

Supplementary Material

Zinc-Catalyzed Regioselective Addition of Alkyl Thiols to Alkenes via Anion or Radical Reactions

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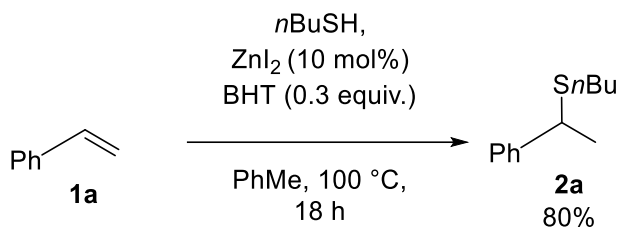
Email: taniguti@fmu.ac.jp

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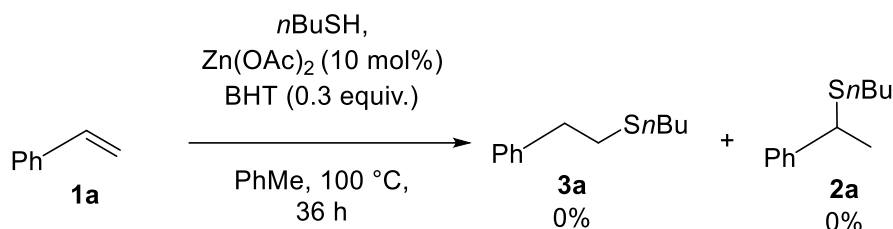
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Additional Experiments

Zn-catalyzed hydrothiolation in the presence of BHT (Scheme 2)

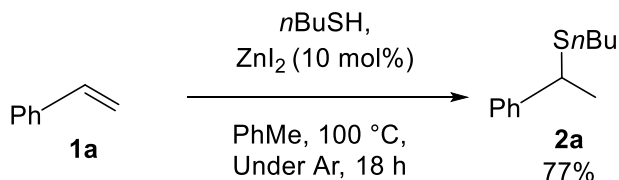


To a mixture of styrene **1a** (31.2 mg, 0.3 mmol), 1-butanethiol (29.8 mg, 0.33 mmol), and BHT (66.1 mg, 0.3 mmol) in CH_2Cl_2 (0.3 mL), ZnI_2 (9.6 mg, 0.03 mmol) was added, and the mixture was stirred at $100\text{ }^\circ\text{C}$ for 18 h in air. After the residue was dissolved in Et_2O , the solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (hexane) gave 1-(1-butylthio)-1-phenylethane **2a** (54.6 mg, 80%).

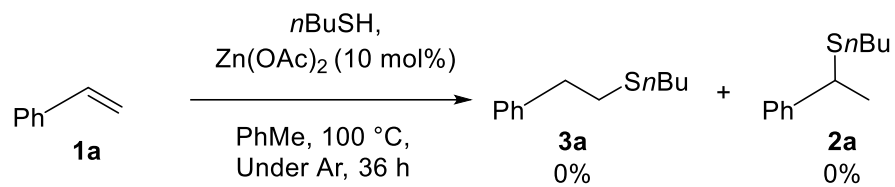


To a mixture of styrene **1a** (31.2 mg, 0.3 mmol), 1-butanethiol (29.8 mg, 0.33 mmol), and BHT (66.1 mg, 0.3 mmol) in CH_2Cl_2 (0.3 mL), $\text{Zn}(\text{OAc})_2$ (5.5 mg, 0.03 mmol) was added, and the mixture was stirred at $100\text{ }^\circ\text{C}$ for 18 h in air. After the residue was dissolved in Et_2O , the solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. The expected 1-(1-butylthio)-2-phenylethane **3a** was not also obtained. The production of **2a** was not observed.

Zn-catalyzed hydrothiolation under Ar (Scheme 3)



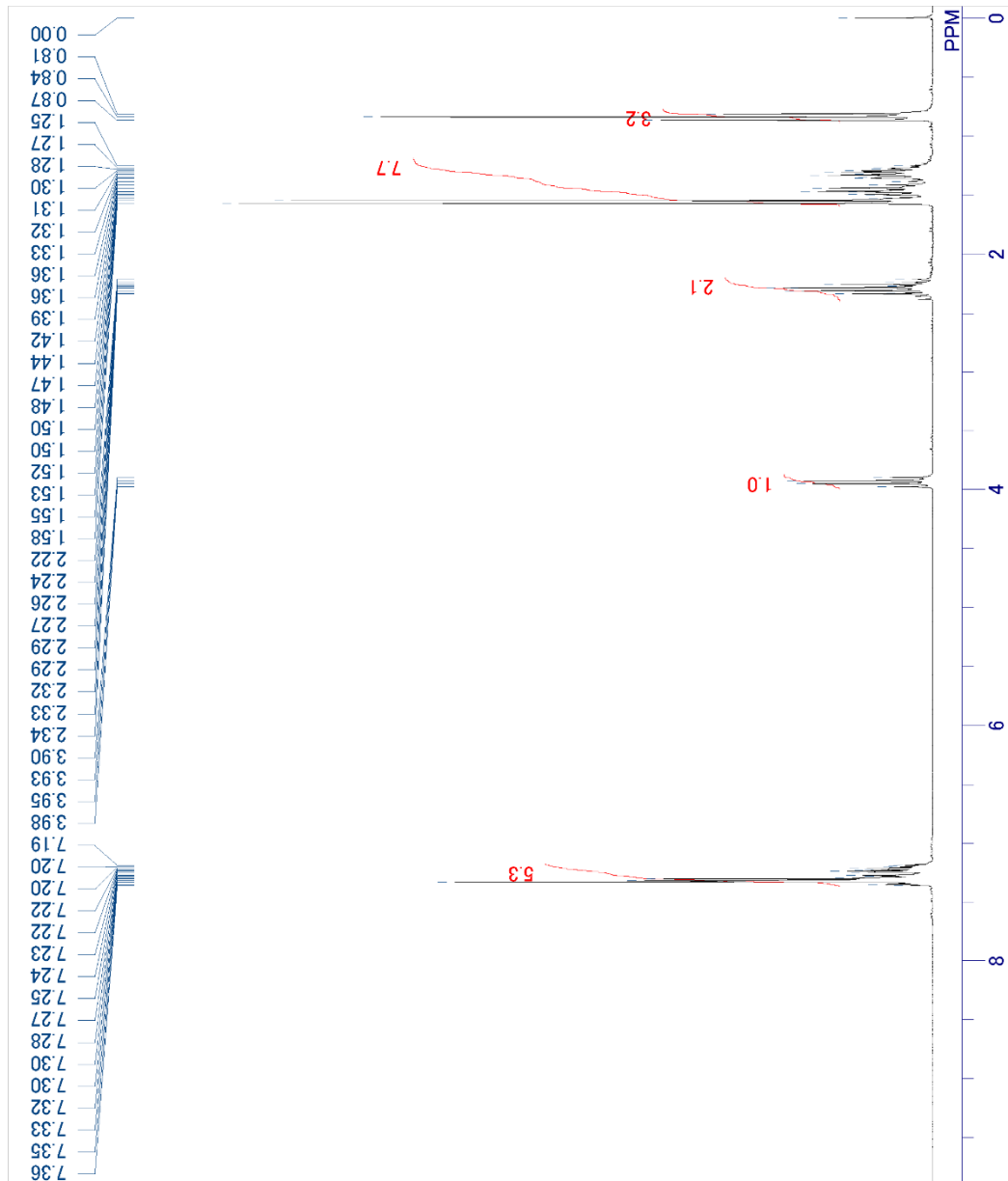
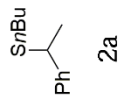
To a mixture of styrene **1a** (31.2 mg, 0.3 mmol) and 1-butanethiol (29.8 mg, 0.33 mmol) in CH_2Cl_2 (0.3 mL), ZnI_2 (9.6 mg, 0.03 mmol) was added, and the mixture was stirred at $100\text{ }^\circ\text{C}$ for 18 h under argon atmosphere. After the residue was dissolved in Et_2O , the solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (hexane) gave 1-(1-butylthio)-1-phenylethane **2a** (45.1 mg, 77%).



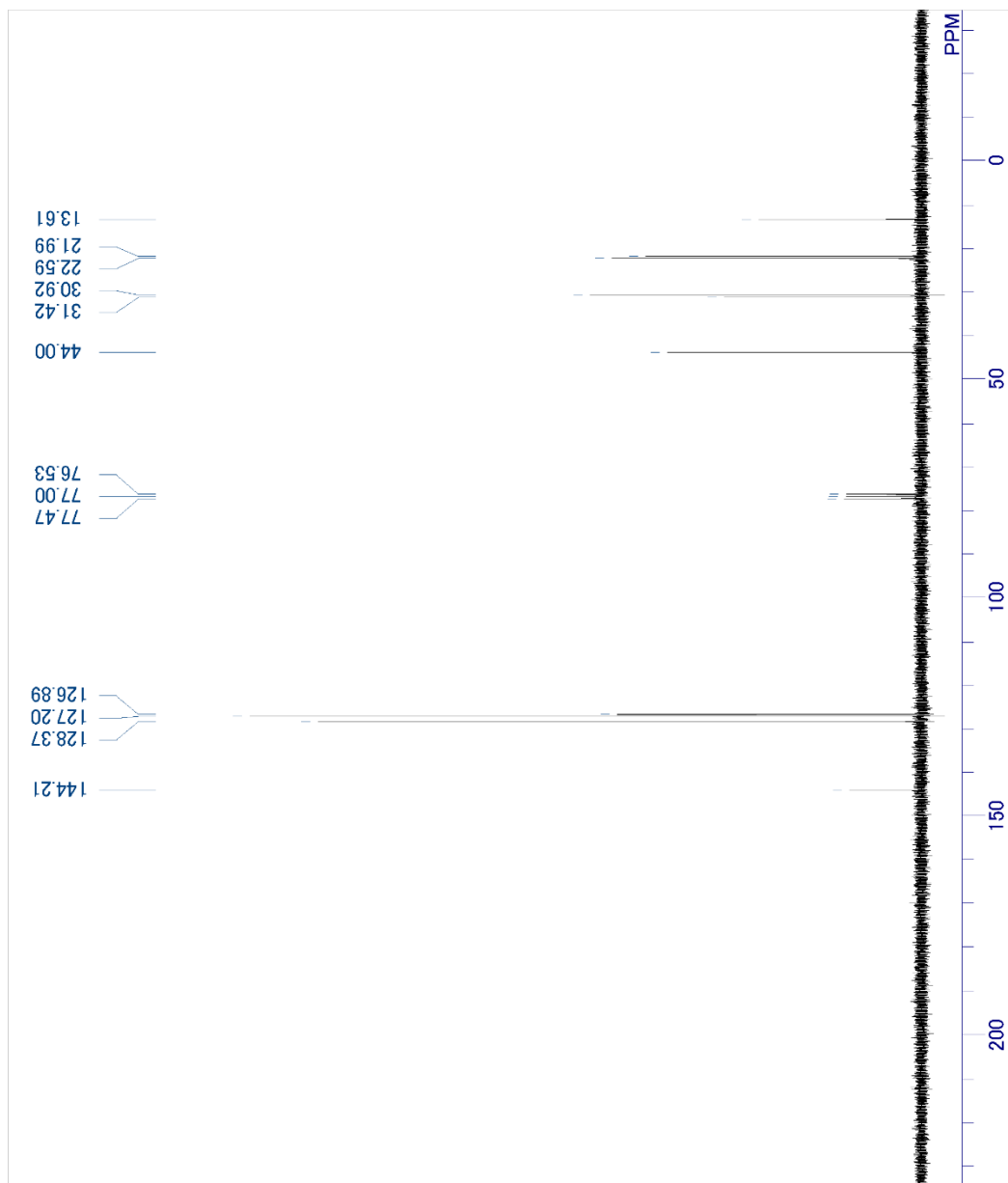
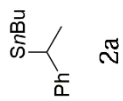
To a mixture of styrene **1a** (31.2 mg, 0.3 mmol) and 1-butanethiol (29.8 mg, 0.33 mmol) in CH₂Cl₂ (0.3 mL), Zn(OAc)₂ (5.5 mg, 0.03 mmol) was added, and the mixture was stirred under argon atmosphere at 100 °C for 18 h. The reaction did not proceed. The production of 3a and 2a was not observed.

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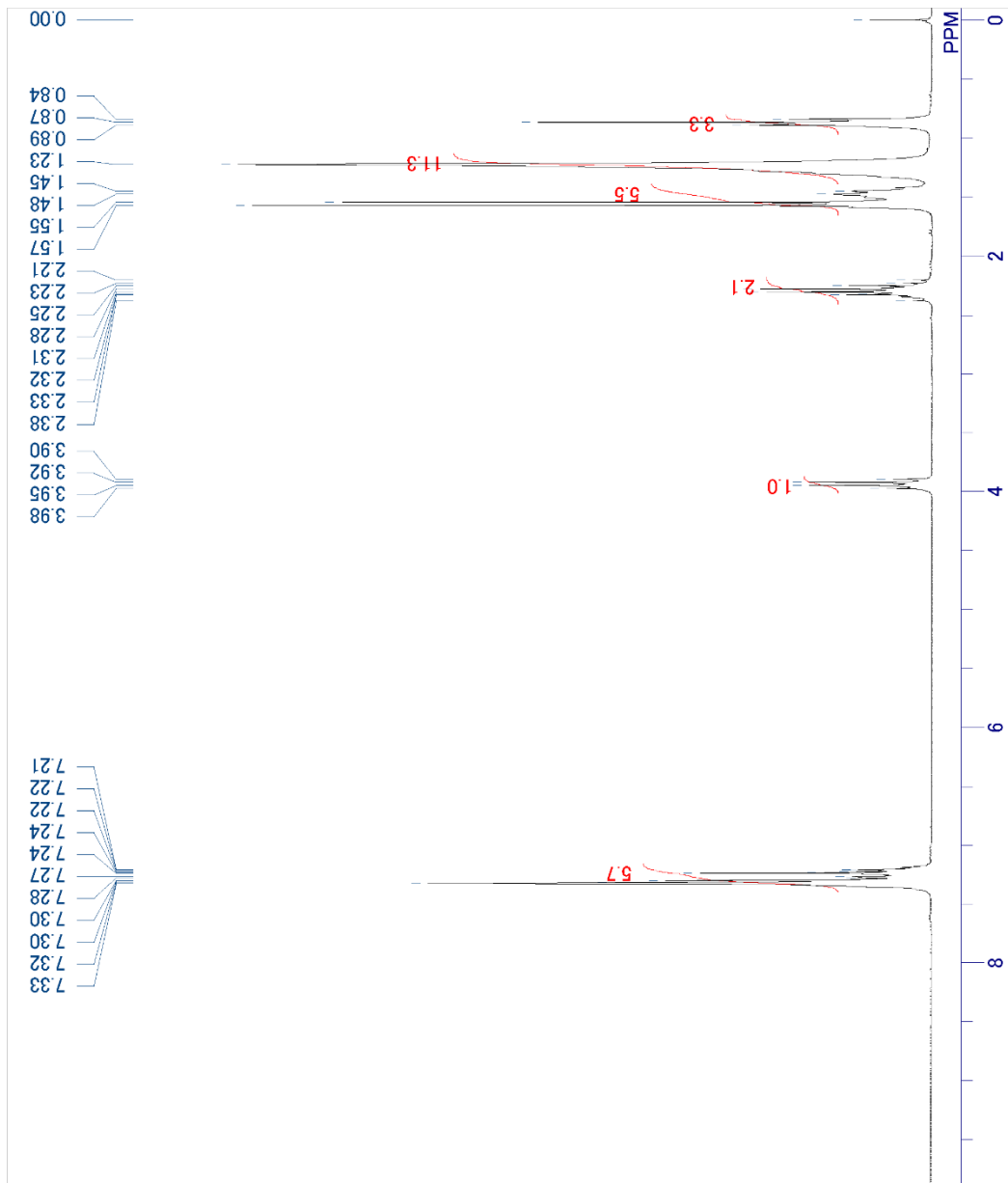
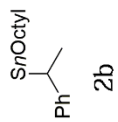
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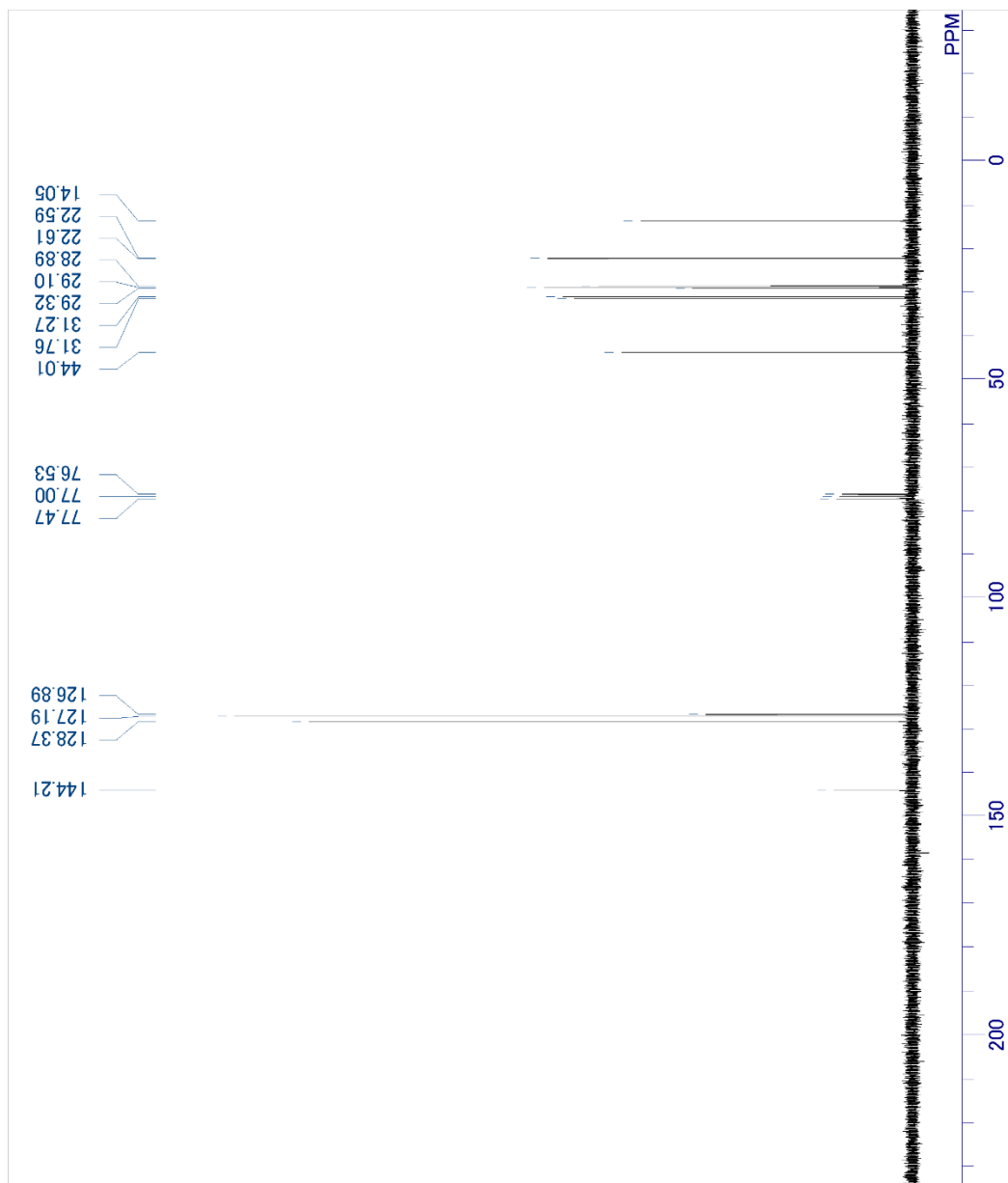
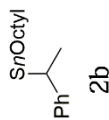
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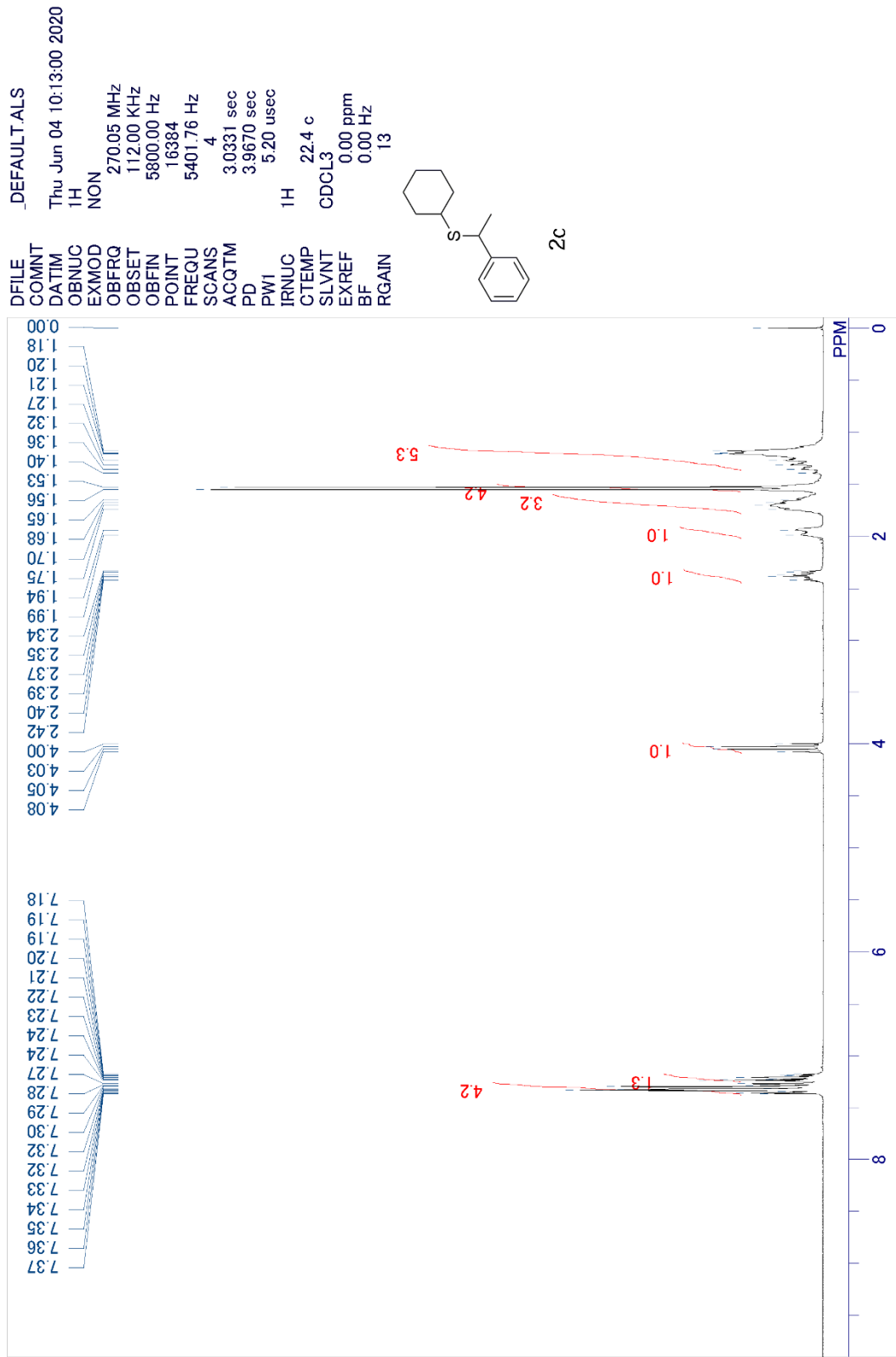


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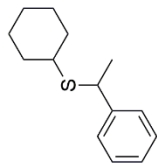


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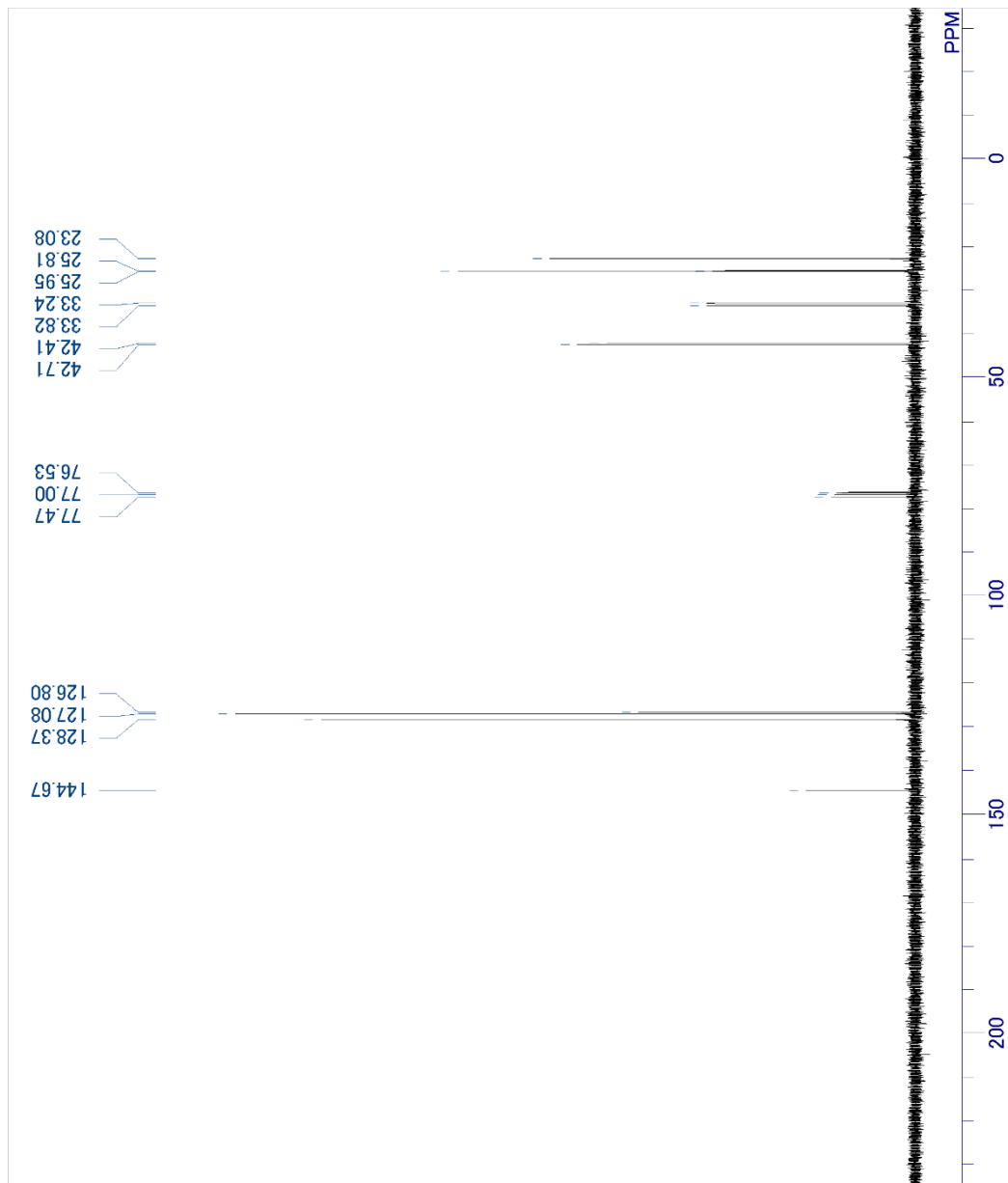


