Supporting Information for:

A Facile and Practical Synthesis of Peracylated 4-Thio-D-ribofuranoses from D-Glucose

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General Information. All ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ (93.94 kG, ^{1}H 400 MHz). Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant. Optical rotations were recorded at 589 nm, and were reported as $[\alpha]_D$ (concentration in grams/100 mL solvent). Melting points were uncorrected.

5,6-Anhydro-3-*O*-benzoyl-1,2-*O*-isopropylidene-α-L-*allo*-pentofuranose (9).

To a stirred solution of mesylate **16** (4.95 g, 9.6 mmol) in 40 mL THF was added dropwise 1M TBAF in THF (11.5 mL) at rt. After 3 h the reaction was quenched by aq. NH_4Cl, THF was removed under reduced pressure and the residue extracted with EtOAc (2×60 mL), the combined organic layer was washed with water and brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give 4.60 g yellow oil. To an ice-cold solution of the crude product in 20 mL DMF under Ar was added NaH (360 mg, 60% in mineral oil, 9 mmol) in one portion under stirring. After 5 min the reaction was quenched by adding ice, the solution was diluted with EtOAc (100 mL), washed with water and brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane=1/6) to afford **9** (1.43 g, 51%) as a white solid.

m.p. 123-124^{o}C; $[\alpha]_D^{23}$ +120.3 (*c* 0.74, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 8.06 (d, 2H, *J* = 7.0 Hz), 7.60 (t, 1H, *J* = 7.4 Hz), 7.47 (t, 2H, *J* = 7.8 Hz), 5.87 (d, 1H, *J* = 3.5 Hz), 5.01 (dd, 1H, *J* = 8.6, 4.7 Hz), 4.96 (m, 1H), 4.20 (dd, 1H, J = 8.6, 4.3 Hz), 3.18 (m, 1H), 2.88-2.80 (m, 2H), 1.54 (s, 3H), 1.33 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.6, 133.5, 129.8, 129.1, 128.5, 113.4, 104.5, 77.5, 77.4, 73.8, 50.9, 43.8, 26.6. ESI-MS *m/z* 307.1 ($M + H^+$); HR-ESI-MS *m/z* Calcd for $C_{16}H_{19}O_6$ 307.1182, Found 307.1187.

5,6-Anhydro-3-*O*-benzoyl-1,2-*O*-isopropylidene-5-thio-α-D-*gluco*-pentofuranose (11).

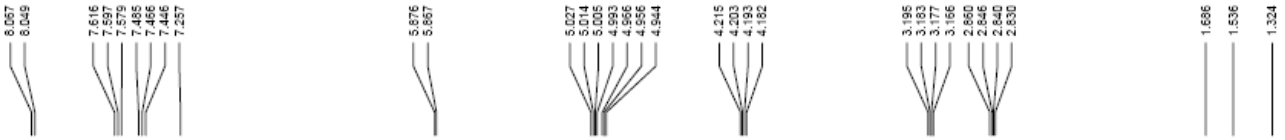
