.002
1.989
1.978
0.007
1.98
2.00
2.07
0.99
1.02
0.94
7.9 7.8
6.9
3.9
3.7 3.6
2.4
2.0
PPM
10
8
6
4
2
0
DFILE 1036C-24-1.jdf
COMNT single_pulse
DATIM 13-02-2009 22:23:40
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 23.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42
O
O
N
N
3c



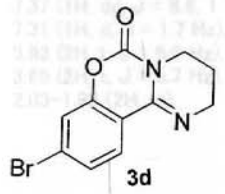

```
DFILE   1036C-24-carbon-1.jdf
COMNT   single pulse decoupled ga
DATIM   13-02-2009 22:49:60
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       39308.18 Hz
SCANS            535
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.50 usec
IRNUC   1H
CTEMP           23.7 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             60
```



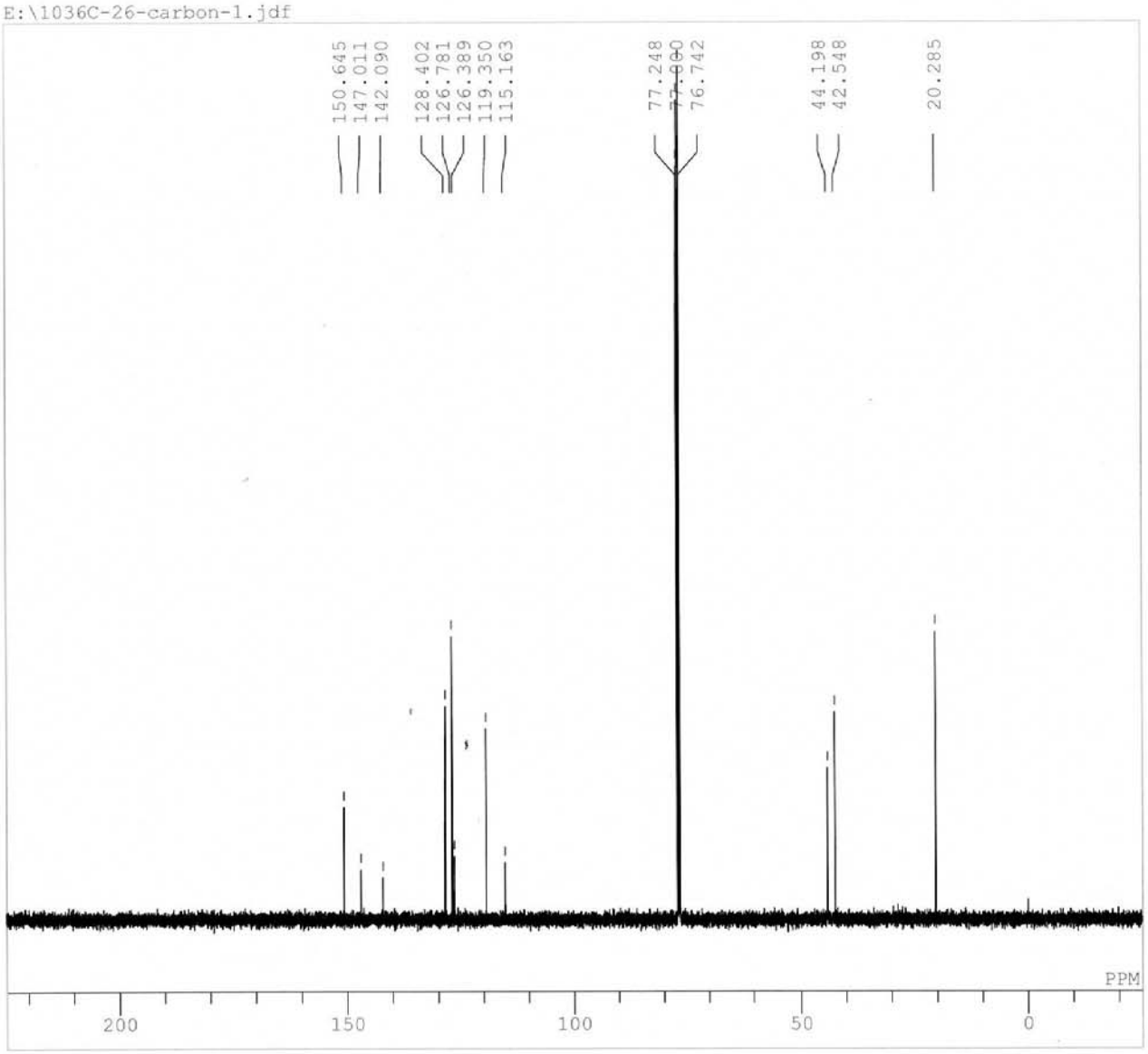
3c



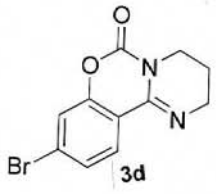
DFILE 1036C-26-1.als
COMNT single_pulse
DATIM 15-02-2009 14:53:40
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44