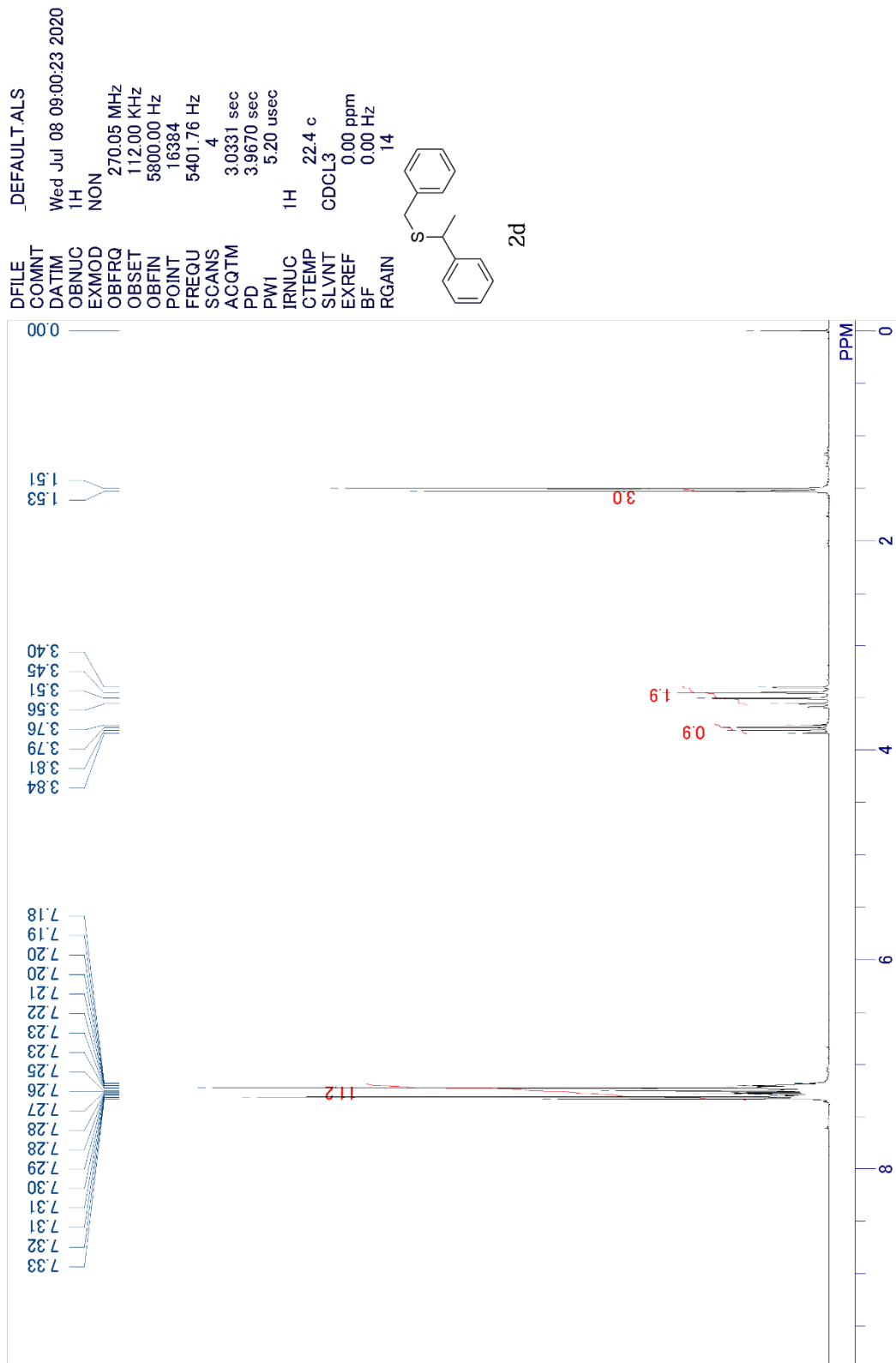


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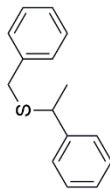


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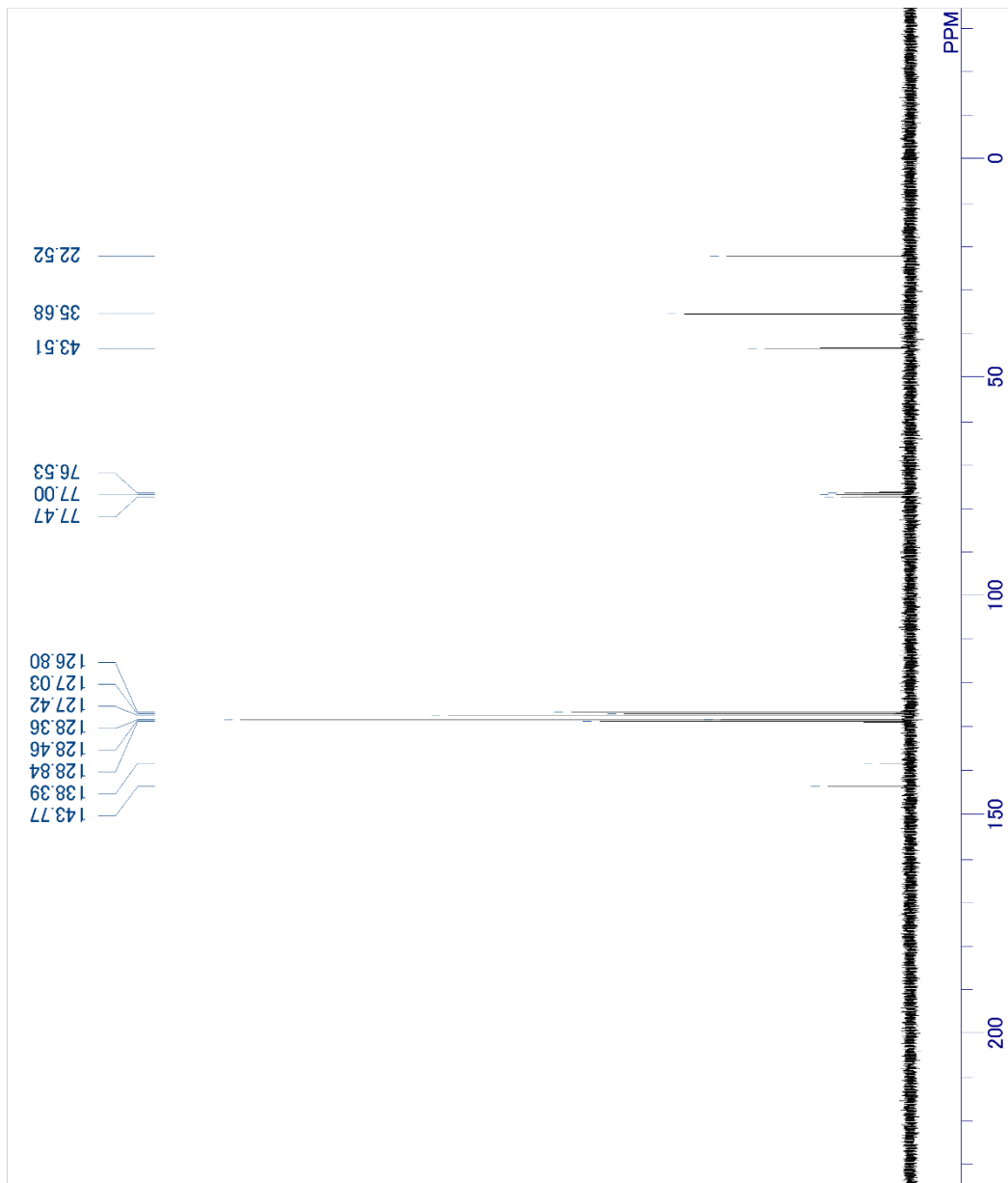


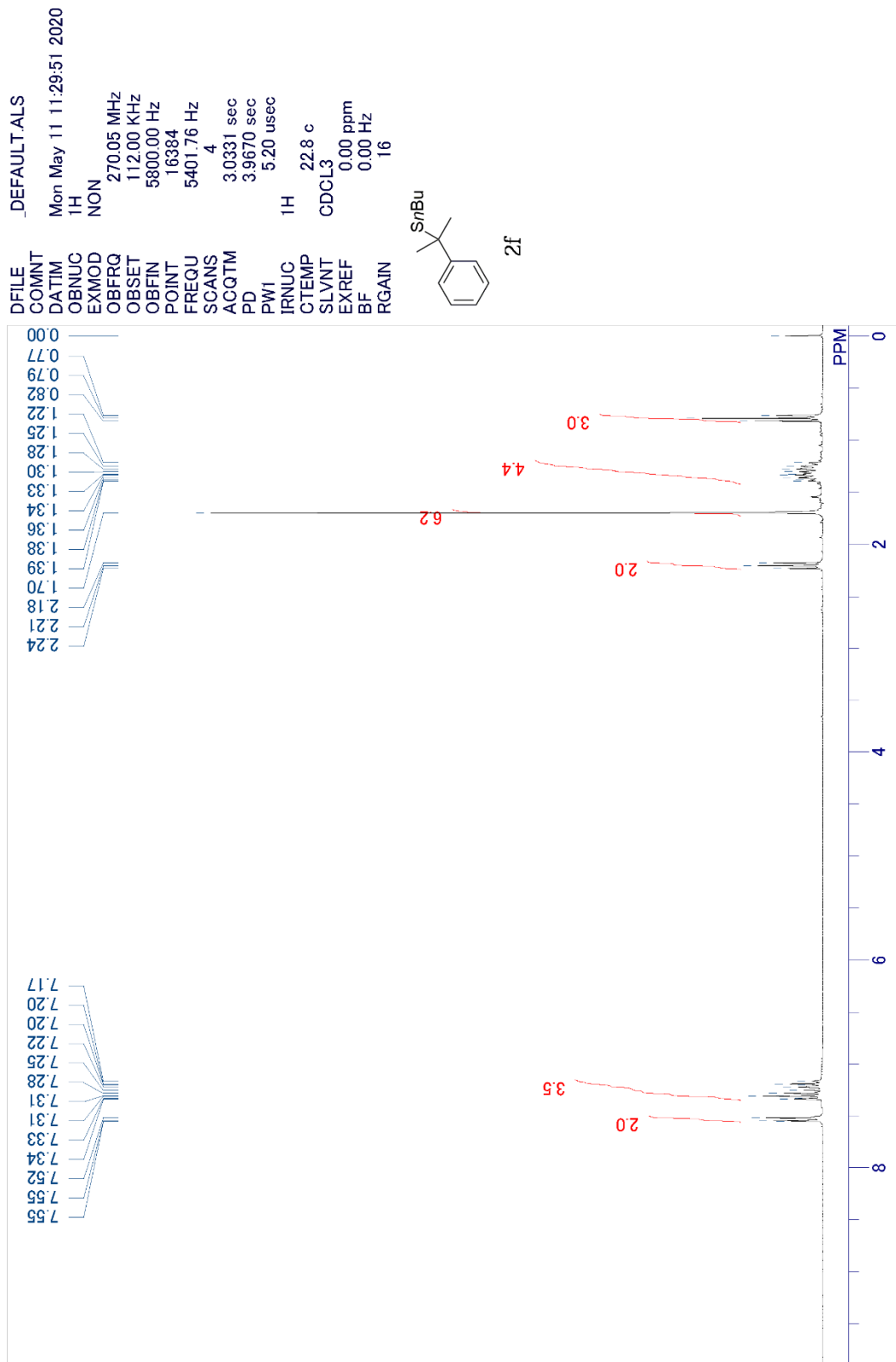


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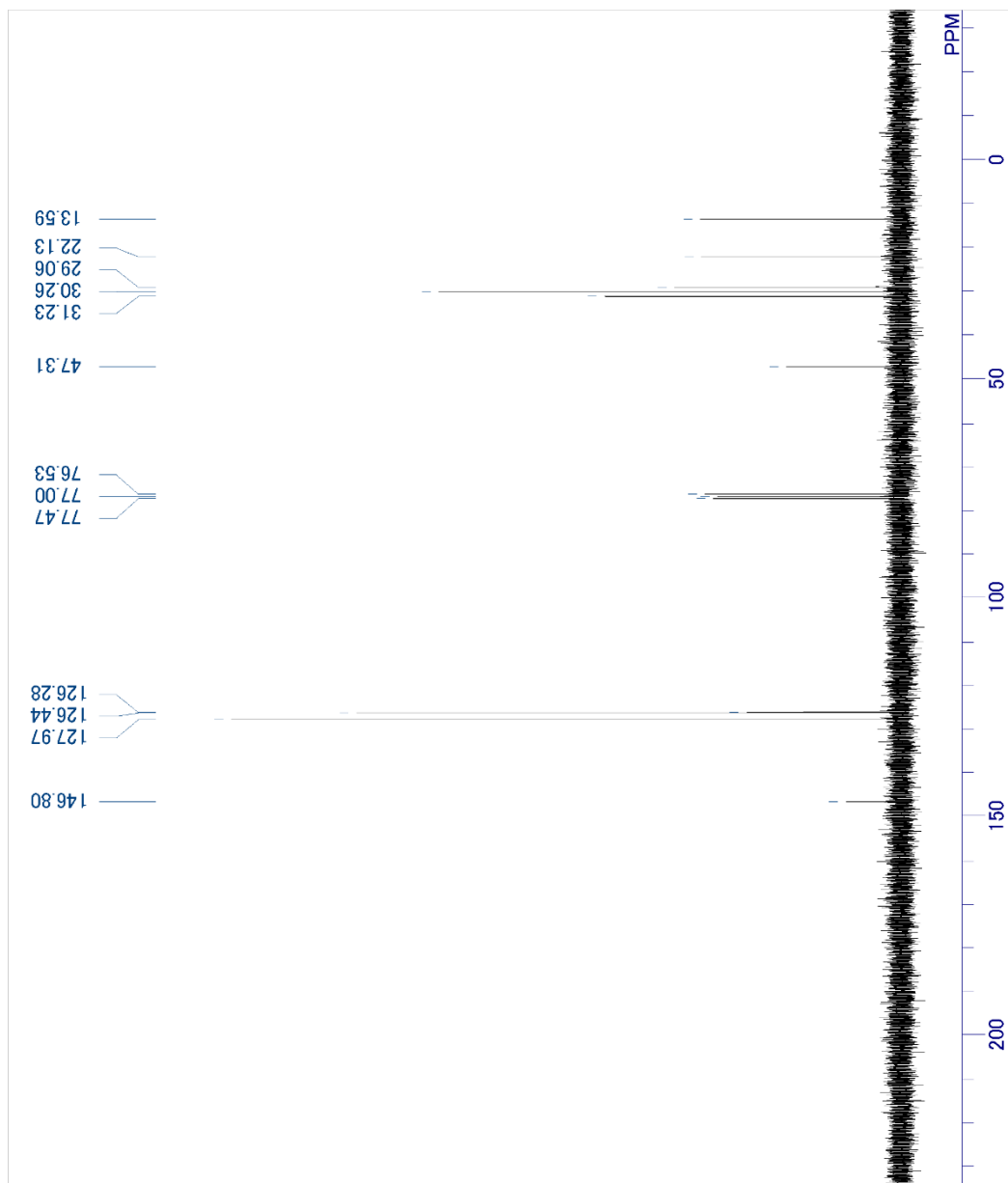
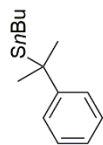


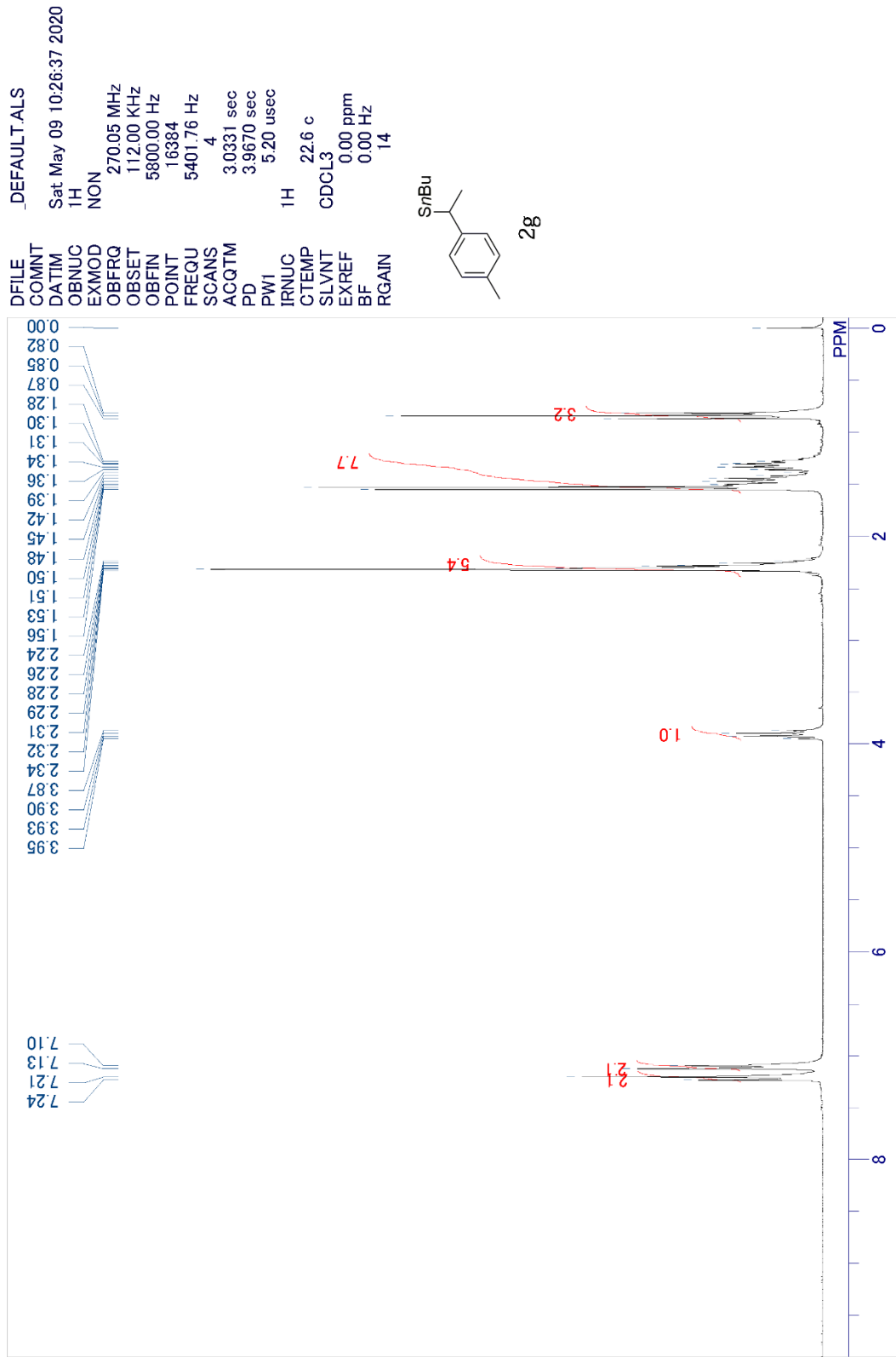
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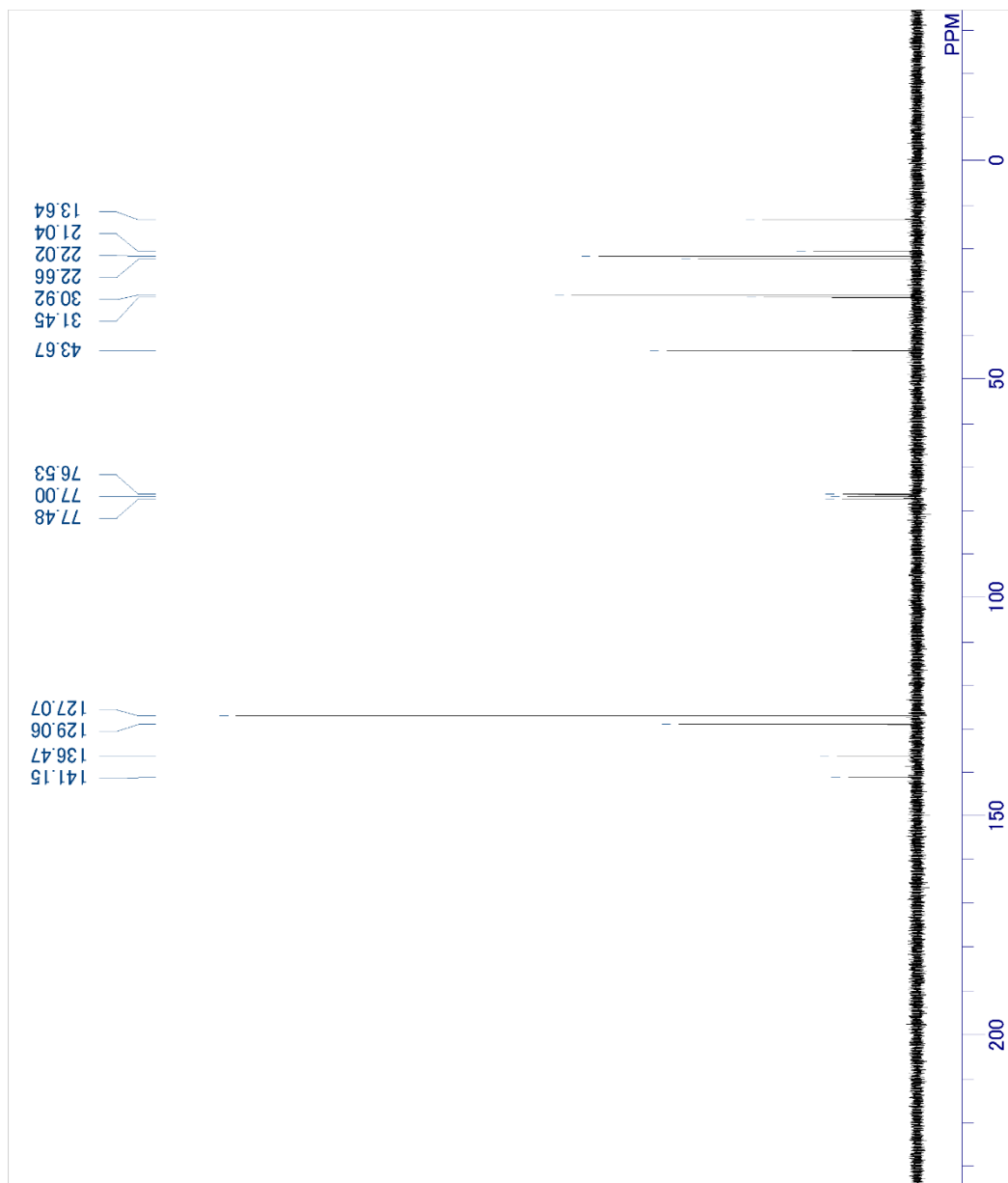
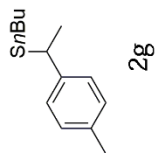