A solution of epoxide **9** (2.01 g, 6.57 mmol) and thiourea (524 mg, 6.9 mmol) in MeOH (25 mL) under Ar was refluxed overnight. After cooling, the solvent was removed under reduced pressure and the residue partitioned between EtOAc and water. The organic layer is washed with water and brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane=1/8 to 1/6) to afford **11** (1.473 g, 73%) as an oil.

$[\alpha]_D^{23}$ +127.6 (*c* 1.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 8.09 (d, 2H, *J* = 7.0 Hz), 7.60 (t, 1H, *J* = 7.4 Hz), 7.47 (t-like, 2H), 5.90 (d, 1H, *J* = 3.9 Hz), 4.99 (t, 1H, *J* = 3.7 Hz), 4.94 (dd, 1H, *J* = 8.6, 5.1 Hz), 3.96 (t-like, 1H), 3.00 (m, 1H), 2.55 (dd, 1H, *J* = 6.3, 1.2 Hz), 2.32 (dd, 1H, *J* = 5.1, 1.6 Hz), 1.52 (s, 3H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.8, 133.4, 130.0, 129.3, 128.5, 113.2, 104.1, 81.3, 77.6, 75.4, 32.6, 26.6, 22.0. ESI-MS *m/z* 345.0 ($M + Na^+$); HR-ESI-MS *m/z* Calcd for $C_{16}H_{18}NaO_5S$ 345.0773, Found 345.0770.

3-*O*-Benzoyl-5,6-di-*O,S*-acetyl-1,2-*O*-isopropylidene-5-thio-*α*-D-*gluco*-pentofuranose (12).

A mixture of **11** (1.33 g, 4.13 mmol), AcOK (1.08 g, 11.0 mmol) in Ac_2O (10.8 mL) and AcOH (2.3 mL) was refluxed for 36 h. After cooling, the volatiles were removed under reduced pressure, the residue was taken up in EtOAc, washed with aq. $NaHCO_3$ and brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane=1/6) to afford **12** (1.61 g, 92%) as an oil.

