Supplementary Material for Organic & Biomolecular Chemistry

Supporting Information

Facile preparation of the Oxetane-Nucleosides

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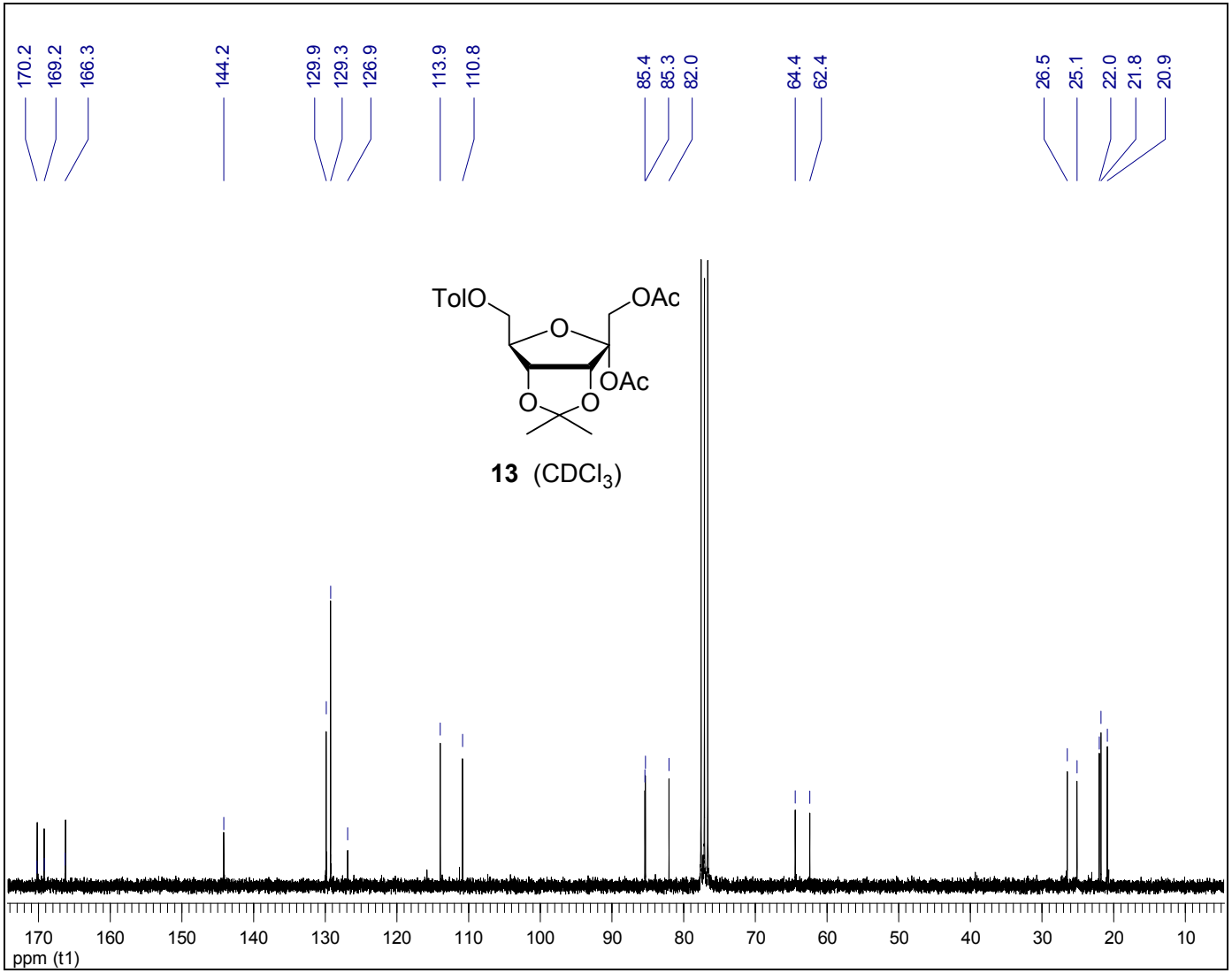
1-[1,6-Di-*O*-methanesulfonyl-*β*-D-psicofuranosyl]uracil (23). A mixture of dimesylate **22** (302 mg, 0.64 mmol) in 90% (v/v) aqueous trifluoroacetic acid (3 ml) was stirred at ambient temperature for 40 min. The mixture was evaporated to dryness *in vacuo* and 3-times co-evaporated with toluene. Remaining solid was triturated with excess of diethyl ether, filtered off and washed with diethyl ether providing after drying in vacuum oven at 60 °C diol **23** (260 mg, 94%) as colorless solid. Mp 134-135 °C (dec.). R_f = 0.35 (CH_2Cl_2/MeOH, 10:1). MALDI-TOF m/z $[M + H]^+$ 431.0 (Calcd. 431.0 for $C_{12}H_{19}N_2O_{11}S_2$).^{1}H NMR (600 MHz, DMSO-d_6): 11.40 (br s, 1H, N*H*), 7.78 (d, 1H, $J_{5\text{-}6}$ = 8.3 Hz, H-6), 5.99 (d, 1H, *J* = 5.2 Hz, O*H*), 5.61 (d, 1H, H-5), 5.45 (d, 1H, *J* = 6.6 Hz, O*H*), 5.01 (d, 1H, J_{gem} = 11.1 Hz, H-1'), 4.74 (t, 1H, *J* = 4.8 Hz, H-3'), 4.57 (br d, 1H, J_{gem} = 11.2 Hz, H-6'), 4.47 (d, 1H, H-1''), 4.37 (dd, 1H, $J_{5'\text{-}6''}$ = 5.0 Hz, H-6''), 4.35-4.30 (m, 1H, H-4'), 3.99-3.94 (m, 1H, H-5'), 3.30, 3.19 (2 × s, 2 × 3H, 2 × C*H*$_3$, Ms). ^{13}C NMR (150.9 MHz, d_6-DMSO): 164.4 (C-4), 151.3 (C-2), 141.3 (C-6), 101.7 (C-5), 97.3 (C-2'), 81.3 (C-4'), 75.3 (C-3'), 70.5 (C-1'), 69.8 (C-5'), 69.0 (C-6'), 37.9, 37.8 (2 × *C*H$_3$, Ms).

