Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

2'-Cyanoethyl Thioglycosides: Effective Nucleophiles for the Synthesis of (Hetero) aryl Thioglycosides under the Catalysis of Cu

Xiaolong Yuan, Yazhen Kou, Lan Yu, Zhan-Xin Zhang, * Weihua Xue *

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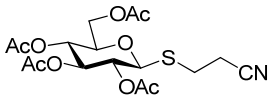
General information

All reactions were conducted using oven-dried glassware under an atmosphere of nitrogen. Dichloromethane was distilled before used from CaH_2, and DMF was distilled from $MgSO_4$. The solvents used in column chromatography, hexane and ethyl acetate, were obtained from commercial suppliers and used without further distillation. TLC was performed on glass-backed plates coated with silica gel F_{254}. Flash chromatography was carried out on using 300-400 Mesh silica gels. Visualization of spots on TLC plate was accomplished with UV light at 254 nm or by dipping the plate into an H_2SO_4-EtOH solution followed by heating. NMR spectra were obtained on a Bruker AVANCE DMX 400 spectrometer operating at 400 MHz for 1H-NMR, 100 MHz for ^{13}C-NMR. Unless otherwise noted, all the NMR spectra were recorded at room temperature. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Coupling constants *J* were reported in hertz unit (Hz). Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of $CDCl_3$. High-resolution mass spectra (HRMS) were obtained using time of flight and quadrupole. Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Analytical and spectral data of all the known compounds are exactly matching with the reported values.

Preparation of donor 2'-cyanoethyl per-*O*-acyl-D-thioglycosides (donor 1a, 1b and 1c)

To the stirred solution of per-*O*-acetyl-D-glucopyranose (per-*O*-acetyl-D-mannopyranose or 2-*N*-phthalimido -1, 3, 4, 6-tetra-*O*-acetyl- D-glucopyranoside [1]) (2 mmol) and 3-mercaptopropionitrile [2] (15 mmol) in anhydrous CH_2Cl_2 (5 mL) at 0 ^oC, $BF_3 \cdot Et_2O$ (0.5 mL, 4 mmol) was added dropwise. When TLC showed the reaction was completed, the reaction mixture was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and concentrated. Pure compounds were obtained through flash column chromatography on silica gel.

2'-Cyanoethyl 2, 3, 4, 6-tetra-*O*-acetyl-α- D-glucopyranoside (1a)



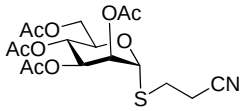
Yield: 726 mg, 87%; colorless oil; $[\alpha]_D^{23}$ +46.6 (*c* 1.0, $CHC1_3$); R_f = 0.28 (petroleum ether-ethyl acetate, 2:1).

1H NMR (400 MHz, $CDCl_3$): δ 5.24 (t, *J* = 10.0 Hz, 1 H), 5.10-5.02 (m, 2 H), 4.58 (d, *J* = 10.0 Hz, 1H), 4.24 (dd, *J* = 4.8, 12.4 Hz, 1 H), 4.17 (dd, *J* = 2.0, 12.4 Hz, 1 H), 3.76 (ddd, *J* =2.4, 4.2 and 7.2 Hz, 1 H), 3.03(dt, *J* = 3.6, 20.8 Hz , 1 H), 2.83 (dt, *J* = 2.8, 20.4 Hz, 1 H), 2.80-2.70 (m, 2 H), 2.07(s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.70, 170.21, 169.61, 169.53, 118.21, 83.51, 75.59, 69.47, 68.15, 62.00, 25.86, 20.87, 20.79, 20.71, 19.79.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{24}O_9NS$ 418.1172, found 418.1174.

2'-Cyanoethyl 2, 3, 4, 6-tetra-O-acetyl-α- D-mannopyranoside (1b)



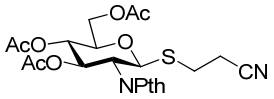
Yield: 684 mg, 82 %; colorless oil; $[\alpha]_D^{23}$ +117.0 (*c* 1.0, $CHC1_3$); R_f = 0.25 (petroleum ether-ethyl acetate, 3:1).

^1H NMR (400 MHz, $CDCl_3$): δ 5.35 (dd, *J* = 1.6, 3.2 Hz, 1 H), 5.29 (d, *J* =1.6 Hz, 1 H), 5.20 (dd, *J* =3.2, 10.0 Hz, 1 H), 4.41 (ddd, *J* =2.0, 5.6, 9.6 Hz, 1 H), 4.29 (dd, *J* = 6.0, 12.4 Hz, 1 H),4.14 (dd, *J* = 2.0, 12.4 Hz, 1 H), 2.96-2.90 (m, 2 H), 2.76 (t, *J* = 6.8 Hz, 2 H), 2.17(s, 3 H), 2.11(s, 3 H), 2.00(s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.49, 169.97, 169.93, 169.74, 140.31, 132.62, 130.11, 118.38, 110.96, 84.37, 70.68, 70.17, 69.31, 66.07, 62.31, 20.96, 20.78, 20.72.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{24}O_9NS$ 418.1172, found 418.1173.

2'-Cyanoethyl 2-dexoyl-2-*N*-phthalimido - 3, 4, 6-tri-*O*-acetyl-β- D-glucopyranoside (1c)



Yield: 887 mg, 88%; colorless oil; $[\alpha]_D^{23}$ +46.3 (*c* 0.5, $CHC1_3$); R_f =0.26 (petroleum ether-ethyl acetate, 2:1).

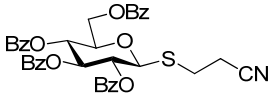
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1 H), 7.85 (s, 1 H), 7.77(d, *J* = 2.4 Hz, 1 H), 7.75 (d, *J* =2.4 Hz, 1 H), 5.83 (t, *J* = 10.0 Hz, 1 H), 5.56 (d, *J* = 10.6 Hz, 1 H), 5.18 (t, *J* = 10.0 Hz, 1 H), 5.39 (t, *J* = 10.6 Hz, 1 H), 4.29 (dd, *J* = 5.2, 12.4 Hz, 1 H), 4.21 (dd, *J* = 1.6, 12.4 Hz, 1 H), 3.95-3.91(m, 1 H), 3.03(dt, *J* = 7.2, 14.0 Hz , 1 H), 2.86-2.79 (m, 1 H), 2.77-2.68 (m, 2 H), 2.13 (s, 3 H), 2.05 (s, 3 H), 1.87 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.55, 169.98, 169.39, 167.71, 167.04, 134.58, 134.45, 131.40, 130.95, 123.80, 117.84, 81.17, 76.16, 71.19, 68.58, 62.03, 53.35, 26.03, 20.71, 20.55, 20.37, 19.52.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{24}O_9NS$ 505.1281, found 505.1280.

Preparation of 2'-cyanoethyl 2, 3, 4, 6-tetra-*O*-benzoyl-β- D-glucopyranoside (1d)

To a solution of the 2, 3, 4, 6-tetra-*O*-benzoyl-β- D-glucopyranosyl bromide (658 mg, 1mmol) and Bu_4NI (369 mg, 1mmol) in CH_2Cl_2 (2 ml) is added NaOH (2ml, 1mol/L) and 2-cyanoethythiol (131mg, 1.5mmol). After the two phase reaction mixture is stirred at room temperature for 24h, CH_2Cl_2 (20 mg) is added. The combine organic extracts are washed with brine and dried with Na_2SO_4, filtered and evaporated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel with petroleum ether-ethyl acetate (2:1) to afford the product.



Yield: 545mg, 82%; colorless oil; $[\alpha]_D^{23}$ +31.9 (*c* 1.0, $CHC1_3$); R_f = 0.42 (petroleum ether-ethyl acetate, 2:1).

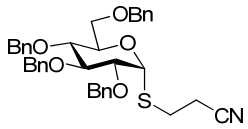
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1 H), 8.04 (s, 1 H), 7.96 (s, 1 H), 7.94 (s, 1 H), 7.92 (s, 1 H), 7.90 (s, 1 H), 7.82 (s, 1 H), 7.80 (s, 1 H), 7.62-7.30 (m, 10 H), 7.30 (s, 1 H), 7.28 (s, 1 H), 5.94 (t, J = 5.6 Hz, 1 H), 5.68 (t, J = 5.6 Hz, 1 H), 5.55 (t, J = 9.6 Hz, 1 H), 4.95 (d, J = 10.0 Hz, 1 H), 4.68 (dd, J = 2.0, 8.4 Hz, 1 H), 4.48 (dd, J = 5.2, 12.4 Hz, 1 H), 4.20 (td, J = 2.8, 5.2, 8.0 Hz, 1 H), 3.11 (dt, J = 7.2, 21.2 Hz, 1 H), 2.87 (m, 1H), 2.77 (dd, J = 6.8, 16.8 Hz, 1 H), 2.70 (dd, J =7.2, 16.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.17, 165.81, 165.36, 165.27, 133.71, 133.51, 130.04, 129.99, 129.82, 129.47, 129.44, 128.82, 128.79, 128.72, 128.69, 128.65, 128.61, 128.48, 83.99, 73.79, 70.26, 69.22, 62.94, 26.12, 19.94.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{37}H_{32}O_9NS$ 666.1798, found 666.1799.

Preparation of 2'-cyanoethyl 2, 3, 4, 6-tetra-*O*-benzyl-α- D-glucopyranoside (1e)

To a stirred solution of 2, 2, 2-trichloroacetimidate 2, 3, 4, 6-tetra-*O*-benzyl-D-glucopyranoside (3.4 g, 5 mmol) and 2-cyanoethythiol (0.65 g, 7.5 mmol) in dry dichloromethane (10 mL) was added boron trifluoride etherate (0.063 ml, 0.5 mmol) under argon at 0 °C. After TLC indicated the completion of the reaction, mixture was quenched with one drop of triethylamine and concentrated under reduced pressure. The residue was subjected to purification by flash chromatography to furnish the titled compound.



Yield: 2.9 g, 86%; colorless oil; $[\alpha]_D^{23}$ +70.2 (c 1.5, $CHC1_3$); R_f = 0.31(petroleum ether-ethyl acetate, 2:1).

1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.12 (m, 20 H), 5.37 (d, J = 4.8 Hz, 1 H), 4.93 (d, J = 10.8 Hz, 1 H), 4.82 (d, J = 10.8 Hz, 1 H), 4.76 (d, J = 10.8 Hz, 1 H), 4.69 (s, 1 H), 4.57 (d, J = 12.0 Hz, 1 H), 4.46 (d, J = 10.8 Hz, 1 H), 4.15 (m, 1 H), 3.85-3.78 (m, 2 H), 3.72-3.62 (m, 2 H), 3.57 (t, J = 9.2 Hz, 1 H), 2.90-2.83 (m, 1 H), 2.77-2.70 (m, 1 H), 2.69-2.62 (m, 2 H).

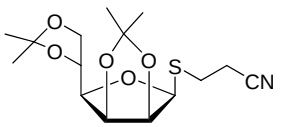
^{13}C NMR (100 MHz, $CDCl_3$): δ 138.57, 138.06, 137.71, 137.06, 128.59, 128.51, 128.34, 128.17, 128.10, 127.99, 127.97, 127.92, 127.88, 127.79, 84.35, 82.37, 79.43, 75.90, 75.22, 73.61, 72.88, 71.02, 68.59, 25.86, 18.99.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{37}H_{40}O_5NS$ 610.2627, found 610.2628.

Preparation of 2'-cyanoethyl 2, 3, 5, 6 -di-*O*-isopropylidene-β-D-mannofuranoside (1f)

2, 3, 5, 6 -Di-*O*-isopropylidene-α-D-mannofuranosyl chloride was prepared using the published procedure. [3] Its α-configuration was characterized by 1HNMR (see page 28). The data for it is fully agreement with the reported ones. [4]

To a stirring solution of 2, 3, 5, 6 -di-*O*-isopropylidene-α-D-mannofuranosyl chloride (576 mg, 2.0 mmol) in DMF (20 mL) containing tetrabutylammonium iodide (73mg, 2.0 mmol), $CsCO_3$ (4.0mmol) and 2-cyanoethythiol (261mg, 3mmol) were added at r.t. The reaction mixture was stirred until reaction completion (control by TLC). The resultant suspension was then poured into water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water (3 x 30 mL) to remove the DMF, brine (30 mL). The organic layer was dried (Na_2SO_4) and filtered, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography to give the donor **1f**.



Yield: 478 mg, 63%; colorless oil; $[\alpha]_D^{23}$ -5.8 (*c* 1.5, $CHC1_3$); R_f = 0.22 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.83 (dd, *J* = 4.0, 6.0 Hz, 1 H), 4.77 (d, *J* = 3.6 Hz, 1 H), 4.75 (t, *J* = 4.0 Hz, 1 H), 4.46 (ddd, *J* = 4.4, 6.0, 7.6 Hz 1 H), 4.11(dd, *J* = 6.0, 8.8 Hz, 1 H), 4.07 (dd, *J* = 6.0, 8.8 Hz, 1 H), 3.58 (dd, *J* = 3.2, 7.6 Hz, 1 H), 3.03-2.91 (m, 2 H), 2.82-2.65 (m, 2 H), 1.51 (s, 3 H), 1.49 (s, 3 H), 1.38 (s, 3 H), 1.38 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 118.16, 113.41, 109.02, 87.88, 82.25, 81.65, 78.96, 72.87, 66.76, 27.79, 26.94, 25.66, 25.16, 24.67, 19.83.

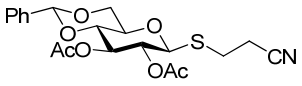
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{24}NO_5S$ 330.1375, found 330.1376.

Preparation of 2'-cyanoethyl 2, 3-di-*O*-acetyl-4, 6-*O*-benzylidene-α-D-glucopyranoside (1g)

The compound was prepared using the slightly modified procedure [5] below.

To a suspension of dry powdered KOH (168 mg, 3mmol), tetrabutylammonium iodide

(320 mg, 1.0 mmol) in anhydrous CH_3CN (20 mL), 3-mercaptopropanenitrile (128mg, 1.5 mmol) and 2, 3-di-*O*-acetyl-4, 6-*O*-benzylidene-α-D-glucopyranosyl bromide [6] (416mg, 1mmol) was added, and the mixture was stirred under a nitrogen atmosphere at room temperature. After 24 h, the resultant suspension was then poured into water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (3 x 30 mL), and dried over sodium sulfate. The filtrate was concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel to obtain donor **1g**.



Yield: 343 mg, 83%; colorless oil; $[\alpha]_D^{23}$ -46.3 (*c* 1.5, $CHC1_3$); R_f= 0.25 (toluene-ethyl acetate, 15:1).

1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1 H), 7.43 (s, 1 H), 7.37-7.35(m, 3 H), 5.51 (s, 1 H), 5.36 (t, *J* = 9.2 Hz, 1 H), 5.05 (t, *J* = 9.6 Hz, 1 H), 4.64 (t, *J* = 10.0 Hz, 1 H), 4.38 (dd, *J* = 10.8 Hz, 1 H), 3.77 (t, *J* = 10.0 Hz, 1 H), 3.71 (t, *J* = 9.6 Hz, 1 H), 3.63-3.57 (m, 1 H), 3.05-2.99 (m, 1 H), 2.89 (m, 1 H), 2.69 (t, *J* = 6.8 Hz, 2 H), 2.09 (s, 3 H), 2.06 (s, 3 H).

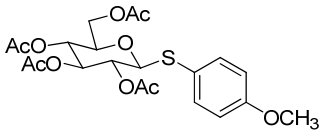
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.09, 169.84, 136.66, 129.32, 128.38, 126.20, 118.11, 101.59, 84.04, 72.48, 70.98, 70.25, 68.36, 25.76, 20.88, 20.83, 19.75.

HRMS (ESI): m/z [M +H]+ calcd for $C_{20}H_{24}O_7NS$ 422.1273, found 422.1272.

Cu (I)-catalyzed Thioglycosidation Reaction of (Hetero) aryl Iodines with 2-cyanoethyl Thioglycosides as Donors

Cs_2CO_3 (66 mg, 0.2 mmol), CuCl (0.01 mmol), 2-cyanoethyl thioglycosides (0.01 mmol) and anhydrous 1, 10-phenanthroline (2 mg, 0.01 mmol) were added to a screw-capped Schlenk tube with a septum. The tube was evacuated with back-filled with nitrogen three times. CH_3CN (2 mL) and (hetero) aryl iodine (0.12 mmol) were added by syringe at room temperature. After the septum of tube was exchanged with a Teflon screw-cap, the reaction mixture was heated under reflux for 24 h, and then allowed to cool to room temperature. The reaction mixture was directly passed through celite. After rinsed with further 50 mL of ethyl acetate, the combined filtrate was evaporated by vacuum. Purification of the residue through flash column chromatography with petroleum ether-ethyl acetate gave the products.

***p*-Methoxylbenzyl 2, 3, 4, 6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (1)** [7]



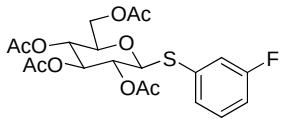
Yield: 46 mg, 98%; white solid, m.p. 80-82 °C; $[\alpha]_D^{23}$ +50.1 (*c* 1.0, $CHC1_3$); R_f=0.30 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.8 Hz, 2 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 5.20 (t, *J* = 9.2 Hz, 1 H), 5.02 (t, *J* = 10.0 Hz, 1 H), 4.89 (t, *J* = 9.2 Hz, 1 H), 4.55 (d, *J* = 10.0 Hz, 1 H), 4.30-4.06 (m, 2 H), 3.82 (s, 3 H), 3.71-3.66 (m, 1 H), 2.11 (s, 3 H), 2.08(s, 3 H), 2.02 (s, 3 H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.63, 170.27, 169.46, 169.32, 160.55, 136.63, 120.96, 114.51, 85.77, 75.84, 74.18, 70.00, 68.30, 62.18, 55.43, 20.89, 20.84, 20.68.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{27}O_{10}S$ 471.1325; found 471.1327.

***m*-Fluorobenzyl 2, 3, 4, 6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (2)**



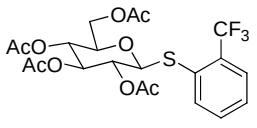
Yield: 90%; white solid, m.p. 73-75 °C; $[\alpha]_D^{23}$ -26.8 (*c* 2.0, $CHC1_3$); R_f = 0.32 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.6 Hz, 1 H), 7.26 (d, *J* = 7.2 Hz, 1 H), 7.23 (d, *J* = 7.6 Hz, 1 H), 7.04-6.99 (m, 1H), 5.24 (t, *J* = 9.2 Hz, 1 H), 5.05 (t, *J* = 10.0 Hz, 1 H), 4.99 (t, *J* = 9.2 Hz, 1 H), 4.74 (d, *J* = 10.0 Hz, 1 H), 4.2 (d, *J* = 4.0 Hz, 1 H), 3.78 (dt, *J* = 4.0 Hz, 10.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.76, 170.24, 169.50, 169.34, 163.86, 161.38, 134.22, 134.15, 130.26, 130.13, 128.14, 128.11, 119.40, 119.18, 115.52, 115.31, 85.42, 73.92, 69.85, 68.24, 62.26, 20.82, 20.73, 20.69.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{24}O_9FS$ 459.1125, found 459.1124.

***o*-Trifluoromethybenzyl 2, 3, 4, 6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (3)**



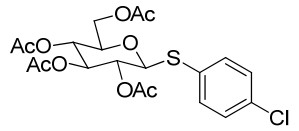
Yield: 45.2 mg, 89%; white solid, m.p. 133-135 °C; $[\alpha]_D^{23}$ -30.4 (*c* 1.0, $CHC1_3$); R_f = 0.21(petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 1 H), 5.23 (t, *J* = 9.2 Hz, 1 H), 5.09 (dd, *J* = 9.2, 11.2 Hz, 1 H), 4.67 (d, *J* =10.4 Hz, 1 H), 4.69 (d, *J* =10 Hz, 1 H), 4.67 (dd, *J* = 5.2, 12.4 Hz, 1 H), 4.18 (dd, *J* = 2.4, 12.4 Hz, 1 H), 3.70 (ddd, *J* = 2.4, 5.2, 7.6 Hz, 1 H), 2.11 (s, 3 H), 2.07 (s, 3 H), 2.03 (s, 3 H), 2.00 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.63, 170.24, 169.60, 169.53, 135.70, 132.31, 132.23, 132.05, 131.75, 131.45, 128.54, 127.03, 126.98, 126.92, 126.87, 124.92, 122.19, 87.01, 75.02, 73.87, 69.75, 68.39, 62.34, 20.87, 20.71, 20.58.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{24}O_9F_3S$ 509.1093, found 509.1095.

***p*-Chlorobenzyl 2, 3, 4, 6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4)** [8, 9]



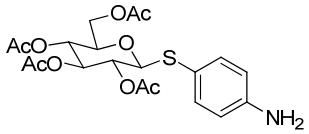
Yield: 45 mg, 95%; white solid, m.p. 111-114 °C; $[\alpha]_D^{23}$ -29.0 (*c* 2.0, $CHC1_3$); R_f= 0.28 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45(d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 9.2 Hz, 2 H), 5.22 (t, *J* = 9.2 Hz, 1 H), 5.04 (t, *J* = 9.6 Hz, 1 H), 4.96 (t, *J* = 10.0 Hz, 1 H), 4.66 (d, *J* = 10.0 Hz, 1H), 4.24-4.16 (m, 2 H), 3.74-3.70(m, 1 H), 3.71 (ddd, *J* = 10.0, 4.4, 2.8 Hz, 1 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.00 (s, 3 H), 1.97 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.0, 169.2, 169.1, 134.9, 134.8, 129.3, 128.9, 85.1, 75.7, 73.7, 69.6, 67.9, 61.9, 20.6, 20.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{24}O_9SCl$ 475.0830, found 475.0829.

***p*-Aminobenzyl 2, 3, 4, 6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (5)** [7]



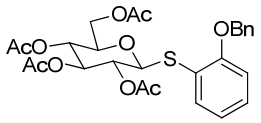
Yield: 41.8 mg, 92%; colorless oil; $[\alpha]_D^{23}$ -22.0 (*c* 1.0, $CHC1_3$); R_f = 0.28 (petroleum ether-ethyl acetate, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.0 Hz, 2 H), 6.62 (d, J = 8.0 Hz, 2 H), 5.19 (t, J = 9.2 Hz, 1 H), 4.98 (t, J = 9.2 Hz, 1 H), 4.91 (t, J = 9.2 Hz,1 H), 4.53 (d, J = 10.0 Hz, 1 H), 4.20-4.18 (m, 2 H), 3.90-3.78 (brs, 2 H), 3.69-3.65 (m, 1 H), 2.11 (s, 3 H), 2.09 (s, 3 H), 2.01 (s, 3 H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.4, 169.54, 169.44, 147.6, 136.8, 117.5, 115.2, 86.02, 75.87, 74.22, 70.05, 68.2, 62.25, 20.94, 20.72.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{26}O_9NS$ 456.1328, found 456.1329.

***o*-Benzyloxybenzyl 2, 3, 4, 6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (6)**



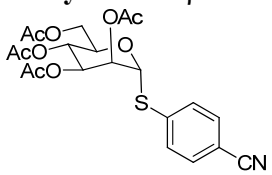
Yield: 48.5 mg, 89 %; white solid, m.p. 171-173°C; $[\alpha]_D^{23}$ -17.0 (*c* 1.0, $CHC1_3$); R_f = 0.25(petroleum ether-ethyl acetate, 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.33 (m, 5 H), 7.22 (t, J = 8.0 Hz, 1 H), 7.13 (t, J = 2.0 Hz, 1 H), 7.06 (d, J = 7.6 Hz, 1 H), 6.92 (dd, J = 2.4, 8.0 Hz, 1H), 5.22 (t, J = 9.2 Hz, 1H), 5.07-5.04 (m, 2 H), 4.99 (t, J = 9.2 Hz, 1 H), 4.72 (d, J = 10.0 Hz, 1H), 4.20 (dd, J = 5.2, 12.4 Hz, 1H), 4.15 (dd, J = 2.4, 12.4 Hz, 1 H), 3.71 (ddd, J = 2.4, 5.2, 7.6 Hz, 1H), 2.94 (s, 3 H), 2.95 (s, 3 H), 1.99(s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.79, 170.29, 169.52, 169.38, 136.68, 133.21, 129.85, 128.75, 128.25, 127.73, 125.20, 119.13, 114.85, 85.88, 75.94, 74.07, 70.23, 69.99, 68.28, 62.21, 20.88, 20.73, 20.70.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{31}O_{10}S$ 547.1638, found 547.1639.

***p*-Cyanobenzyl 2, 3, 4, 6-tetra-*O*-acetyl-1-thio-β-D-mannopyranoside (7)**



Yield: 40.9 mg, 88 %; white solid, m.p. 106-109°C; $[\alpha]_D^{23}$ +81.1 (*c* 1.5, $CHC1_3$); R_f = 0.42 (petroleum ether-ethyl acetate, 2:1).

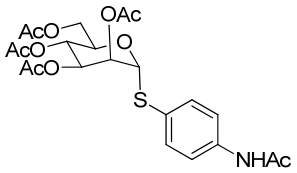
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.4 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 5.66 (d, J = 1.6 Hz, 2 H), 5.47 (t, J = 2.0 Hz, 1 H), 3.56 (t, J = 10.0 Hz, 1 H), 5.27 (dd, J = 3.2, 10.0 Hz, 1 H), 4.44-4.40 (m, 1 H), 4.30 (dd, J = 5.6, 12.4 Hz, 1 H), 4.11 (dd, J = 2.0, 12.4

Hz, 1 H), 2.10(s, 3 H), 2.08 (s, 3 H), 2.04(s, 3 H), 2.03 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.49, 169.97, 169.93, 169.74, 140.31, 132.62, 130.11, 118.38, 110.96, 84.37, 70.68, 70.17, 69.31, 66.07, 62.31, 20.95, 20.78, 20.72.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{24}NO_9S$ 466.1172, found 466.1172.

***p*- Acetamidobenzyl 2, 3, 4, 6-tetra-*O*-benzyl-1-thio-β-D-mannopyranoside (8)**



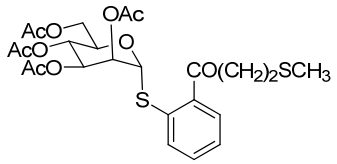
Yield: 42.7 mg, 86 %; white solid, m.p. 133-135°C; $[\alpha]_D^{23}$ +63.4 (*c* 1.0, $CHC1_3$); R_f = 0.33 (petroleum ether-ethyl acetate, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.45 (s, 1 H), 5.48 (dd, *J* = 1.6, 2.4 Hz, 1 H), 5.39 (s, 1H), 5.35-5.28 (m, 2H), 4.55 (t, *J* = 7.2 Hz, 1 H), 4.30 (dd, *J* =5.6, 12.0, Hz, 1 H), 4.10 (dd, *J* = 2.4, 12.0 Hz, 1 H), 2.17(s, 3 H), 2.15(s, 3 H), 2.08 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.76, 170.10, 170.01, 169.88, 168.57, 138.47, 138.71, 127.08, 120.34, 86.20, 70.86, 69.56, 69.45, 66.41, 62.57, 24.73, 21.01, 20.86, 20.84, 20.77.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{28}O_{10}NS$ 498.1434, found 498.1434.

***o*- (2'- Methylthio) ethoxycarbonyl 2, 3, 4, 6-tetra-*O*-benzyl-1-thio-β-D-mannopyranoside (9)**



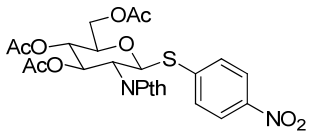
Yield: 48.8 mg, 90 %; colorless oil, $[\alpha]_D^{23}$ +79.9 (*c* 2.0, $CHC1_3$); R_f= 0.33 (petroleum ether-ethyl acetate, 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.46 (td, *J* = 1.6, 8.0 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 1 H), 7.27 (d, *J* = 3.2 Hz, 1 H), 5.67 (d, *J* = 1.2 Hz, 1 H), 5.51 (dd, *J* = 1.2, 2.4 Hz, 1 H), 541-5.34 (m, 2 H), 4.53-4.37 (m, 3 H), 4.34 (dd, *J* = 5.2, 12.4 Hz, 1 H), 4.06 (dd, *J* = 2.4, 12.4Hz, 1 H), 2.2 (s, 3H), 2.18 (s, 3H), 2.06(s, 3 H), 2.03(s, 3 H), 2.01(s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.65, 169.97, 169.89, 169.73, 166.20, 137.15, 132.77, 131.15, 129.83, 128.87, 126.21, 87.74, 71.24, 69.82, 69.54, 66.40, 63.86, 62.33, 32.66, 21.03, 20.82, 20.75,

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{31}O_{10}S_2$ 543.1359, found 543.1360.

***p*-Nitrophenyl 2-dexoyl-2-*N*-phthalimido - 3, 4, 6-tri-*O*-acetyl-β- D-glucopyranoside (10)**



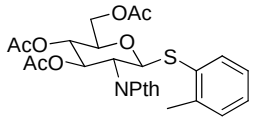
Yield: 53.2 mg, 93 %; yellow solid, m.p. 216-218°C; $[\alpha]_D^{23}$ +63.1 (*c* 1.0, $CHC1_3$); R_f= 0.30 (petroleum ether-ethyl acetate, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4, 2 H), 7.87 (dd, *J* = 3.2, 5.2 Hz, 2 H), 7.78 (dd, *J* = 3.2, 5.2 Hz, 2 H), 7.53 (d, *J* = 8.4, 2H), 5.88 (d, *J* = 10.8, 1 H), 5.83 (d, *J* = 10.0 Hz, 2 H), 5.18 (t, *J* = 10.0 Hz, 1 H), 4.42 (t, *J* = 10.4 Hz, 1 H), 4.32 (dd, *J* = 5.6, 12.4 Hz, 1 H), 4.23 (dd, *J* = 2.0, 12.4 Hz, 1 H), 4.00 (ddd, *J* = 2.0, 5.2, 7.2 Hz, 1 H), 2.13 (s, 3 H), 2.05 (s, 3 H), 1.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.67, 170.22, 169.56, 167.91, 166.99, 147.11, 141.28, 134.84, 131.24, 124.02, 81.97, 76.28, 71.36, 68.50, 62.25, 53.40, 20.96, 20.76, 20.53.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{25}O_{11}N_2S$ 573.1179, found 573.1180.

***o*-Methyphenyl 2-dexoyl-2-*N*-phthalimido - 3, 4, 6-tri-*O*-acetyl-β- D-glucopyranoside (11)**



Yield: 44.9 mg, 83 %; white solid, m.p. 178-180 °C; $[\alpha]_D^{23}$ +33.1 (*c* 1.0, $CHC1_3$); R_f = 0.35 (petroleum ether-ethyl acetate, 2:1).

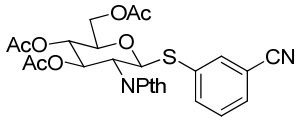
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 2H), 7.78-7.74 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 5.81 (t, *J* =10.4 Hz, 1 H), 5.67 (d, *J* =10.4 Hz, 1 H), 5.18 (t, *J* = 9.2 Hz, 1 H), 4.44 (t, *J* =10.4 Hz, 1 H), 4.28 (dd, *J* =5.6, 12.4 Hz, 1 H), 4.17 (dd, *J* =2.4, 12.0 Hz, 1 H), 3.87 (ddd, 2.4, 5.6, 7.6 Hz, 1 H), 2.19 (s, 3 H), 2.10 (s, 3 H), 2.03(s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.82, 170.30, 169.64, 167.90, 167.13, 140.65, 134.65,

134.51, 133.53, 131.62, 131.22, 131.16, 130.48, 128.57, 126.70, 123.84, 83.61, 75.88, 71.68, 68.89, 62.43, 53.79, 20.99, 20.90, 20.79.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{28}O_9NS$ 542.1485, found542.1486.

***m*-Cynophenyl 2-dexoyl-2-*N*-phthalimido - 3, 4, 6-tri-*O*-acetyl-β- D-glucopyranoside (12)**



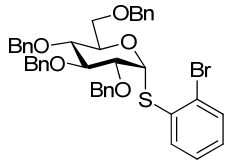
Yield: 48.6 mg, 88 %; white solid; m.p. 157-159 °C; $[\alpha]_D^{23}$ +59.2 (*c* 1.0, $CHC1_3$); R_f = 0.27(petroleum ether-ethyl acetate, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 3.2 Hz, 1 H), 7.88 (d, *J* = 3.2 Hz, 1 H), 7.79 (d, *J* = 3.2 Hz, 1 H), 7.78 (d, *J* = 3.2 Hz, 1 H), 7.74 (s, 1 H), 7.65 (dt, *J* = 1.2, 8.0 Hz, 1 H), 7.60 (dt, *J* = 1.2, 8.0 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 1H), 5.80 (t, *J* = 9.2 Hz, 1 H), 5.74 (d, J = 10.8 Hz, 1 H), 5.14 (t, *J* = 9.6 Hz, 1 H), 5.13 (t, *J* = 9.2 Hz, 1 H), 4.33-4.28 (m, 2H), 4.23 (dd, *J* = 2.0, 12.4 Hz, 1 H), 3.95 (ddd, *J* = 2.0, 4.8, 7.2 Hz, 1 H), 2.15 (s, 3H), 2.04(s, 3H), 1.84(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.88, 170.20, 169.57, 167.93, 166.93, 137.31, 136.11, 134.81, 134.70, 133.20, 131.97, 131.50, 131.04, 129.70, 123.99, 118.14, 113.35, 82.34, 76.23, 71.44, 68.42, 62.19, 53.43, 20.96, 20.76, 20.53.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{25}O_9N_2S$ 553.1281, found 553.1281.

***o*-Bromobenzyl 2, 3, 4, 6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (13)**



Yield: 66 mg, 93 %; colorless oil; $[\alpha]_D^{23}$ +71.7 (*c* 0.5, $CHC1_3$); R_f = 0.34 (petroleum ether-ethyl acetate, 8:1).

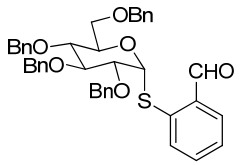
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 2 H), 7.41 (d, *J* = 2.0 Hz, 1 H), 7.40 (d, *J* = 1.2 Hz, 1 H), 7.33-7.26 (m, 16 H), 7.16-7.11(m, 3 H), 7.06 (td, *J* = 1.2, 7.8 Hz, 1 H), 5.80 (d, *J* = 4.0 Hz, 1 H), 5.01 (d, *J* = 10.8 Hz, 1 H), 4.84 (d, *J* = 10.8 Hz, 1 H), 4.83 (dd, *J* = 8.8, 10.8 Hz, 1 H), 4.67 (d, *J* = 11.6 Hz, 1 H), 4.55(d, *J* = 12.0 Hz, 1 H), 4.48 (d, *J* = 10.8 Hz, 1 H), 4.36 (d, *J* = 12.0 Hz, 1 H), 4.29 (d, *J* = 8.8 Hz, 1 H), 3.95-3.92 (m, 2 H), 3.76

(dd, *J* = 2.8, 10.8 Hz, 1 H), 3.73-3.68 (m, 1 H), 3.55 (dd, *J* = 2.0, 10.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.77, 138.27, 137.90, 137.68, 135.49, 133.13, 132.76, 128.56, 128.50, 128.49, 128.44, 128.38, 128.12, 128.06, 128.00, 127.98, 127.94, 127.83, 127.80, 128.75, 126.29, 86.54, 82.65, 79.64, 77.47, 75.94, 75.25, 73.48, 72.61, 71.57, 68.46.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{40}H_{40}O_5SBr$ 711.1780, found711.1781.

***o*-Formybenzyl 2, 3, 4, 6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (14)**



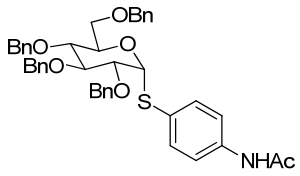
Yield: 59.4 mg, 90 %; colorless oil; $[\alpha]_D^{23}$ +53.5 (*c* 0.5, $CHC1_3$); R_f = 0.42 (petroleum ether-ethyl acetate, 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.55 (s, 1 H), 7.87 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.66 (d, *J* = 3.6 Hz, 1 H), 7.43 (ddd, *J* = 3.6, 8.0, 9.2 Hz, 1 H), 7.34-7.27 (m, 19 H), 7.15 (d, *J* = 2.4 Hz, 1 H), 7.13 (d, *J* = 1.6 Hz, 1 H), 5.59 (d, *J* = 4.8 Hz, 1 H), 5.01 (d, *J* = 10.8 Hz, 1 Hz), 4.83 (dd, *J* = 6.8, 10.8 Hz, 2 H), 4.71 (s, 2H), 4.54 (d, *J* = 12.0 Hz, 1 H), 4.48 (d, *J* = 10.8 Hz, 1 H), 4.38 (d, *J* = 12.0 Hz, 1 H), 4.23 (dd, *J* = 1.2, 9.6 Hz, 1 H), 3.92 (m, 2 H), 3.76-3.67 (m, 2 H), 3.56 (dd, *J* = 1.6, 6.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.67, 139.04, 138.65, 138.19, 137.84, 137.60, 136.06, 134.34, 133.20, 130.06, 128.66, 128.57, 128.49, 128.27, 128.14, 128.05, 127.90, 127.87, 127.54, 87.49, 82.60, 79.82, 75.98, 75.30, 72.05, 68.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{40}H_{41}O_6S$ 649.2624, found 649.2624.

***p*- Acetamidobenzyl 2, 3, 4, 6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (15)**



Yield: 59.2 mg, 89 %; white solid, m.p. 119-120°C; $[\alpha]_D^{23}$ +90.2 (*c* 1.0, $CHC1_3$); R_f = 0.37 (petroleum ether-ethyl acetate, 2:1).

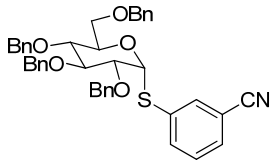
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-4.23 (m, 23 H), 7.16 (d, *J* = 8.0 Hz, 1 H), 7.14 (s, 1

H), 5.53 (d, *J* = 4.0 Hz, 1 H), 5.09 (d, *J* = 10.8 Hz, 1 H), 4.84 (d, *J* = 10.8 Hz, 1 H), 4.79 (d, *J* = 10.8 Hz, 1 H), 4.74 (d, *J* = 11.6 Hz, 1 H), 4.67 (d, *J* = 11.6 Hz, 1 H), 4.54 (d, *J* = 12.0 Hz, 2 H), 4.48 (d, *J* = 12.8 Hz, 1 H), 4.38 (d, *J* = 12.0 Hz, 1 H), 4.34 (d, *J* = 8.0 Hz, 1 H), 3.88 (s, 1 H), 3.87(d, *J* = 2.0, 1 H), 3.77 (dd, *J* = 3.6, 10.4 Hz, 1 H), 3.69-3.64 (m, 1 H), 3.61(dd, *J* = 2.0, 10.8 Hz, 1 H), 2.11 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.39, 138.74, 138.26, 137.95, 137.74, 137.46, 133.15, 129.20, 128.51, 128.47, 128.26, 128.13, 128.04, 128.03, 127.85, 127.79, 127.77, 120.29, 87.62, 82.59, 79.81, 75.90, 75.25, 73.52, 72.65, 71.23, 68.60, 24.74.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{42}H_{44}O_6NS$ 690.2889, found 690.2890.