$[\alpha]_D^{23}$ +117.1 (*c* 1.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 8.08 (m, 2H), 7.60 (t-like, 1H), 7.47 (t-like, 2H), 5.86 (m, 1H), 4.98-4.92 (m, 2H), 4.48 (m, 1H), 4.35 (m, 2H), 4.07 (m, 1H), 2.22 (s, 3H), 2.01 (s, 3H), 1.52 (s, 3H), 1.31 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 193.5, 170.4, 165.4, 133.4, 129.9, 129.2, 128.5, 113.2, 104.0, 77.7, 77.3, 74.8, 63.2, 43.6, 30.4, 26.7, 26.6, 20.6. ESI-MS *m/z* 447.1 ($M + Na^+$); HR-ESI-MS *m/z* Calcd for $C_{20}H_{24}NaO_8S$ 447.1090, Found 447.1071.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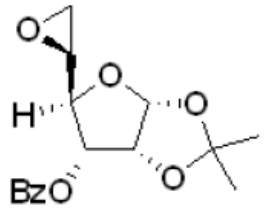
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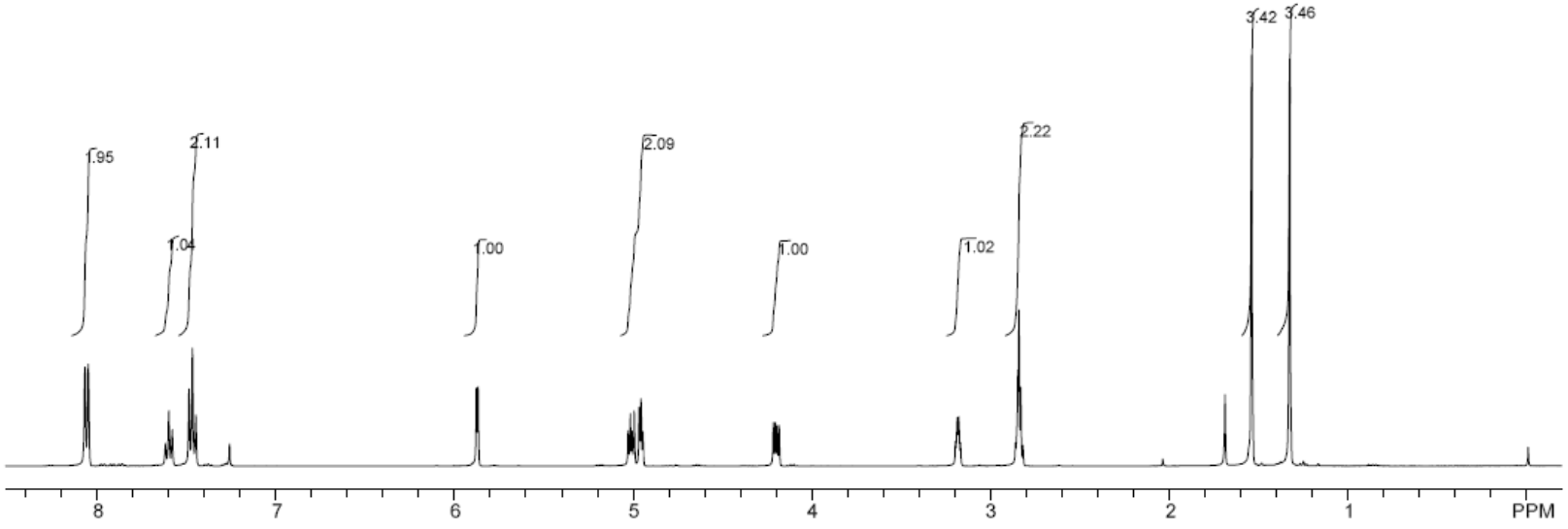
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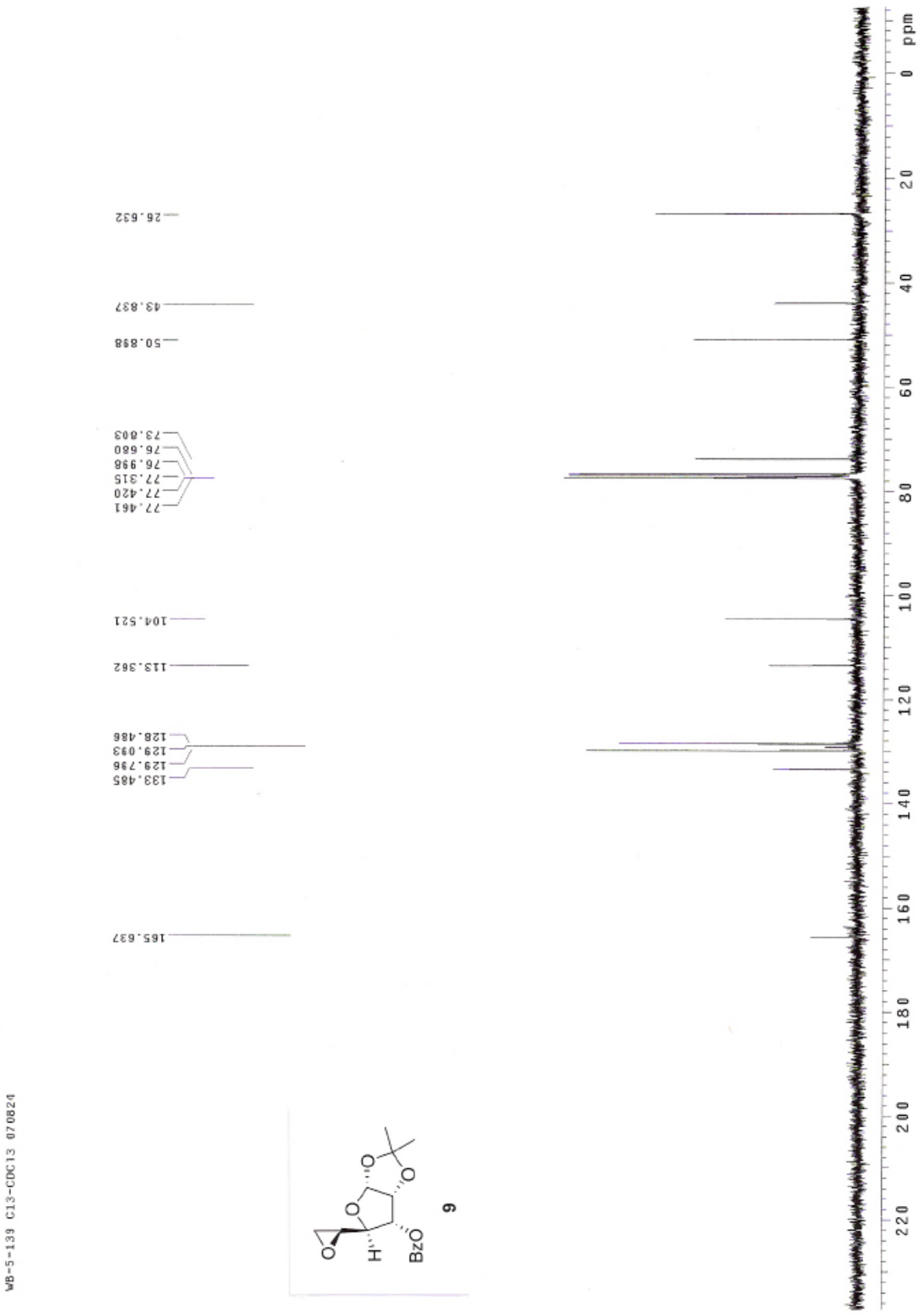
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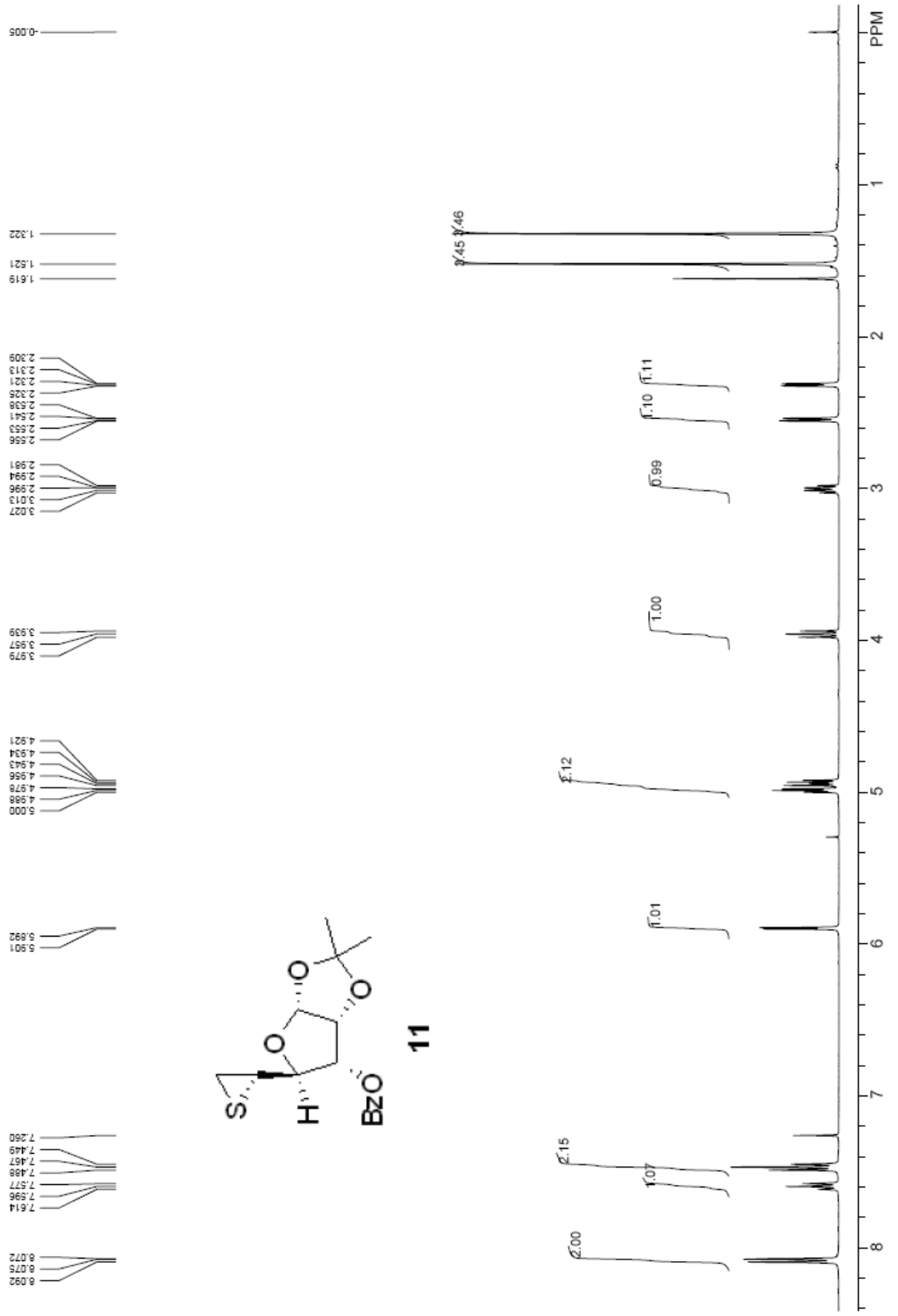
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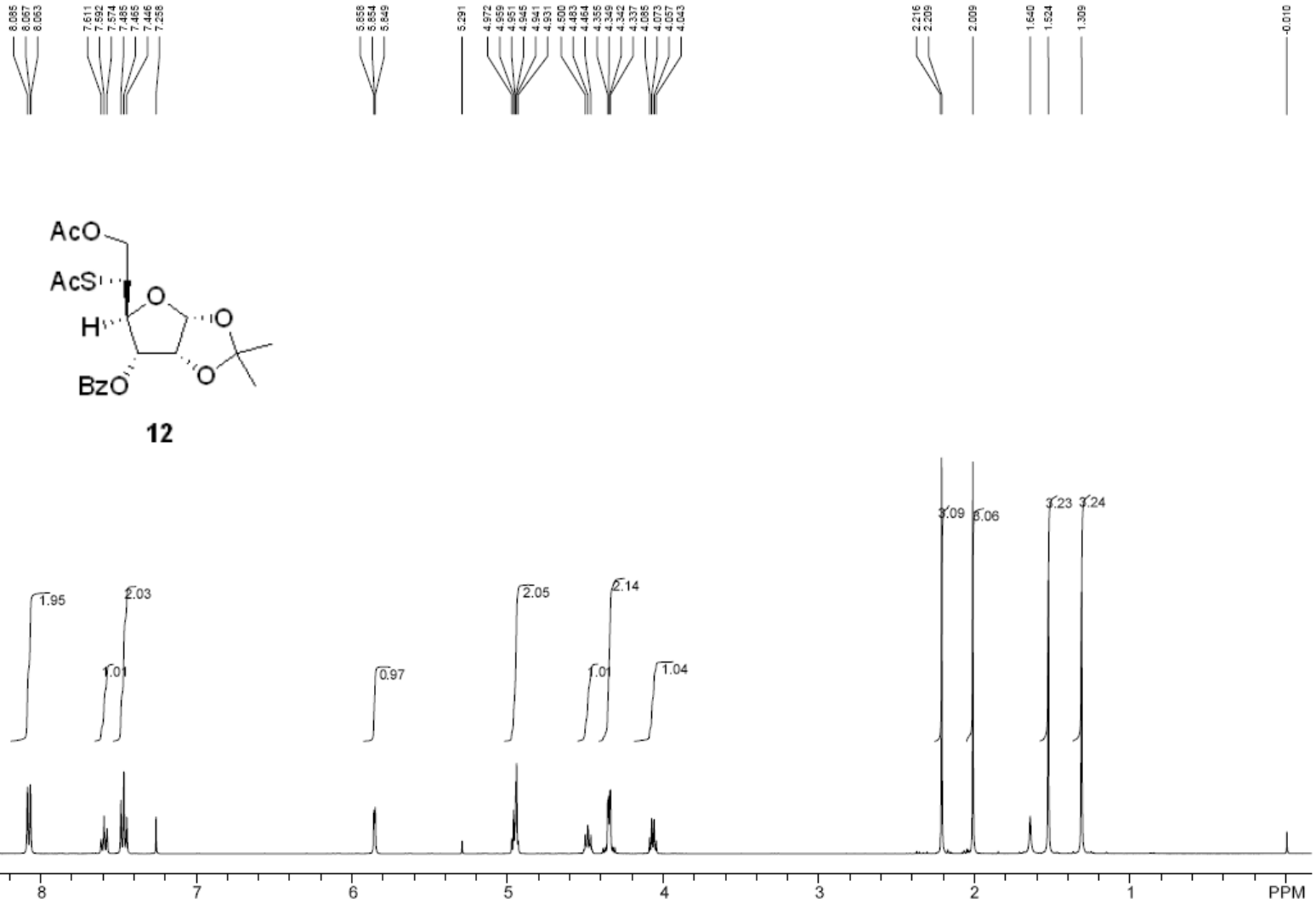
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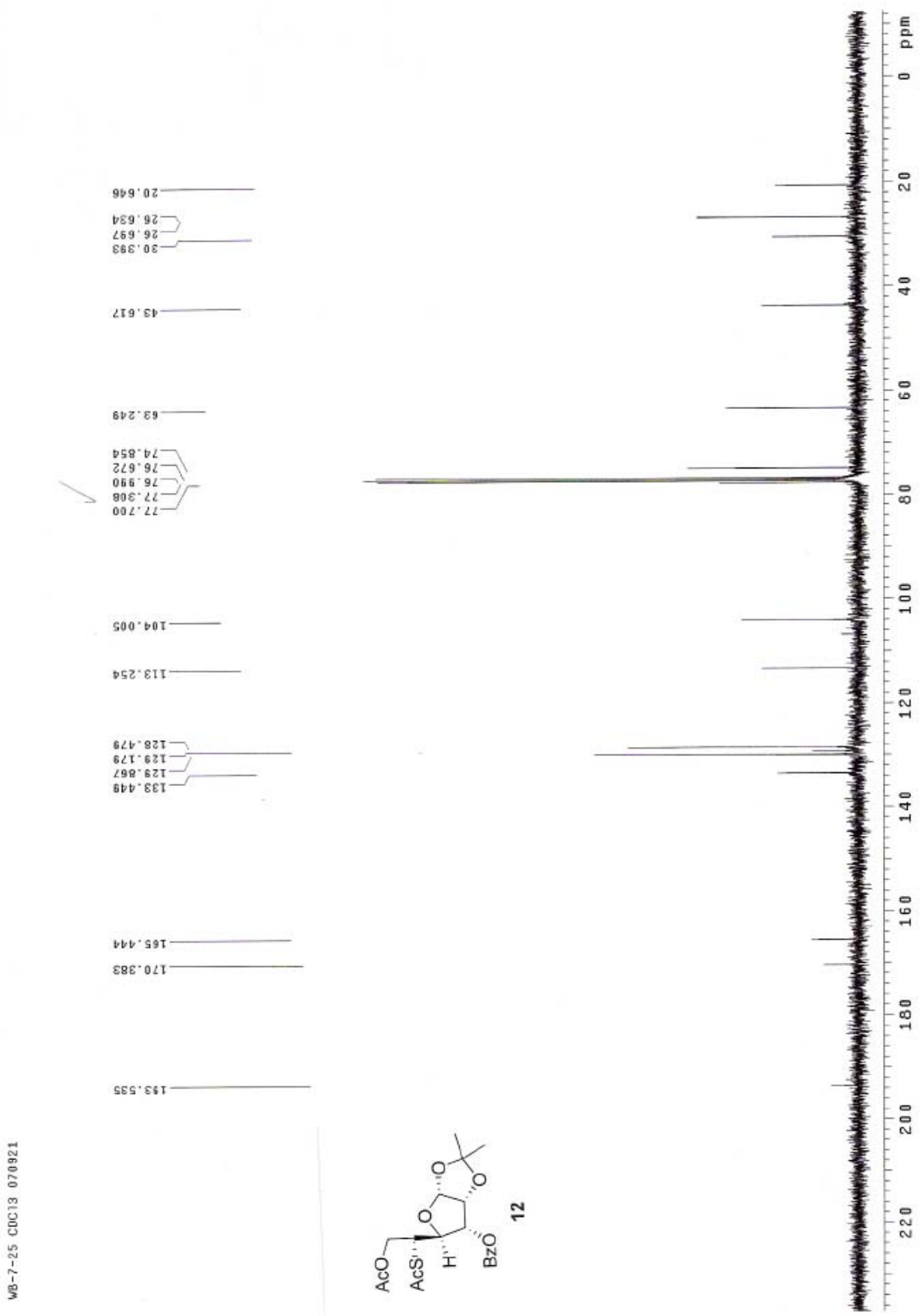
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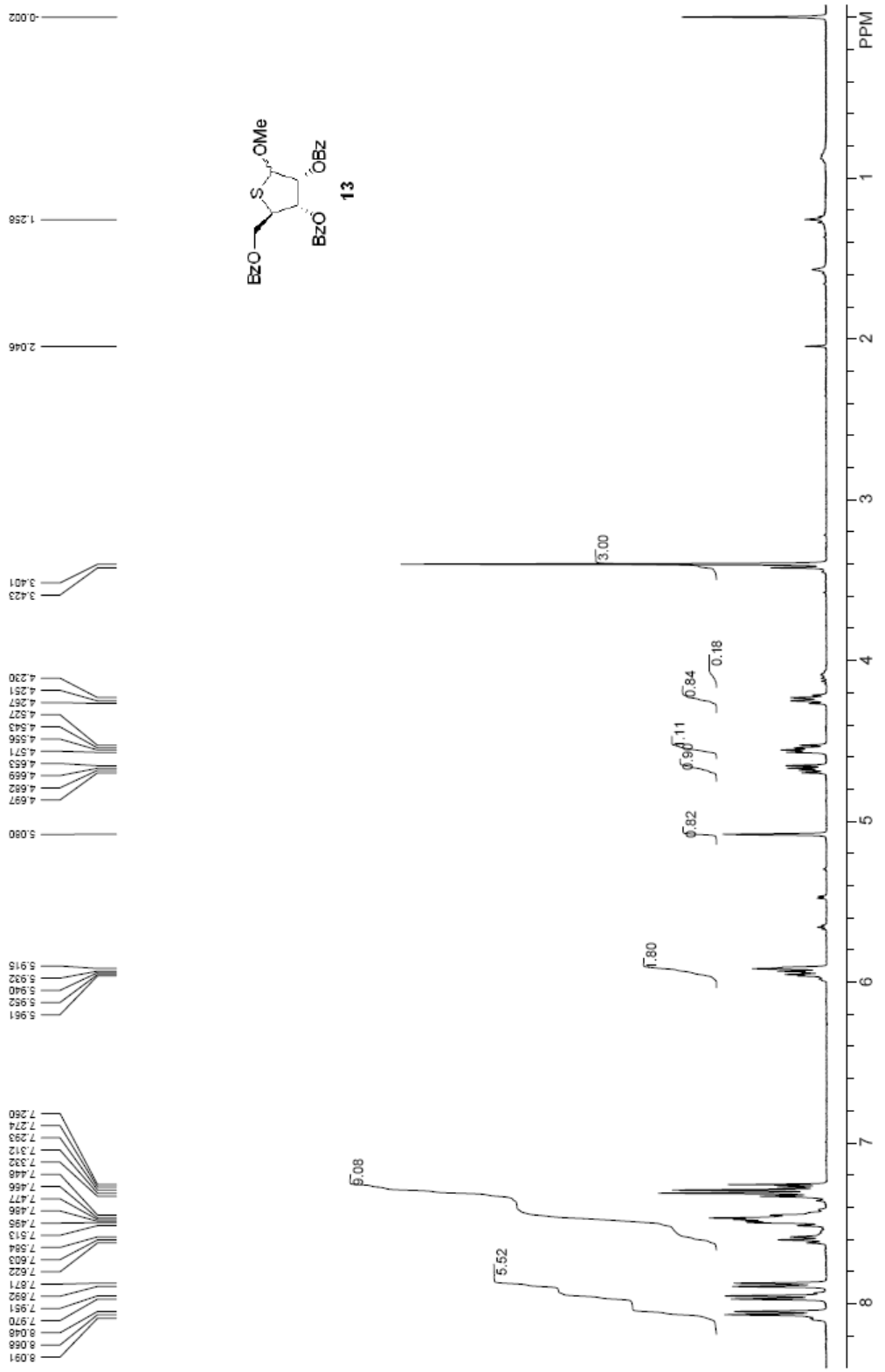
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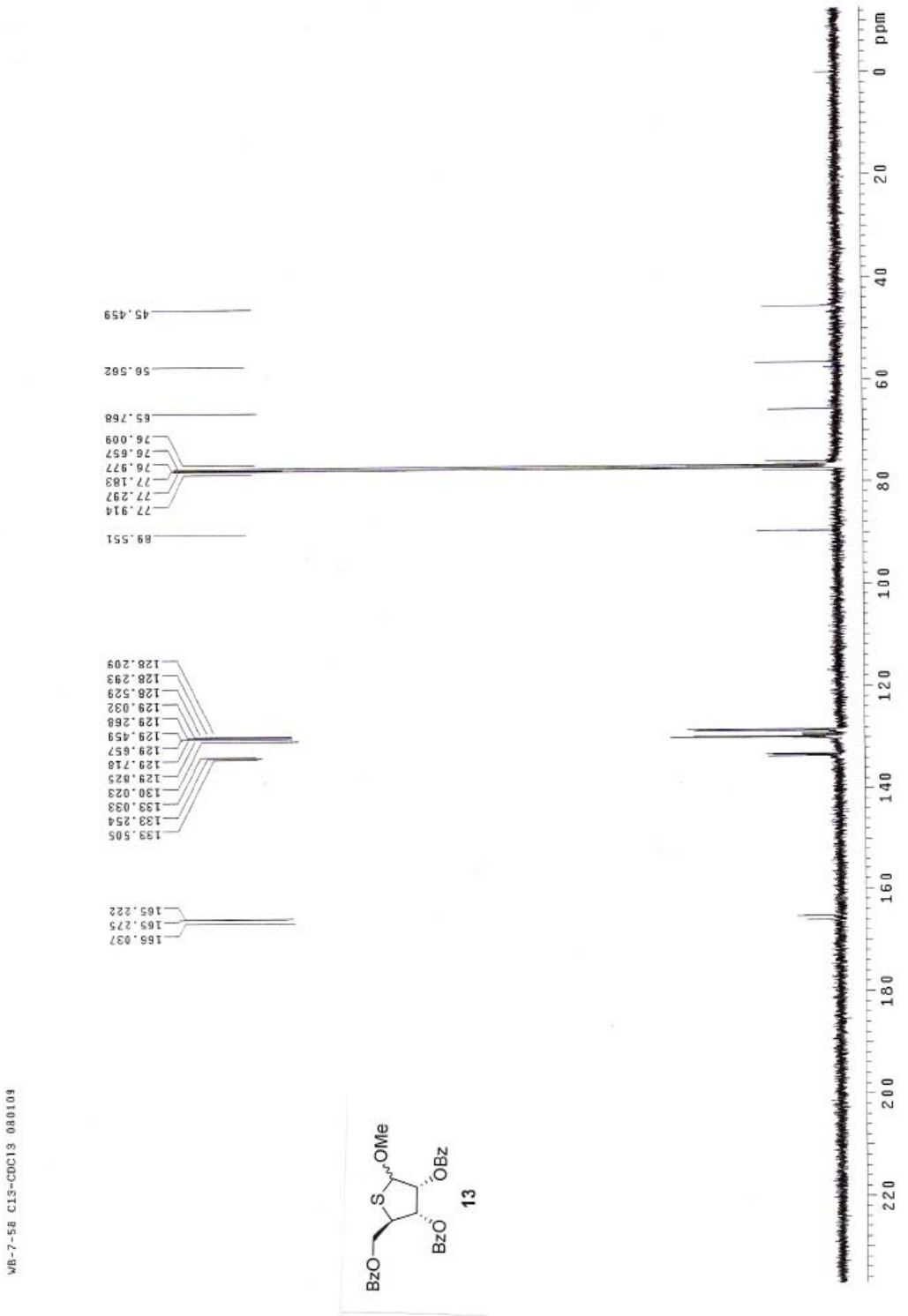
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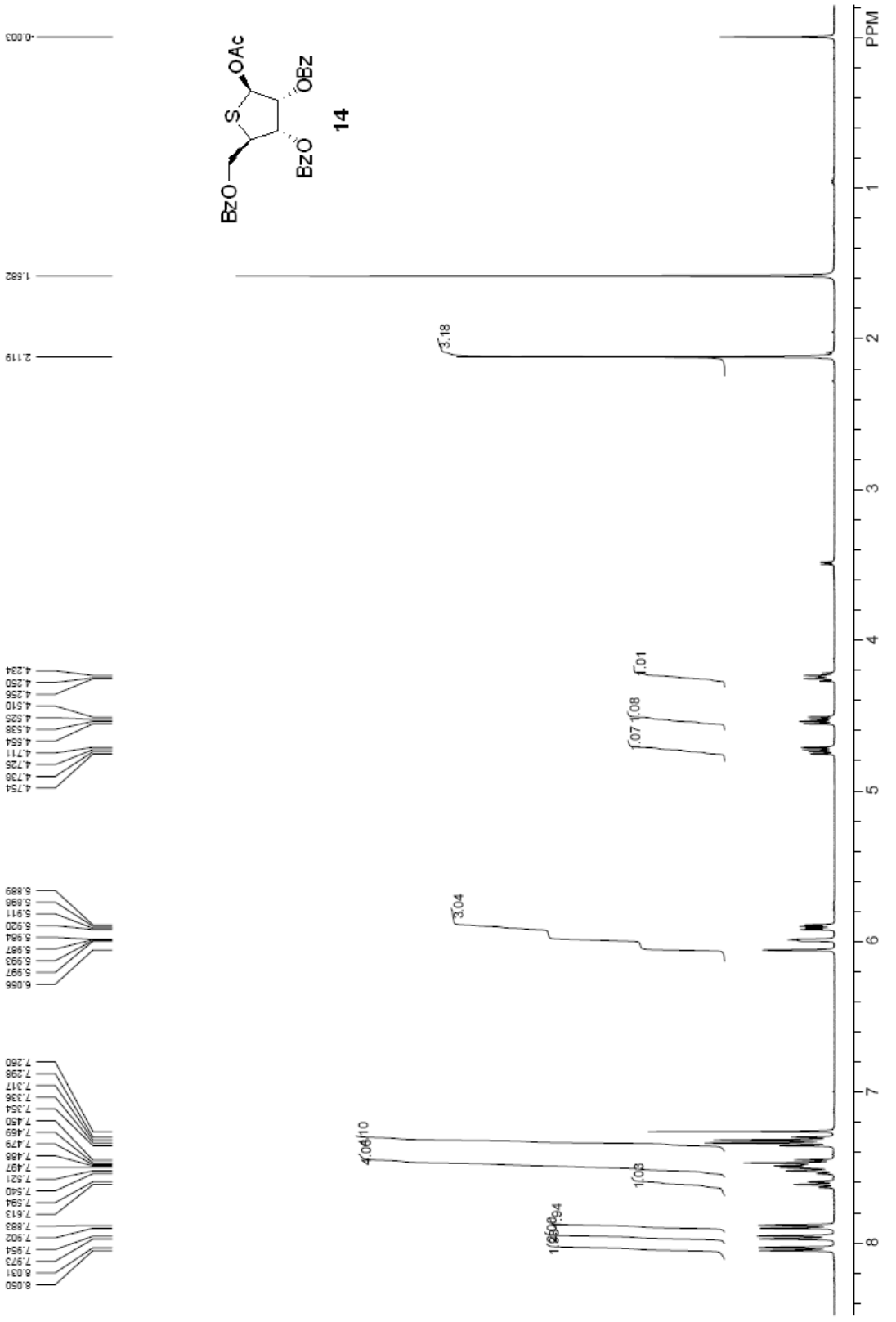