1-[1',3'-*O*-Anhydro-6'-*O*-methanesulfonyl-*β*-D-psicofuranosyl]uracil (24). Sodium bis(trimethylsilyl)amide (1.2 ml, 1.2 mmol, 1M THF sol.) was dropwise added to a stirred mixture of mesylate **23** (252 mg, 0.59 mmol) in THF (6 ml) at -15 °C. The mixture was stirred for 2 h at 0 °C. Then AcOH (0.1 ml) was added and the mixture was evaporated with silica and chromatographed on column of silica (CH_2Cl_2 with gradient of MeOH: 0-3%) affording oxetane **24** (177 mg, 90%) as amorphous foamy solid. R_f = 0.35 (CH_2Cl_2/MeOH, 10:1). MALDI-TOF m/z $[M + H]^+$ 335.05 (Calcd. 335.05 for $C_{11}H_{15}N_2O_8S$). ^{1}H NMR (600 MHz, DMSO-d_6): 7.48

(d, 1H, $J_{5\text{-}6}$ = 7.9 Hz, H-6), 5.65 (d, 1H, H-5), 5.32 (d, 1H, $J_{3'\text{-}4'}$ = 3.9 Hz, H-3'), 5.05 (d, 1H, J_{gem} = 8.2 Hz, H-1'), 4.63 (d, 1H, H-1''), 4.60 (br d, 1H, J_{gem} = 9.9 Hz, H-6'), 4.37-4.31 (m, 2H, H-6'' & H-5'), 4.18 (dd, 1H, $J_{4'\text{-}5'}$ = 8.0 Hz, H-4'), 3.22 (s, 3H, CH_3, Ms). ^{13}C NMR (150.9 MHz, d_6-DMSO): 165.3 (C-4), 150.9 (C-2), 142.2 (C-6), 103.2 (C-5), 92.4 (C-2), 87.3 (C-3'), 80.9 (C-5'), 78.7 (C-1'), 70.8 (C-4'), 70.4 (C-6'), 37.8 (CH$_3$, Ms).

Figure S 1



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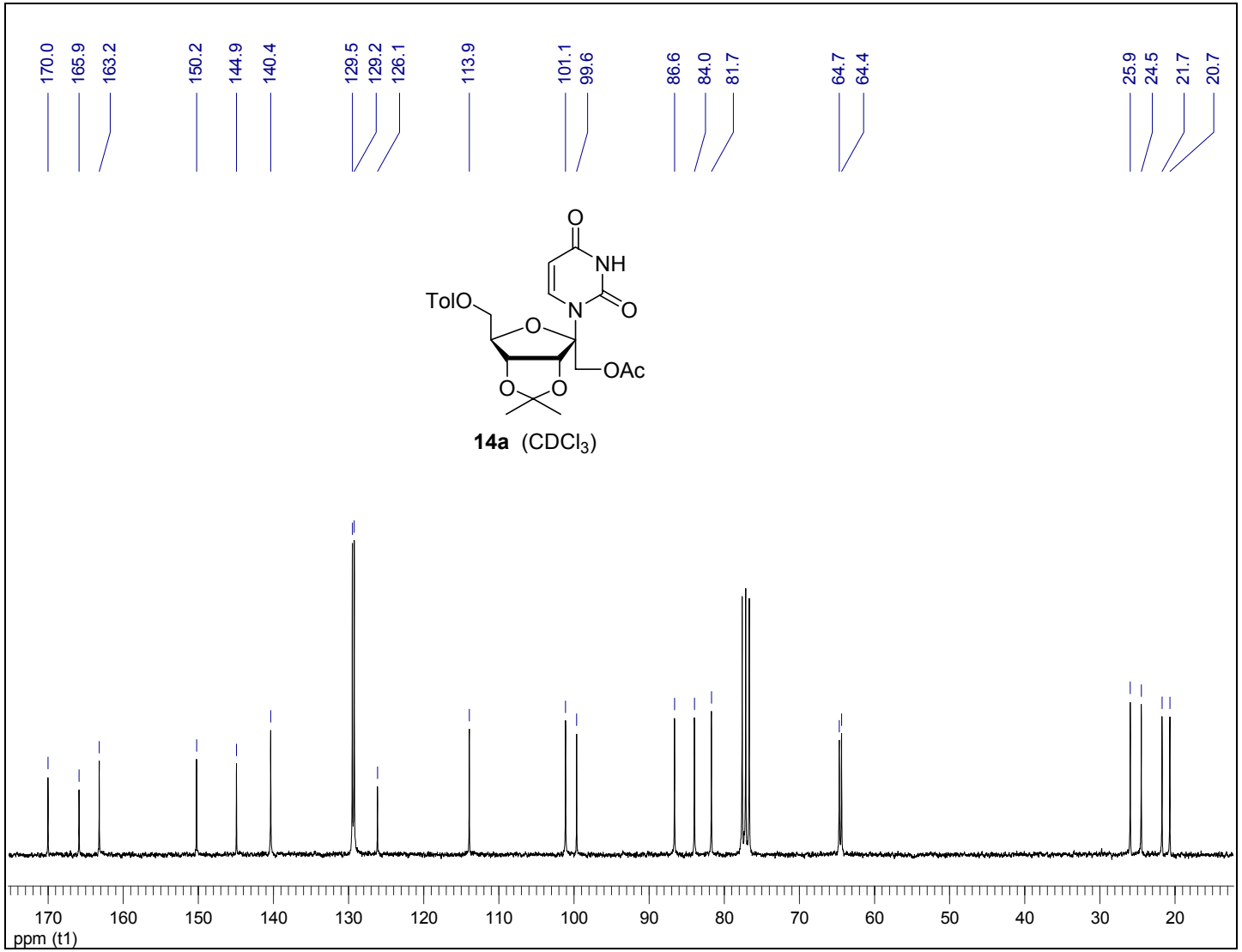