***m*-Cyanobenzyl 2, 3, 4, 6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (16)**



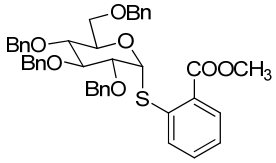
Yield: 57.1 mg, 87 %; colorless oil; $[\alpha]_D^{23}$ +49.6 (*c* 2.0, $CHC1_3$); R_f = 0.25 (petroleum ether-ethyl acetate, 8:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.35-7.28 (m, 19 H), 7.15 (d, *J* = 4.0 Hz, 1 H), 7.13 (d, *J* = 4.0 Hz, 1 H), 5.60 (d, *J* = 1.2 Hz, 1 H), 4.97 (d, *J* = 10.8 Hz, 1 H), 4.82 (t, *J* = 10.8 Hz, 1 H), 4.72 (s, 2 H), 4.57 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 10.4 Hz,1 H), 4.44 (d, *J* = 12.0 Hz, 1 H), 4.22 (ddd, *J* = 1.6, 3.6, 5.2 Hz, 1 H), 3.91 (dd, *J* = 5.2, 9.2 Hz, 1 H), 3.86 (t, *J* = 9.2 Hz, 1 H), 3.57 (dd, *J* = 1.6, 10.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.59, 138.09, 137.77, 137.54, 136.92, 135.46, 134.09, 130.43, 129.54, 128.65, 128.53, 128.55, 128.53, 128.33, 128.26, 128.11, 128.03, 127.95, 127.91, 127.86, , 118.42, 113.23, 86.80, 82.53, 79.73, 75.84, 75.97, 75.33, 73.57, 73.11, 71.66, 68.40.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{41}H_{40}O_5NS$ 658.2627, found 658.2628.

***o*- Ethoxycarbonylphenyl 2, 3, 4, 6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (17)**



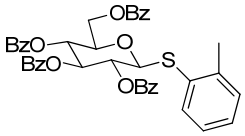
Yield: 57.2 mg, 83 %; white solid, m.p. 221-224°C; $[\alpha]_D^{23}$ -26.8 (*c* 0.5, $CHCl_3$); R_f = 0.23 (petroleum ether-ethyl acetate, 8:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.37 (m, 20 H), 7.15 (d, *J* = 2.4 Hz, 1 H), 7.13 (d, *J* = 1.2 Hz, 1 H), 5.81(d, *J* = 5.6 Hz, 1 H), 5.01(d, *J* = 10.8 Hz, 1 H), 4.84 (d, *J* = 10.8 Hz, 1 H), 4.80 (d, *J* = 10.8 Hz, 1 H), 4.75 (d, *J* = 11.6 Hz, 1 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 10.8 Hz, 1 H), 4.38 (d, *J* = 12.0 Hz, 1 H), 4.25 (d, *J* = 10.0 Hz, 1 H), 4.01(t, *J* = 9.6 Hz, 1Hz), 3.95 (dd, *J* = 9.6, 10.0 Hz,1H), 3.91 (s, 3H), 3.76-3.69 (m, 2H), 3.55 (dd, *J* = 2.0, 10.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.26, 138.82, 138.43, 138.21, 137.90, 132.27, 130.68, 130.59, 129.65, 128.50, 128.46, 128.18, 128.17, 128.01, 127.90, 127.81, 127.73, 125.40, 84.40, 82.65, 79.68, 75.92, 75.11, 73.46, 72.40, 71.39, 68.54, 52.42.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{42}H_{43}O_7S$ 691.2729, found 691.2730.

o-Methybenzyl 2, 3, 4, 6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (18)



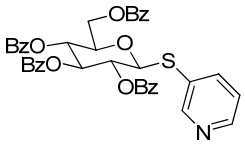
Yield: 61 mg, 87 %; white solid, m.p. 195-197°C; $[\alpha]_D^{23}$ +83.1 (*c* 1.0, $CHCl_3$); R_f = 0.21(petroleum ether-ethyl acetate, 8:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 0.4 Hz, 1 H), 8.01(d, *J* = 1.2 Hz, 1 H), 7.98 (d, *J* = 0.8 Hz, 1 H), 7.96 (d, *J* = 1.2 Hz, 1 H), 7.91 (d, *J* = 0.4 Hz, 1 H), 7.89 (d, *J* = 1.6 Hz, 1 H), 7.82 (d, *J* = 0.4 Hz, 1 H), 7.80 (d, *J* = 1.6 Hz, 1 H), 7.60-7.27 (m, 7 H), 7.17-7.11 (m, 2 H), 6.96-6.91 (m, 1 H), 5.92 (t, *J* = 9.6 Hz, 1 H), 5.65-5.57 (m, 2 H), 5.02 (d, *J* = 10.0 Hz, 1 H), 4.62 (dd, *J* = 2.8, 12.4 Hz, 1 H), 4.47 (dd, *J* = 6.4, 12.0 Hz, 1 H), 4.18 (ddd, *J* = 2.8, 6.4, 9.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.19, 165.90, 165.35, 165.24, 140.65, 133.64, 133.49, 133.39, 132.18, 129.98, 129.93, 129.88, 128.79, 128.56, 128.53, 128.49, 126.73, 87.16, 74.28, 70.78, 69.64, 63.52, 21.06.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{41}H_{35}O_9S$ 703.2002, found6 703.2003.

3'- Pyridyl 2, 3, 4, 6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (19)



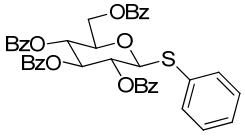
Yield: 59.2 mg, 86 %; white solid, m.p. 182-184°C; $[\alpha]_D^{23}$ +77.4 (*c* 1.0, $CHC1_3$); R_f = 0.22 (petroleum ether-ethyl acetate, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 9.6 Hz, 1 H), 8.50 (dd, *J* = 1.2, 4.8 Hz, 1 H), 8.04 (s, 1 H), 8.02 (d, *J* = 1.2 Hz, 1 H), 7.99 (s, 1H), 7.97 (d, *J* = 1.2 Hz, 1 H), 7.90 (s, 1 H), 7.88 (d, *J* = 1.2 Hz, 1 H), 7.86 (t, *J* = 1.6 Hz, 1 H), 7.08 (s, 1 H), 7.78 (d, *J* = 1.2 Hz, 1 H), 7.58-7.32 (m,), 7.00 (dd, *J* = 2.0, 8.0 Hz, 1 H), 5.93 (t, *J* = 2.0 Hz, 1 H), 5.60 (t, *J* = 5.6 Hz, 1H), 5.47 (t, *J* = 9.6 Hz, 1 H), 5.02 (d, *J* = 10.0 Hz, 1H), 4.67 (dd, *J* = 2.8, 12.0 Hz, 1 H), 4.49 (dd, *J* = 5.6, 12.0 Hz, 1 H), 4.20 (ddd, *J* = 2.8, 5.6, 9.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.10, 165.82, 165.23, 165.14, 153.92, 149.68, 141.51, 133.65, 133.63, 133.41, 133.39, 130.00, 129.94, 129.92, 129.83, 129.59, 129.01, 128.71, 128.68, 128.58, 128.55, 128.40, 123.72, 85.43, 76.52, 70.49, 69.26, 63.04.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{39}H_{32}O_9NS$ 690.1798, found 690.1799.

Benzyl 2, 3, 4, 6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (20)



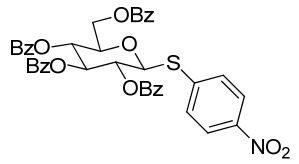
Yield: 57.1 mg, 84 %; colorless oil; $[\alpha]_D^{23}$ +93.7 (*c* 1.0, $CHC1_3$); R_f = 0.3 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 1.2 Hz, 1 H), 8.02 (d, *J* = 1.6 Hz, 1 H), 7.98 (d, *J* = 0.8Hz, 1 H), 7.96 (d, *J* = 1.6 Hz, 1 H), 7.91 (d, *J* = 1.2 Hz, 1 H), 7.89 (d, *J* = 1.2 Hz, 1 H), 7.80 (d, *J* = 1.2 Hz, 1 H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.53 (m, 14 H), 7.28-7.23 (m, 3 H), 7.16-7.12 (m, 2 H), 5.92 (t, *J* = 7.2 Hz, 1 H), 5.61 (t, *J* = 10.0 Hz, 1 H), 5.50 (t, *J* = 9.6 Hz, 1 H), 5.05 (d, *J* = 10.0 Hz, 1 H), 4.68 (dd, *J* = 2.8, 12.0 Hz, 1 H), 4.48 (dd, *J* = 6.0, 12.4 Hz, 1 H), 4.20 (ddd, *J* = 2.8, 6.0, 10.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.21, 165.90, 165.33, 165.20, 133.66, 133.51, 133.39, 133.36, 133.20, 131.90, 130.02, 129.99, 129.96, 129.88, 129.71, 129.27, 129.03, 128.84, 128.78, 128.56, 128.42, 86.37, 74.2, 70.54, 69.48, 63.32.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{40}H_{33}O_9S$ 689.1845, found 689.1846.

***p*-Nitrobenzyl 2, 3, 4, 6-Tetra-*O*-benzoyl-1-thio-α-D-glucopyranoside (21)**



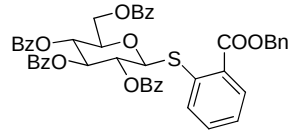
Yield: 69.6 mg, 95 %; white solid, m.p. 233-235°C; $[\alpha]_D^{23}$ +103.5 (*c* 1.0, $CHCl_3$); R_f = 0.25 (petroleum ether-ethyl acetate, 6:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 11.8 Hz, 2 H), 7.93 (t, *J* = 8.0 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 7.80 (d, *J* = 7.2 Hz, 2 H), 7.64 (d, *J* = 7.2 Hz, 2 H), 7.56-7.48 (m, 6 H), 7.42-7.35 (m, 4 H), 7.27 (d, *J* = 7.6 Hz, 1 H), 7.24 (d, *J* = 3.2 Hz, 1 H), 5.99 (t, *J* = 9.6 Hz, 1 H), 5.64 (t, *J* = 10.0 Hz, 1 H), 5.56 (t, *J* = 9.6 Hz, 1 H), 5.21 (d, *J* = 10.0 Hz, 1 H), 4.73 (dd, *J* = 2.4, 12.0 Hz, 1 H), 4.51 (dd, *J* = 6.4, 12.0 Hz, 1 H), 4.51 (ddd, *J* = 2.4, 6.4, 9.6 Hz, 1 H).

^{13}CNMR (400 MHz, $CDCl_3$): δ 166.06, 165.81, 165.32, 165.17, 146.99, 141.82, 133.81, 133.80, 133.75, 133.53, 131.09, 130.01, 129.84, 129.80, 129.46, 128.80, 128.75, 128.63, 128.47, 123.93, 84.75, 73.87, 70.37, 69.26, 63.10,

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{40}H_{32}O_{11}NS$ 734.1696, found 734.1696.

***o*- Benzyloxycarbonyl 2, 3, 4, 6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside (22)**



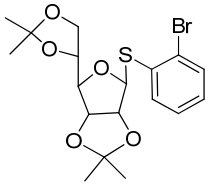
Yield: 70.1 mg, 86 %; white solid, m.p. 262-264°C; $[\alpha]_D^{23}$ +122.1 (*c* 1.0, $CHCl_3$); R_f = 0.25 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2 H), 7.92 (d, *J* = 11.8 Hz, 3 H), 7.82 (t, *J* = 6.4 Hz, 3 H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 7.6, 14.4 Hz, 2 H), 7.44 -7.30(m, 14 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 7.11(t, *J* = 8.0 Hz, 1 H), 5.97 (d, *J* = 8.0 Hz, 1 H), 5.65 (d, *J* = 11.6 Hz, 1 H), 5.22 (d, *J* = 10.0 Hz, 1 H), 5.11 (d, *J* = 12.4 Hz, 1 H), 5.03 (d, *J* = 12.4 Hz, 1 H), 4.67 (d, *J* = 12.0 Hz, 1 H), 4.98 (dd, *J* = 6.8, 12.0 Hz, 1 H), 4.28 (dd, *J* = 7.2, 9.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.19, 166.17, 165.89, 165.39, 165.09, 136.74, 135.63, 133.69, 133.40, 132.40, 130.06, 130.02, 129.93, 129.88, 128.63, 128.60, 128.54, 128.47, 128.44, 128.36, 126.45, 85.07, 74.27, 70.44, 69.64, 67.10, 63.58.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{48}H_{39}O_{11}S$ 823.2213, found 823.2214.

_o_-Bromophenzy 2, 3, 5, 6 -di-_O_-isopropylidene-β-D-mannofuranoside (23)



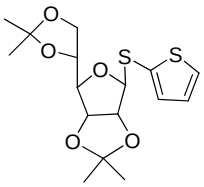
Yield: 39.1 mg, 91%; white solid, m.p. 91-93°C; $[\alpha]_D^{23}$ +26.8 (*c* 1.0, $CHC1_3$); R_f = 0.41 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.58 (d, *J* = 7.6 Hz, 1 H), 7.53 (d, *J* = 7.6 Hz, 1 H), 7.06 (t, *J* = 7.2 Hz, 1 H), 4.98 (m, 1 H), 4.95 (d, *J* = 4.0 Hz, 1 H), 4.83-4.81 (m, 1H), 4.15-4.14 (m, 2 H), 3.63 (dd, *J* = 3.2, 8.0 Hz, 1 H), 1.58 (s, 3 H), 1.46 (s, 3 H), 1.38 (s, 3 H), 1.25 (s, 3 H).

^{13} C NMR (400 MHz, $CDCl_3$): *δ* 137.23, 132.80, 128.84, 128.03, 127.53, 123.49, 113.62, 109.37, 88.26, 82.33, 81.78, 78.77, 72.86, 66.94.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{24}O_5SBr$ 431.0528, found 431.0529.

2'-Thiazolyl 2, 3, 5, 6 -di-_O_-isopropylidene-β-D-mannofuranoside (24)



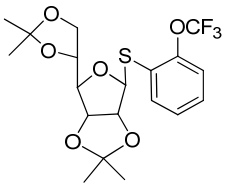
Yield: 30.4 mg, 85%; white solid, m.p. 141-144°C; $[\alpha]_D^{23}$ +44.1 (*c* 1.0, $CHC1_3$); R_f = 0.47 (petroleum ether-ethyl acetate, 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.36 (d, *J* = 5.2 Hz, 1 H), 7.20 (d, *J* = 3.6 Hz, 1 H), 6.87 (t, *J* = 3.6 Hz, 1 H), 4.89 (d, *J* = 4.0 Hz, 1 H), 4.88-4.76 (m, 2 H), 4.14-4.13 (m, 2 H), 3.50 (dd, *J* = 3.2, 8.0 Hz, 1 H), 1.55 (s, 3 H), 1.44 (s, 3 H), 1.38 (s, 3 H), 1.25 (s, 3 H).

^{13} C NMR (400 MHz, $CDCl_3$): *δ* 134.18, 132.34, 129.90, 127.46, 113.52, 109.31, 82.30, 81.83, 81.33, 80.20, 72.90, 68.96.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{23}O_5S_2$ 359.0987, found359.0988.

***o*-Trifluoromethoxyphenyl 2, 3, 5, 6 -di-*O*-isopropylidene-β-D-mannofuranoside (25)**



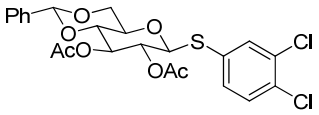
Yield: 40.5 mg, 93%; white solid, m.p. 117-119°C; $[\alpha]_D^{23}$ +49.5 (*c* 1.0, $CHC1_3$); R_f = 0.23 (petroleum ether-ethyl acetate, 8:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-763 (m, 1 H), 7.27-7.25 (m, 3 H), 4.95-4.91 (m, 2H), 4.75 (d, *J* = 4.0 Hz, 1H), 4.54-4.51 (m, 1 H), 4.15-4.14 (m, 2 H), 3.61 (dd, *J* = 3.2, 8.0 Hz, 1 H), 1.55 (s, 3 H), 1.46 (s, 3 H), 1.39 (s, 3 H), 1.25 (s, 3 H).

^{13} C NMR (400 MHz, $CDCl_3$): δ 131.43, 129.73, 127.90, 127.38, 120.85, 113.59, 109.37, 88.30, 82.30, 81.75, 79.80, 72.88, 66.94.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{24}O_6F_3S$ 437.1246, found 437.1247.

***m, p*-Dichlorophenyl 2, 3-di-*O*-acetyl-4, 6-*O*-benzylidene-β-D-thioglucopyranoside (26)**



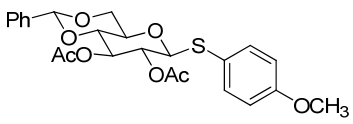
Yield: 48.1 mg, 94%; yellow solid, m.p. 187-189°C; $[\alpha]_D^{23}$ -6.2 (*c* 0.5, $CHC1_3$); R_f = 0.34 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 2.0 Hz, 1 H), 7.43-7.40 (m, 3 H), 7.36-7.34 (m, 3 H), 7.31 (dd, *J* = 2.0, 8.4 Hz, 1 H), 5.49 (s, 1 H), 5.34 (t, *J* = 9.2 Hz, 1 H), 4.96 (dd, *J* = 9.2, 10.4 Hz, 1 H), 4.75 (d, *J* =10.0 Hz, 1 H), 4.39 (dd, *J* = 4.8, 10.4 Hz, 1 H), 3.78 (t, *J* = 9.6 Hz, 1 H), 3.65 (t, *J* = 9.6 Hz, 1 H), 3.59 (dt, *J* = 4.8, 14.0 Hz, 1 H).

^{13} C NMR (400 MHz, $CDCl_3$): δ 170.18, 169.62, 136.68, 134.93, 133.30, 132.95, 132.64, 131.11, 130.82, 129.35, 128.40, 126.24, 101.63, 85.87, 78.05, 72.78, 70.81, 70.88, 68.42, 20.91.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{23}O_7SCl_2$ 513.0542, found513.0544.

***p*- Methoxyphenyl 2, 3-di-*O*-acetyl-4, 6-*O*-benzylidene-β-D-thioglucopyranoside (27)**



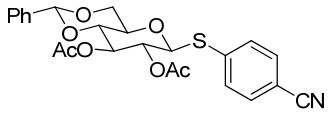
Yield: 42.6, 90%; white solid, m.p. 209-211°C; $[\alpha]_D^{23}$ -15.7 (*c* 0.5, $CHC1_3$); R_f = 0.41(petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.40 (m, 4 H), 7.35-7.33 (m, 3 H), 6.88 (s, 1H), 6.86 (s, 1 H), 5.47 (s, 1 H), 5.31 (t, *J* = 9.2 Hz, 1H), 4.92 (dd, *J* = 9.2, 10.0 Hz, 1 H), 4.64 (d, *J* = 10.0 Hz, 1 H), 4.37 (dd, *J* = 4.8, 10.4 Hz, 1 H), 3.76 (t, *J* = 10.4 Hz, 1 H), 3.60 (t, *J* = 9.2, Hz, 1 H), 3.53 (dt, *J* = 4.8, 14.4 Hz, 1 H), 2.12 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ 170.28, 169.68, 160.48, 136.81, 136.51, 129.27, 128.36, 126.23, 121.0, 114.59, 101.63, 86.66, 78.13, 73.05, 70.73, 70.65, 68.52, 55.47, 21.00, 20.93.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{27}O_8S$ 475.1427, found 475.1428.

***p*-Cyanophenyl 2, 3-di-*O*-acetyl-4, 6-*O*-benzylidene-β-D-thioglucopyranoside (28)**



Yield: 38.9 mg, 83%; white solid, m.p. 234-236°C;$[\alpha]_D^{23}$ -9.3 (*c* 0.5, $CHC1_3$); R_f = 0.28 (petroleum ether-ethyl acetate, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1 H), 7.60 (s, 1 H), 7.53 (s, 1 H), 7.51 (s, 1 H), 7.44-7.35 (m, 4 H), 5.51 (s, 1 H), 5.38 (t, *J* = 9.2 Hz, 1 H), 5.04 (dd, *J* =9.2, 10.0 Hz, 1 H), 4.92 (d, *J* = 10.0 Hz, 1 H), 4.20 (dd, *J* = 4.8, 10.4 Hz, 1 H), 3.80 (t, *J* = 10.0 Hz, 1 H), 3.70 (*t*, J = 9.6 Hz, 1 H), 3.67-3.62 (m, 1 H), 2.09 (s, 3 H), 2.04 (s, 3 H).

^{13}C NMR (400 MHz, CDCl3): δ 170.14, 169.62, 139.29, 136.61, 132.60, 131.36, 129.39, 128.42, 126.24, 118.47, 111.42, 101.70, 85.23, 78.03, 72.68, 70.89, 70.43, 68.41, 20.88, 20.86.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{24}O_7NS$ 470.1273, found 470.1274.

References

(1) Kartha, K.P.; Field, R. A. *Tetrahedron Lett.* **1997**, 53, 11753.

(2) Miller, G. P.; Silverman, A.P.; Kool, E. T. *J. Bioorg. Med. Chem.* **2008**, 16, 56.

(3) Hwang, C. K.; Li, W.S.; Nicolaou, K. C. *Tetrahedron Lett.* **1984**, 25, 2295.

(4) Cicchillo, R.M.; Norris, P. *Carbohydr. Res.* **2000**, 328, 431.

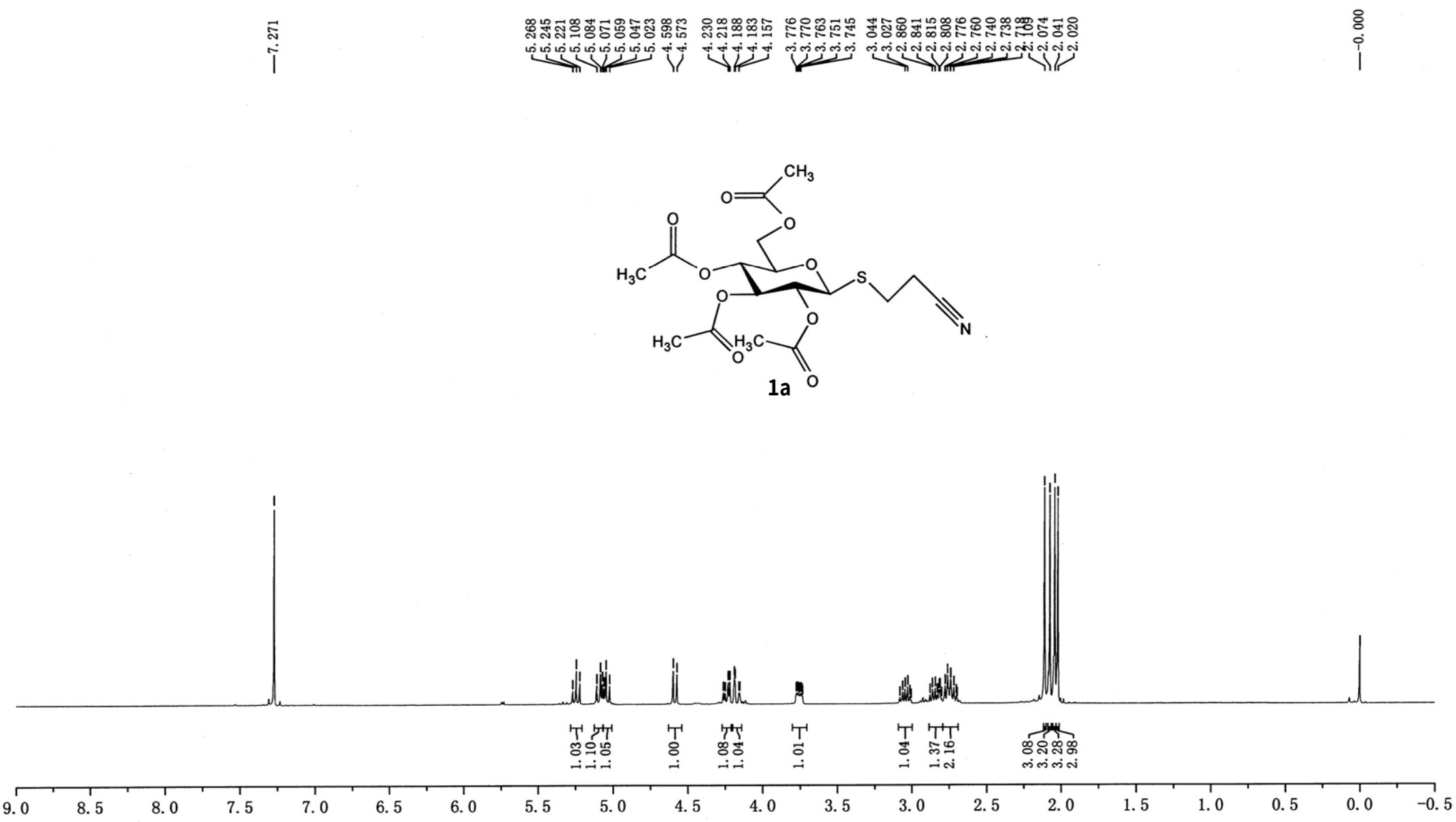
(5) Salvatore, R. N.; Smith, R. A.; Nischwitz, A. K.; Gavin, T. *Tetrahedron Lett.* **2005**, 46, 8931.

(6) Kanakamna, P.P; Mani, N.S. *Syn. Com.* **1992**, 25, 2175.

(7) Brachet, E.; Brion, J. -D.; Messaoudi, S.; Alami, M. *Adv. Synth. Catal.* **2013**, 355, 477.

(8) Pakulski, Z.; Pierozynski, D.; Zamojski, A. *Tetrahedron*, **1996**, 50, 2975.

(9) Weng, S.-S.; Yow-Dzer Lin, Y.-D and Chen, C.-T. *Org. Lett.* **2004**, 8, 5633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4.218
4.188
4.183
4.157
3.776
3.770
3.763
3.751
3.745
3.044
3.027
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2.841
2.815
2.808
2.776
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2.740
2.738
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2.074
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2.020
0.000
1.03
1.10
1.05
1.00
1.08
1.04
1.01
1.04
1.37
2.16
3.08
3.20
3.28
2.98
9.0
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8.0
7.5
7.0
6.5
6.0
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5.0
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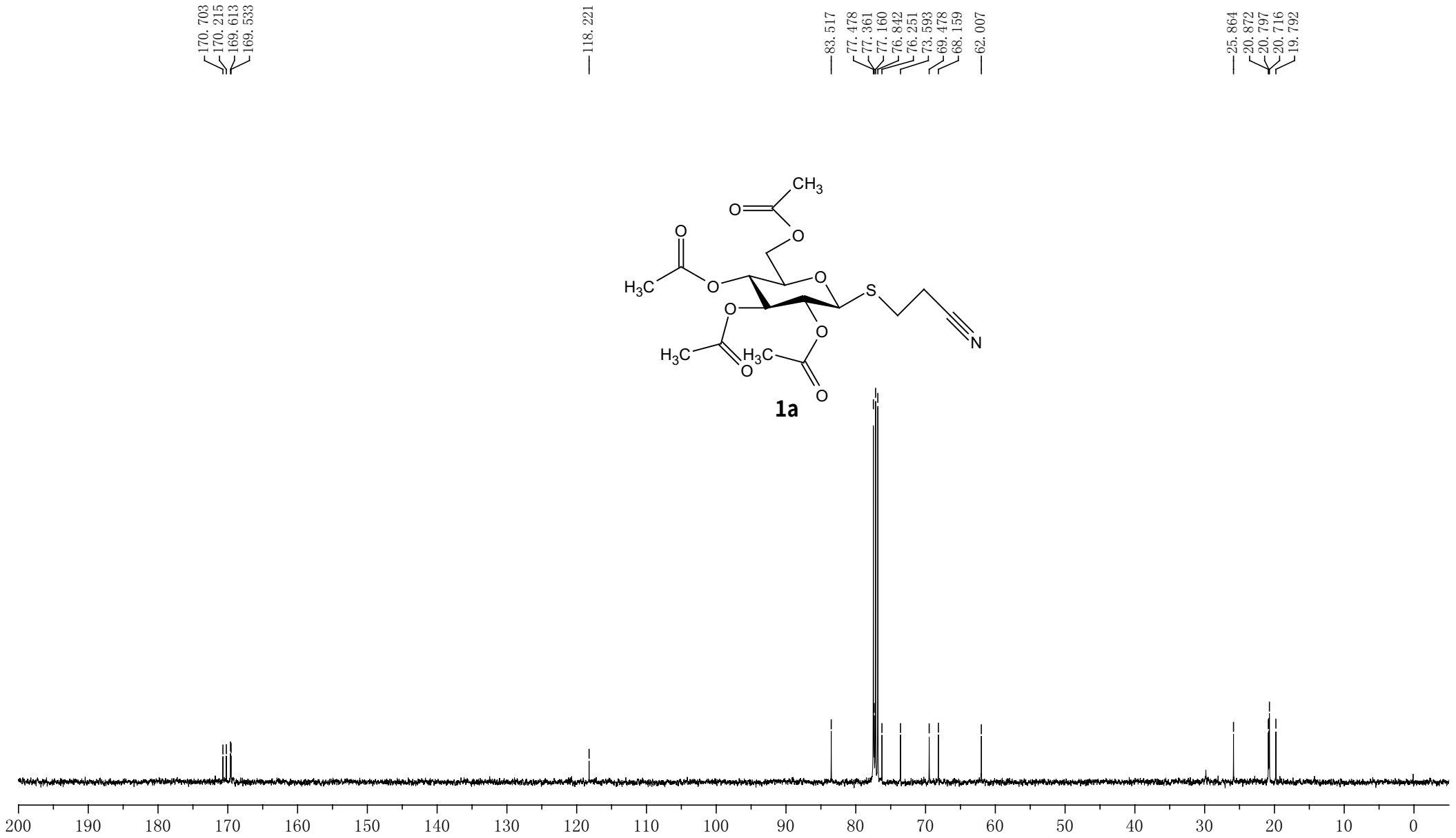
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77.478
77.361
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76.842
76.251
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68.159
62.007
25.864
20.872
20.797
20.716
19.792
CH3
O
O
H3C
O
O
O
S
N
O
H3C
O
H3C
O
O
1a
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10
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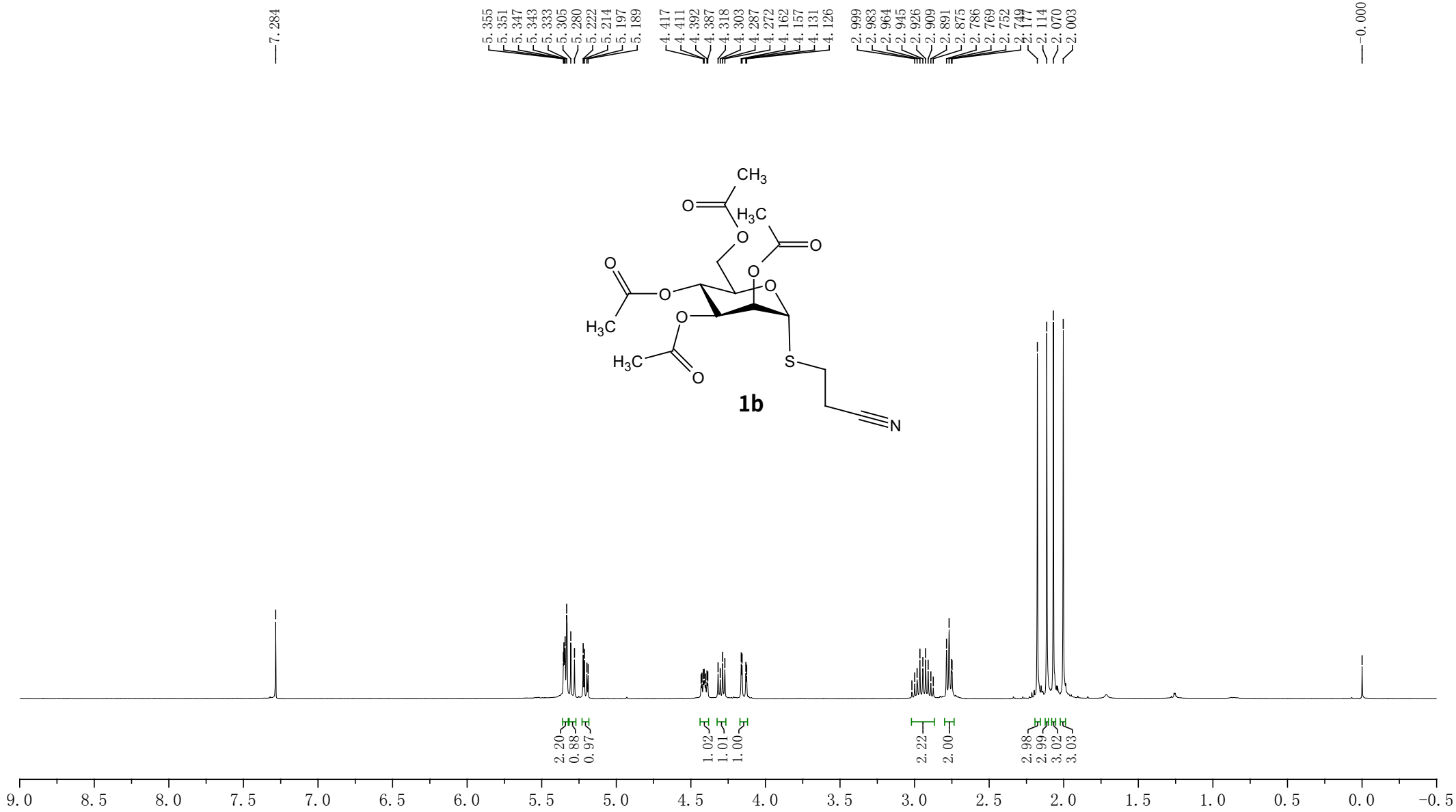
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4.411
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4.387
4.318
4.303
4.287
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4.162
4.157
4.131
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2.945
2.926
2.909
2.891
2.875
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2.769
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2.749
2.114
2.070
2.003
0.000
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O
H3C
O
O
O
O
O
O
H3C
O
H3C
O
S
N
1b
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0.97
1.02
1.01
1.00
2.22
2.00
2.98
2.99
3.02
3.03
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8.5
8.0
7.5
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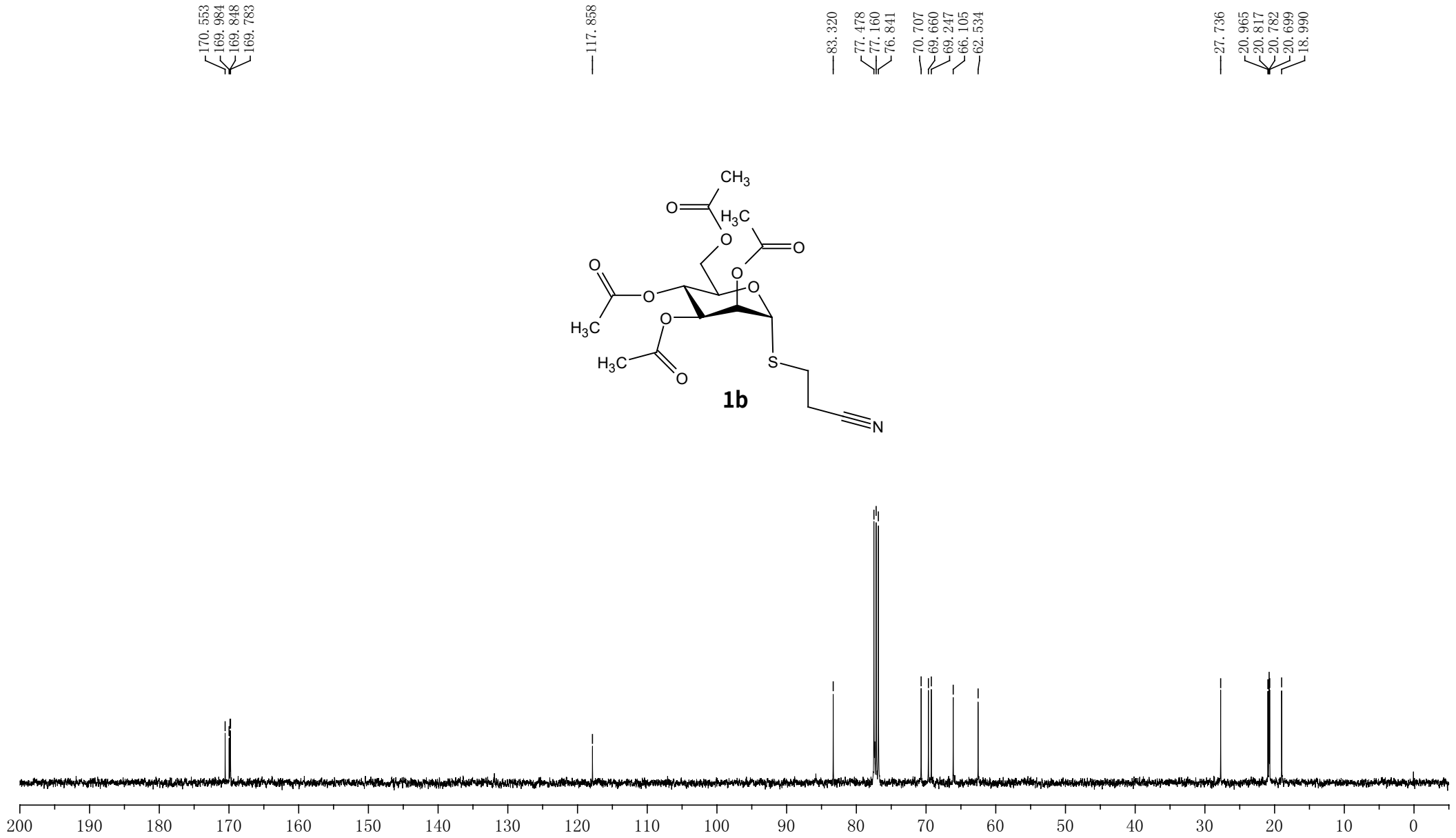
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20.782
20.699
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1b
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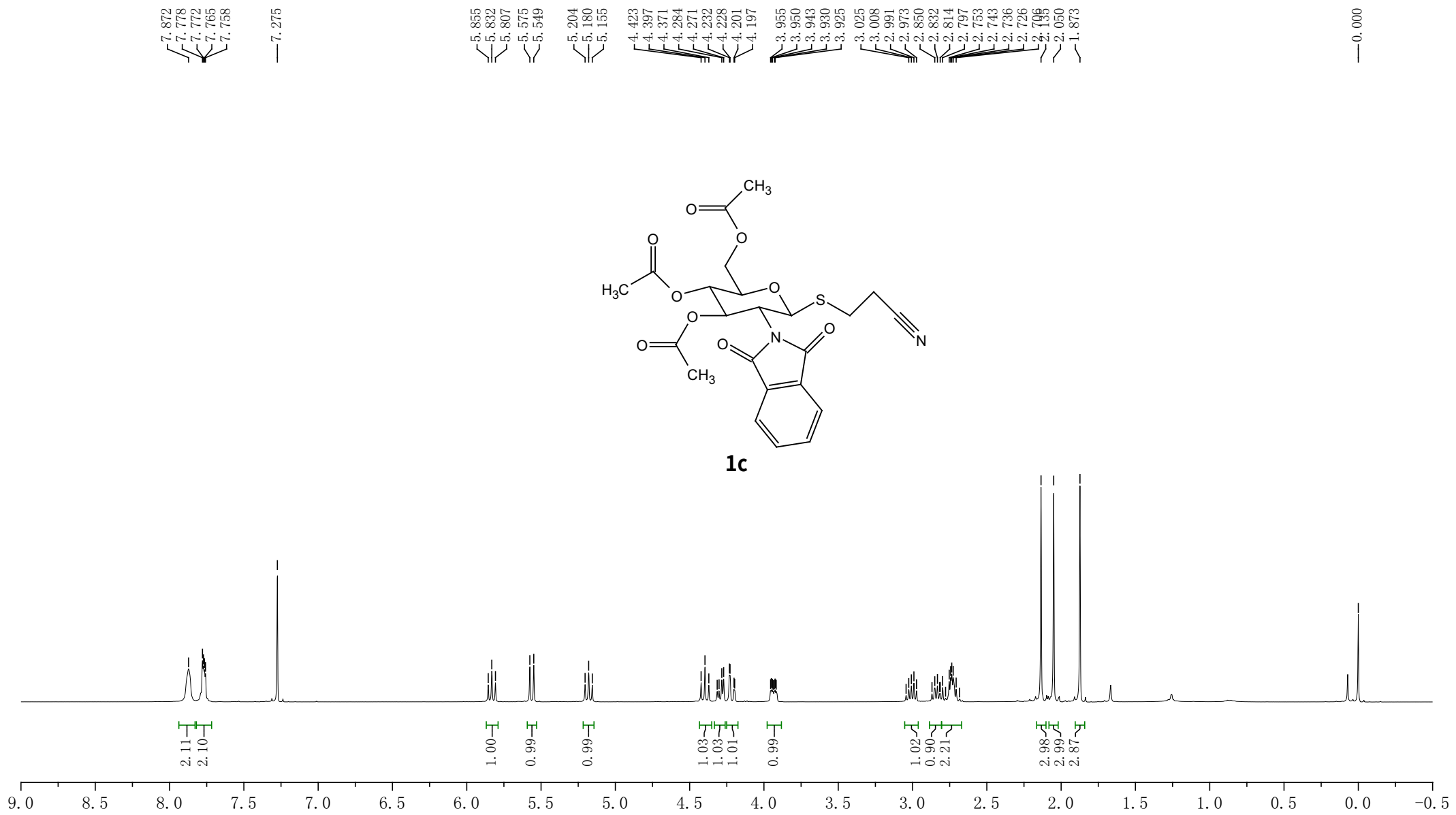
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5.155
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4.271
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4.228
4.201
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3.925
3.025
3.008
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2.850
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2.814
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2.753
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2.736
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O
O
S
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O
O
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0.99
0.99
1.03
1.03
1.01
0.99
1.02
0.90
2.21
2.98
2.99
2.87
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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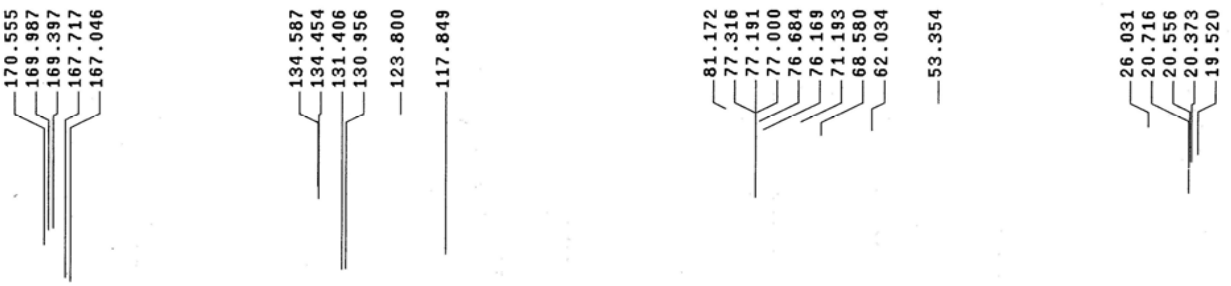
0.5
0.0
-0.5

