Supporting Information

Enantioselective Synthesis of SM-130686 Based on the Development of Asymmetric Cu(I)F-Catalysis to Access 2-Oxindoles Containing a Tetrasubstituted Carbon

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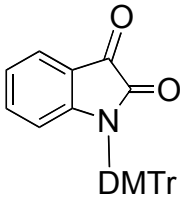
1. General: NMR spectra were recorded on a JEOL JNM-LA500 or ECX500 spectrometer, operating at 500 MHz for ^{1}H-NMR, 125.65 MHz for ^{13}C-NMR, and 202.35 MHz for ^{31}P-NMR. Chemical shifts were reported in ppm on the δ scale relative to TMS (δ = 0) for ^{1}H-NMR, to residual $CHCl_3$ (δ = 77.0) for ^{13}C-NMR as internal references, or to H_3PO_4 (δ = 0) for ^{31}P-NMR as an external standard, unless otherwise mentioned. Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. ESI mass spectra were measured on Waters-ZQ4000. FAB mass spectra were measured on a JEOL JMS-BU20 GCmate or a JEOL JMS-700V. Optical rotations were measured on a JASCO P-1010 polarimeter. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM) or neutral silica gel KANTO CHEMICAL 60N (spherical, neutral, 40–100 μm). The enantiomeric excess (ee) was determined by HPLC analysis. HPLC analysis was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm; mobile phase, hexane/2-propanol. In general, reactions were carried out in dry solvents under an argon atmosphere, unless noted otherwise. Normal glassware can be used to conduct the reactions in this manuscript. CuF•3PPh_3•2EtOH and CuF•3P(C_6H_4–*p*–F)$_3$•2EtOH were synthesized following the reported procedure.[1]

2. Synthesis and Characterization of *N*-DMTr–Protected Isatin Substrates

1–(4,4'–Dimethoxytrityl)–isatin (7a): NaH (660 mg, 16.5 mmol; 60 wt% in mineral oil) was added portionwise to a solution of isatin (2.2 g, 15.0 mmol) in DMF (40 mL) at 0 °C, and the resulting mixture was stirred for 20 min at room temperature. 4,4'–Dimethoxytrityl chloride (6.1 g, 18 mmol) was added, and the mixture was stirred for 4 h at 30 °C. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude mixture was purified by silica gel chlomatography (Hexane/AcOEt = 4/1), affording **7a** as yellow solid (82% yield).



Mp: 145 °C; ^{1}H NMR ($CDCl_3$) δ: 3.74 (s, 6H), 6.37 (d, *J* = 8.3 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 4H), 6.96 (dd, *J* = 7.6 Hz, 7.4 Hz, 1H), 7.15–7.25 (m, 4H), 7.32 (d, *J* = 8.9 Hz, 4H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 7.6 Hz,

1H); ^{13}C NMR ($CDCl_3$) δ: 55.1, 74.7, 113.1, 117.7, 118.9, 123.1, 124.5, 127.0, 127.8, 128.9, 130.5, 133.2, 136.6, 141.8, 152.4, 158.5, 159.2, 183.0; IR (neat): 1739, 1608, 1509, 1462, 1307, 1254, 1181; LRMS: 472.3 $(M+Na)^+$; HRMS Calcd for $C_{29}H_{24}NO_4^+$ 450.1700. Found 450.1699.

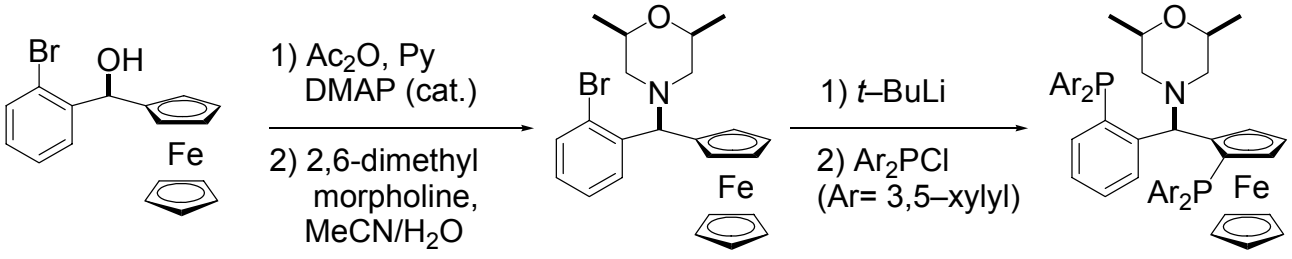
1–(4,4'–Dimethoxytrityl)–5–chloroisatin (7b): This was synthesized from 5-chloroisatin. Orange solid, 85% yield. Mp: 100 °C; ^{1}H NMR ($CDCl_3$) δ:3.74 (s, 6H), 6.32 (d, J = 14.7 Hz, 1H), 6.77 (d, J = 10.3 Hz, 4H), 7.13 (d, J = 7.7 Hz, 1H), 7.19-7.35 (m, 9H), 7.49 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 53.8, 73.6, 111.9, 117.6, 118.4, 122.8, 125.8, 126.5, 127.5, 127.8, 129.1, 131.5, 134.7, 140.0, 149.4, 157.2, 180.7; IR (neat): 1741, 1606, 1508, 1254, 1180, 1034; LRMS: 506.2 $(M+Na)^+$; HRMS Calcd for $C_{29}H_{23}ClNO_4^+$ 484.1310. Found 484.1320.

1–(4,4'–Dimethoxytrityl)–5–methoxyisatin (7c): This was synthesized from 5-methoxyisatin. Red Solid, 80% yield. Mp: 113 °C; ^{1}H NMR ($CDCl_3$) δ: 3.69 (s, 3H), 3.73 (s, 6H), 6.30 (d, J = 8.9 Hz, 1H), 6.78 (d, J = 9.2 Hz, 5H), 7.08 (d, J = 2.8 Hz, 1H), 7.21–7.25 (m, 3H), 7.34 (d, J = 8.9 Hz, 4H), 7.39 (d, J = 8.3 Hz 2H); ^{13}C NMR ($CDCl_3$) δ: 14.0, 20.9, 55.0, 55.6, 60.2, 74.5, 107.7, 112.8, 118.6, 119.3, 123.5, 126.9, 127.4, 128.8, 130.4, 133.2, 141.8, 146.2, 155.5, 158.4, 159.2, 170.9, 183.2; IR (neat): 1738, 1608, 1508, 1488, 1295, 1253, 1180; LRMS: 502.3$(M+Na)^+$; HRMS Calcd for $C_{30}H_{26}NO_5^+$ 480.1805. Found 480.1832.

1–(4,4'–Dimethoxytrityl)–5–methylisatin (7d): This was synthesized from 5-methylisatin. Yellow solid, 88% yield. Mp: 150 °C; ^{1}H NMR ($CDCl_3$) δ: 2.15 (s, 3H), 3.74 (s, 6H), 6.26 (d, J = 8.2 Hz, 1H), 6.77 (d, J = 9.2 Hz, 4H), 6.99 (dd, J = 8.5 Hz, 7.4 Hz, 1H), 7.18–7.26 (m, 3H), 7.32 (d, J = 9.2 Hz, 4H), 7.37–7.39 (m, 3H); ^{13}C NMR ($CDCl_3$) δ: 18.9, 53.7, 73.2, 111.7, 116.1, 117.6, 123.3, 125.6, 126.4, 127.5, 129.1, 131.5, 132.0, 136.0, 140.5, 148.9, 157.1, 158.0, 181.9; IR (neat): 1736, 1622, 1509, 1487, 1303, 1254, 1181; LRMS: 486.3 $(M+Na)^+$; HRMS Calcd for $C_{30}H_{26}NO_4^+$ 464.1856. Found 464.1878.

1–(4,4'–Dimethoxytrityl)–6–chloroisatin (7e): This was synthesized from 6-chloroisatin. Yellow solid, 88% yield. Mp: 101 °C; ^{1}H NMR ($CDCl_3$) δ: 3.74 (s, 6H), 6.36 (s, 1H), 6.83 (d, J = 8.9 Hz, 4H), 6.98 (d, J = 8.3 Hz, 1H), 7.22-7.39 (m, 9H), 7.51 (d, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.1, 75.0, 113.0, 113.2, 117.1, 118.0, 123.5, 125.4, 127.2, 127.9, 128.7, 129.0, 130.4, 132.8, 141.3, 143.0, 153.2, 158.6, 159.1, 181.5; IR (neat): 1743, 1607, 1508, 1254, 1180; LRMS: 506.2 $(M+Na)^+$; HRMS Calcd for $C_{29}H_{23}ClNO_4^+$ 484.1310. Found 484.1317.

3. Synthesis of Chiral Ligand 6



S1 (>99% ee) **S3** **6**

(*R*)–(α–(1–2,6–dimethylmorpholinyl)–*o*–bromophenylmethyl)ferrocene (S3): Prepared following the procedure reported by Knochel.[2] To a mixture of pyridine (1.26 mL), alcohol **S1** (0.9 g, 2.43 mmol, 1.0 eq.), and DMAP (cat.), acetic anhydride (0.54 mL, 5.71 mmol, 2.5 eq.) was added at room temperature, and the mixture was stirred for 30 min. Volatiles were evaporated, then residue was dissolved in an acetonitrile (30

mL)-water (5 mL) mixed solvent. To the solution, 2,6-dimethylmorpholine (1.1 mL, 12.1 mmol, 5.0 eq.) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was then concentrated and extracted with diethyl ether. After washing with water and brine, the organic layer was dried over Na_2SO_4. Extract was filtered off and evaporated, and the crude product was purified by short pad silica gel chromatography (eluent: AcOEt/hexane=1/10 to 1/5) to give the amine **S3** as orange crystals in ca. 88% yield (not completely pure). ^{1}H NMR ($CDCl_3$) δ**:** 0.94 (s, 3H), 0.97 (s, 3H), 1.58 (m, 3H), 2.35 (d, *J* = 11.0 Hz, 1H), 2.43 (d, *J* = 10.7 Hz, 1H), 3.43-3.48 (m, 2H), 4.46 (s, 5H), 4.05-4.08 (m, 3H), 4.15 (s, 1H), 7.09 (m, 1H), 7.31 (m, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H).

1-(S_{FC})-bis(3,5-xylyl)phsphinyl-2-[(*R*)-(α-(1-2,6-dimethyl morpholin-yl)-*o*-bis(3,5-xylyl phosphinylphenylmethyl)ferrocene (6)

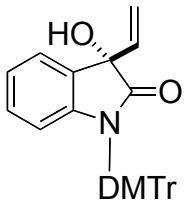
The amine **S3** (2.20 g, 4.7 mmol, 1.0 eq.) was dissolved in anhydrous diethyl ether (20 mL) under argon and cooled to –78 °C. Then, *t*-BuLi (1.59 N in pentane, 11.0 mL, 17.5 mmol, 3.7 eq.) was added dropwise. The mixture was warmed to room temperature and stirred for 1 h. $ClPAr_2$ (3.46 g, 12.5 mmol, 2.5 eq.) was added dropwise at –78 °C, and the mixture was stirred at room temperature overnight. After the addition of NH_4Cl aqueous solution, products were extracted with diethyl ether. The organic layer was washed with brine and dried over Na_2SO_4. Extract was filtered off and evaporated, and the crude mixture was purified by silica gel column chromatography twice (eluent: AcOEt/hexane=1/20 to 1/10) to give ligand **6** as foamy orange solid in 64% yield (1.21 g). Mp: 120 °C; ^{1}H NMR ($CDCl_3$) δ**:** 0.59 (d, *J* = 5.8 Hz, 3H), 0.81 (d, *J* = 6.1 Hz, 3H), 1.29 (br t, *J* = 10.1 Hz, 1H), 1.43 (br t, *J* = 10.1 Hz, 1H), 2.03 (s, 6H), 2.15 (s, 12H), 2.23 (s, 6H), 2.46 (d, *J* = 9.5 Hz, 1H), 2.65 (m, 2H), 3.31 (br, 1H), 3.64 (s, 5H), 3.88 (s, 1H), 4.24 (s, 1H), 4.48 (s, 1H), 5.71 (d, *J* = 9.2 Hz, 1H), 6.54 (d, *J* = 6.7 Hz, 2H), 6.60 (s, 1H), 6.77–7.17 (m, 12H), 7.78 (s, 1H); ^{13}C NMR ($CDCl_3$) δ**:** 18.7, 19.1, 21.3, 57.0, 58.4, 65.1, 68.1, 70.0, 71.2, 71.4, 71.8, 73.9 (d, *J* = 17 Hz), 98.1 (d, *J* = 23 Hz), 126.5, 127.9, 129.1, 129.9, 130.2, 130.3, 130.4, 130.9, 131.4, 131.5, 131.8, 132.0, 134.6, 136.5, 136.5, 136.9, 137.0, 137.4, 137.4, 137.5, 138.6, 138.8, 138.8, 139.1, 139.1 (multiple peaks due to coupling with ^{31}P); ^{31}P NMR ($CDCl_3$) δ: –28.0, –22.1; IR (neat): 3446, 2970, 1457, 1125, 1085; LRMS: 870.4 $(M+Na)^+$; HRMS Calcd for $C_{55}H_{62}FeNOP_2^+$ 870.3651. Found 870.3632, $[\alpha]^{26}_D$ +194.0 (c = 0.83, $CHCl_3$).

4. Catalytic Enantioselective Intermolecular Alkenylation and Arylation of Isatins

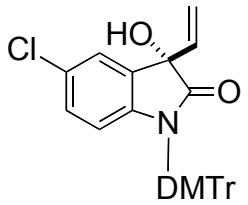
A typical procedure (Table 2, entry 1): A solution of CuF•3P(C_6H_4–*p*–F)$_3$•2EtOH (0.010 mmol), ligand **6** (0.014 mmol), ZnF_2 (0.03 mmol), and protected isatin **7a** (0.2 mmol) in toluene (0.24 mL) was stirred at rt for 5 min. To this solution, trimethoxyvinylsilane (**9a**: 0.4 mmol) was added. After 24 h, TBAF (1 M in THF, 0.3 mL) was added to quench the reaction, and the mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude mixture was purified by silica gel chromatography (neutral spherical SiO_2, eluent: AcOEt/hexane), and pure **8aa** was obtained.

Characterization of Alkenylated and Arylated Products 8

1–(4,4'–Dimethoxytrityl)–3-ethenyl-3-hydroxyoxindole (8aa): amorphous; ^{1}H NMR ($CDCl_3$) δ: 2.90 (br, 1H), 3.66 (s, 6H), 5.26 (d, *J* = 10.4 Hz, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 6.05 (dd, *J* = 10.4, 17.1 Hz, 1H), 6.22 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 4H), 6.85 (m, 2H), 7.10–7.28 (m, 10H); ^{13}C NMR ($CDCl_3$) δ: 55.1, 73.6, 77.1, 112.9, 113.0, 116.3, 116.5, 122.6, 123.9, 126.7, 127.6, 128.2, 128.8, 129.3, 130.5, 133.8, 134.0, 137.2, 142.4, 143.2, 158.2, 178.8; IR (neat): ν 3420, 1732, 1608, 1509, 1464, 1306, 1254, 1181, 1033 cm^{-1}; LRMS m/z: 500.3 $(M+Na)^+$; HRMS Calcd for $C_{31}H_{28}NO_4^+$ 478.2013. Found 478.2007; HPLC: DAICEL CHIRALPAK AD-H, hexane/2-propanol = 9/1, detection at 254 nm, 1.0 mL/min, t_R 19.0 min (minor), 37.0 min (major); $[\alpha]^{26}_D$ +45.6 (c = 2.9, CH_2Cl_2) (90% ee).

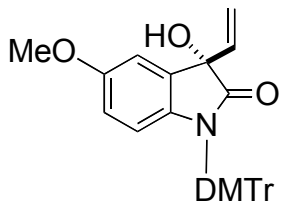


1–(4,4'–Dimethoxytrityl)–5–chloro–3-ethenyl-3-hydroxyoxindole (8ba): amorphous; ^{1}H NMR ($CDCl_3$)



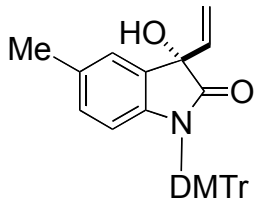
δ: 2.90 (s, 1H), 3.69 (s, 6H), 5.31 (d, *J* = 10.4 Hz, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.95 (dd, *J* = 10.4 Hz, 17.1 Hz, 1H), 6.15 (d, *J* = 8.6 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 4H), 6.81 (dd, *J* = 2.2, 8.9 Hz, 1H), 7.11–7.25 (m, 10H); ^{13}C NMR ($CDCl_3$) δ: 55.1, 73.8, 113.1, 113.1, 117.0, 117.3, 124.3, 126.9, 127.8, 128.2, 128.3, 128.8, 130.4, 131.0, 133.4, 136.7, 141.7, 142.1, 158.4, 178.3;; IR (neat): 3425, 1733, 1607, 1508, 1470, 1254, 1180, 1033 cm^{-1}; LRMS m/z: 534.2 $(M+Na)^+$; HRMS Calcd for $C_{31}H_{27}ClNO_4^+$ 512.1623. Found 512.1642; HPLC: DAICEL CHIRALPAK AD-H, hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 14.8 min (minor), 24.0 min (major); $[\alpha]^{26}_D$ +54.8 (c = 1.9, CH_2Cl_2) (86% ee).

1–(4,4'–Dimethoxytrityl)–5–methoxy–3-ethenyl-3-hydroxyoxindole (8ca): amorphous; ^{1}H NMR



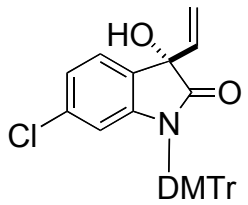
($CDCl_3$) δ: 3.62 (s, 3H), 3.67 (s, 6H), 5.27 (d, *J* = 10.4 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.98 (dd, *J* = 10.4 Hz, 17.1 Hz, 1H), 6.11 (d, *J* = 8.9 Hz, 1H), 6.38 (dd, *J* = 2.8, 8.9 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 4H), 6.79 (d, *J* = 2.8 Hz, 1H), 7.09–7.18 (m, 3H), 7.22 (m, 4H), 7.27 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 55.1, 55.5, 73.5, 77.4, 109.8, 112.9, 113.0, 113.7, 116.5, 117.1, 126.7, 127.6, 128.9, 130.5, 133.9, 134.1, 136.2, 137.3, 142.5, 155.6, 158.2, 178.6; LRMS m/z: 530.3 $(M+Na)^+$; HRMS Calcd for $C_{32}H_{30}NO_5^+$ 508.2118. Found 508.2121; IR (neat): 3416, 1727, 1607, 1508, 1254, 1181, 1033 cm^{-1}; HPLC: DAICEL CHIRALPAK AD-H, hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 45.5 min (minor), 70.2 min (major); $[\alpha]^{27}_D$ +42.1 (c = 3.1, CH_2Cl_2) (81% ee).

1–(4,4'–Dimethoxytrityl)–5–methyl–3-ethenyl-3-hydroxyoxindole (8da): amorphous; ^{1}H NMR



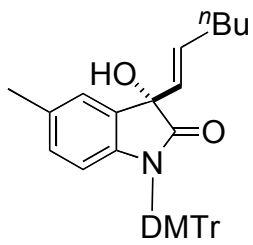
($CDCl_3$) δ: 2.14 (s, 3H), 2.87 (br, 1H), 3.67 (s, 6H), 5.27 (d, *J* = 10.3 Hz, 1H), 5.35 (d, *J* = 17.2 Hz, 1H), 5.99 (dd, *J* = 10.3, 17.2 Hz, 1H), 6.10 (d, *J* = 8.6 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 9.2 Hz, 4H), 7.02 (br d, *J* = 2.3 Hz, 1H), 7.10 (m, 1H), 7.16 (t like, *J* = 7.2 Hz, 2H), 7.22 (m, 4H), 7.27 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 20.7, 55.1, 73.5, 77.2, 112.9, 112.9, 116.1, 116.4, 124.5, 126.7, 127.6, 128.7, 128.9, 129.2, 130.5, 132.3, 133.9, 134.1, 137.3, 140.7, 142.5, 158.2, 178.7; IR (neat): 3426, 1731, 1607, 1508, 1253, 1180, 1033 cm^{-1}; LRMS m/z: 514.3 $(M+Na)^+$; HRMS Calcd for $C_{32}H_{30}NO_4^+$ 492.2169. Found 492.2151; HPLC: DAICEL CHIRALPAK AD-H, hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 29.0 min (minor), 55.9 min (major); $[\alpha]^{26}_D$ +43.0 (c = 1.3, CH_2Cl_2) (84% ee).

1–(4,4'–Dimethoxytrityl)–6–chloro–3-ethenyl-3-hydroxyoxindole (8ea): amorphous; ^{1}H NMR ($CDCl_3$)



δ: 2.89 (s, 1H), 3.70 (s, 4H), 5.29 (d, *J* = 10.4 Hz, 1H), 5.32 (d, *J* = 17.1 Hz, 1H), 5.95 (dd, *J* = 10.4, 17.1 Hz, 1H), 6.18 (d, J = 1.6 Hz, 1H), 6.72 (dd, *J* = 1.8, 7.4 Hz, 4H), 6.88 (dd, *J* = 1.8, 8.0 Hz, 1H), 7.11–7.25 (m, 10H); ^{13}C NMR ($CDCl_3$) δ: 55.2, 73.9, 76.7, 113.1, 113.2, 116.6, 116.9, 122.7, 124.8, 127.0, 127.7, 127.8, 128.8, 130.4, 133.3, 133.6, 134.0, 136.8, 142.0, 144.4, 158.4, 178.6; IR (neat): 3437, 1737, 1608, 1509, 1254, 1180 cm^{-1}; LRMS m/z: 534.2 $(M+Na)^+$; HRMS Calcd for $C_{31}H_{27}ClNO_4^+$ 512.1623. Found 512,1613; HPLC: DAICEL CHIRALPAK AD-H, hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 11.3 min (minor), 19.6 min (major); $[\alpha]^{26}_D$ +63.2 (c = 1.6, CH_2Cl_2) (88% ee).

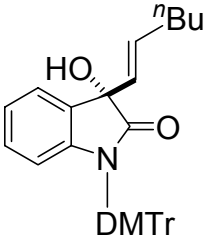
1–(4,4'–Dimethoxytrityl)–5–methyl–3-hexenyl-3-hydroxyoxindole (8db): amorphous; ^{1}H NMR



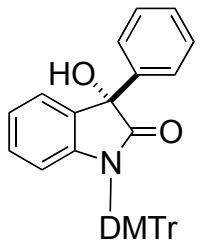
($CDCl_3$) δ: 0.83 (t, *J* = 7.0 Hz, 3H), 1.23–1.34 (m, 4H), 2.04 (q like, *J* = 7.0 Hz, 2H), 2.15 (s, 3H), 3.68 (s, 6H), 5.62–5.72 (m, 2H), 6.07 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 8.9 Hz, 4H), 7.03 (s, 1H), 7.09 (m, 1H), 7.15 (m, 2H), 7.22 (m, 2H), 7.26 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 13.9, 20.8, 22.1, 31.1, 31.9, 55.1, 73.3, 76.6, 112.9, 112.9, 115.9, 124.4, 126.6, 127.6, 128.5, 128.9, 129.5, 129.9, 130.5, 132.0, 132.1, 133.5, 134.0, 134.2, 140.6, 142.6, 158.2, 179.2; IR (neat): 3421, 2929, 1731, 1608, 1509, 1486, 1300, 1253, 1181, 1035 cm^{-1}: LRMS m/z: 570.3 $(M+Na)^+$; HRMS Calcd for $C_{36}H_{38}NO_4^+$ 148.2795. Found 528.2814; HPLC: DAICEL CHIRALCEL OD-H,

hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 5.5 min (minor), 8.9 min (major); $[\alpha]^{27}_D$ +48.3 (c = 2.3, CH_2Cl_2) (80% ee).

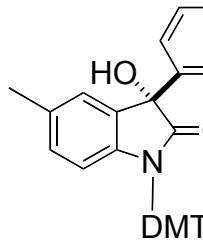
1–(4,4'–Dimethoxytrityl)–3-hexenyl-3-hydroxyoxindole (8ab): oil; ^{1}H NMR ($CDCl_3$) δ: 0.83 (t, *J* = 7.3 Hz, 3H), 1.23–1.34 (m, 4H), 2.05 (q like, *J* = 7.3 Hz, 2H), 3.70 (s, 6H), 5.66–5.69 (m, 2H), 6.21 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 4H), 6.84 (dt, *J* = 1.2, 7.7 Hz, 1H), 6.90 (t, *J* = 7.0 Hz, 1H), 7.12 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.23 (m, 5H), 7.27 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 13.9, 22.1, 31.1, 31.9, 55.1, 73.4, 76.6, 112.9, 113.0, 116.2, 122.5, 123.8, 126.7, 127.6, 128.0, 128.9, 128.9, 129.4, 130.5, 133.8, 133.9, 134.1, 142.6, 143.1, 158.2, 161.3, 179.3; IR (neat): 1732, 1508, 1254, 1181 cm^{-1}; LRMS 556.4 $(M+Na)^+$; HRMS Calcd for $C_{35}H_{36}NO_4^+$ 534.2639. Found 534.2614; HPLC DAICEL CHIRALCEL OD-H, hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 8.2 min (minor), 11.7 min (major); $[\alpha]^{26}_D$ +29.4 (c = 0.56, CH_2Cl_2) (90% ee).



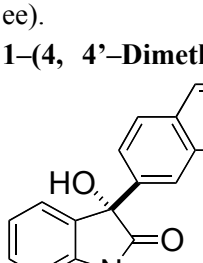
(3*S*)–1–(4,4'–Dimethoxytrityl)–3-phenyl-3-hydroxyoxindole (8ac): colorless oil; ^{1}H NMR ($CDCl_3$) δ: 3.12 (br, 1H), 3.69 (s, 6H), 6.30 (m, 1H), 6.69 (m, 4H), 6.89 (m, 2H), 7.10–7.33 (m, 13 H), 7.38 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 55.1, 73.8, 77.7, 113.0, 113.0, 116.4, 122.9, 124.3, 125.4, 126.7, 127.7, 128.3, 128.7, 128.8, 130.4, 131.7, 133.9, 134.1, 140.6, 142.5, 143.5, 158.2, 179.4; IR (neat): 3437, 1732, 1607, 1509, 1463, 1254, 1181, 1033 cm^{-1}; LRMS m/z 550.3 $(M+Na)^+$; HRMS: Calcd for $C_{35}H_{30}NO_4^+$ 528.2169. Found 528.2169; HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 11.2 min (minor), 19.7 min (major); $[\alpha]^{28}_D$ +11.7 (c = 0.48, CH_2Cl_2) (95% ee).



1–(4, 4'–Dimethoxytrityl)–5–methyl–3-phenyl-3-hydroxyoxindole (8dc): colorless oil; ^{1}H NMR ($CDCl_3$) δ: 2.13 (s, 3H), 3.13 (s, 1H), 3.68 (s, 6H), 6.18 (d, *J* = 8.6 Hz, 1H), 6.69 (m, 5H), 6.99 (s, 1H), 7.10 (m, 1H), 7.15 (t like, *J* = 7.5 Hz, 2H), 7.24 (m, 7H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 20.8, 55.1, 55.1, 73.8, 77.7, 113.0, 113.0, 116.2, 124.9, 125.3, 126.7, 127.7, 128.2, 128.7, 128.8, 128.8, 130.4, 131.7, 132.6, 134.0, 134.2, 140.8, 141.0, 142.6, 158.2, 179.3; IR (neat): 3416, 1732, 1607, 1508, 1254, 1182, 1034 cm^{-1}; LRMS m/z 564.4 $(M+Na)^+$; HRMS: Calcd for $C_{35}H_{32}NO_4^+$ 542.2326. Found 542.2313; HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 9.4 min (minor), 16.1 min (major); $[\alpha]^{28}_D$ +21.7 (c = 1.4, CH_2Cl_2) (96% ee).



1–(4, 4'–Dimethoxytrityl)–5–methyl–3 -naphtyl-3-hydroxyoxindole (8ad): amorphous; ^{1}H NMR ($CDCl_3$) δ: 3.34 (s, 1H), 3.65 (s, 6H), 6.34 (d, *J* = 9.2 Hz, 1H), 6.68 (m, 4H), 6.90 (m, 2H), 7.08–7.15 (m, 3H), 7.12 (m, 1H), 7.24–7.29 (m, 6H), 7.40 (m, 3H), 7.74 (m, 3H), 7.84 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.1, 73.9, 77.8, 113.0, 113.0, 116.4, 122.9, 123.2, 124.4, 124.5, 126.3, 126.3, 126.7, 127.6, 127.7, 128.3, 128.4, 128.6, 128.8, 130.4, 131.6, 133.0, 133.1, 133.9, 134.0, 137.9, 142.5, 143.5, 158.2, 179.2; IR (neat): 3416, 1732, 1607, 1508, 1463, 1254, 1181, 1033 cm^{-1}; LRMS m/z 600.5 $(M+Na)^+$; HRMS: Calcd for $C_{39}H_{32}NO_4^+$ 578.2326. Found 578.2306; HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol 9/1, detection at 254 nm, 1.0 mL/min, t_R 15.0 min (minor), 21.2 min (major); $[\alpha]^{28}_D$ –35.6 (c = 0.9, CH_2Cl_2) (97% ee).

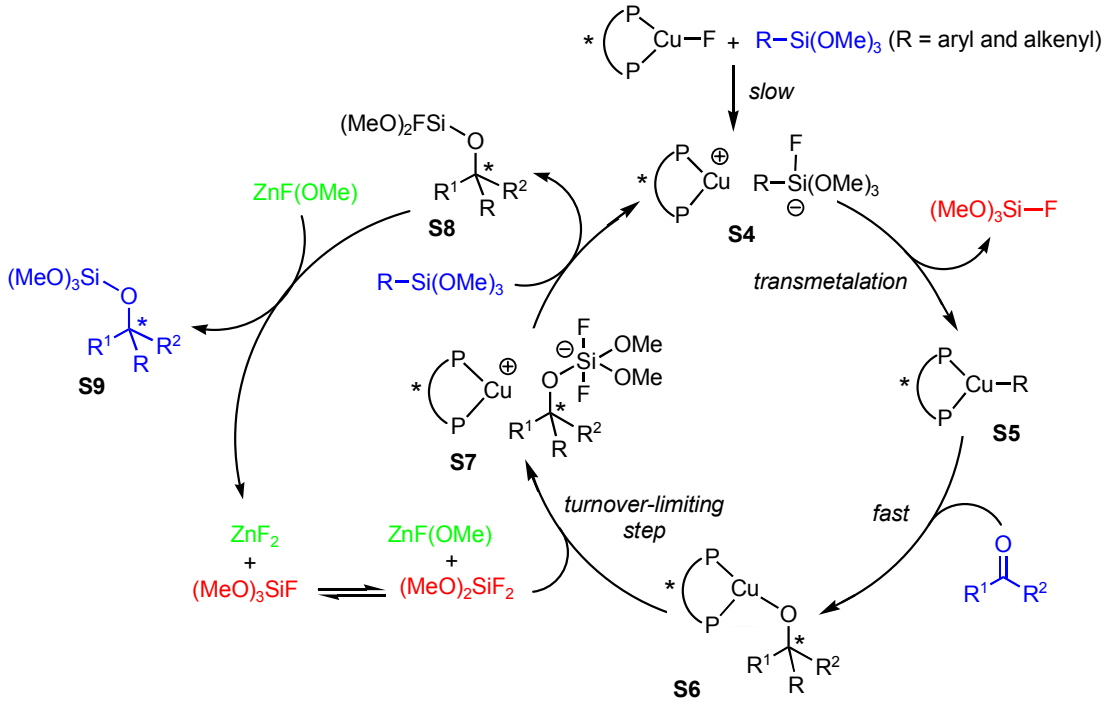


1–(4,4'–Dimethoxytrityl)–3-(2–chlorophenyl)-3-hydroxyoxindole (8ae): amorphous; ^{1}H NMR ($CDCl_3$) δ: 3.33 (s, 1H), 3.65 (s, 6H), 6.34 (m, 1H), 6.67 (m, 4H), 6.89 (m, 2H), 7.08–7.15 (m, 3H), 7.20 (m, 1H), 7.24–7.29 (m, 4H), 7.39 (m, 3H), 7.74 (m, 3H), 7.84 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.1, 73.9, 77.2, 77.8, 113.0, 113.1, 116.4, 122.9, 123.2, 124.4, 124.6, 126.3, 126.3, 126.7, 127.6, 127.7, 128.3, 128.4, 128.6, 128.8, 130.4, 131.7, 133.1, 133.1, 133.9, 134.1, 137.9, 142.5, 143.5, 158.2, 179.2IR (neat): 1732, 1607, 1508, 1463, 1303,

1254, 1181, 1110, 1033 cm^{-1}; ; LRMS m/z 584.3 $(M+Na)^+$; HRMS: Calcd for $C_{35}H_{29}ClNO_4^+$ 562.1780. Found 562.1766; HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol 9/1, 1.0 mL/min, t_R 20.1 min (minor), 28.9 min (major); $[\alpha]^{27}_D$ –35.4 (c = 1.1, CH_2Cl_2) (96% ee).

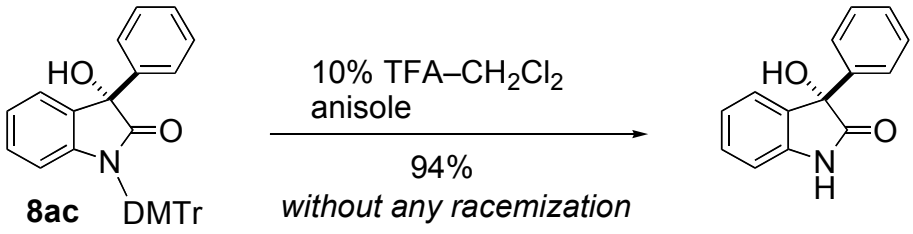
5. Proposed Catalytic Cycle in the Presence of Additive ZnF_2

A plausible catalytic cycle in the presence of catalytic additive ZnF_2 is proposed in the scheme below. A chiral CuF complex transfers hard fluoride anion to the silicon atom of aryl- or alkenyltrimethoxyvinylsilane ($RSi(OMe)_3$) to afford ate-complex **S4**. Transmetalation occurs from **S4**, generating an organocopper species **S5** and $(MeO)_3SiF$. Once **S5** is generated, addition of **S5** to substrate is fast (based on the previous kinetic studies[3]), affording copper alkoxide **S6**. The catalyst turnover-limiting steps are regeneration of the active copper species **S5** from **S6**. The additive ZnF_2 reacts with $(MeO)_3SiF$, which is generated in the transmetalation step (from **S4** to **S5**), and generates a more electrophilic trapping reagent $(MeO)_2SiF_2$ (observed by ^{19}F-NMR[4]), than $(MeO)_3SiF$. $(MeO)_2SiF_2$ quickly reacts with **S6** and generates silicate **S7**. Because the silicon trap of **S6** is the initiating step of the turnover-limiting regeneration of **S5**, the overall catalytic cycle is accelerated in the presence of the reactive trapping reagent, $(MeO)_2SiF_2$. The fluoride transfer from **S7** to a stoichiometric silicon-based nucleophile ($RSi(OMe)_3$) produces **S4** with liberating product **S8**. Through the reaction between **S8** and ZnF(OMe), which was generated through the reaction between ZnF_2 and $(MeO)_3SiF$, trimethoxysilyl protected **S9** was produced with regenerating ZnF_2.



6. Deprotection and Determination of Product's Absolute Configuration

(3*S*)–3-Hydroxy-3-phenyloxindole

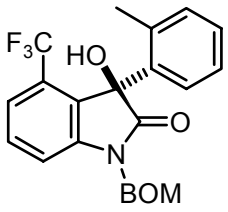


To a mixture of DMTr–protected **8ac** (9.5 mg, 0.018 mmol, 88% ee) and anisole (39 μL, 0.36 mmol), 10% TFA in CH_2Cl_2 (1 mL) was added under ice bath. The mixture was stirred at rt for 2 h, and then the solvent was evaporated. Purification of the resulting crude mixture through silica gel column chromatography (AcOEt/hexane = 1/4) afforded the deprotected oxindole in 94% yield (3.8 mg). The enantiomeric excess of the deprotected compound was determined to be 89% ee by chiral HPLC (DAICEL CHIRALCEL-ODH, ^{i}PrOH/hexane = 1/9, 1.0 mL/min, t_R 28.8 min (major), 36.0 min (minor). The absolute configuration was determined to be (*S*), according to the comparison of the optical rotation to the reported value[5]; $[\alpha]^{25}_D$ = +23.3 (c = 0.06, MeOH).

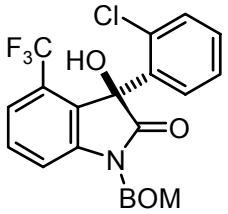
7. Catalytic Asymmetric Intramolecular Arylation

A typical procedure (Table 3, enrty 1): A solution of CuF•3PPh$_3$•2EtOH (12 mg, 0.013 mmol), (*R,R*)–Ph–BPE (9.0 mg, 0.018 mmol), and **10a** (70 mg, 0.13 mmol) in toluene (0.4 mL) was stirred at 55 ^{o}C for 14 h. Water was added to quench the reaction, and the mixture was stirred at room temperature for 30 min. The organic layer was separated, and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated to give a residue, which was purified by silica gel chromatography (EtOAc/hexane, 1/4) to afford **11a** (49 mg, 90%) as colorless needles.

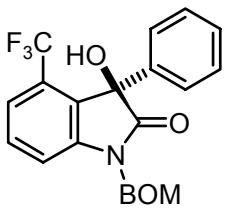
1–Benzyloxymethyl–4–trifluoromethyl–3–*o*-tolyl–3–hydroxyoxindole (11a): colorless needles; mp 139 ^{o}C; ^{1}H NMR ($CDCl_3$) δ: 1.64 (br s, 3H), 3.00 (s, 1H), 4.55 (m, 2H), 5.25 (m, 2H), 6.97 (d, *J* = 7.0 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.24 (m, 6H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.45 (t, *J* = 8.3 Hz, 1H), 7.90 (br, 1H); ^{13}C NMR ($CDCl_3$) δ: 19.3, 70.2, 71.3, 77.2, 113.9, 121.3 (q, *J* = 4.8 Hz), 122.9 (q, *J* = 275 Hz), 126.0, 126.6, 127.9 (q, *J* = 30 Hz), 128.0, 128.1, 128.5, 128.6, 130.8, 131.3, 135.8, 136.8, 144.1, 175.8; IR (neat): 3406, 1739, 1613, 1467, 1337, 1132, 1097, 924, 804, 746, 699, 681cm^{-1}; LRMS m/z 450.2 $(M+Na)^+$; HRMS: Calcd for $C_{24}H_{21}F_3NO_3^+$ 428.1468. Found 428.1460; HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol 2/1, 1.0 mL/min, t_R 18.1 min (minor), 22.7 min (major); $[\alpha]^{26}_D$ +3.7 (c = 2.7, $CHCl_3$) (87% ee).



1–Benzyloxymethyl–4–trifluoromethyl–3–(2-chlorophenyl)–3–hydroxyoxindole (11b): amorphous; ^{1}H NMR ($CDCl_3$) δ: 2.90 (s, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 5.28 (s, 2H), 7.24-7.39 (m, 10H), 7.46 (t, *J* = 8.0 Hz, 1H), 8.03 (br, 1H); ^{13}C NMR ($CDCl_3$) δ: 70.5, 71.3, 113.9, 120.9 (br), 126.8, 128.1, 128.5, 129.0, 130.0, 130.9, 135.7, 137.1, 145.0, 175.1; IR (neat): 3393, 1734, 1467, 1338, 1131, 1097, 800, 748, 699 cm^{-1}; LRMS m/z 470.2 $(M+Na)^+$; HRMS: Calcd for $C_{23}H_{18}ClF_3NO_3^+$ 448.0922. Found 448.0920; HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol 20/1, 1.0 mL/min, t_R 18.9 min (minor), 26.6 min (major); $[\alpha]^{26}_D$ +26.8 (c = 0.97, $CHCl_3$) (77% ee).

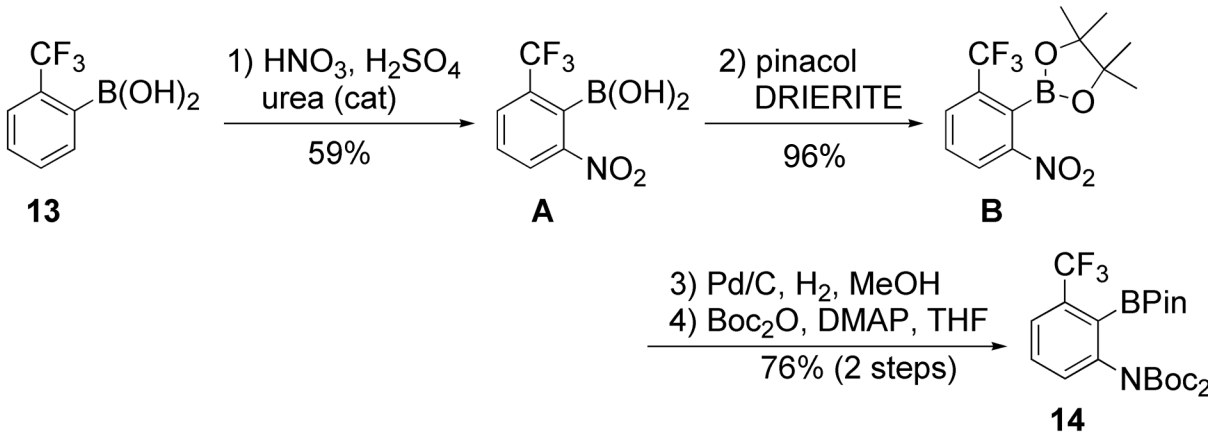


1–Benzyloxymethyl–4–trifluoromethyl–3–phenyl–3–hydroxyoxindole (11c): colorless needles; mp: 120 ^{o}C; ^{1}H NMR ($CDCl_3$) δ:3.01 (s, 1H), 4.41 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 5.23 (m, 2H), 7.15-7.35 (m, 10H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 70.5, 71.3, 78.6, 113.9, 120.9, 126.8, 128.1, 128.5, 129.0, 130.0, 130.9, 135.7, 137.1, 145.0, 175.1; IR (neat): 3421, 1739, 1612, 1466, 1336, 1131, 800, 747, 697 cm^{-1}; LRMS m/z 436.2 $(M+Na)^+$; HRMS: Calcd for $C_{23}H_{19}F_{3N}O_3^+$ 414.1312. Found 414.1320; HPLC: DAICEL CHIRALCEL IC, hexane/2-propanol 30/1, 1.0 mL/min, t_R 20.2 min (major), 23.8 min (minor); $[\alpha]^{26}_D$ –47.8 (c = 0.67, $CHCl_3$) (82% ee).



