# Supporting Information

## Preparation, Structure, and Reactions of Trifluoroacetimidoyl Palladium(II) Complexes

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**General Remarks:**

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. Benzene and toluene were distilled from $CaH_2$. Nitromethane was dried over $CaSO_4$ and distilled. All other reagents and solvents were employed without further purification. Trifluoroacetimidoyl chlorides **1b** and **1c** were prepared in 80-90% yields by refluxing a mixture of TFA (1 equiv.), *p*-anisidine (for **1b**) or *n*-hexylamine (for **1c**) (1 equiv.), triphenylphosphine (3 equiv.) and triethylamine (1 equiv.) in $CCl_4$.[1] Trifluoroacetimidoyl iodide **1a** was prepared by replacement of chlorine atom of the corresponding chloride **1b** with sodium iodide in acetone quantitatively.[1] $^1$H NMR spectra were recorded using $Me_4Si$ as an internal standard (δ 0 ppm). $^{19}$F NMR spectra were recorded using hexafluorobenzene ($C_6F_6$) as an internal standard (δ 0 ppm). $^{31}$P NMR spectra were recorded by the use of phosphoric acid (85 wt% $H_3PO_4$) as an internal standard (δ 0 ppm). Splitting patterns were reported as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

**Iodo[*N*-(*p*-methoxyphenyl)-2,2,2-trifluoroacetiminoacyl]bis(triphenylphosphine)palladium(II) (2a).** To a solution of $Pd(PPh_3)_4$ (0.920 g, 0.80 mmol) in 15 mL of benzene was added *N*-(*p*-methoxyphenyl)-2,2,2-trifluoroacetimidoyl iodide (**1a**) (0.790 g, 2.40 mmol). After stirring for 24 h at room temperature with minimum exposure to light, a pale yellowish suspension was obtained. The solvent was slowly evaporated to ca. one-third of its original volume. Dropwise addition of hexane with sonication provided the precipitate, which was washed with ether by several times to afford orange powder of **2a** (0.761 g, 99%); mp 168.0-170.0 °C; IR (KBr) 1614 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.73 (d, 2H, $J$ = 8.4 Hz), 7.28-7.38 (m, 12H), 7.36-7.44 (m, 6H), 7.52-7.60 (m, 12H), 7.84 (d, 2H, $J$ = 8.4 Hz); $^{19}$F NMR (470 MHz, $CDCl_3$) δ 101.0 (s, 3F); $^{31}$P NMR (203 MHz, $CDCl_3$) δ 18.6 (s, 2P). Anal. Calcd for $C_{45}H_{37}F_3INOP_2Pd$: C, 56.30; H, 3.88; N, 1.46. Found: C, 56.01; H, 3.95; N, 1.19.

**Chloro[*N*-(*p*-methoxyphenyl)-2,2,2-trifluoroacetiminoacyl]bis(triphenylphosphine)palladium(II) (2b).** To a solution of $Pd(PPh_3)_4$ (3.47 g, 3.0 mmol) in 50 mL of benzene was added *N*-(*p*-methoxyphenyl)-2,2,2-trifluoroacetimidoyl chloride (**1b**) (2.12 g, 9.0 mmol). After stirring for 2 days at room temperature, a pale yellowish suspension was given. The solvent was slowly evaporated to ca. one-third of its original volume. Dropwise addition of hexane with sonication provided the precipitate, which was washed with ether by several times to afford the colorless powder of **2b** (2.57 g, 99%); mp 195.0-197.0 °C; IR (KBr) 1610 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.63 (d, 2H, $J$ = 8.4

Hz), 7.28-7.36 (m, 12H), 7.37-7.44 (m, 6H), 7.48-7.58 (m, 12H), 7.76 (d, 2H, $J$ = 8.4 Hz); $^{19}$F NMR (470 MHz, $CDCl_3$) δ 100.2 (s, 3F); $^{31}$P NMR (203 MHz, $CDCl_3$) δ 21.9 (s, 2P). Anal. Calcd for $C_{45}H_{37}ClF_3NOP_2Pd$: C, 62.23; H, 4.29; N, 1.61. Found: C, 62.45; H, 4.38; N, 1.49.

**Chloro(*N*-hexyl-2,2,2-trifluoroacetiminoacyl)bis(triphenylphosphine)palladium(II) (2c).** Using the procedure for **2b**, the reaction of **1c** (2.44 g, 11.3 mmol) and $Pd(PPh_3)_4$ (4.37 g, 3.78 mmol) for over night produced the colorless powder of **2c** (3.22 g, 99%); mp 157.0-159.0 °C; IR (KBr) 1624 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, 3H, $J$ = 6.1 Hz), 1.00-1.17 (m, 4H), 1.20-1.38 (m, 4H), 3.23-3.40 (m, 2H), 7.28-7.42 (m, 18H), 7.55-7.70 (m, 12H); $^{19}$F NMR (470 MHz, $CDCl_3$) δ 99.2 (s, 3F); $^{31}$P NMR (203 MHz, $CDCl_3$) δ 23.1 (s, 2P). Anal. Calcd for $C_{44}H_{43}ClF_3INP_2Pd$: C, 62.42; H, 5.12; N, 1.65. Found: C, 62.32; H, 5.51; N, 1.94.

**Transmetallation Reaction of 2a with Ph-SnBu$_3$. Synthesis of *N*-(*p*-Methoxyphenyl)-1-phenyl-1-trifluoromethylimine (8).** To a solution of complex **2a** (0.288 g, 0.30 mmol) in 4.0 mL of DMF was added Ph-$SnBu_3$ (0.111 g, 0.30 mmol). After stirring for 20 h at 60 °C, then the mixture was poured into brine. The product was extracted with ether, and the combined organic phase was dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (hexane:AcOEt = 5:1) to afford the yellow oil of **8** (45.6 mg, 54%).[2]

**Tetra-μ-iodo-tetrakis{[*N*-(*p*-methoxyphenyl)-2,2,2-trifluoroacetiminoacyl]palladium(II)} (2d).** To a solution of $Pd_2(dba)_3$ •$CHCl_3$ (0.052 g, 0.050 mmol) in 1 mL of toluene was added *N*-(*p*-methoxyphenyl)-2,2,2-trifluoroacetimidoyl iodide (**1a**) (0.036 g, 0.10 mmol). After stirring for 24 h at room temperature with minimum exposure to light, the solvent was evaporated. In order to remove dibenzylideneacetone (dba) from the mixture, recrystallization from ether was carried out, then the solvent of the mother liquor was evaporated. Purification of the residue by column chromatography on silica gel (hexane/ethyl acetate = 25/1) gave red solids of **2d** (0.040 g, 92%); mp 162.0-164.0 °C; IR (KBr) 1608 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 12H), 6.88 (s, 16H); $^{19}$F NMR (470 MHz, $CDCl_3$) δ 104.0 (s, 12F). Anal. Calcd for $C_{36}H_{28}F_{14}I_4N_4O_4Pd_4$: C, 24.82; H, 1.62; N, 3.22. Found: C, 25.22; H, 1.92; N, 3.22.

**Carboalkoxylation of Imidoyl Iodides. Synthesis of *tert*-Butyl 2-[*N*-(*p*-Methoxyphenyl)imino]-3,3,3-trifluoropropanoate (6a).** A two-necked flask with a CO balloon (1 atm) attached was charged with Pd complex **1d** (13.1 mg, 75 μmol) and $K_2CO_3$ (88 mg, 0.64 mmol). Then 100 mg (0.30 mmol) of trifluoroacetimidoyl iodide **1a** in 0.9 mL of *tert*-butyl alcohol was added to the catalyst mixture. Subsequently, 0.1 mL of DMI was added. The reaction vessel was wrapped in aluminum foil to minimize exposure to light, and the mixture was stirred for 3 days at room temperature. The resulting suspension was filtered through a short Florisil column ($CH_2Cl_2$). After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane/ether = 15/1) to give a yellow oil of **6a** (70 mg, 0.23 mmol, 77%).[3]