1c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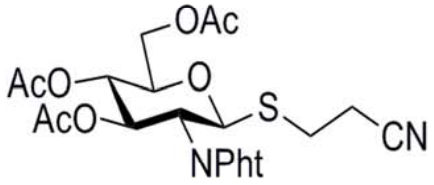
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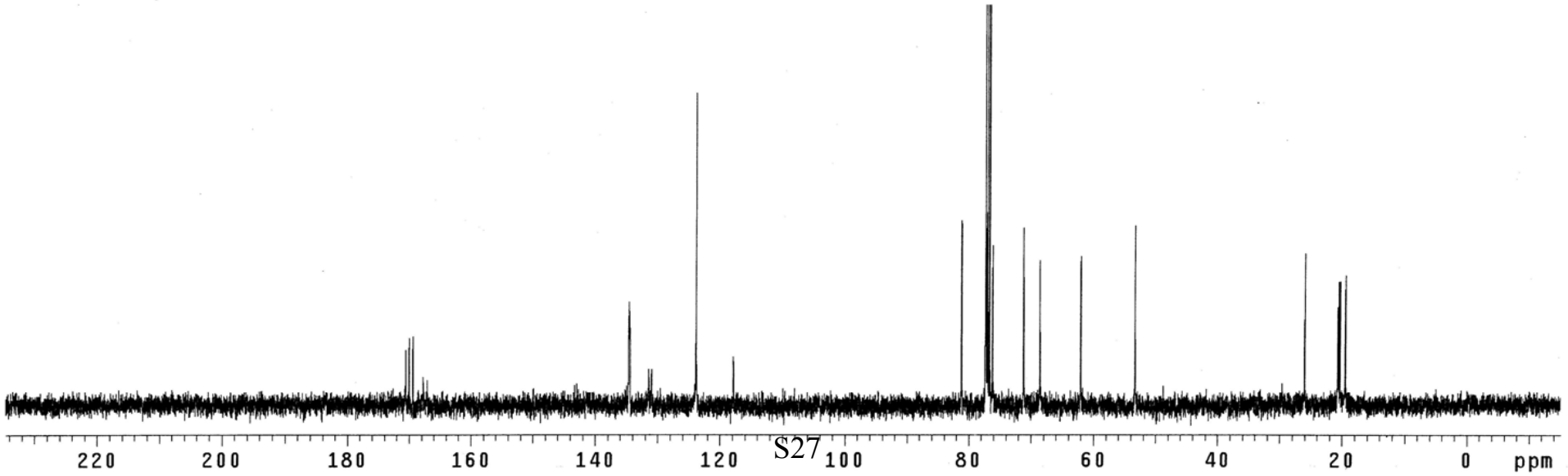
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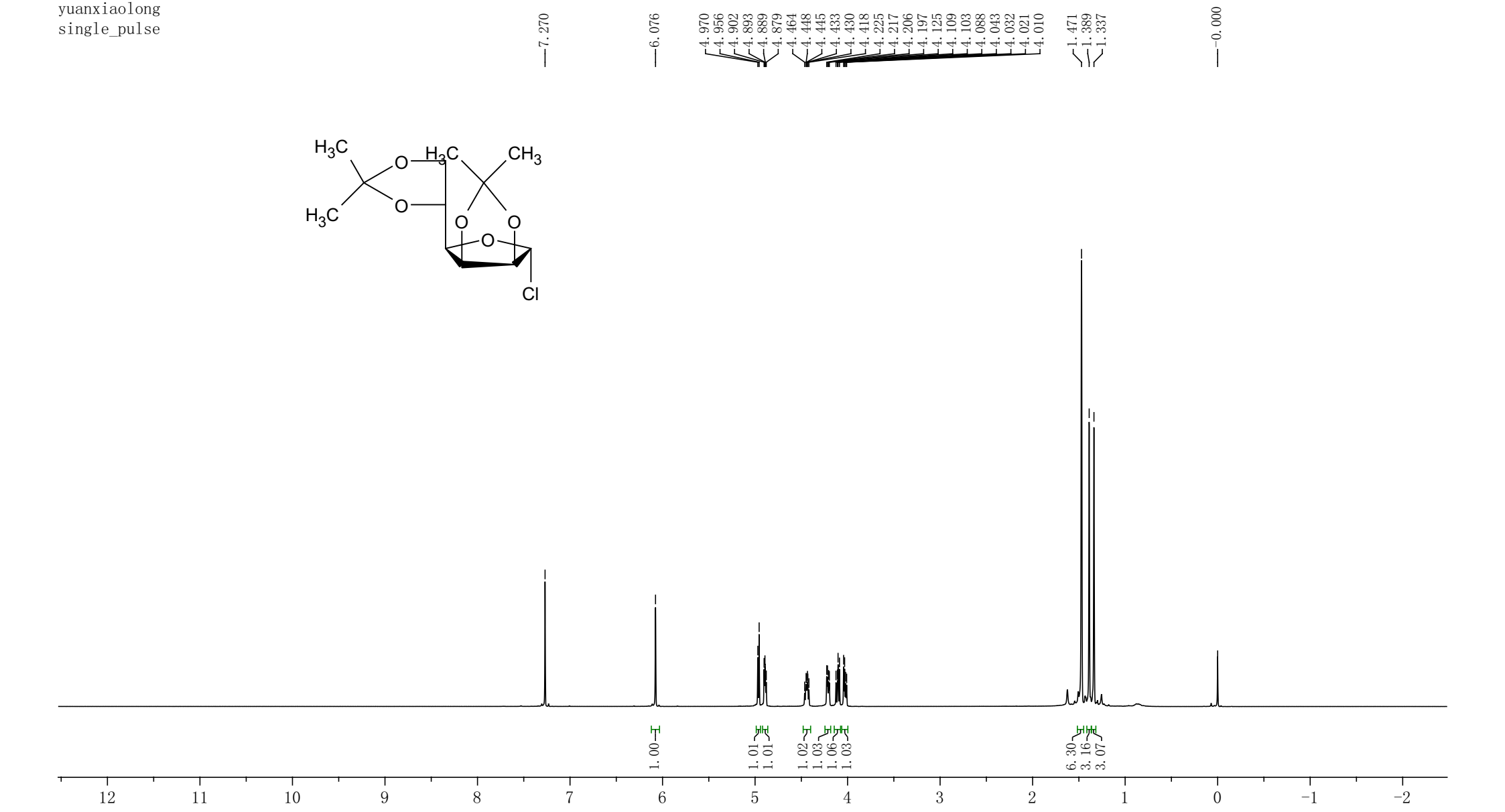
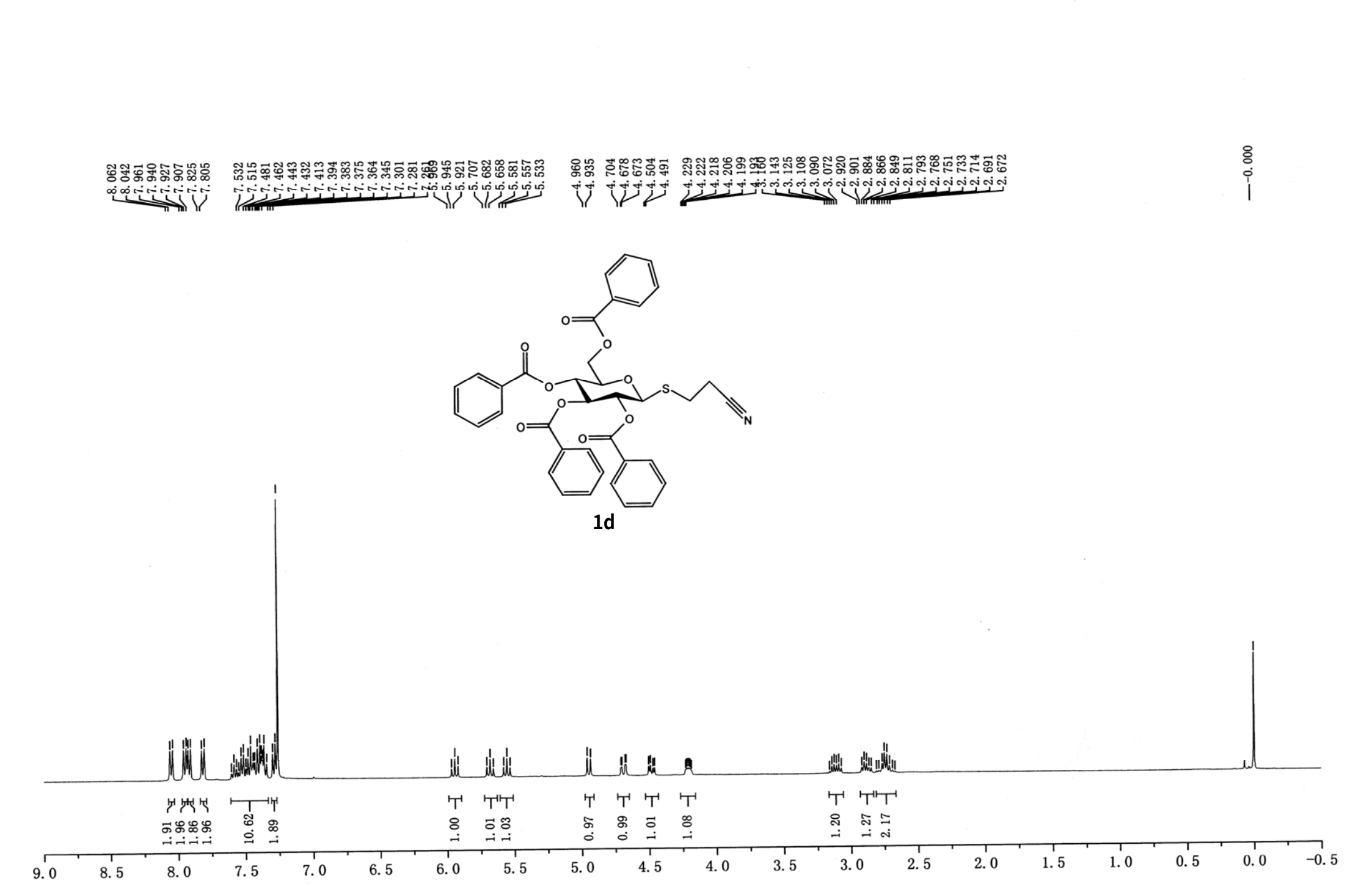
ppm

