

Supporting Information

Dearomatizing Conversion of Pyrazines to 1,4-Dihydropyrazine Derivatives via Transition-Metal-Free Diboration, Silaboration, and Hydroboration

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1. General

All reactions were performed in a drybox under an atmosphere of nitrogen with magnetic stirring. ^1H NMR spectra were recorded on Varian Mercury-400 (400.44 MHz) or 400MR (399.88 MHz) spectrometers. ^{13}C NMR spectra were recorded on a JEOL JNM-A500 (125.65 MHz) spectrometer. ^{11}B NMR spectra were recorded on Varian Mercury-400 (128.48 MHz) or 400MR (128.30 MHz) spectrometers. ^1H NMR data were reported as follows: chemical shift in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (J), and integration. ^{13}C NMR data were reported in ppm downfield from tetramethylsilane. ^{11}B NMR data were reported in ppm downfield from $\text{BF}_3\cdot\text{OEt}_2$. High resolution mass spectra were recorded on a JEOL JMS-SX102A (EI) spectrometer.

2. Materials

THF and pentane were dried and degassed by The Ultimate Solvent System (GlassContour). Bis(pinacolato)diboron (**2**) and 5,5,5',5'-tetramethyl-2,2'-bi-1,3,2-dioxaborinane (**3**) were purchased from Allychem and were purified by recrystallization before use. A silylboronic ester **6**¹ and pinacolborane (**8**)² and were synthesized by the method reported previously. Pyrazine (**1a**) (Aldrich), 2-methylpyrazine (**1b**), 2-pyrazinecarbonitrile (**1e**) (Wako), 2-methoxypyrazine (**1c**), methyl 2-pyrazinecarboxylate (**1d**), and 2,6-dimethylpyrazine (**1f**) (TCI) were used as received from commercial sources.

3. Diboration of Pyrazine (**1a**) with **2** (eq 1)

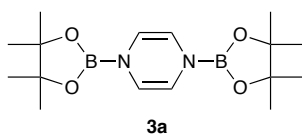
A Procedure for THF as a Solvent: In a drybox, pyrazine (**1a**, 36 mg, 0.45 mmol) and bis(pinacolato)diboron (**2**, 103 mg, 0.40 mmol) were placed in a screw-capped vial equipped with a magnetic stirrer bar. THF (0.4 mL) was added to the vial and the vial was capped by a screw cap. The

(1) T. Ohmura, K. Masuda, H. Furukawa, M. Suginome, *Organometallics* 2007, **26**, 1291.

solution was stirred magnetically in the drybox at room temperature. After 2 h the reaction mixture was concentrated in vacuo to remove volatiles including remaining **1a**. The *N,N'*-diboryl-1,4-dihydropyrazine **3a** (126 mg, 93%) was obtained as a white solid with high purity.

A Procedure for Pentane as a Solvent: In a drybox, pyrazine (**1a**, 35 mg, 0.44 mmol) and bis(pinacolato)diboron (**2**, 103 mg, 0.40 mmol) were placed in a screw-capped vial equipped with a magnetic stirrer bar. Pentane (0.4 mL) was added to the vial and the vial was capped by a screw cap. The solution was stirred magnetically in the drybox at room temperature. A white solid was precipitated. After 2 h the solution was removed by decantation, and the solid was washed with pentane (0.2 mL x 2) and dried in vacuo. The *N,N'*-diboryl-1,4-dihydropyrazine **3a** (122 mg, 90%) was obtained as a white solid with high purity.

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (**3a**)



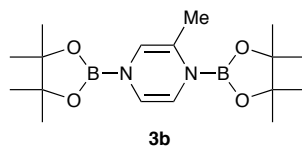
3a: ^1H NMR (400 MHz, CDCl_3) δ 5.13 (s, 4H), 1.19 (s, 24H). ^{13}C NMR (126 MHz, CDCl_3) δ 113.2, 83.0, 24.5. ^{11}B NMR (128 MHz, CDCl_3) δ 21.8. HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{28}\text{B}_2\text{N}_2\text{O}_4$ (M^+): 334.2235, found: 334.2249.

4. Diboration of Substituted Pyrazines 1b-1f (Table 1)

General Procedure for Diboration of Substituted Pyrazines: In a drybox, pyrazine **1** (0.44 mmol) and bis(pinacolato)diboron (**2**, 102 mg, 0.40 mmol) were placed in a screw-capped vial equipped with a magnetic stirrer bar. Pentane (0.4 mL) was added to the vial and the vial was capped by a screw cap. The solution was stirred magnetically in the drybox at room temperature. A white solid was precipitated. After 2 h the solution was removed by decantation, and the solid was washed with pentane (0.2 mL x 2) and dried in vacuo. The *N,N'*-diboryl-1,4-dihydropyrazine **3** was obtained with high purity.

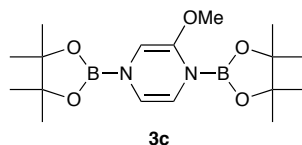
(2) C. E. Tucker, J. Davidson, P. Knochel, *J. Org. Chem.* 1992, **57**, 3484.

2-Methyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (**3b**, entry 1)



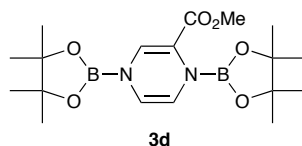
According to the general procedure, 2-methylpyrazine (**1b**, 45 mg, 0.48 mmol) was reacted with **2** (103 mg, 0.40 mmol). The product **3b** (125 mg, 89%) was obtained as a white solid. **3b**: ^1H NMR (400 MHz, CDCl_3) δ 5.36 (d, $J = 6.0$ Hz, 1H), 5.29 (dd, $J = 6.0, 1.2$ Hz, 1H), 5.05 (quintet, $J = 1.2$ Hz, 1H), 1.63 (d, $J = 1.2$ Hz, 3H), 1.19 (s, 12H), 1.18 (s, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 121.9, 114.3, 113.2, 110.4, 82.9, 82.3, 24.5, 24.4, 18.2. ^{11}B NMR (128 MHz, CDCl_3) δ 22.0. HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_4$ (M^+): 348.2392, found: 348.2397.

2-Methoxy-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (**3c**, entry 2)



According to the general procedure, 2-methoxypyrazine (**1c**, 48 mg, 0.44 mmol) was reacted with **2** (103 mg, 0.40 mmol). The product **3c** (119 mg, 81%) was obtained as a white solid. **3c**: ^1H NMR (400 MHz, CDCl_3) δ 6.04 (d, $J = 4.8$ Hz, 1H), 5.95 (d, $J = 4.8$ Hz, 1H), 4.13 (s, 1H), 3.74 (s, 3H), 1.23 (s, 24H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.7, 116.1, 115.9, 83.2, 53.0, 47.5, 25.1, 24.3. ^{11}B NMR (128 MHz, CDCl_3) δ 23.1. HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_5$ (M^+): 364.2341, found: 364.2331.

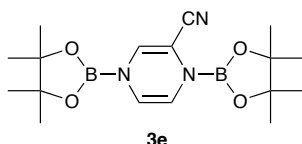
Methyl 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine-2-carboxylate (**3d**, entry 3)



According to the general procedure, methyl 2-pyrazinecarboxylate (**1d**, 61 mg, 0.44 mmol) was reacted with **2** (108 mg, 0.42 mmol). The product **3d** (156 mg, 93%) was obtained as a yellow solid. **3d**:

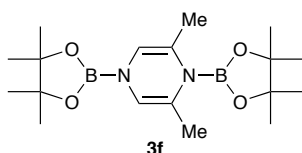
^1H NMR (400 MHz, CDCl_3) δ 6.60 (s, 1H), 5.49 (d, $J = 5.6$ Hz, 1H), 5.35 (d, $J = 5.6$ Hz, 1H), 3.69 (s, 3H), 1.222 (s, 12H), 1.216 (s, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.0, 130.3, 116.6, 116.4, 114.0, 83.7, 82.8, 51.2, 24.41, 24.40. ^{11}B NMR (128 MHz, CDCl_3) δ 22.3. HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_6$ (M^+): 392.2290, found: 392.2279.

2-Cyano-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (**3e**, entry 4)



According to the general procedure, 2-pyrazinecarbonitril (**1e**, 45 mg, 0.43 mmol) was reacted with **2** (103 mg, 0.40 mmol). The product **3e** (140 mg, 96%) was obtained as a yellow solid. **3e**: ^1H NMR (400 MHz, CDCl_3) δ 5.99 (d, $J = 1.2$ Hz, 1H), 5.25 (d, $J = 6.4$ Hz, 1H), 5.08 (dd, $J = 6.4, 1.2$ Hz, 1H), 1.22 (s, 12H), 1.21 (s, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 132.2, 115.6, 115.4, 112.1, 99.6, 84.1, 83.6, 24.43, 24.38. ^{11}B NMR (128 MHz, CDCl_3) δ 21.9. HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{27}\text{B}_2\text{N}_3\text{O}_4$ (M^+): 359.2188, found: 359.2182.

2,6-Dimethyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (**3f**, entry 5)

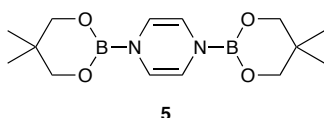


According to the general procedure, 2,6-dimethylpyrazine (**1f**, 48 mg, 0.45 mmol) was reacted with **2** (98 mg, 0.39 mmol). The product **3f** (107 mg, 77%) was obtained as a white solid. This compound was gradually decomposed in CDCl_3 . **3f**: ^1H NMR (400 MHz, C_6D_6) δ 5.96 (q, $J = 1.2$ Hz, 2H), 2.04 (d, $J = 1.2$ Hz, 6H), 1.01 (s, 12H), 0.97 (s, 12H). ^{13}C NMR (126 MHz, C_6D_6) δ 123.7, 115.9, 82.9, 81.9, 24.7, 24.5, 18.4. ^{11}B NMR (128 MHz, CDCl_3) δ 22.8. HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{32}\text{B}_2\text{N}_2\text{O}_4$ (M^+): 362.2548, found: 362.2538.

5. Diboration of Pyrazine (1a) with 4 (eq 2)

In a drybox, pyrazine (**1a**, 36 mg, 0.45 mmol) and 5,5,5',5'-tetramethyl-2,2'-bi-1,3,2-dioxaborinane (**4**, 88 mg, 0.39 mmol) were placed in a screw-capped vial equipped with a magnetic stirrer bar. THF (0.4 mL) was added to the vial and the vial was capped by a screw cap. The solution was stirred magnetically in the drybox at room temperature. After 24 h the reaction mixture was concentrated in vacuo to remove volatiles including remaining **1a**. The *N,N'*-diboryl-1,4-dihydropyrazine **5** (107 mg, 90%) was obtained as a white solid with high purity.

1,4-Bis-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1,4-dihydropyrazine (5)

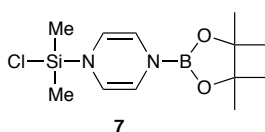


5: ^1H NMR (400 MHz, CDCl_3) δ 5.18 (s, 4H), 3.54 (s, 8H), 0.91 (s, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 112.5, 72.4, 32.1, 21.7. ^{11}B NMR (128 MHz, CDCl_3) δ 17.6. HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{24}\text{B}_2\text{N}_2\text{O}_4$ (M^+): 306.1922, found: 306.1928.

6. Silaboration of Pyrazine (1a) (eq 3)

In a drybox, pyrazine (**1a**, 35 mg, 0.43 mmol) was placed in a screw-capped vial equipped with a magnetic stirrer bar. THF (0.4 mL) and 2-(chlorodimethylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**, 87 mg, 0.39 mmol) were added to the vial and the vial was capped by a screw cap. The solution was stirred magnetically in the drybox at room temperature. After 24 h the reaction mixture was concentrated in vacuo to remove volatiles including remaining **1a**. The *N*-boryl-*N'*-silyl-1,4-dihydropyrazine **7** (97 mg, 82%) was obtained with high purity.

1-(Chlorodimethylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (7)



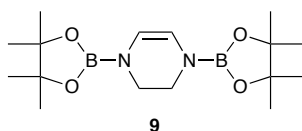
7: ^1H NMR (400 MHz, CDCl_3) δ 5.12 (d, $J = 6.0$ Hz, 2H), 4.85 (d, $J = 6.0$ Hz, 2H), 1.19 (s, 12H), 0.44

(s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 113.8, 113.3, 83.0, 24.5, 0.5. ^{11}B NMR (128 MHz, CDCl_3) δ 21.8.
HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{22}\text{BCIN}_2\text{O}_2\text{Si}$ (M^+):300.1232, found: 300.1238.

7. Hydroboration of Pyrazine (1a) (eq 4)

In a drybox, pyrazine (**1a**, 32 mg, 0.39 mmol) was placed in a screw-capped vial equipped with a magnetic stirrer bar. THF (0.4 mL) and pinacolborane (**8**, 114 mg, 0.89 mmol) were added to the vial and the vial was capped by a screw cap. The solution was stirred magnetically in the drybox at 50 °C. After 72 h the reaction mixture was concentrated in vacuo to remove volatiles including remaining **8**. The *N,N'*-diboryl-1,2,3,4-tetrahydropyrazine **9** (114 mg, 87%) was obtained as a white solid with high purity.

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrazine (**9**)



9: ^1H NMR (400 MHz, CDCl_3) δ 5.66 (s, 2H), 3.31 (s, 4H), 1.22 (s, 24H). ^{13}C NMR (126 MHz, CDCl_3) δ 110.4, 82.6, 41.9, 24.6. ^{11}B NMR (128 MHz, CDCl_3) δ 22.7. HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_4$ (M^+): 336.2392, found: 336.2390.

8. ^1H , ^{13}C , and ^{11}B NMR spectra of **3a-f**, **5**, **7**, and **9**

^1H , ^{13}C , and ^{11}B NMR spectra of **3a-f**, **5**, **7**, and **9** are shown in following pages.