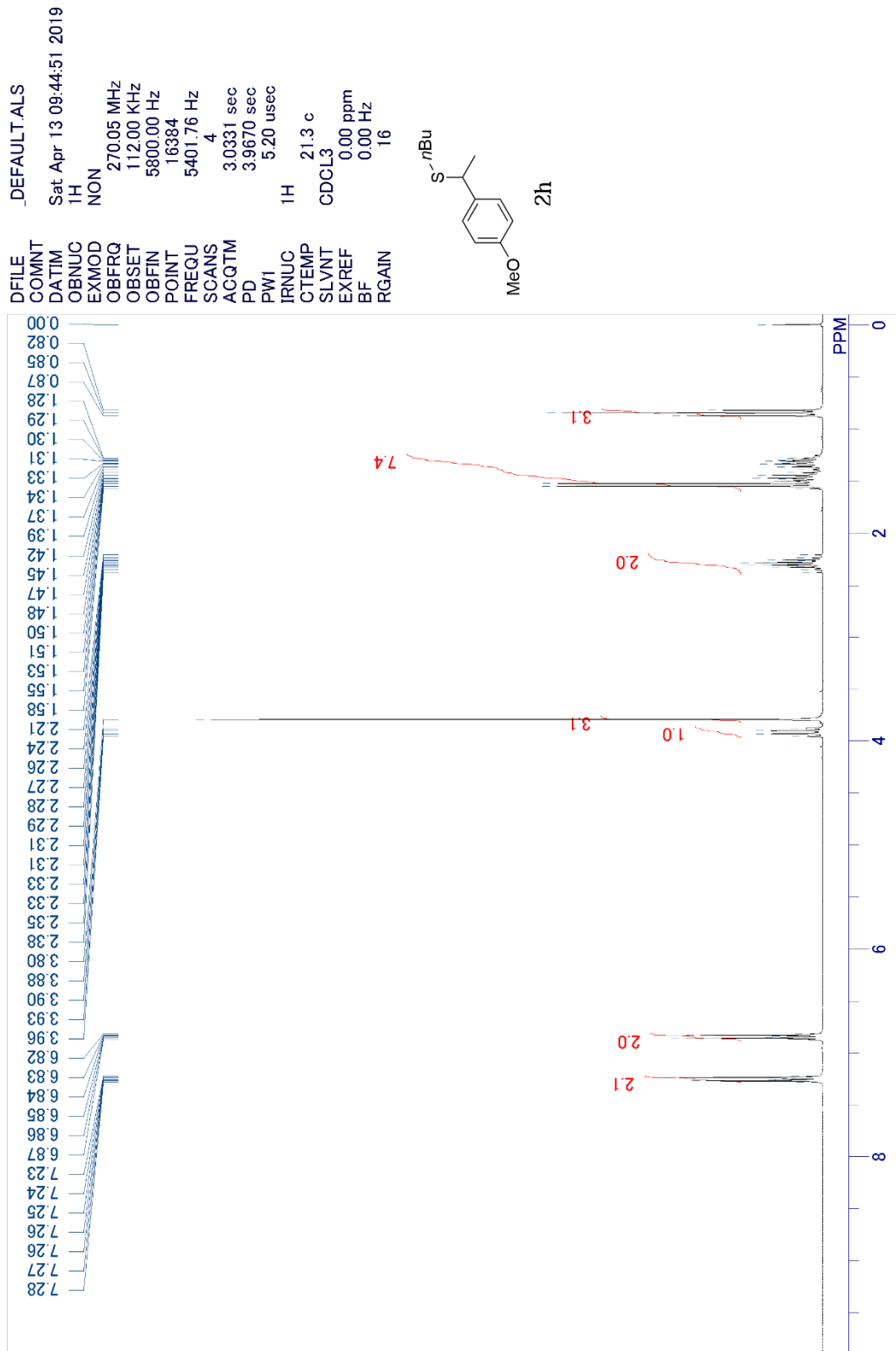
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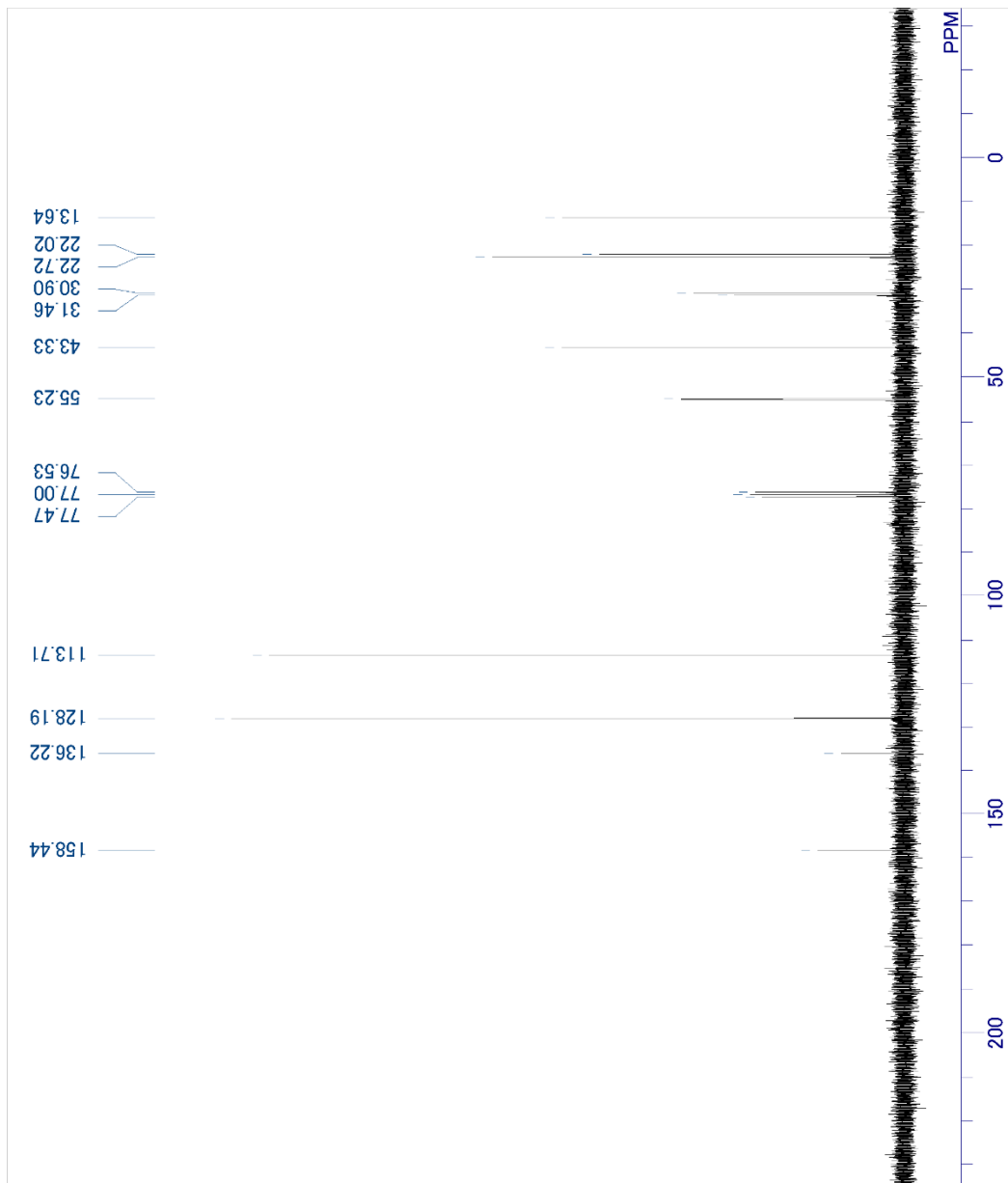
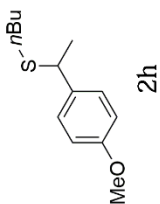


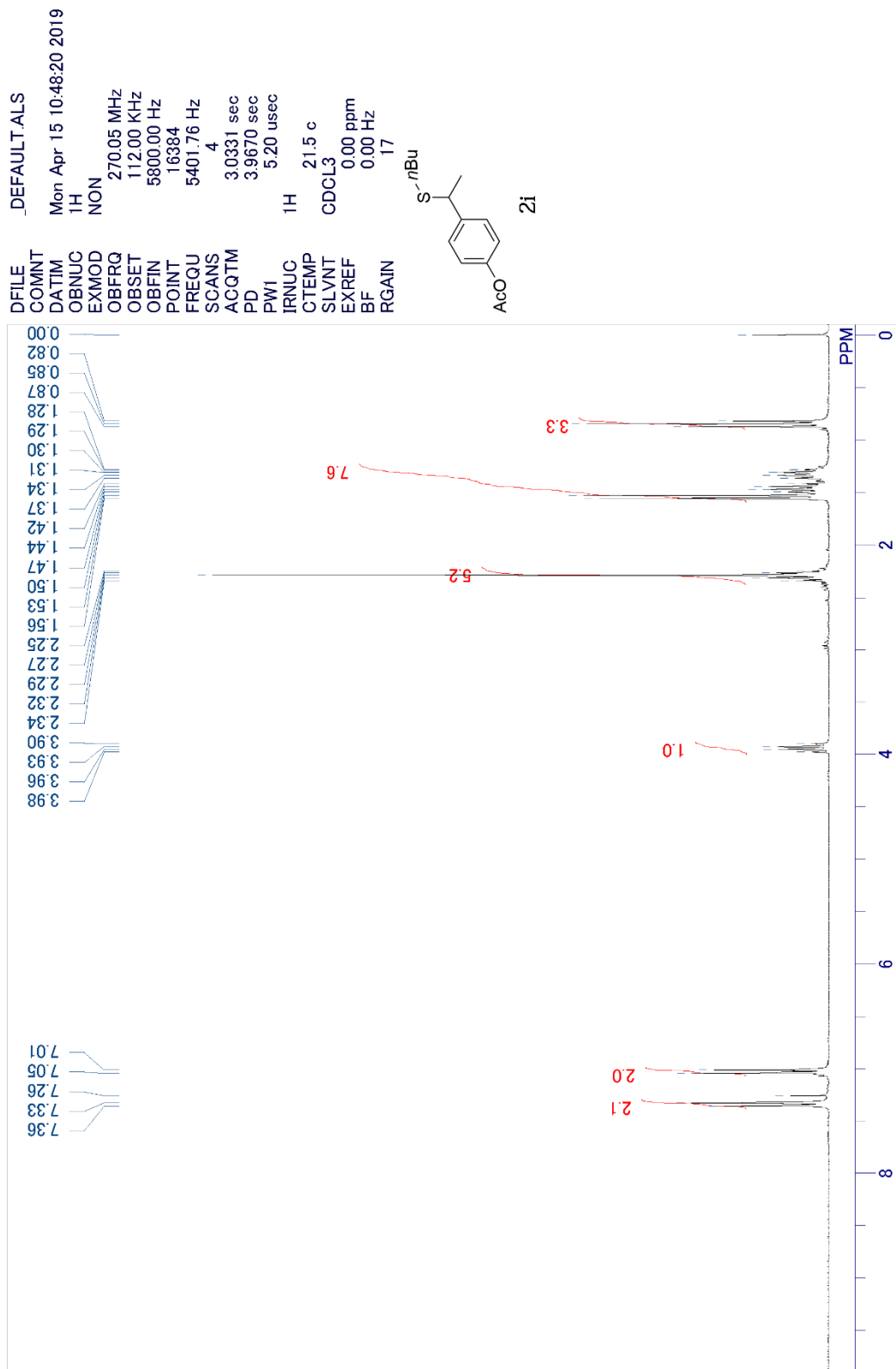
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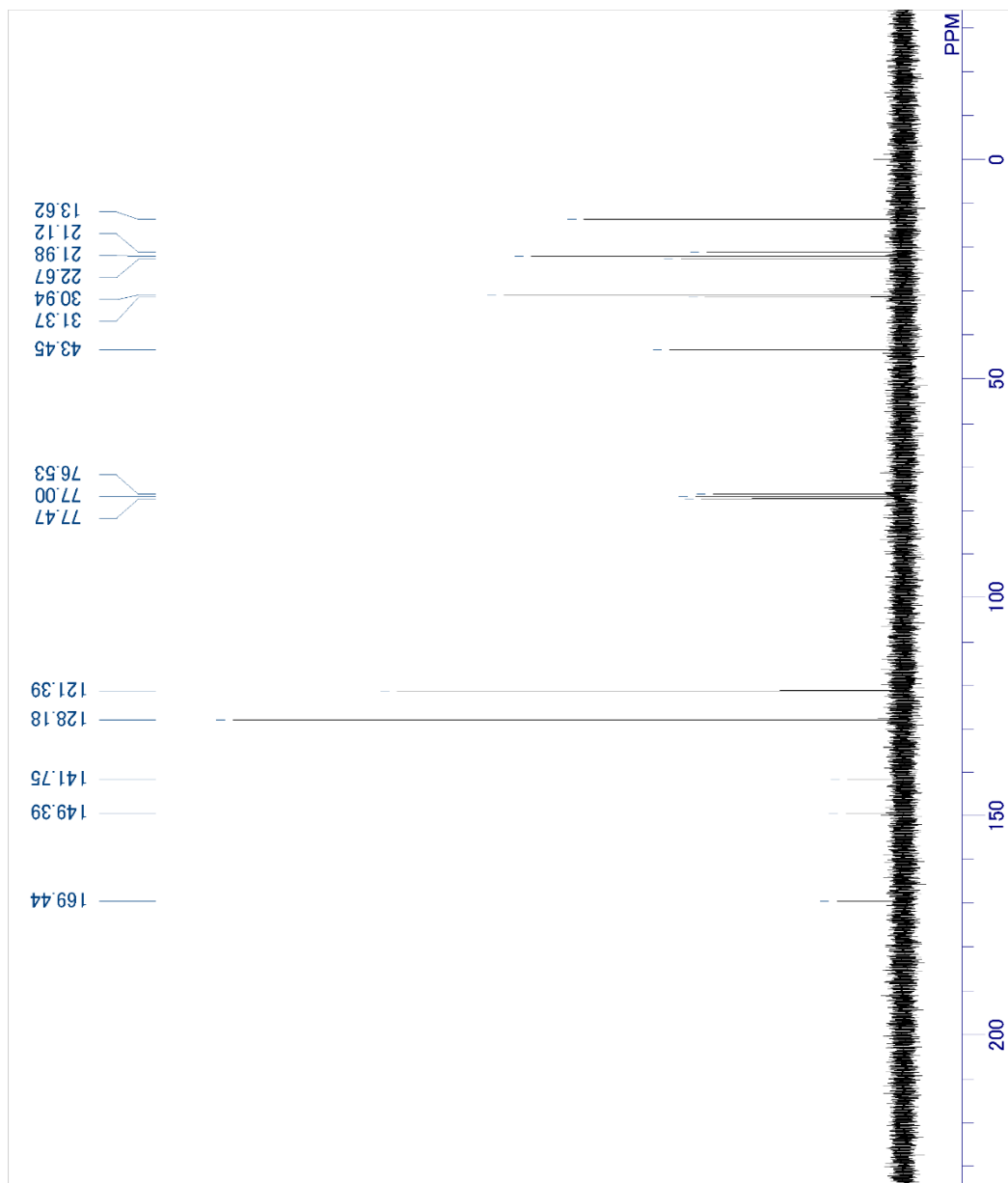
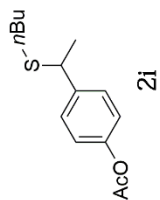


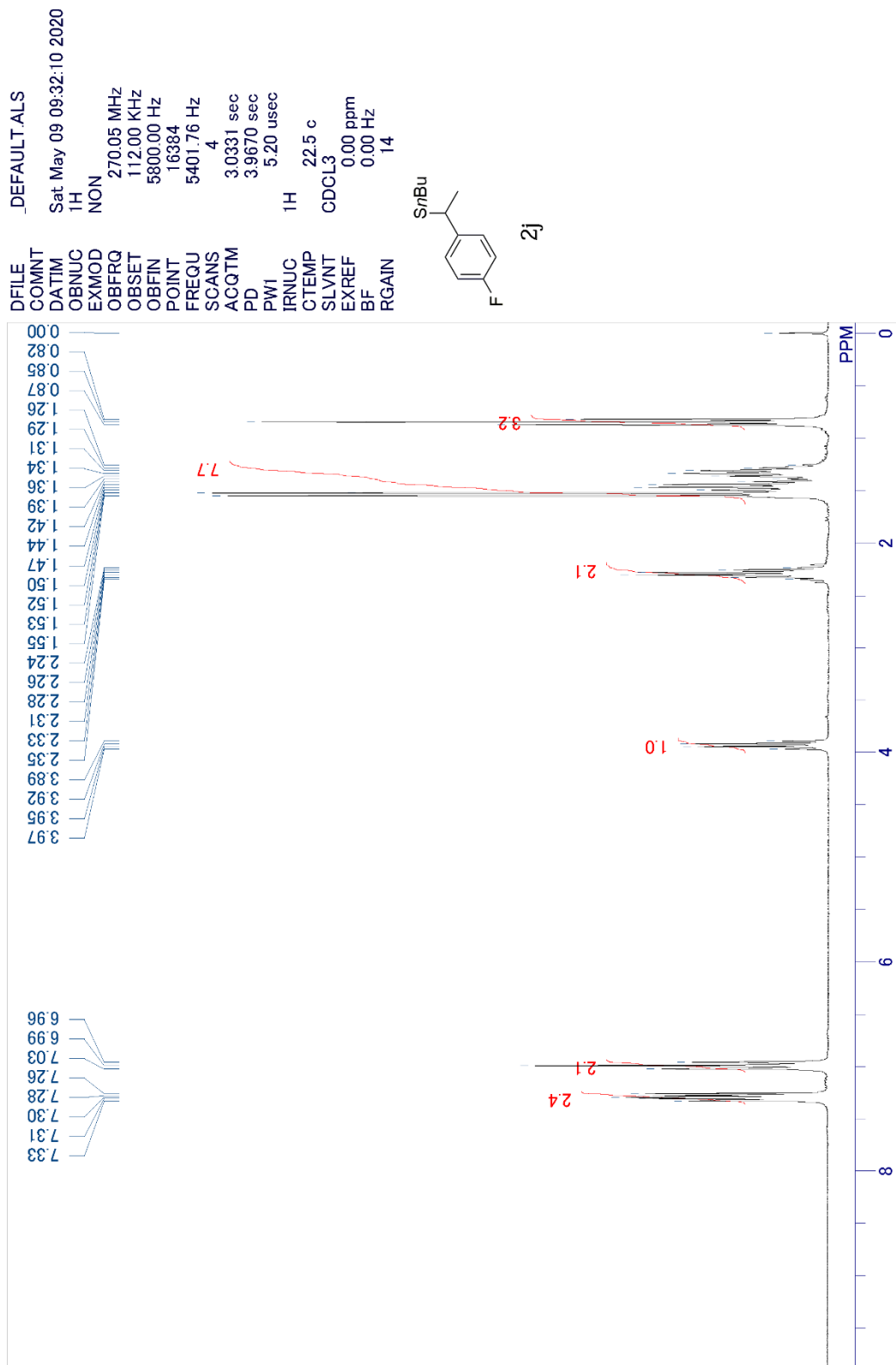
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 1H
 23.0 c
 CDCl3
 77.00 ppm
 0.00 Hz
 27
 RGAIN



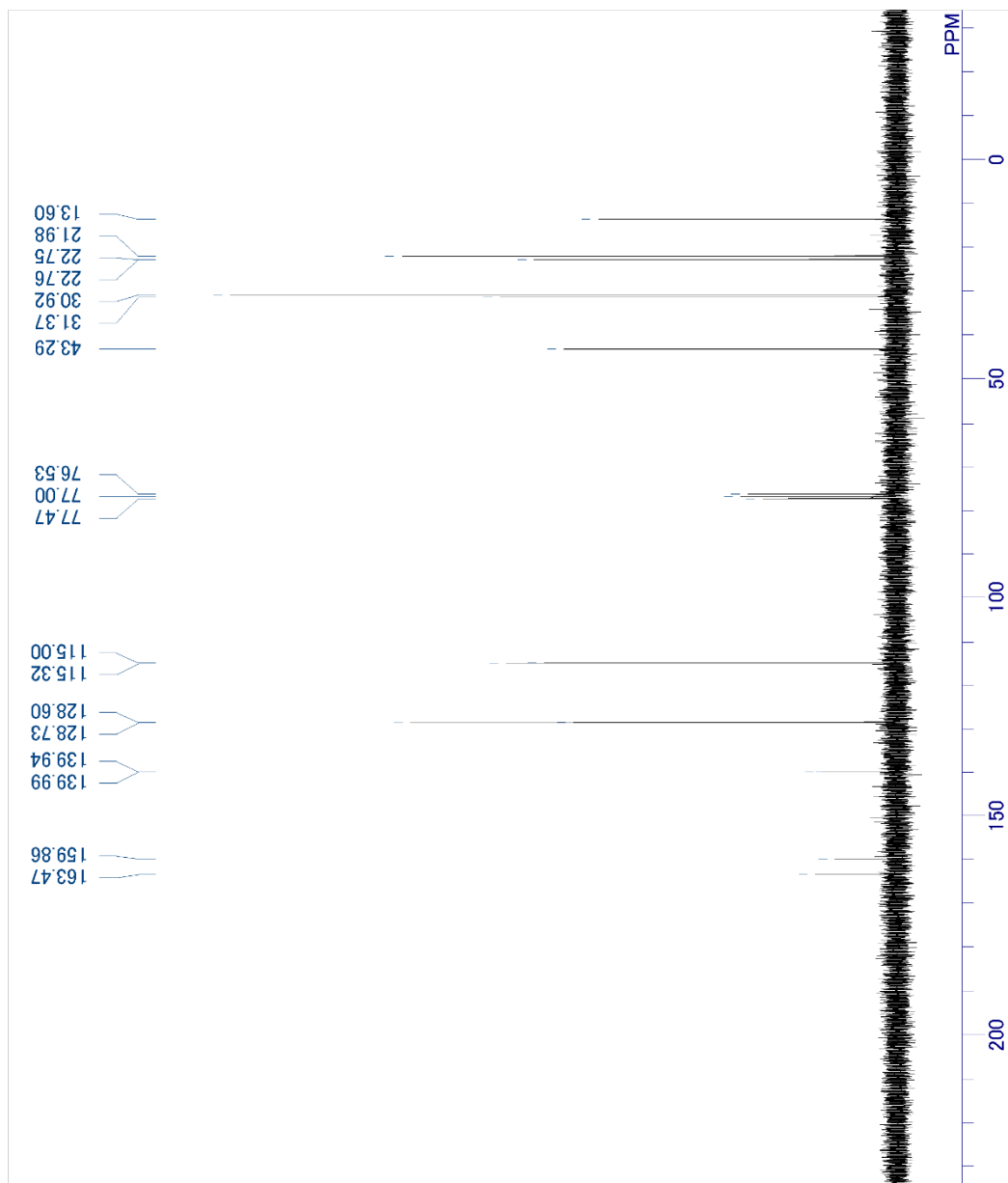
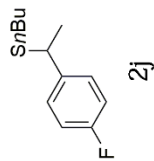


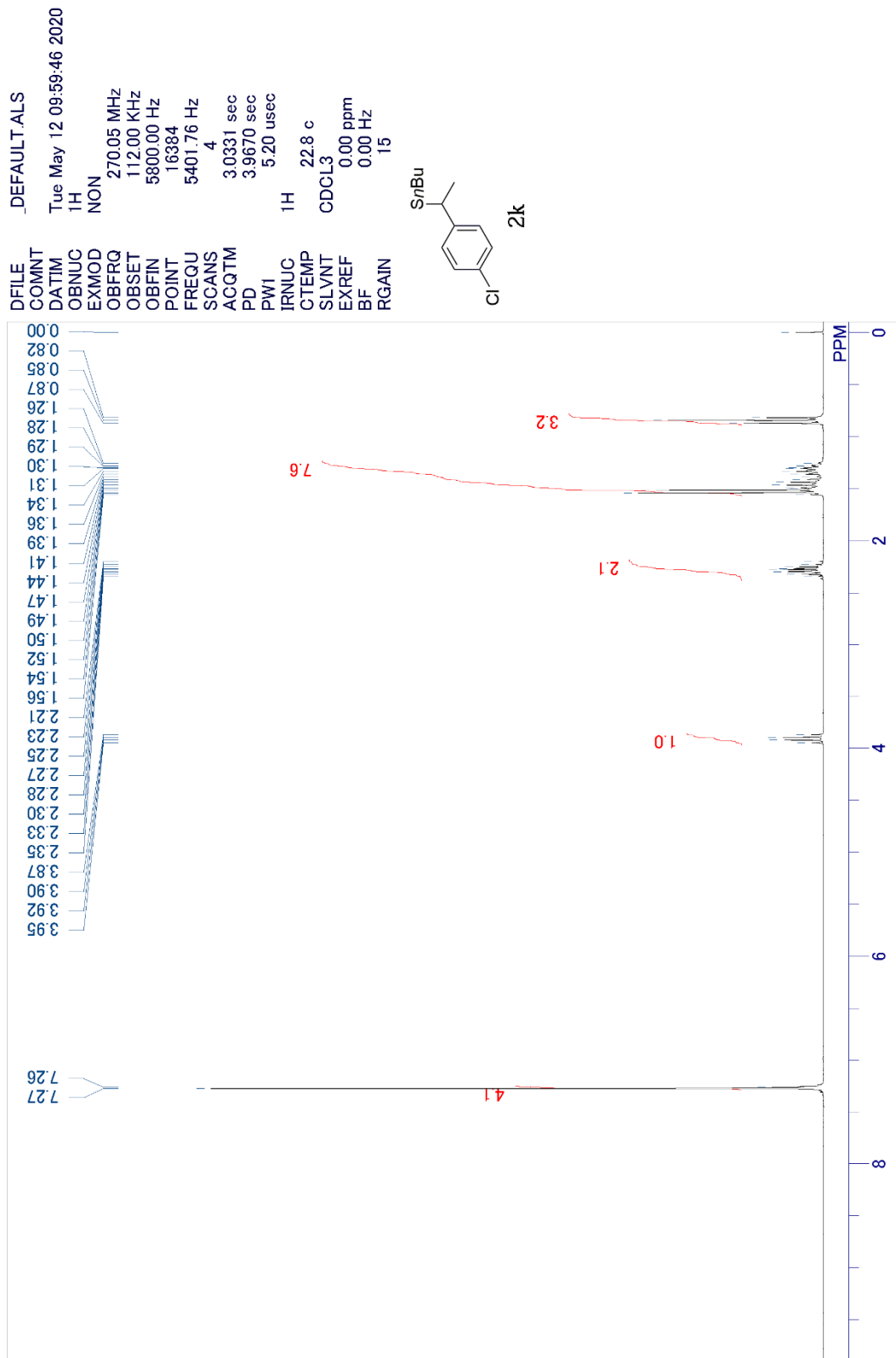
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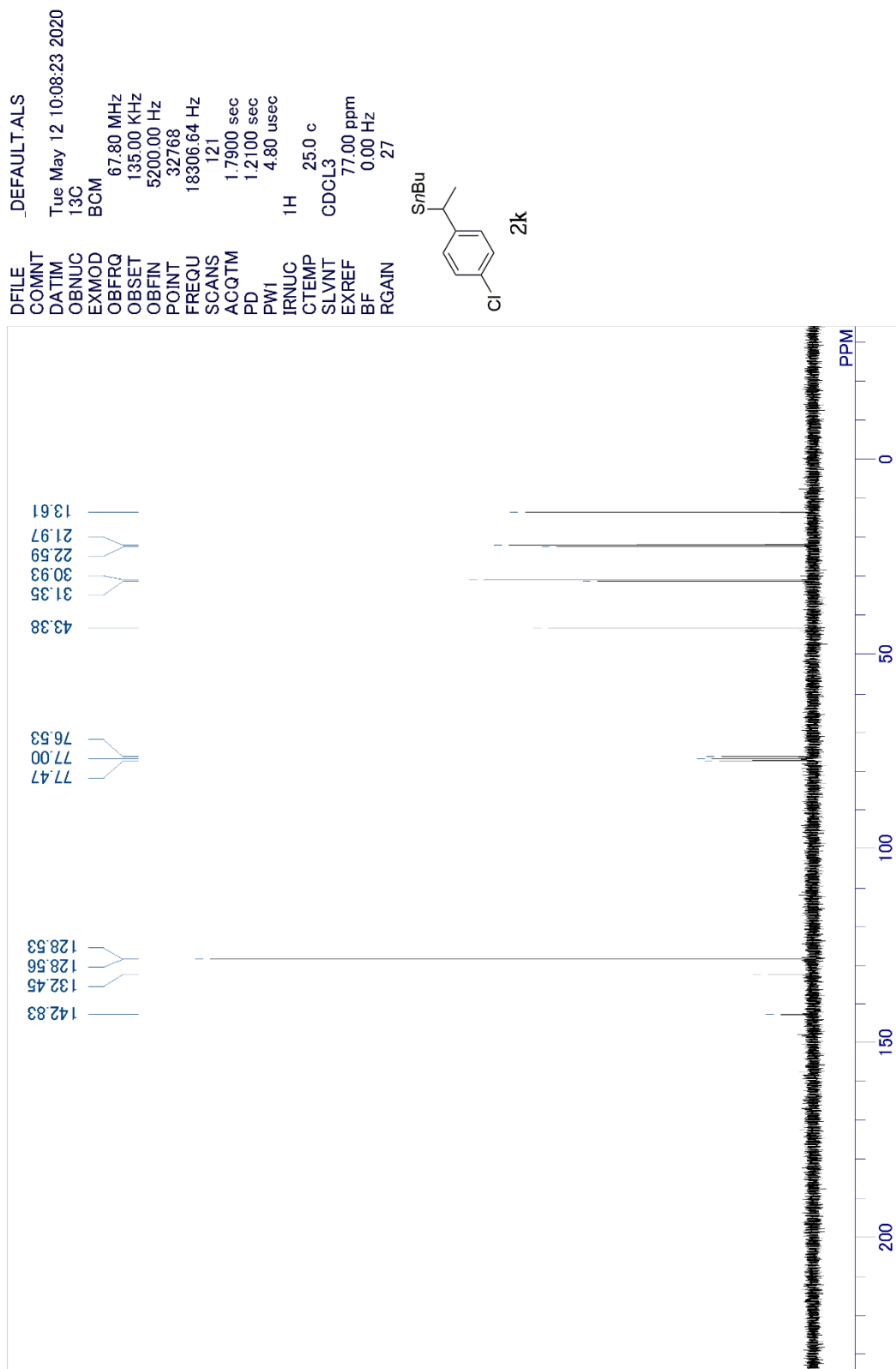


