Supporting Information

Directed ortho-Borylation of Functionalized Arenes Catalyzed by a Silica–Supported Compact Phosphine–Iridium System

Soichiro Kawamorita,[†] Hirohisa Ohmiya,[†] Kenji Hara,[‡] Atsushi Fukuoka[‡] and Masaya Sawamura*[,†]

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan, and Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

Table of Contents

Instrumentation and Chemical

NMR spectra were recorded on a Varian Gemini 2000 spectrometer, operating at 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR. Chemical shift values for ^{1}H and ^{13}C are reference to Me_4Si and the residual solvent resonances respectively. Chemical shifts are reported in δ ppm. Elemental analysis was performed at the Center for Instrument Analysis, Hokkaido University. High-resolution mass spectra were recorded on a JEOL JMS-700TZ mass spectrometer, JEOL JMS-FABmate mass spectrometer or JEOL JMS-T100LC mass spectrometer at the Center for Instrument Analysis, Hokkaido University. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. Gas chromatographic (GC) analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector.

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Silica-SMAP was prepared according to the reported procedure.[1] All solvents for catalytic reactions were degassed via four freeze–pump–thaw cycles before use. $[Ir(OMe)(cod)]_2$ was prepared according to the literature.[2] Bis(pinacolato)diboron was purchased from AllyChem Co., Ltd.

Typical Procedures

Typical Procedure for the ortho-Borylation of Functionalized Arenes (Table 1, entry 1). In a glove box, Silica-SMAP (0.064 mmol P g^{-1}, 39 mg, 0.0025 mmol), bis(pinacolato)diboron (**2**, 127 mg, 0.5 mmol) and anhydrous, degassed hexane (1.1 mL) were placed in a 10 mL-glass tube containing magnetic stirring bar, and the mixture was stirred for 1 min at 25 ˚C. $[Ir(OMe)(cod)]_2$ (0.8 mg, 0.00125 mmol) in hexane (0.4 mL) and methyl benzoate (**1a**, 136 mg, 1.0 mmol) were added in the tube, which was then sealed with a screw cap. The tube was removed from the glove box. After the resulting mixture was stirred at 25 ˚C for 2 hours, the mixture was filtered through a glass pipet equipped with a cotton filter. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the reaction mixture. The yield of the product was determined by ^{1}H NMR. TLC analysis of the crude material revealed that the Rf values of **3a** and the diborylated compound were 0.7 and 0.2, respectively (hexane/diethyl ether = 50/50). Flash silica gel column chromatography (hexane/diethyl ether = 100/0–80/20) of the crude product provided (**3a**, 116.5 mg, 0.44 mmol) in 89% isolated yield.

a **b**

Figure S1. Photographs of the reactor system during (a) and after the reaction (b)

Large-Scale ortho-Borylation of Methyl Benzoate (eq 1). In a glove box, Silica-SMAP (0.065 mmol P g^{-1}, 8.0 mg, 0.0005 mmol), bis(pinacolato)diboron (**2**, 2.54 g, 10.0 mmol) was placed in a 10 mL-glass tube containing magnetic stirring bar. $[Ir(OMe)(cod)]_2$ (0.16 mg, 0.00025 mmol) and methyl benzoate (**1a**, 2.5 mL, 20.0 mmol) were added. After being sealed with a screw cap, the tube was removed from the glove box. The resulting mixture was heated at 100 ˚C for 3 hours. After the mixture was cooled to room temperature, the mixture was filtered through a glass pipet equipped with a cotton filter. Solvent was removed under reduced pressure. Flash silica gel column purification (hexane/diethyl ether = 100:0–80:20) of the crude product provided (**3a**, 2.33 g, 8.8 mmol) in 88% isolated yield.

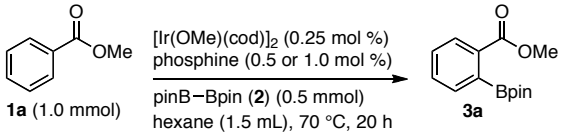
Ir-Catalyzed Borylation of Methyl Benzoate (1a) with Soluble Phosphine Ligands at 70 °C.

Even with Ph_3P, (t-Bu)$_3$P, Cy_3P and Me_3P (Ir/P 1:1 or 1:2) the borylation of **1a** proceeded at 70 ˚C (20 h), but **3a** was obtained in low yields and/or was contaminated with meta and para-borylation products (Table S1). The Ir-to-phosphine ratio of 1:1 provided the borylation

product in much higher yield. In terms of the yield of **3a**, PCy_3 was the best ligand among the homogeneous phosphines examined, but **3a** obtained with PCy_3 was contaminated with meta- and para-borylation products (Table S1, entries 12 and 13).

Typical Procedure for Ir-Catalyzed Borylation of Methyl Benzoate (1a) with Soluble Phosphine Ligands at 70 °C (Table S1). In a glove box, bis(pinacolato)diboron (**2**, 127 mg, 0.5 mmol) and anhydrous, degassed hexane (0.7 or 0.9 mL) were placed in a 10 mL-glass tube containing magnetic stirring bar. Phosphine ligand (0.005 or 0.0025 mmol) in hexane (0.4 or 0.2 mL), $[Ir(OMe)(cod)]_2$ (0.8 mg, 0.00125 mmol) in hexane (0.4 mL) and methyl benzoate (**1a**, 136 mg, 1.0 mmol) were added to the tube in this order. The tube was then sealed with a screw cap, and was removed from the glove box. After the resulting mixture was stirred at 70 ˚C for 20 hours, the mixture was filtered through a short plug of silica gel. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the reaction mixture. The yield of the product was determined by ^1H NMR.

Table S1. Ir-Catalyzed Borylation of Methyl Benzoate (**1a**) with Soluble Phosphine Ligands

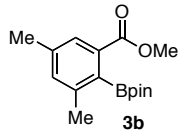


entry	phosphine [P]	[Ir]/[P]	NMR yield (%)	ratio of *o*/(*m*+*p*)
1	none	–	10	>20:1
2	Ph-SMAP	1:1	12	>20:1
3	Ph-SMAP	1:2	0	–
4	4-CF_3-Ph-SMAP	1:1	8	>20:1
5	4-CF_3-Ph-SMAP	1:2	3	>20:1
6	PPh_3	1:1	57	92:8
7	PPh_3	1:2	0	–
8	PMe_3	1:1	31	>20:1
9	PMe_3	1:2	0	–
10	P(*t*-Bu)$_3$	1:1	15	>20:1
11	P(*t*-Bu)$_3$	1:2	9	>20:1
12	PCy_3	1:1	100	90:10
13	PCy_3	1:2	87	96:4

Compounds Characterization

The starting materials shown in Tables 1 and 2 are known compounds. Compound **3a** is found in the literature.[3]

3,5-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid Methyl Ester (3b)

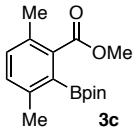


3b

White solid. R_f 0.4 (hexane/diethyl ether = 90/10). ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 12H), 2.31 (s, 3H), 2.40 (s, 3H), 3.89 (s, 3H), 7.13 (s, 1H), 7.59 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 20.86, 21.22, 25.10, 51.98, 83.60, 126.58, 133.28, 134.42, 138.27, 141.21, 168.86. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{23}BO_4Na$, 313.15871; found, 313.15946. m.p. 60.0–62.9 °C.

The characterization of the diborylated compound was performed by GC analysis and ^{1}H NMR spectrum of the isolated product. R_f 0.1 (hexane/diethyl ether = 90/10). ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 24H), 2.38 (s, 6H), 3.90 (s, 3H), 7.08 (s, 1H).

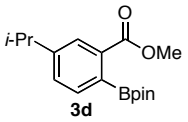
3,6-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid Methyl Ester (3c)



3c

Oil. R_f 0.5 (hexane/diethyl ether = 80/20). ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 12H), 2.41 (s, 6H), 3.90 (s, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 21.06, 21.16, 25.18, 52.07, 83.66, 132.14, 132.51, 134.44, 134.61, 139.46, 171.29. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{23}BO_4Na$, 313.15871; found, 313.15979.

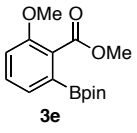
5-Isopropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid Methyl Ester (3d)



3d

Oil. R_f 0.4 (hexane/diethyl ether = 90/10). ^{1}H NMR ($CDCl_3$) δ 1.23 (d, *J* = 6.9 Hz, 6H), 1.40 (s, 12H), 2.93 (q, *J* = 6.9 Hz, 1H), 3.91 (s, 3H), 7.37 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 23.66, 24.74, 33.91, 52.13, 83.88, 126.97, 130.16, 132.48, 133.76, 150.14, 168.86. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{25}BO_4Na$, 327.17436; found, 327.17509.

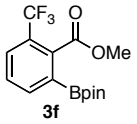
2-Methoxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid Methyl Ester (3e)



3e

Oil. R_f 0.4 (hexane/diethyl ether = 50/50). ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 12H), 3.84 (s, 3H), 3.89 (s, 3H), 7.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.32 (dd, *J* = 7.8 1.2 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.66, 52.19, 55.88, 84.04, 113.79, 126.56, 128.15, 130.58, 156.13, 169.24. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{21}BO_5Na$, 315.13797; found, 315.13800.

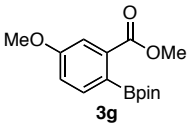
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-6-trifluoromethylbenzoic Acid Methyl Ester (3f)



3f

Oil. R_f 0.4 (benzene). ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 3.91 (s, 3H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.55, 52.53, 84.53, 123.56 (q, *J* = 274.2 Hz, 1C), 126.95 (q, *J* = 32.0 Hz), 128.34 (q, *J* = 4.5 Hz), 128.96, 137.33 (q, *J* = 2.3 Hz), 138.39 (q, *J* = 1.1 Hz), 168.74. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{18}BF_3O_4Na$, 353.11479; found, 353.11422.

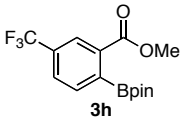
5-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid Methyl Ester (3g)



3g

Oil. R_f 0.3 (hexane/ethyl acetate = 80/20). ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 12H), 3.82 (s, 3H), 3.89 (s, 3H), 7.04 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.65, 52.18, 55.17, 83.76, 113.64, 117.95, 133.86, 135.53, 160.36, 168.42. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{21}BO_5Na$, 315.13797; found, 315.13703.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trifluoromethylbenzoic Acid Methyl Ester (3h)

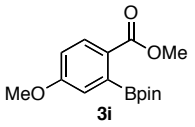


3h

White solid. R_f 0.4 (chloroform). ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 12H), 3.95 (s, 3H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 0.9 Hz, 1H), 8.20 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.69, 52.63, 84.47, 123.71 (q, *J* = 273.0 Hz), 125.52 (q, *J* = 4.0 Hz), 128.29 (q, *J* = 4.0 Hz), 131.43 (q, *J* = 33.2 Hz), 132.86, 134.20, 167.35. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{18}BF_3O_4Na$, 353.11479; found, 353.11417. m.p.

59.1–61.8 ˚C.

4-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid Methyl Ester (3i)

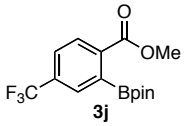


3i

White solid. R_f 0.3 (hexane/diethyl ether = 50/50). ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 12H), 3.84 (s, 3H), 3.88 (s, 3H), 6.88 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.71, 51.96, 55.25, 84.01, 114.15, 117.02, 125.56, 131.04, 162.54, 168.19. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{15}H_{21}BO_5Na$, 315.13797; found, 315.13657. m.p. 76.8–77.3 ˚C.

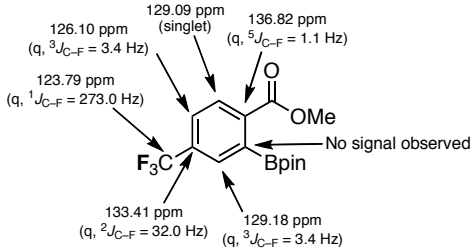
The characterization of the diborylated product was performed by GC analysis and ^{1}H NMR spectrum of the crude material. R_f 0.2 (hexane/diethyl ether = 50/50). ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 24H), 7.02 (s, 2H) (only observed peaks).

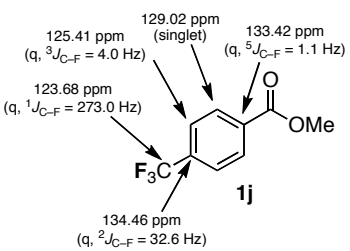
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-trifluoromethyl Benzoic Acid Methyl Ester (3j)

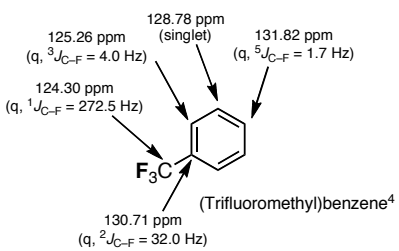


3j

Oil. R_f 0.4 (hexane/diethyl ether = 90/10). ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 12H), 3.95 (s, 3H), 7.68 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.74 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.73, 52.66, 84.52, 123.79 (q, *J* = 273.0 Hz), 126.10 (q, *J* = 3.4 Hz), 129.09, 129.18 (q, *J* = 3.4 Hz), 133.41 (q, *J* = 32.0 Hz), 136.82 (q, *J* = 1.1 Hz), 167.58. A signal for the carbon directly attached to the boron atom was not observed. HRMS–FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{15}H_{19}BF_3O_4$, 331.1331; found, 331.1306. The regioselectivity was assigned on the basis of the J_{C-F} values in the ^{13}C NMR spectrum.

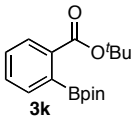






The characterization of the diborylated product was performed by GC analysis and ^{1}H NMR spectrum of the crude material. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 24H), 3.90 (s, 3H), 7.98 (s, 2H).

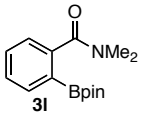
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid *tert*-Butyl Ester (3k)



3k

White solid. R_f 0.5 (hexane/diethyl ether = 80/20). ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 12H), 1.57 (s, 9H), 7.35 (m, 1H), 7.43–7.48 (m, 2H), 7.81 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.69, 28.03, 81.25, 83.73, 128.10, 128.62, 131.28, 131.80, 135.91, 167.56. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{25}BO_4Na$, 327.17436; found, 327.17392. m.p. 76.6–77.6 °C.

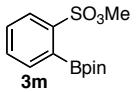
***N,N*-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (3l)**



3l

White solid. R_f 0.3 (hexane/ethyl acetate = 50/50). ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 12H), 2.97 (brs, 6H), 7.30 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.37 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.45 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.80 (dd, *J* = 7.5, 0.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.82, 83.52, 125.59, 128.27, 131.00, 135.09, 142.61, 172.65. A signal for the carbon directly attached to the boron atom was not observed. Anal. Calcd for $C_{15}H_{22}O_3BN$: C, 65.48; H, 8.06%. Found: C, 65.46; H, 8.15%. m.p. 86.0–87.1 °C.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonic Acid Methyl Ester (3m)

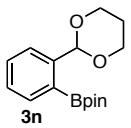


3m

Oil. R_f 0.5 (chloroform). ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 12H), 3.80 (s, 3H), 7.53–7.62 (m, 3H), 7.94 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.54, 56.23, 84.63, 128.19, 129.80, 132.70, 133.30, 137.78. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{19}BO_5SNa$, 321.09439; found, 321.09386.

The characterization of the diborylated product was performed by GC analysis and ^{1}H NMR spectrum of the crude material. R_f 0.1 (chloroform). ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 24H), 3.85 (s, 3H) (only observed peaks).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl-1,3-dioxane (3n)



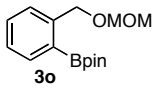
3n

Oil. R_f 0.2 (dichloromethane). ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 12H), 1.41 (dm, *J* = 12.0 Hz, 1H), 2.21 (m, 1H), 4.01 (tm, *J* = 12.0 Hz, 2H), 4.22 (ddm, *J* = 12.0, 3.9 Hz, 2H), 6.02 (s, 1H), 7.30 (td, *J* = 7.2, 1.2 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.68 (dm, *J* = 7.5 Hz, 1H), 7.73 (dd, *J* = 7.2, 1.2

Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.74, 25.70, 67.28, 83.51, 100.34, 124.75, 127.80, 130.59, 134.93, 143.77. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{23}BO_4$, 313.15871; found, 313.16005.

The characterization of the diborylated compound was performed by GC analysis and ^{1}H NMR spectrum of the isolated product. R_f 0.05 (dichloromethane). ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 24H), 1.38 (d, *J* = 12.0 Hz, 1H), 2.24 (m, 1H), 4.01 (td, *J* = 12.0, 2.1 Hz, 2H), 4.24 (dd, *J* = 6.3, 4.8 Hz, 2H), 6.09 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 12.0 Hz, 2H).

2-(2-Methoxymethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)

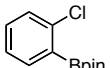


3o

Oil. R_f 0.5 (chloroform). ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 3.42 (s, 3H), 4.75 (s, 2H), 4.85 (s, 2H), 7.30 (dd, *J* = 6.9, 1.8 Hz, 1H), 7.40–7.48 (m, 2H), 7.81 (d, *J* = 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.74, 55.25, 69.12, 83.62, 96.30, 126.89, 128.07, 131.01, 135.93, 144.16. A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{23}BO_4Na$, 301.15871; found, 301.15850.

The characterization of the diborylated compound was performed by GC analysis and ^{1}H NMR spectrum of the isolated product. R_f 0.2 (chloroform). ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 24H), 3.43 (s, 3H), 4.75 (s, 2H), 5.06 (s, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 2H).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-chlorobenzene (3p)

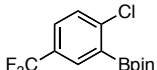


3p

Oil. R_f 0.7 (hexane/diethyl ether = 80/20). ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 12H), 7.22 (m, 1H), 7.32–7.35 (m, 2H), 7.69 (dm, *J* = 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.66, 84.12, 125.87, 129.44, 131.92, 136.49, 139.61. A signal for the carbon directly attached to the boron atom was not observed. HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{12}H_{16}BO_2Cl$, 238.0932; found, 238.0927.

The characterization of the diborylated product was performed by GC analysis and ^{1}H NMR spectrum of the crude material. R_f 0.6 (hexane/diethyl ether = 80/20). ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 24H) (only observed peaks).

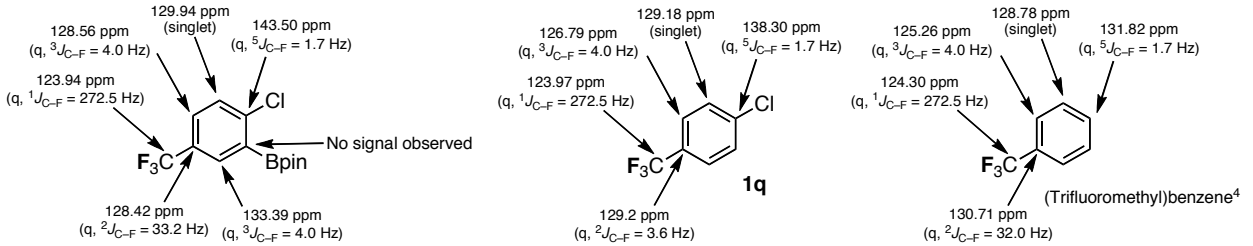
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-trifluoromethyl-1-chlorobenzene (3q)



3q

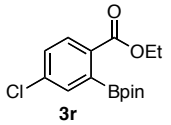
Oil. R_f 0.7 (benzene). ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 12H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.95 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.67, 84.63, 123.94 (q, *J* = 272.5 Hz), 128.42 (q, *J* = 33.2 Hz), 128.56 (q, *J* = 4.0 Hz), 129.94, 133.39 (q, *J* = 4.0 Hz), 143.50 (q, *J* =

1.7 Hz). A signal for the carbon directly attached to the boron atom was not observed. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{16}BClF_3O_2$, 307.08840; found, 306.08721. The regioselectivity was assigned on the basis of the J_{C-F} values in the ^{13}C NMR spectrum.



The characterization of the diborylated product was performed by GC analysis and ^1H NMR spectrum of the crude material. ^1H NMR ($CDCl_3$) δ 1.37 (s, 24H), 7.97 (s, 2H).

4-Chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid Ethyl Ester (3r)



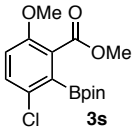
3r

Oil. R_f 0.6 (hexane/diethyl ether = 50/50). ^1H NMR ($CDCl_3$) δ 1.37 (t, *J* = 7.2 Hz, 3H), 1.42 (s, 12H), 4.37 (q, *J* = 7.2 Hz, 2H), 7.37 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.14, 24.71, 61.43, 84.30, 129.06, 130.07, 132.16, 132.17, 138.69, 167.41. A signal for the carbon directly attached to the boron atom was not observed. Anal. Calcd for $C_{15}H_{20}BClO_4$: C, 58.01; H, 6.49%. Found: C, 57.91; H, 6.45%.

The regiochemistry was determined by comparison of the ^1H NMR chemical shifts with the other ortho-borylated benzoate products. The chemical shifts of the proton at the aromatic C6 position are diagnostic of the regiochemitry. On the ortho-borylated benzoate derivatives, the protons at C6 position appeared at the lowest field (δ 7.6–8.2). In the case of **3r**, the C6 proton appeared at the lowest field (δ 7.87), which indicates that **3r** is the ortho isomer.

The characterization of the diborylated compound was performed by GC analysis and ^1H NMR spectrum of the isolated product. R_f 0.3 (hexane/diethyl ether = 50/50). ^1H NMR ($CDCl_3$) δ 1.33 (s, 24H), 1.39 (t, *J* = 7.2 Hz, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 7.68 (s, 2H).

3-Chloro-6-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid Methyl Ester (3s)



3s

White solid. R_f 0.3 (benzene). ^1H NMR ($CDCl_3$) δ 1.42 (s, 12H), 3.84 (s, 3H), 3.91 (s, 3H), 6.90 (d, *J* = 8.7 Hz, 1H) 7.39 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.91, 52.58, 56.18, 84.28, 114.30, 125.12, 129.14, 133.21, 156.85, 168.37. A signal for the carbon directly attached to the boron atom

was not observed. HRMS–ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{15}H_{20}BClO_5Na$, 349.09900; found, 349.09793. m.p. 61.9–63.3 ˚C.

