Supporting information

$Hg(OTf)_2$-Catalyzed Vinylogous Semi-Pinacol Rearrangement Leading to 1,4-Dihydroquinolines

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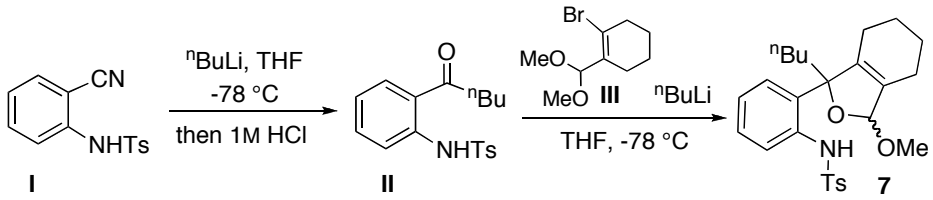
General Procedures and Methods

Melting points were determined with a Mitamura-Riken-Kogyo melting point apparatus and were uncorrected. FTIR spectra were measured on a JASCO FT/IR-4100 infrared spectrophotometer using 5 mm NaCl plates or 35 mm fluorite plate and the data are reported in reciprocal centimeters (cm^{-1}). NMR spectra were recorded on a JEOL JNM-ECA-500 (500 MHz). Chemical shifts are reported in parts per million (ppm). For ^1H NMR spectra ($CDCl_3$ and DMSO-d_6), the residual solvent peak was used as the internal reference (7.24 and 2.54 ppm), whereas the central solvent peak as the reference (77.0, 40.5, and 49.7 ppm) for ^{13}C NMR spectra ($CDCl_3$, DMSO-d_6, and CD_3OD). Mass spectra were recorded on a JEOL the Mstation JMS-700. Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography was performed on Kanto Chemical 60N (0.04-0.05 mm) mesh silica gel. Reagents and solvents are commercial grade and were used as supplied. Anhydrous dichloromethane was purchased from Kanto Chemical Co. Inc. Mercury triflate was prepared by the following procedure: to a suspension of HgO (541.4 mg, 2.5 mmol) in acetonitrile (5 mL) was dropwise added Tf_2O (705.3 mg, 2.5 mmol) at 0 °C, and the mixture was stirred at 0 °C until the yellow color disappeared. The resulting colorless solution was transferred to a 25-mL measuring flask and diluted with anhydrous acetonitrile to give a 0.1M solution.



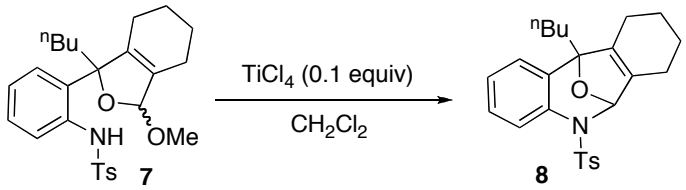
***N*-(2-(1-butyl-3-methoxy-1,3,4,5,6,7-hexahydroisobenzofuran-1-yl)phenyl)-4-methylbenzenesulfonamide (7): Typical procedure for the precursors of vinylogous semi-pinacol rearrangement.**[1,2]

To a solution of 2-cyano-*N*-tosyl-aniline **I** (5.3 g, 19.6 mmol) in THF (200 mL) was added *n*-BuLi (15.6 mL, 2.76 M solution in hexane) at 0 °C. The mixture was stirred at 0 °C for 30 min. The reaction was quenched with 1M HCl (60 mL). The mixture was stirred at room temperature for 30 min and extracted with ethyl acetate (x 3). The combined organic layers were washed with brine (x 2), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with hexane/ethyl acetate = 9/1) to give butyl ketone **II** (5.9 g, 90%) as yellow solid.

To a solution of *n*-BuLi (5.4 mL, 2.76 M solution in hexane) in THF (20 mL) was added a solution of 1-bromo-2-(dimethoxymethyl)cyclohex-1-ene **III**[1] (3.5 g, 15 mmol) in THF (15 mL) at -78 °C. After the mixture was stirred at -78 °C for 1.5 h, the solution of ketone **II** (1.65 g, 5.0 mmol) in THF (15 mL) was added at -78 °C. The mixture was stirred at -78 °C for 1 h, and the reaction was quenched with saturated aqueous $NaHCO_3$ (50 mL). The mixture was extracted with ethyl acetate (x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with hexane/ethyl acetate = 19/1 to 9/1) to give **7** (1.97 g, 86%) as a white solid (3 : 5 diastereomeric mixture). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1Hb), 9.75 (s, 1Ha), 7.62-7.75 (m, 3Ha + 2Hb), 7.57 (d, J = 8.6 Hz, 1Hb), 6.90-7.21 (m, 5Ha + 5Hb), 5.89 (s, 1Ha + 1Hb), 3.55 (d, J = 1.8 Hz, 3Ha), 3.54 (d, J = 1.2 Hz, 3Hb), 2.35 (s, 3Hb), 1.40-2.15 (m, 10Ha + 10 Hb), 0.94-1.32 (m, 4Ha + 4Hb), 0.84 (t, J = 7.5 Hz, 3Ha), 0.81 (t, J = 7.5 Hz, 3Hb); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 143.0, 141.3, 140.3, 137.4, 137.2, 136.4, 136.0, 131.8, 131.2, 130.8, 129.8, 129.4, 129.2, 127.74, 127.72, 127.3, 127.1, 127.0, 126.7, 123.2, 122.9, 120.9, 120.7, 110.8, 109.2, 96.8, 95.0, 56.7, 55.7, 40.3, 39.6, 25.8, 25.5, 22.9 (x2), 22.61, 22.58, 22.31, 22.27, 21.69, 21.62, 21.42, 21.40

(x2) , 21.2 (x2), 14.1, 13.9; HRMS (FD) m/z $[M]^+$ calcd for $[C_{26}H_{33}NO_4S]^+$ 455.2130, found 455.2093.

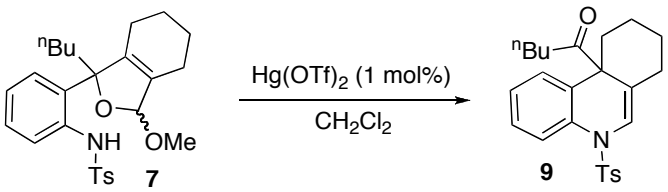
The modified condition for generation of the organolithiums was also established as follows (the case of **14**): To a solution of **III** (171 mg, 0.73 mmol) in THF (2 mL) was added ^{t}BuLi (0.9 mL, 1.6 M in pentane) at -78 °C. After the mixture was stirred at -78 °C for 1.5 h, a solution of 4-methyl-*N*-(5-methyl-2-pentanoylphenyl)benzenesulfonamide (99 mg, 0.29 mmol) in THF (2 mL) was added at -78 °C. The mixture was stirred at -78 °C for 3 h, and the reaction was quenched with saturated aqueous $NaHCO_3$ (4 mL). The mixture was extracted with ethyl acetate (x2). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with hexane/ethyl acetate = 10/1 to 5/1) to give **14** (118 mg, 87%).



11-butyl-5-tosyl-6,7,8,9,10,11-hexahydro-5*H*-6,11-epoxydibenzo[*b*,*e*]azepine (8): Typical procedure of cyclic hemiaminal formation.

To a solution of **7** (45 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was added $TiCl_4$ (1.1 μL, 0.01 mmol) at -78 °C. The mixture was stirred at -78 °C for 1 h and warmed to 40 °C. After the mixture was stirred at 40 °C for 30 min, the reaction was quenched with saturated aqueous $NaHCO_3$ (1 mL). The mixture was extracted with ethyl acetate (x 3). The combined organic layers were washed with brine (x 2), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with hexane/ethyl acetate = 15/1) to give **8** (42 mg, quant.) as a amorphous materials; IR (neat) 3066, 2933, 2860, 2837, 1599, 1477, 1453, 1354, 1167, 1091 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.13 (td, *J* = 8.0, 1.8 Hz, 1H), 6.94 (td, *J* = 7.5, 1.2 Hz, 1H), 6.87 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.60 (s, 1H), 2.32 (s, 3H), 2.14-2.22 (m, 2H), 1.94-2.03 (m, 1H), 1.91 (ddd, *J* = 14.3, 11.5, 4.6 Hz, 1H), 1.75 (ddd, *J* = 14.3, 10.9, 4.6 Hz, 1H), 1.62-1.71 (m, 1H), 1.52-1.63 (m, 2H), 1.38-1.48 (m, 1H), 1.27-1.38 (m,

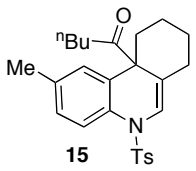
1H), 1.32 (sex, J = 7.5 Hz, 2H), 1.13-1.23 (m, 1H), 0.95-1.07 (m, 1H) 0.86 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 143.4, 135.9, 133.4, 131.6, 129.1, 128.8, 127.6, 127.3, 123.3, 122.8, 121.4, 92.3, 88.2, 29.2, 24.9, 22.9, 21.9, 21.8, 21.3, 20.5, 19.6, 14.0; HRMS (FD) m/z $[M]^+$ calcd for $[C_{25}H_{29}NO_3S]^+$ 423.1868, found 423.1890.



1-(5-tosyl-5,7,8,9,10,10a-hexahydrophenanthridin-10a-yl)pentan-1-one (9): Typical procedure of semi-pinacol rearrangement to give 1,4-dihydroquinolines

To a solution of acetal **7** (91.8 mg, 0.201 mmol) in CH_2Cl_2 (2 mL) was added mercury triflate (20 μL of 0.1 M solution in MeCN, 2.0 μmol) at room temperature. After the mixture was stirred for 5 min, the reaction was quenched with triethylamine (one drop). The mixture was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with hexane/AcOEt = 100/0 to 30/1) to give **8** (82.9 mg, 0.196 mmol 98%) as a colorless crystal. mp 109 °C (recrystallized from pentane-ether); IR (neat) 3066, 2933, 2868, 1712, 1598, 1487, 1360, 1174 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.0, 1.2 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.20 (td, J = 7.5, 1.2 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.02 (td, J = 7.5, 1.1 Hz, 1H), 6.98 (s, 1H), 6.83 (dd, J = 8.0, 1.2 Hz, 1H), 2.53 (br d, J = 12.6 Hz, 1H), 2.36 (s, 3H), 2.26-2.32 (m, 1H), 2.00 (dt, J = 17.8, 6.9 Hz, 1H), 1.70-1.80 (m, 2H), 1.68 (dt, J = 17.8, 6.9 Hz, 1H), 1.50-1.62 (m, 2H), 1.20-1.30 (m, 1H), 1.17 (quint J = 6.9 Hz, 2H), 1.00 (td, J = 13.2, 5.8 Hz, 1H), 0.72-0.97 (m, 2H), 0.67 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 207.9, 144.3, 134.2, 132.9, 129.4, 128.3, 128.0, 127.4, 127.3, 125.7, 123.3, 121.0, 119.7, 55.0, 37.5, 37.2, 31.7, 27.4, 25.5, 23.5, 21.6, 21.3, 13.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $[C_{25}H_{29}NO_3S+Na]^+$ 446.1766, found 446.1759.

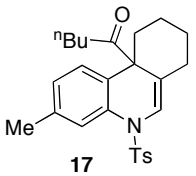
1-(2-methyl-5-tosyl-5,7,8,9,10,10a-hexahydrophenanthridin-10a-yl) pentan-1-one (15)



15

Colorless amorphous material; IR (neat) 3029, 2932, 2867, 1712, 1598, 1496, 1457, 1360, 1261, 1170, 1121, 1074 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.00 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.95 (s, 1H), 6.61 (s, 1H), 2.50 (br d, *J* = 13.2 Hz, 1H), 2.36 (s, 3H), 2.57 (br d, *J* = 13.2 Hz, 1H), 2.19 (s, 3H), 1.98 (dt, *J* = 17.8, 6.9 Hz, 1H), 1.68-1.78 (m, 2H), 1.65 (dt, *J* = 17.8, 6.9 Hz, 1H), 1.50-1.60 (m, 2H), 1.70-1,81 (m, 2H), 1.12-1.34 (m, 3H), 0.73-1.00 (m, 3H), 0.67 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 144.3, 135.6, 134.3, 130.5, 129.5, 128.9, 128.2, 127.8, 127.6, 123.5, 121.2, 119.9, 55.1, 37.7, 37.4, 31.9, 27.6, 25.6, 23.7, 21.8, 21.5, 20.7, 13.8; HRMS (ESI) m/z $[M+Na]^+$ calcd for $[C_{26}H_{31}NO_3S+Na]^+$ 460.1923, found 460.1920.

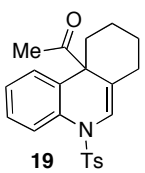
1-(3-methyl-5-tosyl-5,7,8,9,10,10a-hexahydrophenanthridin-10a-yl) pentan-1-one (17)



17

White solids; mp 110 °C (recrystallized from ether-pentane); IR (neat) 2931, 2866, 1712, 1505, 1457, 1361, 1259, 1174, 1122 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 1.2 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 2.51 (br d, *J* = 13.2 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.27 (br d, *J* = 12.6, 1H), 1.98 (dt, *J* = 17.8, 6.9 Hz, 1H), 1.70-1.79 (m, 2H), 1.67 (dt, *J* = 17.8, 6.9 Hz, 1H), 1.48-1.59 (m, 2H), 1.18-1.29 (m, 1H), 1.17 (quint, *J* = 6.9 H, 2H), 0.94 (td, *J* = 12.6, 6.9 Hz, 1H), 0.75-0.95 (m, 2H), 0.68 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.4, 144.4, 138.0, 134.4, 132.8, 129.5, 127.5, 127.2, 126.7, 125.5, 123.5, 121.6, 119.8, 54.8, 37.6, 37.3, 31.8, 27.5, 25.6, 23.7, 21.8, 21.5, 21.4, 13.8; HRMS (ESI) m/z $[M+Na]^+$ calcd for $[C_{26}H_{31}NO_3S+Na]^+$ 460.1923, found 460.1919.

1-(5-tosyl-5,7,8,9,10,10a-hexahydrophenanthridin-10a-yl)ethanone (19)

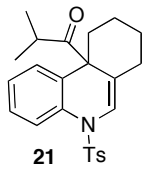


19

Colorless amorphous material; IR (neat) 2935, 2863, 1712, 1597, 1488, 1448, 1359, 1257, 1173, 1121, 1076 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.23 (t, *J* = 8.6 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 6.88 (dd, *J* = 8.1, 1.8 Hz, 1H), 2.50

(br d, J = 12.6 Hz, 1H), 2.35 (s, 3H), 2.30 (br d, J = 13.2 Hz, 1H), 1.72-1.84 (m, 2H), 1.52-1.62 (m, 2H), 1.56 (s, 3H), 1.18-1.33 (m, 1H), 0.97 (td, J = 12.6, 5.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.5, 144.5, 134.2, 133.0, 129.6, 128.3, 128.2, 127.5, 127.4, 126.0, 123.7, 121.5, 119.7, 55.3, 37.1, 31.7, 27.5, 26.1, 23.6, 21.5; HRMS (FD) m/z $[M]^+$ calcd for $[C_{22}H_{23}NO_3S]^+$ 381.1399, found 381.1385.

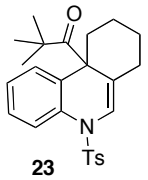
2-methyl-1-(5-tosyl-5,7,8,9,10,10a-hexahydrophenanthridin-10a-yl)propan-1-one (21)



21

White solids; mp 122 °C (recrystallized from hexane-ethyl acetate); IR (neat) 3030, 2934, 2869, 1709, 1598, 1488, 1448, 1360, 1256, 1173, 1122, 1090 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 8.6 Hz, 2H), 7.01 (t, J = 8.0 Hz, 1H), 7.01 (s, 1H), 6.81 (d, J = 7.5 Hz, 1H), 2.53 (br d, J = 12.6 Hz, 1H), 2.36 (s, 3H), 2.23-2.33 (m, 2H), 1.70-1,81 (m, 2H), 1.56-1.67 (m, 2H), 1.18-1.33 (m, 1H), 1.06 (td, J = 12.6, 5.2 Hz, 1H), 0.76 (d, J = 6.9 Hz, 3H), 0.22 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 144.3, 134.3, 133.1, 129.5, 128.2, 127.94, 127.93, 127.4, 125.5, 122.5, 120.8, 120.1, 55.8, 37.2, 36.0, 32.2, 27.6, 23.7, 21.4 (x2) 20.2; HRMS (FD) m/z $[M]^+$ calcd for $[C_{24}H_{27}NO_3S]^+$ 409.1711, found 409.1703.

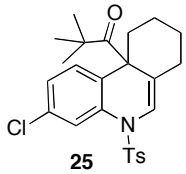
2,2-dimethyl-1-(5-tosyl-5,7,8,9,10,10a-hexahydrophenanthridin-10a-yl)propan-1-one (23)



23

White solids; mp 163 °C (recrystallized from hexane-ethyl acetate); IR (neat) 3115, 2936, 2868, 1693, 1594, 1481, 1360, 1257, 1173, 1076 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 1H), 7.58 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.91 (s, 1H), 6.65 (d, J = 8.1 Hz, 1H), 2.36 (s, 3H), 2.35 (br d, J = 10.9 Hz, 1H), 2.29 (br d, J = 12.6 Hz, 1H), 1.77-1.90 (m, 2H), 1.69 (qt, J = 13.8 Hz, 4.0 Hz, 1H), 1.50 (br d, J = 15.5 Hz, 1H), 1.20-1.35 (m, 2H), 0.90 (s, 9H), 0.70 (td, J = 12.6, 4.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.8, 144.4, 134.5, 133.0, 129.4, 128.0, 127.9, 127.7, 127.5, 125.4, 123.7, 121.2, 119.0, 55.8, 46.8, 41.9, 32.9, 29.33, 29.31, 24.0, 21.5; HRMS (ESI) m/z $[M+Na]^+$ calcd for $[C_{25}H_{29}NO_3S+Na]^+$ 446.1766, found 446.1758.

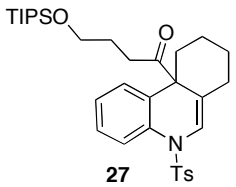
1-(3-chloro-5-tosyl-5,7,8,9,10,10a-hexahydrophenanthridin-10a-yl) -2,2-dimethylpropan-1-one (25)



25

White solids; mp 160 °C (recrystallized from hexane-ethyl acetate); IR (neat) 3020, 2952, 1691, 1489, 1449, 1357, 1216, 1173, 1047 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.8 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6, 1.7 Hz, 1H), 6.91 (s, 1H), 6.57 (d, *J* = 8.6 Hz, 1H), 2.39 (s, 3H), 2.26-2.37 (m, 2H), 1.77-1.89 (m, 2H), 1.65 (qt, *J* = 13.2 Hz, 4.0 Hz, 1H), 1.22-1.34 (m, 2H), 0.91 (s, 9H), 0.76 (td, *J* = 12.6, 4.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.6, 144.8, 134.2, 134.1, 133.7, 129.6, 128.7, 127.6, 126.3, 125.4, 123.3, 120.8, 118.7, 55.5, 46.9, 42.1, 32.8, 29.32, 29.29, 24.0, 21.6; HRMS (ESI) m/z $[M+Na]^+$ calcd for $[C_{25}H_{28}NO_3SCl+Na]^+$ 480.1376, found 480.1374.