STANDARD PROTON PARAMETERS

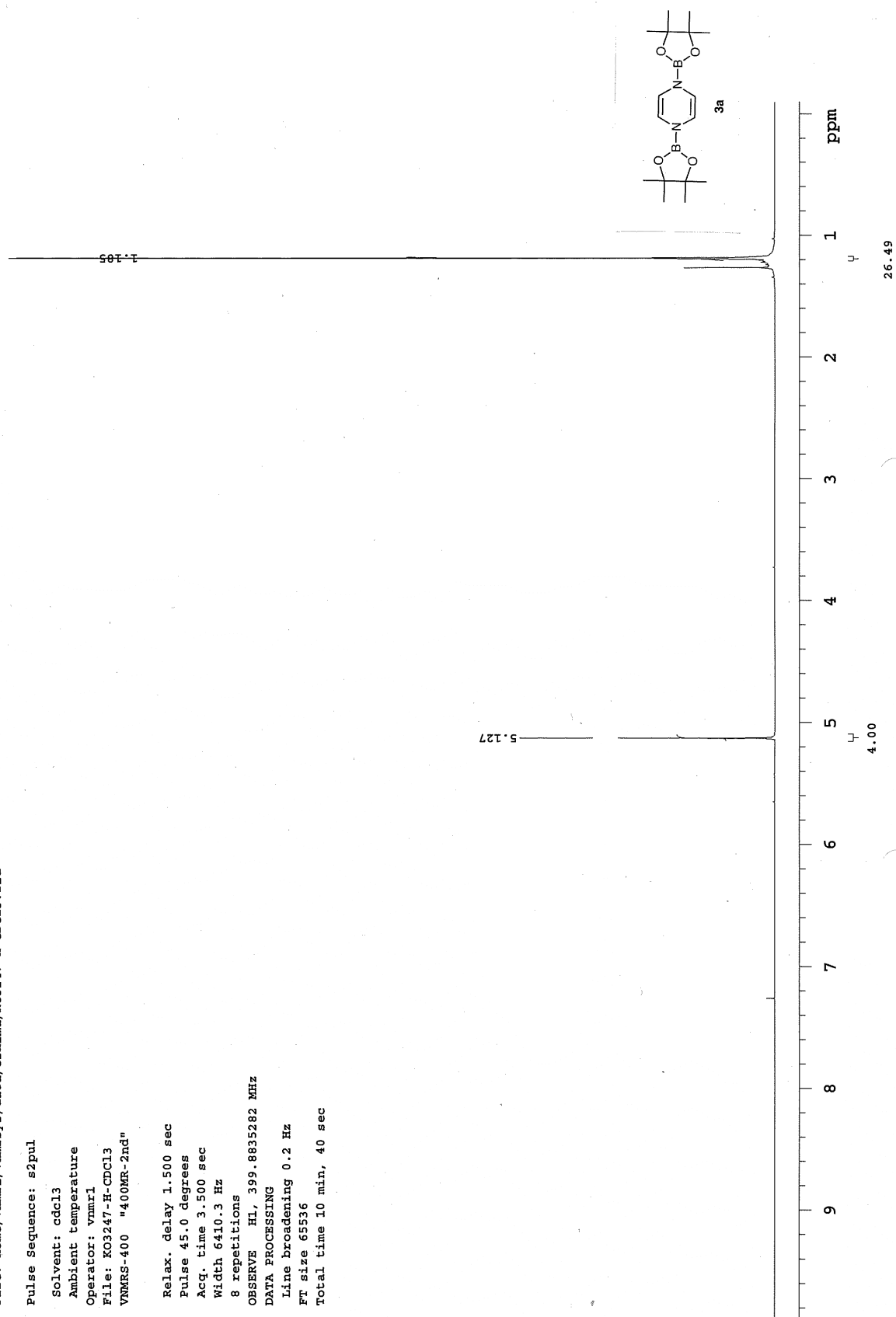
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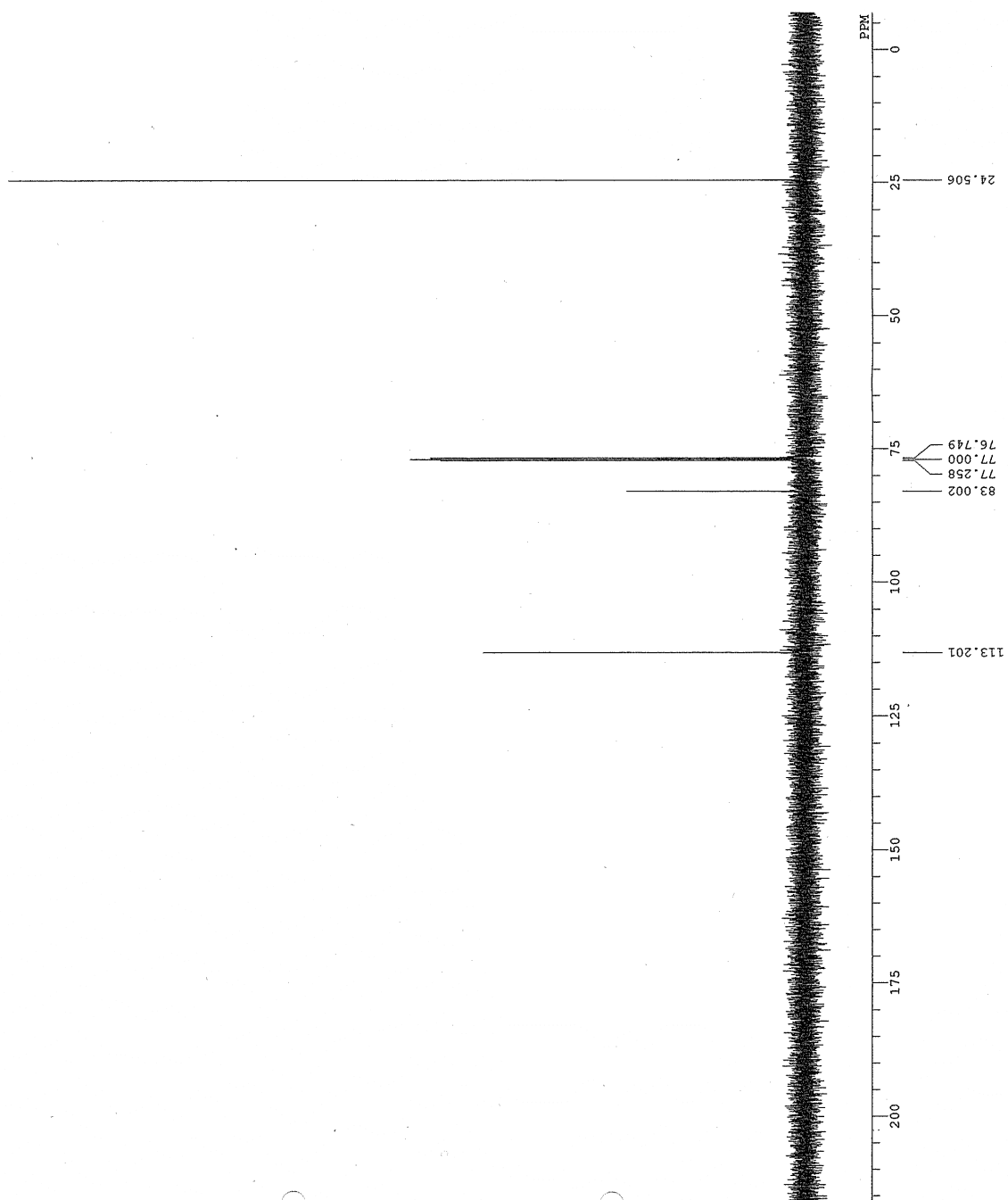
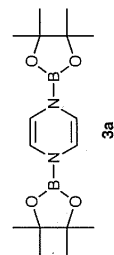
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Width 6410.3 Hz
8 repetitions

OBSERVE H1, 399.8835282 MHZ
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 10 min, 40 sec



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BF 0.16 Hz
RGAIN 33



STANDARD CARBON PARAMETERS

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Ambient temperature

Operator: vnmr1

File: KO3247-B-CDCl3

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Acq. time 0.629 sec

Width 26041.7 Hz

12 repetitions

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DECOUPLE H1, 399.8855705 MHz

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on during acquisition

off during delay

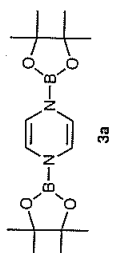
WALTZ-16 modulated

DATA PROCESSING

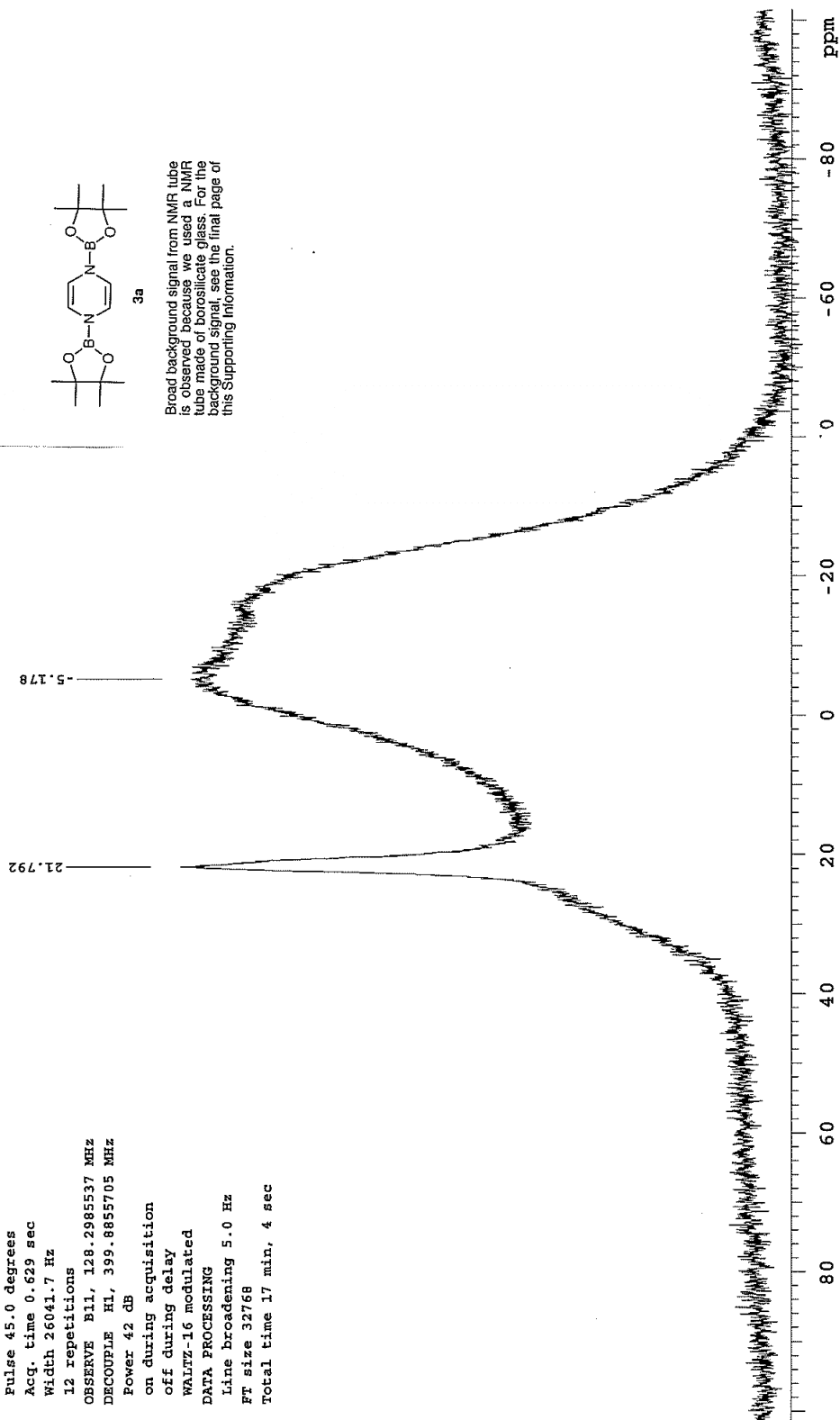
Line broadening 5.0 Hz

FT size 32768

Total time 17 min, 4 sec



Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



STANDARD PROTON PARAMETERS

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Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: K03253-H-CDCl3

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8 repetitions

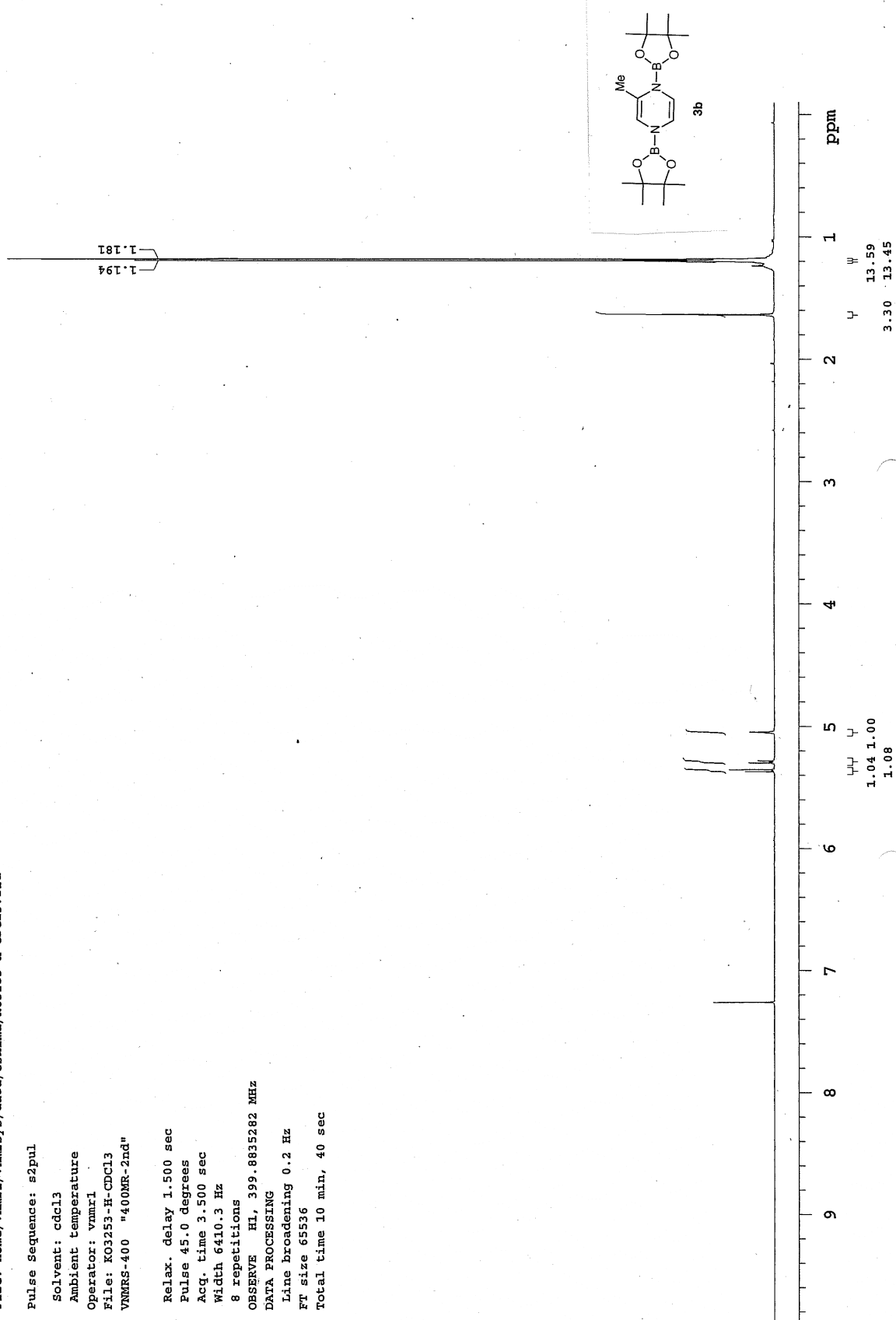
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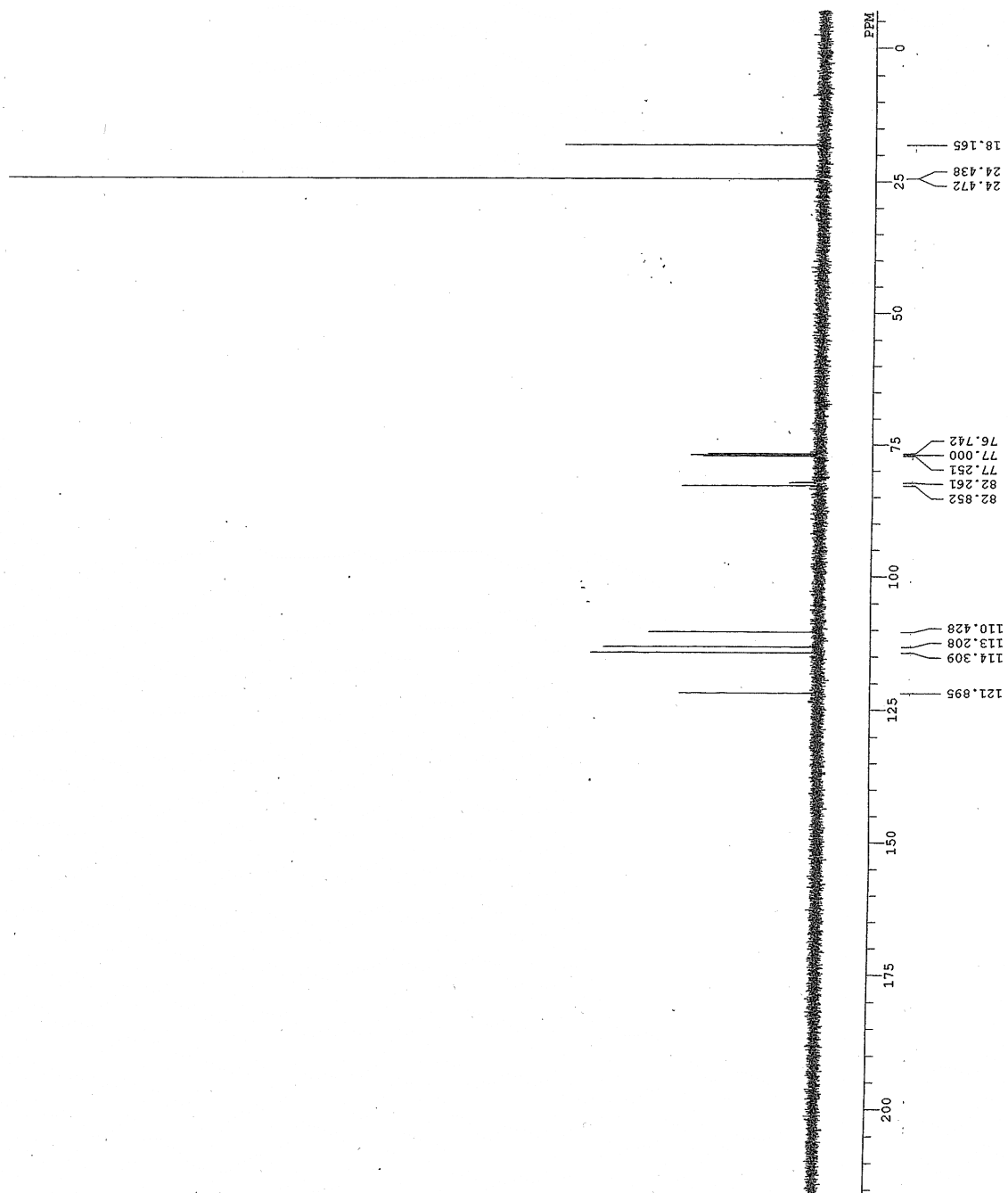
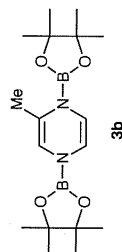
Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