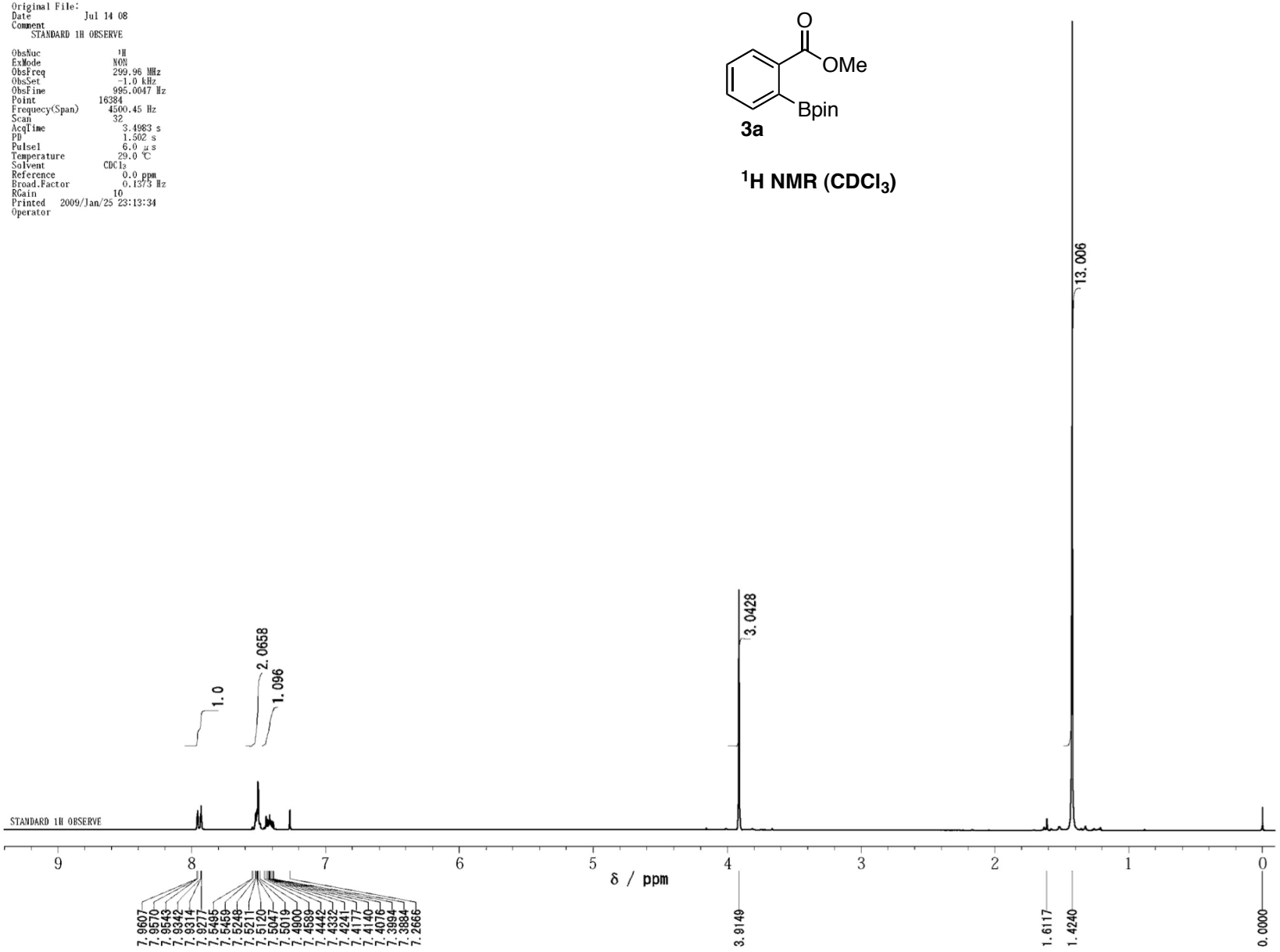
References

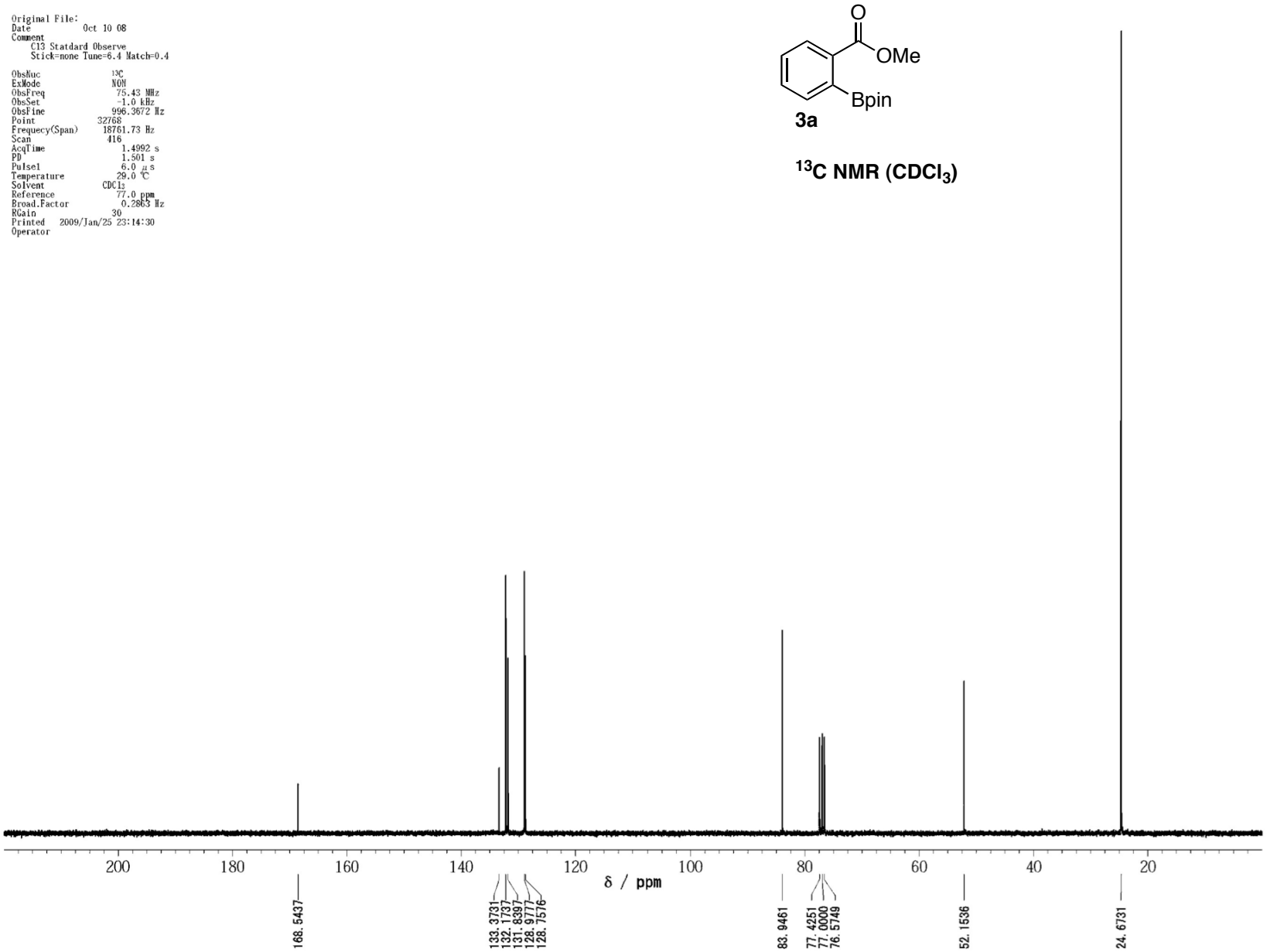
(1) (a) Hamasaka, G.; Ochida, A.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 5381–5383. (b) Hamasaka, G.; Kawamorita, S.; Ochida, A.; Akiyama, R.; Hara, K.; Fukuoka, A.; Asakura, K.; Chun, W. J.; Ohmiya, H.; Sawamura, M. *Organometallics* **2008**, *27*, 6495–6506.

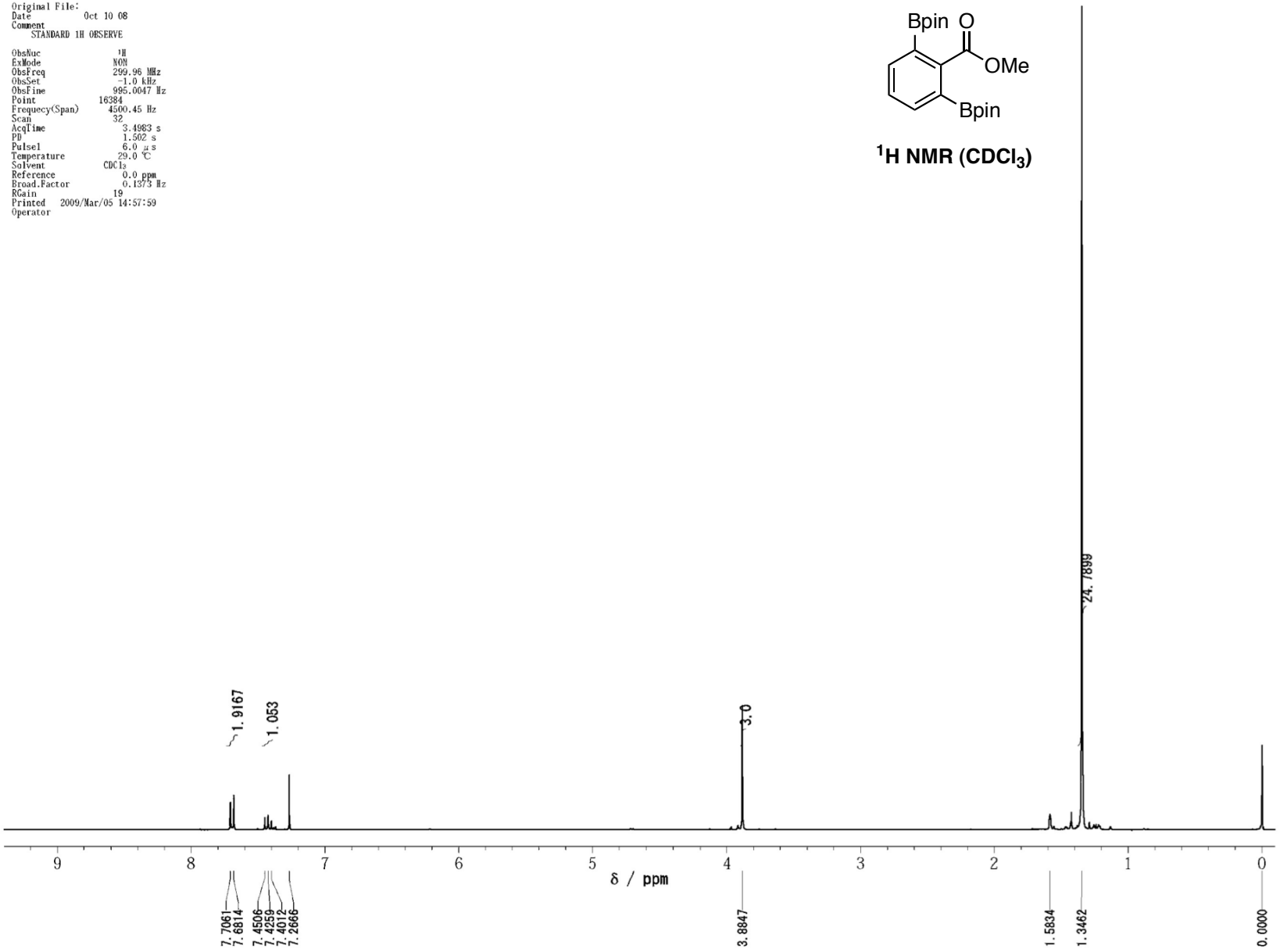
(2) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

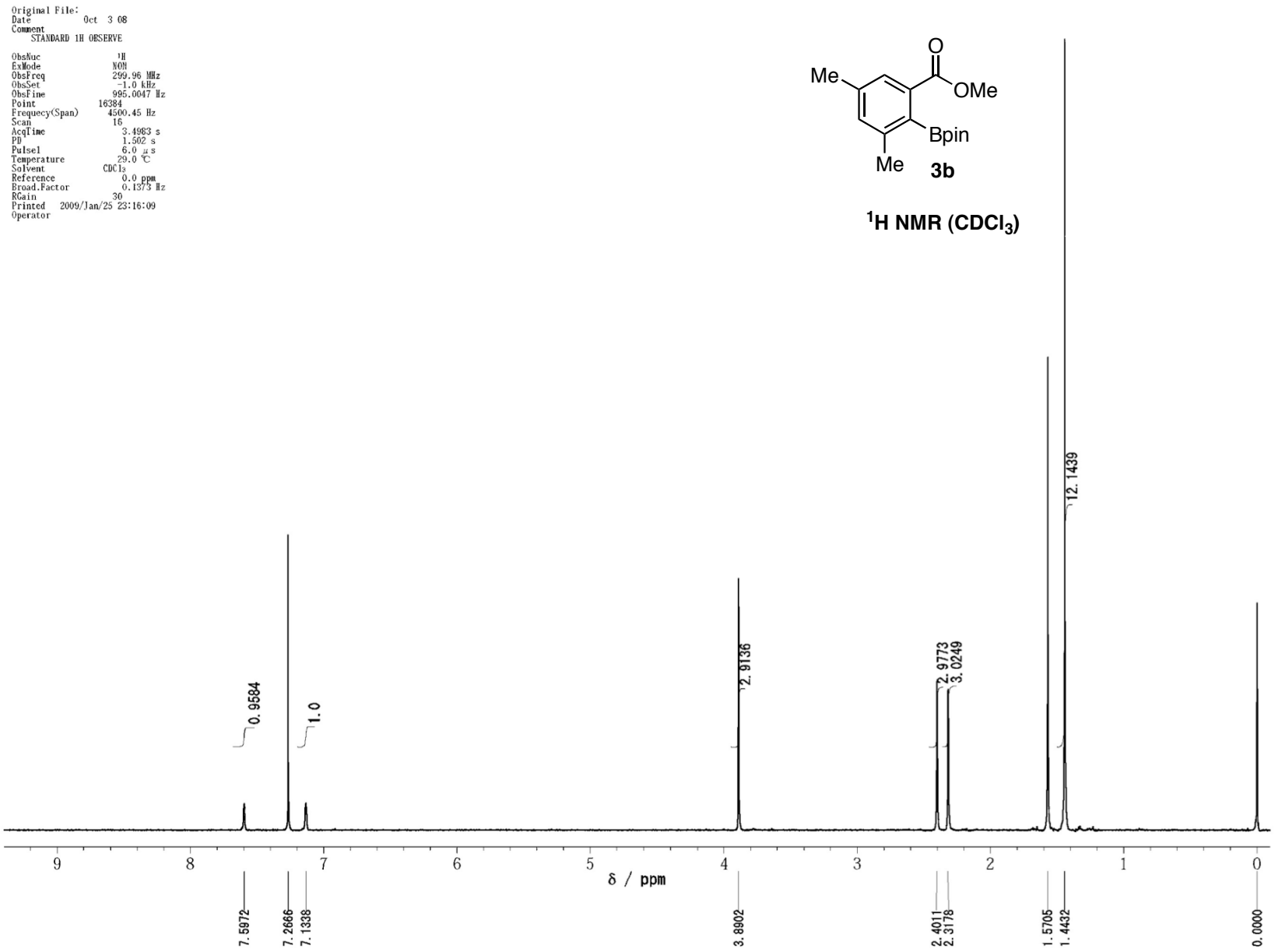
(3) Wolan, A.; Zaidlewicz, M. *Org. Biomol. Chem.* **2003**, *1*, 3274–3276.

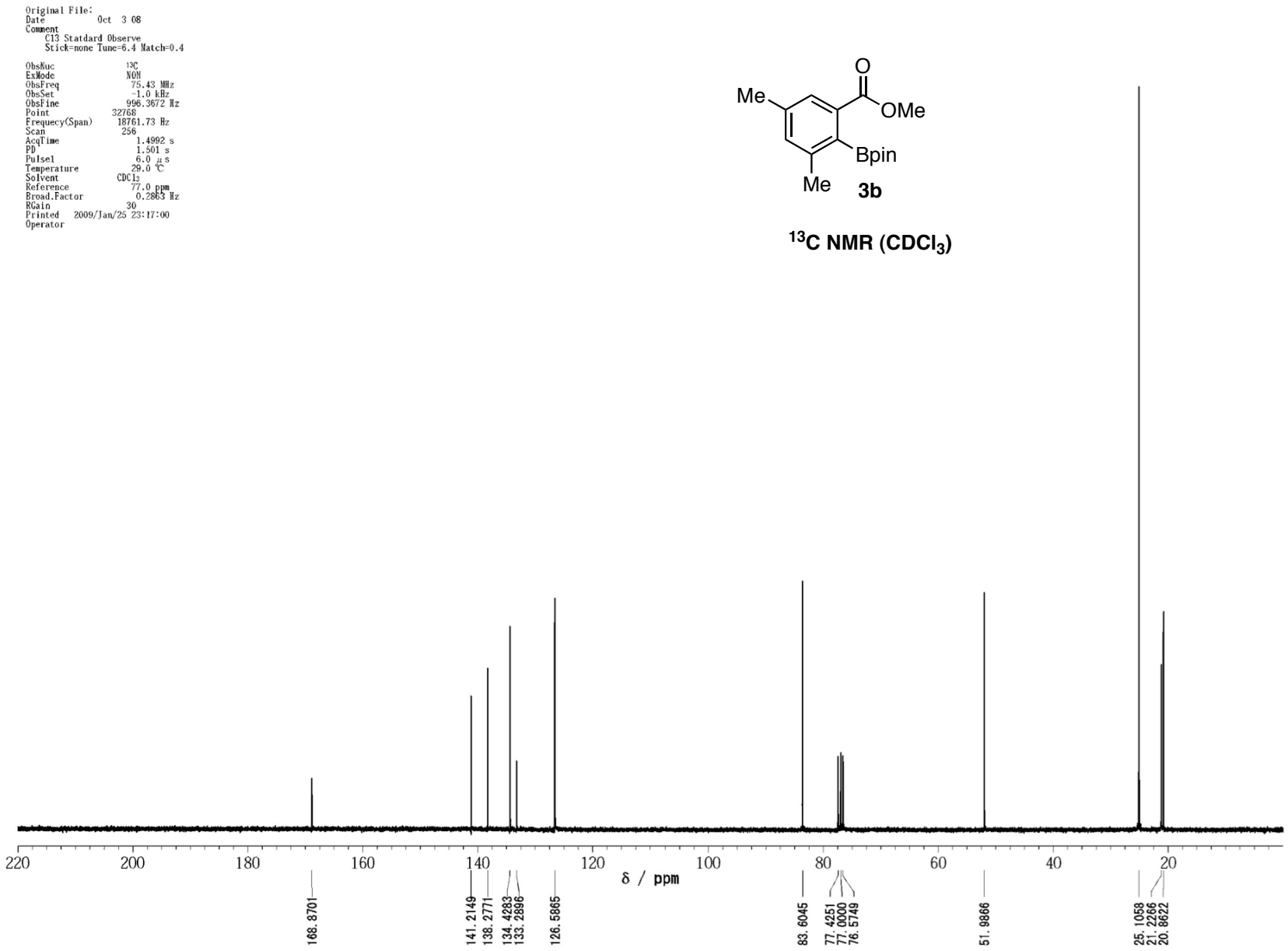
(4) Takahashi, K.; Yoshino, A.; Hosokawa, K.; Muramatsu, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 755–756.

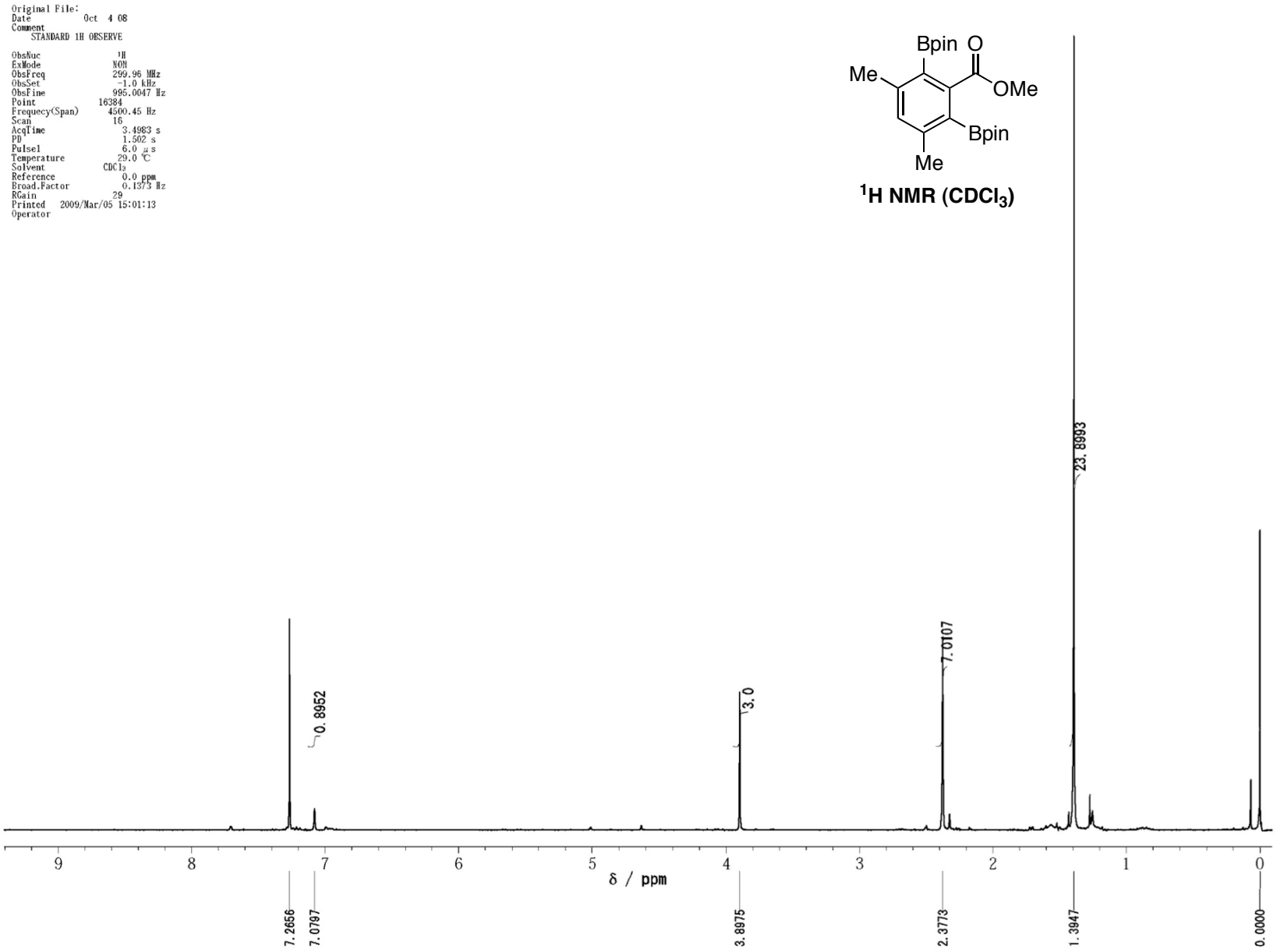

Original File:
Date Jul 14 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 10
Printed 2009/Jan/25 23:13:34
Operator
O
OMe
Bpin
3a
1H NMR (CDCl3)
13.006
3.0428
2.0658
1.096
1.0
STANDARD 1H OBSERVE
δ / ppm
7.9607
7.9570
7.9543
7.9342
7.9314
7.9277
7.5495
7.5459
7.5248
7.5211
7.5120
7.5047
7.5019
7.4900
7.4589
7.4442
7.4332
7.4241
7.4177
7.4140
7.4076
7.3994
7.3884
7.2866
3.9149
1.6117
1.4240
0.0000

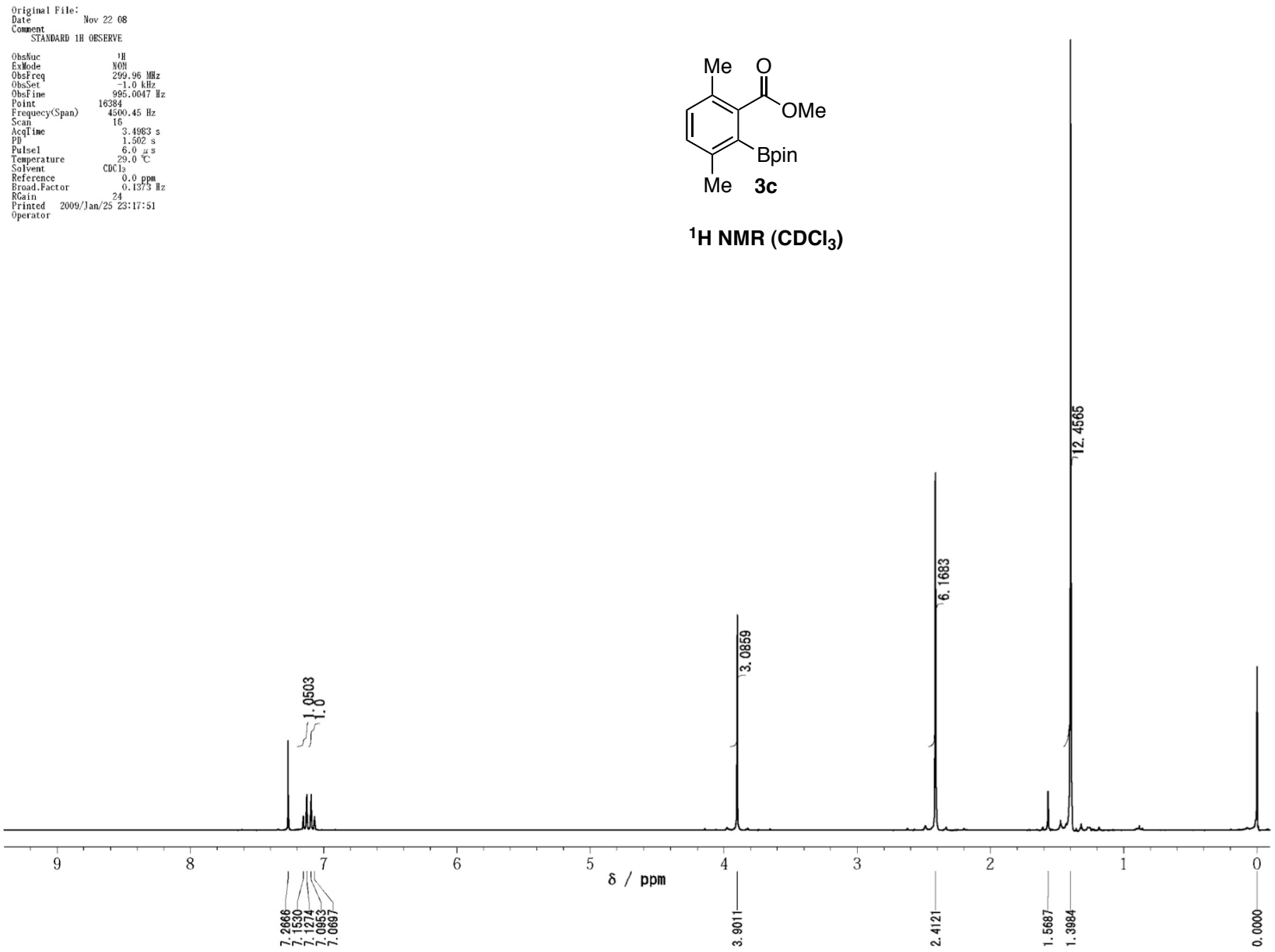

Original File:
Date Oct 10 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 416
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:14:30
Operator
O
OMe
Bpin
3a
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
168.5437
133.3731
132.1737
131.8397
128.9777
128.7576
83.9461
77.4251
77.0000
76.5749
52.1536
24.6731

