

Supplementary Material

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

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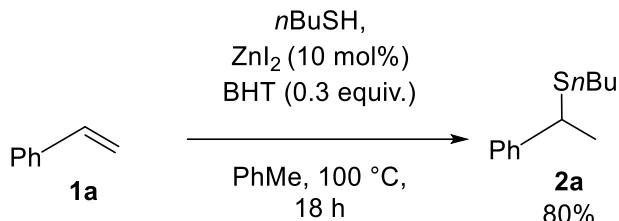
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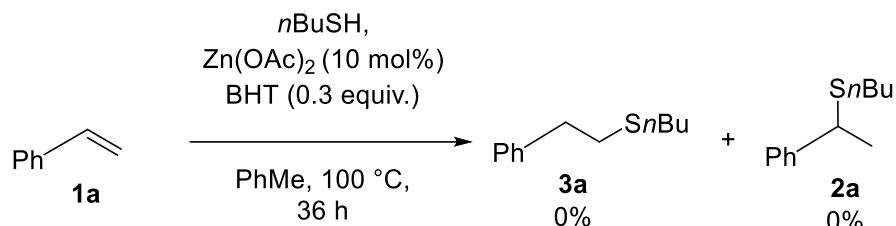
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Additional Experiments

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

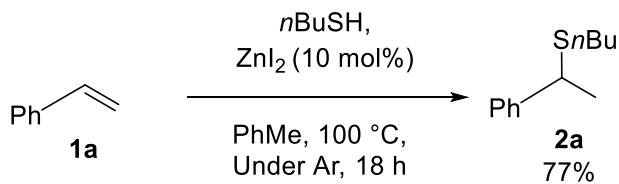


To a mixture of styrene **1a** (31.2 mg, 0.3 mmol), 1-butanethiol (29.8 mg, 0.33 mmol), and BHT (66.1 mg, 0.3 mmol) in CH_2Cl_2 (0.3 mL), ZnI_2 (9.6 mg, 0.03 mmol) was added, and the mixture was stirred at 100°C for 18 h in air. After the residue was dissolved in Et_2O , the solution was washed with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

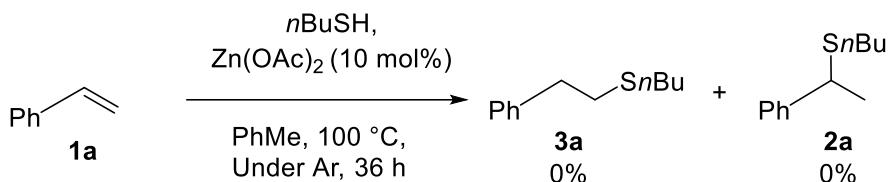


To a mixture of styrene **1a** (31.2 mg, 0.3 mmol), 1-butanethiol (29.8 mg, 0.33 mmol), and BHT (66.1 mg, 0.3 mmol) in CH_2Cl_2 (0.3 mL), Zn(OAc)_2 (5.5 mg, 0.03 mmol) was added, and the mixture was stirred at 100°C for 18 h in air. After the residue was dissolved in Et_2O , the solution was washed with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

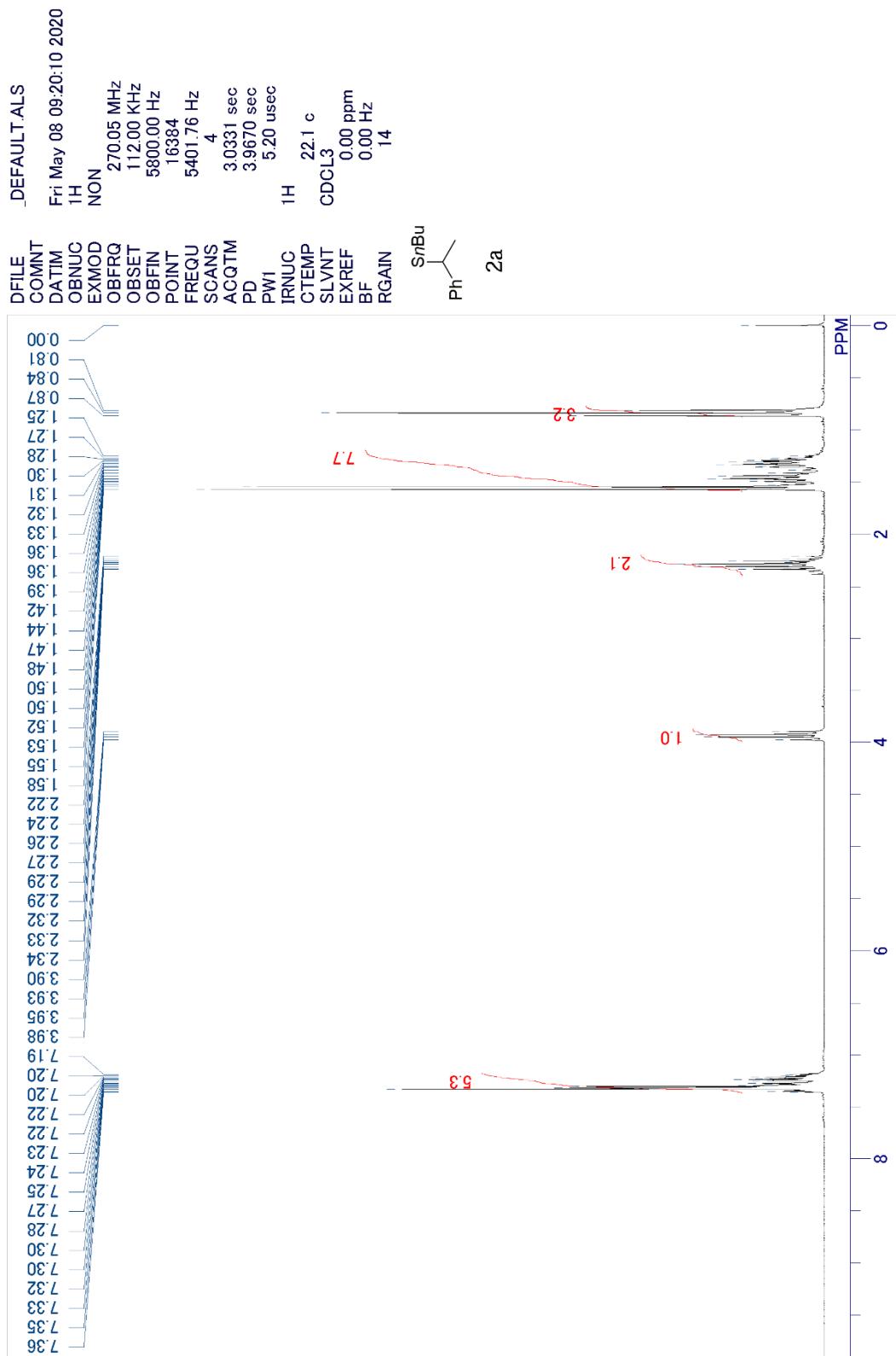
Zn-catalyzed hydrothiolation under Ar (Scheme 3)

