Supplementary information

Dimerization of aldosuloses and aldonolactones into branched higher carbon sugars

Yachen Zhao,[a] Shengyang Wang,[b] and Biao Yu[a,c]*

[a]*State Key Laboratory of Bioorganic and Natural Products Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. E-mail: byu@sioc.ac.cn (Biao Yu)*

[b]*Innovation Research Institute of Traditional Chinese Medicine, Shanghai University of Traditional Chinese Medicine, 1200 Cai Lun Road, Shanghai 201203, China*

[c]*School of Chemistry and Material Sciences, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, 1 Sub-lane Xiangshan, Hangzhou 310024, China*

General remarks

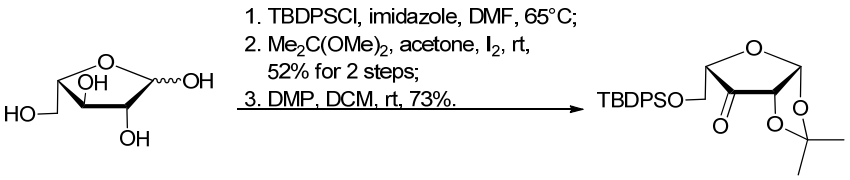
All reactions were carried out under argon with anhydrous solvents in flame-dried glassware, unless otherwise noted. Commercial reagents were used without further purification unless specialized. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compound spots were visualized by UV light (254 nm) or by heating with a solution with 10% H_2SO_4 in ethanol. Flash column chromatography was performed on SiliaFlash® P60 silica gel. ^{1}H, ^{13}C, COSY, HSQC, HMBC, and NOESY NMR spectra were recorded with Brucker AMX 400, Aglient 500/54, and Aglient 600 spectrometers. ^{1}H and ^{13}C NMR signals were calibrated to the residual proton and carbon resonance of the solvent: $CDCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm), $(CD_3)_2CO$ (^{1}H NMR δ = 2.05 ppm, ^{13}C NMR δ = 29.84 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HSQC experiments. Splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and brs (broad singlet) for ^{1}H NMR data. ESI-MS and MALDI-MS were recorded with IonSpec 4.7 Tesla FTMS or APEXIII 7.0 TESLA FTMS. Optical rotations were measured using a JASCO P-1030 polarimeter or Anton Paar MCP 5500, and the wavelength was 589 nm (sodium D-line). Single crystal X-ray

diffraction data were collected on Bruker D8 VENTURE.

Preparation of aldosulose derivatives 1-6 and aldonolactone derivatives 7-11

Compounds **S1**-**S4** and **11** are commercially available. Compounds **1**-**8**, **10** and **11** are known compounds; the ^{1}H NMR spectra of the synthetic compounds were identical to those reported in the literatures.

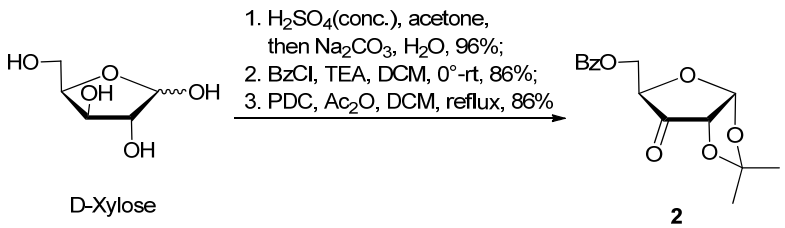
5-*O*-*tert*-Butyldiphenylsilyl-1,2-*O*-isopropylidene-β-L-threo-pentofuranos-3-ulose (1)



L-Arabinose **1**

Compound **1** was prepared according to the literature procedure:[S1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.66 (m, 4H, TBDPS), 7.43–7.36 (m, 6H, TBDPS), 6.02 (d, $J_{1,2}$ = 4.3 Hz, 1H, H-1), 4.38 (d, $J_{2,1}$ = 4.3 Hz, 1H, H-2), 4.28 (dd, $J_{4,5}$ = 6.2, 4.2 Hz, 1H, H-4), 3.93 (m, 2H, H-5), 1.37 (s, 3H, isopropylidene), 1.35 (s, 3H, isopropylidene), 1.06 (s, 9H, TBDPS).

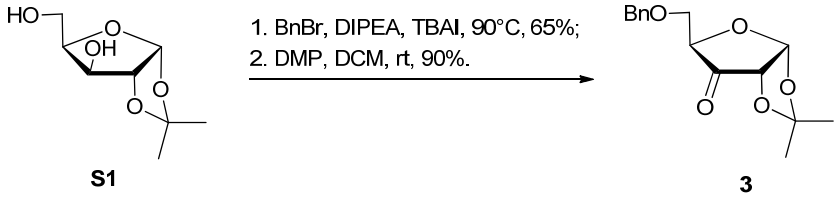
5-*O*-Benzoyl-1,2-*O*-isopropylidene-α-D-erythro-pentofuranos-3-ulose (2)



D-Xylose **2**

Compound **2** was prepared according to the literature procedure:[S2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–7.86 (m, 2H, Bz), 7.58 (t, J = 7.4 Hz, 1H, Bz), 7.45 (t, J = 7.8 Hz, 2H, Bz), 6.14 (d, $J_{1,2}$ = 4.4 Hz, 1H, H-1), 4.71 (m, 2H, H-2 and H-4), 4.51–4.41 (m, 2H, H-5), 1.52 (s, 3H, isopropylidene), 1.44 (s, 3H, isopropylidene).

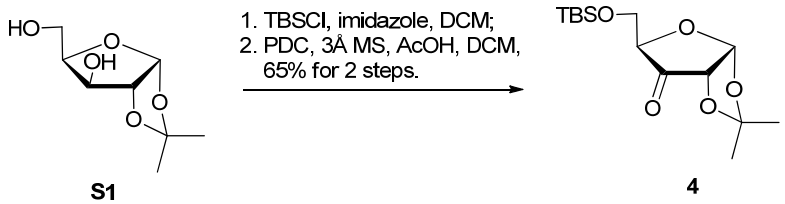
5-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-erythro-pentofuranos-3-ulose (3)



S1 3

Compound **3** was prepared according to the literature procedure:[S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 5H, Bn), 6.13 (d, $J_{1,2}$ = 4.5 Hz, 1H, H-1), 4.56–4.47 (m, 2H, Bn), 4.45 (s, 1H, H-4), 4.35 (d, $J_{2,1}$ = 4.4 Hz, 1H, H-2), 3.73 (d, $J_{5,5}$ = 2.4 Hz, 2H, H-5), 1.46 (s, 3H, isopropylidene), 1.43 (s, 3H, isopropylidene).

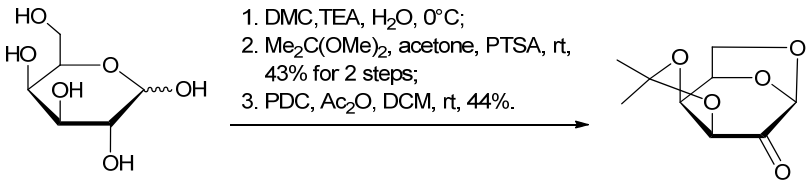
5-*O*-*tert*-Butyldimethylsilyl-1,2-*O*-isopropylidene-α-D-erythro-pentofuranos-3-ulose 4



S1 4

Compound **4** was prepared according to the literature procedure:[S4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (d, $J_{1,2}$ = 4.5 Hz, 1H, H-1), 4.36 (m, 1H, H-4), 4.27 (dd, J = 4.5, 0.9 Hz, 1H, H-2), 3.88 (m, 1H, H-5a), 3.81 (m, 1H, H-5b), 1.45 (s, 3H, isopropylidene), 1.44 (s, 3H, isopropylidene), 0.86 (s, 9H, TBS), 0.05 (s, 3H, TBS), 0.03 (s, 3H, TBS).

1,6-Anhydro-3,4-*O*-isopropylidene-β-D-lyxo-hexopyranos-2-ulose (5)

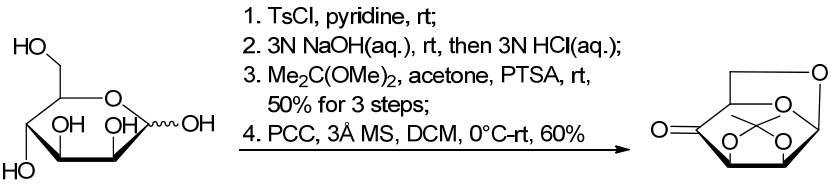


D-Galactose 5

Compound **5** was prepared according to the literature procedure:[S5] $[\alpha]^{25}_D$ = -69.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (s, 1H, H-1), 4.77 (m, 2H, H-3 and H-5), 4.43 (d, $J_{4,5}$ = 7.7 Hz, 1H, H-4), 4.24 (d, $J_{5,6a}$ = 7.8 Hz, 1H, H-6a), 3.79–3.71 (m, 1H,

H-6b), 1.51 (s, 3H, isopropylidene), 1.36 (s, 3H, isopropylidene); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.9 (C-2), 112.0, 98.3 (C-1), 74.1, 73.3, 71.8, 62.9, 25.7, 24.2; HRMS (ESI) *m/z* calcd for $C_{10}H_{16}O_6Na$ $[M+MeOH+Na]^+$ 255.0839, found 255.0842.

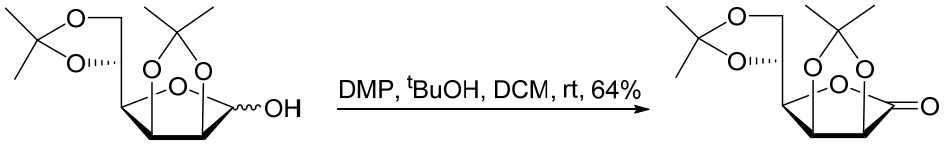
1,6-Anhydro-2,3-*O*-isopropylidene-β-D-lyxo-hexopyranos-4-ulose (6)



D-Mannose **6**

Compound **6** was prepared according to the literature procedure:[S6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63 (s, 1H, H-1), 4.59 (d, $J_{5,6b}$ = 4.8 Hz, 1H, H-5), 4.53–4.41 (m, 2H, H-2 and H-3), 4.03 (d, $J_{5,6a}$ = 7.7 Hz, 1H, H-6a), 3.93–3.85 (m, 1H, H-6b), 1.50 (s, 3H, isopropylidene), 1.34 (s, 3H, isopropylidene).

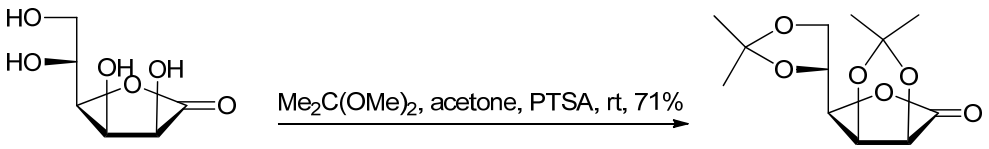
2,3:5,6-Di-*O*-isopropylidene-D-mannono-1,4-lactone (7)



S2 **7**

Compound **7** was prepared according to the literature procedure:[S7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (dd, $J_{2,3/3,4}$ = 5.2, 3.4 Hz, 1H, H-3), 4.83 (d, $J_{2,3}$ = 5.3 Hz, 1H, H-2), 4.44 (ddd, $J_{4,5/5,6a/5,6b}$ = 8.1, 6.0, 3.9 Hz, 1H, H-5), 4.37 (dd, $J_{4,5/3,4}$ = 8.1, 3.4 Hz, 1H, H-4), 4.15 (dd, $J_{5,6/6a,6b}$ = 9.2, 6.0 Hz, 1H, H-6a), 4.08 (dd, $J_{5,6/6a,6b}$ = 9.2, 3.9 Hz, 1H, H-6b), 1.49 (s, 3H, isopropylidene), 1.47 (s, 3H, isopropylidene), 1.43 (s, 3H, isopropylidene), 1.40 (s, 3H, isopropylidene).

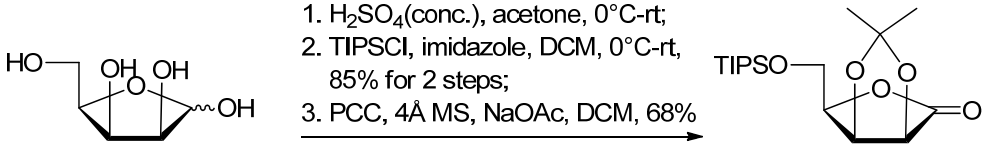
2,3:5,6-Di-*O*-isopropylidene-L-gulono-1,4-lactone (8)



S3 **8**

Compound **8** was prepared according to the literature procedure:[S8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (d, $J_{2,3}$ = 5.6 Hz, 1H, H-2), 4.74 (dd, $J_{2,3/3,4}$ = 5.6, 3.4 Hz, 1H, H-3), 4.42 (m, 2H, H-6a and H-6b), 4.21 (m, 1H, H-4), 3.84–3.79 (m, 1H, H-5), 1.46 (m, 6H, isopropylidene), 1.38 (s, 3H, isopropylidene), 1.37 (s, 3H, isopropylidene).

2,3-*O*-Isopropylidene-5-*O*-triisopropylsilyl-D-lyxono-1,4-lactone (9)



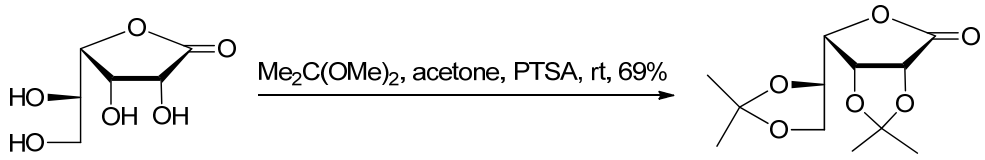
D-Lyxose **9**

To a stirred suspension of D-lyxose (5.052 g, 33.67 mmol) in anhydrous acetone (168 mL, 0.2 M), was added dropwise conc. H_2SO_4 (0.18 mL, 3.36 mmol) at 0 °C. After stirring at 0 °C for 10 min, the mixture was stirred at RT overnight until a clear solution was achieved. The mixture was neutralized with solid Na_2CO_3 (1.414 g, 13.34 mmol) at 0 °C. The solid was filtered through a short pad of Celite, and the Celite pad was washed with ethyl acetate. The filtrate was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to give a colourless syrup.

To a stirred solution of the above syrup and imidazole (4.584 g, 67.34 mmol) in anhydrous CH_2Cl_2 (224 mL, 0.15 M), was added chlorotriisopropylsilane (8.07 mL, 37.71 mmol) at 0 °C. After 10 minutes, the mixture was stirred for additional 1.5 h at RT. The mixture was carefully quenched with dry MeOH (2.2 mL) to consume the remaining chlorotriisopropylsilane, and was then concentrated in vacuo. The resulting residue was dissolved in CH_2Cl_2 and then successively washed with 1N cold aqueous HCl, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting brown syrup was purified by flash column chromatography on silica (petroleum ether/EtOAc, 10:1) to give the corresponding 5-*O*-silyl ether (9.86 g, 85% for 2 steps) as a white solid.

To a stirred solution of the above silyl ether (3.866 g, 11.16 mmol) and 4Å MS (1.208 g) in anhydrous CH_2Cl_2 (75 mL), were added sodium acetate (5.489 g, 66.91 mmol) and pyridinium chlorochromate (9.617 g, 44.62 mmol) at RT. The mixture was stirred for 1 day at RT. The solid was filtered out through a short pad of Celite, and the Celite pad was washed with petroleum ether/ethyl acetate (1:1). The resulting brown syrup was purified by flash column chromatography on silica (petroleum ether/EtOAc, 15:1) to give lactone **9** (2.625 g, 68%) as a white solid:[S9] $[\alpha]^{25}_D$ = 34.1 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.84–4.80 (m, 2H, H-2 and H-3), 4.54 (m, 1H, H-4), 4.11– 4.00 (m, 2H, H-5a and H-5b), 1.46 (s, 3H, isopropylidene), 1.39 (s, 3H, isopropylidene), 1.17–1.05 (m, 21H, TIPS); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 114.2, 79.6, 76.2, 75.9, 61.3, 27.0, 26.0, 18.0, 12.1; HRMS (ESI) *m/z* calcd for $C_{17}H_{33}O_5Si$ $[M+H]^+$ 345.2092, found 345.2096.

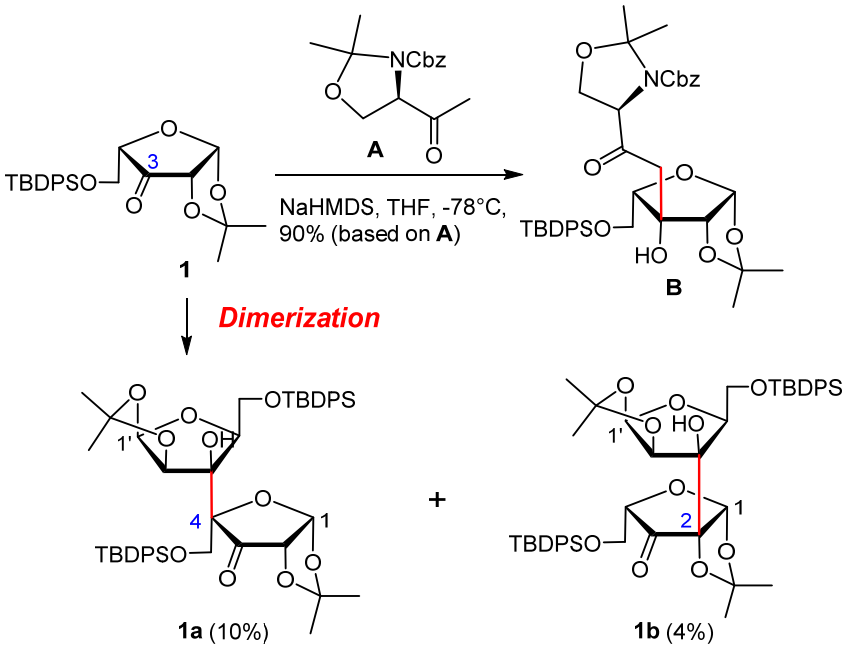
2,3:5,6-Di-*O*-isopropylidene-D-gulono-1,4-lactone (10)



S4 **10**

Compound **10** was prepared according to the literature procedure:[S10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (d, $J_{2,3}$ = 5.6 Hz, 1H, H-2), 4.74 (dd, $J_{2,3/3,4}$ = 5.6, 3.6 Hz, 1H, H-3), 4.47–4.40 (m, 2H, H-6a and H-6b), 4.22 (m, 1H, H-4), 3.82 (m, 1H, H-5), 1.47 (s, 3H, isopropylidene), 1.47 (s, 3H, isopropylidene), 1.40 (s, 3H, isopropylidene), 1.38 (s, 3H, isopropylidene).

5-*O*-*tert*-Butyldiphenylsilyl-3-C-(5-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-β-L-threo-pentofuranos-3-ulose-4-yl)-1,2-*O*-isopropylidene-β-L-lyxofuranose (1a) and 5-*O*-*tert*-Butyldiphenylsilyl-3-C-(5-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-β-L-threo-pentofuranos-3-ulose-2-yl)-1,2-*O*-isopropylidene-β-L-lyxofuranose (1b)



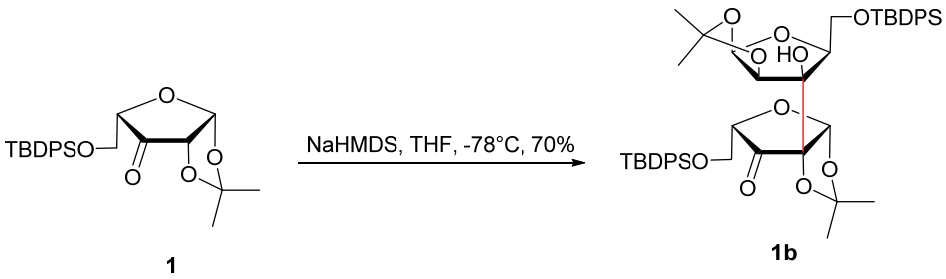
The preparative procedure was reported in the total synthesis of the proposed amipurimycin.[S11] These side products were purified by silica gel column chromatography (petroleum ether/EtOAc, 20:1), providing **1a** (1.62 g, 10%) and **1b** (0.65 g, 4%) as white solids.

1a: $[\alpha]^{25}_{D}$ = 19.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–7.72 (m, 6H, TBDPS), 7.70 (dd, *J* = 7.8, 1.5 Hz, 2H, TBDPS), 7.48–7.38 (m, 12H, TBDPS), 6.08 (d, $J_{1,2}$ = 4.1 Hz, 1H, H-1), 5.59 (d, $J_{1',2'}$ = 4.0 Hz, 1H, H-1'), 5.01 (d, $J_{1',2'}$ = 4.0 Hz, 1H, H-2'), 4.62 (t, $J_{4',5'}$ = 6.1 Hz, 1H, H-4'), 4.43 (d, $J_{1,2}$ = 4.1 Hz, 1H, H-2), 4.11–4.02 (m, 2H, H-5a' and OH), 3.91 (d, $J_{5a,5b}$ = 11.8 Hz, 1H, H-5a), 3.86–3.77 (m, 2H, H-5b and H-5b'), 1.40 (s, 3H, isopropylidene), 1.36 (s, 3H, isopropylidene), 1.33 (s, 3H, isopropylidene), 1.31 (s, 3H, isopropylidene), 1.12 (s, 9H, TBDPS), 1.10 (s, 9H, TBDPS); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.7 (C-3), 135.8, 135.8, 135.7, 135.6, 133.1, 132.9, 132.4, 132.2, 130.0, 129.9, 129.8, 127.9, 127.8, 127.8, 127.8, 115.6, 112.9, 105.3 (C-1'), 103.3 (C-1), 89.4 (C-3'), 83.6 (C-4), 82.3 (C-4'), 79.0 and 79.0 (C-2 and C-2'), 64.5 (C-5), 64.1 (C-5'), 27.7, 27.2, 27.0, 26.8, 26.6, 26.3, 19.2, 19.2; HRMS (ESI) *m/z* calcd for $C_{48}H_{60}O_{10}Si_2Na$ $[M+Na]^+$ 875.3617, found 875.3623.

1b: $[\alpha]^{25}_{D}$ = -17.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H, TBDPS), 7.70 (d, *J* = 7.1 Hz, 6H, TBDPS), 7.35–7.44 (m, 12H, TBDPS), 6.01 (s, 1H, H-1), 5.68 (d, $J_{1',2'}$ = 3.9 Hz, 1H, H-1'), 4.60 (t, $J_{4',5'}$ = 5.1 Hz, 1H, H-4'), 4.52 (d, $J_{1',2'}$ = 3.8 Hz, 1H, H-2'), 4.39 (s, 1H, OH), 4.27 (t, $J_{4,5}$ = 4.0 Hz, 1H, H-4), 4.02 (dd, $J_{5a',5b'/4',5'}$ = 11.1, 5.3 Hz, 1H, H-5a'), 3.96 (d, $J_{4,5}$ = 3.1 Hz, 1H, H-5a), 3.92 (d, $J_{4,5}$ =

5.0 Hz, 1H, H-5b), 3.82 (d, $J_{4',5'}$ = 5.4 Hz, 1H, H-5b'), 1.48 (s, 3H, isopropylidene), 1.45 (s, 3H, isopropylidene), 1.43 (s, 3H, isopropylidene), 1.38 (s, 3H, isopropylidene), 1.04 (s, 18H, TBDPS); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.4 (C-3), 135.8, 135.7, 135.6, 135.6, 133.0, 132.8, 132.7, 132.5, 129.8, 129.8, 129.7, 129.7, 127.8, 127.7, 127.7, 127.7, 115.4, 114.0, 104.8 (C-1'), 104.1 (C-1), 86.5 (C-2), 83.0 (C-4), 81.3 (C-2'), 80.4 (C-3'), 64.1 (C-5'), 62.5 (C-5), 28.6, 27.4, 27.2, 26.8, 26.7, 19.2, 19.1; HRMS (ESI) *m/z* calcd for $C_{48}H_{60}O_{10}Si_2Na$ $[M+Na]^+$ 875.3617, found 875.3621.

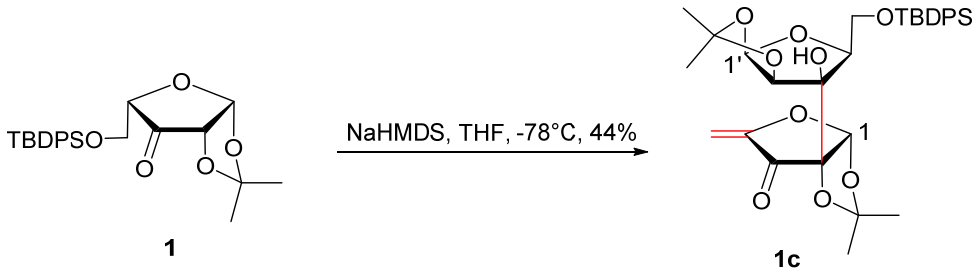
5-*O*-*tert*-Butyldiphenylsilyl-3-C-(5-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-β-L-threo-pentofuranos-3-ulose-2-yl)-1,2-*O*-isopropylidene-β-L-lyxofuranose (1b)



1 **1b**

To a solution of **1** (0.222 g, 0.52 mmol) in dry THF (2.3 mL), was added NaHMDS (2.0 M in THF, 0.26 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and TLC (petroleum ether/EtOAc, 6:1) showed the complete consumption of **1**. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a pale yellow oil. Further purification by column chromatography (petroleum ether/EtOAc, 20:1) gave **1b** (0.155 g, 70%) as a white solid.

5-*O*-*tert*-Butyldiphenylsilyl-3-C-(5-deoxy-1,2-*O*-isopropylidene-β-L-threo-pent-4-enofuranos-3-ulose-2-yl)-1,2-*O*-isopropylidene-β-L-lyxofuranose (1c)

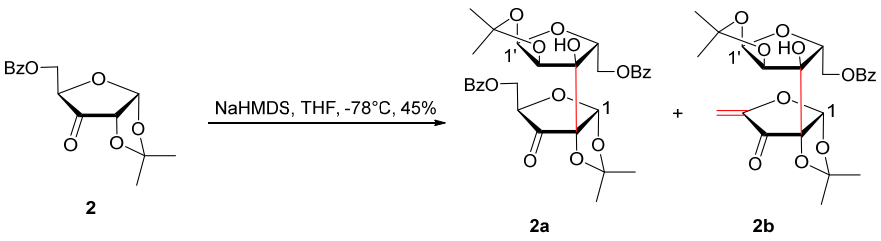


1 **1c**

To a solution of NaHMDS (2.0 M, 0.1 mL) in dry THF (0.34 mL), was added a solution

of **1** (0.058 g, 0.13 mmol) in dry THF (0.5 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and another portion of **1** (0.058 g, 0.13 mmol) in dry THF (0.5 mL) was added to the mixture. After being stirred at the same temperature for 2 h, the reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 25:1) gave **1c** as a colorless oil (0.018 g, 44%): $[\alpha]^{25}_D$ = -11.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, acetone-d6) δ 7.79 (m, 4H, TBDPS), 7.46–7.41 (m, 6H, TBDPS), 6.16 (s, 1H, H-1), 5.83 (d, $J_{1',2'}$ = 4.1 Hz, 1H, H-1'), 5.07 (d, $J_{5a,5b}$ = 2.3 Hz, 1H, H-5a), 4.77 (d, $J_{5a,5b}$ = 2.3 Hz, 1H, H-5b), 4.72 (dd, $J_{3',4'/4',5'}$ = 6.8, 2.8 Hz, 1H, H-4'), 4.65 (d, $J_{1',2'}$ = 4.1 Hz, 1H, H-2'), 4.51 (s, 1H, OH), 4.05 (m, 1H, H-5a'), 3.88 (m, 1H, H-5b'), 1.54 (s, 3H, isopropylidene), 1.41 (s, 3H, isopropylidene), 1.38 (s, 3H, isopropylidene), 1.37 (s, 3H, isopropylidene), 1.06 (s, 9H, TBDPS); ^{13}C NMR (151 MHz, acetone-d6) δ 198.2 (C-3), 154.6 (C-4), 137.1, 136.9, 134.9, 134.7, 131.2, 131.1, 129.2, 129.1, 117.1, 114.9, 106.5 and 106.4 (C-1/1'), 92.0, 86.7, 84.8, 82.6, 80.7, 66.2, 29.4, 28.0, 27.9, 27.7, 27.6, 20.3; HRMS (ESI) *m/z* calcd for $C_{32}H_{40}O_9SiNa$ $[M+Na]^+$ 619.2334, found 619.2342. Compound **1c** was found unstable in $CDCl_3$.

5-*O*-Benzoyl-3-C-(5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-erythro-pentofuranos-3-ulose-2-yl)-1,2-*O*-isopropylidene-α-D-ribofuranose (2a) and 5-*O*-Benzoyl-3-C-(5-deoxy-1,2-*O*-isopropylidene-α-D-erythro-pent-4-enofuranos-3-ulose-2-yl)-1,2-*O*-isopropylidene-α-D-ribofuranose (2b)



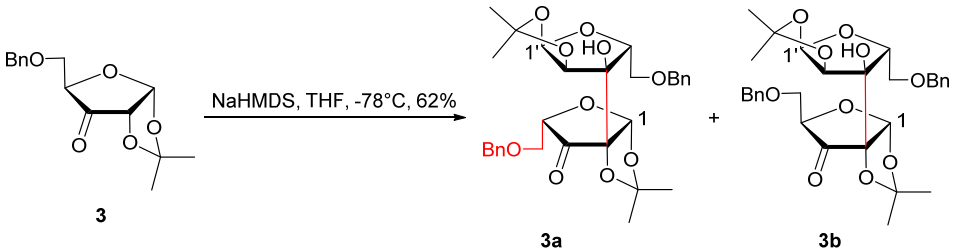
To a solution of **2** (0.303 g, 1.04 mmol) in dry THF (9.9 mL), was added NaHMDS (2.0 M in THF, 0.52 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and TLC (petroleum ether/EtOAc, 2:1) showed the complete consumption of **2**. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum to give

a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 6:1 and 2:1) gave **2a** (0.009 g, 3%) as a white foam and **2b** (0.105 g, 42%) as a colourless oil.

2a: $[\alpha]^{25}_{D}$ = 59.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–8.05 (m, 2H, Bz), 8.03–7.99 (m, 2H, Bz), 7.59–7.50 (m, 2H, Bz), 7.46–7.39 (m, 4H, Bz), 6.10 (s, 1H, H-1), 6.06 (d, $J_{1',2'}$ = 4.5 Hz, 1H, H-1'), 4.84 (d, $J_{1',2'}$ = 4.4 Hz, 1H, H-2'), 4.80 (dd, *J* = 6.9, 3.4 Hz, 1H), 4.76 (d, *J* = 2.2 Hz, 1H), 4.68 (s, 1H), 4.63–4.55 (m, 3H), 3.53 (s, 1H, OH), 1.62 (s, 3H, isopropylidene), 1.47 (s, 3H, isopropylidene), 1.46 (s, 3H, isopropylidene), 1.40 (s, 3H, isopropylidene); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2(C-3), 166.5, 166.3, 133.5, 133.4, 130.2, 130.1, 129.9, 129.8, 129.3, 115.3, 105.7(C-1), 105.3(C-1'), 85.2, 80.7, 79.1, 78.7, 77.5, 63.4, 63.2, 28.4, 28.3, 27.5, 27.1; HRMS (ESI) *m/z* calcd for $C_{30}H_{32}O_{12}Na$ $[M+Na]^+$ 607.1786, found 607.1786.

2b: $[\alpha]^{25}_{D}$ = 24.0 (*c* 1.1, CH_2Cl_2); ^{1}H NMR (600 MHz, acetone-d6) δ 8.03 (dd, *J* = 8.4, 1.3 Hz, 2H, Bz), 7.67–7.63 (m, 1H, Bz), 7.55–7.51 (m, 2H, Bz), 6.27 (s, 1H, H-1), 5.99 (d, $J_{1',2'}$ = 4.4 Hz, 1H, H-1'), 5.08 (d, $J_{5a,5b}$ = 2.3 Hz, 1H, H-5a), 4.93 (d, $J_{1',2'}$ = 4.4 Hz, 1H, H-2'), 4.77 (d, $J_{5a,5b}$ = 2.3 Hz, 1H, H-5b), 4.77 (s, 1H, OH), 4.66–4.56 (m, 2H, H-5a' and H-5b'), 4.53 (dd, $J_{4',5'}$ = 7.7, 3.9 Hz, 1H, H-4'), 1.55 (s, 3H, isopropylidene), 1.48 (s, 3H, isopropylidene), 1.42 (s, 3H, isopropylidene), 1.37 (s, 3H, isopropylidene); ^{13}C NMR (151 MHz, acetone-d6) δ 197.2 (C-3), 166.9, 154.3, 134.6, 131.5, 130.9, 130.0, 117.1, 115.2, 106.3 and 106.2 (C-1/1'), 92.6, 86.8, 81.8, 81.4, 64.0, 61.1, 29.5, 28.1, 27.8, 27.4; HRMS (ESI) *m/z* calcd for $C_{23}H_{26}O_{10}Na$ $[M+Na]^+$ 485.1418, found 485.1419. Compound **2b** was found unstable in $CDCl_3$.

5-*O*-Benzyl-3-C-(5-*O*-benzyl-1,2-*O*-isopropylidene-α-D-erythro-pentofuranos-3-ulose-2-yl)-1,2-*O*-isopropylidene-α-D-ribofuranose (3a) and 5-*O*-Benzyl-3-C-(5-*O*-benzyl-1,2-*O*-isopropylidene-α-D-erythro-pentofuranos-3-ulose-2-yl)-1,2-*O*-isopropylidene-α-D-xylofuranose (3b)



3 3a 3b

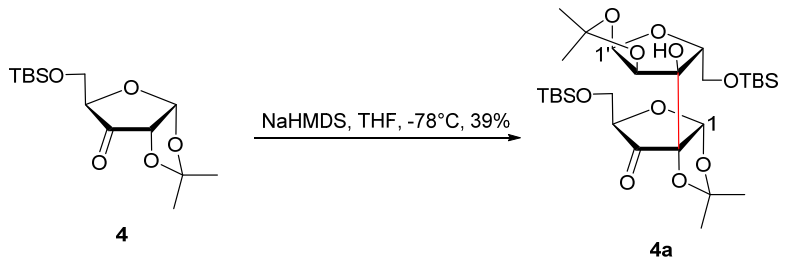
To a solution of **3** (0.347 g, 1.25 mmol) in dry THF (5.9 mL), was added NaHMDS (2.0 M in THF, 0.31 mL) at -78 °C. The mixture was stirred at the same temperature for 30

mins and TLC (petroleum ether/EtOAc, 2:1) showed the complete consumption of **3**. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum to give a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 7:1) gave **3a** (0.042 g, 13%) and **3b** (0.170 g, 49%) as white foams.

3a: $[\alpha]^{25}_D$ = 62.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.28 (m, 10H, Bn), 6.00 (s, 1H, H-1), 5.97 (d, $J_{1',2'}$ = 4.2 Hz, 1H, H-1'), 4.87 (d, $J_{1',2'}$ = 4.2 Hz, 1H, H-2'), 4.60–4.50 (m, 4H, Bn), 4.40 (dd, $J_{4,5}$ = 5.8, 3.6 Hz, 1H, H-4), 4.03 (s, 1H, H-4'), 3.80 (d, $J_{4',5'/5a',5b'}$ = 3.7 Hz, 2H, H-5'), 3.76–3.69 (m, 2H, H-5), 3.22 (s, 1H, OH), 1.58 (s, 3H, isopropylidene), 1.51 (s, 3H, isopropylidene), 1.50 (s, 3H, isopropylidene), 1.42 (s, 3H, isopropylidene); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.0 (C-3), 137.5, 136.9, 128.5, 128.3, 128.2, 128.0, 127.8, 127.7, 115.8, 112.8, 104.8 (C-1), 104.6 (C-1'), 86.1 (C-2), 82.6 (C-4'), 81.8 (C-4), 79.5 (C-3'), 79.4 (C-2'), 73.4 (Bn), 73.3 (Bn), 69.6 (C-5), 66.0 (C-5'), 29.7, 28.6, 27.6, 26.6, 26.3; HRMS (ESI) *m/z* calcd for $C_{30}H_{40}NO_{10}$ $[M+NH_4]^+$ 574.2647, found 574.2650.000

3b: $[\alpha]^{25}_D$ = 51.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 10H, Bn), 6.18 (s, 1H, H-1), 6.00 (d, $J_{1,2}$ = 4.3 Hz, 1H, H-1'), 4.88 (d, $J_{1,2}$ = 4.3 Hz, 1H, H-2'), 4.65 (dd, $J_{4,5}$ = 6.0, 3.0 Hz, 1H, H-4), 4.53 (q, *J* = 12.1 Hz, 2H, Bn), 4.45 (q, *J* = 12.3 Hz, 2H, Bn), 4.17 (s, 1H, H-4'), 3.79 (dd, $J_{4,5/5a,5b}$ = 11.0, 3.0 Hz, 1H, H-5a), 3.69 (m, 3H, H-5b, H-5a' and H-5b'), 3.32 (s, 1H, OH), 1.58 (s, 3H, isopropylidene), 1.50 (s, 3H, isopropylidene), 1.49 (s, 3H, isopropylidene), 1.41 (s, 3H, isopropylidene); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.4(C-3), 137.5, 137.4, 128.4, 127.9, 127.8, 127.8, 127.7, 115.0, 113.0, 104.9 (C-1), 104.7 (C-1'), 85.6 (C-2), 82.8 (C-4'), 80.1 (C-2'), 79.6 (C-3'), 79.2 (C-4), 73.5 (Bn), 73.2 (Bn), 68.4 (C-5), 67.19 (C-5'), 28.3, 28.0, 26.8, 26.4; HRMS (ESI) *m/z* calcd for $C_{30}H_{40}NO_{10}$ $[M+NH_4]^+$ 574.2647, found 574.2646.