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BF -0.10 Hz
RGAIN 33



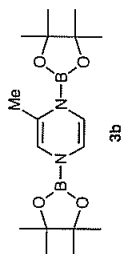
STANDARD CARBON PARAMETERS

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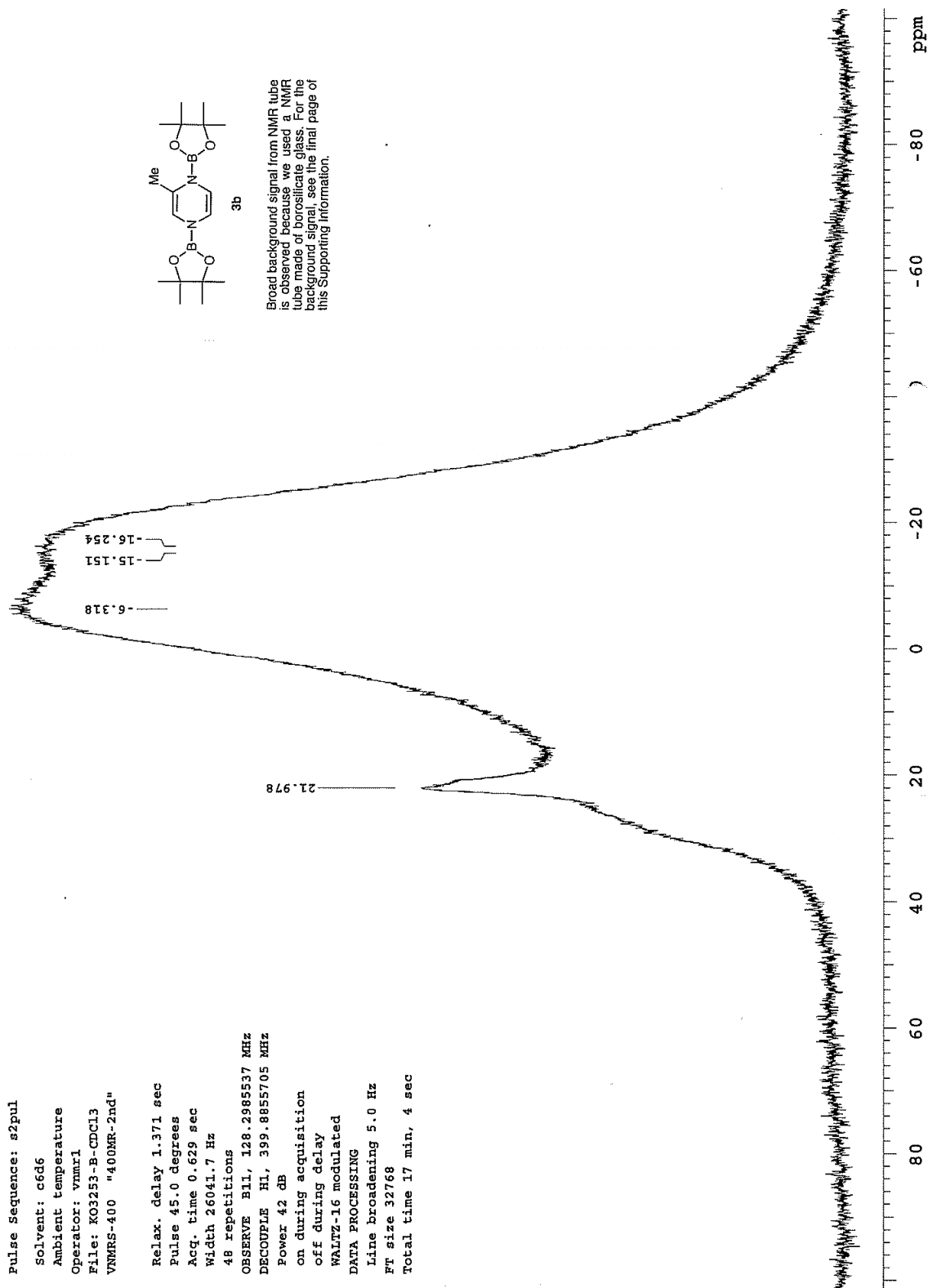
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Ambient temperature
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Acq. time 0.629 sec
Width 26041.7 Hz
48 repetitions
OBSERVE B11, 128.298537 MHz
DECOUPLE H1, 399.885705 MHz
Power 42 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 32768
Total time 17 min, 4 sec



Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



STANDARD PROTON PARAMETERS

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Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: KO3272-H-re-CDCl3

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Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

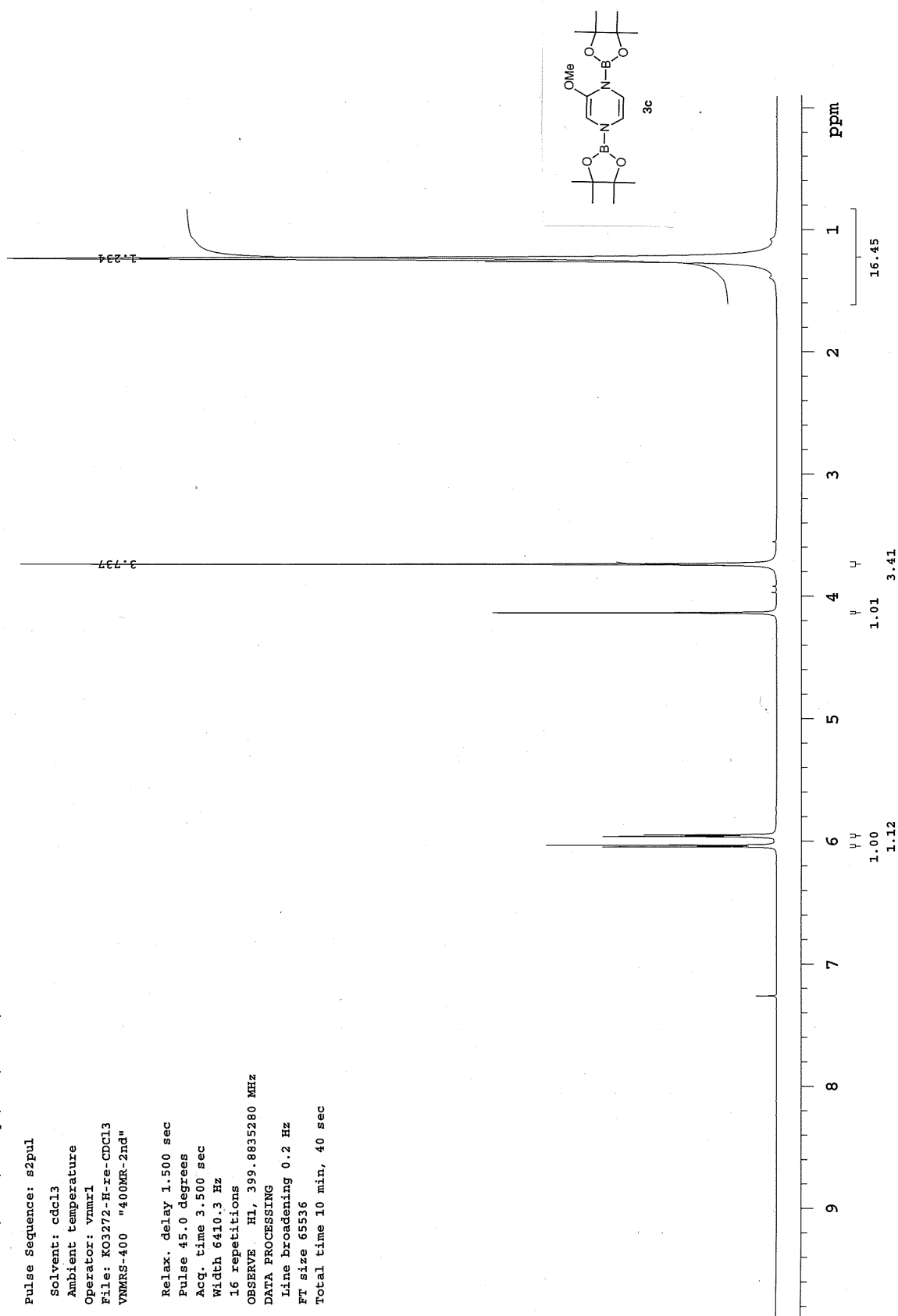
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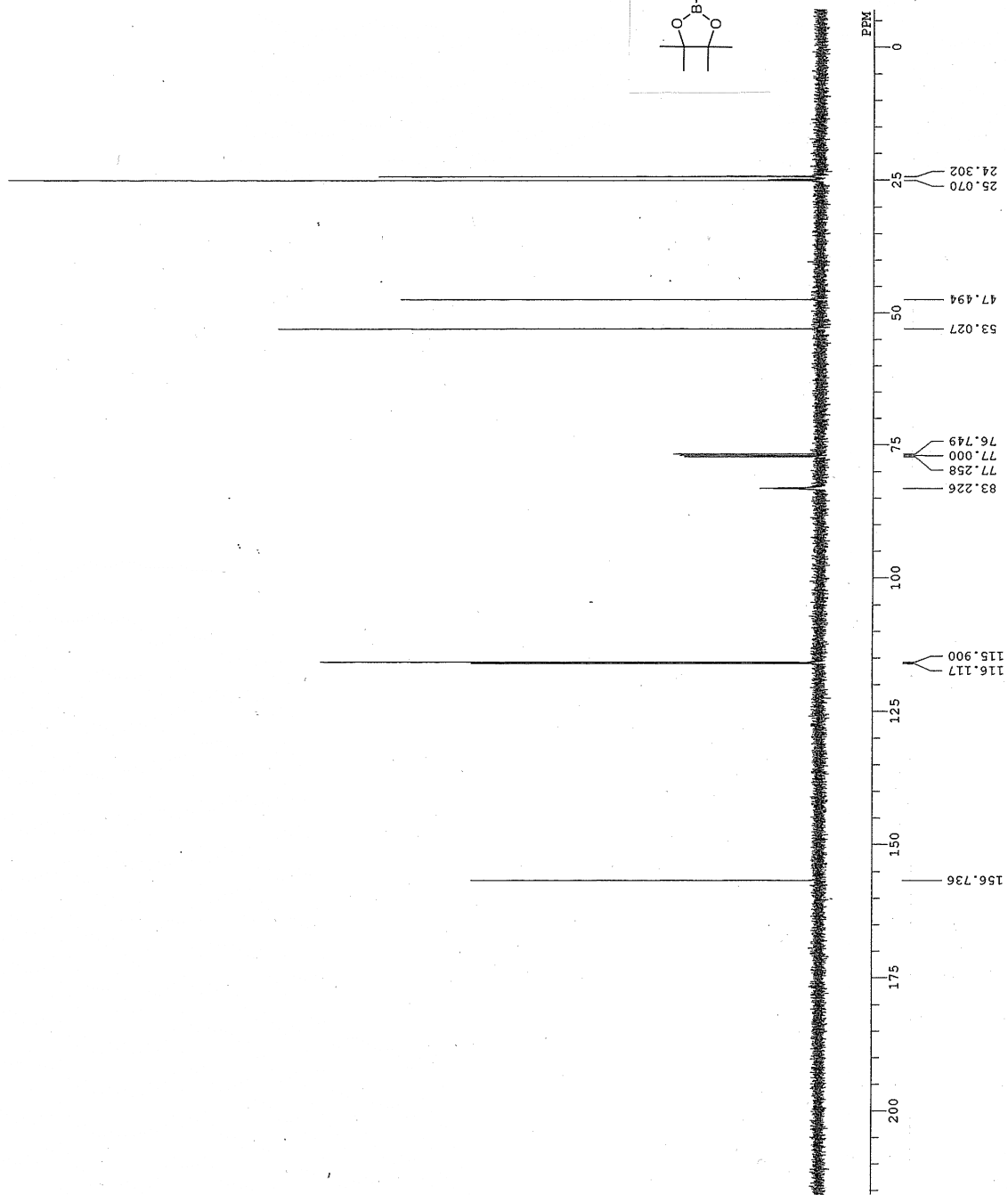
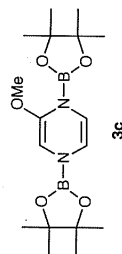
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Total time 10 min, 40 sec



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RGAIN 33



STANDARD CARBON PARAMETERS

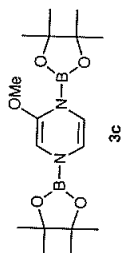
File: home/vnmr1/vnmrSYS/data/oshima/KO3272-B-CDCl3.fid