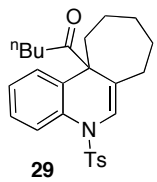
1-(5-tosyl-5,7,8,9,10,10a-hexahydrophenanthridin-10a-yl)-4-((triisopropylsilyl)oxy)butan-1-one (27)



27

Colorless oil; IR (neat) 2940, 2865, 1712, 1488, 1449, 1361, 1257, 1174, 1091 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.17- 7.23 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.02 (td, *J* = 7.5, 1.2 Hz, 1H), 6.96 (s, 1H), 6.84 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.43 (dt, *J* = 9.7, 6.3 Hz, 1H), 3.31 (dt, *J* = 9.7 Hz, 6.3 Hz, 1H), 2.52 (br d, *J* = 13.2 Hz, 1H), 2.35 (s, 3H), 2.22-2.30 (m, 2H), 1.79 (ddd, *J* = 13.2, 4.1, 1.2 Hz, 1H), 1.67-1.77 (m, 2H), 1.47-1.1.60 (m, 3H), 1.37 (sep, *J* = 6.9 Hz, 1H), 1.15-1.28 (m, 1H), 0.97-1.08 (m, 21H), 0.92 (td, *J* = 13.2, 4.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 144.4, 134.2, 133.1, 129.5, 128.5, 128.1, 127.6, 127.3, 125.9, 124.0, 121.6, 119.9, 61.9, 55.1, 37.4, 34.2, 31.8, 27.6, 26.9, 23.7, 21.5, 18.0, 11.9; HRMS (FD) m/z $[M]^+$ calcd for $[C_{33}H_{47}NO_4SSi]^+$ 581.2995, found 581.2978.

1-(5-tosyl-7,8,9,10,11,11a-hexahydro-5H-cyclohepta[c]quinolin-11a-yl)pentan-1-one (29)[1]

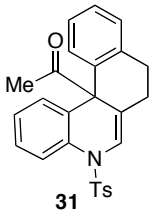


29

Yellow amorphous material; IR (neat) 2923, 2853, 1707, 1489, 1448, 1361, 1172, 1119, 1089 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.25 (td, *J* = 8.6, 1.2 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0, 1.8 Hz, 1H), 6.97 (s, 1H), 2.42 (dt, *J* = 13.8, 4.0 Hz, 1H), 2.35 (s, 3H), 2.10 (ddd, *J* = 14.9, 9.2, 1.2 Hz, 1H), 1.98 (ddd,

J = 14.3, 10.9, 3.5Hz, 1H), 1.79-1.90 (m, 2H), 1.76 (ddd, *J* = 17.8, 7.4, 6.3 Hz, 1H), 1.70 (dd, *J* = 14.9, 10.3 Hz, 1H), 1.48-1.63 (m, 1H), 1.40-1.25 (m, 2H), 1.16-1.05 (m, 3H), 0.85-1.04 (m, 3H), 0.72 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.9, 144.3, 135.1, 134.9, 129.9, 129.6, 129.5, 127.6, 127.4, 127.0, 125.7, 123.6, 121.3, 58.8, 37.9, 36.8, 31.5, 30.8, 29.0, 25.9, 23.7, 22.0, 21.5, 13.9; HRMS (FD) m/z $[M]^+$ calcd for $[C_{26}H_{31}NO_3S]^+$ 437.2025, found 437.2010.

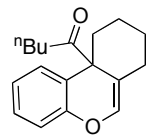
1-(5-tosyl-5,7,8,12b-tetrahydrobenzo[k]phenanthridin-12b-yl)ethan one (31)[1,3]



31

Colorless amorphous material; IR (neat) 3066, 2943, 2847, 1713, 1598, 1478, 1449, 1362, 1263, 1169, 1119, 1089 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.24 (td, *J* = 7.4, 1.1 Hz, 1H), 7.08-7.20 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.76 (dd, *J* = 8.0, 1.8 Hz, 1H), 2.85-2.93 (m, 1H), 2.72-2.80 (m, 1H), 2.55-2.70 (m, 2H), 2.35 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 144.2, 138.6, 136.6, 135.5, 133.0, 129.8, 129.7, 129.5, 129.0, 127.7, 127.5, 127.4, 127.3, 126.1, 126.0, 125.3, 122.6, 121.7, 60.1, 30.1, 28.0, 25.7, 21.6; HRMS (FD) m/z $[M]^+$ calcd for $[C_{26}H_{23}NO_3S]^+$ 429.1399, found 429.1409.

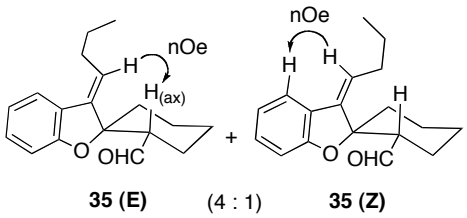
1-(8,9,10,10a-tetrahydro-7*H*-benzo[*c*]chromen-10a-yl)pentan-1-one (34)



34

Yellow oil; IR (neat) 2955, 2931, 2859, 1712, 1608, 1581, 1486, 1453, 1245, 1219, 1188, 1123, 1080 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (ddd, *J* = 8.6, 5.7, 2.3 Hz, 1H), 6.90-6.97 (m, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 1.7 Hz, 1H), 2.78 (br d, *J* = 12.6 Hz, 1H), 2.50 (dt, *J* = 17.8, 7.6 Hz, 1H), 2.45 (dt, *J* = 17.8, 7.6 Hz, 1H), 2.13-2.22 (m, 1H), 1.68-1.82 (m, 3H), 1.60 (qt, *J* = 13.5, 3.5 Hz, 1H), 1.48 (td, *J* = 13.2, 4.0 Hz, 1H), 1.24-1.46 (m, 3H), 0.98-1.15 (m, 2H), 0.74 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.7, 149.8, 134.7, 128.7, 127.2, 123.4, 123.0, 116.7, 114.7, 52.5, 38.3, 35.8, 28.9, 27.1, 26.1, 24.0, 22.0, 13.7; HRMS (EI) m/z $[M]^+$ calcd for $[C_{18}H_{22}O_2]^+$ 270.1620, found 270.1610.

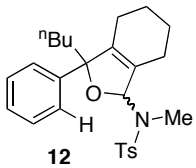
3-butylidene-3*H*-spiro[benzofuran-2,1'-cycloh exane]-2'-carbaldehyde (35)



35 (E) (4 : 1) **35 (Z)**

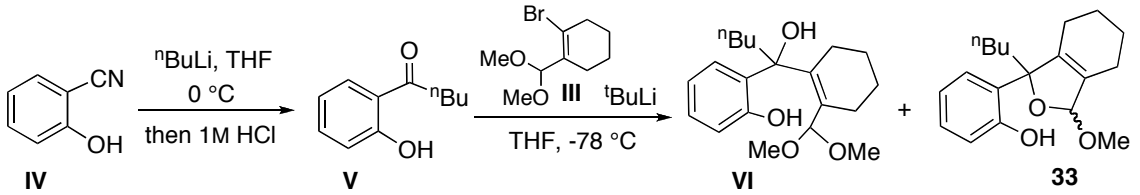
Yellow oil as a 4 : 1 geometric mixtures; IR (neat) 3036, 2934, 2863, 2737, 1724, 1605, 1587, 1461, 1269, 1234, 1104 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.48 (d, *J* = 1.7 Hz, $1H_{(Z)}$), 9.43 (d, *J* = 1.8 Hz, $1H_{(E)}$), 7.53 (d, *J* = 7.5 Hz, $1H_{(E)}$), 7.29 (d, *J* = 7.5 Hz, $1H_{(Z)}$), 7.18 (t, *J* = 8.6 Hz, 1H), 7.13 (t, *J* = 8.6 Hz, $1H_{(Z)}$), 6.91 (td, *J* = 7.5, 1.2 Hz, $1H_{(E)}$), 6.86 (t, *J* = 7.5 Hz, $1H_{(Z)}$), 6.85 (d, *J* = 8.0 Hz, $1H_{(E)}$), 6.79 (d, *J* = 8.1 Hz, $1H_{(Z)}$), 5.93 (t, *J* = 8.0 Hz, $1H_{(Z)}$), 5.38 (t, *J* = 7.5 Hz, $1H_{(E)}$), 2.75 (ddd, *J* = 10.3, 6.3, 1.7 Hz, $1H_{(z)}$), 2.49 (dt, *J* = 18.3, 7.5, $1H_{(E)}$), 2.44 (dt, *J* = 18.3, 7.5 Hz, $1H_{(E)}$), 2.37 (ddd, *J* = 10.4, 6.3, 2.2, Hz, $1H_{(E)}$), 2.31 (q, *J* = 7.5 Hz, $1H_{(E)}$), 1.72-1.97 (m, 6H), 1.62-1.72 (m, $1H_{(E)}$ + $1H_{(Z)}$), 1.46-1.60 (m, 3H), 1.32-1.46 (m, 2H), 0.99 (t, *J* = 7.5 Hz, $3H_{(E)}$), 0.98 (t, *J* = 7.5 Hz, $1H_{(Z)}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 141.0, 129.7, 125.5, 124.5, 122.3, 120.7, 110.5, 88.8, 58.7, 56.3, 39.1, 30.4, 24.3, 22.9, 22.7, 21.6, 13.8 (E-isomer); HRMS (EI) m/z $[M]^+$ calcd for $[C_{18}H_{22}O_2]^+$ 270.1620, found 270.1628.

***N*-(3-butyl-3-phenyl-1,3,4,5,6,7-hexahydroisobenzofuran-1-yl)-*N*, 4-dimethylbenzenesulfonamide (12)**



12

White solids as a 1 : 1 diastereomeric mixtures; IR (neat) 3057, 3027, 2933, 2859, 2340, 1599, 1445, 1343, 1171 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.20-7.38 (m, 9H), 7.05-7.18 (m, 3H), 6.90 (dd, *J* = 8.0, 2.3 Hz, 2H), 6.67 (s, 1H), 6.50 (s, 1H), 2.54 (s, 3H), 2.46 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H), 2.13-2.23 (m, 1H), 1.98-2.12 (m, 3H), 1.45-2.25 (m, 16 H), 1.39 (ddd, *J* = 16.1, 8.6, 7.5 Hz), 1.25 (sex, *J* = 7.5 Hz, 2H), 0.93-1.16 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.78 (quint, *J* = 8.1 Hz, 2H), 0.64 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 144.0, 143.7, 143.2, 143.1, 141.8, 135.9, 135.5, 129. 5, 129.2, 129.1, 128.4, 128.3, 128.2, 127.7, 126.9, 126.6, 126,3, 125.1, 124.7, 94.2, 93.7, 93.1, 92.9, 41.0, 37.6, 28.8, 28.2, 25.9, 25.4, 23.0, 22.8, 22.7, 22.6, 22.4, 22.0, 21.9, 21.6, 21.53, 21.50, 21.4, 21.2, 14.1, 13.9; HRMS (FD) m/z $[M]^+$ calcd for $[C_{26}H_{33}NO_3S]^+$ 439.2181, found 439.2167.

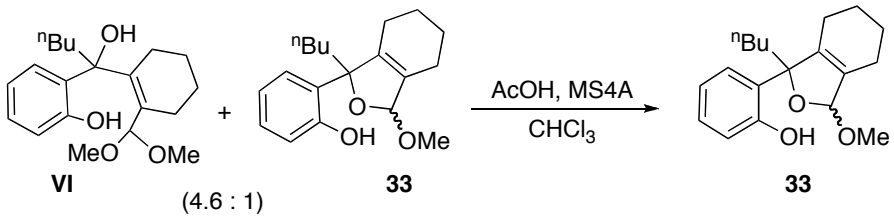


2-(1-butyl-3-methoxy-1,3,4,5,6,7-hexahydroisobenzofuran-1-yl)phenol (33):

Typical procedure for the phenol derivatives as a rearrangement precursor.

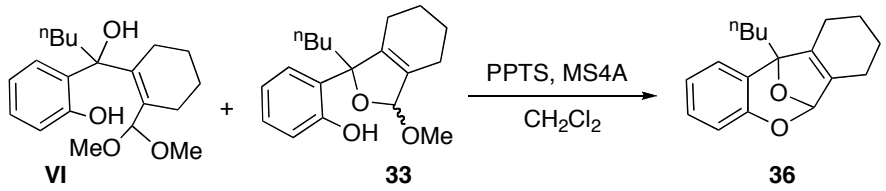
To a solution of 2-hydroxybenzonitrile **IV** (451 mg, 3.79 mmol) in THF (30 mL) was added *n*-BuLi (3.0 mL, 2.69 M solution in hexane) at 0 °C. The mixture was stirred at 0 °C for 10 min. The reaction was quenched with 1M HCl (30 mL). The mixture was stirred at room temperature for 45 min and extracted with ethyl acetate (x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with hexane/ethyl acetate = 10/1) to give butyl ketone **V** (354 mg, 52%) as a colorless oil.

To a solution of 1-bromo-2-(dimethoxymethyl)cyclohex-1-ene **III**[1] (300 mg, 1.27 mmol) in THF (3.8 mL) was added ^{t}BuLi (1.7 mL, 1.54 M solution in pentane) at -78 °C. After the mixture was stirred at -78 °C for 1 h, the solution of ketone **V** (99 mg, 0.51 mmol) in THF (1.3 mL) was added at -78 °C. The mixture was stirred at -78 °C for 20 min, and the reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL). The mixture was extracted with ethyl acetate (x 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure to give crude **VI** in 74% ^{1}H NMR yield. The residue was purified by dimethylaniline-treated silica gel flash column chromatography (elution with hexane/ethyl acetate = 20/1 to 10/1) to give the 4.6 : 1 mixture of dimethyl acetal **VI** and cyclic hemiacetal **33** (104 mg, 63%) as a colorless oil, in later of which was formed during silica gel column chromatography. **VI**: ^{1}H NMR (500 MHz, C_6D_6) δ 10.12 (s, 1H), 7.09 (dd, J = 8.6, 1.8 Hz, 1H), 7.02 (td, *J* = 8.6, 1.7 Hz, 1H), 6.77 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.67 (td, *J* = 8.1, 1,8 Hz, 1H), 5.15 (s, 1H), 4.22 (s, 1H), 3.17 (s, 3H), 2.74 (s, 3H), 2.30-2.40 (m, 1H), 2.14-2.26 (m, 1H), 2.04-2.14 (m, 1H), 1.93-2.03 (m, 1H), 1.89 (ddd, *J* = 13.8, 12.1, 5.2 Hz, 1H), 1.81 (ddd, *J* = 13.2, 11.5, 4.1 Hz, 1H), 1.54-1.67 (m, 1H), 1.38-1.56 (m, 2H), 1.16-1.38 (m, 5H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 143.4, 135.0, 130.5, 128.4, 126.4, 119.0, 117.1, 103.8, 82.4, 55.0, 54.9, 41.5, 28.7, 25.3, 24.8, 23.1, 22.9, 21.8, 14.1.



2-(1-butyl-3-methoxy-1,3,4,5,6,7-hexahydroisobenzofuran-1-yl)phenol (33)

To the 4.6 : 1 mixture of dimethyl acetal **VI** and cyclic hemiaminal **33** (31 mg, 0.094 mmol) in $CHCl_3$ was added MS4A (51 mg) at room temperature. After the mixture was stirred at room temperature for 15 h, acetic acid (50 μL) was added. The mixture was stirred for 10 min, filtered through celite, washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by dimethylaniline-treated silica gel flash column chromatography (elution with hexane/ethyl acetate = 100/1 to 20/1 to 9/1) to give **33** (15 mg, 53%) as a colorless oil, the 4.6 : 1 mixture of **VI** and **33** (4 mg, 13%), and **36** (1.2 mg, 5%) as a colorless amorphous material. **33** (2 : 1 diastereomeric mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1H), 9.08 (s, 1H), 7.12 (td, *J* = 7.5, 1.8 Hz, 1H), 7.11 (td, *J* = 6.9, 1.7 Hz, 1H), 7.05 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.00 (dd, *J* = 8.0, 1,7 Hz, 1H), 6.81-6.86 (m, 2H), 6.76-6.81 (m, 2H), 5.65 (s, 1H), 5.64 (s, 1H), 3.51 (s, 3H), 3.50 (s, 3H), 1.88-2.20 (m, 10H), 1.63-1.82 (m, 6H), 1.44-1.64 (m, 4H), 1.18-1.43 (m, 8H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 155.5, 141.6, 140.9, 130.8, 130.3, 128.5, 128.3, 126.3, 126.2, 125.1, 120.2, 118.9, 118.8, 118.2, 117.8, 110.7, 109.3, 97.9, 95.8, 55.9, 55.3, 40.6, 39.7, 25.8, 25.6, 22.7, 22.6, 22.5, 22.48, 22.44, 22.3, 21.8, 21.7, 21.3, 21.2, 14.1, 14.0; HRMS (EI) m/z $[M]^+$ calcd for $[C_{19}H_{26}O_3]^+$ 302.1882, found 302.1886.



11-butyl-6,7,8,9,10,11-hexahydro-6,11-epoxydibenzo[*b*,*e*]oxepine (36)

To the 4.6 : 1 mixture of dimethyl acetal **VI** and cyclic hemiaminal **33** (30 mg, 0.090 mmol) in CH_2Cl_2 (0.9 mL) was added PPTS (5.2 mg, 0.021 mmol) and MS4A (60 mg) at room temperature. After the mixture was stirred at room temperature for 5.5 h, more PPTS (5.2 mg, 0.021 mmol) was added. The mixture was further stirred at room temperature for 24 h, filtered through celite, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with hexane/ethyl acetate = 100/1 to 30/1) to give **36** (18.8 mg, 77%) and **33** (2.9 mg, 11%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.23 (td, *J* = 8.0, 1.8 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.12 (d, *J* = 1.7 Hz, 1H), 2.33 (dd, *J* = 14.0 Hz, 4.3 Hz, 1H), 2.19 (tdd, *J* = 13.5, 4.6, 1.7 Hz, 1H), 1.82-2.07 (m, 6H), 1.75 (td, *J* = 13.2 Hz, 4.0 Hz, 1H), 1.25-1.55 (m, 5H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 139.2, 130.3, 129.1, 125.1, 120.3, 114.3, 110.6, 99.2, 94.6, 34.1, 32.0, 26.3, 26.2, 23.4, 22.4, 21.5, 14.0.

1. For the Vilsmeier reaction: see, Gurnos, J.; Stephen, P. *Organic Reactions*; Paquette, L. A. Ed.; John Wiley & Sons, Inc; New York, **2000**, 56, 355-660.
2. For the formation of dimethyl acetal **III** from the Vilsmeier adduct and its lithiation, see Takemoto, Y.; Ohra, T.; Sugiyama, K.; Imanishi, T.; Iwata, C. *Chem. Pharm. Bull.* **1995**, *43*, 571-577.
3. For the Vilsmeier reaction of 3,4-dihydronaphthalen-1(2*H*)-one: see, Gilchrist, T. L.; Healy, M. A. M. *Tetrahedron*, **1993**, *49*, 2543-2556.

