

Supporting Information

Silver-Catalyzed Stereoselective Formation of Glucosides Using Glucosyl Ynenoates as Donors

Xu Dong,^a Li Chen,^{*ab} Zhitong Zheng,^b Xu Ma,^b Zaigang Luo^b and Liming Zhang^{*b}

^a State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, P.R. China

^b Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA

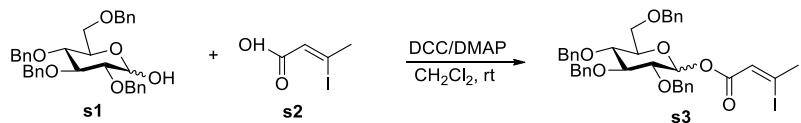
Table of Contents

1. General Information.....	S2
2. Synthesis of Compound s3	S2
3. Synthesis of Compound 1	S3
4. Synthesis of Compounds 2 and 3	S5
5. References	S12
6. NMR Spectra for New Compounds.....	S13

1. General Information

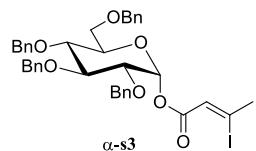
Ethyl acetate (ACS grade), hexanes (ACS grade) and diethyl ether (ACS grade) were purchased from Fisher Scientific and used without further purification. Anhydrous dichloromethane (HPLC grade), 1,2-dichloroethane (HPLC grade) were purified by distillation over calcium hydride. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates. Organic solutions were concentrated by rotary evaporation. Flash column chromatography was performed over Silicycle silica gel (230-400 mesh). Melting points were measured on an X-4 binocular microscope melting point apparatus (Beijing Tech Instruments Co., Beijing, China) and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 500 MHz and 600 MHz spectrometers using residue solvent peaks as internal standards (CHCl_3 , ^1H : 7.26 ppm; ^{13}C : 77.00 ppm). Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Xevo G2-XS QTOF Quadrupole Time-of-Flight Mass Spectrometry using electron spray ionization. Optical rotations were measured by using a Rudolph Autopol III polarimeter with a sodium lamp (D line, 589 nm). All pure α/β substrates were separated by multiple silica gel columns chromatography (hexane/ethyl acetate, 5:1).

2. Synthesis of Compound s3

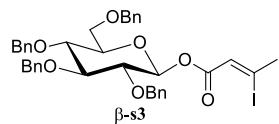


A solution of **s1** (1 mmol), acid **s2** (1 mmol), DMAP (12.2 mg, 0.1 mmol), and DCC (0.227 g, 1.1 mmol) in dry CH_2Cl_2 (10 mL) was stirred for 4 h at room temperature. The mixture was filtrated and concentrated in vacuum. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 6:1) to provide **s3**.

Compound α -s3 + β -s3: 0.68 g, 94% yield, $\alpha/\beta = 1.1:1$.



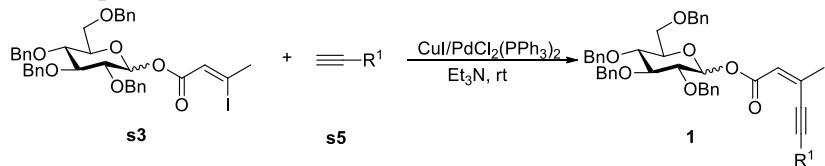
Compound α -s3: White crystals, mp 43–44 °C; $[\alpha]_D^{24}$ 70.2 (c 0.54, CHCl_3); IR (KBr) ν_{\max} 2866, 1736, 1622, 1454, 1138, 1072, 1014, 772, 736; ^1H NMR (600 MHz, CDCl_3) δ 7.36 – 7.24 (m, 18H), 7.17 – 7.13 (m, 2H), 6.51 (d, $J = 3.5$ Hz, 1H), 6.39 (d, $J = 1.3$ Hz, 1H), 4.96 (d, $J = 10.9$ Hz, 1H), 4.85 (d, $J = 10.7$ Hz, 1H), 4.82 (d, $J = 10.9$ Hz, 1H), 4.75 (d, $J = 11.4$ Hz, 1H), 4.64 (d, $J = 11.4$ Hz, 1H), 4.61 (d, $J = 12.2$ Hz, 1H), 4.52 (d, $J = 10.7$ Hz, 1H), 4.49 (d, $J = 12.1$ Hz, 1H), 3.98 (t, $J = 9.3$ Hz, 1H), 3.91 (dt, $J = 9.9$ Hz, 3Hz, 1H), 3.79 – 3.72 (m, 3H), 3.66 (dd, $J = 10.9$, 1.8 Hz, 1H), 2.76 (d, $J = 1.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 162.44, 138.62, 138.07, 137.80, 137.50, 128.46, 128.39, 128.26, 127.95, 127.94, 127.92, 127.85, 127.77, 127.73, 127.63, 125.11, 115.78, 90.14, 81.69, 78.84, 76.89, 75.66, 75.24, 73.55, 73.17, 73.00, 68.06, 36.82; HRMS (EI) m/z calcd for $\text{C}_{38}\text{H}_{39}\text{InaO}_7$ [M + Na] $^+$ 757.1638, found 757.1650.



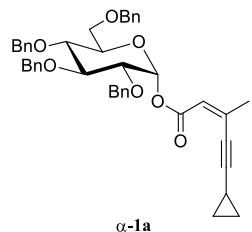
Compound β -s3: White crystals, mp 48–49 °C; $[\alpha]_D^{25}$ 5.9 (c 2.8, CHCl_3); IR (KBr) ν_{\max} 2868, 1743,

1624, 1454, 1159, 1076, 1057, 736; ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.27 (m, 18H), 7.19 – 7.14 (m, 2H), 6.24 (d, J = 1.4 Hz, 1H), 5.74 (d, J = 8.1 Hz, 1H), 4.93 (d, J = 11.0 Hz, 1H), 4.86 (d, J = 7.2 Hz, 1H), 4.84 (d, J = 7.0 Hz, 1H), 4.80 (d, J = 11.4 Hz, 1H), 4.77 (d, J = 11.4 Hz, 1H), 4.66 (d, J = 12.1 Hz, 1H), 4.57 (d, J = 10.7 Hz, 1H), 4.50 (d, J = 12.1 Hz, 1H), 3.83 – 3.74 (m, 4H), 3.65 (t, J = 8.5 Hz, 1H), 3.63 – 3.59 (m, 1H), 2.77 (d, J = 1.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.38, 138.41, 138.11, 138.04, 137.96, 128.43, 128.42, 128.38, 128.01, 127.97, 127.91, 127.89, 127.80, 127.73, 127.71, 127.68, 124.60, 116.68, 94.14, 84.86, 81.06, 77.23, 75.75, 75.60, 75.05, 73.54, 68.07, 36.90; HRMS (EI) m/z calcd for $\text{C}_{38}\text{H}_{39}\text{InaO}_7$ [M + Na]⁺ 757.1638, found 757.1650.

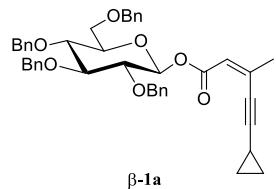
3. Synthesis of Compound 1



Under an argon atmosphere, to a solution of **s3** (1 mmol) in Et_3N (5 mL) were added compound **s-5** (2 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.021 g, 0.03 mmol) and CuI (0.019 g, 0.1 mmol) at room temperature. Then the mixture was stirred for 12 h. The mixture was filtrated and the filtrate was evaporated to remove Et_3N under reduce pressure. The residue was purified by chromatography on silica gel (eluent: hexane/ethyl acetate = 5:1) afforded compound **1**.

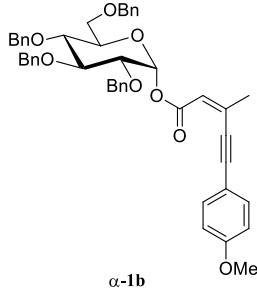


Compound $\alpha\text{-1a}$: White crystals, 0.64 g, 95% yield, mp 34–34 °C (recrystallized from ethyl acetate and hexane); $[\alpha]_D^{25}$ 71.5 (*c* 0.50, CHCl_3); IR (KBr) ν_{max} 2866, 2210, 1731, 1704, 1454, 1154, 1107, 1027, 735; ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.24 (m, 18H), 7.12 (dd, J = 6.5, 3.0 Hz, 2H), 6.52 (d, J = 3.5 Hz, 1H), 5.97 (d, J = 1.4 Hz, 1H), 4.99 (d, J = 10.9 Hz, 1H), 4.85 (d, J = 10.6 Hz, 1H), 4.82 (d, J = 10.9 Hz, 1H), 4.76 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.8 Hz, 2H), 4.51 (t, J = 11.5 Hz, 2H), 4.06 (t, J = 9.4 Hz, 1H), 4.01 – 3.97 (m, 1H), 3.78 (ddd, J = 9.1, 5.7, 2.4 Hz, 2H), 3.74 (dd, J = 9.6, 3.5 Hz, 1H), 3.67 (dd, J = 10.9, 1.9 Hz, 1H), 2.02 (d, J = 1.4 Hz, 3H), 1.59 (ddd, J = 8.2, 5.5, 3.1 Hz, 1H), 0.84 – 0.76 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.34, 138.80, 138.26, 137.94, 137.74, 137.43, 128.41, 128.38, 128.29, 128.21, 127.97, 127.85, 127.83, 127.69, 127.67, 127.58, 122.42, 108.11, 89.73, 81.88, 78.94, 76.98, 75.88, 75.67, 75.15, 73.54, 72.96, 72.89, 68.17, 26.09, 9.57, 9.56, 0.94; HRMS (EI) m/z calcd for $\text{C}_{43}\text{H}_{44}\text{NaO}_7$ [M + Na]⁺ 695.2985, found 695.3016.

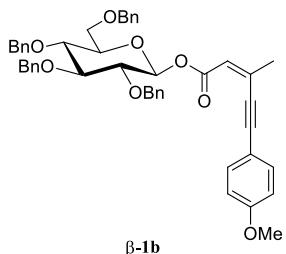


Compound $\beta\text{-1a}$: White crystals, 0.65 g, 96% yield, mp 40–41 °C (recrystallized from ethyl acetate and hexane); $[\alpha]_D^{25}$ 26.6 (*c* 0.50, CHCl_3); IR (KBr) ν_{max} 2867, 2212, 1738, 1609, 1360, 1150, 1075, 1028, 736; ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.22 (m, 18H), 7.17 – 7.14 (m, 2H), 5.89 (d, J = 1.4 Hz, 1H),

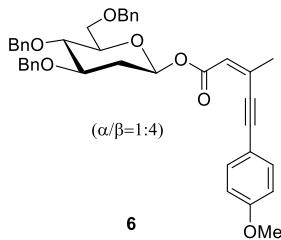
5.71 (d, $J = 8.1$ Hz, 1H), 4.90 (d, $J = 10.9$ Hz, 1H), 4.82 (d, $J = 10.5$ Hz, 2H), 4.79 (d, $J = 11.2$ Hz, 1H), 4.73 (d, $J = 11.2$ Hz, 1H), 4.63 (d, $J = 12.1$ Hz, 1H), 4.55 (d, $J = 10.7$ Hz, 1H), 4.48 (d, $J = 12.1$ Hz, 1H), 3.79 – 3.70 (m, 4H), 3.63 – 3.57 (m, 2H), 2.02 (d, $J = 1.3$ Hz, 3H), 1.53 – 1.47 (m, 1H), 0.94 – 0.87 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.07, 138.50, 138.48, 138.14, 138.11, 138.04, 128.39, 128.36, 128.33, 128.08, 127.92, 127.90, 127.89, 127.75, 127.68, 127.66, 127.61, 121.83, 108.48, 93.82, 84.84, 81.19, 77.31, 75.74, 75.60, 75.50, 75.02, 74.96, 73.50, 68.19, 25.85, 9.64, 9.63, 0.97; HRMS (EI) m/z calcd for $\text{C}_{43}\text{H}_{44}\text{NaO}_7$ [M + Na]⁺ 695.2985, found 695.3016.



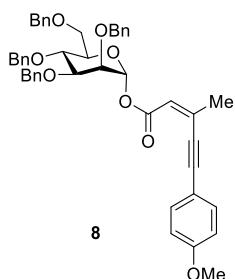
Compound $\alpha\text{-1b}$: White crystals, 0.67 g, 92% yield, mp 59–60 °C (recrystallized from ethyl acetate and hexane); $[\alpha]_D^{25}$ 50.8 (c 0.51, CHCl_3); IR (KBr) ν_{max} 2918, 2196, 1730, 1599, 1510, 1250, 1157, 1109, 1072, 1027, 736; ^1H NMR (500 MHz, CDCl_3) δ 7.52 (d, $J = 8.9$ Hz, 2H), 7.37 – 7.24 (m, 18H), 7.15 (dd, $J = 7.2, 2.2$ Hz, 2H), 6.76 (d, $J = 8.9$ Hz, 2H), 6.51 (d, $J = 3.5$ Hz, 1H), 6.06 (d, $J = 1.4$ Hz, 1H), 4.90 (d, $J = 10.9$ Hz, 1H), 4.84 (d, $J = 10.7$ Hz, 1H), 4.76 (d, $J = 11.4$ Hz, 1H), 4.70 (d, $J = 10.9$ Hz, 1H), 4.64 (d, $J = 11.5$ Hz, 1H), 4.61 (d, $J = 12.2$ Hz, 1H), 4.52 (d, $J = 10.7$ Hz, 1H), 4.47 (d, $J = 12.1$ Hz, 1H), 4.01 (t, $J = 9.3$ Hz, 1H), 3.97 – 3.93 (m, 1H), 3.79 – 3.72 (m, 6H), 3.65 (dd, $J = 10.9, 1.9$ Hz, 1H), 2.16 (d, $J = 1.3$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.28, 160.38, 138.79, 138.25, 137.91, 137.70, 136.96, 133.90, 128.42, 128.36, 128.34, 128.24, 127.95, 127.94, 127.86, 127.80, 127.70, 127.67, 127.54, 122.53, 114.66, 114.00, 102.13, 89.78, 87.79, 81.87, 79.00, 77.08, 75.55, 75.22, 73.54, 73.06, 72.79, 68.16, 55.29, 25.73; HRMS (EI) m/z calcd for $\text{C}_{47}\text{H}_{46}\text{NaO}_8$ [M + Na]⁺ 761.3090, found 761.3074.



Compound $\beta\text{-1b}$: White crystals, 0.66 g, 91% yield, mp 65–65 °C (recrystallized from ethyl acetate and hexane); $[\alpha]_D^{25}$ 49.0 (c 0.51, CHCl_3); IR (KBr) ν_{max} 2916, 2196, 1736, 1597, 1510, 1250, 1164, 1075, 1028, 736; ^1H NMR (500 MHz, CDCl_3) δ 7.53 (d, $J = 8.9$ Hz, 2H), 7.36 – 7.23 (m, 18H), 7.17 (d, $J = 7.7$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 5.97 (d, $J = 1.3$ Hz, 1H), 5.78 (d, $J = 8.1$ Hz, 1H), 4.91 (d, $J = 10.9$ Hz, 1H), 4.86 – 4.78 (m, 3H), 4.73 (d, $J = 11.2$ Hz, 1H), 4.65 (d, $J = 12.1$ Hz, 1H), 4.57 (d, $J = 10.7$ Hz, 1H), 4.50 (d, $J = 12.1$ Hz, 1H), 3.82 (s, 3H), 3.81 – 3.72 (m, 4H), 3.64 (t, $J = 8.4$ Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.02, 160.49, 138.48, 138.13, 138.11, 138.04, 137.68, 133.98, 128.39, 128.35, 128.34, 128.09, 127.94, 127.91, 127.89, 127.75, 127.67, 127.65, 127.61, 122.15, 114.68, 114.08, 102.39, 93.89, 87.79, 84.84, 81.24, 77.32, 75.72, 75.56, 75.03, 74.98, 73.54, 68.25, 55.33, 25.49; HRMS (EI) m/z calcd for $\text{C}_{47}\text{H}_{46}\text{NaO}_8$ [M + Na]⁺ 761.3090, found 761.3074.



Compound 6: colorless oil, 0.40 g, 63% yield, recrystallization was not successful (α/β anomeric ratio 1:4); IR (KBr) ν_{\max} ; ^1H NMR (500 MHz, CDCl_3) δ 7.54 – 7.47 (m, 2H), 7.36 – 7.24 (m, 13H), 7.21 – 7.17 (m, 2H), 6.85 (dd, J = 8.6, 1.5 Hz, 1.6H), 6.74 (dd, J = 8.7, 1.4 Hz, 0.4H), 6.42 – 6.37 (m, 0.2H), 6.02 (d, J = 1.4 Hz, 0.8H), 5.95 (d, J = 1.4 Hz, 0.2H), 5.82 (dd, J = 10.1, 2.1 Hz, 0.8H), 4.90 (d, J = 10.8 Hz, 2H), 4.71 – 4.47 (m, 5H), 4.03 (ddd, J = 11.6, 9.0, 4.9 Hz, 0.2H), 3.97 – 3.92 (m, 0.2H), 3.87 – 3.71 (m, 6H), 3.67 (t, J = 9.4 Hz, 1H), 3.56 (ddd, J = 9.5, 3.7, 2.1 Hz, 0.8H), 2.47 – 2.39 (m, 0.8H), 2.37 (ddd, J = 13.5, 5.0, 1.6 Hz, 0.2H), 2.15 (d, J = 1.4 Hz, 3H), 1.88 (ddd, J = 13.7, 11.4, 3.6 Hz, 0.2H), 1.83 – 1.75 (m, 0.8H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.29, 163.00, 160.45, 160.39, 138.53, 138.47, 138.33, 138.19, 138.14, 138.09, 137.32, 136.43, 133.89, 133.81, 133.64, 128.46, 128.36, 128.34, 128.33, 128.19, 127.98, 127.94, 127.73, 127.71, 127.69, 127.61, 127.58, 127.57, 122.72, 122.36, 114.69, 114.55, 114.06, 114.04, 102.08, 101.95, 92.15, 92.01, 87.67, 87.60, 79.11, 77.75, 77.45, 77.20, 75.88, 75.08, 75.01, 73.53, 73.51, 73.46, 71.77, 71.64, 68.69, 68.52, 55.31, 55.29, 35.59, 34.52, 25.75, 25.46.; HRMS (EI) m/z calcd for $\text{C}_{40}\text{H}_{40}\text{NaO}_7$ [M + Na]⁺ 655.2672, found.



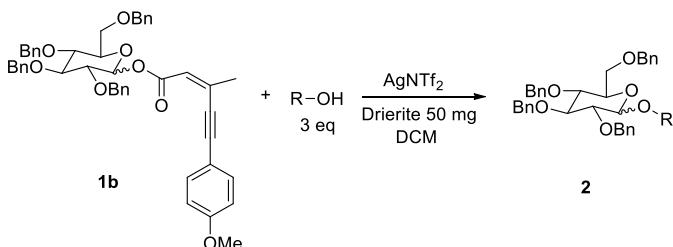
Compound 8: colorless oil, 0.55 g, 74% yield; $[\alpha]_D^{25}$; IR (KBr) ν_{\max} ; ^1H NMR (500 MHz, CDCl_3) δ 7.50 – 7.45 (m, 2H), 7.41 (dd, J = 7.7, 1.8 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.31 – 7.22 (m, 14H), 7.17 (dd, J = 7.5, 2.0 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 6.38 (d, J = 2.0 Hz, 1H), 5.90 (d, J = 1.5 Hz, 1H), 4.87 (d, J = 10.7 Hz, 1H), 4.81 (d, J = 12.4 Hz, 1H), 4.73 (d, J = 12.4 Hz, 1H), 4.67 (d, J = 12.1 Hz, 1H), 4.53 (dd, J = 14.8, 11.4 Hz, 2H), 4.45 – 4.39 (m, 2H), 4.11 (t, J = 9.7 Hz, 1H), 3.93 (ddd, J = 10.0, 4.6, 2.3 Hz, 2H), 3.83 (dd, J = 3.2, 2.1 Hz, 1H), 3.79 (dd, J = 11.2, 4.5 Hz, 1H), 3.73 (s, 3H), 3.71 (dd, J = 11.2, 1.9 Hz, 1H), 2.13 (d, J = 1.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.97, 160.46, 138.53, 138.37, 138.28, 137.98, 136.96, 133.87, 128.40, 128.34, 128.31, 128.30, 128.28, 128.27, 128.08, 127.99, 127.98, 127.87, 127.65, 127.60, 127.58, 127.53, 127.44, 122.21, 114.43, 114.06, 102.32, 91.74, 87.62, 79.57, 77.23, 75.23, 74.45, 74.34, 73.59, 73.49, 72.37, 71.95, 68.92, 55.30, 25.77; HRMS (EI) m/z calcd for $\text{C}_{47}\text{H}_{46}\text{NaO}_8$ [M + Na]⁺ 761.3090, found.

4. Synthesis of Compounds 2 and 3:

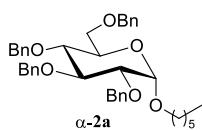
Table S1. AgNTf₂-catalyzed glycosidation reactions of **1b**

Entry	sub- strate	Acceptor	Temp (°C)	Time (h)	2	Yield ^b	$\alpha:\beta^c$
-------	----------------	----------	--------------	----------	----------	--------------------	------------------

1	α-1b	isopropanol	-30 → -20	50	2c	92%	1:7.5
2	β-1b		-40	48	2c	91%	9:1
3	α-1b		-40 → -30	48	2d	88%	1:4
4	β-1b		-40 → -30	36	2d	87%	23:1
5	α-1b	BnOH	-40 → -30	48	2e	93%	1:6.7
6	β-1b		-40	48	2e	95%	10:1
7	α-1b	t-BuOH	-40 → -30	48	2f	91%	1:6.5
8	β-1b		-30	36	2f	92%	6.7:1
9	α-1b		-40 → -30	48	2g	87%	1:11
10	β-1b		-30	36	2g	89%	10:1
11	α-1b	cholesterol	-20	36	2h	85%	1:8
12	β-1b		-30	36	2h	86%	8:1
13	α-1b		-20	36	2i	60%	1:2
14	β-1b		-30	36	2i	85%	2.2:1
15	β-1b		rt	8	2i	58%	1.6:1
16	β-1b		0	8	2j	83%	2:1

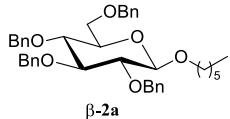


To a mixture of compound **1b** (50 mg, 0.068 mmol), alcohol (2.0 mmol) and 50 mg drierite in CH_2Cl_2 (0.5 mL) cooled to the appropriate temperature (shown in Table S1) was added AgNTf_2 (5 mg, 0.014 mmol). The mixture was stirred for 5–48 hours monitored by TLC, quenched with $n\text{-Bu}_4\text{NCl}$ and then concentrated. The residue was purified by column chromatography (petroleum hexane/ethyl acetate = 10:1) on silica gel to afford compound **2**.

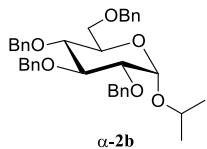


Compound α-2a: viscous liquid; $[\alpha]_D^{25}$ 36.2 (*c* 0.35, CHCl_3); IR (KBr) ν_{max} 2925, 2860, 1497, 1454, 1360, 1159, 1089, 1072, 1028, 735; ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.26 (m, 18H), 7.16 (dd, *J* =

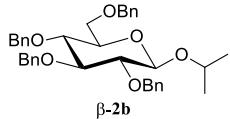
7.3, 2.0 Hz, 2H), 4.99 (d, J = 10.9 Hz, 1H), 4.83 (d, J = 7.9 Hz, 1H), 4.81 (d, J = 8.1 Hz, 1H), 4.80 – 4.74 (m, 2H), 4.65 (d, J = 12.1 Hz, 1H), 4.61 (d, J = 12.1 Hz, 1H), 4.47 (d, J = 11.7 Hz, 2H), 3.99 (t, J = 9.3 Hz, 1H), 3.80 – 3.76 (m, 1H), 3.72 (dd, J = 10.6, 3.7 Hz, 1H), 3.62 – 3.59 (m, 3H), 3.55 (dd, J = 9.6, 3.6 Hz, 1H), 3.42 (dt, J = 9.8, 6.8 Hz, 1H), 1.66 – 1.59 (m, 2H), 1.36 – 1.27 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.93, 138.37, 138.28, 137.97, 128.38, 128.35, 128.35, 128.32, 128.01, 127.92, 127.87, 127.78, 127.66, 127.63, 127.51, 96.87, 82.12, 80.12, 77.80, 75.66, 75.06, 73.46, 73.10, 70.08, 68.56, 68.23, 31.64, 29.37, 25.83, 22.58; 14.07. HRMS (EI) m/z calcd for $\text{C}_{40}\text{H}_{48}\text{NaO}_6$ [M + Na]⁺ 647.3349, found 647.3330.



Compound $\beta\text{-}2\text{a}$: White crystals, mp 30–31 °C (from ethyl acetate and hexane); $[\alpha]_D^{25}$ 3.4 (c 0.43, CHCl_3); IR (KBr) ν_{max} 2926, 2858, 1497, 1454, 1361, 1071, 1029, 734; ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.26 (m, 18H), 7.16 (dd, J = 7.3, 2.1 Hz, 2H), 4.95 (d, J = 11.0 Hz, 1H), 4.93 (d, J = 11.0 Hz, 1H), 4.81 (d, J = 10.8 Hz, 1H), 4.78 (d, J = 10.9 Hz, 1H), 4.72 (d, J = 11.0 Hz, 1H), 4.61 (d, J = 12.2 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 4.53 (d, J = 10.8 Hz, 1H), 4.39 (d, J = 7.8 Hz, 1H), 3.96 (dt, J = 9.5, 6.5 Hz, 1H), 3.74 (dd, J = 10.8, 1.9 Hz, 1H), 3.69 – 3.62 (m, 2H), 3.59 – 3.50 (m, 2H), 3.48 – 3.42 (m, 2H), 1.69 – 1.62 (m, 2H), 1.43 – 1.37 (m, 2H), 1.30 (dd, J = 7.3, 3.6 Hz, 4H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.64, 138.52, 138.22, 138.11, 128.36, 128.34, 128.32, 128.13, 127.96, 127.86, 127.74, 127.72, 127.61, 127.56, 103.65, 84.72, 82.28, 77.96, 75.67, 74.99, 74.85, 74.78, 73.47, 70.17, 69.04, 31.65, 29.76, 25.86, 22.59, 14.04; HRMS (EI) m/z calcd for $\text{C}_{40}\text{H}_{48}\text{NaO}_6$ [M + Na]⁺ 647.3349, found 647.3382.

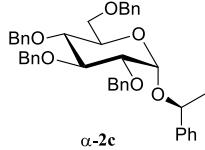


Compound $\alpha\text{-}2\text{b}$: viscous liquid; $[\alpha]_D^{25}$ 33.1 (c 0.66, CHCl_3); IR (KBr) ν_{max} 2922, 2866, 1497, 1454, 1072, 1039, 735; ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.26 (m, 18H), 7.14 – 7.11 (m, 2H), 5.00 (d, J = 10.8 Hz, 1H), 4.88 (d, J = 3.7 Hz, 1H), 4.83 (d, J = 7.3 Hz, 1H), 4.81 (d, J = 7.5 Hz, 1H), 4.77 (d, J = 12.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.1 Hz, 1H), 4.48 (s, 1H), 4.45 (d, J = 2.1 Hz, 1H), 3.99 (t, J = 9.3 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.84 (ddd, J = 10.1, 3.3, 2.1 Hz, 1H), 3.73 (dd, J = 10.6, 3.6 Hz, 1H), 3.66 – 3.60 (m, 2H), 3.55 (dd, J = 9.7, 3.7 Hz, 1H), 1.22 (d, J = 6.3 Hz, 3H), 1.18 (d, J = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.96, 138.27, 138.24, 137.97, 128.40, 128.36, 128.33, 128.15, 127.98, 127.91, 127.88, 127.83, 127.69, 127.64, 127.51, 94.77, 82.13, 79.93, 77.89, 75.66, 75.13, 73.45, 73.14, 70.03, 69.03, 68.55, 23.17, 21.16; HRMS (EI) m/z calcd for $\text{C}_{37}\text{H}_{42}\text{NaO}_6$ [M + Na]⁺ 605.2879, found 605.2911.

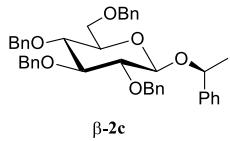


Compound $\beta\text{-}2\text{b}$: White crystals, mp 109–110 °C (from ethyl acetate and hexane); $[\alpha]_D^{25}$ 10.5 (c 0.44, CHCl_3); IR (KBr) ν_{max} 2904, 2864, 1497, 1453, 1068, 1039, 731; ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.26 (m, 18H), 7.19 – 7.15 (m, 2H), 4.97 (d, J = 10.8 Hz, 1H), 4.92 (d, J = 10.9 Hz, 1H), 4.82 (d, J = 10.8 Hz, 1H), 4.78 (d, J = 10.9 Hz, 1H), 4.71 (d, J = 10.9 Hz, 1H), 4.61 (d, J = 12.2 Hz, 1H), 4.58 – 4.52 (m, 2H), 4.47 (d, J = 7.8 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.74 (d, J = 10.0 Hz, 1H), 3.68 – 3.61 (m, 2H),

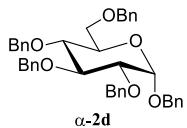
3.55 (t, $J = 9.3$ Hz, 1H), 3.48 – 3.41 (m, 2H), 1.32 (d, $J = 6.2$ Hz, 3H), 1.25 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.67, 138.54, 138.29, 138.14, 128.36, 128.34, 128.31, 128.20, 127.98, 127.87, 127.72, 127.68, 127.63, 127.55, 127.52, 102.18, 84.85, 82.31, 78.00, 75.67, 74.97, 74.82, 73.43, 72.35, 69.19, 23.73, 22.23; HRMS (EI) m/z calcd for $\text{C}_{37}\text{H}_{42}\text{NaO}_6$ [$\text{M} + \text{Na}]^+$ 605.2879, found 605.2911.