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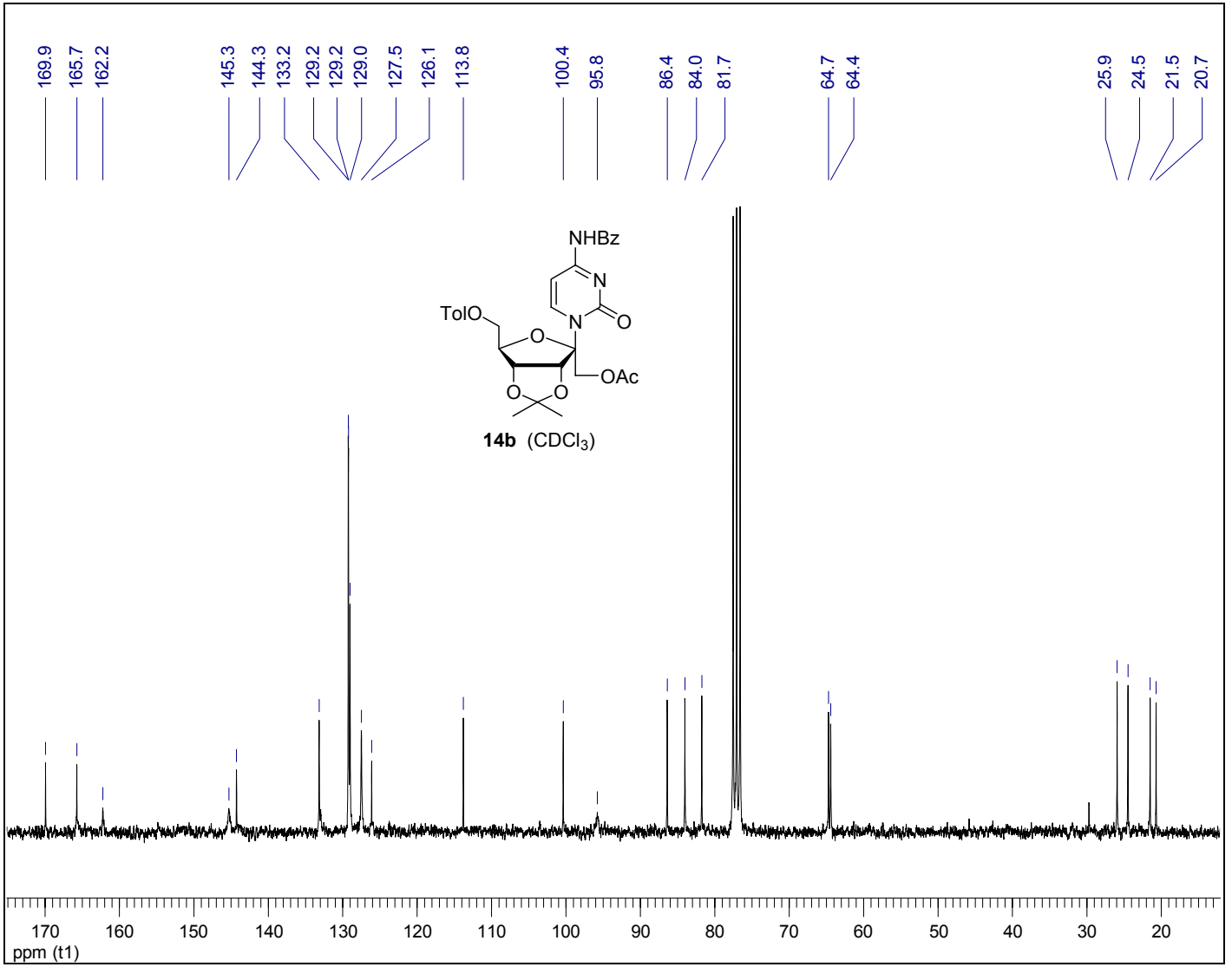

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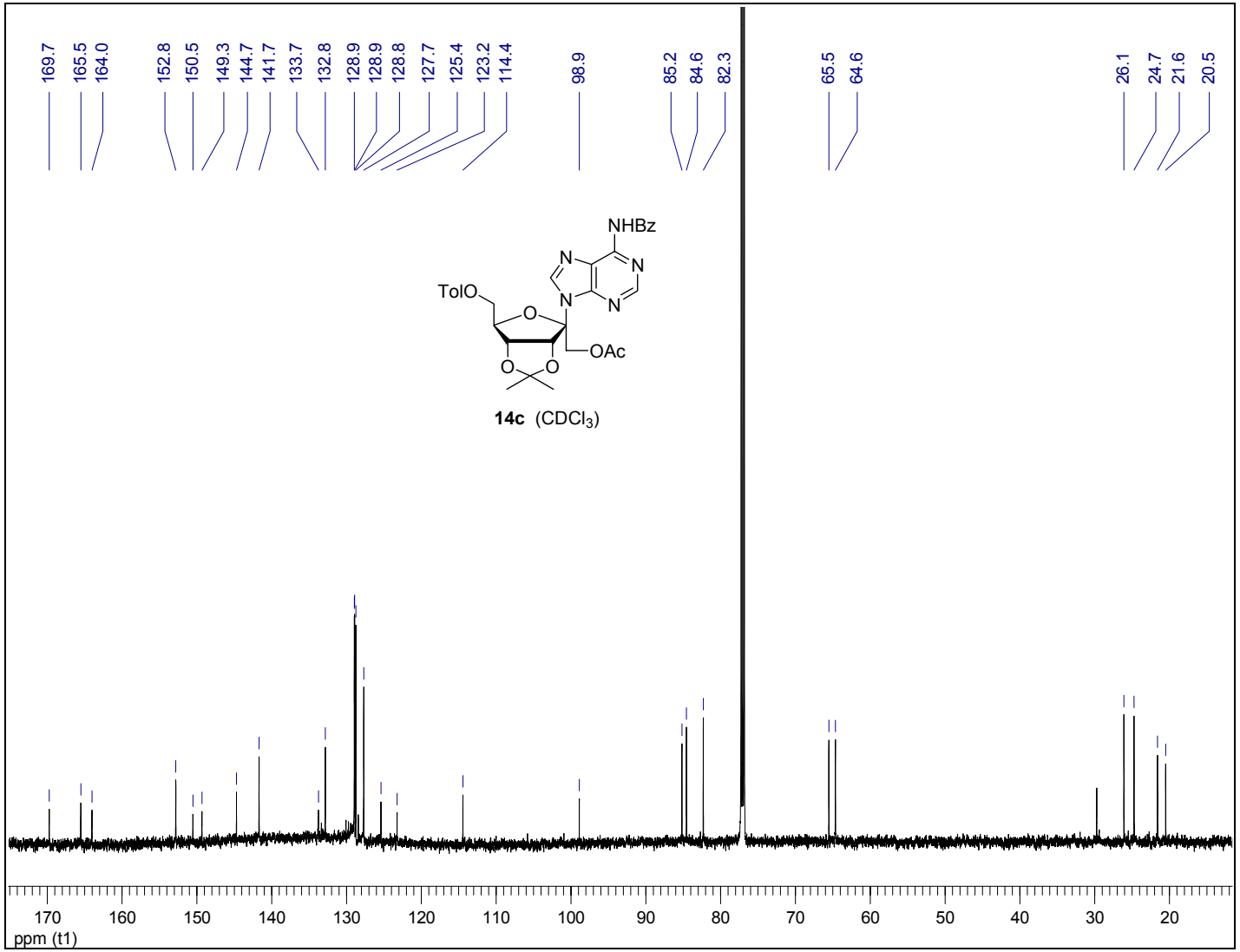