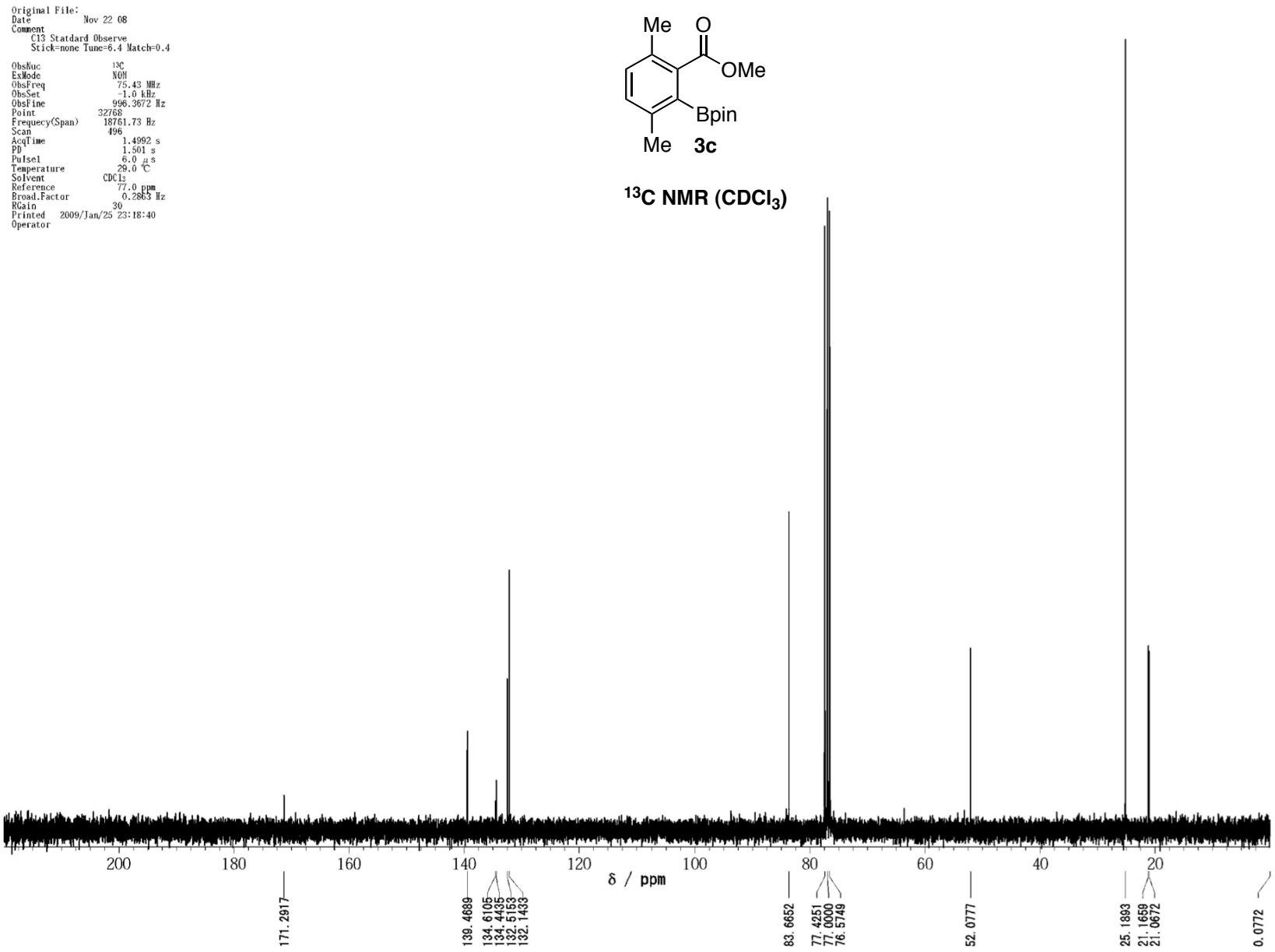

Original File:
Date Oct 10 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 19
Printed 2009/Mar/05 14:57:59
Operator
Bpin
O
OMe
Bpin
1H NMR (CDCl3)
1.9167
1.053
3.0
24.7899
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.7061
7.6814
7.4506
7.4259
7.4012
7.2666
3.8847
1.5834
1.3462
0.0000

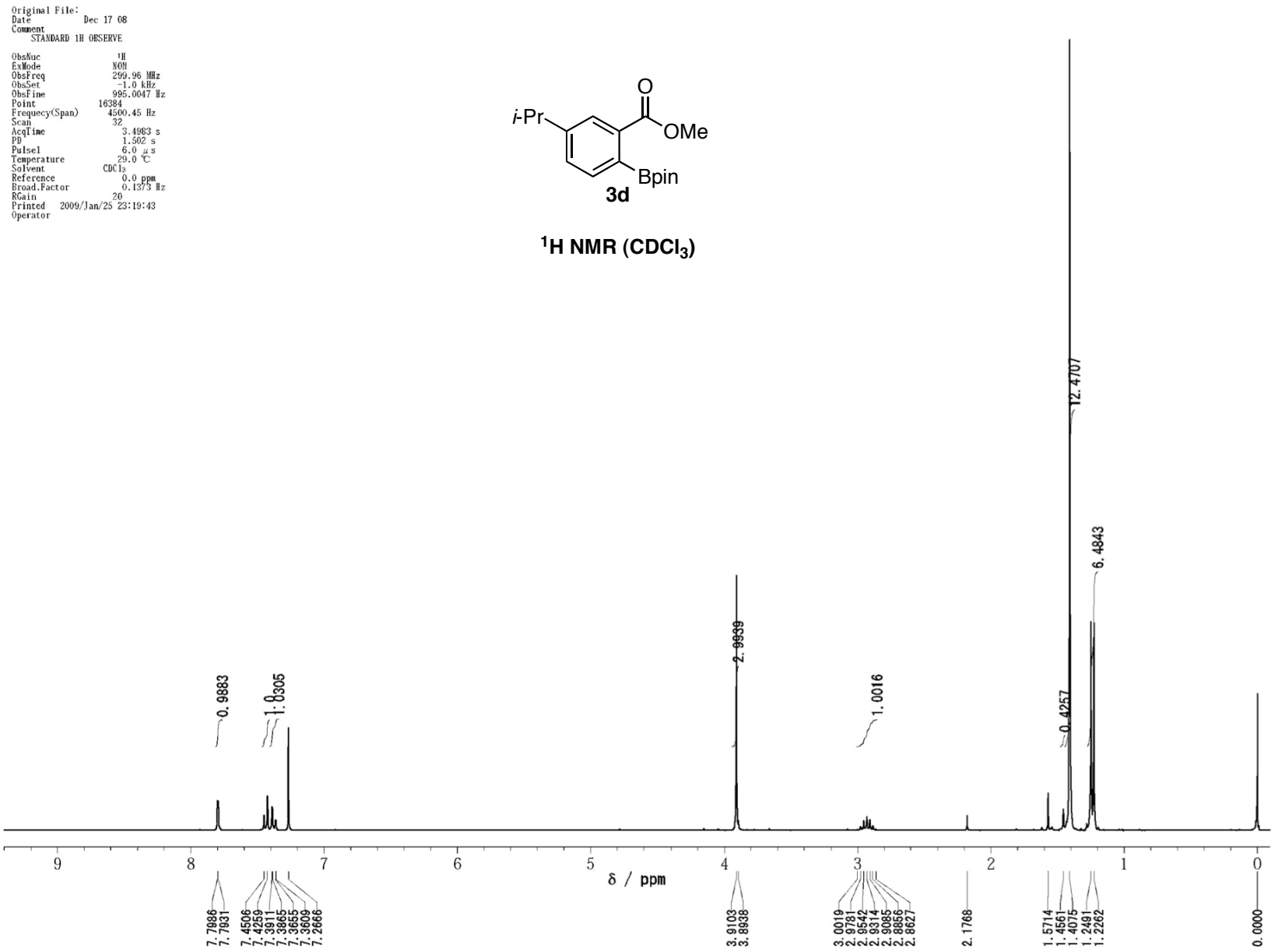

Original File:
Date Oct 3 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 30
Printed 2009/Jan/25 23:16:09
Operator
Me
O
OMe
Bpin
Me
3b
1H NMR (CDCl3)
0.9584
1.0
2.9136
2.9773
3.0249
12.1439
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.5972
7.2666
7.1338
3.8902
2.4011
2.3178
1.5705
1.4432
0.0000


Original File:
Date Oct 3 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 256
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:17:00
Operator
Me
O
OMe
Bpin
Me
3b
13C NMR (CDCl3)
220
200
180
160
140
120
100
80
60
40
20
δ / ppm
168.8701
141.2149
138.2771
134.4283
133.2896
126.5865
83.6045
77.4251
77.0000
76.5749
51.9866
25.1058
21.2266
20.8622

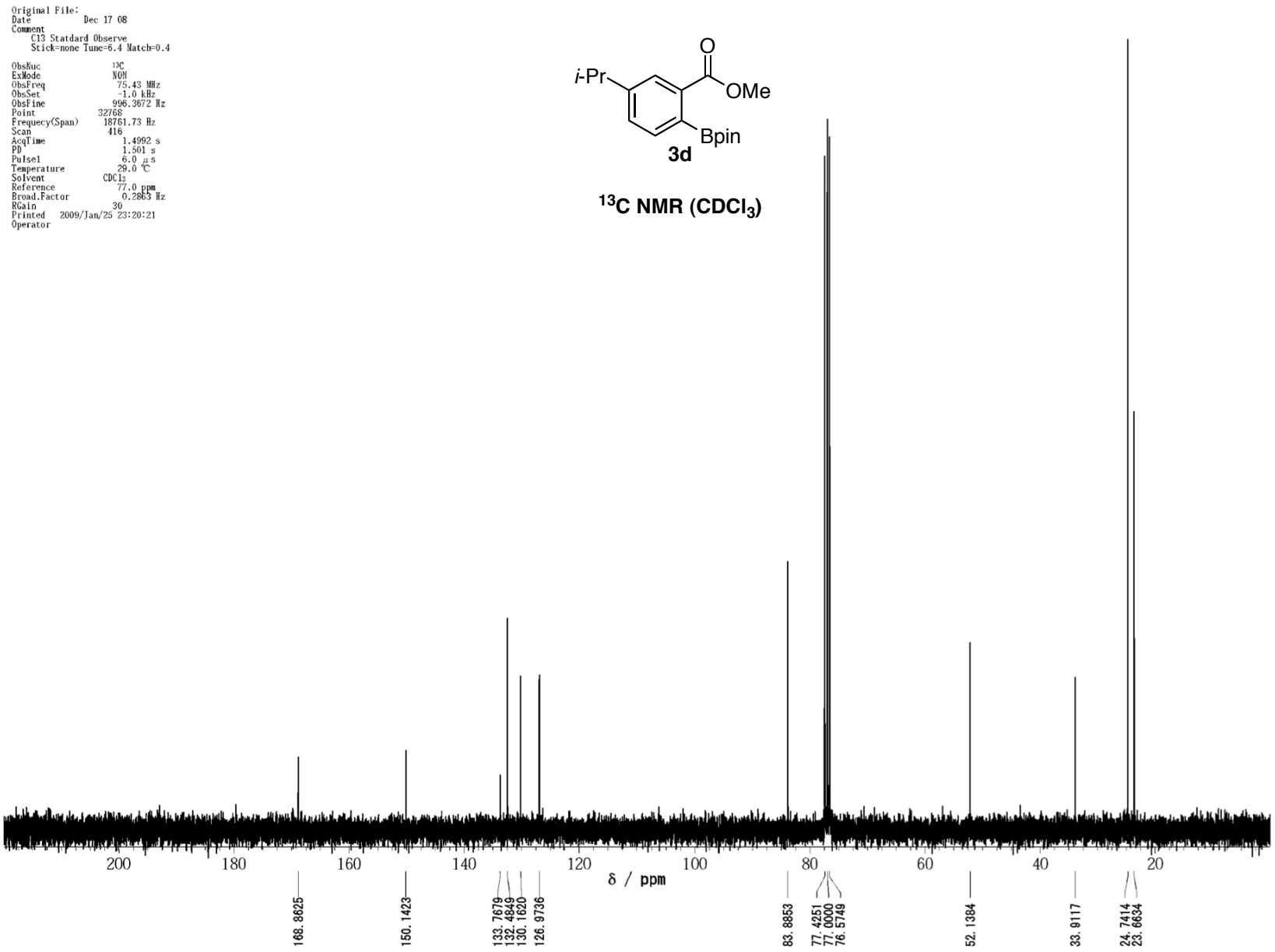

Original File:
Date Oct 4 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 29
Printed 2009/Mar/05 15:01:13
Operator
Bpin
O
Me
OMe
Bpin
Me
1H NMR (CDCl3)
0.8952
3.0
7.0107
23.8993
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2656
7.0797
3.8975
2.3773
1.3947
0.0000

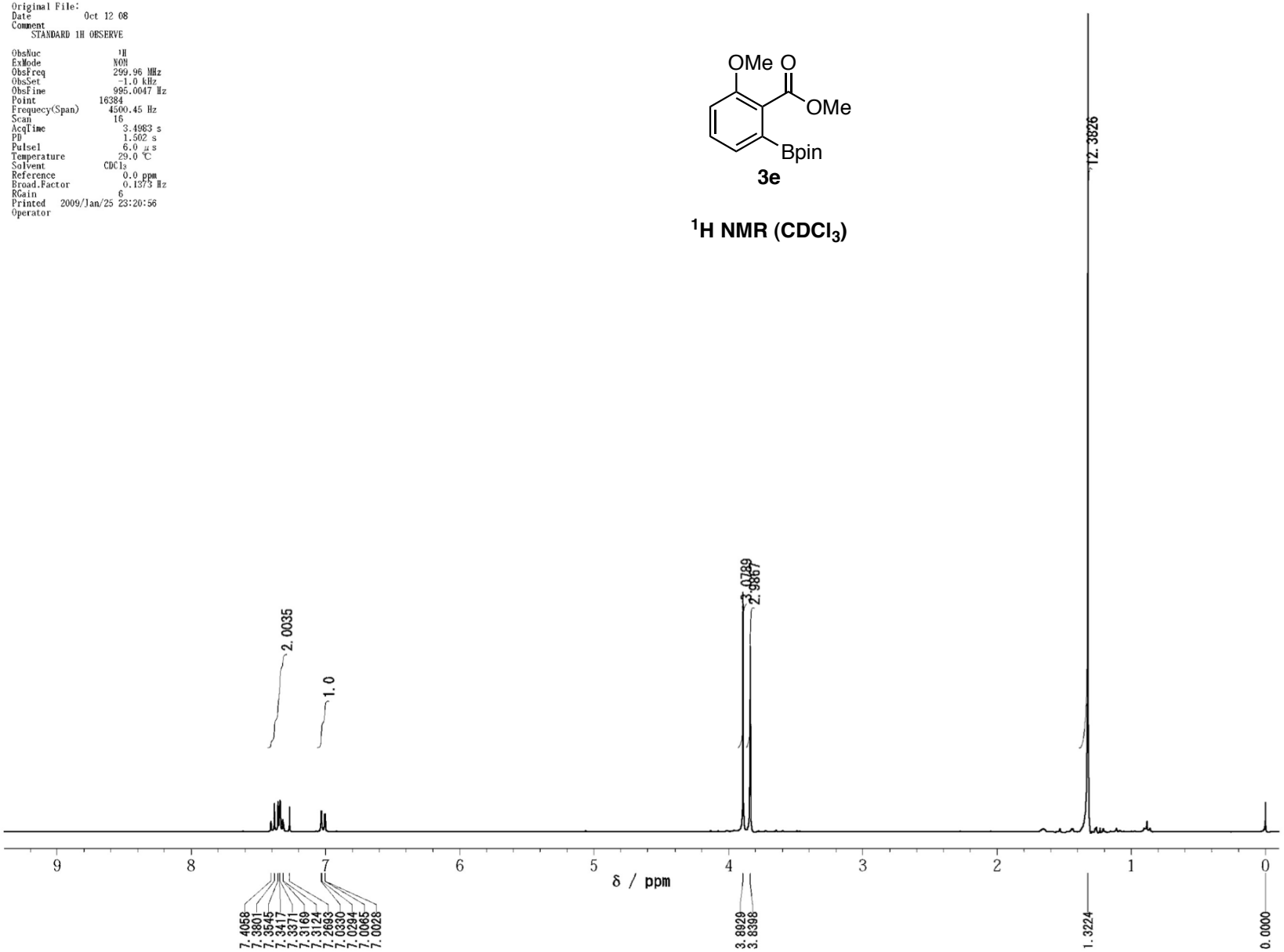

Original File:
Date Nov 22 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 24
Printed 2009/Jan/25 23:17:51
Operator
Me
O
OMe
Bpin
Me
3c
1H NMR (CDCl3)
12.4565
6.1683
3.0859
1.0503
1.0
δ / ppm
7.2666
7.1530
7.1274
7.0953
7.0697
3.9011
2.4121
1.5687
1.3984
0.0000

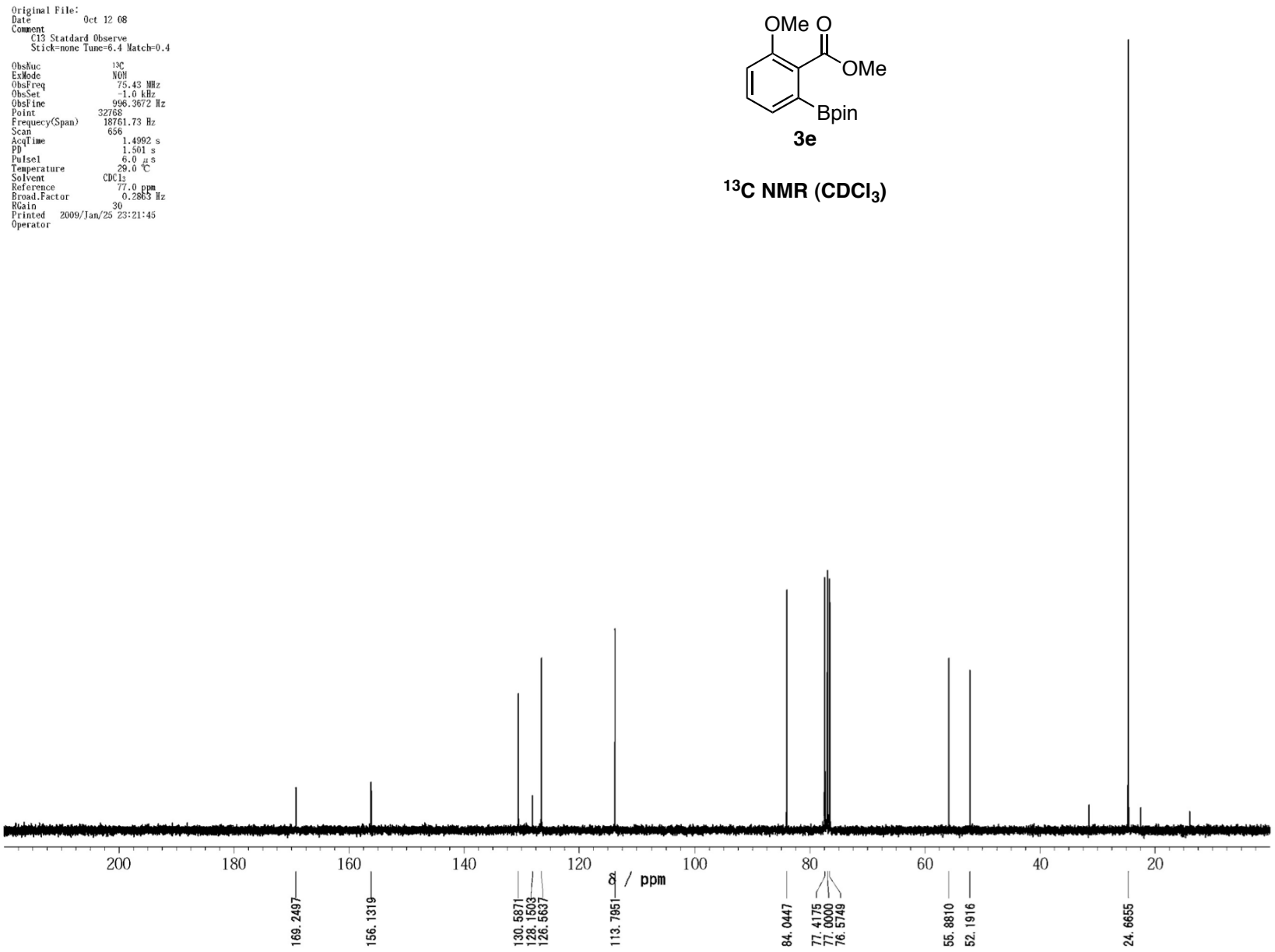

Original File:
Date Nov 22 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 496
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:18:40
Operator
Me
O
OMe
Bpin
Me
3c
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
171.2917
139.4689
134.6105
134.4435
132.5153
132.1433
83.6652
77.4251
77.0000
76.5749
52.0777
25.1893
21.1659
21.0672
0.0772

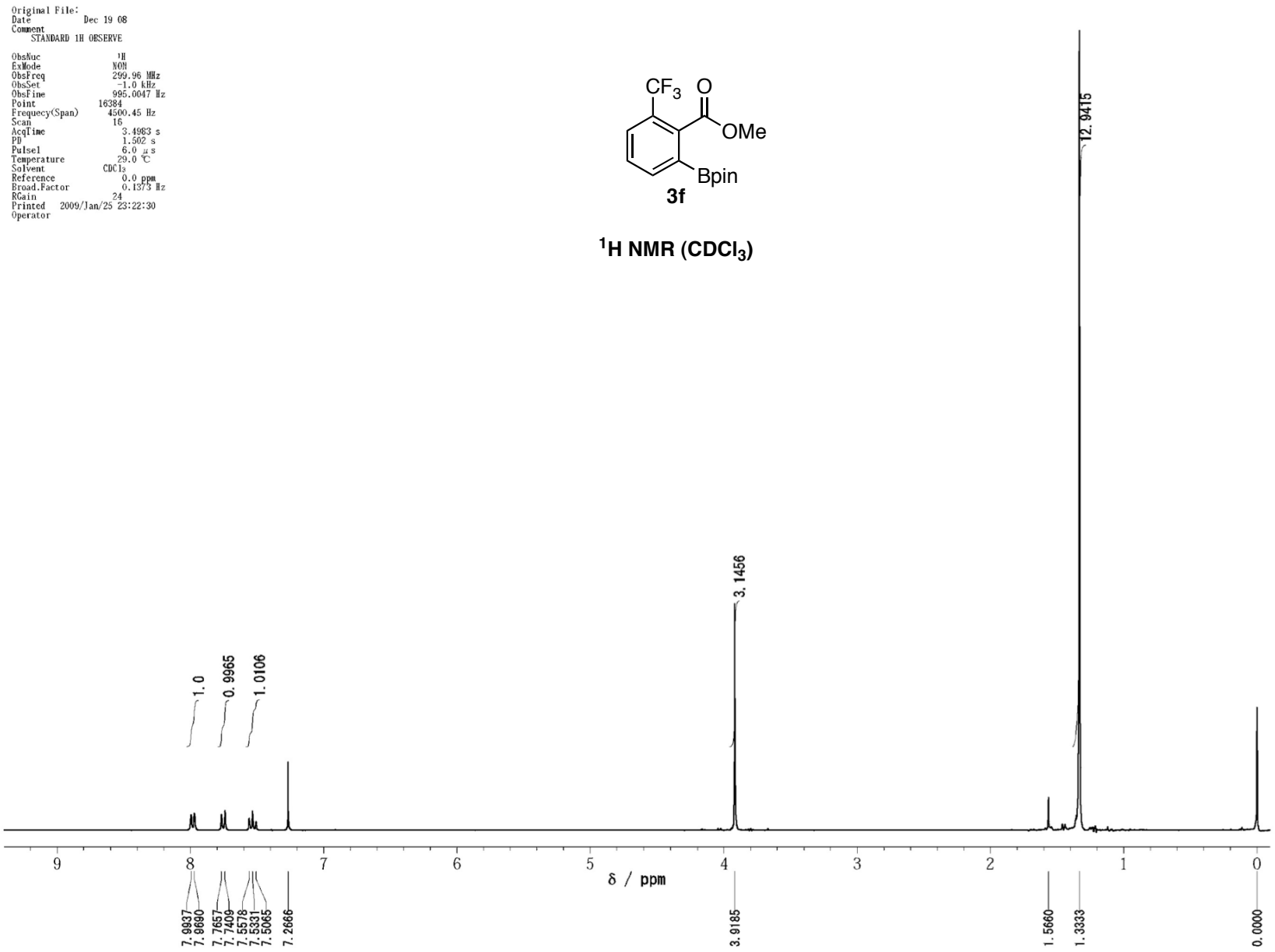

Original File:
Date Dec 17 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 20
Printed 2009/Jan/25 23:19:43
Operator
i-Pr
O
OMe
Bpin
3d
0.9883
1.0305
2.9939
1.0016
0.4257
12.4707
6.4843
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.7986
7.7931
7.4506
7.4259
7.3911
7.3865
7.3655
7.3609
7.2866
3.9103
3.8938
3.0019
2.9781
2.9542
2.9314
2.9085
2.8856
2.8627
2.1768
1.5714
1.4561
1.4075
1.2491
1.2262
0.0000

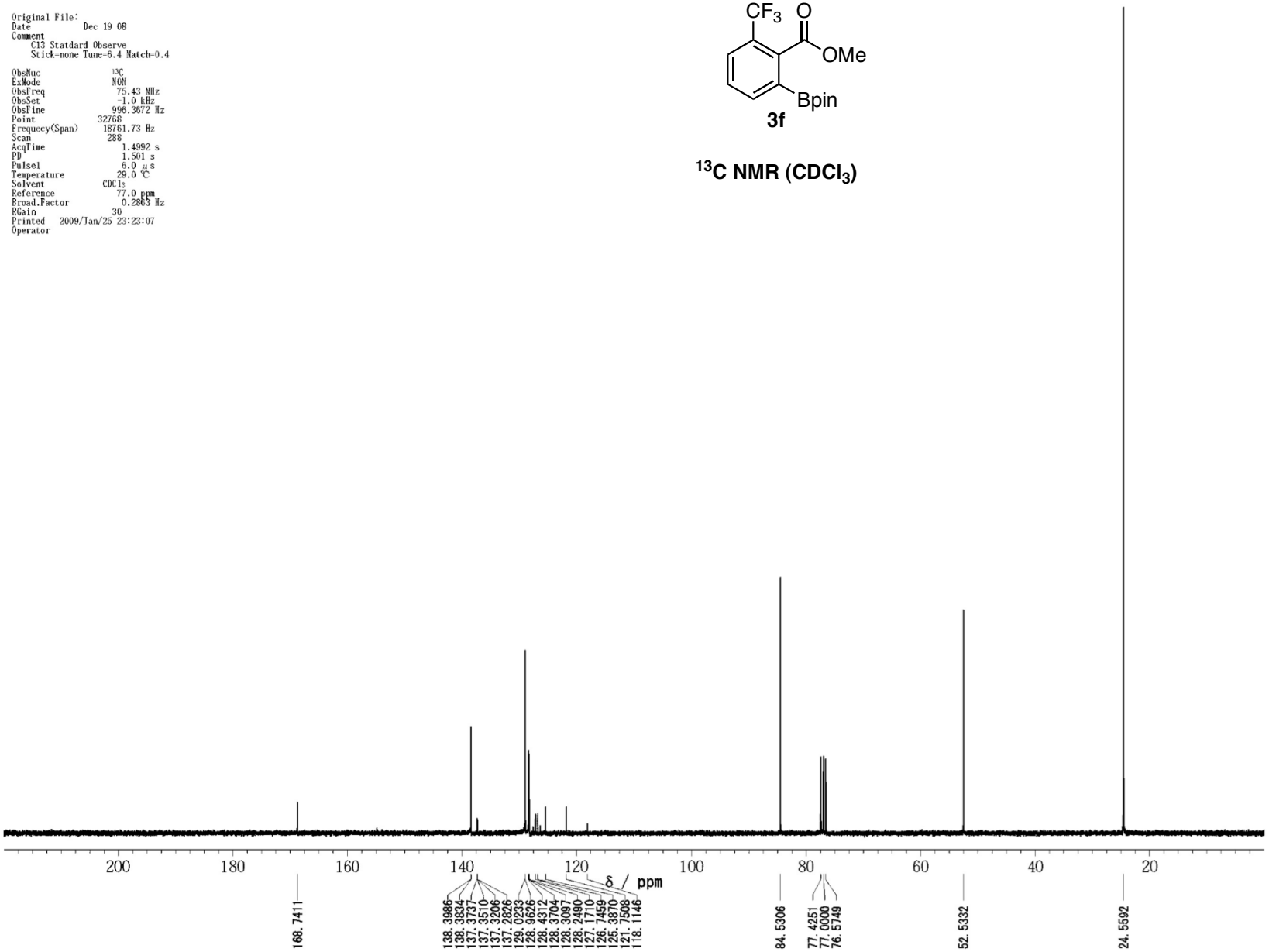
^{1}H NMR ($CDCl_3$)