yuanxiaolong
single_pulse

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6.0
5.5
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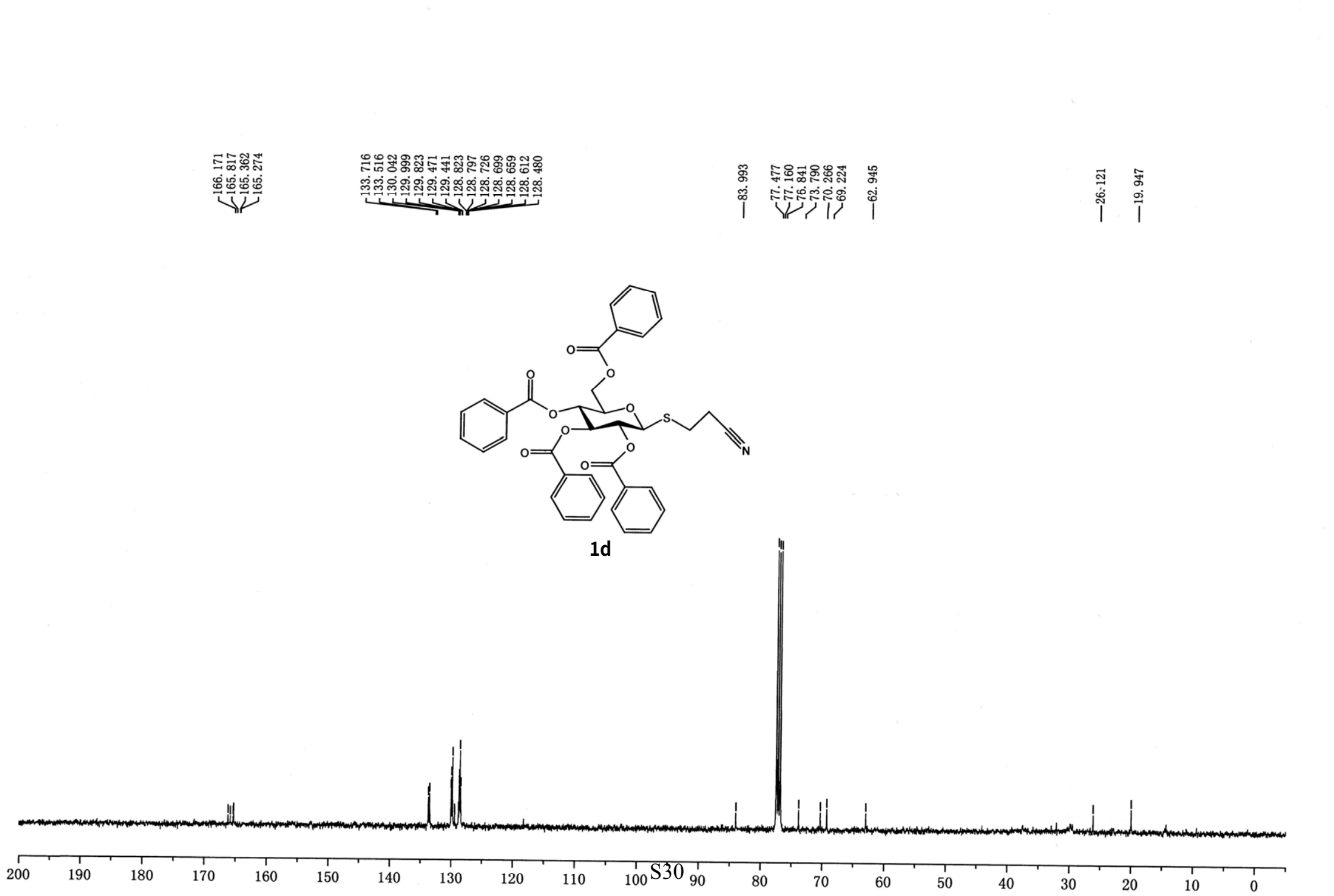
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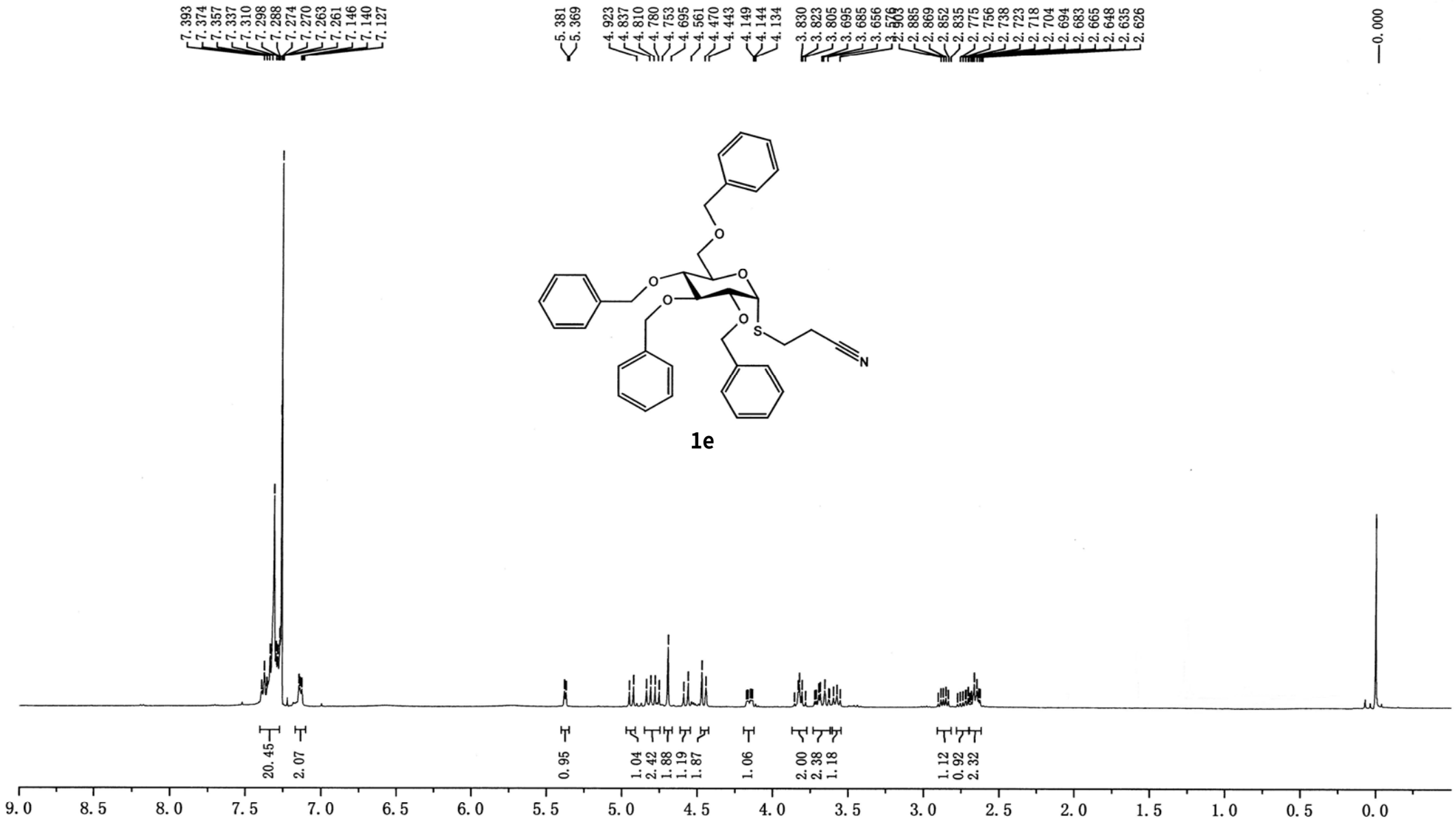
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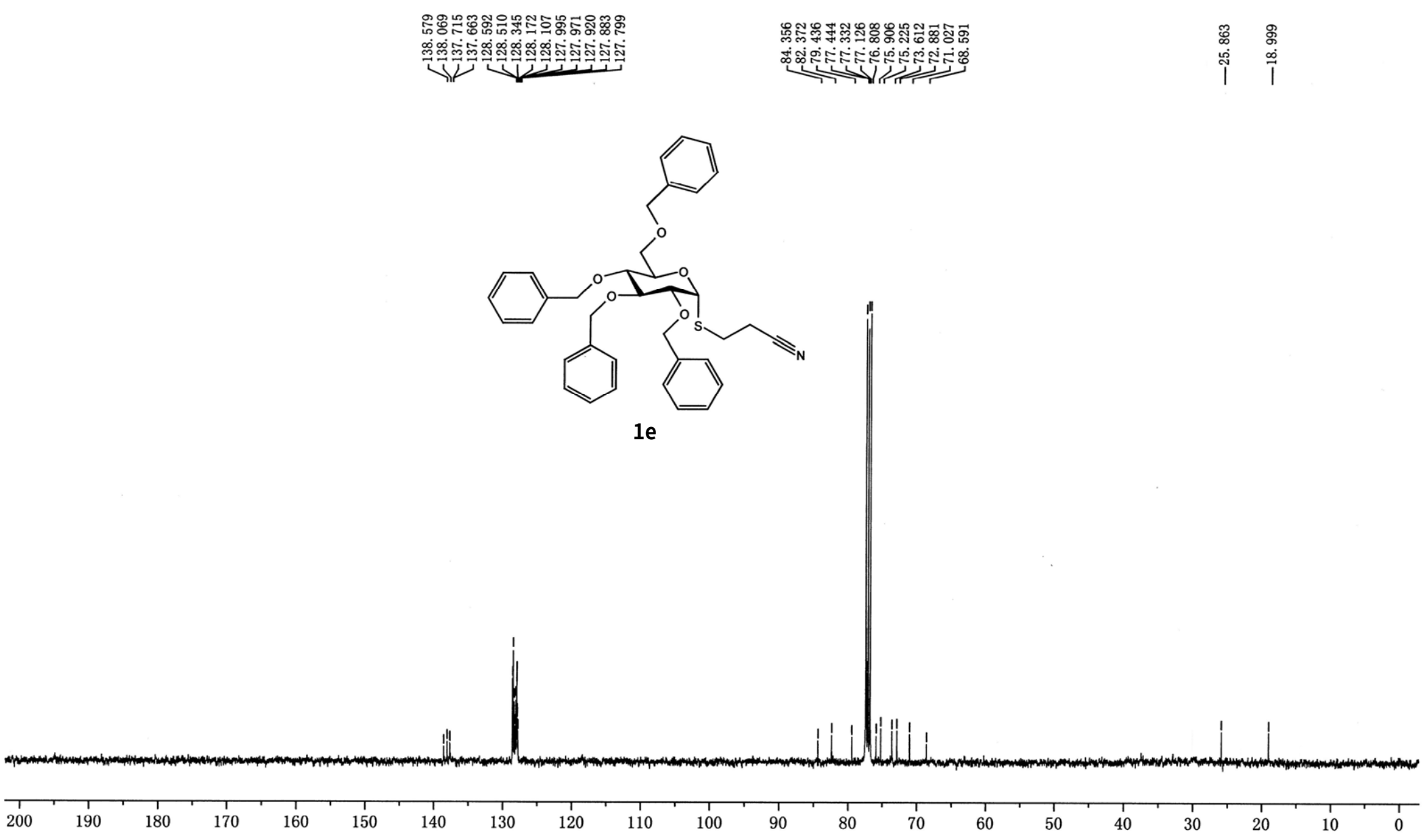
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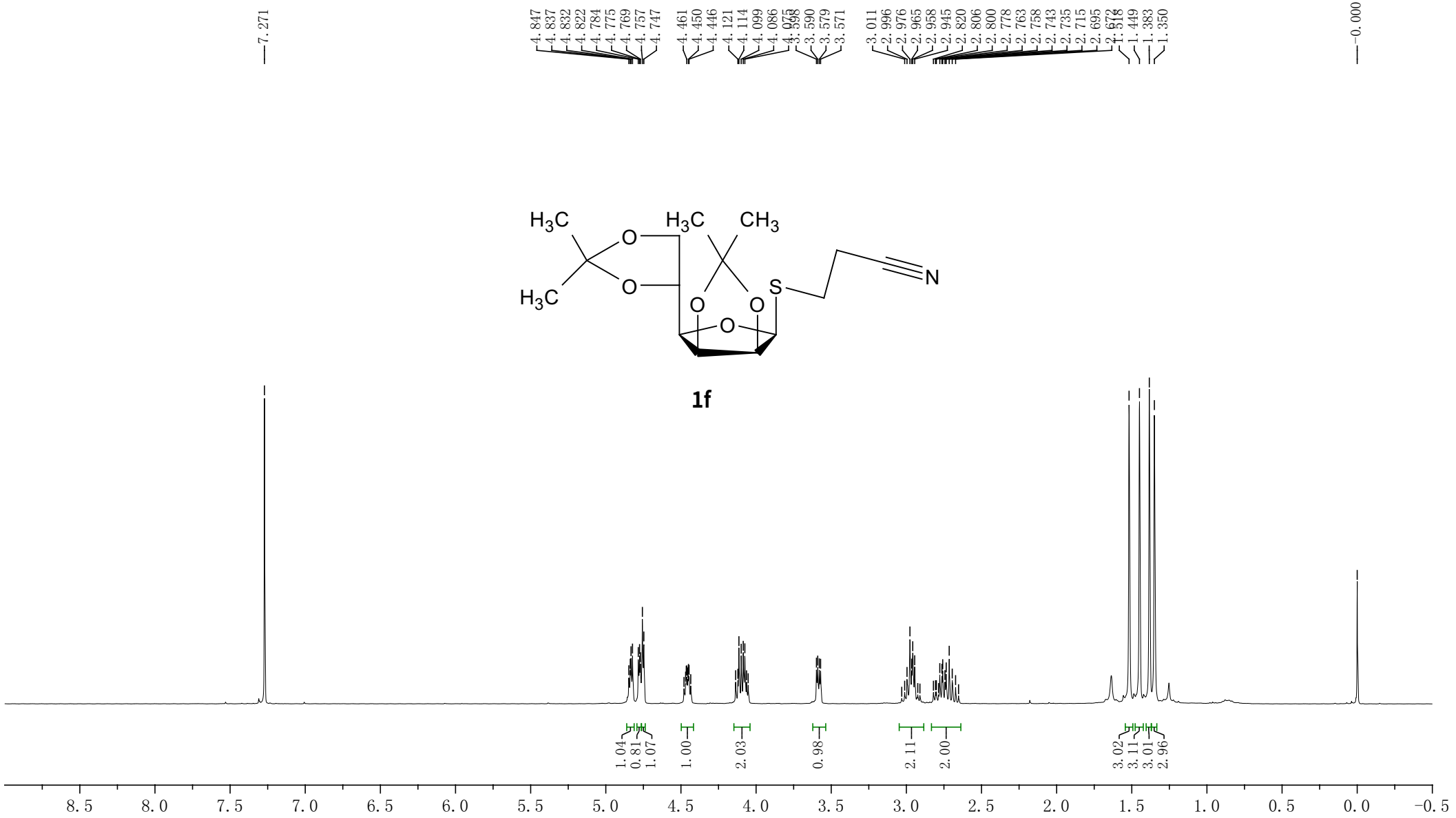
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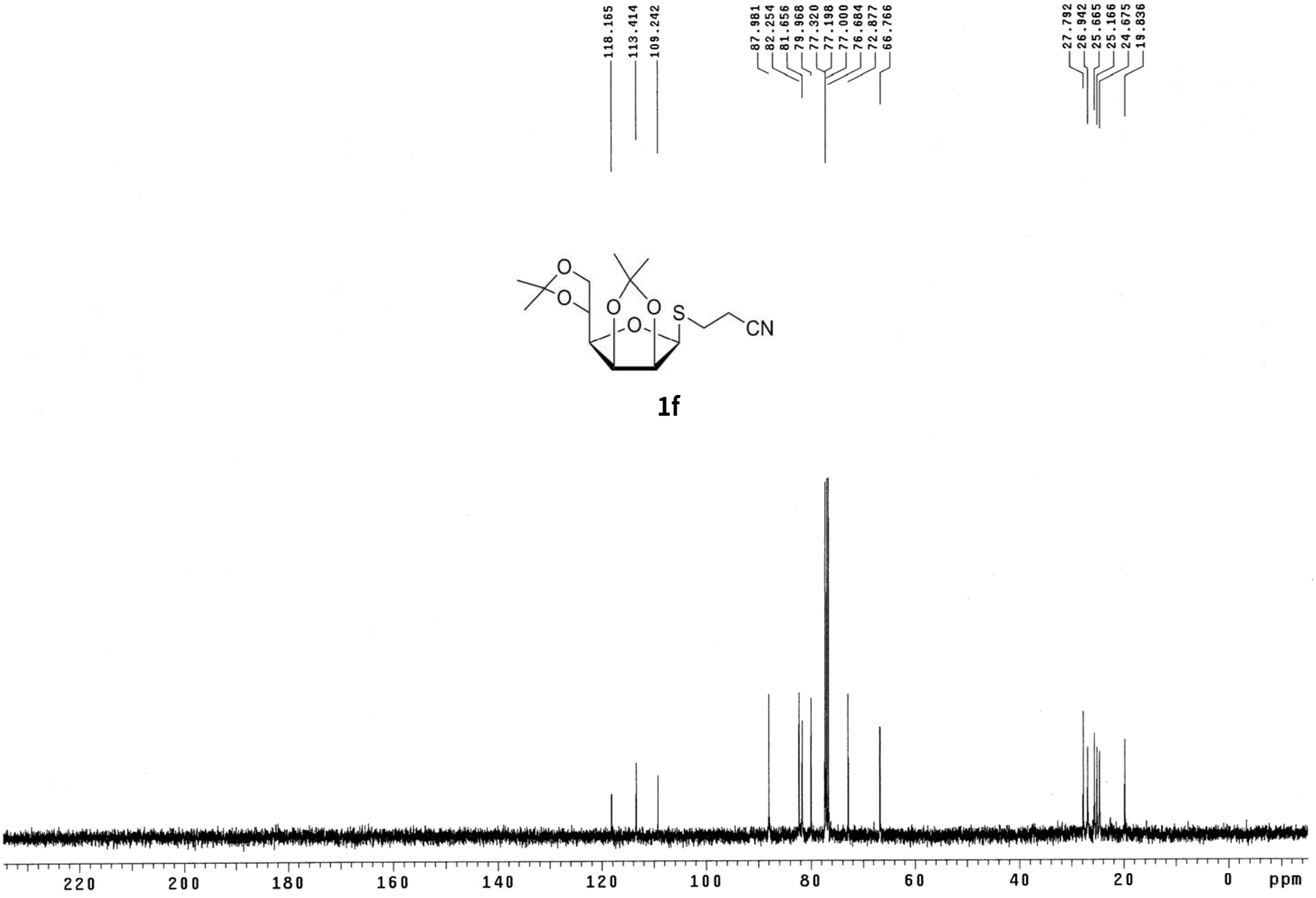
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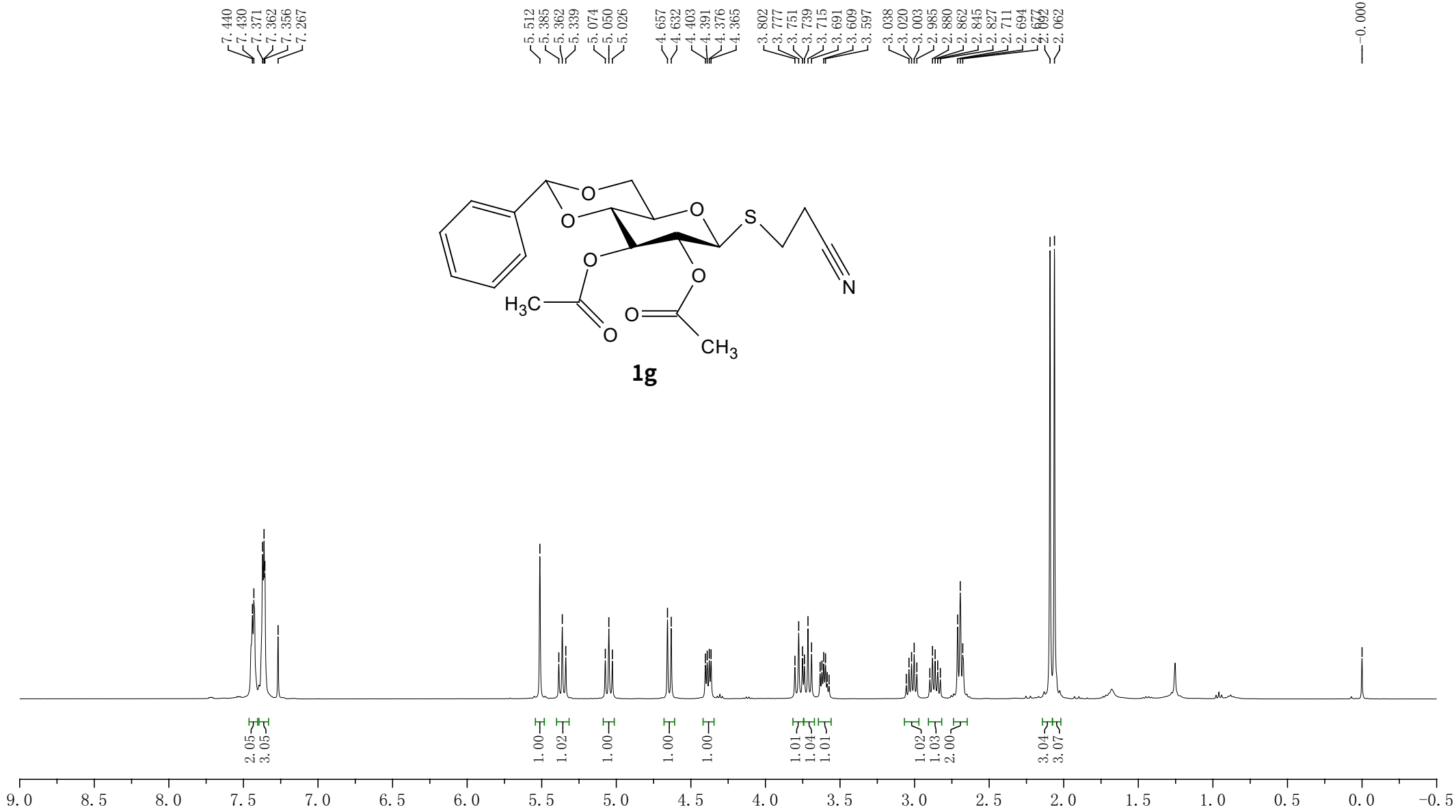
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1.00
1.00
1.01
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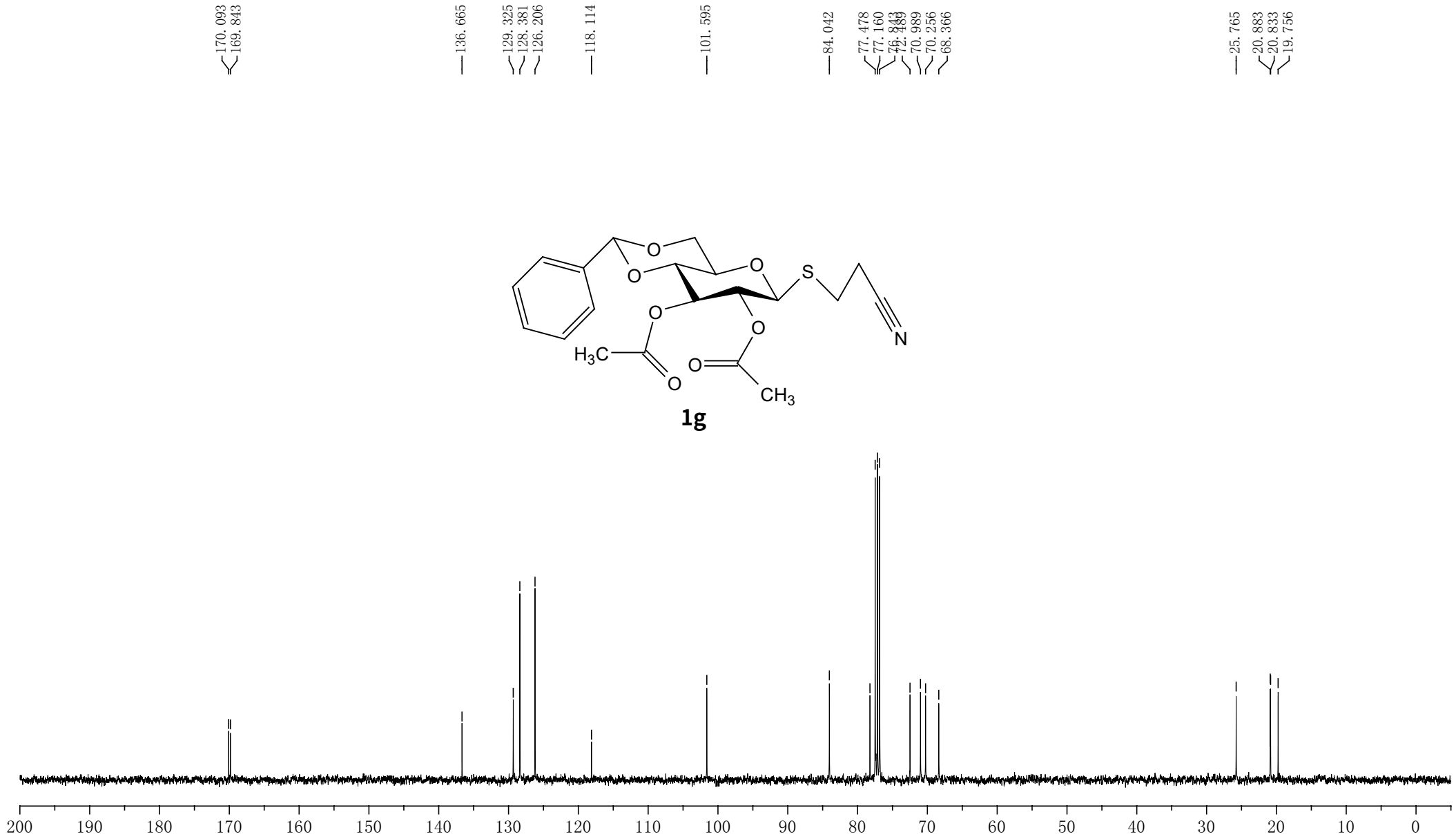
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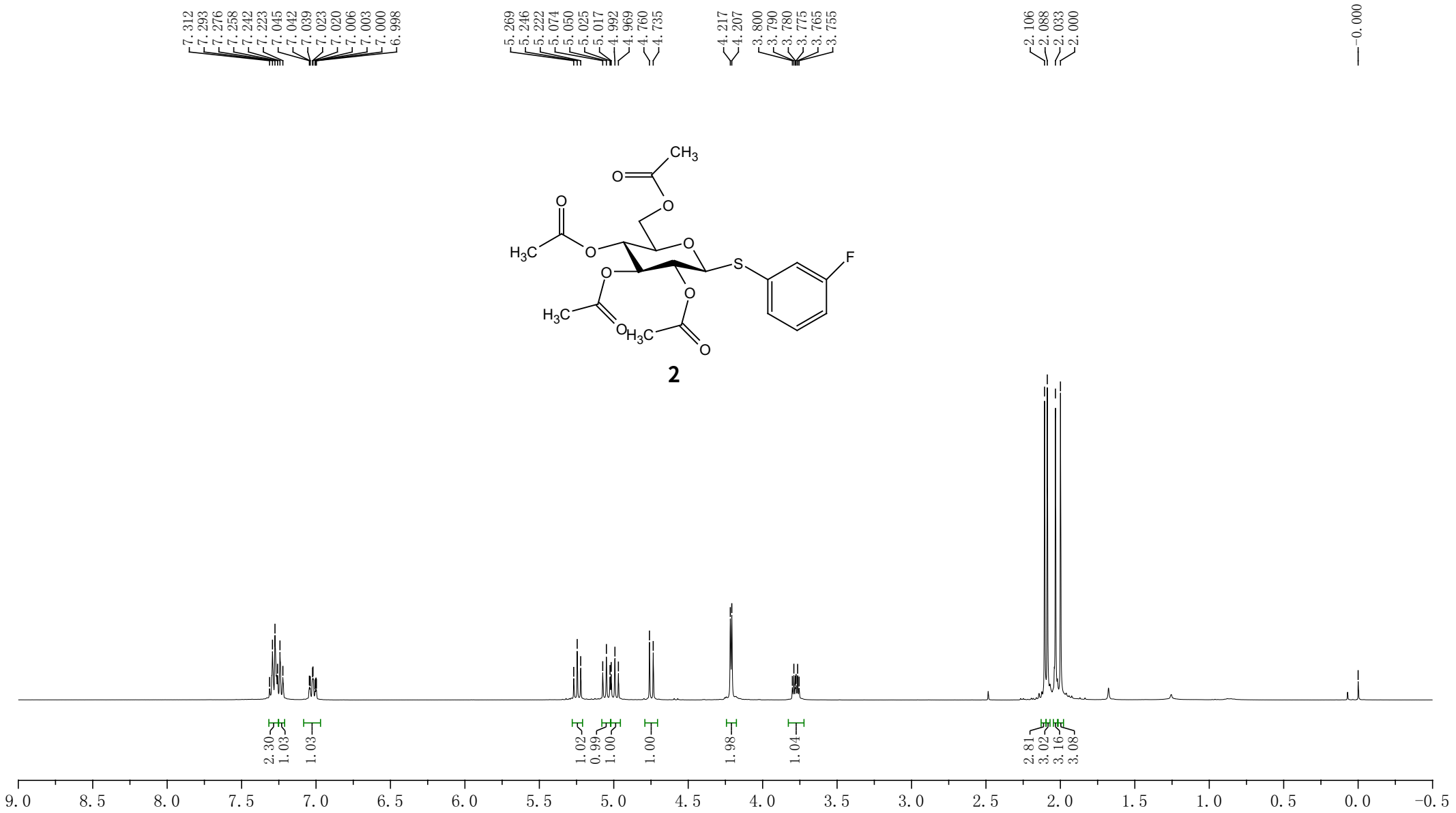
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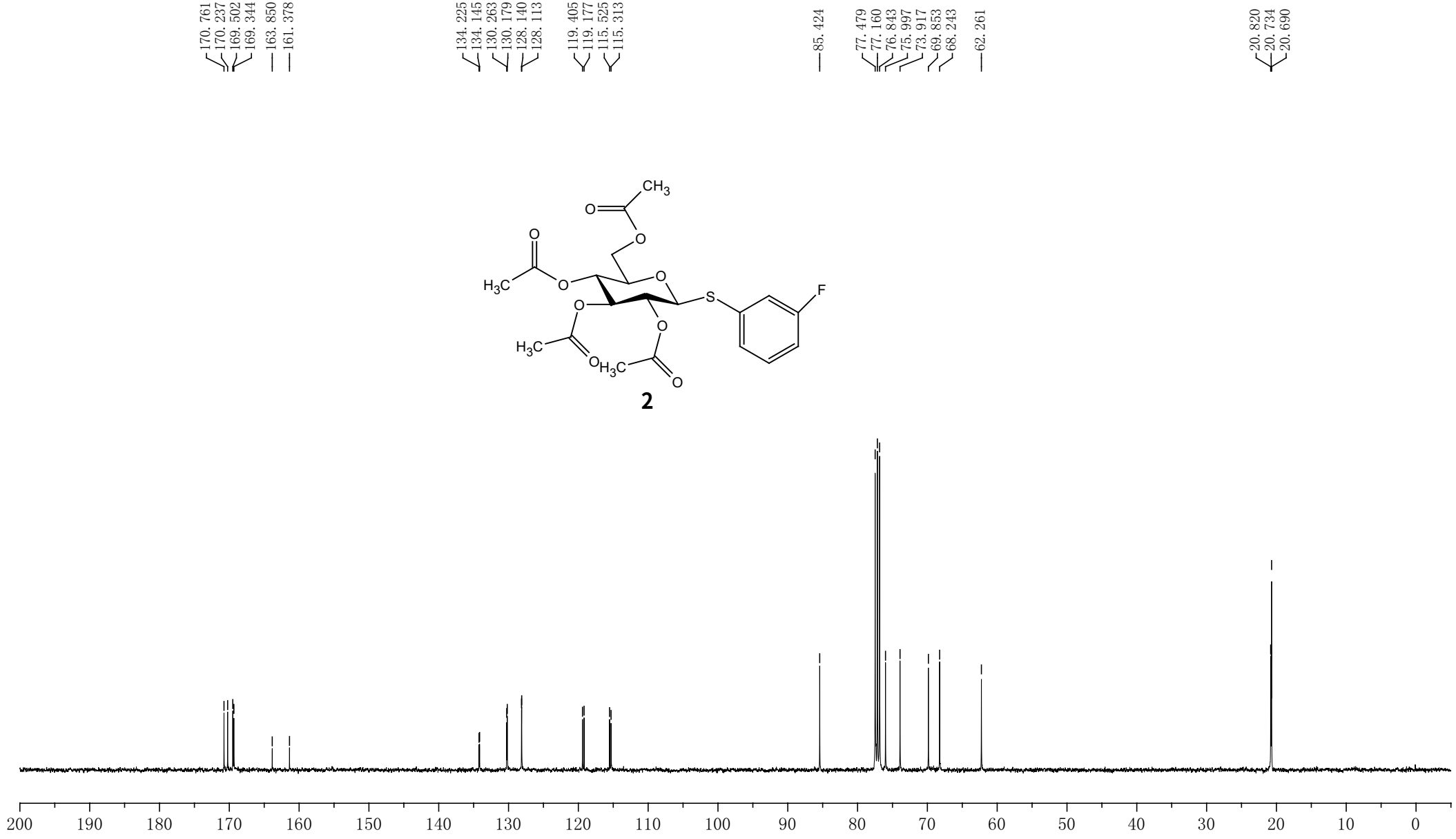
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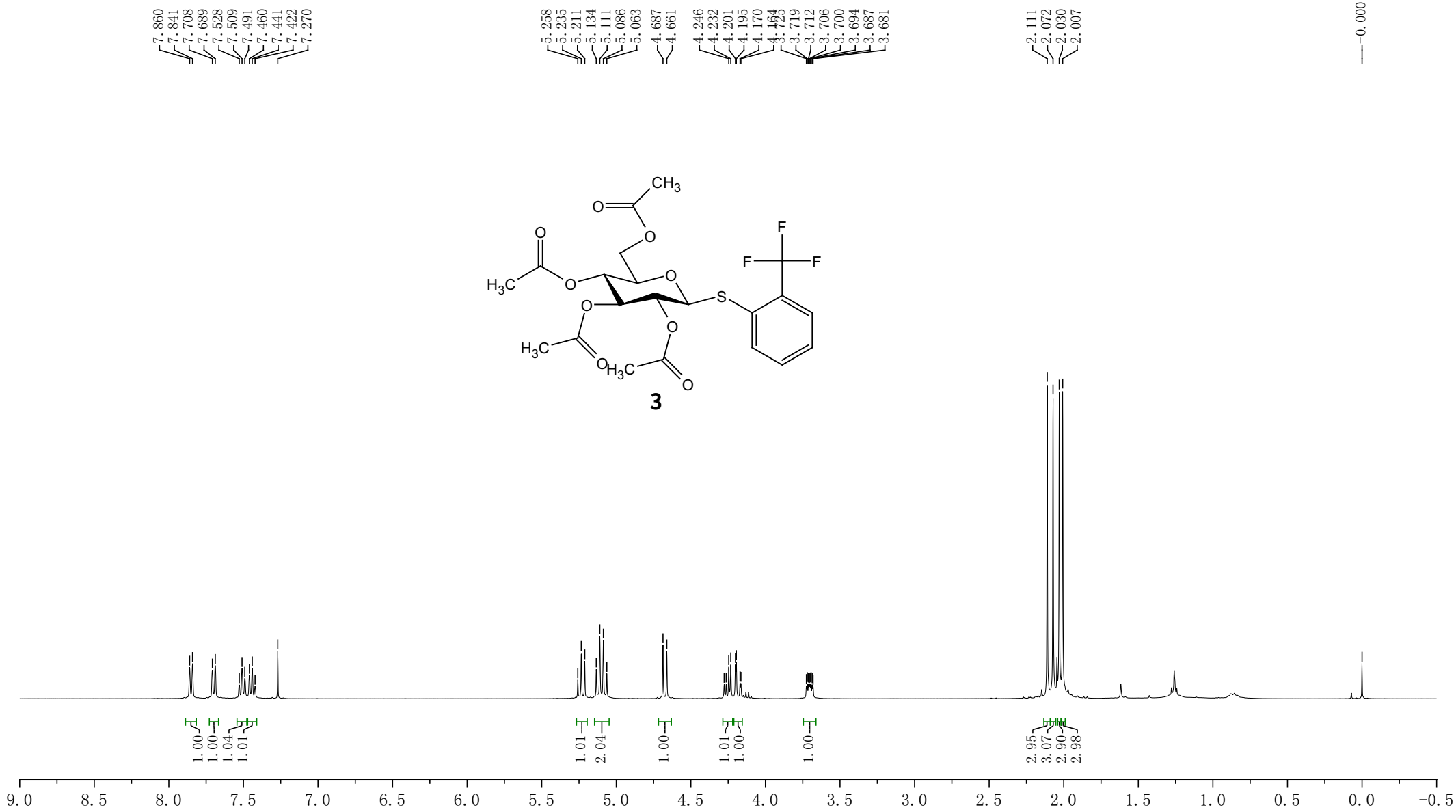
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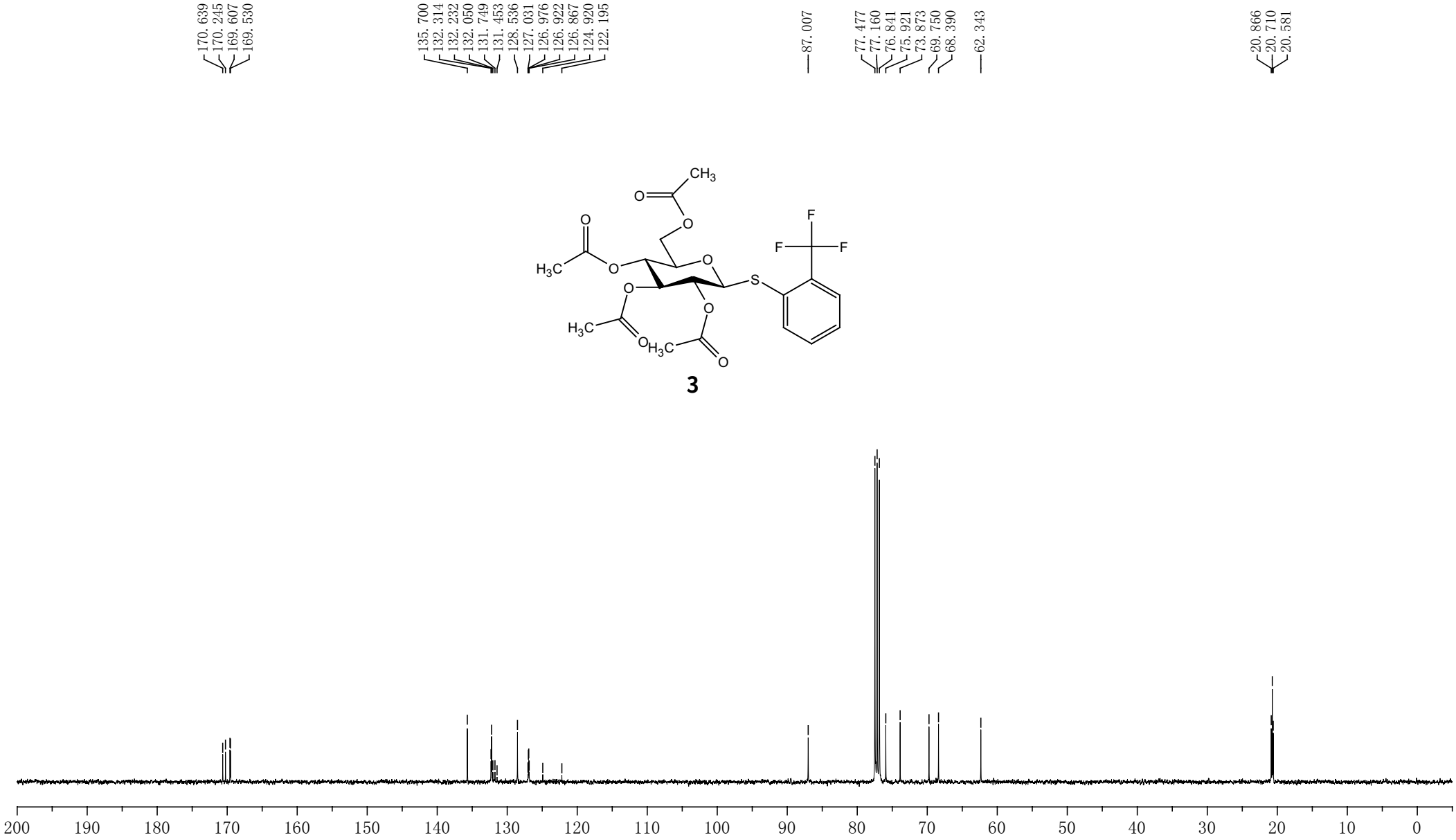
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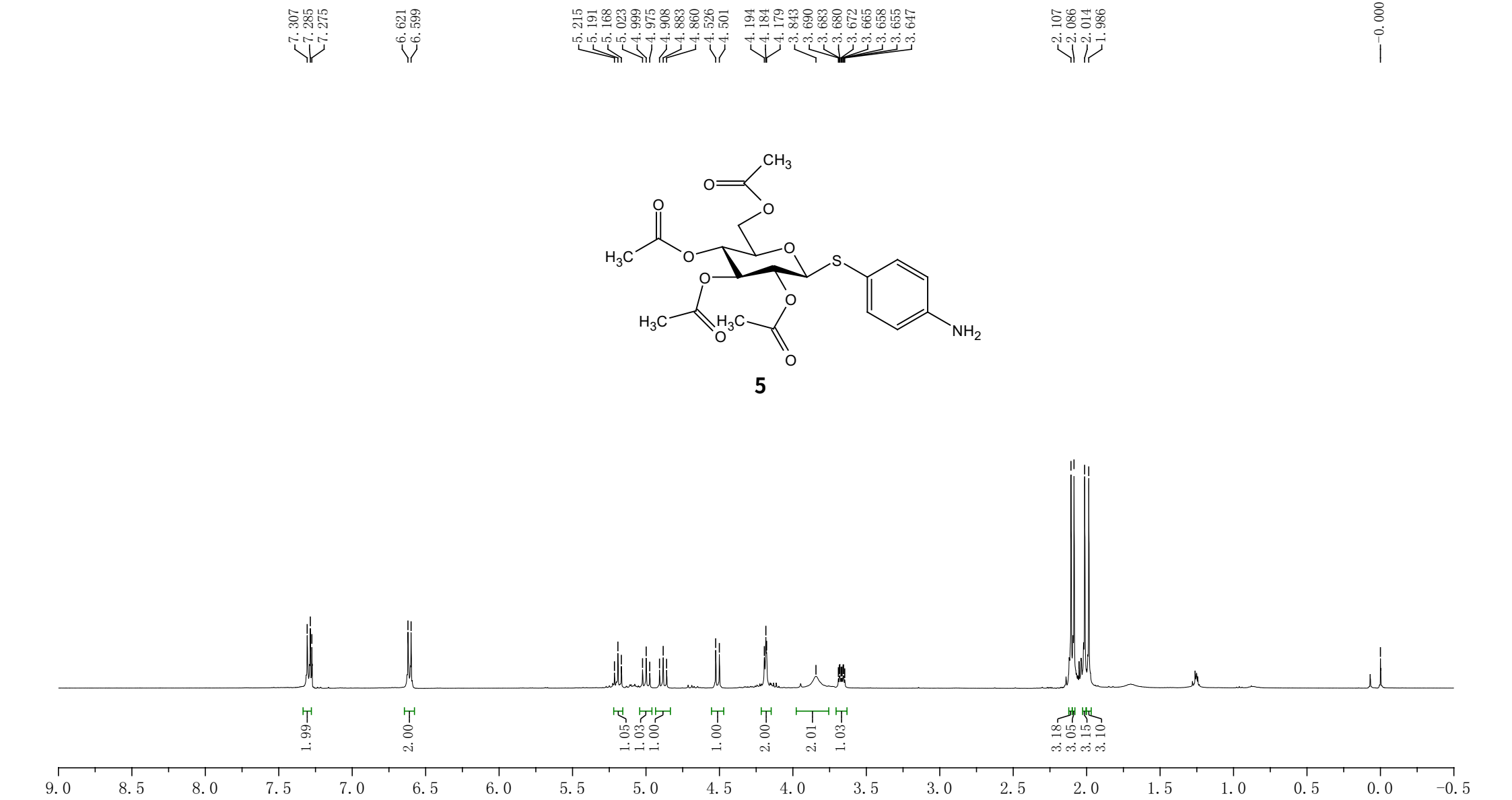
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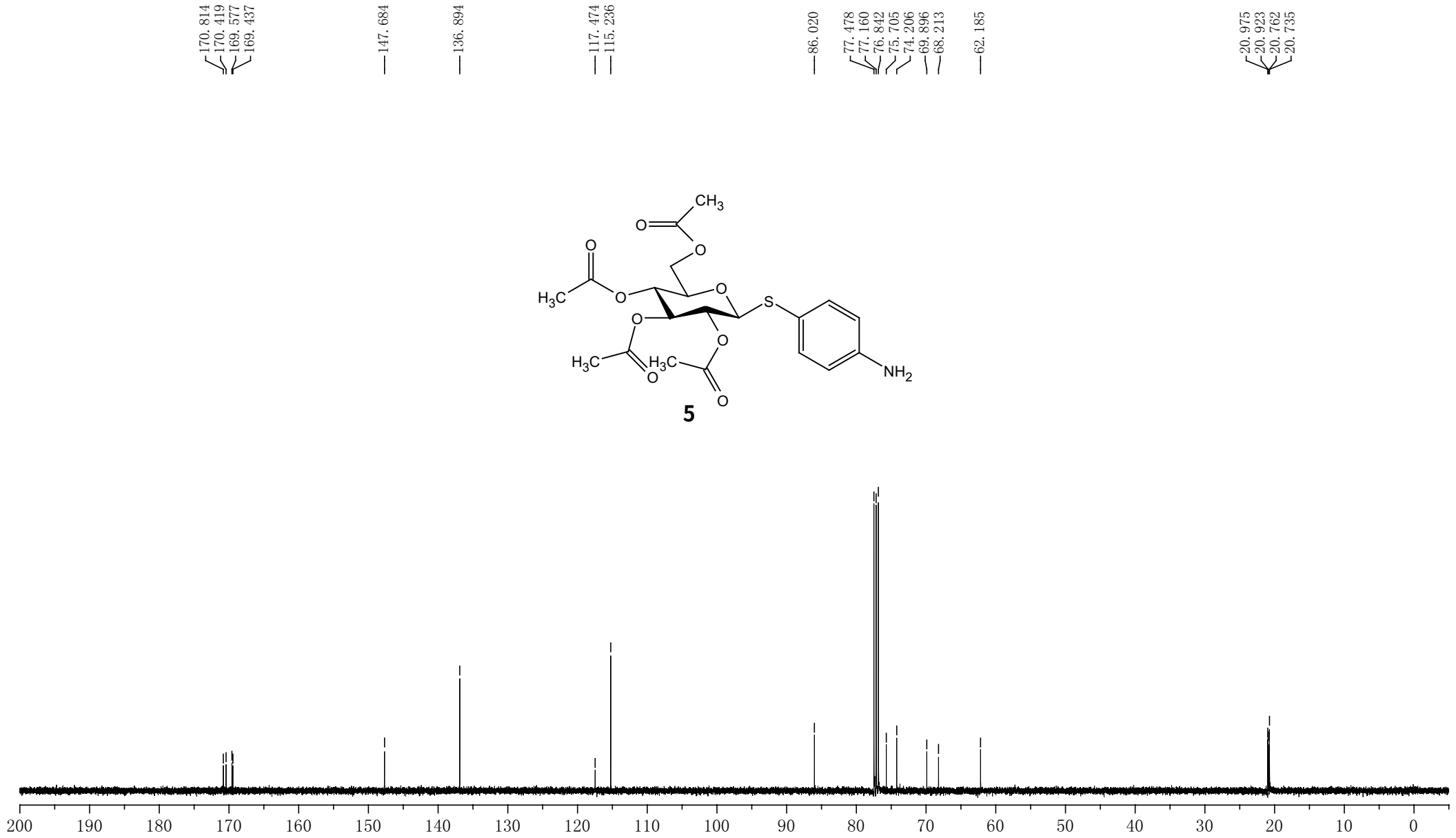
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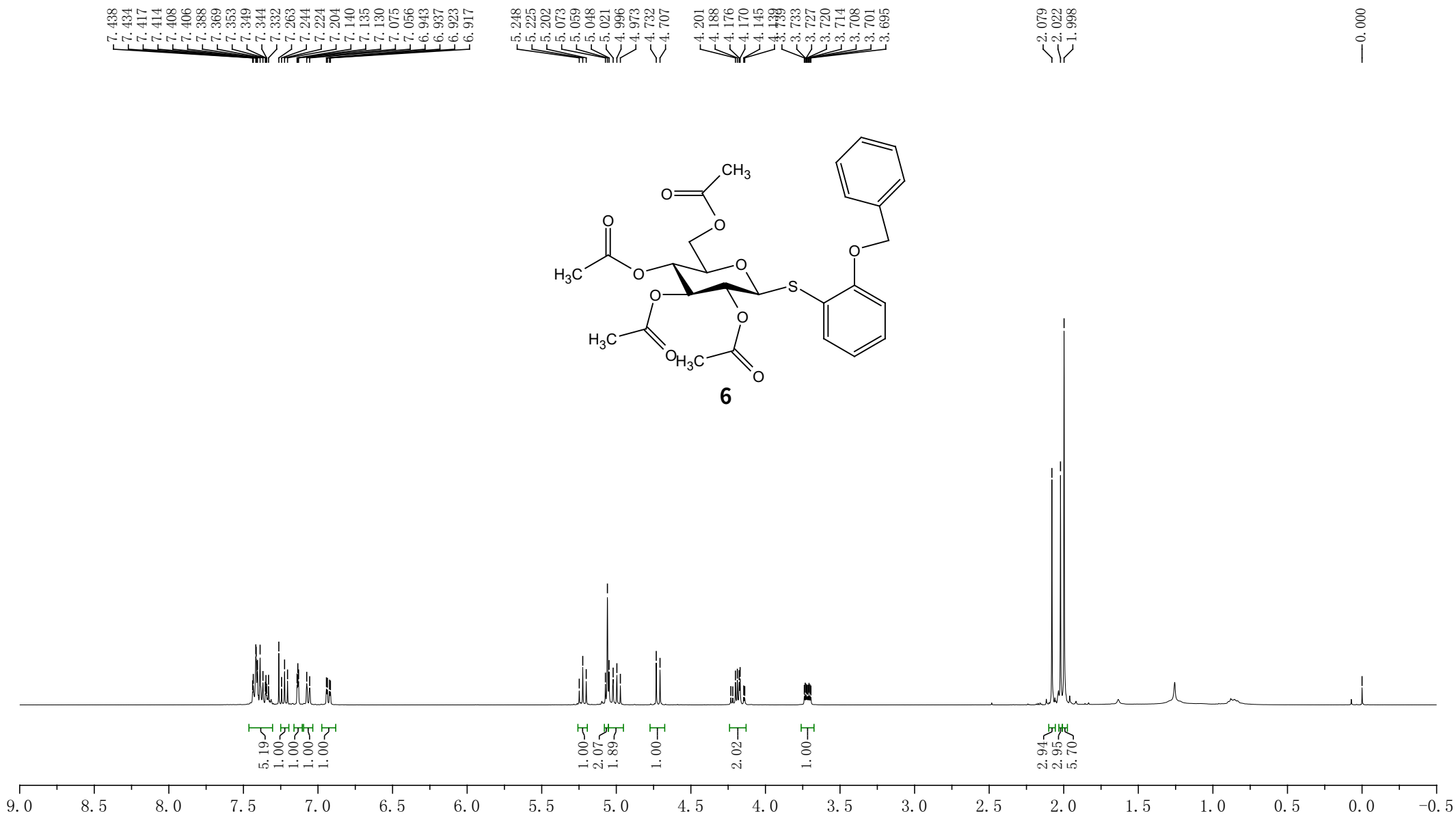
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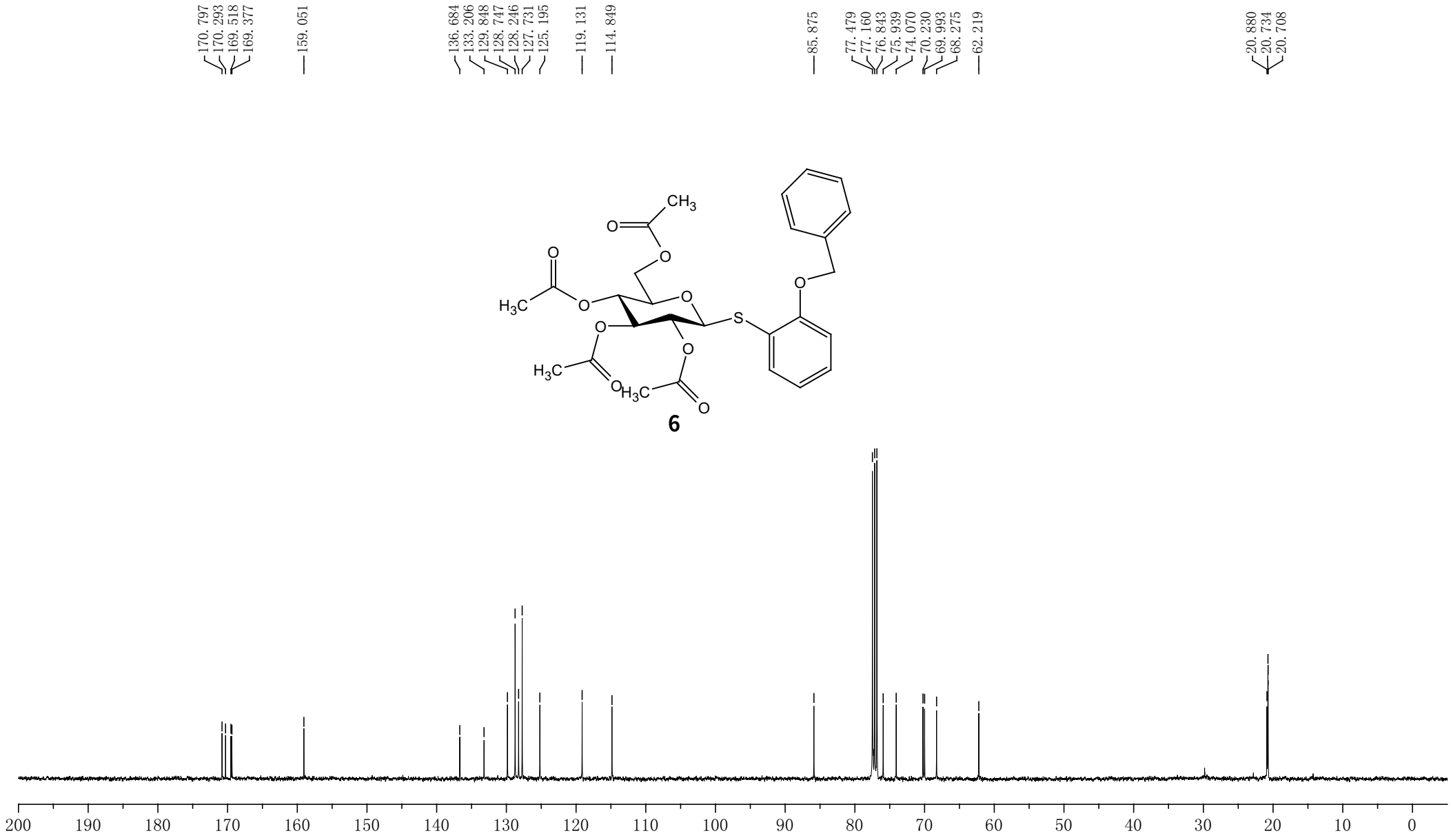
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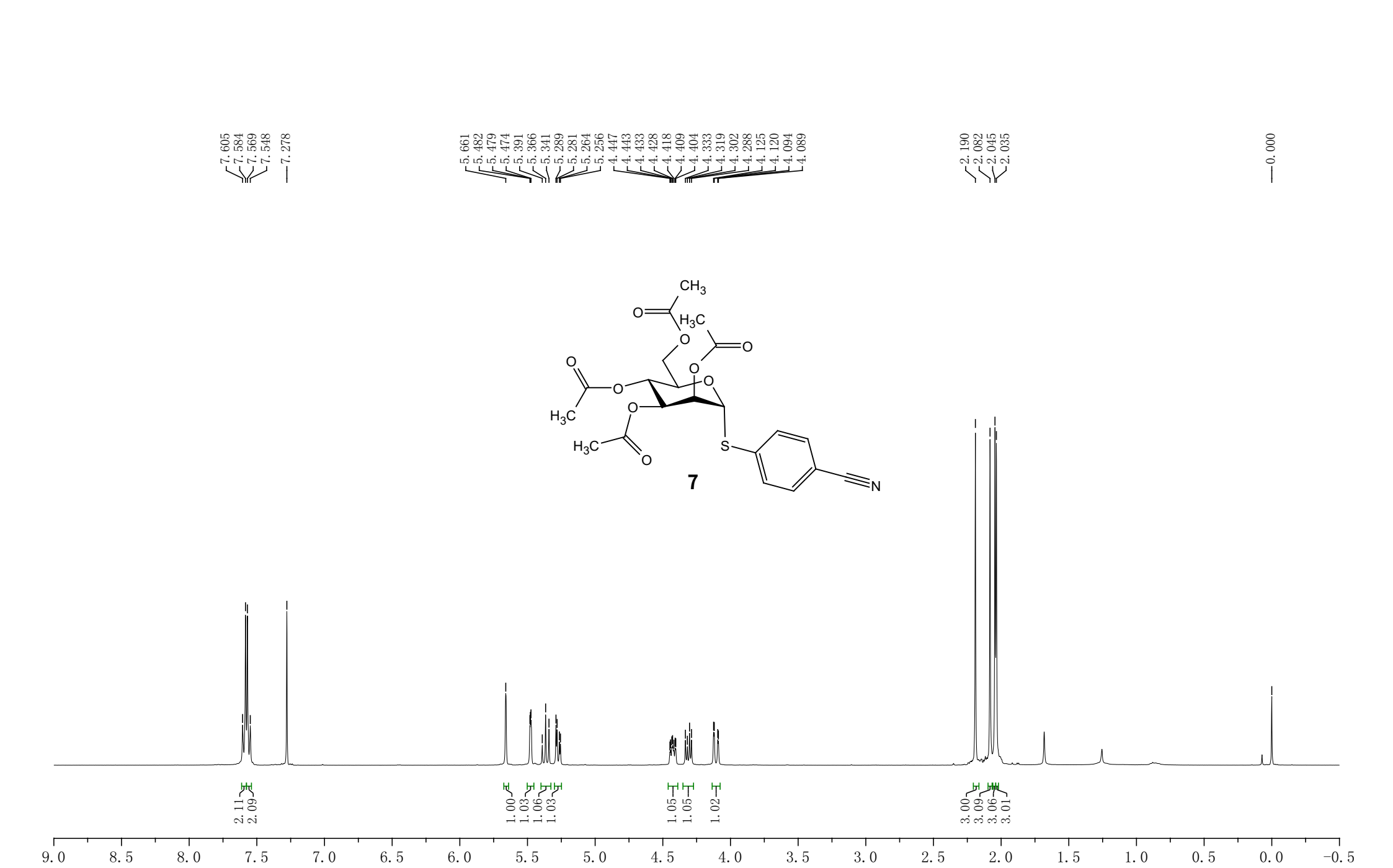
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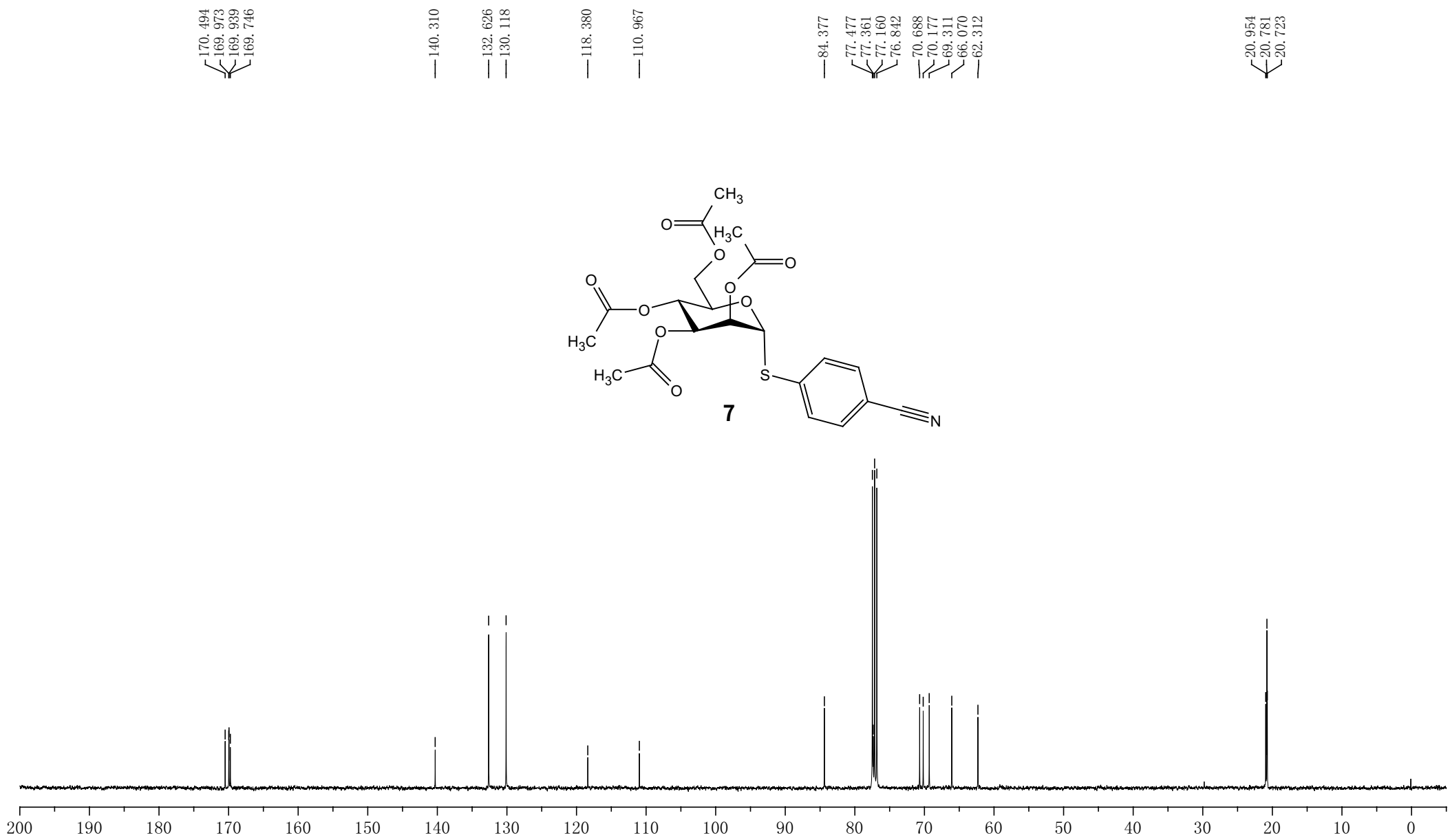
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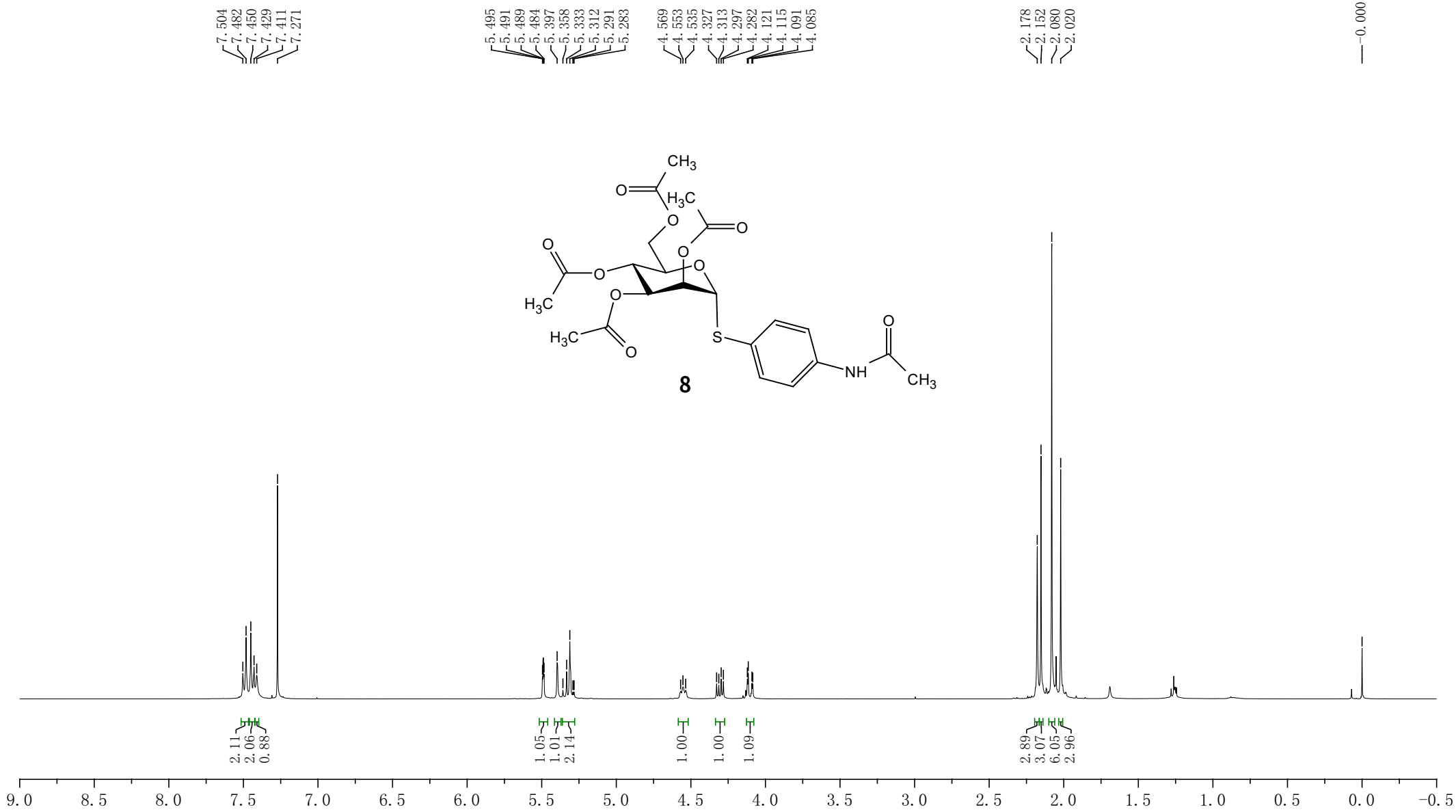
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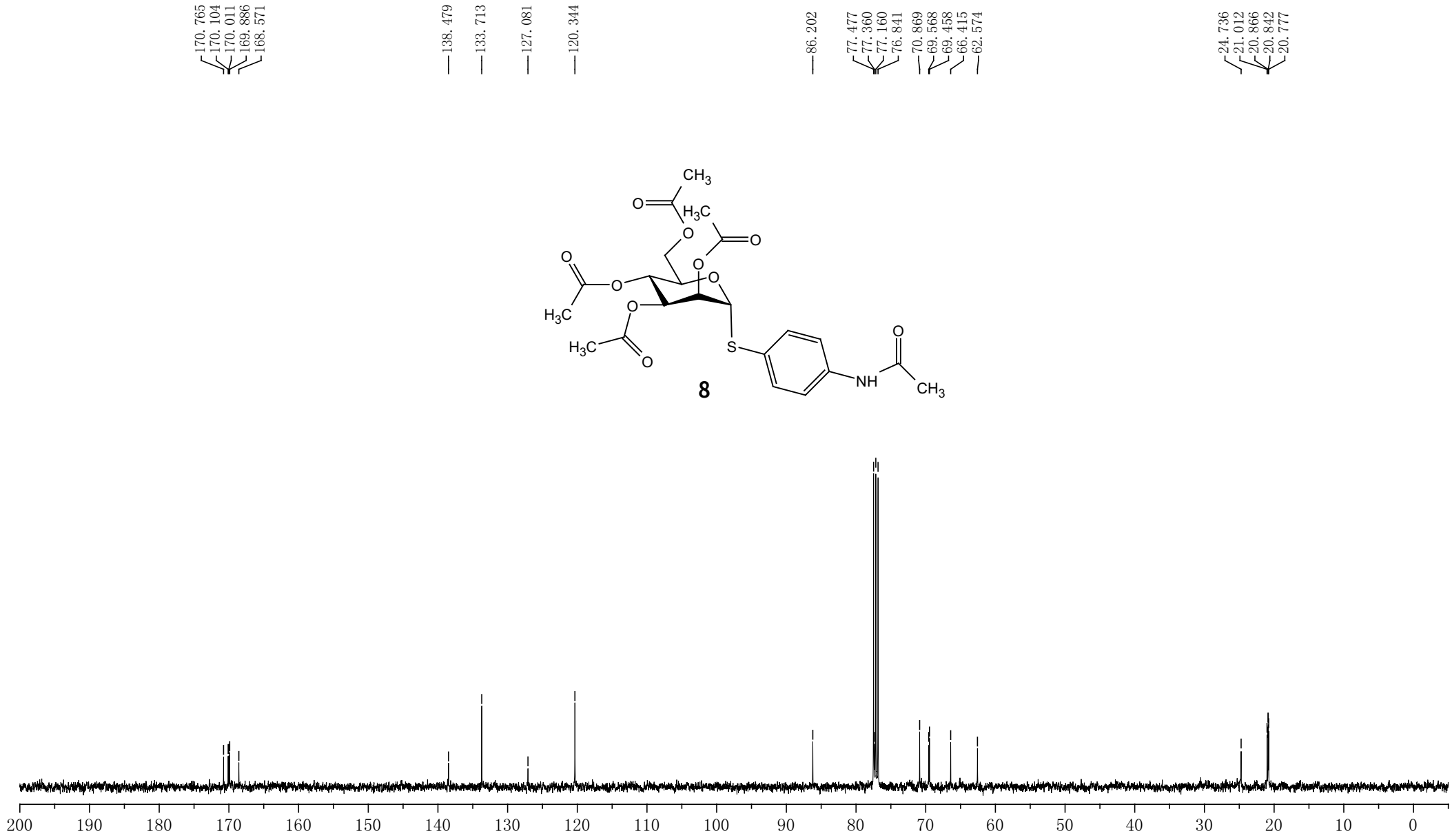
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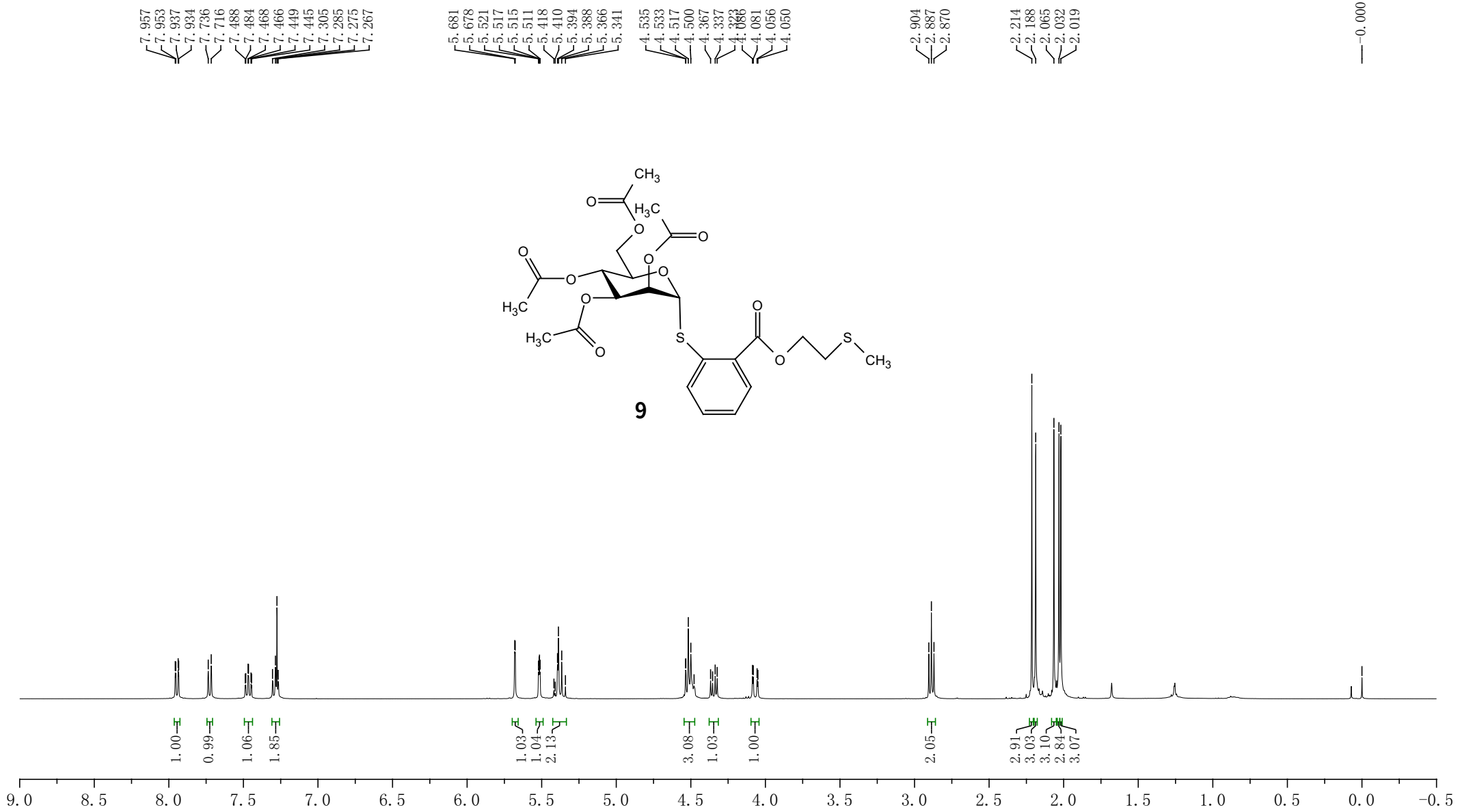
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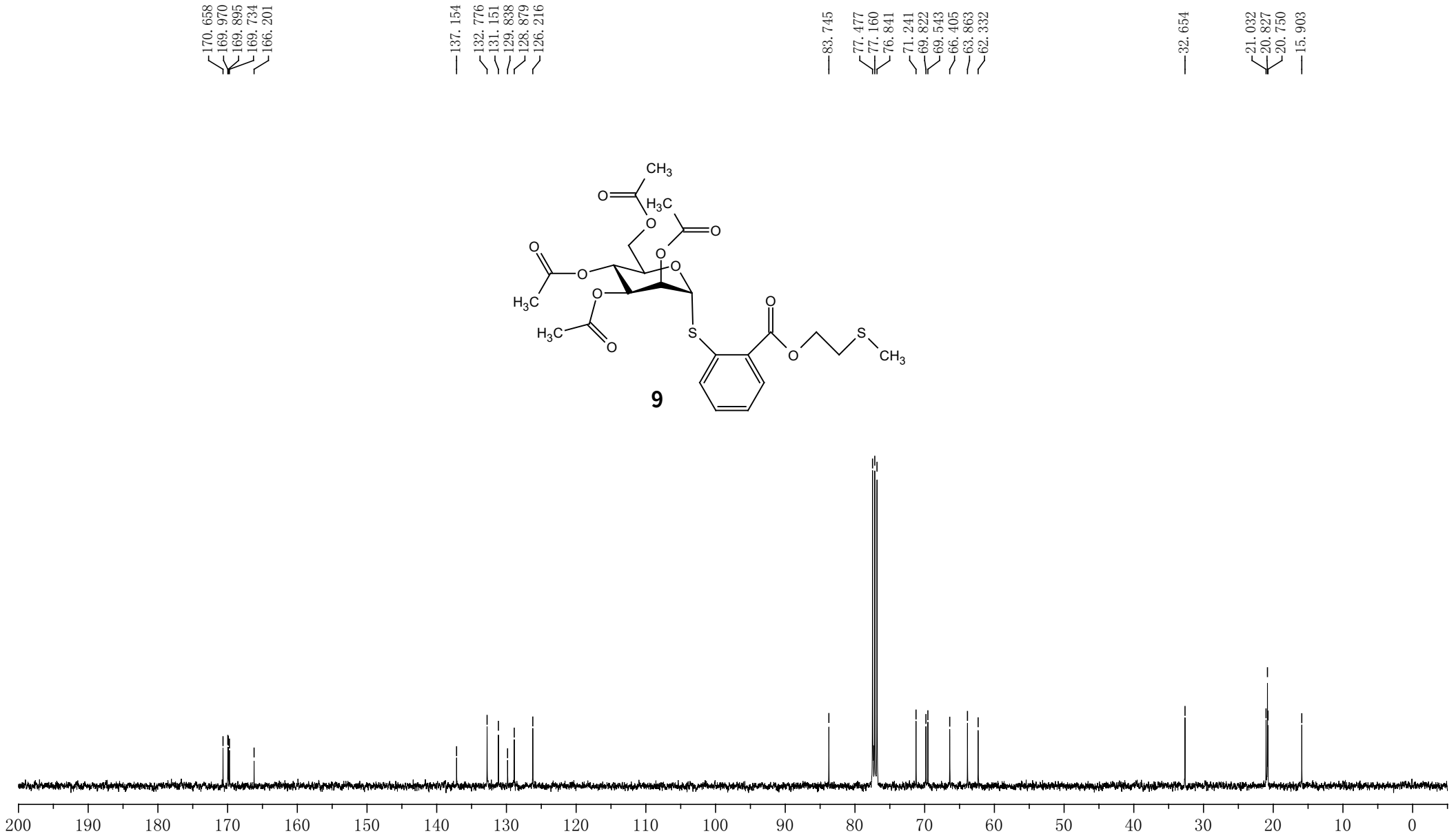
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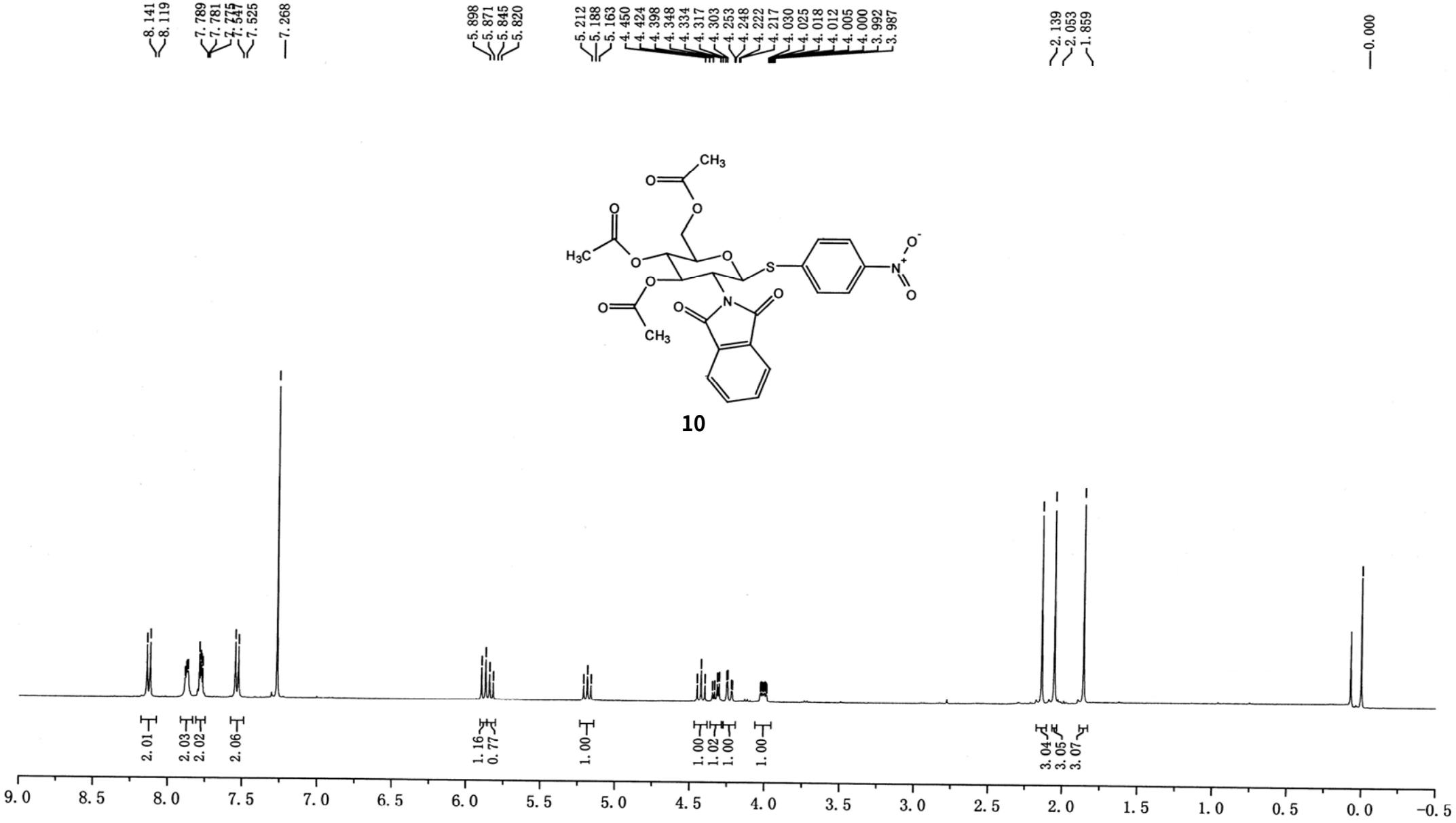
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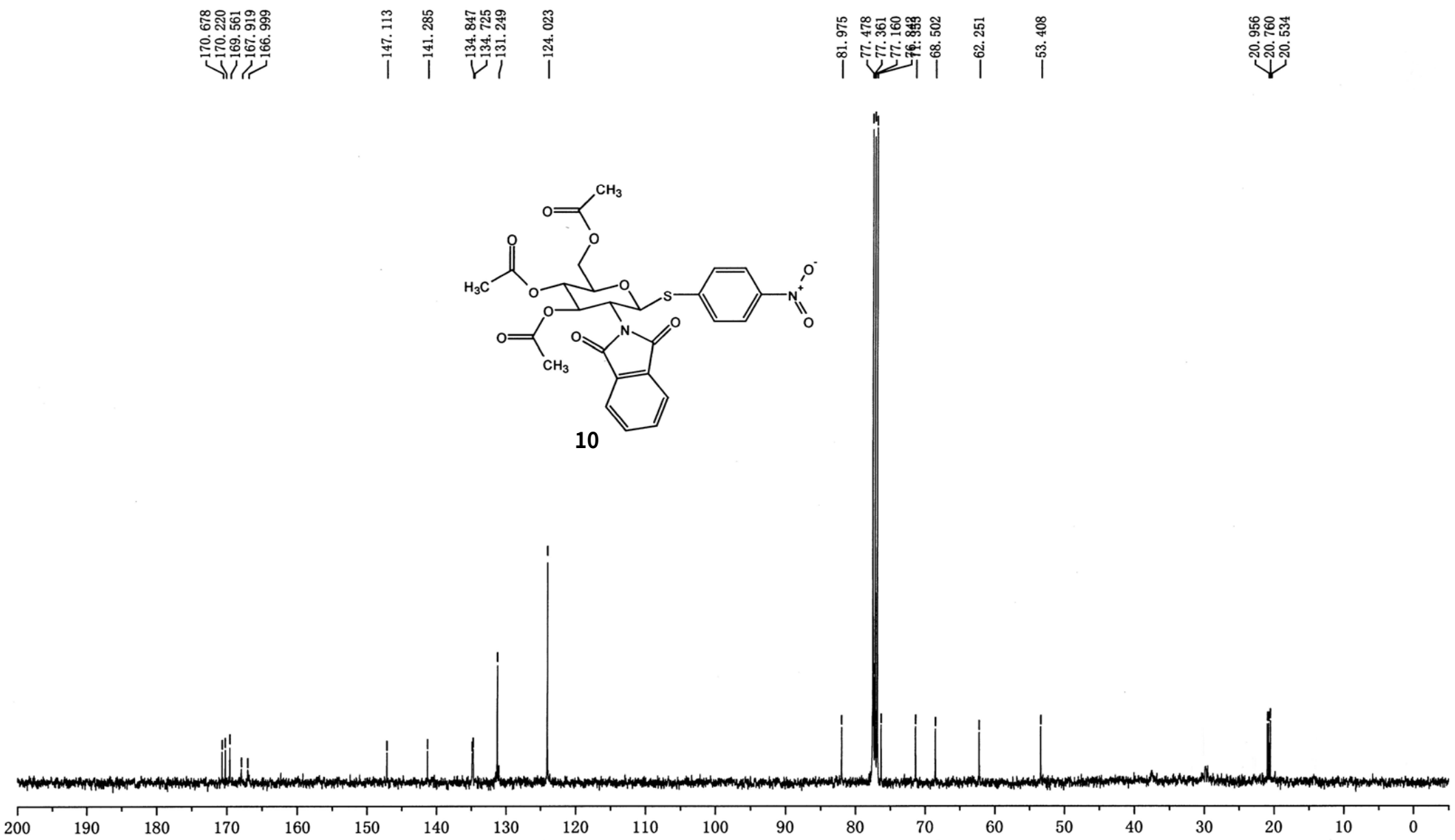
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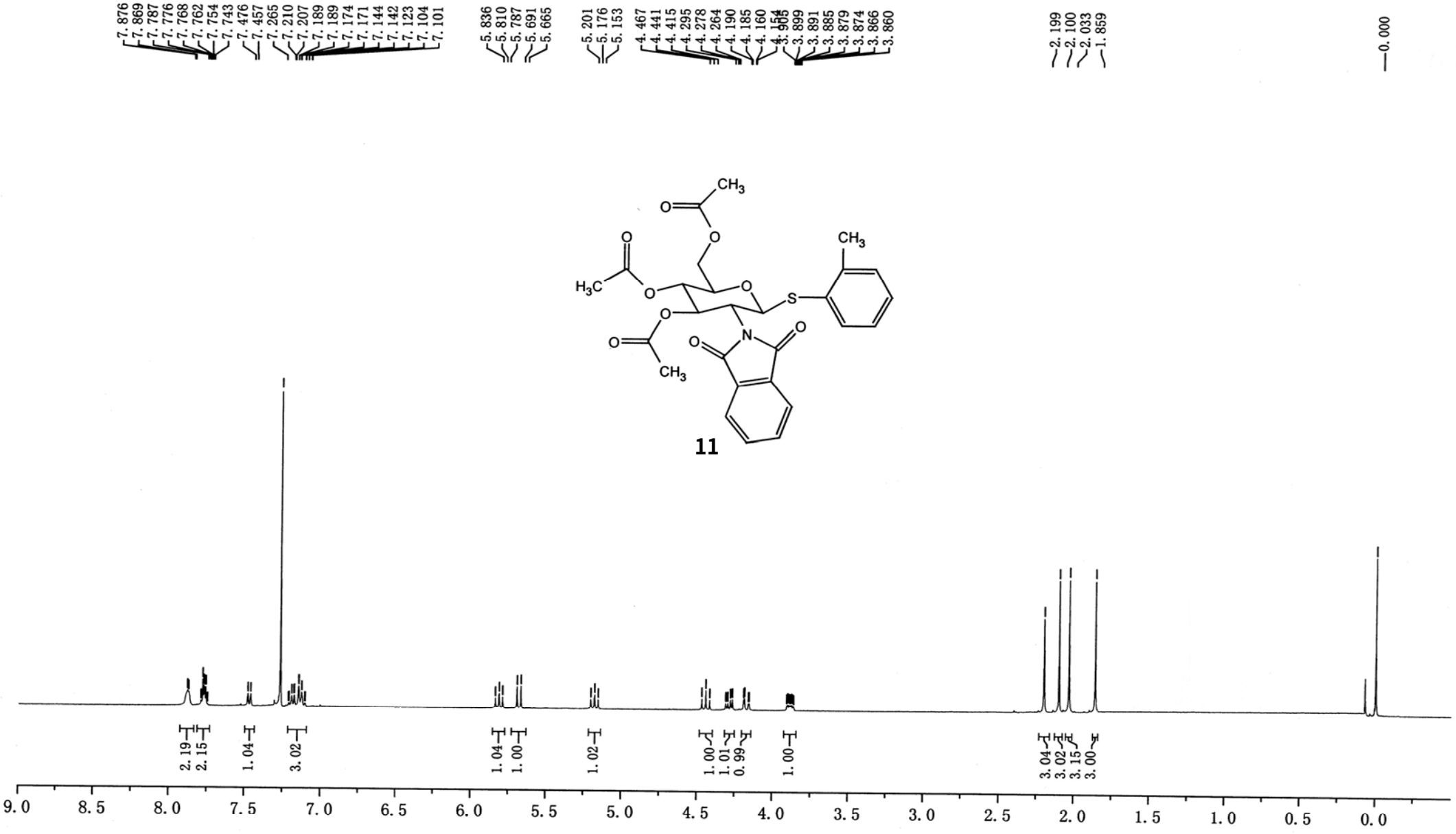
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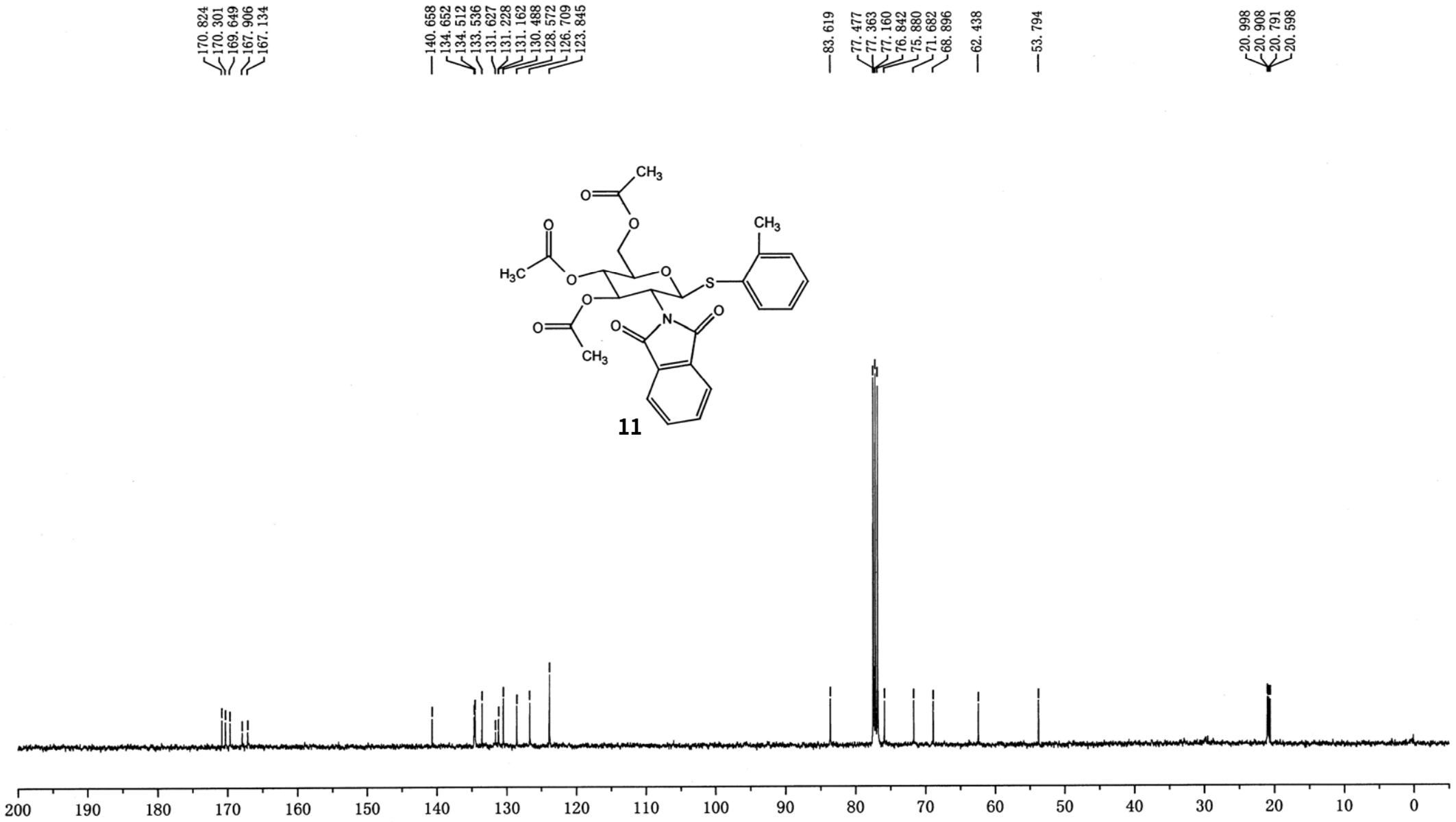
