

Supporting Information

Catalytic Activation of *cis*-Vicinal Diols by Boronic Acids: Site-Selective Acylation of Carbohydrates

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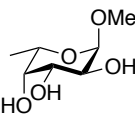
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1. General information

NMR spectra were recorded on Agilent Technologies 400-MR DD2 (400 MHz for ^1H , 100 MHz for ^{13}C), 400-MR (400 MHz for ^1H , 100 MHz for ^{13}C), NMR DD2 400NB (128 MHz for ^{11}B) spectrometers. ^1H -NMR data are reported as follows; chemical shift in parts per million (ppm) downfield or upfield from CDCl_3 (δ 7.26), CD_3OD (δ 3.31) integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sep = septet, dd = double doublet, ddd = double double doublet, dddd = double double double doublet, ddt = double double triplet, dt = double triplet, dq = double quartet, and m = multiplet), and coupling constants (Hz). ^{13}C -NMR chemical shifts are reported in ppm downfield or upfield from CDCl_3 (δ 77.0) or CD_3OD (δ 49.0). ^{11}B -NMR chemical shifts are reported in ppm downfield or upfield from $\text{PhB}(\text{OH})_2$ (δ 28.82). Mass spectra were measured with JEOL JMS-AX505HA, JMS-700 MStation, and JEOL JMS-T100LP spectrometers. Melting points (mp) were obtained on Stanford Research Systems *MPA100* melting point apparatus. Thin-layer chromatography (TLC) was carried out on Merck 60F-254 or Fuji NH KP20610 (NH) precoated silica gel plates and were visualized by fluorescence quenching under UV light. Column chromatography was performed using Silica Gel 60N (spherical, neutral, 63-210 μm) (Kanto Chemical Co., Inc.) and Silica Gel NH (Fuji Silysia Chemical LTD, HU50100, DM1020). Air- and/or moisture-sensitive reactions were carried out under argon or nitrogen atmosphere using oven-dried glassware. Boronic acid **1a**¹ and **1b**², borinic acid **SI-2**³ and **SI-3**³ were synthesized according to the literature.

2. Supplementary information

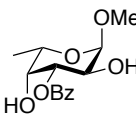
SI-Table 1. Initial solvent screening for site-selective benzylation of **2a**.



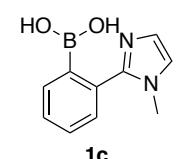
2a

1c (5.0 mol%)
BzCl (1.5 equiv)
*i*Pr₂NEt (1.5 equiv)

solvent (0.2 M)
rt, 4 h



3a

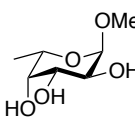


1c

entry	solvent	yield (%) ^a
1	CH ₂ Cl ₂	>99
2	DCE	91
3	CH ₃ CN	96
4	THF	89
5	1,4-dioxane	78
6	toluene	55
7	EtOAc	49
8	acetone	46
9	DMF	3

^aDetermined by ¹H-NMR of crude mixture.

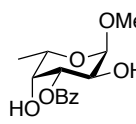
SI-Table 2. Optimization of base for site-selective benzylation of **2a**.



2a

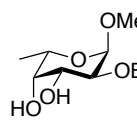
1c (5.0 mol%)
BzCl (1.5 equiv)
base (1.5 equiv)

CH₂Cl₂ (0.2 M)
rt, 4 h



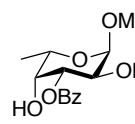
3a

+



4

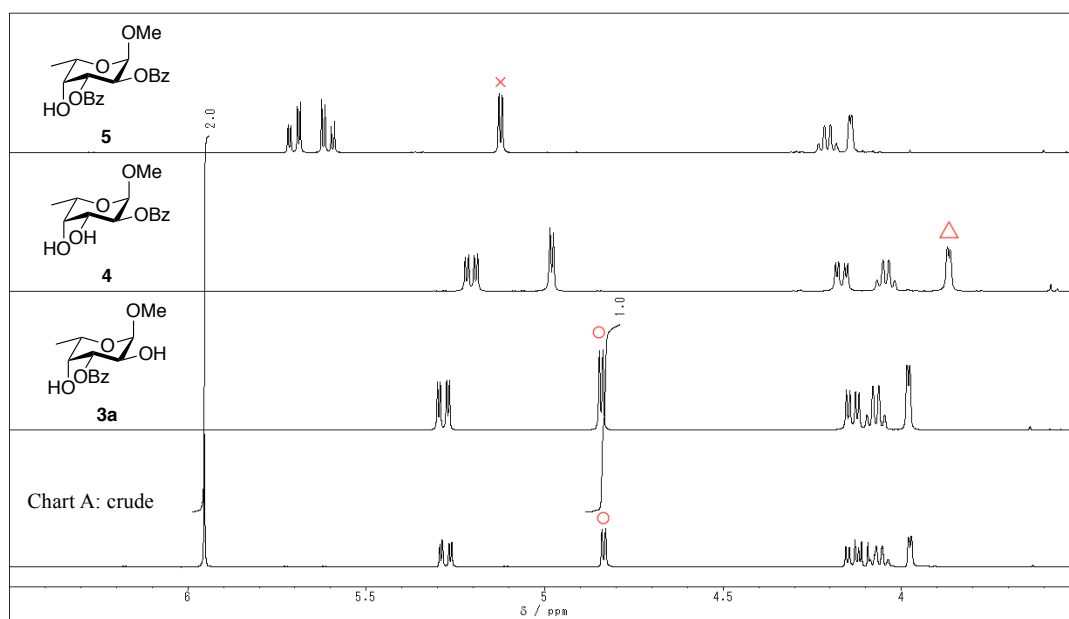
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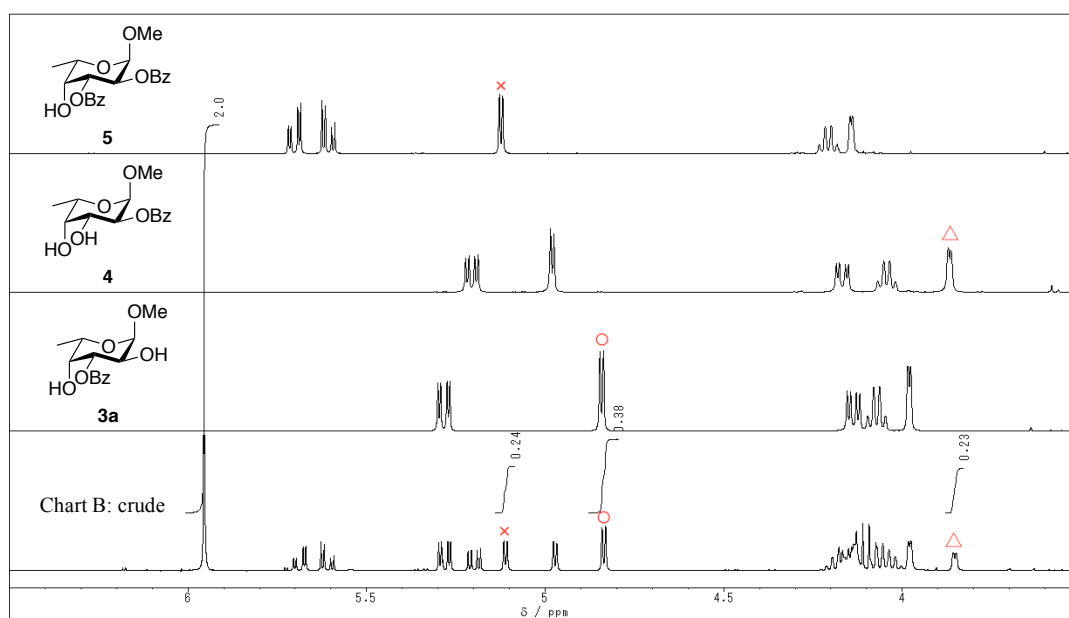
5

entry	base	yield (3a / 4 / 5) (%) ^a	total (%) ^a
1	<i>i</i> Pr ₂ NEt	>99 / – / –	>99
2	DABCO	44 / 9 / 7	60
3	NEt ₃	38 / 23 / 24	85
4	2,6-lutidine	94 / 1 / 2	97
5	2,4,6-collidine	94 / 2 / 2	98
6	pyridine	46 / 16 / 15	77
7	imidazole	15 / 12 / 24	51
8	1-methylimidazole	17 / 25 / 51	93
9	1,2-dimethylimidazole	16 / 41 / 24	81

^aDetermined by ¹H-NMR of crude mixture.

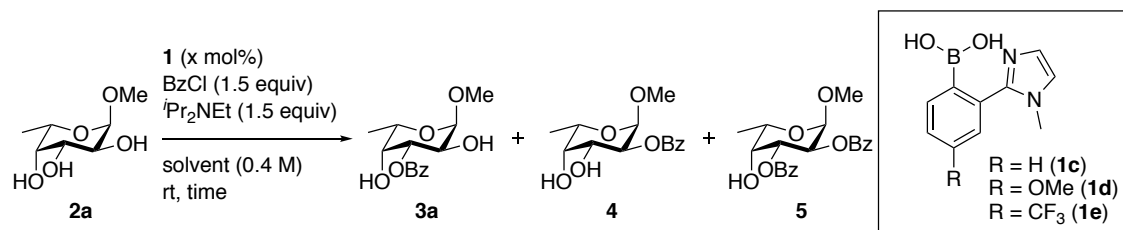


SI-Figure 1. Chart A: ^1H -NMR spectrum of crude reaction mixture for site-selective benzylation of **2a** by using *N,N*-diisopropylethylamine as base (SI-Table 2, entry 1).



SI-Figure 2. Chart B: ^1H -NMR spectrum of crude reaction mixture for site-selective benzylation of **2a** by using triethylamine as base (SI-Table 2, entry 3).

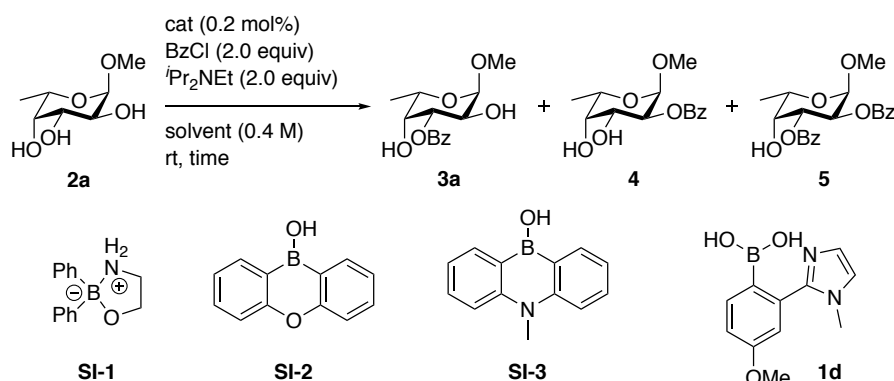
SI-Table 3. Optimization of reaction conditions for site-selective benzylation of 2a.



entry	cat (x mol%)	solvent	time (h)	yield (3a / 4 / 5) (%) ^a	total (%) ^a
1	1c (1)	CH ₂ Cl ₂	4	92 / 5 / 1	98
2	1c (0.5)	CH ₂ Cl ₂	4	84 / 3 / 7	94
3	1c (0.5)	1,4-dioxane	17.5	99 / – / <1	99
4	1d (0.5)	1,4-dioxane	4	>99 / <1 / –	>99
5	1e (0.5)	1,4-dioxane	24	93 / <1 / <1	93

^aDetermined by ¹H-NMR of crude mixture.

SI-Table 4. Comparison of catalysts for site-selective benzylation of 2a.



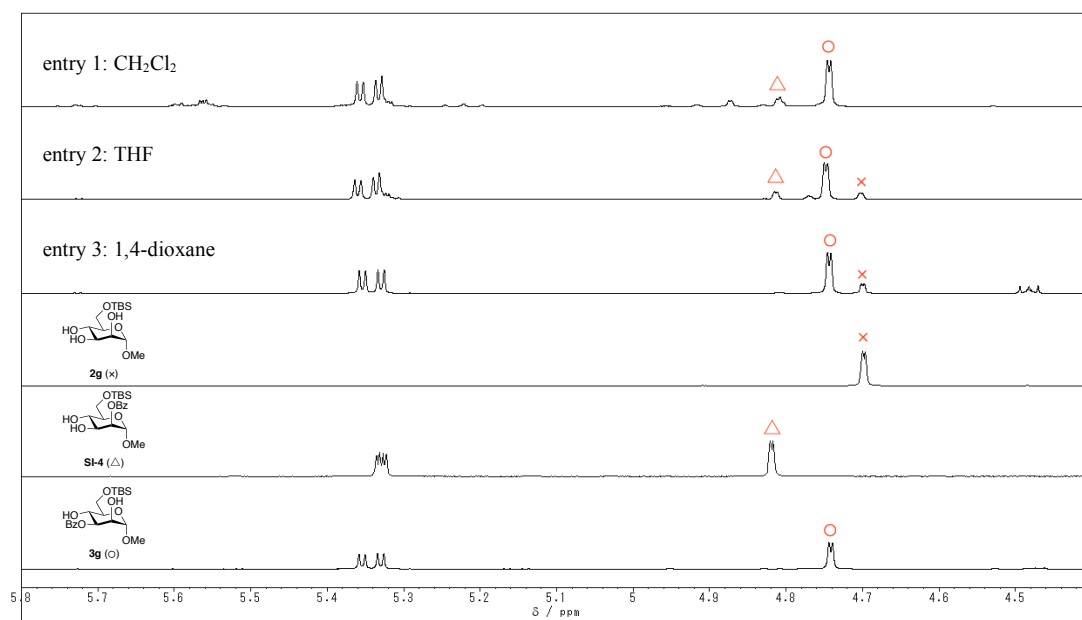
entry	cat	solvent	time (h)	yield (3a / 4 / 5) (%) ^a	total (%)
1	SI-1	1,4-dioxane	24	24 / 4 / 1	29
2	SI-2	1,4-dioxane	24	23 / 6 / 2	31
3	SI-3	1,4-dioxane	24	21 / 4 / 2	27
4	1d	1,4-dioxane	7	>99 / – / <1	>99 [99] ^b
5	none	1,4-dioxane	7	1 / 1 / –	2
6	SI-1	MeCN	7	35 / 3 / 4	42
7	SI-1	MeCN	24	43 / 5 / 4	52
8	SI-2	MeCN	7	66 / 3 / 3	72
9	SI-3	MeCN	7	46 / 5 / 5	56

^aDetermined by ¹H-NMR of crude mixture. ^bIsolated yield of **3a**.

SI-Table 5. Solvent screening for site-selective benzylation of 2g.

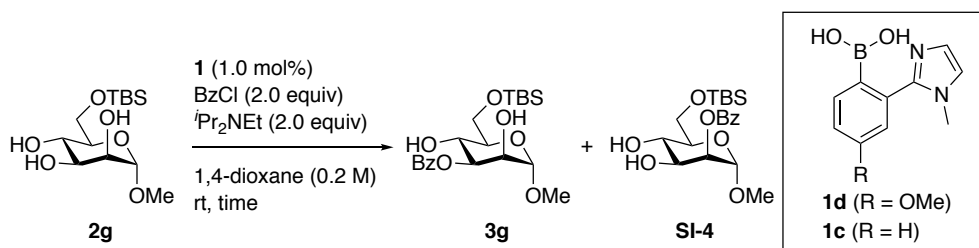
entry	solvent	time (h)	yield (3g / SI-4) (%) ^a	3g : SI-4	total (%) ^a
1	CH ₂ Cl ₂	22	73 / 8	9.1 : 1	81
2	THF	4	72 / 14	5.1 : 1	86
3	1,4-dioxane	4	83 / 1	>30 : 1	84

^aDetermined by ¹H-NMR of crude mixture.



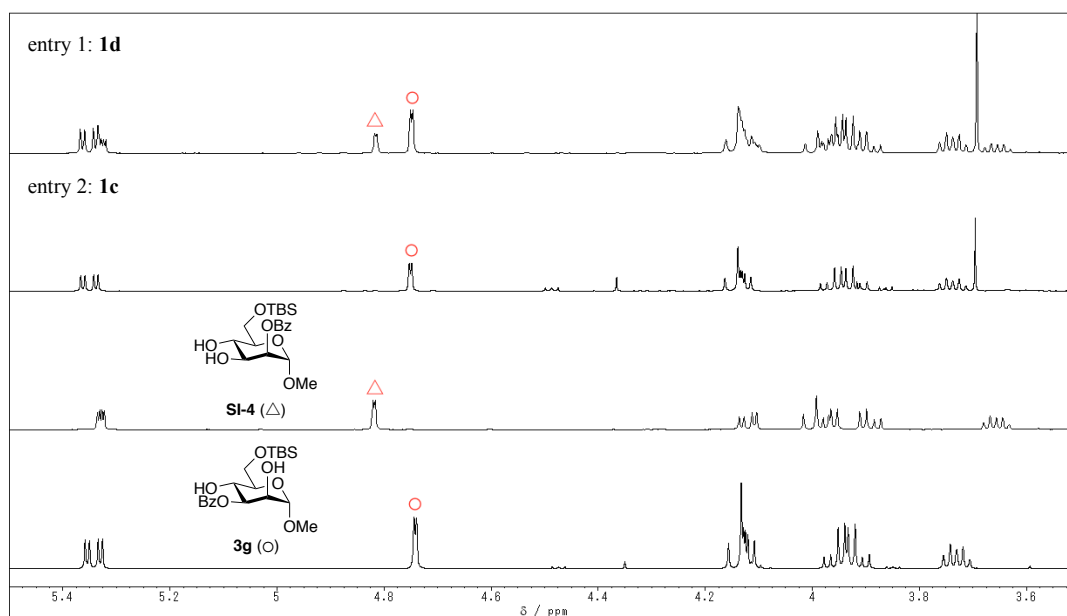
SI-Figure 3. ¹H-NMR spectra of crude reaction mixtures for SI-Table 5.

SI-Table 6. Optimization of catalyst for site-selective benzoylation of 2g.



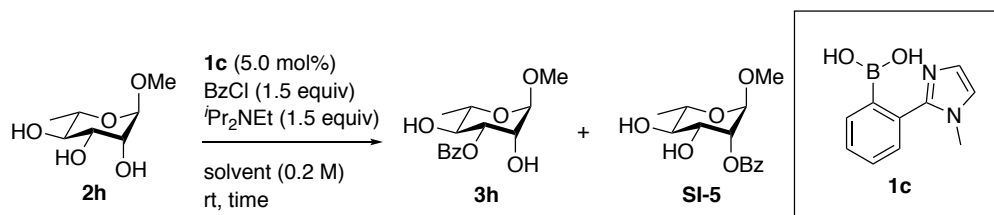
entry	1	time	yield (3g / SI-4) (%) ^a	3g : SI-4 ^a	total (%) ^a
1	1d (R = OMe)	2	69 / 31	2.2 : 1	100
2	1c (R = H)	24	98 / 2	>30 : 1	100 [97] ^b

^aDetermined by ¹H-NMR of crude mixture. ^bIsolated yield of **3g**.



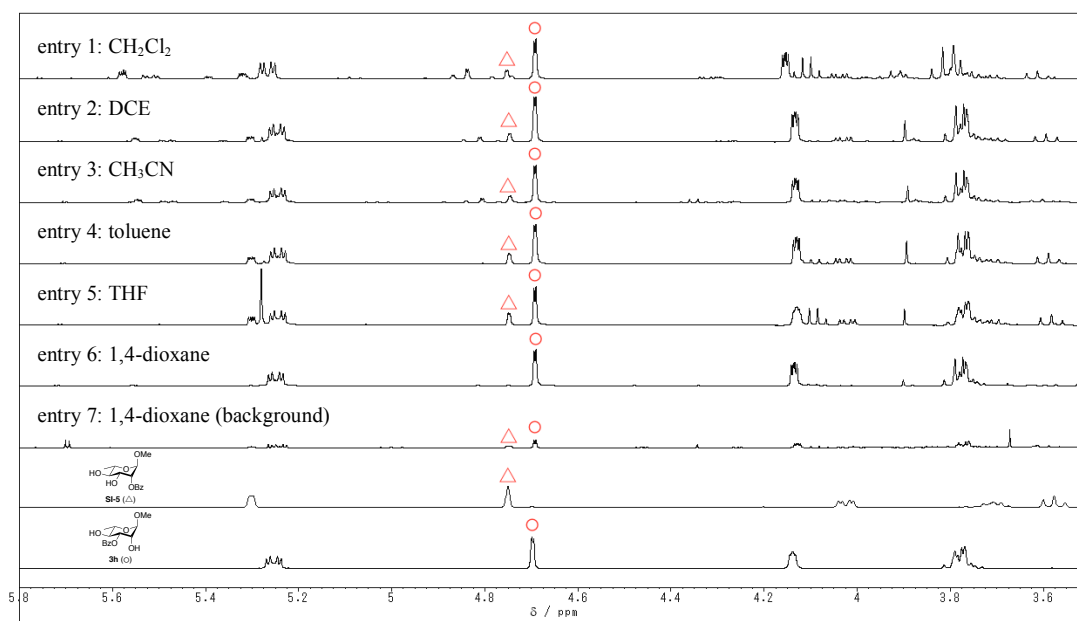
SI-Figure 4. ¹H-NMR spectra of crude reaction mixtures for SI-Table 6.

SI-Table 7. Solvent screening for site-selective benzylation of 2h.



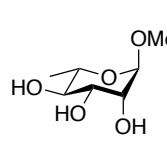
entry	solvent	1c	time (h)	yield (3h / SI-5) (%) ^a	3h : SI-5	total (%) ^a
1	CH ₂ Cl ₂	+	4	54 / 14	3.9 : 1	68
2	DCE	+	4	72 / 13	5.5 : 1	85
3	CH ₃ CN	+	4	66 / 12	5.5 : 1	78
4	toluene	+	4	62 / 15	4.1 : 1	77
5	THF	+	4	74 / 25	3.0 : 1	99
6	1,4-dioxane	+	4	84 / 1	>30 : 1	85
7	1,4-dioxane	–	24	2 / 1	2 : 1	3

^aDetermined by ¹H-NMR of crude mixture.



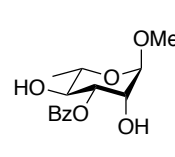
SI-Figure 5. ¹H-NMR spectra of crude reaction mixtures for SI-Table 7.

SI-Table 8. Optimization of catalyst for site-selective benzoylation of 2h.



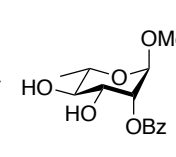
2h

1 (1.0 mol%)
BzCl (2.0 equiv)
^tPr₂NEt (2.0 equiv)
1,4-dioxane (0.2 M)
rt, time

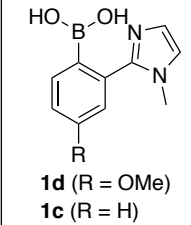


3h

+



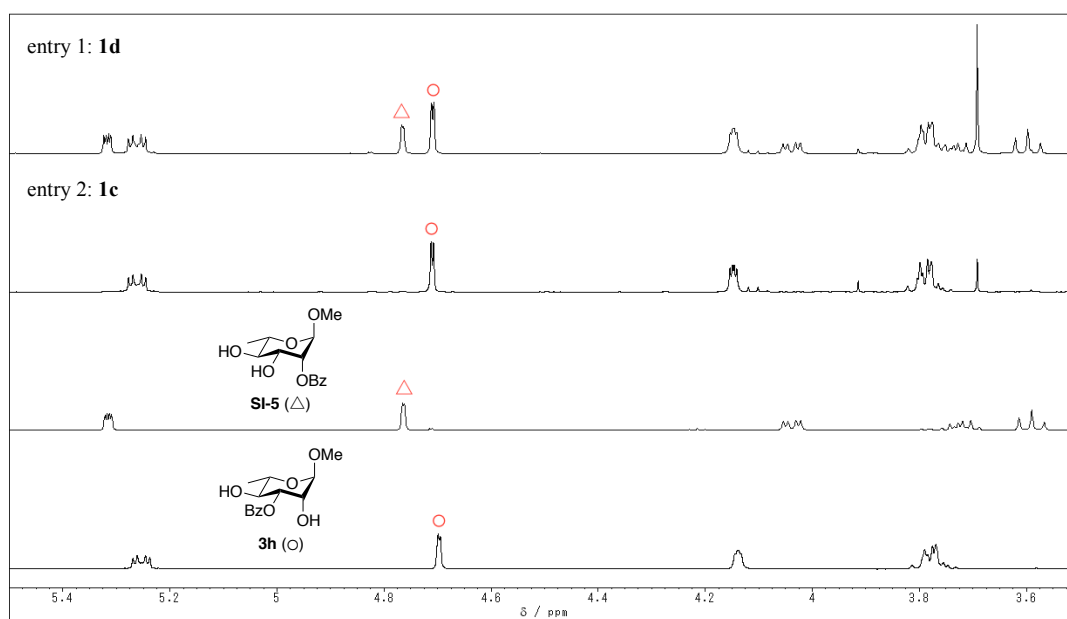
SI-5



1d (R = OMe)
1c (R = H)

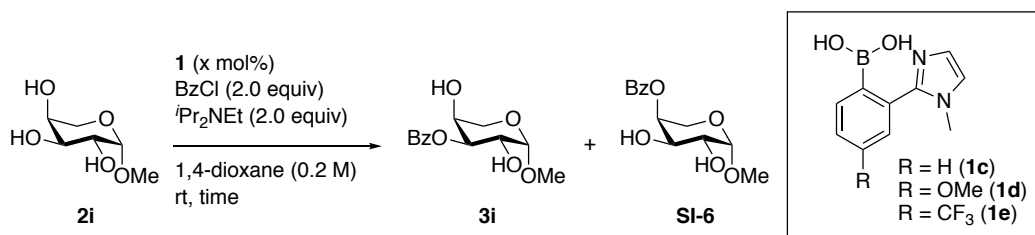
entry	1	time (h)	yield (3h / SI-5) (%) ^a	3h : SI-5	total (%) ^a
1	1d (R = OMe)	2	63 / 37	1.7 : 1	100
2	1c (R = H)	12	98 / 2	>30 : 1	100 [97] ^b

^aDetermined by ¹H-NMR of crude mixture. ^bIsolated yield of **3h**.



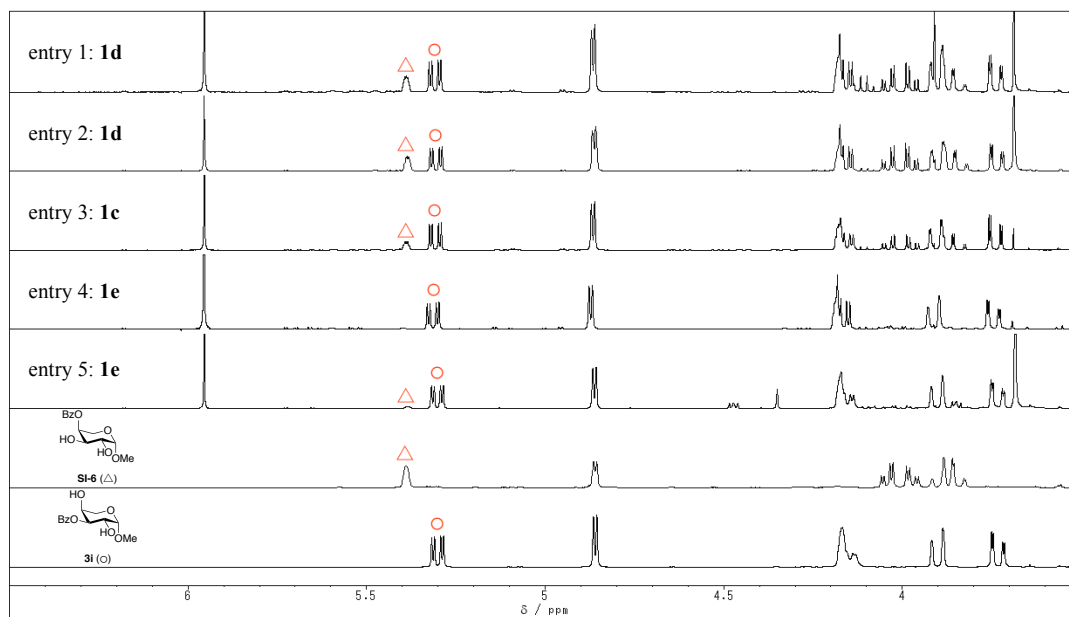
SI-Figure 6. ¹H-NMR spectra of crude reaction mixtures for SI-Table 8.

SI-Table 9. Optimization of catalyst for site-selective benzoylation of **2i.**



entry	1 (x mol%)	time (h)	yield (3i / SI-6) (%) ^a	3i : SI-6	total yield (%) ^a
1	1d (0.5)	2	53 / 45	1.2 : 1	98
2	1d (1.0)	2	60 / 40	1.5 : 1	100
3	1c (1.0)	15	73 / 23	3.2 : 1	96
4	1e (1.0)	24	43 / 1	>30 : 1	44
5	1e (2.0)	24	94 / 6	16 : 1	100 [93] ^b

^aDetermined by ¹H-NMR of crude mixture. ^bIsolated yield of **3i**.



SI-Figure 7. ¹H-NMR spectra of crude reaction mixtures for SI-Table 9.

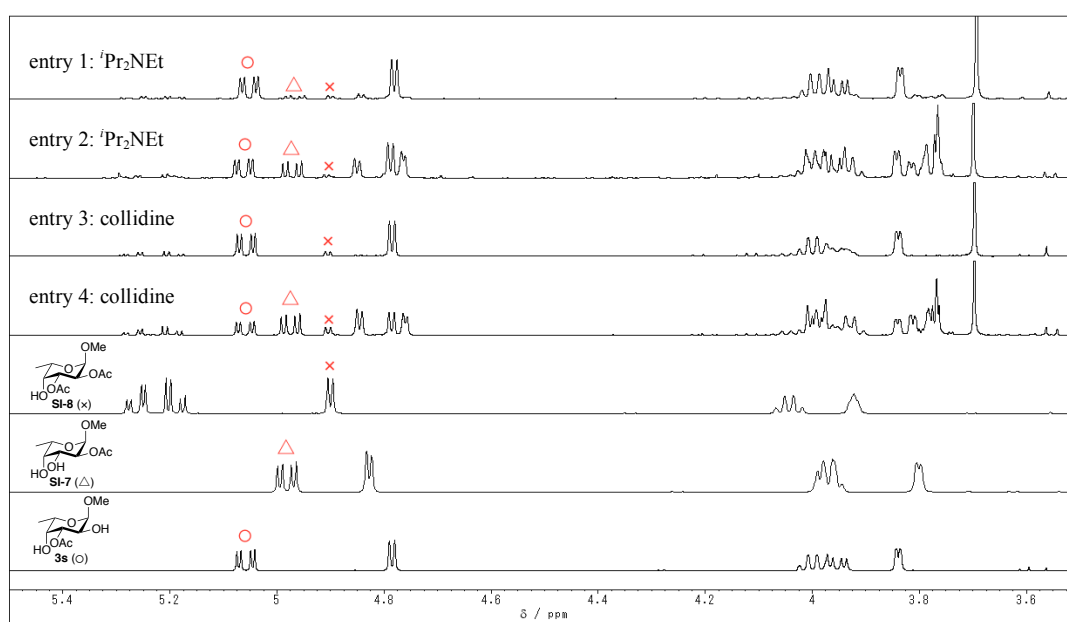
SI-Table 10. Optimization of base for site-selective acetylation of 2a.

2a → **3s** + **SI-7** + **SI-8**

1d

entry	1d	base	yield (3s / SI-7 / SI-8) (%) ^a	3s : SI-7	total (%) ^a
1	+	<i>i</i> Pr ₂ NEt	78 / 11 / 7	7.1 : 1	96
2	–	<i>i</i> Pr ₂ NEt	32 / 20 / 3	1.6 : 1	55
3	+	collidine	90 / <1 / 9	>90 : 1	99 [90] ^b
4	–	collidine	24 / 32 / 9	1 : 1.7	65

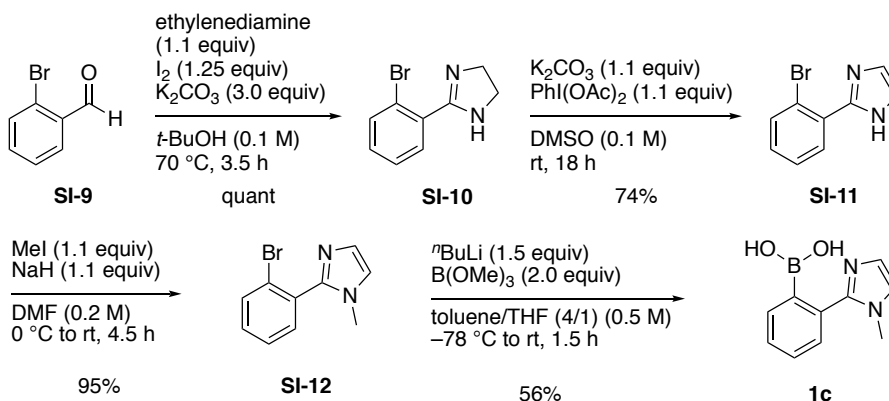
^aDetermined by ¹H-NMR of crude mixture. ^bIsolated yield of **3s**.



SI-Figure 8. ¹H-NMR spectra of crude reaction mixtures for SI-Table 10.

3. Preparation of boronic acid **1c**, **1d** and **1e**

Preparation of (2-(1-Methyl-1*H*-imidazol-2-yl)phenyl)boronic acid (**1c**)⁴



Ethylenediamine (2.01 mL, 29.7 mmol, 1.1 equiv) was added to a stirred solution of 2-bromobenzaldehyde (**SI-9**) (5.00 g, 27.0 mmol, 1.0 equiv) in *t*-BuOH (270 mL, 0.1 M). After stirring at room temperature for 30 minutes under nitrogen, I_2 (8.57 g, 33.8 mmol, 1.25 equiv)⁵ and K_2CO_3 (11.2 g, 81.0 mmol, 3.0 equiv) were added. After stirring at 70 °C for 3 hours, the reaction was quenched by addition of sat. Na_2SO_3 aq. and the resulting mixture was extracted three times with chloroform. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to give crude imidazoline **SI-10** (7.01 g). The resulting crude material was used in the next step without further purification.

$PhI(OAc)_2$ (4.88 g, 15.1 mmol, 1.1 equiv)⁵ was added to a stirred solution of the crude imidazoline **SI-10** (3.10 g, 13.8 mmol, 1.0 equiv) and K_2CO_3 (2.08 g, 15.1 mmol, 1.1 equiv) in DMSO (138 mL, 0.1 M). After stirring at room temperature for 18 hours, the reaction was quenched by addition of sat. $NaHCO_3$ aq. and the resulting mixture was extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by recrystallization from chloroform to give **SI-11** (2.27 g, 10.2 mmol, 74%) as a white solid.

Data for **SI-11**: R_f = 0.40 (20/1 $CHCl_3$ / MeOH); mp 142-145 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.0, 1.6 Hz, 1H) 7.62 (dd, J = 8.0, 1.2 Hz, 1H), 7.39 (dt, J = 8.0, 1.2 Hz, 1H), 7.23–7.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 133.7, 131.5, 130.5, 129.8, 127.9, 119.2; IR (KBr) ν = 3140, 3019, 2965, 2897, 2801, 1560, 1489, 1446, 1408, 1360, 1171, 1103, 1026, 959, 767, 731, 645 cm^{-1} ; HRMS (ESI) m/z calcd for $C_9H_8^{79}BrN_2$ $[M+H]^+$ 222.9871, found 222.9867.

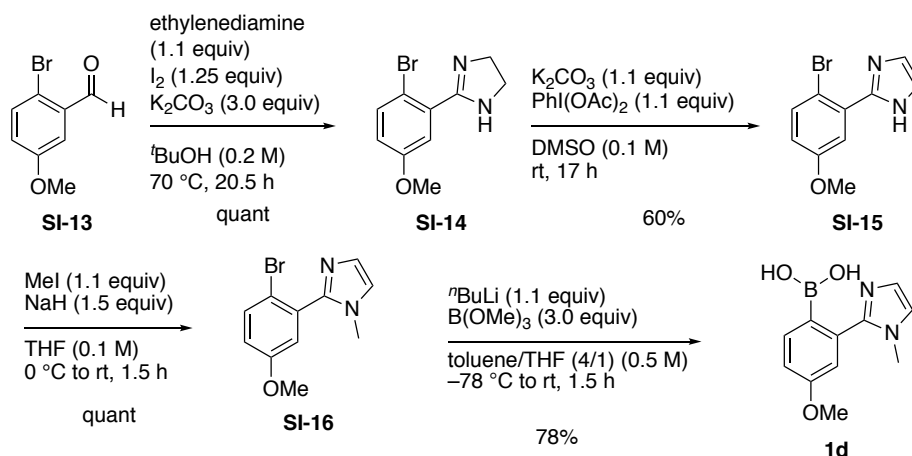
A solution of imidazole **SI-11** (2.00 g, 8.96 mmol, 1.0 equiv) in DMF (22 mL, 0.4 M) was added to a stirred suspension of NaH (237 mg, 9.86 mmol, 1.1 equiv) in DMF (22 mL, 0.4 M). After stirring at 0 °C for 30 minutes, iodomethane (0.61 mL, 9.86 mmol, 1.1 equiv) was added. After stirring at room temperature for 4 hours, the resulting mixture was poured onto ice and extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (CHCl₃ : methanol = 20 : 1) to give **SI-12** (2.03 g, 8.56 mmol, 95%) as a pale yellow oil.

Data for **SI-12**: *R*_f = 0.40 (20/1 CHCl₃ / MeOH); ¹H NMR (400 MHz, CD₃OD) δ 7.66 (br d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.40 (br t, *J* = 7.6 Hz, 1H), 7.31 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.15 (d, *J* = 1.2 Hz, 1H), 7.00 (d, *J* = 1.2 Hz, 1H), 3.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 132.6, 132.4, 132.3, 130.8, 128.2, 127.3, 124.4, 120.9, 33.4; IR (neat) ν = 3383, 3106, 3057, 2948, 1659, 1596, 1562, 1496, 1464, 1436, 1403, 1281, 1136, 1029, 1016, 765, 733, 644 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₀H₁₀⁷⁹BrN₂ [M+H]⁺ 237.0027, found 237.0022.

n-BuLi in *n*-hexane (1.60 M, 3.96 mL, 6.33 mmol, 1.5 equiv) was added to a stirred solution of **SI-12** (1.00 g, 4.22 mmol, 1.0 equiv) in dry toluene/THF (4 / 1, 8.4 mL, 0.5 M) at -78 °C under argon. After stirring at -78 °C for 30 minutes, B(OMe)₃ (0.941 mL, 8.44 mmol, 2.0 equiv) was added at -78 °C, and then the resulting mixture was warmed to room temperature. After stirring for 1 hour, the mixture was concentrated. The resulting crude material was purified by amino silica gel chromatography (dichloromethane to dichloromethane : methanol = 50 : 1) to give **1c** (477 mg, 2.36 mmol, 56%) as a white solid.

Data for **1c**: *R*_f (NH) = 0.20 (20/1 CH₂Cl₂ / MeOH); 125 °C (decomp.); ¹H NMR (400 MHz, CD₃OD) δ 7.74 (br d, *J* = 7.6 Hz, 1H), 7.55 (br d, *J* = 7.6 Hz, 1H), 7.39 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.35 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.27 (d, *J* = 1.6 Hz, 1H), 7.20 (d, *J* = 1.6 Hz, 1H), 4.06 (s, 3H); ¹³C NMR (100 MHz, CD₃OD) δ 134.6, 133.6, 132.8, 130.5, 127.0, 121.9, 121.7, 35.3; IR (KBr) ν = 3372, 3114, 3093, 3049, 2929, 2888, 2818, 1564, 1510, 1463, 1432, 1360, 1295, 1278, 1210, 1166, 1118, 997, 954, 801, 738, 718, 648 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₀H₁₂¹¹BN₂O₂ [M+H]⁺ 203.0992, found 203.0986.

Preparation of (4-Methoxy-2-(1-methyl-1*H*-imidazol-2-yl)phenyl)boronic acid (**1d**)



Ethylenediamine (1.37 mL, 20.4 mmol, 1.1 equiv) was added to a stirred solution of 2-bromo-5-methoxybenzaldehyde (**SI-13**) (3.98 g, 18.5 mmol, 1.0 equiv) in *t*-BuOH (93 mL, 0.2 M). After stirring at room temperature for 30 minutes under nitrogen, I₂ (5.87 g, 23.1 mmol, 1.25 equiv)⁵ and K₂CO₃ (7.66 g, 55.5 mmol, 3.0 equiv) were added. After stirring at 70 °C for 20 hours, the reaction was quenched by addition of sat. Na₂SO₃ aq. and the resulting mixture was extracted three times with chloroform. The combined organic layers were washed with sat. NaHCO₃ aq. and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give crude imidazoline **SI-14** (4.73 g). The resulting crude material was used in the next step without further purification.

PhI(OAc)₂ (4.03 g, 12.5 mmol, 1.1 equiv)⁵ was added to a stirred solution of imidazoline **SI-14** (2.90 g, 11.8 mmol, 1.0 equiv) and K₂CO₃ (1.73 g, 12.5 mmol, 1.1 equiv) in DMSO (114 mL, 0.1 M). After stirring at room temperature for 17 hours, the reaction was quenched by addition of sat. NaHCO₃ aq. and the resulting mixture was extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting crude material was purified by recrystallization from chloroform to give **SI-15** (1.73 g, 6.84 mmol, 60%) as a white solid.

Data for **SI-15**: R_f = 0.10 (2/1 *n*-hexane / EtOAc); mp 162-165 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 3.2 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.22 (s, 2H), 6.79 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CD₃OD) δ 160.5, 146.4, 135.3, 134.0, 117.84, 117.80, 112.9, 56.1; IR (KBr) ν = 3011, 2962, 1593, 1557, 1487, 1465, 1105, 1017, 861, 809, 766, 628 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₀H₁₀⁷⁹BrN₂O [M+H]⁺ 252.9977, Found 252.9979.

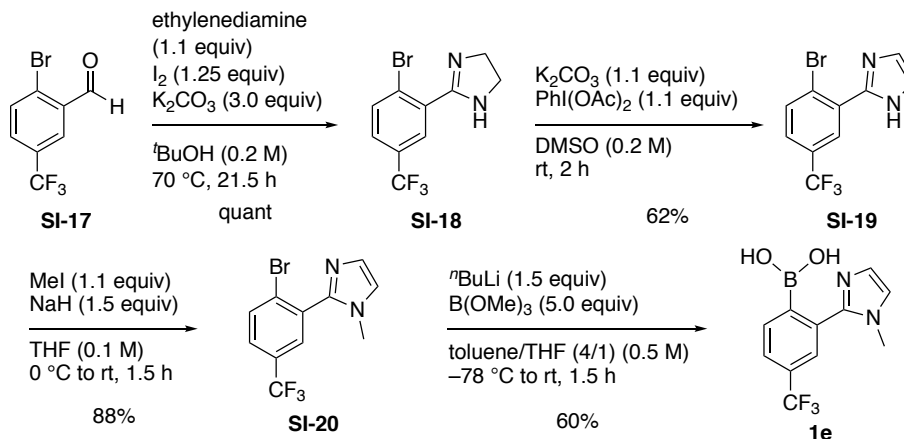
A solution of imidazole **SI-15** (100 mg, 0.395 mmol, 1.0 equiv) in THF (2 mL, 0.2 M) was added to a stirred suspension of NaH (14.2 mg, 0.593 mmol, 1.5 equiv) in THF (2.0 mL, 0.2 M). After stirring at 0 °C for 30 minutes, iodomethane (27.1 μ L, 0.435 mmol, 1.1 equiv) was added. After stirring at room temperature for 1 hour, the resulting mixture was poured onto ice and extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 2) to give **SI-16** (107 mg, 0.401 mmol, >99%) as a pale yellow oil.

Data for **SI-16**: R_f = 0.20 (1/2 *n*-hexane / EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.8 Hz, 1H), 7.14 (d, J = 1.2 Hz, 1H), 6.99 (d, J = 1.2 Hz, 1H), 6.98 (d, J = 3.2 Hz, 1H), 6.89 (dd, J = 8.8, 3.2 Hz, 1H), 3.80 (s, 3H), 3.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 146.7, 133.2, 133.0, 128.2, 120.9, 117.4, 117.2, 114.6, 55.5, 33.4; IR (neat) ν = 3344, 2951, 1598, 1572, 1460, 1434, 1285, 1238, 1209, 1178, 1091, 1208, 728 cm⁻¹; HRMS (ESI) m/z calcd for C₁₁H₁₂⁷⁹BrN₂O [M+H]⁺ 267.0133, Found 267.0123.

n-BuLi in *n*-hexane (1.60 M, 257 μ L, 0.411 mmol, 1.1 equiv) was added to a stirred solution of **SI-16** (100 mg, 0.374 mmol, 1.0 equiv) in dry toluene/THF (4 / 1, 0.75 mL, 0.5 M) at -78 °C under argon. After stirring at -78 °C for 30 minutes, B(OMe)₃ (125 μ L, 1.12 mmol, 3.0 equiv) was added at -78 °C, and then the resulting mixture was warmed to room temperature. After stirring for 1 hour, the mixture was concentrated. The resulting crude material was purified by amino silica gel chromatography (dichloromethane to dichloromethane : methanol = 50 : 1) to give **1d** (67.3 mg, 0.290 mmol, 78%) as a pale yellow solid.

Data for **1d**: R_f (NH) = 0.37 (20/1 CH₂Cl₂ / MeOH); 144 °C (decomp.); ¹H NMR (400 MHz, CD₃OD) δ 7.44 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 1.7 Hz, 1H), 7.19 (d, J = 1.7 Hz, 1H), 6.98 (dd, J = 8.0, 2.0 Hz, 1H), 4.06 (s, 3H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CD₃OD) δ 161.2, 151.8, 133.0, 132.4, 126.4, 121.4, 115.8, 108.6, 55.9, 35.2; IR (KBr) ν = 3114, 3087, 2931, 2826, 1513, 1309, 1294, 1215, 1162, 1108, 1091, 1045, 985, 856, 811, 727 cm⁻¹; HRMS (ESI) m/z calcd for C₁₁H₁₄¹¹BN₂O₃ [M+H]⁺ 233.1097, Found 233.1089.

Preparation of (2-(1-Methyl-1H-imidazol-2-yl)-4-(trifluoromethyl)phenyl)boronic acid (**1e**)



Ethylenediamine (0.580 mL, 8.69 mmol, 1.1 equiv) was added to a stirred solution of 2-bromo-5-(trifluoromethyl)benzaldehyde (**SI-17**) (2.00 g, 7.90 mmol, 1.0 equiv) in t -BuOH (40 mL, 0.2 M). After stirring at room temperature for 30 minutes under nitrogen, I_2 (2.51 g, 9.88 mmol, 1.25 equiv)⁵ and K_2CO_3 (3.28 g, 23.7 mmol, 3.0 equiv) were added. After stirring at 70 °C for 21 hours, the reaction was quenched by addition of sat. Na_2SO_3 aq. and the resulting mixture was extracted three times with chloroform. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to give crude imidazoline **SI-18** (2.48 g). The resulting crude material was used in the next step without further purification.

$PhI(OAc)_2$ (1.40 g, 4.35 mmol, 1.1 equiv)⁵ was added to a stirred solution of imidazoline **SI-18** (1.16 g, 3.95 mmol, 1.0 equiv) and K_2CO_3 (602 mg, 4.35 mmol, 3.0 equiv) in DMSO (19.8 mL, 0.2 M). After stirring at room temperature for 2 hours, the reaction was quenched by addition of sat. $NaHCO_3$ aq. and the resulting mixture was extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by recrystallization from chloroform to give **SI-19** (713 mg, 2.45 mmol, 62%) as a pale yellow solid.

Data for **SI-19**: R_f = 0.40 (2/1 n -hexane / EtOAc); mp 170-175 °C; 1H NMR (400 MHz, $CDCl_3$) δ 10.3 (br, 1H), 8.56 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.44 (dd, J = 8.4, 2.0 Hz, 1H), 7.26 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 134.5, 134.3, 131.3, 130.5 (q, $^2J_{C-F}$ = 33.2 Hz), 128.4 (q, $^3J_{C-F}$ = 3.8 Hz), 126.0 (q, $^3J_{C-F}$ = 3.5 Hz), 123.4 (q, $^1J_{C-F}$ = 271.5 Hz), 122.6 (q, $^4J_{C-F}$ = 1.5 Hz); IR (KBr) ν = 3034, 2798, 1612,

1402, 1327, 1185, 1123, 1076, 1029, 971, 828, 730 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_7^{79}\text{BrF}_3\text{N}_2$ $[\text{M}+\text{H}]^+$ 290.9745, Found 290.9744.

A solution of imidazole **SI-19** (100 mg, 0.344 mmol, 1.0 equiv) in THF (1.7 mL, 0.2 M) was added to a stirred suspension of NaH (12.4 mg, 0.516 mmol, 1.5 equiv) in THF (1.7 mL, 0.2 M). After stirring at 0 °C for 30 minutes, iodomethane (23.5 μL , 0.378 mmol, 1.1 equiv) was added. After stirring at room temperature for 1 hour, the resulting mixture was poured onto ice and extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **SI-20** (91.8 mg, 0.301 mmol, 88%) as a pale yellow oil.

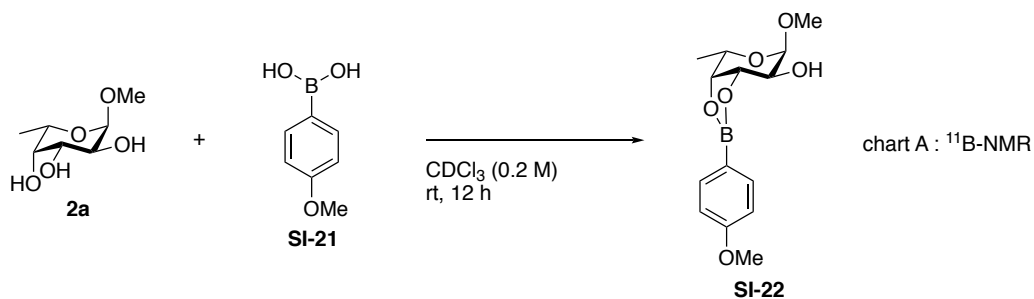
Data for **SI-20**: R_f = 0.25 (2/1 *n*-hexane / EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 2.3 Hz, 1H), 7.58 (dd, J = 8.4, 2.3 Hz, 1H), 7.17 (d, J = 1.2 Hz, 1H), 7.02 (d, J = 1.2 Hz, 1H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 133.39, 133.36, 130.0 (q, $^2J_{\text{C-F}}$ = 33.2 Hz), 129.5 (q, $^3J_{\text{C-F}}$ = 3.8 Hz), 128.7, 128.4 (q, $^4J_{\text{C-F}}$ = 1.5 Hz), 127.4 (q, $^3J_{\text{C-F}}$ = 3.5 Hz), 123.4 (q, $^1J_{\text{C-F}}$ = 271.5 Hz), 121.4, 33.5; IR (neat) ν = 1610, 1327, 1280, 1258, 1174, 1131, 1022, 908, 830, 750, 689 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_9^{79}\text{BrF}_3\text{N}_2$ $[\text{M}+\text{H}]^+$ 304.9901, Found 304.9902.

n-BuLi in *n*-hexane (1.55 M, 194 μL , 0.300 mmol, 1.5 equiv) was added to a stirred solution of **SI-20** (61.0 mg, 0.200 mmol, 1.0 equiv) in dry toluene/THF (4 / 1, 0.4 mL, 0.5 M) at -78 °C under argon. After stirring at -78 °C for 30 minutes, $\text{B}(\text{OMe})_3$ (111 μL , 1.0 mmol, 5.0 equiv) was added at -78 °C, and then the resulting mixture was warmed to room temperature. After stirring for 1 hour, the mixture was concentrated. The resulting crude material was purified by amino silica gel chromatography (dichloromethane to dichloromethane : methanol = 50 : 1) to give **1e** (32 mg, 1.20 mmol, 60%) as a pale yellow amorphous material.

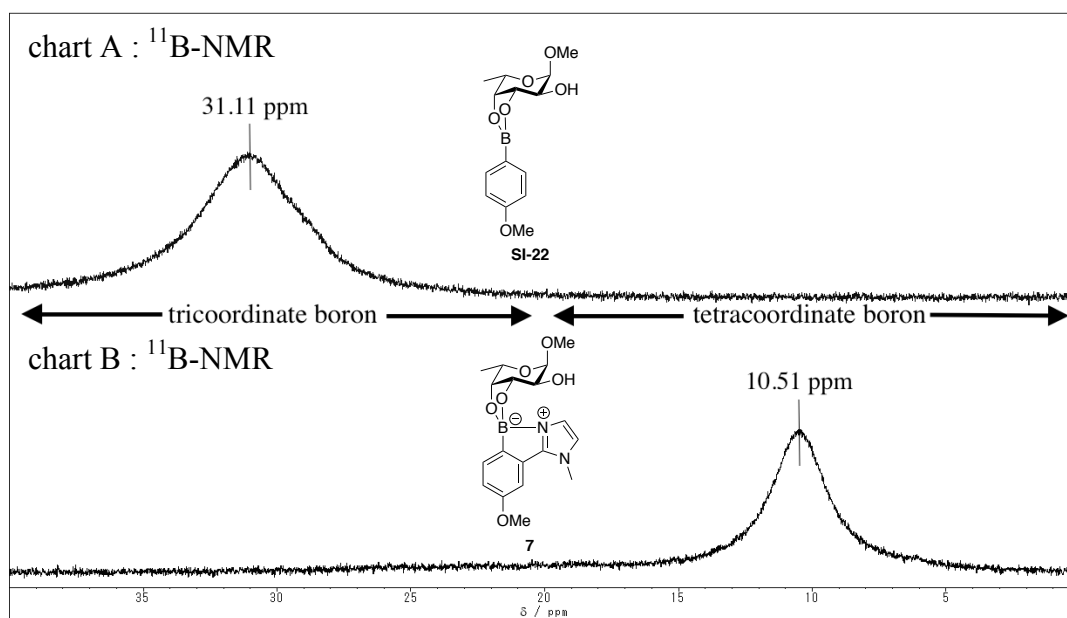
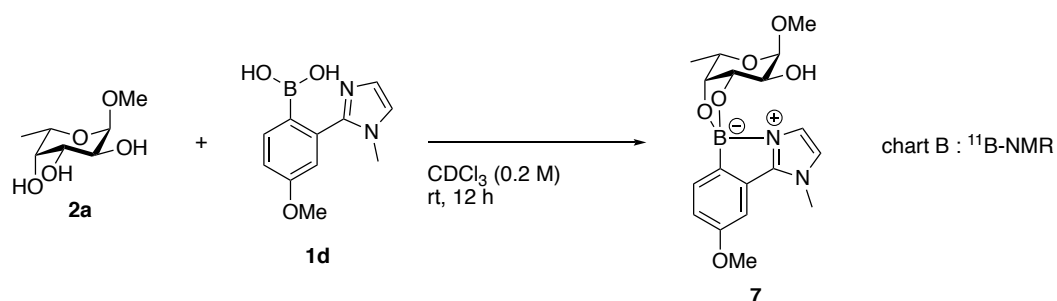
Data for **1e**: R_f (NH) = 0.43 (20/1 CH_2Cl_2 / MeOH); ^1H NMR (400 MHz, CD_3OD) δ 7.95 (s, 1H), 7.72 (br d, J = 7.6 Hz, 1H), 7.69 (br d, J = 7.6 Hz, 1H), 7.37 (d, J = 1.6 Hz, 1H), 7.28 (d, J = 1.6 Hz, 1H), 4.12 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 150.6, 132.7, 132.0, 131.1 (q, $^2J_{\text{C-F}}$ = 32.0 Hz), 127.4 (q, $^3J_{\text{C-F}}$ = 4.0 Hz), 127.3, 125.7 (q, $^1J_{\text{C-F}}$ = 270.1 Hz), 121.7, 118.1 (q, $^3J_{\text{C-F}}$ = 4.0 Hz), 35.4; IR (neat) ν = 3107, 2957, 1563, 1460, 1394, 1330, 1121, 989, 834, 730, 664, 583 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}^{11}\text{BF}_3\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 271.0866, Found 271.0859.

4. Supplementary data for boronic acids

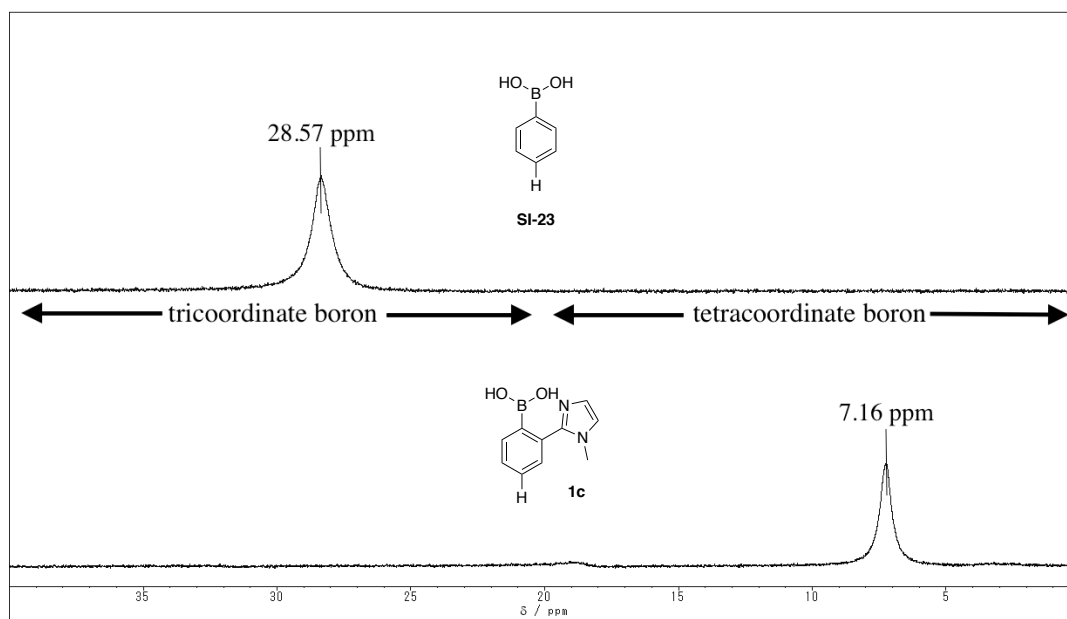
SI-Scheme 1. Preparation of boronic ester SI-22.



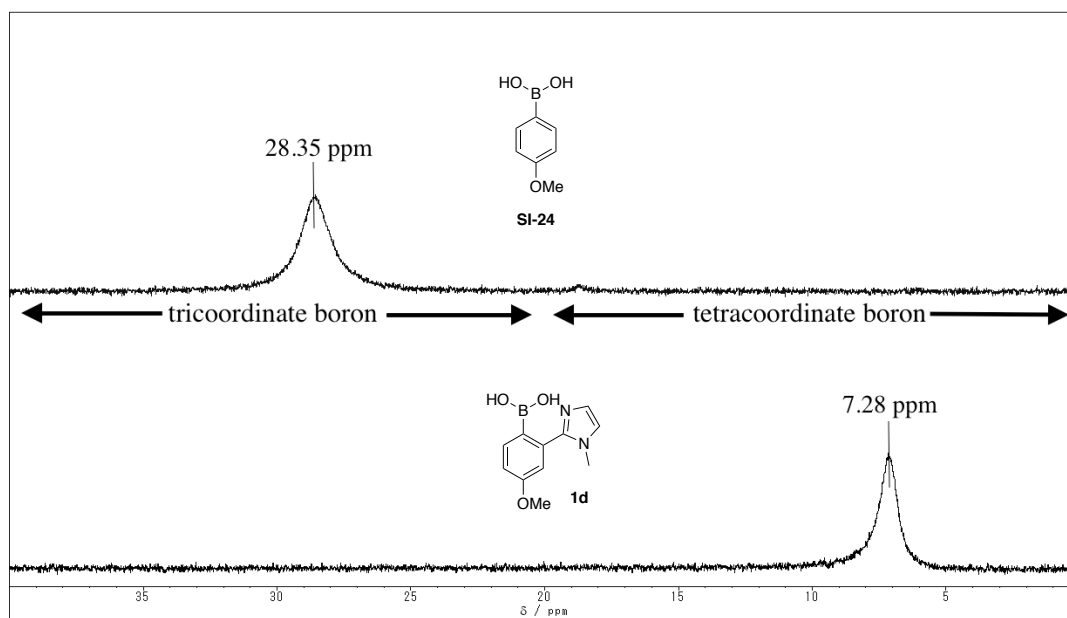
SI-Scheme 2. Preparation of borate complex 7.



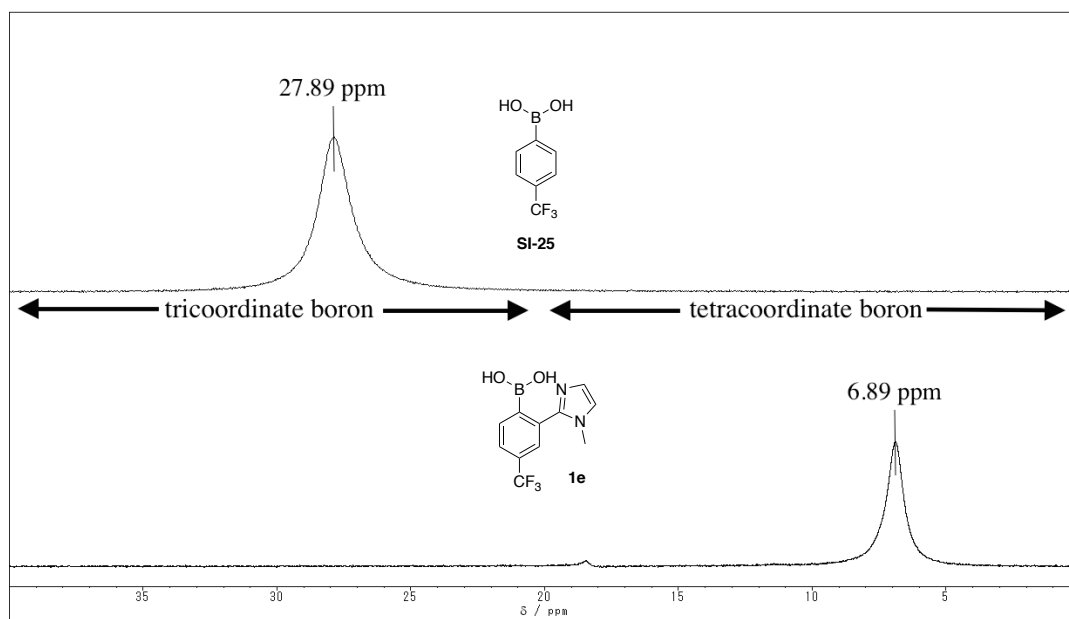
SI-Figure 9. Chart A: ^{11}B -NMR spectrum of SI-22. Chart B: ^{11}B -NMR spectrum of 7.



SI-Figure 10 . ^{11}B -NMR spectra of SI-23 and 1c in CD_3OD .



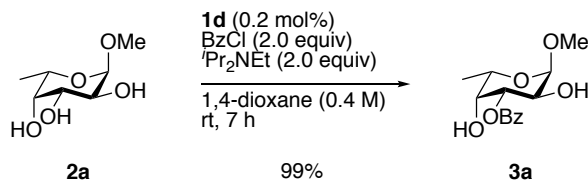
SI-Figure 11 . ^{11}B -NMR spectra of SI-24 and 1d in CD_3OD .



SI-Figure 12. ^{11}B -NMR spectra of **SI-25** and **1e** in CD_3OD .

5. Boronic acid catalyzed site-selective benzylation of **2a** (Table 1)

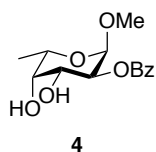
Methyl 3-*O*-benzoyl- α -L-fucopyranoside (**3a**)⁶



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred solution of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 200 μL , 0.400 μmol , 0.2 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) in dry 1,4-dioxane (300 μL , total 0.4 M) under ambient atmosphere. After stirring for 7 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 1) to give **3a** (56.3 mg, 0.199 mmol, 99%) as a white solid.

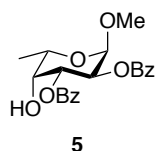
Data for **3a**: R_f = 0.28 (1/1 *n*-hexane / EtOAc); mp 81–84 $^\circ\text{C}$; $[\alpha]_D^{23}$ -184.0° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.08 (m, 2H), 7.59–7.55 (m, 1H), 7.46–7.43 (m, 2H), 5.28 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.84 (d, J = 4.0 Hz, 1H, *H*-1), 4.14 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 4.07 (q, J = 6.4 Hz, 1H, *H*-5), 3.98 (d, J = 3.2 Hz, 1H, *H*-4), 3.46 (s, 3H), 2.13 (br, 2H, *OH*-2, *OH*-4), 1.31 (d, J = 6.4 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 133.3, 129.8, 129.7, 128.4, 99.7, 74.5, 70.8, 67.1, 65.7, 55.5, 16.0; IR (KBr) ν = 3470, 2937, 1709, 1451, 1280, 1128, 1052, 961, 848, 756, 713 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 305.1001, found 305.0994.

Methyl 2-*O*-benzoyl- α -L-fucopyranoside (**4**)



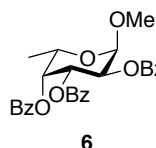
Data for **4**: white solid; R_f = 0.32 (20/1 CHCl_3 / MeOH); mp 168–171 °C; $[\alpha]_D^{25}$ -137.7° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.08–8.06 (m, 2H), 7.59–7.55 (m, 1H), 7.45–7.41 (m, 2H), 5.21 (dd, J = 10.0, 4.0 Hz, 1H, H -2), 4.98 (d, J = 4.0 Hz, 1H, H -1), 4.17 (dd, J = 10.0, 3.2 Hz, 1H, H -3), 4.04 (q, J = 6.4 Hz, 1H, H -5), 3.87 (d, J = 3.2 Hz, 1H, H -4), 3.39 (s, 3H), 1.83 (br, 2H, OH-3, OH-4), 1.34 (d, J = 6.4 Hz, 3H, H -6); ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 133.3, 129.9, 129.6, 128.4, 97.5, 72.4, 72.3, 68.9, 65.3, 55.5, 16.1; IR (KBr) ν = 3524, 2987, 2936, 1718, 1691, 1457, 1339, 1289, 1257, 1126, 1095, 1039, 998, 963, 901, 716 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 305.1001, found 305.1001.

Methyl 2,3-*O*-dibenzoyl- α -L-fucopyranoside (**5**)



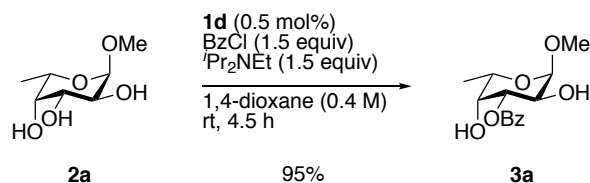
Data for **5**: colorless oil; R_f = 0.38 (3/1 *n*-hexane / EtOAc); $[\alpha]_D^{25}$ -147.4° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.01–7.97 (m, 4H), 7.53–7.48 (m, 2H), 7.40–7.35 (m, 4H), 5.70 (dd, J = 10.8, 3.2 Hz, 1H, H -3), 5.61 (dd, J = 10.8, 3.6 Hz, 1H, H -2), 5.12 (d, J = 3.6 Hz, 1H, H -1), 4.21 (q, J = 6.4 Hz, 1H, H -5), 4.14 (d, J = 3.2 Hz, 1H, H -4), 3.43 (s, 3H), 1.36 (d, J = 6.4 Hz, 3H, H -6); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 165.8, 133.3, 133.2, 129.82, 129.75, 129.5, 129.4, 128.44, 128.36, 97.5, 71.5, 70.9, 68.9, 65.4, 55.5, 16.0; IR (neat) ν = 3502, 2934, 1722, 1602, 1452, 1282, 1109, 1071, 1051, 1030, 965, 763, 710 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$ 409.1263, found 409.1261.

Methyl 2,3,4-*O*-tribenzoyl- α -L-fucopyranoside (**6**)



Data for **6**: colorless oil; R_f = 0.28 (10/1 *n*-hexane / EtOAc); $[\alpha]_D^{25}$ -251.7° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.13–8.11 (m, 2H), 8.00–7.98 (m, 2H), 7.81–7.79 (m, 2H), 7.64–7.59 (m, 1H), 7.53–7.48 (m, 3H), 7.44–7.35 (m, 3H), 7.26–7.22 (m, 2H), 5.97 (dd, J = 10.8, 3.6 Hz, 1H, H -3), 5.77 (dd, J = 3.6, 0.8 Hz, 1H, H -4), 5.66 (dd, J = 10.8, 3.6 Hz, 1H, H -2), 5.25 (d, J = 3.6 Hz, 1H, H -1), 4.40 (dq, J = 6.4, 0.8 Hz, 1H, H -5), 3.48 (s, 3H), 1.30 (d, J = 6.4 Hz, 3H, H -6); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 166.0, 165.6, 133.33, 133.25, 133.0, 129.9, 129.8, 129.6, 129.4, 129.3, 128.5, 128.4, 128.2, 97.6, 72.0, 69.4, 68.7, 64.7, 55.6, 16.1; IR (neat) ν = 2938, 1727, 1602, 1452, 1285, 1108, 1071, 1053, 1027, 759, 712 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{26}\text{NaO}_8$ $[\text{M}+\text{Na}]^+$ 513.1525, found 513.1520.

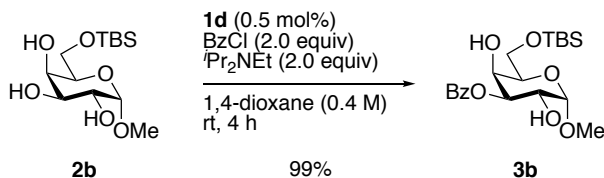
6. Gram-scale synthesis (Scheme 1)



Benzoyl chloride (9.86 mL, 8.42 mmol, 1.5 equiv) was added to a stirred solution of methyl α -L-fucopyranoside (**2a**) (1.00 g, 5.61 mmol, 1.0 equiv), boronic acid **1d** (6.5 mg, 0.5 mol%) and N,N -diisopropylethylamine (1.47 mL, 8.42 mmol, 1.5 equiv) in dry 1,4-dioxane (14 mL, 0.4 M) under ambient atmosphere. After stirring for 4.5 hours, the reaction was quenched by addition of 1 M HCl (10 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 1) to give **3a** (1.51 g, 5.35 mmol, 95%) as a colorless amorphous material.

7. Boronic acid catalyzed site-selective mono-benzoylation of carbohydrates (Scheme 2)

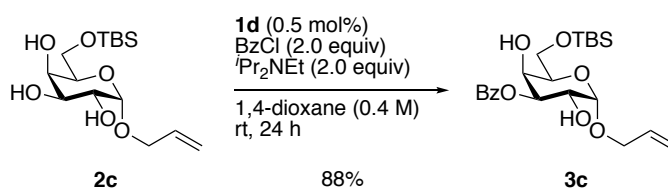
Methyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- α -D-galactopyranoside (**3b**)⁶



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl 6-((*tert*-butyldimethylsilyl)oxy)- α -D-galactopyranoside (**2b**) (61.7 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 500 μL , 1.00 μmol , 0.5 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 4 hours, the resulting mixture was diluted with chloroform and washed with 1 M HCl, sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 3 : 1) to give **3b** (81.9 mg, 0.199 mmol, 99%) as a white solid.

Data for **3b**: R_f = 0.30 (2/1 *n*-hexane / EtOAc); mp 98–101 $^\circ\text{C}$; $[\alpha]_D^{23} +128.3^\circ$ (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.13–8.10 (m, 2H), 7.59–7.55 (m, 1H), 7.47–7.43 (m, 2H), 5.27 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.91 (d, J = 3.6 Hz, 1H, *H*-1), 4.32 (br d, J = 3.2 Hz, 1H, *H*-4), 4.25 (dt, J = 10.4, 3.6 Hz, 1H, *H*-2), 3.95 (dd, J = 10.8, 5.2 Hz, 1H, *H*-6), 3.90 (dd, J = 10.8, 4.4 Hz, 1H, *H*-6), 3.86–3.84 (m, 1H, *H*-5), 3.47 (s, 3H), 3.12 (br, 1H, OH-4), 2.06 (br, 1H, OH-2), 0.90 (s, 9H), 0.101 (s, 3H), 0.099 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 133.2, 129.9, 129.8, 128.4, 99.9, 74.2, 69.34, 69.28, 67.4, 63.6, 55.4, 25.8, 18.3, –5.52, –5.54; IR (KBr) ν = 3569, 3304, 2937, 2853, 1771, 1450, 1318, 1292, 1253, 1143, 1092, 1054, 1038, 837, 773, 716 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{NaO}_7\text{Si}$ $[\text{M}+\text{Na}]^+$ 435.1815, found 435.1805.

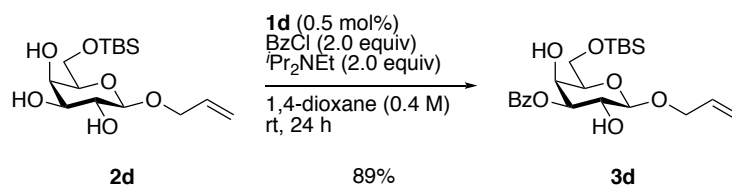
Allyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- α -D-galactopyranoside (**3c**)



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of allyl 6-((*tert*-butyldimethylsilyl)oxy)- α -D-galactopyranoside (**2c**) (66.9 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 500 μL , 1.00 μmol , 0.5 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 24 hours, the resulting mixture was diluted with chloroform and washed with 1 M HCl, sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 4 : 1) to give **3c** (77.2 mg, 0.176 mmol, 88%) as a white solid.

Data for **3c**: R_f = 0.45 (2/1 *n*-hexane / EtOAc); mp 60–64 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23} +127.5^{\circ}$ (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.12–8.10 (m, 2H), 7.58–7.54 (m, 1H), 7.45–7.41 (m, 2H), 5.93 (dddd, J = 17.2, 10.4, 6.1, 5.4 Hz, 1H), 5.32 (dq, J = 17.2, 1.6 Hz, 1H), 5.30 (dd, J = 10.2, 3.0 Hz, 1H, *H*-3), 5.23 (ddt, J = 10.4, 1.6, 1.2 Hz, 1H), 5.05 (d, J = 4.0 Hz, 1H, *H*-1), 4.32 (br d, J = 3.0 Hz, 1H, *H*-4), 4.28–4.23 (m, 2H, *H*-2, *H*-6), 4.10–4.04 (m, 1H, *H*-6), 3.93–3.87 (m, 3H, *H*-5, $\text{OCH}_2\text{CHCH}_2$), 0.90 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 133.5, 133.2, 129.9, 129.8, 128.3, 117.9, 98.1, 74.2, 69.6, 69.3, 68.7, 67.3, 63.6, 25.8, 18.2, –5.53, –5.54; IR (KBr) ν = 3527, 3450, 2930, 2857, 1701, 1281, 1254, 1094, 1028, 933, 839, 777, 713 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{34}\text{NaO}_7\text{Si}$ $[\text{M}+\text{Na}]^+$ 461.1972, found 461.1967.

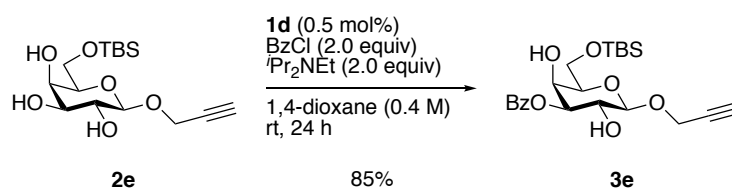
Allyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- β -D-galactopyranoside (**3d**)



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of allyl 6-((*tert*-butyldimethylsilyl)oxy)- β -D-galactopyranoside (**2d**) (66.9 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 500 μL , 1.00 μmol , 0.5 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) in dry 1,4-dioxane under ambient atmosphere. After stirring for 24 hours, the resulting mixture was diluted with chloroform and washed with 1 M HCl, sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 4 : 1) to give **3d** (78.1 mg, 0.178 mmol, 89%) as a colorless oil.

Data for **3d**: R_f = 0.23 (4/1 *n*-hexane / EtOAc); $[\alpha]_D^{24} +17.1^\circ$ (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.11–8.09 (m, 2H), 7.58–7.54 (m, 1H), 7.46–7.42 (m, 2H), 5.95 (dddd, J = 17.2, 10.0, 6.4, 5.2 Hz, 1H), 5.32 (dq, J = 17.2, 1.6 Hz, 1H), 5.22 (ddt, J = 10.4, 1.6, 1.2 Hz, 1H), 5.08 (dd, J = 10.0, 3.2 Hz, 1H, *H*-3), 4.44 (d, J = 7.6 Hz, 1H, *H*-1), 4.41 (ddt, J = 12.4, 5.2, 1.2 Hz, 1H), 4.28 (d, J = 3.2 Hz, 1H, *H*-4), 4.16 (ddt, J = 12.4, 6.4, 1.2 Hz, 1H), 4.07 (dd, J = 10.0, 7.6 Hz, 1H, *H*-2), 3.95 (dd, J = 10.4, 5.6 Hz, 1H, *H*-6), 3.89 (dd, J = 10.4, 5.6 Hz, 1H, *H*-6), 3.59 (t, J = 5.6 Hz, 1H, *H*-5), 2.84 (br, 1H, OH), 2.47 (br, 1H, OH), 0.89 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 133.7, 133.3, 129.9, 129.7, 128.4, 118.0, 102.3, 75.8, 74.0, 70.1, 69.4, 68.0, 62.8, 25.8, 18.3, –5.50; IR (neat) ν = 3480, 2954, 2929, 2884, 2857, 1719, 1452, 1281, 1111, 1071, 997, 930, 839, 780, 713 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{34}\text{NaO}_7\text{Si}$ $[\text{M}+\text{Na}]^+$ 461.1972, found 461.1966.

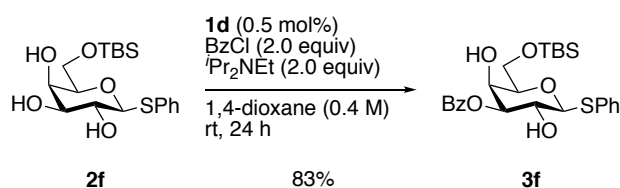
Propargyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- β -D-galactopyranoside (**3e**)



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of propargyl 6-((*tert*-butyldimethylsilyl)oxy)- β -D-galactopyranoside (**2e**) (66.5 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 500 μL , 1.00 μmol , 0.5 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 24 hours, the resulting mixture was diluted with chloroform and washed with 1 M HCl, sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 4 : 1) to give **3e** (74.1 mg, 0.170 mmol, 85%) as a colorless oil.

Data for **3e**: R_f = 0.18 (4/1 *n*-hexane / EtOAc); $[\alpha]_D^{24}$ -7.4° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.11–8.08 (m, 2H), 7.58–7.53 (m, 1H), 7.45–7.41 (m, 2H), 5.11 (dd, J = 10.0, 3.1 Hz, 1H, *H*-3), 4.62 (d, J = 7.7 Hz, 1H, *H*-1), 4.46 (dd, J = 15.8, 2.4 Hz, 1H, OCH_2CCH), 4.40 (dd, J = 15.8, 2.4 Hz, 1H, OCH_2CCH), 4.29 (br, 1H, *H*-4), 4.08 (dd, J = 10.0, 7.7 Hz, 1H, *H*-2), 3.95 (dd, J = 10.6, 5.7 Hz, 1H, *H*-6), 3.89 (dd, J = 10.6, 4.7 Hz, 1H, *H*-6), 3.63–3.60 (m, 1H, *H*-5), 2.49 (t, J = 2.4 Hz, 1H, OCH_2CCH), 0.89 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 133.3, 129.9, 129.6, 128.4, 101.0, 78.5, 75.7, 75.4, 74.0, 69.1, 68.0, 62.8, 55.7, 25.8, 18.2, -5.51 ; IR (neat) ν = 3452, 2930, 1714, 1280, 1109, 839, 781, 713 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{32}\text{NaO}_7\text{Si}$ $[\text{M}+\text{Na}]^+$ 459.1815, found 459.1819.

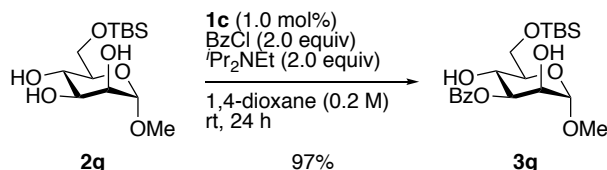
Phenylthio 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- β -D-galactopyranoside (**3f**)



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of phenylthio 6-((*tert*-butyldimethylsilyl)oxy)- β -D-galactopyranoside (**2f**) (77.3 mg, 0.20 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 500 μL , 1.00 μmol , 0.5 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) in dry 1,4-dioxane under ambient atmosphere. After stirring for 24 hours, the resulting mixture was diluted with chloroform and washed with 1 M HCl, sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 4 : 1) to give **3f** (81.7 mg, 0.167 mmol, 83%) as a white solid.

Data for **3f**: R_f = 0.33 (4/1 *n*-hexane / EtOAc); mp 76–80 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23} +9.6^{\circ}$ (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.07 (m, 2H), 7.62–7.59 (m, 2H), 7.58–7.53 (m, 1H), 7.44–7.41 (m, 2H), 7.33–7.30 (m, 3H), 5.11 (dd, J = 9.6, 3.0 Hz, 1H, *H*-3), 4.65 (d, J = 9.6 Hz, 1H, *H*-1), 4.35 (br, 1H, *H*-4), 4.09 (t, J = 9.6 Hz, 1H, *H*-2), 4.00 (dd, J = 10.8, 5.0 Hz, 1H, *H*-6), 3.93 (dd, J = 10.8, 4.3 Hz, 1H, *H*-6), 3.65–3.63 (m, 1H, *H*-5), 3.15 (br, 1H, *OH*-4), 2.54 (br, 1H, *OH*-2), 0.91 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 133.3, 132.7, 131.8, 129.9, 129.6, 129.0, 128.4, 128.1, 89.0, 77.6, 77.1, 68.7, 67.2, 63.6, 25.8, 18.2, –5.51, –5.53; IR (KBr) ν = 3512, 2928, 2856, 1703, 1279, 1104, 1071, 839, 778, 743, 714, 689 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{34}\text{NaO}_6\text{SSi}$ $[\text{M}+\text{Na}]^+$ 513.1743, found 513.1736.

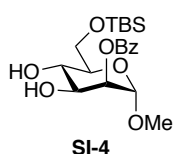
Methyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- α -D-mannopyranoside (**3g**)⁶



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl 6-((*tert*-butyldimethylsilyl)oxy)- α -D-mannopyranoside (**2g**) (61.7 mg, 0.200 mmol, 1.0 equiv), boronic acid **1c** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 24 hours, the resulting mixture was diluted with chloroform and washed with 1 M HCl, sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 4 : 1) to give **3g** (79.6 mg, 0.193 mmol, 97%) as a colorless oil.

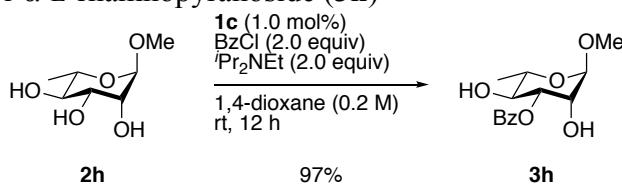
Data for **3g**: R_f = 0.25 (4/1 *n*-hexane / EtOAc); $[\alpha]_D^{24} +31.7^\circ$ (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.11–8.08 (m, 2H), 7.59–7.54 (m, 1H), 7.46–7.42 (m, 2H), 5.34 (dd, J = 9.8, 3.3 Hz, 1H, *H*-3), 4.74 (d, J = 1.8 Hz, 1H, *H*-1), 4.13 (t, J = 9.8 Hz, 1H, *H*-4), 4.13 (dd, J = 3.3, 1.8 Hz, 1H, *H*-2), 3.96 (dd, J = 10.6, 5.0 Hz, 1H, *H*-6), 3.92 (dd, J = 10.6, 5.3 Hz, 1H, *H*-6), 3.75–3.71 (m, 1H, *H*-5), 3.42 (s, 3H), 0.91 (s, 9H), 0.11 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 133.3, 129.9, 129.7, 128.4, 100.6, 75.0, 71.4, 69.2, 68.0, 64.4, 55.0, 25.9, 18.3, –5.47; IR (neat) ν = 3478, 2929, 2857, 1703, 1603, 1452, 1281, 1109, 973, 838, 758, 713, 668 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{NaO}_7\text{Si}$ $[\text{M}+\text{Na}]^+$ 435.1815, found 435.1809.

Methyl 6-((*tert*-butyldimethylsilyl)oxy)-2-*O*-benzoyl- α -D-mannopyranoside (**SI-4**)



Data for **SI-4**: colorless oil; R_f = 0.28 (2/1 *n*-hexane / EtOAc); $[\alpha]_D^{24} +11.8^\circ$ (c = 1.0, CH_3OH); ^1H NMR (400 MHz, CDCl_3) δ 8.06–8.03 (m, 2H), 7.59–7.55 (m, 1H), 7.45–7.41 (m, 2H), 5.33 (dd, J = 3.6, 1.6 Hz, 1H, *H*-2), 4.82 (d, J = 1.6 Hz, 1H, *H*-1), 4.12 (dd, J = 9.6, 3.6 Hz, 1H, *H*-3), 3.99 (t, J = 9.6 Hz, 1H, *H*-4), 3.97 (dd, J = 10.8, 4.8 Hz, 1H, *H*-6), 3.89 (dd, J = 10.8, 4.8 Hz, 1H, *H*-6), 3.66 (dt, J = 9.6, 4.8 Hz, 1H, *H*-5), 3.40 (s, 3H), 0.93 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 133.3, 129.9, 129.6, 128.4, 98.7, 72.2, 71.0, 70.4, 70.2, 64.1, 55.1, 25.9, 18.3, –5.43, –5.48; IR (neat) ν = 3429, 2954, 2929, 2856, 1724, 1603, 1452, 1363, 1272, 1116, 1072, 972, 837, 778, 711, 685 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{NaO}_7\text{Si}$ $[\text{M}+\text{Na}]^+$ 435.1815, found 435.1806.

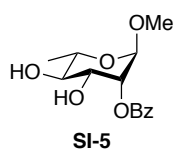
Methyl 3-*O*-benzoyl- α -L-rhamnopyranoside (**3h**)⁶



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-rhamnopyranoside (**2h**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1c** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 12 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3h** (54.8 mg, 0.194 mmol, 97%) as a white solid.

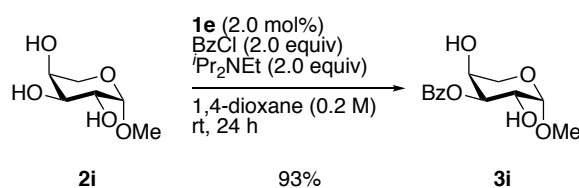
Data for **3h**: R_f = 0.37 (20/1 CHCl_3 / MeOH); mp 68–71 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{23}$ -52.8° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (br d, J = 7.8 Hz, 2H), 7.60–7.56 (m, 1H), 7.44 (br t, J = 7.8 Hz, 2H), 5.26 (dd, J = 9.5, 3.2 Hz, 1H, *H*-3), 4.70 (d, J = 1.7 Hz, 1H, *H*-1), 4.14 (br, dd, J = 3.2, 1.7 Hz, 1H, *H*-2), 3.79–3.76 (m, 2H, *H*-4, *H*-5), 3.40 (s, 3H), 2.47 (br, 1H, OH), 2.28 (br, 1H, OH), 1.29 (d, J = 6.4 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 133.5, 129.8, 129.5, 128.5, 100.6, 75.5, 71.4, 69.7, 68.4, 55.0, 17.6; IR (KBr) ν = 3423, 2979, 2938, 1709, 1452, 1319, 1282, 1130, 1056, 986, 806, 716 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 305.1001, found 305.0993.

Methyl 2-*O*-benzoyl- α -L-rhamnopyranoside (**SI-5**)



Data for **SI-5**: colorless oil; R_f = 0.34 (20/1 CHCl_3 / MeOH); $[\alpha]_{\text{D}}^{25}$ $+6.7^\circ$ (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 5.32–5.31 (m, 1H, *H*-2), 4.76 (br, 1H, *H*-1), 4.04 (dd, J = 9.2, 3.2 Hz, 1H, *H*-3), 3.76–3.69 (m, 1H, *H*-5), 3.59 (t, J = 9.2 Hz, 1H, *H*-4), 3.40 (s, 3H), 2.64 (br, 2H, OH-2, OH-4), 1.37 (d, J = 6.0 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 133.5, 129.9, 129.5, 128.5, 98.6, 73.7, 72.9, 70.6, 67.9, 55.0, 17.6; IR (neat) ν = 3438, 2930, 1719, 1452, 1359, 1277, 1135, 1118, 1078, 995, 887, 765, 714 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 305.1001, found 305.1002.

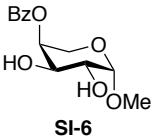
Methyl 3-*O*-benzoyl- β -L-arabinopyranoside (**3i**)⁶



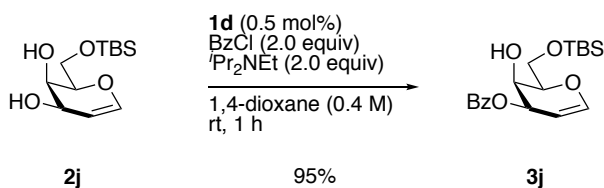
Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl β -L-arabinopyranoside (**2i**) (32.8 mg, 0.200 mmol, 1.0 equiv), boronic acid **1e** (0.004 M in 1,4-dioxane, 1.00 mL, 4.00 μmol , 2.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 24 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3i** (49.9 mg, 0.186 mmol, 93%) as a colorless oil.

Data for **3i**: R_f = 0.32 (20/1 CHCl_3 / MeOH); $[\alpha]_D^{24}$ +214.8° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.07 (m, 2H), 7.60–7.55 (m, 1H), 7.46–7.43 (m, 2H), 5.30 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.86 (d, J = 4.0 Hz, 1H, *H*-1), 4.17 (br, 1H, *H*-4), 4.14 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.90 (br d, J = 12.4 Hz, 1H, *H*-5), 3.73 (dd, J = 12.4, 2.4 Hz, 1H, *H*-5), 3.47 (s, 3H), 2.32 (br, 1H, *OH*), 2.16 (br, 1H, *OH*); ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 133.4, 129.8, 129.6, 128.4, 100.1, 73.6, 68.2, 67.5, 62.3, 55.6; IR (neat) ν = 3454, 2934, 1717, 1452, 1317, 1282, 1142, 1065, 1034, 995, 765, 715 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 291.0845, found 291.0842.

Methyl 4-*O*-benzoyl- β -L-arabinopyranoside (**SI-6**)

 Data for **SI-6**: colorless oil; R_f = 0.28 (20/1 CHCl_3 / MeOH); $[\alpha]_D^{24}$ +181.8° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.07–8.05 (m, 2H), 7.59–7.55 (m, 1H), 7.46–7.42 (m, 2H), 5.39–5.38 (m, 1H, *H*-4), 4.86 (d, J = 3.6 Hz, 1H, *H*-1), 4.04 (dd, J = 9.6, 3.6 Hz, 1H, *H*-3), 3.97 (dd, J = 9.6, 3.6 Hz, 1H, *H*-2), 3.90 (br d, J = 12.8 Hz, 1H, *H*-5), 3.84 (dd, J = 12.8, 2.0 Hz, 1H, *H*-5), 3.45 (s, 3H), 2.55 (br, 2H, *OH*-2, *OH*-3); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 133.3, 129.8, 128.4, 99.7, 71.9, 70.1, 69.2, 60.7, 55.7; IR (neat) ν = 3438, 2933, 1722, 1452, 1376, 1274, 1118, 1071, 1027, 974, 713 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 291.0845, found 291.0846.

6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl-D-galactal (**3j**)

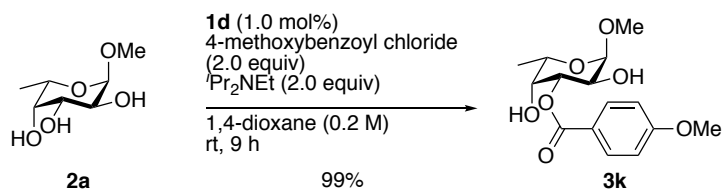


Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of phenyl 6-((*tert*-butyldimethylsilyl)oxy)-D-galactal (**2j**) (52.1 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 500 μL , 1.00 μmol , 0.5 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 1 hour, the resulting mixture was diluted with chloroform and washed with 1 M HCl, sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 15 : 1) to give **3j** (69.2 mg, 0.0190 mmol, 95%) as a colorless oil.

Data for **3j**: R_f = 0.18 (10/1 *n*-hexane / EtOAc); $[\alpha]_{\text{D}}^{23}$ -67.6° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.09–8.07 (m, 2H), 7.58–7.55 (m, 1H), 7.46–7.42 (m, 2H), 6.52 (dd, J = 6.0, 2.0 Hz, 1H, *H*-1), 5.68 (dt, J = 4.0, 2.0 Hz, 1H, *H*-3), 4.81 (dt, J = 6.0, 2.0 Hz, 1H, *H*-2), 4.41 (br, 1H, *H*-4), 4.08–4.02 (m, 2H, *H*-5, *H*-6), 3.92 (dd, J = 9.6, 3.6 Hz, 1H, *H*-6), 2.94 (d, J = 3.6, 1H, *OH*-4), 0.91 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 146.1, 133.2, 129.9, 129.8, 128.4, 98.6, 75.9, 68.1, 64.1, 62.9, 25.8, 18.3, -5.48 , -5.50 ; IR (neat) ν = 3493, 2929, 2885, 2857, 1720, 1644, 1603, 1471, 1452, 1273, 1110, 1028, 839, 779, 713, 549, 496 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{28}\text{NaO}_5\text{Si}$ $[\text{M}+\text{Na}]^+$ 387.1604, found 387.1595.

8. Boronic acid catalyzed site-selective mono-acylations of **2a** (Scheme 3)

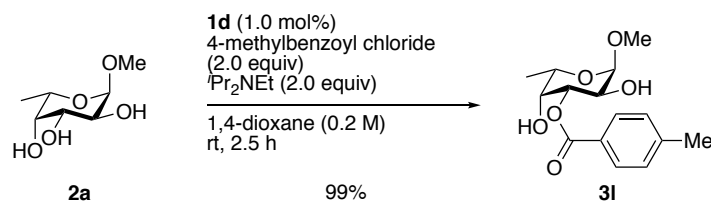
Methyl 3-*O*-4-methoxybenzoyl- α -L-fucopyranoside (**3k**)



4-Methoxybenzoyl chloride (54.2 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 9 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3k** (61.8 mg, 0.198 mmol, 99%) as a white solid.

Data for **3k**: R_f = 0.39 (20/1 CHCl_3 / MeOH); mp 88-92 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{23}$ -163.2° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (dt, J = 9.6, 2.8 Hz, 2H), 6.90 (dt, J = 9.6, 2.8 Hz, 2H), 5.24 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.82 (d, J = 4.0 Hz, 1H, *H*-1), 4.11 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 4.05 (q, J = 6.8 Hz, 1H, *H*-5), 3.96 (d, J = 3.2 Hz, 1H, *H*-4), 3.85 (s, 3H), 3.45 (s, 3H), 2.22 (br, 2H, *OH*-2, *OH*-4), 1.29 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 163.6, 131.9, 122.0, 113.7, 99.7, 74.2, 70.9, 67.1, 65.7, 55.5, 55.4, 16.0; IR (KBr) ν = 3338, 2993, 2942, 2842, 1694, 1606, 1579, 1514, 1421, 1364, 1286, 1265, 1169, 1129, 1044, 963, 842, 770, 683, 615, 500 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$ 335.1107, found 335.1094.

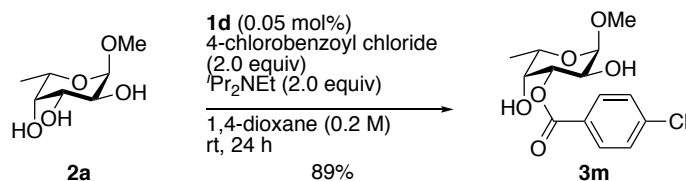
Methyl 3-*O*-4-methylbenzoyl- α -L-fucopyranoside (**3I**)



4-Methylbenzoyl chloride (52.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 2.5 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3I** (58.7 mg, 0.198 mmol, 99%) as a white solid.

Data for **3I**: R_f = 0.39 (20/1 CHCl_3 / MeOH); mp 108-111 $^\circ\text{C}$; $[\alpha]_D^{23}$ -175.8° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 5.26 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.83 (d, J = 4.0 Hz, 1H, *H*-1), 4.12 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 4.05 (dq, J = 6.8, 0.8 Hz, 1H, *H*-5), 3.96 (dd, J = 3.2, 0.8 Hz, 1H, *H*-4), 3.45 (s, 3H), 2.40 (s, 3H), 2.09 (br, 2H, *OH*-2, *OH*-4), 1.30 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 144.1, 129.9, 129.1, 126.9, 99.7, 74.3, 70.9, 67.1, 65.7, 55.5, 21.7, 16.0; IR (KBr) ν = 3380, 2992, 2979, 2938, 1705, 1638, 1612, 1449, 1365, 1282, 1181, 1125, 1036, 963, 845, 761, 681, 640 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 319.1158, found 319.1148.

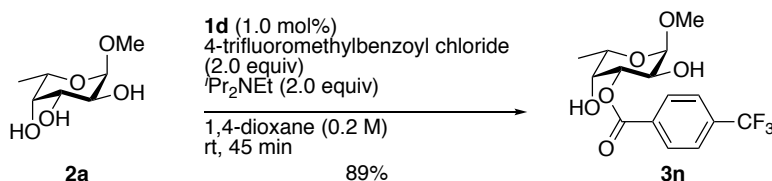
Methyl 3-*O*-4-chlorobenzoyl- α -L-fucopyranoside (**3m**)



4-Chlorobenzoyl chloride (51.1 μL , 0.400 mmol, 2.0 equiv) was added to a stirred solution of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 50.0 μL , 0.100 μmol , 0.05 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) in dry 1,4-dioxane (950 μL , total 0.20 M) under ambient atmosphere. After stirring for 24 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3m** (56.4 mg, 0.178 mmol, 89%) as a white solid.

Data for **3m**: R_f = 0.39 (20/1 CHCl_3 / MeOH); mp 134-137 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{23}$ -175.2° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 5.25 (dd, J = 10.0, 2.8 Hz, 1H, *H*-3), 4.83 (d, J = 3.6 Hz, 1H, *H*-1), 4.11 (dd, J = 10.0, 3.6 Hz, 1H, *H*-2), 4.06 (q, J = 6.4 Hz, 1H, *H*-5), 3.97 (d, J = 2.8 Hz, 1H, *H*-4), 3.46 (s, 3H), 2.08 (br, 2H, *OH*-2, *OH*-4), 1.30 (d, J = 6.4 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 139.8, 131.2, 128.8, 128.2, 99.7, 74.8, 70.8, 67.1, 65.7, 55.6, 16.0; IR (KBr) ν = 3512, 3435, 2982, 2941, 2923, 2835, 1708, 1594, 1400, 1359, 1312, 1279, 1091, 1052, 959, 850, 761, 679 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{ClNaO}_6$ $[\text{M}+\text{Na}]^+$ 339.0611, found 339.0603.

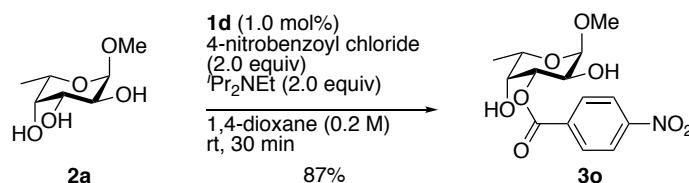
Methyl 3-*O*-4-trifluoromethylbenzoyl- α -L-fucopyranoside (**3n**)



4-Trifluoromethylbenzoyl chloride (59.2 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 45 minutes, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3n** (62.5 mg, 0.178 mmol, 89%) as a white solid.

Data for **3n**: R_f = 0.39 (20/1 CHCl_3 / MeOH); mp 121-124 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{23}$ -157.9° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 5.29 (dd, J = 10.0, 2.8 Hz, 1H, *H*-3), 4.85 (d, J = 4.0 Hz, 1H, *H*-1), 4.13 (dd, J = 10.0, 4.0 Hz, 1H, *H*-2), 4.08 (q, J = 6.8 Hz, 1H, *H*-5), 3.99 (d, J = 2.8 Hz, 1H, *H*-4), 3.47 (s, 3H), 2.04 (br, 2H, *OH*-2, *OH*-4), 1.31 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 134.8 (q, $^2J_{\text{C-F}}$ = 32.5 Hz), 133.0 (q, $^4J_{\text{C-F}}$ = 1.3 Hz), 130.3, 125.5 (q, $^3J_{\text{C-F}}$ = 3.9 Hz), 123.5 (q, $^1J_{\text{C-F}}$ = 271.6 Hz), 99.6, 75.2, 70.8, 67.1, 65.8, 55.6, 16.0; IR (KBr) ν = 3529, 3430, 2934, 1709, 1414, 1335, 1290, 1168, 1121, 1054, 961, 866, 776, 752, 709 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{F}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 373.0875, found 373.0859.

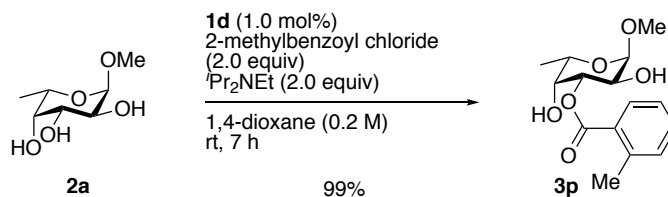
Methyl 3-*O*-4-nitrobenzoyl- α -L-fucopyranoside (**3o**)



4-Nitrobenzoyl chloride (74.2 mg, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 30 minutes, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3o** (56.7 mg, 0.173 mmol, 87%) as a white solid.

Data for **3o**: R_f = 0.37 (20/1 CHCl_3 / MeOH); mp 133-136 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{23}$ -185.2° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.29–8.24 (m, 4H), 5.29 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.85 (d, J = 4.0 Hz, 1H, *H*-1), 4.13 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 4.09 (q, J = 6.8 Hz, 1H, *H*-5), 3.99 (d, J = 3.2 Hz, 1H, *H*-4), 3.48 (s, 3H), 2.05 (br, 2H, OH-2, OH-4), 1.31 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 150.7, 135.2, 131.0, 123.5, 99.6, 75.6, 70.8, 67.0, 65.8, 55.6, 16.0; IR (KBr) ν = 3524, 3434, 2984, 2942, 2839, 1708, 1608, 1525, 1352, 1306, 1282, 1129, 1090, 1048, 959, 863, 759, 719, 684 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{NNaO}_8$ $[\text{M}+\text{Na}]^+$ 350.0852, found 350.0847.

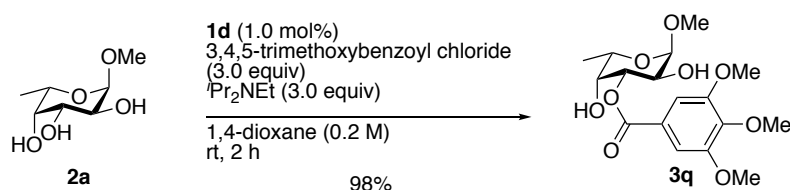
Methyl 3-*O*-2-methylbenzoyl- α -L-fucopyranoside (**3p**)



2-Methylbenzoyl chloride (52.0 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 7 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3p** (58.7 mg, 0.198 mmol, 99%) as a white solid.

Data for **3p**: R_f = 0.39 (20/1 CHCl_3 / MeOH); mp 94-97 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{23}$ -175.9° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.98–7.96 (m, 1H), 7.44–7.39 (m, 1H), 7.27–7.24 (m, 2H), 5.29 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.84 (d, J = 4.0 Hz, 1H, *H*-1), 4.11 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 4.08 (q, J = 6.8 Hz, 1H, *H*-5), 3.99 (d, J = 3.2 Hz, 1H, *H*-4), 3.47 (s, 3H), 2.61 (s, 3H), 1.94 (br, 2H, *OH*-2, *OH*-4), 1.31 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 140.3, 132.3, 131.7, 130.7, 129.3, 125.8, 99.7, 74.3, 70.9, 67.2, 65.7, 55.6, 21.7, 16.0; IR (KBr) ν = 3491, 2993, 2920, 2831, 1693, 1601, 1443, 1358, 1303, 1270, 1192, 1144, 1093, 1046, 959, 754, 740 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 319.1158, found 319.1148.

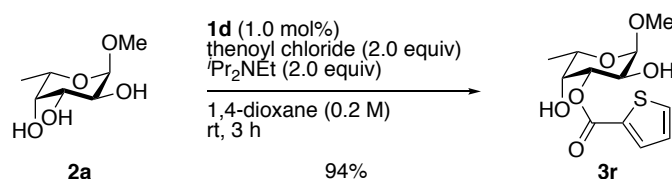
Methyl 3-*O*-3,4,5-trimethylgalloyl- α -L-fucopyranoside (**3q**)



3,4,5-Trimethylgalloyl chloride (138 μL , 0.600 mmol, 3.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 2.00 μmol , 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 0.00200 mmol, 1.0 mol%) and *N,N*-diisopropylethylamine (105 μL , 0.600 mmol, 3.0 equiv) under ambient atmosphere. After stirring for 2 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3q** (70.3 mg, 0.196 mmol, 98%) as a white solid.

Data for **3q**: R_f = 0.34 (20/1 CHCl_3 / MeOH); mp 132-136 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{23}$ -142.4° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.32 (s, 2H), 5.25 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.84 (d, J = 4.0 Hz, 1H, *H*-1), 4.13 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 4.08 (q, J = 6.4 Hz, 1H, *H*-5), 3.98 (d, J = 3.2 Hz, 1H, *H*-4), 3.90 (s, 6H), 3.89 (s, 3H), 3.47 (s, 3H), 2.00 (br, 2H, *OH*-2, *OH*-4), 1.31 (d, J = 6.4 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 152.9, 142.6, 124.7, 107.1, 99.7, 74.8, 70.8, 67.1, 65.7, 60.9, 56.3, 55.5, 16.0; IR (KBr) ν = 3312, 2943, 1703, 1590, 1508, 1459, 1418, 1362, 1337, 1231, 1130, 1037, 1007, 965, 868, 774 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{24}\text{NaO}_9$ $[\text{M}+\text{Na}]^+$ 395.1318, found 395.1299.

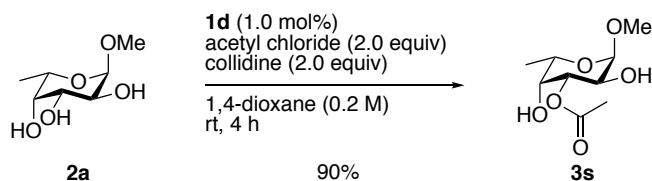
Methyl 3-*O*-2-thenoyl- α -L-fucopyranoside (**3r**)



2-Thenoyl chloride (42.5 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 3 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO₃ aq., water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 1) to give **3r** (54.2 mg, 0.189 mmol, 94%) as a white solid.

Data for **3r**: R_f = 0.38 (1/2 *n*-hexane / EtOAc); mp 124-126 °C; $[\alpha]_D^{23}$ -176.6° (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (dd, J = 4.0, 1.2 Hz, 1H), 7.59 (dd, J = 4.8, 1.2 Hz, 1H), 7.12 (dd, J = 4.8, 4.0 Hz, 1H), 5.24 (dd, J = 10.0, 2.8 Hz, 1H, *H*-3), 4.83 (d, J = 4.0 Hz, 1H, *H*-1), 4.10 (dd, J = 10.0, 4.0 Hz, 1H, *H*-2), 4.06 (q, J = 6.8 Hz, 1H, *H*-5), 3.97 (d, J = 2.8 Hz, 1H, *H*-4), 3.46 (s, 3H), 2.02 (br, 2H, OH-2, OH-4), 1.31 (d, J = 6.8 Hz, 3H, *H*-6); ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 134.1, 133.1, 133.0, 127.9, 99.7, 74.8, 70.9, 67.1, 65.7, 55.5, 16.0; IR (KBr) ν = 3357, 2992, 2938, 1710, 1525, 1450, 1419, 1364, 1260, 1170, 1088, 1041, 1006, 963, 859, 761, 749, 681, 636, 491 cm⁻¹; HRMS (ESI) m/z calcd for C₁₂H₁₆NaO₆S [M+Na]⁺ 311.0565, found 311.0551.

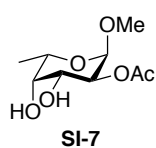
Methyl 3-*O*-acetyl- α -L-fucopyranoside (**3s**)



Acetyl chloride (28.3 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 4 hours, the resulting mixture was filtered through a short pad of silica gel by using pipette and washed with ethyl acetate and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3s** (39.6 mg, 0.180 mmol, 90%) as a white solid.

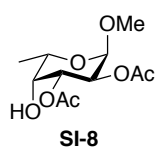
Data for **3s**: R_f = 0.24 (20/1 CHCl_3 / MeOH); mp 112-114 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23}$ -213.4° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.06 (dd, J = 10.4, 2.8 Hz, 1H, H -3), 4.79 (d, J = 4.0 Hz, 1H, H -1), 4.00 (q, J = 6.8 Hz, 1H, H -5), 3.95 (dd, J = 10.4, 4.0 Hz, 1H, H -2), 3.84 (d, J = 2.8 Hz, 1H, H -4), 3.44 (s, 3H), 2.16 (s, 3H), 1.91 (br, 2H, OH -2, OH -4), 1.28 (d, J = 6.8 Hz, 3H, H -6); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 99.6, 73.8, 70.8, 67.1, 65.7, 55.5, 21.1, 16.0; IR (KBr) ν = 3499, 3435, 2989, 2969, 2947, 2920, 2849, 1711, 1388, 1261, 1085, 1028, 963, 803, 755, 646, 483 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{16}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 243.0845, found 243.0839.

