

Supporting Information

**Iridium-Catalysed Borylation of Sterically Hindered C(sp³)–H bonds:
Remarkable Rate Acceleration by the Catalytic Amount of Potassium
tert-Butoxide**

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1. General

All iridium- and palladium-catalyzed reactions and homologation of **3i** were performed in glove box or using Schlenk technique under an atmosphere of nitrogen with magnetic stirring. Materials were weighed by an electric balance, Sartorius CPA225D (readability: 0.01 mg). Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm , 60 \AA). Gas chromatography (GC) was performed by Shimadzu GC-2010 (detector: FID) with Agilent J&W GC Column DB-1 (ϕ 0.32 mm x 15 m). The GC yields of all products were calculated using the relative response factors against the standard. The factors were obtained by the calibration curves, which were prepared by measurement of three samples (the product:standard ratio of 0.5:1, 1:1, and 1.5:1). ^1H NMR spectra were recorded on a Varian 400-MR (399.89 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian 400-MR (100.55 MHz) spectrometers. ^{11}B NMR spectra were recorded on a Varian 400-MR (128.30 MHz) spectrometer. ^1H NMR data were reported as follows: chemical shifts in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, and m = multiplet), coupling constant (J), and integration. ^{13}C and ^{11}B NMR data were reported in ppm downfield from tetramethylsilane (^{13}C) and $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B), respectively. High resolution mass spectra were recorded on JEOL JMS-MS700 (EI) or Thermo Scientific Exactive (APCI) spectrometers. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer.

2. Materials

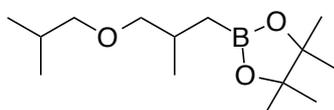
Solvents and reagents: Tetrahydrofuran (THF, **1e**, Wako) was degassed by purging with argon (15 min + 10 min) and then dried by The Ultimate Solvent System (GlassContour). Diisobutyl ether (**1a**, TCI), diisopropyl ether (**1b**, nacalai), diisopentyl ether (**1c**, TCI), di-*n*-butyl ether (**1d**, nacalai), tetrahydropyran (**1f**, TCI), triisobutylamine (**1g**, TCI), 1,3,5-triisopropylbenzene (**1h**, TCI), 2,4-dimethylpentane (**1i**, Aldrich), isooctane (**1j**, Wako), and cyclohexane (**1k**, nacalai) were distilled over calcium hydride and degassed prior to use. Bis(pinacolato)diboron (**2**) was purchased from ChemICHIBA and was purified by

recrystallization (pentane) before use. Pinacolborane was synthesized by the reported method.¹ 4-Bromotoluene (Wako) was distilled under reducing pressure. BrCH₂Cl (TCI) and *n*-BuLi (1.6 M solution in hexane, nacalai) were used as received from commercial sources.

Catalysts and ligands: [Ir(OMe)(cod)]₂ was synthesized by the method reported previously.² XPhos-Pd-G3 was purchased from Aldrich. 3,4,7,8-Tetramethyl-1,10-phenanthroline (Me₄phen, TCI), 4,7-dimethyl-1,10-phenanthroline (4,7-Me₂phen, TCI), 1,10-phenanthroline (phen, Aldrich), 4,4'-dimethyl-2,2'-bipyridine (4,4'-Me₂bpy, Aldrich), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, Aldrich), and CsOH•H₂O (nacalai) were used as received from commercial sources. *t*-BuOK (nacalai), NaOMe (Wako), Cs₂CO₃ (Wako), and CsF (Wako) were dried in vacuo (rt, 12-20 h) before use.

3. Effect of additives and ligands in iridium-catalysed borylation of **1a** (Table 1)

General Procedure: In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with [Ir(OMe)(cod)]₂ (13.3 mg, 0.020 mmol), a ligand (0.040-0.042 mmol), an additive (0-0.06 mmol), bis(pinacolato)diboron (**2**) (127 mg, 0.50 mmol), and diisobutyl ether (**1a**) (0.35 mL, 260 mg, 2.0 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 110 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 20 h, the mixture was cooled to room temperature and undecane (39 mg, 0.25 mmol, internal standard) was added. The resulting mixture was analyzed by GC to determine the yield of the borylated product **3a**.



3a

2-(3-Isobutoxy-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a, entry 6): According to the general procedure, the reaction was carried out using [Ir(OMe)(cod)]₂ (26.5 mg, 0.040 mmol),

(1) C. E. Tucker, J. Davidson and P. Knochel, *J. Org. Chem.* 1992, **57**, 3484.

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

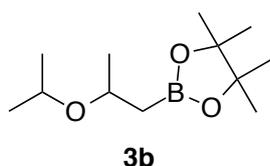
Me₄phen (19 mg, 0.080 mmol), **2** (254 mg, 1.0 mmol), and **1a** (0.69 mL, 521 mg, 4.0 mmol). The product **3a** (197 mg, 77%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 10:1). **3a**: ¹H NMR (400 MHz, CDCl₃) δ 3.11-3.21 (m, 4H), 1.92-2.05 (m, 1H), 1.84 (septet, *J* = 6.8 Hz, 1 H), 1.24 (s, 12H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 6H), 0.87 (dd, *J* = 15.6, 5.6 Hz, 1H, partially overlapped with the peaks at 0.88), 0.61 (dd, *J* = 15.6, 6.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 82.9, 78.1, 77.8, 29.8, 28.3, 24.9 [CH₃ of B(pin), 2C], 24.8 [CH₃ of B(pin), 2C], 19.44, 19.40, 16.2 (C–B, broad). ¹¹B NMR (128 MHz, CDCl₃) δ 33.4. HRMS (APCI) *m/z* calcd for C₁₄H₃₀BO₃⁺ [M + H]⁺: 257.2283, found: 257.2282.

4. Iridium-catalysed C(sp³)–H borylation with or without *t*-BuOK (Table 2)

General Procedure for the reaction without t-BuOK (General Procedure A): In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with [Ir(OMe)(cod)]₂ (0.020-0.050 mmol), Me₄phen (0.040-0.10 mmol, Ir:Me₄phen = 1:1), bis(pinacolato)diboron (**2**) (254 mg, 1.0 mmol), and an aliphatic substrate **1** (4.0 or 6.0 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 110 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 20 h, the mixture was cooled to room temperature and undecane (39 mg, 0.25 mmol, internal standard) was added. The resulting mixture was analyzed by GC to determine the yield of the borylated product.

General Procedure for the reaction with t-BuOK (General Procedure B): In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with [Ir(OMe)(cod)]₂ (0.020-0.050 mmol), Me₄phen (0.040-0.10 mmol, Ir:Me₄phen = 1:1), *t*-BuOK (0.01-0.025 mmol, Ir:*t*-BuOK = 1:0.25), bis(pinacolato)diboron (**2**) (254 mg, 1.0 mmol), and an aliphatic substrate **1** (4.0 or 6.0 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 110 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 20 h, the mixture was cooled to room

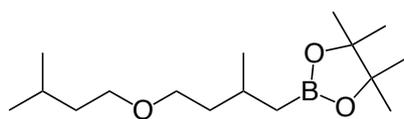
temperature and undecane (39 mg, 0.25 mmol, internal standard) was added. The resulting mixture was analyzed by GC to determine the yield of the borylated products. After removal of the volatiles including HB(pin) under reduced pressure, the crude product was purified by column chromatography on silica gel and/or bulb-to-bulb distillation. *Caution: HB(pin) is readily decomposed by protic compounds such as water and generates hydrogen gas. The collected volatile materials during the concentration process should be treated carefully with MeOH to convert HB(pin) into MeOB(pin) before throw them away.*



2-(2-Isopropoxypropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**, entry 1)

The reaction without t-BuOK: According to the *General Procedure A*, the reaction was carried out using [Ir(OMe)(cod)]₂ (19.9 mg, 0.030 mmol), Me₄phen (14.5 mg, 0.061 mmol), **2** (254 mg, 1.0 mmol), and diisopropyl ether (**1b**) (0.84 mL, 613 mg, 6.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3b** in 10% yield.

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (19.9 mg, 0.030 mmol), Me₄phen (14.5 mg, 0.061 mmol), *t*-BuOK (1.7 mg, 0.015 mmol), **2** (254 mg, 1.0 mmol), and **1b** (0.84 mL, 613 mg, 6.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3b** in 96% yield. The product **3b** (162 mg, 71%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 10:1). **3b**: ¹H NMR (400 MHz, C₆D₆) δ 3.87-3.95 (m, 1H), 3.58 (septet, *J* = 6.0 Hz, 1H), 1.41 (dd, *J* = 15.2, 6.0 Hz, 1H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.22 (dd, *J* = 15.2, 7.6 Hz, 1H), 1.14 (d, *J* = 6.0 Hz, 3H), 1.10 (d, *J* = 6.0 Hz, 3H), 1.07, (s, 12H). ¹³C NMR (101 MHz, C₆D₆) δ 82.8, 70.0, 68.0, 25.0 [CH₃ of B(pin), 2C], 24.8 [CH₃ of B(pin), 2C], 23.3 (CH₃ of *i*-Pr, 1C), 23.2 (CH₃ of *i*-Pr, 1C), 23.0, 21.7 (C–B, broad). ¹¹B NMR (128 MHz, C₆D₆) δ 33.1. HRMS (APCI) *m/z* calcd for C₁₂H₂₆BO₃⁺ [M + H]⁺: 229.1970, found: 229.1967.

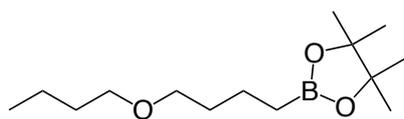


3c

2-[4-(Isopentyloxy)-2-methylbutyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**, entry 2)

*The reaction without *t*-BuOK:* According to the *General Procedure A*, the reaction was carried out using $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (26.5 mg, 0.040 mmol), Me_4phen (19 mg, 0.080 mmol), **2** (254 mg, 1.0 mmol), and diisopentyl ether (**1c**) (0.81 mL, 633 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3c** in 15% yield.

*The reaction with *t*-BuOK:* According to the *General Procedure B*, the reaction was carried out using $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (26.5 mg, 0.040 mmol), Me_4phen (19 mg, 0.080 mmol), *t*-BuOK (2.2 mg, 0.020 mmol), **2** (254 mg, 1.0 mmol), and **1c** (0.81 mL, 633 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3c** in 73% yield. The product **3c** (179 mg, 63%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 10:1). **3c**: ¹H NMR (400 MHz, CDCl₃) δ 3.36-3.45 (m, 4H), 1.77-1.86 (m, 1H), 1.68 (septet, *J* = 6.8 Hz, 1H), 1.52-1.62 (m, 1H), 1.39-1.51 (m, 3H), 1.24 (s, 12H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 6H), 0.86 (dd, *J* = 15.6, 5.6 Hz, 1H, partially overlapped with the peaks at 0.89), 0.67 (dd, *J* = 15.6, 8.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 82.9, 69.4, 69.2, 39.1, 38.6, 26.7, 25.1, 24.9 [CH₃ of B(pin), 2C], 24.8 [CH₃ of B(pin), 2C], 22.7, 22.4, 19.7 (C–B, broad). ¹¹B NMR (128 MHz, CDCl₃) δ 33.3. HRMS (APCI) *m/z* calcd for C₁₆H₃₄BO₃⁺ [M + H]⁺: 285.2596, found: 285.2593.



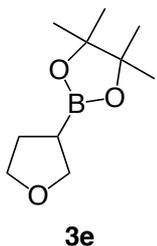
3d

2-(4-Butoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**, entry 3)

*The reaction without *t*-BuOK:* According to the *General Procedure A*, the reaction was carried out using $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (19.9 mg, 0.030 mmol), Me_4phen (14.5 mg, 0.061 mmol), **2** (254 mg, 1.0 mmol),

and di-*n*-butyl ether (**1d**) (0.68 mL, 521 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3d** in 13% yield.

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (19.9 mg, 0.030 mmol), Me₄phen (14.5 mg, 0.061 mmol), *t*-BuOK (1.7 mg, 0.015 mmol), **2** (254 mg, 1.0 mmol), and **1d** (0.68 mL, 521 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3d** in 88% yield. The product **3d** (192 mg, 75%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 10:1). **3d**³: ¹H NMR (400 MHz, CDCl₃) δ 3.389 (t, *J* = 6.8 Hz, 2H), 3.386 (t, *J* = 6.8 Hz, 2H), 1.50-1.62 (m, 4H), 1.41-1.50 (m, 2H), 1.31-1.41 (m, 2H), 1.24 (s, 12H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 82.9, 70.7, 70.6, 32.3, 31.9, 24.8, 20.6, 19.4, 13.9, 10.9 (C–B, broad). ¹¹B NMR (128 MHz, CDCl₃) δ 33.5. HRMS (APCI) *m/z* calcd for C₁₄H₃₀BO₃⁺ [M + H]⁺: 257.2283, found: 257.2286.



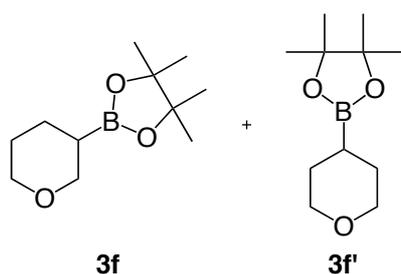
4,4,5,5-Tetramethyl-2-(tetrahydrofuran-3-yl)-1,3,2-dioxaborolane (**3e**, entry 4)

The reaction without t-BuOK: According to the *General Procedure A*, the reaction was carried out using [Ir(OMe)(cod)]₂ (13 mg, 0.020 mmol), Me₄phen (9.5 mg, 0.040 mmol), **2** (254 mg, 1.0 mmol), and tetrahydrofuran (**1e**) (0.49 mL, 433 mg, 6.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3e** in 87% yield.

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (13 mg, 0.020 mmol), Me₄phen (9.5 mg, 0.040 mmol), *t*-BuOK (1.1 mg, 0.010 mmol), **2** (254 mg, 1.0 mmol), and **1e** (0.49 mL, 433 mg, 6.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3e** in 109% yield, indicating that HB(pin) formed as a byproduct also

(3) H. Chen and J. F. Hartwig, *Angew. Chem. Int. Ed.* 1999, **38**, 3391.

participated in the C–H borylation. The product **3e** (174 mg, 88%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 5:1). **3e**⁴: ¹H NMR (400 MHz, CDCl₃) δ 3.99 (t, *J* = 8.0 Hz, 1H), 3.81 (td, *J* = 8.0, 4.0 Hz, 1H), 3.70 (dt, *J* = 8.0, 7.2 Hz, 1H), 3.61 (dd, *J* = 10.0, 8.0 Hz, 1H), 1.98-2.10 (m, 1H), 1.78-1.87 (m, 1H), 1.55-1.65 (m, 1H), 1.25 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 83.3, 70.2, 68.4, 28.7, 24.7, 22.8 (C–B, broad). ¹¹B NMR (128 MHz, CDCl₃) δ 33.3. HRMS (APCI) *m/z* calcd for C₁₀H₂₀BO₃⁺ [M + H]⁺: 199.1500, found: 199.1505.



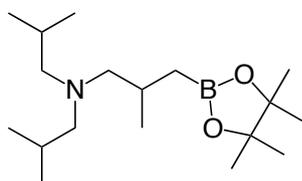
4,4,5,5-Tetramethyl-2-(tetrahydro-2H-pyran-3-yl)-1,3,2-dioxaborolane (3f) and 4,4,5,5-tetramethyl-2-(tetrahydro-2H-pyran-4-yl)-1,3,2-dioxaborolane (3f') (entry 5)

The reaction without t-BuOK: According to the *General Procedure A*, the reaction was carried out using [Ir(OMe)(cod)]₂ (19.9 mg, 0.030 mmol), Me₄phen (14.5 mg, 0.061 mmol), **2** (254 mg, 1.0 mmol), and tetrahydropyran (**1f**) (0.58 mL, 517 mg, 6.0 mmol). GC analysis of the crude reaction mixture indicated the formation of a mixture of **3f** and **3f'** in 35% yield. The ratio of **3f**:**3f'** was determined as 92:8 by ¹H NMR analysis (in C₆D₆) after purification by column chromatography on silica gel (hexane:Et₂O = 5:1).

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (19.9 mg, 0.030 mmol), Me₄phen (14.5 mg, 0.061 mmol), *t*-BuOK (1.7 mg, 0.015 mmol), **2** (254 mg, 1.0 mmol), and **1f** (0.58 mL, 517 mg, 6.0 mmol). GC analysis of the crude reaction mixture indicated the formation of a mixture of **3f** and **3f'** in 87% yield. The products (172 mg, 81%, **3f**:**3f'** = 92:8) was obtained as a colorless liquid after purification by column chromatography on silica gel

(4) C. W. Liskey and J. F. Hartwig, *J. Am. Chem. Soc.* 2012, **134**, 12422.

(hexane:Et₂O = 5:1). The ratio of **3f** and **3f'** was determined by ¹H NMR analysis in C₆D₆. **3f**⁴: ¹H NMR (400 MHz, CDCl₃) δ 3.79-3.93 (m, 2H), 3.42-3.55 (m, 2H), 1.79-1.87 (m, 1H), 1.48-1.66 (m, 3H), 1.28-1.40 (m, 1H), 1.23 (s, 12H). ¹H NMR (400 MHz, C₆D₆) δ 4.11 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.72-3.84 (m, 2H), 3.41-3.48 (m, 1H), 1.80-1.88 (m, 1H), 1.60-1.73 (m, 1H), 1.37-1.55 (m, 3H), 1.02 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 83.1, 69.7, 68.5, 26.7, 24.9, 24.74 [CH₃ of B(pin), 2C], 24.66 [CH₃ of B(pin), 2C], 22.6 (C–B, broad). ¹¹B NMR (128 MHz, CDCl₃) δ 32.6. HRMS (APCI) *m/z* calcd for C₁₁H₂₂BO₃⁺ [M + H]⁺: 213.1657, found: 213.1656. **3f'**⁵: The authentic sample of **3f'** was prepared via the reaction of 4-bromotetrahydropyran (Frontier Scientific) with **2** in the presence of a CuCl/Xantphos catalyst with *t*-BuOK.⁶ ¹H NMR (400 MHz, CDCl₃) δ 3.82 (dt, *J* = 11.2, 4.0 Hz, 2H), 3.46 (dt, *J* = 11.2, 6.4 Hz, 2H), 1.58-1.64 (m, 4H), 1.16-1.28 (m, 1H), 1.24 (s, 12H). ¹H NMR (400 MHz, C₆D₆) δ 3.87 (dt, *J* = 11.2, 4.0 Hz, 2H), 3.41-3.47 (m, 2H), 1.75-1.84 (m, 2H), 1.60-1.68 (m, 2H), 1.16-1.26 (m, 1H), 1.03 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 83.1, 68.8, 27.6, 24.7, 18.9 (C–B, broad).



3g

2-[3-(Diisobutylamino)-2-methylpropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**, entry 6)

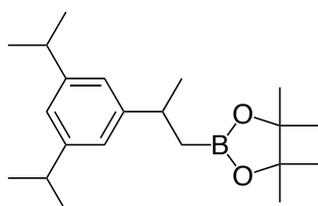
The reaction without t-BuOK: According to the *General Procedure A*, the reaction was carried out using [Ir(OMe)(cod)]₂ (26.5 mg, 0.040 mmol), Me₄phen (19 mg, 0.080 mmol), **2** (254 mg, 1.0 mmol), and triisobutylamine (**1g**) (0.96 mL, 741 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3g** in 17% yield.

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (26.5 mg, 0.040 mmol), Me₄phen (19 mg, 0.080 mmol), *t*-BuOK (2.2 mg, 0.020 mmol),

(5) S. K. Bose, K. Fucke, L. Liu, P. G. Steel and T. B. Marder, *Angew. Chem. Int. Ed.* 2014, **53**, 1799.