Compound $\alpha\text{-}2\text{c}$: viscous liquid; $[\alpha]_D^{25}$ 36.4 (c 0.20, CHCl_3); IR (KBr) ν_{max} 2923, 2854, 1497, 1454, 1072, 1028, 735; ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.22 (m, 23H), 7.08 (dd, $J = 6.6, 2.9$ Hz, 2H), 5.00 (dd, $J = 7.3, 3.5$ Hz, 2H), 4.82 (d, $J = 7.3$ Hz, 1H), 4.80 (d, $J = 8.5$ Hz, 1H), 4.77 (d, $J = 10.7$ Hz, 1H), 4.67 (dd, $J = 9.2, 5.7$ Hz, 2H), 4.50 (d, $J = 12.2$ Hz, 1H), 4.42 (d, $J = 10.7$ Hz, 1H), 4.33 (d, $J = 12.1$ Hz, 1H), 3.97 (t, $J = 9.3$ Hz, 1H), 3.63 – 3.56 (m, 2H), 3.51 (q, $J = 2.8$ Hz, 2H), 3.15 (dd, $J = 11.9, 3.4$ Hz, 1H), 1.50 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.48, 138.96, 138.37, 138.22, 137.97, 128.44, 128.35, 128.32, 128.26, 128.22, 128.08, 127.98, 127.88, 127.84, 127.83, 127.65, 127.56, 127.50, 127.34, 126.32, 96.27, 82.09, 80.22, 77.80, 76.27, 75.63, 75.09, 73.29, 73.16, 70.13, 68.03, 22.20; HRMS (EI) m/z calcd for $\text{C}_{42}\text{H}_{44}\text{NaO}_6$ [$\text{M} + \text{Na}]^+$ 667.3036, found 667.3059.

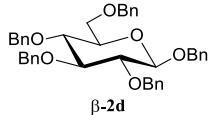


Compound $\beta\text{-}2\text{c}$: White crystals, mp 29–31 °C (from ethyl acetate and hexane); $[\alpha]_D^{25}$ – 16.1 (c 0.20, CHCl_3); IR (KBr) ν_{max} 2923, 2857, 1496, 1454, 1071, 1028, 735; ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.24 (m, 23H), 7.15 (dd, $J = 7.4, 2.0$ Hz, 2H), 5.01 (d, $J = 11.0$ Hz, 1H), 4.98 (q, $J = 6.6$ Hz, 1H), 4.86 (d, $J = 10.9$ Hz, 1H), 4.80 (d, $J = 11.0$ Hz, 1H), 4.75 (d, $J = 11.0$ Hz, 1H), 4.72 (d, $J = 10.9$ Hz, 1H), 4.64 (d, $J = 12.2$ Hz, 1H), 4.58 (d, $J = 12.2$ Hz, 1H), 4.52 (d, $J = 10.9$ Hz, 1H), 4.27 (d, $J = 7.4$ Hz, 1H), 3.74 (dd, $J = 10.8, 1.9$ Hz, 1H), 3.67 (dd, $J = 10.8, 4.9$ Hz, 1H), 3.57 (t, $J = 9.2$ Hz, 1H), 3.55 – 3.48 (m, 2H), 3.32 (ddd, $J = 9.4, 4.9, 1.9$ Hz, 1H), 1.55 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 142.34, 138.63, 138.52, 138.27, 138.19, 128.45, 128.34, 128.32, 128.31, 128.27, 128.08, 127.84, 127.72, 127.67, 127.64, 127.58, 127.53, 127.52, 126.70, 100.47, 84.82, 82.30, 77.96, 75.71, 75.63, 74.83, 74.76, 74.69, 73.40, 69.03, 24.22; HRMS (EI) m/z calcd for $\text{C}_{42}\text{H}_{44}\text{NaO}_6$ [$\text{M} + \text{Na}]^+$ 667.3036, found 667.3059.

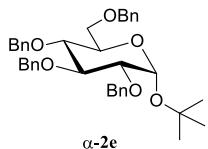


Compound $\alpha\text{-}2\text{d}$: White crystals, mp 36–38 °C (from ethyl acetate and hexane); $[\alpha]_D^{25}$ 57.9 (c 0.28, CHCl_3); IR (KBr) ν_{max} 2920, 2866, 1496, 1454, 1071, 1028, 735; ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.26 (m, 21H), 7.16 – 7.12 (m, 2H), 5.00 (d, $J = 10.9$ Hz, 1H), 4.85 (d, $J = 3.6$ Hz, 1H), 4.84 (d, $J = 4.8$ Hz, 1H), 4.82 (d, $J = 4.8$ Hz, 1H), 4.69 (dd, $J = 12.1, 8.1$ Hz, 2H), 4.61 (d, $J = 12.1$ Hz, 1H), 4.56 (dd, $J = 12.1, 1.6$ Hz, 2H), 4.47 (d, $J = 11.7$ Hz, 2H), 4.04 (t, $J = 9.3$ Hz, 1H), 3.81 (ddd, $J = 10.1, 3.4, 2.1$ Hz, 1H), 3.70 (dd, $J = 10.6, 3.6$ Hz, 1H), 3.67 – 3.63 (m, 1H), 3.60 – 3.54 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.87, 138.26, 138.18, 137.96, 137.19, 128.42, 128.36, 128.34, 127.93, 127.92, 127.88, 127.88, 127.81, 127.74, 127.73, 127.66, 127.53, 95.63, 82.14, 79.91, 77.73, 75.70, 75.07,

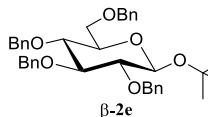
73.47, 73.00, 70.38, 69.13, 68.43; HRMS (EI) m/z calcd for $C_{41}H_{42}NaO_6$ [M + Na]⁺ 653.2879, found 653.2902.



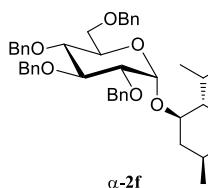
Compound $\beta\text{-2d}$: White crystals, mp 44–46 °C (from ethyl acetate and hexane); $[\alpha]_D^{25} -6.9$ (c 0.25, $CHCl_3$); IR (KBr) ν_{max} 2919, 2861, 1497, 1454, 1070, 1028, 734; 1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 23H), 7.19 – 7.14 (m, 2H), 4.98 (d, $J = 11.6$ Hz, 1H), 4.96 (d, $J = 11.6$ Hz, 1H), 4.92 (d, $J = 11.0$ Hz, 1H), 4.82 (d, $J = 10.9$ Hz, 1H), 4.78 (d, $J = 10.9$ Hz, 1H), 4.72 (d, $J = 10.9$ Hz, 1H), 4.68 (d, $J = 11.9$ Hz, 1H), 4.64 (d, $J = 12.2$ Hz, 1H), 4.57 (d, $J = 12.2$ Hz, 1H), 4.54 (d, $J = 10.9$ Hz, 1H), 4.52 (d, $J = 8.0$ Hz, 1H), 3.77 (dd, $J = 10.7$ Hz, 1.5Hz, 1H), 3.71 (dd, $J = 10.8$, 4.8 Hz, 1H), 3.68 – 3.59 (m, 2H), 3.53 (t, $J = 8.2$ Hz, 1H), 3.49 – 3.44 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.59, 138.40, 138.20, 138.12, 137.48, 128.38, 128.37, 128.35, 128.32, 128.16, 127.93, 127.85, 127.74, 127.73, 127.62, 127.59, 127.58, 102.60, 84.74, 82.31, 77.90, 75.69, 74.98, 74.91, 74.88, 73.49, 71.15, 68.96; HRMS (EI) m/z calcd for $C_{41}H_{42}NaO_6$ [M + Na]⁺ 653.2879, found 653.2902.



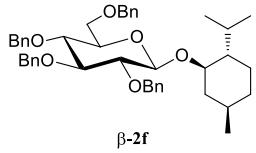
Compound $\alpha\text{-2e}$: viscous liquid; $[\alpha]_D^{25} 57.6$ (c 0.25, $CHCl_3$); IR (KBr) ν_{max} 2919, 2849, 1646, 1497, 1454, 1069, 735; 1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 18H), 7.16 – 7.11 (m, 2H), 5.14 (d, $J = 3.6$ Hz, 1H), 4.99 (d, $J = 10.8$ Hz, 1H), 4.84 (d, $J = 7.0$ Hz, 1H), 4.82 (d, $J = 7.3$ Hz, 1H), 4.73 (d, $J = 11.8$ Hz, 1H), 4.67 (d, $J = 11.9$ Hz, 1H), 4.65 (d, $J = 12.4$ Hz, 1H), 4.46 (dd, $J = 11.4$, 4.6 Hz, 2H), 4.04 – 3.94 (m, 2H), 3.77 (dd, $J = 10.4$, 3.3 Hz, 1H), 3.68 (t, $J = 9.5$ Hz, 1H), 3.60 (dd, $J = 10.4$, 1.7 Hz, 1H), 3.55 (dd, $J = 9.7$, 3.6 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.01, 138.32, 138.29, 138.04, 128.36, 128.36, 128.34, 128.30, 128.10, 127.97, 127.87, 127.74, 127.66, 127.59, 127.47, 91.48, 82.08, 80.14, 78.12, 75.52, 75.24, 75.10, 73.45, 73.08, 69.64, 68.66; 28.63. HRMS (EI) m/z calcd for $C_{38}H_{44}NaO_6$ [M + Na]⁺ 619.3036, found 619.3040.



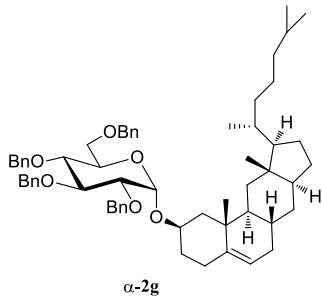
Compound $\beta\text{-2e}$: White crystals, mp 38–40 °C (from ethyl acetate and hexane); $[\alpha]_D^{25} 19.2$ (c 0.25, $CHCl_3$); IR (KBr) ν_{max} 2921, 2851, 1658, 1496, 1454, 1069, 1028, 737; 1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 18H), 7.18 (dd, $J = 7.3$, 2.1 Hz, 2H), 4.98 (d, $J = 10.9$ Hz, 1H), 4.92 (d, $J = 10.9$ Hz, 1H), 4.82 (d, $J = 10.9$ Hz, 1H), 4.78 (d, $J = 10.9$ Hz, 1H), 4.71 (d, $J = 10.9$ Hz, 1H), 4.64 – 4.49 (m, 4H), 3.71 (dd, $J = 10.6$, 1.8 Hz, 1H), 3.68 – 3.59 (m, 2H), 3.53 (t, $J = 9.2$ Hz, 1H), 3.49 – 3.39 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.63, 137.46, 137.31, 137.14, 127.34, 127.27, 127.15, 126.93, 126.87, 126.70, 126.59, 126.45, 96.81, 84.08, 81.34, 77.10, 75.04, 74.72, 73.91, 73.9, 73.59, 72.33, 68.32, 27.87; HRMS (EI) m/z calcd for $C_{38}H_{44}NaO_6$ [M + Na]⁺ 619.3036, found 619.3040.



Compound α -2f: viscous liquid; $[\alpha]_D^{25}$ 33.4 (*c* 0.25, CHCl₃); IR (KBr) ν_{max} 2922, 2869, 1497, 1454, 1360, 1072, 1028, 735; ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.26 (m, 18H), 7.13 (dd, *J* = 7.3, 2.0 Hz, 2H), 5.02 (d, *J* = 3.6 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 7.0 Hz, 1H), 4.81 (d, *J* = 7.2 Hz, 1H), 4.69 (q, *J* = 11.7 Hz, 2H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.46 (dd, *J* = 11.4, 5.8 Hz, 2H), 4.01 (t, *J* = 9.4 Hz, 1H), 3.97 (ddd, *J* = 10.3, 3.5, 2.1 Hz, 1H), 3.75 (dd, *J* = 10.5, 3.8 Hz, 1H), 3.65 – 3.61 (m, 2H), 3.54 (dd, *J* = 9.8, 3.6 Hz, 1H), 3.35 (td, *J* = 10.6, 4.3 Hz, 1H), 2.41 (dtd, *J* = 14.0, 6.9, 2.4 Hz, 1H), 2.12 (d, *J* = 12.1 Hz, 1H), 1.63 – 1.58 (m, 2H), 1.40 – 1.33 (m, 1H), 1.31 – 1.26 (m, 1H), 1.03 (dd, *J* = 23.2, 12.1 Hz, 1H), 0.94 (dd, *J* = 12.7, 2.9 Hz, 1H), 0.85 (d, *J* = 6.8, 3H), 0.84 (d, *J* = 6.8, 3H), 0.81 (dd, *J* = 11.9, 2.9 Hz, 1H), 0.70 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.91, 138.38, 138.31, 138.05, 128.34, 128.32, 128.31, 128.24, 127.90, 127.87, 127.63, 127.62, 127.61, 127.49, 127.46, 98.62, 81.97, 81.01, 80.55, 78.10, 75.47, 75.03, 73.44, 73.18, 70.29, 68.68, 48.75, 43.04, 34.26, 31.73, 24.57, 22.96, 22.27, 21.10, 16.05; HRMS (EI) *m/z* calcd for C₄₄H₅₄NaO₆ [M + Na]⁺ 701.3818, found 701.3803.

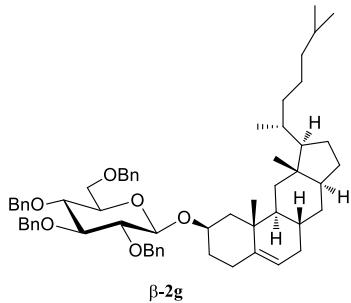


Compound β -2f: White crystals, mp 39–41 °C (from ethyl acetate and hexane); $[\alpha]_D^{25}$ – 28.4 (*c* 0.35, CHCl₃); IR (KBr) ν_{max} 2921, 2867, 1497, 1454, 1360, 1070, 1029, 734; ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.24 (m, 18H), 7.22 – 7.18 (m, 2H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.93 (d, *J* = 11.1 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 11.1 Hz, 1H), 4.69 (d, *J* = 10.9 Hz, 1H), 4.60 (t, *J* = 11.9 Hz, 2H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 3.70 (d, *J* = 3.2 Hz, 2H), 3.62 (dt, *J* = 18.4, 9.0 Hz, 2H), 3.50 (td, *J* = 10.7, 4.2 Hz, 1H), 3.44 – 3.38 (m, 2H), 2.35 (dtd, *J* = 13.9, 7.0, 2.3 Hz, 1H), 2.14 (d, *J* = 11.9 Hz, 1H), 1.66 (d, *J* = 12.0 Hz, 2H), 1.37 – 1.26 (m, 2H), 1.04 – 0.85 (m, 9H), 0.83 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.83, 138.57, 138.39, 138.23, 128.36, 128.31, 128.30, 128.27, 128.06, 127.76, 127.70, 127.62, 127.58, 127.48, 127.46, 100.75, 84.97, 82.22, 77.97, 77.74, 75.57, 74.97, 74.82, 74.81, 73.67, 69.34, 48.13, 40.96, 34.46, 31.47, 25.28, 23.23, 22.23, 21.07, 15.97; HRMS (EI) *m/z* calcd for C₄₄H₅₄NaO₆ [M + Na]⁺ 701.3818, found 701.3803.

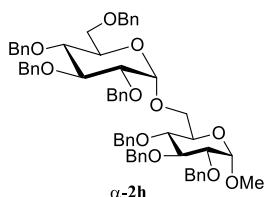


Compound α -2g: White crystals, mp 46–48°C (from ethyl acetate and hexane); $[\alpha]_D^{25}$ 28.2 (*c* 0.20, CHCl₃); IR (KBr) ν_{max} 2928, 2866, 1497, 1454, 1364, 1072, 1030, 733; ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.26 (m, 18H), 7.14 (dd, *J* = 7.3, 1.9 Hz, 2H), 5.28 (d, *J* = 5.2 Hz, 1H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1H), 4.83 (d, *J* = 7.9 Hz, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.47 (d, *J* = 6.7 Hz, 1H), 4.45 (d, *J* = 8.2 Hz, 1H), 4.00 (t, *J* = 9.3 Hz, 1H), 3.88 (d, *J* = 9.5 Hz, 1H), 3.74 (dd, *J* = 10.6, 3.7 Hz, 1H), 3.66 – 3.61 (m, 2H), 3.55 (dd, *J* = 9.7, 3.7 Hz, 1H), 3.51 – 3.43 (m, 1H), 2.42 (t, *J* = 12.3 Hz, 1H), 2.30 – 2.25 (m, 1H), 2.01 (d, *J* = 12.5 Hz, 1H), 1.95 (d, *J* = 17.0 Hz, 1H), 1.90 – 1.79 (m, 3H), 1.51 – 1.42 (m, 5H), 1.34 (d, *J* = 9.0 Hz, 3H), 1.17 – 0.99 (m, 12H), 0.93 – 0.84 (m, 13H), 0.68 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ

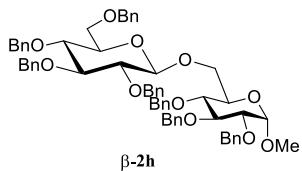
140.84, 138.96, 138.26, 138.25, 137.97, 128.41, 128.37, 128.36, 128.32, 128.13, 127.97, 127.90, 127.83, 127.69, 127.62, 127.51, 121.70, 94.61, 82.12, 79.93, 77.88, 76.52, 75.67, 75.12, 73.42, 73.06, 70.04, 68.59, 56.78, 56.16, 50.12, 42.32, 39.88, 39.78, 39.52, 37.11, 36.79, 36.19, 35.78, 31.93, 31.88, 29.96, 28.23, 28.01, 24.29, 23.82, 22.81, 22.56, 21.06, 19.39, 18.72, 11.85; HRMS (EI) m/z calcd for $C_{61}H_{80}NaO_6 [M + Na]^+$ 931.5853, found 931.5886.



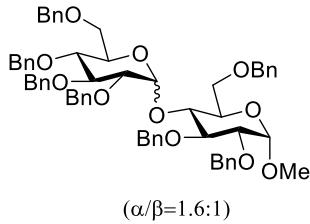
Compound $\beta\text{-}2\text{g}$: White crystals, mp 66–68 °C (from ethyl acetate and hexane); $[\alpha]_D^{25} - 0.2$ (c 0.33, $CHCl_3$); IR (KBr) ν_{max} 2934, 2867, 1497, 1454, 1363, 1070, 1028, 733; 1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 18H), 7.17 (dd, $J = 7.3, 1.8$ Hz, 2H), 5.34 (d, $J = 5.2$ Hz, 1H), 4.97 (d, $J = 10.9$ Hz, 1H), 4.92 (d, $J = 11.0$ Hz, 1H), 4.82 (d, $J = 10.8$ Hz, 1H), 4.78 (d, $J = 10.9$ Hz, 1H), 4.72 (d, $J = 10.9$ Hz, 1H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.54 (d, $J = 11.0$ Hz, 1H), 4.50 (d, $J = 7.8$ Hz, 1H), 3.73 (dd, $J = 10.7, 1.7$ Hz, 1H), 3.67 – 3.57 (m, 3H), 3.54 (t, $J = 9.3$ Hz, 1H), 3.45 (dd, $J = 14.7, 5.7$ Hz, 2H), 2.41 (ddd, $J = 13.2, 4.8, 1.9$ Hz, 1H), 2.33 (t, $J = 12.2$ Hz, 1H), 2.07 – 1.94 (m, 3H), 1.89 – 1.79 (m, 2H), 1.71 – 1.62 (m, 1H), 1.52 – 0.91 (m, 26H), 0.87 (dd, $J = 6.6, 2.2$ Hz, 6H), 0.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.59, 138.66, 138.52, 138.30, 138.13, 128.36, 128.33, 128.30, 128.23, 127.97, 127.87, 127.71, 127.66, 127.65, 127.55, 127.51, 121.91, 102.23, 84.83, 82.36, 79.69, 78.00, 75.67, 74.97, 74.92, 74.79, 73.39, 69.17, 56.76, 56.15, 50.19, 42.33, 39.79, 39.52, 39.11, 37.32, 36.76, 36.19, 35.78, 31.95, 31.89, 29.97, 28.23, 28.01, 24.29, 23.82, 22.81, 22.56, 21.07, 19.42, 18.72, 11.86; HRMS (EI) m/z calcd for $C_{61}H_{80}NaO_6 [M + Na]^+$ 931.5853, found 931.5823.



Compound $\alpha\text{-}2\text{h}$:¹ viscous liquid; 1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 33H), 7.14 – 7.23 (m, 2H), 4.99 – 4.88 (m, 4H), 4.84 – 4.54 (m, 10H), 4.48 – 4.38 (m, 2H), 4.00 – 3.91 (m, 2H), 3.84 – 3.50 (m, 7H), 3.54 (d, $J = 10.5$ Hz, 2H), 3.44 (d, $J = 9.5$ Hz, 1H), 3.35 (s, 3H).

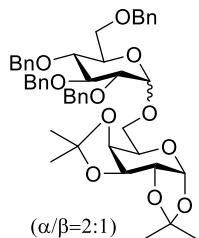


Compound $\beta\text{-}2\text{h}$:¹ viscous liquid; 1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 29H), 7.21 – 7.14 (m, 6H), 4.98 (d, $J = 3.0$ Hz, 1H), 4.95 (d, $J = 2.8$ Hz, 1H), 4.90 (d, $J = 10.9$ Hz, 1H), 4.83 – 4.48 (m, 12H), 4.34 (d, $J = 7.7$ Hz, 1H), 4.18 (dd, $J = 11.0, 1.7$ Hz, 1H), 3.99 (t, $J = 9.2$ Hz, 1H), 3.86 – 3.79 (m, 1H), 3.75 – 3.40 (m, 9H), 3.32 (s, 3H).



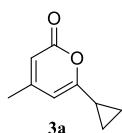
2i

Compound 2i: viscous liquid; , α/β anomeric ratio 1.6:1, known compound; ^1H NMR (500 MHz, CDCl_3) δ 7.43-7.38(m, 2H), 7.32-7.18(m, 85.8H), 7.11-7.07(m, 3.2H), 5.69(d, $J=3.6$ Hz, 1.6H), 5.08(d, $J=11.6$ Hz, 1H), 5.02(d, $J=11.3$ Hz, 3.2H), 4.91-4.24(m, 37.4H), 4.12-3.32(m, 38H), 3.28 (ddd, $J = 10.0, 4.7, 1.9$ Hz, 1H) ^{13}C NMR (126 MHz, Chloroform-d) δ 139.57, 138.96, 138.76, 138.59, 138.56, 138.49, 138.39, 138.31, 138.17, 137.98, 137.94, 137.84, 128.43, 128.41, 128.34, 128.33, 128.31, 128.30, 128.28, 128.27, 128.23, 128.22, 128.20, 128.18, 128.16, 128.08, 127.99, 127.98, 127.95, 127.94, 127.89, 127.86, 127.80, 127.79, 127.77, 127.75, 127.74, 127.71, 127.68, 127.61, 127.60, 127.56, 127.54, 127.51, 127.48, 127.47, 127.34, 127.28, 127.24, 127.05, 126.74, 102.47, 98.41, 97.76, 96.63, 84.86, 82.81, 82.03, 82.01, 80.41, 80.21, 79.47, 78.83, 78.04, 77.65, 76.59, 75.57, 75.52, 75.36, 75.16, 74.92, 74.90, 74.77, 74.40, 73.62, 73.44, 73.36, 73.34, 73.33, 73.22, 73.14, 72.37, 70.97, 69.97, 69.54, 69.03, 68.19, 67.86, 55.29, 55.14.



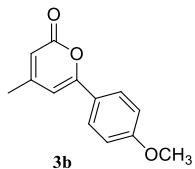
2j

Compound 2j: viscous liquid; , α/β anomeric ratio 2:1, known compound; ^1H NMR (500 MHz, CDCl_3) δ 7.10-7.45 (m, 30H), 5.57 (d, $J = 5.0$ Hz, 0.5H), 5.53 (d, $J = 5.0$ Hz, 1H), 4.45-5.08 (m, 15H), 4.36 (dd, $J=1.9$ Hz, $J=7.9$ Hz, 1H) 4.31-4.34 (m, 1.5H), 4.25 (dd, $J=1.9$ Hz, $J=7.9$ Hz, 0.5H), 4.17 (dd, $J=3.8$ Hz, $J=10.6$ Hz, 0.5H), 4.03-4.12(m, 1.5H), 3.99(t, 1H), 3.42-3.85 (m, 10.5H) 1.32, 1.46, 1.51, 1.54 (4 s, 18H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.93, 138.69, 138.34, 138.33, 138.15, 138.14, 137.97, 128.60, 128.33, 128.31, 128.30, 128.17, 127.91, 127.89, 127.86, 127.84, 127.82, 127.78, 127.67, 127.65, 127.61, 127.59, 127.56, 127.50, 127.47, 127.43, 109.35, 109.17, 108.56, 108.54, 104.37, 97.03, 96.37, 96.29, 84.54, 81.95, 81.62, 79.80, 77.72, 77.57, 77.26, 77.20, 77.00, 76.75, 75.63, 75.59, 74.96, 74.75, 74.32, 73.51, 73.48, 73.45, 72.32, 71.43, 70.80, 70.77, 70.65, 70.62, 70.47, 70.21, 69.68, 68.77, 68.36, 67.34, 66.19, 65.68, 26.16, 26.06, 26.02, 25.99, 25.01, 24.91, 24.63, 24.43.

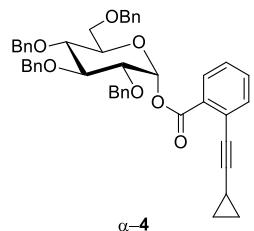


Compound 3a: viscous oil; IR (KBr) ν_{max} 2923, 2854, 1717, 1640, 1552, 1415, 1063, 952, 810; ^1H NMR (500 MHz, CDCl_3) δ 5.91 (d, $J = 1.4$ Hz, 1H), 5.89 – 5.85 (m, 1H), 2.10 (d, $J = 1.1$ Hz, 3H), 1.72 (tt, $J = 8.3, 5.0$ Hz, 1H), 1.10 – 1.05 (m, 2H), 0.96 – 0.91 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 165.49, 162.93,

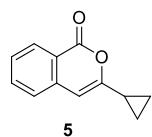
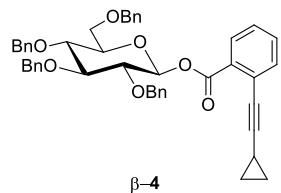
156.40, 109.48, 104.38, 21.36, 14.06, 8.06; HRMS (EI) m/z calcd for C₉H₁₁O₂ [M + H]⁺ 151.0759, found 151.0756.



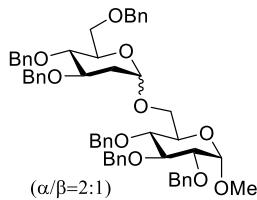
Compound 3b: White crystals, mp 54–56 °C (from ethyl acetate and hexane); IR (KBr) ν_{max} 2921, 2851, 1720, 1634, 1546, 1508, 1255, 1176, 1028, 783; ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 6.42 (d, J = 1.3 Hz, 1H), 6.05 – 5.99 (m, 1H), 3.86 (s, 3H), 2.21 (d, J = 1.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.63, 161.68, 159.64, 156.27, 127.29, 123.89, 114.30, 110.51, 102.67, 55.43, 21.68; HRMS (EI) m/z calcd for C₁₃H₁₃O₃ [M + H]⁺ 217.0865, found 217.0863.



Compound α-4: viscous oil; IR (KBr) ν_{max} 2921, 2852, 1734, 1685, 1456, 1243, 1160, 1073, 745; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 7.8 Hz, 1H), 7.55 – 7.38 (m, 3H), 7.28 (m, 18H), 7.16 – 7.03 (m, 2H), 6.68 (m, 1H), 5.07 – 4.92 (m, 1H), 4.90 – 4.74 (m, 3H), 4.69 – 4.61 (m, 2H), 4.51 (t, J = 11.5 Hz, 2H), 4.18 – 4.03 (m, 2H), 3.89 – 3.74 (m, 3H), 3.70 – 3.67 (m, 1H), 1.27 – 1.24 (m, 1H), 0.82 – 0.73 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 137.90, 137.33, 137.03, 136.94, 133.85, 131.17, 130.13, 130.07, 127.61, 127.56, 127.34, 127.20, 127.16, 127.12, 127.03, 126.97, 126.95, 126.82, 126.23, 124.25, 99.15, 90.07, 80.98, 78.23, 76.11, 74.90, 74.51, 74.16, 72.76, 72.45, 72.21, 67.25, 8.22; HRMS (EI) m/z calcd for C₄₆H₄₄NaO₇ [M + Na]⁺ 731.2985, found 731.3435.

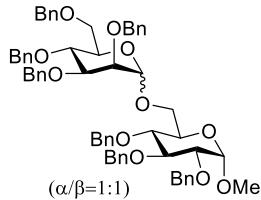


Compound 5: viscous oil; IR (KBr) ν_{max} 2920, 2849, 1732, 1649, 1483, 1161, 1071, 965, 813; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 7.9 Hz, 1H), 7.71 – 7.61 (m, 1H), 7.45 – 7.36 (m, 1H), 7.32 (d, J = 7.9 Hz, 1H), 6.30 (s, 1H), 1.81 (m, 1H), 1.06 (m, 2H), 0.98 – 0.89 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 161.70, 157.36, 136.88, 133.71, 128.50, 126.06, 123.55, 118.89, 100.34, 12.78, 5.94; HRMS (EI) m/z calcd for C₁₂H₁₀NaO₂ [M + Na]⁺ 209.0578, found 209.0578.



7

Compound 7: viscous oil, α/β anomeric ratio 2:1, known compound; ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.08 (m, 30H), 5.00 (dd, $J = 10.7$ Hz, 1.33H), 4.93 (d, $J = 11.1$ Hz, 0.66H), 4.88 (dd, $J = 11.0$ Hz, 1.33H), 4.85 – 4.76 (m, 2H), 4.72 – 4.51 (m, 6.33H), 4.49 (d, $J = 10.9$ Hz, 0.66H), 4.41 (d, $J = 12.1$ Hz, 0.66H), 4.18 (dd, $J = 9.7$, 1.9 Hz, 0.33H), 4.09 (dd, $J = 10.7$, 2.1 Hz, 0.33H), 4.00 (t, $J = 9.3$ Hz, 1H), 3.98 – 3.91 (m, 0.66H), 3.82 (dd, $J = 11.4$, 4.4 Hz, 0.66H), 3.78 – 3.71 (m, 1.33H), 3.71 – 3.65 (m, 1H), 3.64 – 3.48 (m, 5H), 3.44 (t, $J = 9.1$ Hz, 0.33H), 3.37 (s, 1H), 3.35 (s, 2H), 2.31 (ddd, $J = 12.9$, 5.1, 1.4 Hz, 0.66H), 2.20 – 2.14 (m, 0.33H), 1.73 – 1.66 (m, 0.66H), 1.66 – 1.62 (m, 0.33H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.79, 138.70, 138.68, 138.57, 138.45, 138.39, 138.33, 138.16, 138.14, 138.13, 128.47, 128.46, 128.44, 128.41, 128.40, 128.36, 128.35, 128.33, 128.30, 128.29, 128.22, 128.20, 128.17, 128.09, 128.05, 128.02, 128.01, 127.92, 127.91, 127.89, 127.87, 127.77, 127.73, 127.70, 127.68, 127.67, 127.64, 127.61, 127.59, 127.56, 127.53, 127.48, 127.45, 127.42, 100.02, 98.02, 97.92, 97.80, 82.25, 82.22, 80.02, 79.78, 79.29, 78.18, 78.14, 77.76, 77.41, 77.23, 75.79, 75.75, 75.32, 74.99, 74.87, 74.82, 74.79, 73.40, 73.36, 73.28, 71.70, 71.42, 70.89, 69.75, 69.65, 69.48, 68.69, 67.61, 65.67, 60.40, 57.08, 55.14, 55.11, 36.51, 35.27, 29.71, 21.06, 14.21.