8. Catalytic Enantioselective Synthesis of SM-130686

***N,N'*–di–*tert*-butyl–2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl) phenylcarbamate (14)**



13 **A** **B** **14**

To a mixture of concentrated HNO_3 (15 mL), H_2SO_4 (45 mL), and urea (62 mg, 1 mmol) in a 1 L flask, commercially available **13** (20.0 g, 105 mmol) in Ac_2O (250 mL) was added very carefully at –20 °C (*Be careful!* Violent reaction can occur if added rapidly). The reaction temperature was allowed to gradually increase to rt, and the reaction was continued for 12 h. After cooling under ice bath, 30% aqueous solution of NaOH was added to adjust pH = 3 ~ 5. Water was added, and products were extracted with AcOEt (x 3). The organic layer was washed with saturated NaCl aqueous solution, and dried over Na_2SO_4. Filtration and evaporation of the solvent afforded crude oil, which was purified through silica gel column chromatography, giving the known nitrated compound **A**[6] in 59% yield (15 g).

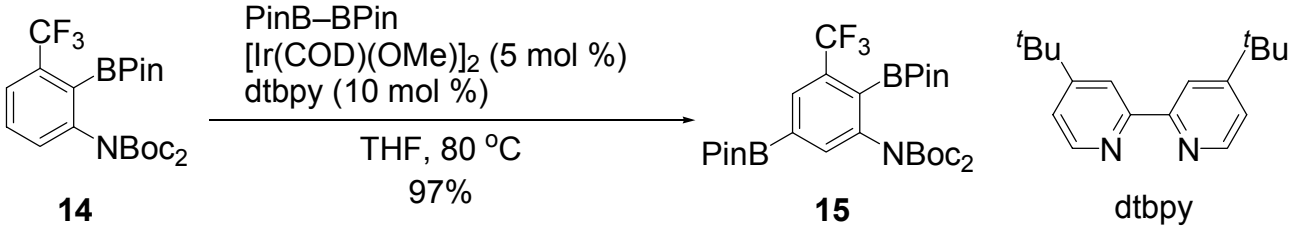
Compound **A** (4.1 g, 17.4 mmol) and pinacol (2.2 g, 18.6 mmol) were dissolved in toluene (50 mL) in the presence of DRIERITE (1 g), and the whole was stirred at 90 °C for 15 h. After filtration and washing with toluene, the filtrate was directly loaded on silica gel column chromatography (eluent: hexane/AcOEt = 100/1), giving compound **B** in 96% yield (5.3 g, 16.7 mmol) as off-white solid.

Mp: 119 °C; ^{1}H NMR ($CDCl_3$) δ: 1.49 (s, 12H), 7.66 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 23.9, 83.8, 120.9, 123.0, 124.8, 129.0, 129.8, 133.7, 150.4; IR (neat): 2982, 1539, 1340, 1138, 961, 853, 819, 743, 704, 657 cm^{-1}; LRMS m/z 340.2 $(M+Na)^+$; HRMS: Calcd for $C_{13}H_{16}BF_3NO_4^+$ 318.1119. Found 318.1131.

A mixture of **B** (2.9 g, 9.2 mmol) and Pd/C (500 mg) in MeOH (30 mL) was stirred under hydrogen atmosphere at room temperature. After 1 h, the reaction mixture was filtered through short pad of Celite, and the filtrate was concentrated under reduced pressure. The residue and DMAP (335 mg, 2.8 mmol) were dissolved in THF (100 mL), and Boc_2O (10.0 g, 45.8 mmol) was added at room temperature. The reaction mixture was warmed up to 50 °C. After 10 h, the solvent was evaporated under reduced pressure, water was added, and products were extracted with ethyl acetate. The organic layer was separated, and concentrated under vacuum. The target product **14** was purified by silica gel column chromatography using hexane–ethyl acetate (4:1) as eluent, affording **14** (3.4 g, 7.0 mmol) as white solid in 76% yield.

Mp 123 °C; ^{1}H NMR ($CDCl_3$) δ: 1.31 (s, 12H), 1.34 (s, 18H), 7.22 (d, J = 7.9 Hz, 1H), 7.43 (dd, J = 8.0 Hz, 7.9 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 24.8, 27.8, 82.6, 82.6, 84.6,123.0, 124.1 (q, J = 251 Hz), 124.4 (br, J = 4.8 Hz), 129.5, 131.3, 133.9 (q, J = 33 Hz), 143.6, 150.7; IR (neat): 2982, 1759, 1718, 1473, 1337, 1272, 1135, 850, 775, 677 cm^{-1}. LRMS m/z 510.3 $(M+Na)^+$; HRMS: Calcd for $C_{23}H_{34}BF_3NO_6^+$ 488.2426. Found 488.2444.

***N,N'*–di–*tert*-butyl–2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl) phenylcarbamate (15)**

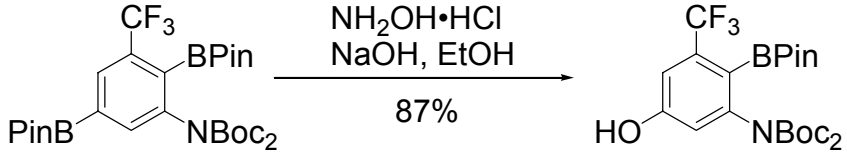


14 **15** dtbpy

In a glove box, **14** (2.3 g, 4.7 mmol), $(BPin)_2$ (830 mg, 3.3 mmol), $[Ir(COD)(OMe)]_2$ (160 mg, 0.24 mmol), dtbpy (130 mg, 0.48 mmol), and THF (7.0 mL) were combined.[7] The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction mixture was then cooled to room temperature, and the volatile materials were evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (Et_2O/hexane = 1/2), affording **15** as white solid in 97% yield (2.8 g, 4.6 mmol).

Mp 162 °C; ^{1}H NMR ($CDCl_3$) δ: 1.31 (s, 12H), 1.37 (s, 18H), 7.59 (s, 1H), 7.96 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 24.5, 27.5, 82.2, 84.0, 84.3, 122.5, 125.0, 130.0 (br d, J = 4.1 Hz), 133.1, 133.3, 137.1, 142.7, 150.6; IR (neat): 2981, 1798, 1757, 1488, 1370, 1336, 1300, 1272, 1142, 963, 854, 691 cm^{-1}; LRMS m/z 636.4 $(M+Na)^+$; HRMS: Calcd for $C_{29}H_{45}B_2F_3NO_8^+$ 614.3278. Found 614.3305.

***N,N'*–di–*tert*-butyl–5-hydroxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl) phenylcarbamate (16)**

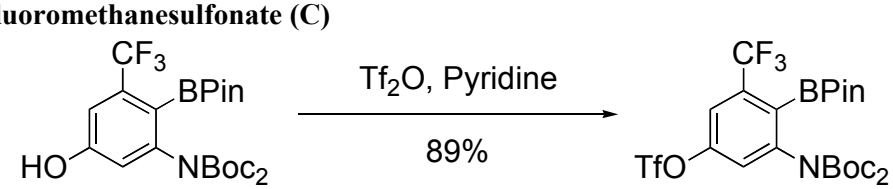


15 **16**

To a solution of **15** (680 mg, 1.1 mmol) in ethanol (10 mL), hydroxyl ammonium chloride (224 mg, 3.2 mmol) and sodium hydroxide (184 mg, 4.6 mmol) were added, and the mixture was stirred at room temperature for 48 h. The reaction progress was monitored by TLC. Workup of the reaction involved evaporating the solvent under reduced pressure, addition of water, and then extraction with ethyl acetate. The solvent was removed under vacuum and the product was purified by silica gel column chromatography using hexane–ethyl acetate (4:1) as eluent, affording **16** as white solid in 87% yield (486 mg, 0.96 mmol).[8]

Mp 177 °C; ^{1}H NMR ($CDCl_3$) δ: 1.28 (s, 12H), 1.36 (s, 18H), 6.69 (d, J = 2.5 Hz, 1H), 7.08 (d, J = 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 24.7, 27.8, 83.0, 84.3, 112.5, 112.6, 118.4, 124.9, 135.2, 144.9, 150.9, 156.9; IR (neat): 3376, 2980, 1769, 1333, 1138, 945, 853, 782 cm^{-1}; LRMS m/z 526.3 $(M+Na)^+$; HRMS: Calcd for $C_{23}H_{33}BF_3NNaO_7^+$ 526.2194. Found 526.2217.

3-(*N,N'*–di–*tert*-butoxycarbonylamino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenyl trifluoromethanesulfonate (C)

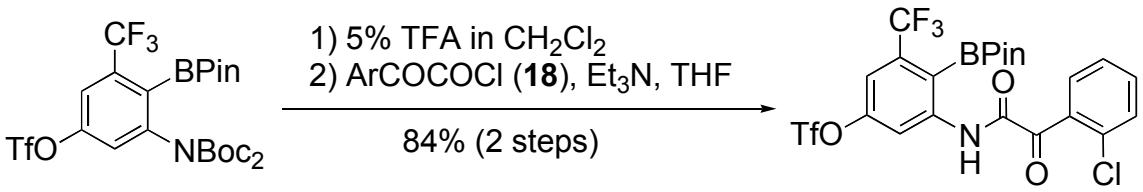


16 **C**

A solution of **16** (310 mg, 0.62 mmol) in pyridine (1.2 mL) was stirred at 0 °C for 10 min. To this solution, triflic anhydride (204 μL, 1.2 mmol) was added. Then, the reaction mixture was stirred at 0 °C for 2 h. H_2O was added to quench the reaction. Products were extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford crude **C**, which was purified by silica gel column

chromatography using hexane–ethyl acetate (4:1) as eluent, affording **C** as white solid in 89% yield.
Mp: 117 °C; ^{1}H NMR ($CDCl_3$) δ: 1.35 (s, 12H), 1.43 (s, 18H), 7.24 (d, J = 2.2 Hz, 1H), 7.51 (d, J = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 24.8, 27.6, 83.5, 85.2, 117.4, 117.8 (d, J = 5.1 Hz), 119.9, 121.8, 124.0, 124.7, 135.8 (d, J = 33 Hz), 145.6, 149.3, 149.7; LRMS m/z 636 $(M+H)^+$; HRMS Calcd for $C_{24}H_{32}BF_6NO_9S^+$ 636.1868. Found 636.1880; IR (neat): 2983, 1803, 1766, 1731, 1606, 1430, 1337, 1139, 939, 887, 852, 799, 777, 762, 701 cm^{-1}.

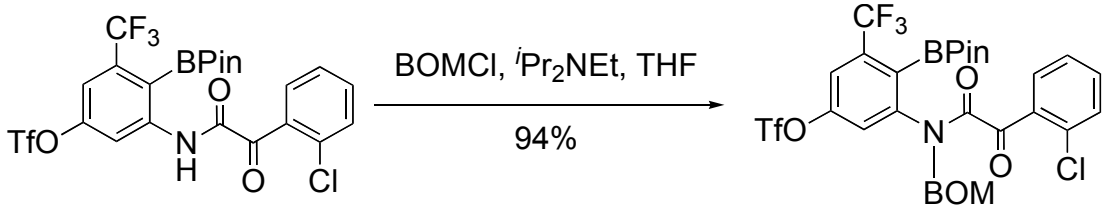
3-(2-(2-chlorophenyl)-2-oxoacetamido)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenyl trifluoromethanesulfonate (D)



17 **D**

To a solution of **17** (513 mg, 0.81 mmol) in CH_2Cl_2 (3 mL) at 0 °C, TFA (11.6 mL of 5% solution in CH_2Cl_2, 3.2 mmol) was added dropwise via syringe over 10 min. After 2 h, the reaction mixture was evaporated. The residue was mixed with 2-(2-chlorophenyl)-2-oxoacetyl chloride (436 mg, 2.1 mmol, freshly prepared from the corresponding keto acid and 10 eq. of dichloromethyl methyl ether in neat conditions at 50 °C for 1 h, and then evaporation) in THF (8 mL), and Et_3N (0.49 mL, 3.5 mmmol) was added at 0 °C. The solution was stirred at room temperature for 2 h. After adding water, products were extracted with AcOEt. This compound is not very stable, and was only partially purified by silica gel column chromatography (AcOEt/hexane = 1/4), affording compound **D** in ca. 84% yield (408 mg, 0.68 mmol).
^{1}H NMR ($CDCl_3$) δ: 1.46 (s, 12H), 7.40 (dt, J = 2.2, 7.3 Hz, 2H), 7.46–7.51 (m, 2H), 7.67 (dd, J = 1.5, 7.5 Hz, 8.72 (d, J = 2.2 Hz, 1H), 10.74 (s, 1H); LRMS m/z 647.1 $(M+Na)^+$.

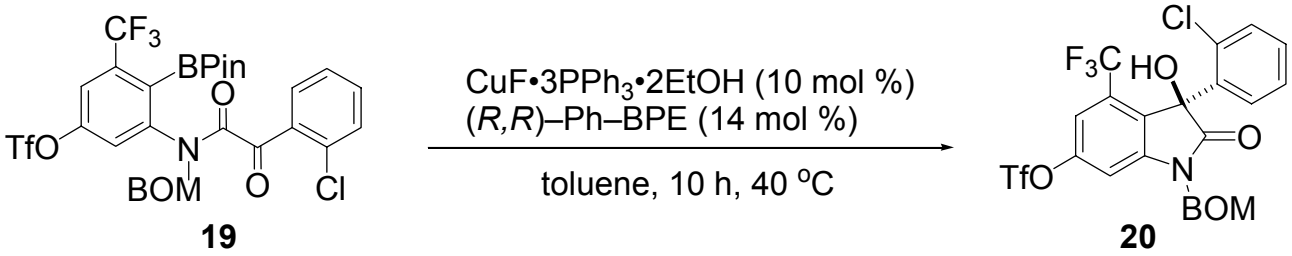
3-(*N*-(benzyloxymethyl)-2-(2-chlorophenyl)-2-oxoacetamido)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenyl trifluoromethanesulfonate (19)



D **19**

To a solution of **D** (80 mg, 0.13 mmol) and BOMCl (0.27 mL, 1.9 mmol) in THF, ^{i}Pr$_2$NEt (0.35 mL, 2.0 mmol) was added dropwise at 0 °C. After stirring at room temperature for 2 h, saturated NH_4Cl was added to quench the reaction. The organic phase was separated and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/5) to afford **19** as a pale yellow oil (88 mg, 0.12 mmol, 94% yield). The compound was pure, but NMR charts are not very informative due to the existence of amide rotamers. LRMS m/z 744.2 $(M+Na)^+$.

(3*S*)–1-(benzyloxymethyl)-3-(2-chlorophenyl)-3-hydroxy-2-oxo-4-(trifluoromethyl)indolin-6-yl trifluoromethanesulfonate (20)

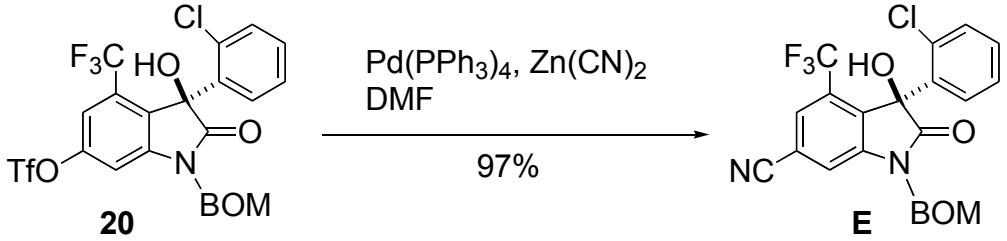


19 **20**

A solution of CuF•3PPh$_3$•2EtOH (4.7 mg, 0.0049 mmol), (*R,R*)–Ph–BPE (3.4 mg, 0.0068 mmol), and **19** (35 mg, 0.049 mmol) in toluene (0.3 mL) was stirred at 40 °C for 10 h. Water was added to quench the reaction, and the mixture was stirred at room temperature for 30 min. The organic layer was separated, and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated to give a residue, which was purified by silica gel chromatography (EtOAc/hexane, 1/4) to afford **20** (27 mg, 90%) as amorphous.

^{1}H NMR ($CDCl_3$) δ: 2.99 (br s, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), .5.24 (s, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 7.09–7.29 (m, 8H), 7.37 (br t, *J* = 7.6 Hz, 1H), 7.97 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 70.6, 71.7, 77.1, 107.7, 113.7 (q, *J* = 6 Hz), 118.4 (q, *J* = 320 Hz), 121.9 (q, *J* = 273 Hz), 126.5, 126.8, 127.0, 127.8, 128.0, 128.3, 128.5, 129.0, 130.0, 130.5, 134.8, 136.6, 146.9, 150.3, 174.7; LRMS m/z 618.1 $(M+Na)^+$; HRMS: Calcd for $C_{24}H_{17}ClF_6NO_6S$ 596.0364. Found 596.0381; IR (neat): 3386, 1747, 1613, 1430, 1218, 1140, 941, 823, 747 cm^{-1}; HPLC: DAICEL CHIRALCEL OD-H, ^{i}PrOH/hexane = 1/20, t_R = 12.6 min (minor) and 14.5 min (major); $[\alpha]^{26}_D$ +46.0 (c = 1.0, $CHCl_3$) (85% ee).

(3*S*)–1-(benzyloxymethyl)-3-(2-chlorophenyl)-3-hydroxy-2-oxo-4-(trifluoromethyl)indoline-6-carbonitrile (E)

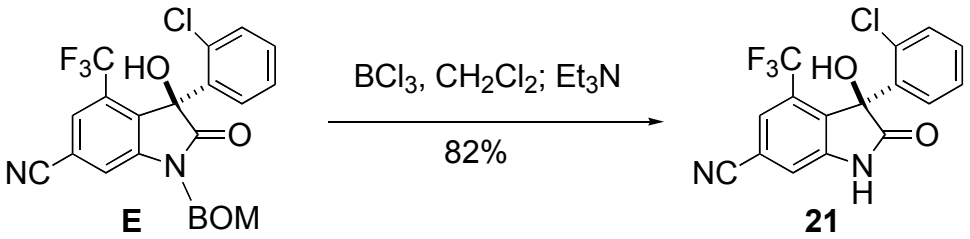


20 **E**

A solution of **20** (30 mg, 0.050 mmol), $Pd(PPh_3)_4$ (28 mg, 0.024 mmol), and $Zn(CN)_2$ (23 mg, 0.20 mmol) in DMF (0.75 mL) was stirred at 60 °C for 2 h. Saturated aqueous solution of $NaHCO_3$ was added to quench the reaction, and the mixture was stirred at room temperature for 30 min. The organic layer was separated, and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated to give a residue, which was purified by silica gel chromatography (EtOAc/hexane, 1/4) to afford **E** (23 mg, 0.049 mmol, 97% yield) as amorphous.

^{1}H NMR ($CDCl_3$) δ: 2.99 (br, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.69 (d, *J* = 11.8 Hz, 1H), 5.32 (m, 2H), 7.24-7.36 (m, 8H), 7.45 (dd, *J* = 7.6, 7.7 Hz, 1H), 7.58 (s, 1H), 7.61 (s, 1H), 8.03 (br, 1H); ^{13}C NMR ($CDCl_3$) δ: 70.5, 71.7, 77.3, 114.9, 116.2, 116.9, 121.5 (q, *J* = 273 Hz), 124.9 (q, *J* = 5.1 Hz), 127.1, 127.8, 128.1, 128.4, 129.7, 130.0, 130.5, 131.4, 134.6, 136.5, 145.9, 174.3; IR (neat): 3393, 2930, 1745, 1620, 1449, 1368, 1141, 1032, 937, 877, 748, 700, 626 cm^{-1}; LRMS m/z 495.2 $(M+Na)^+$; HRMS: Calcd for $C_{24}H_{16}ClF_3N_2O_3$ 473.0874. Found 473.0883; $[\alpha]^{26}_D$ +73.6 (c = 0.44, $CHCl_3$).

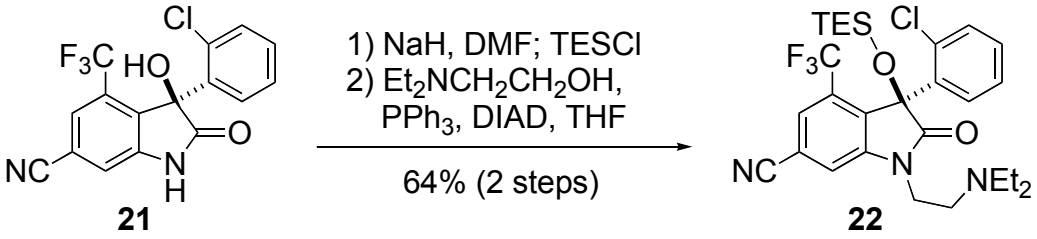
(3*S*)–3-(2-chlorophenyl)-3-hydroxy-2-oxo-4-(trifluoromethyl)indoline-6-carbonitrile (21)



To a solution of **E** (10 mg, 0.021 mmol) in CH_2Cl_2 (1.1 mL) at –78 °C was added BCl_3 (0.21 mL, 1.0 M in CH_2Cl_2, 0.21 mmol) dropwise via syringe over 2 min. After 1 h at –78 °C, the reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL), and the mixture was extracted with EtOAc. After evaporation, the resulting crude solid was dissolved in MeOH (1.1 mL). Et_3N (55 μL) was added, and the solution was heated at 50 °C for 2 h. After evaporation, the product was purified by column chromatography (AcOEt/hexane. 1/2 to 1/1) to give 6.0 mg (82%) of **21** as a white solid.

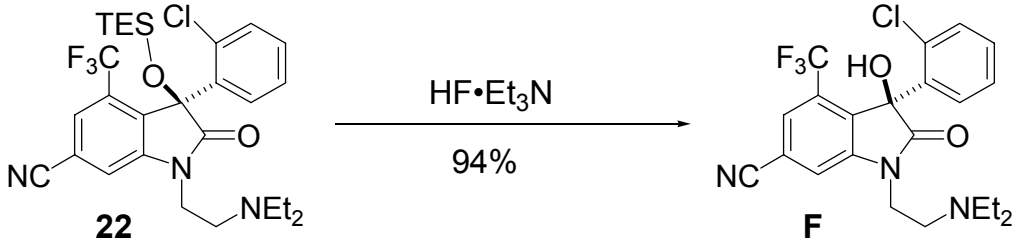
Mp: 190 °C; ^{1}H NMR ($CDCl_3$) δ: 4.01 (s, 1H), 7.16 (s, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.53 (s, 1H), 8.00 (br, 1H), 9.10 (s, 1H); ^{13}C NMR (CD_3OD) δ: 77.6, 115.3, 117.4, 118.3, 121.3 (q, J = 275 Hz), 124.8 (q, J = 5.9 Hz), 127.6, 129.4 (q, J = 35 Hz), 130.5, 131.0, 131.1, 132.1, 135.1, 137.4, 147.5, 178.3; LRMS m/z 374.8 $(M+Na)^+$; HRMS: Calcd for $C_{16}H_9ClF_3N_2O_2^+$ 352.0299. Found 352.0300; IR (neat): 3277, 1735, 1627, 1444, 1339, 1142, 1006, 879, 705 cm^{-1}; $[\alpha]^{22}_D$ +96.3 (c = 0.06, $CHCl_3$).

(3*S*)–3-(2-chlorophenyl)-1-(2-(diethylamino)ethyl)-2-oxo-3-(triethylsilyloxy)-4-(trifluoromethyl) indoline-6-carbonitrile (22)



To a solution of **21** (8.0 mg, 0.023 mmol) in DMF (0.1 mL) at 0 °C was added NaH (1.8 mg, 0.045 mmol; 60 wt% in mineral oil). After 30 min at 0 °C, TESCl (15 μL, 0.089 mmol) was added to the reaction mixture. After further 3 h, the reaction was quenched with H_2O. The TES-protected compound was extracted with EtOAc, and the solvent was evaporated. The resulting crude solid was dissolved in THF (0.24 mL), and 2–diethylaminoethanol (21.1 μL, 0.158 mmol), DIAD (28.8 μL, 0.146 mmol), and PPh_3 (40.3 mg, 0.15 mmol) were added. The mixture was stirred at room temperature for 12 h. The solvent was evaporated, and the residue was partially purified by silica gel chromatography (EtOAc/hexane, 1/4) to afford **22** (8.2 mg, 0.015 mmol, ca. 64%, containing inseparale hydrazine byproduct derived from DIAD). LRMS m/z 565.3 $(M+Na)^+$.

(3*S*)–3-(2-chlorophenyl)-1-(2-(diethylamino)ethyl)-3-hydroxy-2-oxo-4-(trifluoromethyl) indoline-6-carbonitrile (F)

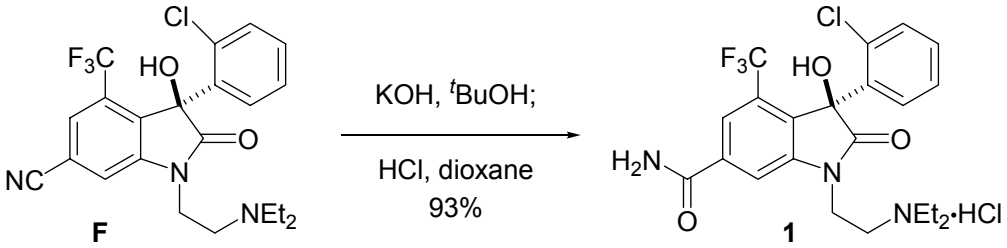


TES-protected **22** (38.3 mg, calcd 0.068 mmol; conatining hydrazine byproduct) was dissolved in THF (0.68 mL), and 50.3 μL of 1.5 M 3HF·Et_3N solution in THF (0.074 mmol) was added at rt. After 10 h, volatiles were evaporated to give crude **F**, which was purified with silica gel column chromatography (AcOEt/hexane = 1/2

to AcOEt/MeOH = 20/1), affording known compound **F**[9] (28.6 mg, 0.063 mmol) as white solid in 94% yield. The absolute configuration of **F** was determined through comparison of the sign of optical rotation to the reported value[9]; $[\alpha]^{25}_{D}$ +66.4 (c = 0.31, MeOH). ^{1}H NMR chemical shifts completely matched with the reported values.

Mp: 175 °C; ^{1}H NMR ($CDCl_3$) δ: 1.05 (t, *J* = 7.2 Hz, 3H), 2.78 (m, 5H), 3.03 (m, 1H), 3.70 (dt, *J* = 5.2, 14.9 Hz, 1H), 4.23 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.29 (dt, *J* = 1.8, 8.0 Hz, 1H), 7.37 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.56 (s, 1H), 8.12 (br d, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 10.4, 38.5, 46.3, 49.2, 76.3, 114.3, 114.7, 117.4, 122.0 (q, *J* = 275 Hz), 124.6 (q, *J* = 5.9 Hz), 127.0, 128.7 (q, *J* = 36 Hz), 129.8, 129.8, 130.3, 130.6, 133.4, 135.2, 146.6, 175.1; LRMS m/z 452.2 $(M+H)^+$; IR (neat): 3390, 2975, 2235, 1732, 1617, 1453, 1384, 1167, 1140 cm^{-1}.

SM-130686 (1)

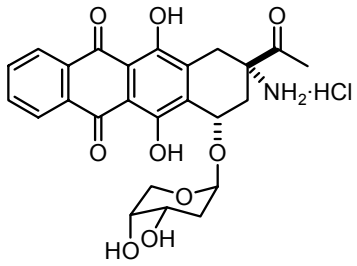


To a solution of **F** (10 mg, 0.022 mmol) in ^{t}BuOH (0.44 mL), powdered KOH (34 mg, 0.61 mmol) was added. The mixture was stirred at 50 °C for 1 h. After cooling to room temperature, the mixture was filtered through Celite pad, and the filtrate was evaporated. To the residue, EtOAc and H_2O were added, and the mixture was stirred for 5 min. Organic layer was separated, dried over Na_2SO_4, and concentrated. The residue was dissolved in 1,4-dioxane (0.2 mL), and 4 N HCl in 1,4-dioxane (110 μL, 0.44 mmol) was added at room temperature. Evaporation of the solvent afforded **1**[9] (10.4 mg, 0.021 mmol) as white solid in 93% yield.

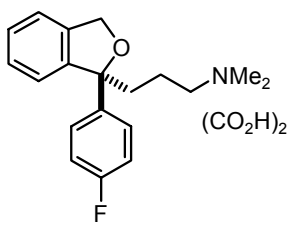
Mp: 173 °C; ^{1}H NMR (DMSO-d_6) δ: 1.25 (t, *J* = 7.2 Hz, 3H), 3.27 (m, 5H), 3.44 (m, 1H), 4.19 (m, 1H), 4.33 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.41 (s, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.81 (s, 1H), 7.83 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.17 (s, 1H), 8.37 (s, 1H), 10.5 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ: 8.3, 8.5, 34.9, 45.5, 46.7, 75.4, 111.8, 119.4 (br), 122.8 (q, *J* = 274 Hz), 125.2, 125.6 (q, *J* = 33 Hz), 126.6, 129.3, 129.8, 129.9, 131.1, 136.4, 136.5, 145.1, 165.8, 174.5; LRMS m/z 470.0 $(M–HCl+H)^+$; IR (neat): 3366, 1733, 1671, 1446, 1351, 1167, 1134 cm^{-19}; $[\alpha]^{22}_{D}$ +52.1 (c = 0.41, MeOH).

9. Examples which justify the statement in reference 2 in the text

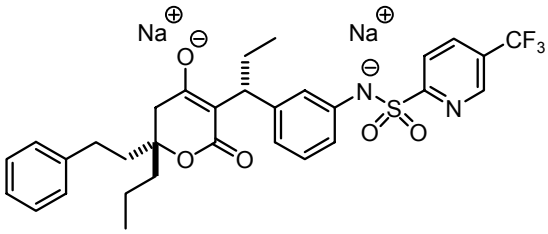
The followings are typical examples that justify the satatement of ref. 2 in the text (on an industrial scale, pharmaceuticals that are not derived from natural sources containing chiral tetrasubstituted carbons are almost always produced through resolution).



amurubicin hydrochloride[10]
(anticancer)



escitalopram oxalate[11]
(antidepressant)



tipranavir disodium[12]
(HIV protease inhibitor)

10. References

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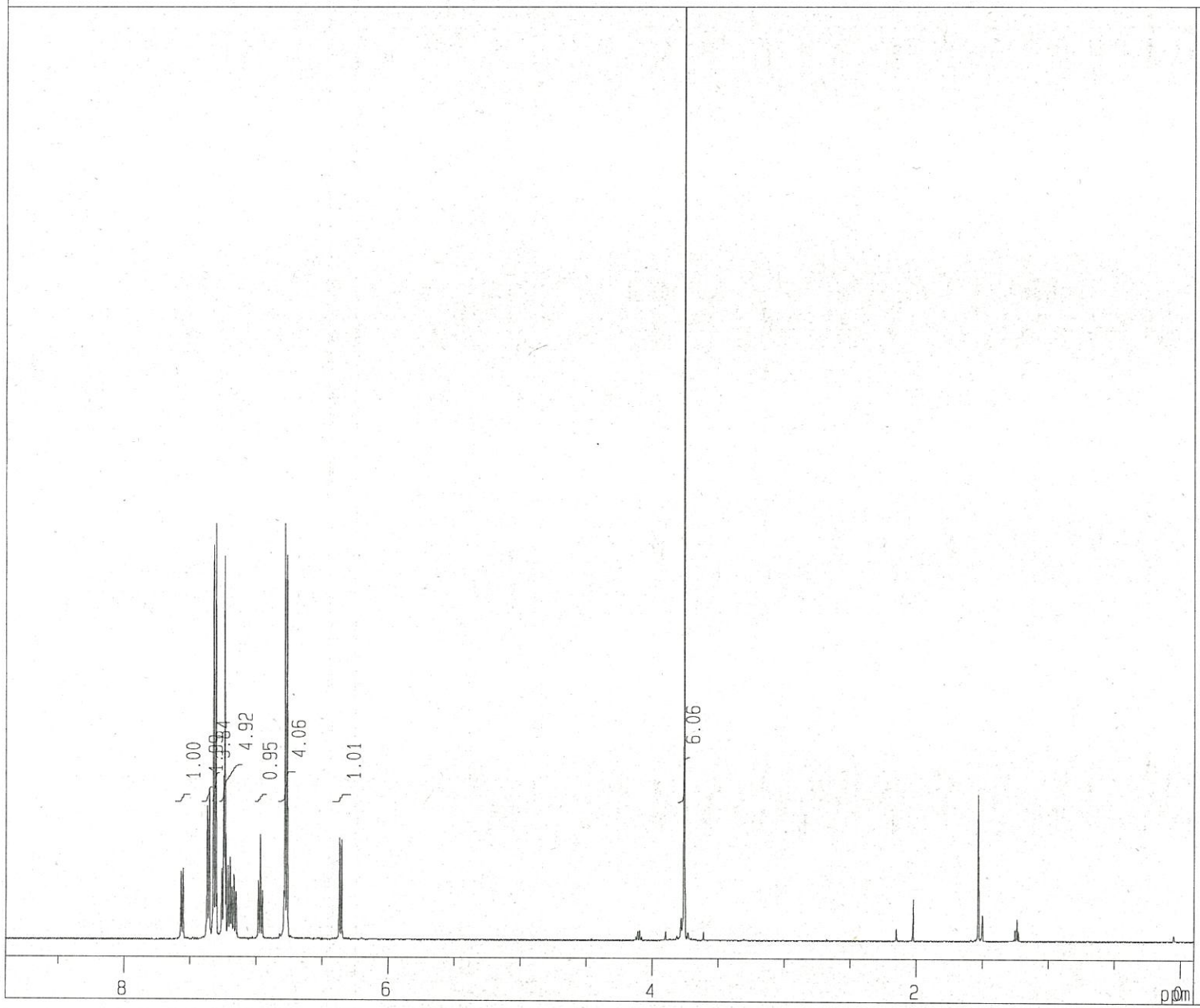
normal



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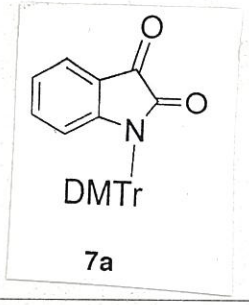
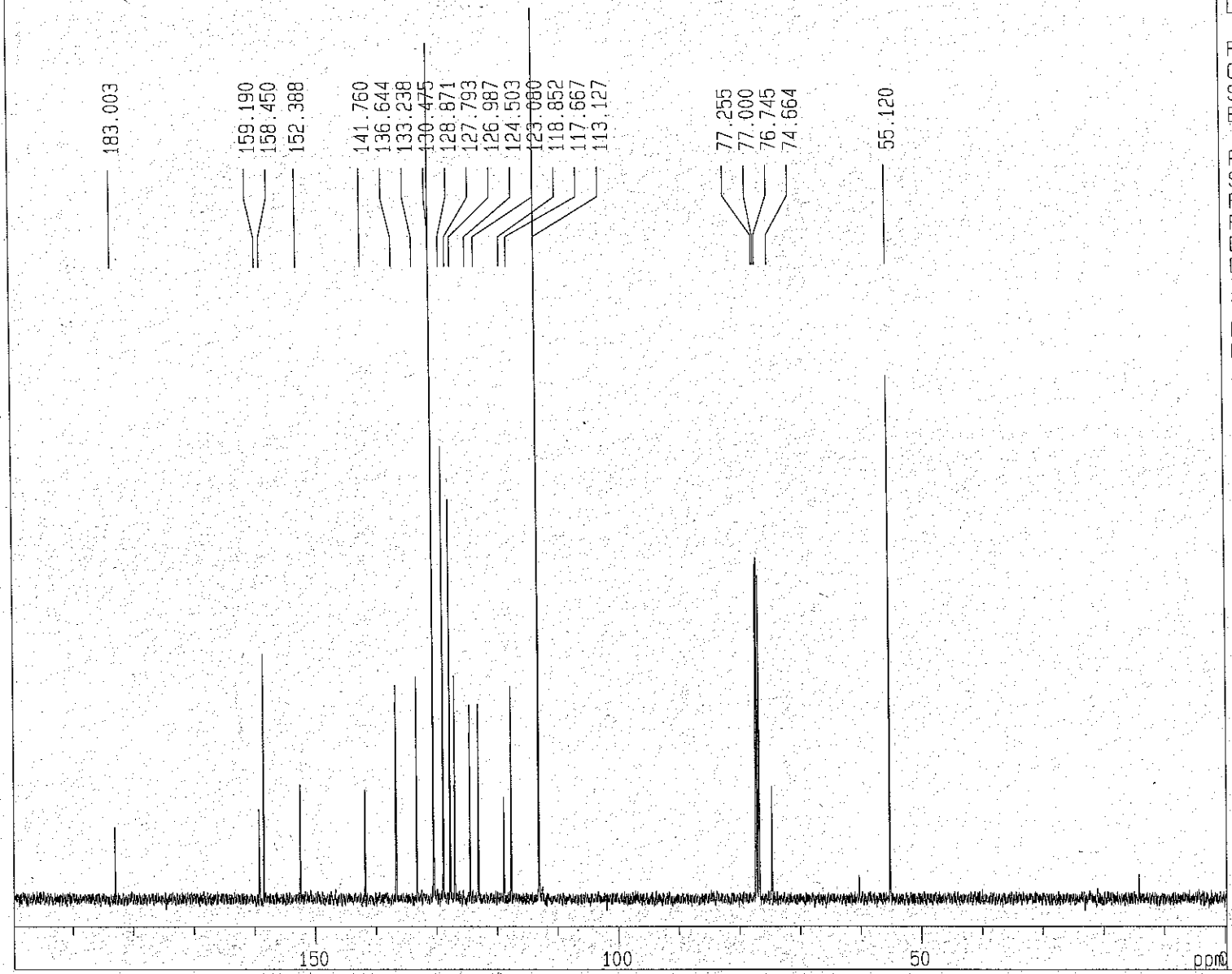


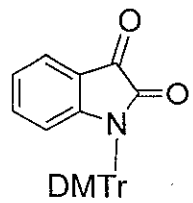
7a

Substrate Ph 13C



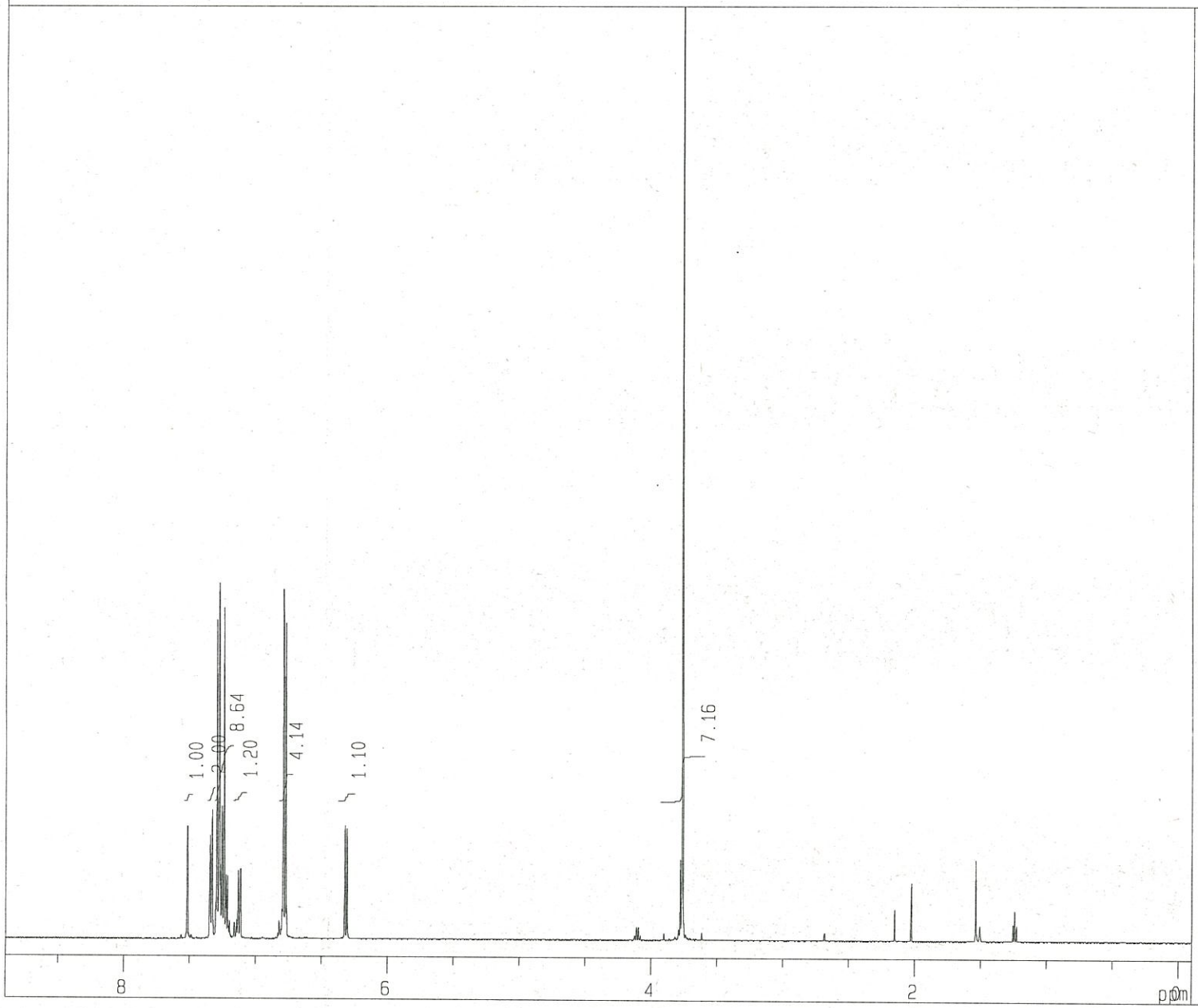
Date : Tue Mar 10 16:05:59 2009

FileName	:	.LoadingFID.nmdata
Comment	:	Substrate Ph 13C
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	300 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	99 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	25.7 C