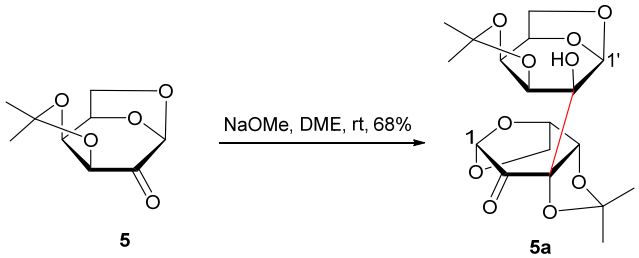
5-*O*-*tert*-Butyldimethylsilyl-3-C-(5-*O*-*tert*-butyldimethylsilyl-1,2-*O*-isopropylidene-α-D-erythro-pentofuranos-3-ulose-2-yl)-1,2-*O*-isopropylidene-α-D-ribofuranose (4a)



4 **4a**

To a solution of **4** (0.128 g, 0.42 mmol) in dry THF (2.0 mL), was added NaHMDS (2.0 M in THF, 0.11 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and TLC (petroleum ether/EtOAc, 5:1) showed the complete consumption of **4**. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum to give a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 20:1) gave **4a** (0.049 g, 39%) as a white solid: $[\alpha]^{25}_D$ = 62.9 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.24 (s, 1H, H-1), 5.92 (d, $J_{1',2'}$ = 4.4 Hz, 1H, H-1'), 4.86 (d, $J_{1',2'}$ = 4.4 Hz, 1H, H-2'), 4.47 (dd, $J_{4,5}$ = 5.9, 3.5 Hz, 1H, H-4), 4.14 (s, 1H, H-4'), 3.96–3.81 (m, 4H, H-5 and H-5'), 3.24 (s, 1H, OH), 1.59 (s, 3H, isopropylidene), 1.50 (s, 3H, isopropylidene), 1.47 (s, 3H, isopropylidene), 1.40 (s, 3H, isopropylidene), 0.91 (s, 9H, TBS), 0.89 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.08 (s, 3H, TBS), 0.07 (s, 3H, TBS), 0.07 (s, 3H, TBS); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.8 (C-3), 114.8, 113.6, 105.0 (C-1 and C-1'), 85.7 (C-2 and C-4'), 81.1 (C-4), 80.6 (C-2'), 80.1 (C-3'), 62.9 (C-5), 61.8 (C-5'), 28.5, 28.4, 27.1, 26.7, 26.2, 26.2, 18.8, 18.5, 1.3, -4.9, -5.0, -5.1, -5.1; HRMS (ESI) *m/z* calcd for $C_{28}H_{52}O_{10}Si_2Na$ $[M+Na]^+$ 627.2991, found 627.2996.

1,6-Anhydro-2-*C*-(1,6-anhydro-3,4-*O*-isopropylidene-β-D-lyxo-hexopyranos-2-ulose-3-yl)-3,4-*O*-isopropylidene-β-D-talopyranose (5a)

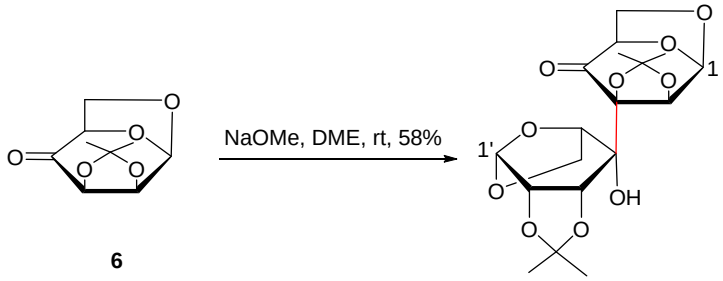


5 **5a**

To a solution of **5** (0.208 g, 1.04 mmol) in dry DME (10.0 mL), was added NaOMe (6 mg) at rt. The mixture was stirred at the same temperature for 1h and TLC (petroleum ether/EtOAc, 2:1) showed the complete consumption of **5**. The reaction was quenched

by addition of saturated aq. NH_4Cl. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a colourless oil. Purification by column chromatography (petroleum ether/EtOAc, 6:1) gave **5a** (0.141 g, 68%) as a colorless syrup: $[\alpha]^{25}_D$ = -65.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (s, 1H, H-1), 5.24 (s, 1H, H-1'), 5.20 (d, $J_{3',4'}$ = 7.4 Hz, 1H, H-3'), 4.96 (ddd, $J_{3',4'/4',5'}$ = 6.9, 5.5, 1.0 Hz, 1H, H-4'), 4.89 (d, $J_{4,5}$ = 7.0 Hz, 1H, H-4), 4.37 (m, 2H, H-6a and H-6b), 4.23 (t, $J_{4,5/5,6}$ = 6.5 Hz, 1H, H-5), 4.20 (d, $J_{5,6b/6a,6b}$ = 7.6 Hz, 1H, H-6b), 3.68 (dd, $J_{4',5'/5',6'}$ = 7.8, 5.5 Hz, 1H, H-5'), 3.57 (dd, $J_{5,6a/6a,6b}$ = 7.5, 5.0 Hz, 1H, H-6a), 3.47 (s, 1H, OH), 1.54 (s, 3H, isopropylidene), 1.52 (s, 3H, isopropylidene), 1.42 (s, 3H, isopropylidene), 1.41 (s, 3H, isopropylidene); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8 (C-2), 113.1, 109.3, 99.5 and 98.4 (C-1/1'), 85.6, 77.2, 73.9, 73.4, 73.1, 71.0, 70.7, 65.2, 62.6, 28.0, 27.2, 25.8, 25.0; HRMS (ESI) *m/z* calcd for $C_{18}H_{24}O_{10}Na$ $[M+Na]^+$ 423.1262, found 423.1259.

1,6-Anhydro-4-*C*-(1,6-anhydro-2,3-*O*-isopropylidene-β-D-lyxo-hexopyranos-4-ulose-3-yl)-2,3-*O*-isopropylidene-β-D-talopyranose (6a)

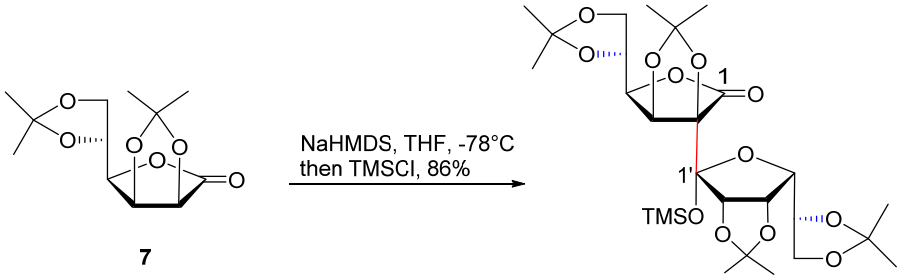


6 **6a**

To a solution of **6** (0.077 g, 0.39 mmol) in dry DME (3.8 mL), was added NaOMe (2 mg) at rt. The mixture was stirred at the same temperature for 1h and TLC (petroleum ether/EtOAc, 1:1) showed the complete consumption of **6**. The reaction was quenched by addition of saturated aq. NH_4Cl. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a colourless oil. Purification by column chromatography (petroleum ether/EtOAc, 5:1) gave **6a** (0.045 g, 58%) as a white solid: $[\alpha]^{25}_D$ = -13.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (d, *J* = 3.8 Hz, 1H, H-1), 5.22 (d, *J* = 3.1 Hz, 1H, H-1'), 4.82 (d, *J* = 3.8 Hz, 1H, H-2), 4.79 (d, *J* = 6.3 Hz, 1H, H-3'), 4.73 (d, *J* = 4.5 Hz, 1H, H-5), 4.62 (d, *J* = 6.2 Hz, 1H, H-5'), 4.28 (dd, *J* = 7.7, 0.9 Hz, 1H, H-6a'), 3.95 (dd, *J* = 6.3, 3.2 Hz, 1H, H-2'), 3.88 (d, *J* = 7.6 Hz, 1H, H-6a), 3.82–3.74

(m, 2H, H-6b and H-6b'), 3.44 (s, 1H, OH), 1.55 (s, 3H, isopropylidene), 1.52 (s, 3H, isopropylidene), 1.40 (s, 3H, isopropylidene), 1.38 (s, 3H, isopropylidene); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.7 (C-4), 114.7, 110.6, 99.4 and 98.8 (C-1/1'), 88.9, 78.5, 76.9, 76.4, 74.8, 73.3, 73.0, 68.3, 63.7, 28.1, 28.0, 26.2, 25.9; HRMS (Dart Positive Ion Mode) *m/z* calcd for $C_{18}H_{25}O_{10}$ $[M+H]^+$ 401.1442, found 401.1442.

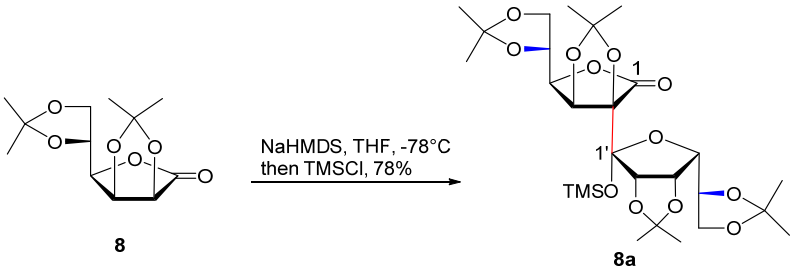
2,3:5,6-Di-*O*-isopropylidene-2-*C*-(2,3;5,6-di-*O*-isopropylidene-1-*O*-trimethylsilyl-β-D-mannofuranosyl)-D-mannono-1,4-lactone (7a)



7 **7a**

To a solution of **7** (0.108 g, 0.42 mmol) in dry THF (2.6 mL), was added NaHMDS (2.0 M in THF, 0.15 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and TLC (petroleum ether/EtOAc, 2:1) showed the complete consumption of **7**. Then TMSCl (0.037 mL, 0.29 mmol) was added and the reaction mixture was stirred at the same temperature for another 30 mins. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 4:1) gave **7a** (0.106 g, 86%) as a white solid: [S12] $[\alpha]^{25}_D$ = 14.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 (d, *J* = 3.3 Hz, 1H), 4.76 (dd, *J* = 6.0, 4.8 Hz, 1H), 4.68 (d, *J* = 6.1 Hz, 1H), 4.35 (s, 1H), 4.32–4.28 (m, 1H), 4.26 (dd, *J* = 8.9, 3.3 Hz, 1H), 4.15–4.01 (m, 5H), 1.58 (s, 3H, isopropylidene), 1.46 (s, 3H, isopropylidene), 1.44 (s, 3H, isopropylidene), 1.42 (s, 3H, isopropylidene), 1.41 (s, 3H, isopropylidene), 1.37 (s, 9H, isopropylidene), 0.15 (s, 9H, TMS); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2 (C-1), 115.0, 112.8, 109.9, 109.6, 105.8 (C-1'), 89.2, 81.0, 80.1, 79.8, 79.5, 78.8, 72.9, 72.6, 67.4, 66.8, 27.3, 27.1, 26.9, 26.7, 25.3, 25.3, 25.2, 23.4, 2.0; HRMS (ESI) *m/z* calcd for $C_{27}H_{44}O_{12}SiNa$ $[M+Na]^+$ 611.2494, found 611.2495.

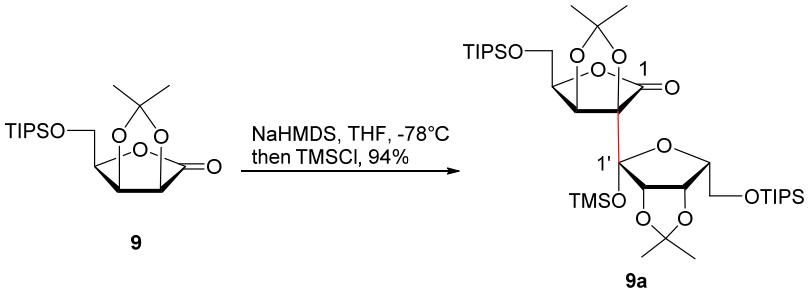
2,3:5,6-Di-*O*-isopropylidene-2-*C*-(2,3;5,6-di-*O*-isopropylidene-1-*O*-trimethylsilyl-α-L-gulofuranosyl)-L-gulono-1,4-lactone (8a)



8 **8a**

To a solution of **8** (1.247 g, 4.83 mmol) in dry THF (30.2 mL), was added NaHMDS (2.0 M in THF, 1.70 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and TLC (petroleum ether/EtOAc, 2:1) showed the complete consumption of **8**. Then TMSCl (0.43 mL, 3.37 mmol) was added and the reaction mixture was stirred at the same temperature for another 30 mins. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 8:1) gave **8a** (1.104 g, 78%) as a white solid: $[\alpha]^{25}_D$ = 19.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.91 (d, $J_{2',3'}$ = 6.4 Hz, 1H, H-2'), 4.74 (d, $J_{3,4}$ = 3.5 Hz, 1H, H-3), 4.70–4.65 (m, 1H, H-3'), 4.47–4.37 (m, 2H, H-4 and H-5), 4.27 (dt, $J_{4',5'/5',6'}$ = 8.3, 6.4 Hz, 1H, H-5'), 4.18 (dd, $J_{5,6a/6a,6b}$ = 8.7, 6.4 Hz, 1H, H-6a), 4.08 (dd, $J_{5',6a'/6a',6b'}$ = 8.7, 6.6 Hz, 1H, H-6a'), 3.89 (dd, $J_{3',4'/4',5'}$ = 8.4, 5.4 Hz, 1H, H-4'), 3.80 (dd, $J_{5,6b/6a,6b}$ = 8.7, 6.1 Hz, 1H, H-6b), 3.62 (dd, $J_{5',6b'/6a',6b'}$ = 8.7, 6.3 Hz, 1H, H-6b'), 1.54 (s, 3H, isopropylidene), 1.45 (s, 3H, isopropylidene), 1.42 (s, 3H, isopropylidene), 1.42 (s, 3H, isopropylidene), 1.41 (s, 3H, isopropylidene), 1.38 (s, 3H, isopropylidene), 1.34 (s, 3H, isopropylidene), 1.32 (s, 3H, isopropylidene), 0.25 (s, 9H, TMS); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6 (C-1), 115.2, 112.9, 110.4, 109.5, 106.2 (C-1'), 88.9, 81.7, 81.6, 80.8, 80.4, 78.8, 76.4, 75.1, 66.0, 65.1, 27.3, 26.9, 26.7, 26.6, 25.4, 25.3, 25.2, 23.5; HRMS (ESI) *m/z* calcd for $C_{27}H_{44}O_{12}SiNa$ $[M+Na]^+$ 611.2494, found 611.2496.

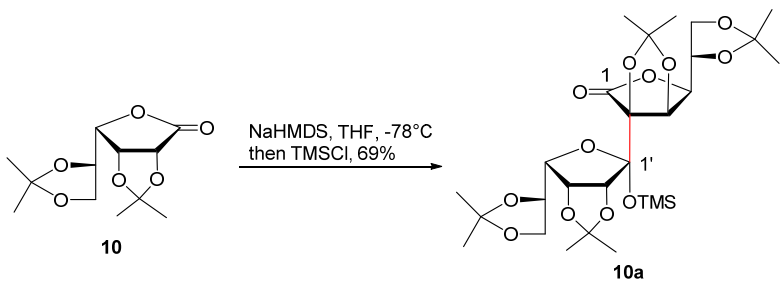
2,3-*O*-Isopropylidene-2-*C*-(2,3-*O*-isopropylidene-5-*O*-triisopropylsilyl-1-*O*-trimethylsilyl-β-D-lyxofuranosyl)-5-*O*-triisopropylsilyl-D-lyxono-1,4-lactone (9a)



9 9a

To a solution of **9** (0.564 g, 1.64 mmol) in dry THF (10.2 mL), was added NaHMDS (2.0 M in THF, 0.57 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and TLC (petroleum ether/EtOAc, 9:1) showed the complete consumption of **9**. Then TMSCl (0.15 mL, 1.17 mmol) was added and the reaction mixture was stirred at the same temperature for another 30 mins. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 40:1) gave **9a** (0.588 g, 94%) as a white solid: $[\alpha]^{25}_D$ = 4.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (d, $J_{2',3'}$ = 6.4 Hz, 1H, H-2'), 4.81 (d, $J_{3,4}$ = 3.3 Hz, 1H, H-3), 4.74–4.69 (m, 1H, H-3'), 4.54 (td, $J_{3,4/4,5}$ = 6.6, 3.4 Hz, 1H, H-4), 4.10 (q, $J_{3',4'/4',5'}$ = 5.5 Hz, 1H, H-4'), 3.99 (qd, $J_{4,5/5a,5b}$ = 10.2, 6.6 Hz, 2H, H-5a and H-5b), 3.91 (dd, J $J_{4',5b'/5a',5b'}$ = 10.2, 5.5 Hz, 1H, H-5b'), 3.83 (dd, $J_{4',5a'/5a',5b'}$ = 10.2, 6.5 Hz, 1H, H-5a'), 1.54 (s, 3H, isopropylidene), 1.41 (s, 3H, isopropylidene), 1.41 (s, 3H, isopropylidene), 1.34 (s, 3H, isopropylidene), 1.14–1.00 (m, 42H, TIPS), 0.21 (s, 9H, TMS); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1 (C-1), 114.1, 112.3, 105.6 (C-1'), 88.8, 80.9, 80.5, 80.1, 80.0, 78.8, 62.0, 60.9, 27.2, 26.5, 25.2, 23.5, 17.9, 17.8, 11.9, 11.9, 2.1; HRMS (ESI) *m/z* calcd for $C_{37}H_{72}O_{10}Si_3Na$ $[M+Na]^+$ 783.4325, found 783.4325.

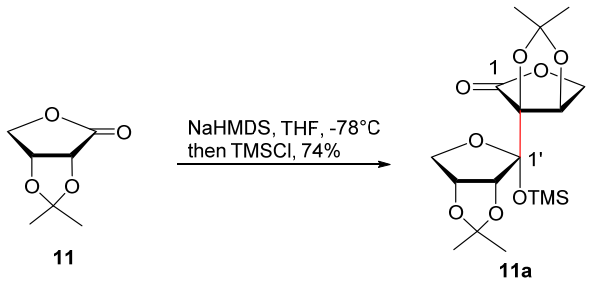
2,3:5,6-Di-*O*-isopropylidene-2-*C*-(2,3;5,6-di-*O*-isopropylidene-1-*O*-trimethylsilyl-β-D-gulofuranosyl)-D-gulono-1,4-lactone (10a)



10 10a

To a solution of **10** (0.128 g, 0.50 mmol) in dry THF (3.1 mL), was added NaHMDS (2.0 M in THF, 0.17 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and TLC (petroleum ether/EtOAc, 2:1) showed the complete consumption of **10**. Then TMSCl (0.044 mL, 0.34 mmol) was added and the reaction mixture was stirred at the same temperature for another 30 mins. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 8:1) gave **10a** (0.100 g, 69%) as a white solid: $[\alpha]^{25}_D$ = -21.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (d, $J_{2',3'}$ = 6.3 Hz, 1H, H-2'), 4.73 (d, $J_{3,4}$ = 3.0 Hz, 1H, H-3), 4.66 (t, $J_{2',3'/3',4'}$ = 5.8 Hz, 1H, H-3'), 4.41 (m, 2H, H-4 and H-5), 4.25 (q, $J_{4',5'/5a',5b'}$ = 6.6 Hz, 1H, H-5'), 4.20–4.14 (m, 1H, H-6a), 4.10–4.04 (m, 1H, H-6a'), 3.90–3.85 (m, 1H, H-4'), 3.82–3.77 (m, 1H, H-6b), 3.63–3.57 (m, 1H, H-6b'), 1.53 (s, 3H, isopropylidene), 1.43 (s, 3H, isopropylidene), 1.42–1.38 (m, 9H, isopropylidene), 1.37 (s, 3H, isopropylidene), 1.32 (s, 3H, isopropylidene), 1.31 (s, 3H, isopropylidene), 0.23 (s, 9H, TMS); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6 (C-1), 115.2, 112.8, 110.4, 109.5, 106.2 (C-1'), 88.8, 81.7, 81.6, 80.8, 80.4, 78.8, 76.4, 75.1, 66.0, 65.1, 27.3, 26.9, 26.7, 26.6, 25.4, 25.3, 25.2, 23.5, 2.3; HRMS (ESI) *m/z* calcd for $C_{27}H_{44}O_{12}SiNa$ $[M+Na]^+$ 611.2494, found 611.2501.

2,3-*O*-Isopropylidene-2-*C*-(2,3-*O*-isopropylidene-1-*O*-trimethylsilyl-α-D-erythrosyl)-D-erythrono-1,4-lactone (11a)



11 **11a**

To a solution of **11** (0.148 g, 0.99 mmol) in dry THF (6.2 mL), was added NaHMDS (2.0 M in THF, 0.34 mL) at -78 °C. The mixture was stirred at the same temperature for 30 mins and TLC (petroleum ether/EtOAc, 2:1) showed the complete consumption of **11**. Then TMSCl (0.009 mL, 0.07 mmol) was added and the reaction mixture was stirred at the same temperature for another 30 mins. The reaction was quenched by addition of saturated aq. NH_4Cl. After warming to RT, the mixture was extracted with CH_2Cl_2 three

times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a pale yellow oil. Purification by column chromatography (petroleum ether/EtOAc, 12:1) gave **11a** (0.134 g, 74%) as a white solid:[S12] $[\alpha]^{25}_D$ = -33.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87–4.76 (m, 3H, H-3, H-2' and H-3'), 4.32 (d, *J* = 10.5 Hz, 2H), 4.03–3.90 (m, 2H), 1.57 (s, 3H, isopropylidene), 1.42 (s, 3H, isopropylidene), 1.42 (s, 3H, isopropylidene), 1.35 (s, 3H, isopropylidene), 0.19 (s, 9H, TMS); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2 (C-1), 114.2, 113.1, 107.0 (C-1'), 87.6, 80.8, 80.3, 78.6, 72.5, 70.6, 27.2, 26.5, 25.8, 23.9, 1.9; HRMS (ESI) *m/z* calcd for $C_{17}H_{28}O_8SiNa$ $[M+Na]^+$ 411.1446, found 411.1450.

3. References

[S1] M. T. de Oliveira, D. L. Hughes, S. A. Nepogodiev and R. A. Field, *Carbohydr. Res.,* 2008, **343**, 211-220.

[S2] (a) J. Moravcová, J. Čapková and J. Staněk, *Carbohydr. Res.,* 1994, **263**, 61-66; (b) S. D. Lucas, A. P. Rauter, J. Schneider and H. P. Wessel, *J. Carbohydr. Chem.,* 2009, **28**, 431-446.

[S3] (a) R. D. Marwood, D. J. Jenkins, V. Correa, C. W. Taylor and B. V. L. Potter, *J. Med. Chem.,* 2000, **43**, 4278-4287; (b) M. Giordano and A. Iadonisi, *Tetrahedron Lett.,* 2013, **54**, 1550-1552.

[S4] T. Bauer, M. Majdecki and J. Jurczak, *Tetrahedron,* 2013, **69**, 1930-1939.

[S5] (a) D. Horton and J. S. Jewell, *Carbohydr. Res.,* 1967, **5**, 149-160; (b) M. Kloosterman, D. de Wit, J. H. van Boom and H. T. de Hey, *Recueil des Travaux Chimiques des Pays-Bas,* 1986, **105**, 229-231; (c) T. Tanaka, W. C. Huang, M. Noguchi, A. Kobayashi and S.-i. Shoda, *Tetrahedron Lett.,* 2009, **50**, 2154-2157.

[S6] (a) M. Kloosterman, M. P. De Nijs and J. H. Van Boom, *J. Carbohydr. Chem.* 1986, **5**, 215-233; (b) N. Boissièere-Junot, C. Tellier and C. Rabiller, *J. Carbohydr. Chem.,* 1998, **17**, 99-115; (c) M. Georges and B. Fraser-Reid, *Carbohydr. Res.* 1984, **127**, 162-164; (d) M. A. Zottola, R. Alonso, G. D. Vite and B. Fraser-Reid, *J. Org. Chem.,* 1989, **54**, 6123-6125; (e) T. Susana, N. Beatriz, B. Vicen and A. Ricardo, *J. Org. Chem.,* 2003, **68**, 4772-4783.

[S7] (a) R. Csuk and P. Dörr, *J. Carbohydr. Chem.,* 1995, **14**, 35-44; (b) A. Oddo and R. Holl, *Carbohydr. Res.,* 2012, **359**, 59-64.

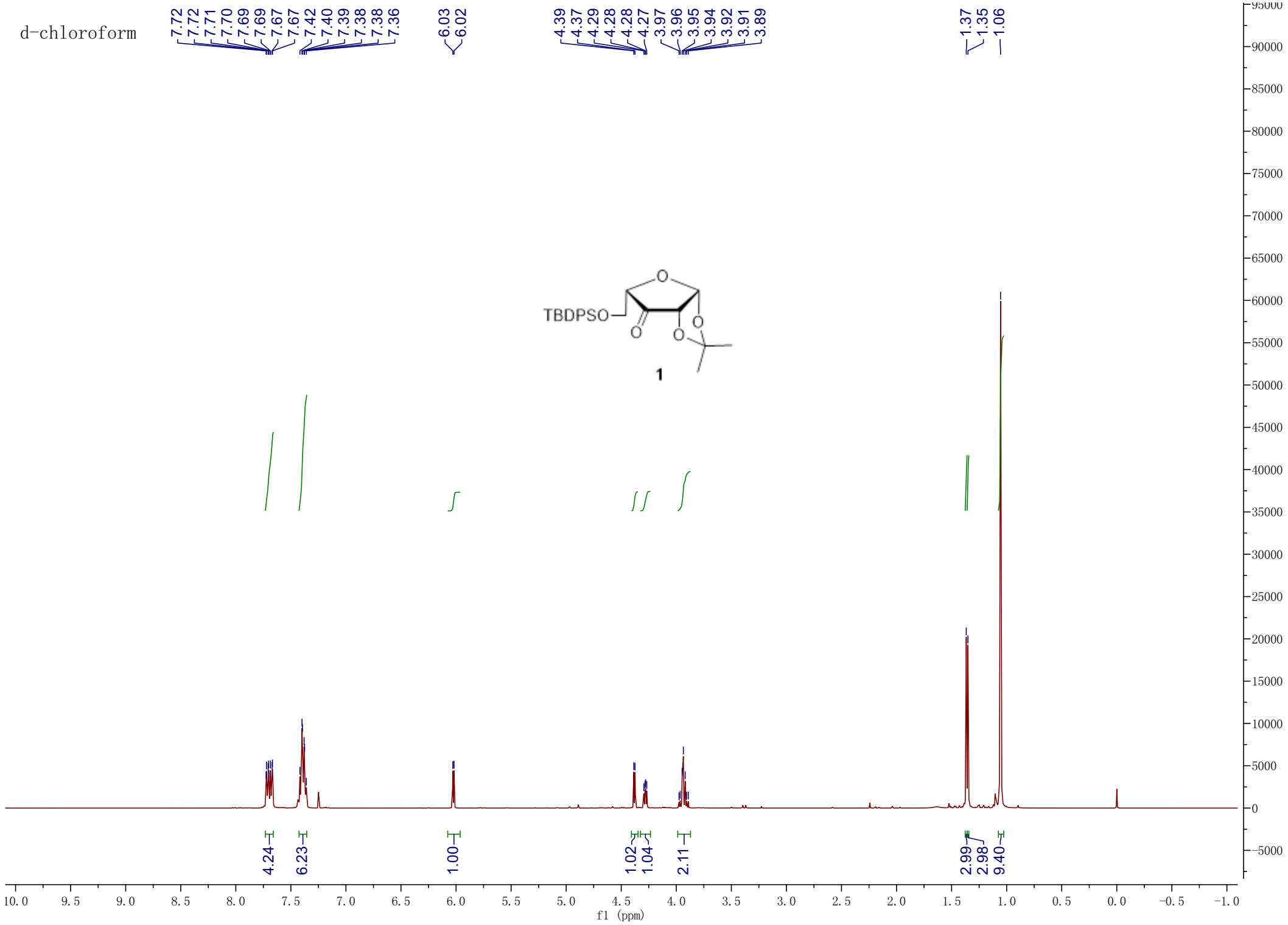
[S8] S. Thopate and G. Dhage, *Synlett,* 2017, **28**, 970-972.

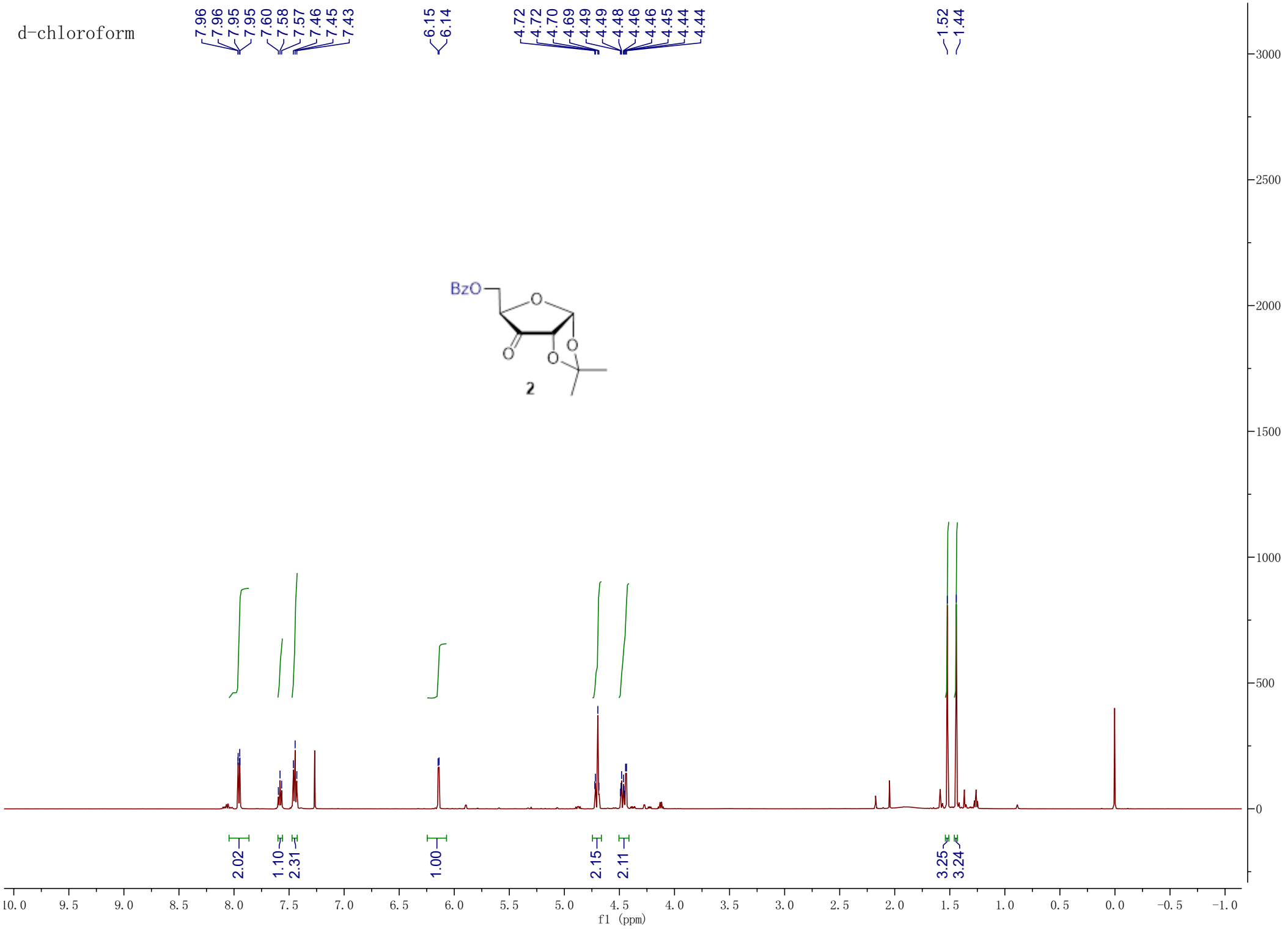
[S9] (a) Y.-F. Tsai, C.-C. Huang, S.-H. Lin, P.-M. Su, Y.-J. Chen and T.-Y. Wu, *Heterocycles,* 2012, **85**, 299; (b) Y. F. Wu, Y. F. Tsai, J. R. Guo, C. P. Yu, H. M. Yu and C. C. Liao, *Org. Biomol. Chem.,* 2014, **12**, 9345-9349.

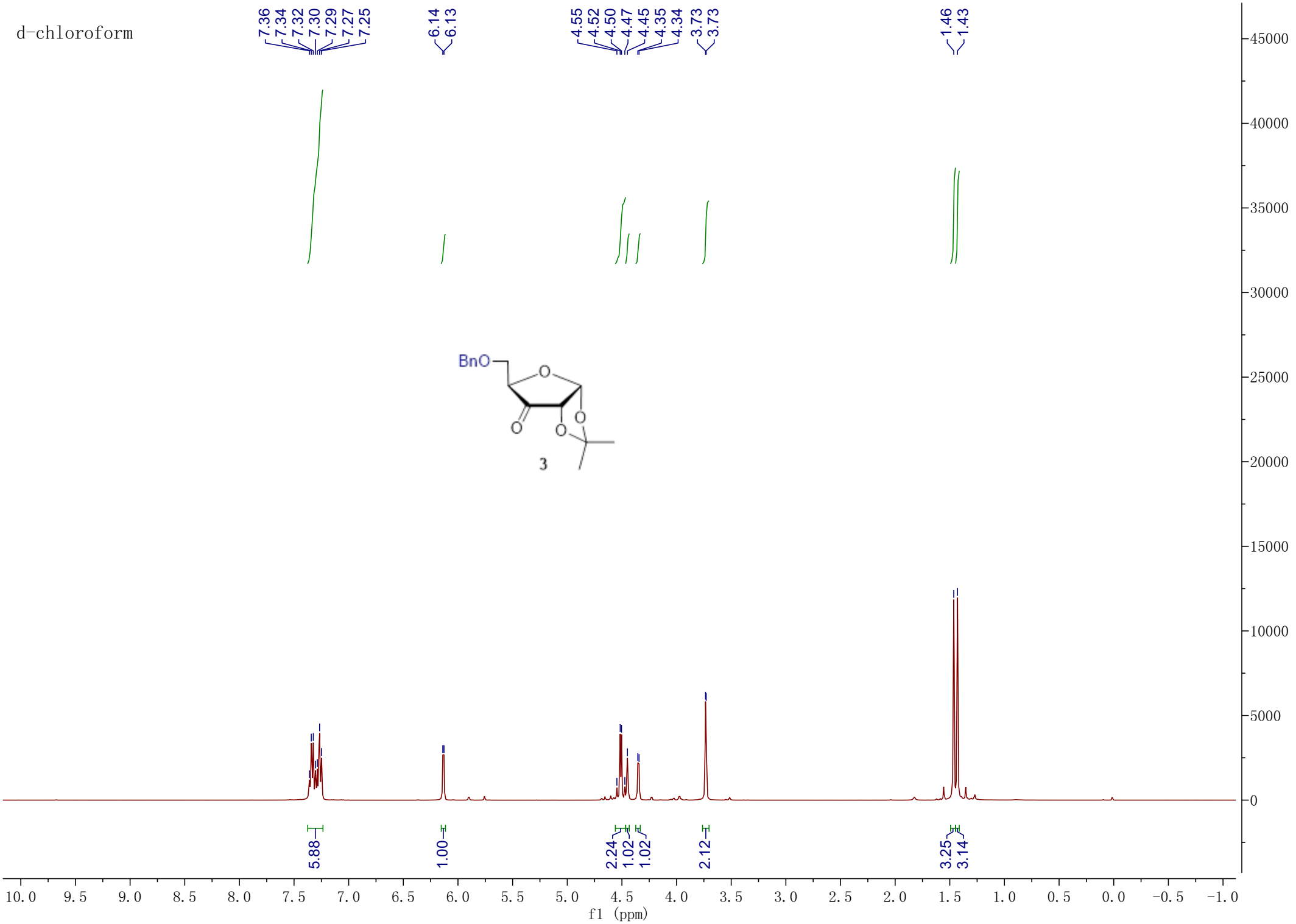
[S10] (a) C. Bello, M. Cea, G. D. Bello, A. Garuti, I. Rocco, G. Cirmena, E. Moran, A. Nahimana, M. A. Duchosal, F. Fruscione, P. Pronzato, F. Grossi, F. Patrone, A. Ballestrero, M. Dupuis, B. Sordat, A. Nencioni and P. Vogel, *Bioorg. Med. Chem.,* 2010, **18**, 3320-3334; (b) J. Hoberg, J. Singleton and K. Sahteli, *Synthesis,* 2008, **22**, 3682-3686.

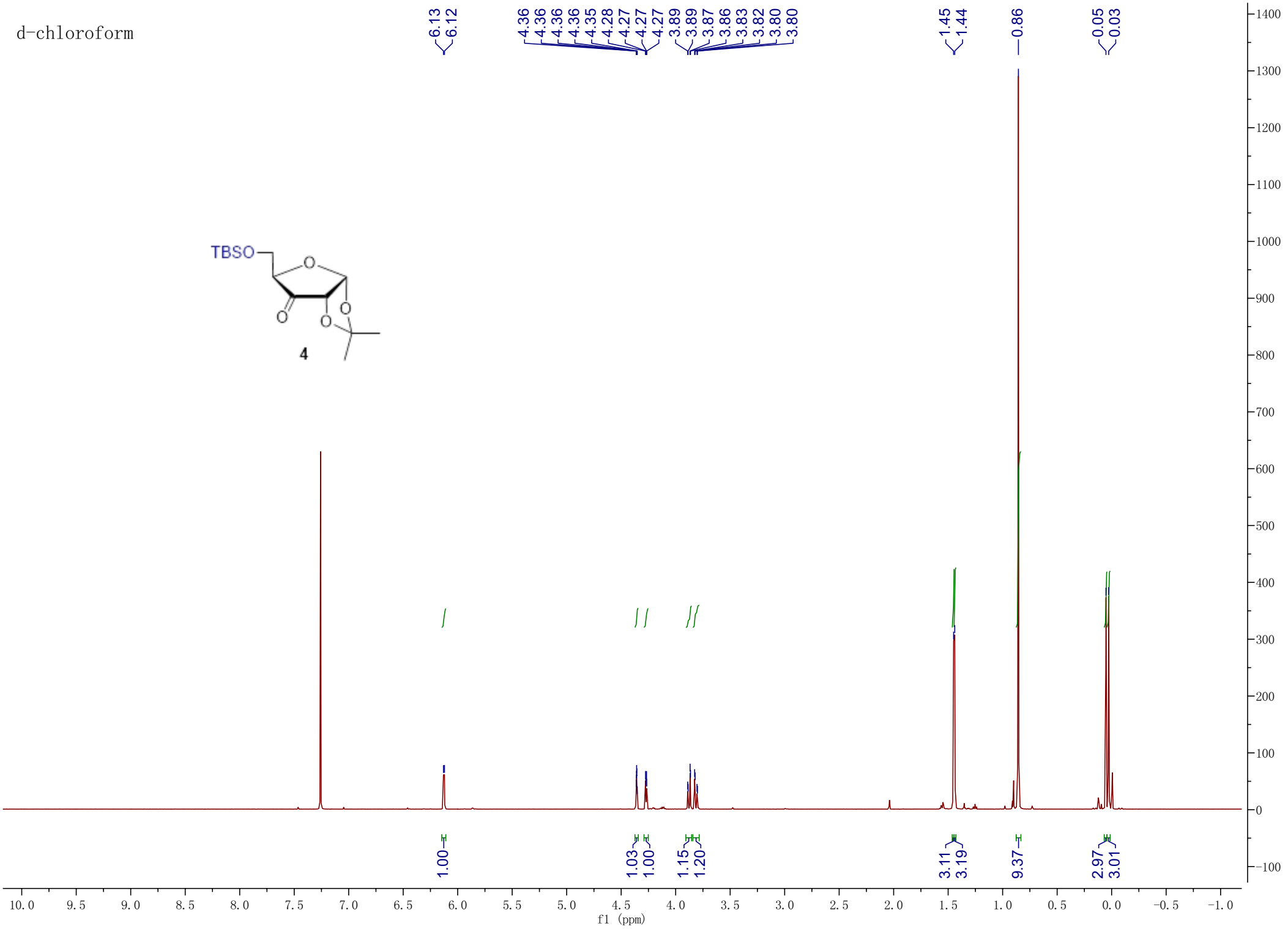
[S11] S. Wang, J. Sun, Q. Zhang, X. Cao, Y. Zhao, G. Tang and B. Yu, *Angew. Chem. Int. Ed. Engl.*, 2018, **57**, 2884-2888.