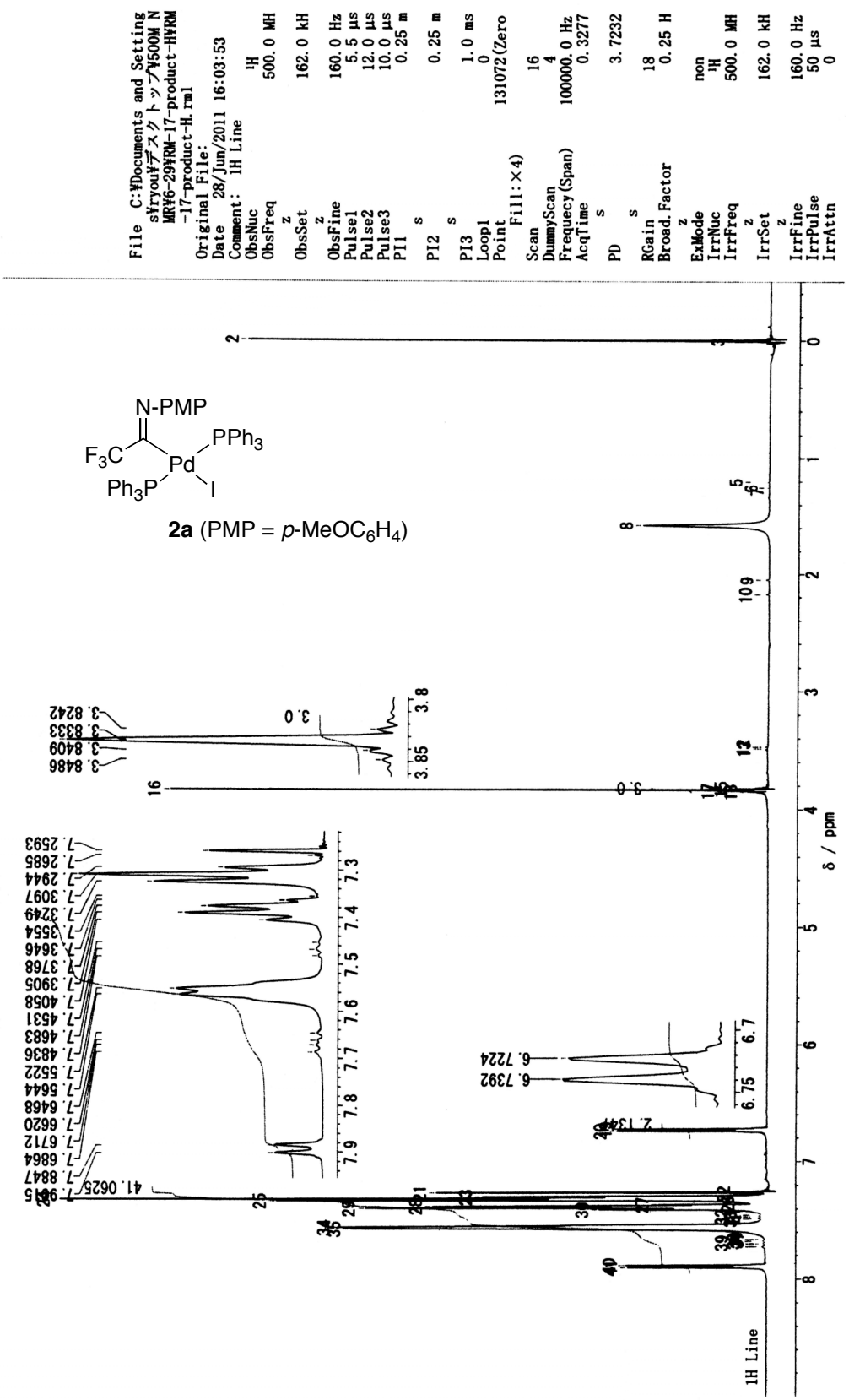
**Synthesis of (*N*-Hexyl-*N*-methylamino)(trifluoromethyl)carbene Palladium(II) Complex (11).** A two-necked flask with a septum cap was charged with **2c** (4.45 g, 5.26 mmol) and activated molecular sieves 4A. Trimethyloxonium tetrafluoroborate (95%, 0.855 g, 5.78 mmol) was speedily added as a solid, and then nitromethane (30 mL) was added under an argon atmosphere. The mixture was stirred for 2 h at room temperature and passed through a short column of Celite (eluent: nitromethane). After exhaustive evaporation of solvent, 5 mL of dichloromethane was added. Dropwise addition of ether with sonication provided the precipitate, which was washed with ether by several times to afford the pale yellowish powder of **11** (4.25 g, 85%); IR (KBr) 1484, 1438 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J$ = 7.0 Hz), 0.97-1.12 (m, 2H), 1.18-1.36 (m, 4H), 1.50-1.68 (m, 2H), 3.19 (s, 3H), 4.40-4.50 (m, 2H), 7.33-7.78 (m, 30H); $^{19}F$ NMR (470 MHz, $CDCl_3$) δ 8.86 (s, 4F), 100.9 (s, 3F). Anal. Calcd for $C_{45}H_{46}BClF_7NP_2Pd$: C, 56.99; H, 4.89; N, 1.48. Found: C, 56.69; H, 4.86; N, 1.51.

**Reaction of 11 with Elemental Sulfur: Synthesis of *N*-Hexyl-*N*-methyl-2,2,2-trifluoroethanethioamide (13).** A glass tube was charged with the Pd-complex **18** (94.8 mg, 0.10 mmol) and elemental sulfur (32.0 mg, 1.0 mmol). The tube was sealed with a flame, then the mixture was immersed into an oil bath at 70 °C. After warming to 160 °C, the bath temperature was kept for 24 h and passed through a Celite pad (eluent: ether). The solvent was removed under reduced pressure. The residue was purified by preparative thin layer chromatography (hexane:AcOEt = 5:1) to afford the yellow oil of **13** (44.4 mg, 44% yield, a mixture of two geometrical isomer, isomer ratio was 1.18:1.00); IR (neat) 1514 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.86-0.93 (m, 3H), 1.24-1.38 (m, 6H), 1.66-1.76 (m, 2H), 3.38 (s, 3H, minor isomer), 3.40 (s, 3H, major isomer), 3.69 (t, 2H, $J$ = 8.0 Hz, major isomer), 3.93 (t, 2H, $J$ = 7.9 Hz, minor isomer); $^{19}F$ NMR (470 MHz, $CDCl_3$) δ 99.0 (s, 3F, minor isomer), 100.3 (s,

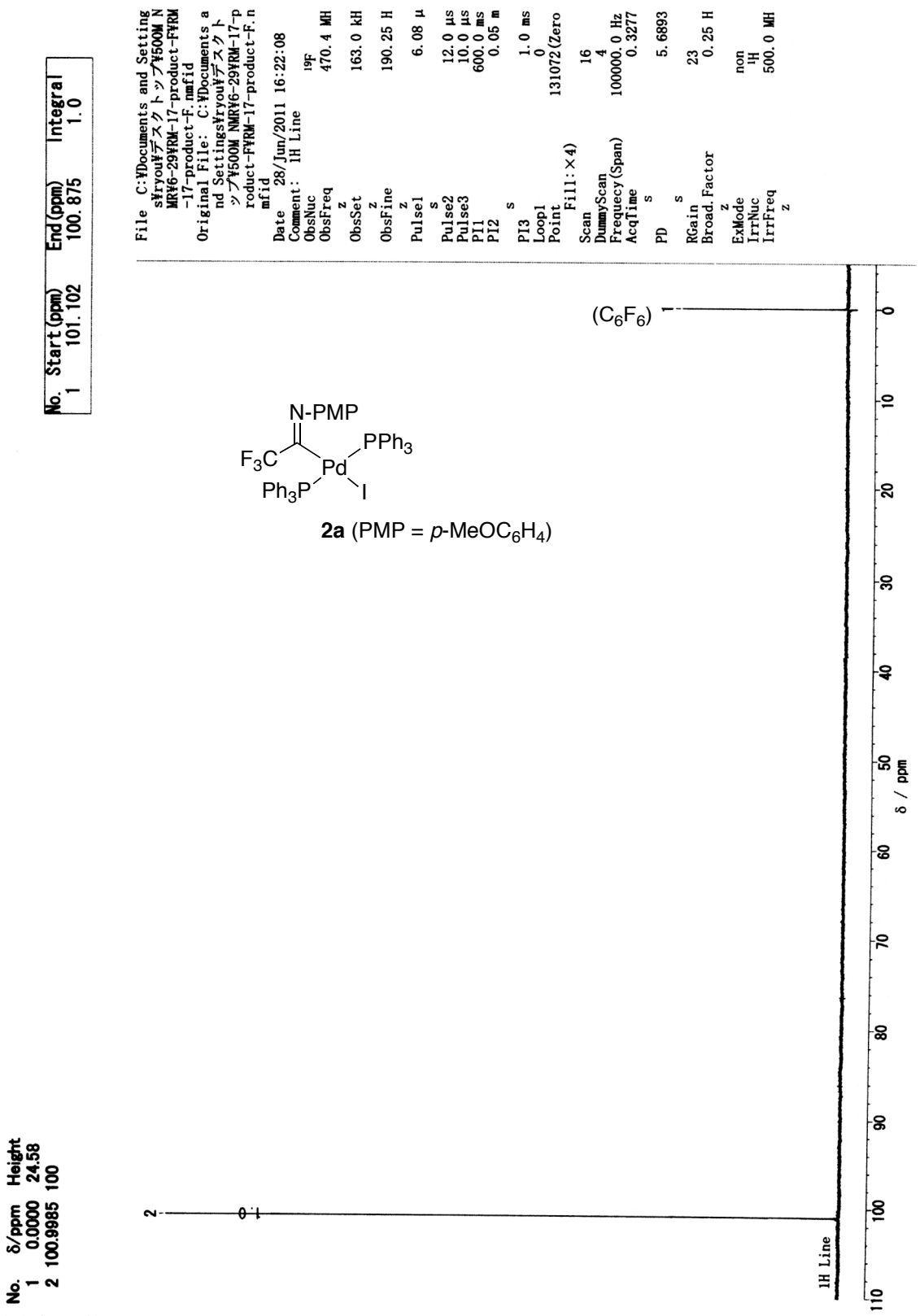
3F, major isomer); EI-MS *m/z* (%) 227 ($M^+$, 36), 194 (81), 184 (34), 157 (24), 138 (32), 110 (100). Anal. Calcd for $C_9H_{16}F_3NS$: C, 47.56; H, 7.10; N, 6.16. Found: C, 47.44; H, 6.75; N, 6.15.

**Reaction of Chloro[*N*-(*n*-hexyl)-2,2,2-trifluoroacetiminoacyl]bis(triphenylphosphine)palladium(II) (2c) with Methyl Thioglycolate: Synthesis of 3-Hexyl-2-(trifluoromethyl)thiazolidin-4-one (14).** A glass tube was charged with complex **2c** (169.2 mg, 0.20 mmol) and methyl thioglycolate (42.5 mg, 0.40 mmol). The tube was sealed with a flame, then the mixture was immersed into an oil bath at 90 °C. After warming to 170 °C, the bath temperature was kept at 170 °C for 24 h and passed through a Celite pad (eluent: ether). The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (hexane:AcOEt = 10:1) to provide the colorless powder and oil. Further distillation of the obtained mixture was performed (ca. 0.1 mmHg, 100 °C) to afford the colorless oil of **14** (0.120 g, 47%); IR (neat) 1694 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.80-0.90 (m, 3H), 1.10-1.20 (m, 6H), 1.55-1.78 (m, 2H), 3.10-3.20 (m, 1H), 3.44 (d, 1H, *J* = 15.5 Hz), 3.75 (d, 1H, *J* = 15.5 Hz), 3.81-3.89 (m, 1H), 4.83 (q, 1H, *J* = 5.3 Hz); $^{19}F$ NMR (470 MHz, $CDCl_3$) δ 86.2 (d, 3F, *J* = 5.3 Hz); EI-MS *m/z* (%) 170 ($M^+$, 100), 142 (9). Anal. Calcd for $C_{10}H_{16}F_3NOS$: C, 47.05; H, 6.31; N, 5.49. Found: C, 47.22; H, 6.37; N, 5.30.