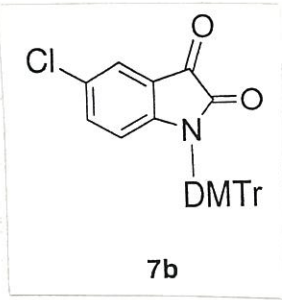
7a

ue



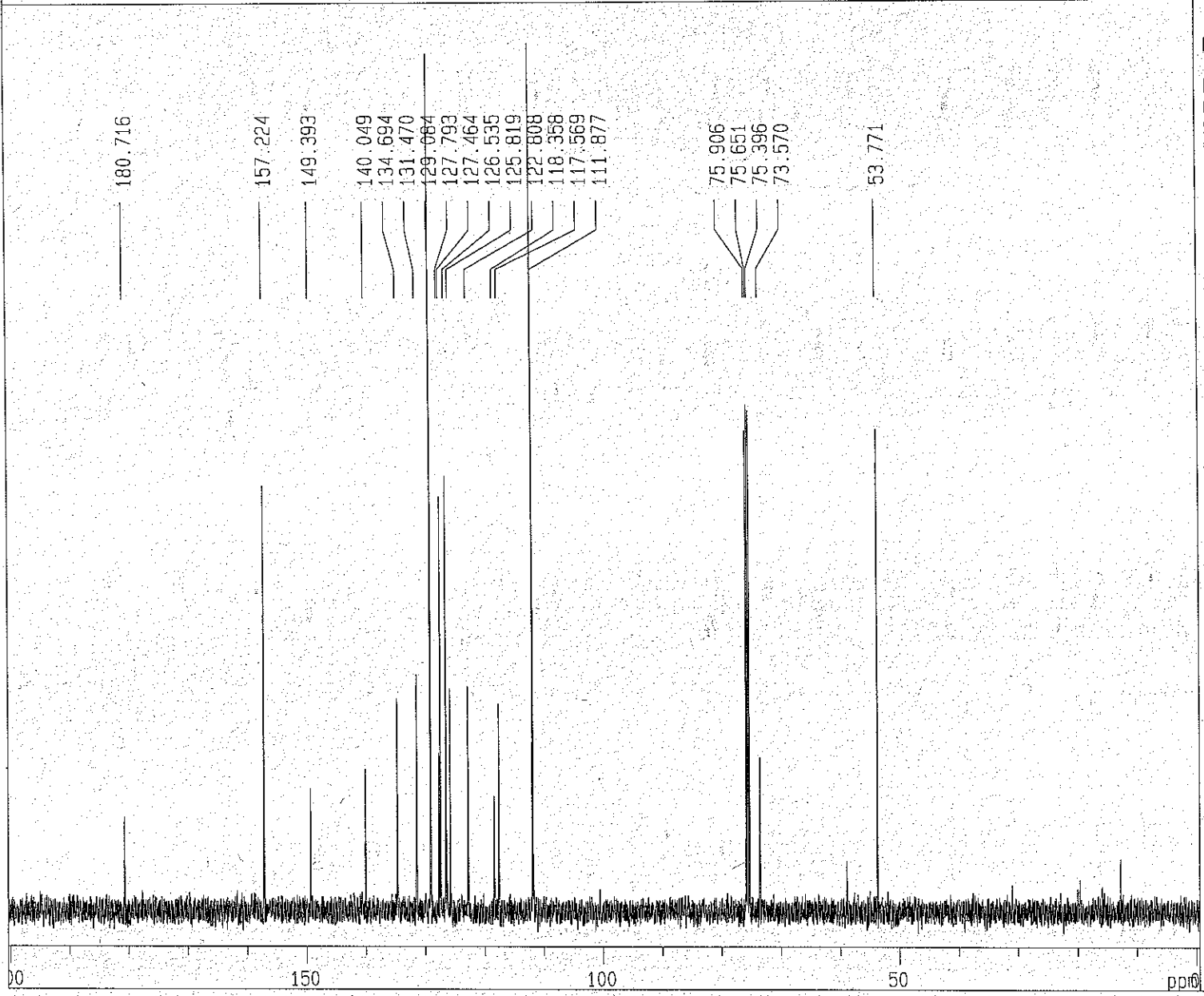
Date : Thu Apr 23 20:40:23 2009

FileName	:	.LoadingFID.nmdata
Comment	:	ue
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	512 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	22
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	26.2 C



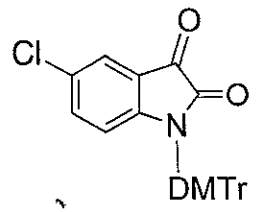
7b

5-Cl 13C



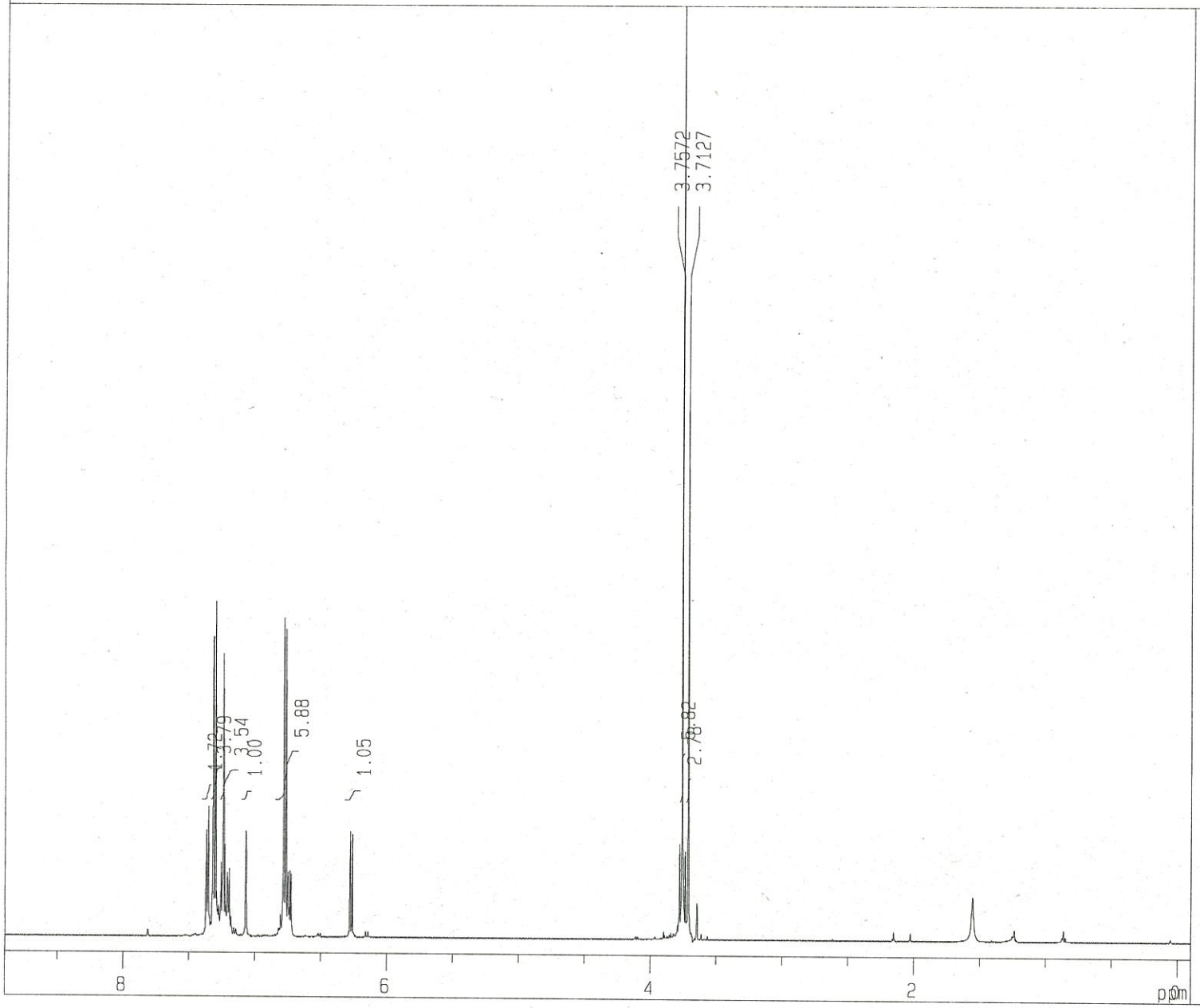
Date : Fri Mar 13 22:47:25 2009

FileName	:	.LoadingFID.nmdata
Comment	:	5-Cl 13C
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	500 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	32
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	72 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	25.7 C



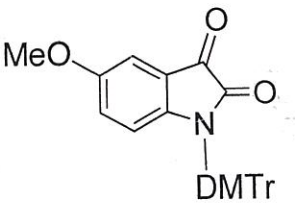
7b

MeO-isatin



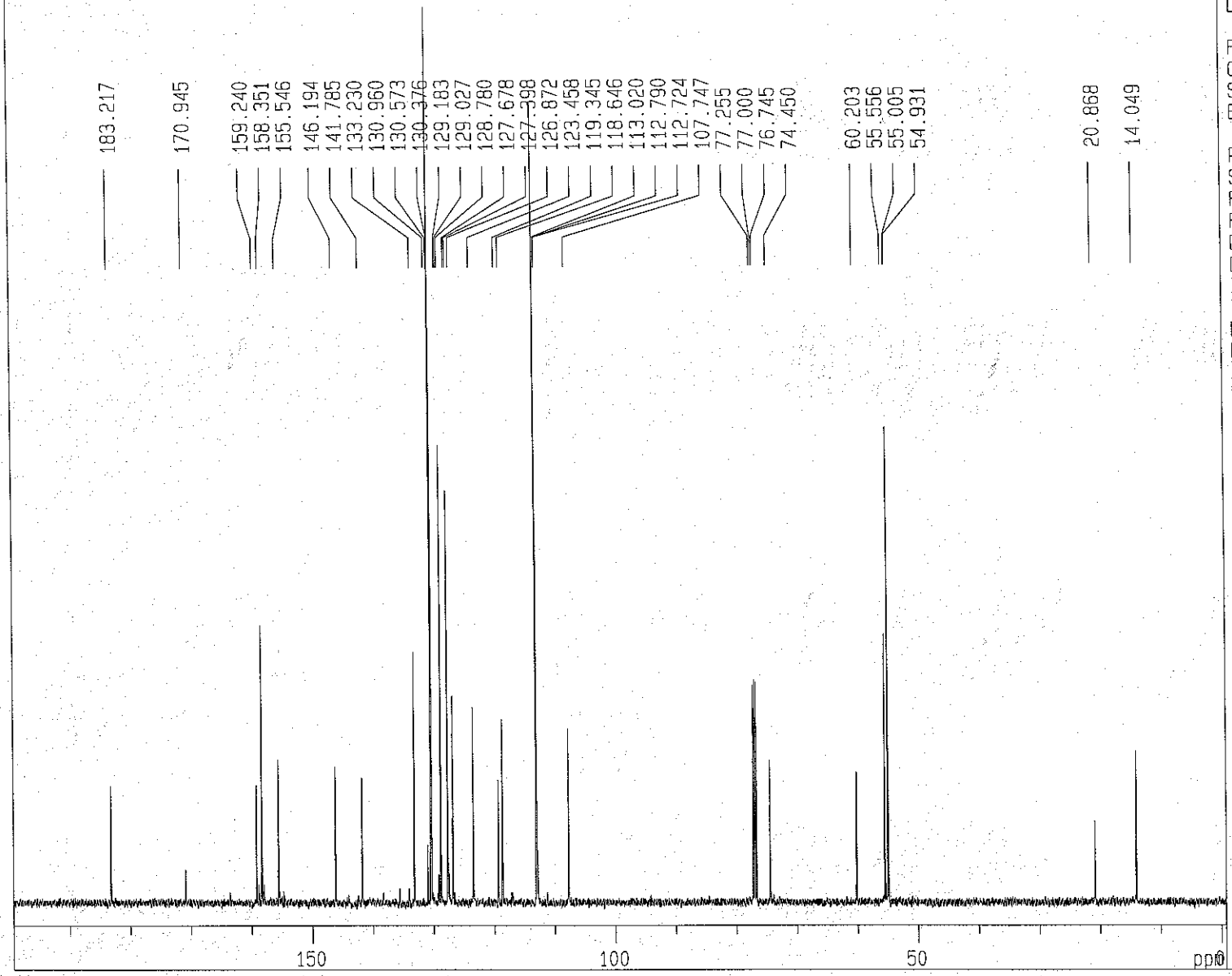
Date : Wed Apr 15 11:48:05 2009

FileName	:	.LoadingFID.nmdata
Comment	:	MeO-isatin
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	20 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	21
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	17 Hz
TEMP	:	25.7 C



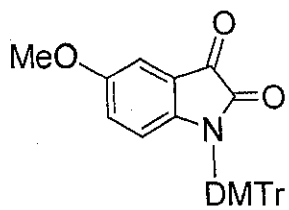
7c

090120-7-48 13C



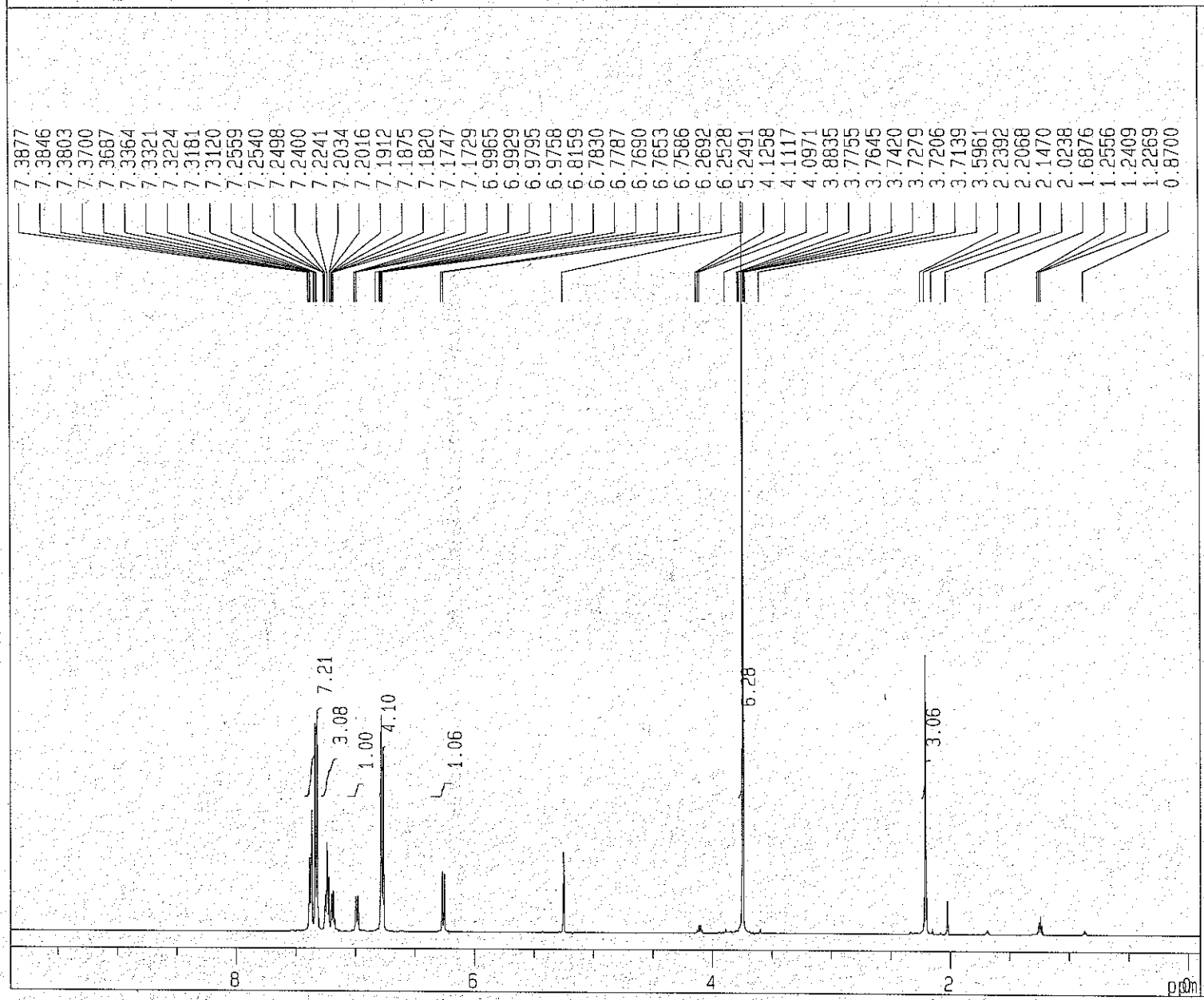
Date : Tue Jan 20 21:05:38 2009

FileName	:	.LoadingFID.nmdata
Comment	:	090120-7-48 13C
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	1000 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	138 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	24.9 C



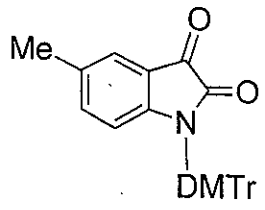
7c

Substrate -Me



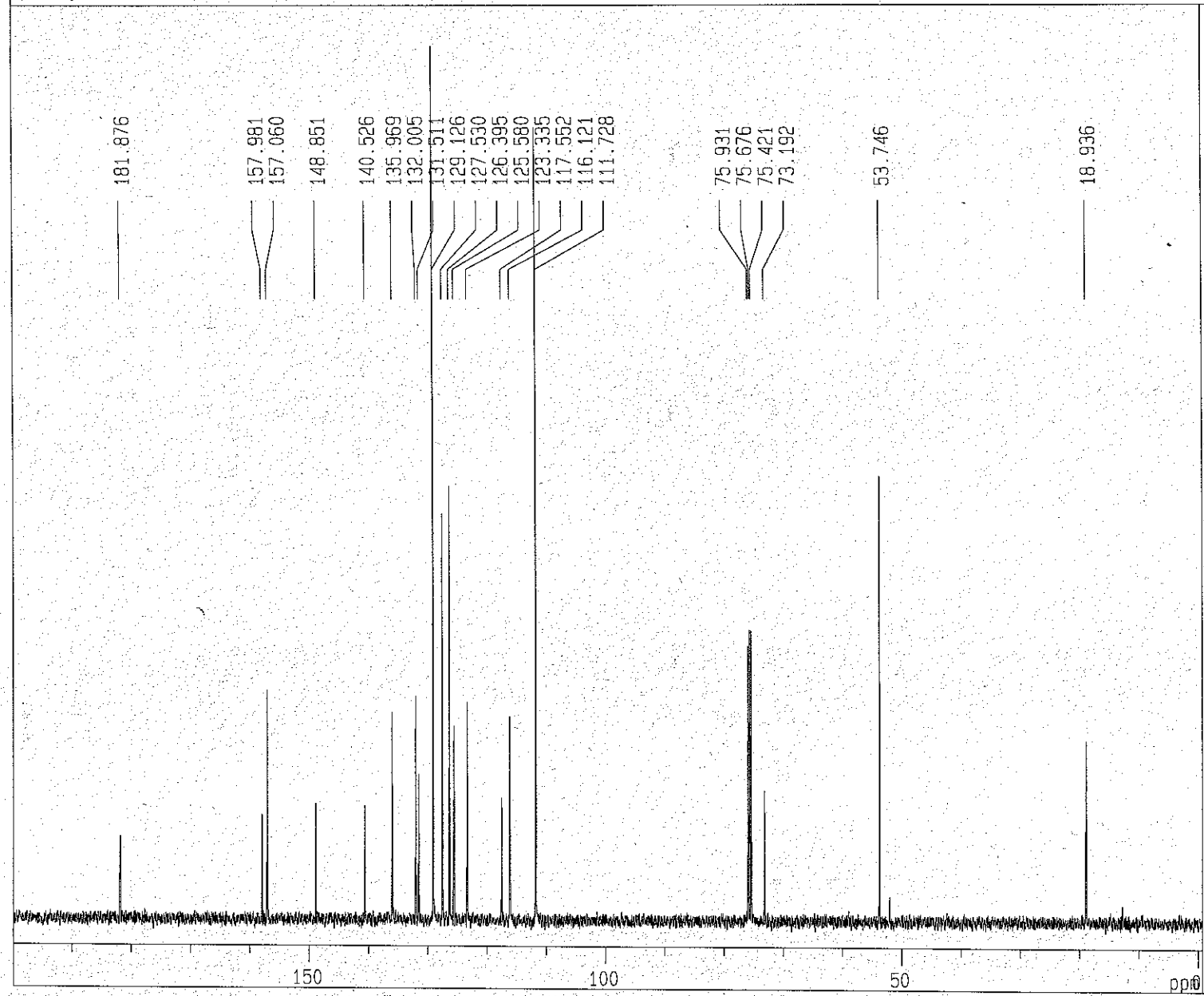
Date : Tue Mar 10 16:15:48 2009

FileName	:	.LoadingFID.nmdata
Comment	:	Substrate -Me
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	300 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	13
SCANS	:	9 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	25.3 C



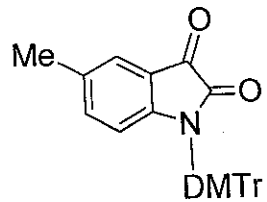
7d

Substrate -Me 13C



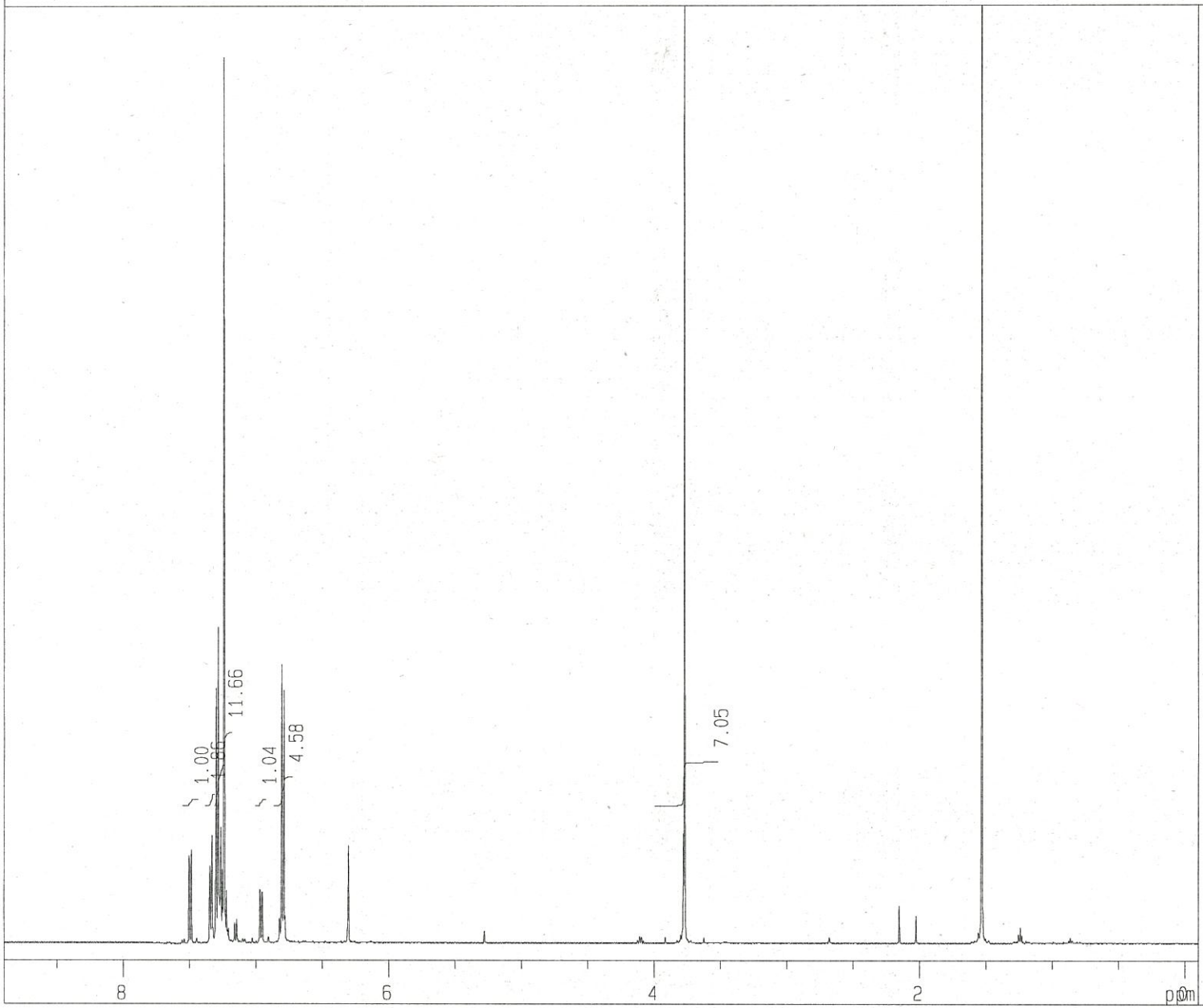
Date : Tue Mar 10 16:12:44 2009

FileName	:	.LoadingFID.nmdata
Comment	:	Substrate -Me 13C
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	300 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	57 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	25.6 C



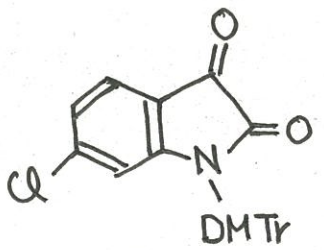
7d

shita



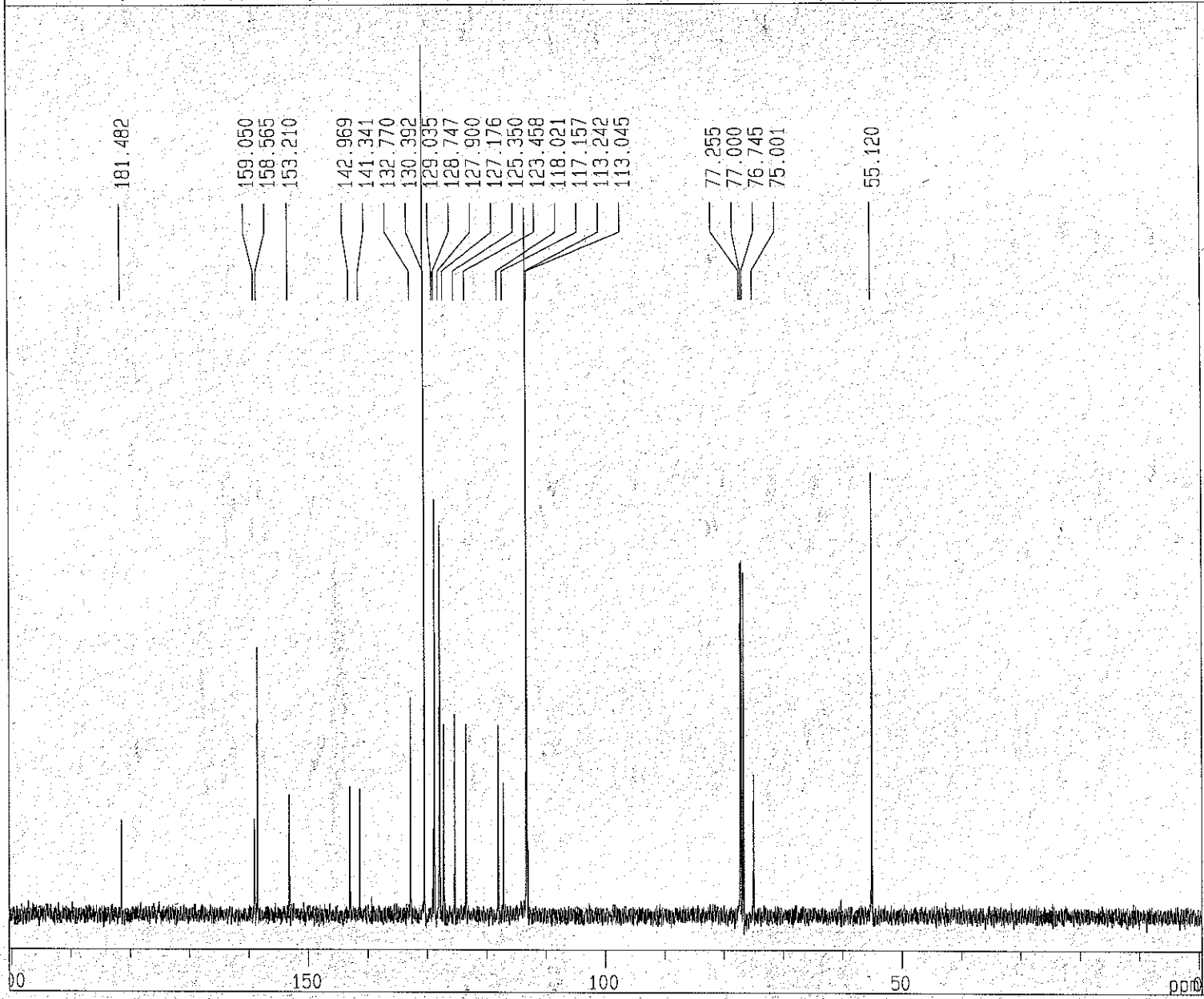
Date : Thu Apr 23 19:29:45 2009

FileName	:	.LoadingFID.nmdata
Comment	:	shita
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	160 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	26
SCANS	:	32 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	25.9 C



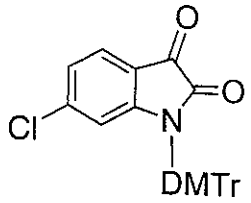
7e

6-Cl 13C



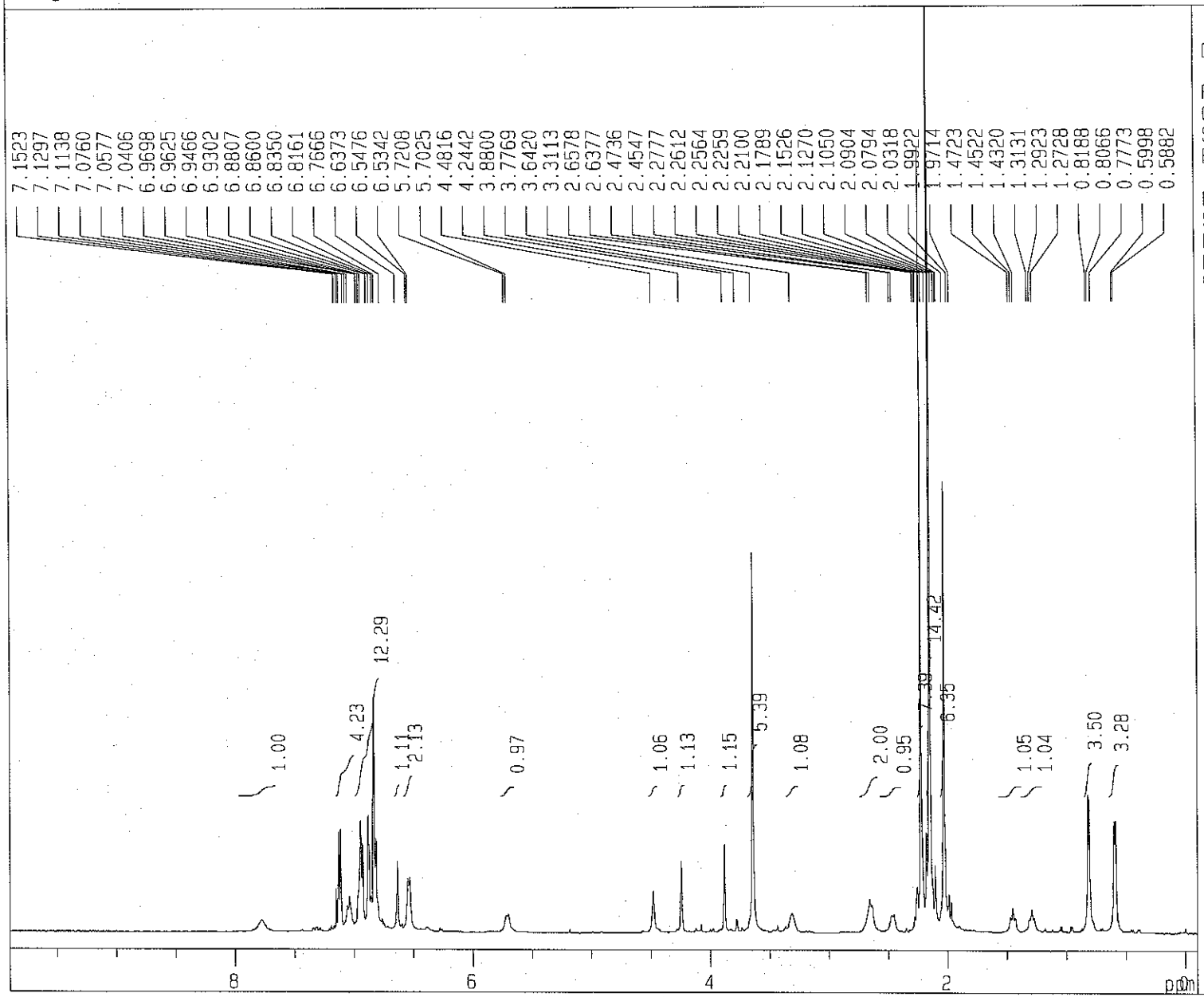
Date : Fri Mar 13 22:40:49 2009

FileName	:	.LoadingFID.nmdata
Comment	:	6-Cl 13C
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	500 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	31
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	77 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	25.4 C



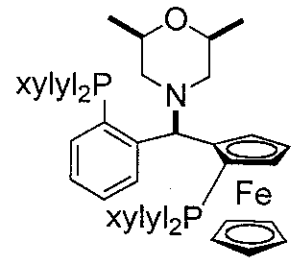
7e

Ligand



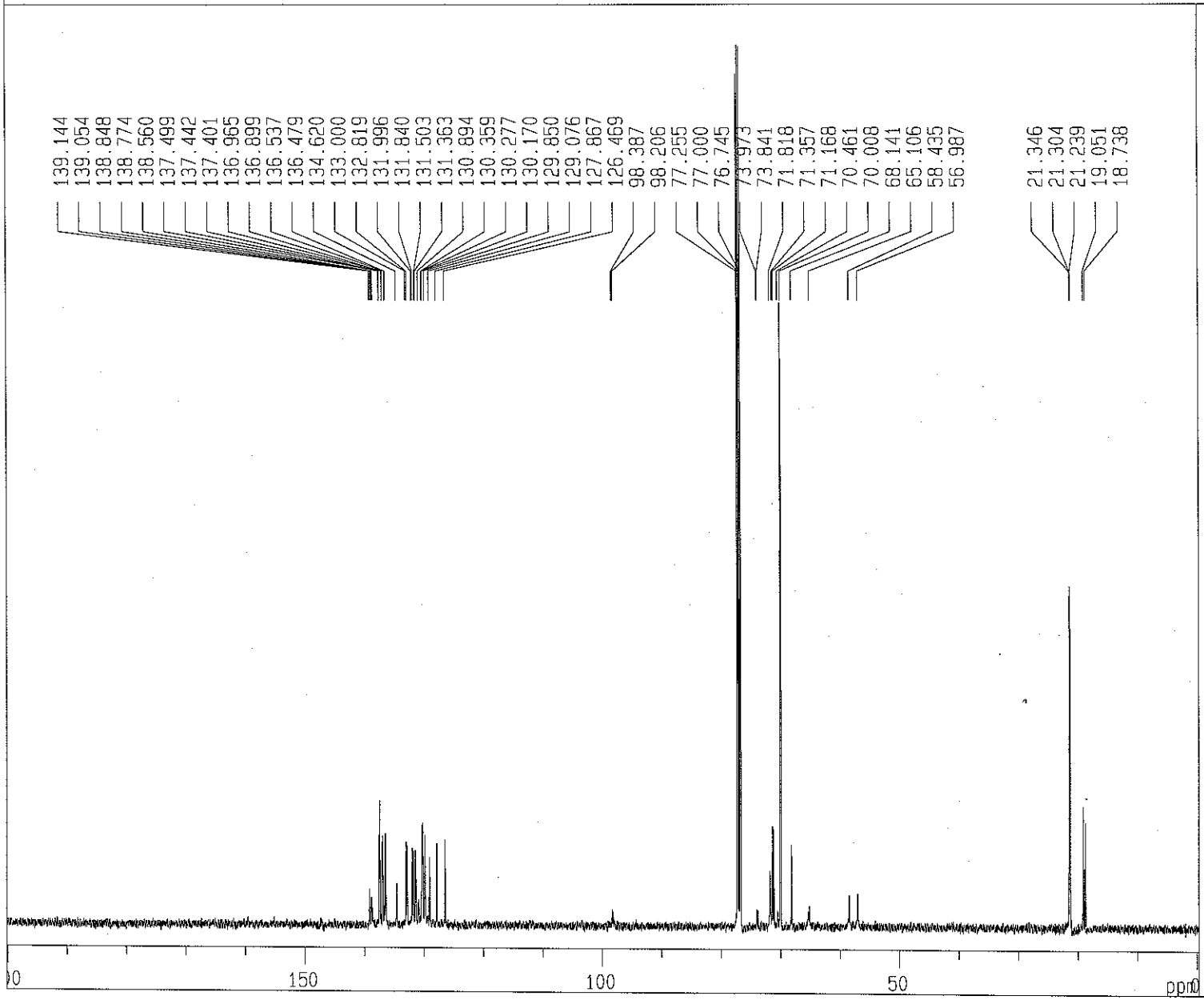
Date : Fri Feb 20 17:09:07 2009

FileName	:	.LoadingFID.nmdata
Comment	:	Ligand
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	10000 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	13
SCANS	:	13 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	24.9 C



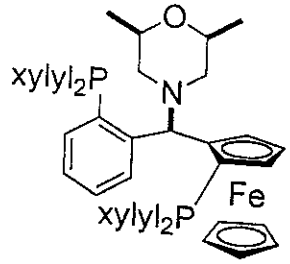
6

Ligand

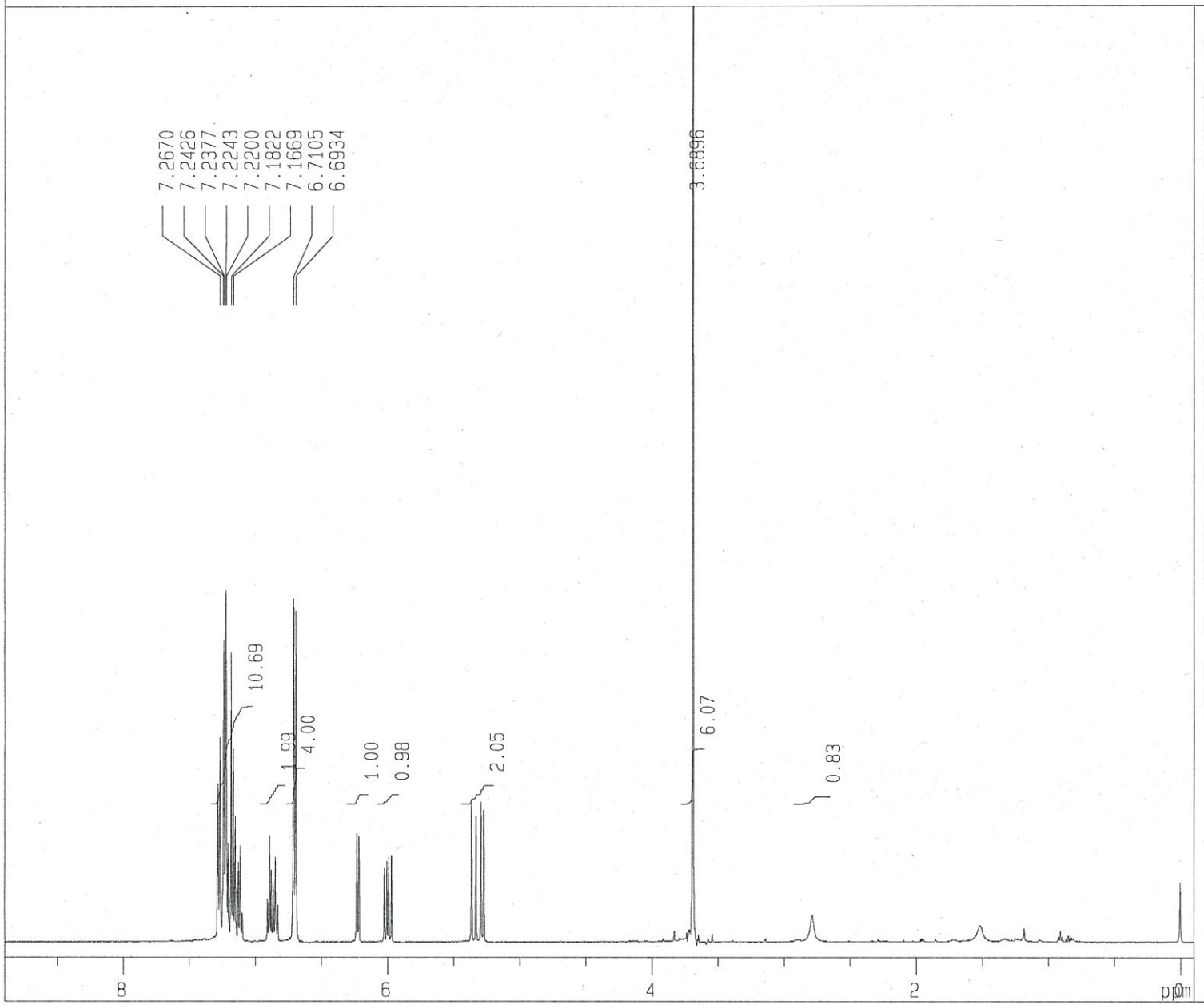


Date : Fri Feb 20 17:25:20 2009

FileName	:	.LoadingFID.nmdata
Comment	:	Ligand
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	10000 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	300 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	