[S12] R. Csuk, M. Schaade and A. Schmidt, *Tetrahedron*, 1994, **50**, 11885-11892.


d-chloroform
7.72
7.72
7.71
7.70
7.69
7.69
7.67
7.67
7.42
7.40
7.39
7.38
7.38
7.36
6.03
6.02
4.39
4.37
4.29
4.28
4.28
4.27
3.97
3.96
3.95
3.94
3.92
3.91
3.89
1.37
1.35
1.06
TBDPSO
O
O
O
O
1
4.24
6.23
1.00
1.02
1.04
2.11
2.99
2.98
9.40
f1 (ppm)

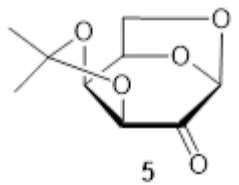

d-chloroform
7.96
7.96
7.95
7.95
7.60
7.58
7.57
7.46
7.45
7.43
6.15
6.14
4.72
4.72
4.70
4.69
4.49
4.49
4.48
4.46
4.46
4.45
4.44
4.44
1.52
1.44
BzO
O
O
O
O
2
3000
2500
2000
1500
1000
500
0
2.02
1.10
2.31
1.00
2.15
2.11
3.25
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


d-chloroform
7.36
7.34
7.32
7.30
7.29
7.27
7.25
6.14
6.13
4.55
4.52
4.50
4.47
4.45
4.35
4.34
3.73
3.73
1.46
1.43
BnO
O
O
O
O
3
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
5.88
1.00
2.24
1.02
1.02
2.12
3.25
3.14
10.0
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
-0.5
-1.0
f1 (ppm)


d-chloroform
6.13
6.12
4.36
4.36
4.36
4.36
4.35
4.28
4.27
4.27
4.27
3.89
3.89
3.87
3.86
3.83
3.82
3.80
3.80
1.45
1.44
0.86
0.05
0.03
TBSO
O
O
O
O
4
1.00
1.03
1.00
1.15
1.20
3.11
3.19
9.37
2.97
3.01
f1 (ppm)

d-chloroform

5.17
4.79
4.78
4.77
4.75
4.74
4.44
4.42
4.24
4.23
3.76
3.75
3.73
1.51
1.36

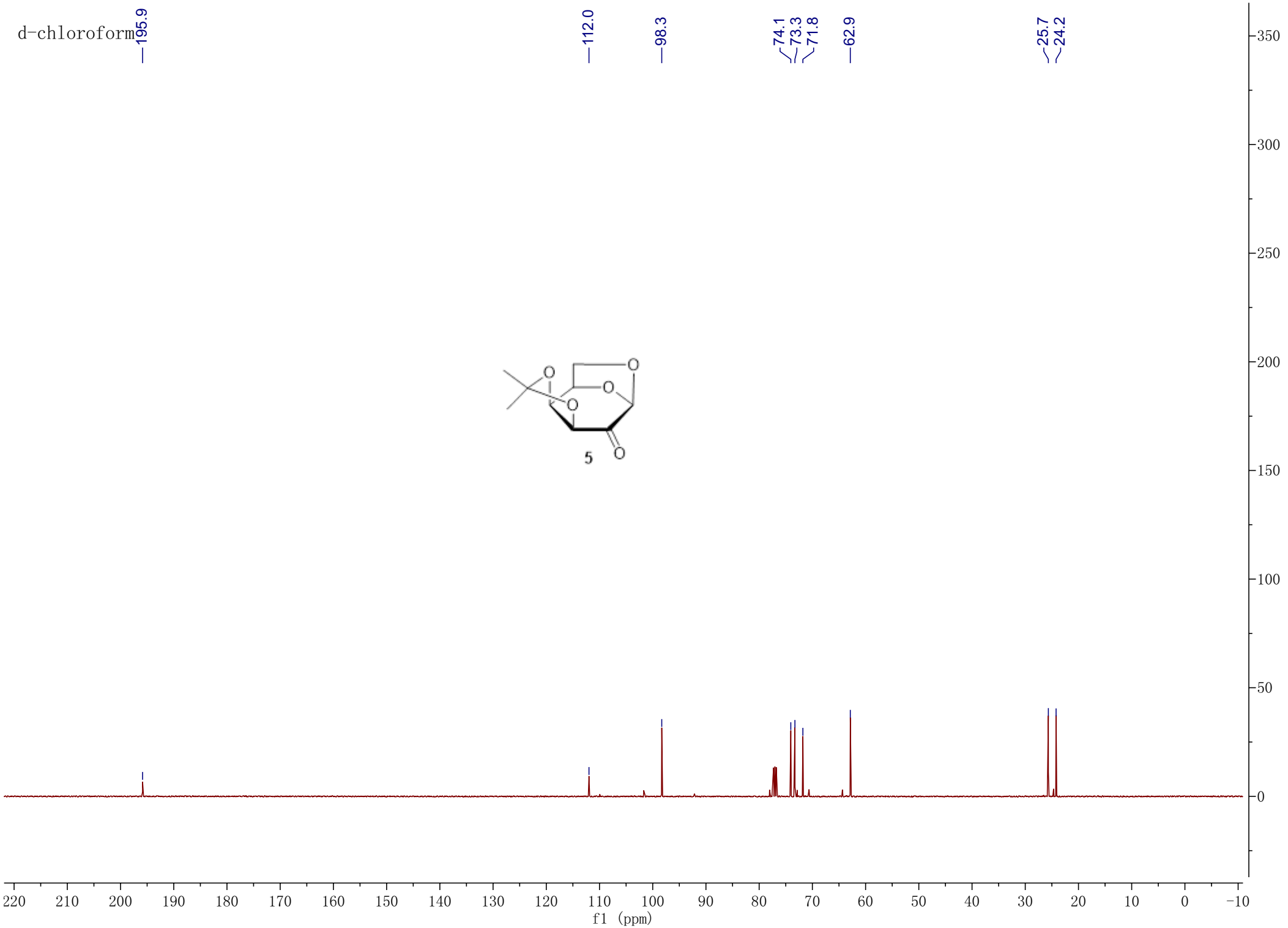


5

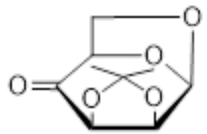
0.92
2.07
1.03
1.12
1.14
3.00
3.14

f1 (ppm)


d-chloroform
O
O
O
O
O
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
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

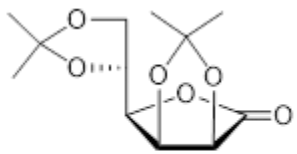

d-chloroform
195.9
112.0
98.3
74.1
73.3
71.8
62.9
25.7
24.2
O
O
O
O
O
5
350
300
250
200
150
100
50
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

d-chloroform

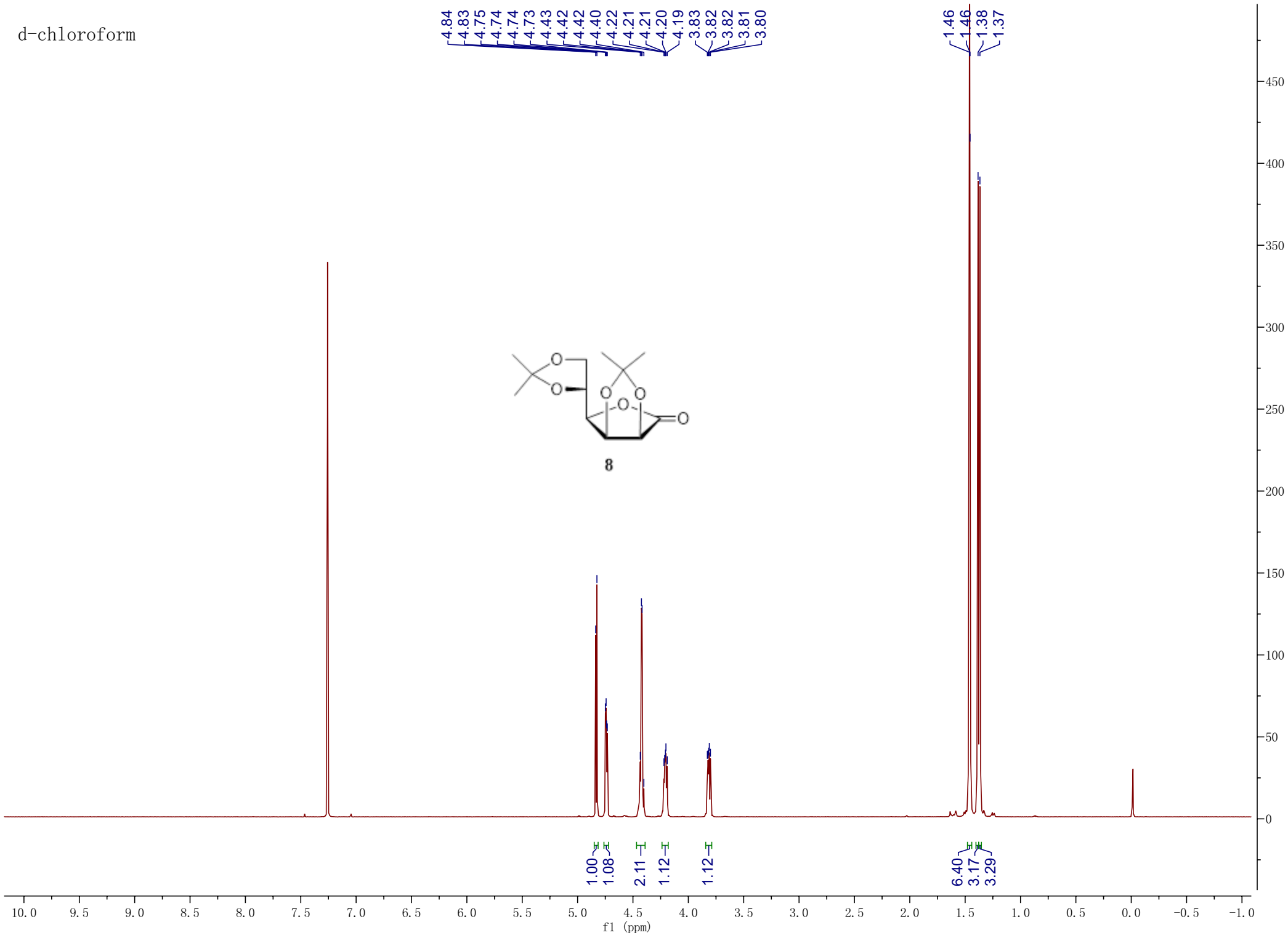


6

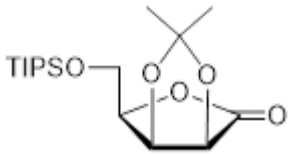
d-chloroform



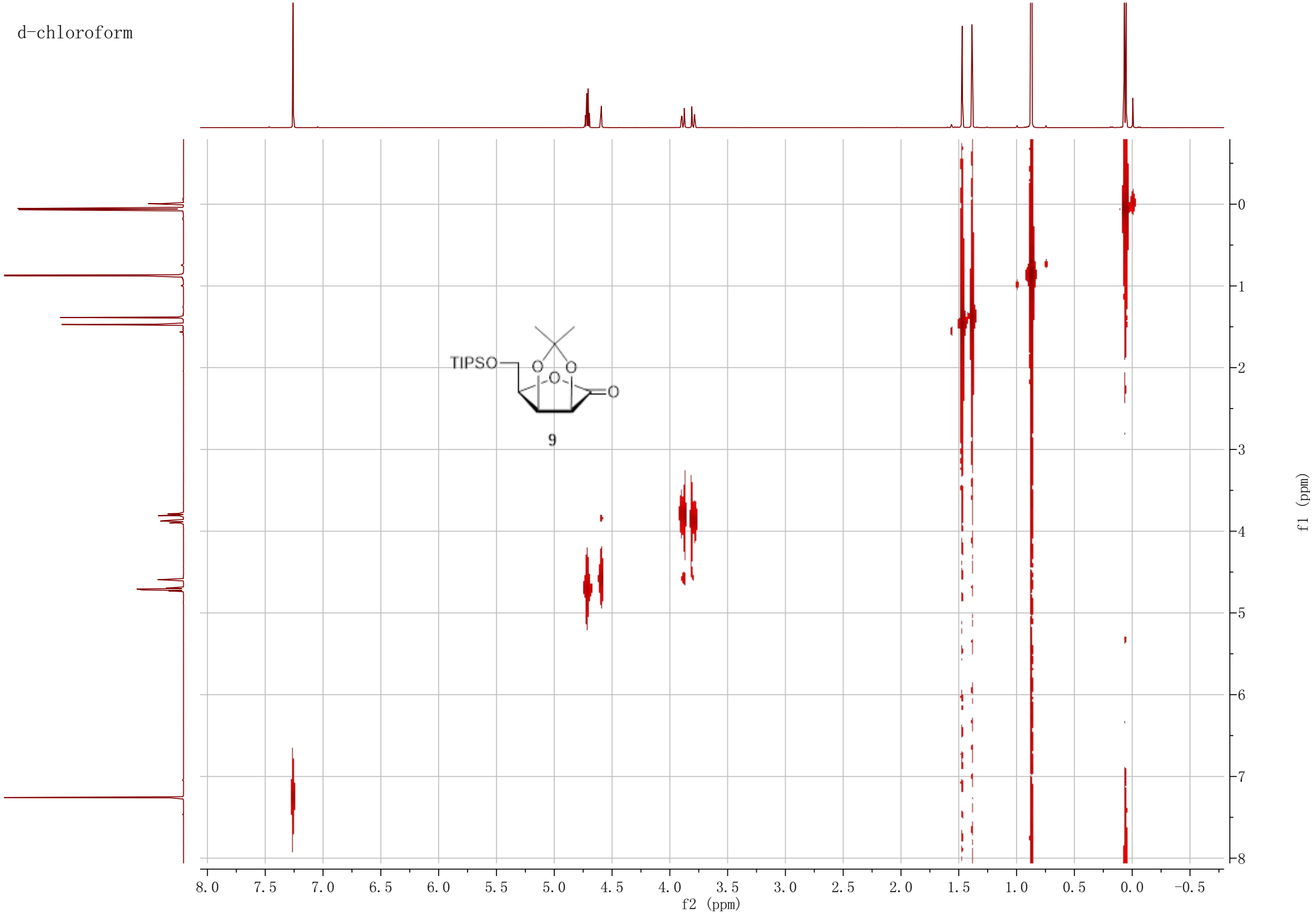
7


d-chloroform
4.84
4.83
4.75
4.74
4.74
4.73
4.43
4.42
4.42
4.40
4.22
4.21
4.21
4.20
4.19
3.83
3.82
3.82
3.81
3.80
1.46
1.46
1.38
1.37
8
1.00
1.08
2.11
1.12
1.12
6.40
3.17
3.29
f1 (ppm)

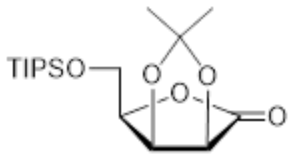
d-chloroform



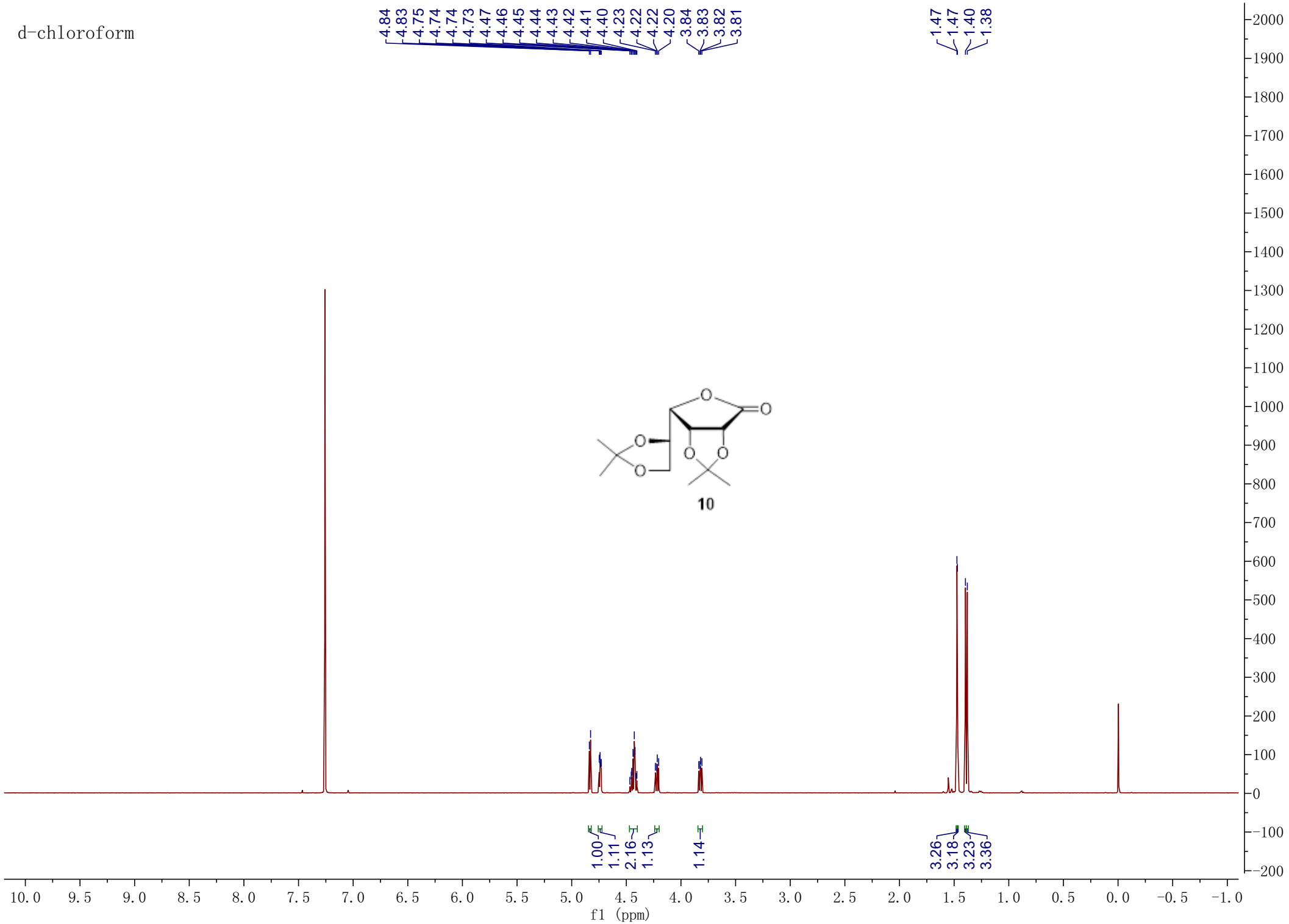
9

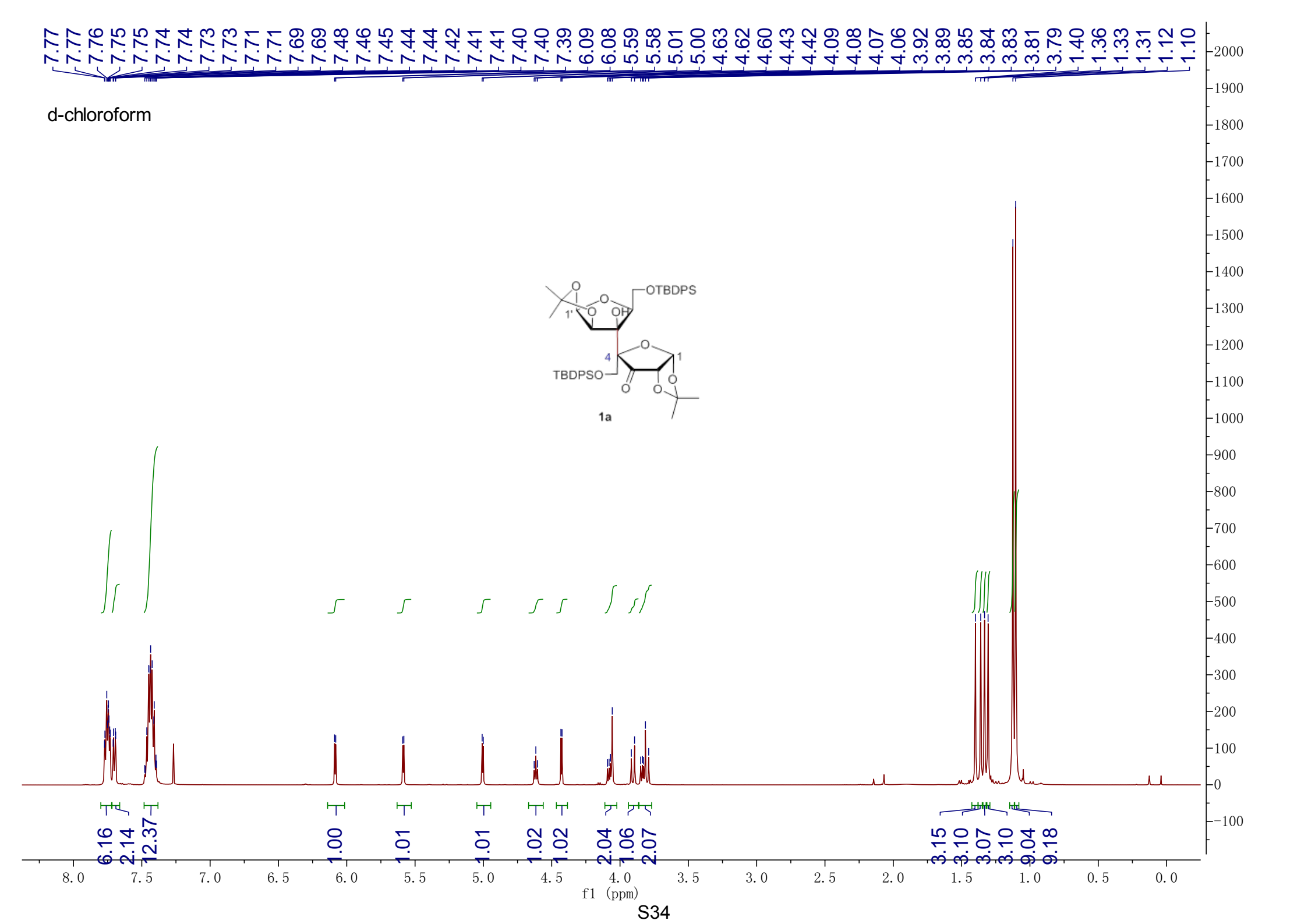

d-chloroform
TIPSO
O
O
O
O
9
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

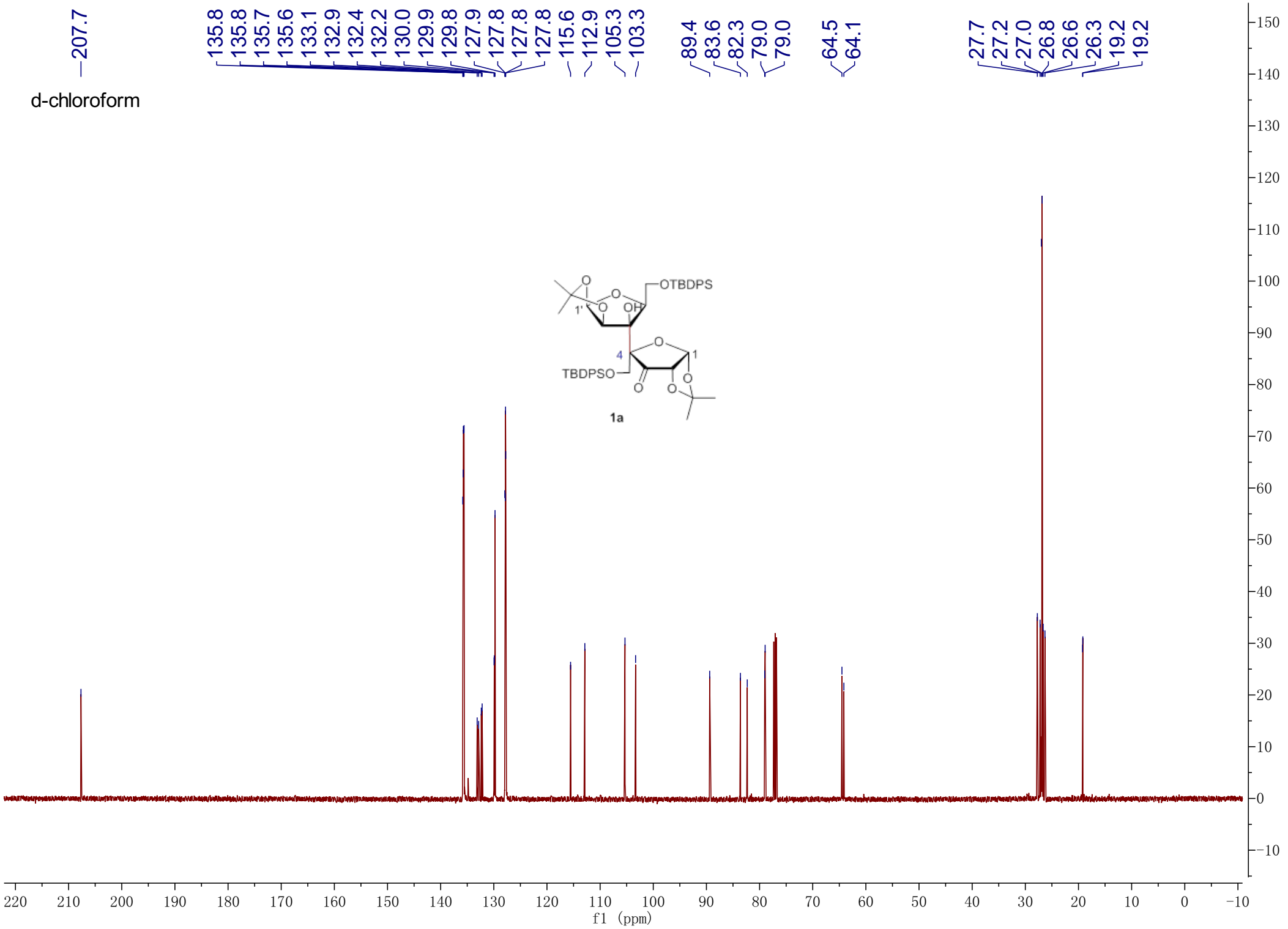
d-chloroform



9

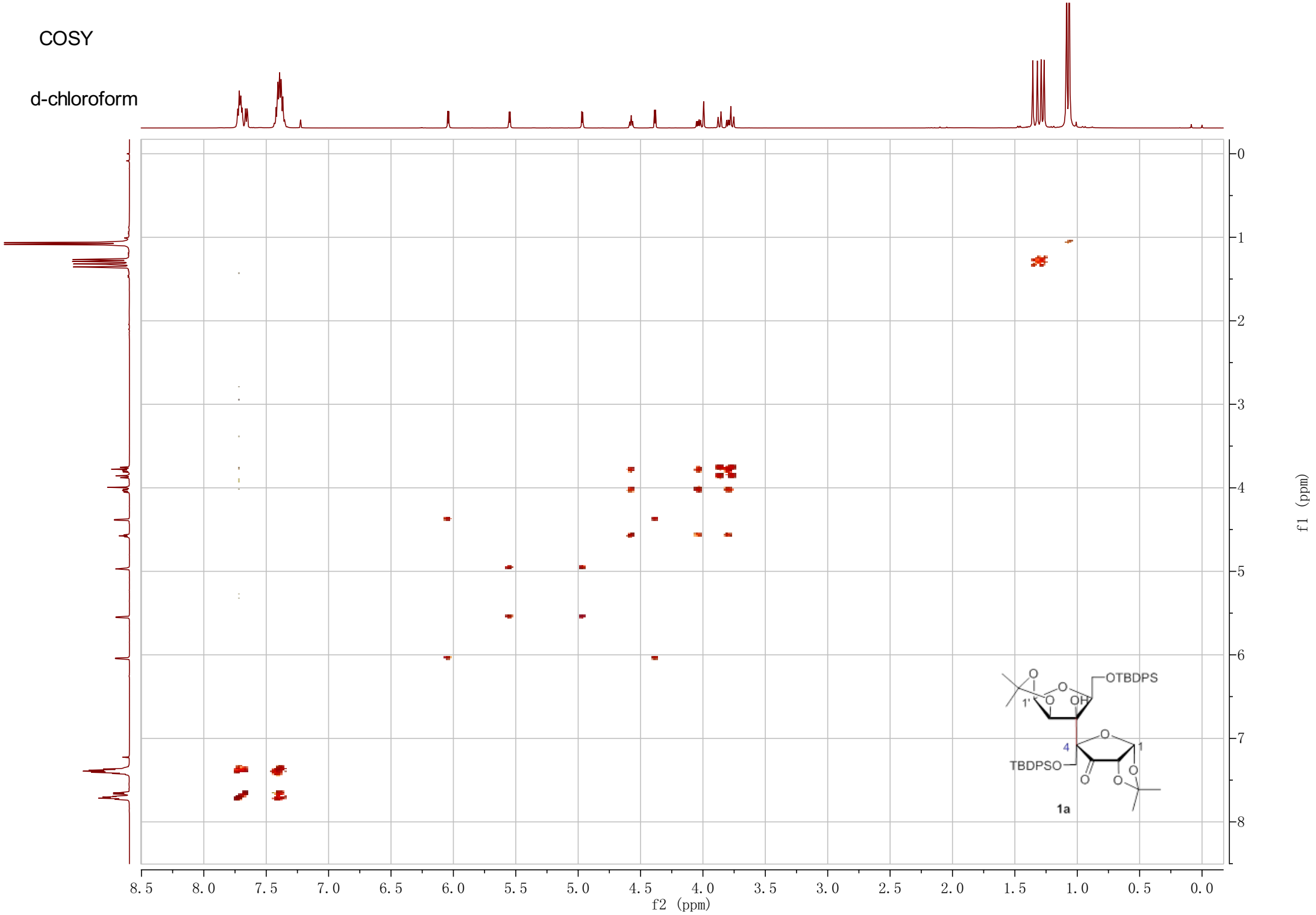

d-chloroform
4.84
4.83
4.75
4.74
4.74
4.73
4.47
4.46
4.45
4.44
4.43
4.42
4.41
4.40
4.23
4.22
4.22
4.20
3.84
3.83
3.82
3.81
1.47
1.47
1.40
1.38
10
1.00
1.11
2.16
1.13
1.14
3.26
3.18
3.23
3.36
f1 (ppm)

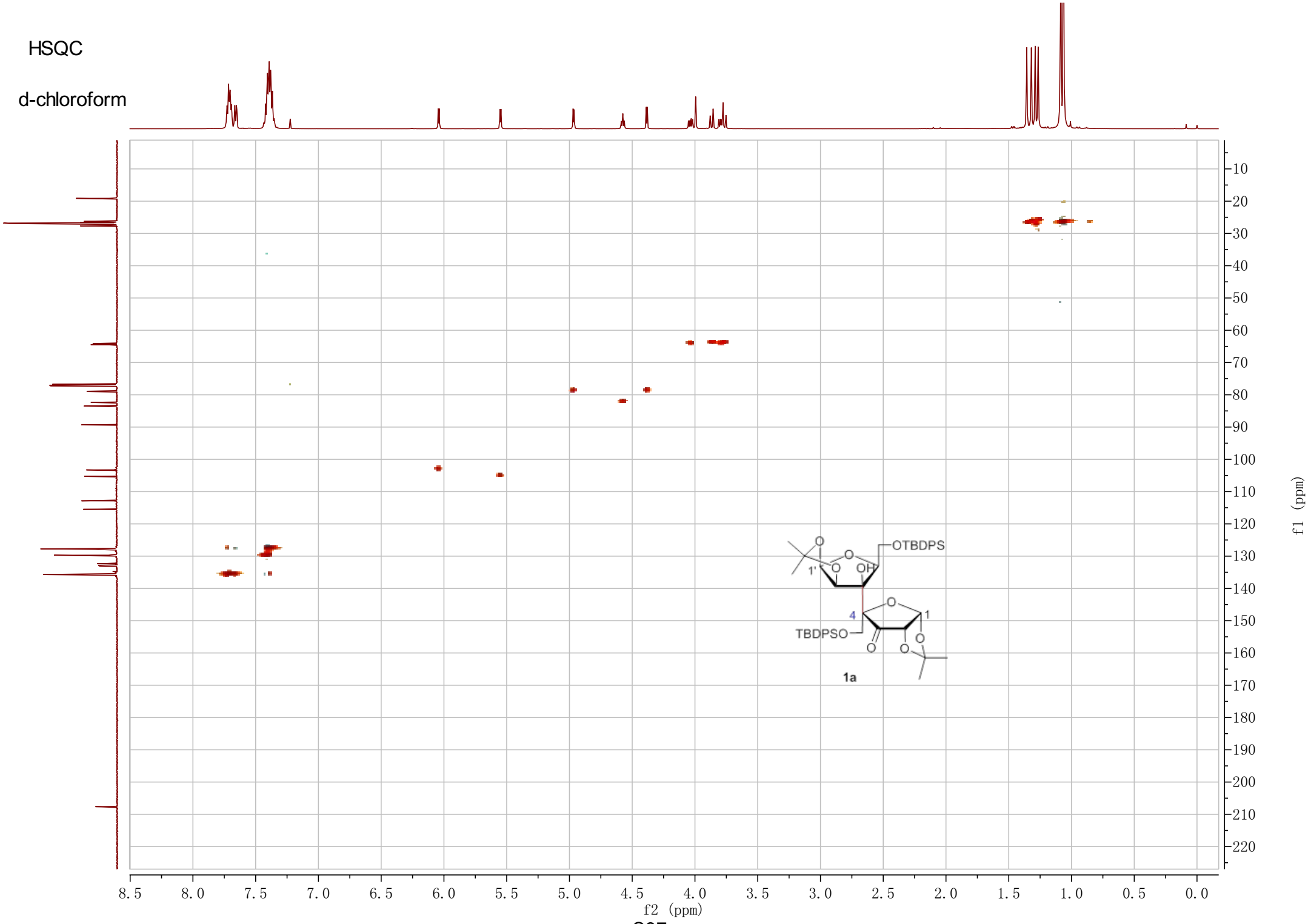

7.77 7.77 7.76 7.75 7.75 7.74 7.74 7.73 7.73 7.71 7.71 7.69 7.69 7.48 7.46 7.45 7.44 7.44 7.42 7.41 7.41 7.40 7.40 7.39 6.09 6.08 5.59 5.58 5.01 5.00 4.63 4.62 4.60 4.43 4.42 4.09 4.08 4.07 4.06 3.92 3.89 3.85 3.84 3.83 3.81 3.79 1.40 1.36 1.33 1.31 1.12 1.10
d-chloroform
OTBDPS
OH
TBDPSO
1a
6.16 2.14 12.37 1.00 1.01 1.01 1.02 1.02 2.04 1.06 2.07 3.15 3.10 3.07 3.10 9.04 9.18
f1 (ppm)


207.7
135.8
135.8
135.7
135.6
133.1
132.9
132.4
132.2
130.0
129.9
129.8
127.9
127.8
127.8
127.8
115.6
112.9
105.3
103.3
89.4
83.6
82.3
79.0
79.0
64.5
64.1
27.7
27.2
27.0
26.8
26.6
26.3
19.2
19.2
d-chloroform
OTBDPS
TBDPSO
OH
1'
4
1
1a
f1 (ppm)