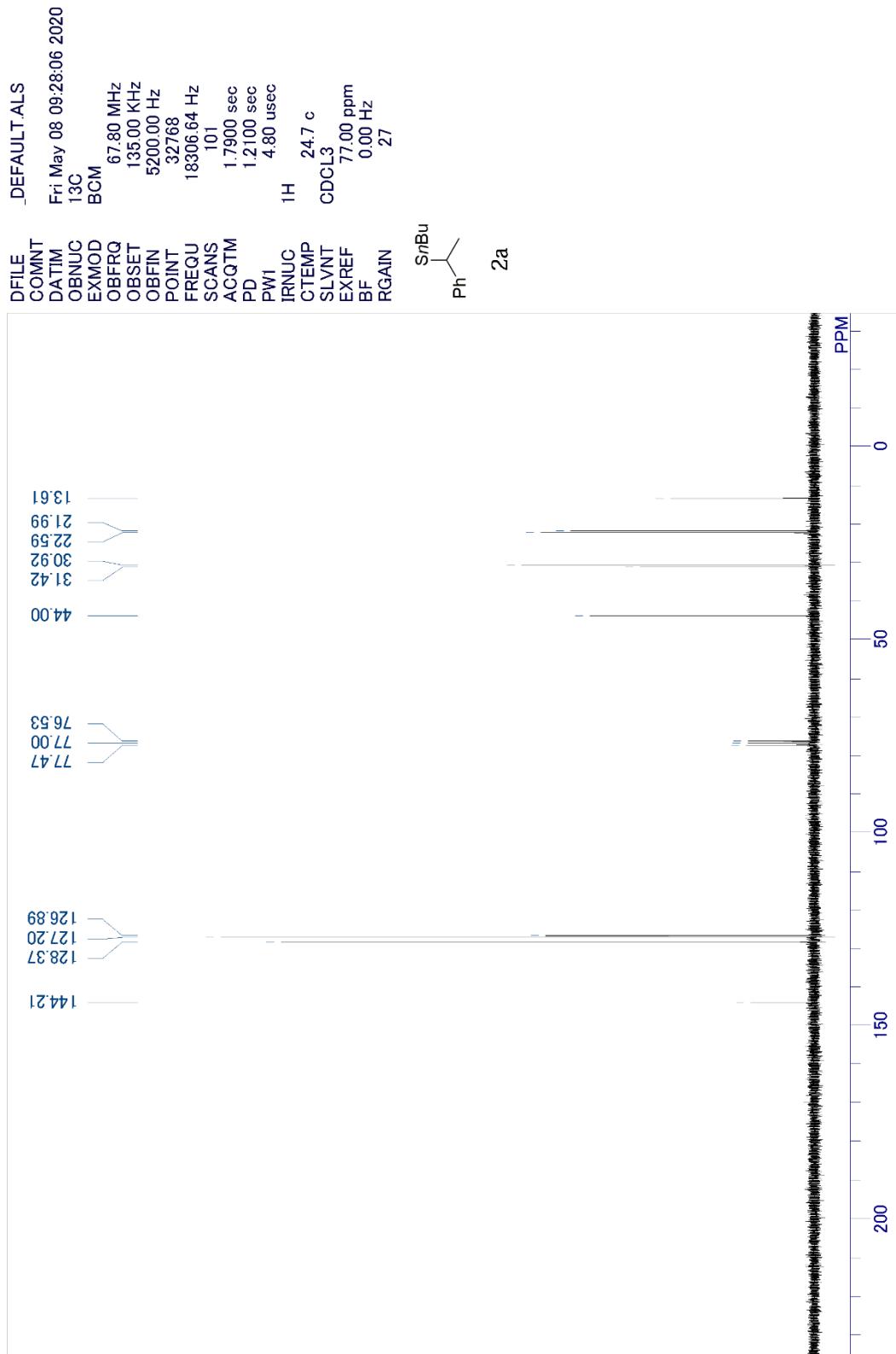


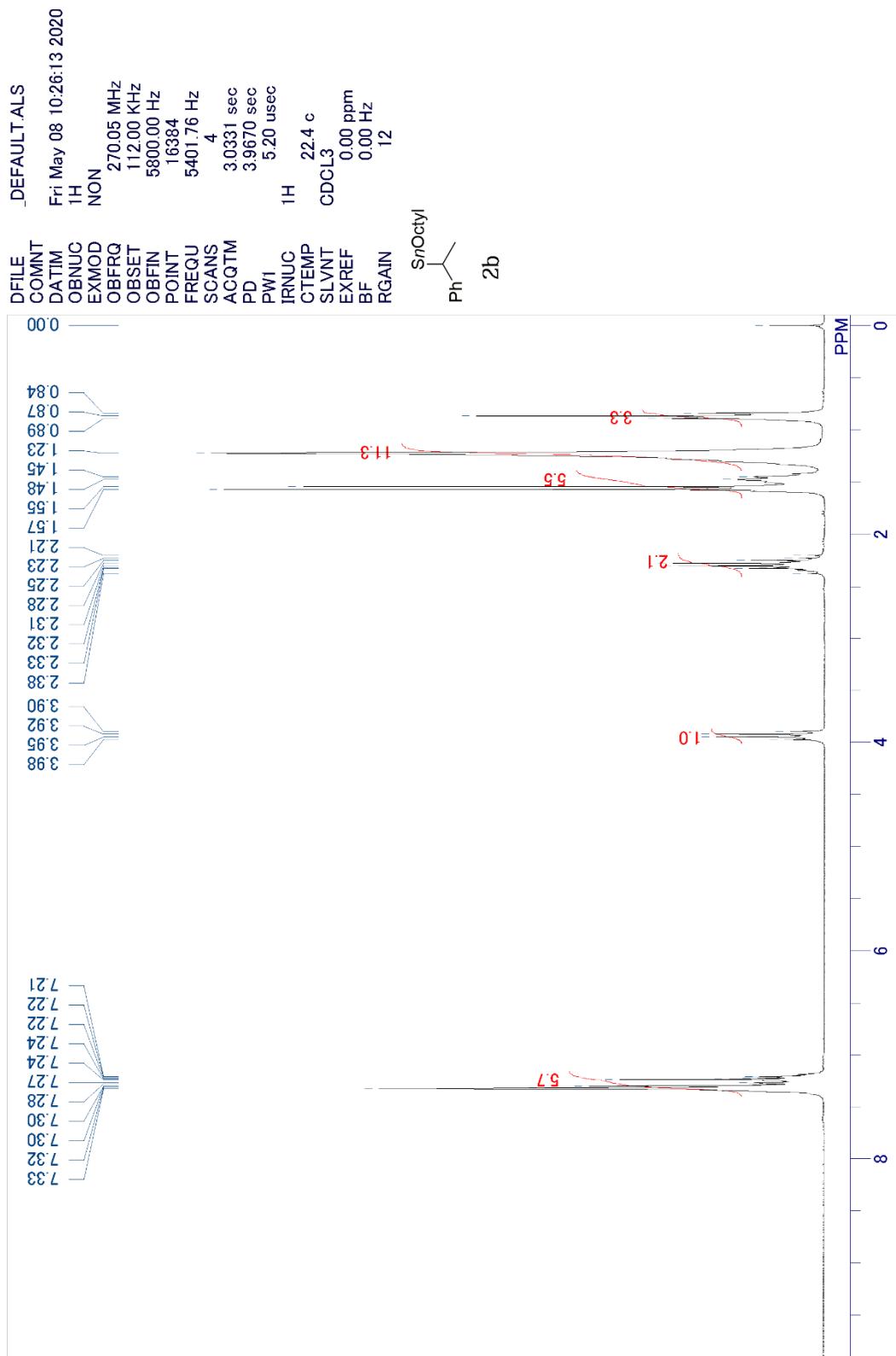
To a mixture of styrene **1a** (31.2 mg, 0.3 mmol) and 1-butanethiol (29.8 mg, 0.33 mmol) in CH_2Cl_2 (0.3 mL), ZnI_2 (9.6 mg, 0.03 mmol) was added, and the mixture was stirred at 100°C for 18 h under argon atmosphere. After the residue was dissolved in Et_2O , the solution was washed with H_2O and saturated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