Pulse Sequence: s2pul

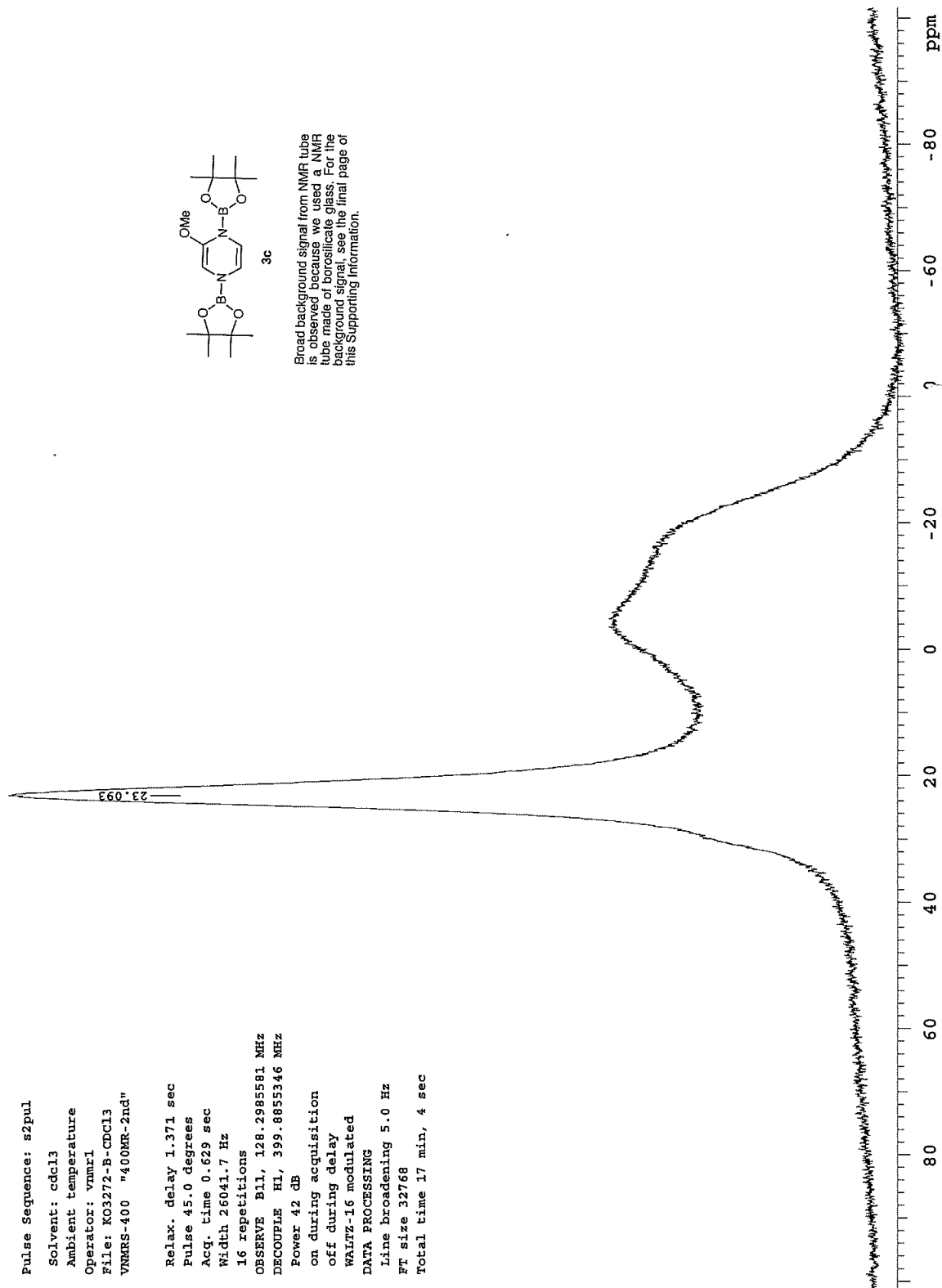
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: KO3272-B-CDCl3
VNMR5-400 "400MR-2nd"

Relax. delay 1.371 sec
Pulse 45.0 degrees
Acq. time 0.629 sec
Width 26041.7 Hz
16 repetitions
OBSERVE B11, 128.2985581 MHz
DECOUPLE H1, 399.8855346 MHz

Power 42 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 32768
Total time 17 min, 4 sec



Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



STANDARD PROTON PARAMETERS

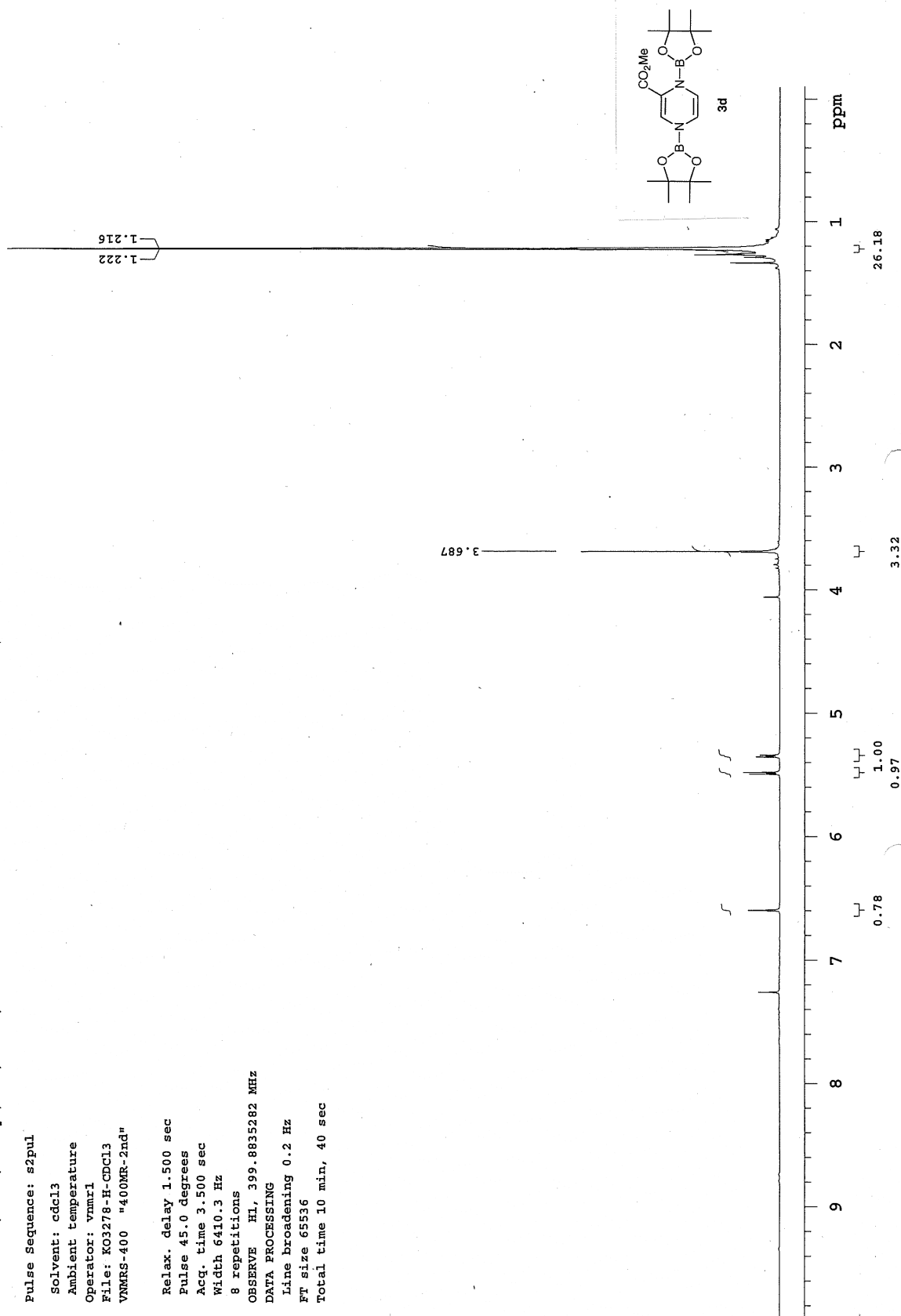
File: home/vnmr1/vnmrsys/data/oshima/K03278-H-CDCl3.fid

Pulse Sequence: s2pul

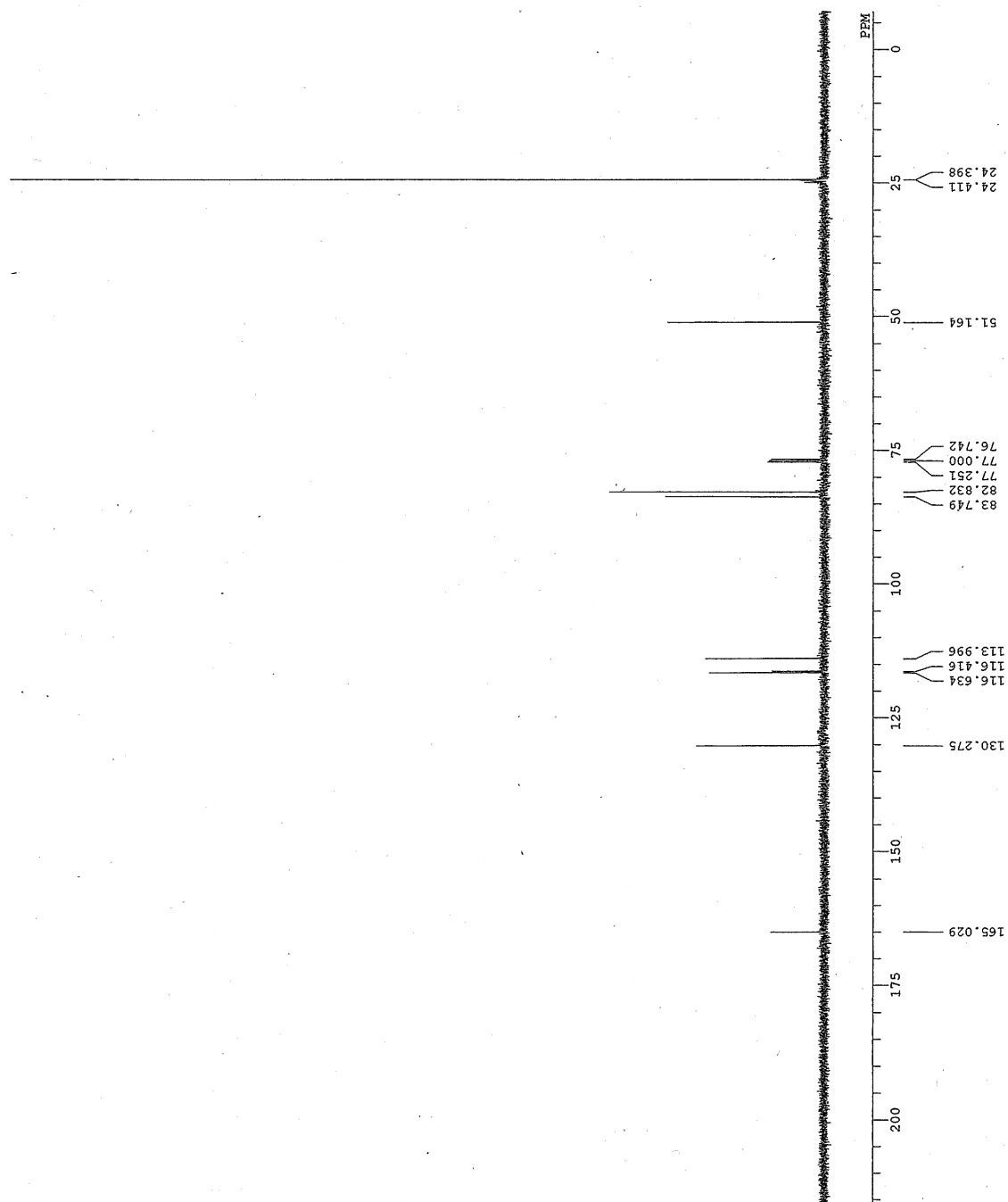
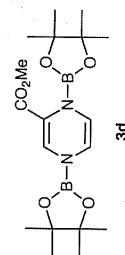
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: K03278-H-CDCl3
VNMRS-400 "400MF-2nd"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
8 repetitions

OBSERVE H1, 399.8835282 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 10 min, 40 sec



DFILE K03278-ECM-CDC13.ALS
CONNT Wed Mar 07 17:22:51 20
DAYM 13C
OBNUC 13C
EXMOD SINGL
OBFREQ 125.65 MHz
OBFIN 128449.48 Hz
POINT 32768
FREQU 28011.20 Hz
SCANS 85
ACQTM 1.1698 sec
PD 2.0000 sec
PWL 4.50 usec
IRNUC 1H
CTEMP 21.9 c
SIVNT CDCL3
EXREF 77.00 PPM
BF 0.43 Hz
RGAIN 33



STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrSYS/data/oshima/K03278-B-CDCl3.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: K03278-B-CDCl3
VNMR5-400 "400MR-2nd"

Relax. delay 1.371 sec
Pulse 45.0 degrees
Acq. time 0.629 sec
Width 26041.7 Hz
16 repetitions

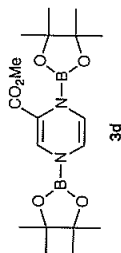
OBSERVE B11, 128.2985565 MHz
DECOUPLE H1, 399.8855346 MHz