(6) H. Ito and K. Kubota, *Org. Lett.* 2012, **14**, 890.

2 (254 mg, 1.0 mmol), and **1g** (0.96 mL, 741 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3g** in 69% yield. The product **3g** (199 mg, 64%) was obtained as a colorless liquid after purification by bulb-to-bulb distillation (0.2 mmHg, 50 °C to 90 °C). **3g**: ¹H NMR (400 MHz, C₆D₆) δ 1.99-2.25 (m, 7H), 1.71 (septet, *J* = 6.8 Hz, 2H), 1.26 (dd, *J* = 15.6, 4.4 Hz, 1H), 1.18 (d, *J* = 6.0 Hz, 3H), 1.08 (s, 12H), 0.95 (d, *J* = 6.8 Hz, 6H), 0.92 (d, *J* = 6.8 Hz, 6H), 0.86 (dd, *J* = 15.6, 8.0 Hz, 1H). ¹³C NMR (101 MHz, C₆D₆) δ 82.7, 65.6, 65.0, 28.5, 26.8, 25.0 [CH₃ of B(pin), 2C], 24.9 [CH₃ of B(pin), 2C], 21.2, 21.1, 18.2 (C–B, broad). ¹¹B NMR (128 MHz, C₆D₆) δ 33.8. HRMS (APCI) *m/z*. calcd for C₁₈H₃₉BNO₂⁺ [M + H]⁺: 312.2068, found: 312.3058.



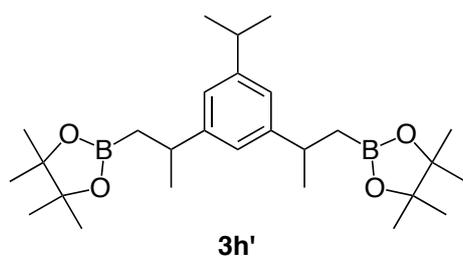
3h

2-[2-(3,5-Diisopropylphenyl)propyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**, entry 7)

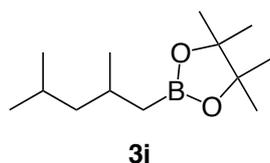
The reaction without t-BuOK: According to the *General Procedure A*, the reaction was carried out using [Ir(OMe)(cod)]₂ (26.5 mg, 0.040 mmol), Me₄phen (19 mg, 0.080 mmol), **2** (254 mg, 1.0 mmol), and 1,3,5-triisopropylbenzene (**1h**) (0.96 mL, 817 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3h** in 17% yield.

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (26.5 mg, 0.040 mmol), Me₄phen (19 mg, 0.080 mmol), *t*-BuOK (2.2 mg, 0.020 mmol), **2** (254 mg, 1.0 mmol), and **1h** (0.96 mL, 817 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3h** (86% yield) with formation of diborylated product **3h'** (5% yield, see below). The product **3h** (281 mg, 85%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 20:1). **3h**: ¹H NMR (400 MHz, C₆D₆) δ 7.09 (d, *J* = 1.6 Hz, 2H), 6.97 (t, *J* = 1.6 Hz, 1H), 3.28 (sextet, *J* = 7.2 Hz, 1H), 2.81 (septet, *J* = 6.8 Hz, 2H), 1.46 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.36 (dd, *J* = 15.6 Hz, 8.0 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 12H),

1.00 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 149.7, 148.8, 122.7, 122.2, 82.7, 36.6, 34.8, 25.6. 24.9 [CH_3 of B(pin), 2C], 24.8 [CH_3 of B(pin), 2C], 24.44 (CH_3 of *i*-Pr, 2C), 24.38 (CH_3 of *i*-Pr, 2C), 21.8 (C–B, broad). ^{11}B NMR (128 MHz, C_6D_6) δ 33.3. HRMS (APCI) m/z calcd for $\text{C}_{21}\text{H}_{36}\text{BO}_2^+$ [$\text{M} + \text{H}$] $^+$: 331.2803, found: 331.2798.



1,3-Bis[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propyl]-5-isopropylbenzene (3h'): The titled compound **3h'** was obtained as a diastereomer mixture (ca 1:1) by column chromatography on silica gel (hexane:Et₂O = 10:1). **3h'**: ^1H NMR (400 MHz, C_6D_6) δ 7.16 (s, 1H, overlapped with C_6H_6 in C_6D_6), 7.06 (d, $J = 1.2$ Hz, 2H), 3.22-3.33 (m, 2H), 2.81 (septet, $J = 6.8$ Hz, 1H), 1.45 (dd, $J = 15.6, 7.2$ Hz, 2H), 1.420 (d, $J = 6.8$ Hz, 3H), 1.418 (d, $J = 6.8$ Hz, 3H), 1.35 (dd, $J = 15.6, 8.0$ Hz, 2H), 1.25 (d, $J = 6.8$ Hz, 6H), 1.00 (s, 24H). A single set of peaks was observed despite of a diastereomer mixture (ca. 1:1). ^{13}C NMR (101 MHz, C_6D_6) δ 149.5, 148.61, 148.60, 123.1, 123.0, 122.60, 122.57, 82.7, 36.5, 34.8, 25.5, 25.4, 24.89, 24.86, 24.5, 24.41, 24.35, 21.9 (C–B, broad). Two sets of peaks were observed corresponding to the diastereomers. ^{11}B NMR (128 MHz, C_6D_6) δ 32.9. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{47}\text{B}_2\text{O}_4^+$ [$\text{M} + \text{H}$] $^+$: 457.3655, found: 457.3656.

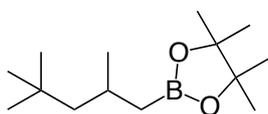


2-(2,4-Dimethylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i, entry 8)

The reaction without t-BuOK: According to the *General Procedure A*, the reaction was carried out using $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (33 mg, 0.050 mmol), Me_4phen (24 mg, 0.10 mmol), **2** (254 mg, 1.0 mmol), and

2,4-dimethylpentane (**1i**) (0.59 mL, 401 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3i** in 26% yield.

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (33 mg, 0.050 mmol), Me₄phen (24 mg, 0.10 mmol), *t*-BuOK (2.8 mg, 0.025 mmol), **2** (254 mg, 1.0 mmol), and **1i** (0.59 mL, 401 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3i** in 71% yield. The product **3i** (152 mg, 67%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 20:1) and bulb-to-bulb distillation (50 °C/0.2 mmHg) to remove the high-boiling-point materials. **3i**: ¹H NMR (400 MHz, CDCl₃) δ 1.70-1.81 (m, 1H), 1.54-1.67 (m, 1H), 1.25 (s, 12H), 1.01-1.12 (m, 2H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 3H), 0.80 (dd, *J* = 15.2, 6.4 Hz, 1H), 0.62 (dd, *J* = 15.2, 8.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 82.8, 49.4, 27.1, 25.5, 24.9 [CH₃ of B(pin), 2C], 24.8 [CH₃ of B(pin), 2C], 23.3, 22.4, 20.2 (C–B, broad). ¹¹B NMR (128 MHz, CDCl₃) δ 33.5. HRMS (APCI) *m/z* calcd for C₁₃H₂₈BO₂⁺ [M + H]⁺: 227.2177, found: 227.2176.



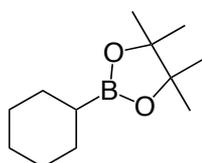
3j

4,4,5,5-Tetramethyl-2-(2,4,4-trimethylpentyl)-1,3,2-dioxaborolane (3j, entry 9)

The reaction without t-BuOK: According to the *General Procedure A*, the reaction was carried out using [Ir(OMe)(cod)]₂ (33 mg, 0.050 mmol), Me₄phen (24 mg, 0.10 mmol), **2** (254 mg, 1.0 mmol), and isooctane (**1j**) (0.66 mL, 457 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3j** in 10% yield.

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (33 mg, 0.050 mmol), Me₄phen (24 mg, 0.10 mmol), *t*-BuOK (2.8 mg, 0.025 mmol), **2** (254 mg, 1.0 mmol), and **1j** (0.66 mL, 457 mg, 4.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3j** in 45% yield. The product **3j** (101 mg, 42%) was obtained as a colorless

liquid after purification by column chromatography on silica gel (hexane:Et₂O = 20:1) and bulb-to-bulb distillation (50 °C/0.2 mmHg) to remove the high-boiling-point materials. **3j**: ¹H NMR (400 MHz, CDCl₃) δ 1.75-1.88 (m, 1H), 1.24 (s, 12H), 1.22 (dd, *J* = 14.0, 4.4 Hz, 1H, partially overlapped with the peaks at 1.24), 1.12 (dd, *J* = 14.0, 6.8 Hz, 1H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 9H), 0.85 (dd, *J* = 15.2, 6.0 Hz, 1H), 0.70 (dd, *J* = 15.2, 8.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 82.8, 53.7, 31.1, 30.2, 26.1, 25.1, 24.9 [CH₃ of B(pin), 2C], 24.8 [CH₃ of B(pin), 2C], 22.8 (C–B, broad). ¹¹B NMR (128 MHz, CDCl₃) δ 33.2. HRMS (APCI) *m/z* calcd for C₁₄H₃₀BO₂⁺ [M + H]⁺: 241.2333, found: 241.2331.



3k

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3k**, entry 10)

The reaction without t-BuOK: According to the *General Procedure A*, the reaction was carried out using [Ir(OMe)(cod)]₂ (33 mg, 0.050 mmol), Me₄phen (24 mg, 0.10 mmol), **2** (254 mg, 1.0 mmol), and cyclohexane (**1k**) (0.65 mL, 505 mg, 6.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3k** in 8% yield.

The reaction with t-BuOK: According to the *General Procedure B*, the reaction was carried out using [Ir(OMe)(cod)]₂ (33 mg, 0.050 mmol), Me₄phen (24 mg, 0.10 mmol), *t*-BuOK (2.8 mg, 0.025 mmol), **2** (254 mg, 1.0 mmol), and **1k** (0.65 mL, 505 mg, 6.0 mmol). GC analysis of the crude reaction mixture indicated the formation of **3k** in 42% yield. The product **3k** (80 mg, 38%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 20:1) and bulb-to-bulb distillation (50 °C/0.2 mmHg) to remove the high-boiling-point materials. **3i**^{5,6}: ¹H NMR (400 MHz, CDCl₃) δ 1.50-1.72 (m, 5H), 1.18-1.39 (m, 5H), 1.22 (s, 12H), 0.92-1.02 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 82.7, 28.0, 27.1, 26.8, 24.7, 22.0 (C–B, broad). ¹¹B NMR (128 MHz, CDCl₃) δ 33.6. HRMS (APCI) *m/z* calcd for C₁₂H₂₄BO₂⁺ [M + H]⁺: 211.1864, found: 211.1864.

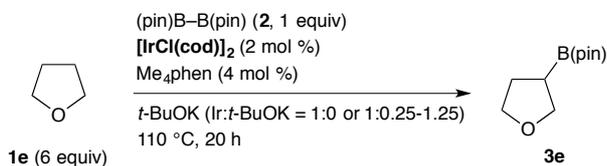
5. Gram-scale synthesis of **3a** (eq 1)

A 50 mL two-necked, round-bottomed flask, equipped with a Dimroth condenser and a magnetic stirring bar, was charged with **2** (2.54 g, 10.0 mmol), [Ir(OMe)(cod)]₂ (265 mg, 0.40 mmol), and Me₄phen (199 mg, 0.84 mmol). The flask was evacuated and backfilled with nitrogen. **1a** (6.9 mL, 5.2 g, 40.0 mmol) was added to the flask. The resulting mixture was reacted at 110 °C using an oil bath with stirring for 20 h. After cooling to room temperature, volatiles were removed in vacuo. The product **3a** (1.9 g, 74%) was obtained as a colorless liquid after purification by column chromatography on silica gel (hexane:Et₂O = 10:1).

6. C–H borylation of **1e** using [IrCl(cod)]₂ as a catalyst precursor (Table S1)

The C(sp³)–H borylation of THF (**1e**) was examined using [IrCl(cod)]₂ as a catalyst precursor. The results are summarized in Table S1. As expected, low catalyst activity was observed in the absence of *t*-BuOK (entry 1), while in the presence of *t*-BuOK (Ir:*t*-BuOK = 1:0.95) the borylation took place more efficiently by formation of the alkoxyiridium species in situ, giving **3e** in reasonable yield (74%, entry 3). Use of the chloride with *t*-BuOK with the ratio of 1:1.25 resulted in formation of **3e** in 104% yield based on **2** (entry 4). This catalyst efficiency is comparable to that observed with [Ir(OMe)(cod)]₂ (entry 4, Table 2).

Table S1. C(sp³)–H borylation of **1e** using [IrCl(cod)]₂ as a catalyst precursor^a

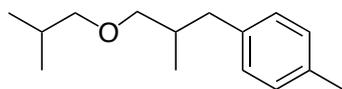


entry	<i>t</i> -BuOK (mmol)	<i>t</i> -BuOK/Ir	yield (%) ^b
1	0	0	8
2	1	0.25	14
3	3.8	0.95	74
4	5	1.25	104

^a **1e** (6.0 mmol), **2** (1.0 mmol), [IrCl(cod)]₂ (0.020 mmol), Me₄phen (Ir:Me₄phen = 1:1), and *t*-BuOK (Ir:*t*-BuOK = 1:0-1.25) were stirred at 110 °C for 20 h. ^b GC yield based on **2** (average of two runs).

7. Synthetic conversion of borylated products **3a** and **3i** (eqs 2 and 3)

Suzuki-Miyaura coupling of 3a with 4-bromotoluene to give 4 (eq 2): In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with XPhos-Pd-G3 (17 mg, 0.020 mmol), CsOH•H₂O (101 mg, 0.60 mmol), THF (1 mL), **3a** (51 mg, 0.20 mmol), 4-bromotoluene (51 mg, 0.30 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The stopcock was removed temporarily under nitrogen flow. Degassed water (0.10 mL) was added to the tube and the tube was sealed by the stopcock again. The mixture was reacted at 110 °C for 24 h. After cooling to room temperature, water (10 mL) was added to the tube. The organic materials were extracted with ether (10 mL x 3), and the combined organic layer was washed with water (1 mL x 3), washed with brine (1 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles under reduced pressure, the crude product was purified by column chromatography on silica gel (hexane:Et₂O = 20:1) and bulb-to-bulb distillation (70 °C/0.2 mmHg, to remove the high-boiling-point materials) to afford **4** (27 mg, 61%) as a colorless oil.

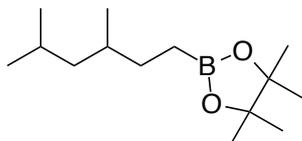


4

1-(3-Isobutyloxy-2-methylpropyl)-4-methylbenzene (4): ¹H NMR (400 MHz, CDCl₃) δ 7.09 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.25 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.20 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.16 (d, *J* = 6.8 Hz, 2H) 2.74 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.35 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.32 (s, 3H), 1.95-2.04 (m, 1H), 1.84 (septet, *J* = 6.8 Hz, 1H), 0.919 (d, *J* = 6.8 Hz, 3H), 0.916 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.8, 135.1, 129.1, 128.8, 77.8, 75.6, 39.5, 35.5, 28.5, 21.0, 19.5 (CH₃ of *i*-Bu, 1C), 19.4 (CH₃ of *i*-Bu, 1C), 16.8. HRMS (APCI) *m/z* calcd for C₁₅H₂₅O⁺ [M + H]⁺: 221.1900, found: 221.1899. IR (neat) 1109 (ν_{C-O-C}) cm⁻¹.

Homologation of 3i to give 5 (eq 3): A Schlenk tube equipped with a magnetic stirring bar, was evacuated and backfilled with nitrogen. THF (0.6 mL), BrCH₂Cl (52 mg, 0.40 mmol), and **3i** (45mg, 0.20

mmol) were added to the tube, and the tube was cooled to $-78\text{ }^{\circ}\text{C}$ by dry ice-acetone bath. A hexane solution of *n*-BuLi (1.6 M, 0.25 mL, 0.40 mmol) was added slowly to the mixture via syringe and the resulting solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 0.5 h. The dry ice-acetone bath was removed and the mixture was stirred at room temperature for 12 h. Water (1.0 mL) was added to the tube. The organic materials were extracted with hexane, and dried over anhydrous magnesium sulfate. After removal of the volatiles under reduced pressure, product **5** (44 mg, 92%) was obtained as a colorless liquid.



5

2-(3,5-Dimethylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5): ^1H NMR (400 MHz, CDCl_3) δ 1.58-1.68 (m, 1H), 1.35-1.45 (m, 2H), 1.24 (s, 12H), 1.08-1.22 (m, 2H), 0.92-1.00 (m, 1H), 0.86 (d, $J = 6.4$ Hz, 3H), 0.822 (d, $J = 6.8$ Hz, 6H), 0.62-0.80 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 82.8, 46.4, 32.4, 31.3, 25.2, 24.82 [CH_3 of B(pin), 2C], 24.80 [CH_3 of B(pin), 2C], 23.4 [$\text{CH}(\text{CH}_3)_2$, 1C], 22.3 [$\text{CH}(\text{CH}_3)_2$, 1C], 19.3, 8.3 (C–B, broad). ^{11}B NMR (128 MHz, CDCl_3) δ 33.7. HRMS (EI, positive) m/z calcd for $\text{C}_{14}\text{H}_{29}\text{BO}_2$ [M]: 240.2261, found: 240.2266.

8. ^1H and ^{13}C NMR spectra of products

^1H and ^{13}C NMR spectra of **3a-3f**, **3f'**, **3g-3h**, **3h'**, **3i-3k**, **4**, and **5** are given in following pages.