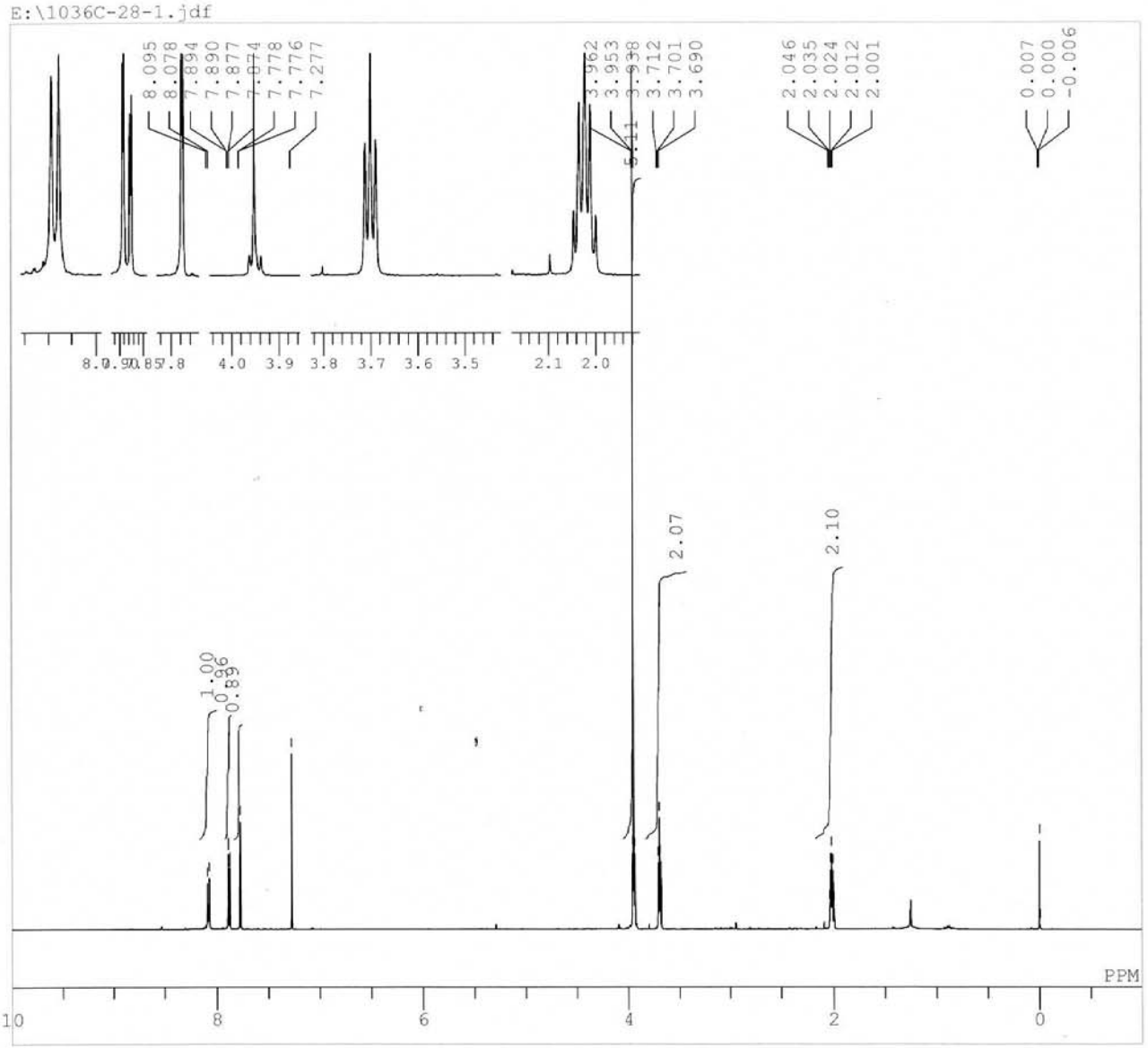
3d



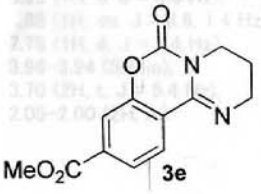

```
DFILE   1036C-26-carbon-1.jdf
COMNT   single pulse decoupled ga
DATIM   15-02-2009 15:34:57
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       39308.18 Hz
SCANS            855
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.50 usec
IRNUC   1H
CTEMP           24.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              58
```