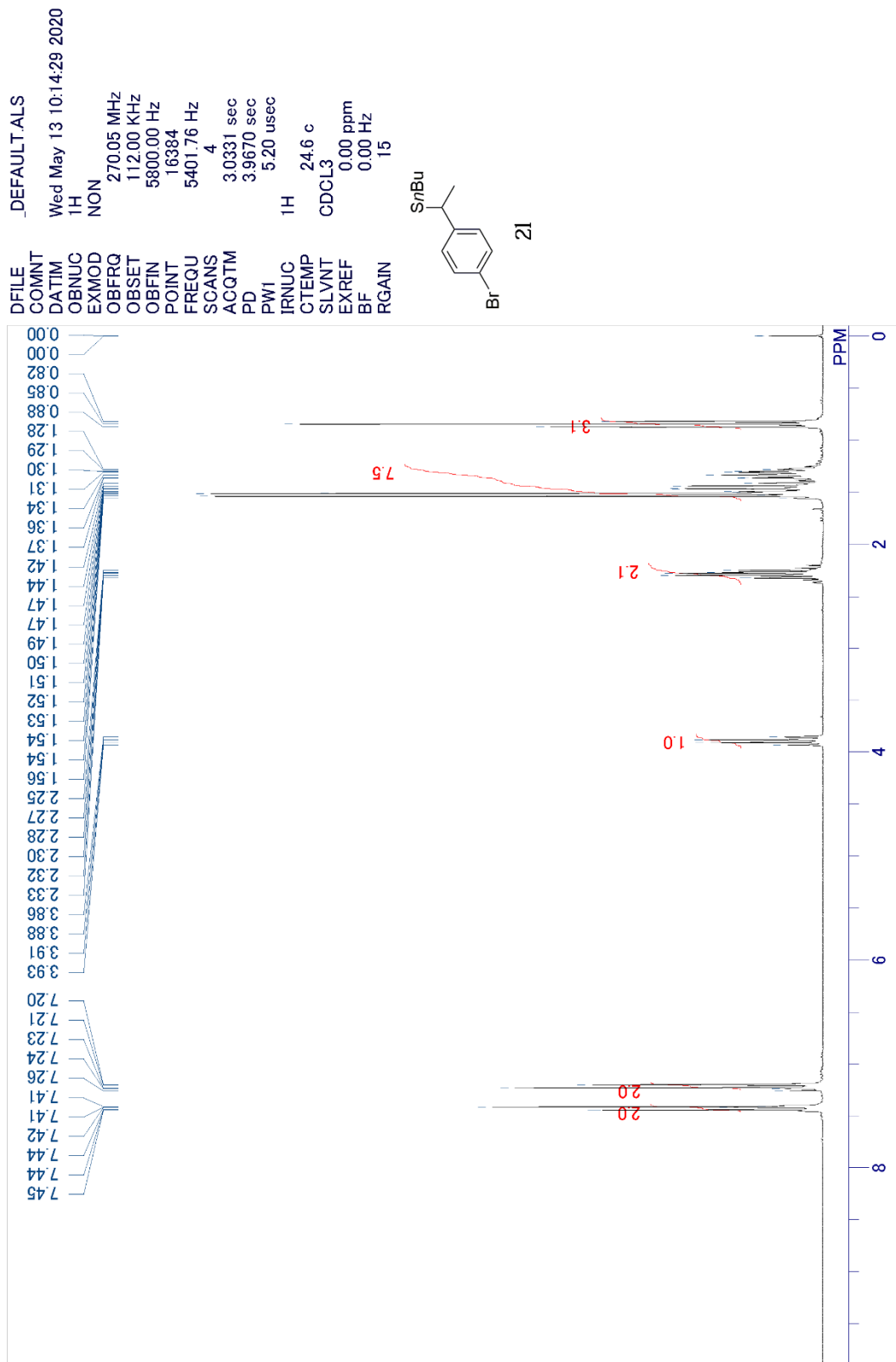


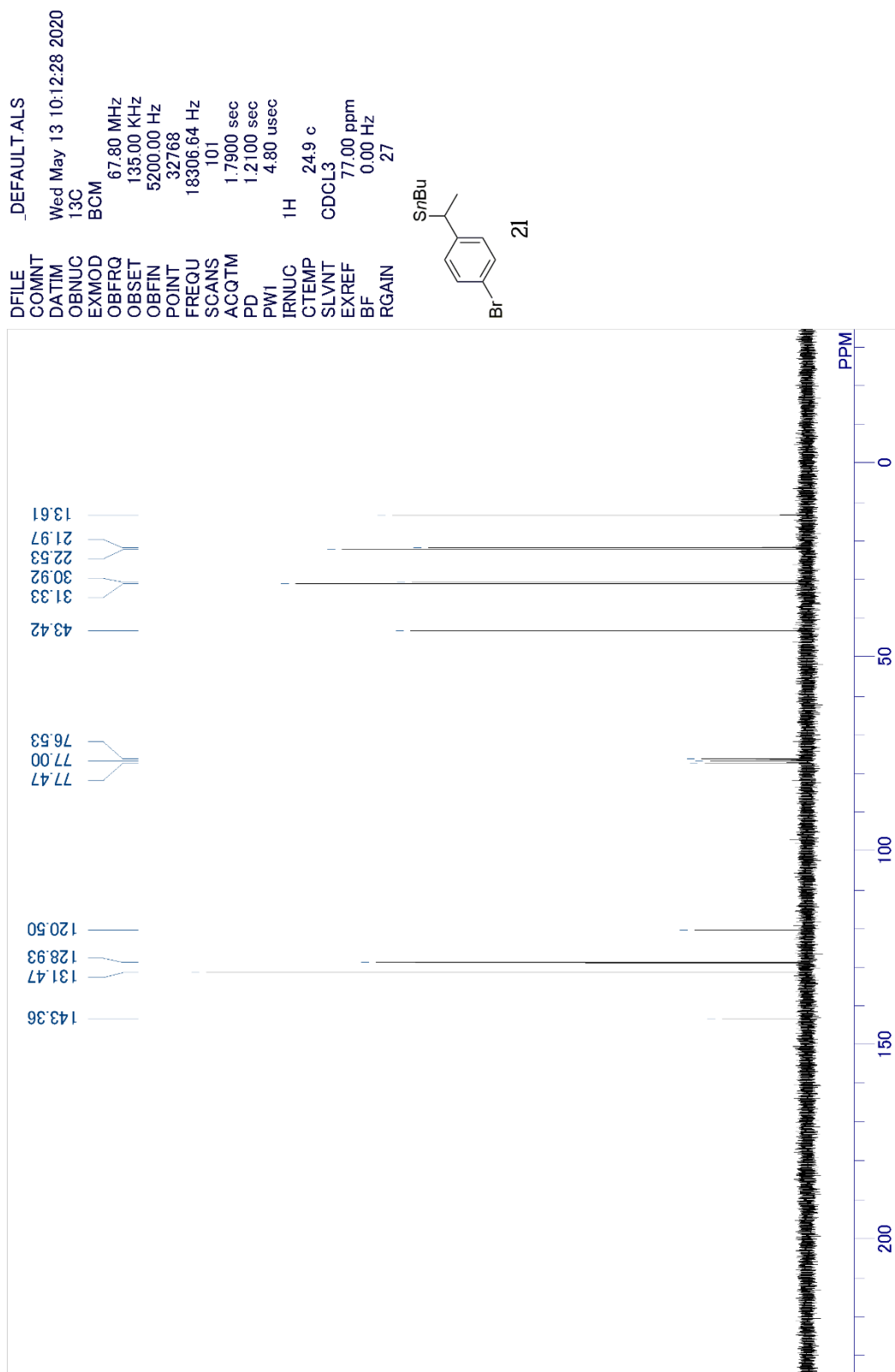
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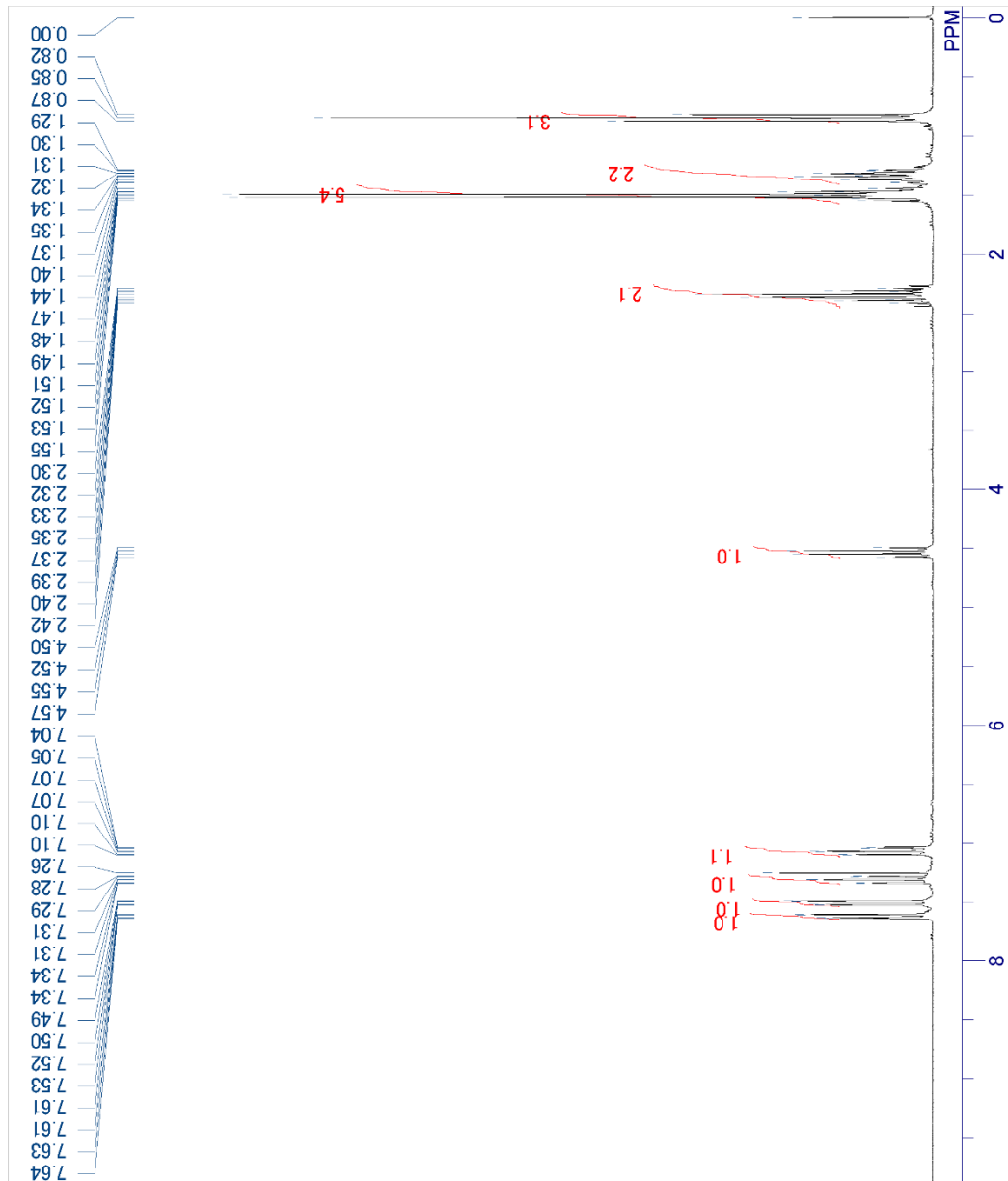
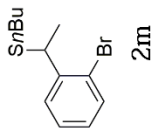




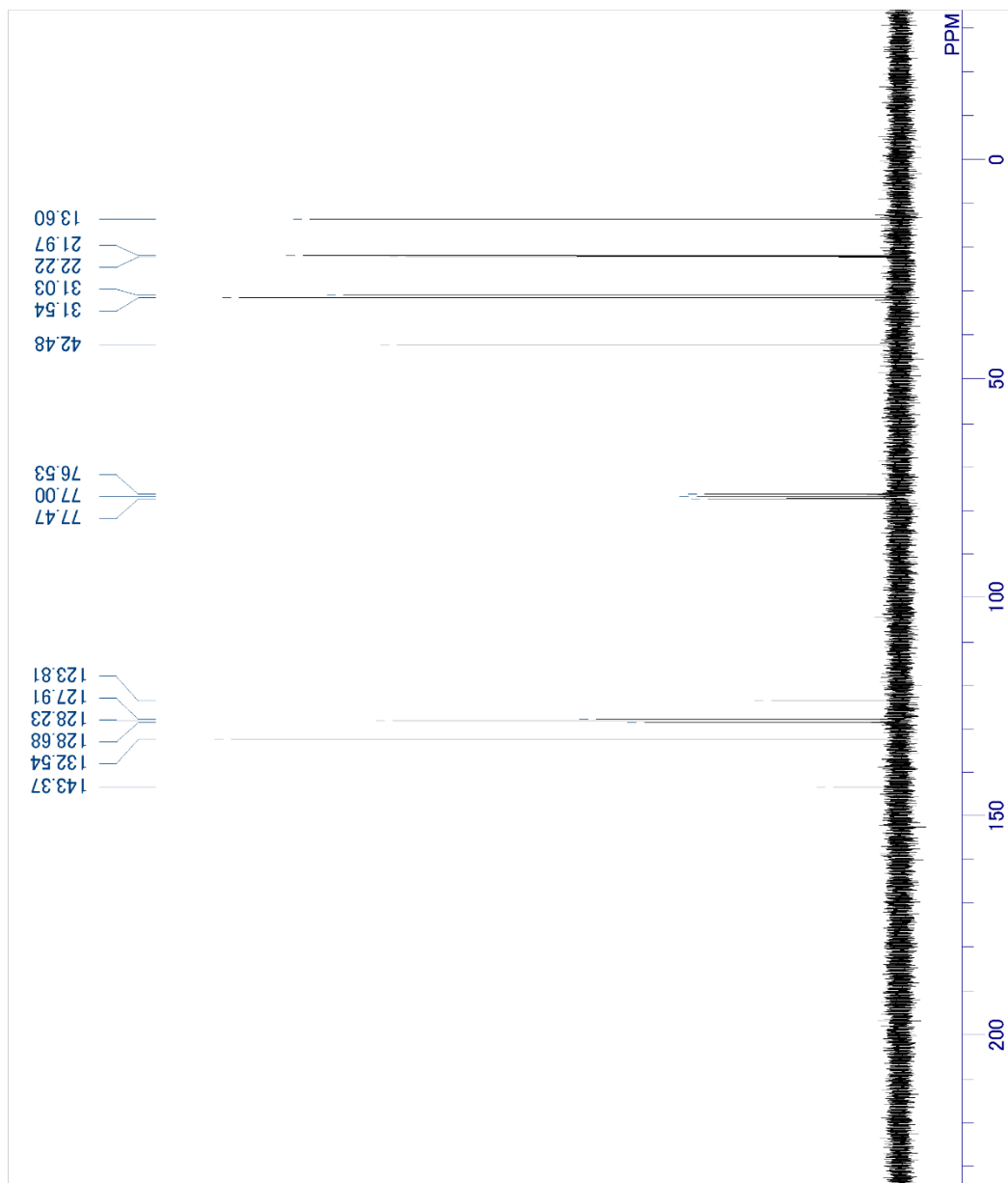
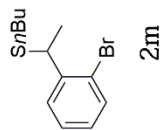




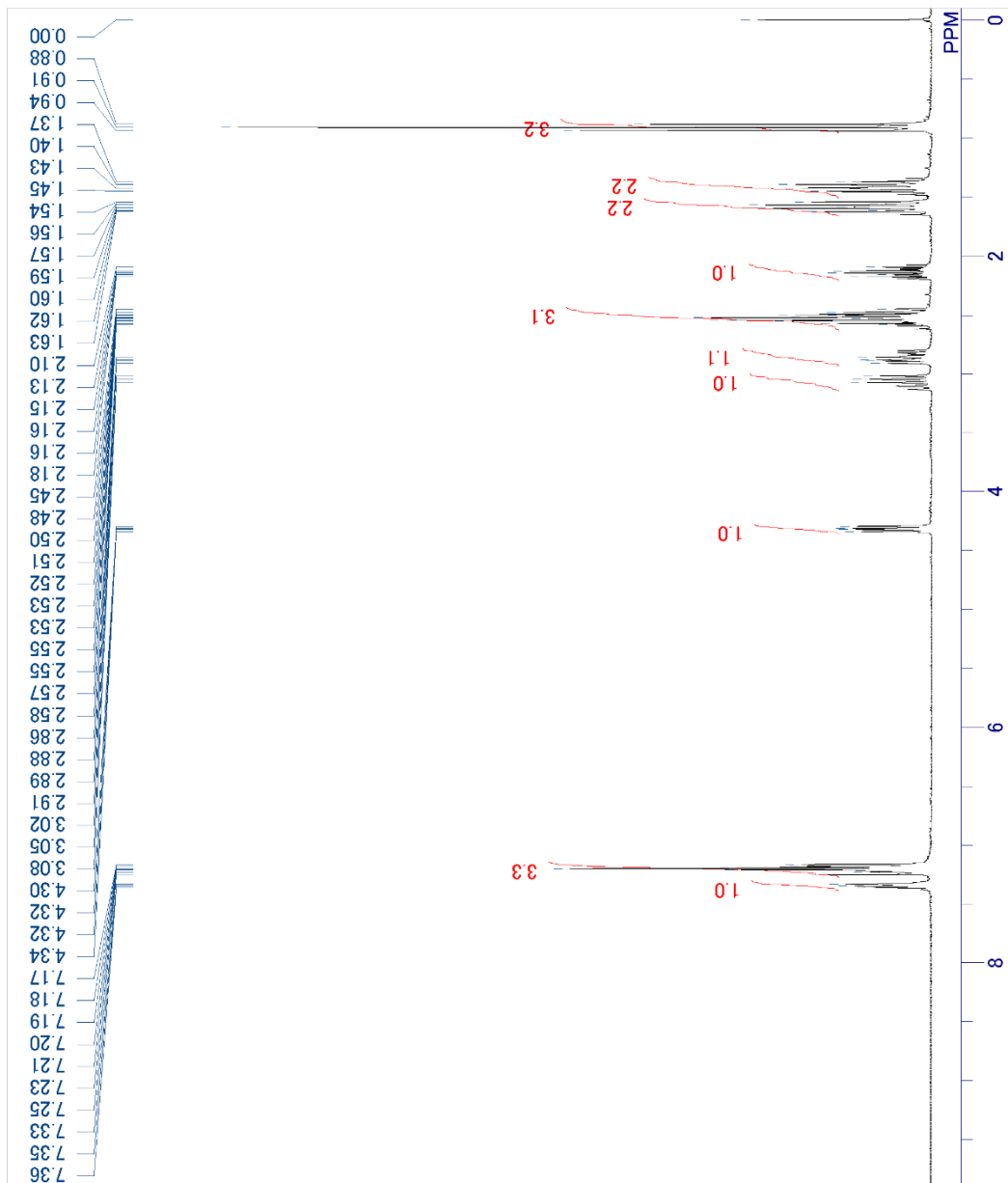
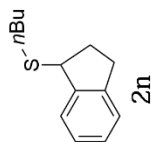
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CDCL3
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0.00 Hz
16



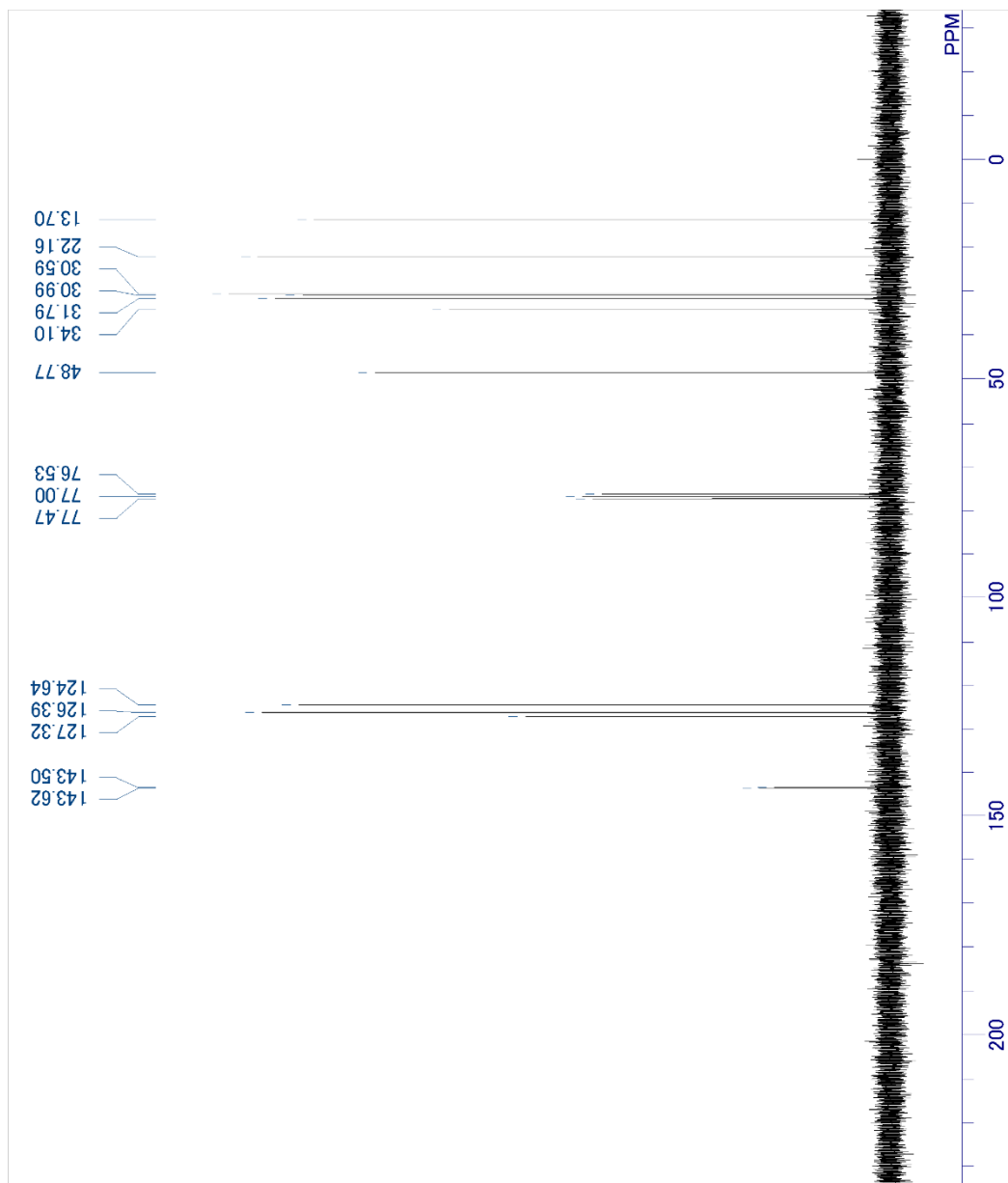
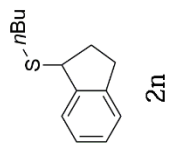
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SLVNT 77.00 ppm
EXREF 0.00 Hz
BF 27
RGAIN