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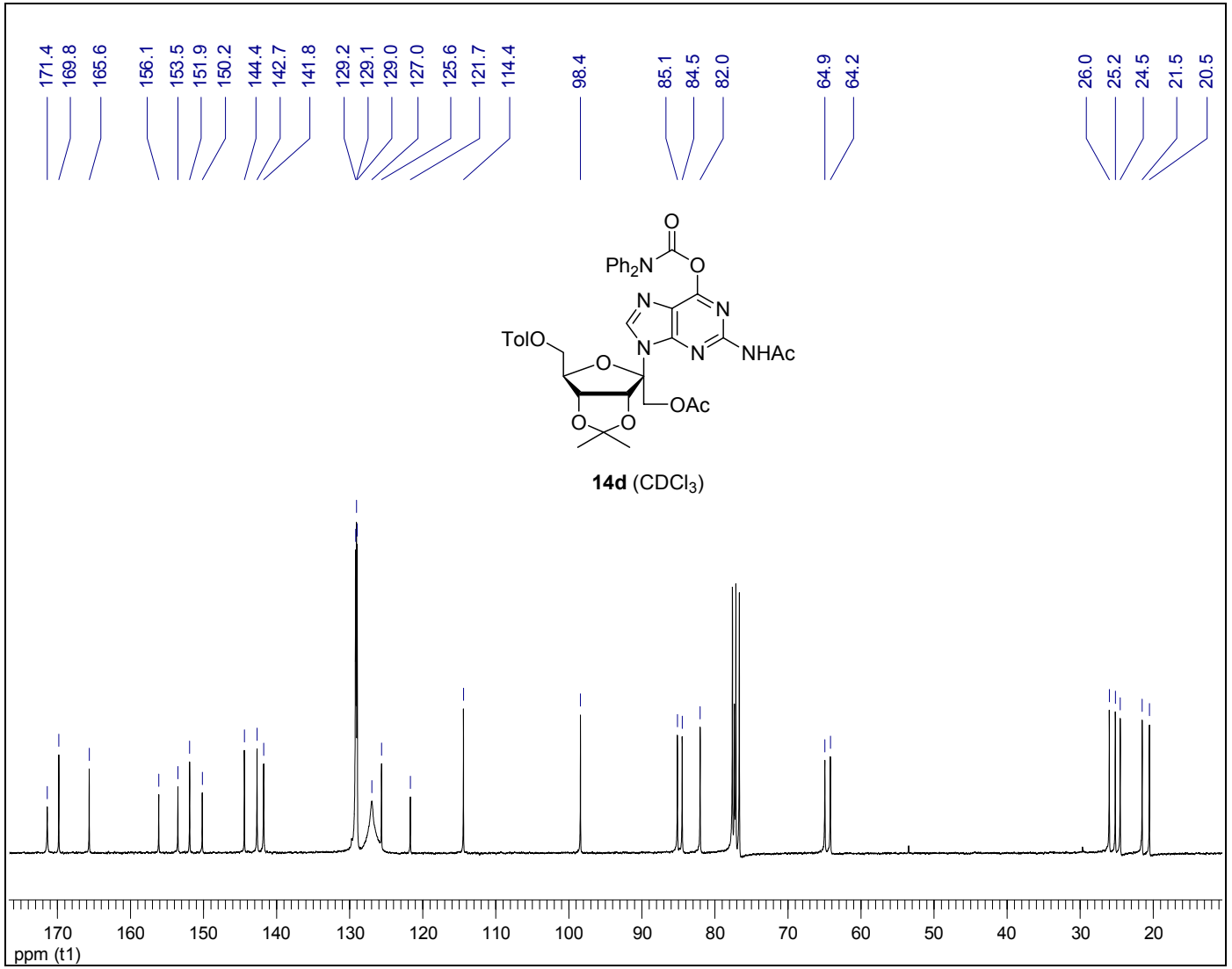

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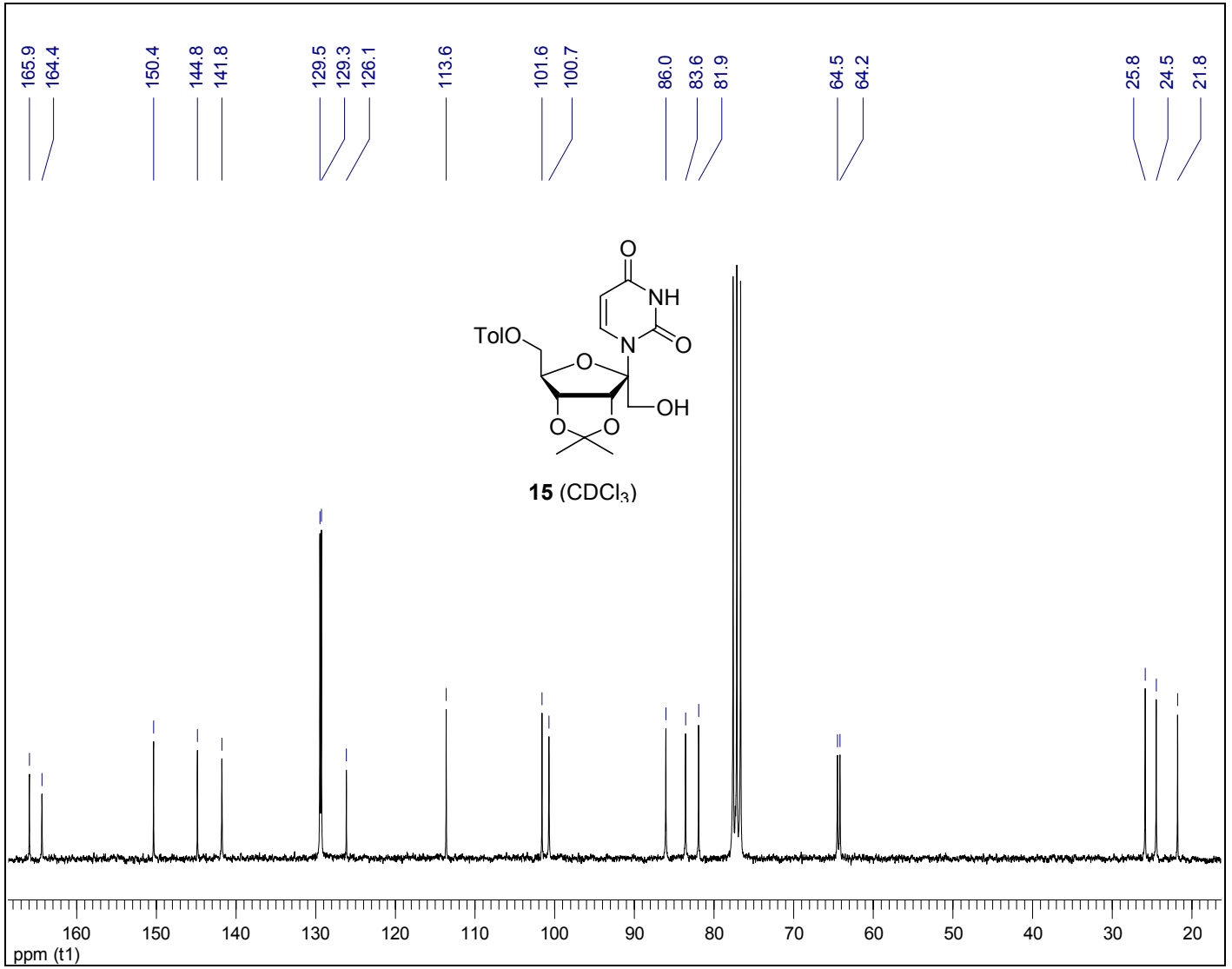