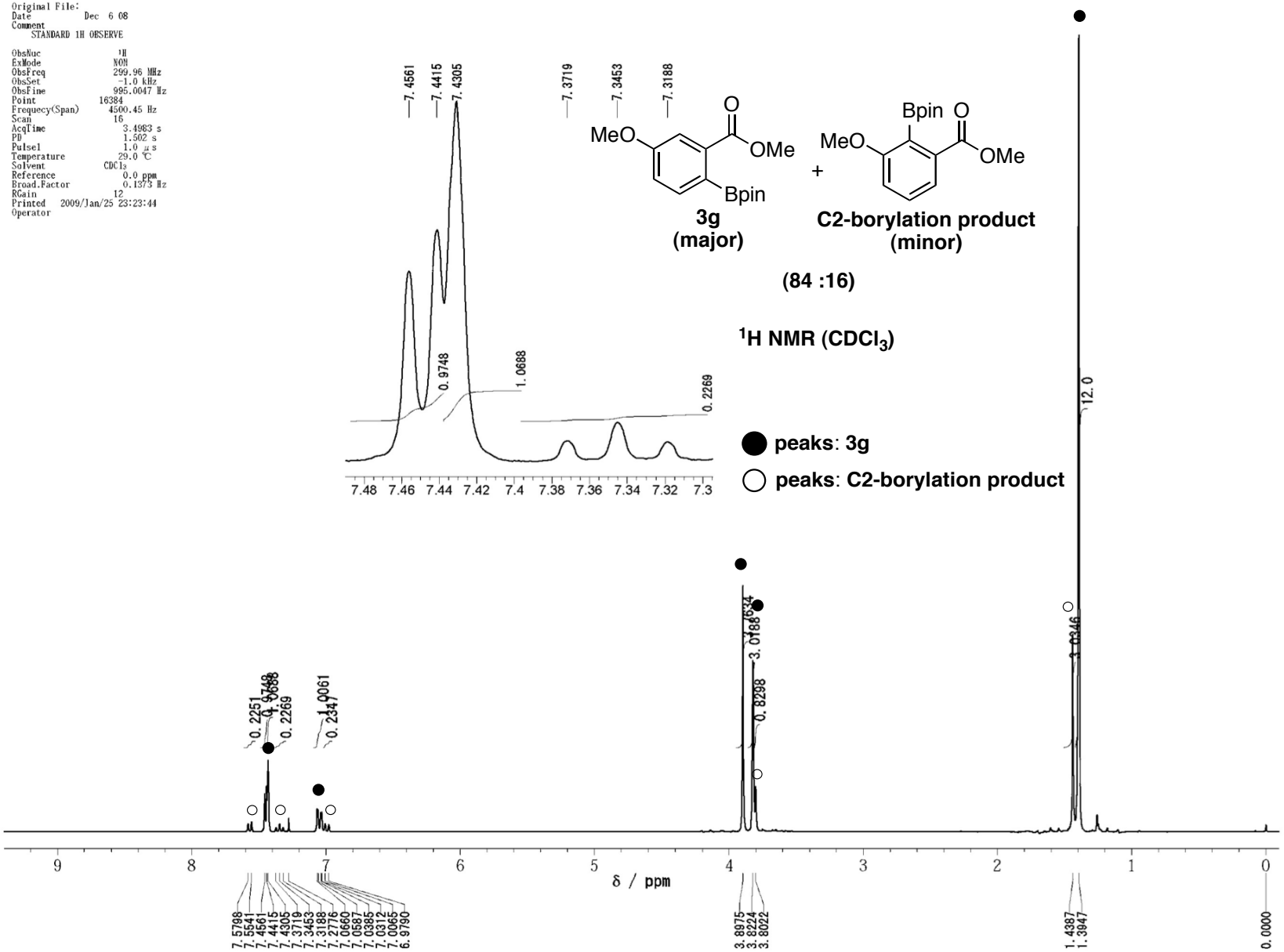

Original File:
Date Dec 17 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NOM
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 416
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:20:21
Operator
i-Pr
O
OMe
Bpin
3d
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
168.8625
150.1423
133.7679
132.4849
130.1620
126.9736
83.8853
77.4251
77.0000
76.5749
52.1384
33.9117
24.7414
23.6634

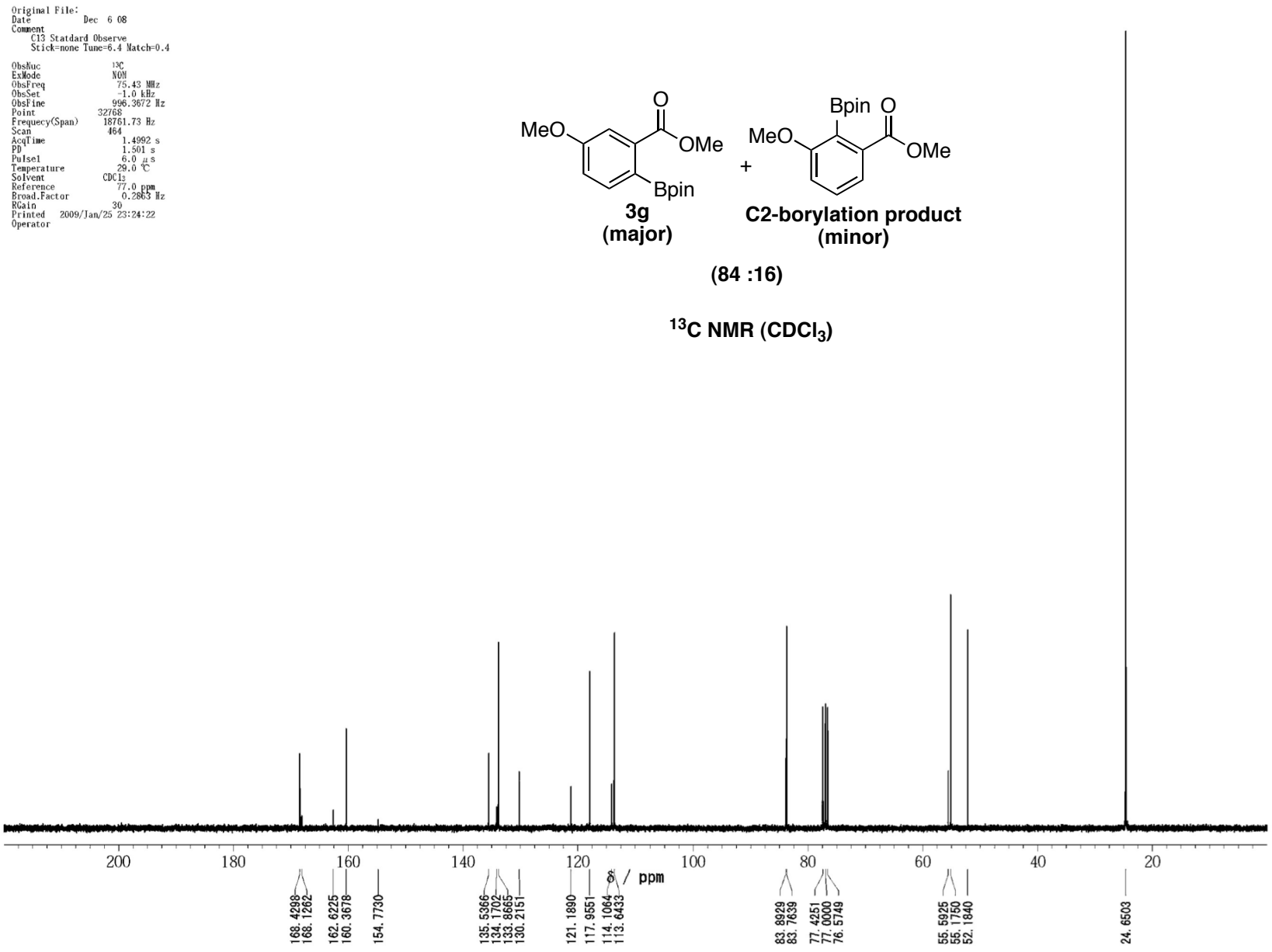

Original File:
Date Oct 12 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2009/Jan/25 23:20:56
Operator
OMe O
OMe
Bpin
3e
1H NMR (CDCl3)
12.3826
2.0035
1.0
δ / ppm
1.3224
0.0000

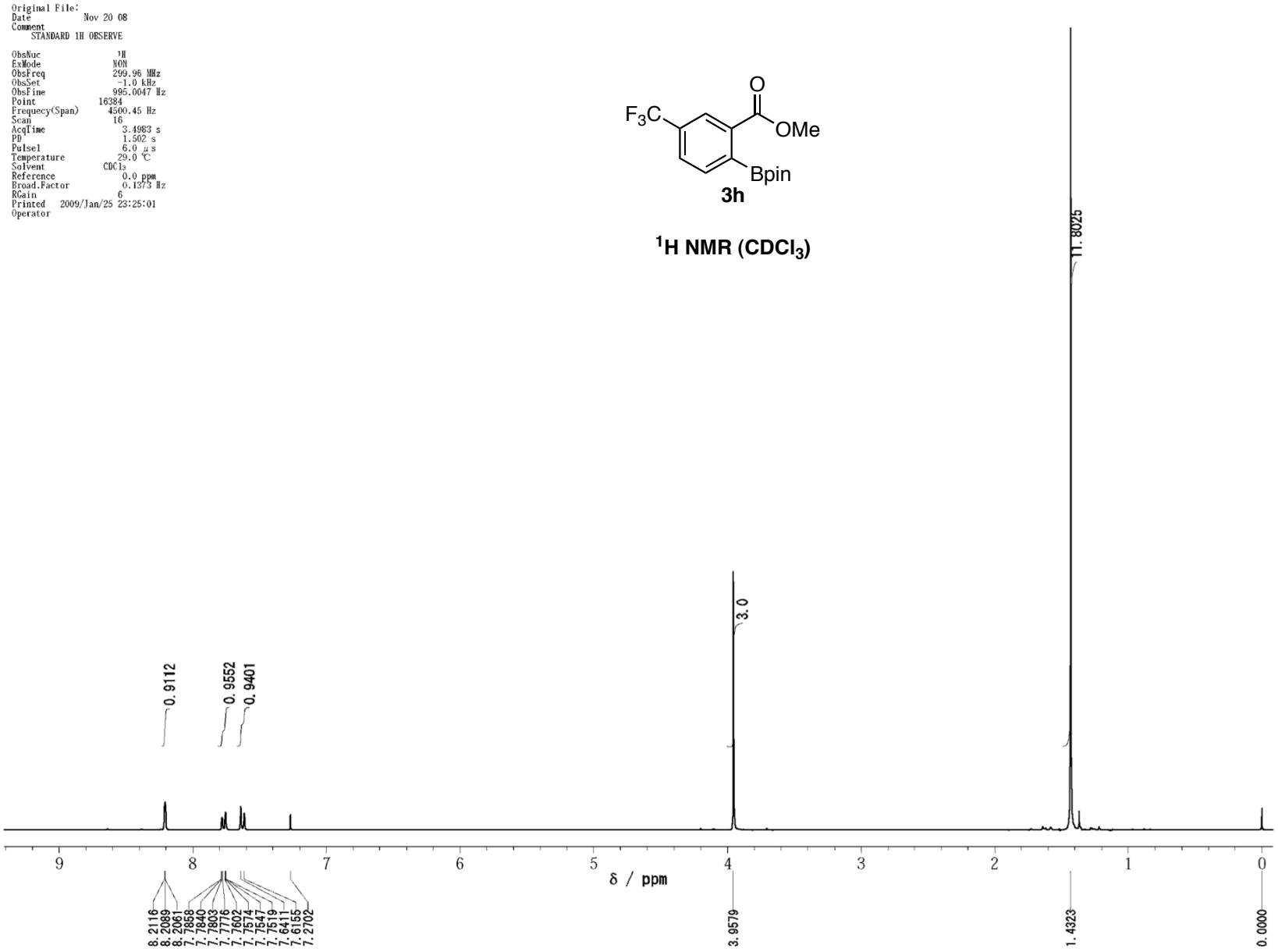

Original File:
Date Oct 12 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 656
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:21:45
Operator
OMe O
OMe
Bpin
3e
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
169.2497
156.1319
130.5871
128.1503
126.5637
113.7851
84.0447
77.4175
77.0000
76.5749
55.8810
52.1916
24.6655


Original File:
Date Dec 19 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 24
Printed 2009/Jan/25 23:22:30
Operator
CF3
O
OMe
Bpin
3f
1H NMR (CDCl3)
12.9415
3.1456
1.0
0.9965
1.0106
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.9937
7.9690
7.7657
7.7409
7.5578
7.5331
7.5065
7.2666
3.9185
1.5660
1.3333
0.0000


Original File:
Date Dec 19 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 288
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:23:07
Operator
CF3
O
OMe
Bpin
3f
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
168.7411
138.3986
138.3834
137.3737
137.3510
137.3206
137.2826
129.0233
128.9626
128.4312
128.3704
128.3097
126.2480
127.1710
126.7459
125.3870
121.7508
118.1146
84.5306
77.4251
77.0000
76.5749
52.5332
24.5592

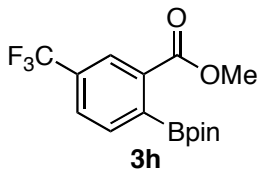

Original File:
Date Dec 6 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 1.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 12
Printed 2009/Jan/25 23:23:44
Operator
7.4561
7.4415
7.4305
7.3719
7.3453
7.3188
MeO
OMe
Bpin
3g
(major)
+
C2-borylation product
(minor)
(84 :16)
1H NMR (CDCl3)
peaks: 3g
peaks: C2-borylation product
0.9748
1.0688
0.2269
12.0
δ / ppm


Original File:
Date Dec 6 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 464
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:24:22
Operator
MeO
OMe
Bpin
3g
(major)
Bpin
O
MeO
OMe
+
C2-borylation product
(minor)
(84 :16)
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
168.4298
168.1262
162.6225
160.3678
154.7730
135.5366
134.1702
133.8665
130.2151
121.1890
117.9551
114.1064
113.6433
83.8929
83.7639
77.4251
77.0000
76.5749
55.5925
55.1750
52.1840
24.6503


Original File:
Date Nov 20 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2009/Jan/25 23:25:01
Operator
O
F3C
OMe
Bpin
3h
1H NMR (CDCl3)
11.8025
3.0
0.9112
0.9552
0.9401
δ / ppm
8.2116
8.2089
8.2061
7.7858
7.7840
7.7803
7.7776
7.7602
7.7574
7.7547
7.7519
7.6411
7.6155
7.2702
3.9579
1.4323
0.0000

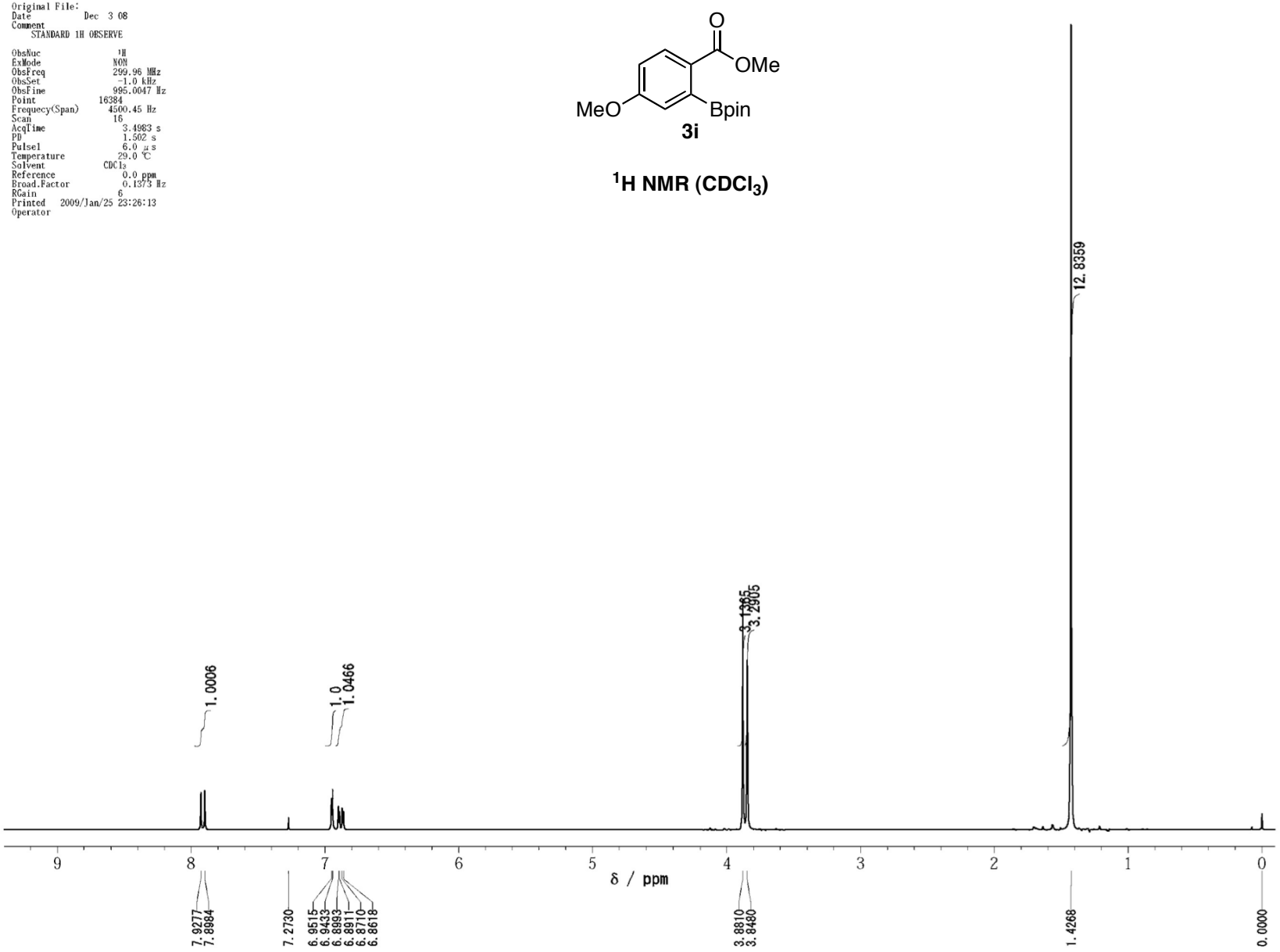
Original File:
Date Nov 20 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

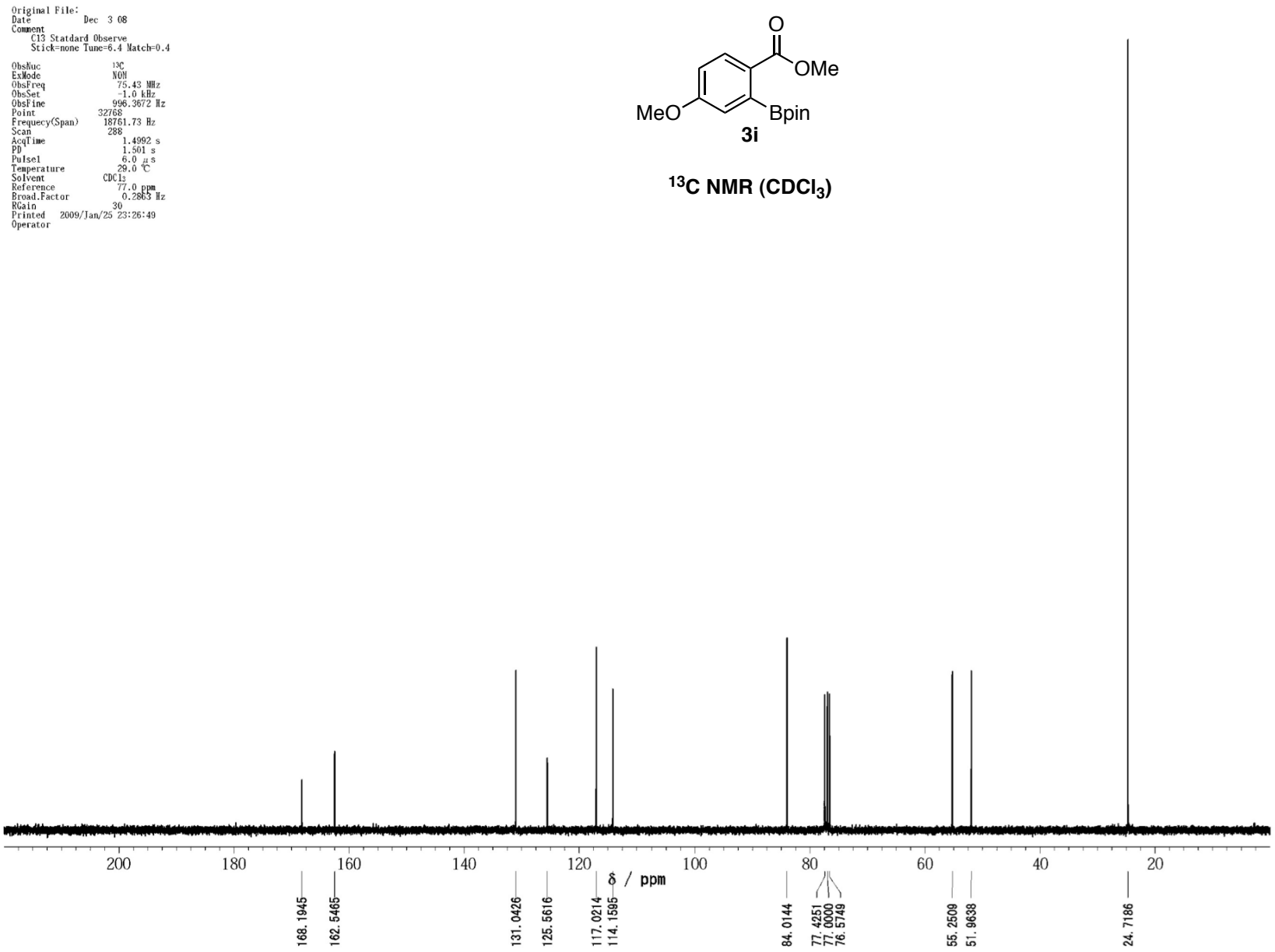
ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	32768
Frequecy(Span)	18761.73 Hz
Scan	432
AcqTime	1.4992 s
PD	1.501 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2009/Jan/25 23:25:40
Operator	



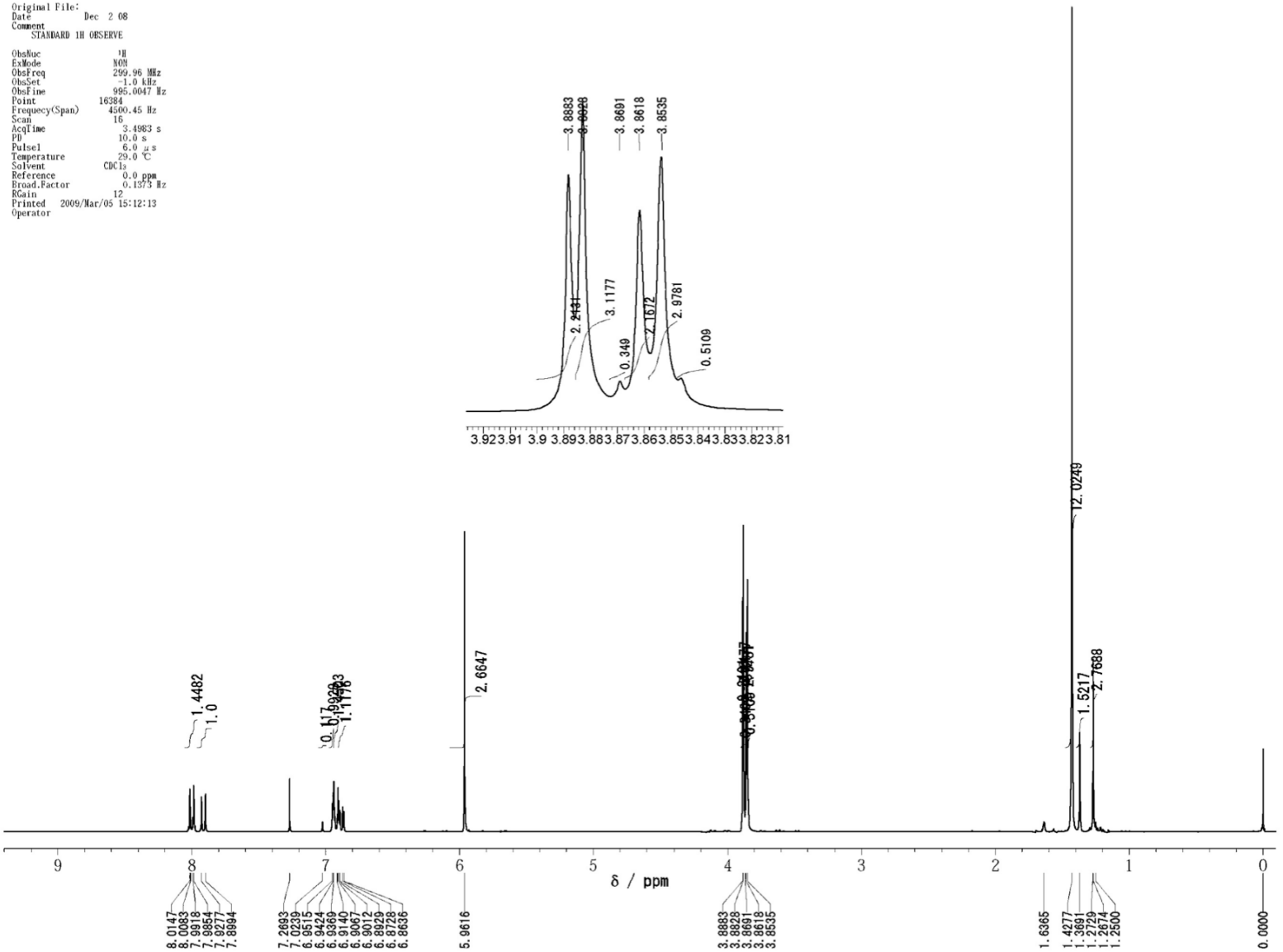
3h

^{13}C NMR ($CDCl_3$)