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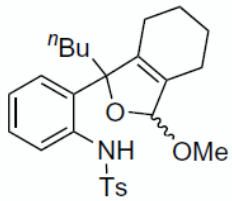

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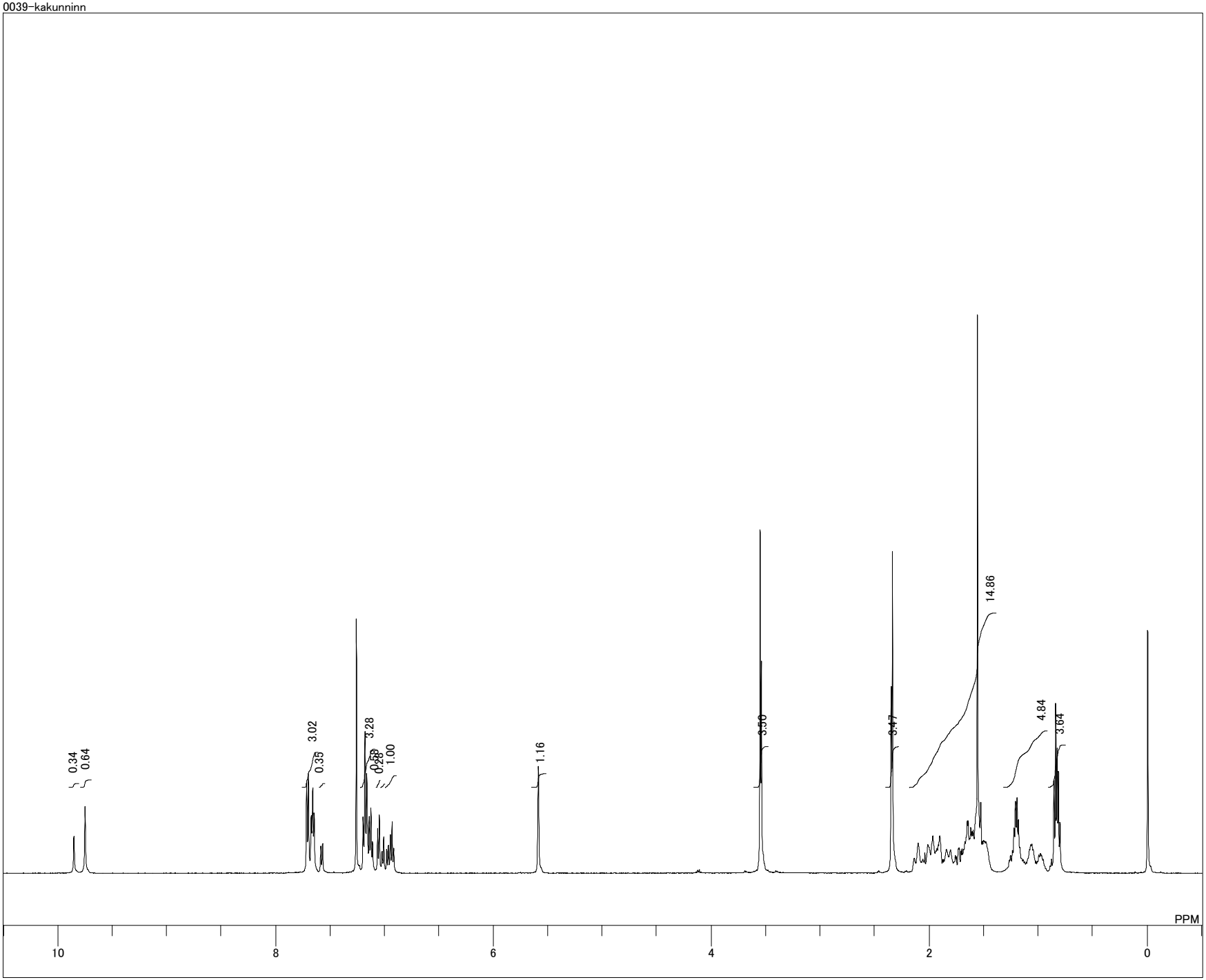
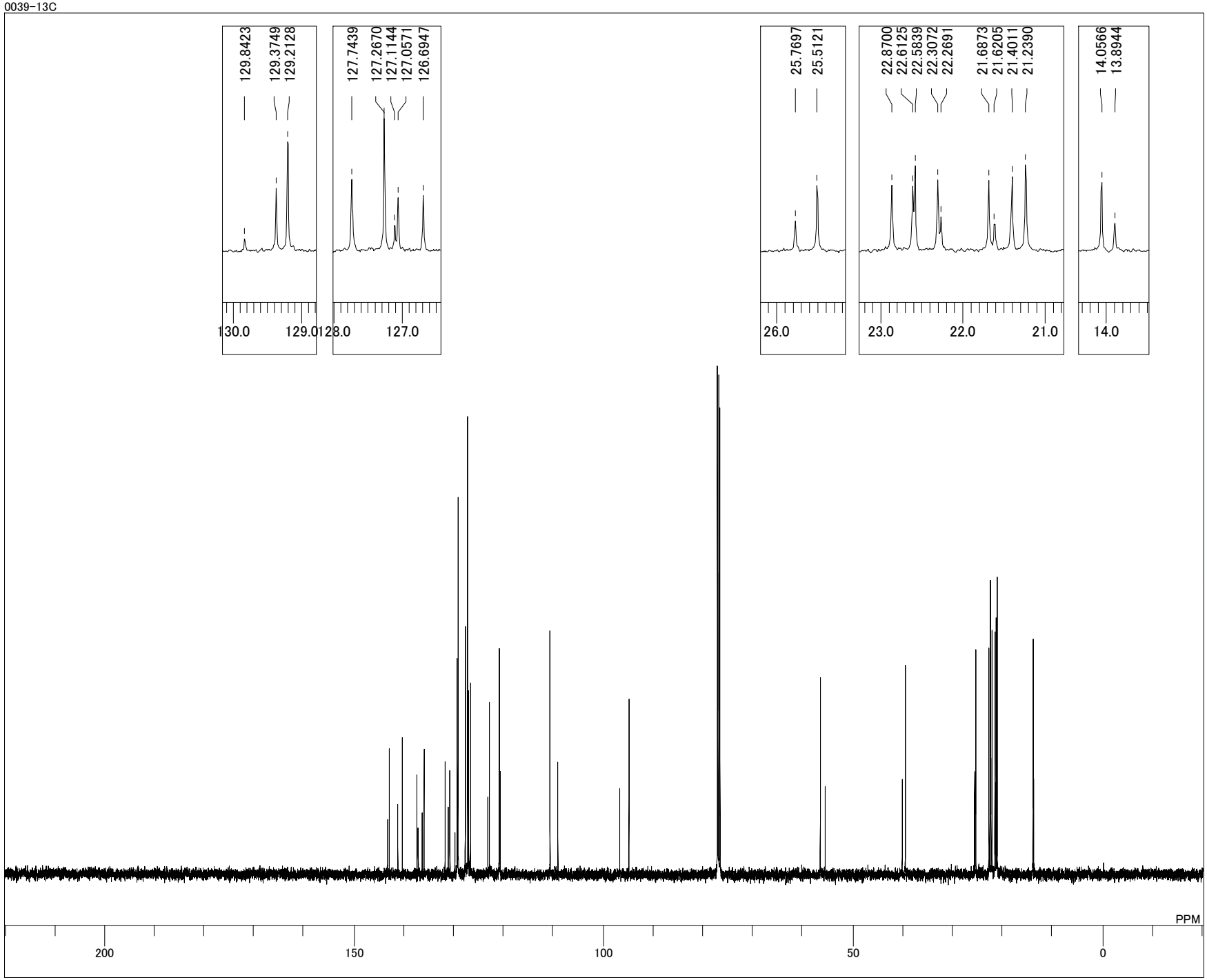


0039-13C



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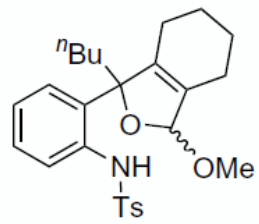
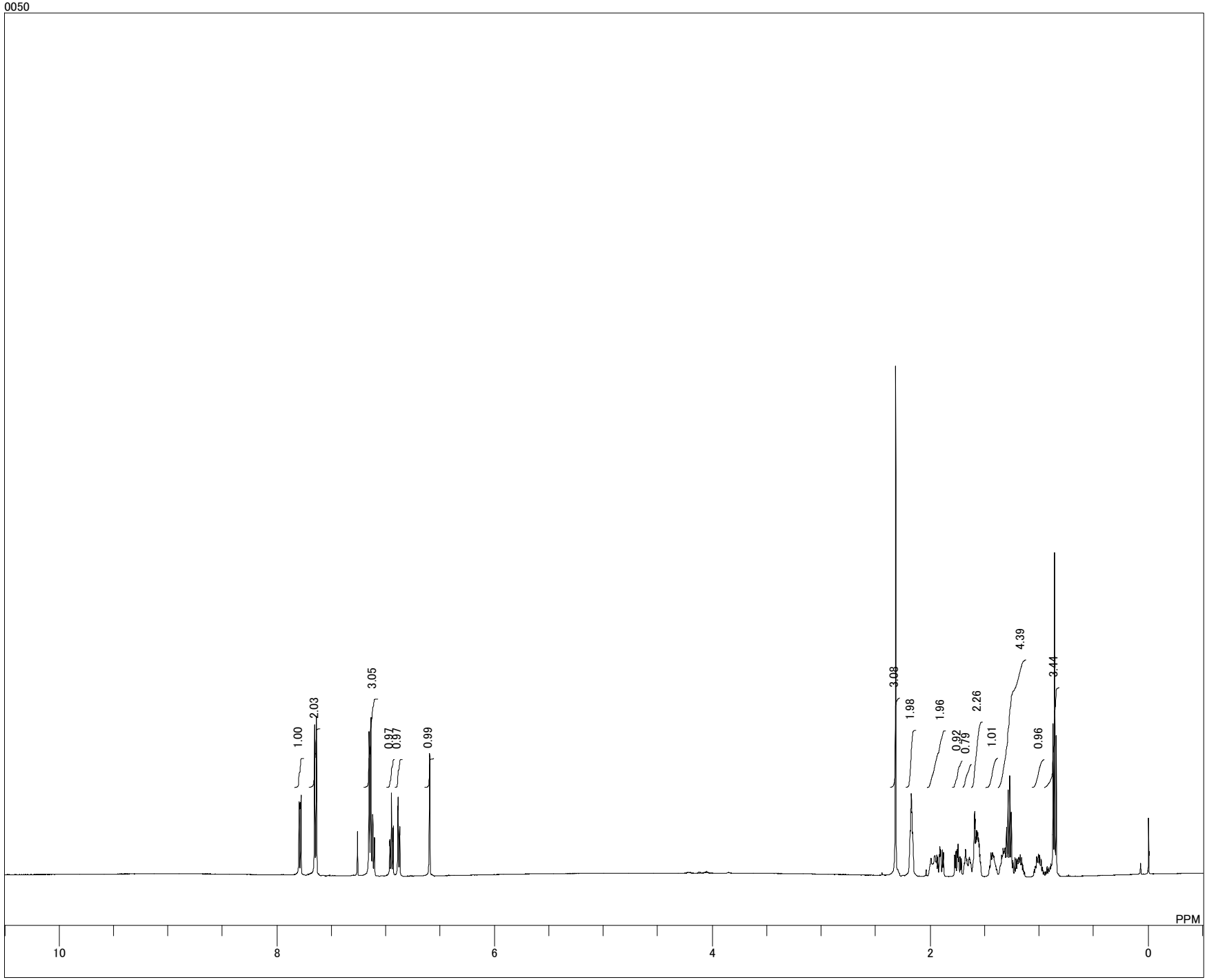
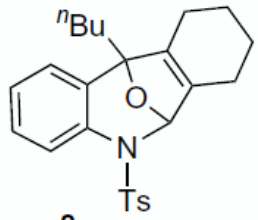


7

0050

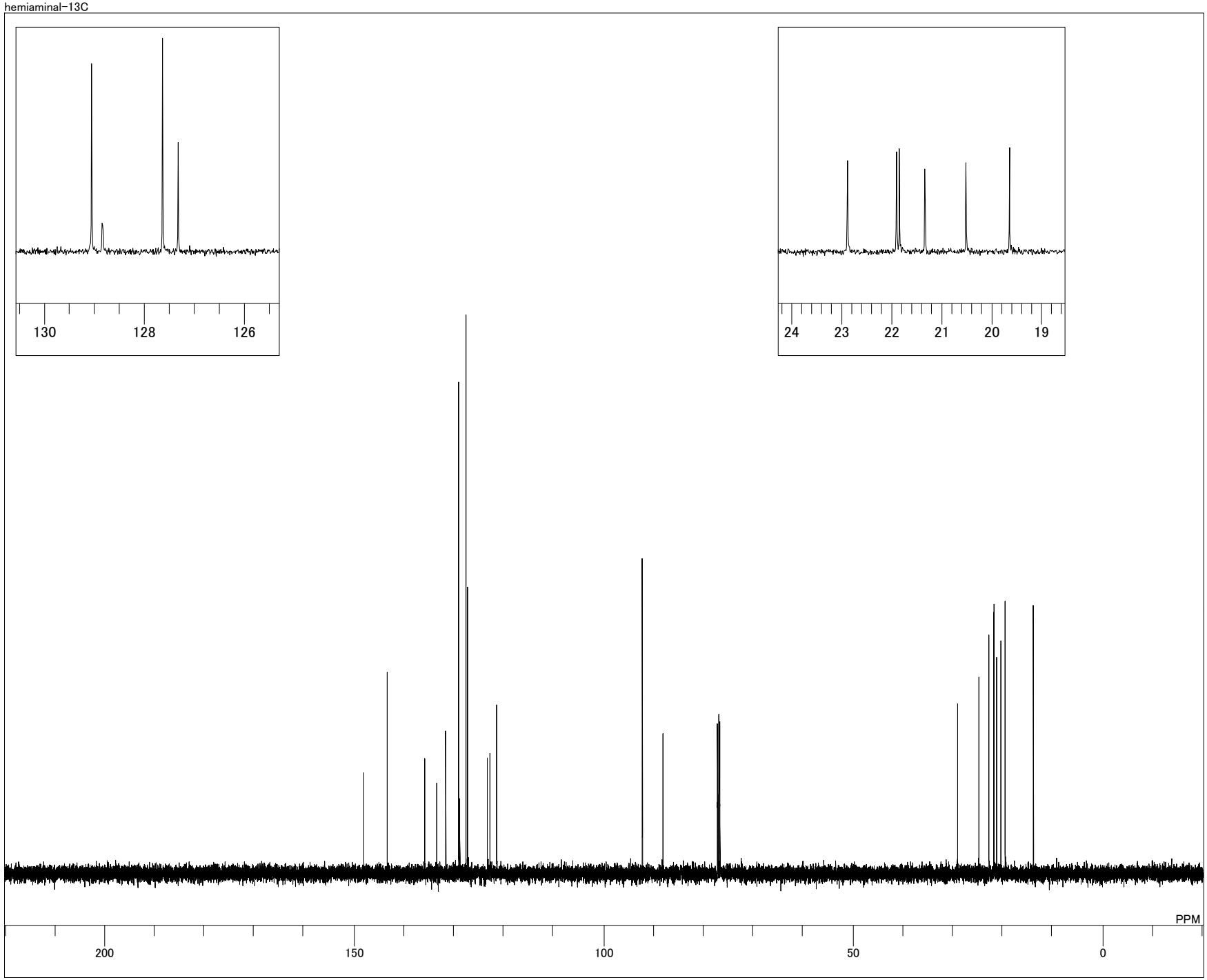


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0050
DATIM	03-09-2010 16:32:40
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	23.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	50

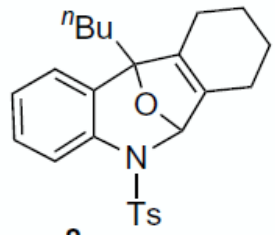


8

hemiaminal-13C

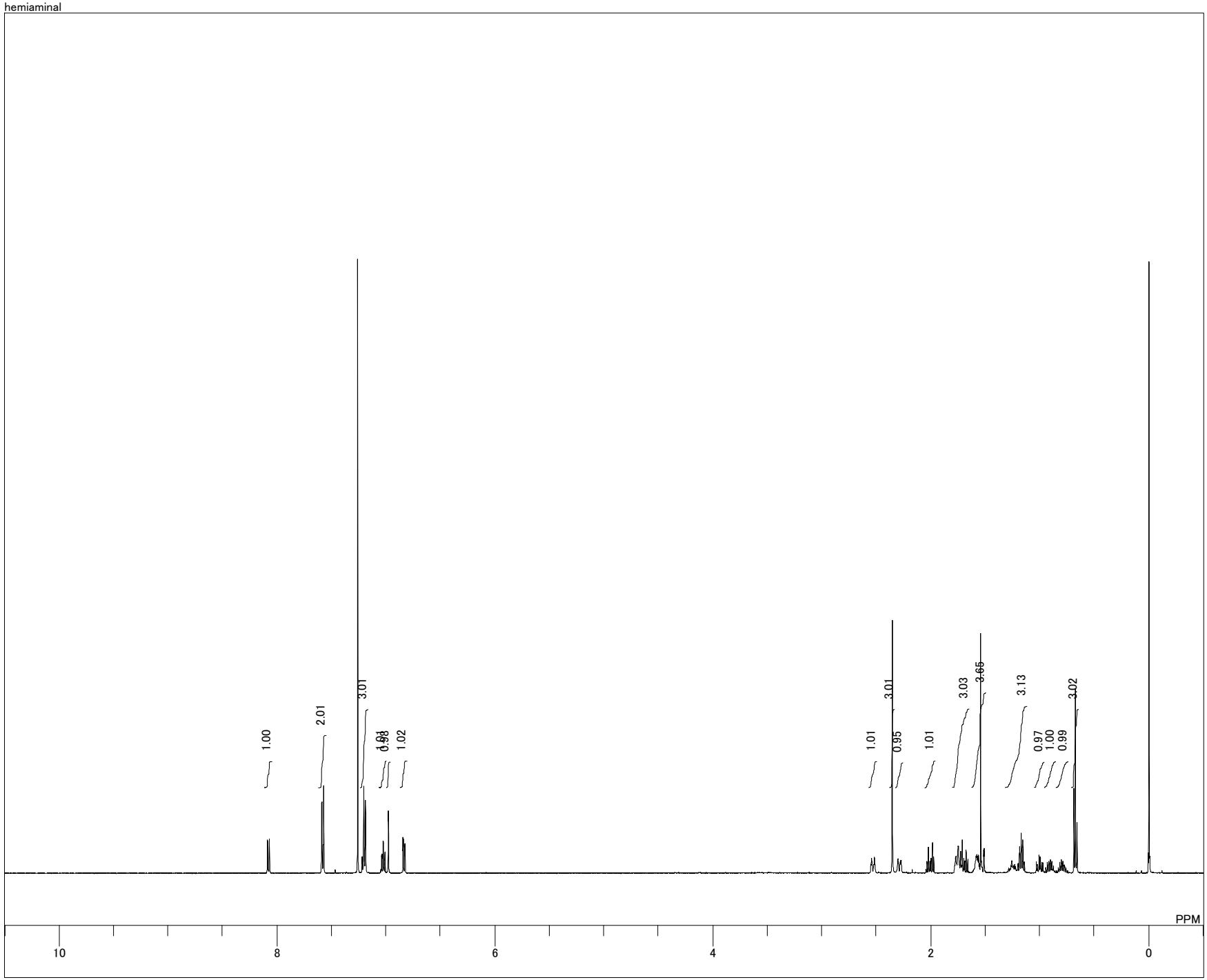


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	hemiaminal-13C
DATIM	05-03-2011 15:33:05
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	202
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.58 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