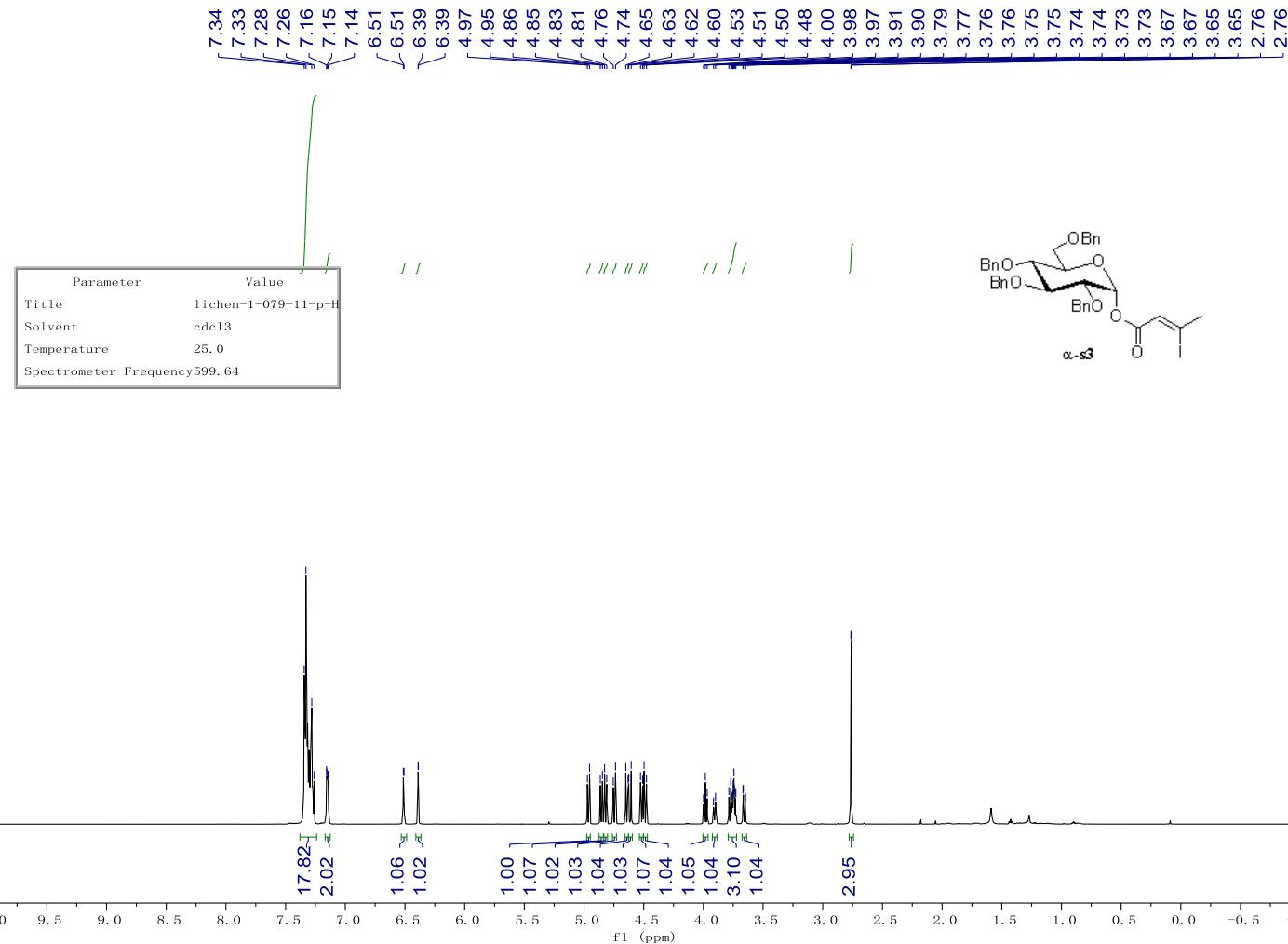
9

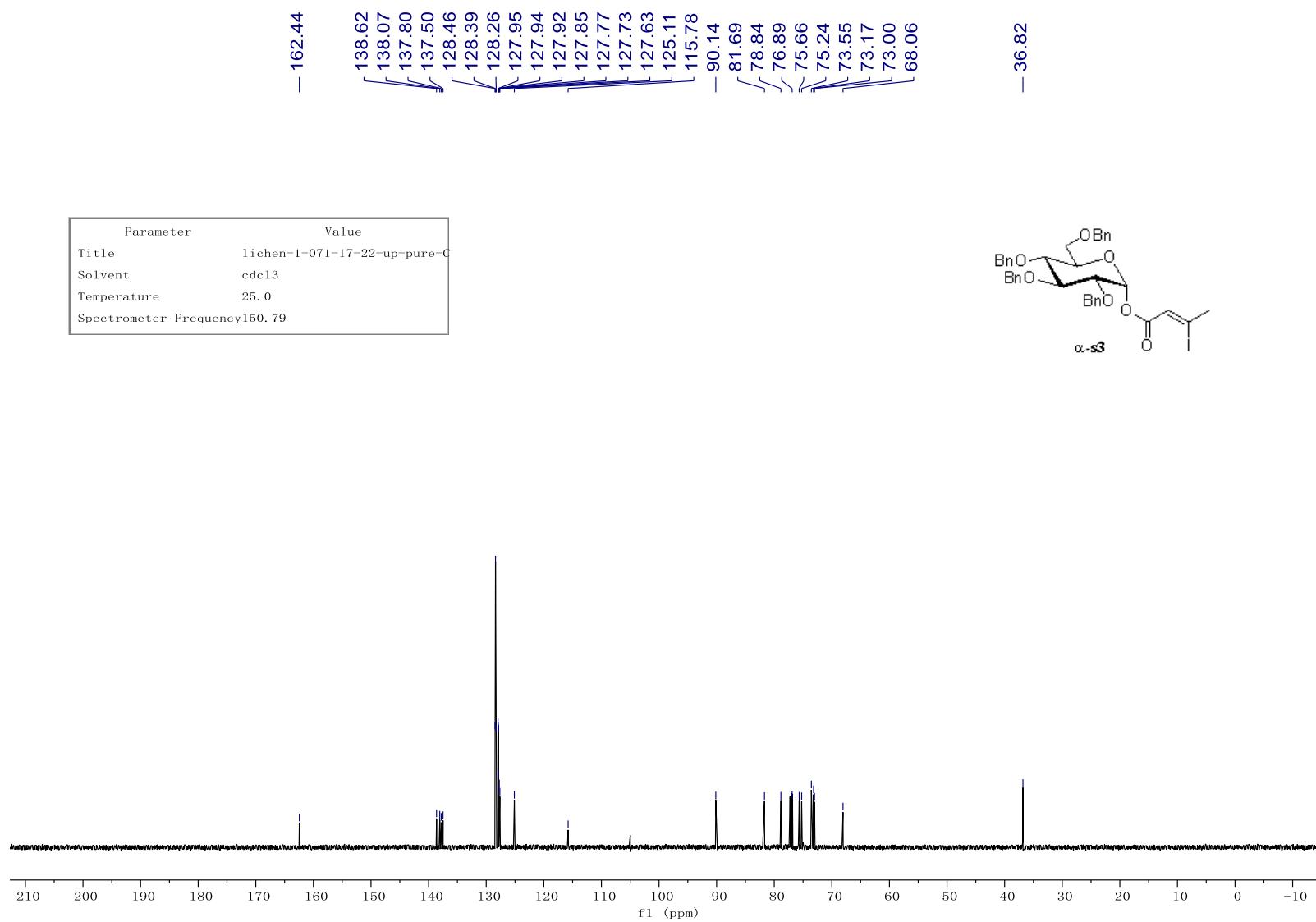
Compound 9: viscous oil, α/β anomeric ratio 1:1, known compound; ^1H NMR (500 MHz, CDCl_3) δ 7.49 – 7.10 (m, 35H), 5.07 – 4.77 (m, 6H), 4.75 – 4.42 (m, 9H), 4.17 (dd, $J = 10.5$, 2.0 Hz, 0.5H), 4.13 (s, 0.5H), 4.10 – 3.95 (m, 1.5H), 3.91 – 3.76 (m, 2.5H), 3.76 – 3.58 (m, 3.5H), 3.52 (dd, $J = 9.7$, 3.5 Hz, 0.5H), 3.49 – 3.37 (m, 3H), 3.35 – 3.30 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.84, 138.74, 138.68, 138.65, 138.47, 138.43, 138.37, 138.30, 138.20, 138.18, 138.15, 138.08, 128.59, 128.58, 128.49, 128.47, 128.41, 128.40, 128.39, 128.37, 128.35, 128.34, 128.28, 128.26, 128.23, 128.17, 128.16, 128.13, 128.12, 128.09, 128.05, 128.02, 128.00, 127.94, 127.87, 127.85, 127.85, 127.81, 127.76, 127.74, 127.72, 127.68, 127.66, 127.62, 127.60, 127.57, 127.56, 127.50, 127.45, 127.39, 101.51, 98.27, 97.83, 97.80, 97.58, 82.29, 82.16, 82.15, 80.01, 79.89, 79.58, 79.52, 77.68, 77.65, 77.49, 77.24, 77.11, 76.02, 75.80, 75.71, 75.17, 75.02, 74.99, 74.93, 74.88, 74.74, 74.67, 74.56, 73.69, 73.62, 73.53, 73.49, 73.34, 73.27, 73.07, 72.45, 72.00, 71.95, 71.57, 69.83, 69.81, 69.76, 69.66, 69.13, 68.54, 68.31, 65.82, 55.18, 55.09, 55.05.

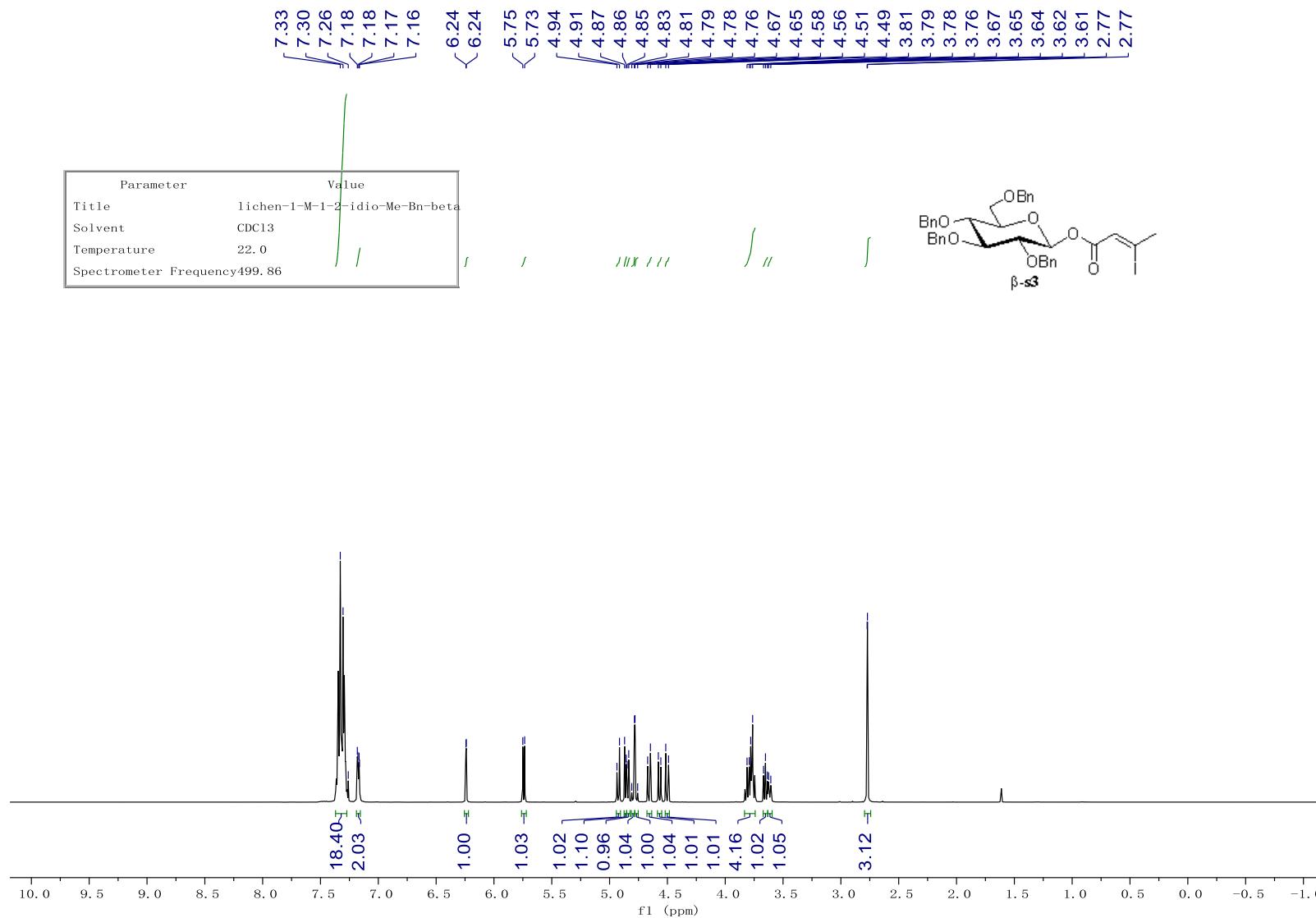
5. Reference

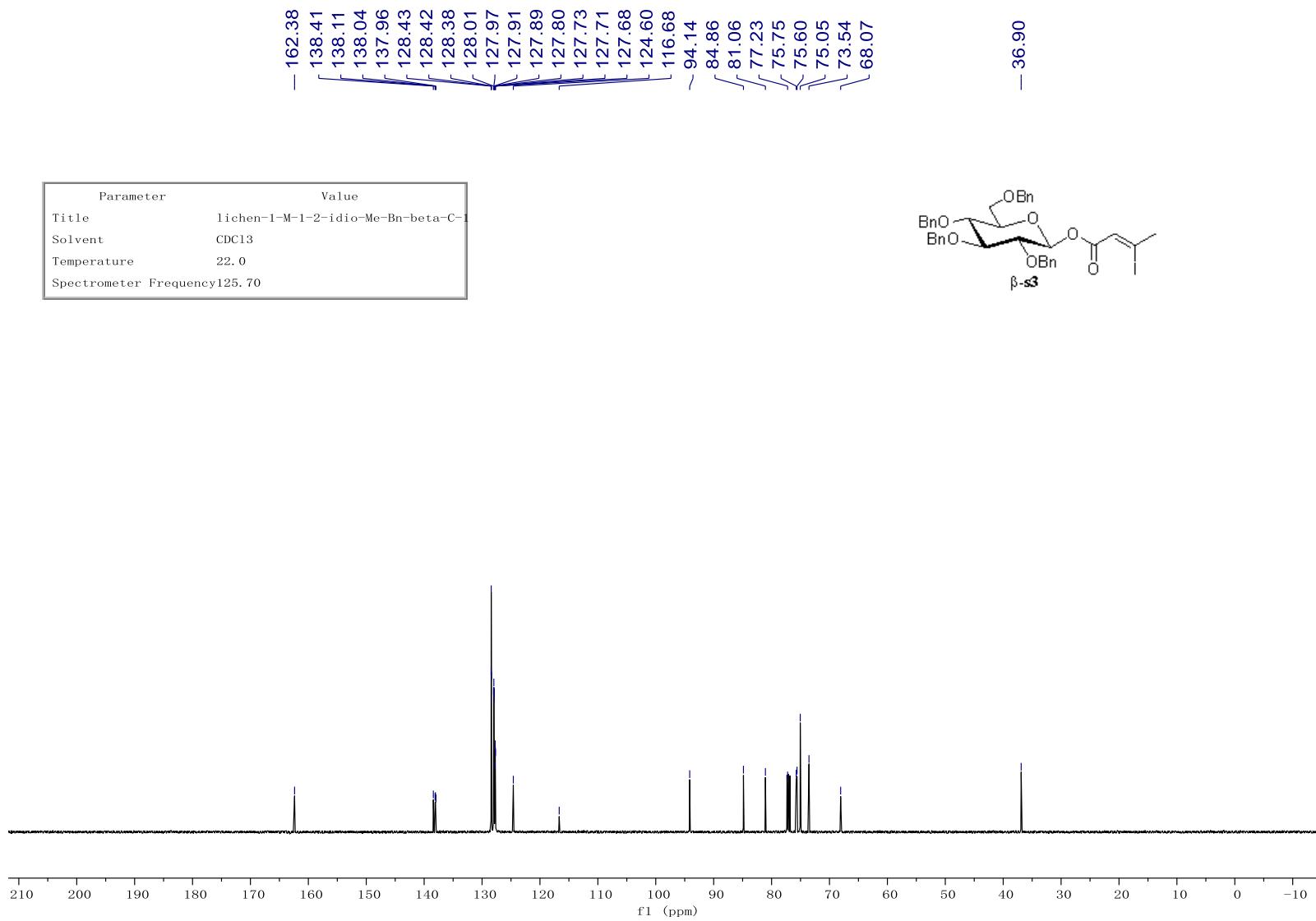
- (1) Iwata, R.; Uda, K.; Takahashi, D.; Toshima, K. *Chem. Commun.* **2014**, 73, 10695–10698.

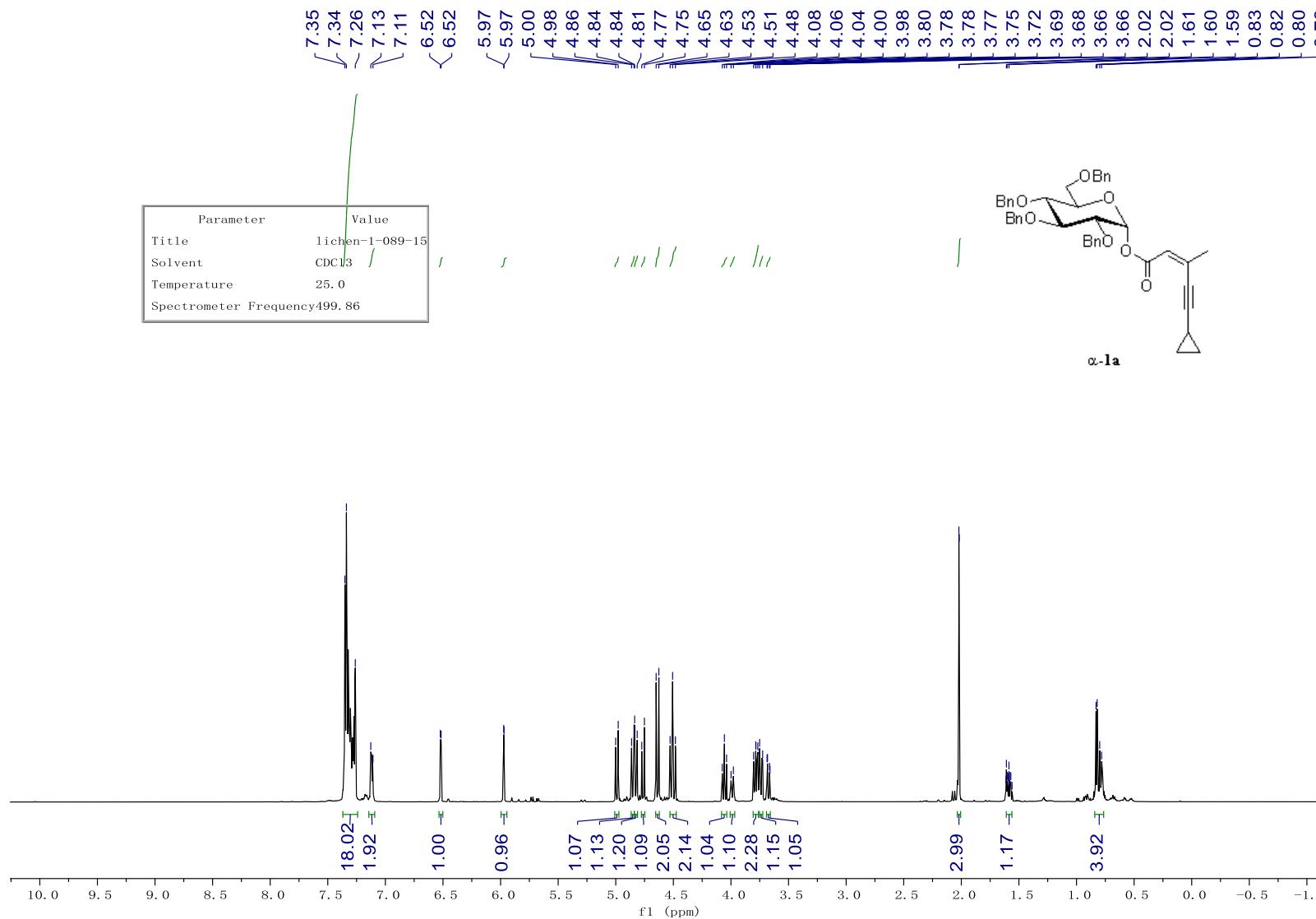
6. NMR Spectra for New Compounds

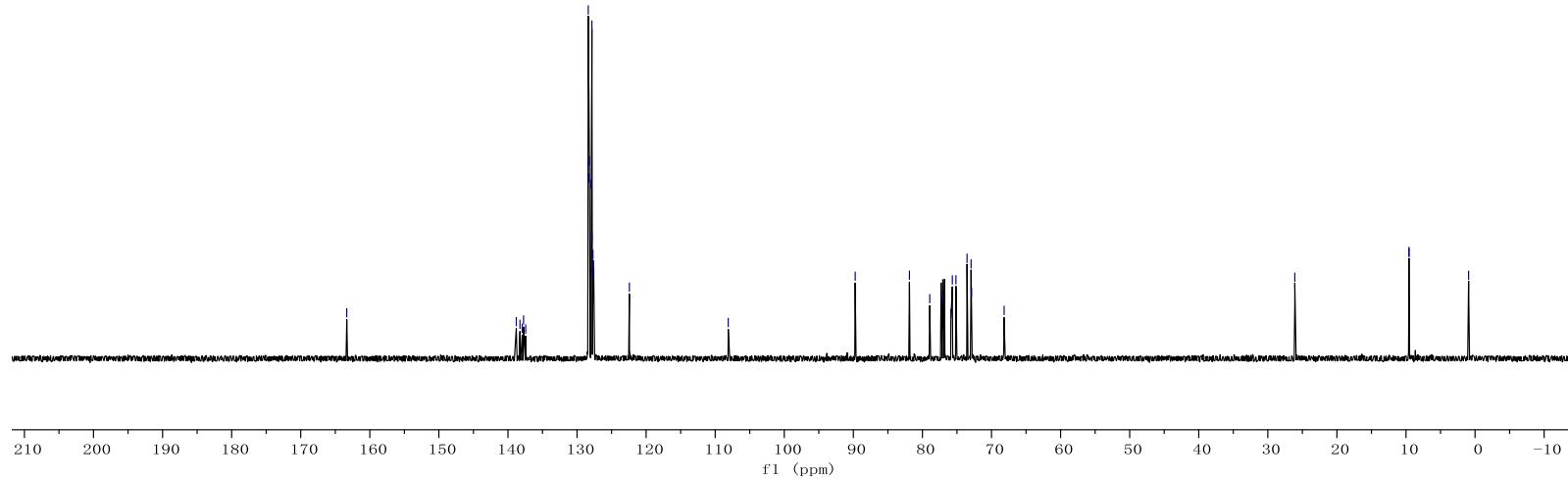




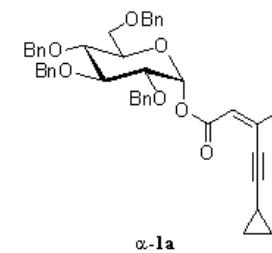








Parameter	Value
Title	lichen-1-089-15-C
Solvent	CDCl ₃
Temperature	25.0
Spectrometer Frequency	125.70



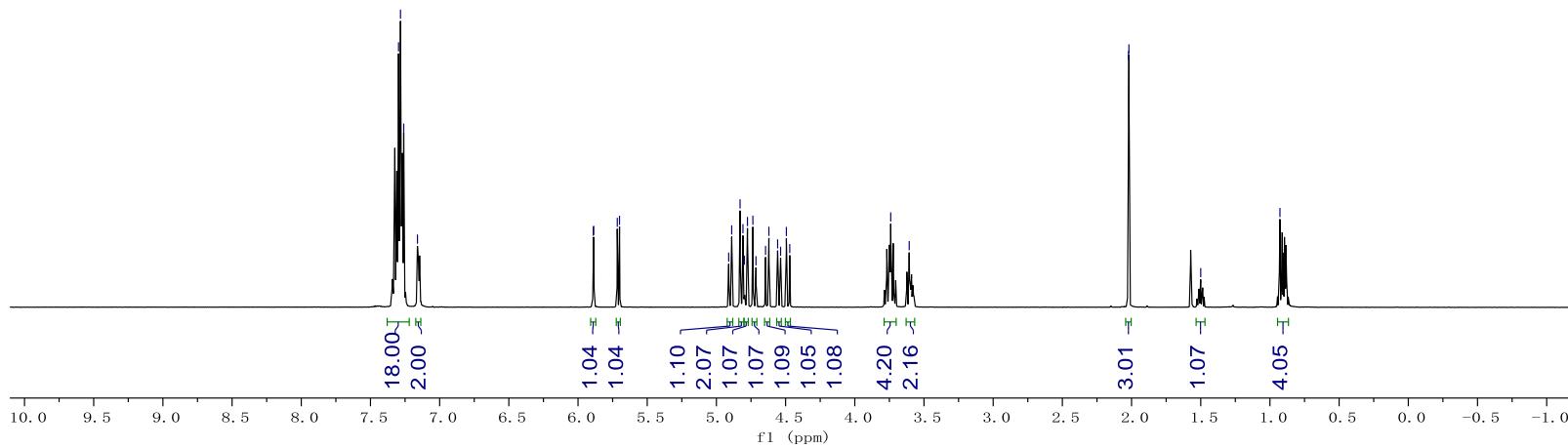
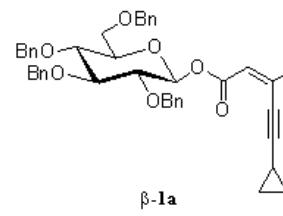
Parameter	Value
Title	lichen-1-165-A-p
Solvent	CDCl ₃
Temperature	25.0
Spectrometer Frequency	499.86

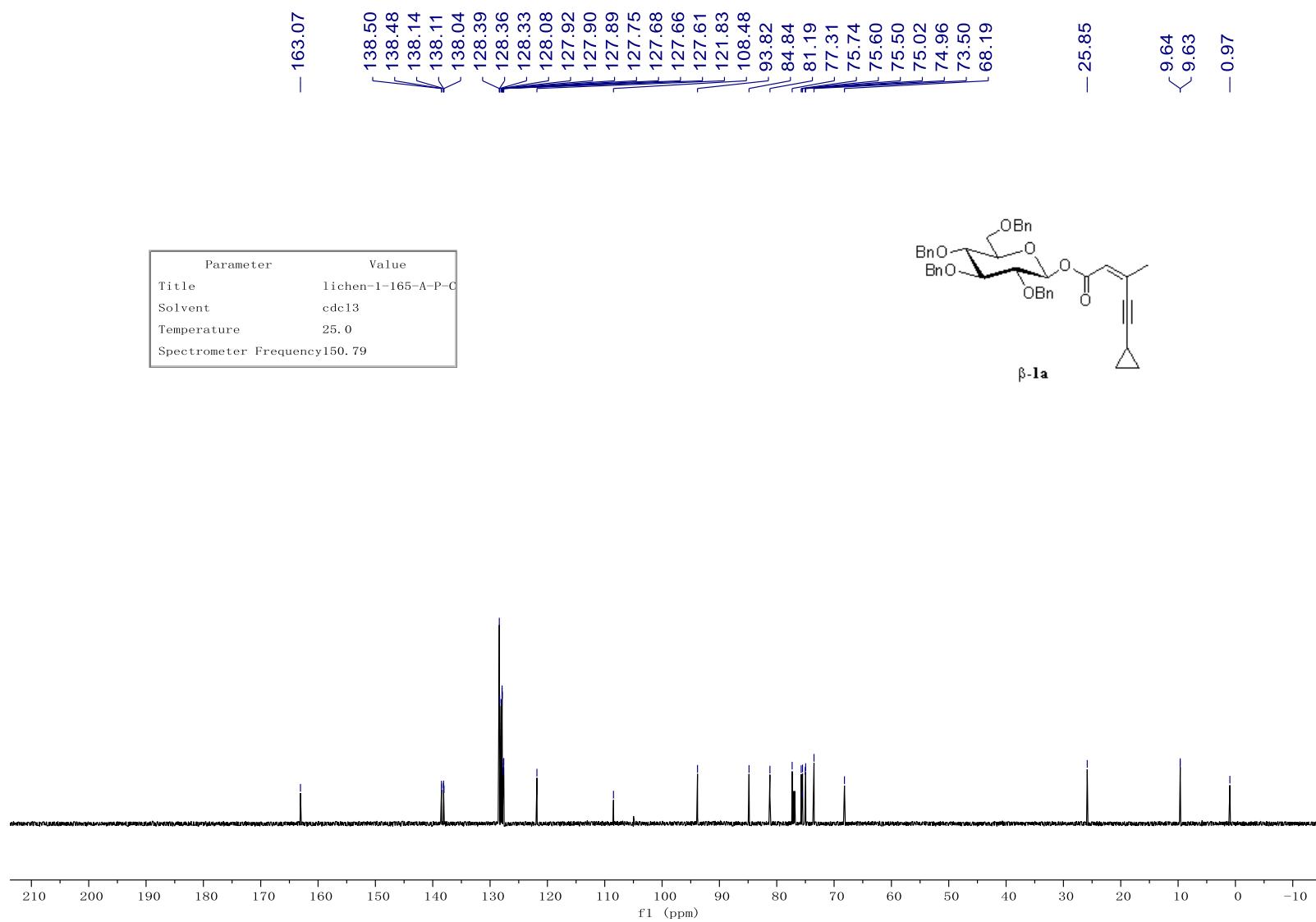
7.30
7.28
7.26
7.16

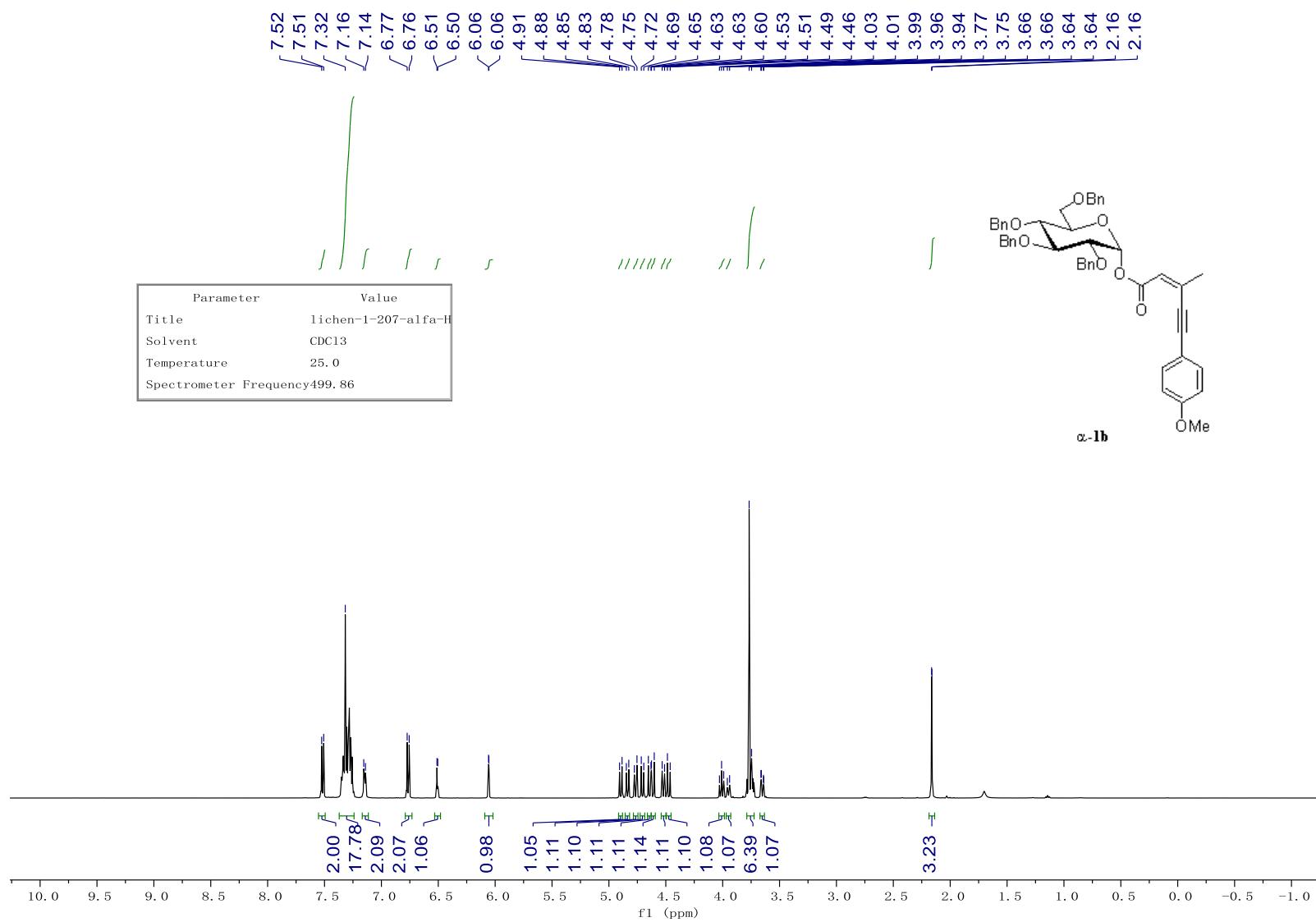
5.89
5.89
5.72
5.70
4.91
4.89
4.83
4.81
4.80
4.78
4.74
4.71
4.65
4.62
4.56
4.54
4.49
4.47
3.74
3.61