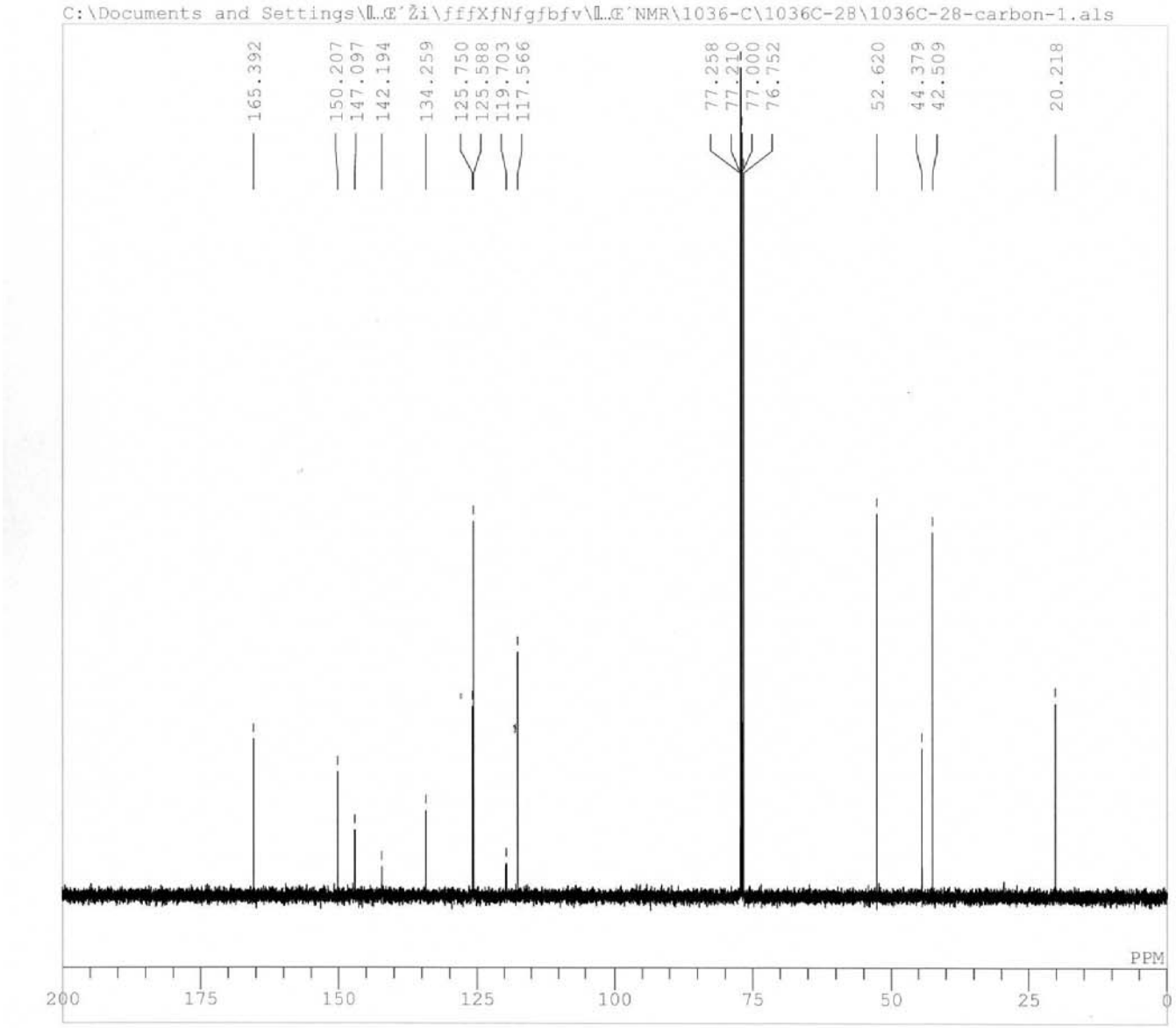
3d



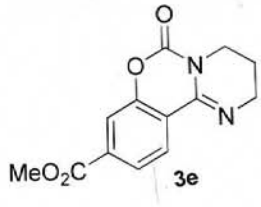
DFILE 1036C-28-1.jdf
COMNT single_pulse
DATIM 16-02-2009 21:39:16
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42



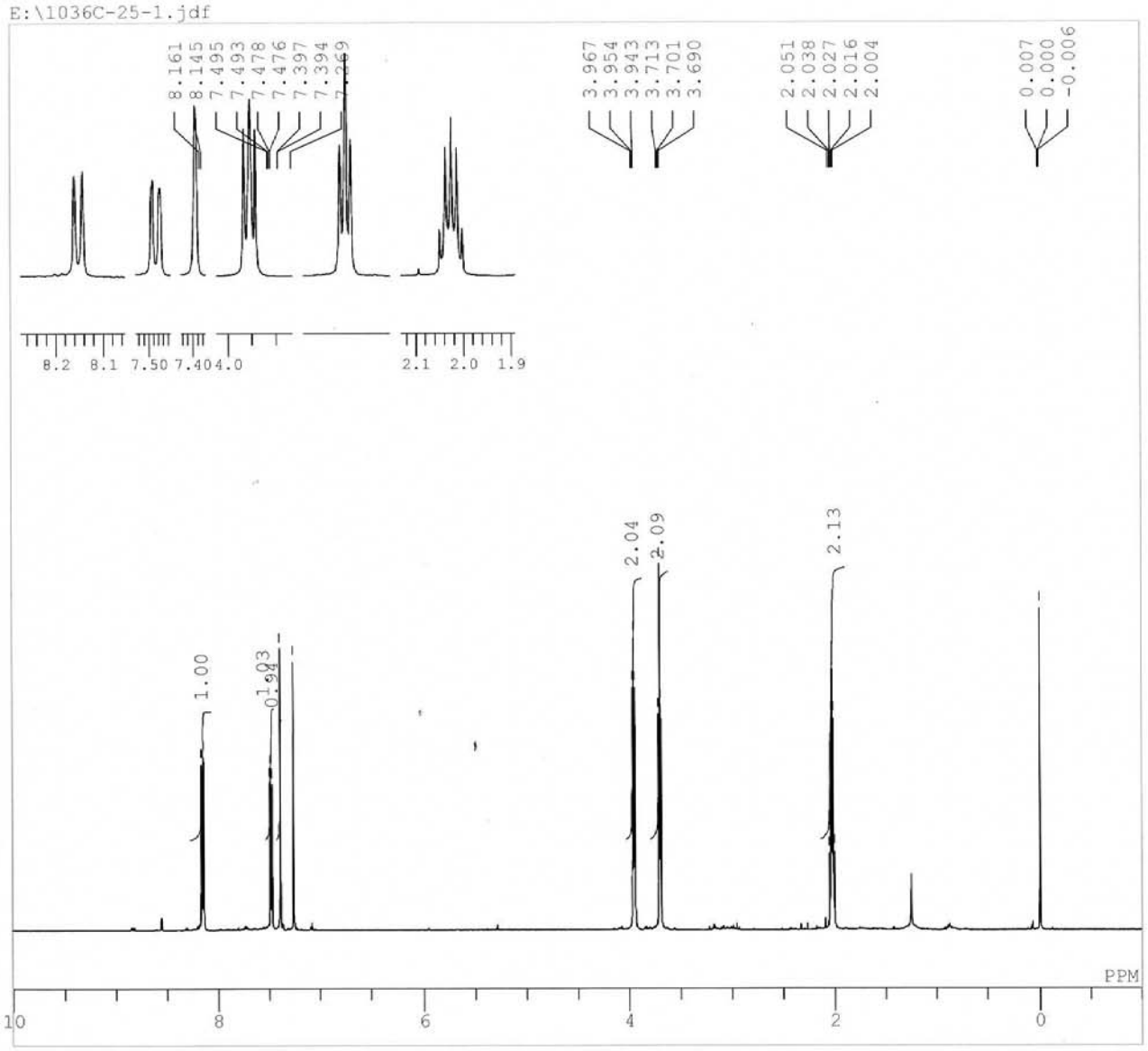
3e



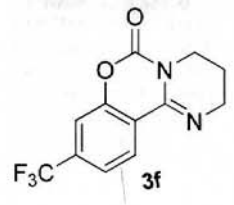

```
DFILE   1036C-28-carbon-1.als
COMNT   single pulse decoupled ga
DATIM   16-02-2009 22:01:55
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       39308.18 Hz
SCANS            460
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.50 usec
IRNUC   1H
CTEMP           21.9 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             60
```