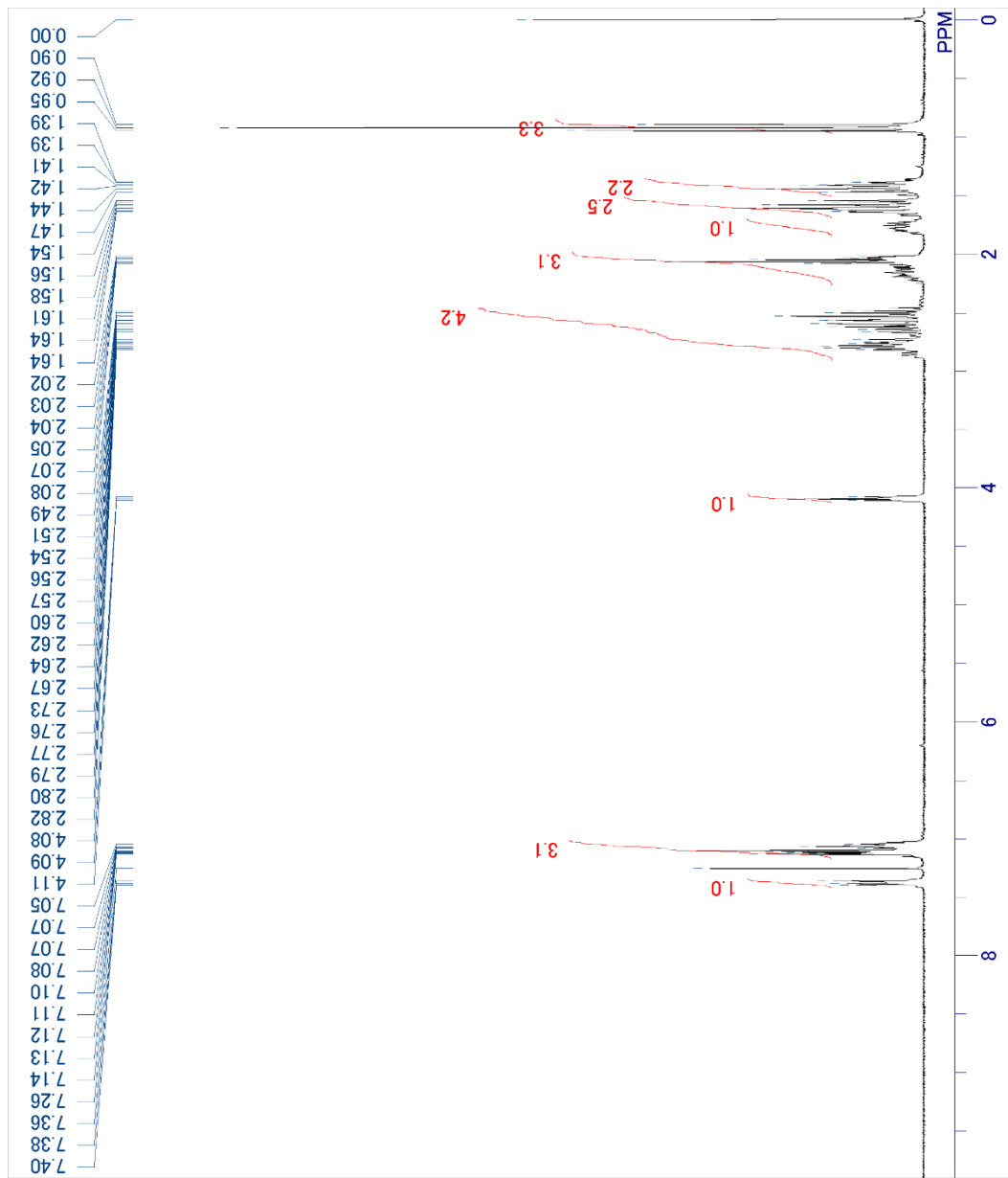
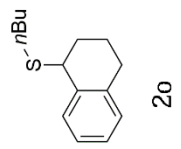
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CDCL3
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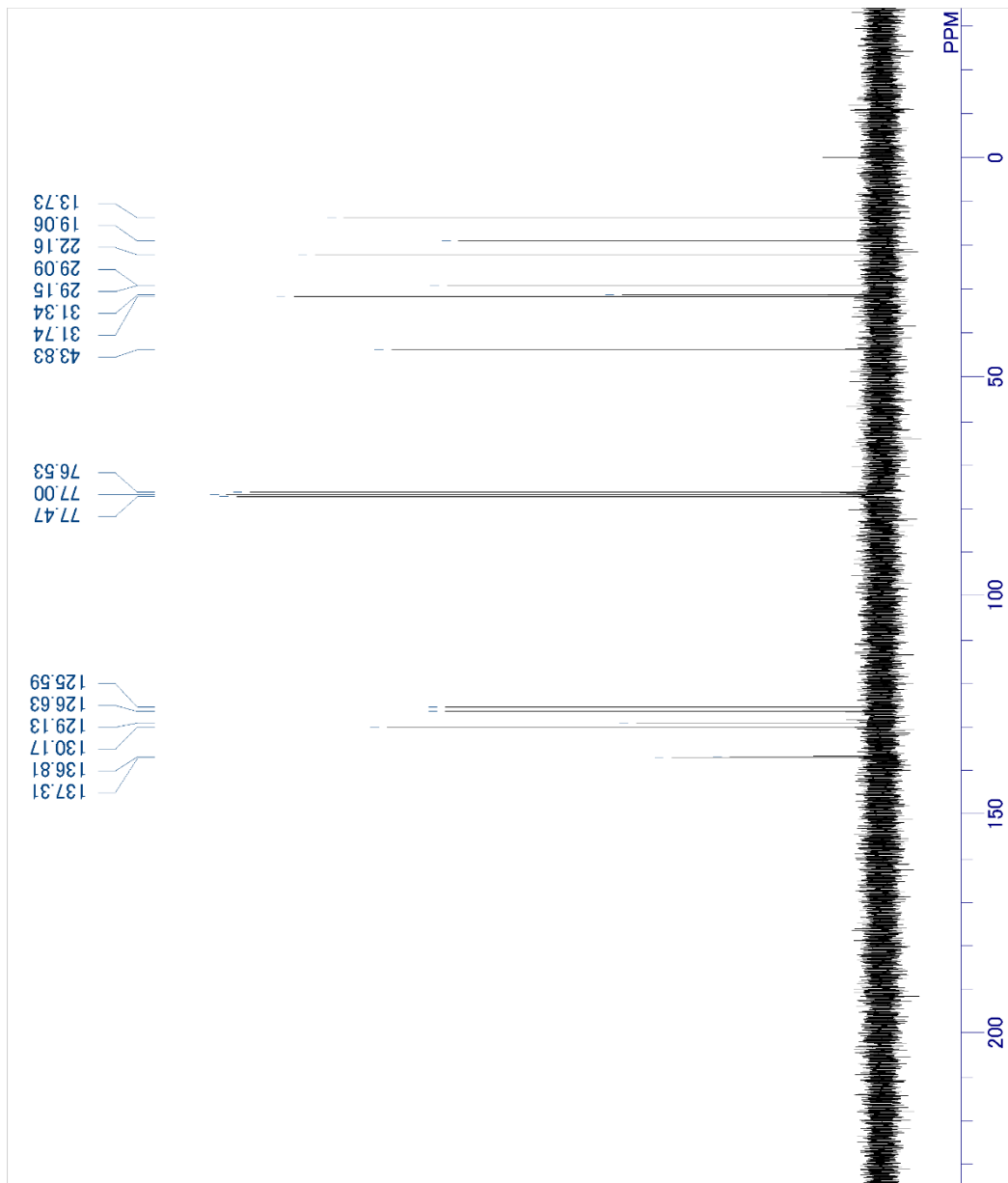
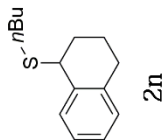
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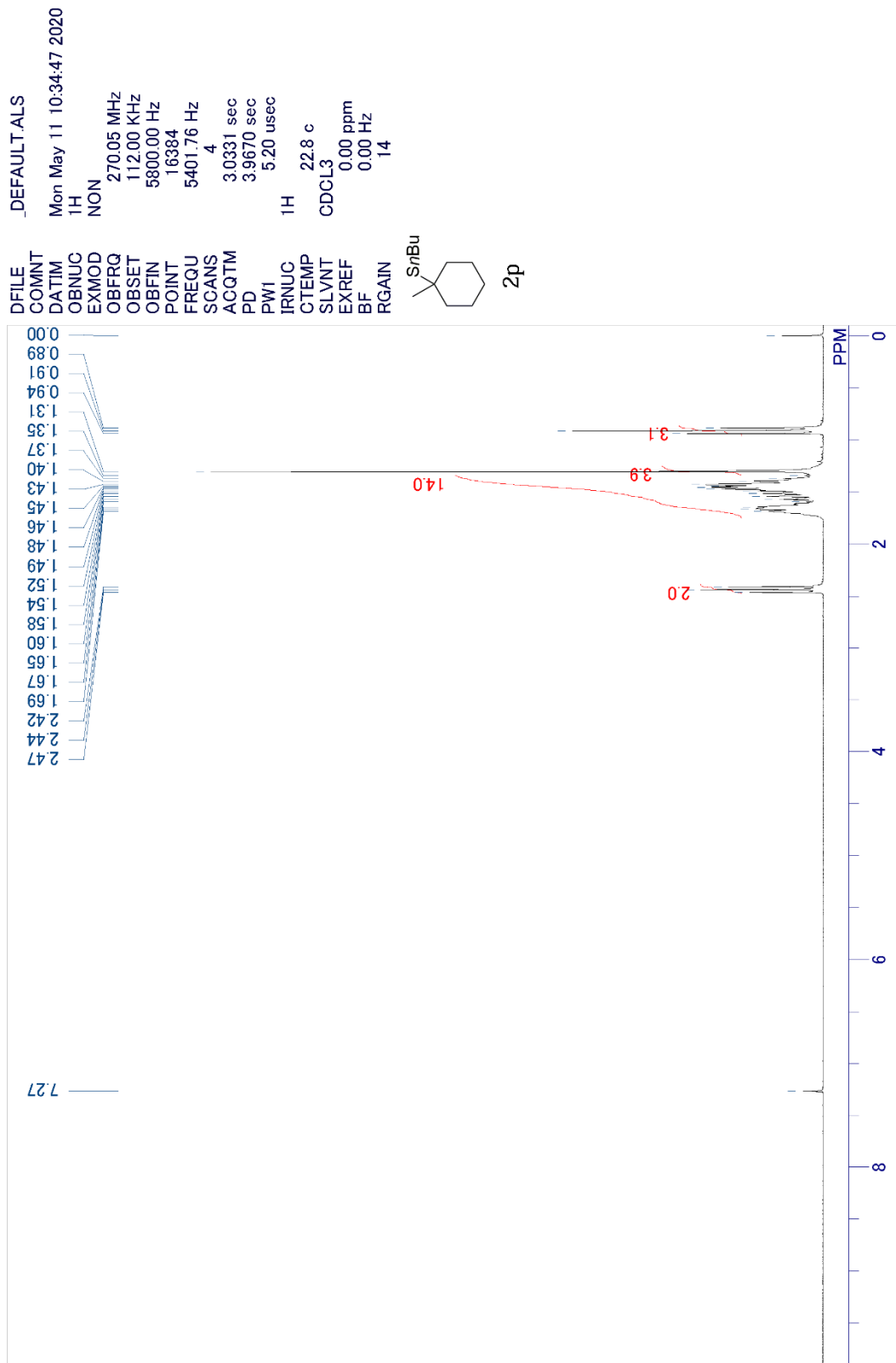


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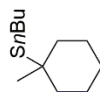
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 RGAIN



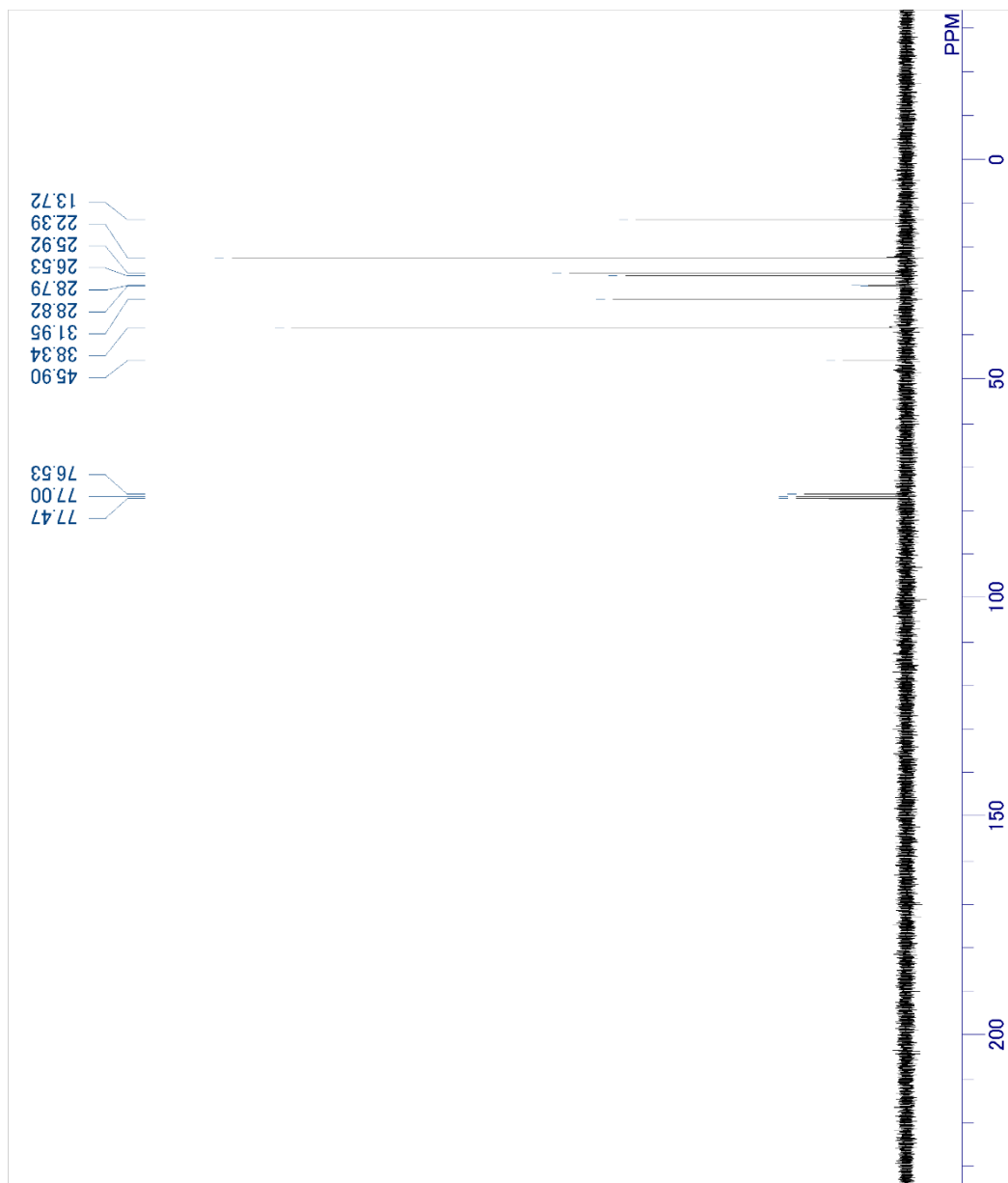


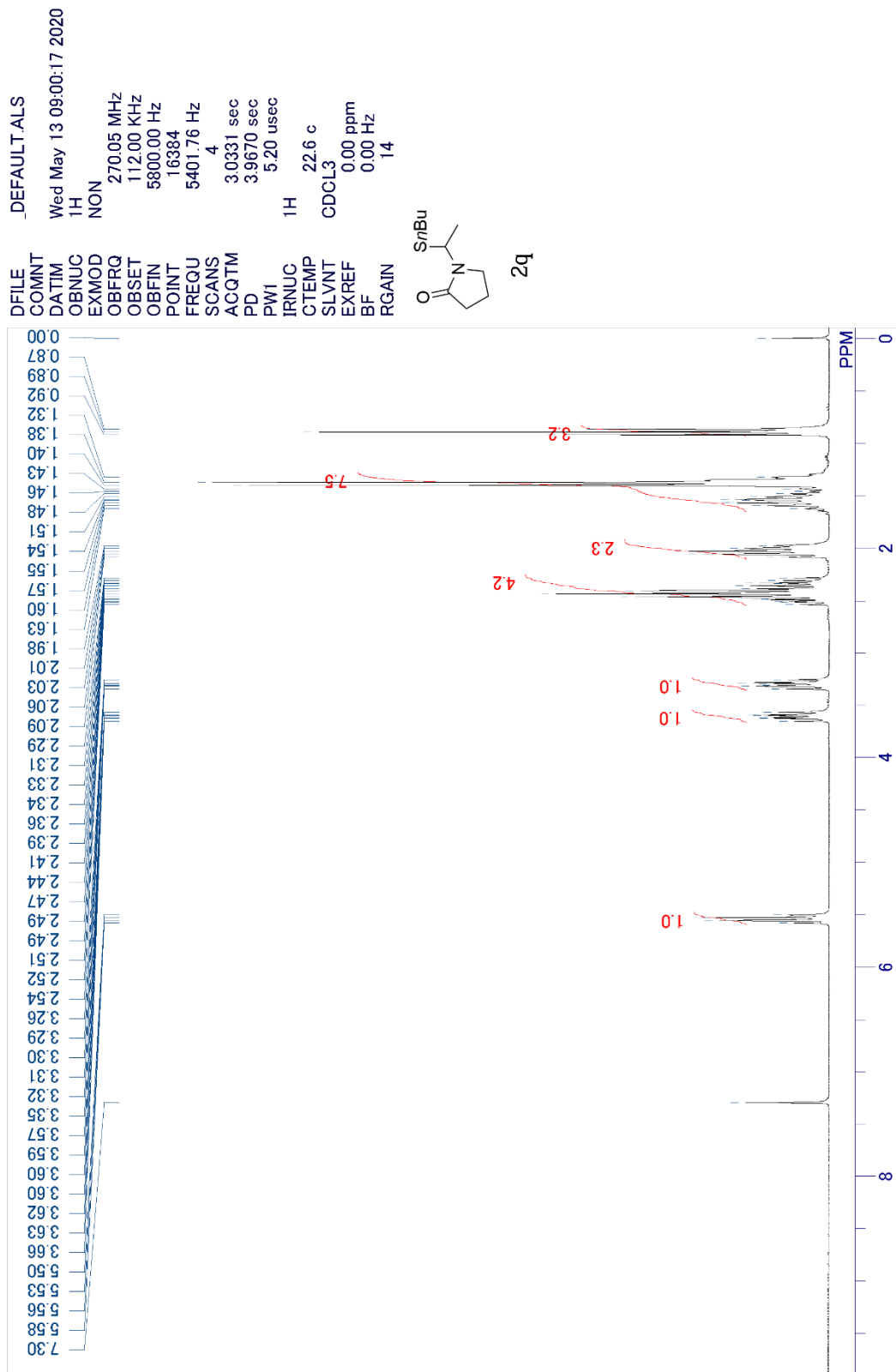
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DFILE
COMNT
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OBNUC
EXMOD
OBFRQ
OBSET
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CTEMP
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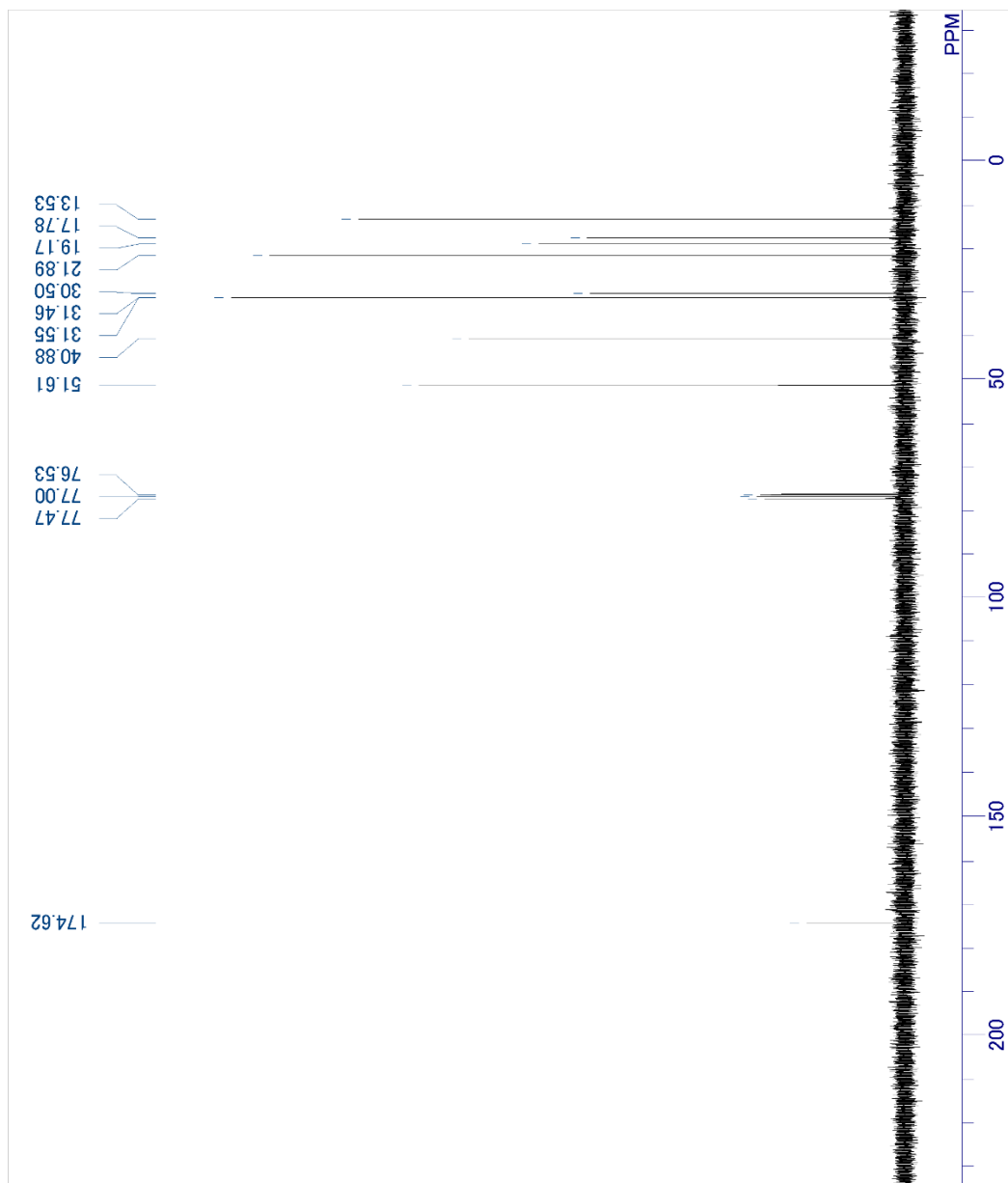
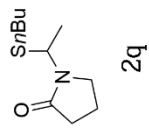