15 ($CDCl_3$)

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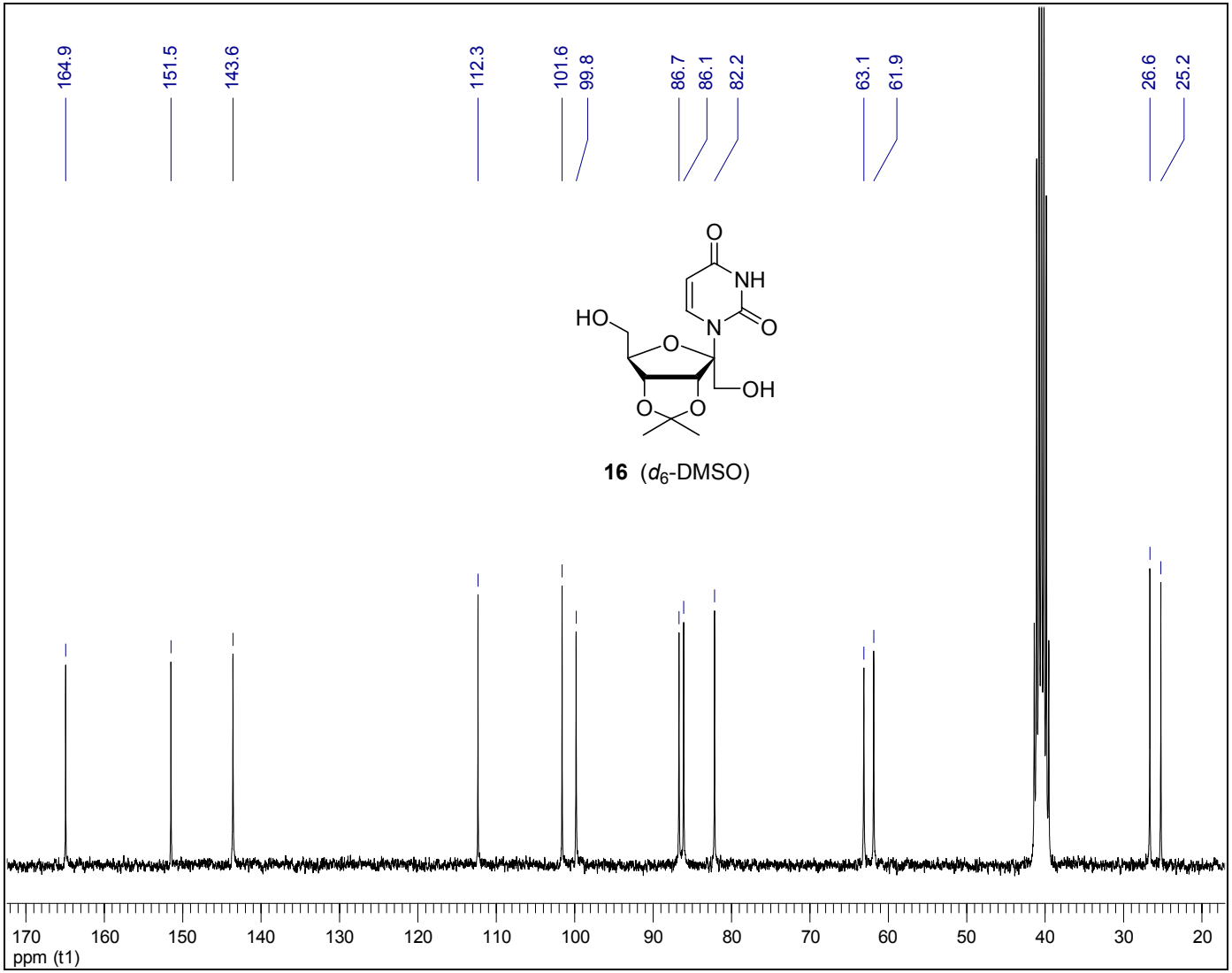

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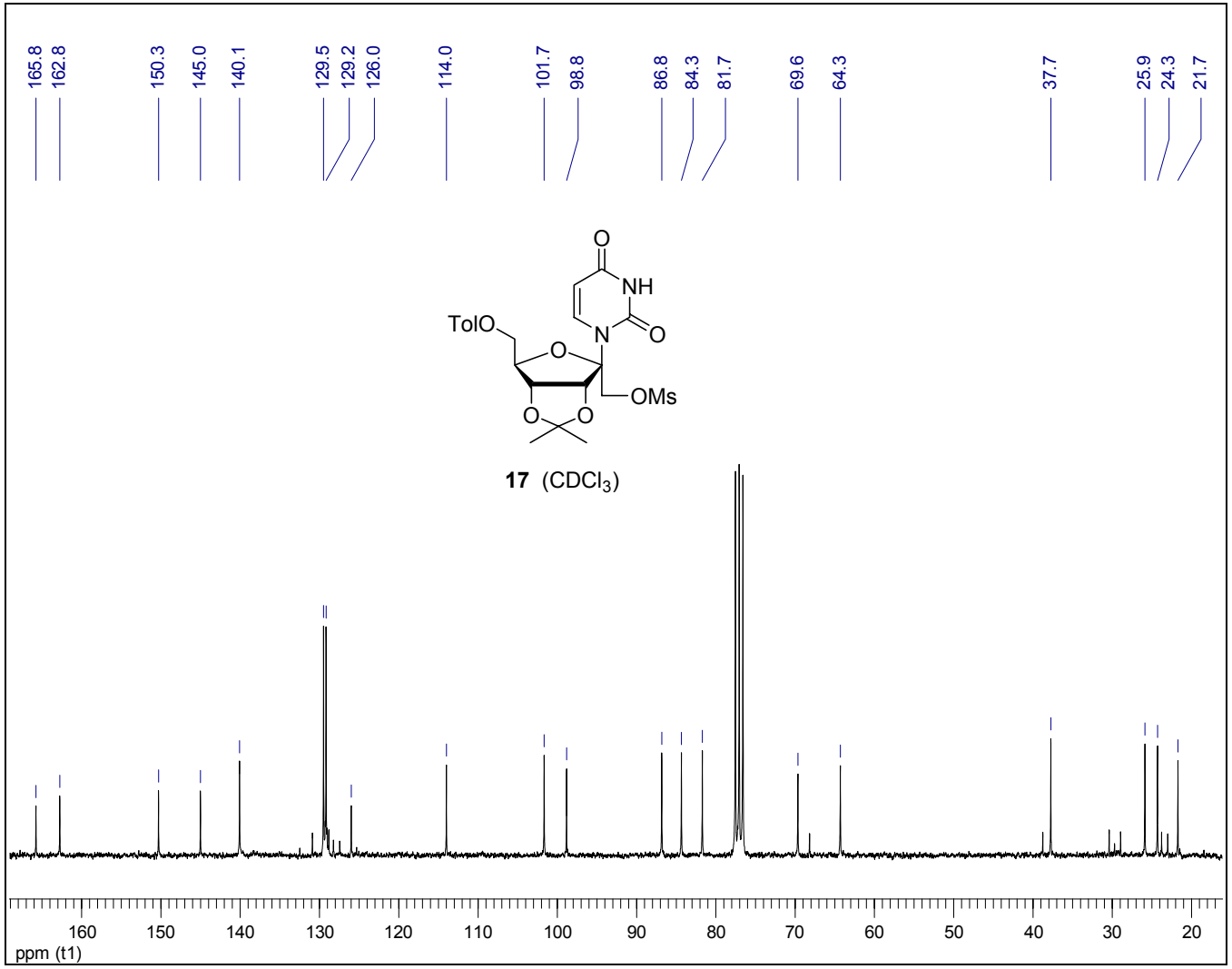