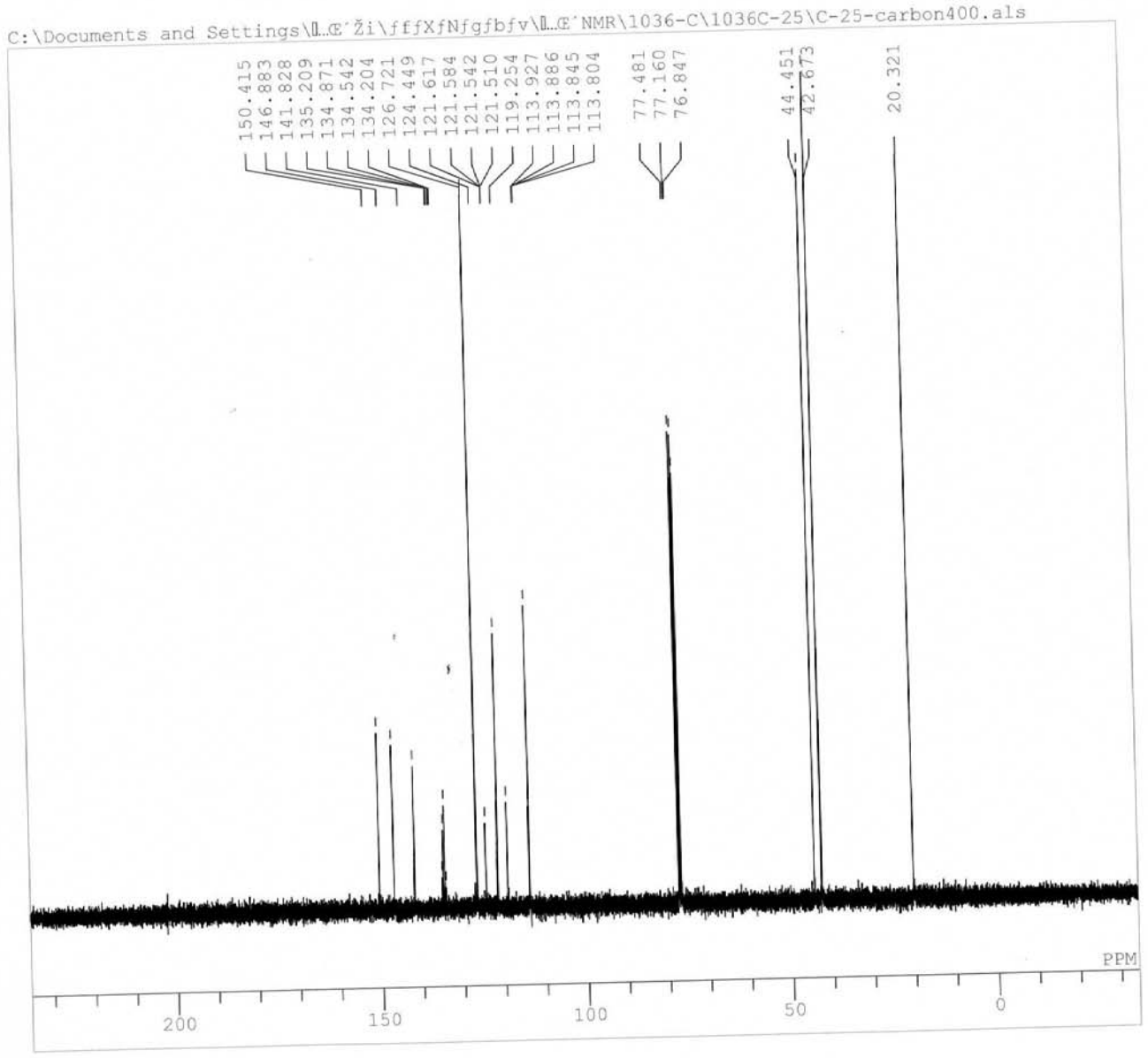
3e



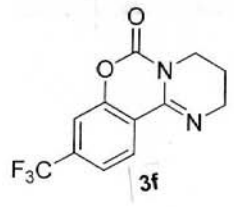
DFILE 1036C-25-1.jdf
COMNT single_pulse
DATIM 15-02-2009 13:57:27
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 23.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44