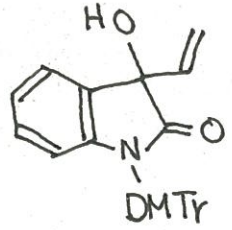


nor-vinyl



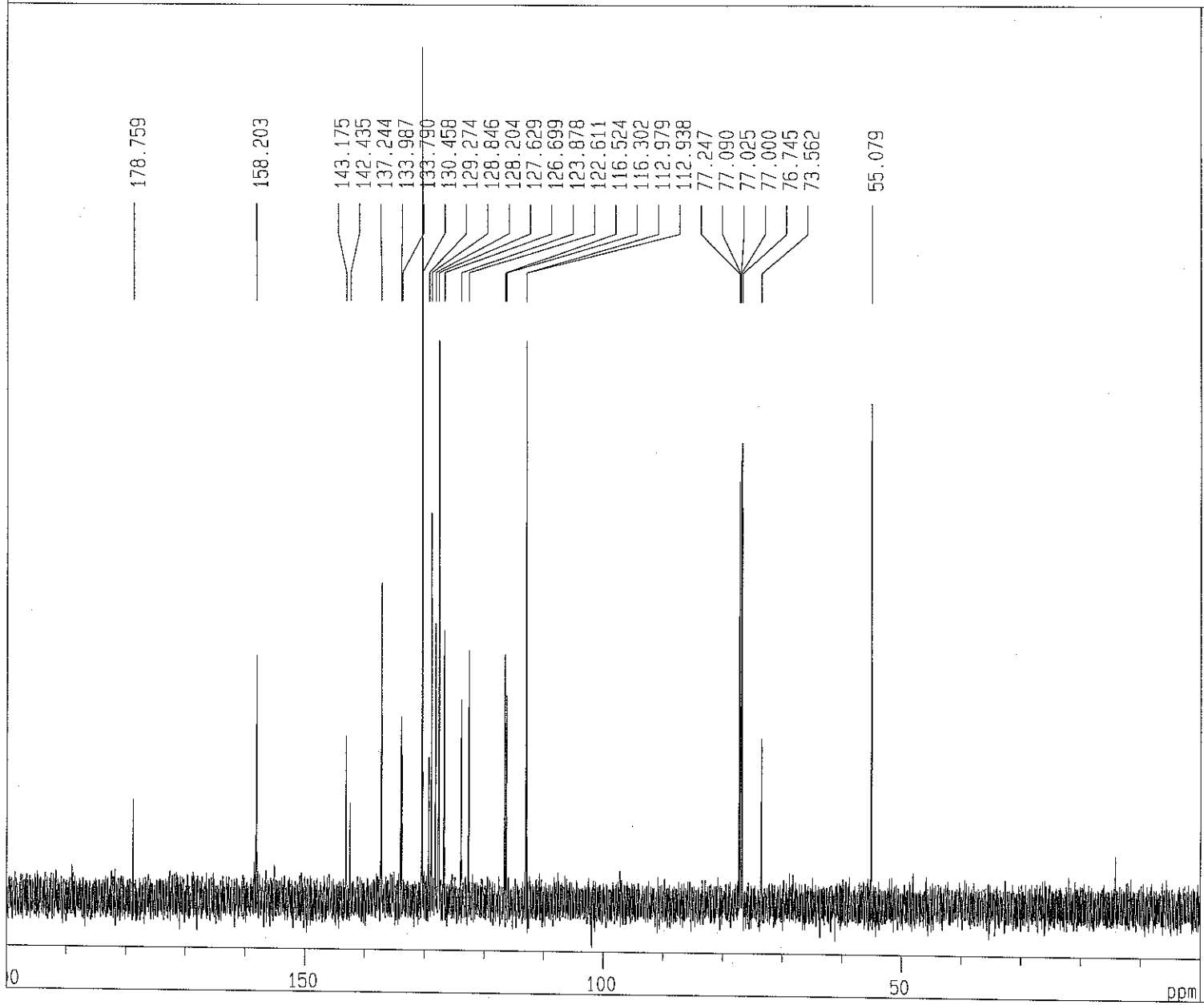
Date : Wed Apr 15 11:54:58 2009

FileName	:	.LoadingFID.nmdata
Comment	:	nor-vinyl
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	20 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	20
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	20 Hz
TEMP	:	25.9 C



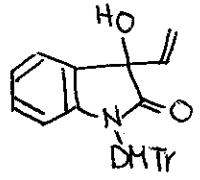
8aa

nor



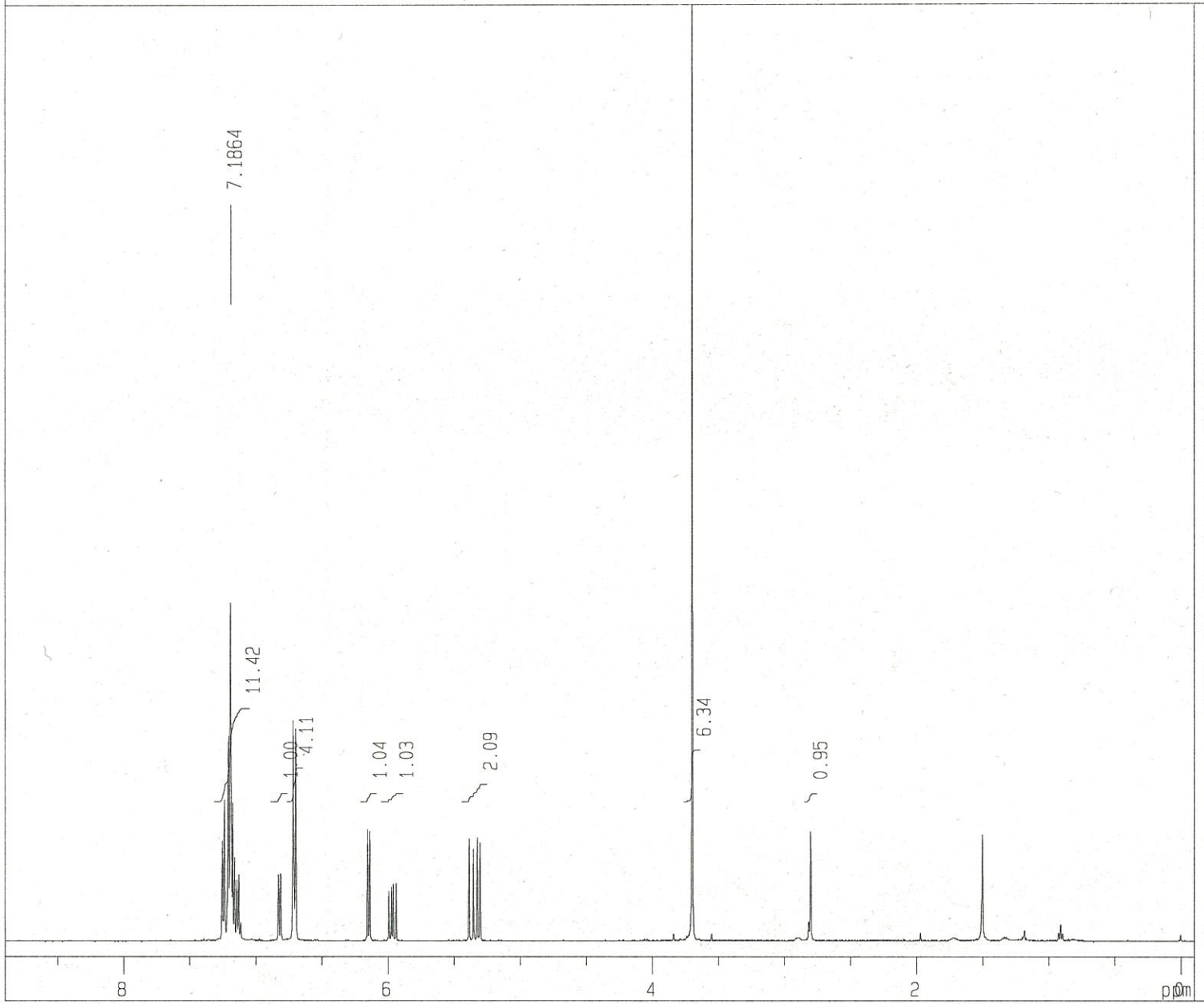
Date : Wed Feb 4 10:05:30 2009

FileName	:	.LoadingFID.nmdata
Comment	:	nor
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	3200 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	31
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	56 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	23.5 C



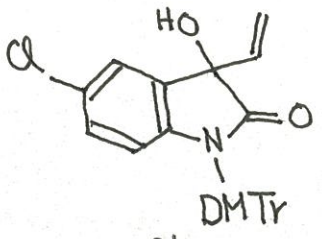
829

5-Cl-vinyl



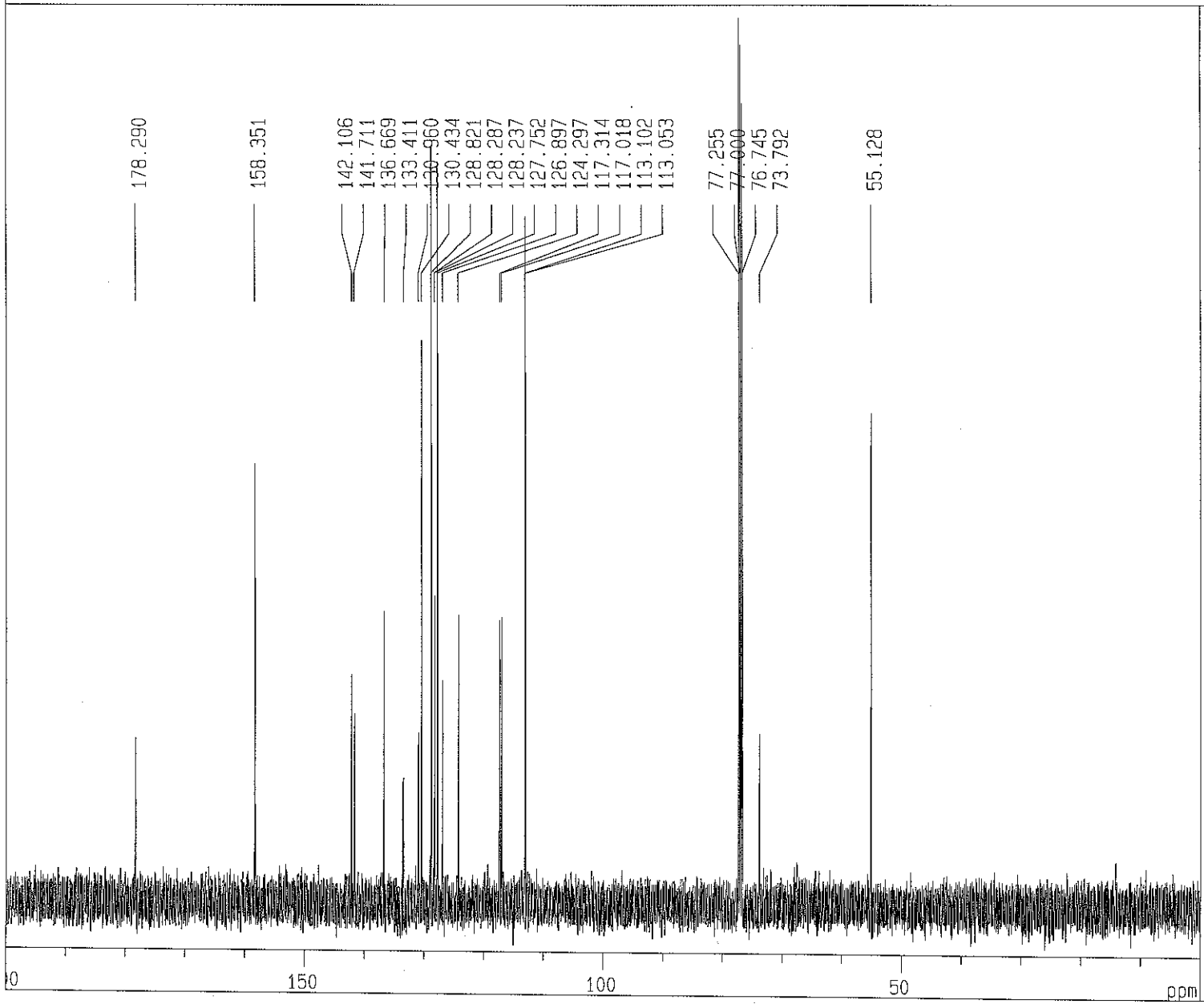
Date : Wed Apr 15 11:59:04 2009

FileName	:	.LoadingFID.nmdata
Comment	:	4-Cl-vinyl
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	20 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	21
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	21 Hz
TEMP	:	26.1 C



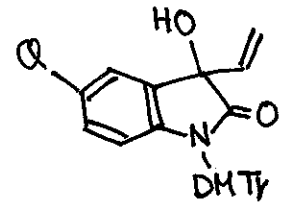
8ba

5-Cl



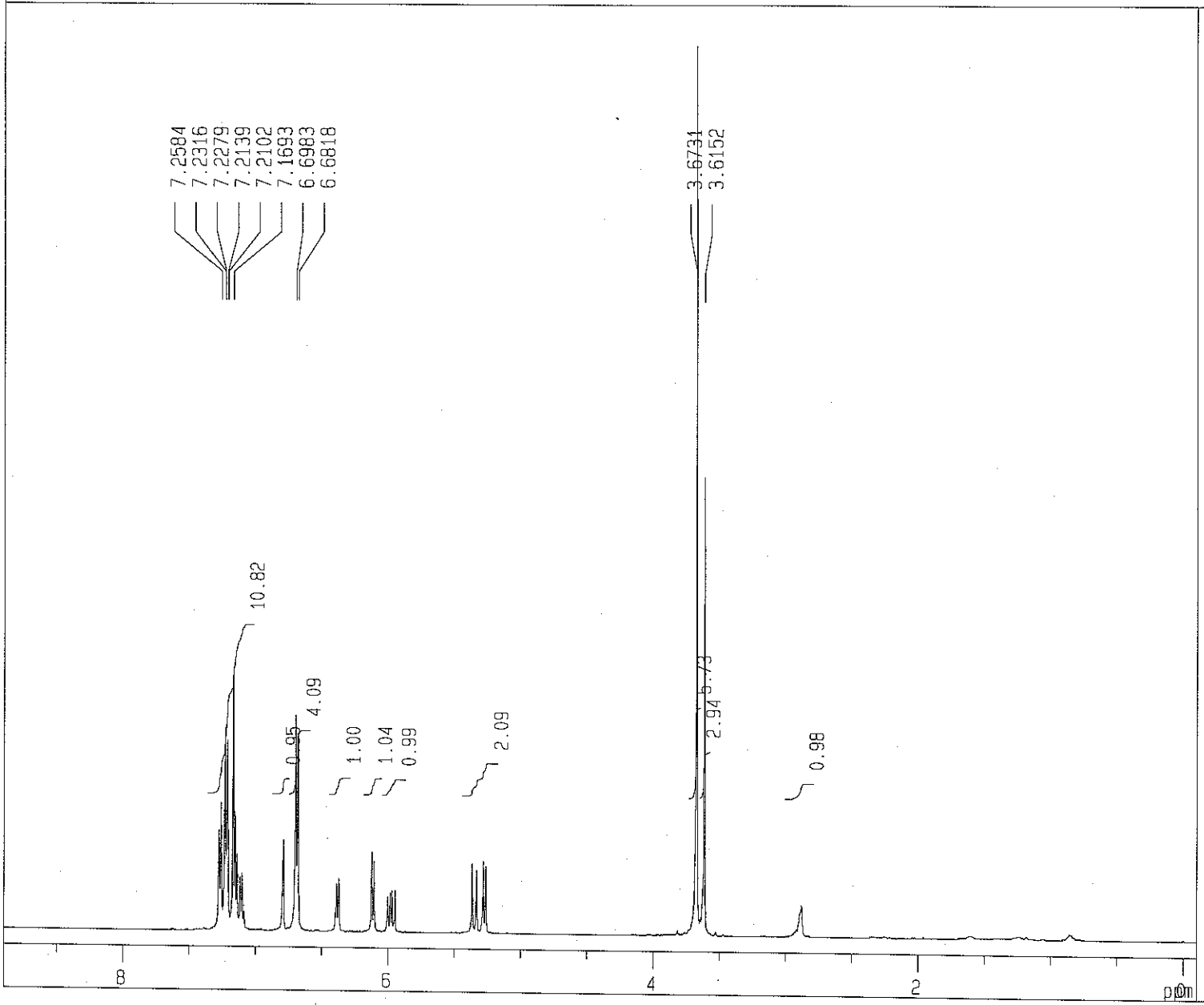
Date : Tue Feb 3 10:36:18 2009

FileName	:	.LoadingFID.nmdata
Comment	:	5-Cl
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	400 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	31
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	88 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	24.8 C



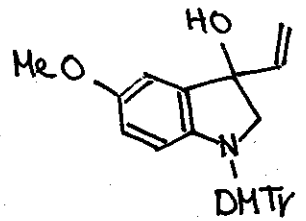
8ba

MeO



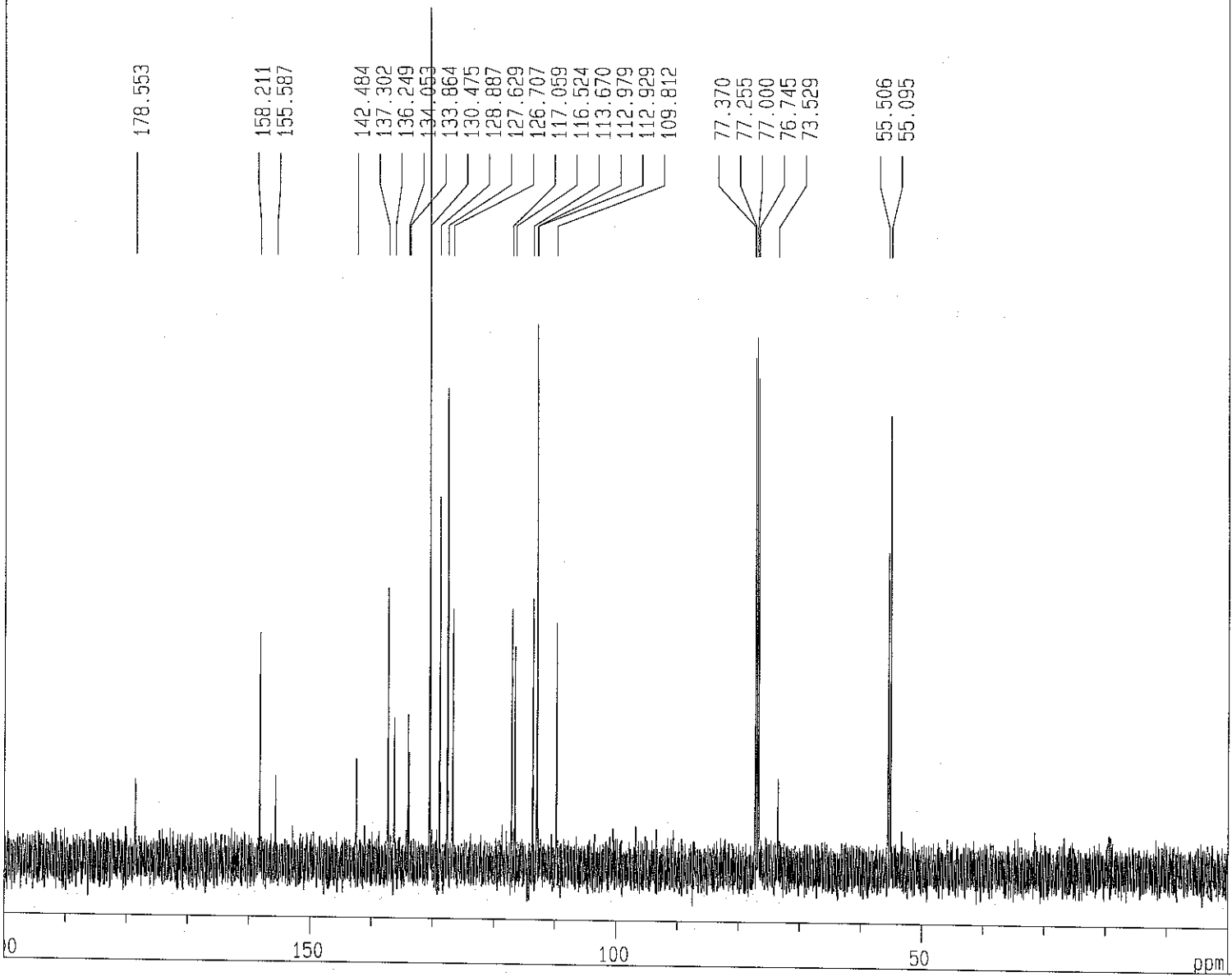
Date : Tue Feb 3 11:21:58 2009

FileName	:	.LoadingFID.nmdata
Comment	:	5-
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	400 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	16
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	23.9 C



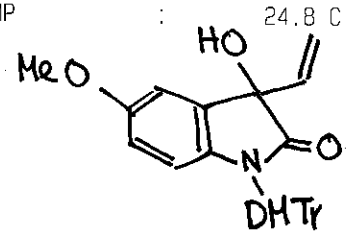
8'cg

OMe



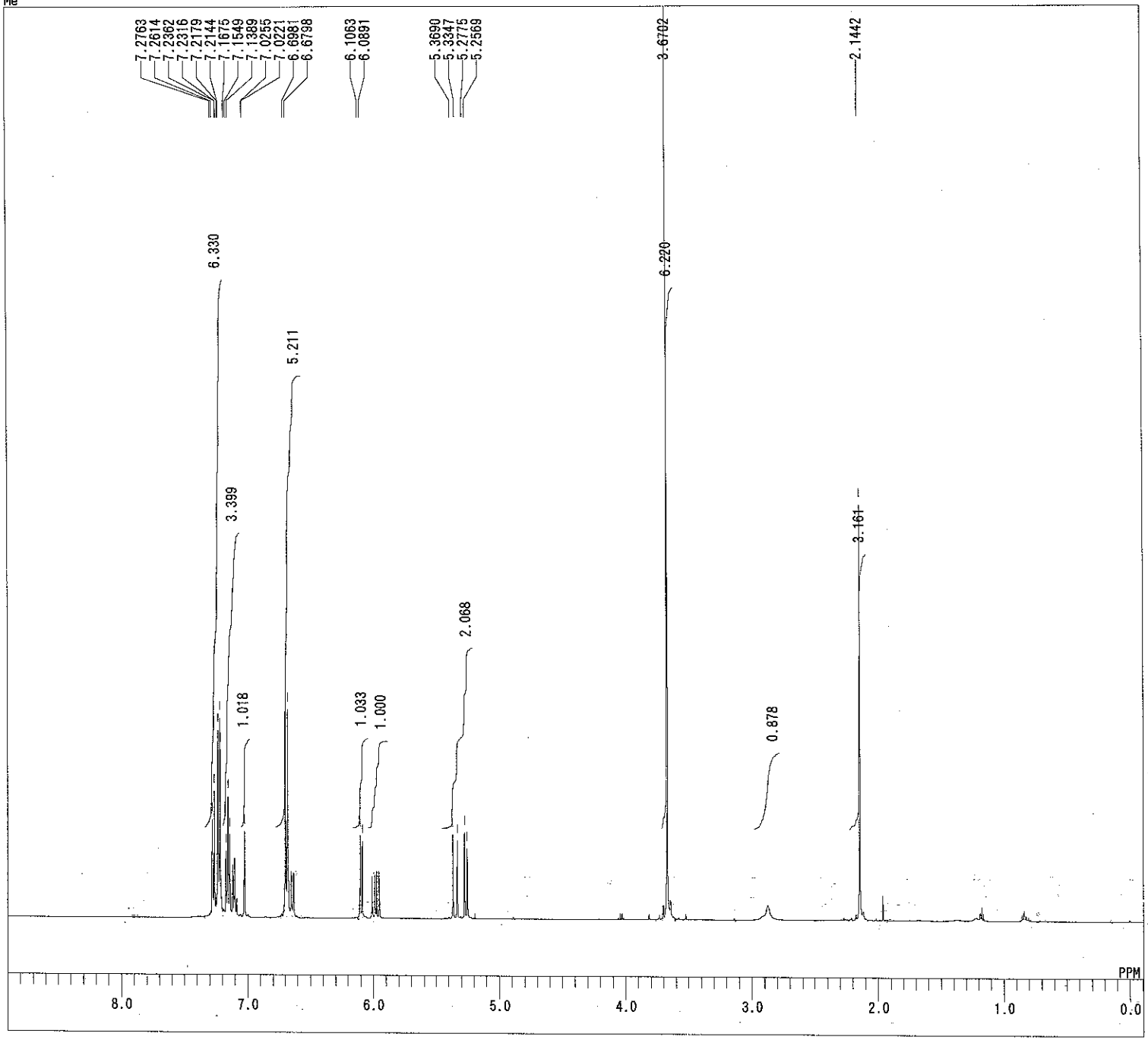
Date : Tue Feb 3 15:01:11 2009

FileName	:	.LoadingFID.nmdata
Comment	:	OMe
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	100 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	60 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	24.8 C

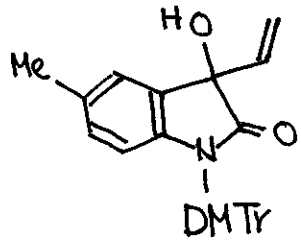


80a

C:¥My Documents¥PGousei¥KANAI¥single_pulse.53
Me

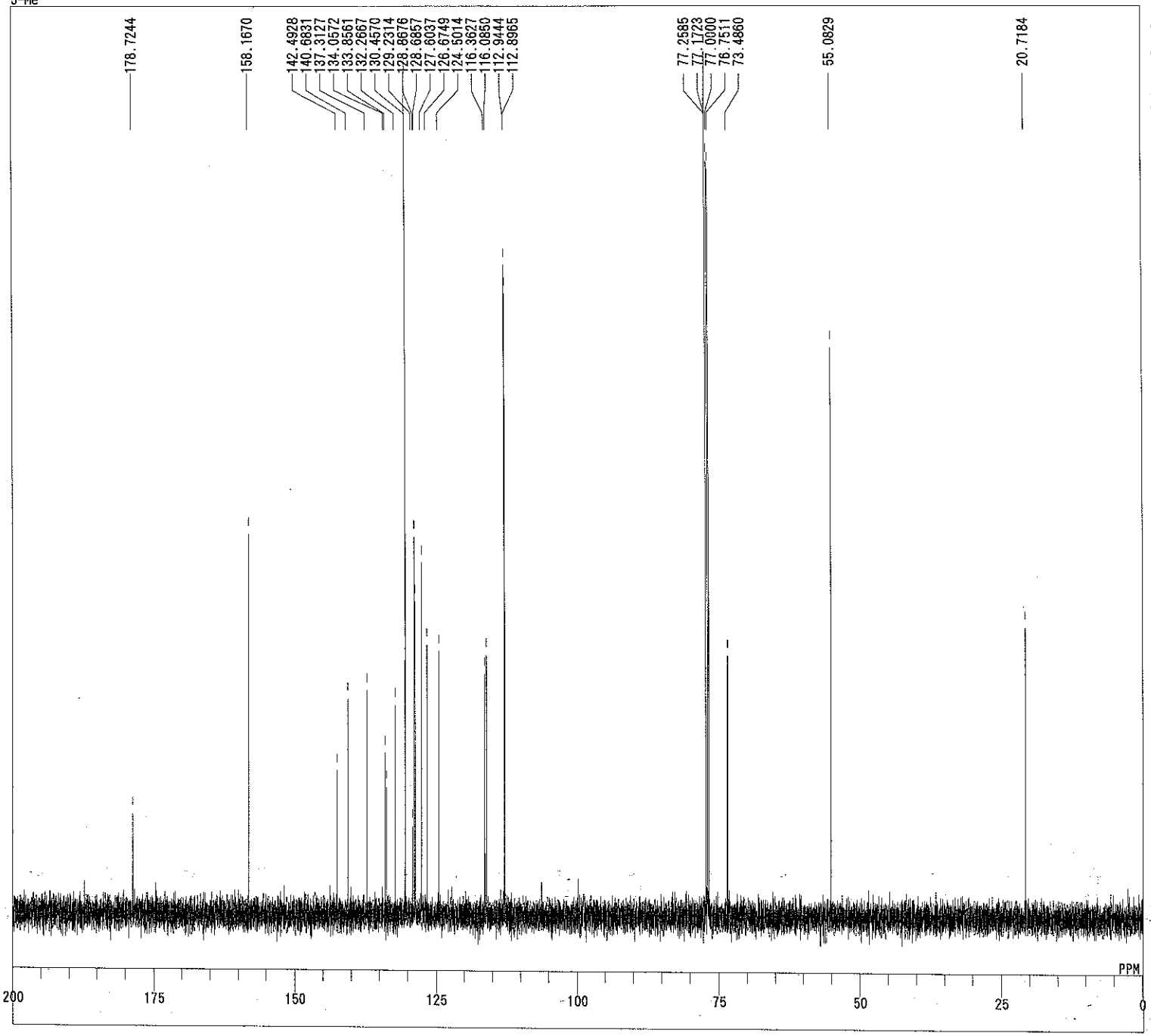


DFILE C:¥My Documents¥PGousei¥KANAI¥single_pulse.53
COMNT Me
DATIM 02-02-2009 20:59:24
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
POINT 16384
FREQU 9286.78 Hz
SCANS 4
ACQTM 1.7642 sec
PD 5.0000 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 17.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.01 Hz
RGAIN 40

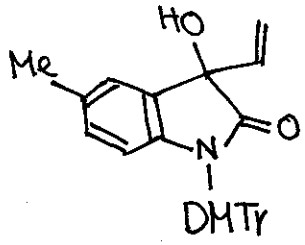


8da

C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.11
5-Me

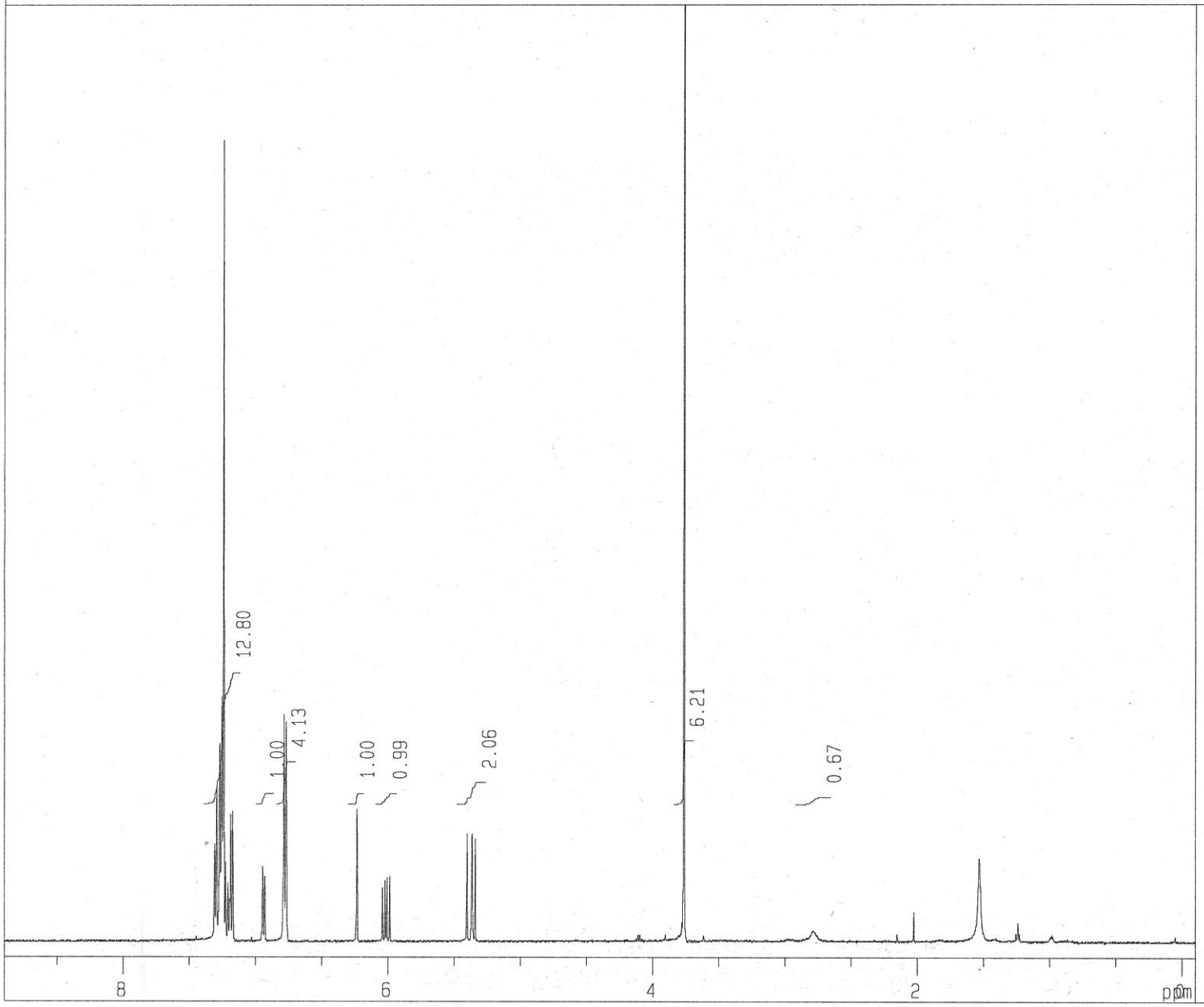



```
DFILE  C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.11
COMNT  5-Me
DATIM  02-02-2009 21:05:47
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        124.51 MHz
OBSET          3.45 KHz
OBFIN          6.00 Hz
POINT         32768
FREQU      39062.50 Hz
SCANS           113
ACQTM        0.8389 sec
PD           2.0000 sec
PW1             3.57 usec
IRNUC  1H
CTEMP          18.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.01 Hz
RGAIN            60
```



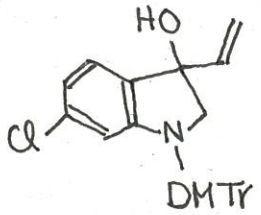
8da

6-Cl-vinyl



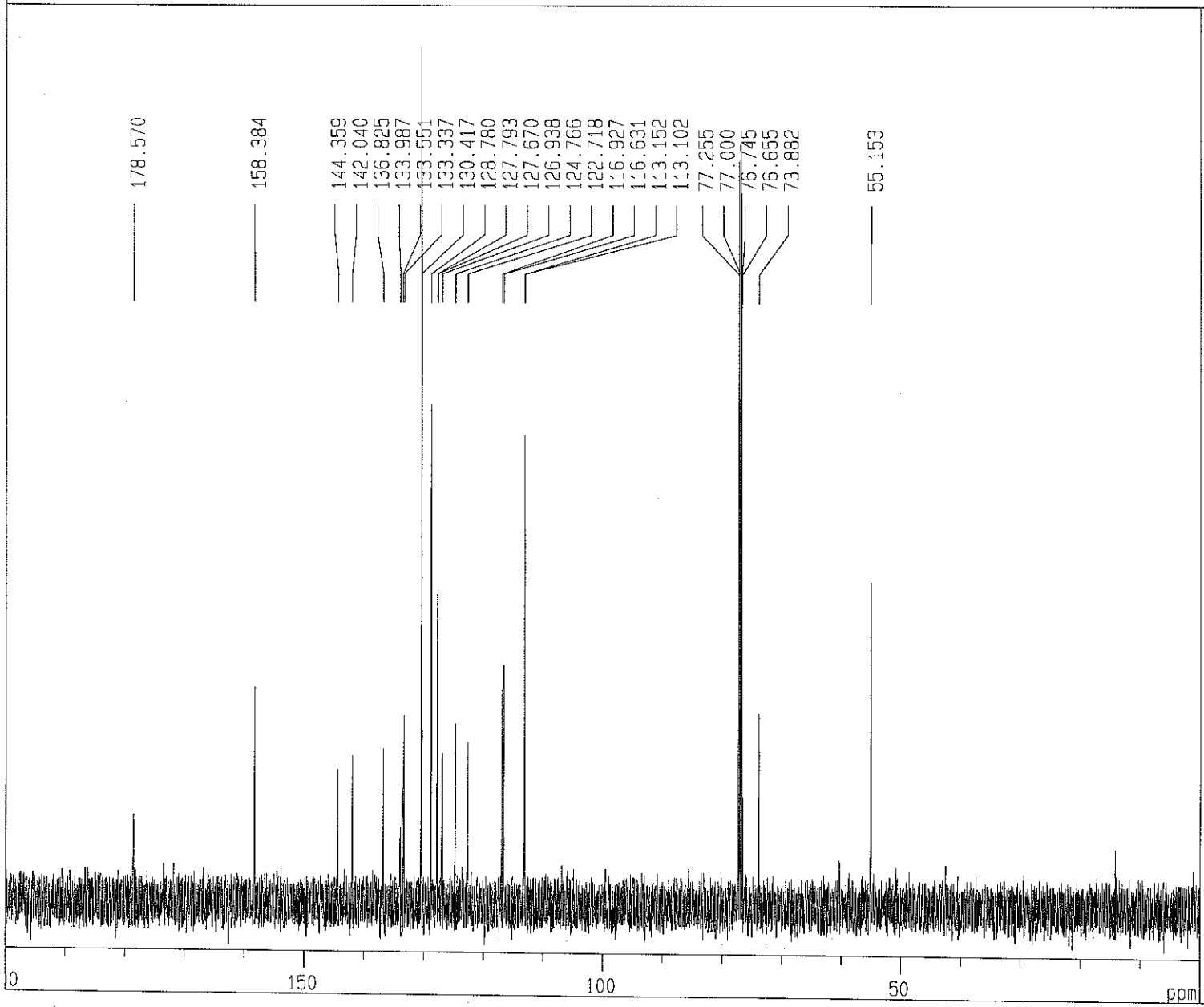
Date : Wed Apr 15 12:03:56 2009

FileName	:	.LoadingFID.nmdata
Comment	:	5-Cl-vinyl
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	20 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	25
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	19 Hz
TEMP	:	26.2 C



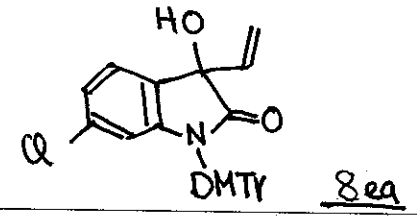
8ea

6-Cl

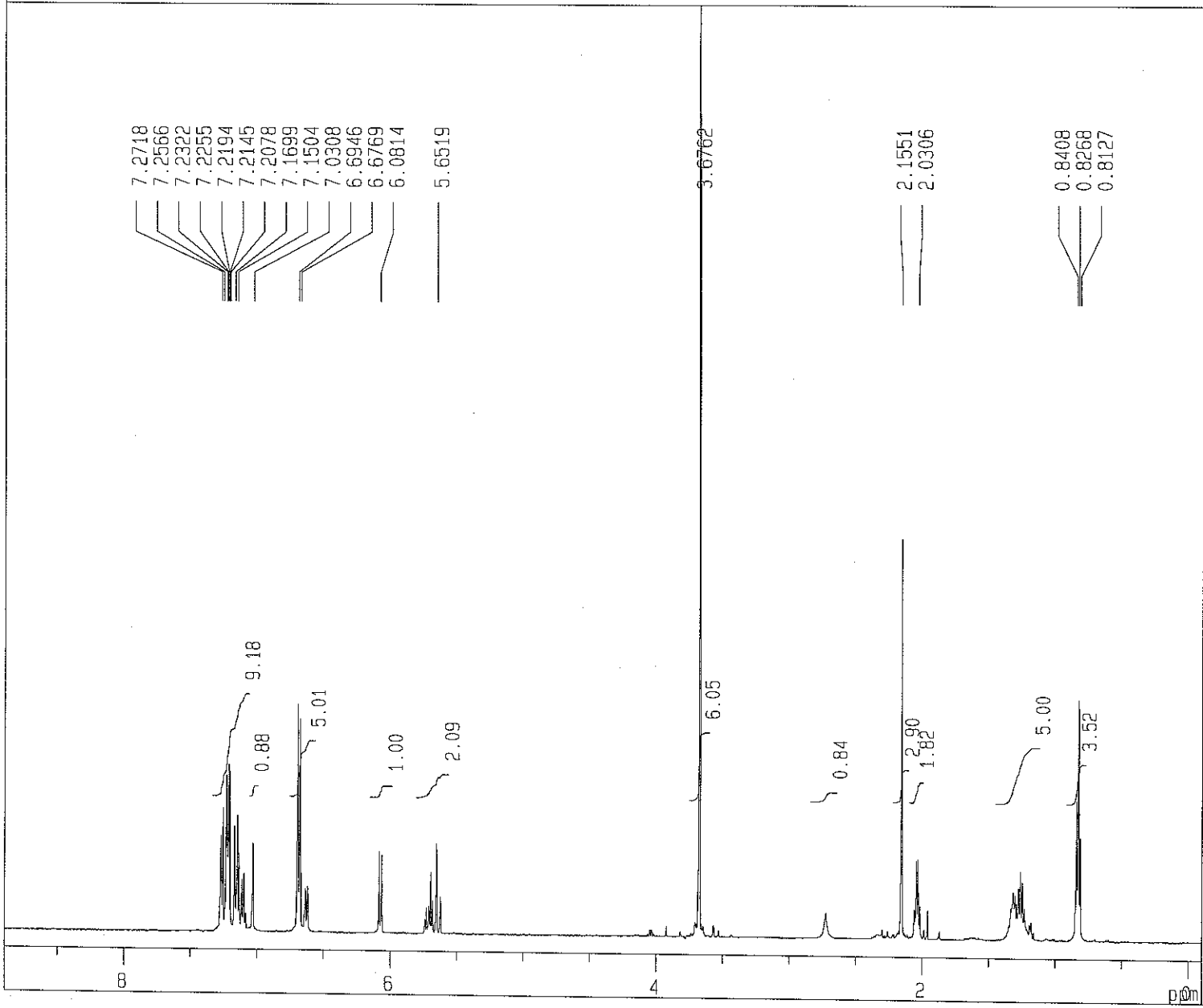


Date : Tue Feb 3 10:44:43 2009

FileName	:	.LoadingFID.nmdata
Comment	:	6-Cl
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	400 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	60 times
SLVNT	:	CDCL3
SPINNING	:	9 Hz
TEMP	:	25.3 C