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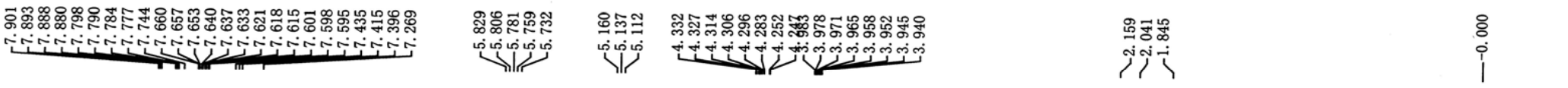
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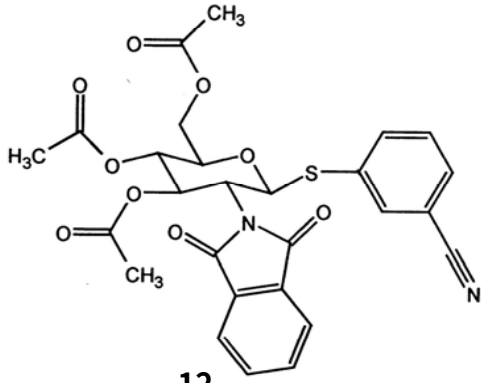
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CH3
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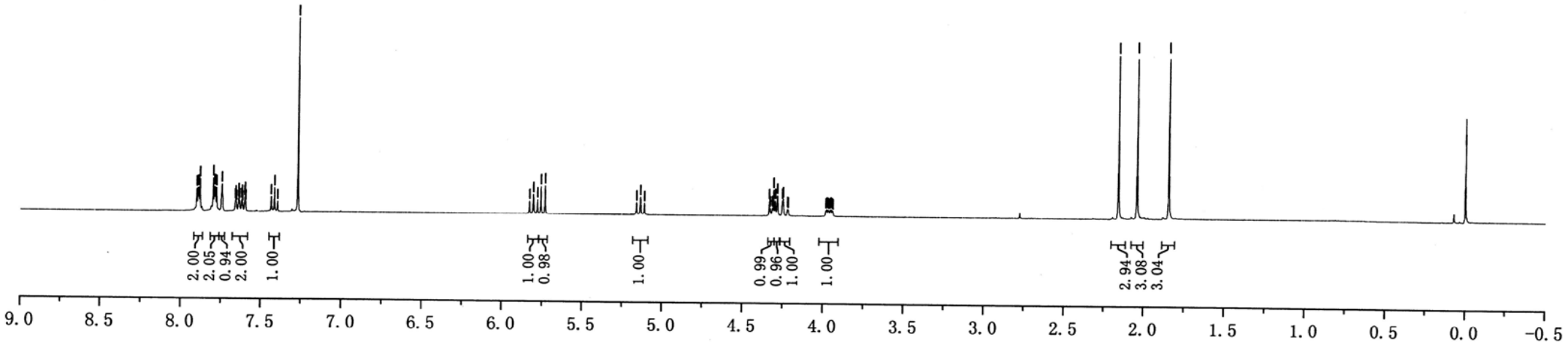
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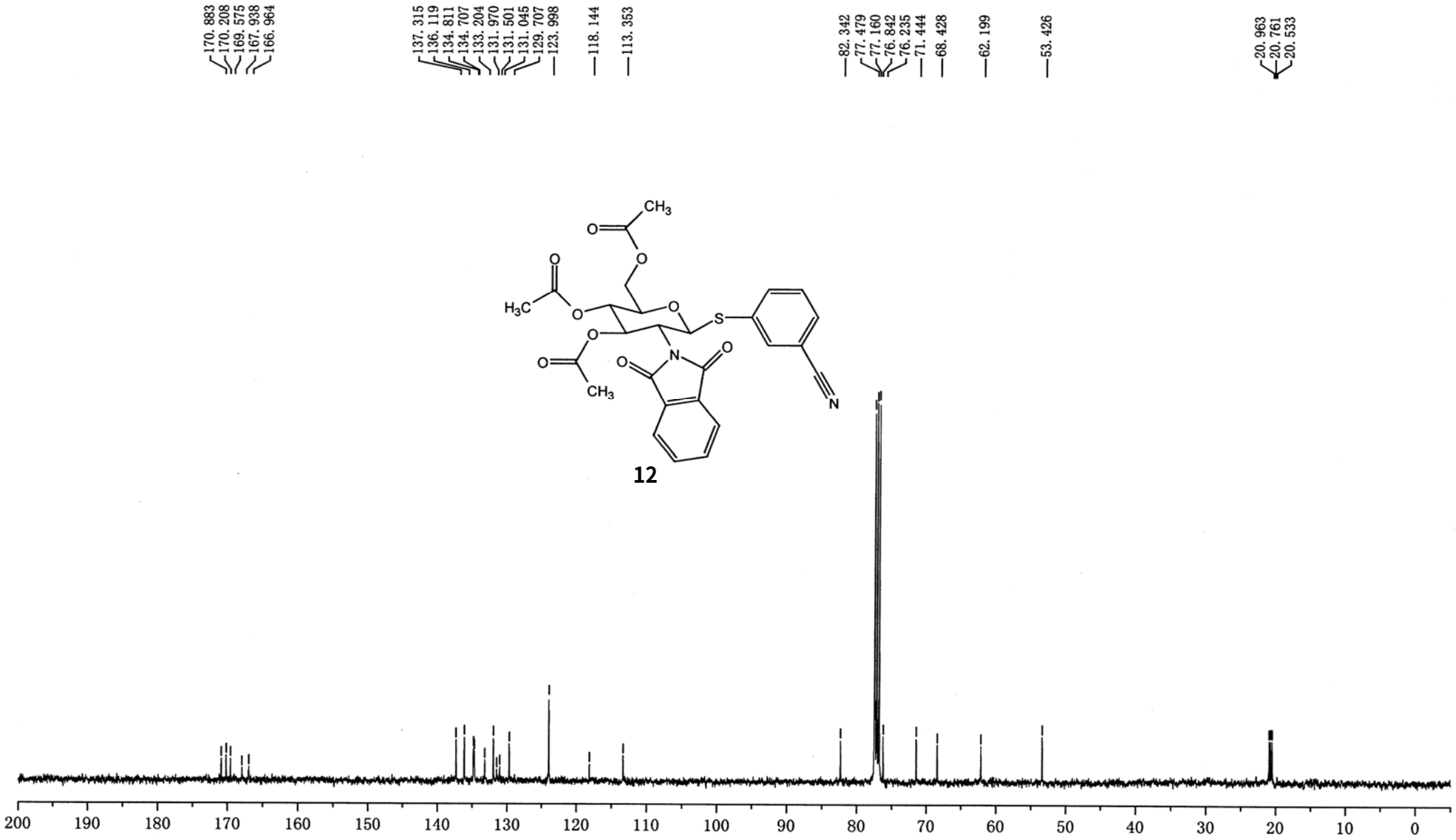
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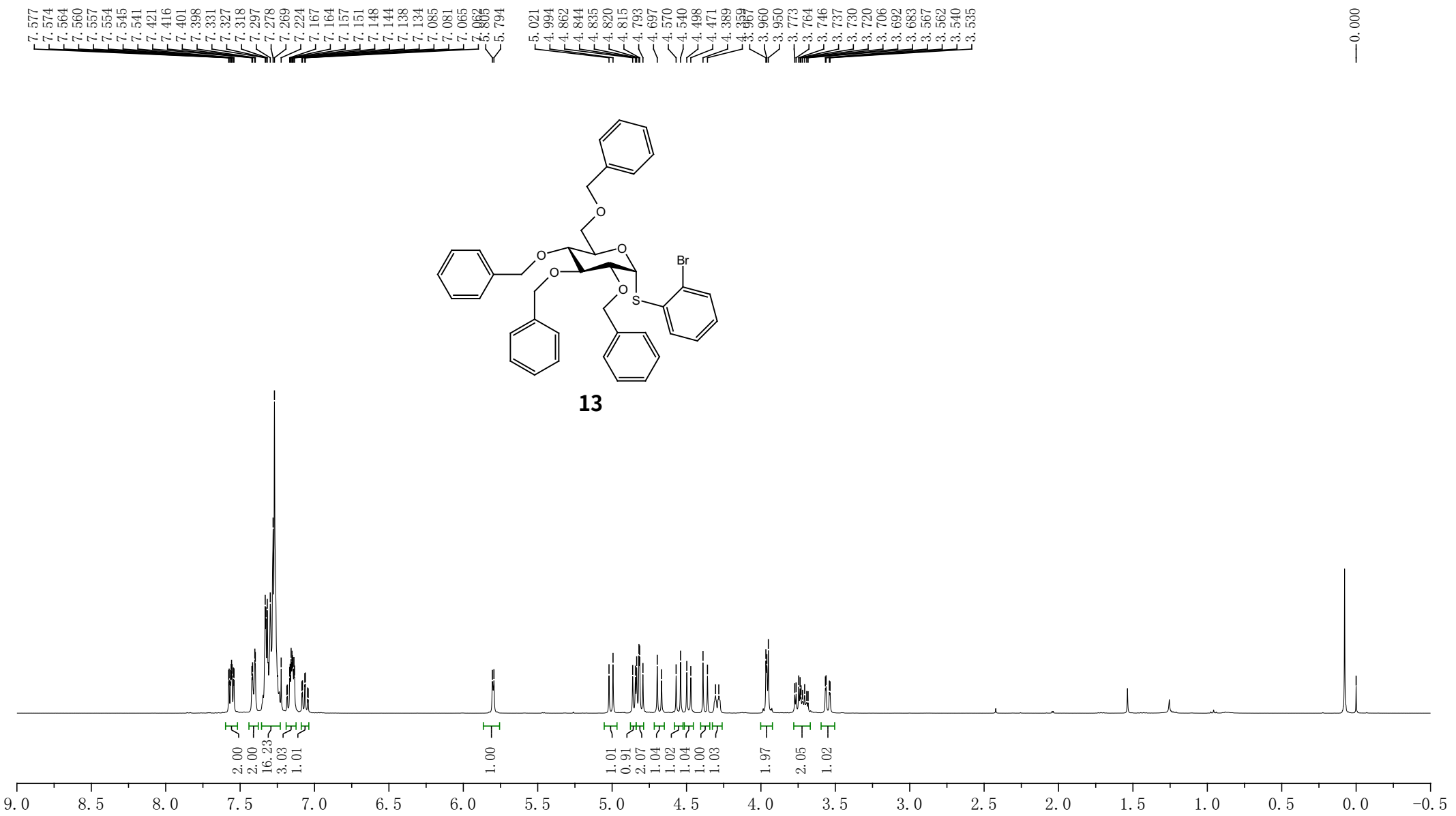
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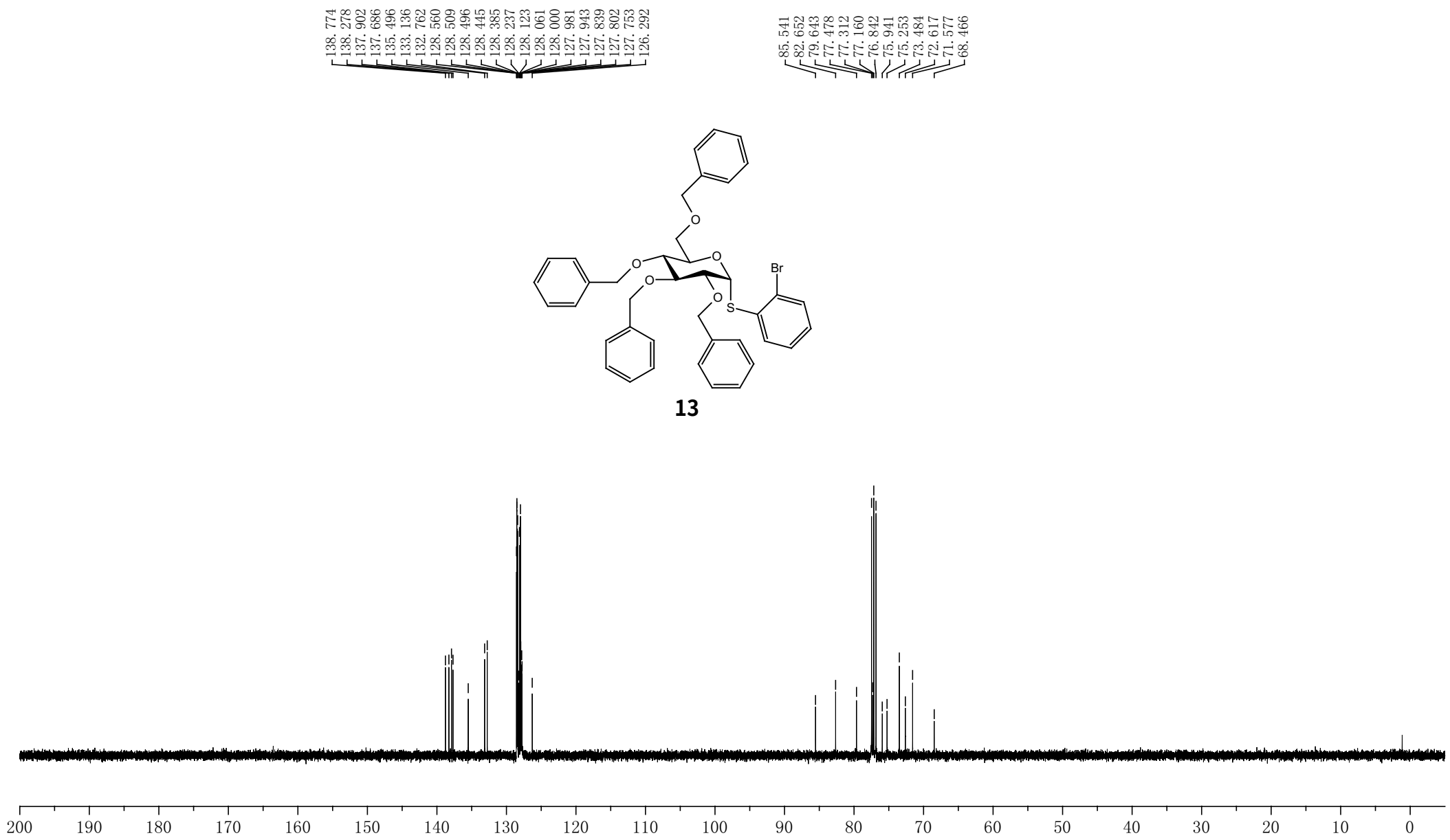
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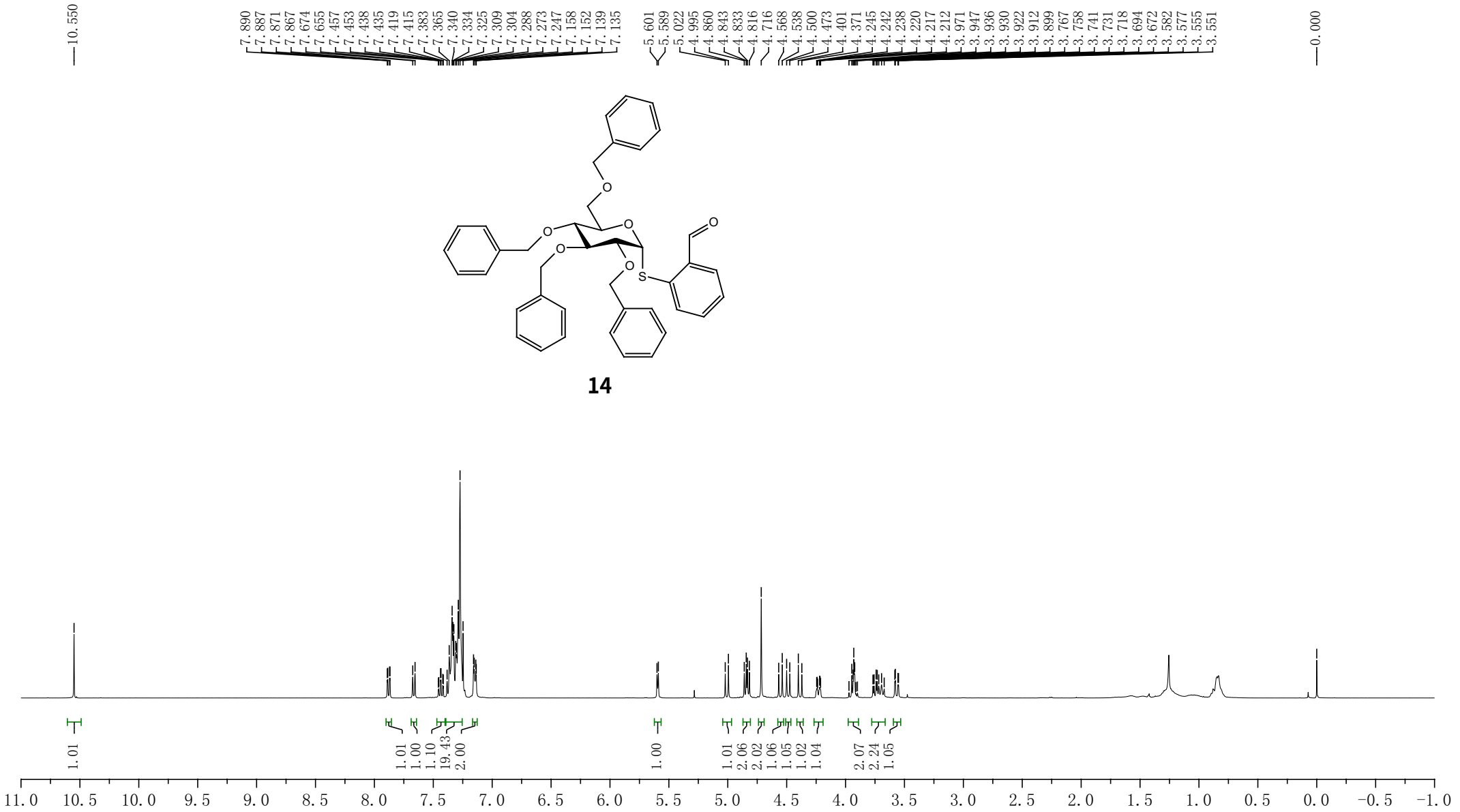
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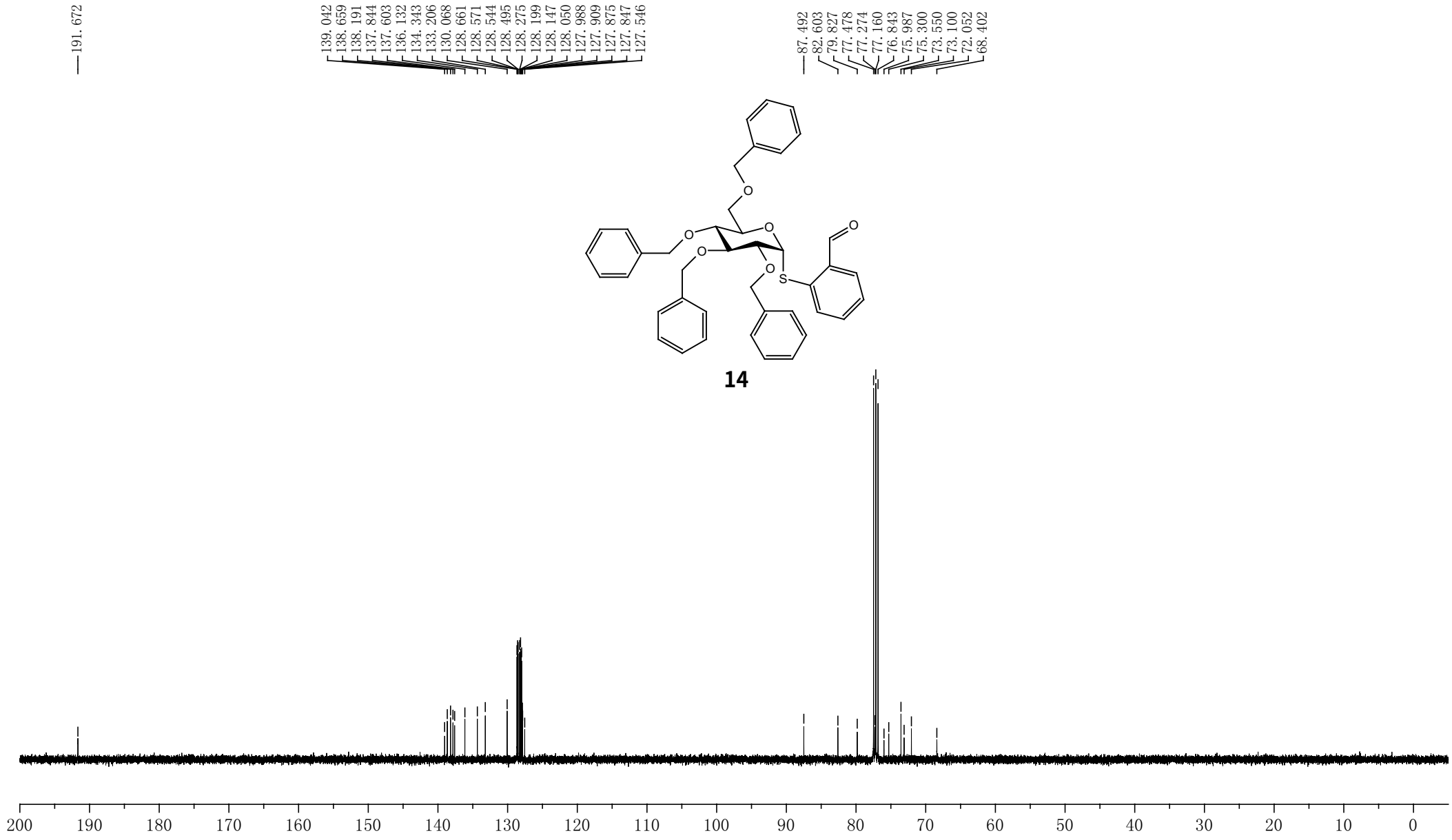
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S
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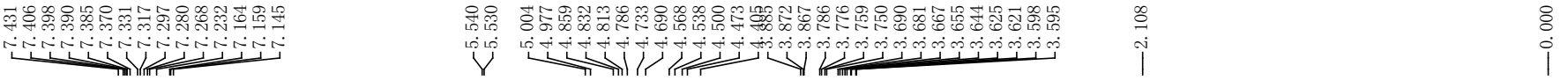
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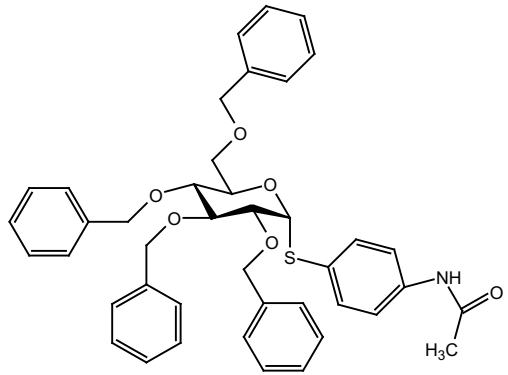
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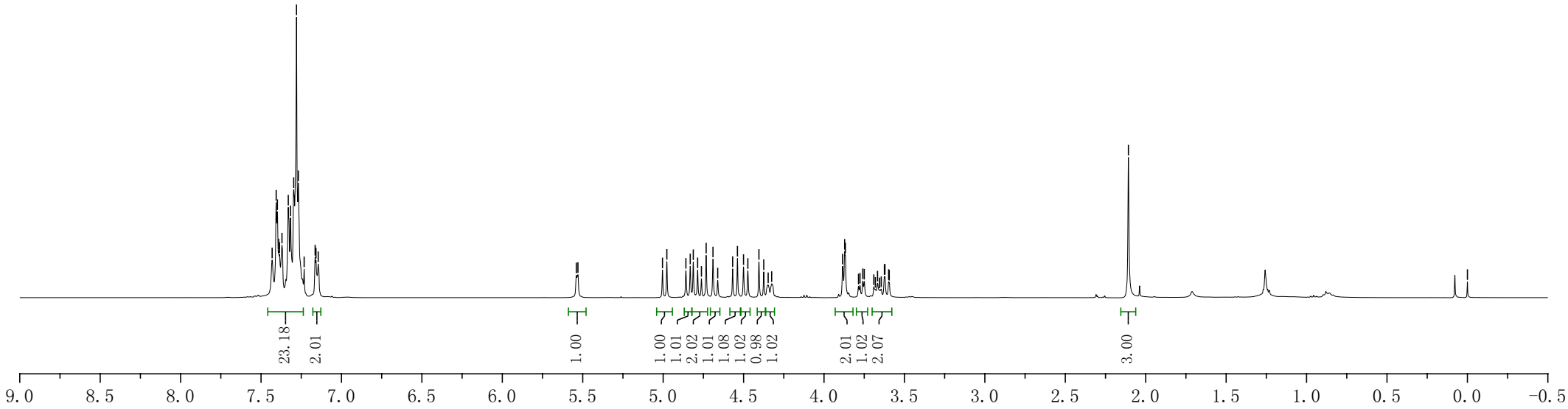
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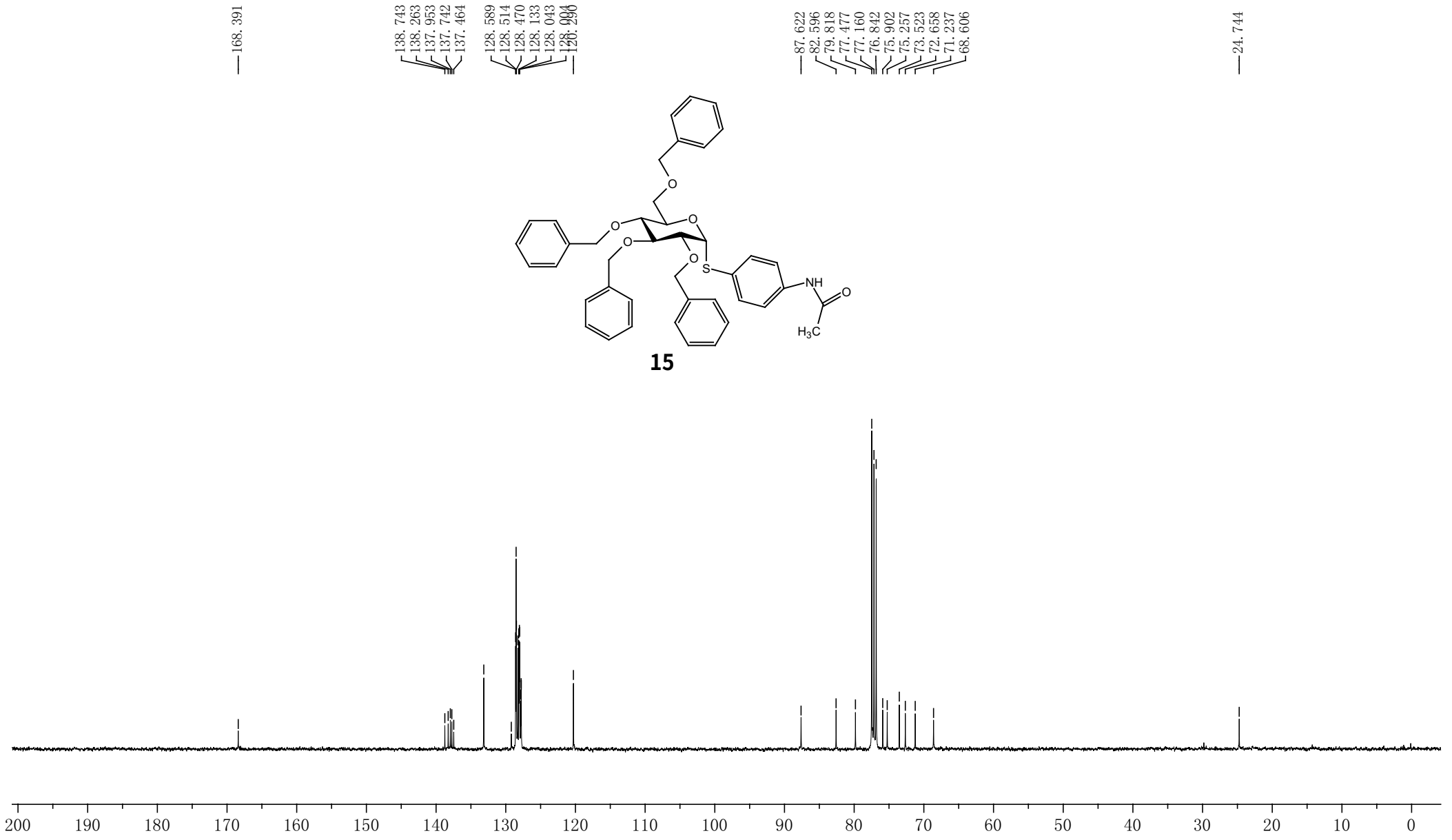
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H3C
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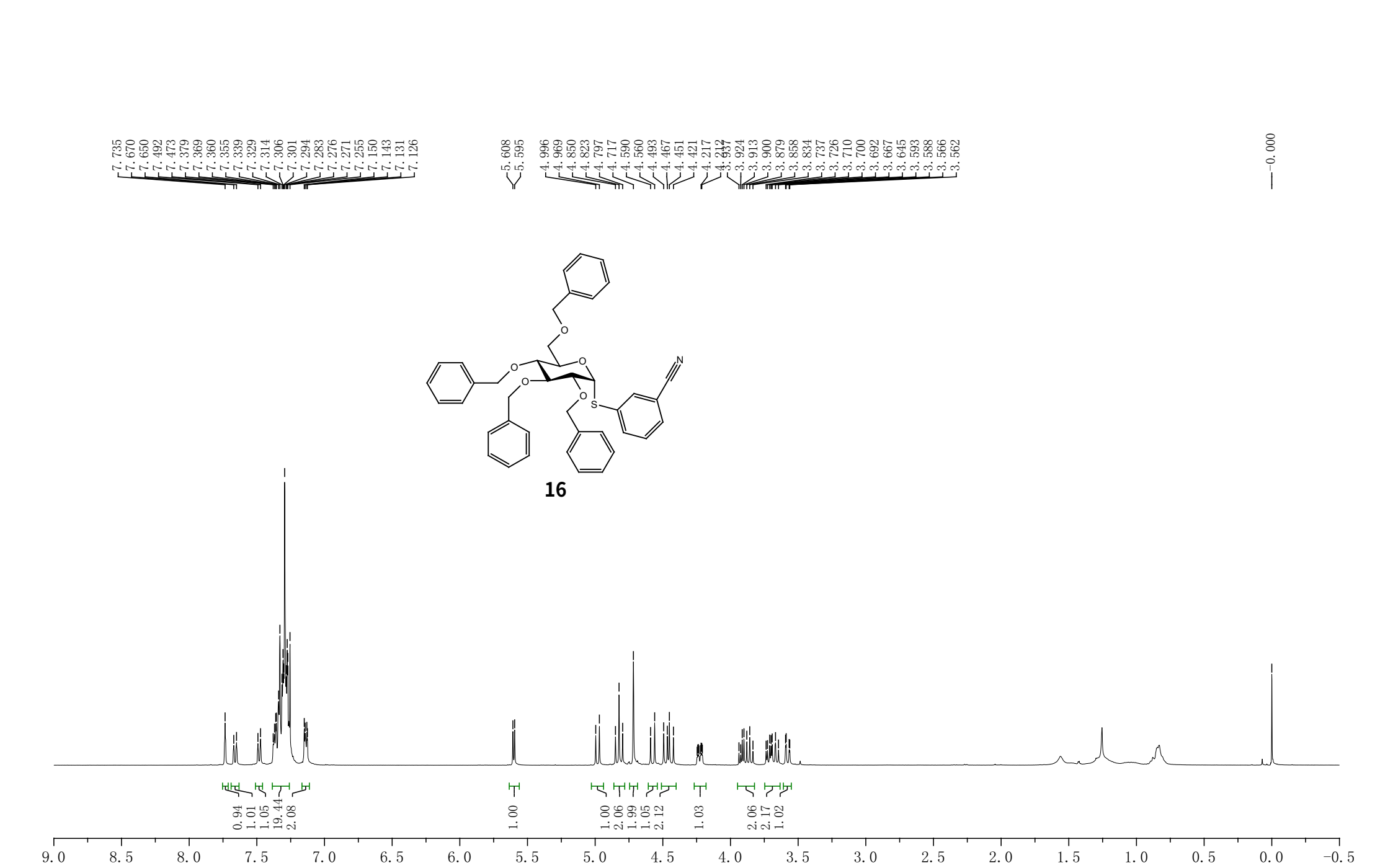
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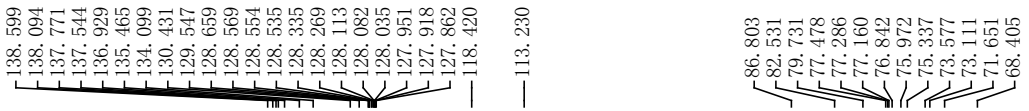
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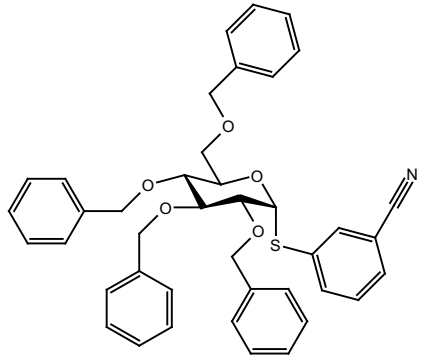
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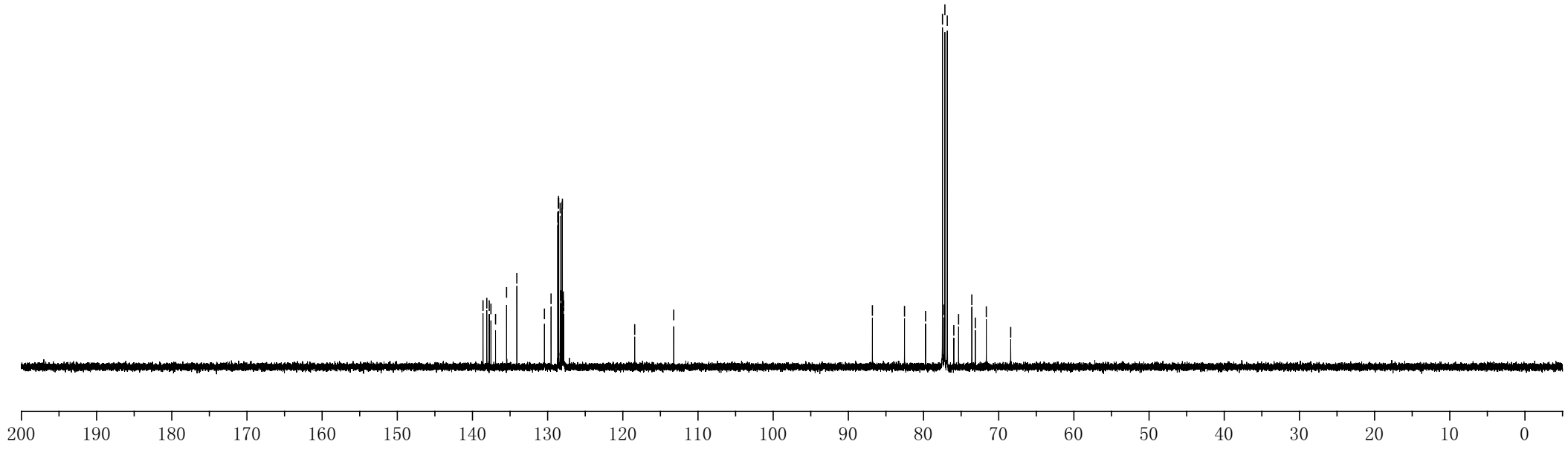
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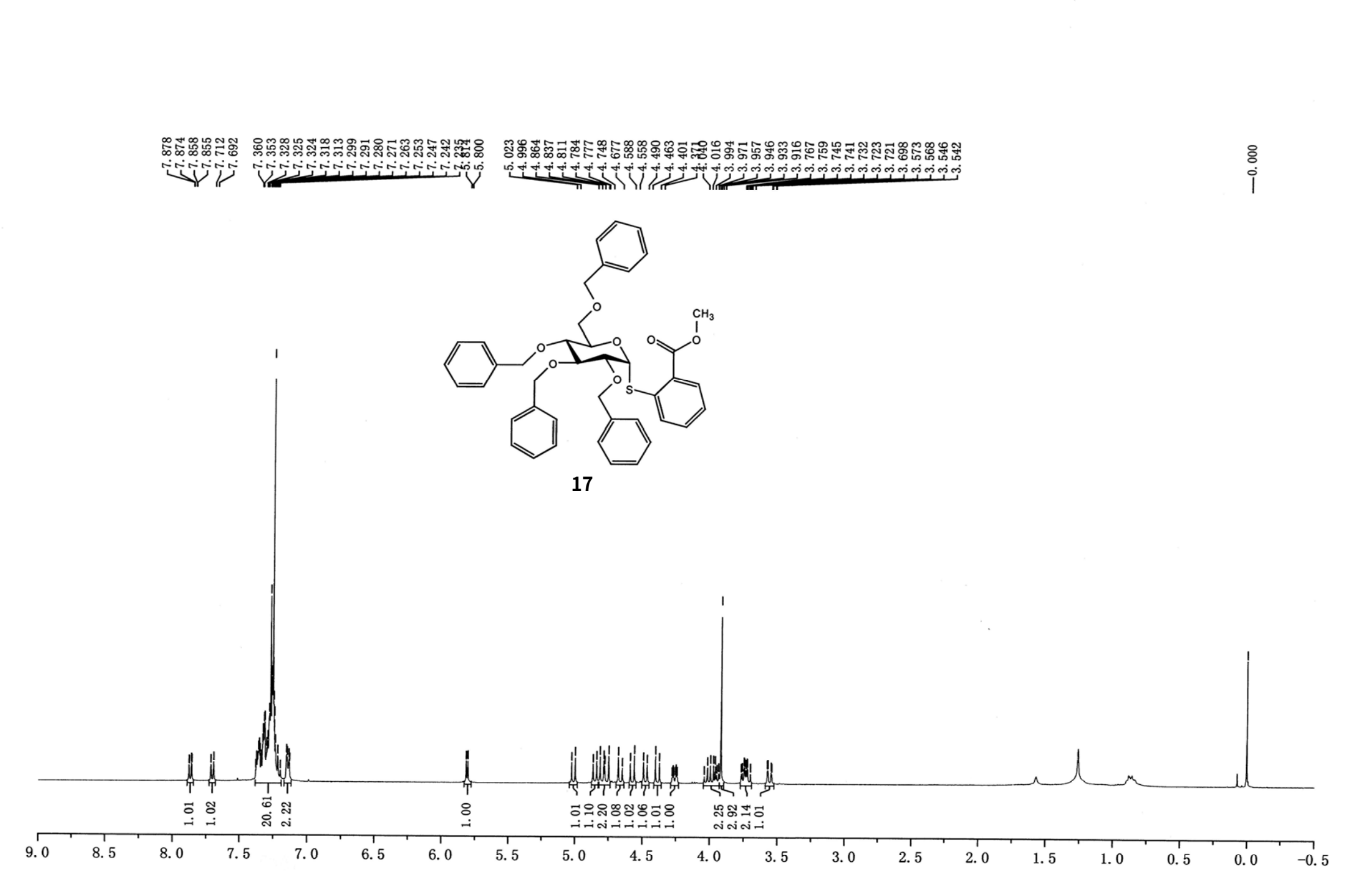
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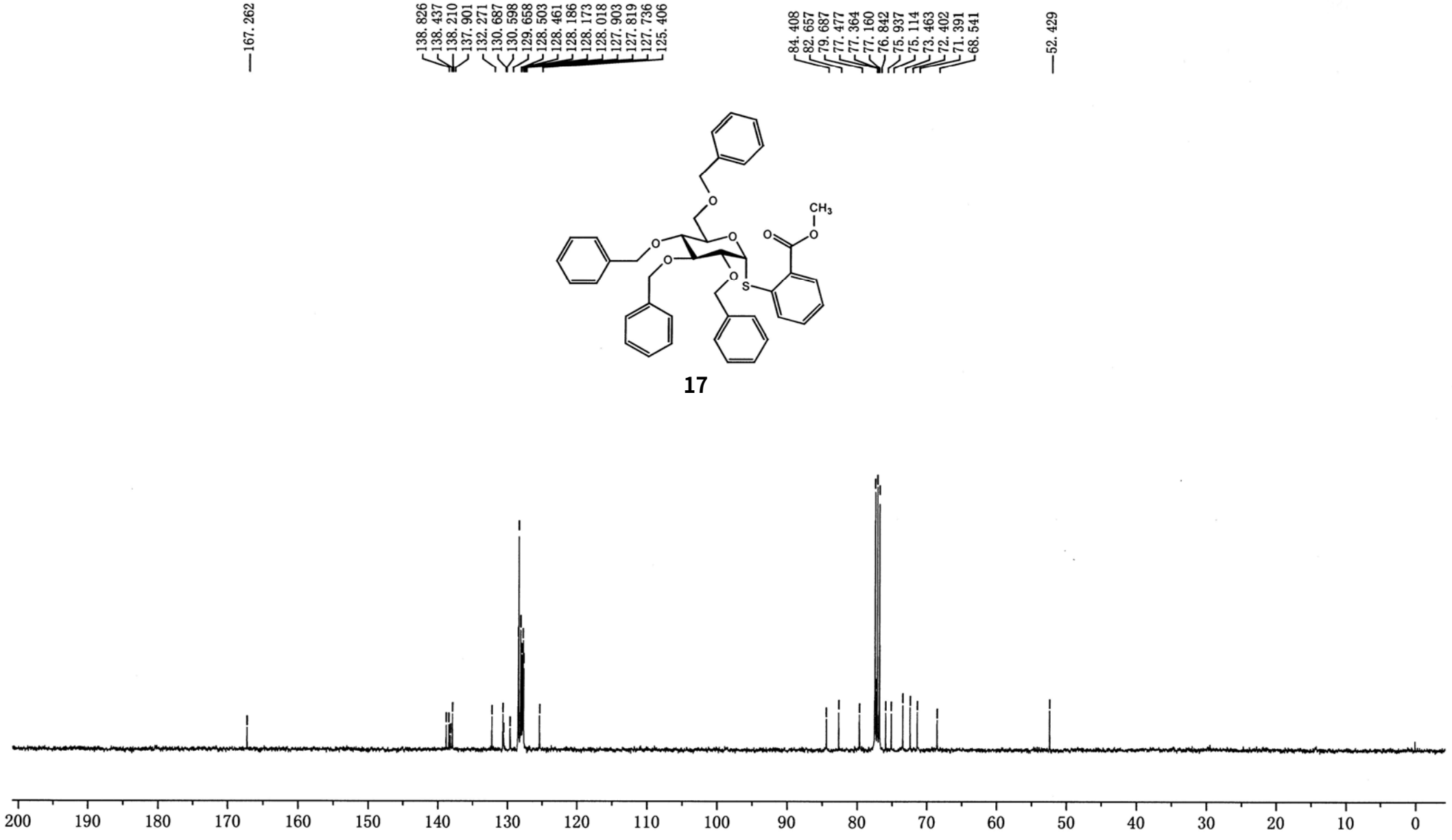
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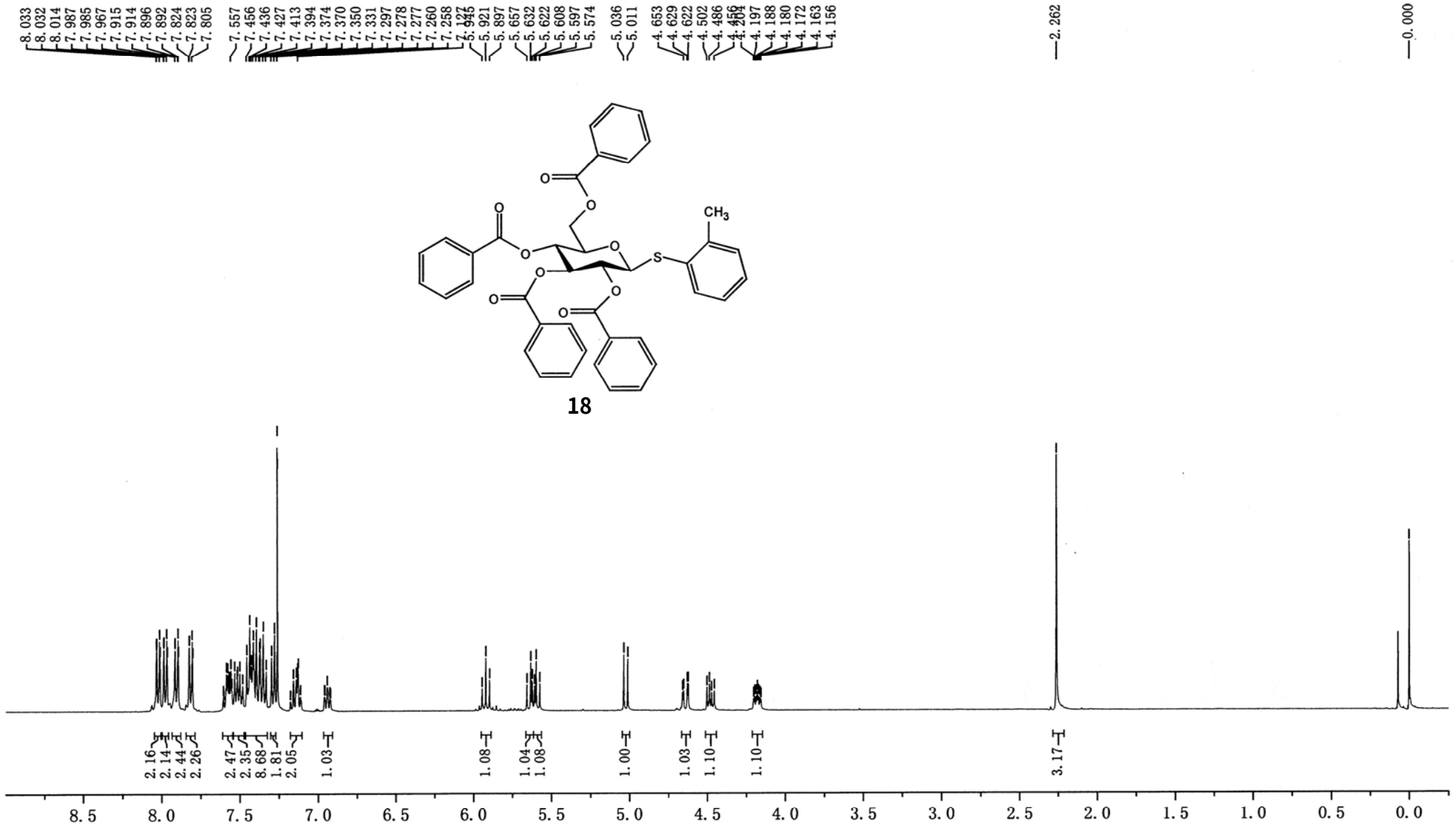
17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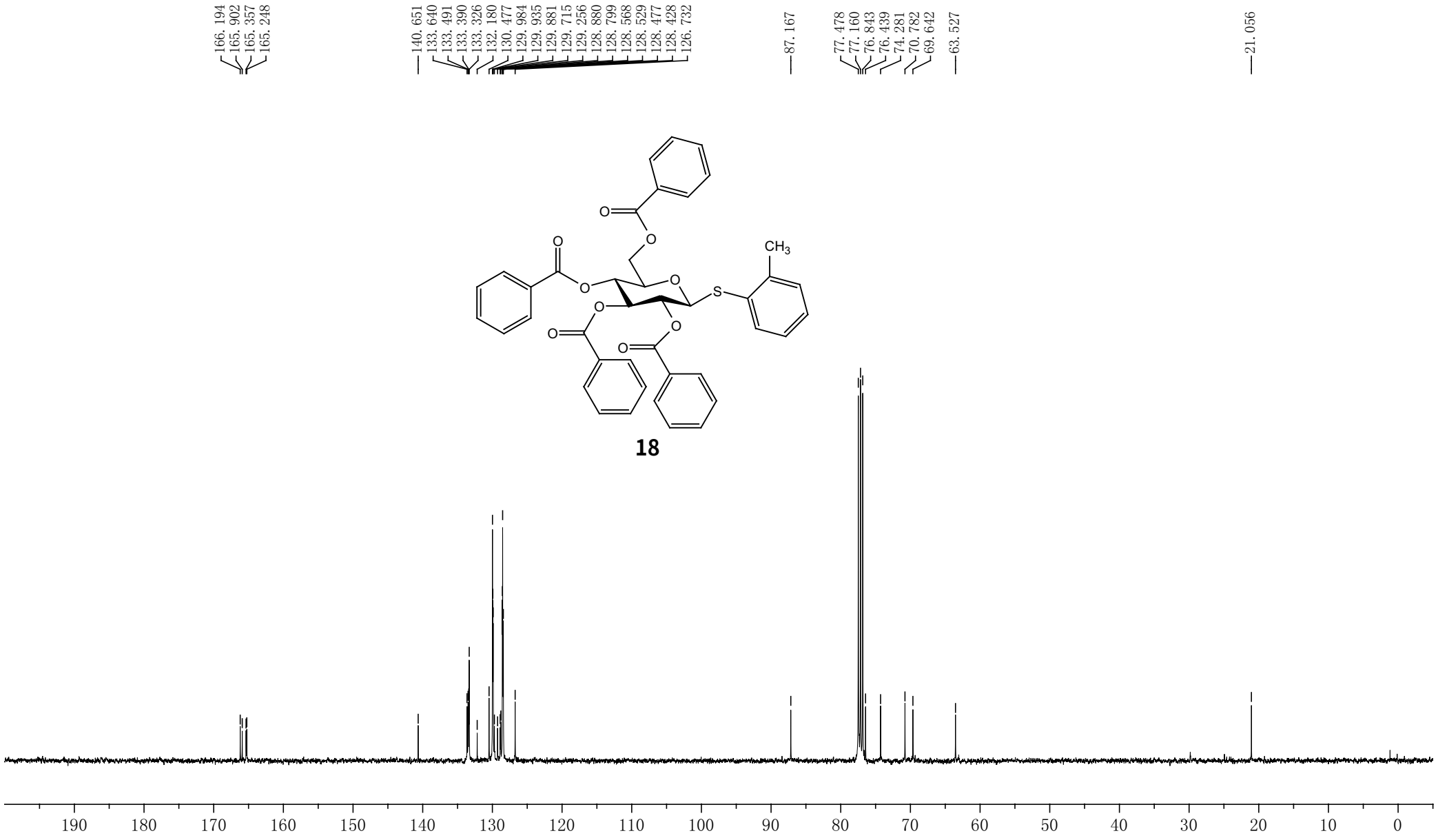
18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CH3
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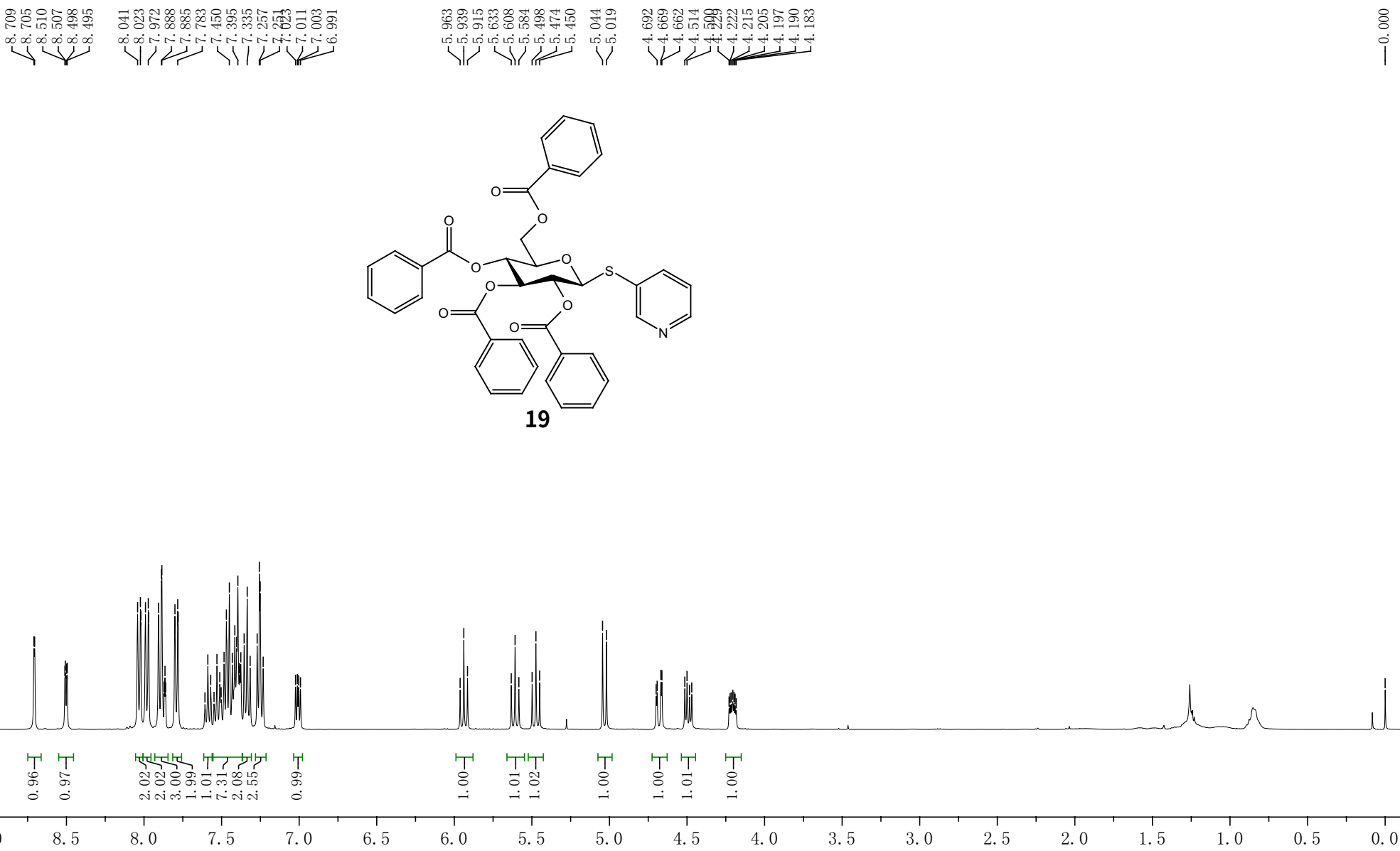
18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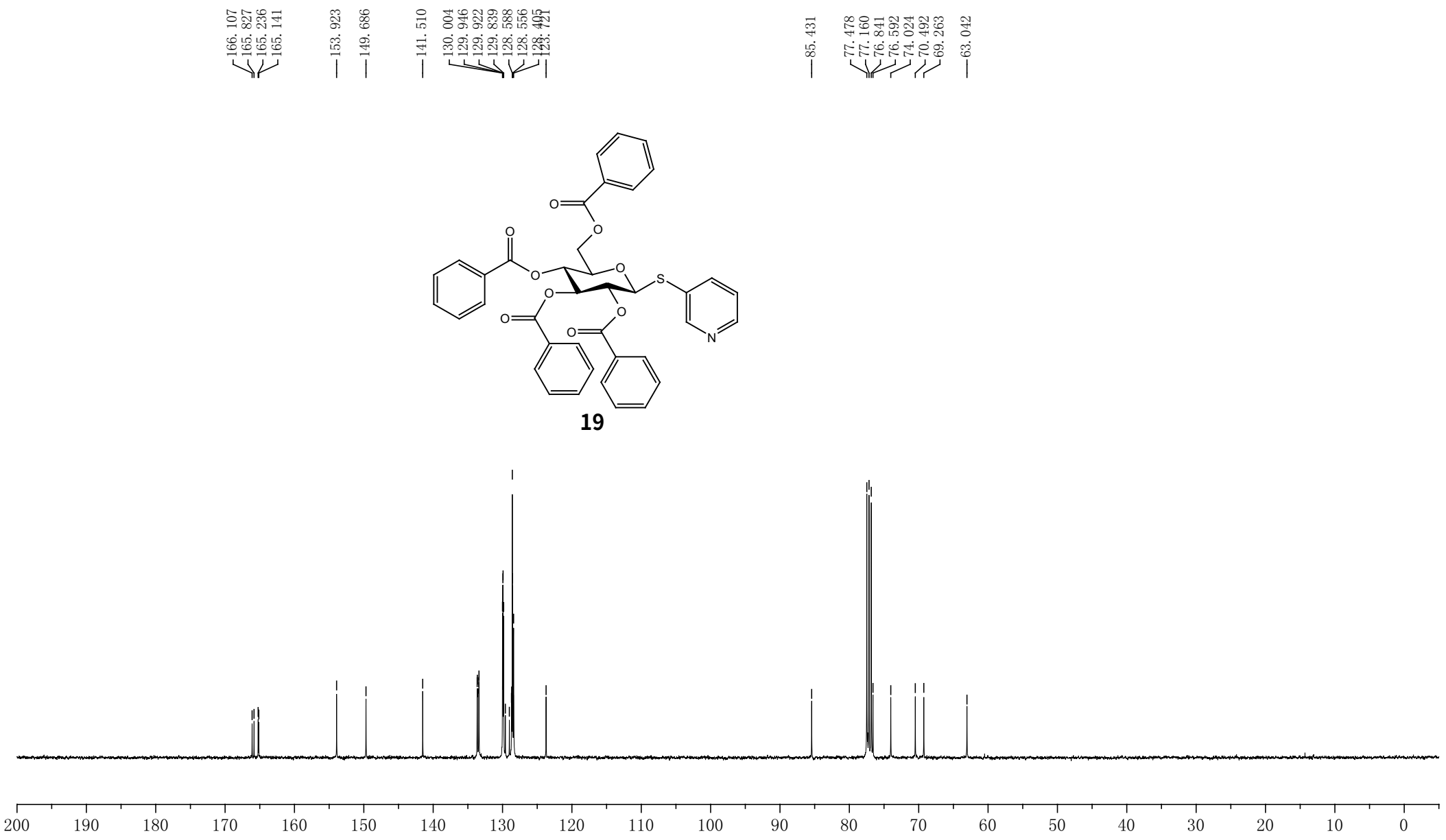
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O
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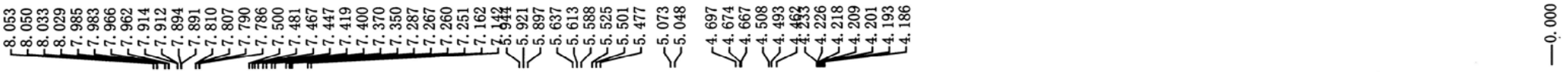
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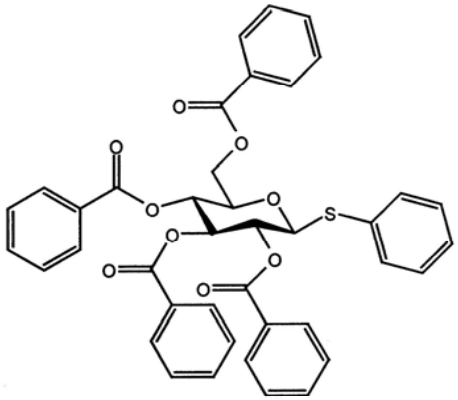