COSY

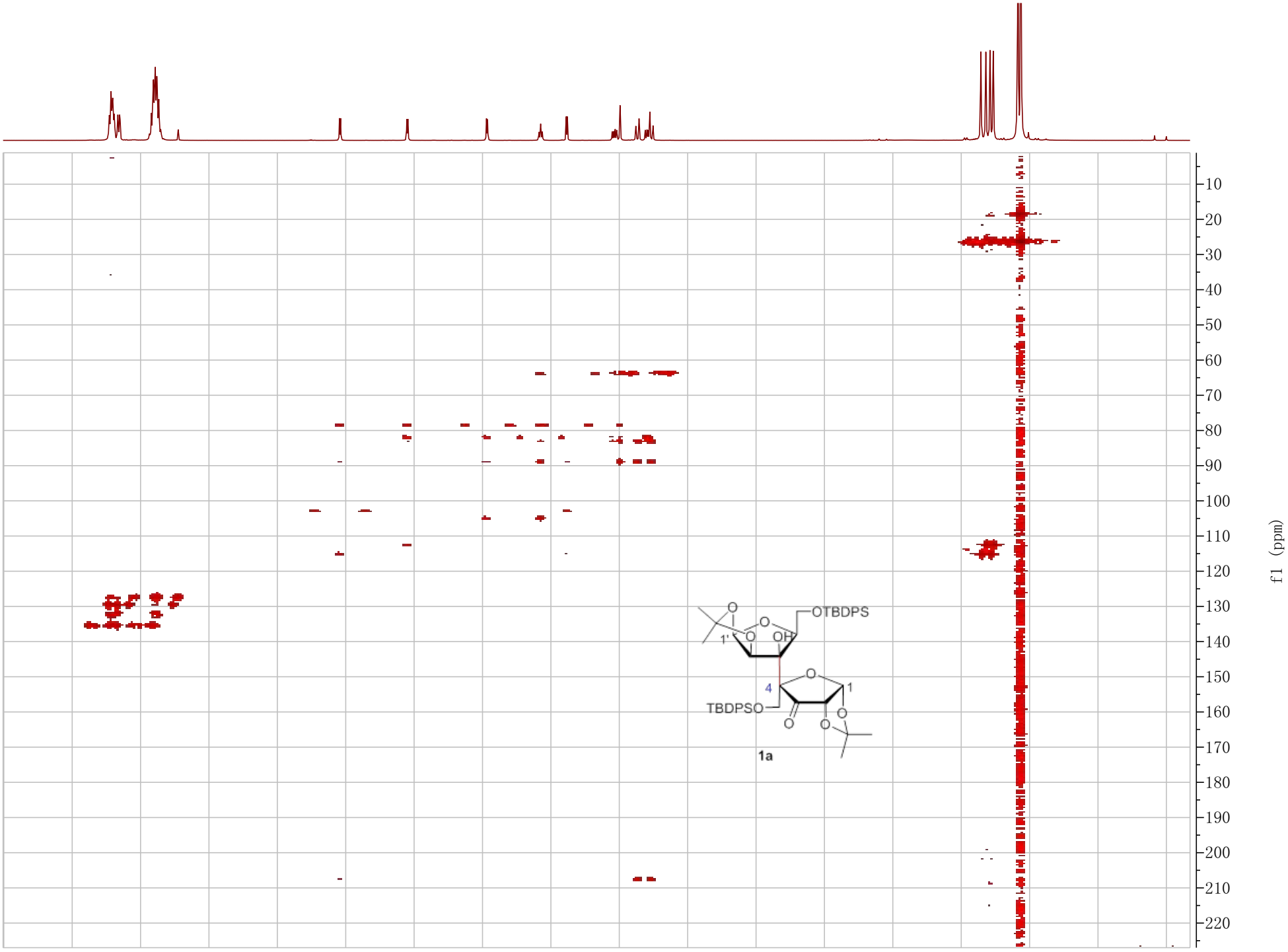
d-chloroform

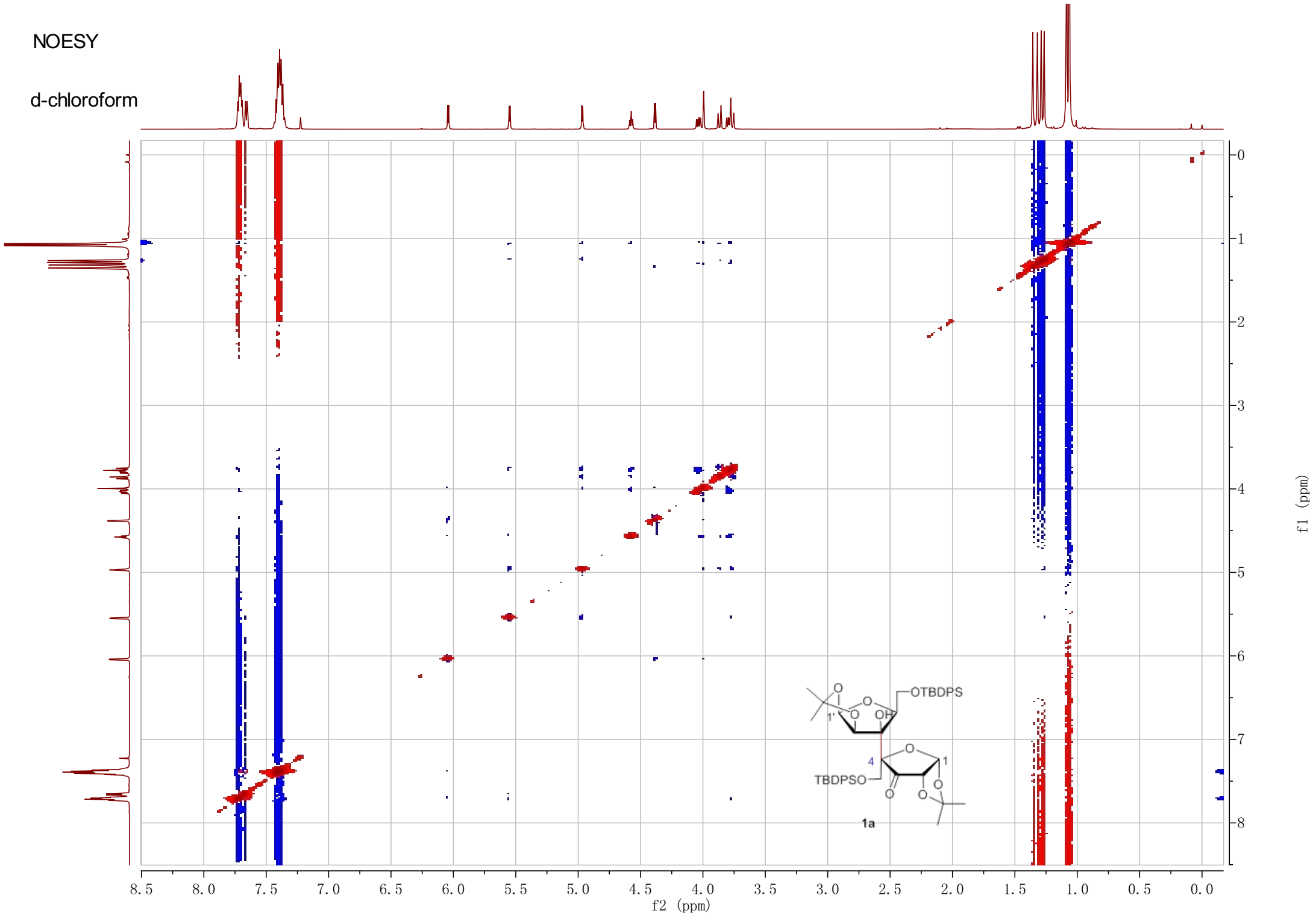



HSQC
d-chloroform
OTBDPS
OH
1'
4
1
TBDPSO
1a
f2 (ppm)
f1 (ppm)

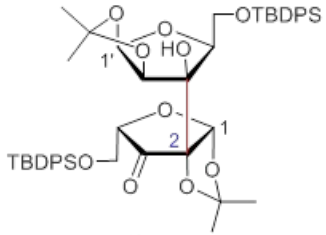
HMBC

d-chloroform



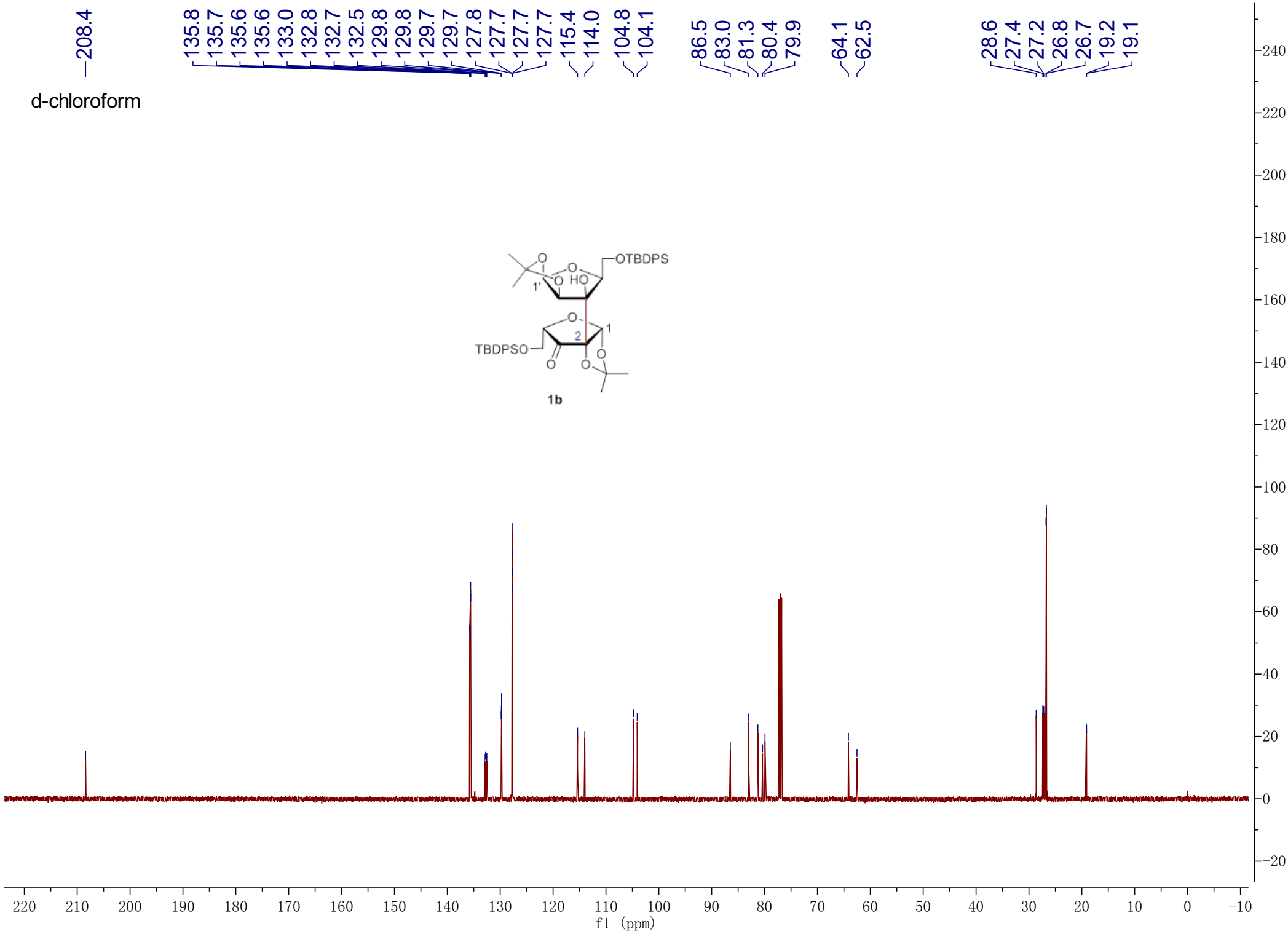

NOESY
d-chloroform
OTBDPS
OH
TBDPSO
1a
f2 (ppm)
f1 (ppm)

d-chloroform



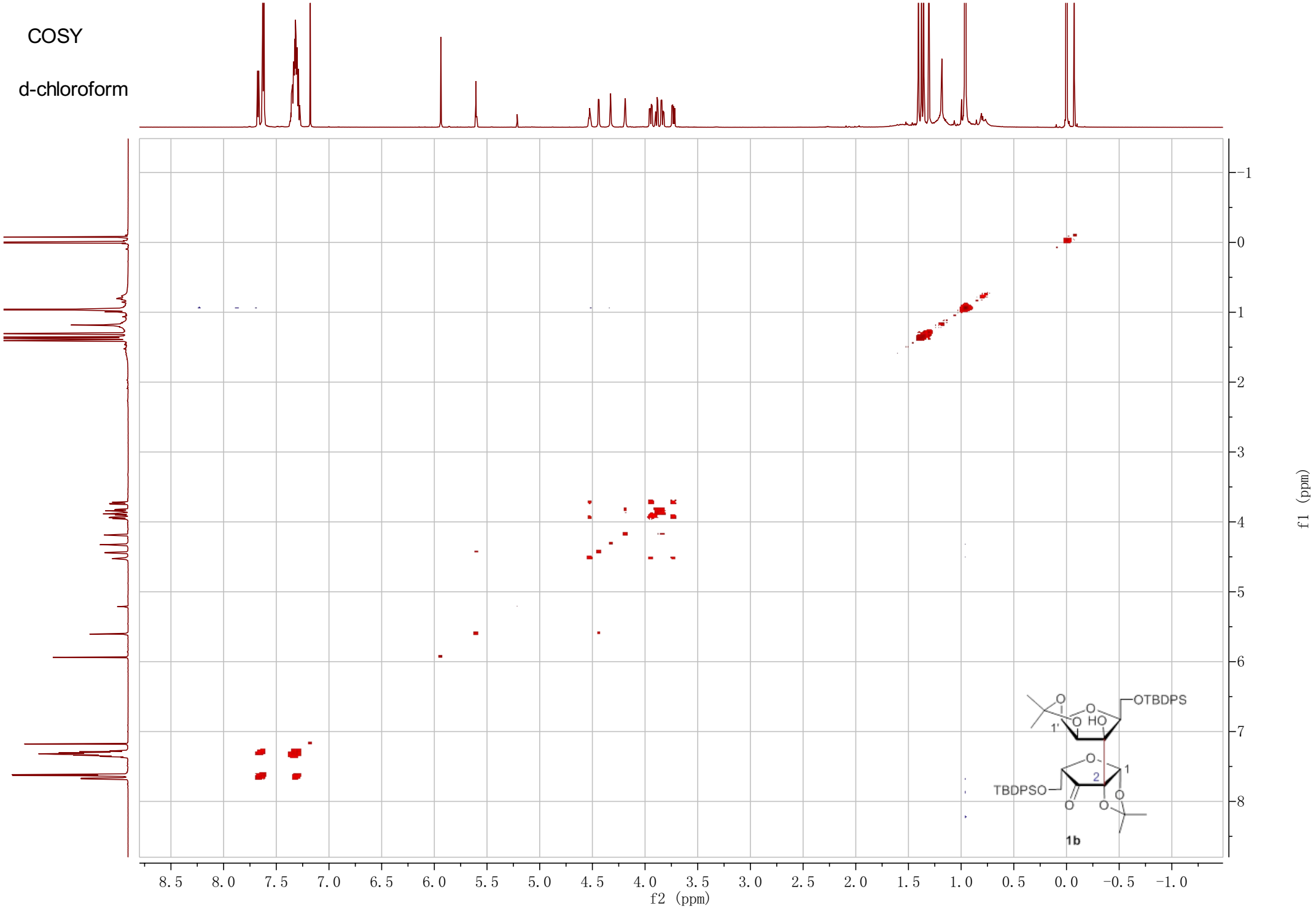
1b

f1 (ppm)


208.4
135.8
135.7
135.6
135.6
133.0
132.8
132.7
132.5
129.8
129.8
129.7
129.7
127.8
127.7
127.7
127.7
115.4
114.0
104.8
104.1
86.5
83.0
81.3
80.4
79.9
64.1
62.5
28.6
27.4
27.2
26.8
26.7
19.2
19.1
d-chloroform
OTBDPS
HO
TBDPSO
1'
1
2
1b
f1 (ppm)

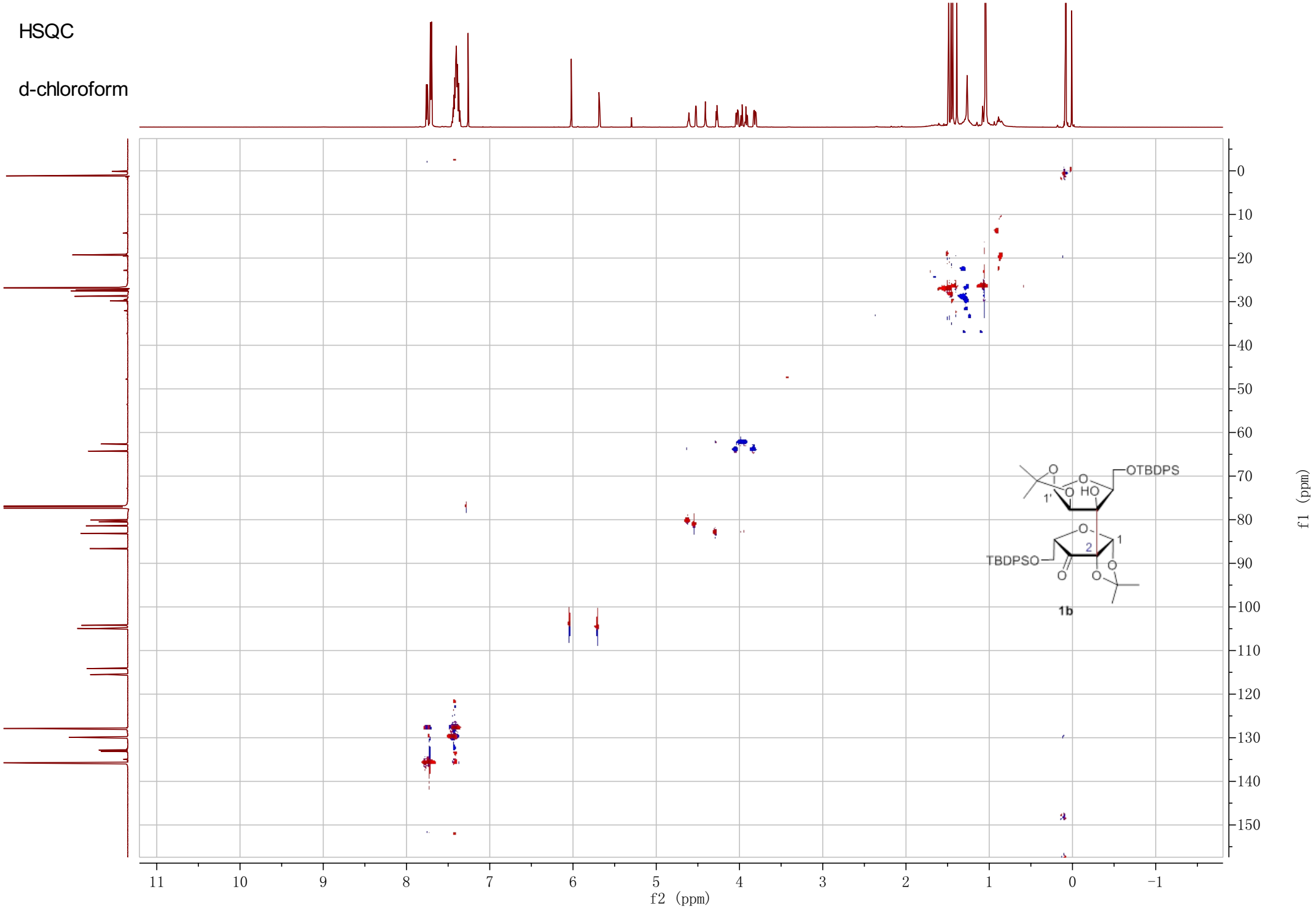
COSY

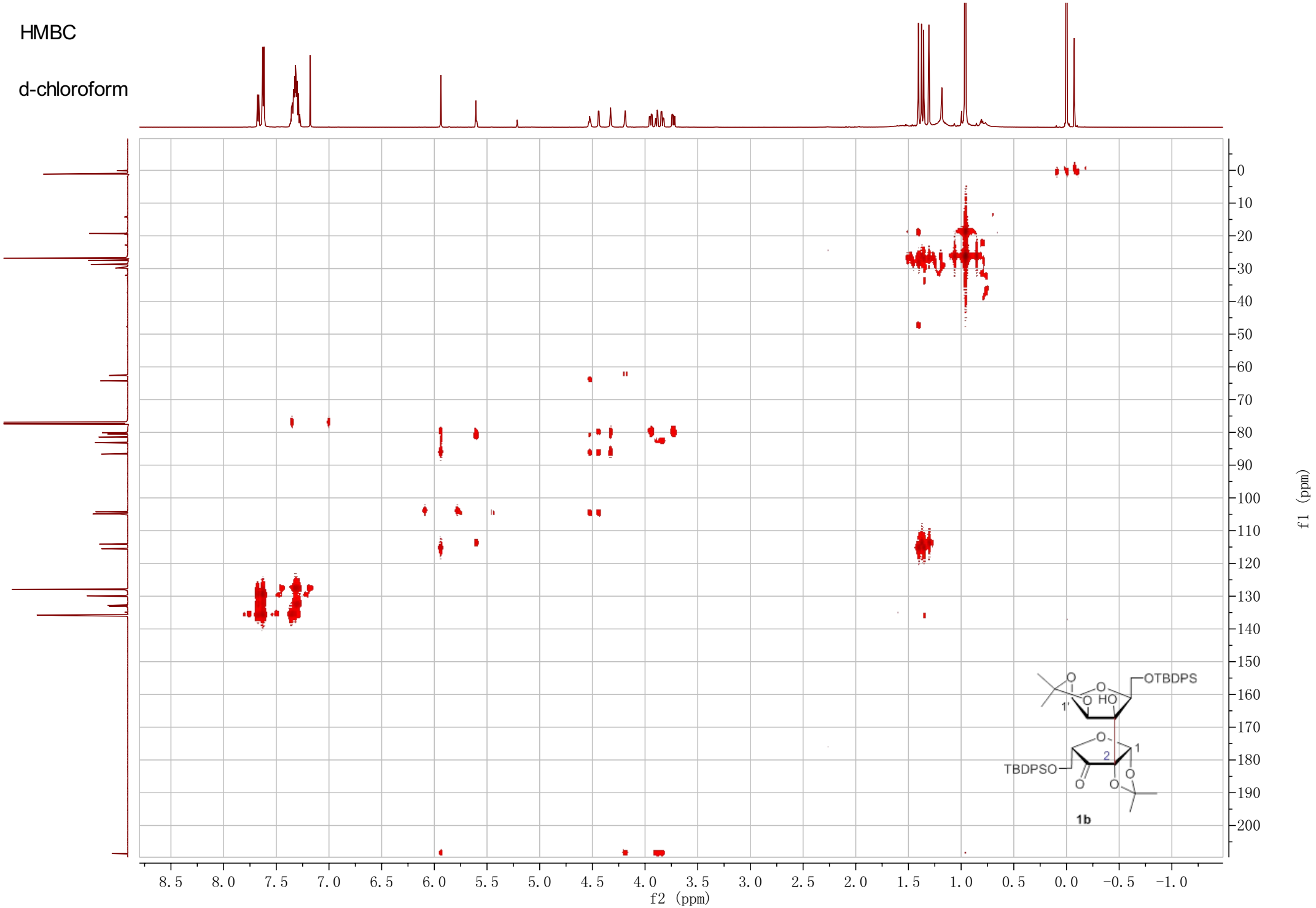
d-chloroform

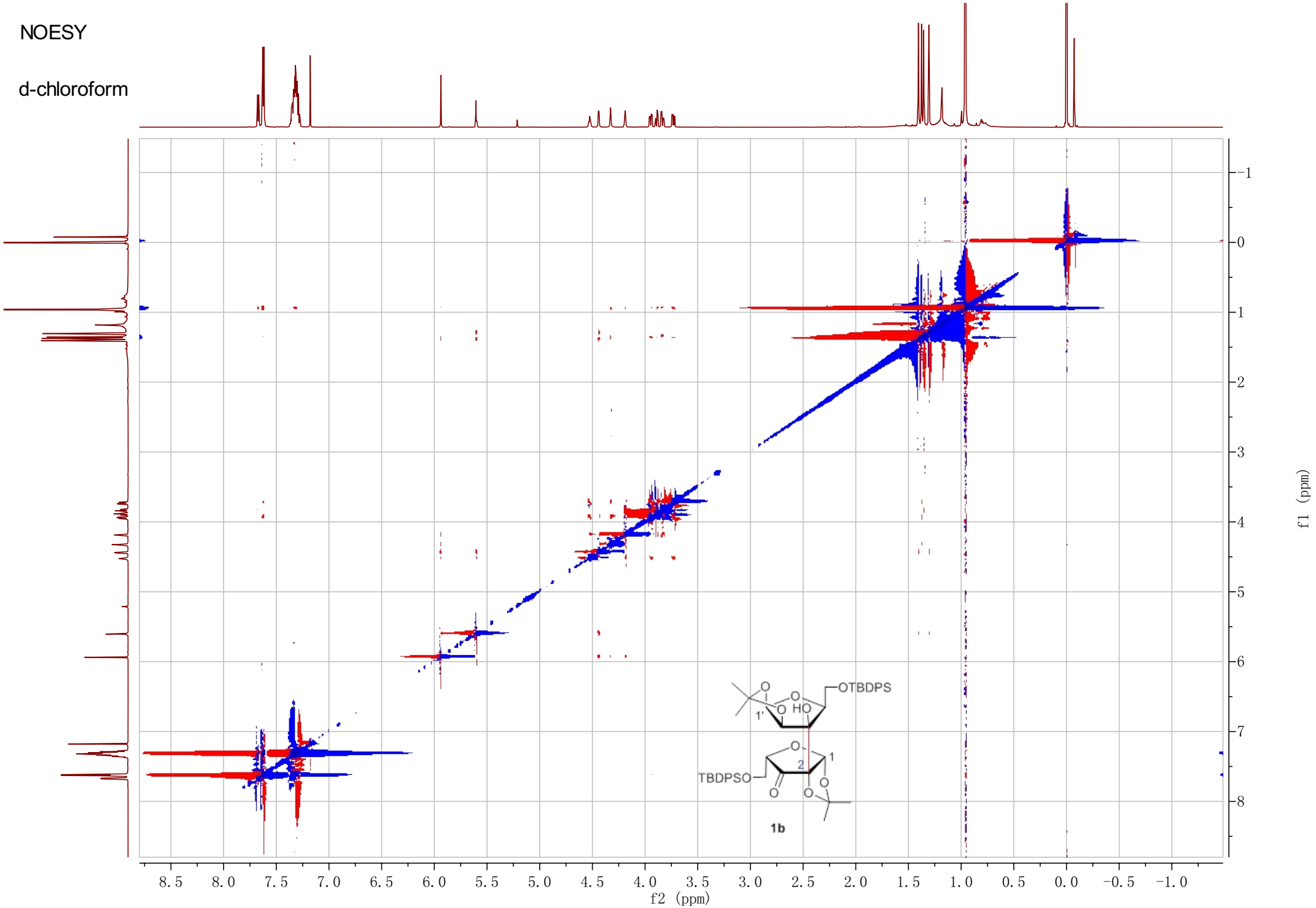


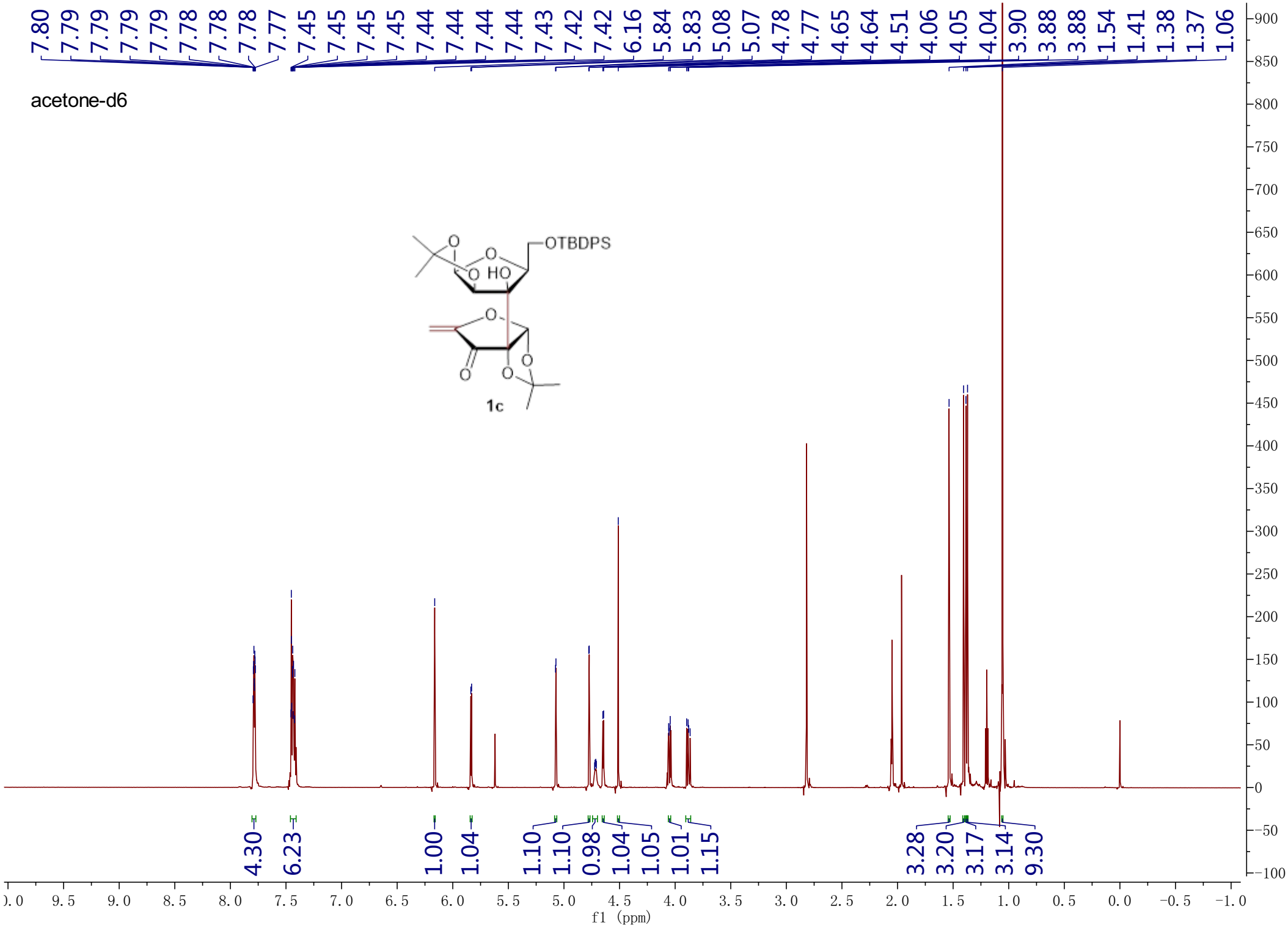
HSQC

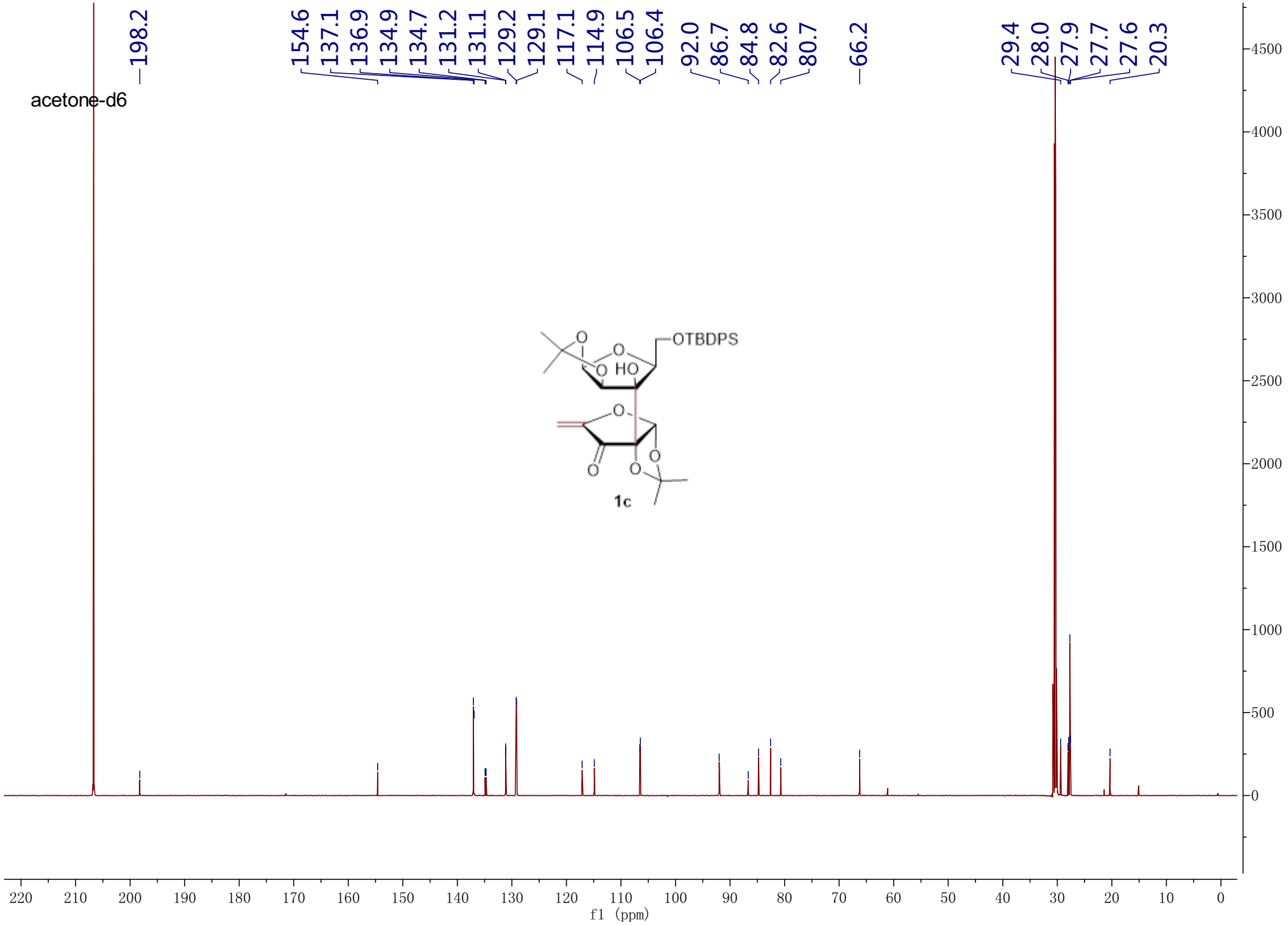
d-chloroform

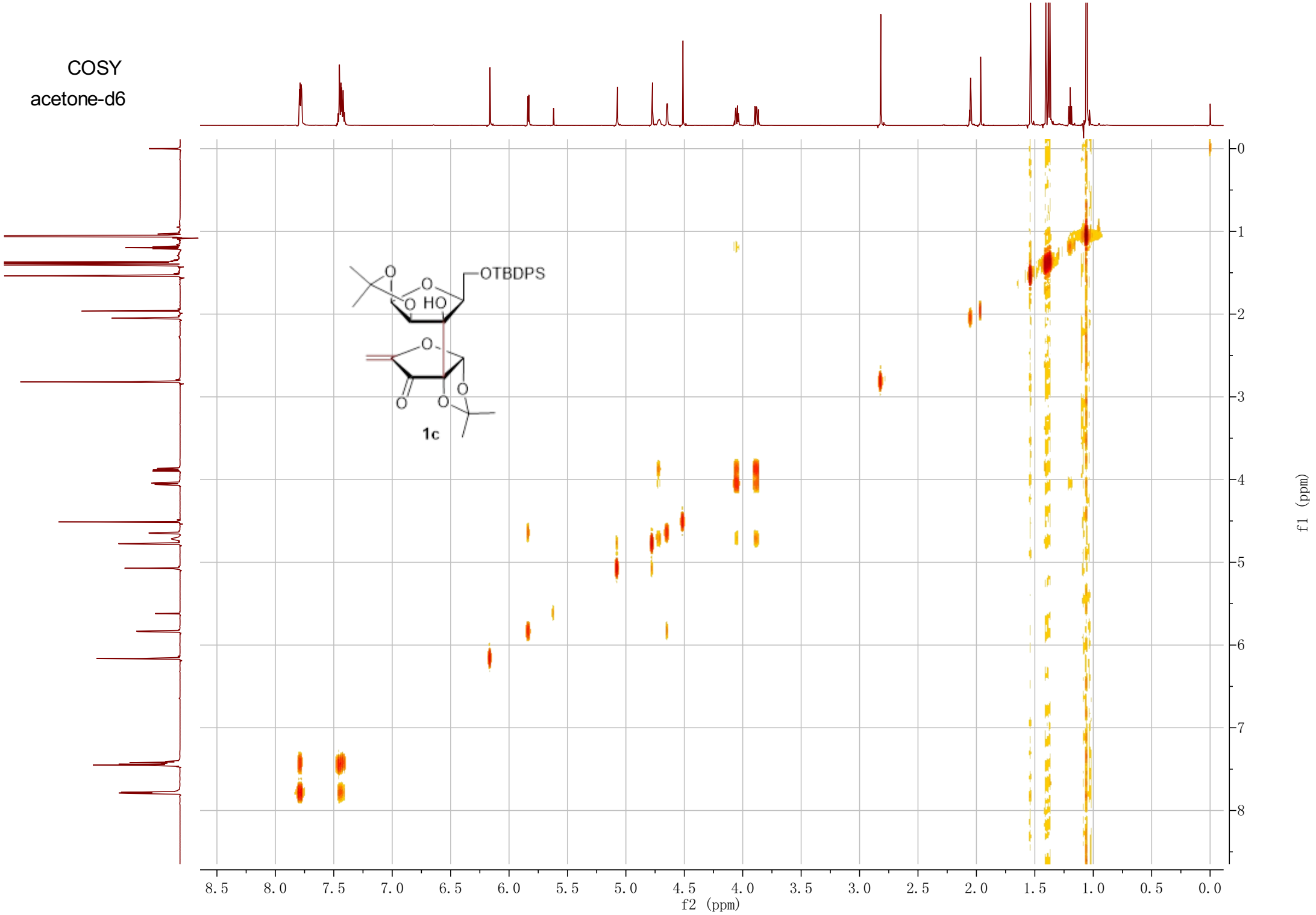


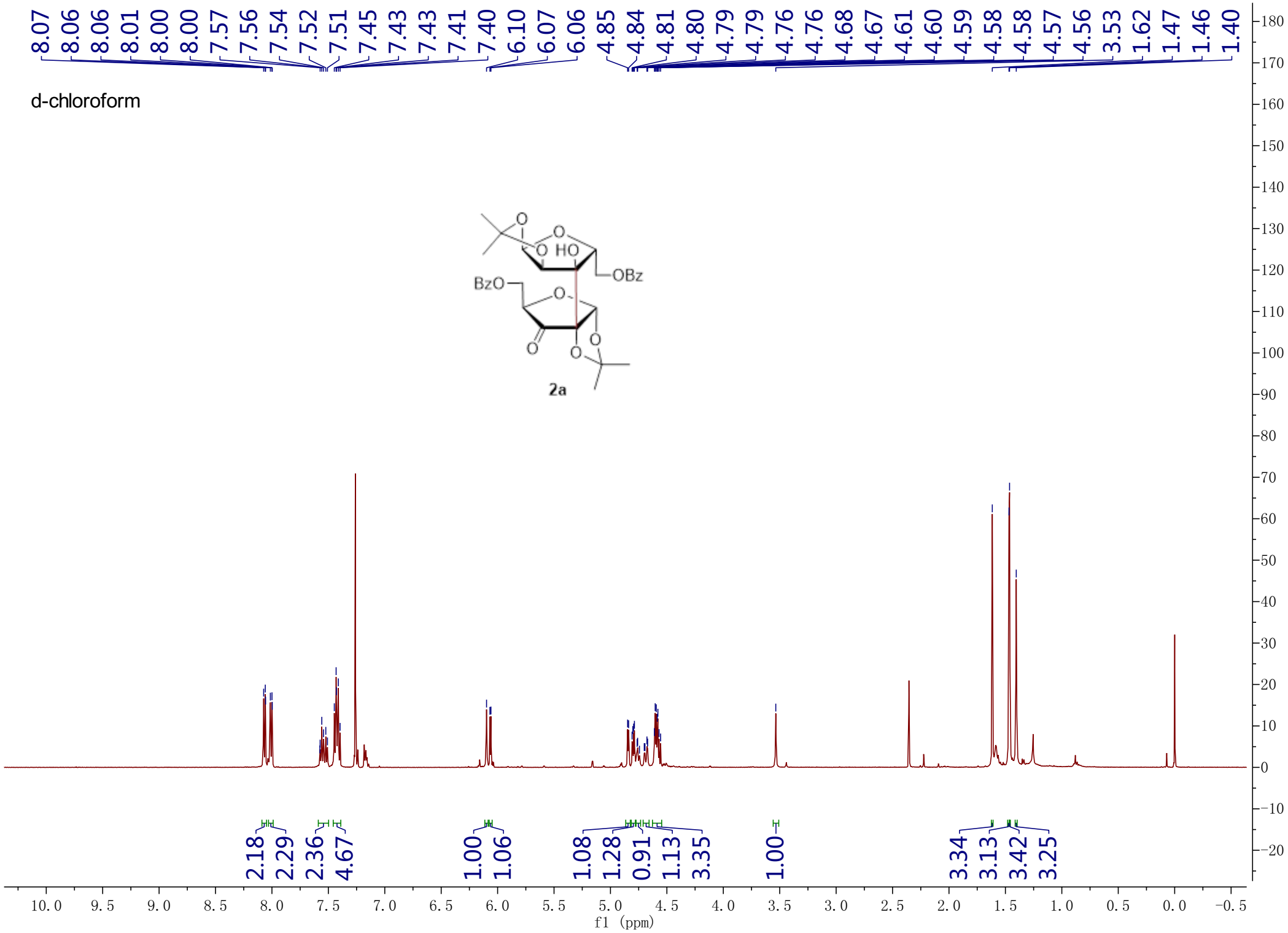

HMBC
d-chloroform
f2 (ppm)
f1 (ppm)
OTBDPS
HO
TBDPSO
1b

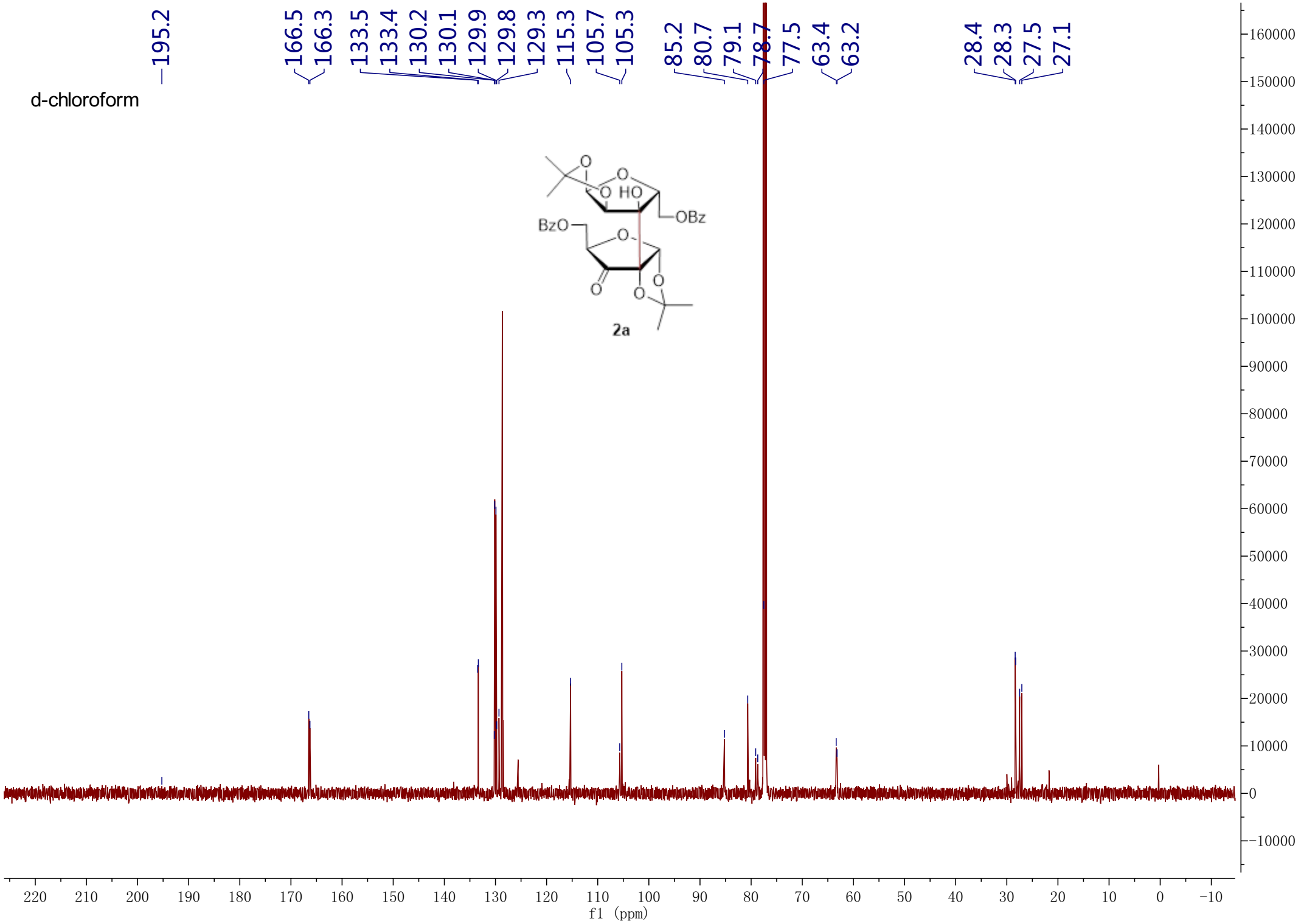

NOESY
d-chloroform
OTBDPS
HO
TBDPSO
1b
f2 (ppm)
f1 (ppm)