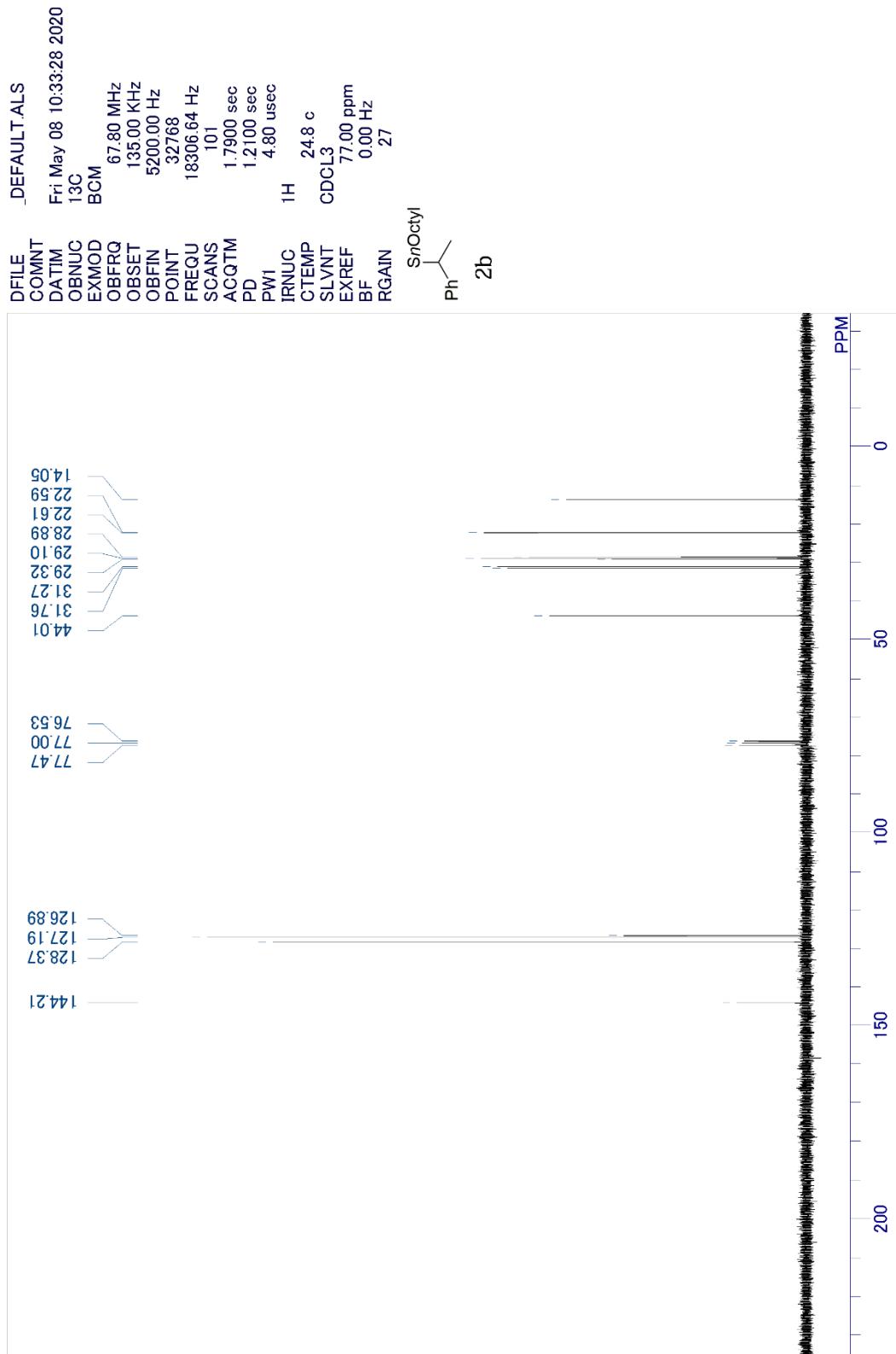


To a mixture of styrene **1a** (31.2 mg, 0.3 mmol) and 1-butanethiol (29.8 mg, 0.33 mmol) in CH₂Cl₂ (0.3 mL), Zn(OAc)₂ (5.5 mg, 0.03 mmol) was added, and the mixture was stirred under argon atmosphere at 100 °C for 18 h. The reaction did not proceed. The production of **3a** and **2a** was not observed.



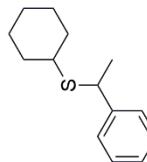




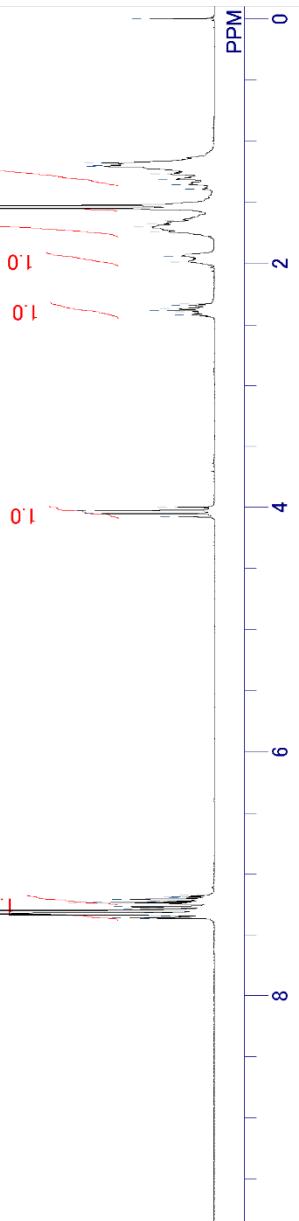


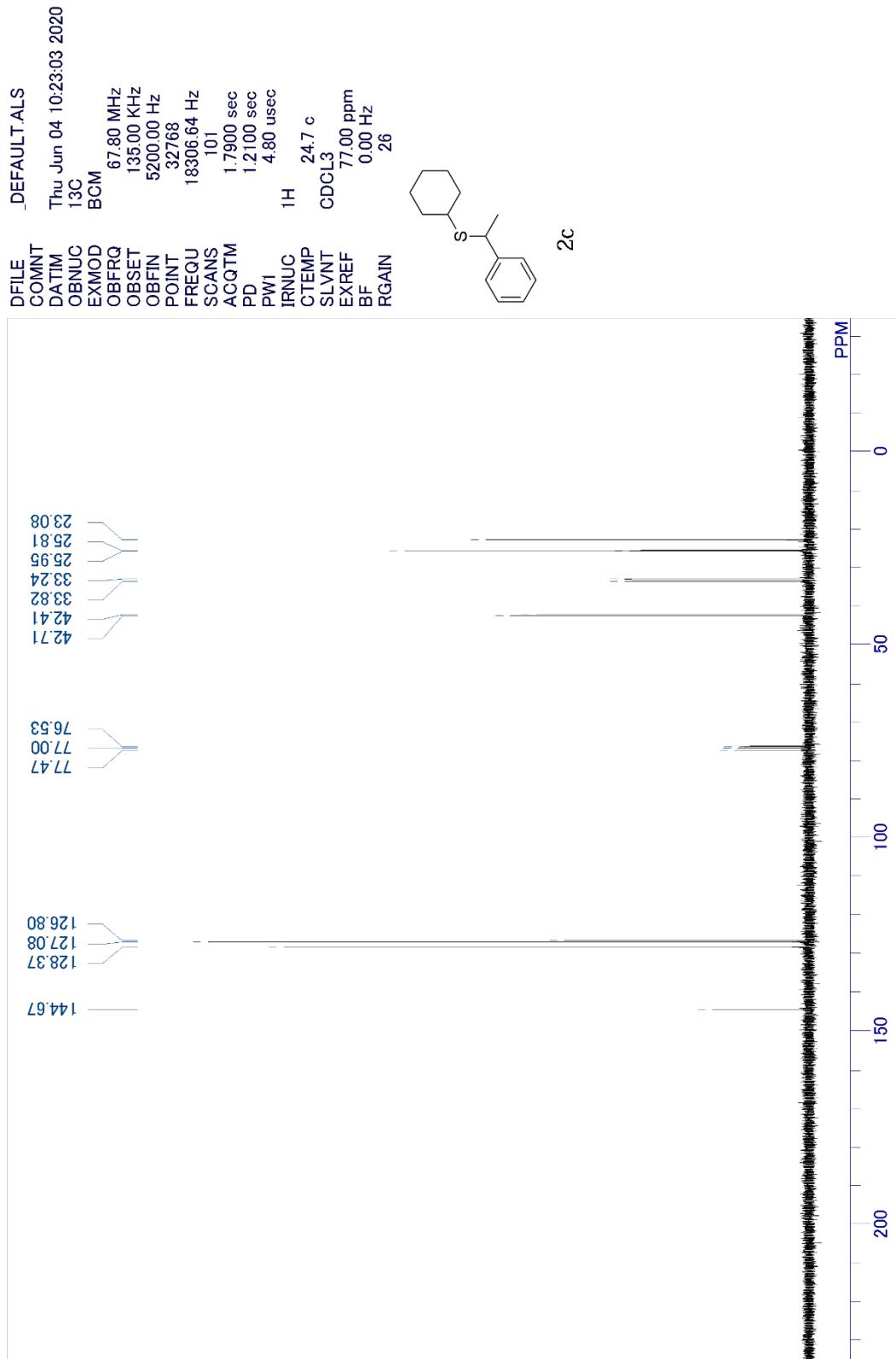
Detailed NMR Peak Data:

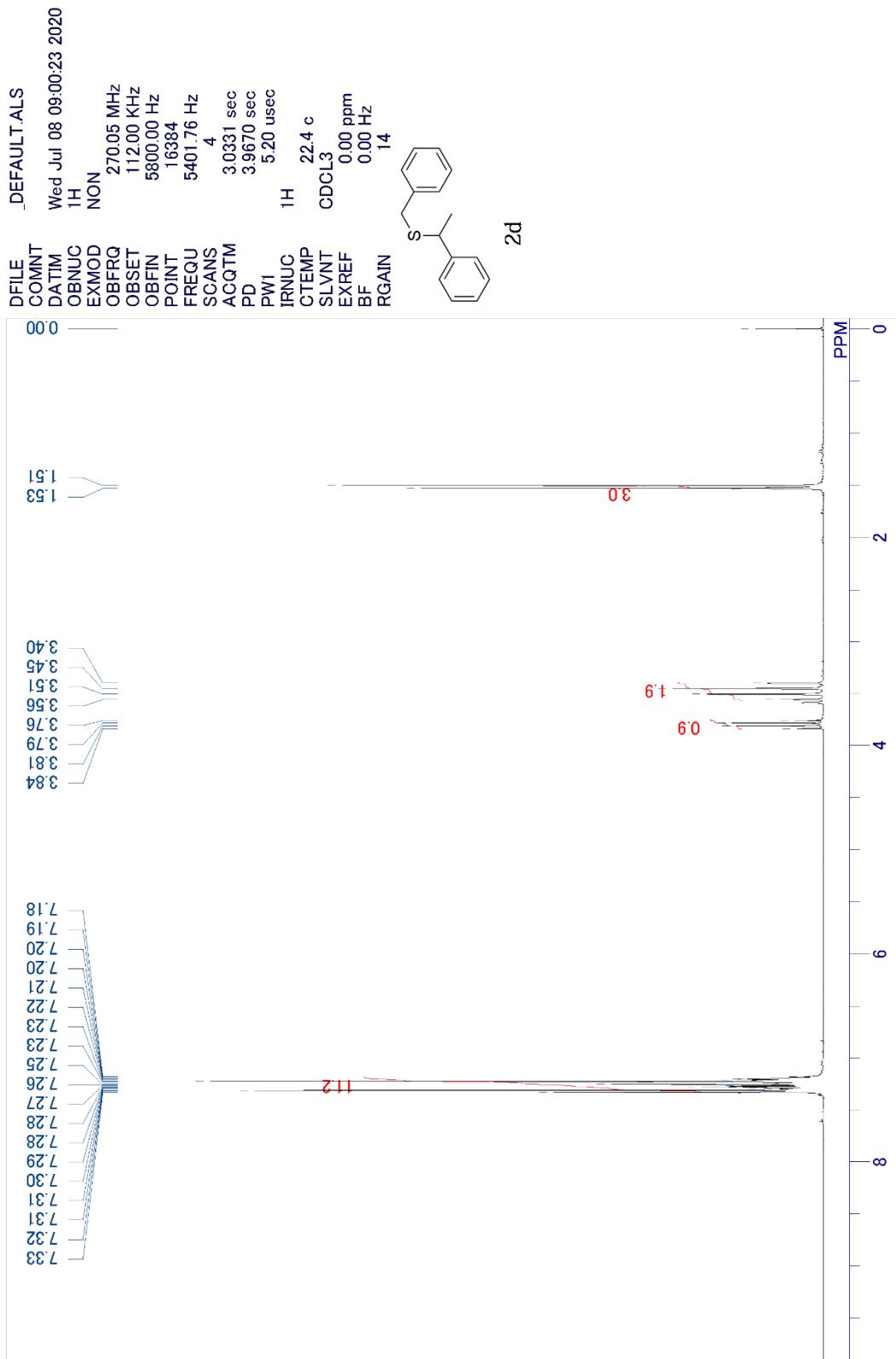
Chemical Shift (ppm)	Integration
1.18	0.00
1.19	0.00
1.20	0.00
1.21	0.00
1.27	0.00
1.32	0.00
1.36	0.00
1.40	0.00
1.43	0.00
1.53	0.00
1.56	0.00
1.65	0.00
1.68	0.00
1.70	0.00
1.75	0.00
1.94	0.00
1.99	0.00
2.34	0.00
2.35	0.00
2.39	0.00
2.40	0.00
2.42	0.00
4.00	0.00
4.03	0.00
4.05	0.00
4.08	0.00
7.18	0.00
7.19	0.00
7.20	0.00
7.21	0.00
7.22	0.00
7.24	0.00
7.27	0.00
7.28	0.00
7.29	0.00
7.30	0.00
7.32	0.00
7.33	0.00
7.34	0.00
7.35	0.00
7.36	0.00
7.37	0.00