Methyl 2-*O*-acetyl- α -L-fucopyranoside (**SI-7**)



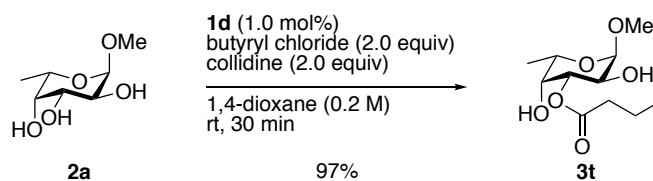
Data for **SI-7**: colorless amorphous material; R_f = 0.20 (1/2 *n*-hexane / EtOAc); $[\alpha]_D^{23}$ -182.3° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 4.98 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 4.83 (d, J = 4.0 Hz, 1H, *H*-1), 3.99–3.94 (m, 2H, *H*-3, *H*-5), 3.80 (d, J = 3.2 Hz, 1H, *H*-4), 3.36 (s, 3H), 3.00 (br, 1H, OH), 2.89 (br, 1H, OH), 2.14 (s, 3H), 1.29 (d, J = 6.4 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 97.3, 72.4, 71.6, 68.6, 65.4, 55.3, 21.1, 16.0; IR (neat) ν = 3561, 3330, 2993, 2924, 1736, 1490, 1366, 1249, 1193, 1163, 1141, 1098, 1054, 997, 961, 926, 896, 869, 804, 674, 419 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{16}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 243.0845, found 243.0837.

Methyl 2,3-*O*-diacetyl- α -L-fucopyranoside (**SI-8**)



Data for **SI-8**: colorless oil; R_f = 0.36 (1/1 *n*-hexane / EtOAc); $[\alpha]_D^{24}$ -158.1° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.26 (dd, J = 10.8, 2.8 Hz, 1H, *H*-3), 5.19 (dd, J = 10.8, 3.6 Hz, 1H, *H*-2), 4.90 (d, J = 3.6 Hz, 1H, *H*-1), 4.04 (q, J = 6.8 Hz, 1H, *H*-5), 3.92 (br, 1H, *H*-4), 3.38 (s, 3H), 2.11 (br, 1H, OH-4), 2.09 (s, 3H), 2.07 (s, 3H), 1.28 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 170.0, 97.2, 70.7, 70.6, 68.1, 65.2, 55.3, 20.9, 20.8, 15.9; IR (neat) ν = 3495, 2939, 1742, 1373, 1234, 1197, 1164, 1120, 1056, 966, 931, 770 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$ 285.0950, found 285.0944.

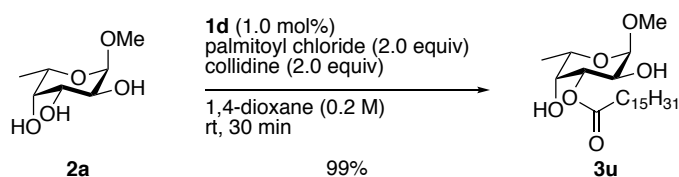
Methyl 3-*O*-butyryl- α -L-fucopyranoside (**3t**)



Butyryl chloride (41.8 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 30 minutes, the resulting mixture was filtered through a short pad of silica gel by using pipette and washed with ethyl acetate and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 1) to give **3t** (48.1 mg, 0.194 mmol, 97%) as a colorless amorphous material.

Data for **3t**: R_f = 0.23 (1/1 *n*-hexane / EtOAc); $[\alpha]_D^{23}$ -169.5° (c = 1.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.08 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.79 (d, J = 4.0 Hz, 1H, *H*-1), 3.99 (br q, J = 6.8 Hz, 1H, *H*-5), 3.95 (dt, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.83 (br t, J = 3.2 Hz, 1H, *H*-4), 3.44 (s, 3H), 2.41 (dt, J = 15.2, 7.6 Hz, 1H), 2.38 (dt, J = 15.2, 7.6 Hz, 1H), 1.97 (br d, J = 10.4 Hz, 1H, *OH*-2), 1.94 (br d, J = 3.2 Hz, 1H, *OH*-4), 1.69 (sext, J = 7.6 Hz, 2H), 1.28 (d, J = 6.8 Hz, 3H, *H*-6), 0.97 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 99.7, 73.5, 70.9, 67.1, 65.6, 55.5, 36.2, 18.5, 16.0, 13.6; IR (neat) ν = 3486, 2936, 1720, 1289, 1159, 1051, 961, 871 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{20}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 271.1158, found 271.1158.

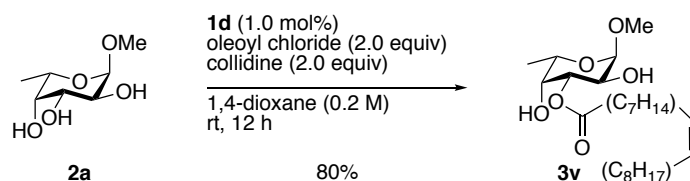
Methyl 3-*O*-palmitoyl- α -L-fucopyranoside (**3u**)



Palmitoyl chloride (121 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%, 0.2 M) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 30 minutes, the resulting mixture was filtered through a short pad of silica gel by using pipette and washed with ethyl acetate and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **3u** (82.4 mg, 0.198 mmol, 99%) as a white solid.

Data for **3u**: R_f = 0.20 (2/1 *n*-hexane / EtOAc); mp 66-68 $^{\circ}$ C; $[\alpha]_D^{23}$ -111.4° (c = 1.0, CHCl₃); ^1H NMR (400 MHz, CDCl₃) δ 5.08 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.79 (d, J = 4.0 Hz, 1H, *H*-1), 4.01 (br q, J = 6.8 Hz, 1H, *H*-5), 3.95 (dt, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.84 (br t, J = 3.2 Hz, 1H, *H*-4), 3.44 (s, 3H), 2.42 (dt, J = 15.6, 7.6 Hz, 1H), 2.39 (dt, J = 15.6, 7.6 Hz, 1H), 1.97 (br d, J = 10.4 Hz, 1H, OH-2), 1.94 (br d, J = 3.2 Hz, 1H, OH-4), 1.65 (quint, J = 7.6 Hz, 2H), 1.29 (d, J = 6.8 Hz, 3H, *H*-6), 1.25 (br s, 24H), 0.88 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl₃) δ 173.7, 99.7, 73.5, 70.9, 67.1, 65.7, 55.5, 34.3, 31.9, 29.67, 29.66, 29.65, 29.63, 29.62, 29.58, 29.4, 29.3, 29.2, 29.1, 25.0, 22.6, 16.0, 14.1; IR (KBr) ν = 3518, 3436, 2915, 2847, 1708, 1467, 1425, 1383, 1343, 1245, 1225, 1204, 1186, 1155, 1090, 1062, 1003, 967, 769, 720 cm^{-1} ; HRMS (ESI) m/z calcd for C₂₃H₄₄NaO₆ [M+Na]⁺ 439.3036, found 439.3030.

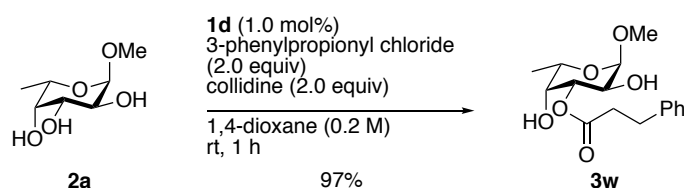
Methyl 3-*O*-oleoyl- α -L-fucopyranoside (**3v**)



Oleoyl chloride (132 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 12 hours, the resulting mixture was filtered through a short pad of silica gel by using pipette and washed with ethyl acetate and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 4 : 1) to give **3v** (70.9 mg, 0.160 mmol, 80%) as a colorless oil.

Data for **3v**: R_f = 0.30 (2/1 *n*-hexane / EtOAc); $[\alpha]_D^{23}$ -109.5° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.37–5.28 (m, 2H), 5.05 (dd, J = 10.4, 2.8 Hz, 1H, *H*-3), 4.77 (d, J = 4.0 Hz, 1H, *H*-1), 3.99 (q, J = 6.8 Hz, 1H, *H*-5), 3.94 (dt, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.82 (br, 1H, *H*-4), 3.42 (s, 3H), 2.42 (quin, J = 8.0 Hz, 1H), 2.37 (quin, J = 8.0 Hz, 1H), 2.01–1.97 (m, 6H), 1.64 (quin, J = 8.0 Hz, 2H), 1.29–1.26 (m, 23H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.7, 123.0, 129.7, 99.7, 73.5, 70.8, 67.1, 65.6, 55.4, 34.3, 31.9, 29.7, 29.6, 29.5, 29.3, 29.12, 29.05, 29.0, 27.2, 27.1, 24.9, 22.6, 16.0, 14.1; IR (neat) ν = 3460, 2926, 2854, 1737, 1465, 1383, 1364, 1194, 1163, 1055, 961, 759, 723, 680 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{46}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 465.3192, found 465.3185.

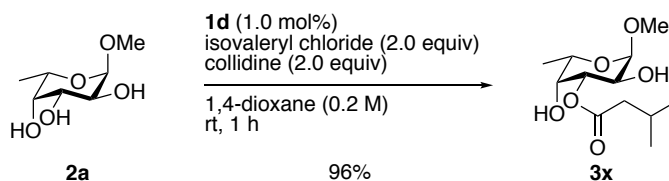
Methyl 3-*O*-3-phenylpropionyl- α -L-fucopyranoside (**3w**)



3-Phenylpropionyl chloride (59.2 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 1 hour, the resulting mixture was filtered through a short pad of silica gel by using pipette and washed with ethyl acetate and extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 1) to give **3w** (60.2 mg, 0.194 mmol, 97%) as a white solid.

Data for **3w**: R_f = 0.38 (1/2 *n*-hexane / EtOAc); mp 108-110 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23}$ -151.4° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.28 (m, 2H), 7.23–7.20 (m, 3H), 5.02 (dd, J = 10.4, 2.8 Hz, 1H, *H*-3), 4.76 (d, J = 4.0 Hz, 1H, *H*-1), 3.95 (q, J = 6.4 Hz, 1H, *H*-5), 3.92 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.68 (d, J = 2.8 Hz, 1H, *H*-4), 3.42 (s, 3H), 3.01 (dt, J = 15.2, 7.6 Hz, 1H), 2.96 (dt, J = 15.2, 7.6 Hz, 1H), 2.78 (dt, J = 15.2, 7.6 Hz, 1H), 2.75 (dt, J = 15.2, 7.6 Hz, 1H), 1.25 (d, J = 6.4 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 140.2, 128.5, 128.3, 126.4, 99.6, 73.9, 70.7, 66.9, 65.6, 55.5, 35.8, 31.0, 16.0; IR (KBr) ν = 3374, 3005, 2938, 2890, 1697, 1415, 1390, 1359, 1309, 1198, 1166, 1091, 1069, 960, 758, 698 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{22}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 333.1314, found 333.1298.

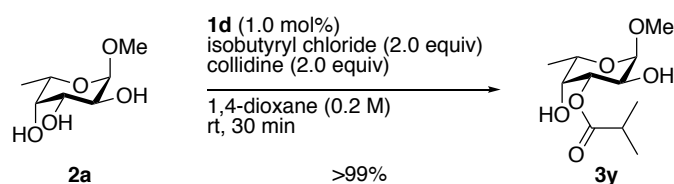
Methyl 3-*O*-isovaleryl- α -L-fucopyranoside (**3x**)



Isovaleryl chloride (48.7 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%, 0.2 M) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 1 hour, the resulting mixture was filtered through a short pad of silica gel by using pipette and washed with ethyl acetate and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **3x** (50.4 mg, 0.192 mmol, 96%) as a white solid.

Data for **3x**: R_f = 0.30 (1/1 *n*-hexane / EtOAc); mp 92-94 $^{\circ}$ C; $[\alpha]_D^{23}$ -192.3° (c = 1.0, CHCl₃); ^1H NMR (400 MHz, CDCl₃) δ 5.09 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.79 (d, J = 4.0 Hz, 1H, *H*-1), 4.01 (br q, J = 6.8 Hz, 1H, *H*-5), 3.95 (dt, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.84 (br t, J = 3.2 Hz, 1H, *H*-4), 3.44 (s, 3H), 2.32 (dd, J = 14.8, 7.2 Hz, 1H), 2.28 (dd, J = 14.8, 7.2 Hz, 1H), 2.19–2.09 (m, 1H), 1.93 (d, J = 10.4 Hz, 1H, *OH*-2), 1.88 (br d, J = 3.2 Hz, 1H, *OH*-4), 1.29 (d, J = 6.8 Hz, 3H, *H*-6), 0.99 (d, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CDCl₃) δ 172.9, 99.7, 73.5, 71.0, 67.1, 65.7, 55.5, 43.4, 25.9, 22.33, 22.32, 16.0; IR (KBr) ν = 3472, 2958, 1719, 1368, 1296, 1052, 961, 871 cm^{-1} ; HRMS (ESI) m/z calcd for C₁₂H₂₂NaO₆ $[M+\text{Na}]^+$ 285.1314, found 285.1315.

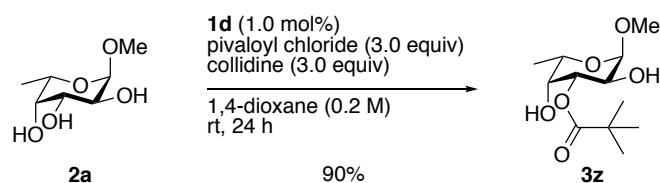
Methyl 3-*O*-isobutyryl- α -L-fucopyranoside (**3y**)



Isobutyryl chloride (42.2 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.20 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 30 minutes, the resulting mixture was filtered through a short pad of silica gel by using pipette and washed with ethyl acetate and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 1) to give **3y** (50.0 mg, 0.201 mmol, >99%) as a white solid.

Data for **3y**: R_f = 0.25 (1/1 *n*-hexane / EtOAc); mp 97-100 $^{\circ}$ C; $[\alpha]_D^{23}$ -200.8° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.05 (dd, J = 10.4, 3.2 Hz, 1H, H -3), 4.79 (d, J = 4.0 Hz, 1H, H -1), 4.01 (br q, J = 6.8 Hz, 1H, H -5), 3.96 (dt, J = 10.4, 4.0 Hz, 1H, H -2), 3.84 (br, 1H, H -4), 3.44 (s, 3H), 2.66 (sept, J = 6.8 Hz, 1H), 1.94 (d, J = 10.4 Hz, 1H, OH -2), 1.92 (br d, J = 3.2 Hz, 1H, OH -4), 1.28 (d, J = 6.8 Hz, 3H, H -6), 1.21 (d, J = 6.8 Hz, 3H), 1.20 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.0, 99.7, 73.5, 70.9, 67.2, 65.7, 55.5, 34.1, 19.01, 19.00, 16.0; IR (KBr) ν = 3480, 2938, 1728, 1196, 1158, 1051, 961, 758 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{20}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 271.1158, found 271.1163.

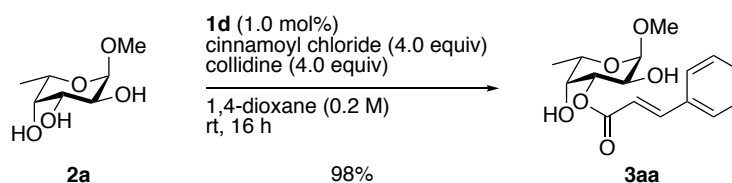
Methyl 3-*O*-pivaloyl- α -L-fucopyranoside (**3z**)



Pivaloyl chloride (73.1 μ L, 0.600 mmol, 3.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (79.8 μ L, 0.600 mmol, 3.0 equiv) in dry 1,4-dioxane under ambient atmosphere. After stirring for 24 hours, the resulting mixture was filtered through a short pad of silica gel by using pipette and washed with ethyl acetate and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3z** (47.3 mg, 0.180 mmol, 90%) as a white solid.

Data for **3z**: R_f = 0.45 (20/1 CHCl_3 / MeOH); mp 96-98 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23}$ -188.1° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.04 (dd, J = 10.4, 3.2 Hz, 1H, H -3), 4.78 (d, J = 4.0 Hz, 1H, H -1), 4.01 (br q, J = 6.8 Hz, 1H, H -5), 3.96 (br, 1H, H -2), 3.83 (d, J = 3.2 Hz, 1H, H -4), 3.44 (s, 3H), 1.89 (br, 2H, OH -2, OH -4), 1.29 (d, J = 6.8 Hz, 3H, H -6), 1.25 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.3, 99.7, 73.5, 70.9, 67.2, 65.7, 55.5, 39.0, 27.2, 16.0; IR (KBr) ν = 3465, 2929, 1734, 1191, 1050, 961, 755 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{22}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$ 285.1314, found 285.1328.

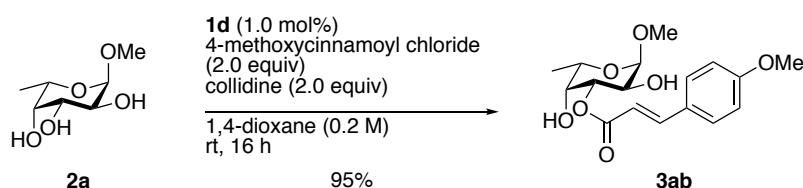
Methyl 3-*O*-cinnamoyl- α -L-fucopyranoside (**3aa**)



Cinnamoyl chloride (133 mg, 0.800 mmol, 4.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (106 μ L, 0.800 mmol, 4.0 equiv) under ambient atmosphere. After stirring for 16 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO₃ aq., water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **3aa** (60.4 mg, 0.196 mmol, 98%) as a colorless amorphous material.

Data for **3aa**: R_f = 0.25 (1/1 *n*-hexane / EtOAc); $[\alpha]_D^{23}$ -190.5° (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, 16.0 Hz, 1H), 7.54–7.52 (m, 2H), 7.40–7.38 (m, 3H), 6.54 (d, J = 16.0 Hz, 1H), 5.18 (dd, J = 10.0 Hz, 2.8 Hz, 1H, *H*-3), 4.83 (d, J = 4.0 Hz, 1H, *H*-1), 4.08–4.03 (m, 2H, *H*-2, *H*-5), 3.93 (br d, J = 2.8 Hz, 1H, *H*-4), 3.46 (s, 3H), 1.97 (br, 2H, *OH*-2, *OH*-4), 1.30 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.8, 145.9, 134.2, 130.5, 128.9, 128.2, 117.5, 99.7, 74.0, 70.9, 67.1, 65.7, 55.5, 16.0; IR (neat) ν = 3463, 2933, 1698, 1636, 1313, 1161, 1051, 961, 768 cm⁻¹; HRMS (ESI) m/z calcd for C₁₆H₂₀NaO₆ [M+Na]⁺ 331.1158, found 331.1164.

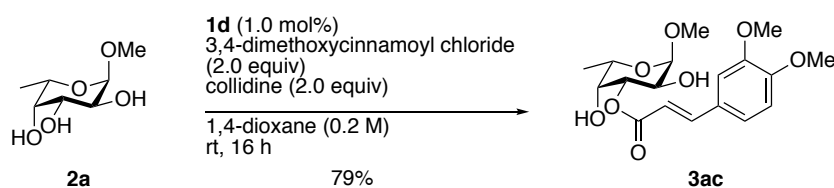
Methyl 3-*O*-4-methoxycinnamoyl- α -L-fucopyranoside (**3ab**)



4-Methoxycinnamoyl chloride (78.7 mg, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 16 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO₃ aq., water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **3ab** (64.2 mg, 0.190 mmol, 95%) as a colorless amorphous material.

Data for **3ab**: R_f = 0.18 (2/1 *n*-hexane / EtOAc); $[\alpha]_D^{24}$ -183.3° (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 5.16 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.81 (d, J = 4.0 Hz, 1H, *H*-1), 4.06 (dt, J = 10.4, 4.0 Hz, 1H, *H*-2), 4.04 (br q, J = 6.8 Hz, 1H, *H*-5), 3.92 (br, 1H, *H*-4), 3.82 (s, 3H), 3.44 (s, 3H), 2.19 (br, 1H, OH-4), 2.14 (d, J = 10.4 Hz, 1H, OH-2), 1.29 (d, J = 6.8 Hz, 3H, *H*-6); ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 161.5, 145.6, 129.9, 126.9, 114.8, 114.3, 99.7, 73.8, 70.8, 67.1, 65.7, 55.5, 55.3, 16.0; IR (neat) ν = 3461, 2936, 1699, 1605, 1514, 1423, 1255, 1174, 1053, 961, 830, 756 cm⁻¹; HRMS (ESI) m/z calcd for C₁₇H₂₂NaO₇ [M+Na]⁺ 361.1263, found 361.1255.

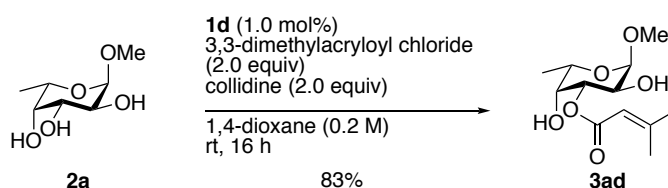
Methyl 3-*O*-3,4-dimethoxycinnamoyl- α -L-fucopyranoside (**3ac**)



3,4-Dimethoxycinnamoyl chloride (90.7 mg, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 16 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO₃ aq., water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3ac** (58.2 mg, 0.158 mmol, 79%) as a colorless amorphous material.

Data for **3ac**: R_f = 0.43 (20/1 CHCl₃ / MeOH); $[\alpha]_D^{23}$ -142.7° (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 16.0 Hz, 1H), 7.09 (dd, J = 8.4, 1.6 Hz, 1H), 7.04 (d, J = 1.6 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 5.16 (dd, J = 10.0, 2.8 Hz, 1H, *H*-3), 4.82 (d, J = 4.0 Hz, 1H, *H*-1), 4.06 (dd, J = 10.0, 4.0 Hz, 1H, *H*-2), 4.04 (q, J = 6.8 Hz, 1H, *H*-5), 3.93 (d, J = 2.8 Hz, 1H, *H*-4), 3.90 (s, 3H), 3.89 (s, 3H), 3.45 (s, 3H), 2.21 (br, 2H, *OH*-2, *OH*-4), 1.29 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 151.3, 149.1, 145.8, 127.1, 122.9, 115.0, 110.9, 109.5, 99.7, 73.9, 70.8, 67.1, 65.7, 55.9, 55.8, 55.5, 16.0; IR (neat) ν = 3483, 2937, 1703, 1633, 1599, 1514, 1465, 1262, 1159, 1140, 1052, 809, 755 cm⁻¹; HRMS (ESI) m/z calcd for C₁₈H₂₄NaO₈ [M+Na]⁺ 391.1369, found 391.1367.

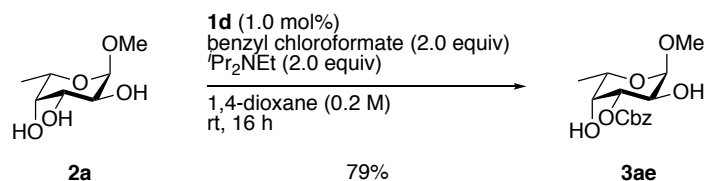
Methyl 3-*O*-3,3-dimethylacryloyl- α -L-fucopyranoside (**3ad**)



3,3-Dimethylacryloyl chloride (44.5 μ L, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μ mol, 1.0 mol%) and collidine (53.2 μ L, 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 16 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO₃ aq., water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3ad** (43.2 mg, 0.166 mmol, 83%) as a white solid.

Data for **3ad**: R_f = 0.37 (20/1 CHCl₃ / MeOH); mp 91-93 °C; $[\alpha]_D^{23}$ -209.9° (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 5.80 (sep, J = 1.2 Hz, 1H), 5.10 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.80 (d, J = 4.0 Hz, 1H, *H*-1), 4.02 (br q, J = 6.4 Hz, 1H, *H*-5), 3.98 (dt, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.87 (br t, J = 3.2 Hz, 1H, *H*-4), 3.44 (s, 3H), 2.18 (d, J = 1.2 Hz, 3H), 2.00 (br d, J = 10.4 Hz, 1H, *OH*-2), 1.92 (br d, J = 3.2 Hz, 1H, *OH*-4), 1.92 (d, J = 1.2 Hz, 3H), 1.29 (d, J = 6.4 Hz, 3H, *H*-6); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 158.7, 115.5, 99.7, 72.8, 71.0, 67.2, 65.7, 55.5, 27.5, 20.4, 16.0; IR (KBr) ν = 3574, 3369, 2984, 2937, 1714, 1652, 1450, 1383, 1234, 1197, 1151, 1087, 1039, 960, 853, 750 cm⁻¹; HRMS (ESI) m/z calcd for C₁₂H₂₀NaO₆ [M+Na]⁺ 283.1158, found 283.1154.

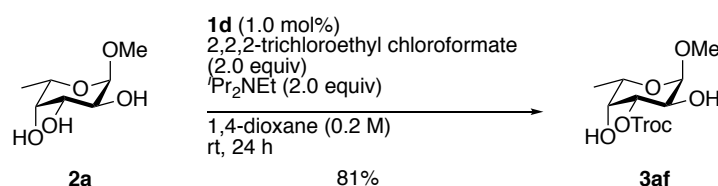
Methyl 3-*O*-benzyloxycarbonyl- α -L-fucopyranoside (**3ae**)



Benzyl chloroformate (56.4 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 16 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **3ae** (49.1 mg, 0.157 mmol, 79%) as a colorless amorphous material.

Data for **3ae**: R_f = 0.37 (1/1 *n*-hexane / EtOAc); $[\alpha]_{\text{D}}^{23}$ -138.6° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.34 (m, 5H), 5.21 (d, J = 12.0 Hz, 1H), 5.17 (d, J = 12.0 Hz, 1H), 4.91 (dd, J = 10.0, 2.8 Hz, 1H, *H*-3), 4.80 (d, J = 4.0 Hz, 1H, *H*-1), 4.02 (dd, J = 10.0, 4.0 Hz, 1H, *H*-2), 3.99 (q, J = 6.8 Hz, 1H, *H*-5), 3.92 (br d, J = 2.8 Hz, 1H, *H*-4), 3.44 (s, 3H), 2.00 (br, 2H, *OH*-2, *OH*-4), 1.29 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 134.8, 128.64, 128.61, 128.4, 99.6, 77.9, 70.5, 70.1, 67.0, 65.6, 55.5, 16.0; IR (neat) ν = 3471, 2937, 1743, 1455, 1387, 1269, 1055, 963, 758 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$ 335.1107, found 335.1119.

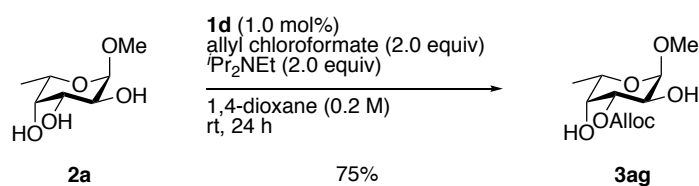
Methyl 3-*O*-2,2,2-trichloroethyloxycarbonyl- α -L-fucopyranoside (**3af**)



2,2,2-Trichloroethyl chloroformate (53.6 μL , 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 0.00200 mmol, 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 24 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (chloroform : methanol = 100 : 1) to give **3af** (57.5 mg, 0.163 mmol, 81%) as a white solid.

Data for **3af**: R_f = 0.39 (20/1 CHCl_3 / MeOH); mp 114-117 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{23}$ -127.6° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 4.94 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.83 (d, J = 12.0 Hz, 1H), 4.80 (d, J = 4.0 Hz, 1H, *H*-1), 4.75 (d, J = 12.0 Hz, 1H), 4.06 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.99 (q, J = 6.8 Hz, 1H, *H*-5), 3.96 (d, J = 3.2 Hz, 1H, *H*-4), 3.44 (s, 3H), 2.14 (br, 2H, *OH*-2, *OH*-4), 1.29 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 153.8, 99.5, 94.2, 79.1, 77.0, 70.3, 66.9, 65.7, 55.5, 16.0; IR (KBr) ν = 3521, 3403, 2992, 2919, 1761, 1449, 1388, 1274, 1248, 1168, 1140, 1054, 964, 825, 764, 733, 713, 568 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{15}^{35}\text{Cl}_3\text{NaO}_7$ $[\text{M}+\text{Na}]^+$ 374.9781, found 374.9777.

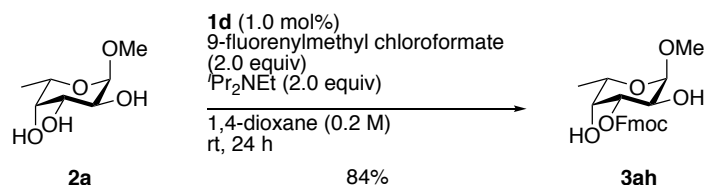
Methyl 3-*O*-allyloxycarbonyl- α -L-fucopyranoside (**3ag**)



Allyl chloroformate (42.1 μL , 0.400 mmol, 2.0 equiv) was added to a stirred solution of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 0.00200 mmol, 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 24 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 1) to give **3ag** (39.4 mg, 0.150 mmol, 75%) as a white solid.

Data for **3ag**: R_f = 0.40 (1/2 *n*-hexane / EtOAc); mp 112-114 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23}$ -171.1° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 5.94 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.38 (dq, J = 17.2, 1.2 Hz, 1H), 5.29 (dq, J = 10.4, 1.2 Hz, 1H), 4.89 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3), 4.80 (d, J = 4.0 Hz, 1H, *H*-1), 4.65 (dt, J = 5.6, 1.2 Hz, 2H), 4.02 (dd, J = 10.4, 4.0 Hz, 1H, *H*-2), 3.99 (q, J = 6.8 Hz, 1H, *H*-5), 3.92 (d, J = 3.2 Hz, 1H, *H*-4), 3.44 (s, 3H), 2.01 (br, 2H, *OH*-2, *OH*-4), 1.29 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 131.2, 119.3, 99.6, 77.8, 70.5, 68.9, 67.0, 65.6, 55.5, 16.0; IR (KBr) ν = 3575, 3345, 2986, 2941, 2839, 1740, 1458, 1389, 1277, 1199, 1159, 1089, 1054, 960, 786, 764 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$ 285.0950, found 285.0946.

Methyl 3-*O*-9-fluorenylmethyloxycarbonyl- α -L-fucopyranoside (**3ah**)

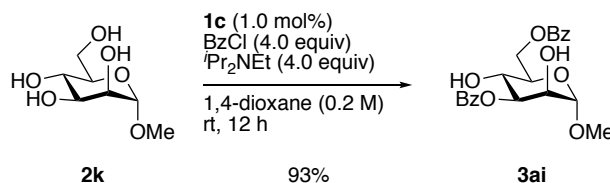


9-Fluorenylmethyl chloroformate (51.7 mg, 0.400 mmol, 2.0 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 24 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **3ah** (67.1 mg, 0.168 mmol, 84%) as a white solid.

Data for **3ah**: R_f = 0.50 (1/2 *n*-hexane / EtOAc); mp 174-178 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23}$ -121.3° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 4.89 (dd, J = 10.0, 2.8 Hz, 1H, *H*-3), 4.81 (d, J = 3.6 Hz, 1H, *H*-1), 4.51 (dd, J = 10.4, 7.2 Hz, 1H), 4.42 (dd, J = 10.4, 7.2 Hz, 1H), 4.28 (t, J = 7.2 Hz, 1H), 4.06 (dd, J = 10.0, 3.6 Hz, 1H, *H*-2), 3.98 (q, J = 6.8 Hz, 1H, *H*-5), 3.90 (d, J = 2.8 Hz, 1H, *H*-4), 3.44 (s, 3H), 2.06 (br, 2H, *OH*-2, *OH*-4), 1.30 (d, J = 6.8 Hz, 3H, *H*-6); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 143.3, 143.1, 141.3, 141.2, 127.9, 127.2, 125.2, 125.1, 120.04, 120.02, 99.6, 77.9, 70.5, 70.1, 67.0, 65.7, 55.5, 46.7, 16.0; IR (KBr) ν = 3510, 3429, 2988, 2936, 2892, 2839, 1728, 1450, 1393, 1282, 1202, 1164, 1096, 1058, 969, 759, 736 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{24}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$ 423.1420, found 423.1414.

9. Boronic acid catalyzed site-selective dibenzoylations (Scheme 4)

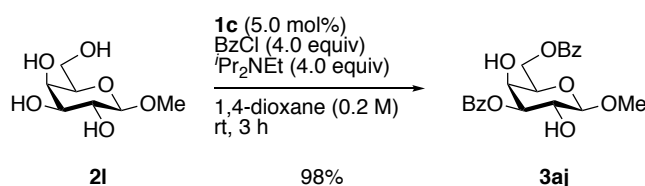
Methyl 3,6-*O*-dibenzoyl- α -D-mannopyranoside (**3ai**)



Benzoyl chloride (93.8 μL , 0.800 mmol, 4.0 equiv) was added to a stirred mixture of methyl α -D-mannopyranoside (**2k**) (38.8 mg, 0.200 mmol, 1.0 equiv), boronic acid **1c** (0.002 M in 1,4-dioxane, 1.00 mL, 2.00 μmol , 1.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) under ambient atmosphere. After stirring for 12 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **3ai** (74.4 mg, 0.185 mmol, 93%) as a colorless oil.

Data for **3ai**: R_f = 0.31 (2/1 *n*-hexane / EtOAc); $[\alpha]_{\text{D}}^{24}$ +61.9° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.08–8.05 (m, 4H), 7.58–7.53 (m, 2H), 7.44–7.39 (m, 4H), 5.36 (dd, J = 9.8, 3.2 Hz, 1H, *H*-3), 4.78 (d, J = 1.8 Hz, 1H, *H*-1), 4.73 (dd, J = 12.0, 5.2 Hz, 1H, *H*-6), 4.61 (dd, J = 12.0, 2.2 Hz, 1H, *H*-6), 4.17 (dd, J = 3.2, 1.8 Hz, 1H, *H*-2), 4.13 (t, J = 9.8 Hz, 1H, *H*-4), 4.61 (ddd, J = 9.8, 5.2, 2.2 Hz, 1H, *H*-5), 3.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 166.7, 133.4, 133.2, 129.9, 129.8, 129.7, 129.5, 128.41, 128.39, 100.7, 75.0, 70.9, 69.3, 65.9, 64.0, 55.0; IR (neat) ν = 3454, 1714, 1452, 1277, 1117, 1059, 757, 712 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{NaO}_8$ $[\text{M}+\text{Na}]^+$ 425.1212, found 425.1202.

Methyl 3,6-*O*-dibenzoyl-β-D-galactopyranoside (**3aj**)⁶

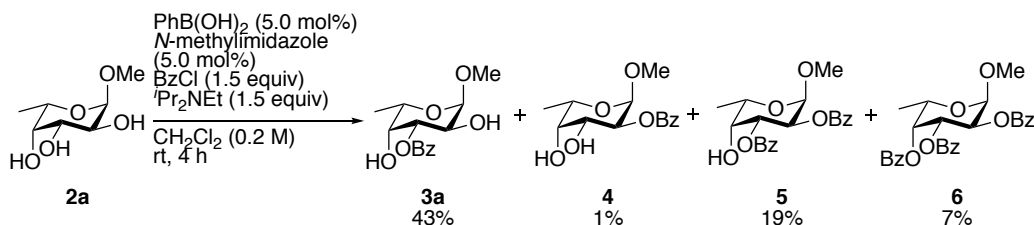


Benzoyl chloride (46.9 μL , 0.400 mmol, 4.0 equiv) was added to a stirred solution of methyl β -D-galactopyranoside (**2l**) (19.4 mg, 0.10 mmol, 1.0 equiv), boronic acid **1c** (1.01 mg, 5.00 μmol , 5.0 mol%) and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 4.0 equiv) in dry 1,4-dioxane (0.5 mL, 0.2 M) under ambient atmosphere. After stirring for 3 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography (hexane : ethyl acetate = 2 : 1) to give **3aj** (29.3 mg, 0.0982 mmol, 98%) as a white solid.

Data for **3aj**: R_f = 0.13 (2/1 *n*-hexane / EtOAc); mp 132–134 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{23}$ -5.6° (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.08 (m, 2H), 8.04–8.02 (m, 2H), 7.59–7.55 (m, 2H), 7.46–7.42 (m, 4H), 5.14 (dd, J = 10.1, 3.3 Hz, 1H, *H*-3), 4.65 (dd, J = 11.4, 6.6 Hz, 1H, *H*-6), 4.56 (dd, J = 11.4, 6.6 Hz, 1H, *H*-6), 4.36 (d, J = 7.7 Hz, 1H, *H*-1), 4.24 (br, 1H, *H*-4), 4.05 (dd, J = 10.1, 7.7 Hz, 1H, *H*-2), 3.97 (t, J = 6.6 Hz, 1H, *H*-5), 3.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 166.1, 133.5, 133.3, 129.9, 129.7, 129.5, 129.4, 128.46, 128.45, 104.3, 75.4, 72.3, 69.4, 67.2, 62.6, 57.2; IR (KBr) ν = 3548, 2920, 1715, 1450, 1284, 1121, 1070, 712, 772 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{NaO}_8$ $[\text{M}+\text{Na}]^+$ 425.1212, found 425.1202.

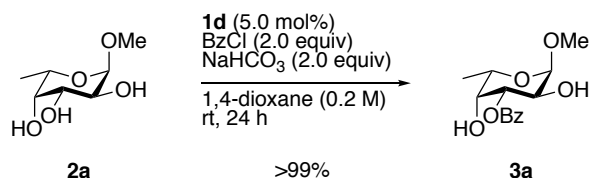
10. Control experiments for mechanistic studies (Scheme 5)

a) PhB(OH)₂ / *N*-methylimidazole as catalyst



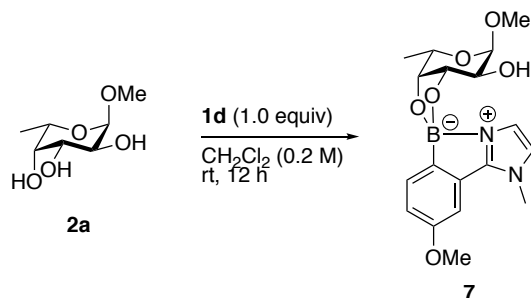
Benzoyl chloride (17.6 μL , 0.150 mmol, 1.5 equiv) was added to a stirred mixture of methyl α -L-fucopyranoside (**2a**) (17.8 mg, 0.100 mmol, 1.0 equiv), phenyl boronic acid (0.610 mg, 5.00 μmol , 5.0 mol%), *N*-methylimidazole (0.01 M in dichloromethane, 0.5 mL, 5.00 μmol , 5 mol%) and *N,N*-diisopropylethylamine (26.1 μL , 0.150 mmol, 1.5 equiv) under ambient atmosphere. After stirring for 4 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The yields were determined by ^1H -NMR analysis of crude product mixture using 1,1,2,2-tetrachloroethane as an internal standard.

b) **1d** as catalyst with NaHCO_3



Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred solution of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), boronic acid **1d** (2.32 mg, 10.0 μmol , 5.0 mol%), and NaHCO_3 (33.6 mg, 0.400 mmol, 2.0 equiv) in dry 1,4-dioxane (1.0 mL, 0.2 M) under ambient atmosphere. After stirring for 4 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The yield was determined by ^1H -NMR analysis of crude product mixture using 1,1,2,2-tetrachloroethane as an internal standard.

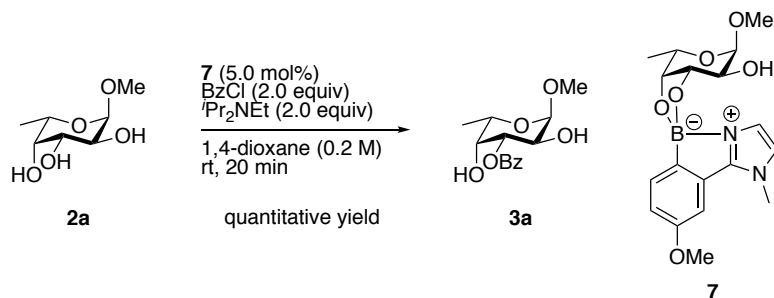
Preparation of 7



Methyl α -L-fucopyranoside (**2a**) (17.6 mg, 0.100 mmol, 1.0 equiv) and boronic acid **1d** (23.2 mg, 0.100 mmol, 1.0 equiv) were dissolved in dry dichloromethane (0.5 mL, 0.2 M) under ambient atmosphere. After stirring for 12 hours, the resulting mixture was concentrated *in vacuo*. The resulting crude material was used in the next reaction without further purification.

Data for **7**: $[\alpha]_{\text{D}}^{25} -67.3^\circ$ ($c = 1.0$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.0$ Hz, 1H), 7.09 (d, $J = 0.8$ Hz, 1H), 6.98 (d, $J = 1.6$ Hz, 1H), 6.89 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.80 (d, $J = 0.8$ Hz, 1H), 4.84 (br, 1H, H -1), 4.34 (t, $J = 5.2$ Hz, 1H, H -3), 4.19–4.15 (m, 2H, H -4, H -5), 4.02 (br, 1H, H -2), 3.85 (s, 3H), 3.81 (s, 3H), 3.48 (s, 3H), 2.62 (br, 1H, OH -2), 1.32 (d, $J = 6.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 132.5, 131.6, 123.7, 121.2, 114.3, 107.7, 98.8, 75.9, 75.1, 71.1, 65.6, 55.5, 55.2, 34.5, 16.4; IR (neat) $\nu = 3404, 2934, 1614, 1567, 1515, 1255, 1173, 1074, 982, 752\text{ cm}^{-1}$; HRMS (FAB) m/z calcd for $\text{C}_{18}\text{H}_{24}^{11}\text{BN}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ 375.1727, found 375.1727.

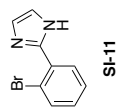
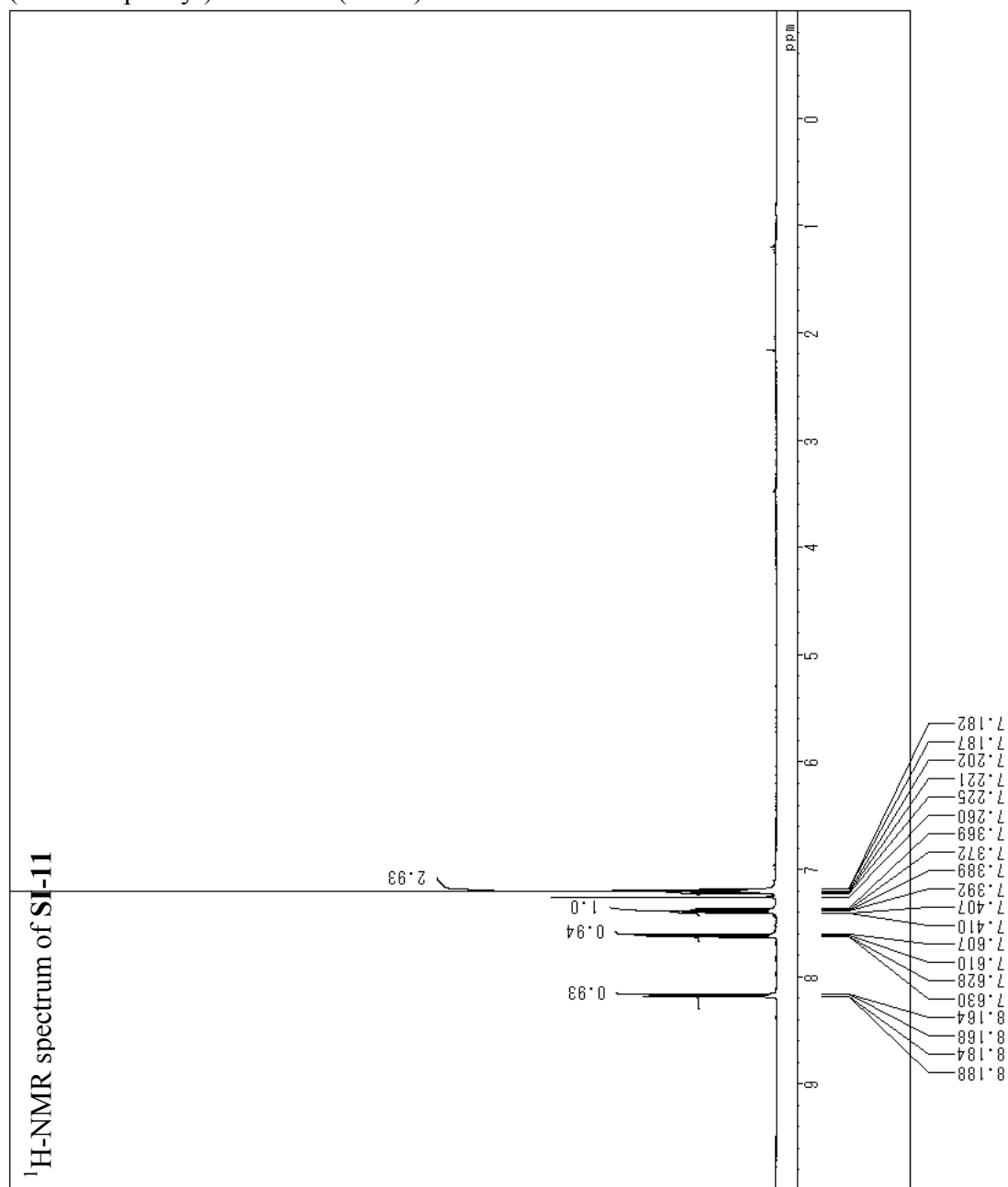
c) **7** as catalyst



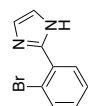
Benzoyl chloride (46.9 μL , 0.400 mmol, 2.0 equiv) was added to a stirred solution of methyl α -L-fucopyranoside (**2a**) (35.6 mg, 0.200 mmol, 1.0 equiv), **7** (3.74 mg, 10.0 μmol , 5.0 mol%), and *N,N*-diisopropylethylamine (69.6 μL , 0.400 mmol, 2.0 equiv) in dry 1,4-dioxane (1.0 mL, 0.2 M) under ambient atmosphere. After stirring for 4 hours, the reaction was quenched by addition of 1 M HCl (2.0 mL) and the resulting mixture was extracted two times with ethyl acetate. The combined organic layers were washed with sat. NaHCO_3 aq., water and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The yield was determined by ^1H -NMR analysis of crude product mixture using 1,1,2,2-tetrachloroethane as an internal standard.

11. ^1H , ^1H - ^1H COSY, ^{13}C NMR spectra

2-(2-Bromophenyl)imidazole (SI-11)



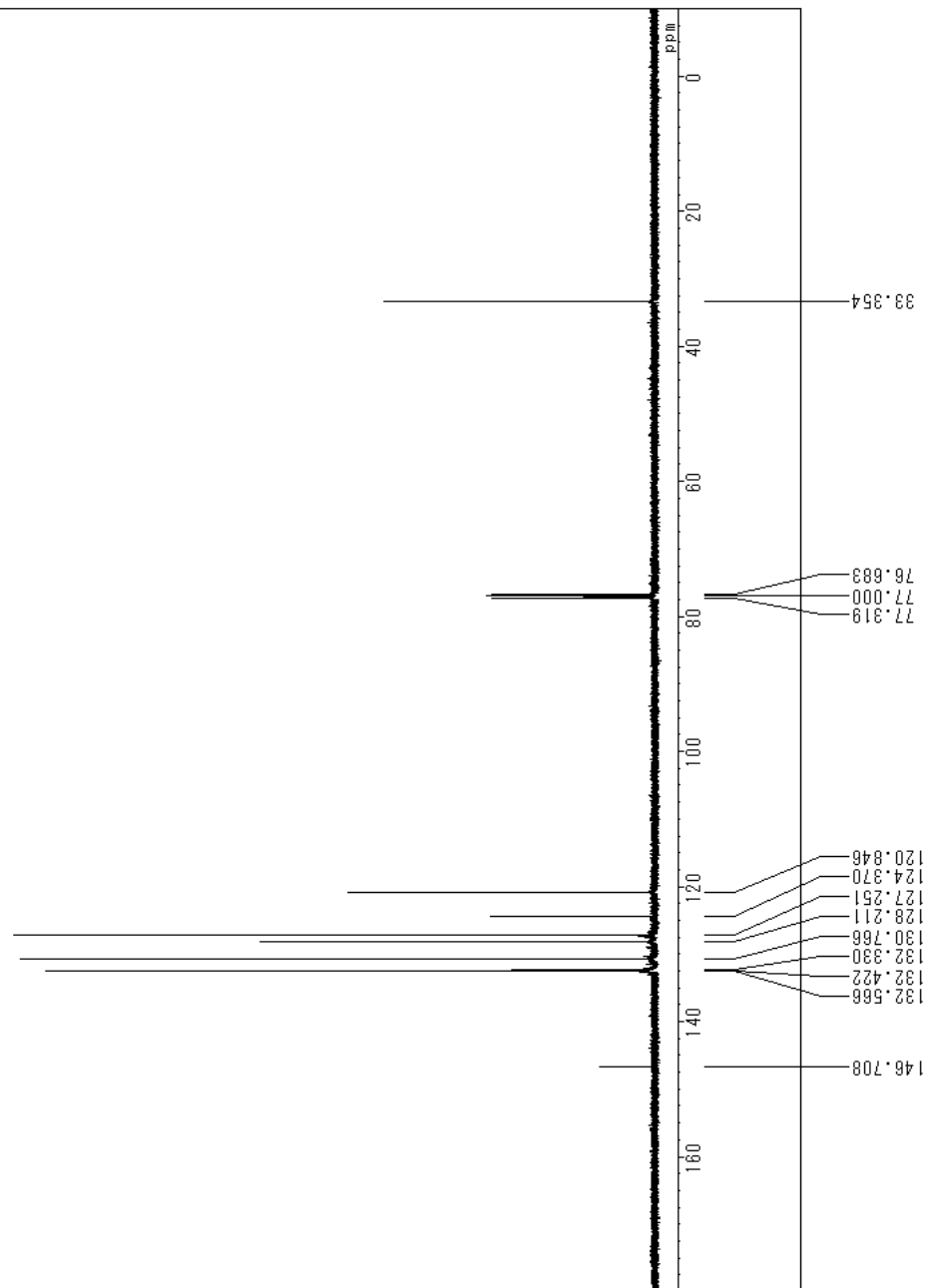
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 ExMode: PROTON_001
 ObsFreq: 400.28 MHz
 Scan: 8
 AcqTime: 2.5559 s
 Acc. Interval: 5.5559 s
 Spinning: 16.0 Hz
 Temperature: 25.0 $^{\circ}\text{C}$
 Solvent: cdcl_3



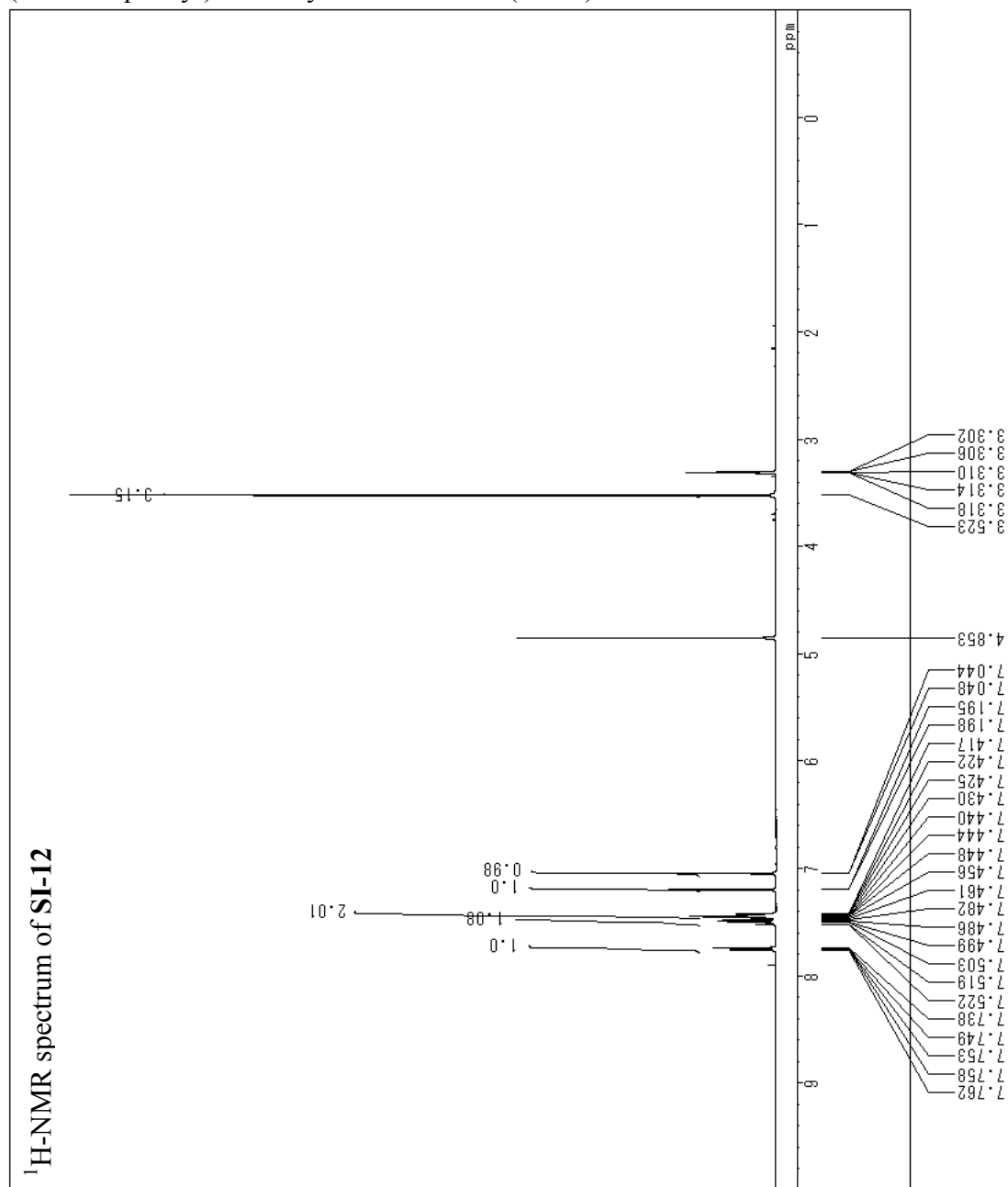
SI-11

Comment T40-17-23-C 20151221_01
 Date 2015/Dec/21
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 256
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

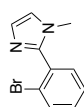
¹³C-NMR spectrum of SI-11



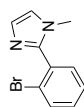
2-(2-Bromophenyl)-1-methyl-1*H*-imidazole (SI-12)



Comment BNO_01_003_pure_20170217
 Date_01 2017/Feb/17
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 400.28 MHz
 Scan 32
 AcqTime 2.5559 s
 Acc. Interval 5.5559 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

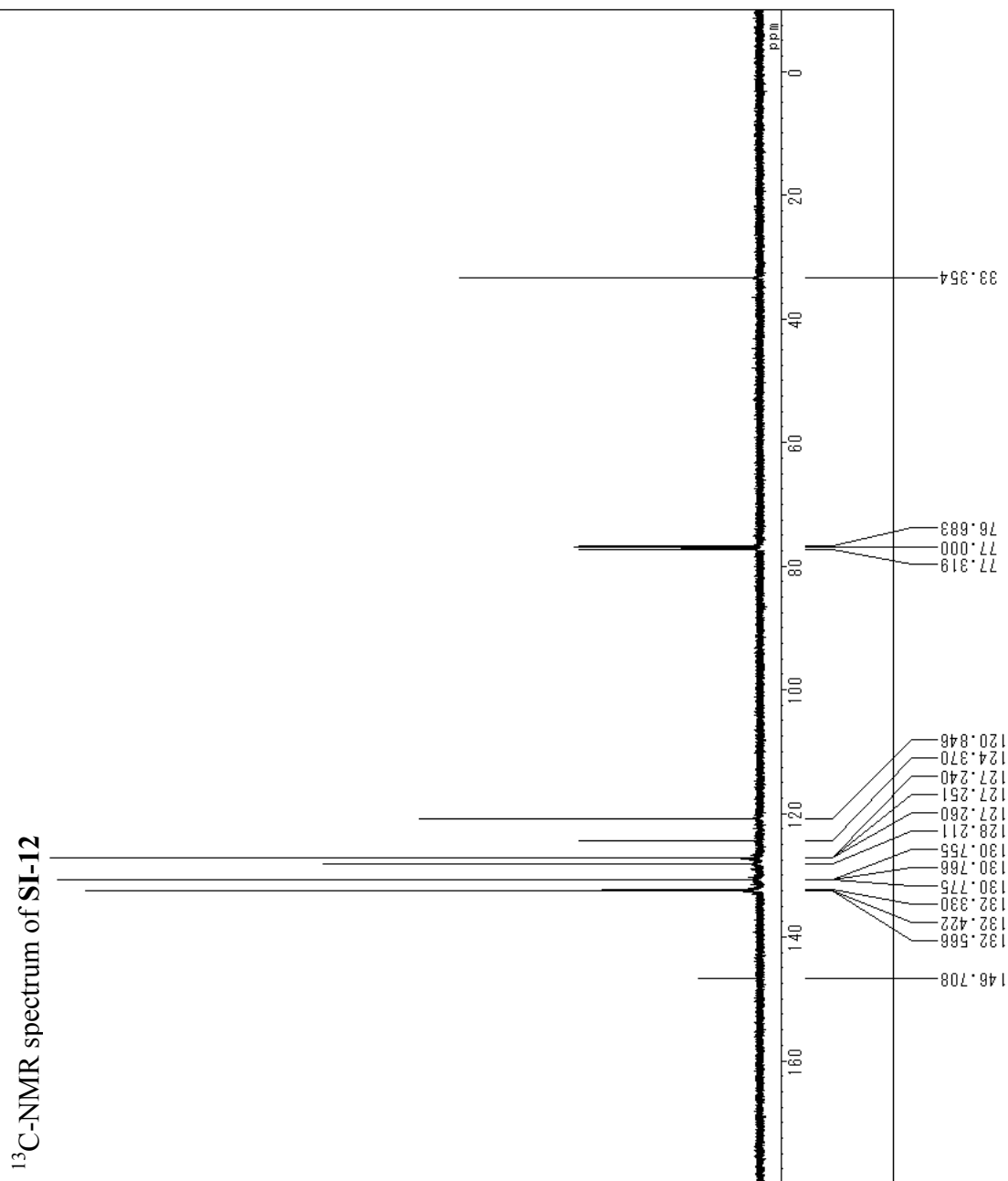


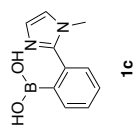
SI-12



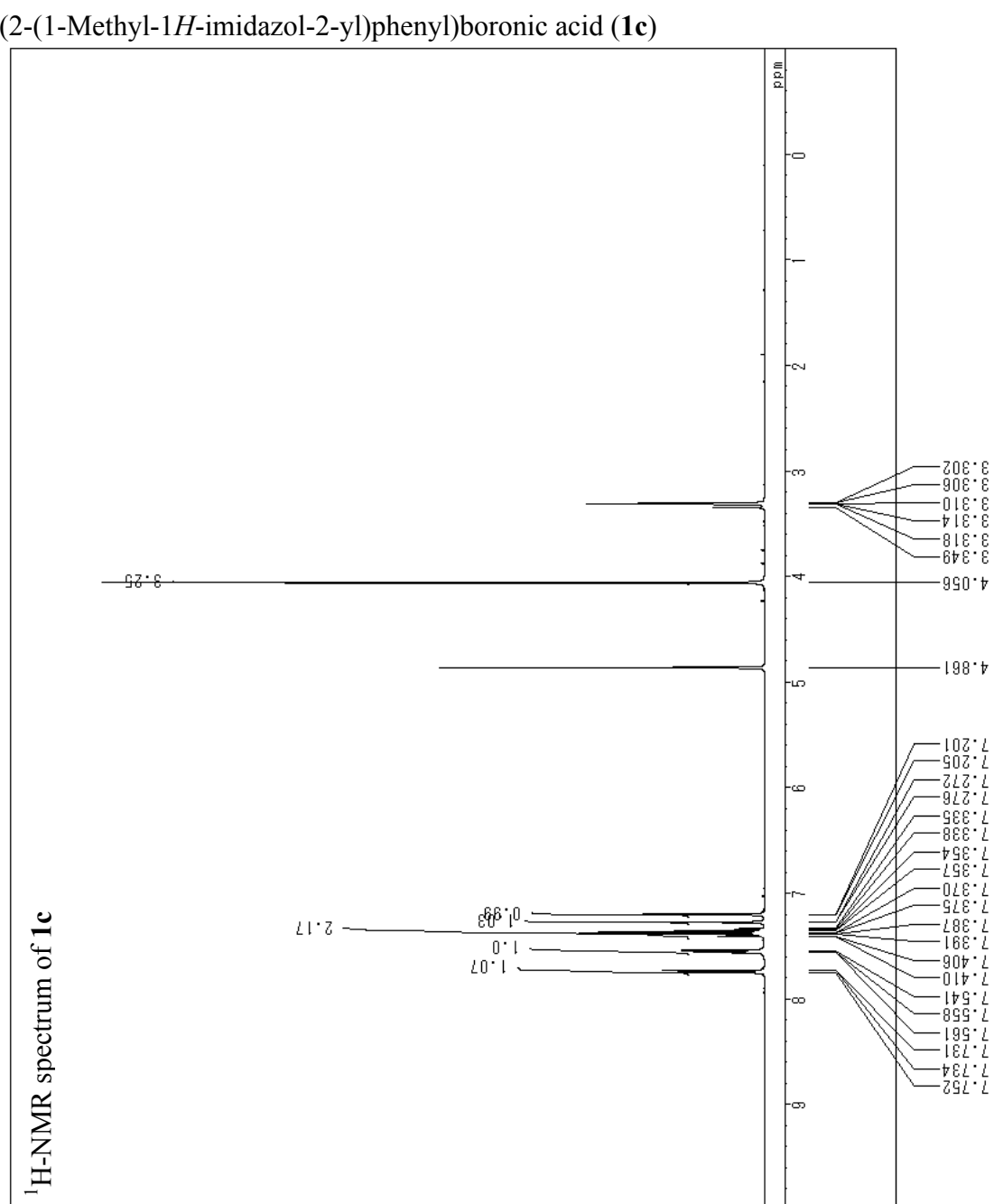
SI-12

Comment TMO-17-23-C-20151221_01
 Date 2015/Dec/21
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 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 256
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

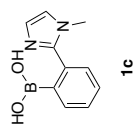




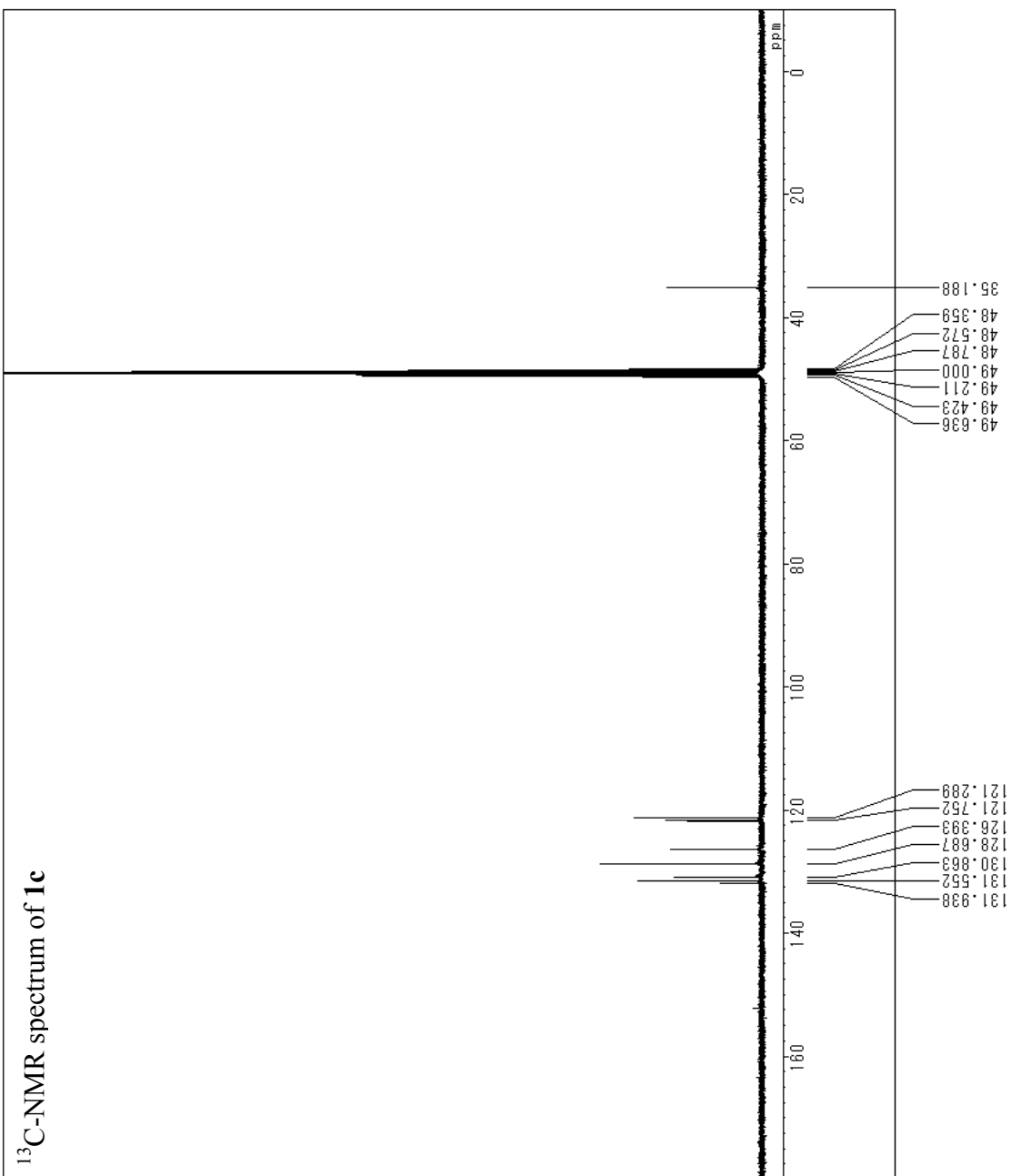
Comment cat_H 13C_20190118_01
 Date 2019/Jan/18
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 400.28 MHz
 Scan 16
 AcqTime 2.5559 s
 Acc. Interval 5.5559 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdso₃d



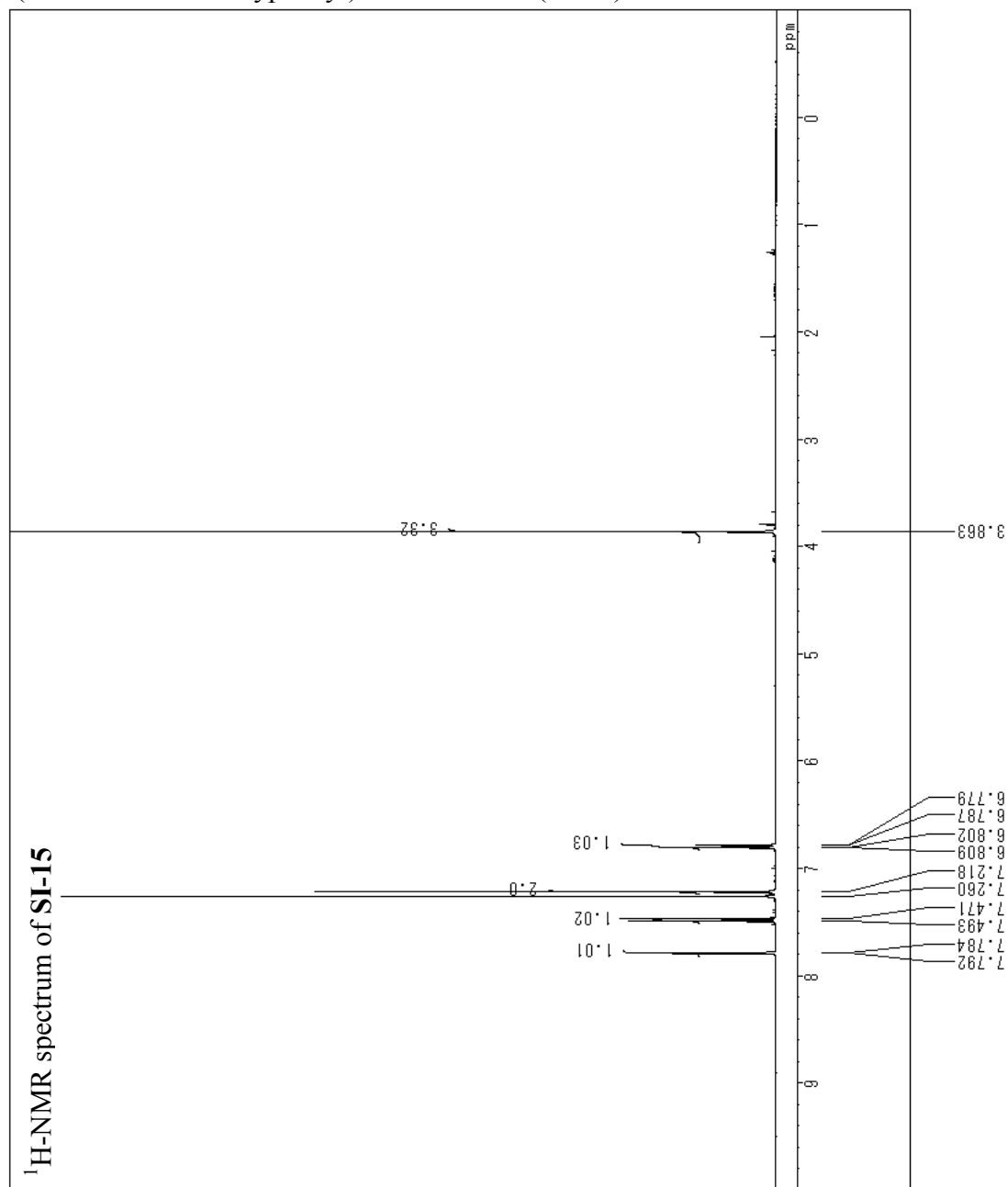
(2-(1-Methyl-1*H*-imidazol-2-yl)phenyl)boronic acid (**1c**)



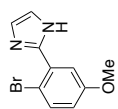
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 Date 2019/Jan/18
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 1024
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdso₃d



2- (2-Bromo-5-methoxyphenyl)-1*H*-imidazole (**SI-15**)



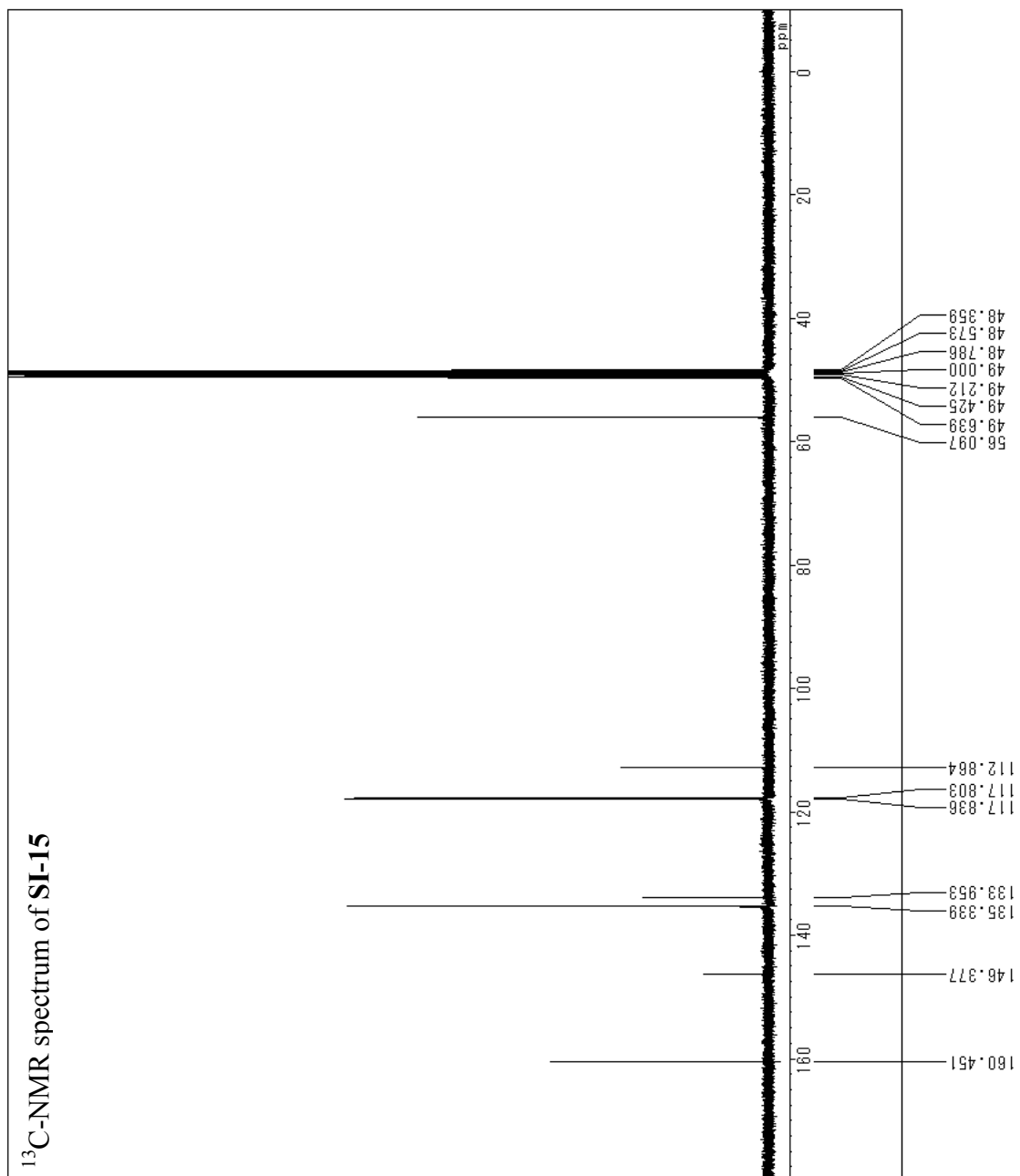
Comment TSV05039_pure_20160329_01
 Date 2016/Mar/29
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 32
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 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



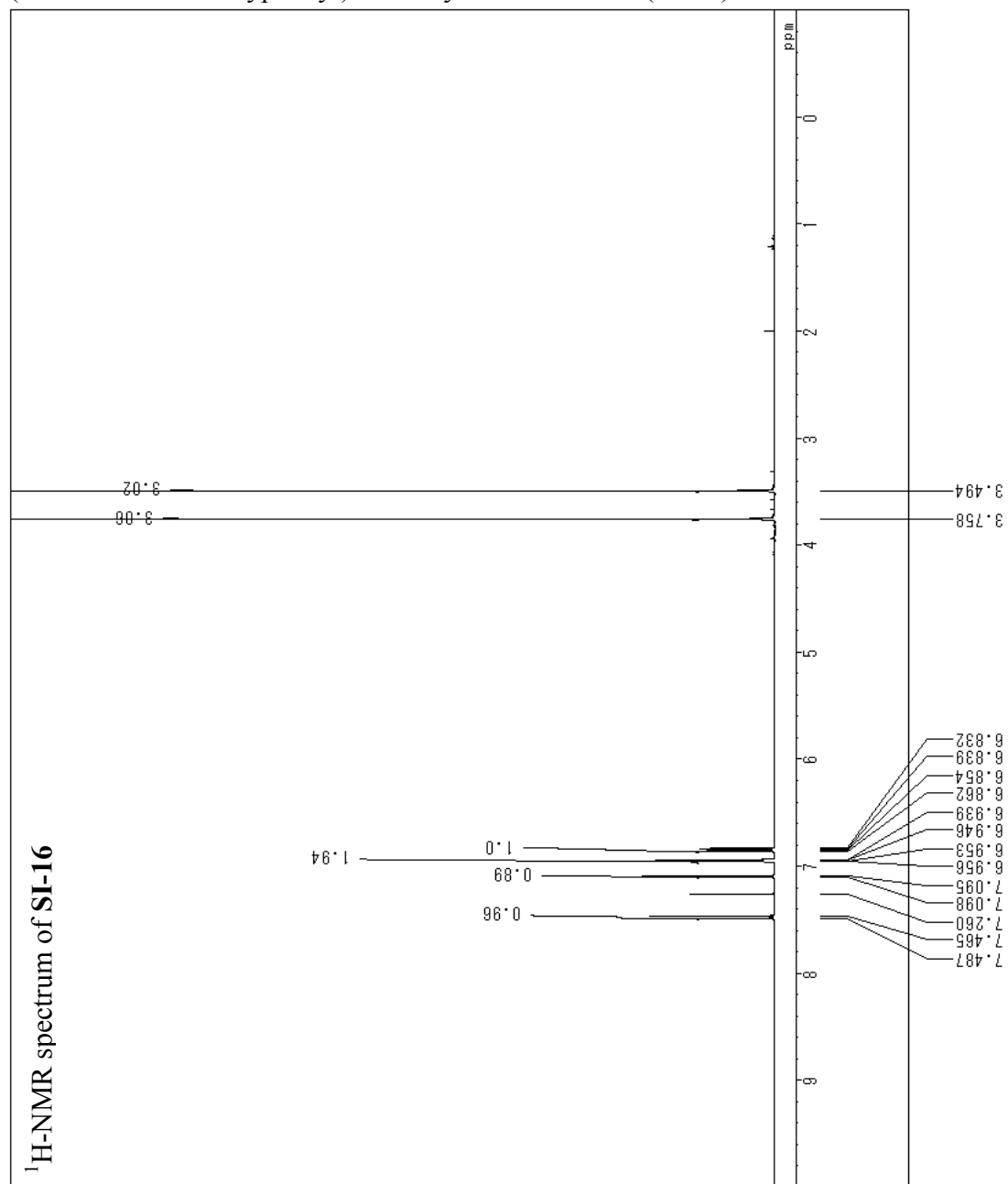
SI-15

¹³C-NMR spectrum of SI-15

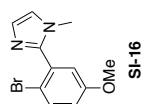
Comment TSV07003_SM_13C_20180518
 Date_01 2018/May/18
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 256
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdsod

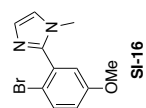


2-(2-Bromo-5-methoxyphenyl)-1-methyl-1*H*-imidazole (SI-16)

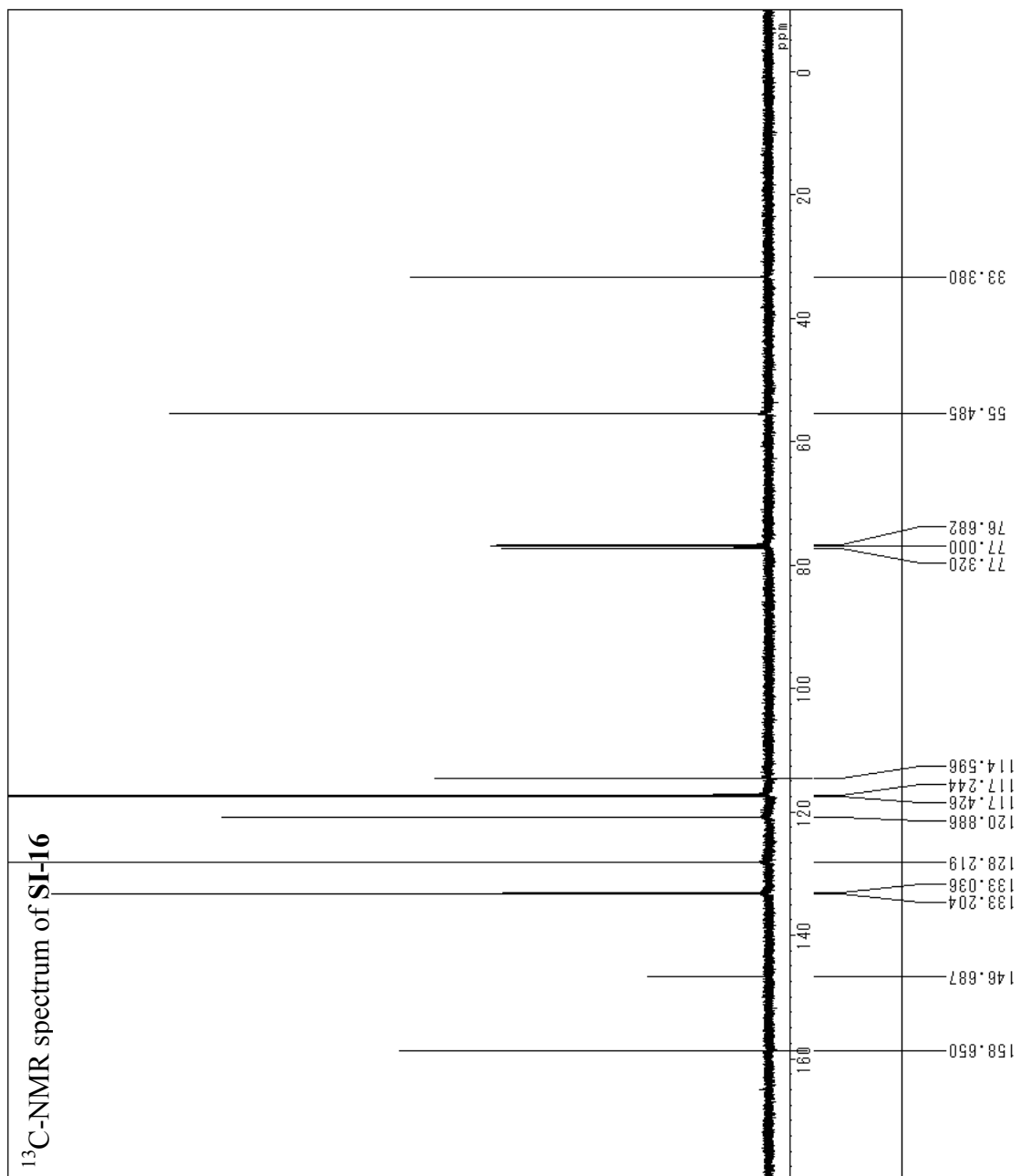


Comment TSV07003_column_20180512
 Date_01 2018/May/12
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl3

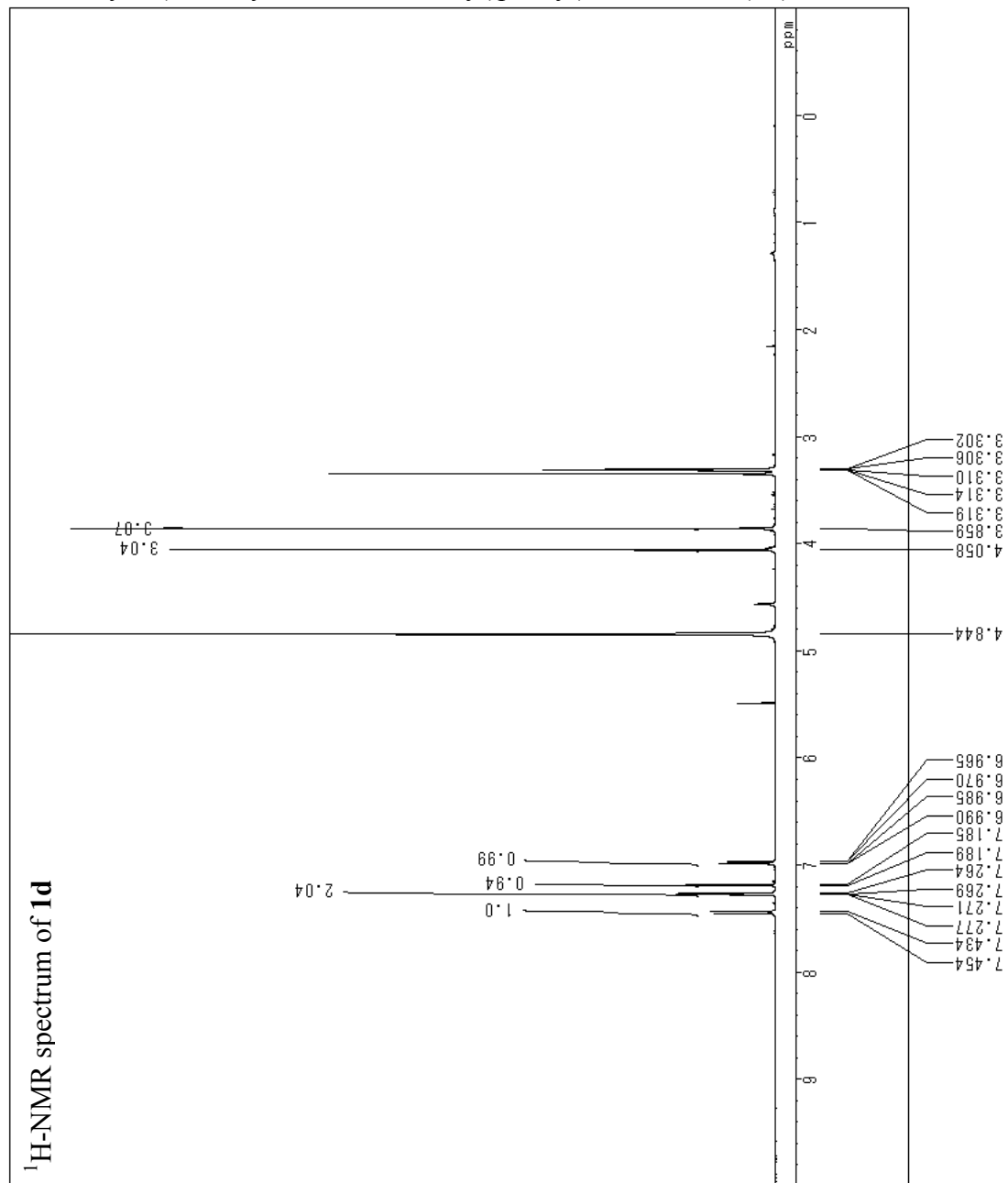




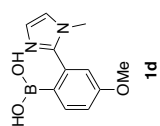
Comment TSV07003_13C_20180512_01
 Date 2018/May/12
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 256
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

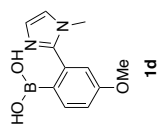


(4-Methoxy-2-(1-methyl-1*H*-imidazol-2-yl)phenyl)boronic acid (**1d**)



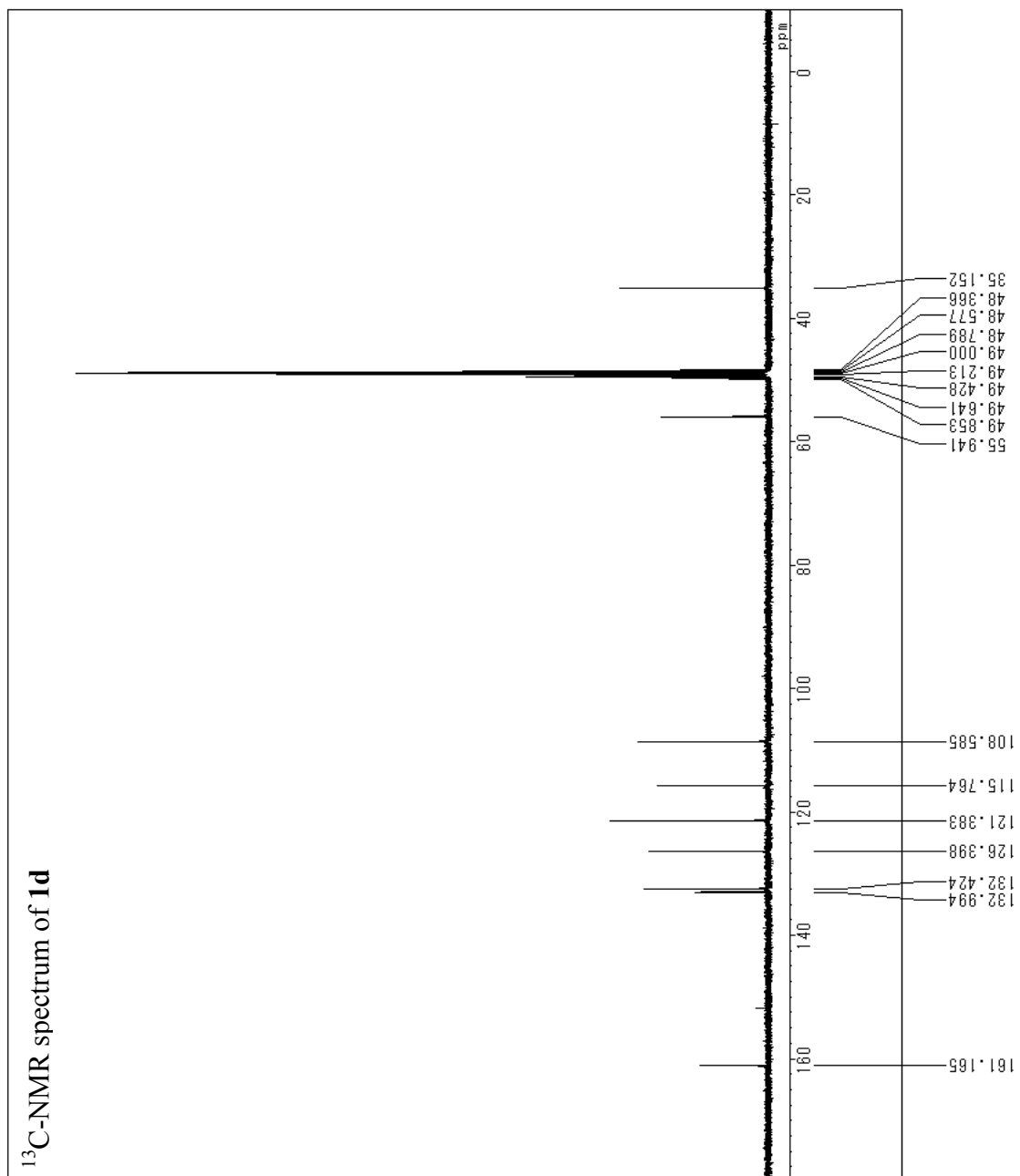
Comment_RYU02033_pure_column_20170612_01
 Date_2017/Jun/12
 ObsNuc_1H
 ExMode_PROTON_001
 ObsFreq_399.45 MHz
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 Acc. Interval_5.589 s
 Spinning_16.0 Hz
 Temperature_25.0 °C
 Solvent_cdsod



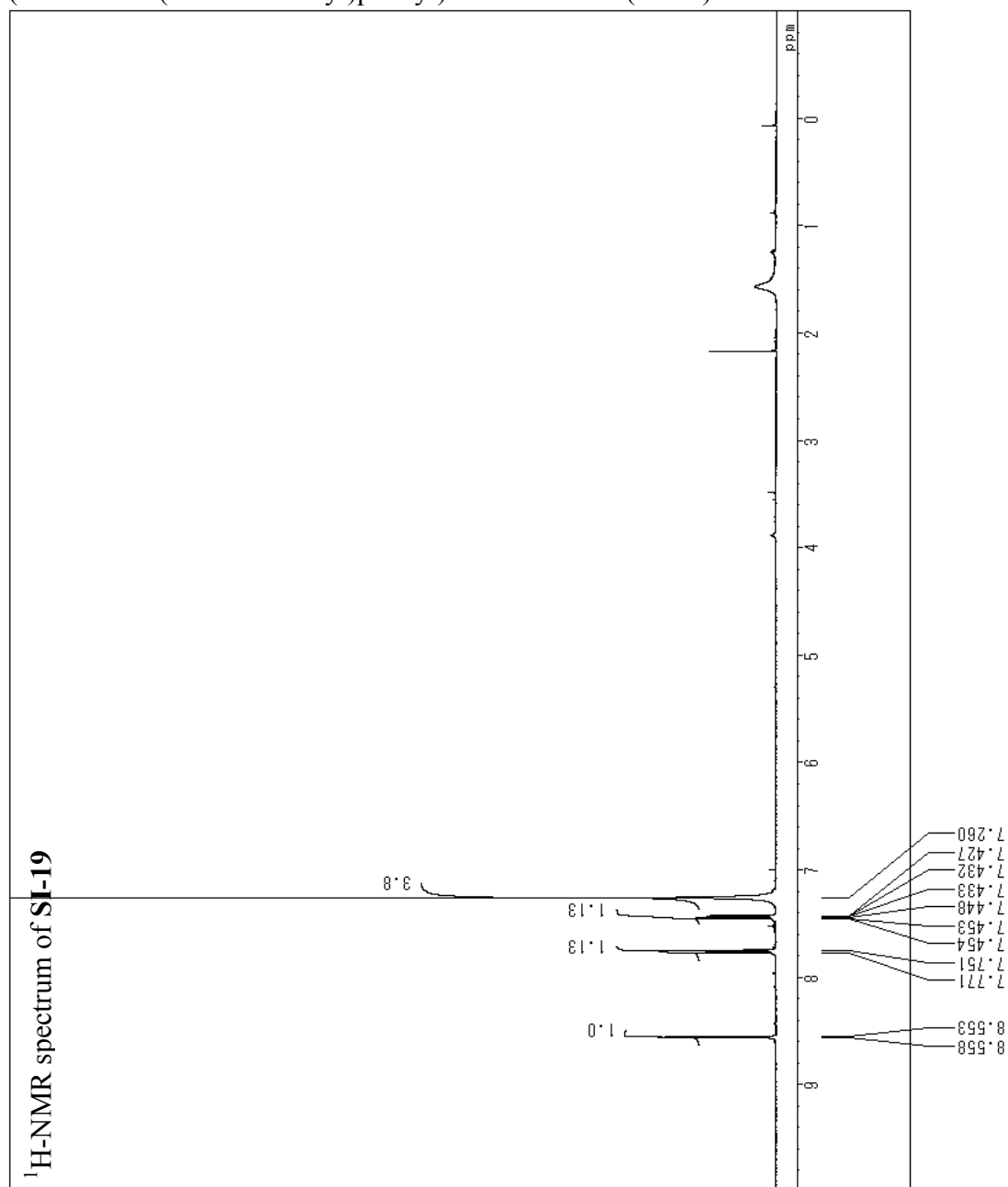


Comment_RVU02033_pure_CARBON_MeO
 Date_D_20170813_01
 ObsNuc_2017/Jun/13
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 CARBON_001
 ObsFreq_100.66 MHz
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 Acc. Interval_3.3831 s
 Spinning_20.0 Hz
 Temperature_25.0 °C
 Solvent_cdsod

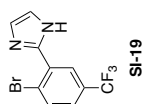
¹³C-NMR spectrum of **1d**

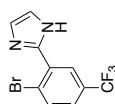


2-(2-Bromo-5-(trifluoromethyl)phenyl)-1*H*-imidazole (SI-19)



Comment TSV_recrystal_20170131_0
 Date 2017/Jan/31
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 300.45 MHz
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 AcqTime 2.569 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

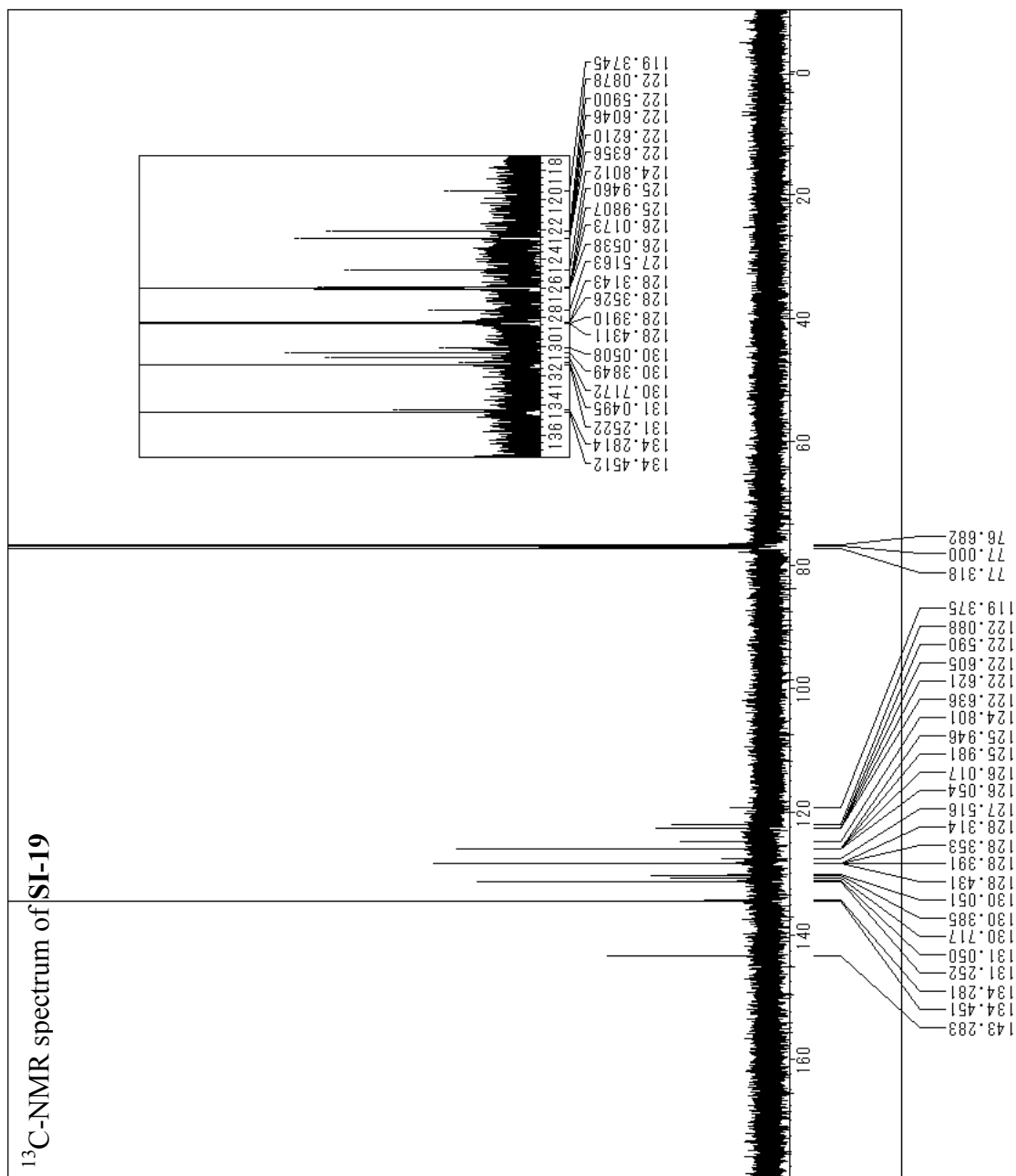




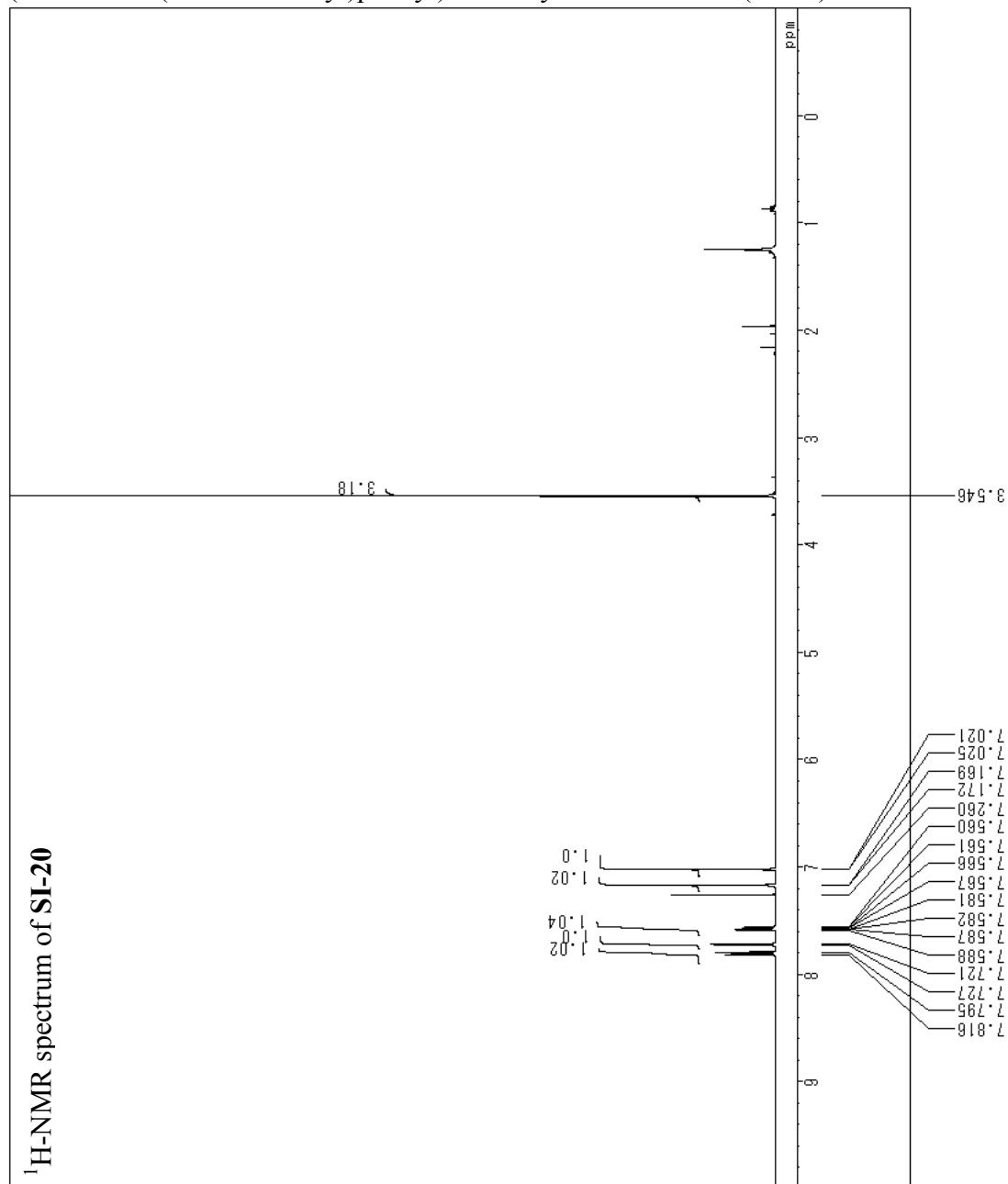
SI-19

Comment TSV06008.13C.20160406_01
 Date 2016/Apr/06
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
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 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

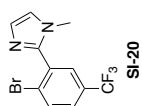
¹³C-NMR spectrum of SI-19

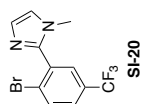


2-(2-Bromo-5-(trifluoromethyl)phenyl)-1-methyl-1*H*-imidazole (SI-20)

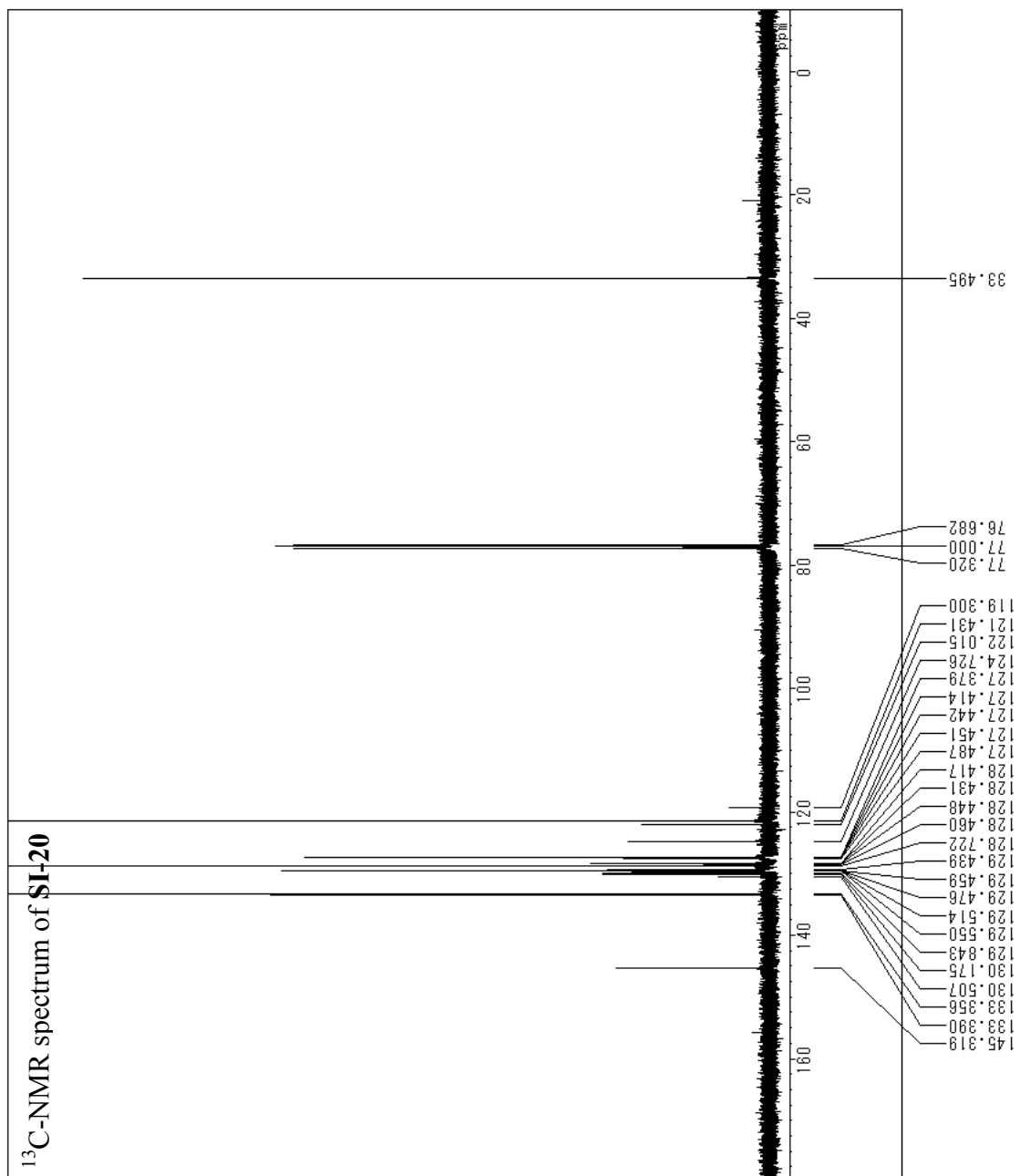


Comment: TSV06010_column_20160408
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 ObsNuc: ¹H
 ExMode: PROTON_001
 ObsFreq: 399.45 MHz
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 Acc. Interval: 5.589 s
 Spinning: 16.0 Hz
 Temperature: 25.0 °C
 Solvent: cdcl₃

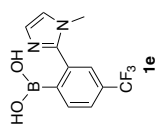
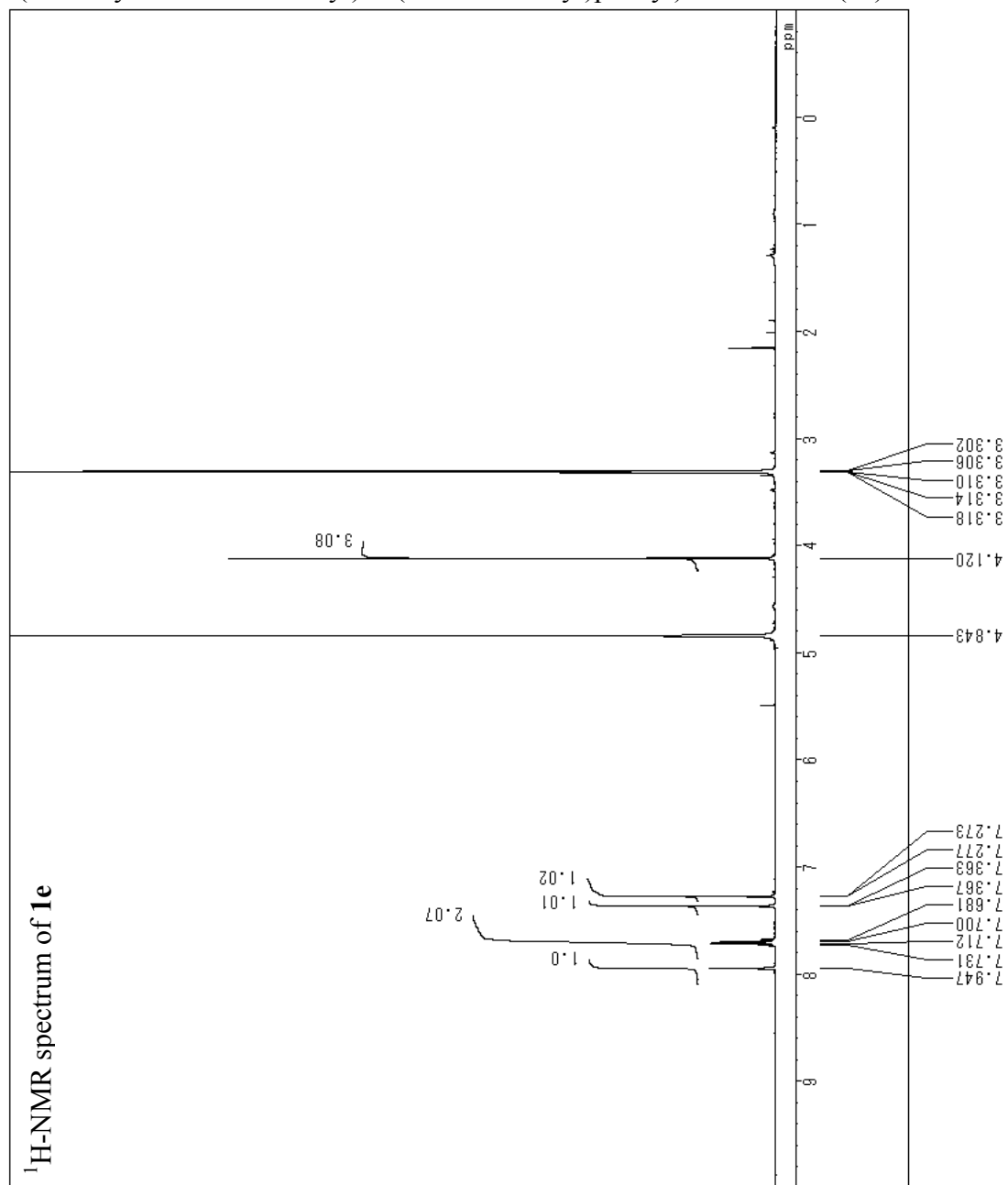




