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Supporting Information

Ortho-(Methyltosylaminoethynyl)benzyl Glycosides as New Glycosyl Donors for Latent-Active Glycosylation

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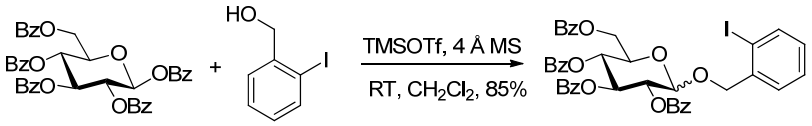
Contents

1. General information. Commercial reagents were used without further purification unless specialized. Solvents were dried and redistilled prior to use in the usual way. Thin layer chromatographies (TLCs) were performed on precoated plates of Silica Gel HF254 (0.5 mm, Yantai, China). Flash column chromatography was performed on Silica Gel H (10-40 μ, Yantai, China). Optical rotations were determined with a Perkin-Elmer Model 241 MC polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 or Bruker AM 500 spectrometer with Me_4Si as the internal standard. Chemical shifts were recorded in δ values and *J* values were given in Hz. Mass spectra were obtained on an HP5989A or a VG Quatro mass spectrometer.

2. Experimental details and characterization data of new compounds

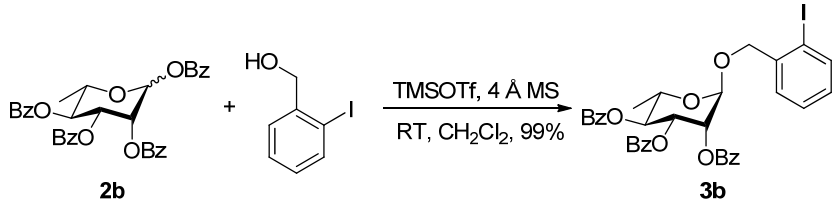
2.1. *Ortho*-Iodobenzyl 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranoside (3a)



2a **3a**

A mixture of **2a** (10 g, 14.3 mmol), 2-iodobenzyl alcohol (4.0 g, 17.1 mmol), and 4Å MS in dry CH_2Cl_2 (100 mL) under argon atmosphere was stirred at room temperature for 30 minutes. TMSOTf (1.3 mL, 7.2 mmol) was injected to the mixture and the mixture was stirred at room temperature for another hour before it was quenched with Et_3N (5 mL). The mixture was filtered through Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 4:1) to provide **3a** as a colorless syrup (9.8 g, 85%, α/β = 1:20): $[\alpha]^{25}_D$ = 5.6 (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–8.02 (m, 2 H), 7.96–7.89 (m, 4 H), 7.87–7.82 (m, 2 H), 7.74 (d, *J* = 7.9 Hz, 1 H), 7.61–7.47 (m, 3 H), 7.47–7.27 (m, 11 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 6.93 (t, *J* = 7.6 Hz, 1 H), 5.90 (t, *J* = 9.6 Hz, 1 H), 5.70 (t, *J* = 9.7 Hz, 1 H), 5.65 (dd, *J* = 9.6, 8.0 Hz, 1 H), 4.93–4.86 (m, 2H), 4.76 (d, *J* = 13.2 Hz, 1 H), 4.69 (dd, *J* = 12.1, 2.9 Hz, 1 H), 4.54 (dd, *J* = 12.1, 5.8 Hz, 1 H), 4.24–4.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 165.2, 165.1, 139.1, 139.0, 133.4, 133.2, 133.1, 130.2, 129.9, 129.8, 129.8, 129.7, 129.4, 129.1, 128.8, 128.7, 128.4, 128.4, 128.3, 128.2, 99.6, 98.1, 97.8, 74.3, 72.9, 72.4, 71.8, 69.7, 63.2; HRMS (MALDI) *m*/*z* calcd for $C_{41}H_{33}O_{10}INa$ $[M+Na]^+$ 835.1011, found 835.0993.

2.2. *Ortho*-Iodobenzyl 2,3,4-tri-*O*-benzoyl-L-rhamnopyranoside (3b)

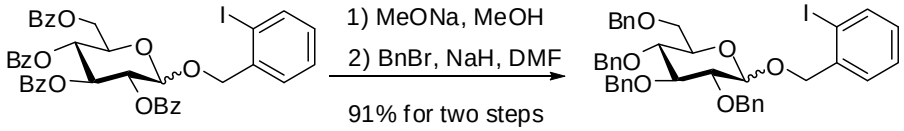


2b **3b**

To a solution of **2b** (291 mg, 0.50 mmol) and 2-iodobenzyl alcohol (141 mg, 0.60 mmol) in dry CH_2Cl_2 (5 mL) containing 4Å MS (400 mg) under the protection of

argon, was added TMSOTf (10 μL, 0.05 mmol) dropwise. The mixture was allowed to be stirred at ambient temperature for 2 h before it was quenched with Et_3N (1 mL). The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 3:1) to give **3b** as a colorless foam (343 mg, 99%): $[\alpha]^{25}_D$ = 83.3 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.3, 1.4 Hz, 2 H), 7.97 (dd, *J* = 8.4, 1.4 Hz, 2 H), 7.85 (ddd, *J* = 17.6, 8.2, 1.4 Hz, 3 H), 7.64–7.53 (m, 2 H), 7.49 (td, *J* = 7.5, 5.9 Hz, 3 H), 7.47–7.29 (m, 4 H), 7.28–7.21 (m, 2 H), 7.04 (td, *J* = 7.7, 1.7 Hz, 1 H), 5.92 (dd, *J* = 10.1, 3.5 Hz, 1 H), 5.79 (dd, *J* = 3.5, 1.8 Hz, 1 H), 5.72 (t, *J* = 10.0 Hz, 1 H), 5.19 (d, *J* = 1.7 Hz, 1 H), 4.86 (d, *J* = 12.7 Hz, 1 H), 4.65 (d, *J* = 12.6 Hz, 1 H), 4.29 (dq, *J* = 9.8, 6.2 Hz, 1 H), 1.38 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 165.6, 165.5, 139.4, 139.2, 133.5, 133.3, 133.1, 129.9, 129.8, 129.7, 129.7, 129.4, 129.3, 129.2, 129.1, 128.6, 128.5, 128.4, 128.3, 98.0, 97.5, 73.9, 71.8, 70.8, 70.1, 67.2, 17.7; HRMS (ESI) *m*/*z* calcd for $C_{34}H_{33}O_8NI$ $[M+NH_4]^+$ 710.1245, found 710.1241.

2.3. *Ortho*-Iodobenzyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside (3c)

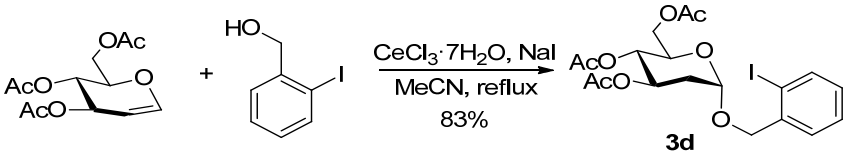


3a **3c**

Compound **3a** (2.0 g, 2.46 mmol) was treated with NaOMe (100 mg) in methanol (10 mL) for 2 h at room temperature. The mixture was neutralized with Amberlite IRA-120B(H^+) resin and then concentrated. The syrupy residue was stirred with benzyl bromide (1.46 mL, 12.3 mmol) in dry DMF (15 mL) in the presence of 50% sodium hydride (0.78 g, 19.7 mmol) for 3 h at room temperature. After treatment with water, the mixture was diluted with CH_2Cl_2, washed with water, and concentrated. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 7:1) to afford **3c** as a colorless oil (1.7 g, 91 % for two steps, α/β = 1:20). **3cα**: $[\alpha]^{25}_D$ = 35.2 (*c* 1.1 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.9, 0.9 Hz, 1 H), 7.55 (dd, *J* = 7.7, 1.2 Hz, 1 H), 7.38–7.22 (m, 20 H), 7.14 (m, 2 H), 6.97 (td, *J* = 7.7, 1.6 Hz, 1 H), 5.01 (d, *J* = 10.9 Hz, 1 H), 4.94 (d, *J* = 3.6 Hz, 1 H), 4.63 (m, 9 H), 4.07

(t, *J* = 9.3 Hz, 1 H), 3.85 (ddd, *J* = 10.0, 3.1, 2.2 Hz, 1 H), 3.76–3.59 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.0 138.9, 138.3, 138.0, 129.2, 129.0, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 97.5, 96.7, 82.7, 82.1, 80.7, 80.2, 77.7, 75.7, 75.1, 73.5, 73.3, 73.2, 70.6, 68.4; HRMS (MALDI) *m*/*z* calcd for $C_{41}H_{41}O_6INa$ $[M+Na]^+$ 779.1840, found 779.1844. **3cβ:** $[\alpha]^{25}_D$ = –4.1 (*c* 1.0 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.2 Hz, 1 H), 7.52 (dd, *J* = 7.8, 1.7 Hz, 1 H), 7.39–7.21 (m, 19 H), 7.17 (dd, *J* = 7.3, 2.2 Hz, 2 H), 6.98 (td, *J* = 7.6, 1.7 Hz, 1 H), 5.00 (d, *J* = 10.9 Hz, 1 H), 4.95 (d, *J* = 10.4 Hz, 1 H), 4.92 (d, *J* = 8.3 Hz, 1 H), 4.83 (d, *J* = 10.8 Hz, 1 H), 4.79 (d, *J* = 10.9 Hz, 1 H), 4.76–4.69 (m, 2 H), 4.64 (d, *J* = 12.2 Hz, 1 H), 4.59–4.51 (m, 3 H), 3.79 (dd, *J* = 10.9, 2.1 Hz, 1 H), 3.72 (dd, *J* = 10.8, 4.6 Hz, 1 H), 3.68–3.62 (m, 2 H), 3.60–3.53 (m, 1 H), 3.49 (ddt, *J* = 6.9, 4.6, 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.2, 138.7, 138.4, 138.3, 138.2, 129.4, 129.2, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 102.6, 98.0, 84.9, 82.4, 77.9, 75.8, 75.2, 75.1, 75.1, 74.7, 73.6, 68.9; LRMS (ESI) *m*/*z* $[M+Na]^+$ 779.2, found 779.6.

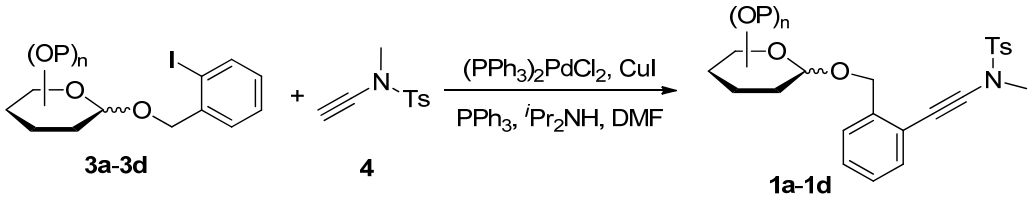
2.4. *Ortho*-Iodobenzyl 3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranoside (3d)



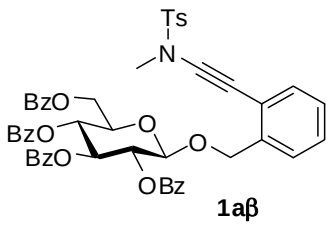
A mixture of 3,4,6-tri-*O*-acetyl-D-glucal (5.2 g, 19.1 mmol), the alcohol (9.0 g, 38,2 mmol), $CeCl_3 \cdot 7H_2O$ (10.6 g, 28.7 mmol), and NaI (4.3 g, 28.7 mmol) in acetonitrile (100 mL) was stirred at reflux temperature for 5 h; the reaction completed as monitored by TLC. The reaction mixture was diluted with water (15 mL) and extracted with ethyl acetate (2×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1) to afford glycoside **3d** as a colorless oil (83%, α/β = 15:1): $[\alpha]^{25}_D$ = 71.0 (*c* 1.3 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.0 Hz, 1 H), 7.44 (dd, *J* = 7.6, 1.5 Hz, 1 H), 7.37 (td, *J* = 7.6, 1.1 Hz, 1 H), 7.02 (td, *J* = 7.7, 1.7 Hz, 1 H), 5.39 (ddd, *J* = 11.6, 9.5, 5.4 Hz, 1 H),

5.12 (d, J = 3.0 Hz, 1 H), 5.03 (t, J = 9.7 Hz, 1 H), 4.69 (d, J = 12.8 Hz, 1 H), 4.48 (d, J = 12.8 Hz, 1 H), 4.31 (dd, J = 12.7, 5.3 Hz, 1 H), 4.09–4.01 (m, 2 H), 2.36 (ddd, J = 13.0, 5.4, 0.9 Hz, 1 H), 2.11 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H), 1.90 (ddd, J = 13.0, 11.8, 3.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.2, 169.9, 139.5, 139.2, 129.5, 128.8, 128.3, 97.8, 96.8, 73.3, 69.3, 69.1, 68.3, 62.34, 34.9, 21.0, 20.8, 20.7; HRMS (MALDI) m/z calcd for $C_{19}H_{23}O_8INa$ $[M+Na]^+$ 529.0330, found, 529.0326.

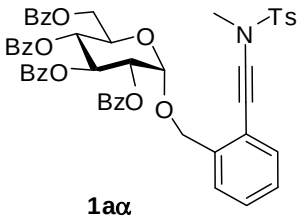
2.5. Preparation of the *ortho*-(methyltosylaminoethynyl)benzyl glycosides



General Sonogashira coupling procedure. A mixture of the *ortho*-iodobenzyl glycoside (**3a-3d**) (0.22 mmol), Ph_3P (24 mg, 0.08 mmol), $Pd(PPh_3)_2Cl_2$ (32 mg, 0.04 mmol), and CuI (8.6 mg, 0.04 mmol) in DMF (2 mL) and $^iPr_2NH$(4 mL) was deoxygenated, and a solution of ynamide **4** (187 mg, 0.88 mmol) in DMF (2 mL) was injected dropwise. After 5 h, the reaction was quenched with NH_4Cl and extracted with CH_2Cl_2 (3×15 mL). The organic phase was washed with brine and dried under Na_2SO_4. The volatiles were removed under reduce pressure. The residue was purified by column chromatography on silica gel to afford the desired glycoside (**1a-1d**).



1aβ

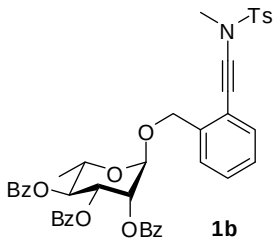


1aα

Compound **1aβ/α** (90% yield, α/β = 1:20, a white solid). **1aβ**: $[\alpha]^{25}_D$ =50.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.97 (m, 2 H), 7.92–7.86 (m, 4 H), 7.86–7.77 (m, 4 H), 7.57–7.20 (m, 12 H), 7.12 (td, J = 7.6, 1.2 Hz, 1 H), 7.02 (td, J = 7.6, 1.3 Hz, 1 H), 5.88 (t, J = 9.6 Hz, 1 H), 5.74 (t, J = 9.7 Hz, 1 H), 5.61 (dd, J = 9.7, 7.9 Hz, 1 H), 4.99 (d, J = 13.3 Hz, 1 H), 4.98 (d, J = 8.0 Hz, 1 H), 4.88 (d, J = 13.3 Hz, 1 H), 4.65 (dd, J = 12.2, 3.1 Hz, 1 H), 4.49 (dd, J = 12.2, 4.5 Hz, 1 H), 4.21 (ddd, J =

9.7, 4.3, 3.3 Hz, 1 H), 3.05 (s, 3 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 165.1, 165.1, 144.9, 138.0, 133.3, 133.3, 133.1, 133.1, 133.1, 131.2, 129.9, 129.8, 129.8, 129.7, 129.6, 129.3, 128.9, 128.8, 128.3, 128.2, 127.8, 127.7, 127.5, 121.4, 100.3, 88.5, 73.0, 72.2, 71.9, 69.6, 69.4, 66.7, 63.0, 39.1, 21.6; HRMS (MALDI) *m*/*z* calcd for $C_{51}H_{43}NO_{12}SNa$ $[M+Na]^+$ 916.2398, found 916.2392.

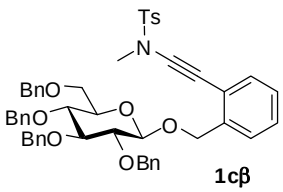
1aα: $[\alpha]^{25}_D$ = 46.8 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.93 (m, 2 H), 7.91–7.77 (m, 6 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 7.50–7.19 (m, 12 H), 7.08 (td, *J* = 7.6, 1.0 Hz, 1 H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1 H), 6.18 (t, *J* = 9.9 Hz, 1 H), 5.68 (t, *J* = 9.9 Hz, 1 H), 5.36–5.31 (m, 1 H), 5.28 (dd, *J* = 10.2, 3.7 Hz, 1 H), 4.86 (d, *J* = 13.3 Hz, 1 H), 4.70 (d, *J* = 13.2 Hz, 1 H), 4.50–4.40 (m, 2 H), 4.36 (dd, *J* = 12.0, 4.1 Hz, 1 H), 3.00(s, 3 H), 2.31(s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 165.7, 165.3, 144.9, 138.1, 133.4, 133.1, 131.5, 129.9, 129.9, 129.7, 129.7, 129.2, 129.1, 128.9, 128.4, 128.4, 128.3, 127.9, 127.8, 127.6, 121.4, 95.7, 88.7, 71.9, 70.6, 69.4, 68.3, 68.1, 66.6, 62.8, 39.1, 21.6; HRMS (MALDI) *m*/*z* calcd for $C_{51}H_{43}NO_{12}SNa$ $[M+Na]^+$ 916.2398, found 916.2398.



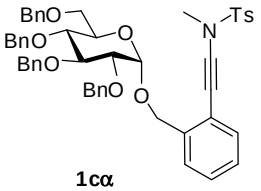
1b

Compound **1b** (90% yield, a white foam): $[\alpha]^{25}_D$ = 79.9 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.3, 1.4 Hz, 2 H), 7.96 (dd, *J* = 8.3, 1.4 Hz, 2 H), 7.89–7.78 (m, 4 H), 7.66–7.55 (m, 2 H), 7.54–7.46 (m, 3 H), 7.45–7.23 (m, 11 H), 5.88 (dd, *J* = 10.1, 3.4 Hz, 1 H), 5.73 (dd, *J* = 3.5, 1.8 Hz, 1 H), 5.69 (t, *J* = 10.0 Hz, 1 H), 5.11 (d, *J* = 1.7 Hz, 1 H), 4.94 (d, *J* = 12.9 Hz, 1 H), 4.77 (d, *J* = 12.8 Hz, 1 H), 4.24 (dq, *J* = 9.8, 6.3 Hz, 1 H), 3.21 (s, 3 H), 2.40 (s, 3 H), 1.34 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 165.5, 165.5, 144.9, 138.2, 133.4, 133.4, 133.3, 133.1, 131.7, 129.9, 129.9, 129.7, 129.7, 129.4, 129.3, 129.2, 128.6, 128.4, 128.2, 128.1, 127.8, 127.7, 127.6, 121.5, 97.3, 88.6, 71.9, 70.8, 70.1, 68.0, 67.0, 66.7, 39.3, 21.6, 17.6; HRMS (ESI) *m*/*z* calcd for $C_{44}H_{43}N_2O_{10}S$ $[M+NH_4]^+$ 791.2633, found

791.2636.



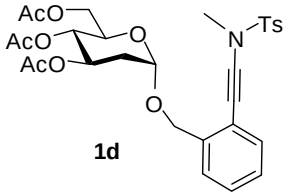
1cβ



1cα

Compound **1c** (88% yield, α/β = 1:20, a colorless oil). **1cβ**: $[\alpha]^{25}_{D}$ = 48.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2 H), 7.56 (d, *J* = 7.3 Hz, 1 H), 7.42–7.19 (m, 19 H), 7.18–6.96 (m, 2 H), 5.00 (d, *J* = 10.7 Hz, 1 H), 4.98 (d, *J* = 2.3 Hz, 1 H), 4.85–4.41(m, $PhCH_2$, 9 H), 4.07 (t, *J* = 9.3 Hz, 1 H), 3.86–3.80 (m, 1 H), 3.77–3.68 (m, 2 H), 3.60 (ddd, *J* = 12.6, 10.2, 2.7 Hz, 1 H), 3.10 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.0, 138.9, 138.4, 138.3, 138.0, 133.4, 131.3, 129.9, 128.3, 128.3, 128.3, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.2, 121.3, 96.4, 88.5, 82.1, 80.1, 77.7, 75.6, 75.1, 73.4, 72.9, 70.5, 68.4, 67.3, 66.9, 39.2, 21.6; HRMS (MALDI) *m*/*z* calcd for $C_{51}H_{51}NO_8SNa$ $[M+Na]^+$ 860.3228, found 860.3205.

1cα: $[\alpha]^{25}_{D}$ = 24.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.74 (m, 2 H), 7.56–7.46 (m, 1 H), 7.38–7.21 (m, 19 H), 7.19–7.13 (m, 2 H), 5.05 (d, *J* = 12.9 Hz, 1 H), 4.93 (d, *J* = 4.8 Hz, 1 H), 4.91 (d, *J* = 4.9 Hz, 1 H), 4.85–4.46 (m, 8 H), 3.81–3.71 (m, 2 H), 3.71–3.59 (m, 2 H), 3.57–3.45 (m, 2 H), 3.08 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.0, 138.6, 138.4, 138.2, 133.3, 131.4, 129.9, 128.4, 128.3, 128.3, 128.3, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 121.4, 103.1, 88.4, 84.7, 82.4, 77.8, 75.7, 74.9, 73.4, 69.4, 68.8, 66.9, 39.2, 21.6; HRMS (MALDI) *m*/*z* calcd for $C_{51}H_{51}NO_8SNa$ $[M+Na]^+$ 860.3228, found 860.3217.

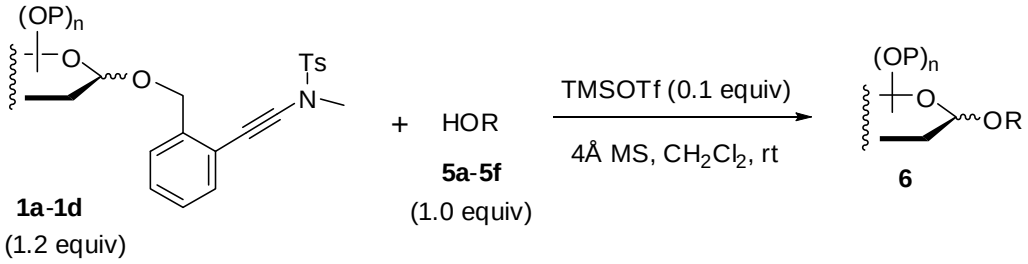


1d

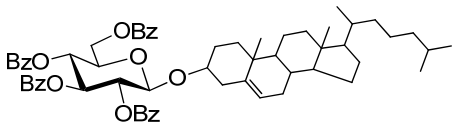
Compound **1d** (83% yield, a white solid): $[\alpha]^{25}_{D}$ = 91.9 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2 H), 7.46–7.20 (m, 6 H), 5.37 (ddd, *J* = 11.6, 9.6, 5.4 Hz, 1 H), 5.10 (d, *J* = 2.7 Hz, 1 H), 5.03 (t, *J* = 9.8 Hz, 1 H), 4.76 (d, *J* = 12.7 Hz, 1 H), 4.64 (d, *J* = 12.6 Hz, 1 H), 4.31 (dd, *J* = 12.3, 4.2 Hz, 1 H), 4.07–3.94 (m, 1 H),

3.16 (s, 3 H), 2.45 (s, 3 H), 2.31 (dd, J = 13.0, 5.4 Hz, 1 H), 2.07 (s, 3 H), 2.02 (s, 3 H), 2.00 (s, 3 H), 1.86 (td, J = 13.0, 3.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.2, 169. 9, 144.8, 138.6, 133.3, 131.6, 129.9, 127.9, 127.8, 127.8, 127.5, 121.6, 96.8, 88.4, 69.3, 69.1, 68.0, 67.9, 66.7, 62.2, 39.2, 35.0, 21.6, 21.0, 20.7, 20.7; HRMS (MALDI) m/z calcd for $C_{29}H_{33}NO_{10}SNa$ $[M+Na]^+$ 610.1717, found 610.1722.

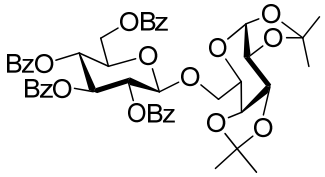
2.6. General procedure for the glycosylation



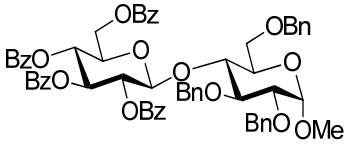
To a solution of the donor (**1a-1d**) (0.12 mmol), acceptor (**5a-5f**) (0.10 mmol), and 4Å MS (100 mg) in dry CH_2Cl_2 (2 mL) under the protection of argon, was added TMSOTf (1.85 μL, 0.01 mmol). The mixture was allowed to be stirred at ambient temperature for 2 h before it was quenched with Et_3N (10 mL). The mixture was filtered and concentrated *in vacuo*. The residue was purified with silica gel column chromatography to afford glycoside **6**.



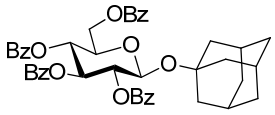
6aa[1] (91% yield, β only)



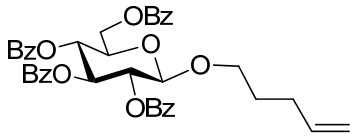
6ab[2] (91% yield, β only)



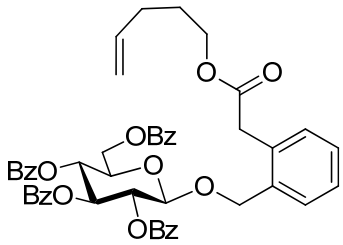
6ac[3] (98% yield, β only)



6ad (94% yield, β only; a white solid): $[\alpha]^{25}_{D}$ = 5.8 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.90 (m, 2 H), 7.90–7.85 (m, 2 H), 7.85–7.81 (m, 2 H), 7.78–7.71 (m, 2 H), 7.47–7.37 (m, 3 H), 7.34–7.24 (m, 7 H), 7.22–7.15 (m, 2 H), 5.85 (t, *J* = 9.6 Hz, 1 H), 5.48 (t, *J* = 9.7 Hz, 1 H), 5.42 (dd, *J* = 9.7, 8.0 Hz, 1 H), 5.05 (d, *J* = 7.9 Hz, 1 H), 4.51 (dd, *J* = 11.9, 3.0 Hz, 1 H), 4.41 (dd, *J* = 11.9, 7.1 Hz, 1 H), 4.11 (ddd, *J* = 10.0, 7.1, 3.1 Hz, 1 H), 1.93 (s, 3 H), 1.74 (d, *J* = 11.3 Hz, 3 H), 1.57 (d, *J* = 11.4 Hz, 3 H), 1.43 (dd, *J* = 29.1, 12.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.8, 165.3, 164.9, 133.4, 133.1, 133.0, 129.8, 129.7, 129.6, 129.6, 129.5, 128.9, 128.8, 128.3, 128.3, 128.2, 128.2, 94.3, 75.9, 73.2, 72.0, 71.9, 70.3, 63.6, 42.3, 36.0, 30.5; HRMS (MALDI) *m*/*z* calcd for $C_{44}H_{42}O_{10}Na$ $[M+Na]^+$ 753.2670, found 753.2669.

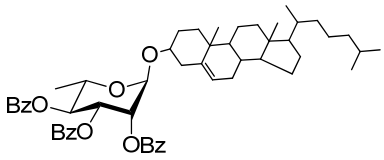


6af[4] (62% yield, β only)

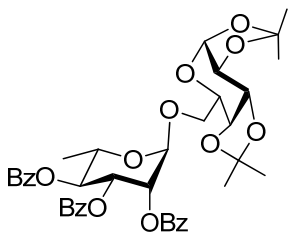


7 (34% yield, β only; a white solid): $[\alpha]^{25}_{D}$ = –11.7 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.03 (m, 2 H), 7.89 (dt, *J* = 8.4, 1.4 Hz, 4 H), 7.85–7.79 (m, 2 H), 7.60–7.17 (m, 14 H), 7.16–7.03 (m, 2 H), 5.84 (t, *J* = 9.6 Hz, 1 H), 5.77–5.64 (m, 2 H), 5.59 (dd, *J* = 9.7, 7.9 Hz, 1 H), 5.07–4.90 (m, 3 H), 4.86–4.73 (m, 2 H), 4.66 (dd, *J* = 12.1, 3.1 Hz, 1 H), 4.52 (dd, *J* = 12.1, 5.3 Hz, 1 H), 4.18–4.07 (m, 1 H), 3.98 (t, *J*

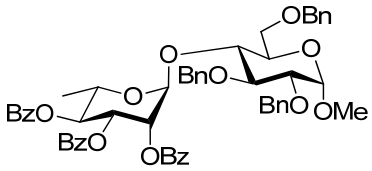
= 6.6 Hz, 2 H), 3.59 (d, *J* = 15.6 Hz, 1 H), 3.36 (d, *J* = 15.6 Hz, 1 H), 2.06–1.93 (m, 2 H), 1.69–1.55 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 166.1, 165.8, 165.2, 165.0, 137.3, 134.7, 133.5, 133.4, 133.2, 133.2, 133.1, 130.6, 129.8, 129.8, 129.7, 129.6, 129.1, 128.8, 128.8, 128.6, 128.4, 128.4, 128.3, 128.3, 127.3, 115.3, 98.9, 72.9, 72.2, 71.7, 69.7, 68.6, 64.2, 63.1, 37.9, 29.9, 27.6; HRMS (ESI) *m*/*z* calcd for $C_{48}H_{44}O_{12}Na$ $[M+Na]^+$ 835.2725, found 835.2746.



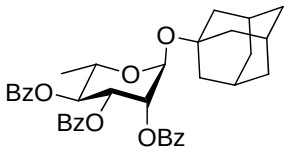
6ba (90% yield, α only; a colorless syrup): $[\alpha]^{25}_D$ = 43.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14–8.08 (m, 2 H), 7.99 (d, *J* = 7.6 Hz, 2 H), 7.83 (d, *J* = 7.6 Hz, 2 H), 7.65–7.58 (m, 1 H), 7.51 (dt, *J* = 12.7, 7.8 Hz, 3 H), 7.41 (dt, *J* = 15.6, 7.7 Hz, 3 H), 7.29–7.23 (m, 2 H), 5.87 (dd, *J* = 10.1, 3.4 Hz, 1 H), 5.71–5.60 (m, 2 H), 5.39 (d, *J* = 5.0 Hz, 1 H), 5.18 (s, 1 H), 4.28 (dq, *J* = 12.5, 6.4 Hz, 1 H), 3.60 (tt, *J* = 11.0, 4.7 Hz, 1 H), 2.44 (ddd, *J* = 13.0, 5.2, 2.1 Hz, 1 H), 2.03 (dt, *J* = 13.1, 3.4 Hz, 2 H), 1.98 (s, 2 H), 1.98–1.68 (m, 3 H), 1.64–1.43 (m, 5 H), 1.35 (d, *J* = 6.4 Hz, 5 H), 1.33–1.22 (m, 1 H), 1.23–1.08 (m, 3 H), 1.07 (s, 3 H), 1.07–0.96 (m, 2 H), 0.99–0.91 (m, 4 H), 0.88 (dd, *J* = 6.7, 2.1 Hz, 6 H), 0.70 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 165.7, 165.5, 140.2, 133.4, 133.2, 133.0, 129.9, 129.7, 129.7, 129.5, 129.4, 129.3, 128.5, 128.4, 128.2, 122.2, 95.8, 78.0, 77.3, 72.1, 71.5, 70.1, 66.7, 56.8, 56.2, 50.2, 42.3, 39.8, 39.5, 38.5, 37.3, 36.7, 36.2, 35.8, 32.0, 31.9, 29.5, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 17.7, 11.9; HRMS (ESI) *m*/*z* calcd for $C_{54}H_{72}NO_8$ $[M+NH_4]^+$ 862.5252, found 862.5250.



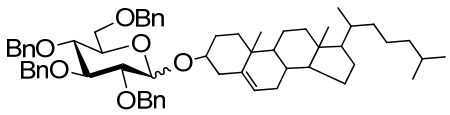
6bb[5] (95% yield, α only)



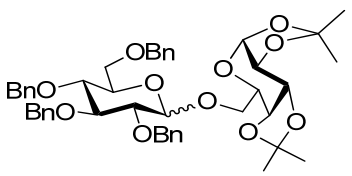
6bc[6] (88% yield, α only)



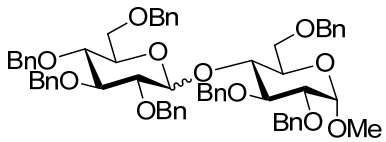
6bd (91% yield, α only; a colorless syrup): $[\alpha]^{25}_{D}$ = 56.5 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.09 (m, 2 H), 8.03–7.97 (m, 2 H), 7.87–7.81 (m, 2 H), 7.65–7.57 (m, 1 H), 7.56–7.36 (m, 7 H), 7.30–7.23 (m, 1 H), 5.91 (dd, *J* = 10.1, 3.3 Hz, 1 H), 5.66 (t, *J* = 10.0 Hz, 1 H), 5.50–5.42 (m, 2 H), 4.38 (dq, *J* = 9.8, 6.3 Hz, 1 H), 2.20 (p, *J* = 3.1 Hz, 3 H), 1.97–1.87 (m, 7 H), 1.66 (d, *J* = 3.7 Hz, 6 H), 1.57 (s, 1 H), 1.35–1.24 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.8, 165.6, 133.3, 133.2, 133.0, 129.9, 129.7, 129.7, 129.6, 129.5, 129.4, 128.5, 128.4, 128.2, 90.7, 75.6, 72.7, 72.3, 70.2, 66.2, 42.3, 36.2, 30.7, 17.7; HRMS (ESI) *m*/*z* calcd for $C_{37}H_{42}NO_8$ $[M+NH_4]^+$ 628.2905, found 628.2906.