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Solvent: cdd13

Ambient temperature

Operator: vnmr1

File: TTI247

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24 repetitions

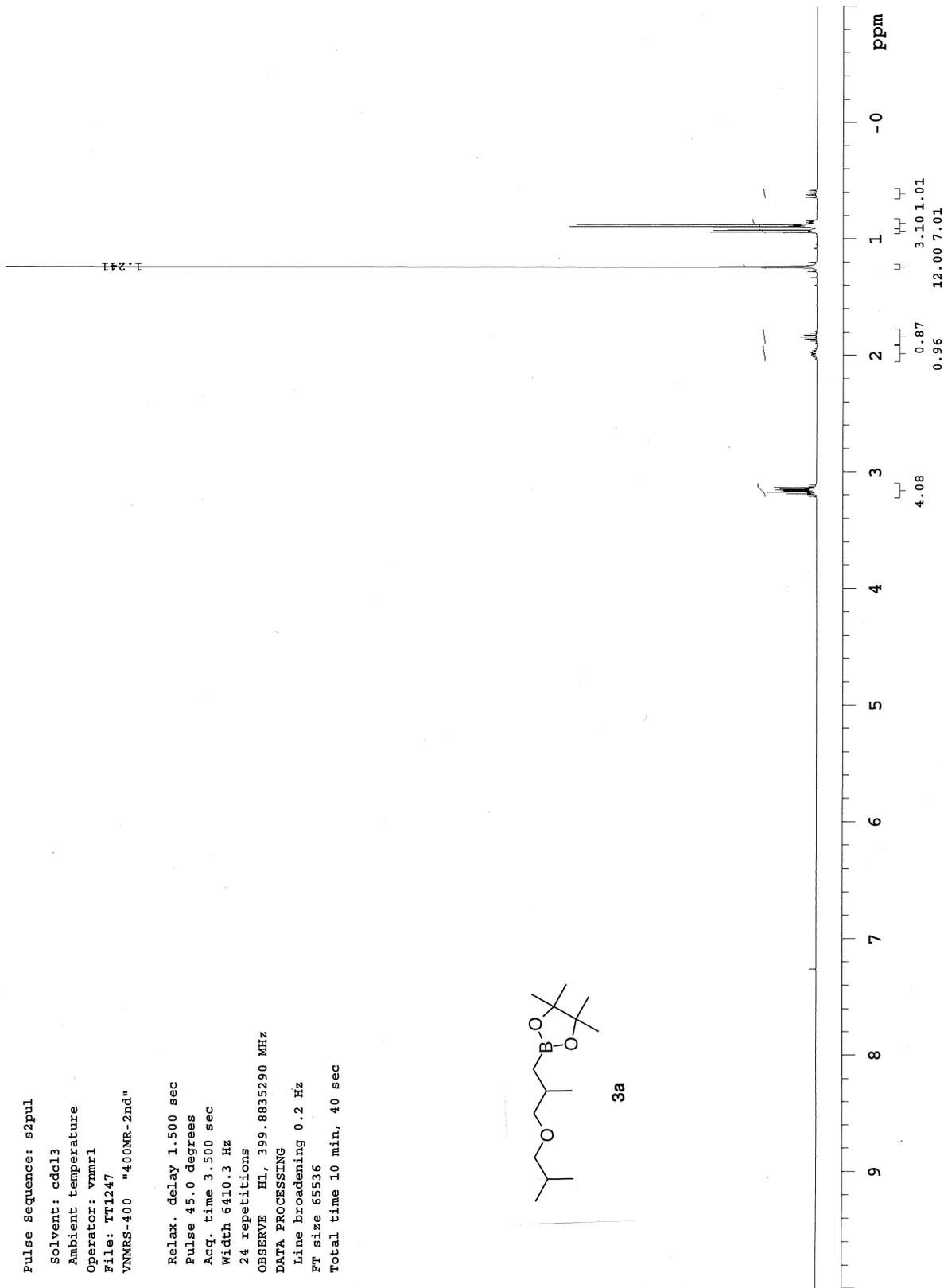
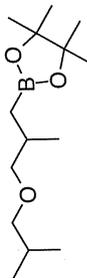
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DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



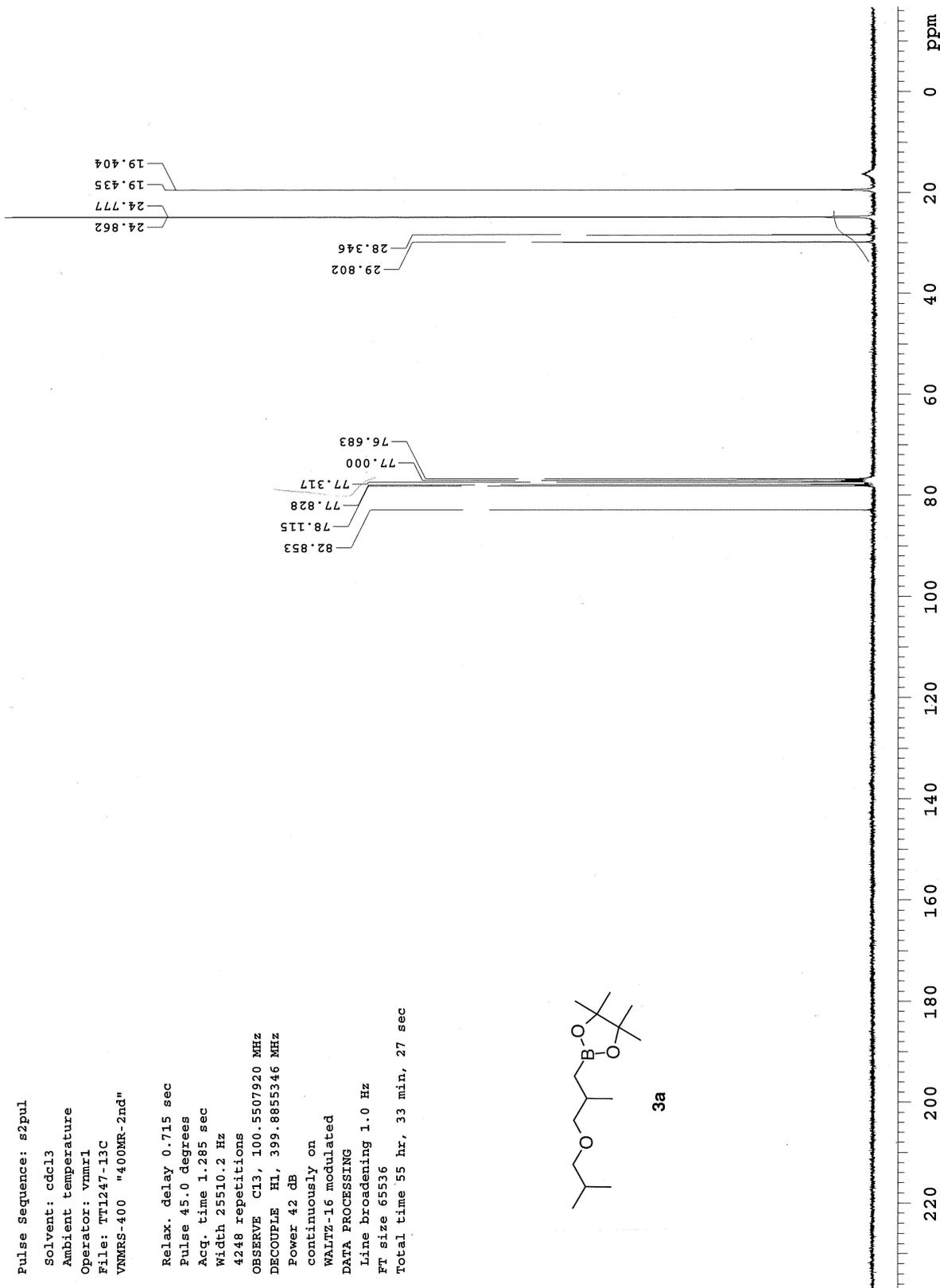
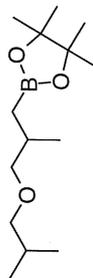
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Ambient temperature
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Relax. delay 0.715 sec
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4248 repetitions
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DECOUPLE H1, 399.8855346 MHZ
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
Ft size 65536
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STANDARD PROTON PARAMETERS

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Ambient temperature

Operator: vnmr1

File: TT1045-C6D6

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Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

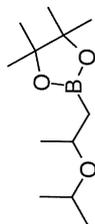
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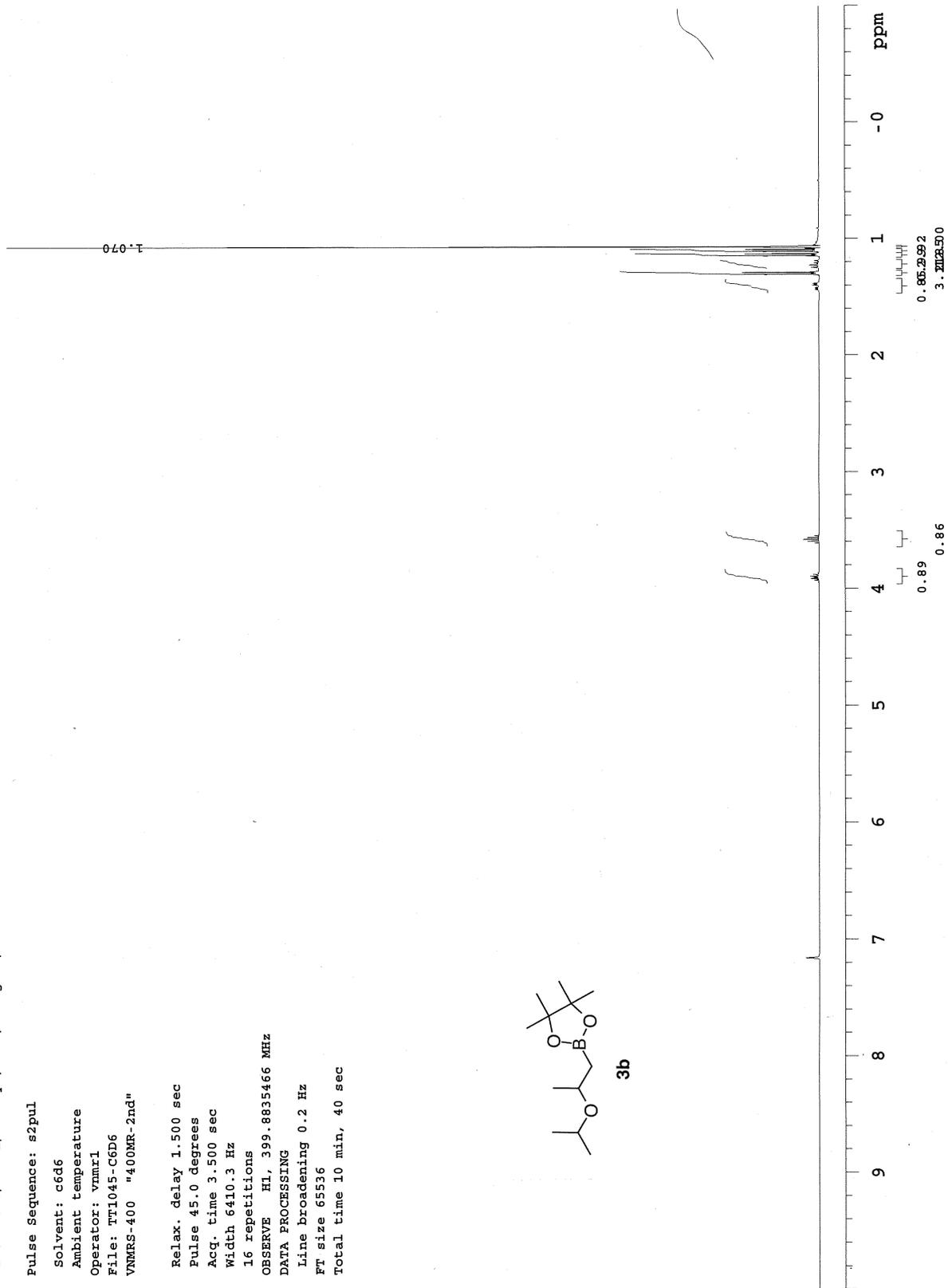
Line broadening 0.2 Hz

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Total time 10 min, 40 sec



3b



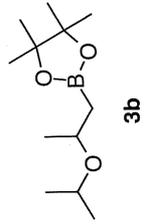
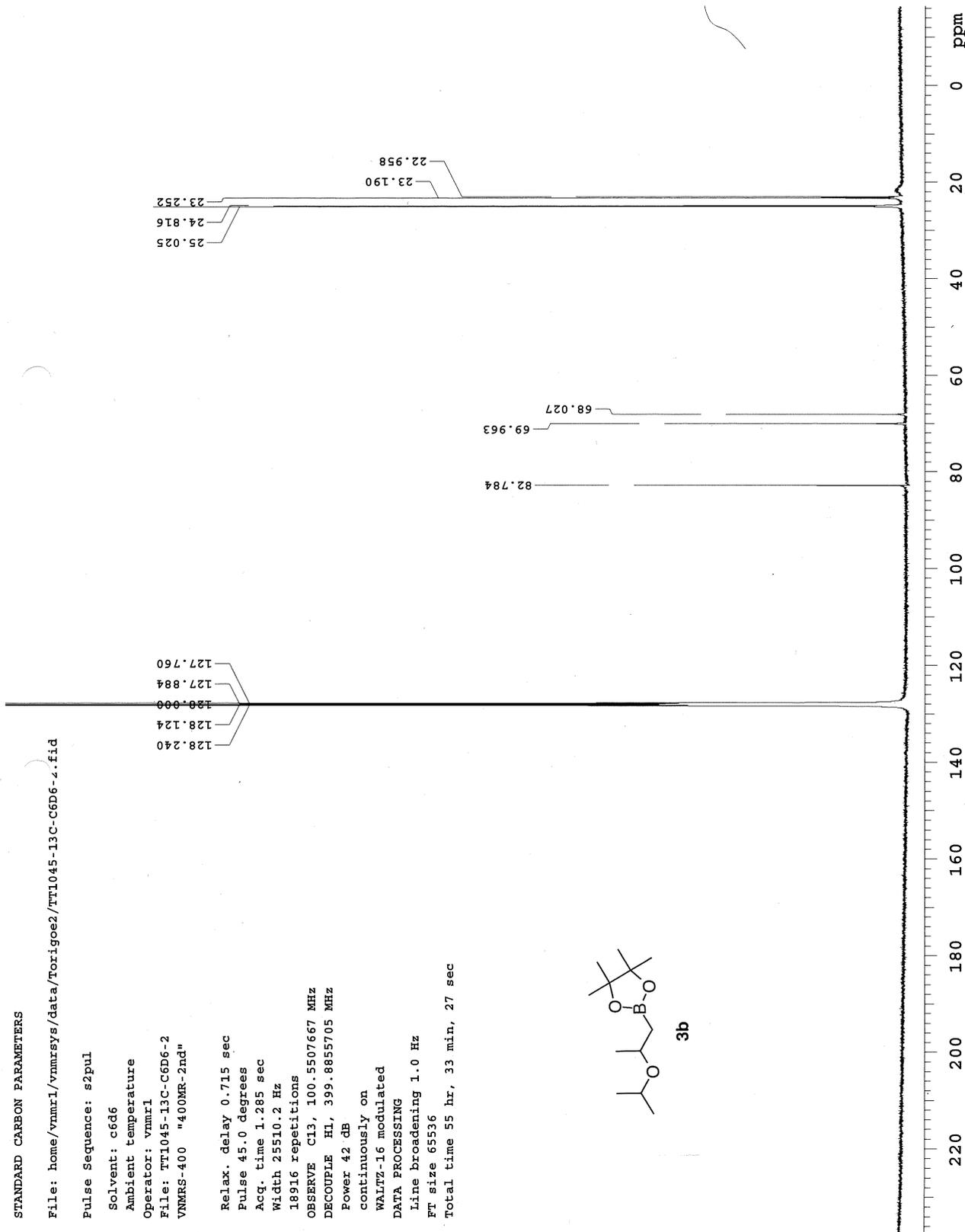
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 18916 repetitions
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 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 55 hr, 33 min, 27 sec



STANDARD PROTON PARAMETERS

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Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: TT1248

VNMRS-400 "400MR-2nd"

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Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

24 repetitions

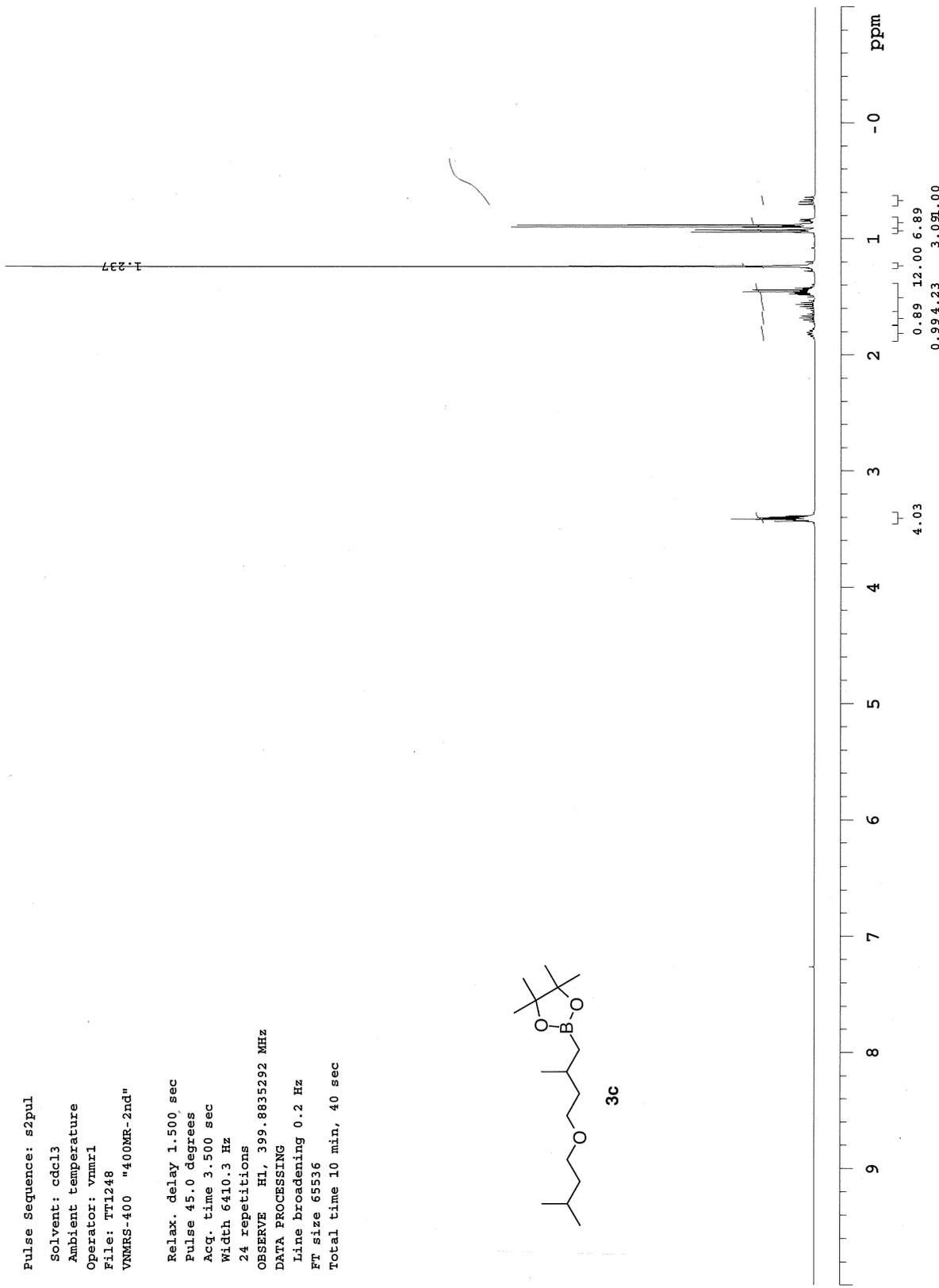
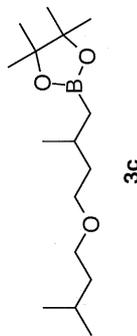
OBSERVE H1, 399.8835292 MHZ

DATA PROCESSING

Line broadening 0.2 Hz

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Total time 10 min, 40 sec



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Ambient temperature

Operator: vnmr1

File: TT1300

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Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