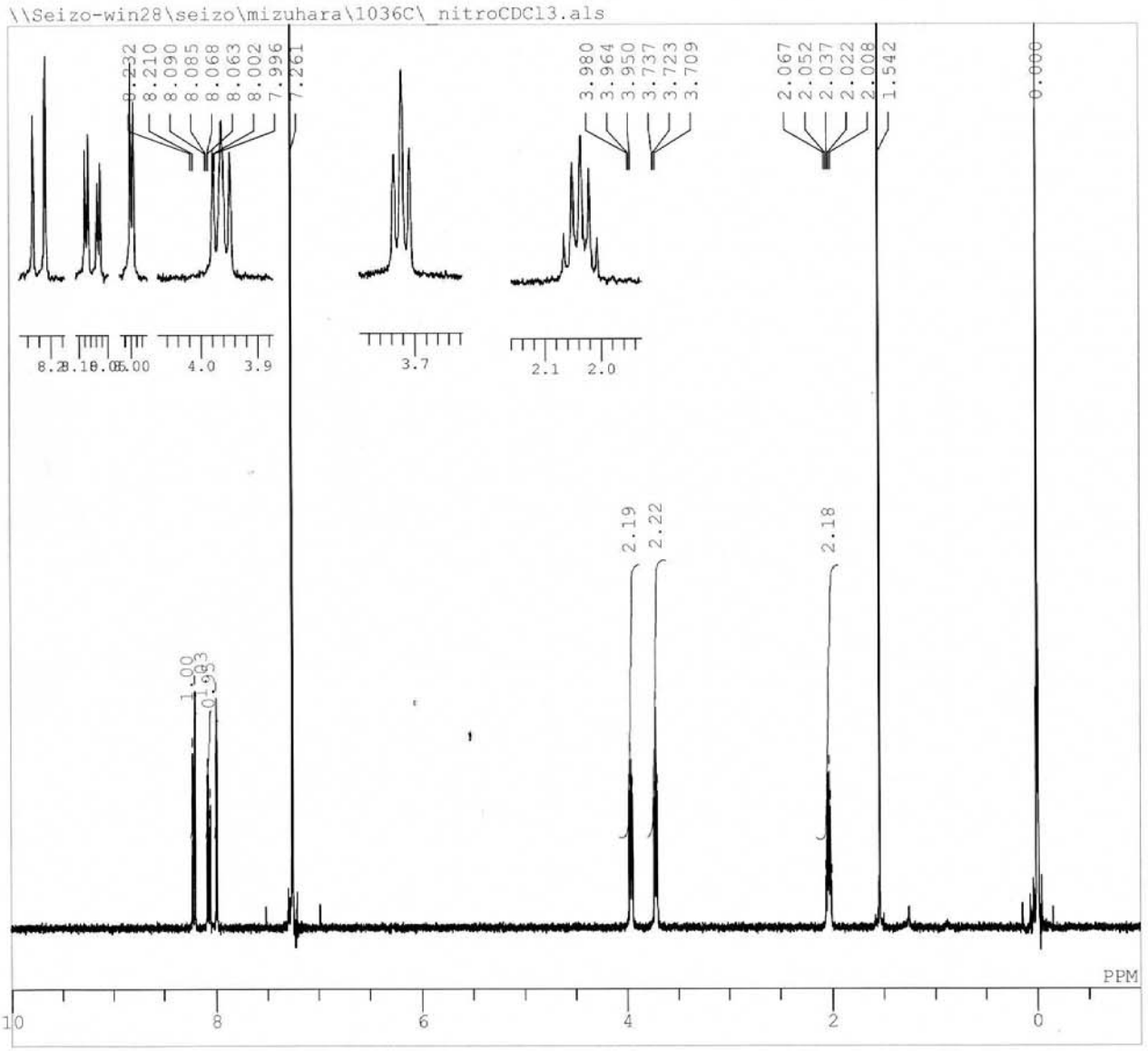
3f



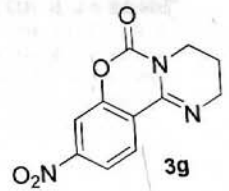
DFILE C-25-carbon400.als
COMNT
DATIM Thu Feb 26 23:39:43 2009
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 799
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.10 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 0.12 Hz
RGAIN 25



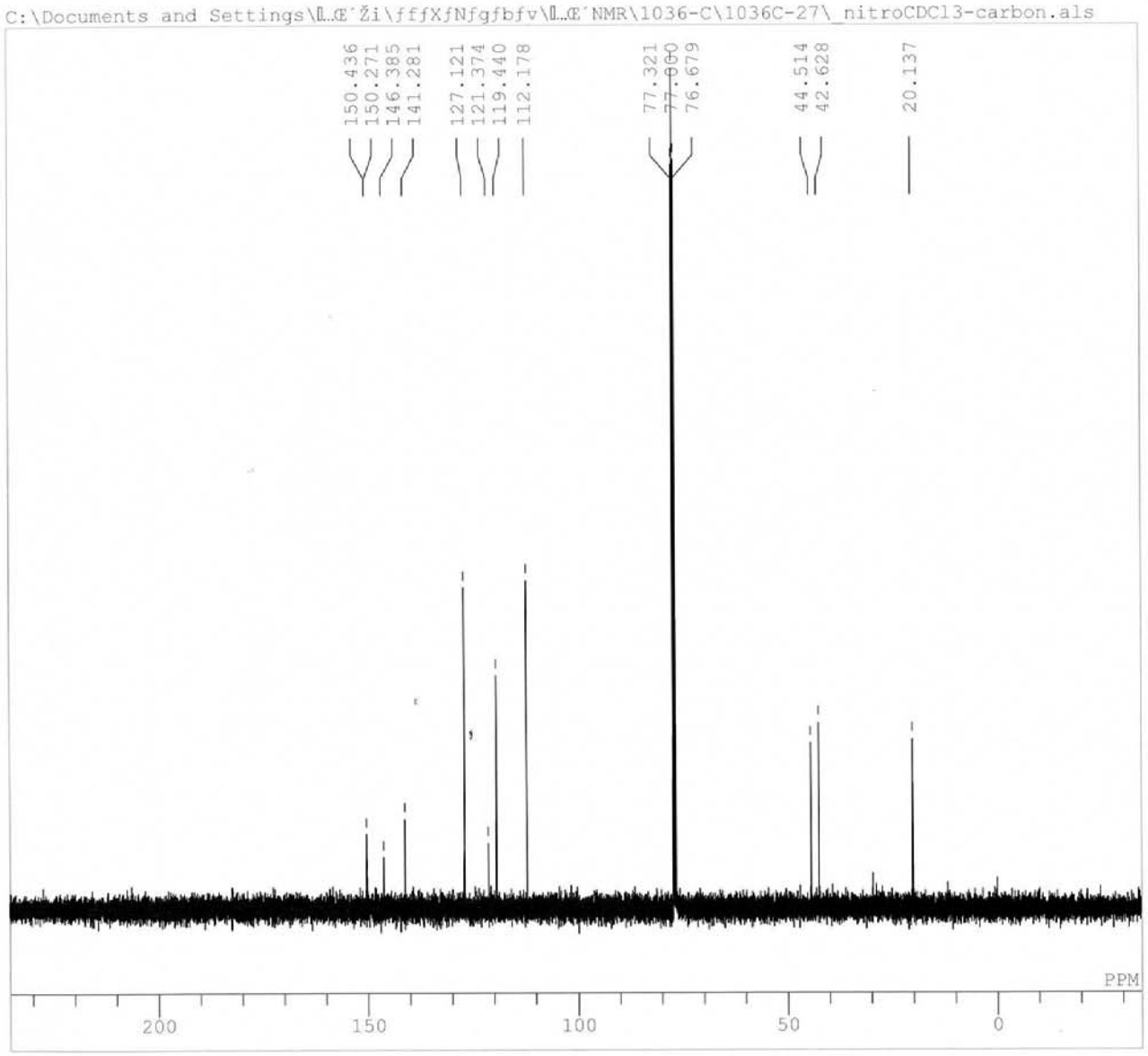
3f



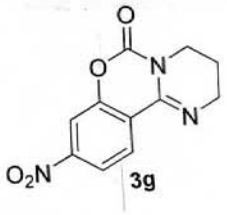
DFILE _nitroCDCl3.als
COMNT
DATIM Thu Feb 26 00:41:00 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 8
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 25