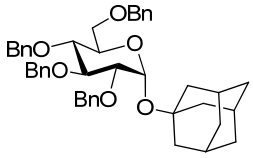
6ca[7] (95% yield, α/β = 1:1)



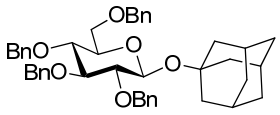
6cb[8] (93% yield, α/β = 1.5:1)



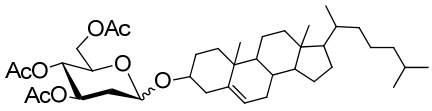
6cc[9] (85% yield, α/β = 1.2:1)



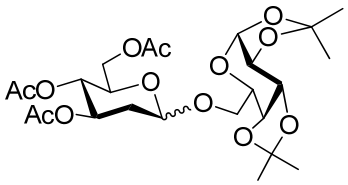
6cd (89% yield, α/β = 1.2:1; a colorless oil): $[\alpha]^{25}_{D}$ = 44.7 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.20 (m, 18 H), 7.18–7.10 (m, 2 H), 5.28 (d, *J* = 3.6 Hz, 1 H), 4.98 (d, *J* = 10.9 Hz, 1 H), 4.87–4.42 (m, 7 H), 4.04–3.96 (m, 2 H), 3.76 (dd, *J* = 10.5, 3.6 Hz, 1 H), 3.69–3.58 (m, 2 H), 3.53 (dd, *J* = 9.7, 3.7 Hz, 1 H), 2.13 (s, 3 H), 1.83 (q, *J* = 11.6 Hz, 6 H), 1.68–1.52 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.4, 138.3, 138.1, 128.3, 128.3, 128.3, 128.1, 127.9, 127.9, 127.8, 127.7 127.6, 127.6, 127.4, 89.8, 82.1, 80.1, 78.2, 75.5, 75.1, 74.5, 73.4, 72.8, 69.7, 68.8, 42.4, 36.3, 30.6; HRMS (MALDI) *m*/*z* calcd for $C_{44}H_{50}O_6Na$ $[M+Na]^+$ 697.3500, found 697.3496.



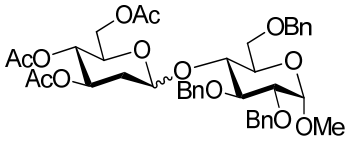
6cd (89% yield, α/β = 1.2:1; a colorless oil): $[\alpha]^{25}_{D}$ = 7.8 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 18 H), 7.22–7.16 (m, 2 H), 5.00 (d, *J* = 11.0 Hz, 1 H), 4.91 (d, *J* = 10.9 Hz, 1 H), 4.82 (d, *J* = 10.9 Hz, 1 H), 4.77 (d, *J* = 10.9 Hz, 1 H), 4.71 (d, *J* = 7.5 Hz, 1 H), 4.69 (d, *J* = 4.3 Hz, 1 H), 4.61–4.50 (m, 3 H), 3.73 (dd, *J* = 10.6, 1.6 Hz, 1 H), 3.68–3.58 (m, 2 H), 3.55–3.39 (m, 3 H), 2.15 (s, 3 H), 1.94 (d, *J* = 11.6 Hz, 3 H), 1.83 (d, *J* = 11.6 Hz, 1 H), 1.69–1.53 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.6, 138.4, 138.2, 128.3, 128.3, 128.3, 128.2, 127.9, 127.9, 127.7, 127.6, 127.5, 127.4, 85.1, 82.3, 78.2, 75.7, 75.3, 74. 9, 74.6, 73.4, 69.5, 42.8, 36.3, 30.7; HRMS (MALDI) *m*/*z* calcd for $C_{44}H_{50}O_6Na$ $[M+Na]^+$ 697.3500, found 697.3479.



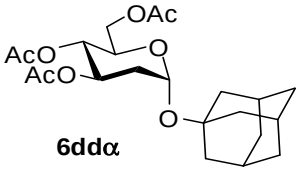
6da[10] (98% yield, α/β = 1.8:1)



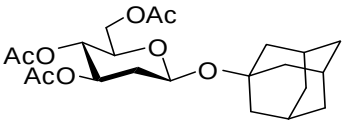
6db[11] (99% yield, α/β = 2.5:1)



6dc[11] (83% yield, α/β = 10:1)



6ddα



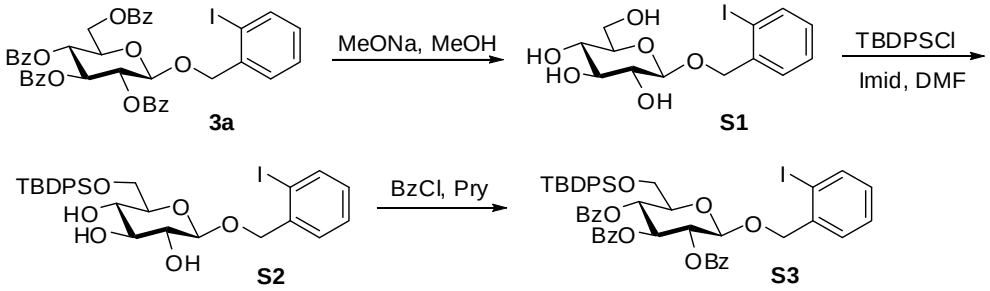
6ddβ

6dd (89% yield, α/β = 3:1; a colorless oil). **6ddα**: $[\alpha]^{25}_{D}$ = 114.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50–5.31 (m, 2 H), 4.96 (t, *J* = 9.8 Hz, 1 H), 4.30 (dd, *J* = 12.1, 4.8 Hz, 1 H), 4.19 (ddd, *J* = 10.1, 4.8, 2.2 Hz, 1 H), 4.02 (dd, *J* = 12.0, 2.2 Hz, 1 H), 2.14 (s, 3 H), 2.08 (s, 3 H), 2.04 (s, 3 H), 2.00 (s, 3 H), 1.88–1.74 (m, 6 H), 1.62 (dd, *J* = 21.5, 12.4 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.3, 170.0, 90.1, 74.6, 69.9, 69.4, 67.4, 62.6, 42.4, 36.5, 36.2, 30.6, 29.7, 21.0, 20.7; HRMS (MALDI) *m*/*z* calcd for $C_{44}H_{50}O_6Na$ $[M+Na]^+$ 447.1989, found 447.1989.

6ddβ: $[\alpha]^{25}_{D}$ = –14.7 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (ddd, *J* = 11.6, 9.3, 5.3 Hz, 1 H), 4.93 (t, *J* = 9.6 Hz, 1 H), 4.86 (dd, *J* = 9.7, 2.0 Hz, 1 H), 4.25 (dd, *J* = 12.0, 5.9 Hz, 1 H), 4.07 (dd, *J* = 12.0, 2.5 Hz, 1 H), 3.60 (ddd, *J* = 9.6, 5.9, 2.6 Hz, 1 H), 2.20–2.10 (m, 4 H), 2.06 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.79 (dt, *J*

= 11.9, 6.8 Hz, 6 H), 1.63 (q, J = 12.5 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.4, 169.8, 92.5, 75.3, 71.7, 71.1, 69.4, 62.9, 42.4, 37.5, 36.2, 30.7, 29.7, 20.9, 20.8, 20.7; HRMS (MALDI) m/z calcd for $C_{44}H_{50}O_6Na$ $[M+Na]^+$ 447.1989, found 447.1987.

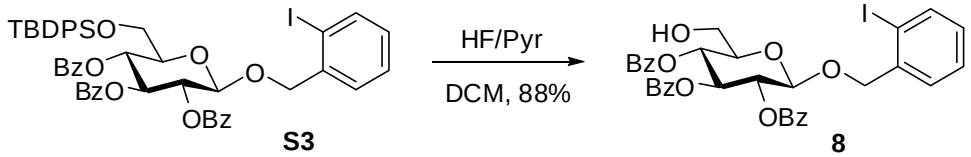
2.7. Synthesis of *Ortho*-iodobenzyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranoside (S3)



Compound **3a** (2.0 g, 2.46 mmol) was treated with sodium methoxide (100 mg) in methanol (10 mL) for 2 h at room temperature. The mixture was neutralized with Amberlite IRA-120B(H^+) resin and then concentrated to give **S1**. To a solution of **S1** (2.1 g, 5.3 mmol) and imidazole (805 mg, 10.6 mmol) in DMF (50 mL), was added dropwise a solution of *tert*-butyldiphenylchlorosilane (1.5 mL, 7.9 mmol). After the reaction mixture was stirred overnight at ambient temperature, the mixture was concentrated to afford a yellowish oily foam **S2**. To a solution of **S2** in pyridine (10 mL) was added benzoyl chloride (2.8 mL, 21.2 mmol). The reaction mixture was stirred at ambient temperature and monitored by TLC. Quantitative conversion of the starting material to a single product was observed after 6 h. The mixture was cooled using an ice-bath, quenched by addition of MeOH (5 mL), and extracted with CH_2Cl_2 (3×30 mL). The organic phase was washed with brine, dried over sodium sulfate, and evaporated to dryness. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 10:1) to give **S3** (88% for three steps) as a white solid: $[\alpha]^{25}_D$ = –10.2 (c 5.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.3, 1.2 Hz, 2 H), 7.89 (ddd, J = 8.5, 5.7, 1.2 Hz, 4 H), 7.79 (dd, J = 7.9, 1.1 Hz, 1 H), 7.75 (dd, J = 8.0, 1.4 Hz, 2 H), 7.65 (dd, J = 8.0, 1.3 Hz, 2 H), 7.58–7.49 (m, 2 H),

7.47–7.29 (m, 12 H), 7.25 (t, *J* = 7.4 Hz, 2 H), 7.17 (td, *J* = 7.6, 1.1 Hz, 1 H), 6.96 (td, *J* = 7.7, 1.6 Hz, 1 H), 5.88 (t, *J* = 9.6 Hz, 1 H), 5.74 (t, *J* = 9.3 Hz, 1 H), 5.67 (dd, *J* = 9.7, 7.9 Hz, 1 H), 4.98 (d, *J* = 13.3 Hz, 1 H), 4.92 (d, *J* = 7.9 Hz, 1 H), 4.78 (d, *J* = 13.3 Hz, 1 H), 3.96–3.90 (m, 3 H), 1.10 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.1, 164.9, 139.3, 139.0, 135.6, 135.5, 133.2, 133.1, 133.0, 133.0, 129.8, 129.8, 129.7, 129.6, 129.6, 129.4, 129.3, 129.2, 128.9, 128.9, 128.3, 128.2, 128.2, 128.2, 127.7, 127.6, 99.8, 97.5, 75.2, 74.2, 73.3, 72.8, 72.0, 69.2, 62.6, 26.7, 19.2; HRMS (MALDI) *m*/*z* calcd for $C_{50}H_{47}O_9SiINa$ $[M+Na]^+$ 969.1926, found 969.1941.

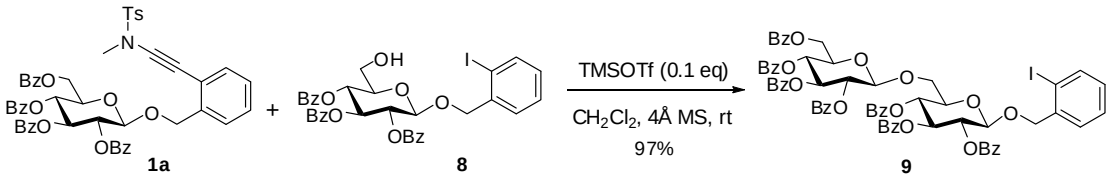
2.8. *Ortho*-Iodobenzyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (8)



S3 **8**

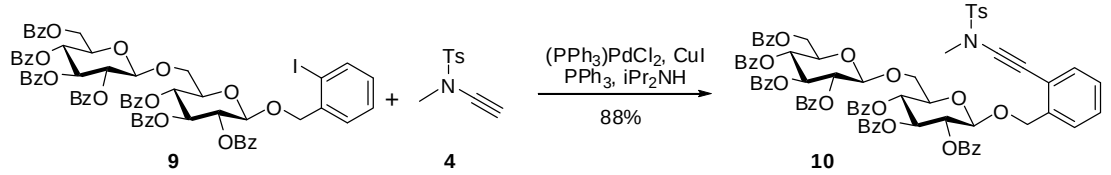
To a solution of **S3** (283 mg, 0.3 mmol) in THF (3 mL) was added HF·pyridine (0.3 mL) at 0℃. After being stirred at room temperature for 8 h under nitrogen, the reaction mixture was evaporated under vacuum. The residue was dissolved in CH_2Cl_2 and washed with sat. $NaHCO_3$, H_2O, and brine, respectively. The organic layer was dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel (hexane/ethyl acetate, 5:1) to afford **8** (88%) as a white solid: $[\alpha]^{25}_D$ = –14.7 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (td, *J* = 8.4, 1.2 Hz, 4 H), 7.86 (dd, *J* = 8.4, 1.3 Hz, 2 H), 7.76 (dd, *J* = 7.9, 1.1 Hz, 1 H), 7.56–7.48 (m, 2 H), 7.45–7.36 (m, 5 H), 7.34–7.27 (m, 3 H), 7.15 (td, *J* = 7.5, 1.1 Hz, 1 H), 6.95 (td, *J* = 7.7, 1.7 Hz, 1 H), 5.94 (t, *J* = 9.7 Hz, 1 H), 5.64 (dd, *J* = 9.8, 7.9 Hz, 1 H), 5.56 (t, *J* = 9.7 Hz, 1 H), 4.93 (d, *J* = 13.2 Hz, 1 H), 4.92 (d, *J* = 7.9 Hz, 1 H), 4.78 (d, *J* = 13.2 Hz, 1 H), 3.93 (dd, *J* = 12.6, 1.8 Hz, 1 H), 3.84 (ddd, *J* = 9.7, 4.3, 2.1 Hz, 1 H), 3.79 (dd, *J* = 12.6, 4.4 Hz, 1 H), 2.64 (brs, 1 H); ^{13}C NMR (125 MHz, $CHCl_3$) δ 166.0, 165.8, 165.0, 139.1, 139.1, 133.6, 133.2, 133.2, 129.9, 129.8, 129.7, 129.4, 129.2, 129.1, 128.5, 128.5, 128.3, 128.2, 99.9, 97.8, 74.7, 74.6, 72.7, 71.8, 69.8, 61.3; HRMS (MALDI) *m*/*z* calcd for $C_{34}H_{29}O_9INa$ $[M+Na]^+$ 731.0749, found 731.0761.

2.9. Disaccharide 9



The general glycosylation procedure was applied to provide **9** (97% yield, β only) as a white solid: $[\alpha]^{25}_{D}$ = –18.4 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.94 (m, 4 H), 7.93–7.71 (m, 11 H), 7.57–7.45 (m, 4 H), 7.44–7.38 (m, 5 H), 7.33 (dd, *J* = 13.8, 7.2 Hz, 6 H), 7.29–7.23 (m, 6 H), 7.23–7.16 (m, 1 H), 7.15 (td, *J* = 7.5, 1.1 Hz, 1 H), 6.93 (td, *J* = 7.6, 1.8 Hz, 1 H), 5.92 (t, *J* = 9.6 Hz, 1 H), 5.77 (t, *J* = 9.6 Hz, 1 H), 5.63 (t, *J* = 9.7 Hz, 1 H), 5.55 (dd, *J* = 9.8, 7.9 Hz, 1 H), 5.48 (dd, *J* = 9.8, 7.9 Hz, 1 H), 5.33 (t, *J* = 9.6 Hz, 1 H), 5.05 (d, *J* = 7.9 Hz, 1 H), 4.72 (d, *J* = 7.9 Hz, 1 H), 4.69 (d, *J* = 12.9 Hz, 1 H), 4.59 (dd, *J* = 12.2, 3.1 Hz, 1 H), 4.48–4.37 (m, 2 H), 4.15–4.05 (m, 2 H), 4.05–3.98 (m, 1 H), 3.94 (dd, *J* = 11.2, 7.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.7, 165.7, 165.4, 165.2, 165.0, 139.2, 138.9, 133.5, 133.4, 133.1, 129.9, 129.8, 129.8, 129.5, 129.5, 129.4, 129.2, 128.8, 128.7, 128.4, 128.4, 128.3, 128.2, 128.1, 101.1, 99.5, 98.2, 74.3, 72.9, 72.8, 72.3, 71.9, 71.7, 69.8, 69.62, 68.2, 63.0; HRMS (MALDI) *m*/*z* calcd for $C_{68}H_{55}O_{18}INa$ $[M+Na]^+$ 1309.2325, found 1309.2318.

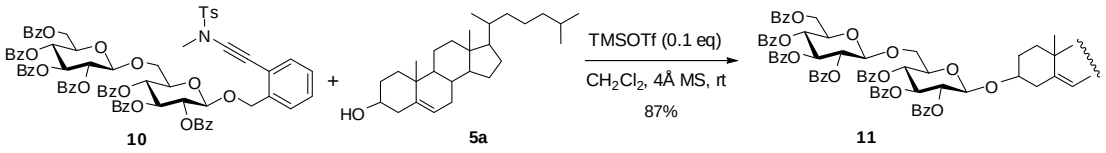
2.10. Disaccharide donor 10



The general Sonogashira procedure was applied to provide **10** (88% yield) as a white solid: $[\alpha]^{25}_{D}$ = –4.2 (*c* 3.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.96 (m, 2 H), 7.96–7.92 (m, 2 H), 7.91–7.87 (m, 2 H), 7.78 (ddd, *J* = 16.4, 13.2, 5.1 Hz, 10 H), 7.57–7.12 (m, 26 H), 7.09 (td, *J* = 7.4, 1.3 Hz, 1 H), 5.85 (t, *J* = 9.6 Hz, 1 H), 5.73 (t, *J* = 9.6 Hz, 1 H), 5.59 (t, *J* = 9.7 Hz, 1 H), 5.51 (dd, *J* = 9.7, 7.9 Hz, 1 H), 5.42 (dd, *J* = 9.7, 7.9 Hz, 1 H), 5.35 (t, *J* = 9.7 Hz, 1 H), 4.94 (d, *J* = 7.8 Hz, 1 H), 4.78–4.69 (m,

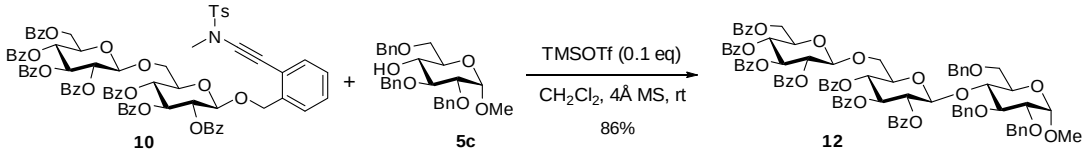
2 H), 4.55 (d, J = 13.2 Hz, 1 H), 4.38 (dd, J = 12.2, 5.0 Hz, 1 H), 4.17–4.08 (m, 1 H), 4.05–3.97 (m, 2 H), 3.86 (dd, J = 11.4, 6.9 Hz, 1 H), 3.04 (s, 3 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.7, 165.6, 165.3, 165.1, 165.1, 165.0, 144.8, 138.0, 133.4, 133.1, 133.1, 133.0, 131.4, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.3, 129.2, 128.9, 128.8, 128.8, 128.5, 128.4, 128.2, 128.2, 128.1, 127.8, 127.6, 121.9, 101.2, 99.7, 88.4, 73.8, 73.0, 72.9, 72.1, 71.8, 71.7, 69.9, 69.6, 69.2, 68.4, 66.7, 63.0, 39.0, 21.6; HRMS (MALDI) *m*/*z* calcd for $C_{78}H_{65}NO_{20}SNa$ $[M+Na]^+$ 1390.3713, found 1390.3712.

2.11. Disaccharides 11



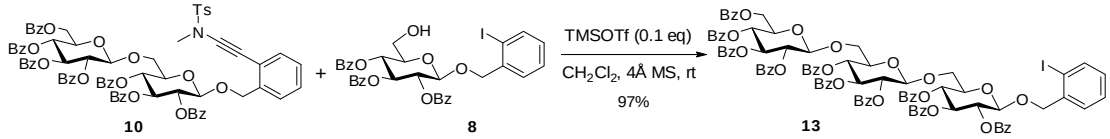
The general glycosylation procedure was applied to provide **11** (87% yield, β only) as a white solid: $[\alpha]^{25}_D$ = 5.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.99 (m, 2 H), 7.97–7.90 (m, 4 H), 7.89–7.76 (m, 8 H), 7.58–7.26 (m, 21 H), 5.83 (t, J = 8.7 Hz, 1 H), 5.78 (t, J = 8.8 Hz, 1 H), 5.59 (t, J = 9.6 Hz, 1 H), 5.48 (dd, J = 9.7, 7.8 Hz, 1 H), 5.37 (dd, J = 9.8, 7.9 Hz, 1 H), 5.31 (t, J = 9.5 Hz, 1 H), 5.23 (d, J = 4.8 Hz, 1 H), 5.04 (d, J = 7.8 Hz, 1 H), 4.79 (d, J = 7.9 Hz, 1 H), 4.58 (dd, J = 12.1, 3.1 Hz, 1 H), 4.41 (dd, J = 12.2, 5.1 Hz, 1 H), 4.08 (ddd, J = 9.6, 5.0, 3.3 Hz, 1 H), 4.04–3.91 (m, 3 H), 3.52–3.40 (m, 1 H), 0.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.7, 165.6, 165.4, 165.1, 165.1, 165.0, 140.4, 133.4, 133.1, 133.1, 129.8, 129.8, 129.7, 129.7, 129.6, 129.5, 129.3, 128.9, 128.8, 128.4, 128.4, 128.3, 128.2, 128.2, 121.9, 100.9, 100.2, 80.6, 74.2, 72.9, 72.4, 72.1, 71.8, 69.9, 69.6, 68.1, 63.0, 56.7, 56.2, 49.9, 42.3, 39.8, 39.5, 39.0, 37.1, 36.6, 36.2, 35.7, 31.9, 31.8, 29.7, 28.2, 28.0, 24.3, 23.8, 22.8, 22.5, 21.1, 19.2, 18.7, 11.8; HRMS (MALDI) *m*/*z* calcd for $C_{88}H_{94}O_{18}Na$ $[M+Na]^+$ 1461.6332, found 1461.6348.

2.12. Trisaccharides 12



The general glycosylation procedure was applied to provide **12** (86% yield, β only) as a white solid: $[\alpha]^{25}_{D}$ = 5.9 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3 Hz, 4 H), 7.95–7.89 (m, 2 H), 7.83–7.70 (m, 8 H), 7.63 (d, *J* = 7.1 Hz, 2 H), 7.57–7.09 (m, 34 H), 5.82 (t, *J* = 9.8 Hz, 1 H), 5.55 (t, *J* = 9.6 Hz, 1 H), 5.50 (t, *J* = 9.8 Hz, 1 H), 5.39 (td, *J* = 10.1, 8.0 Hz, 2 H), 5.31 (t, *J* = 9.8 Hz, 1 H), 5.24 (d, *J* = 8.0 Hz, 1 H), 5.15 (d, *J* = 11.7 Hz, 1 H), 5.10 (d, *J* = 11.7 Hz, 1 H), 4.92 (d, *J* = 11.7 Hz, 1 H), 4.87 (d, *J* = 11.7 Hz, 1 H), 4.73 (d, *J* = 3.3 Hz, 1 H), 4.68 (d, *J* = 8.0 Hz, 1 H), 4.17 (dd, *J* = 12.2, 3.0 Hz, 2 H), 4.04–3.81 (m, 7 H), 3.68 (ddd, *J* = 9.8, 5.8, 2.7 Hz, 1 H), 3.58 (dd, *J* = 9.6, 2.1 Hz, 1 H), 3.50 (dd, *J* = 10.5, 4.0 Hz, 1 H), 3.40–3.22 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 165.6, 165.5, 165.5, 165.3, 164.9, 164.7, 139.7, 138.9, 137.7, 133.5, 133.2, 133.2, 133.2, 133.1, 133.0, 132.9, 132.9, 130.2, 129.8, 129.7, 129.6, 129.6, 128.9, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.1, 127.6, 100.1, 99.8, 96.9, 81.5, 80.2, 76.8, 76.5, 76.4, 74.7, 73.7, 73.2, 72.9, 72.2, 71.1, 70.0, 69.6, 55.3; HRMS (ESI) *m*/*z* calcd for $C_{89}H_{80}O_{23}Na$ $[M+Na]^+$ 1539.4983, found 1539.4962.

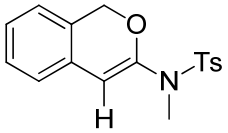
2.13. Trisaccharides 13



The general glycosylation procedure was applied to provide **13** (97% yield, β only) as a white solid:$[\alpha]^{25}_{D}$ = –29.1 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.98 (m, 4 H), 7.99–7.68 (m, 18 H), 7.59–7.30 (m, 22 H), 7.29–7.08 (m, 9 H), 6.91 (td, *J* = 7.7, 1.7 Hz, 1 H), 6.12 (t, *J* = 9.7 Hz, 1 H), 5.84 (t, *J* = 9.6 Hz, 1 H), 5.75–5.61 (m, 2 H), 5.55 (t, *J* = 8.3 Hz, 1 H), 5.51 (dd, *J* = 8.5, 6.5 Hz, 1 H), 5.25 (dd, *J* = 9.7, 7.8 Hz, 1 H), 5.15–5.03 (m, 2 H), 4.81–4.73 (m, 2 H), 4.66 (d, *J* = 7.8 Hz, 1 H), 4.61 (dd, *J* = 12.1, 3.0 Hz, 1 H), 4.52 (d, *J* = 13.0 Hz, 1 H), 4.46 (dd, *J* = 12.1, 5.4 Hz, 1 H),

4.35–4.29 (m, 1 H), 4.07 (dd, J = 11.2, 3.3 Hz, 1 H), 3.98 (d, J = 10.2 Hz, 1 H), 3.94–3.79 (m, 3 H), 3.70 (dd, J = 11.2, 5.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.7, 165.7, 165.5, 165.4, 165.3, 165.2, 165.0, 164.9, 139.1, 139.0, 133.4, 133.4, 133.2, 133.1, 133.0, 129.9, 129.8, 129.8, 129.8, 129.7, 129.7, 129.7, 129.6, 129.5, 129.4, 129.3, 129.1, 128.9, 128.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 101.4, 100.7, 99.9, 97.9, 74.4, 74.2, 73.6, 72.9, 72.8, 72.7, 72.3, 72.1, 71.9, 71.8, 70.7, 69.7, 68.6, 68.3, 63.2; HRMS (MALDI) m/z calcd for $C_{95}H_{78}O_{26}INa$ $[M+Na]^+$ 1784.3718, found 1784.3700.

2.14. 1*H*-isochromene D



Compound D: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.62 (m, 2 H), 7.23–7.19 (m, 2 H), 7.15 (td, J = 7.5, 1.3 Hz, 1 H), 7.07 (td, J = 7.4, 1.3 Hz, 1 H), 6.97–6.89 (m, 2 H), 5.77 (s, 1 H), 4.94 (s, 2 H), 3.03 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 144.0, 135.6, 132.0, 129.7, 128.4, 127.9, 127.4, 126.6, 123.9, 123.8, 98.6, 70.0, 36.3, 21.7; HRMS (ESI) m/z calcd for $C_{17}H_{17}NO_3SNa$ $[M+Na]^+$ 338.0821, found 338.0826.