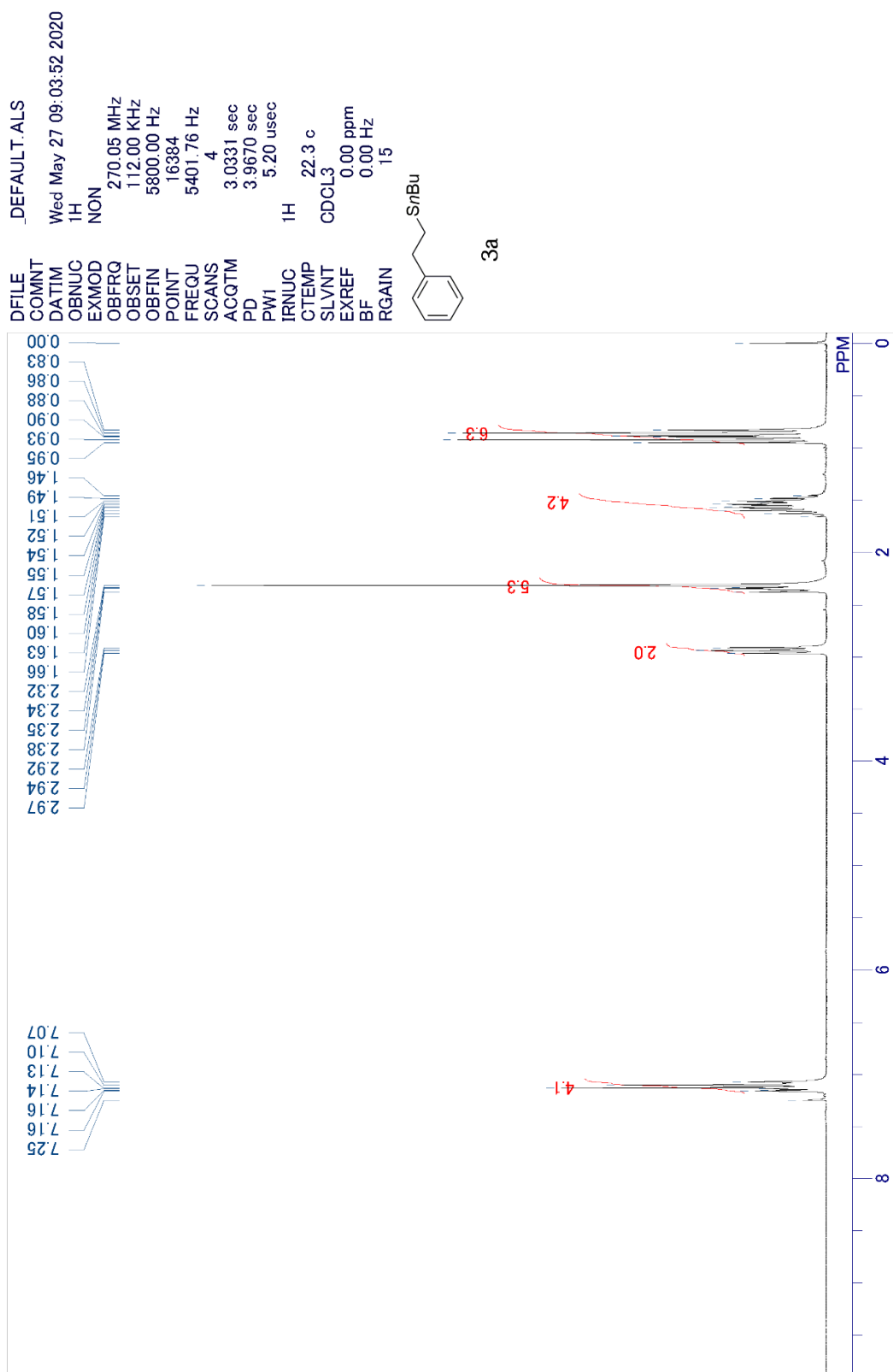
2p

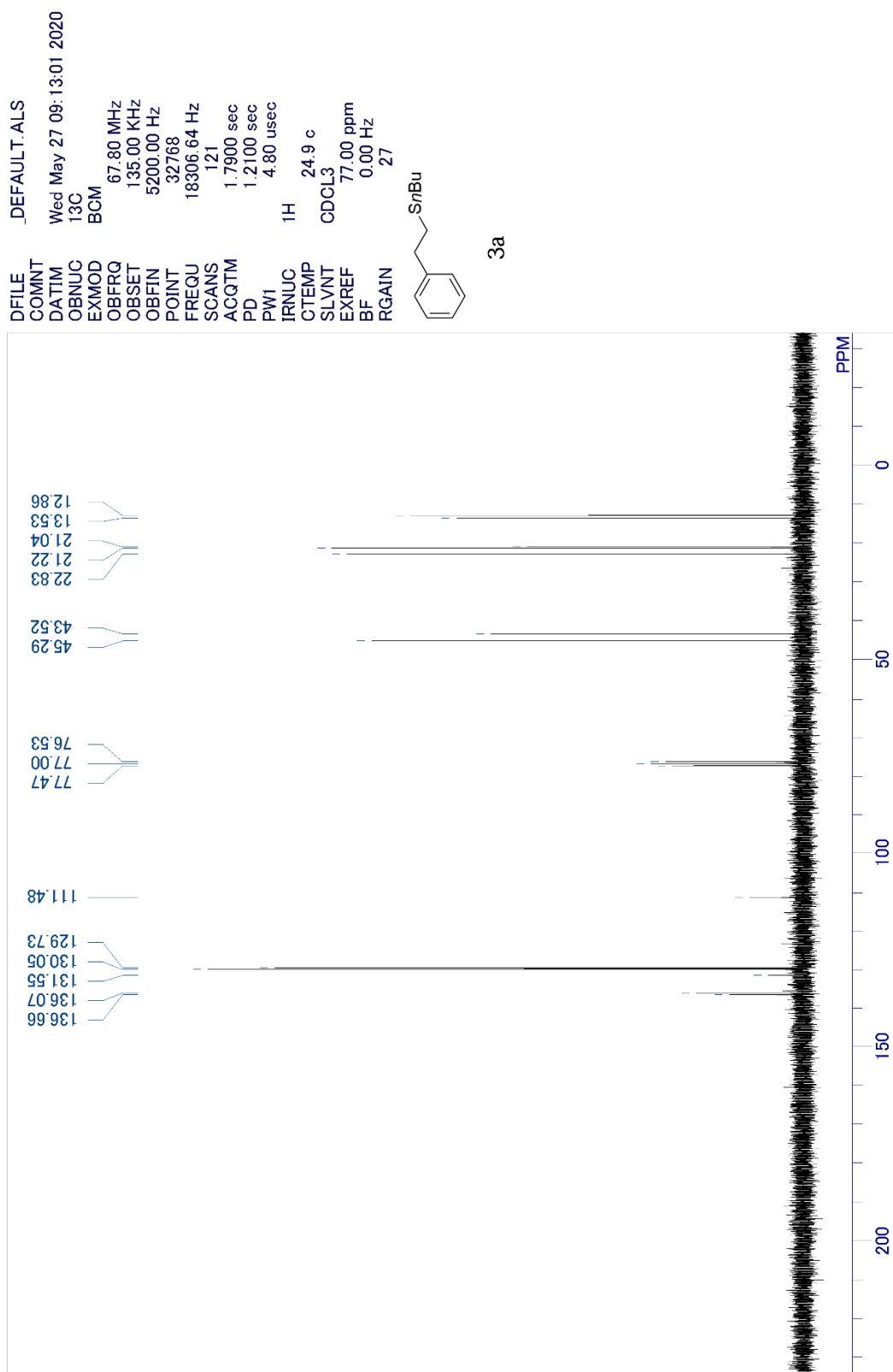


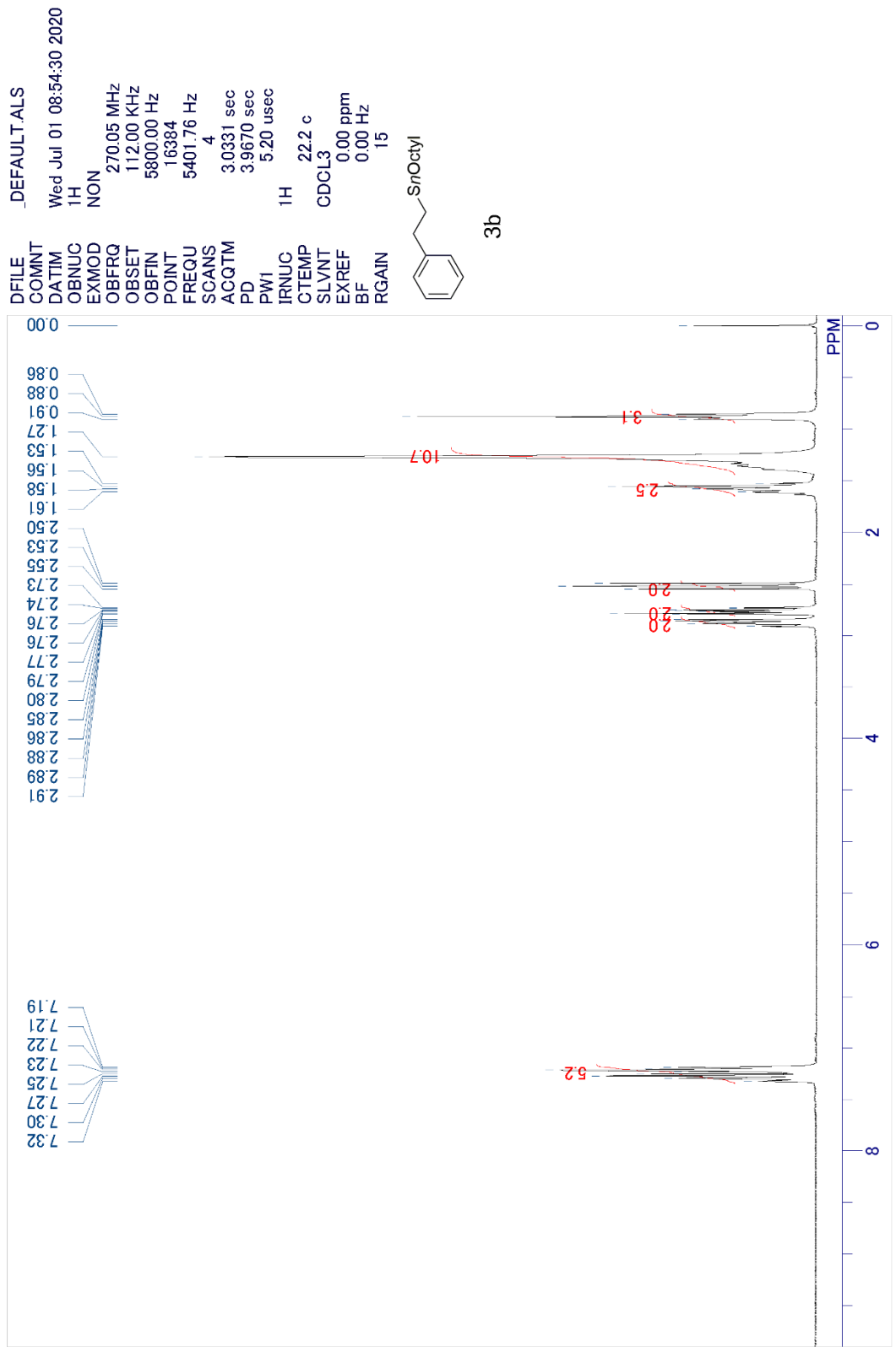


DFILE _DEFAULT.ALS
COMNT Wed May 13 09:08:34 2020
DATIM 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18306.64 Hz
SCANS 121
ACQTM 1.7900 sec
PD 1.2100 sec
PWI 4.80 usec
IRNUC 1H
CTEMP 24.9 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 27

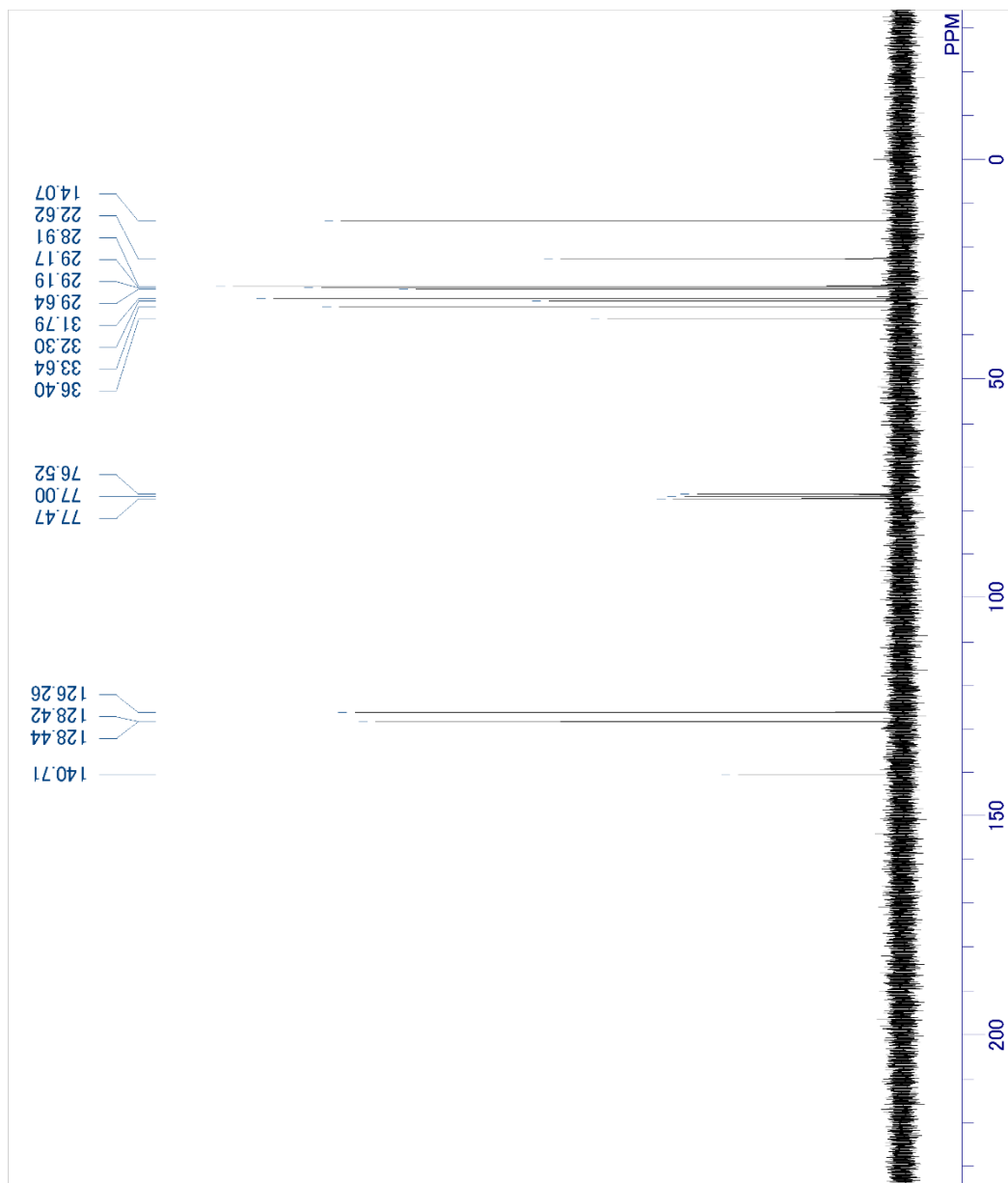


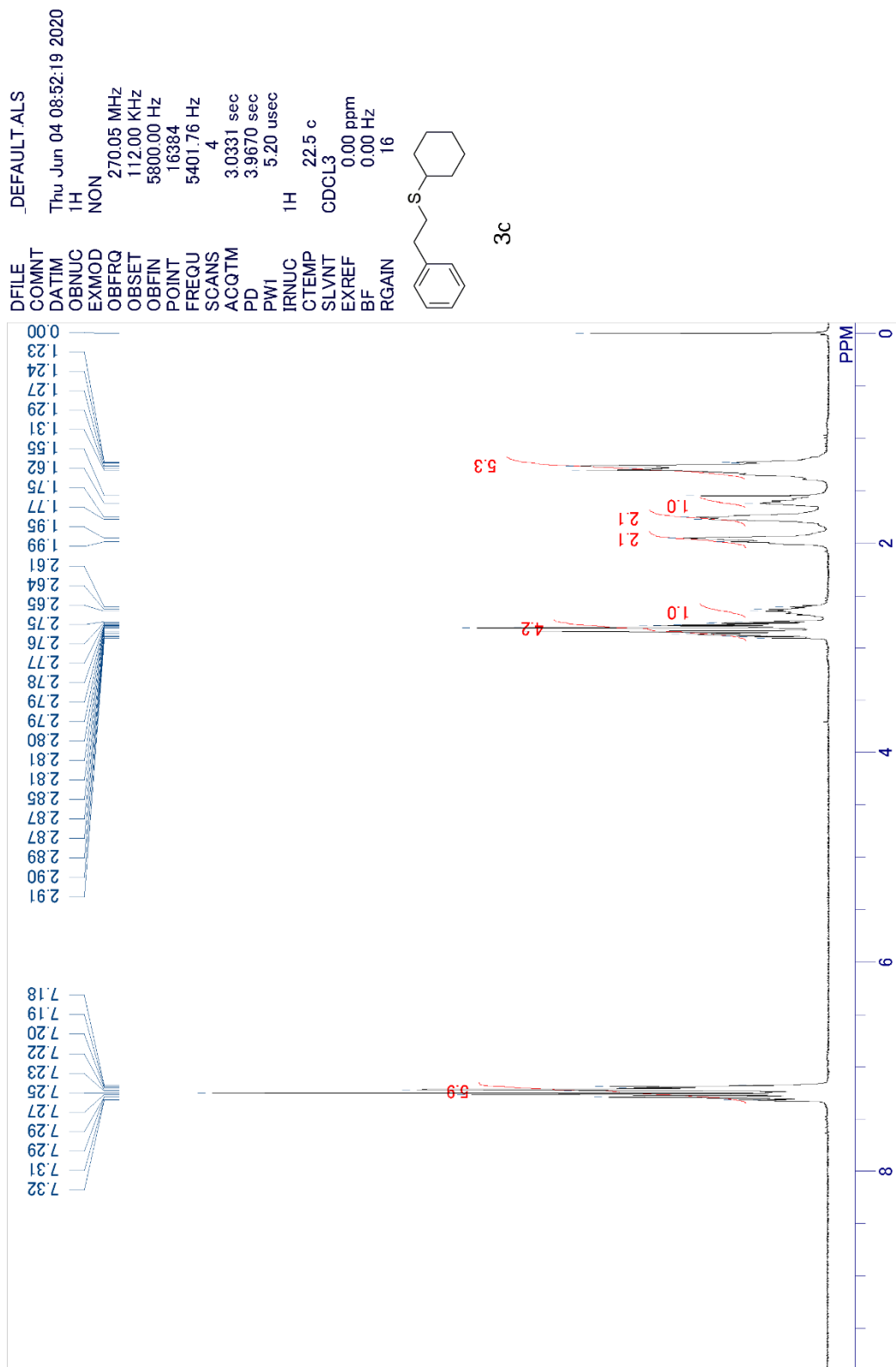




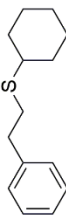


DFILE _DEFAULT.ALS
COMNT Wed Jul 01 09:07:39 2020
DATIM 13C
OBRUC BCM
EXMOD 67.80 MHz
OBFRQ 135.00 KHz
OBSET 5200.00 Hz
OBFIN 32768
POINT 18306.64 Hz
FREQU 202
SCANS 17900 sec
ACQTM 1.2100 sec
PD 4.80 usec
PWI 1H
IRNUC 24.4 c
CTEMP CDC13
SLVNT 77.00 ppm
EXREF 0.00 Hz
BF 27
RGAIN

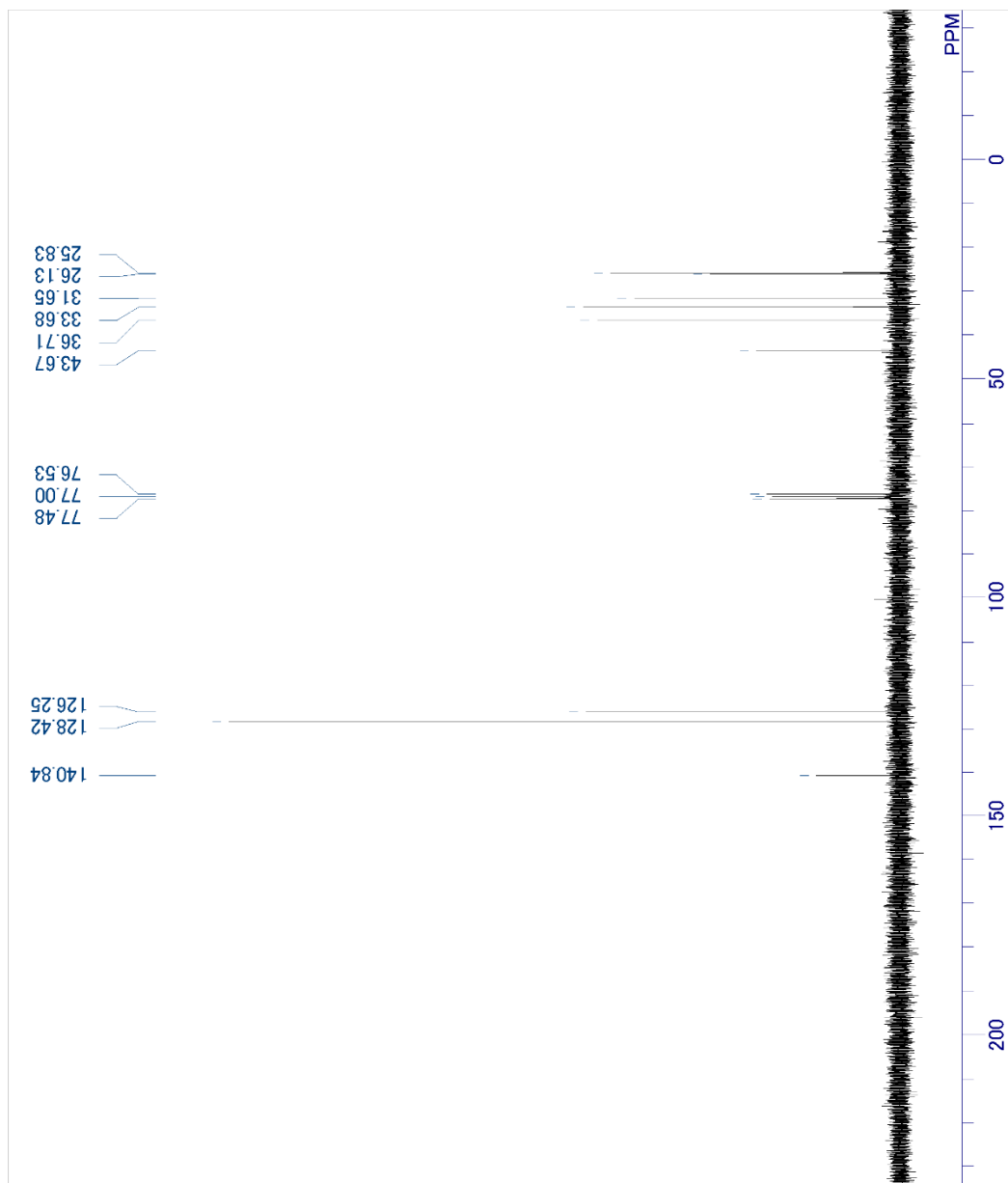




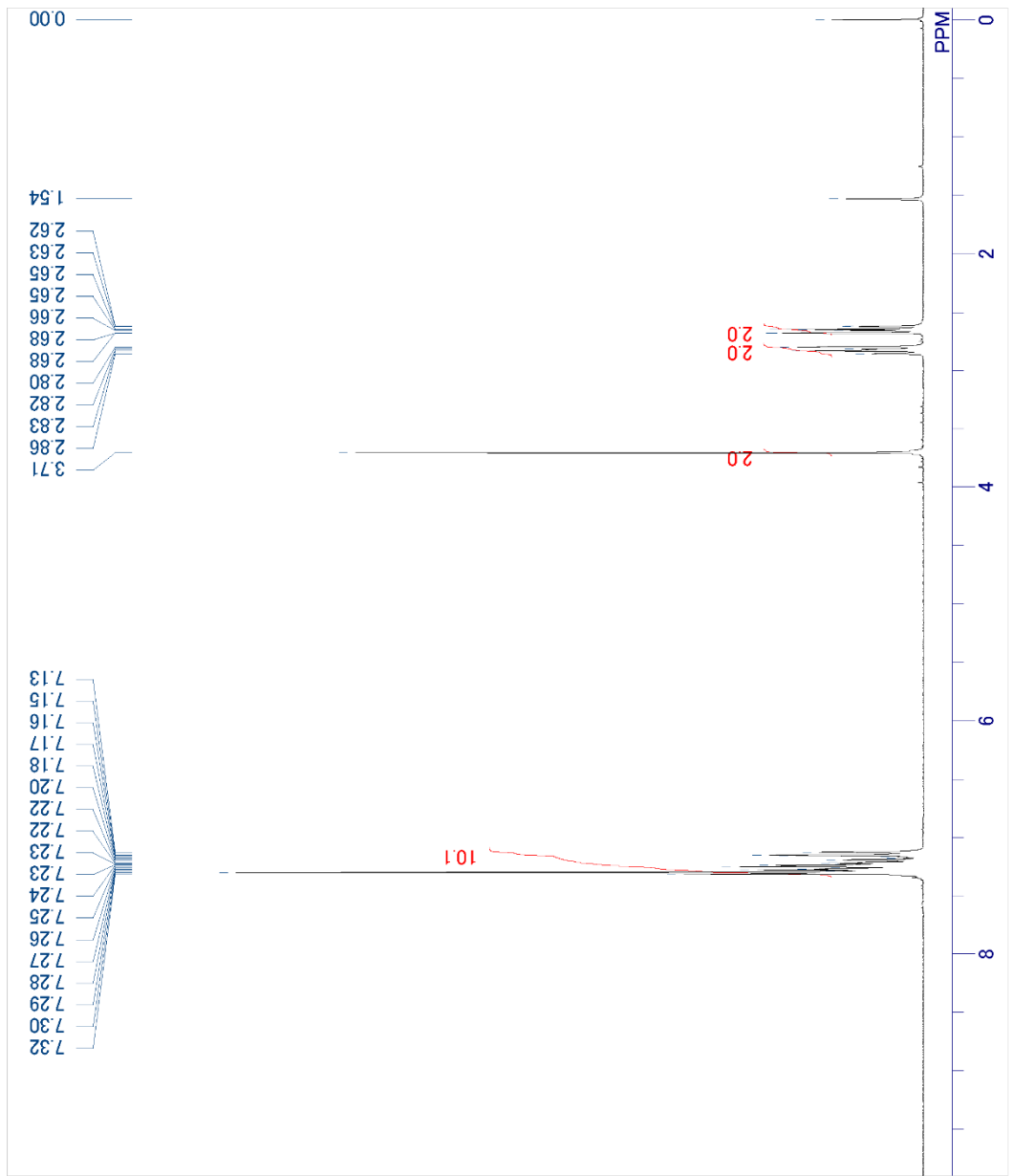
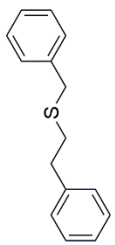
DFILE _DEFAULT.ALS
COMNT Thu Jun 04 09:02:14 2020
DATIM 13C
OBNUC BCM
EXMOD 67.80 MHz
OBFRQ 135.00 KHz
OBSET 5200.00 Hz
OBFIN 32768
POINT 18306.64 Hz
FREQU 101
SCANS 1.7900 sec
ACQTM 1.2100 sec
PD 4.80 usec
PWI 1H
IRNUC 24.8 c
CTEMP CDC13
SLVNT 77.00 ppm
EXREF 0.00 Hz
BF 27
RGAIN



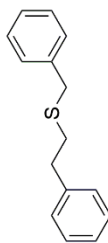
3c



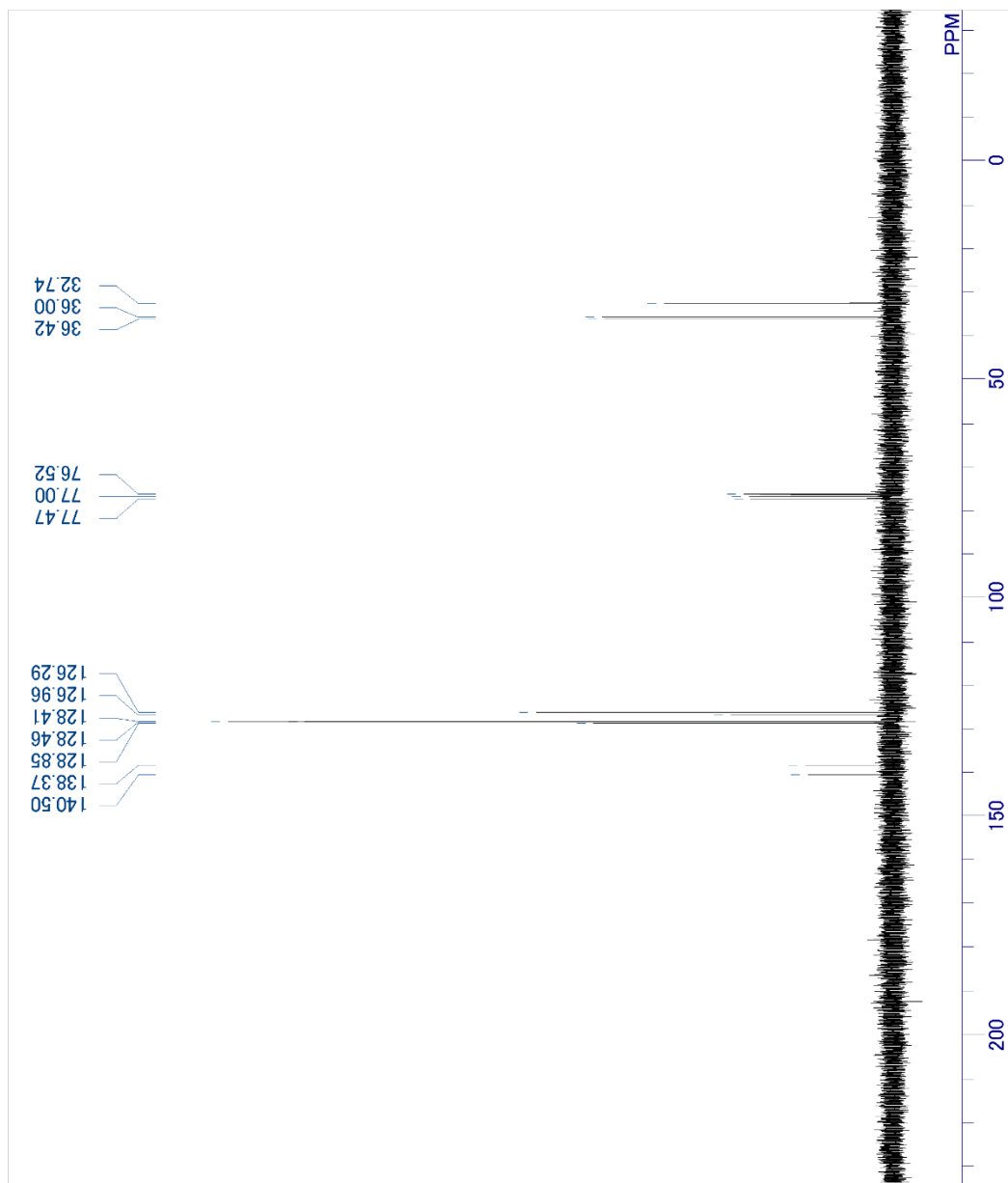
DFILE _DEFAULT.ALS
COMNT Fri Jul 03 09:24:24 2020
DATIM 1H
OBNUC NON
EXMOD 270.05 MHz
OBFREQ 112.00 KHz
OBSET 5800.00 Hz
OBFIN 16384
POINT 5401.76 Hz
FREQU 4
SCANS 30331 sec
ACQTM 3.9670 sec
PD 5.20 usec
PWI 1H
IRNUC 22.1 c
CTEMP CDCL3
SLVNT 0.00 ppm
EXREF 0.00 Hz
BF 16
RGAIN