Original File:
Date Dec 3 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2009/Jan/25 23:26:13
Operator
O
OMe
MeO
Bpin
3i
1H NMR (CDCl3)
12.8359
3.1285
3.2905
1.0006
1.0
1.0466
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.9277
7.8984
7.2730
6.9515
6.9433
6.8993
6.8911
6.8710
6.8618
3.8810
3.8480
1.4268
0.0000

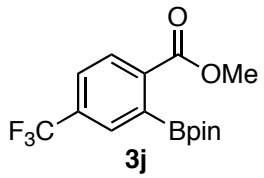

Original File:
Date Dec 3 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NOM
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 288
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:26:49
Operator
O
OMe
MeO
Bpin
3i
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
168.1945
162.5465
131.0426
125.5616
117.0214
114.1595
84.0144
77.4251
77.0000
76.5749
55.2509
51.9638
24.7186

^{1}H NMR spectrum of the crude material on a reaction of 1i (Table 1, entry 9)



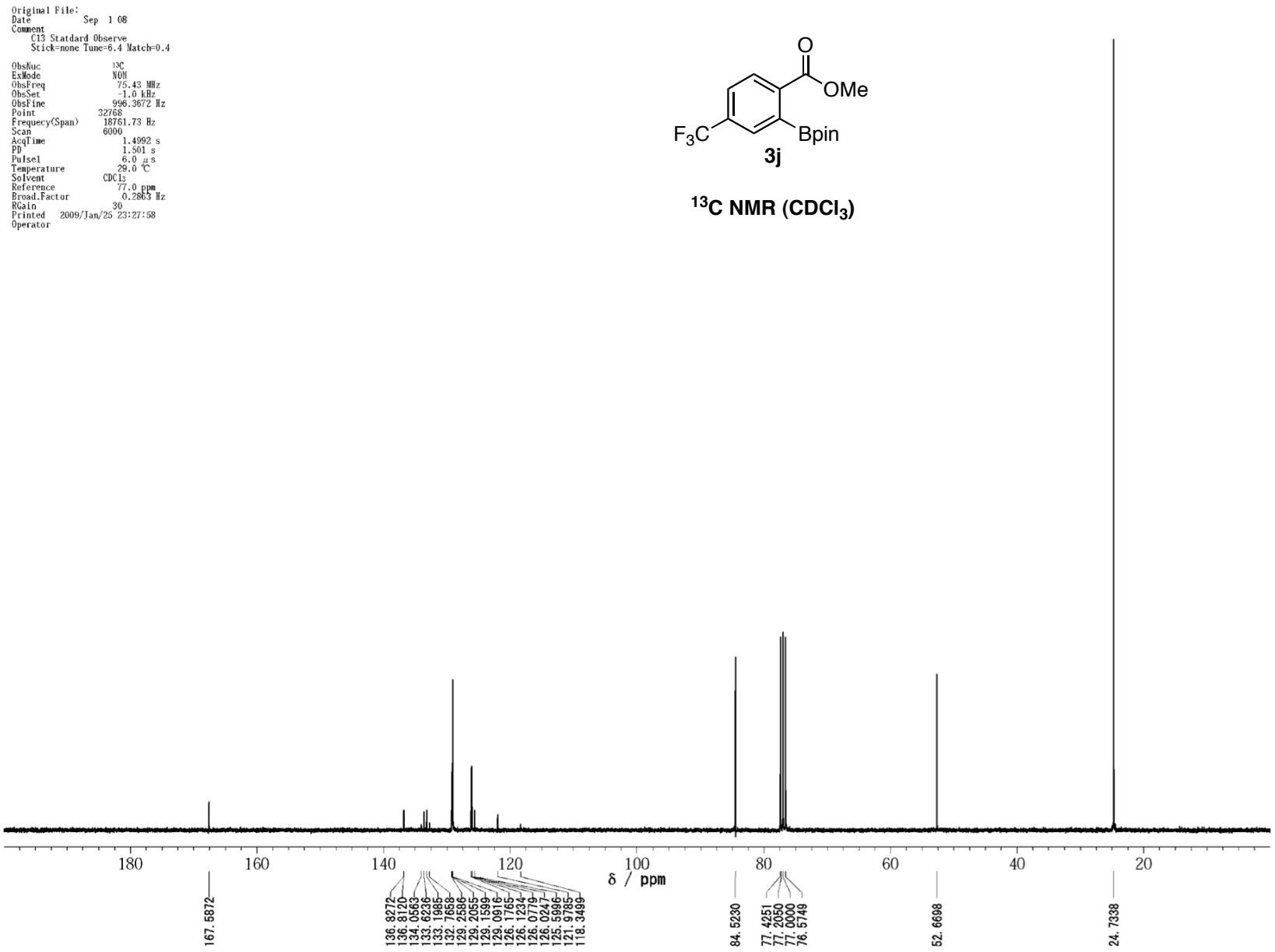
Original File:
Date Aug 26 08
Comment
STANDARD 1H OBSERVE

ObsNuc	^{1}H
ExMode	NON
ObsFreq	299.96 MHz
ObsSet	-1.0 kHz
ObsFine	995.0047 Hz
Point	16384
Frequecy(Span)	4500.45 Hz
Scan	32
AcqTime	3.4983 s
PD	1.502 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	$CDCl_3$
Reference	0.0 ppm
Broad.Factor	0.1373 Hz
RGain	30
Printed	2009/Jan/25 23:27:24
Operator	

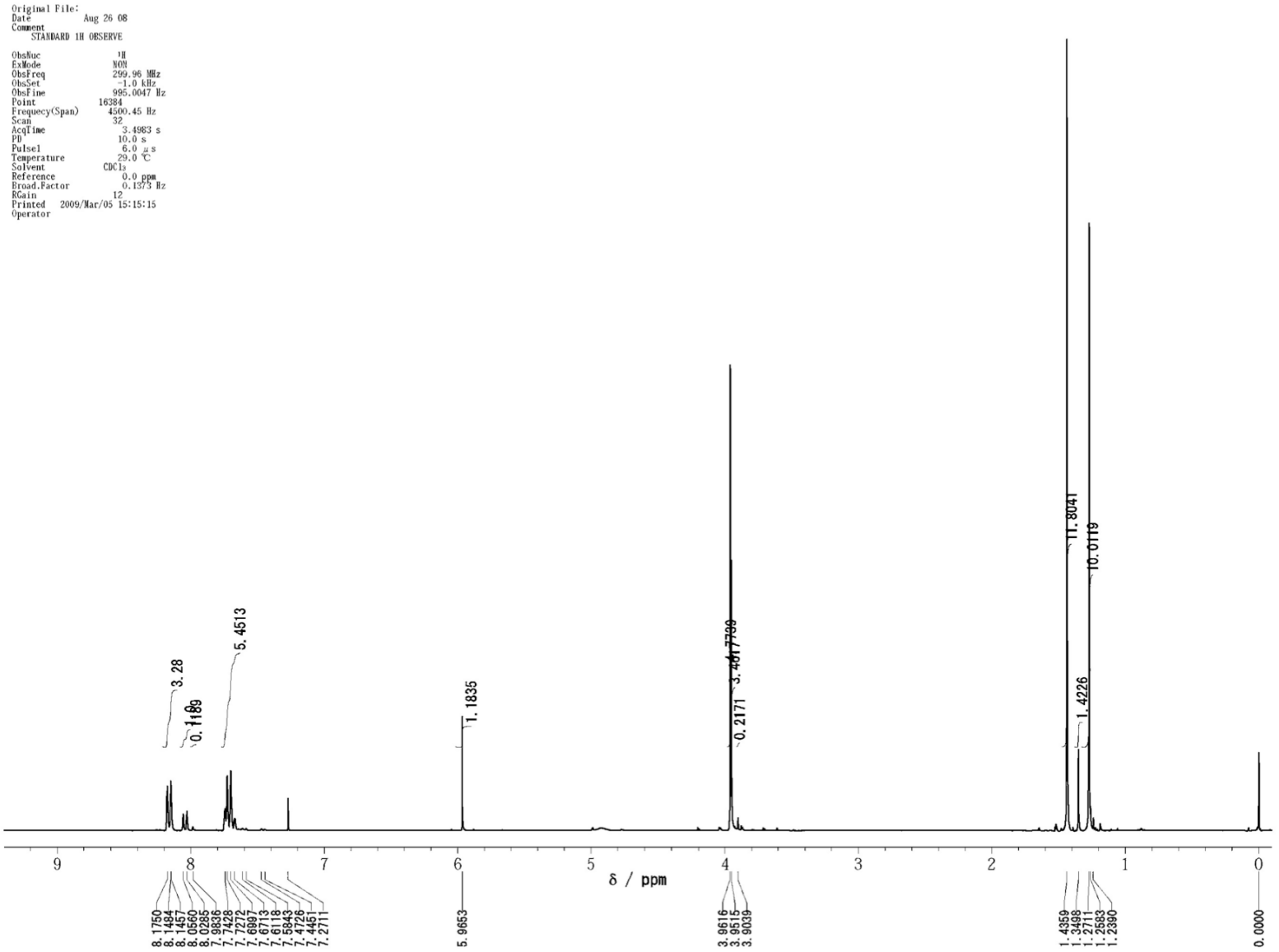


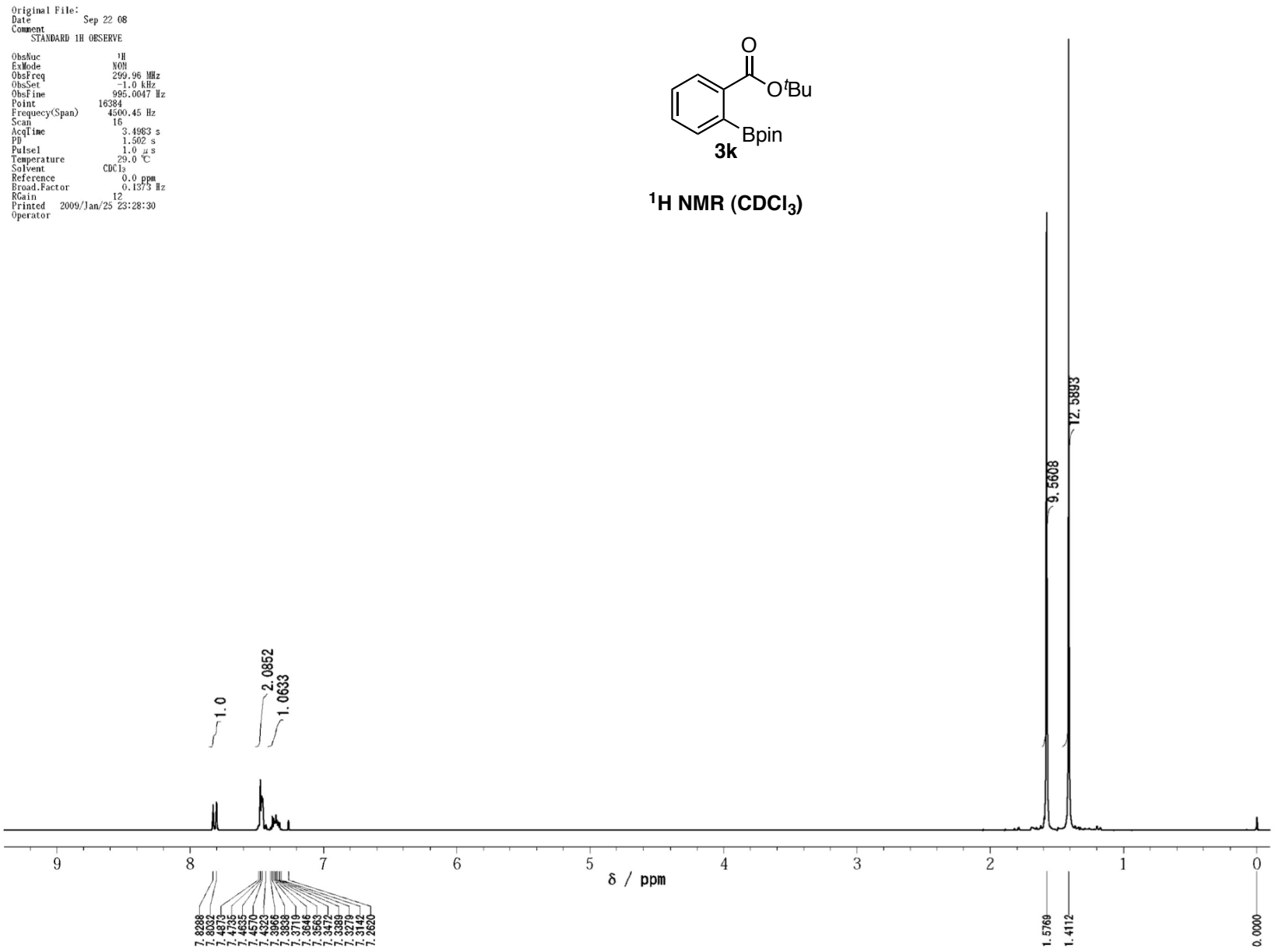
3j

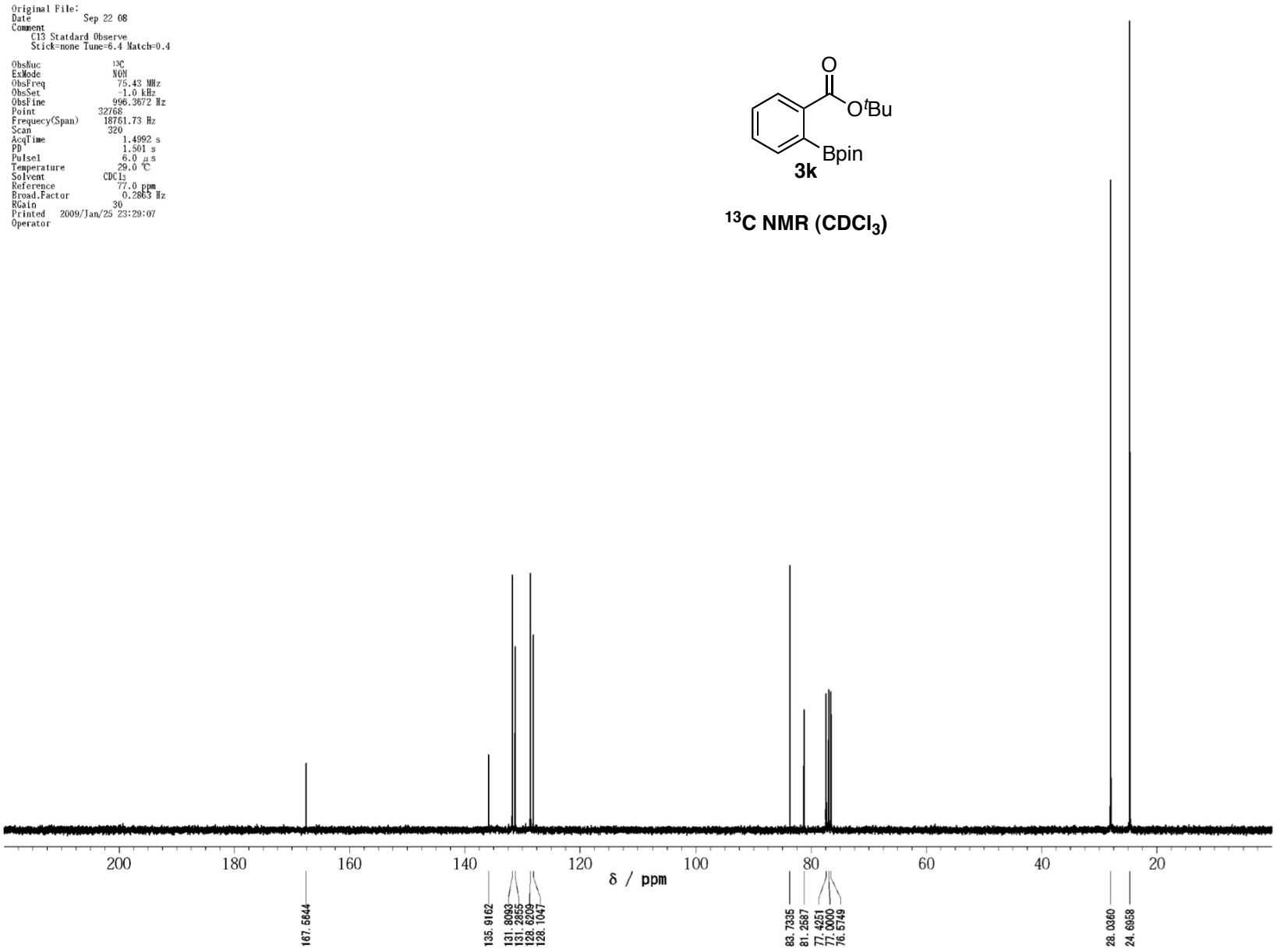
^{1}H NMR ($CDCl_3$)

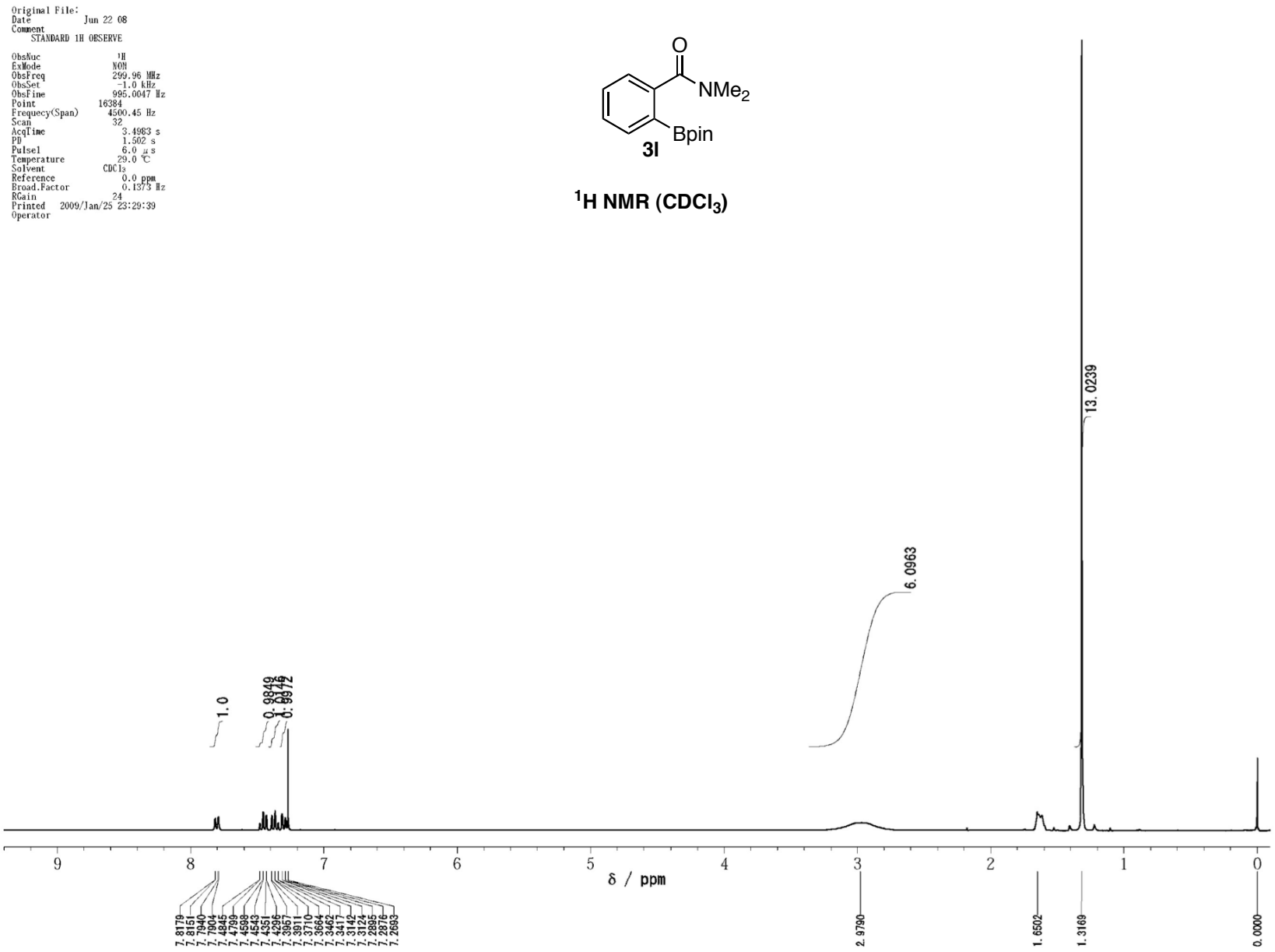

Original File:
Date Sep 1 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 6000
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:27:58
Operator
O
OMe
F3C
Bpin
3j
13C NMR (CDCl3)
180
160
140
120
100
80
60
40
20
δ / ppm
167.5872
136.8272
136.8120
134.0563
133.6236
133.1985
132.7658
129.2586
129.2055
129.1599
129.0916
126.1765
126.1234
126.0779
126.0247
125.5996
121.9785
118.3499
84.5230
77.4251
77.2050
77.0000
76.5749
52.6698
24.7338

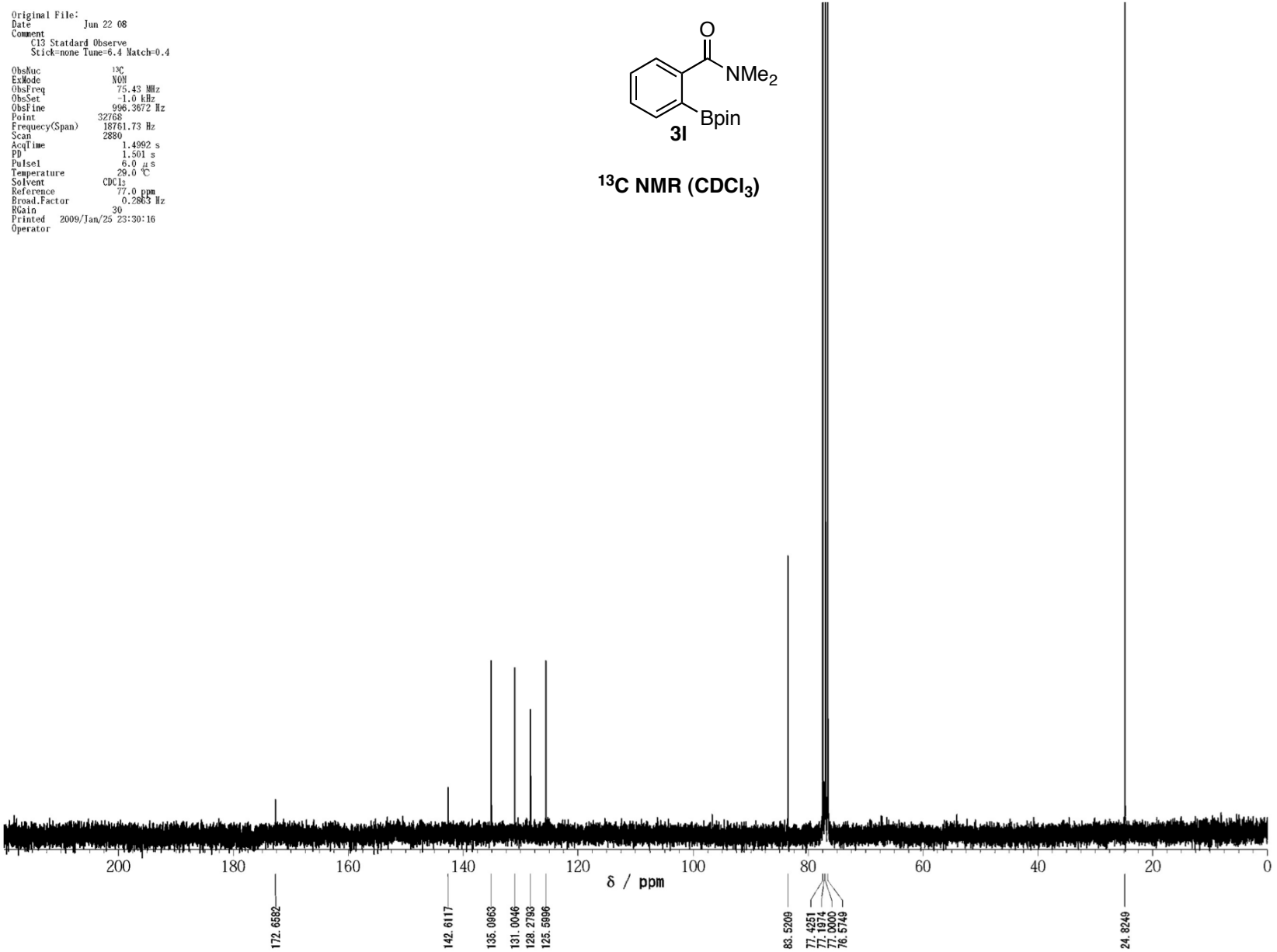
^{1}H NMR spectrum of the crude material on a reaction of 1j (Table 1, entry 10)