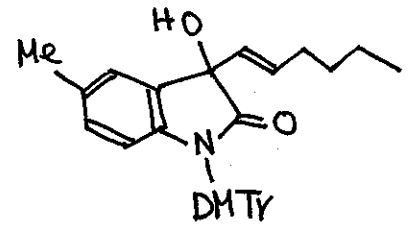


Me long chain



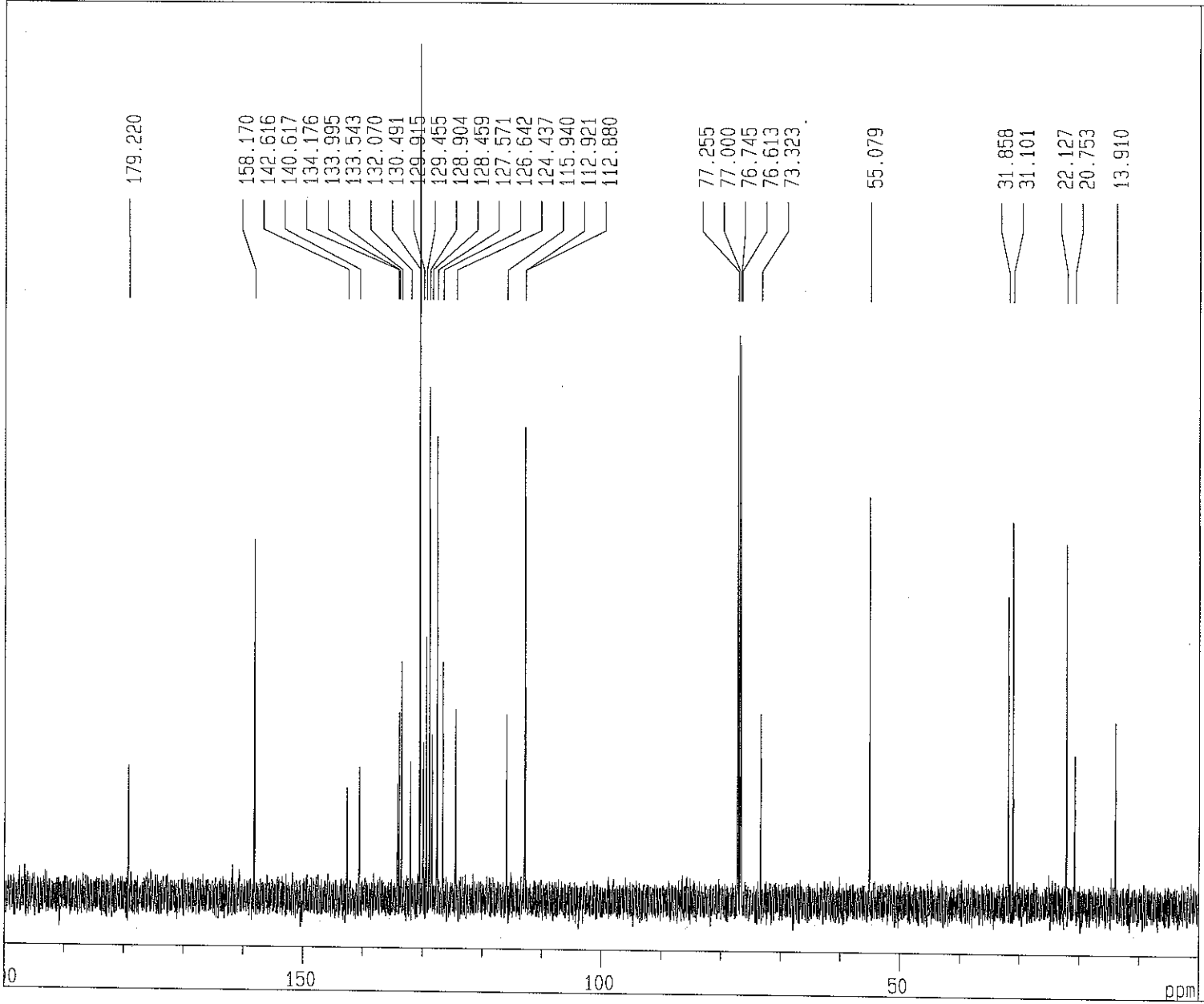
Date : Wed Feb 4 10:32:09 2009

FileName	:	.LoadingFID.nmdata
Comment	:	Me long chain
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	3200 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	16
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	9 Hz
TEMP	:	24.6 C



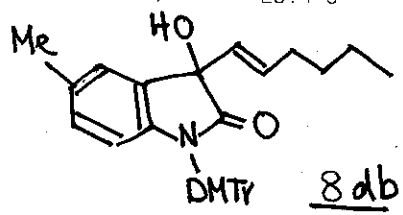
8db

Me long chain



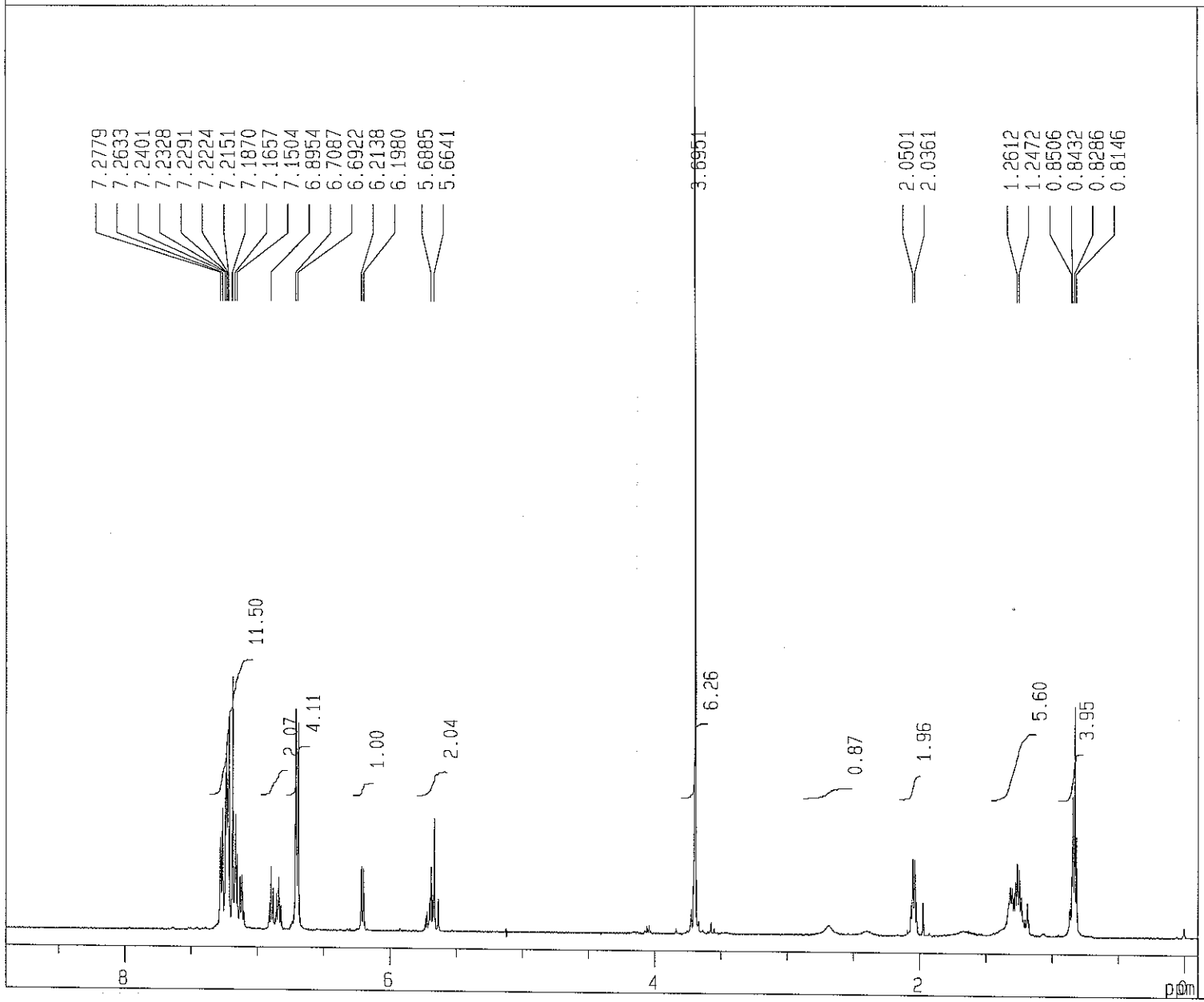
Date : Wed Feb 4 10:36:13 2009

FileName	:	.LoadingFID.nmdata
Comment	:	Me long chain
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	3200 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	31
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	64 times
SLVNT	:	CDCL3
SPINNING	:	10 Hz
TEMP	:	25.4 C



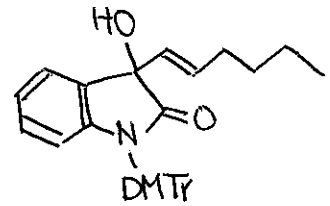
8db

nor-long chain



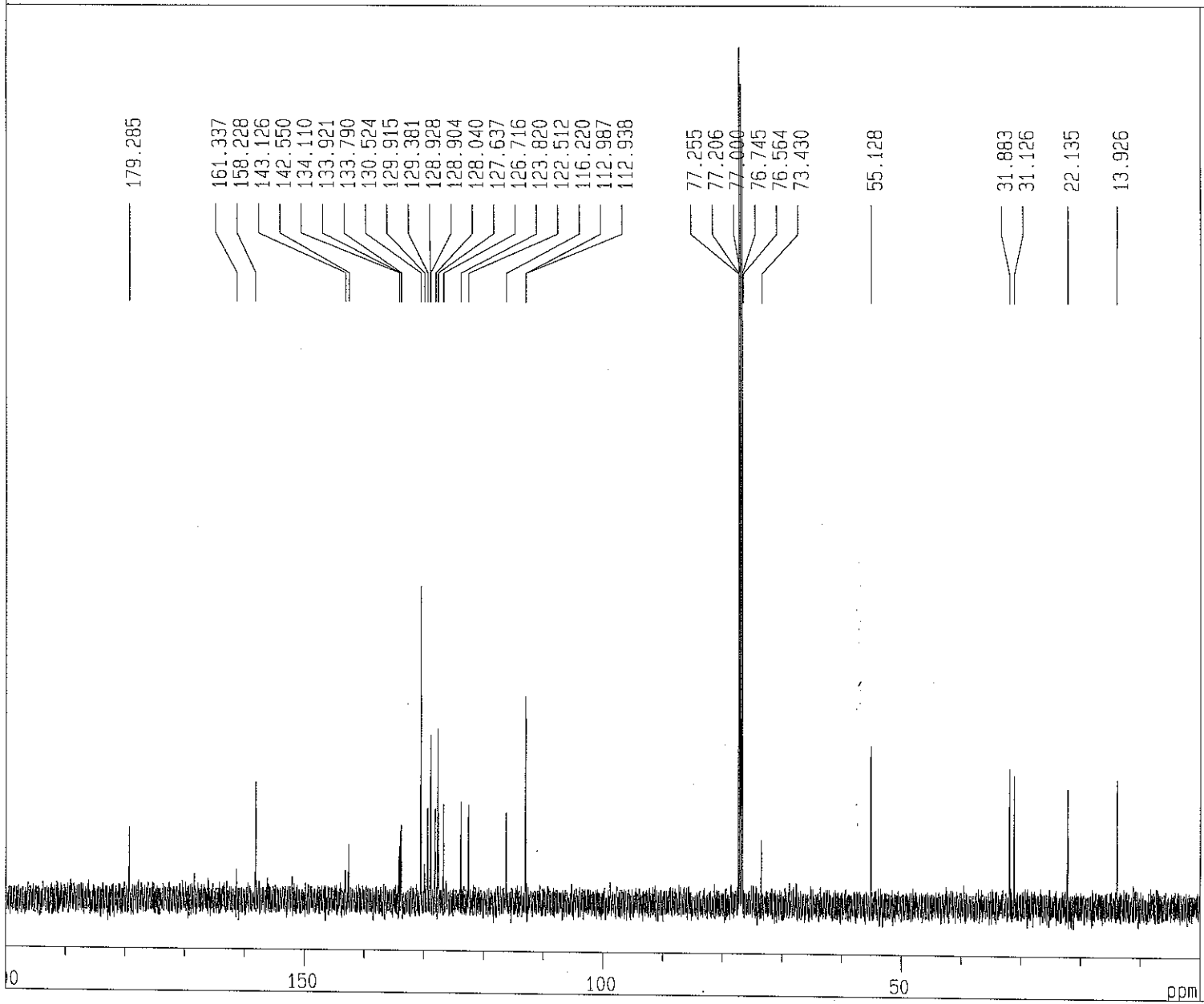
Date : Wed Feb 4 10:09:43 2009

FileName	:	.LoadingFID.nmdata
Comment	:	nor-long chain
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	3200 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	21
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	23.4 C



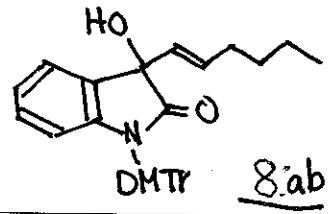
8.ab

nor long chain



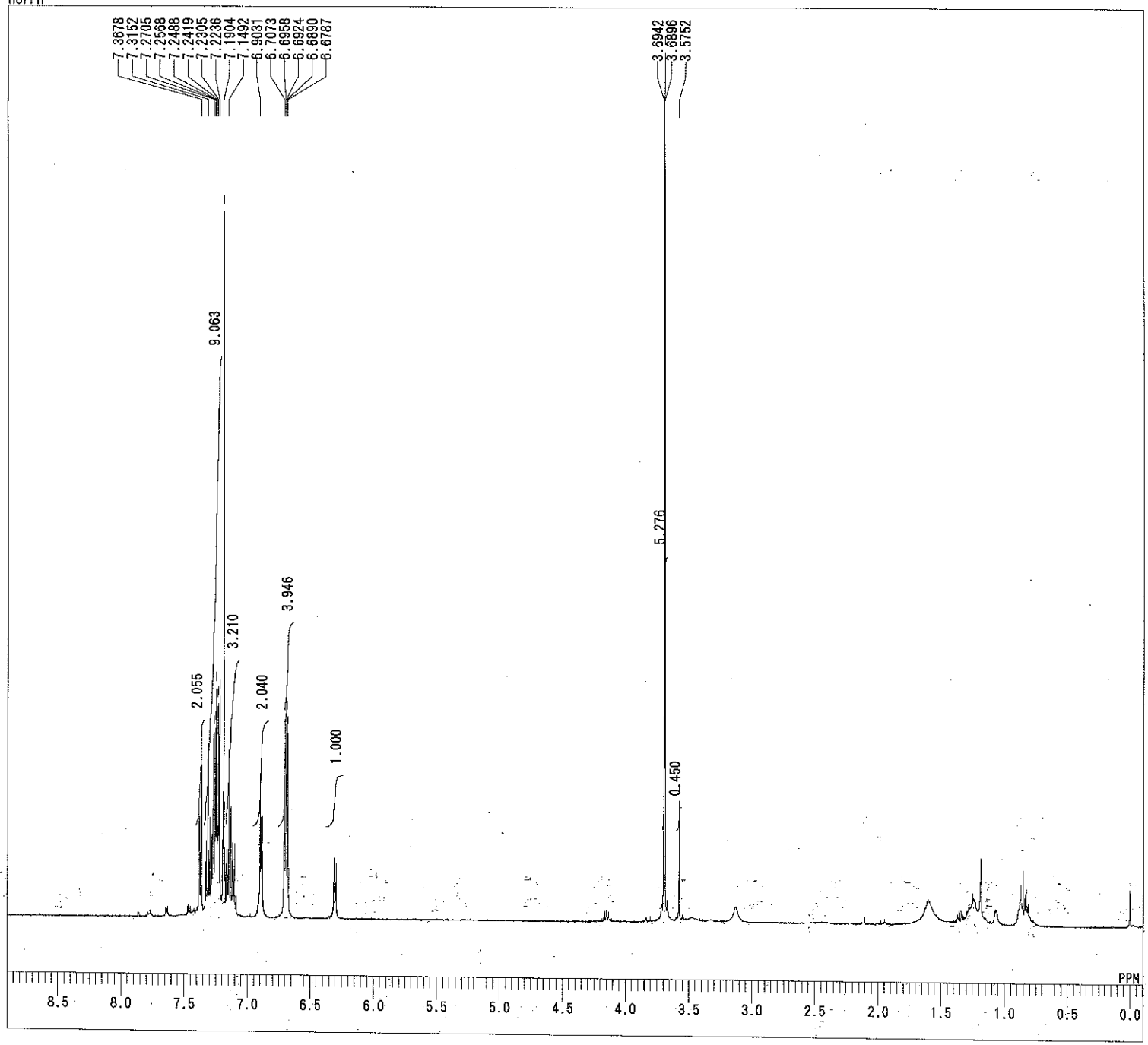
Date : Wed Feb 4 10:26:48 2009

FileName	:	.LoadingFID.nmdata
Comment	:	nor long chain
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	3200 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	300 times
SLVNT	:	CDCL3
SPINNING	:	10 Hz
TEMP	:	24.6 C

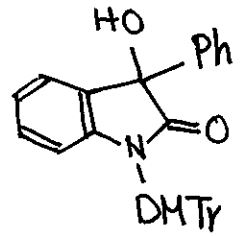


8ab

C:¥My Documents¥PGousei¥KANAI¥single_pulse.63
norPh

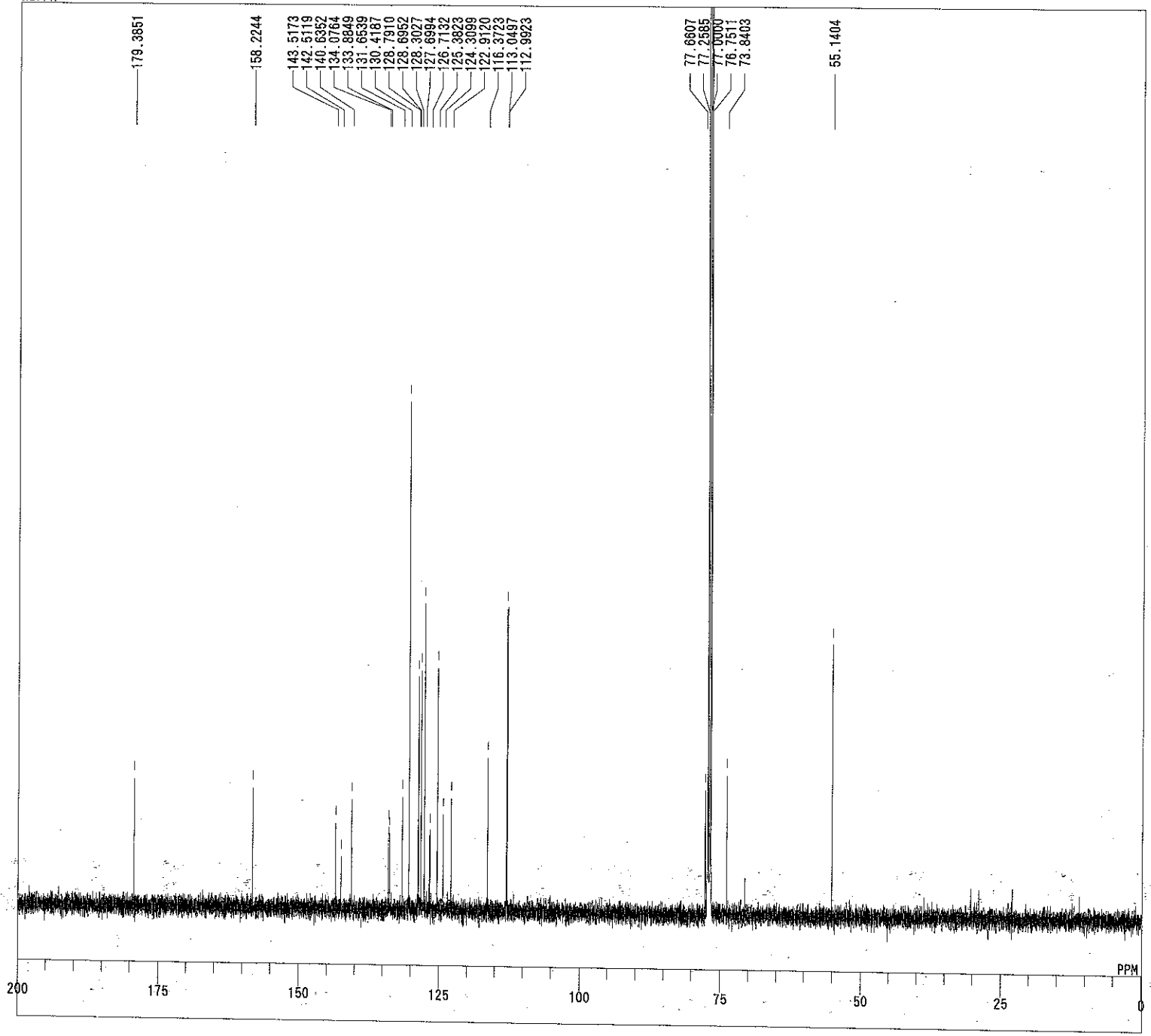


DFILE C:¥My Documents¥PGousei¥KANAI¥single_pulse.63
COMNT norPh
DATIM 05-02-2009 09:26:03
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
POINT 16384
FREQU 9286.78 Hz
SCANS 8
ACQTM 1.7642 sec
PD 5.0000 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 18.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.01 Hz
RGAIN 54

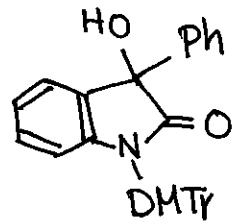


8ac

C:¥My Documents¥PGousei¥KANAI¥phenylation of isatin.1
norPh

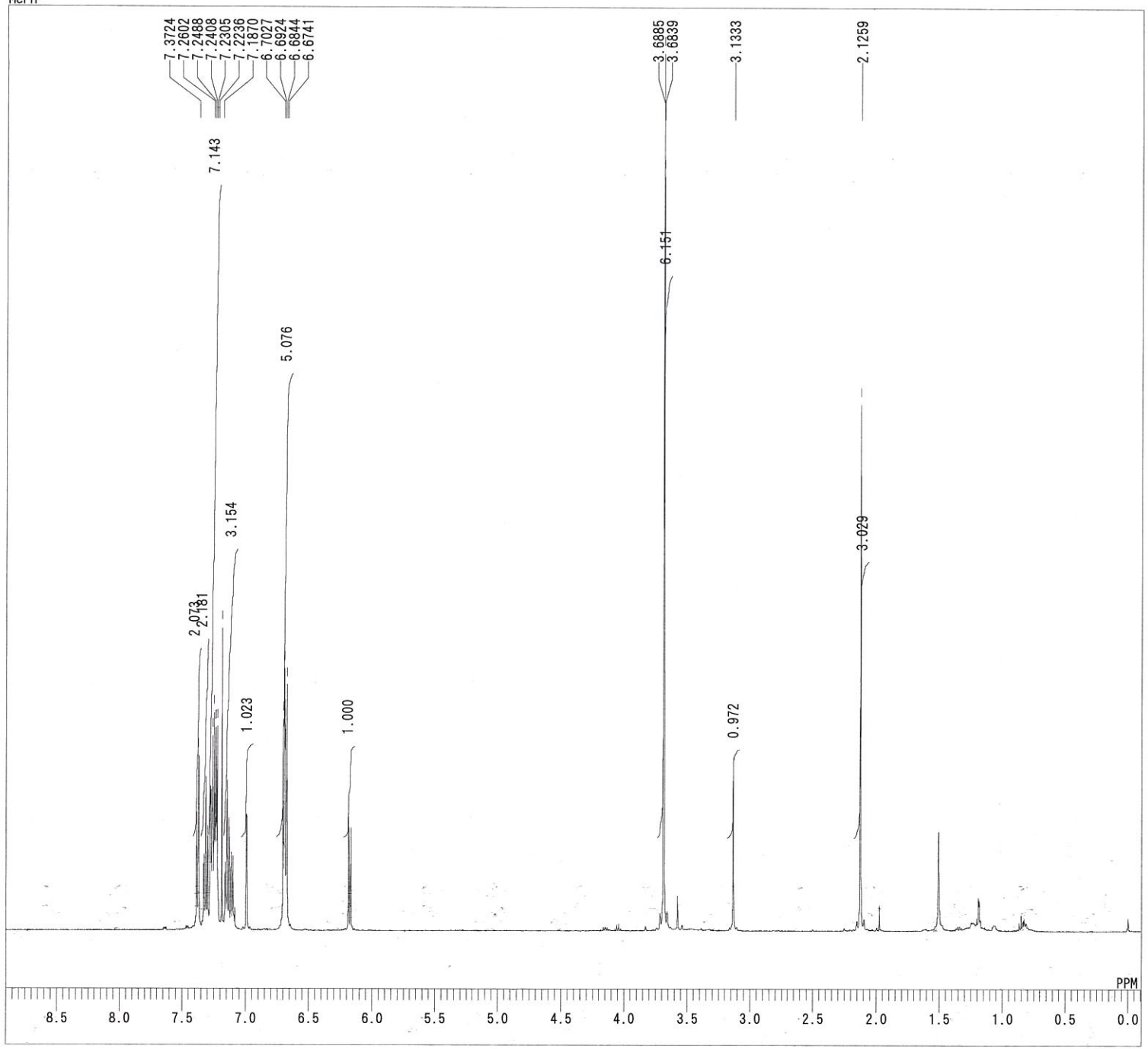


DFILE C:¥My Documents¥PGousei¥KANAI¥phenylation of isatin.1
COMNT norPh
DATIM 05-02-2009 08:12:09
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32768
FREQU 39062.50 Hz
SCANS 11500
ACQTM 0.8389 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 19.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 60

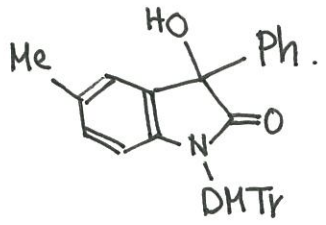


8ac

C:¥My Documents¥PGousei¥KANAI¥single_pulse.64
MePh

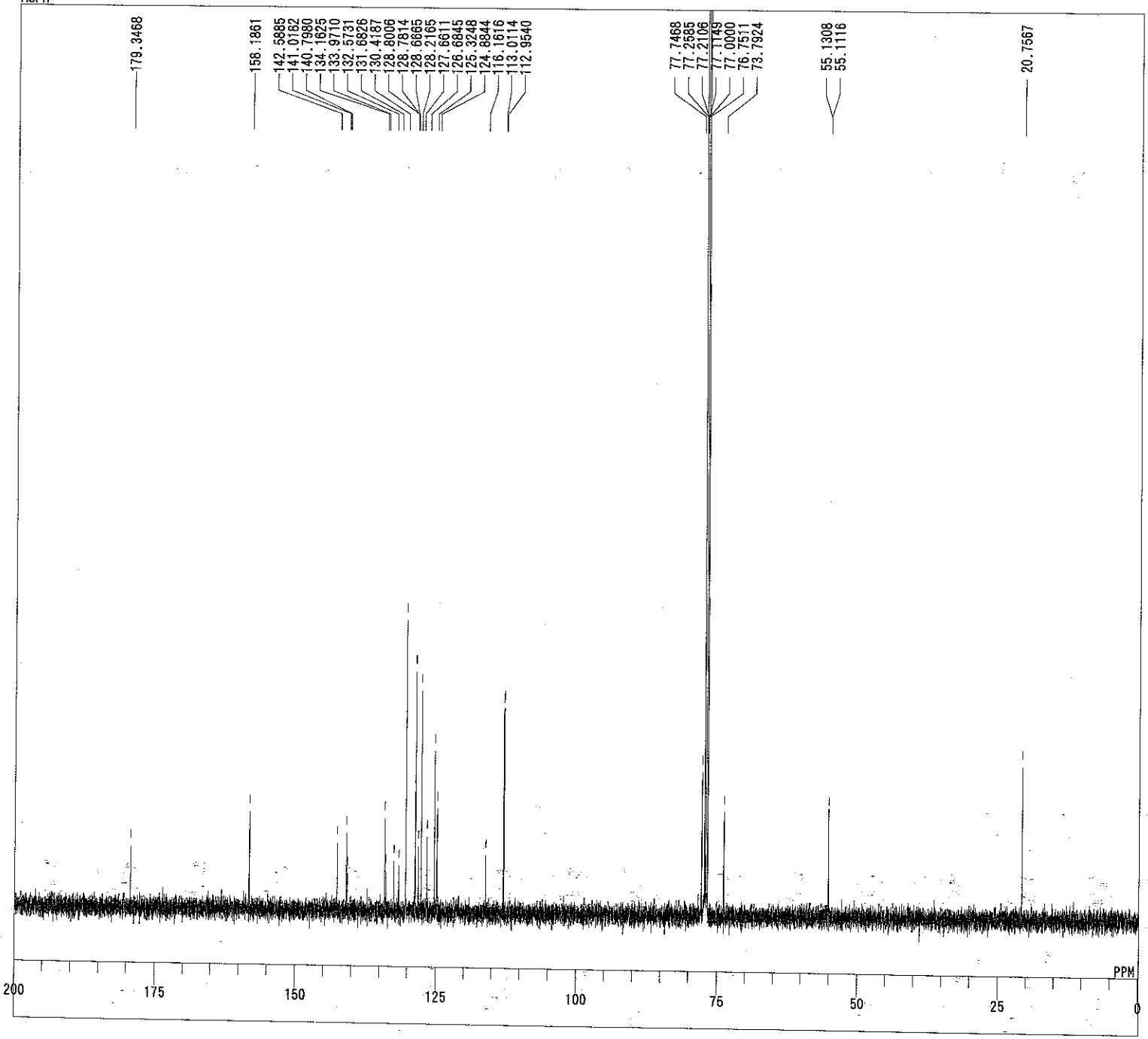


DFILE C:¥My Documents¥PGousei¥KANAI¥single_pulse.64
COMNT MePh
DATIM 05-02-2009 09:57:58
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
POINT 16384
FREQU 9286.78 Hz
SCANS 7
ACQTM 1.7642 sec
PD 5.0000 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 17.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.01 Hz
RGAIN 50

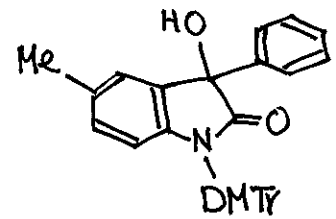


8dc

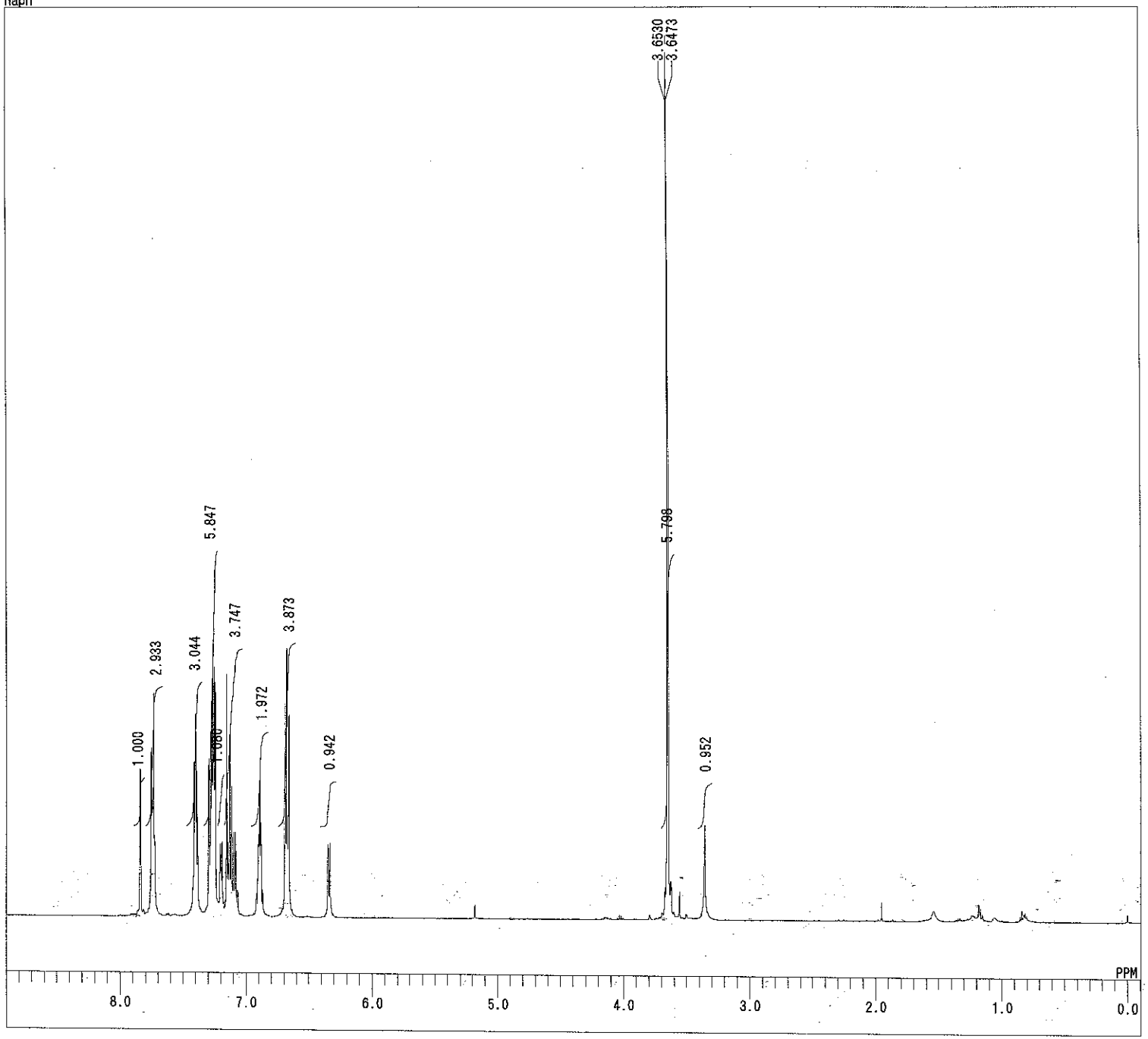
C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.14
MePh



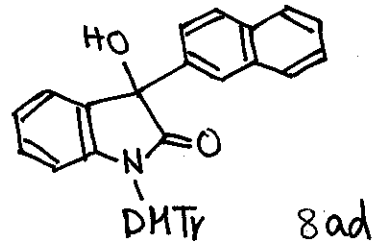
DFILE C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.14
COMNT MePh
DATIM 05-02-2009 10:47:51
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32768
FREQU 39062.50 Hz
SCANS 1000
ACQTM 0.8389 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 60



C:¥My Documents¥PGousei¥KANAI¥single_pulse.61
naph

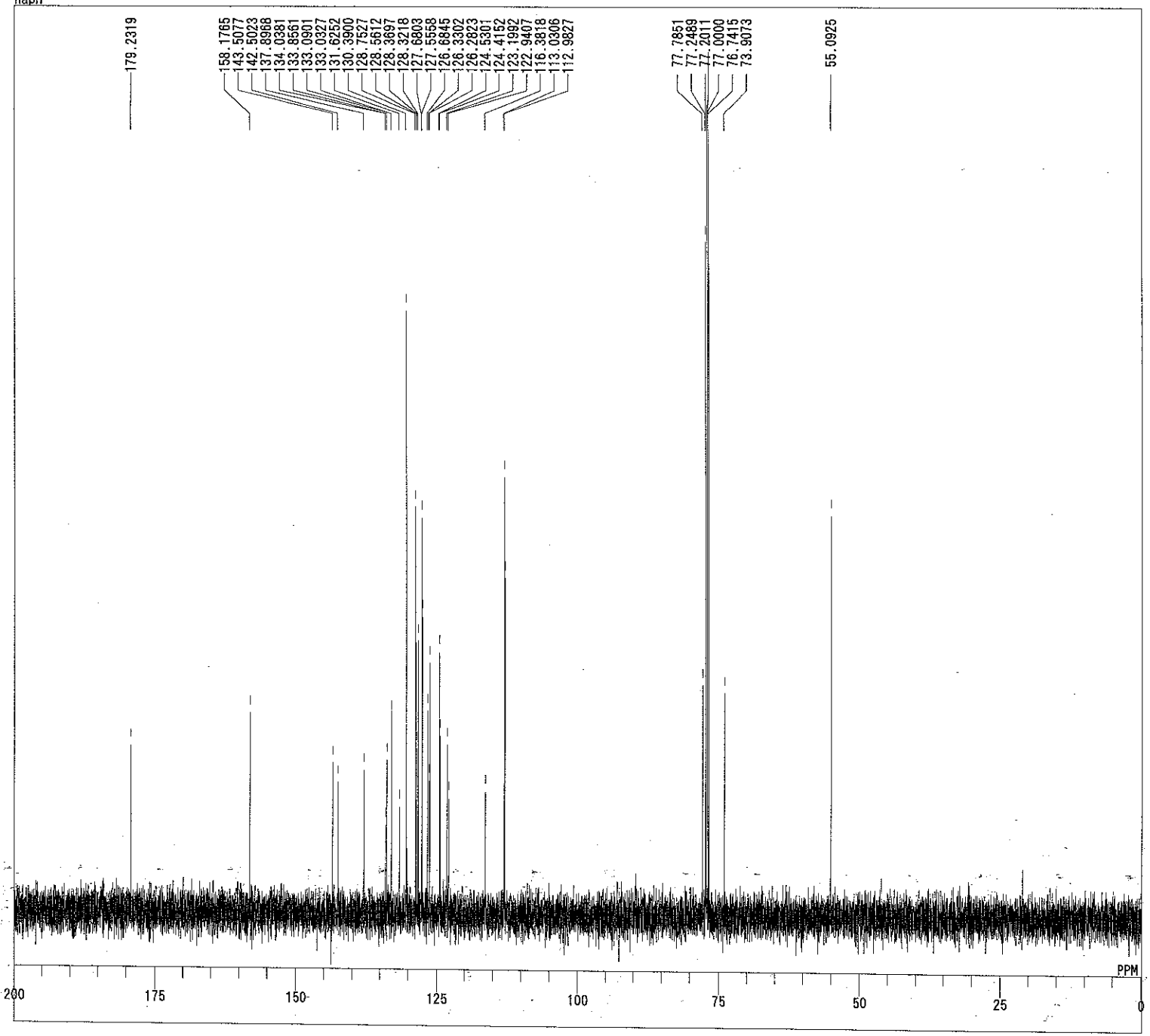



```
DFILE  C:¥My Documents¥PGousei¥KANAI¥single_pulse.61
COMNT  naph
DATIM  04-02-2009 20:24:35
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        495.13 MHz
OBSET          4.38 KHz
OBFIN          9.64 Hz
POINT         16384
FREQU       9286.78 Hz
SCANS             4
ACQTM         1.7642 sec
PD            5.0000 sec
PW1             6.20 usec
IRNUC  1H
CTEMP          17.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.01 Hz
RGAIN            40
```

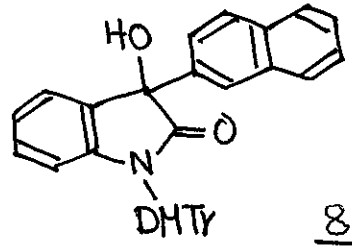


8ad

C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.13
naph

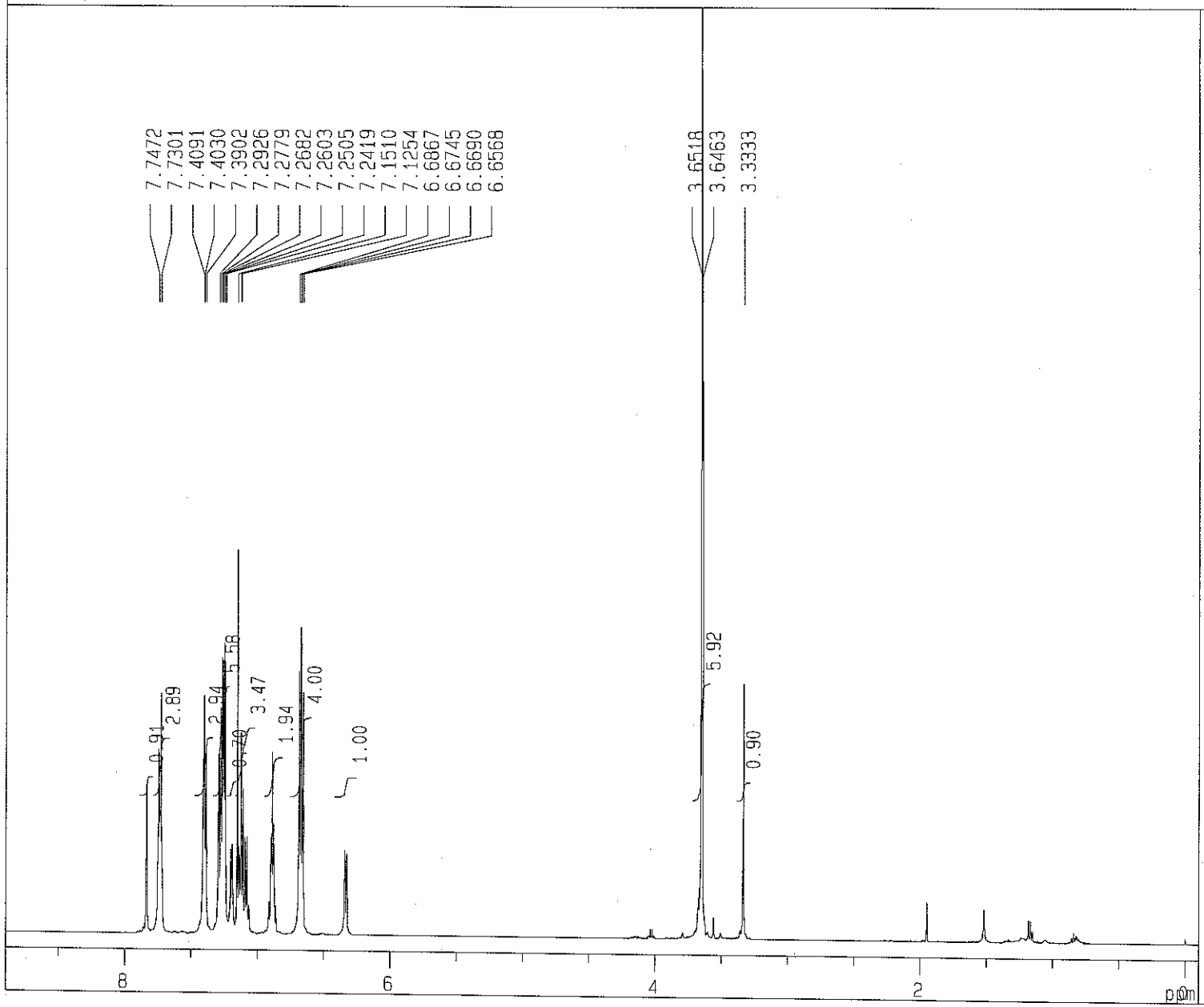


DFILE C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.13
COMNT naph
DATIM 04-02-2009 20:28:53
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32768
FREQU 39062.50 Hz
SCANS 73
ACQTM 0.8389 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 60