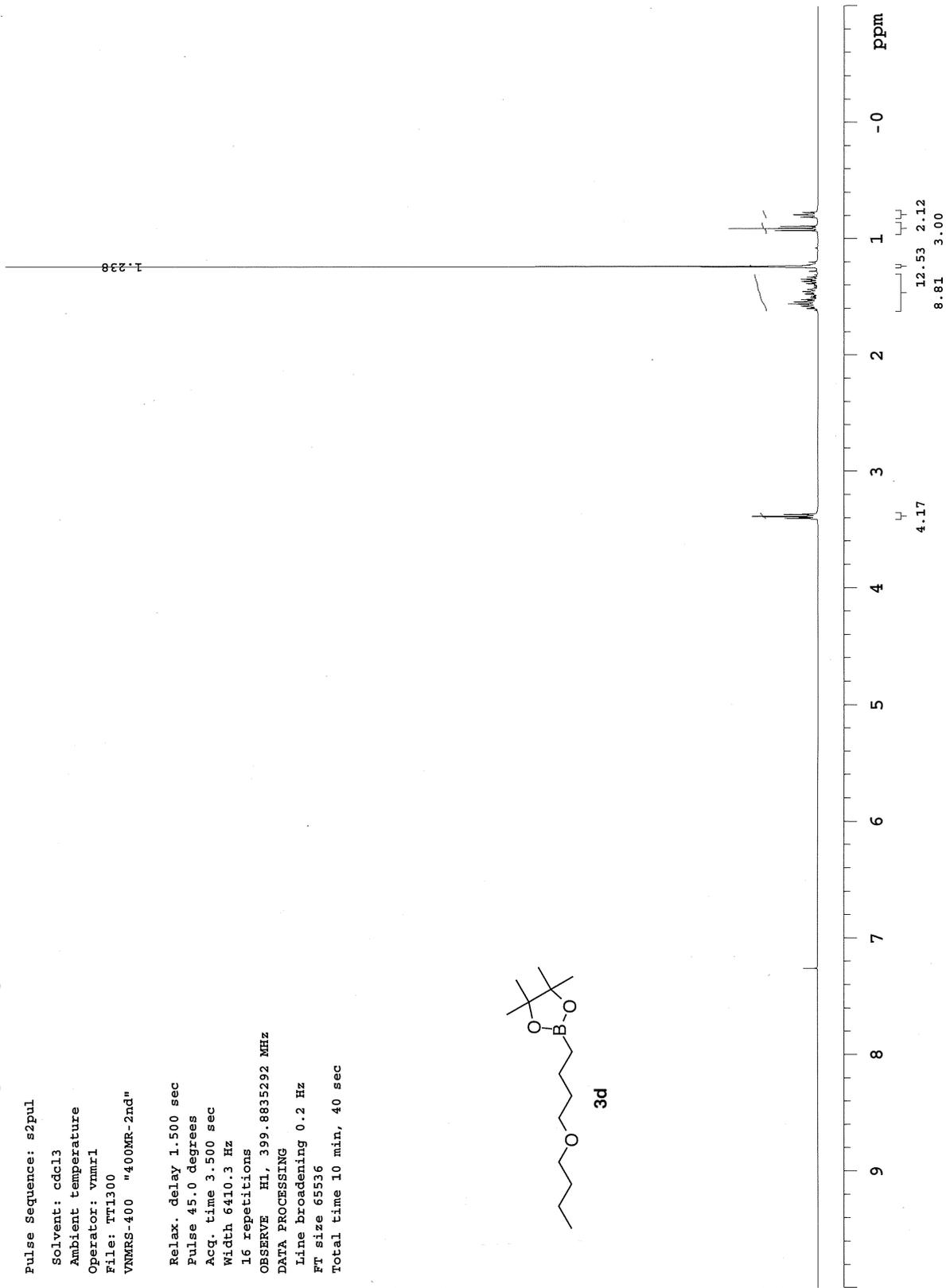
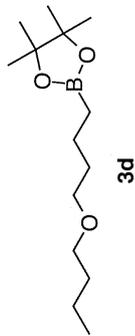
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DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



STANDARD CARBON PARAMETERS

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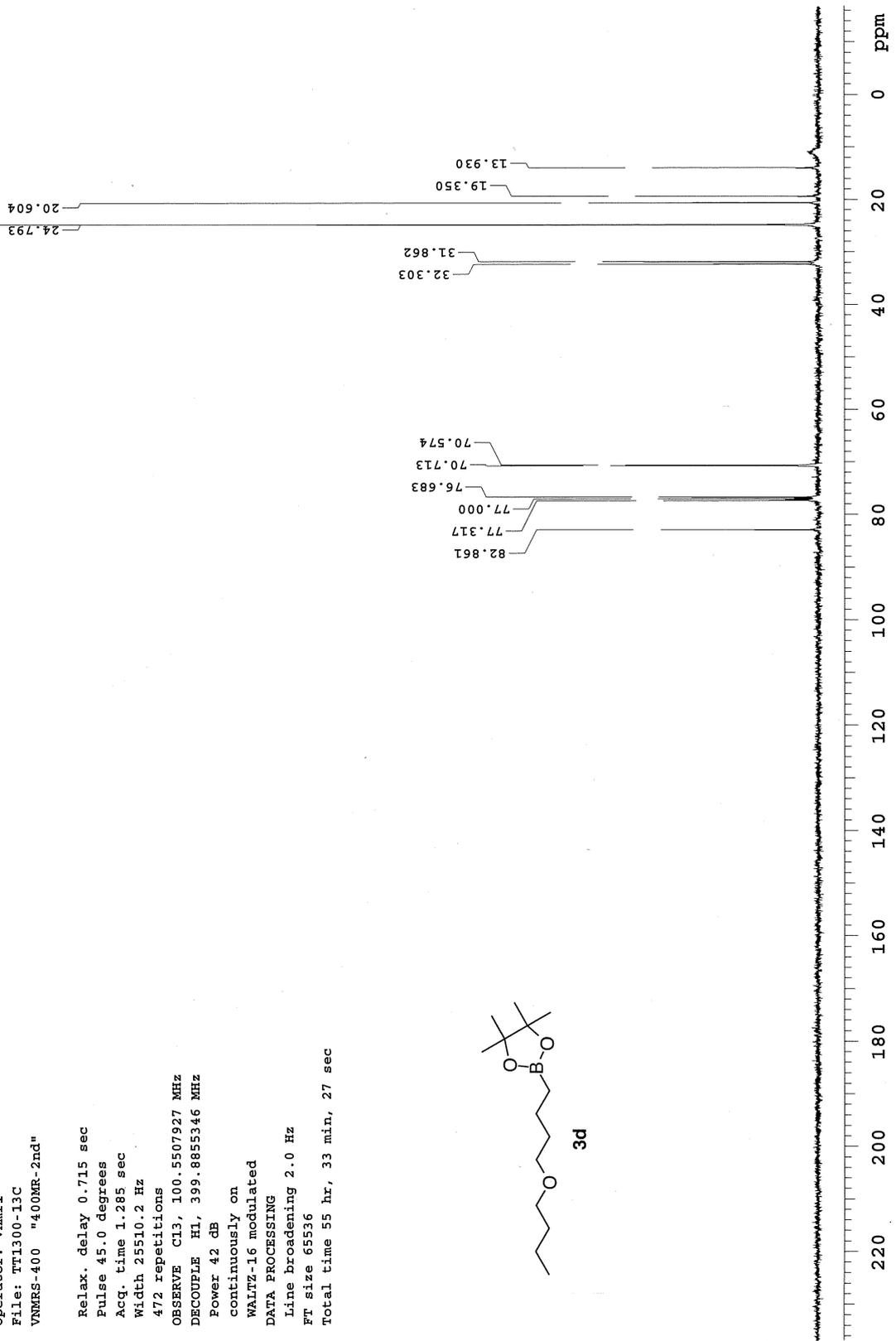
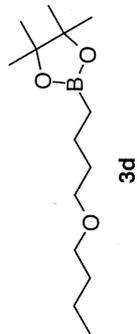
Solvent: cdc13
 Ambient temperature
 Operator: vnmr1
 File: Tt1300-13C
 VNMR-400 "400MR-2nd"

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 472 repetitions

OBSERVE C13, 100.5507927 MHz
 DECOUPLE H1, 399.8855346 MHz
 Power 42 dB

continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 2.0 Hz
 FT size 65536

Total time 55 hr, 33 min, 27 sec



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1306.fid

Pulse Sequence: s2pul

Solvent: cdc13

Ambient temperature

Operator: vnmr1

File: Tt1306

VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

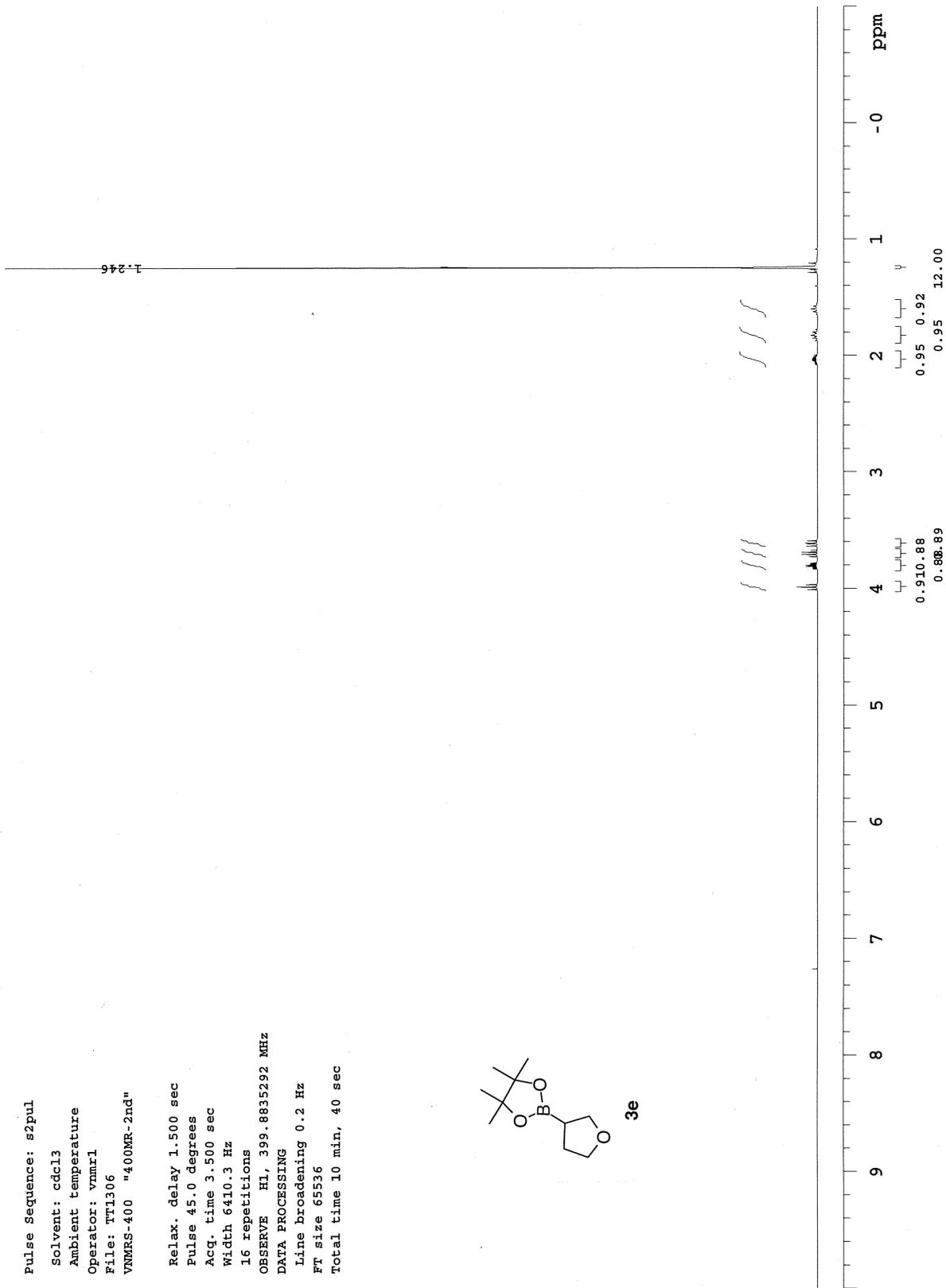
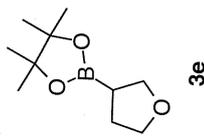
OBSERVE H1, 399.8835292 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



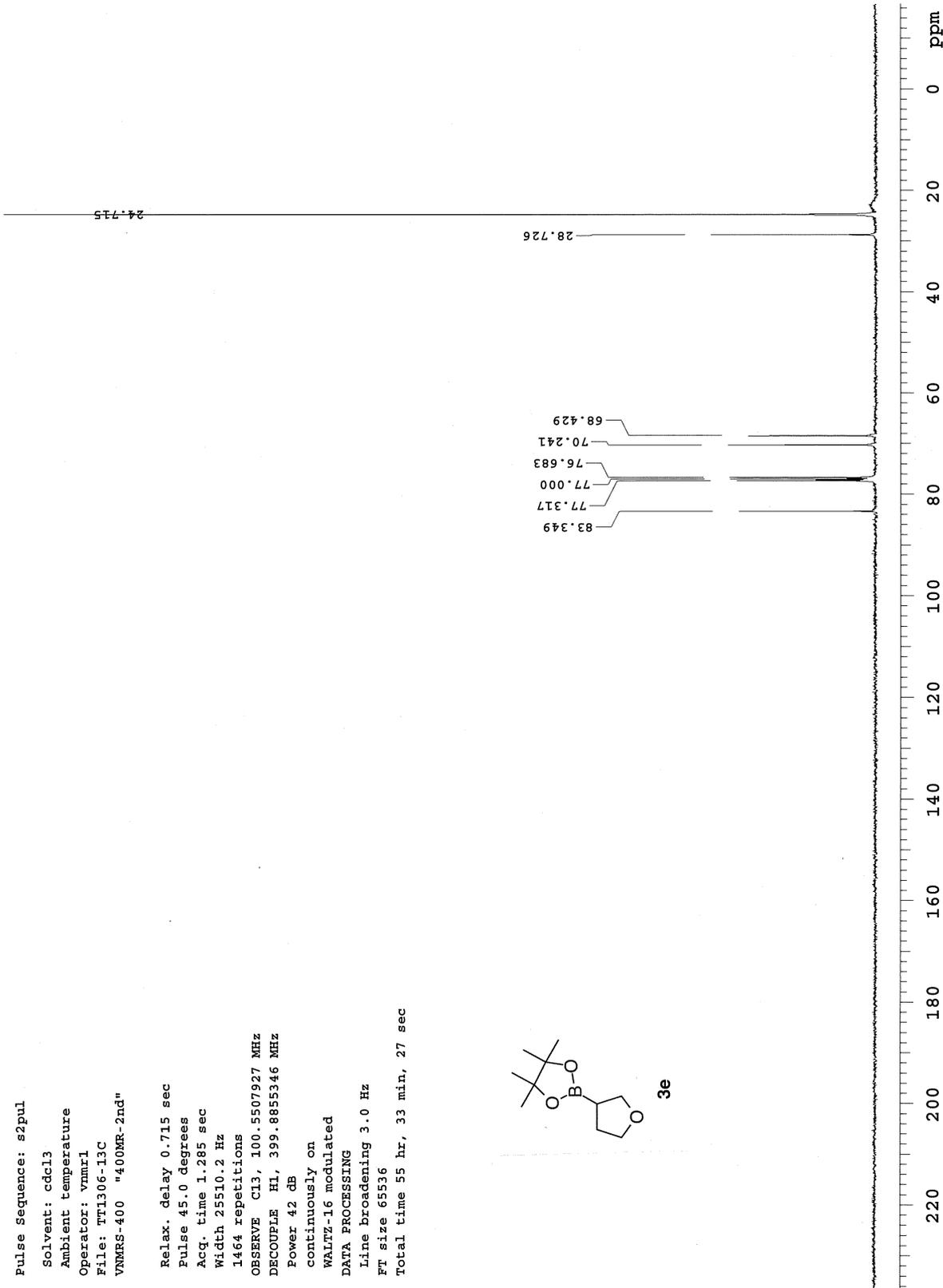
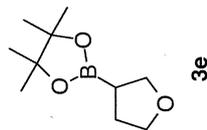
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1306-13C.fid

Pulse Sequence: s2pul

Solvent: cdcl3
 Ambient temperature
 Operator: vnmr1
 File: Tt1306-13C
 VNMR-400 "400MR-2nd"

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 1454 repetitions
 OBSERVE C13, 100.5507927 MHz
 DECOUPLE H1, 399.8855346 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 3.0 Hz
 FT size 65536
 Total time 55 hr, 33 min, 27 sec



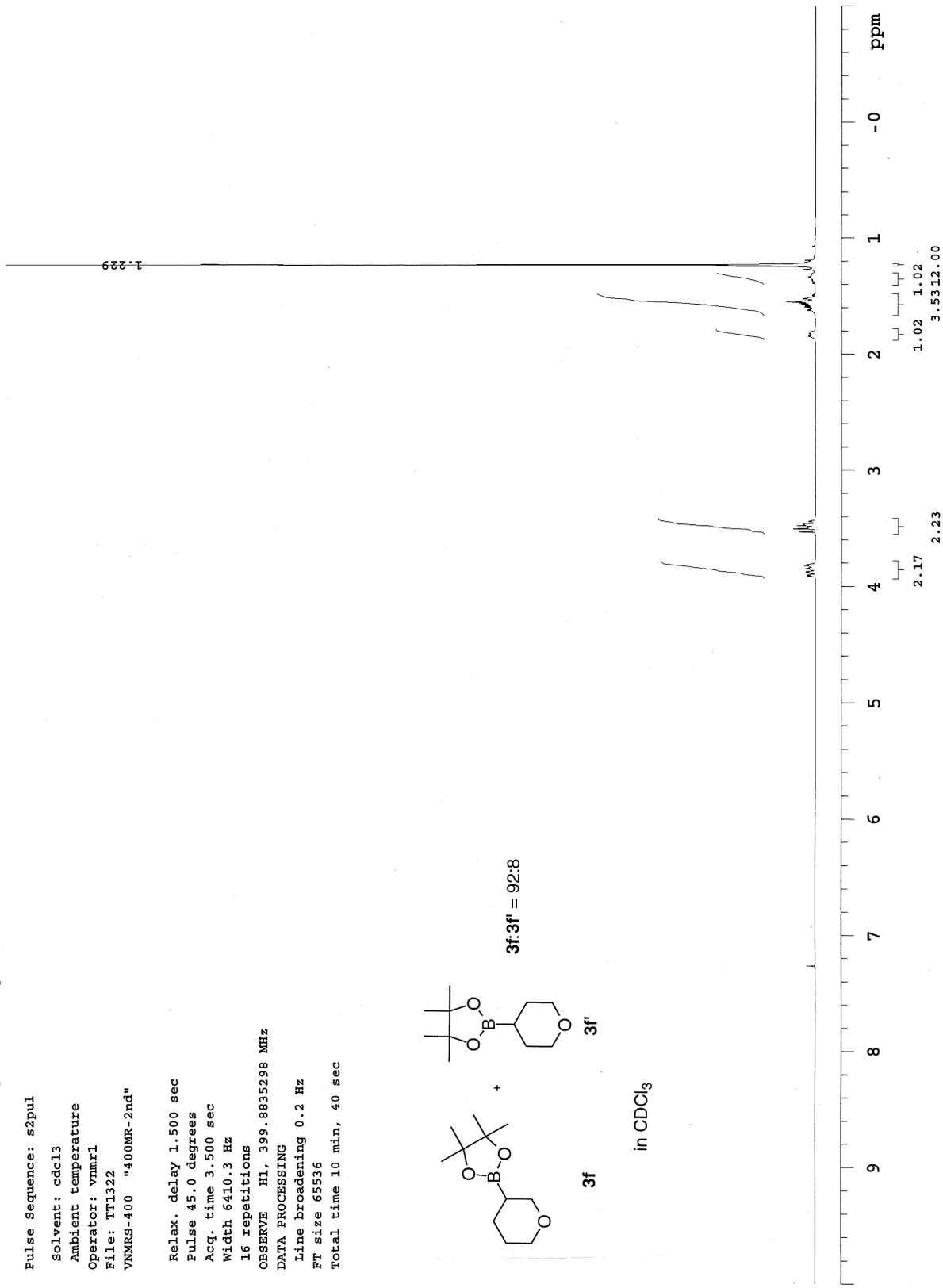
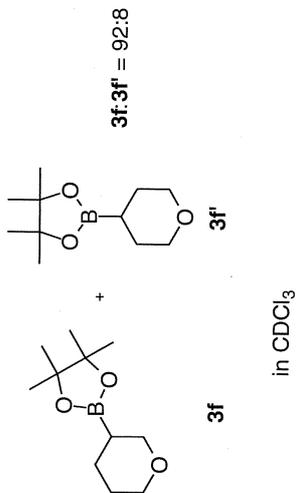
STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1322.fid