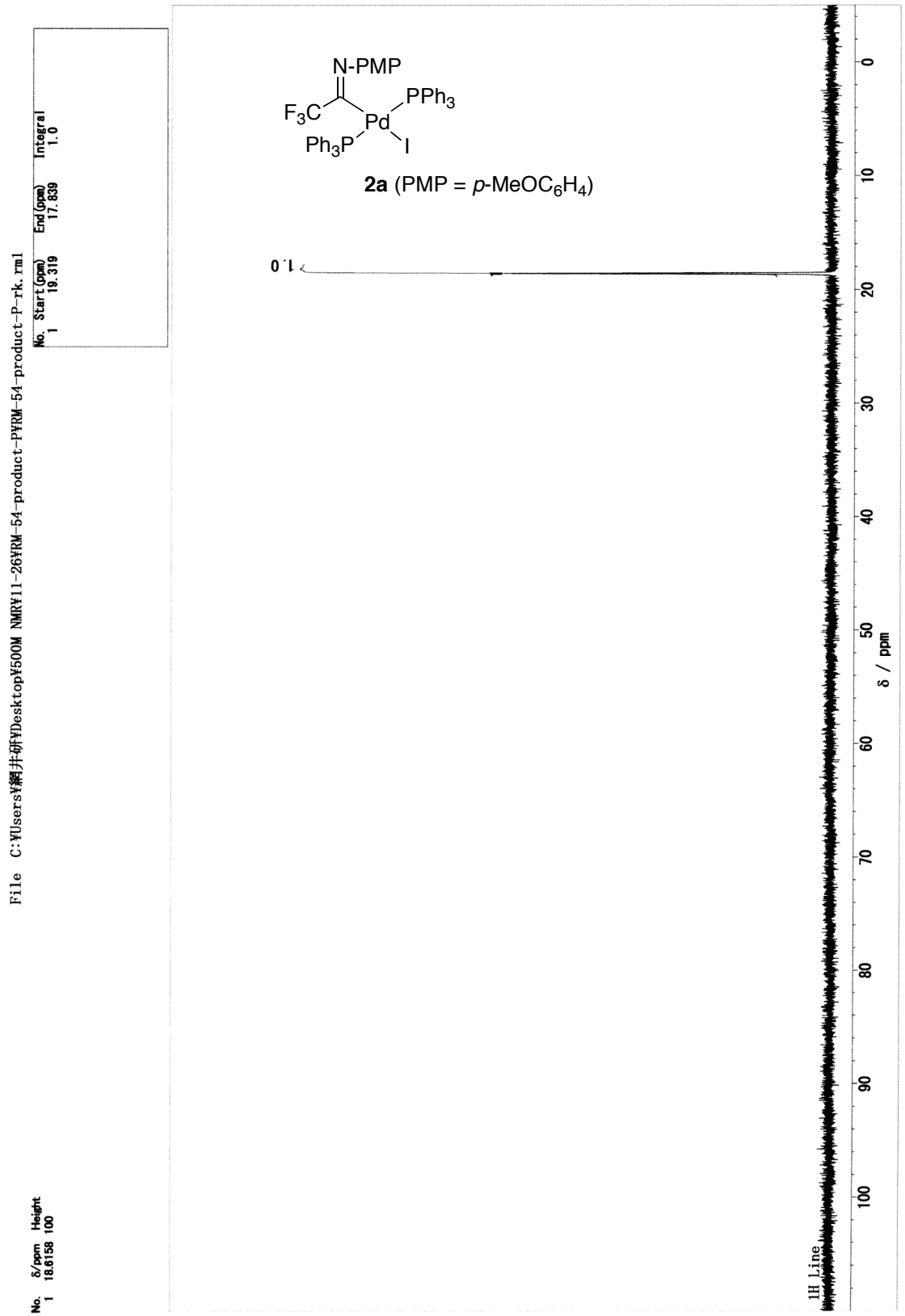
$^{1}$H NMR Spectrum of Compound **2a**



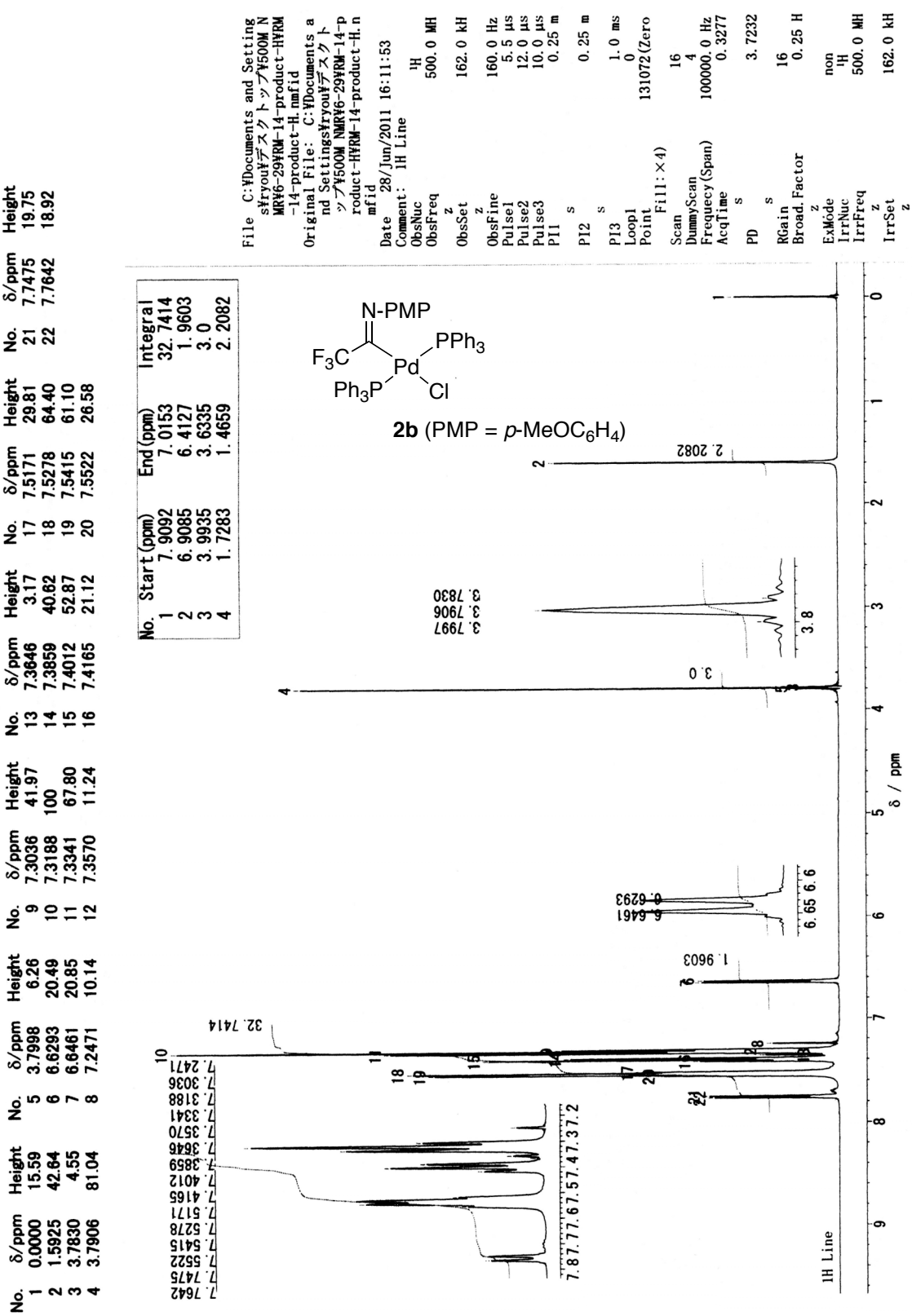
$^{19}$F NMR Spectrum of Compound **2a**



$^{31}$P NMR Spectrum of Compound **2a**



$^{1}$H NMR Spectrum of Compound **2b**



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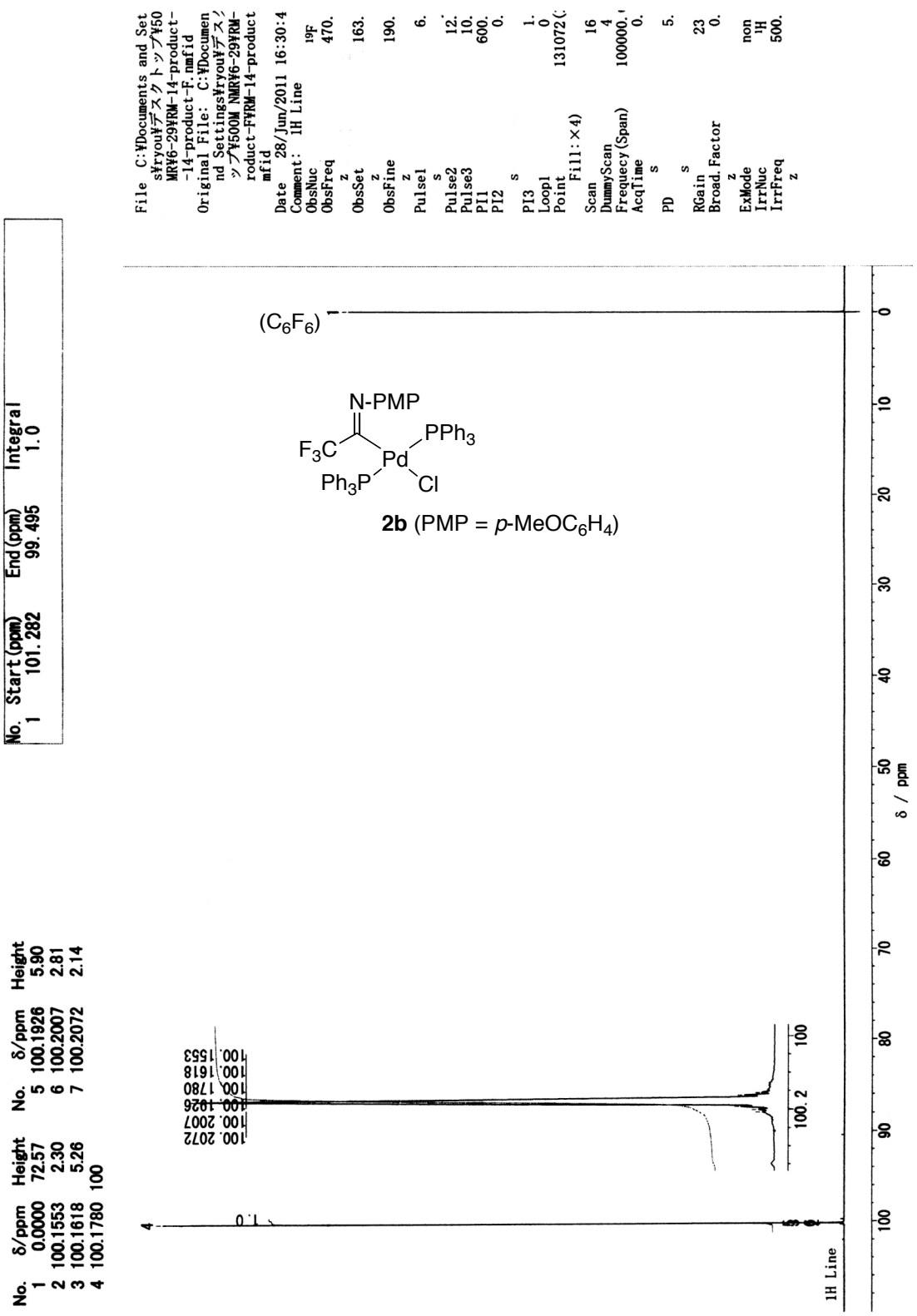