7.80 7.79 7.79 7.79 7.79 7.78 7.78 7.78 7.77 7.45 7.45 7.45 7.45 7.44 7.44 7.44 7.44 7.43 7.42 7.42 6.16 5.84 5.83 5.08 5.07 4.78 4.77 4.65 4.64 4.51 4.06 4.05 4.04 3.90 3.88 3.88 1.54 1.41 1.38 1.37 1.06
acetone-d6
OTBDPS
HO
1c
4.30 6.23 1.00 1.04 1.10 1.10 0.98 1.04 1.05 1.01 1.15 3.28 3.20 3.17 3.14 9.30
f1 (ppm)


198.2
154.6
137.1
136.9
134.9
134.7
131.2
131.1
129.2
129.1
117.1
114.9
106.5
106.4
92.0
86.7
84.8
82.6
80.7
66.2
29.4
28.0
27.9
27.7
27.6
20.3
acetone-d6
OTBDPS
HO
1c
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

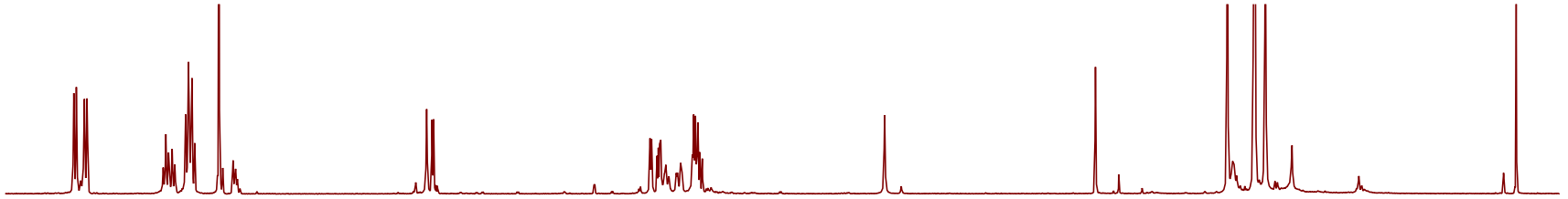

COSY
acetone-d6
OTBDPS
HO
1c
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

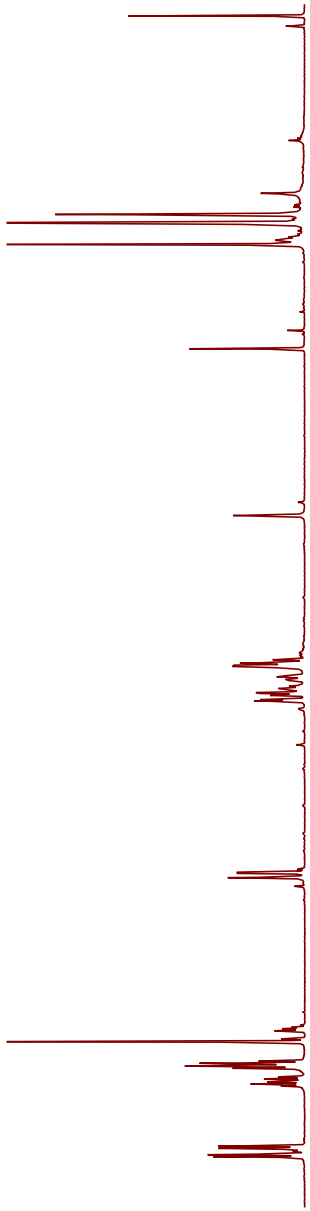

8.07
8.06
8.06
8.01
8.00
8.00
7.57
7.56
7.54
7.52
7.51
7.45
7.43
7.43
7.41
7.40
6.10
6.07
6.06
4.85
4.84
4.81
4.80
4.79
4.79
4.76
4.76
4.68
4.67
4.61
4.60
4.59
4.58
4.58
4.57
4.56
3.53
1.62
1.47
1.46
1.40
d-chloroform
HO
OBz
BzO
2a
2.18
2.29
2.36
4.67
1.00
1.06
1.08
1.28
0.91
1.13
3.35
1.00
3.34
3.13
3.42
3.25
f1 (ppm)

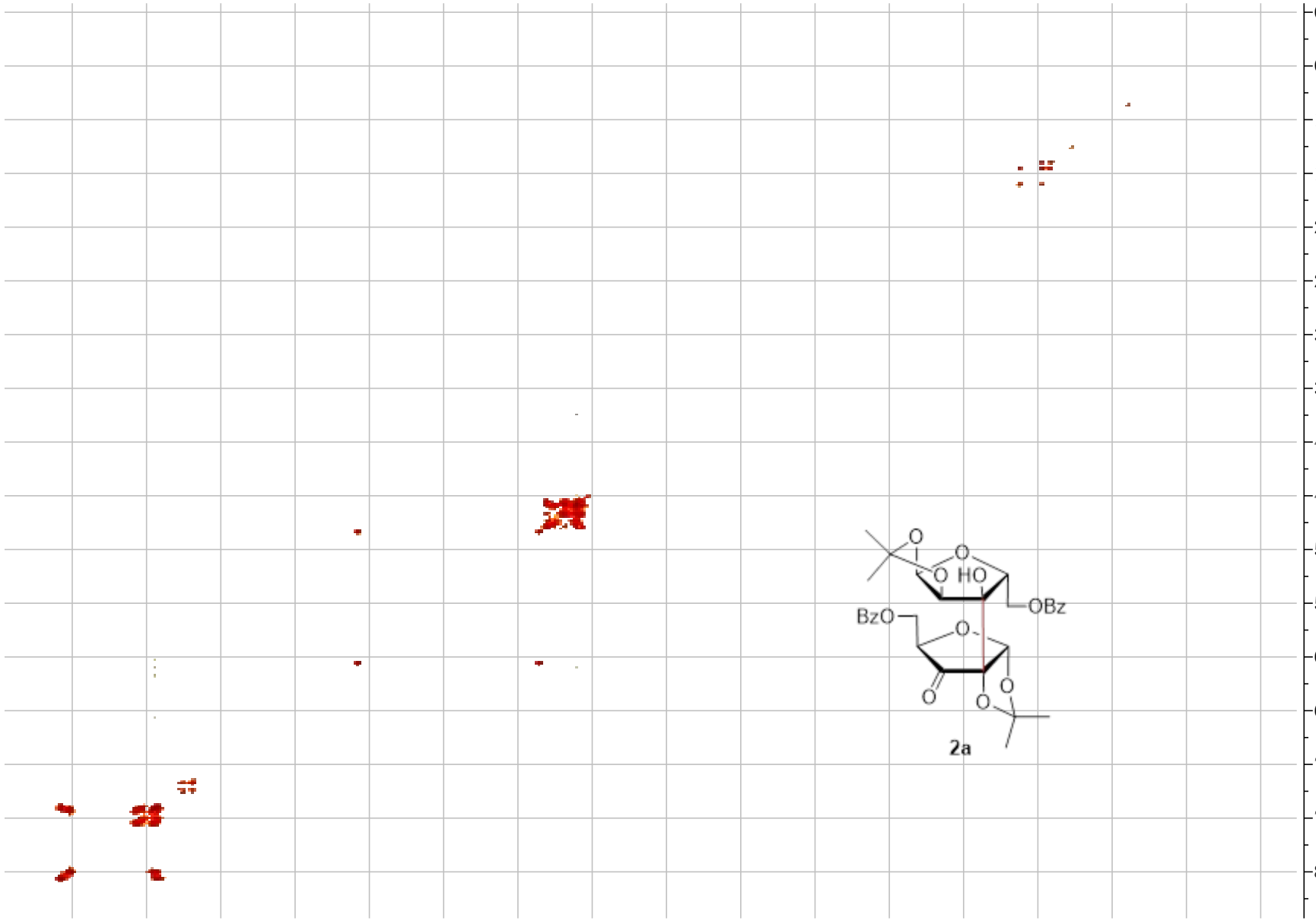

195.2
166.5
166.3
133.5
133.4
130.2
130.1
129.9
129.8
129.3
115.3
105.7
105.3
85.2
80.7
79.1
78.7
77.5
63.4
63.2
28.4
28.3
27.5
27.1
d-chloroform
BzO
OBz
HO
2a
f1 (ppm)

COSY

d-chloroform



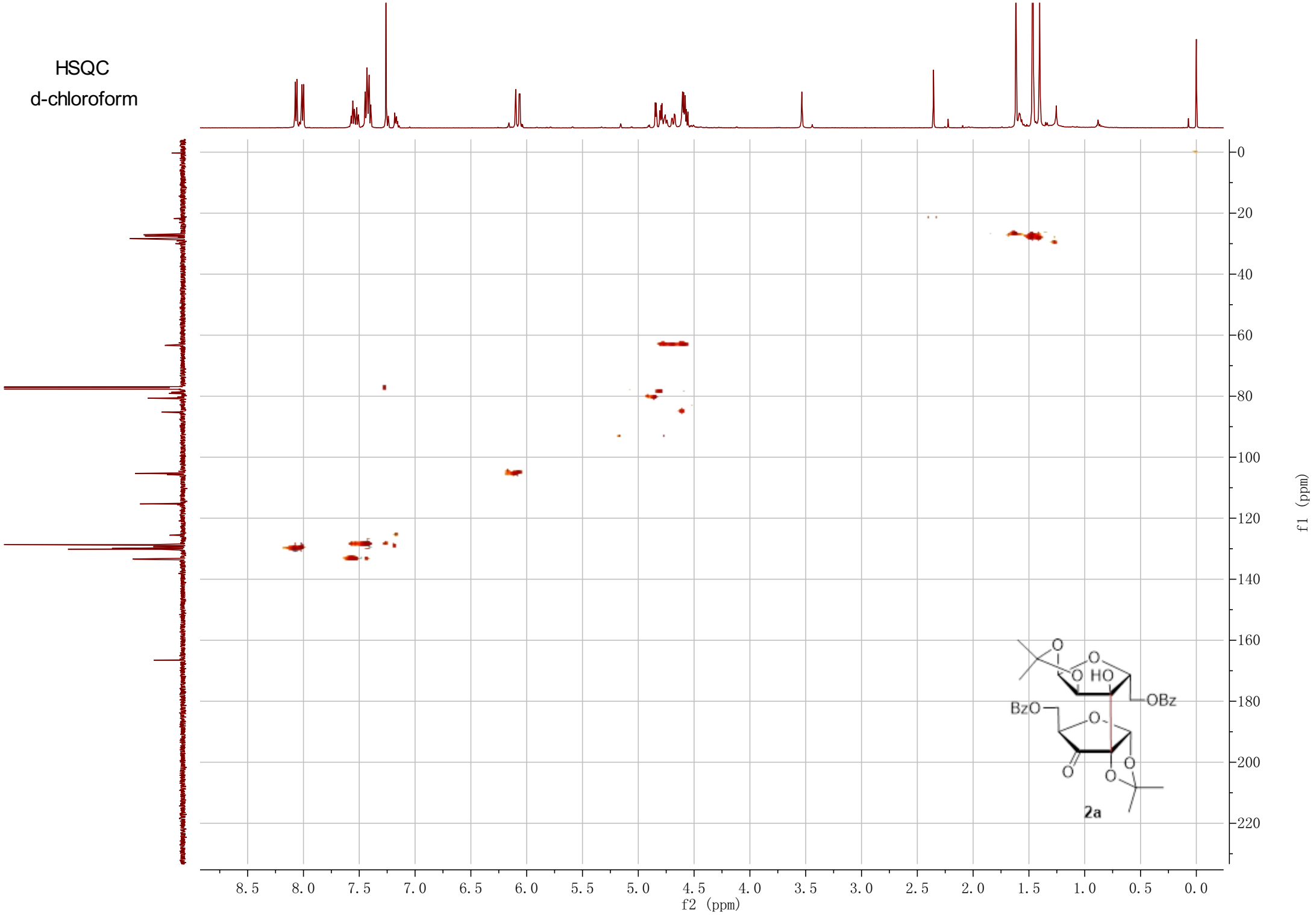




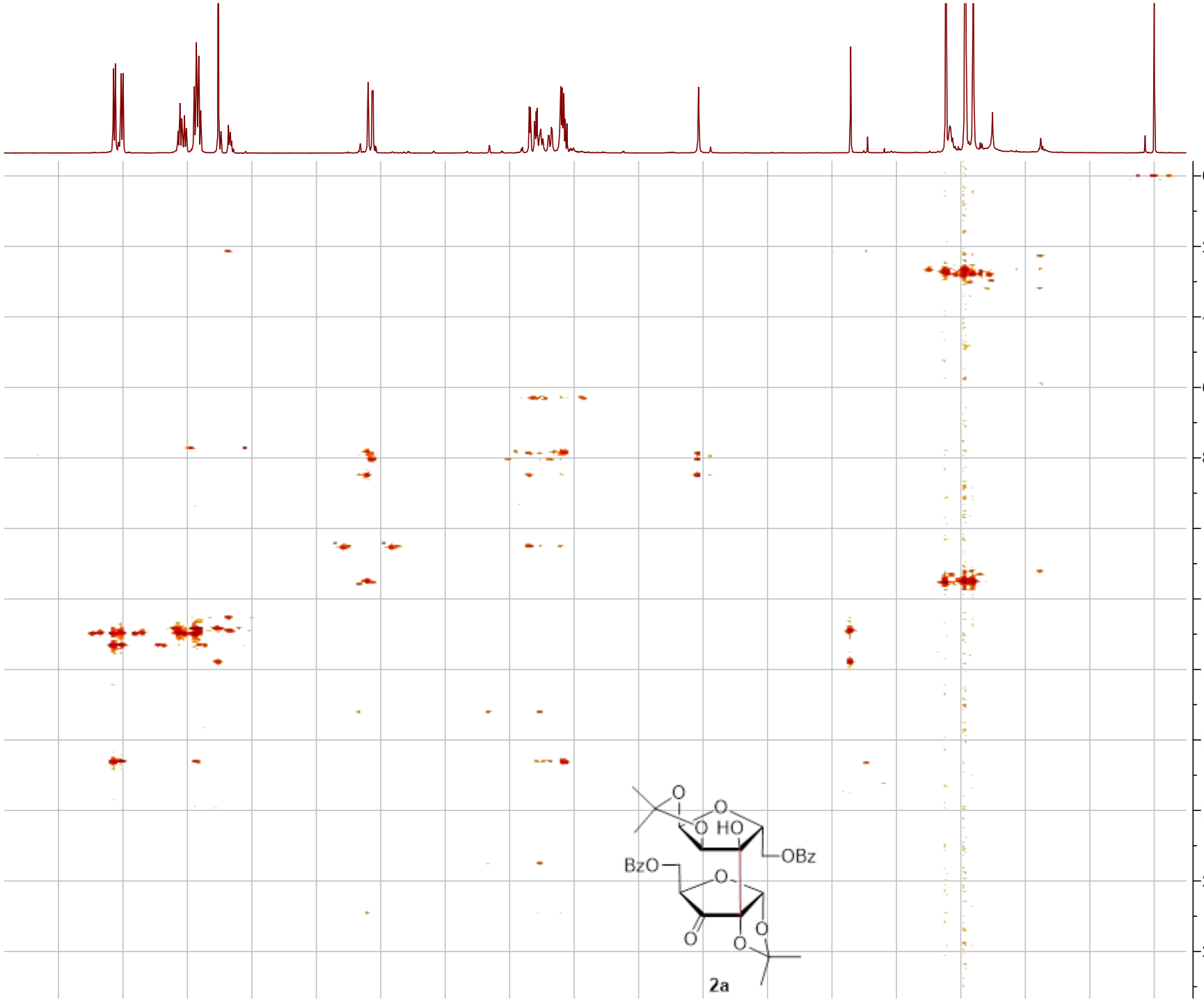
2a

HSQC

d-chloroform

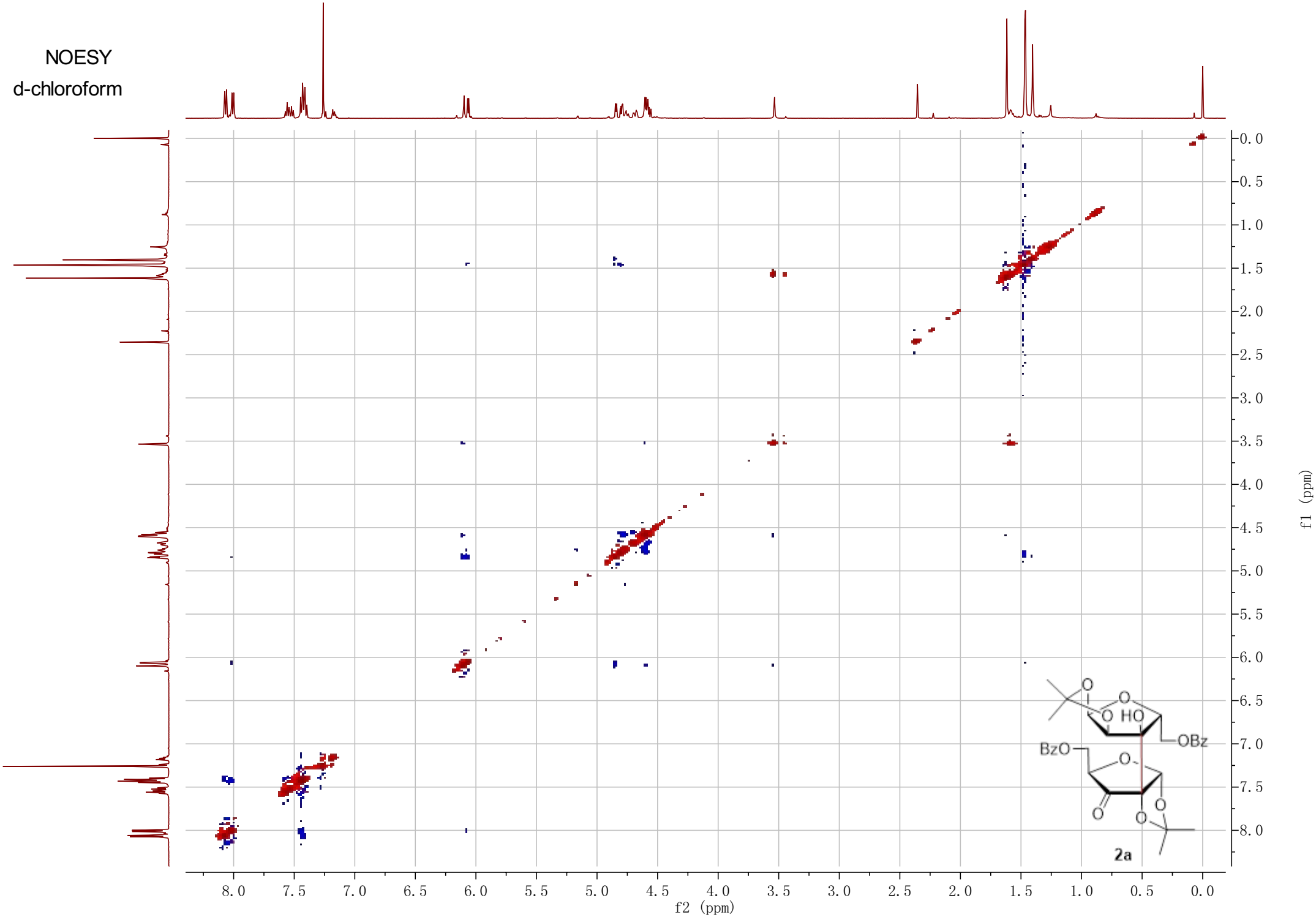


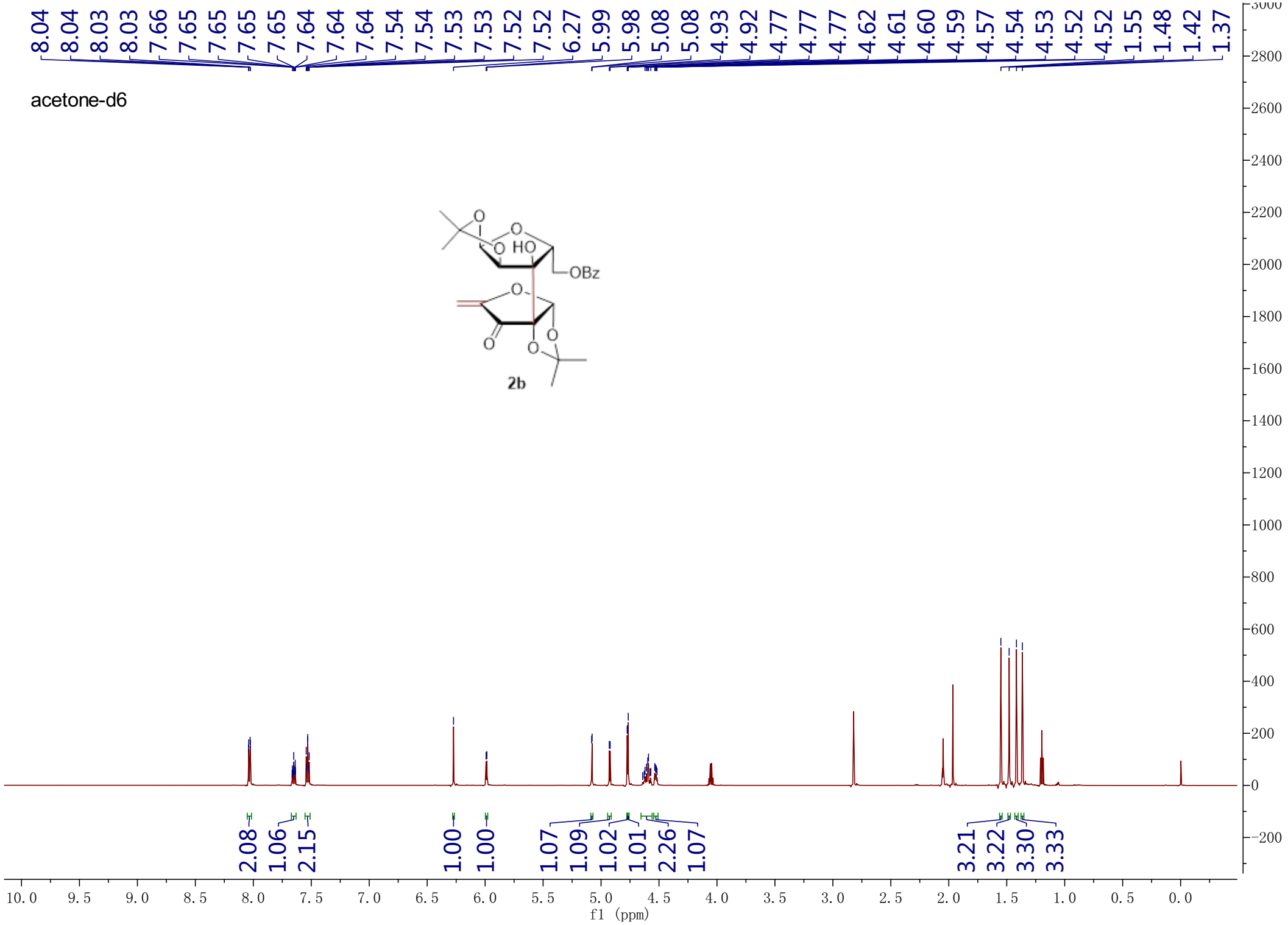
HMBC
d-chloroform

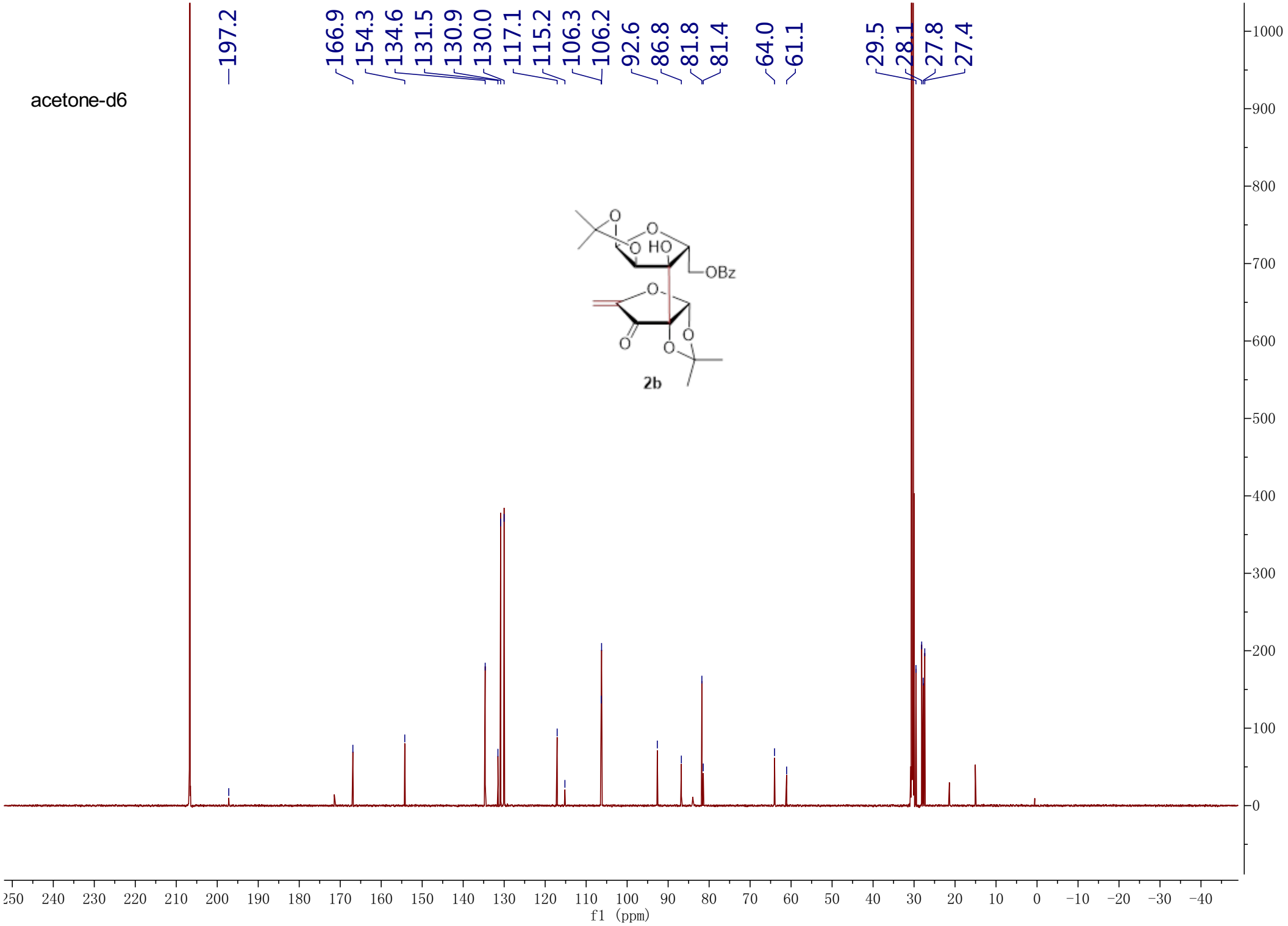


NOESY

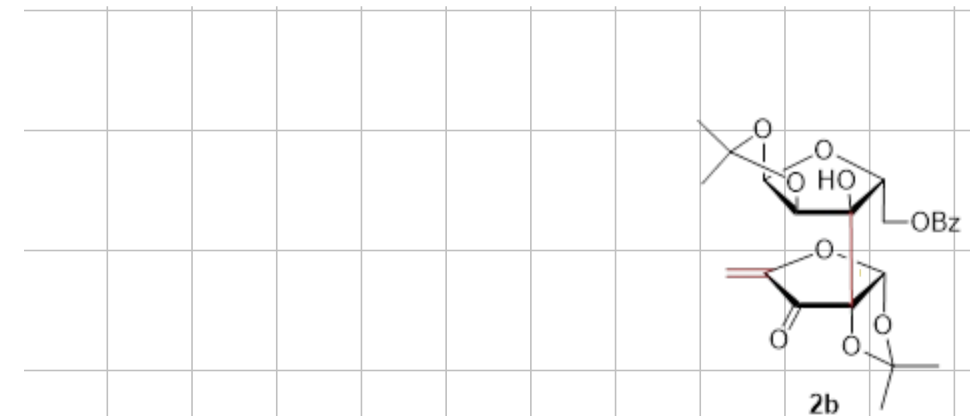
d-chloroform




8.04 8.04 8.03 8.03 7.66 7.65 7.65 7.65 7.65 7.64 7.64 7.64 7.54 7.54 7.53 7.53 7.52 7.52 6.27 5.99 5.98 5.08 5.08 4.93 4.92 4.77 4.77 4.77 4.62 4.61 4.60 4.59 4.57 4.54 4.53 4.52 4.52 1.55 1.48 1.42 1.37
acetone-d6
HO
OBz
2b
2.08 1.06 2.15 1.00 1.00 1.07 1.09 1.02 1.01 2.26 1.07 3.21 3.22 3.30 3.33
f1 (ppm)


acetone-d6
197.2
166.9
154.3
134.6
131.5
130.9
130.0
117.1
115.2
106.3
106.2
92.6
86.8
81.8
81.4
64.0
61.1
29.5
28.1
27.8
27.4
HO
OBz
2b
f1 (ppm)

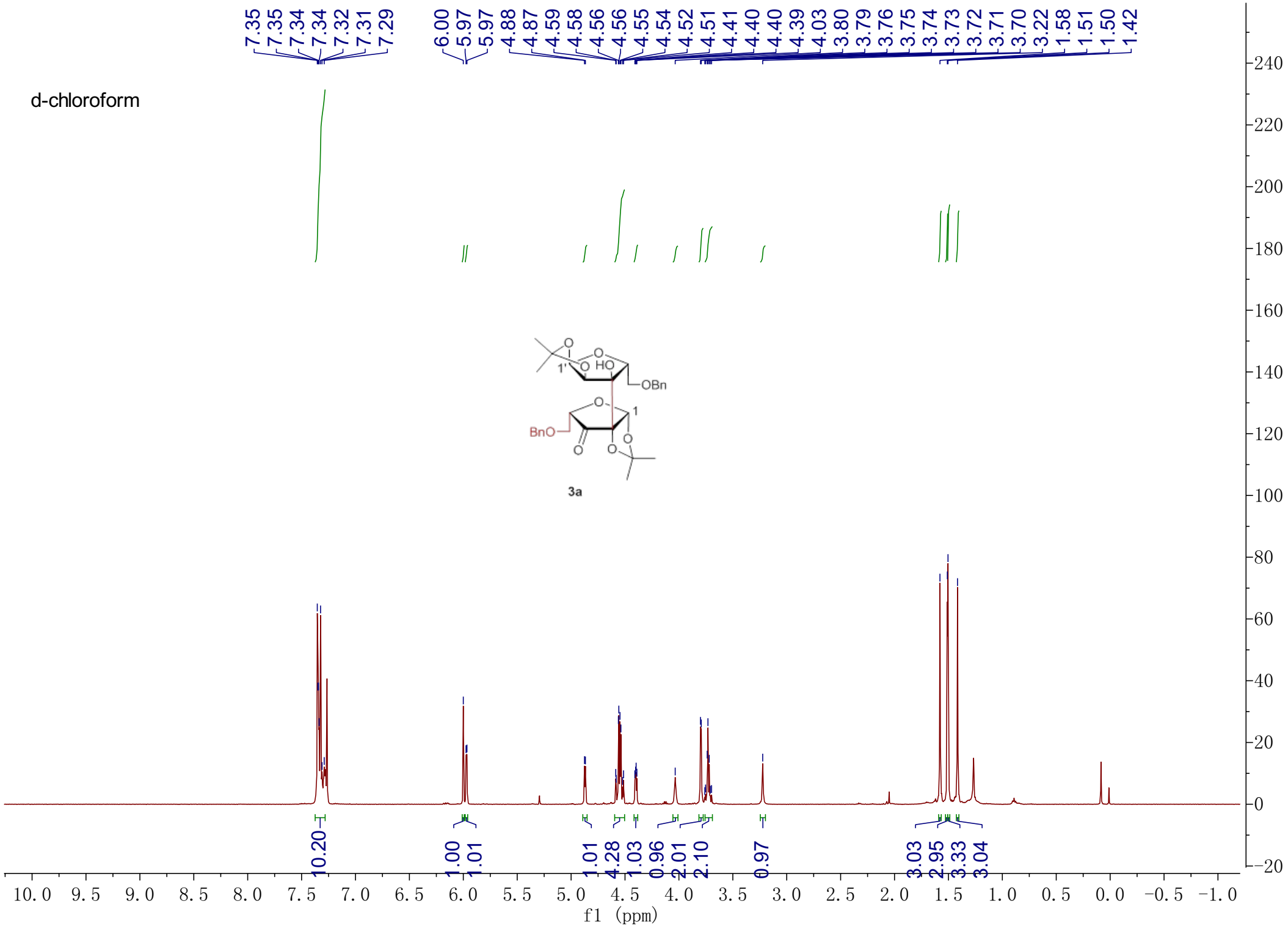
COSY
acetone-d6

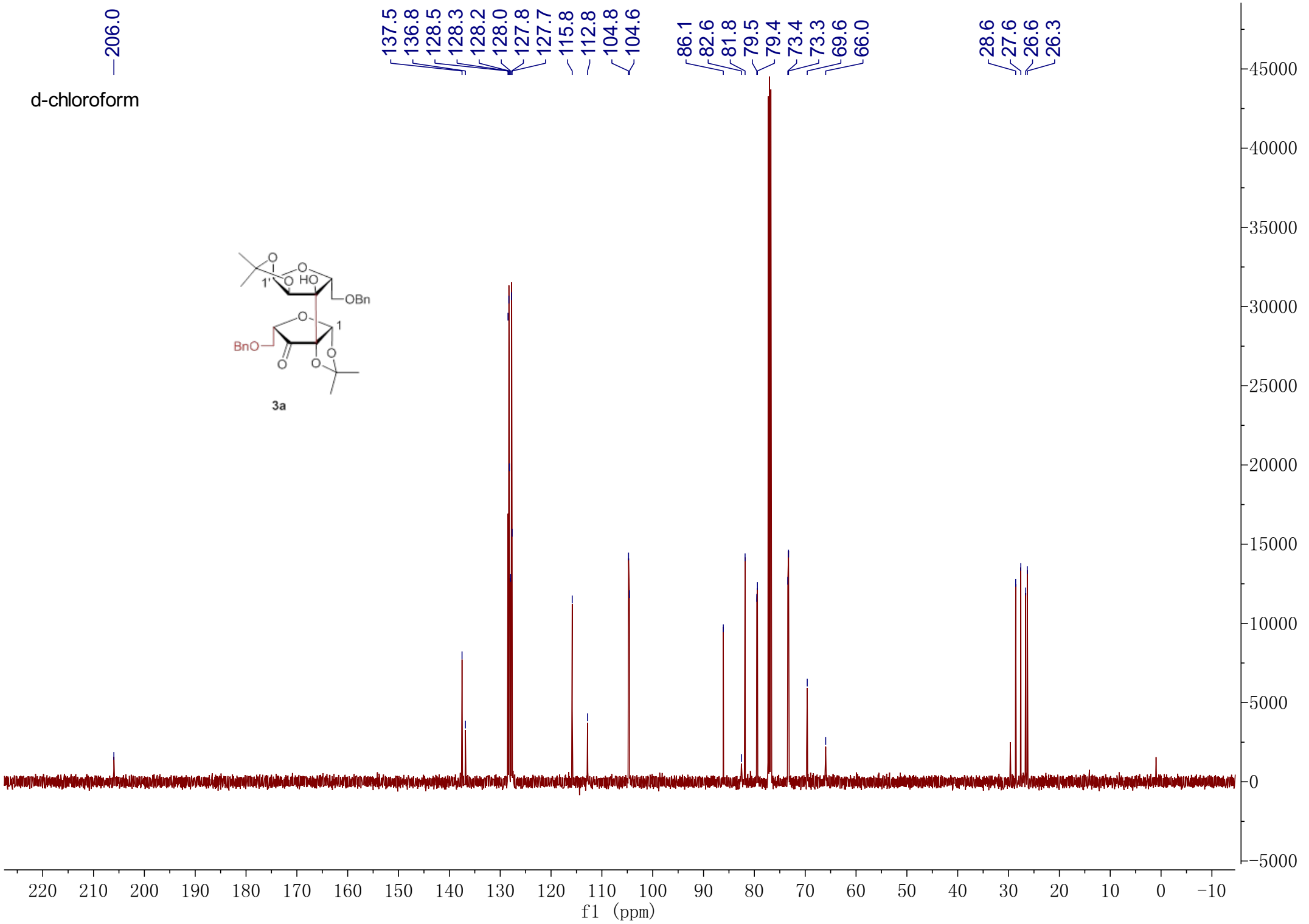


2b

f2 (ppm)