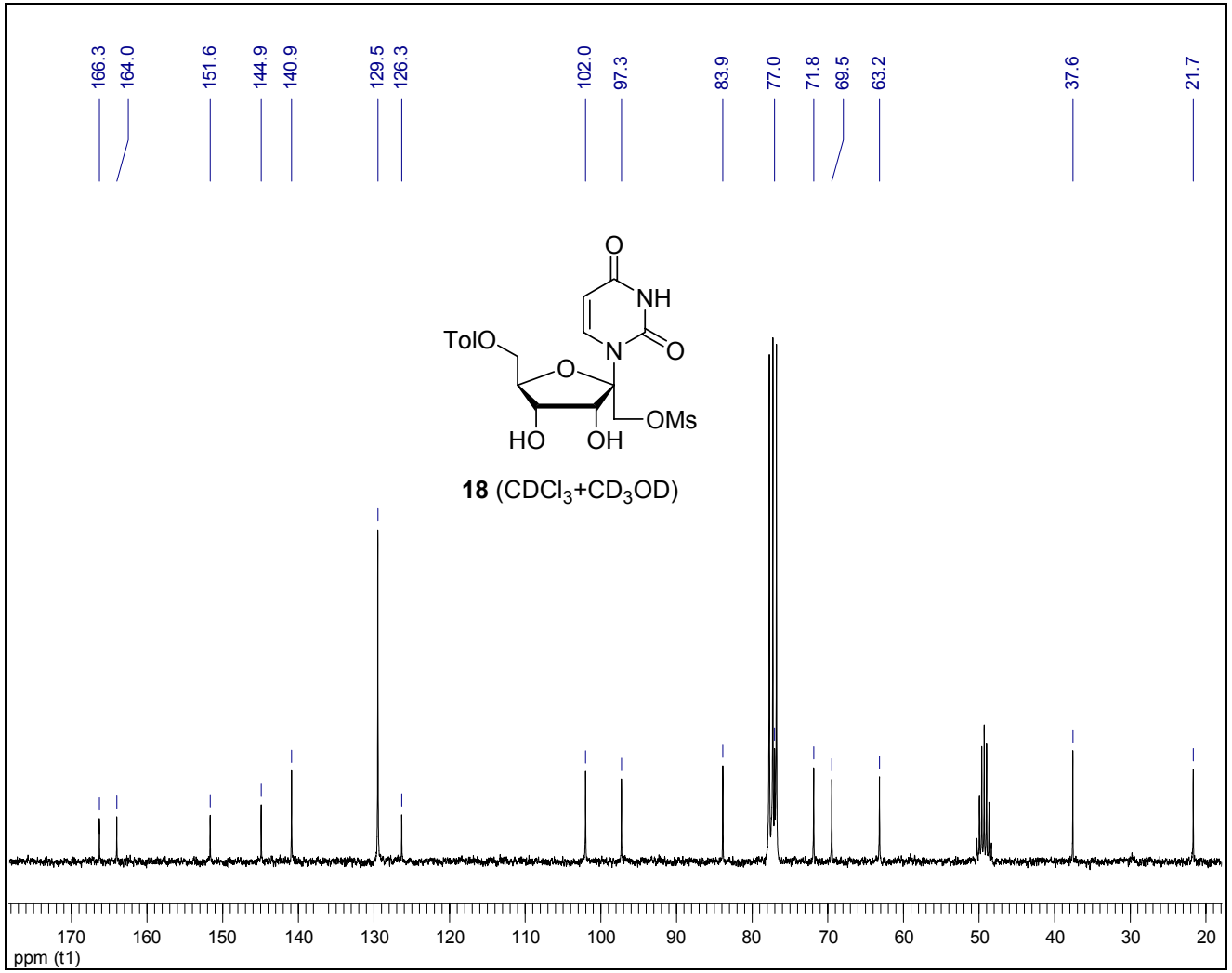

Figure S9

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