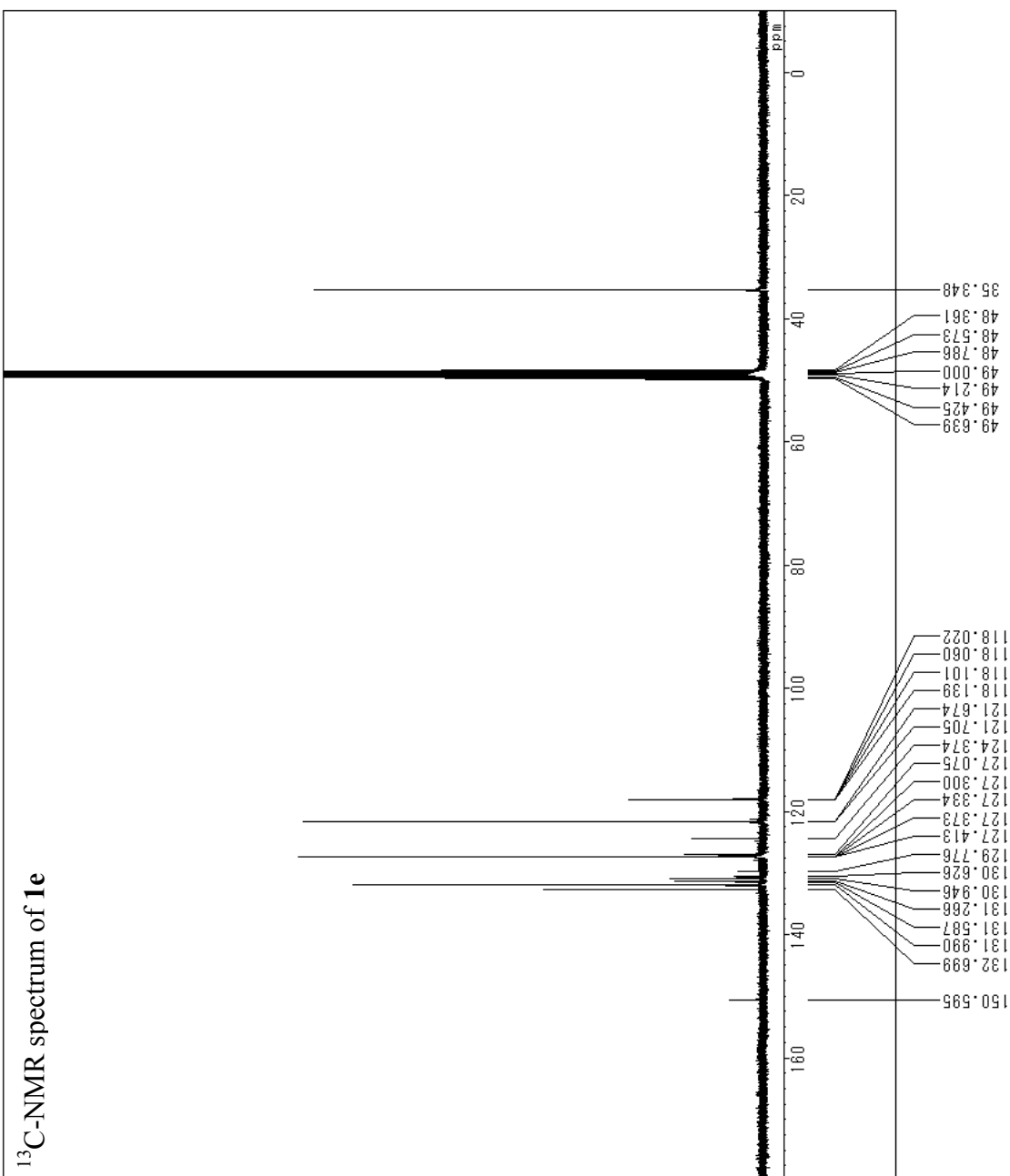
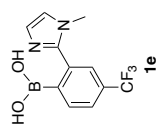
Comment TSV07010_13C_20180517_01
 Date 2018/May/17
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 256
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



(2-(1-Methyl-1*H*-imidazol-2-yl)-4-(trifluoromethyl)phenyl)boronic acid (**1e**)

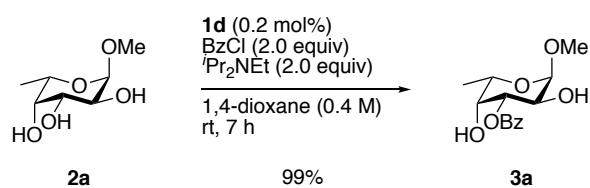


Comment ST001009_pure_20170224_0
 1
 Date 2017/Feb/24
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 32
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 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

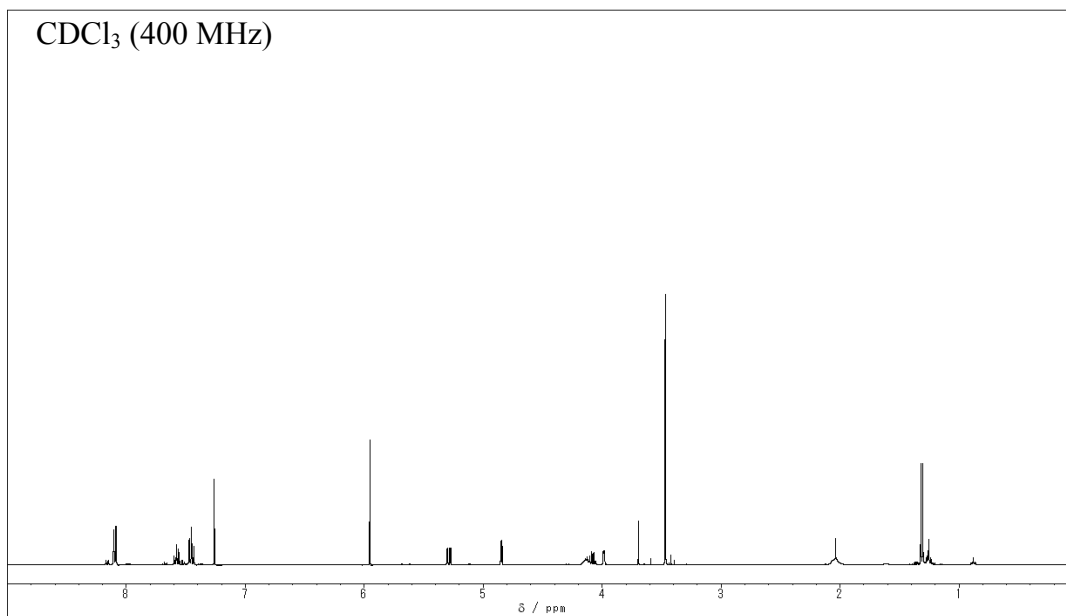


Comment TSV_cat_CF3_imidazole_13
 C_20180201_01
 Date 2018/Feb/01
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 1868
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdsod

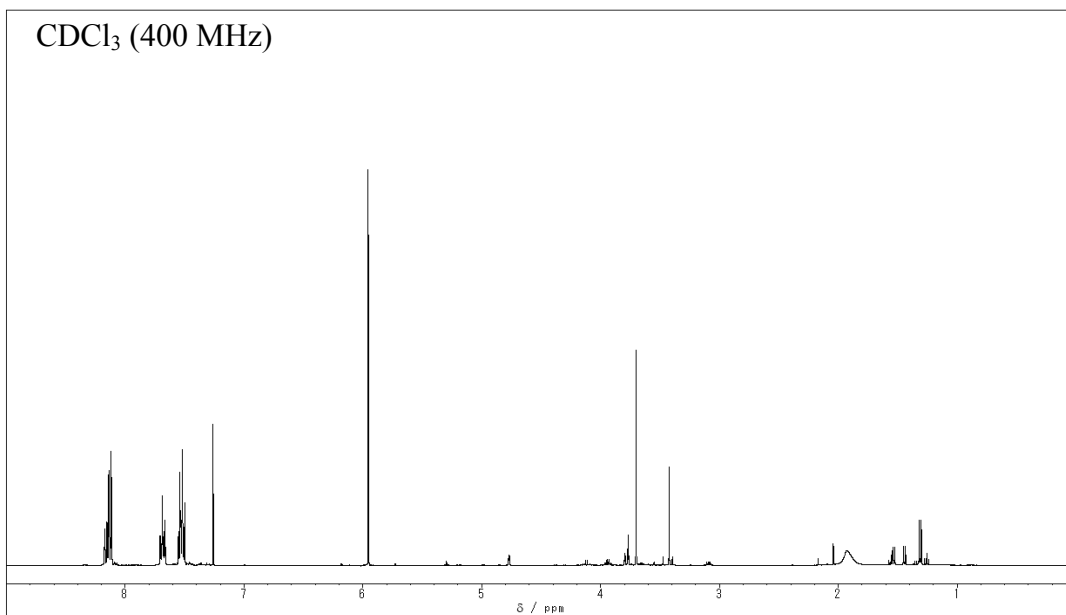
Methyl 3-*O*-benzoyl- α -L-fucopyranoside (**3a**)

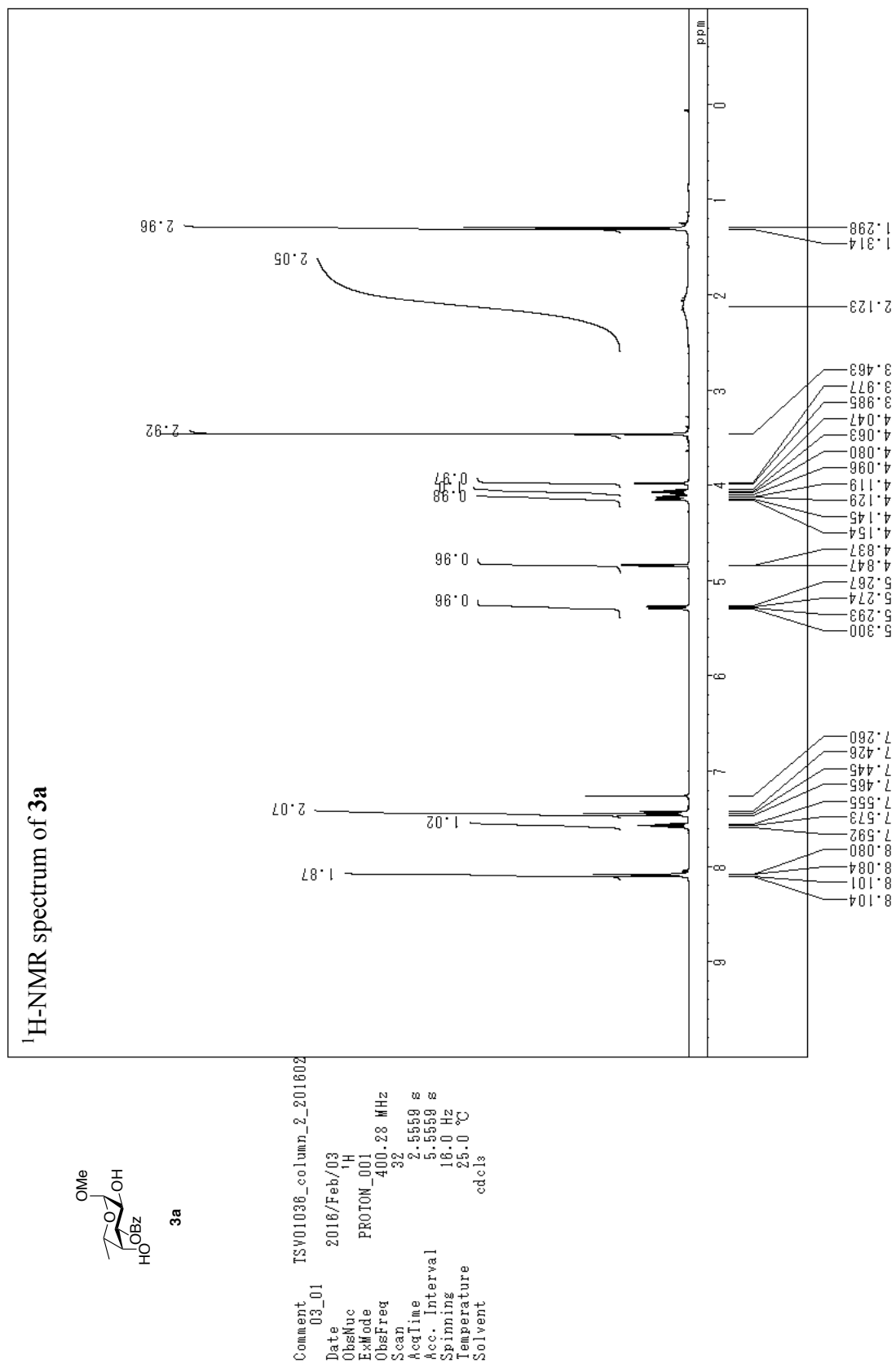


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

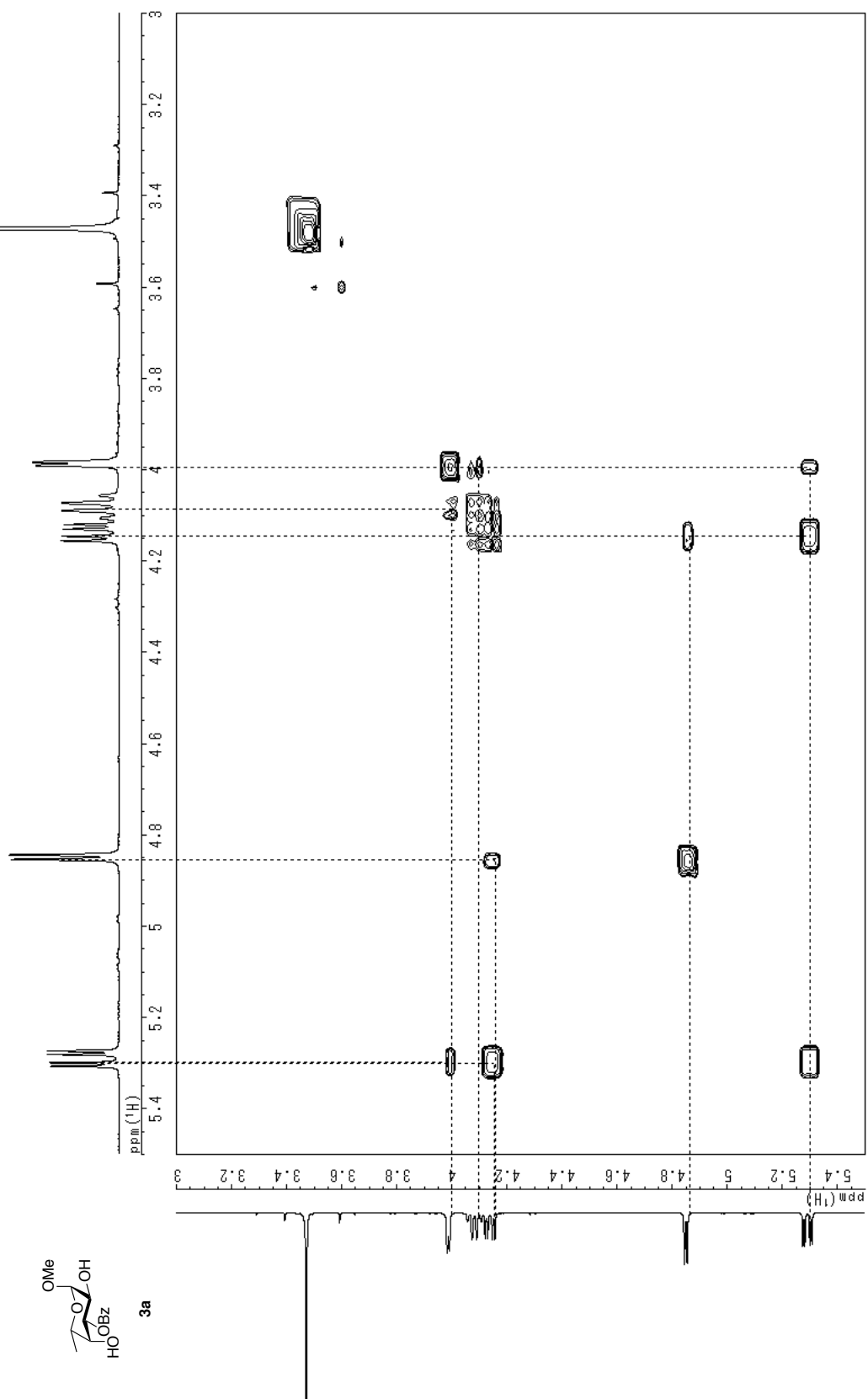


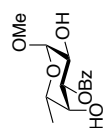
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



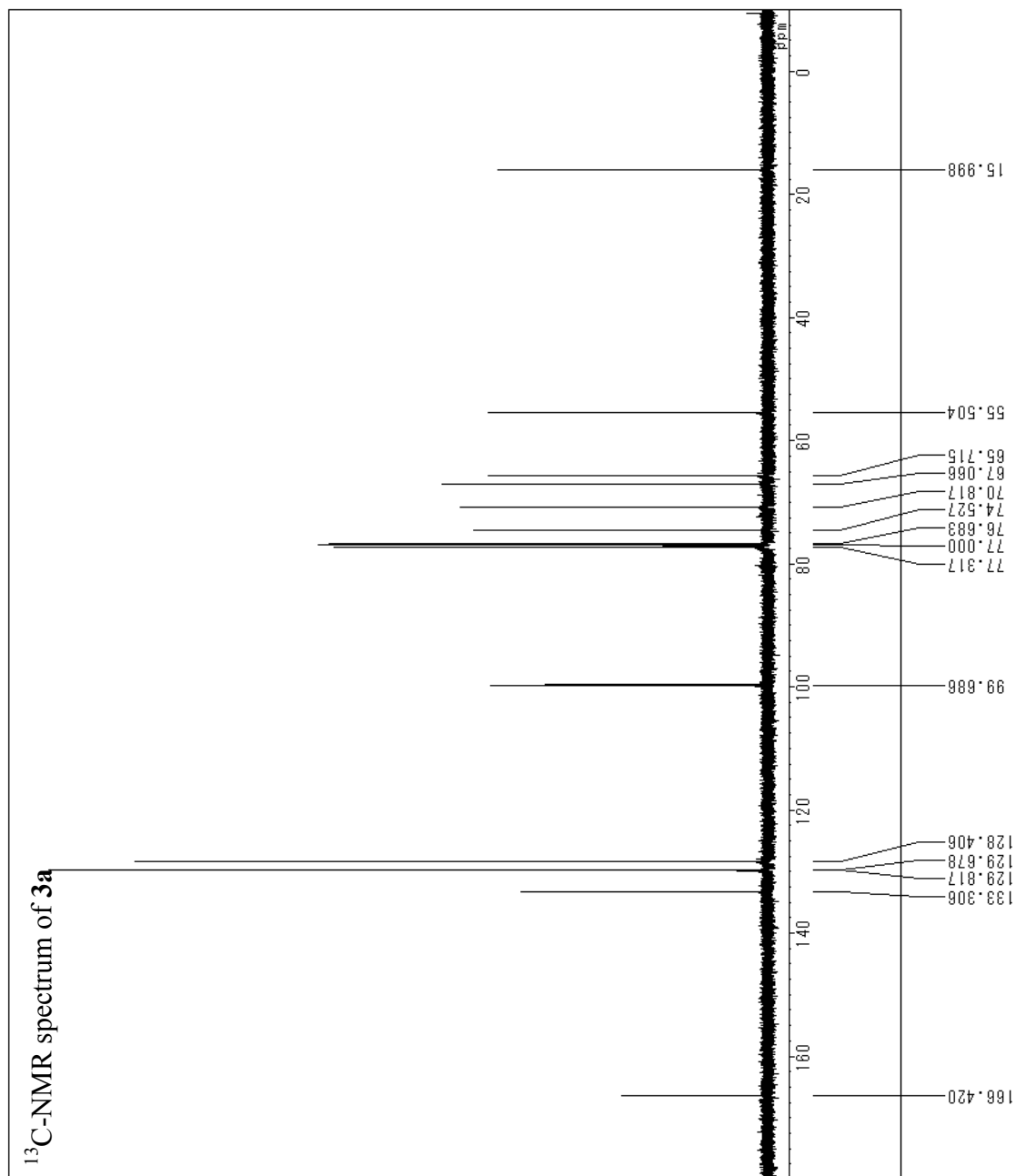


^1H - ^1H COSY spectrum of **3a**

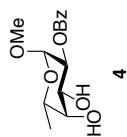
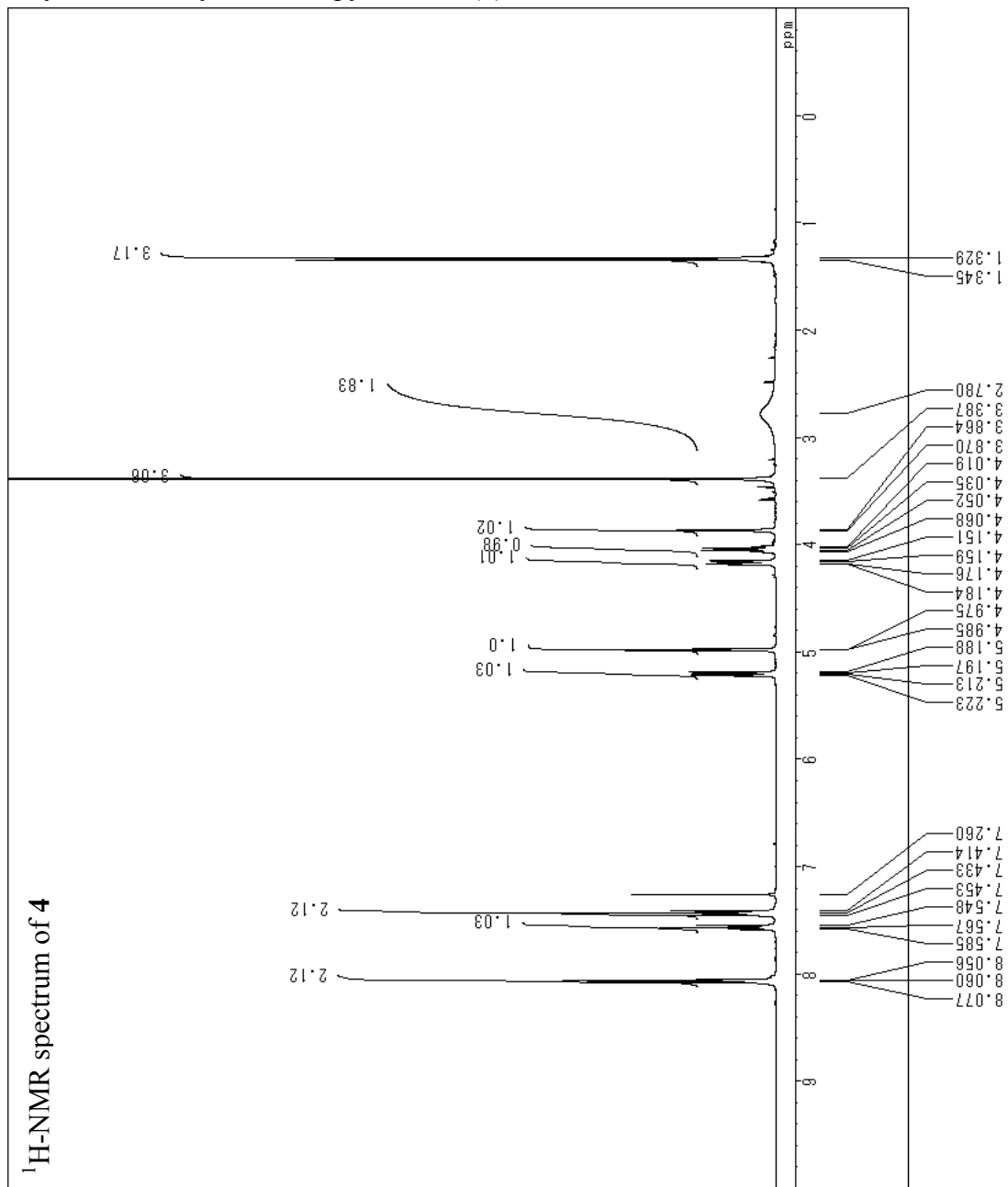




3a

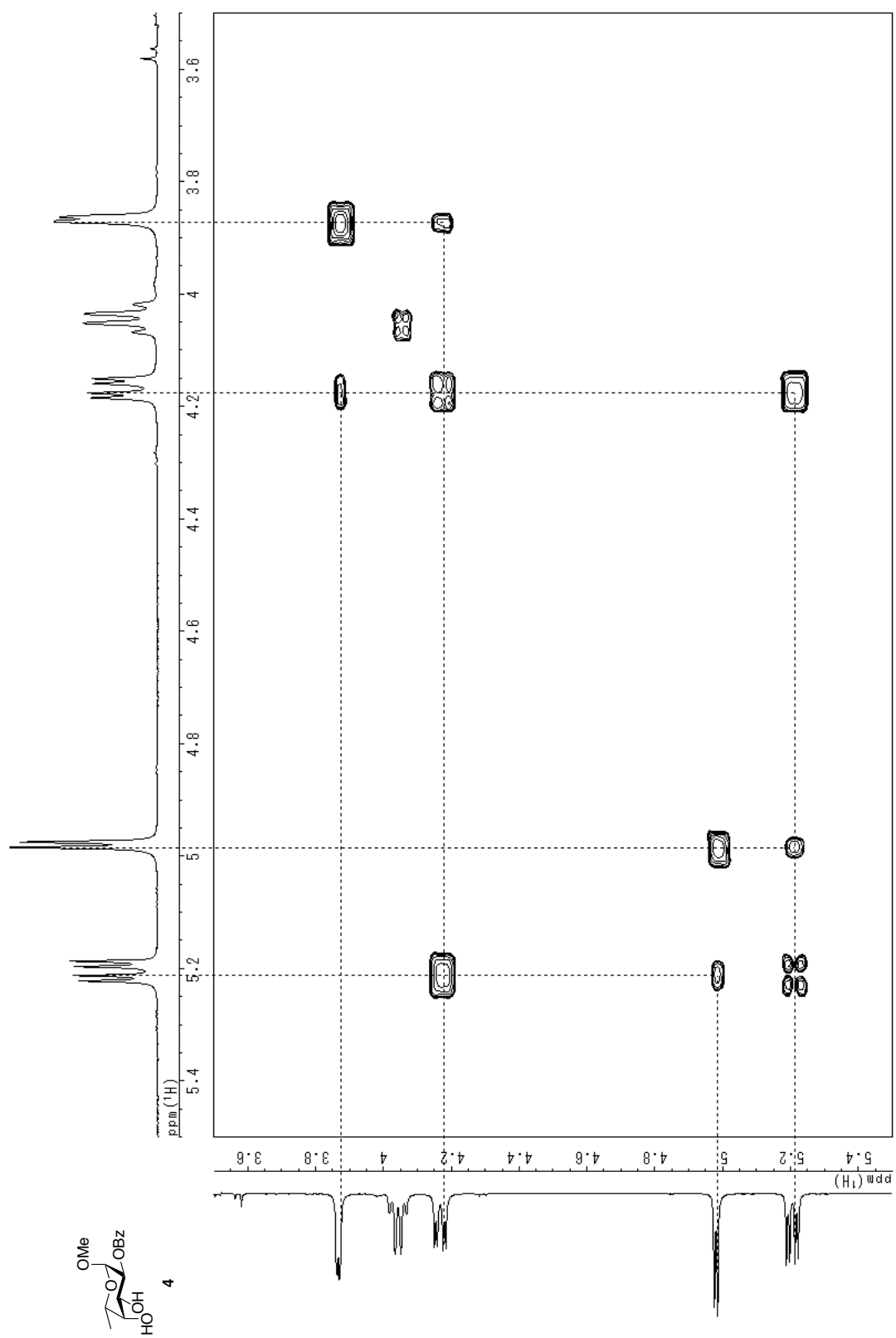


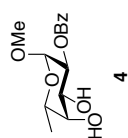
Comment TAO-14-11-19-38-C_201512
 30_01
 Date 2015/Dec/30
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 256
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

Methyl 2-*O*-benzoyl- α -L-fucopyranoside (**4**)

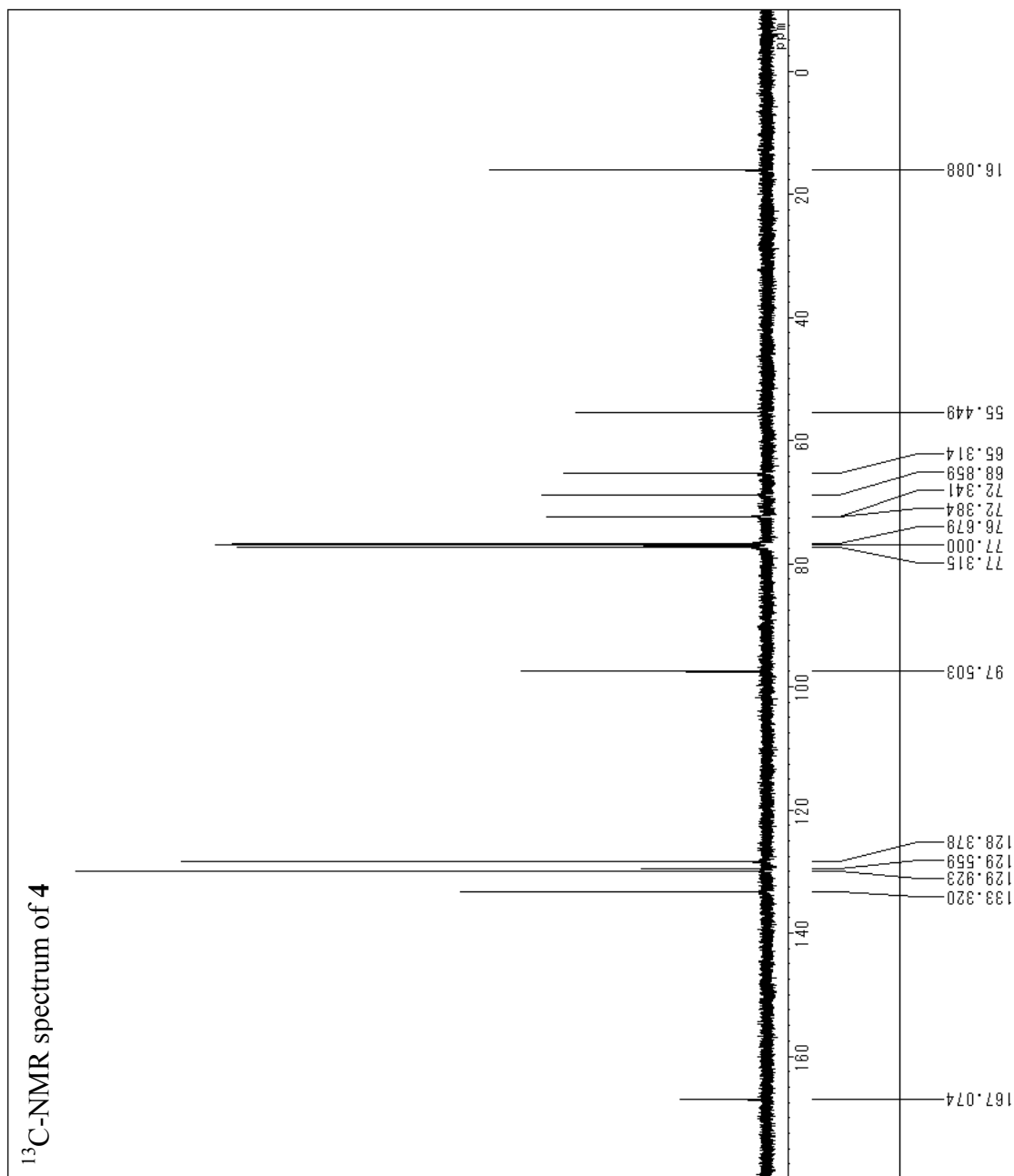
Comment	TSY250228_13C-COSY_201901
18_01	
Date	2019/Jan/18
ObsNuc	¹ H
ExMode	PROTON_001
ObsFreq	400.27 MHz
Scan	16
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	15.0 Hz
Temperature	25.0 °C
Solvent	cdcl3

^1H - ^1H COSY spectrum of **4**



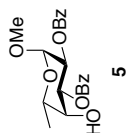
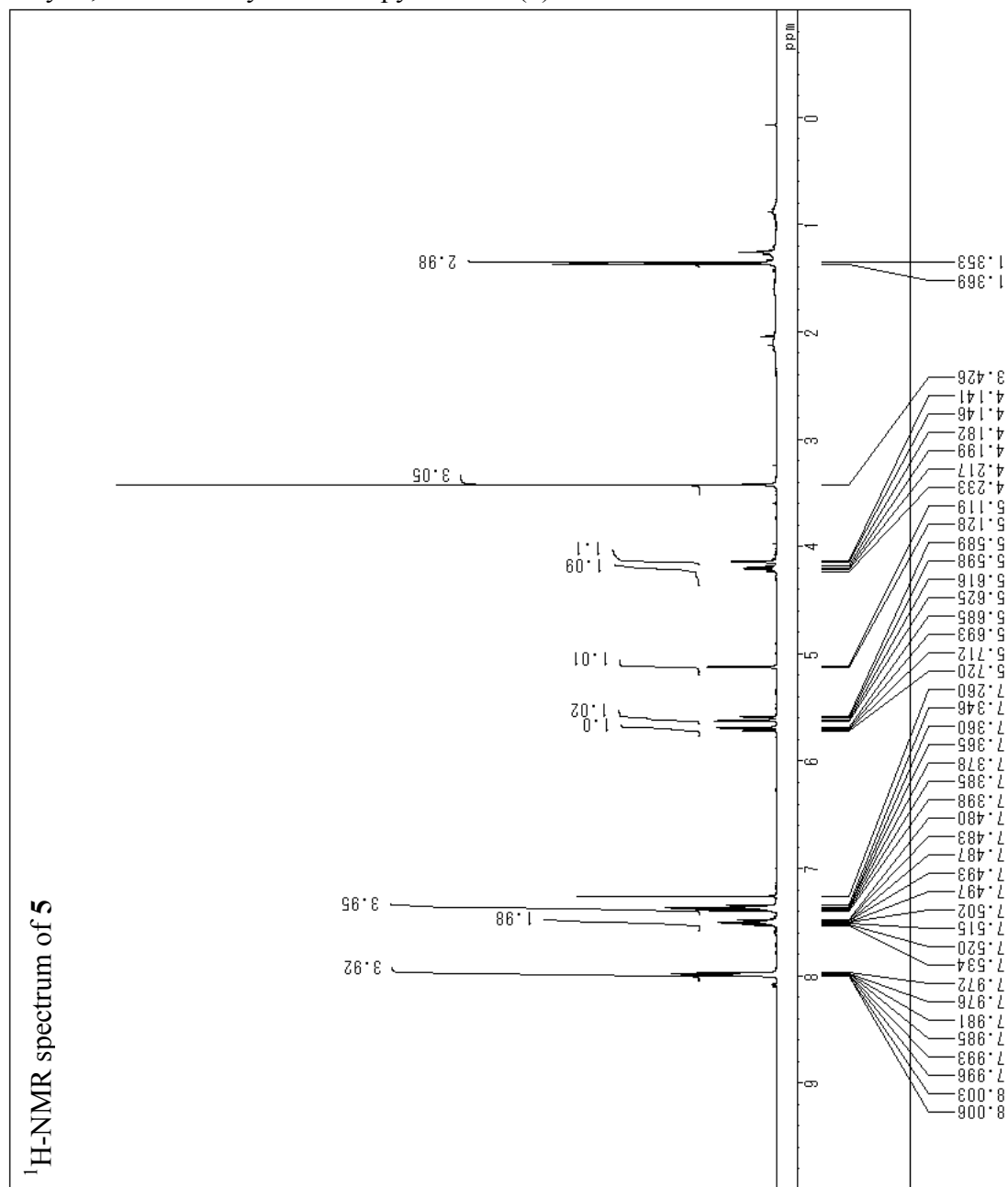


¹³C-NMR spectrum of 4



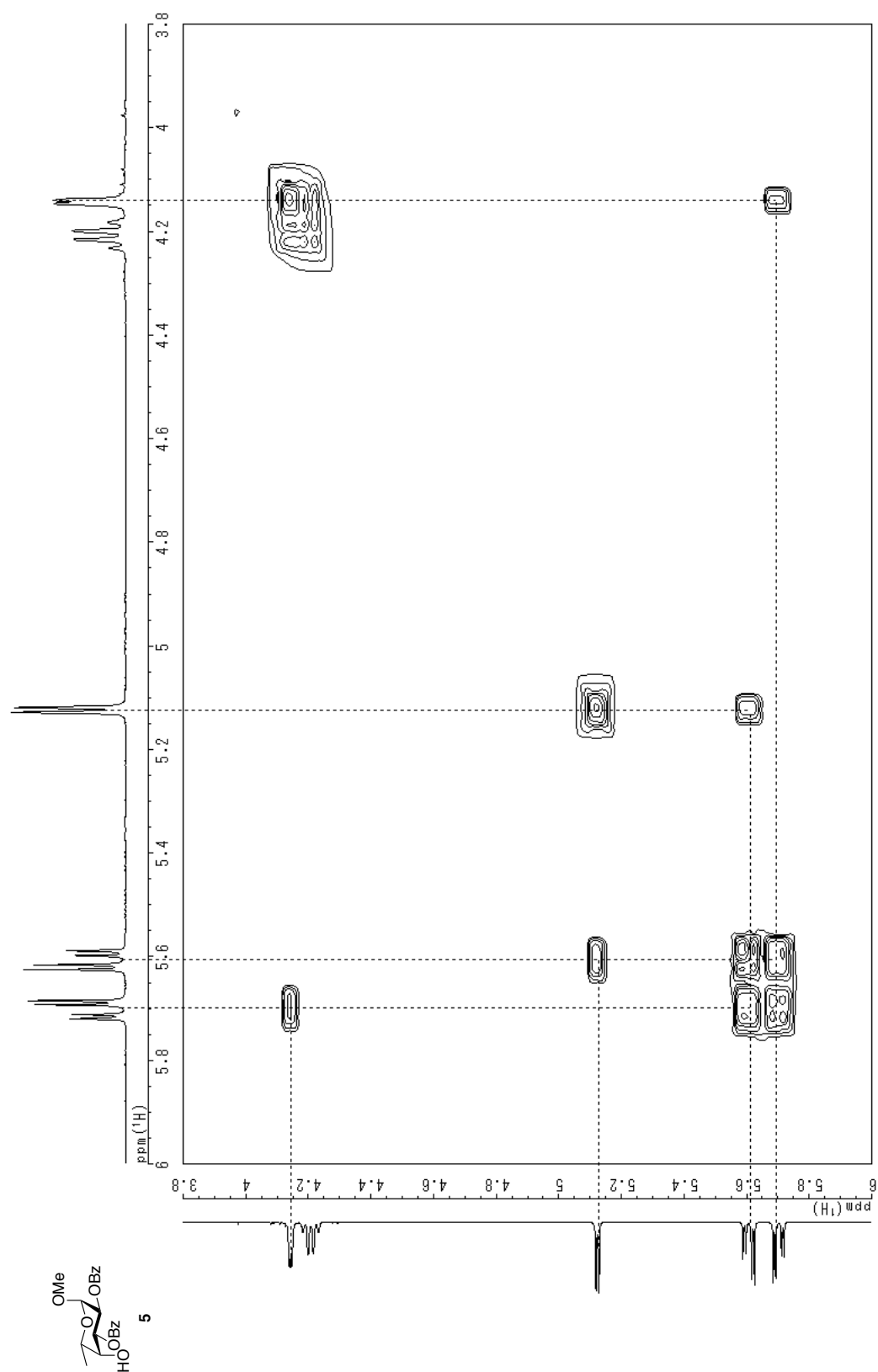
Comment TSV25028_13C_COSY_20180118_01
 Date 2018/Jan/18
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

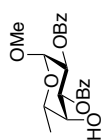
Methyl 2,3-*O*-dibenzoyl- α -L-fucopyranoside (**5**)



Comment: TSV25029_pure_13C_COSY_2
 0190127_01
 Date: 2019/Jan/27
 ObsNuc: ¹H
 ExMode: PROTON_001
 ObsFreq: 399.45 MHz
 Scan: 16
 AcqTime: 2.589 s
 Acc. Interval: 5.589 s
 Spinning: 16.0 Hz
 Temperature: 25.0 °C
 Solvent: cdcl3

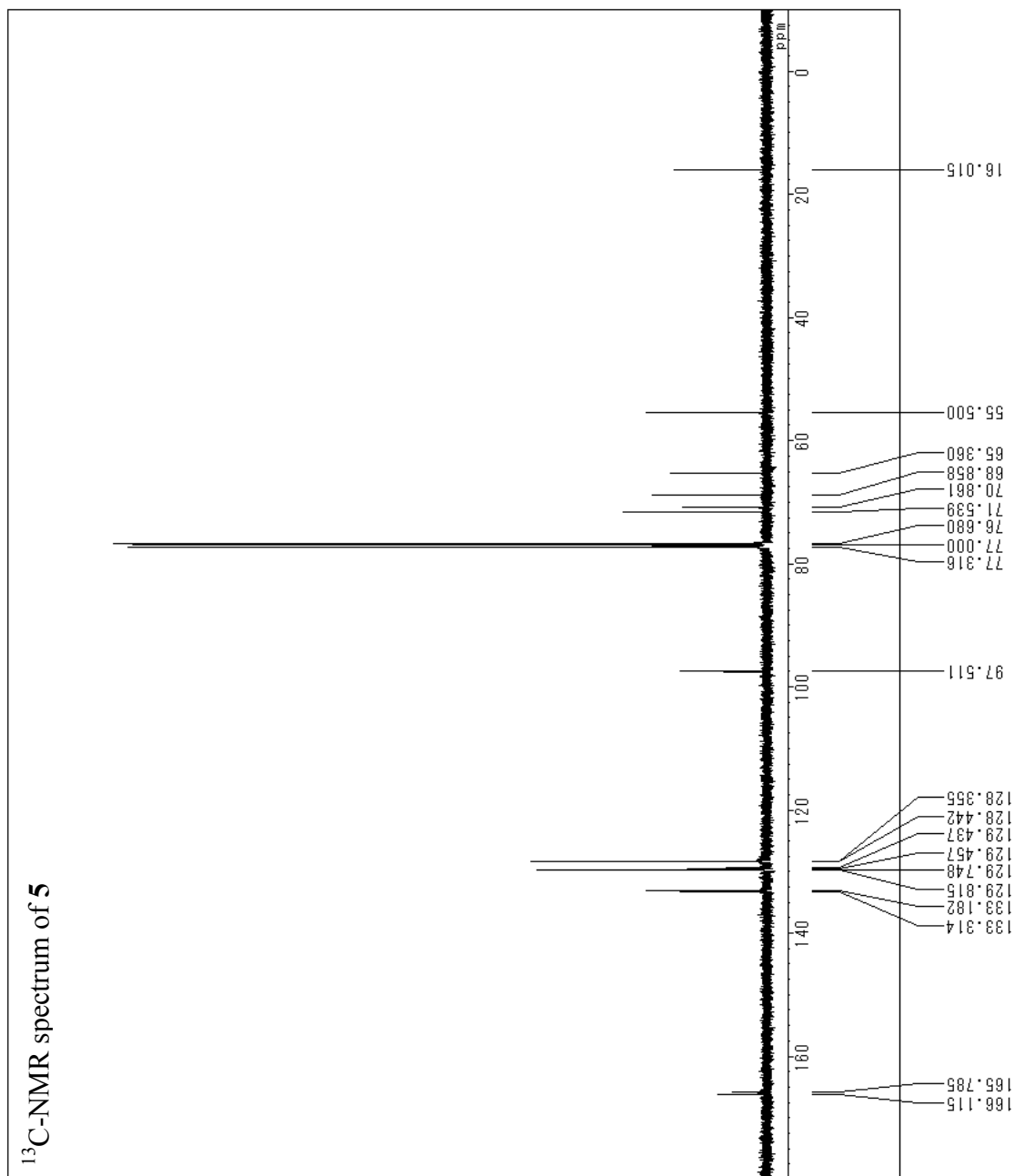
^1H - ^1H COSY spectrum of **5**



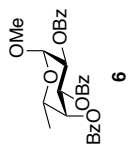
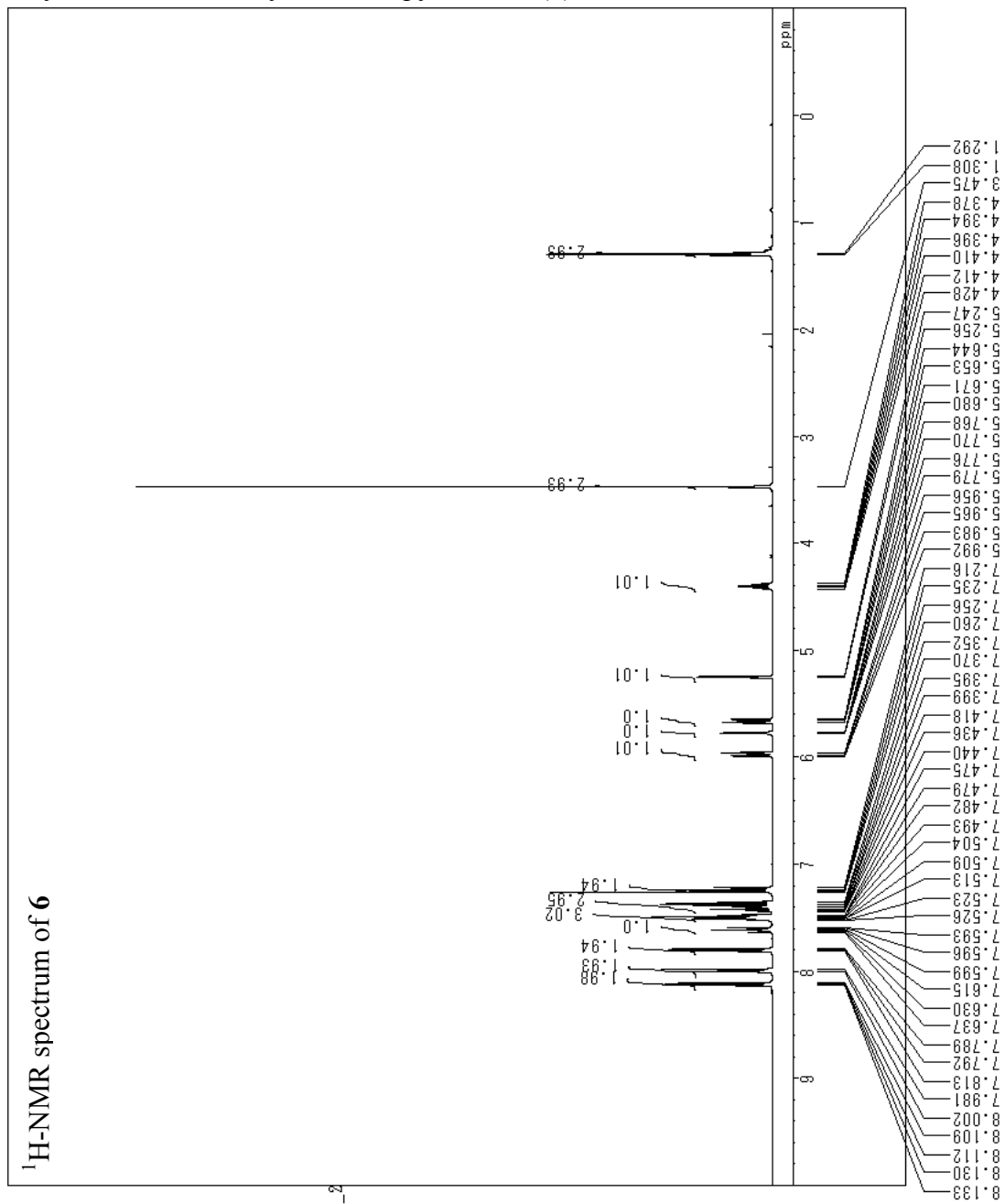


5

¹³C-NMR spectrum of 5

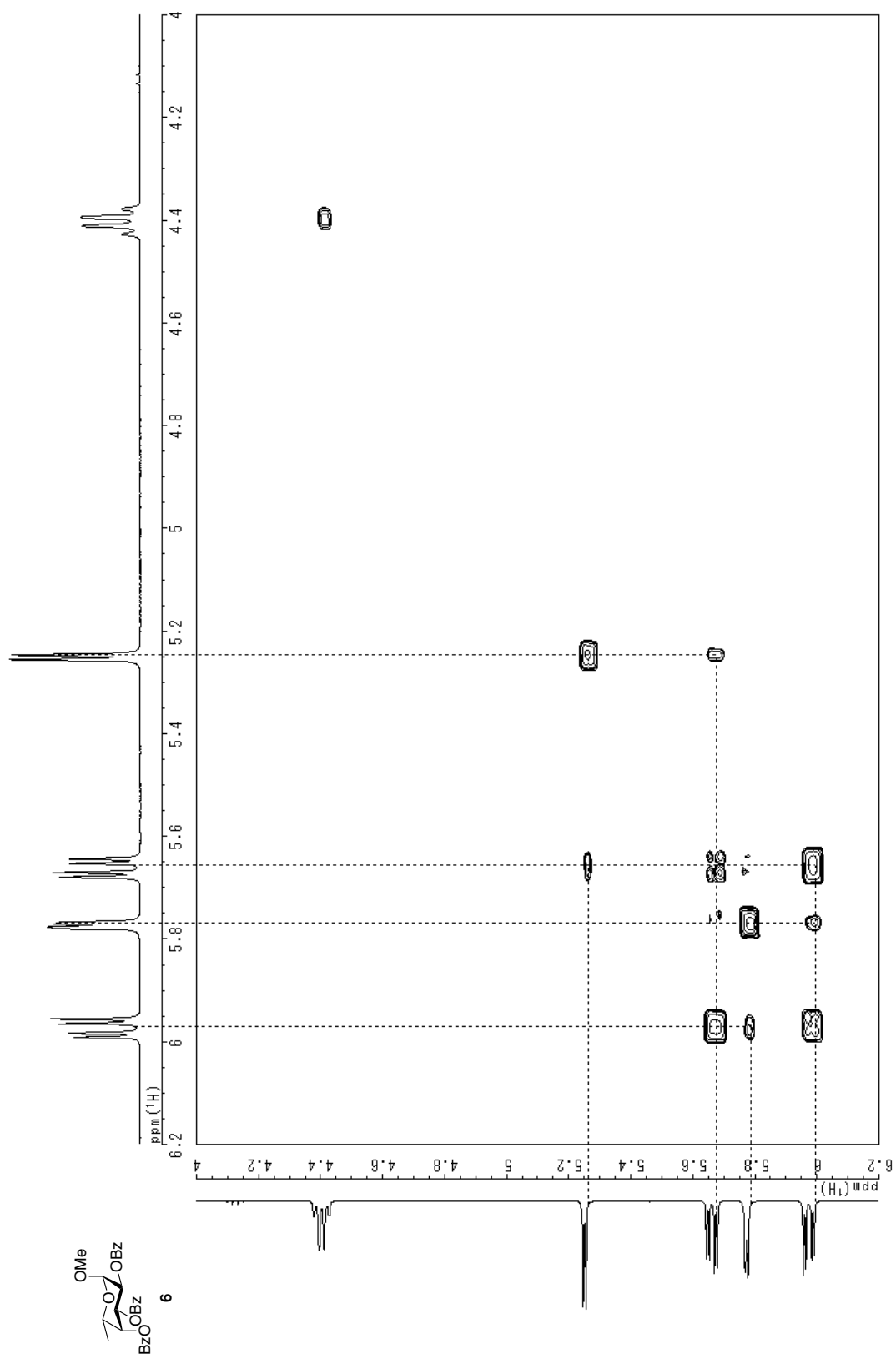


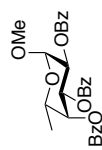
Comment TSV25029_pure_13C_COSY_2
0190127_01
Date 2019/Jan/27
ObsNuc ¹³C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 1024
AcqTime 1.3831 s
Acc. Interval 3.3831 s
Spinning 20.0 Hz
Temperature 25.0 °C
Solvent cdcl₃

Methyl 2,3,4-*O*-tribenzoyl- α -L-fucopyranoside (**6**)

Comment	TS/25034_pure_13C_COSY_2
Date	0180129_01
ObsNuc	1H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	16
AcqTime	2.568 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 °C
Solvent	cdcl3

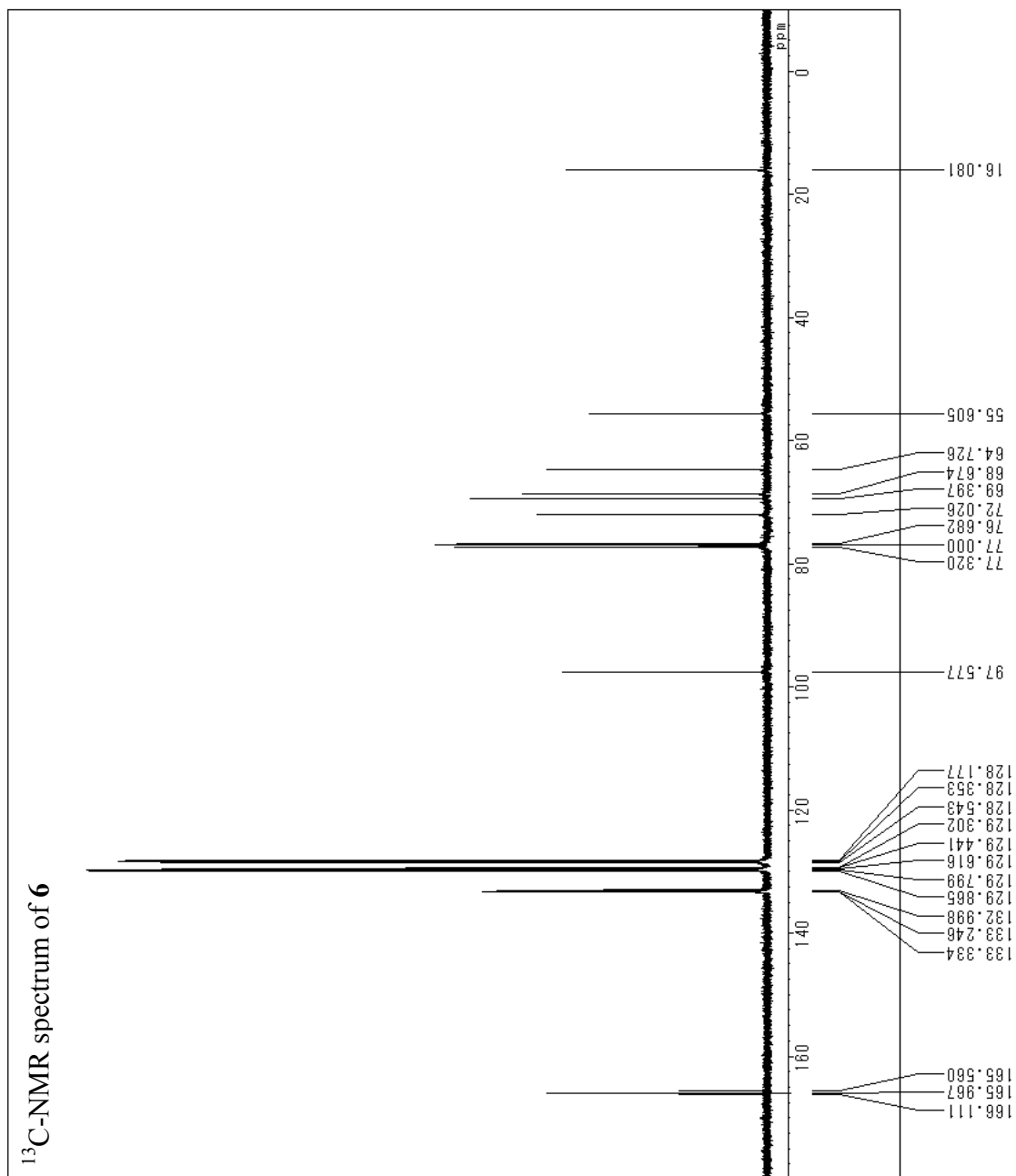
^1H - ^1H COSY spectrum of **6**



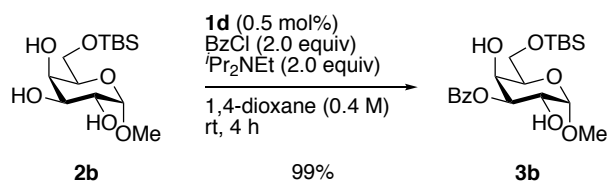


¹³C-NMR spectrum of 6

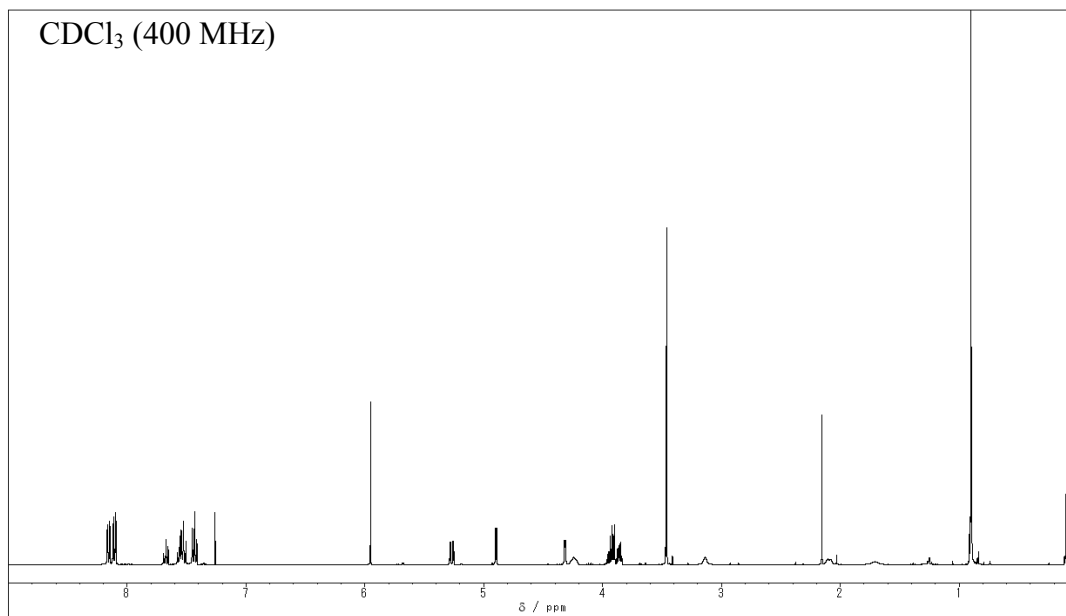
Comment TSV25034_pure_13C_COSY_2
 0190129_01
 Date 2019/Jan/29
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



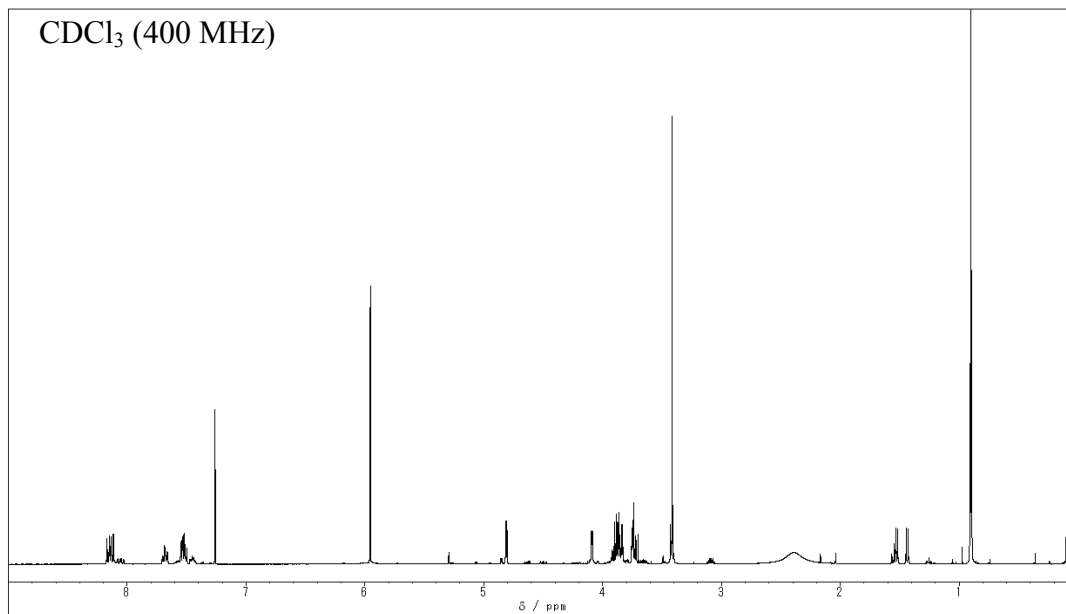
Methyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- α -D-galactopyranoside (**3b**)

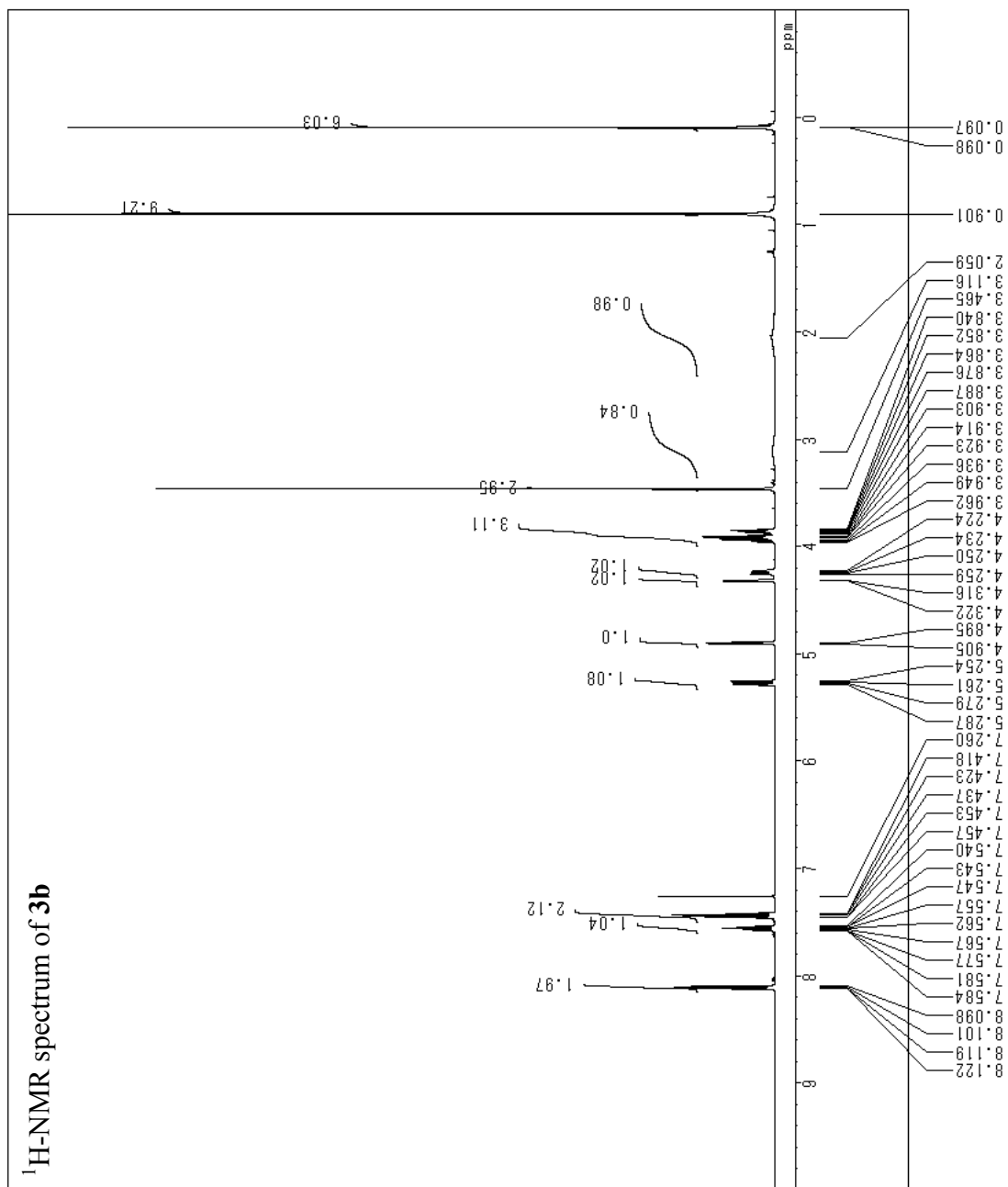
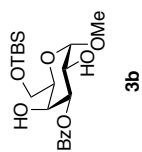


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



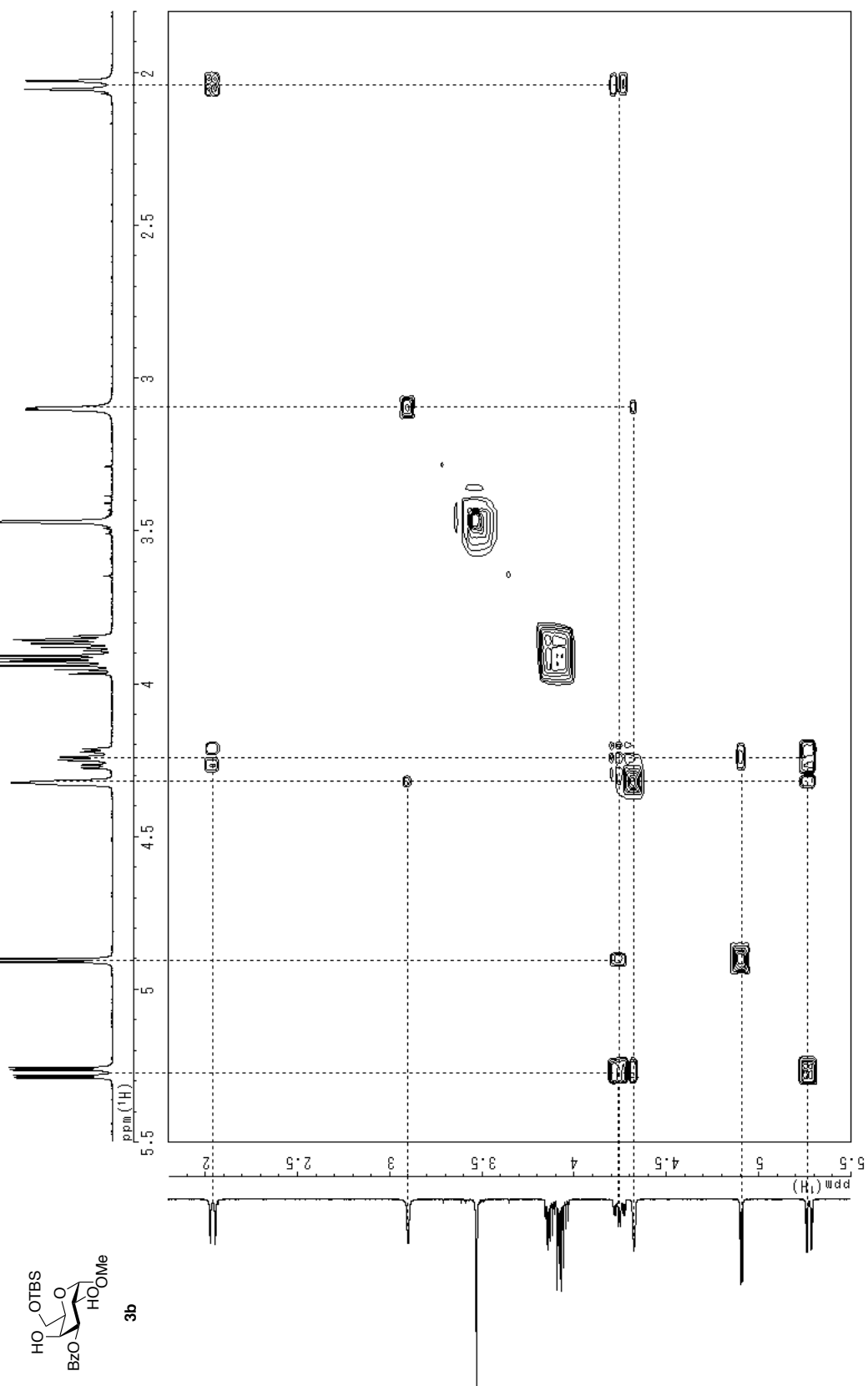
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

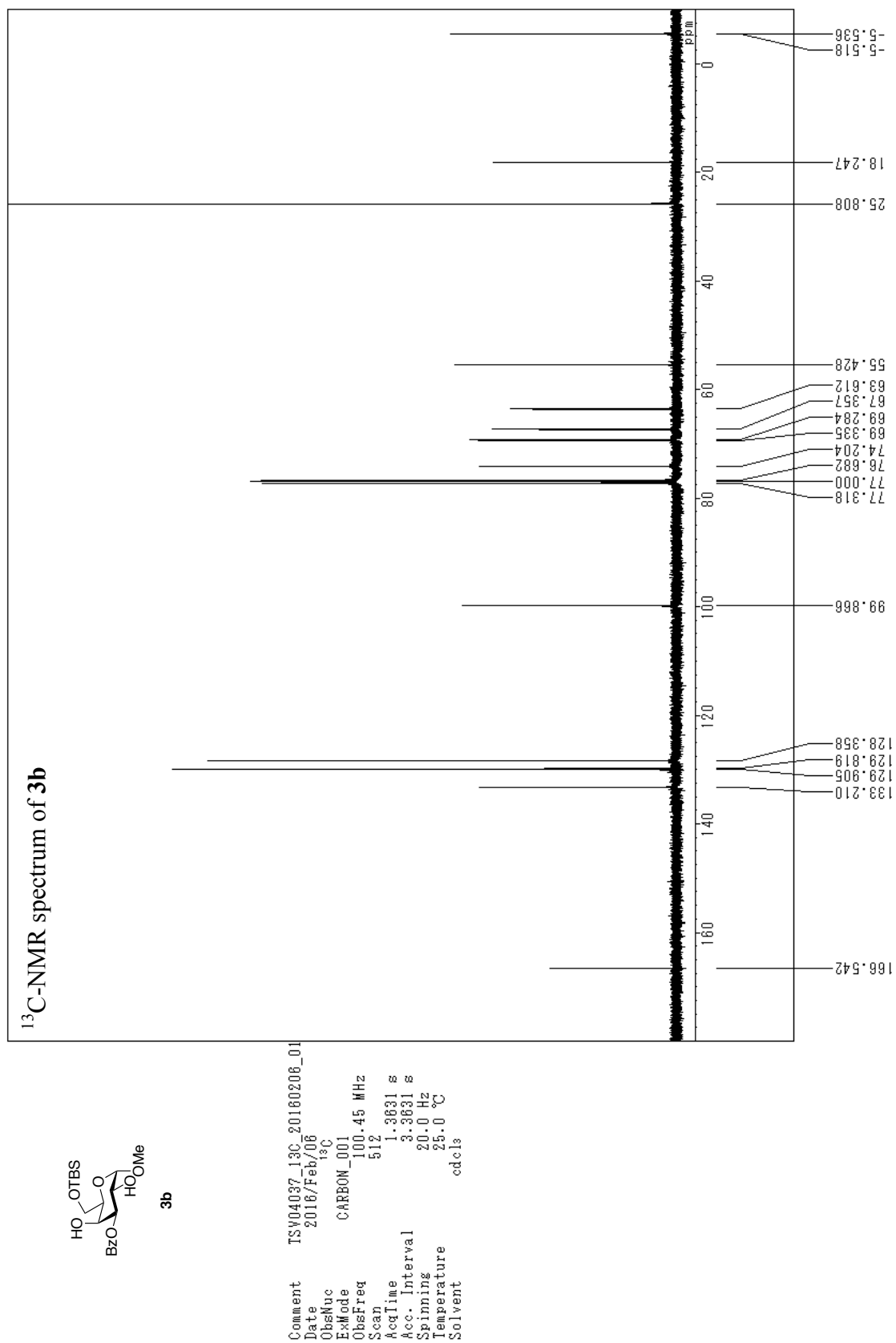




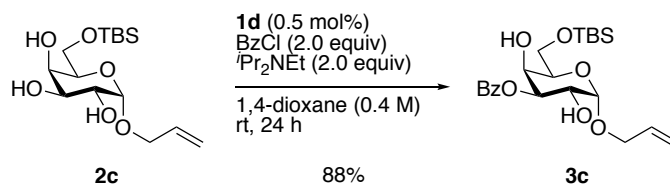
Comment TSV04037_column_20180208
 Date_01 2016/Feb/08
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 32
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **3b**

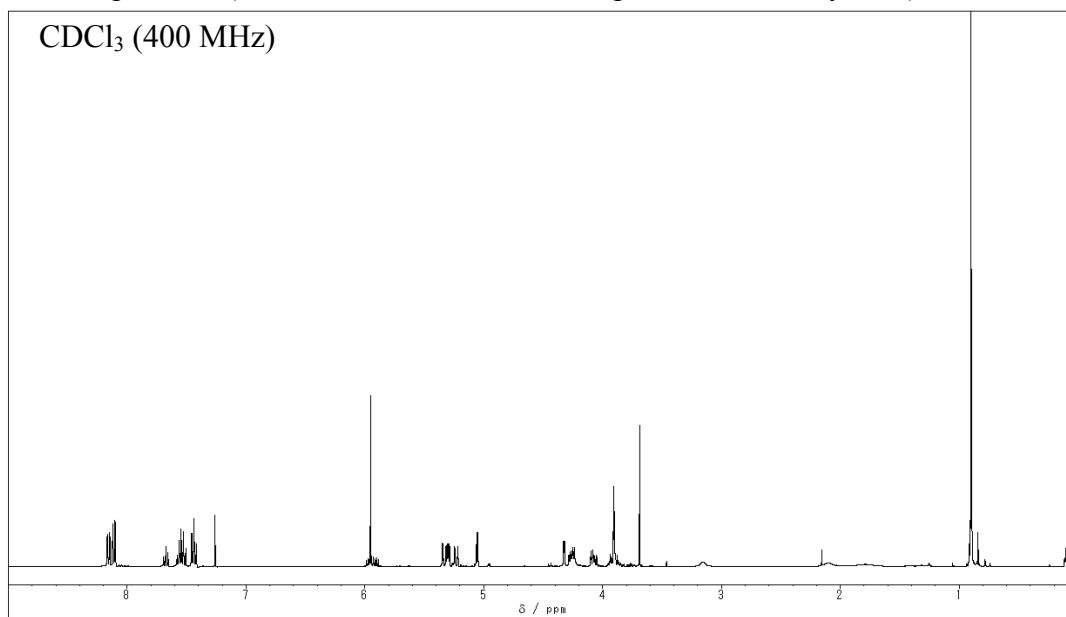




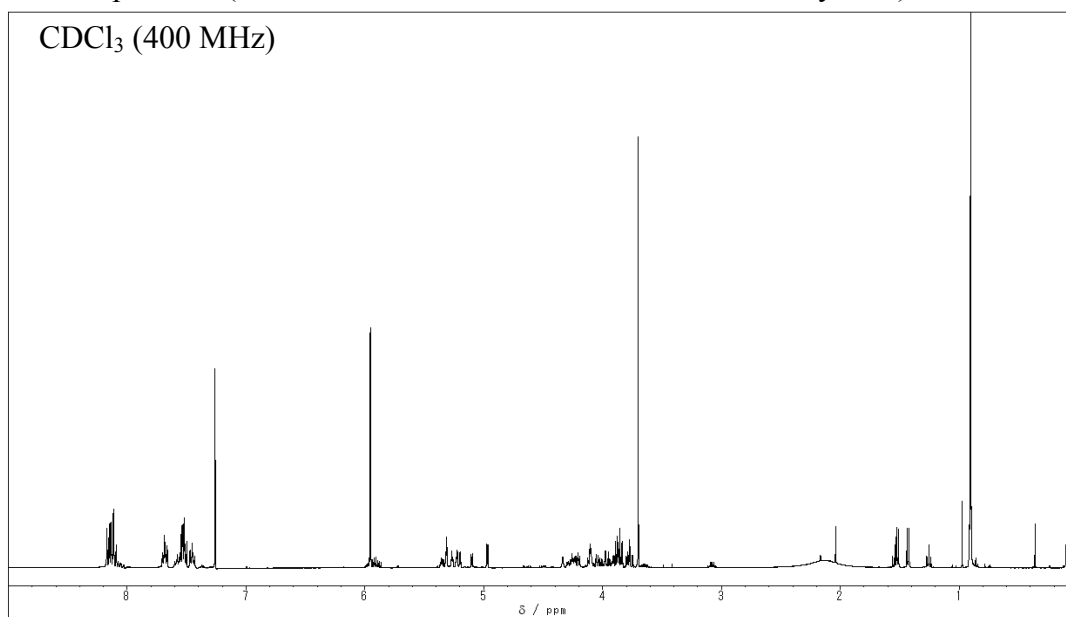
Allyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- α -D-galactopyranoside (**3c**)

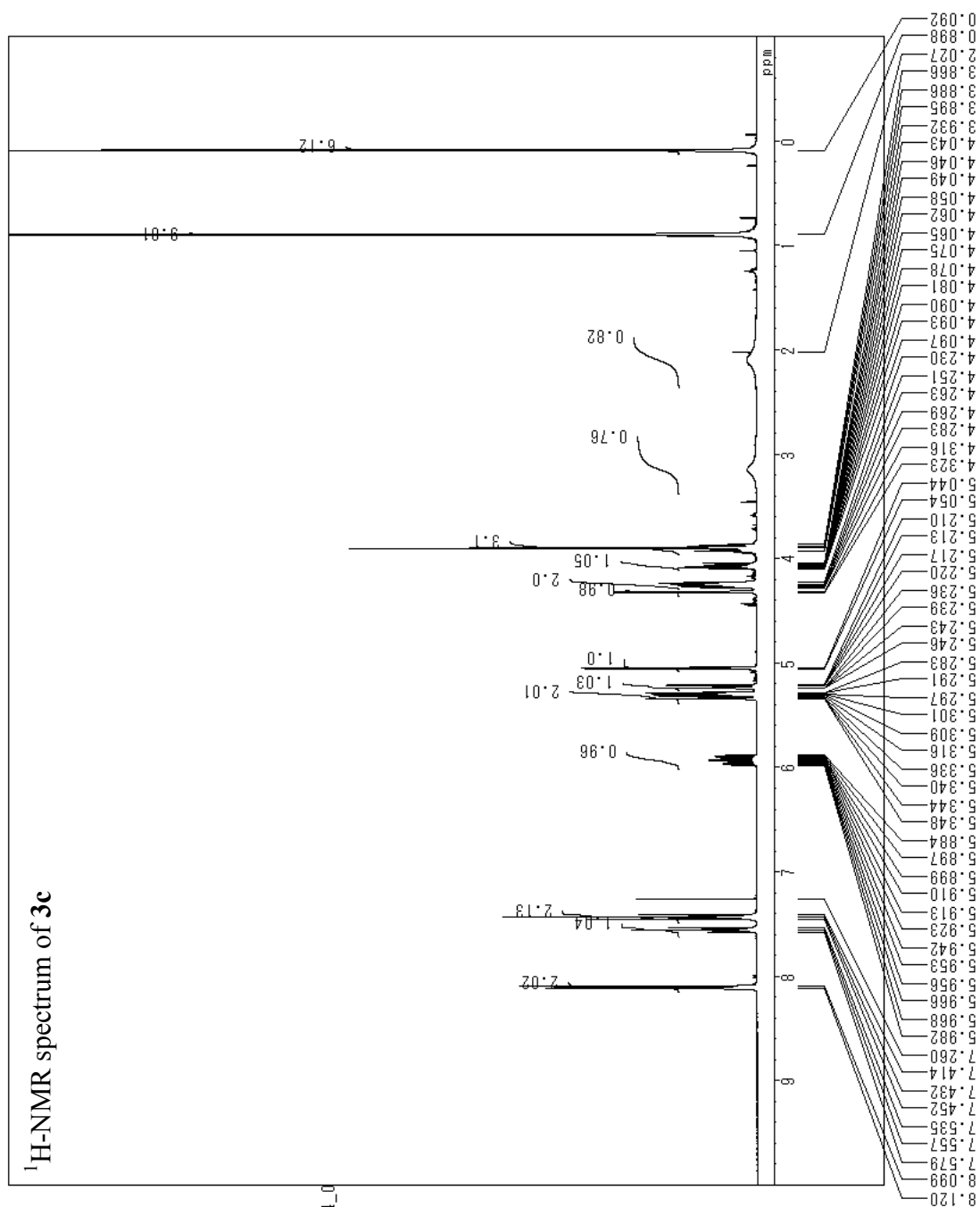
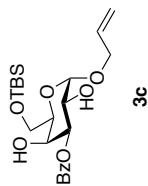


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



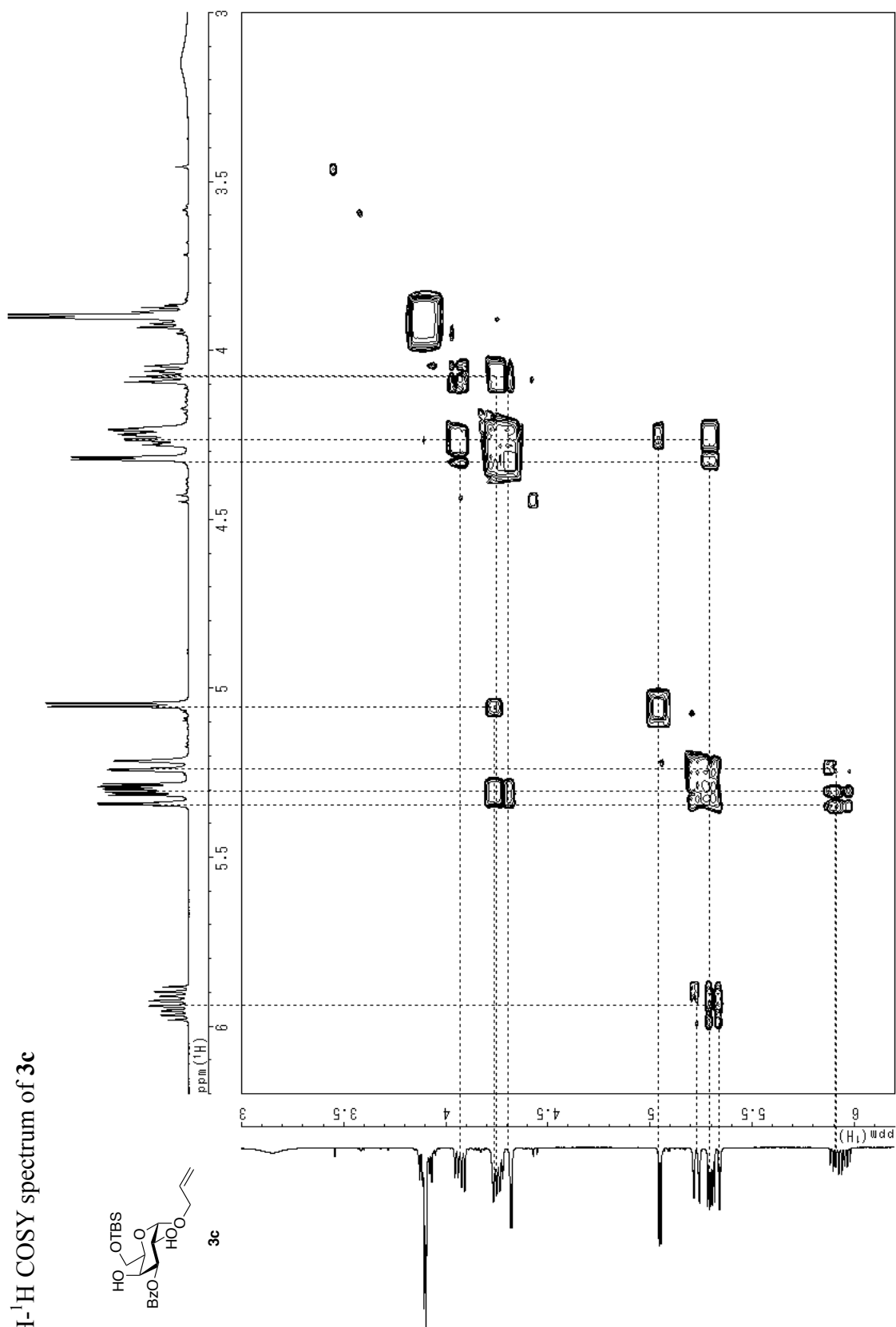
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

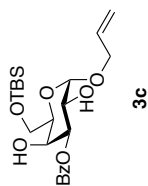




Comment TSV03026_COSY_20160714_0
 Date 2016/Jul/14
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.569 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

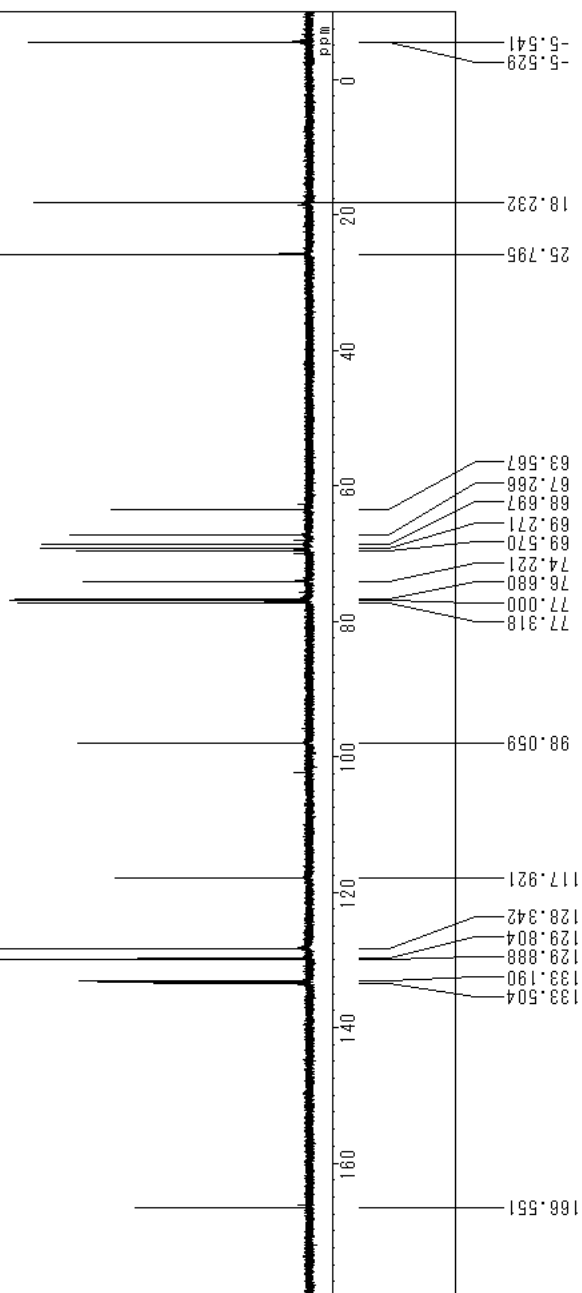
^1H - ^1H COSY spectrum of **3c**



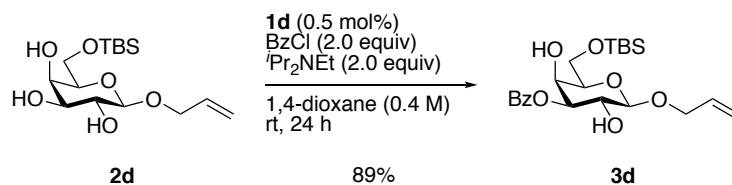


^{13}C -NMR spectrum of **3c**

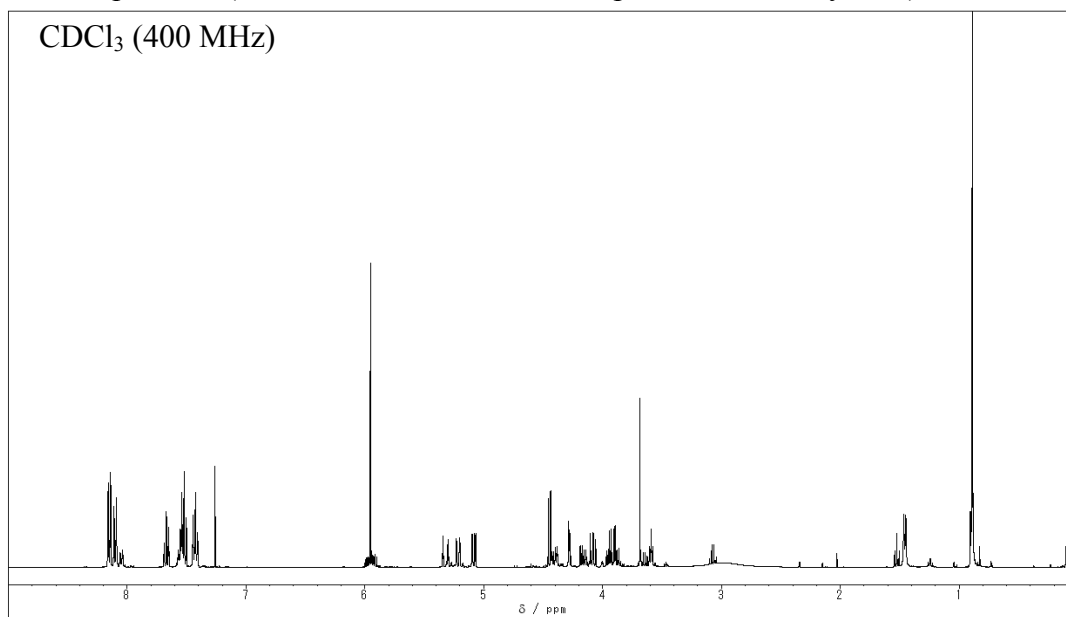
Comment TSV08026_13C_20160714_01
 Date 2016/Jul/14
 ObsNuc ^{13}C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 $^{\circ}\text{C}$
 Solvent cdCl_3



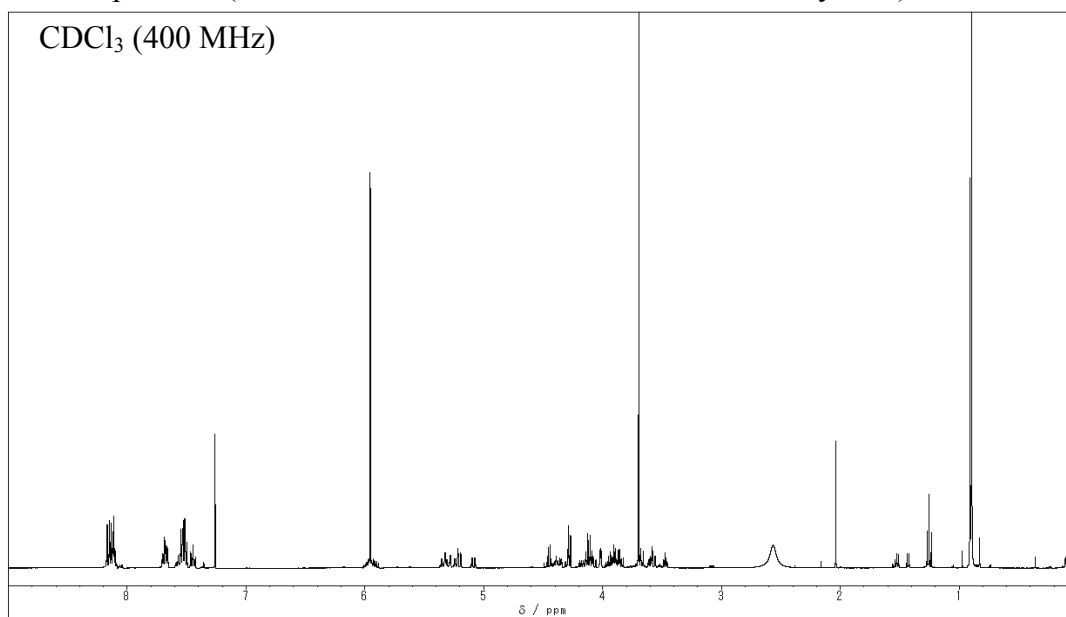
Allyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- β -D-galactopyranoside (**3d**)

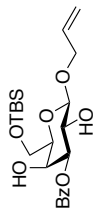


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



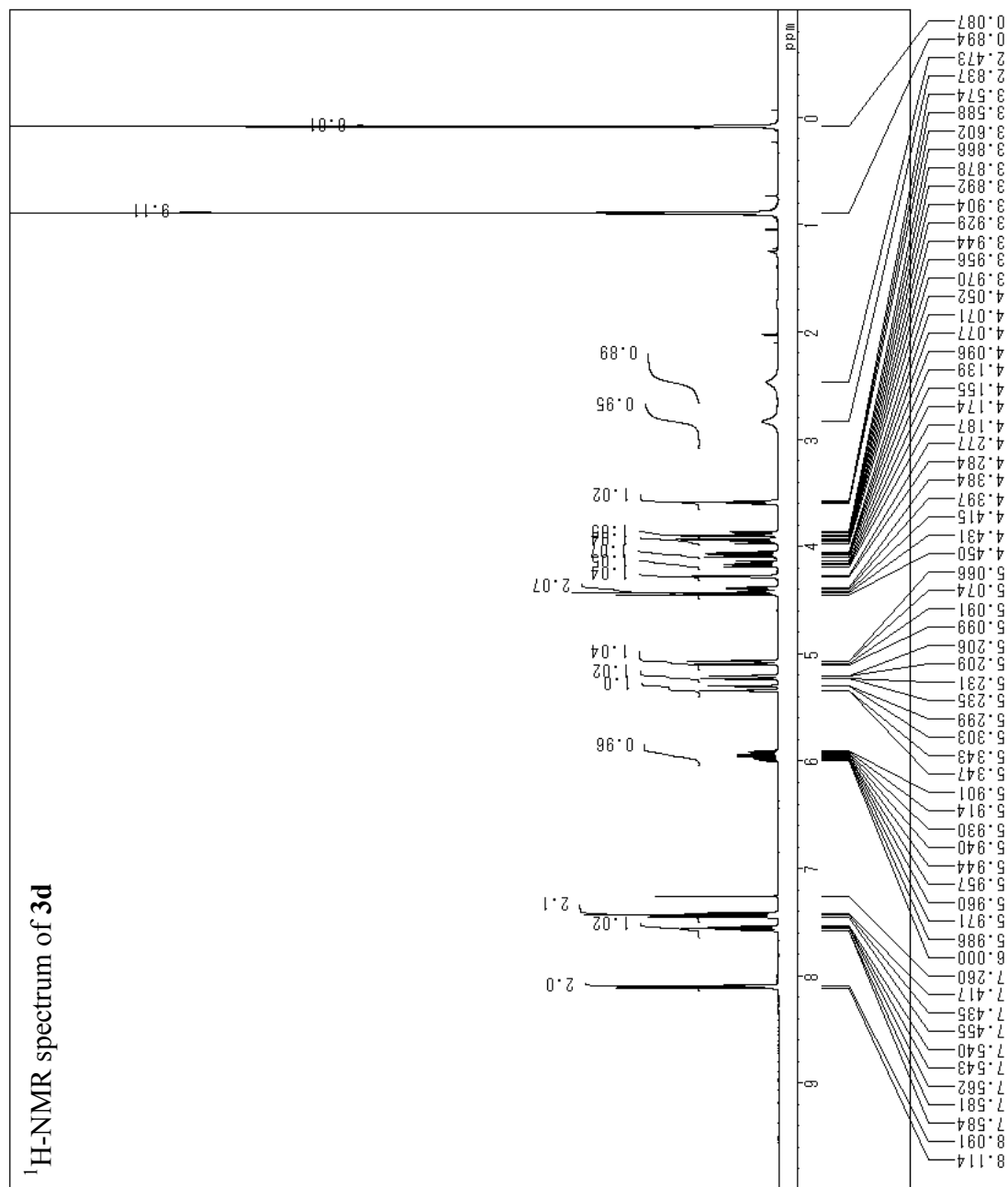
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)





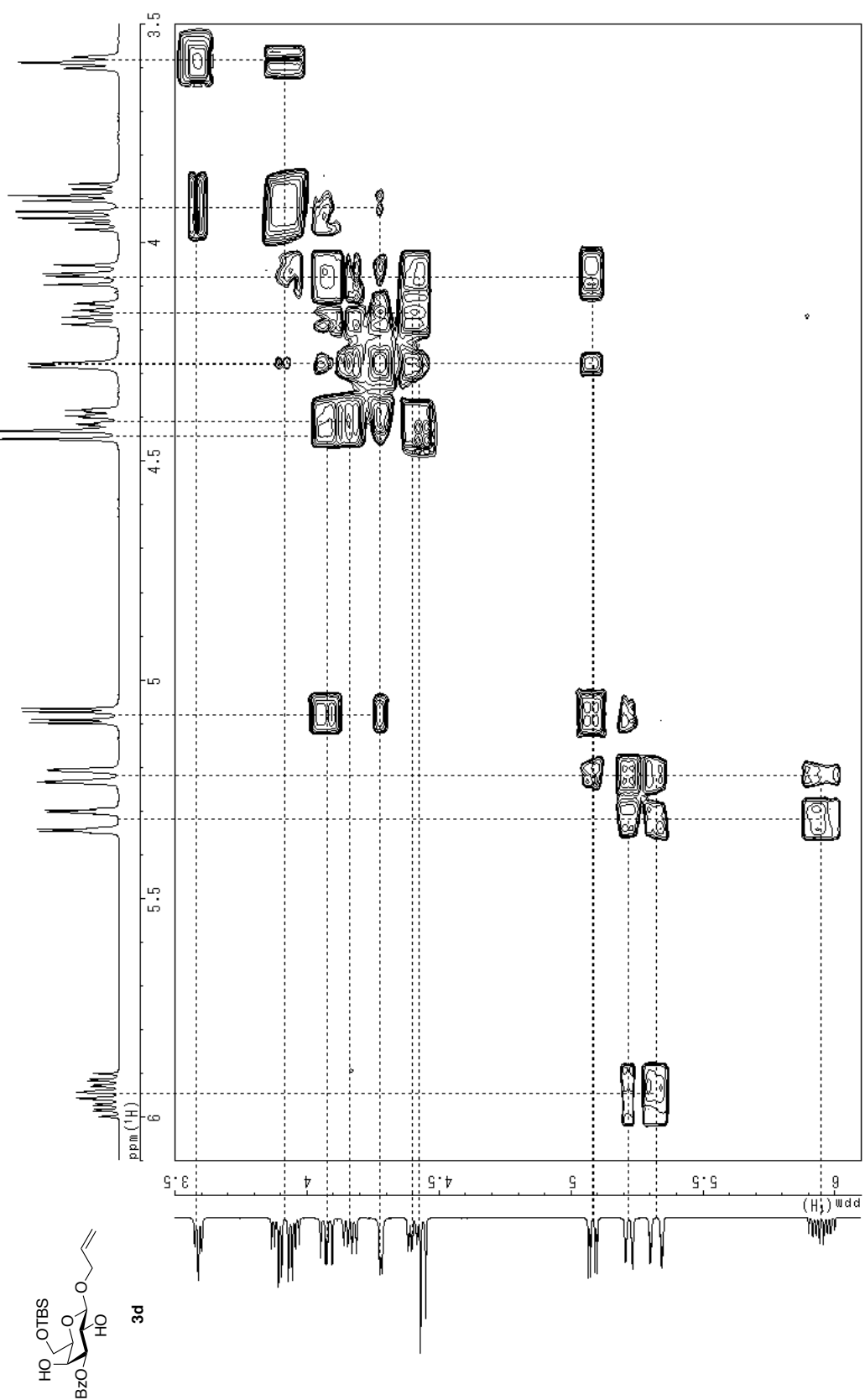
3d

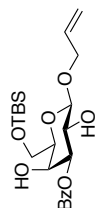
¹H-NMR spectrum of **3d**



Comment TSV25026_pure_13C_COSY_2
0190114_01
Date 2019/Jan/14
ObsNuc ¹H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 16
AcqTime 2.589 s
Acc. Interval 5.589 s
Spinning 16.0 Hz
Temperature 25.0 °C
Solvent cdcl3

^1H - ^1H COSY spectrum of **3d**

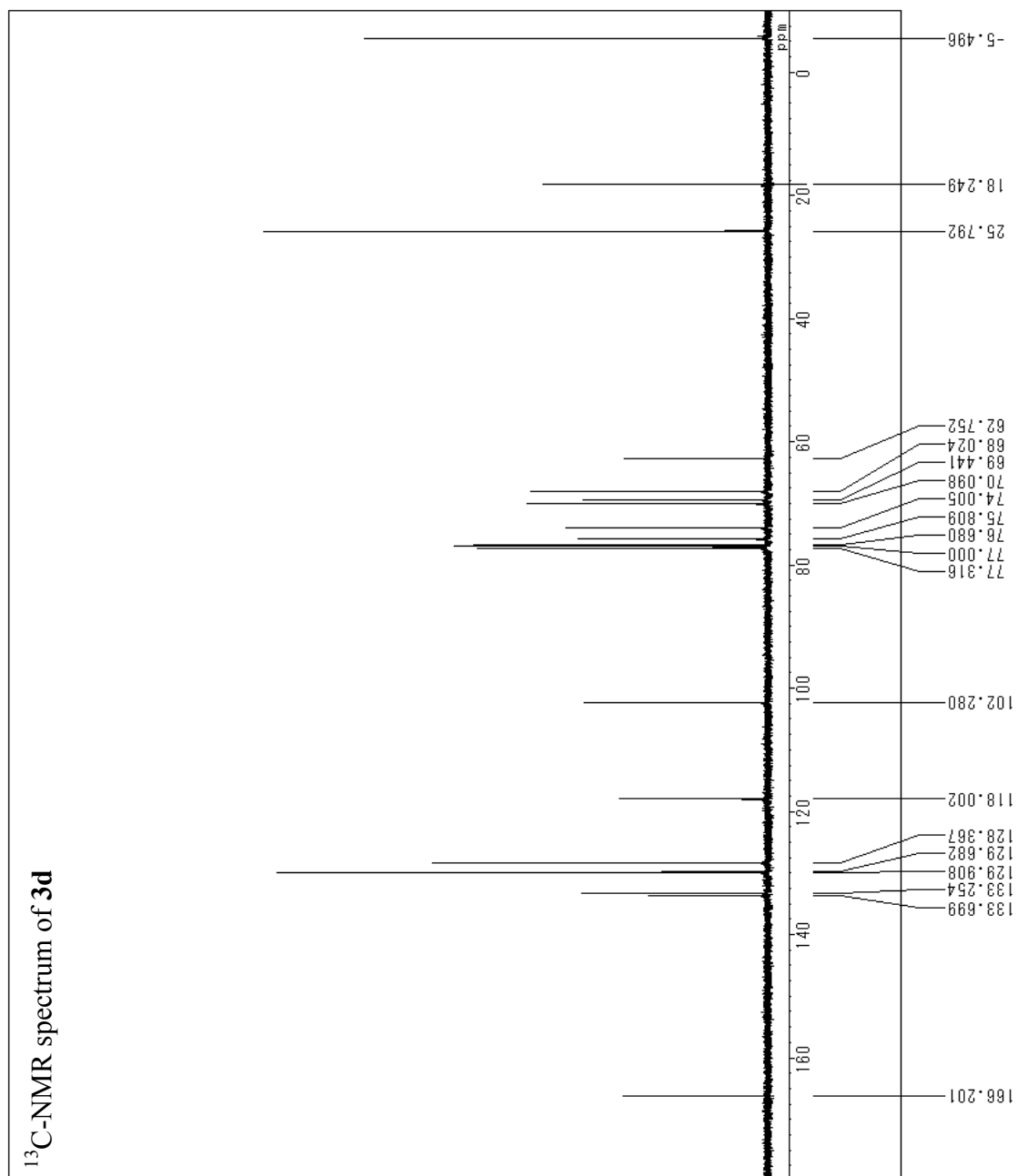




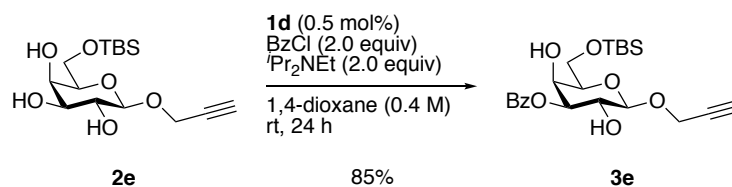
3d

¹³C-NMR spectrum of **3d**

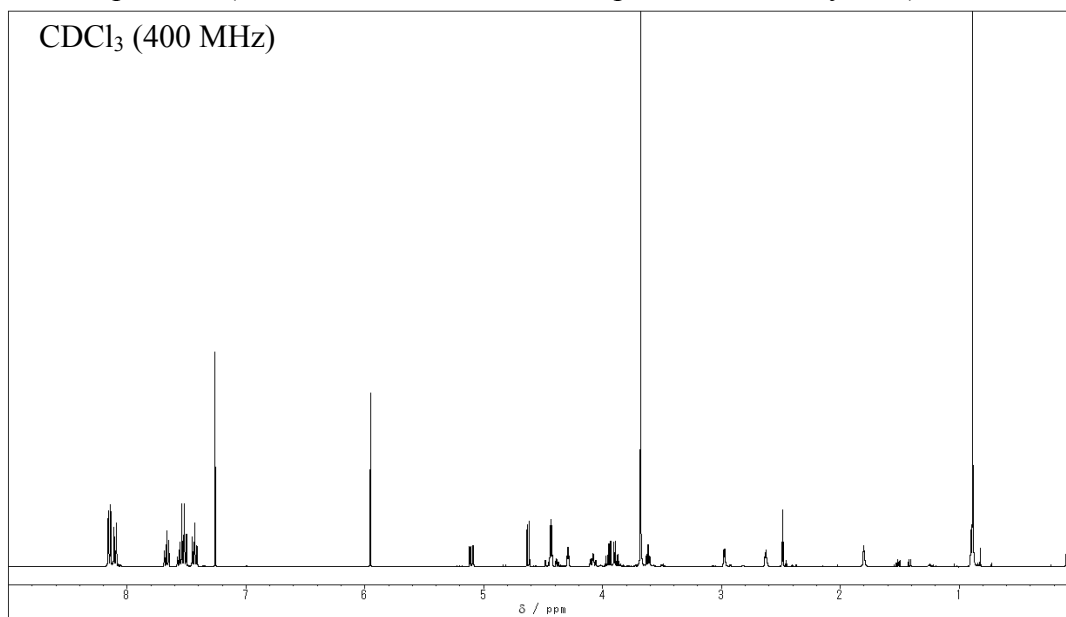
Comment TSV25026_pure_13C_COSY_2
 0190114_01
 Date 2019/Jan/14
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



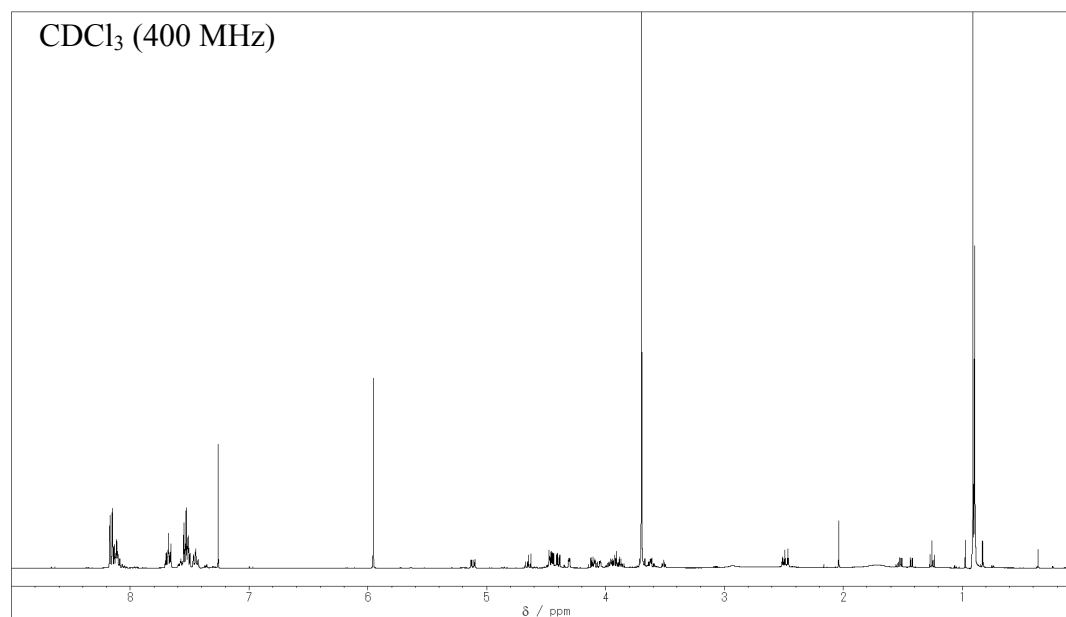
Propargyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- β -D-galactopyranoside (**3e**)

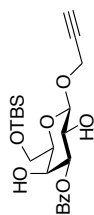


¹H-NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



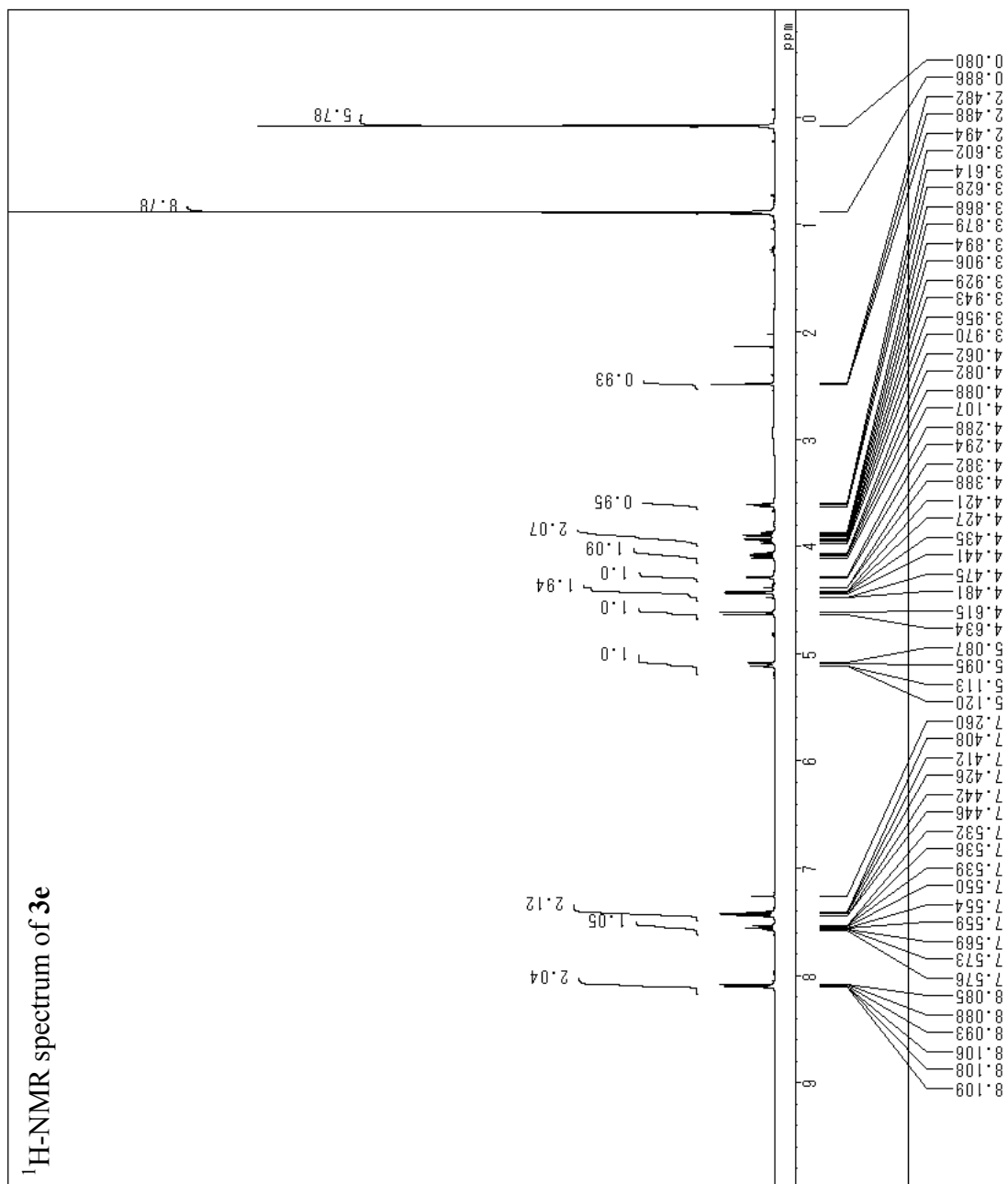
¹H-NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