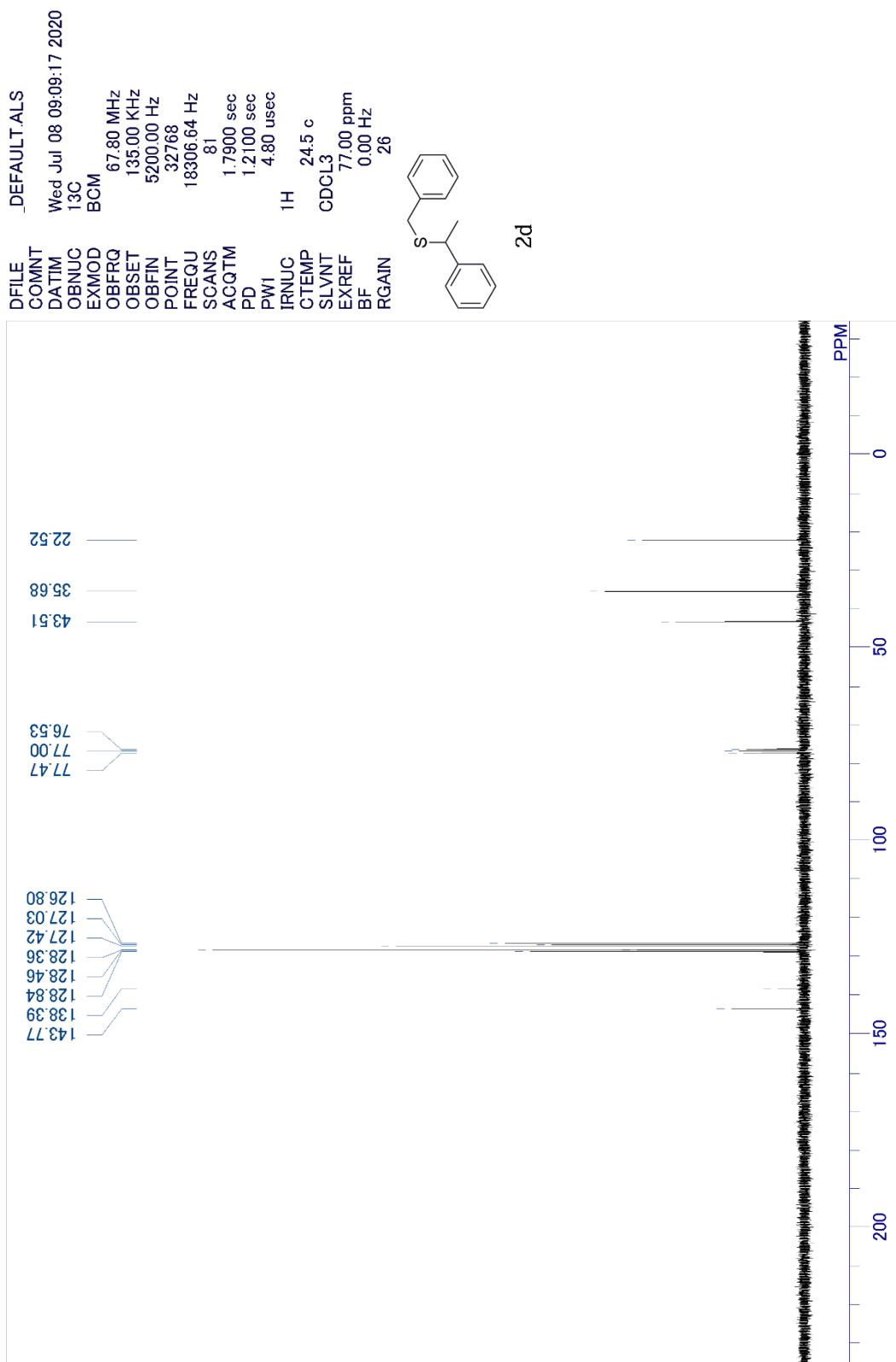


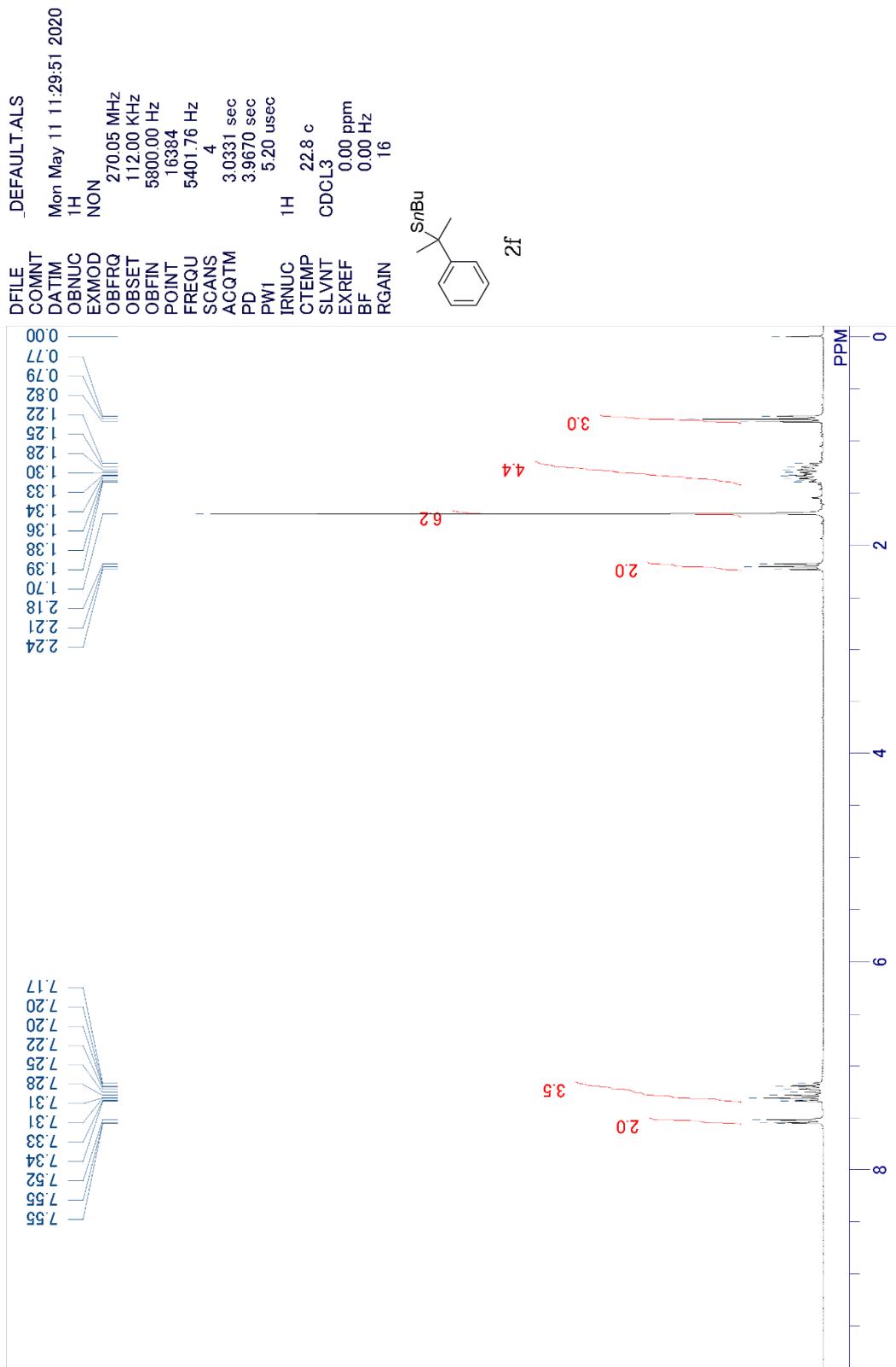
2c

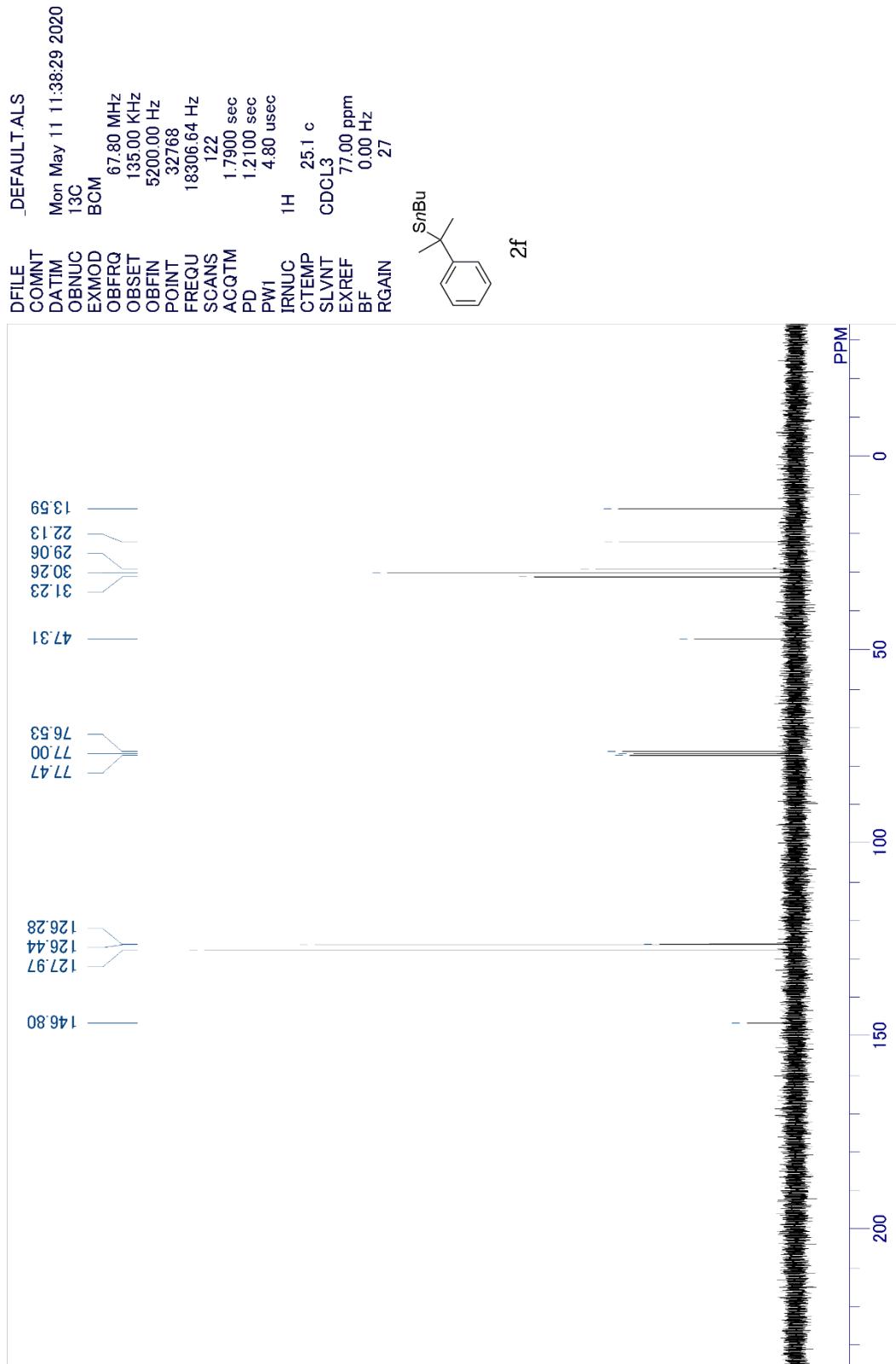


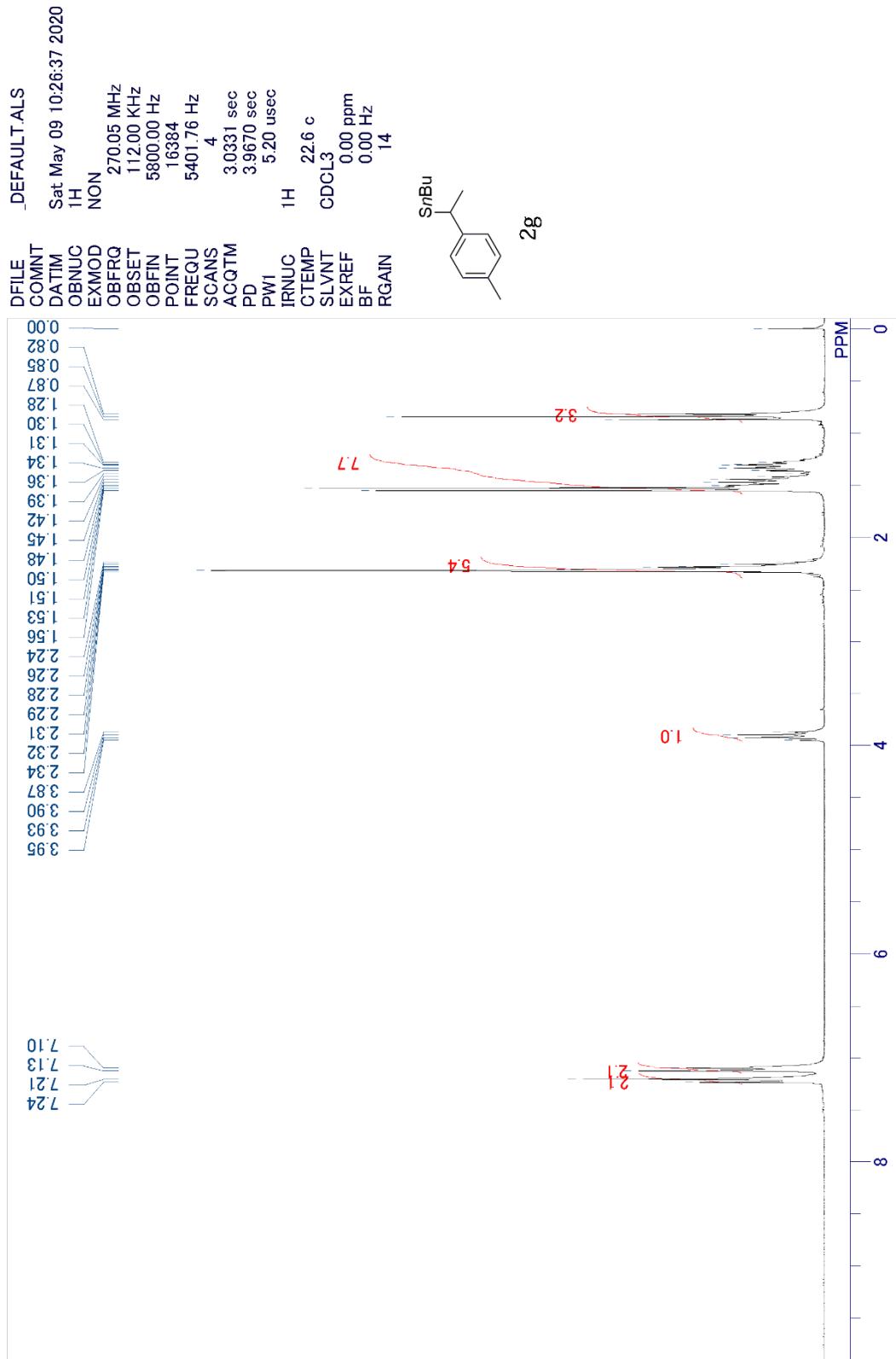