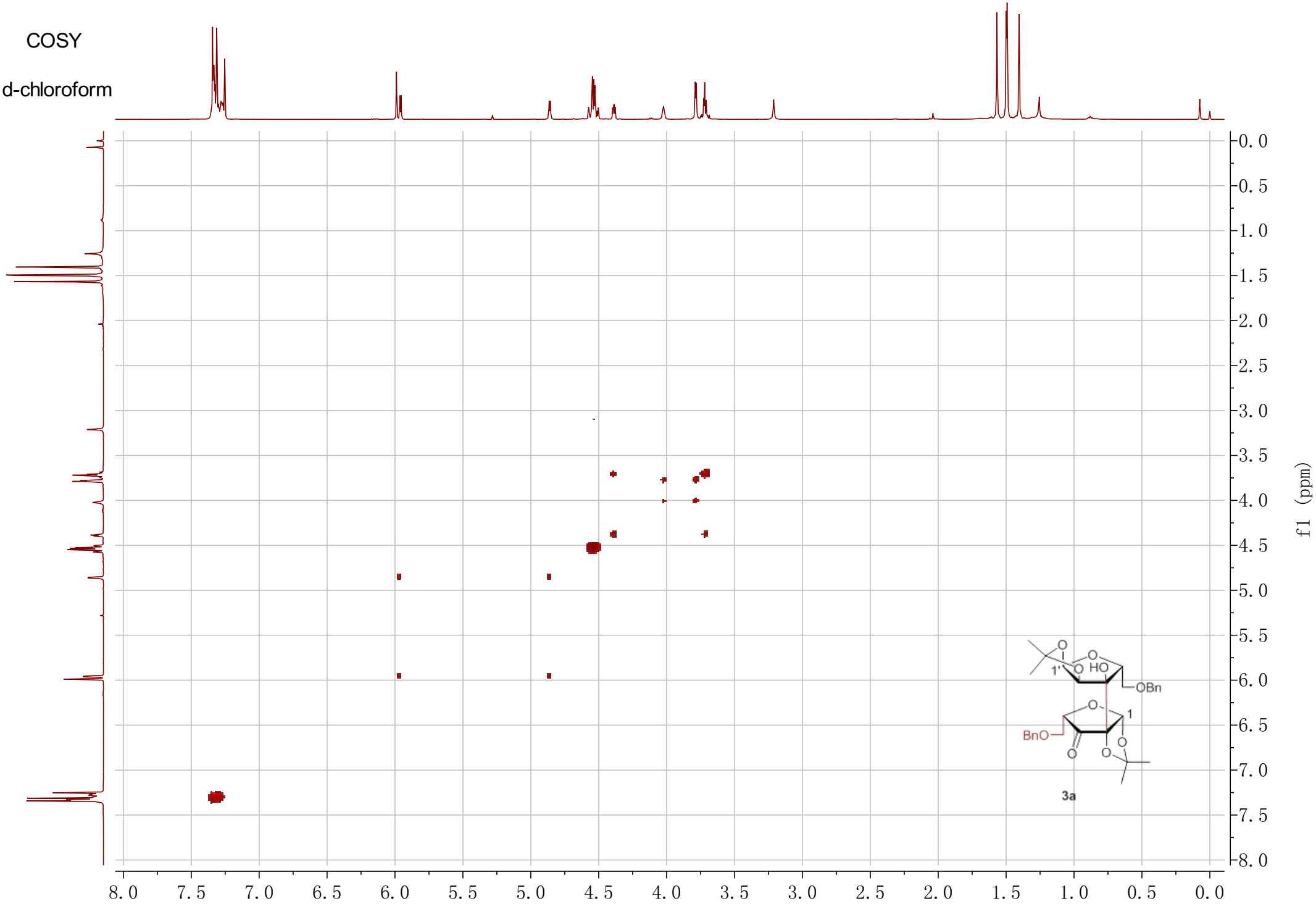
f1 (ppm)


d-chloroform
7.35
7.35
7.34
7.34
7.32
7.31
7.29
6.00
5.97
5.97
4.88
4.87
4.59
4.58
4.56
4.56
4.55
4.54
4.52
4.51
4.41
4.40
4.40
4.39
4.03
3.80
3.79
3.76
3.75
3.74
3.73
3.72
3.71
3.70
3.22
1.58
1.51
1.50
1.42
HO
OBn
BnO
1'
1
3a
10.20
1.00
1.01
1.01
4.28
1.03
0.96
2.01
2.10
0.97
3.03
2.95
3.33
3.04
f1 (ppm)


206.0
137.5
136.8
128.5
128.3
128.2
128.0
127.8
127.7
115.8
112.8
104.8
104.6
86.1
82.6
81.8
79.5
79.4
73.4
73.3
69.6
66.0
28.6
27.6
26.6
26.3
d-chloroform
3a
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
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)

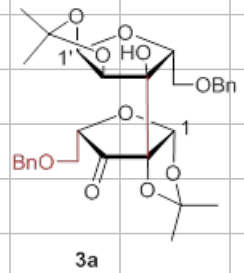
COSY

d-chloroform



HSQC

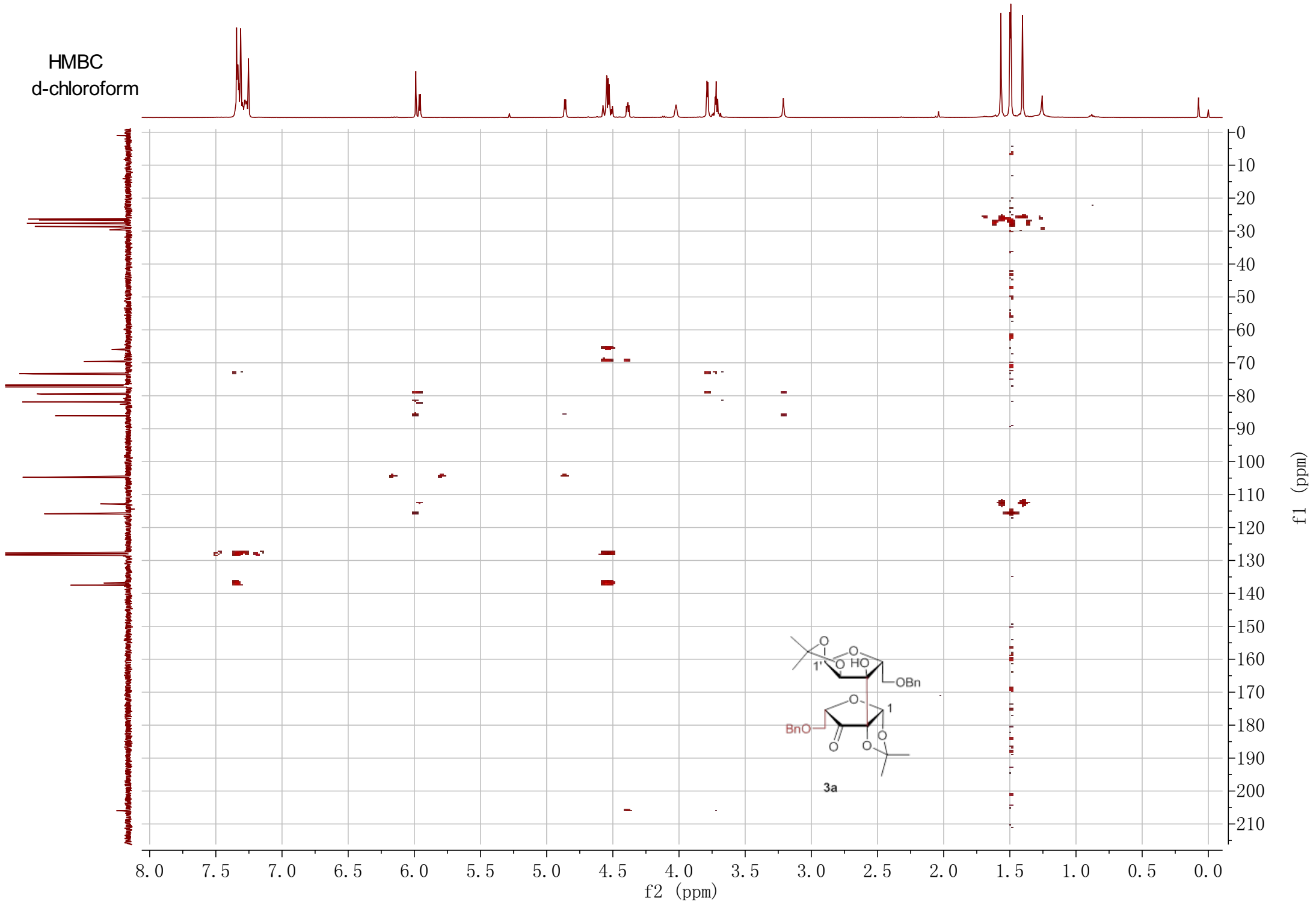
d-chloroform

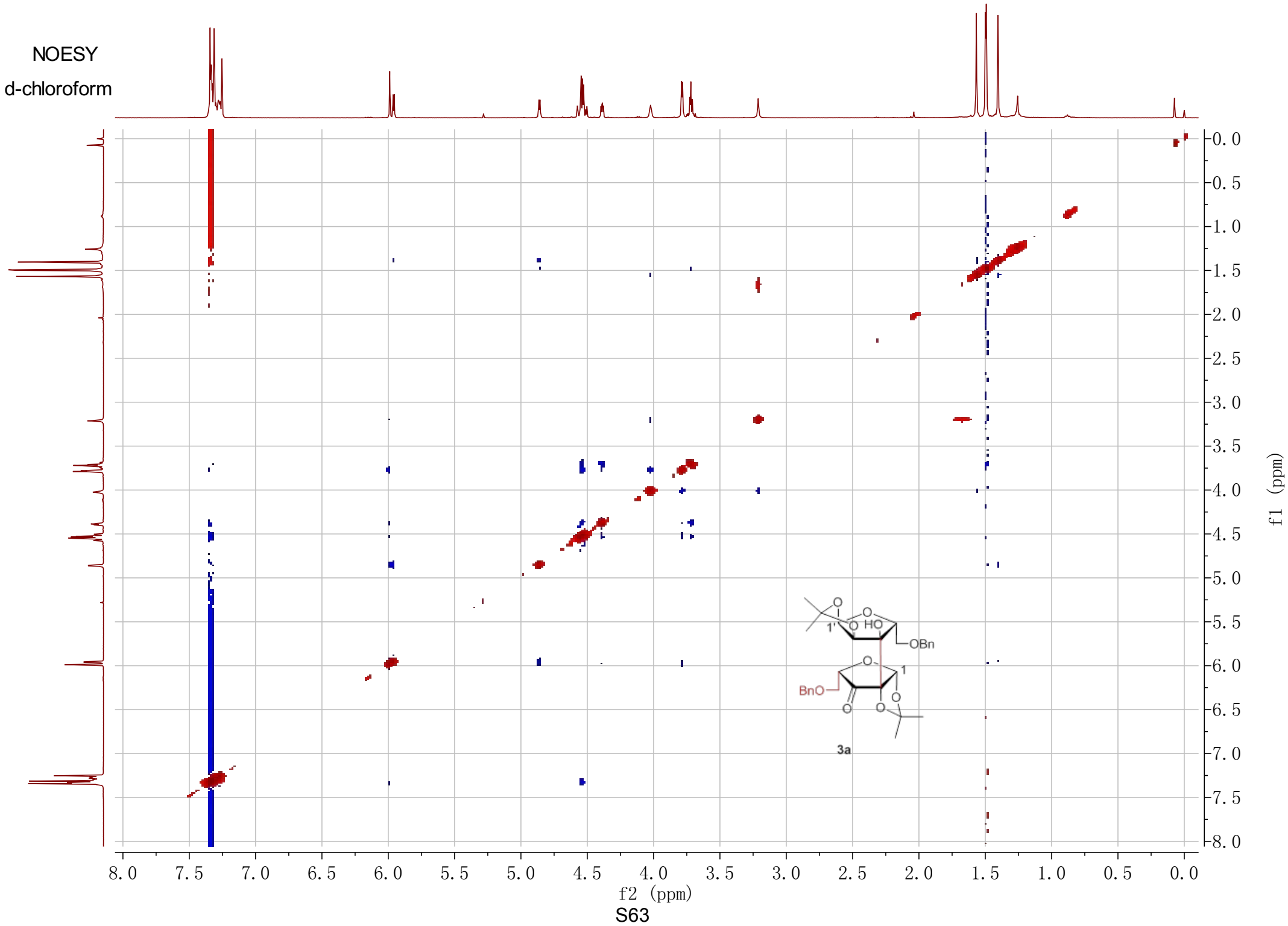


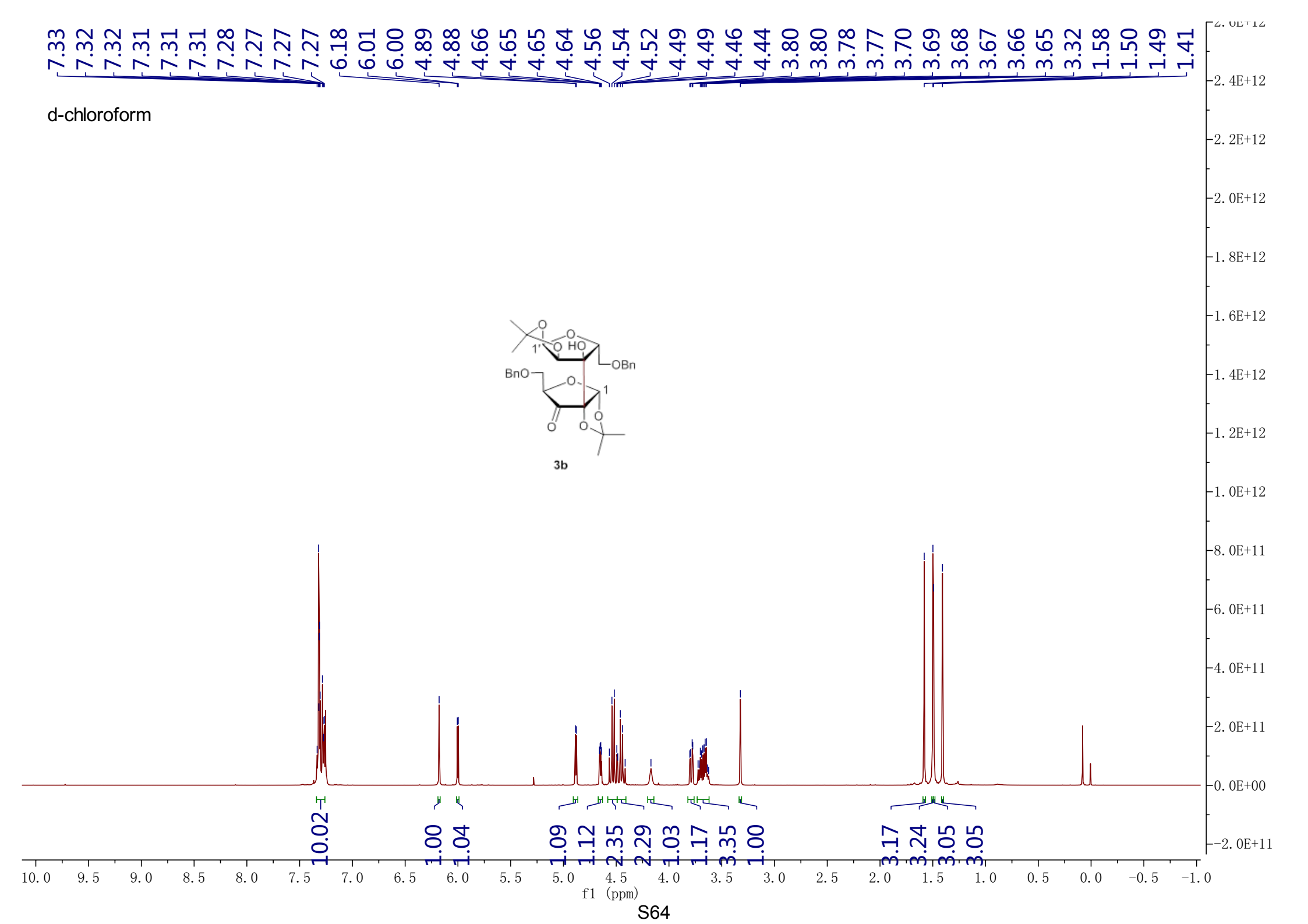
3a

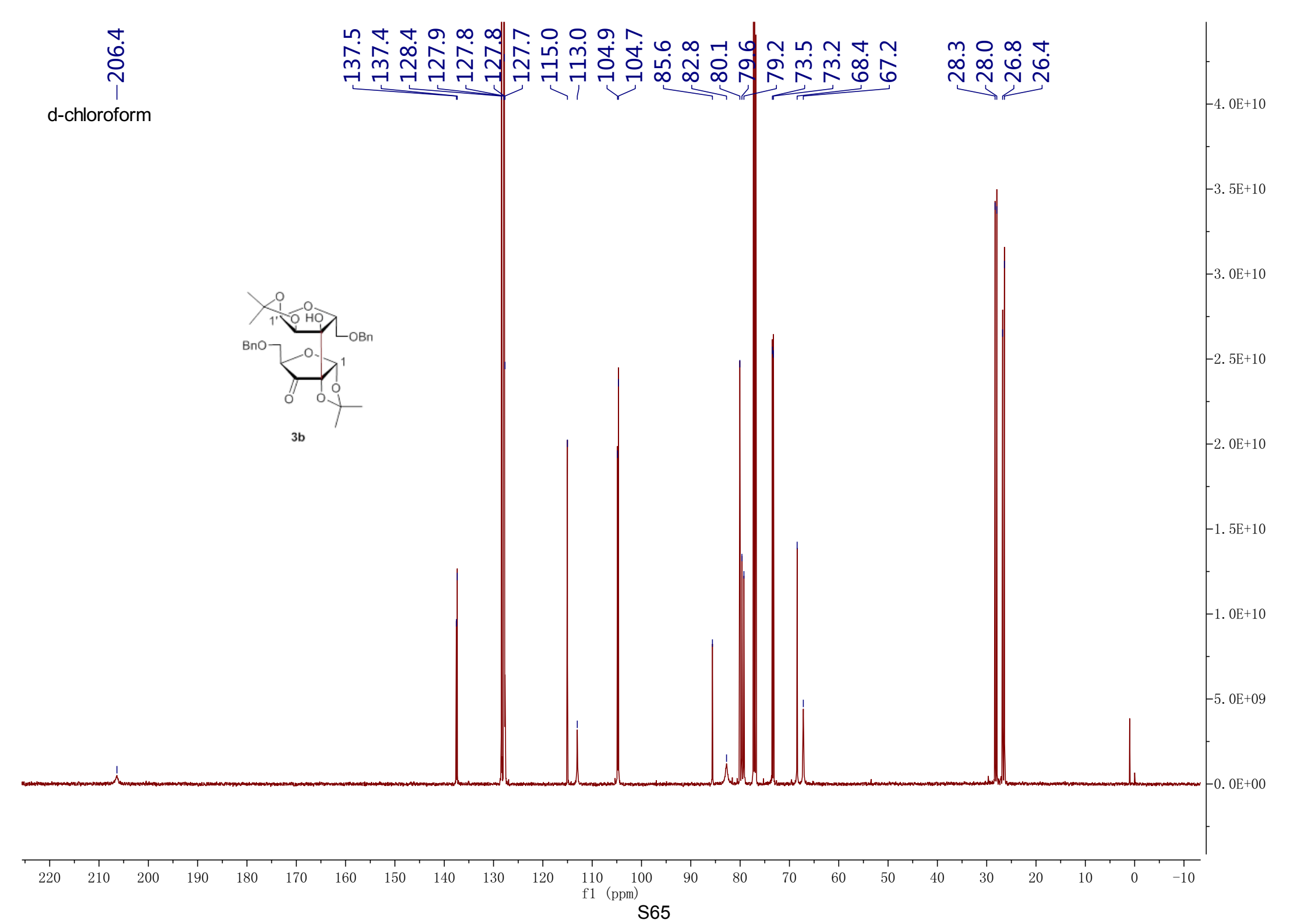
f2 (ppm)

f1 (ppm)

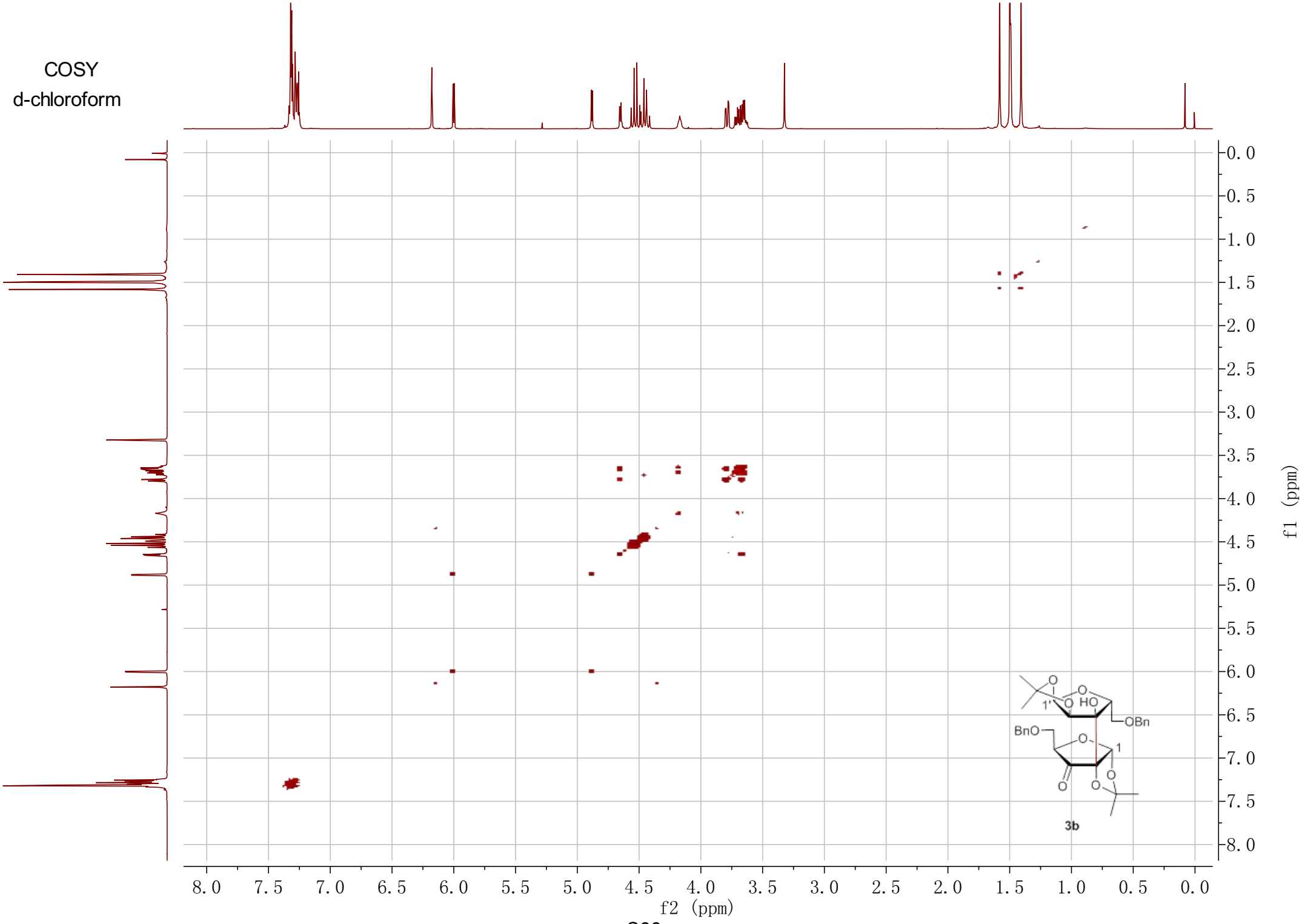

HMBC
d-chloroform
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
HO
OBn
BnO
1'
1
3a


NOESY
d-chloroform
f2 (ppm)
f1 (ppm)
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
HO
OBn
BnO
1'
1
3a

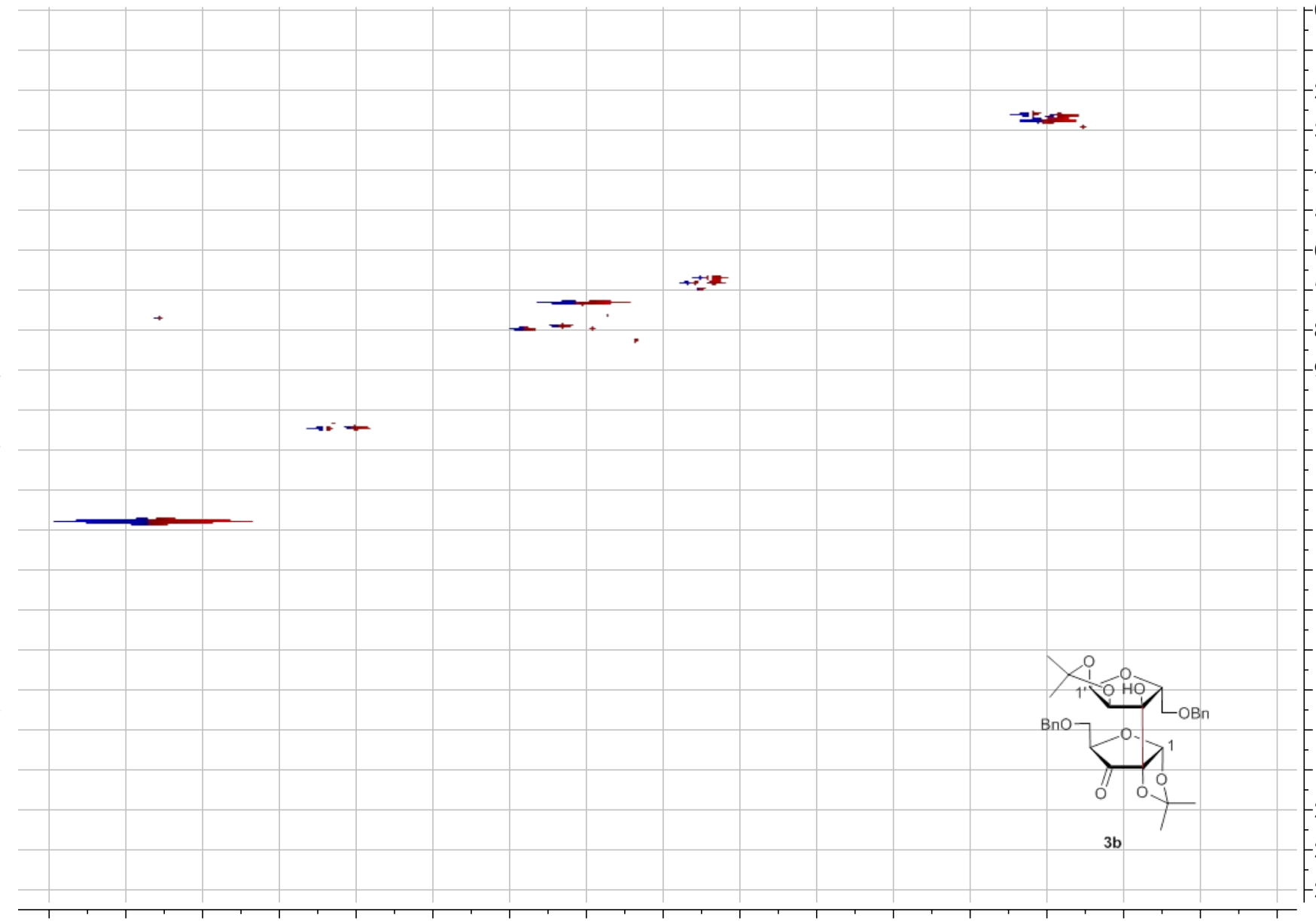

7.33
7.32
7.32
7.31
7.31
7.31
7.28
7.27
7.27
7.27
6.18
6.01
6.00
4.89
4.88
4.66
4.65
4.65
4.64
4.56
4.54
4.52
4.49
4.49
4.46
4.44
3.80
3.80
3.78
3.77
3.70
3.69
3.68
3.67
3.66
3.65
3.32
1.58
1.50
1.49
1.41
d-chloroform
BnO
OBn
HO
1'
1
3b
10.02
1.00
1.04
1.09
1.12
2.35
2.29
1.03
1.17
3.35
1.00
3.17
3.24
3.05
3.05
f1 (ppm)

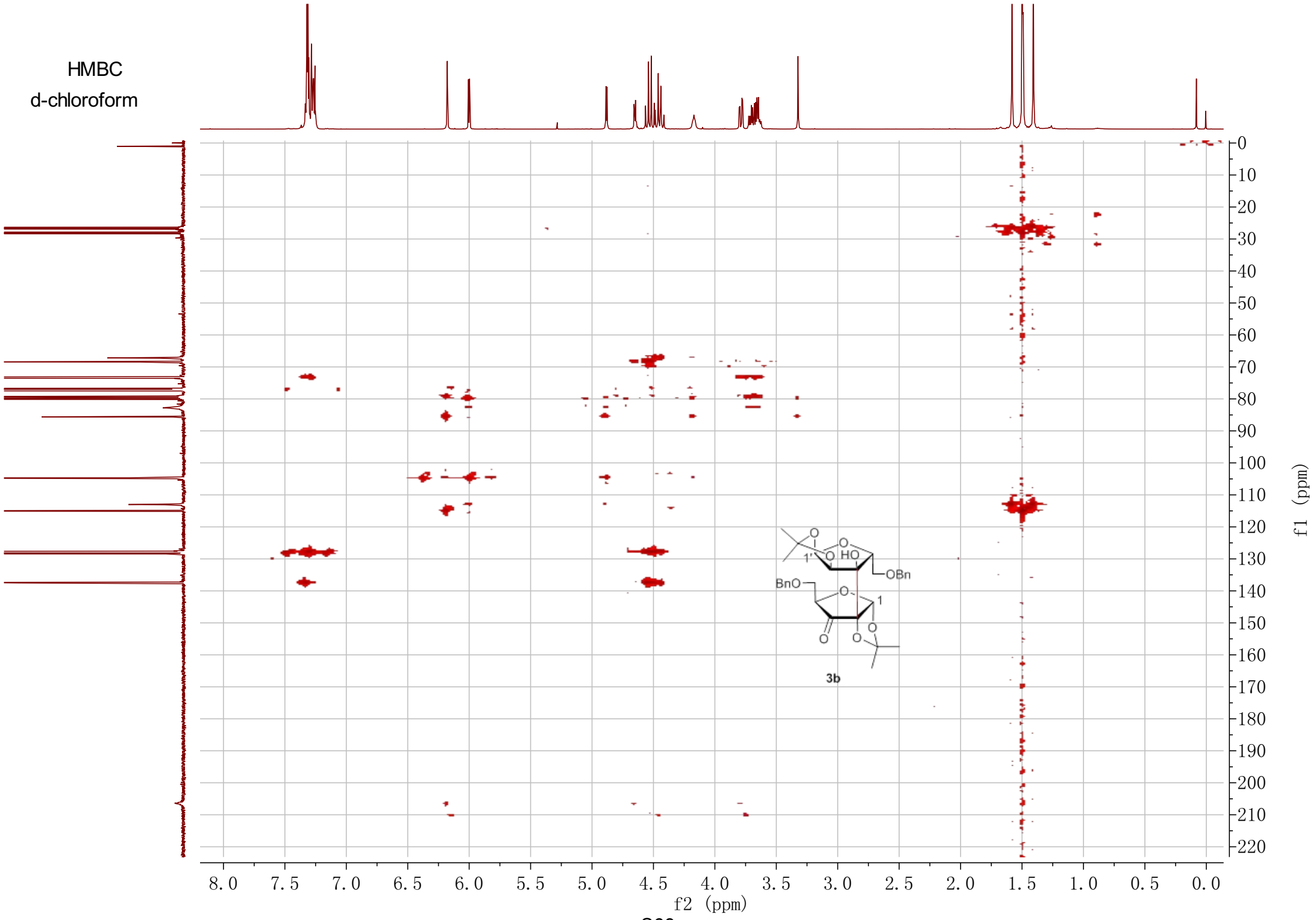

206.4
d-chloroform
137.5
137.4
128.4
127.9
127.8
127.8
127.7
115.0
113.0
104.9
104.7
85.6
82.8
80.1
79.6
79.2
73.5
73.2
68.4
67.2
28.3
28.0
26.8
26.4
4.0E+10
3.5E+10
3.0E+10
2.5E+10
2.0E+10
1.5E+10
1.0E+10
5.0E+09
0.0E+00
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
BnO
OBn
HO
1'
1
3b