Pulse Sequence: s2pul

Solvent: cdcl3
 Ambient temperature
 Operator: vnmr1
 File: Tt1322
 VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8835298 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 10 min, 40 sec



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigoe2/Tt1322.fid

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: Tt1322

VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

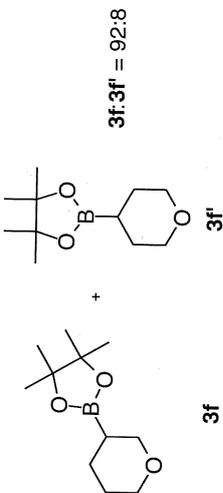
OBSERVE HL, 399.8835298 MHz

DATA PROCESSING

Line broadening 0.2 Hz

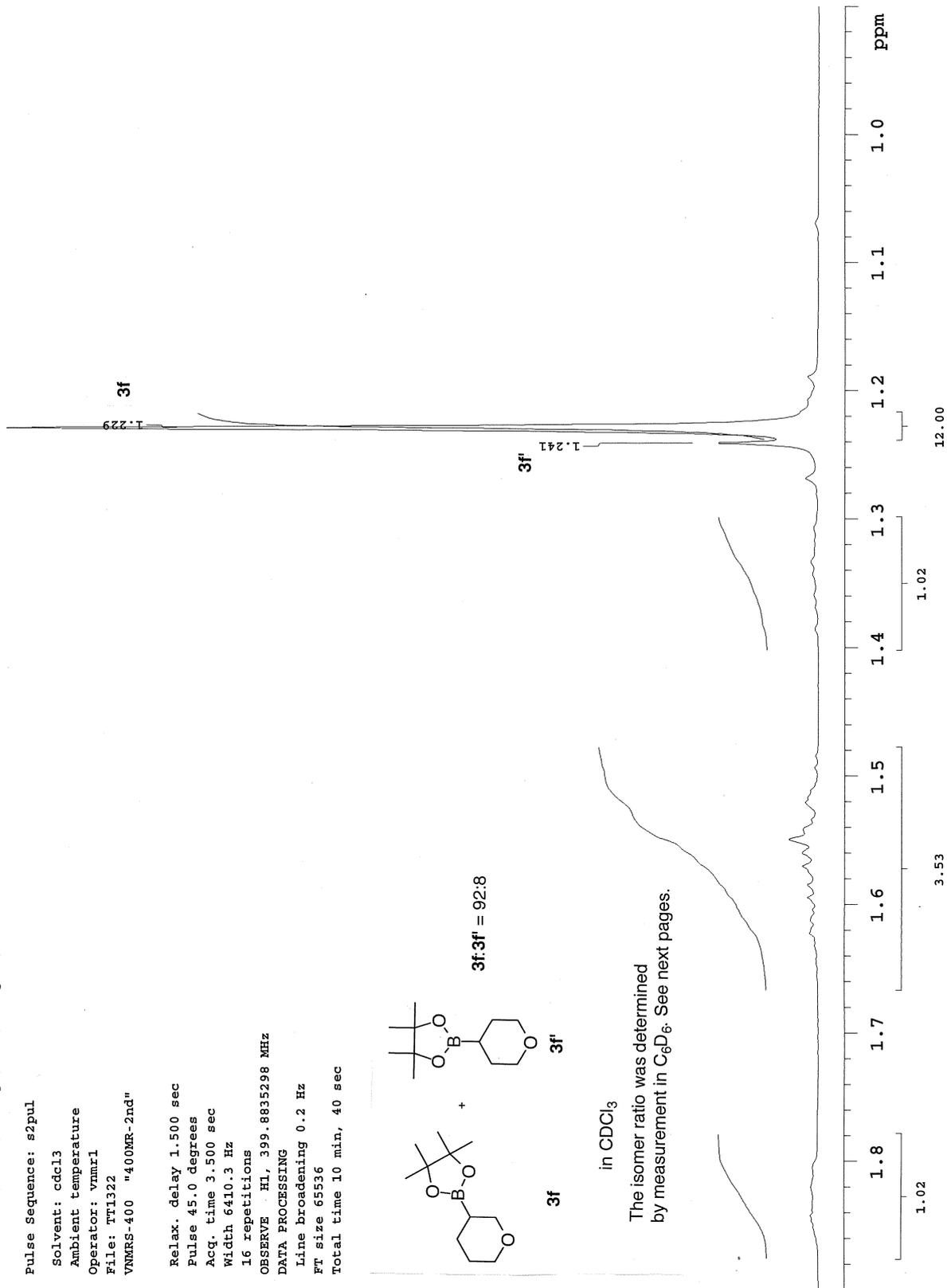
FT size 65536

Total time 10 min, 40 sec



in CDCl₃

The isomer ratio was determined by measurement in C₆D₆. See next pages.



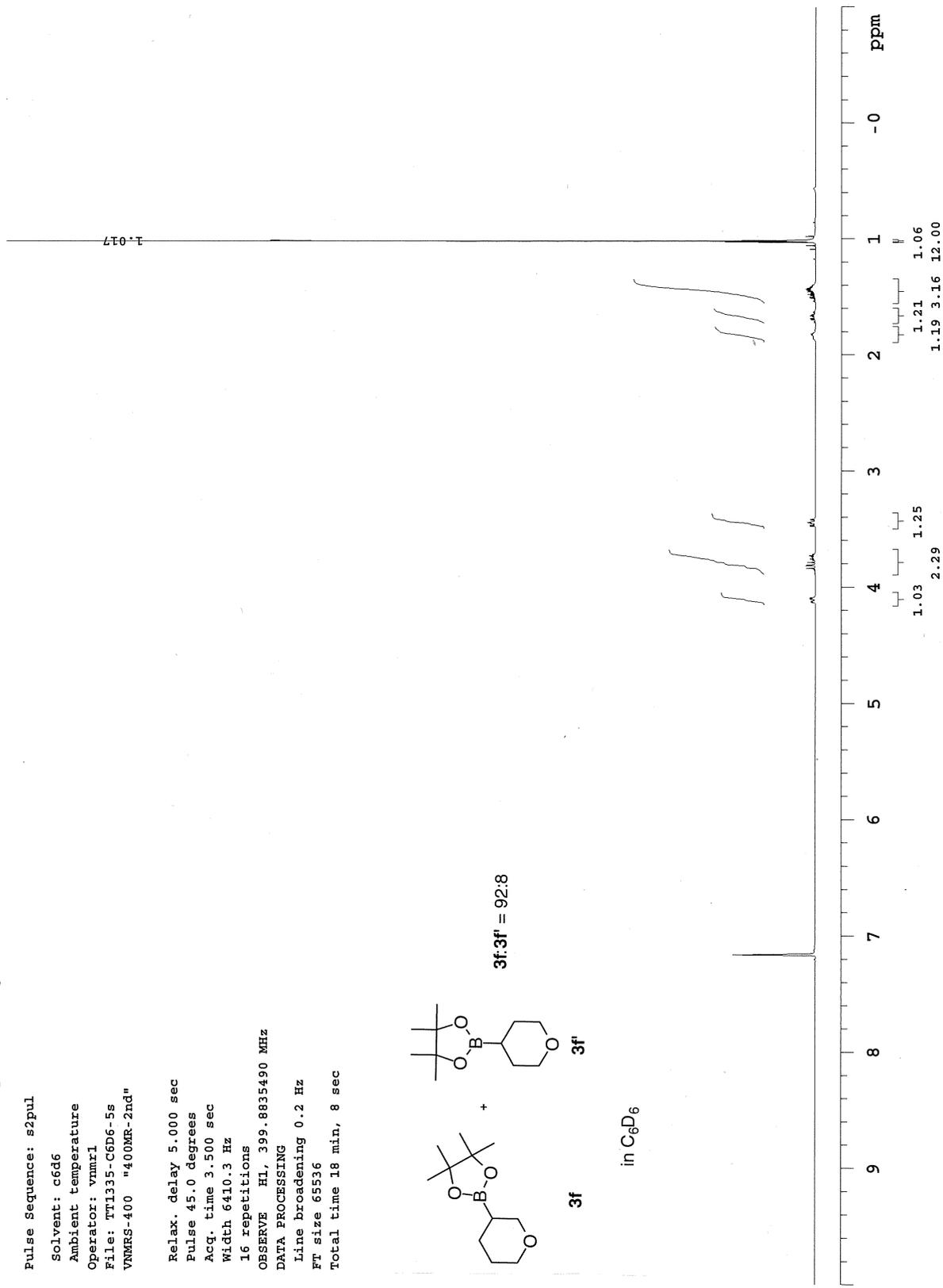
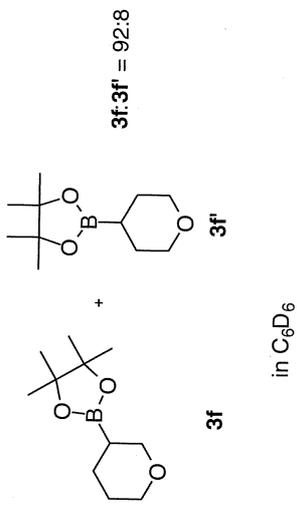
STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigoe2/TI1335-C6D6-5s.fid

Pulse Sequence: s2pul

Solvent: c6d6
 Ambient temperature
 Operator: vnmr1
 File: TI1335-C6D6-5s
 VNMRS-400 "400MR-2nd"

Relax. delay 5.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8835490 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 18 min, 8 sec



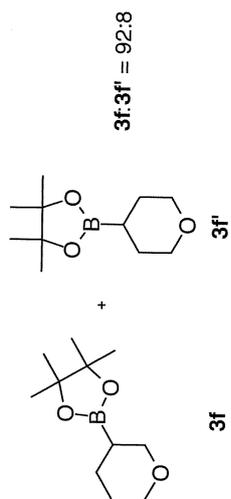
STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigce2/TI1335-C6D6-5s.fid

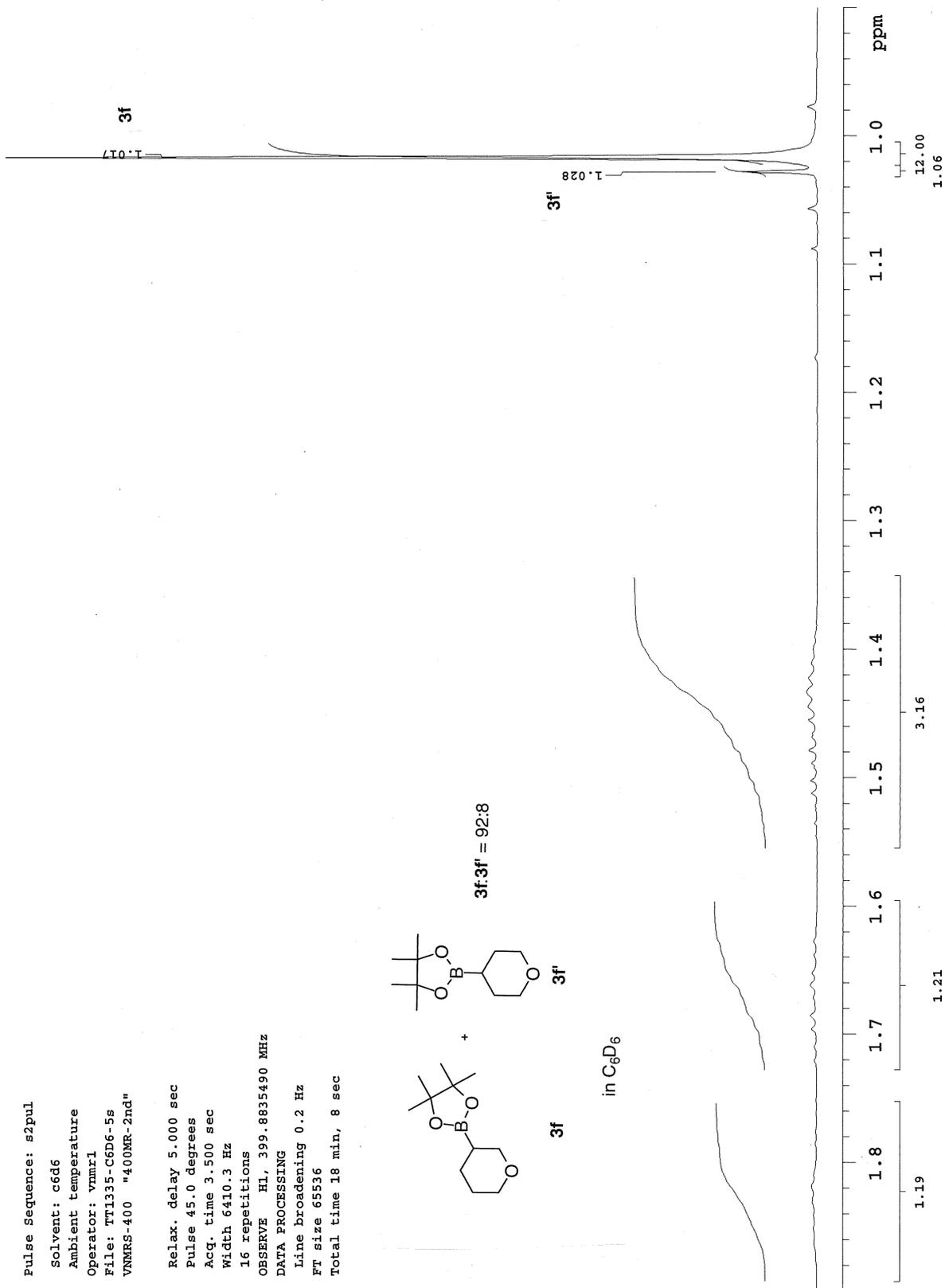
Pulse Sequence: s2pul

Solvent: c6d6
 Ambient temperature
 Operator: vnmr1
 File: TI1335-C6D6-5s
 VNMRS-400 "400MR-2nd"

Relax. delay 5.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8835490 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 18 min, 8 sec



in C₆D₆



STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1322-3-13C.fid

Pulse Sequence: s2pul

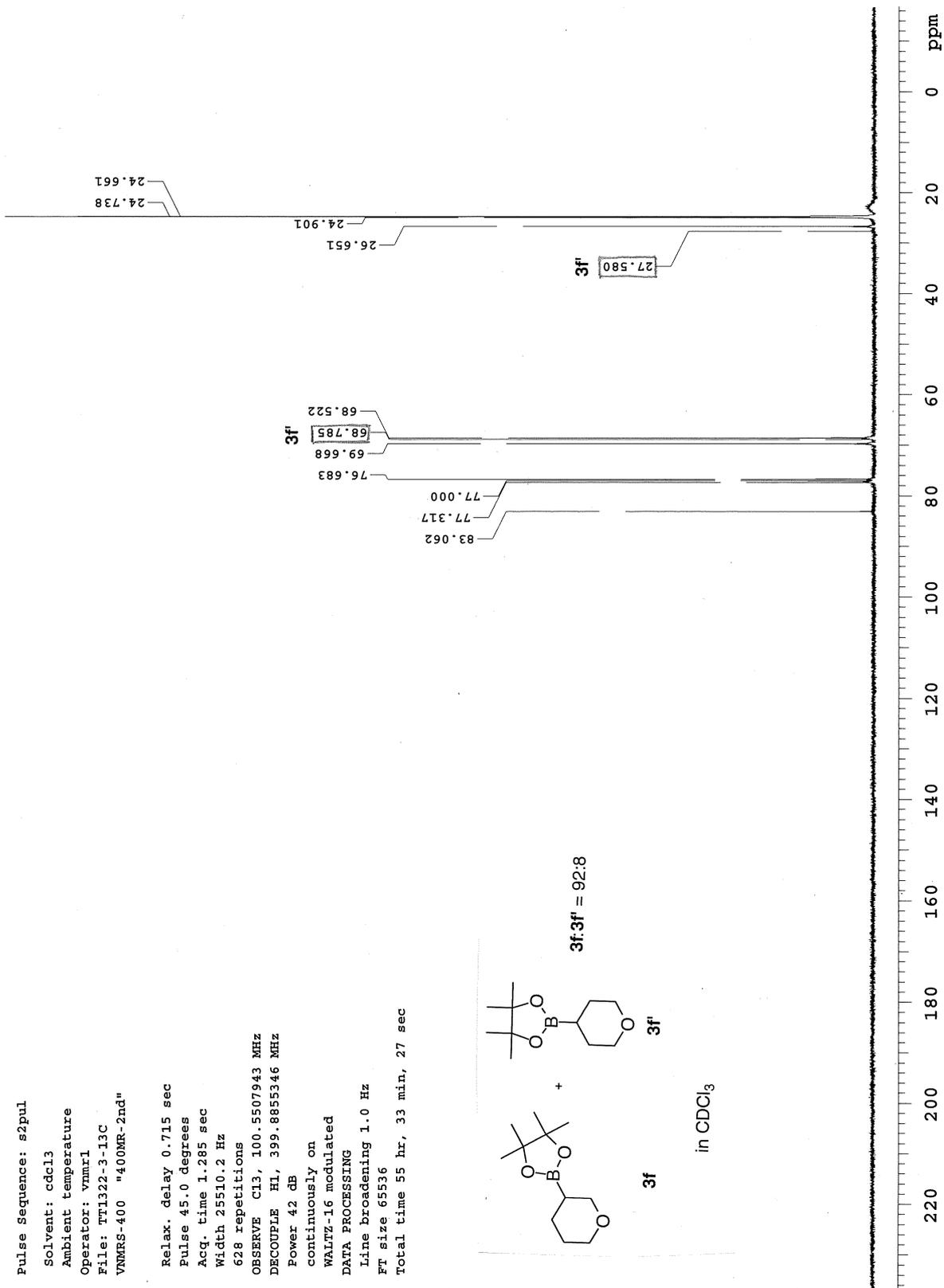
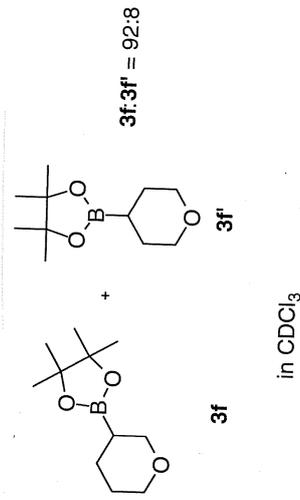
Solvent: cdc13
 Ambient temperature
 Operator: vnmr1
 File: Tt1322-3-13C
 VNMR-400 "400MR-2nd"