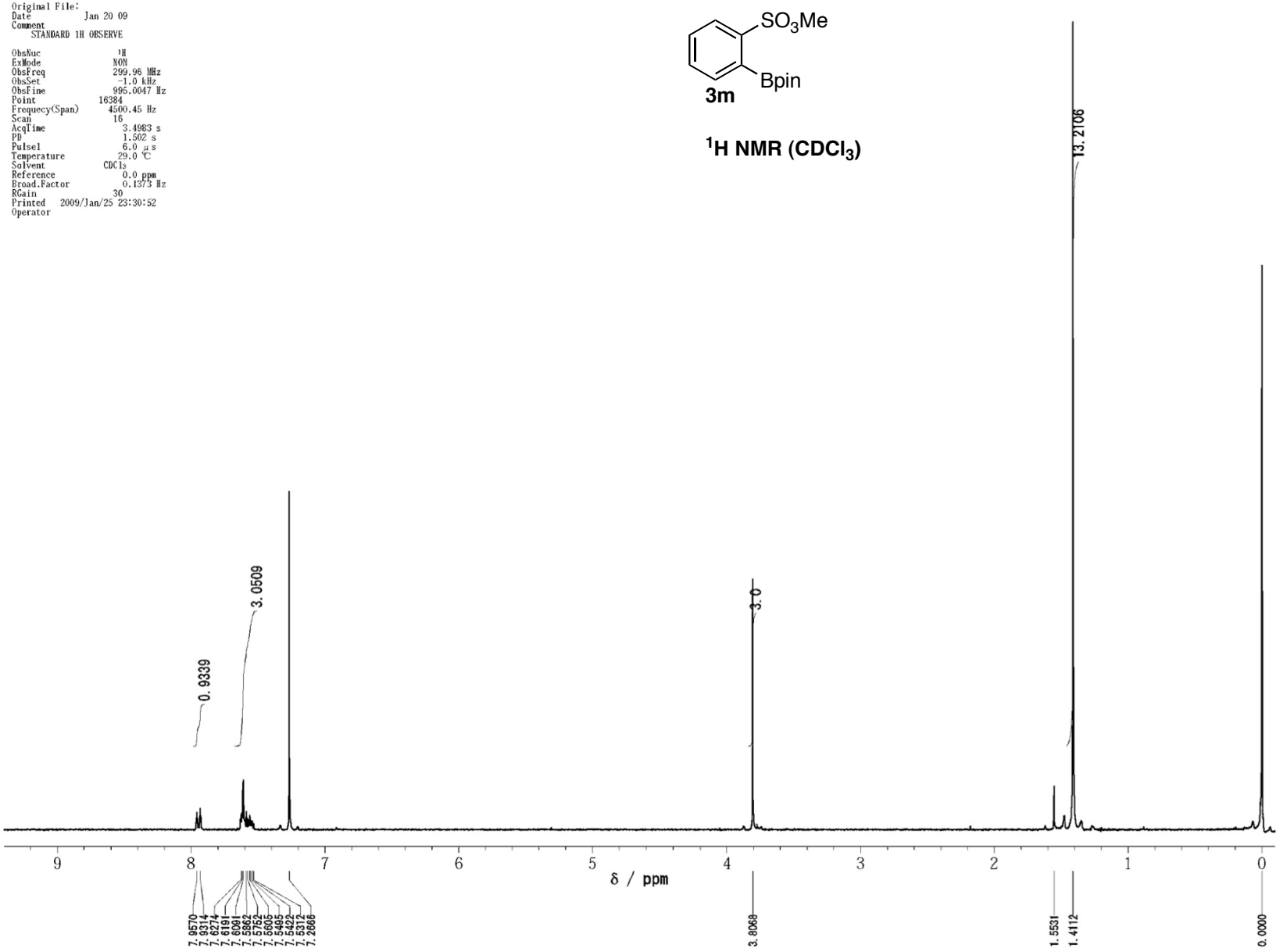


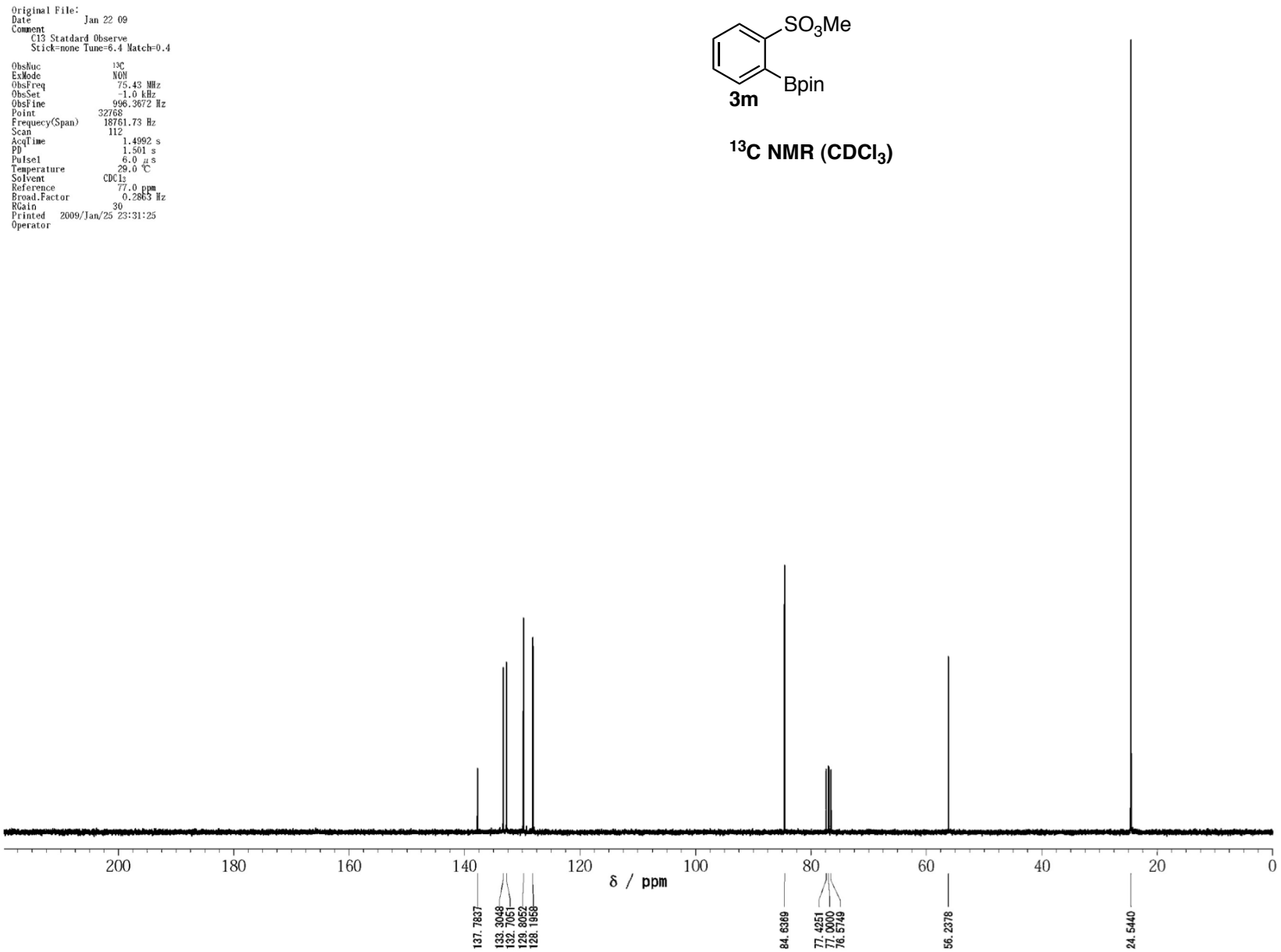

Original File:
Date Sep 22 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 1.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 12
Printed 2009/Jan/25 23:28:30
Operator
O
O tBu
Bpin
3k
1H NMR (CDCl3)
1.0
2.0852
1.0633
9.5608
12.5893
δ / ppm
7.8288
7.8032
7.4873
7.4736
7.4635
7.4570
7.4323
7.3966
7.3838
7.3719
7.3646
7.3563
7.3472
7.3389
7.3279
7.3142
7.2620
1.5769
1.4112
0.0000


Original File:
Date Sep 22 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 320
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:29:07
Operator
O
OtBu
Bpin
3k
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
167.5644
135.9162
131.8093
131.2855
128.6209
128.1047
83.7335
81.2687
77.4251
77.0000
76.5749
28.0360
24.6958

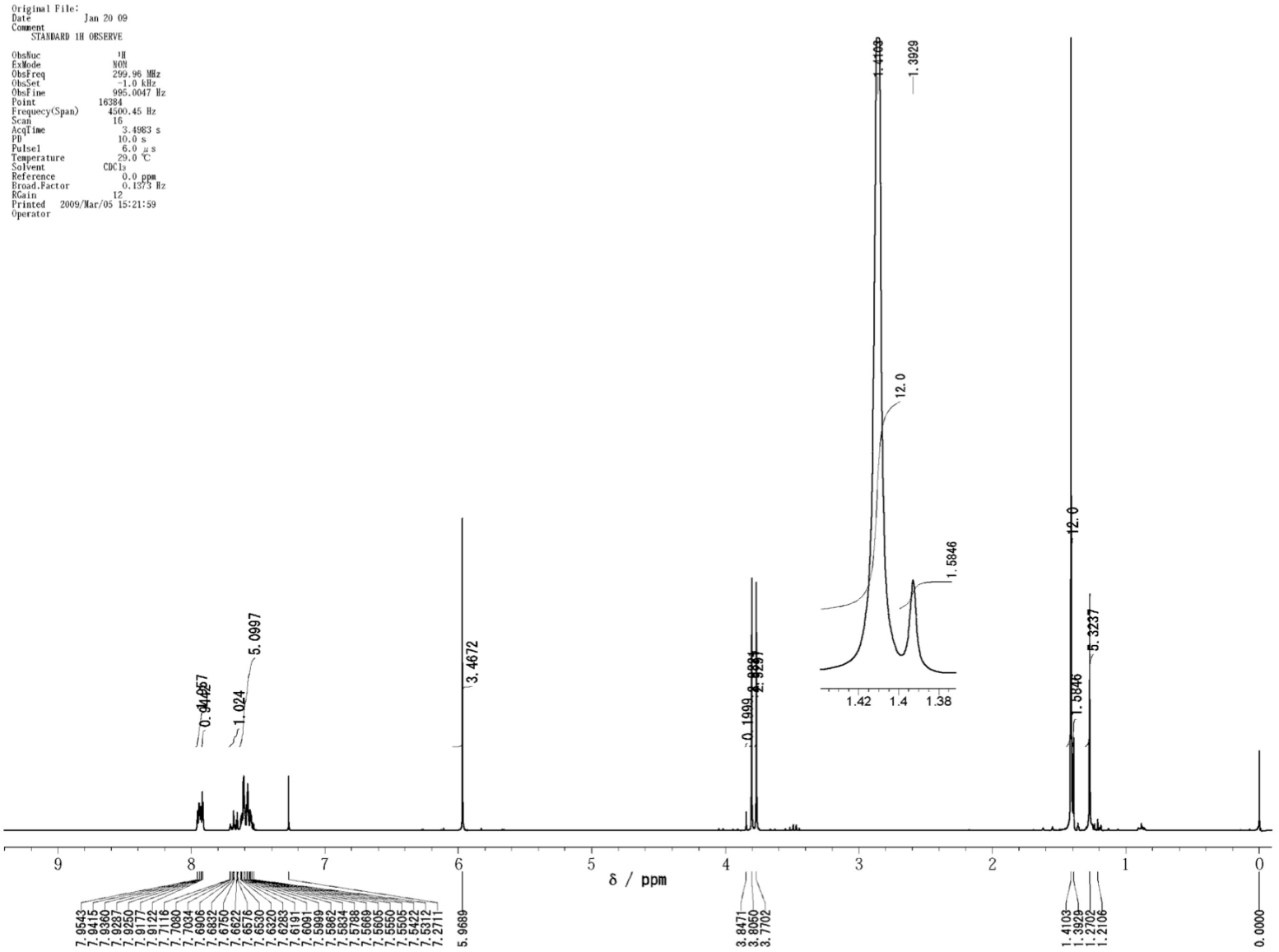

Original File:
Date Jun 22 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 24
Printed 2009/Jan/25 23:29:39
Operator
O
NMe2
Bpin
3l
1H NMR (CDCl3)
13.0239
6.0963
1.0
δ / ppm
2.9790
1.6502
1.3169
0.0000

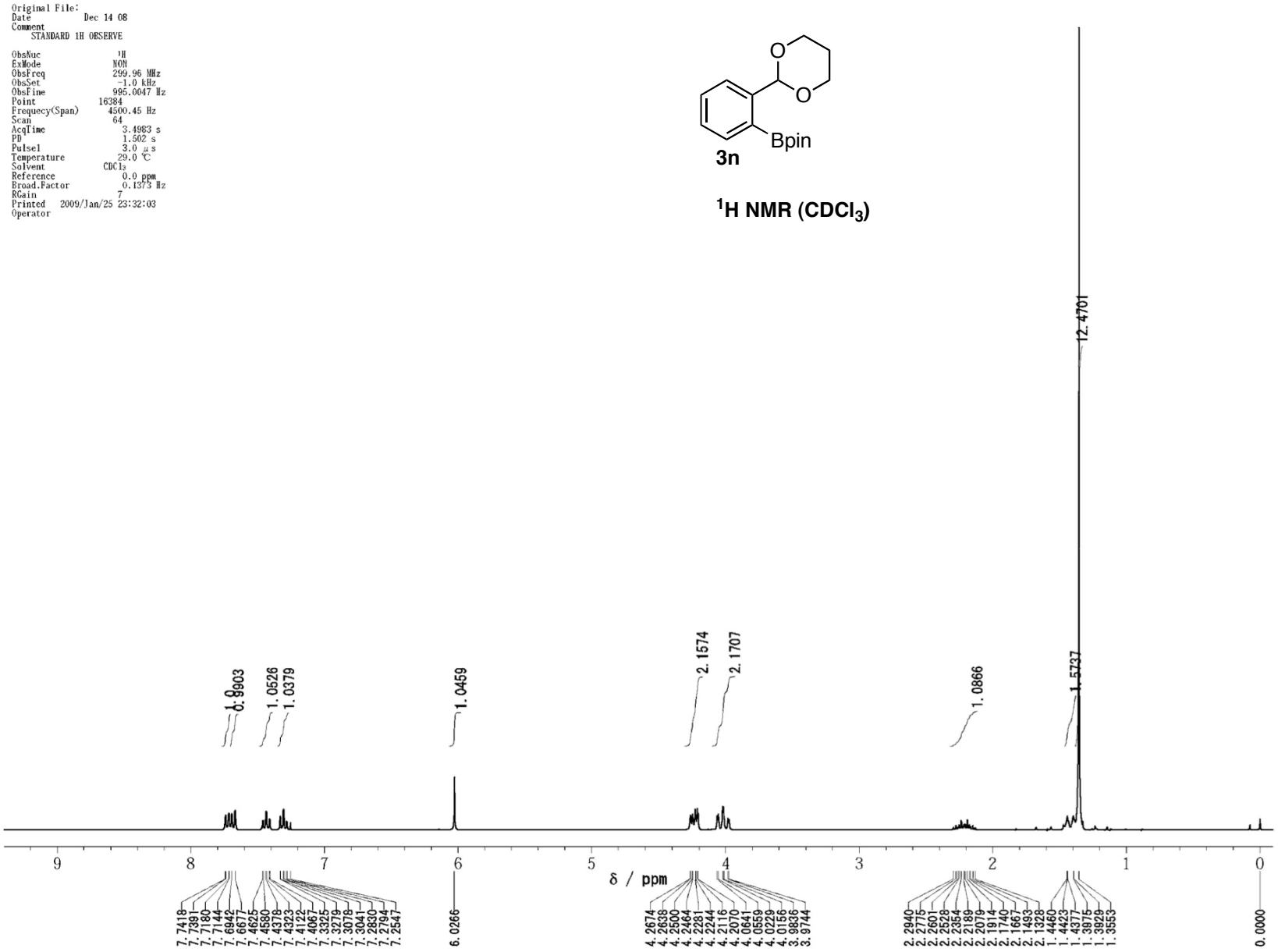

Original File:
Date Jun 22 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 2880
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:30:16
Operator
O
NMe2
Bpin
3l
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
172.6582
142.6117
135.0963
131.0046
128.2793
125.5996
83.5209
77.4251
77.1974
77.0000
76.5749
24.8249

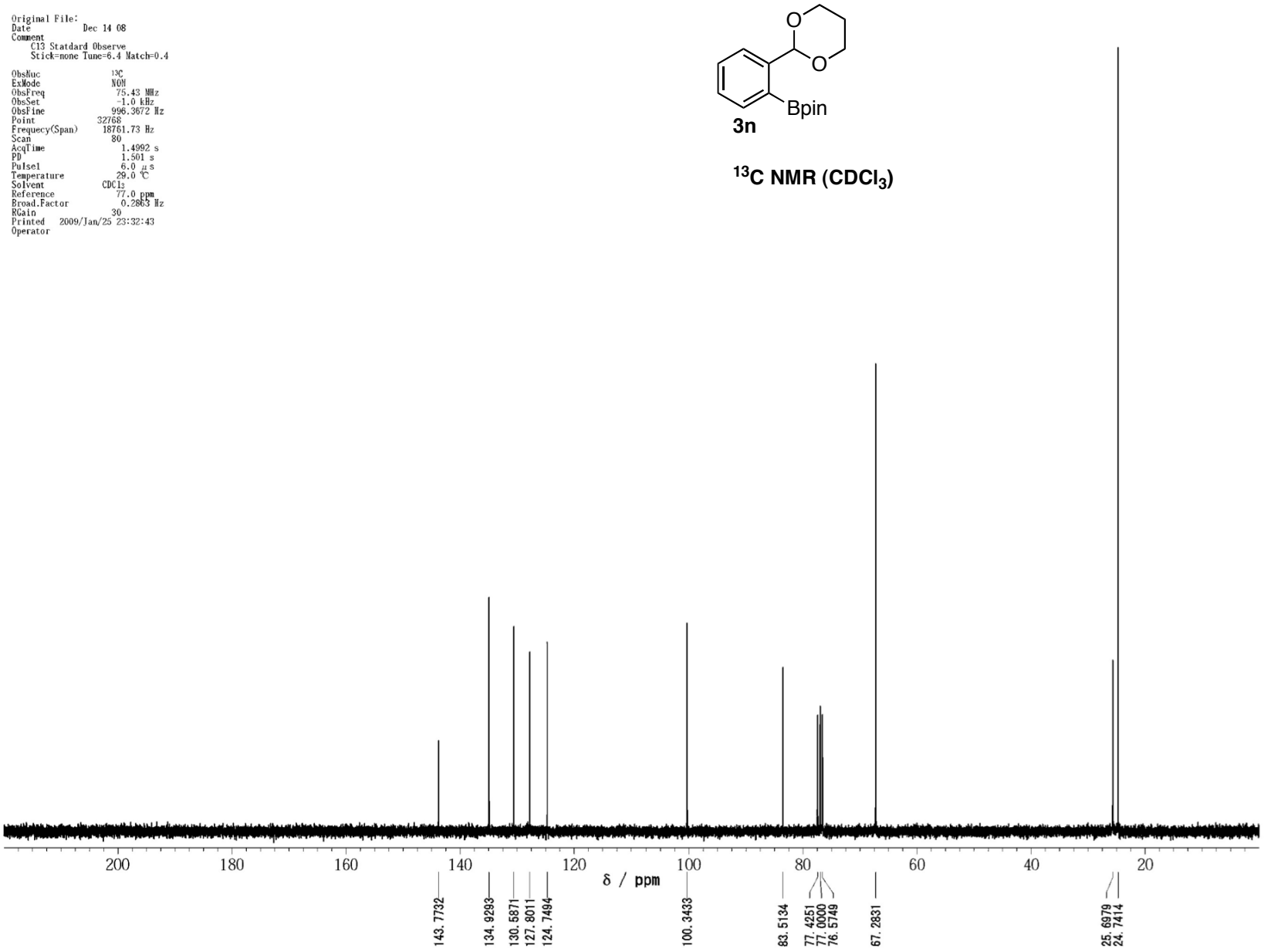

Original File:
Date Jan 20 09
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 30
Printed 2009/Jan/25 23:30:52
Operator
SO3Me
Bpin
3m
1H NMR (CDCl3)
13.2106
3.0509
3.0
0.9339
δ / ppm
7.9570
7.9314
7.6274
7.6191
7.6091
7.5862
7.5762
7.5605
7.5495
7.5422
7.5312
7.2666
3.8068
1.5531
1.4112
0.0000

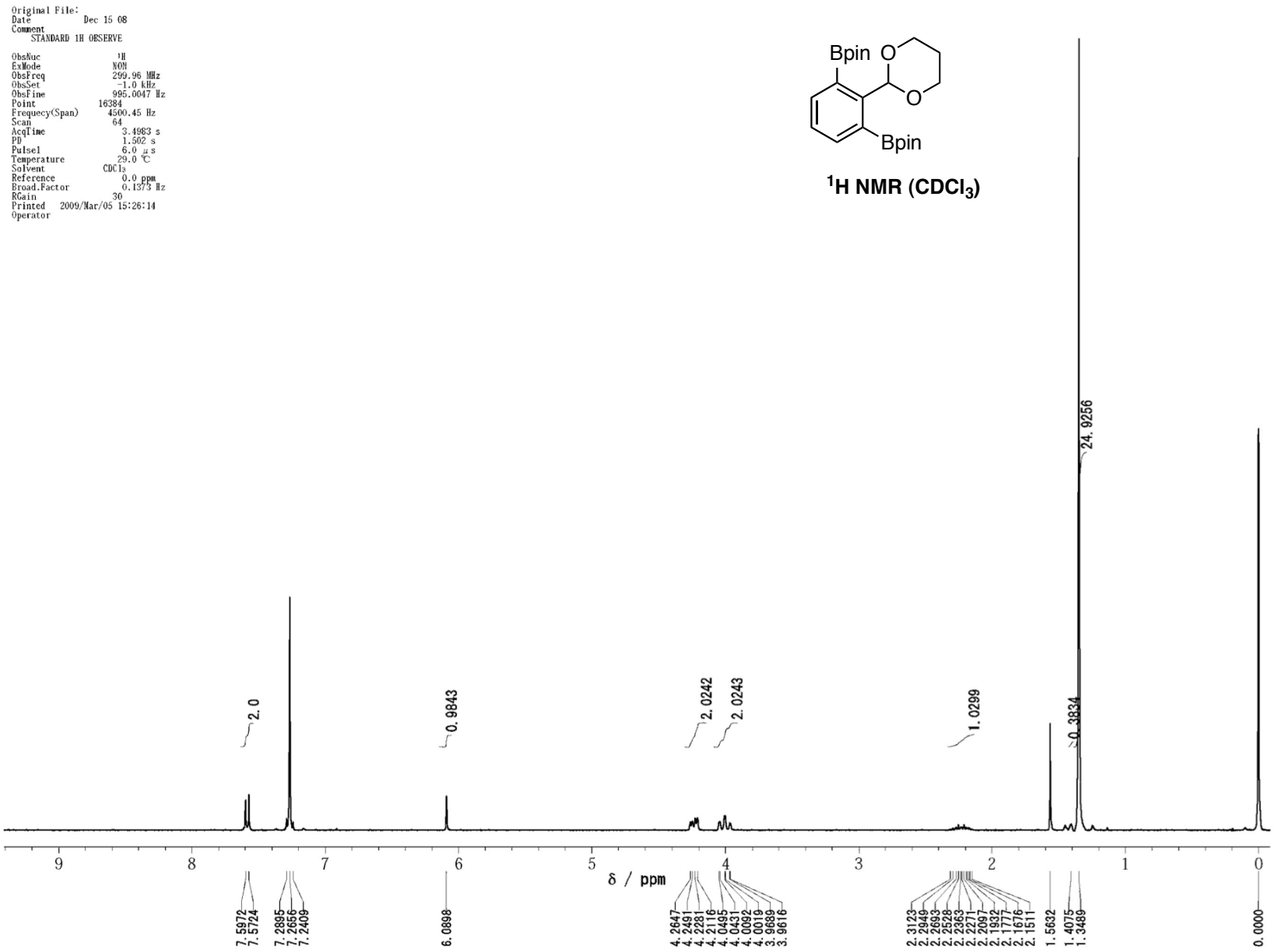

Original File:
Date Jan 22 09
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 112
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:31:25
Operator
SO3Me
Bpin
3m
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
137.7837
133.3048
132.7051
129.8052
128.1958
84.6369
77.4251
77.0000
76.5749
56.2378
24.5440