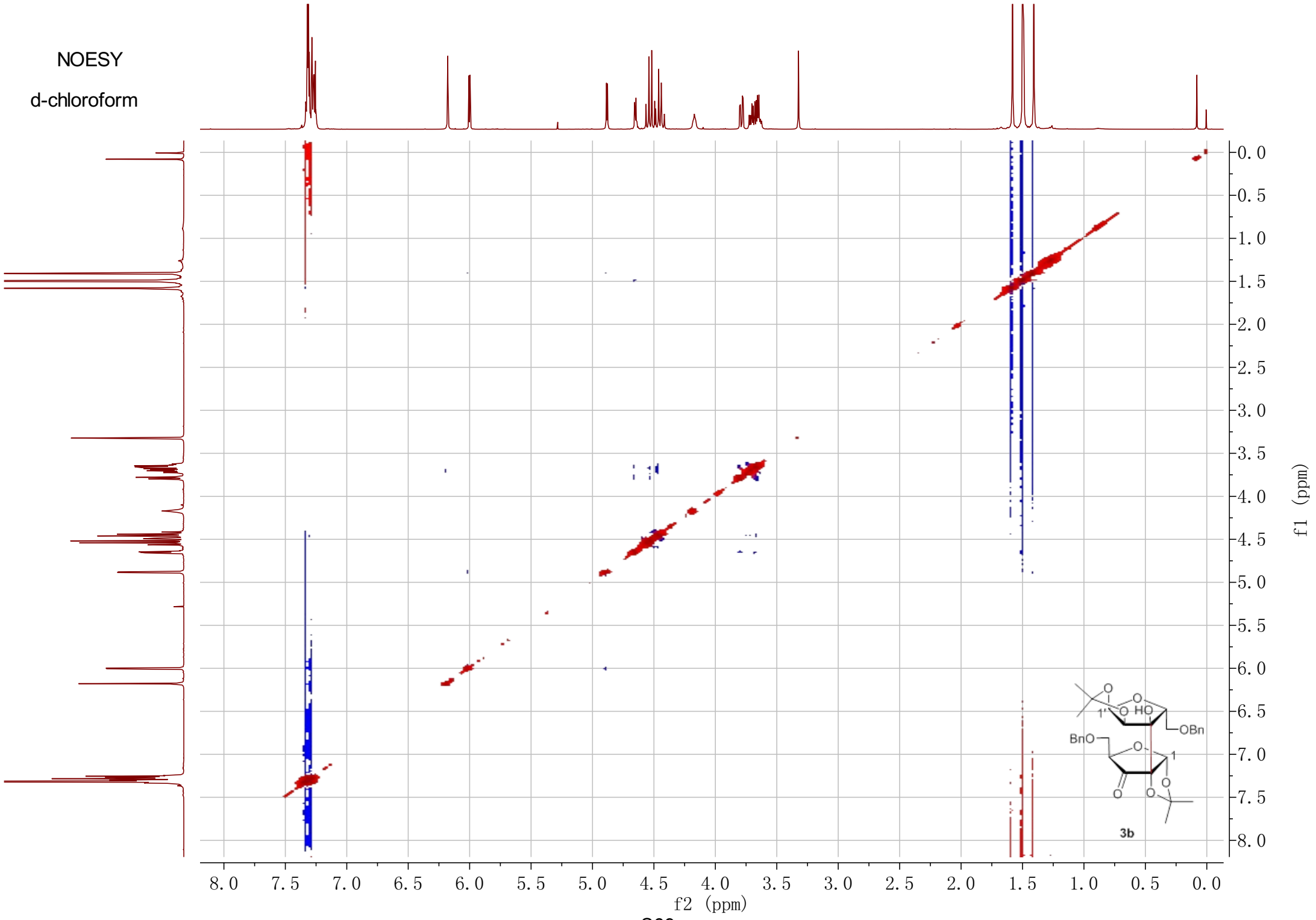
COSY
d-chloroform

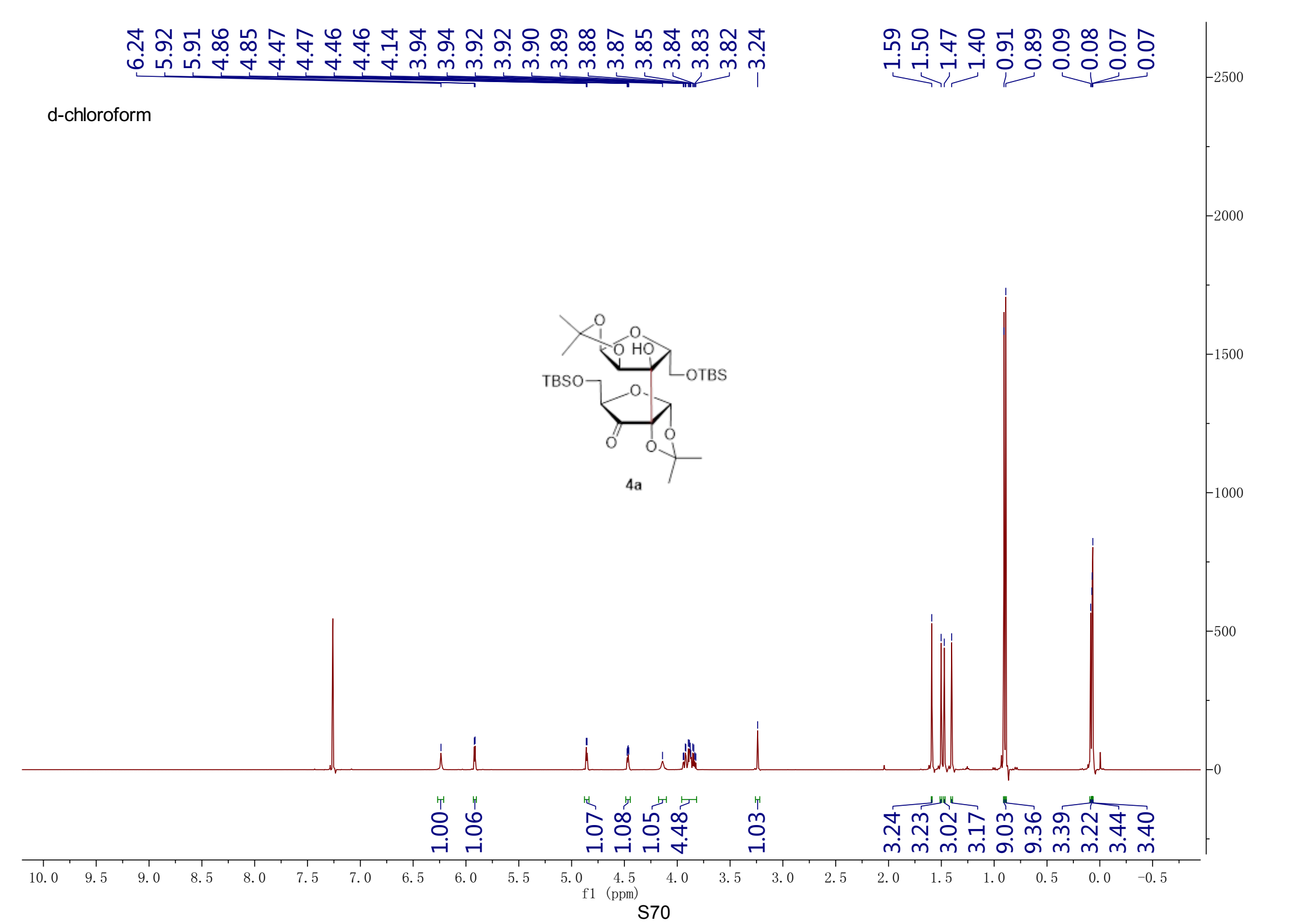


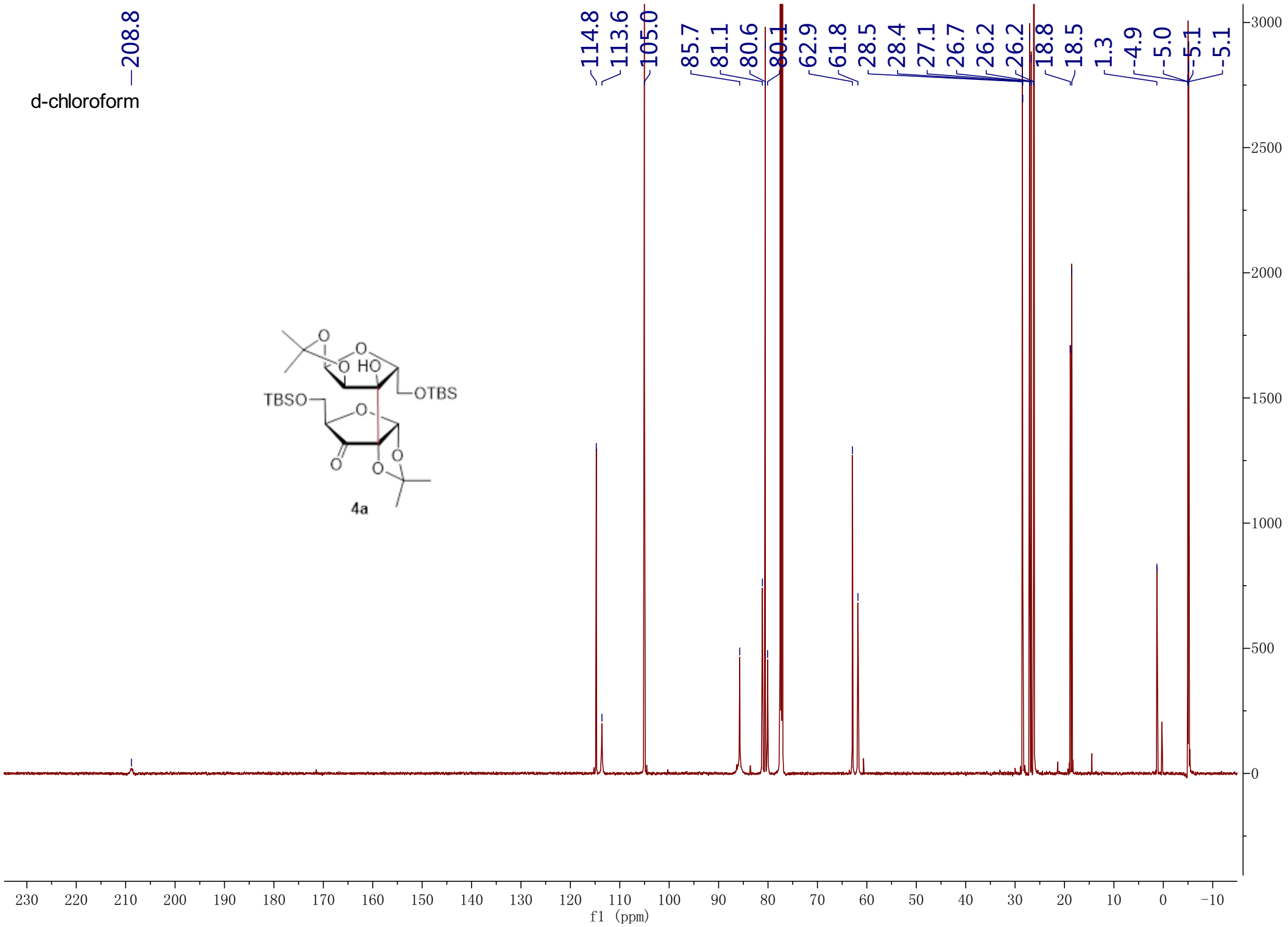
HSQC
d-chloroform

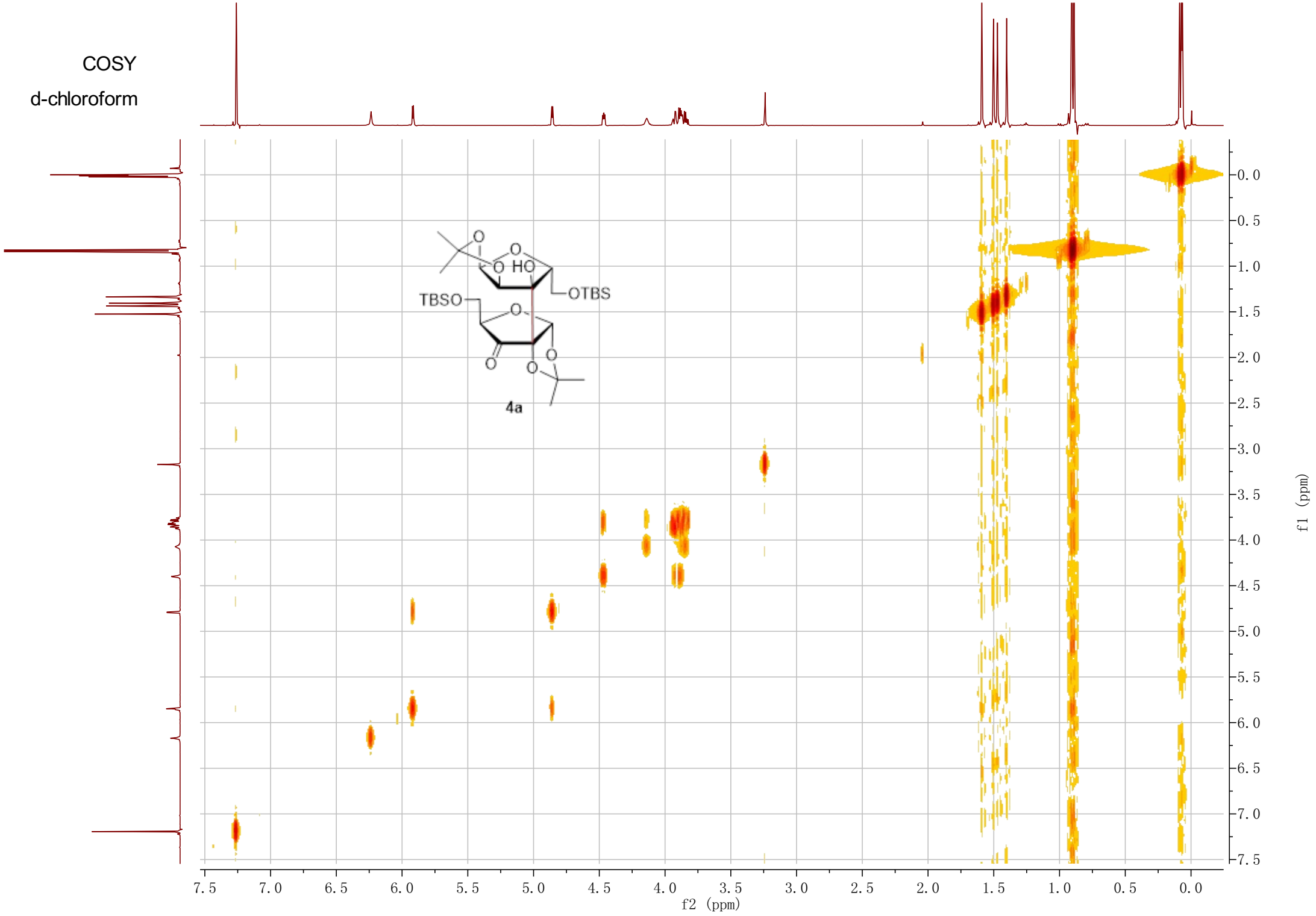


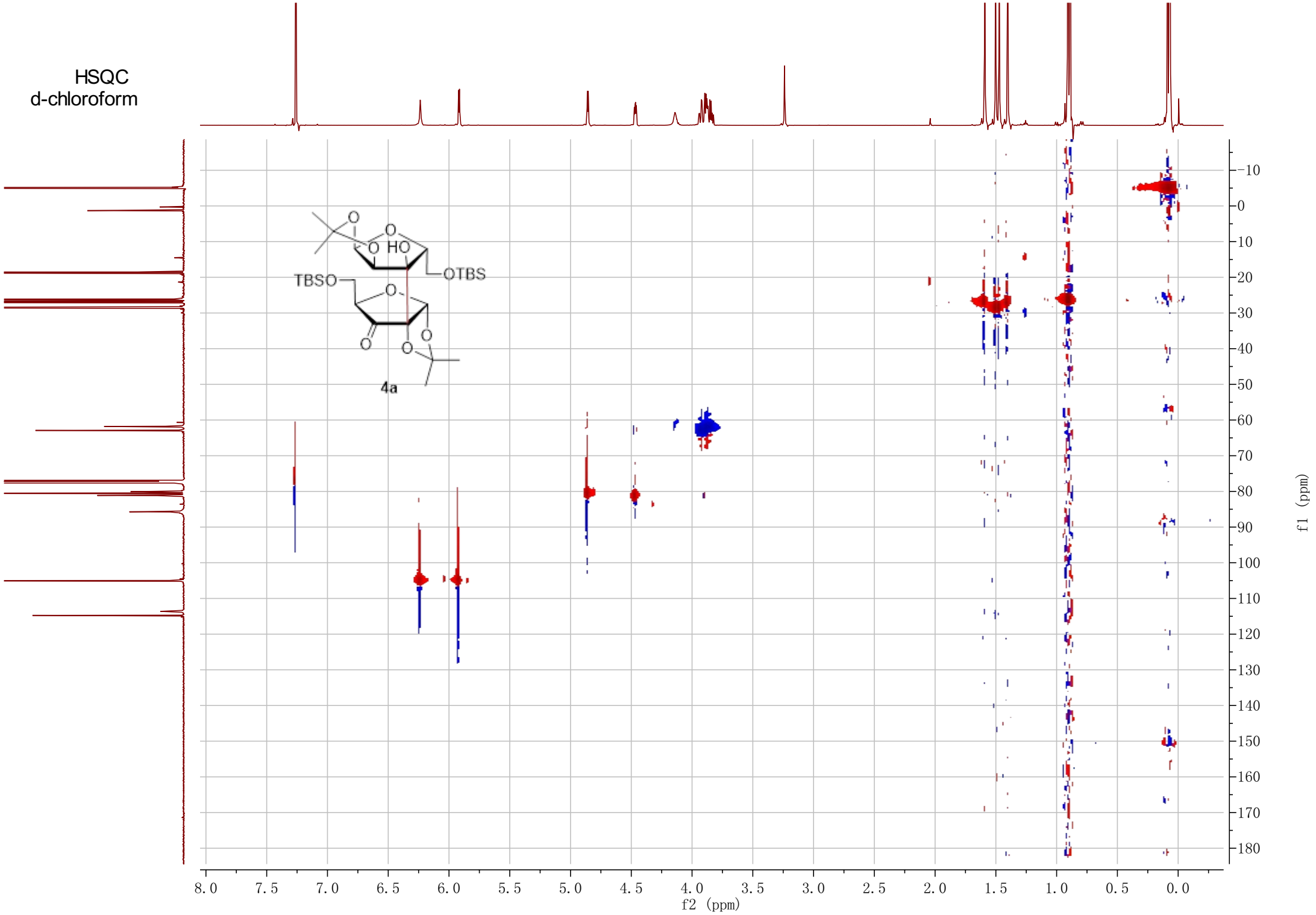

HMBC
d-chloroform
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
HO
OBn
BnO
1''
1
3b

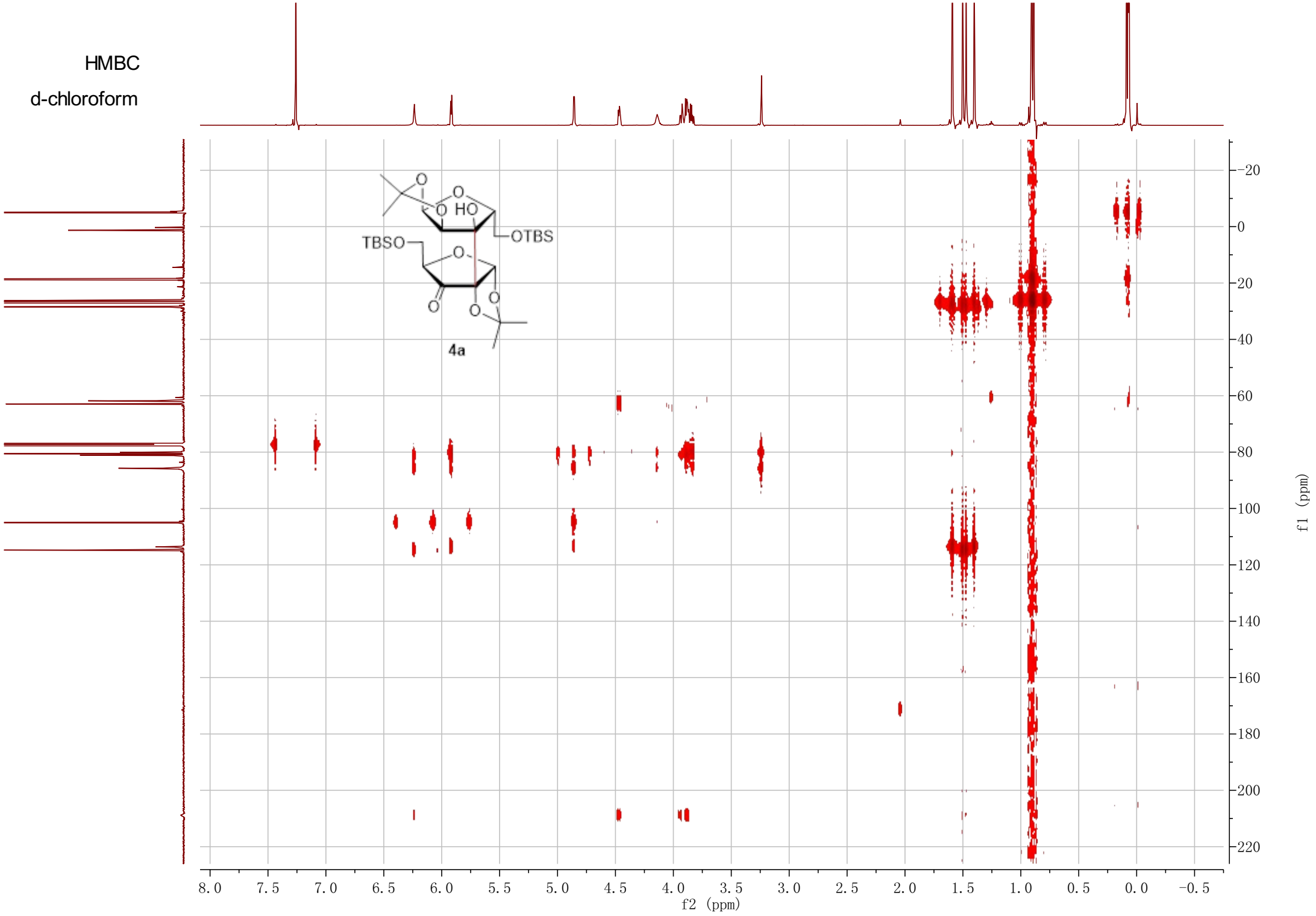

NOESY
d-chloroform
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
HO
OBn
BnO
3b

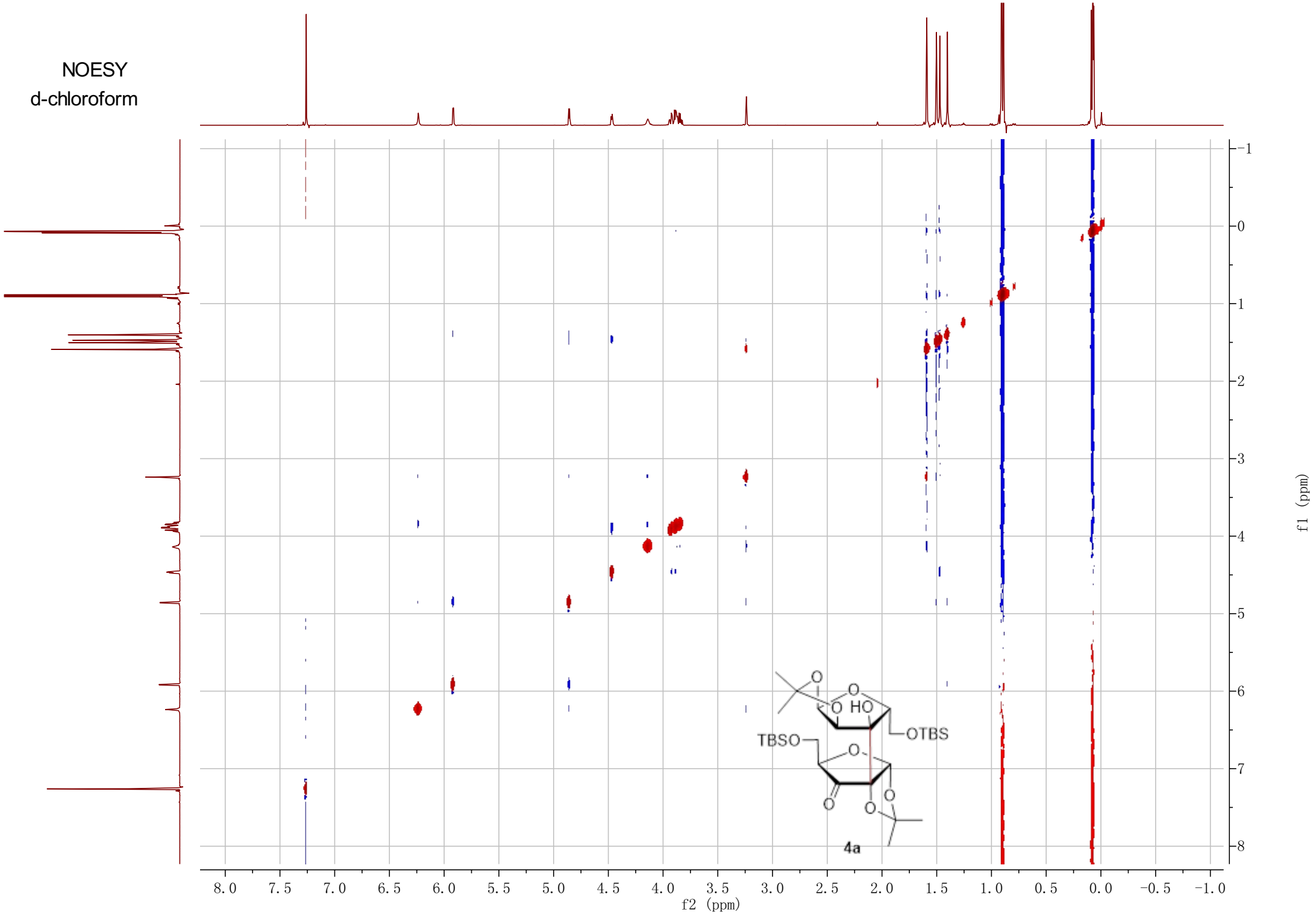

6.24
5.92
5.91
4.86
4.85
4.47
4.47
4.46
4.46
4.14
3.94
3.94
3.92
3.92
3.90
3.89
3.88
3.87
3.85
3.84
3.83
3.82
3.24
1.59
1.50
1.47
1.40
0.91
0.89
0.09
0.08
0.07
0.07
d-chloroform
TBSO
HO
OTBS
4a
1.00
1.06
1.07
1.08
1.05
4.48
1.03
3.24
3.23
3.02
3.17
9.03
9.36
3.39
3.22
3.44
3.40
f1 (ppm)


208.8
d-chloroform
114.8
113.6
105.0
85.7
81.1
80.6
80.1
62.9
61.8
28.5
28.4
27.1
26.7
26.2
26.2
18.8
18.5
1.3
-4.9
-5.0
-5.1
-5.1
HO
TBSO
OTBS
4a
3000
2500
2000
1500
1000
500
0
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)

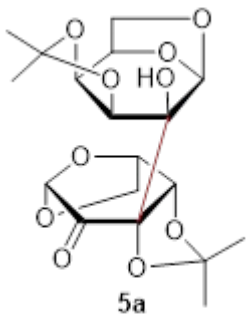

COSY
d-chloroform
TBSO
HO
OTBS
4a
f2 (ppm)
f1 (ppm)


HSQC
d-chloroform
TBSO
HO
OTBS
4a
f2 (ppm)
f1 (ppm)

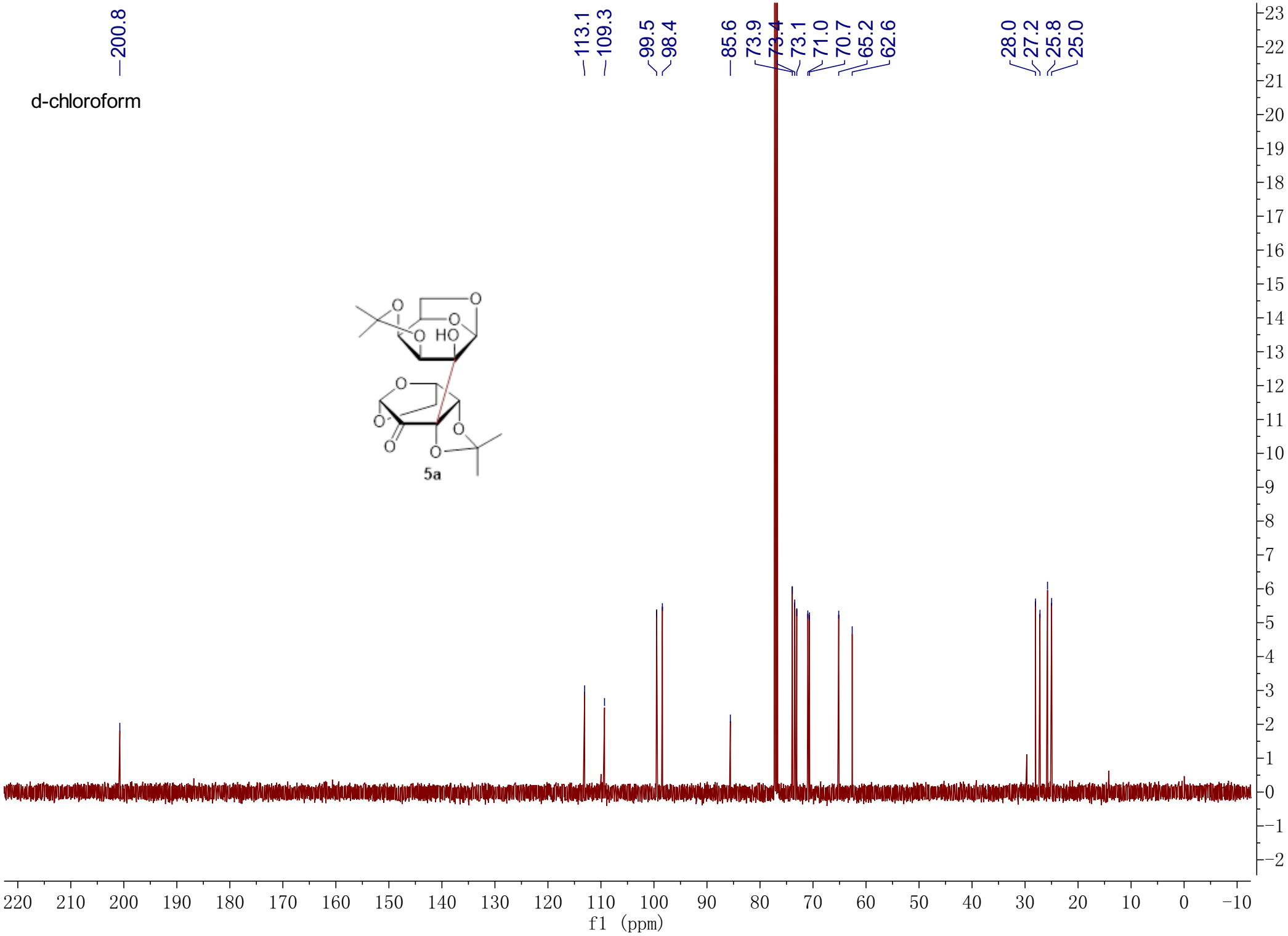

HMBC
d-chloroform
TBSO
HO
OTBS
4a
f2 (ppm)
f1 (ppm)

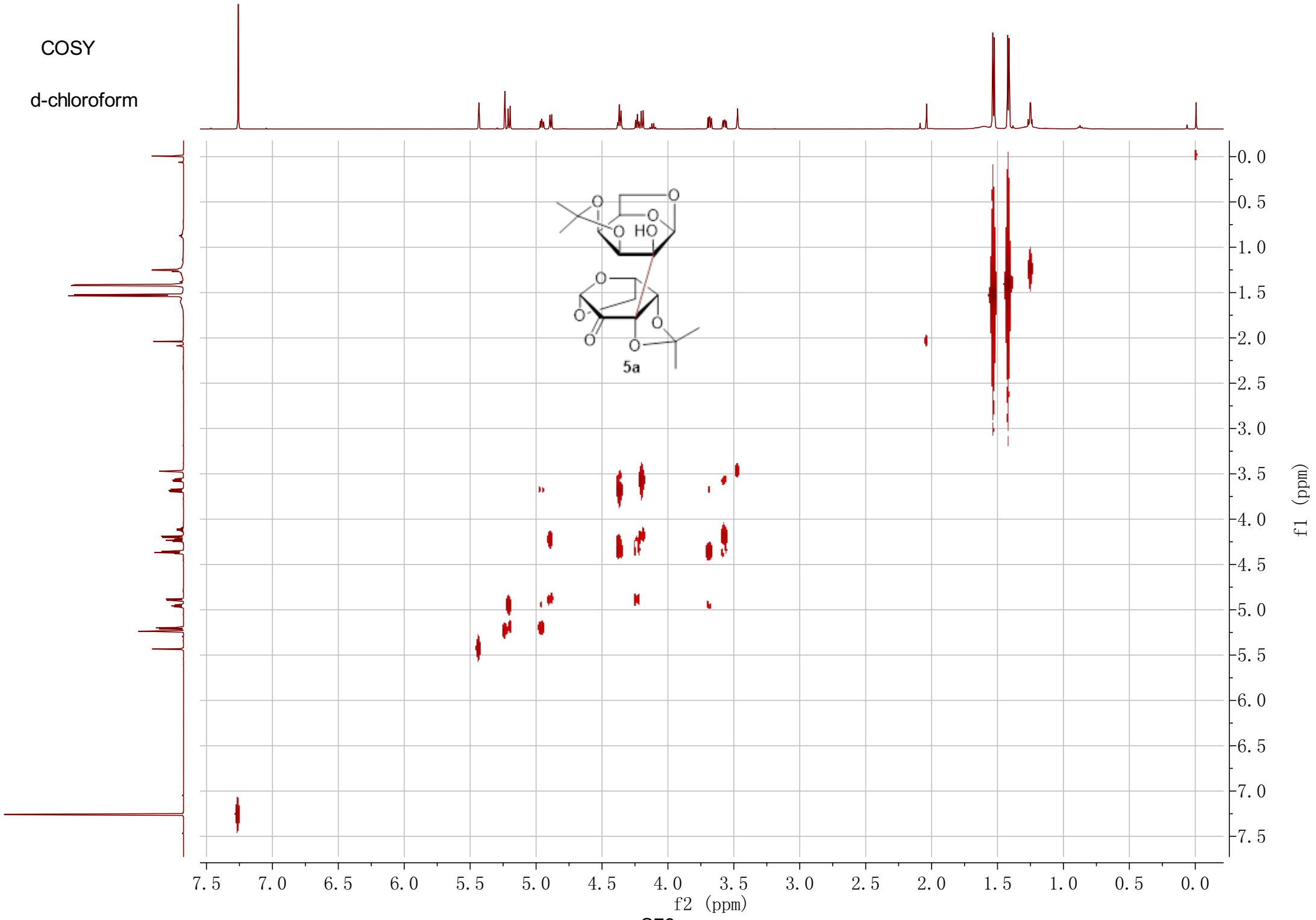

NOESY
d-chloroform
f2 (ppm)
f1 (ppm)
HO
OTBS
TBSO
4a

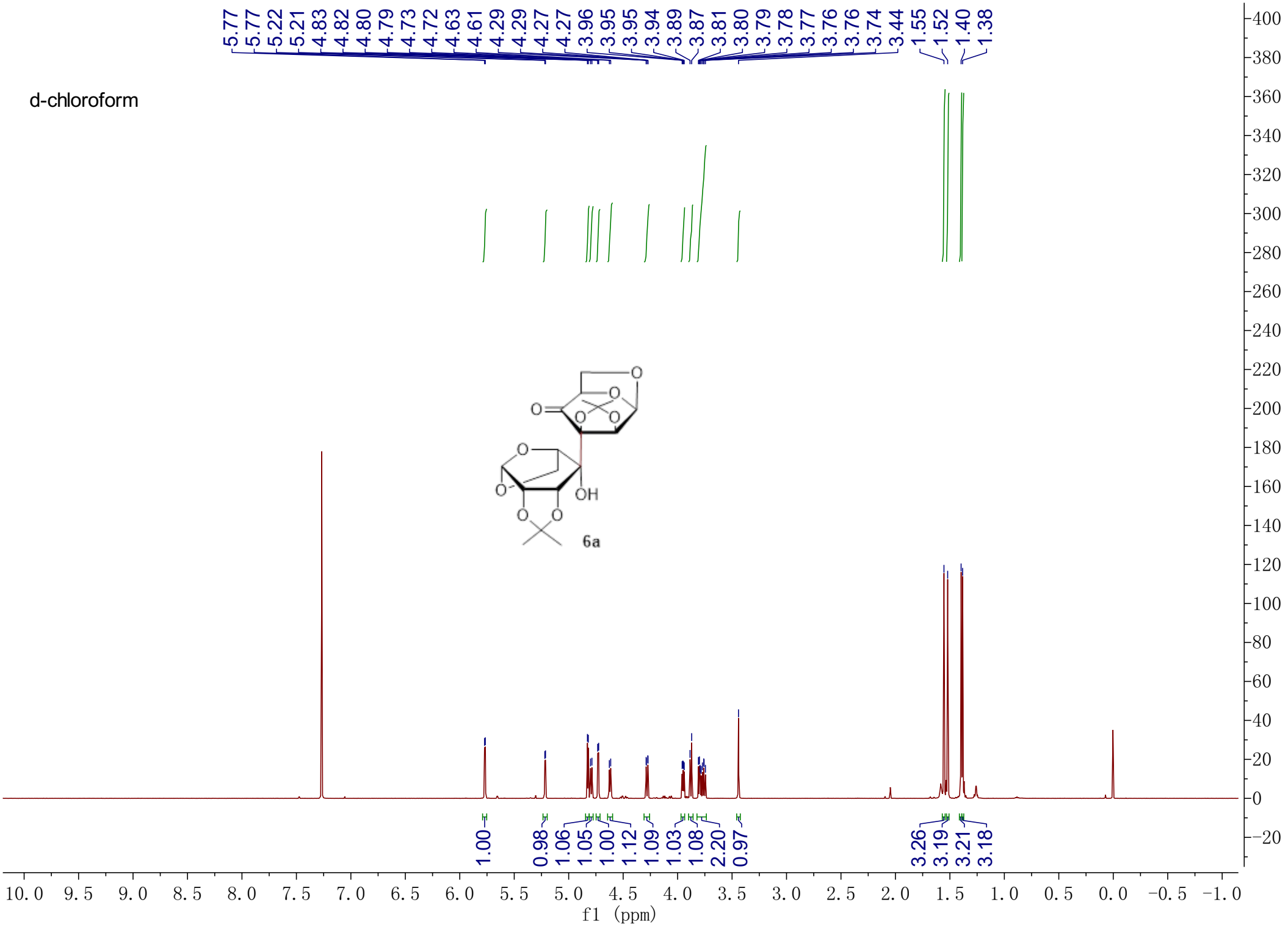
d-chloroform

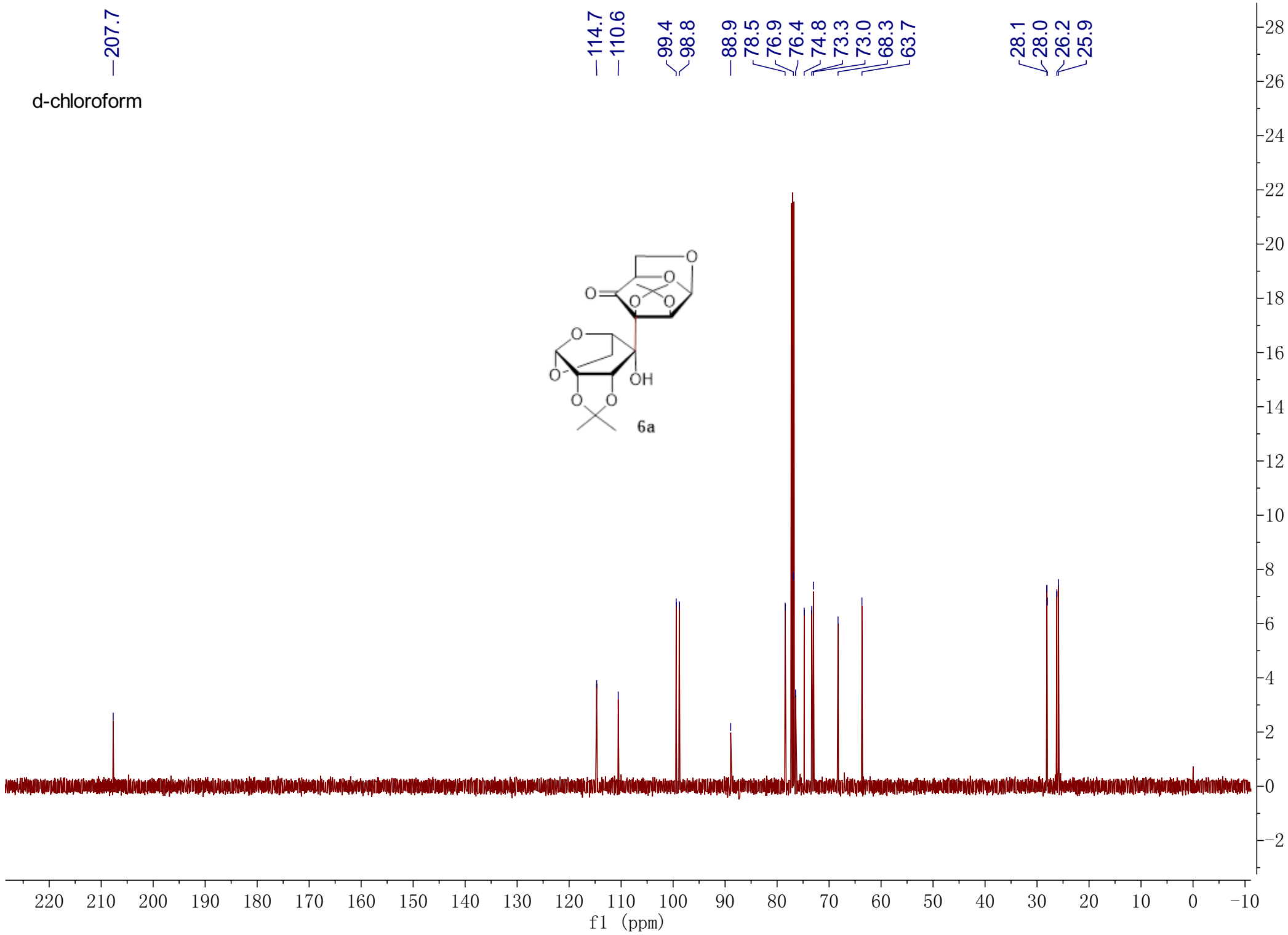


5a


200.8
113.1
109.3
99.5
98.4
85.6
73.9
73.4
73.1
71.0
70.7
65.2
62.6
28.0
27.2
25.8
25.0
d-chloroform
HO
5a
f1 (ppm)

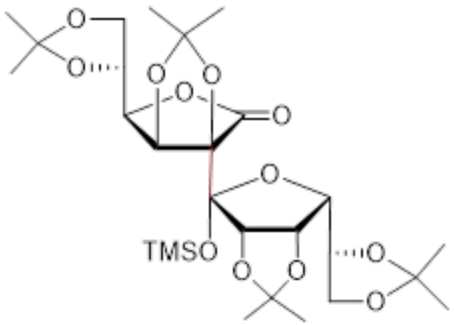

COSY
d-chloroform
HO
5a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)


5.77
5.77
5.22
5.21
4.83
4.82
4.80
4.79
4.73
4.72
4.63
4.61
4.29
4.29
4.27
4.27
3.96
3.95
3.95
3.94
3.89
3.87
3.81
3.80
3.79
3.78
3.77
3.76
3.76
3.74
3.44
1.55
1.52
1.40
1.38
d-chloroform
O
O
O
O
O
O
O
O
OH
6a
1.00
0.98
1.06
1.05
1.00
1.12
1.09
1.03
1.08
2.20
0.97
3.26
3.19
3.21
3.18
f1 (ppm)