Power 42 dB
on during acquisition
off during delay

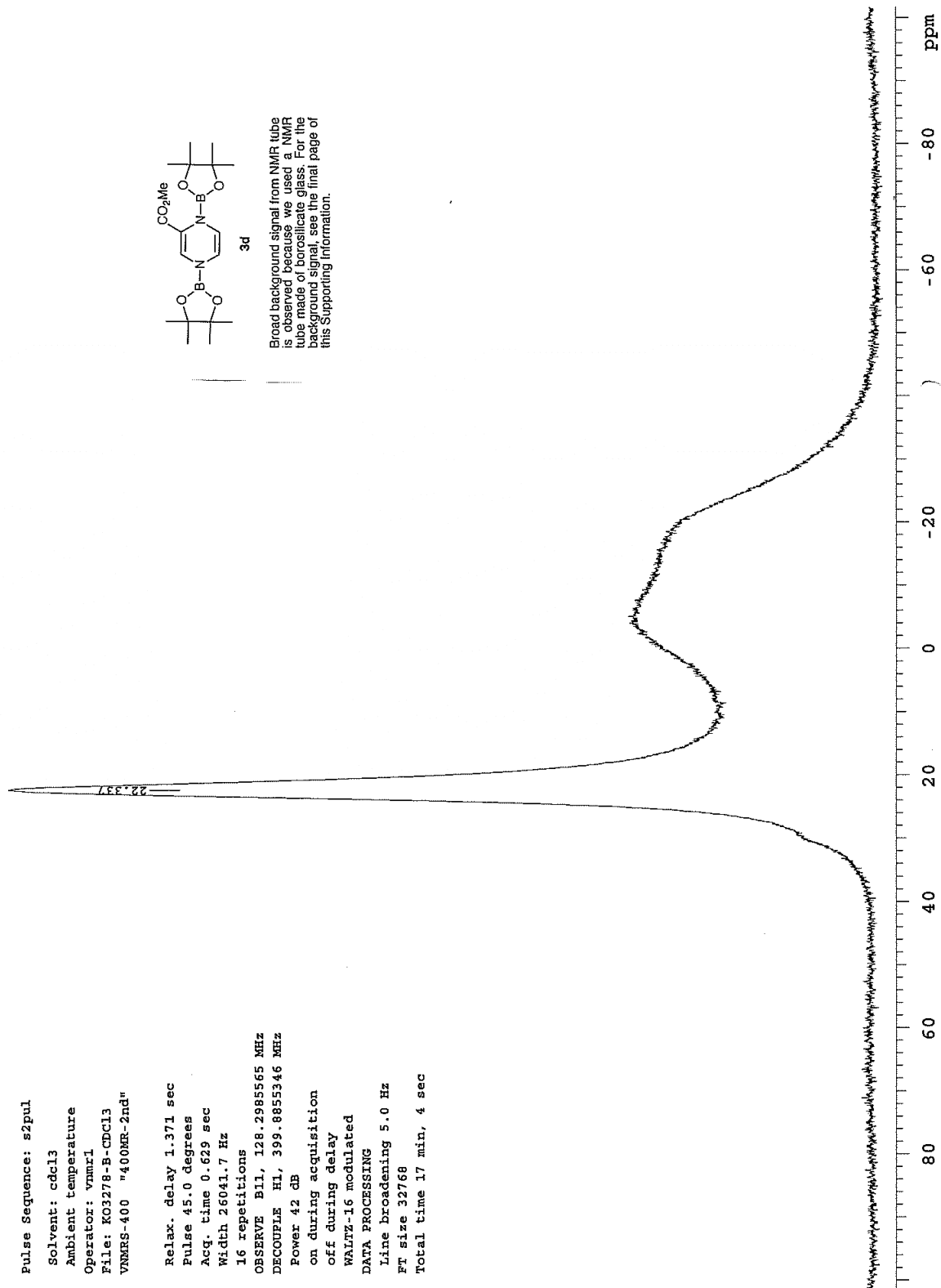
WALTZ-16 modulated

DATA PROCESSING

Line broadening 5.0 Hz
FT size 32768
Total time 17 min, 4 sec



Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



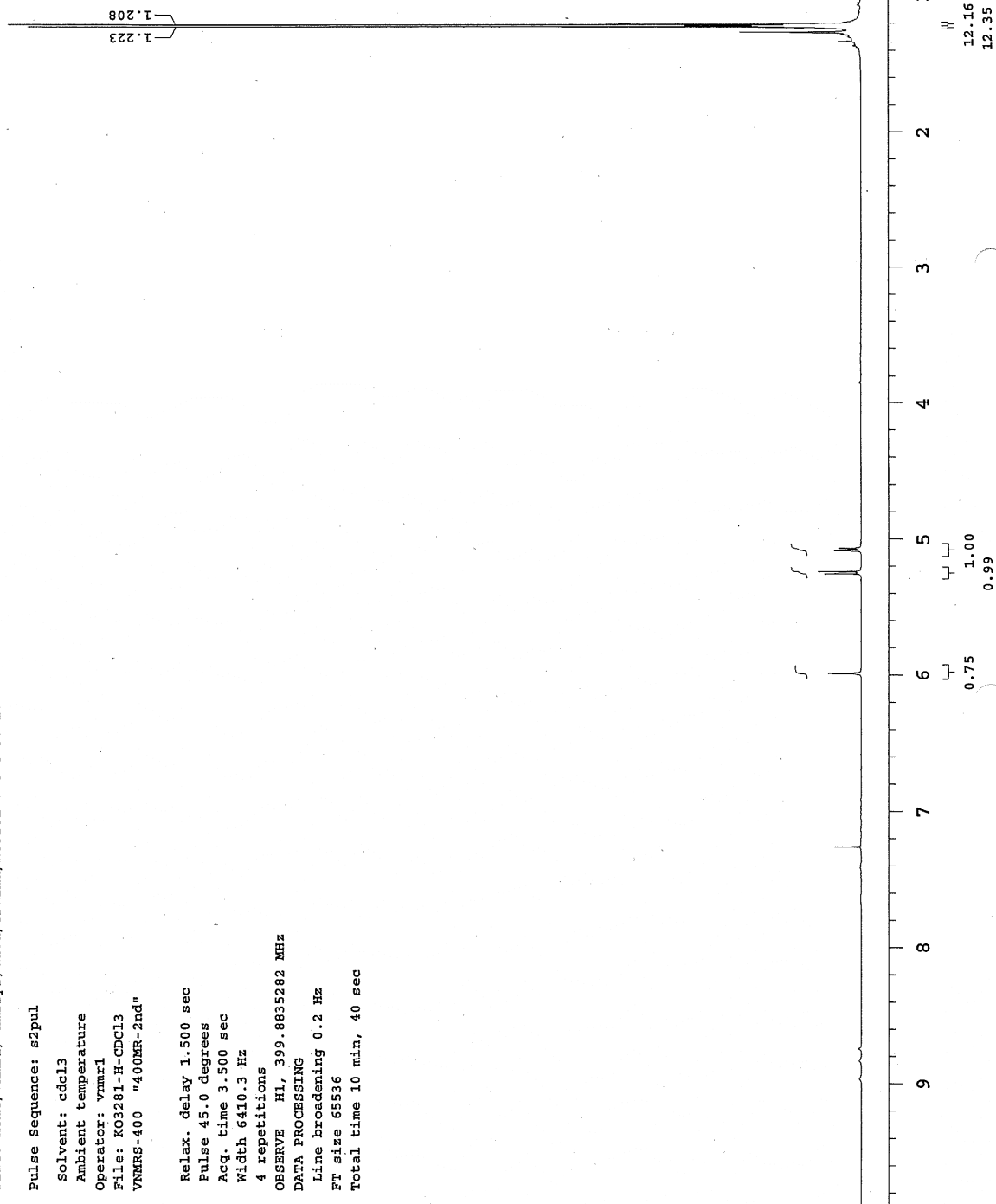
STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/oshima/KO3281-H-CDCl3.fid

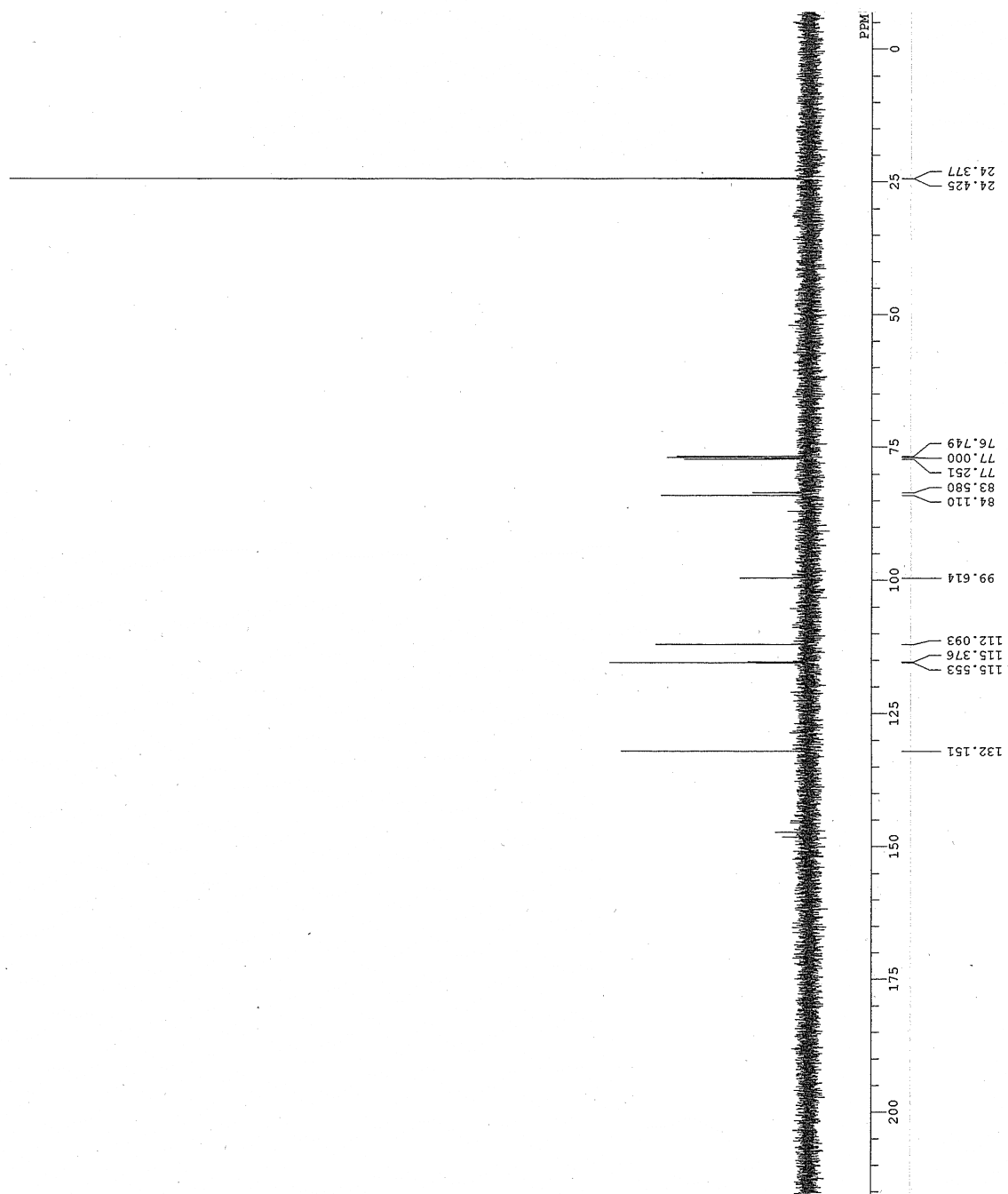
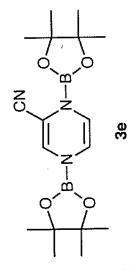
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: KO3281-H-CDCl3
VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
4 repetitions
OBSERVE H1, 399.8635282 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 10 min, 40 sec



DFILE K03281-C4-CDCl3.als
COMNT
DATIM Tue Mar 06 17:06:55 20
ORNUC 13C
EXMOD SINGL
OBFOC 125.65 MHz
OBFIN 128443.48 Hz
FOINT 32768
FREQU 28011.20 Hz
SCANS 20
ACQTM 1.1698 sec
PD 2.0000 sec
FWI 4.50 usec
IRNUC 1H
CTEMP 22.0 C
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.49 Hz
RGAIN 35



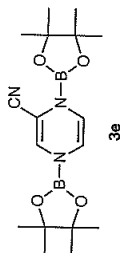
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrSYS/data/oshima/KO3281-B-CDCl3.fid

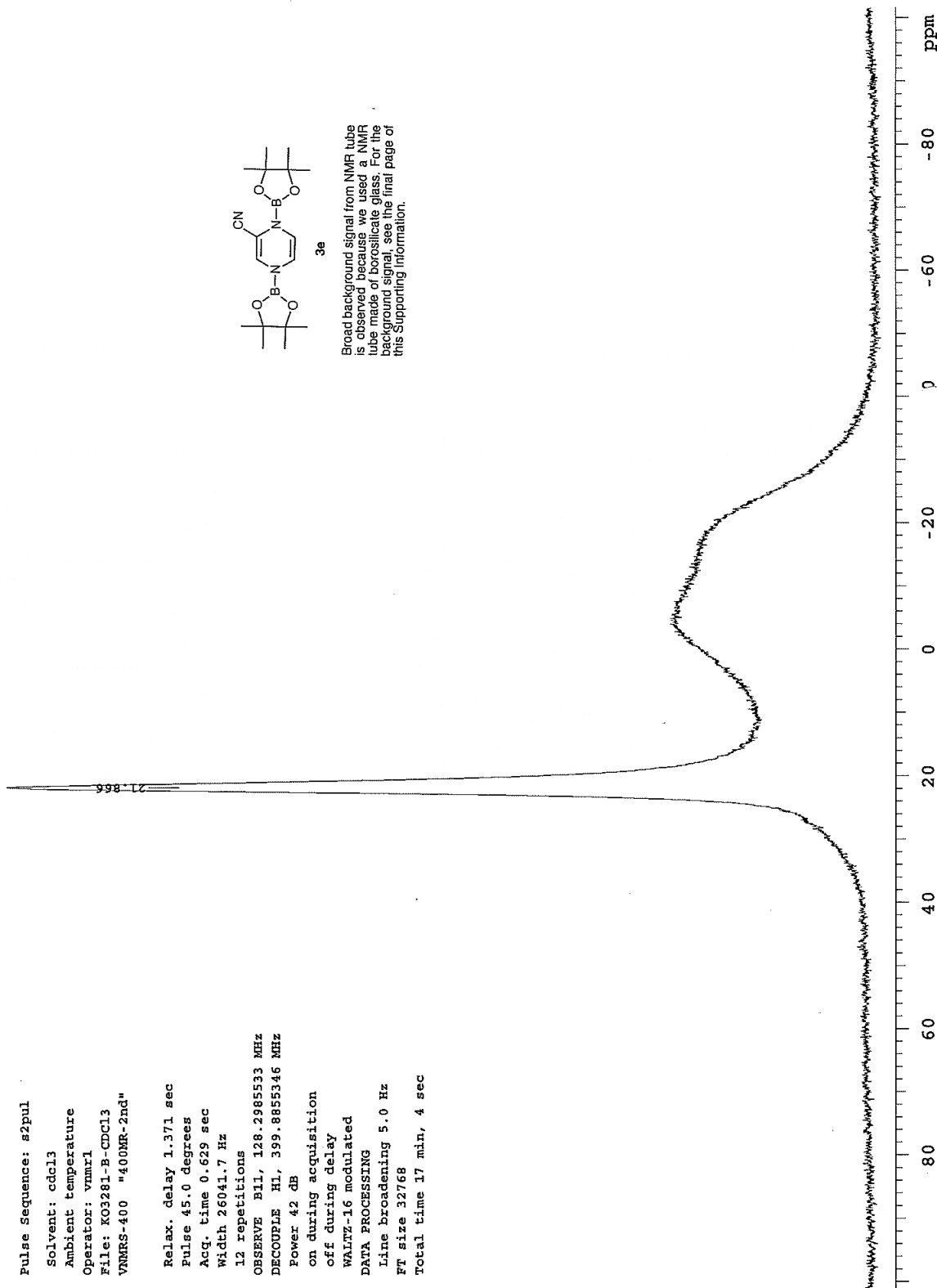
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: KO3281-B-CDCl3
VNMRS-400 "400MR-2nd"

Relax. delay 1.371 sec
Pulse 45.0 degrees
Acq. time 0.629 sec
Width 26041.7 Hz
12 repetitions
OBSERVE B11, 128.2985533 MHz
DECOUPLE H1, 399.8855346 MHz
Power 42 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 32768
Total time 17 min, 4 sec



Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrsys/data/oshima/KO3254-H-C6D6.fid