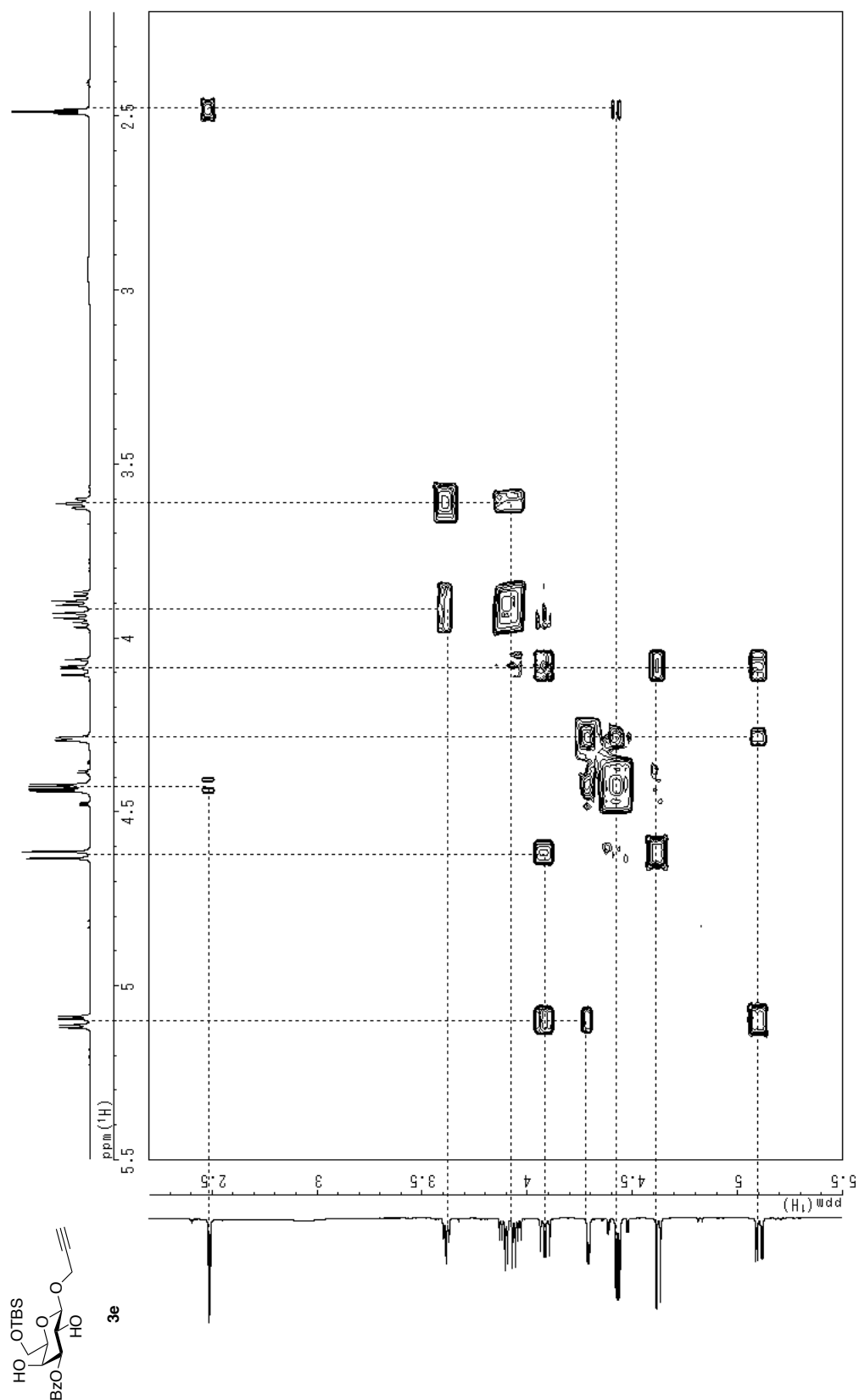


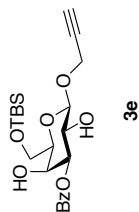
3e

Comment TSV09016_COSY_20160801_0
 1
 Date 2016/Aug/01
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

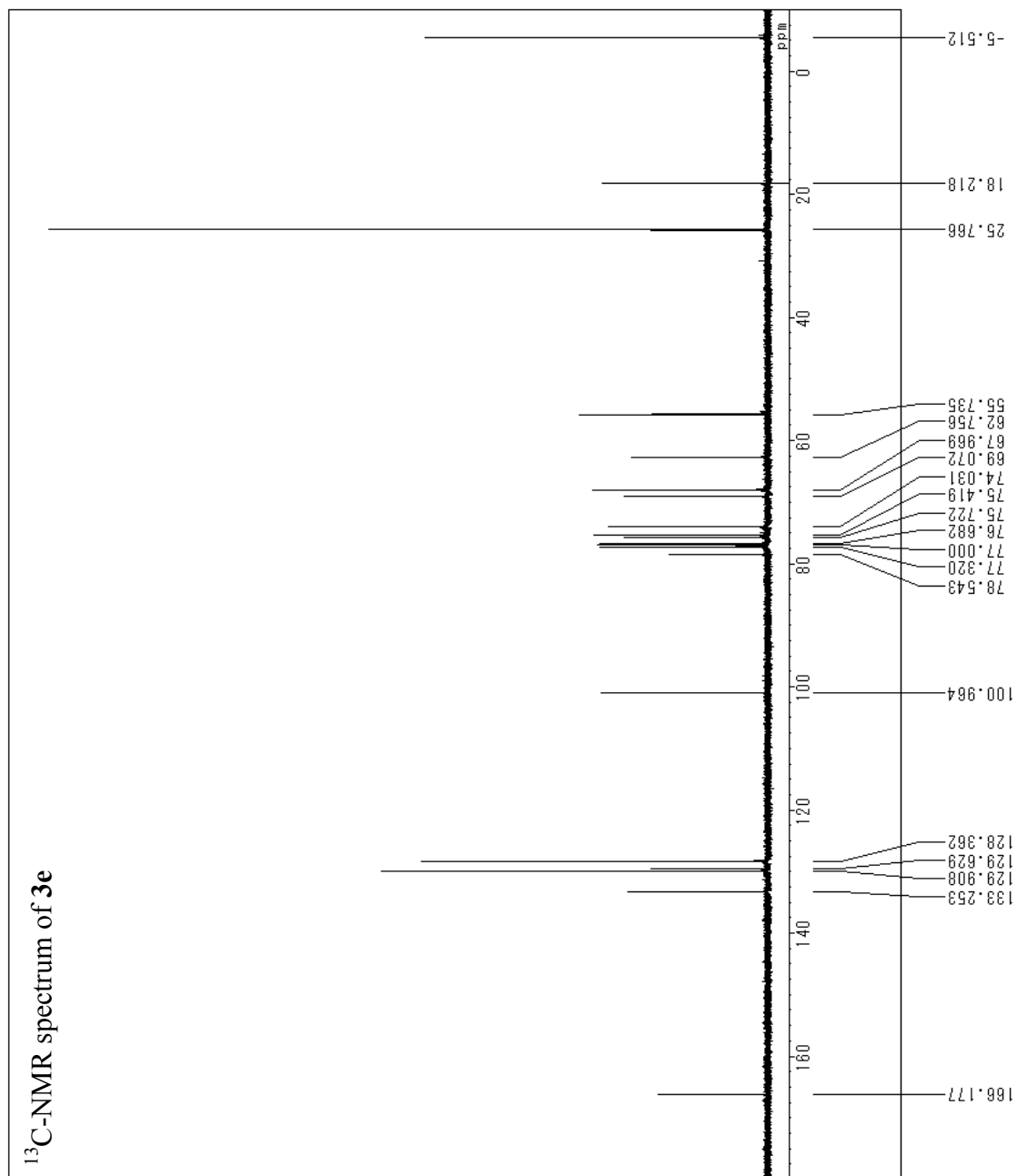


^1H - ^1H COSY spectrum of **3e**



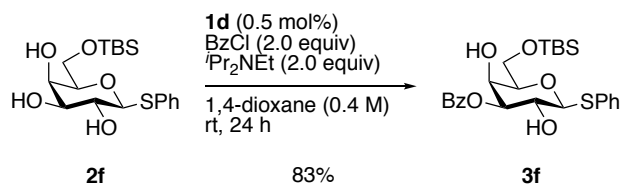


¹³C-NMR spectrum of **3e**

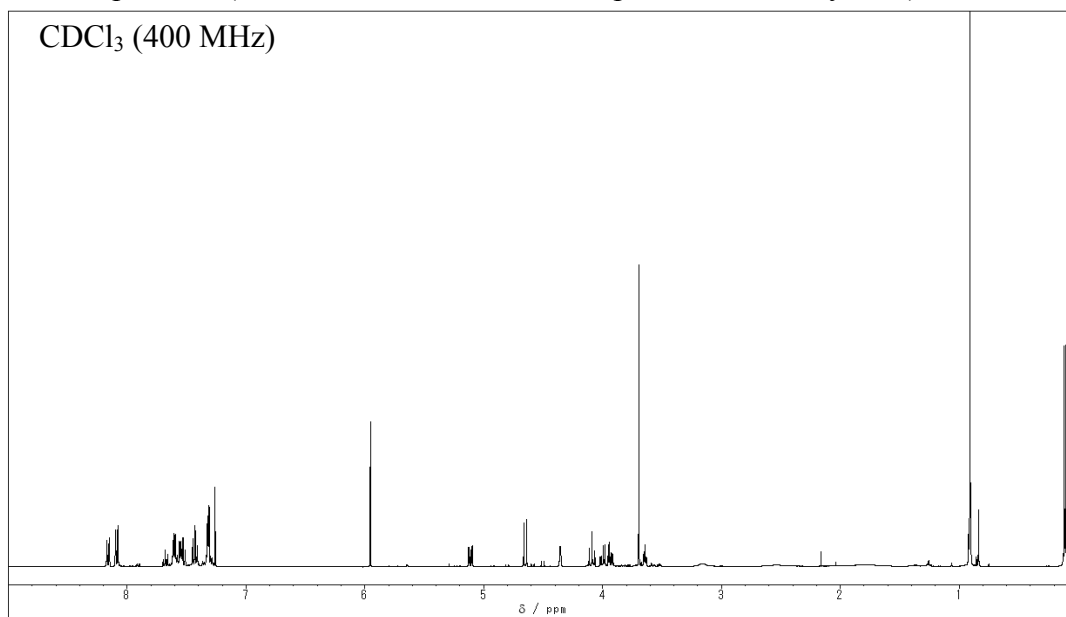


Comment TSV09016_13C_2_20180801
 01
 Date 2018/Aug/01
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 256
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

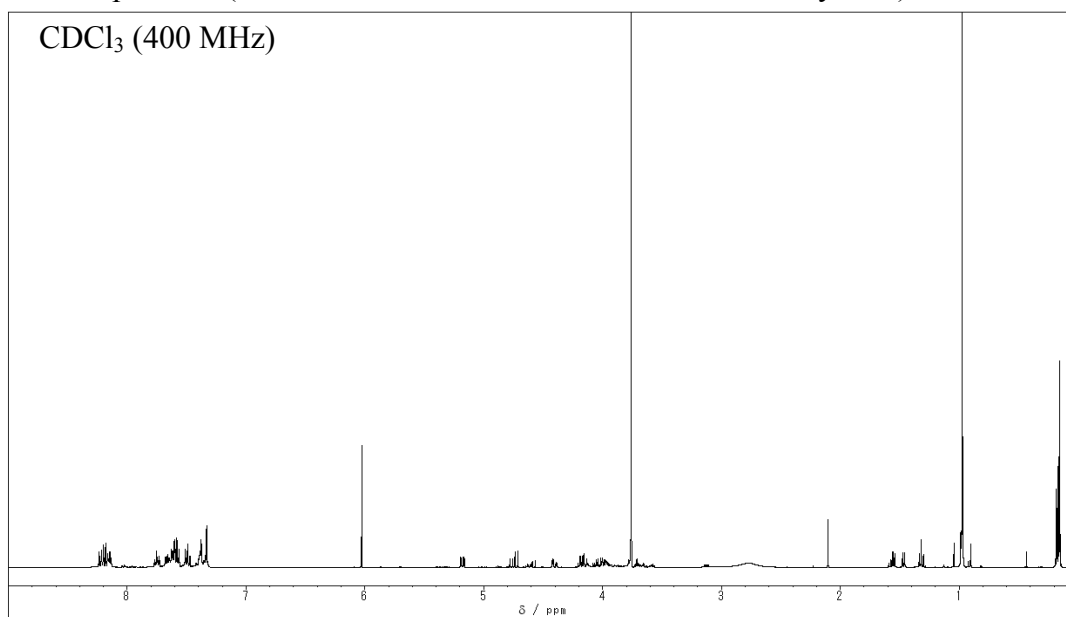
Phenylthio 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- β -D-galactopyranoside (**3f**)



$^1\text{H-NMR}$ spectrum (crude reaction mixture in the presence of catalyst **1d**)



$^1\text{H-NMR}$ spectrum (crude reaction mixture in the absence of catalyst **1d**)



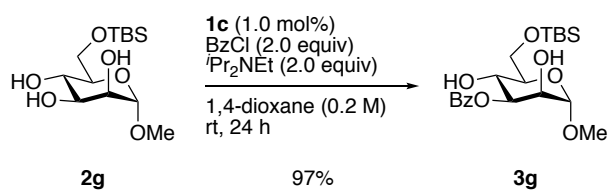


Comment	1	
Date	2016/Jul/12	
ObsNuc	¹ H	
ExMode	PROTON_001	
ObsFreq	399.45 MHz	
Scan	8	
AcqTime	2.569 s	
Acc. Interval	5.569 s	
Spinning	16.0 Hz	
Temperature	25.0 °C	
Solvent	cdcl3	

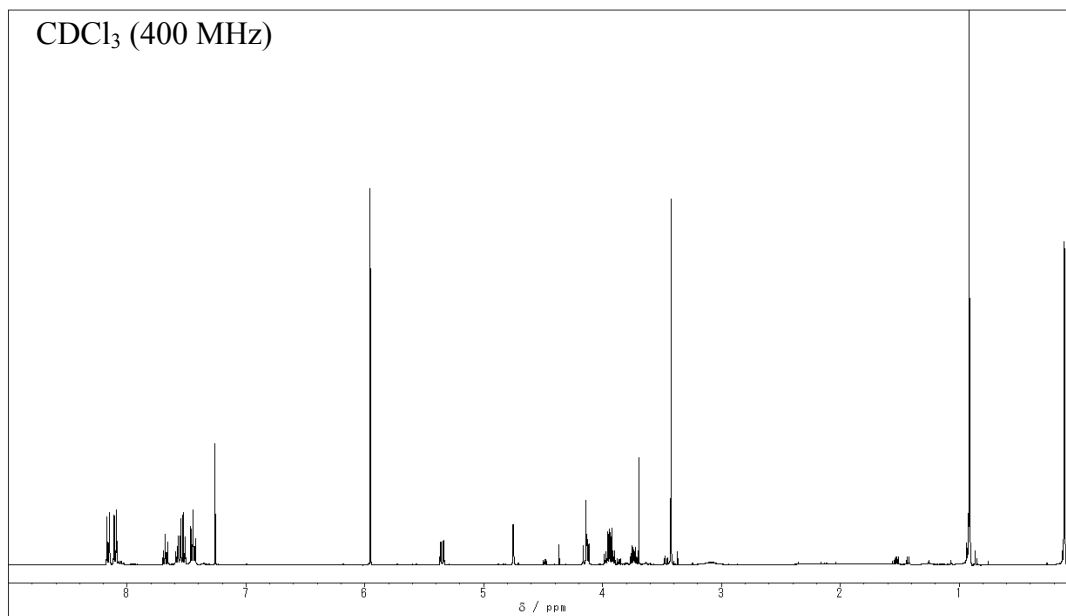
Chemical structure of **3f** is shown as a chair conformation of a cyclohexane ring with an OTBS group at C1 (axial), a BzO group at C2 (equatorial), and a Ph group at C3 (equatorial).

¹H NMR spectrum (CDCl₃) of **3f** is displayed, showing peaks from 2.5 to 5.5 ppm. Key assignments include: aromatic protons (7.2-7.4 ppm), BzO protons (4.5-4.7 ppm), C3-H (3.9 ppm), C2-H (3.7 ppm), C1-H (2.5 ppm), and solvent (7.26 ppm). Integration values are provided for several peaks.

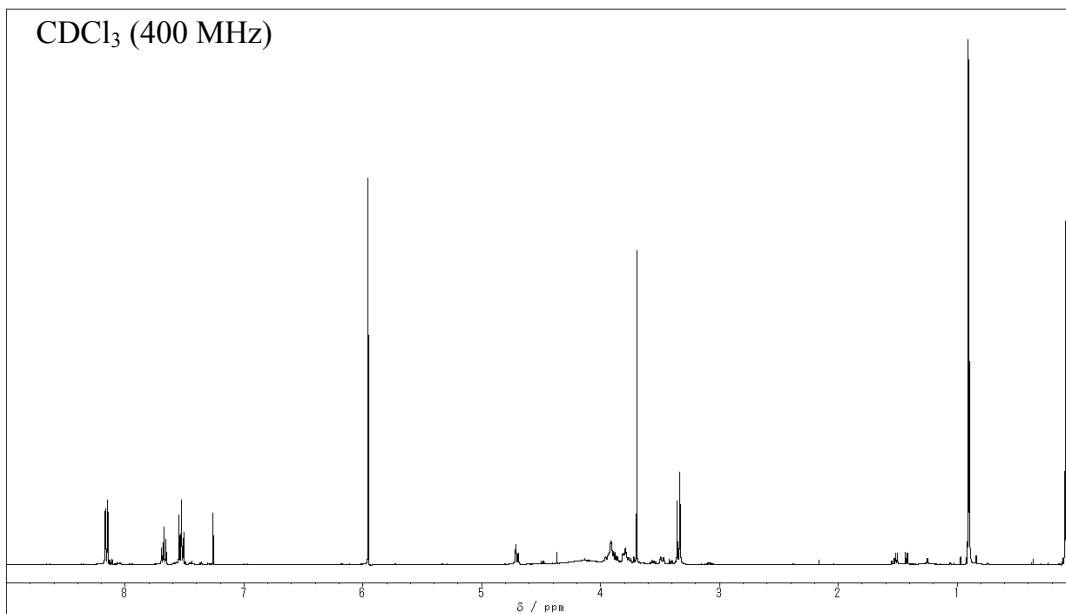
Methyl 6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl- α -D-mannopyranoside (**3g**)

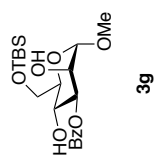


$^1\text{H-NMR}$ spectrum (crude reaction mixture in the presence of catalyst **1c**)

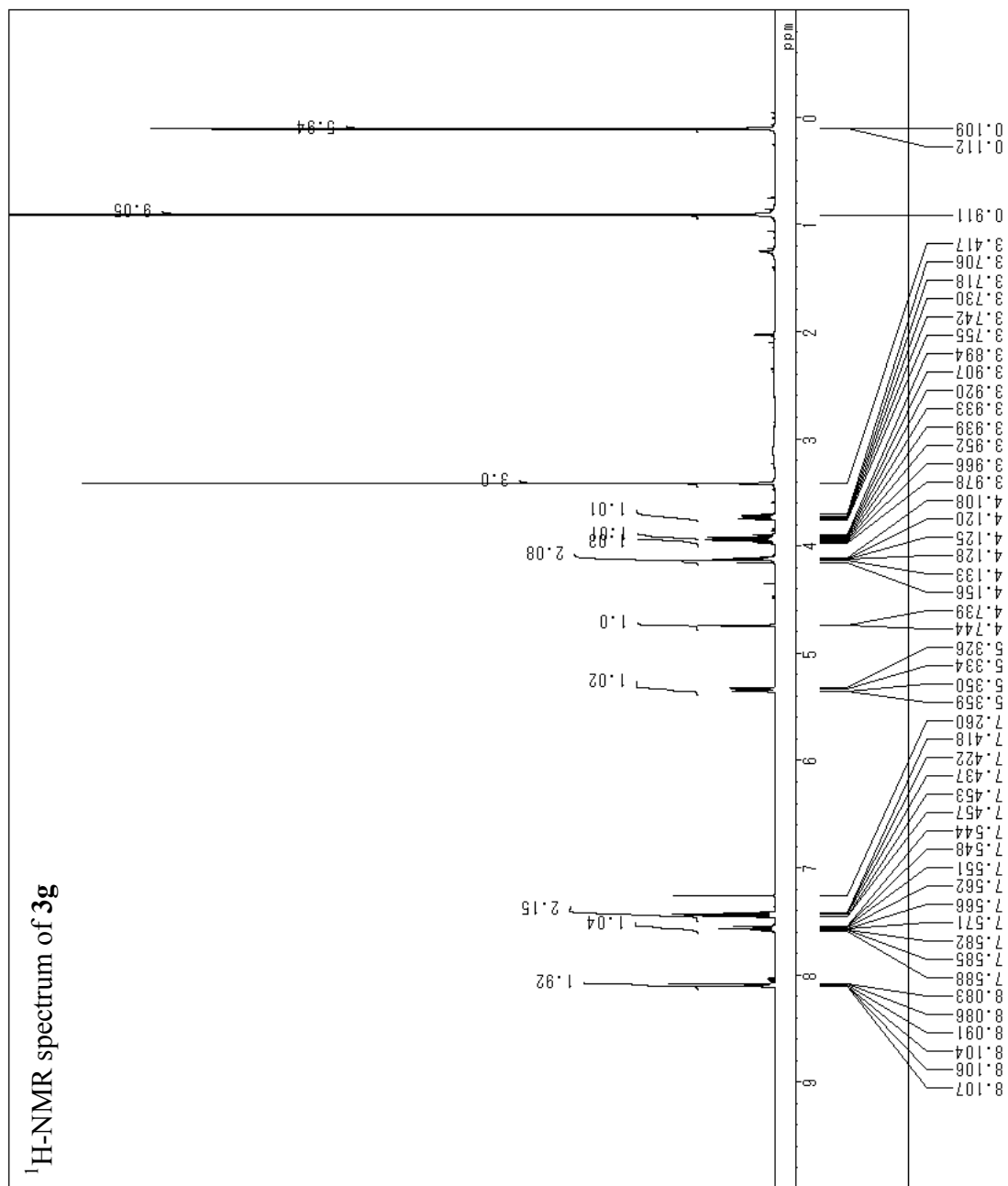


$^1\text{H-NMR}$ spectrum (crude reaction mixture in the absence of catalyst **1c**)

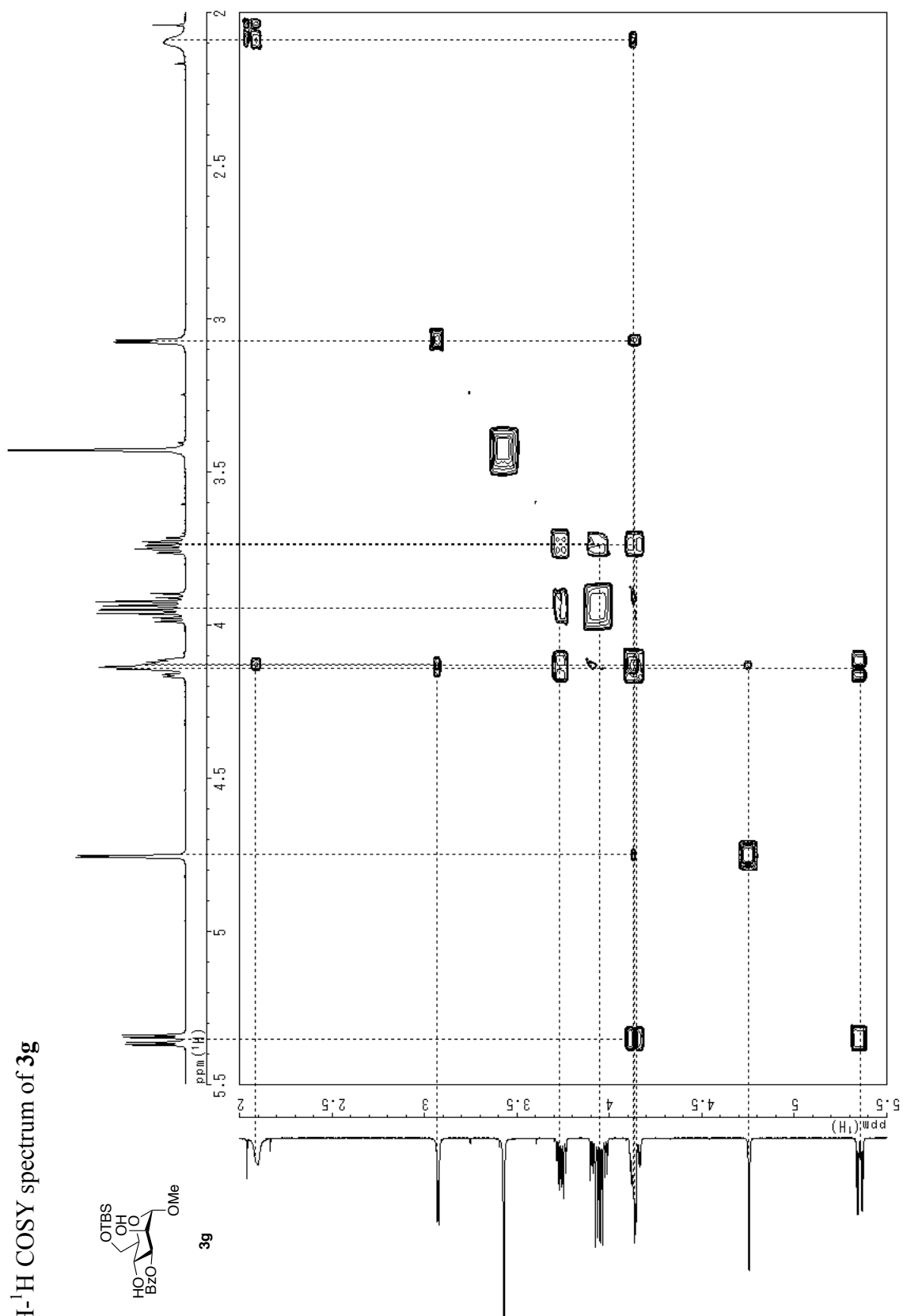


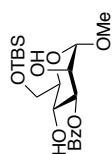
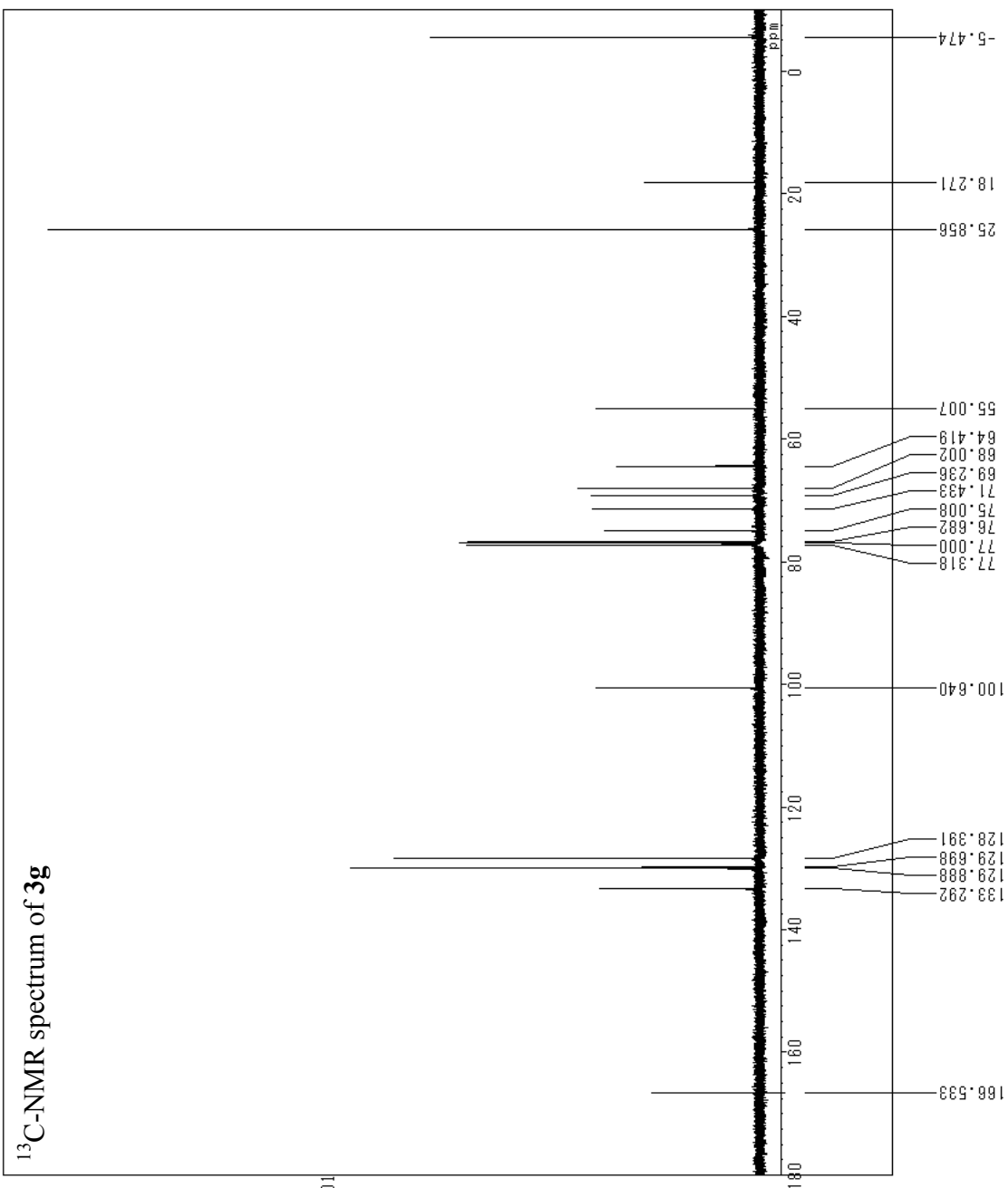


Comment	2016/Mar/25
Date_01	1H
ObsNuc	PROTON_001
ObsMuc	399.45 MHz
ExMode	16
ObsFreq	2.568 s
Scan	5.569 s
AcqTime	Acc. Interval
Spinning	16.0 Hz
Temperature	25.0 °C
Solvent	cdcl3



^1H - ^1H COSY spectrum of **3g**

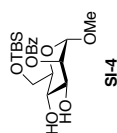
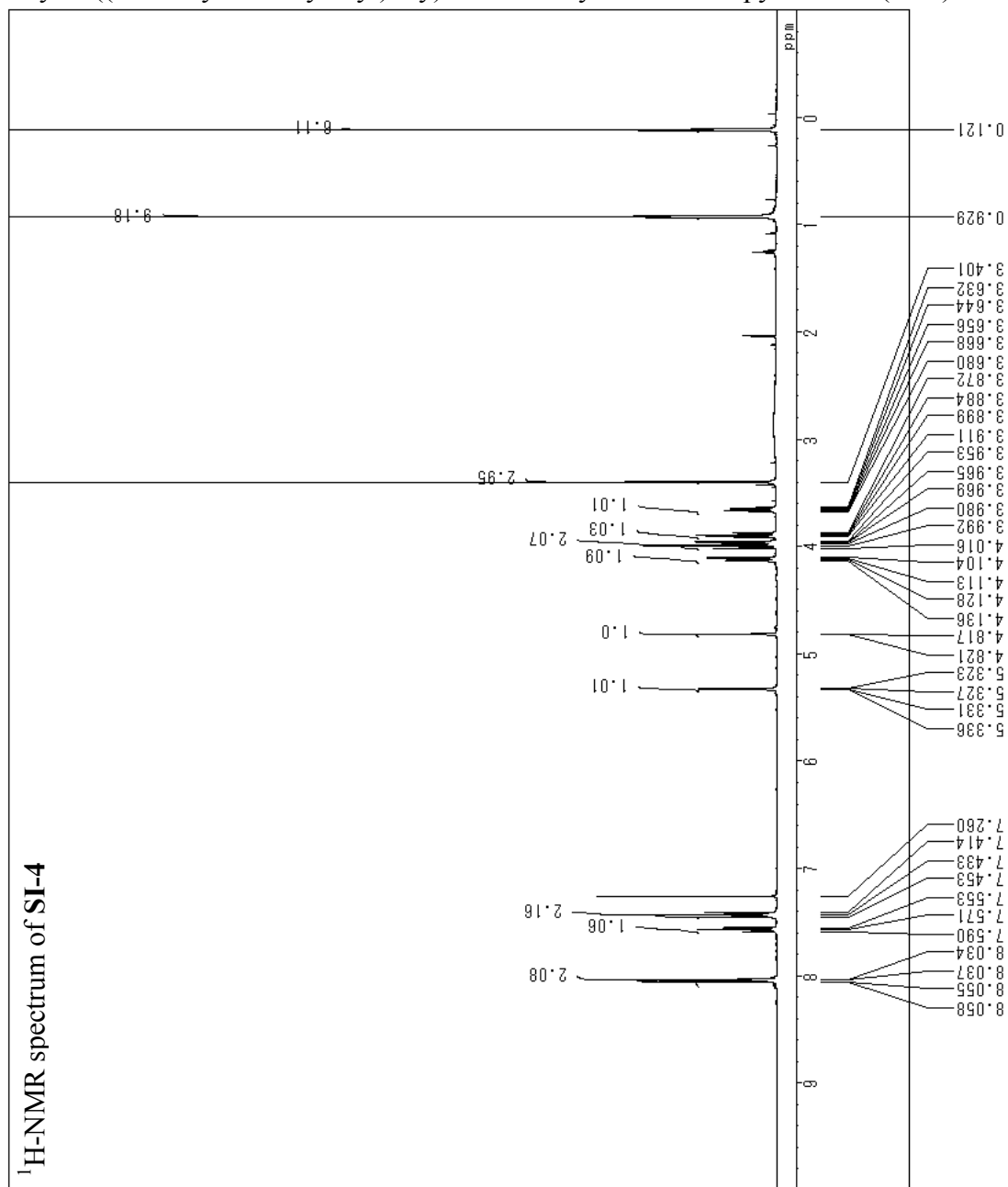




3g

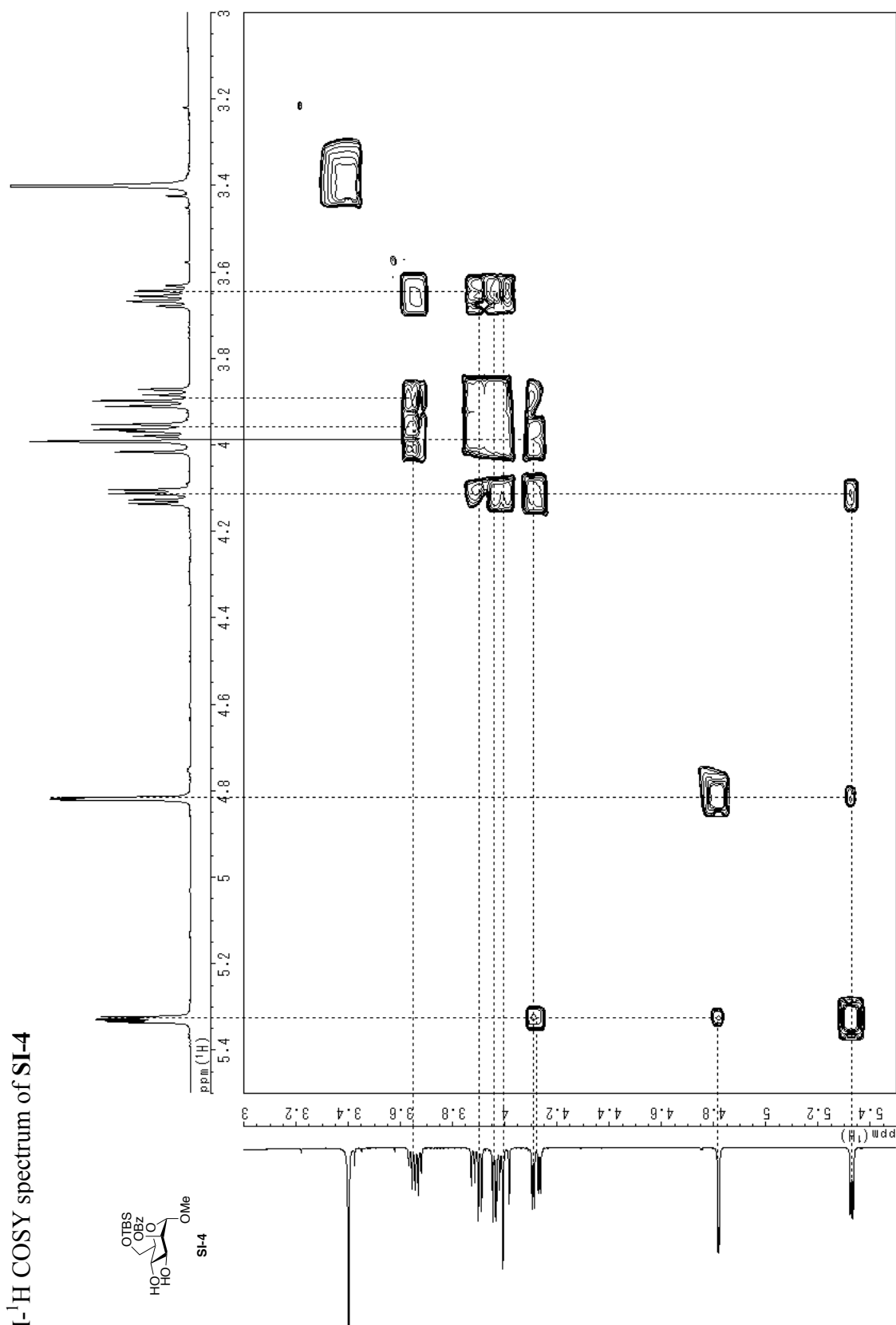
Comment TSV05029_13C_20180325_01
 Date 2016/Mar/25
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 256
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

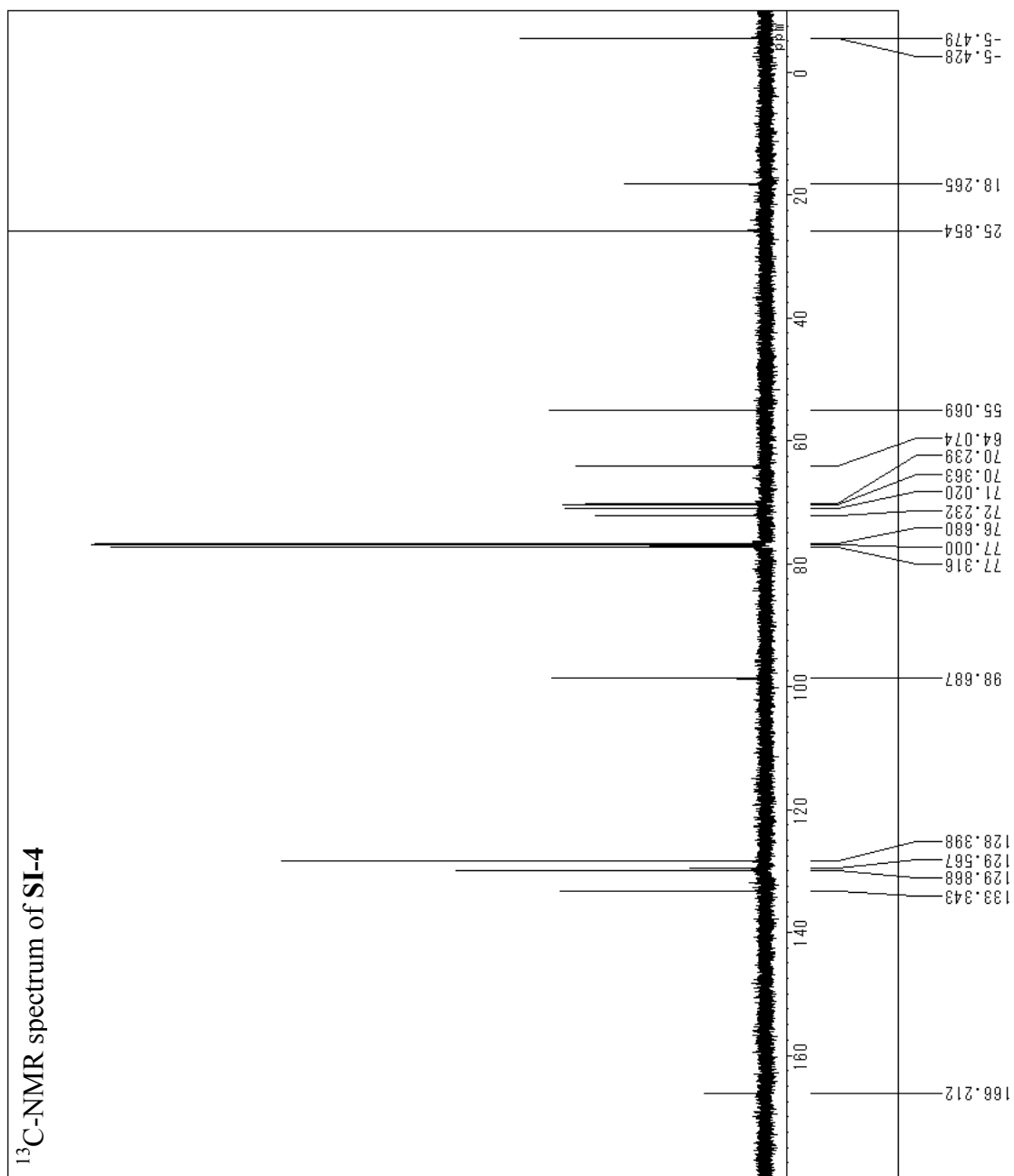
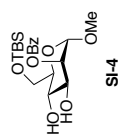
Methyl 6-((*tert*-butyldimethylsilyl)oxy)-2-*O*-benzoyl- α -D-mannopyranoside (**SI-4**)



Comment TSV25019_pure_13C_COSY_2
0181225_01
Date 2018/Dec/25
ObsNuc ¹H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 16
AcqTime 2.588 s
Acc.Interval 5.588 s
Spinning 16.0 Hz
Temperature 25.0 °C
Solvent cdcl3

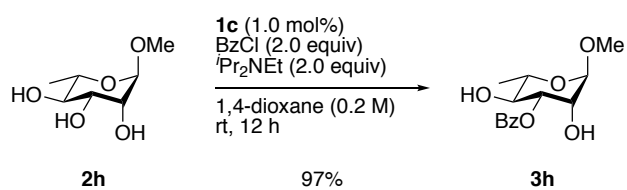
^1H - ^1H COSY spectrum of **SI-4**



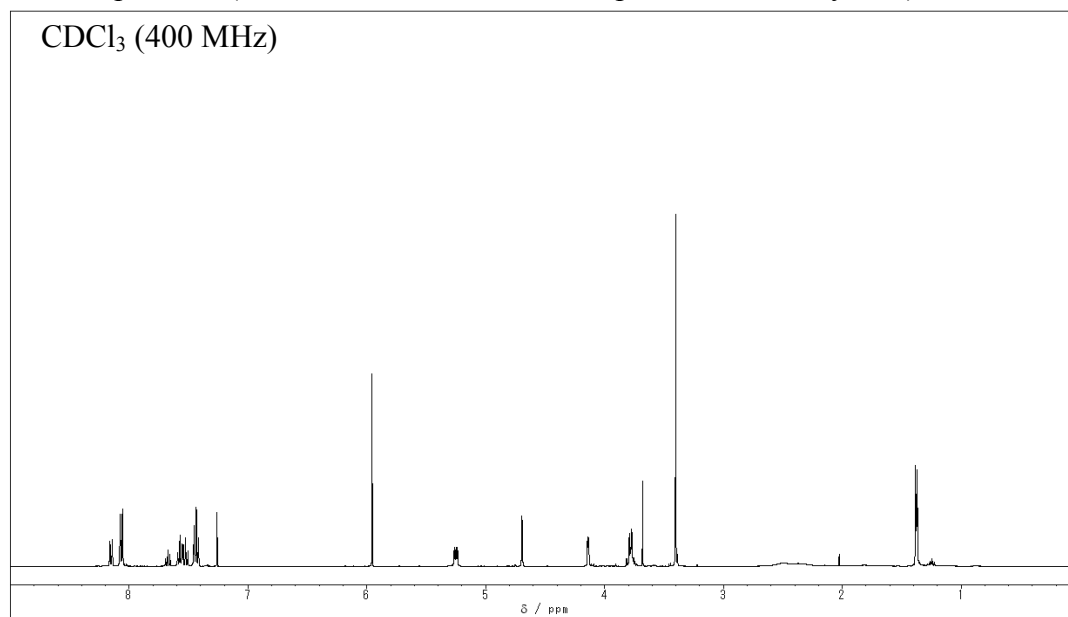


Comment TSY25019_pure_13C_COSY_2
 0181225_01
 Date 2018/Dec/25
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl3

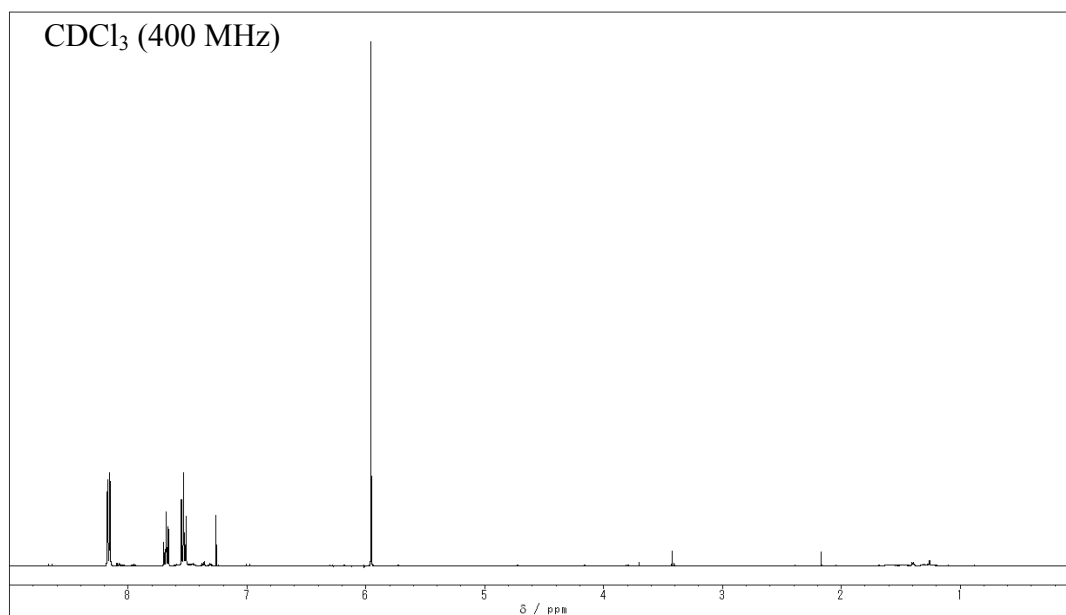
Methyl 3-*O*-benzoyl- α -L-rhamnopyranoside (**3h**)

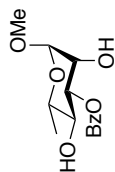


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1c**)



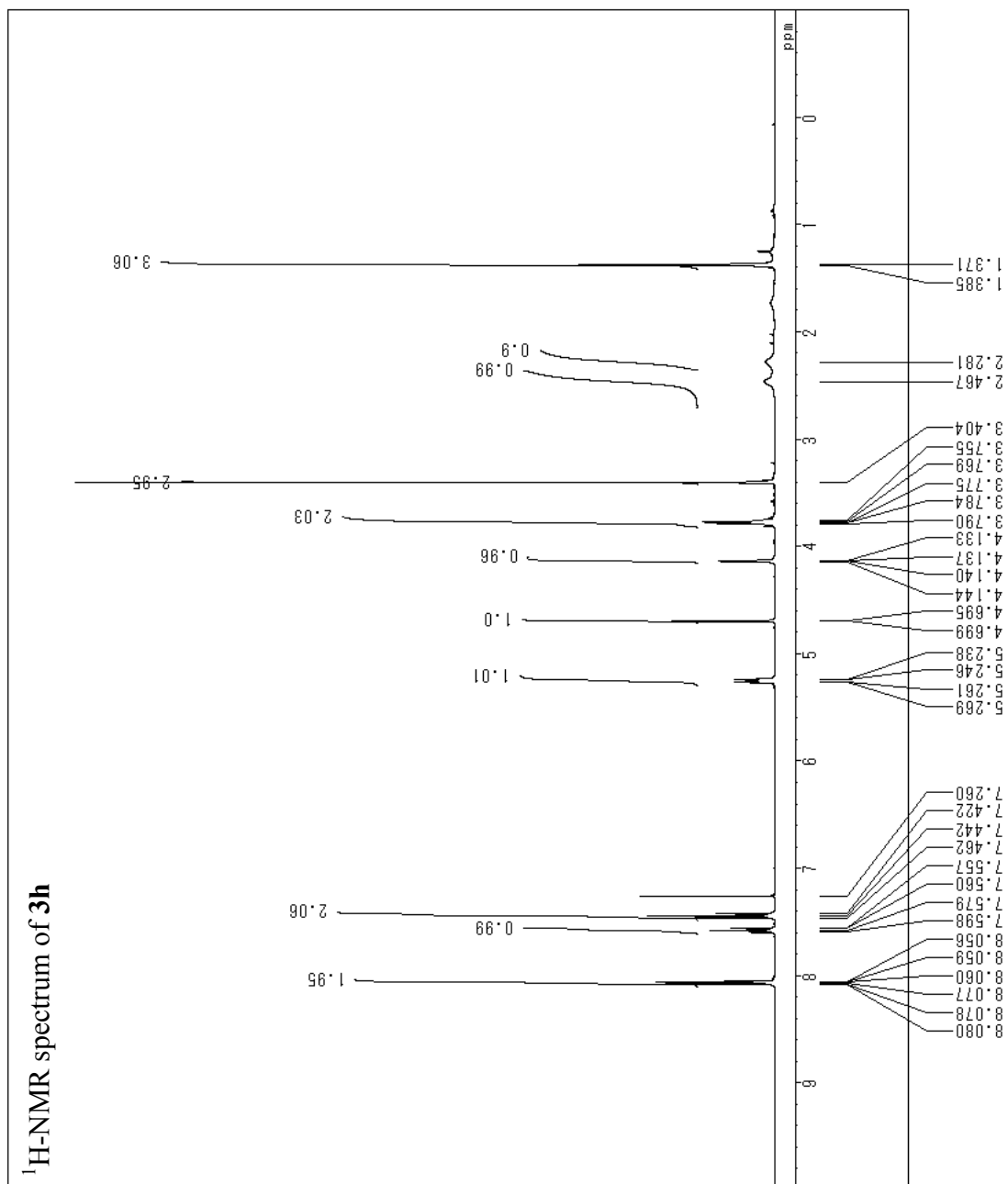
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1c**)



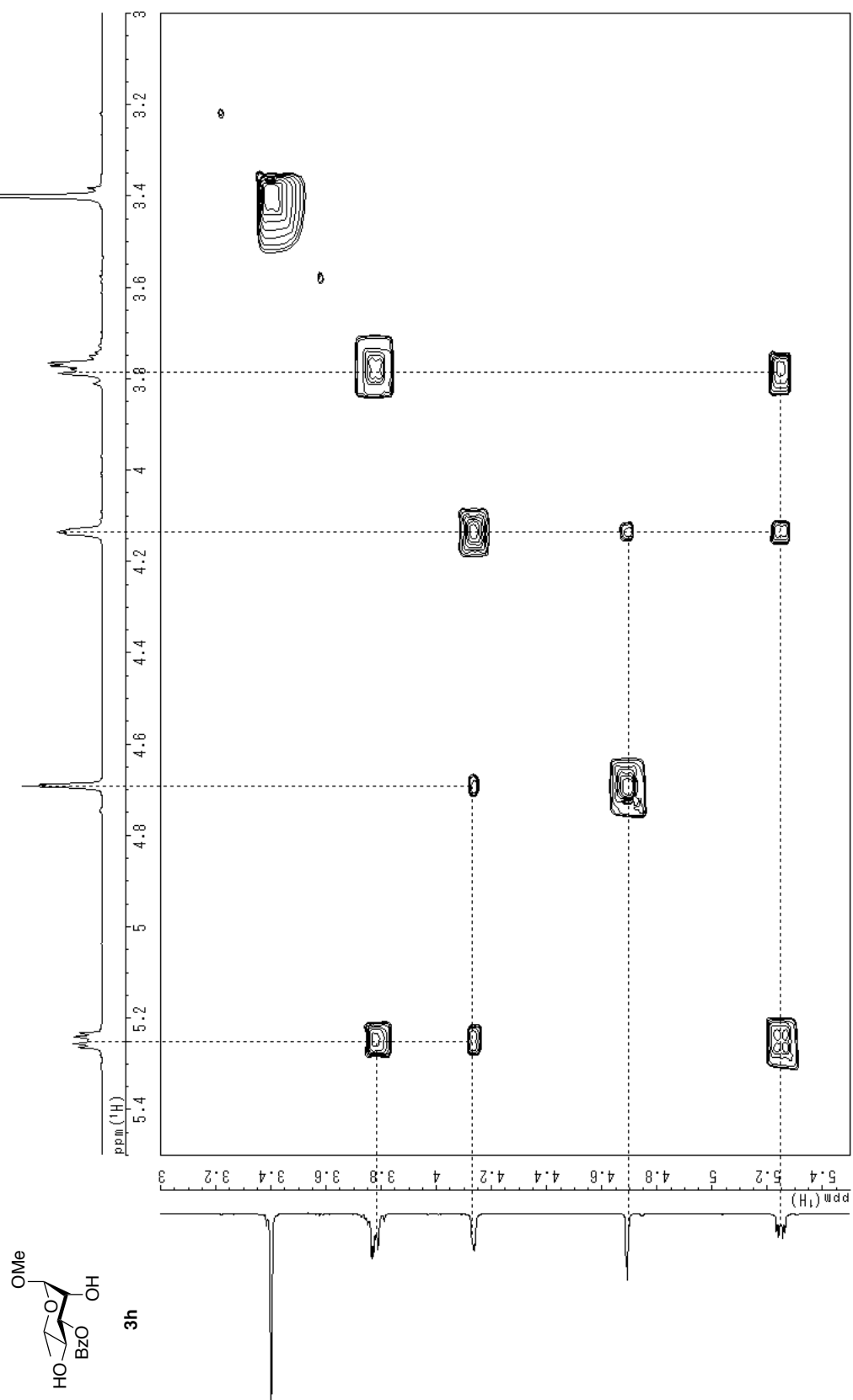


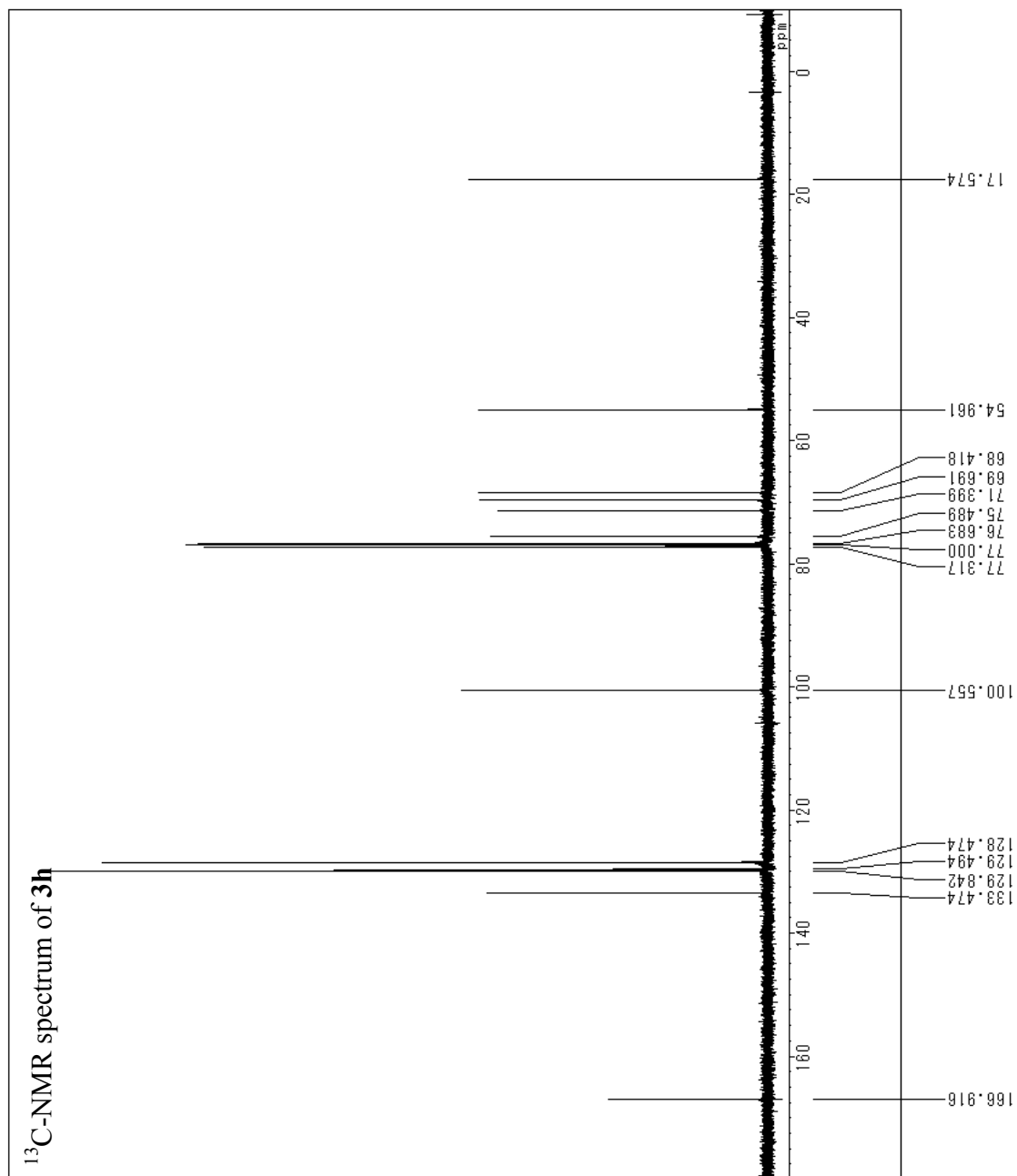
3h

Comment TSV05020_column_20180314
 Date_01 2018/Mar/14
 ObsNuc ^1H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 32
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 $^{\circ}\text{C}$
 Solvent cdcl_3



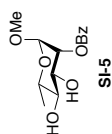
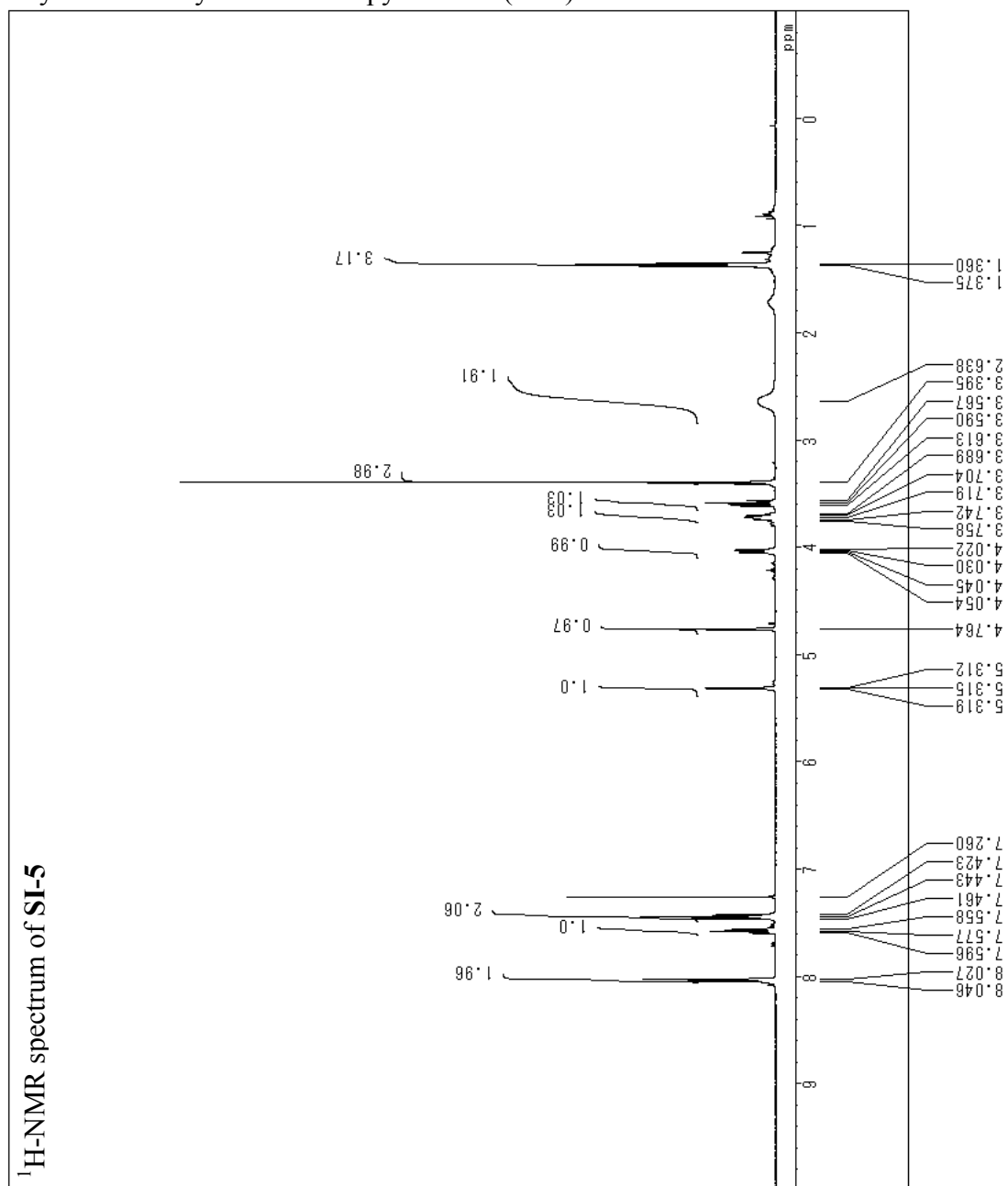
^1H - ^1H COSY spectrum of **3h**





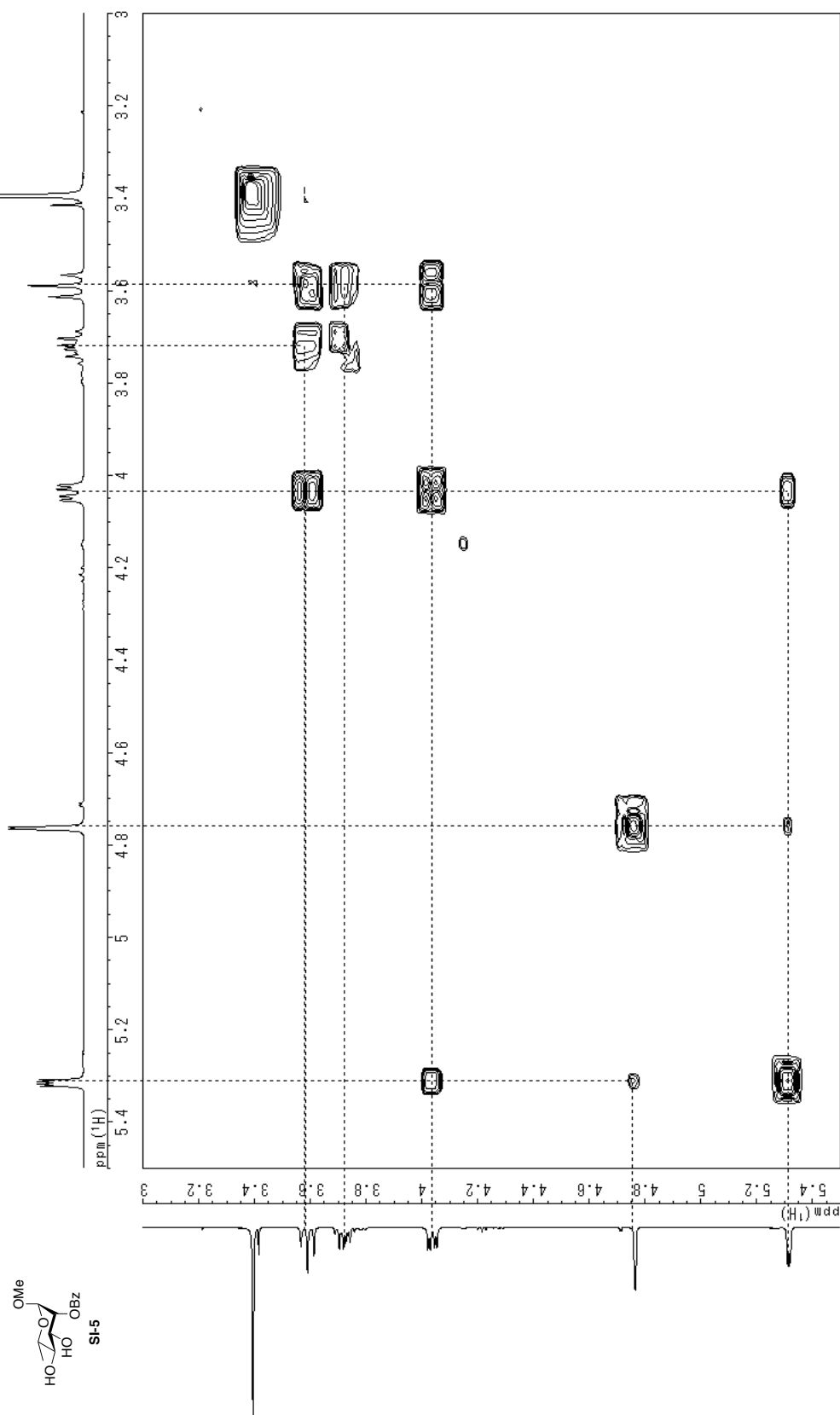
Comment TSV05020_13C_20180314_01
 Date 2016/Mar/14
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

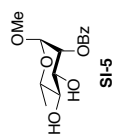
Methyl 2-*O*-benzoyl- α -L-rhamnopyranoside (SI-5)



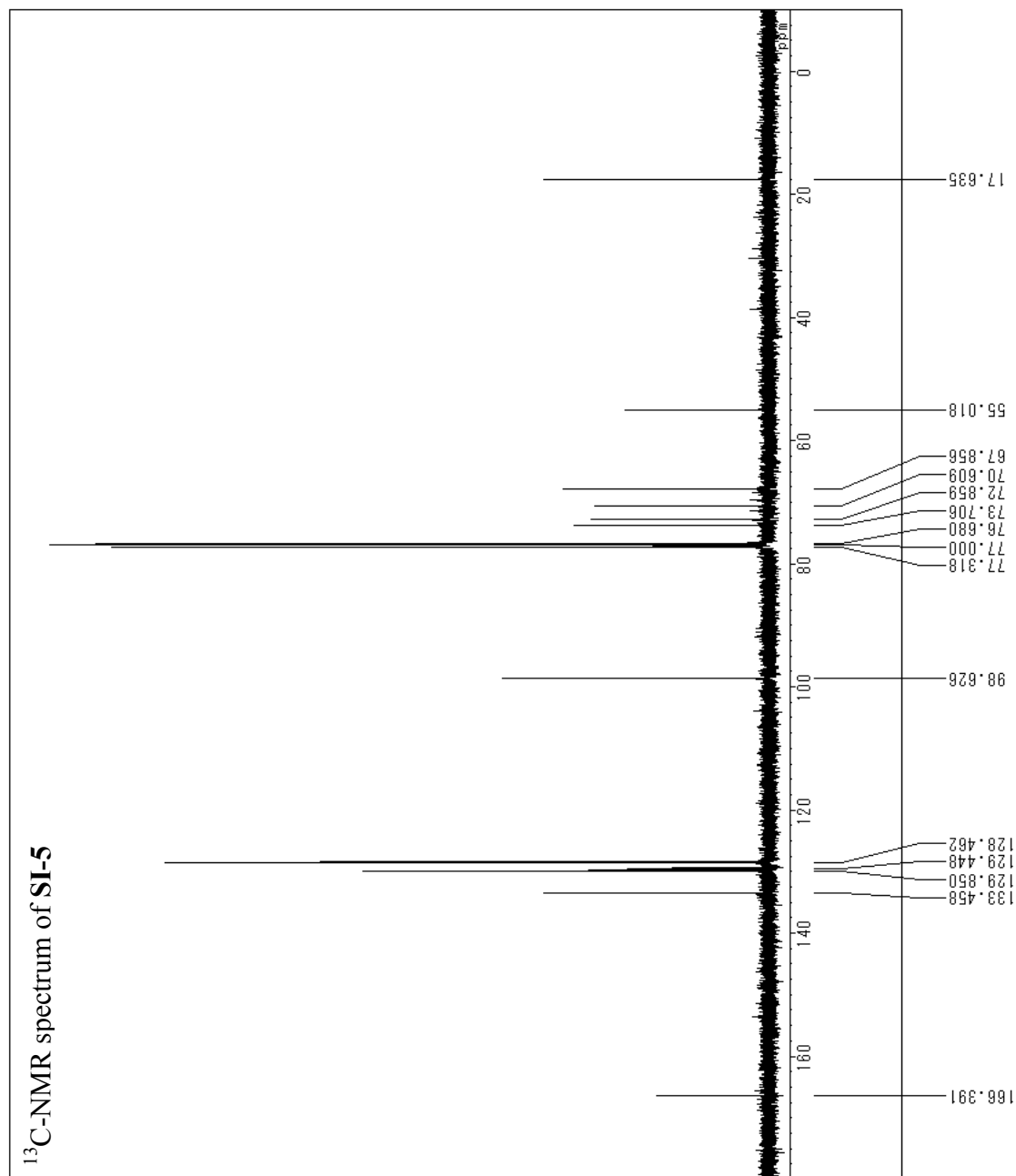
Comment TSV25018_pure_2_20181228
 Date_01 2018/Dec/28
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 400.27 MHz
 Scan 16
 AcqTime 2.5559 s
 Acc. Interval 3.5559 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **SI-5**



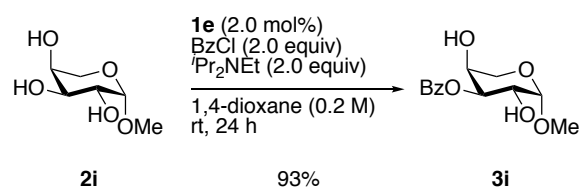


¹³C-NMR spectrum of SI-5

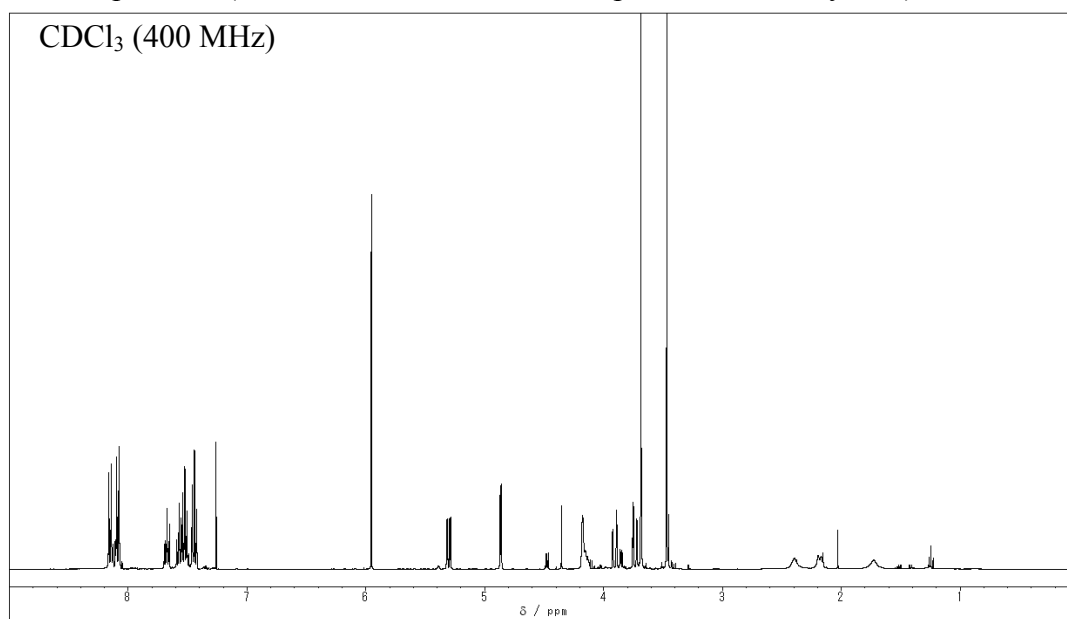


Comment TSV25018_pure_2_13C_COSY
 Date_20181228_01
 Date 2018/Dec/28
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

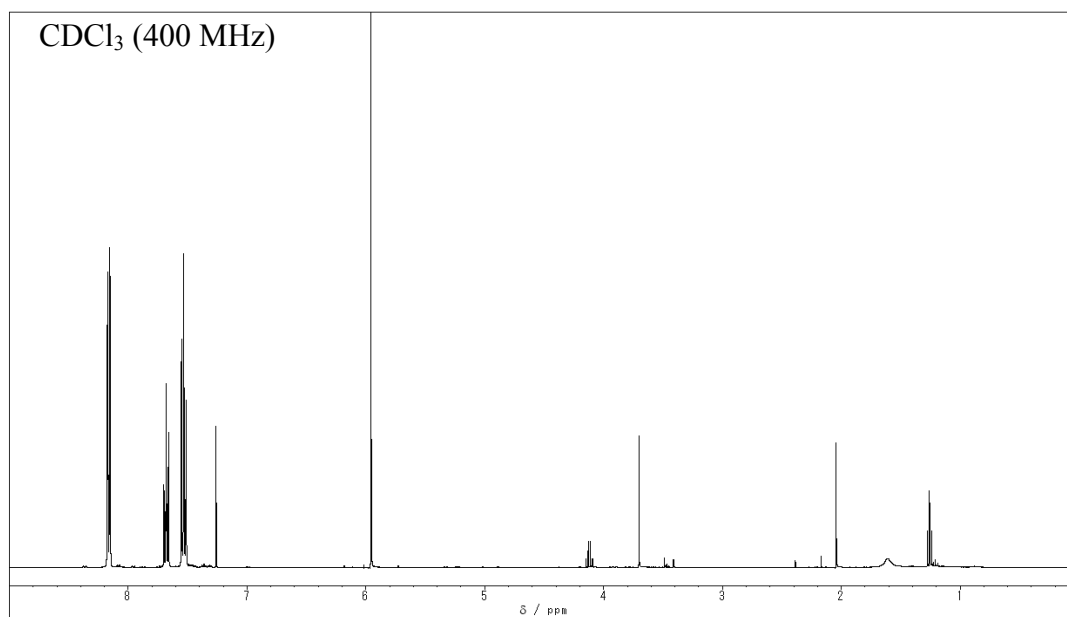
Methyl 3-*O*-benzoyl- β -D-arabinopyranoside (**3i**)

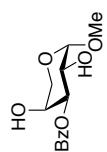


$^1\text{H-NMR}$ spectrum (crude reaction mixture in the presence of catalyst **1e**)



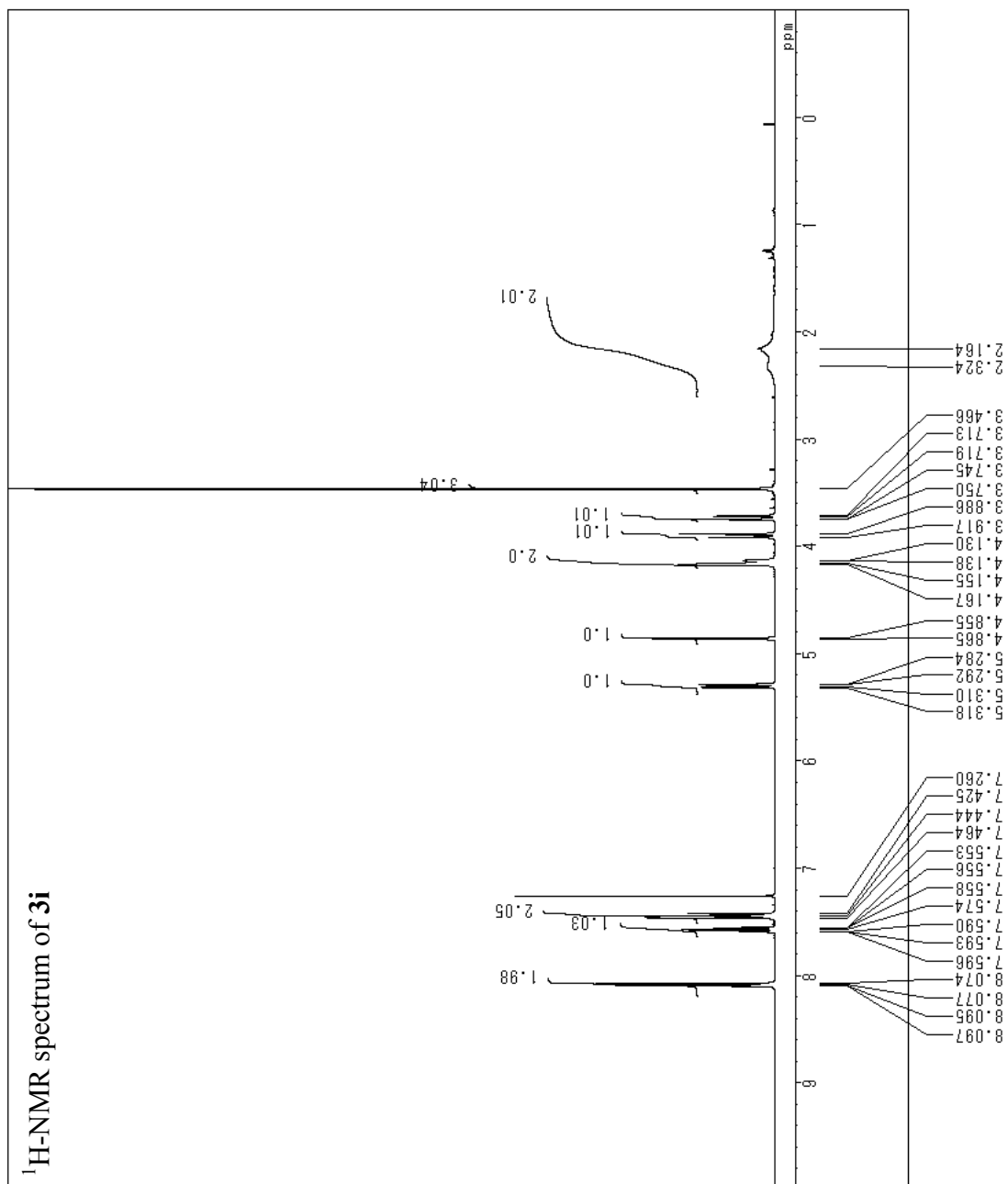
$^1\text{H-NMR}$ spectrum (crude reaction mixture in the absence of catalyst **1e**)





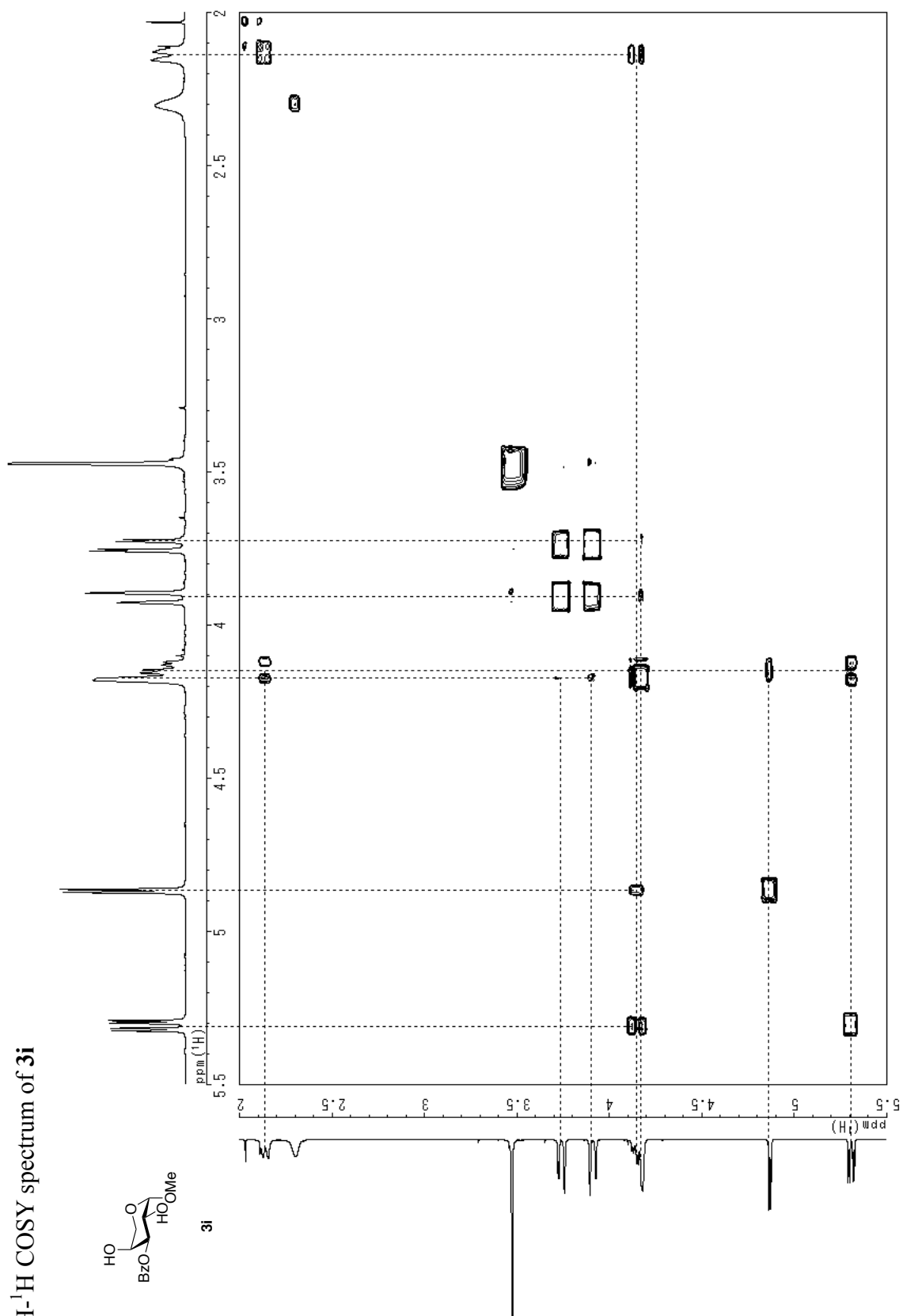
3i

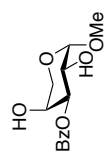
¹H-NMR spectrum of 3i



Comment TSV04038_column_20180208
 Date_01 2016/Feb/05
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl3

^1H - ^1H COSY spectrum of **3i**

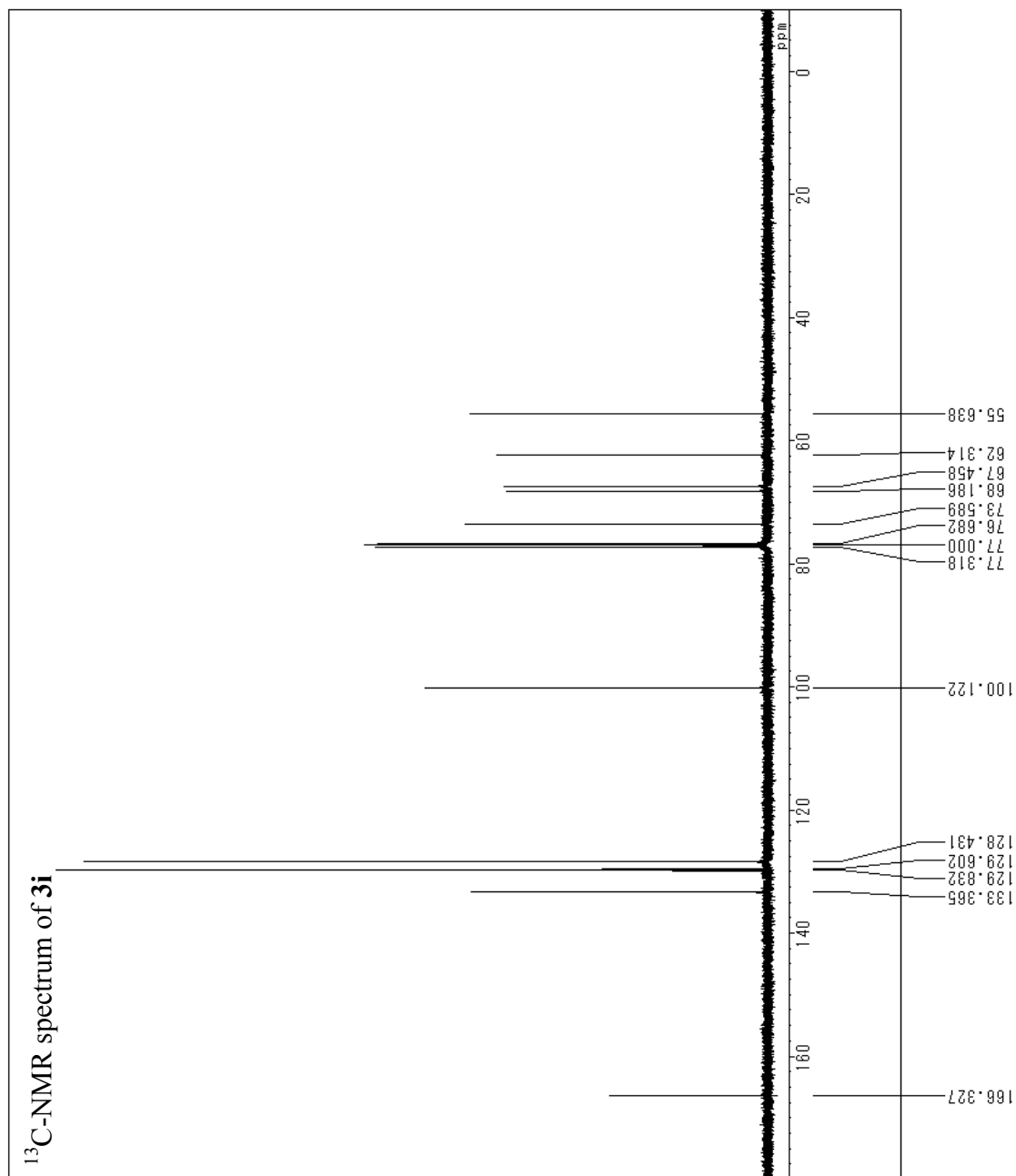




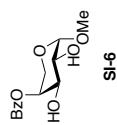
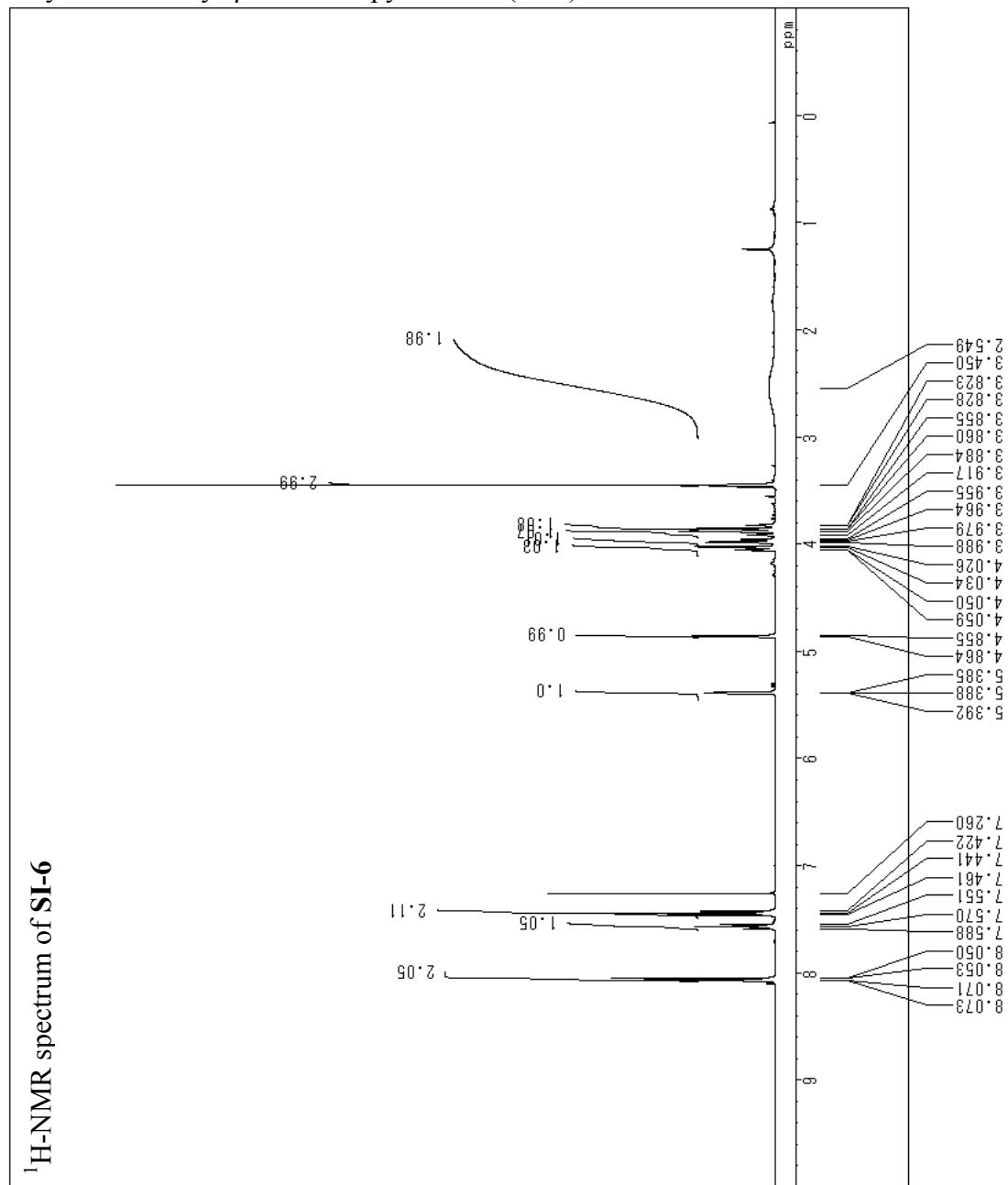
3i

¹³C-NMR spectrum of 3i

Comment TSV04038.13C.20180205_01
 Date 2016/Feb/05
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

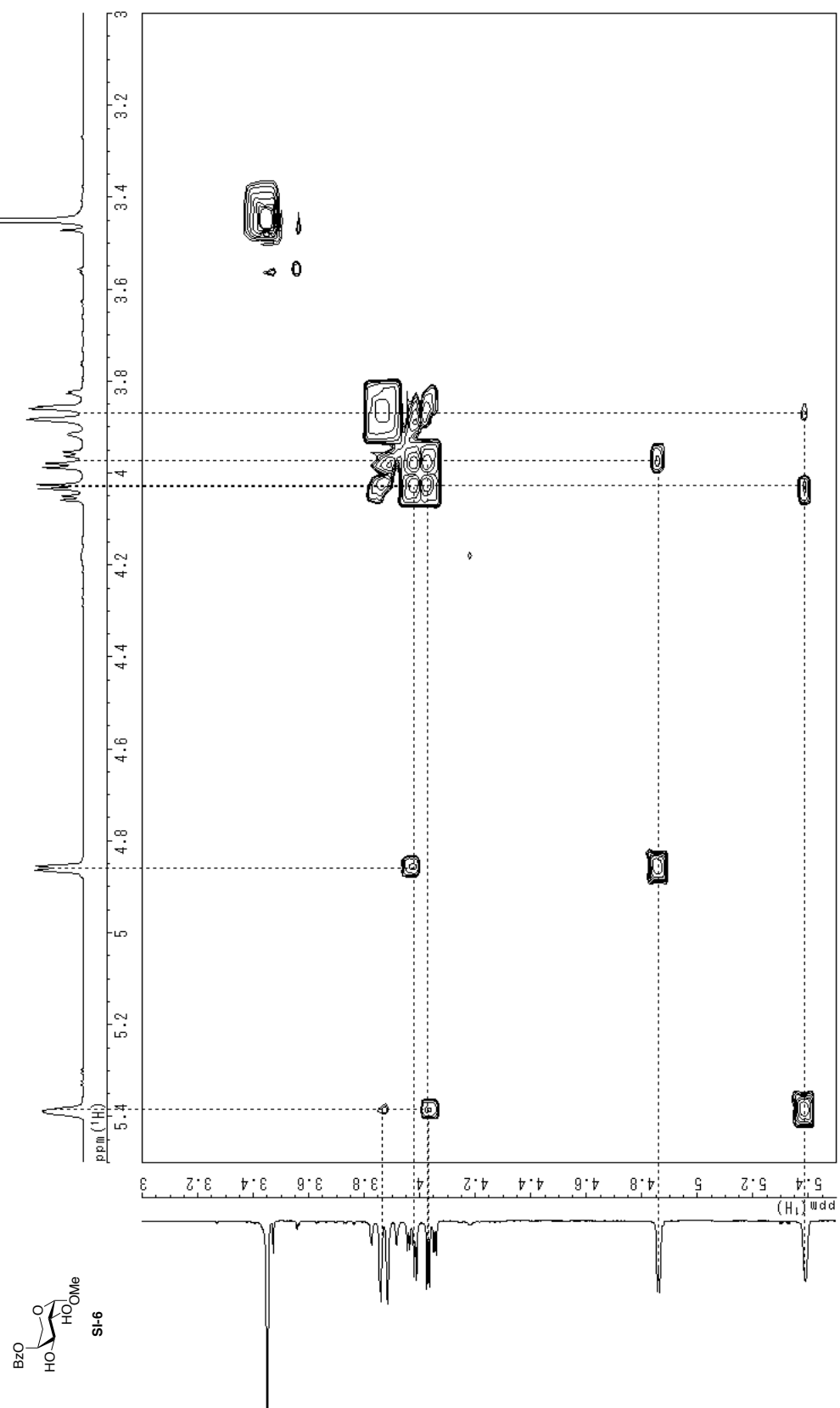


Methyl 4-*O*-benzoyl- β -L-arabinopyranoside (SI-6)

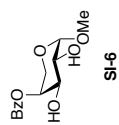


Comment: TSV25020_pure_13C_COSY_2
 0181227_01
 Date: 2018/Dec/27
 ObsNuc: ¹H
 ExMode: PROTON_001
 ObsFreq: 399.45 MHz
 Scan: 16
 AcqTime: 2.569 s
 Acc. Interval: 5.589 s
 Spinning: 16.0 Hz
 Temperature: 25.0 °C
 Solvent: cdcl₃

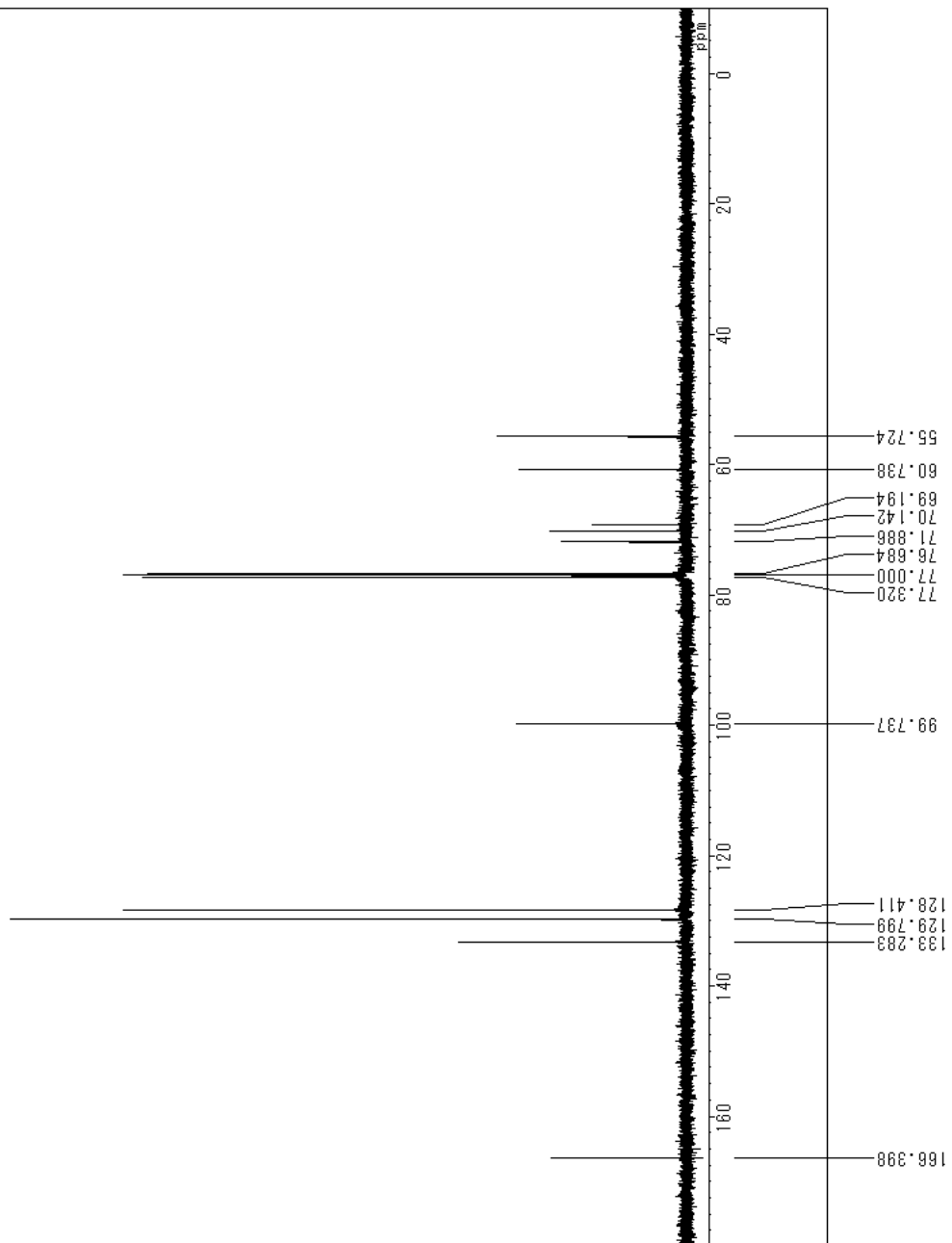
^1H - ^1H COSY spectrum of **SI-6**



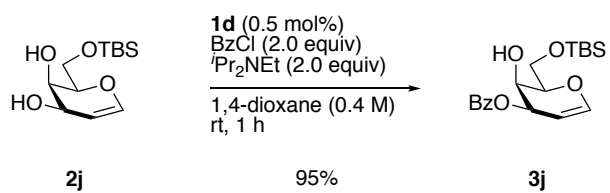
¹³C-NMR spectrum of **SI-6**



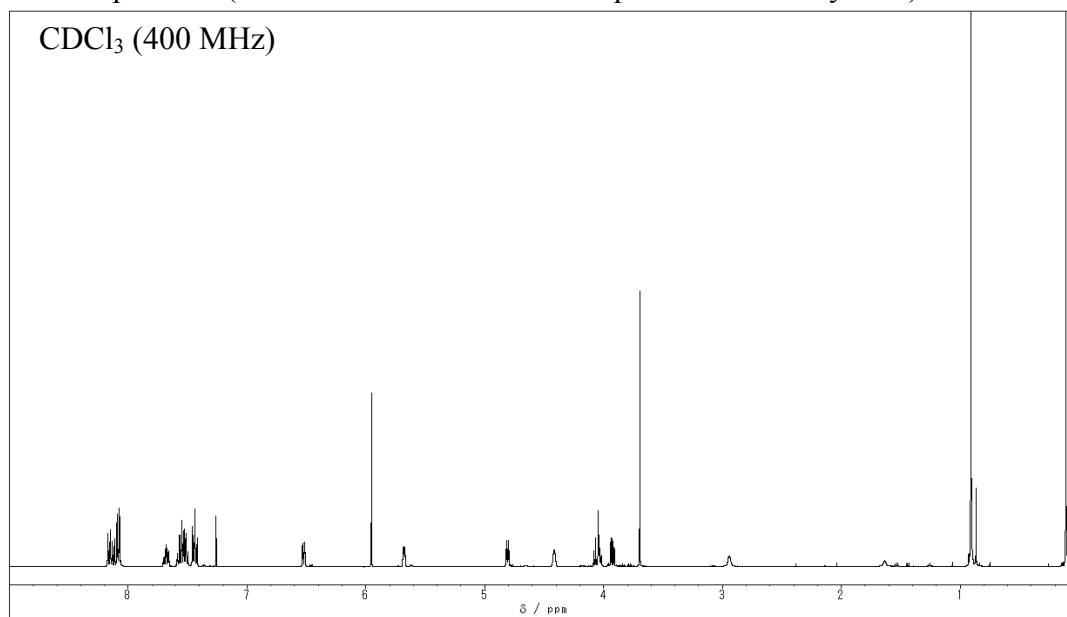
Comment TSV25020_pure_13C_COSY_2
 0181227_01 2018/Dec/27
 Date
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



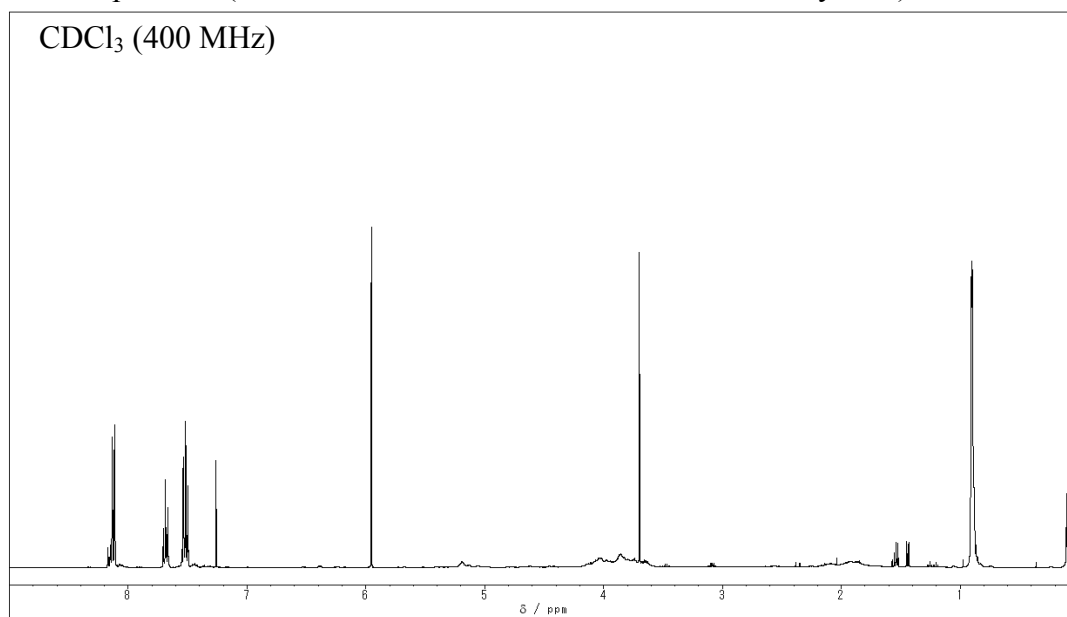
6-((*tert*-butyldimethylsilyl)oxy)-3-*O*-benzoyl-D-galactal (**3j**)



^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



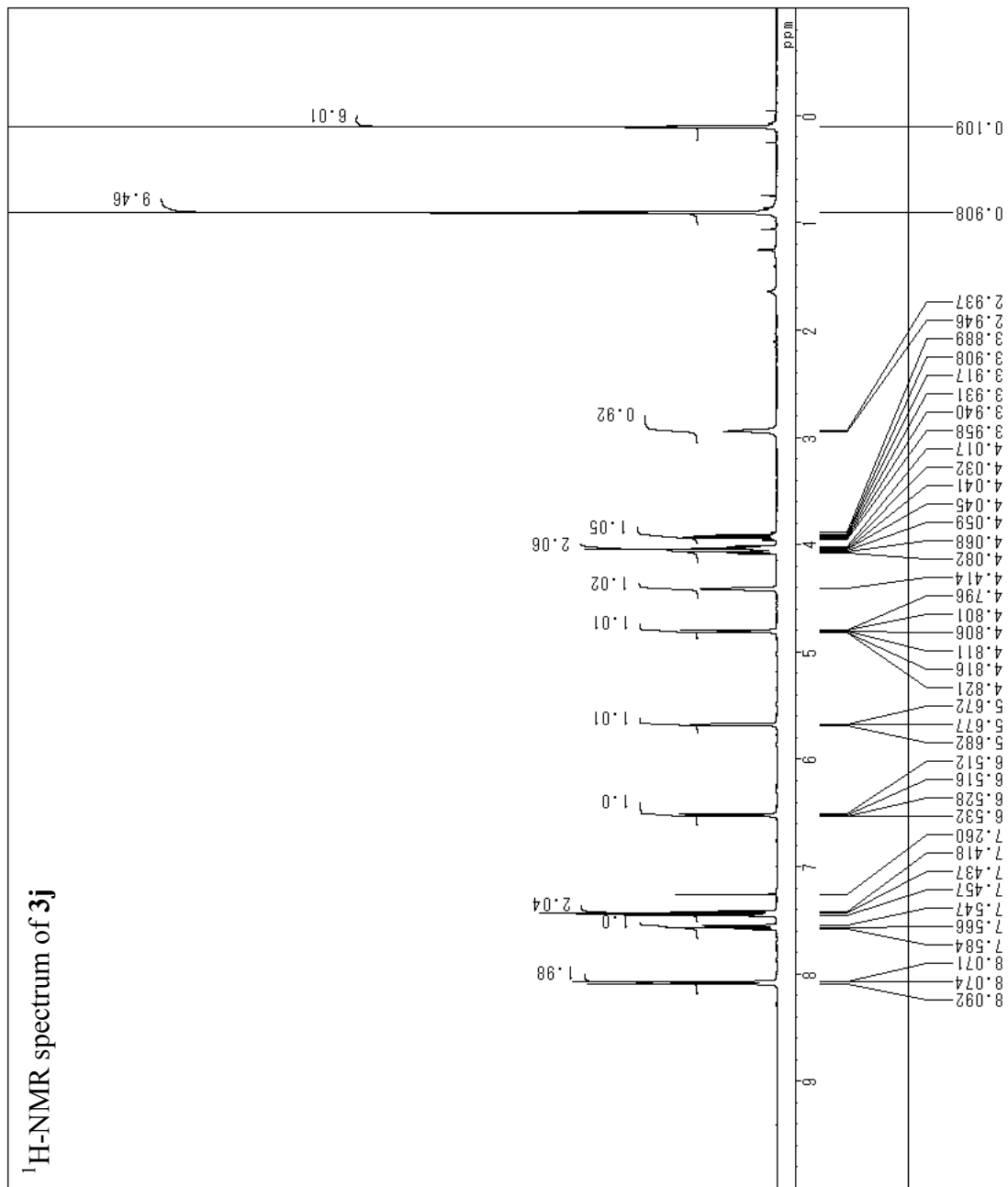
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)