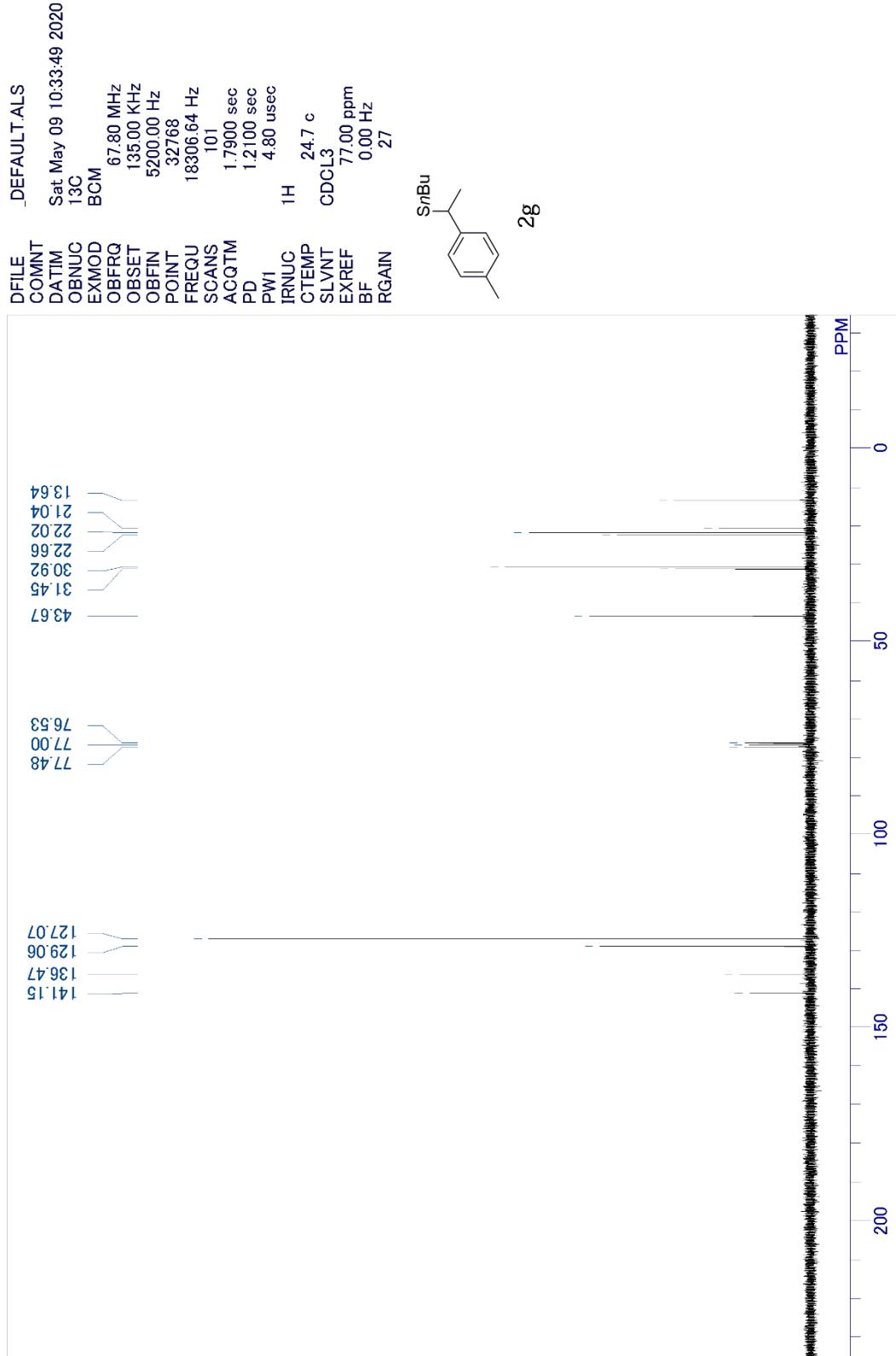


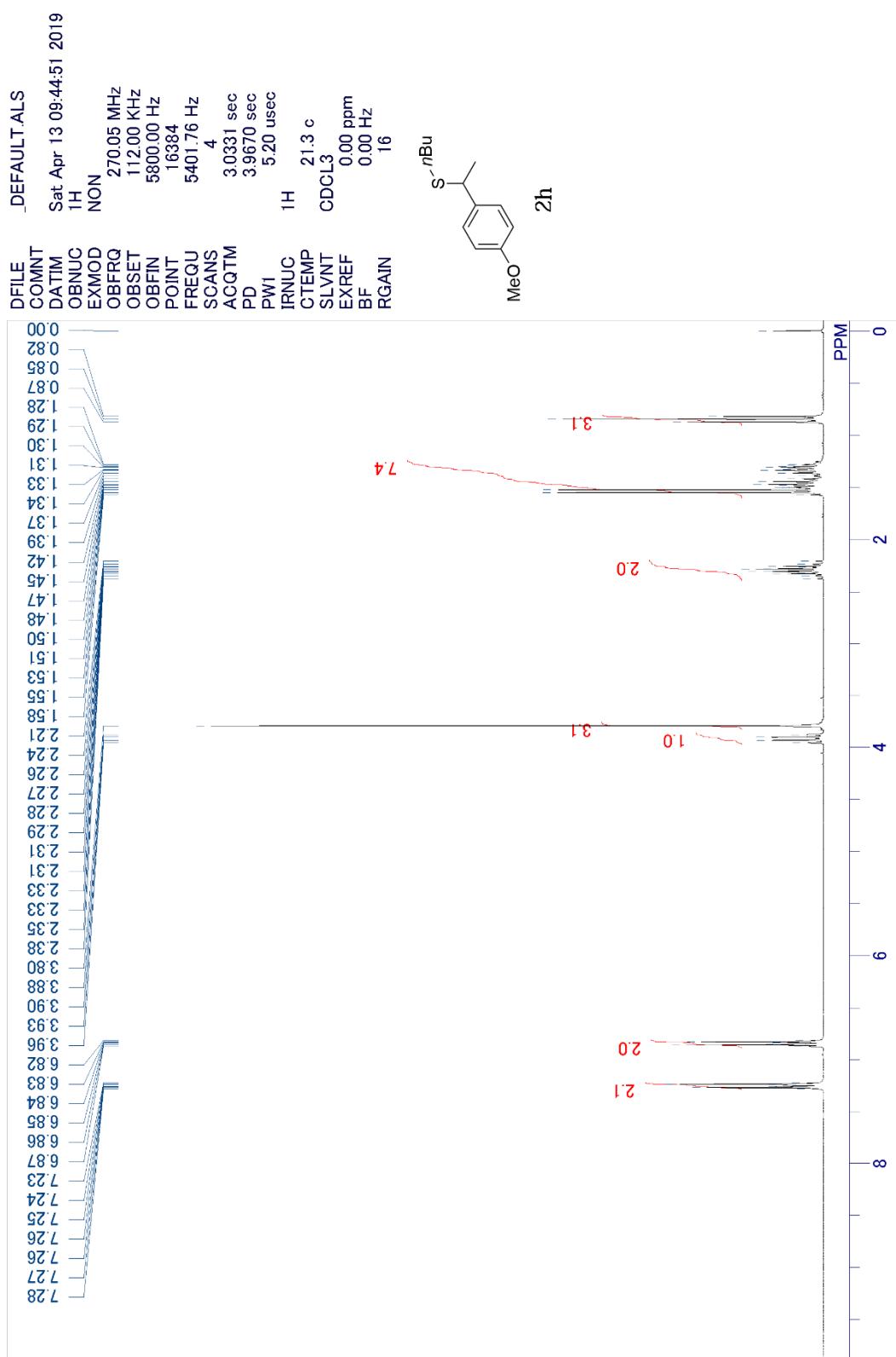


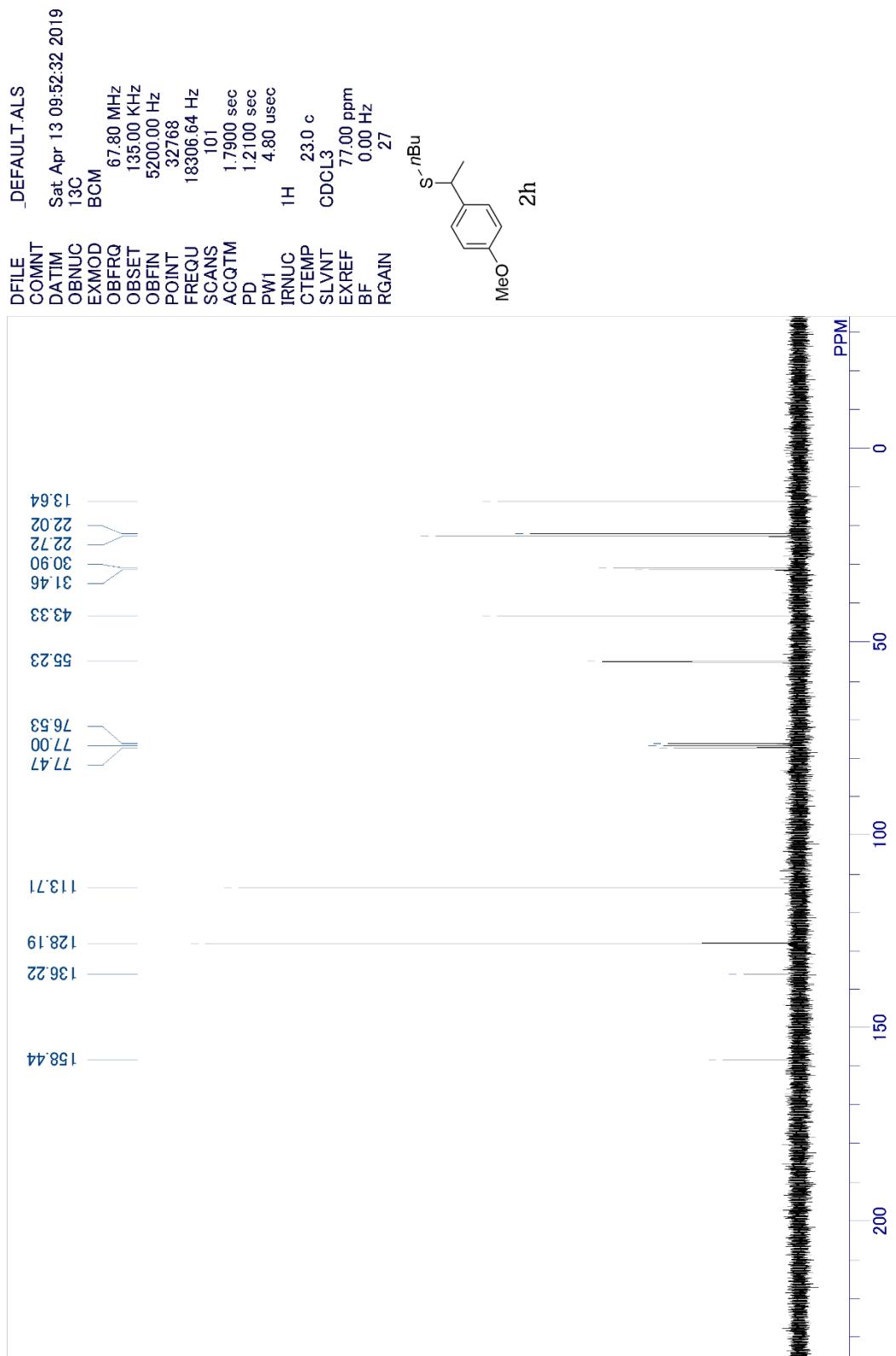