3. References

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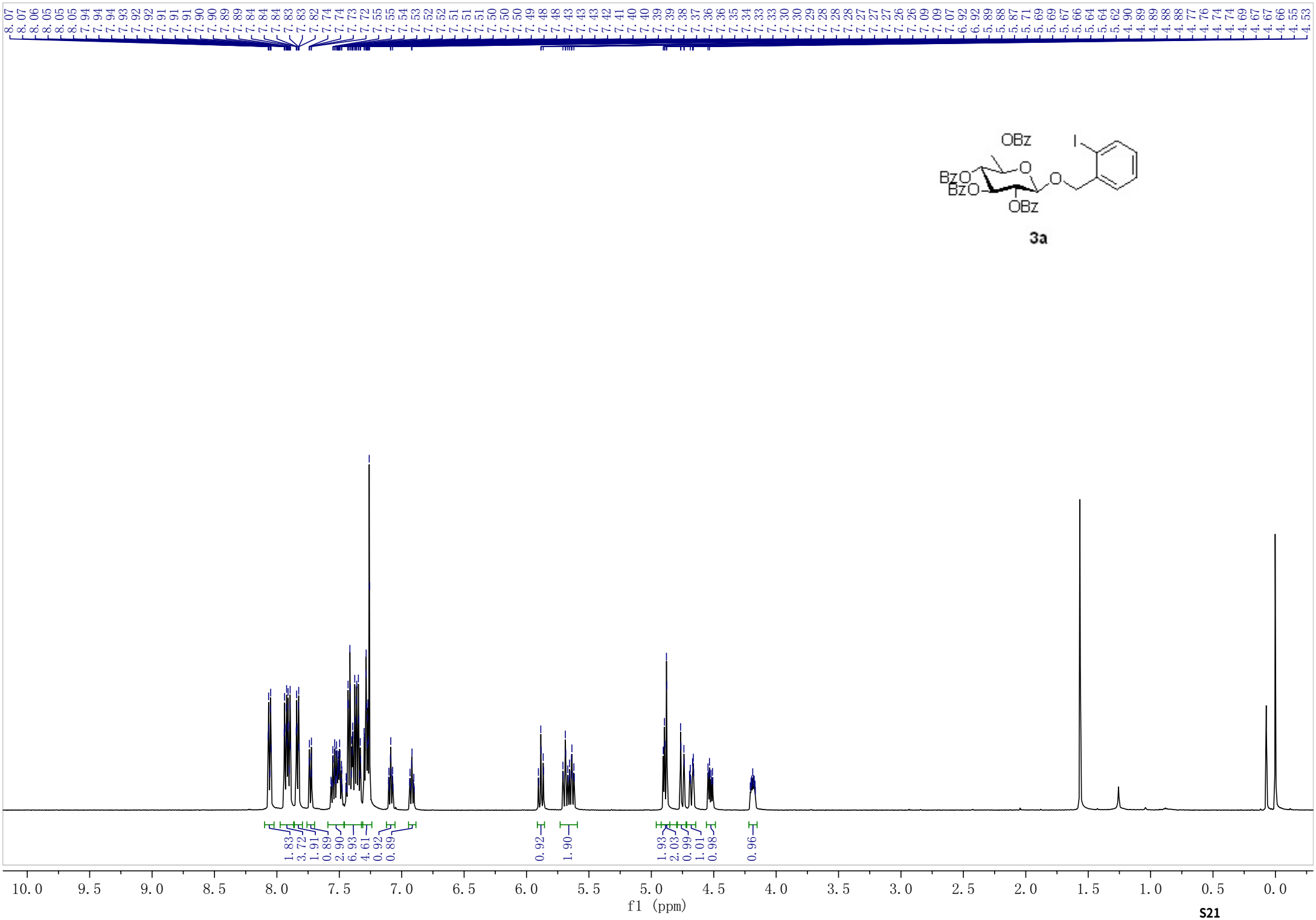
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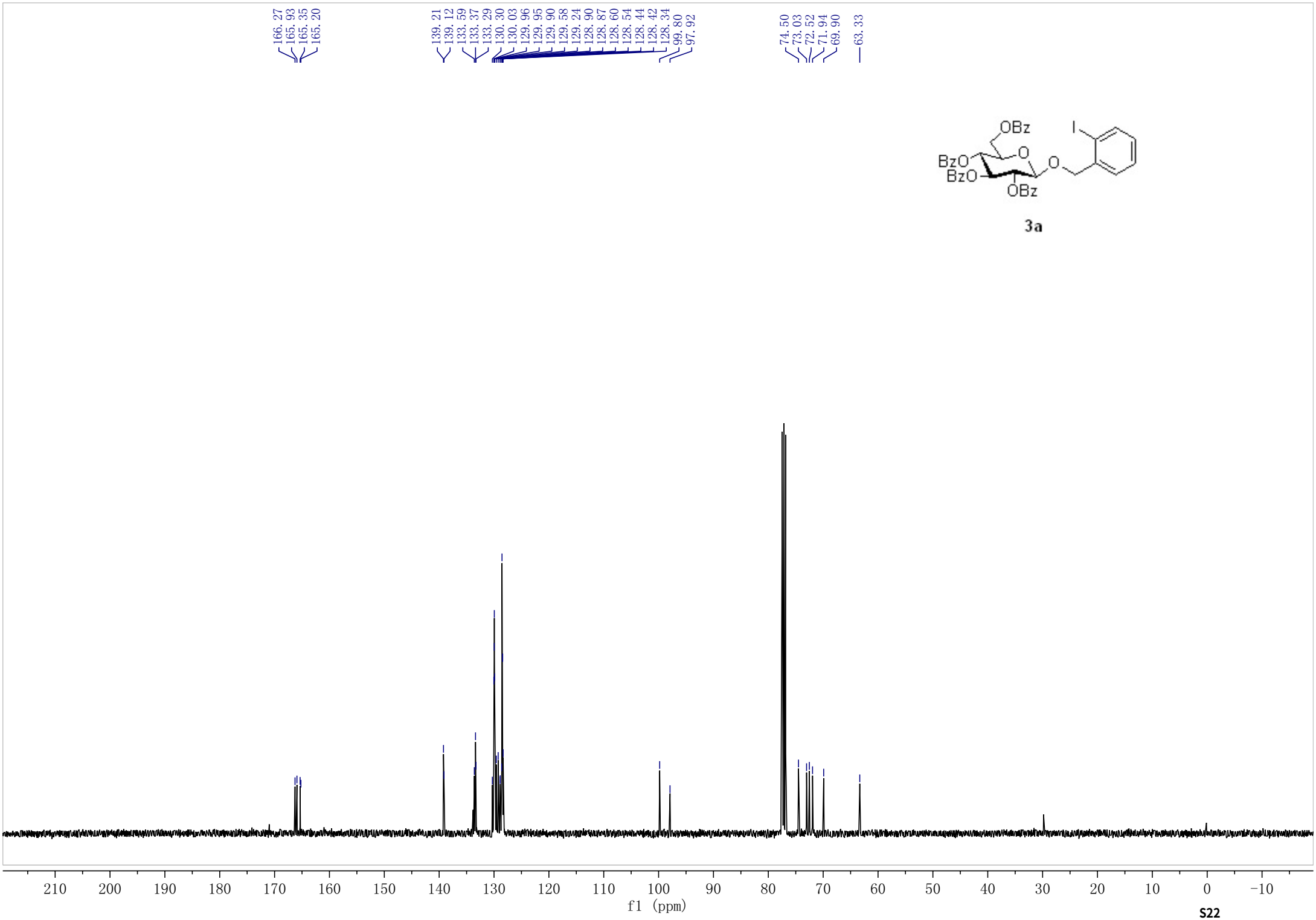
BzO
BzO
O
O
OBz
3a
f1 (ppm)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133.59
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128.42
128.34
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97.92
74.50
73.03
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69.90
63.33
OBz
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BzO
BzO
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3a
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200
190
180
170
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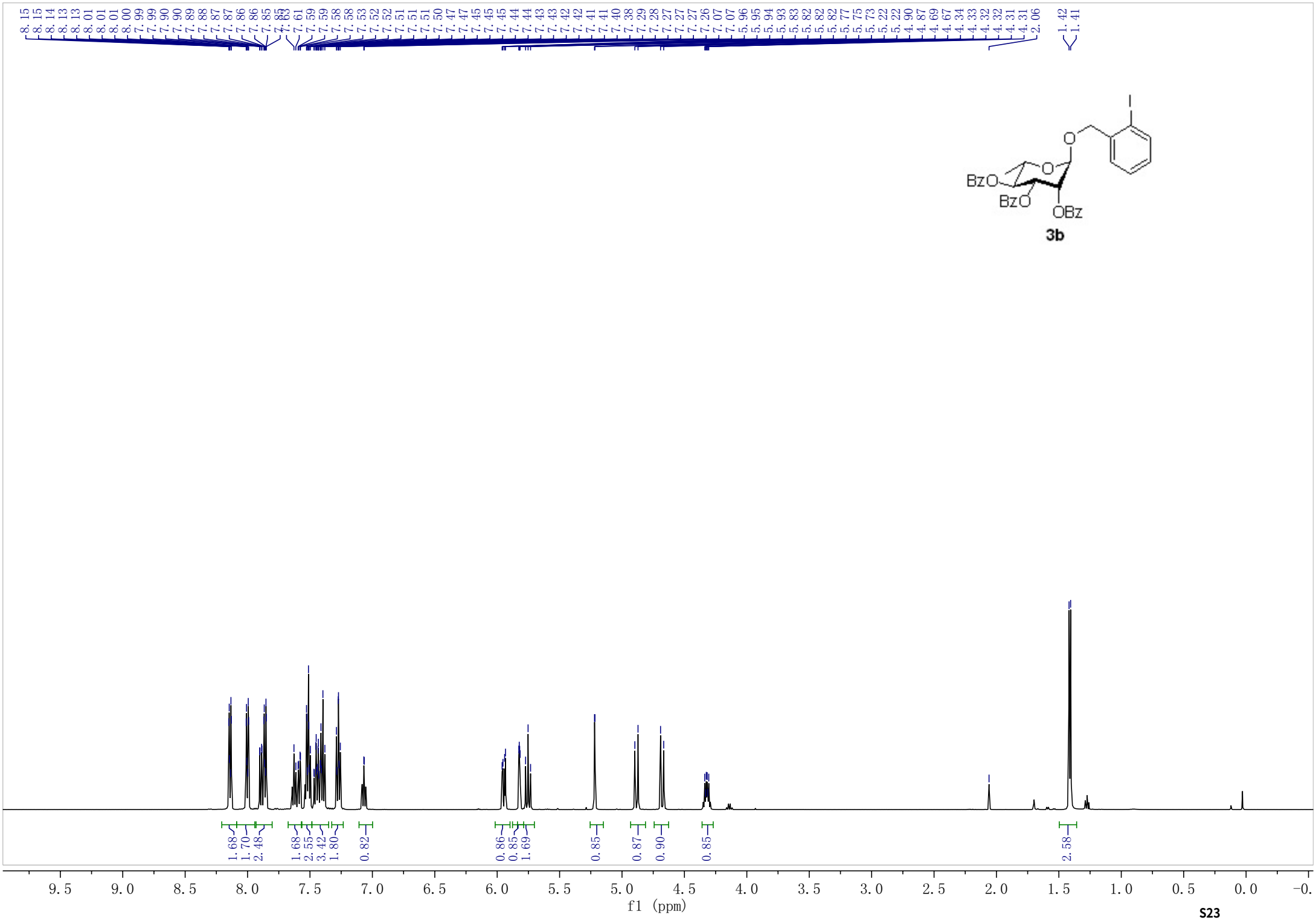
f1 (ppm)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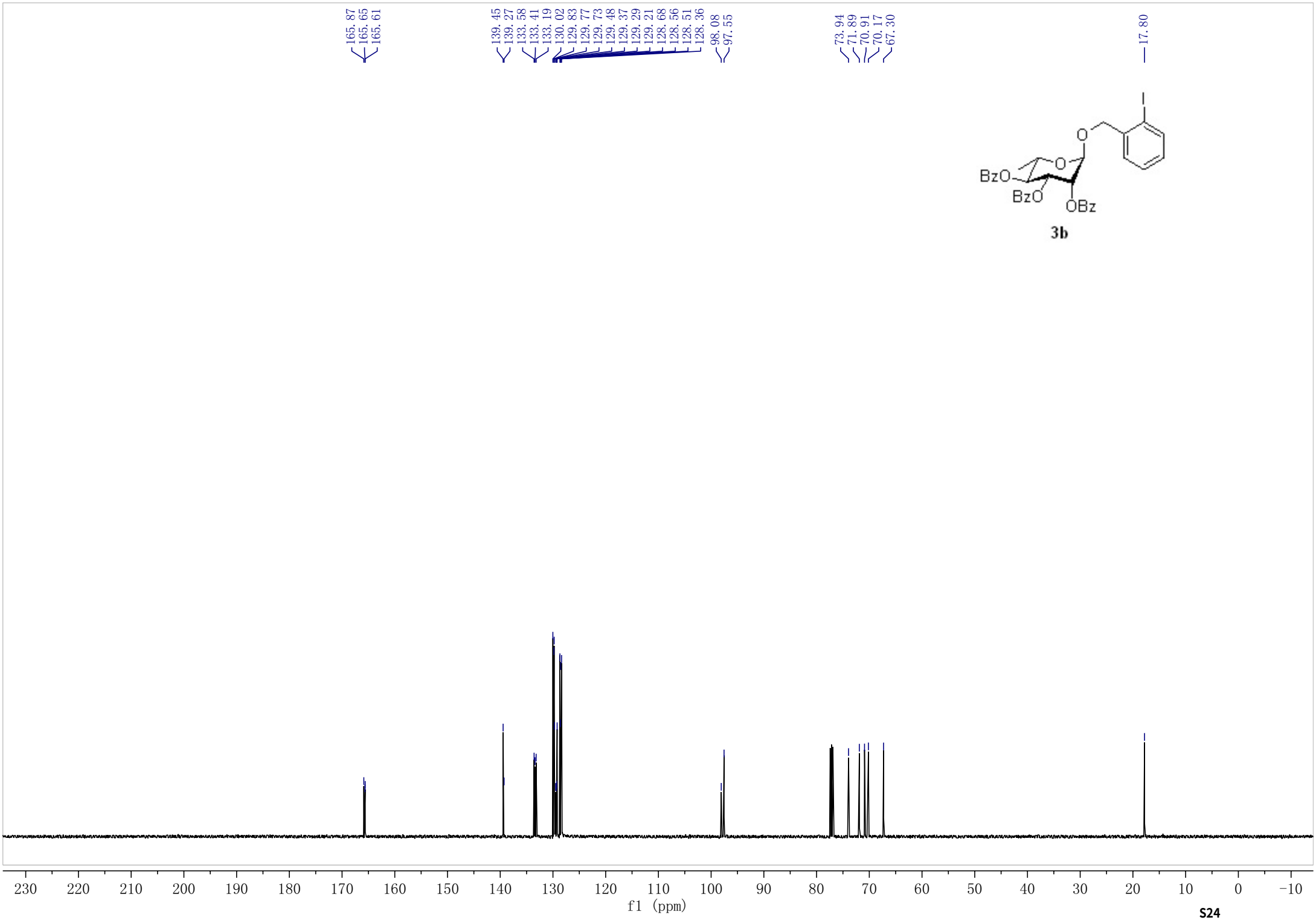
I
O
O
BzO
BzO
OBz
3b
1.68 1.70 2.48 1.68 2.55 3.42 1.80 0.82 0.86 0.85 1.69 0.85 0.87 0.90 0.85 2.58
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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165.65
165.61
139.45
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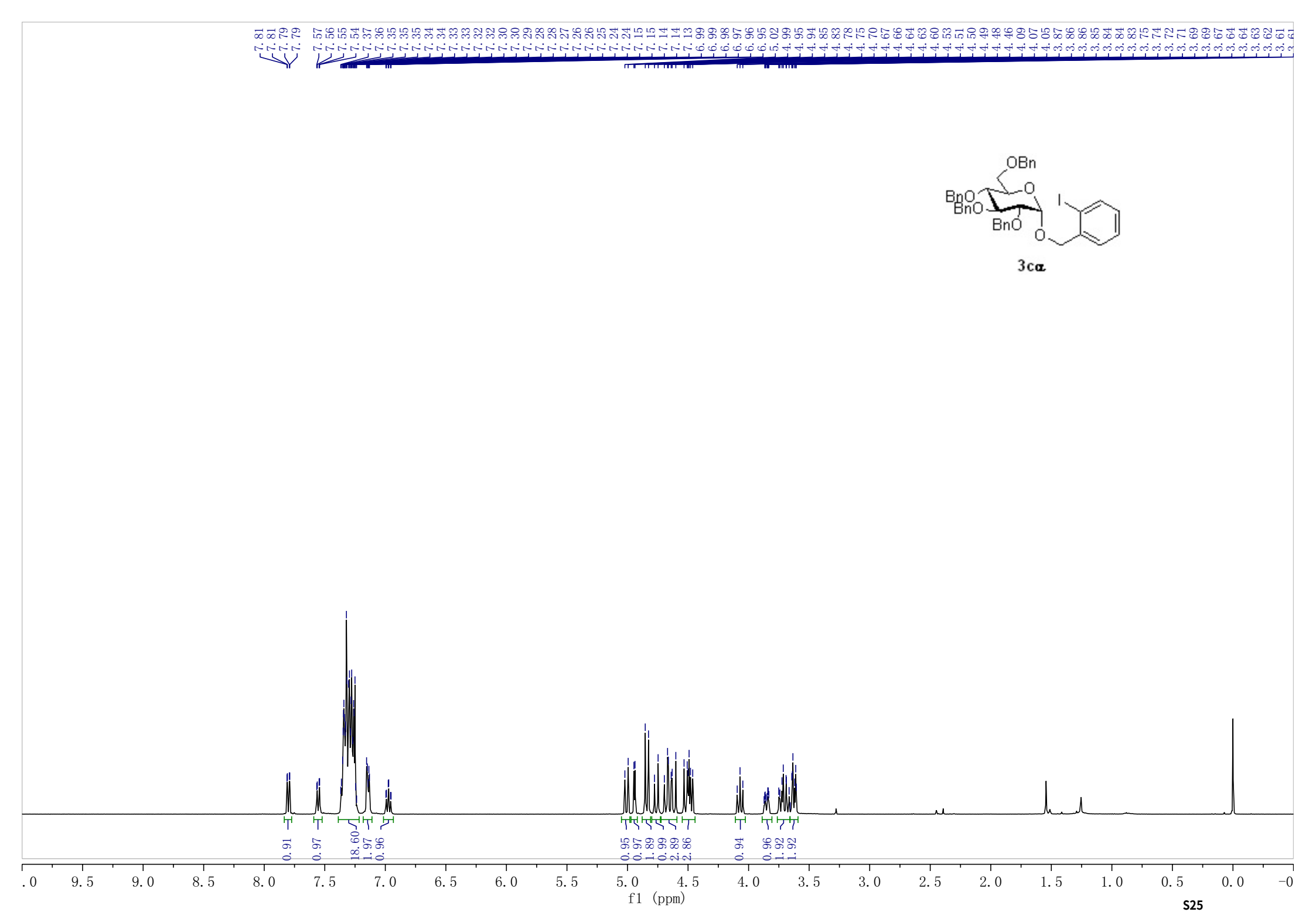
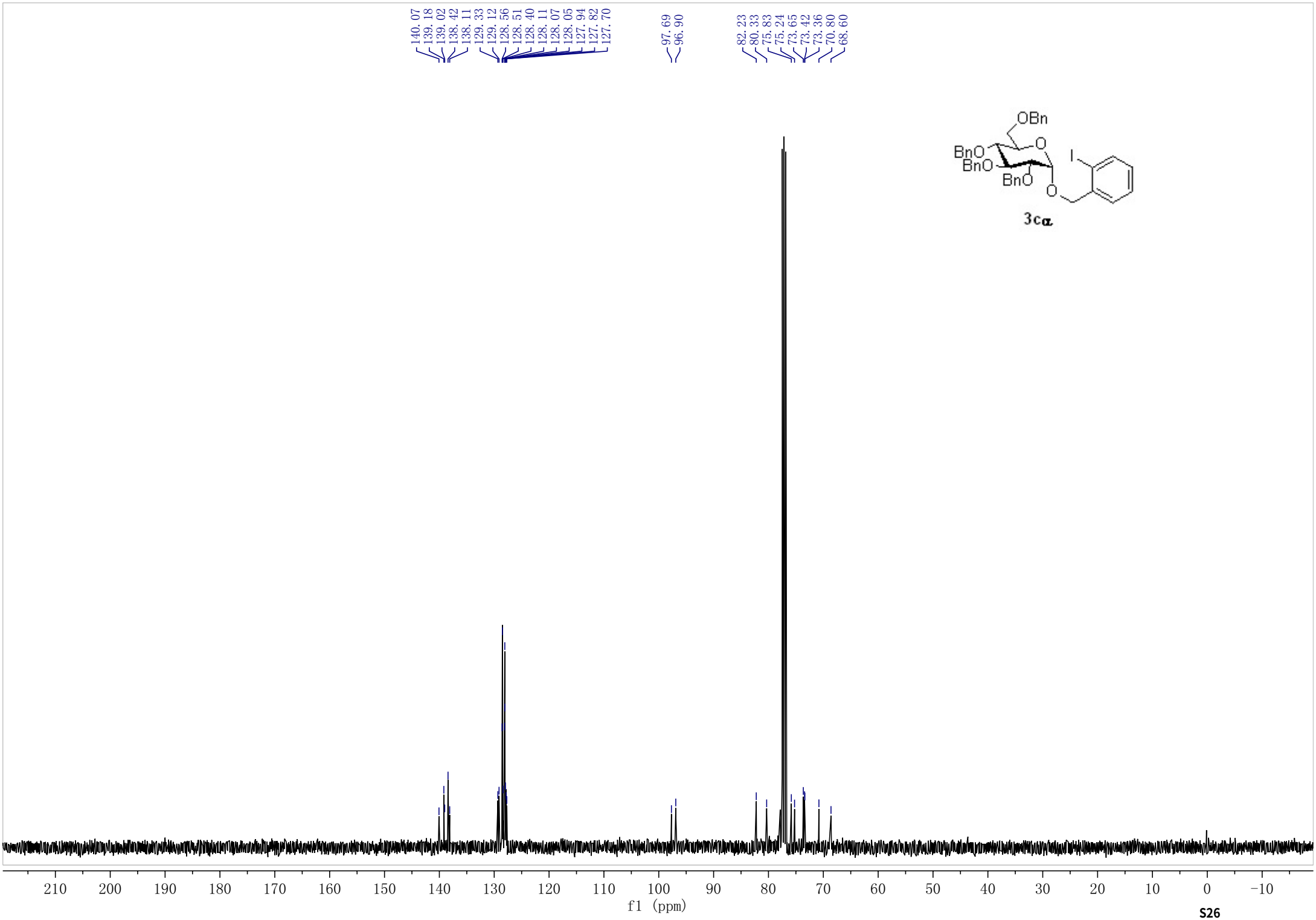
133.41
133.19
130.02
129.83
129.77
129.73
129.48
129.37
129.29
129.21
128.68
128.56
128.51
128.36
98.08
97.55
73.94
71.89
70.91
70.17
67.30
17.80
I
O
O
BzO
BzO
OBz
3b
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.81 7.81 7.79 7.79 7.57 7.56 7.55 7.54 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.30 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.24 7.15 7.15 7.14 7.13 6.99 6.99 6.98 6.97 6.96 6.95 5.02 4.99 4.95 4.94 4.85 4.83 4.78 4.75 4.70 4.67 4.66 4.64 4.63 4.60 4.53 4.51 4.50 4.49 4.48 4.46 4.09 4.07 4.05 3.87 3.86 3.86 3.85 3.84 3.84 3.83 3.75 3.74 3.72 3.71 3.69 3.69 3.67 3.64 3.64 3.63 3.62 3.61 3.61
OBn
BnO
BnO
BnO
O
O
I
3cα
0.91 0.97 18.60 1.97 0.96 0.95 0.97 1.89 0.99 2.89 2.86 0.94 0.96 1.92 1.92
f1 (ppm)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139.18
139.02
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129.12
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128.40
128.11
128.07
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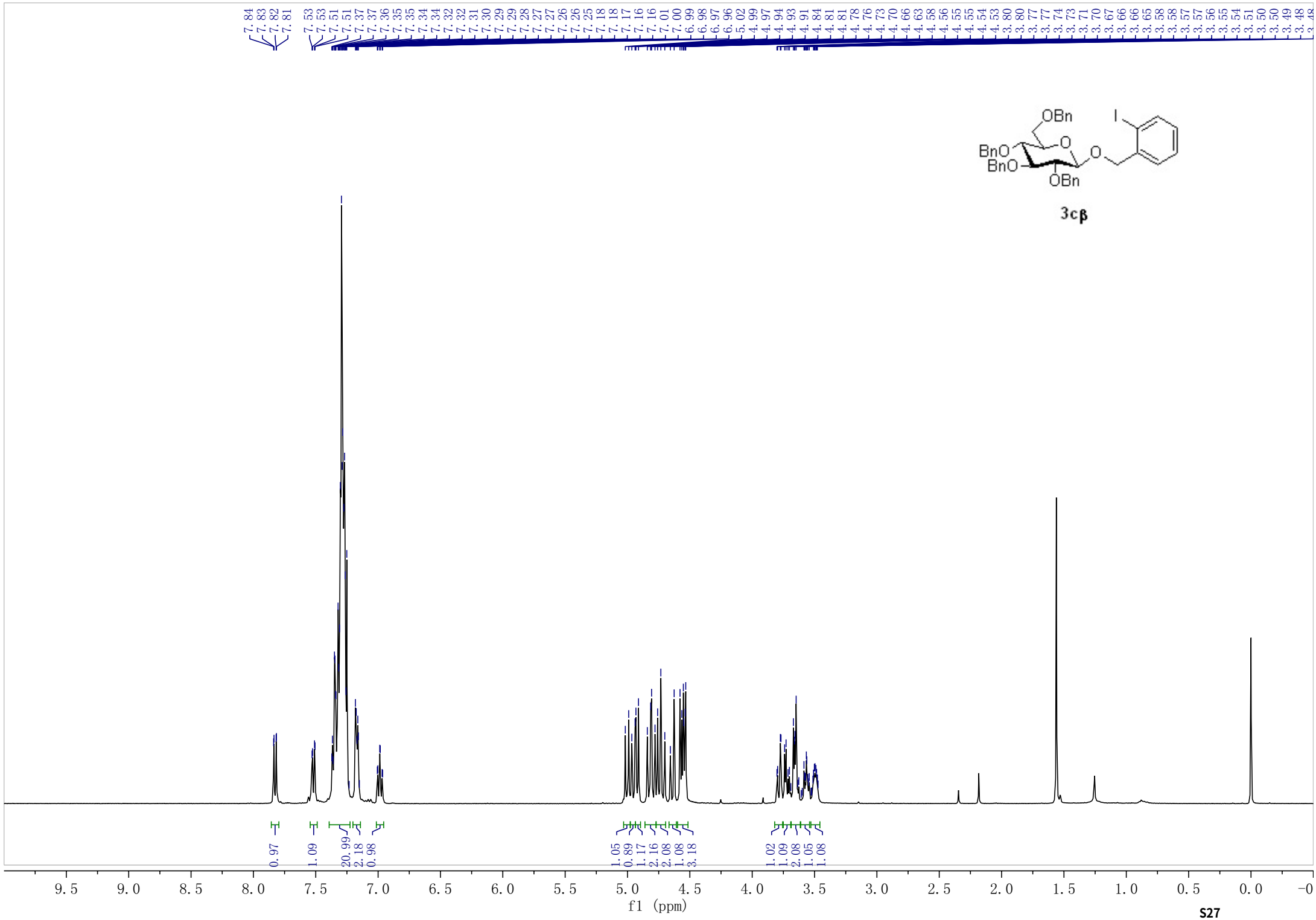
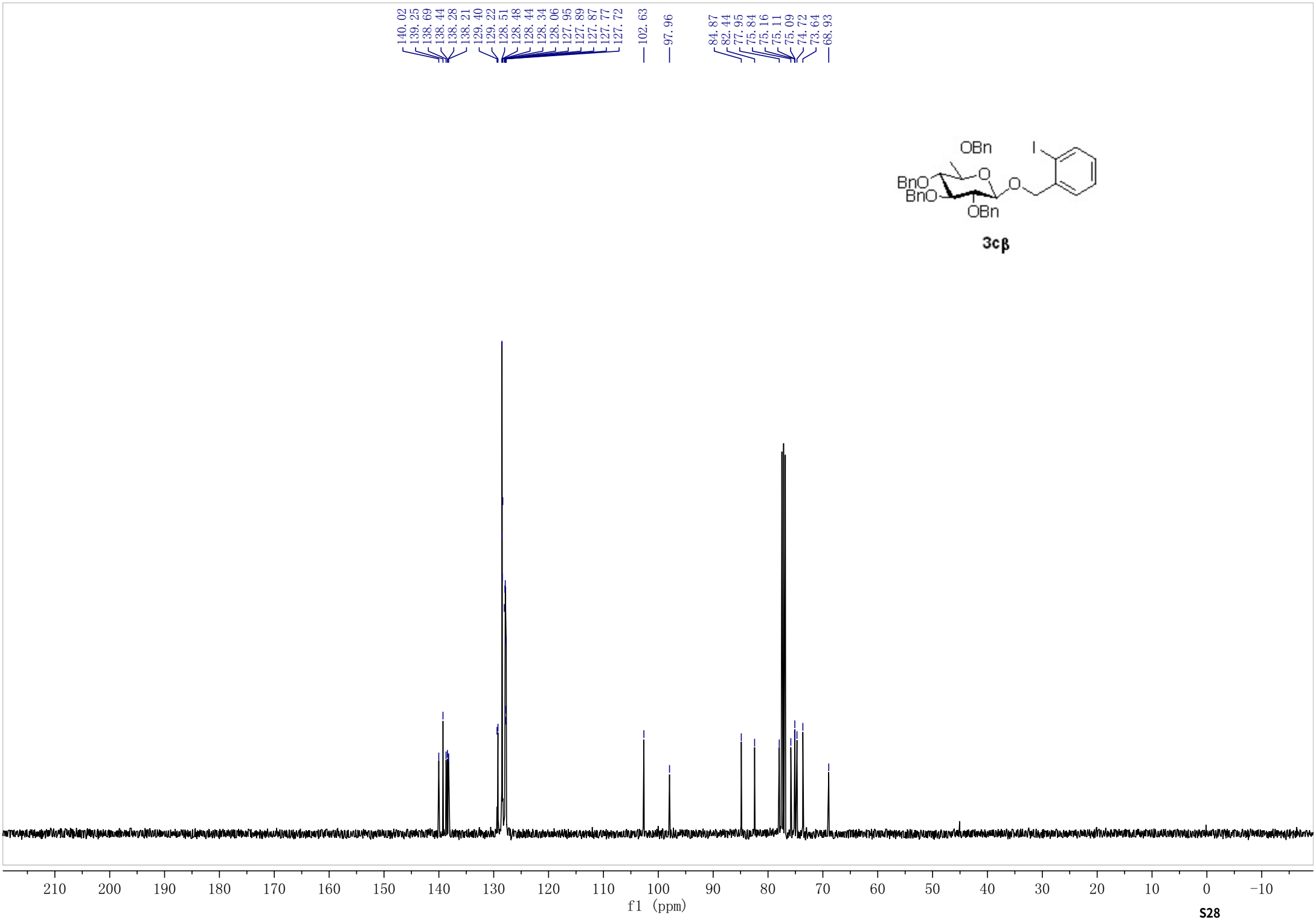
127.94
127.82
127.70
97.69
96.90
82.23
80.33
75.83
75.24
73.65
73.42
73.36
70.80
68.60
OBn
BnO
BnO
BnO
O
O
I
3cα
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OBn
I
BnO
BnO
O
O
OBn
3cβ
f1 (ppm)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138.69
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138.28
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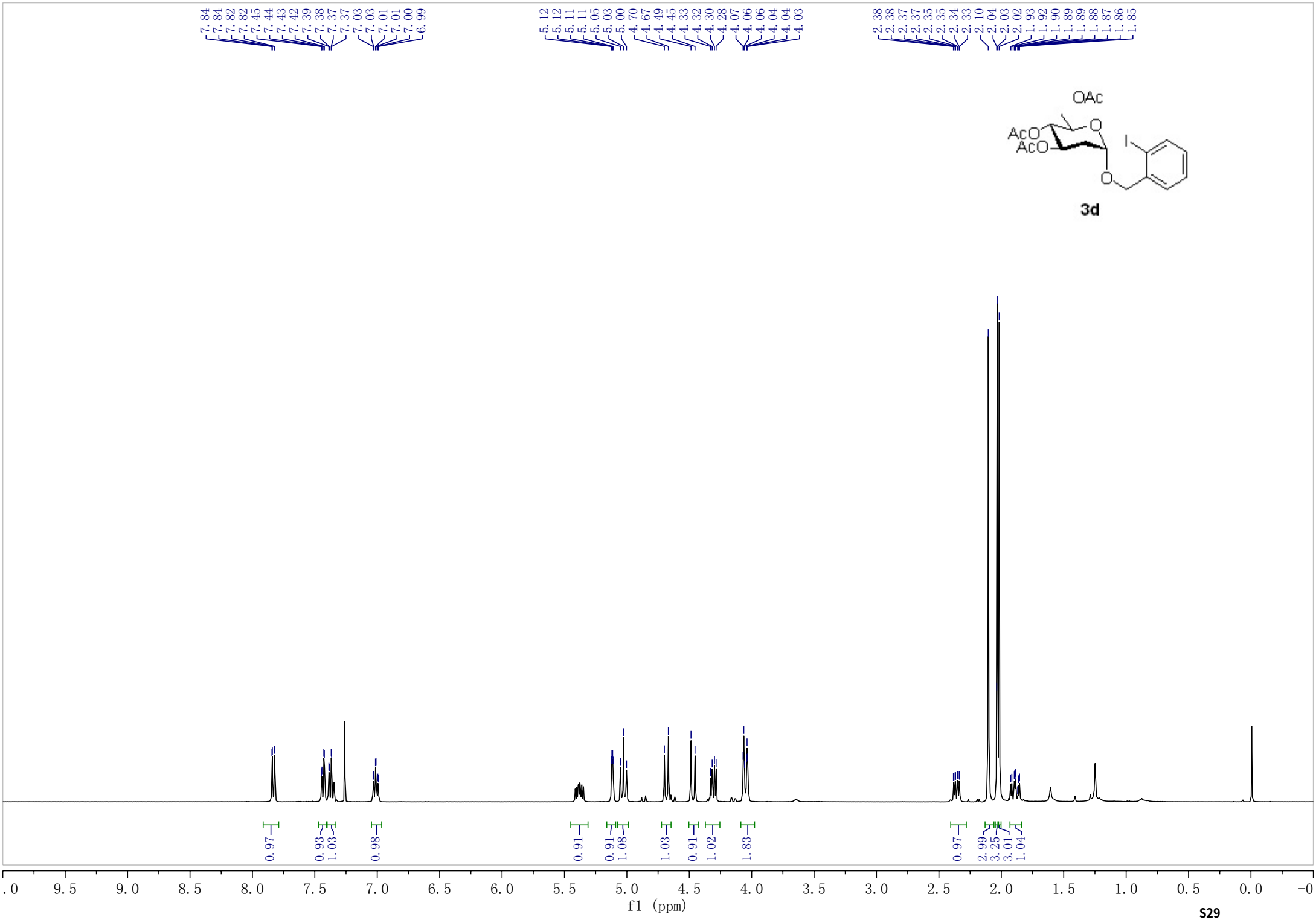
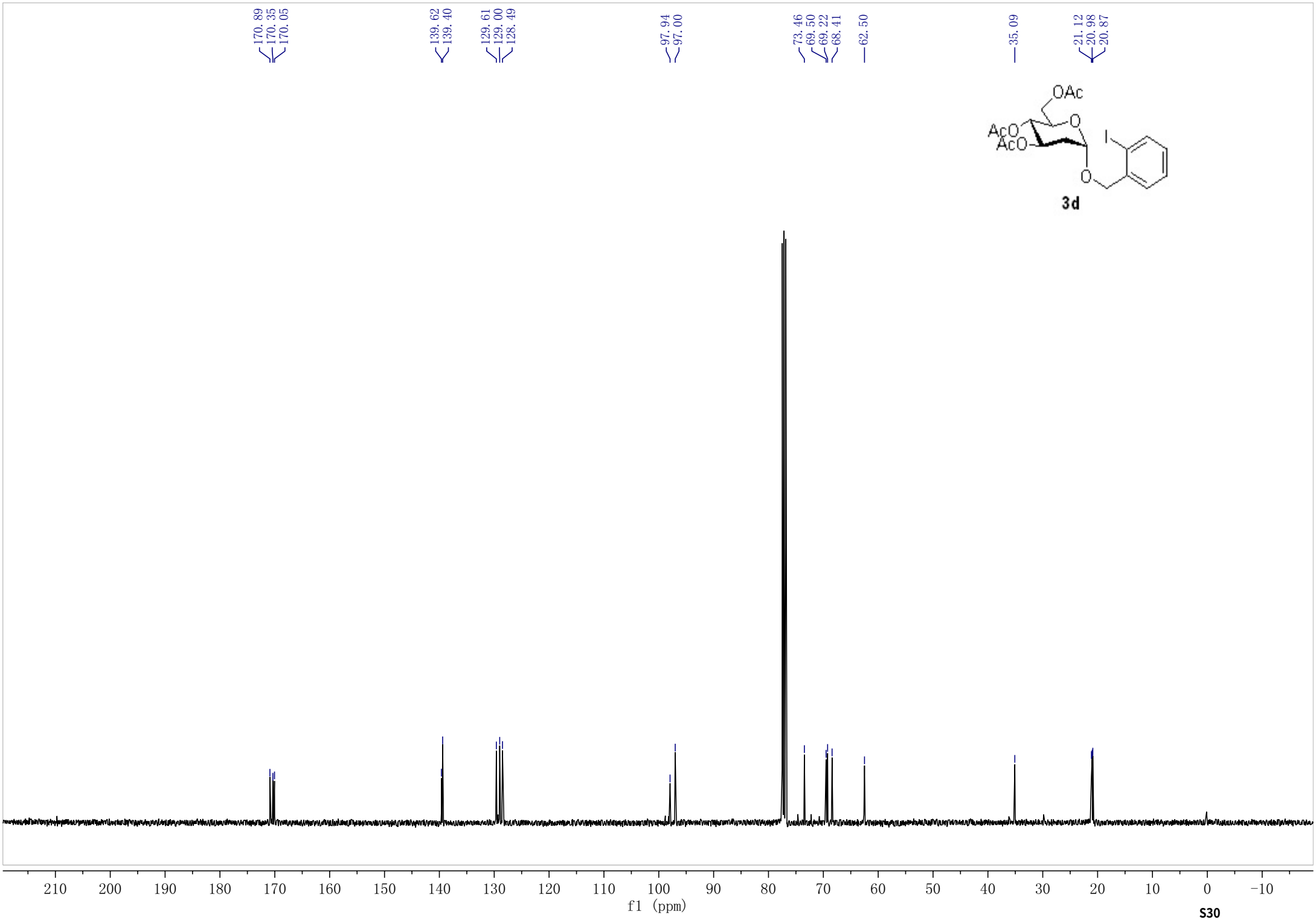
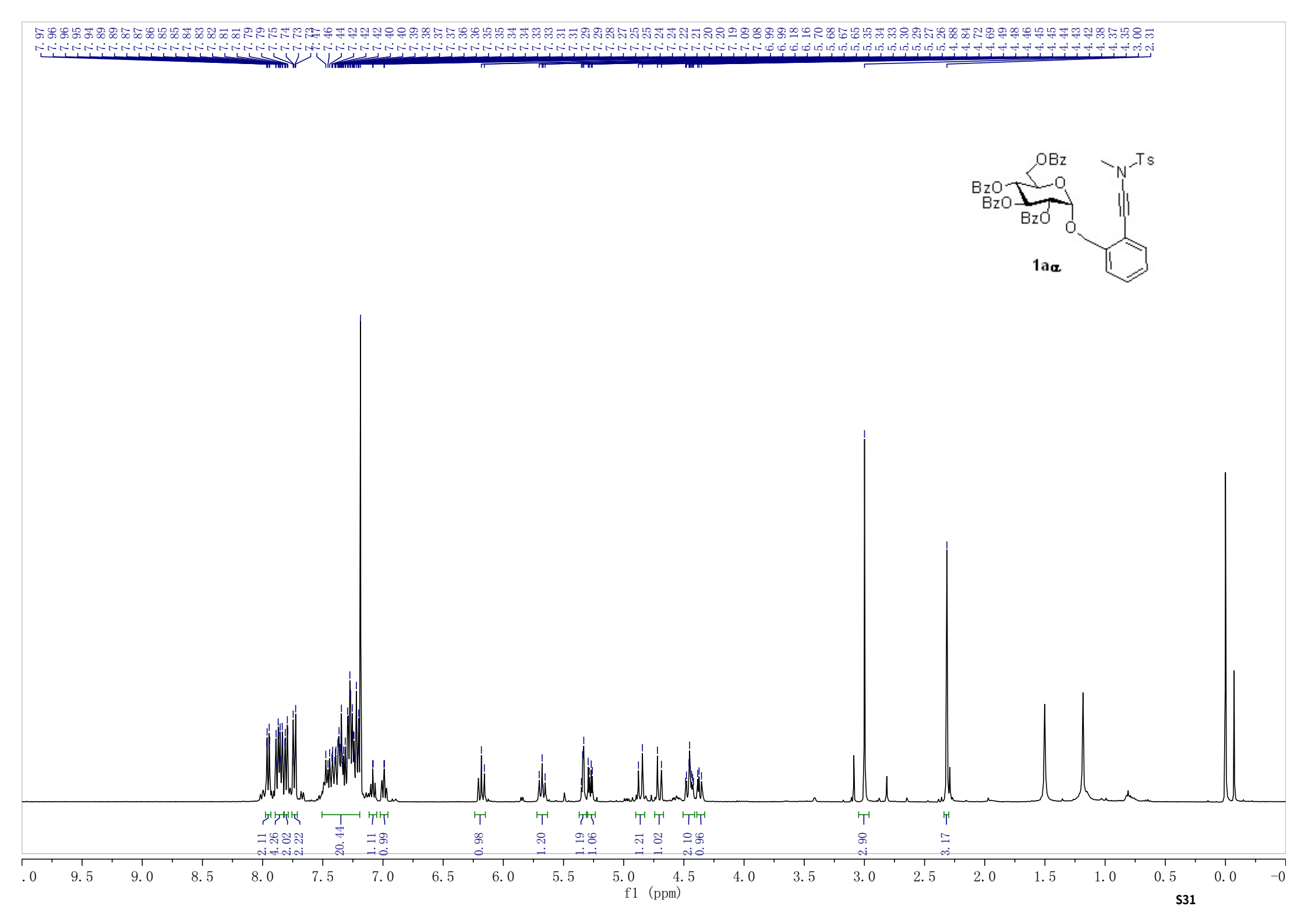
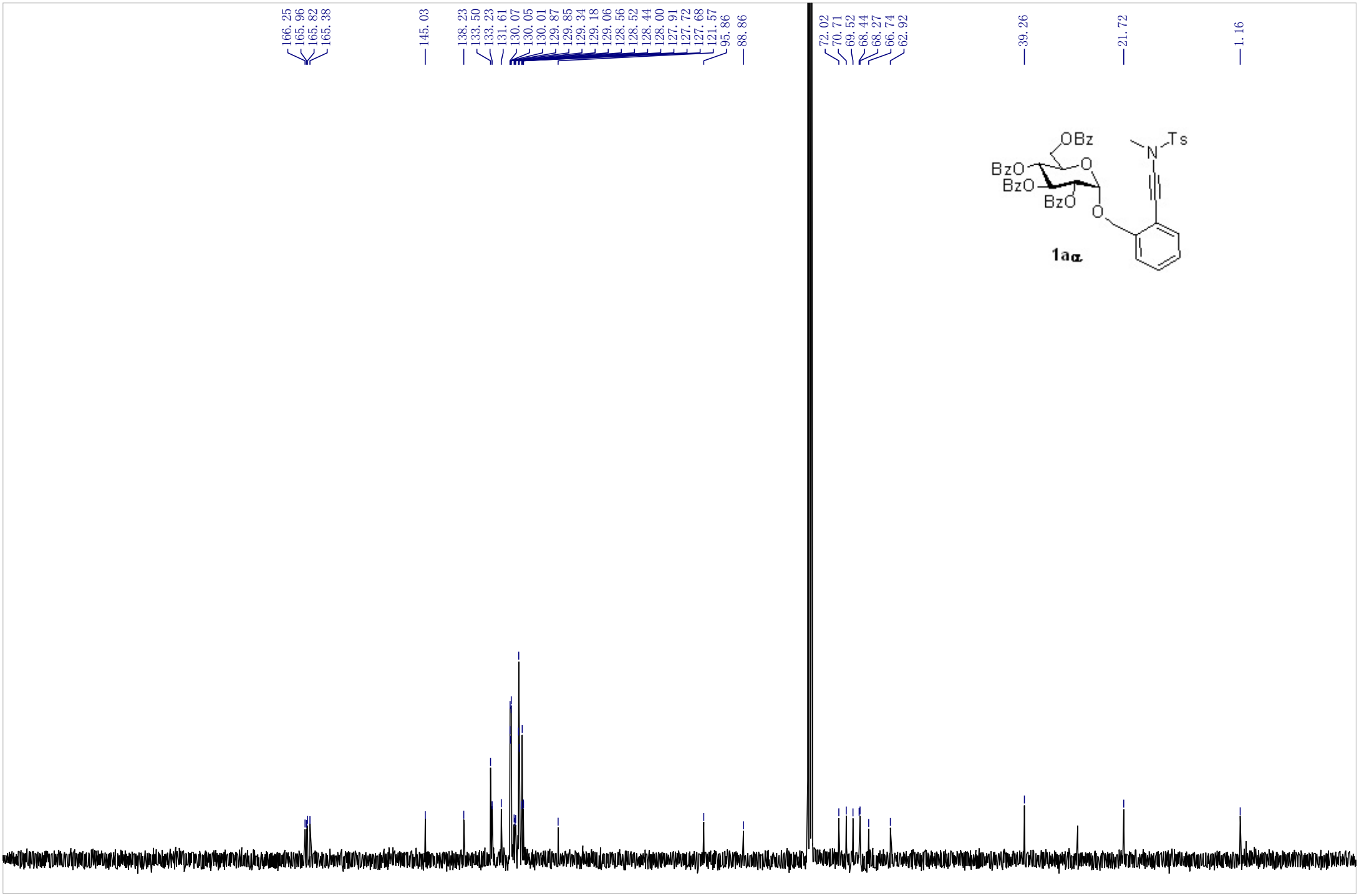
129.40
129.22
128.51
128.48
128.44
128.34
128.06
127.95
127.89
127.87
127.77
127.72
102.63
97.96
84.87
82.44
77.95
75.84
75.16
75.11
75.09
74.72
73.64
68.93
OBn
I
BnO
BnO
O
O
OBn
3cβ
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.84 7.84 7.82 7.82 7.45 7.44 7.43 7.42 7.39 7.38 7.37 7.37 7.03 7.01 7.01 7.00 6.99
5.12 5.12 5.11 5.11 5.05 5.03 5.00 4.70 4.67 4.49 4.45 4.33 4.32 4.30 4.28 4.07 4.06 4.06 4.04 4.04 4.03
2.38 2.38 2.37 2.37 2.35 2.35 2.34 2.33 2.10 2.04 2.03 2.02 1.93 1.92 1.90 1.89 1.89 1.88 1.87 1.86 1.85
OAc
AcO
AcO
O
O
I
3d
0.97 0.93 1.03 0.98 0.91 0.91 1.08 1.03 0.91 1.02 1.83 0.97 2.99 3.25 3.01 1.04
f1 (ppm)