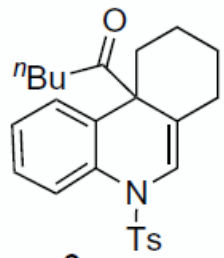


8

hemiaminal

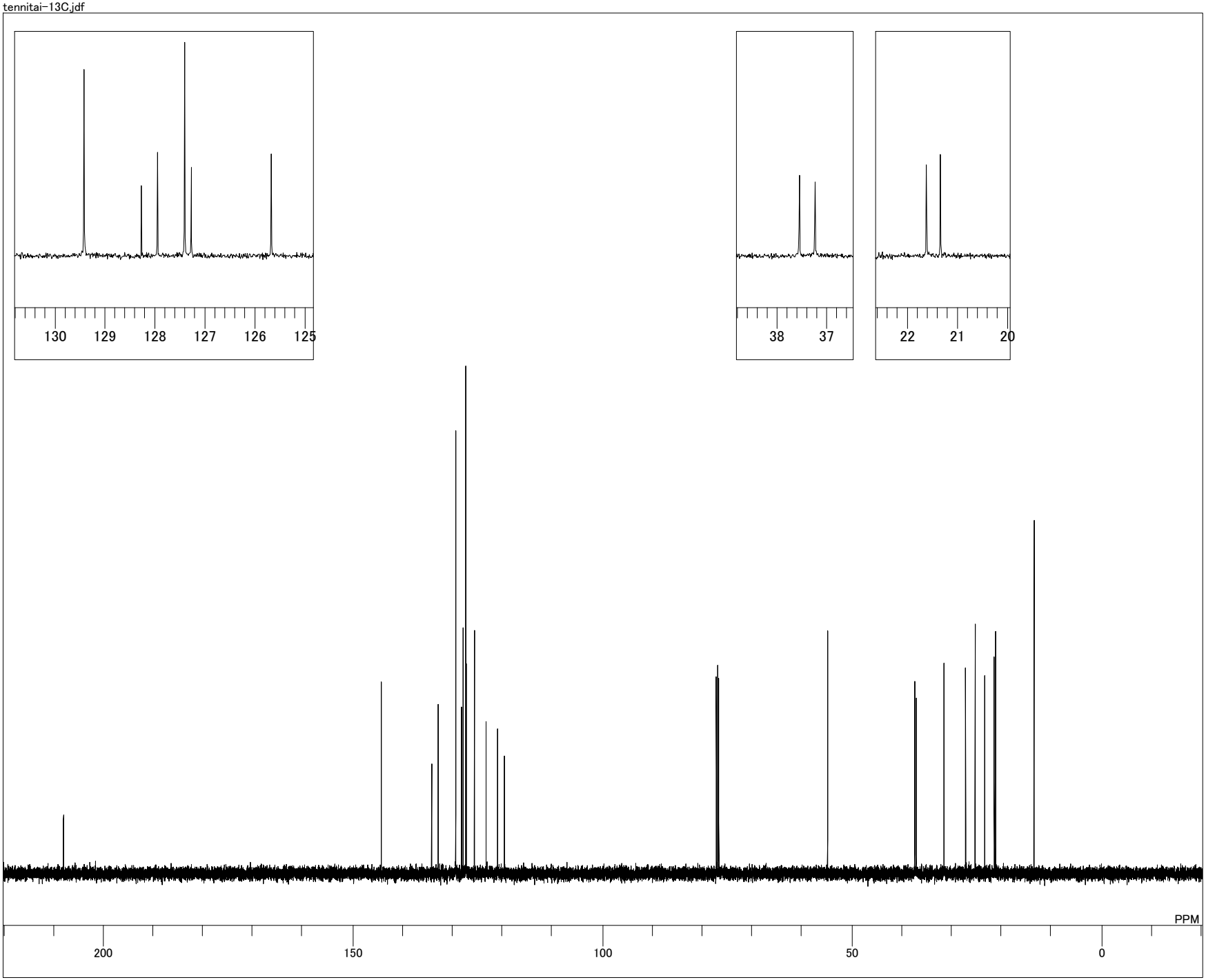


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	hemiaminal
DATIM	02-03-2011 19:06:13
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	56

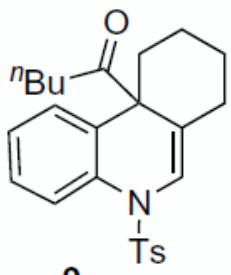


9

tennitai-13C.jdf



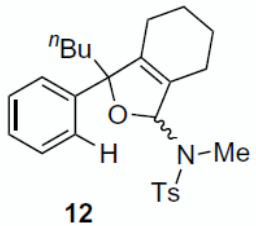
DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	tennitai-13C.jdf
DATIM	05-03-2011 15:57:36
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	154
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.58 usec
IRNUC	1H
CTEMP	25.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



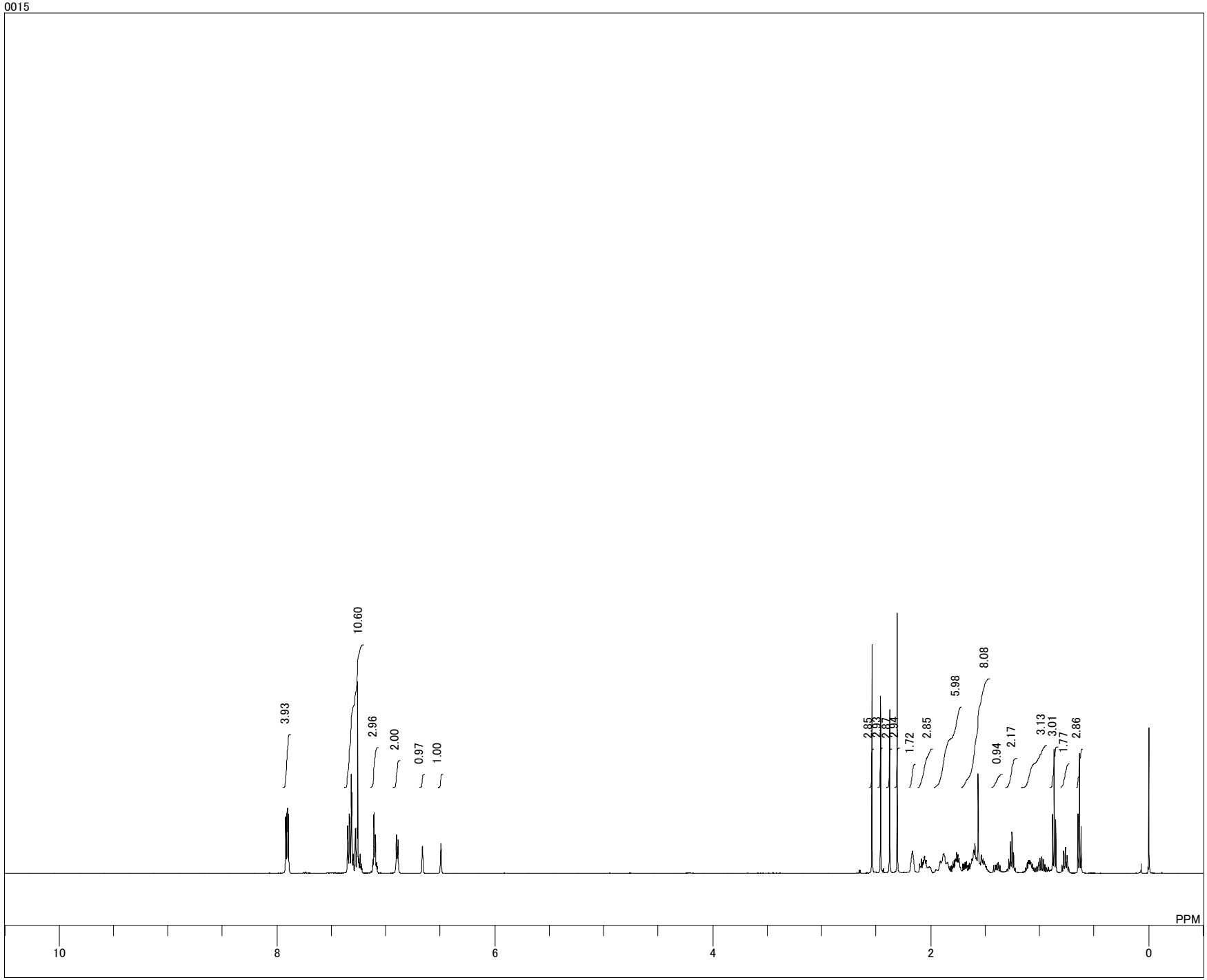
9

0015

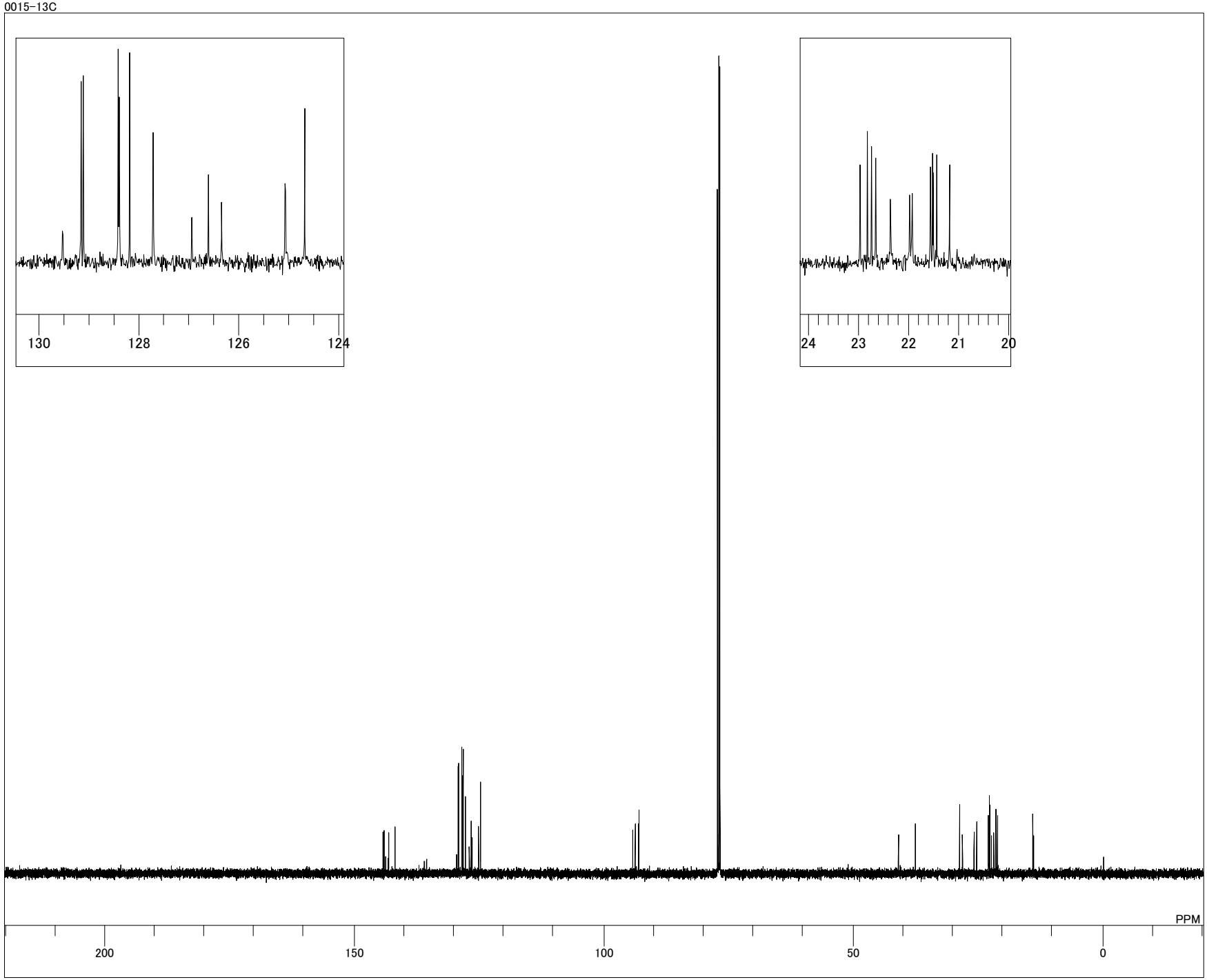
DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0015
DATIM	04-06-2011 14:48:34
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	22.2 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	50



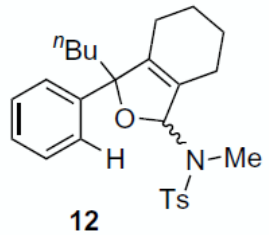
12



0015-13C



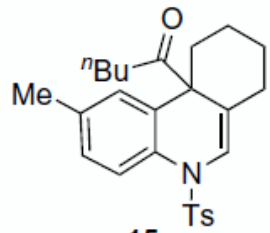
DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0015-13C
DATIM	05-06-2011 12:44:20
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	733
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.58 usec
IRNUC	1H
CTEMP	23.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58



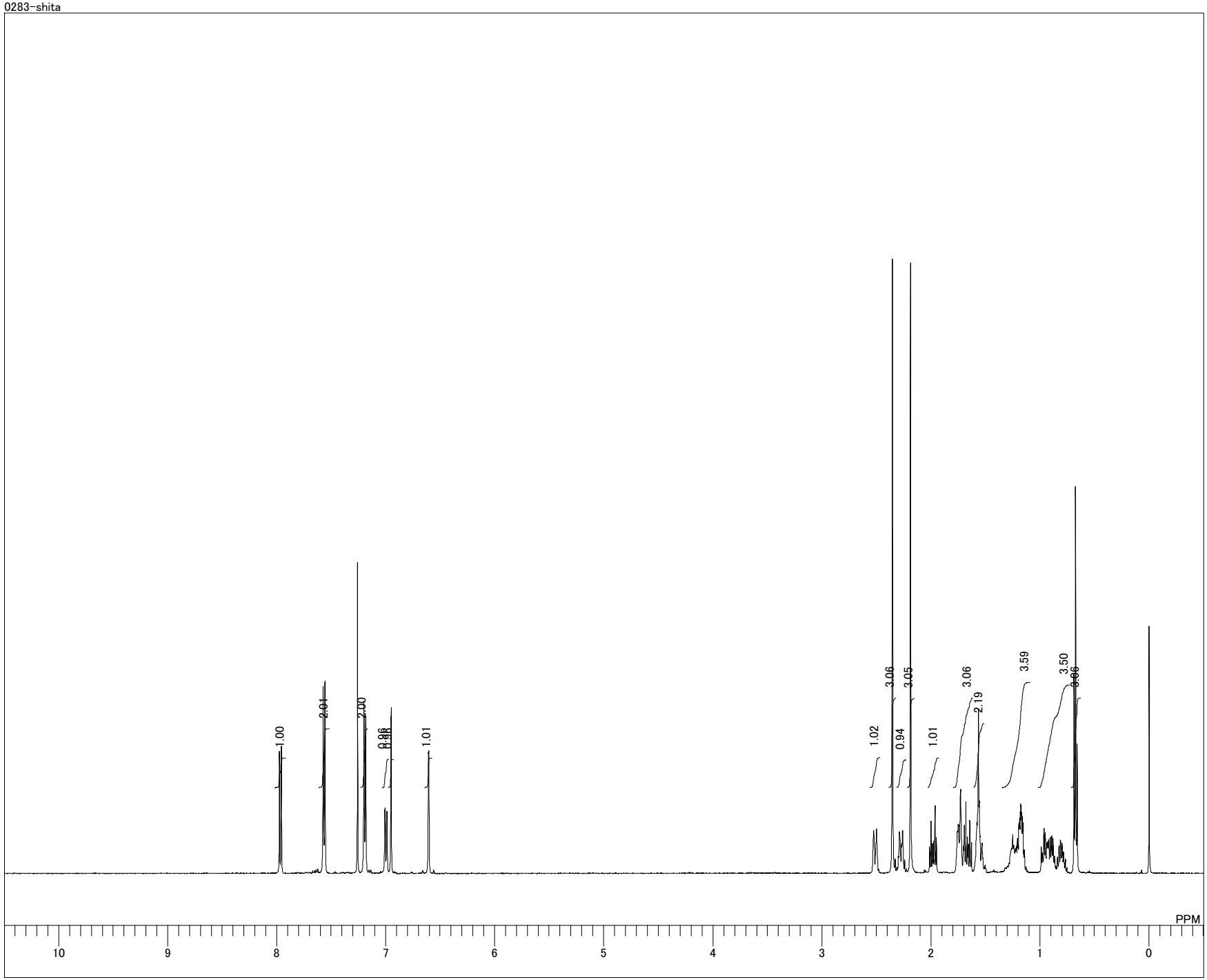
12

0283-shita

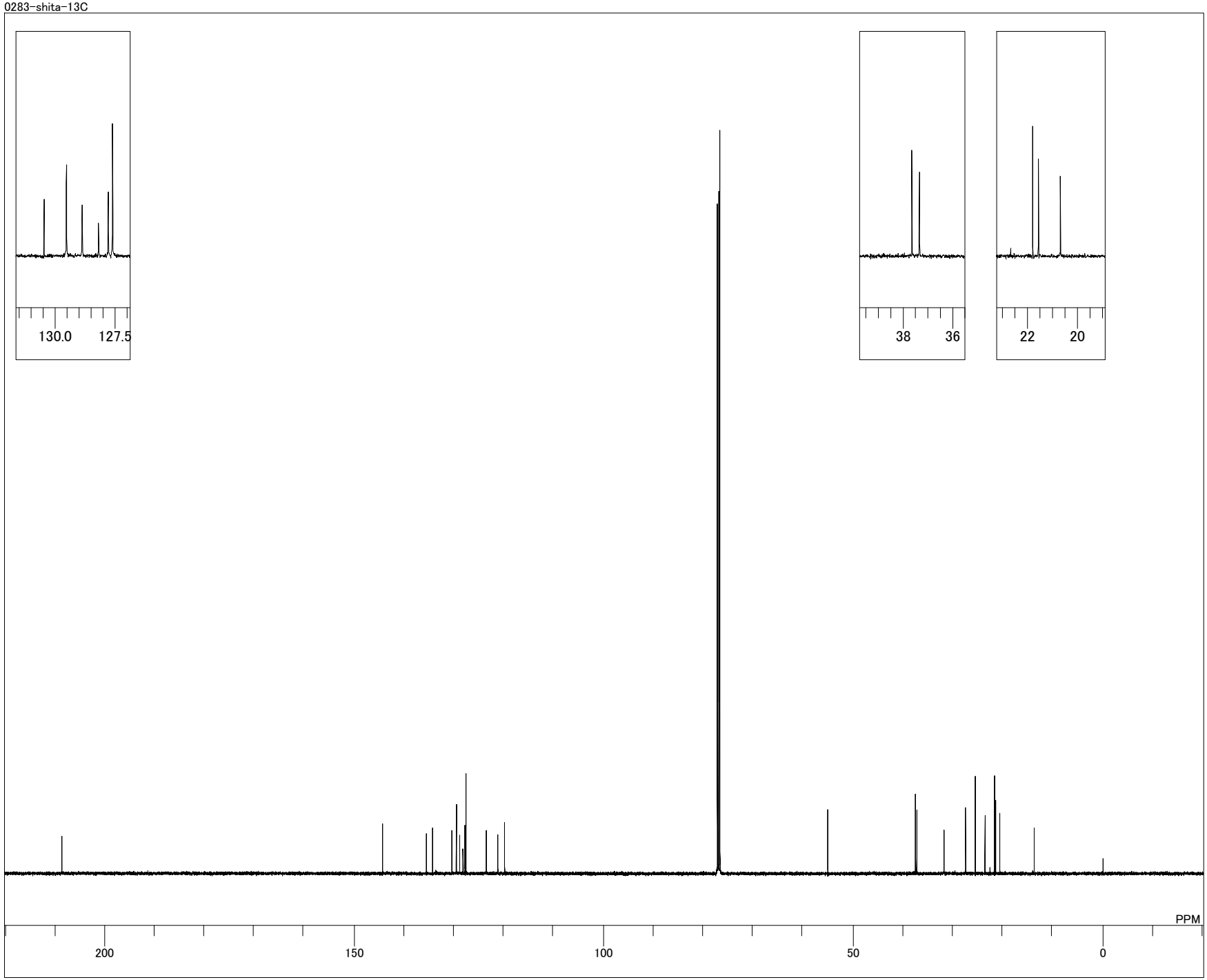
DFILE	E:¥Hg論文用データ¥追加
COMNT	0283-shita
DATIM	04-02-2012 23:05:44
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	16384
FREQU	9384.38 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.75 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	48