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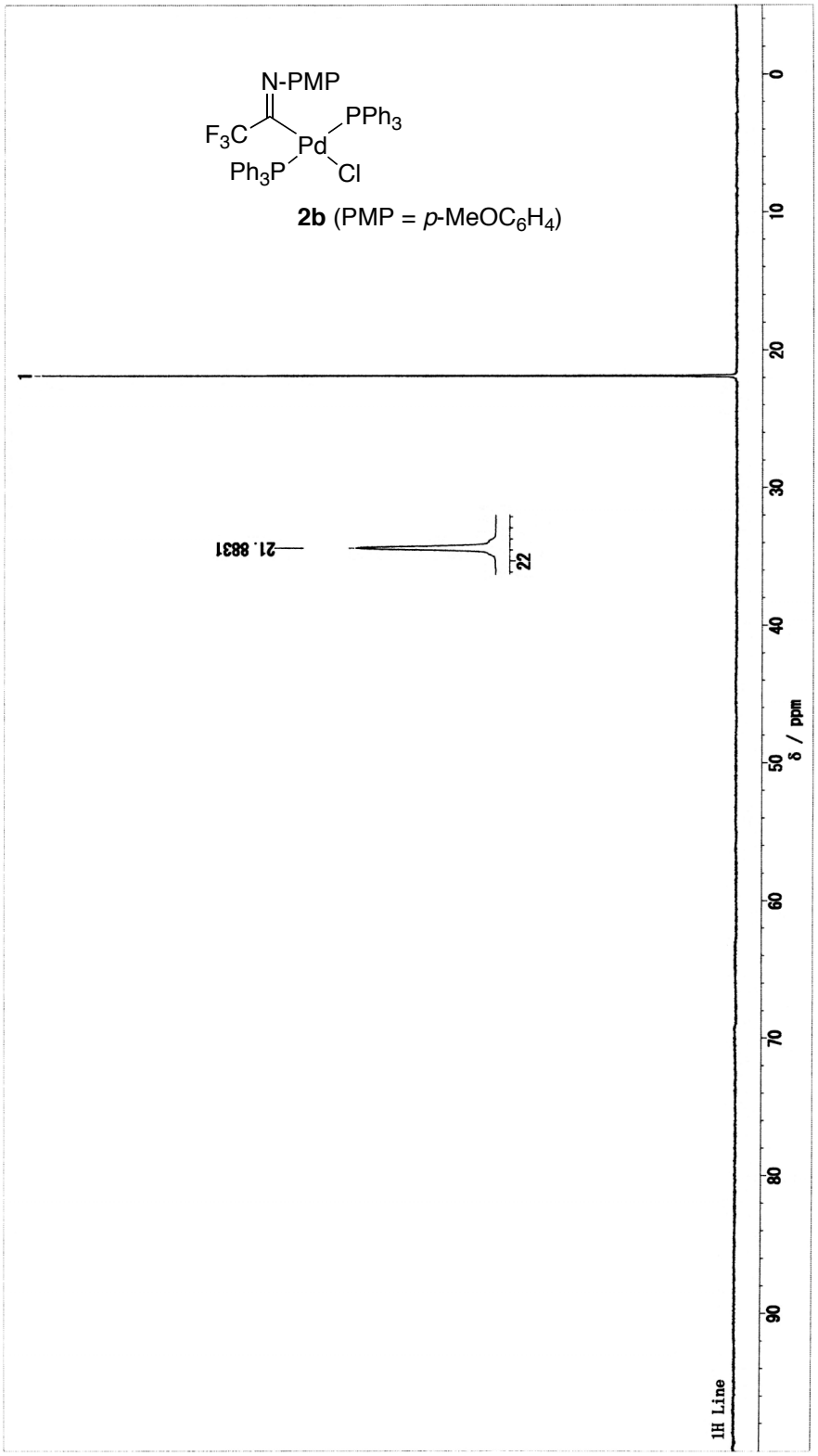
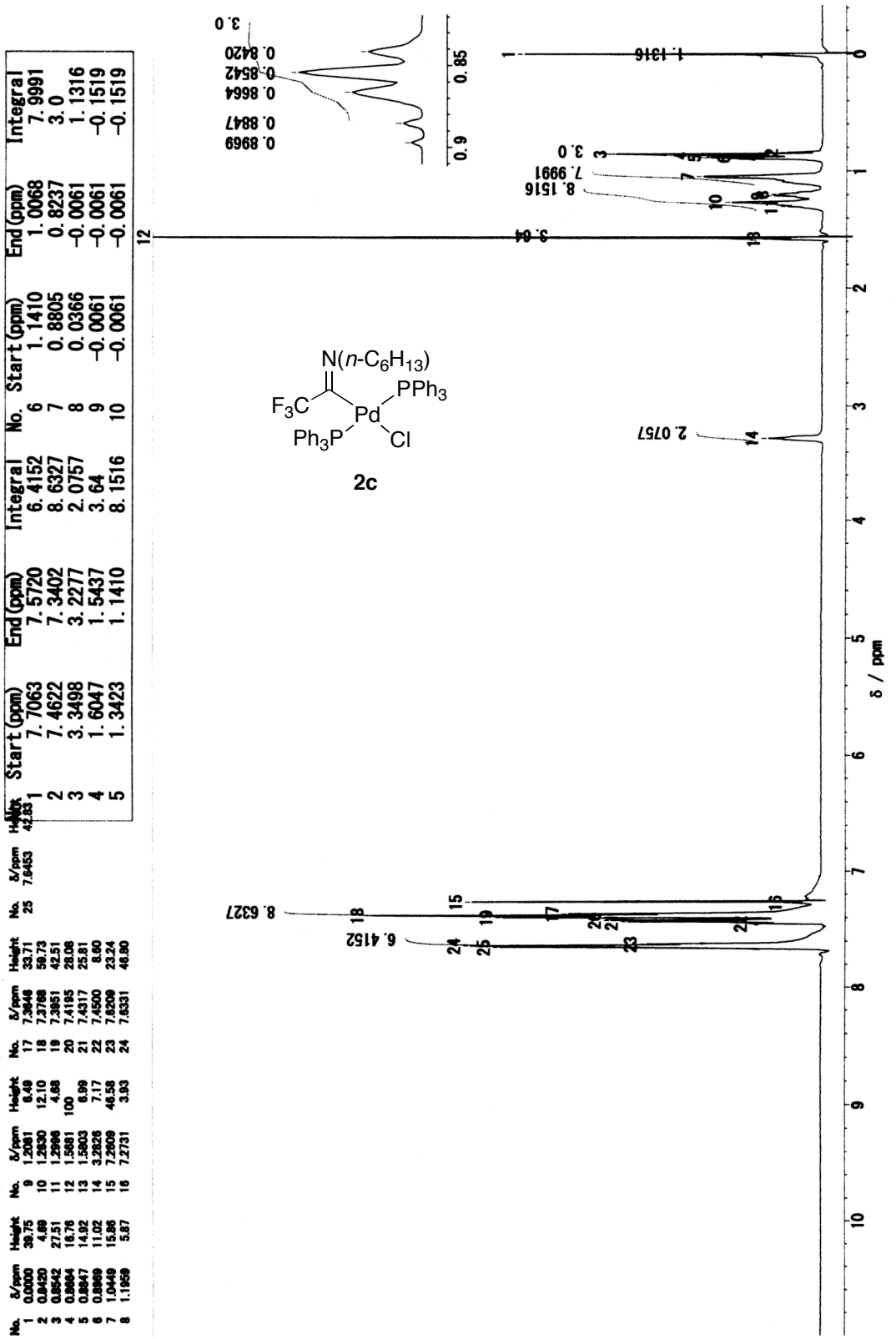