170.89
170.35
170.05
139.62
139.40
129.61
129.00
128.49
97.94
97.00
73.46
69.50
69.22
68.41
62.50
35.09
21.12
20.98
20.87
OAc
AcO
AcO
O
O
I
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.97 7.96 7.96 7.95 7.94 7.89 7.89 7.87 7.87 7.86 7.85 7.85 7.84 7.83 7.82 7.81 7.81 7.79 7.79 7.75 7.74 7.73 7.73 7.47 7.46 7.44 7.42 7.42 7.42 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.31 7.31 7.29 7.29 7.28 7.27 7.25 7.25 7.24 7.24 7.22 7.21 7.20 7.20 7.19 7.09 7.08 6.99 6.99 6.18 6.16 5.70 5.68 5.67 5.65 5.35 5.34 5.33 5.30 5.29 5.27 5.26 4.88 4.84 4.72 4.69 4.49 4.48 4.46 4.45 4.45 4.44 4.43 4.42 4.38 4.37 4.35 3.00 2.31
OBz
BzO
BzO
BzO
O
O
N
Ts
1aα
2.11 4.26 2.02 2.22 20.44 1.11 0.99 0.98 1.20 1.19 1.06 1.21 1.02 2.10 0.96 2.90 3.17
f1 (ppm)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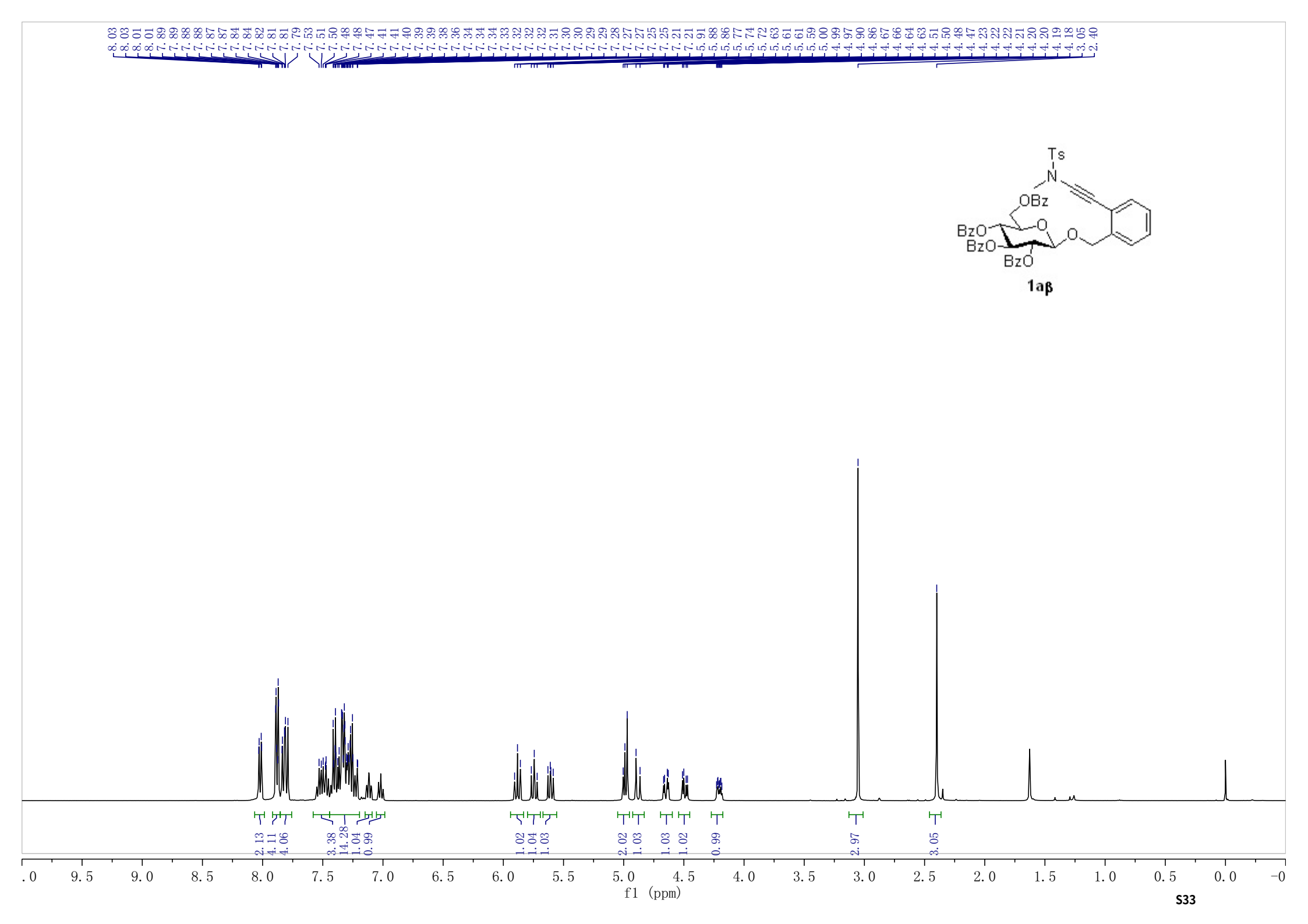
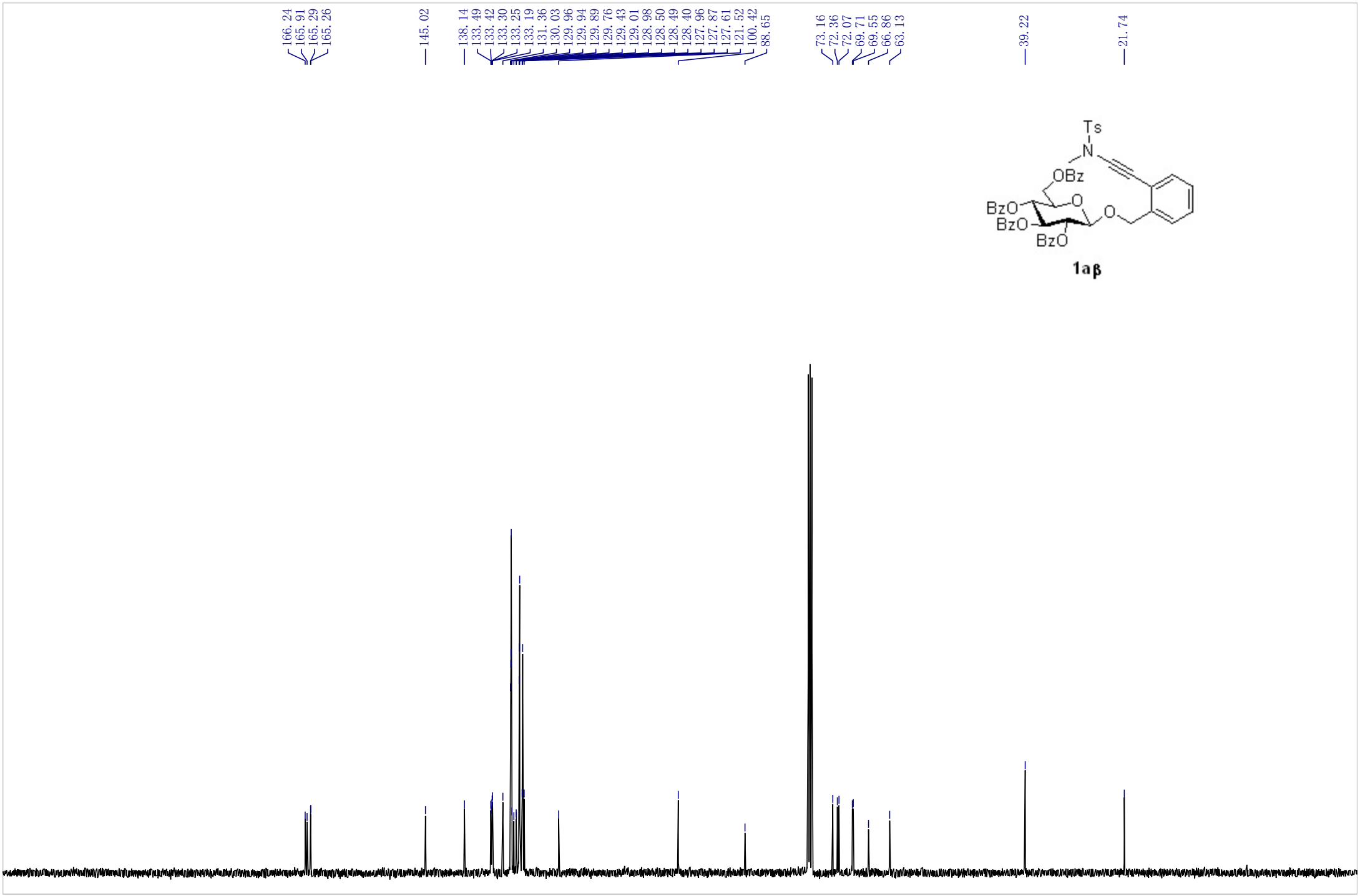
165.96
165.82
165.38
145.03
138.23
133.50
133.23
131.61
130.07
130.05
130.01
129.87
129.85
129.34
129.18
129.06
128.56
128.52
128.44
128.00
127.91
127.72
127.68
121.57
95.86
88.86
72.02
70.71
69.52
68.44
68.27
66.74
62.92
39.26
21.72
1.16
OBz
BzO
BzO
BzO
O
O
N
Ts
1aα
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.03 8.03 8.01 7.89 7.89 7.88 7.88 7.87 7.87 7.84 7.84 7.82 7.81 7.81 7.79 7.53 7.51 7.50 7.48 7.48 7.47 7.41 7.41 7.40 7.39 7.39 7.38 7.36 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.25 7.25 7.21 7.21 5.91 5.88 5.86 5.77 5.74 5.72 5.63 5.61 5.61 5.59 5.00 4.99 4.97 4.90 4.86 4.67 4.66 4.64 4.63 4.51 4.50 4.48 4.47 4.23 4.22 4.22 4.21 4.20 4.20 4.19 4.18 3.05 2.40
Ts
N
OBz
BzO
BzO
BzO
O
O
1aβ
2.13 4.11 4.06 3.38 14.28 1.04 0.99 1.02 1.04 1.03 2.02 1.03 1.03 1.02 0.99 2.97 3.05
f1 (ppm)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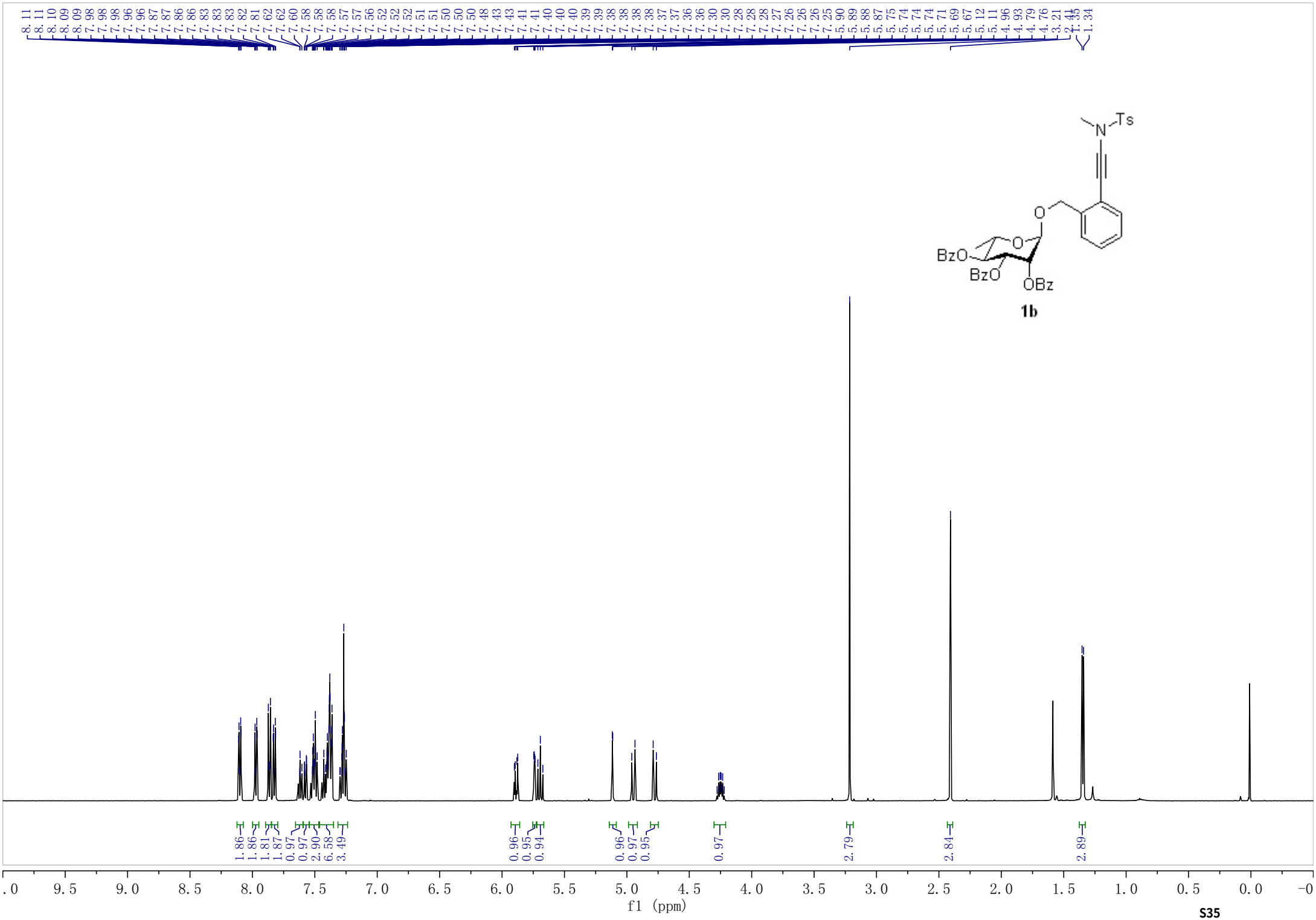
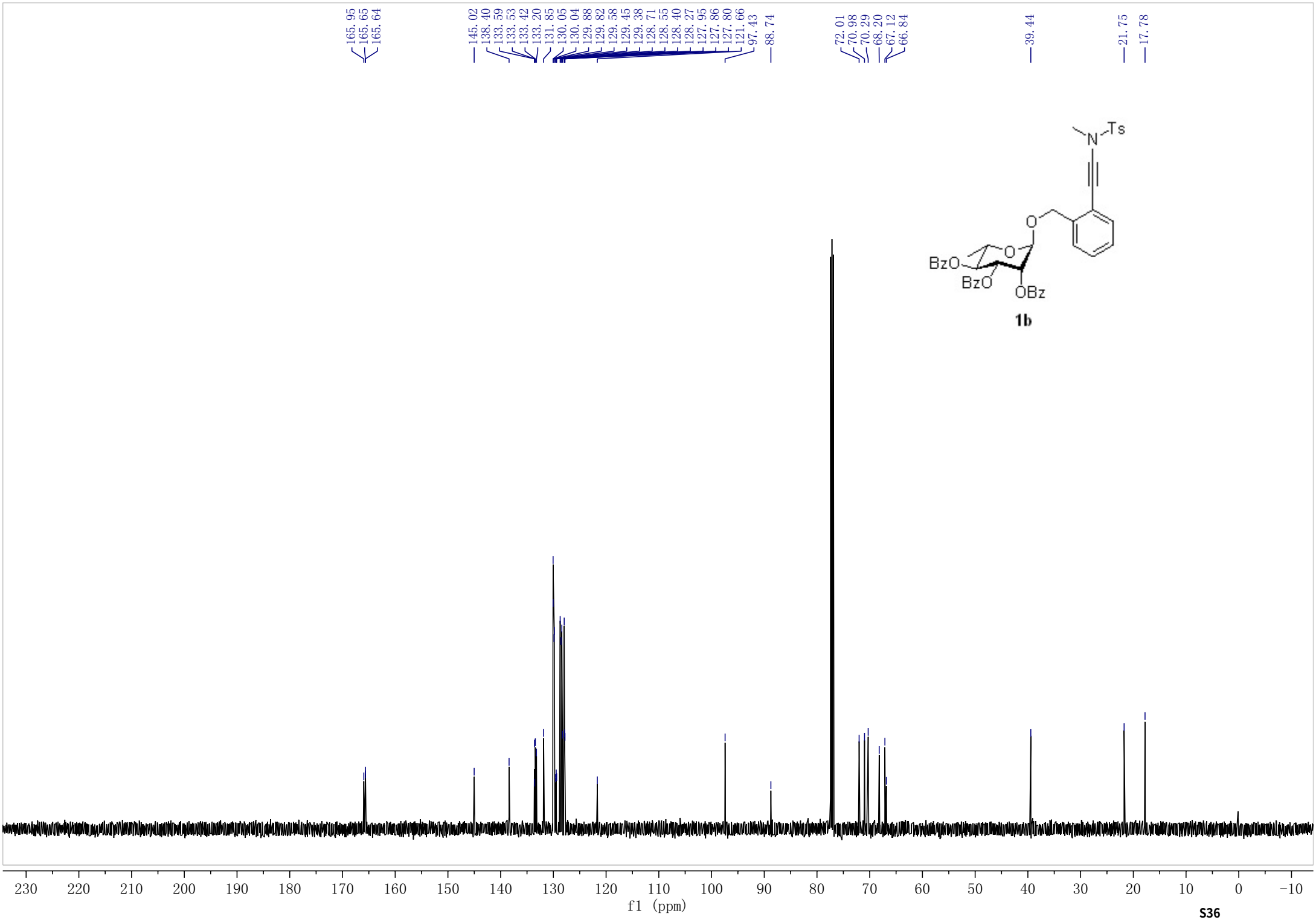
165.91
165.29
165.26
145.02
138.14
133.49
133.42
133.30
133.25
133.19
131.36
130.03
129.96
129.94
129.89
129.76
129.43
129.01
128.98
128.50
128.49
128.40
127.96
127.87
127.61
121.52
100.42
88.65
73.16
72.36
72.07
69.71
69.55
66.86
63.13
39.22
21.74
Ts
N
OBz
BzO
BzO
BzO
O
O
1aβ
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.11 8.11 8.10 8.09 8.09 7.98 7.98 7.98 7.96 7.96 7.87 7.87 7.86 7.86 7.83 7.83 7.82 7.81 7.62 7.62 7.60 7.58 7.58 7.58 7.57 7.57 7.56 7.52 7.52 7.52 7.51 7.51 7.50 7.50 7.50 7.48 7.43 7.43 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.30 7.28 7.28 7.28 7.27 7.26 7.26 7.26 7.25 5.90 5.89 5.88 5.87 5.75 5.74 5.74 5.74 5.71 5.69 5.67 5.12 5.11 4.96 4.93 4.79 4.76 3.21 2.41 1.35 1.34
N
Ts
O
O
BzO
BzO
OBz
1b
1.86 1.86 1.81 1.87 0.97 0.97 2.90 6.58 3.49
0.96 0.95 0.94
0.96 0.97 0.95
0.97
2.79
2.84
2.89
f1 (ppm)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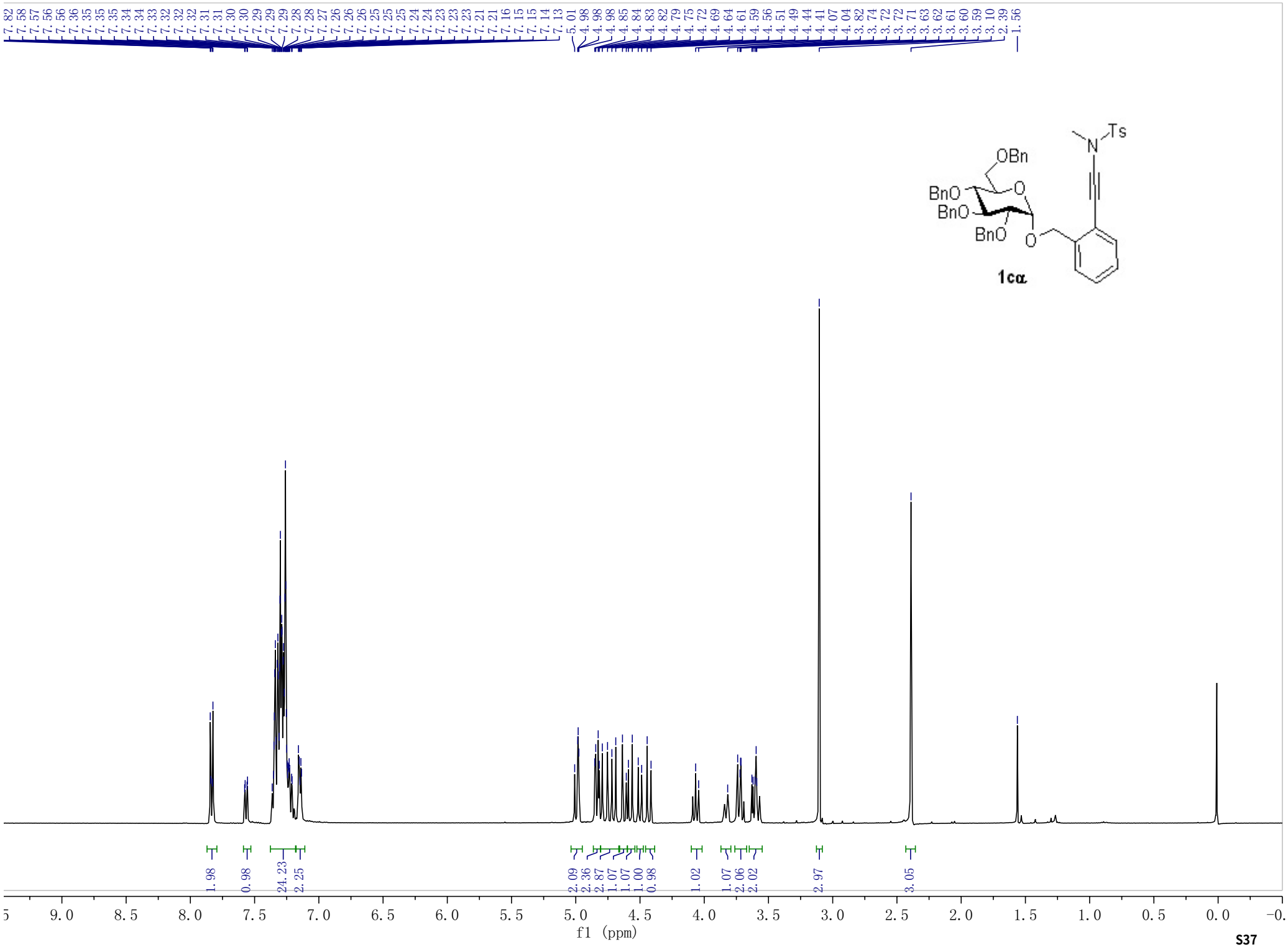
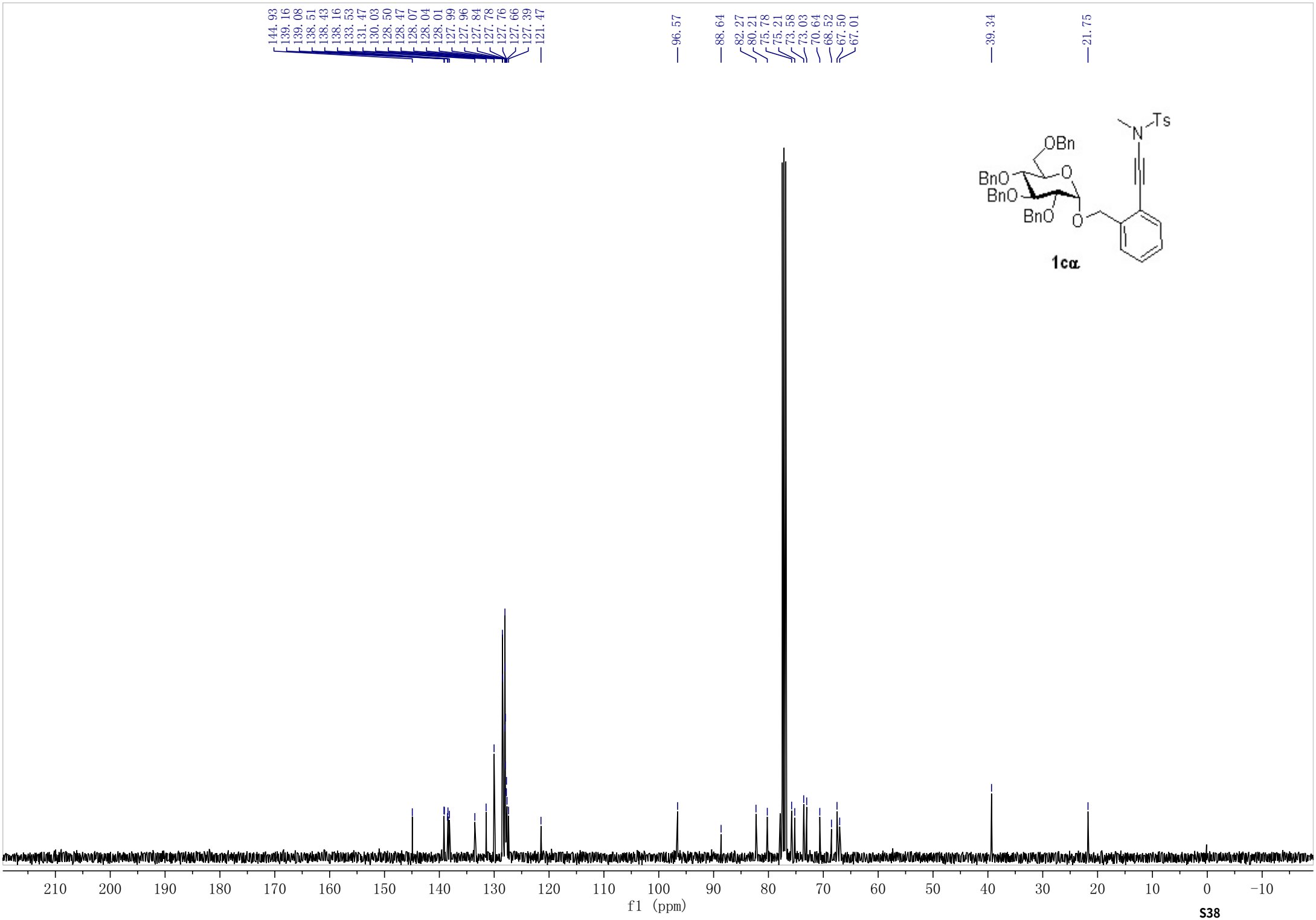
165.65
165.64
145.02
138.40
133.59
133.53
133.42
133.20
131.85
130.05
130.04
129.88
129.82
129.58
129.45
129.38
128.71
128.55
128.40
128.27
127.95
127.86
127.80
121.66
97.43
88.74
72.01
70.98
70.29
68.20
67.12
66.84
39.44
21.75
17.78
N
Ts
O
O
BzO
BzO
OBz
1b
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.82 7.58 7.57 7.56 7.56 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.23 7.23 7.21 7.21 7.16 7.15 7.15 7.14 7.13 5.01 4.98 4.98 4.98 4.85 4.84 4.83 4.82 4.79 4.75 4.72 4.69 4.64 4.61 4.59 4.56 4.51 4.49 4.44 4.41 4.07 4.04 3.82 3.74 3.72 3.72 3.71 3.63 3.62 3.61 3.60 3.59 3.10 2.39 1.56
OBn
BnO
BnO
BnO
O
O
N
Ts
1cα
1.98 0.98 24.23 2.25 2.09 2.36 2.87 1.07 1.07 1.00 0.98 1.02 1.07 2.06 2.02 2.97 3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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139.16
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131.47
130.03
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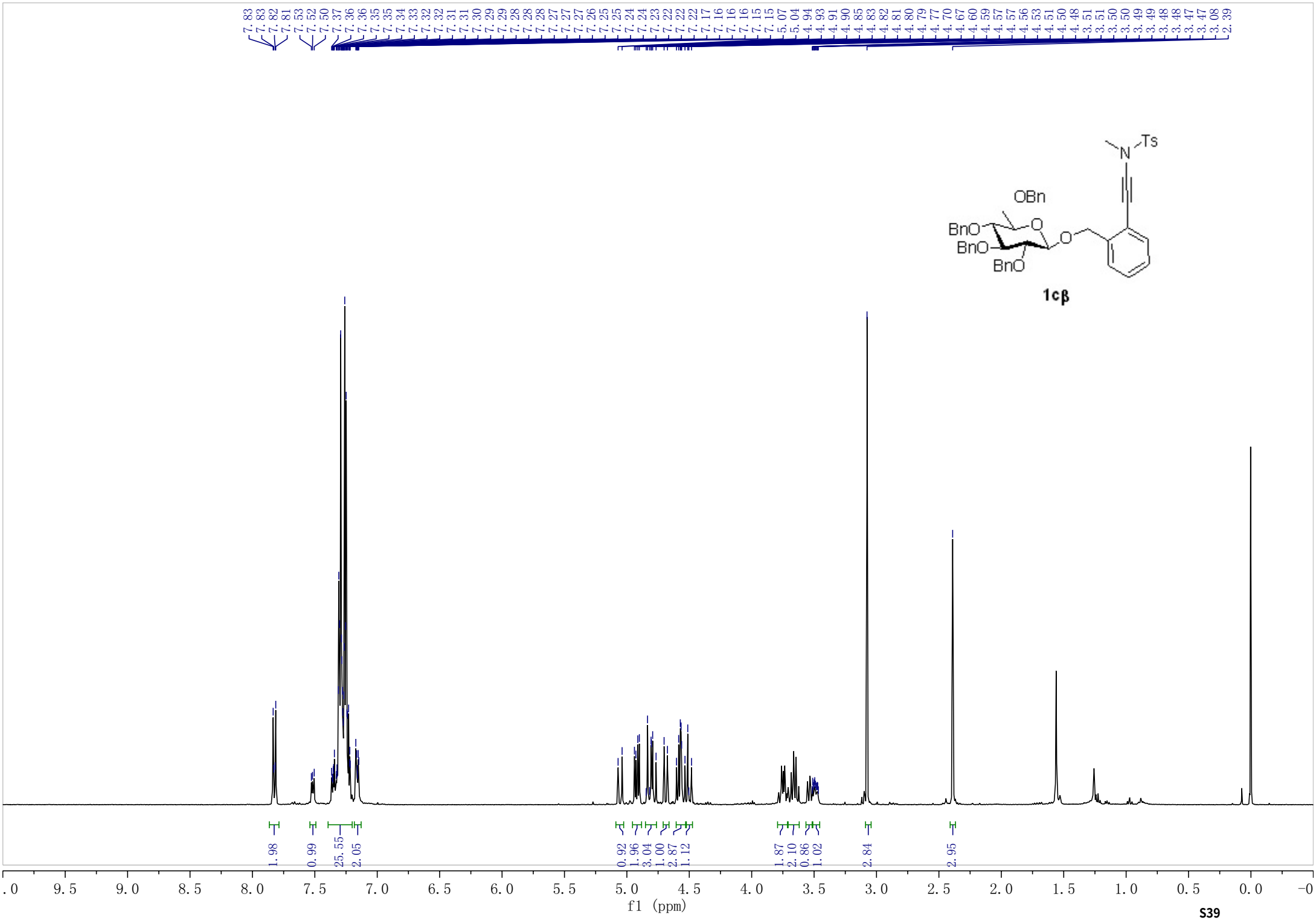
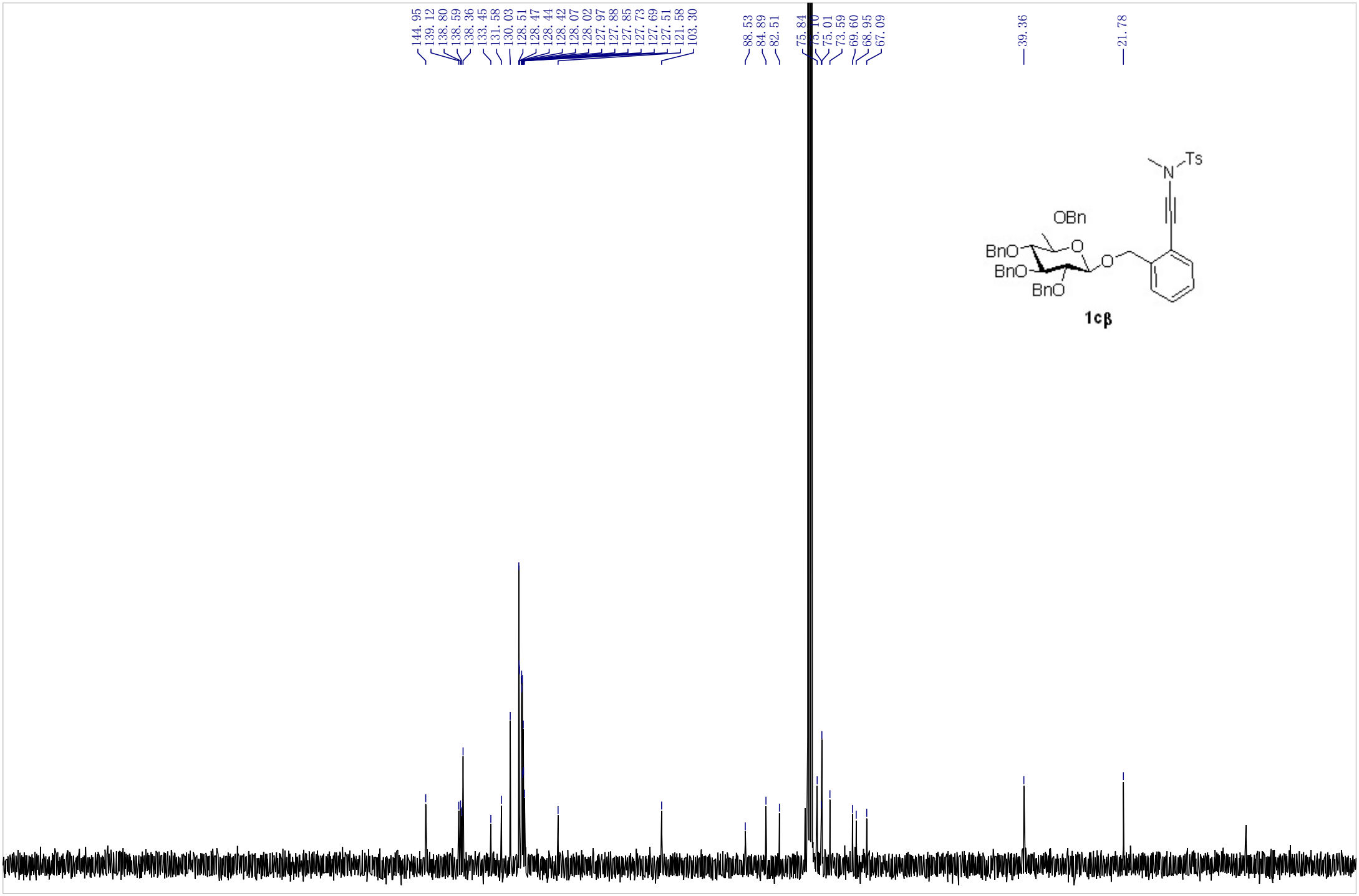
128.07
128.04
128.01
127.99
127.96
127.84
127.78
127.76
127.66
127.39
121.47
96.57
88.64
82.27
80.21
75.78
75.21
73.58
73.03
70.64
68.52
67.50
67.01
39.34
21.75
OBn
BnO
BnO
BnO
O
O
N
Ts
1cα
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.83 7.83 7.82 7.81 7.53 7.52 7.50 7.37 7.36 7.36 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.17 7.16 7.16 7.15 7.15 5.07 5.04 4.94 4.93 4.91 4.90 4.85 4.83 4.82 4.81 4.80 4.79 4.77 4.70 4.67 4.60 4.59 4.57 4.57 4.56 4.53 4.51 4.50 4.48 3.51 3.51 3.50 3.50 3.49 3.49 3.48 3.48 3.47 3.47 3.08 2.39