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 628 repetitions

OBSERVE C13, 100.5507943 MHz
 DECOUPLE H1, 399.8855346 MHz
 Power 42 dB

continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536

Total time 55 hr, 33 min, 27 sec



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/T11375.fid

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: T11375

VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

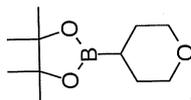
OBSERVE HL, 399.8835276 MHz

DATA PROCESSING

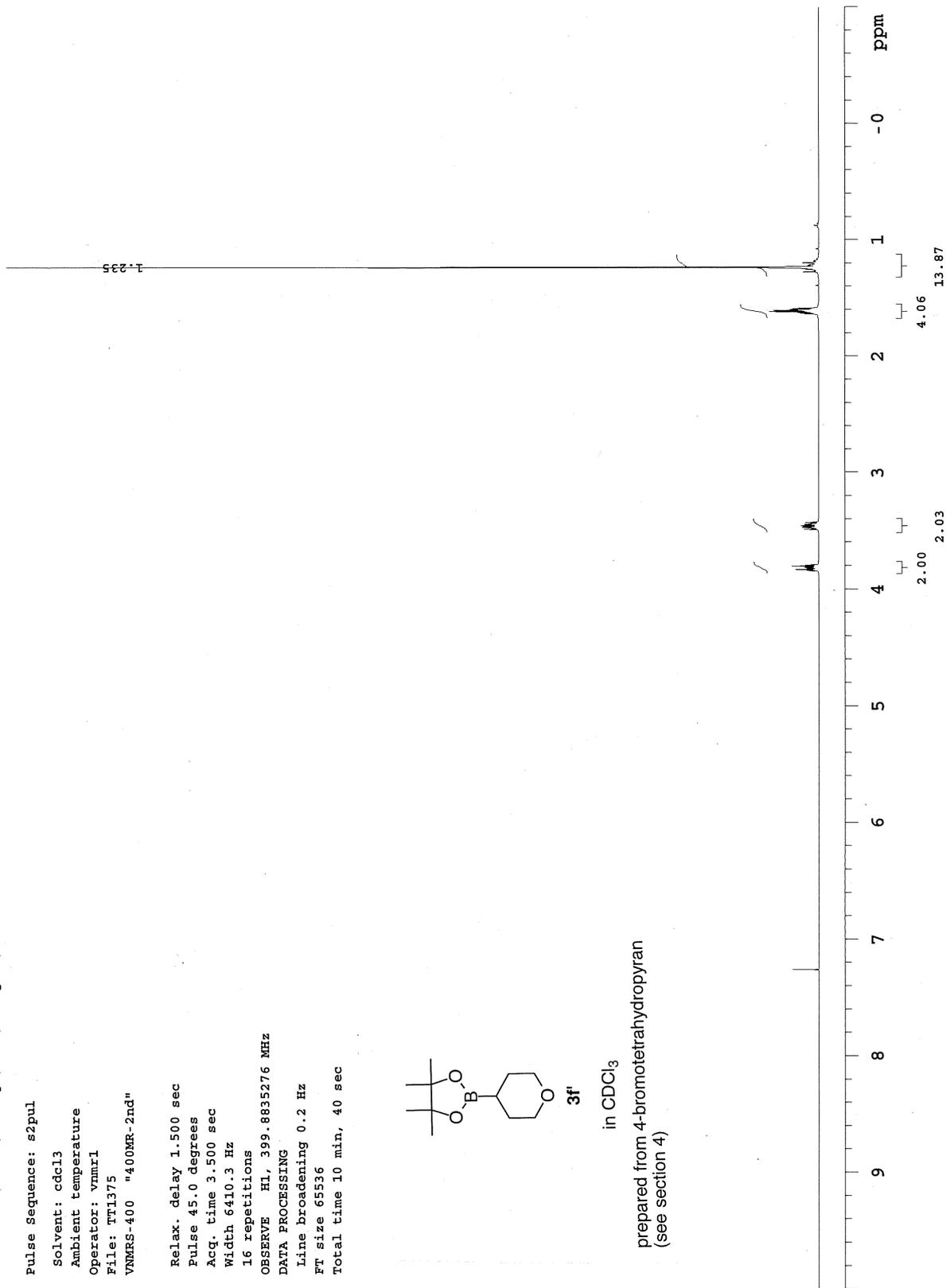
Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



in CDCl₃
prepared from 4-bromotetrahydropyran
(see section 4)



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1375-C6D6.fid

Pulse Sequence: s2pul

Solvent: c6d6

Ambient temperature

Operator: vnmr1

File: Tt1375-C6D6

VNMR-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

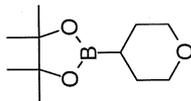
OBSERVE HL, 399.8835466 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

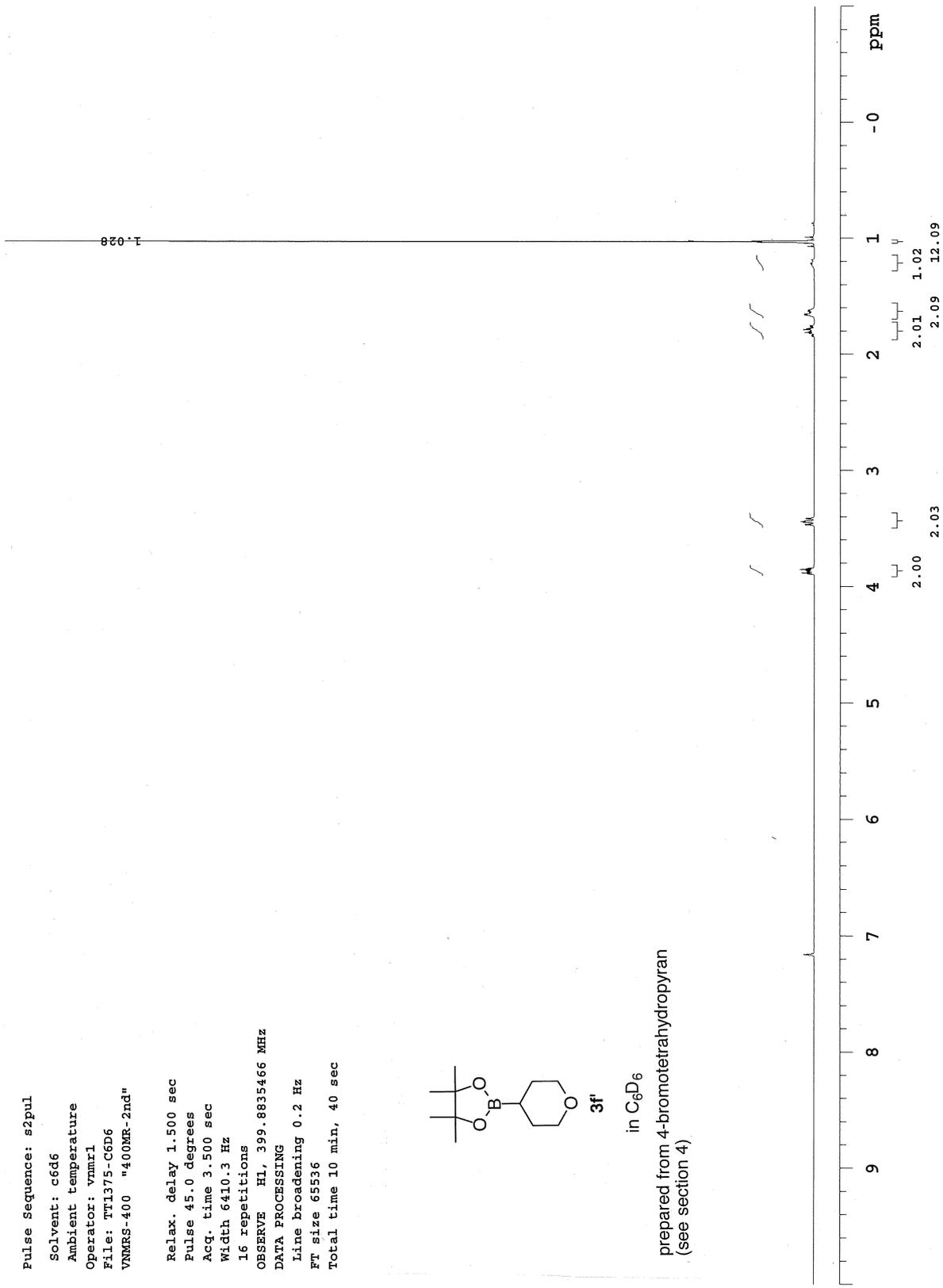
Total time 10 min, 40 sec



3f

in C₆D₆

prepared from 4-bromotetrahydropyran
(see section 4)



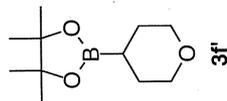
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1375-13C.fid

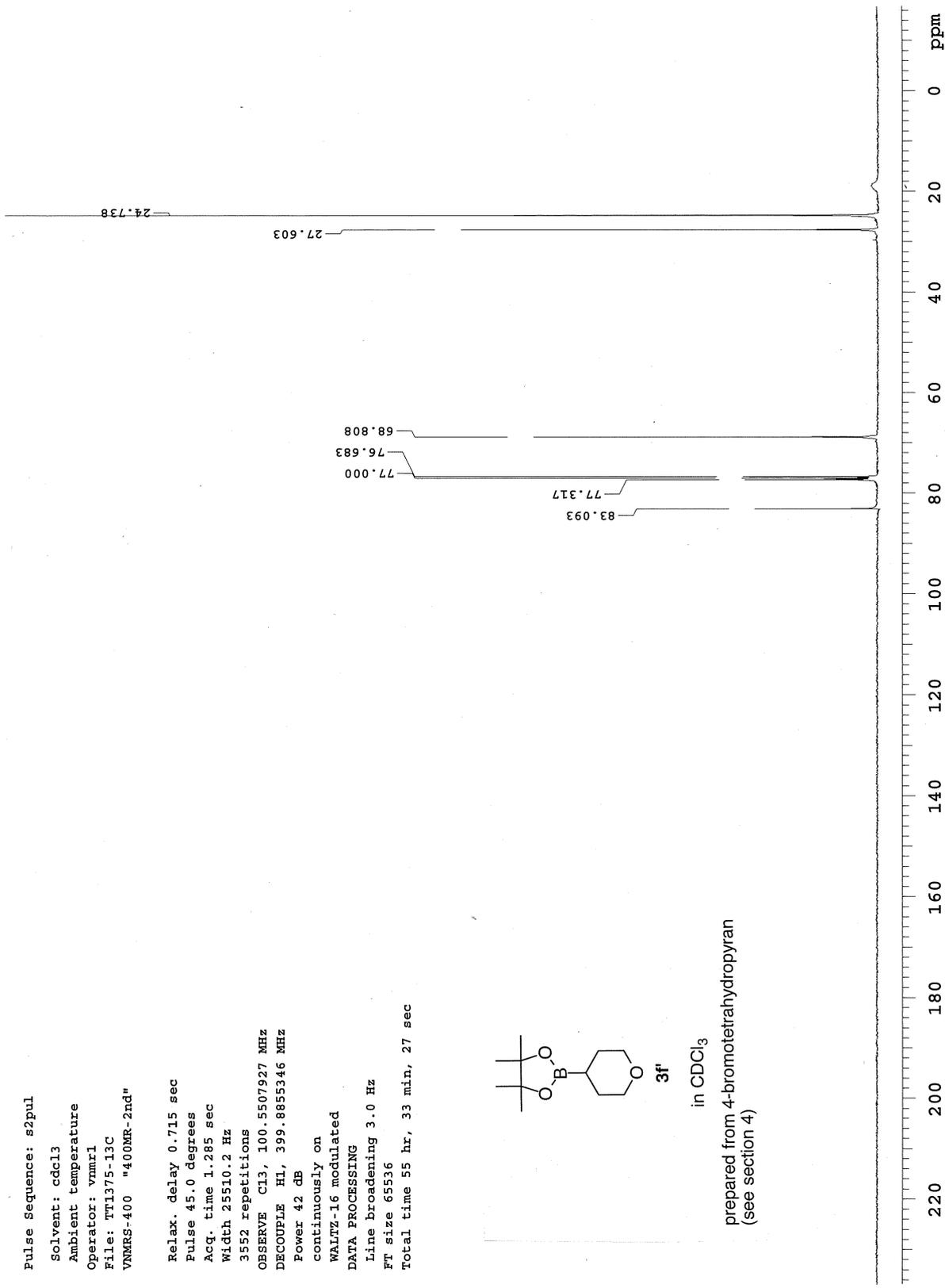
Pulse Sequence: s2pul

Solvent: cdc13
Ambient temperature
Operator: vnmr1
File: Tt1375-13C
VNMRS-400 "400MR-2nd"

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
3552 repetitions
OBSERVE C13, 100.5507927 MHz
DECOUPLE H1, 399.8855346 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
Ft size 65536
Total time 55 hr, 33 min, 27 sec



in CDCl₃
prepared from 4-bromotetrahydropyran
(see section 4)



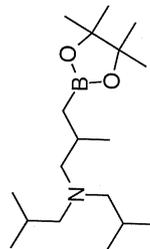
STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1304-C6D6.fid

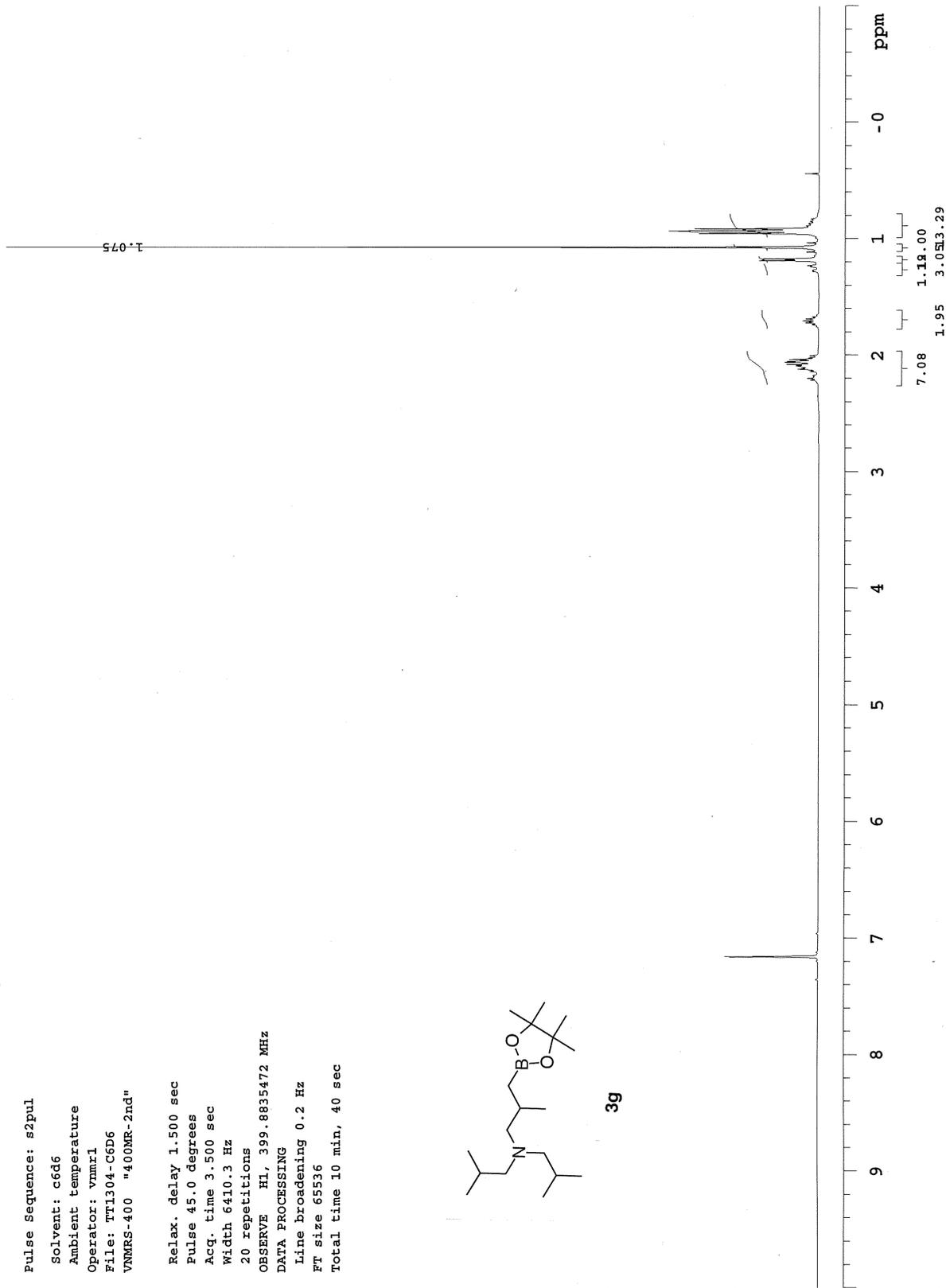
Pulse Sequence: s2pul

Solvent: c6d6
Ambient temperature
Operator: vnmr1
File: Tt1304-C6D6
VNMR-400 "400MR-2nd"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
20 repetitions
OBSERVE HL, 399.8835472 MHz
DATA PROCESSING
Line broadening 0.2 Hz
Ft size 65536
Total time 10 min, 40 sec



3g



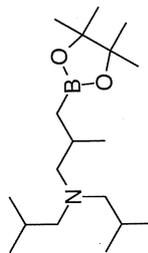
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigoe2/T11304-C6D6-13C...d

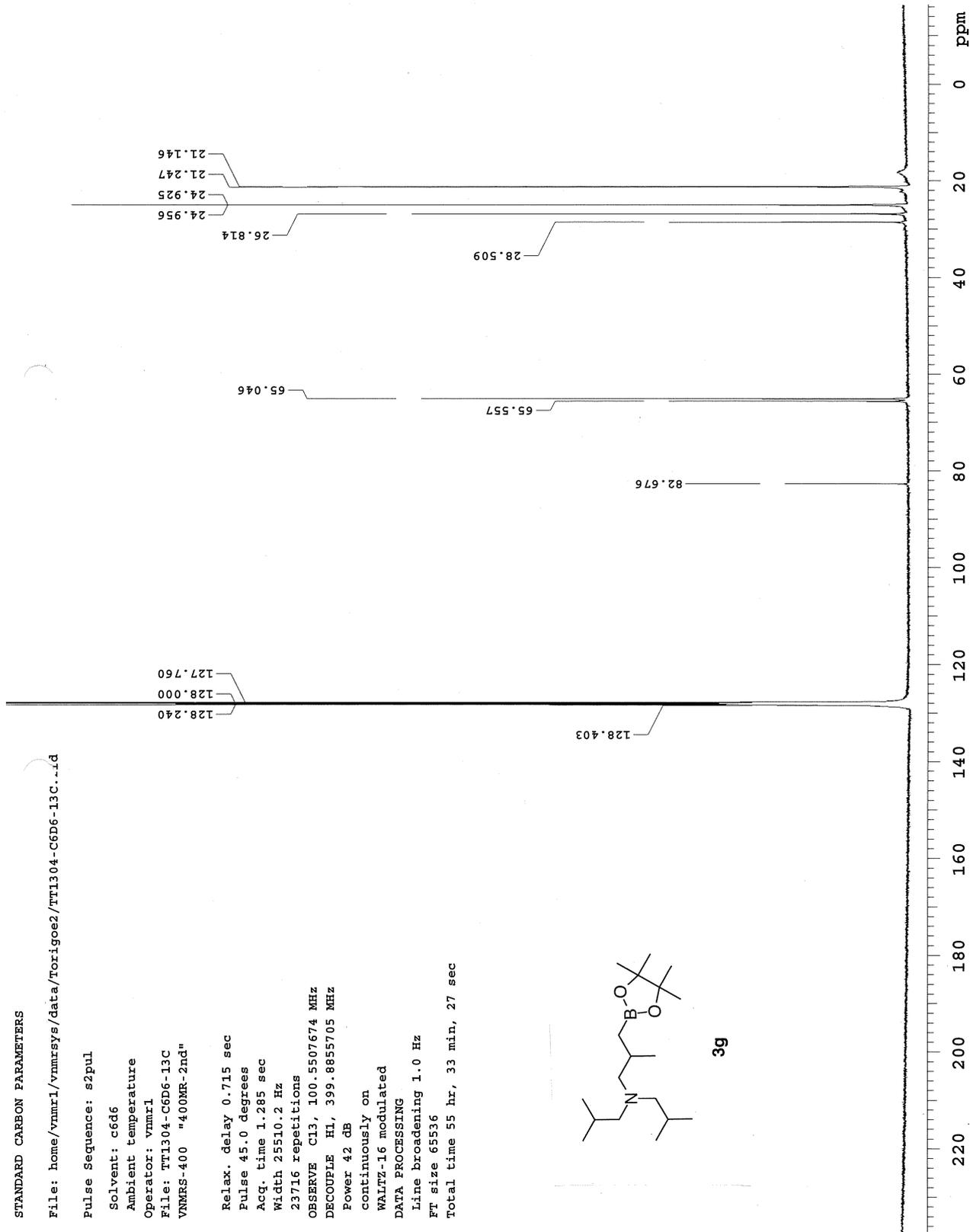
Pulse Sequence: s2pul

Solvent: c6d6
 Ambient temperature
 Operator: vnmr1
 File: T11304-C6D6-13C
 VNMR-400 "400MR-2nd"