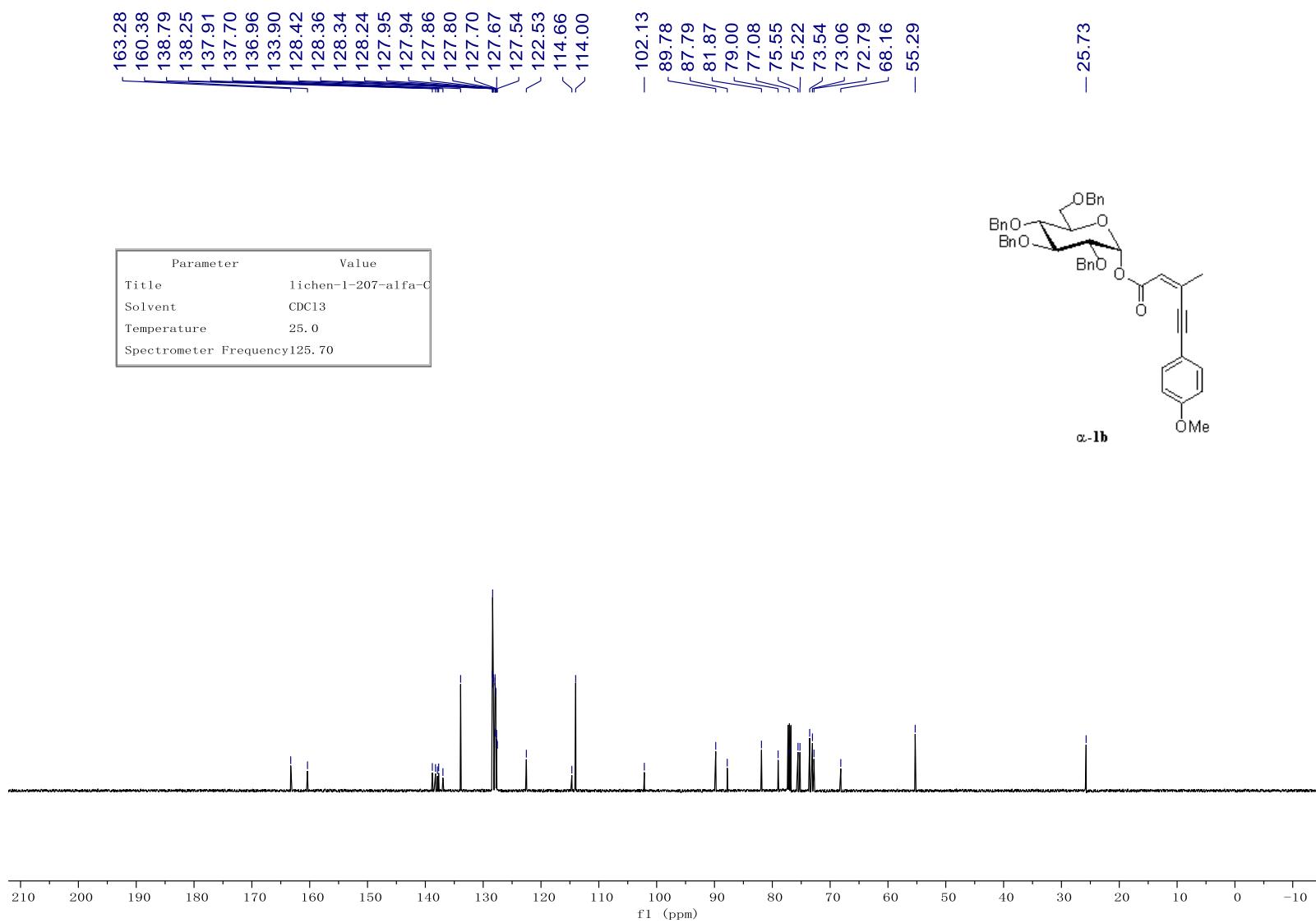
— 1.50

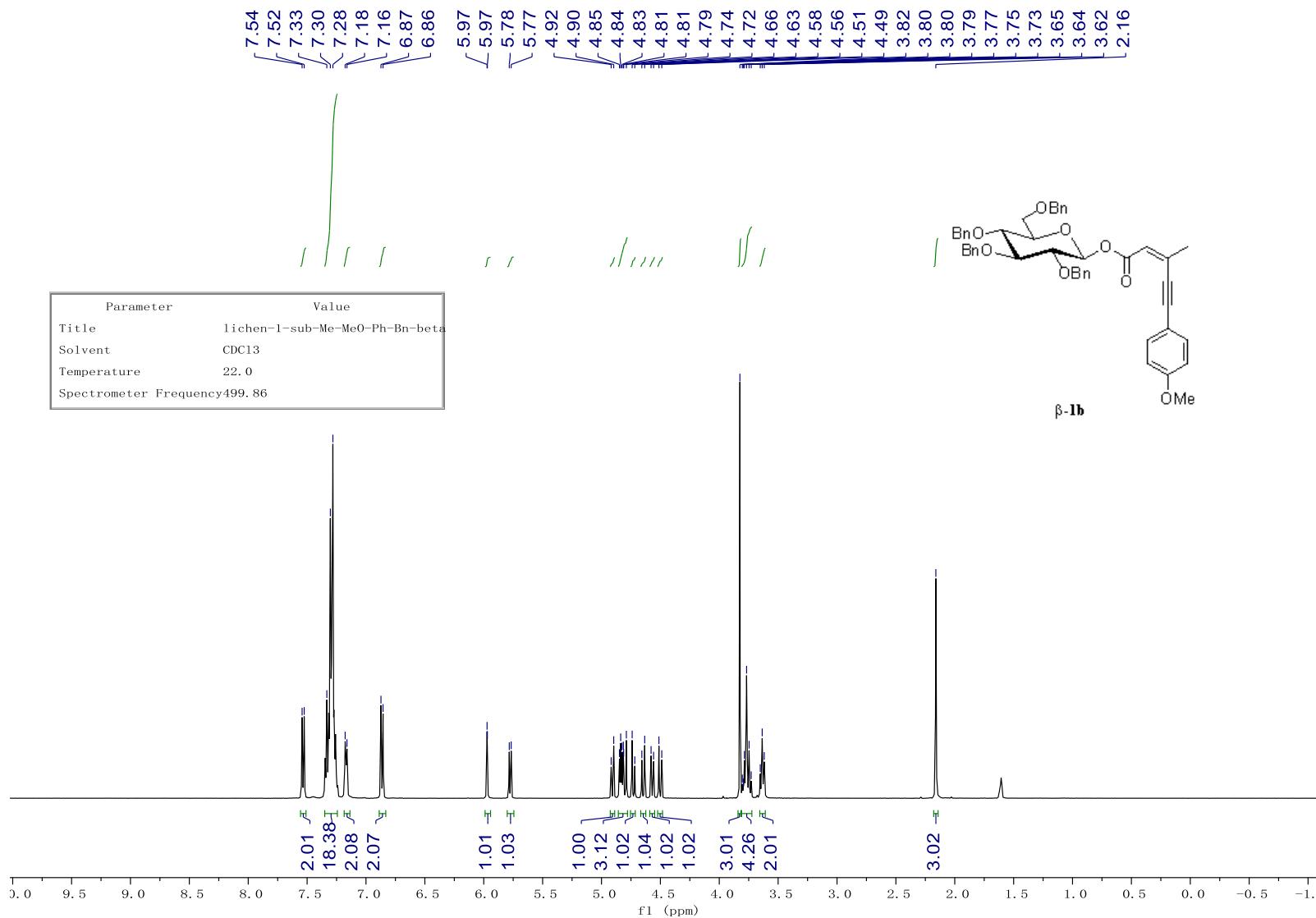
— 0.93

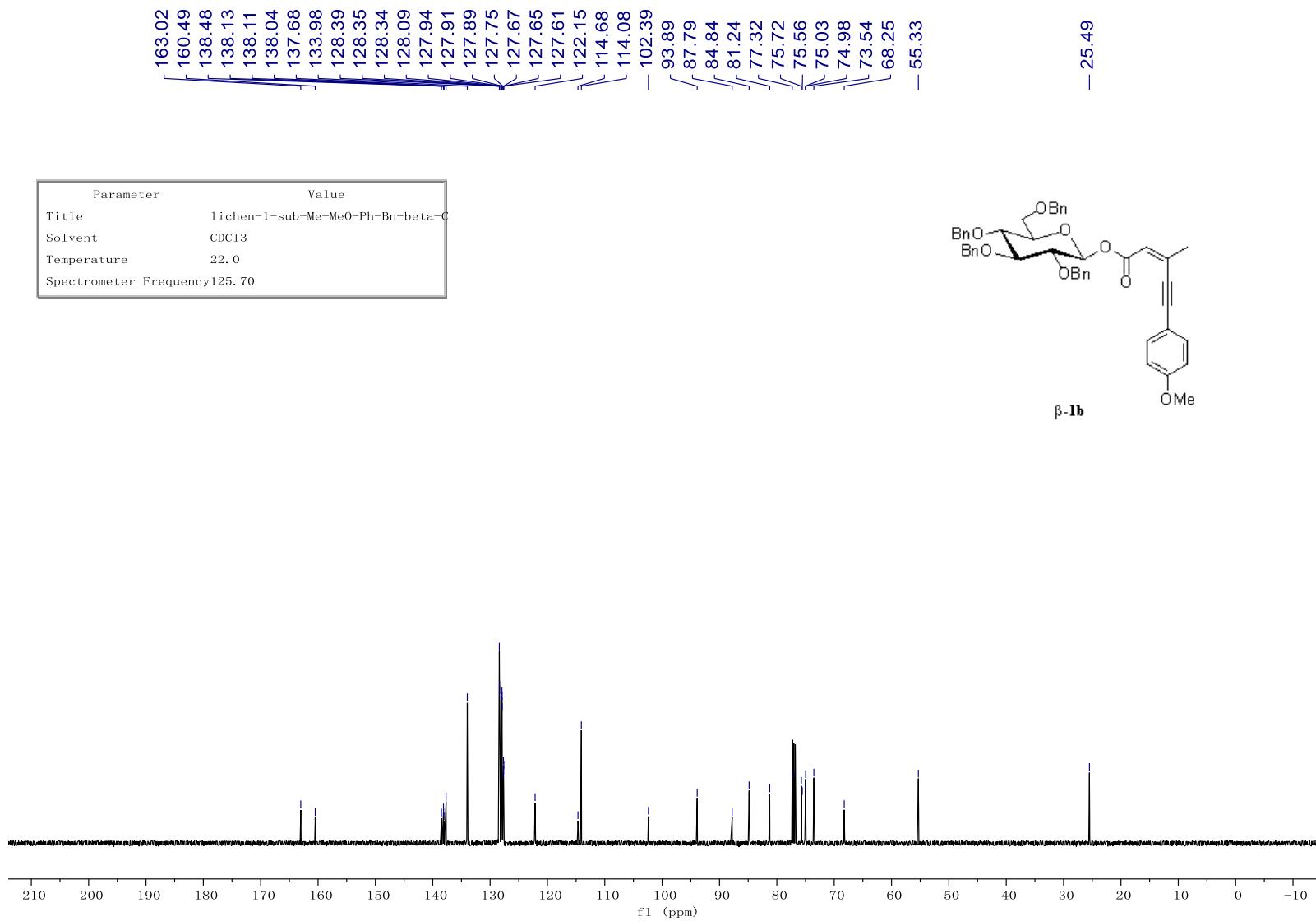


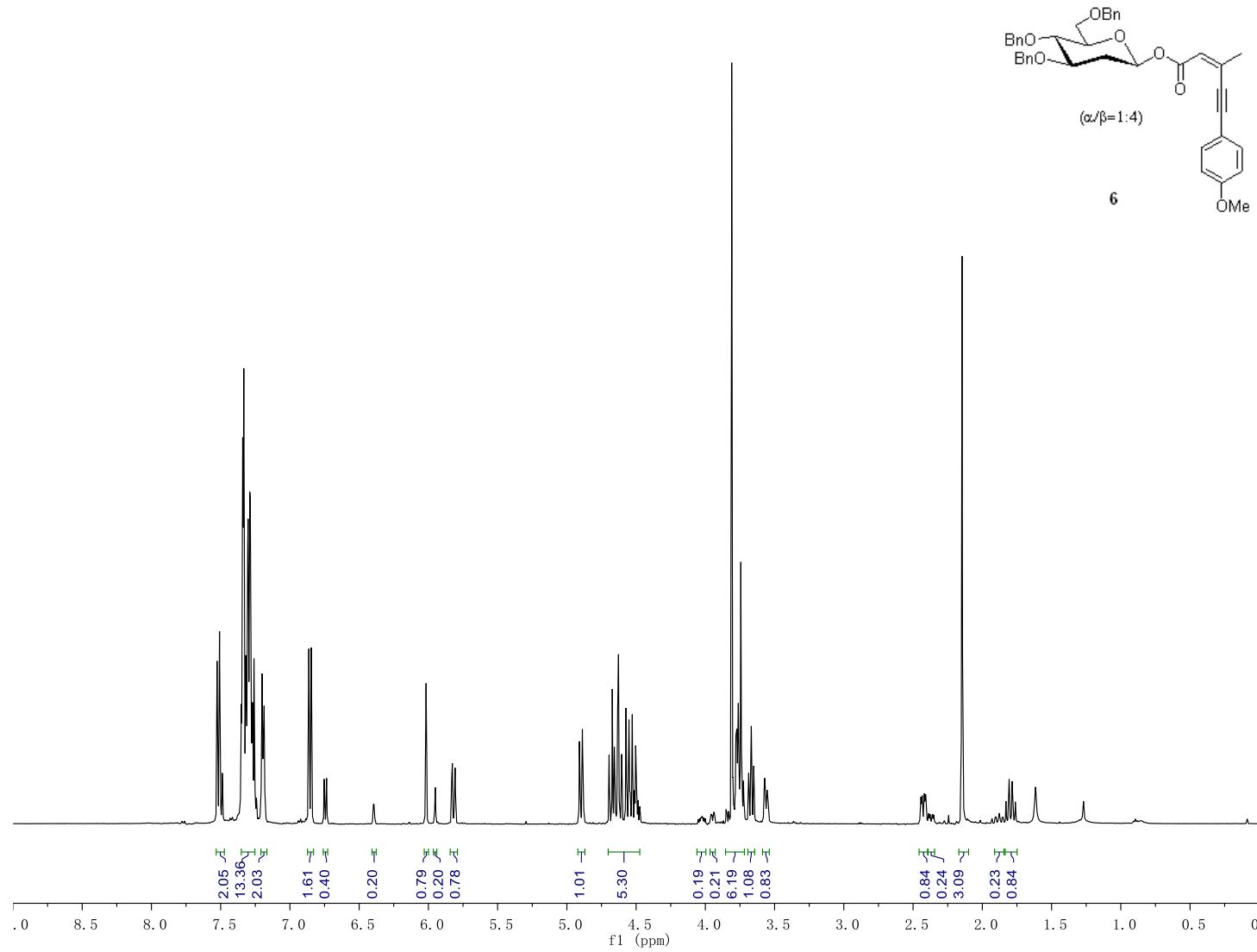


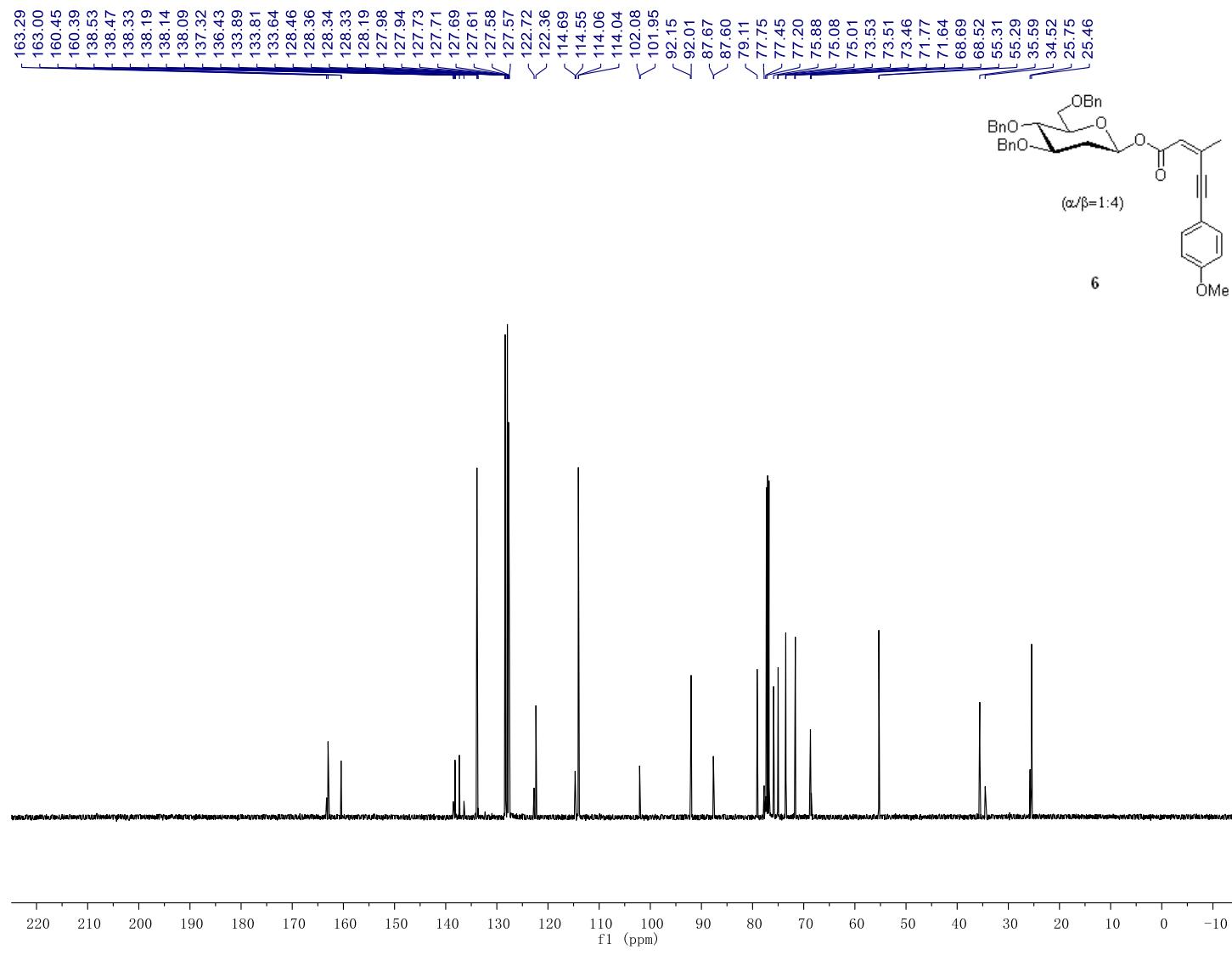


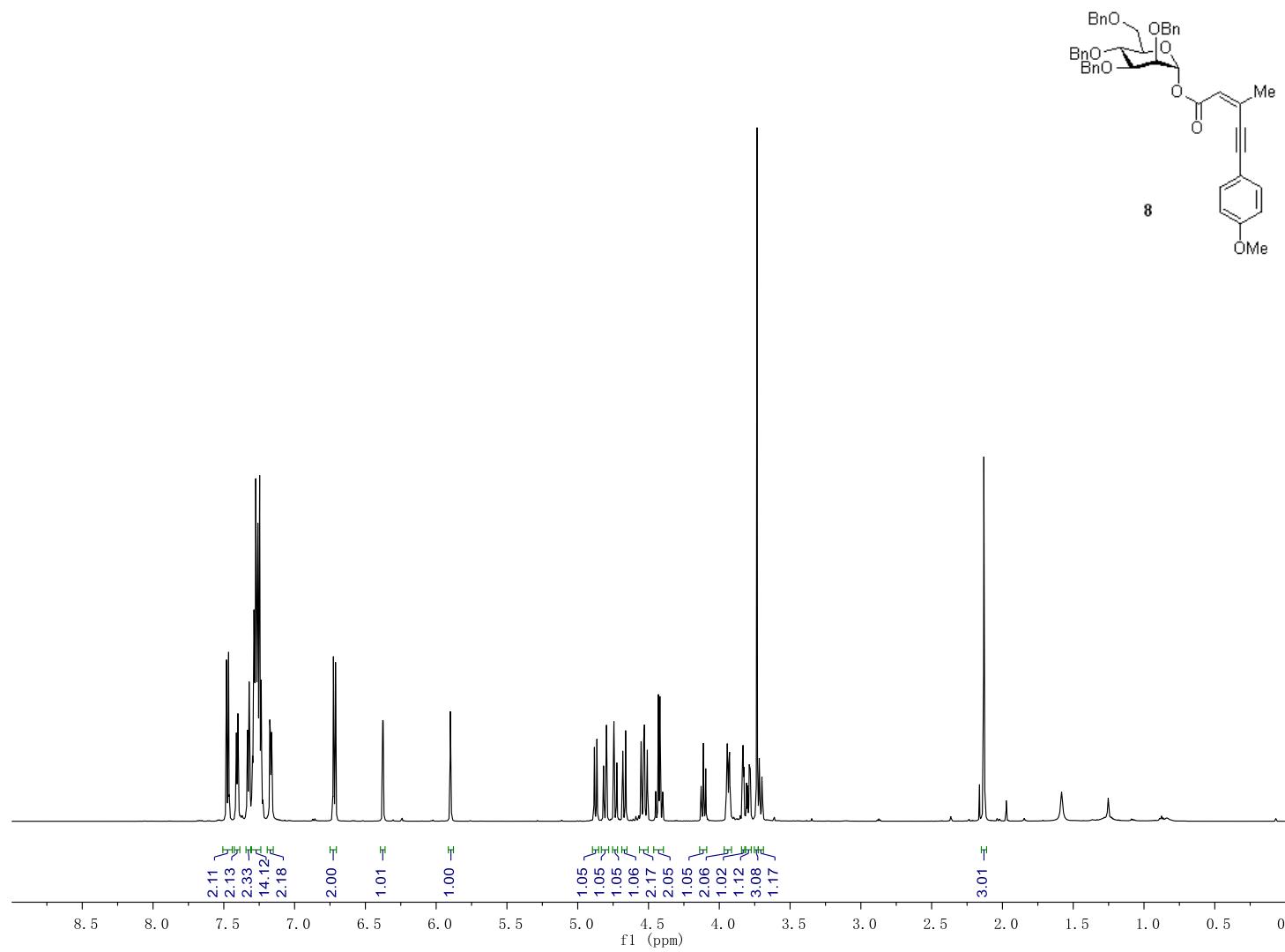


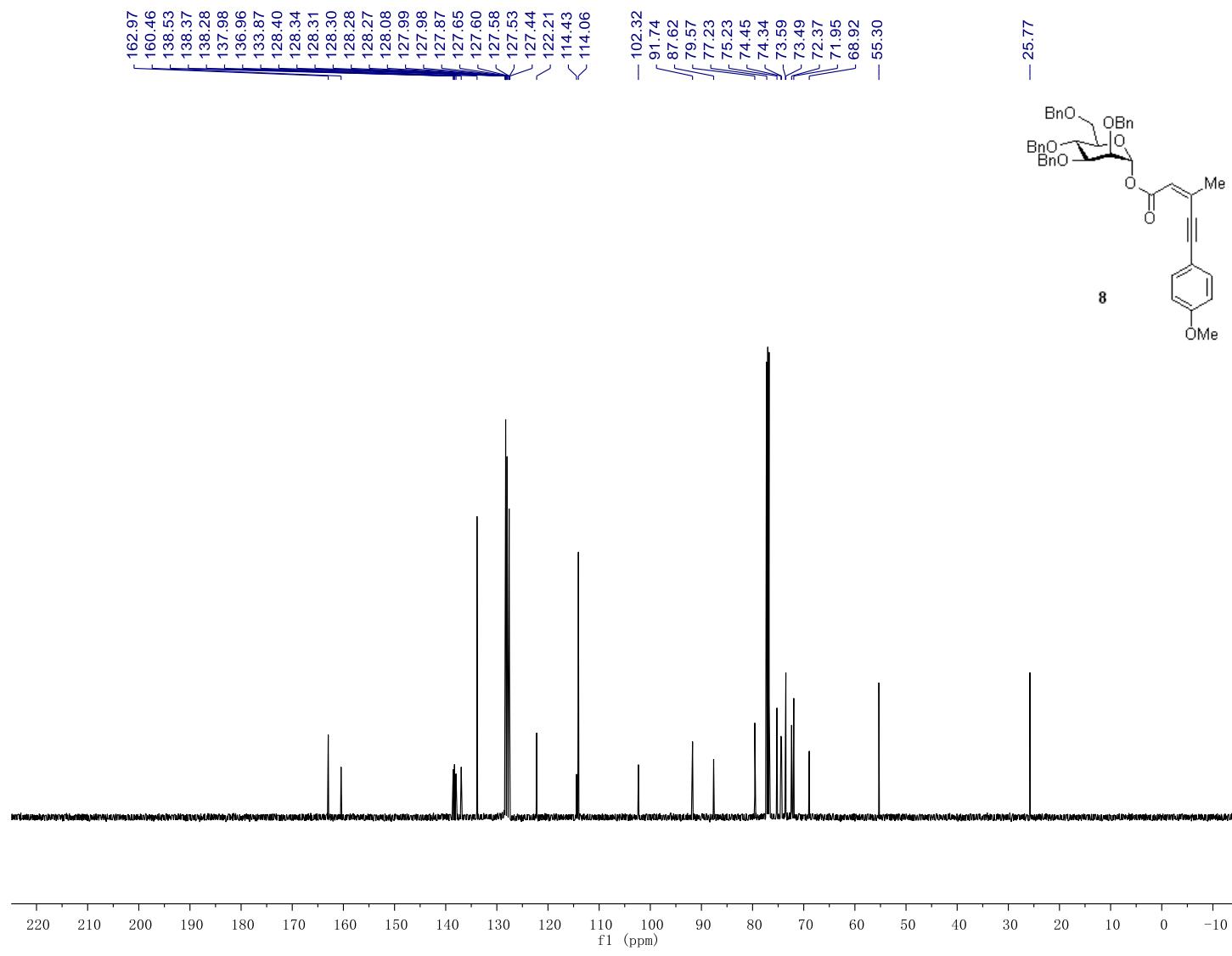


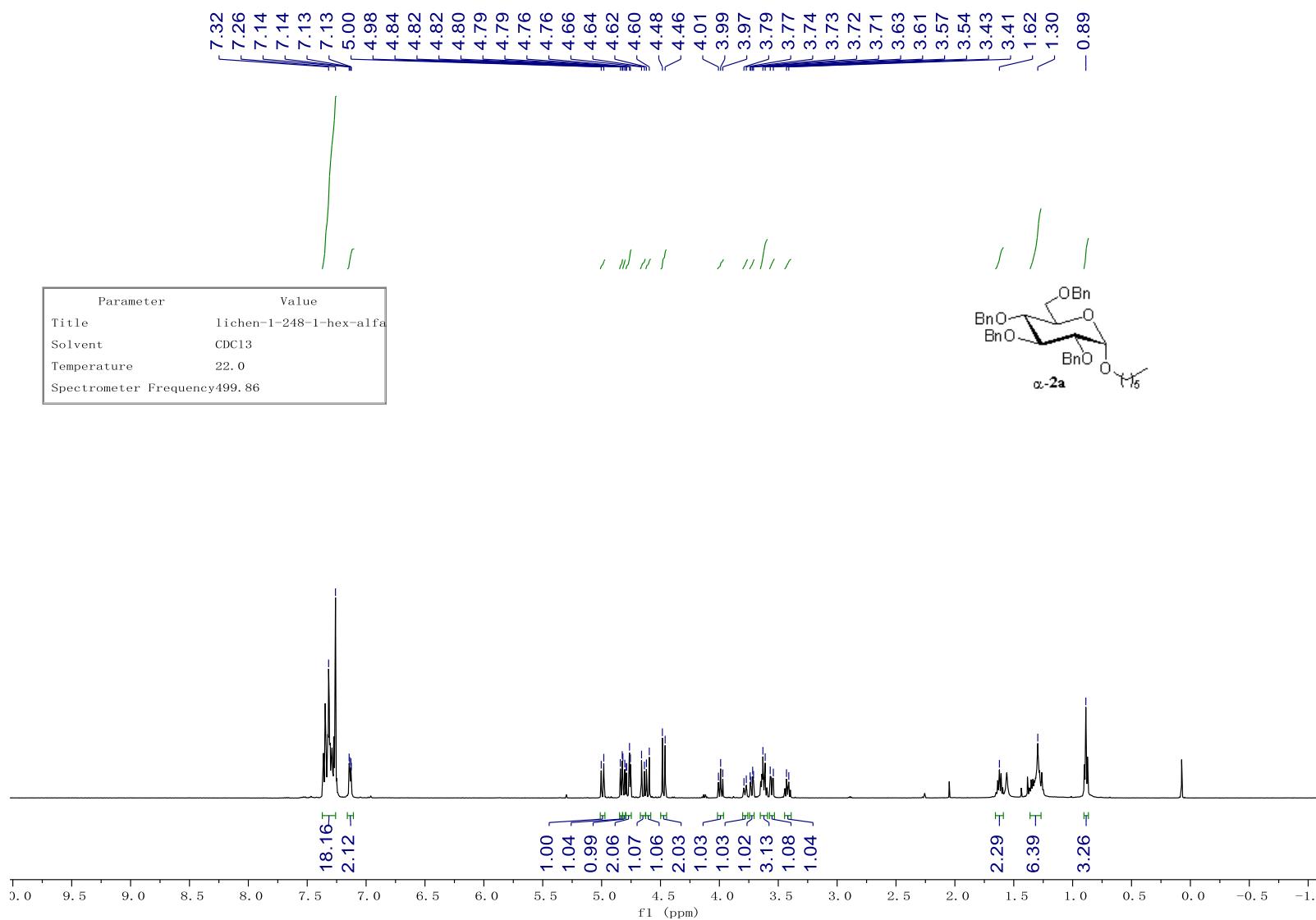


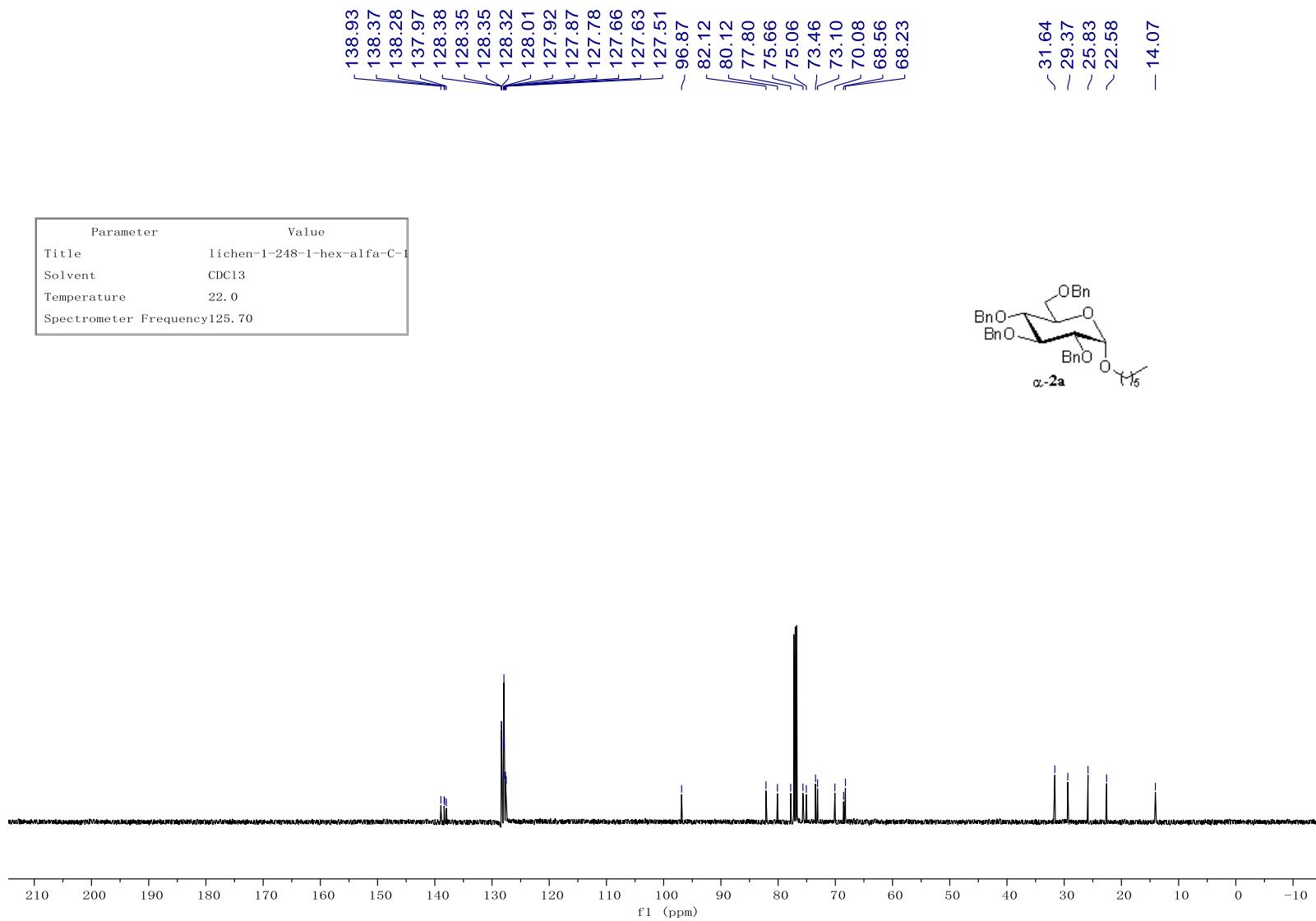