$^{1}$H NMR Spectrum of Compound **2c**



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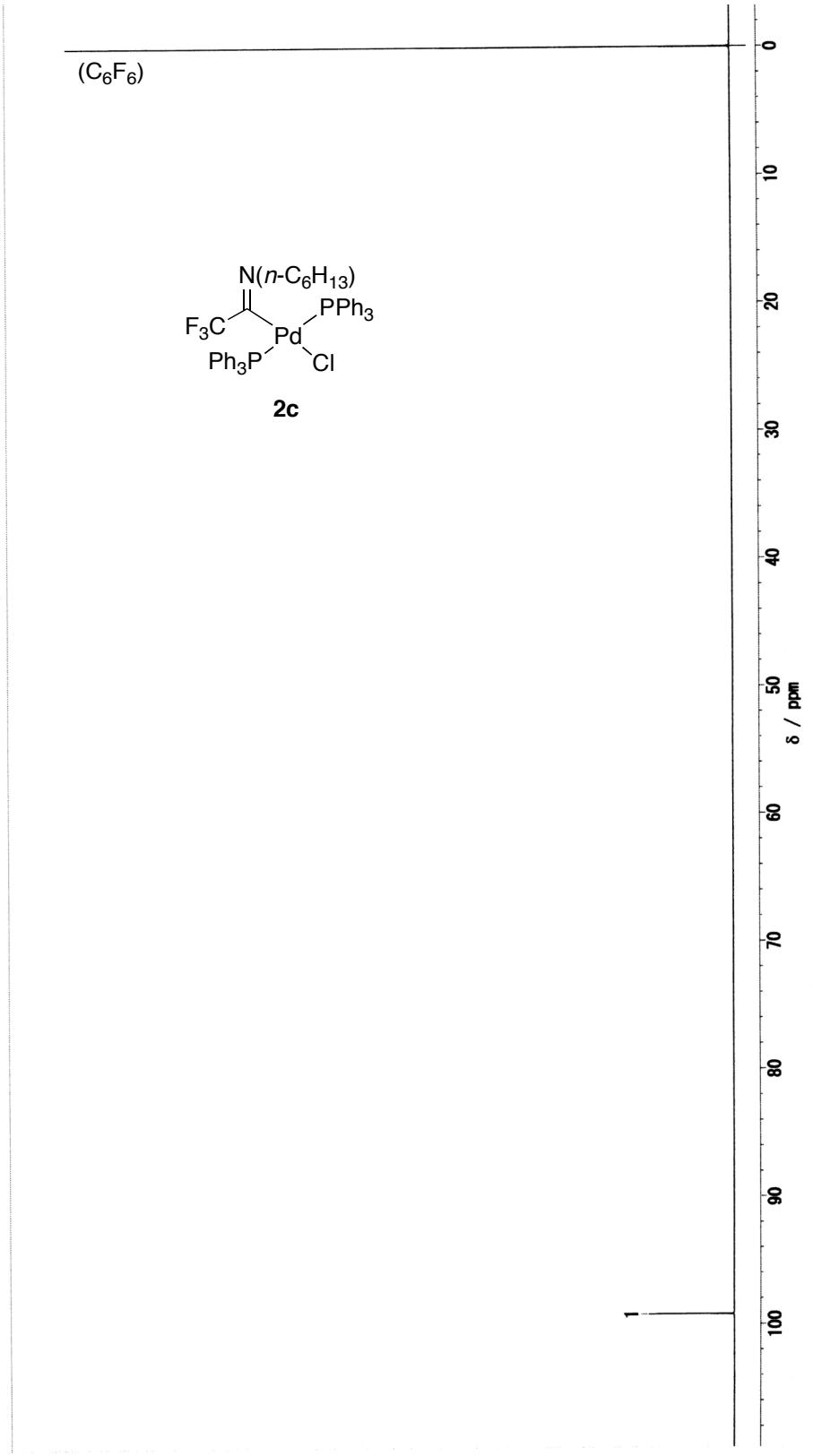

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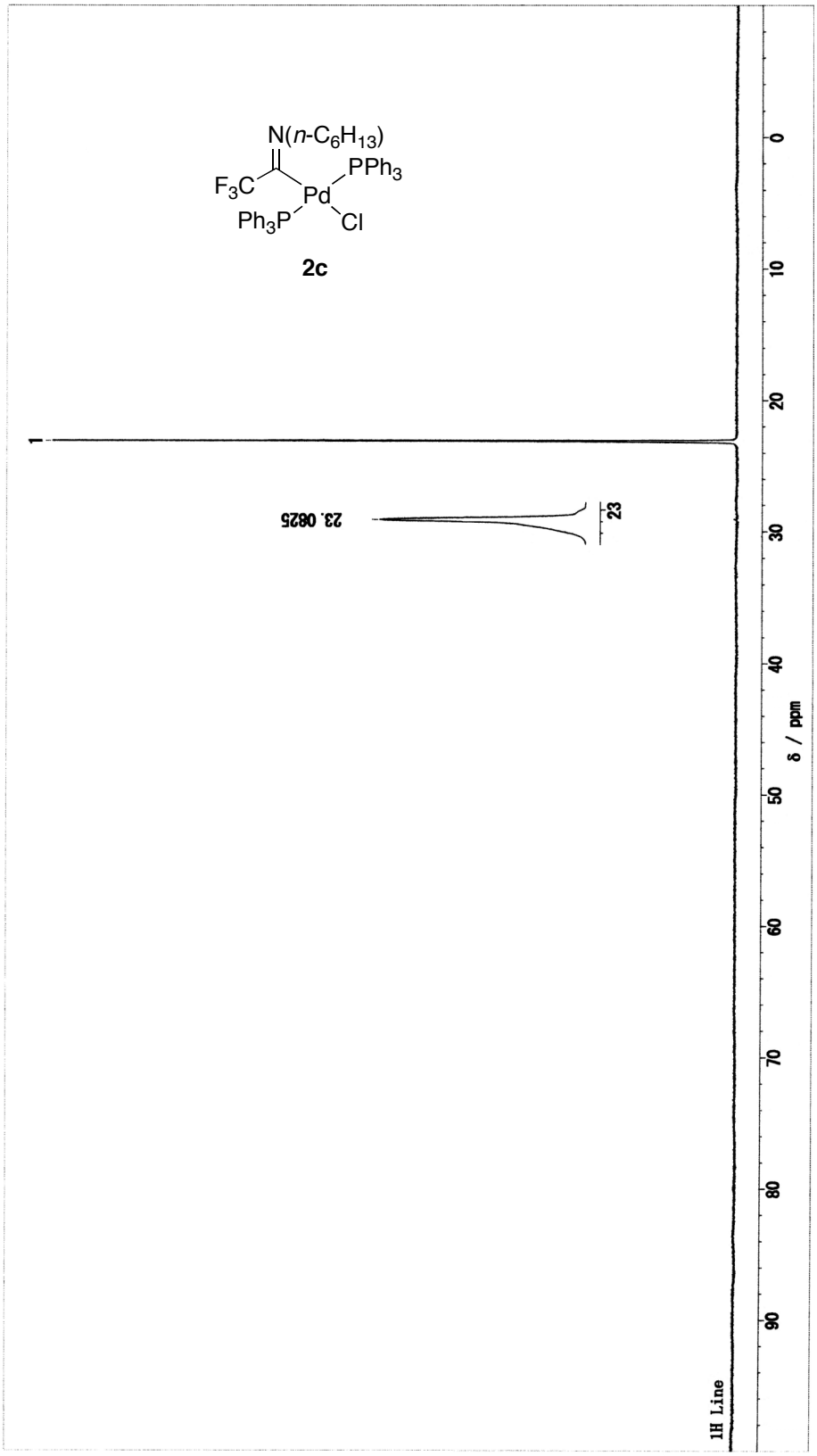
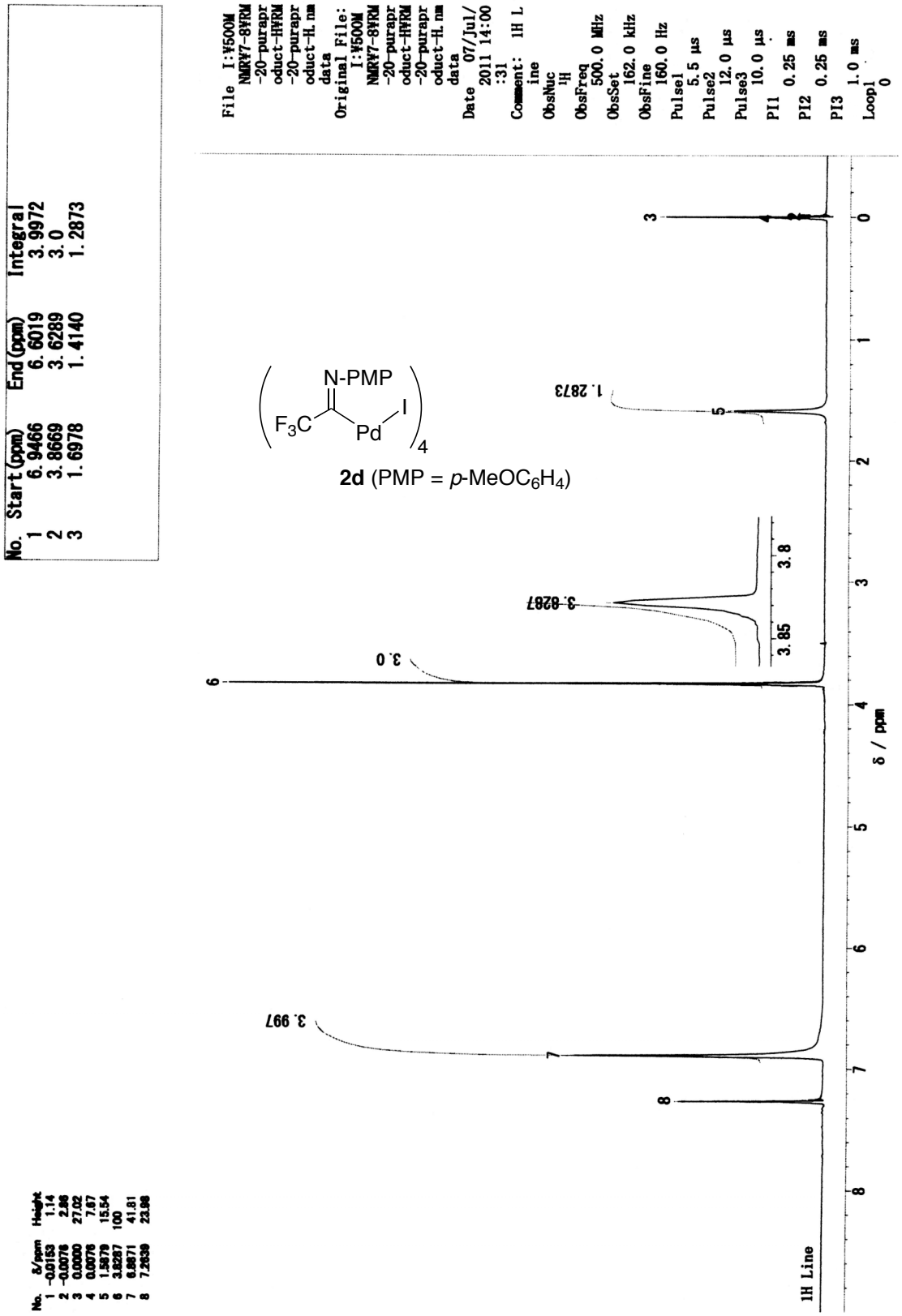