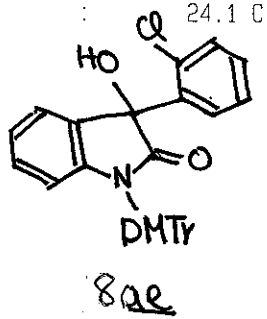
8'ad

ClPh



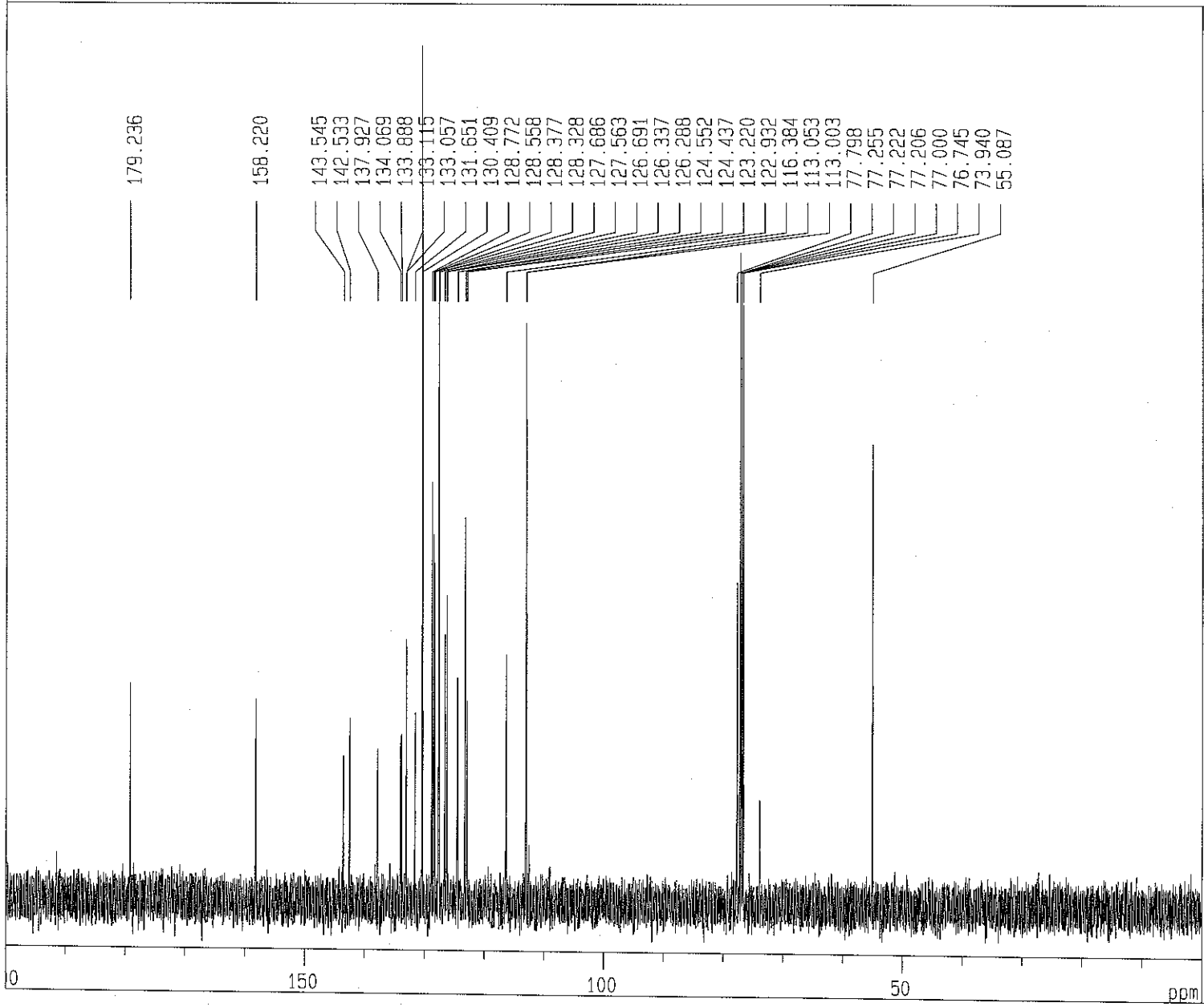
Date : Wed Feb 4 11:16:02 2009

FileName	:	.LoadingFID.nmdata
Comment	:	ClPh
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	8 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	16
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	24.1 C



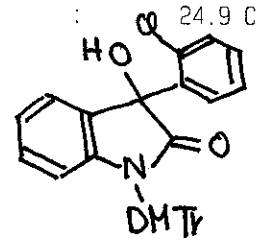
8ae

ClPh



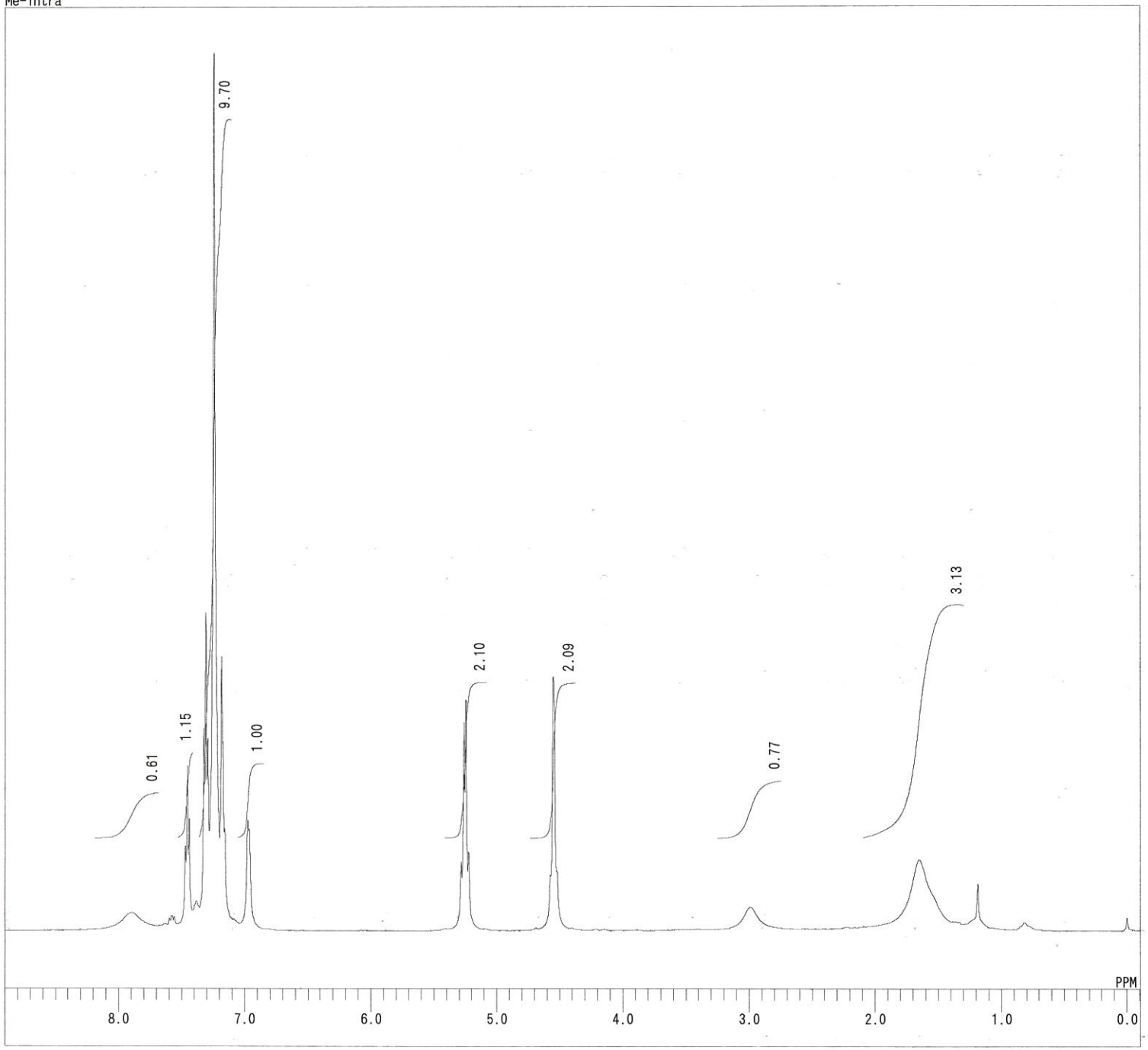
Date : Wed Feb 4 11:19:20 2009

FileName	:	.LoadingFID.nmdata
Comment	:	ClPh
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	800 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	52 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	24.9 C

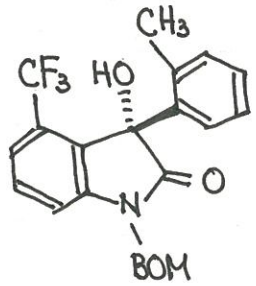


8ae

C:¥My Documents¥PGousei¥KANAI¥single_pulse.138
Me-intra

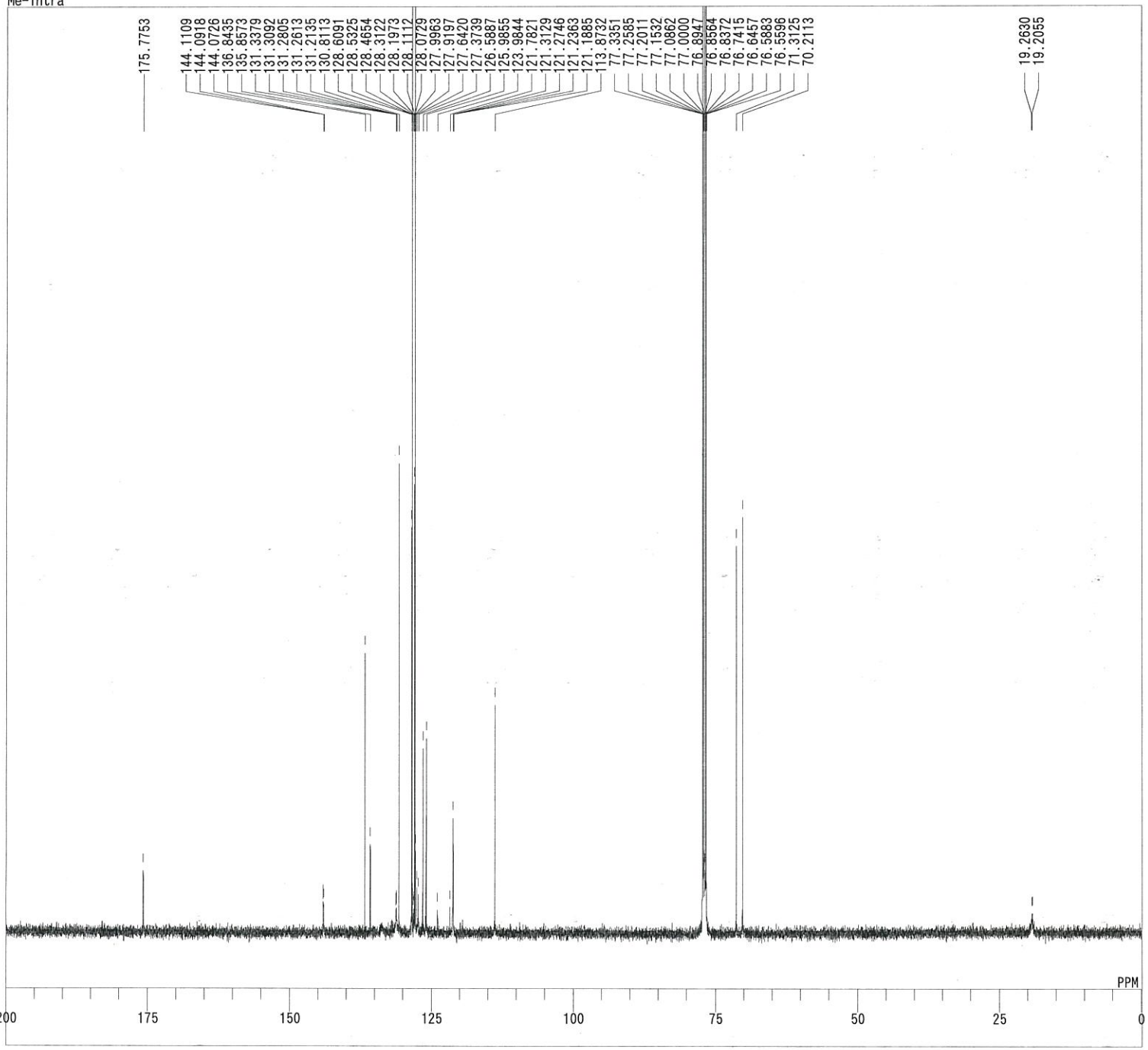



```
DFILE  C:¥My Documents¥PGousei¥KANAI¥single_pulse.138
COMNT  Me-intra
DATIM  17-04-2009 11:07:42
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        495.13 MHz
OBSET          4.38 KHz
OBFIN          9.64 Hz
POINT         16384
FREQU       9286.78 Hz
SCANS             8
ACQTM         1.7642 sec
PD            5.0000 sec
PW1             6.20 usec
IRNUC  1H
CTEMP          25.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             3.00 Hz
RGAIN            50
```

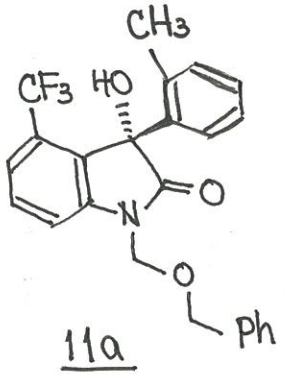


11a

C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.27
Me-intra

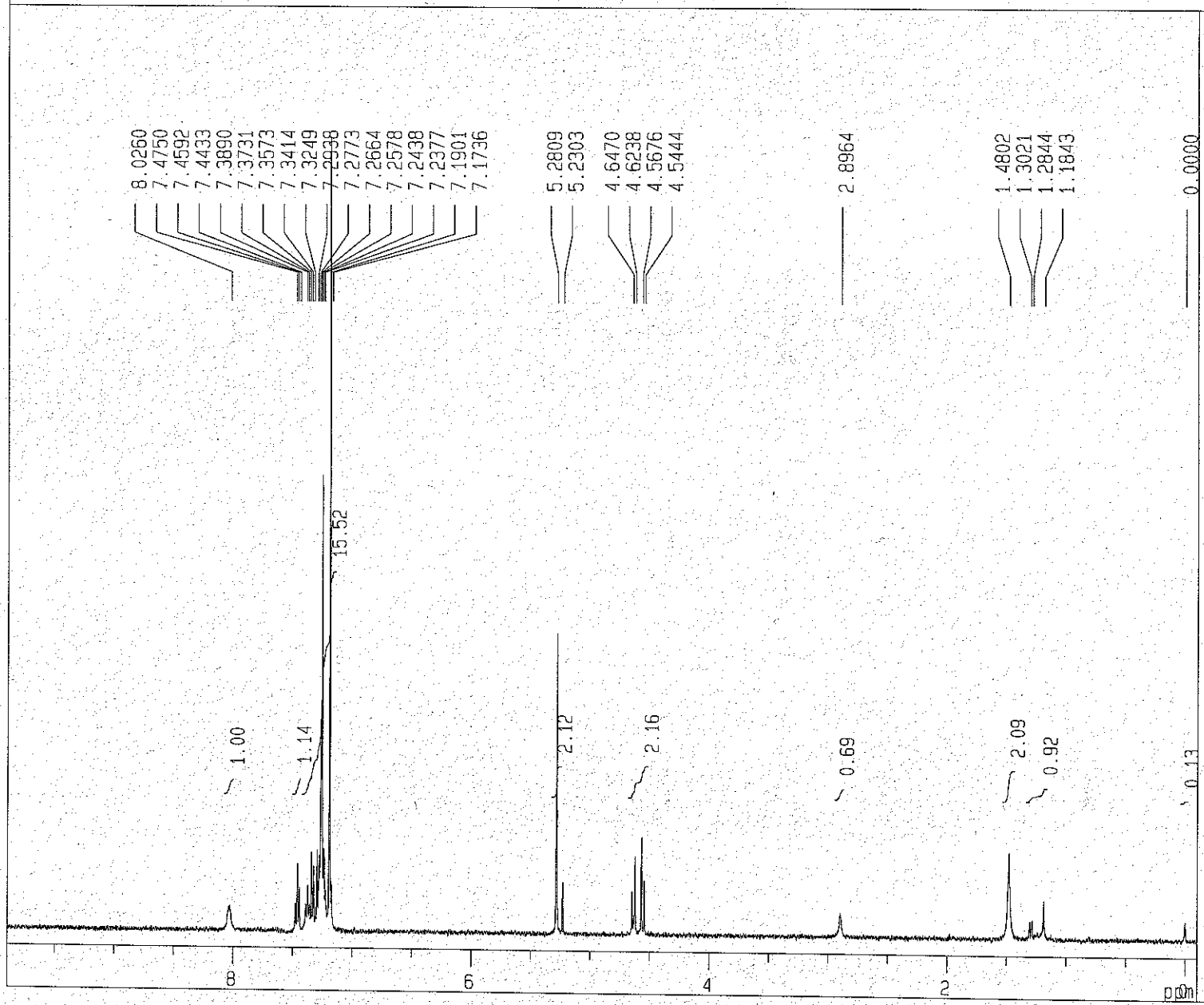


DFILE C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.27
COMNT Me-intra
DATIM 18-04-2009 09:39:47
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32768
FREQU 39062.50 Hz
SCANS 14922
ACQTM 0.8389 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 60



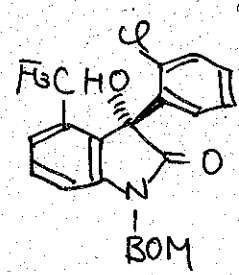
11a

Intramolecular o-Cl Ph



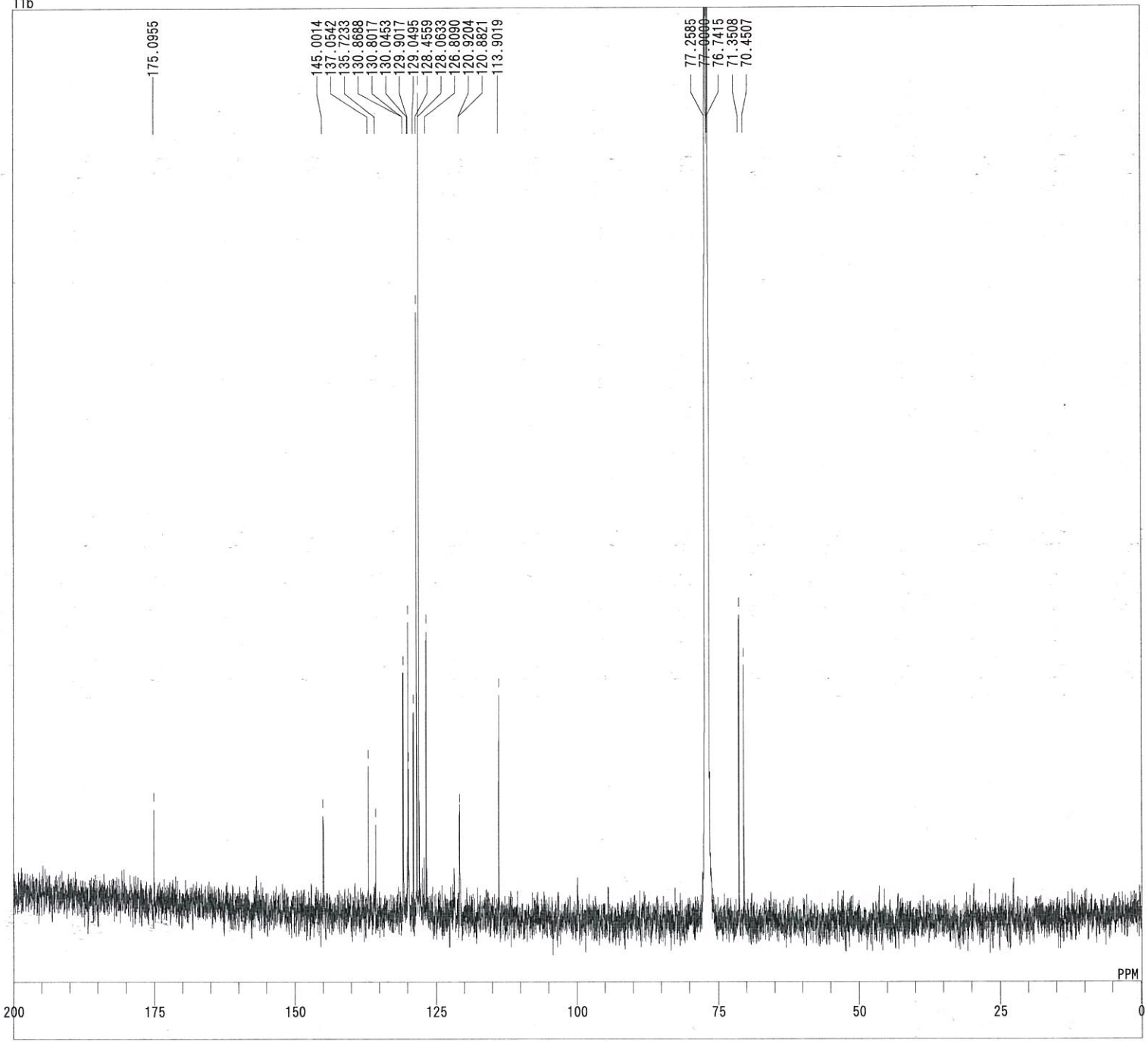
Date : Sun Mar 8 16:25:37 2009

FileName	:	.LoadingFID.nmdata
Comment	:	Intramolecular o-Cl Ph
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	32 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	26
SCANS	:	3 times
SLVNT	:	CDCL3
SPINNING	:	15 Hz
TEMP	:	23.8 C

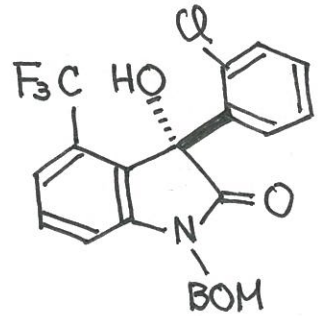


11b

C:¥My Documents¥PGousei¥卒業生¥tomita¥DTEX090208Intramolecular2.2
11b

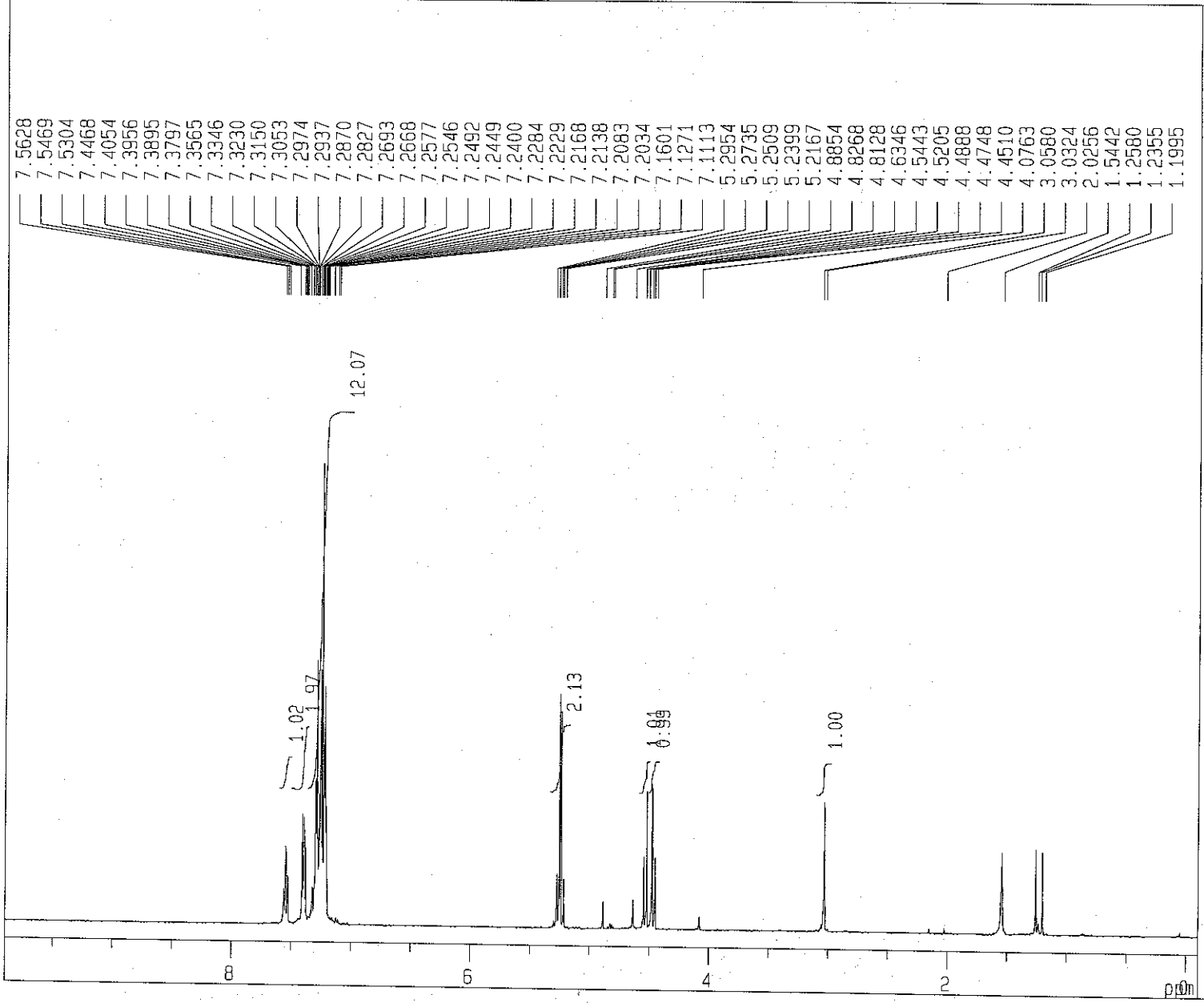



```
DFILE  C:¥My Documents¥PGousei¥卒業生¥tomita¥DTEX090208Intramole
COMNT  11b
DATIM  09-03-2009 07:49:30
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        124.51 MHz
OBSET          3.45 KHz
OBFIN          6.00 Hz
POINT         40961
FREQU      48828.87 Hz
SCANS         20000
ACQTM         0.8389 sec
PD            2.0000 sec
PW1           3.57 usec
IRNUC  1H
CTEMP         25.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.01 Hz
RGAIN            60
```



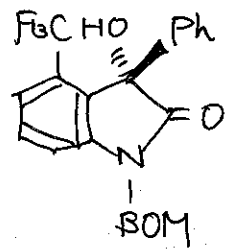
11b

1H Line



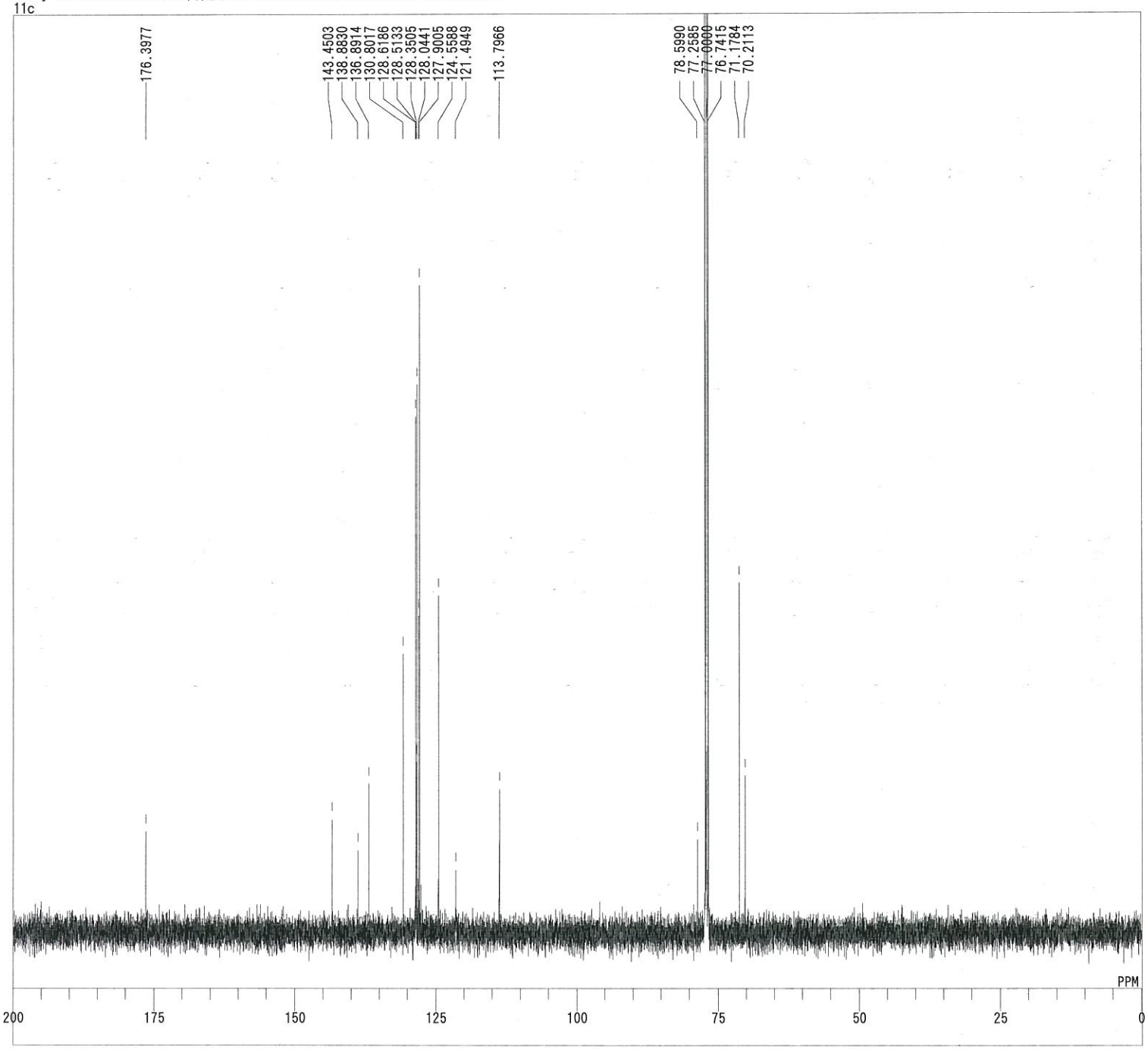
Date : Tue Feb 10 21:33:42 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	166 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	22
SCANS	:	13 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	23.8 C

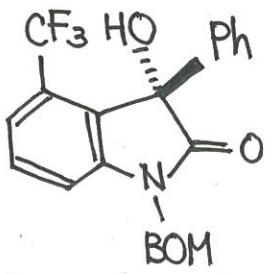


11C

C:¥My Documents¥PGousei¥卒業生¥tomita¥dtexIntramolecularPh.ecx.ecx.als
11c

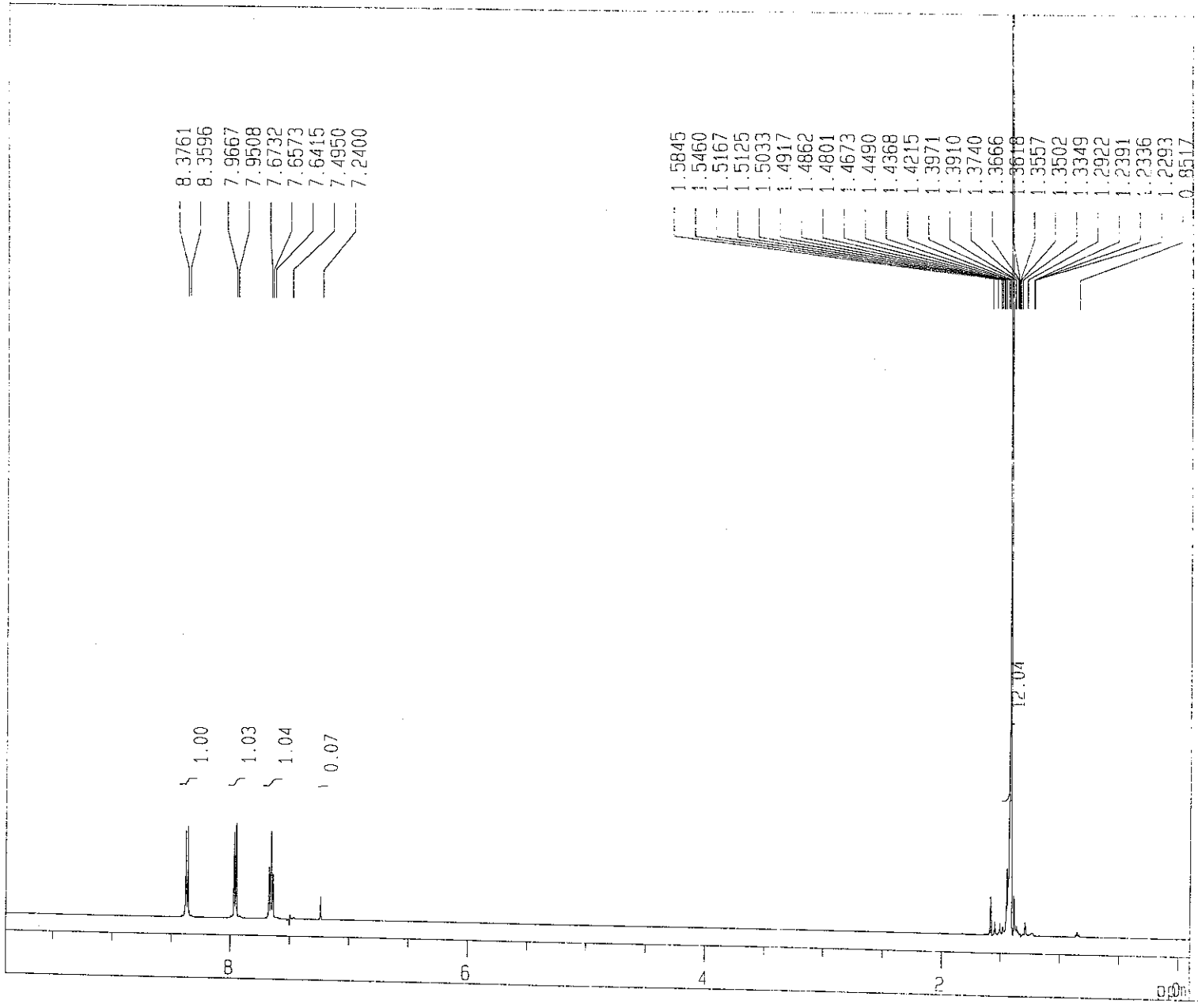


DFILE C:¥My Documents¥PGousei¥卒業生¥tomita¥dtexIntramolecularP
COMNT 11c
DATIM 20-02-2009 22:52:39
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 26214
FREQU 31249.52 Hz
SCANS 2000
ACQTM 0.8389 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 60



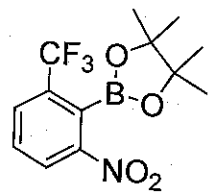
11c

081027-6-165 Column



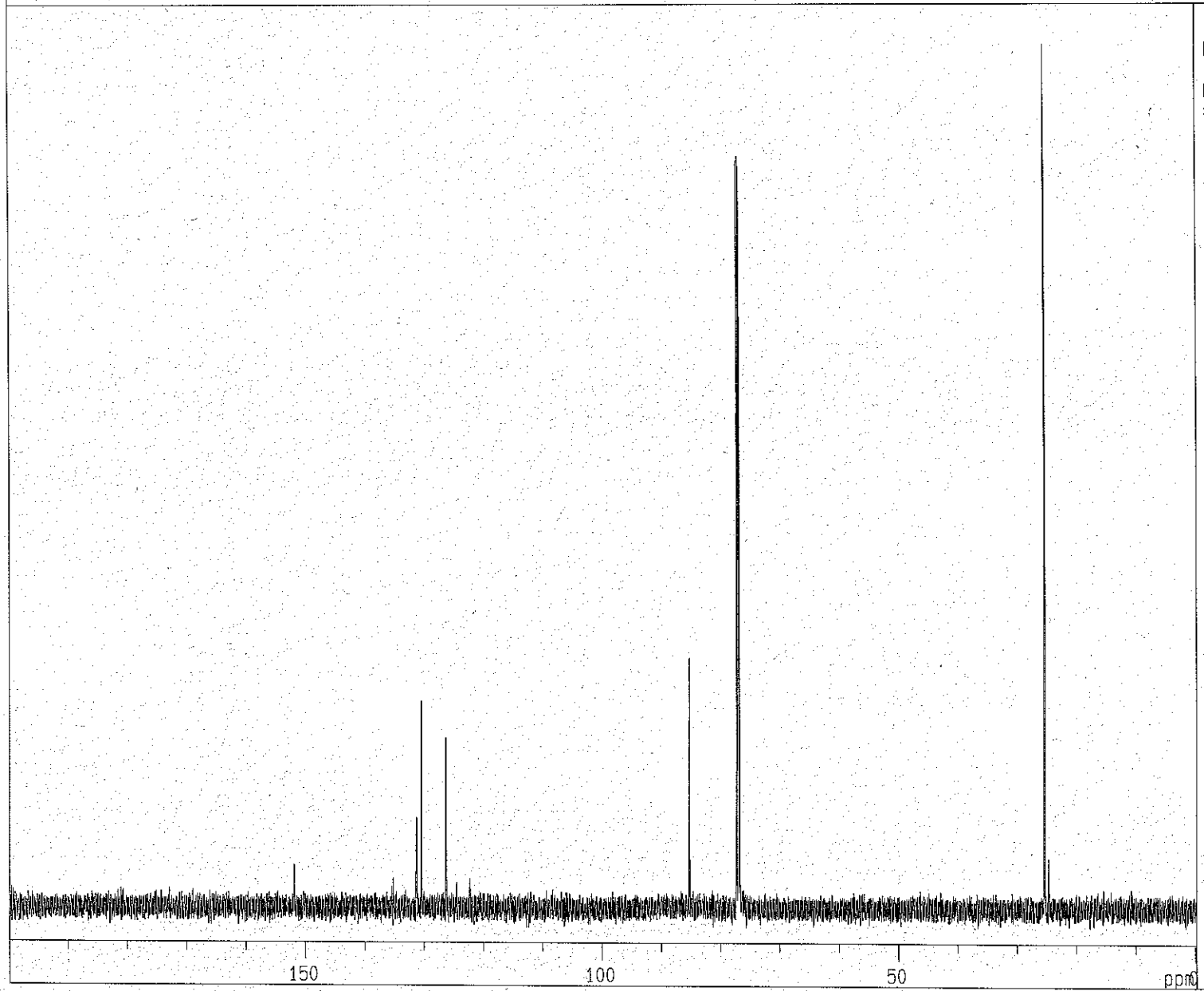
Date : Mon Oct 27 14:28:08 2008

FileName	:	.\081027-6-165.nmdata
Comment	:	081027-6-165 Column
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	128 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3275.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	14
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	14 Hz
TEMP	:	25.0 C



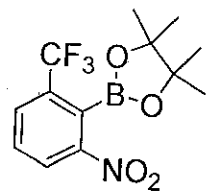
B

1H Line



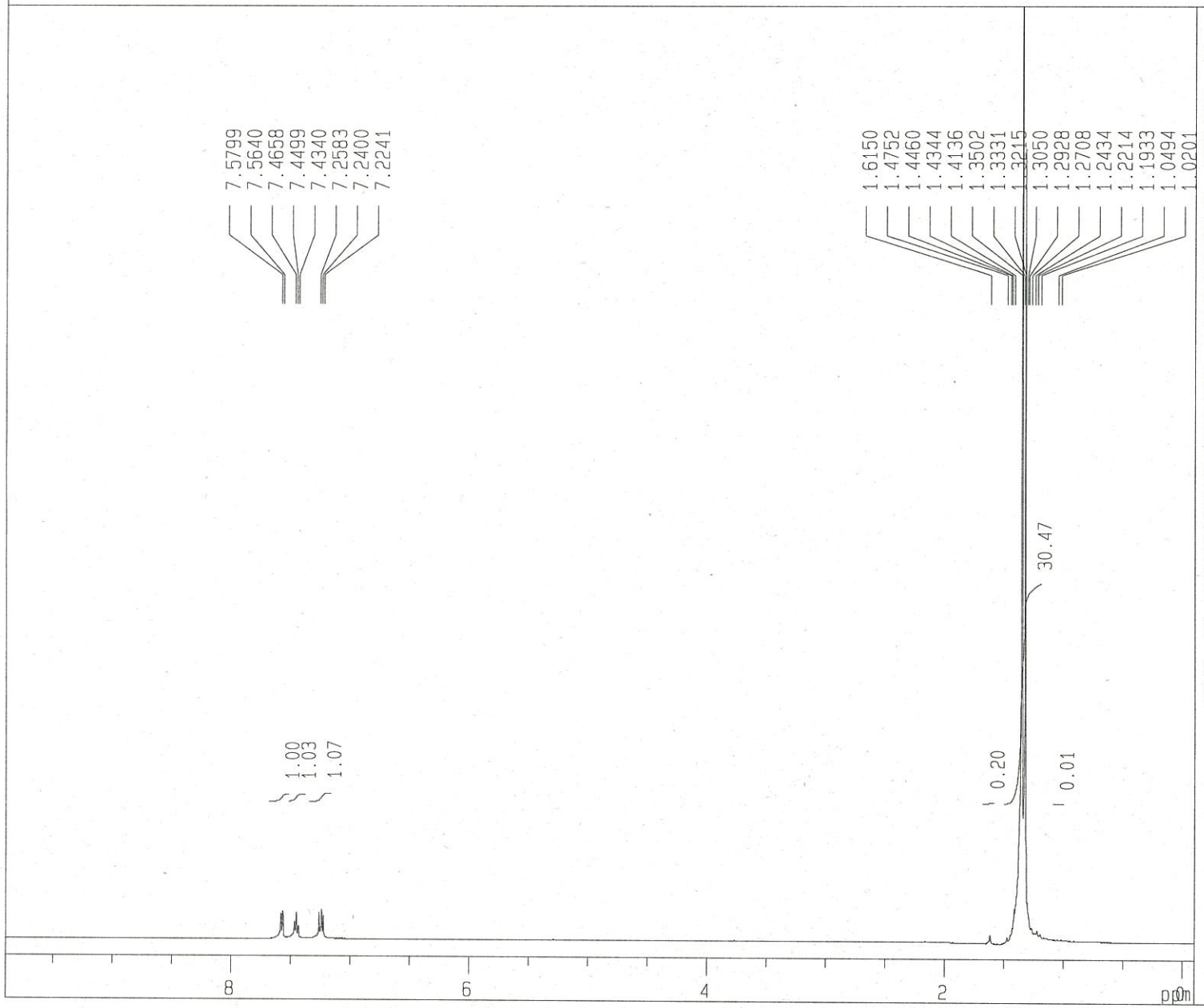
Date : Sat Mar 14 16:35:51 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	3000 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	32
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	2762 times
SLVNT	:	CDCL3
SPINNING	:	0 Hz
TEMP		