N
Ts
OBn
BnO
BnO
BnO
O
O
1cβ
1.98 0.99 25.55 2.05 0.92 1.96 3.04 1.00 2.87 1.12 1.87 2.10 0.86 1.02 2.84 2.95
f1 (ppm)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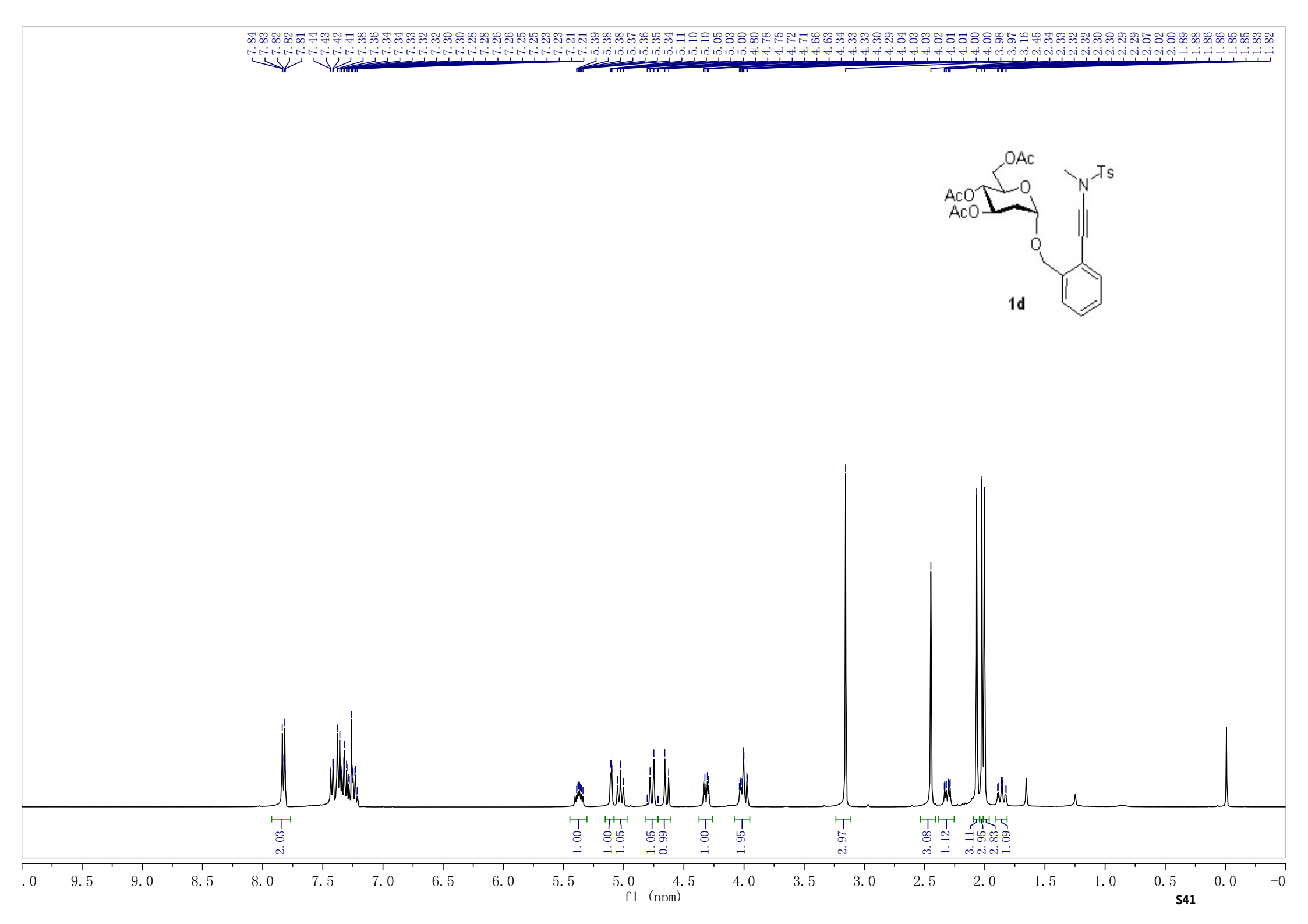
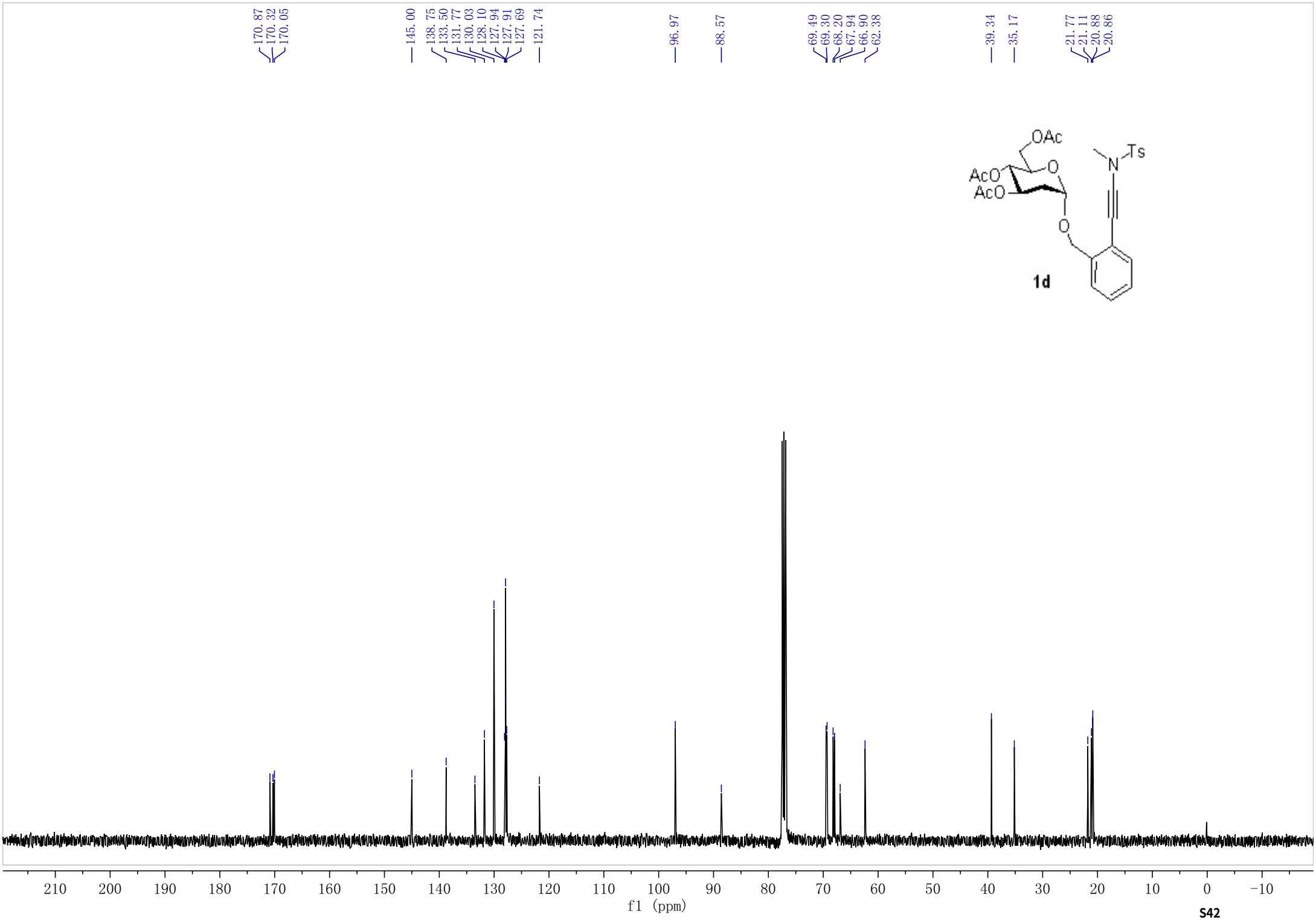
131.58
130.03
128.51
128.47
128.44
128.42
128.07
128.02
127.97
127.88
127.85
127.73
127.69
127.51
121.58
103.30
88.53
84.89
82.51
75.84
75.01
73.59
69.60
68.95
67.09
39.36
21.78
Ts
N
OBn
BnO
BnO
BnO
O
O
1cβ
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.84 7.83 7.82 7.82 7.81 7.44 7.43 7.42 7.41 7.38 7.36 7.34 7.34 7.33 7.32 7.32 7.30 7.30 7.28 7.28 7.26 7.26 7.25 7.25 7.23 7.23 7.21 7.21 5.39 5.38 5.38 5.37 5.36 5.35 5.34 5.11 5.10 5.10 5.05 5.03 5.00 4.80 4.78 4.75 4.72 4.71 4.66 4.63 4.34 4.33 4.33 4.30 4.29 4.04 4.03 4.03 4.02 4.01 4.01 4.00 4.00 3.98 3.97 3.16 2.45 2.34 2.33 2.32 2.32 2.30 2.30 2.29 2.29 2.07 2.02 2.00 1.89 1.88 1.86 1.86 1.85 1.85 1.83 1.82
OAc
AcO
AcO
O
O
N
Ts
1d
2.03
1.00
1.00
1.05
1.05
0.99
1.00
1.95
2.97
3.08
1.12
3.11
2.95
2.83
1.09
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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145.00
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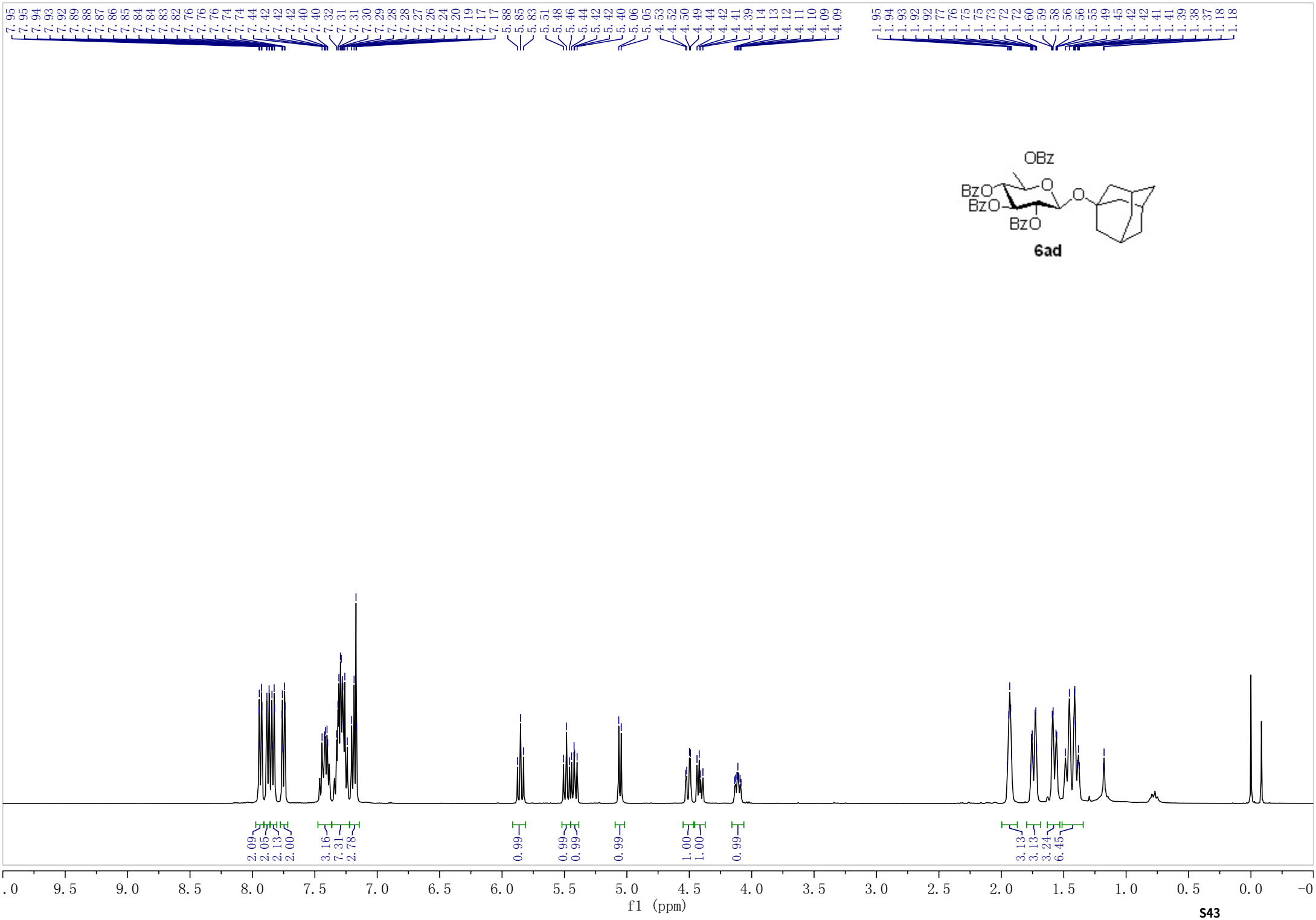
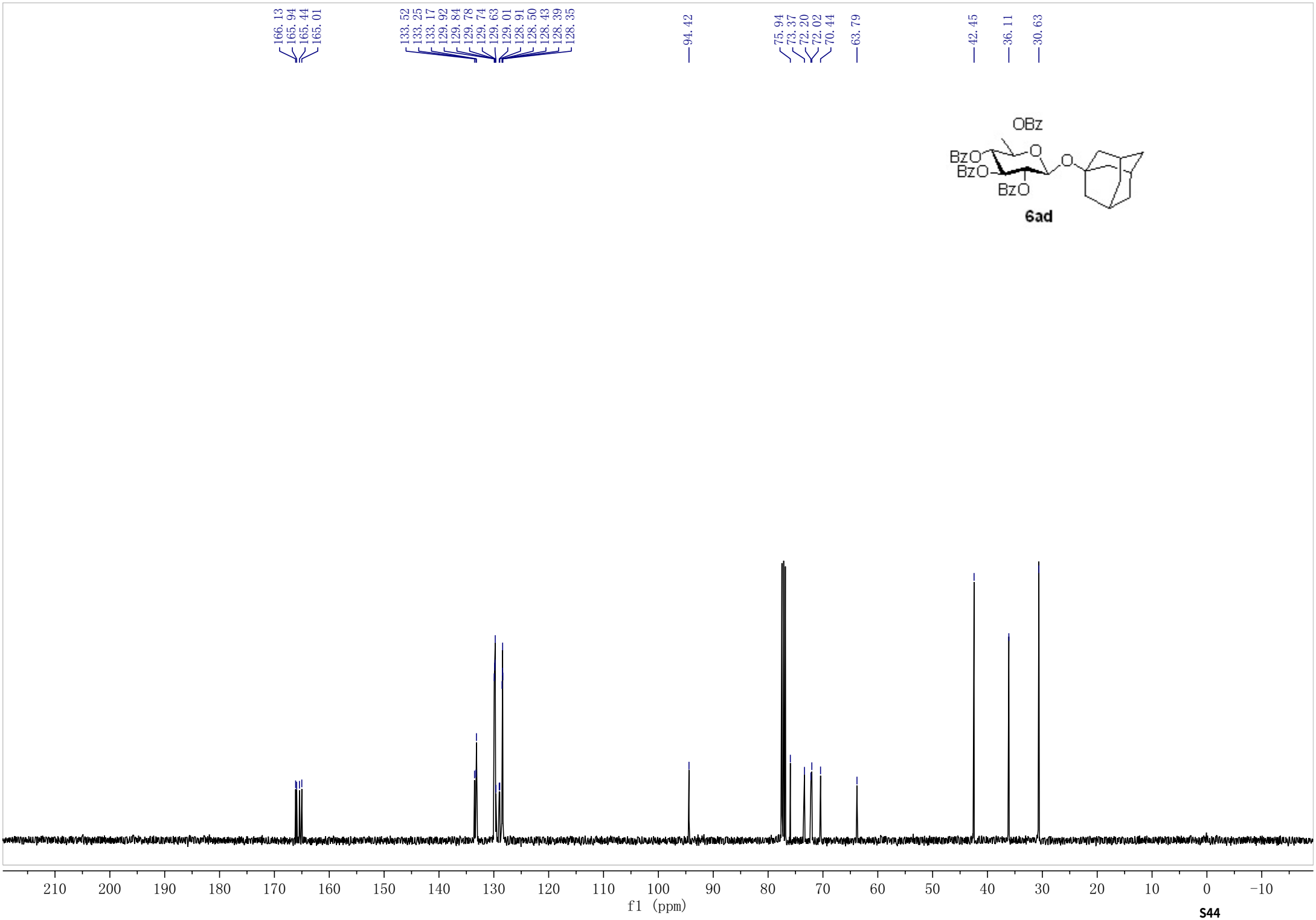
133.50
131.77
130.03
128.10
127.94
127.91
127.69
121.74
96.97
88.57
69.49
69.30
68.20
67.94
66.90
62.38
39.34
35.17
21.77
21.11
20.88
20.86
OAc
AcO
AcO
O
O
N
Ts
1d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.95 7.95 7.94 7.93 7.92 7.89 7.88 7.87 7.86 7.85 7.84 7.84 7.83 7.82 7.76 7.76 7.76 7.74 7.74 7.44 7.42 7.42 7.42 7.40 7.40 7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.26 7.24 7.20 7.19 7.17 7.17
5.88 5.85 5.83 5.51 5.48 5.46 5.44 5.42 5.40 5.06 5.05 4.53 4.52 4.50 4.49 4.44 4.42 4.41 4.39 4.14 4.13 4.12 4.11 4.10 4.09 4.09
1.95 1.94 1.93 1.92 1.92 1.77 1.76 1.75 1.75 1.73 1.72 1.72 1.60 1.59 1.58 1.56 1.56 1.55 1.49 1.45 1.42 1.42 1.41 1.41 1.39 1.38 1.37 1.18 1.18
OBz
BzO
BzO
BzO
O
O
6ad
2.09 2.05 2.13 2.00 3.16 7.31 2.78 0.99 0.99 0.99 0.99 1.00 1.00 0.99 3.13 3.13 3.24 6.45
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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129.78
129.74
129.63
129.01
128.91
128.50
128.43
128.39
128.35
94.42
75.94
73.37
72.20
72.02
70.44
63.79
42.45
36.11
30.63
OBz
BzO
BzO
BzO
O
O
6ad
210
200
190
180
170
160
150
140
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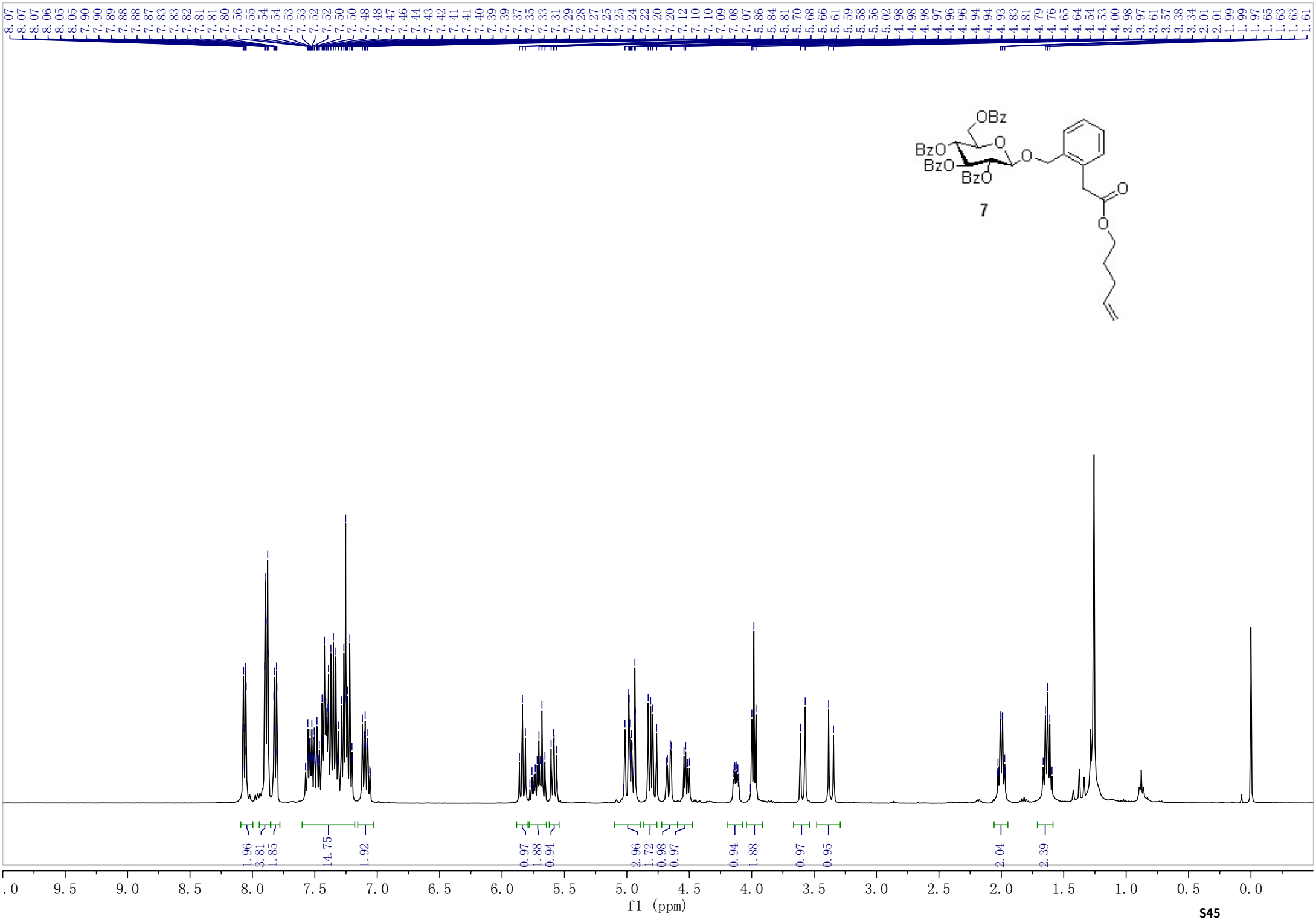
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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BzO
BzO
BzO
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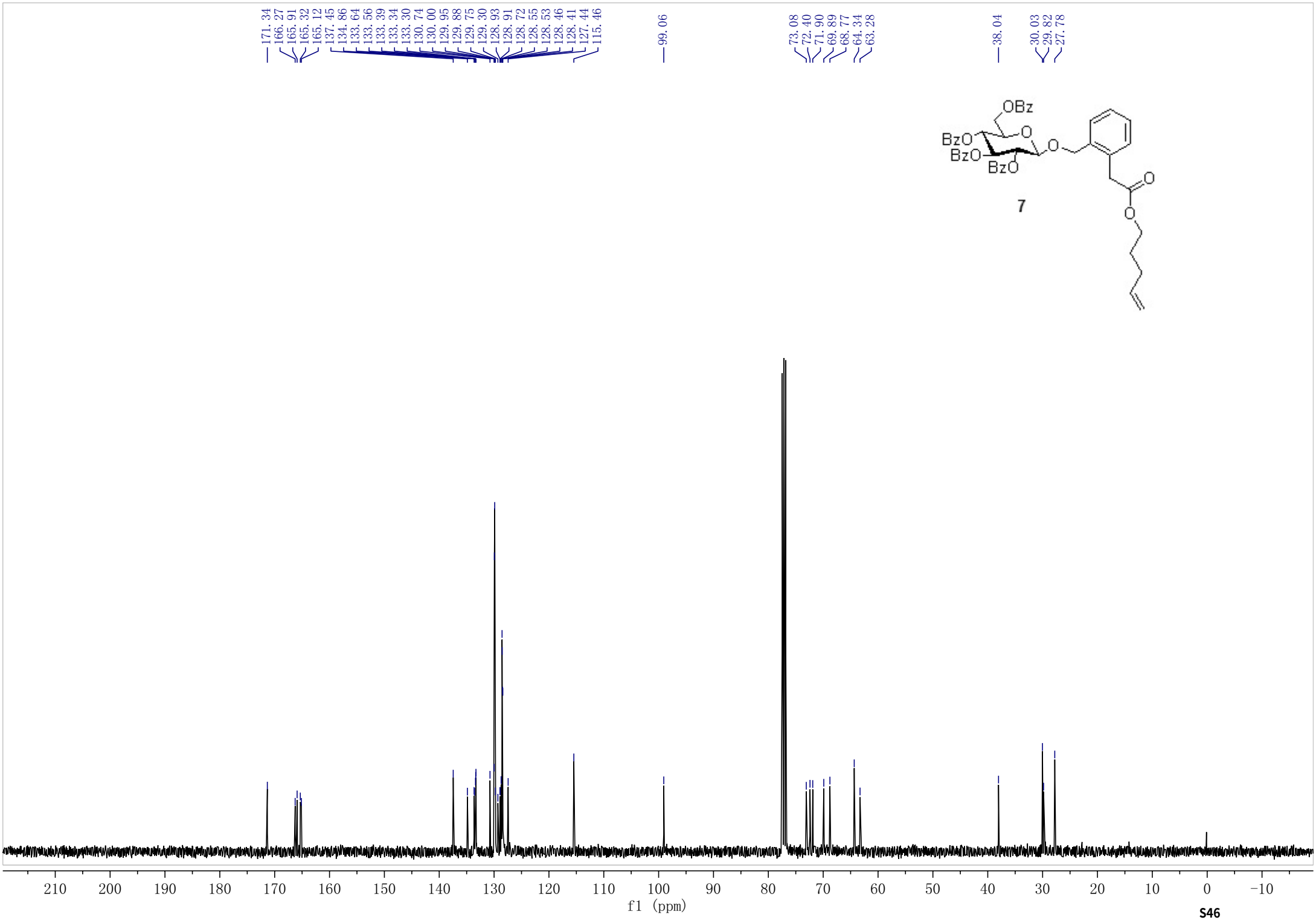
O
O
O
7
1.96
3.81
1.85
14.75
1.92
0.97
1.88
0.94
2.96
1.72
0.98
0.97
0.94
1.88
0.97
0.95
2.04
2.39
f1 (ppm)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166.27
165.91
165.32
165.12
137.45
134.86
133.64
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133.39
133.34
133.30
130.74
130.00
129.95
129.88
129.75
129.30
128.93
128.91
128.72
128.55
128.53
128.46
128.41
127.44
115.46
99.06
73.08
72.40
71.90
69.89
68.77
64.34
63.28
38.04
30.03
29.82
27.78
OBz
BzO
BzO
BzO
O
O
O
O
7
210
200
190
180
170
160
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140
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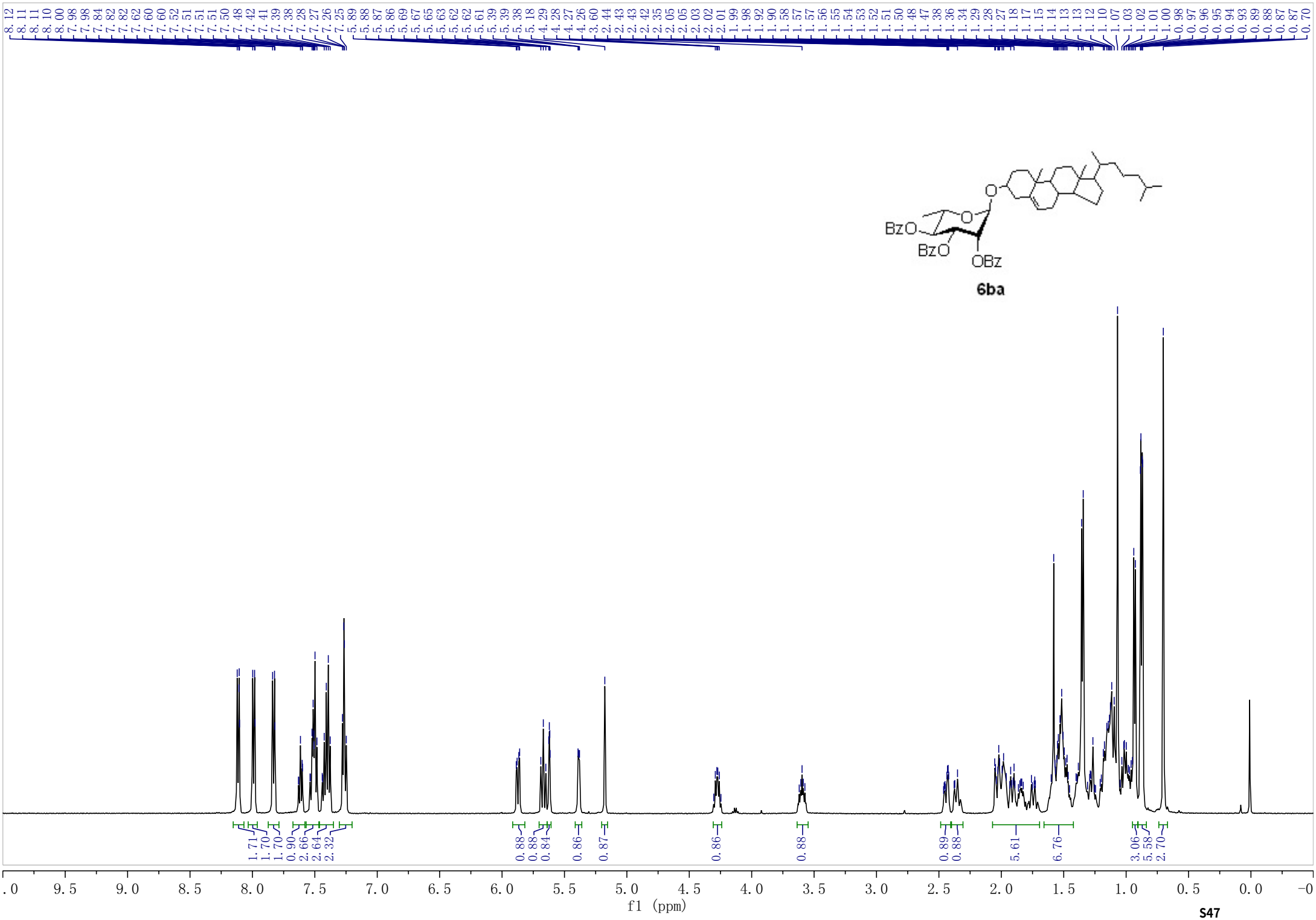
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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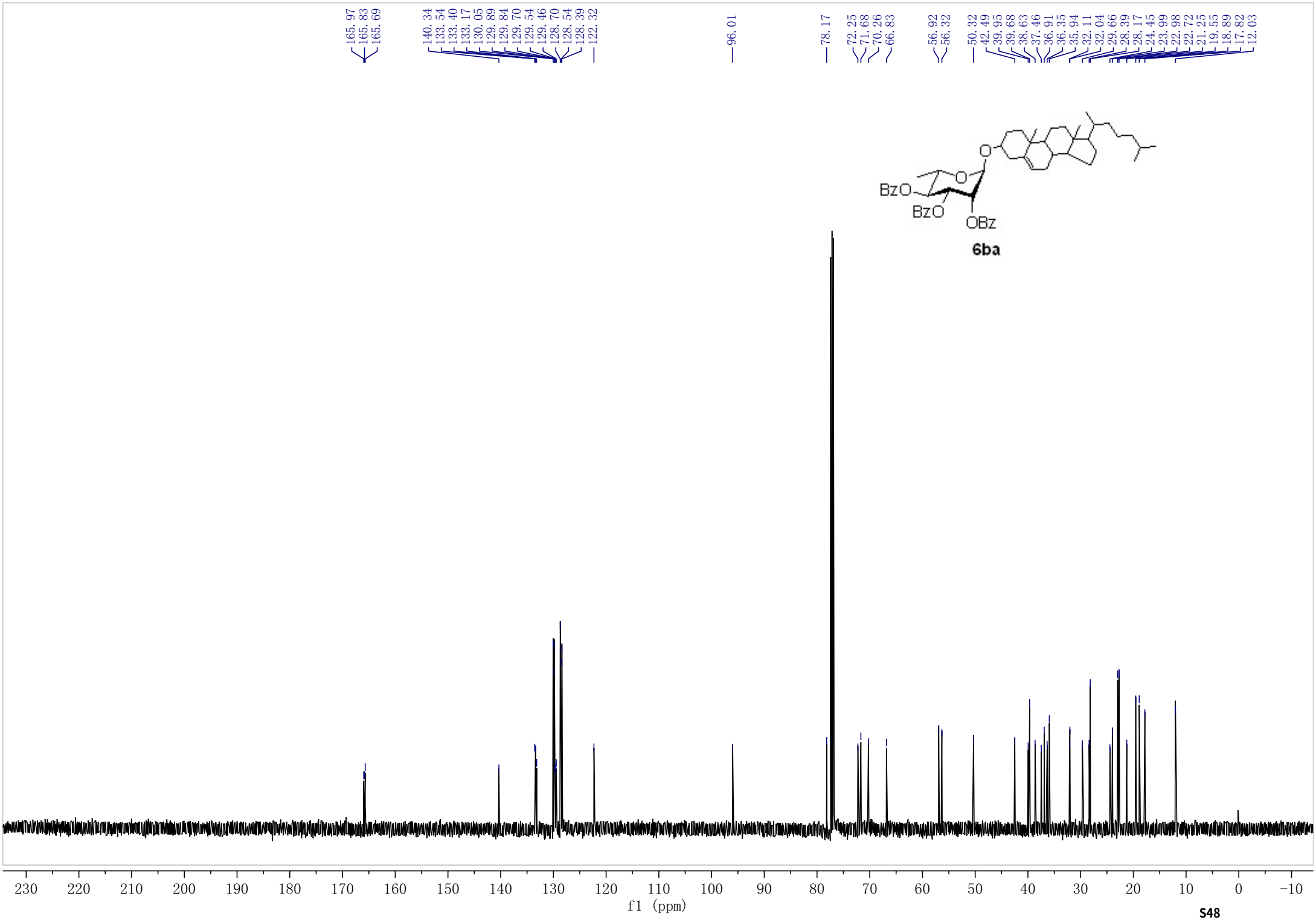
BzO
BzO
OBz
O
O
6ba
1.71 1.70 1.70 0.90 2.66 2.64 2.32 0.88 0.88 0.84 0.86 0.87 0.86 0.88 0.89 0.88 5.61 6.76 3.06 5.58 2.70
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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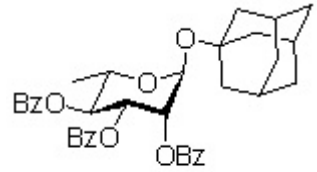
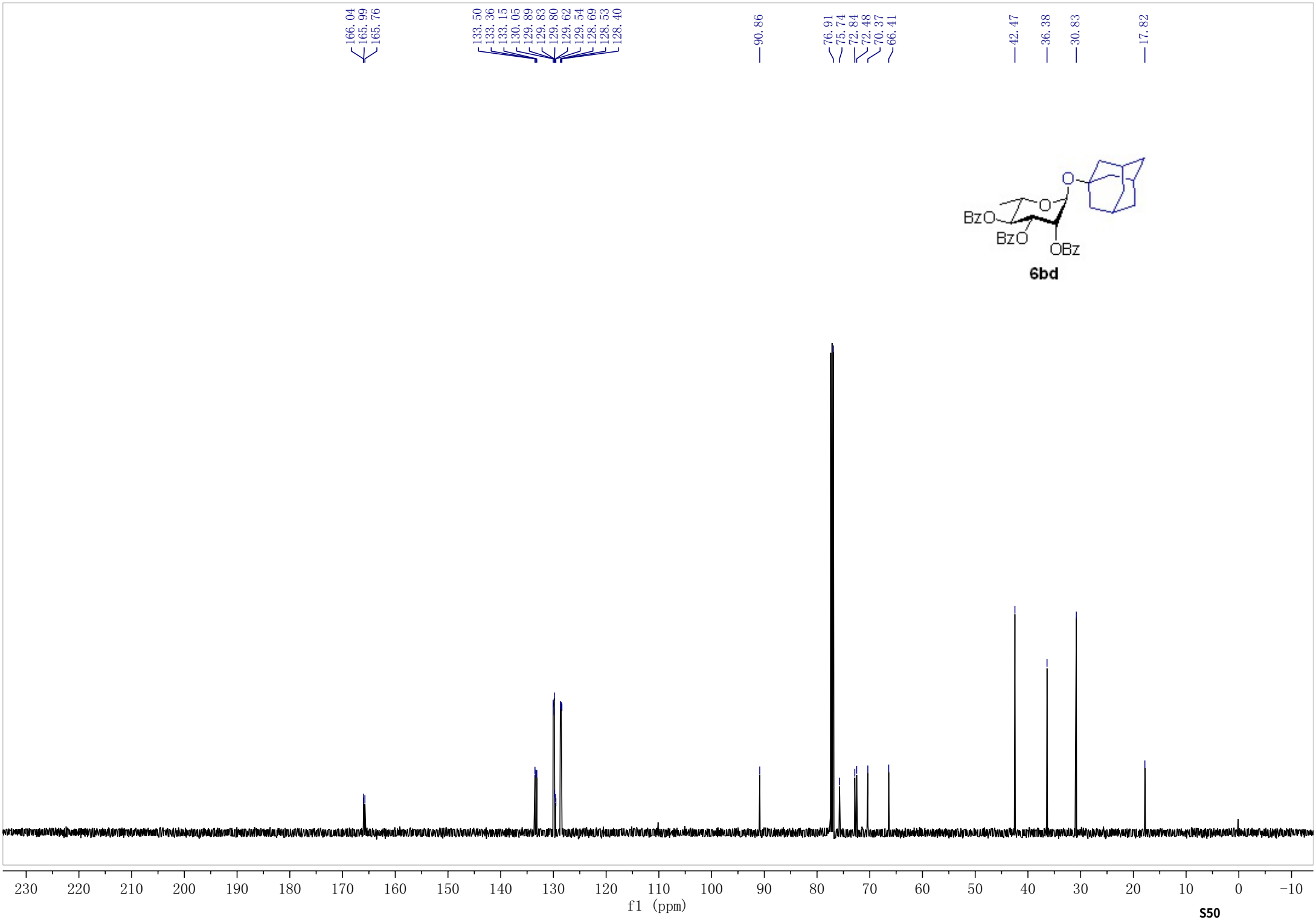
165.69
140.34
133.54
133.40
133.17
130.05
129.89
129.84
129.70
129.54
129.46
128.70
128.54
128.39
122.32
96.01
78.17
72.25
71.68
70.26
66.83
56.92
56.32
50.32
42.49
39.95
39.68
38.63
37.46
36.91
36.35
35.94
32.11
32.04
29.66
28.39
28.17
24.45
23.99
22.98
22.72
21.25
19.55
18.89
17.82
12.03
BzO
BzO
OBz
6ba
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