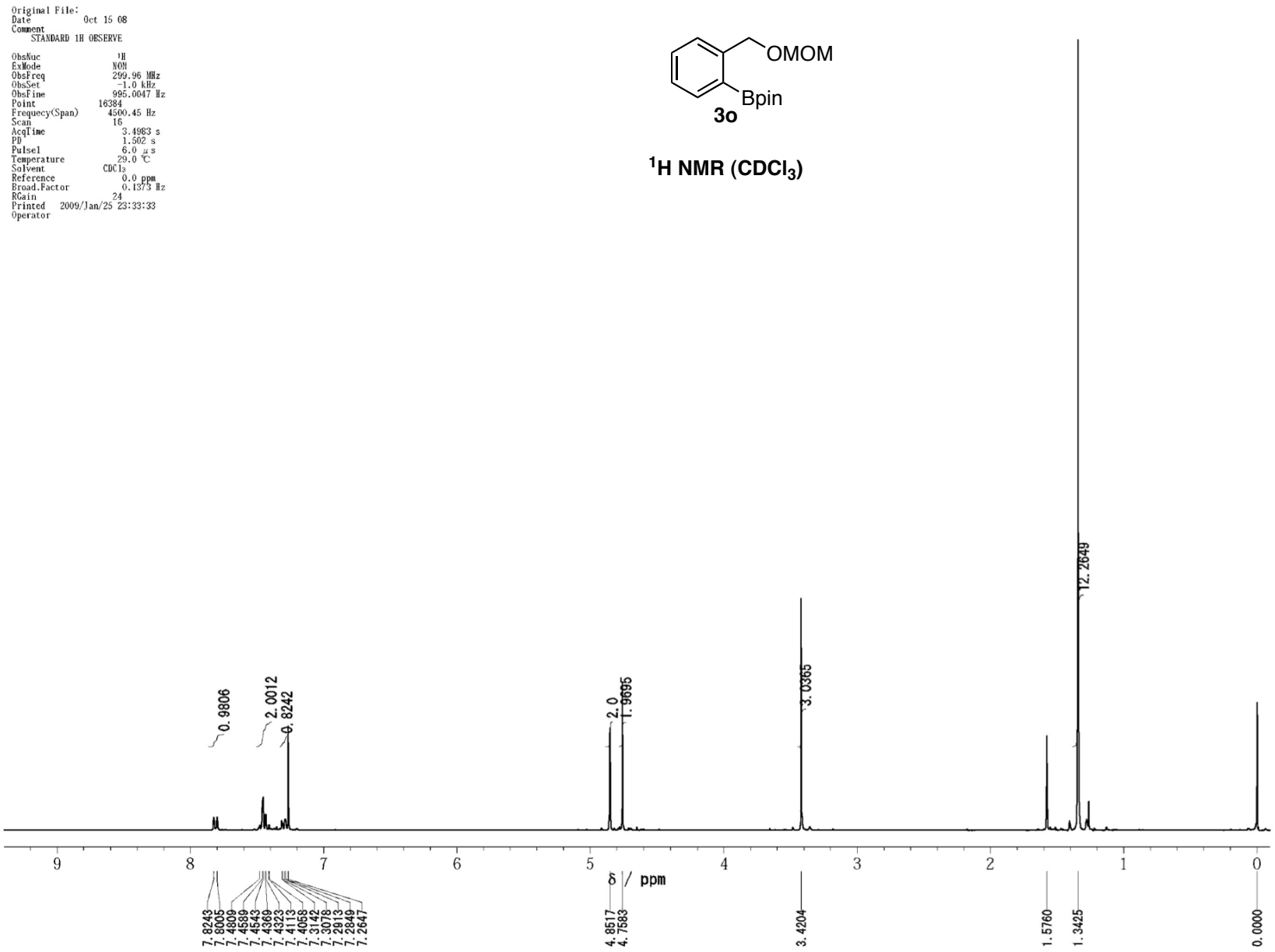
^{1}H NMR spectrum of the crude material on a reaction of 1m (Table 2, entry 3)



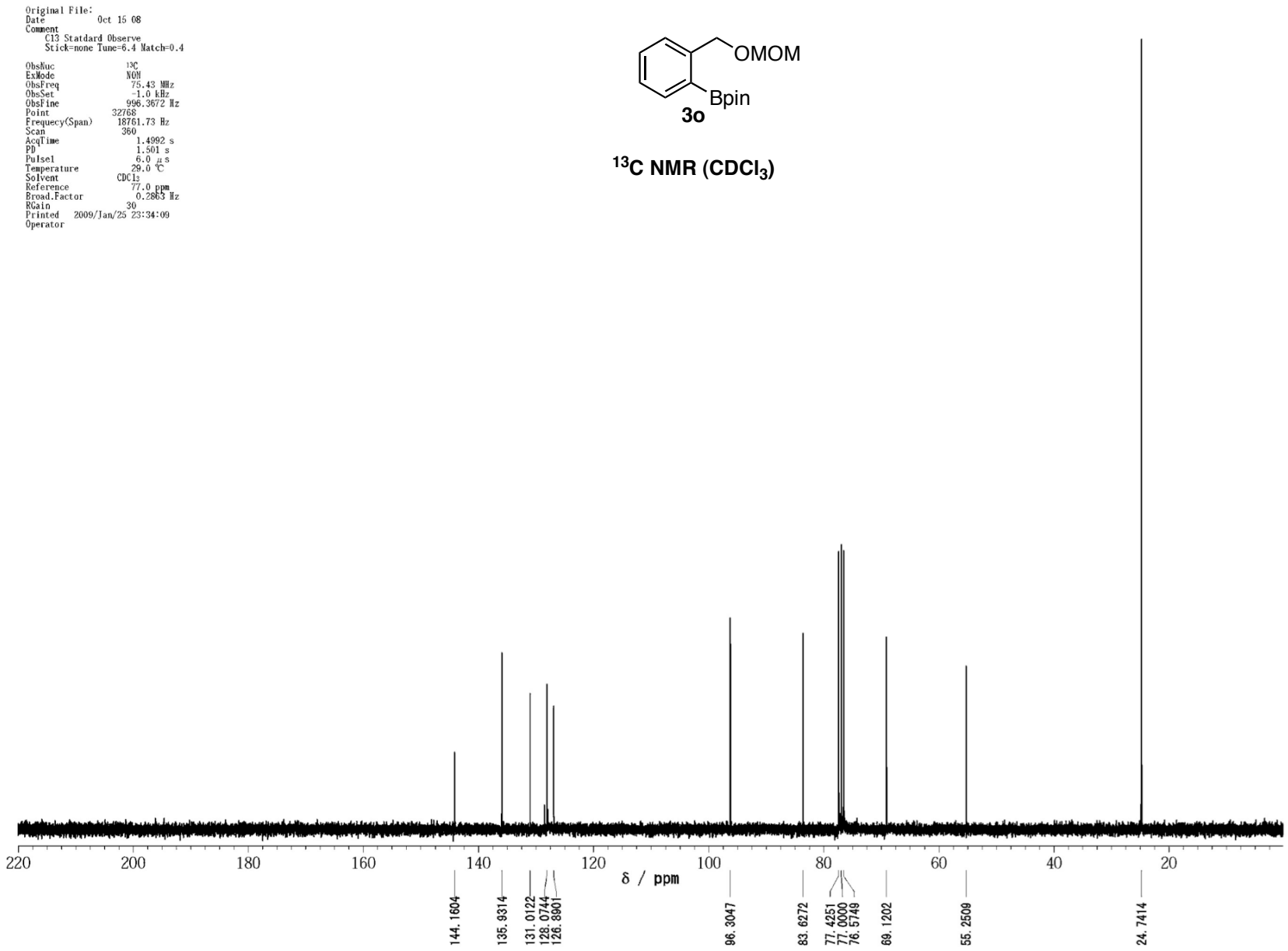

Original File:
Date Dec 14 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 64
AcqTime 3.4983 s
PD 1.502 s
Pulse1 3.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 7
Printed 2009/Jan/25 23:32:03
Operator
O
O
Bpin
3n
1H NMR (CDCl3)
12.4701
2.1574
2.1707
1.0866
1.5737
1.0459
1.0526
1.0379
δ / ppm

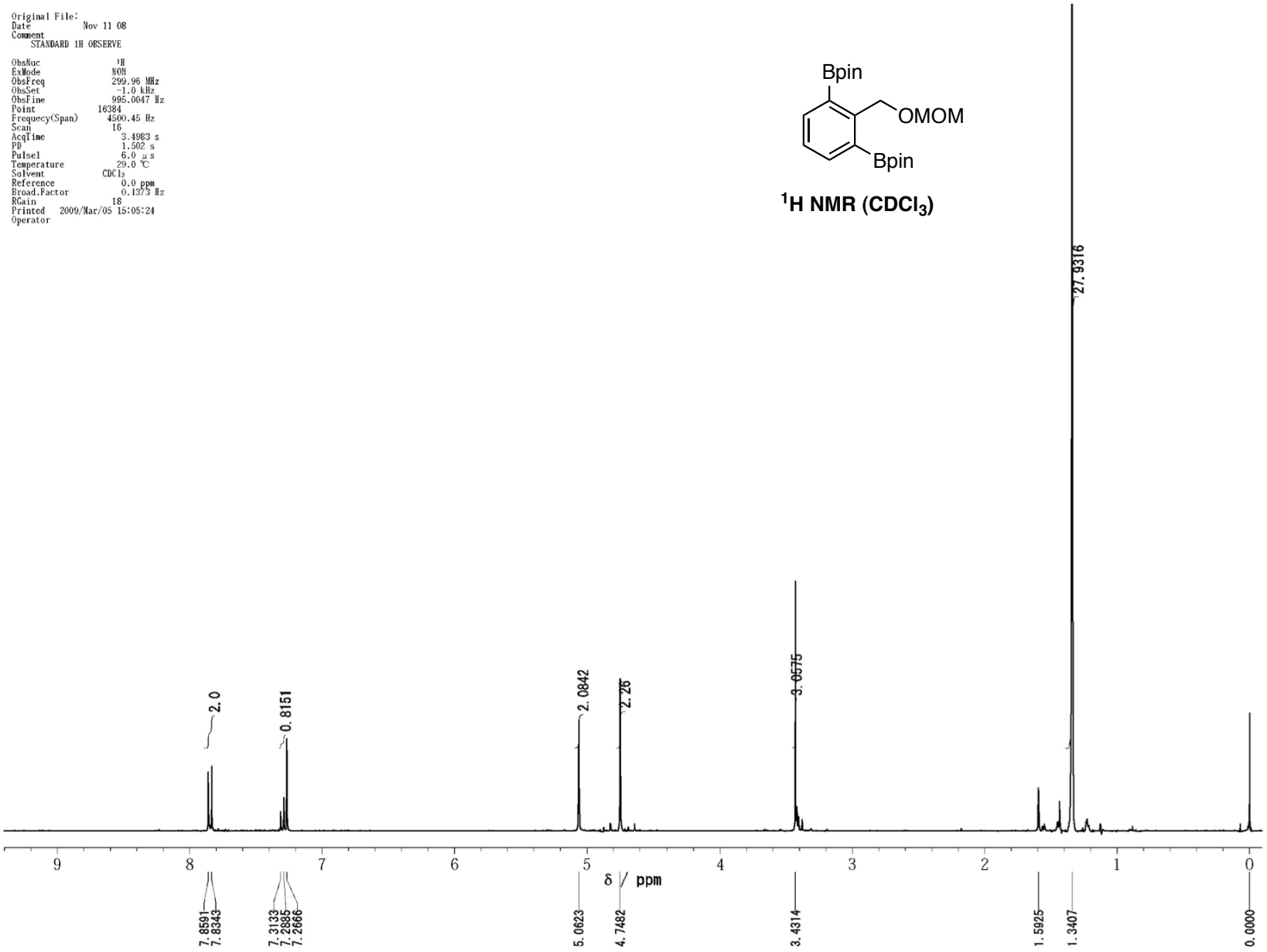

Original File:
Date Dec 14 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 80
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:32:43
Operator
O
O
Bpin
3n
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
143.7732
134.9293
130.5871
127.8011
124.7494
100.3433
83.5134
77.4251
77.0000
76.5749
67.2831
25.6979
24.7414

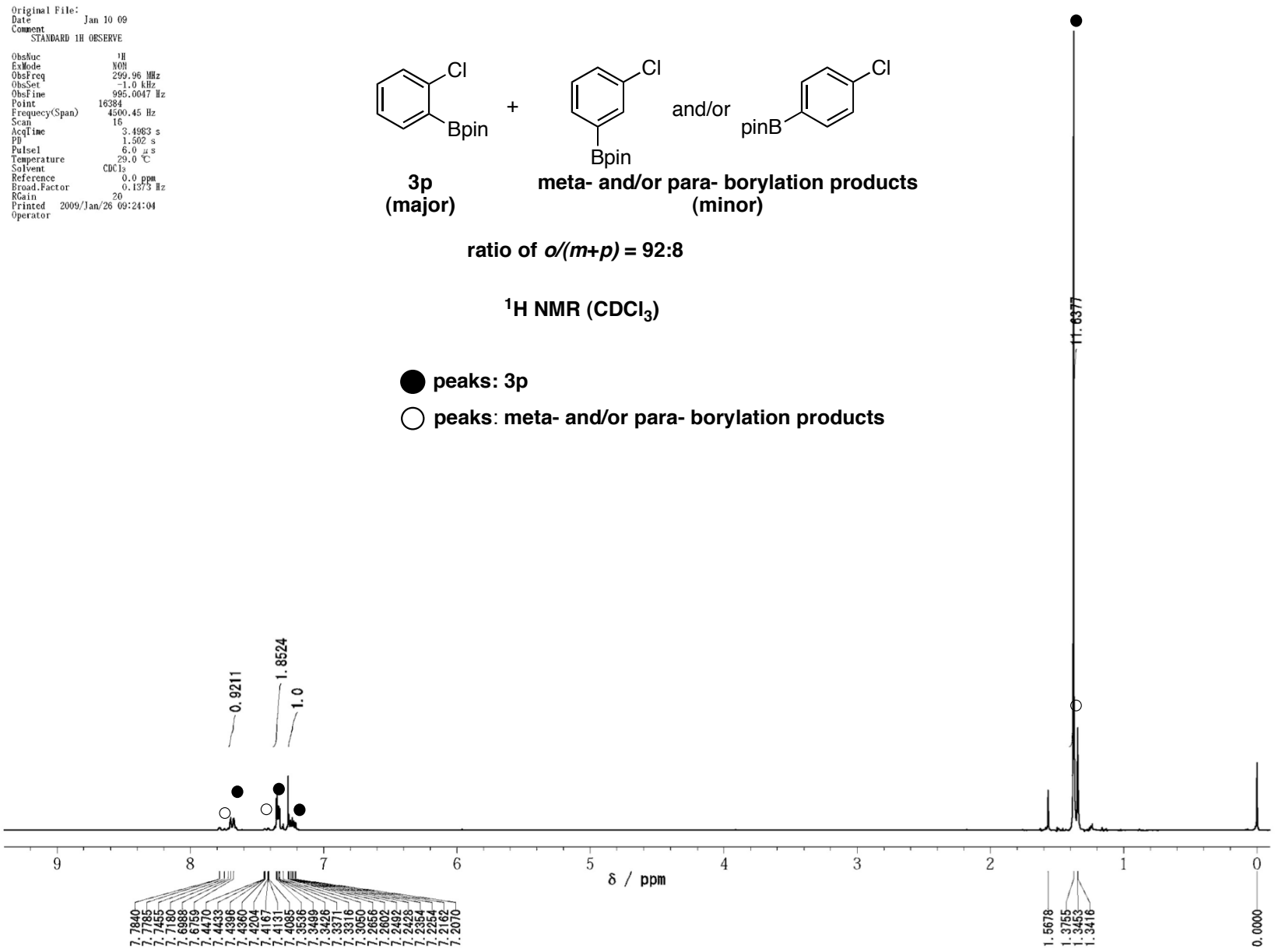

Original File:
Date Dec 15 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 64
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 30
Printed 2009/Mar/05 15:26:14
Operator
Bpin
O
O
Bpin
1H NMR (CDCl3)
2.0
0.9843
2.0242
2.0243
1.0299
0.3834
24.9256
δ / ppm
7.5972
7.5724
7.2895
7.2656
7.2409
6.0898
4.2647
4.2491
4.2281
4.2116
4.0495
4.0431
4.0092
4.0019
3.9689
3.9616
2.3123
2.2949
2.2693
2.2528
2.2363
2.2271
2.2097
2.1932
2.1777
2.1676
2.1511
1.5632
1.4075
1.3489
0.0000

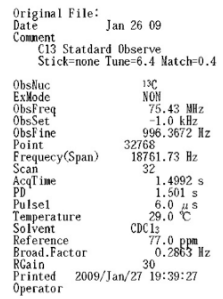

Original File:
Date Oct 15 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 24
Printed 2009/Jan/25 23:33:33
Operator
OMOM
Bpin
3o
0.9806
2.0012
0.8242
2.0
1.9695
3.0365
12.2649
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.8243
7.8005
7.4809
7.4589
7.4543
7.4369
7.4323
7.4113
7.4058
7.3142
7.3076
7.2913
7.2849
7.2647
4.8517
4.7583
3.4204
1.5760
1.3425
0.0000

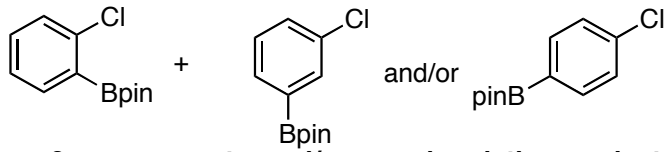
^{1}H NMR ($CDCl_3$)


Original File:
Date Oct 15 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 360
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:34:09
Operator
OMOM
Bpin
3o
13C NMR (CDCl3)
220
200
180
160
140
120
100
80
60
40
20
δ / ppm
144.1604
135.9314
131.0122
128.0744
126.8901
96.3047
83.6272
77.4251
77.0000
76.5749
69.1202
55.2509
24.7414


Original File:
Date Nov 11 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 18
Printed 2009/Mar/05 15:05:24
Operator
Bpin
OMOM
Bpin
1H NMR (CDCl3)
27.9316
2.0
0.8151
2.0842
2.26
3.0575
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.8591
7.8343
7.3133
7.2885
7.2666
5.0623
4.7482
3.4314
1.5925
1.3407
0.0000


Original File:
Date Jan 10 09
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 20
Printed 2009/Jan/26 09:24:04
Operator
Cl
Bpin
+
Cl
Bpin
and/or
pinB
Cl
3p
(major)
meta- and/or para- borylation products
(minor)
ratio of o/(m+p) = 92:8
1H NMR (CDCl3)
peaks: 3p
peaks: meta- and/or para- borylation products
0.9211
1.8524
1.0
11.6377
δ / ppm
7.7840
7.7785
7.7455
7.7180
7.6988
7.6759
7.4470
7.4433
7.4396
7.4360
7.4204
7.4167
7.4131
7.4085
7.3536
7.3499
7.3426
7.3371
7.3316
7.3050
7.2656
7.2602
7.2492
7.2428
7.2354
7.2254
7.2162
7.2070
1.5678
1.3755
1.3453
1.3416
0.0000



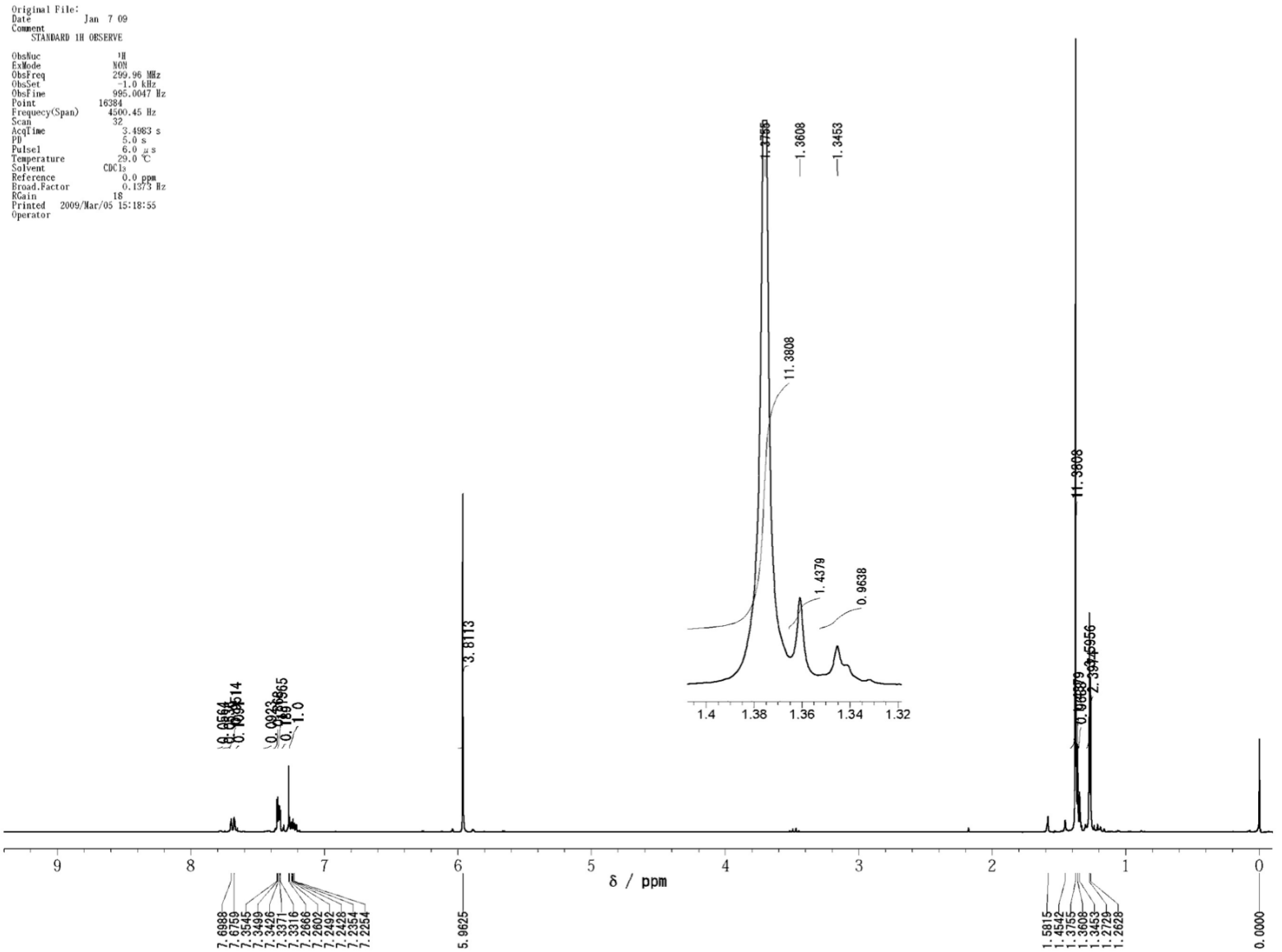


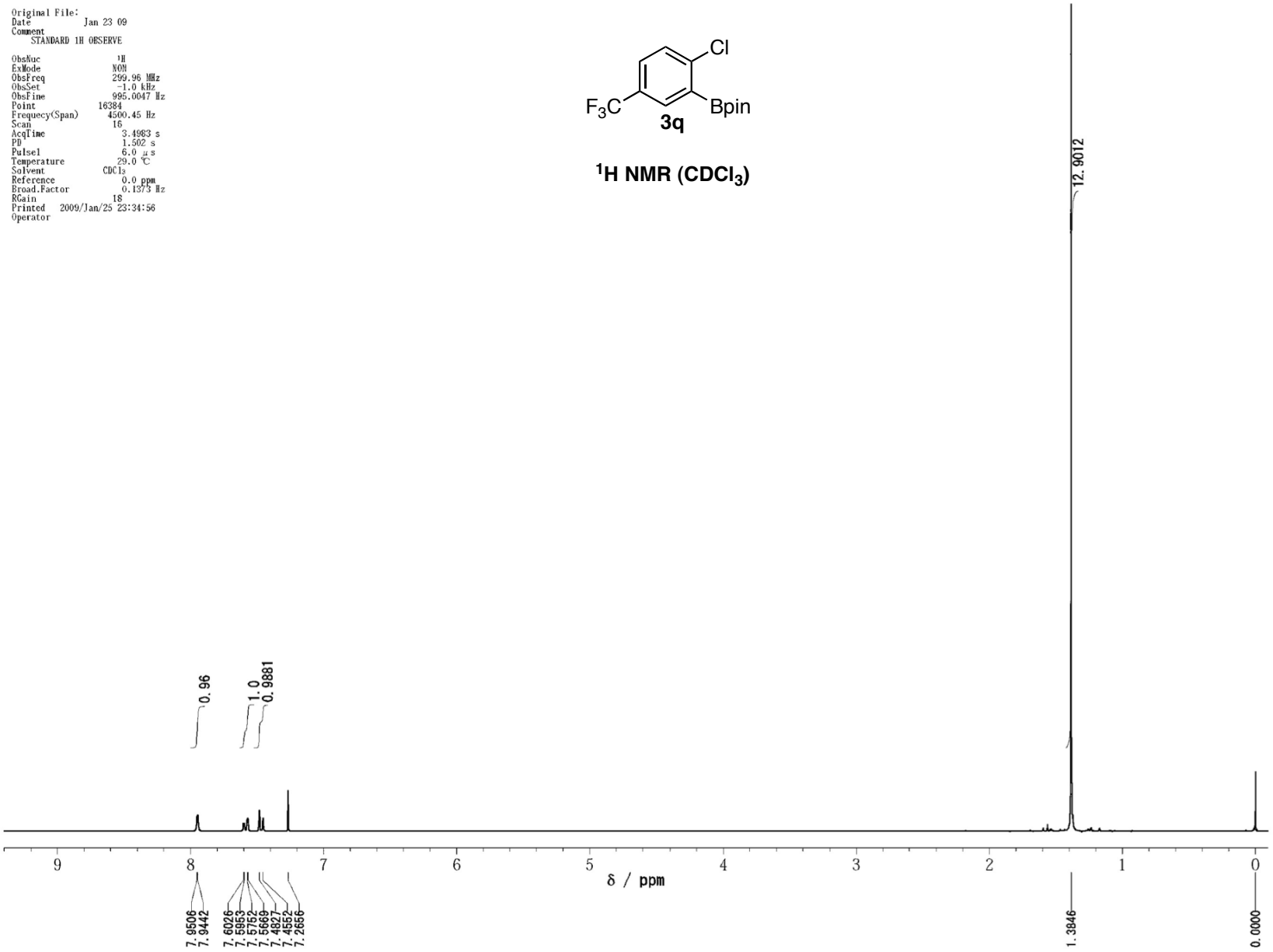
3p (major) **meta- and/or para- borylation products (minor)**