Pulse Sequence: s2pul

Solvent: c6d6

Ambient temperature

Operator: vnmr1

File: KO3254-H-C6D6

VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

12 repetitions

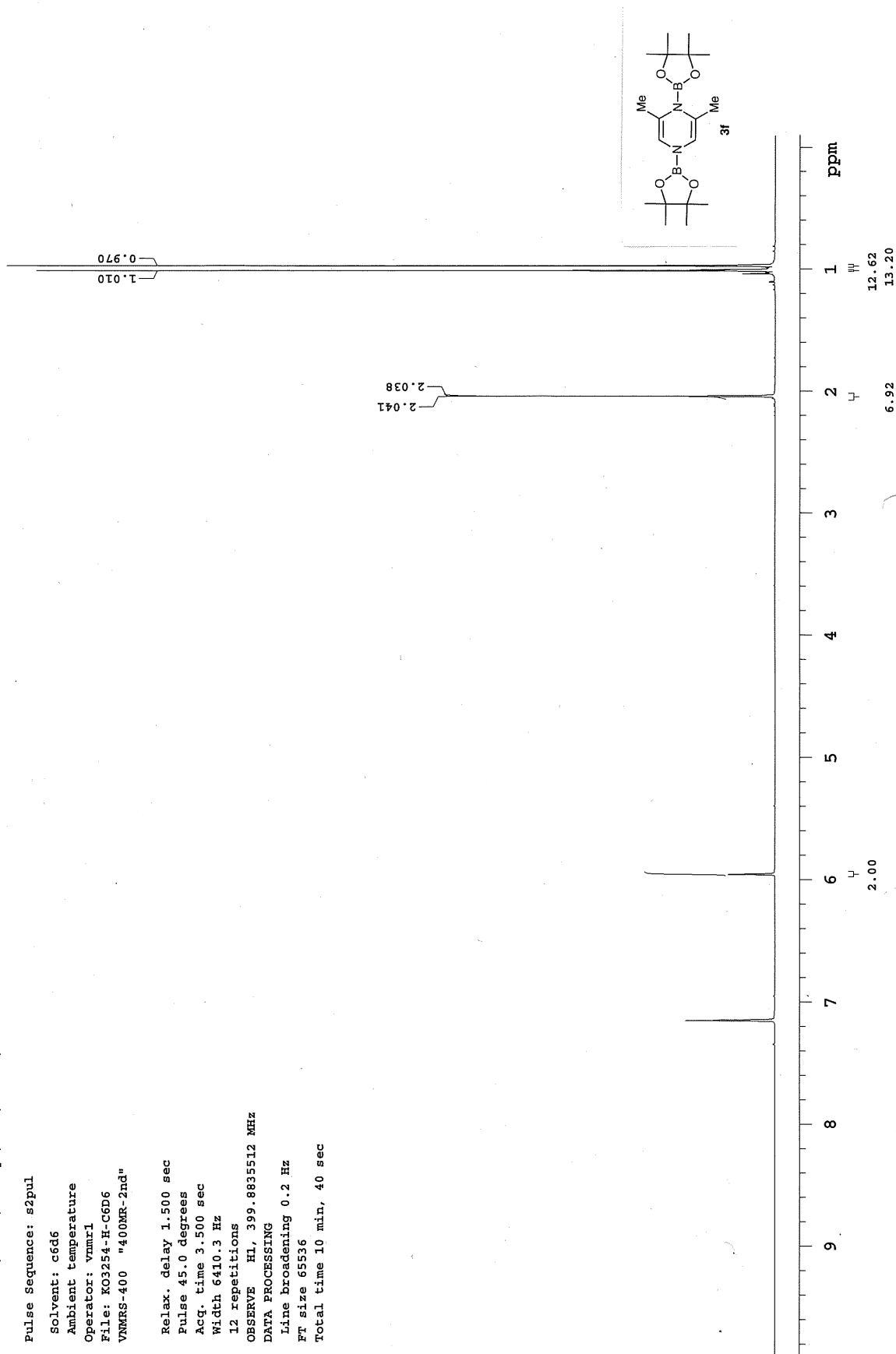
OBSERVE H1, 399.8835512 MHz

DATA PROCESSING

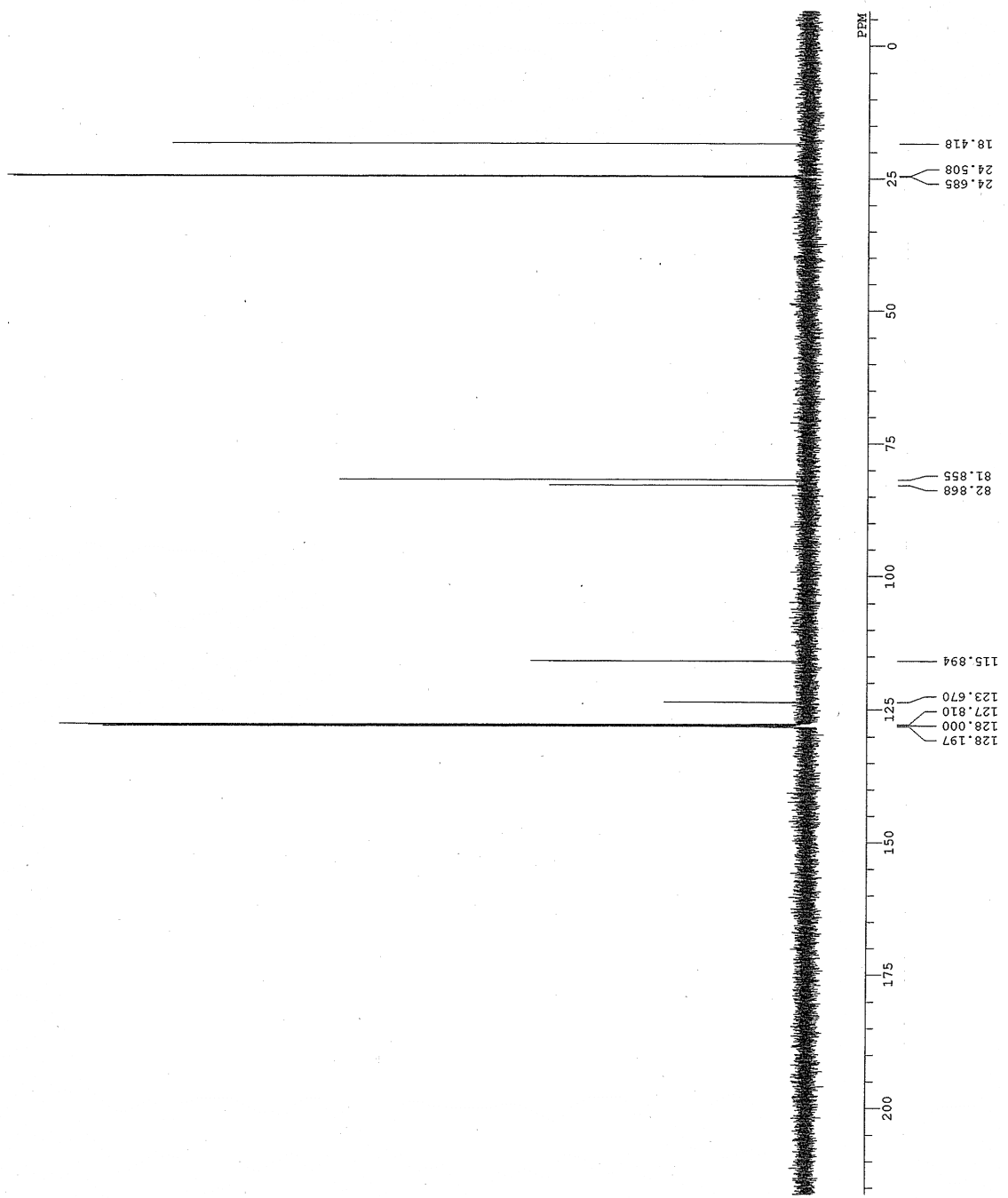
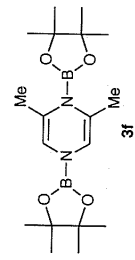
Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



DFILE _DEFAULT.ALS
COMNT
DATIM Sat Mar 03 00:19:58 20
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBFIN 128449.48 Hz
POINT 32768
FREOU 28011.20 Hz
SCANS 1.1688 sec
ACQTM 2.0000 sec
PUL 4.50 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT C6D6
EXREF 128.00 PPM
BF -0.10 Hz
RGAIN 32



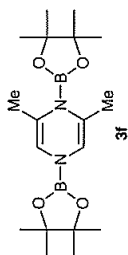
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrSYS/data/oshima/K03254-B-C6D6.fid

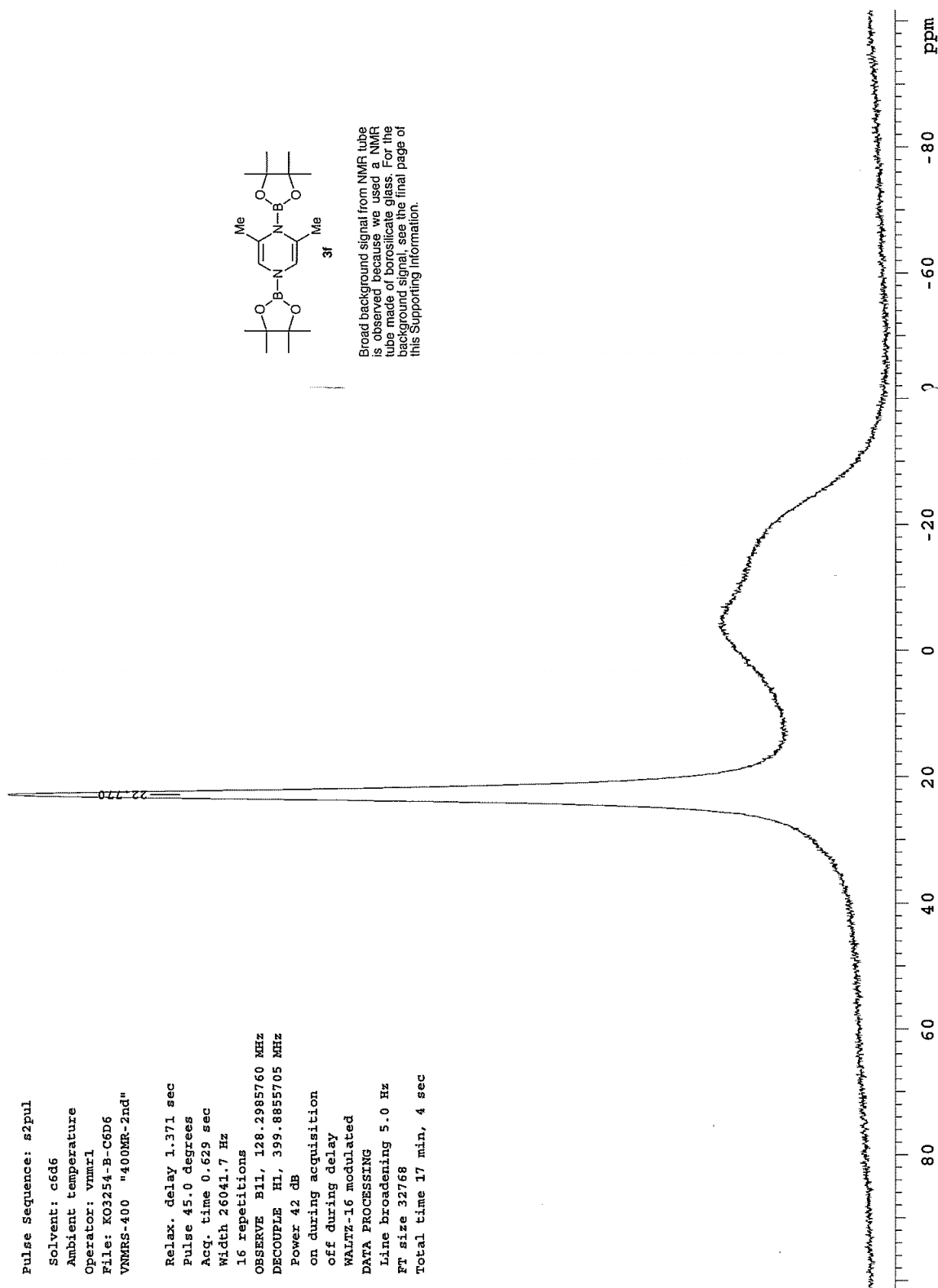
Pulse Sequence: s2pul

Solvent: c6d6
Ambient temperature
Operator: vnmr1
File: K03254-B-C6D6
VNMRS-400 "400MR-2nd"

Relax. delay 1.371 sec
Pulse 45.0 degrees
Acq. time 0.629 sec
Width 26041.7 Hz
16 repetitions
OBSERVE B11, 128.2985760 MHz
DECOUPLE H1, 399.8855705 MHz
Power 42 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
Ft size 32768
Total time 17 min, 4 sec



Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrSYS/data/oshima/K03296-H-CDCl3.fid

Pulse Sequence: s2pul

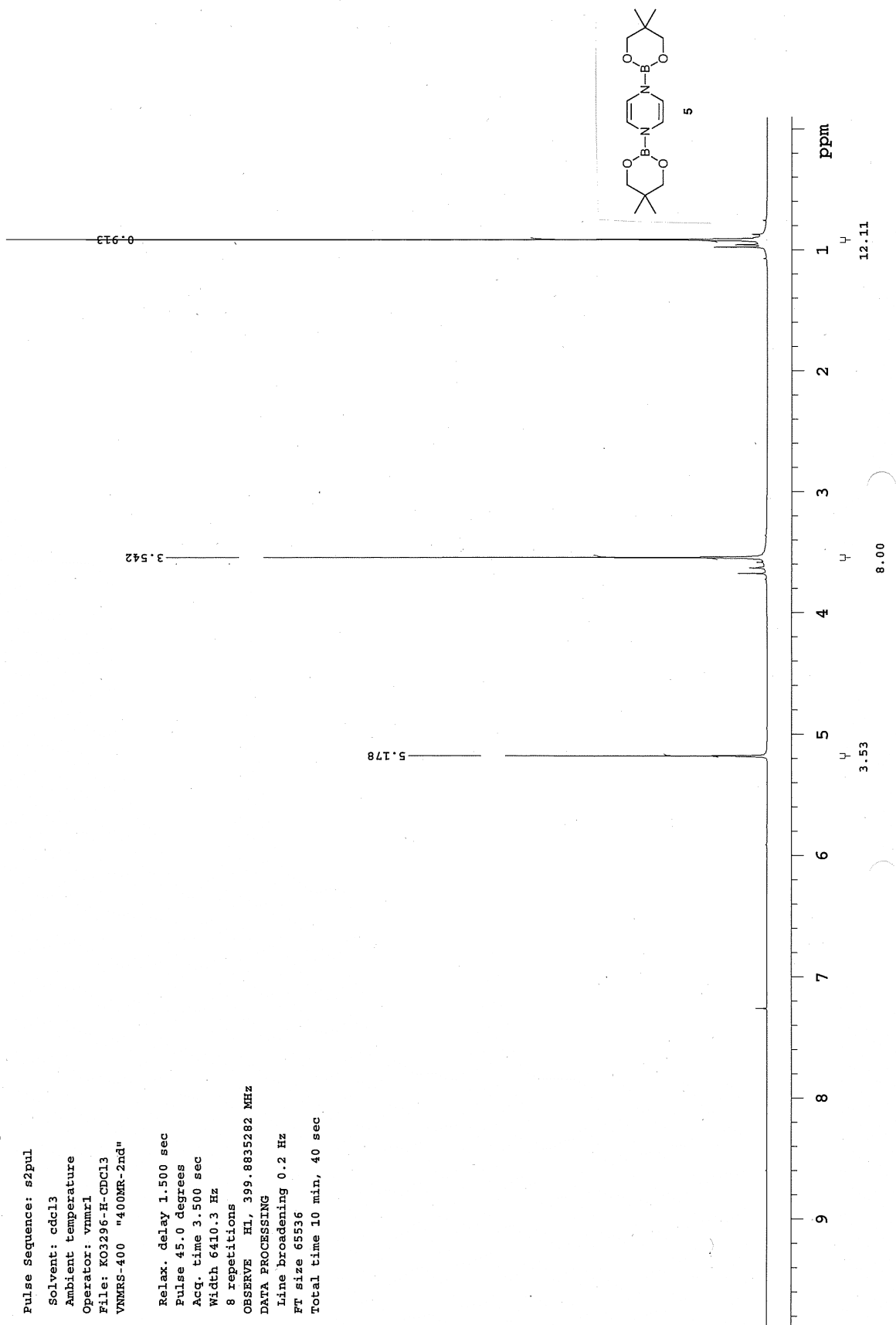
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: K03296-H-CDCl3
VNMRS-400 "400MR-2nd"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
8 repetitions