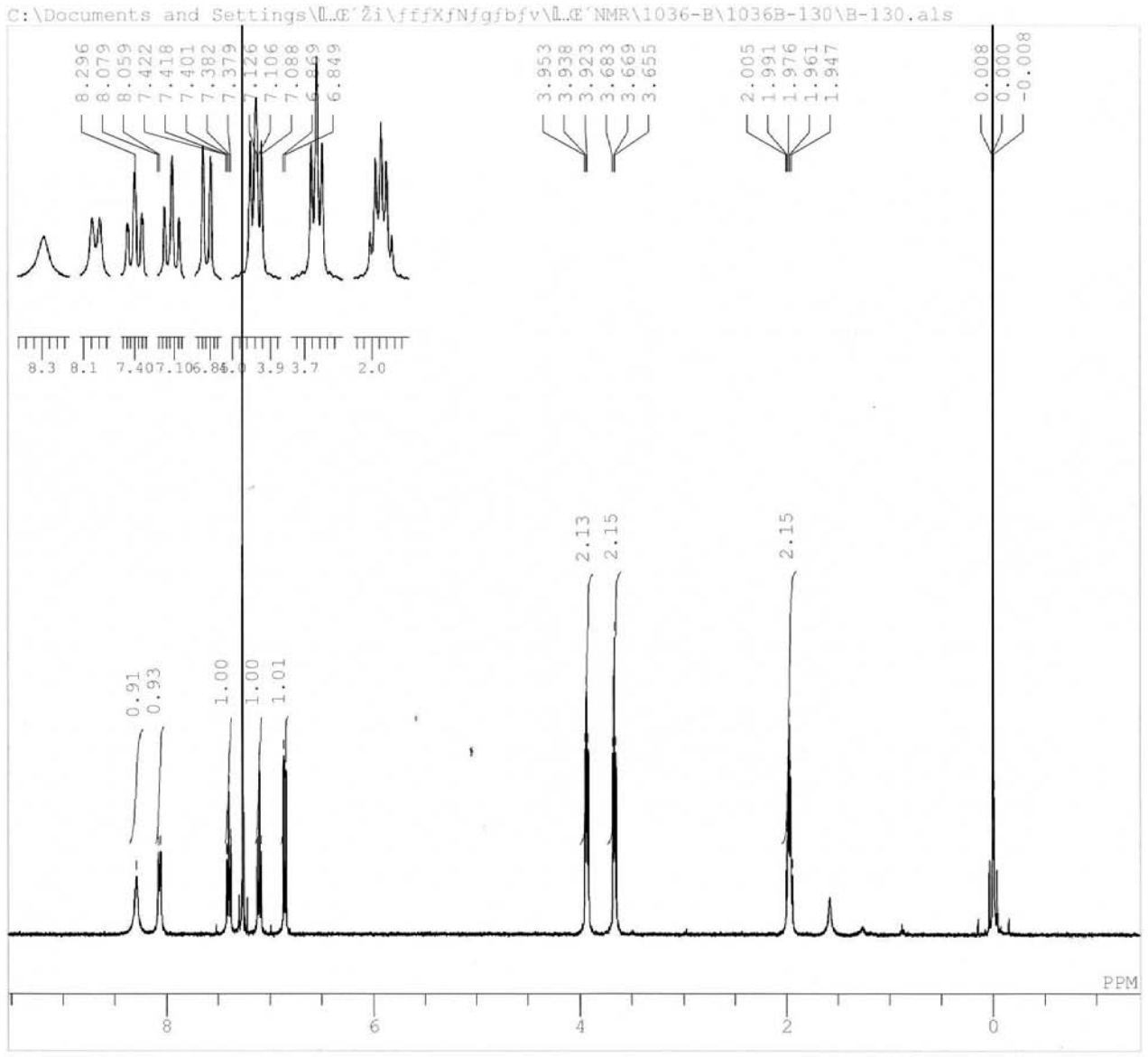
3g



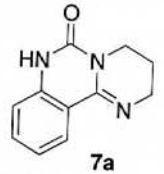

```
DFILE   _nitroCDCl3-carbon.als
COMNT
DATIM   Thu Feb 26 00:30:43 2009
OBNUC   13C
EXMOD   BCM
OBFRQ         100.40 MHz
OBSET         125.00 KHz
OBFIN       10500.00 Hz
POINT         32768
FREQU       27118.64 Hz
SCANS          1241
ACQTM          1.2083 sec
PD             1.7920 sec
PW1            5.10 usec
IRNUC   1H
CTEMP          20.3 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.12 Hz
RGAIN            25
```