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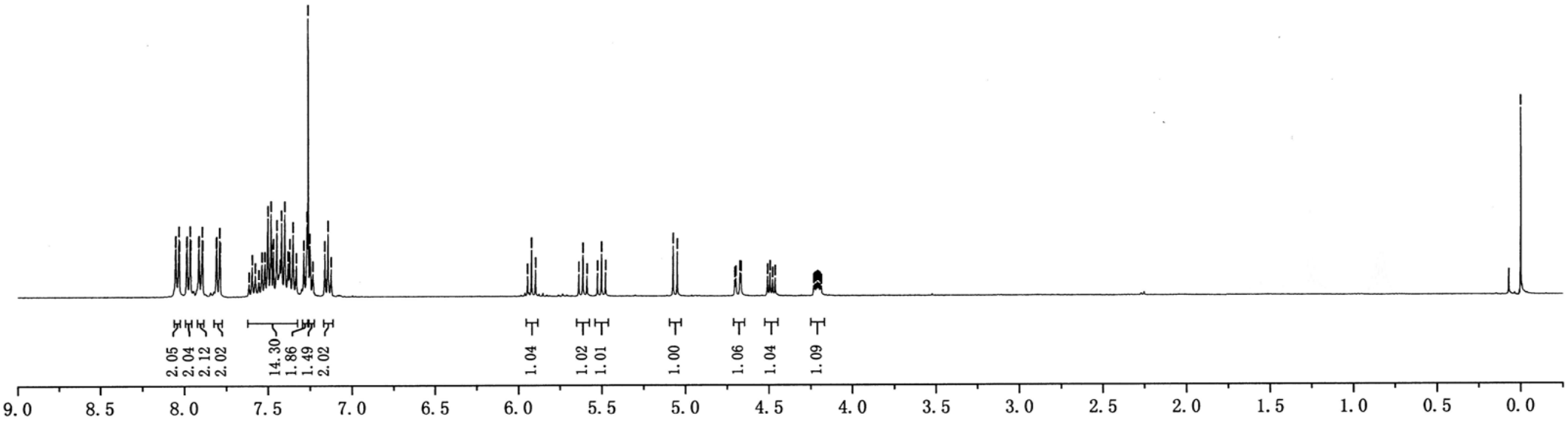
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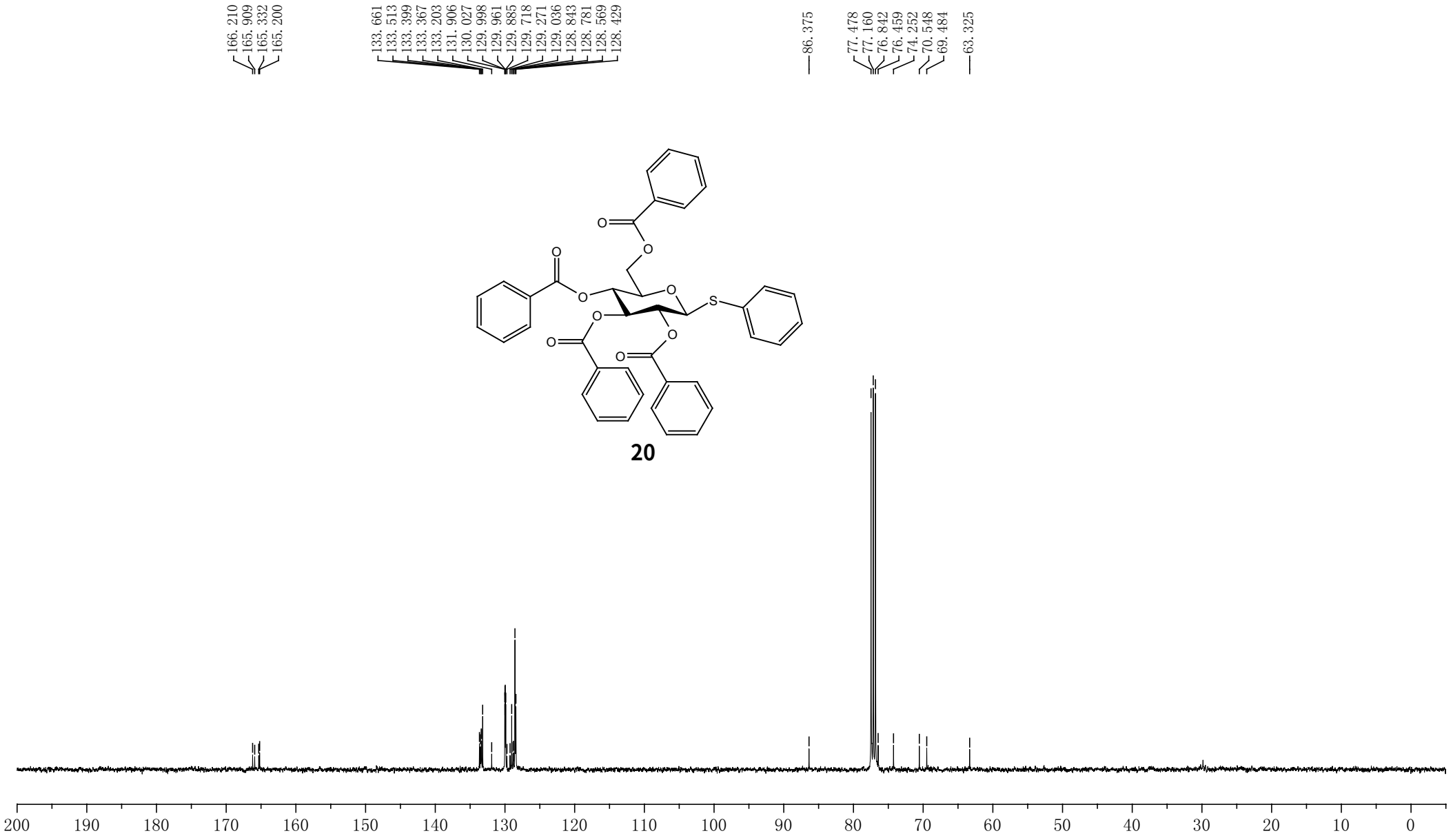
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S
200
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180
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20
10
0