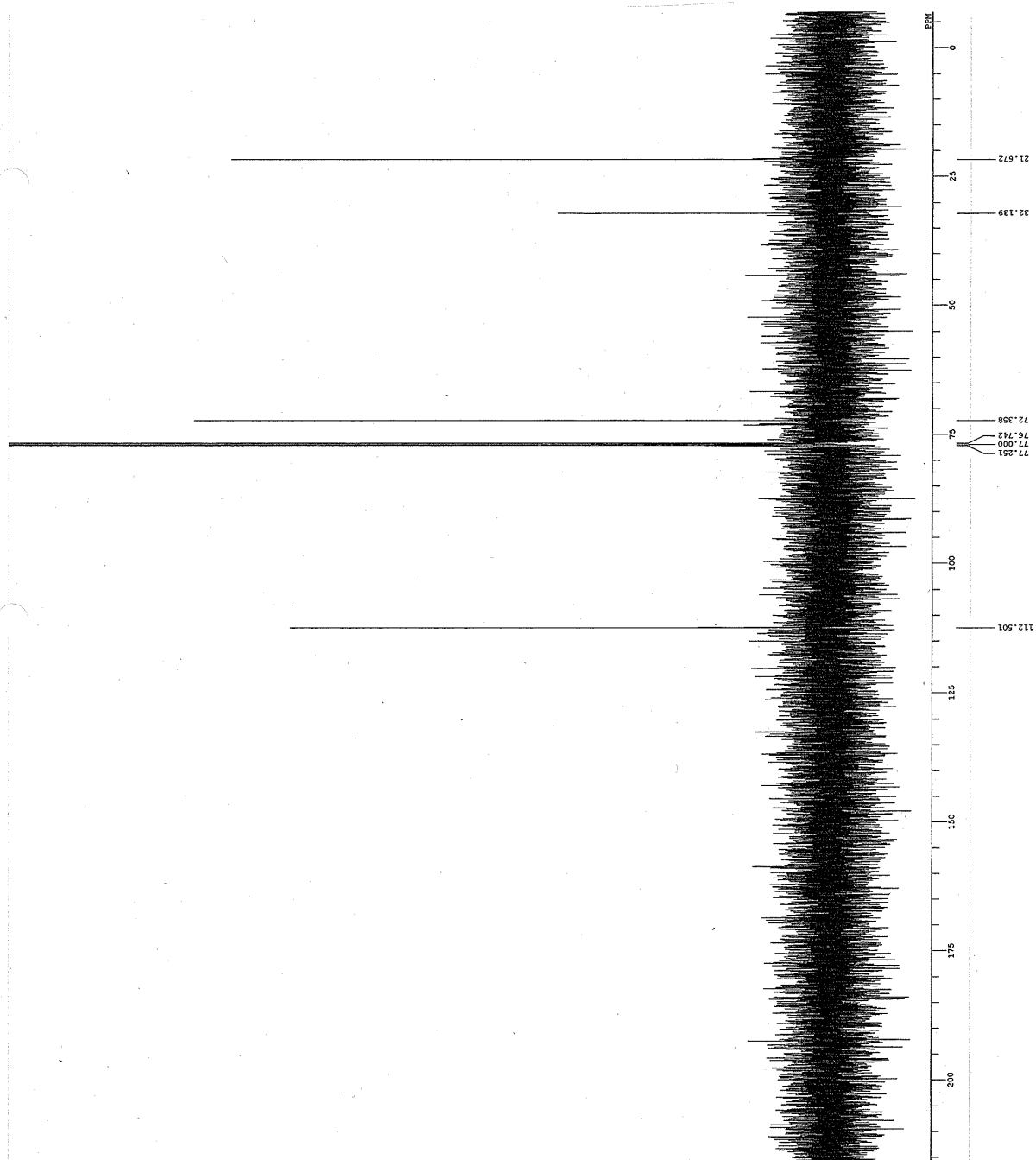
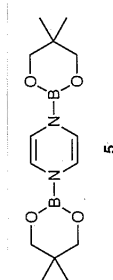
OBSERVE H1, 399.8835282 MHz

DATA PROCESSING

Line broadening 0.2 Hz
FT size 65536
Total time 10 min, 40 sec



DETAILS_DEFAULT.ALS
CONNT 15 Mar 16 14:06:13 2012
NAME 15
ORIG F1
EXPOD SINGL
SOLVENT CDCl3
PULPROG zgpg30
AQTIME 1.2698 sec
F2 41.50 MHz
P1 12.00
RG 19.35
INSTRUM IH
PROBHD 5
SOLVENT CDCl3
NUC1 13C
NUC2 13C
RGAIN 19.35



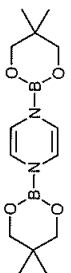
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrSYS/data/oshima/K03296-B-CDCl3.fid

Pulse Sequence: s2pul

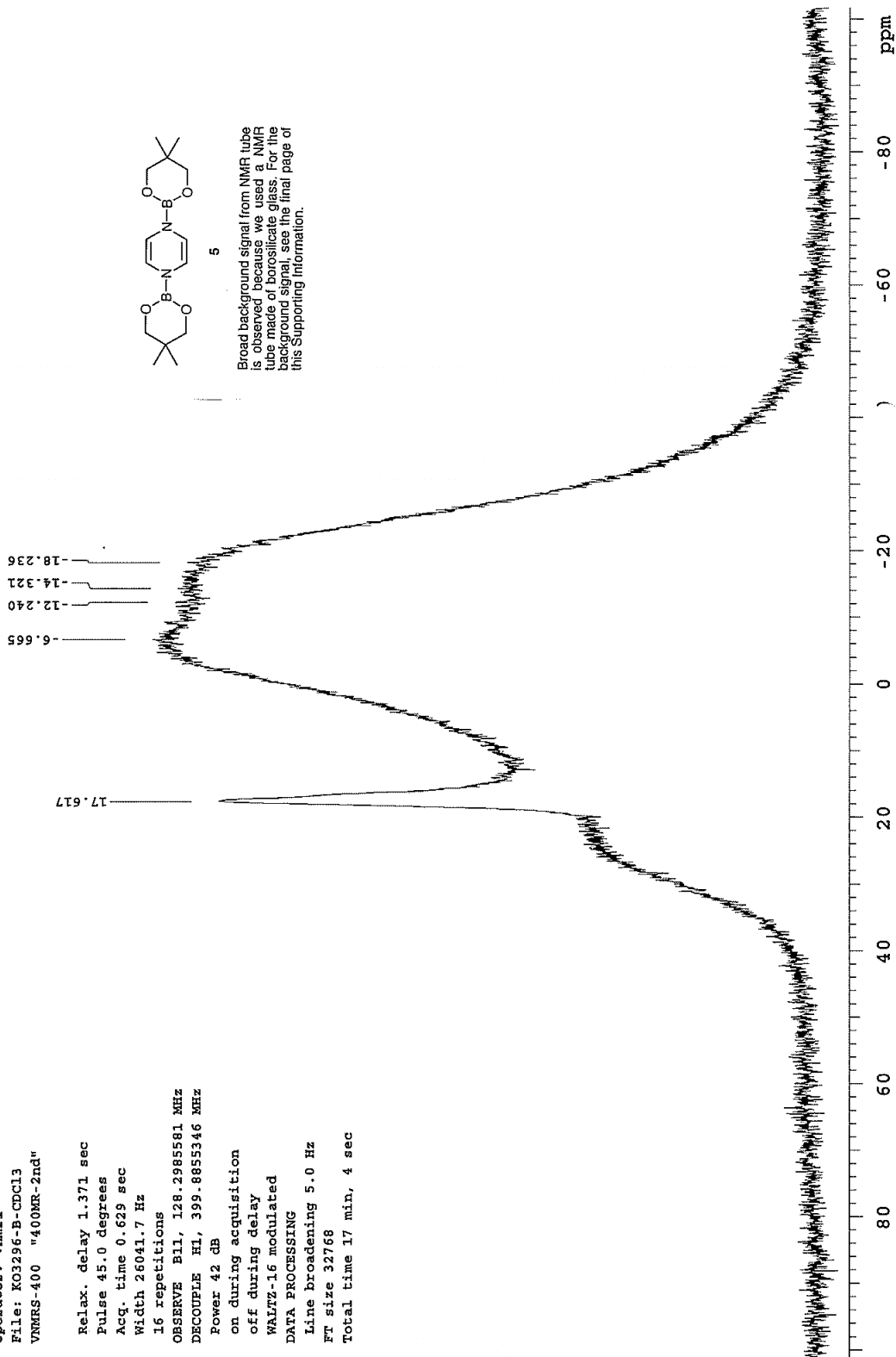
Solvent: cdcl3
Ambient temperature
Operator: vnmz1
File: K03296-B-CDCl3
VNMR5-400 "400MR-2nd"

Relax. delay 1.371 sec
Pulse 45.0 degrees
Acq. time 0.629 sec
Width 26041.7 Hz
16 repetitions
OBSERVE B11, 128.2985581 MHz
DECOUPLE H1, 399.8855346 MHz
Power 42 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 32768
Total time 17 min, 4 sec



5

Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



STANDARD PROTON PARAMETERS

File: home/vnmr1/vnmrsys/data/oshima/KO3273-H-re-CDCl3.fid

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vnmr1

File: KO3273-H-re-CDCl3

VNMR5-400 "400MR-2nd"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

12 repetitions

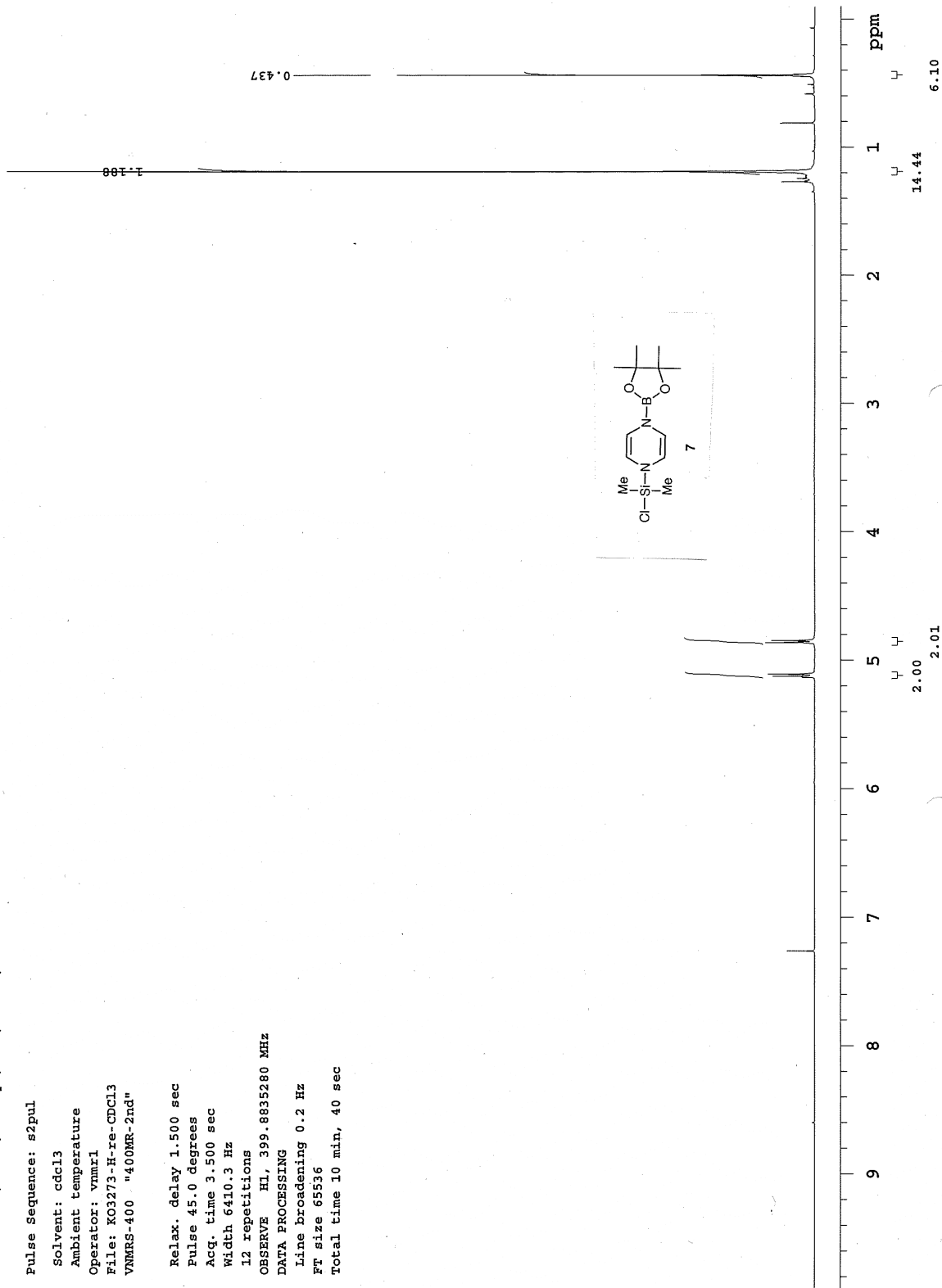
OBSERVE H1, 399.8835280 MHz

DATA PROCESSING

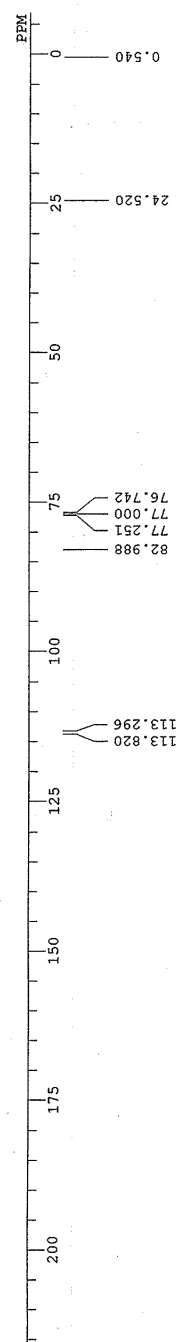
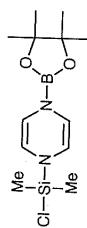
Line broadening 0.2 Hz

FT size 65536

Total time 10 min, 40 sec



DFILE _DEFAULT.ALS
COMMENT
DATEM Sat Mar 03 01:46:20 20
ORNUC 13C
EXMOD SINGL
ORFREQ 125.65 MHz
ORFIN 128449.48 Hz
POINT 32768
FREOU 28011.20 Hz
SCANS 280
ACQTM 1.1698 sec
PD 2.0000 sec
PWI 4.50 usec
IRNUC 1H
CTEMP 21.6 C
SIVANT CDCl3
EXREF 77.00 ppm
BF -0.10 Hz
RGAIN 33



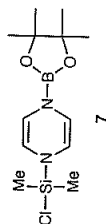
STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrsys/data/oshima/KO3273-B-CDCl3.fid

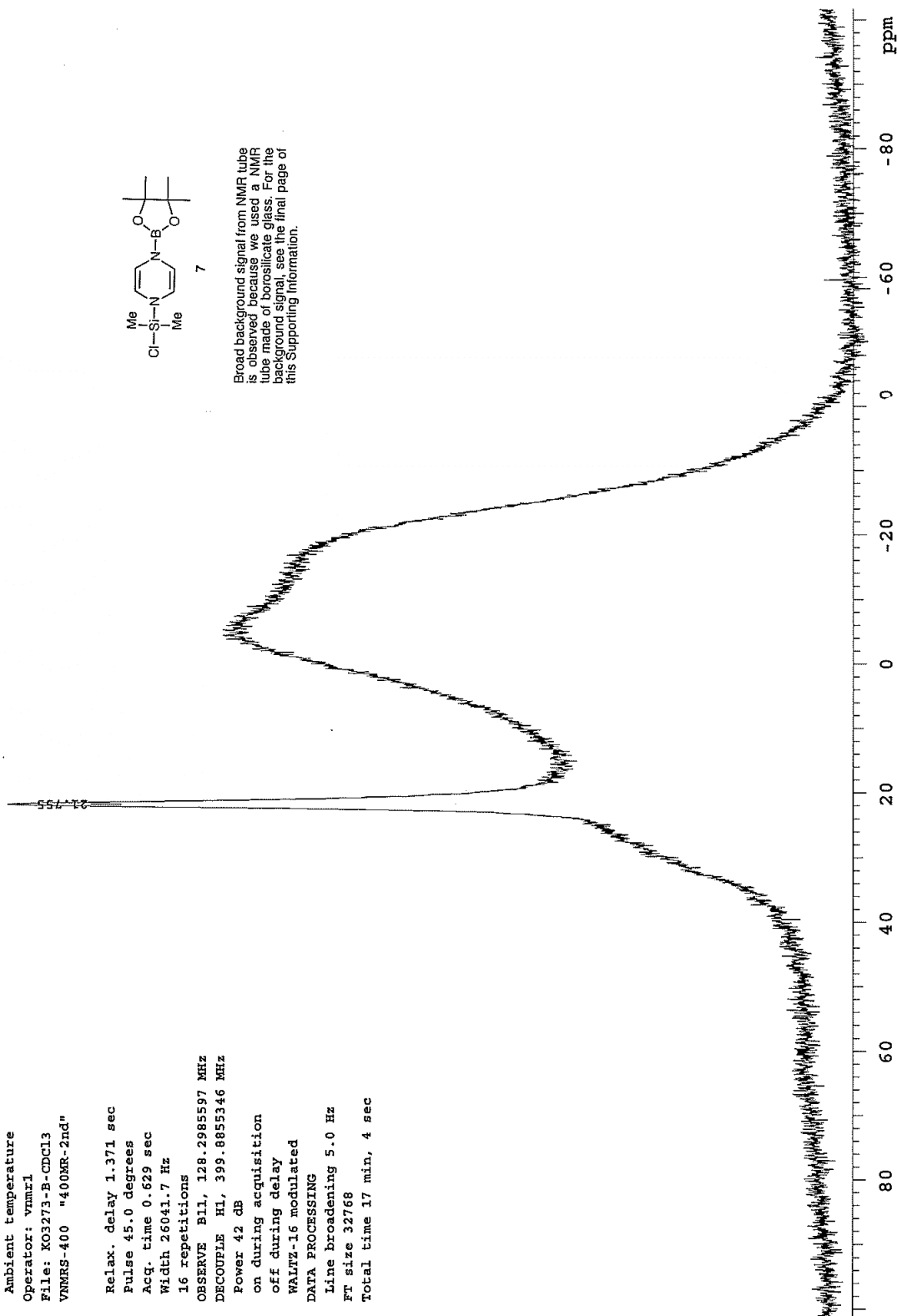
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: KO3273-B-CDCl3
VNMRS-400 "400MR-2nd"