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 23716 repetitions
 OBSERVE C13, 100.5507674 MHz
 DECOUPLE H1, 399.8855705 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 Ft size 65536
 Total time 55 hr, 33 min, 27 sec



3g



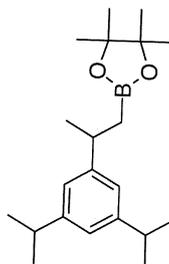
STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/TI1310-C6D6.fid

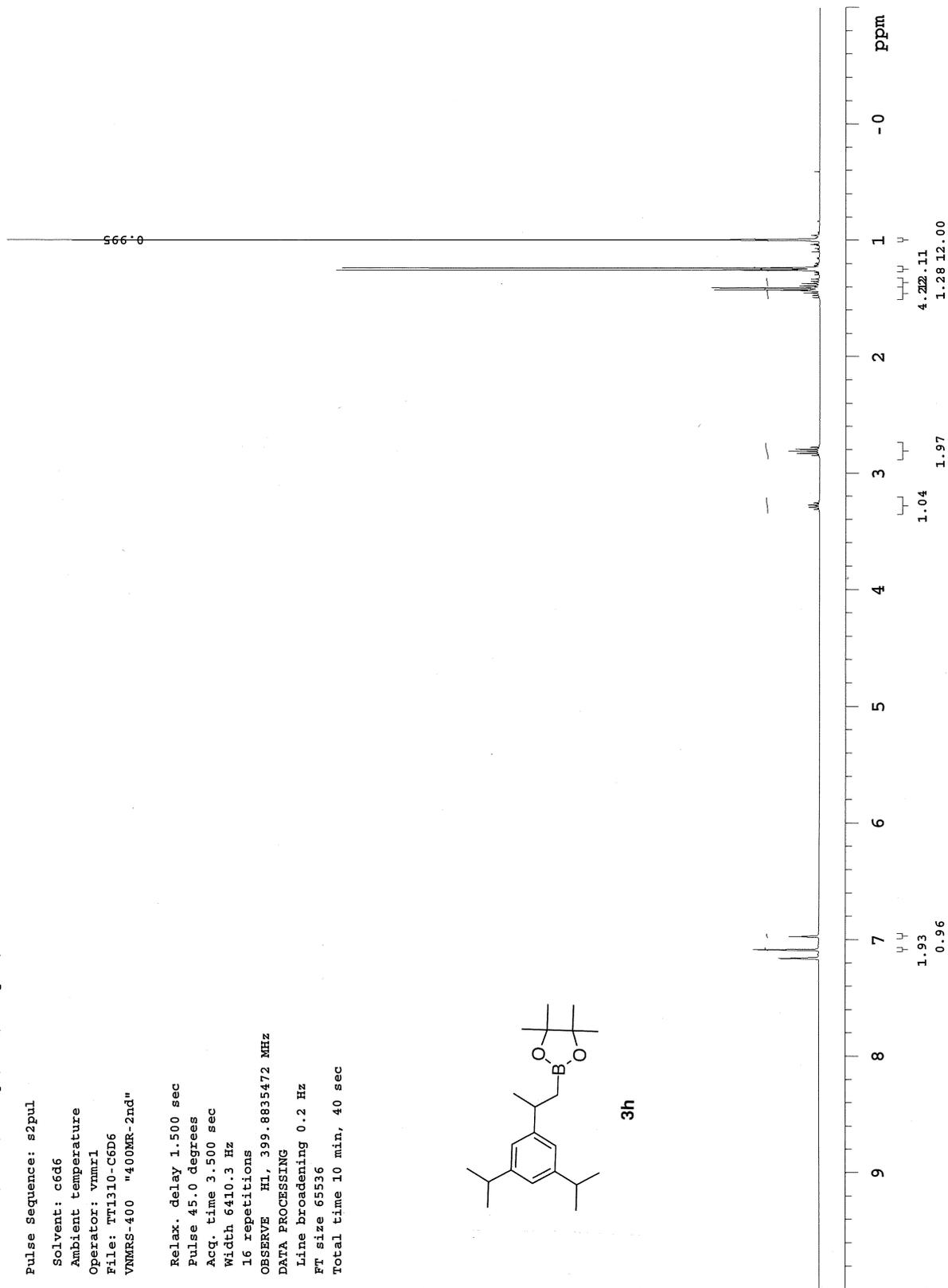
Pulse Sequence: s2pul

Solvent: c6d6
 Ambient temperature
 Operator: vnmr1
 File: TI1310-C6D6
 VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8835472 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 10 min, 40 sec



3h



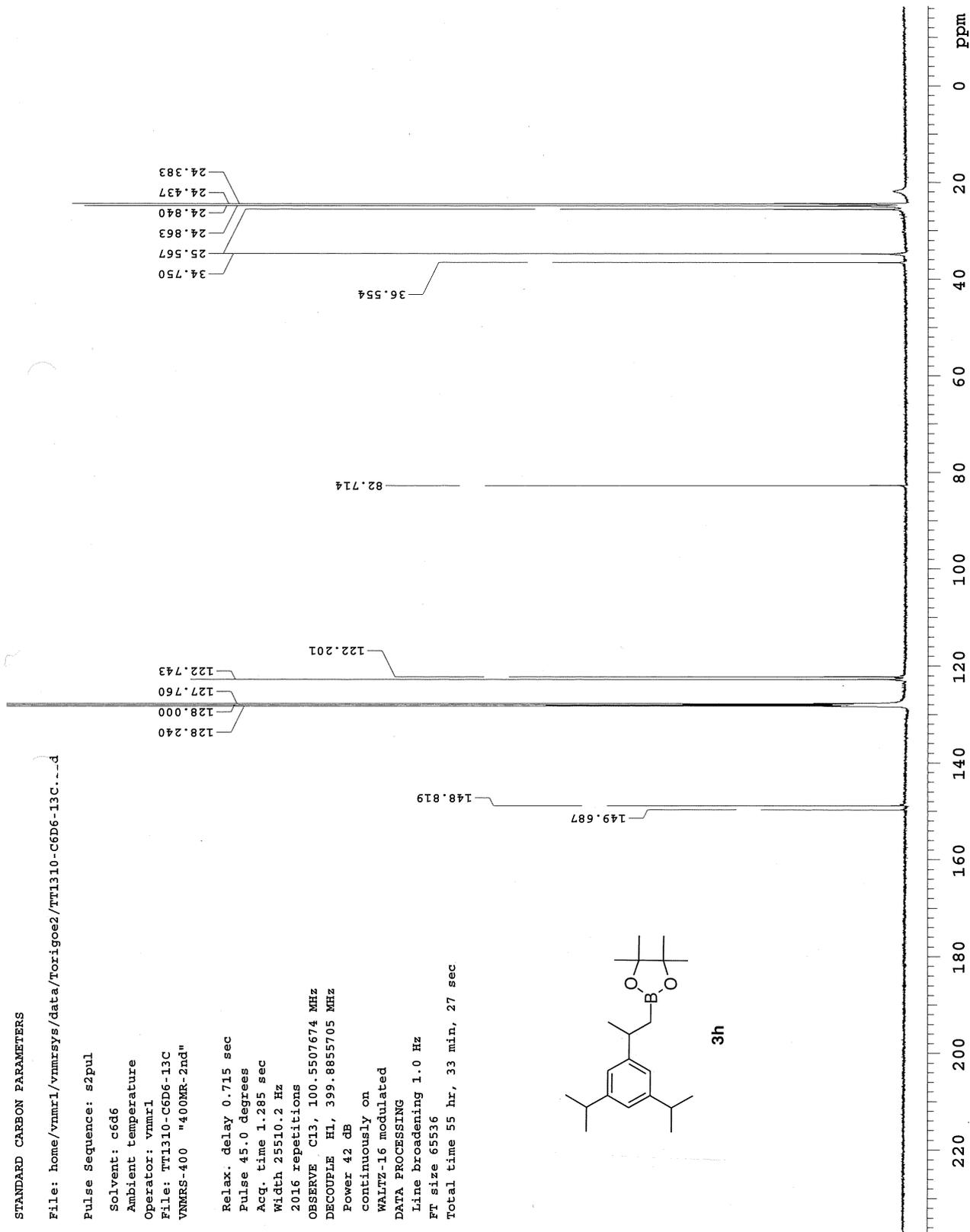
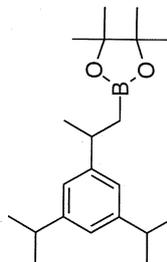
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigce2/TT1310-C6D6-13C...d

Pulse Sequence: s2pul

Solvent: c6d6
 Ambient temperature
 Operator: vnmr1
 File: TT1310-C6D6-13C
 VNMRS-400 "400MR-2nd"

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 2016 repetitions
 OBSERVE C13, 100.507674 MHz
 DECOUPLE H1, 399.8855705 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 Ft size 65536
 Total time 55 hr, 33 min, 27 sec



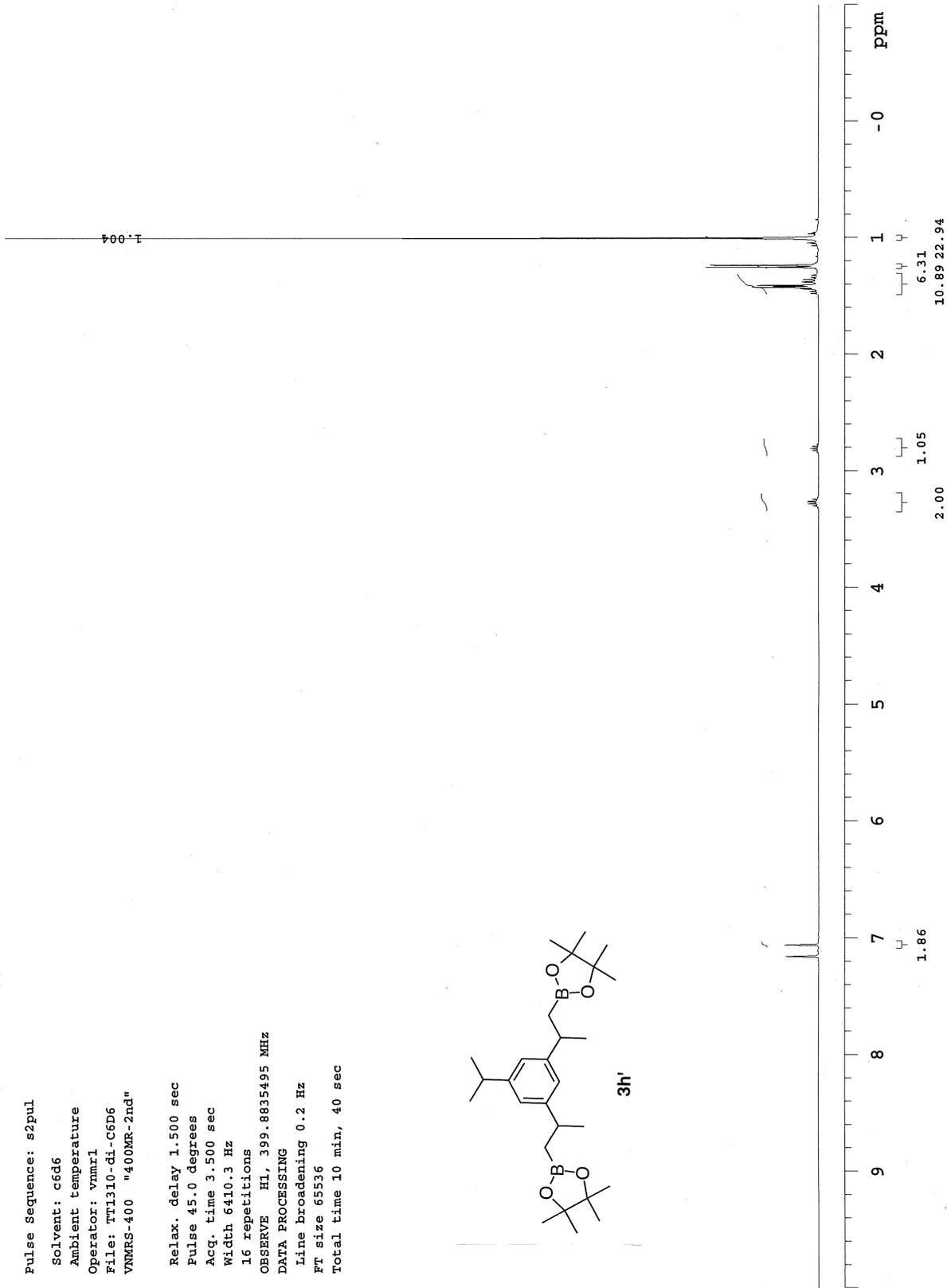
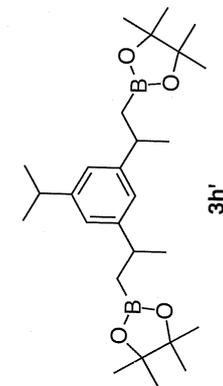
STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1310-di-C6D6.1..1

Pulse Sequence: s2pul

Solvent: c6d6
 Ambient temperature
 Operator: vnmr1
 File: Tt1310-di-C6D6
 VNMR-400 "400MR-2nd"

Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8835495 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 10 min, 40 sec



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1295.fid

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: Tt1295

VNMR-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

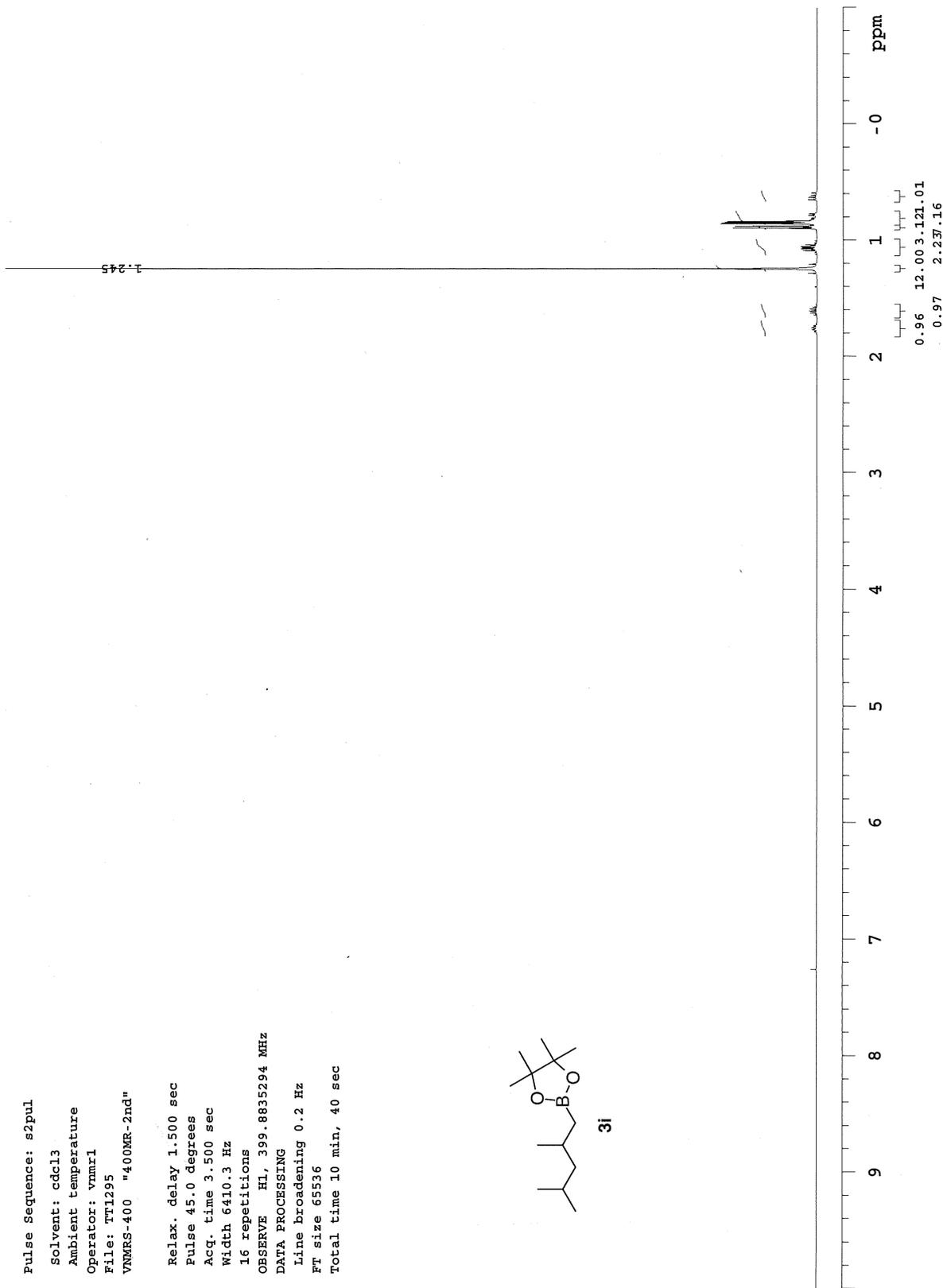
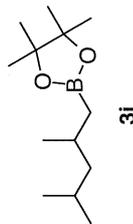
OBSERVE H1, 399.8835294 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