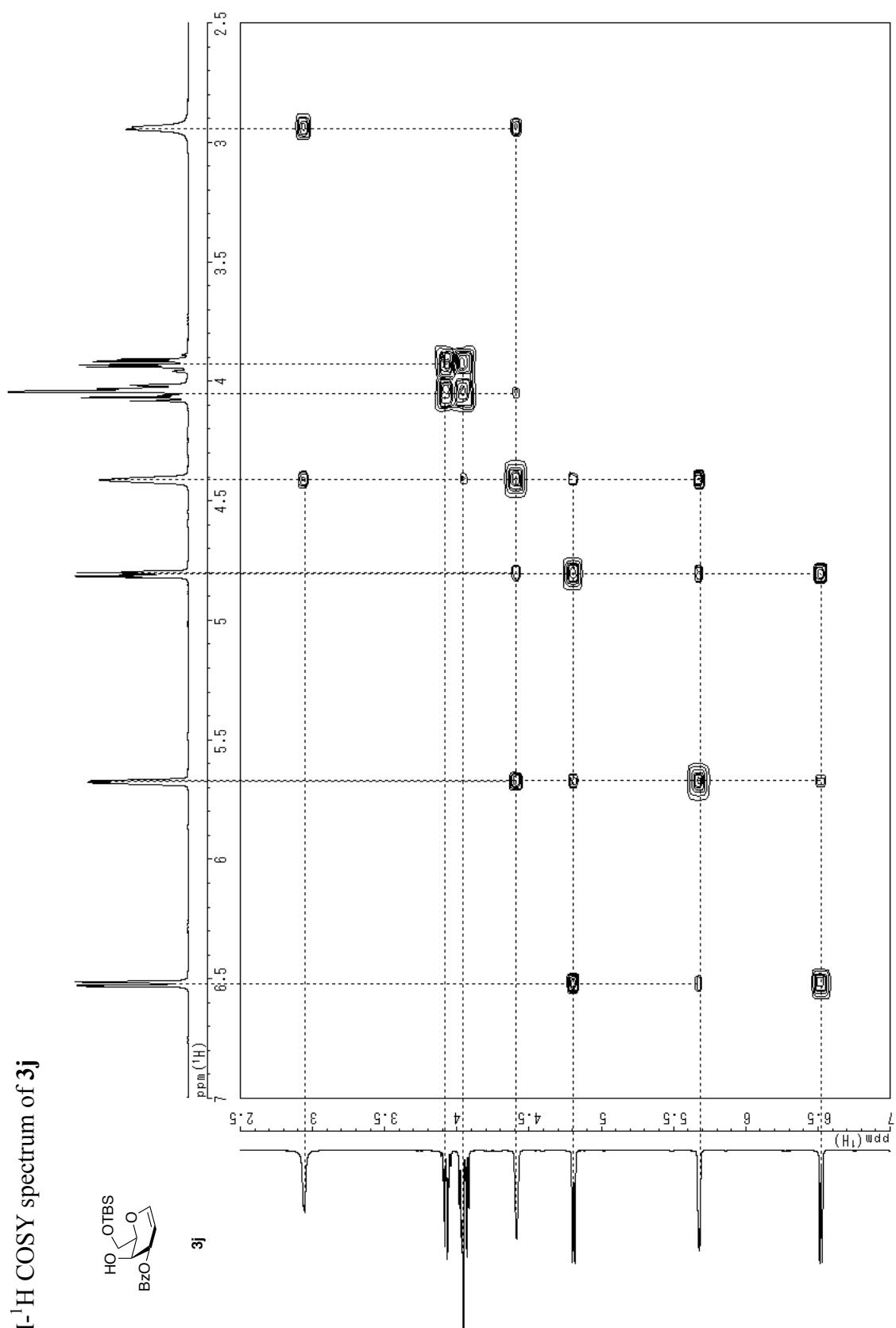
3j

¹H-NMR spectrum of 3j



Comment TSV21017_pure_13C_COSY_2
0180131_01
Date 2018/Jan/31
ObsNuc ¹H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 16
AcqTime 2.589 s
Acc. Interval 5.589 s
Spinning 16.0 Hz
Temperature 25.0 °C
Solvent cdcl3

^1H - ^1H COSY spectrum of **3j**

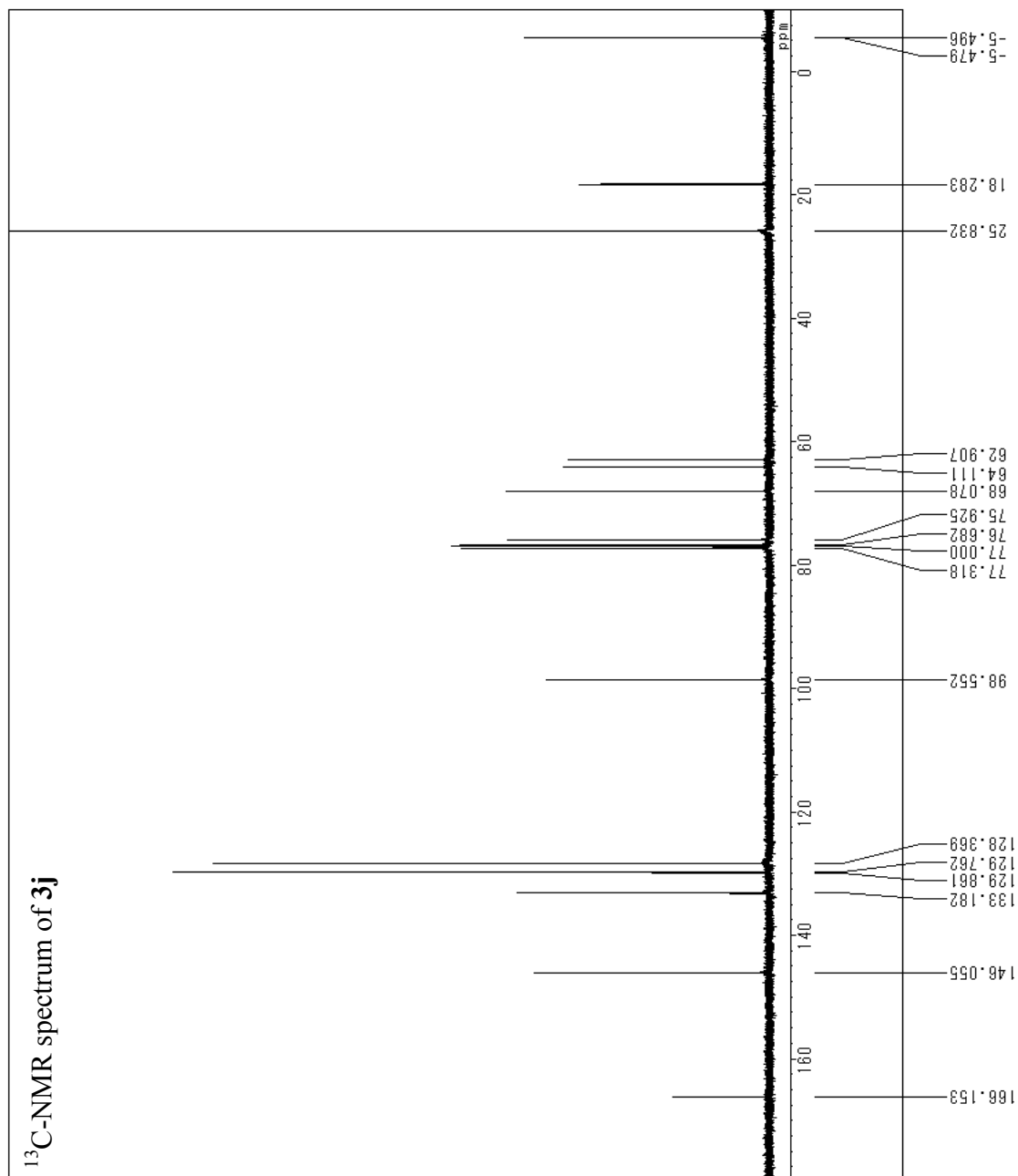




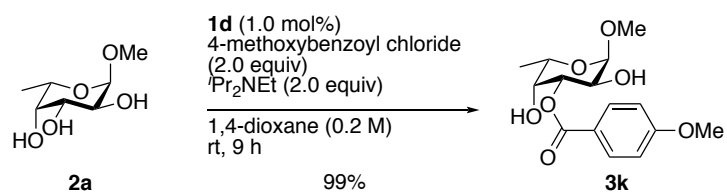
3j

¹³C-NMR spectrum of 3j

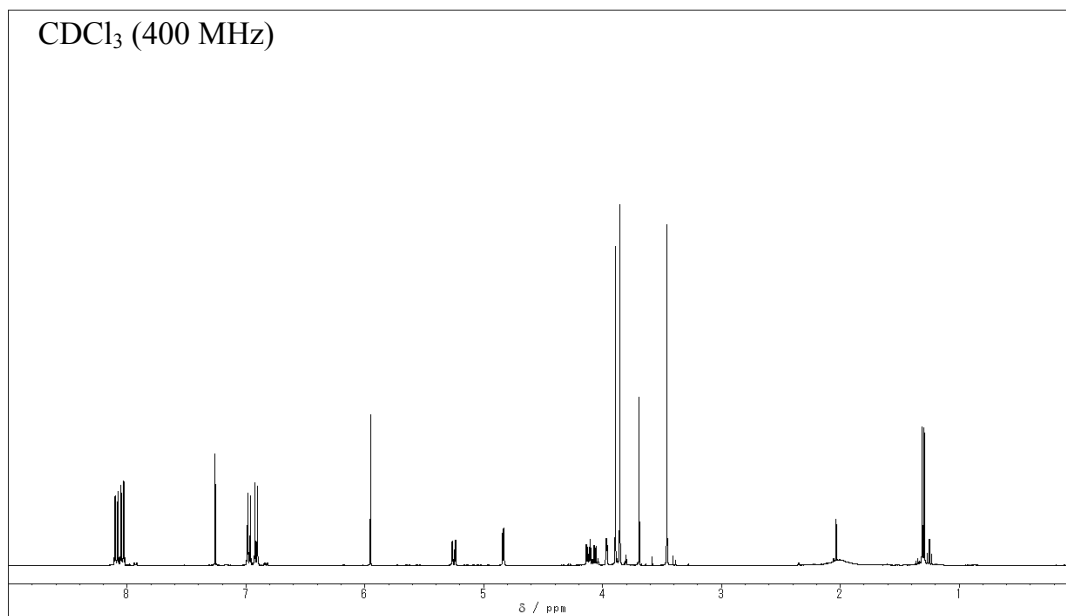
Comment TSV21017_pure_13C_COSY_2
 0180131_01
 Date 2018/Jan/31
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



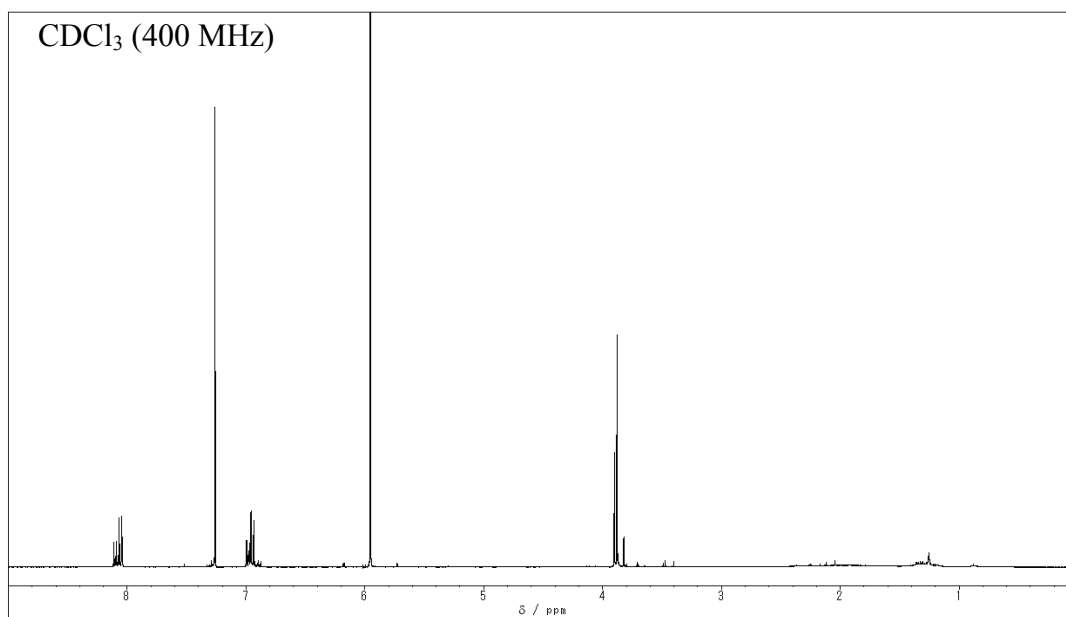
Methyl 3-*O*-4-methoxybenzoyl- α -L-fucopyranoside (**3k**)

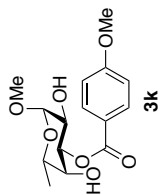


$^1\text{H-NMR}$ spectrum (crude reaction mixture in the presence of catalyst **1d**)



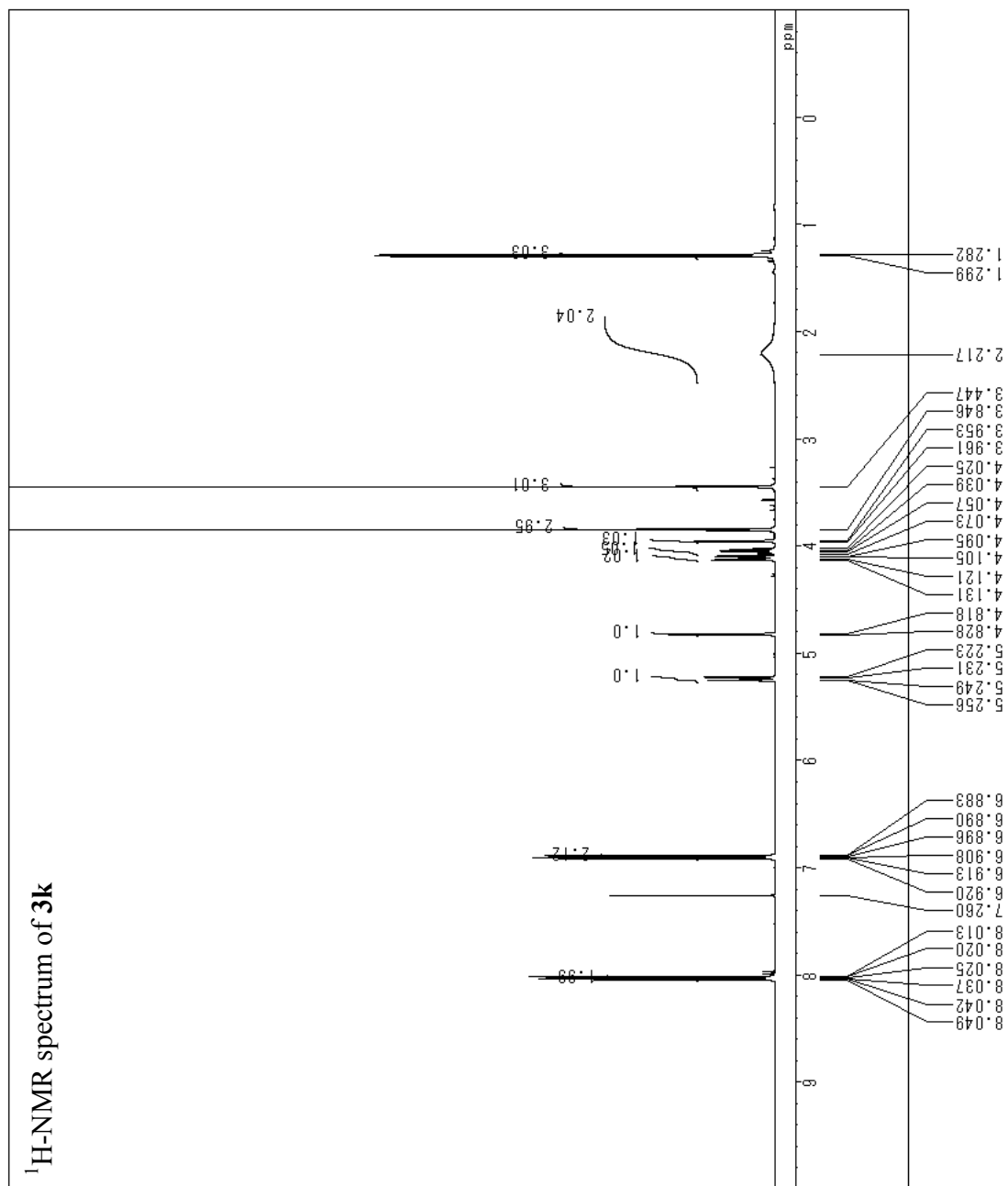
$^1\text{H-NMR}$ spectrum (crude reaction mixture in the absence of catalyst **1d**)



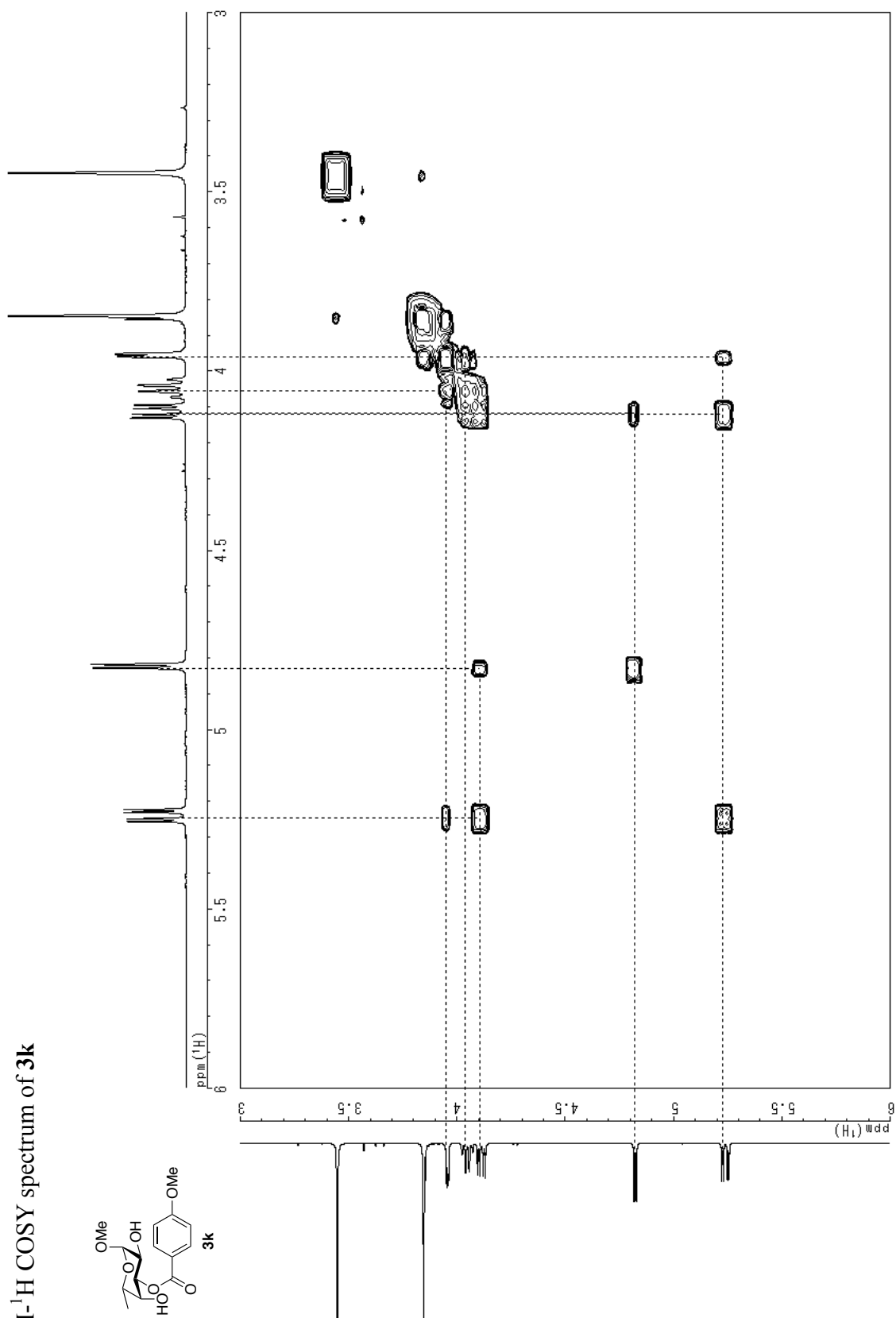
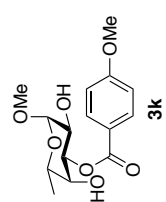


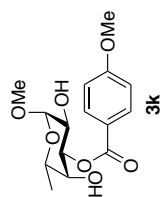
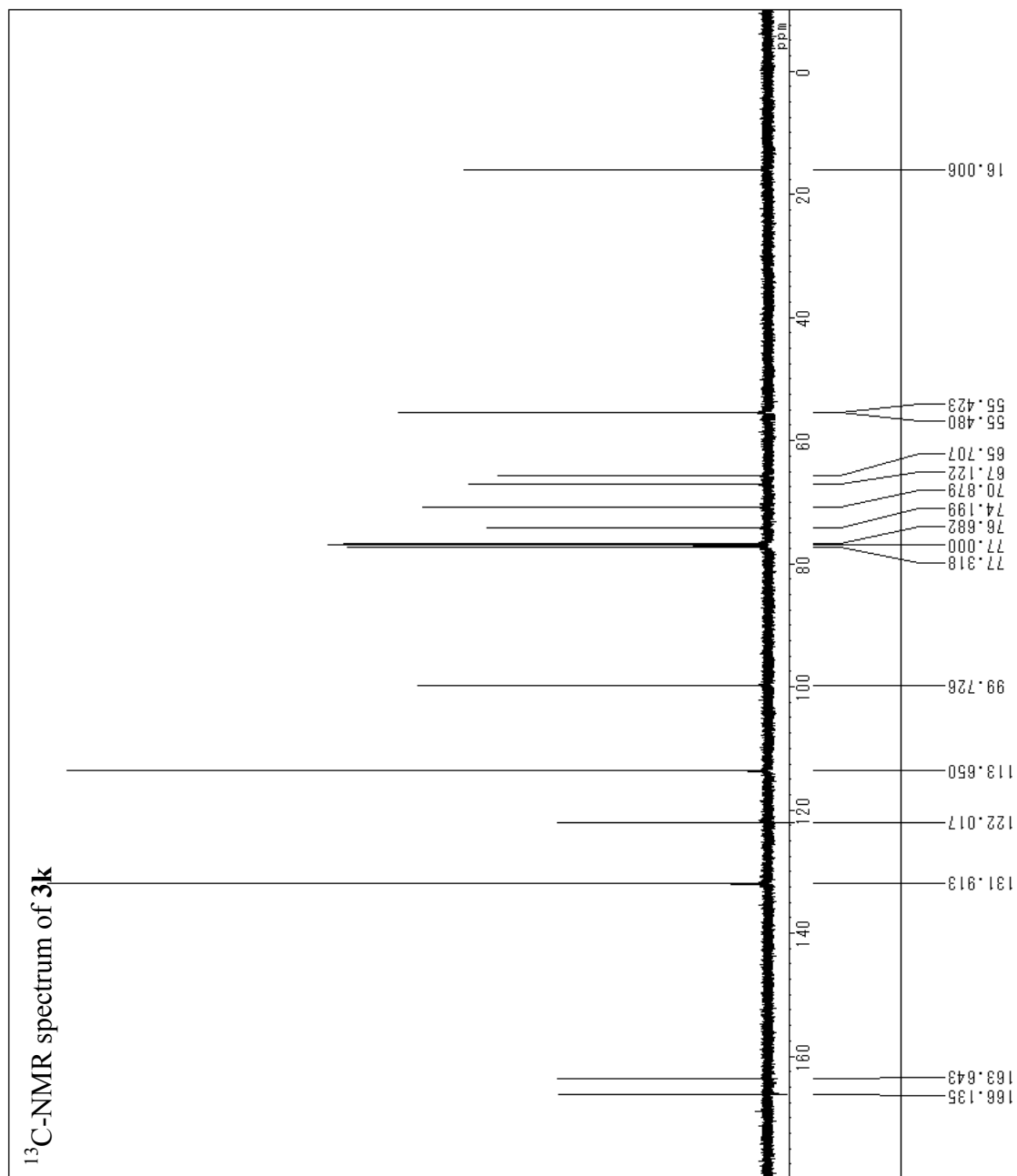
¹H-NMR spectrum of **3k**

Comment TSV17037_pure_13C_COSY_2
 0170920_01
 Date 2017/Sep/20
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



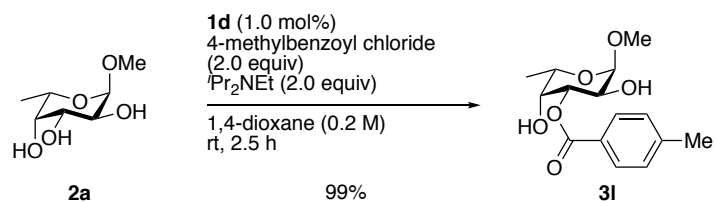
^1H - ^1H COSY spectrum of **3k**



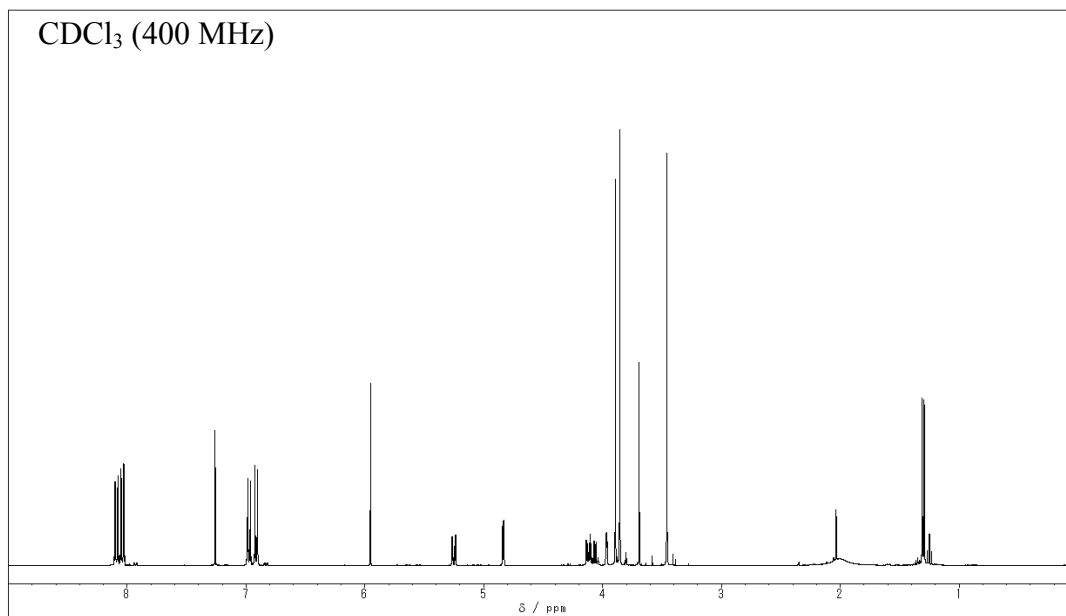


Comment TSV17037_13C_20170920_01
 Date 2017/Sep/20
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

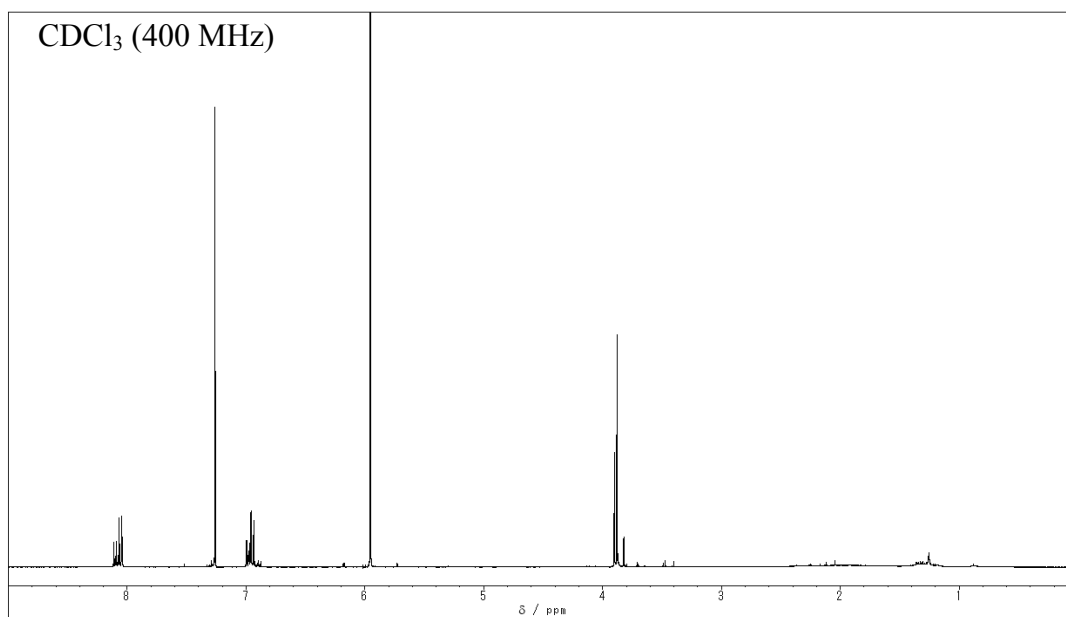
Methyl 3-*O*-4-methylbenzoyl - α -L-fucopyranoside (**3I**)

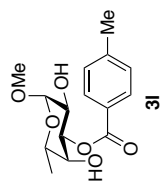


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

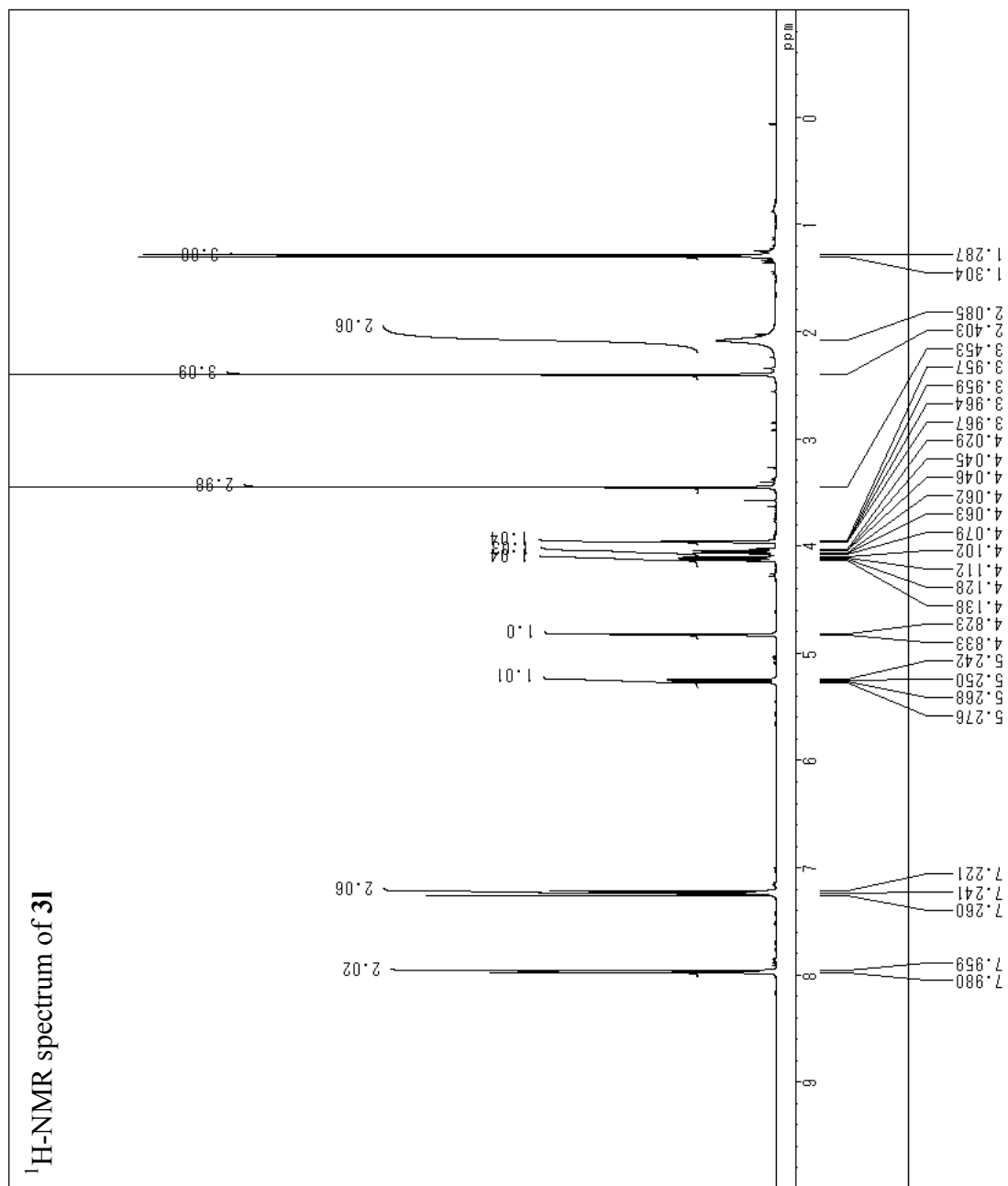


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



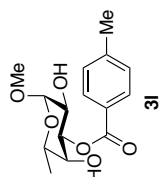


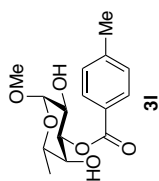
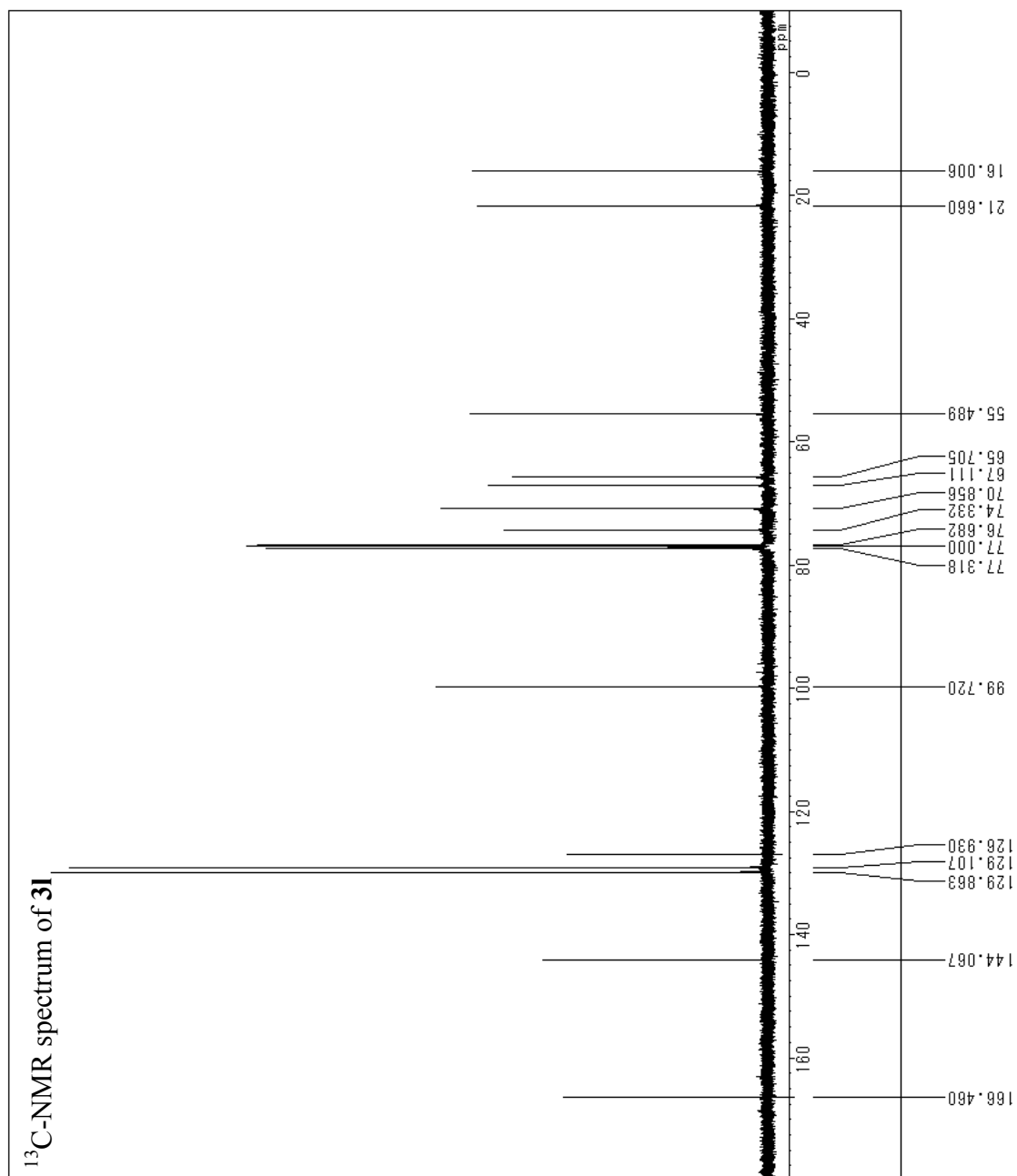
¹H-NMR spectrum of **31**



Comment TSV18037_pure_13C_COSY_2
 0171011_01
 Date 2017/Oct/11
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

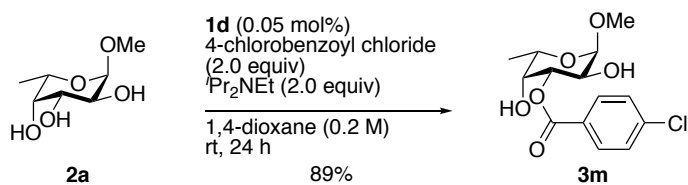
¹H COSY spectrum of **31**



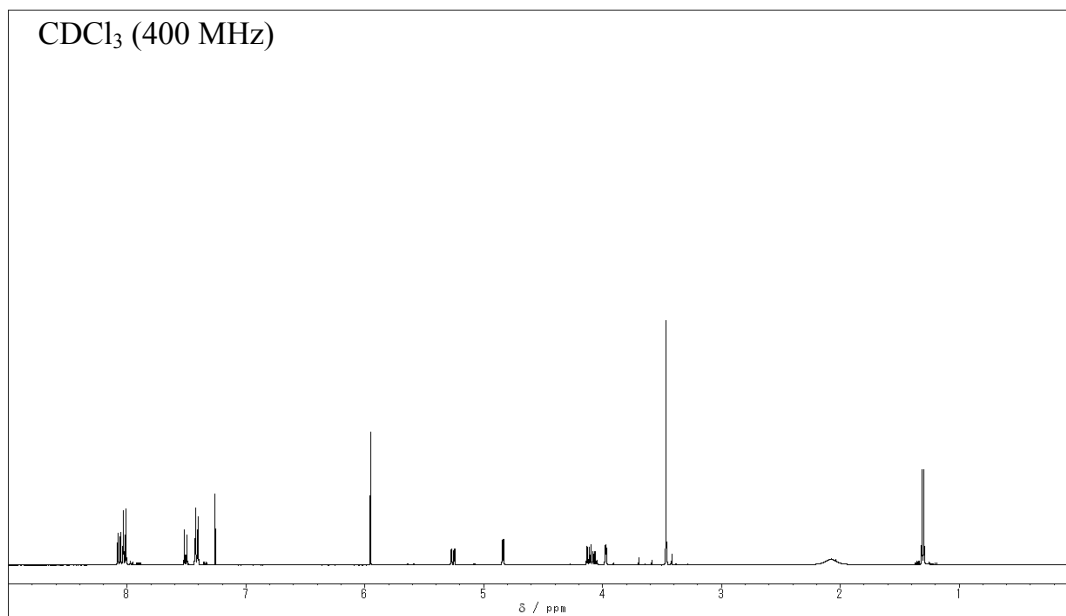


Comment TSV18037_pure_13C_COSY_2
 0171011_01
 Date 2017/Oct/11
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

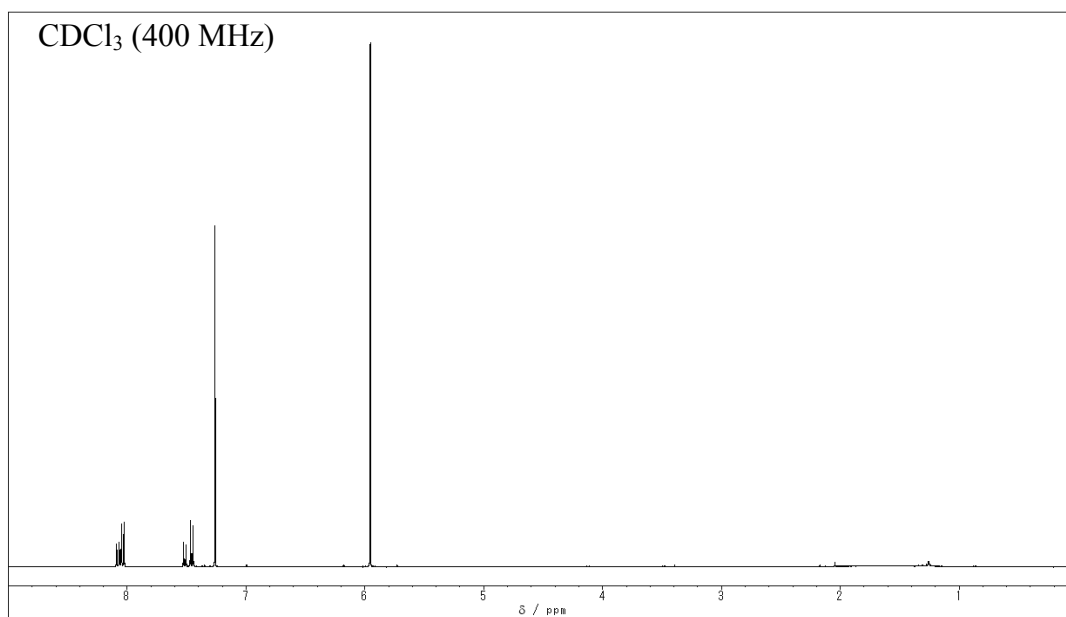
Methyl 3-*O*-4-chlorobenzoyl- α -L-fucopyranoside (**3m**)

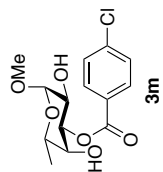


¹H-NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



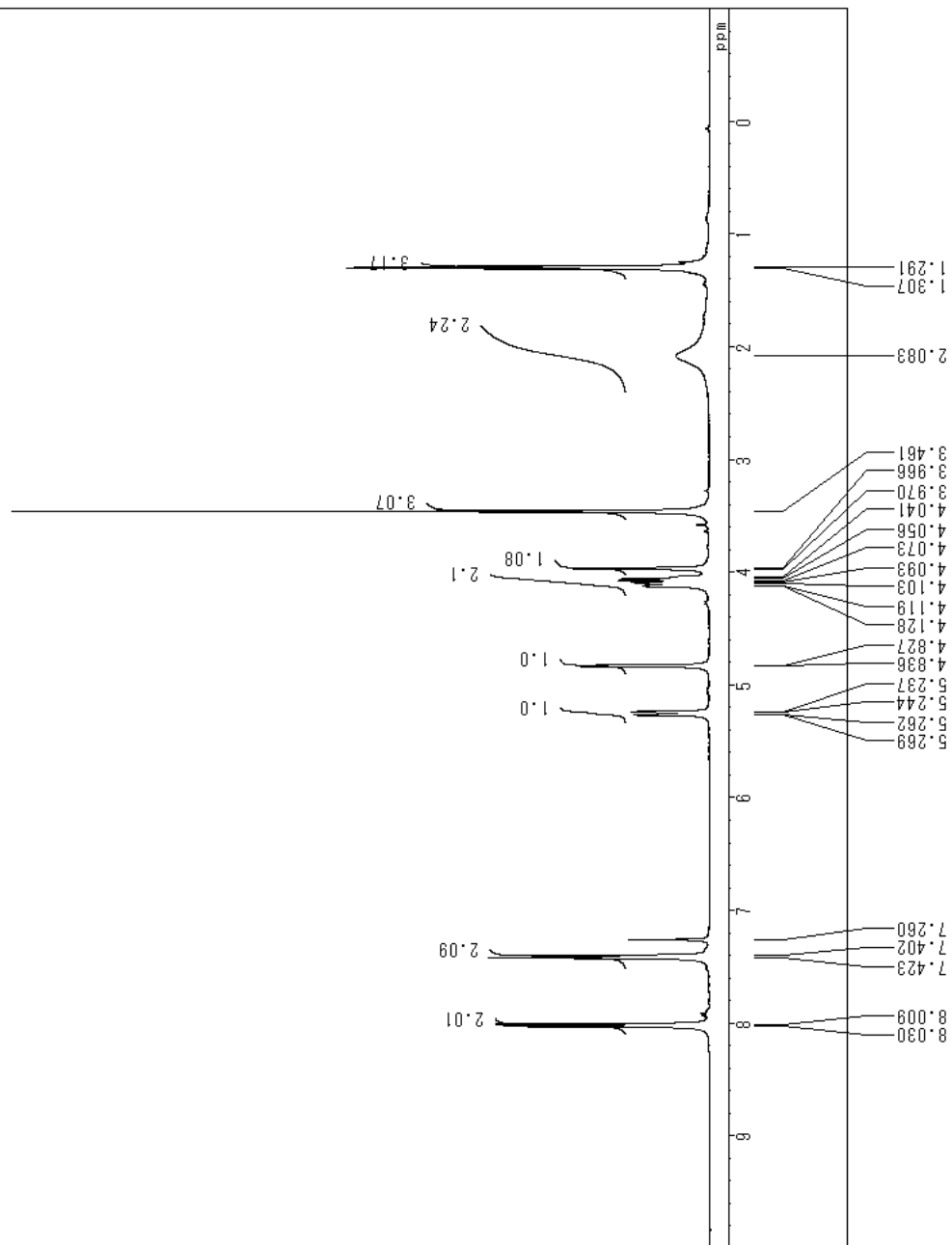
¹H-NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



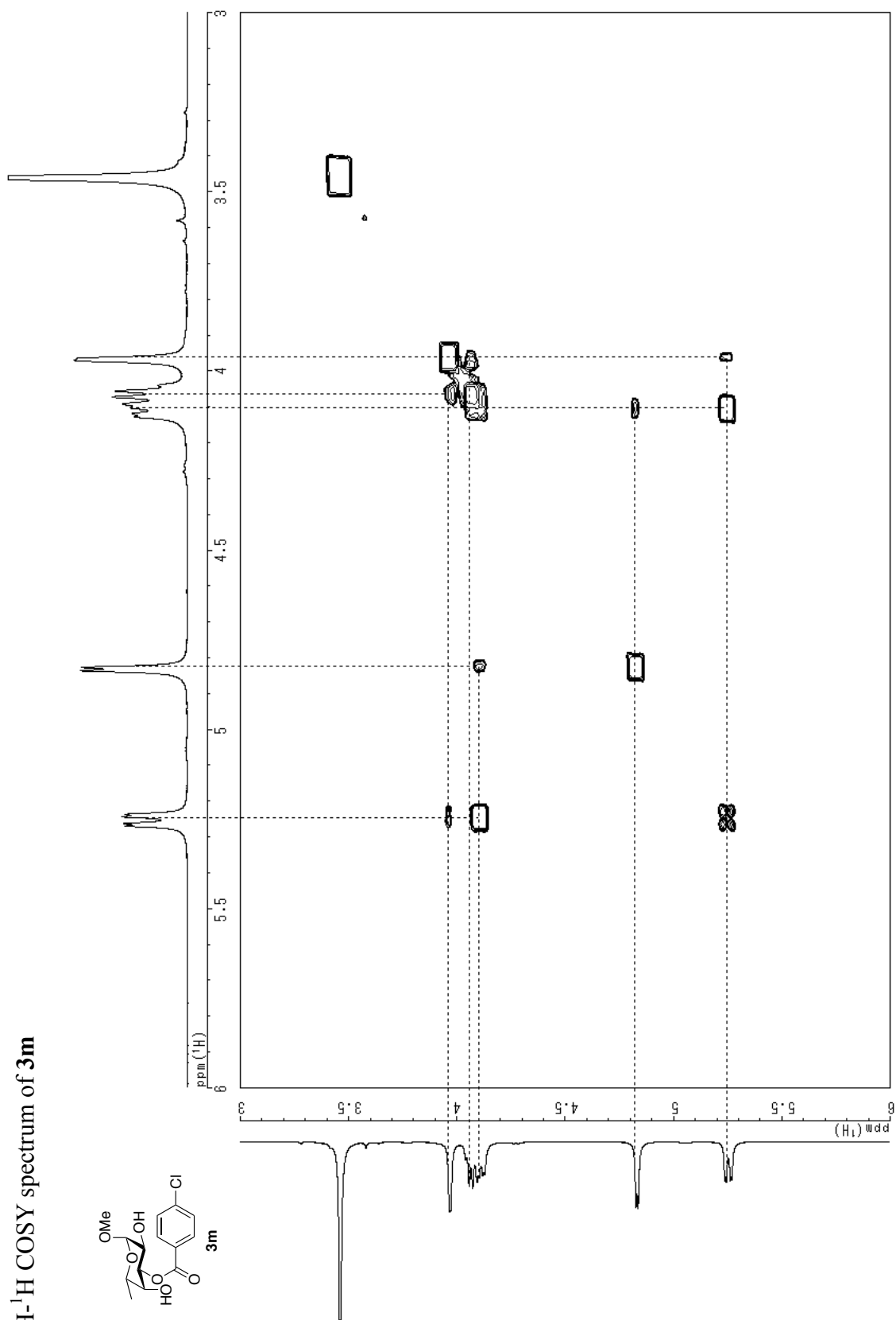


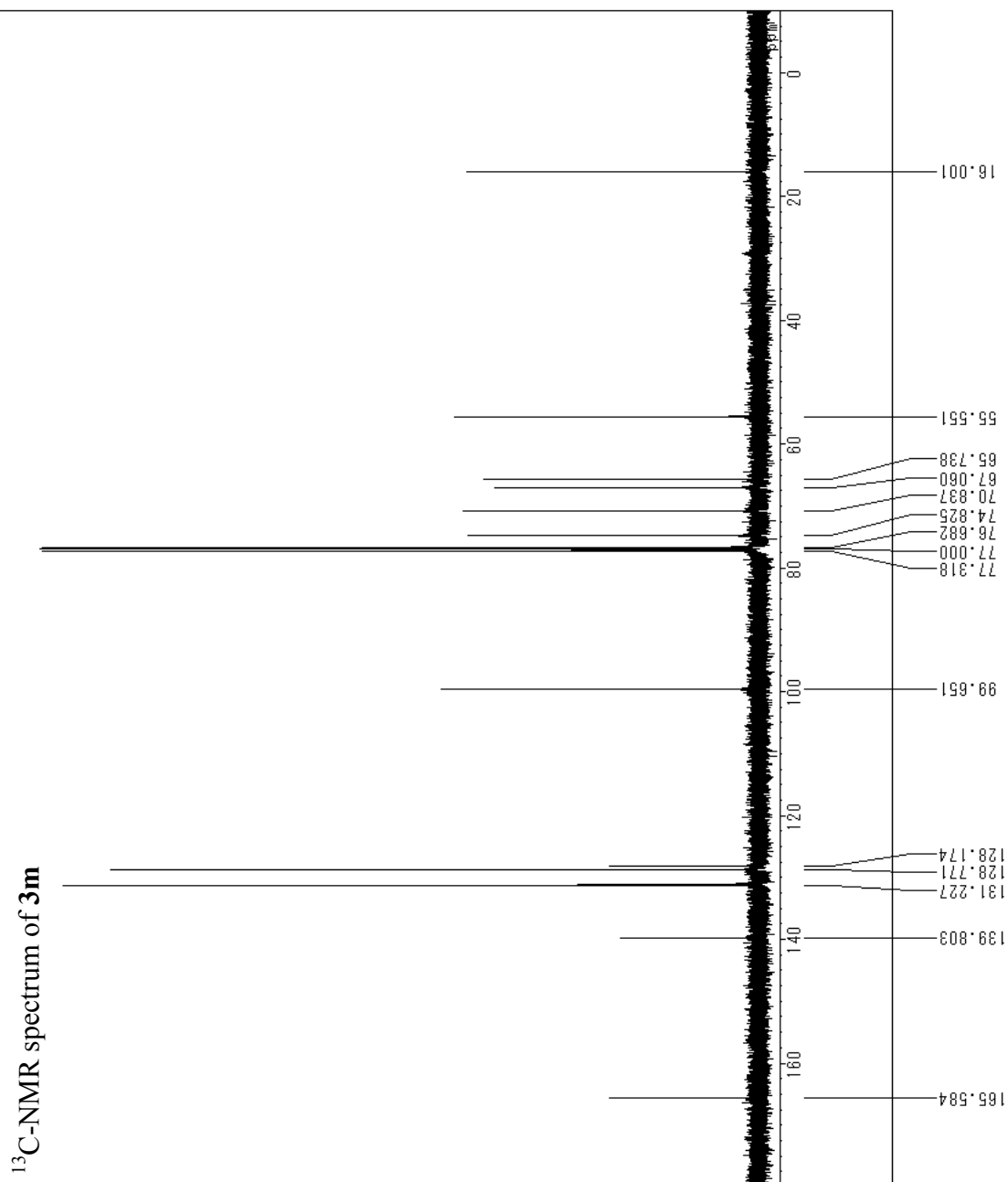
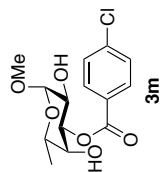
Comment TSV17035_pure_13C_COSY_2
 0170918_01
 Date 2017/Sep/19
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

¹H-NMR spectrum of **3m**



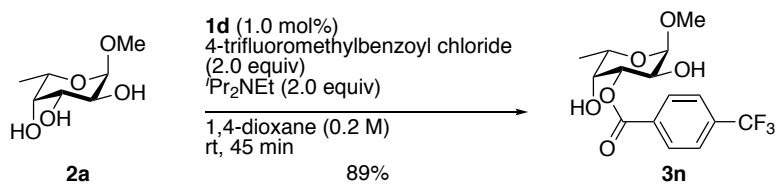
^1H - ^1H COSY spectrum of **3m**



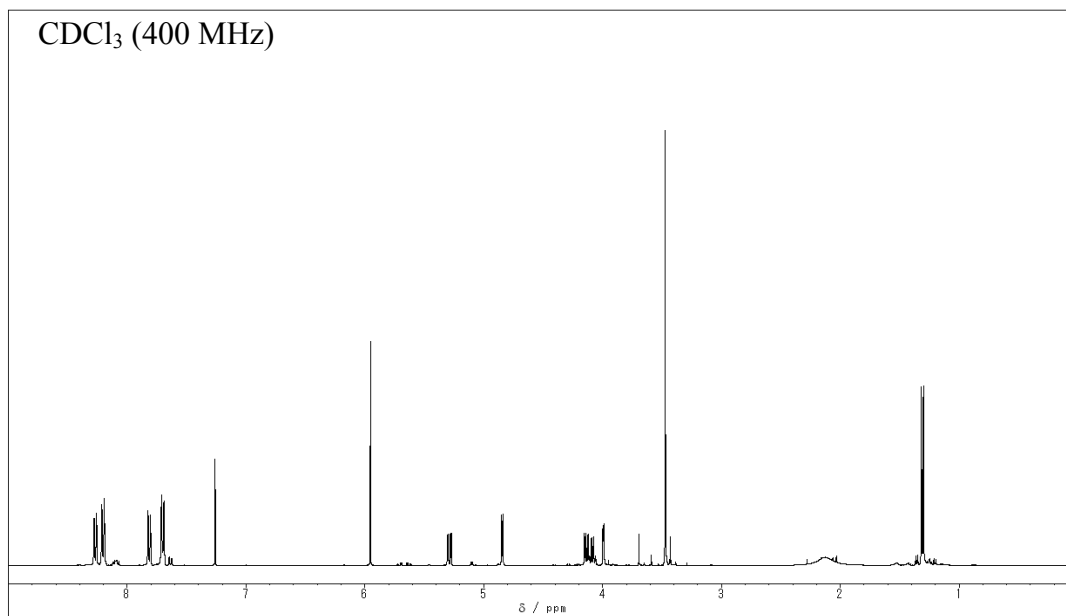


Comment TSV17035_pure_13C_COSY_2
 0170919_01
 Date 2017/Sep/19
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

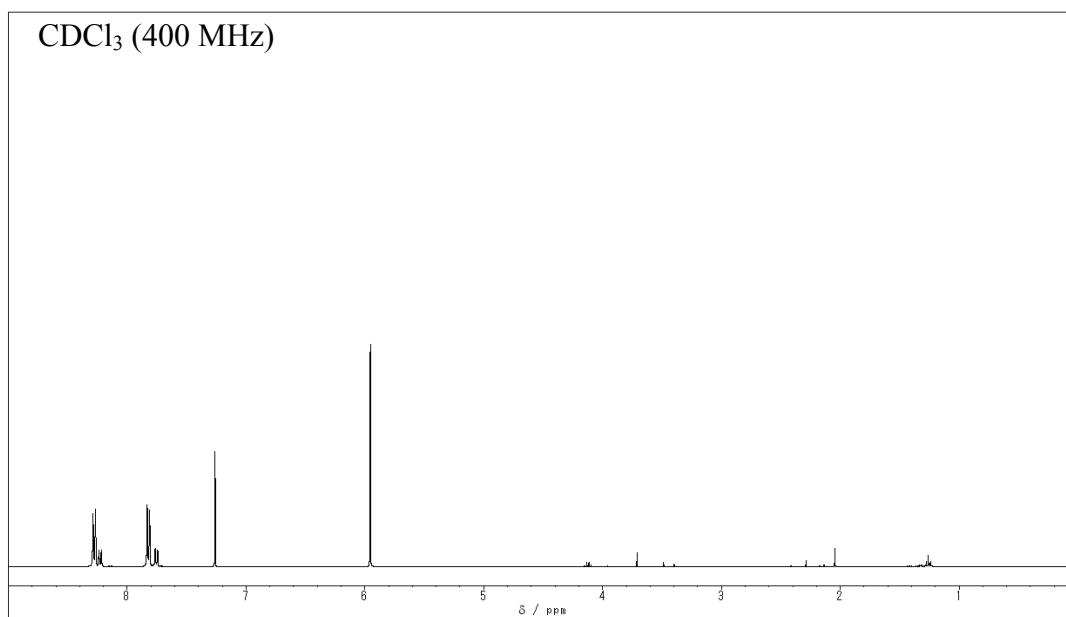
Methyl 3-*O*-4-trifluoromethylbenzoyl- α -L-fucopyranoside (**3n**)

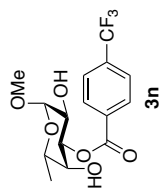


$^1\text{H-NMR}$ spectrum (crude reaction mixture in the presence of catalyst **1d**)

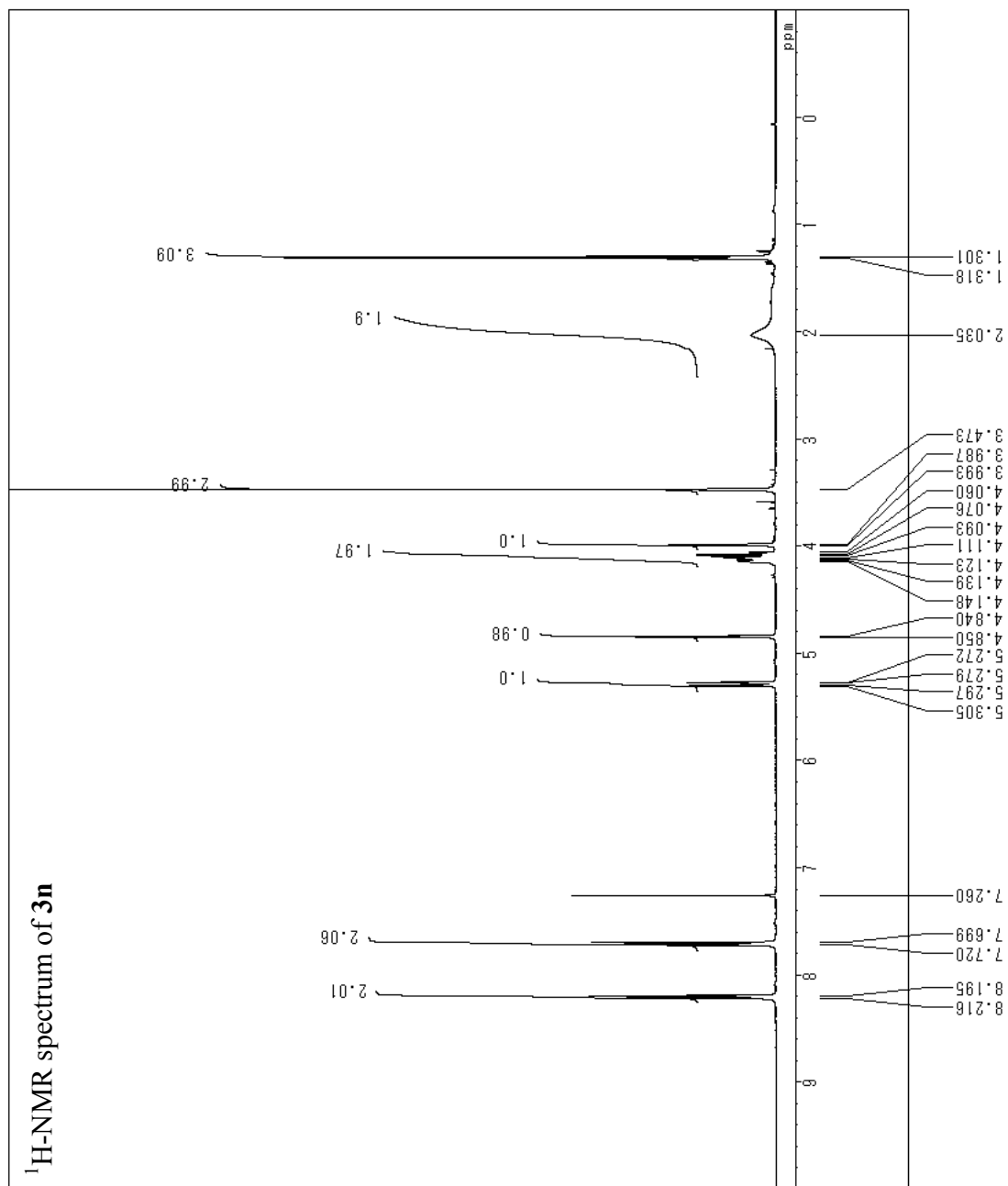


$^1\text{H-NMR}$ spectrum (crude reaction mixture in the absence of catalyst **1d**)



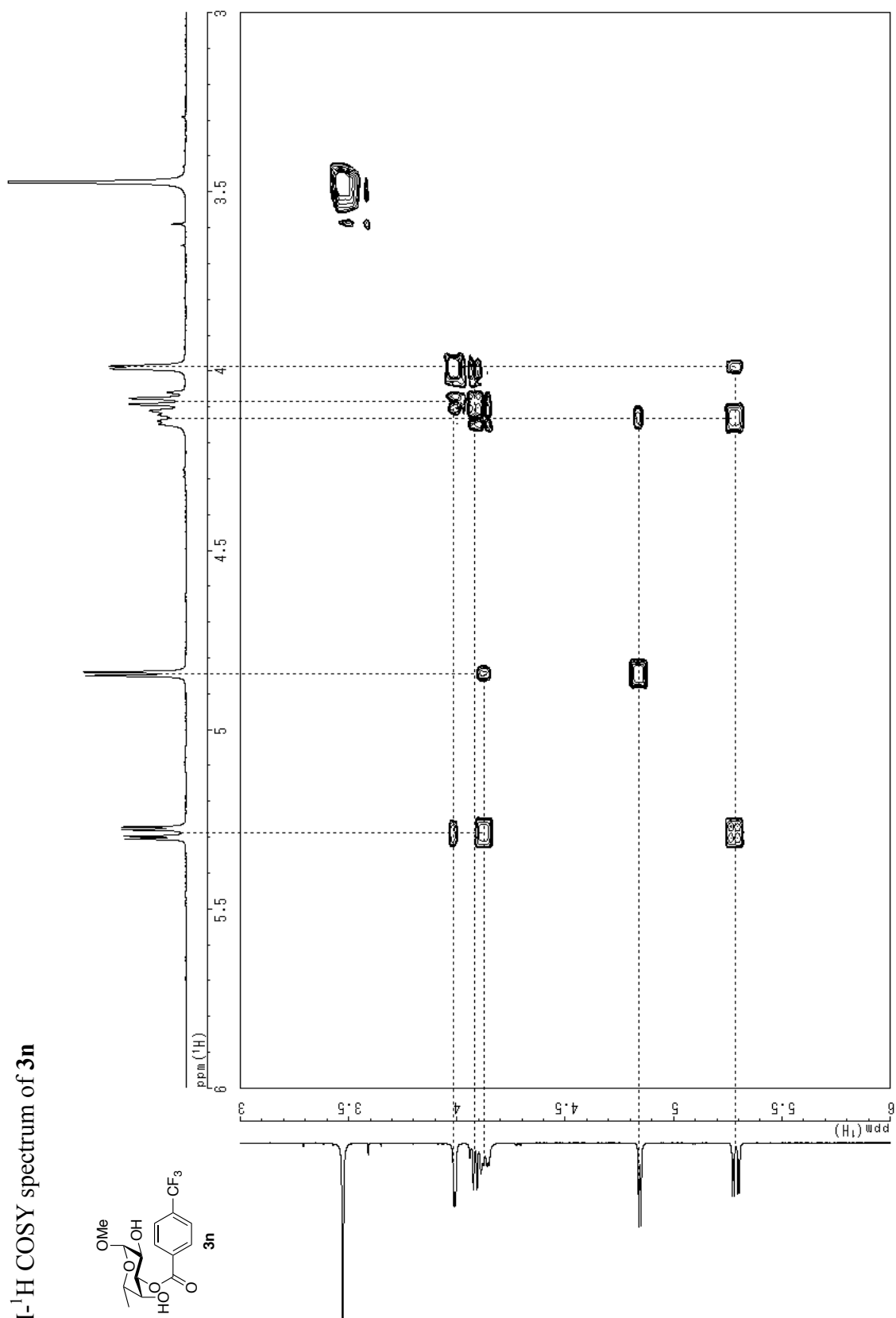
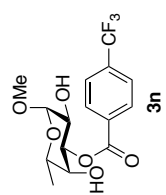


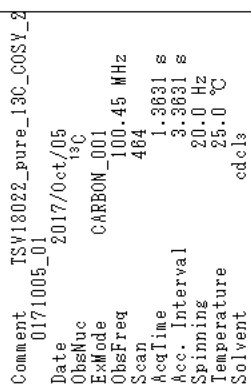
¹H-NMR spectrum of **3n**



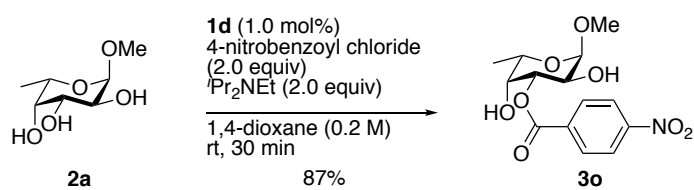
Comment TSV18022_pure_13C_COSY_2
 0171005_01
 Date 2017/Oct/05
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **3n**

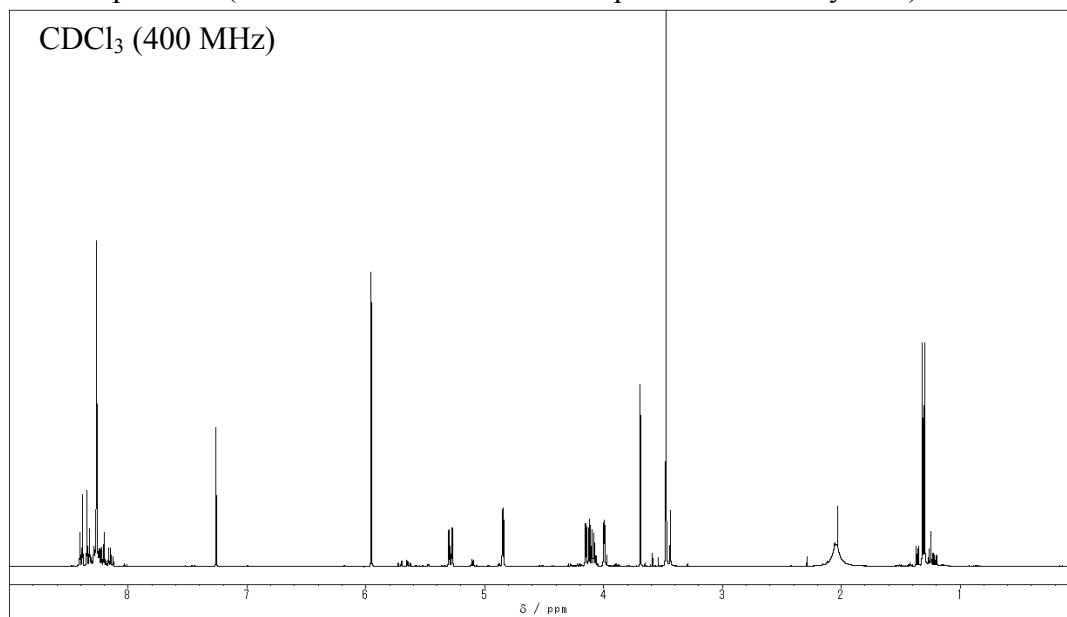




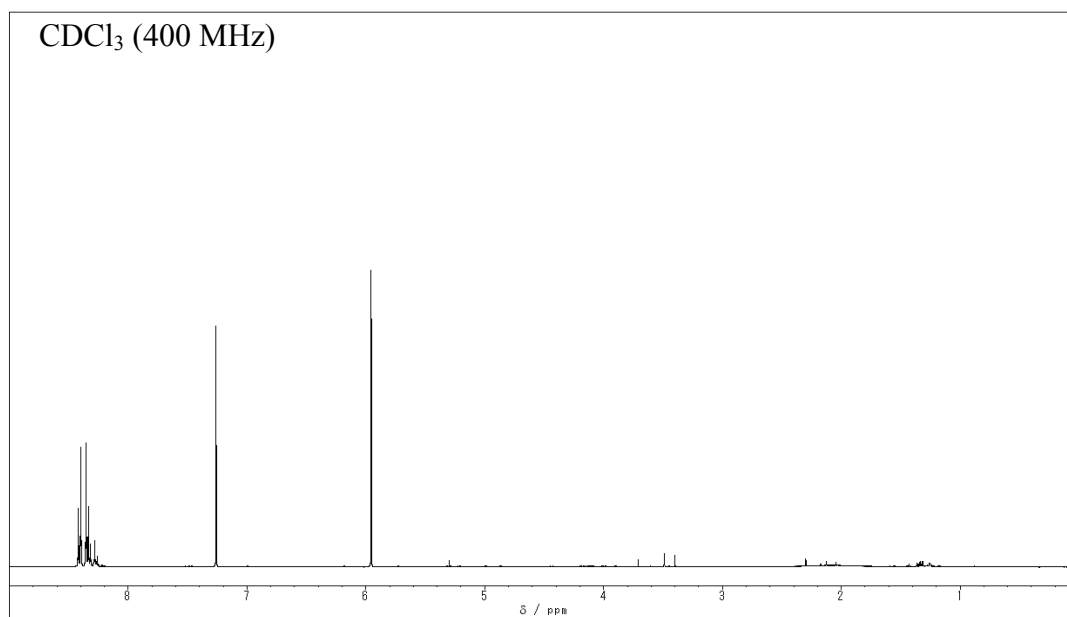
Methyl 3-*O*-4-nitrobenzoyl- α -L-fucopyranoside (**3o**)

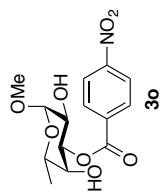


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

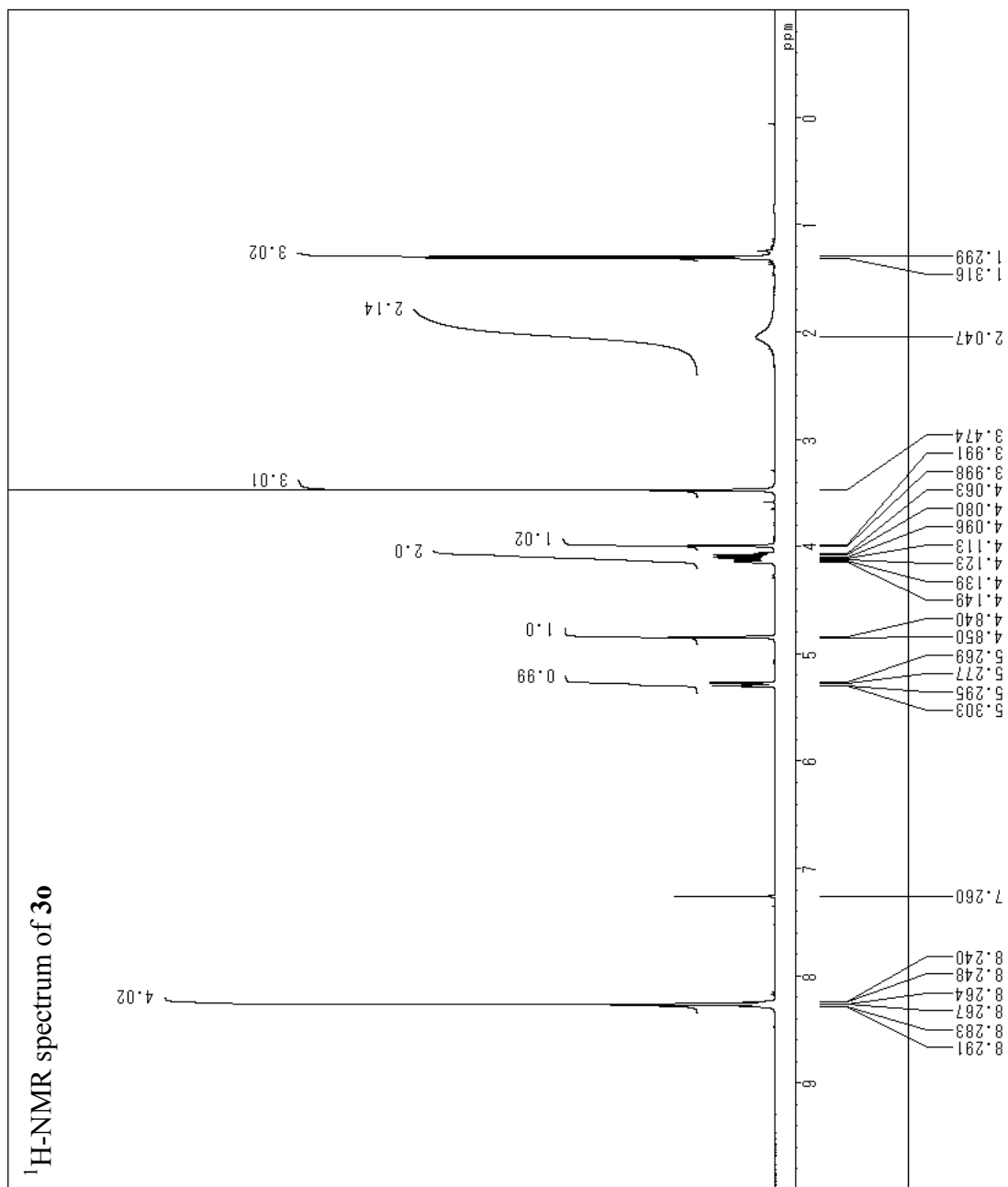


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



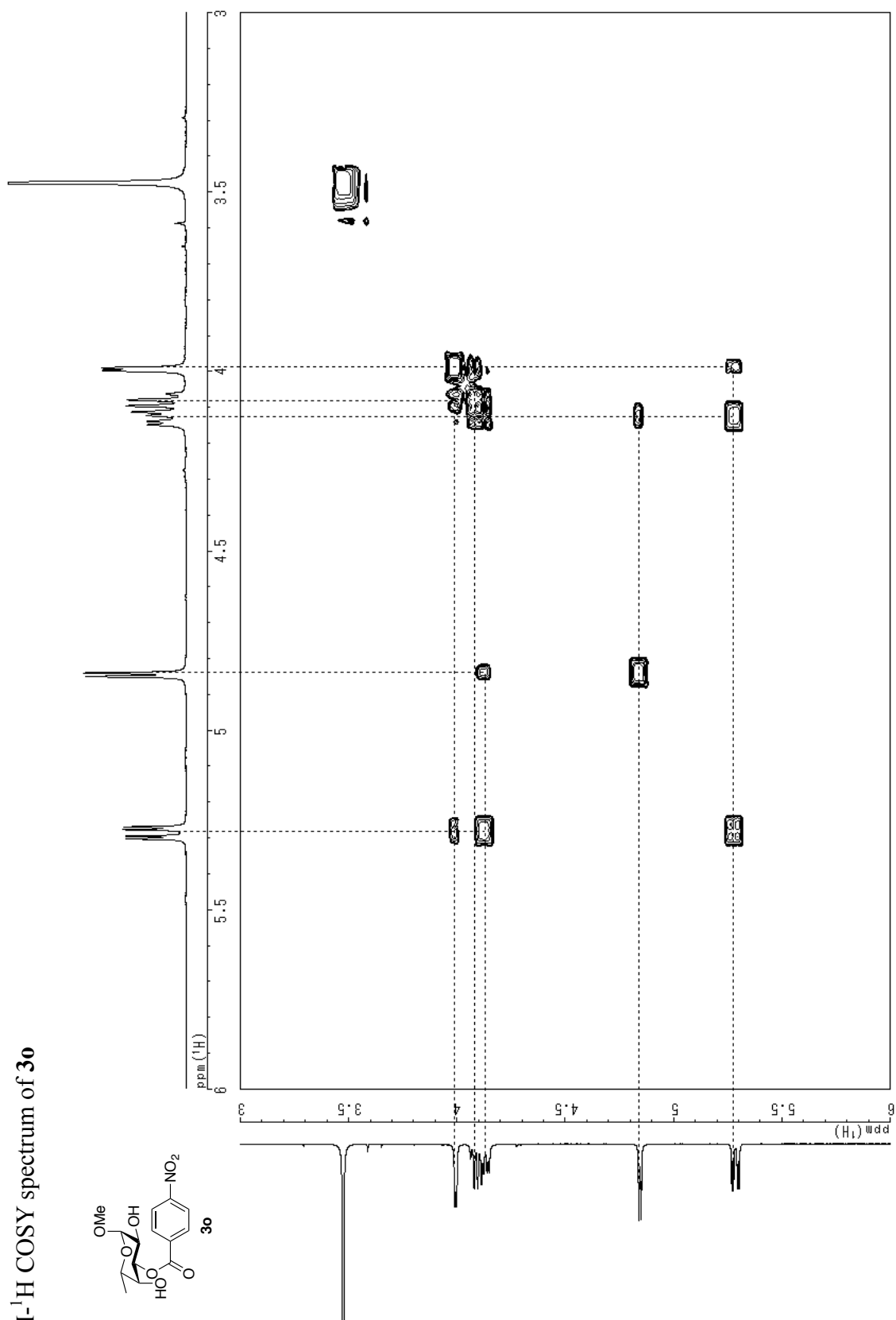
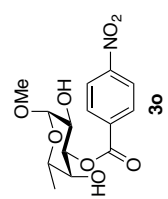


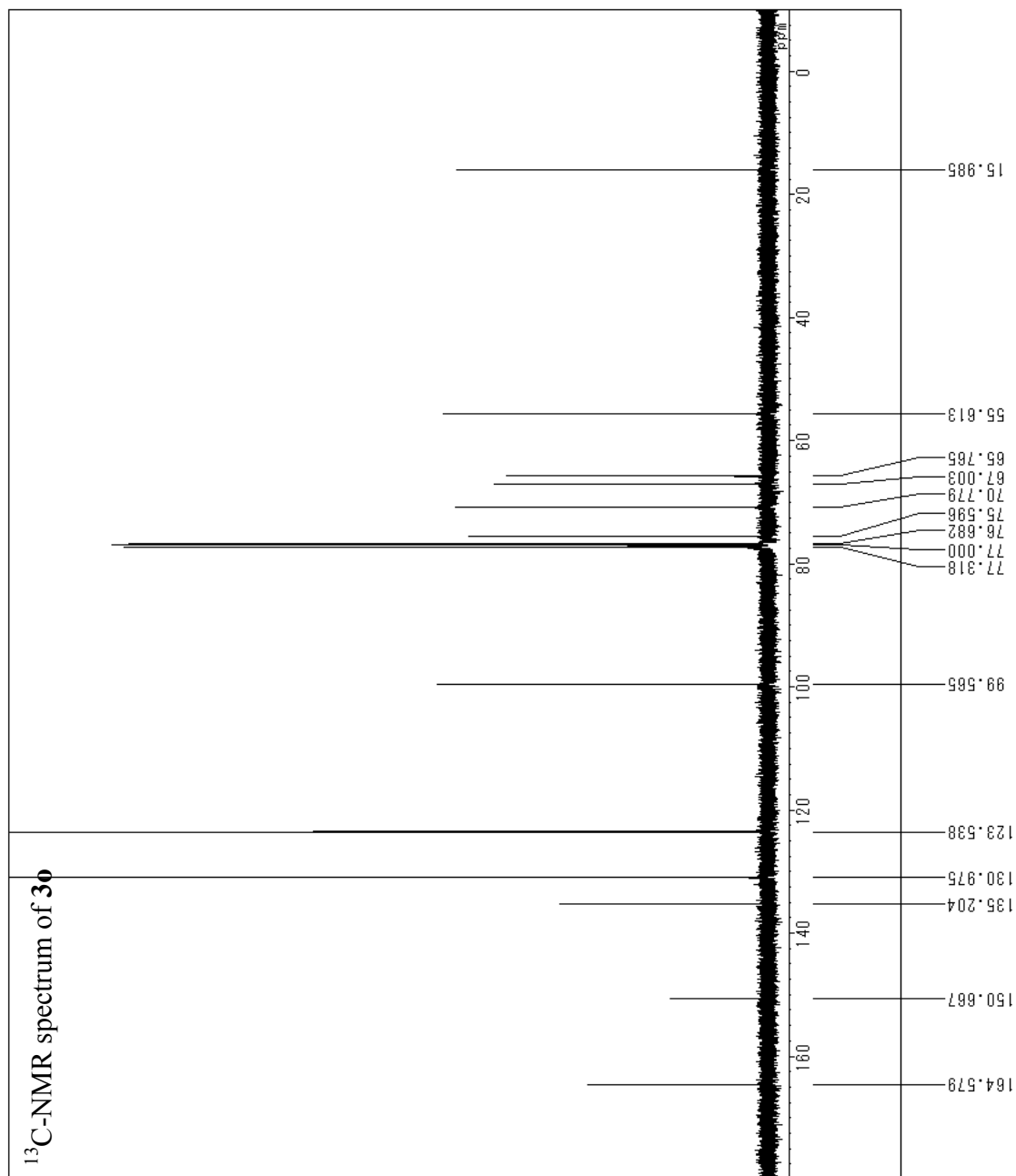
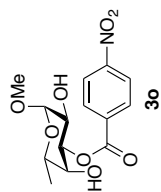
¹H-NMR spectrum of **3o**



Comment TSV18008_pure_13C_COSY_2
 0170928_01
 Date 2017/Sep/28
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

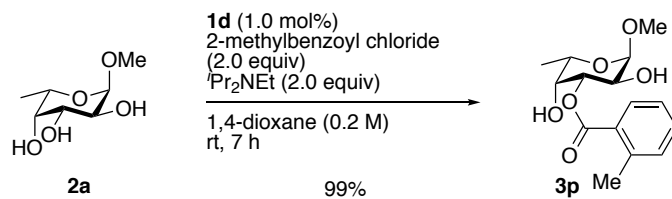
^1H - ^1H COSY spectrum of **3o**



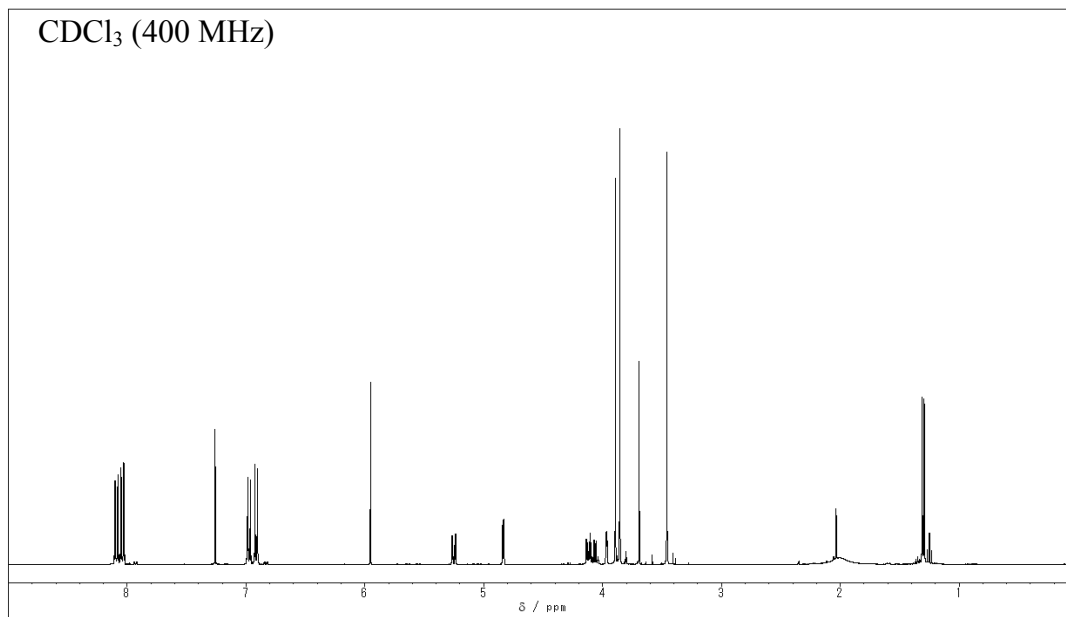


Comment TSV18008_pure_13C_COSY_2
 Date 0170928_01
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

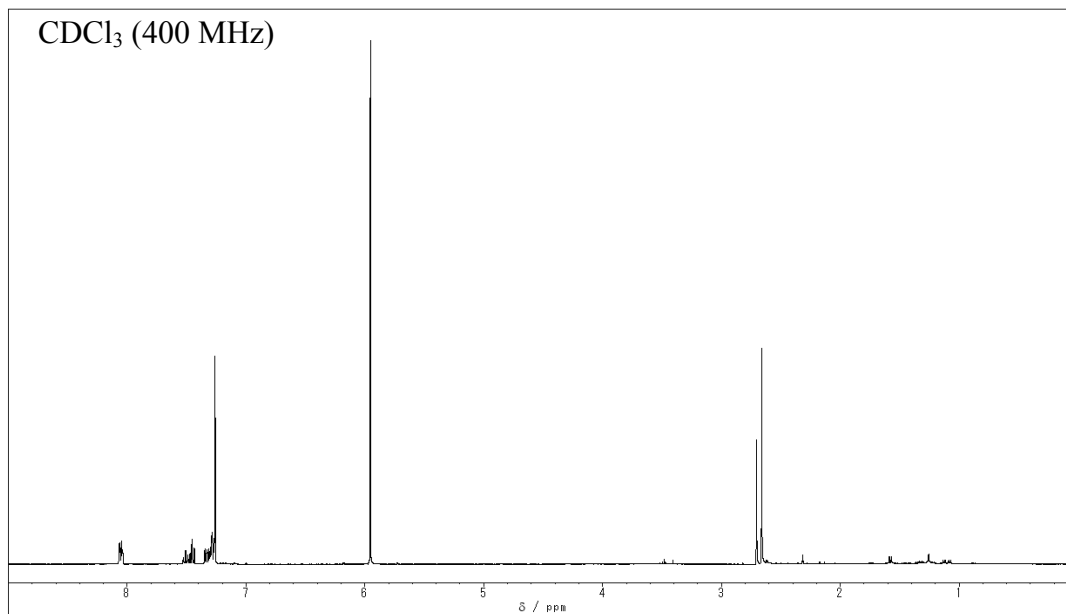
Methyl 3-*O*-2-methylbenzoyl- α -L-fucopyranoside (**3p**)

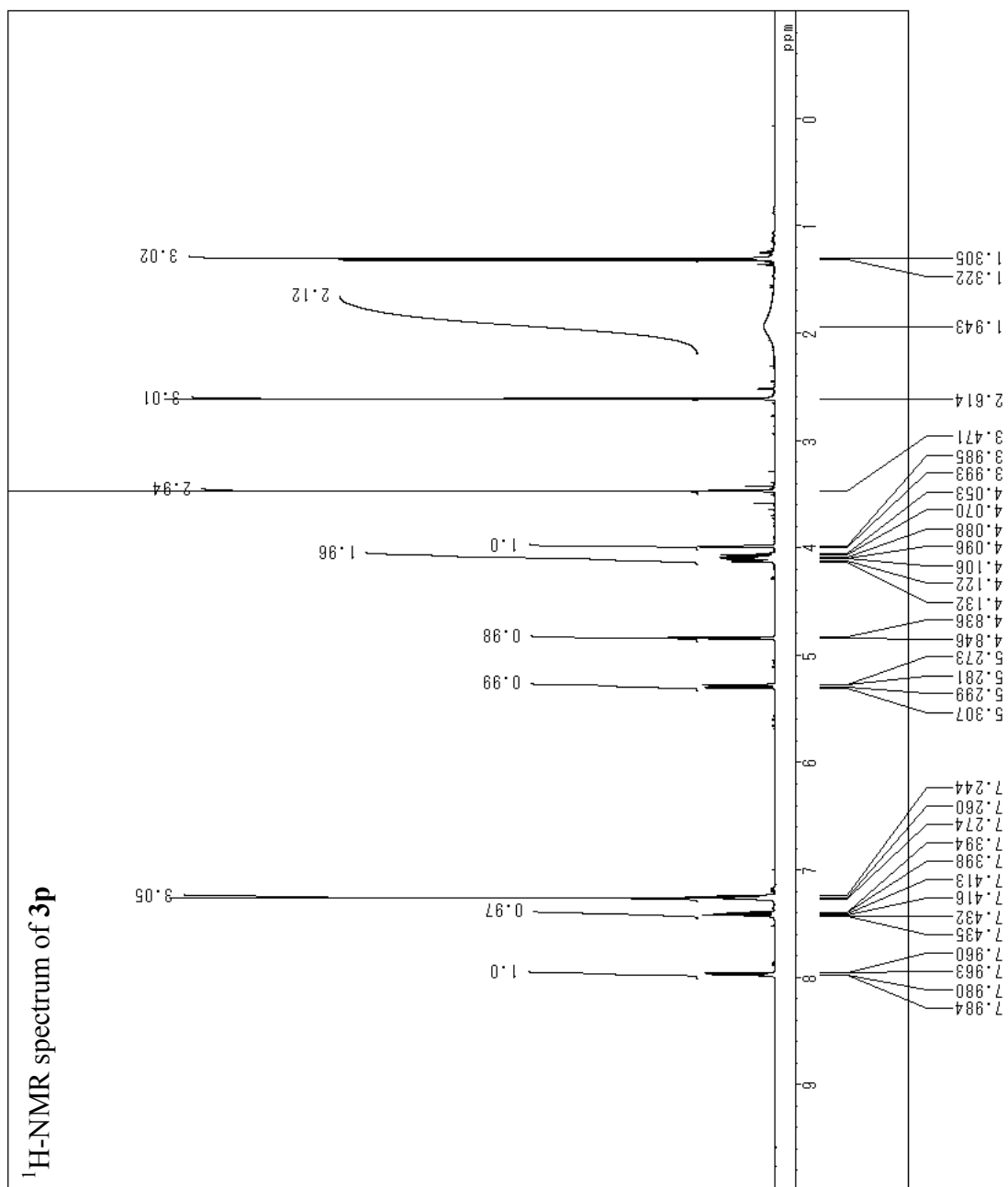


$^1\text{H-NMR}$ spectrum (crude reaction mixture in the presence of catalyst **1d**)



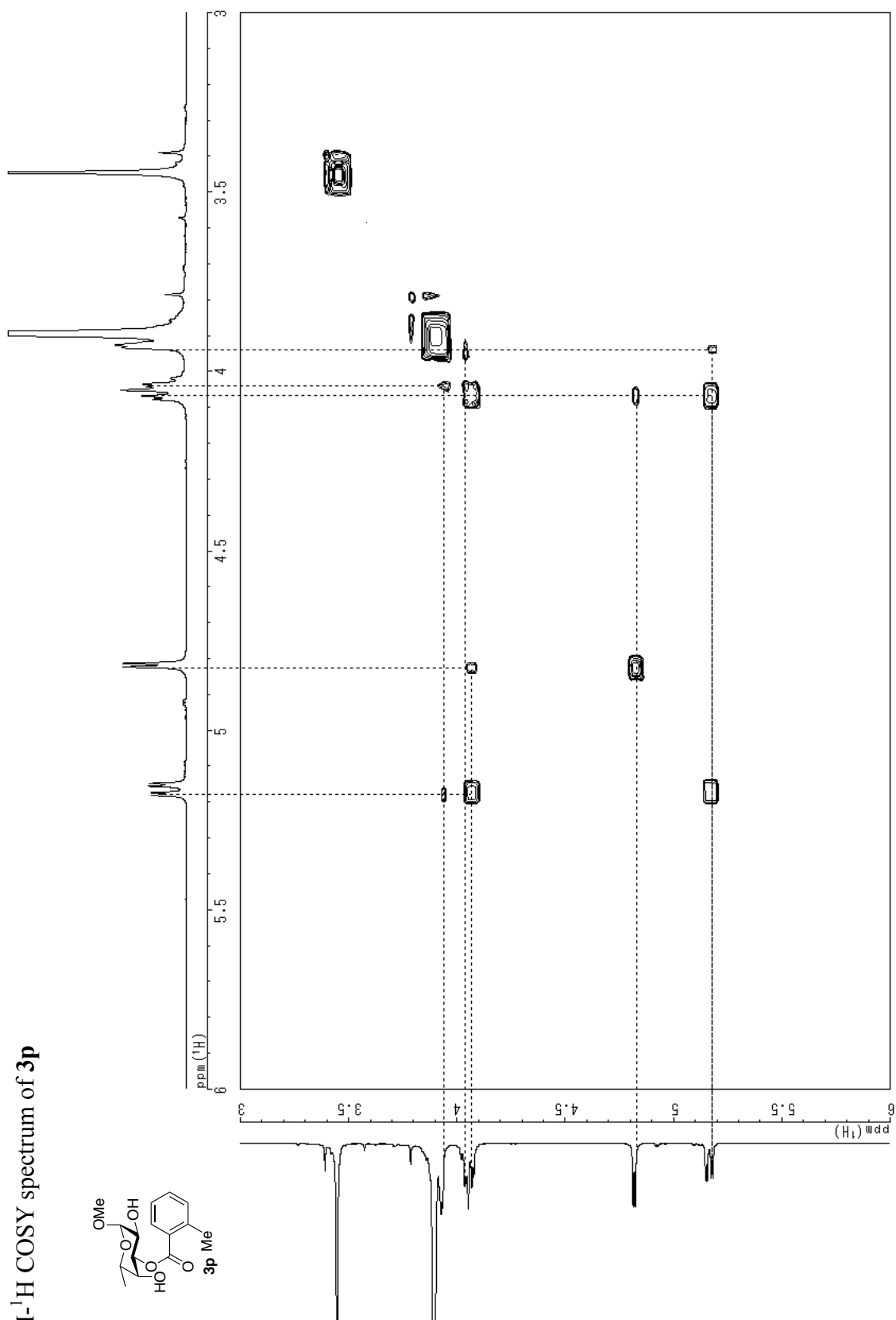
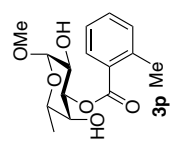
$^1\text{H-NMR}$ spectrum (crude reaction mixture in the absence of catalyst **1d**)

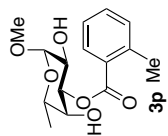




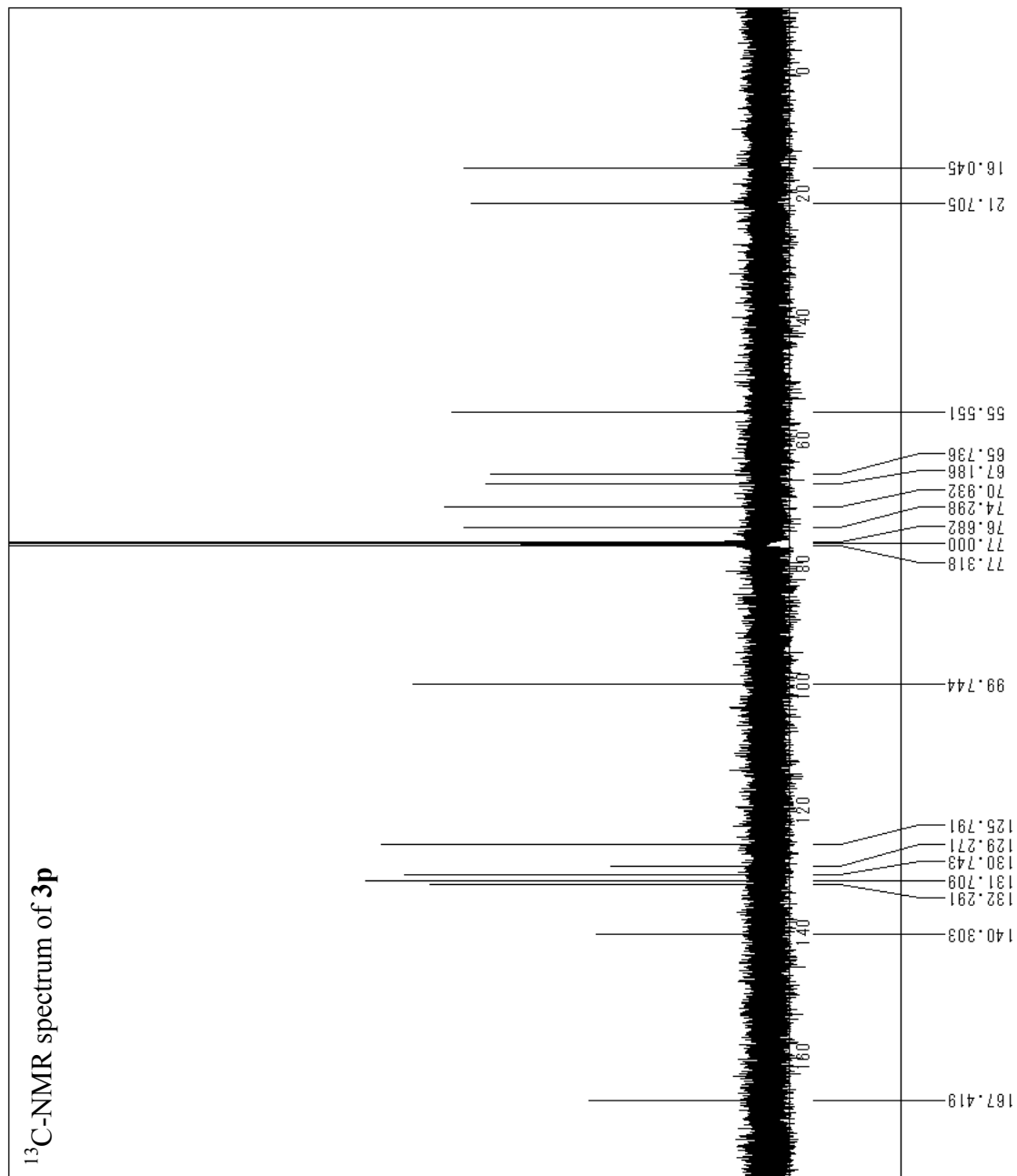
Comment TSV17030_pure_20170909_0
 1
 Date 2017/Sep/09
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **3p**



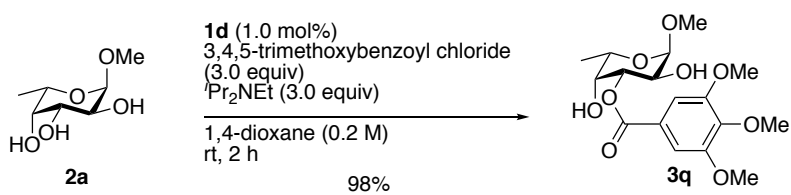


¹³C-NMR spectrum of 3p

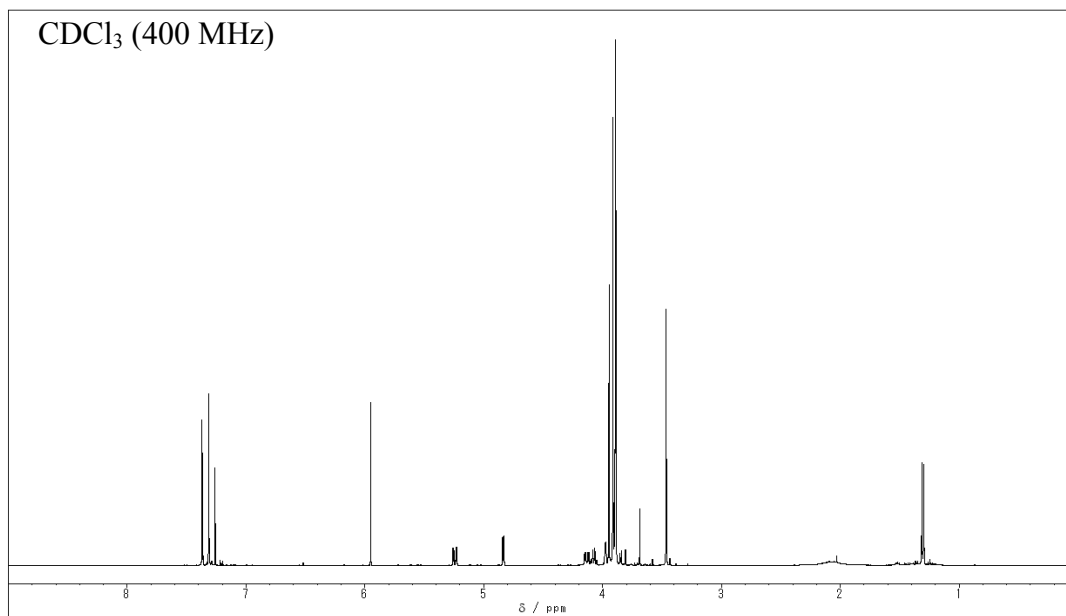


Comment TSV17030_COSY_13C_20170809_01
 Date 2017/Sep/09
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 256
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

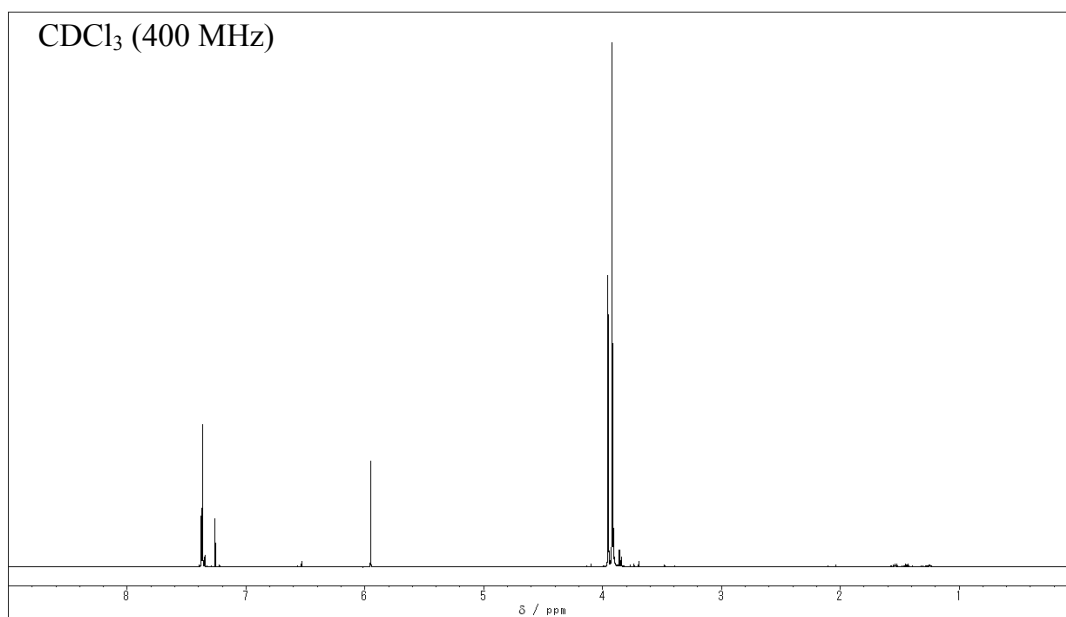
Methyl 3-*O*-3,4,5-trimethylgalloyl- α -L-fucopyranoside (**3q**)

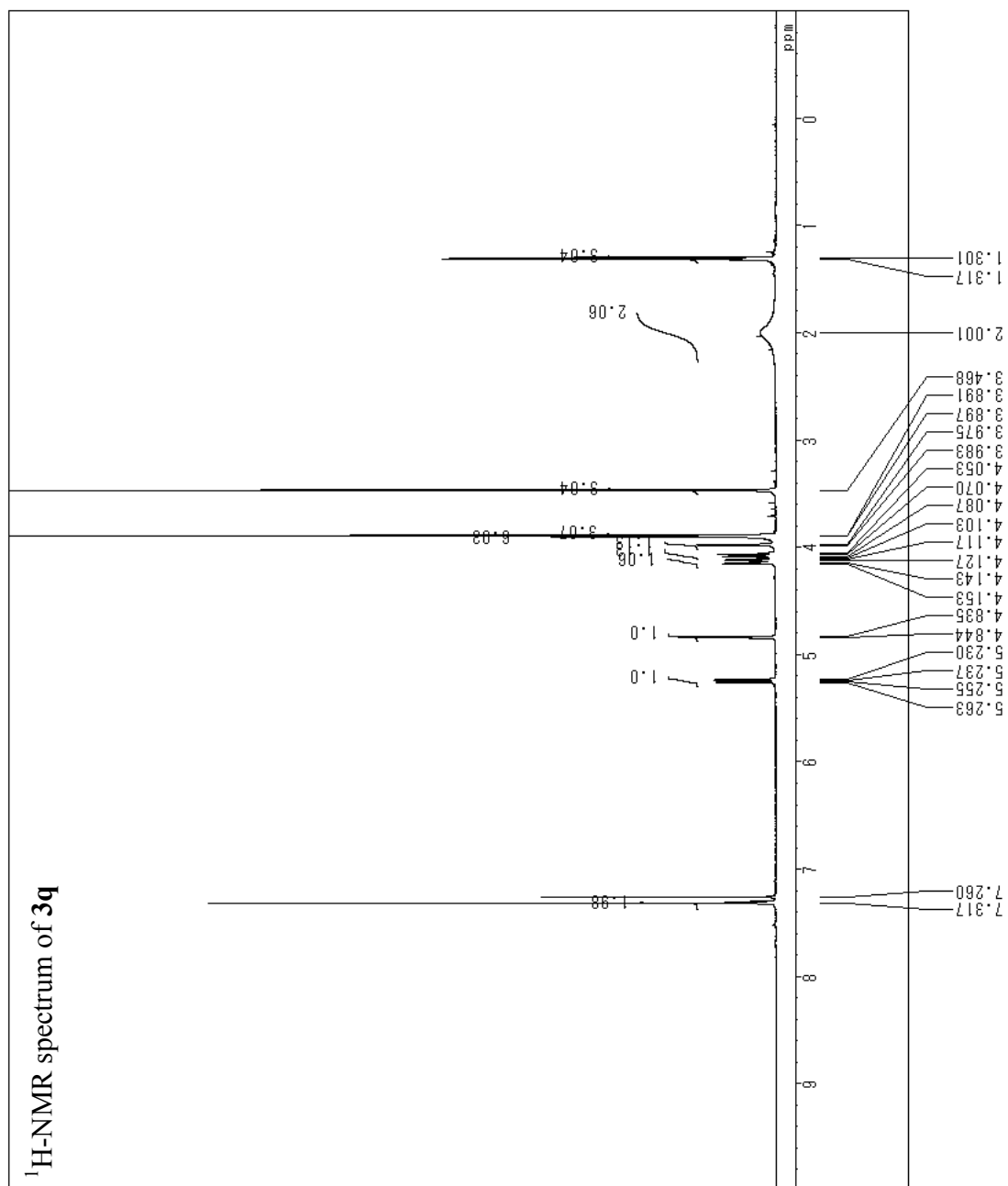


$^1\text{H-NMR}$ spectrum (crude reaction mixture in the presence of catalyst **1d**)



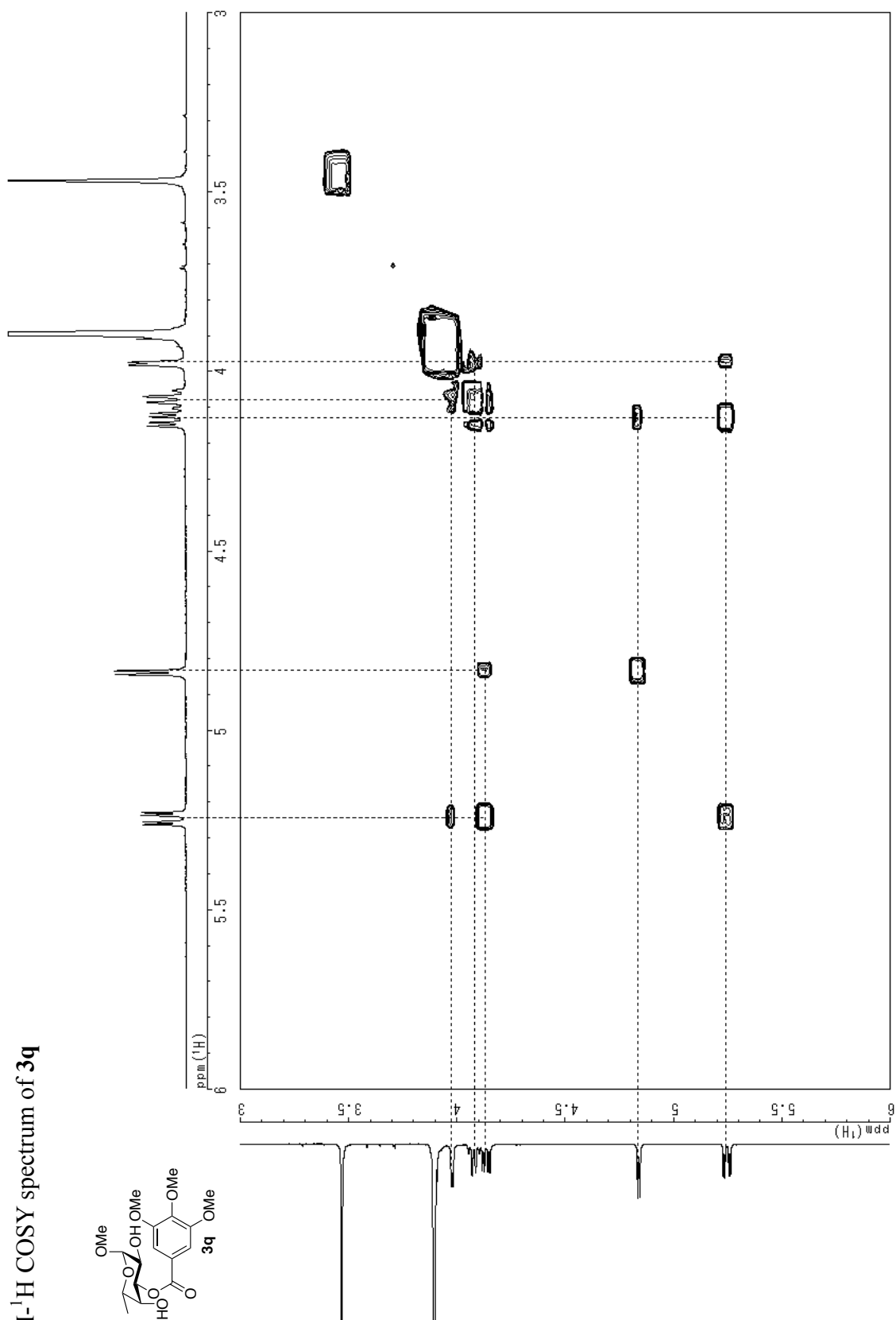
$^1\text{H-NMR}$ spectrum (crude reaction mixture in the absence of catalyst **1d**)