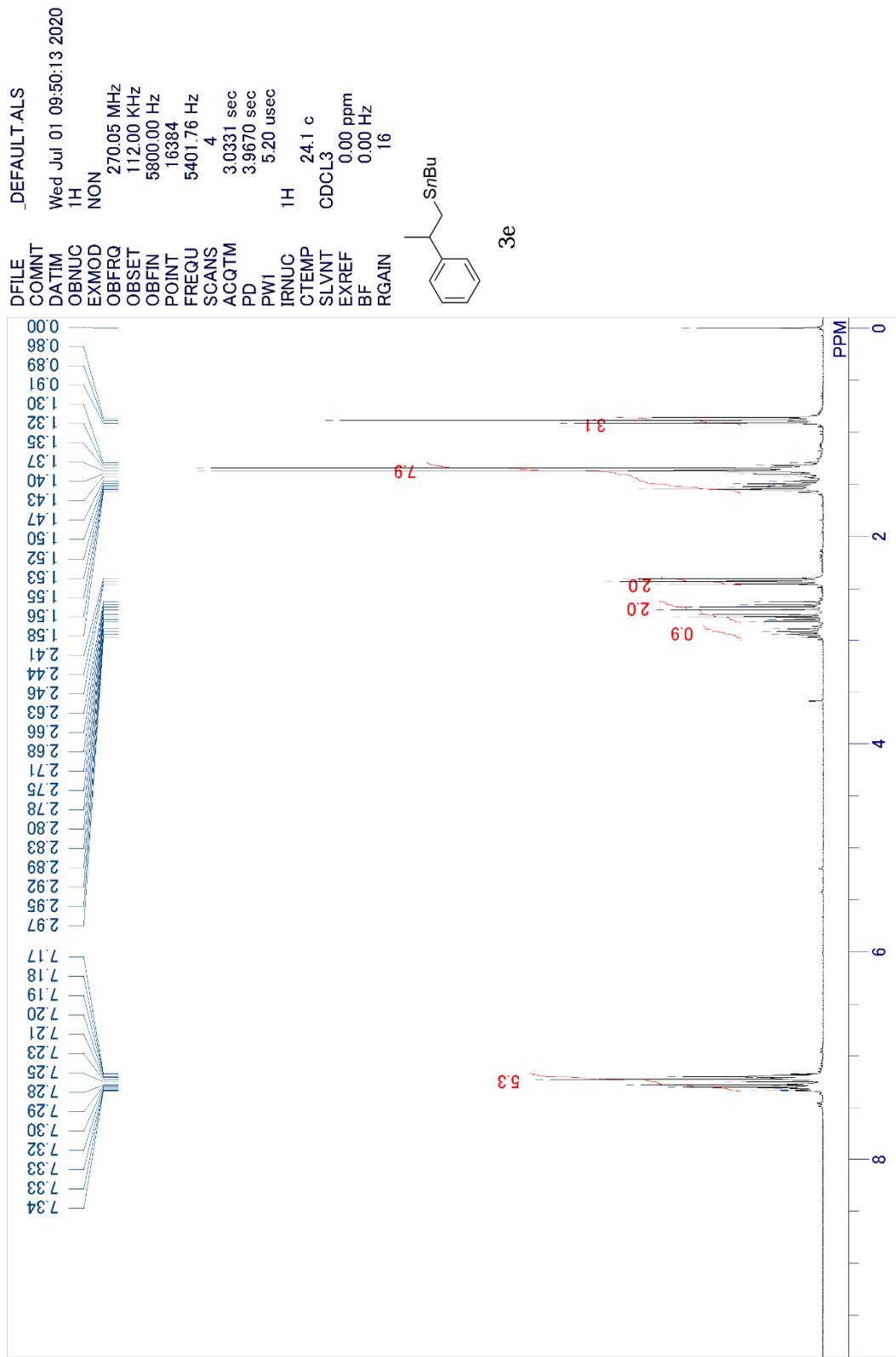


DFILE _DEFAULT.ALS
COMNT
DATIM Fri Jul 03 09:31:50 2020
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18306.64 Hz
SCANS 101
ACQTM 1.7900 sec
PD 1.2100 sec
PWI 4.80 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 27

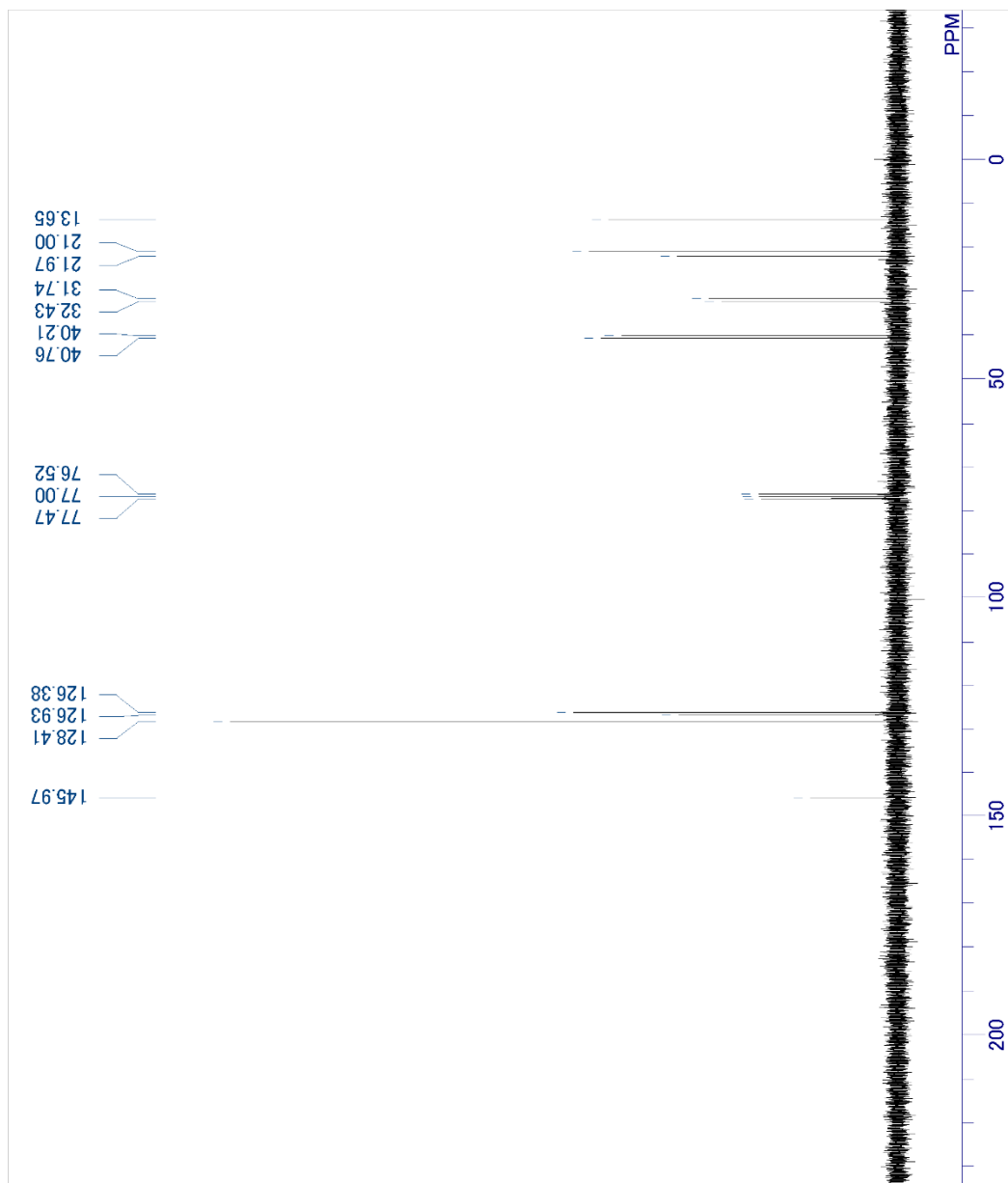
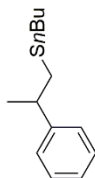


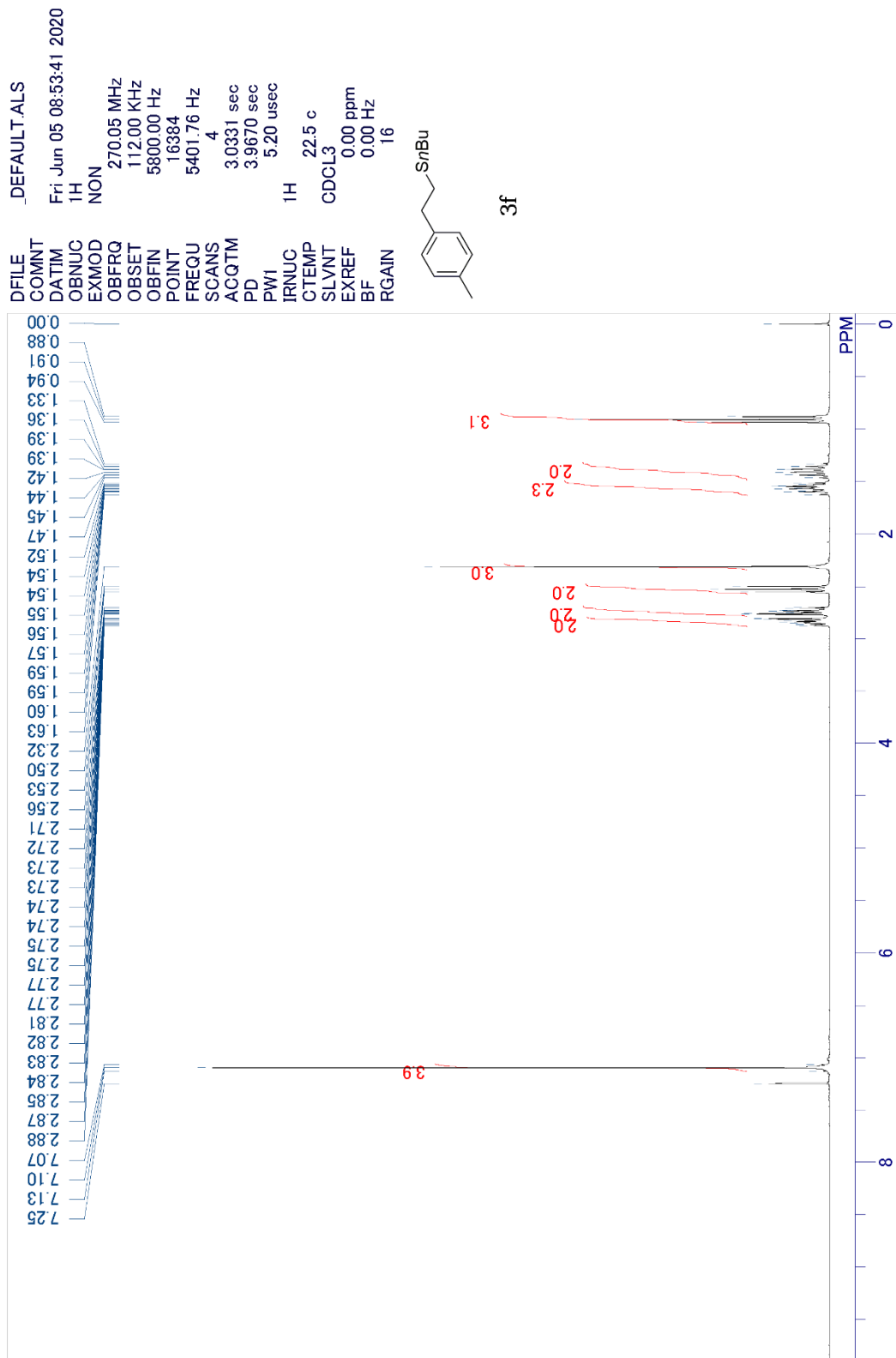
3d



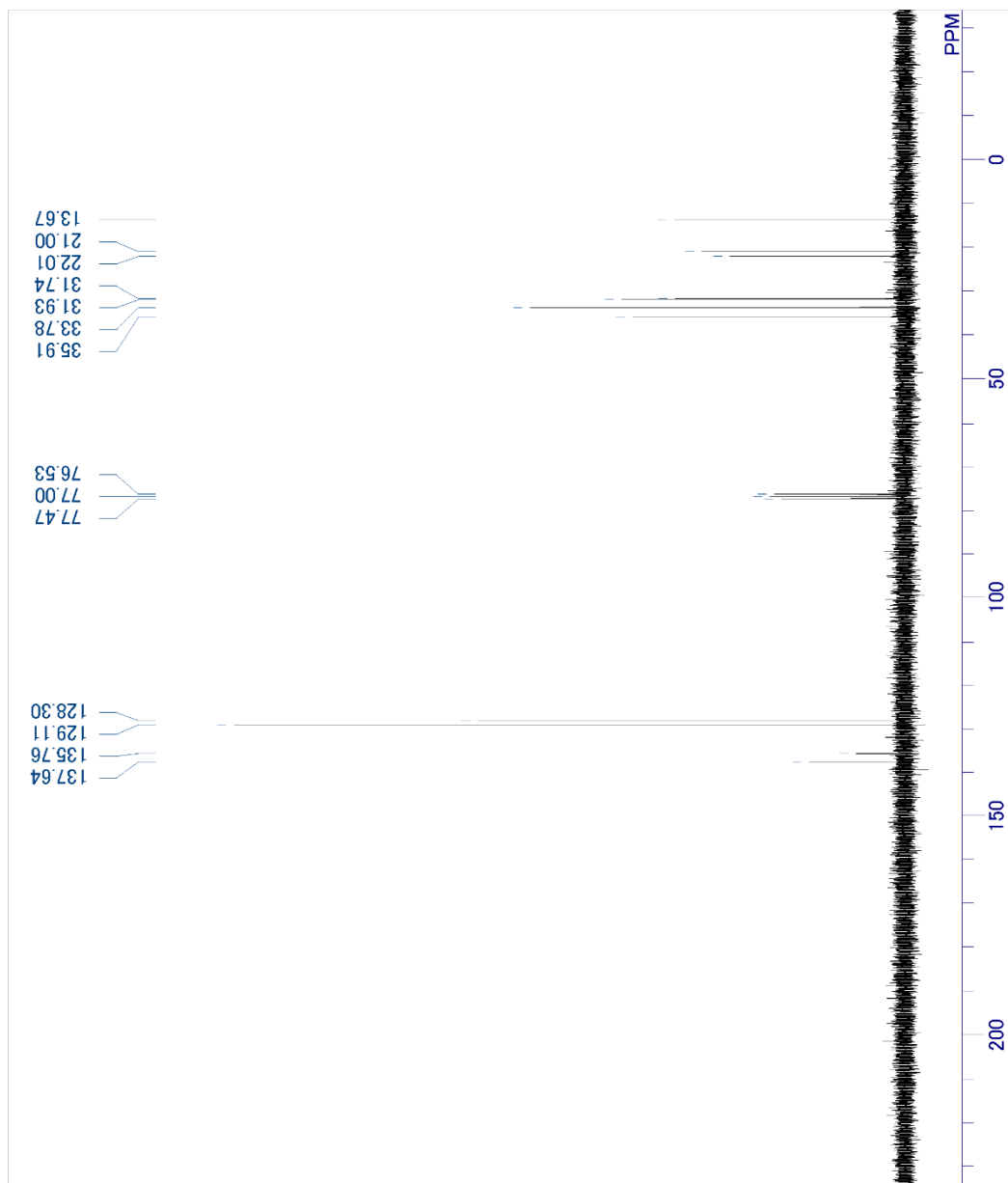
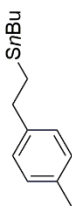


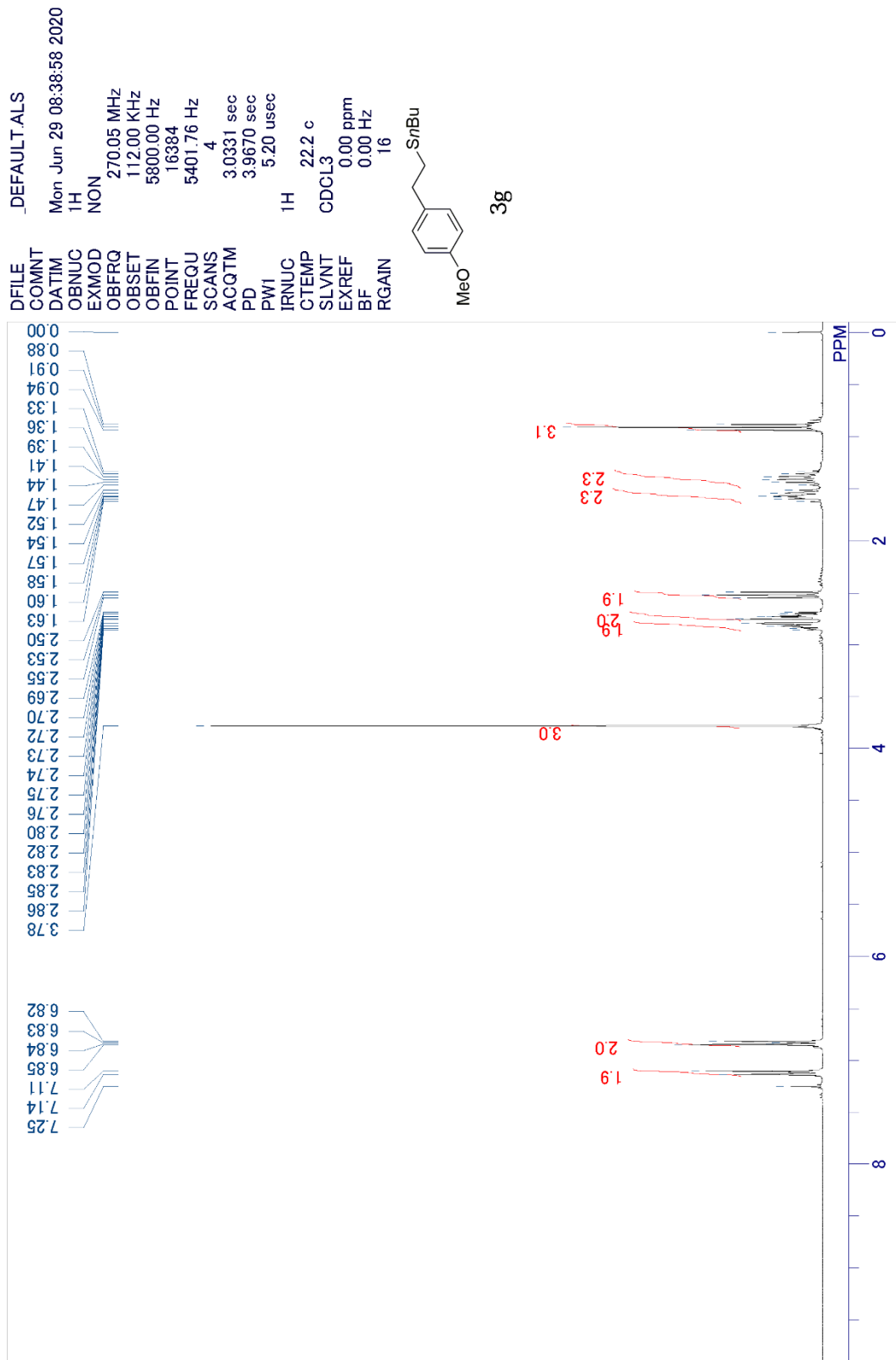
_DEFAULT.ALS
 COMNT Wed Jul 01 09:47:56 2020
 DATIM 13C
 OBRUC BCM
 EXMOD 67.80 MHz
 OBFRQ 135.00 KHz
 OBSET 5200.00 Hz
 OBFIN 32768
 POINT 18306.64 Hz
 FREQU 121
 SCANS 17900 sec
 ACQTM 1.2100 sec
 PD 4.80 usec
 PW1 1H
 IRNUC 24.3 c
 CTEMP CDC13
 SLVNT 77.00 ppm
 EXREF 0.00 Hz
 BF 27
 RGAIN



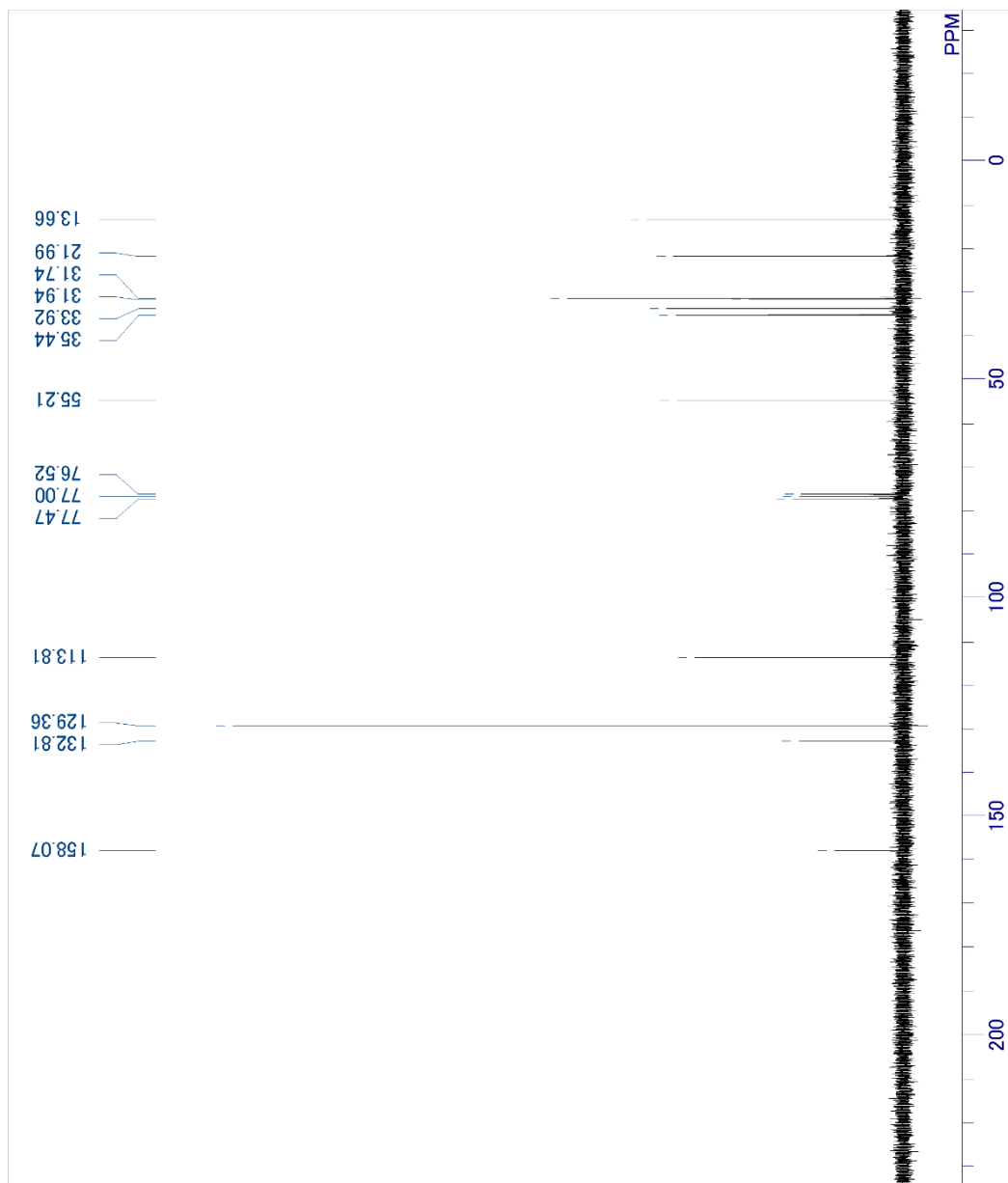
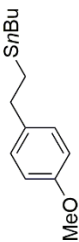


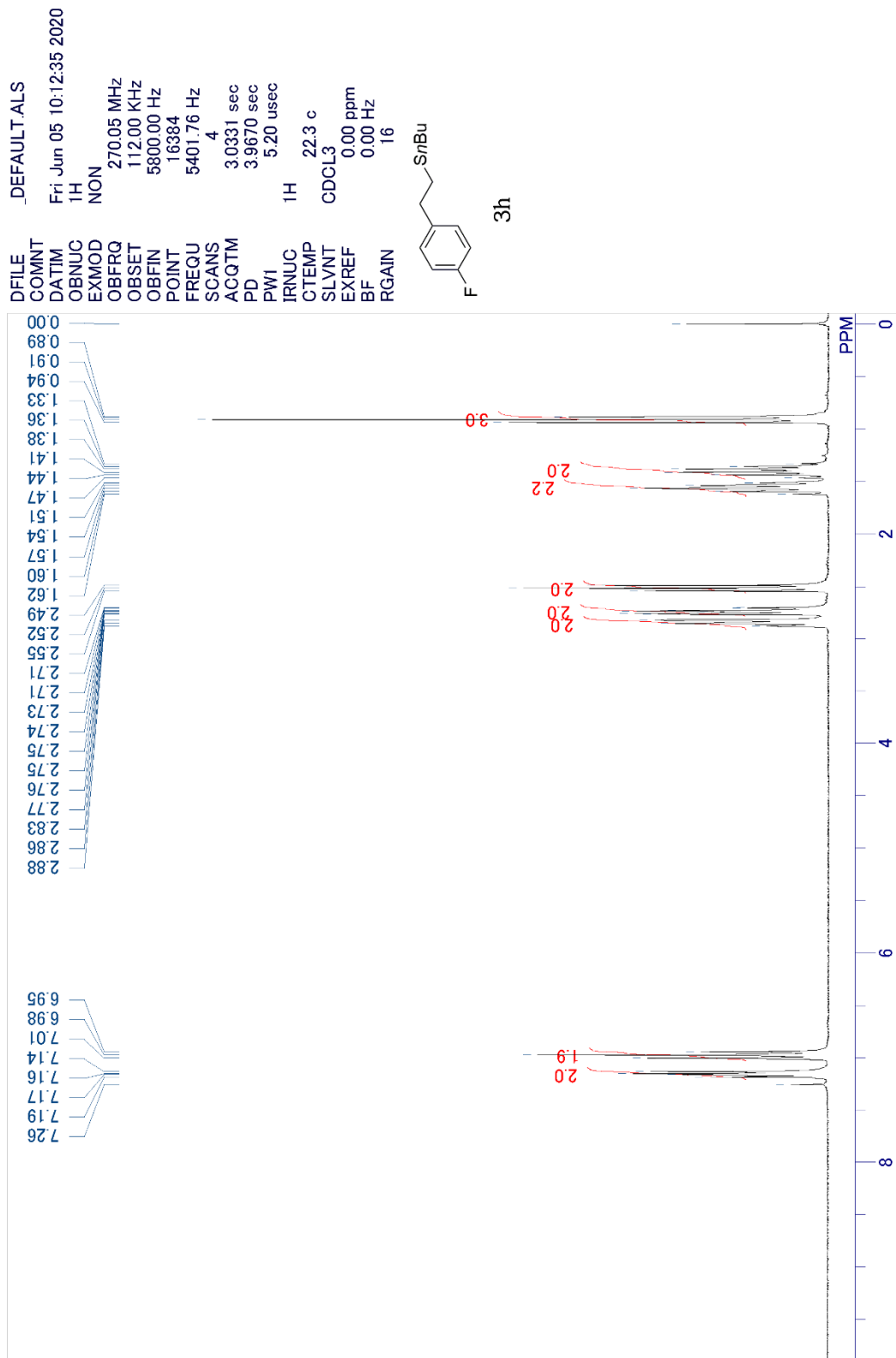
DFILE _DEFAULT.ALS
COMNT Fri Jun 05 09:01:31 2020
DATIM 13C
EXMOD BCM
OBNUC 67.80 MHz
OBFRQ 135.00 KHz
OBSET 5200.00 Hz
OBFIN 32768
POINT 18306.64 Hz
FREQU 101
SCANS 1.7900 sec
ACQTM 1.2100 sec
PD 4.80 usec
PWI 1H
IRNUC 24.8 c
CTEMP CDC13
SLVNT 77.00 ppm
EXREF 0.00 Hz
BF 27
RGAIN