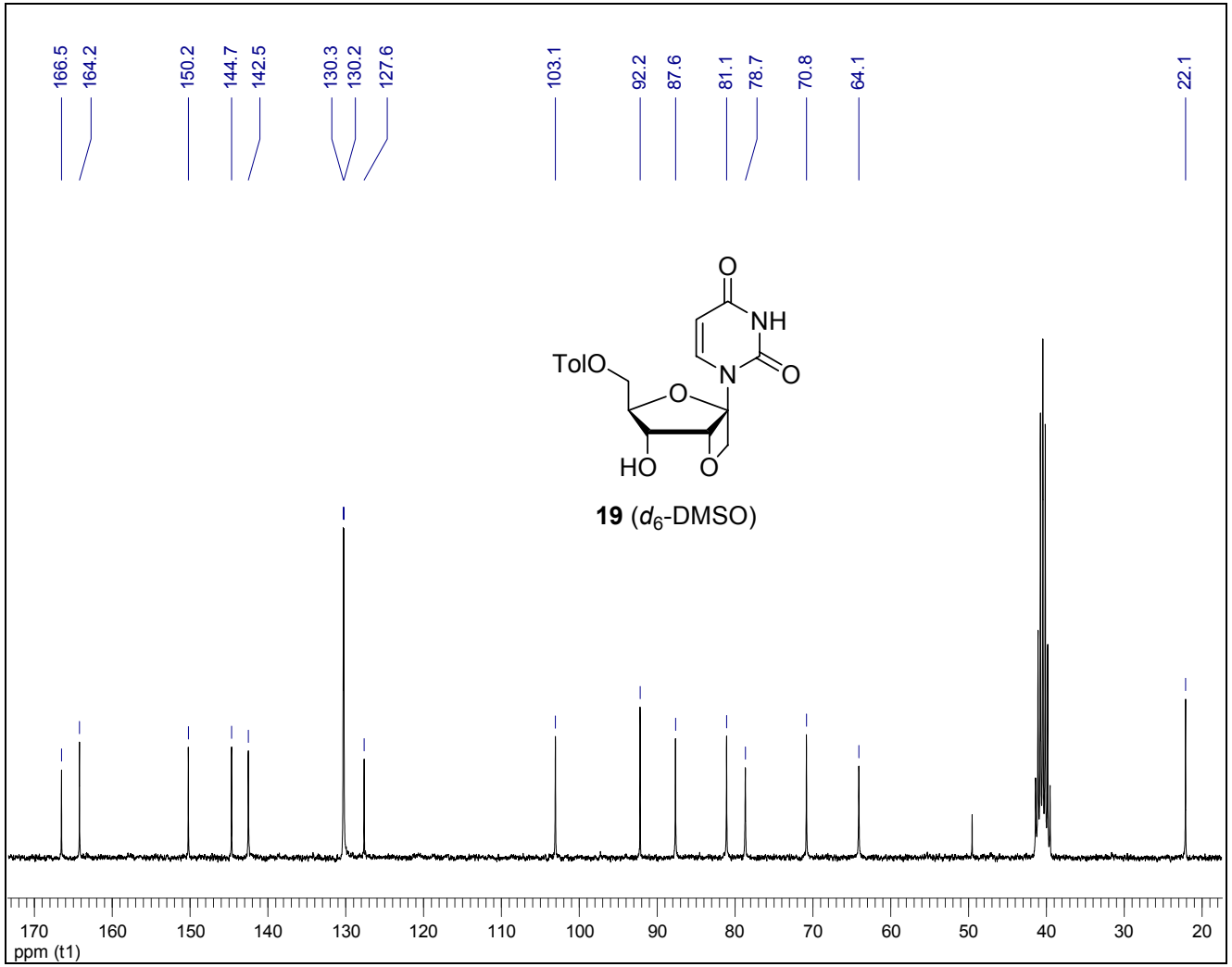

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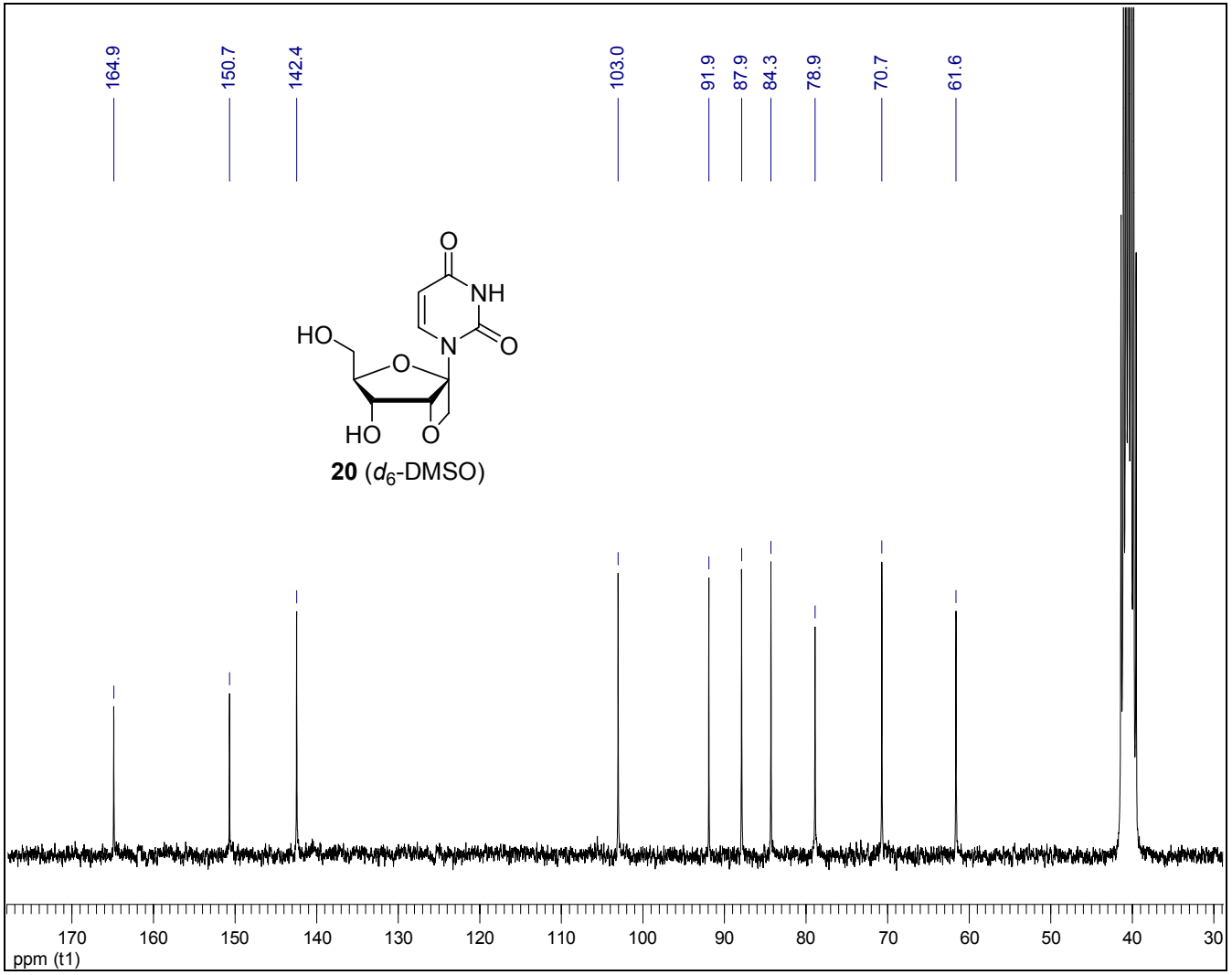