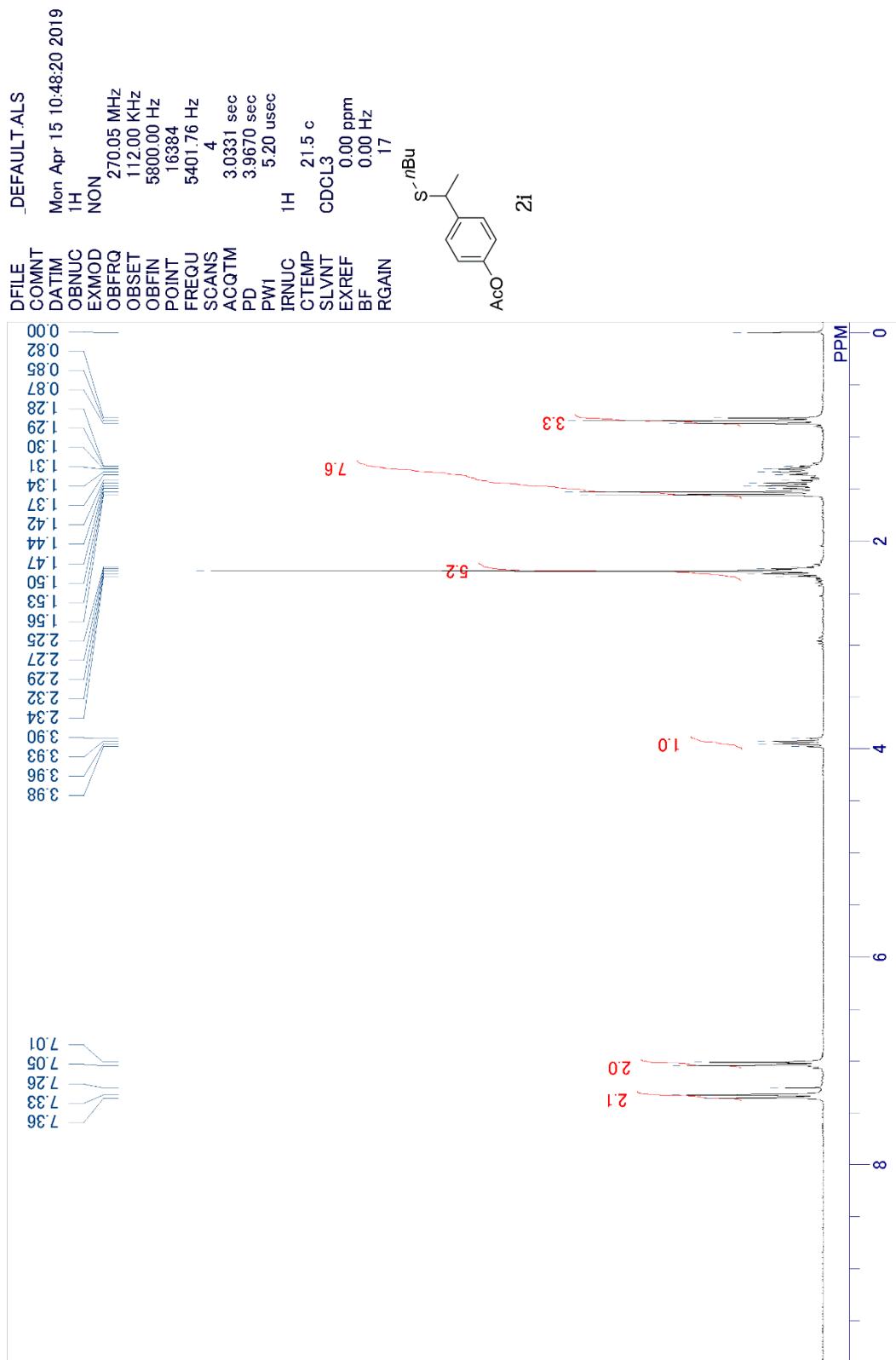












_DETAILS	
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OBNUC	BCM
EXMOD	67.80 MHz
OBJFRQ	13500 kHz
OBSSET	5200.00 Hz
OBFIN	32768
POINT	18306.64 Hz
FREQU	161
SCAN	1.7900 sec
ACQTM	1.2100 sec
PPD	4.80 usec
PPW1	1H
IRNUC	24.0 c
CTTEMP	CDCL3
SLVNT	77.00 ppm
EXREF	0.00 Hz
BF	RGGAIN