6bd

f1 (ppm)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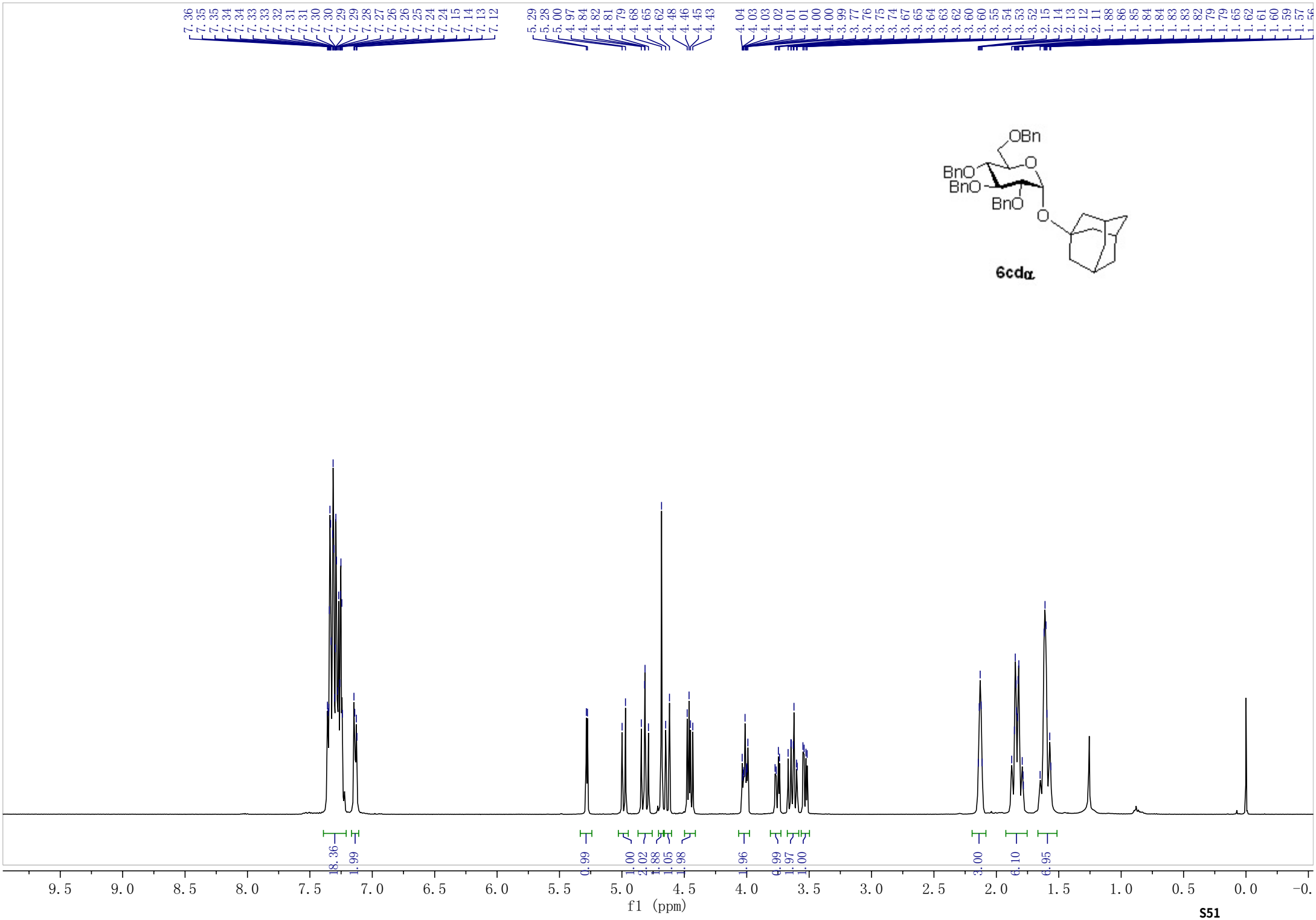
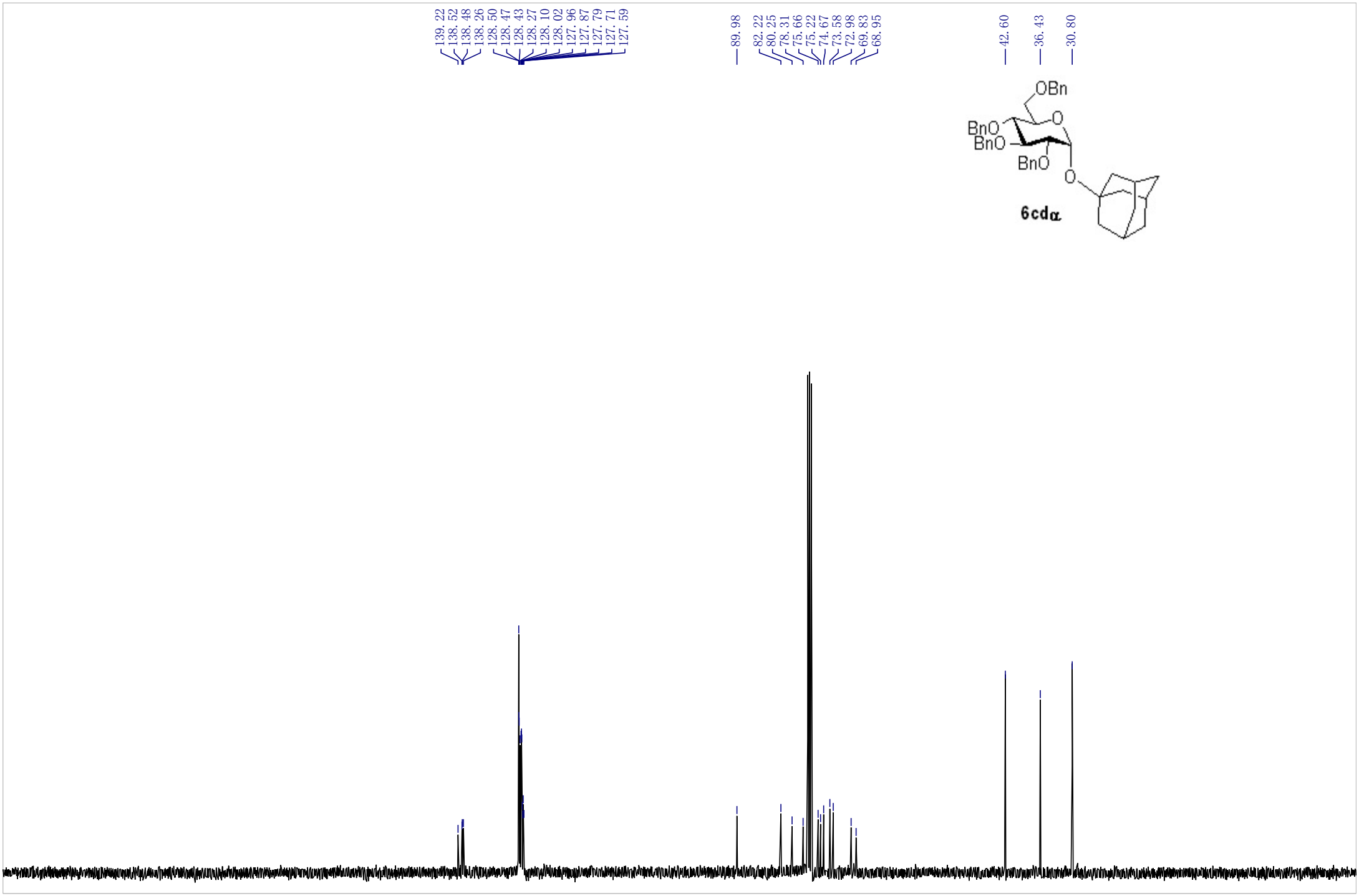
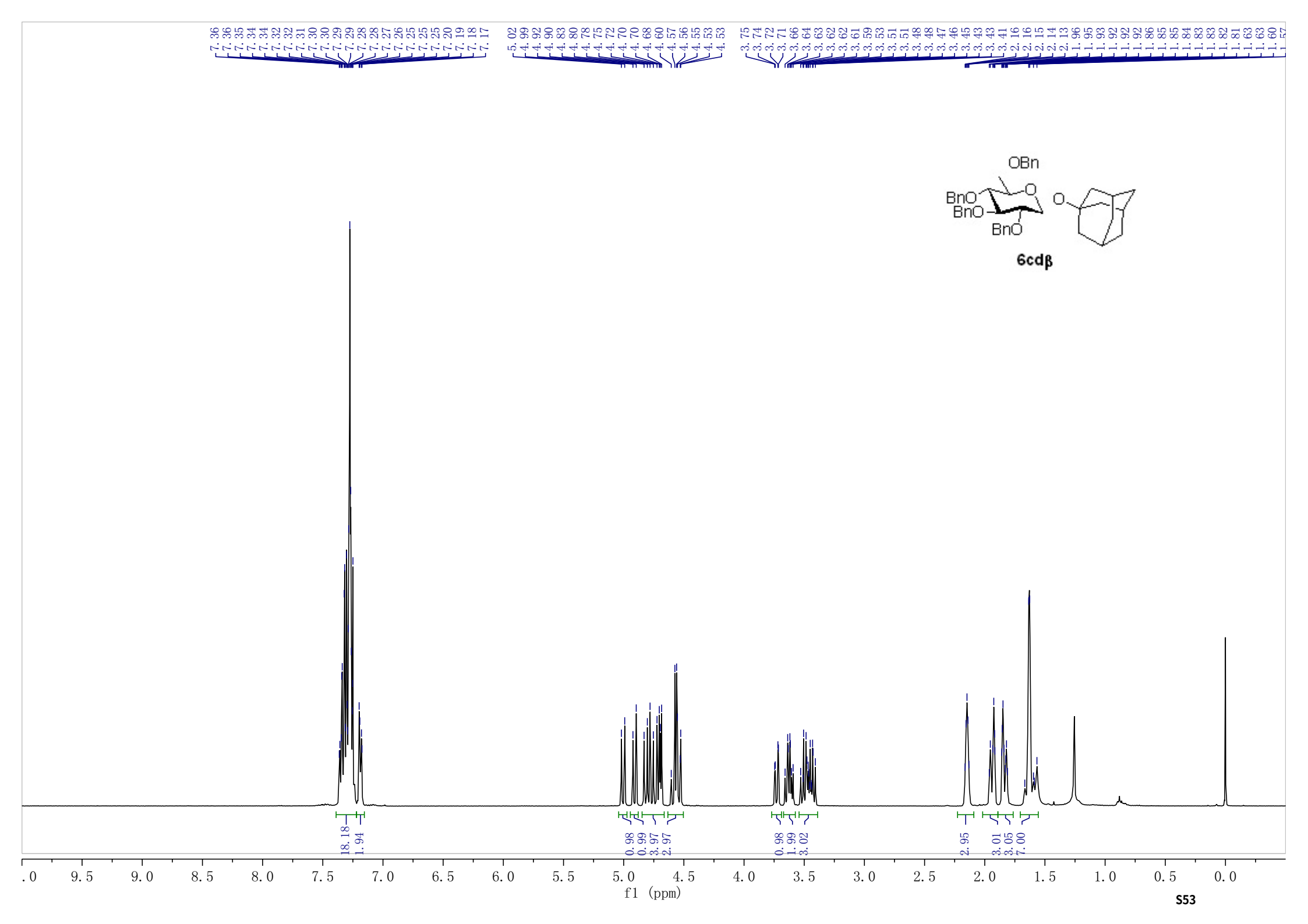
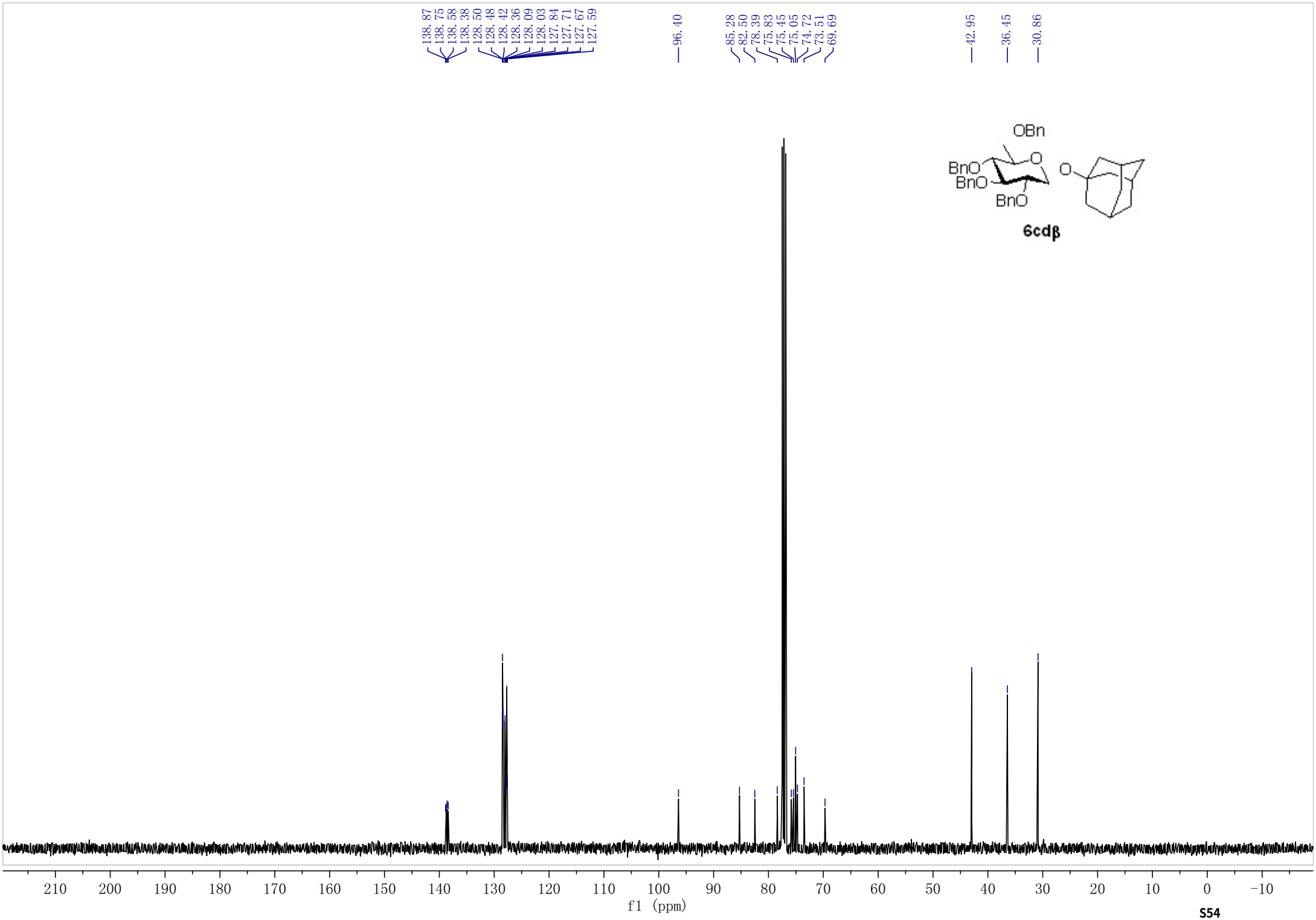
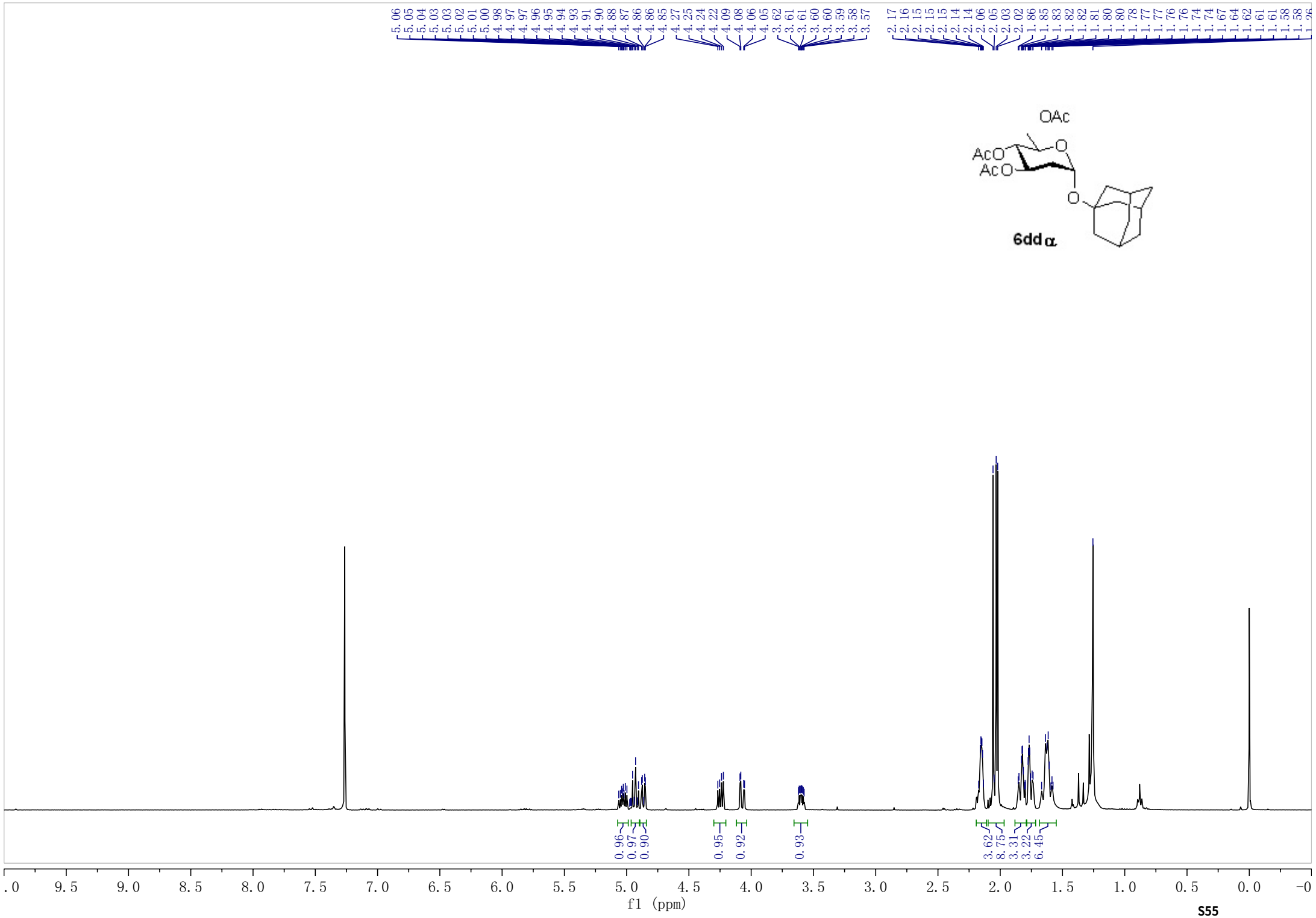
165.99
165.76
133.50
133.36
133.15
130.05
129.89
129.83
129.80
129.62
129.54
128.69
128.53
128.40
90.86
76.91
75.74
72.84
72.48
70.37
66.41
42.47
36.38
30.83
17.82
BzO
BzO
OBz
O
O
6bd
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