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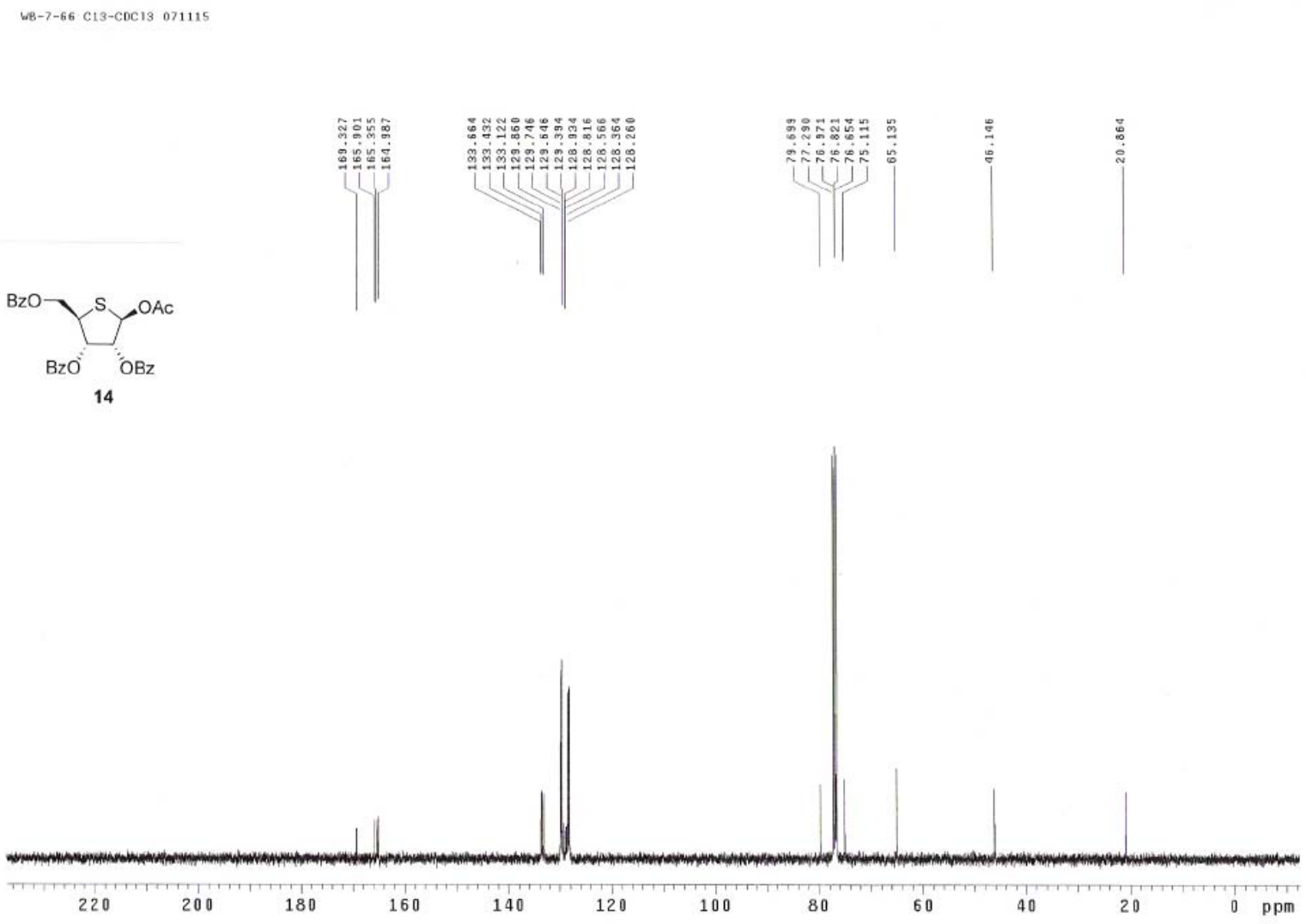
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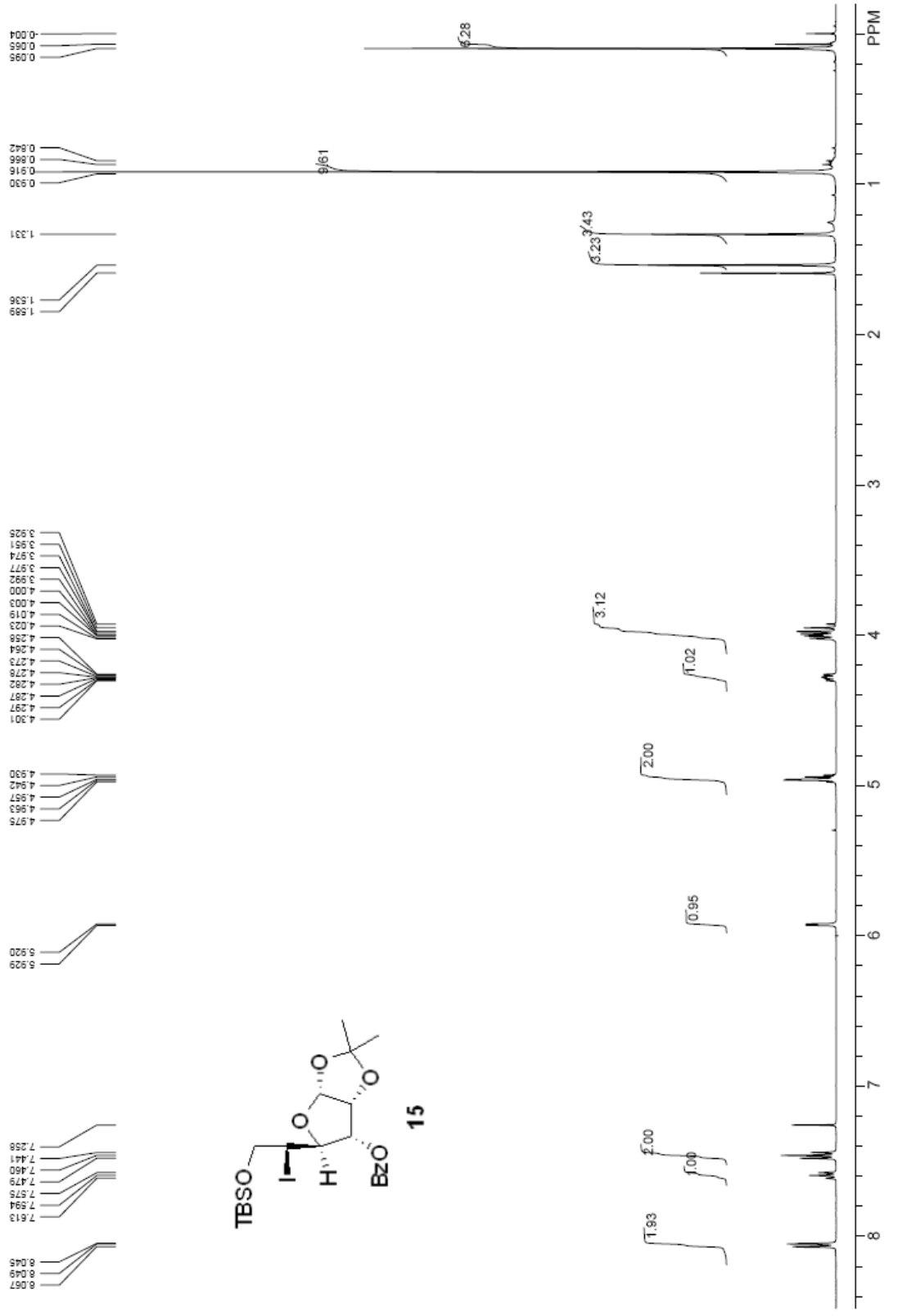
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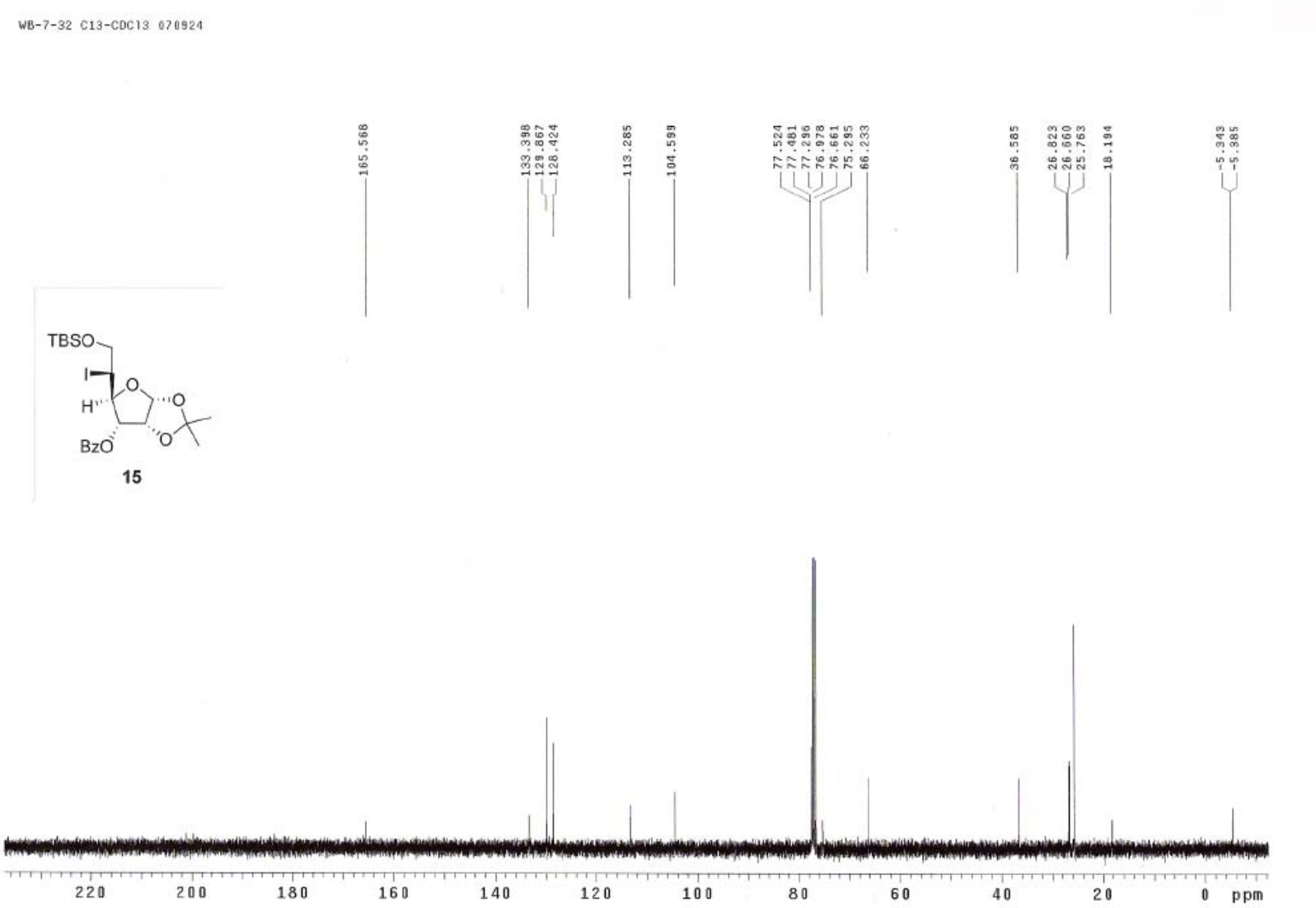
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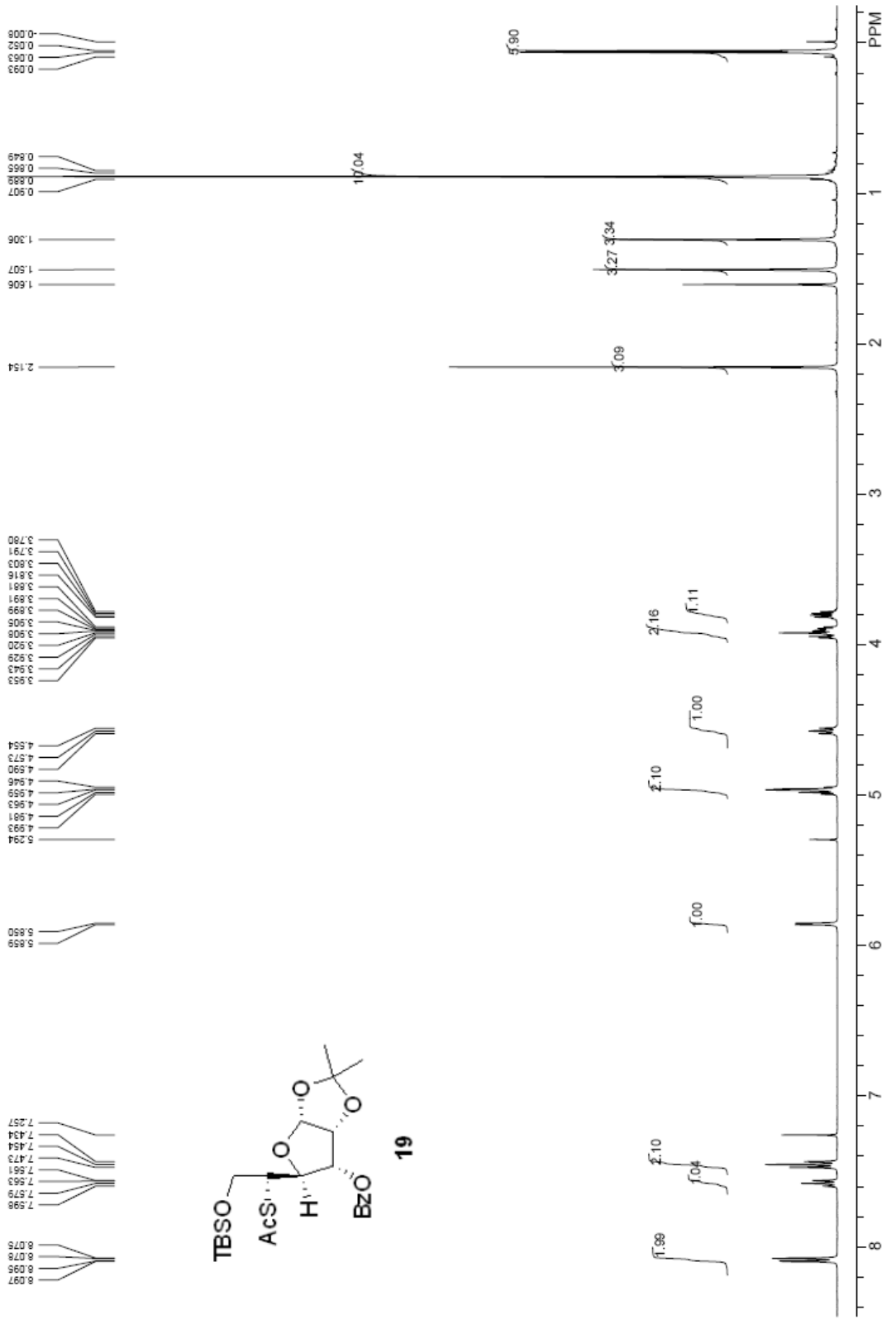
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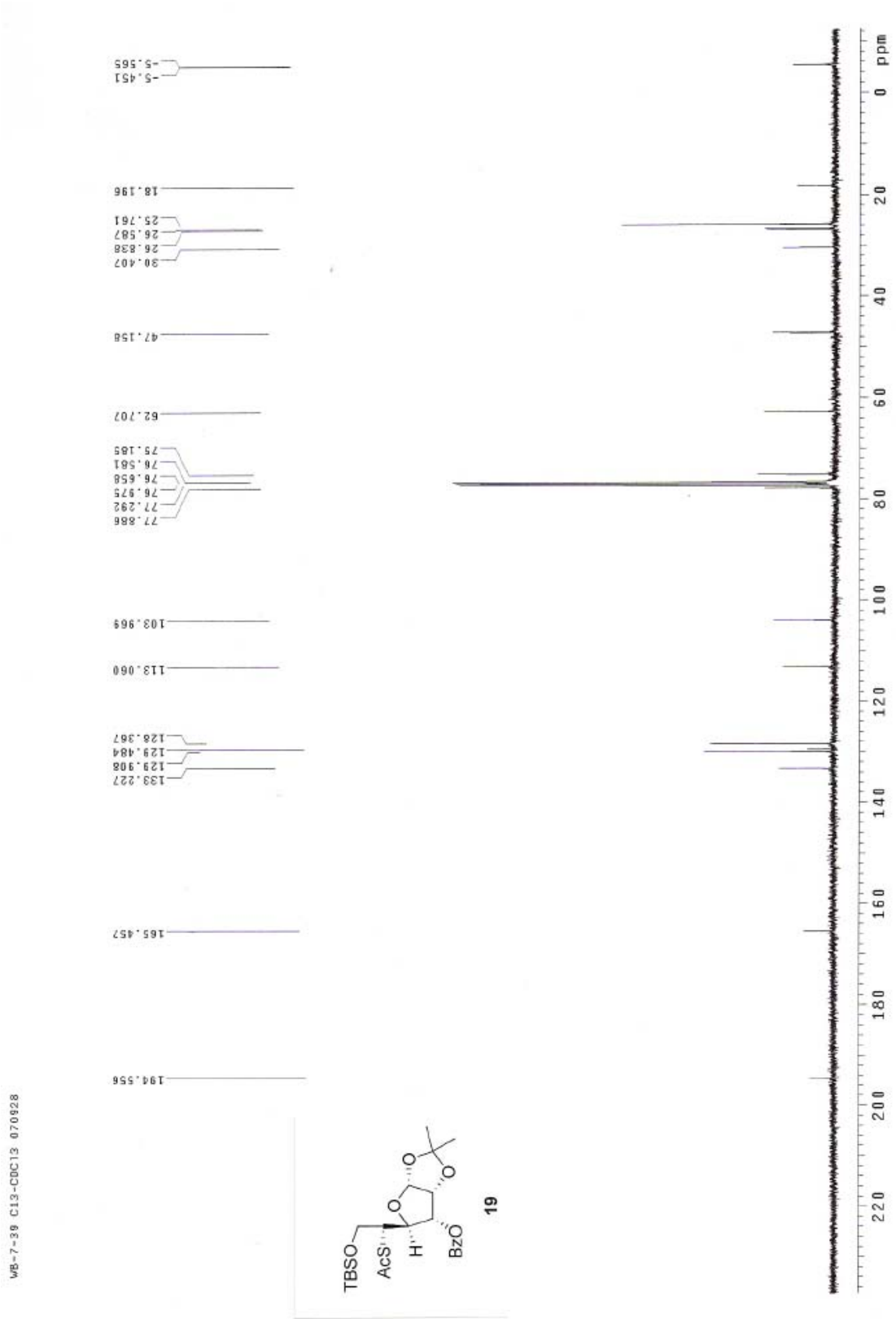
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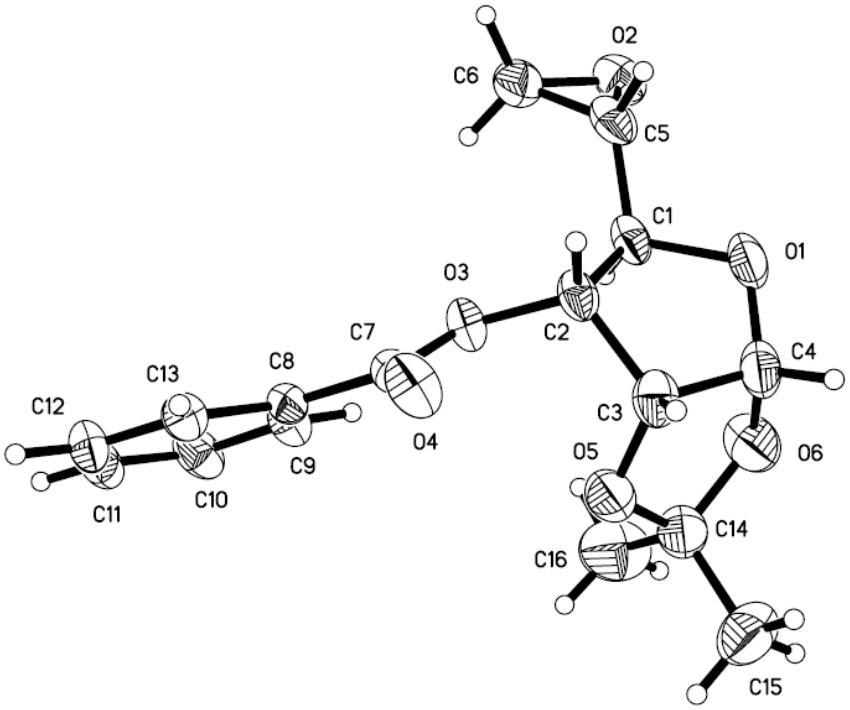

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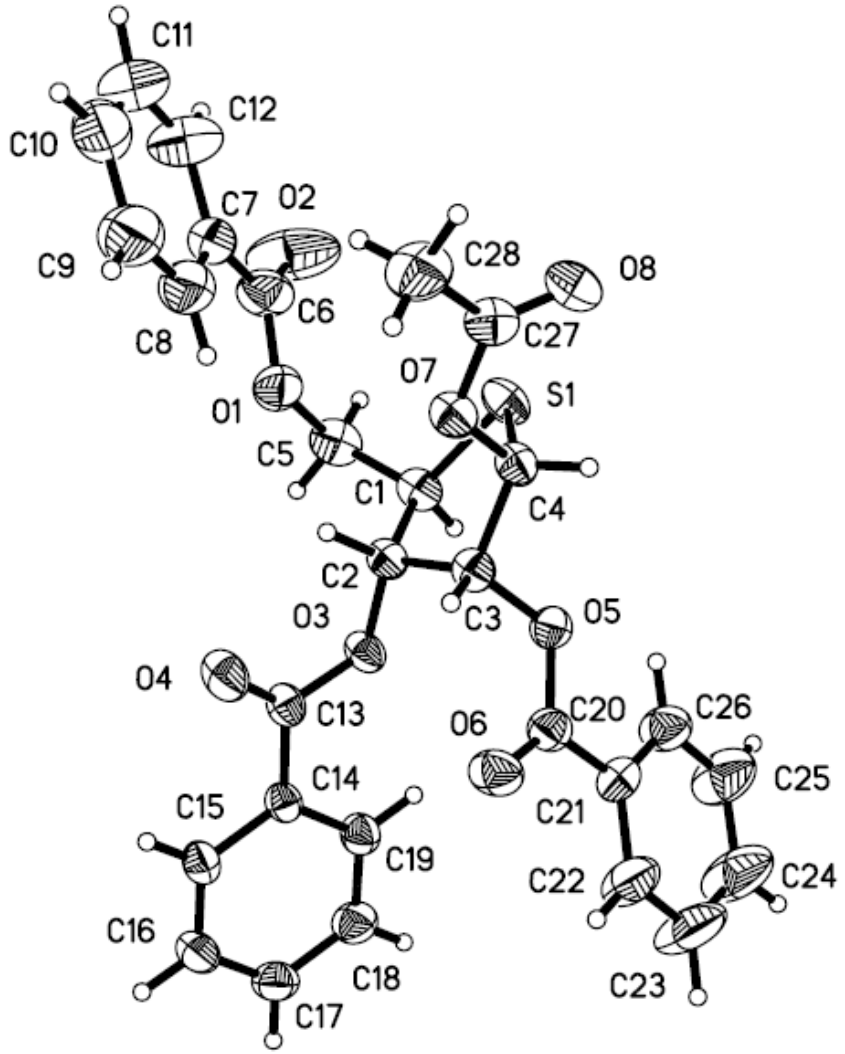

ORTEP drawing for compound **14**.