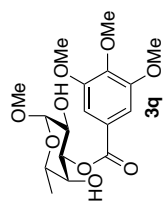
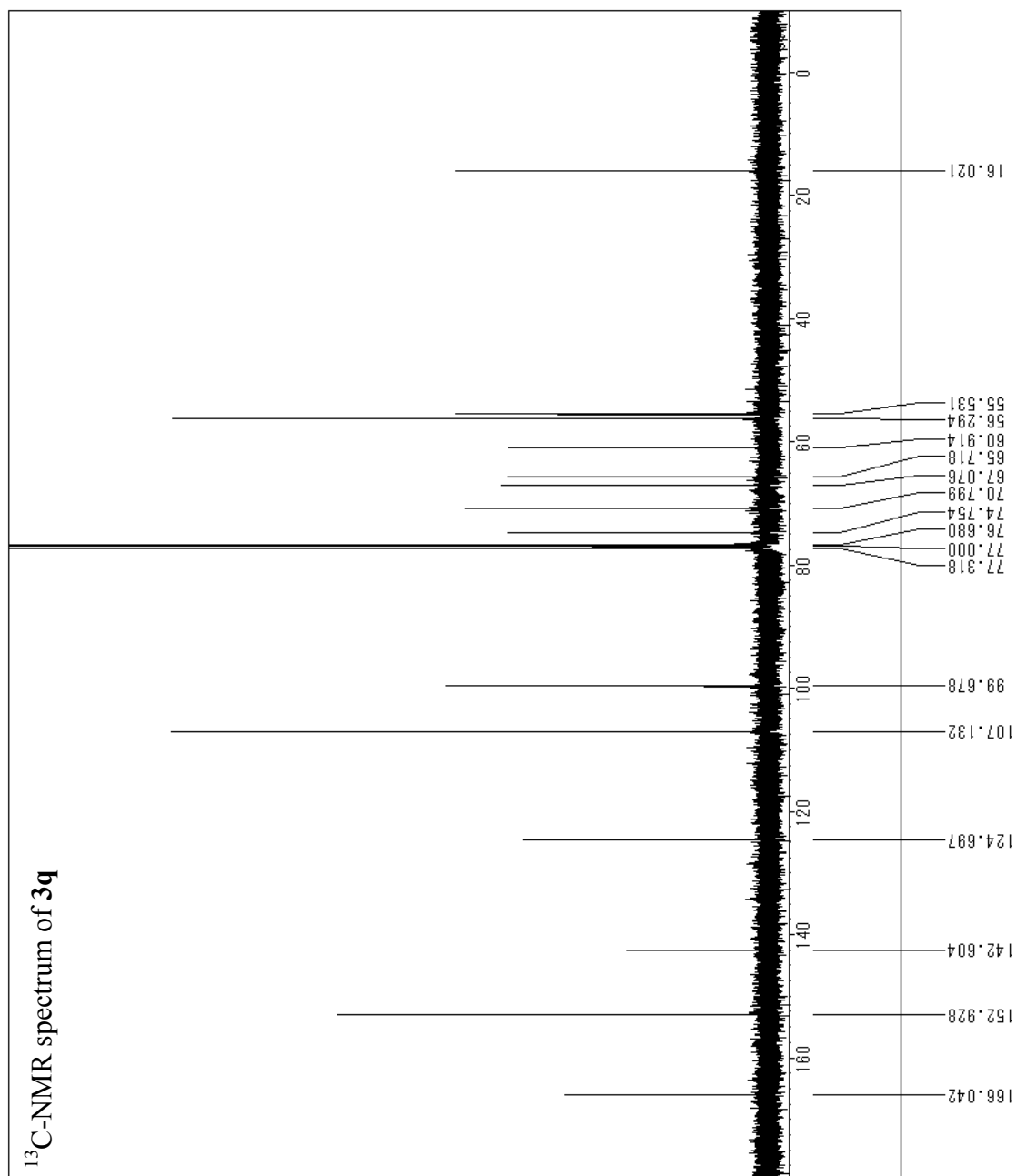




Comment TSV18002_pure_13C_COSY_2
 0170928_01
 Date 2017/Sep/28
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.569 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

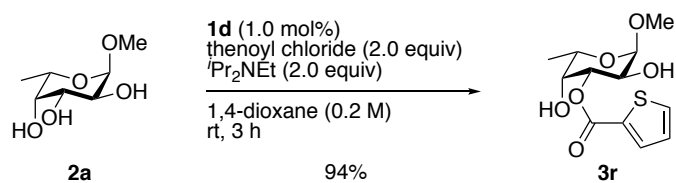
^1H - ^1H COSY spectrum of **3q**



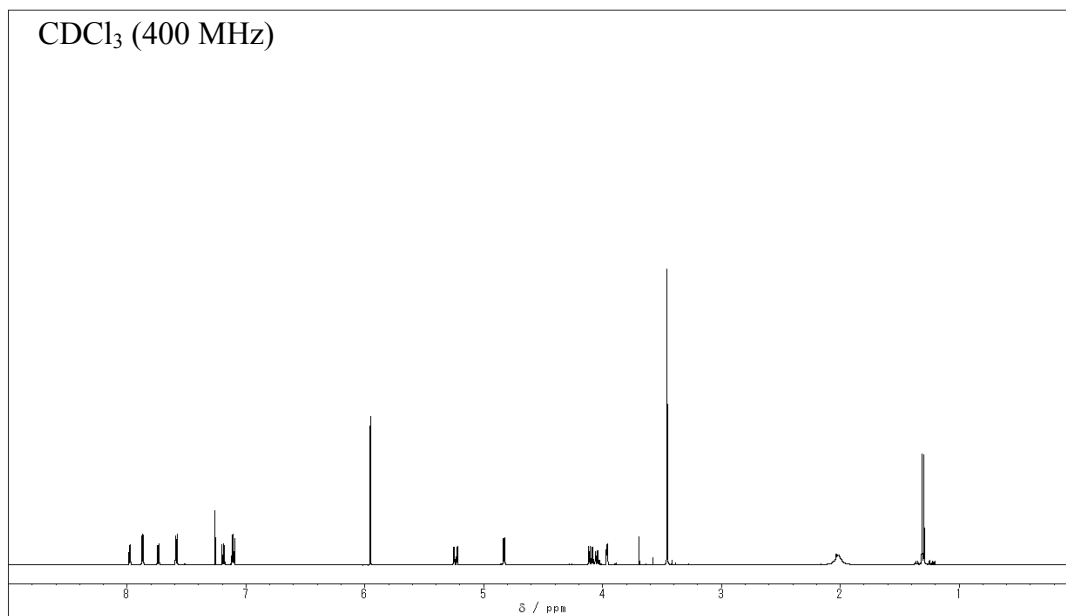


Comment TSV18002_pure_13C_COSY_2
 0170928_01
 Date 2017/Sep/28
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

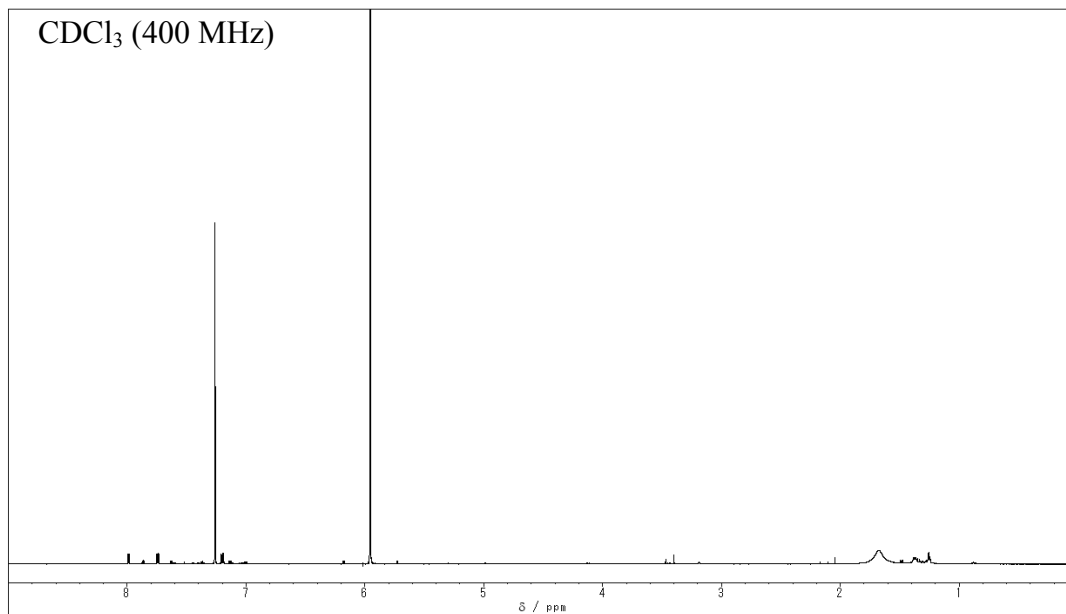
Methyl 3-*O*-2-thenoyl- α -L-fucopyranoside (**3r**)

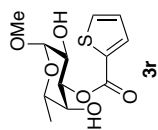


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



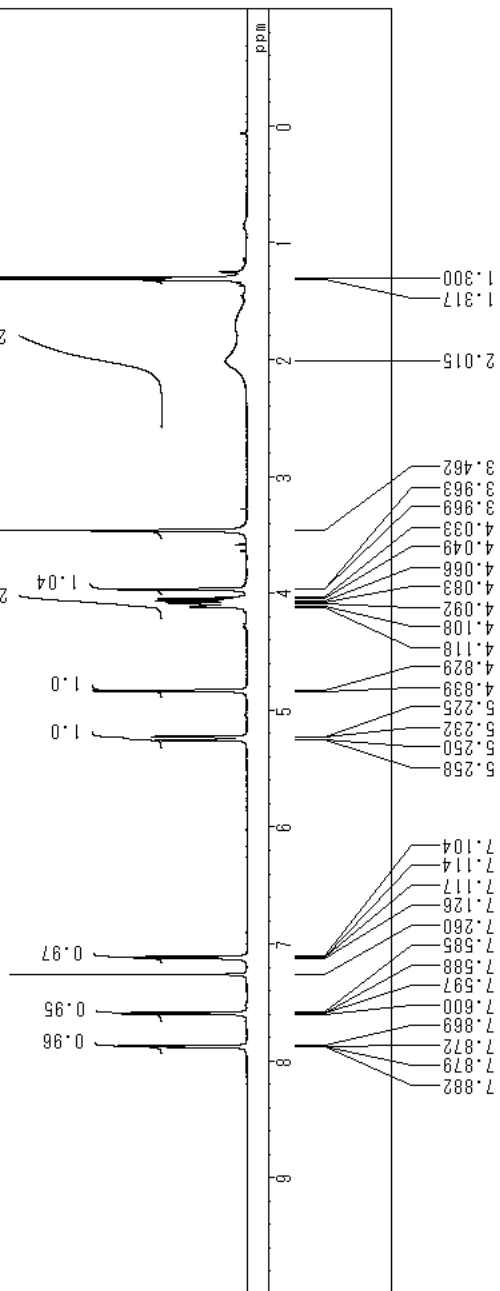
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



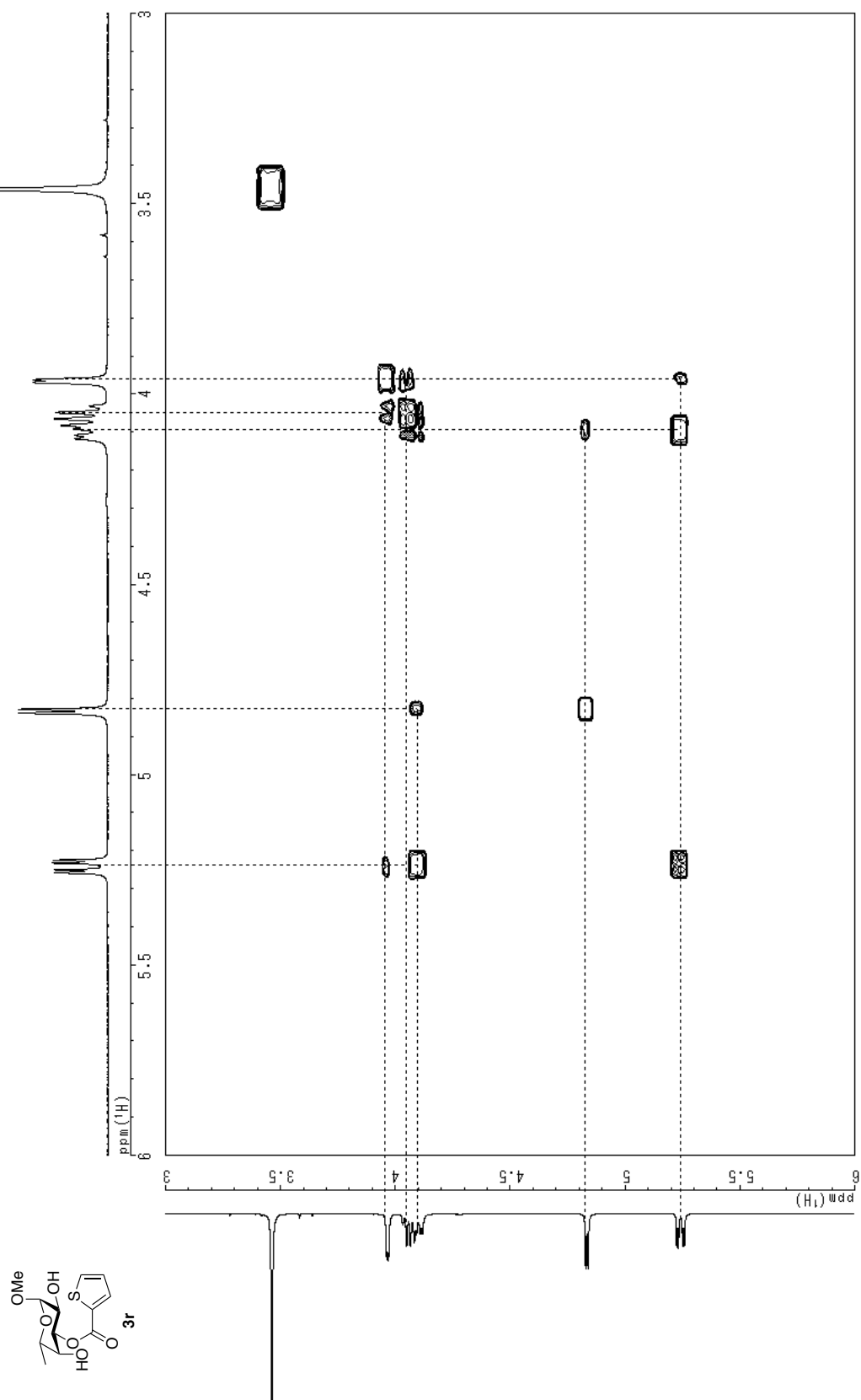


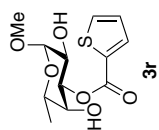
¹H-NMR spectrum of **3r**

Comment TSV17033_pure_13C_COSY_2
 0170918_01
 Date 2017/Sep/19
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

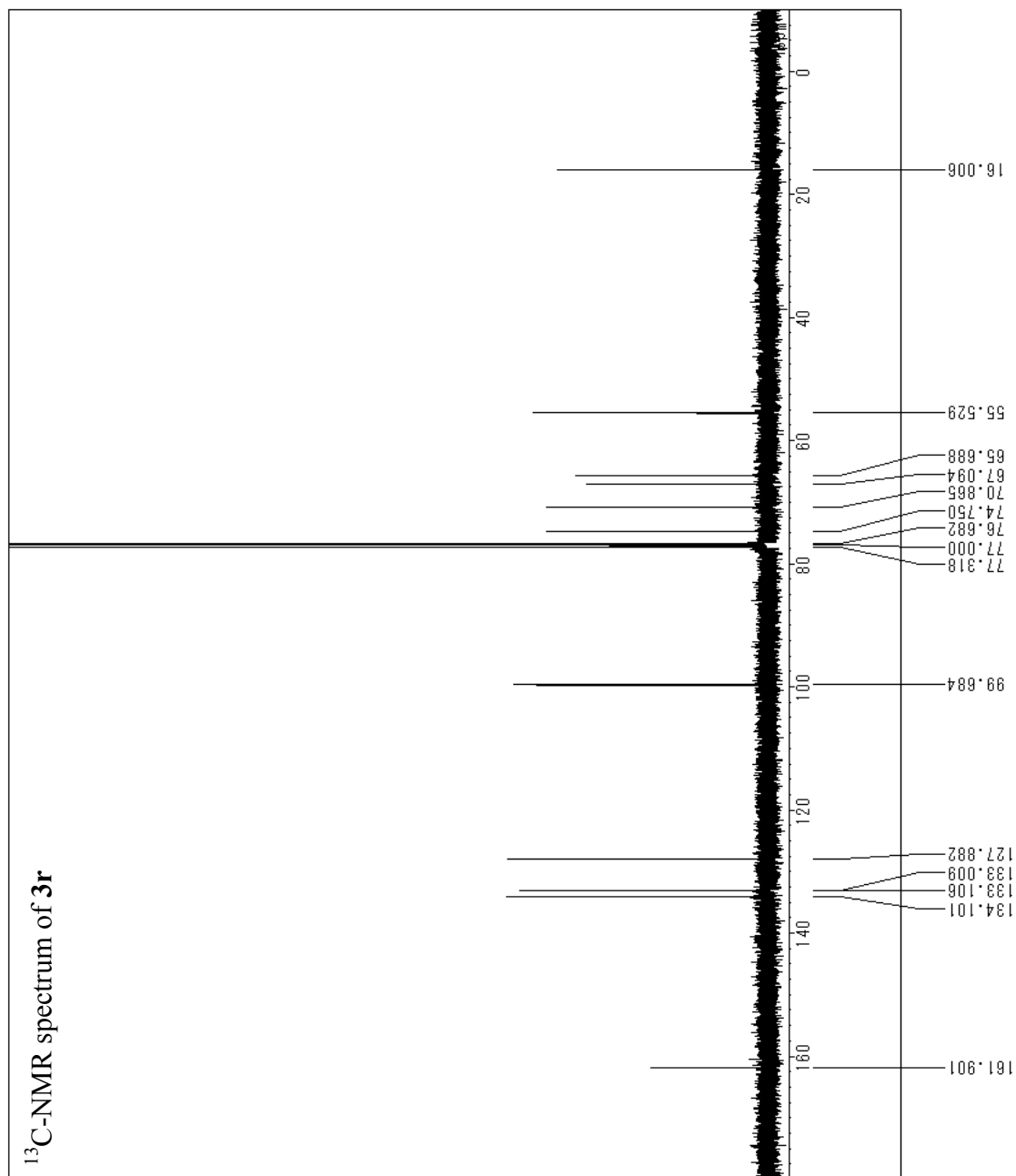


^1H - ^1H COSY spectrum of **3r**



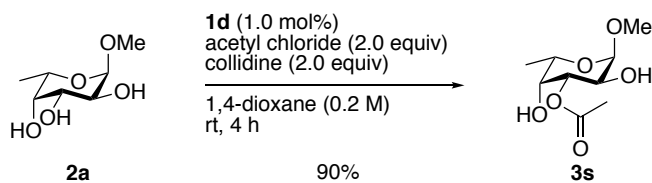


¹³C-NMR spectrum of **3r**

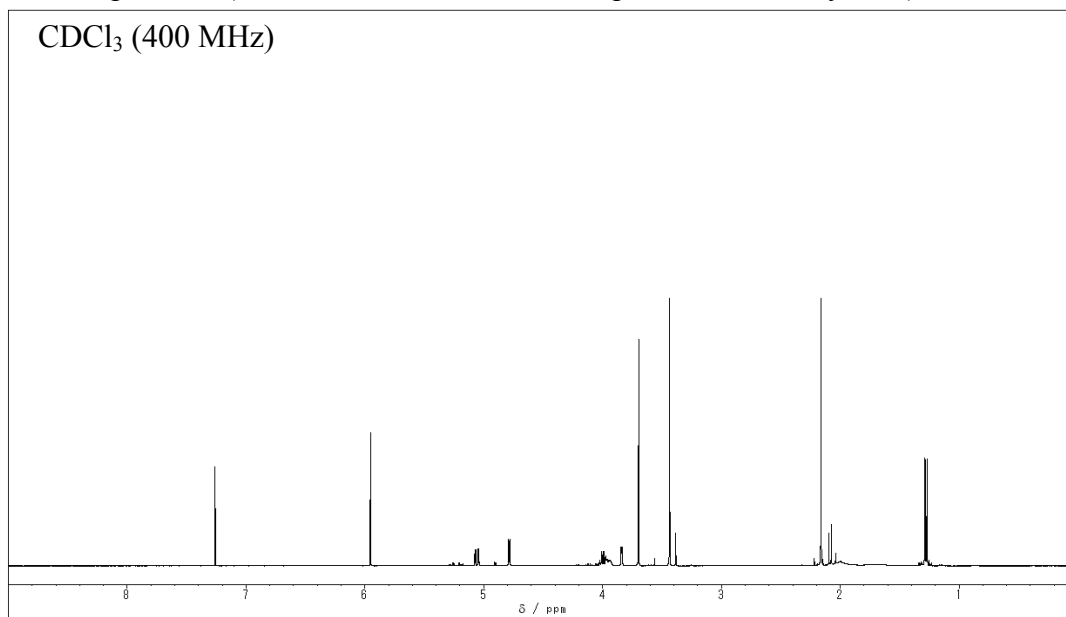


Comment TSV17033_pure_13C_COSY_2
 0170918_01
 Date 2017/Sep/19
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

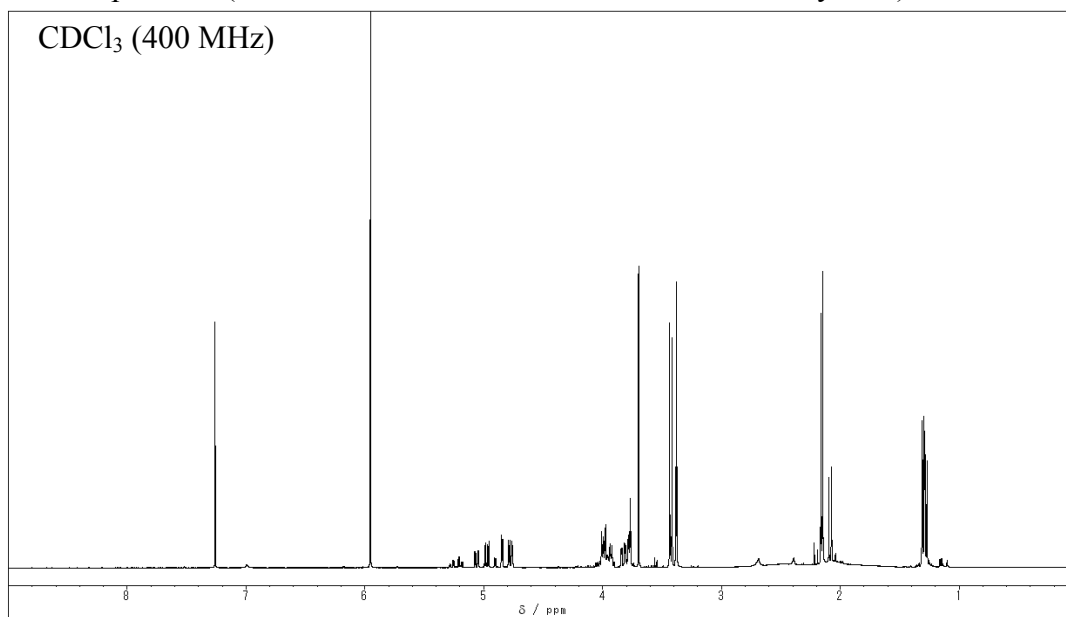
Methyl 3-*O*-acetyl- α -L-fucopyranoside (**3s**)

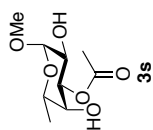


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

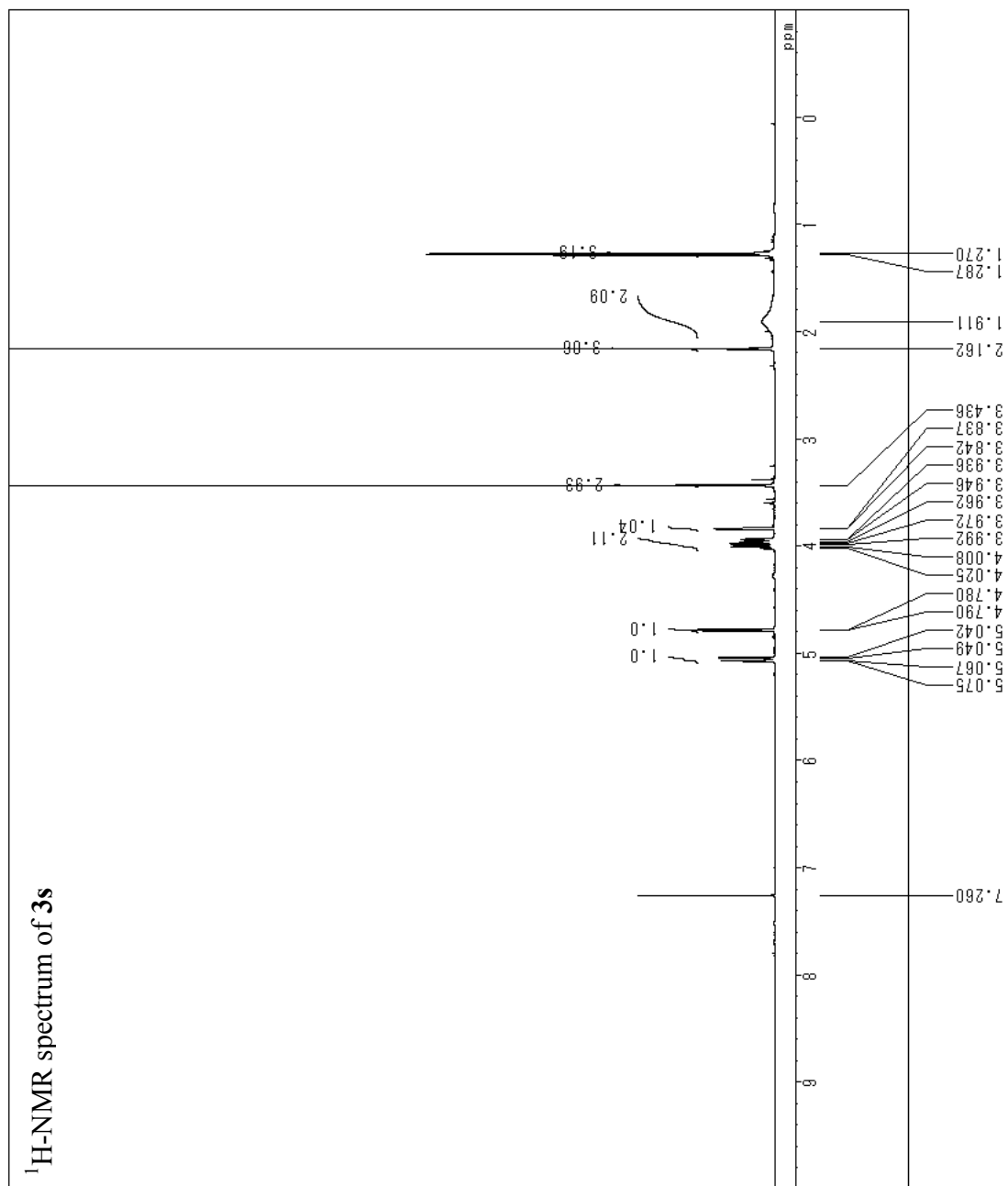


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



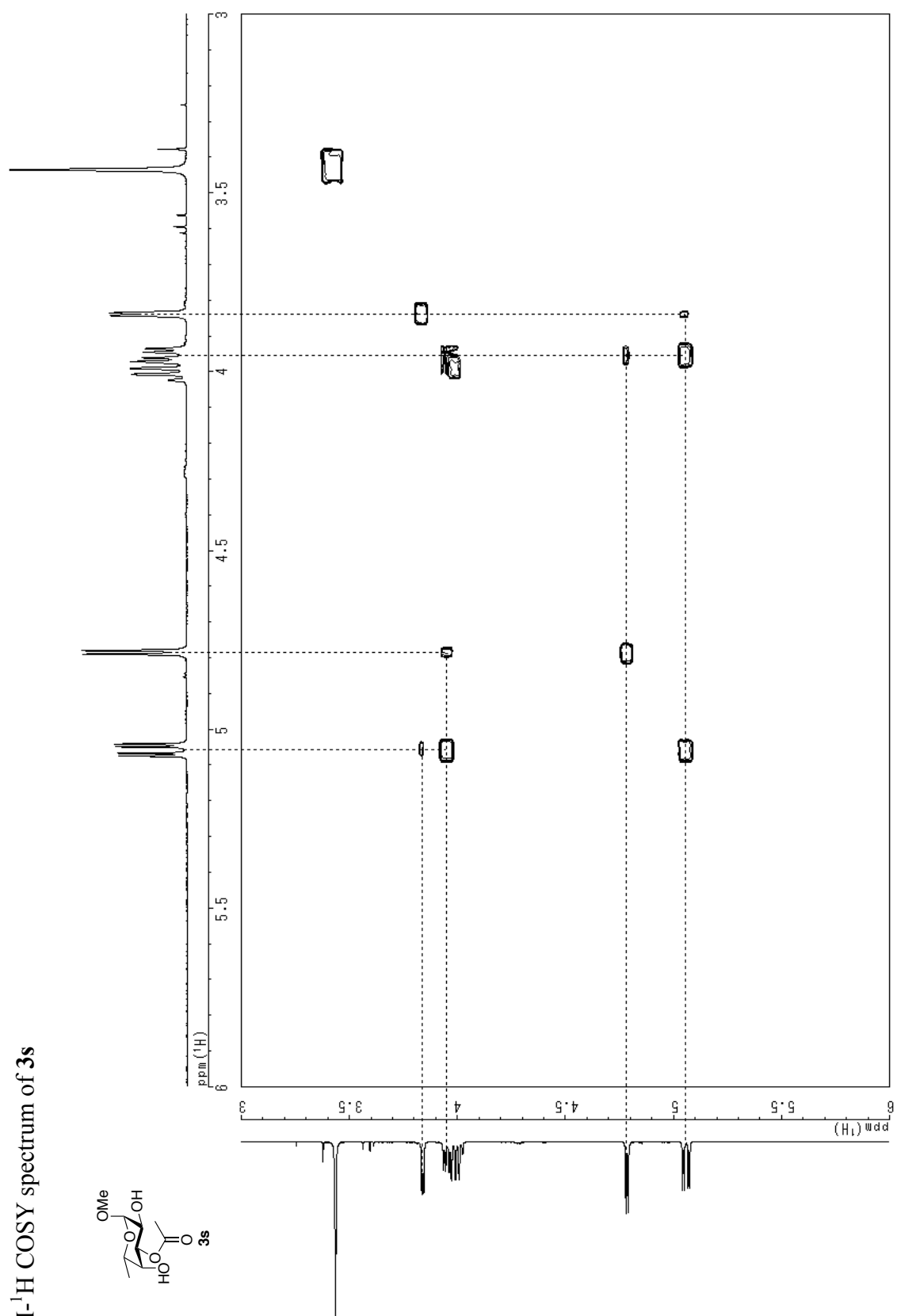


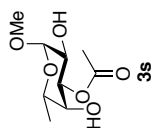
¹H-NMR spectrum of **3s**



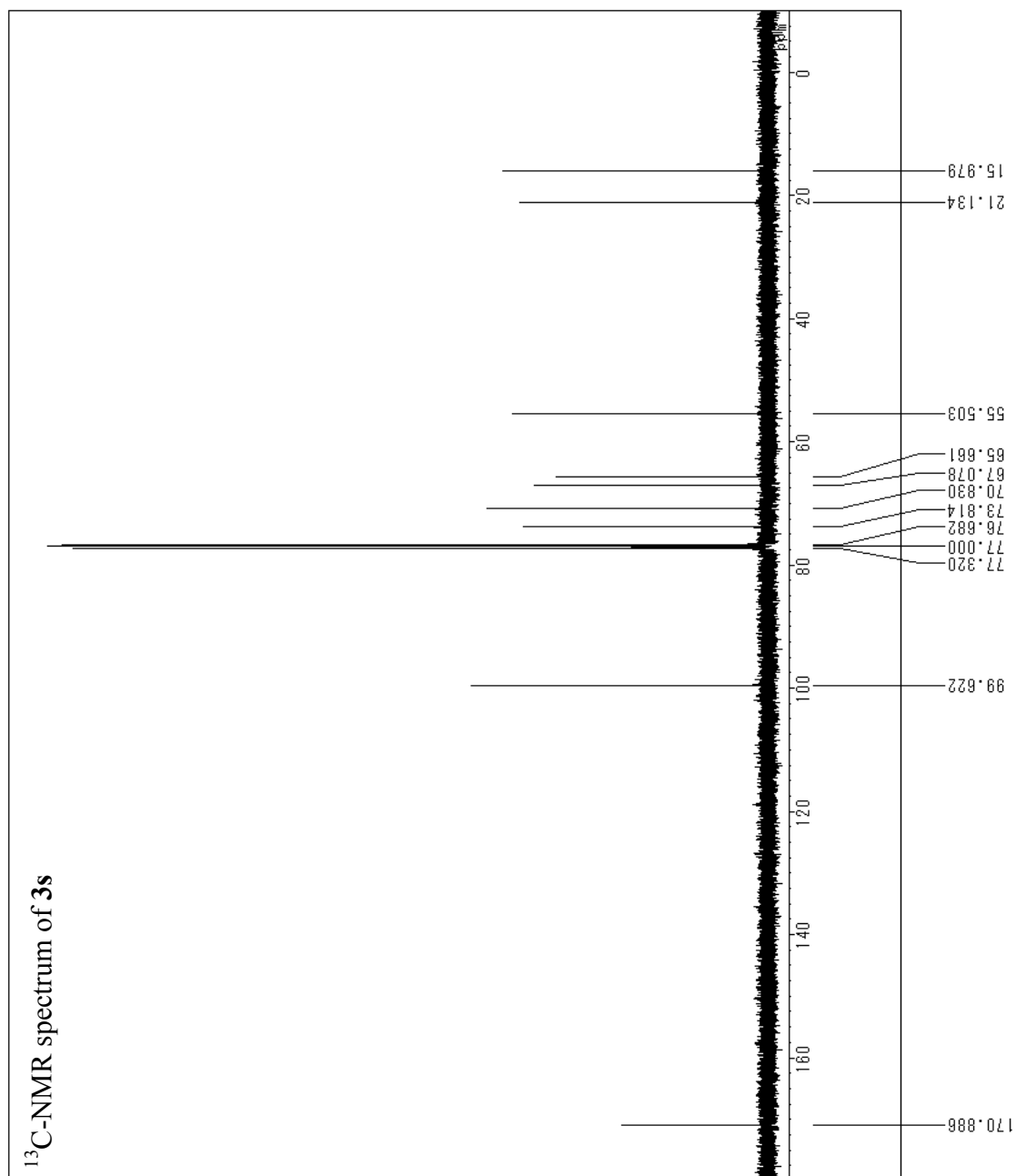
Comment TSV18020_pure_13C_COSY_2
 0171003_01
 Date 2017/Oct/03
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **3s**



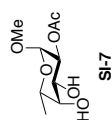
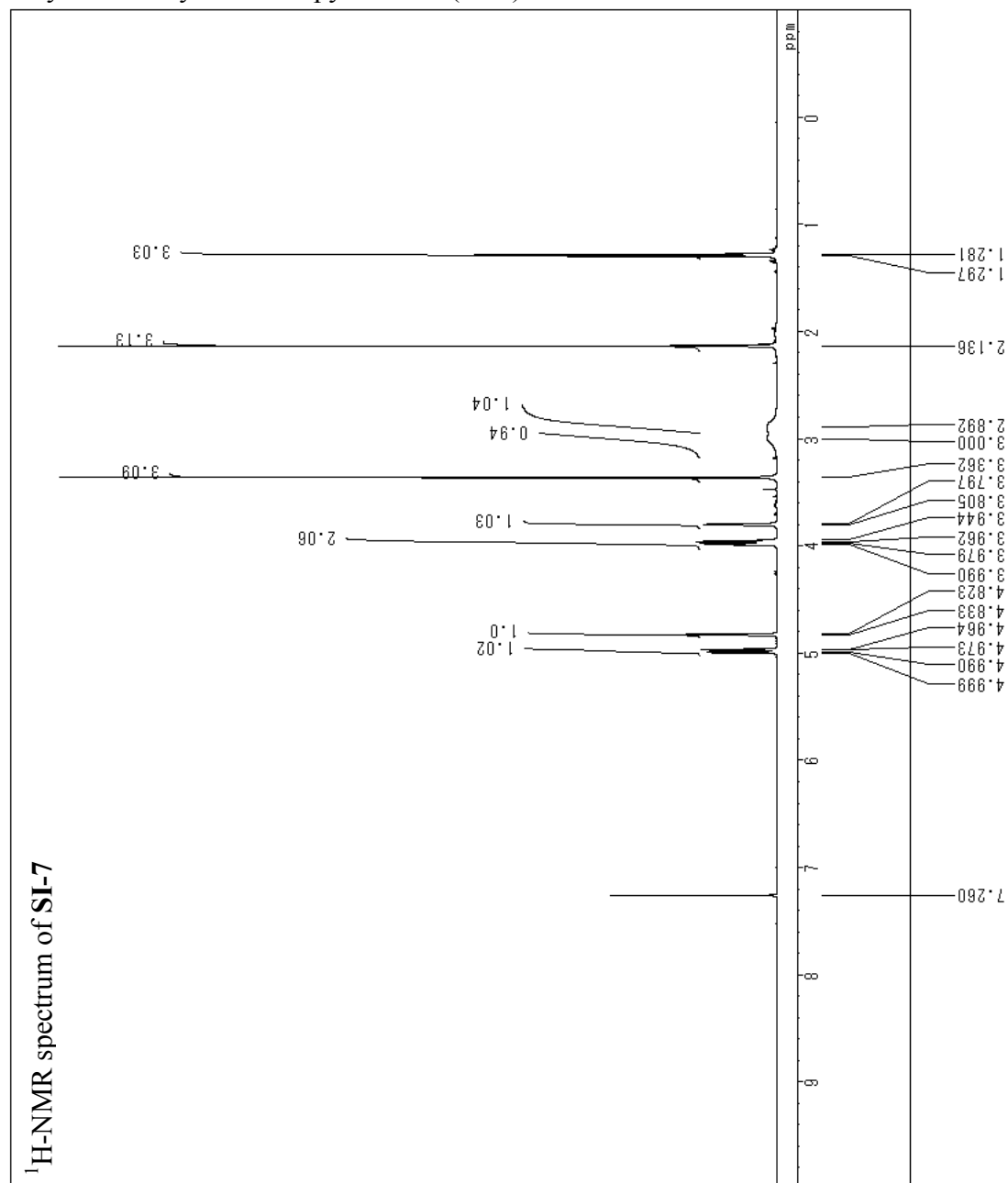


¹³C-NMR spectrum of **3s**



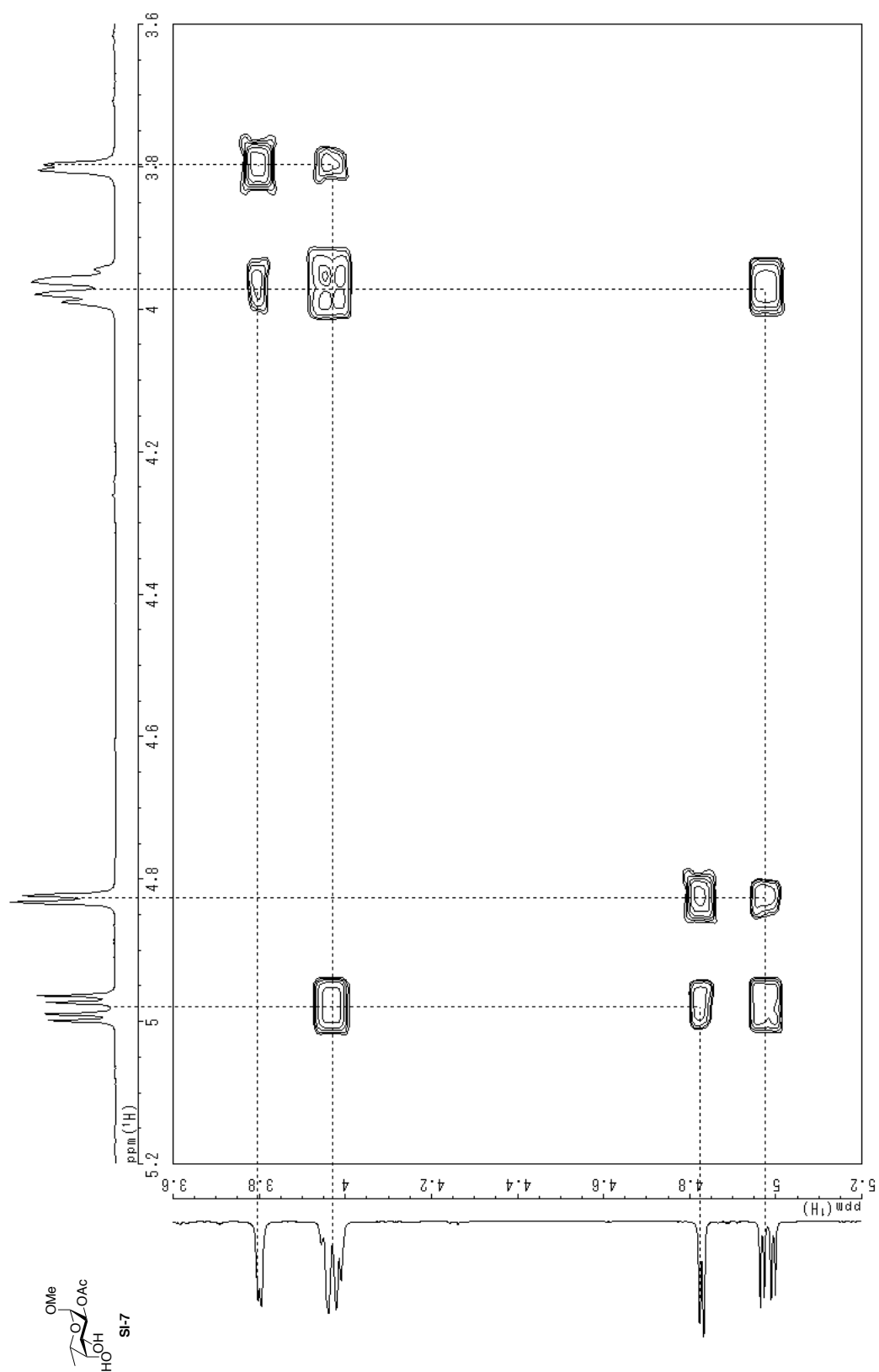
Comment TSV18020_pure_13C_COSY_2
 0171003_01
 Date 2017/Oct/03
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

Methyl 2-*O*-acetyl- α -L-fucopyranoside (SI-7)

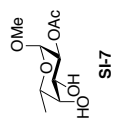


Comment TSV25039_pure_13C_COSY_2
0190210_01
Date 2019/Feb/10
ObsNuc ¹H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 16
AcqTime 2.589 s
Acc. Interval 5.589 s
Spinning 16.0 Hz
Temperature 25.0 °C
Solvent cdcl₃

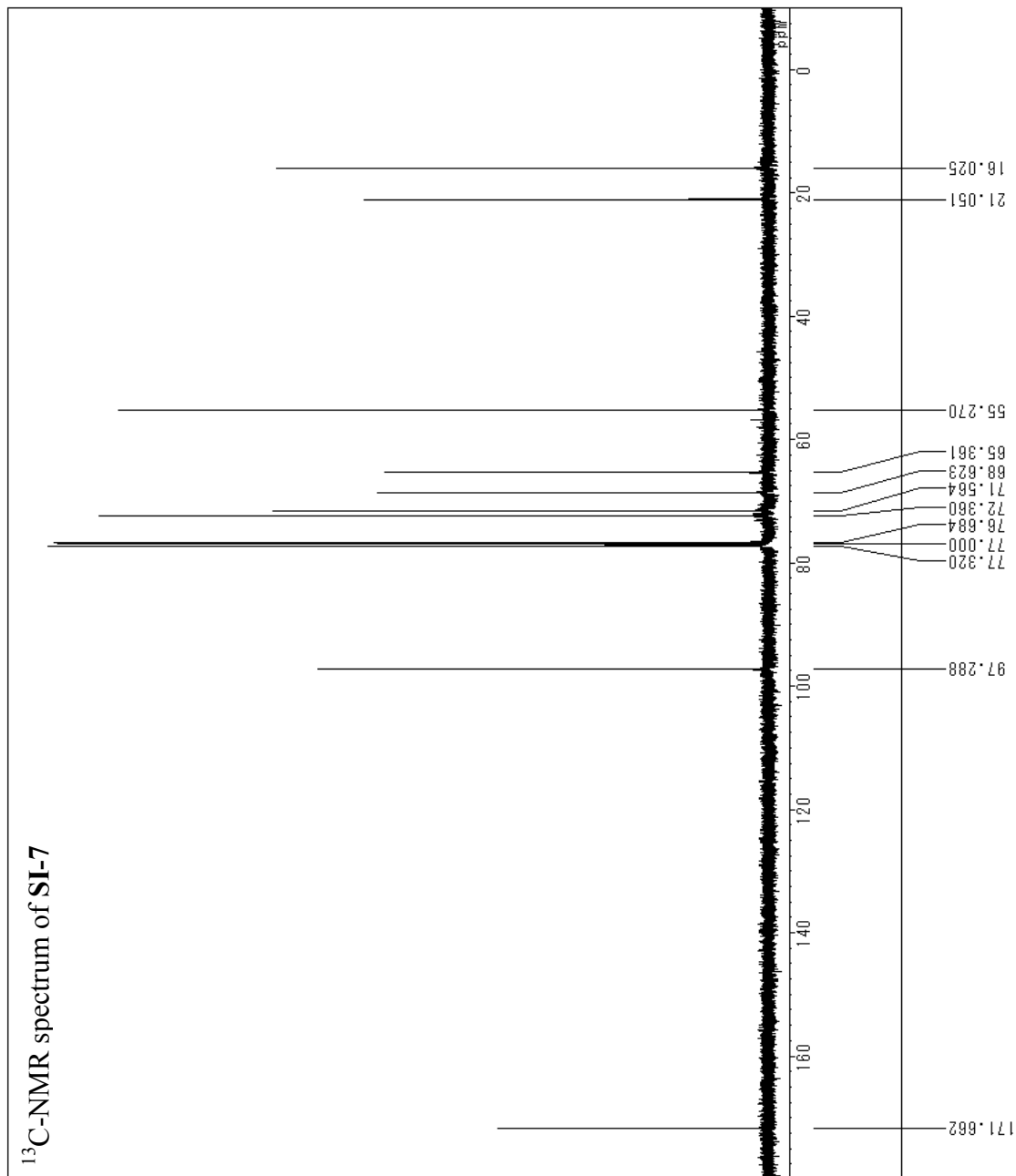
^1H - ^1H COSY spectrum of **SI-7**



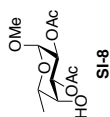
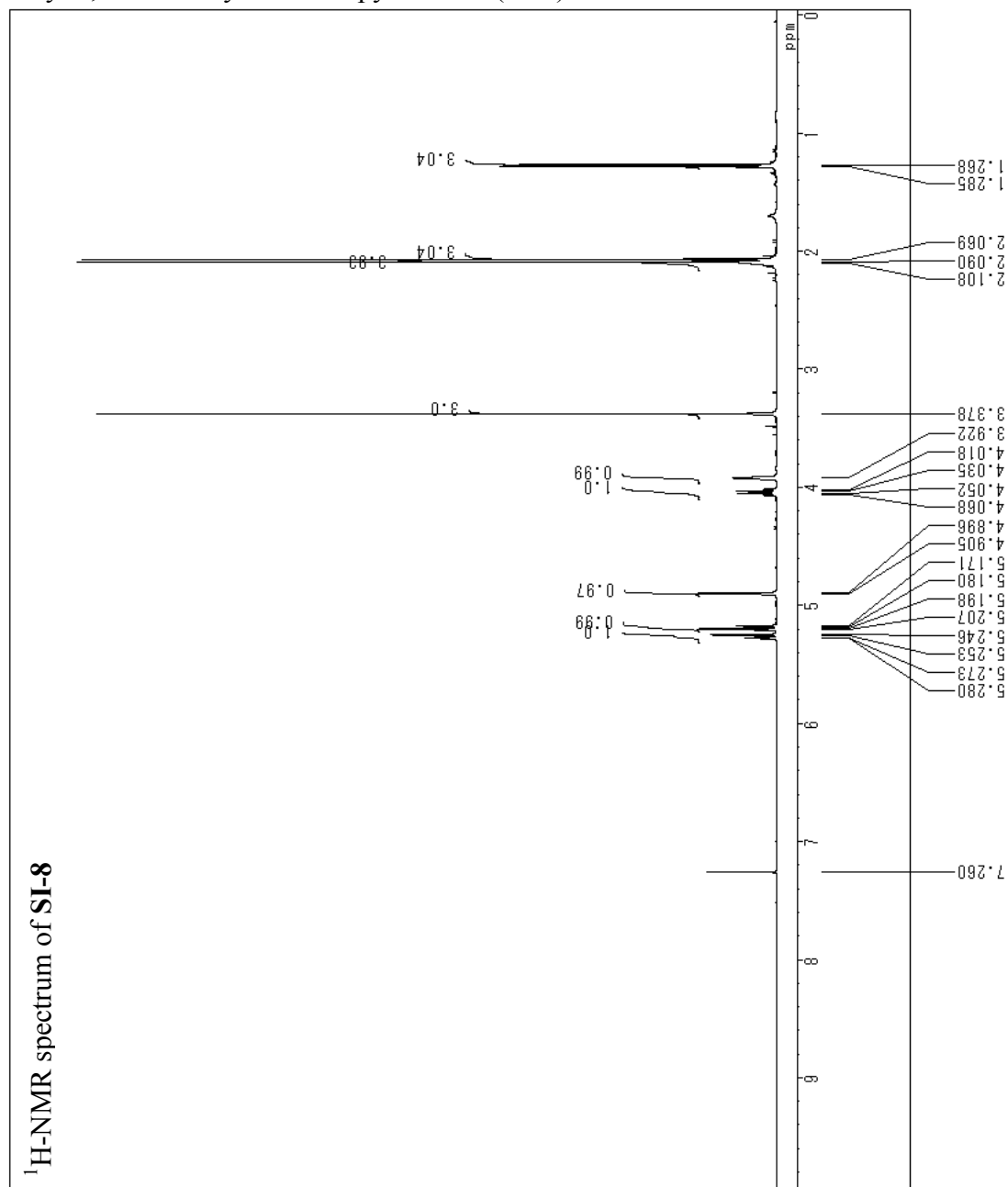
¹³C-NMR spectrum of SI-7



Comment TSV25039_pure_13C_COSY_2
0190210_01
Date 2019/Feb/10
ObsNuc ¹³C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 512
AcqTime 1.3831 s
Acc. Interval 3.3831 s
Spinning 20.0 Hz
Temperature 25.0 °C
Solvent cdcl₃

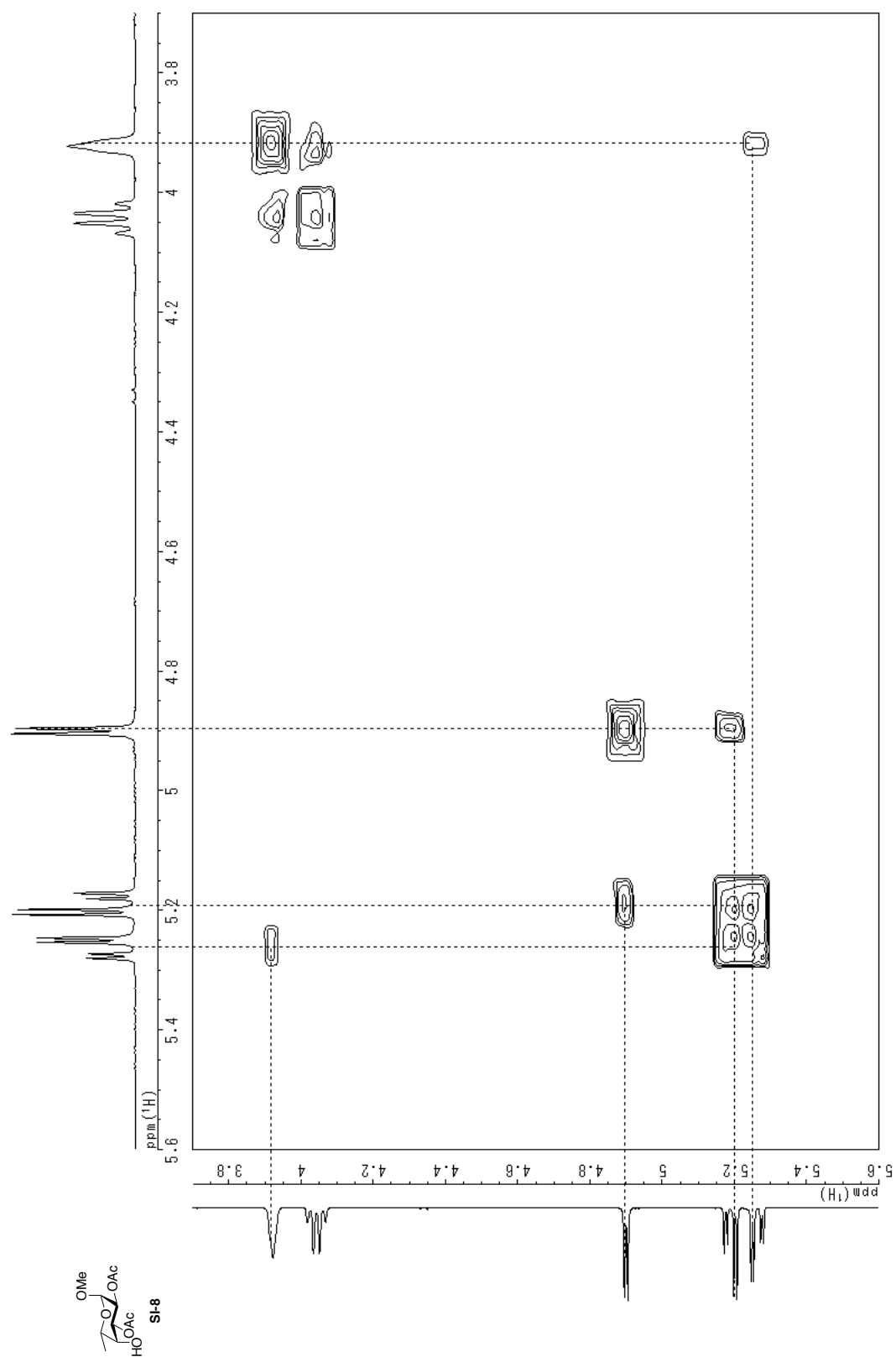


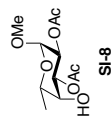
Methyl 2,3-*O*-diacetyl- α -L-fucopyranoside (**SI-8**)



Comment TSV25040_pure_13C_COSY_2
 0180213_01
 Date 2019/Feb/13
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

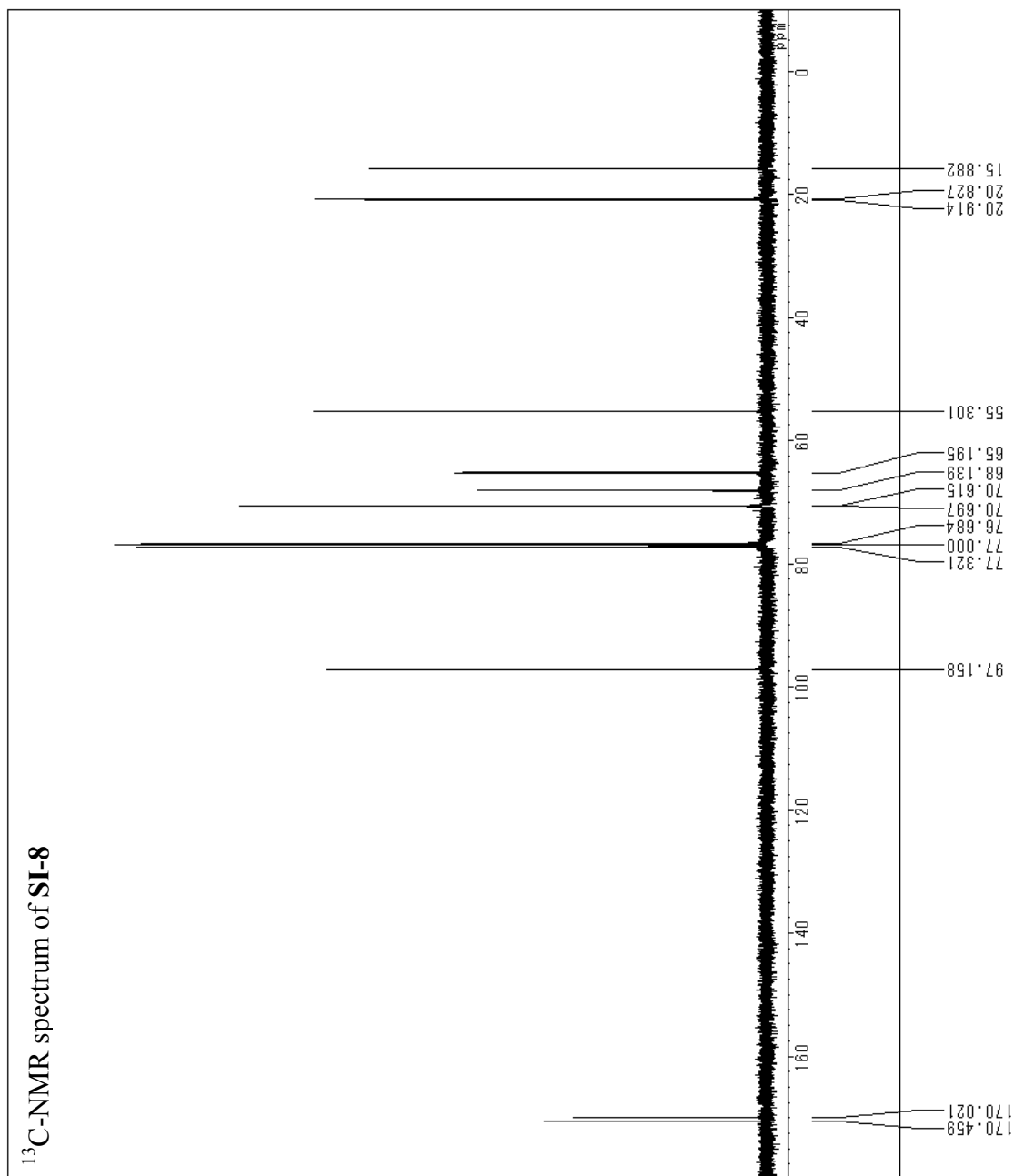
^1H - ^1H COSY spectrum of **SI-8**



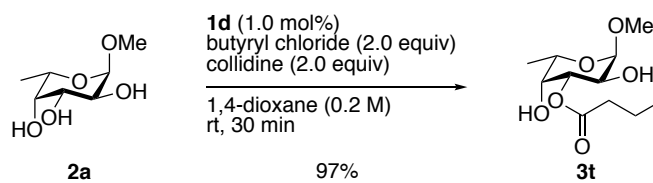


¹³C-NMR spectrum of SI-8

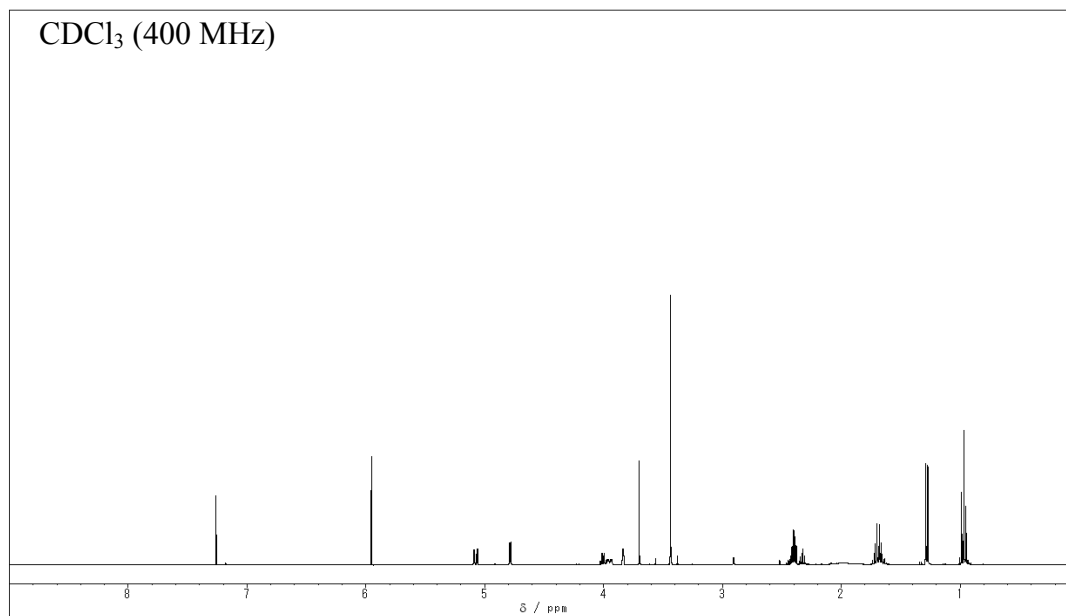
Comment TSV25040_pure_13C_COSY_2
 0190213_01
 Date 2019/Feb/13
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



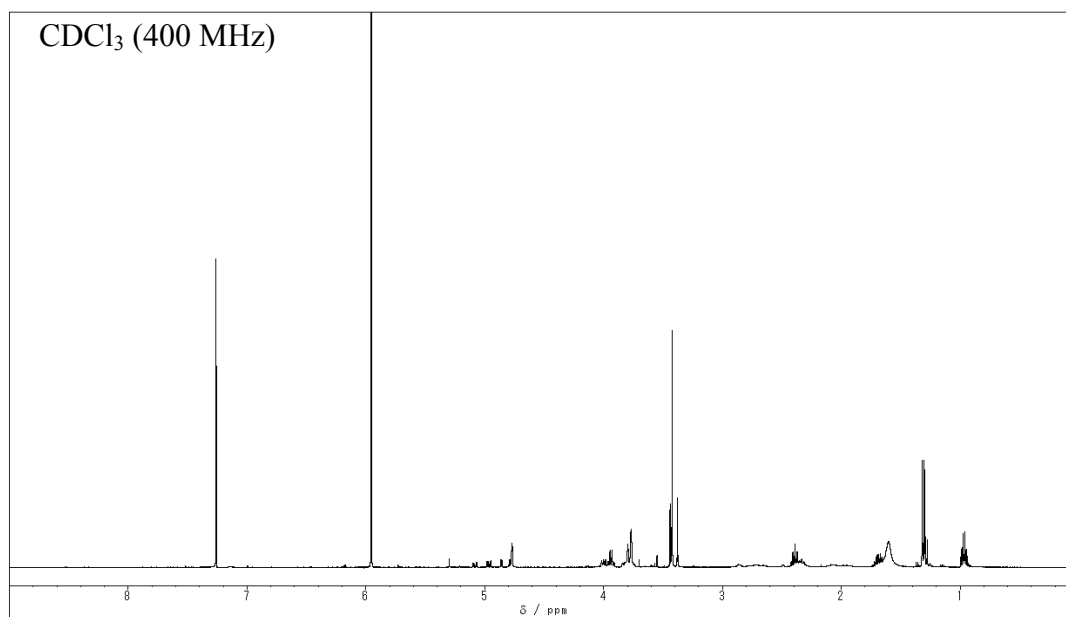
Methyl 3-*O*-butyryl- α -L-fucopyranoside (**3t**)

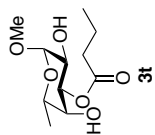


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

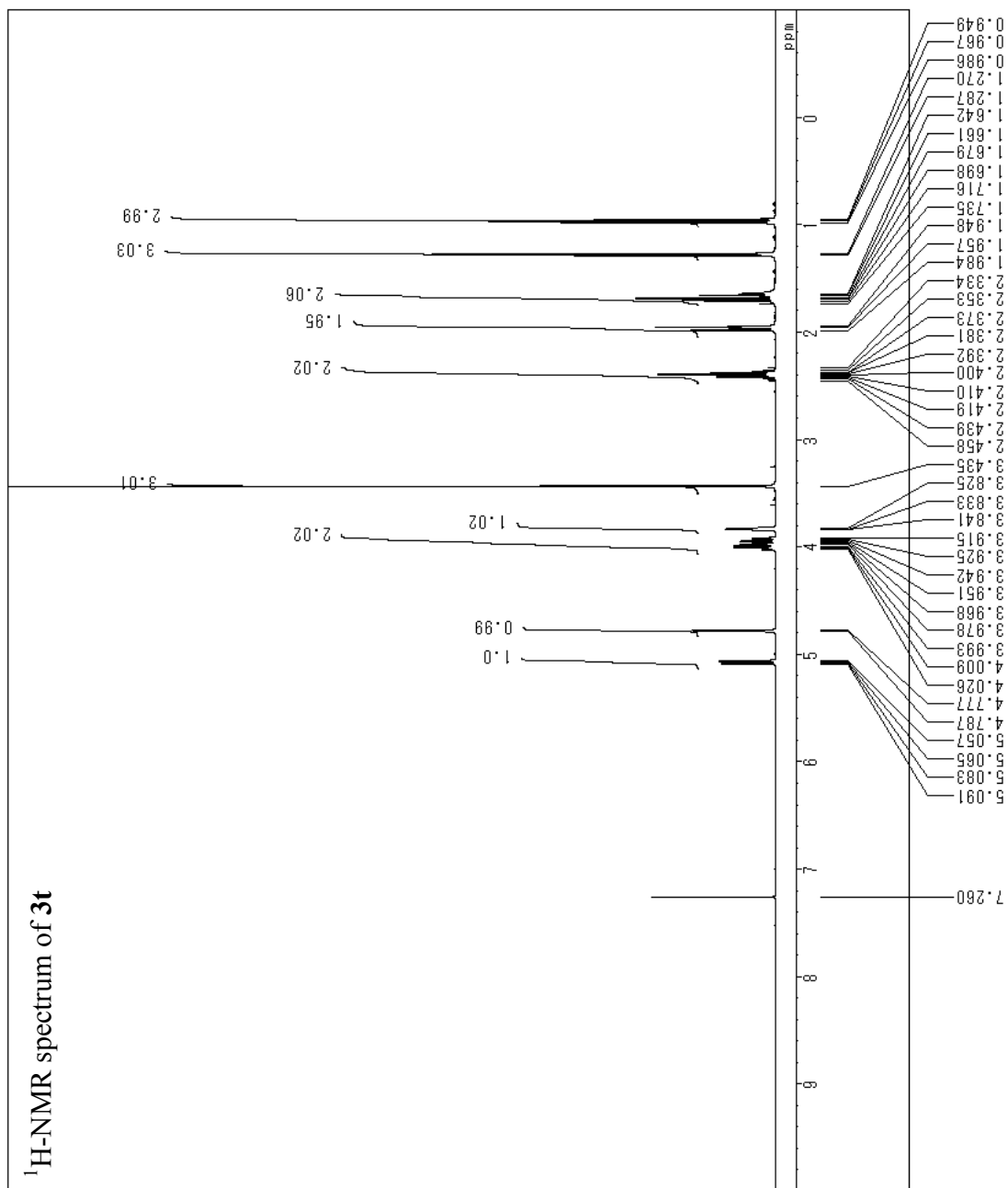


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

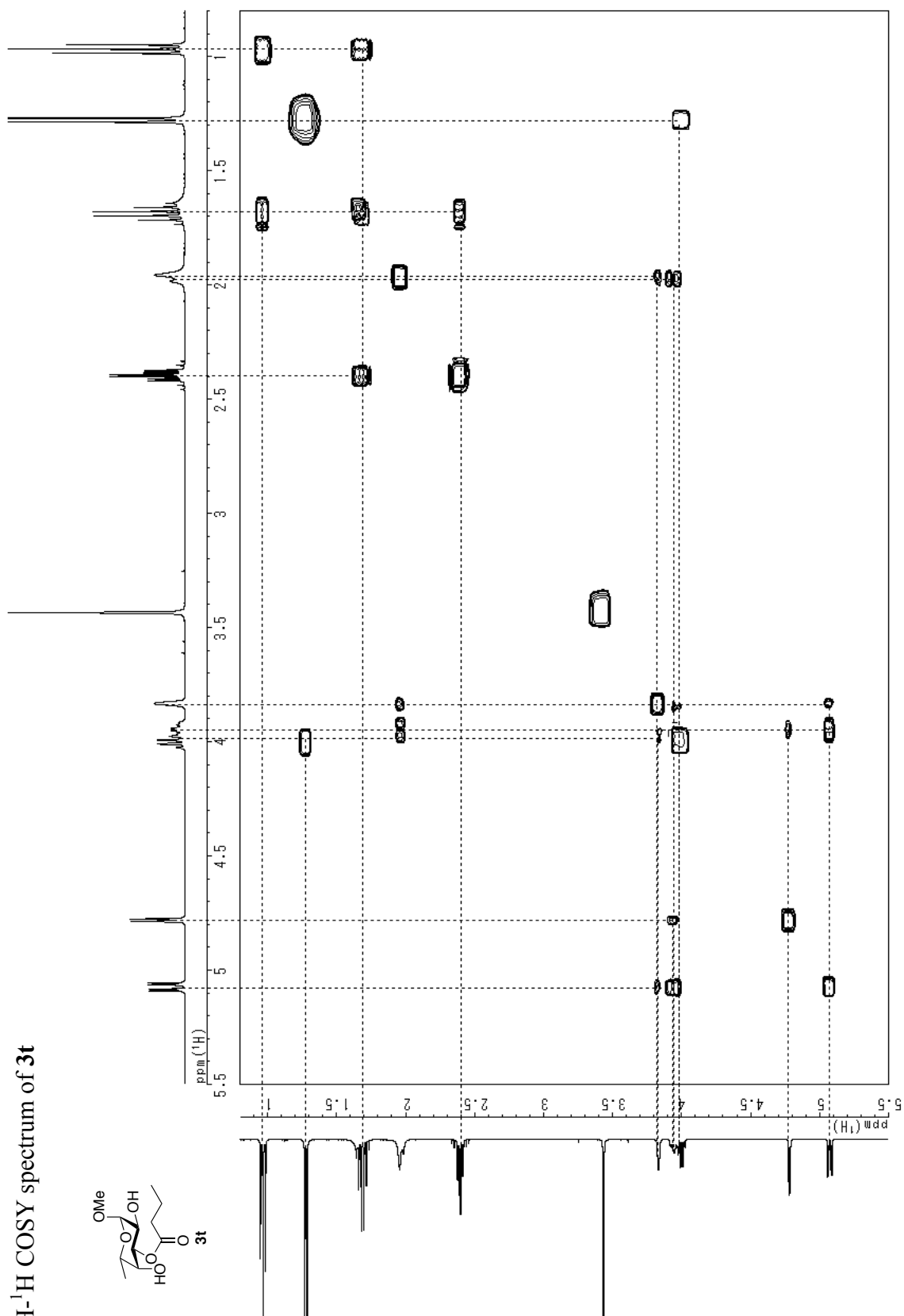


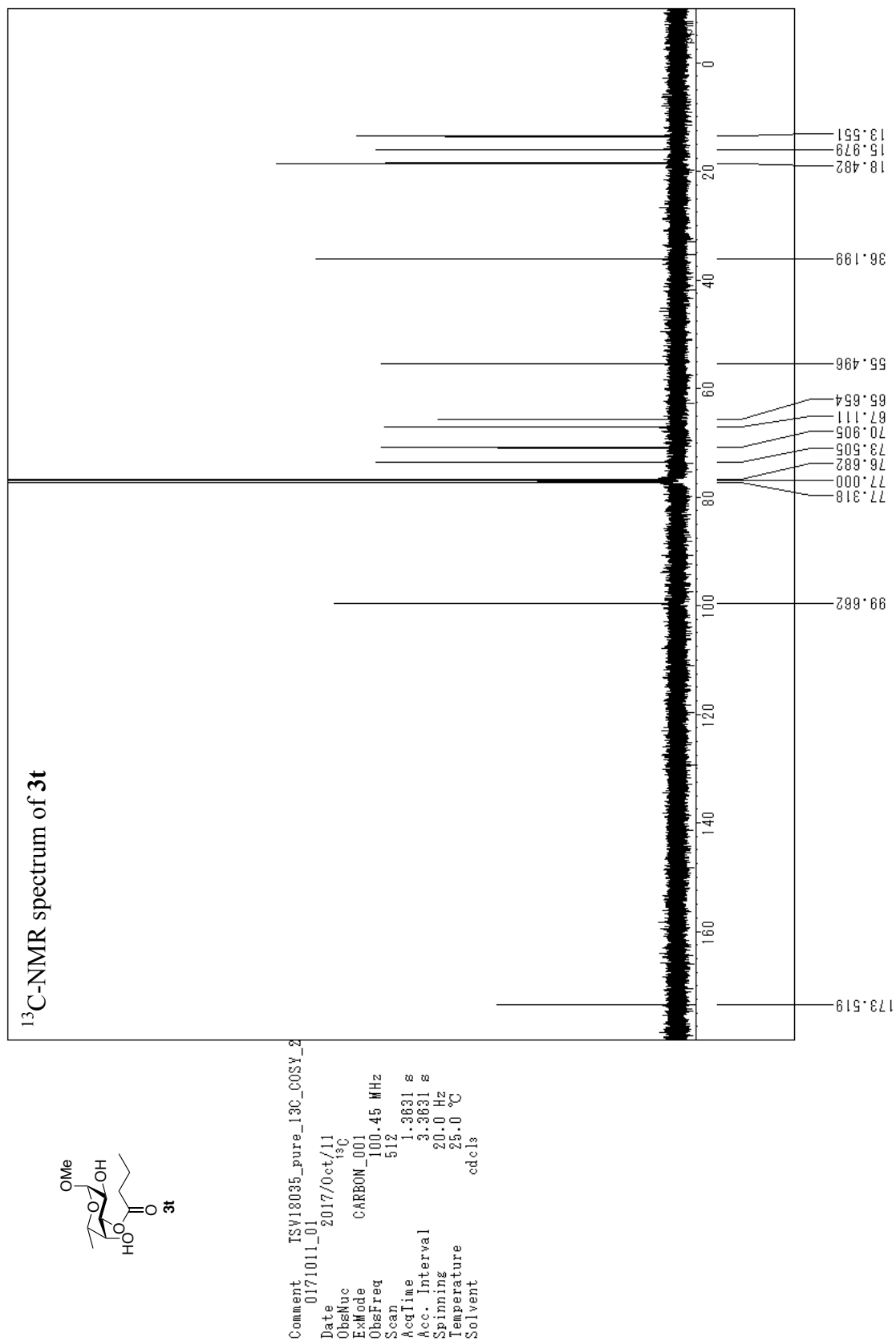
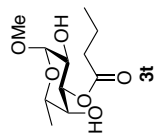


Comment TSV18035_pure_20171011_0
 1
 Date 2017/Oct/11
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 300.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

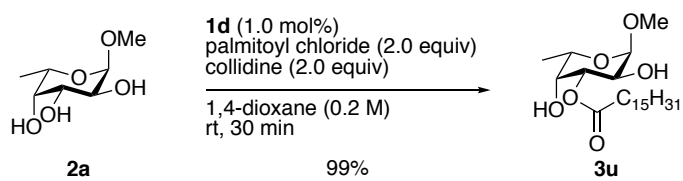


^1H - ^1H COSY spectrum of **3t**

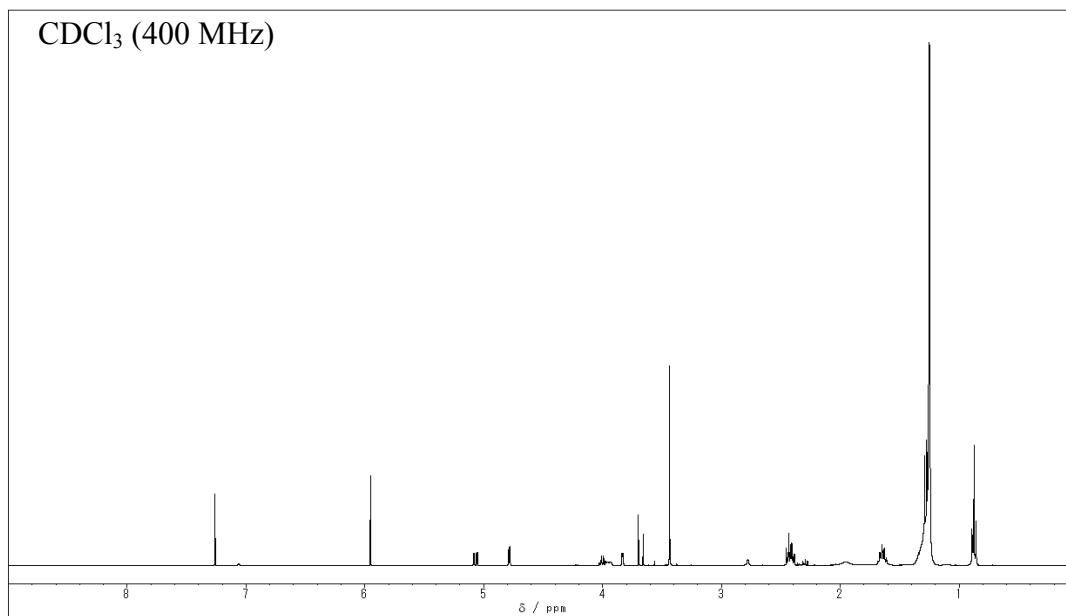




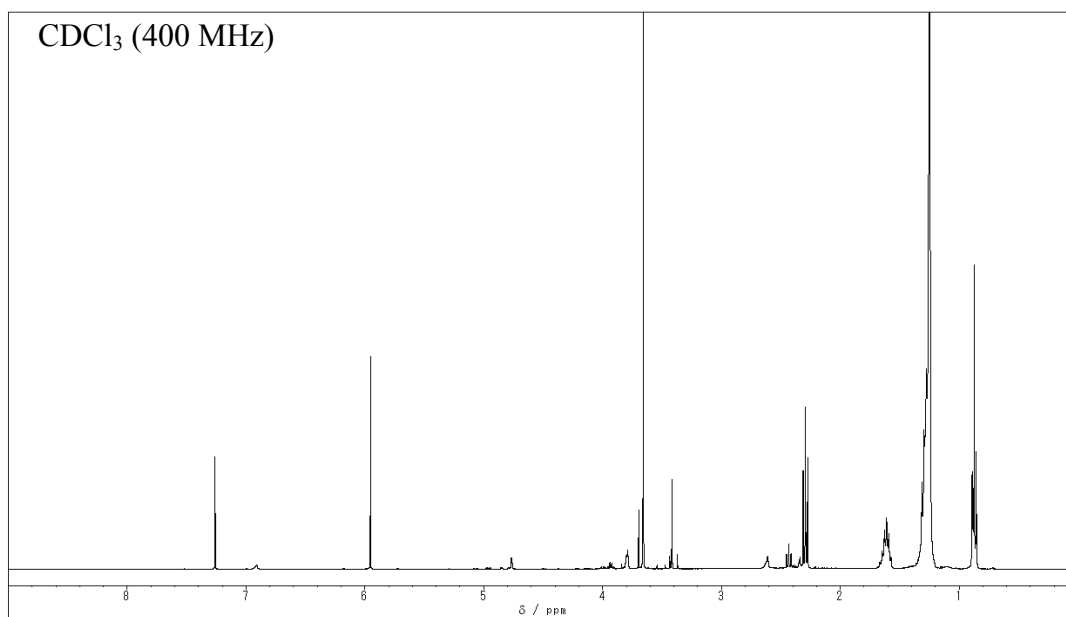
Methyl 3-*O*-palmitoyl- α -L-fucopyranoside (**3u**)

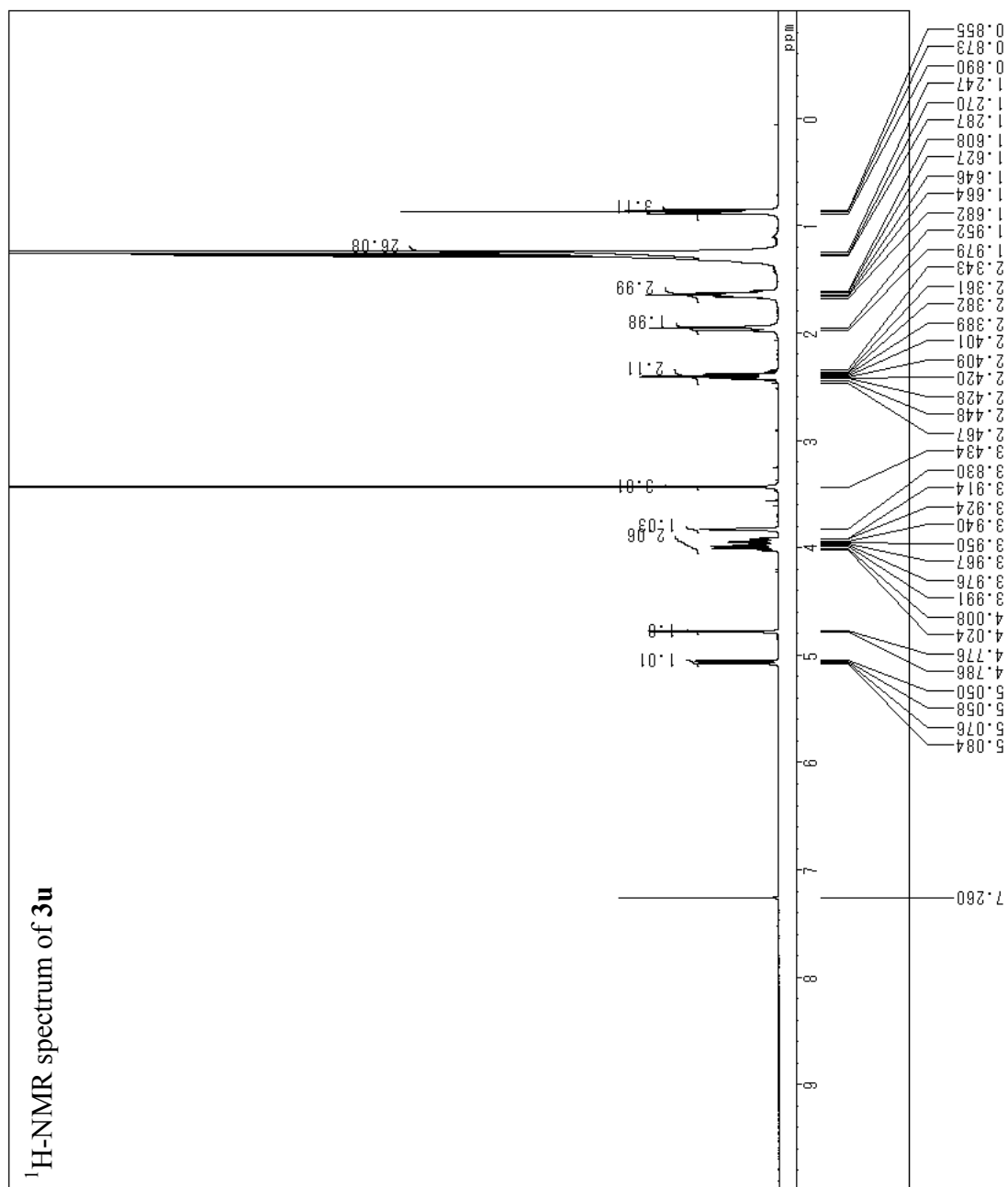


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



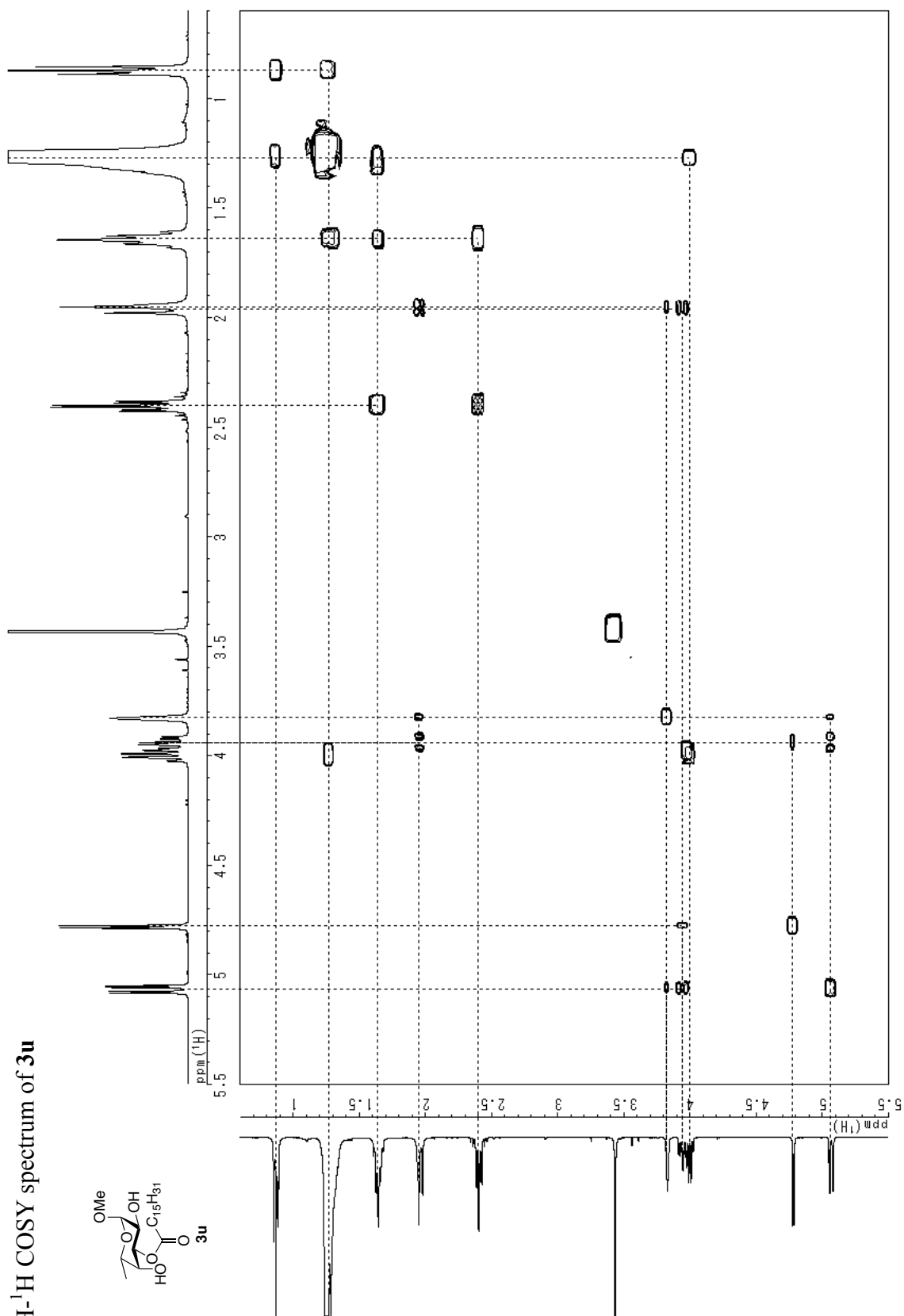
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

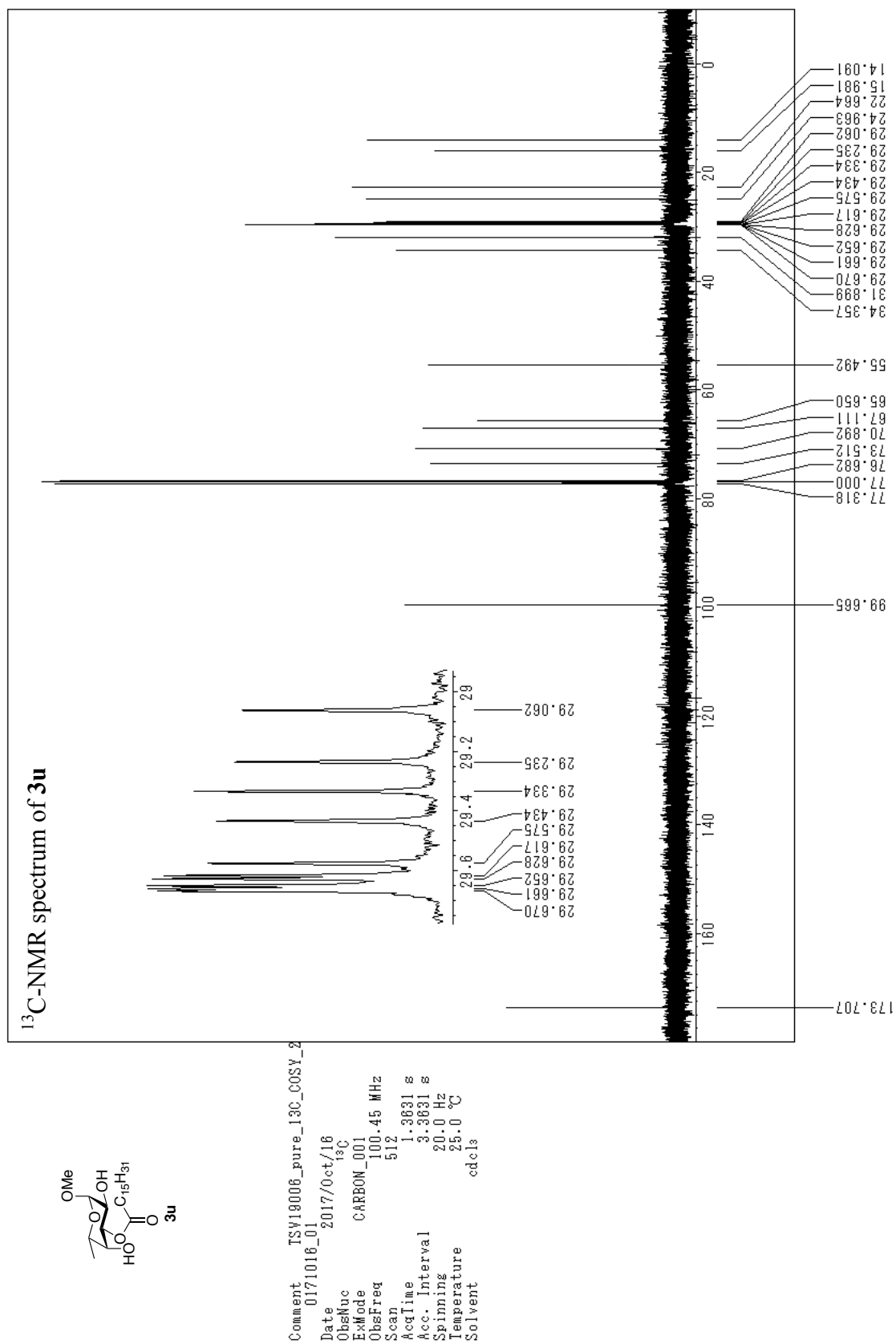




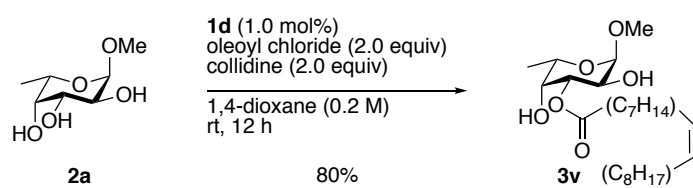
Comment TSV19006_pure_13C_COSY_2
 0171016_01
 Date 2017/0ct/18
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.569 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **3u**

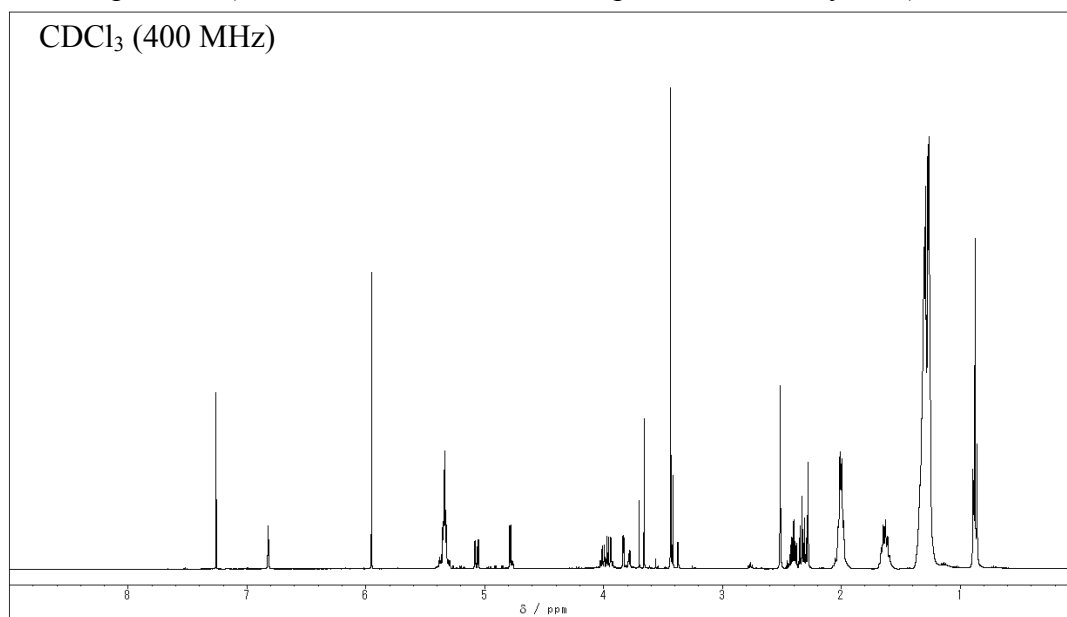




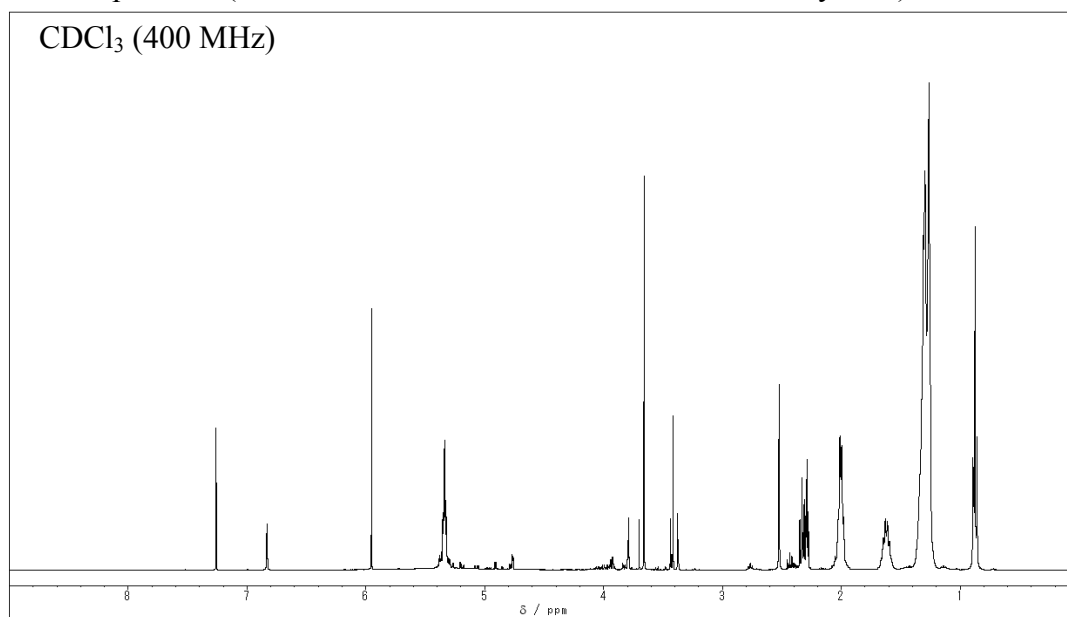
Methyl 3-*O*-oleoyl- α -L-fucopyranoside (**3v**)

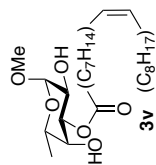


¹H-NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

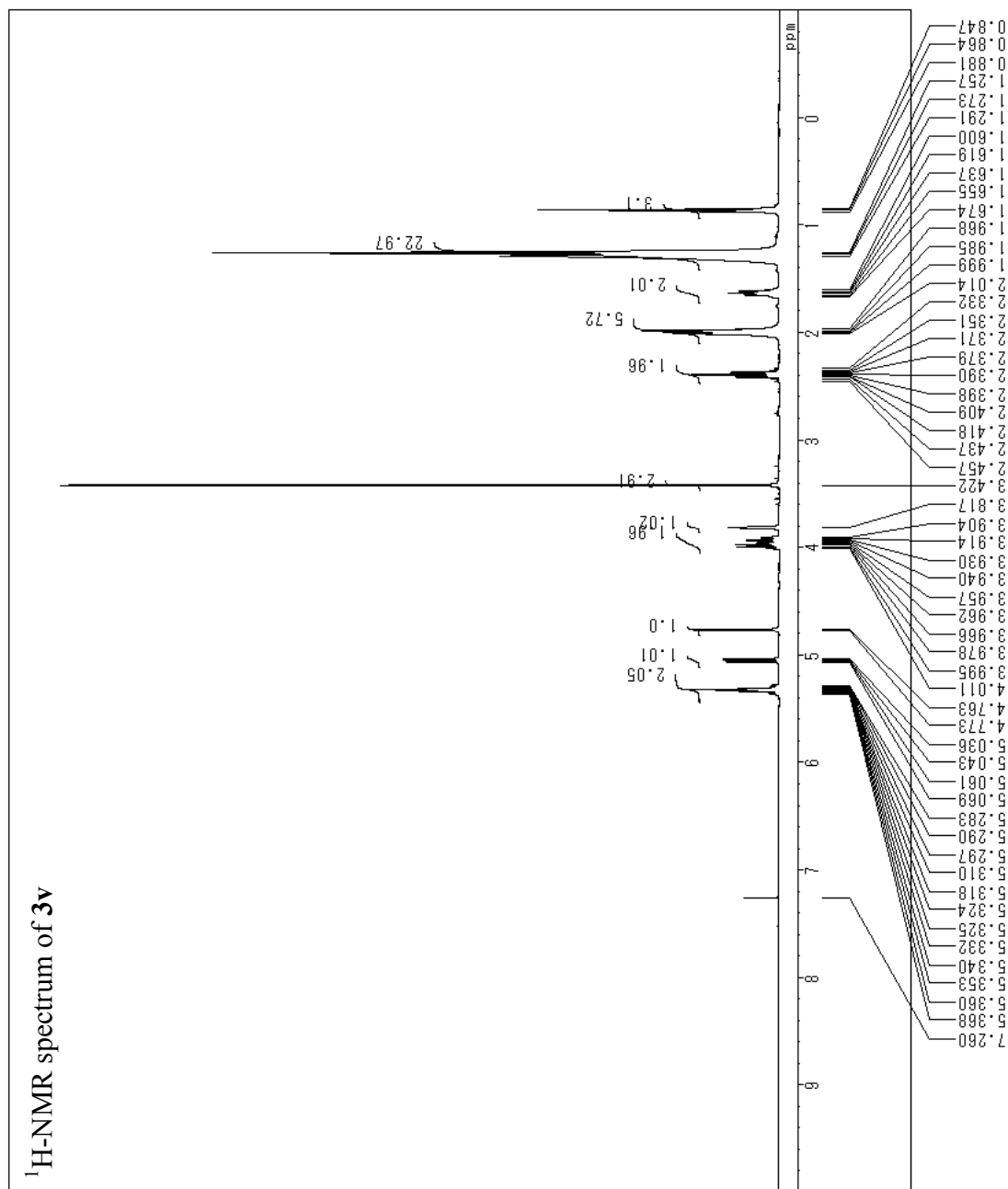


¹H-NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



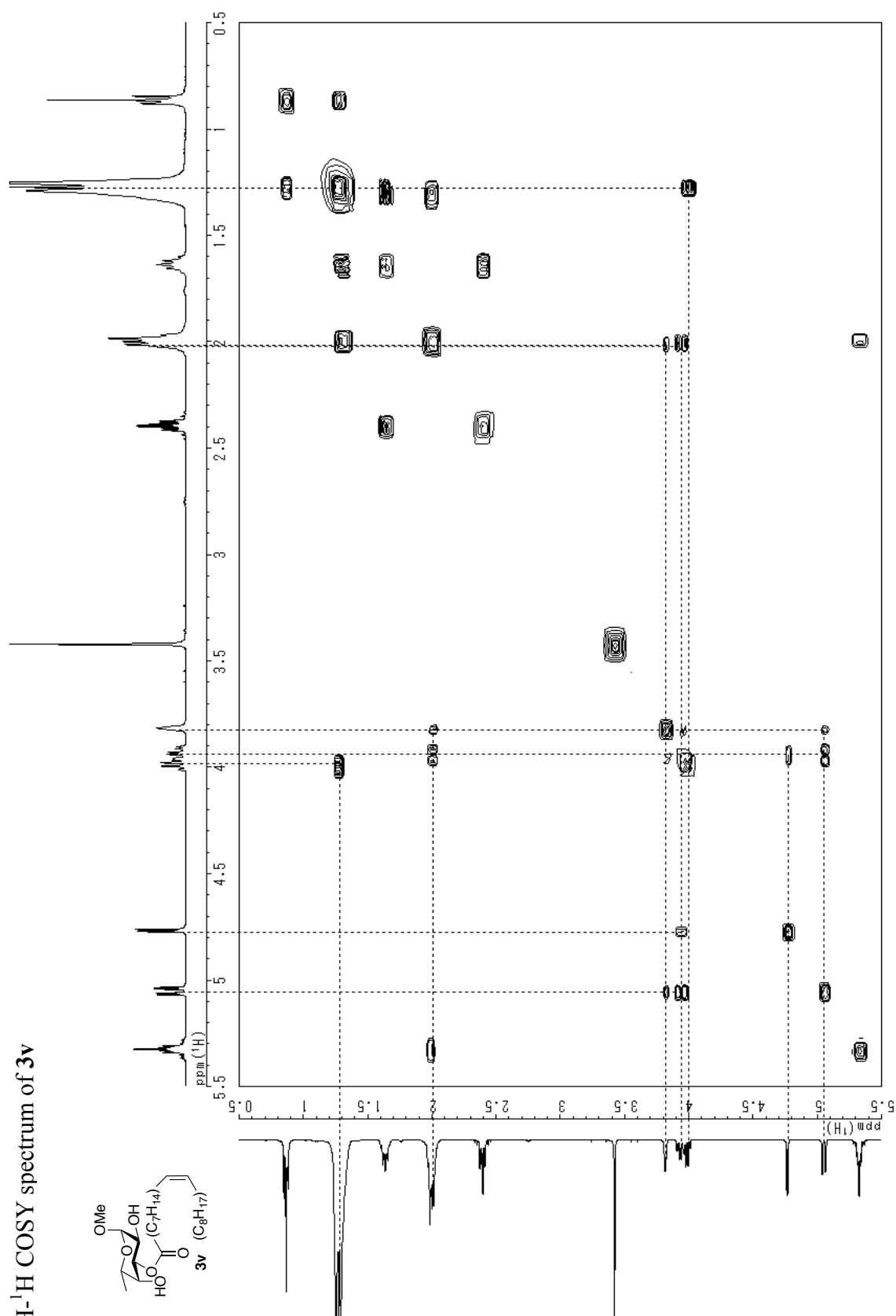


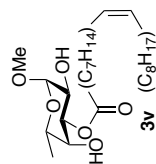
¹H-NMR spectrum of **3v**



Comment TSV25031_column2_13C_COSY
 Date y_20190213_01
 Date 2019/Feb/13
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 400.27 MHz
 Scan 16
 AcqTime 2.5559 s
 Acc. Interval 5.5559 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

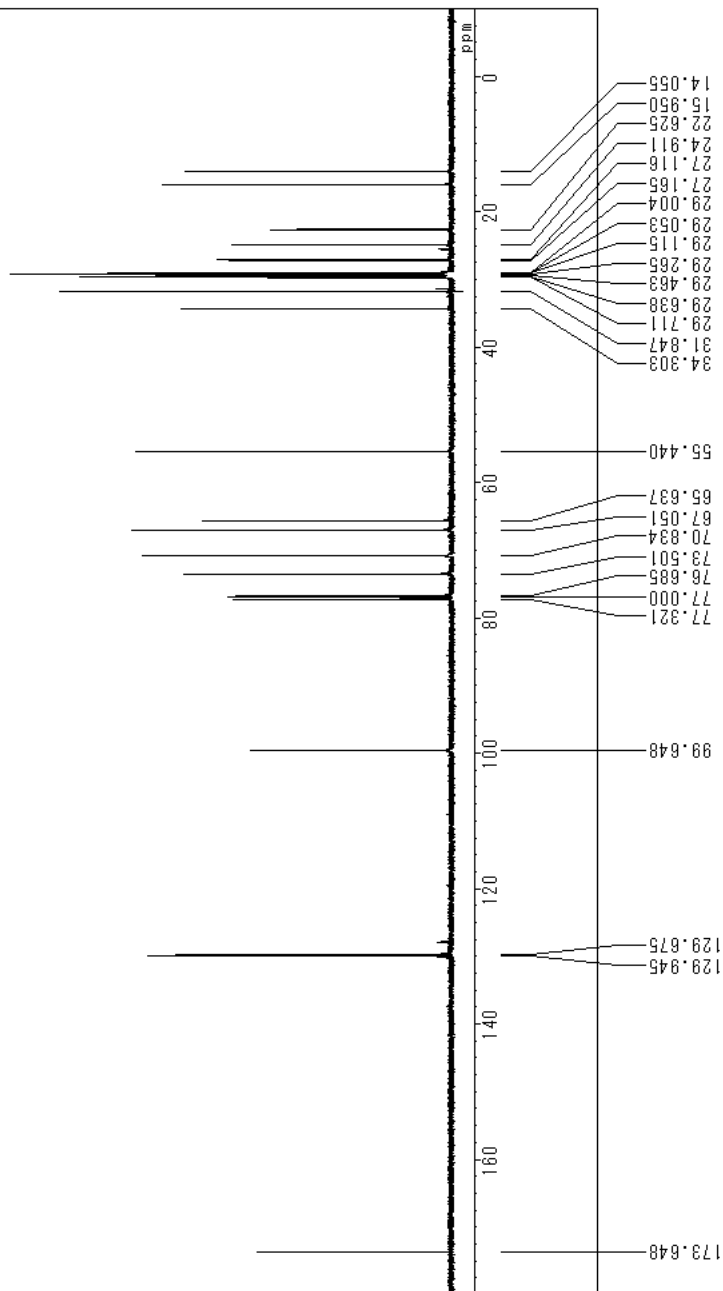
^1H - ^1H COSY spectrum of **3v**



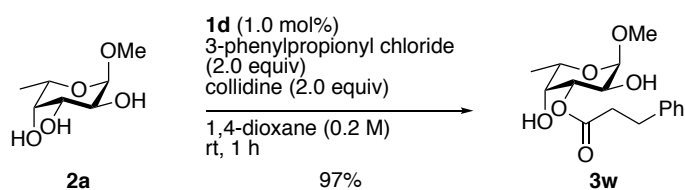


¹³C-NMR spectrum of **3v**

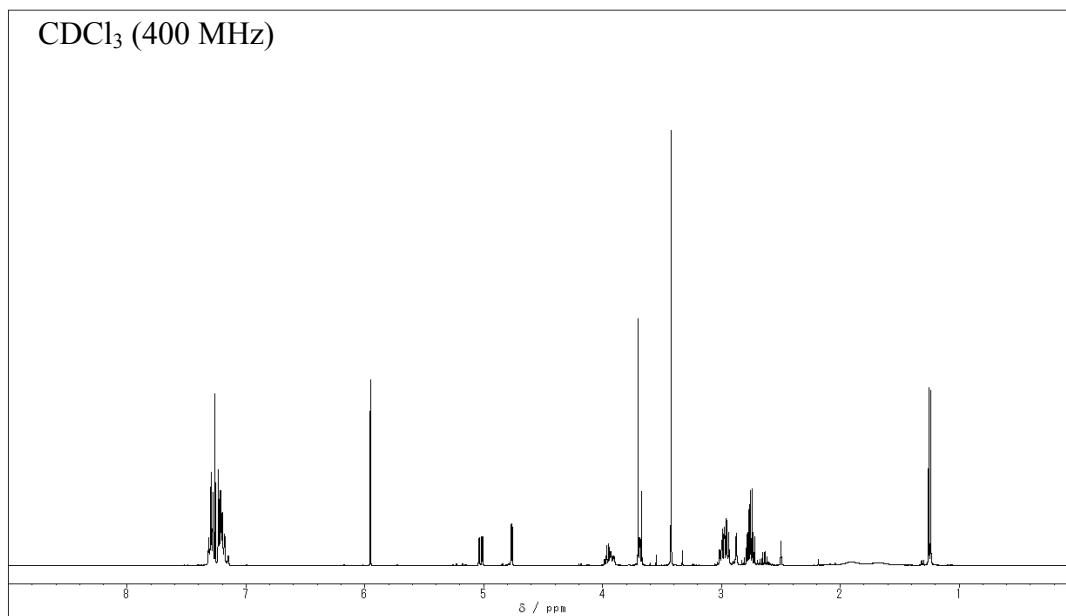
Comment TSV25031_column2_13C_COSY
 Date 20190213_01
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl3