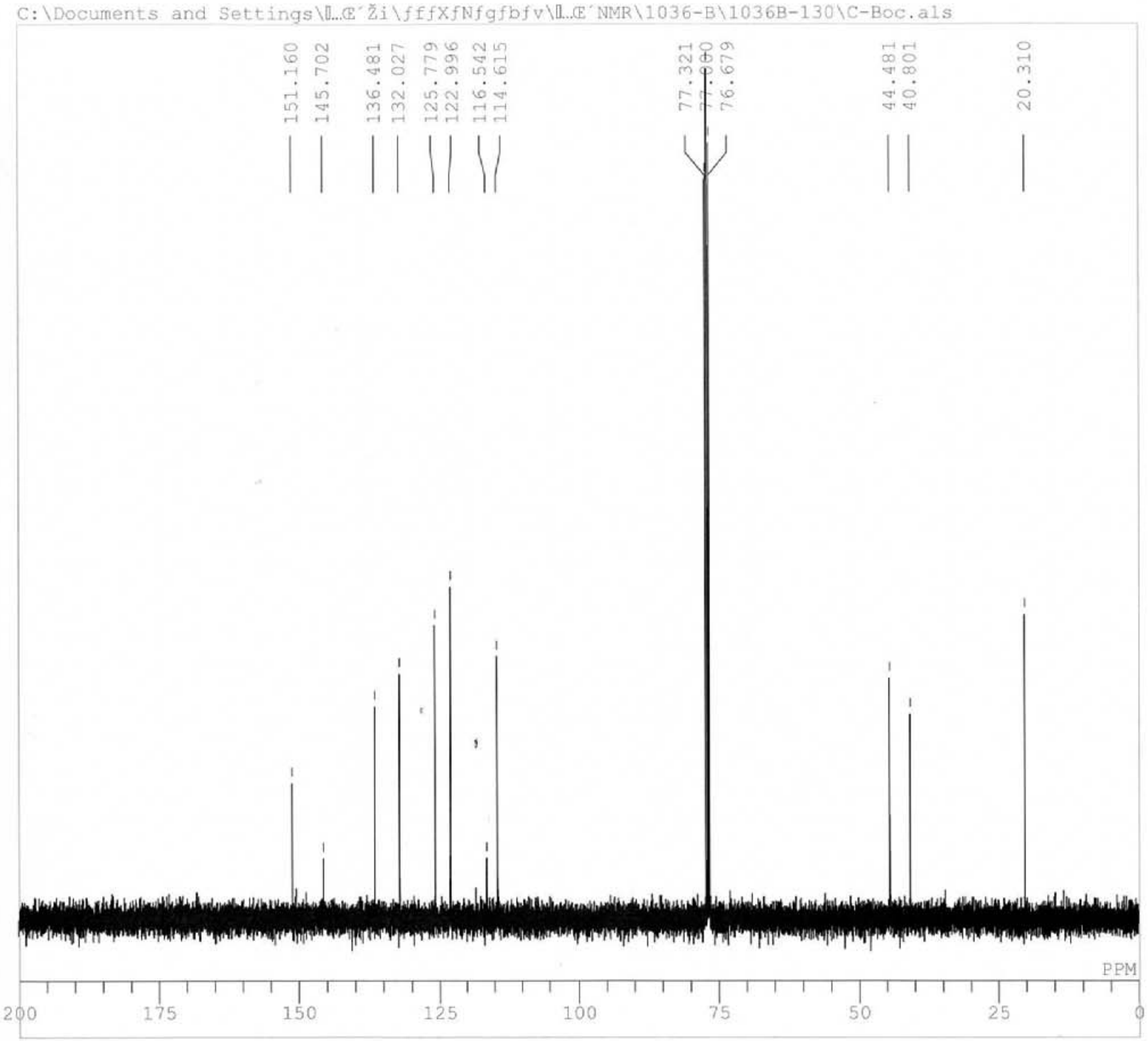
3g



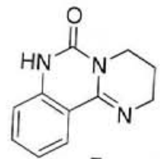
DFILE B-130.als
COMNT
DATIM Thu Jan 08 17:05:31 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 16
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23