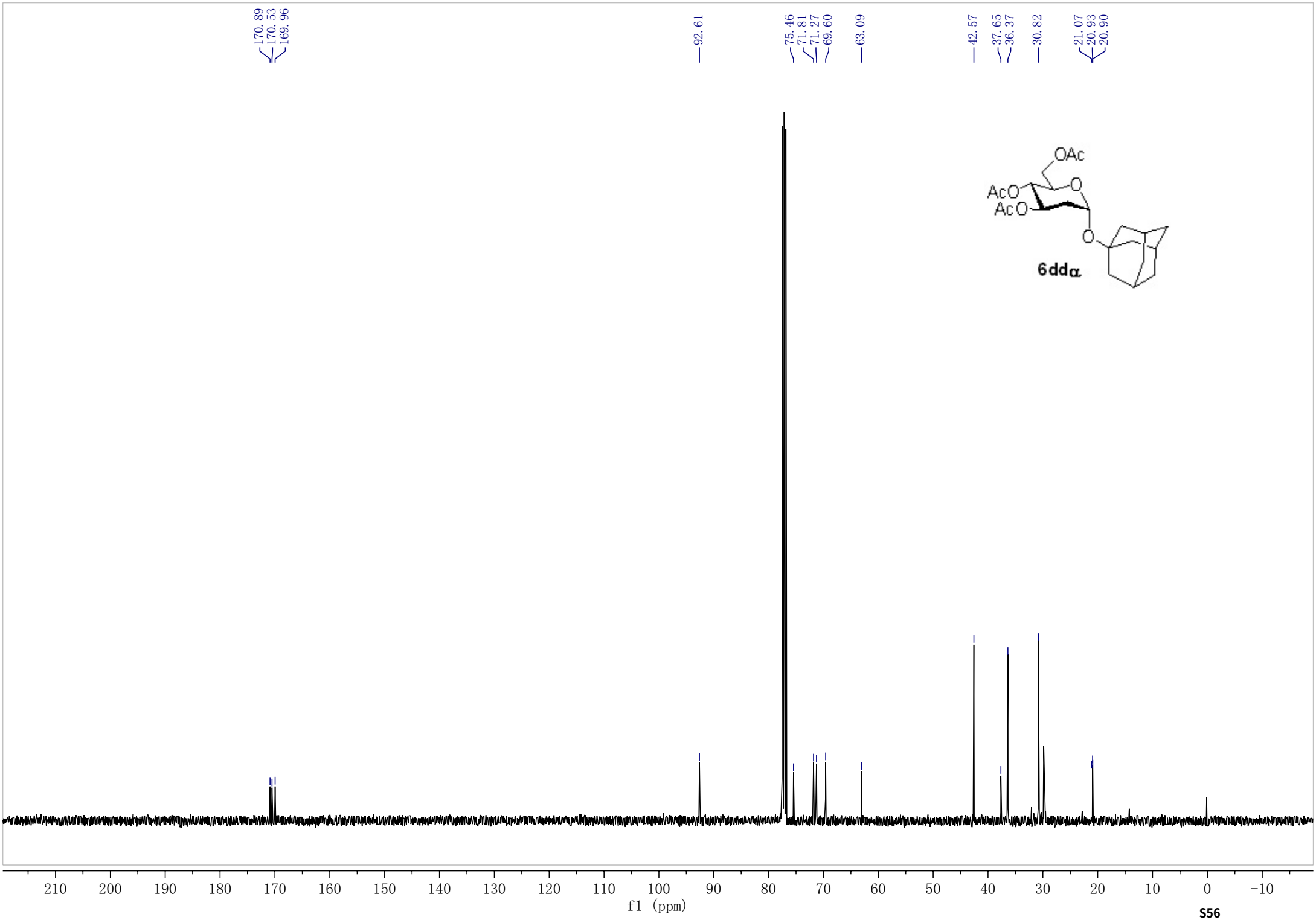

OBn
BnO
BnO
BnO
O
O
6cdα
f1 (ppm)


139.22
138.52
138.48
138.26
128.50
128.47
128.43
128.27
128.10
128.02
127.96
127.87
127.79
127.71
127.59
89.98
82.22
80.25
78.31
75.66
75.22
74.67
73.58
72.98
69.83
68.95
42.60
36.43
30.80
OBn
O
BnO
BnO
BnO
O
6cdα
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OBn
BnO
BnO
BnO
O
O
6cdβ
f1 (ppm)


138.87
138.75
138.58
138.38
128.50
128.48
128.42
128.36
128.09
128.03
127.84
127.71
127.67
127.59
96.40
85.28
82.50
78.39
75.83
75.45
75.05
74.72
73.51
69.69
42.95
36.45
30.86
OBn
BnO
BnO
BnO
O
O
6cdβ
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OAc
AcO
AcO
O
O
6ddα
f1 (ppm)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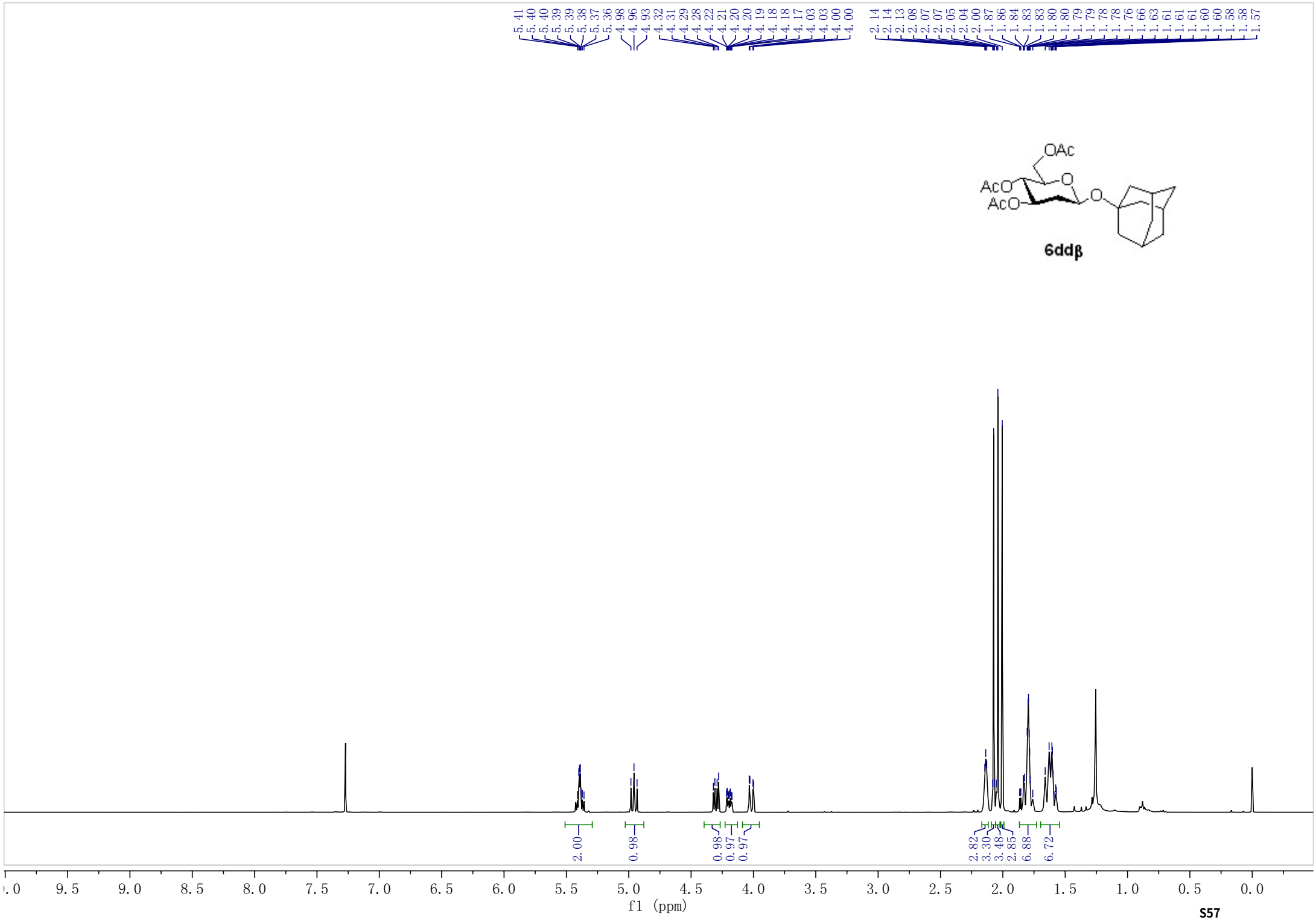
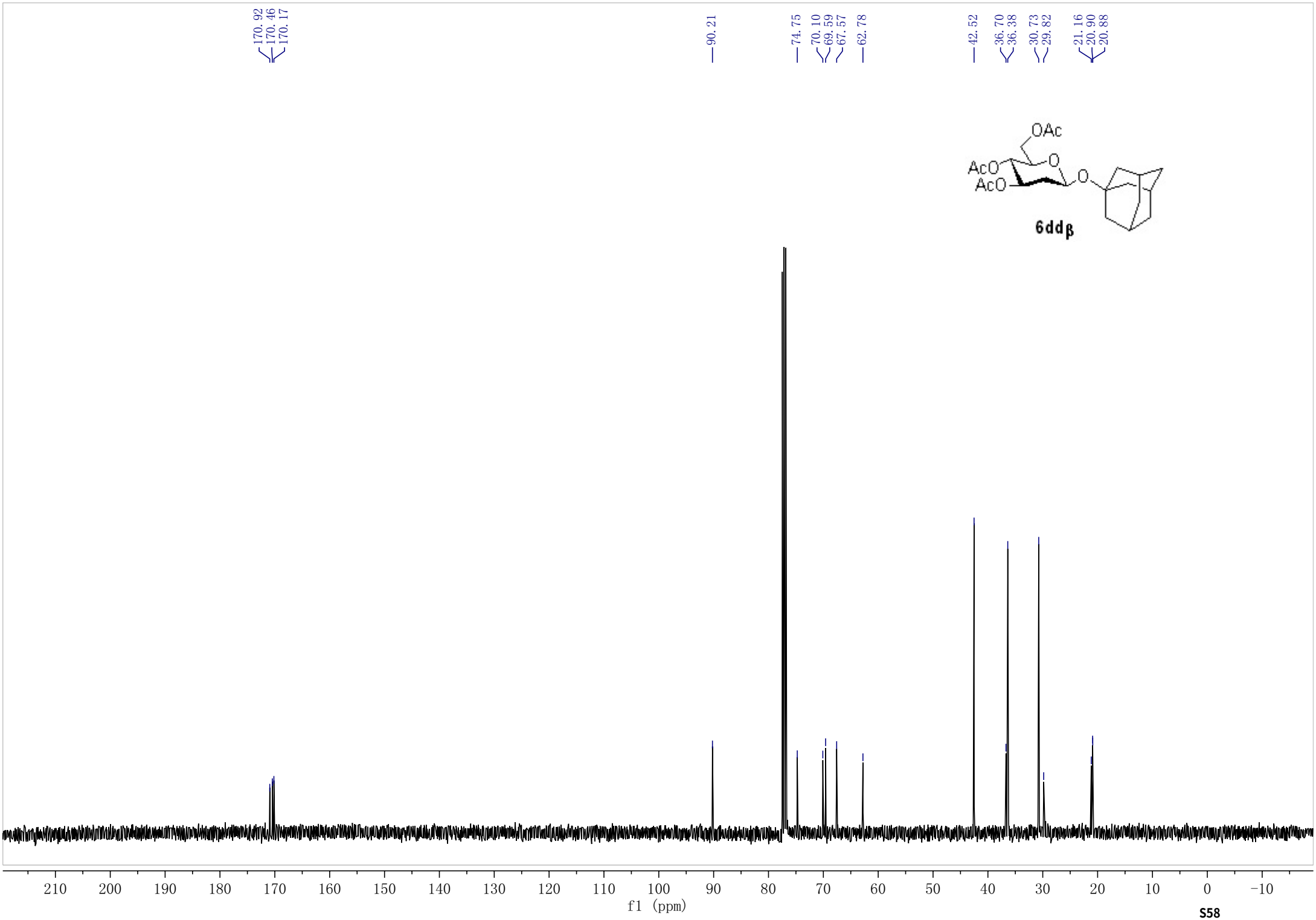
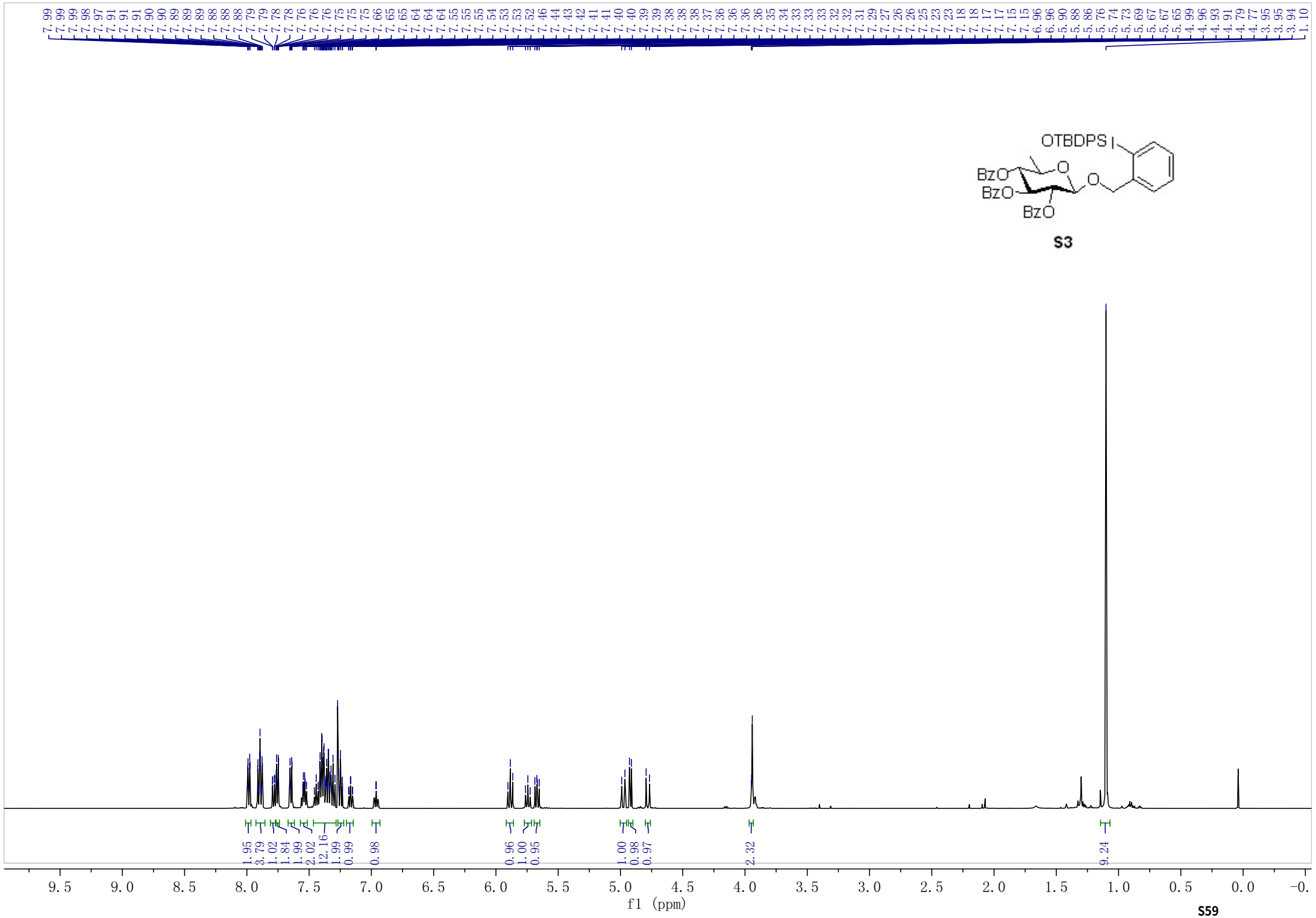
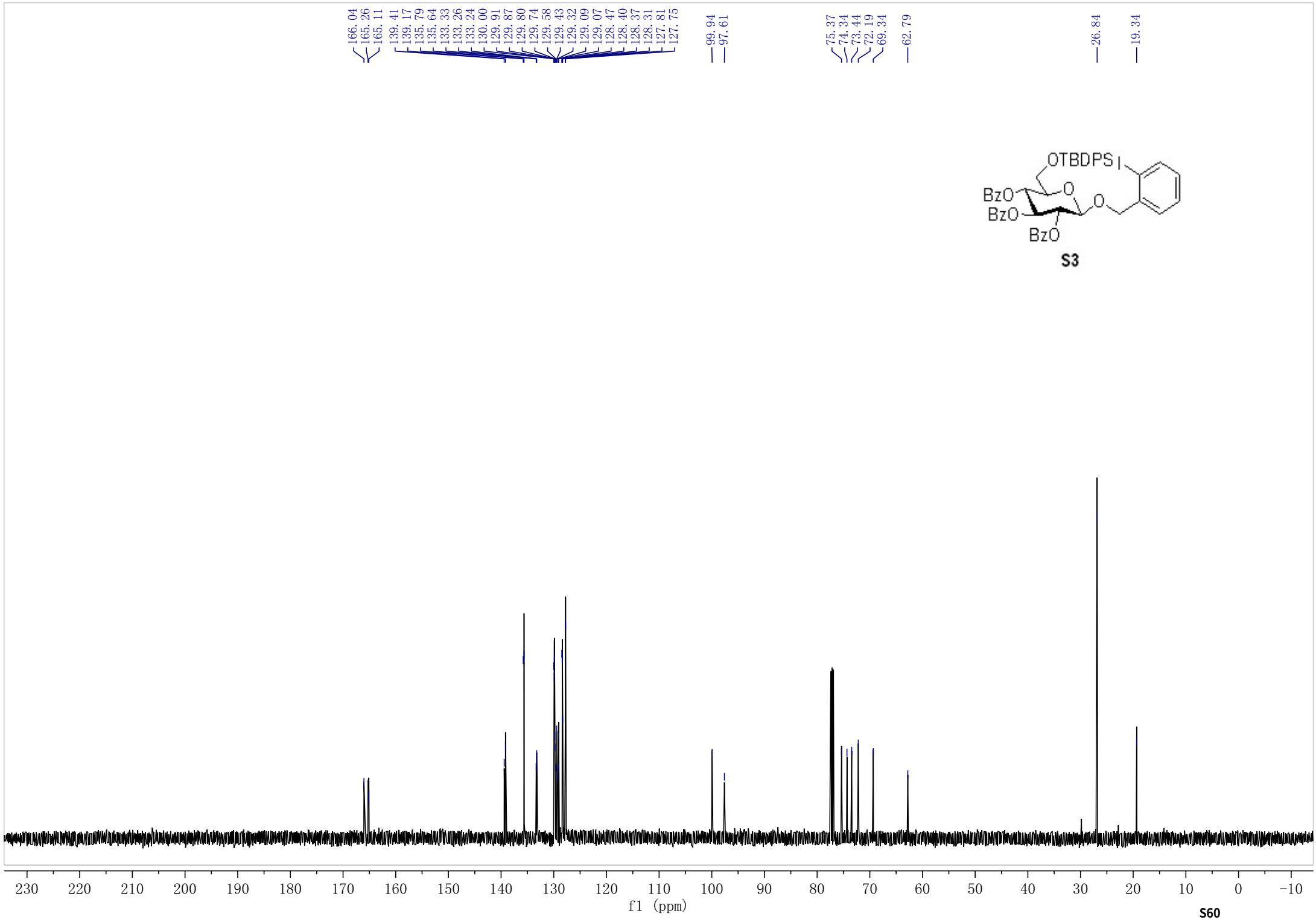
169.96
92.61
75.46
71.81
71.27
69.60
63.09
42.57
37.65
36.37
30.82
21.07
20.93
20.90
OAc
AcO
AcO
O
O
6ddα
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5.41 5.40 5.40 5.39 5.39 5.38 5.37 5.36 4.98 4.96 4.93 4.32 4.31 4.29 4.28 4.22 4.21 4.20 4.20 4.19 4.18 4.18 4.17 4.03 4.03 4.00 4.00
2.14 2.14 2.13 2.08 2.07 2.07 2.05 2.04 2.00 1.87 1.86 1.84 1.83 1.83 1.80 1.80 1.79 1.79 1.78 1.78 1.76 1.66 1.63 1.61 1.61 1.61 1.60 1.60 1.58 1.58 1.57
OAc
AcO
AcO
O
O
6ddβ
2.00
0.98
0.98
0.97
0.97
2.82
3.30
3.48
2.85
6.88
6.72
f1 (ppm)


170.92
170.46
170.17
90.21
74.75
70.10
69.59
67.57
62.78
42.52
36.70
36.38
30.73
29.82
21.16
20.90
20.88
OAc
AcO
AcO
O
O
6ddβ
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


OTBDPS
BzO
BzO
BzO
O
O
S3
f1 (ppm)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165.11
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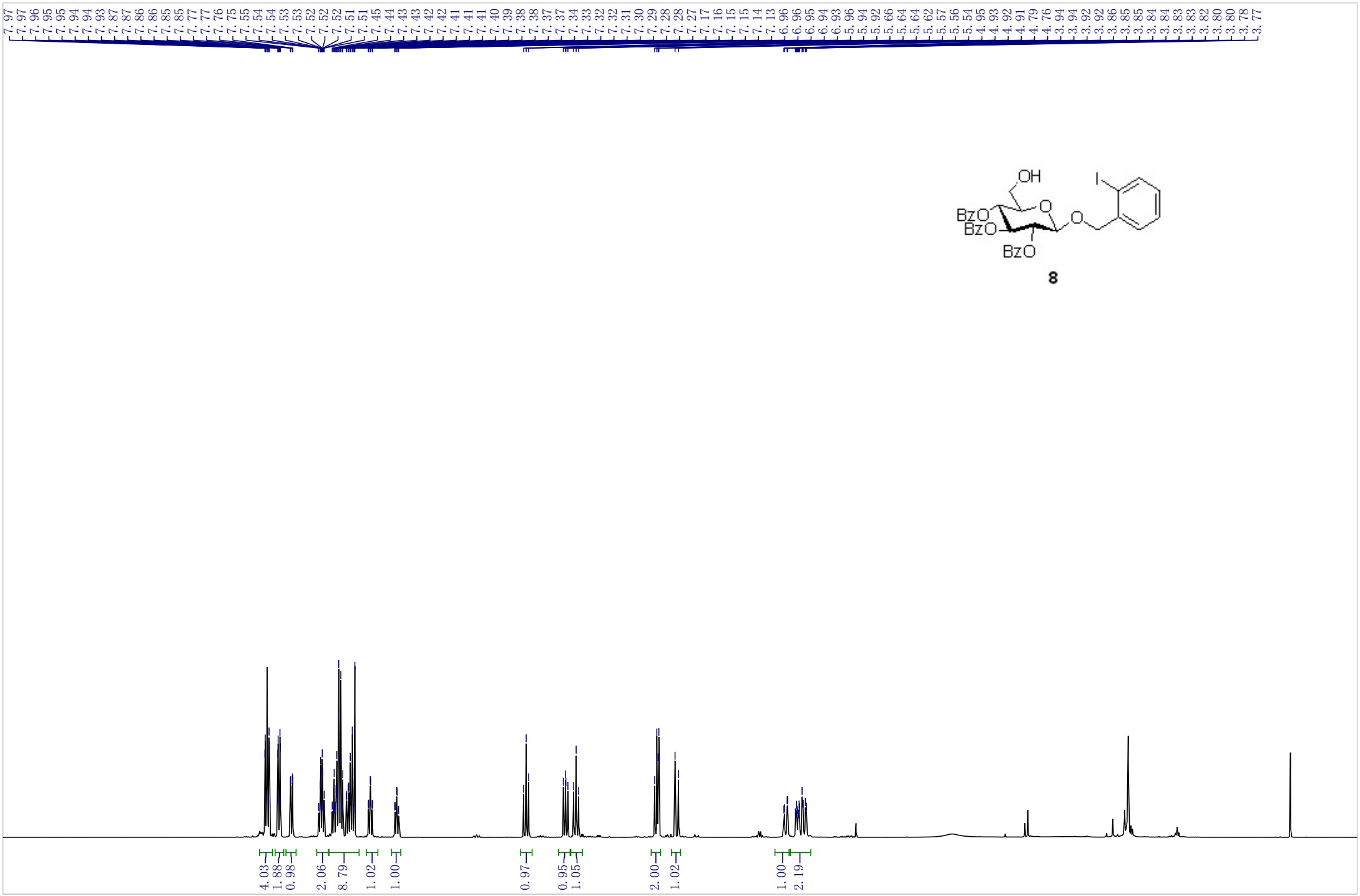
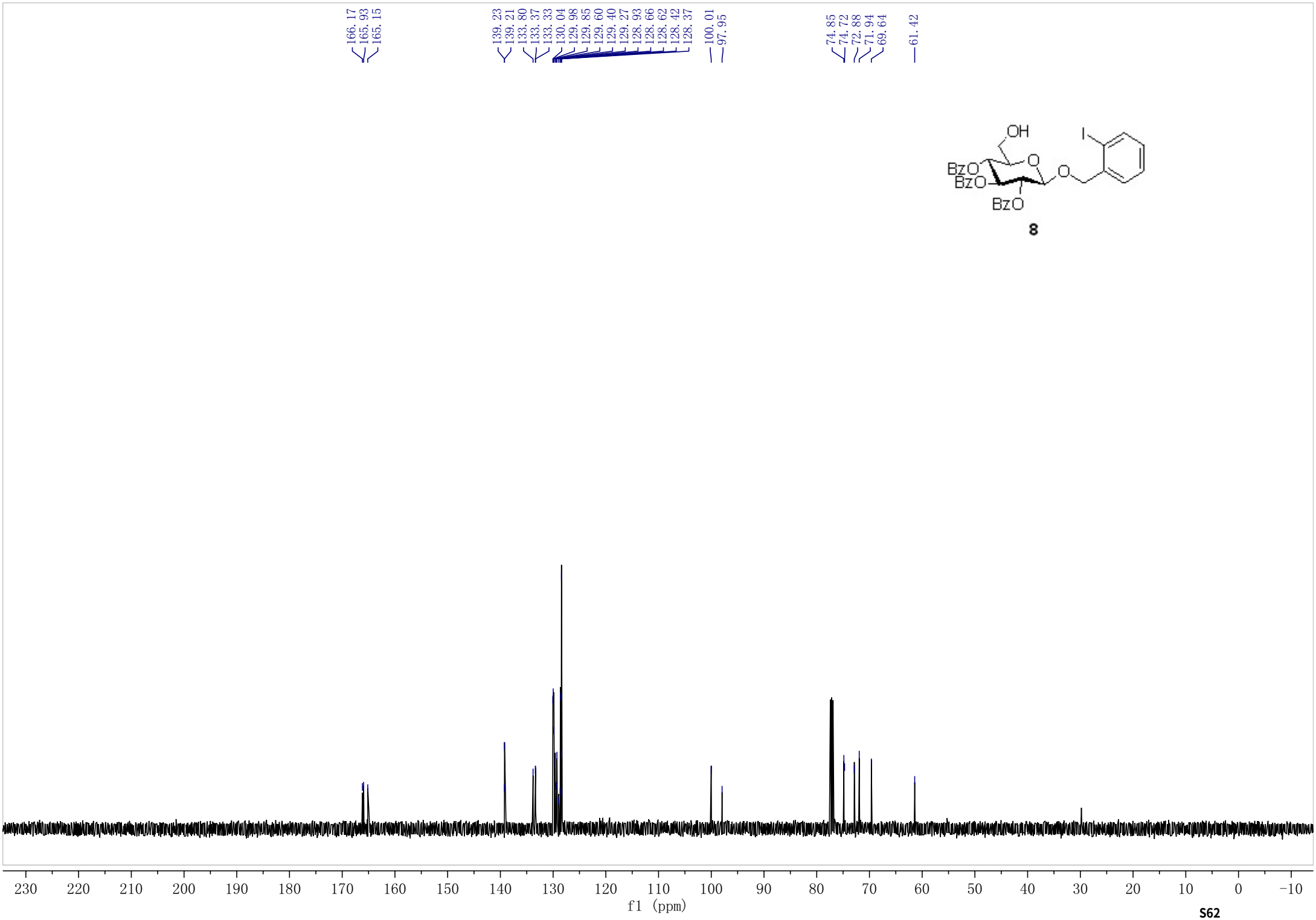
139.17
135.79
135.64
133.33
133.26
133.24
130.00
129.91
129.87
129.80
129.74
129.58
129.43
129.32
129.09
129.07
128.47
128.40
128.37
128.31
127.81
127.75
99.94
97.61
75.37
74.34
73.44
72.19
69.34
62.79
26.84
19.34
OTBDPS
O
BzO
BzO
BzO
O
S3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OH
I
BzO
BzO
BzO
O
O
8
4.03
1.88
0.98
2.06
8.79
1.02
1.00
0.97
0.95
1.05
2.00
1.02
1.00
2.19
f1 (ppm)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139.21
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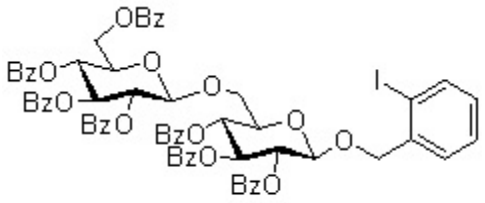
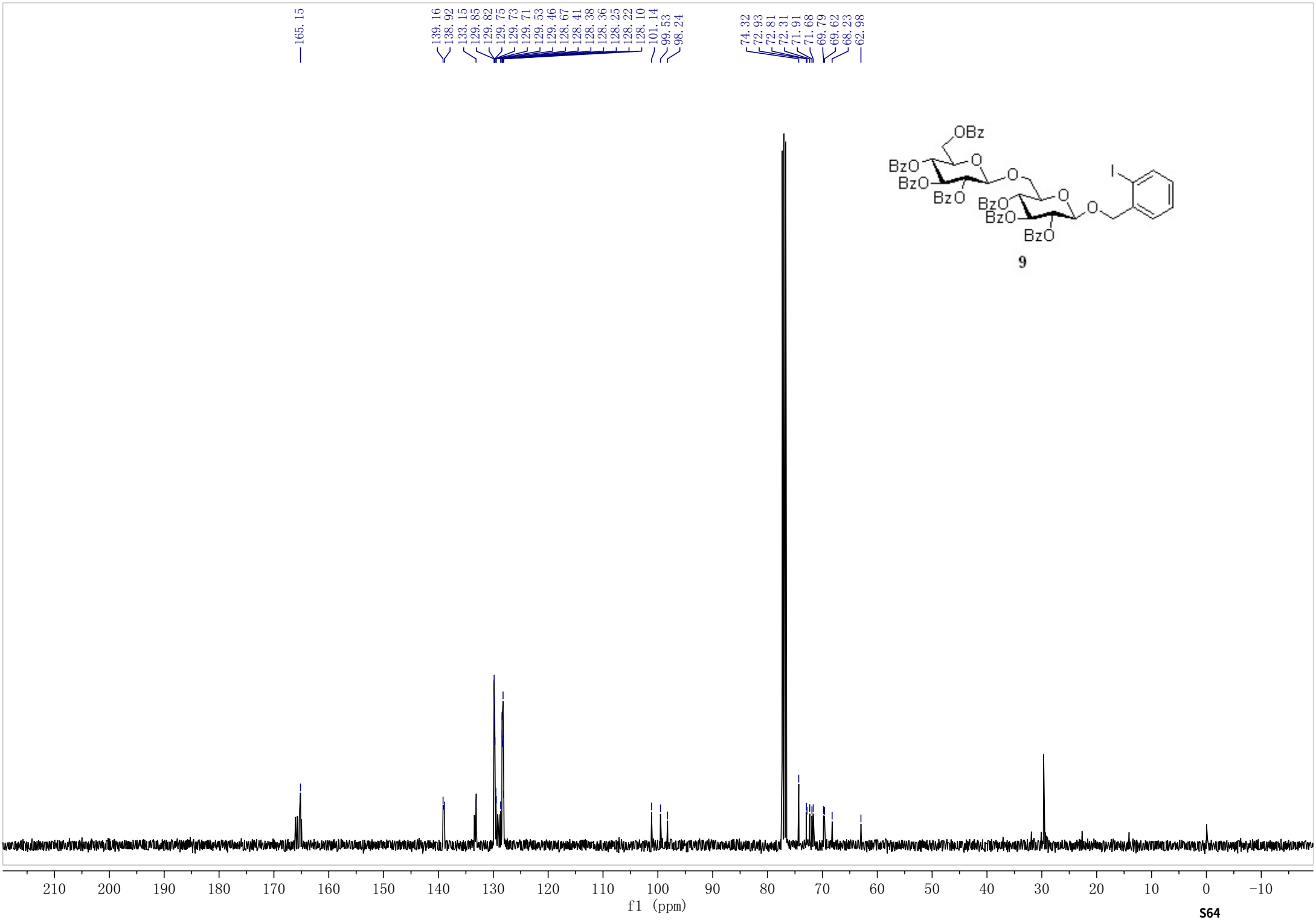
133.33
130.04
129.98
129.85
129.60
129.40
129.27
128.93
128.66
128.62
128.42
128.37
100.01
97.95
74.85
74.72
72.88
71.94
69.64
61.42
OH
O
I
BzO
BzO
BzO
O
8
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