$^1$H NMR Spectrum of Compound **2d**



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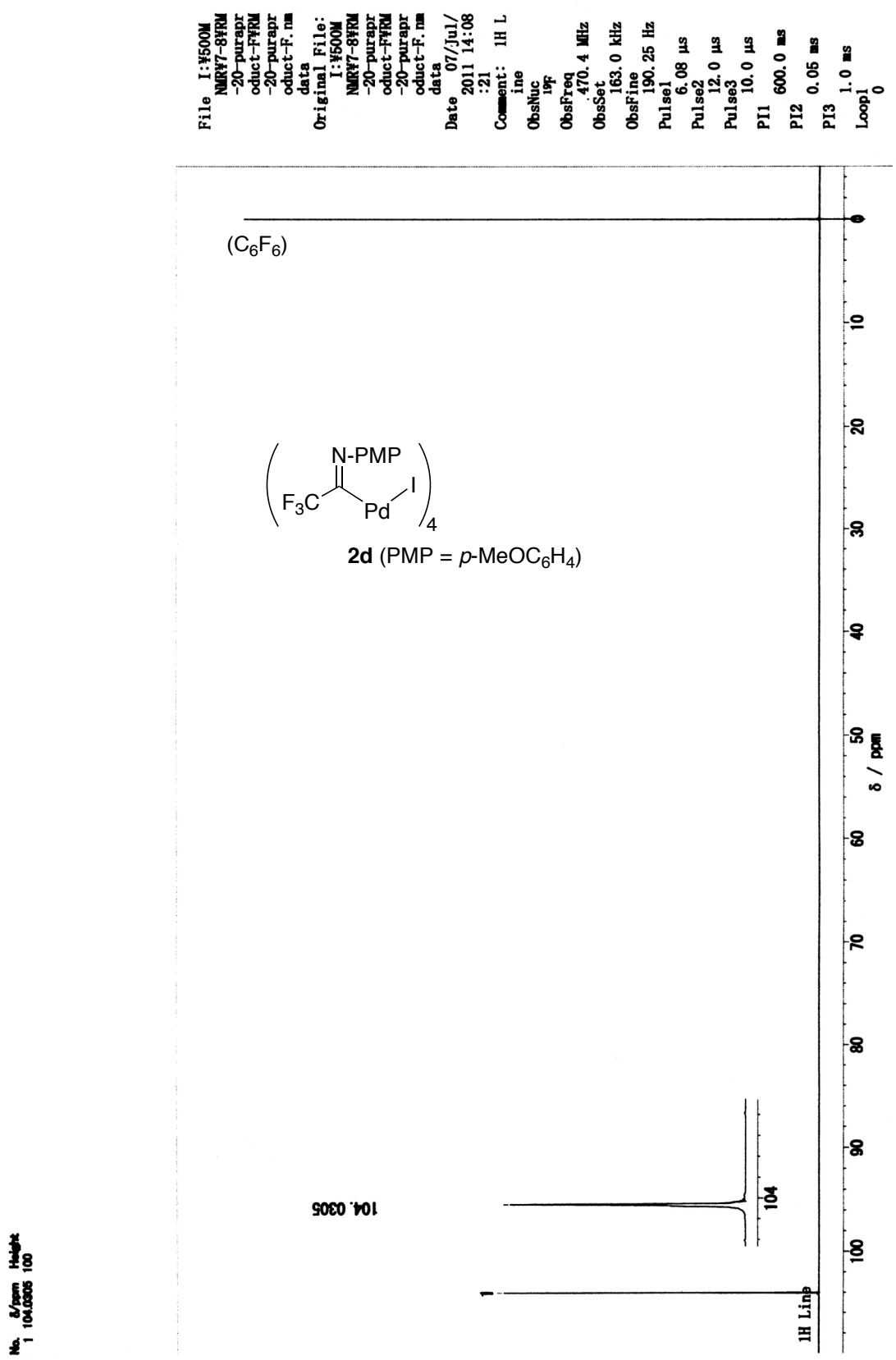

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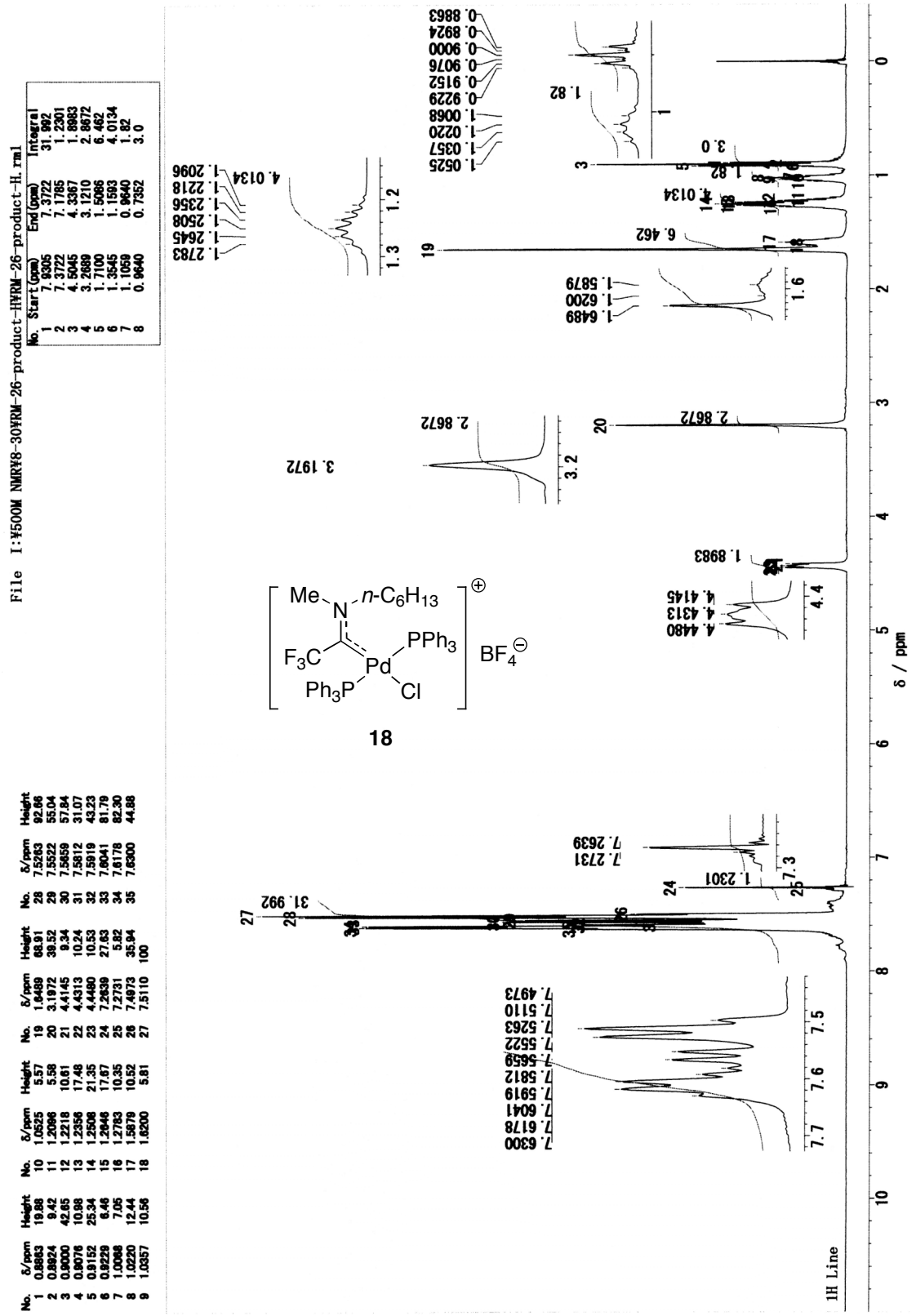