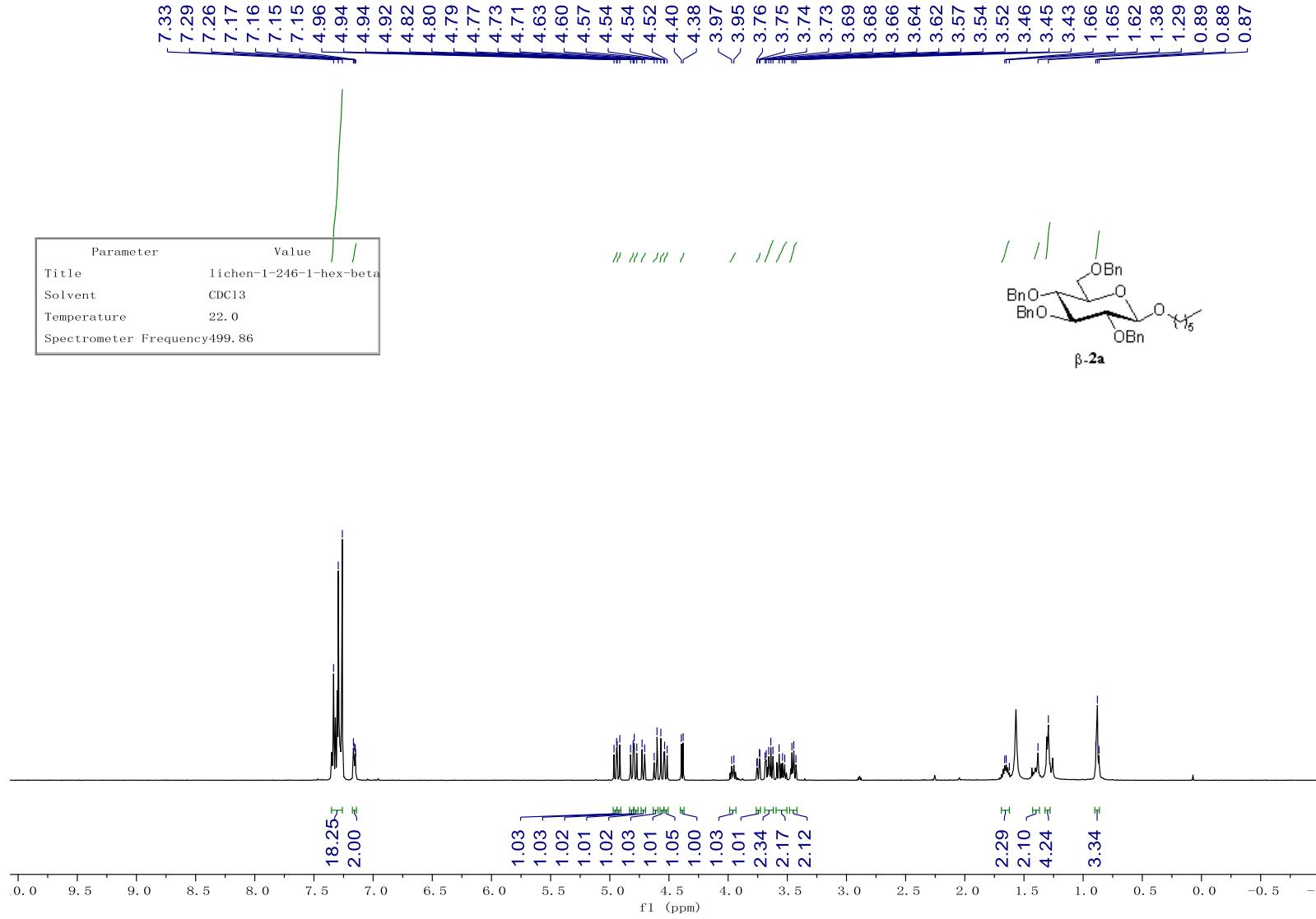


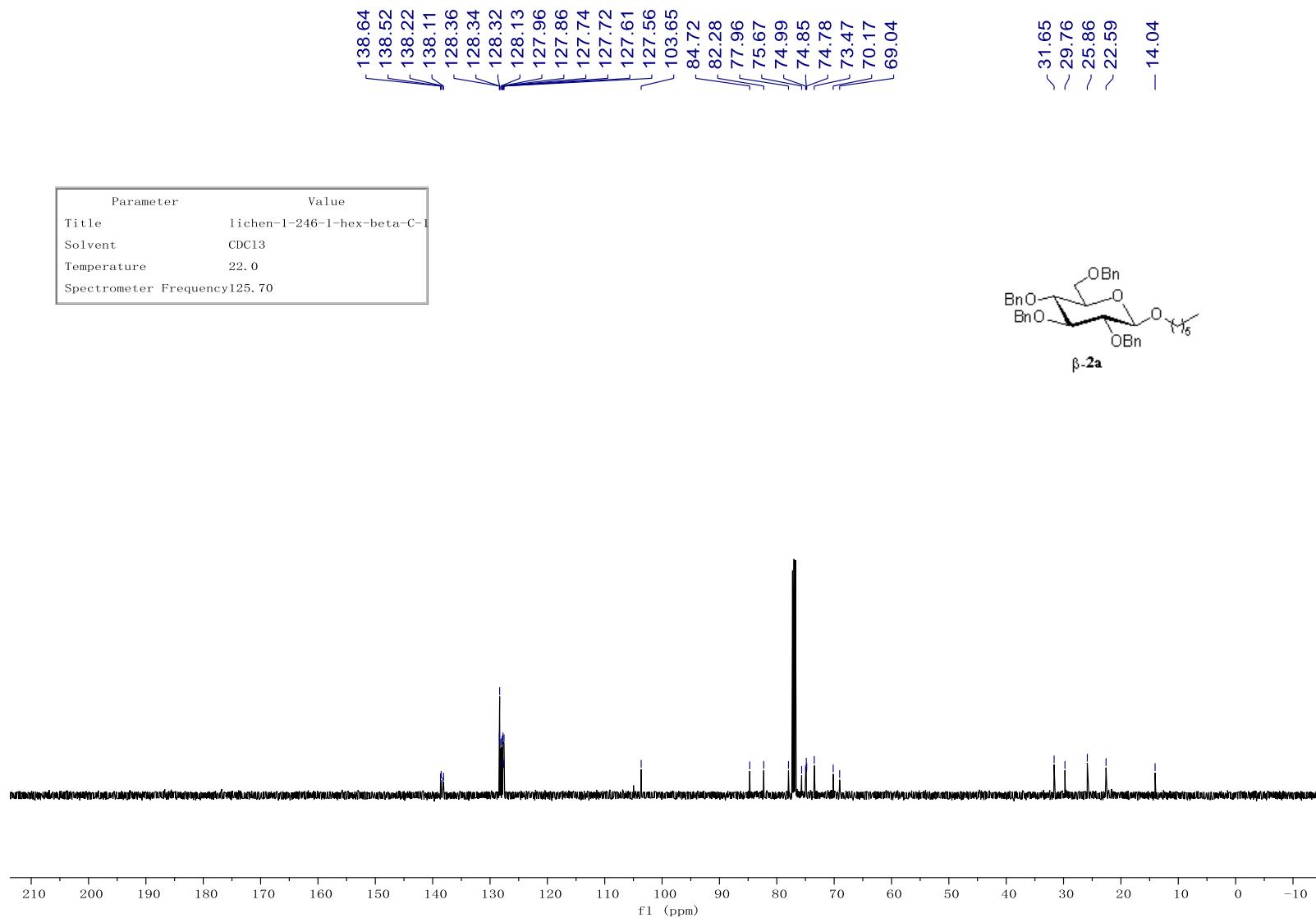


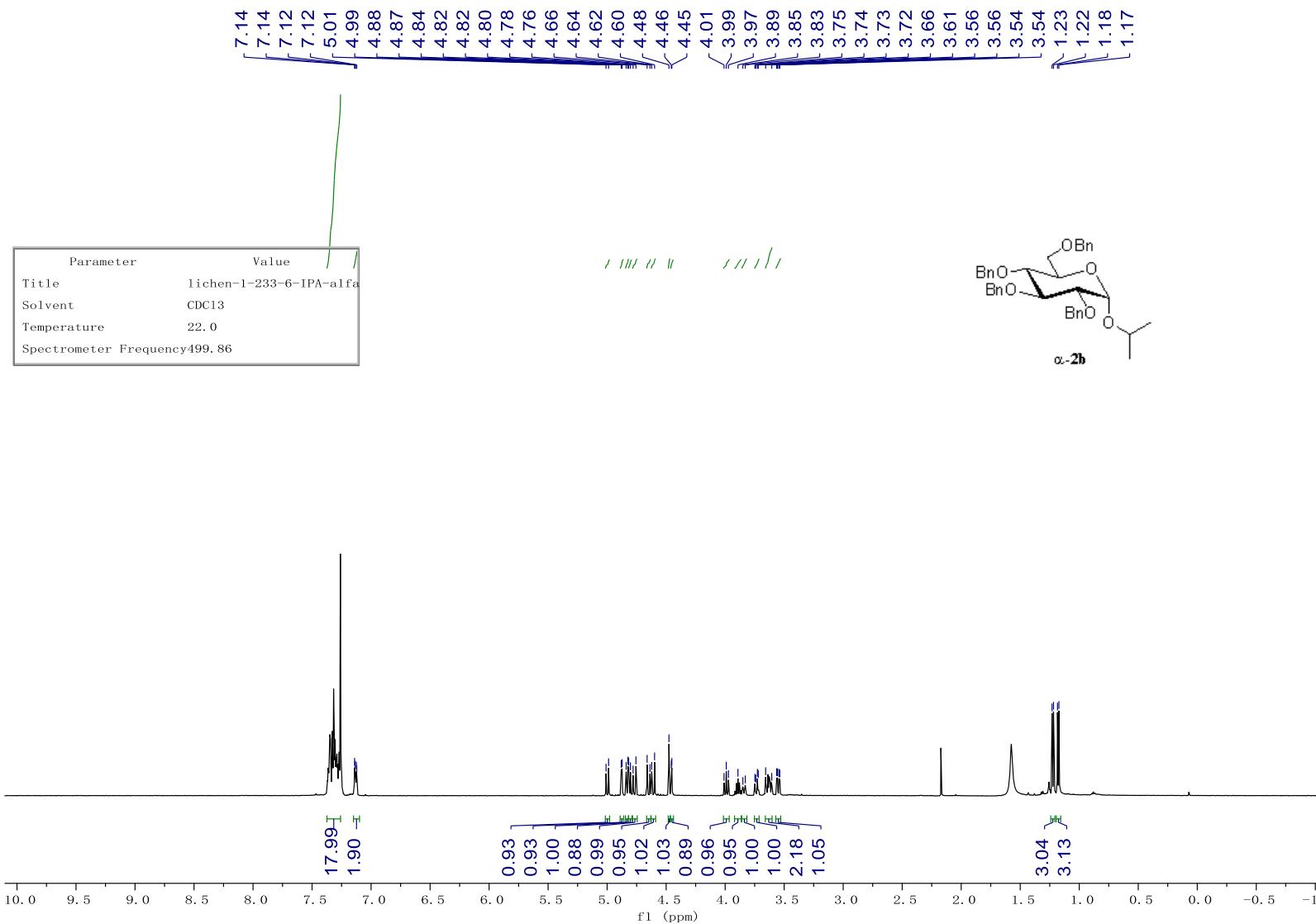


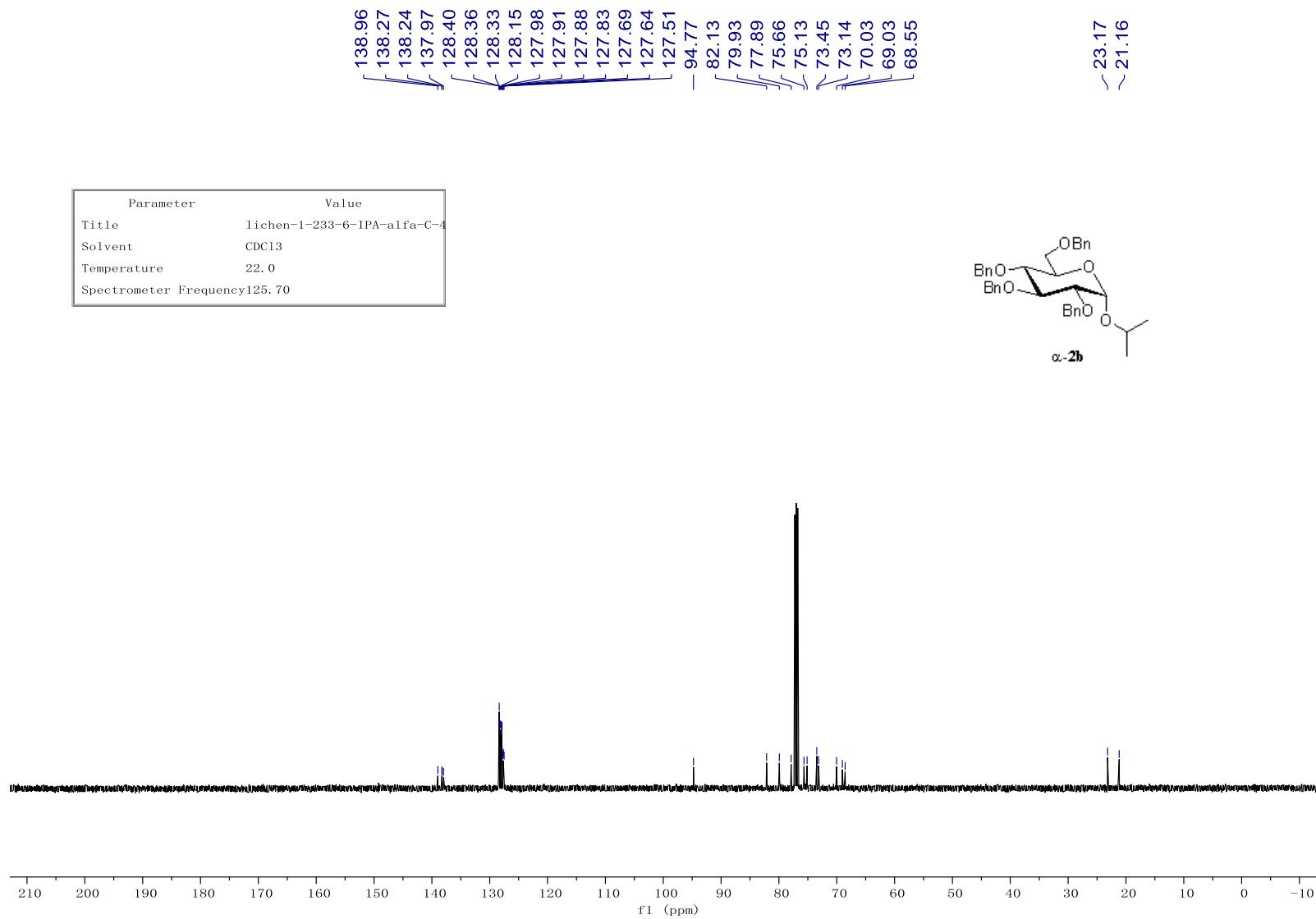


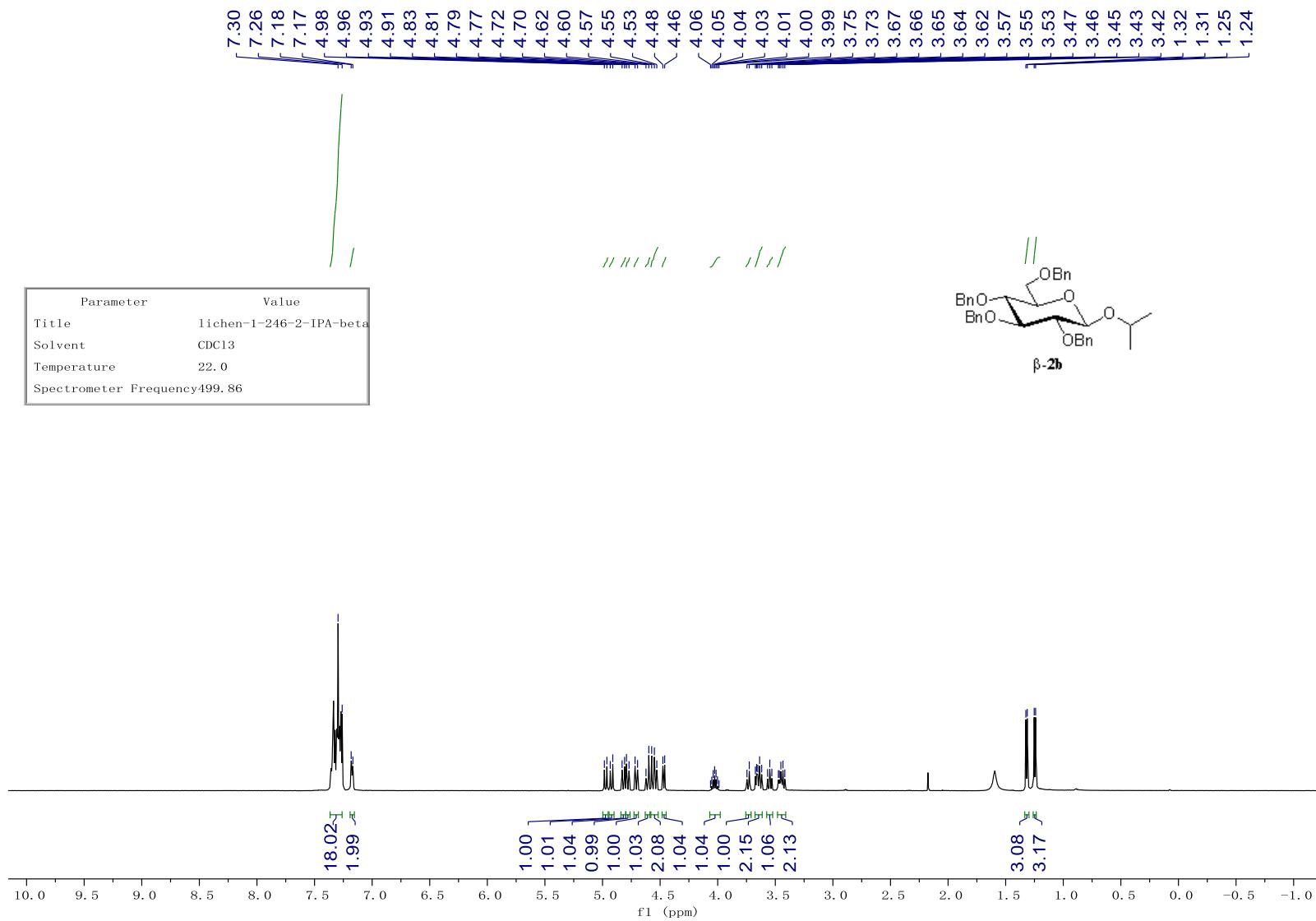


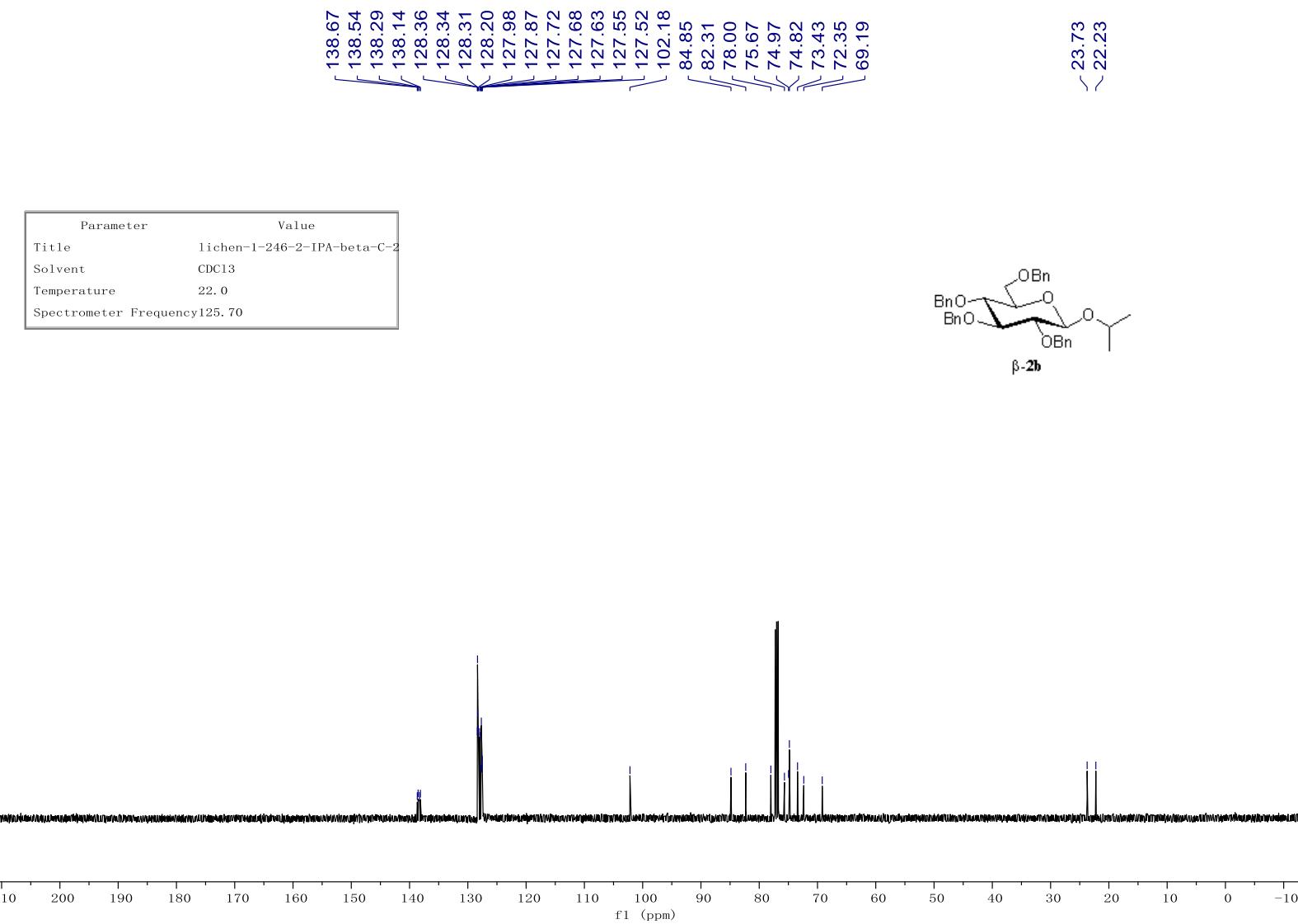


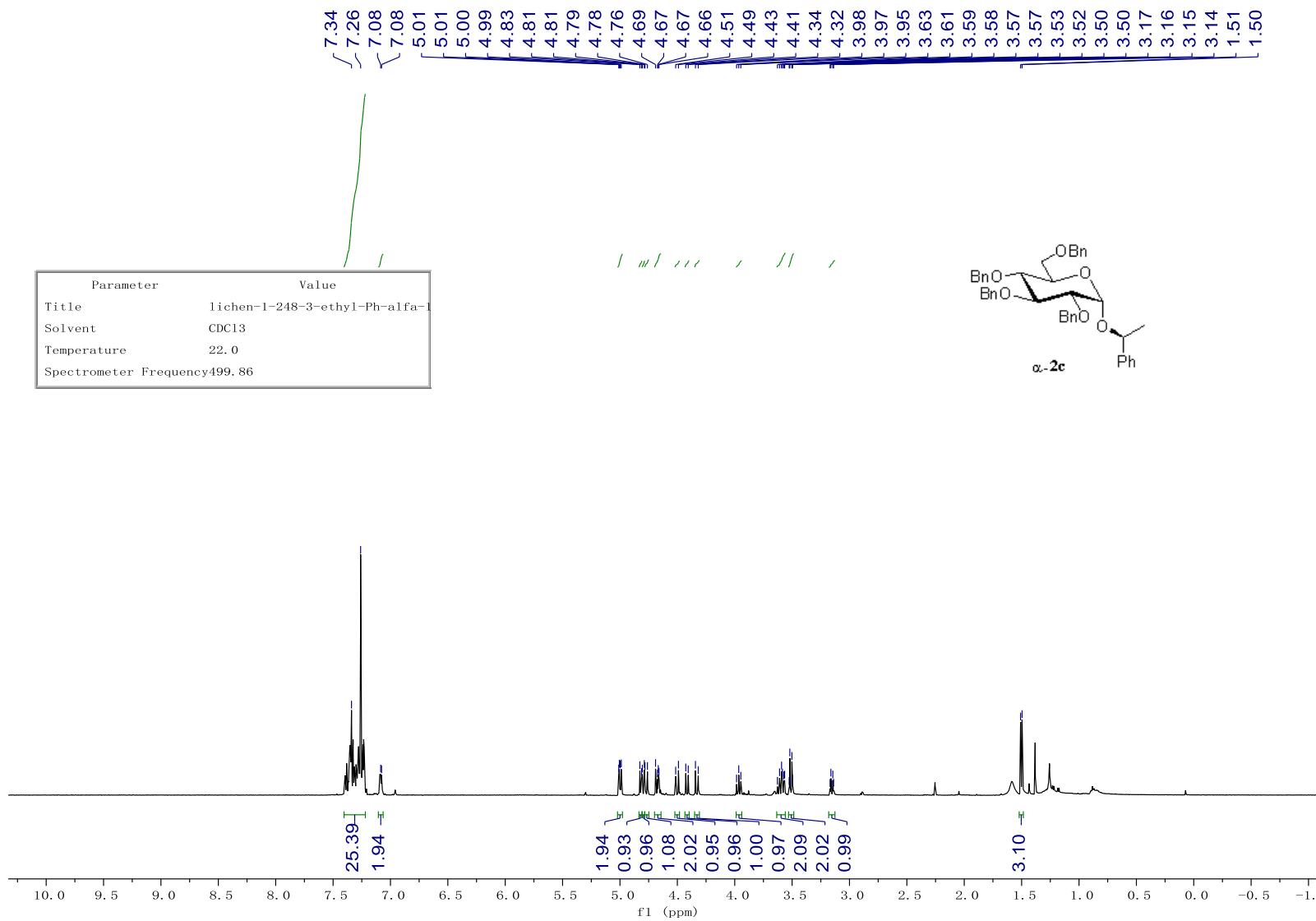


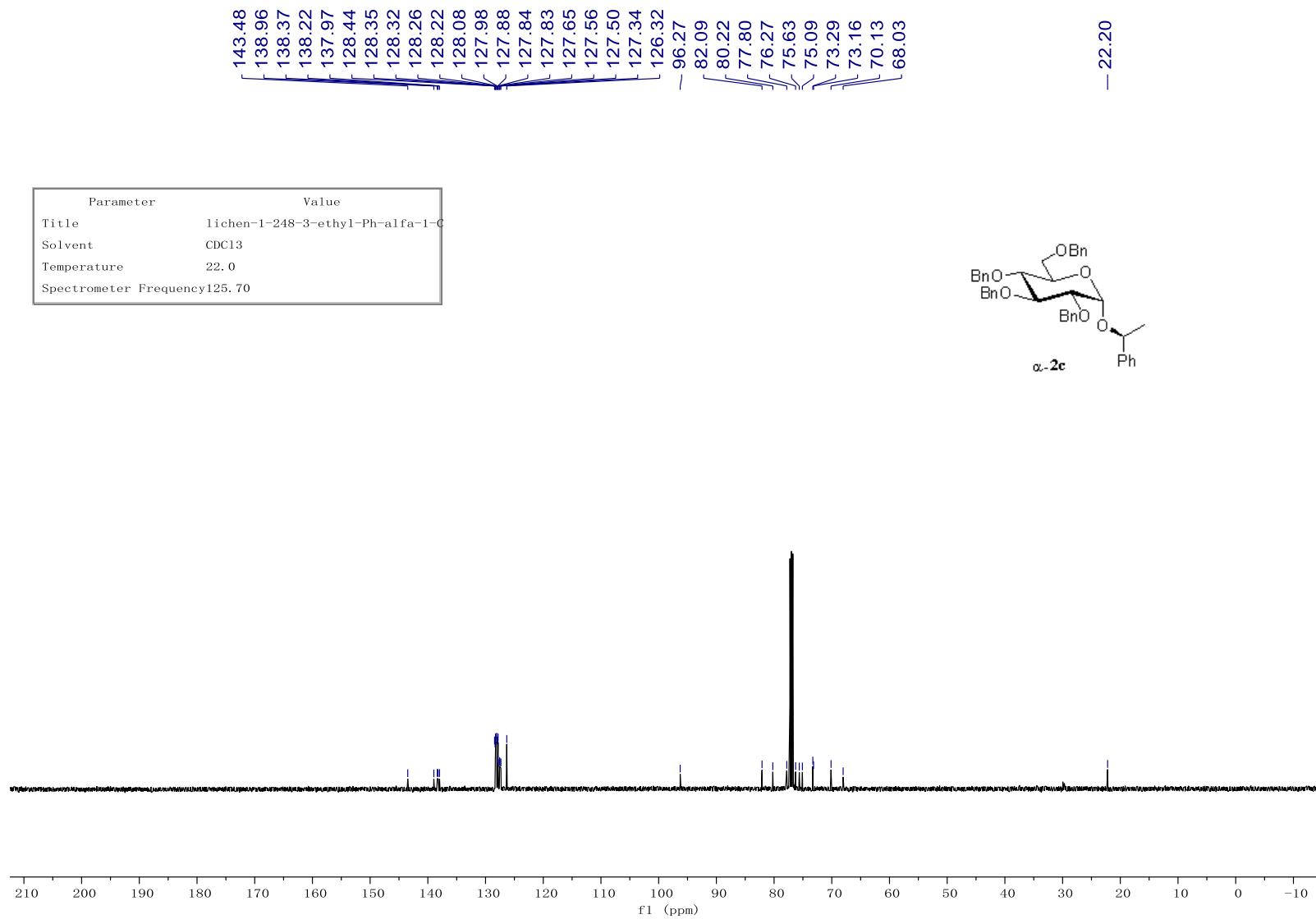


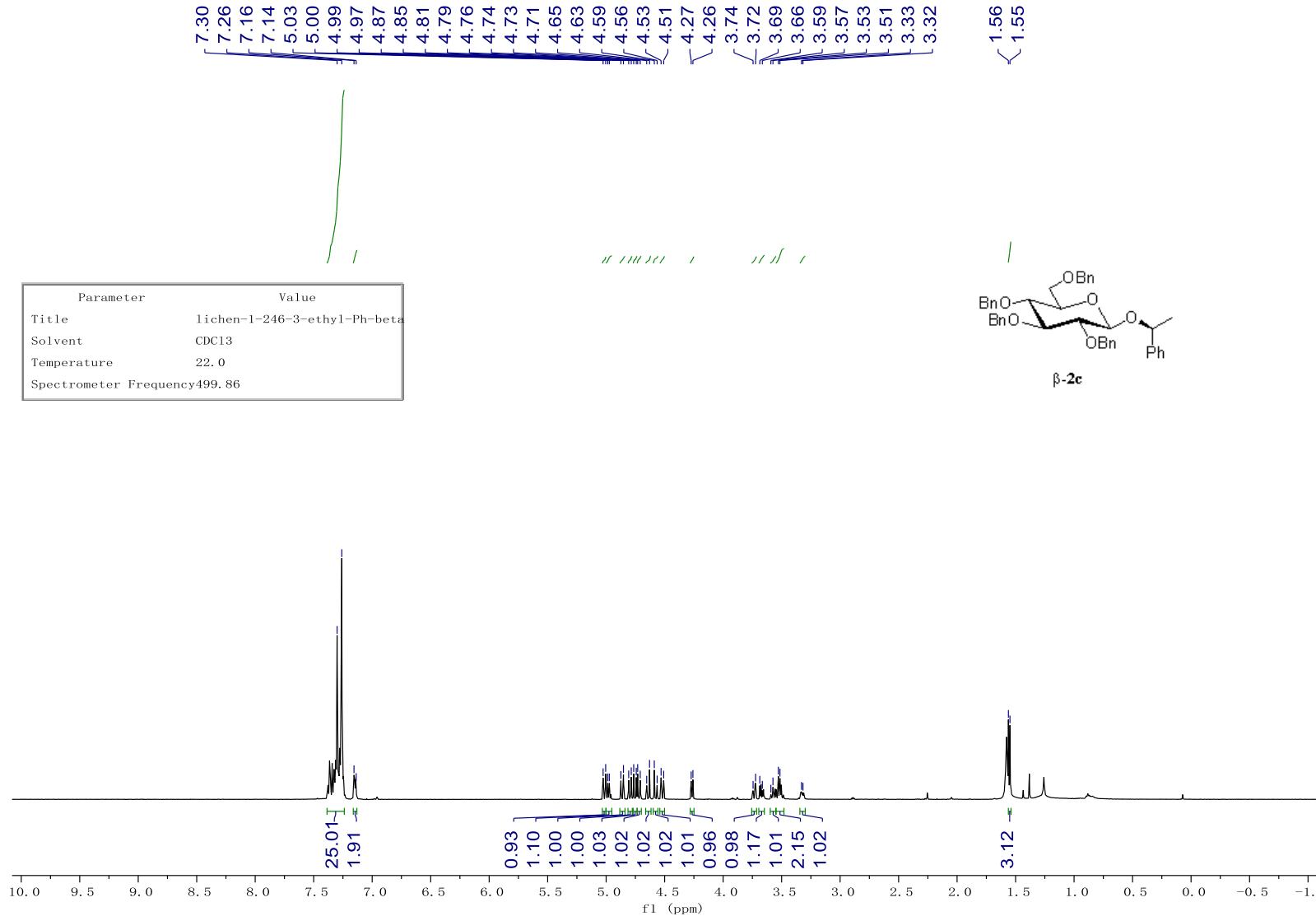