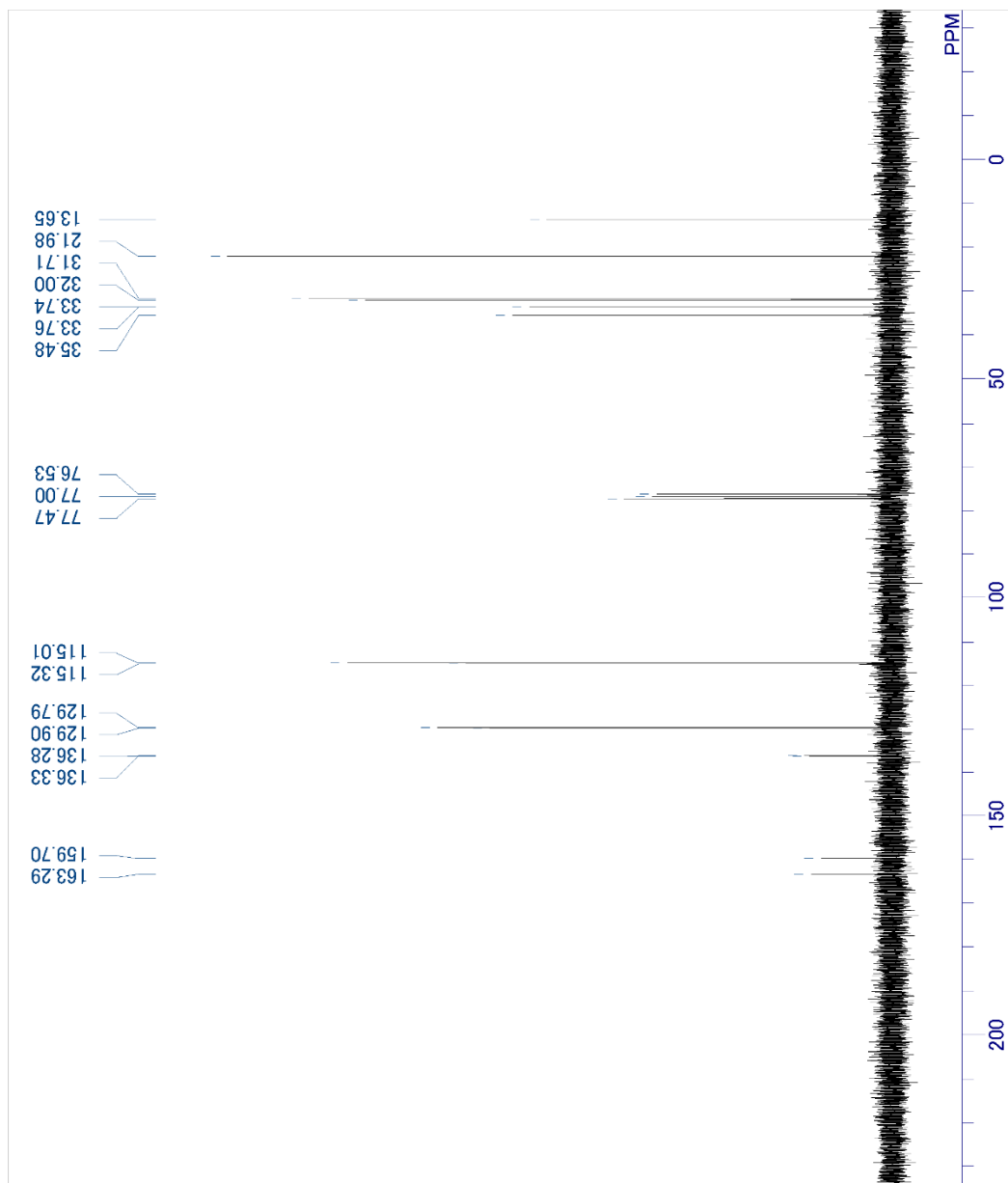
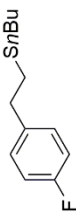


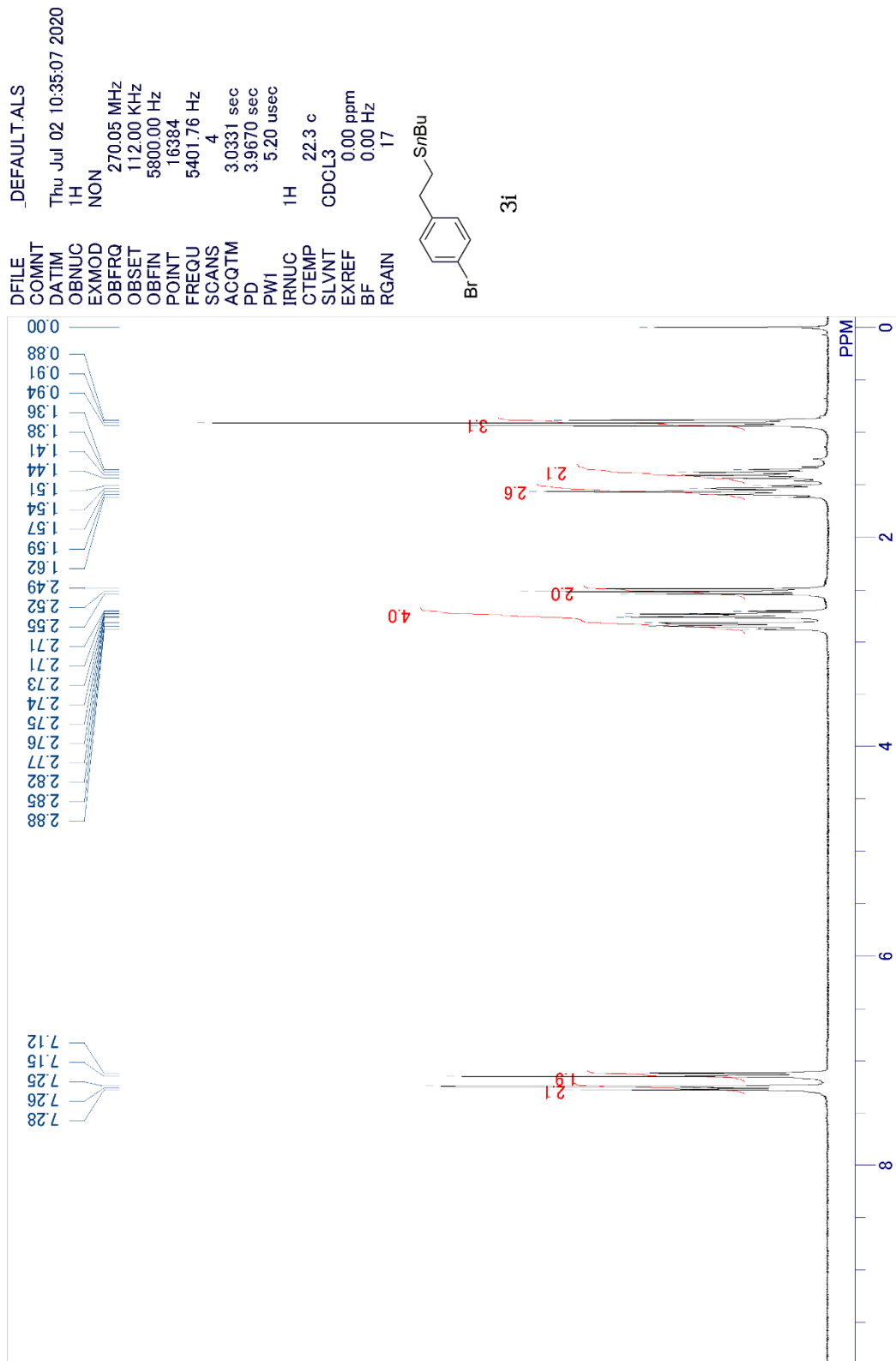
DFILE _DEFAULT.ALS
COMNT Mon Jun 29 08:47:39 2020
DATIM 13C
OBNUC BCM
EXMOD 67.80 MHz
OBFRQ 135.00 KHz
OBSET 5200.00 Hz
OBFIN 32768
POINT 18306.64 Hz
FREQU 101
SCANS 1.7900 sec
ACQTM 1.2100 sec
PD 4.80 usec
PWI 1H
IRNUC 24.4 c
CTEMP CDC13
SLVNT 77.00 ppm
EXREF 0.00 Hz
BF 27
RGAIN



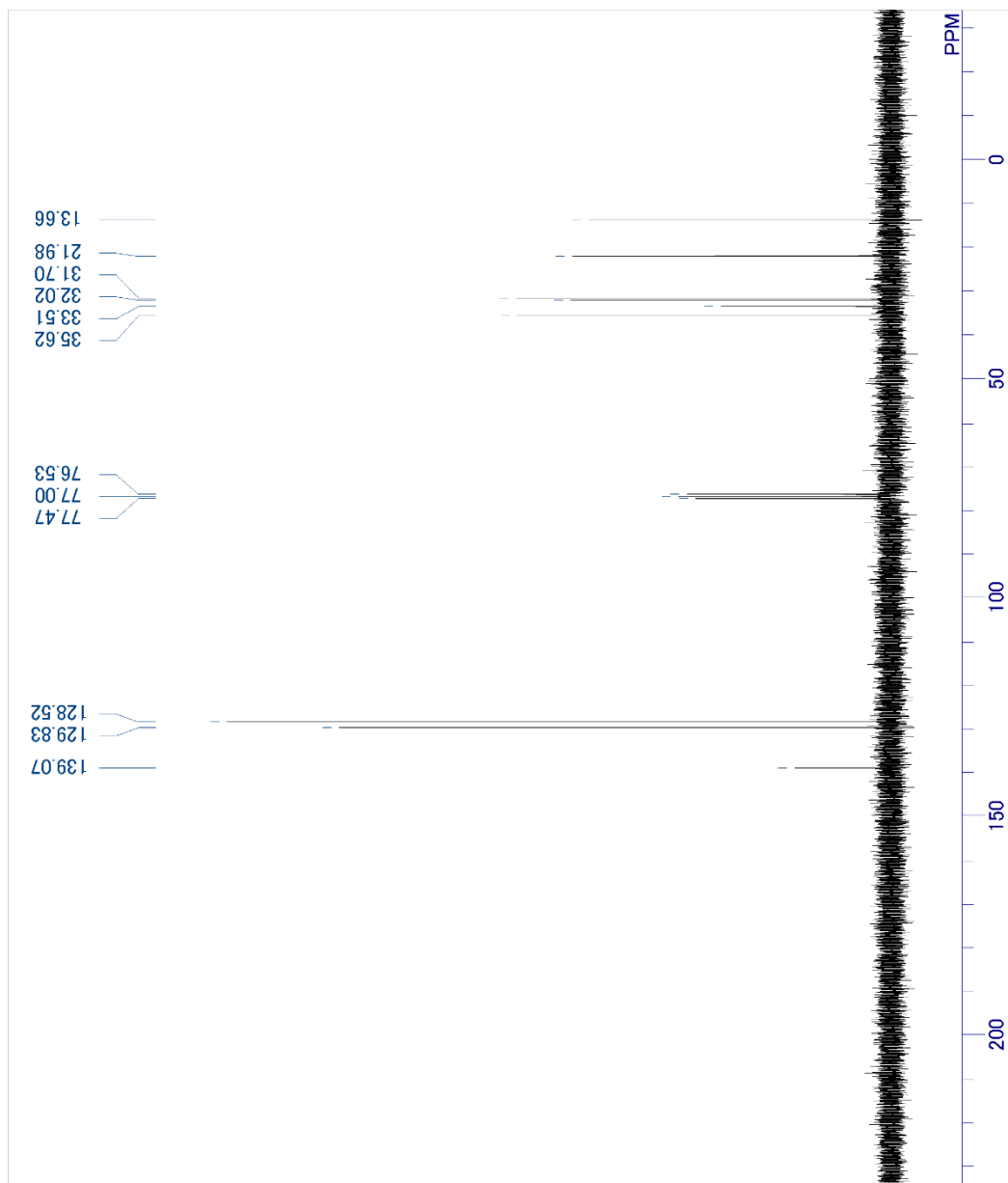
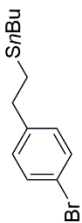


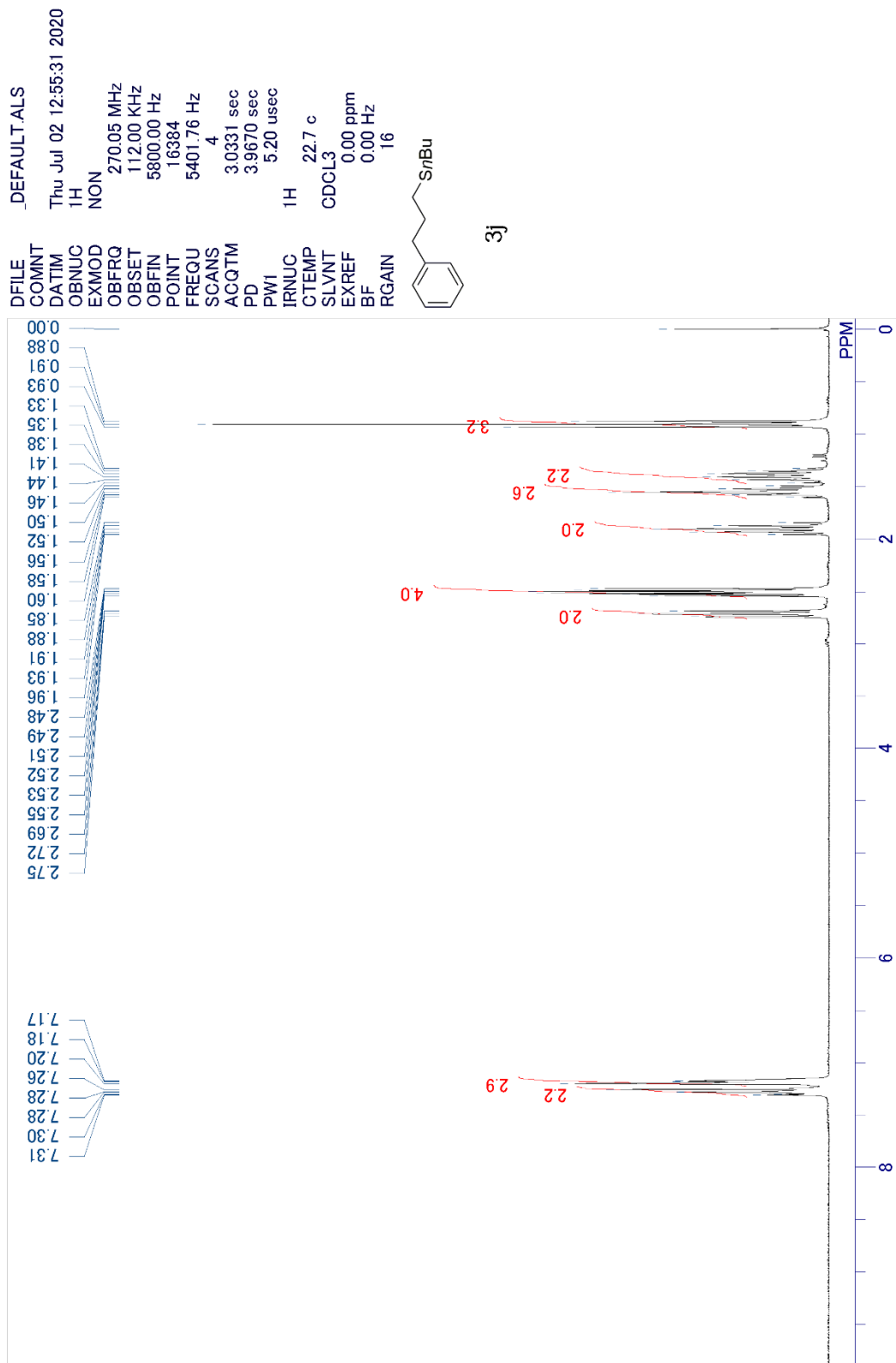
DFILE _DEFAULT.ALS
COMNT
DATIM Fri Jun 05 10:25:25 2020
OBRNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18306.64 Hz
SCANS 201
ACQTM 1.7900 sec
PD 1.2100 sec
PWI 4.80 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 27



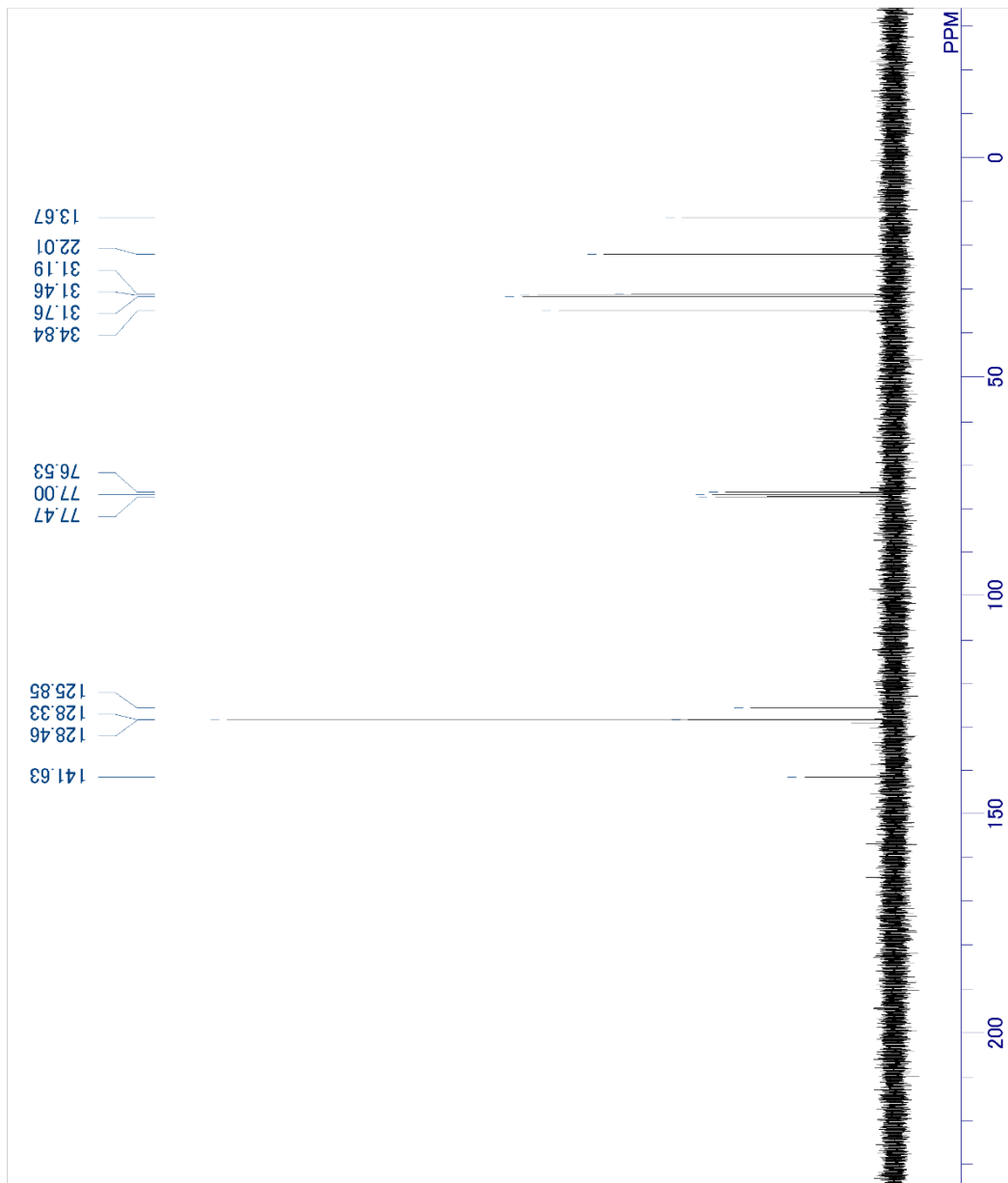


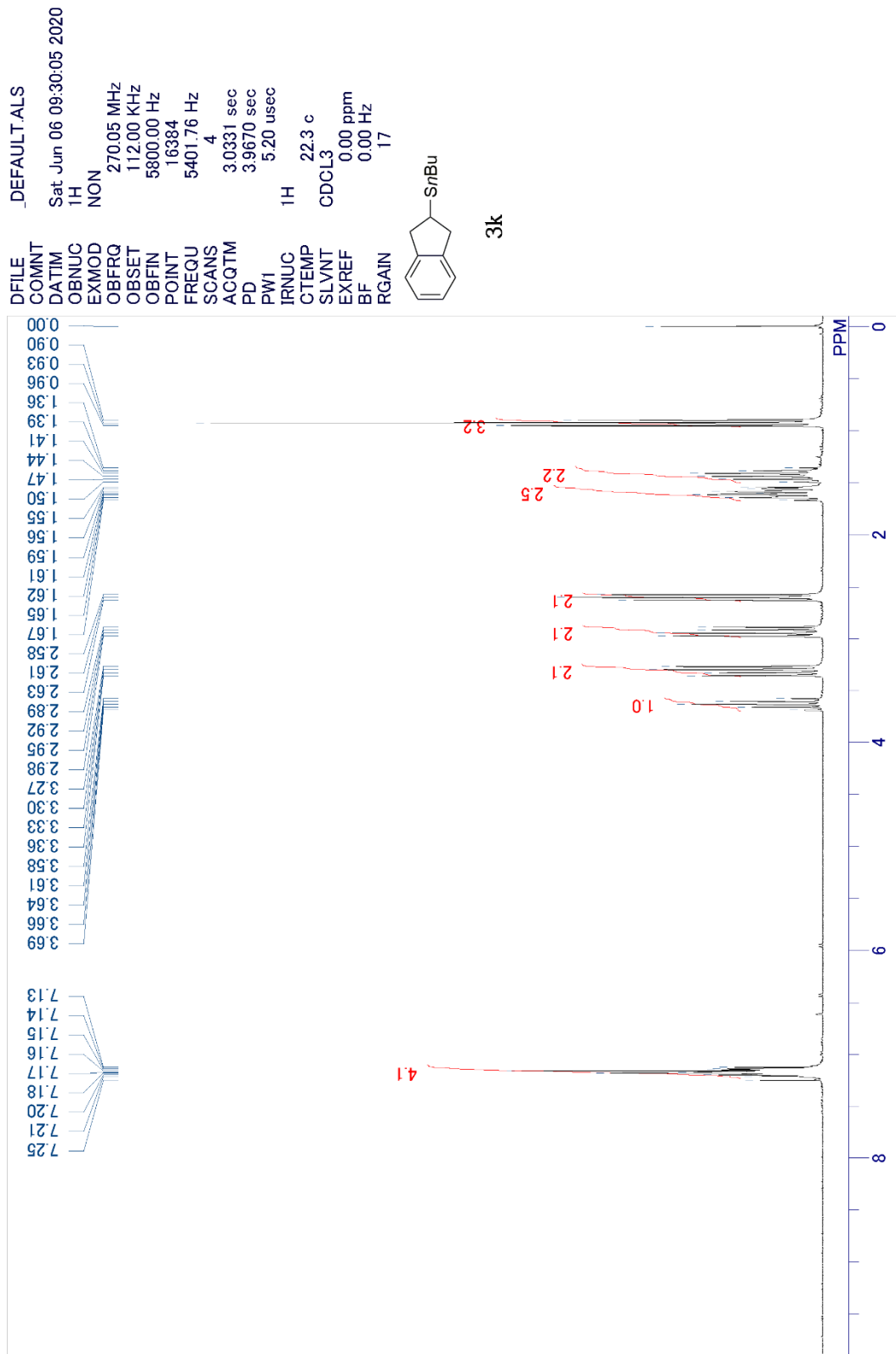
DFILE _DEFAULT.ALS
COMNT Thu Jul 02 10:49:20 2020
DATIM 13C
EXMOD BCM
OBFREQ 67.80 MHz
OBSETE 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18306.64 Hz
SCANS 241
ACQTM 1.7900 sec
PD 1.2100 sec
PWI 4.80 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 27



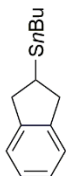


_DEFAULT.ALS
 COMINT Thu Jul 02 13:04:08 2020
 DATIM 13C
 OBNUC BCM
 EXMOD 67.80 MHz
 OBFRQ 135.00 KHz
 OBSET 5200.00 Hz
 OBFIN 32768
 POINT 18306.64 Hz
 FREQU 121
 SCANS 17900 sec
 ACQTM 1.2100 sec
 PD 4.80 usec
 PW1 1H
 IRNUC 24.8 c
 CTEMP CDC13
 SLVNT 77.00 ppm
 EXREF 0.00 Hz
 BF 27
 RGAIN





DFILE _DEFAULT.ALS
COMINT Sat Jun 06 09:40:39 2020
DATIM 13C
OBNUC BCM
EXMOD 67.80 MHz
OBFRQ 135.00 KHz
OBSET 5200.00 Hz
OBFIN 32768
POINT 18306.64 Hz
FREQU 162
SCANS 17900 sec
ACQTM 1.2100 sec
PD 4.80 usec
PWI 1H
IRNUC 24.7 c
CTEMP CDC13
SLVNT 77.00 ppm
EXREF 0.00 Hz
BF 27
RGAIN



3k