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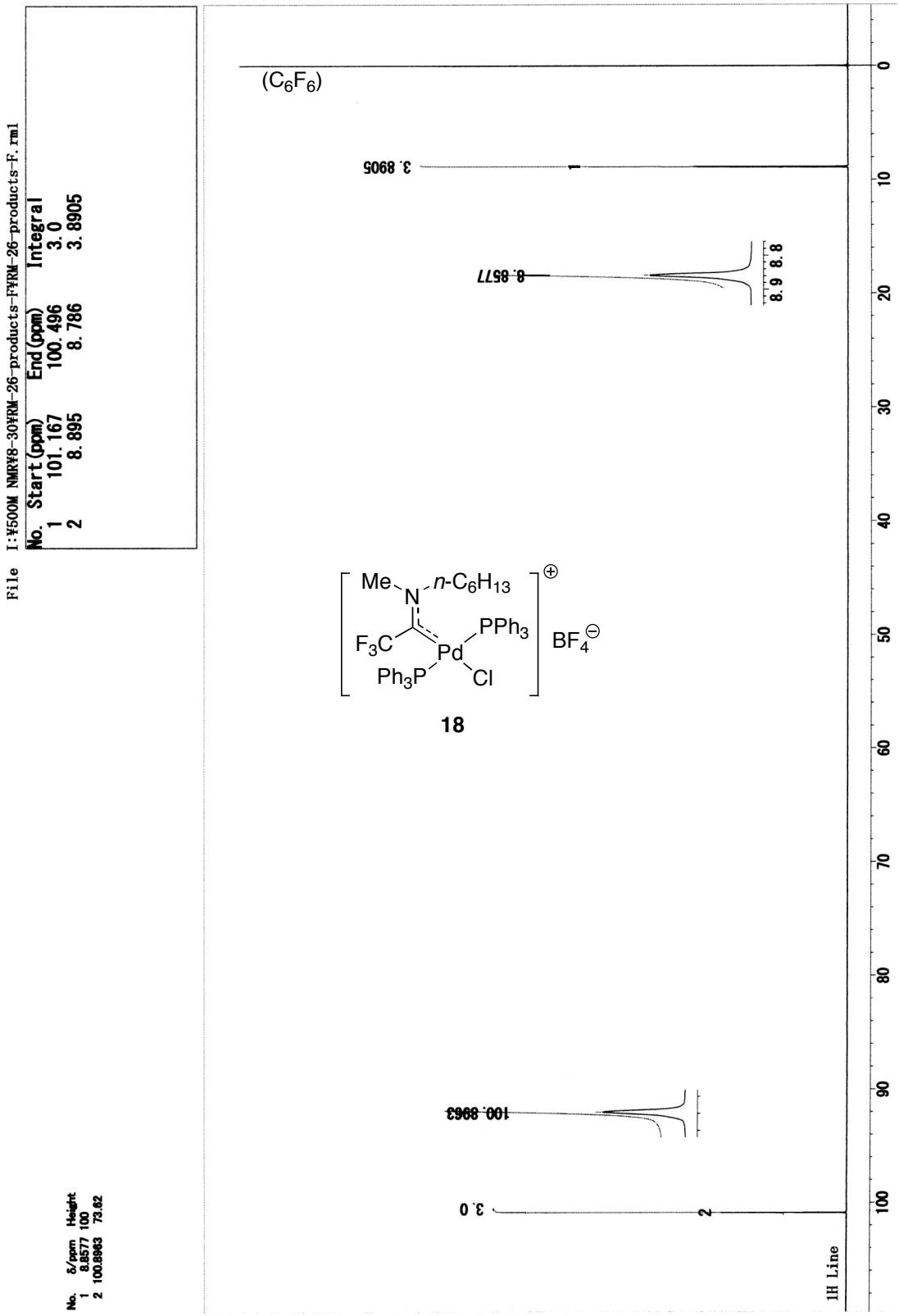
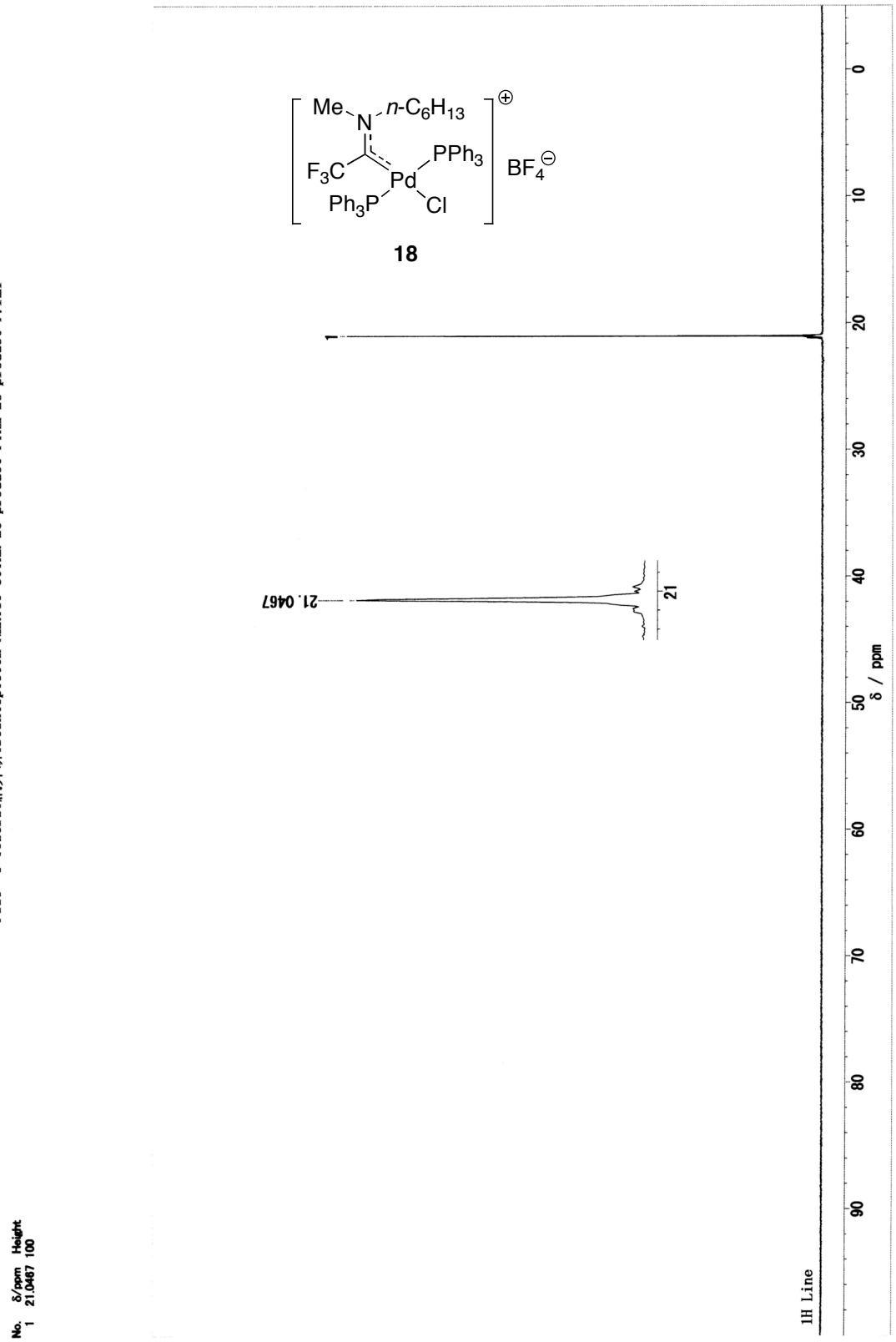


$^{31}$P NMR Spectrum of Compound **18**



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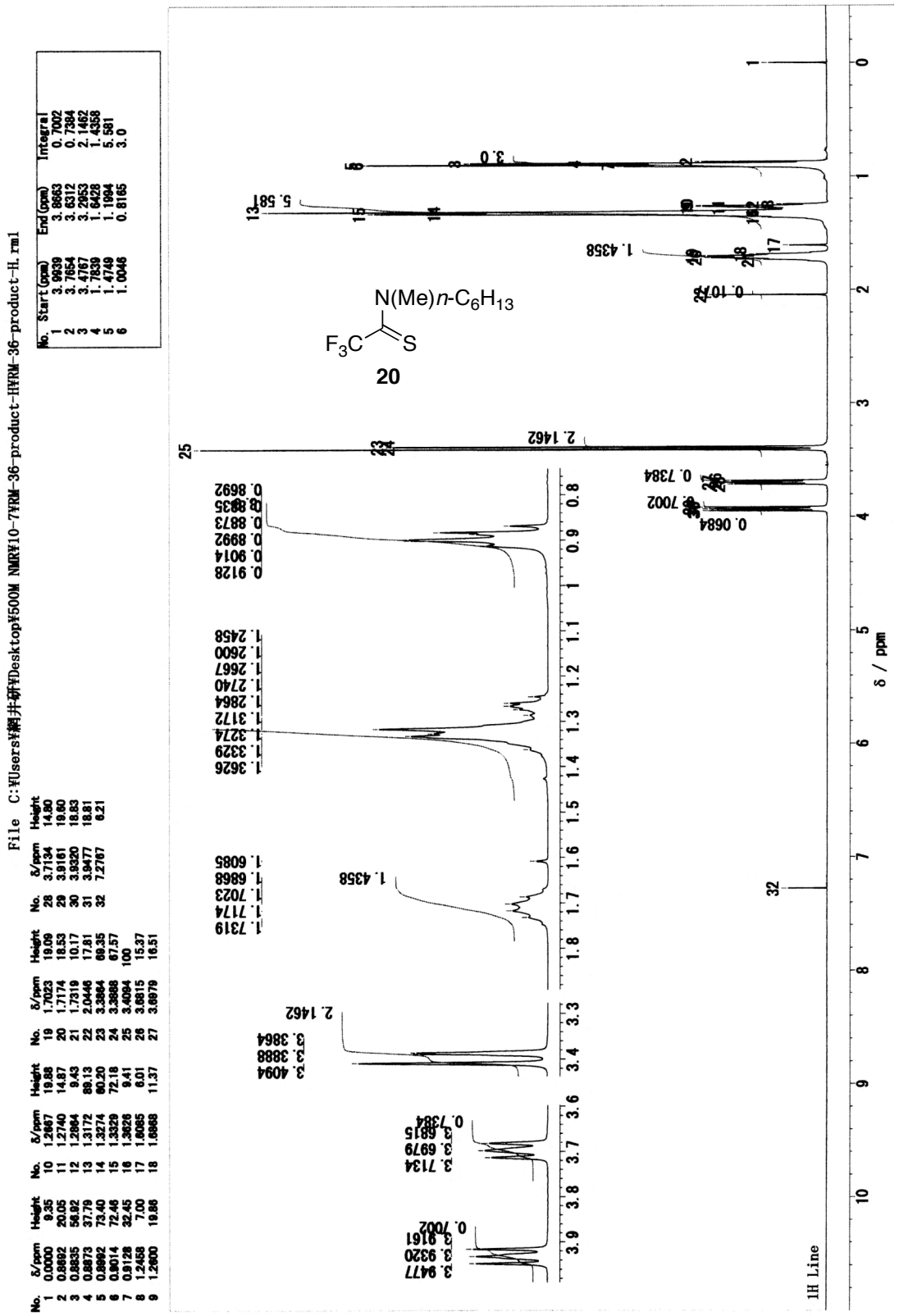