20


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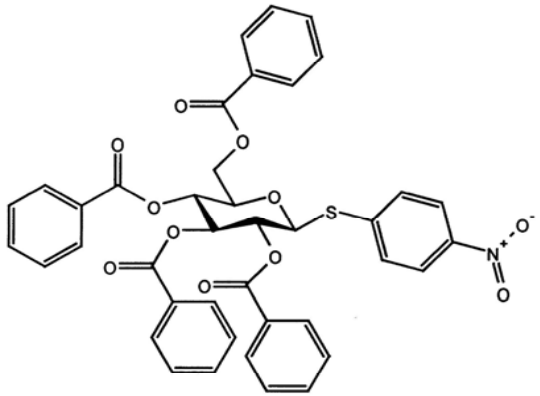

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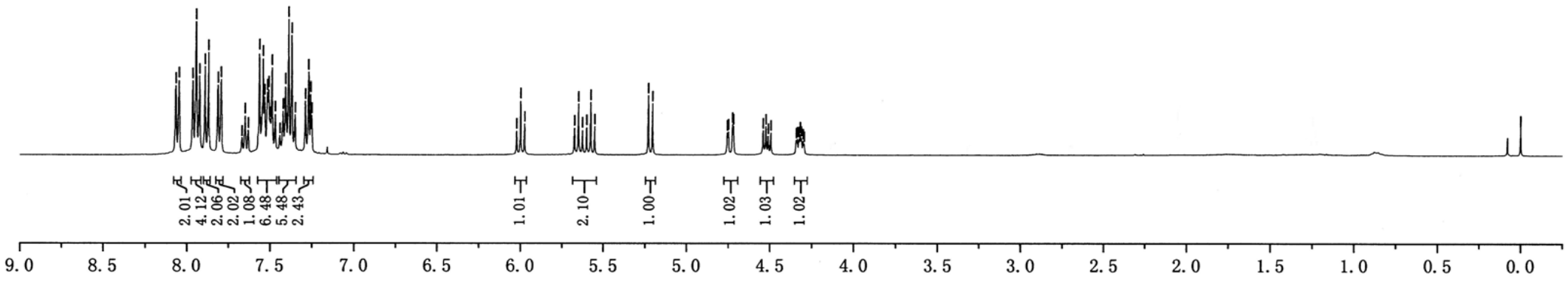
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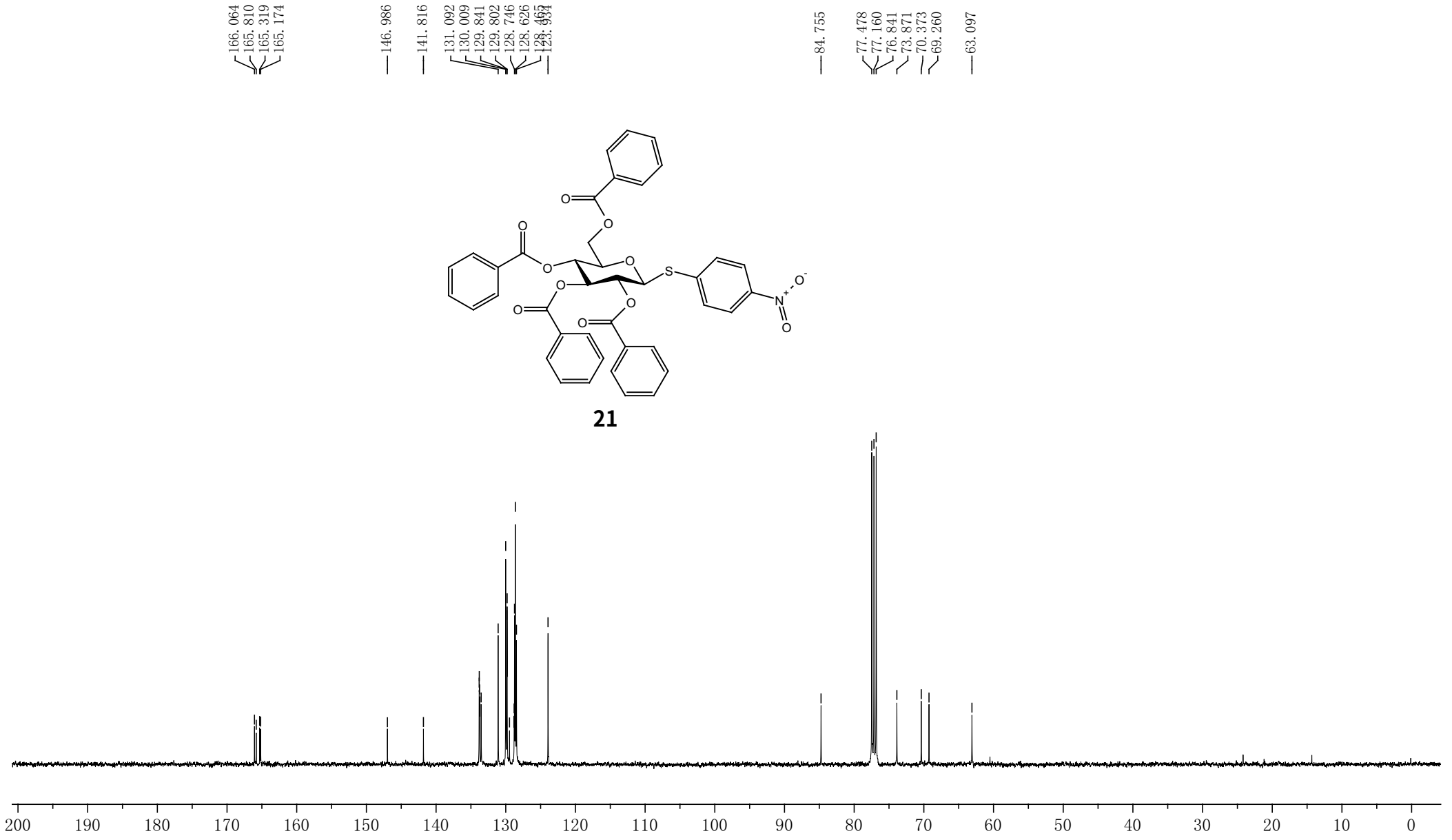
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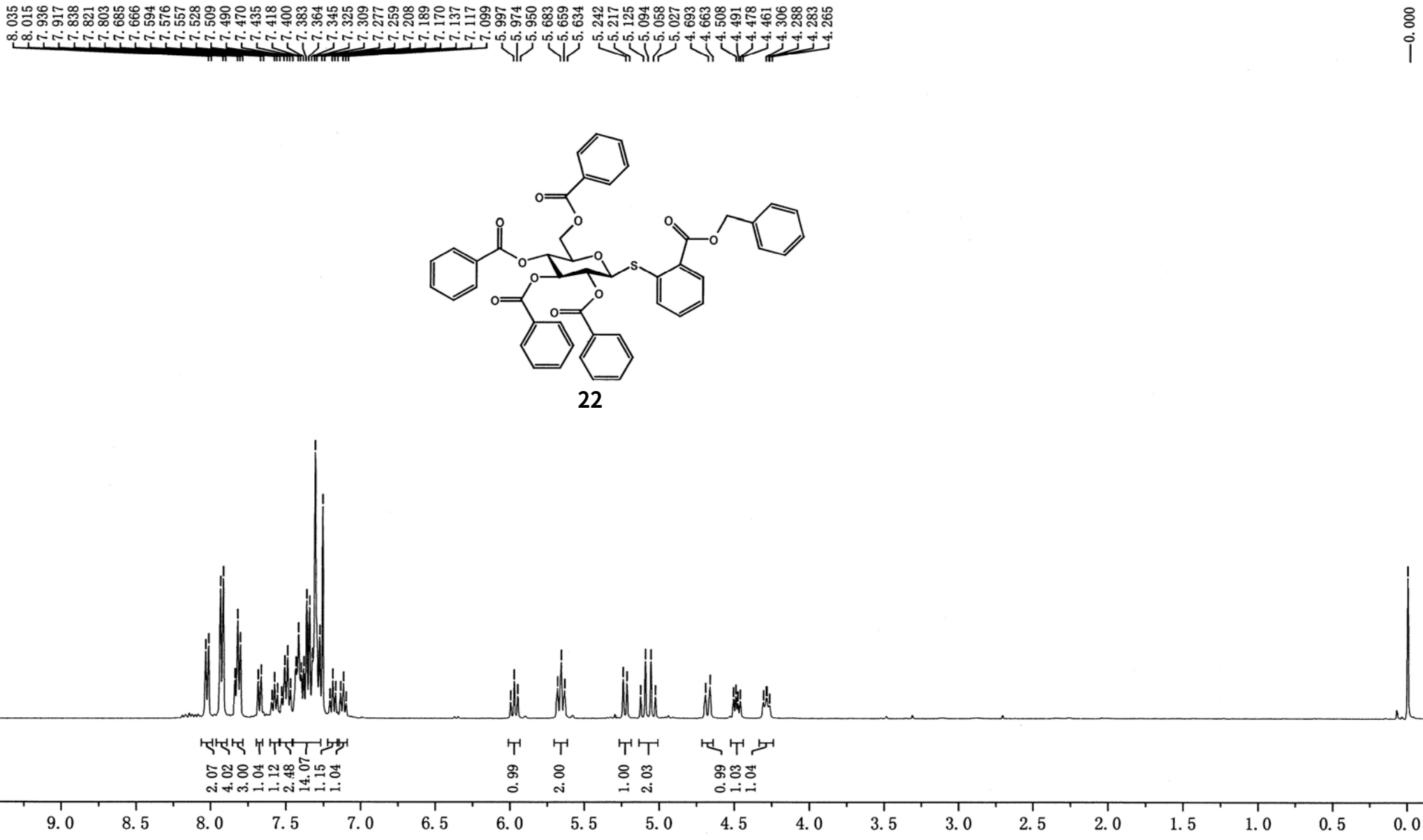
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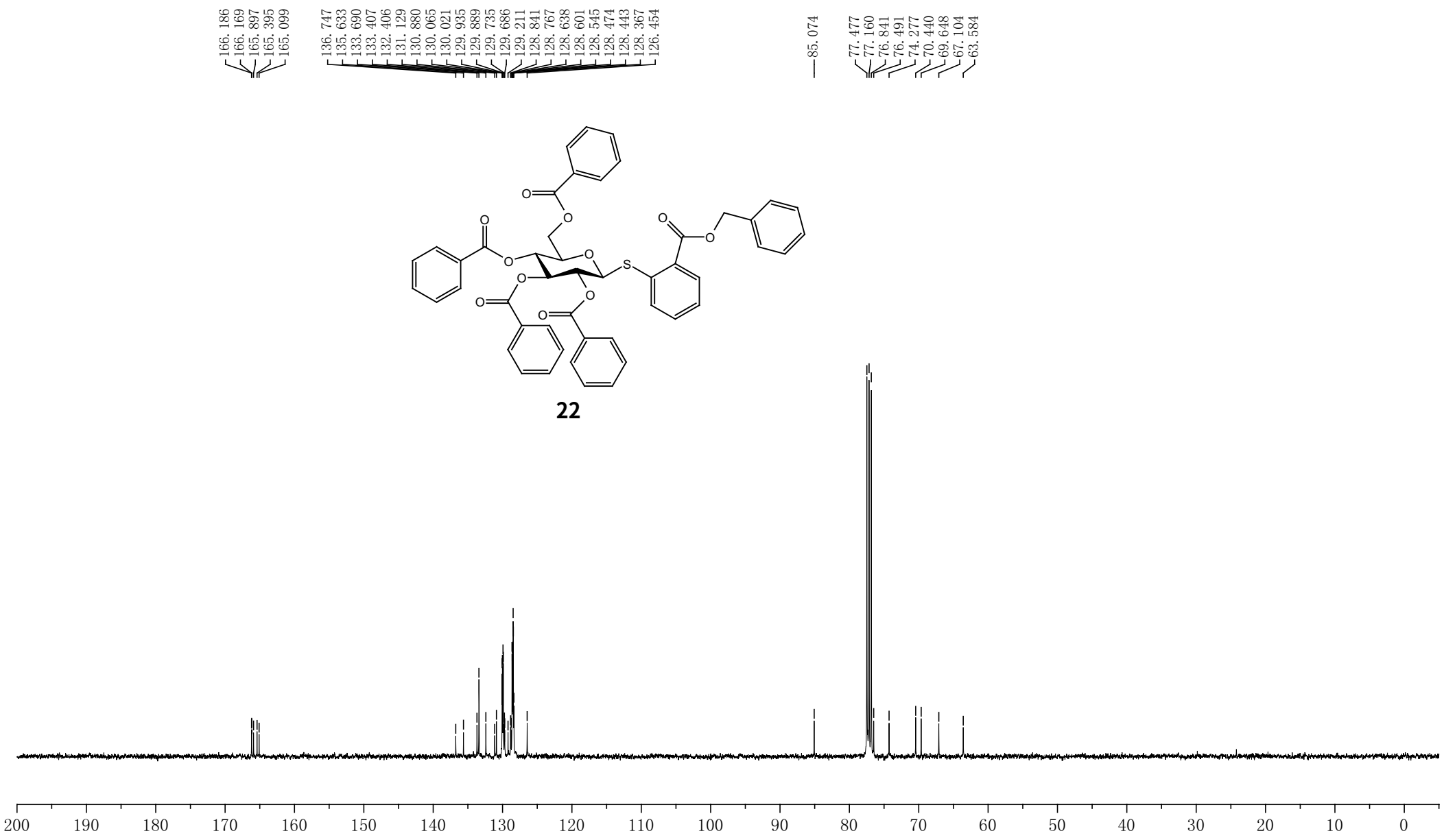
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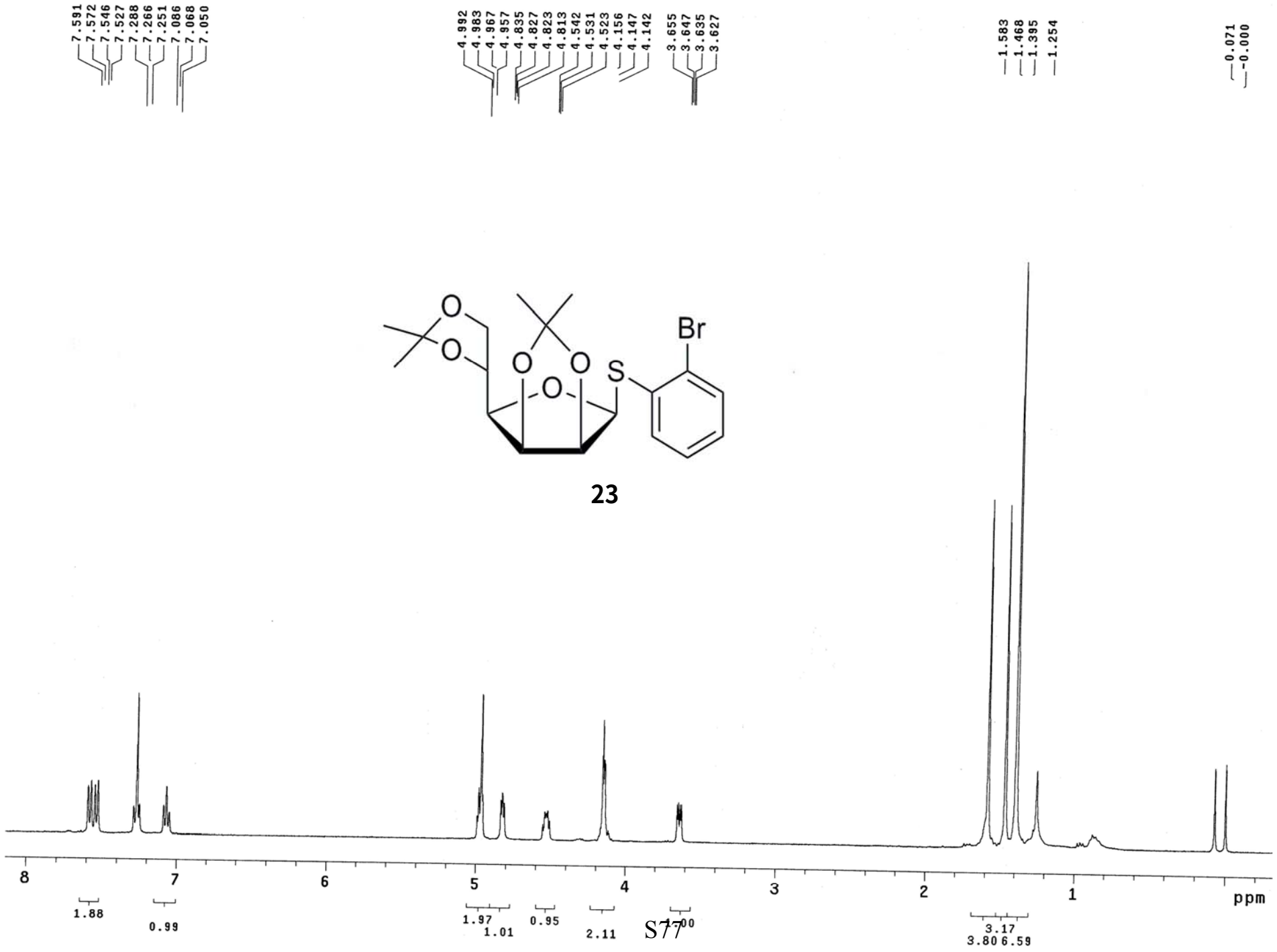
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O
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O
O
S
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6
5
4
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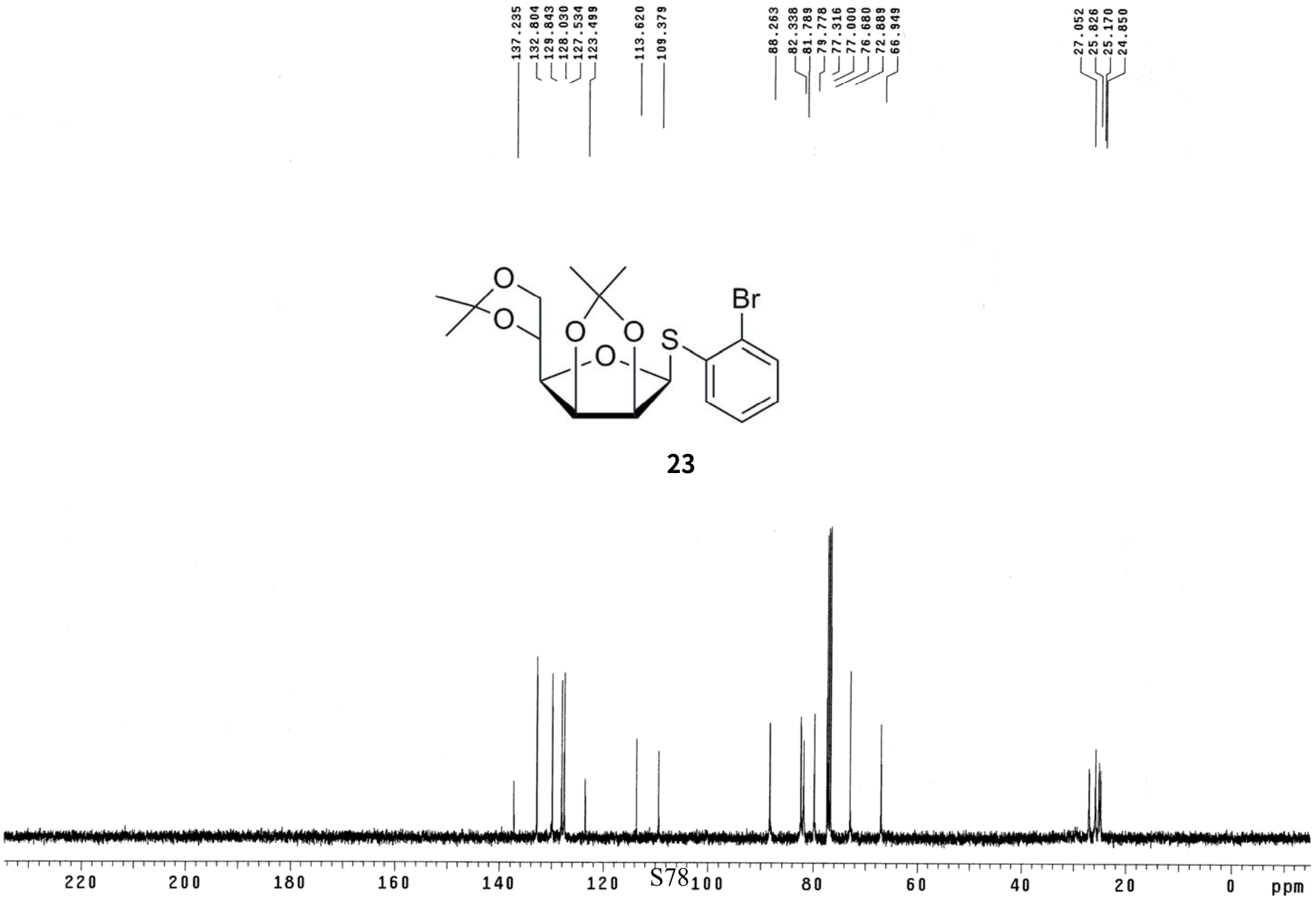
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20
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ppm