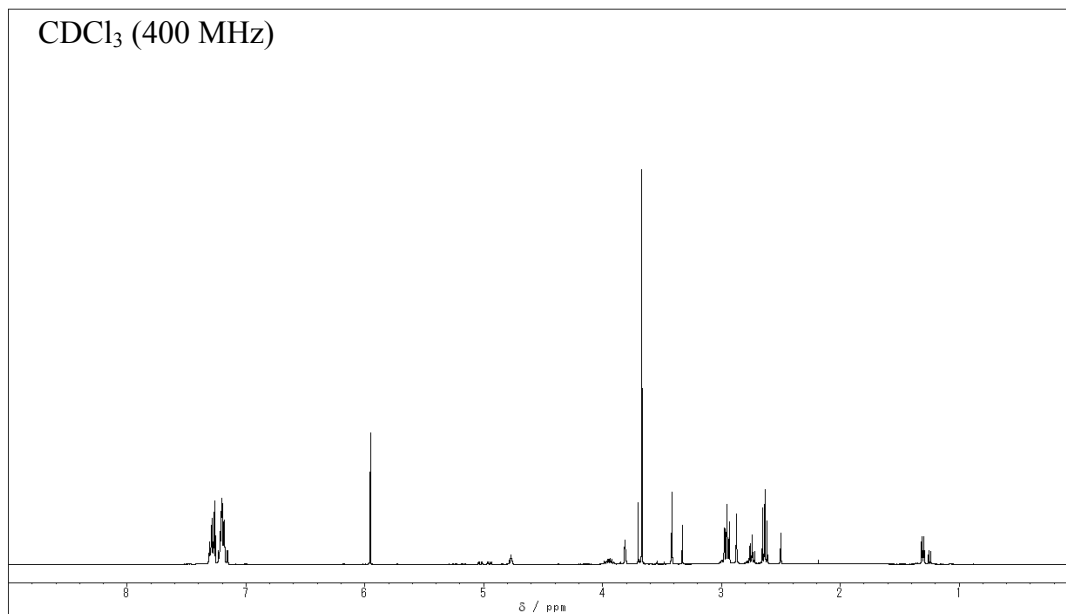
Methyl 3-*O*-3-phenylpropionyl- α -L-fucopyranoside (**3w**)

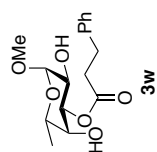


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



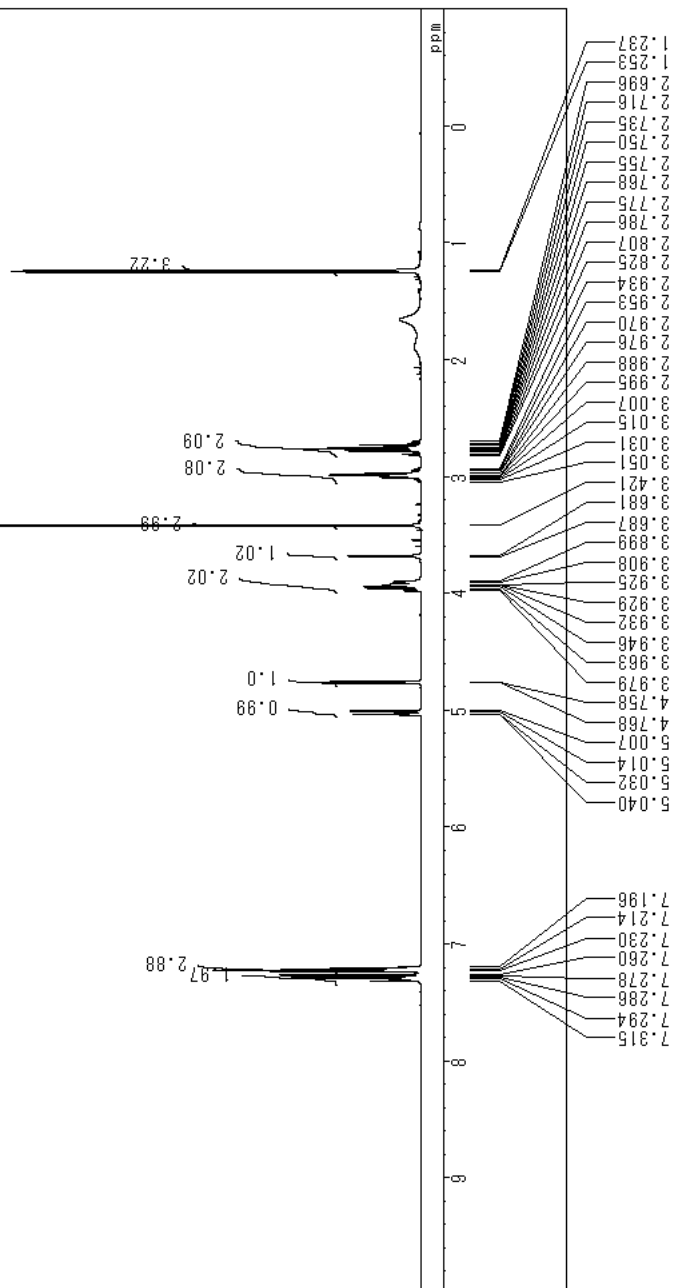
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



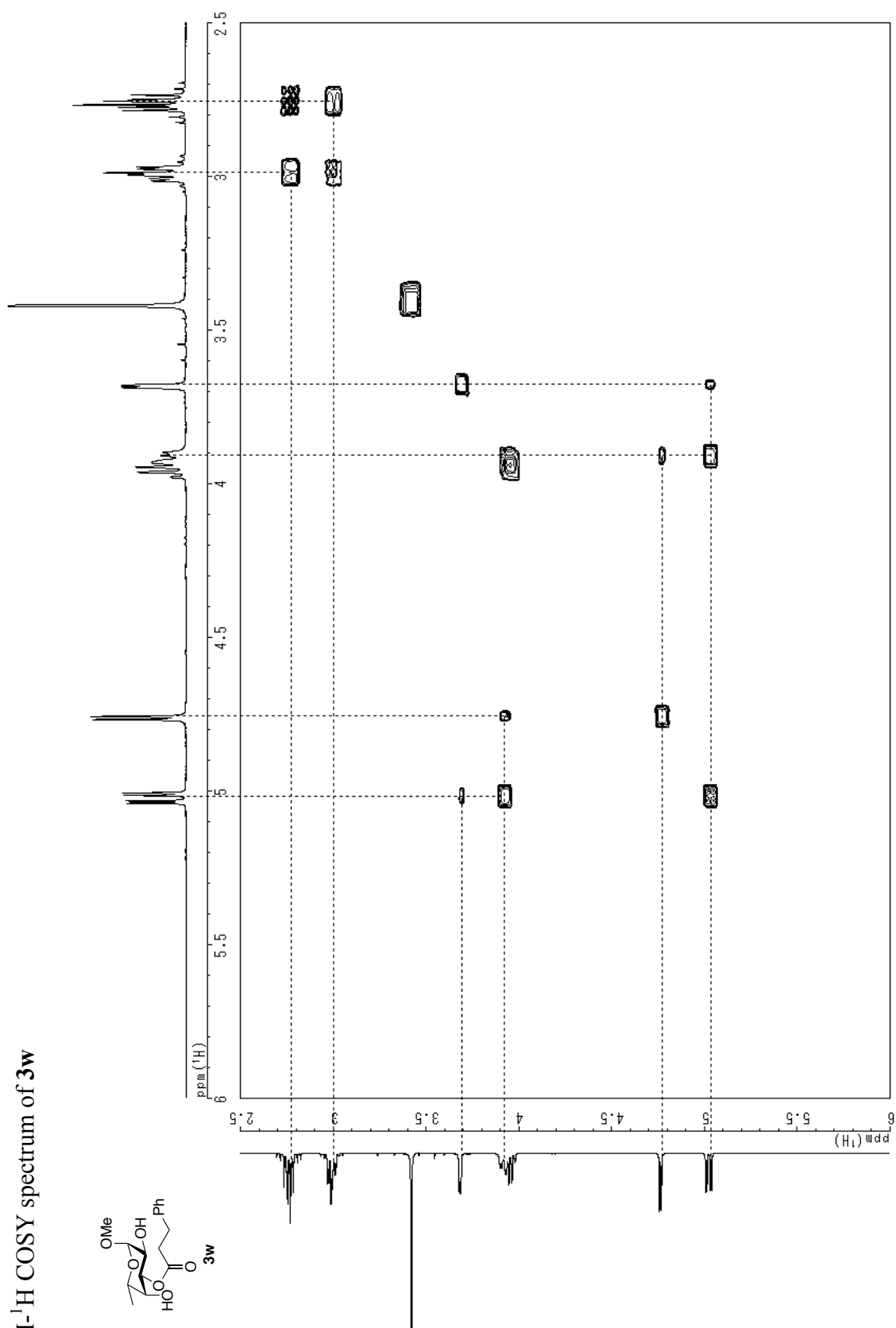


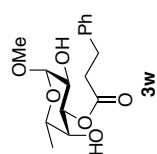
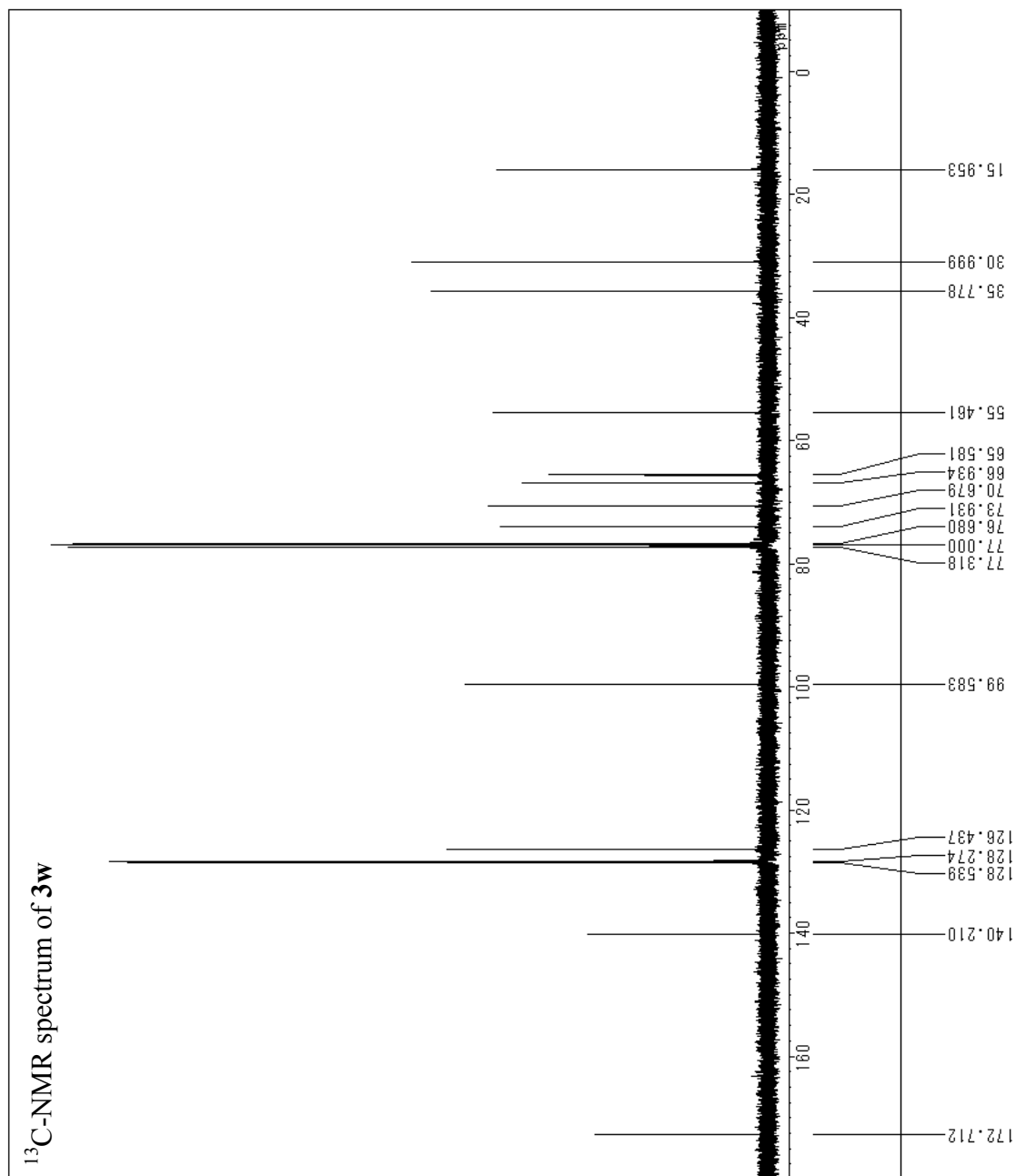
¹H-NMR spectrum of **3w**

Comment TSV17039_pure_13C_COSY_2
 Date_20170824_01
 Date_2017/Sep/24
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



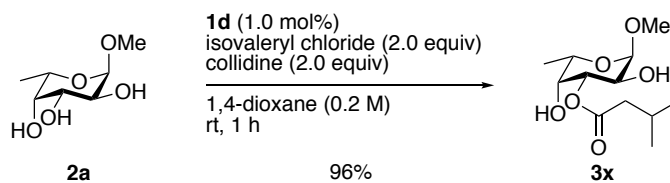
^1H - ^1H COSY spectrum of **3w**



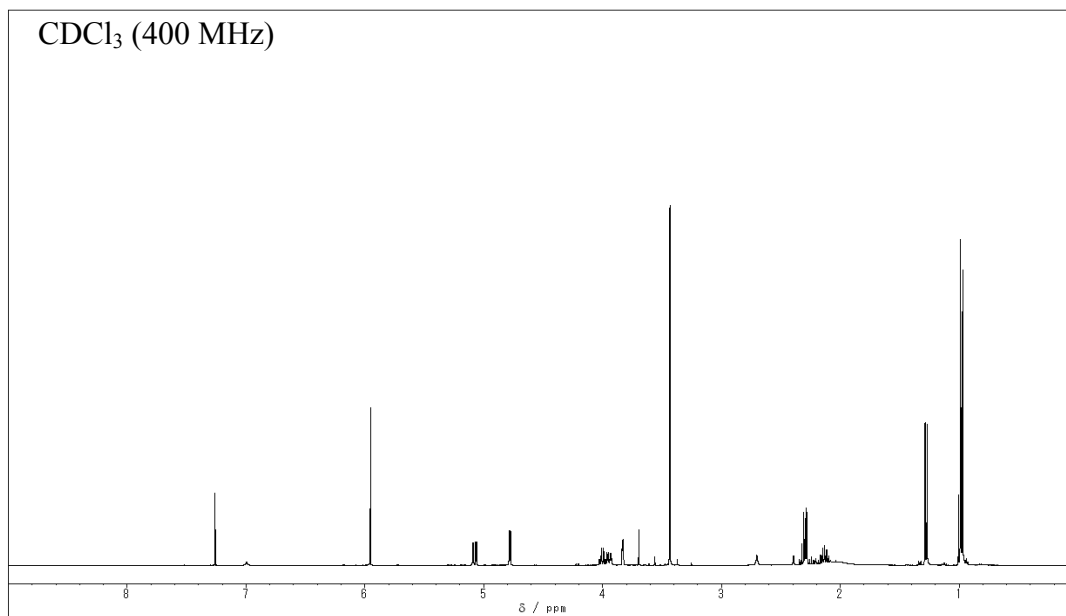


Comment TSV17039_pure_13C_COSY_2
 Date_20170824_01
 Date_2017/Sep/24
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

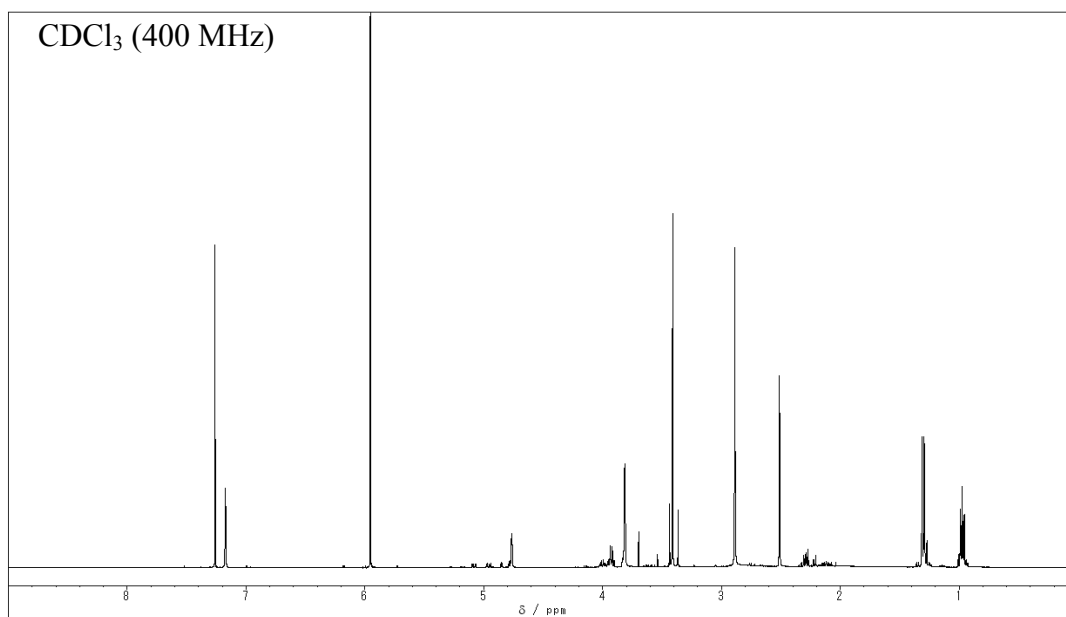
Methyl 3-*O*-isovaleryl- α -L-fucopyranoside (**3x**)

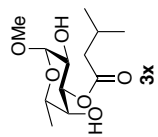


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

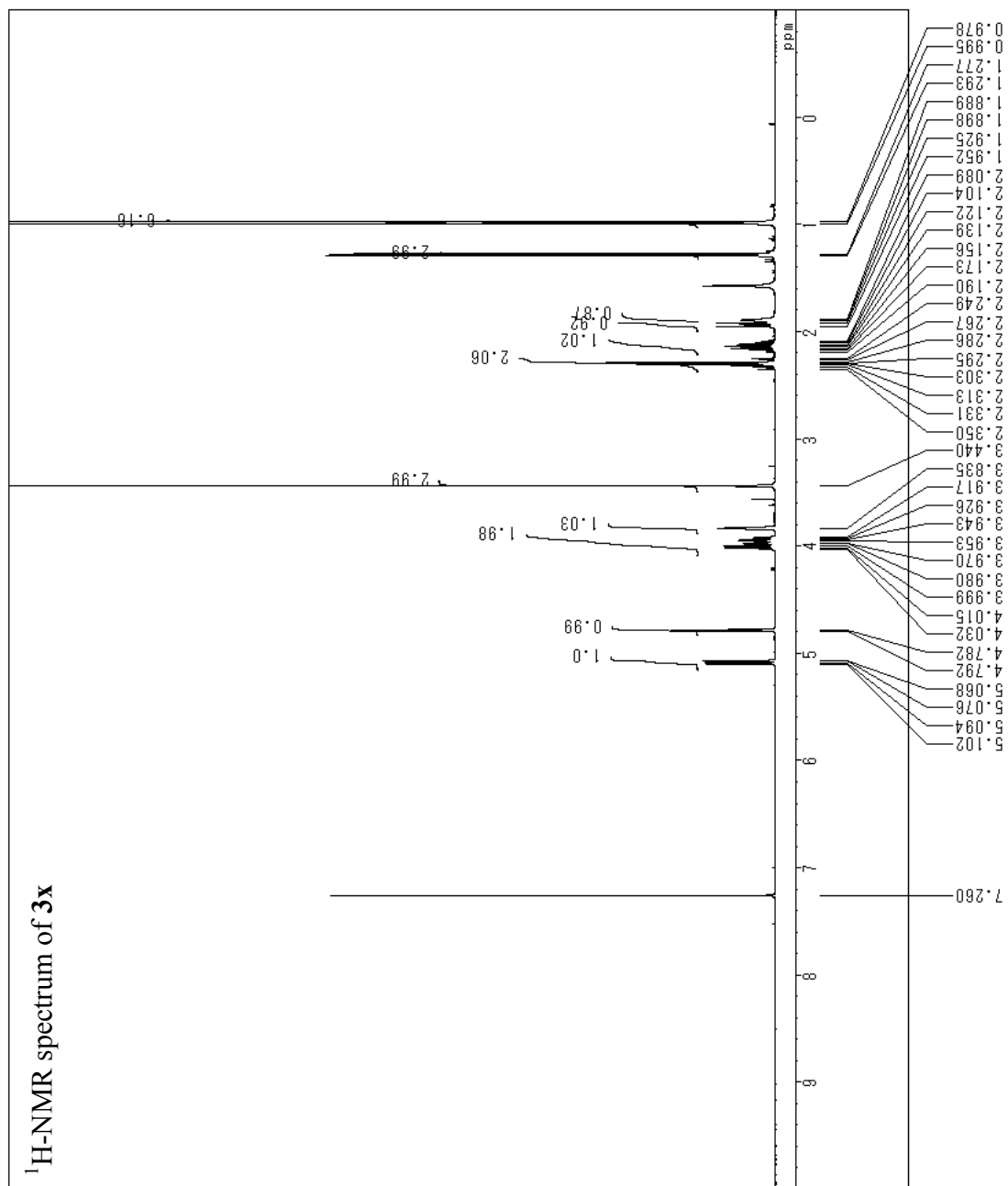


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



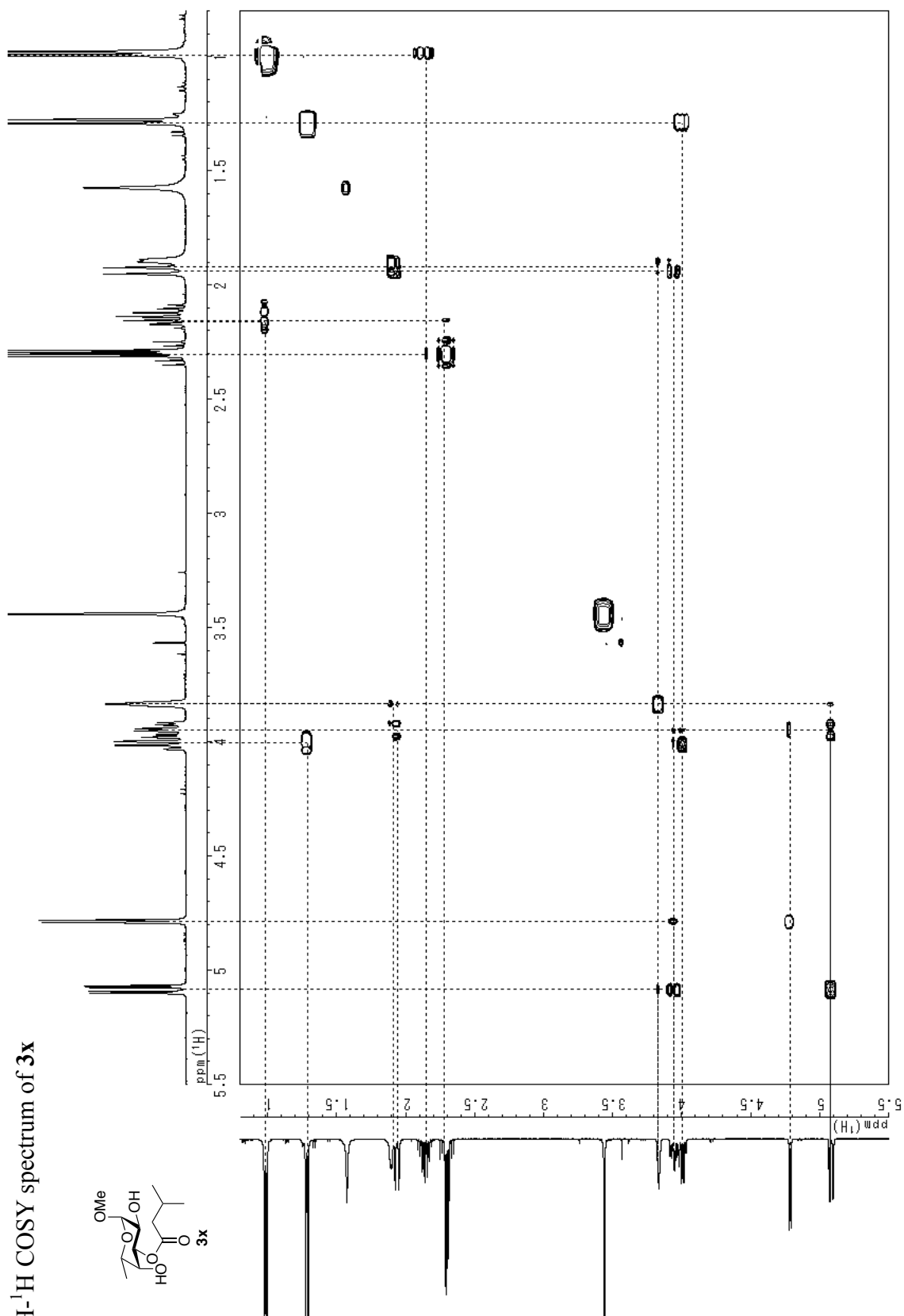


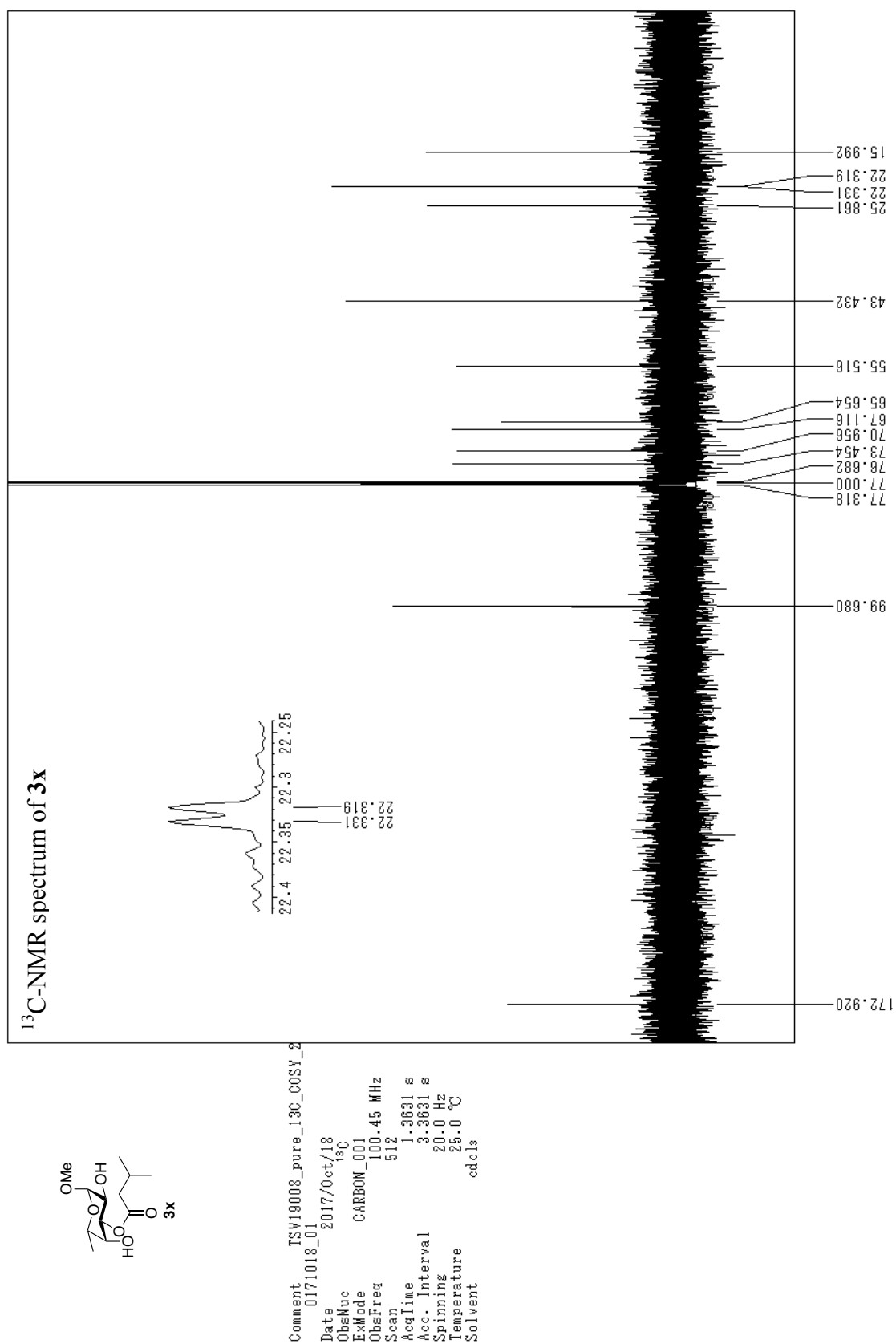
¹H-NMR spectrum of 3x



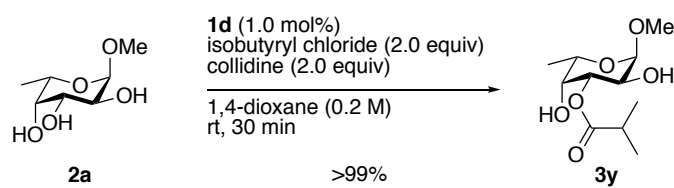
Comment TSV19008_pure_13C_COSY_2
 0171018_01
 Date 2017/Oct/18
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **3x**

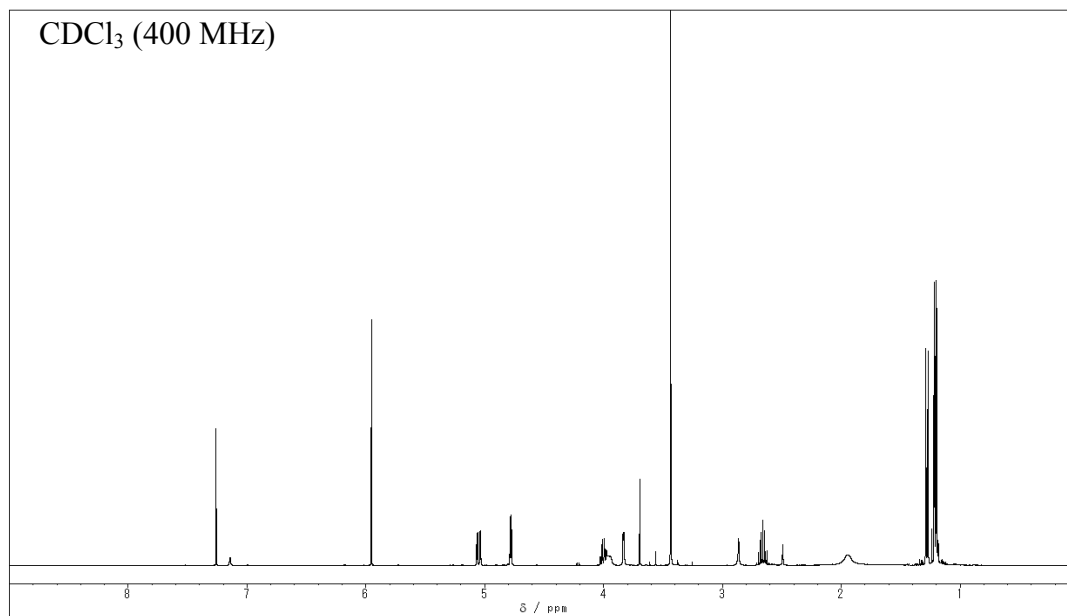




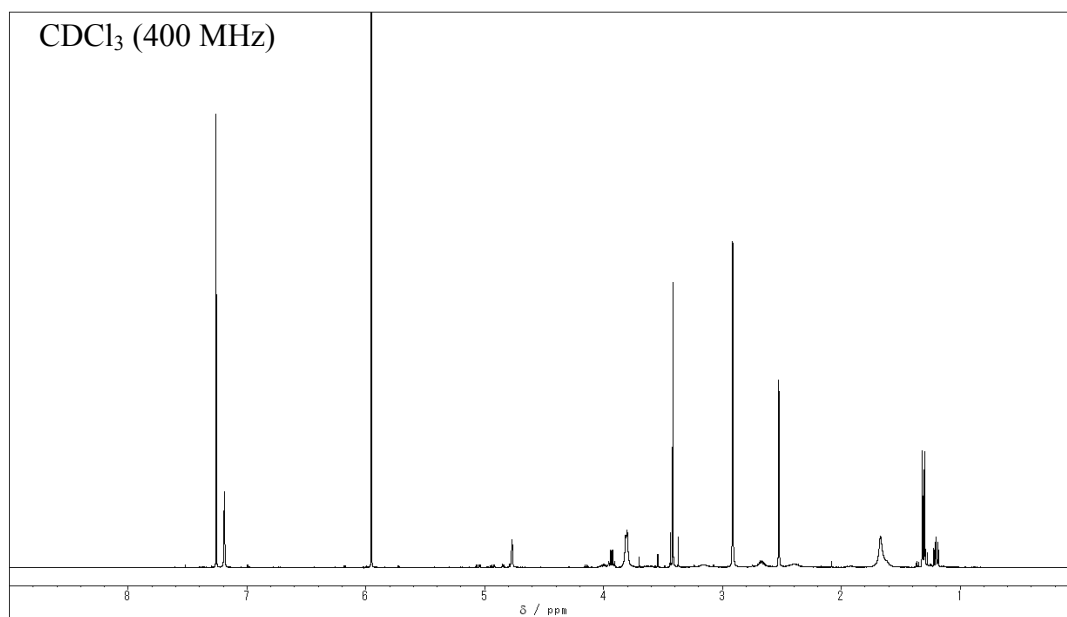
Methyl 3-*O*-isobutyryl- α -L-fucopyranoside (**3y**)

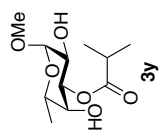


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



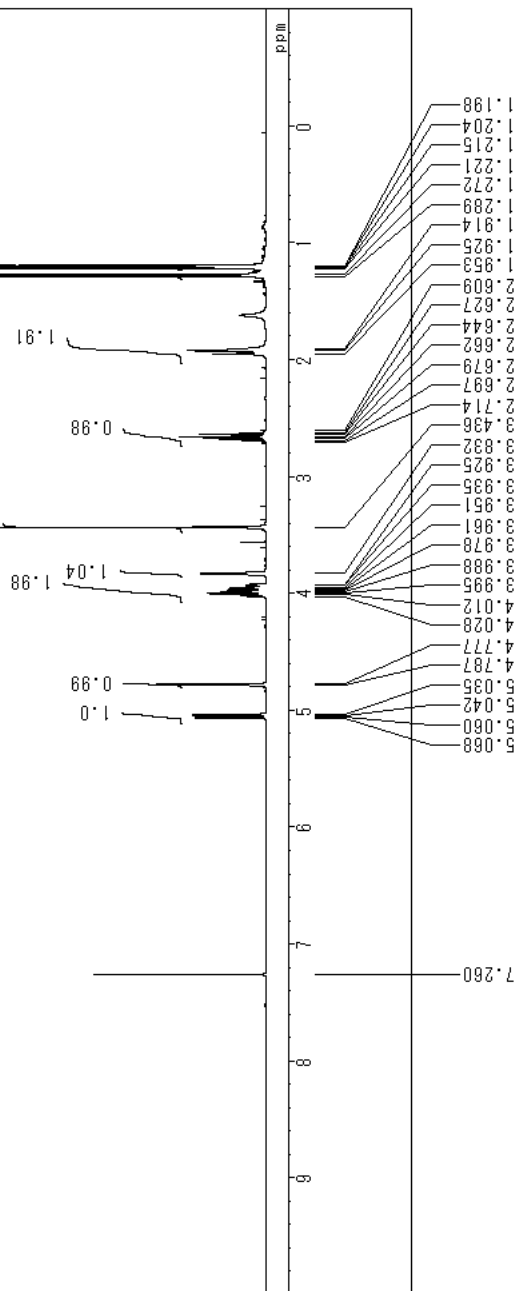
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



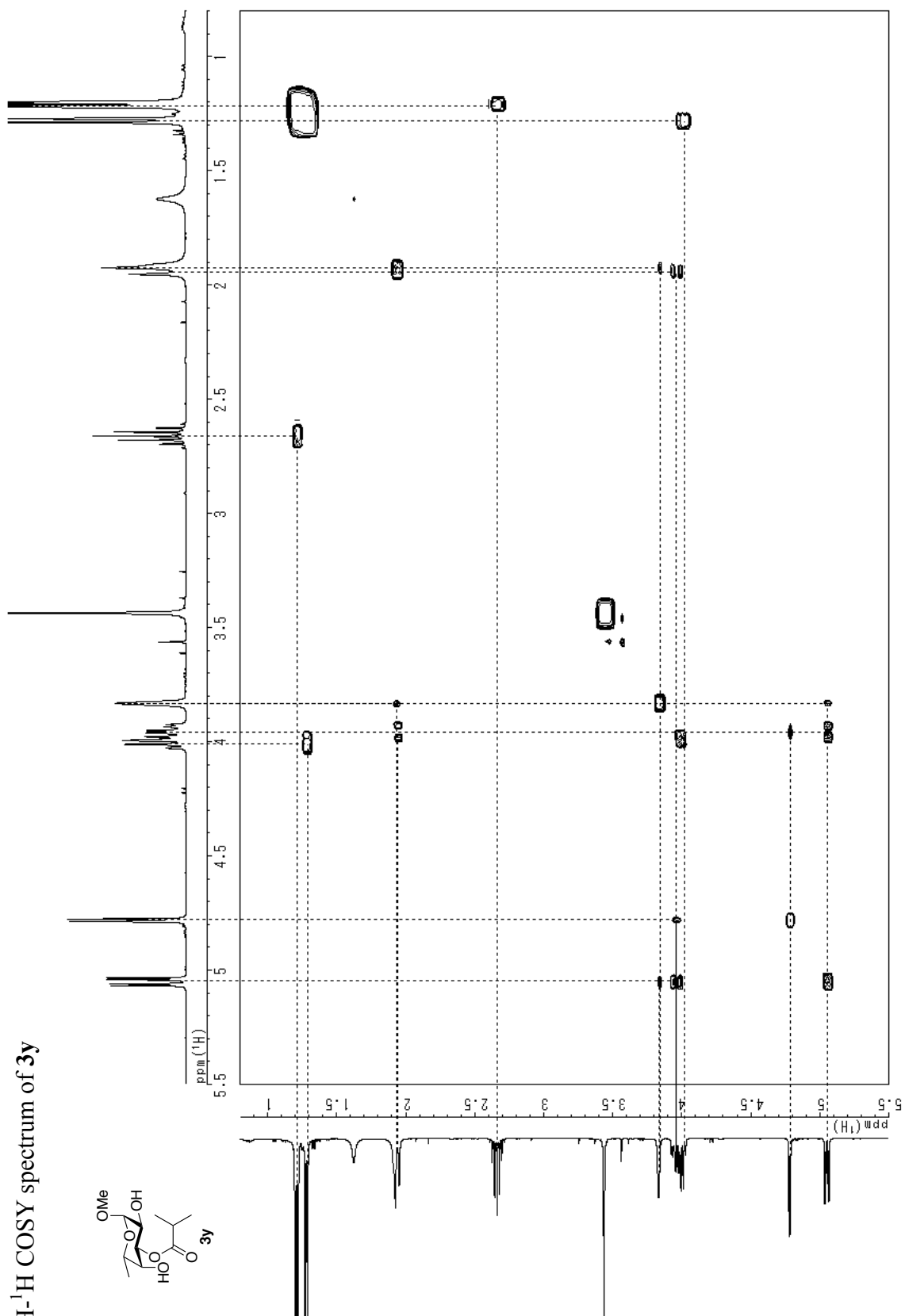


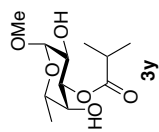
¹H-NMR spectrum of **3y**

Comment TSV19010_pure_13C_COSY_2
 0171017_01
 Date 2017/Oct/17
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 400.27 MHz
 Scan 16
 AcqTime 2.5559 s
 Acc. Interval 5.5559 s
 Spinning 18.0 Hz
 Temperature 25.0 °C

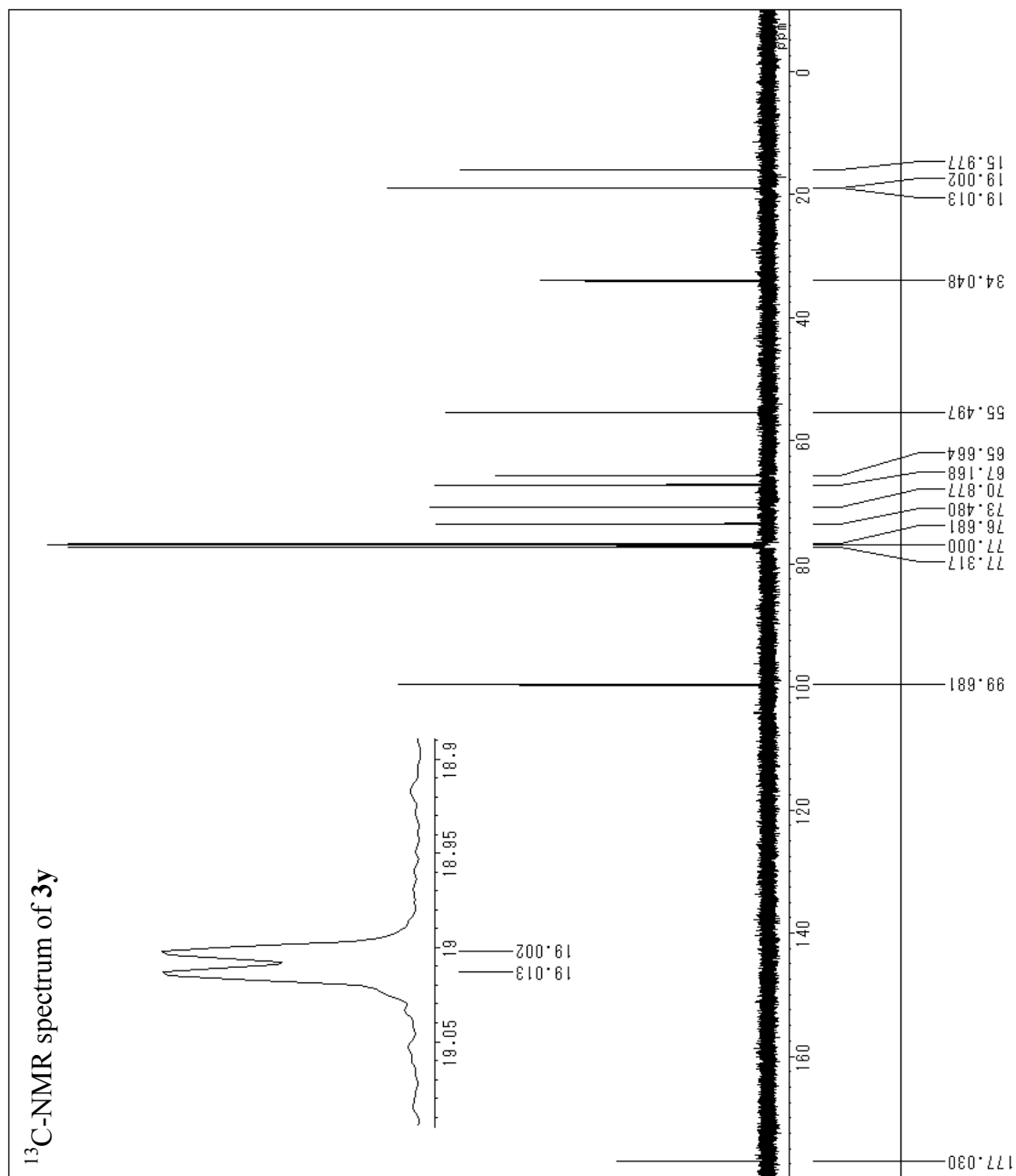


^1H - ^1H COSY spectrum of **3y**



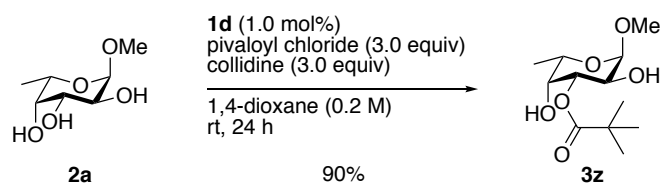


¹³C-NMR spectrum of **3y**

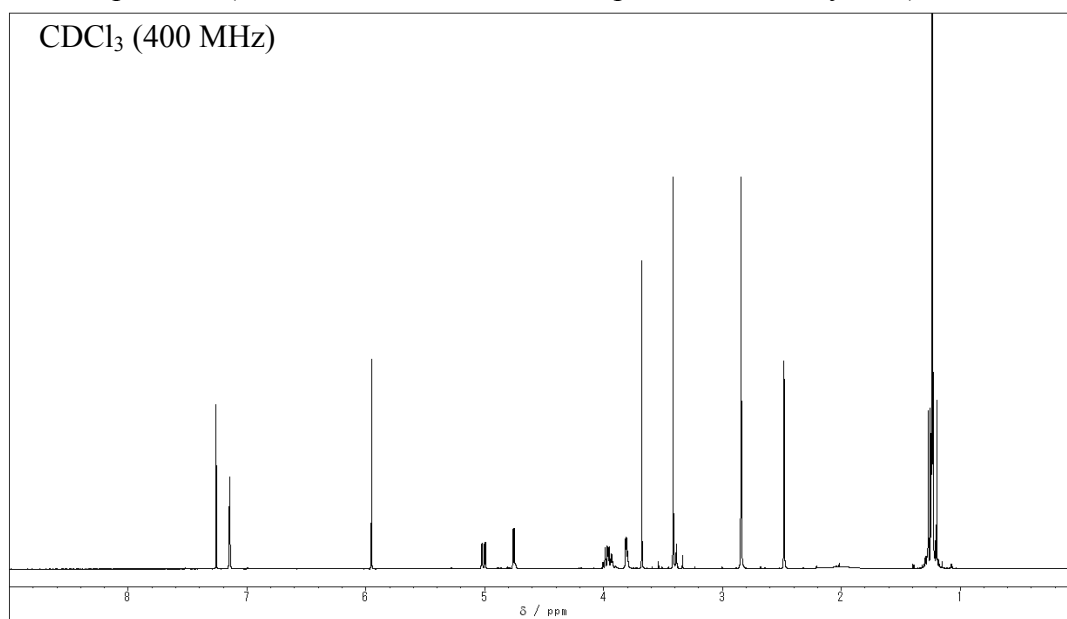


Comment TSV19010_pure_13C_COSY_2
 0171017_01
 Date 2017/Oct/17
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

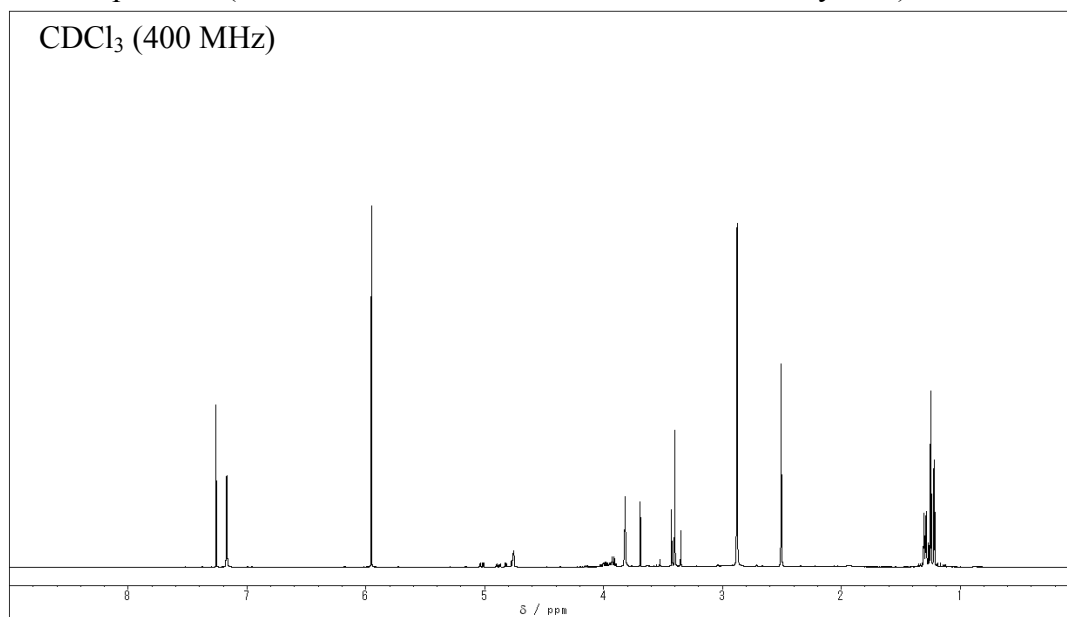
Methyl 3-*O*-pivaloyl- α -L-fucopyranoside (**3z**)

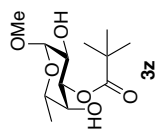


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

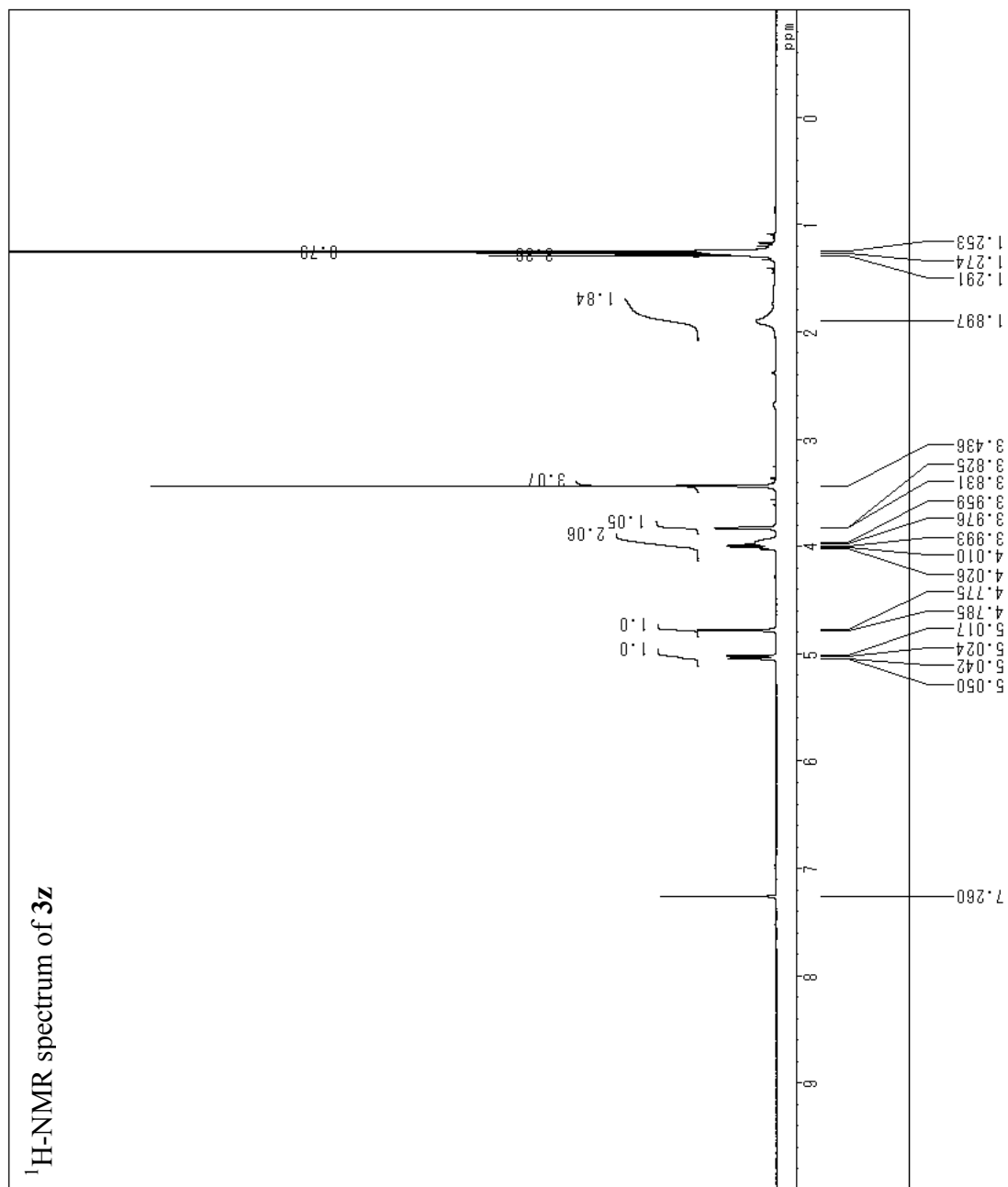


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



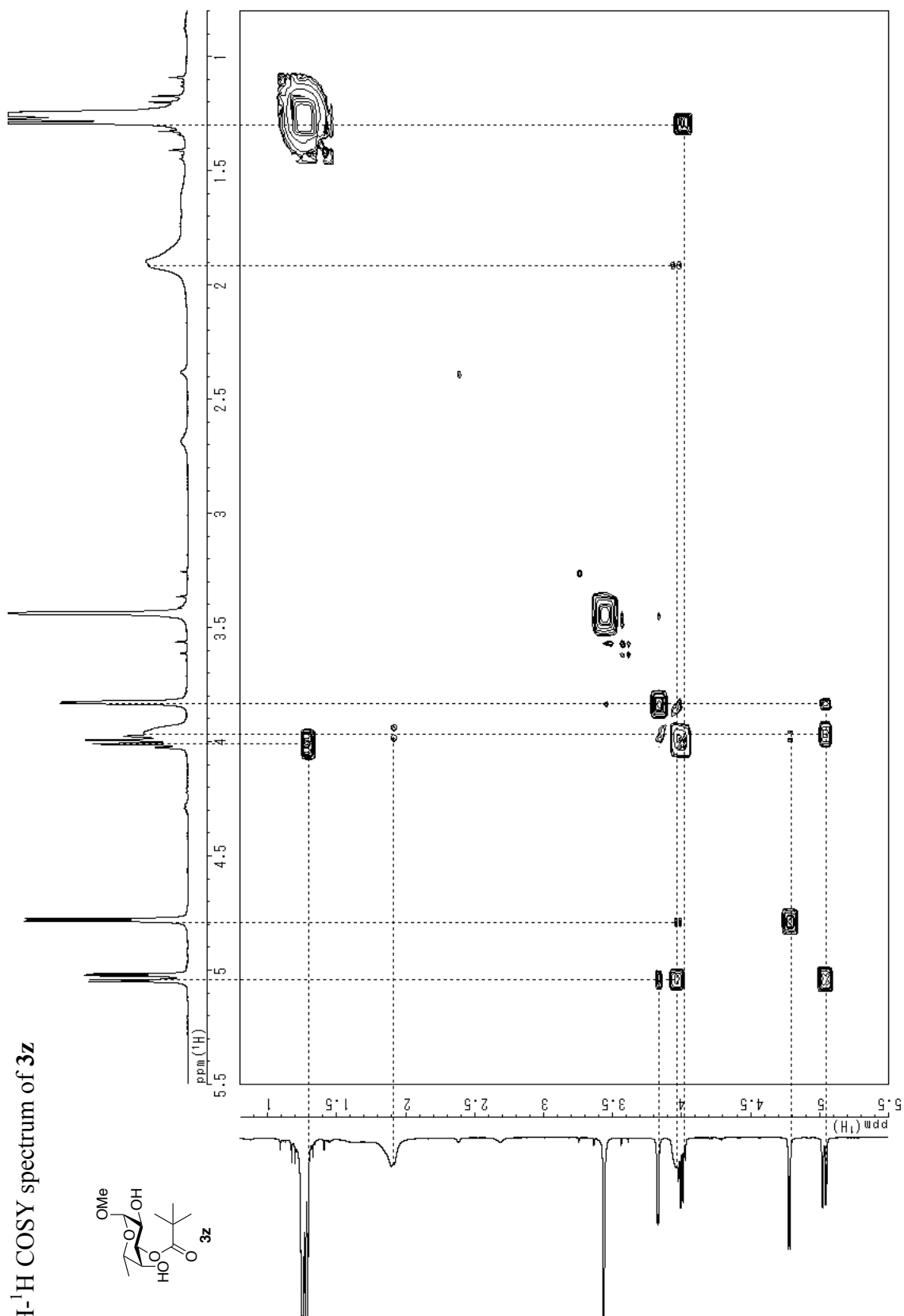


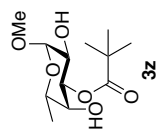
¹H-NMR spectrum of **3z**



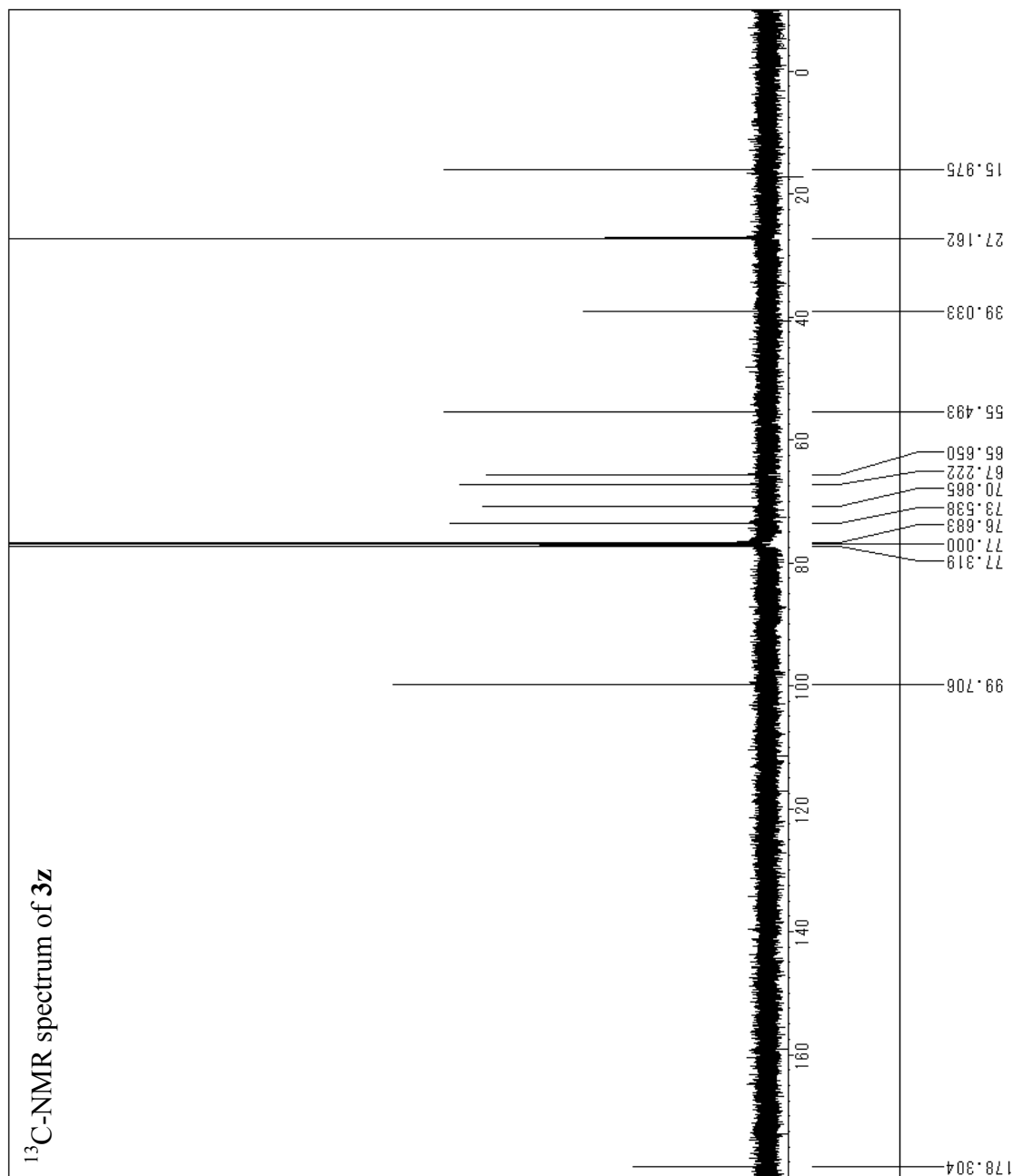
Comment TSV19020_pure_13C_COSY_2
 0171025_01
 Date 2017/Oct/25
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 400.27 MHz
 Scan 16
 AcqTime 2.5559 s
 Acc. Interval 5.5559 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **3z**



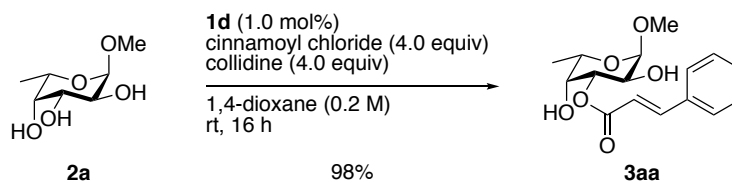


¹³C-NMR spectrum of 3z

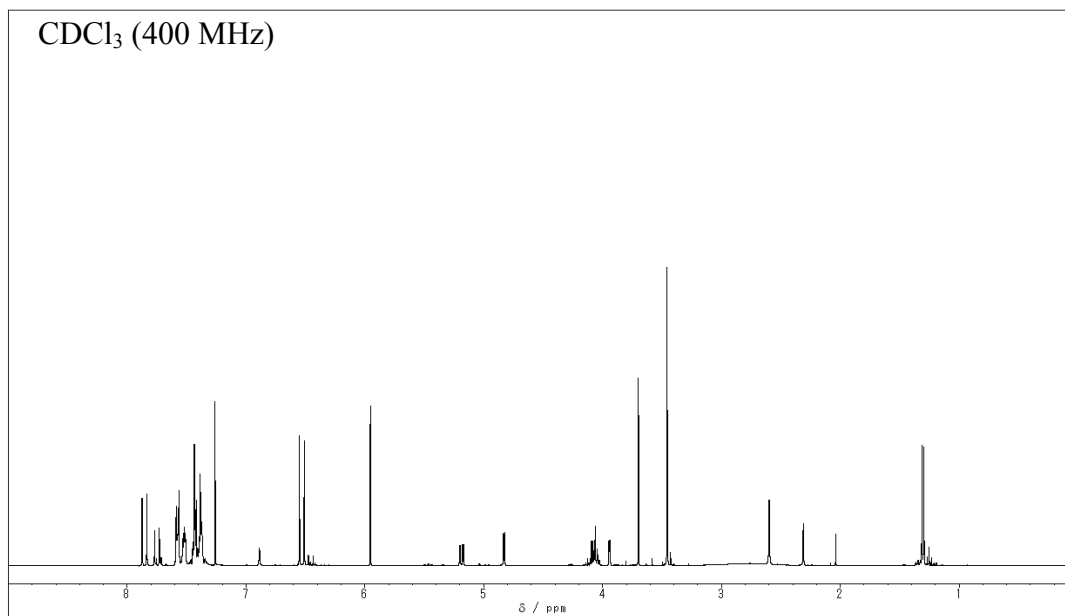


Comment TSV19020_pure_13C_COSY_2
 0171025_01
 Date 2017/Oct/25
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

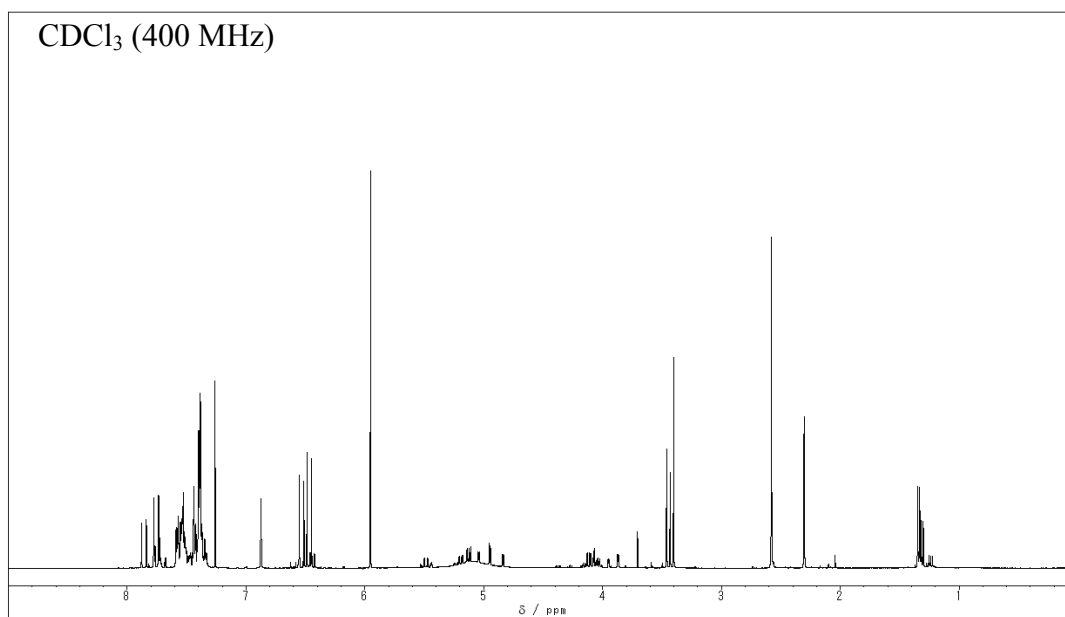
Methyl 3-*O*-cinnamoyl- α -L-fucopyranoside (**3aa**)

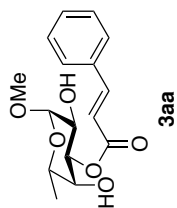


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



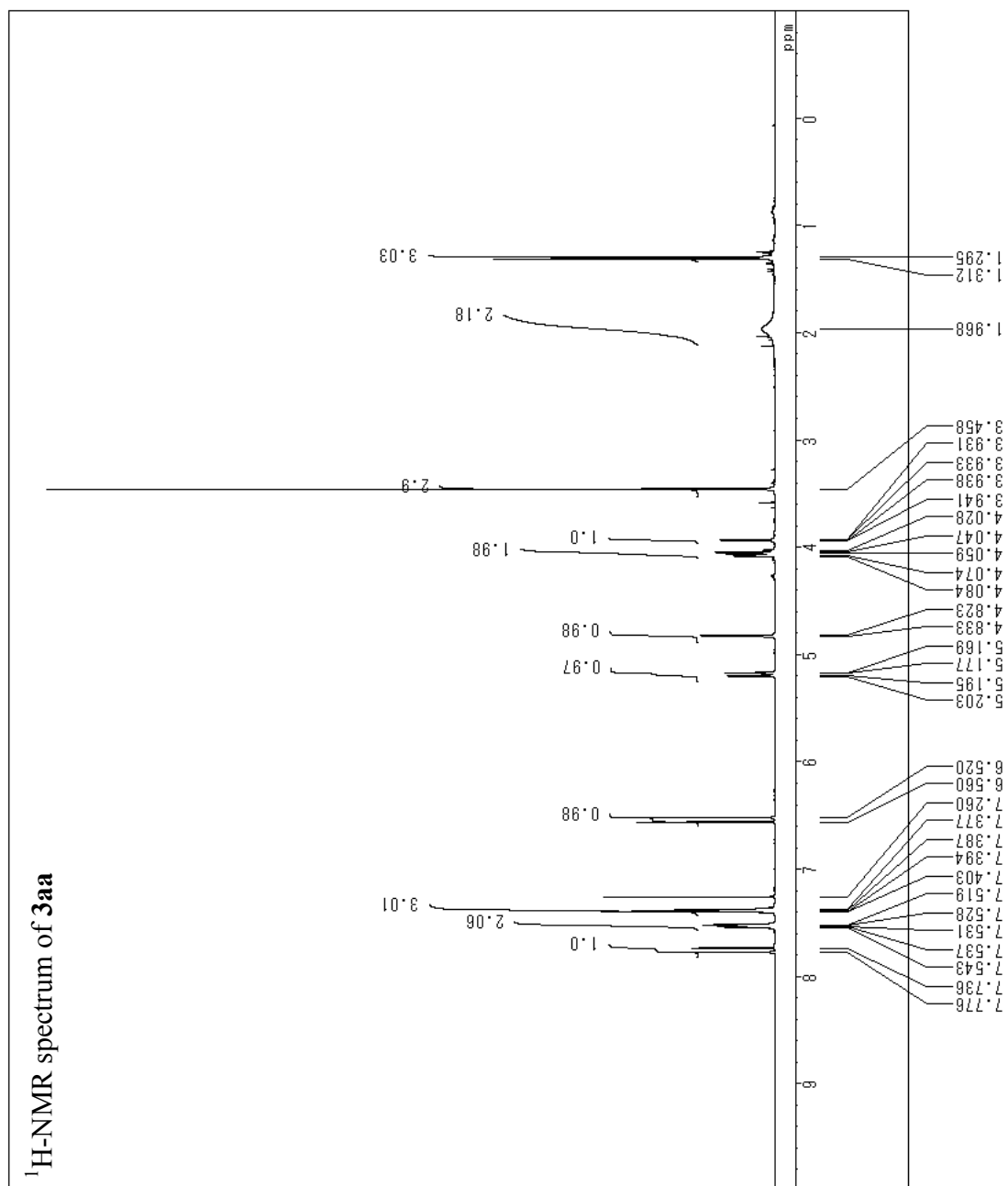
^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)



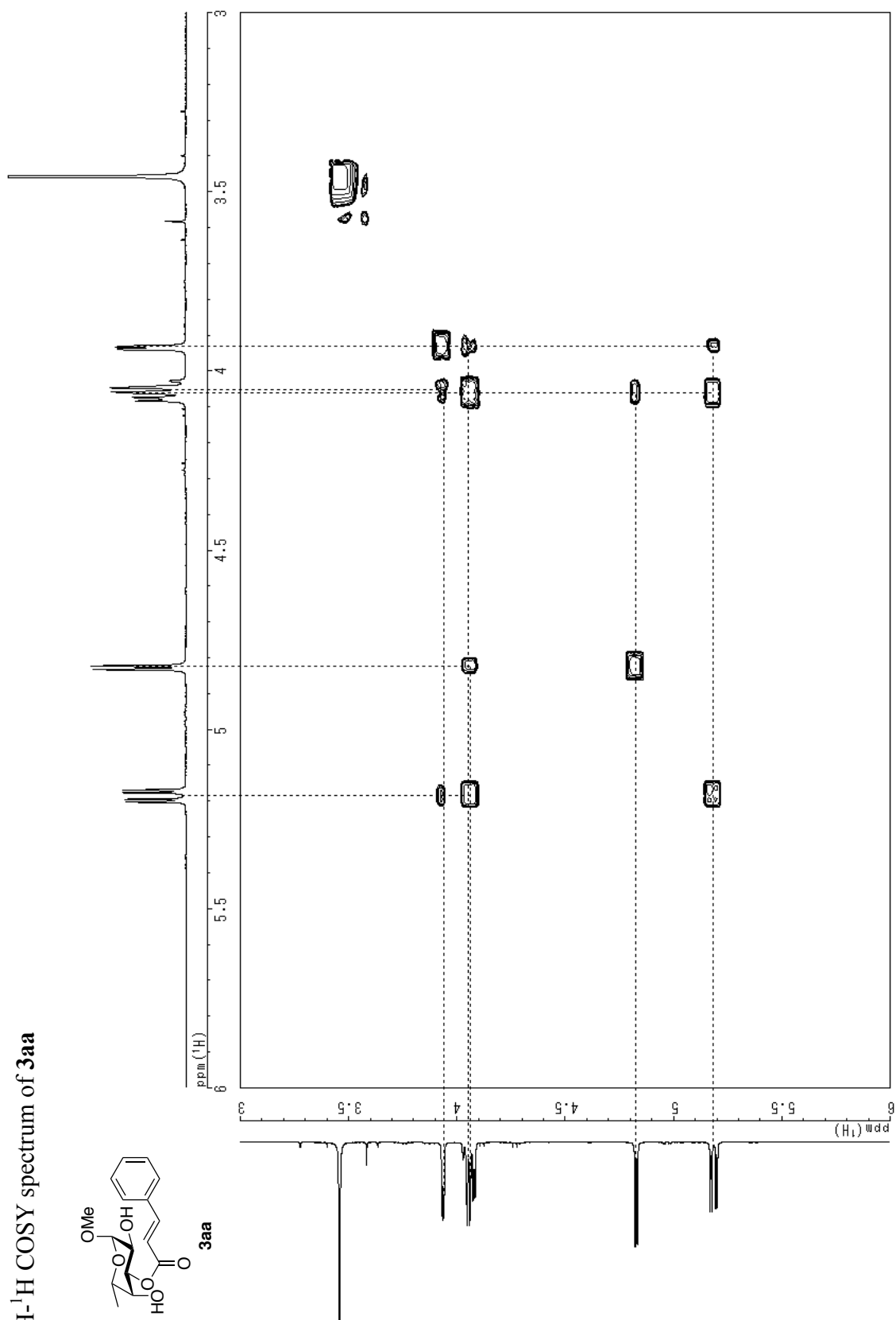


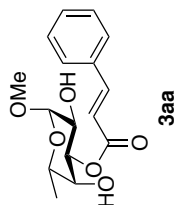
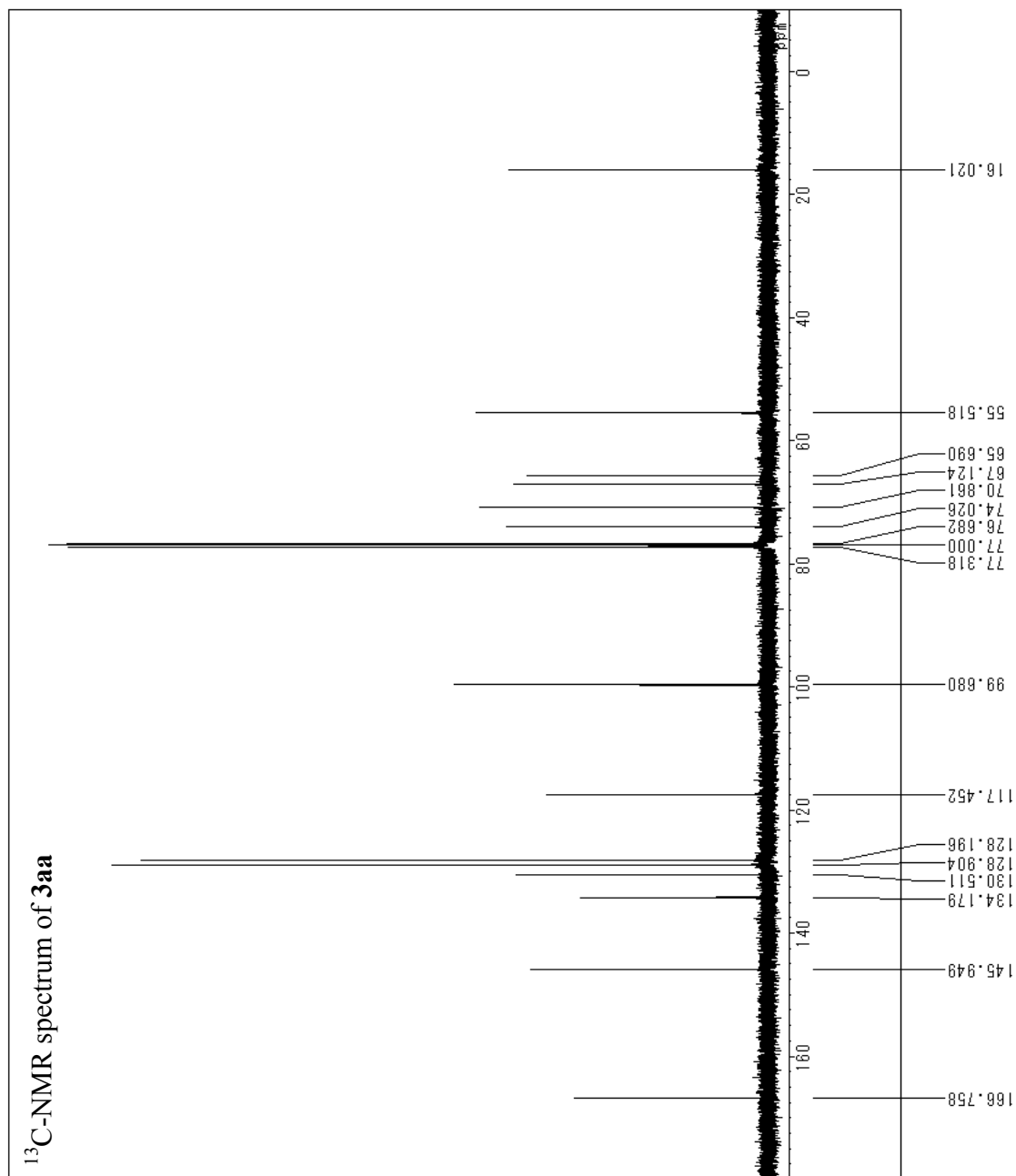
Comment TSV18006_pure_13C_COSY_2
 0170928_01
 Date 2017/Sep/28
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.569 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

¹H-NMR spectrum of **3aa**



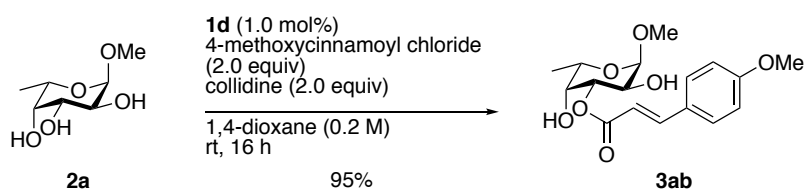
^1H - ^1H COSY spectrum of **3aa**



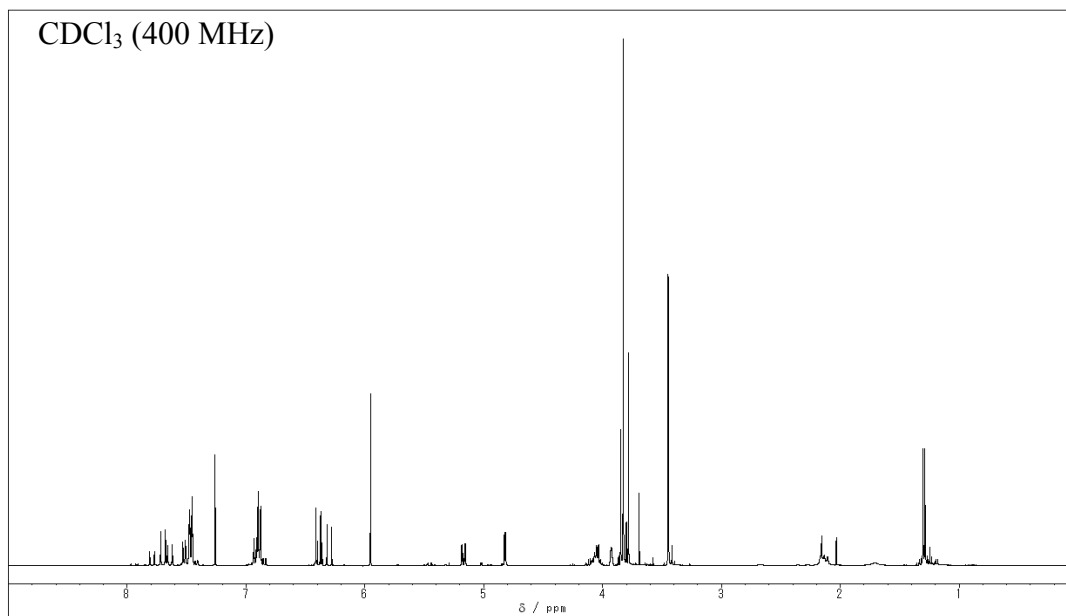


Comment TSV18006_pure_13C_COSY_2
 0170928_01
 Date 2017/Sep/28
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

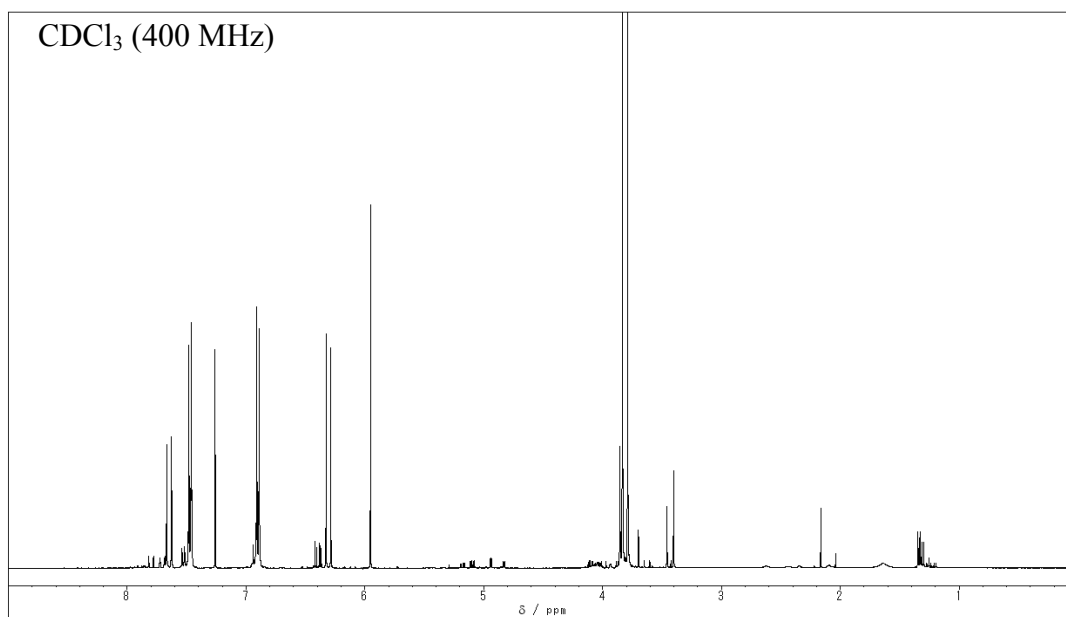
Methyl 3-*O*-4-methoxycinnamoyl- α -L-fucopyranoside (**3ab**)

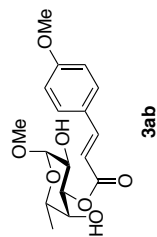


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

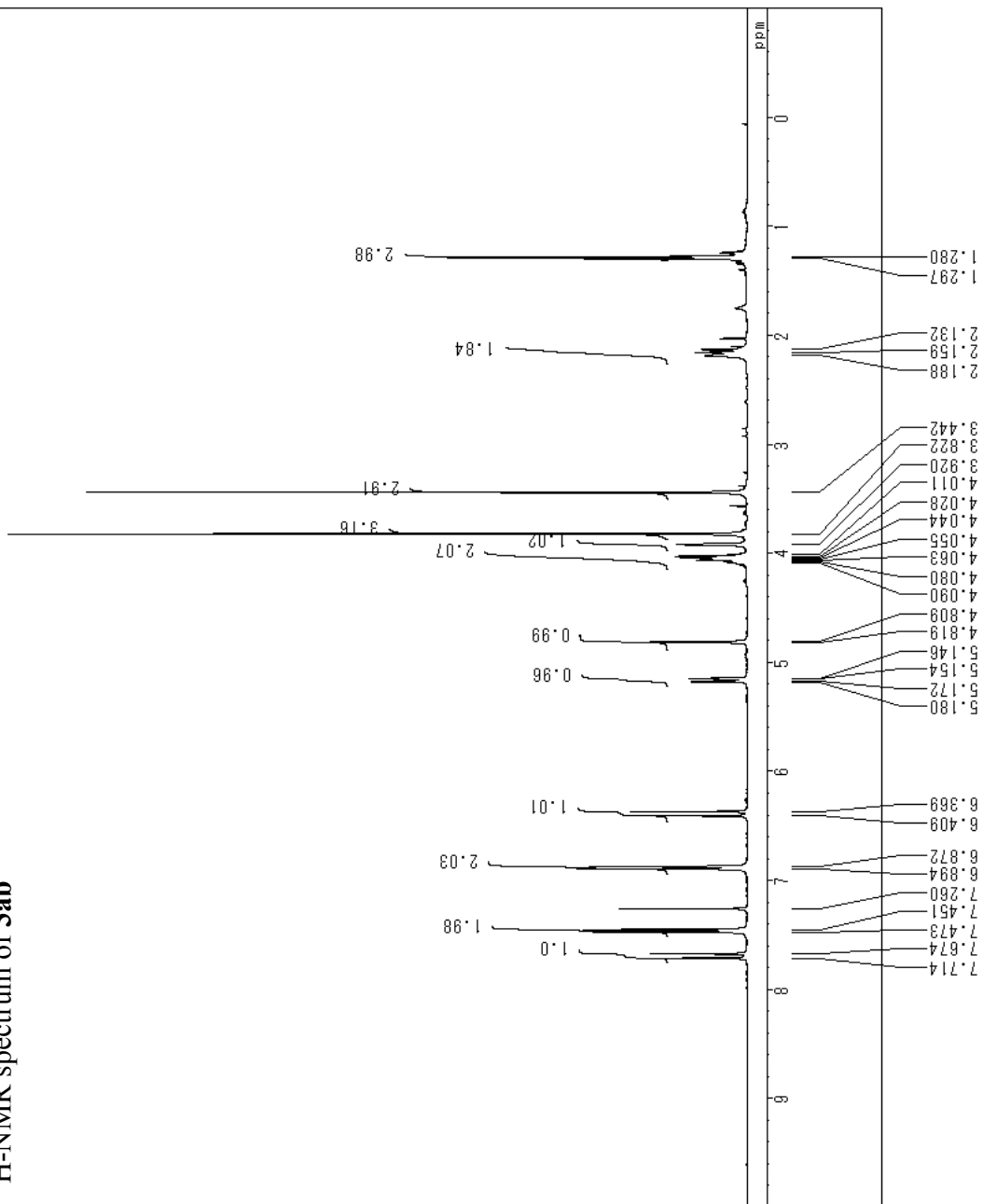




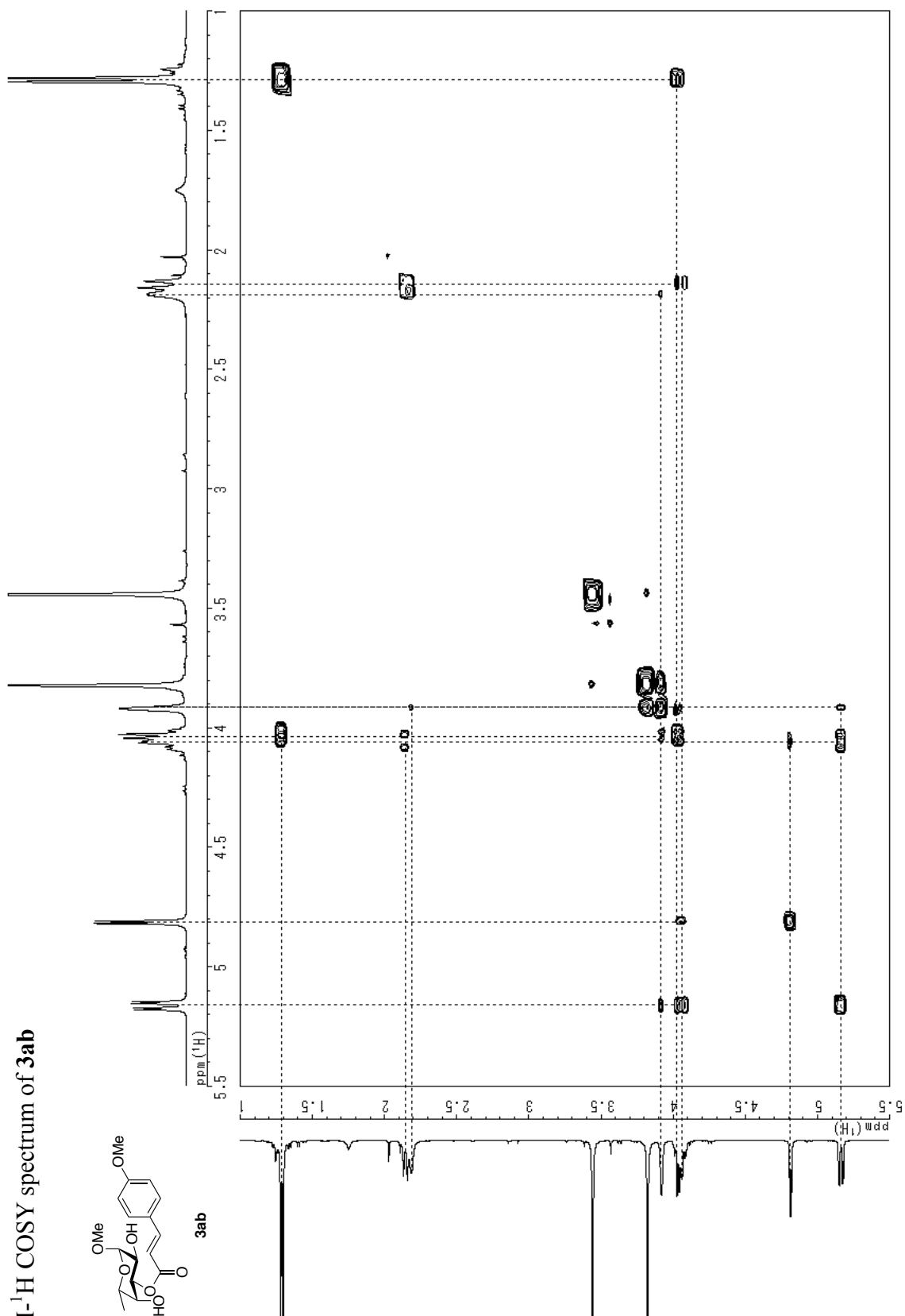
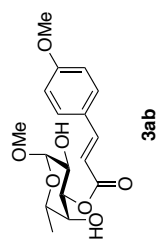
3ab

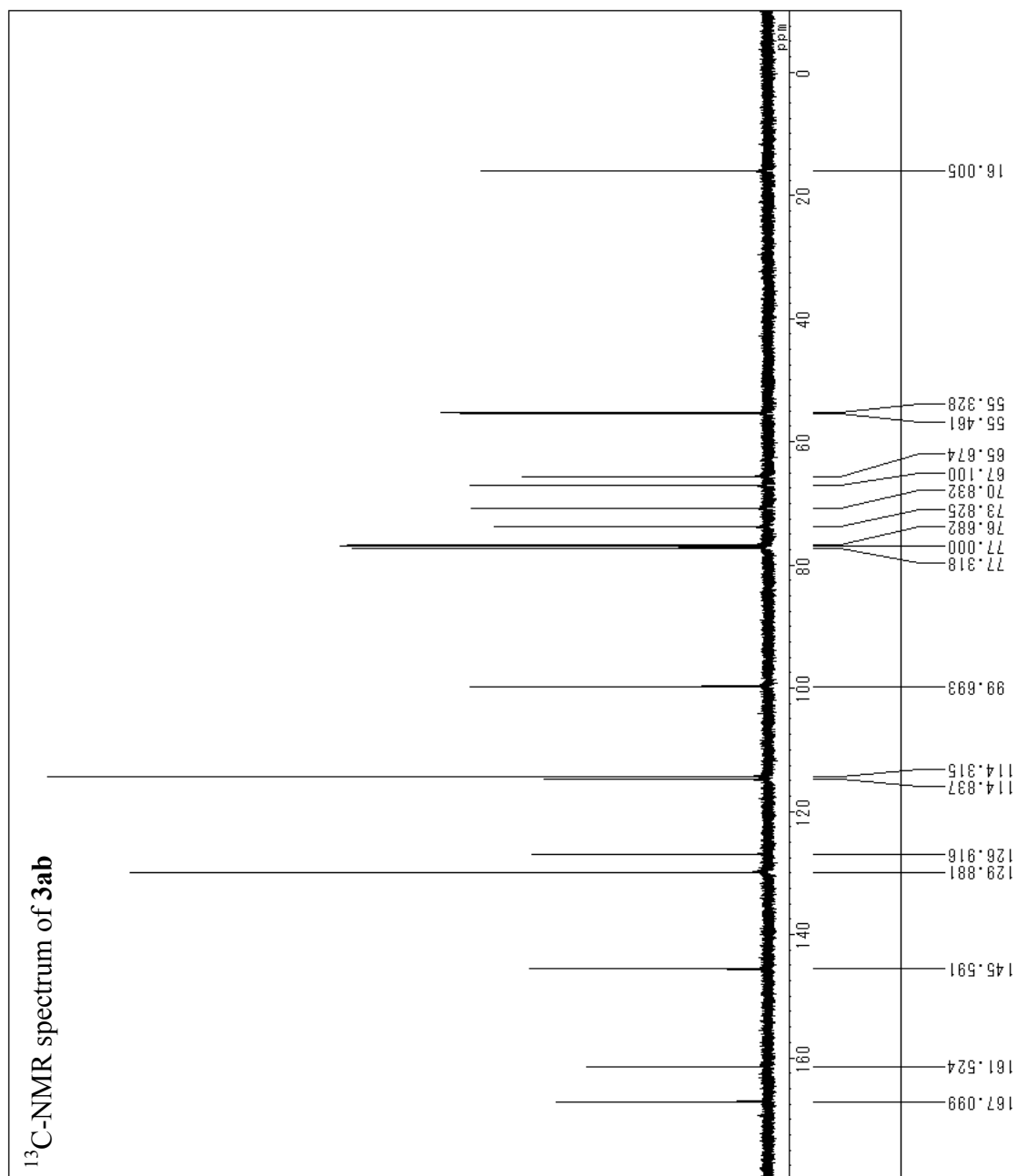
Comment TSV20034_pure_13C_COSY_2
 0171206_01
 Date 2017/Dec/08
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

¹H-NMR spectrum of 3ab



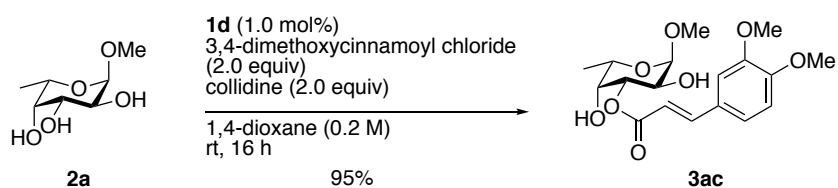
^1H - ^1H COSY spectrum of **3ab**



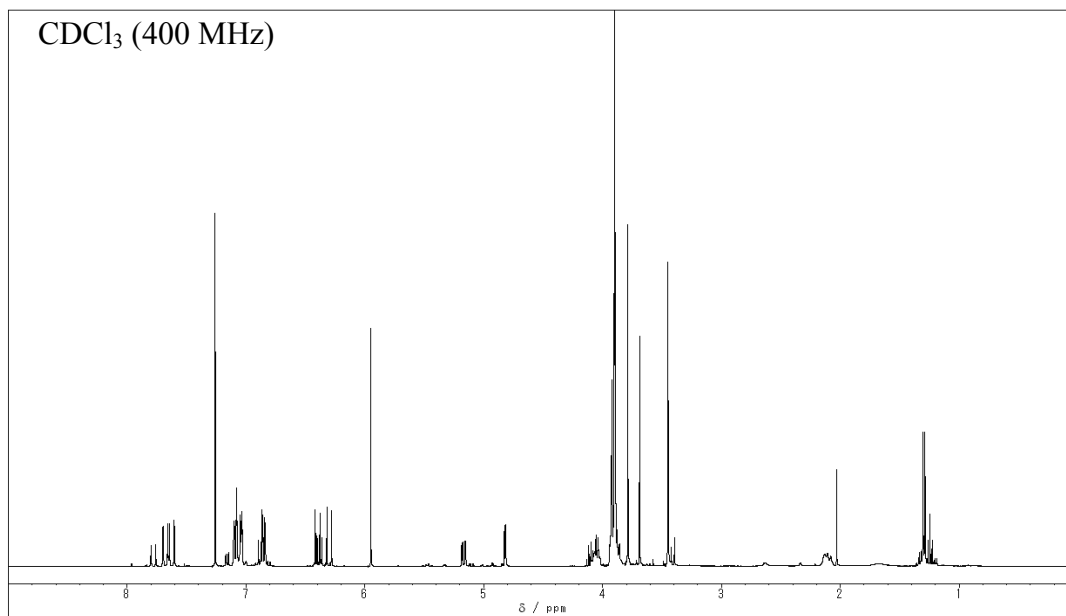


Comment TSV20034_pure_13C_COSY_2
 0171208_01
 Date 2017/Dec/08
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

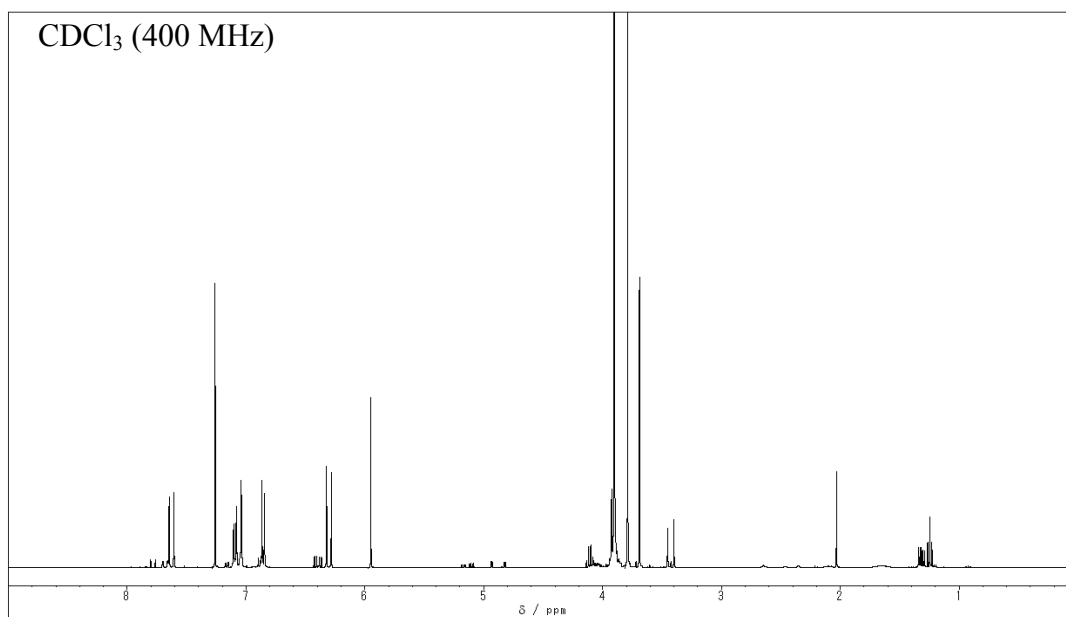
Methyl 3-*O*-3,4-dimethoxycinnamoyl- α -L-fucopyranoside (**3ac**)

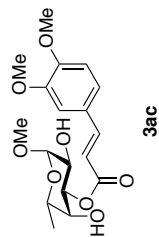


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

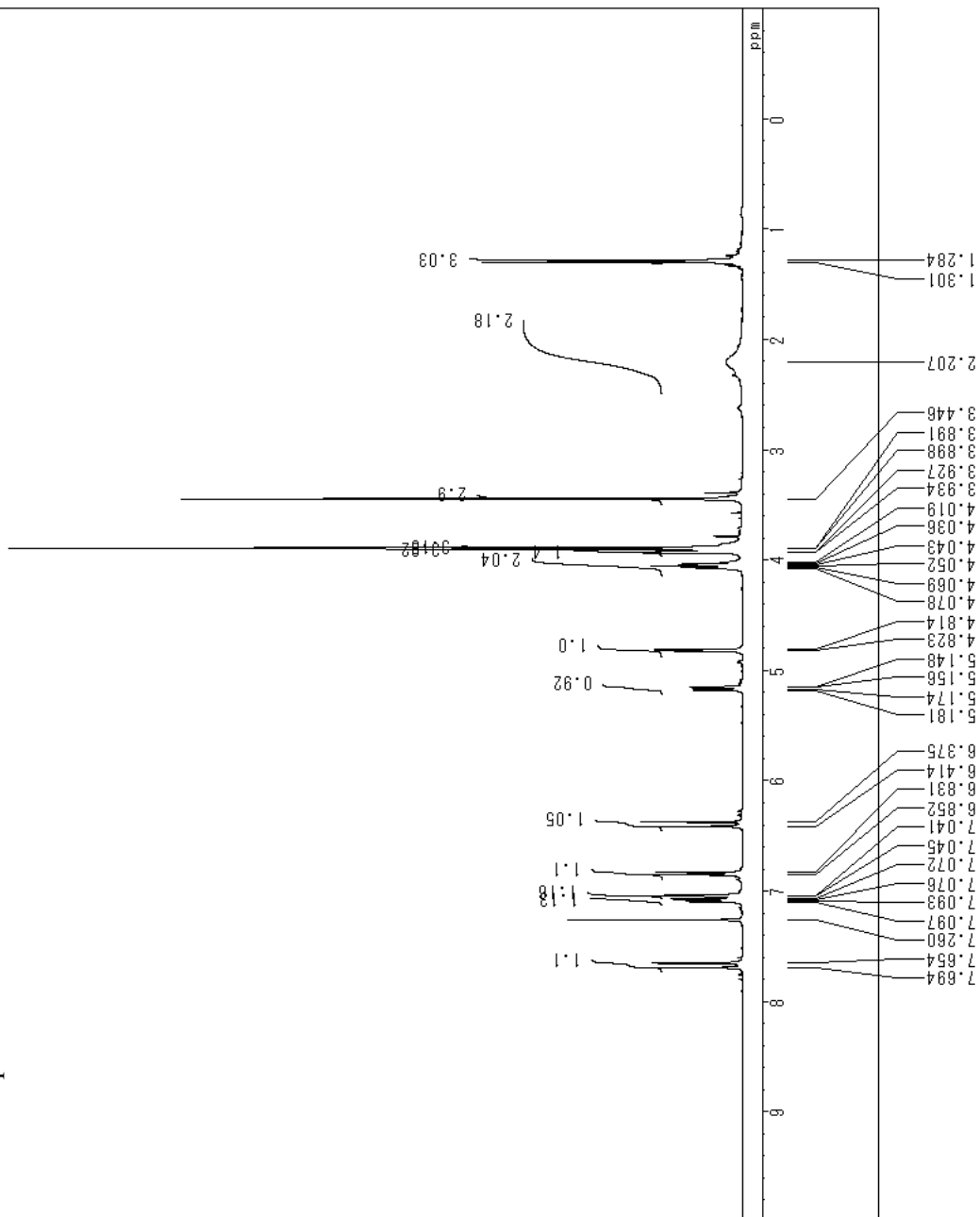




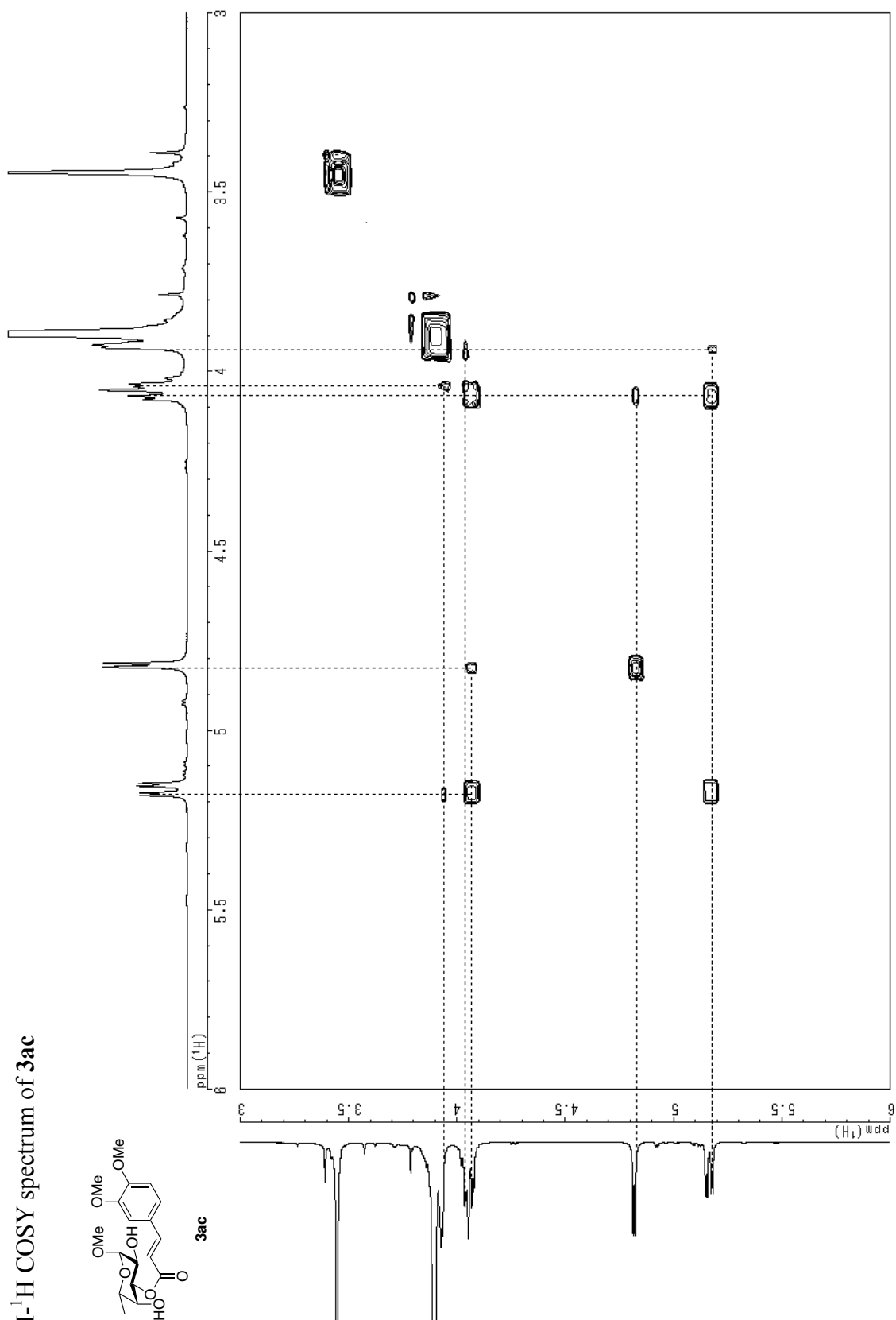
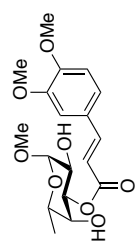
3ac

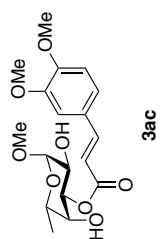
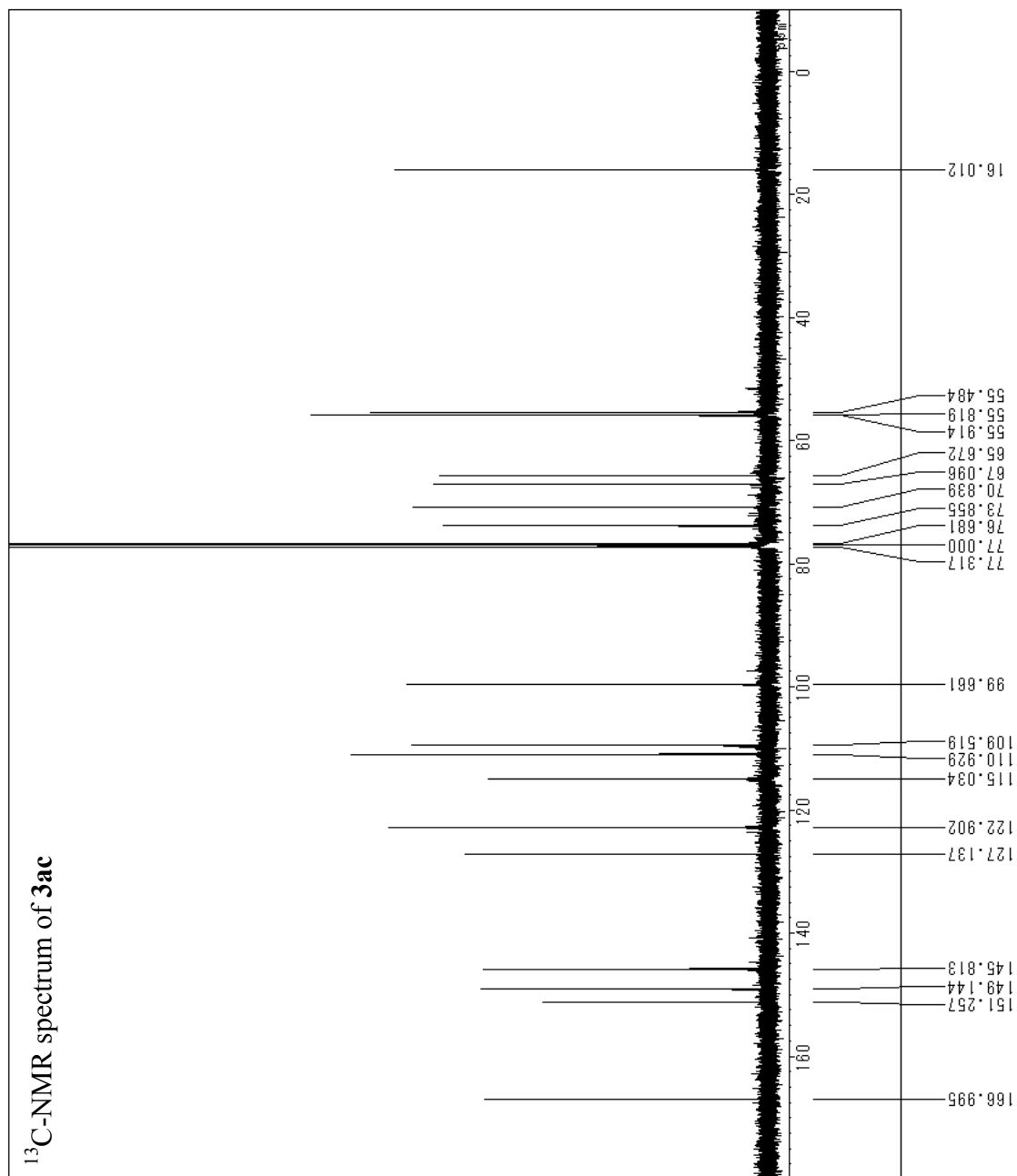
Comment TSV20036_pure_13C_COSY_2
 0180124_01
 Date 2018/Jan/24
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 400.27 MHz
 Scan 8
 AcqTime 2.5559 s
 Acc. Interval 5.5559 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