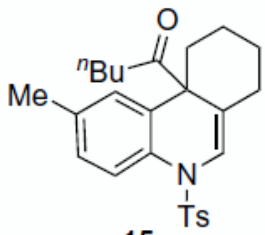
15



0283-shita-13C

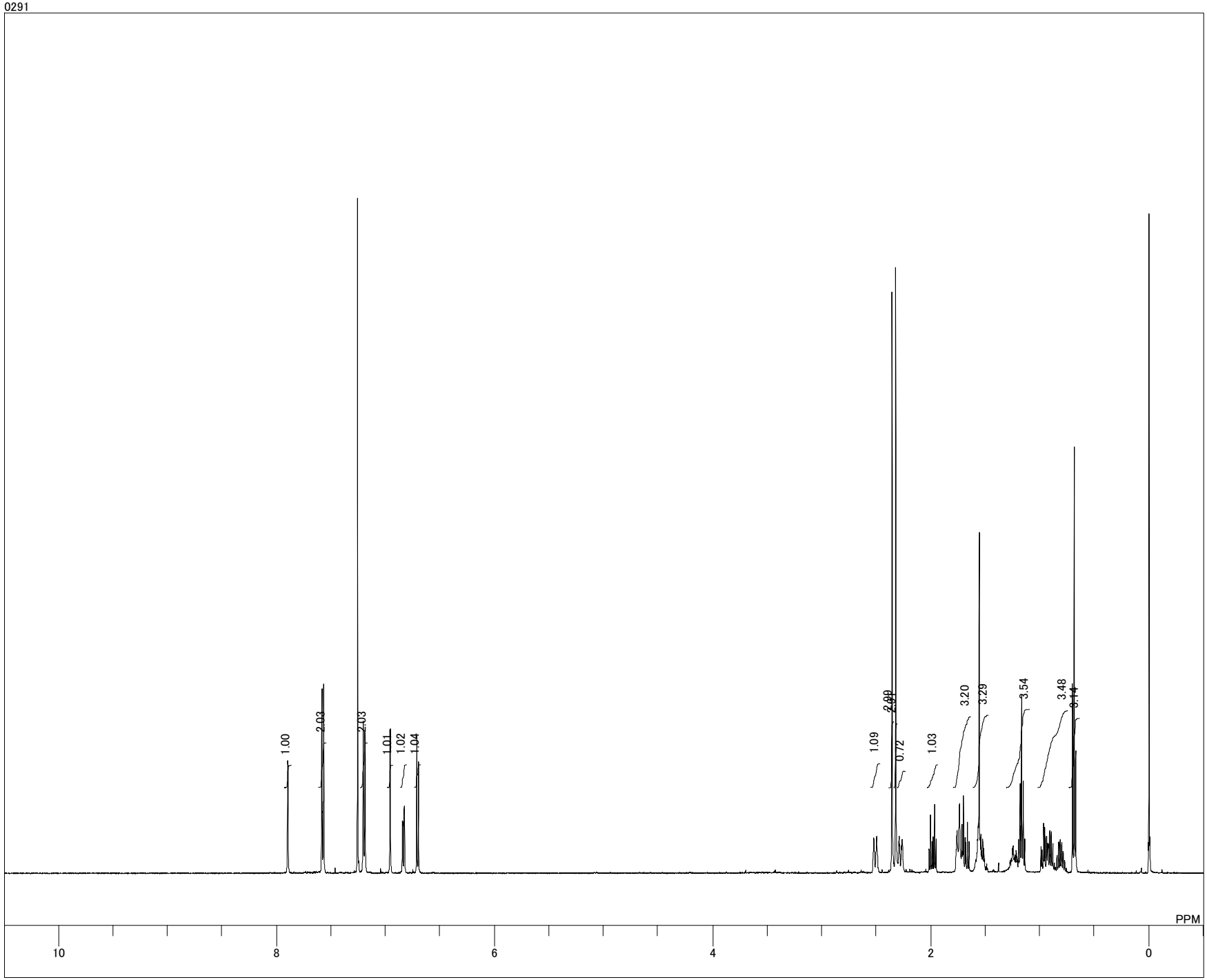


DFILE	E:¥Hg論文用データ¥追加
COMNT	0283-shita-13C
DATIM	05-02-2012 08:19:18
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32768
FREQU	39308.18 Hz
SCANS	10000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	4.33 usec
IRNUC	1H
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	58

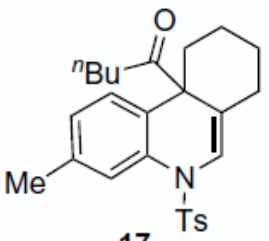


15

0291

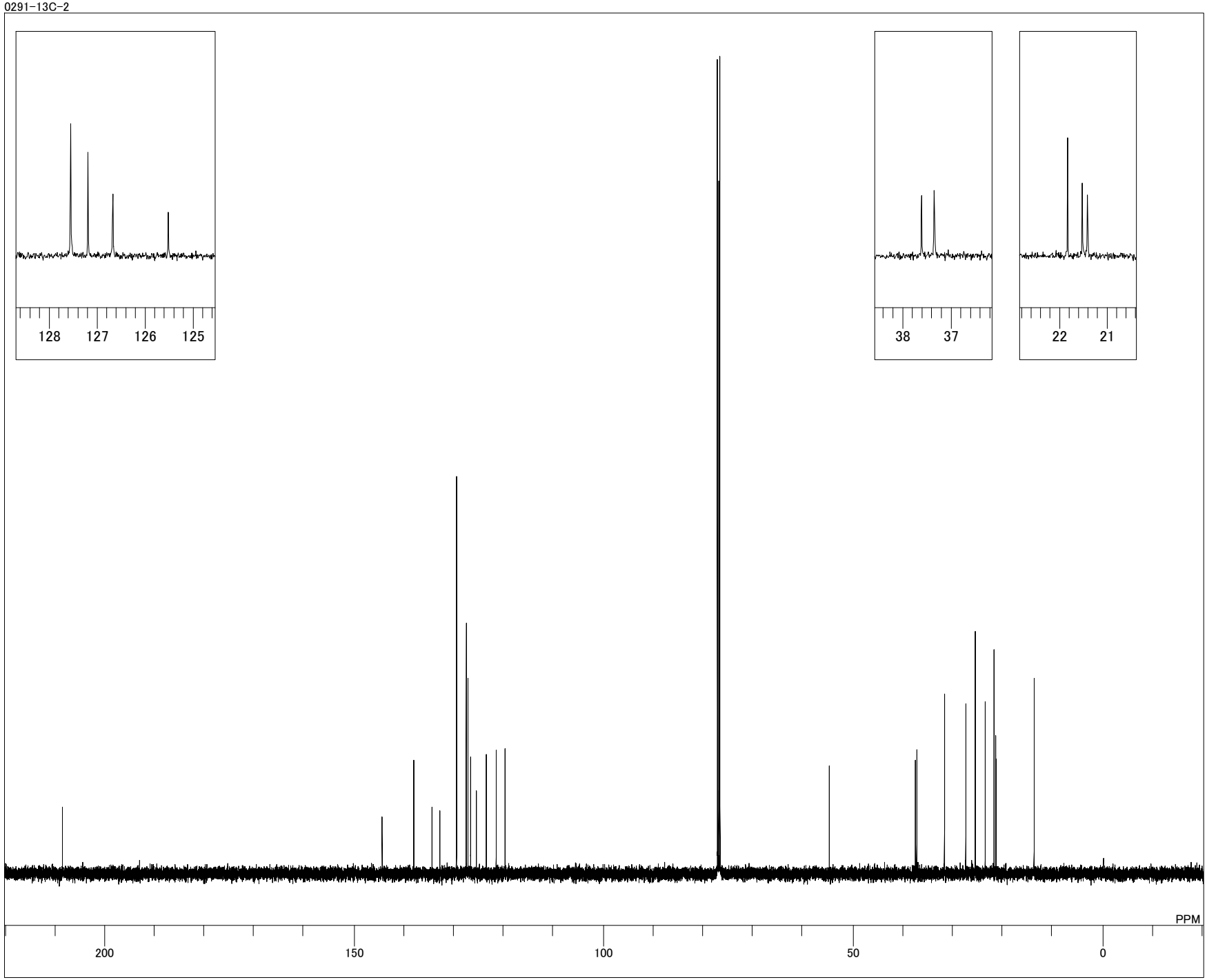


DFILE	E:¥Hg論文用データ¥追加
COMNT	0291
DATIM	04-02-2012 17:42:49
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	16384
FREQU	9384.38 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.75 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	54

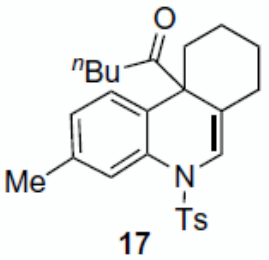


17

0291-13C-2

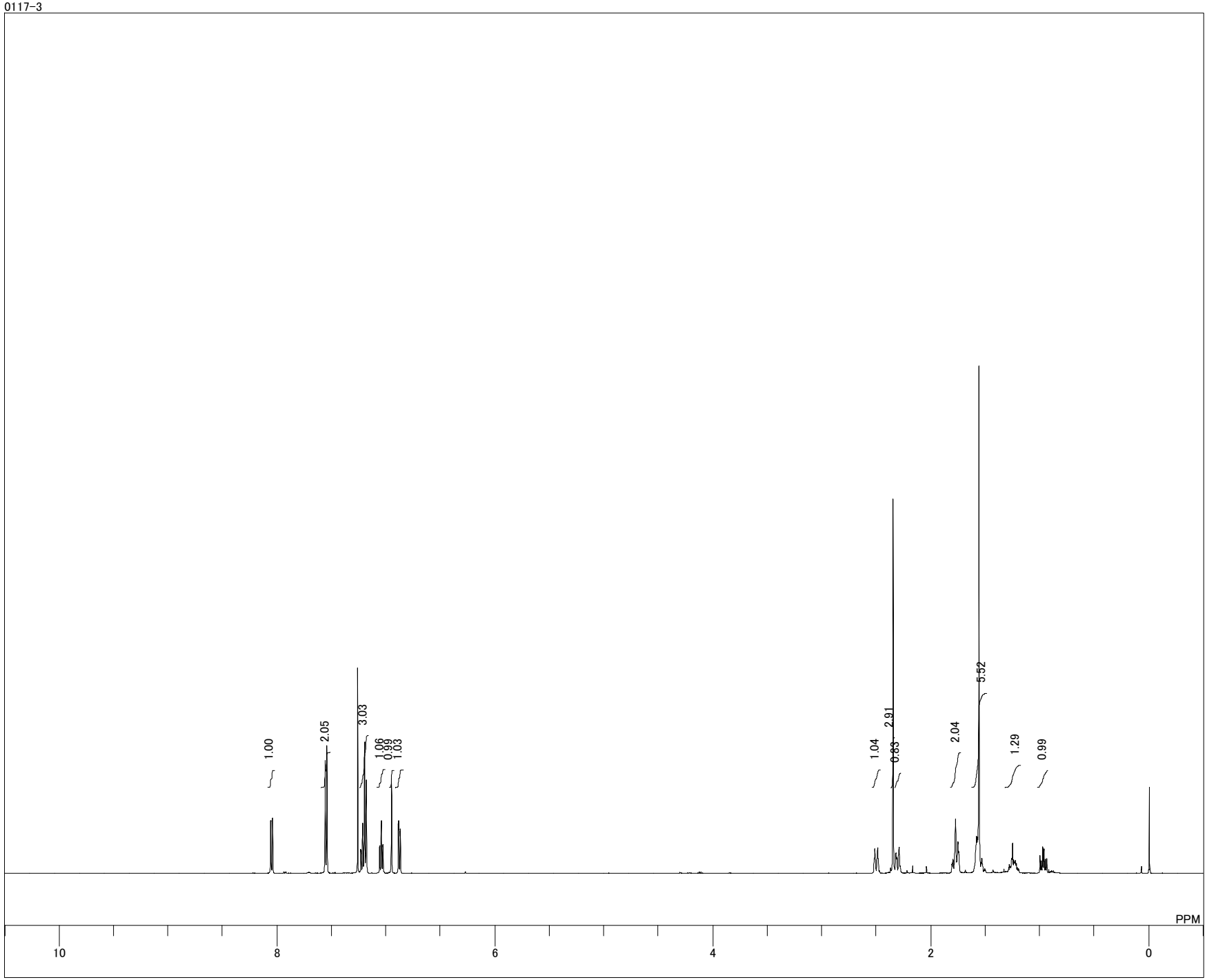


DFILE	E:¥Hg論文用データ¥追加
COMNT	0291-13C-2
DATIM	06-02-2012 22:44:19
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32768
FREQU	39308.18 Hz
SCANS	681
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	4.33 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

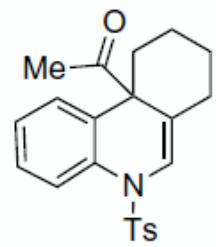


17

0117-3

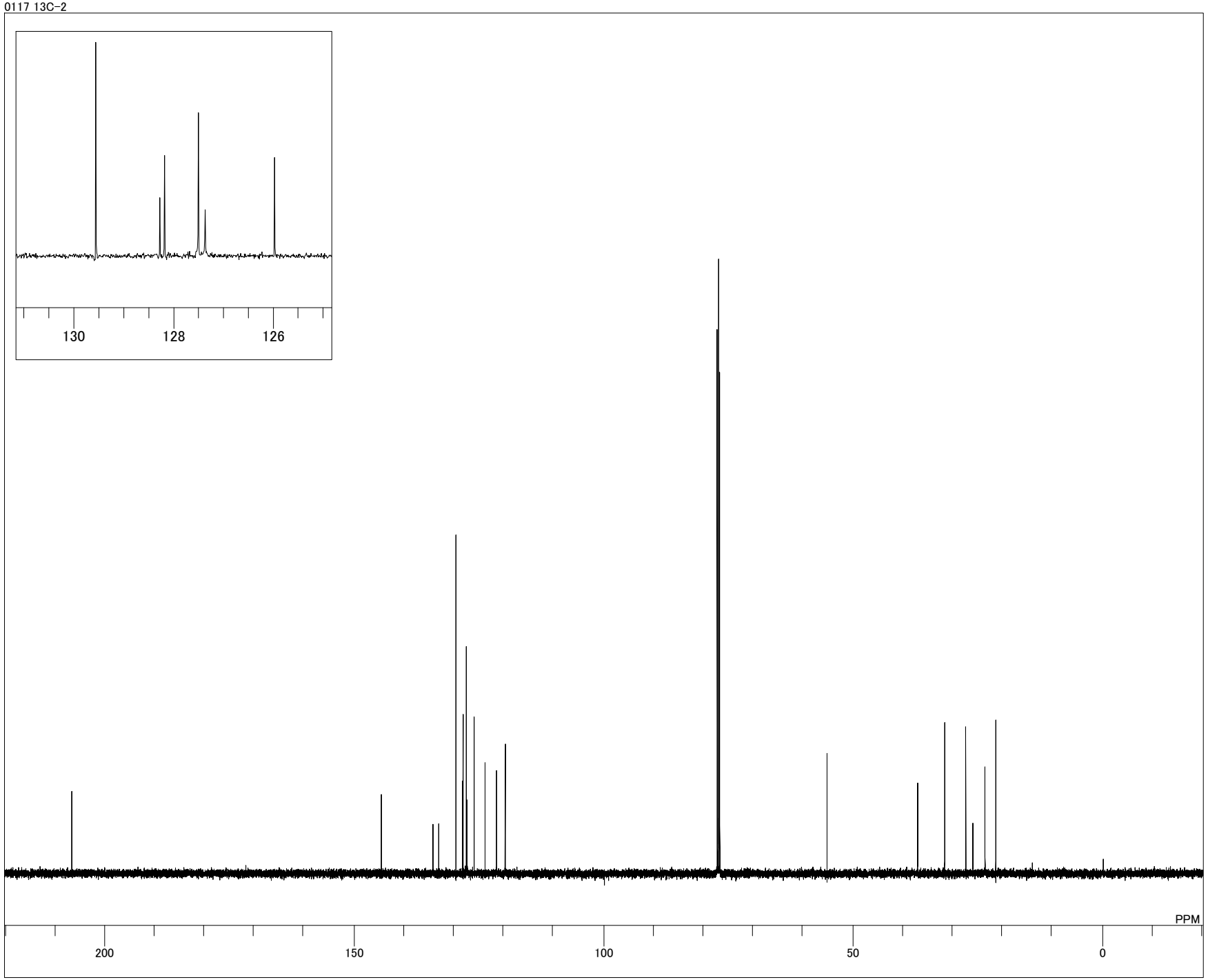


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0117-3
DATIM	28-05-2011 19:19:60
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	46