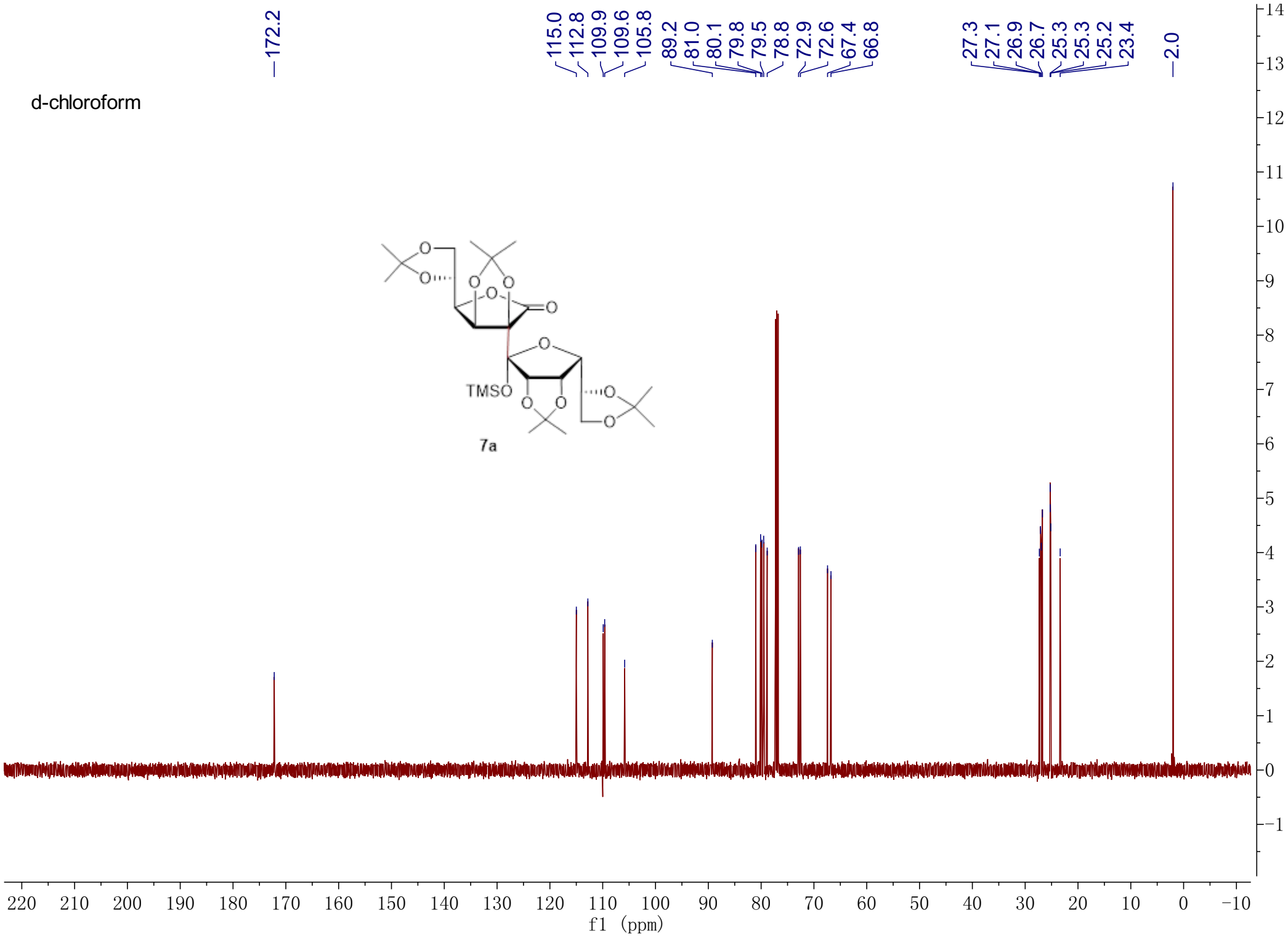

207.7
114.7
110.6
99.4
98.8
88.9
78.5
76.9
76.4
74.8
73.3
73.0
68.3
63.7
28.1
28.0
26.2
25.9
d-chloroform
OH
6a
f1 (ppm)

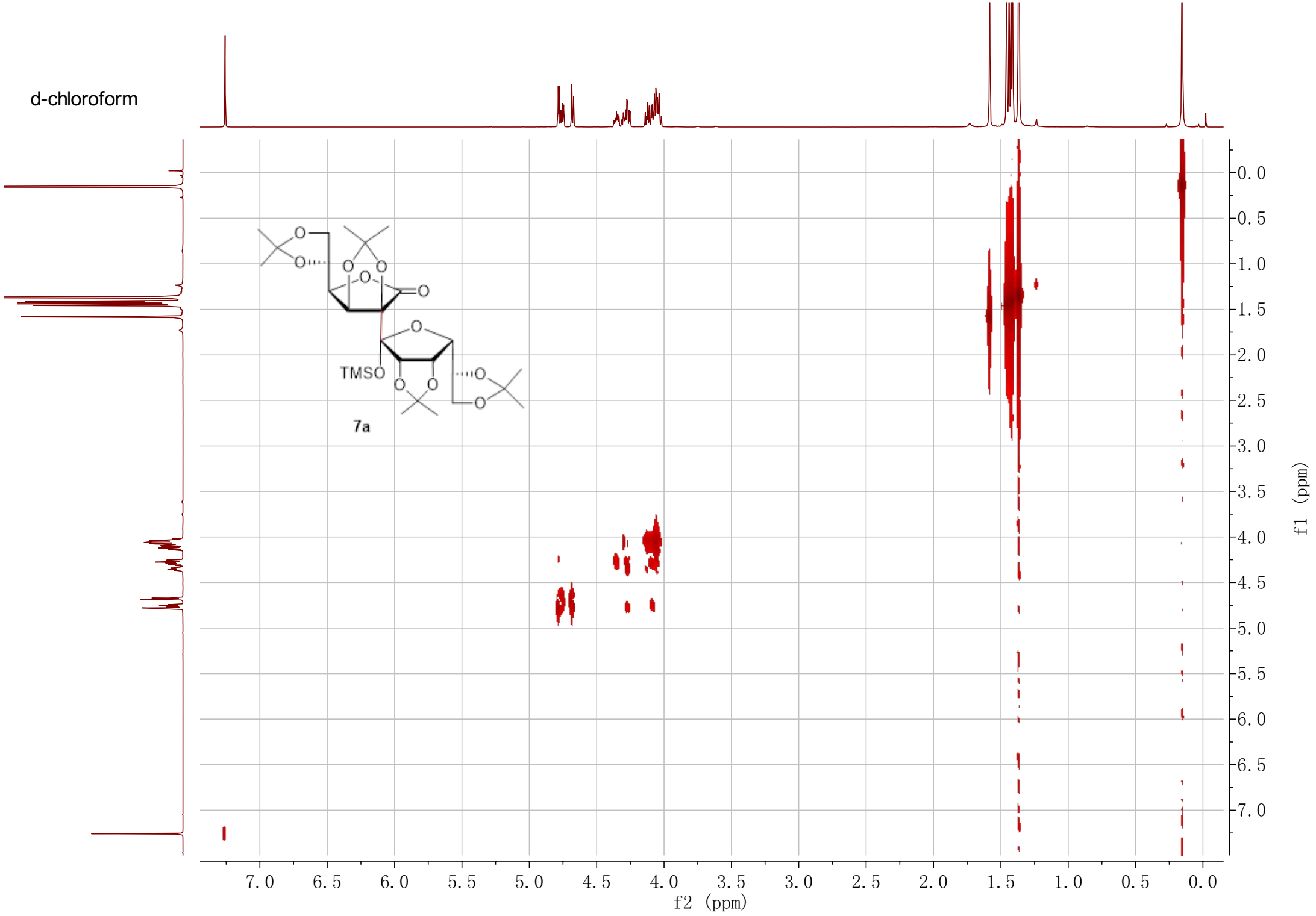

COSY
d-chloroform
OH
6a
f2 (ppm)
f1 (ppm)

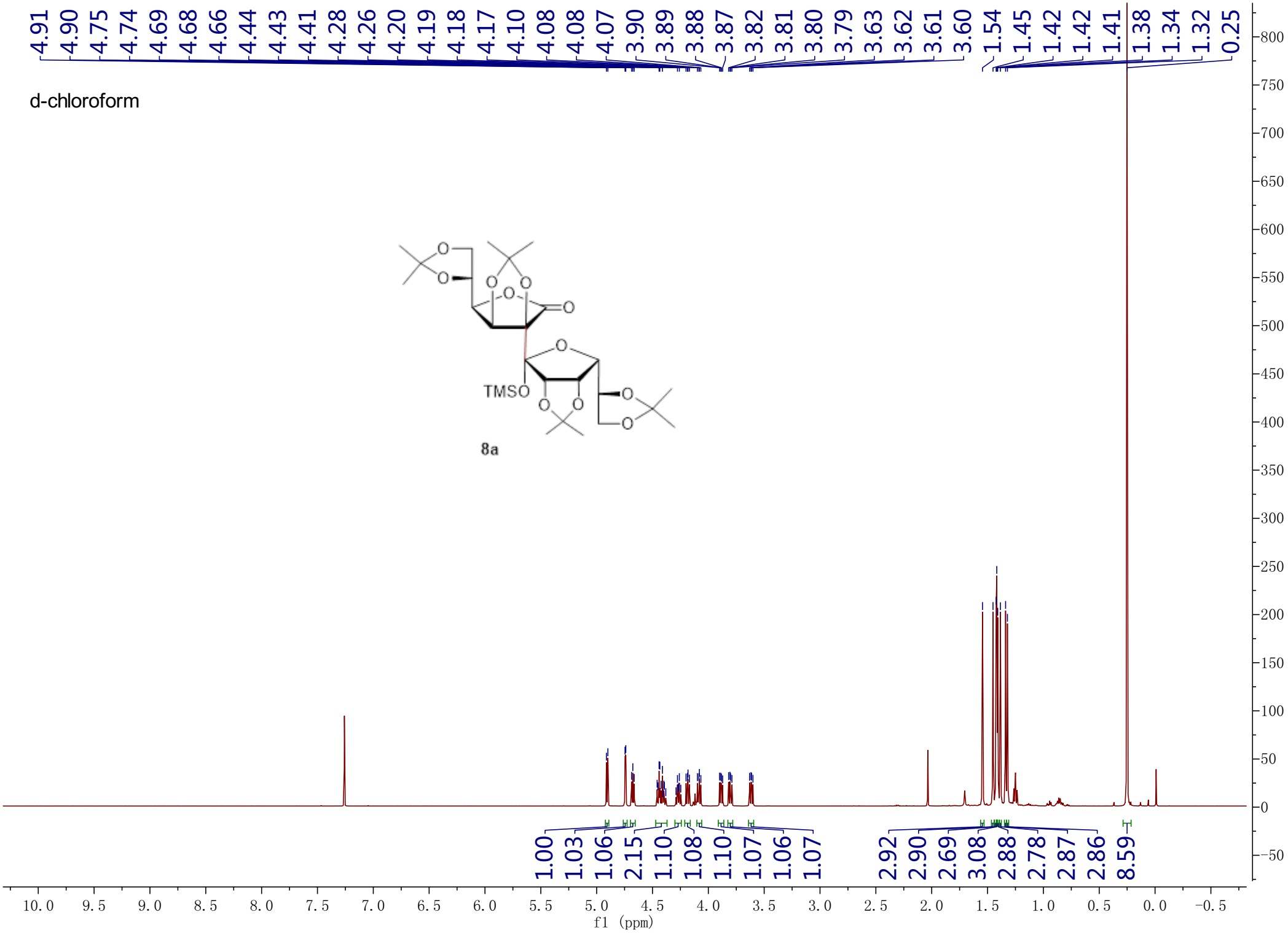
d-chloroform

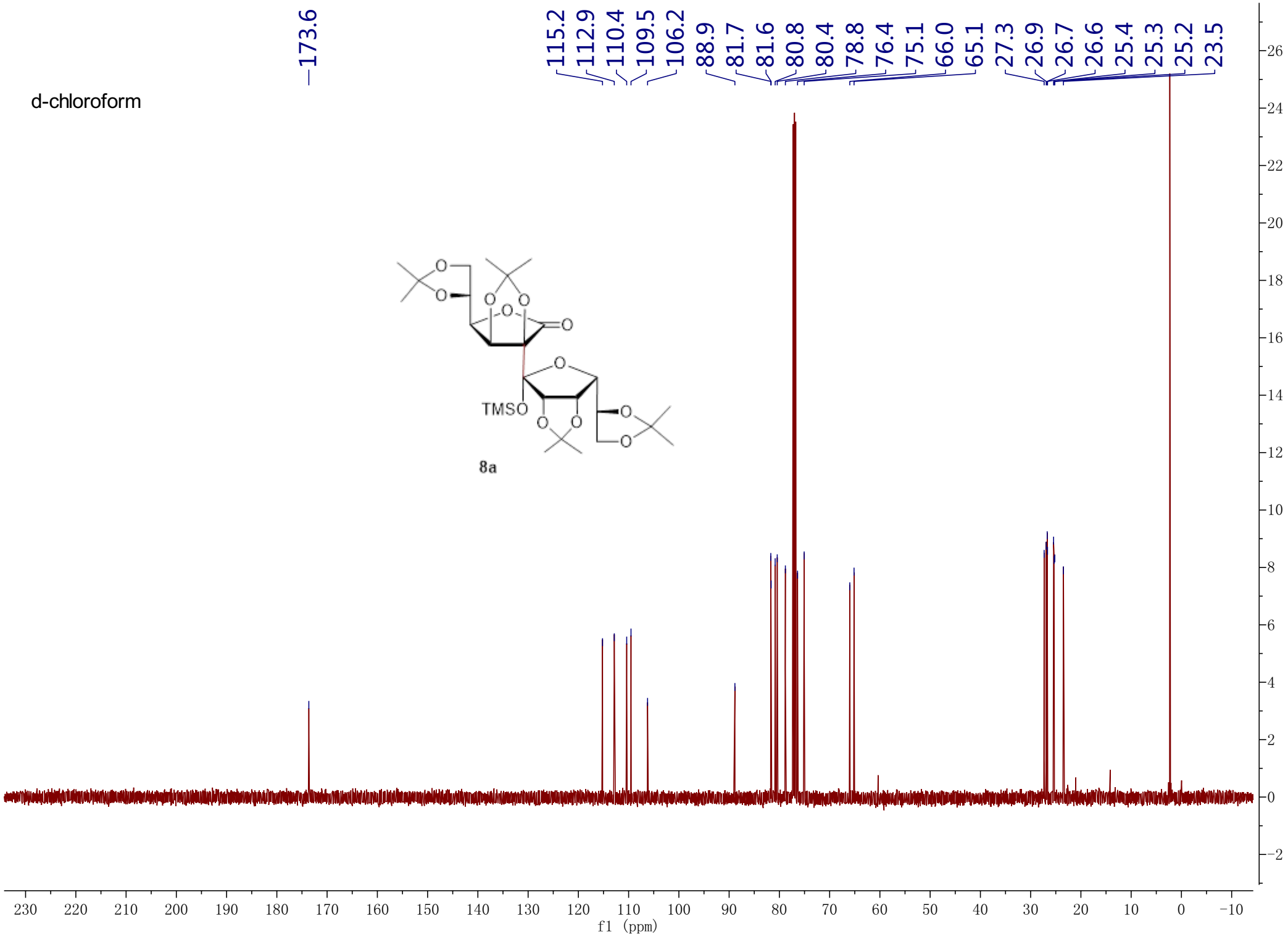


7a

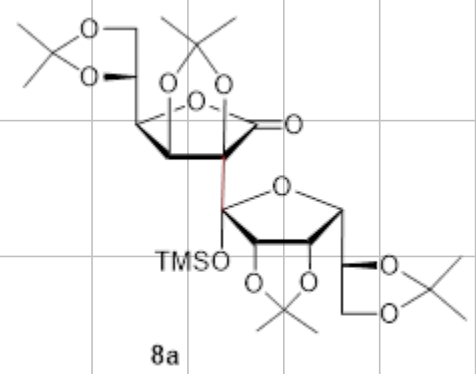

172.2
115.0
112.8
109.9
109.6
105.8
89.2
81.0
80.1
79.8
79.5
78.8
72.9
72.6
67.4
66.8
27.3
27.1
26.9
26.7
25.3
25.3
25.2
23.4
2.0
d-chloroform
TMSO
7a
f1 (ppm)


d-chloroform
TMSO
7a
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
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
f1 (ppm)


4.91
4.90
4.75
4.74
4.69
4.68
4.66
4.44
4.43
4.41
4.28
4.26
4.20
4.19
4.18
4.17
4.10
4.08
4.08
4.07
3.90
3.89
3.88
3.87
3.82
3.81
3.80
3.79
3.63
3.62
3.61
3.60
1.54
1.45
1.42
1.42
1.41
1.38
1.34
1.32
0.25
d-chloroform
TMSO
8a
1.00
1.03
1.06
2.15
1.10
1.08
1.10
1.07
1.06
1.07
2.92
2.90
2.69
3.08
2.88
2.78
2.87
2.86
8.59
f1 (ppm)


173.6
115.2
112.9
110.4
109.5
106.2
88.9
81.7
81.6
80.8
80.4
78.8
76.4
75.1
66.0
65.1
27.3
26.9
26.7
26.6
25.4
25.3
25.2
23.5
d-chloroform
TMSO
8a
f1 (ppm)

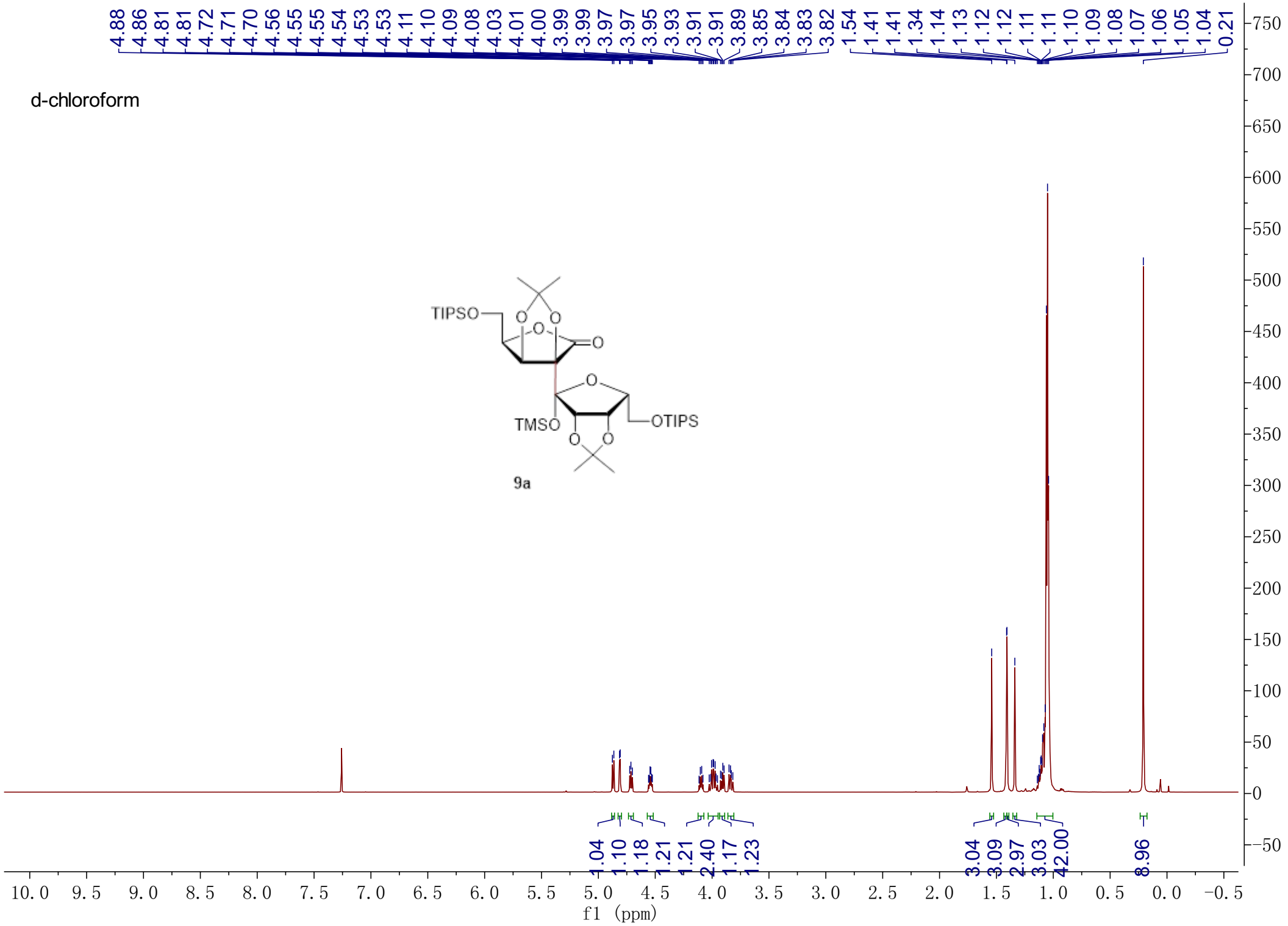
COSY
d-chloroform

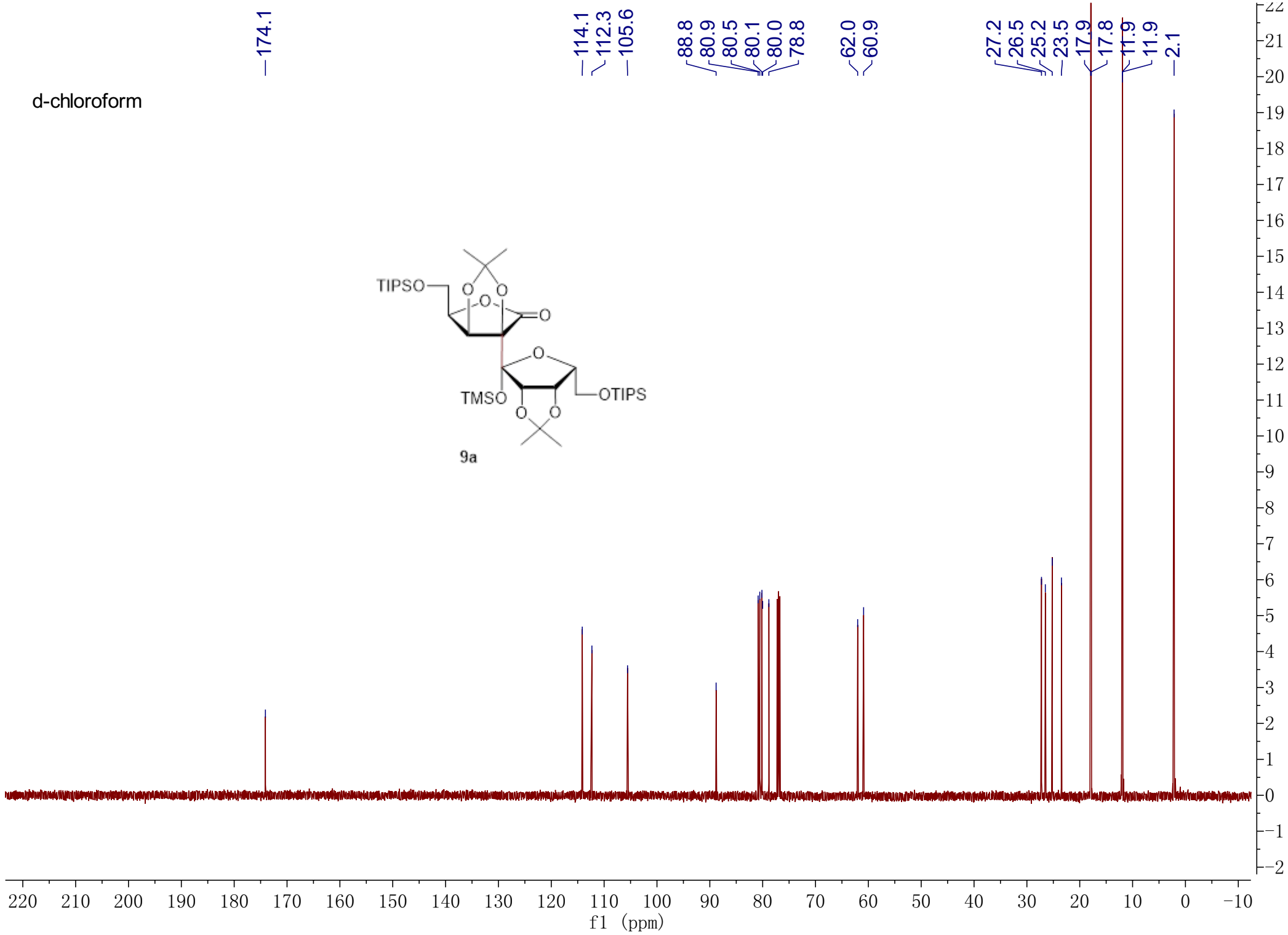


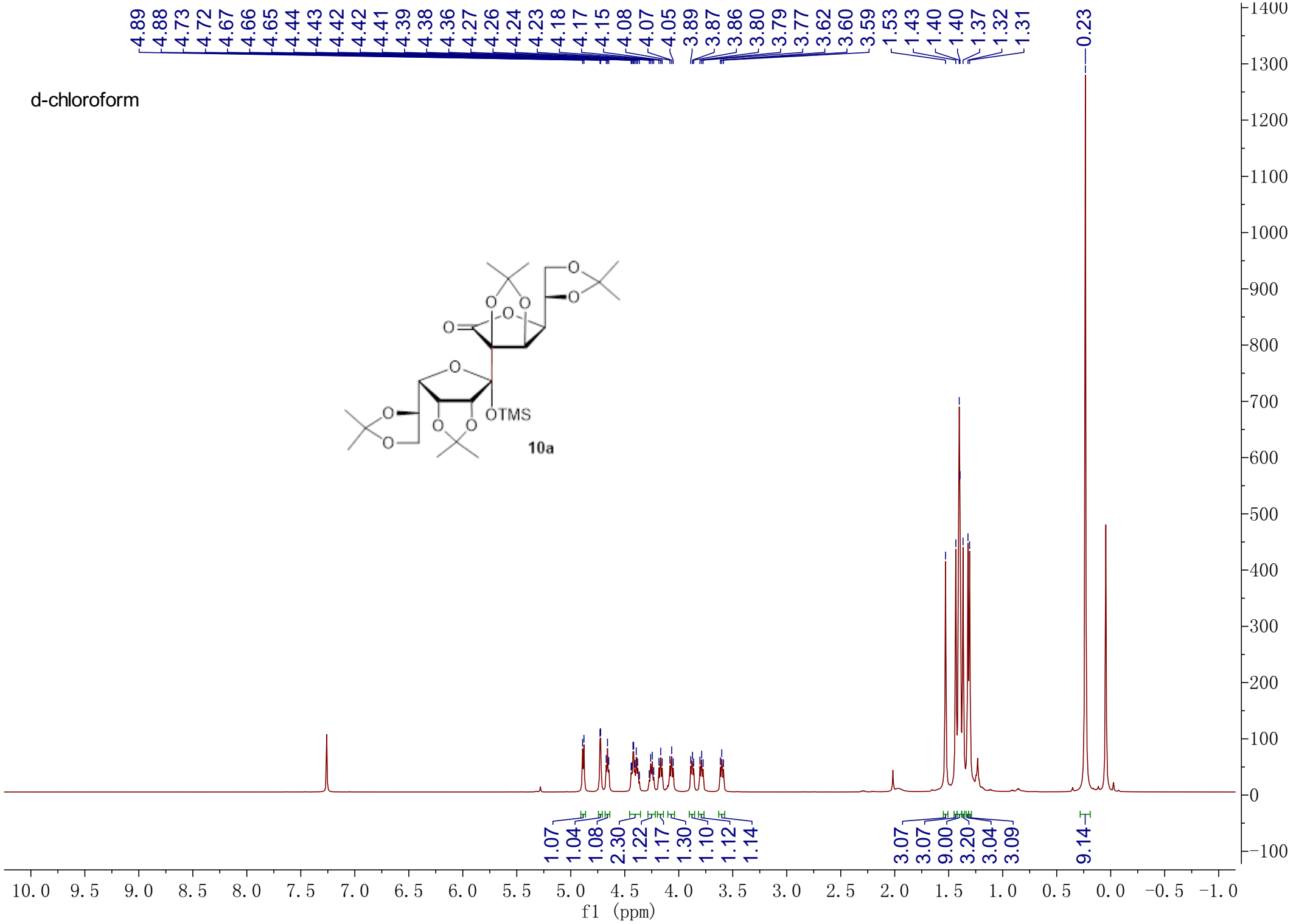
8a

f2 (ppm)

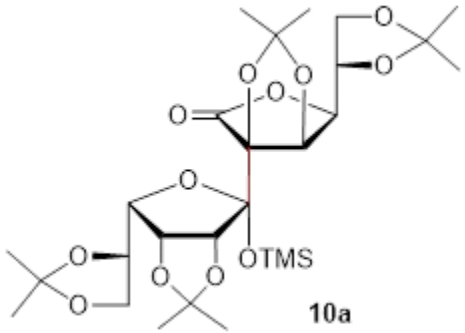
f1 (ppm)


4.88 4.86 4.81 4.81 4.72 4.71 4.70 4.56 4.55 4.55 4.54 4.53 4.53 4.11 4.10 4.09 4.08 4.03 4.01 4.00 3.99 3.99 3.97 3.97 3.95 3.93 3.91 3.91 3.89 3.85 3.84 3.83 3.82 1.54 1.41 1.41 1.34 1.14 1.13 1.12 1.12 1.11 1.11 1.10 1.09 1.08 1.07 1.06 1.05 1.04 0.21
d-chloroform
TIPSO
TMSO
OTIPS
9a
1.04 1.10 1.18 1.21 1.21 2.40 1.17 1.23
3.04 3.09 2.97 3.03 42.00
8.96
f1 (ppm)


174.1
114.1
112.3
105.6
88.8
80.9
80.5
80.1
80.0
78.8
62.0
60.9
27.2
26.5
25.2
23.5
17.9
17.8
11.9
11.9
2.1
d-chloroform
TIPSO
TMSO
OTIPS
9a
f1 (ppm)

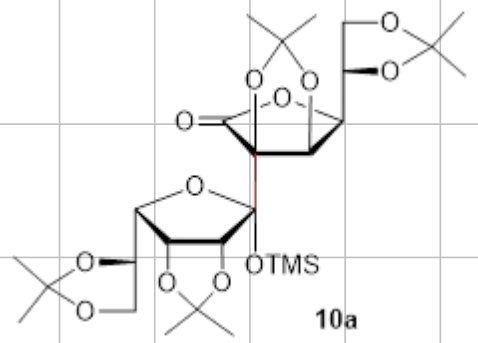

4.89
4.88
4.73
4.72
4.67
4.66
4.65
4.44
4.43
4.42
4.42
4.41
4.39
4.38
4.36
4.27
4.26
4.24
4.23
4.18
4.17
4.15
4.08
4.07
4.05
3.89
3.87
3.86
3.80
3.79
3.77
3.62
3.60
3.59
1.53
1.43
1.40
1.40
1.37
1.32
1.31
0.23
d-chloroform
OTMS
10a
1.07
1.04
1.08
2.30
1.22
1.17
1.30
1.10
1.12
1.14
3.07
3.07
9.00
3.20
3.04
3.09
9.14
f1 (ppm)

d-chloroform



10a

COSY
d-chloroform



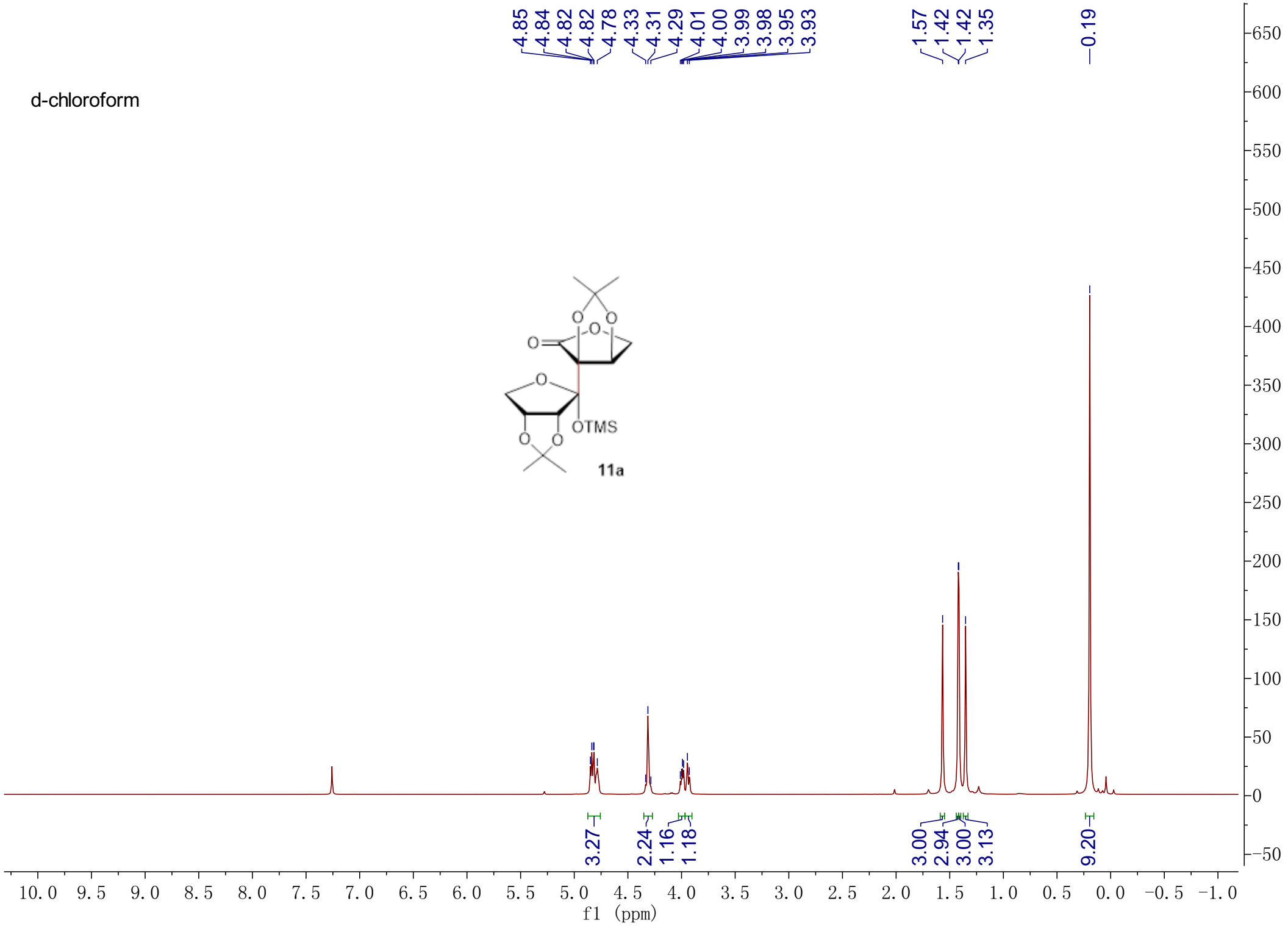
10a

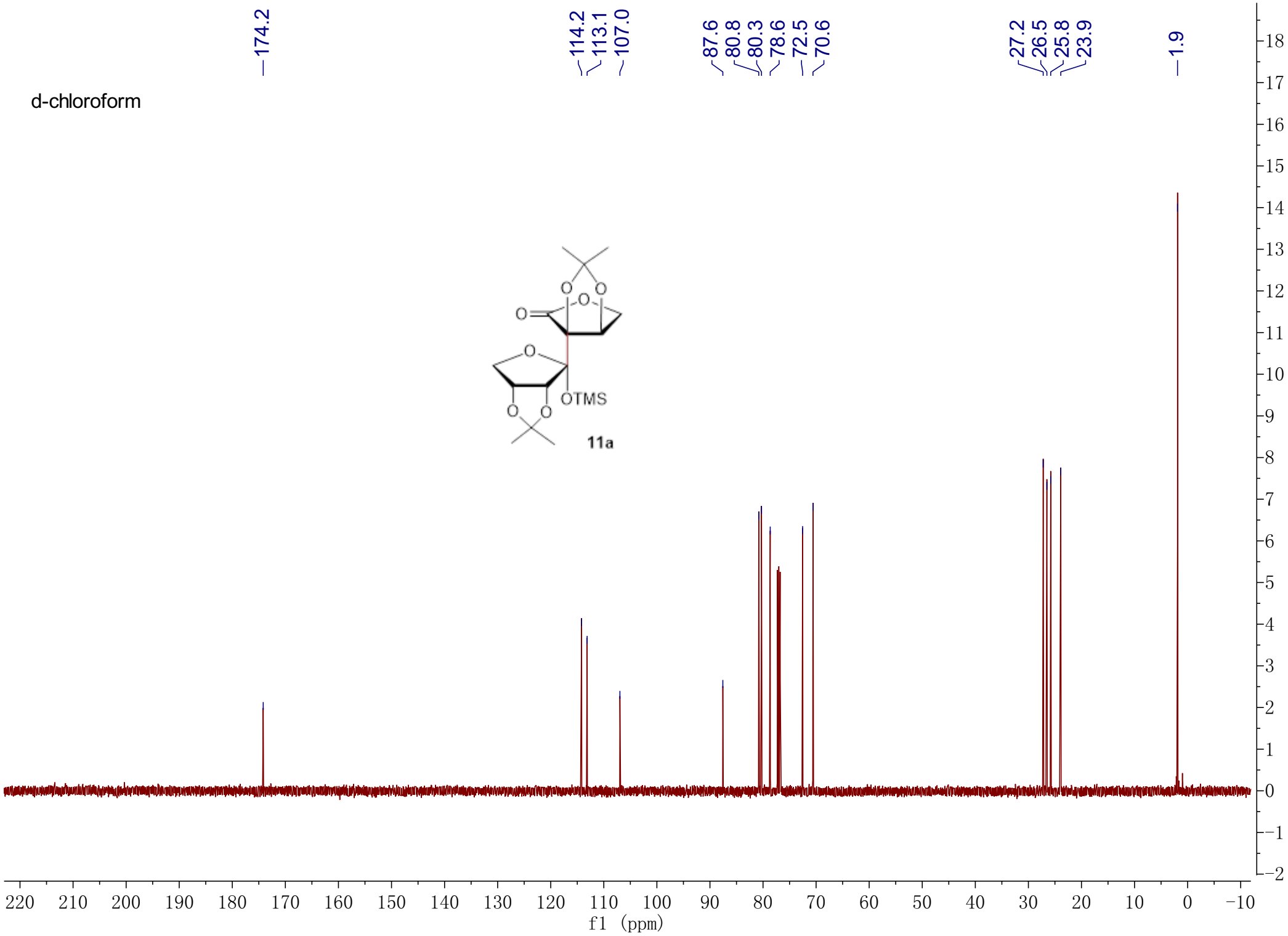
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

f2 (ppm)

0 1 2 3 4 5 6 7 8

f1 (ppm)


4.85
4.84
4.82
4.82
4.78
4.33
4.31
4.29
4.01
4.00
3.99
3.98
3.95
3.93
1.57
1.42
1.42
1.35
0.19
d-chloroform
OTMS
11a
3.27
2.24
1.16
1.18
3.00
2.94
3.00
3.13
9.20
f1 (ppm)


174.2
114.2
113.1
107.0
87.6
80.8
80.3
78.6
72.5
70.6
27.2
26.5
25.8
23.9
1.9
d-chloroform
OTMS
11a
f1 (ppm)

COSY

d-chloroform