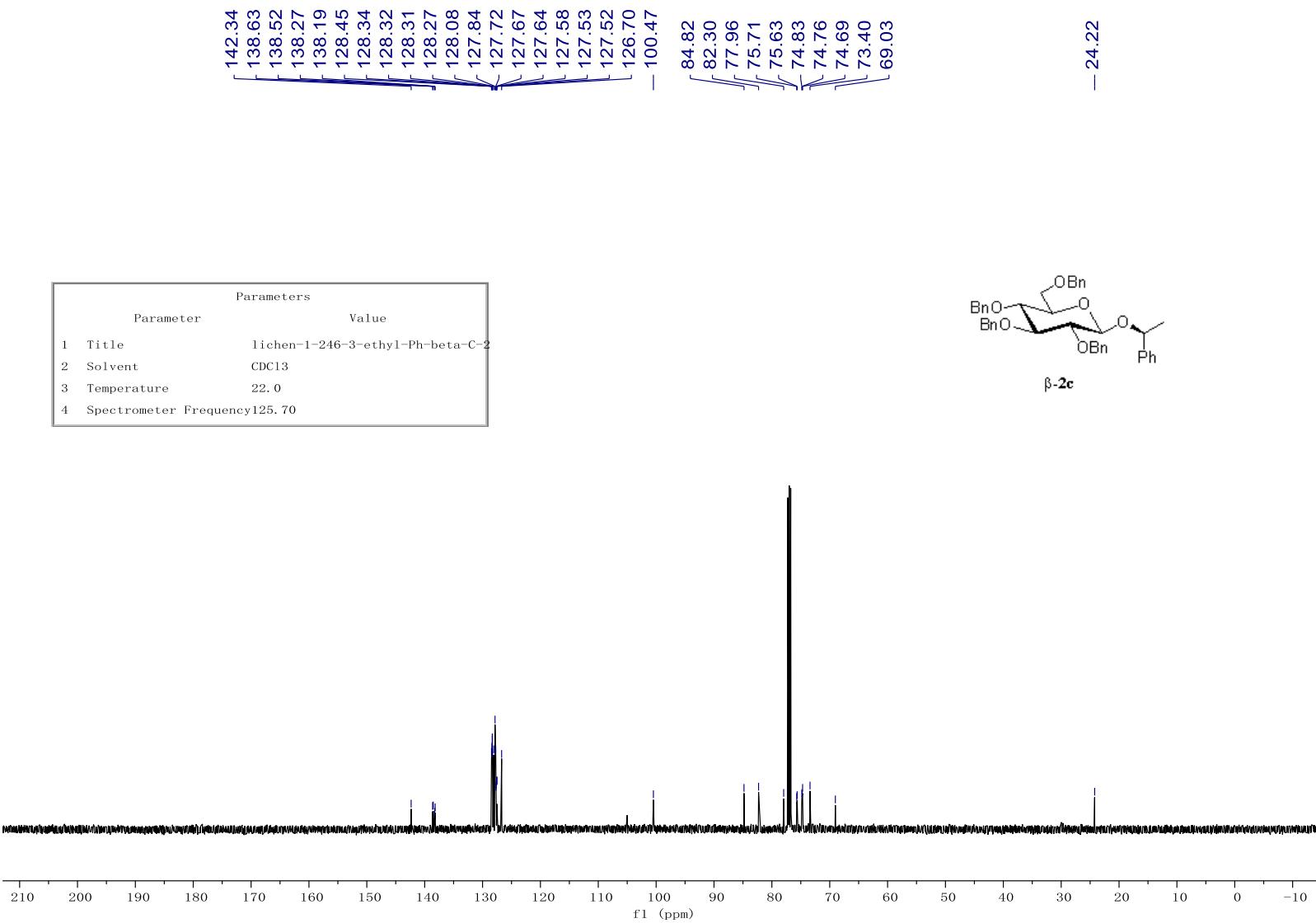


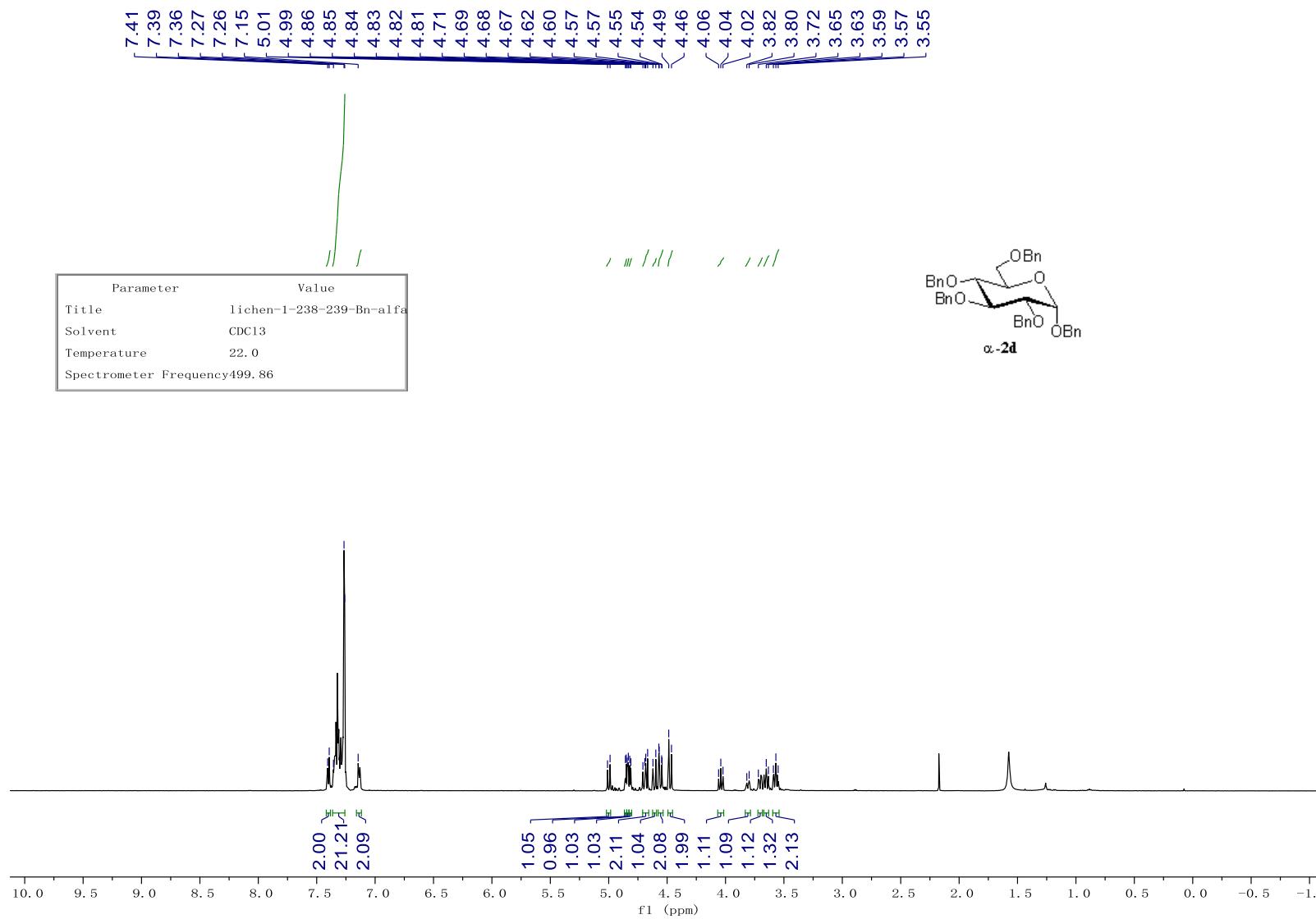


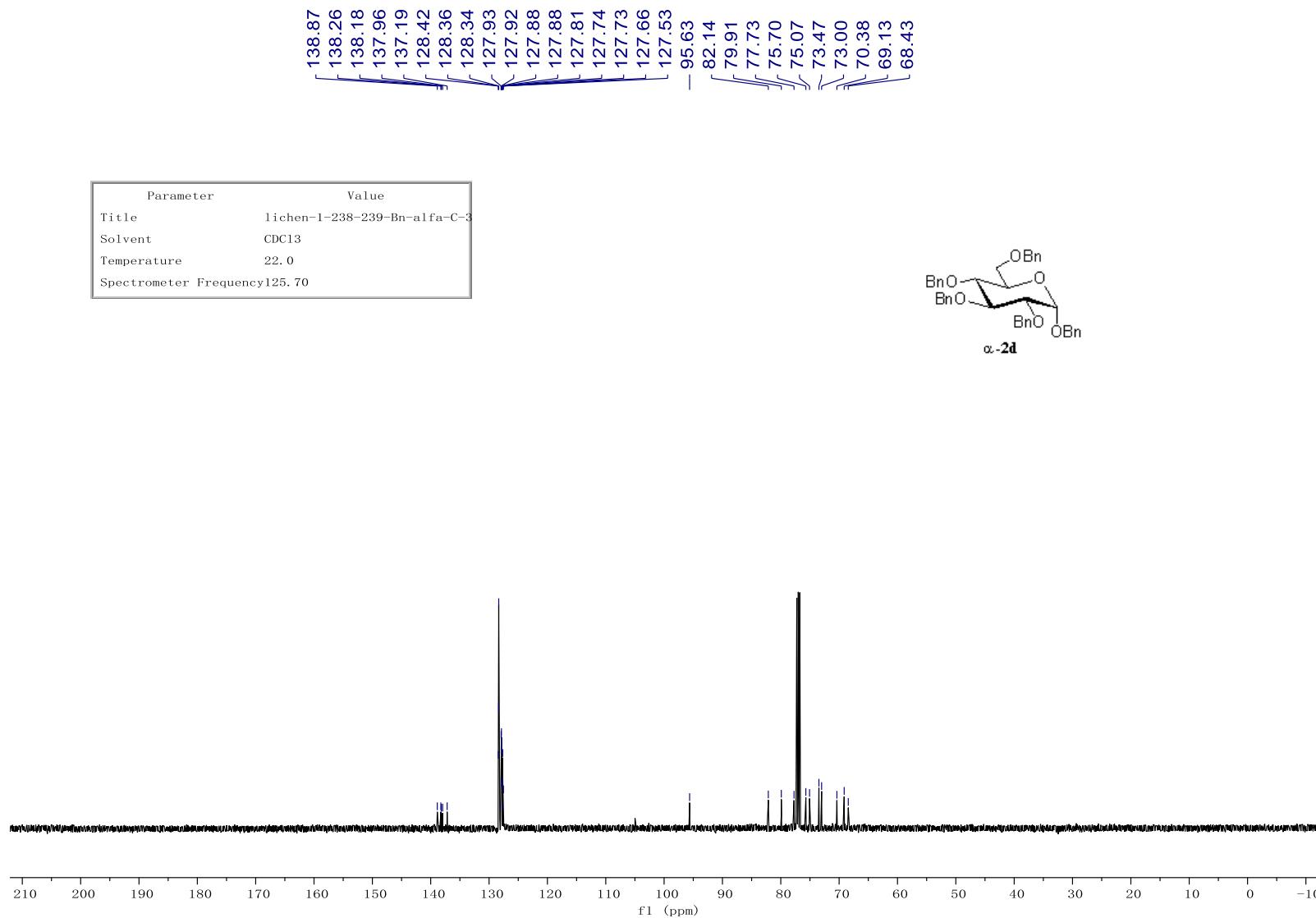


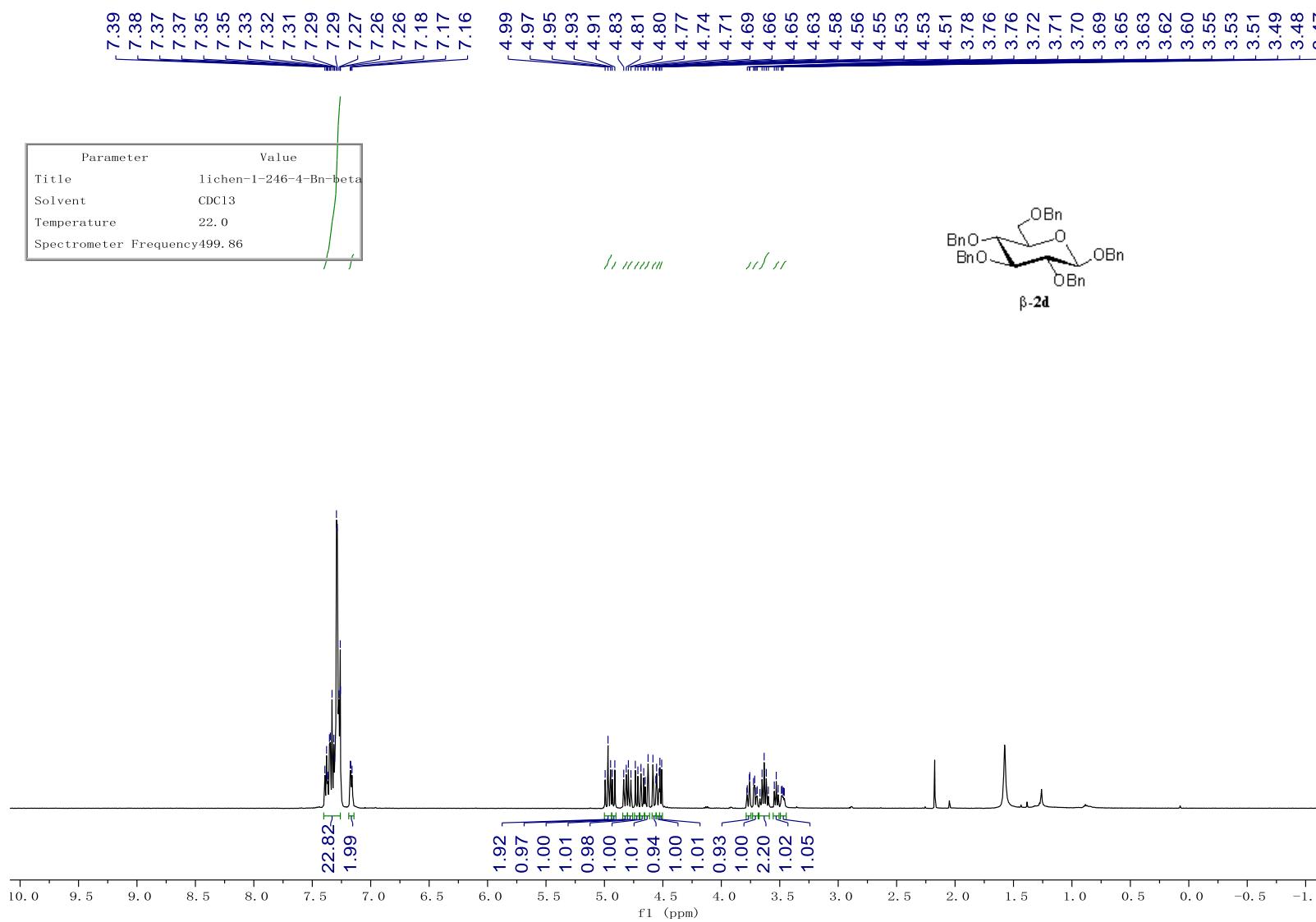


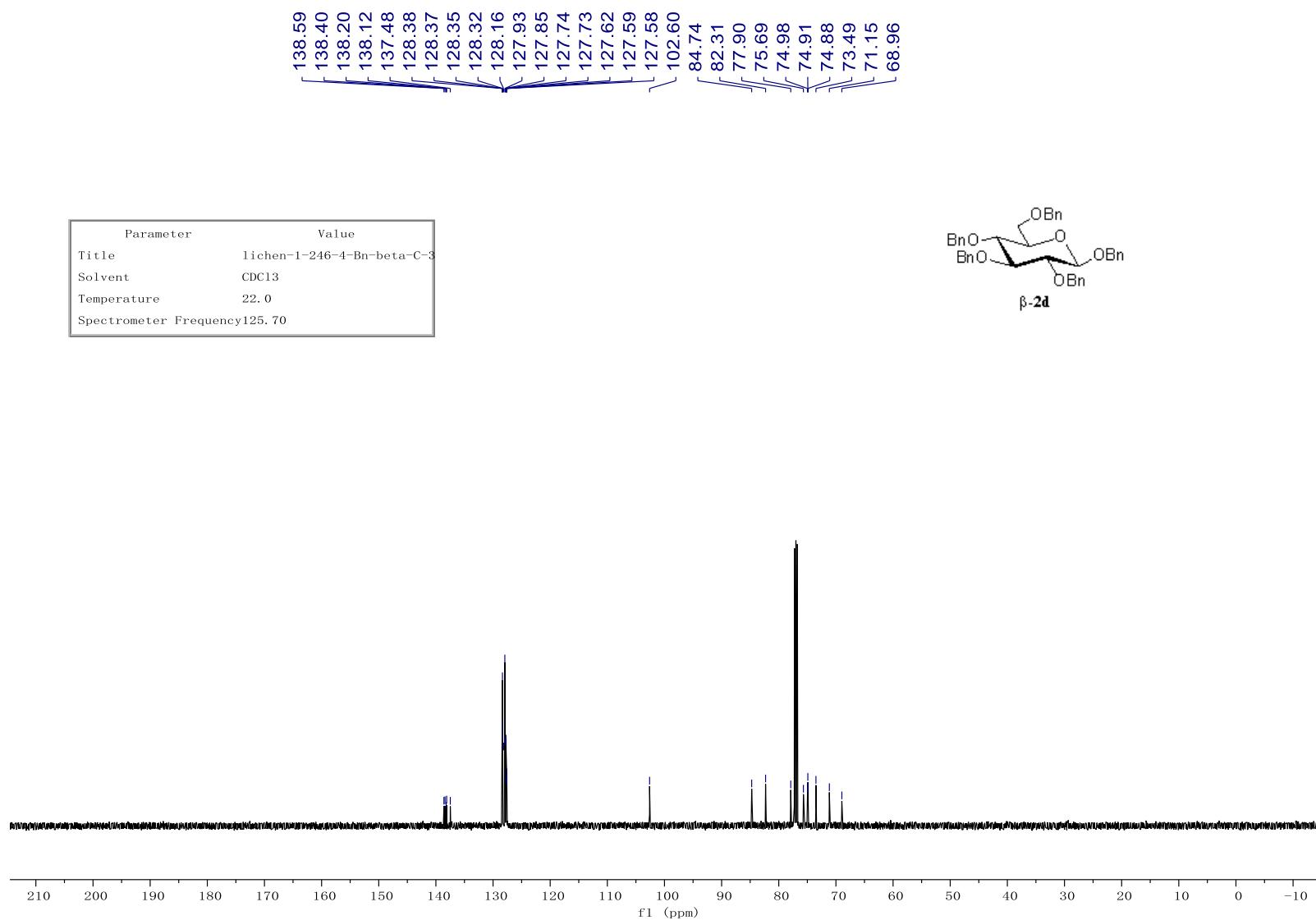


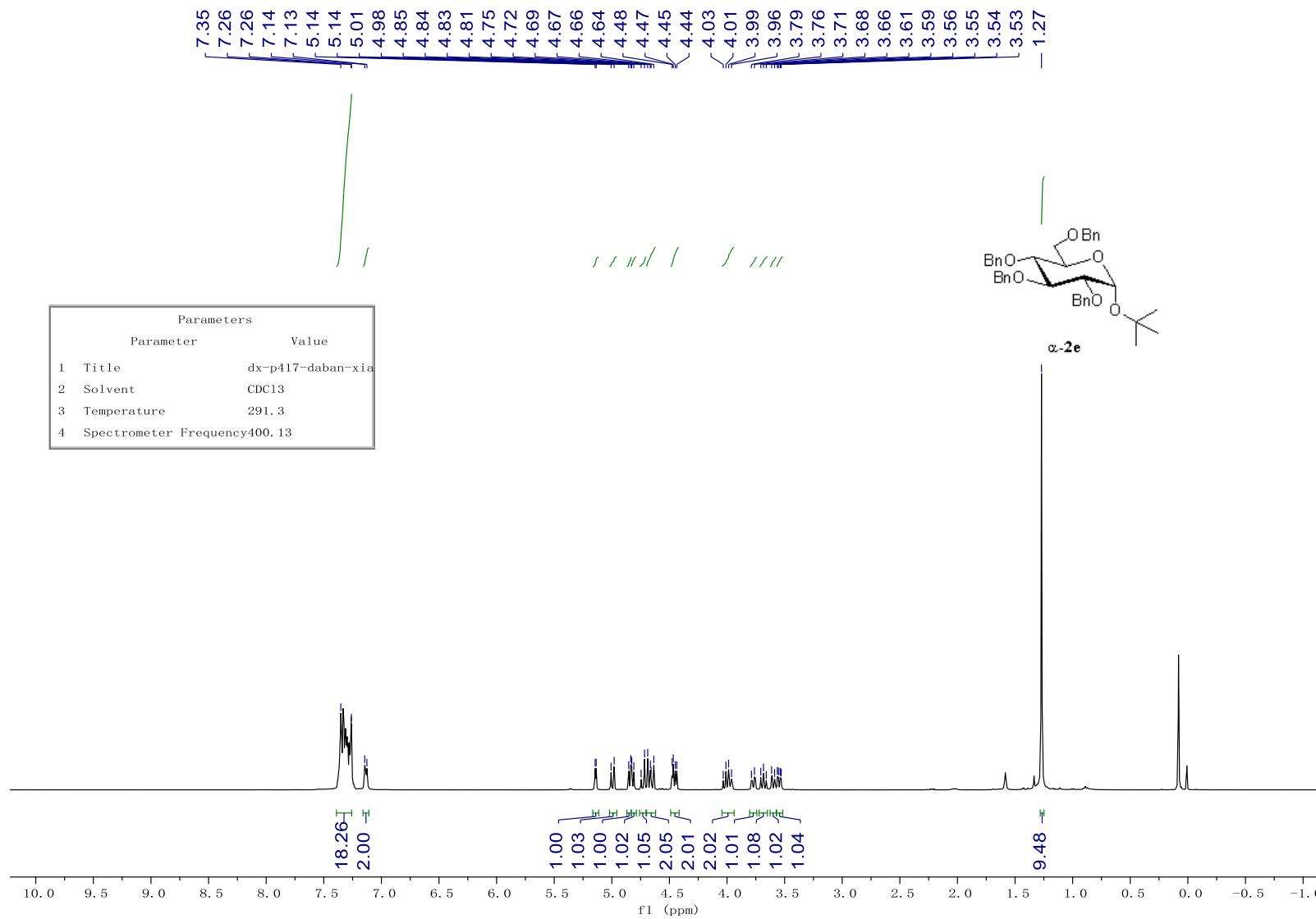


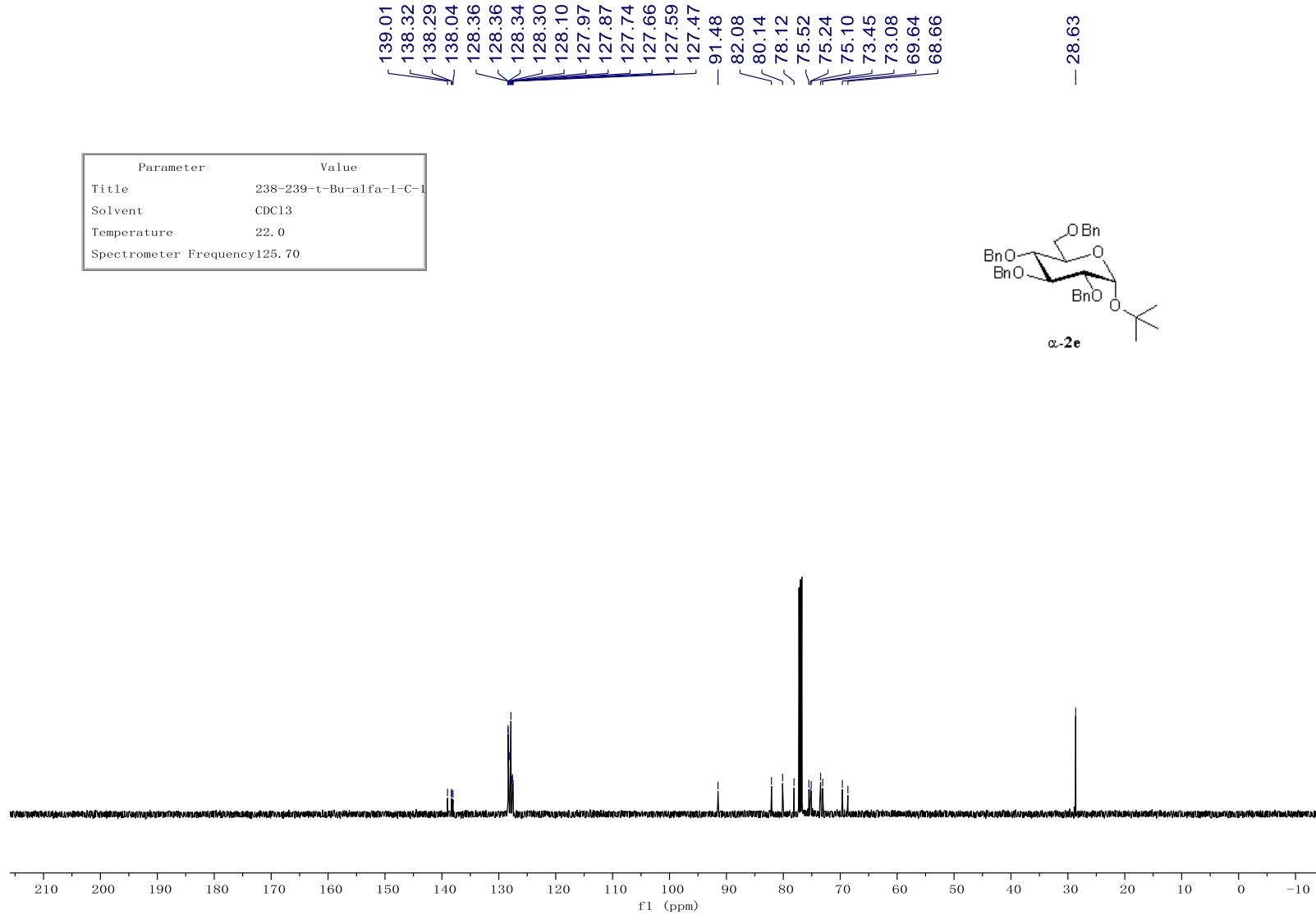


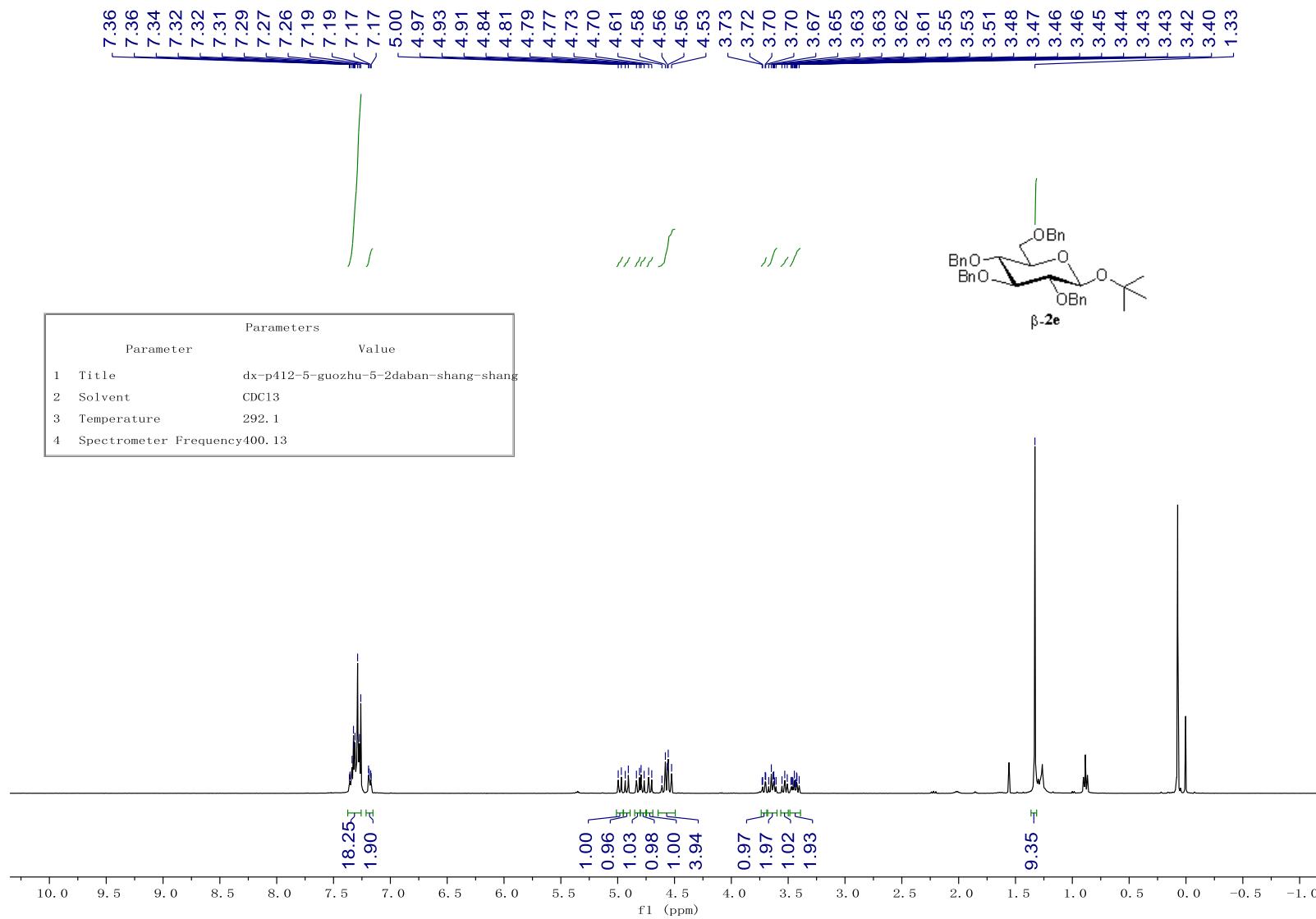


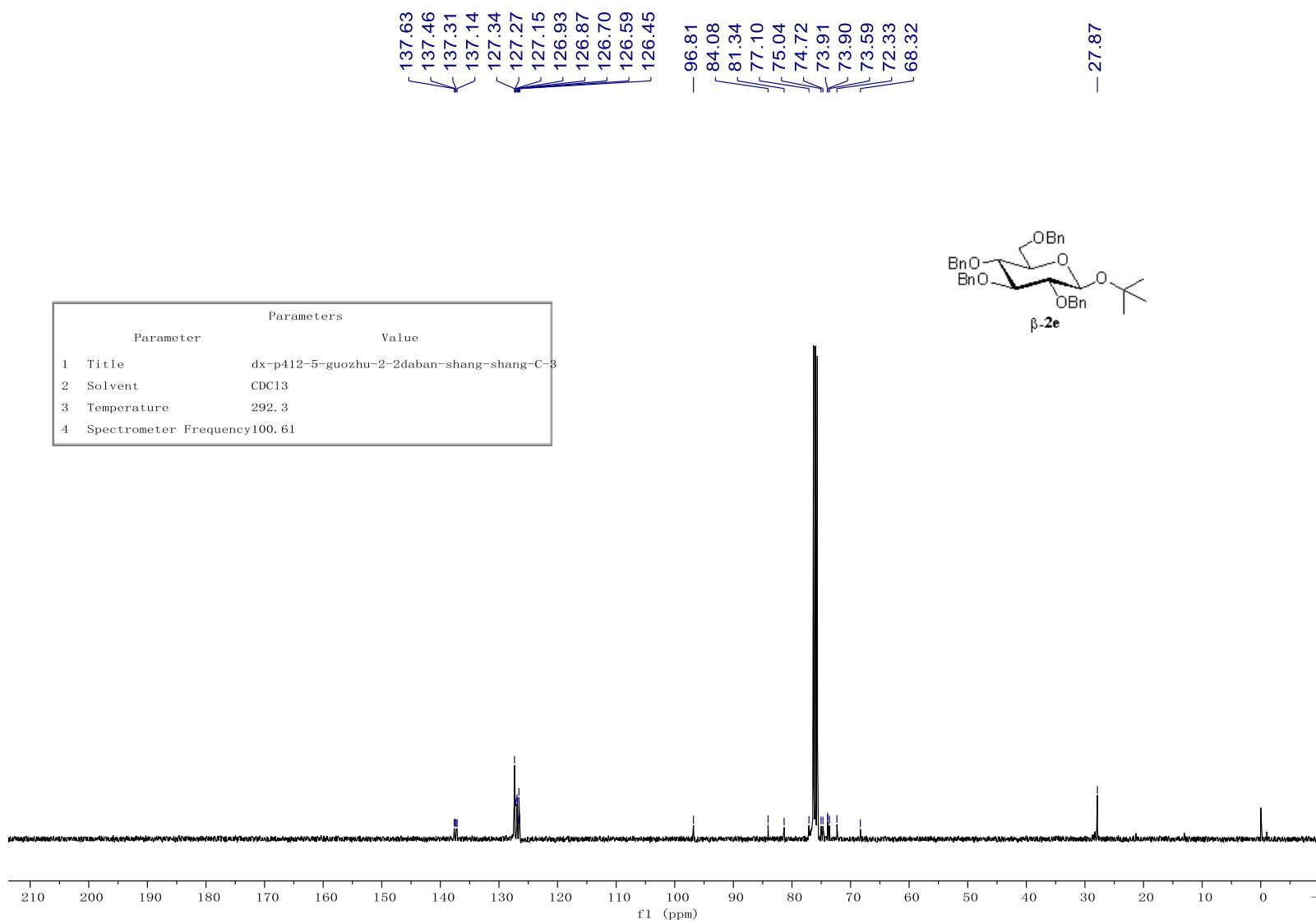


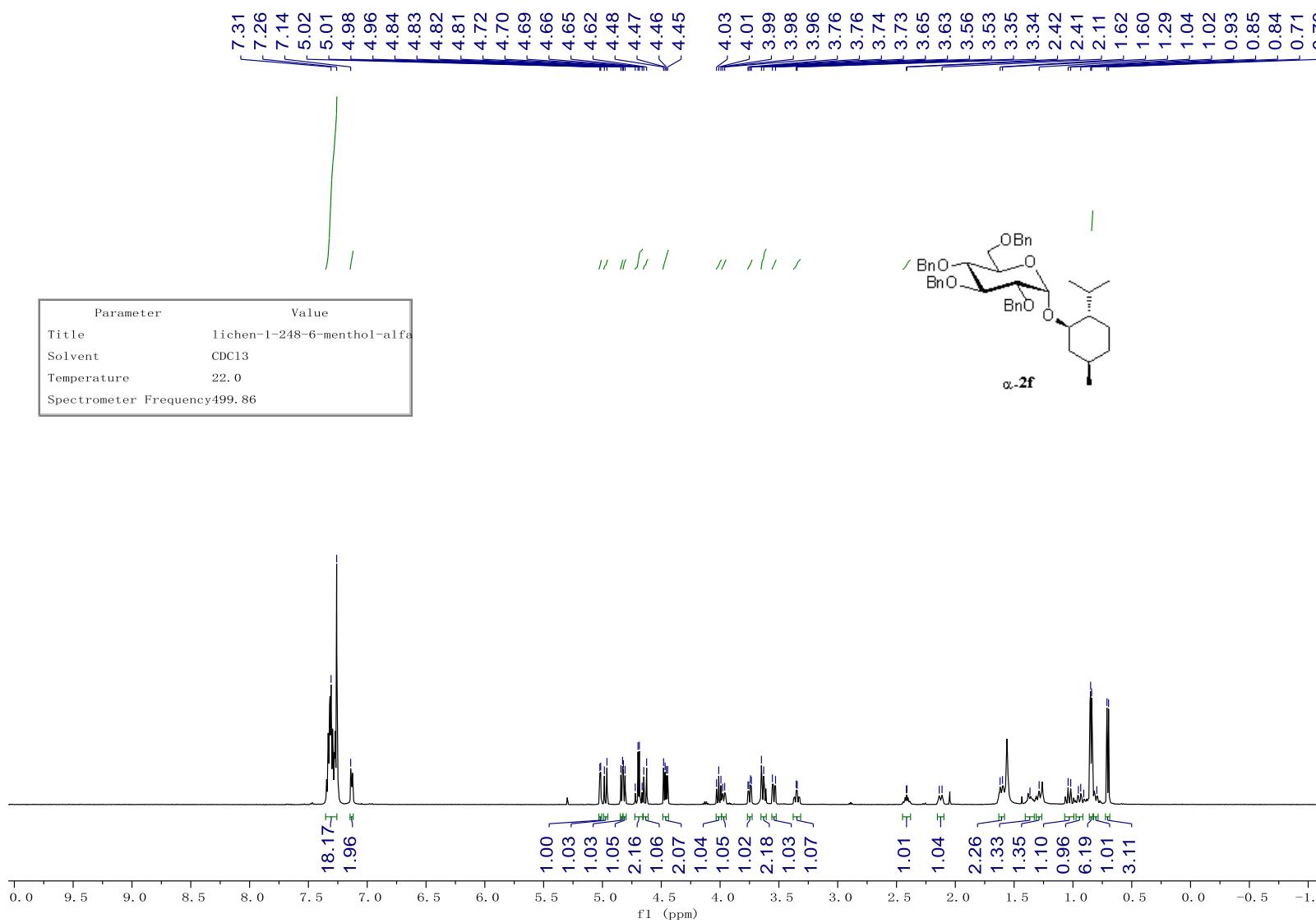