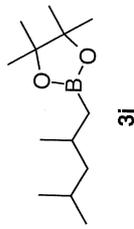
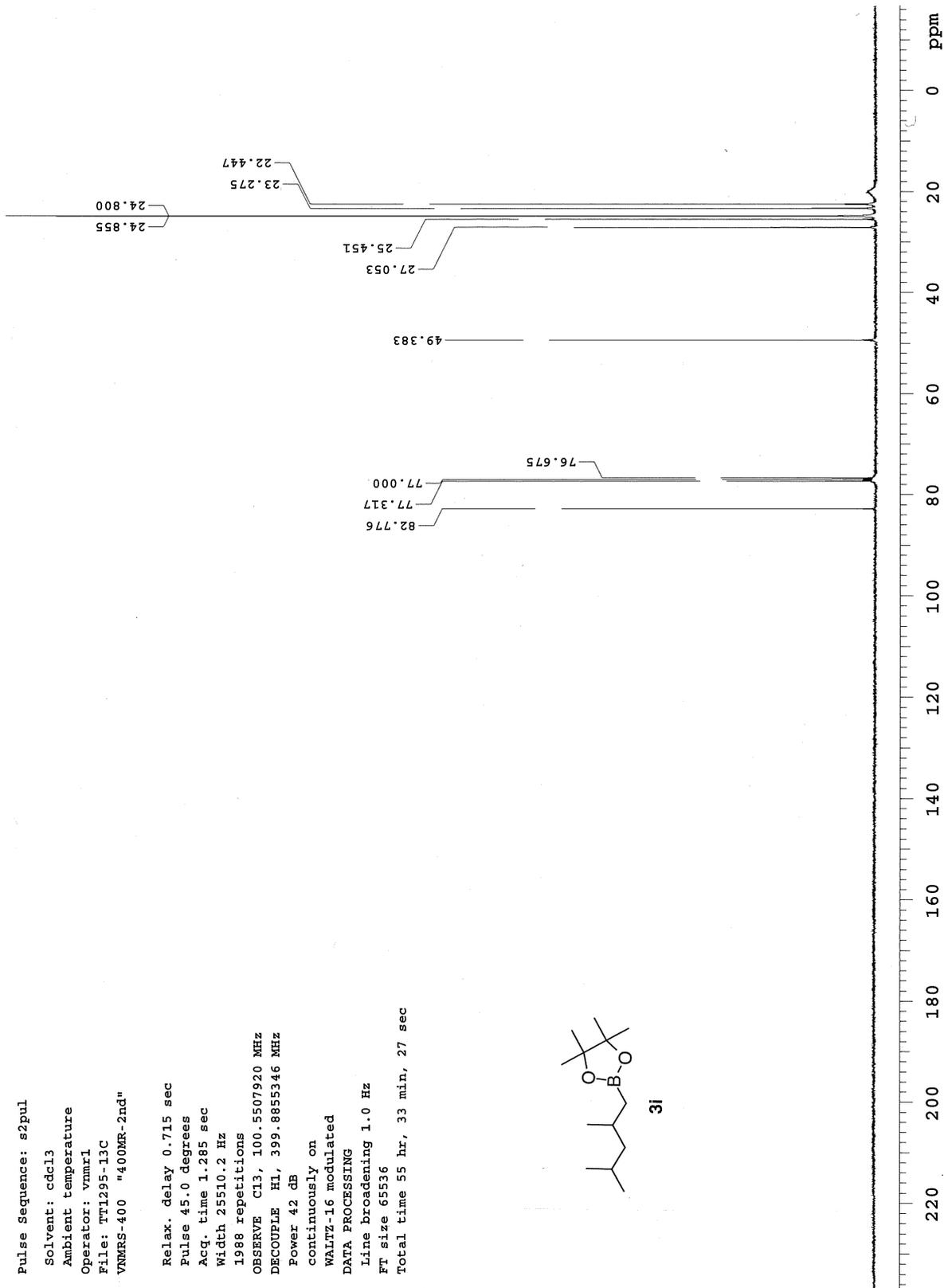
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/TI1295-13C.fid

Pulse Sequence: s2pul

Solvent: cdcl3
 Ambient temperature
 Operator: vnmr1
 File: TI1295-13C
 VNMR-400 "400MR-2nd"

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 1988 repetitions
 OBSERVE C13, 100.5507920 MHz
 DECOUPLE H1, 399.8855346 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 Ft size 65536
 Total time 55 hr, 33 min, 27 sec



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigoe2/Ttl1308.fid

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: Ttl1308

VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

24 repetitions

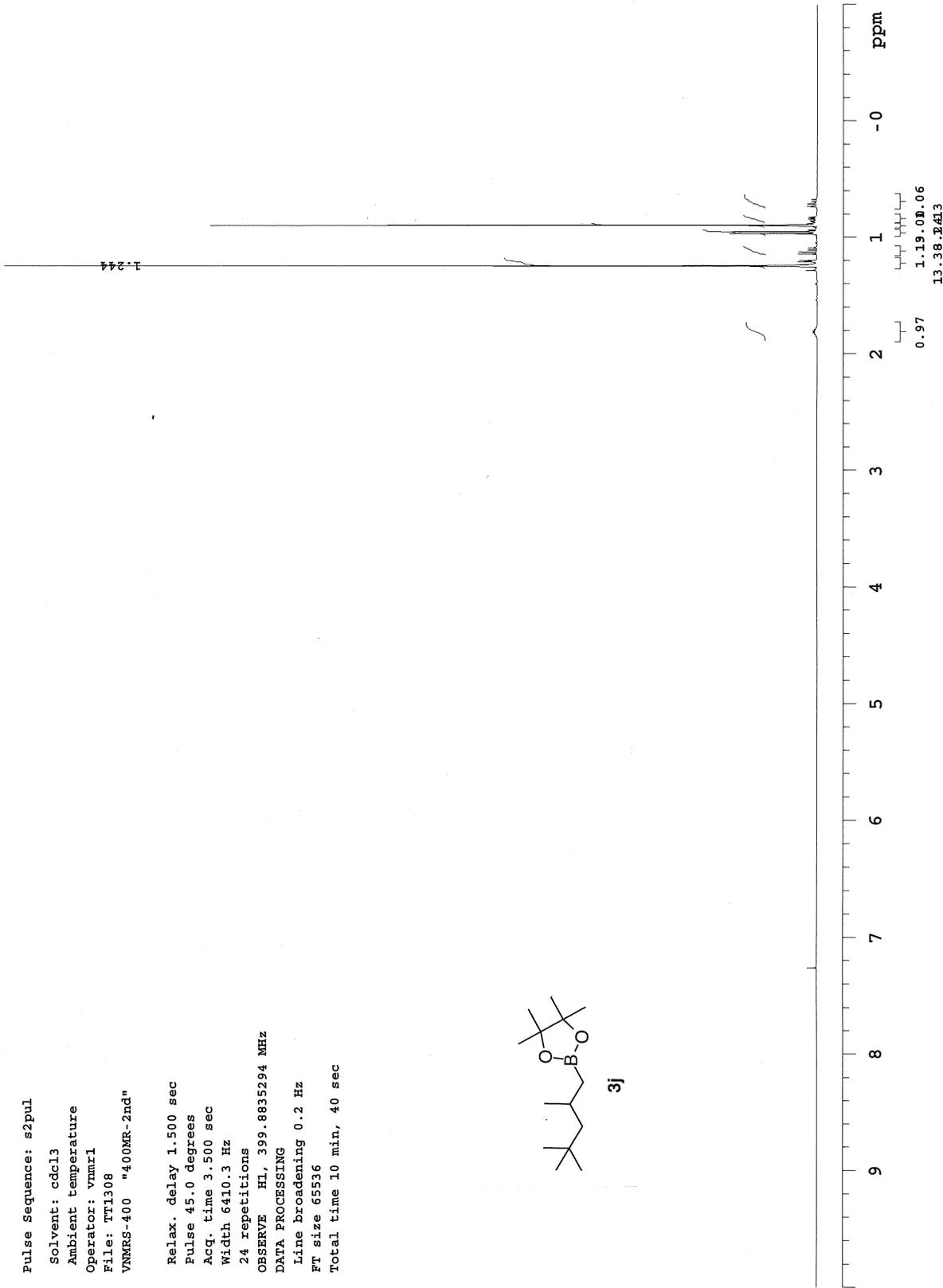
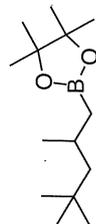
OBSERVE H1, 399.8835294 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/Torigoe2/Tt1314.fid

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: Tt1314

VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

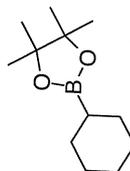
OBSERVE HL, 399.8835280 MHz

DATA PROCESSING

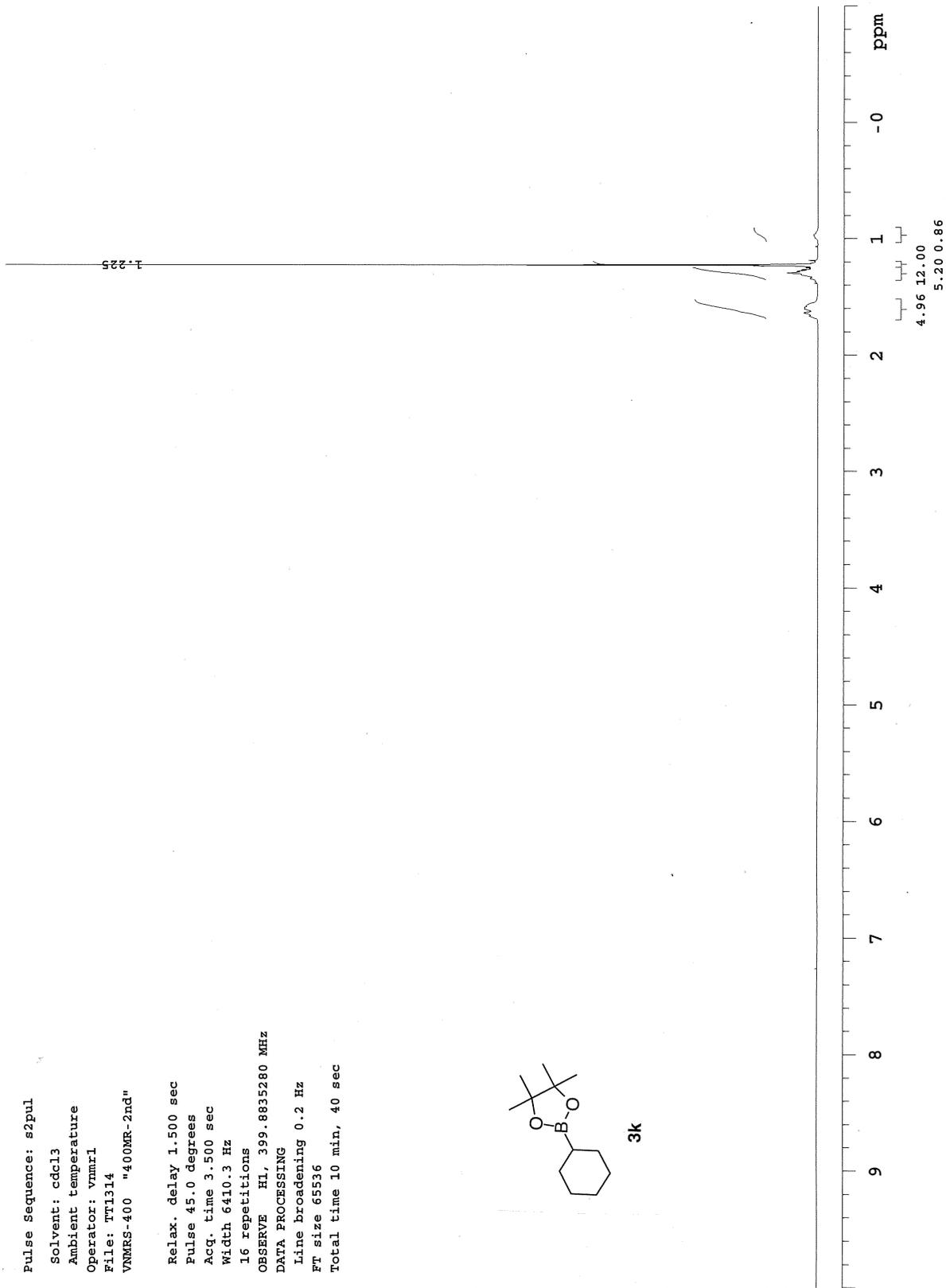
Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



3k



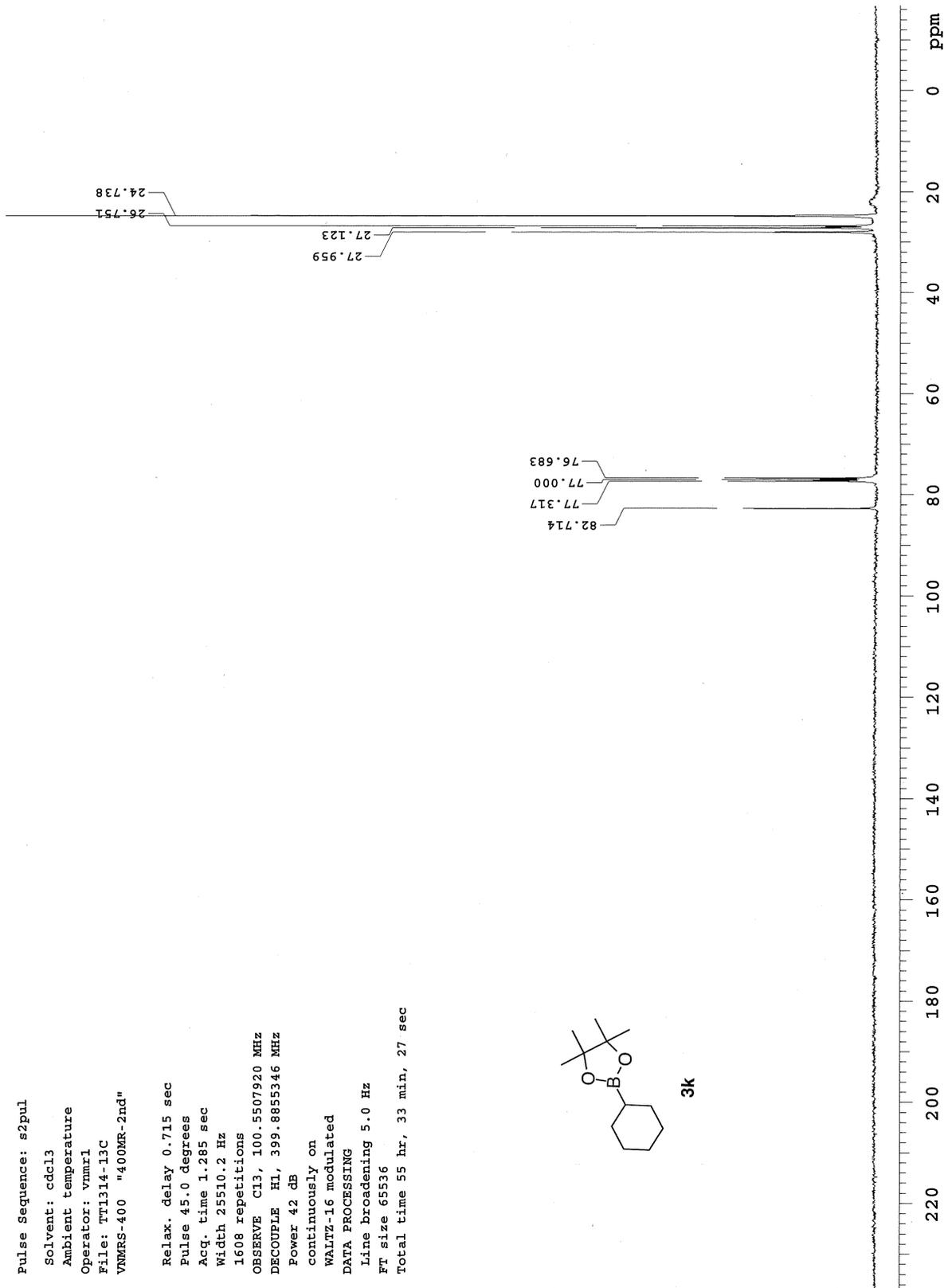
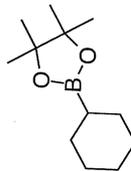
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigoe2/T11314-13C.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: T11314-13C
VNMR-400 "400MR-2nd"

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
1608 repetitions
OBSERVE C13, 100.5507920 MHz
DECOUPLE H1, 399.8855346 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
Ft size 65536
Total time 55 hr, 33 min, 27 sec



STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigoe2/Tt1352-13C.fid

Pulse Sequence: s2pul

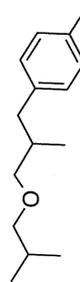
Solvent: cdcl3
 Ambient temperature
 Operator: vnmr1
 File: Tt1352-13C
 VNMR-400 "400MR-2nd"

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 740 repetitions

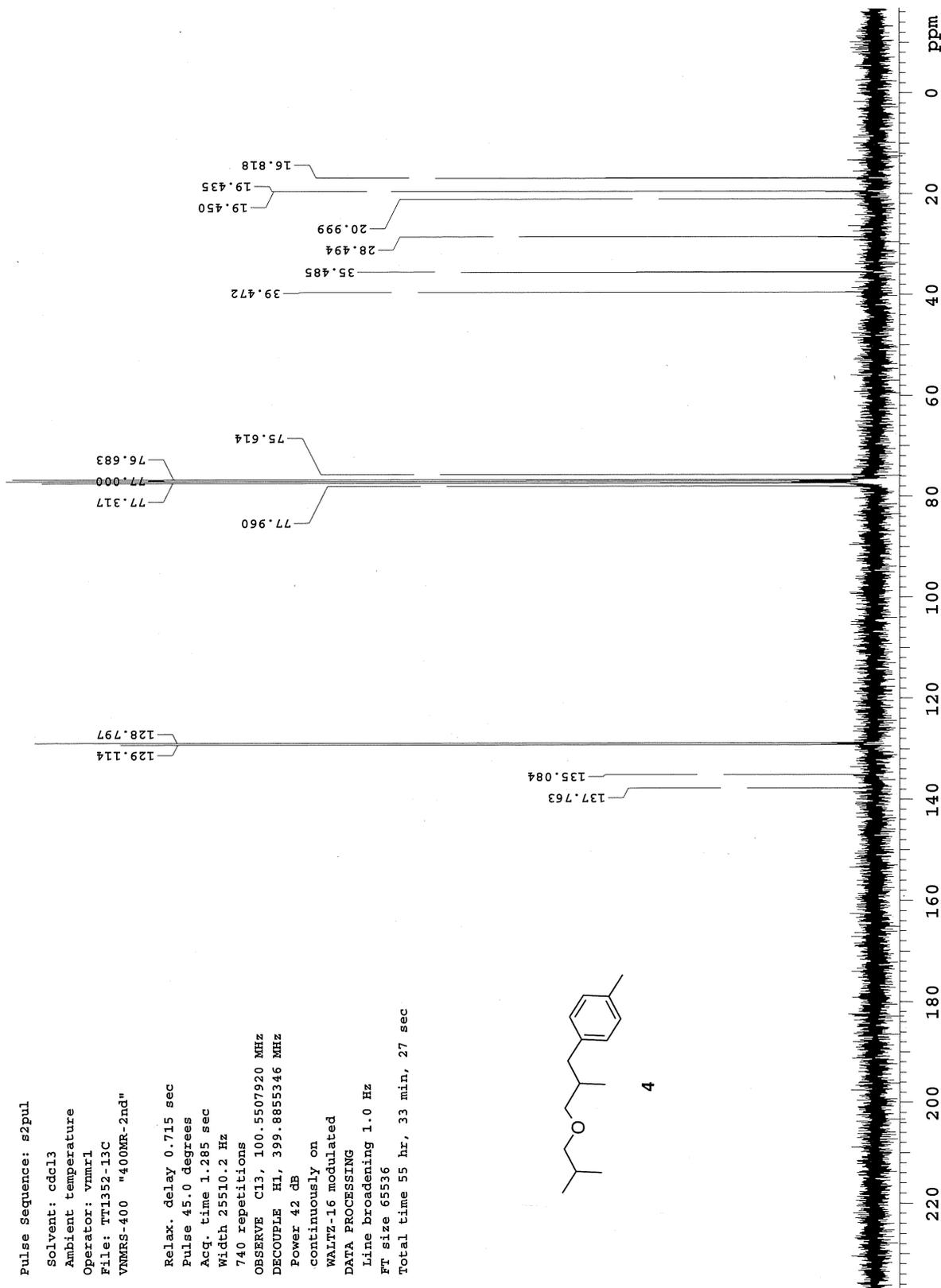
OBSERVE C13, 100.5507920 MHz
 DECOUPLE H1, 399.885346 MHz
 Power 42 dB

continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz

FT size 65536
 Total time 55 hr, 33 min, 27 sec



4



STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigoe2/TT1341-13C-2.fi

Pulse Sequence: s2pul

Solvent: cdc13
 Ambient temperature
 Operator: vnmr1
 File: TT1341-13C-2
 VNMRS-400 "400MR-2nd"

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 1996 repetitions
 OBSERVE C13, 100.5507920 MHz
 DECOUPLE H1, 399.8855346 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 55 hr, 33 min, 27 sec