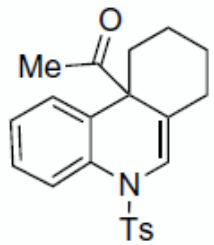


19

0117 13C-2

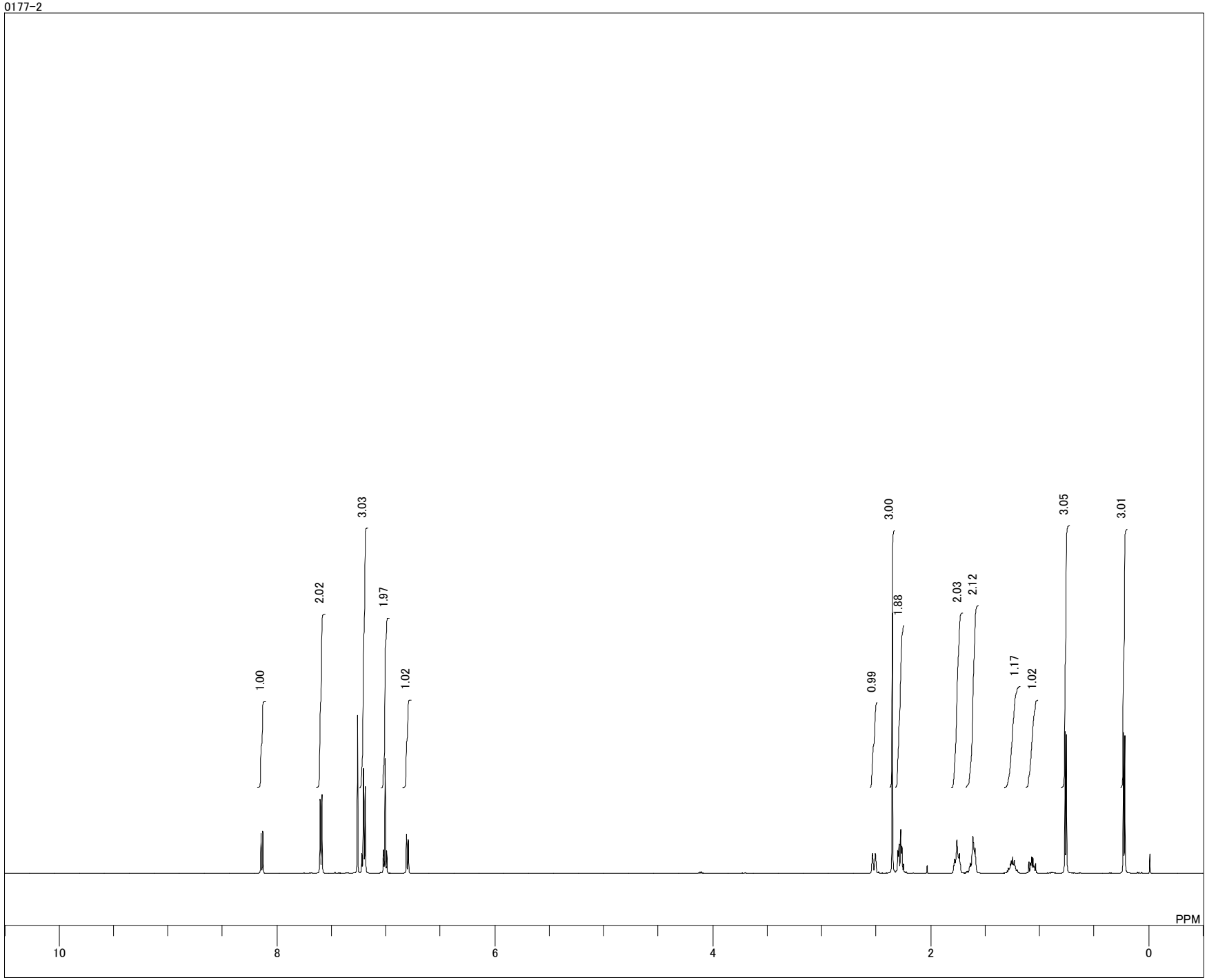


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0117 13C-2
DATIM	30-05-2011 11:32:54
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	521
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.58 usec
IRNUC	1H
CTEMP	23.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

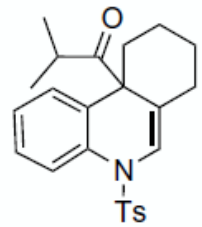


19

0177-2

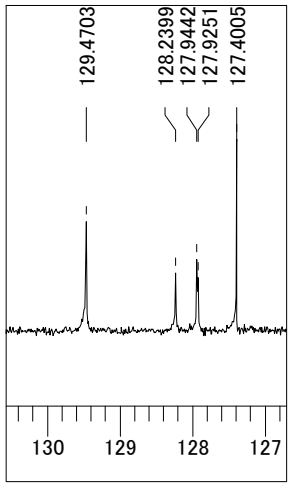


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0177-2
DATIM	28-05-2011 17:52:41
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40

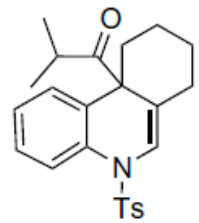


21

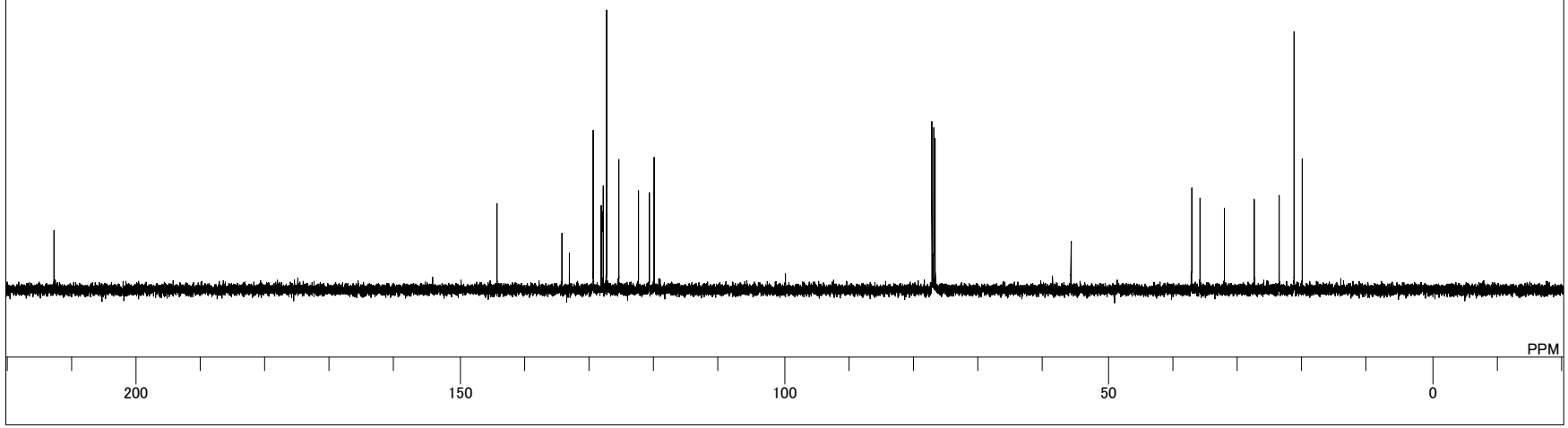
0177 13C



DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0177 13C
DATIM	22-03-2011 11:51:24
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	145
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.58 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

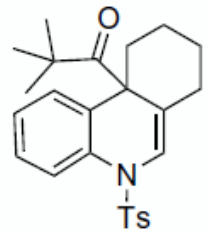


21

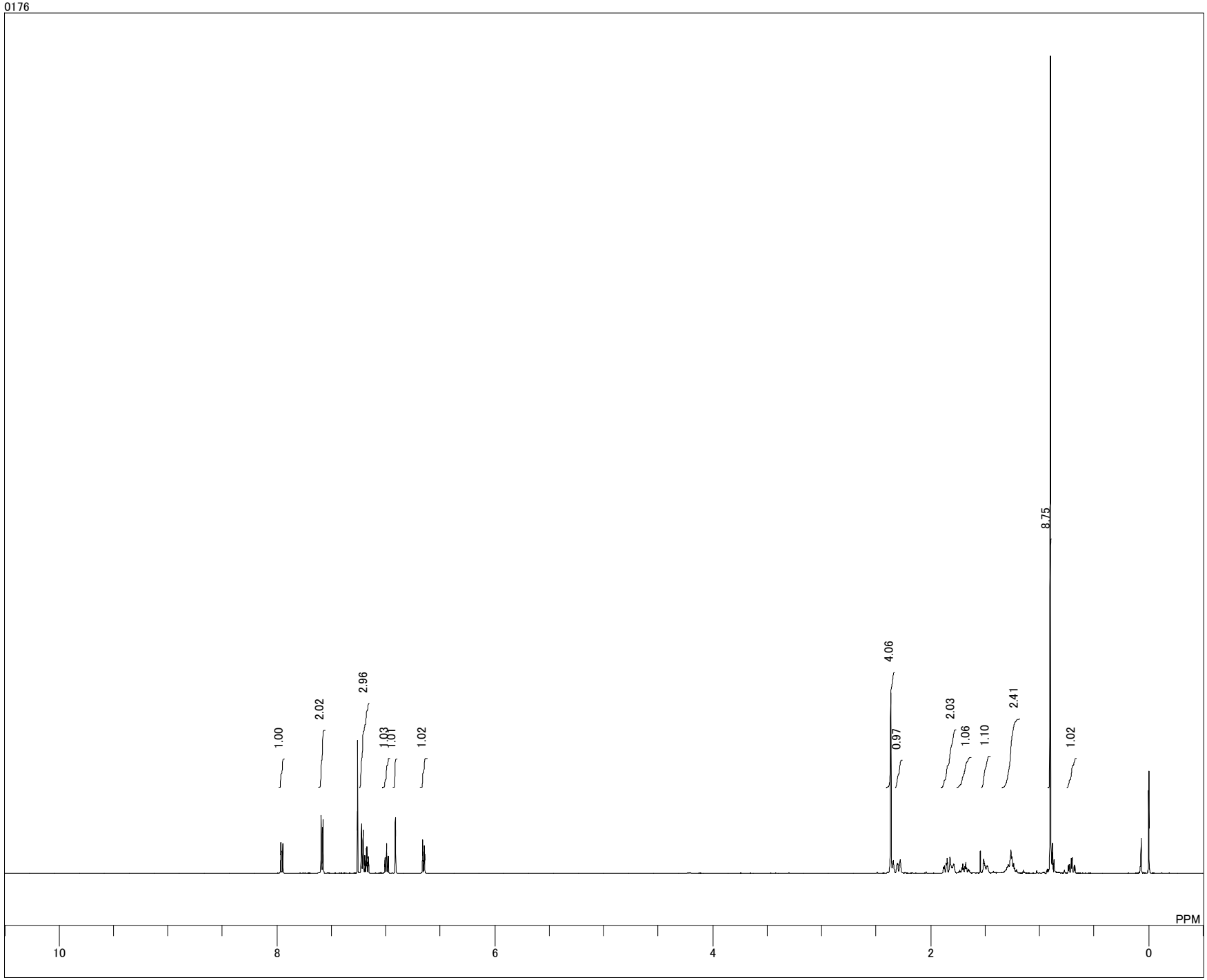


0176

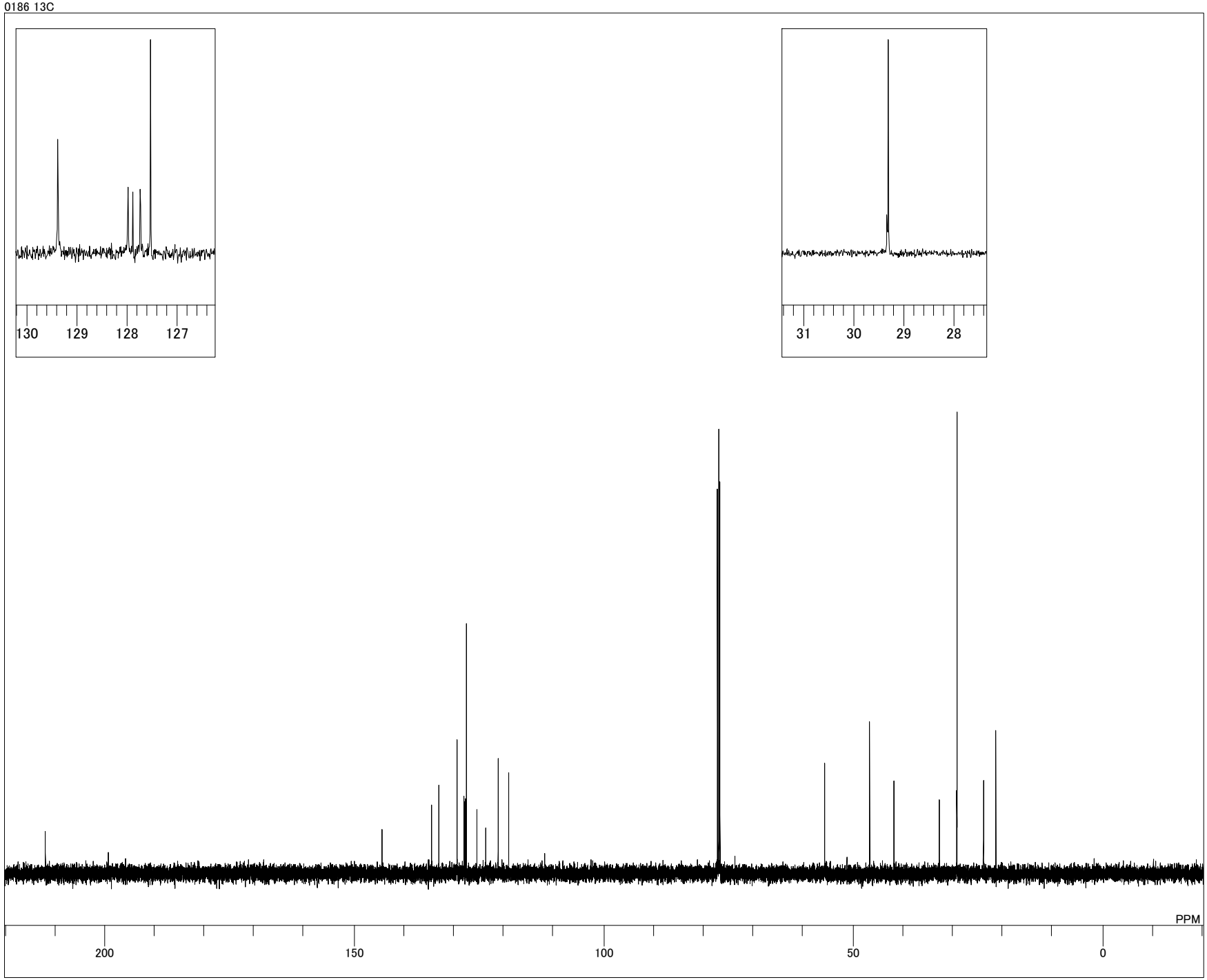
DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0176
DATIM	12-03-2011 13:43:13
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	50



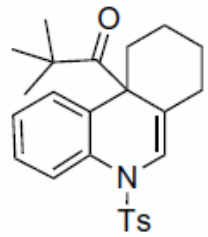
23



0186 13C

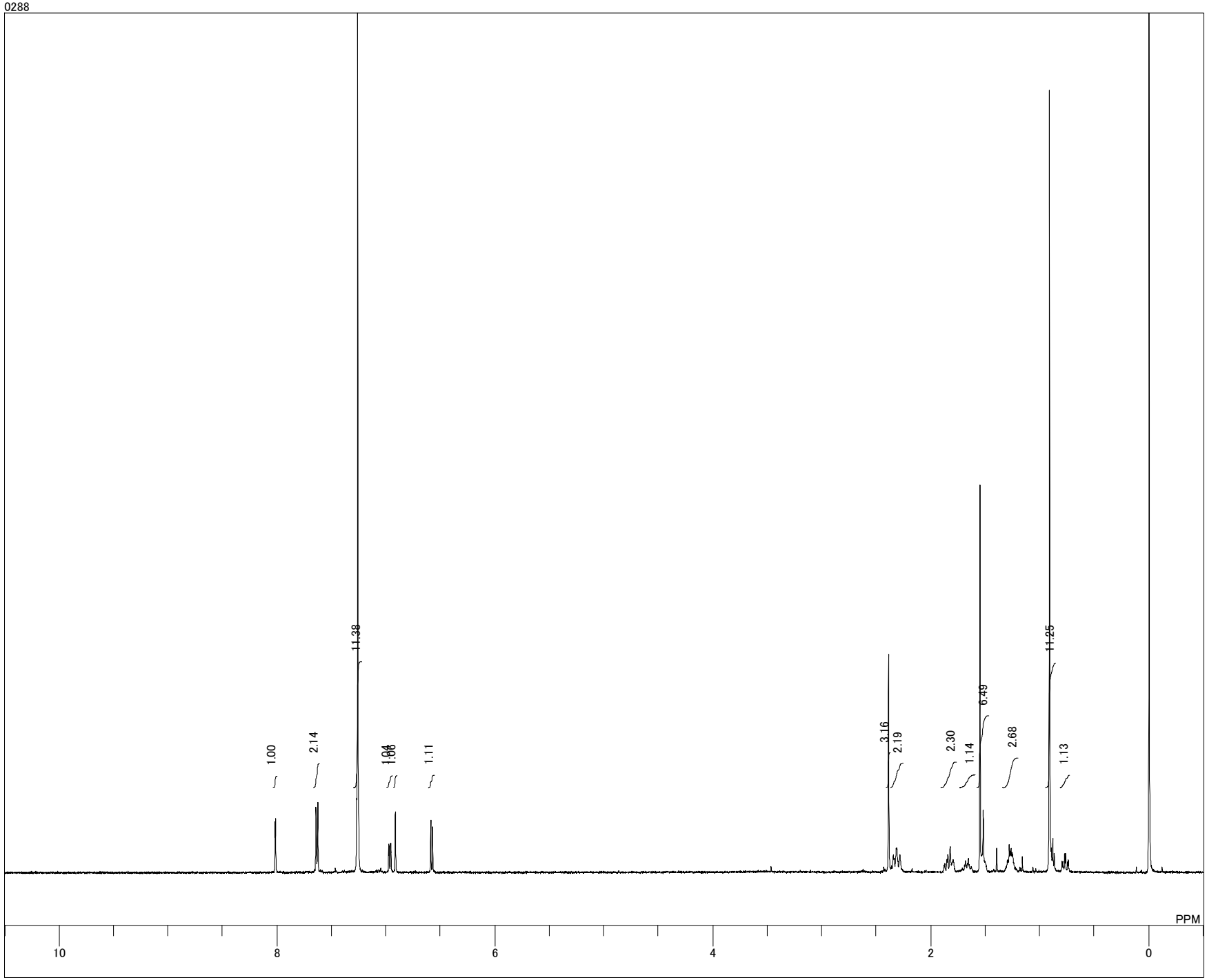


DFILE E:¥Hg論文用データ¥Hg-1
COMNT 0186 13C
DATIM 19-03-2011 15:46:04
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 262
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.58 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