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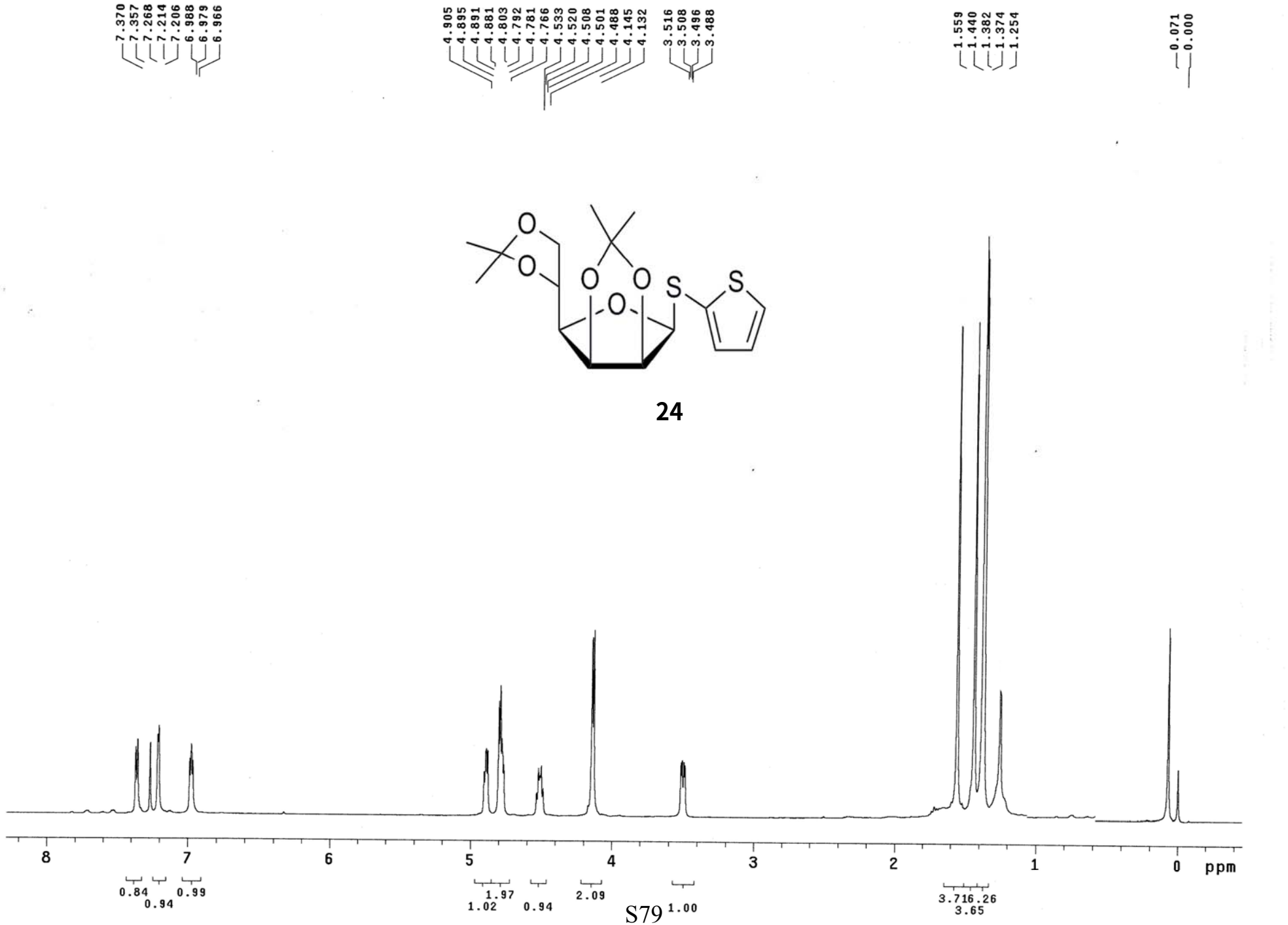
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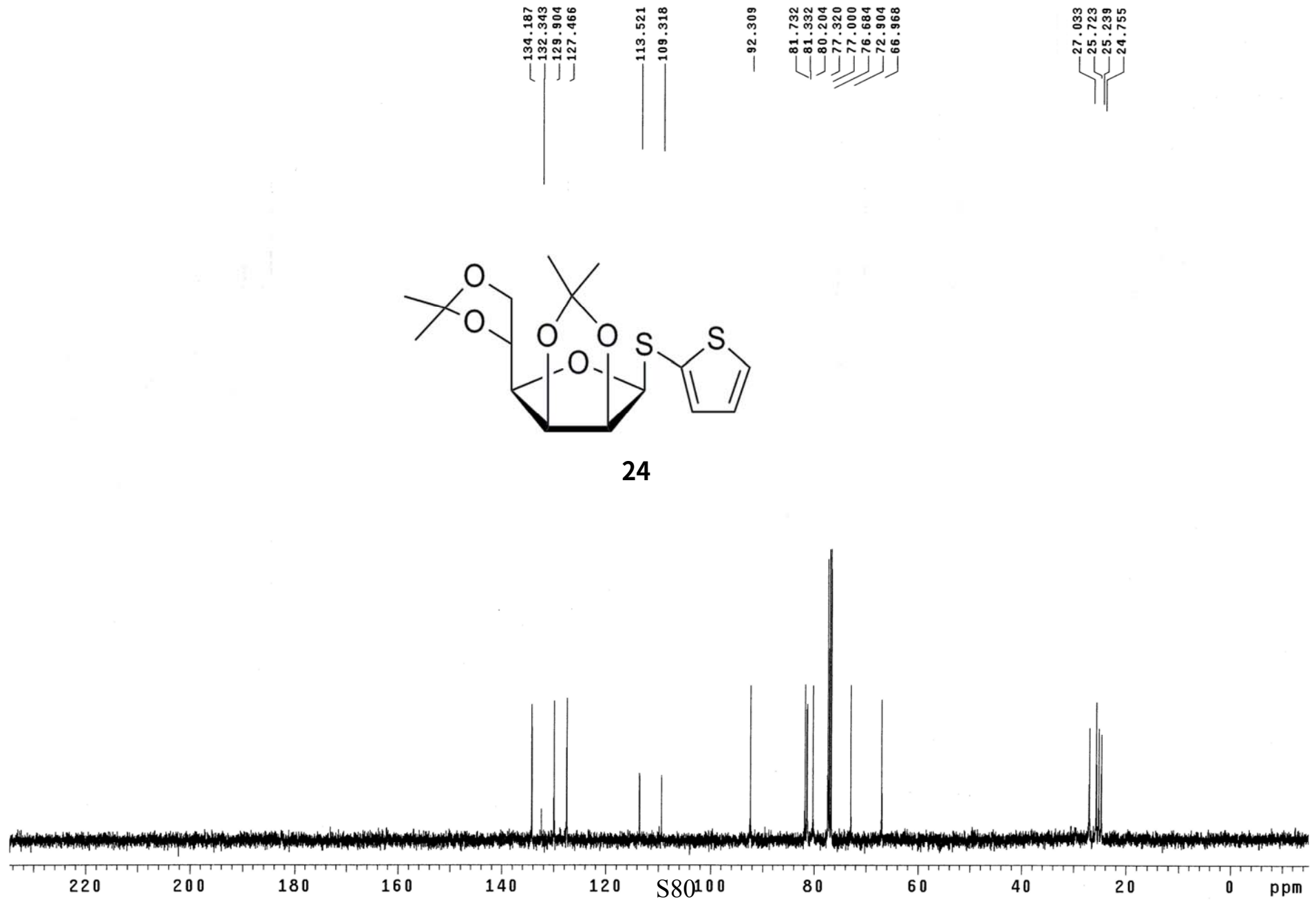
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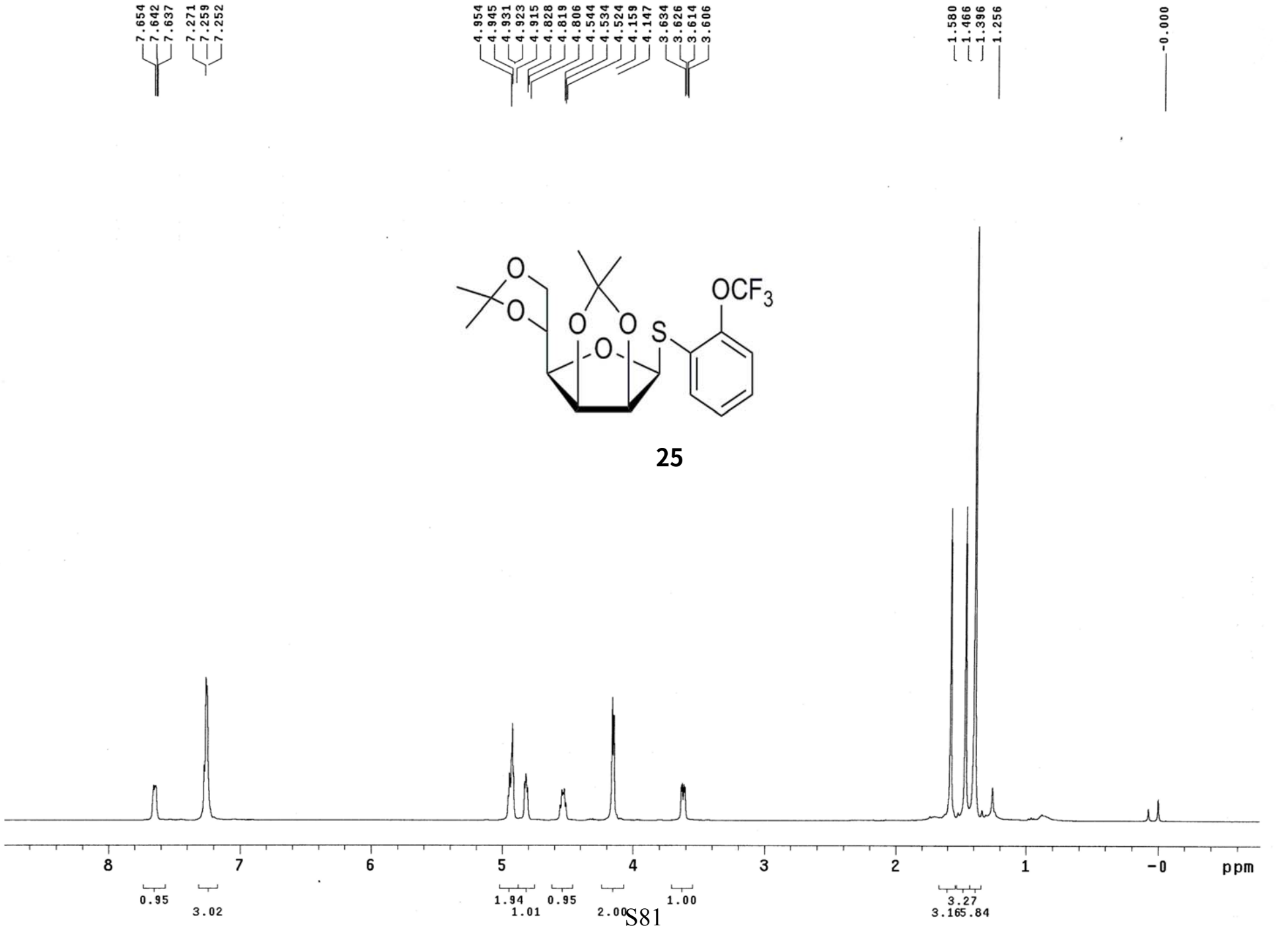
24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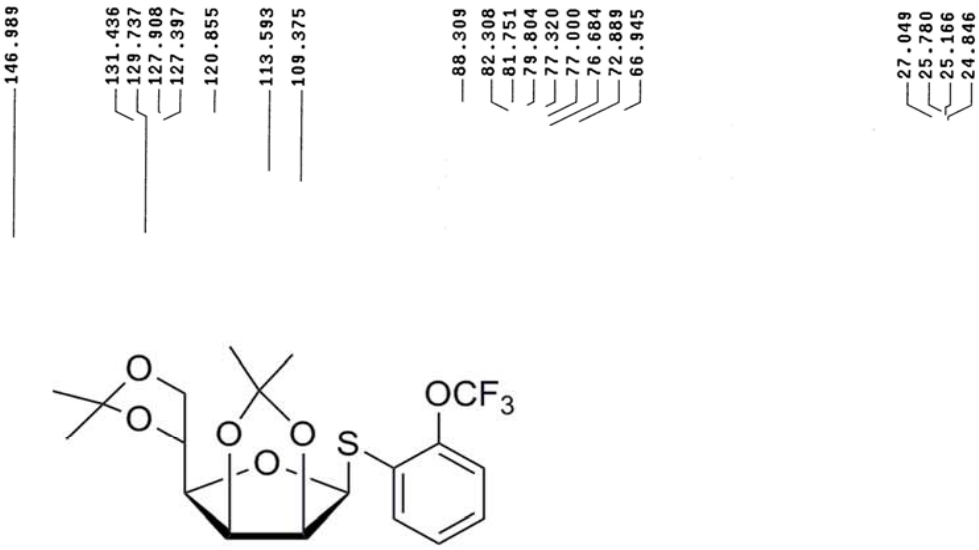
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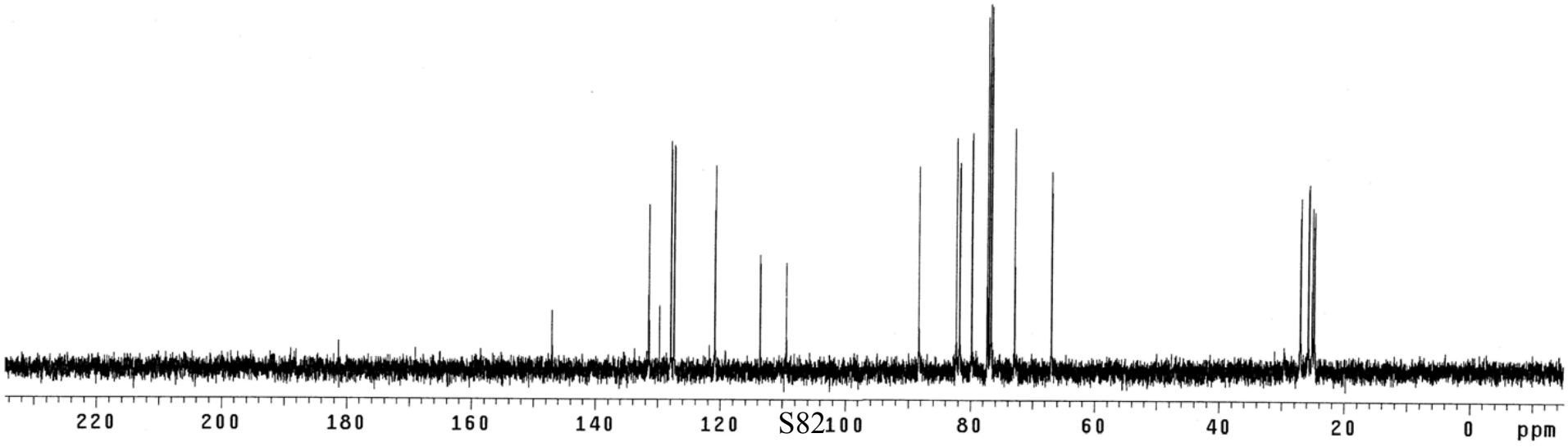
25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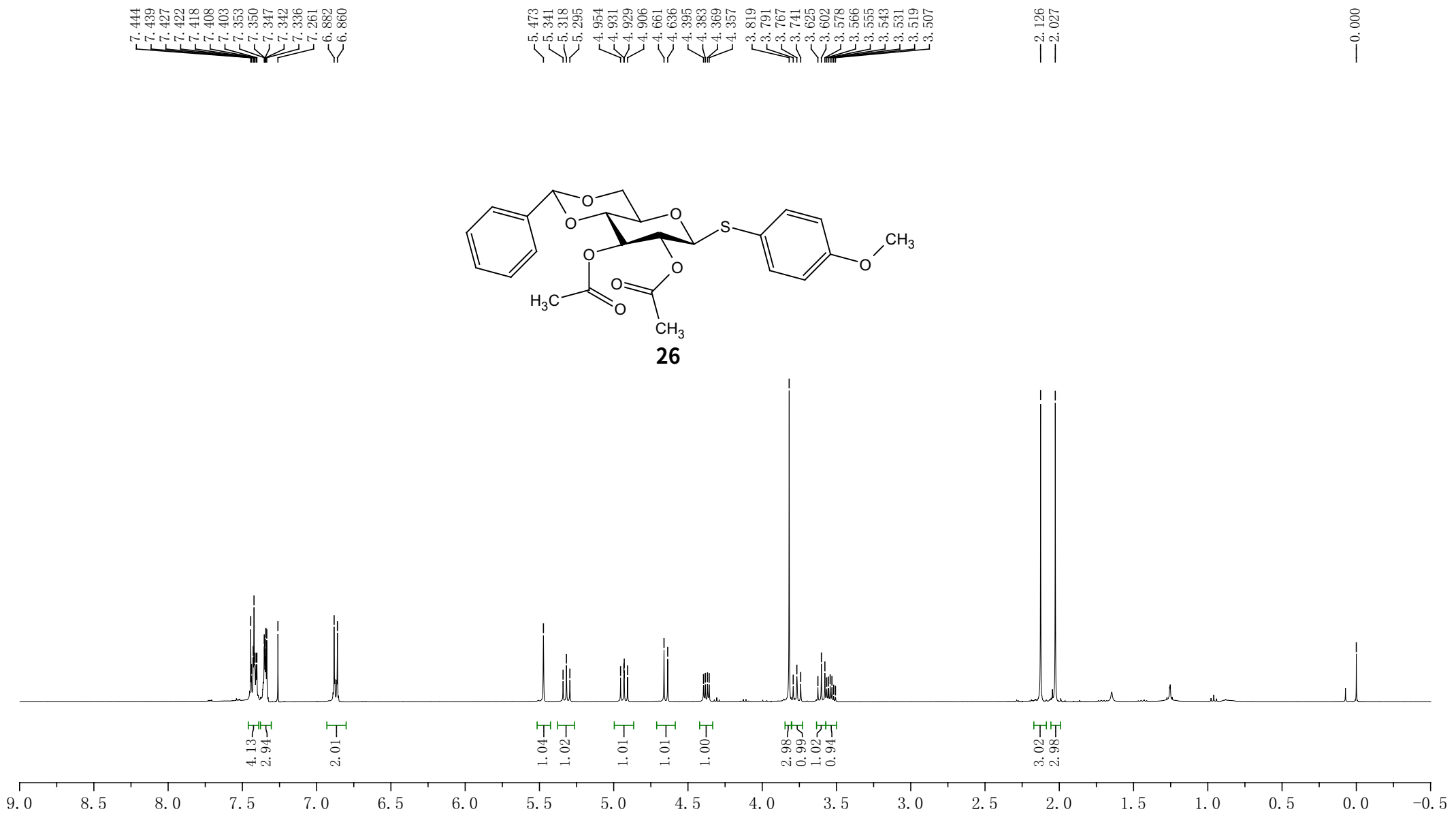
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O
S
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CH3
O
O
H3C
O
CH3
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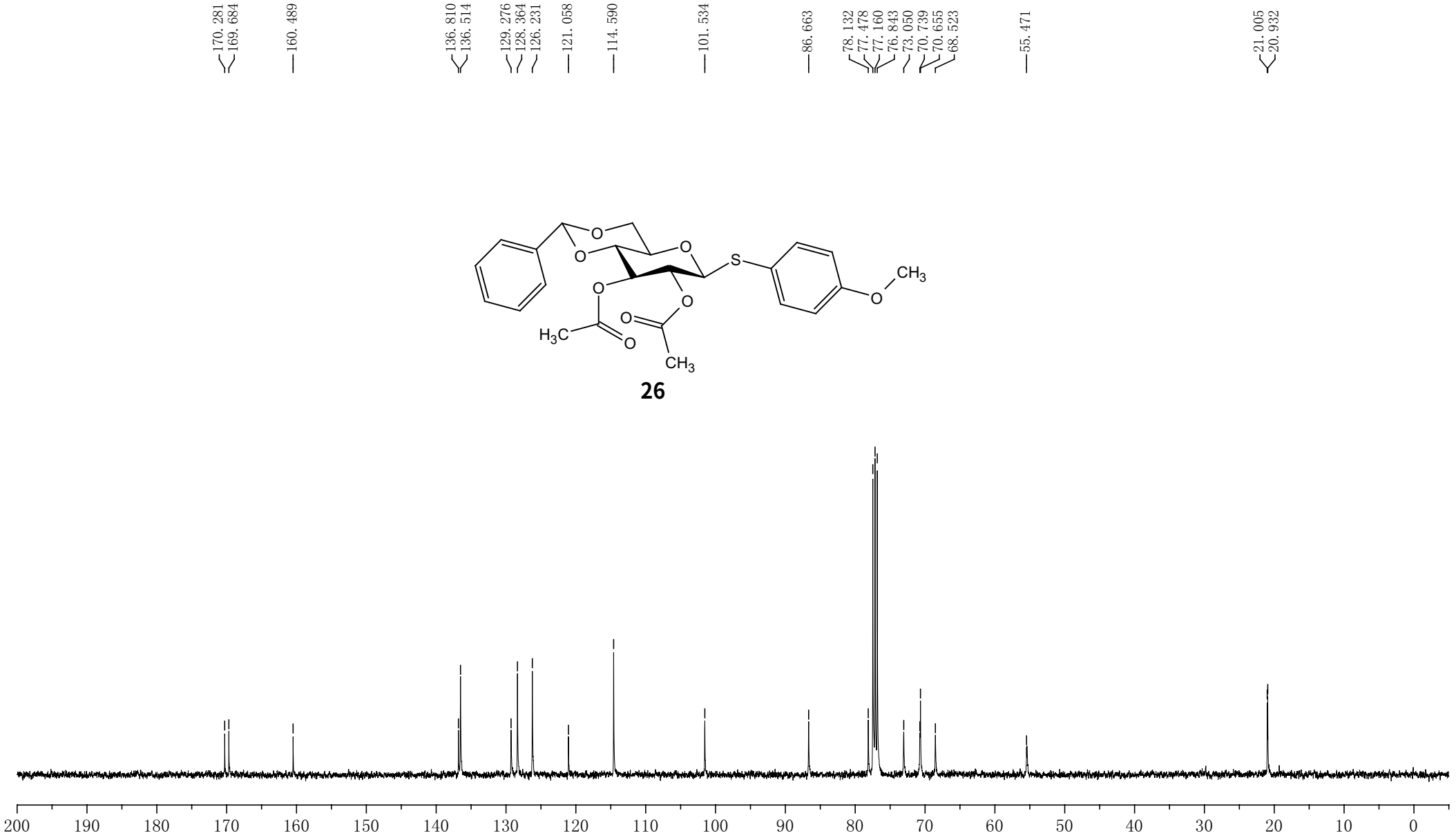
26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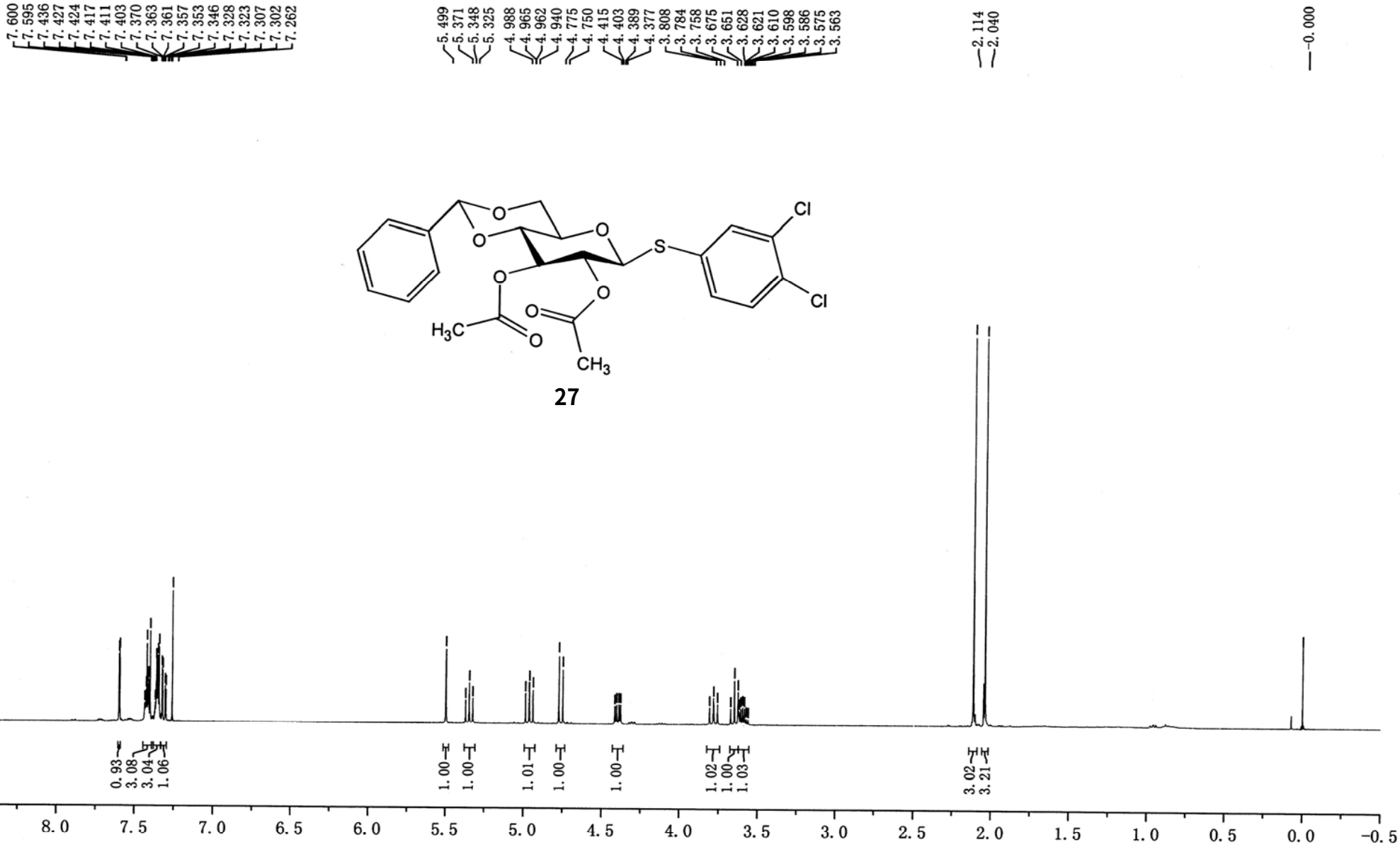
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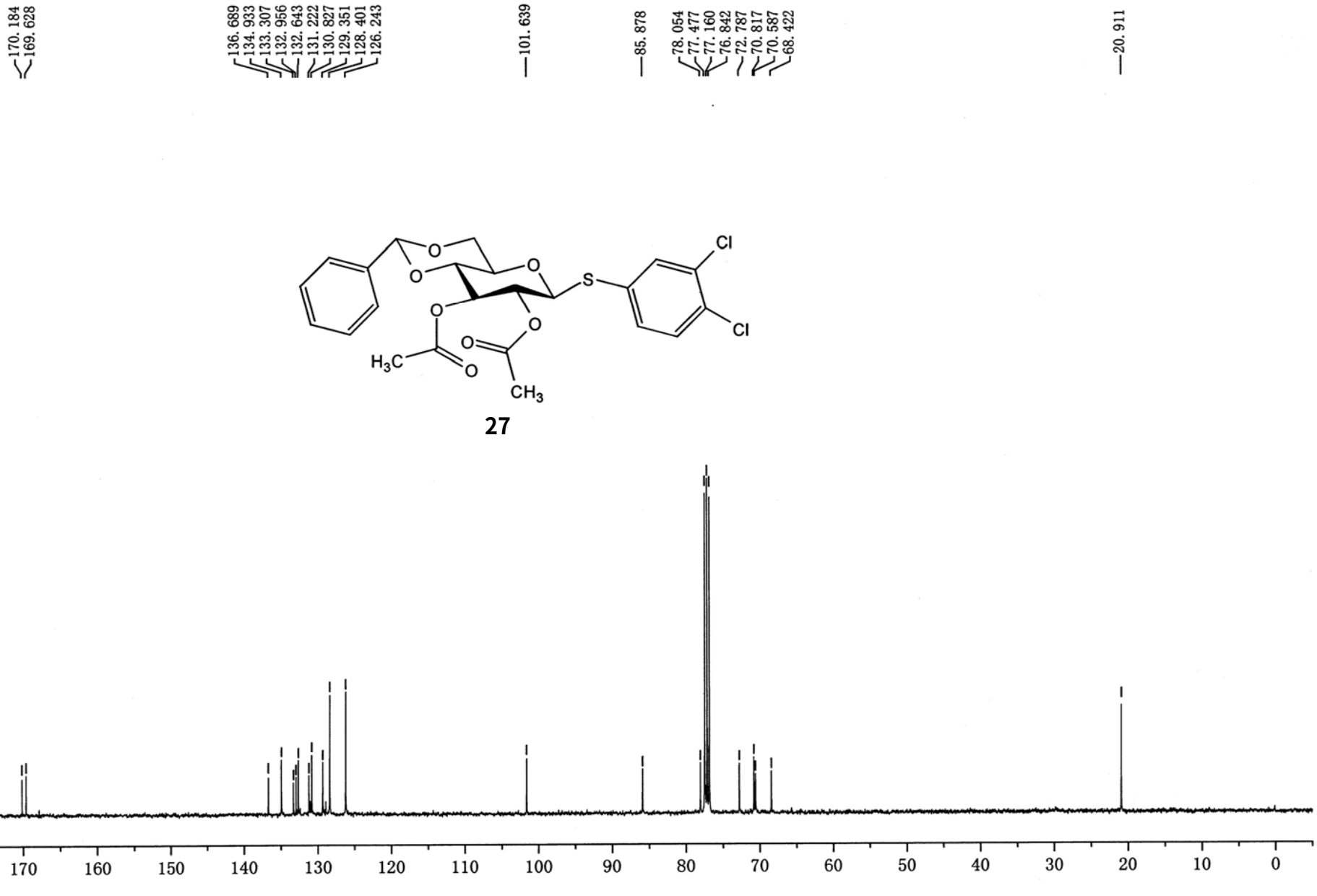
27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Cl
S
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H3C
CH3
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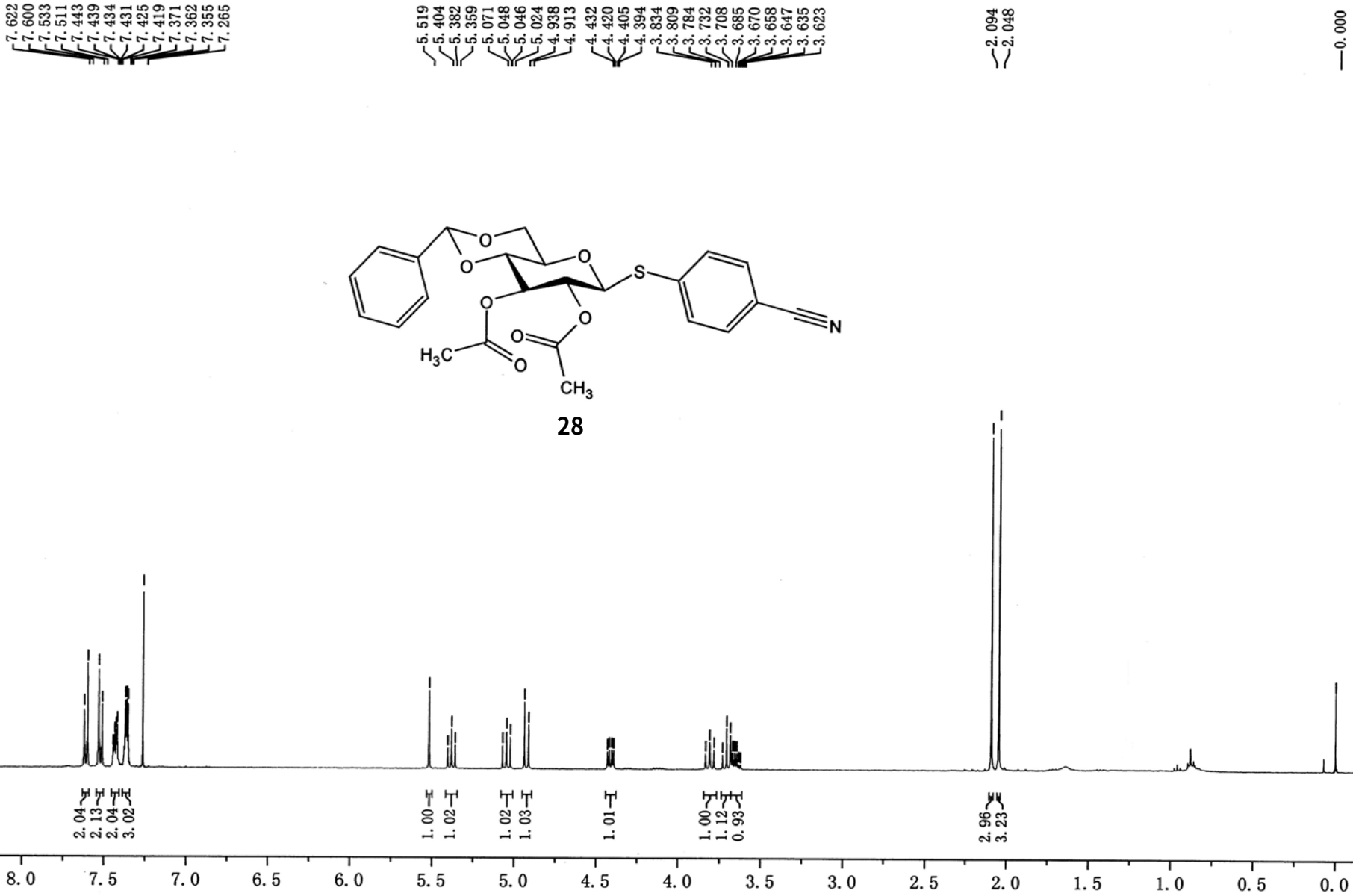
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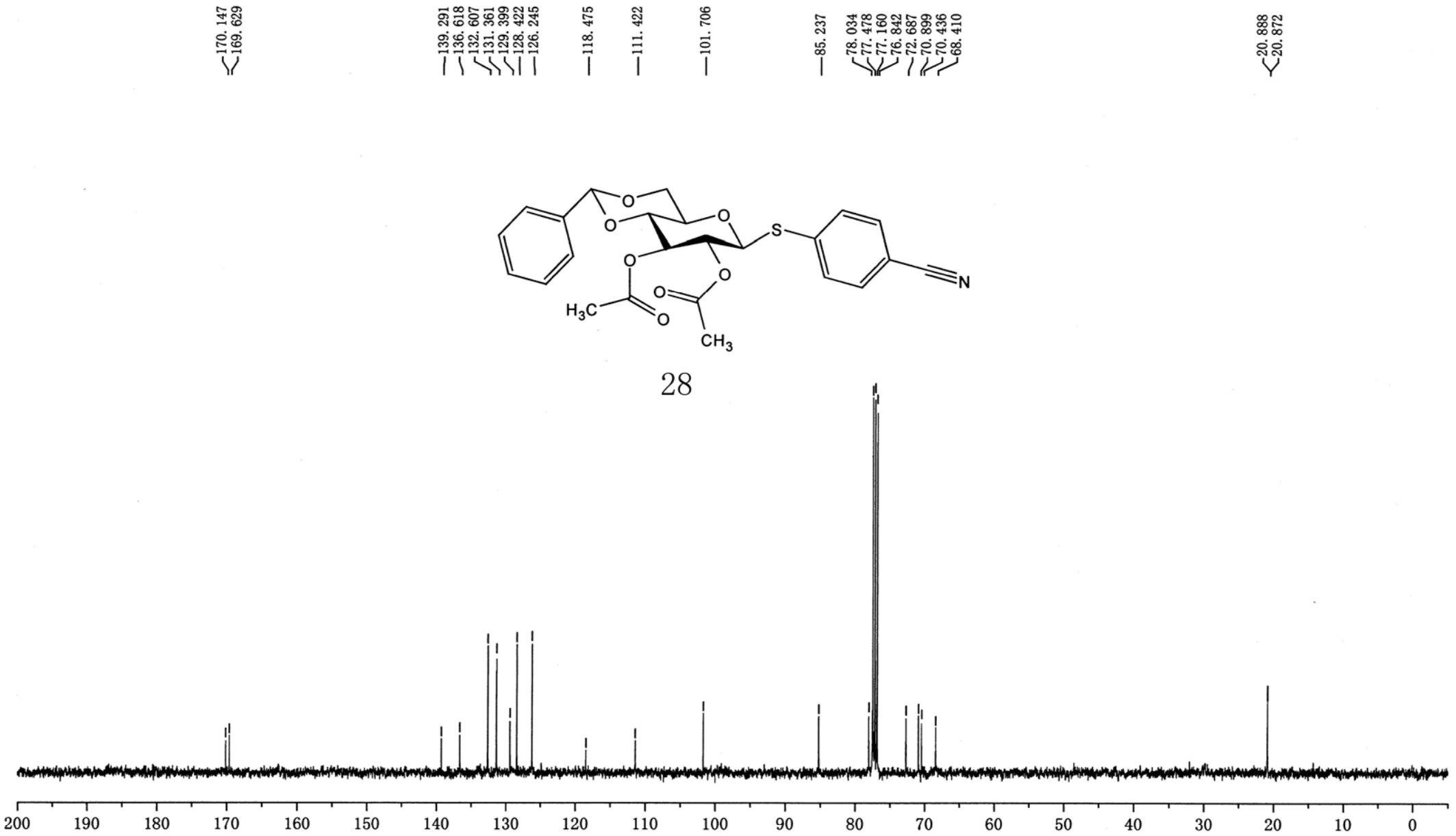
-0.5

28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O
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O
S
N
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O
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H3C
CH3
200
190
180
170
160
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140
130
120
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100
90
80
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28