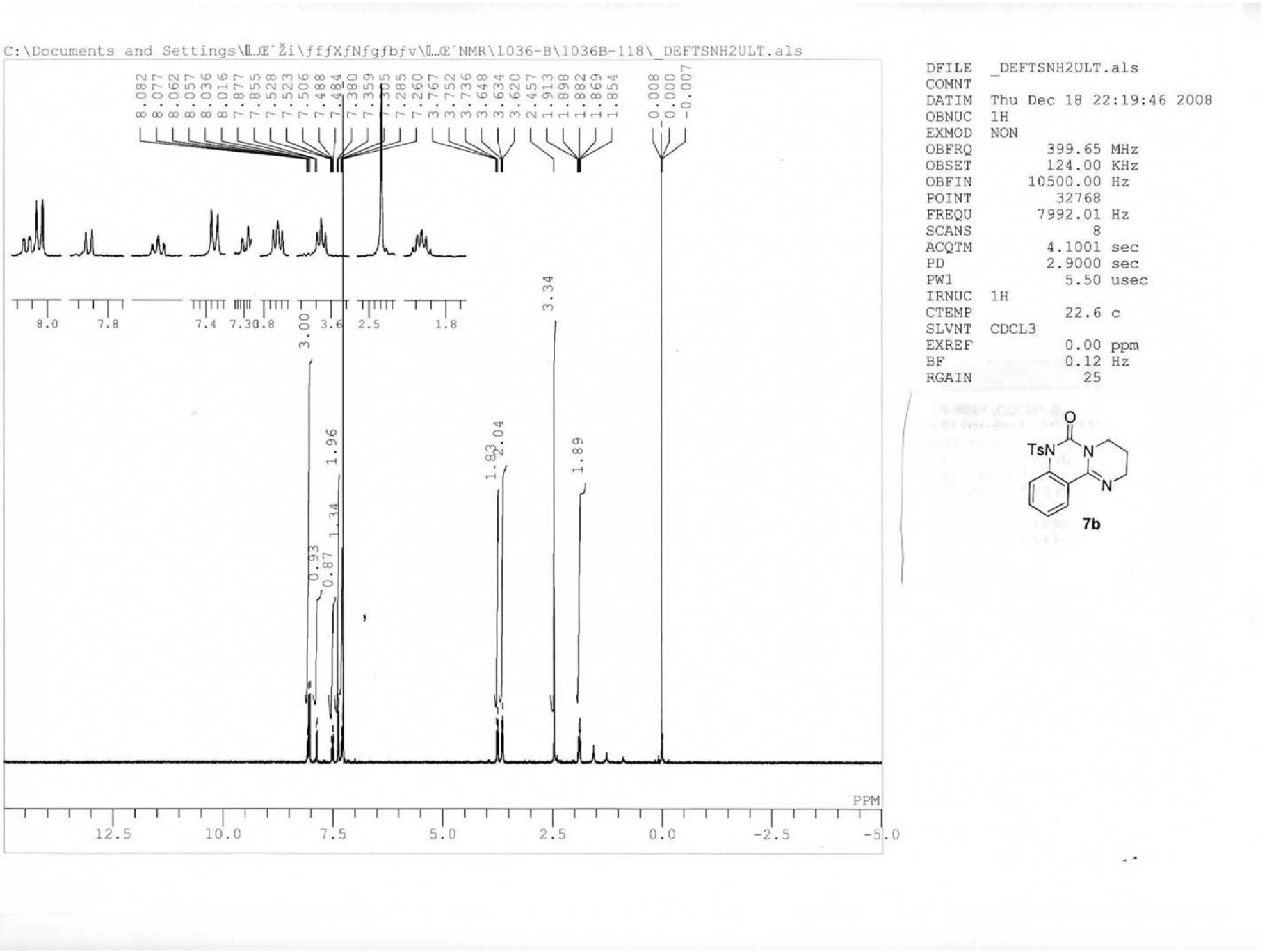
7a



DFILE	C-Boc.als
COMNT	
DATIM	Sat Feb 28 19:06:34 2009
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	194
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	5.10 usec
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25

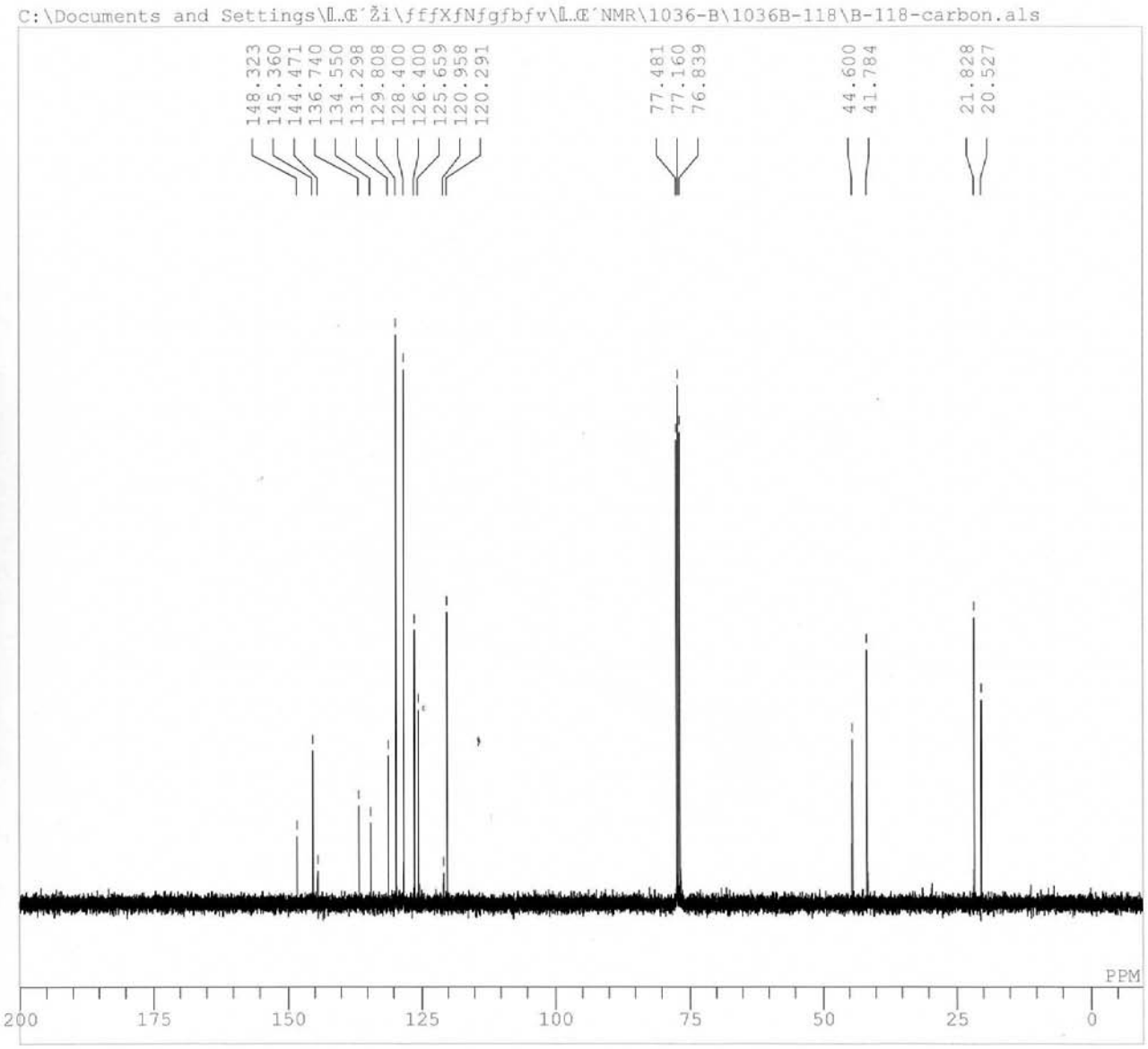


7a




```
DFILE   _DEFTSNH2ULT.als
COMNT
DATIM   Thu Dec 18 22:19:46 2008
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.00 Hz
POINT         32768
FREQU        7992.01 Hz
SCANS             8
ACQTM         4.1001 sec
PD            2.9000 sec
PW1             5.50 usec
IRNUC   1H
CTEMP            22.6 c
SLVNT   CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              25
```


7b

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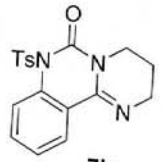
DFILE   B-118-carbon.als
COMNT
DATIM   Tue Feb 10 22:25:10 2009
OBNUC   13C
EXMOD   BCM
OBFRQ         100.40 MHz
OBSET         125.00 KHz
OBFIN       10500.00 Hz
POINT         32768
FREQU       27118.64 Hz
SCANS           197
ACQTM         1.2083 sec
PD            1.7920 sec
PW1             5.10 usec
IRNUC   1H
CTEMP           20.8 c
SLVNT   CDCL3
EXREF           77.16 ppm
BF              0.12 Hz
RGAIN             25
```



7b