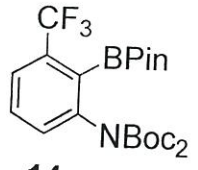
B

1H Line



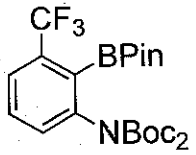
Date : Sat Mar 14 11:44:04 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	32 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	16
SCANS	:	4 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	24.8 C

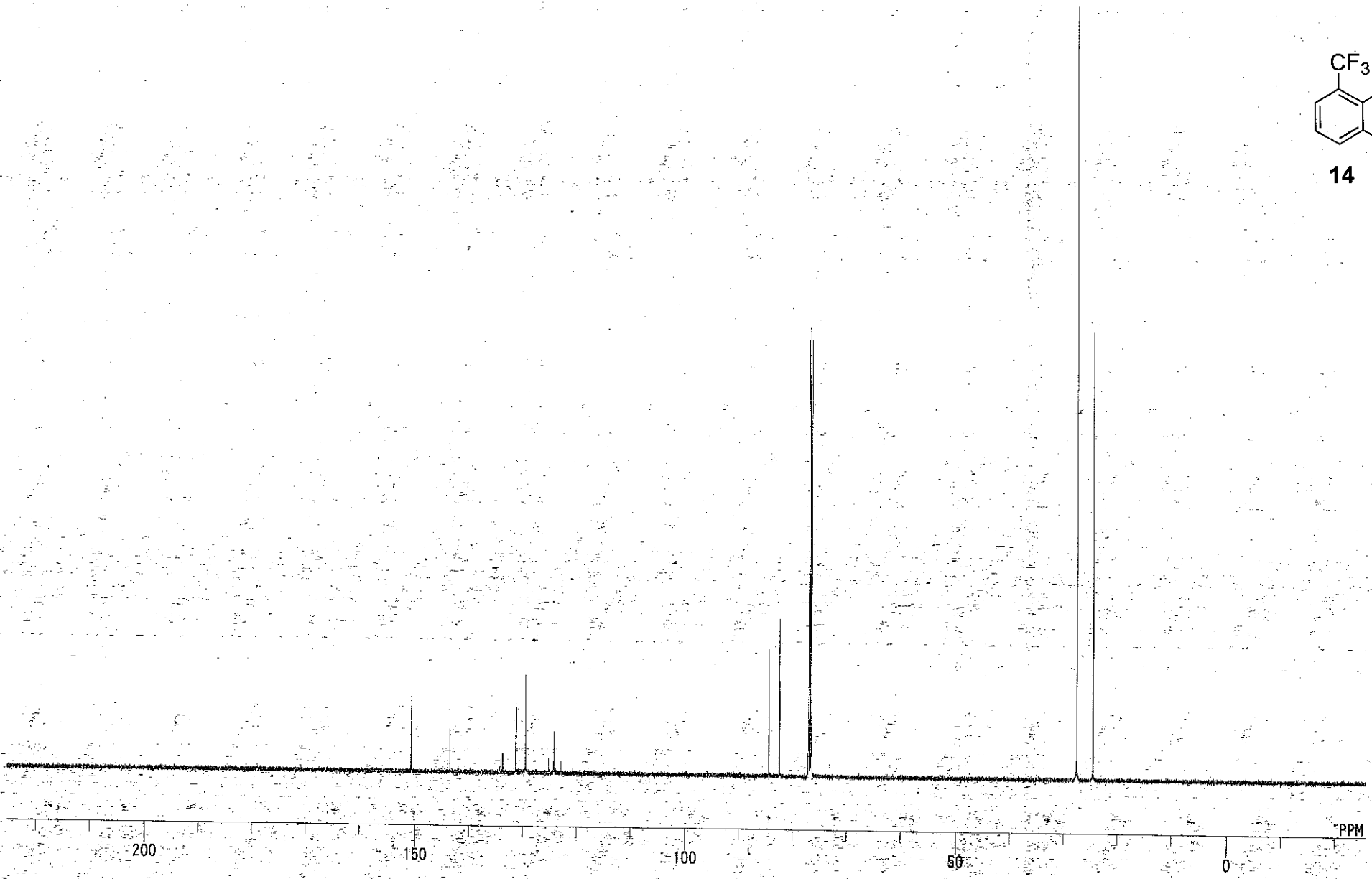


14

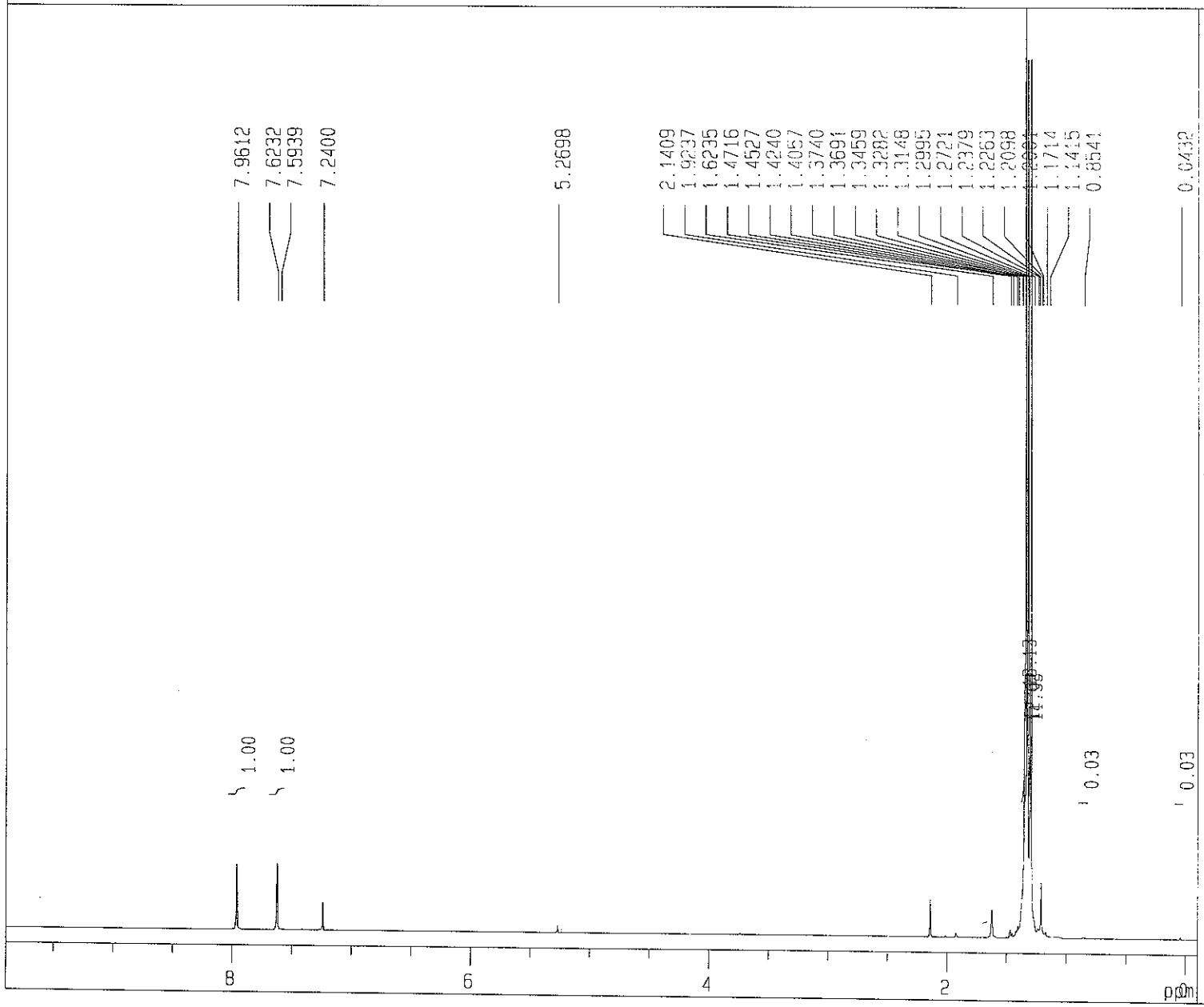
C:¥My Documents¥Pgousel¥tomita¥datexb002.1
single pulse decoupled gated NOE



14

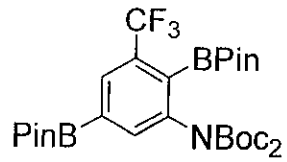


081002-6-137 for submission

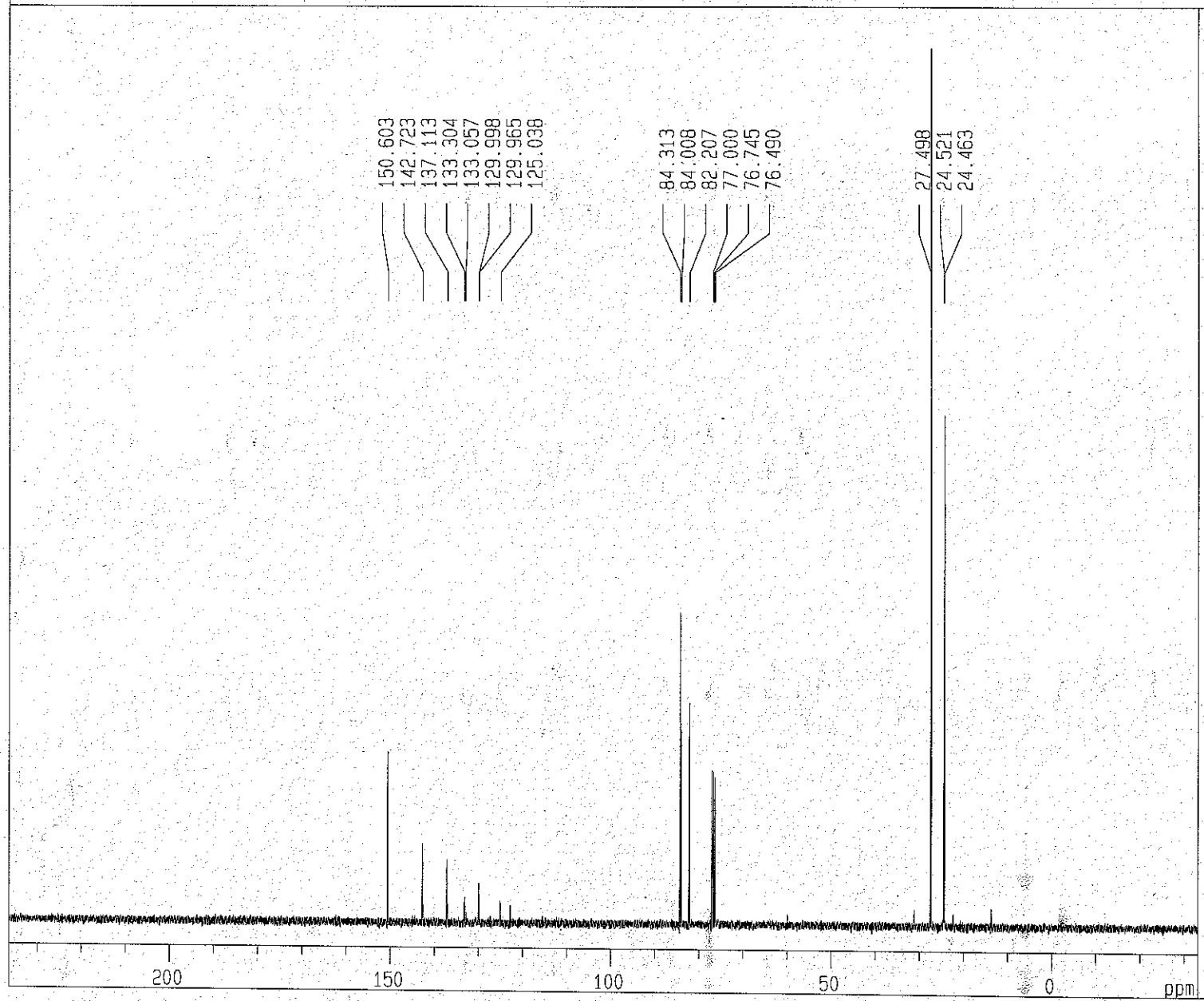


Date : Thu Oct 2 19:41:37 2008

FileName	:	.\LoadingFID.nmrdata
Comment	:	081002-6-137 for submis
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	16 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3275.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	15
SCANS	:	8 times
SLVNT	:	CDCL3
SPINNING	:	14 Hz
TEMP	:	25.8 C

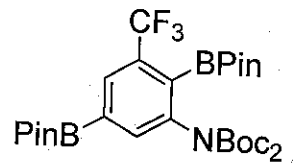


15



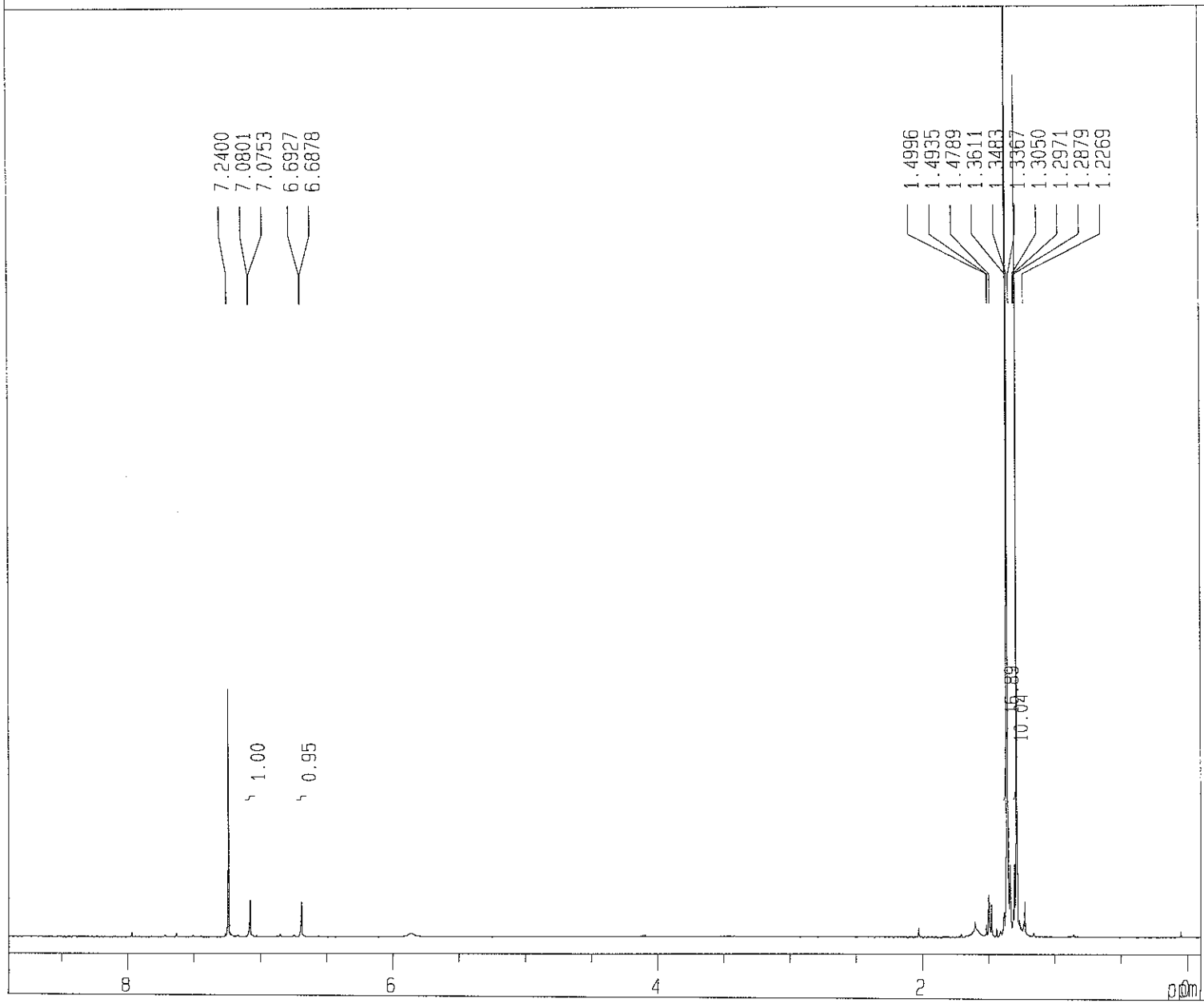
Date : Fri Mar 13 23:44:02 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	800 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	32
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	262 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	26.0 C



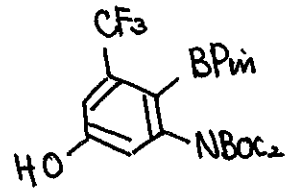
15

3028 -3

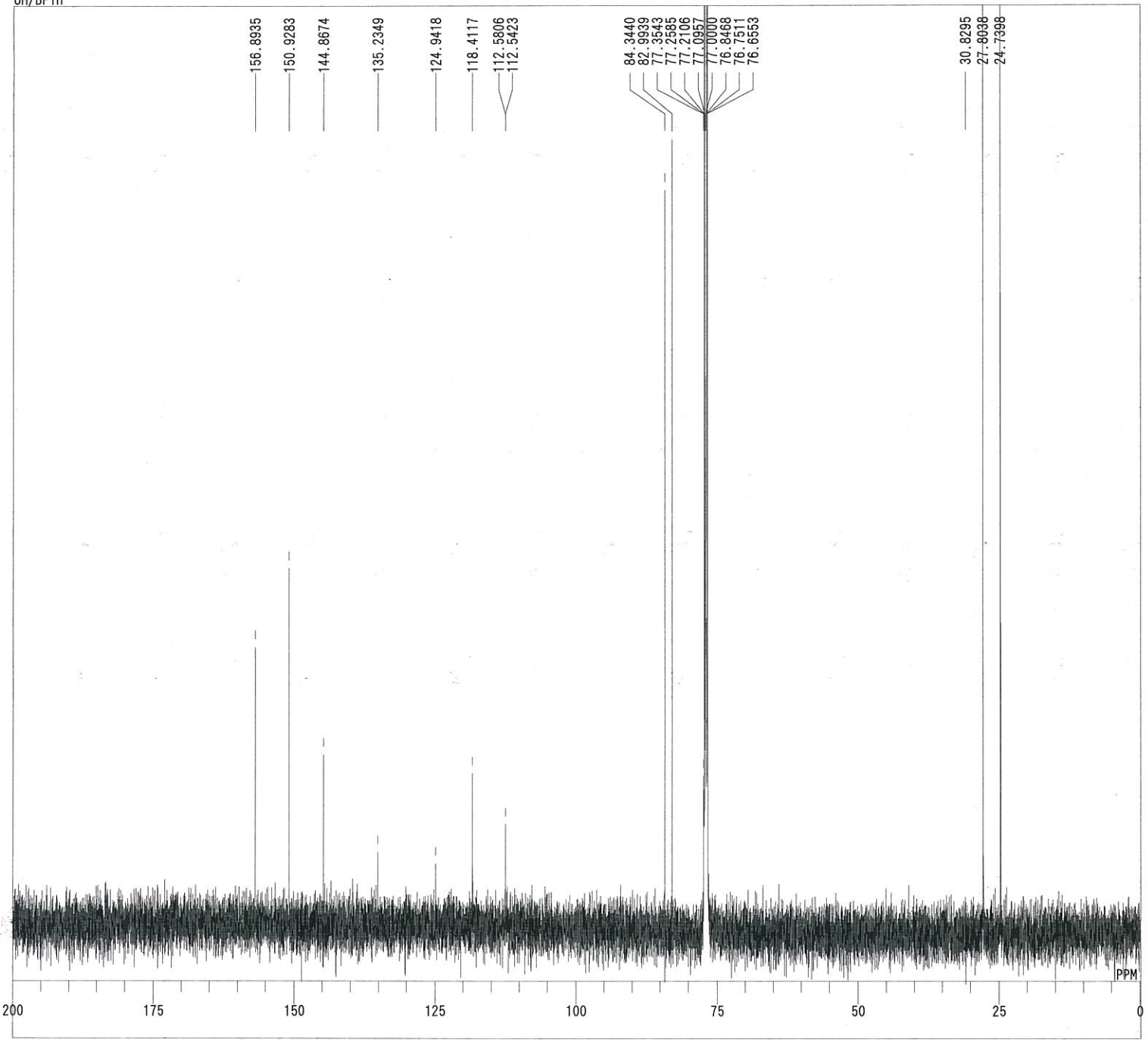


Date : Fri Oct 31 15:31:42 2008

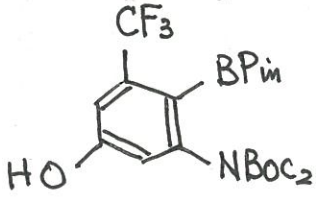
FileName	:	.LoadingFID.nmdata
Comment	:	-3
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	16 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	22
SCANS	:	8 times
SLVNT	:	CDCL3
SPINNING	:	10 Hz
TEMP	:	25.7 C



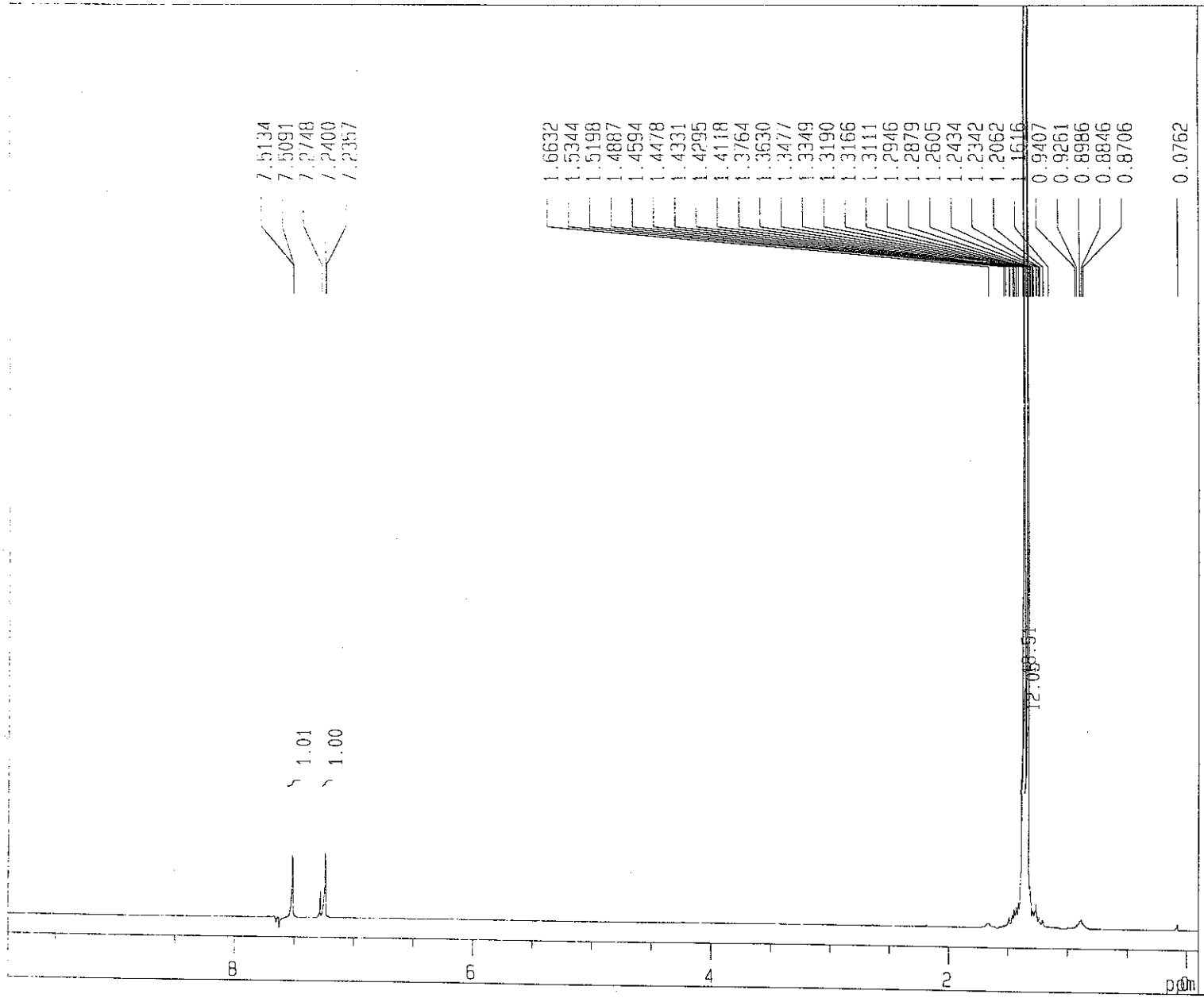
C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.0
OH/BPin




```
DFILE  C:¥My Documents¥PGousei¥KANAI¥single_pulse_dec.0
COMNT  OH/BPin
DATIM  23-04-2009 09:28:44
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        124.51 MHz
OBSET          3.45 KHz
OBFIN          6.00 Hz
POINT         32768
FREQU      39062.50 Hz
SCANS         14390
ACQTM         0.8389 sec
PD            2.0000 sec
PW1           3.57 usec
IRNUC  1H
CTEMP         21.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.01 Hz
RGAIN            50
```

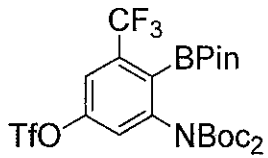


16

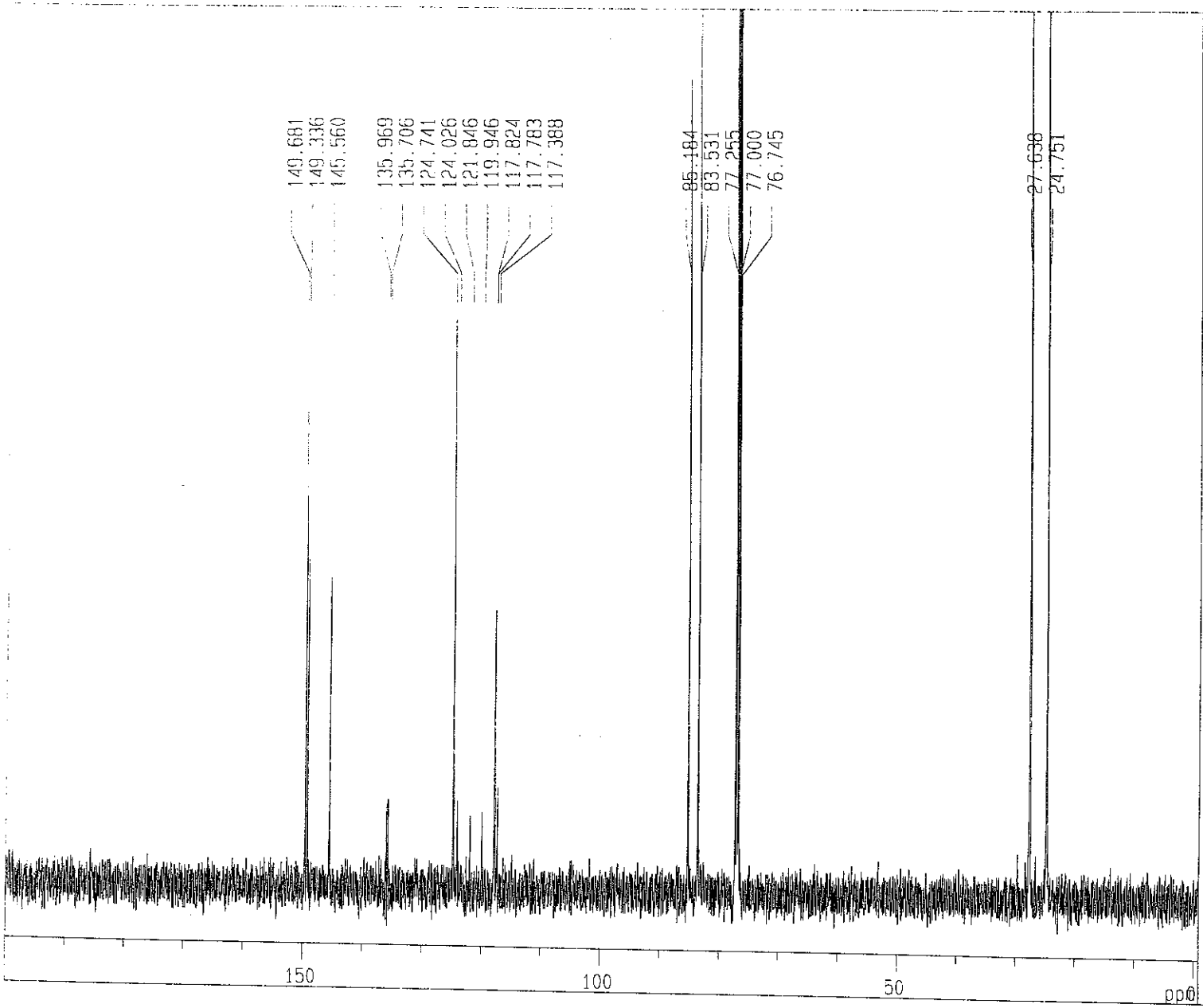


Date : Fri Nov 21 14:53:11 2008

FileName	:	.LoadingFID.nmdata
Comment	:	081121-7-7 Column
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	80 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	13
SCANS	:	3 times
SLVNT	:	CDCL3
SPINNING	:	10 Hz
TEMP	:	25.9 C

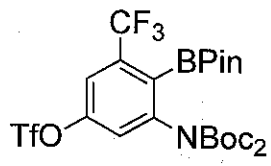


C



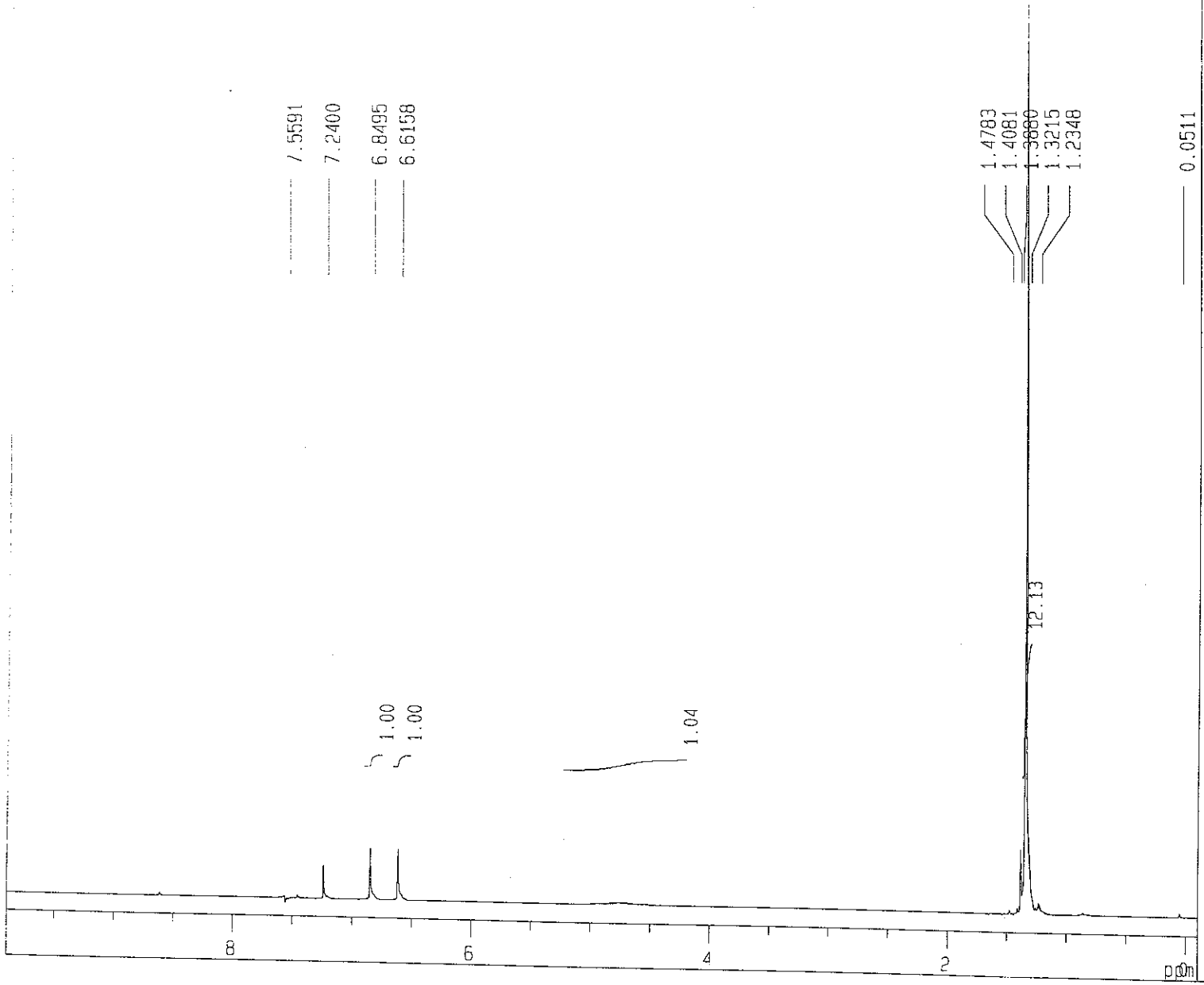
Date : Fri Nov 21 15:03:33 2008

FileName	:	.LoadingFID.nmdata
Comment	:	081121-7-7 Column
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	300 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	6.25 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	192 times
SLVNT	:	CDCL3
SPINNING	:	10 Hz
TEMP	:	26.9 C



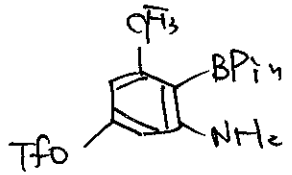
C

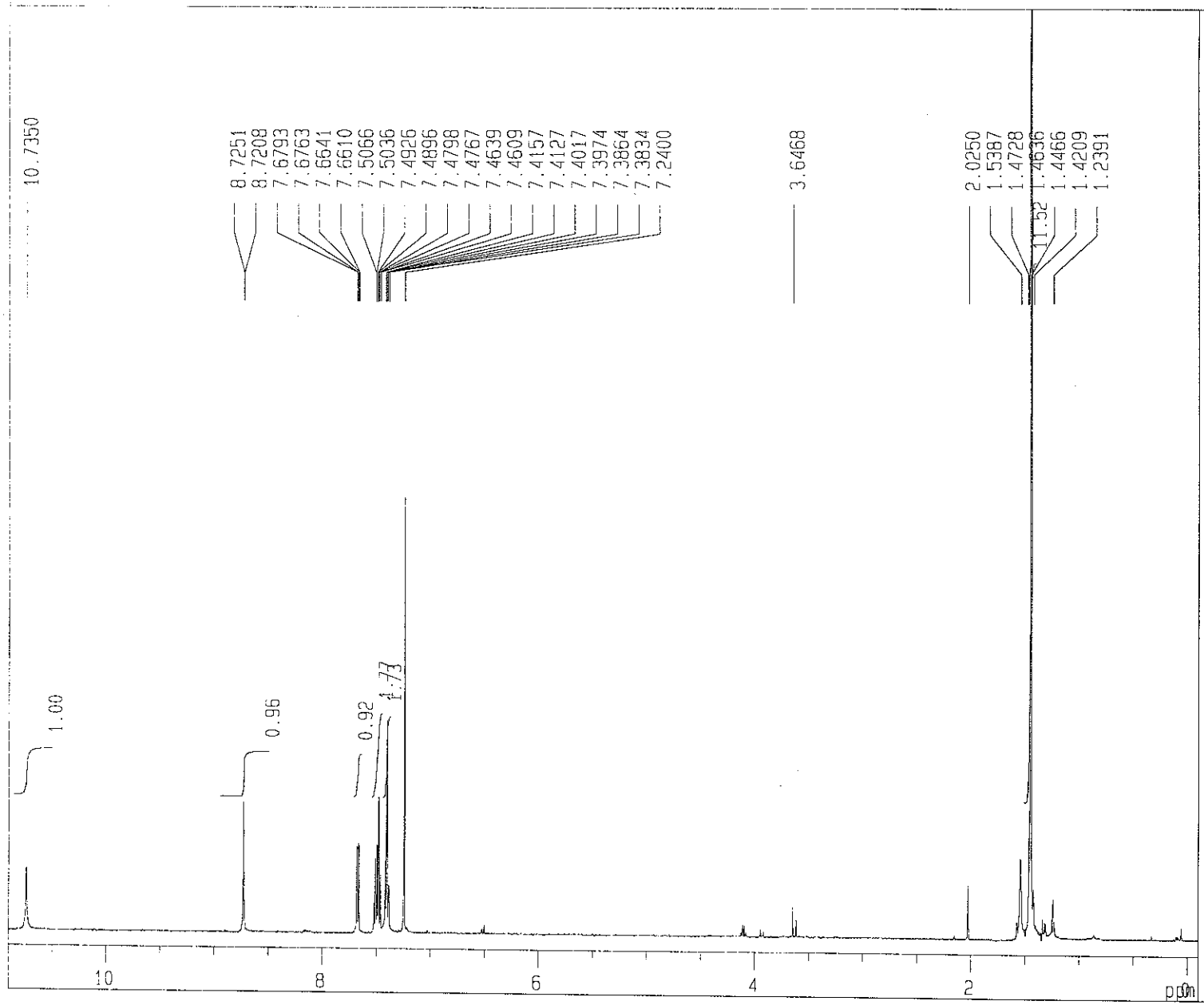
081122-7-8 Column



Date : Sat Nov 22 12:26:57 2008

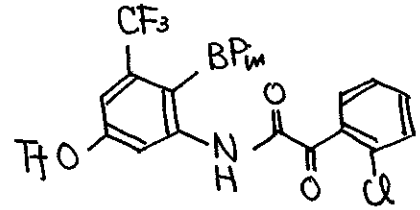
FileName	:	.LoadingFID.nmdata
Comment	:	081122-7-8 Column
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	64 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	19
SCANS	:	3 times
SLVNT	:	CDCL3
SPINNING	:	14 Hz
TEMP	:	25.7 C



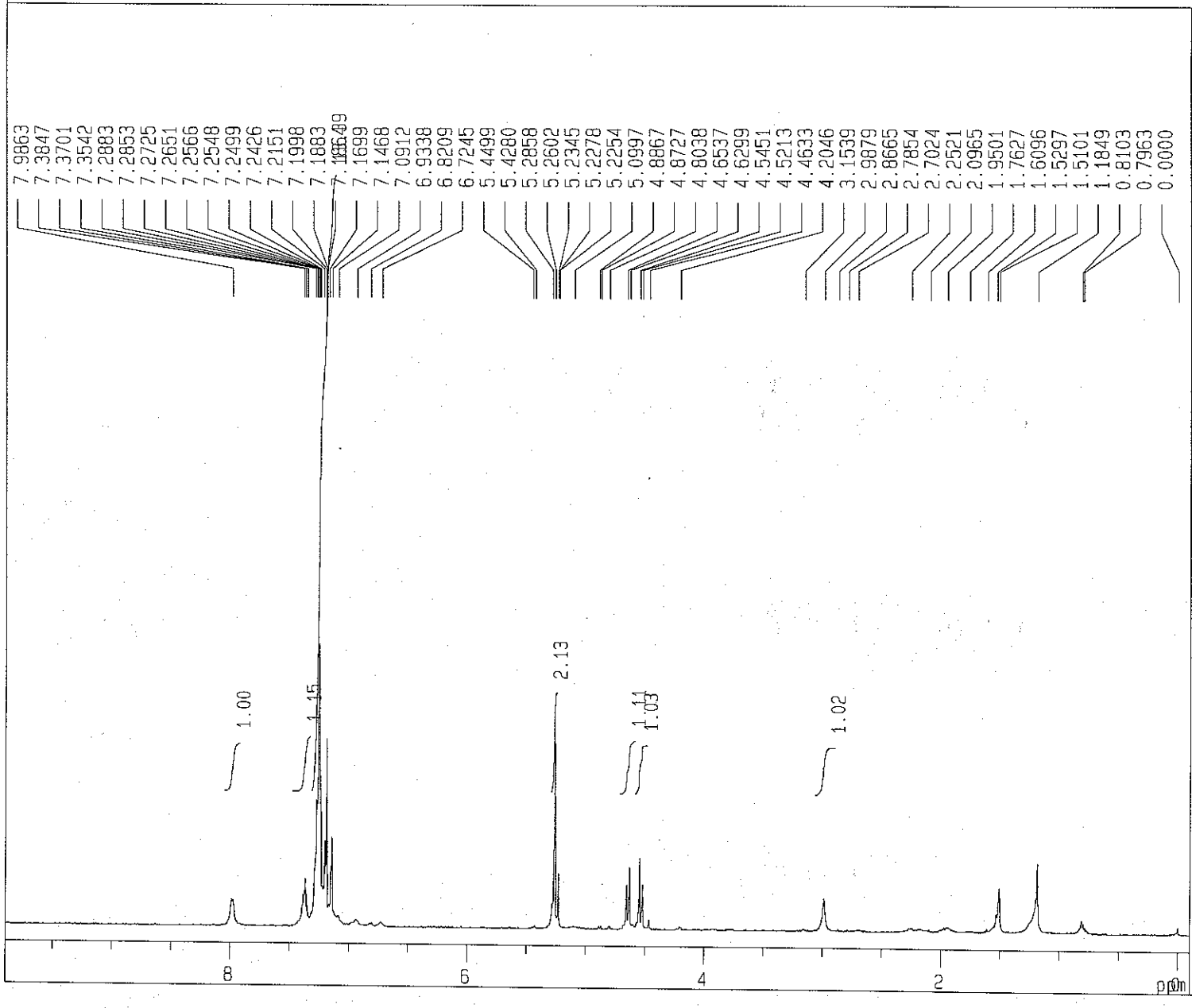


Date : Sat Nov 15 13:17:30 2008

FileName	:	.LoadingFID.nmdata
Comment	:	-2
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	128 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.31 Hz
RGAIN	:	22
SCANS	:	8 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	25.4 C