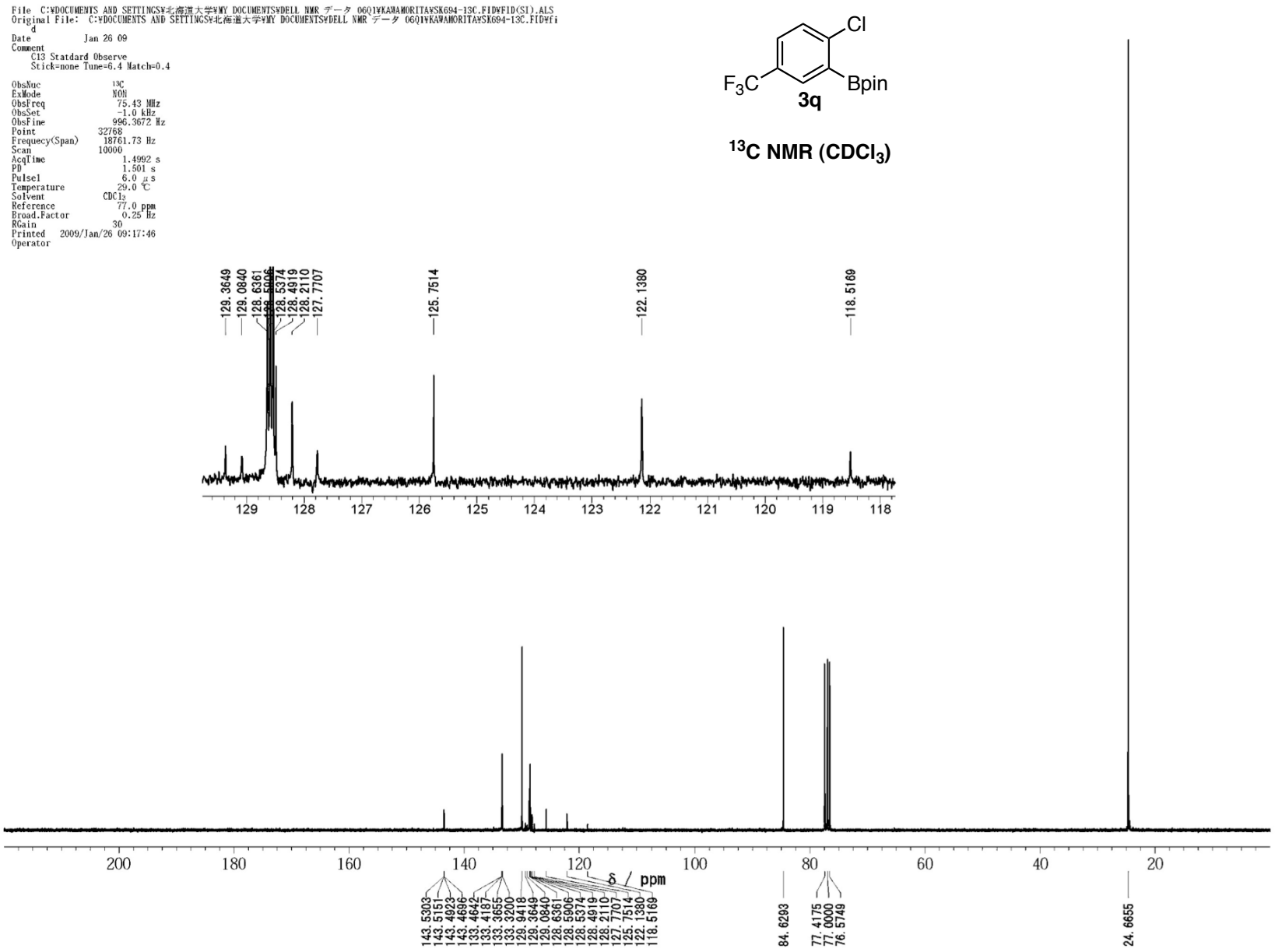
ratio of *o/(m+p)* = 92:8

^{13}C NMR ($CDCl_3$)

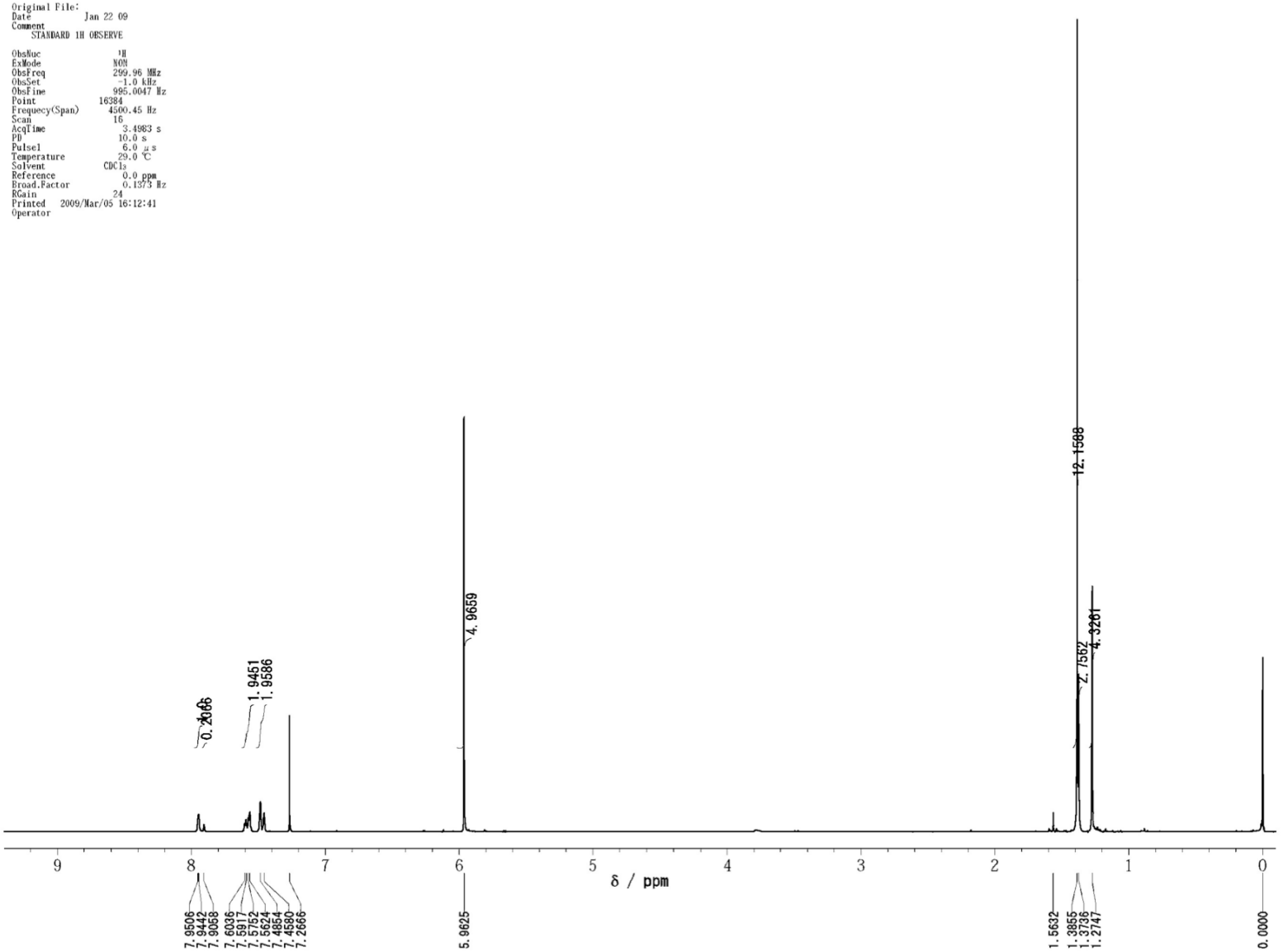
^{1}H NMR spectrum of the crude material on a reaction of 1p (Table 2, entry 6)

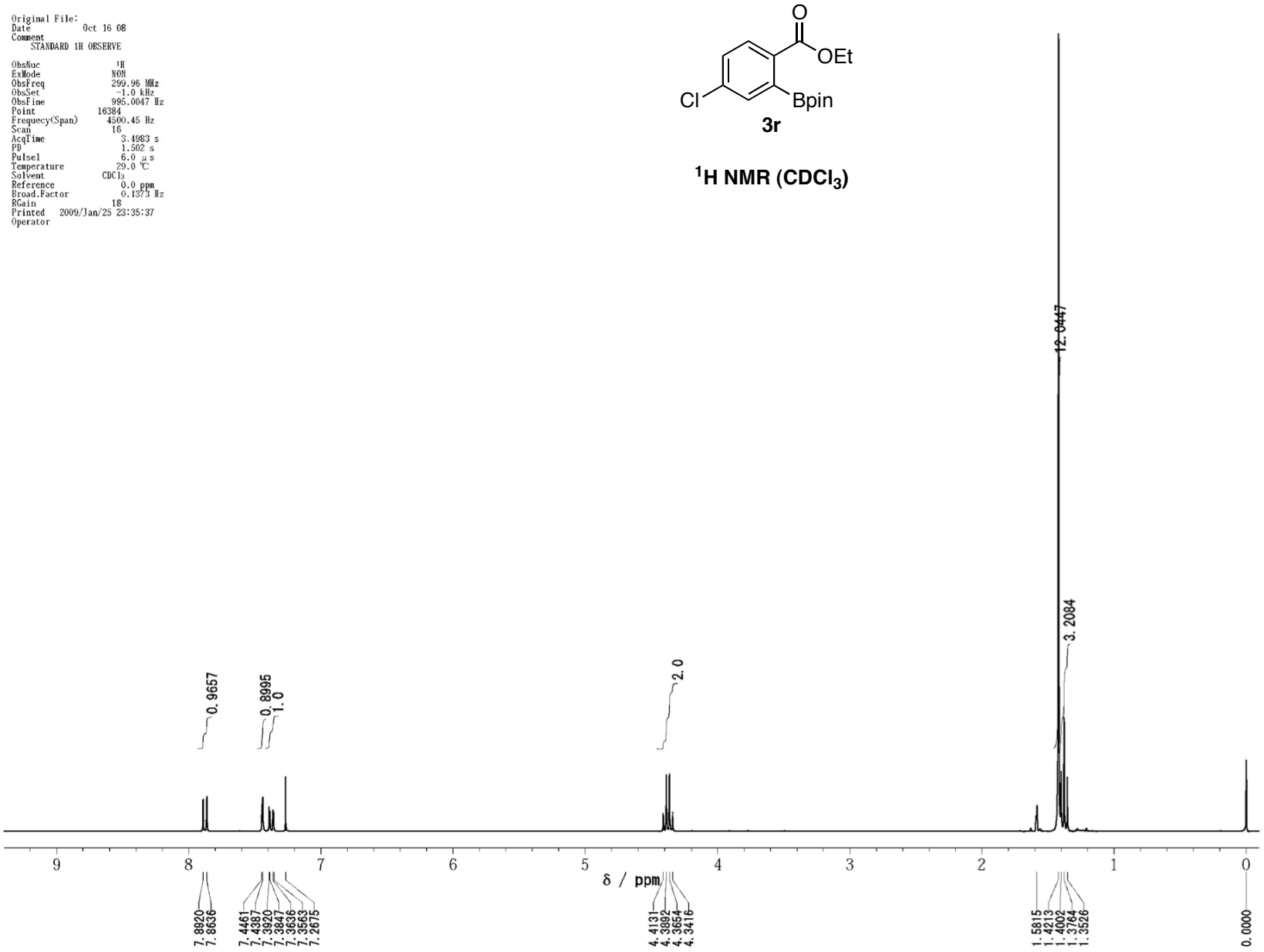



Original File:
Date Jan 23 09
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 18
Printed 2009/Jan/25 23:34:56
Operator
Cl
F3C
Bpin
3q
1H NMR (CDCl3)
12.9012
0.96
1.0
0.9881
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.9506
7.9442
7.6026
7.5953
7.5752
7.5669
7.4827
7.4552
7.2656
1.3846
0.0000

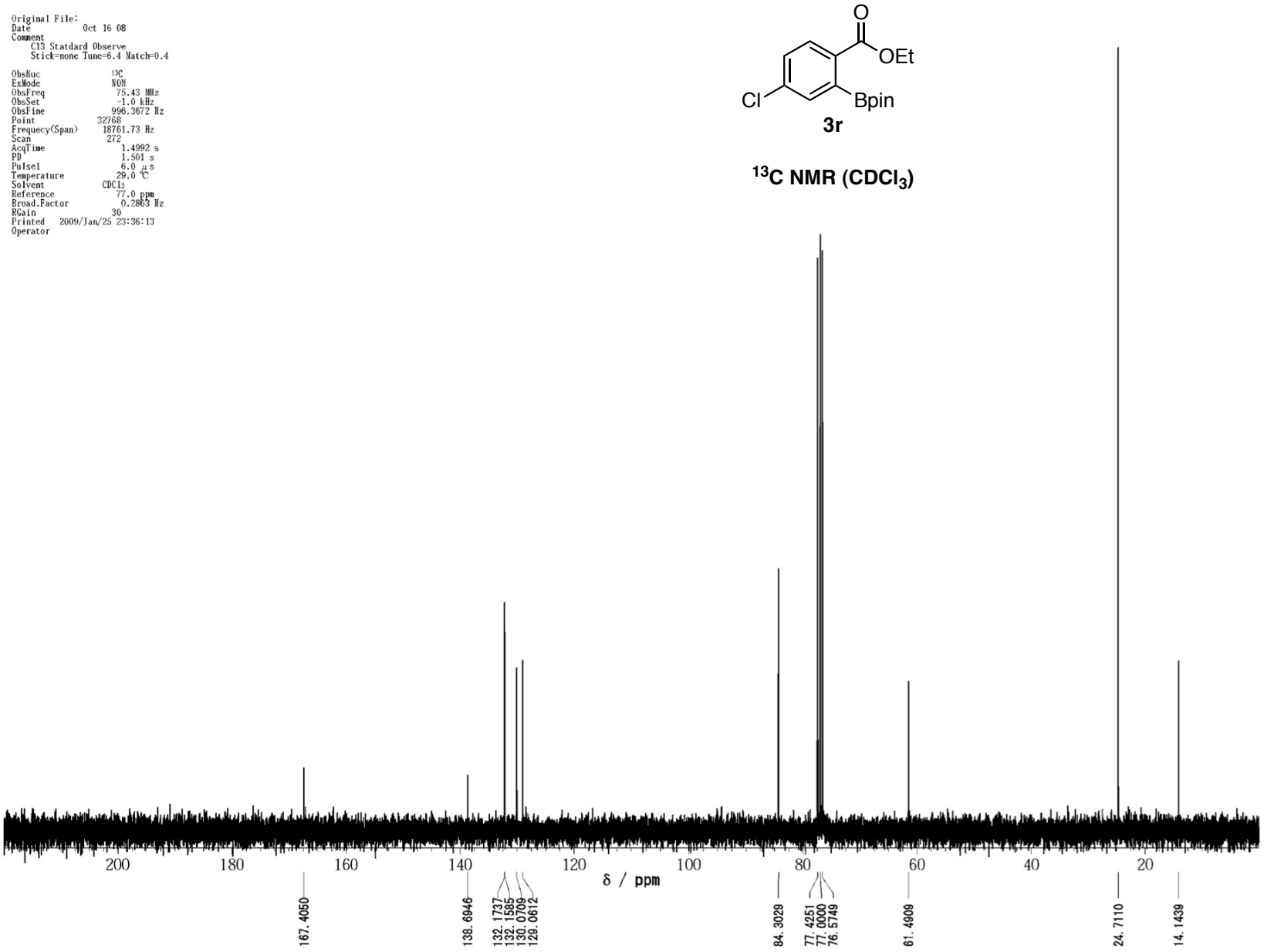

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥KAWAMORITA¥SK694-13C.FID¥FID(SI).ALS
Original File: C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥KAWAMORITA¥SK694-13C.FID¥fid
Date Jan 26 09
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 10000
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.25 Hz
RGain 30
Printed 2009/Jan/26 09:17:46
Operator
Cl
F3C
Bpin
3q
13C NMR (CDCl3)
129.3649
129.0840
128.6361
128.5906
128.5374
128.4919
128.2110
127.7707
125.7514
122.1380
118.5169
δ / ppm
143.5303
143.5151
143.4923
143.4696
133.4642
133.4187
133.3655
133.3200
129.9418
129.3649
129.0840
128.6361
128.5906
128.5374
128.4919
128.2110
127.7707
125.7514
122.1380
118.5169
84.6293
77.4175
77.0000
76.5749
24.6655

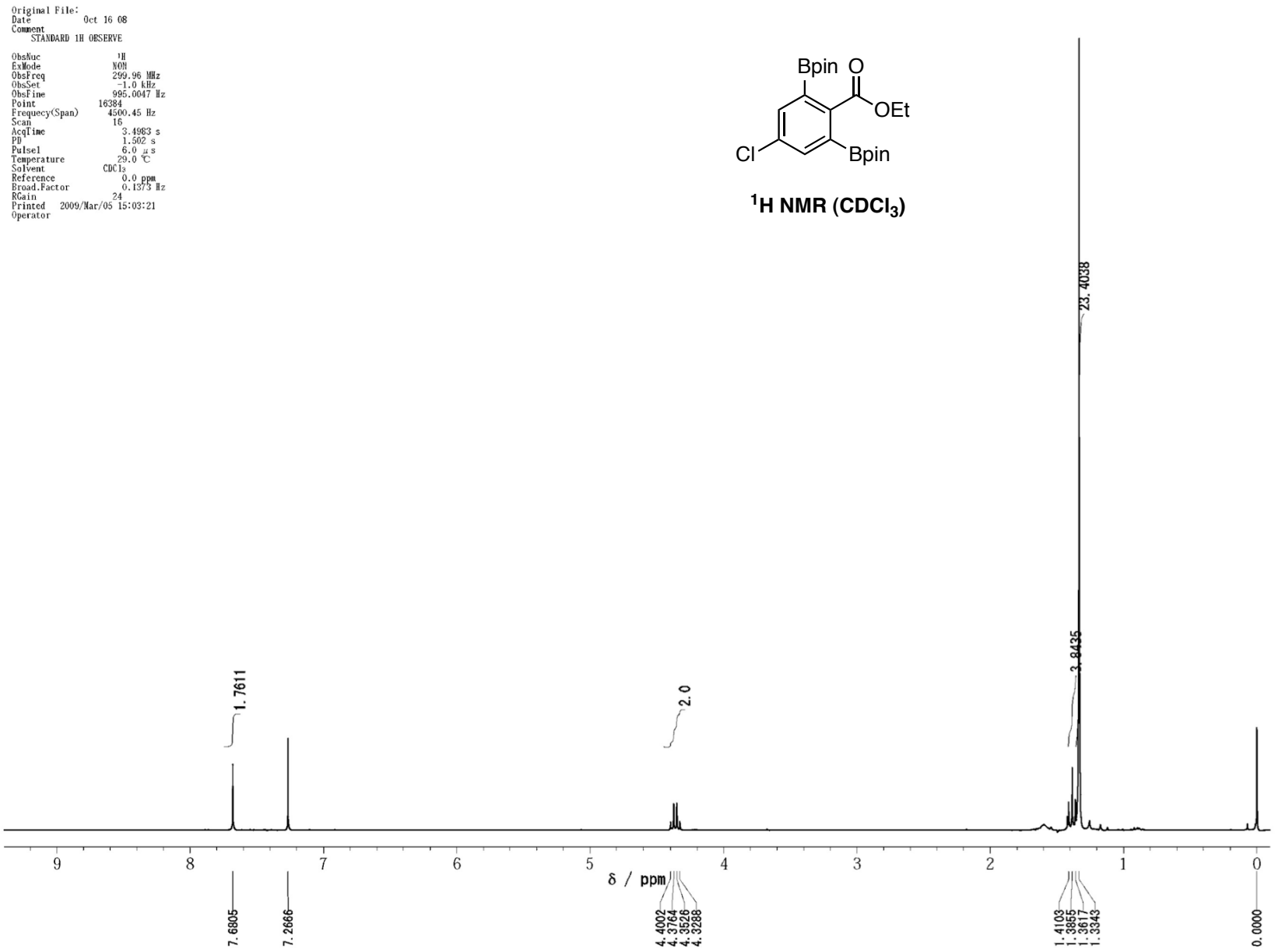
^{1}H NMR spectrum of the crude material on a reaction of 1q (Table 2, entry 7)

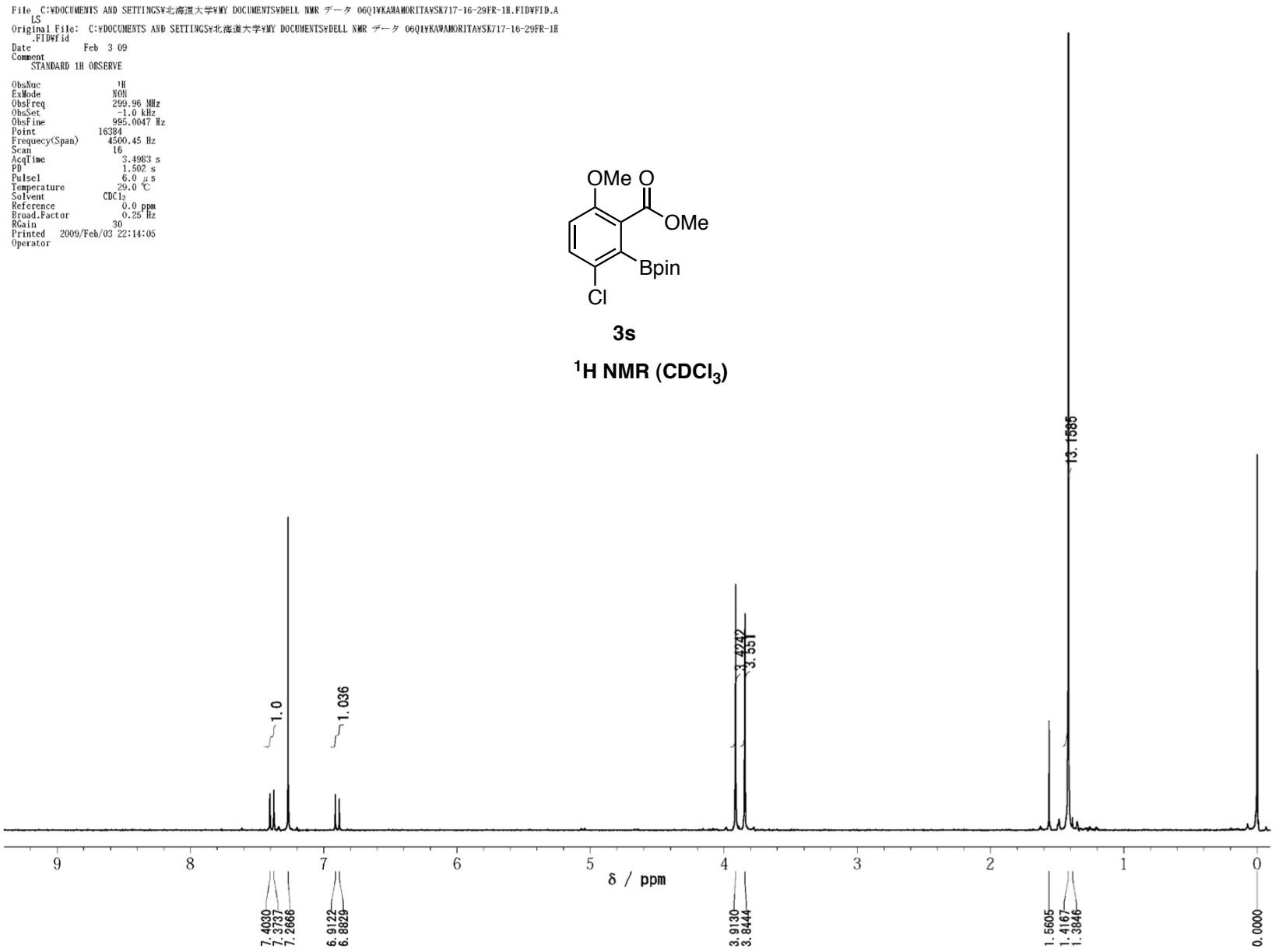



Original File:
Date Oct 16 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 18
Printed 2009/Jan/25 23:35:37
Operator
O
OEt
Cl
Bpin
3r
12.0447
3.2084
2.0
0.9657
0.8995
1.0
δ / ppm
7.8820
7.8636
7.4461
7.4387
7.3920
7.3847
7.3636
7.3568
7.2675
4.4131
4.3892
4.3654
4.3416
1.5815
1.4213
1.4002
1.3764
1.3526
0.0000

^{1}H NMR ($CDCl_3$)

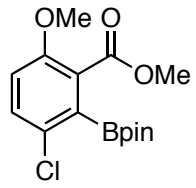

Original File:
Date Oct 16 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NOM
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 272
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2009/Jan/25 23:36:13
Operator
O
OEt
Cl
Bpin
3r
13C NMR (CDCl3)
200
180
160
140
120
100
80
60
40
20
δ / ppm
167.4050
138.6946
132.1737
132.1585
130.0709
129.0612
84.3029
77.4251
77.0000
76.5749
61.4909
24.7110
14.1439


Original File:
Date Oct 16 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 24
Printed 2009/Mar/05 15:03:21
Operator
Bpin
O
OEt
Cl
Bpin
1H NMR (CDCl3)
23.4038
3.8435
2.0
1.7611
δ / ppm
7.6805
7.2666
4.4002
4.3764
4.3526
4.3288
1.4103
1.3865
1.3617
1.3343
0.0000


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥KAWAMORITA¥SK717-16-29FR-1H.FID¥FID.A
LS
Original File: C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥KAWAMORITA¥SK717-16-29FR-1H
.FID¥fid
Date Feb 3 09
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.25 Hz
RGain 30
Printed 2009/Feb/03 22:14:05
Operator
OMe O
OMe
Bpin
Cl
3s
1H NMR (CDCl3)
13.1585
3.4747
3.5551
1.0
1.036
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.4030
7.3737
7.2868
6.9122
6.8829
3.9130
3.8444
1.5605
1.4167
1.3846
0.0000

Original File:
Date Jan 25 09
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	32768
Frequecy(Span)	18761.73 Hz
Scan	64
AcqTime	1.4992 s
PD	1.501 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	$CDCl_3$
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2009/Jan/25 23:37:35
Operator	



3s

^{13}C NMR ($CDCl_3$)