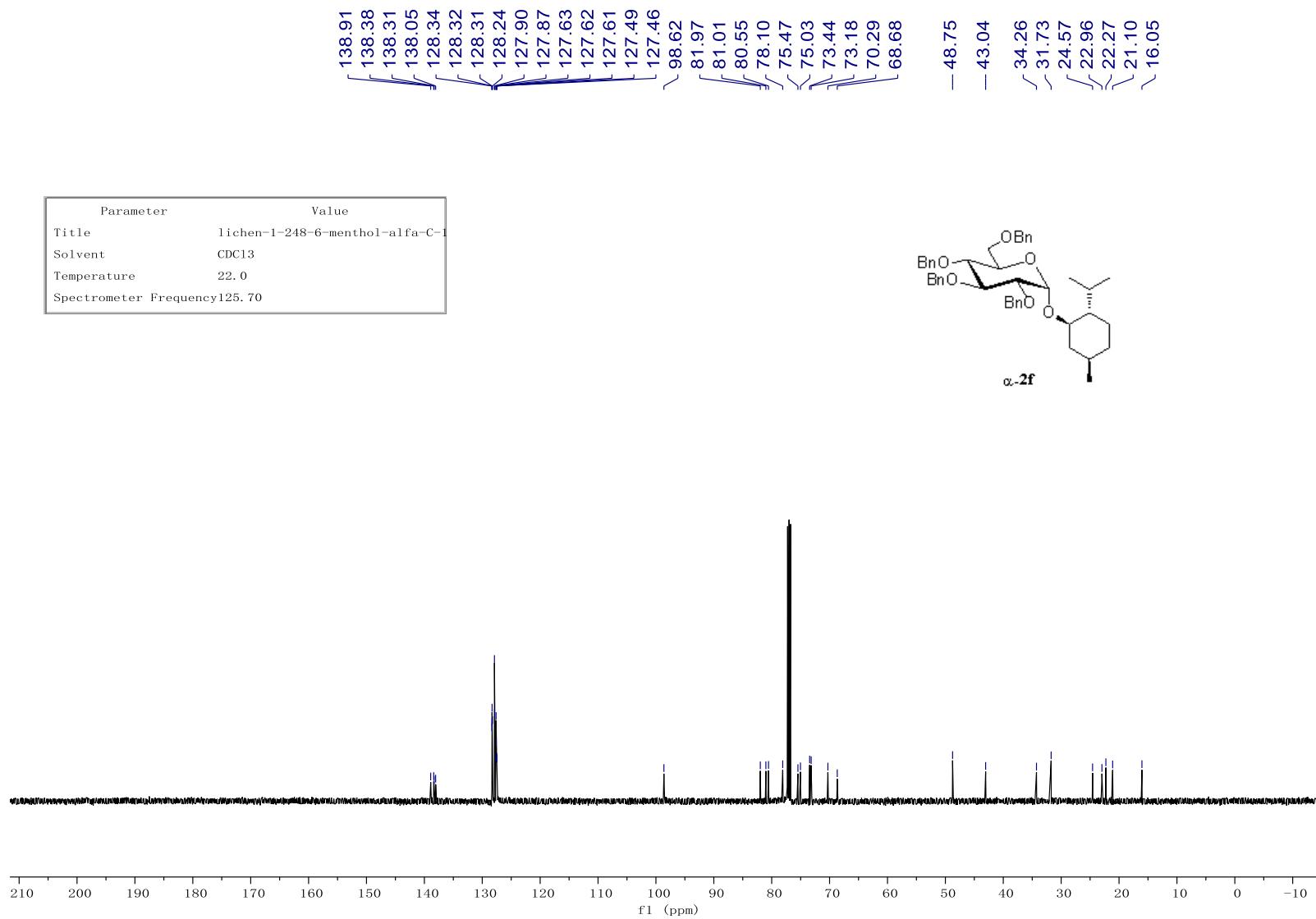


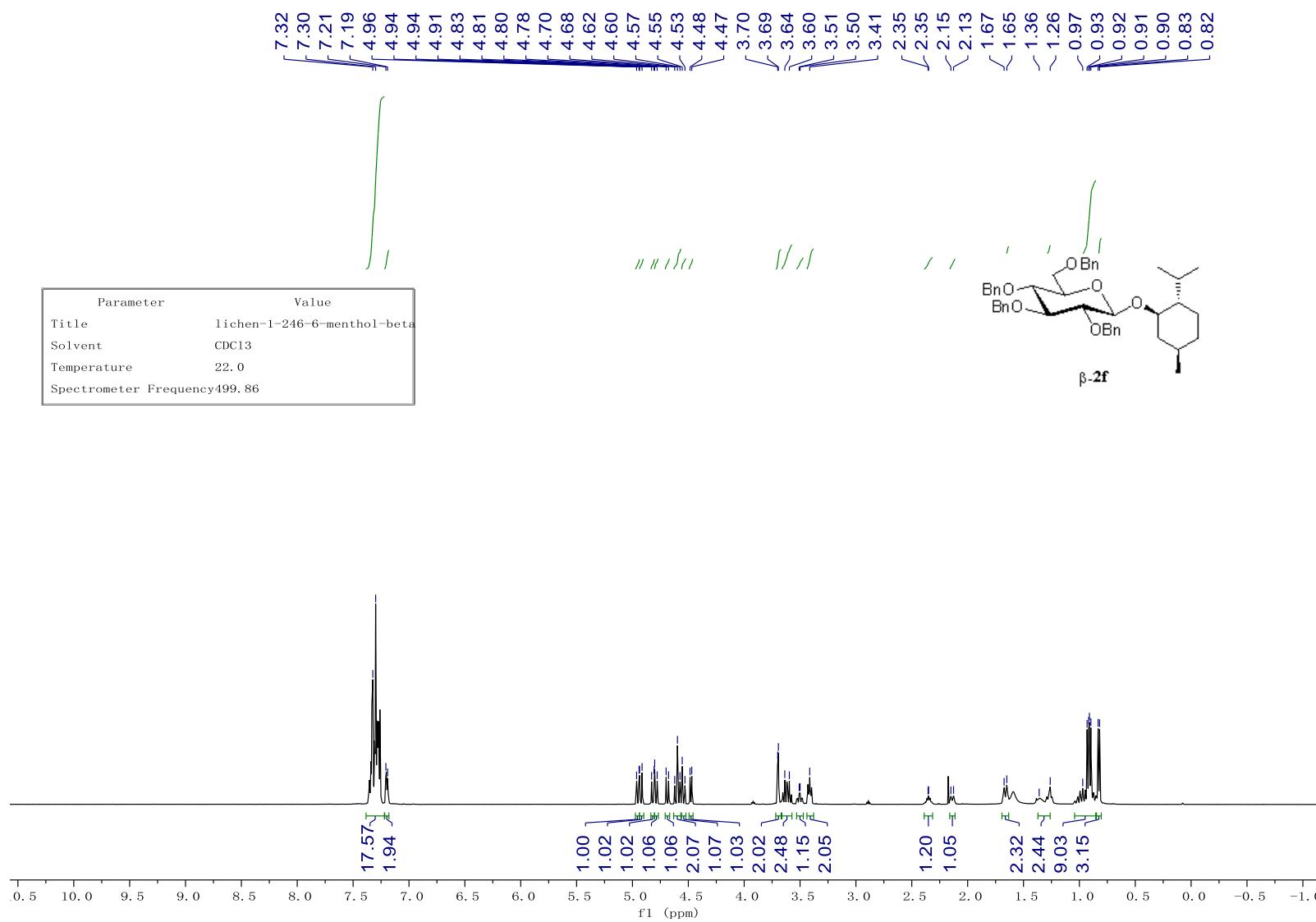


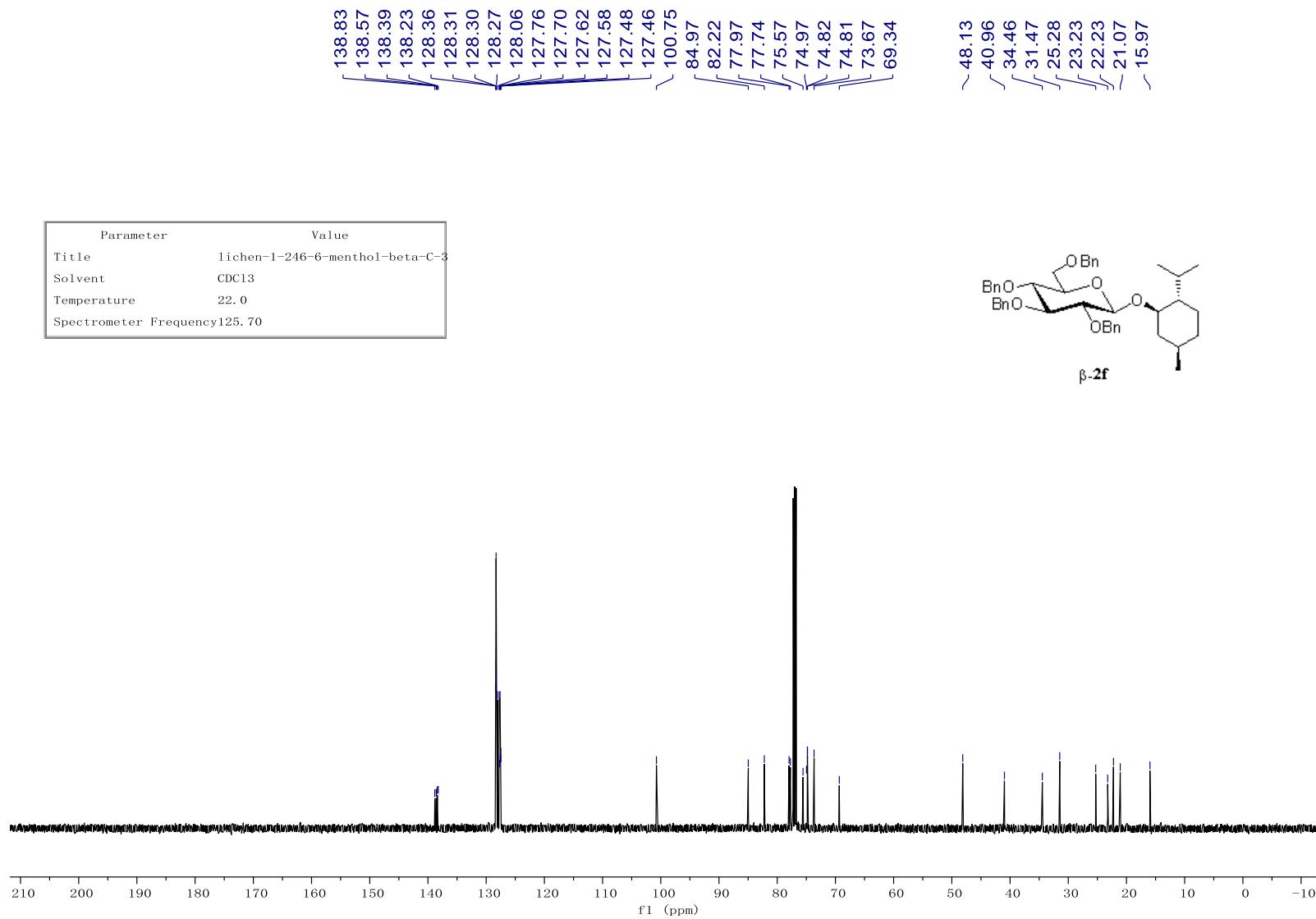


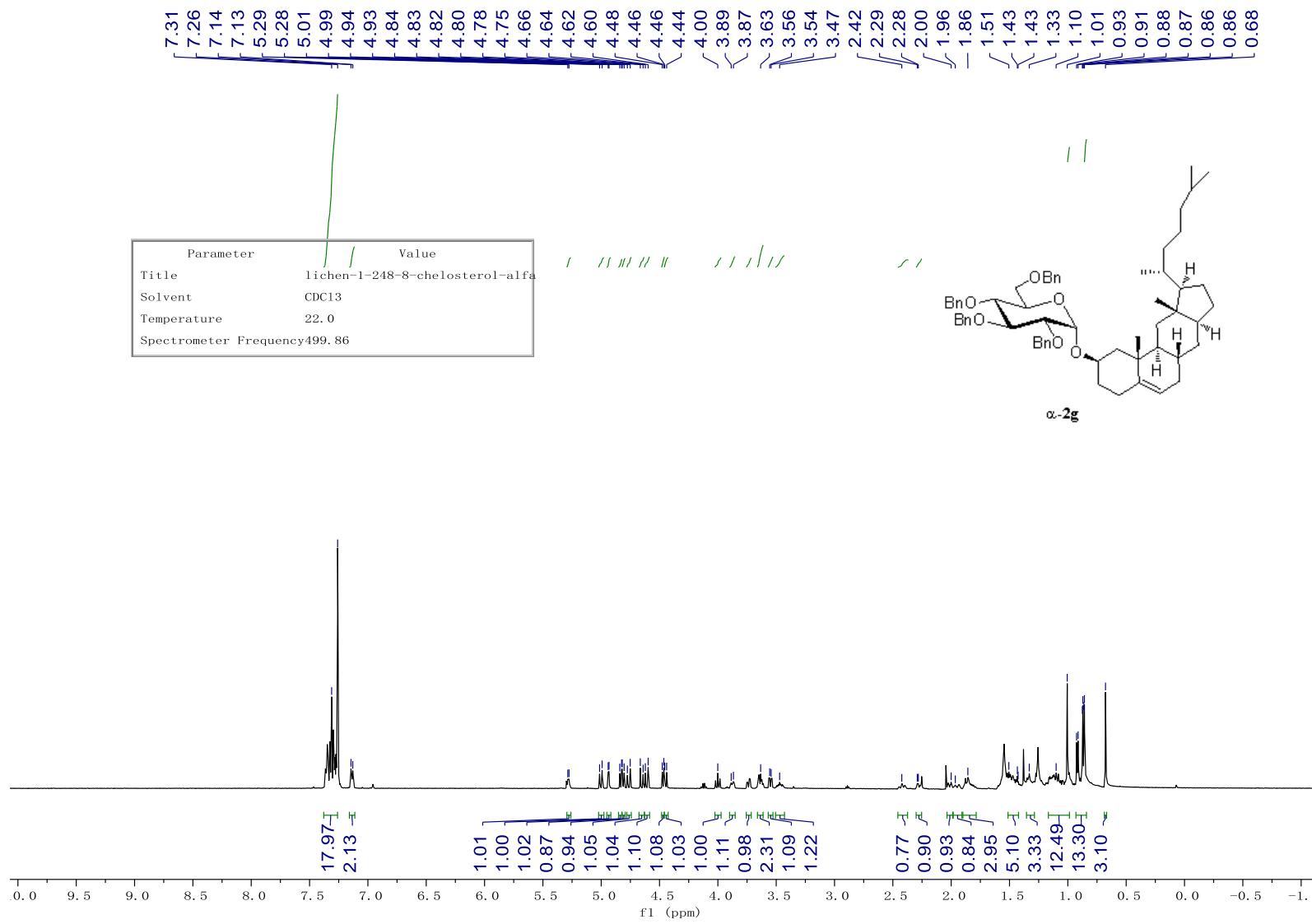


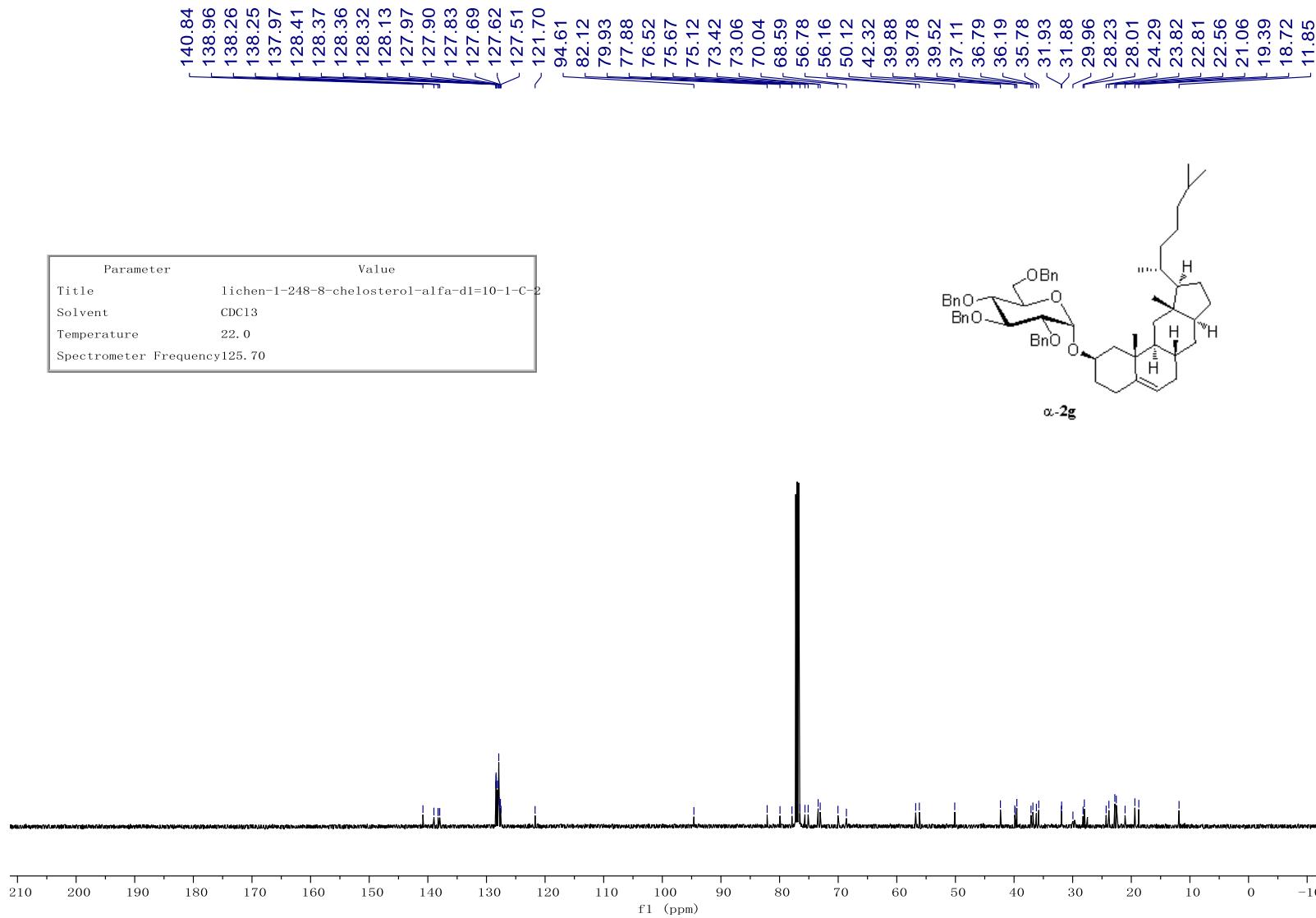


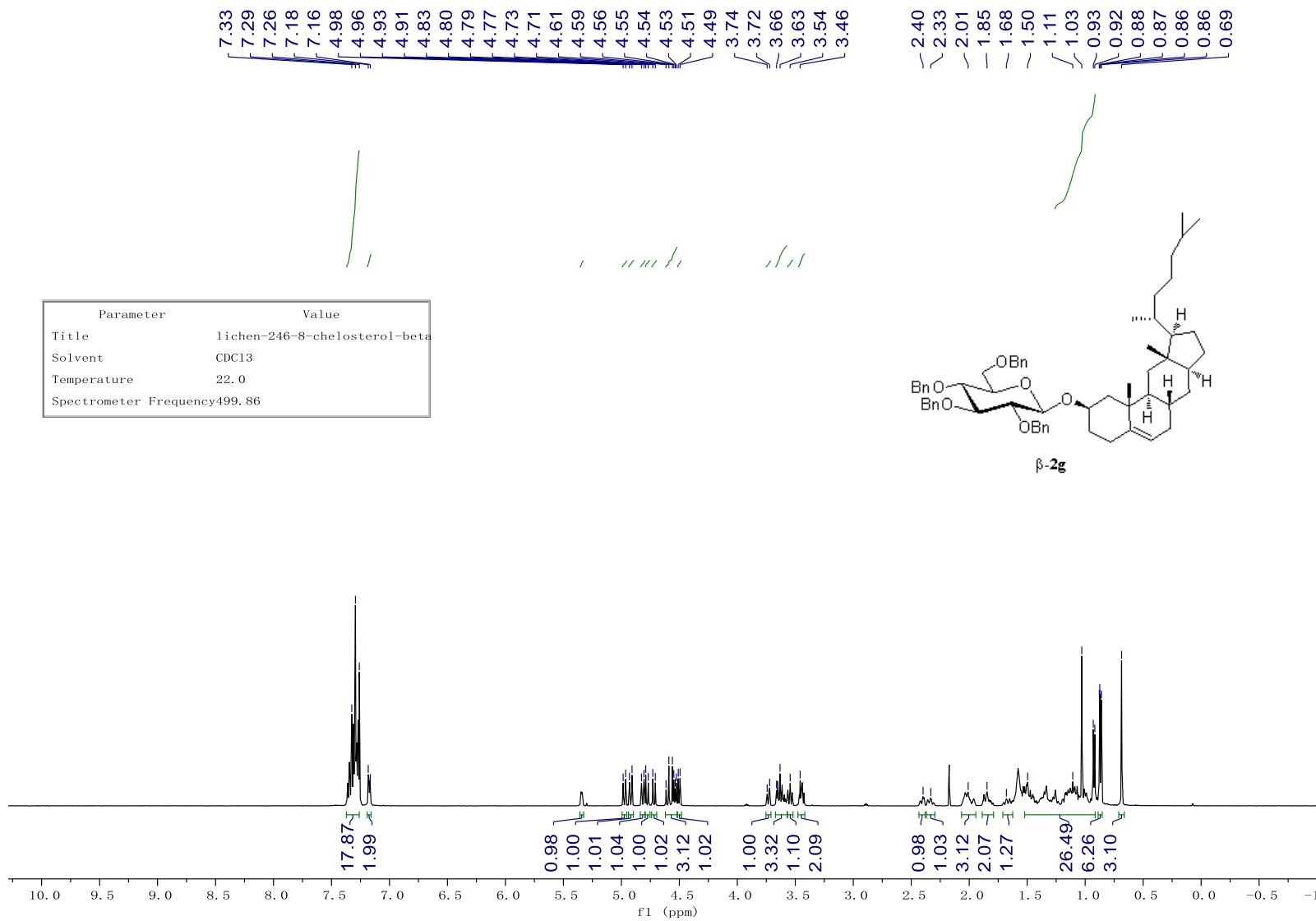


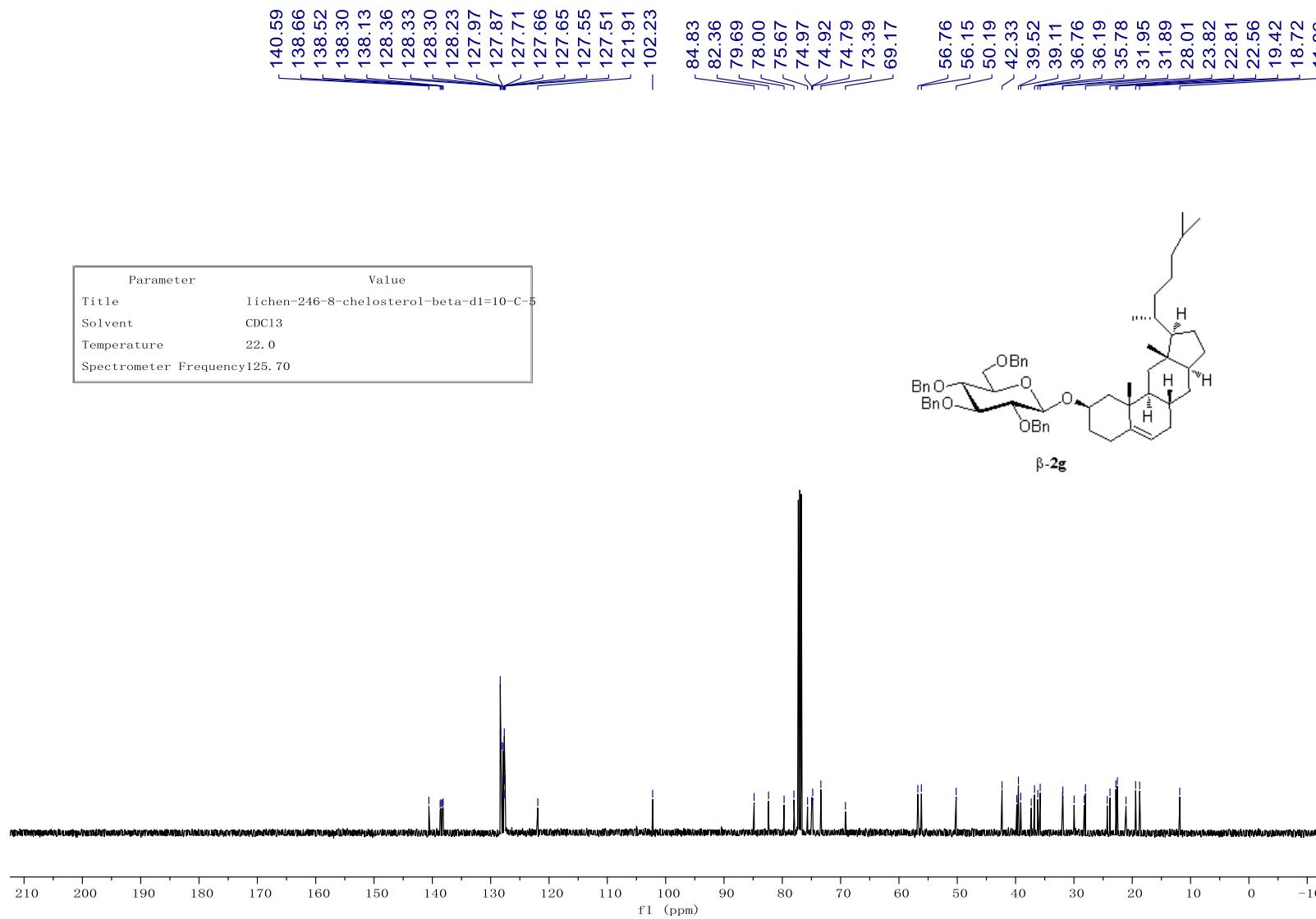


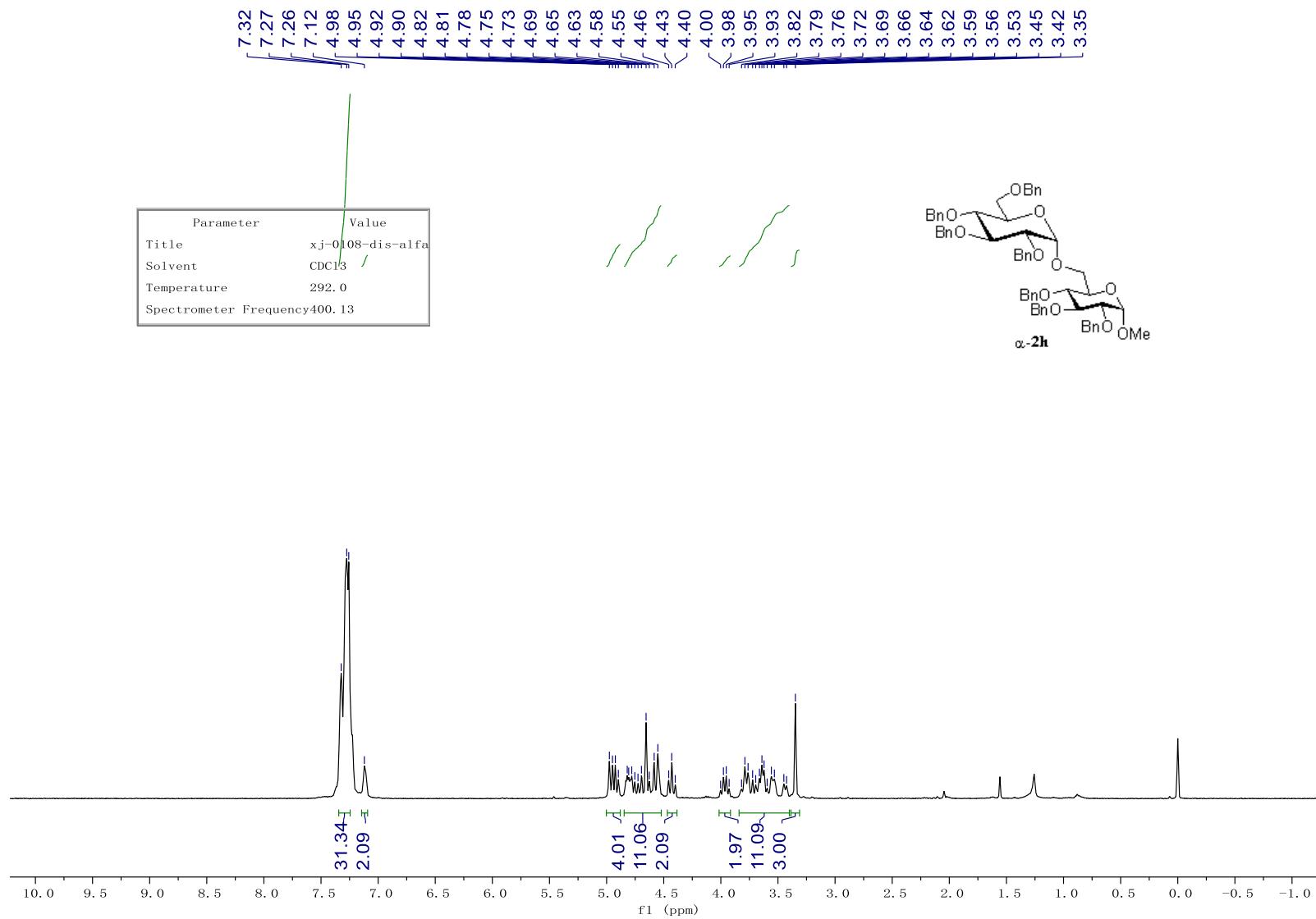


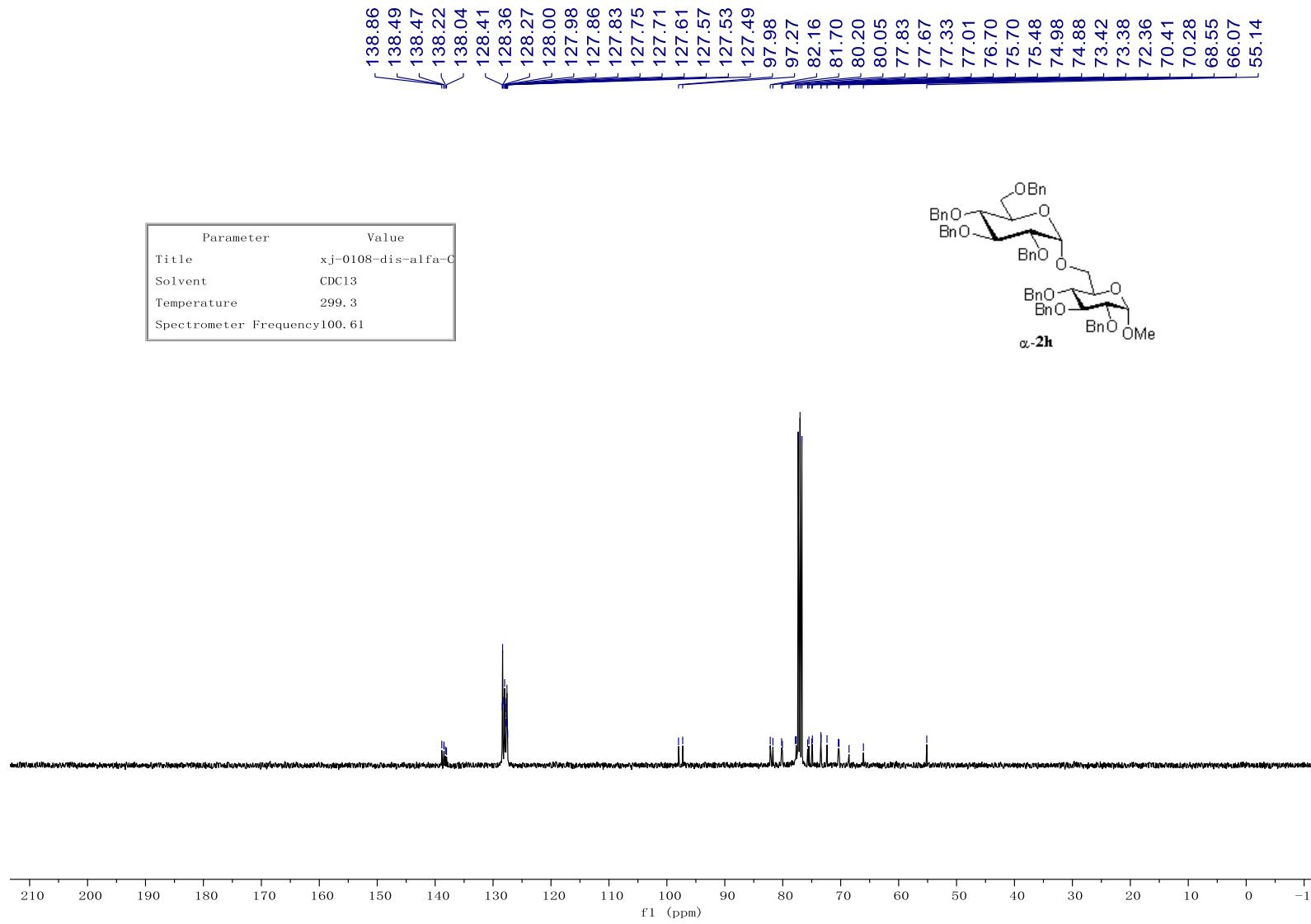