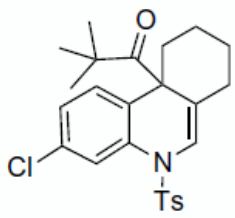


23

0288

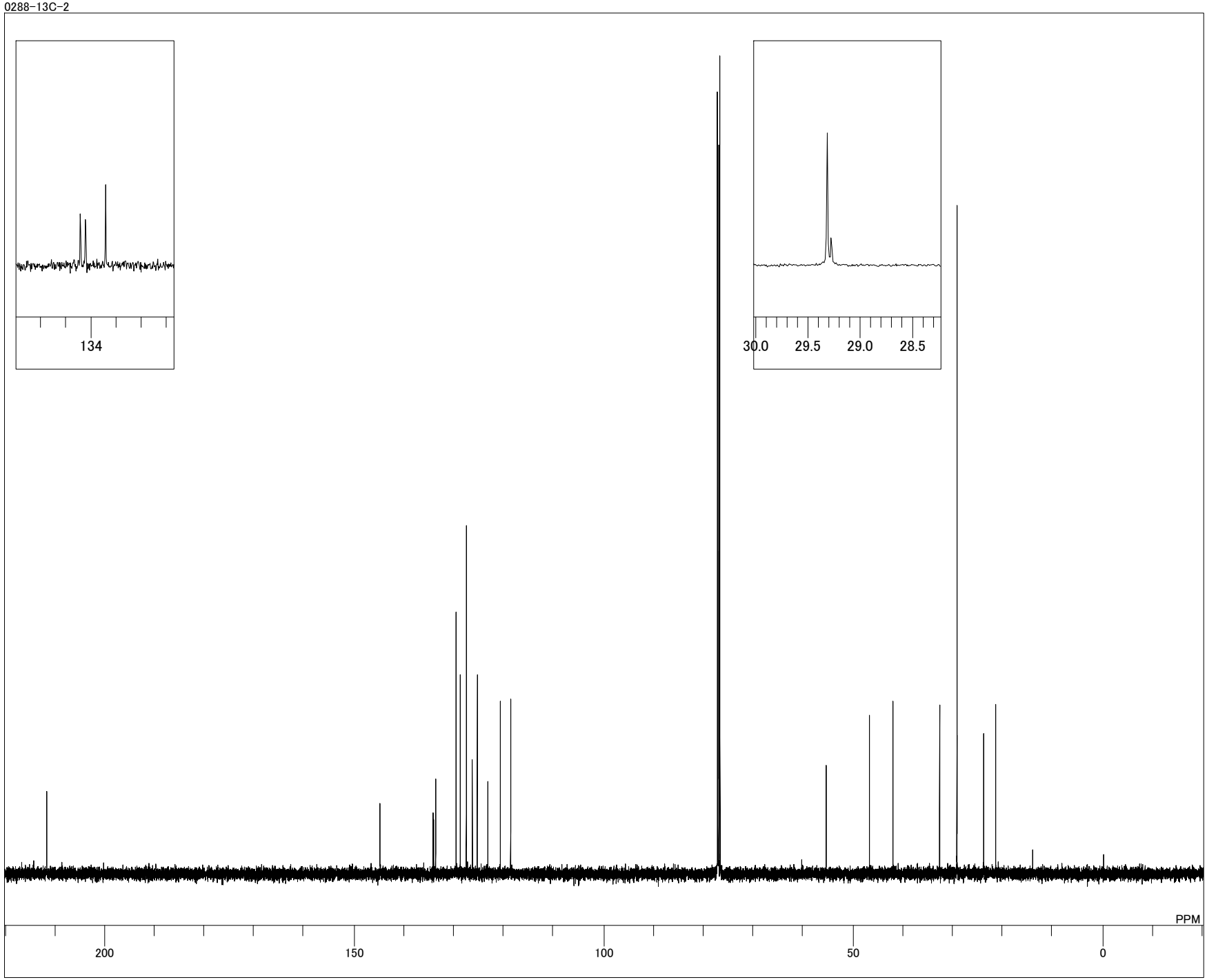


DFILE	E:¥Hg論文用データ¥追加
COMNT	0288
DATIM	03-02-2012 16:48:39
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	16384
FREQU	9384.38 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.75 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	58

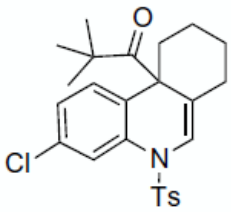


25

0288-13C-2

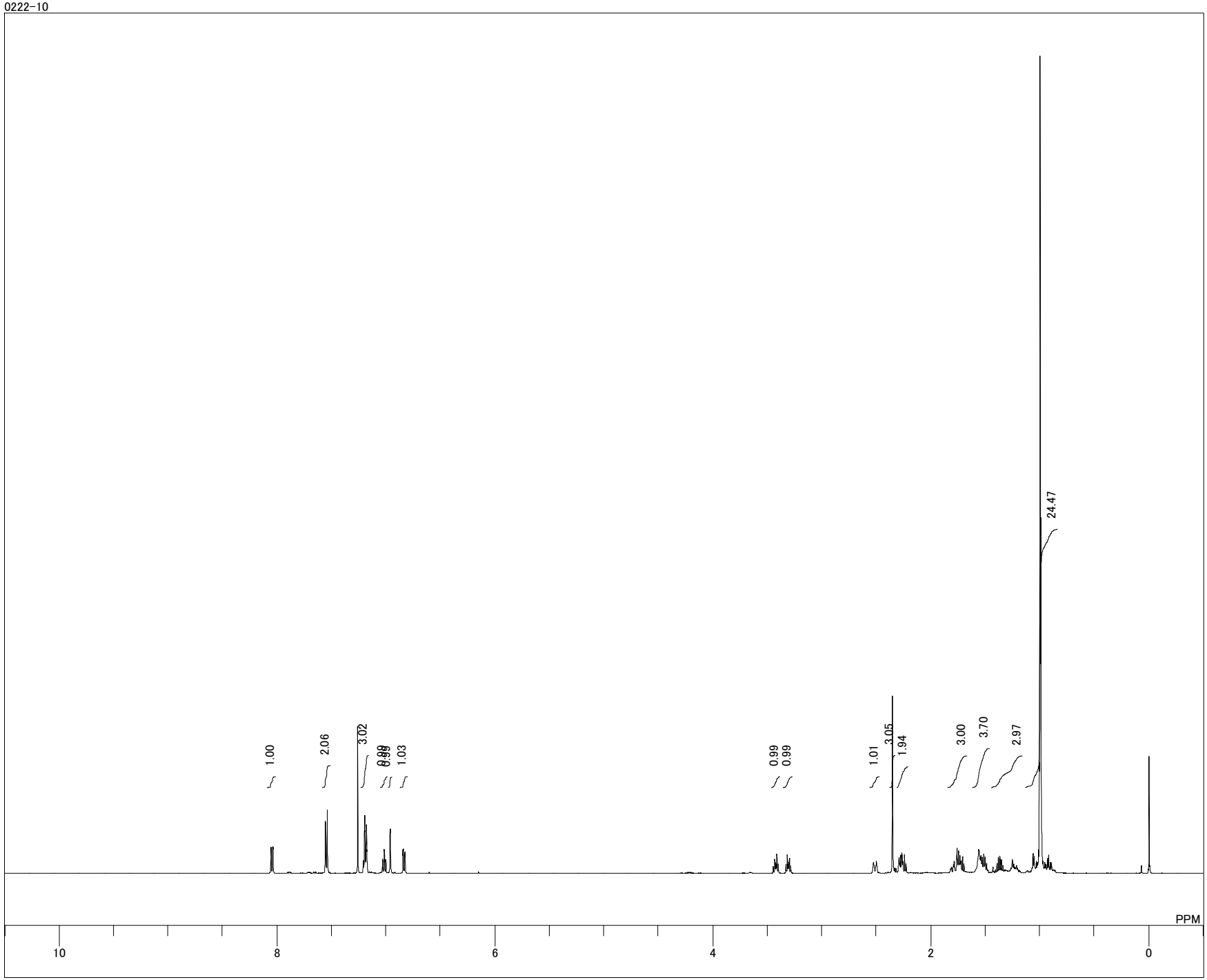


DFILE	E:¥Hg論文用データ¥追加
COMNT	0288-13C-2
DATIM	06-02-2012 23:33:08
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32768
FREQU	39308.18 Hz
SCANS	823
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	4.33 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

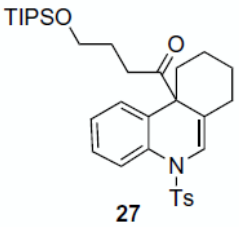


25

0222-10

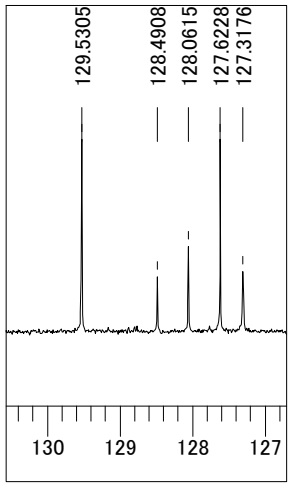


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0222-10
DATIM	02-06-2011 19:31:40
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	22.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	48

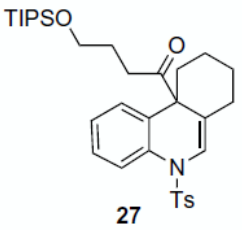


27

0222-13C



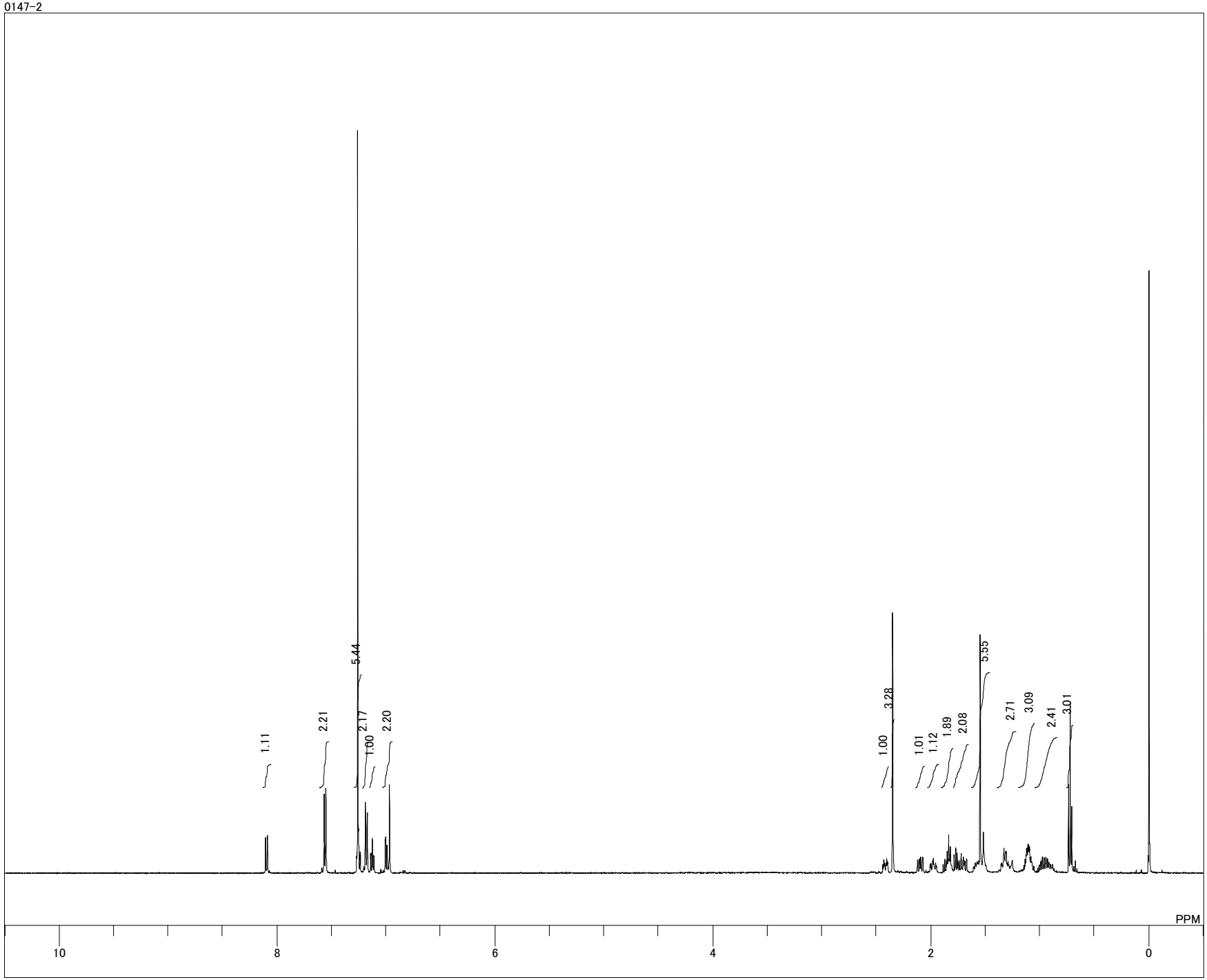
DFILE E:¥Hg論文用データ¥Hg-1
COMNT 0222-13C
DATIM 06-06-2011 10:12:42
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 14866
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.58 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 60



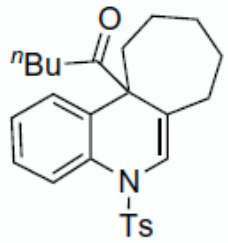
27

PPM
200
150
100
50
0

0147-2

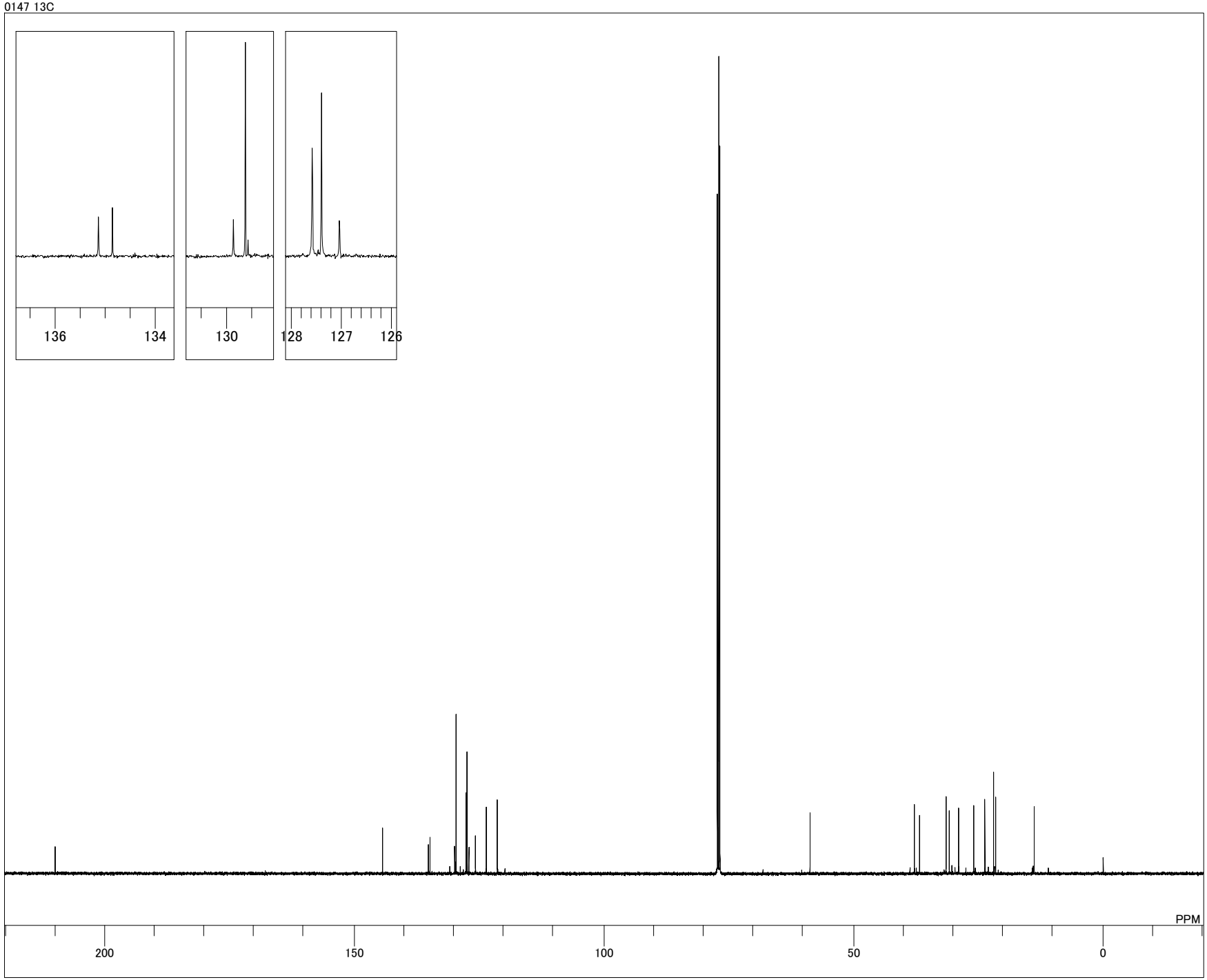


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0147-2
DATIM	03-06-2011 21:56:46
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	56

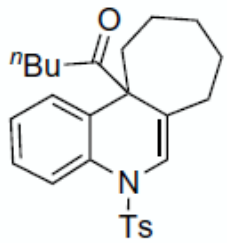


29

0147 13C

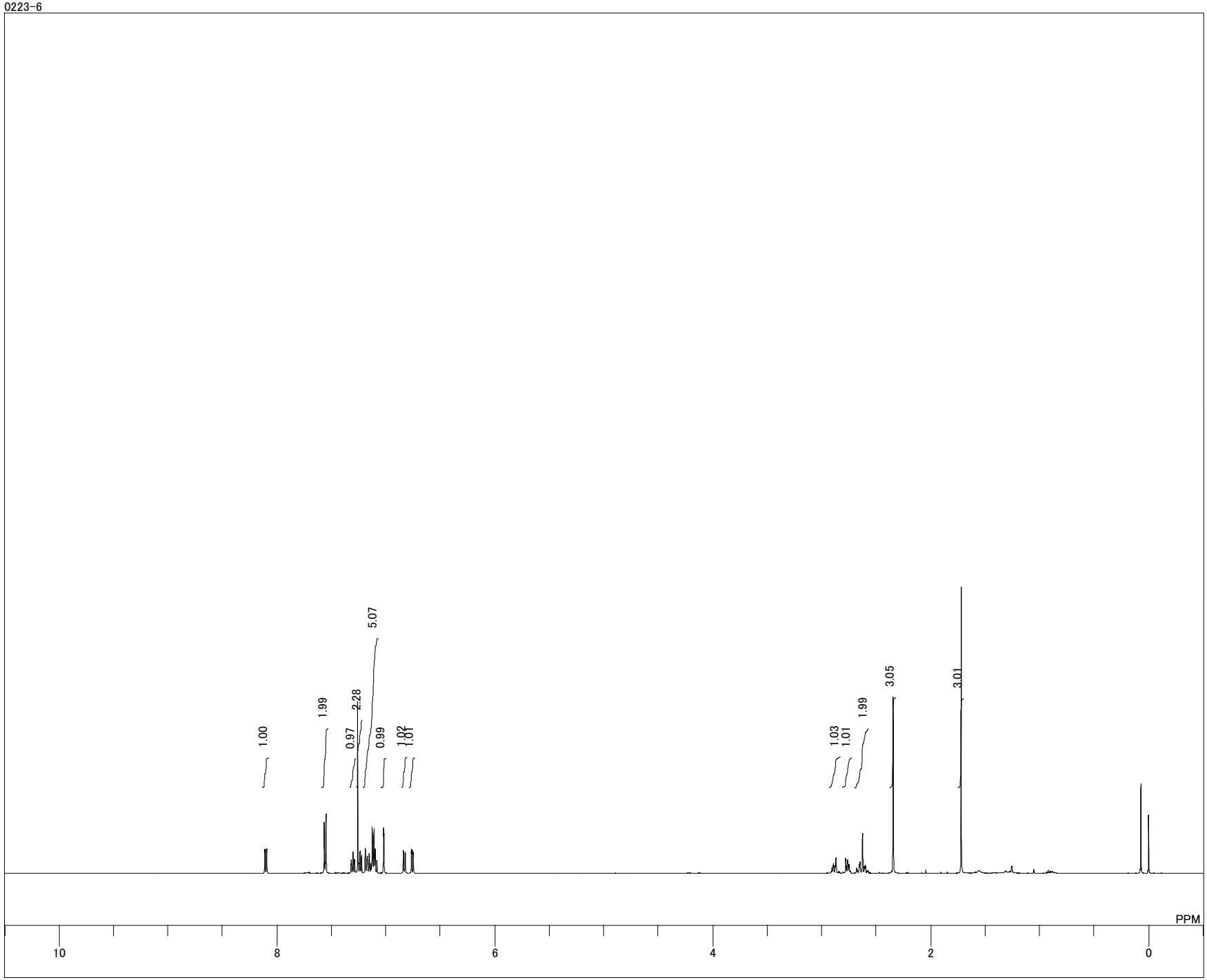


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0147 13C
DATIM	31-05-2011 09:39:14
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	13000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.58 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	60