¹H-NMR spectrum of **3ac**



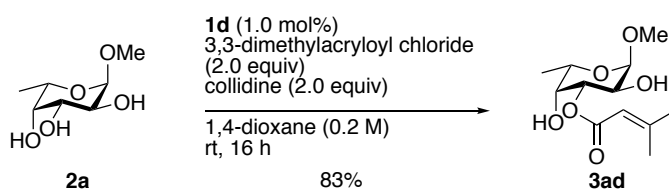
^1H - ^1H COSY spectrum of **3ac**



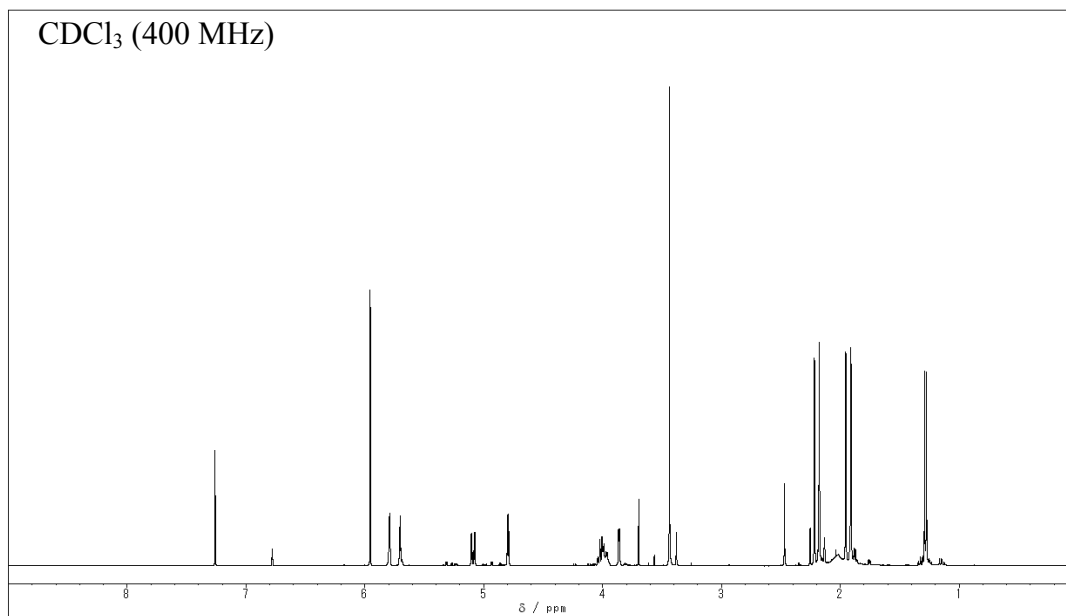


Comment TSV20036_pure_13C_COSY_2
 0180124_01
 Date 2018/Jan/24
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 432
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

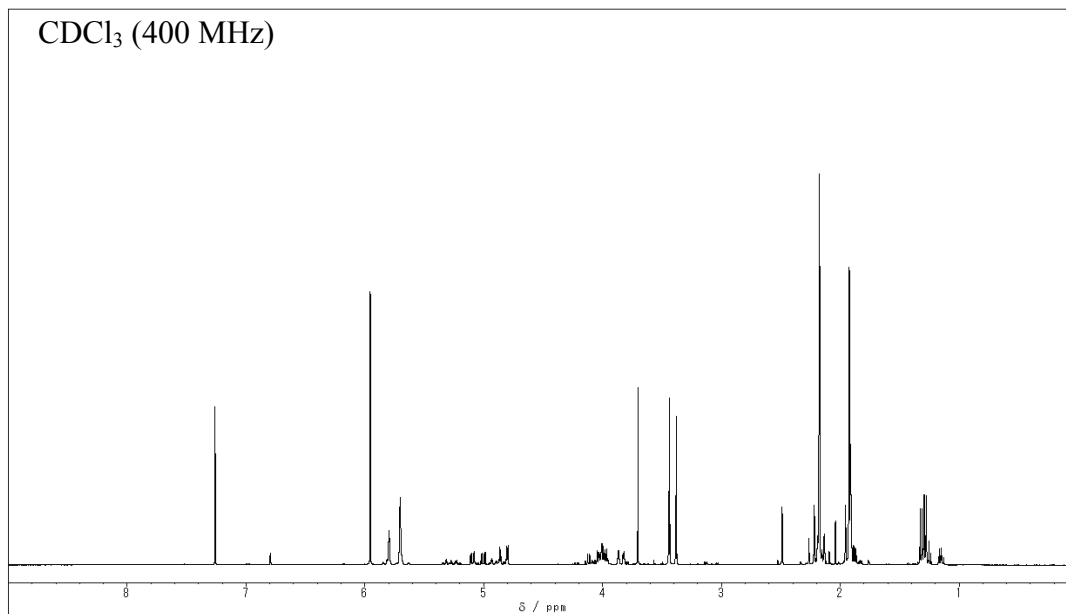
Methyl 3-*O*-3,3-dimethylacryloyl- α -L-fucopyranoside (**3ad**)

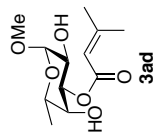


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

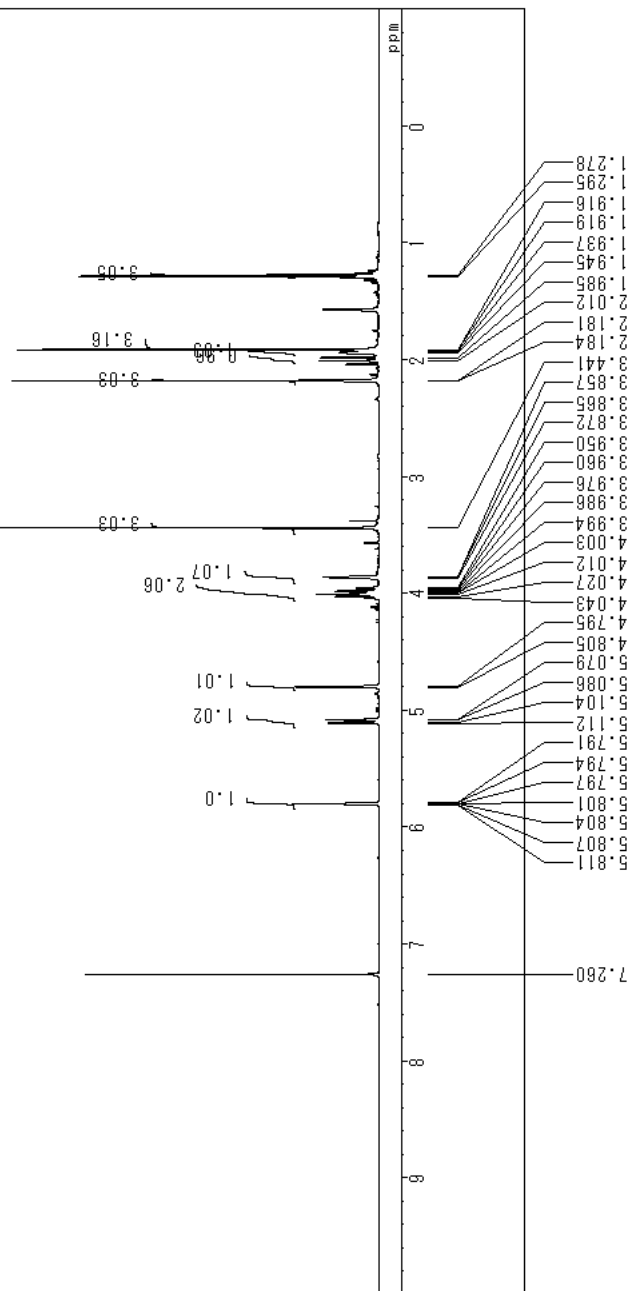




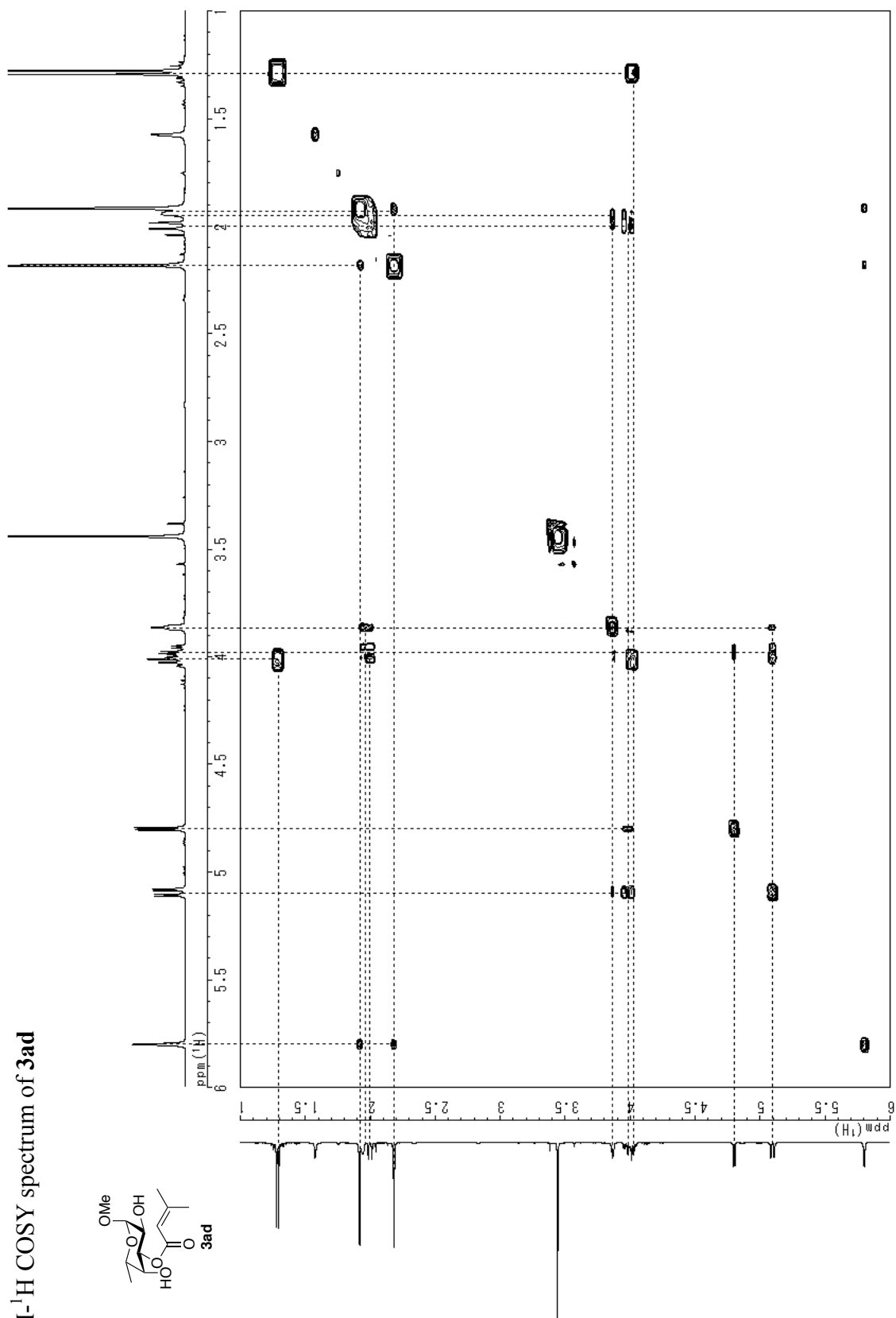
¹H-NMR spectrum of 3ad

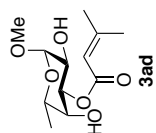
Comment TSV13020_COSY_20170224_0
 Date 2017/Feb/24
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

S222

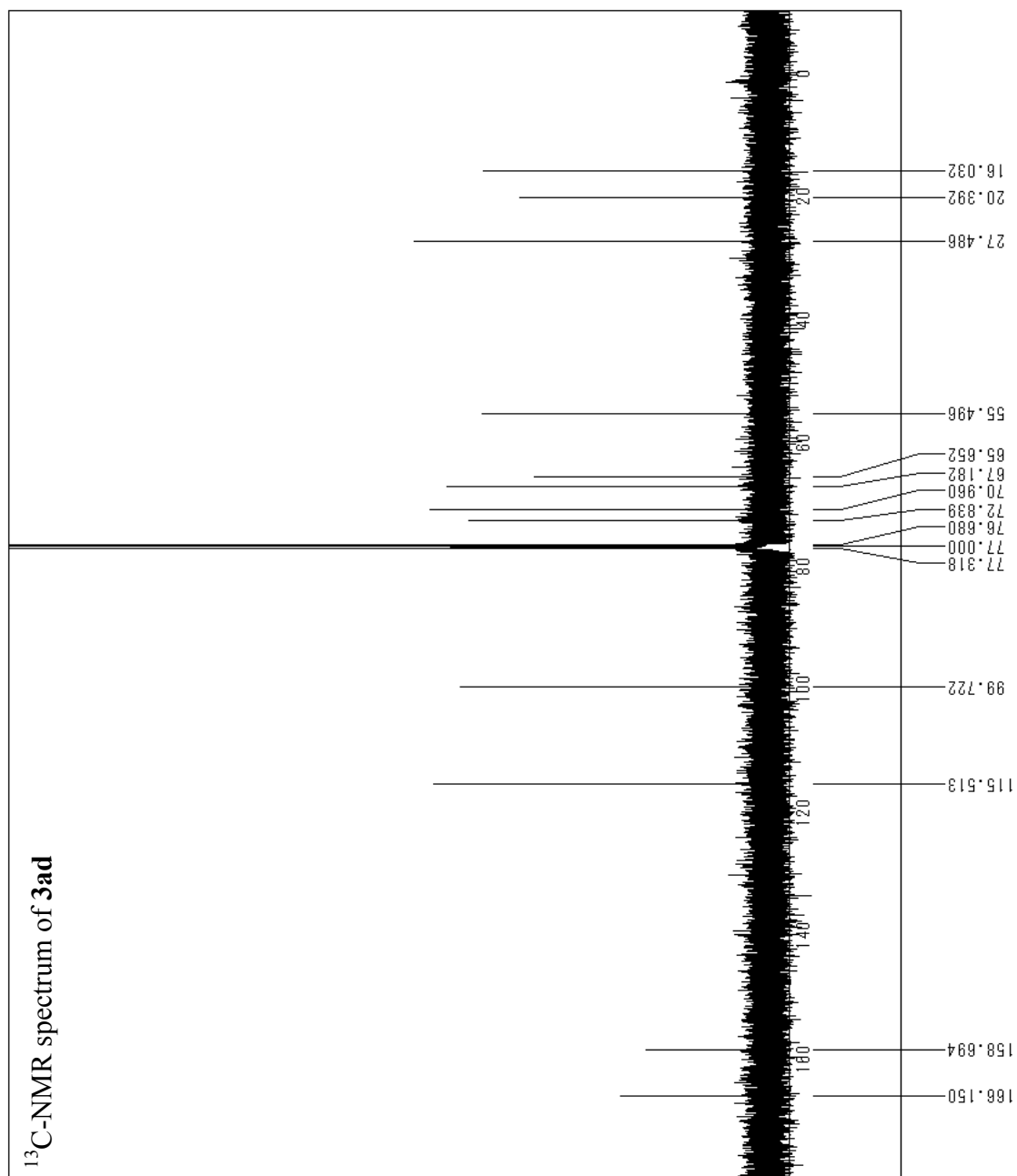


^1H - ^1H COSY spectrum of **3ad**

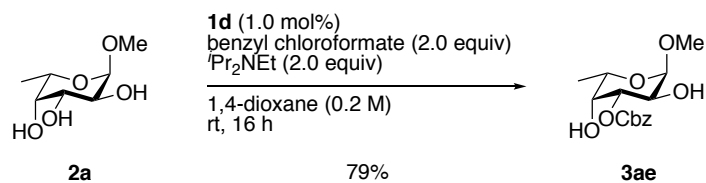




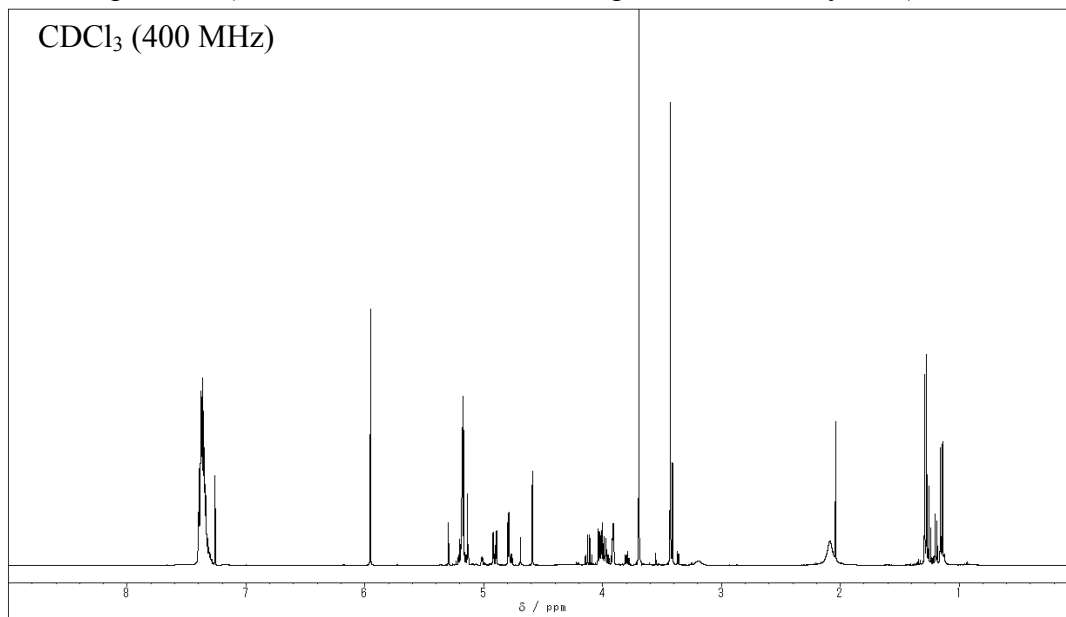
Comment TSV13020_13C_20170224_01
 Date 2017/Feb/24
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



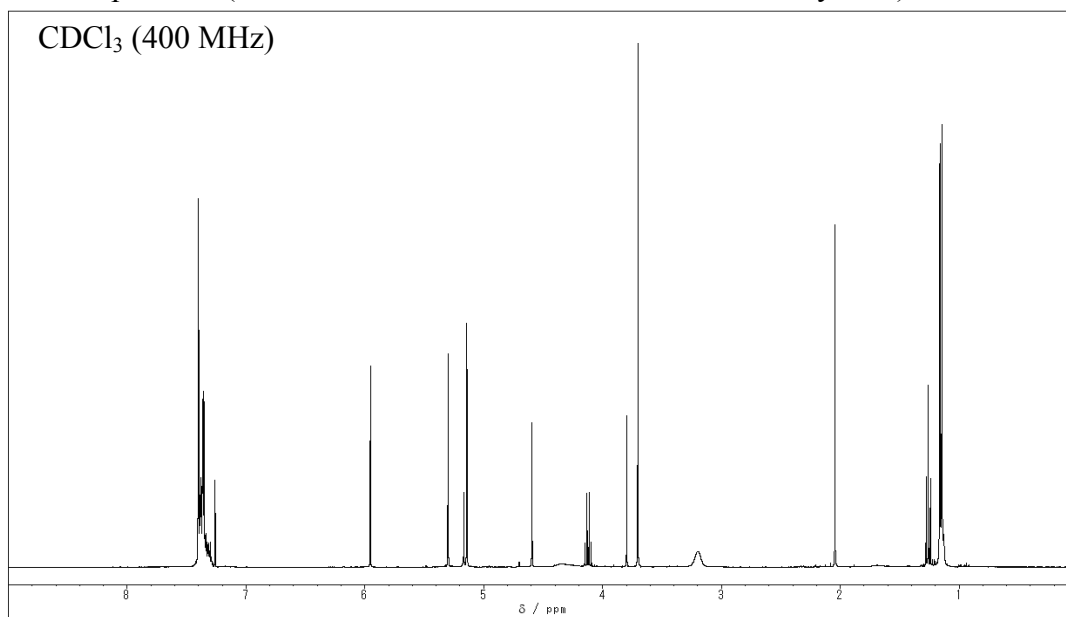
Methyl 3-*O*-benzyloxycarbonyl- α -L-fucopyranoside (**3ae**)

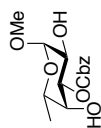


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

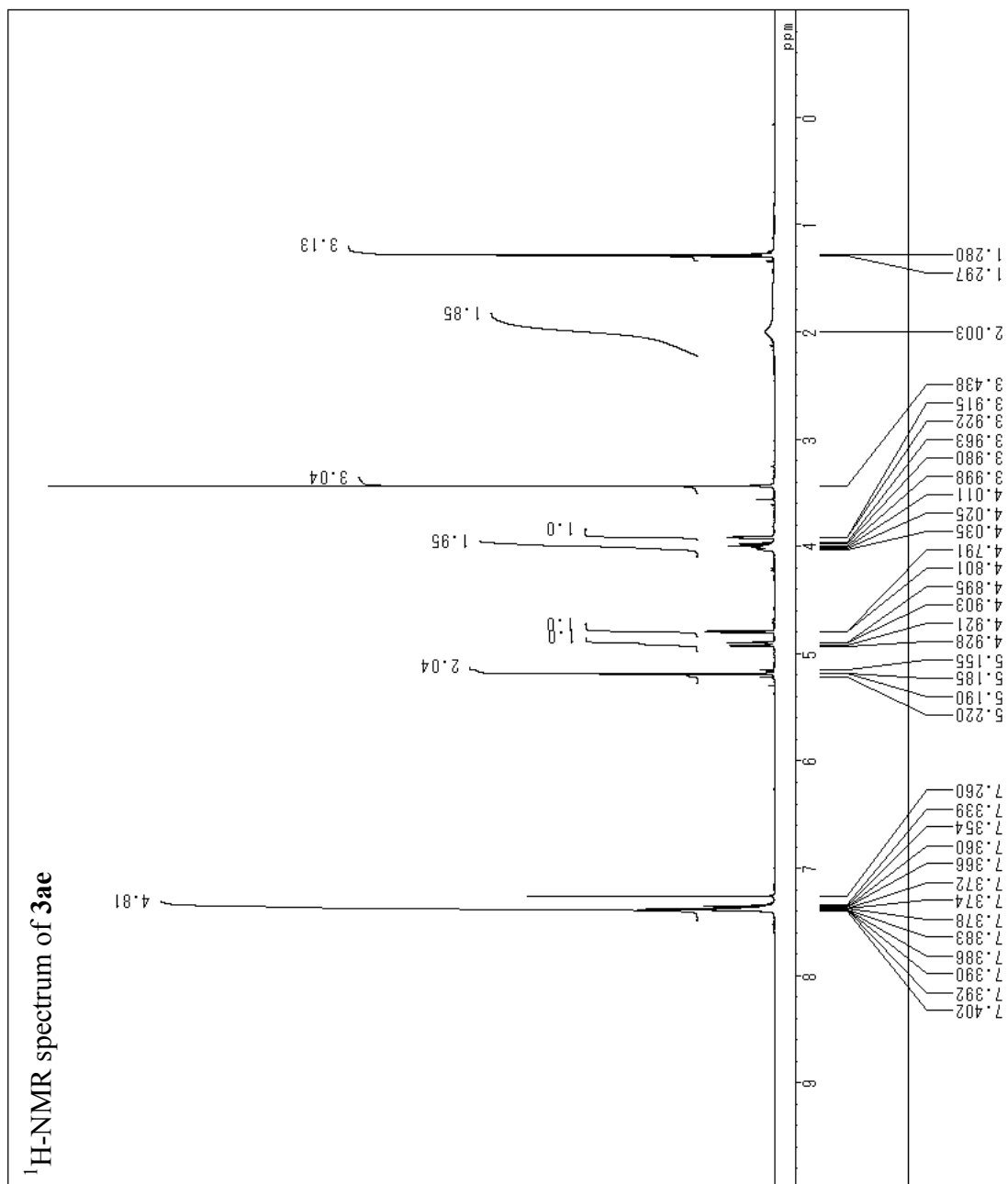




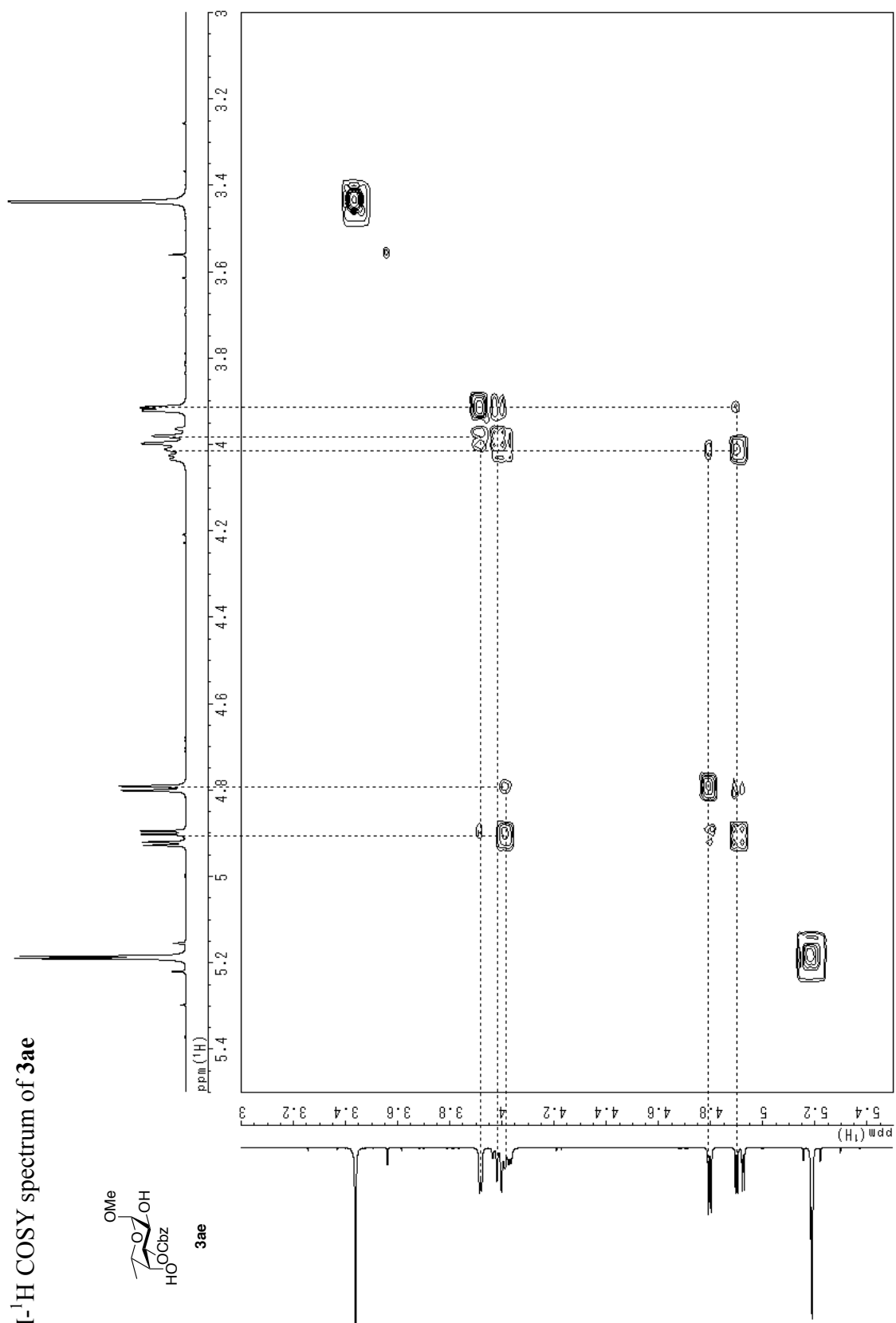
3ae

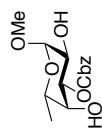
Comment TSV21019_pure_COSY_20180
 204_01
 Date 2018/Feb/04
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 16
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 16.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

¹H-NMR spectrum of 3ae



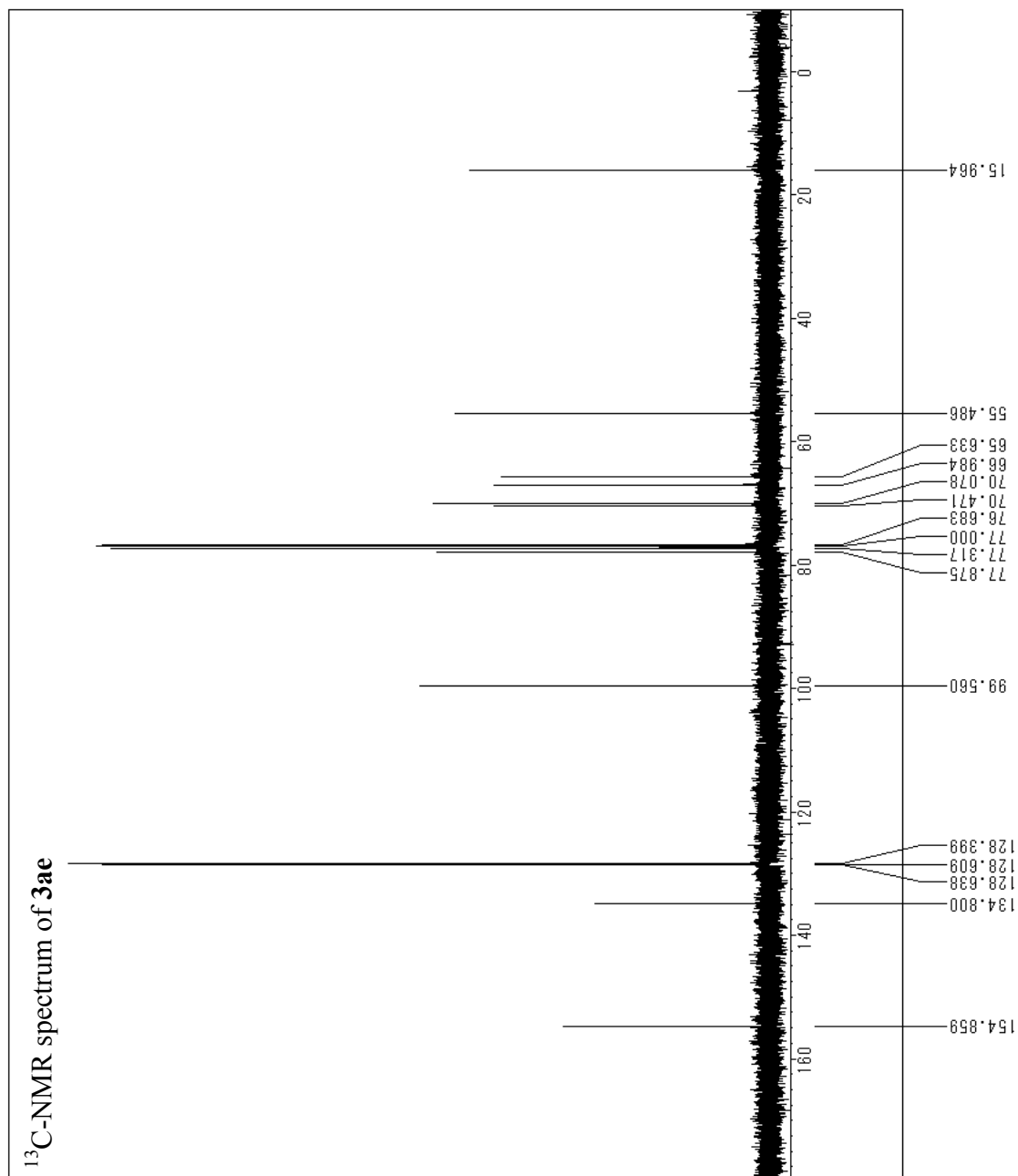
^1H - ^1H COSY spectrum of **3ae**



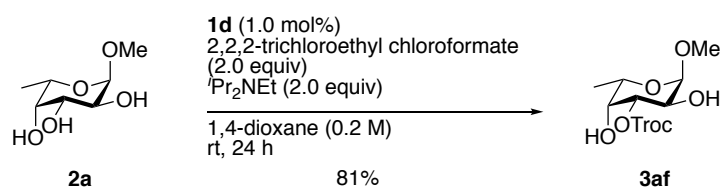


3ae

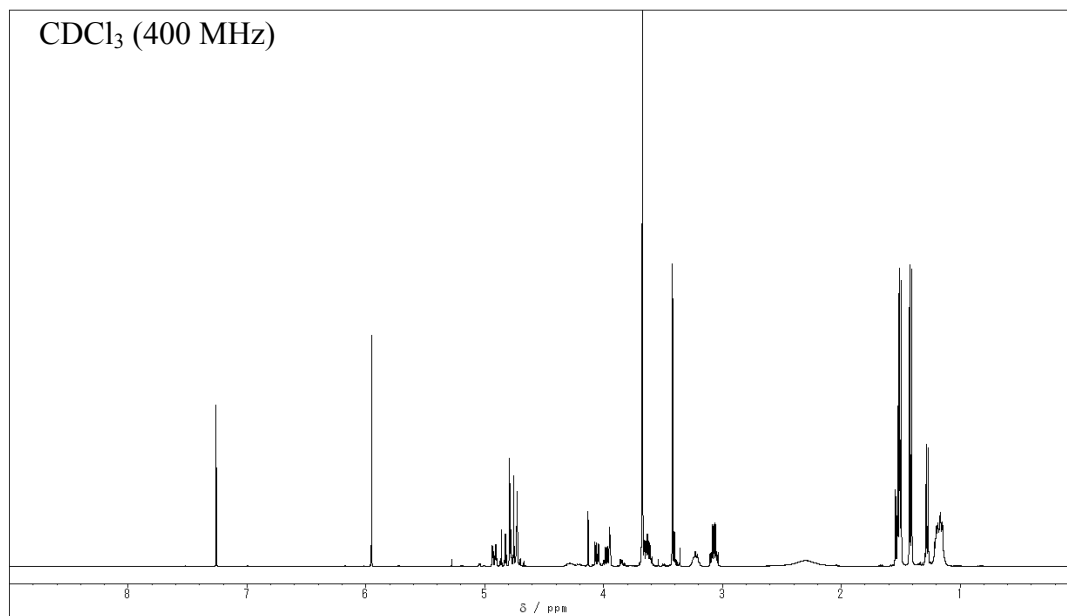
Comment TAO-18-22-17-27_20180108
 Date_01 2018/Jan/08
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 96
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



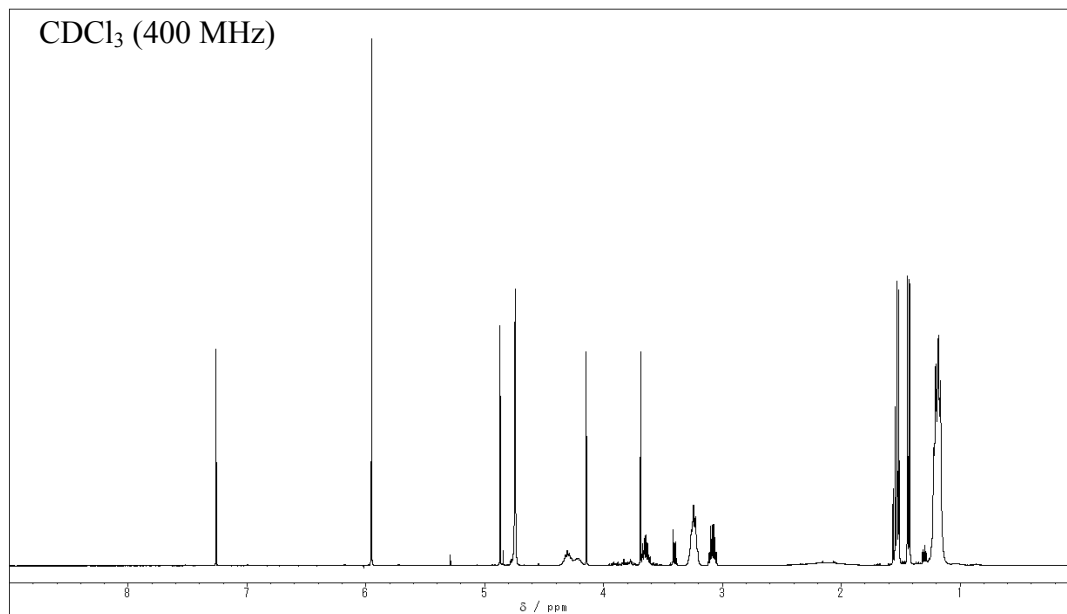
Methyl 3-*O*-2,2,2-trichloroethyloxycarbonyl- α -L-fucopyranoside (**3af**)

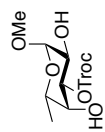


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

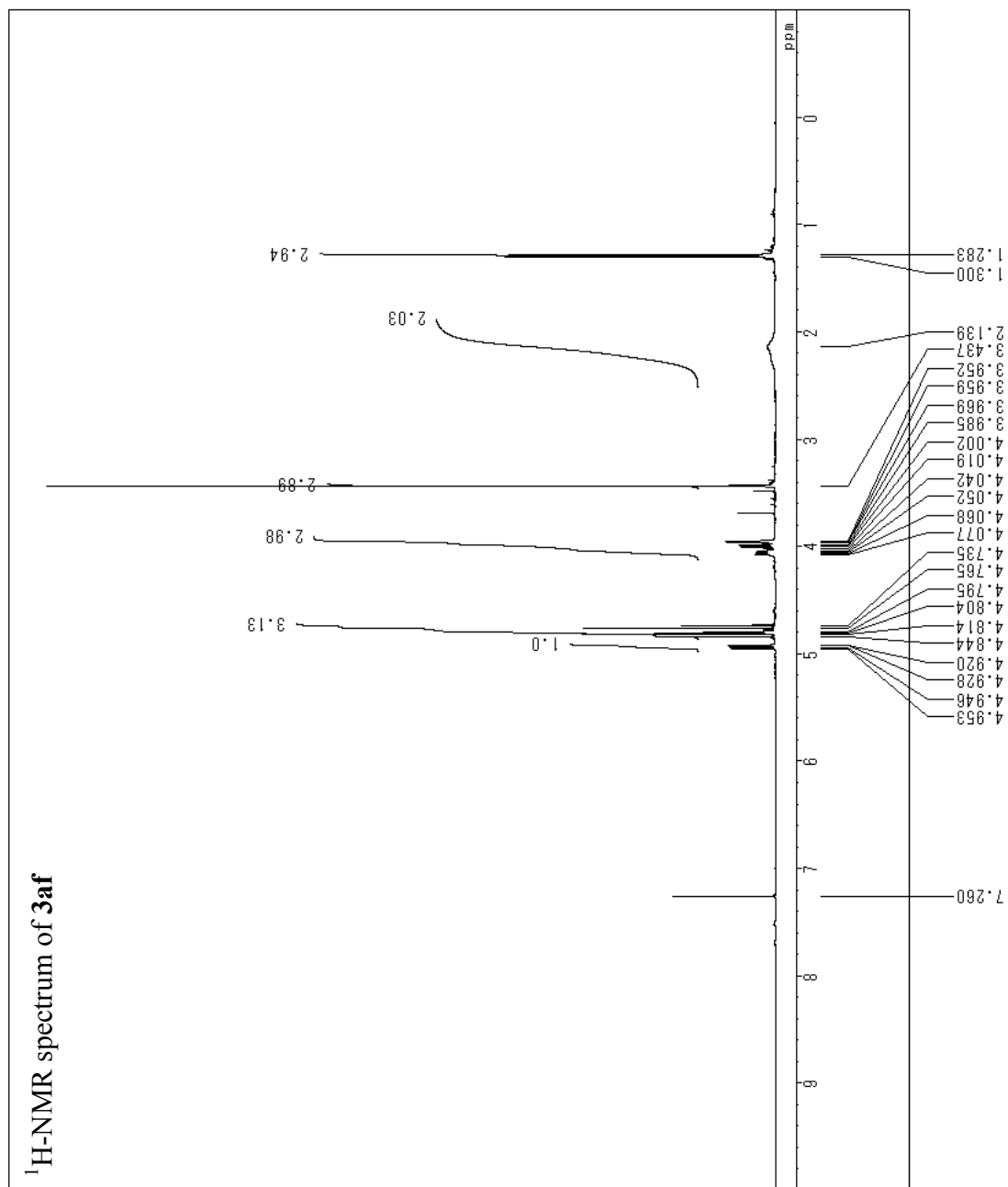




3af

Comment TSV19018_pure_13C_COSY_2
 0171018_01
 Date 2017/Oct/18
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

¹H-NMR spectrum of **3af**



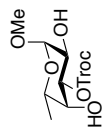
¹H COSY spectrum of **3af**

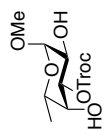
COc1ccc(O)cc1O

3af

ppm (¹H)

ppm (¹H)

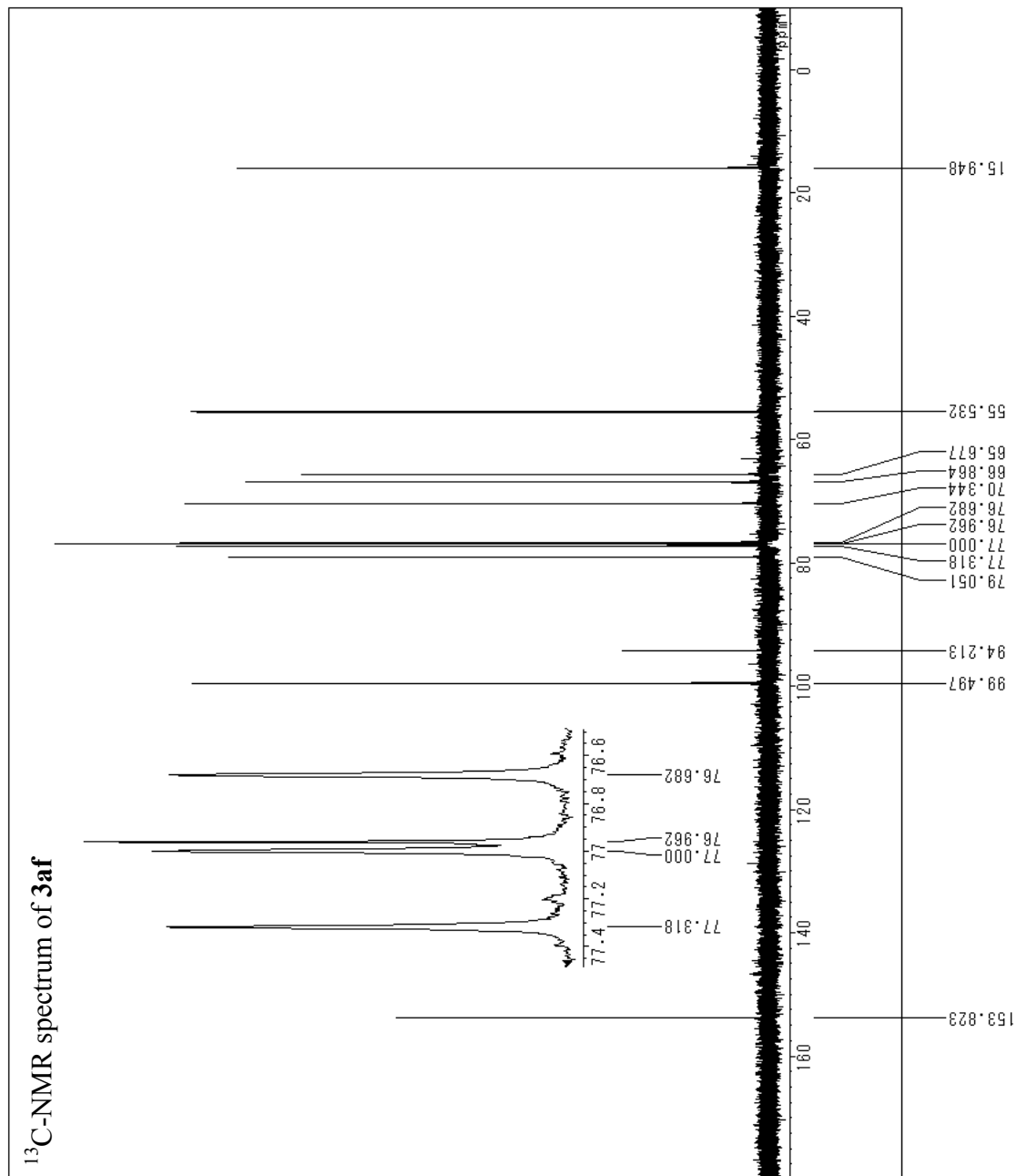




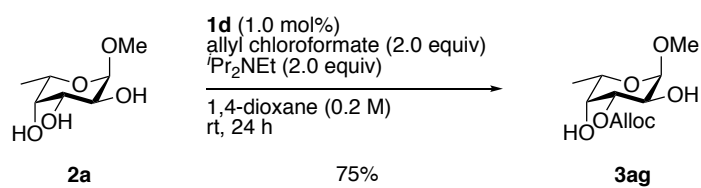
3af

Comment TSV19018_pure_13C_COSY_2
 0171018_01
 Date 2017/Oct/18
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

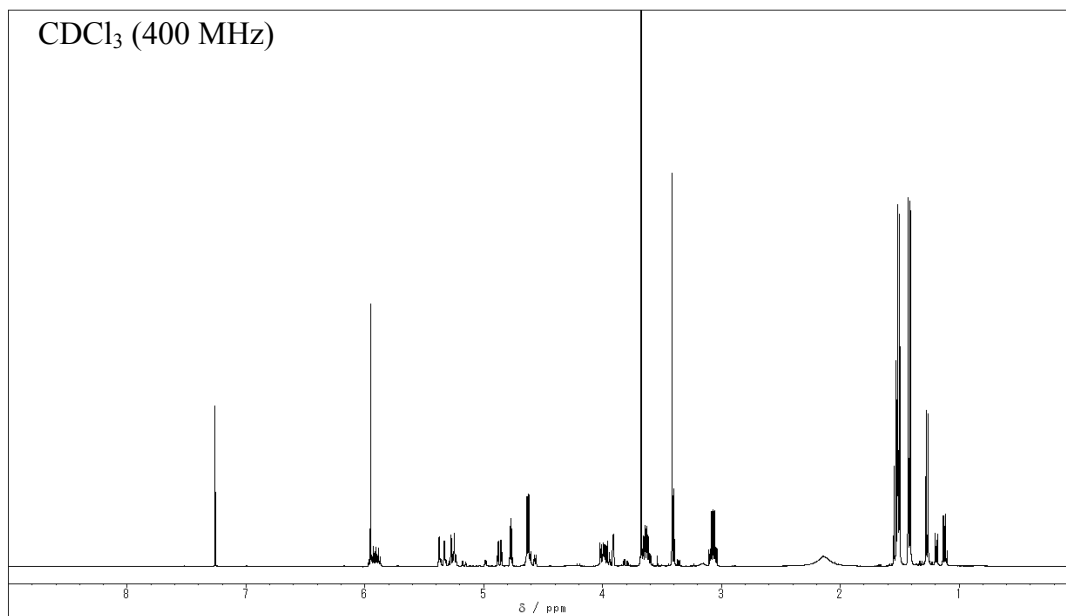
¹³C-NMR spectrum of 3af



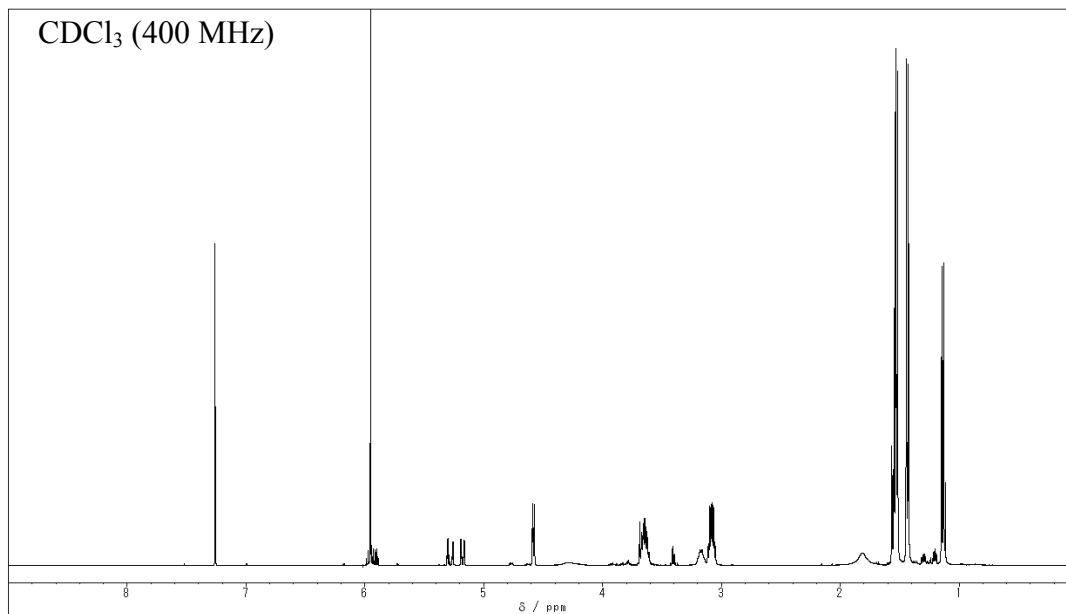
Methyl 3-*O*-allyloxycarbonyl- α -L-fucopyranoside (**3ag**)

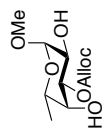


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)



^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

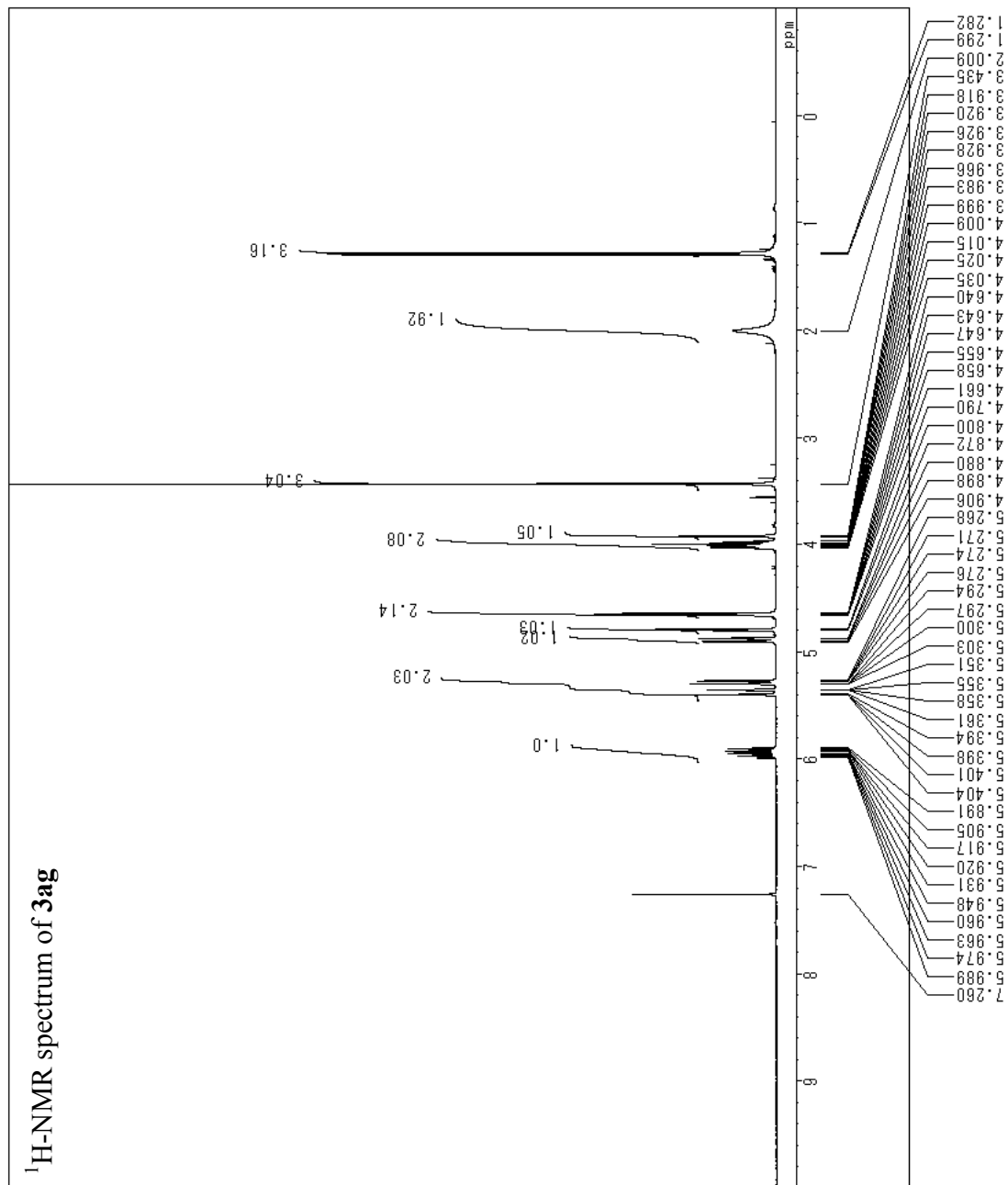




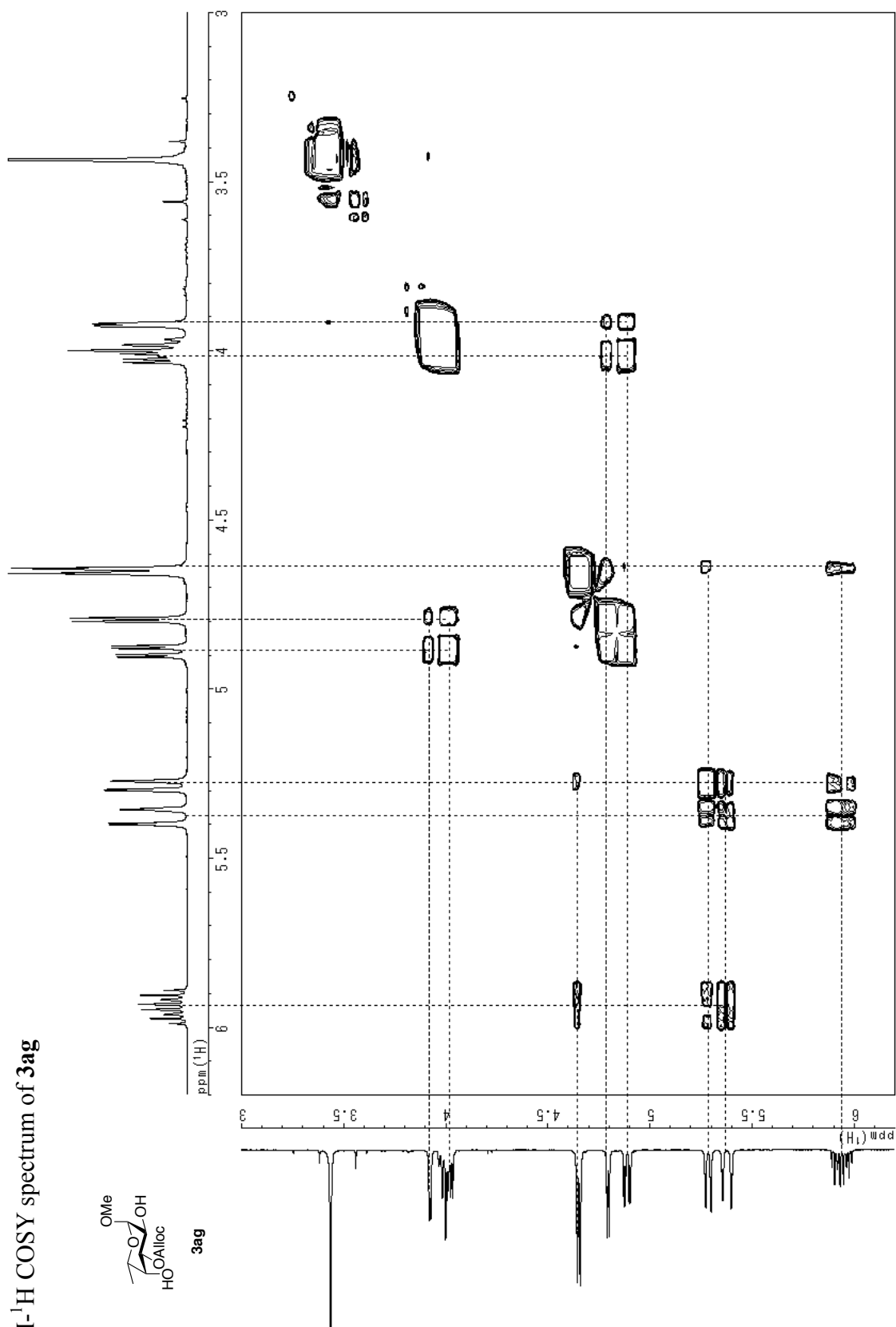
3ag

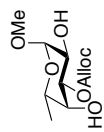
Comment TSV19016_pure_13C_COSY_2
 0171018_01
 Date 2017/Oct/18
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 8
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

¹H-NMR spectrum of **3ag**

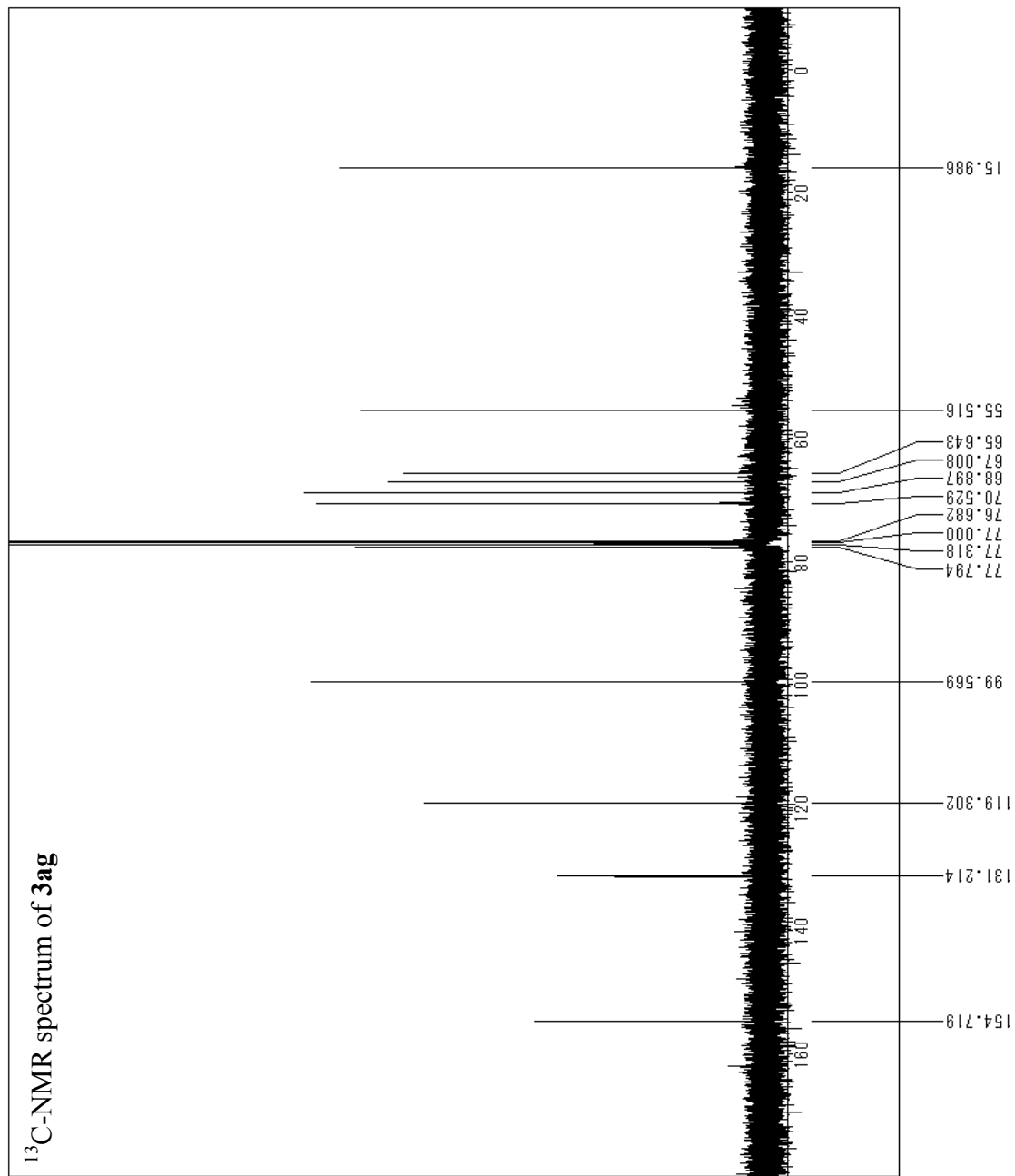


^1H - ^1H COSY spectrum of **3ag**



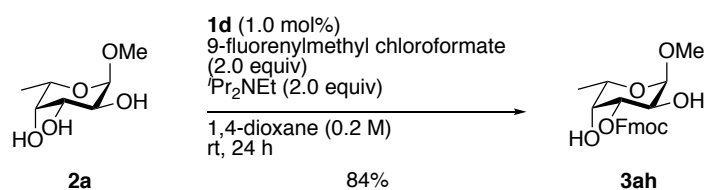


3ag

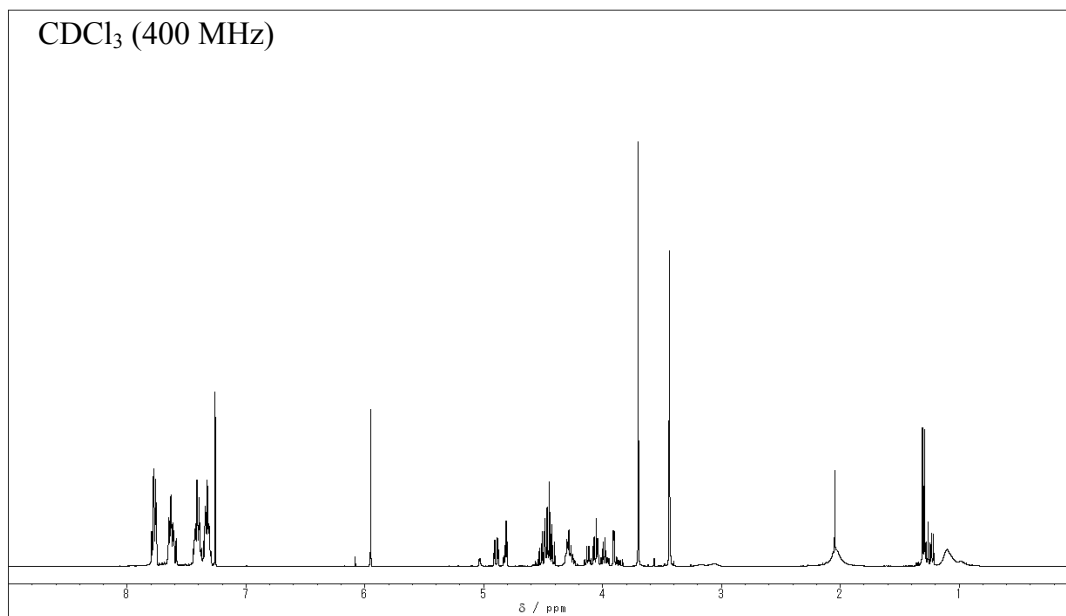


Comment TSV19016_pure_13C_COSY_2
 0171018_01
 Date 2017/Oct/18
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3631 s
 Acc. Interval 3.3631 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

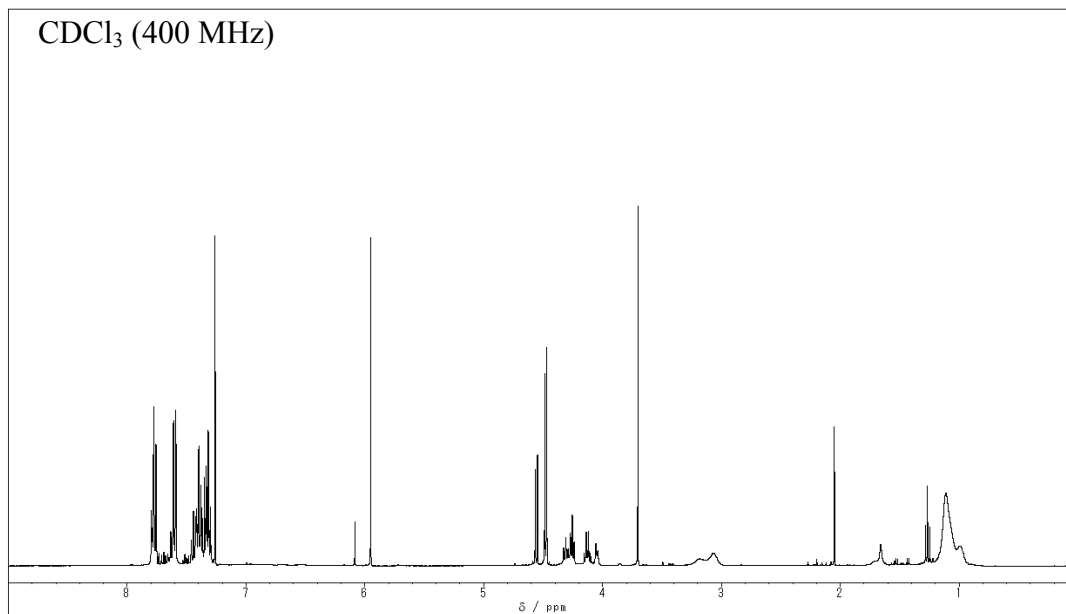
Methyl 3-*O*-9-fluorenylmethyloxycarbonyl- α -L-fucopyranoside (**3ah**)

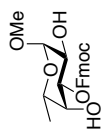


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1d**)

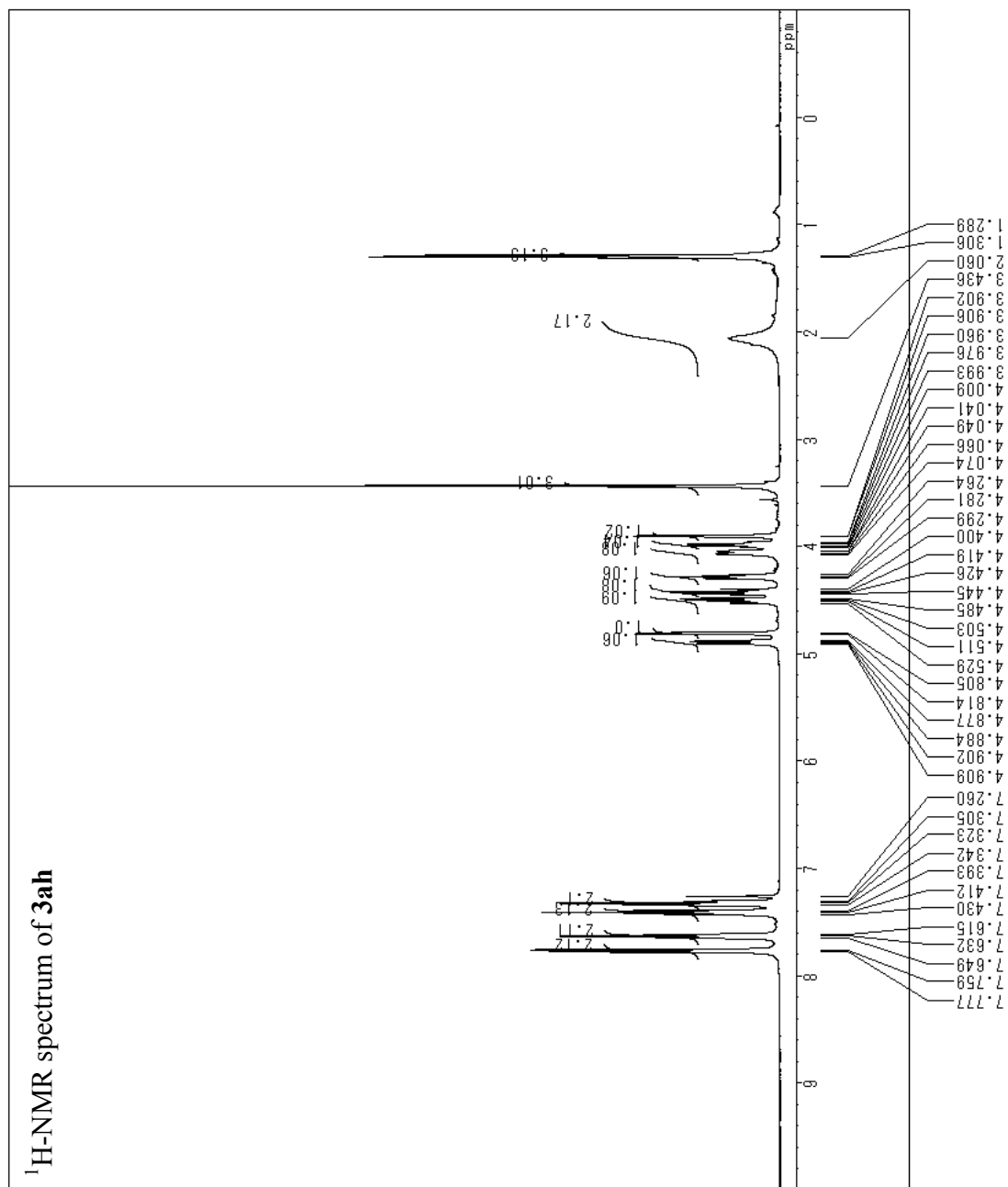


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1d**)

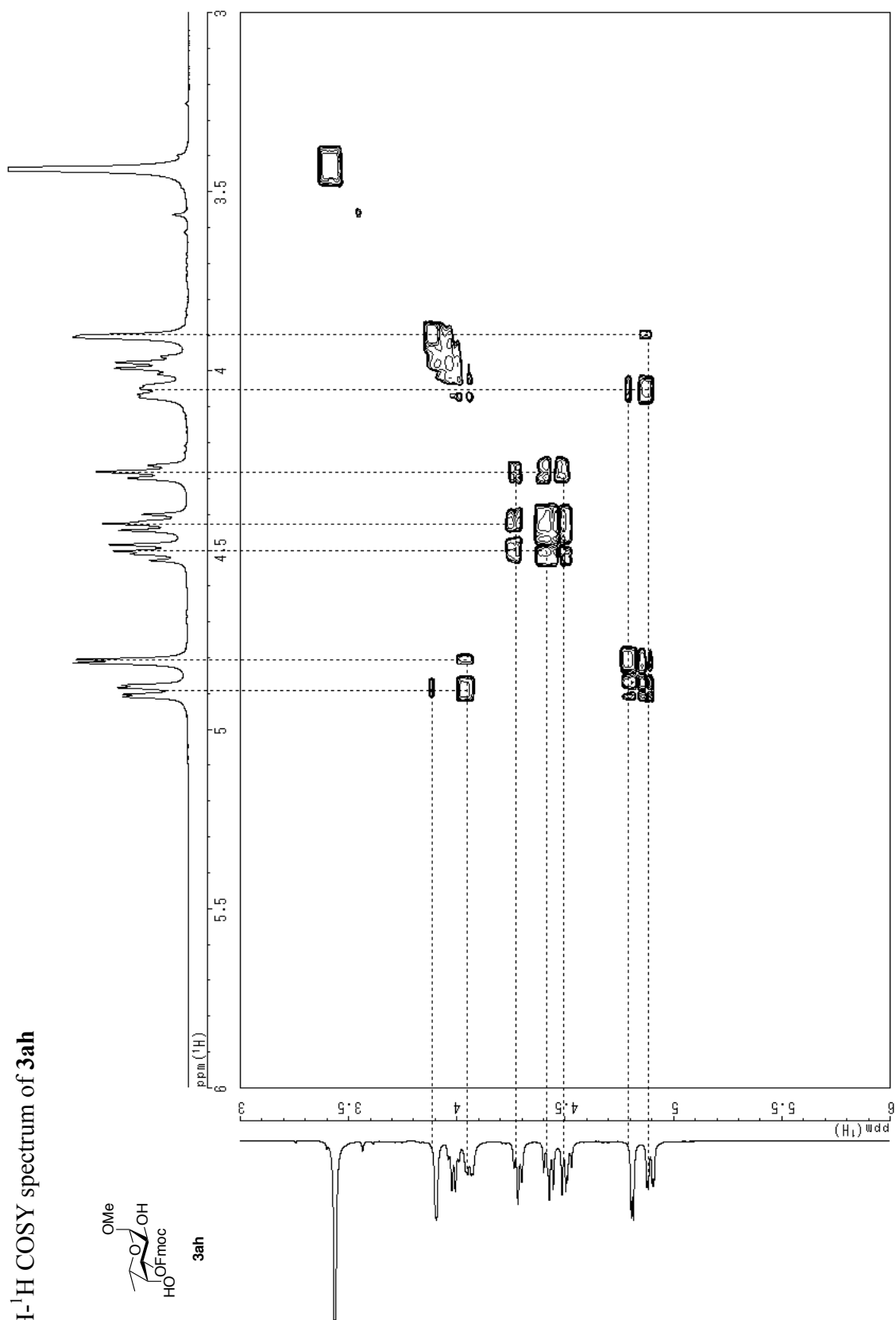


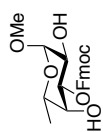
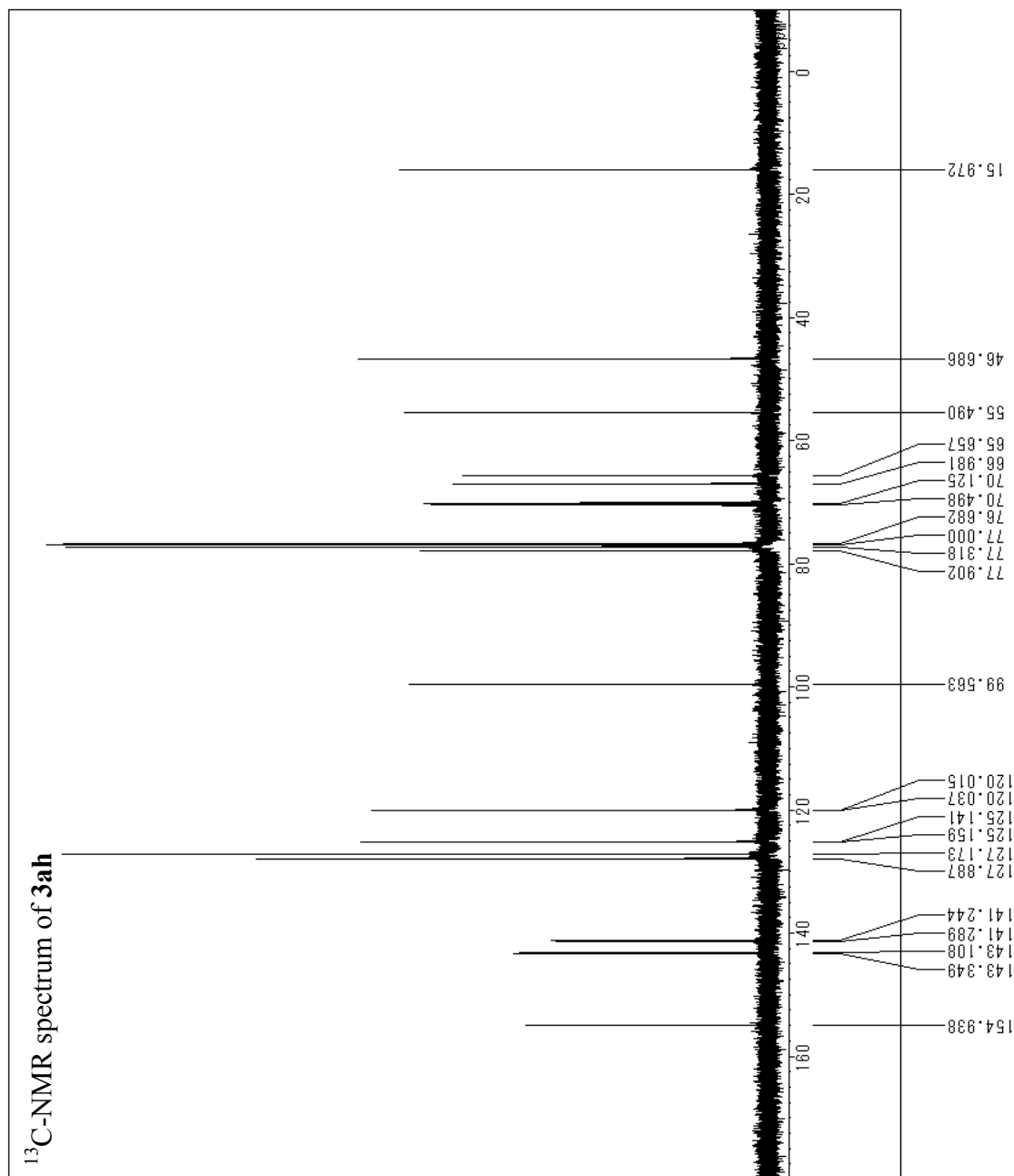


Comment	TSV18014_pure_13C_COSY_2
Date	01/7/2005_01
Date	2017/0ct/05
ObsNuc	¹ H
ObsProg	PROTON_001
ExMode	8
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acq. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 °C
Solvent	cdcl ₃



^1H - ^1H COSY spectrum of **3ah**

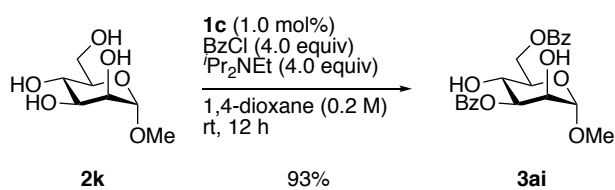




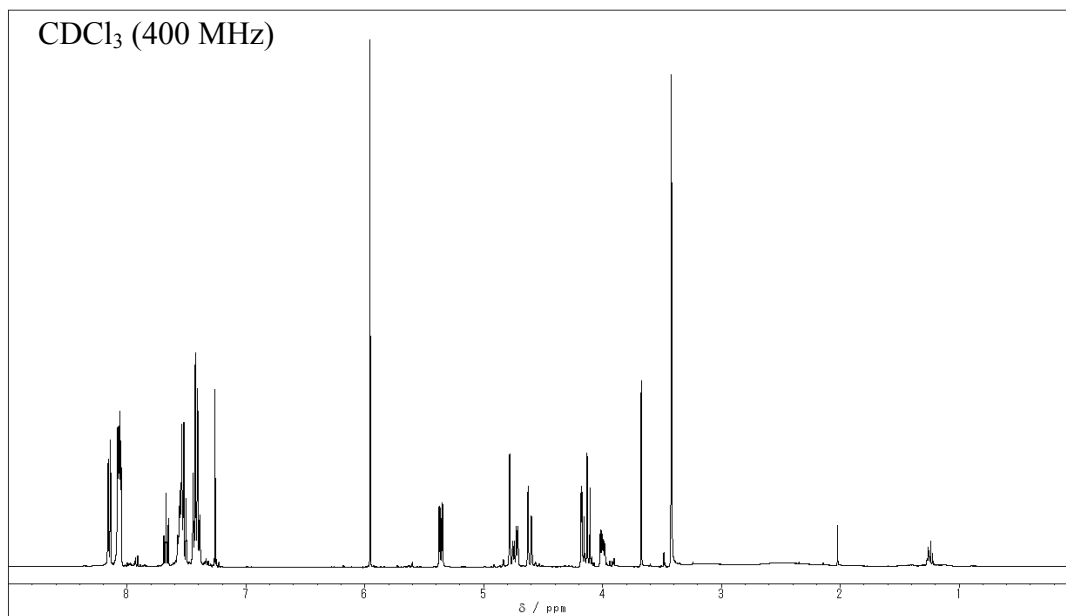
3ah

Comment TSV18014_pure_13C_COSY_2
 0171005_01
 Date 2017/Oct/05
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

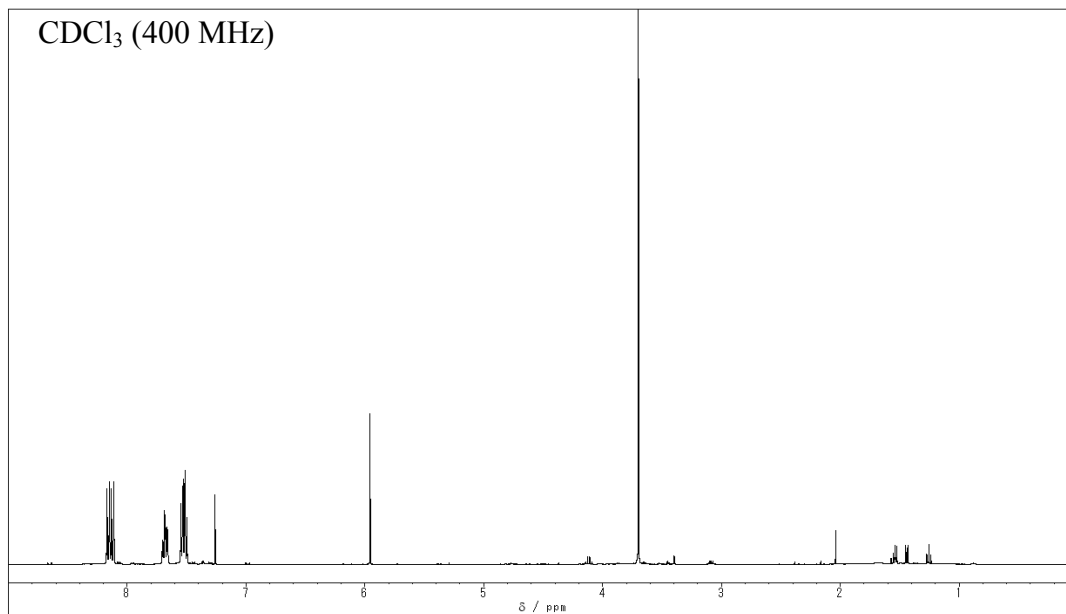
Methyl 3,6-*O*-dibenzoyl- α -D-mannopyranoside (**3ai**)

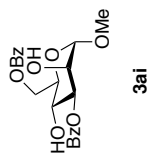


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1c**)

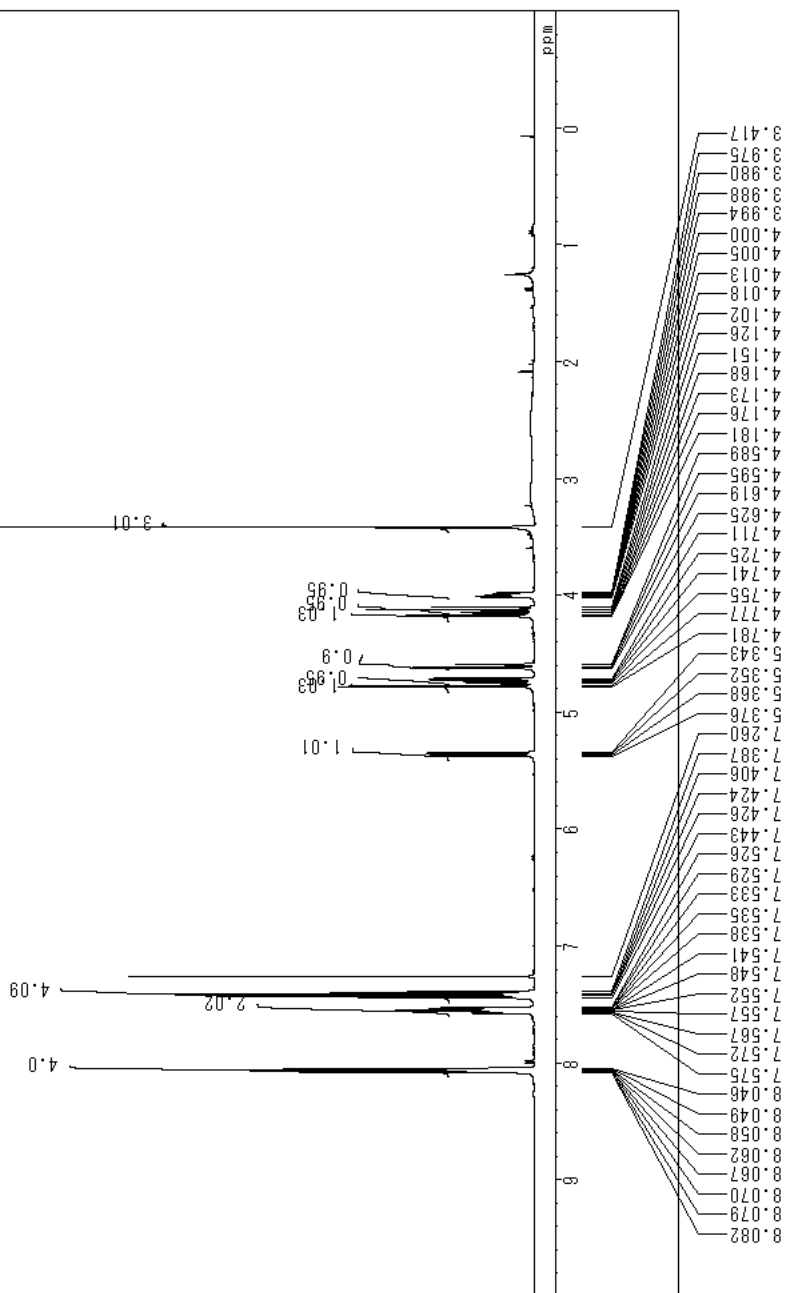


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1c**)



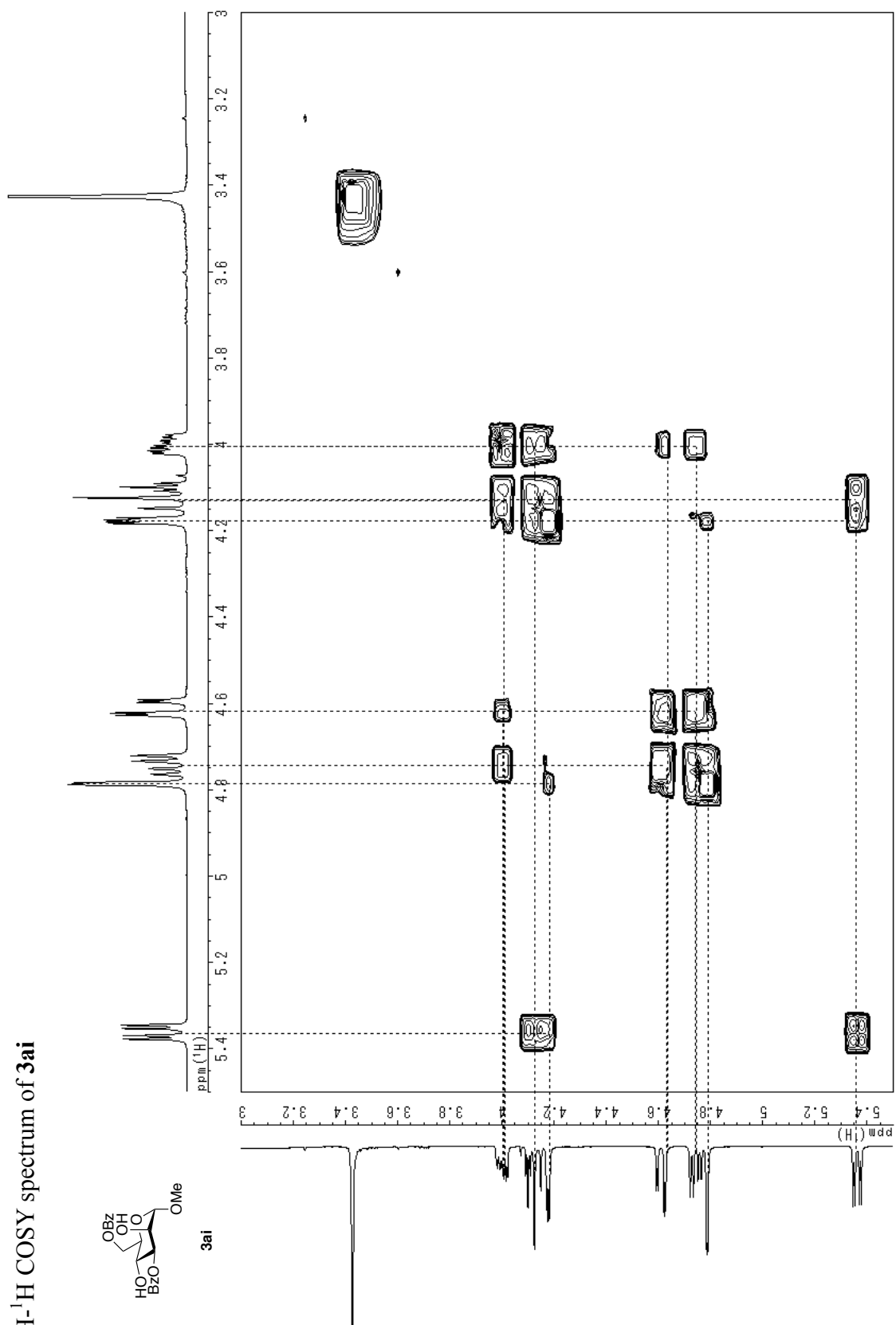


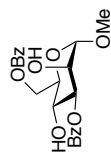
¹H-NMR spectrum of 3ai



Comment TSV05018_column_2_201803
 Date 07_01 2018/Mar/07
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 399.45 MHz
 Scan 32
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

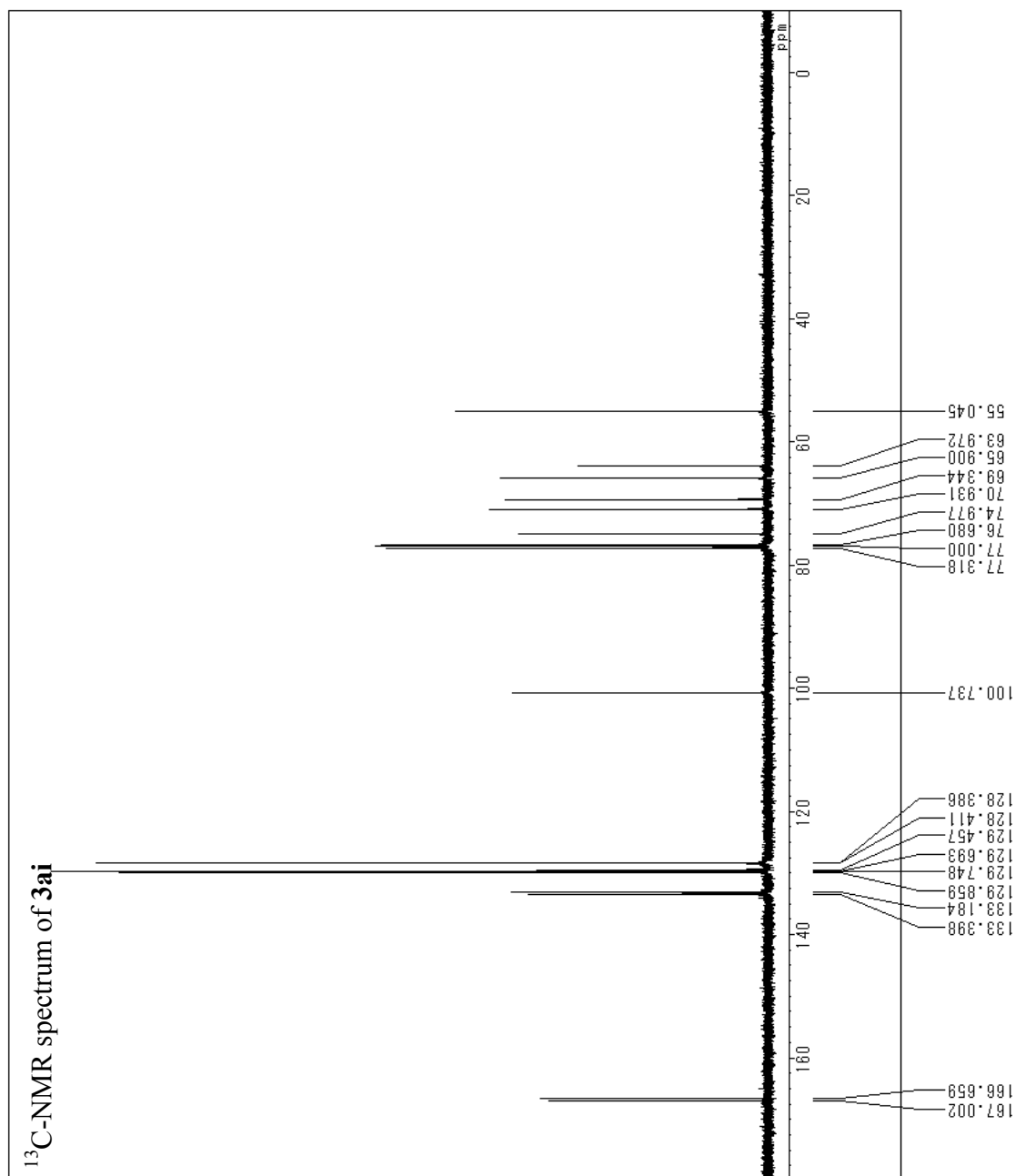
^1H - ^1H COSY spectrum of **3ai**



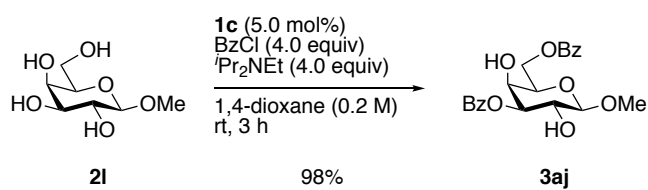


3ai

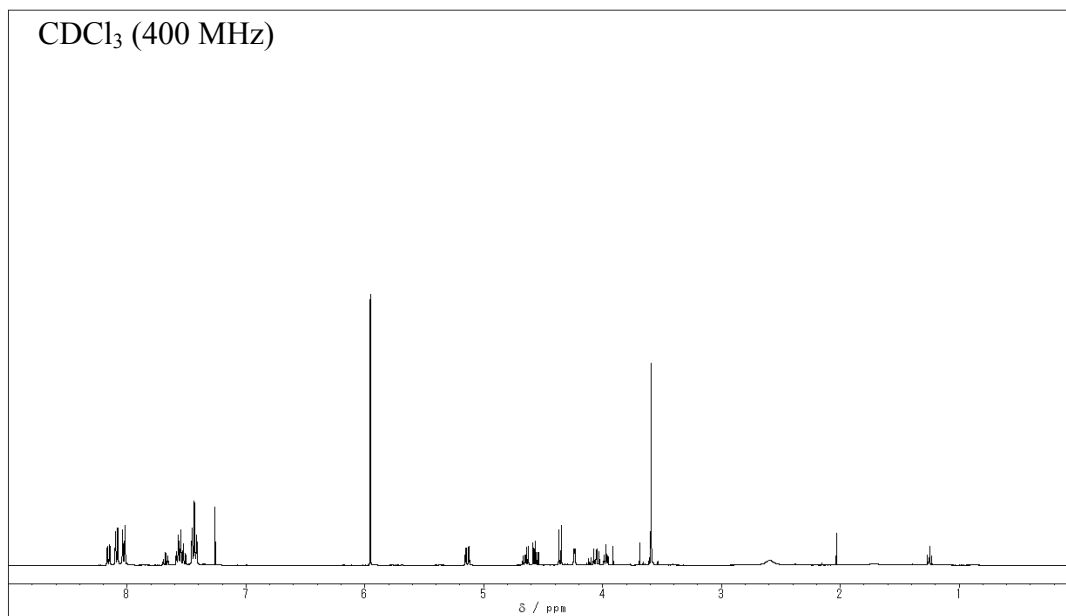
Comment TSV05018_13C_20180308_01
 Date 2018/Mar/08
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.45 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃



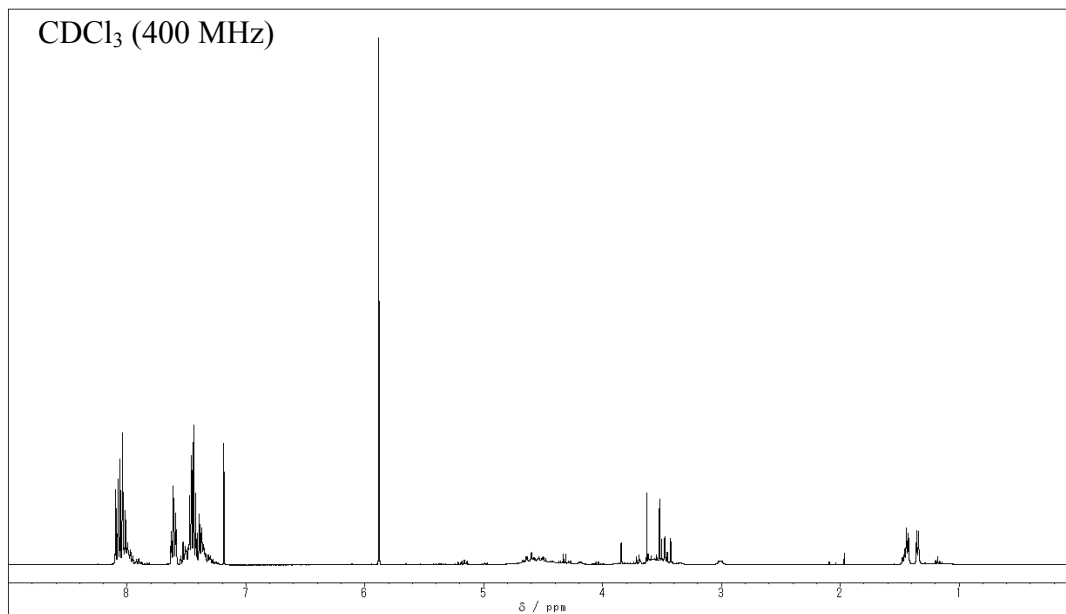
Methyl 3,6-*O*-dibenzoyl- β -D-galactopyranoside (**3aj**)

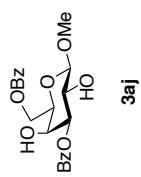


^1H -NMR spectrum (crude reaction mixture in the presence of catalyst **1c**)

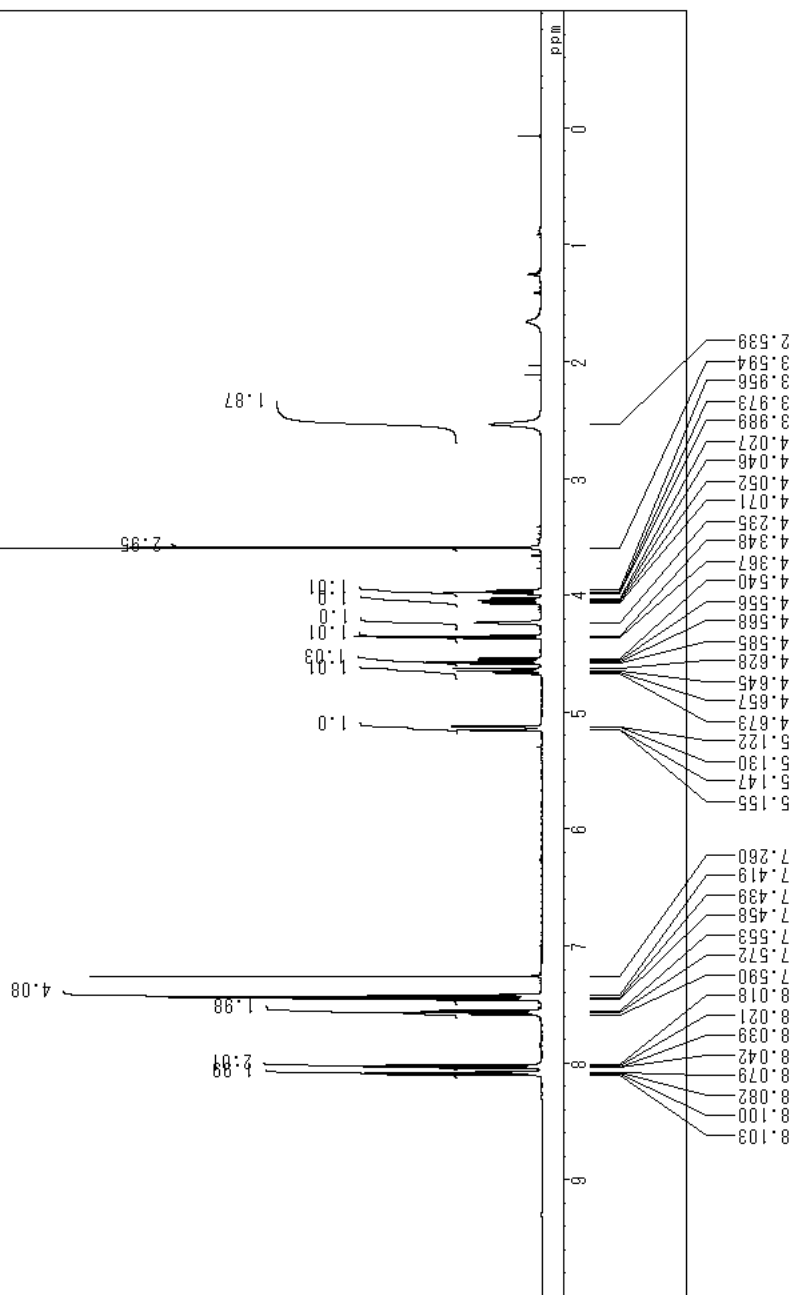


^1H -NMR spectrum (crude reaction mixture in the absence of catalyst **1c**)



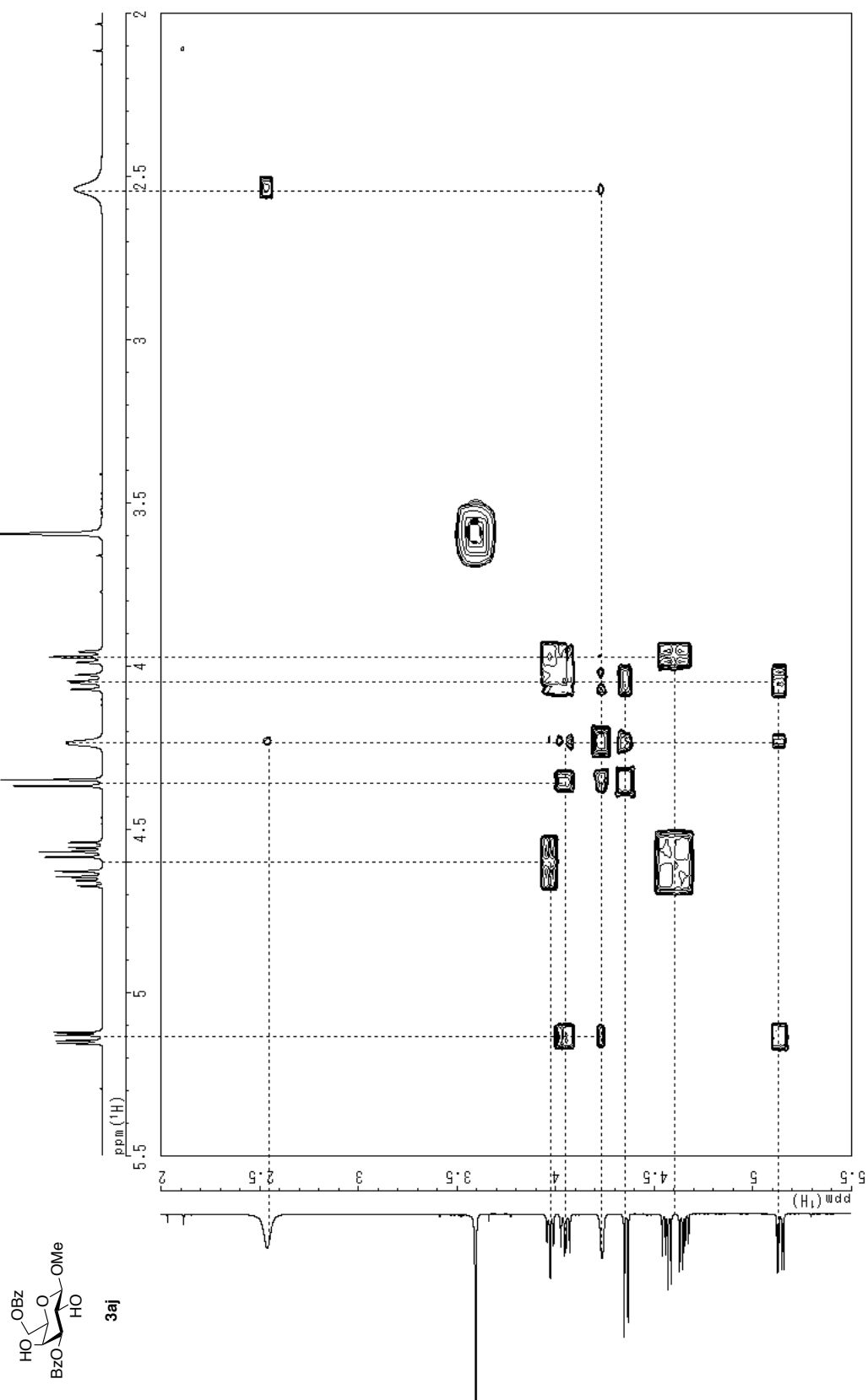


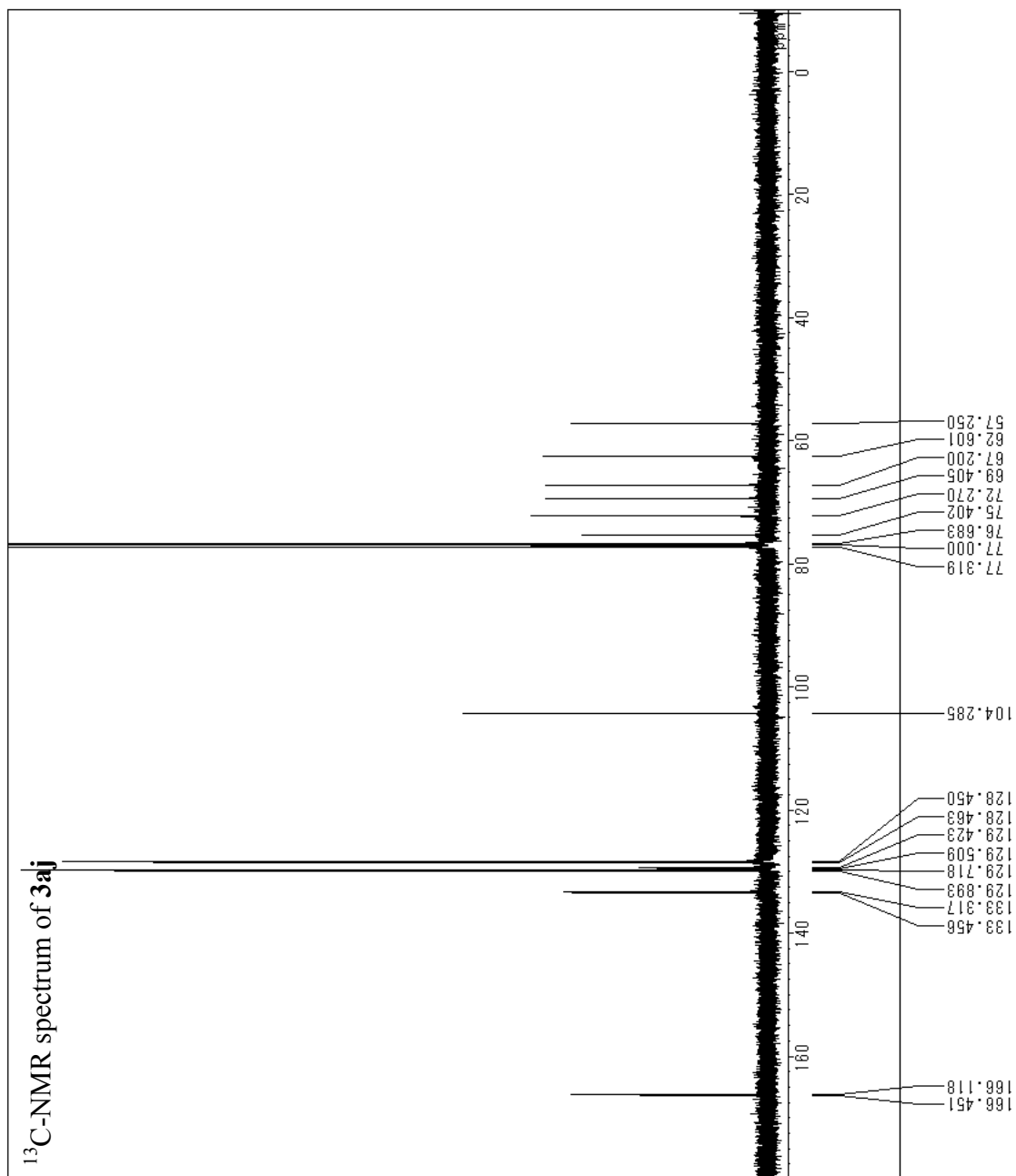
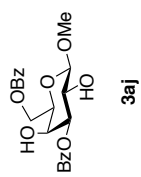
¹H-NMR spectrum of **3aj**



Comment TSV05023_column_20180318
 Date_01 2018/Mar/18
 ObsNuc ¹H
 ExMode PROTON_001
 ObsFreq 300.45 MHz
 Scan 32
 AcqTime 2.589 s
 Acc. Interval 5.589 s
 Spinning 18.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

^1H - ^1H COSY spectrum of **3aj**





Comment TSV05023_13C_20180316_01
 Date 2016/Mar/16
 ObsNuc ¹³C
 ExMode CARBON_001
 ObsFreq 100.66 MHz
 Scan 512
 AcqTime 1.3831 s
 Acc. Interval 3.3831 s
 Spinning 20.0 Hz
 Temperature 25.0 °C
 Solvent cdcl₃

12. References

- (1) Coghlan, S. W.; Giles, R. L.; Howard, J. A. K.; Patrick, L. G. F.; Probert, M. R.; Smith, G. E.; Whiting, A. Synthesis and structure of potential Lewis acid–Lewis base bifunctional catalysts: 2-*N,N*-diisopropylaminophenylboronate derivatives. *J. Organomet. Chem.* **2005**, *690*, 4784–4793.
- (2) Ishihara, K.; Sakakura, A. Process for producing carboxylic anhydride, and arylboronic acid compound. WO 2010/103976 A1.
- (3) Dimitrijević, E.; Taylor, M. S. 9-Hetero-10- boraanthracene-derived borinic acid catalysts for regioselective activation of polyols. *Chem. Sci.* **2013**, *4*, 3298–3303.
- (4) Sakakura, A.; Yamashita, R.; Ohkubo, T.; Akakura, M.; Ishihara, K. Intramolecular dehydrative condensation of dicarboxylic acids with Brønsted base-assisted boronic acid catalysts. *Aust. J. Chem.* **2011**, *64*, 1458–1465.
- (5) Ishihara, M.; Togo, H. An efficient preparation of 2-imidazolines and imidazoles from aldehydes with molecular iodine and (diacetoxyiodo)benzene. *Synlett*, **2006**, 227–230.
- (6) Lee, D.; Taylor, M. S. Borinic acid-catalyzed regioselective acylation of carbohydrate derivatives. *J. Am. Chem. Soc.* **2011**, *133*, 3724–3727.