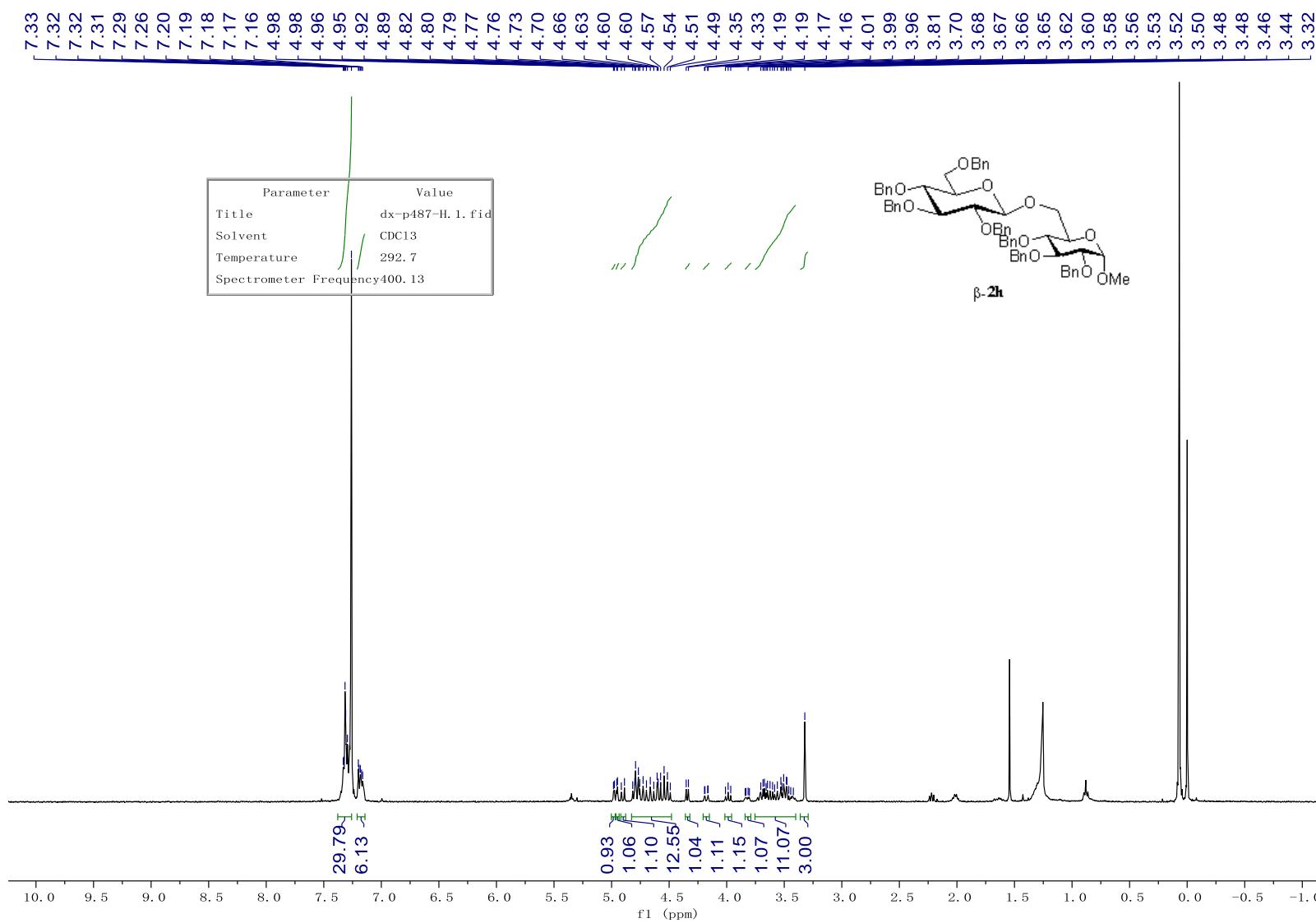




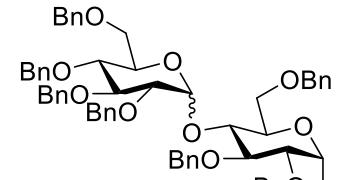






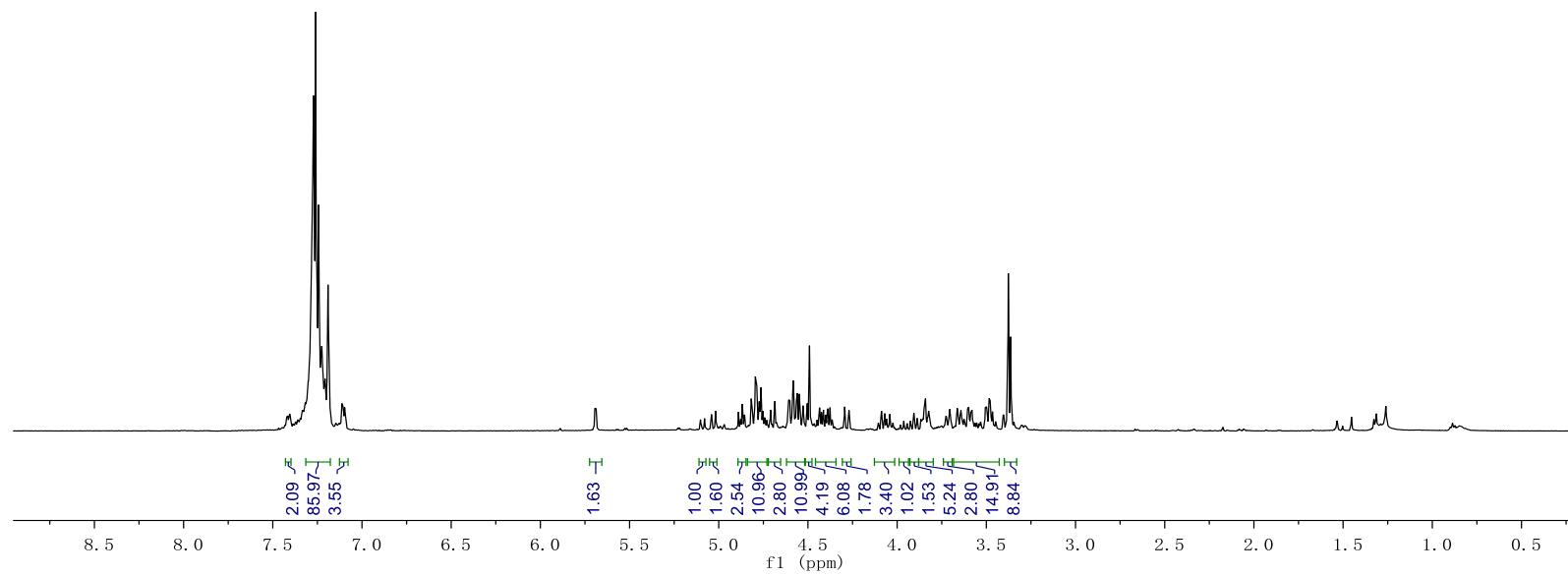


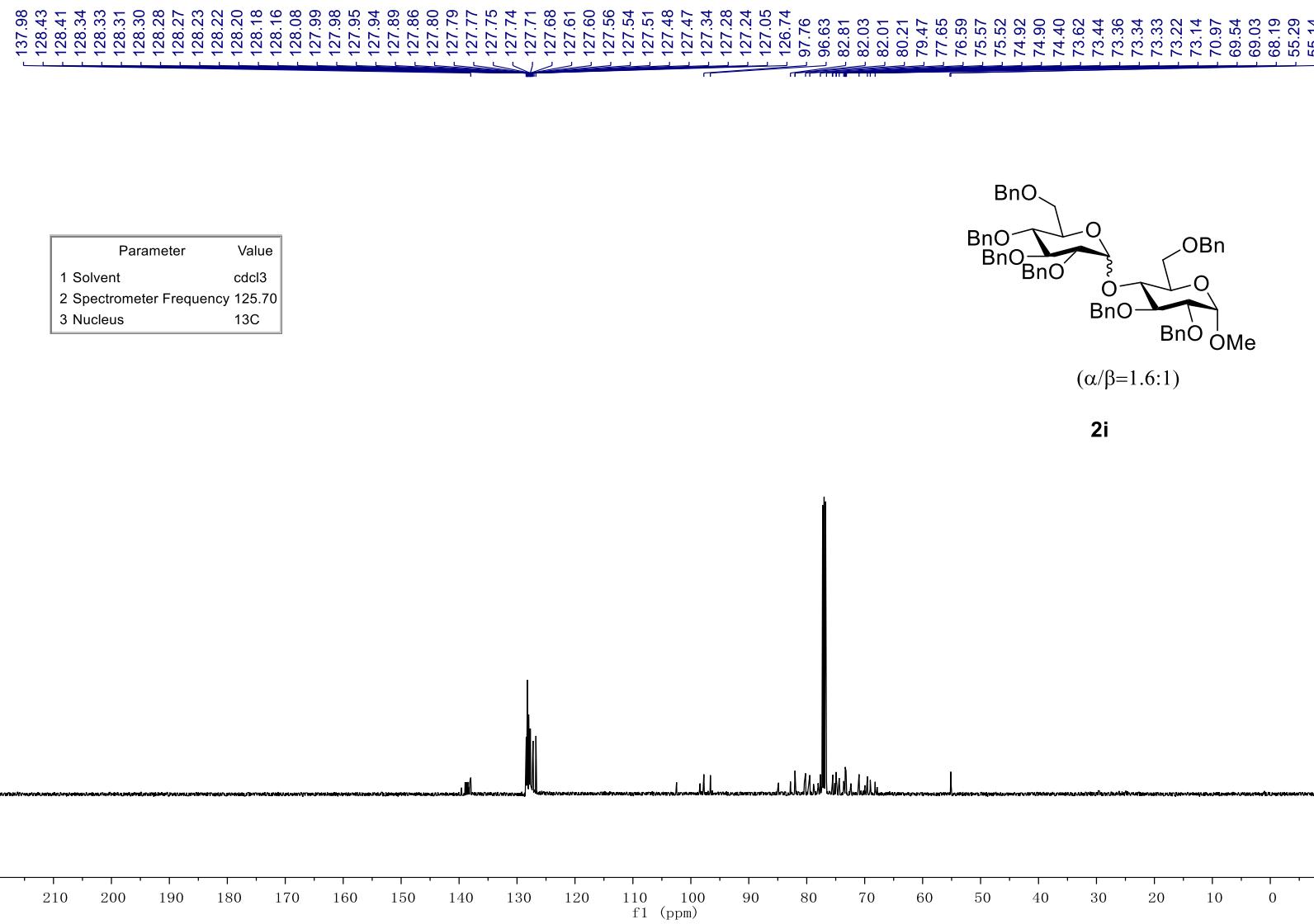
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.85
3 Nucleus	1H



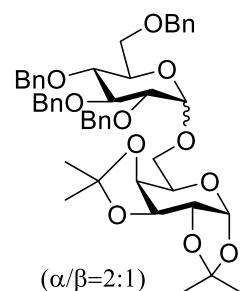
($\alpha/\beta=1.6:1$)

2i





Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.85
3 Nucleus	1H



2j