9

f1 (ppm)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133.15
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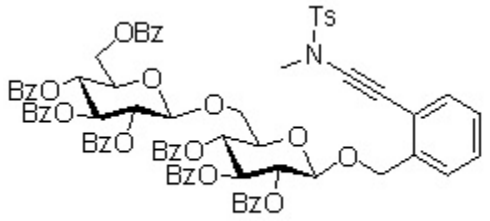
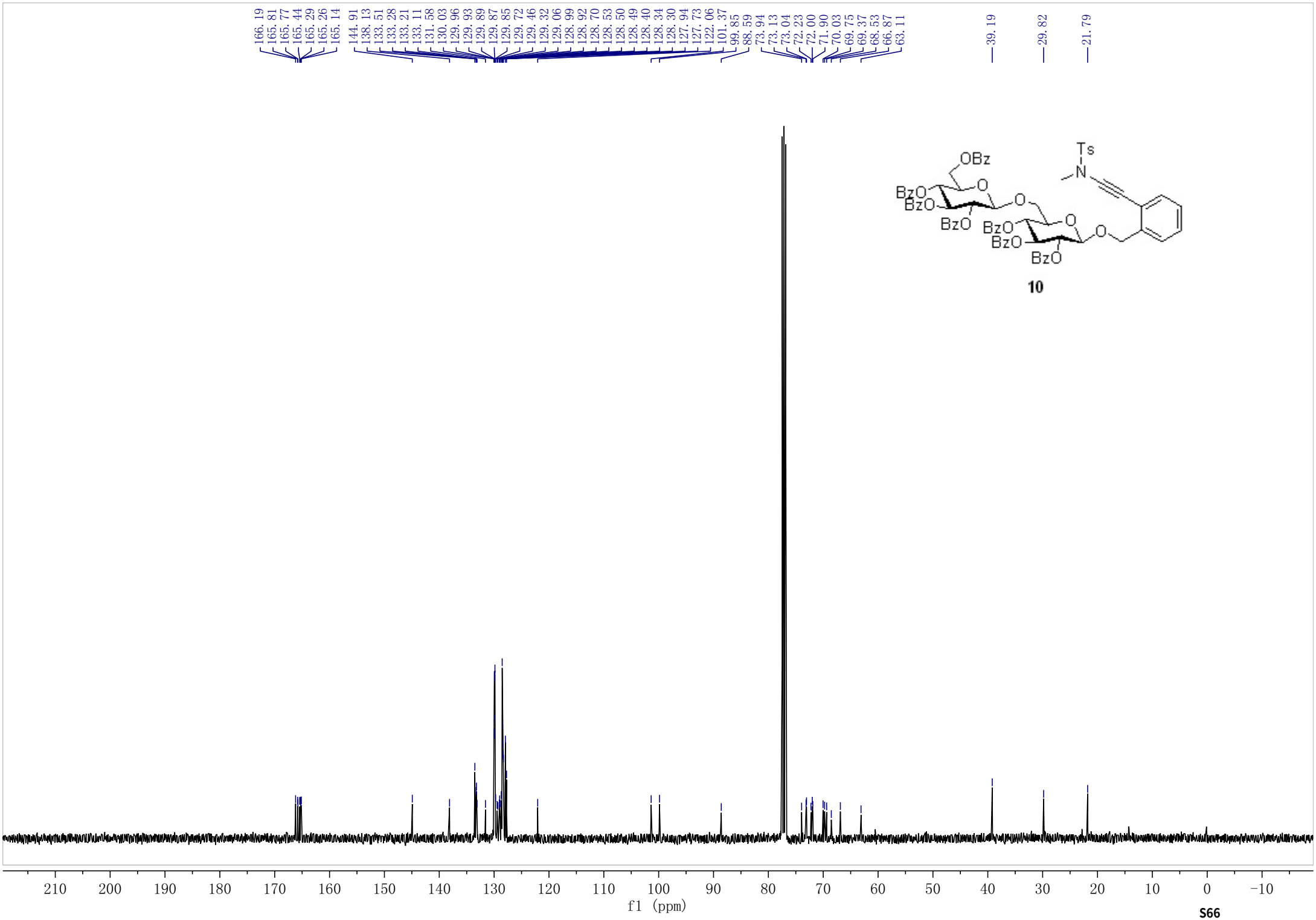
129.82
129.75
129.73
129.71
129.53
129.46
128.67
128.41
128.38
128.36
128.25
128.22
128.10
101.14
99.53
98.24
74.32
72.93
72.81
72.31
71.91
71.68
69.79
69.62
68.23
62.98
OBz
BzO
BzO
BzO
BzO
BzO
BzO
O
O
O
O
I
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



10

f1 (ppm)


166.19
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165.44
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165.26
165.14
144.91
138.13
133.51
133.28
133.21
133.11
131.58
130.03
129.96
129.93
129.89
129.87
129.85
129.72
129.46
129.32
129.06
128.99
128.92
128.70
128.53
128.50
128.49
128.40
128.34
128.30
127.94
127.73
122.06
101.37
99.85
88.59
73.94
73.13
73.04
72.23
72.00
71.90
70.03
69.75
69.37
68.53
66.87
63.11
39.19
29.82
21.79
OBz
BzO
BzO
BzO
BzO
BzO
BzO
O
O
O
O
Ts
N
10
210
200
190
180
170
160
150
140
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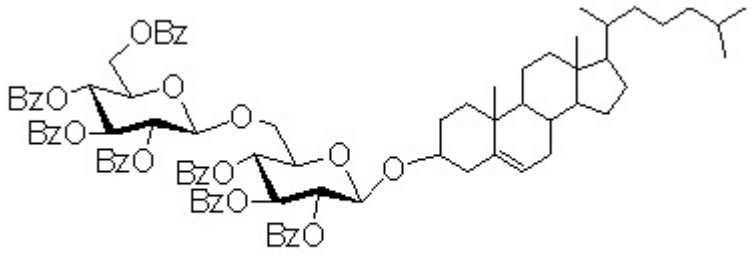
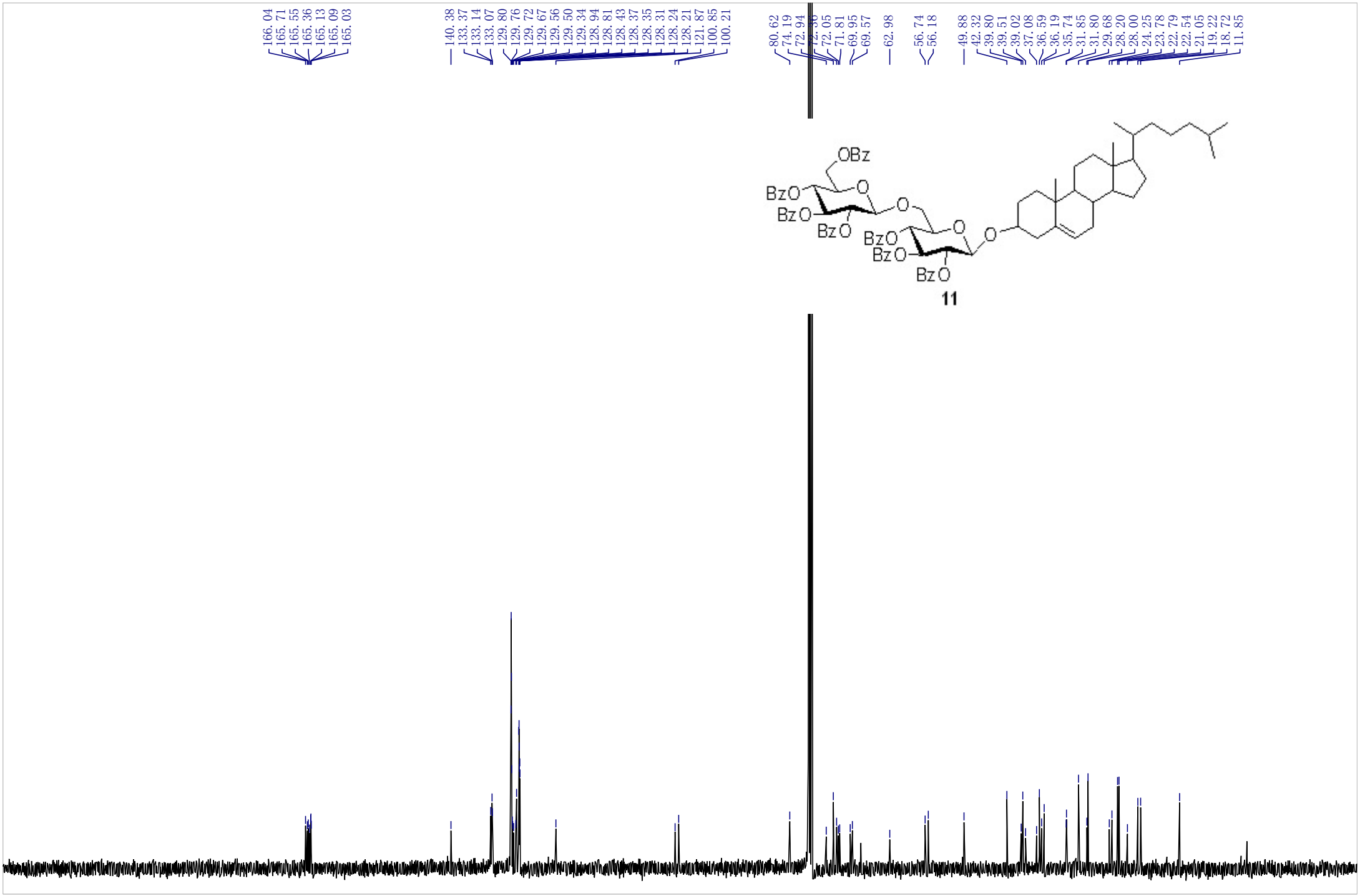
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



11

f1 (ppm)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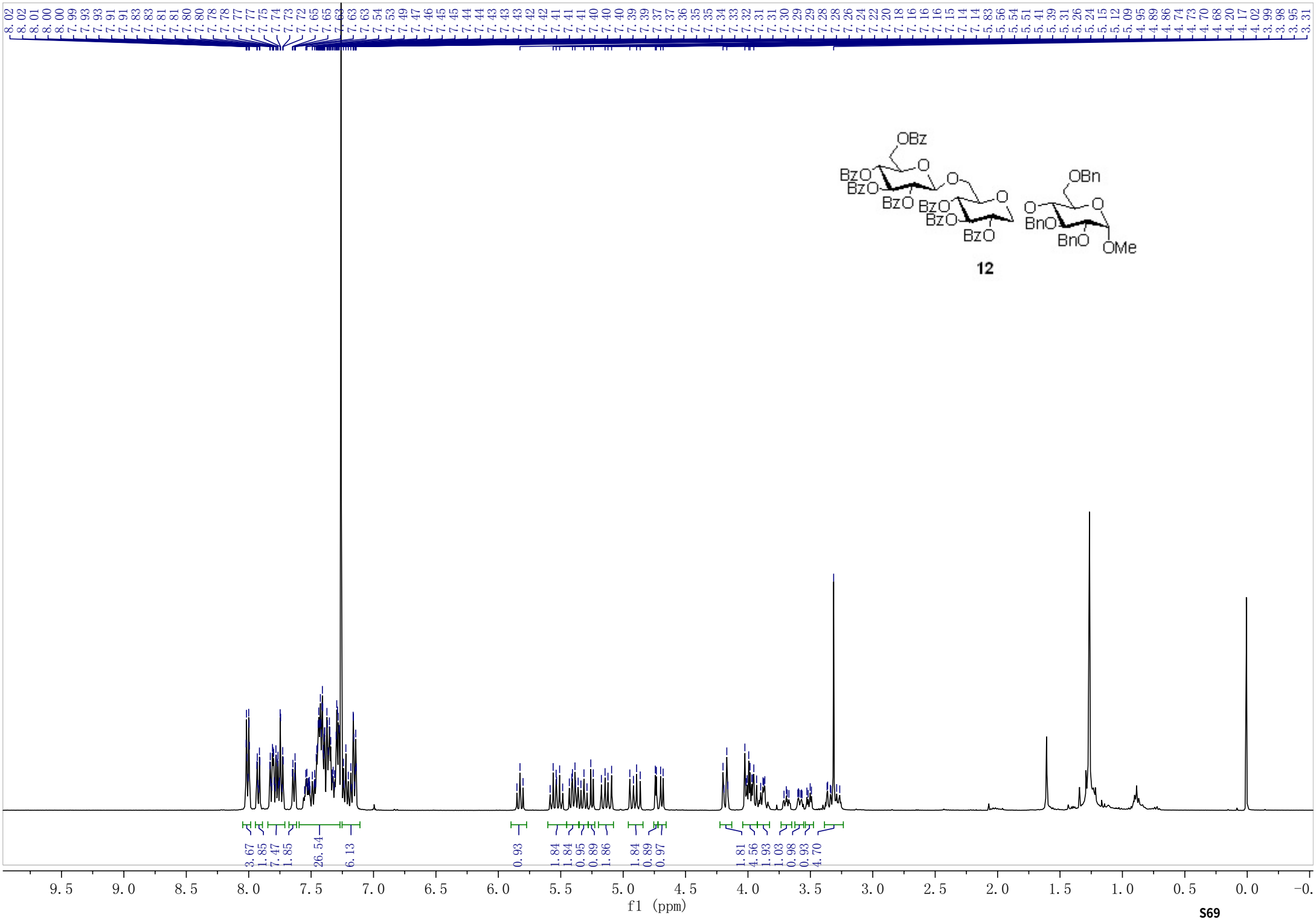
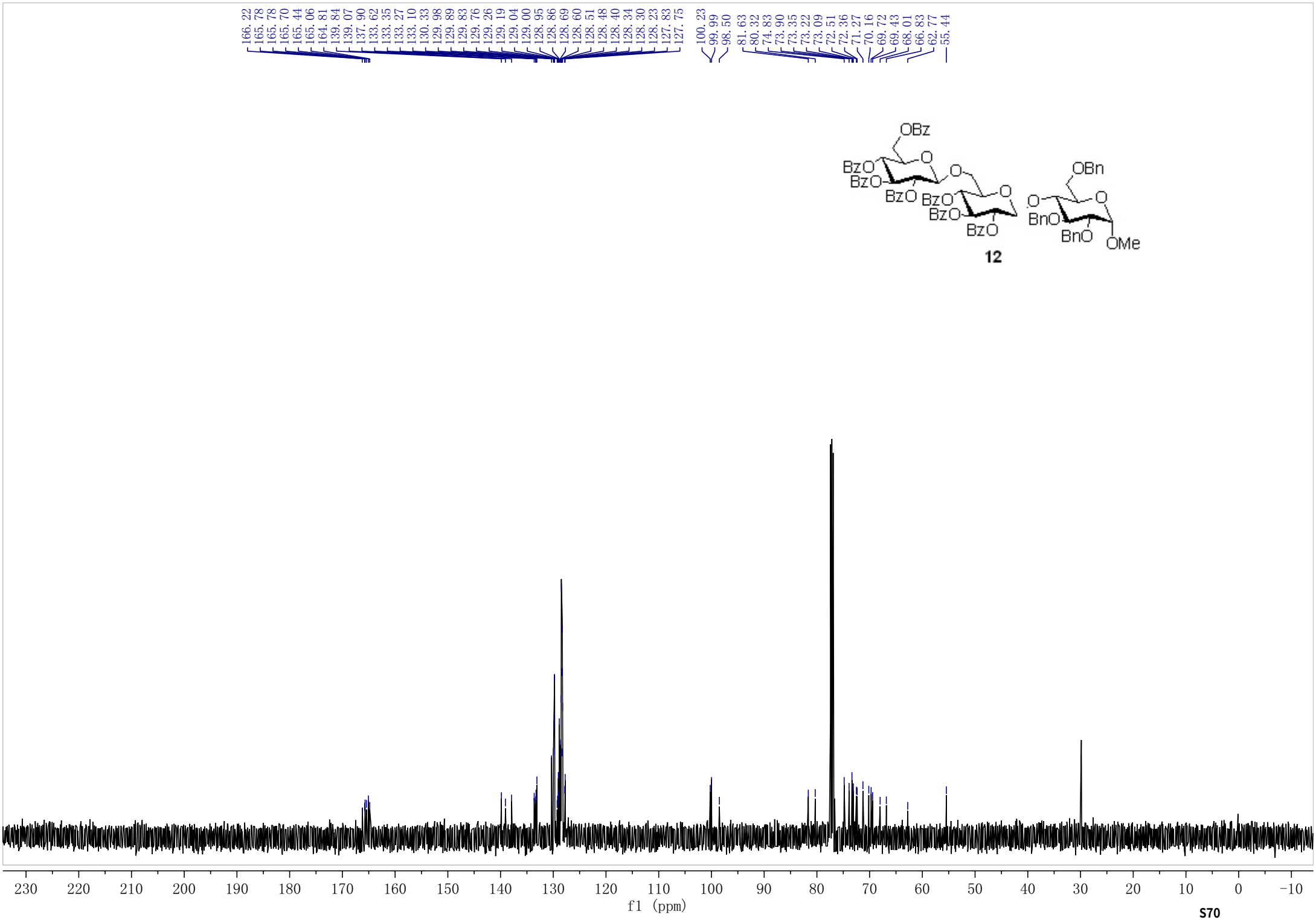
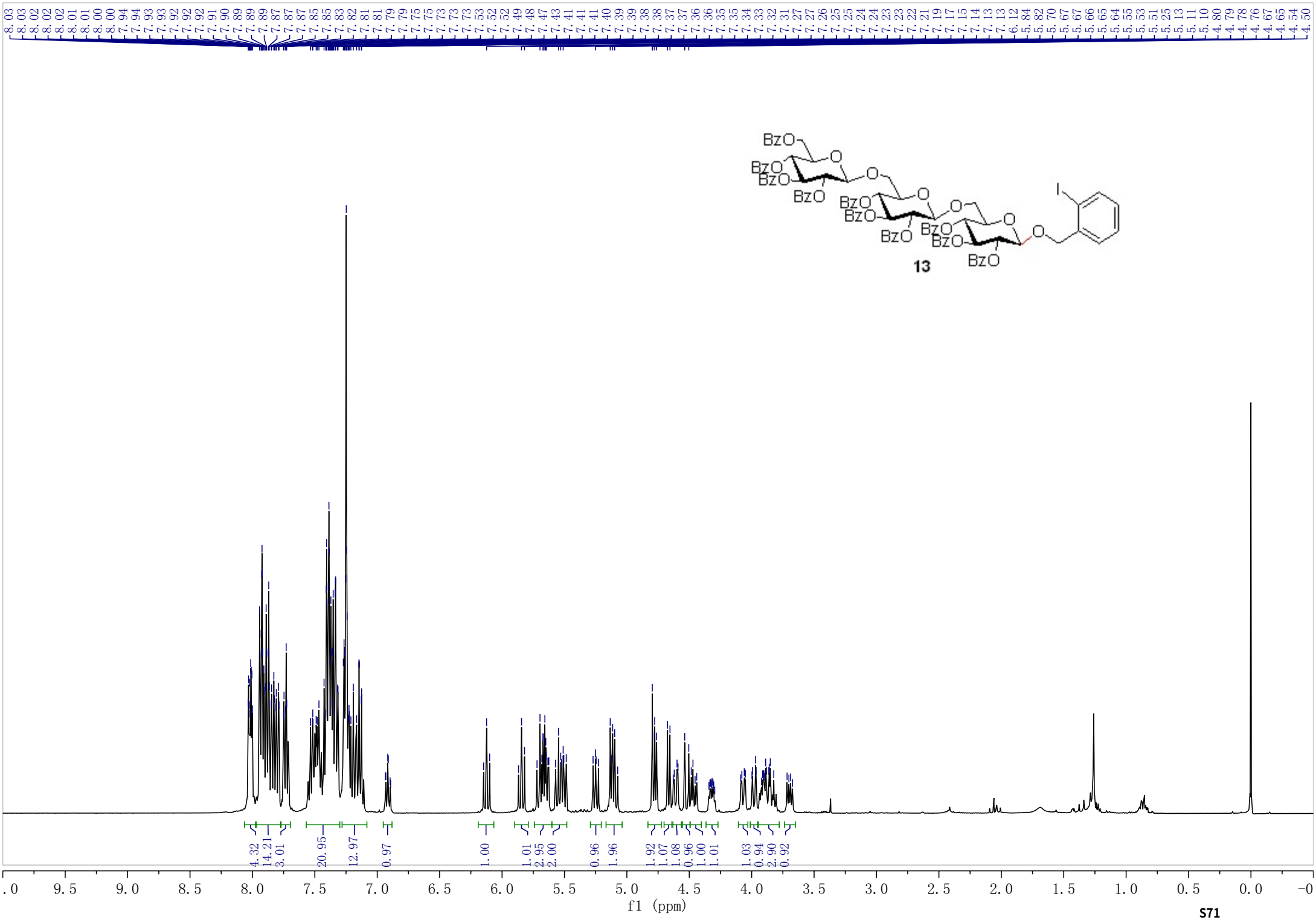
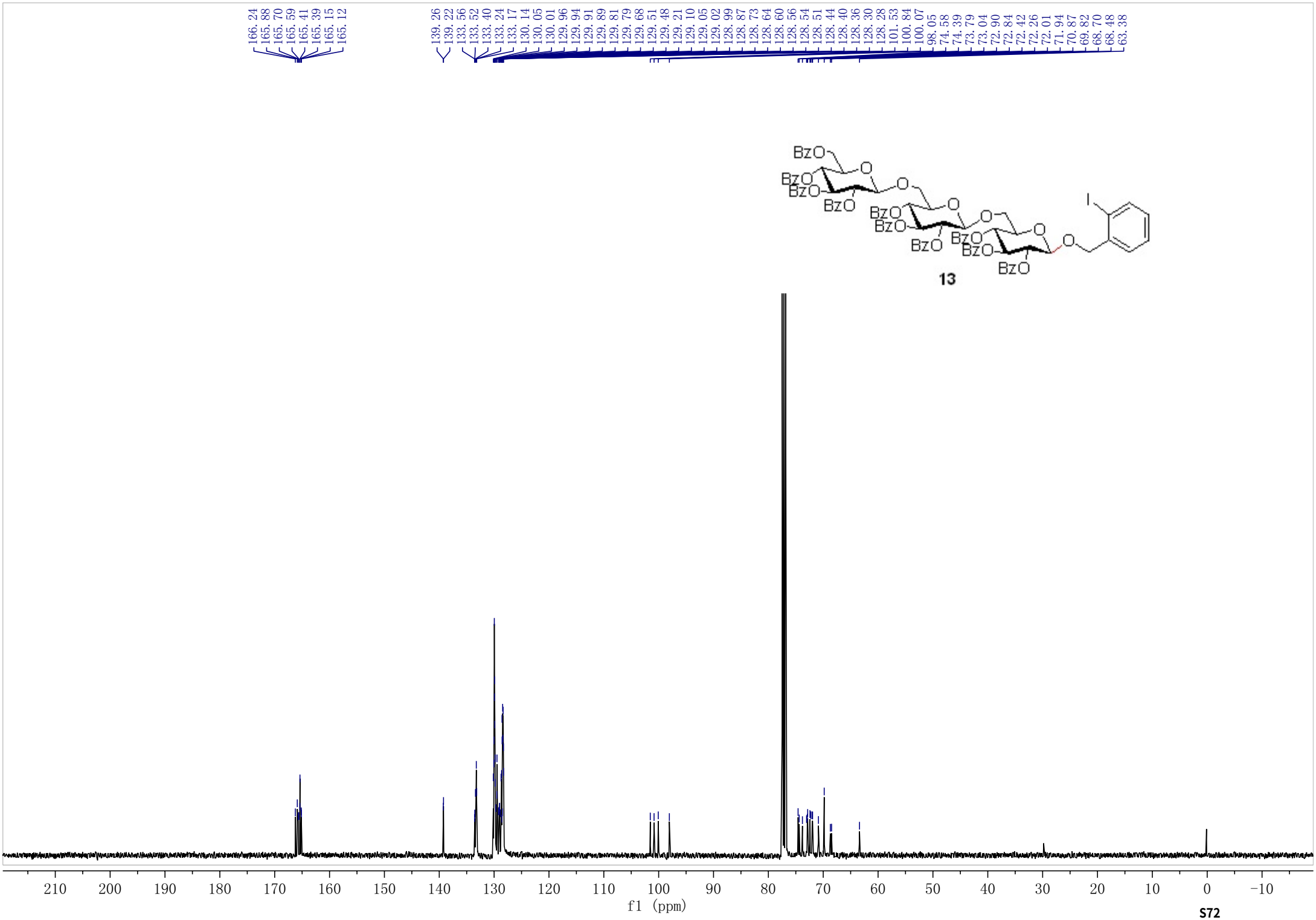
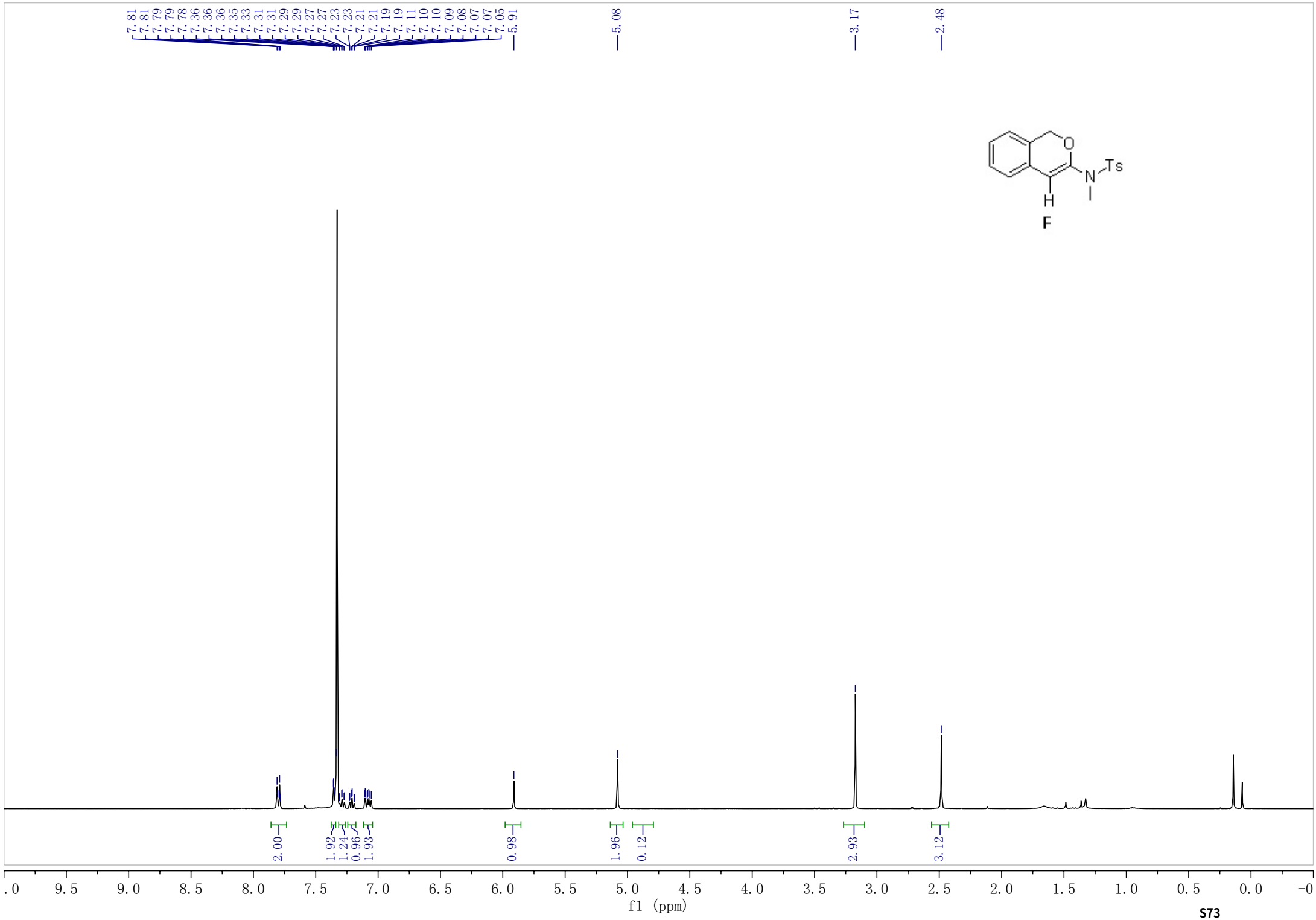
165.71
165.55
165.36
165.13
165.09
165.03
140.38
133.37
133.14
133.07
129.80
129.76
129.72
129.67
129.56
129.50
129.34
128.94
128.81
128.43
128.37
128.35
128.31
128.24
128.21
121.87
100.85
100.21
80.62
74.19
72.94
72.36
72.05
71.81
69.95
69.57
62.98
56.74
56.18
49.88
42.32
39.80
39.51
39.02
37.08
36.59
36.19
35.74
31.85
31.80
29.68
28.20
28.00
24.25
23.78
22.79
22.54
21.05
19.22
18.72
11.85
OBz
BzO
BzO
BzO
BzO
BzO
BzO
O
O
O
O
O
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

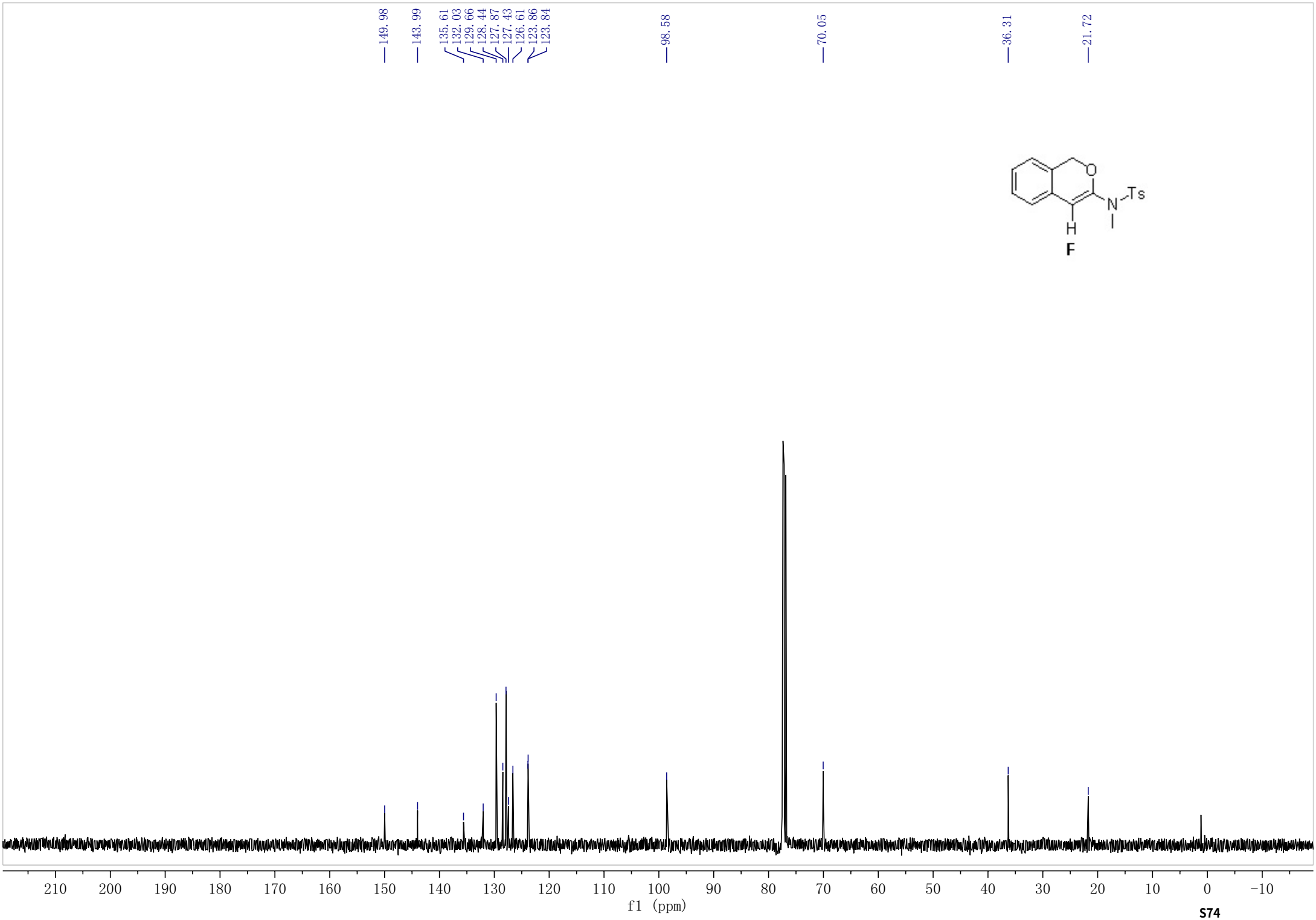

OBz
BzO
BzO
BzO
BzO
BzO
BzO
OBn
BnO
BnO
OMe
12
f1 (ppm)


166.22
165.78
165.78
165.70
165.44
165.06
164.81
139.84
139.07
137.90
133.62
133.35
133.27
133.10
130.33
129.98
129.89
129.83
129.76
129.26
129.19
129.04
129.00
128.95
128.86
128.69
128.60
128.51
128.48
128.40
128.34
128.30
128.23
127.83
127.75
100.23
99.99
98.50
81.63
80.32
74.83
73.90
73.35
73.22
73.09
72.51
72.36
71.27
70.16
69.72
69.43
68.01
66.83
62.77
55.44
OBz
BzO
BzO
BzO
BzO
BzO
BzO
OBn
BnO
BnO
OMe
12
f1 (ppm)


BzO
BzO
BzO
BzO
O
O
O
O
O
O
BzO
BzO
BzO
BzO
BzO
BzO
BzO
I
13
f1 (ppm)


166.24
165.88
165.70
165.59
165.41
165.39
165.15
165.12
139.26
139.22
133.56
133.52
133.40
133.24
133.17
130.14
130.05
130.01
129.96
129.94
129.91
129.89
129.81
129.79
129.68
129.51
129.48
129.21
129.10
129.05
129.02
128.99
128.87
128.73
128.64
128.60
128.56
128.54
128.51
128.44
128.40
128.36
128.30
128.28
101.53
100.84
100.07
98.05
74.58
74.39
73.79
73.04
72.90
72.84
72.42
72.26
72.01
71.94
70.87
69.82
68.70
68.48
63.38
BzO
I
13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.81
7.81
7.79
7.79
7.78
7.36
7.36
7.35
7.33
7.31
7.31
7.29
7.29
7.27
7.27
7.23
7.23
7.21
7.21
7.19
7.19
7.11
7.10
7.10
7.09
7.08
7.07
7.07
7.05
5.91
5.08
3.17
2.48
O
N
Ts
H
F
2.00
1.92
1.24
0.96
1.93
0.98
1.96
0.12
2.93
3.12
f1 (ppm)


149.98
143.99
135.61
132.03
129.66
128.44
127.87
127.43
126.61
123.86
123.84
98.58
70.05
36.31
21.72
O
N
Ts
H
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)