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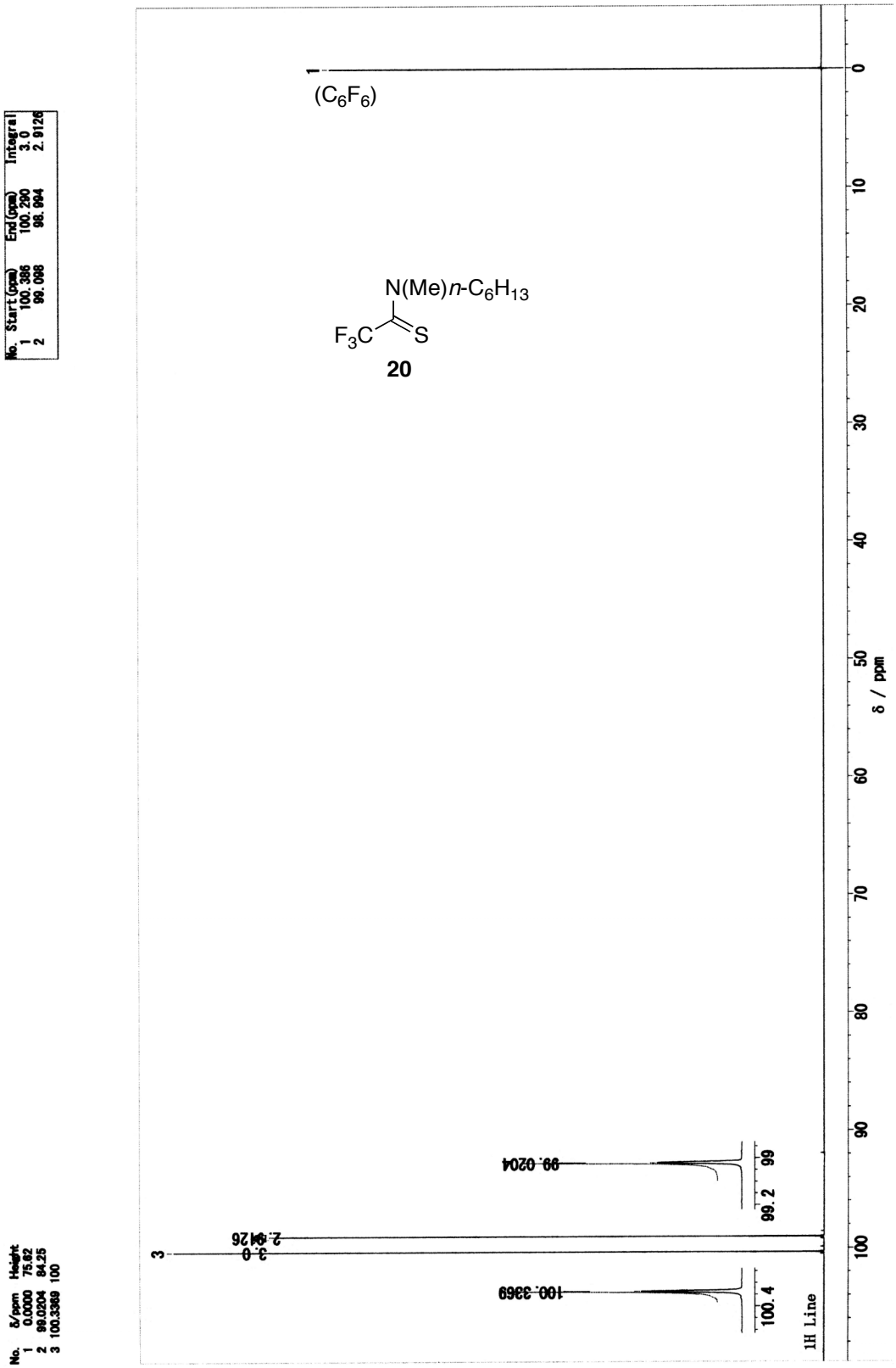

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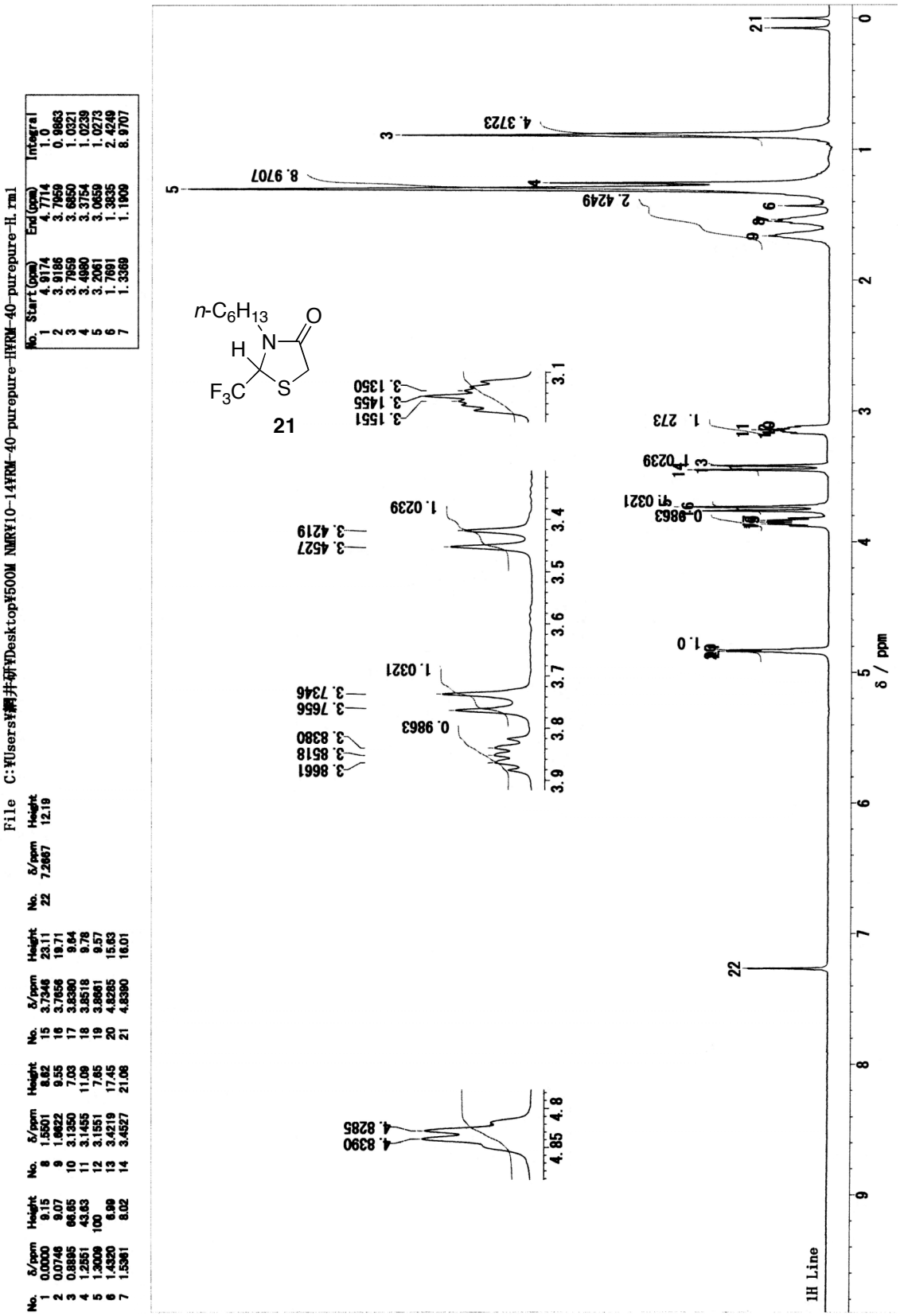

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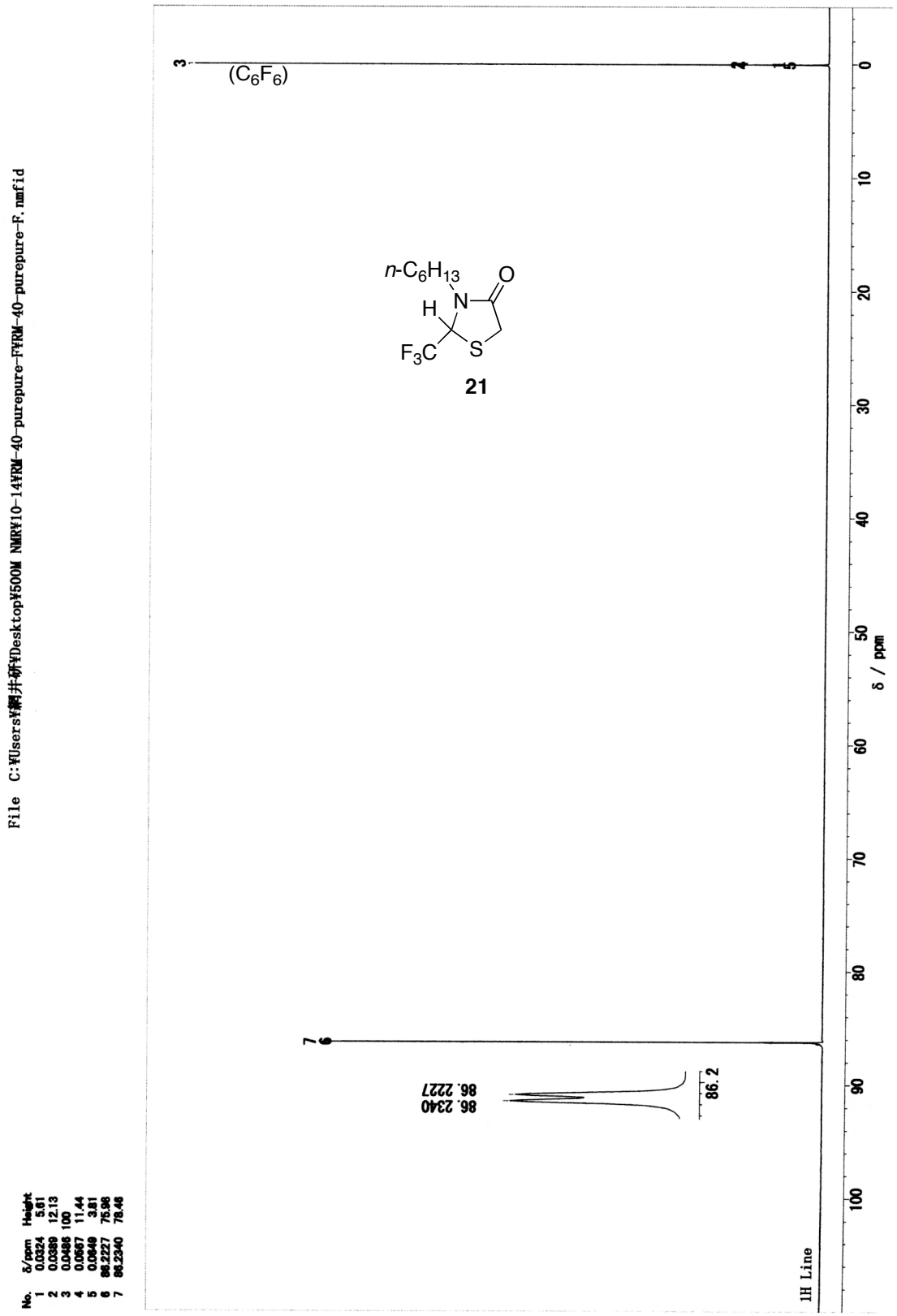

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3) Amii, H.; Kishikawa, Y.; Kageyama, K.; Uneyama, K. *J. Org. Chem.* **2000**, *65*, 3404.