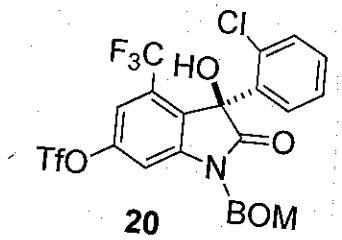


1H Line



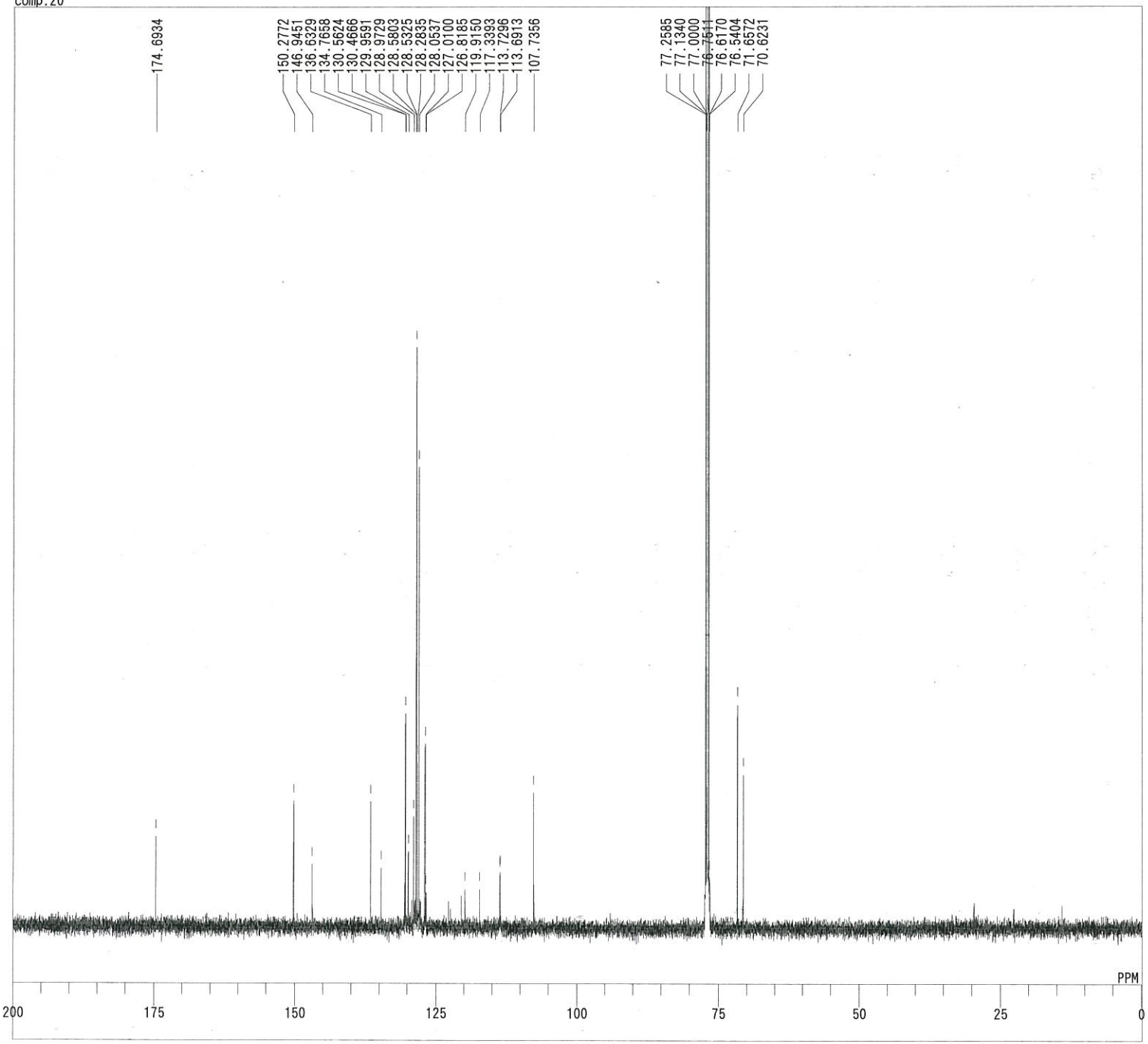
Date : Wed Feb 11 15:00:38 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	1024 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	22
SCANS	:	21 times
SLVNT	:	CDCL3
SPINNING	:	10 Hz
TEMP	:	23.8 C

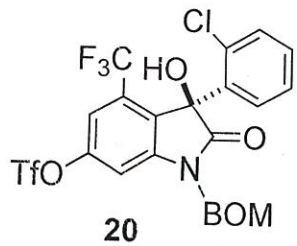


20

C:¥My Documents¥PGousei¥tomita¥dtex759.1
comp.20



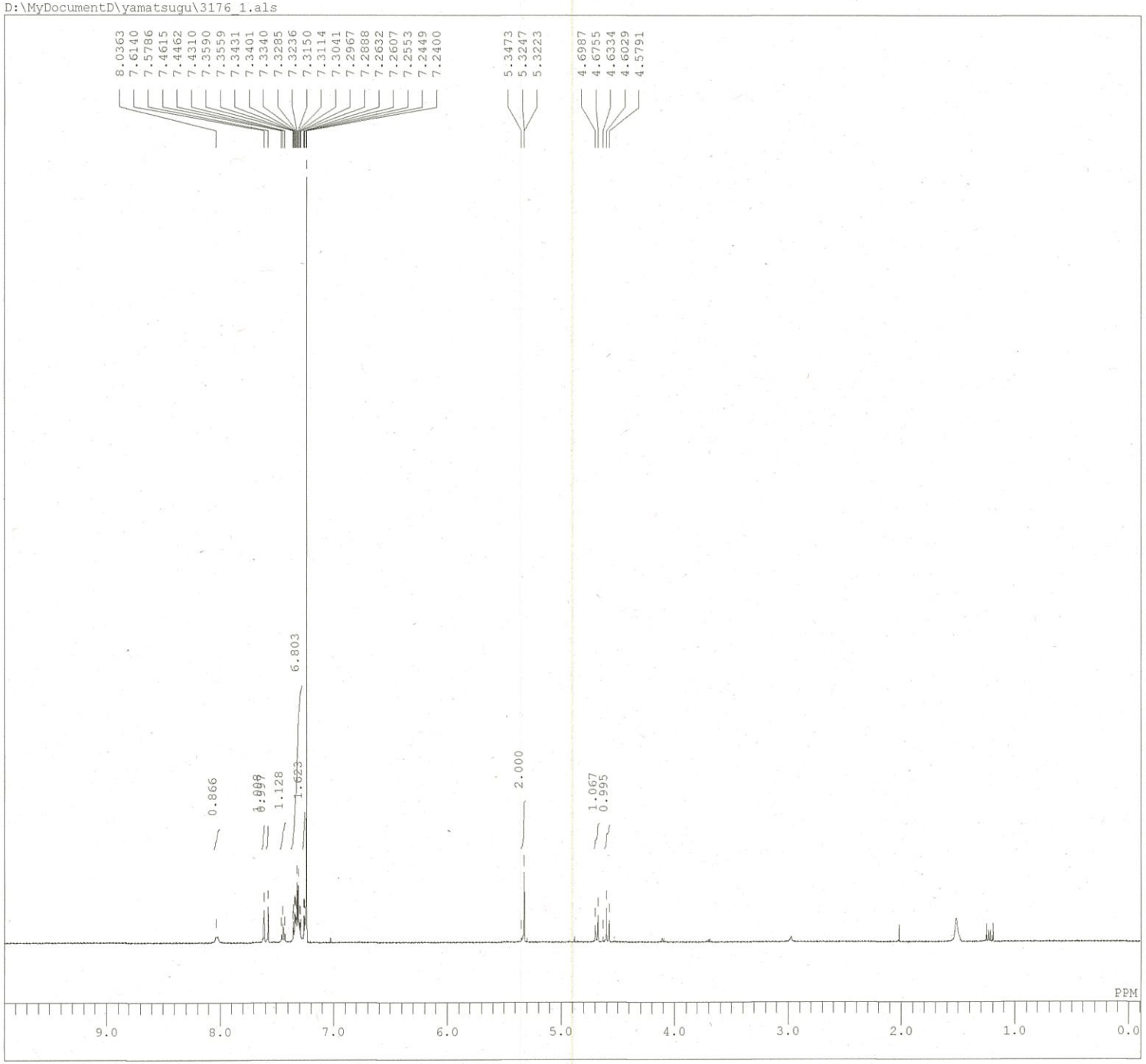

```
DFILE  C:¥My Documents¥PGousei¥tomita¥dtex759.1
COMNT  comp.20
DATIM  11-02-2009 09:50:58
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        124.51 MHz
OBSET          3.45 KHz
OBFIN          6.00 Hz
POINT         32768
FREQU      39062.50 Hz
SCANS         12800
ACQTM         0.8389 sec
PD            2.0000 sec
PW1           3.57 usec
IRNUC  1H
CTEMP          19.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.01 Hz
RGAIN            60
```



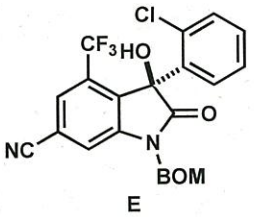
20

3176-1

D:\MyDocumentD\yamatsugu\3176_1.als

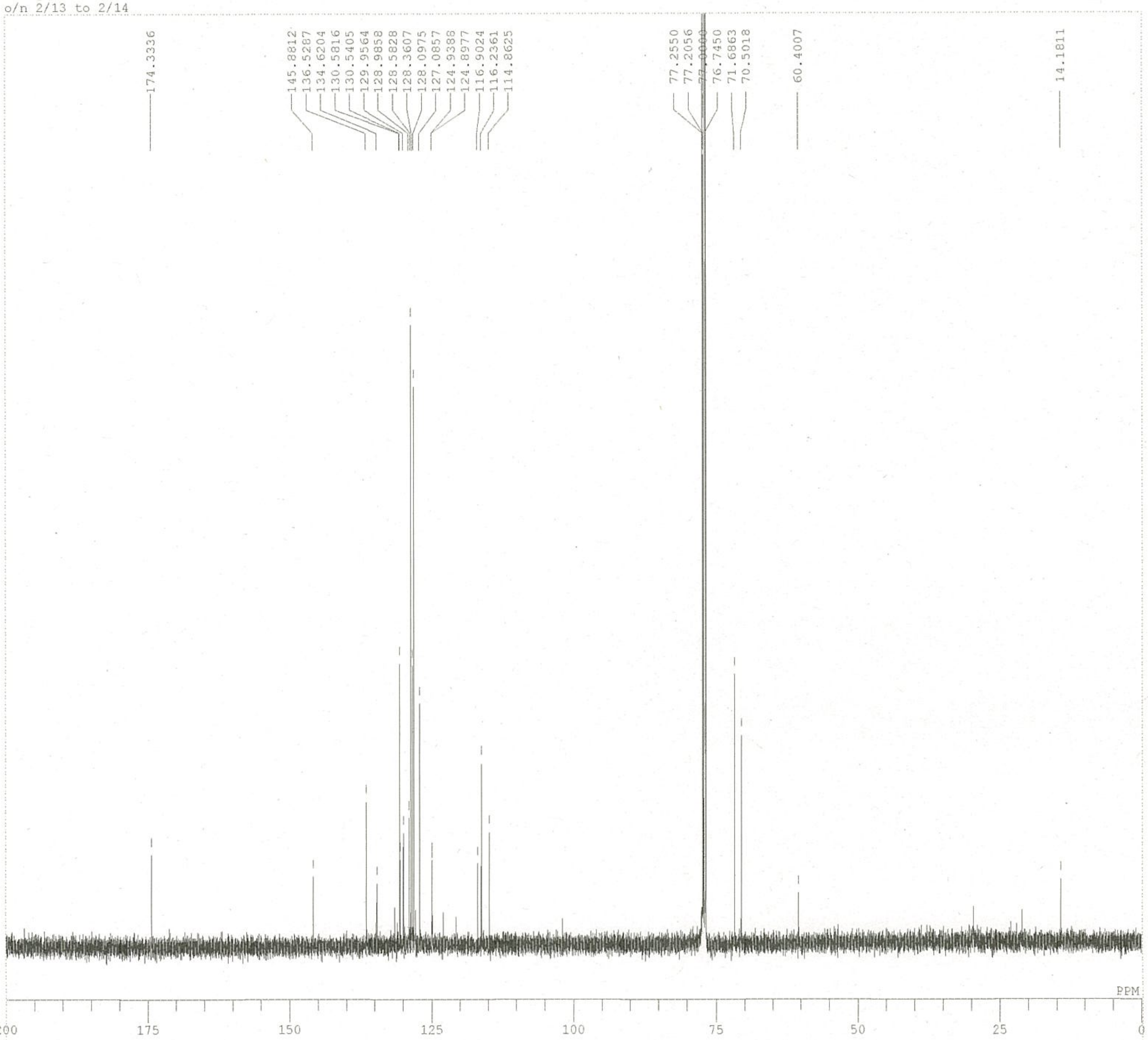



```
DFILE   3176_1.als
COMNT   3176-1
DATIM   Mon Apr 20 20:16:24 2009
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU        10000.00 Hz
SCANS             16
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               5.70 usec
IRNUC   1H
CTEMP            25.7 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                1.20 Hz
RGAIN               27
```

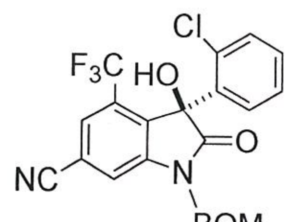


E

D:\MyDocumentD\'²‹廓¶\tomita\tomitachan\tomitachan.nmfid
o/n 2/13 to 2/14

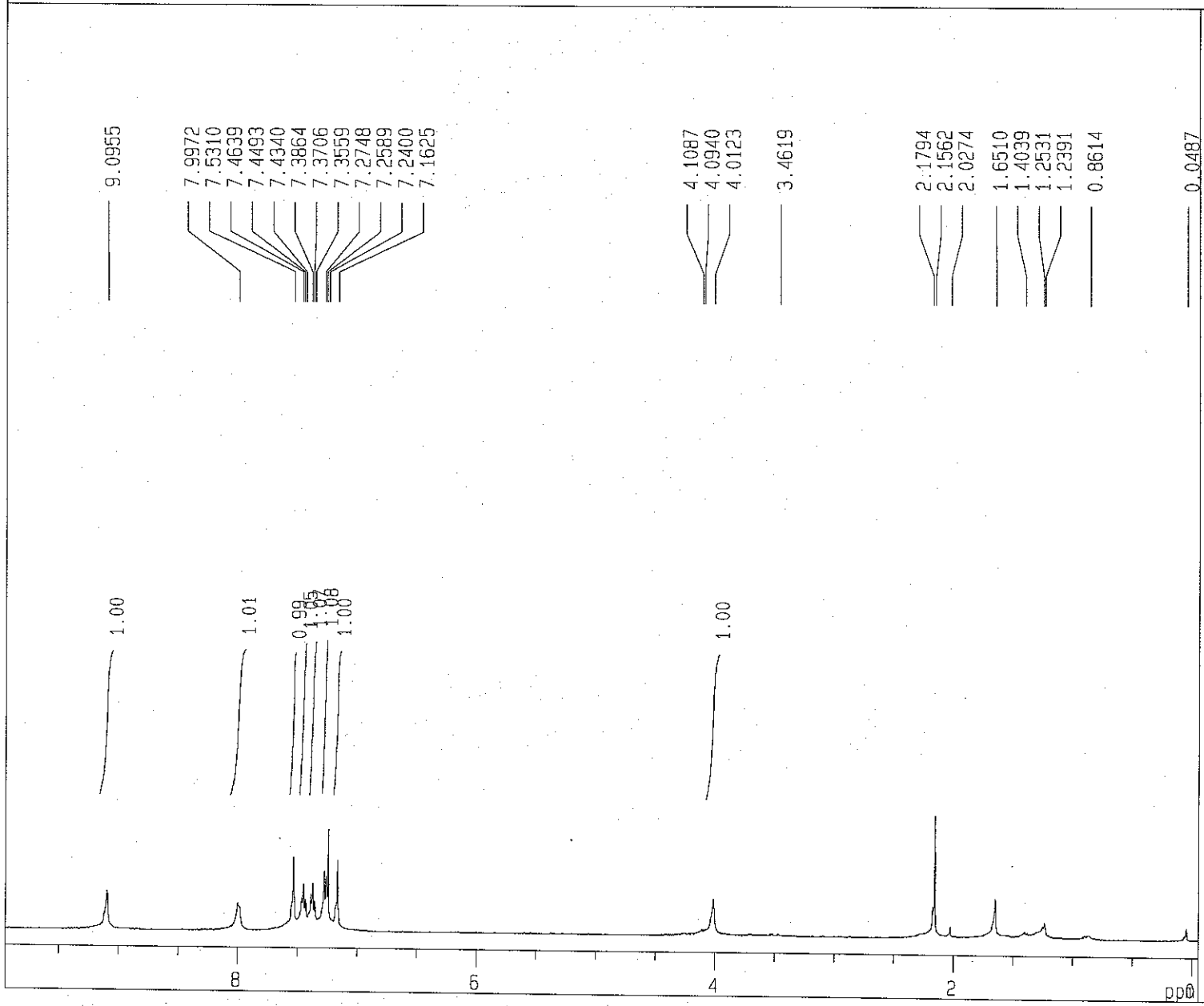


DFILE	D:\MyDocumentD\'²‹廓¶\tomita\tomitachan\tomitachan.n
COMNT	o/n 2/13 to 2/14
DATIM	Sat Feb 14 10:18:07 2009
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.0 Hz
POINT	32768
FREQU	33898.3 Hz
SCANS	9241
ACQTM	0.967 sec
PD	2.033 sec
PW1	6.2 us
IRNUC	1H
CTEMP	26.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	31



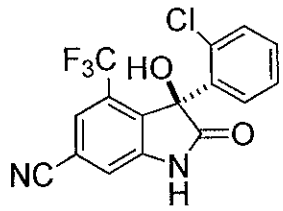
E

1H Line



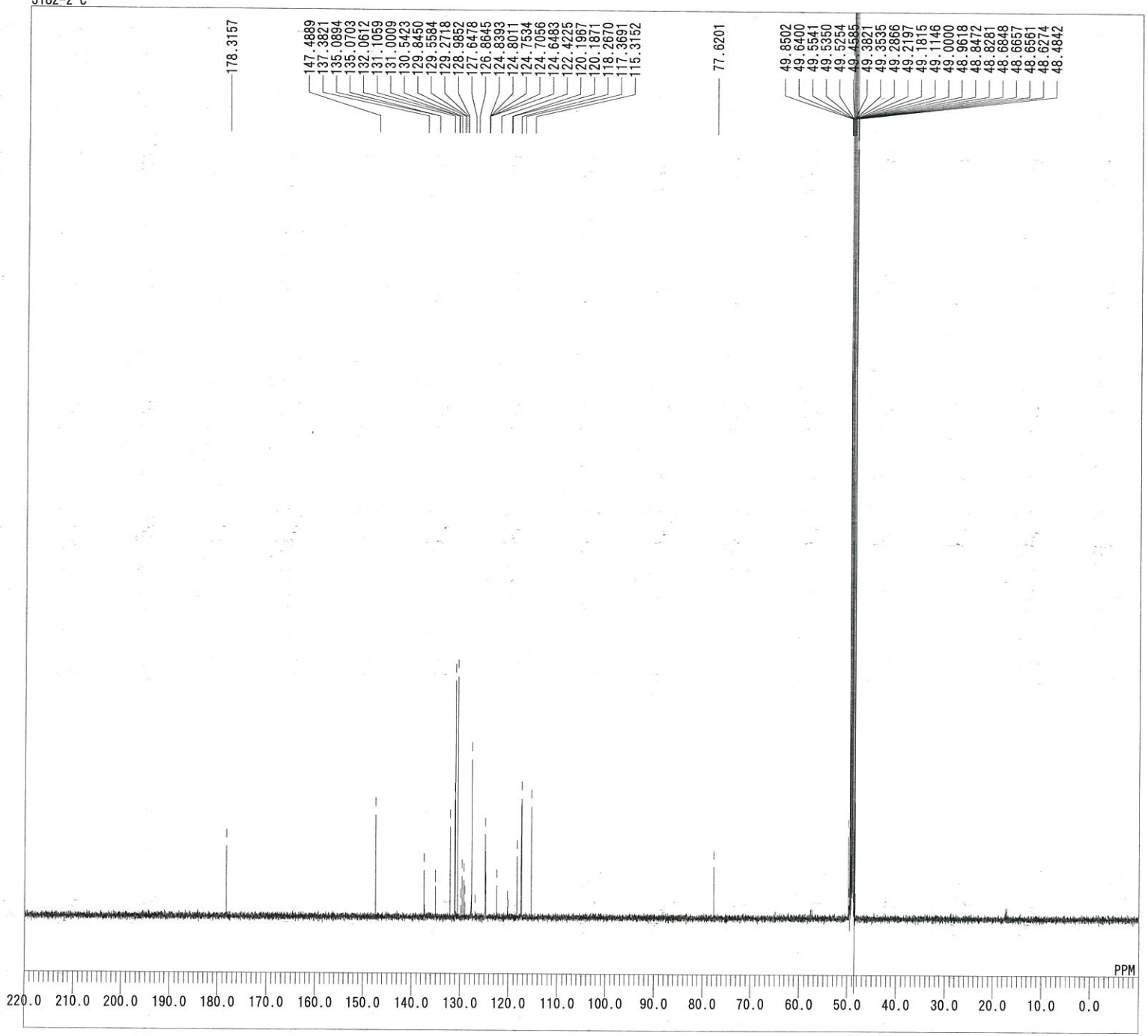
Date : Wed Feb 18 20:43:31 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	32 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	24
SCANS	:	32 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	24.0 C

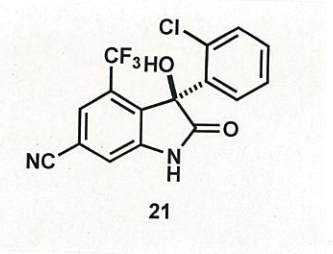


21

C:¥My Documents¥PGousei¥yamatsugu¥3182_2_C.als
3182-2 C

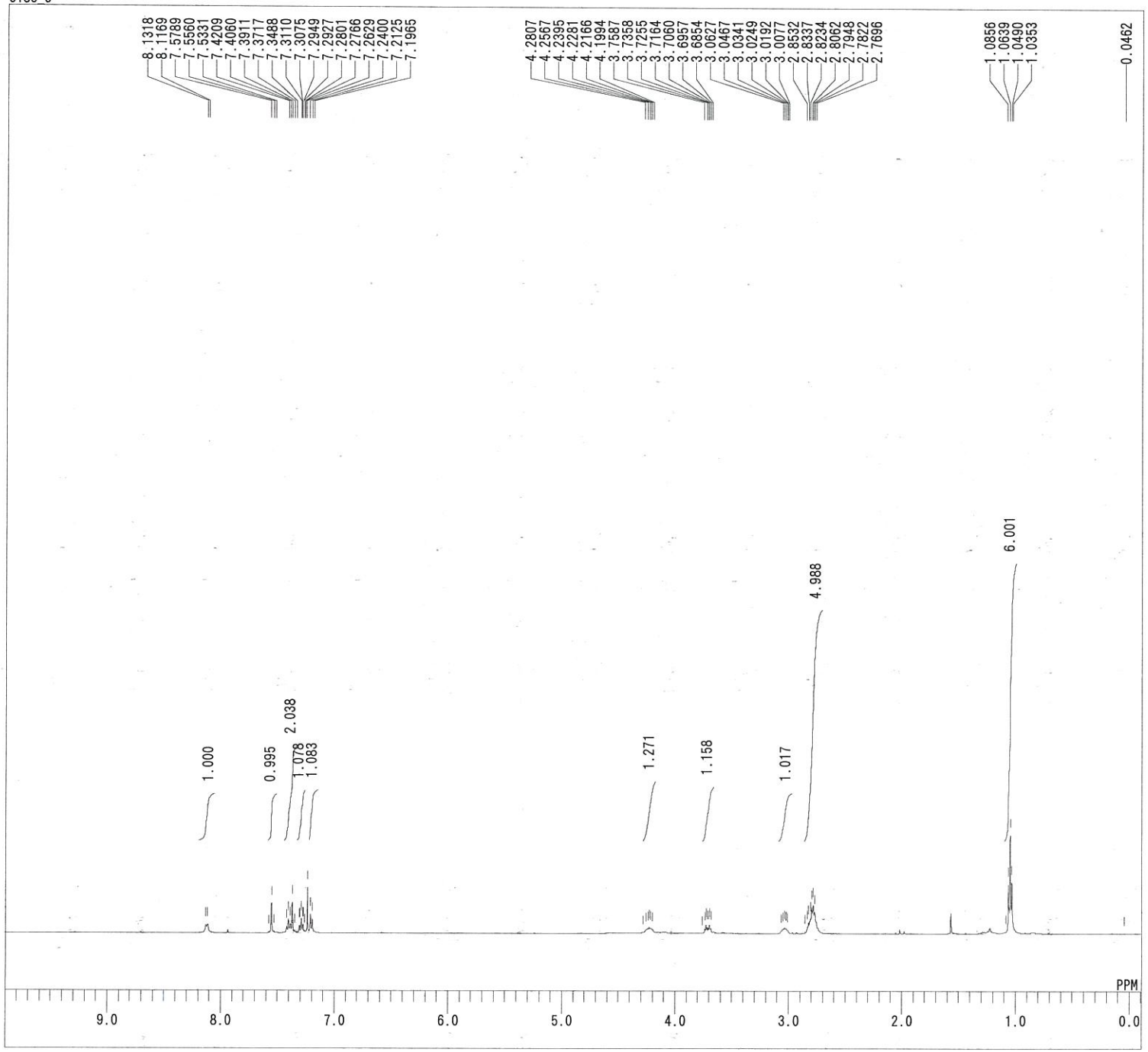


DFILE C:¥My Documents¥PGousei¥yamatsugu¥3182_2_C.als
COMNT 3182-2 C
DATIM 24-04-2009 21:41:54
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 123.26 MHz
OBSET 2.31 KHz
OBFIN 6.71 Hz
POINT 26214
FREQU 30863.73 Hz
SCANS 4800
ACQTM 0.8493 sec
PD 2.0000 sec
PW1 3.20 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CD3OD
EXREF 49.00 ppm
BF 0.01 Hz
RGAIN 60

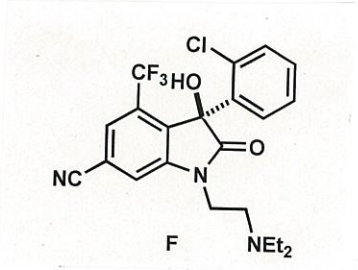


21

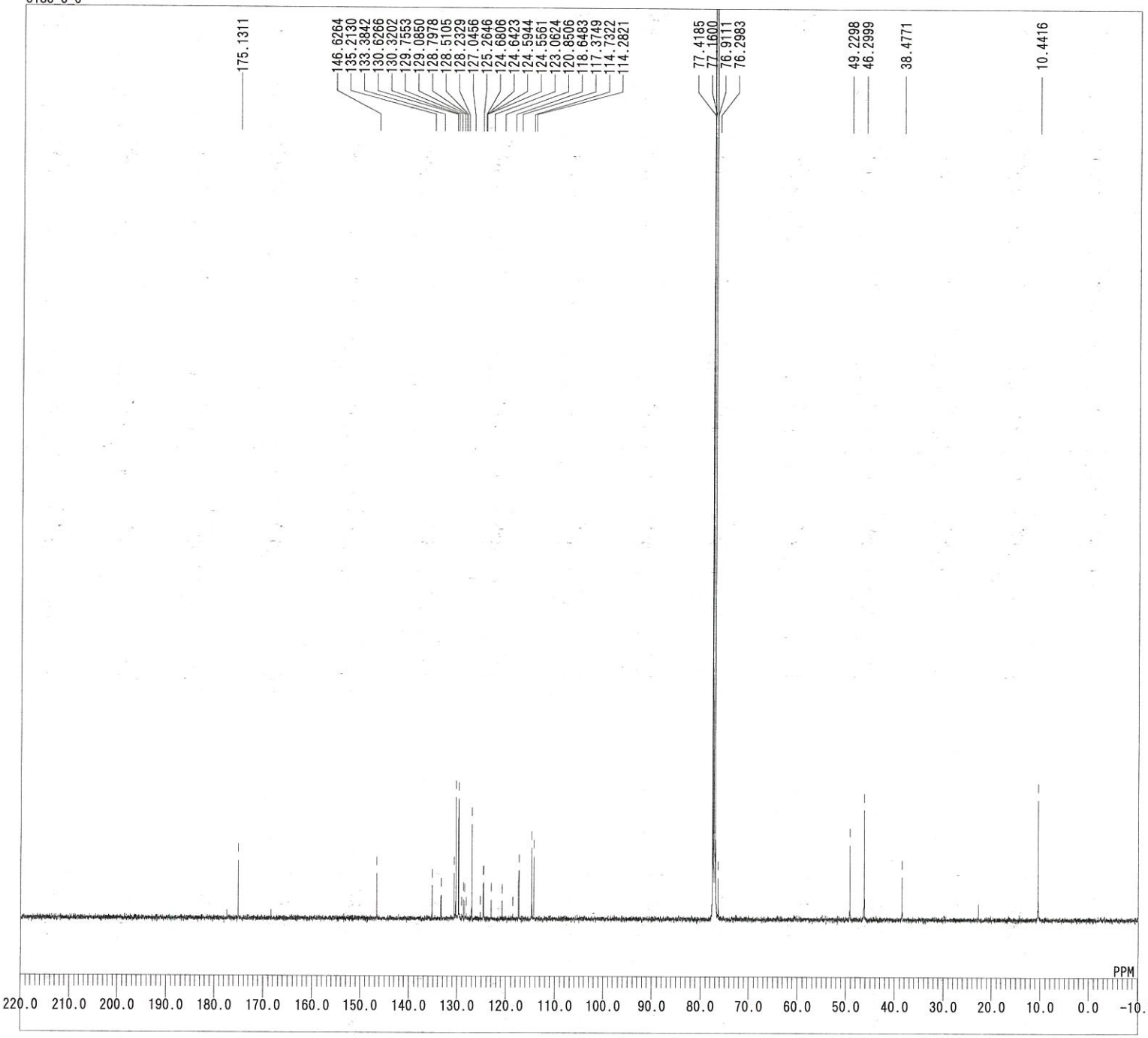
C:¥My Documents¥PGousei¥yamatsugu¥3183_3.als
3183_3



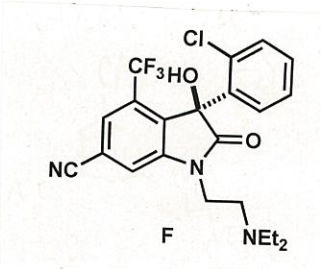
DFILE C:¥My Documents¥PGousei¥yamatsugu¥3183_3.als
COMNT 3183_3
DATIM 25-04-2009 01:18:37
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
POINT 13107
FREQU 7429.31 Hz
SCANS 8
ACQTM 1.7642 sec
PD 5.0000 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 1.00 Hz
RGAIN 50



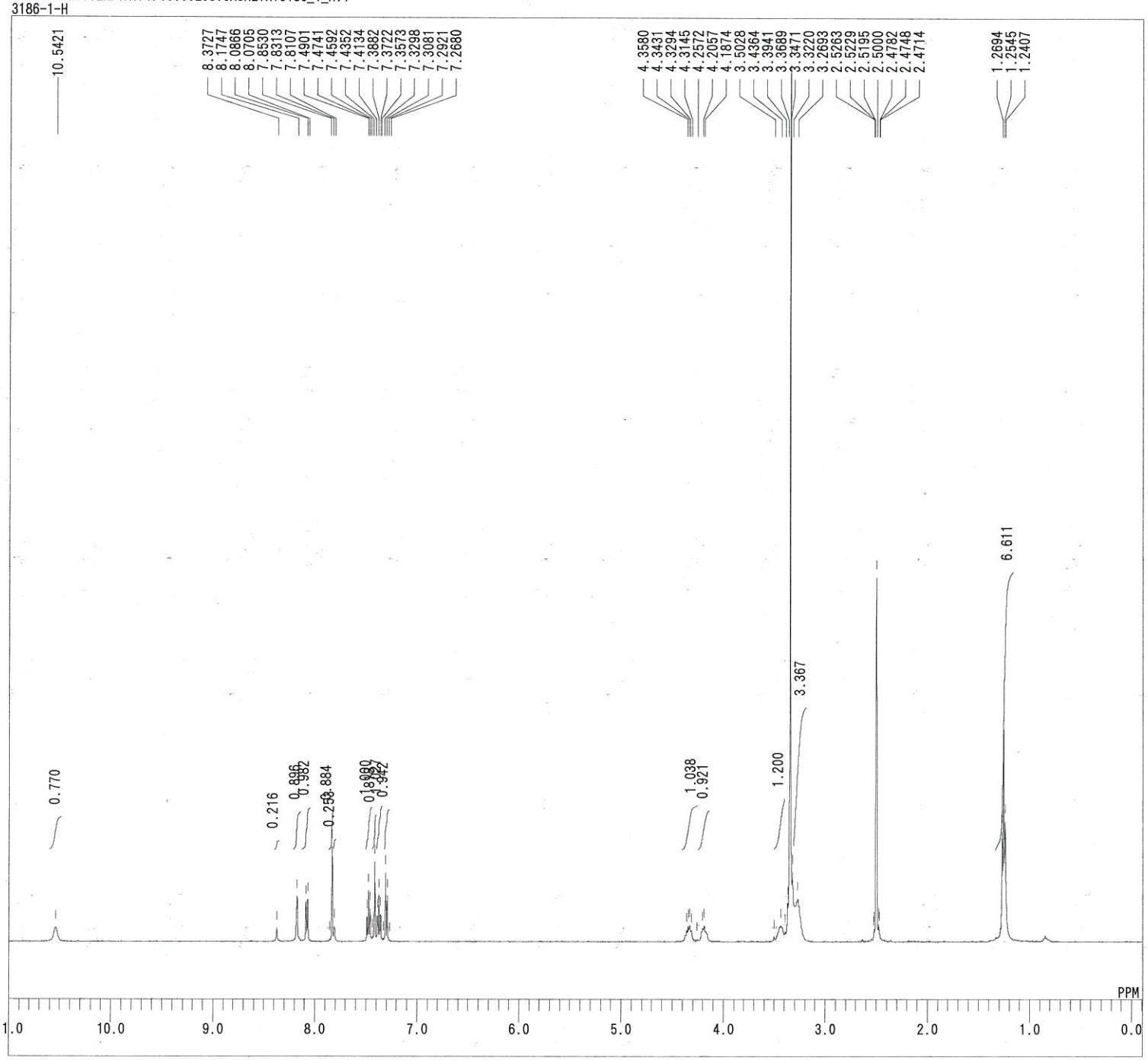
C:¥My Documents¥PGousei¥yamatsugu¥3183_3_C.als
3183_3_C



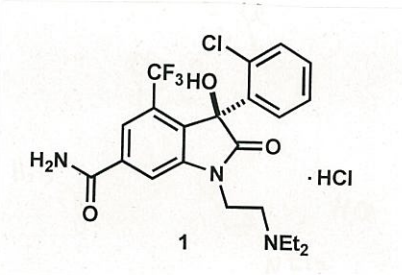

```
DFILE  C:¥My Documents¥PGousei¥yamatsugu¥3183_3_C.als
COMNT  3183_3_C
DATIM  25-04-2009 09:13:14
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        124.51 MHz
OBSET          3.45 KHz
OBFIN          6.00 Hz
POINT         26214
FREQU      31249.52 Hz
SCANS         10000
ACQTM         0.8389 sec
PD            2.0000 sec
PW1             3.57 usec
IRNUC  1H
CTEMP          21.1 c
SLVNT  CDCL3
EXREF         77.16 ppm
BF             1.00 Hz
RGAIN            60
```



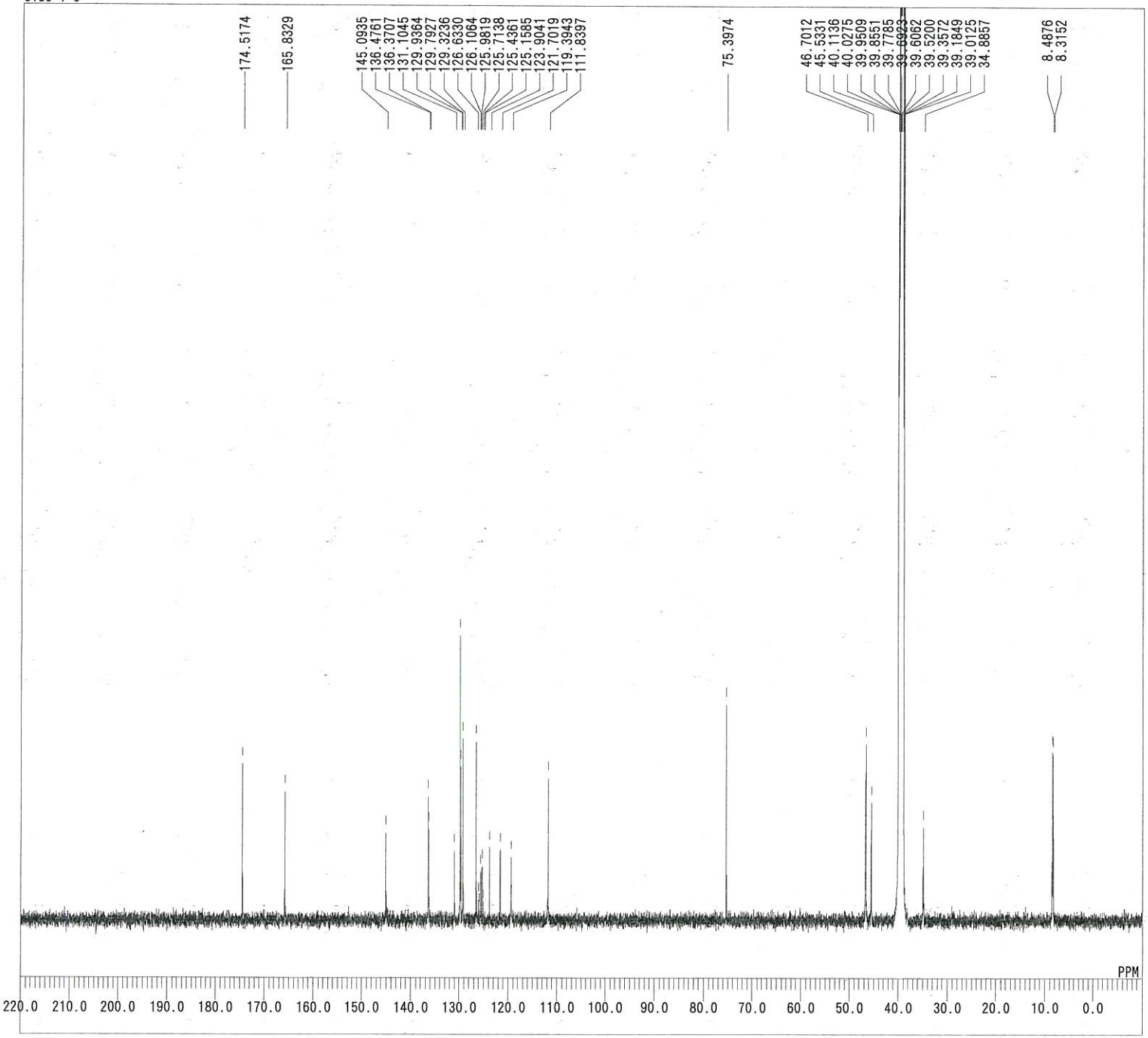
C:¥WINDOWS¥TEMP¥ATFTP00000EC8.CACHE¥KY3186_1_H.1
3186-1-H



DFILE C:¥WINDOWS¥TEMP¥ATFTP00000EC8.CACHE¥KY3186_1_H.1
COMNT 3186-1-H
DATIM 25-04-2009 23:19:34
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
POINT 16384
FREQU 9286.78 Hz
SCANS 8
ACQTM 1.7642 sec
PD 5.0000 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT DMSO
EXREF 2.50 ppm
BF 0.01 Hz
RGAIN 50



C:¥My Documents¥PGousei¥yamatsugu¥3186_1_C.als
3186-1-C



DFILE	C:¥My Documents¥PGousei¥yamatsugu¥3186_1_C.als
COMNT	3186-1-C
DATIM	27-04-2009 06:52:55
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.00 Hz
POINT	26214
FREQU	31249.52 Hz
SCANS	40000
ACQTM	0.8389 sec
PD	2.0000 sec
PW1	3.57 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	DMSO
EXREF	39.52 ppm
BF	1.00 Hz
RGAIN	60