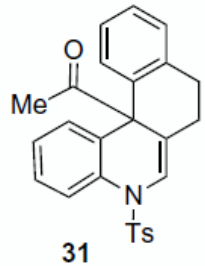


29

0223-6

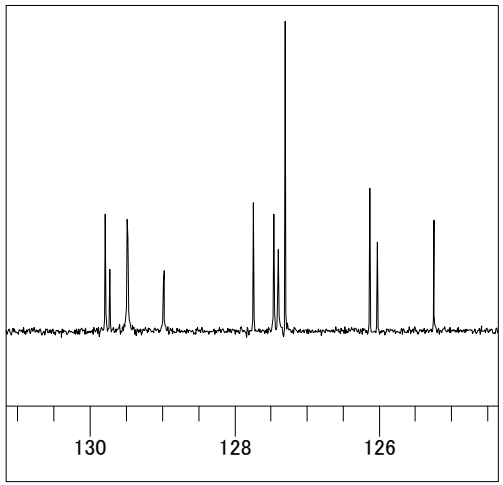


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0223-6
DATIM	30-05-2011 16:36:57
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	48

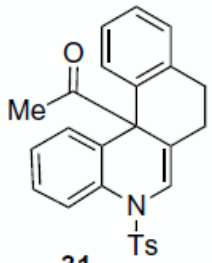


31

0223 13C

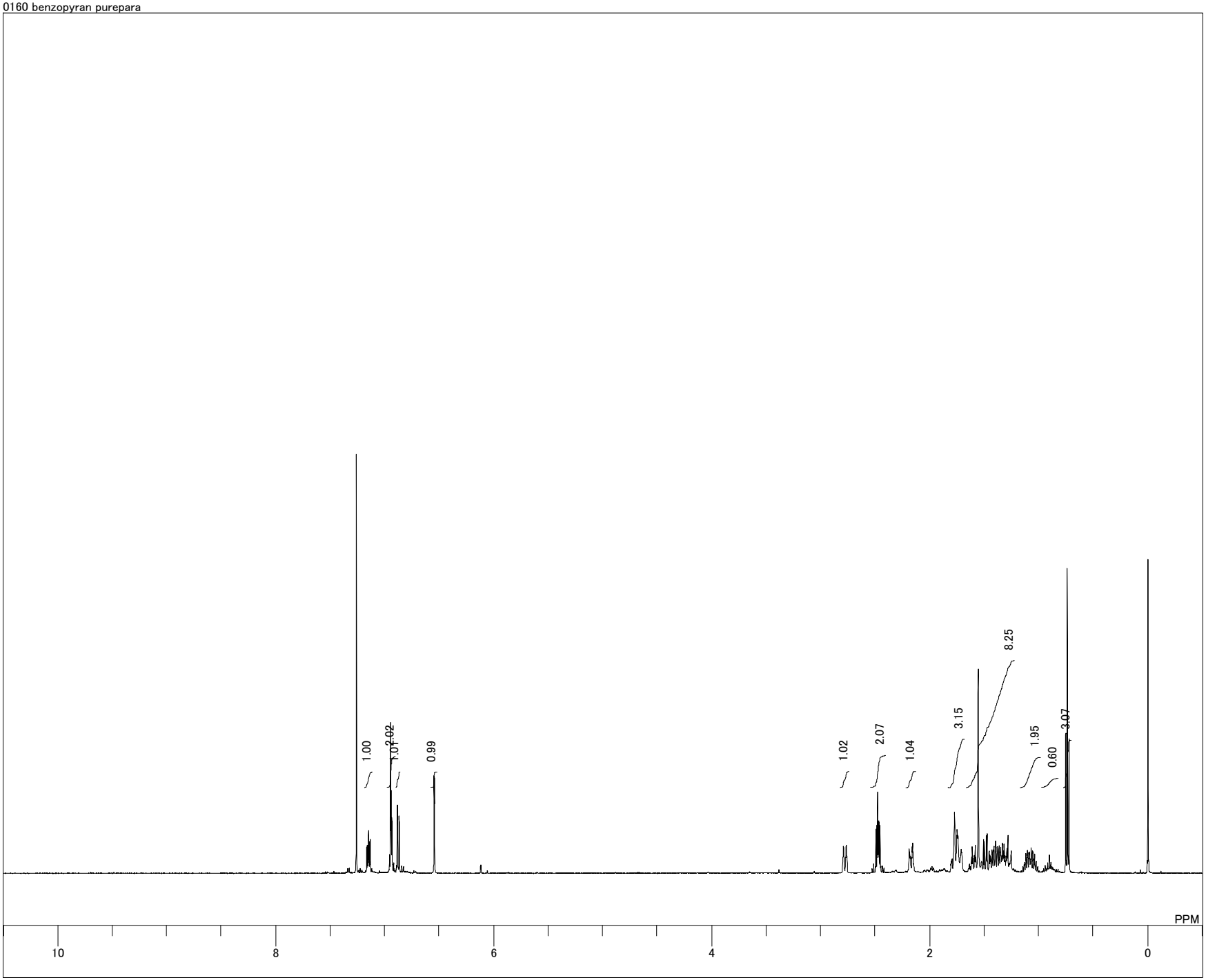


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0223 13C
DATIM	27-05-2011 14:14:59
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	274
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.58 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

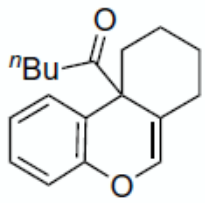


31

0160 benzopyran purepara

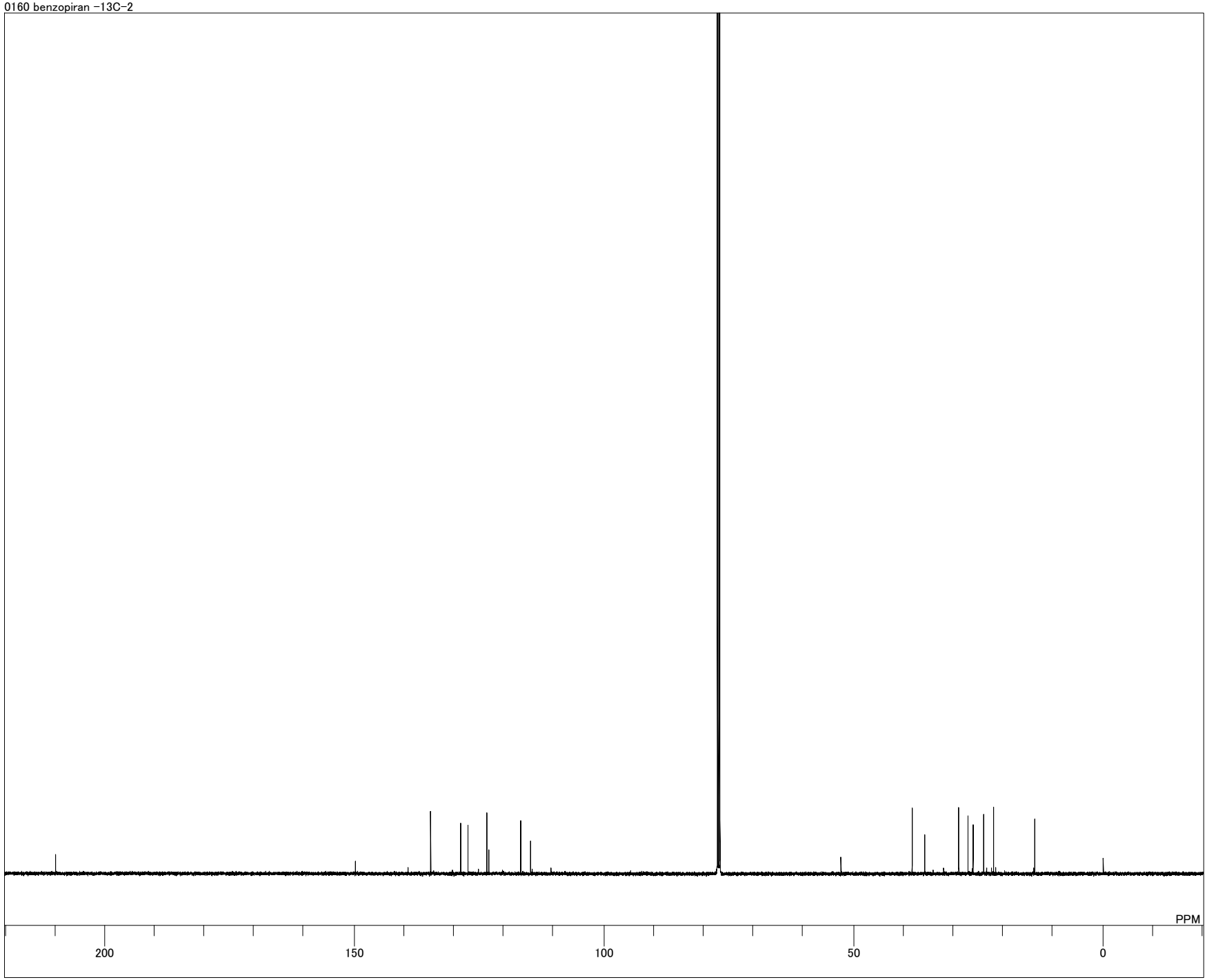


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0160 benzopyran purepara
DATIM	03-06-2011 19:41:29
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	22.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	54

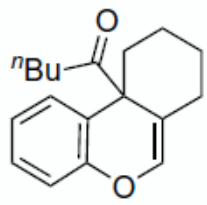


34

0160 benzopiran -13C-2

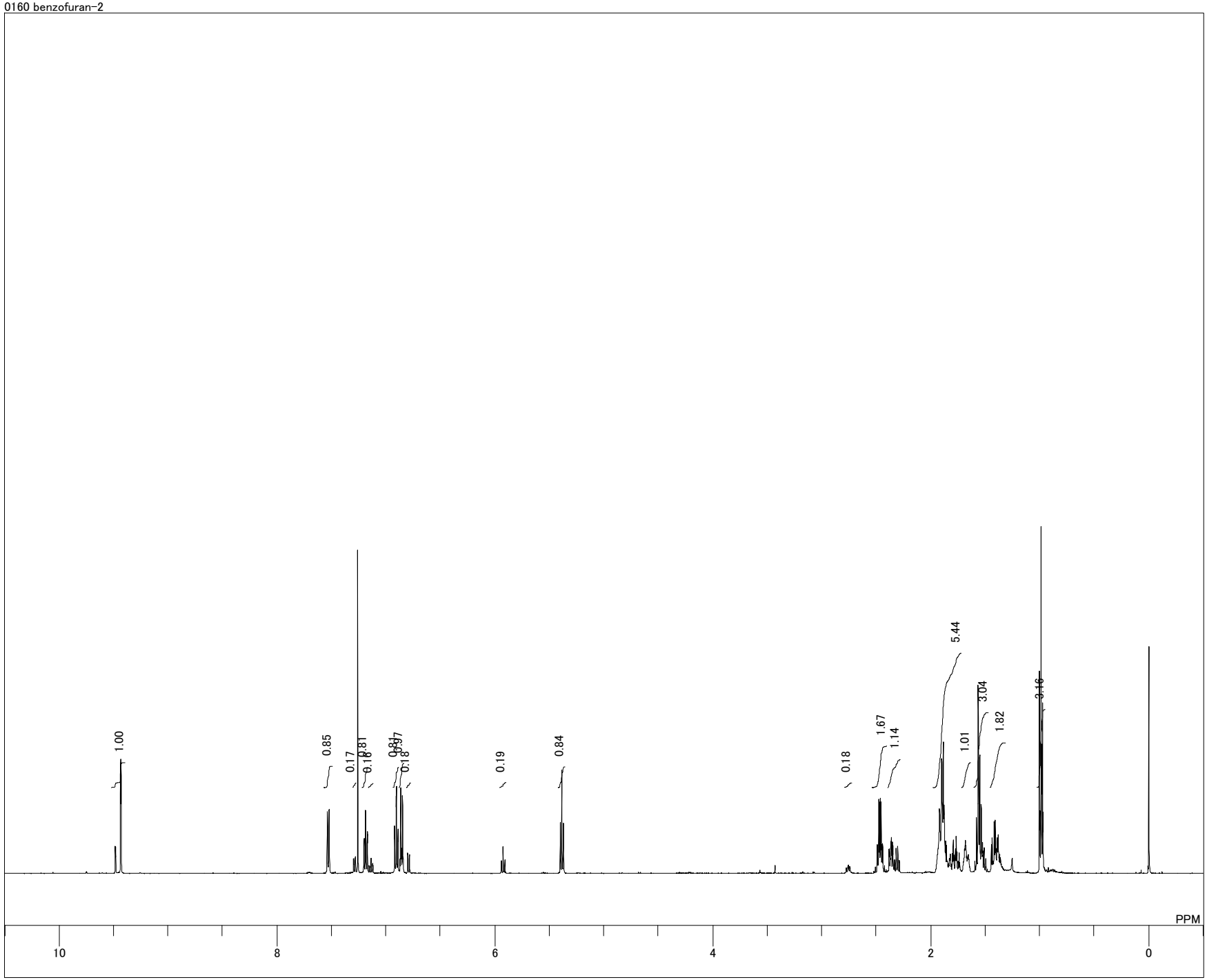


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0160 benzopiran -13C-2
DATIM	05-06-2011 12:04:38
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	18348
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.58 usec
IRNUC	1H
CTEMP	23.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	60

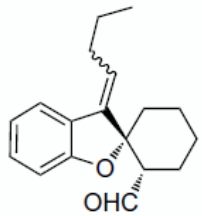


34

0160 benzofuran-2

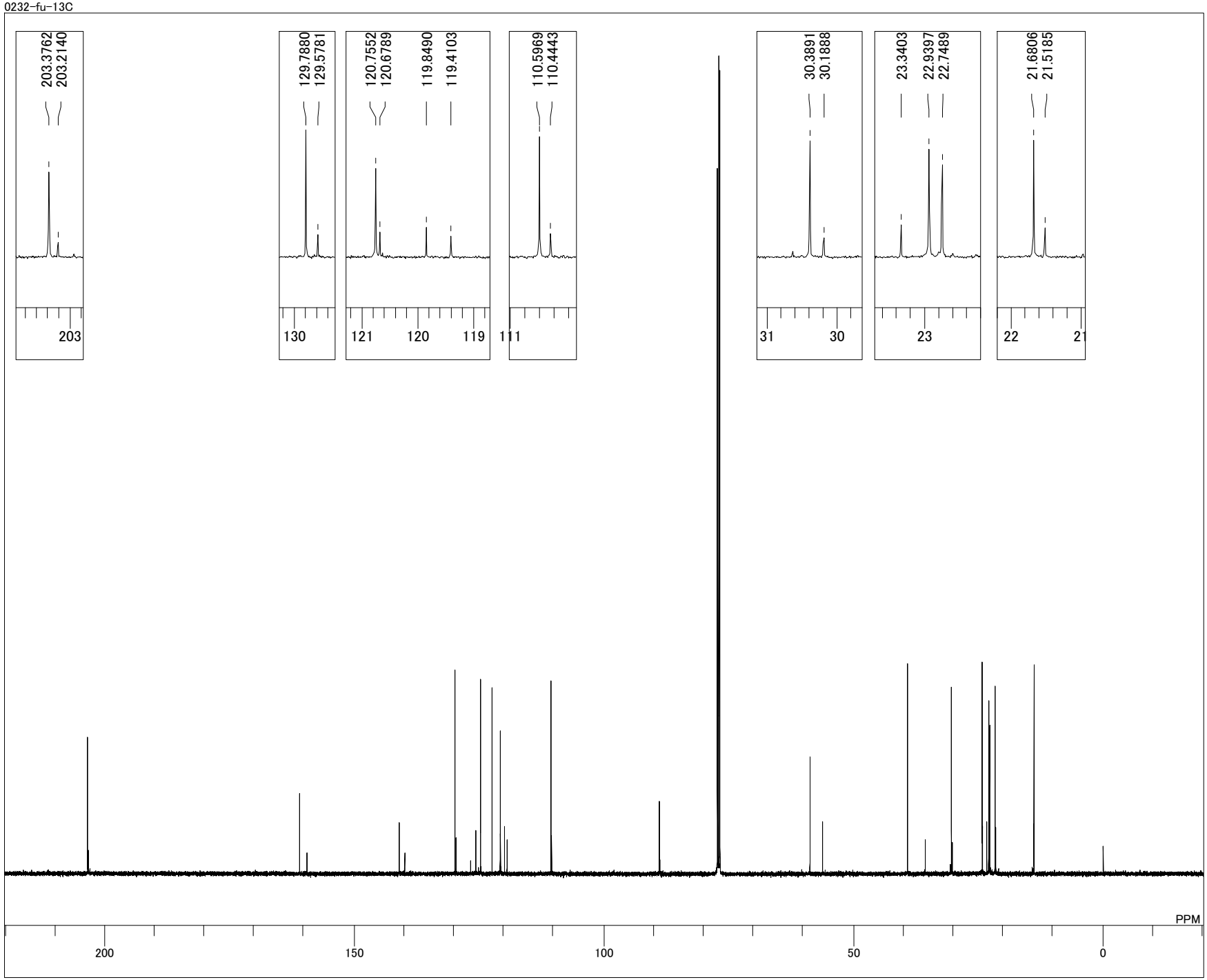


DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0160 benzofuran-2
DATIM	06-06-2011 20:05:25
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	54

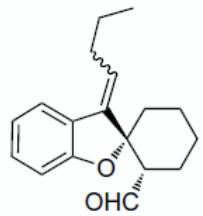


35

0232-fu-13C



DFILE	E:¥Hg論文用データ¥Hg-1
COMNT	0232-fu-13C
DATIM	18-11-2011 10:11:16
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32768
FREQU	39308.18 Hz
SCANS	11949
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	4.33 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	60



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