Relax. delay 1.371 sec
Pulse 45.0 degrees
Acq. time 0.629 sec
Width 26041.7 Hz
16 repetitions
OBSERVE B1, 128.2985597 MHz
DECOUPLE H1, 399.8855346 MHz
Power 42 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 32768
Total time 17 min, 4 sec



Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



STANDARD PROTON PARAMETERS

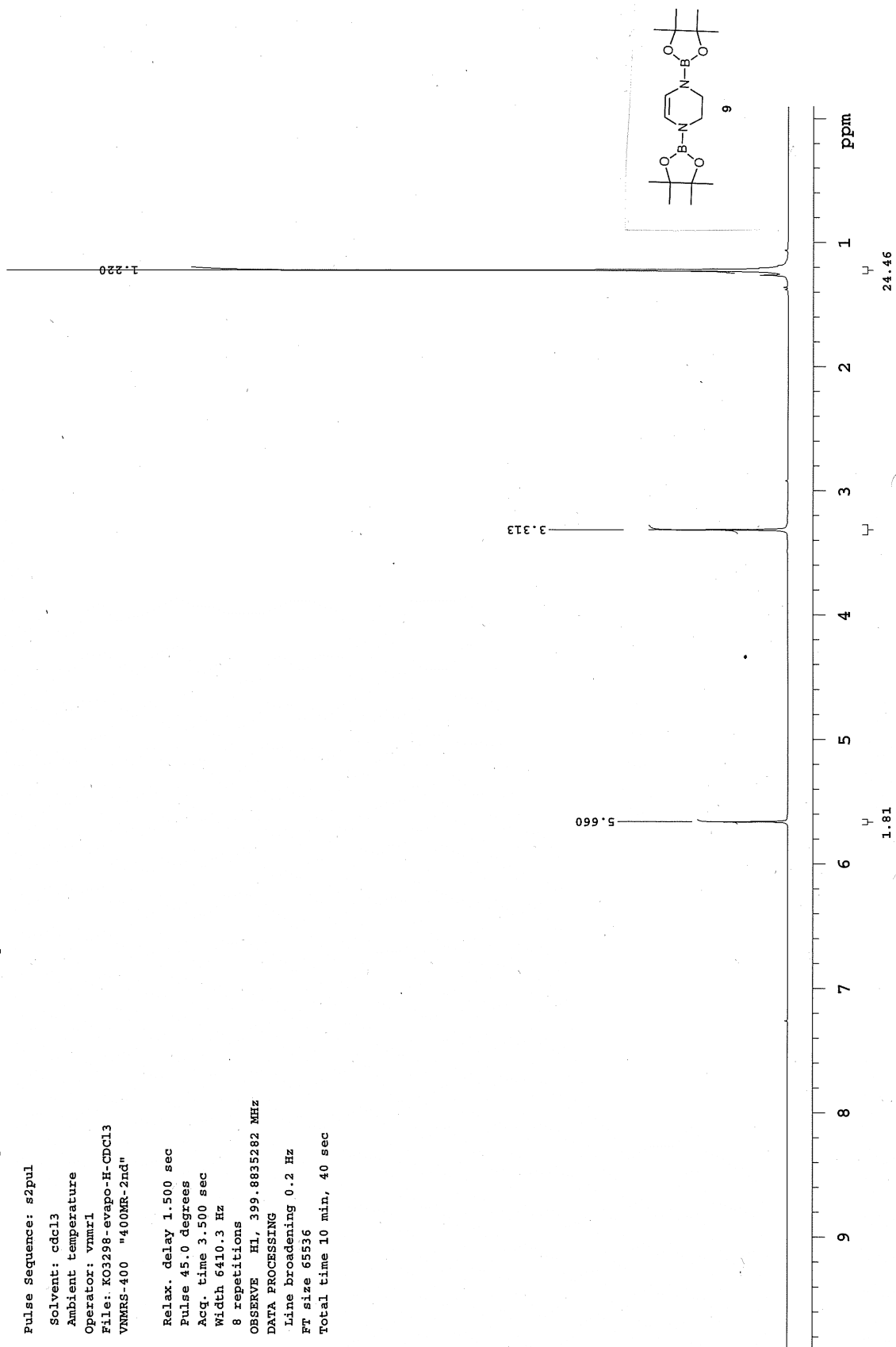
File: home/vnmr1/vnmrSYS/data/oshima/KO3298-evapo-H-CDCl3.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: KO3298-evapo-H-CDCl3
VNMRS-400 "400MR-2nd"

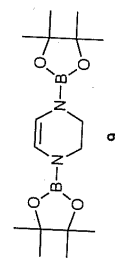
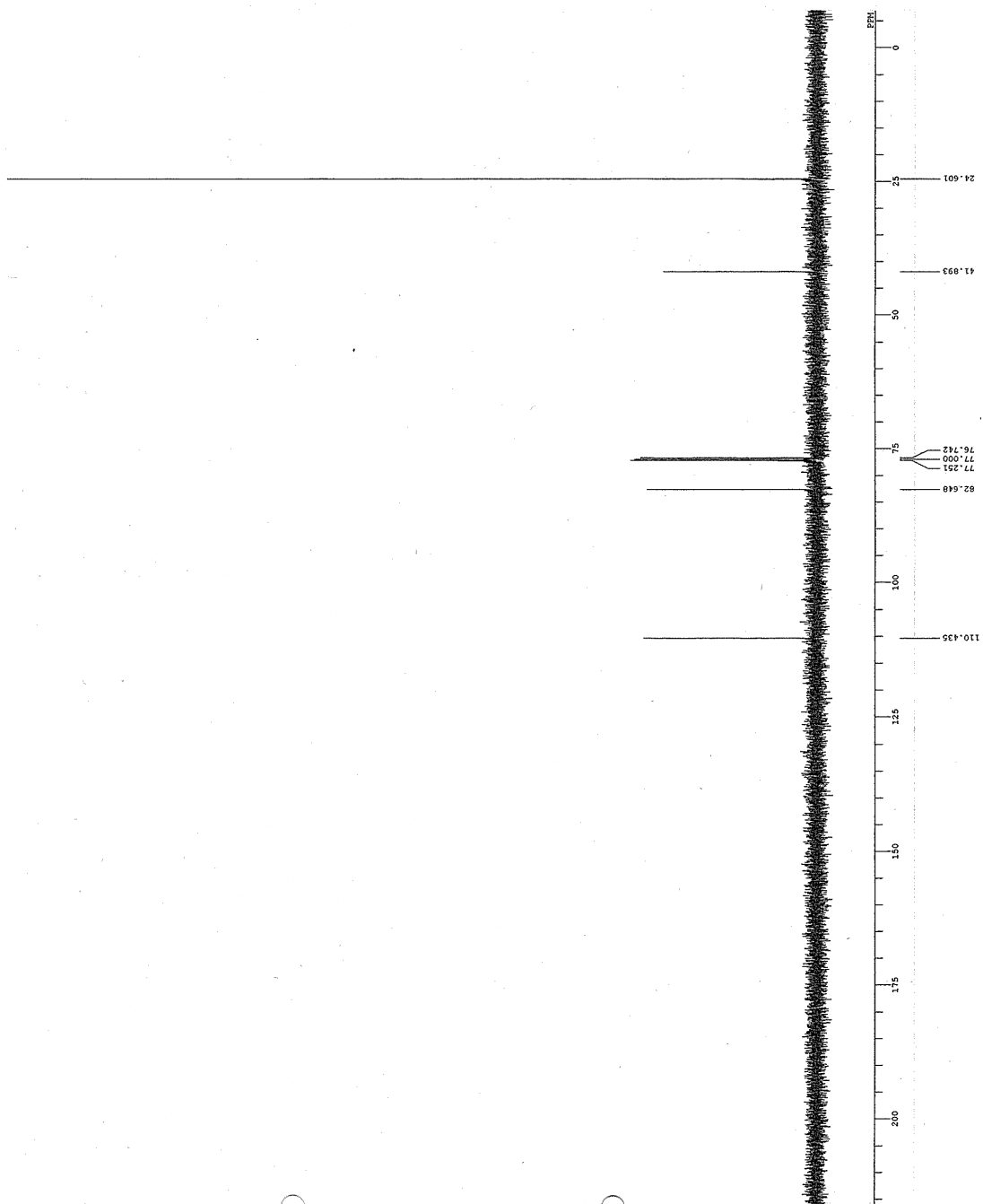
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
8 repetitions

OBSERVE H1, 399.8835282 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 10 min, 40 sec



C:\NMR\ESI\COCC\CA_DEFAULT.ALS

DFILE _DEFAULT.ALS
CONV F1 Mar 16 12:30:18 2012
CHNAC 13C
PULPROG zgpg30
SFO 125.60 MHz
AQ 128445.48 Hz
RG 128445.48 Hz
FREQ 125.60 MHz
SCANS 1
DELTA 1.80
PC 2.0000 sec
PD 0.0000 sec
PDEL 0.0000 sec
PRG 1H
RG 4.50 usec
SFO 400.146 MHz
CT 21.5 c
SLANT 0DC13 71.00 Hz
RF 12.64 MHz
BF 0.19 Hz
RGAIN 33



STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrsys/data/oshima/KO3298-B-CDCl3.fid

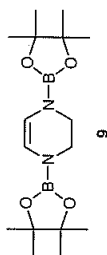
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: KO3298-B-CDCl3
VNMRS-400 "400MR-2nd"

Relax. delay 1.371 sec
Pulse 45.0 degrees
Acq. time 0.629 sec
Width 26041.7 Hz

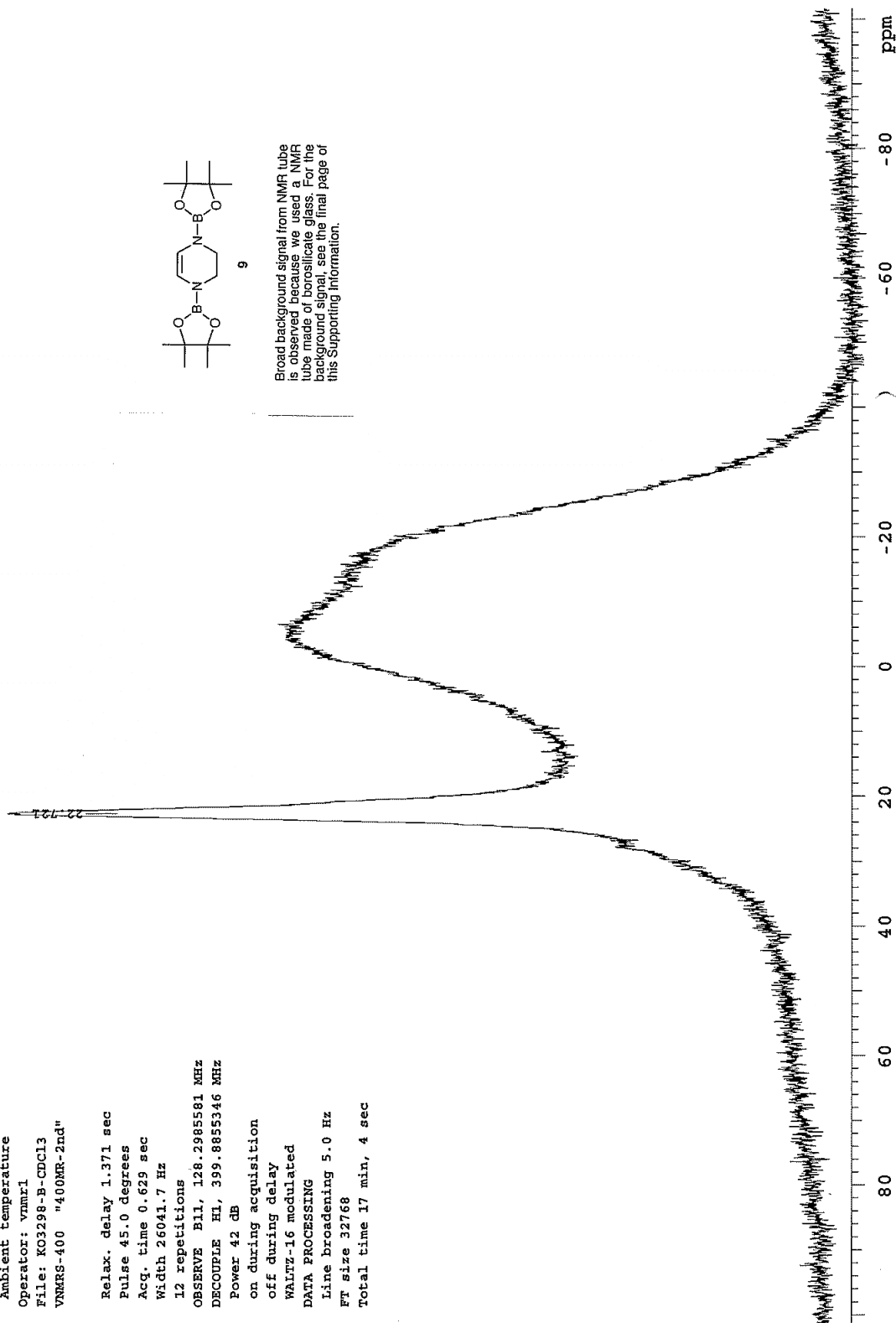
12 repetitions
OBSERVE B11, 128.2985581 MHz
DECOUPLE H1, 399.8855346 MHz
Power 42 dB

on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 32768
Total time 17 min, 4 sec



9

Broad background signal from NMR tube is observed because we used a NMR tube made of borosilicate glass. For the background signal, see the final page of this Supporting Information.



STANDARD CARBON PARAMETERS

File: home/vnmr1/vnmrsys/data/Torigoe/cdcl3-NMRtube-11B.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: CDCl3-NMRtube-11B
VNMRS-400 "400MR-2nd"

Relax. delay 1.371 sec
Pulse 45.0 degrees
Acq. time 0.629 sec
Width 26041.7 Hz
100 repetitions
OBSERVE B1, 128.2985645 MHz
DECODEPLE H1, 399.8855346 MHz
Power 42 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 32768
Total time 17 min, 4 sec

Background signal from NMR tube