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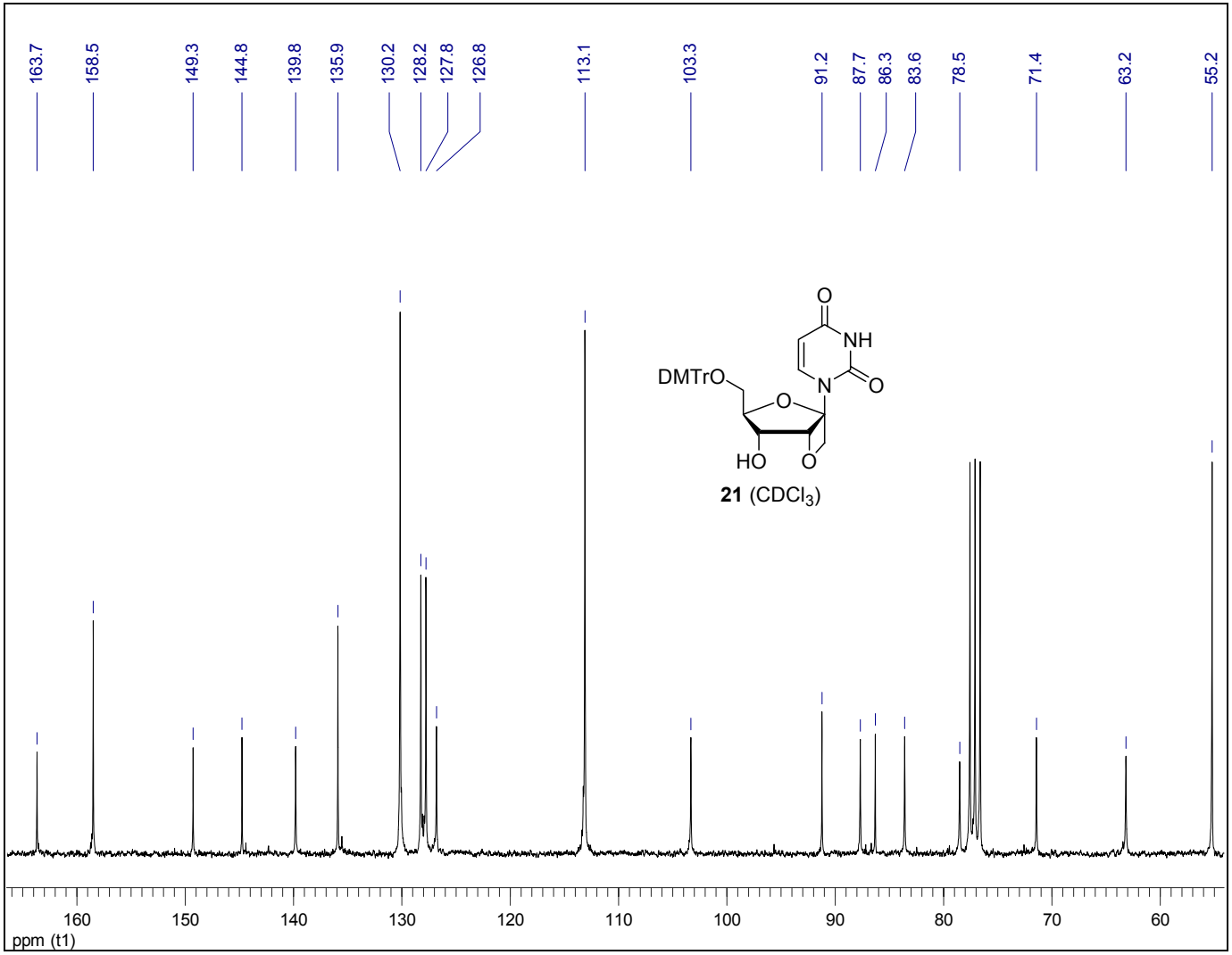

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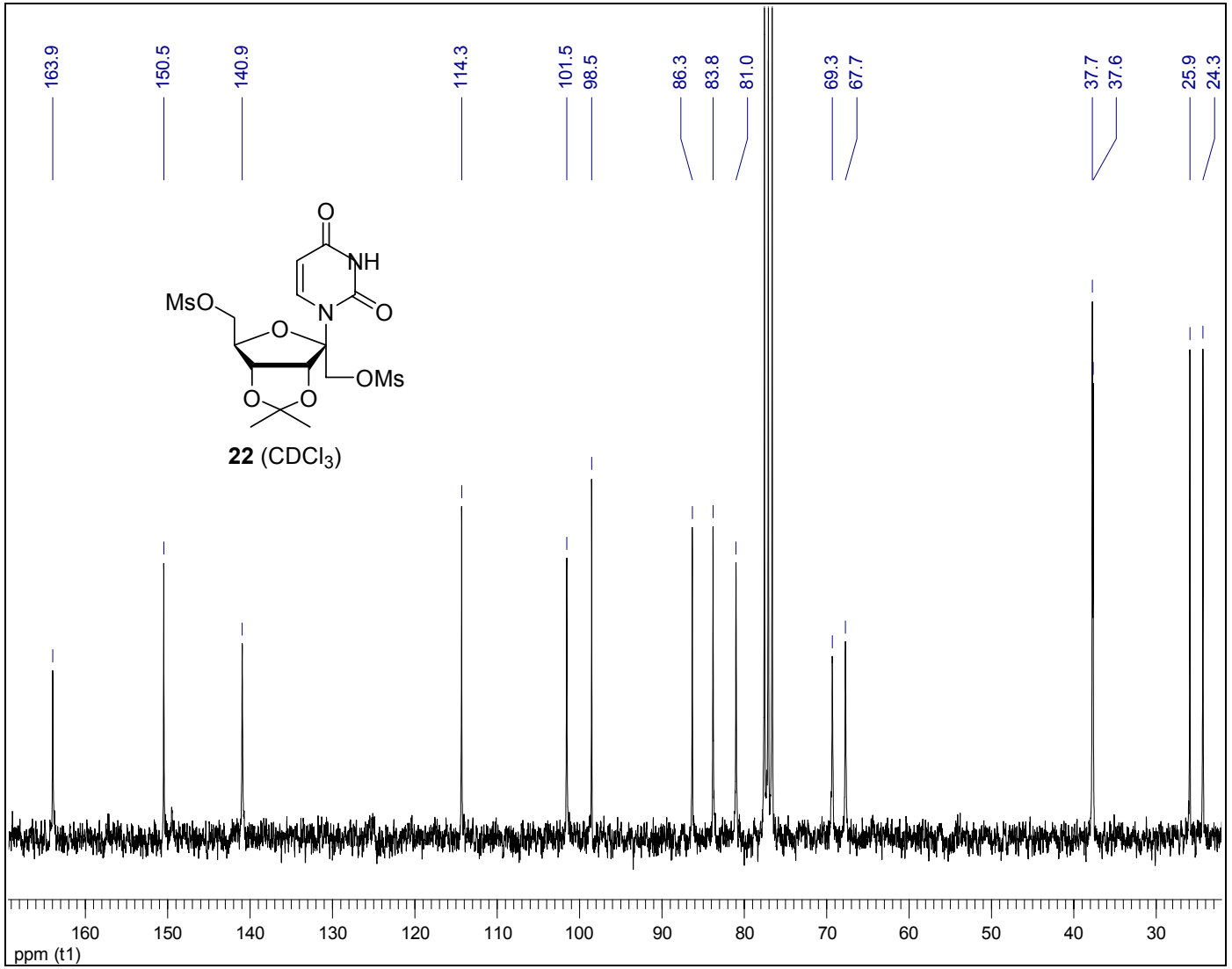

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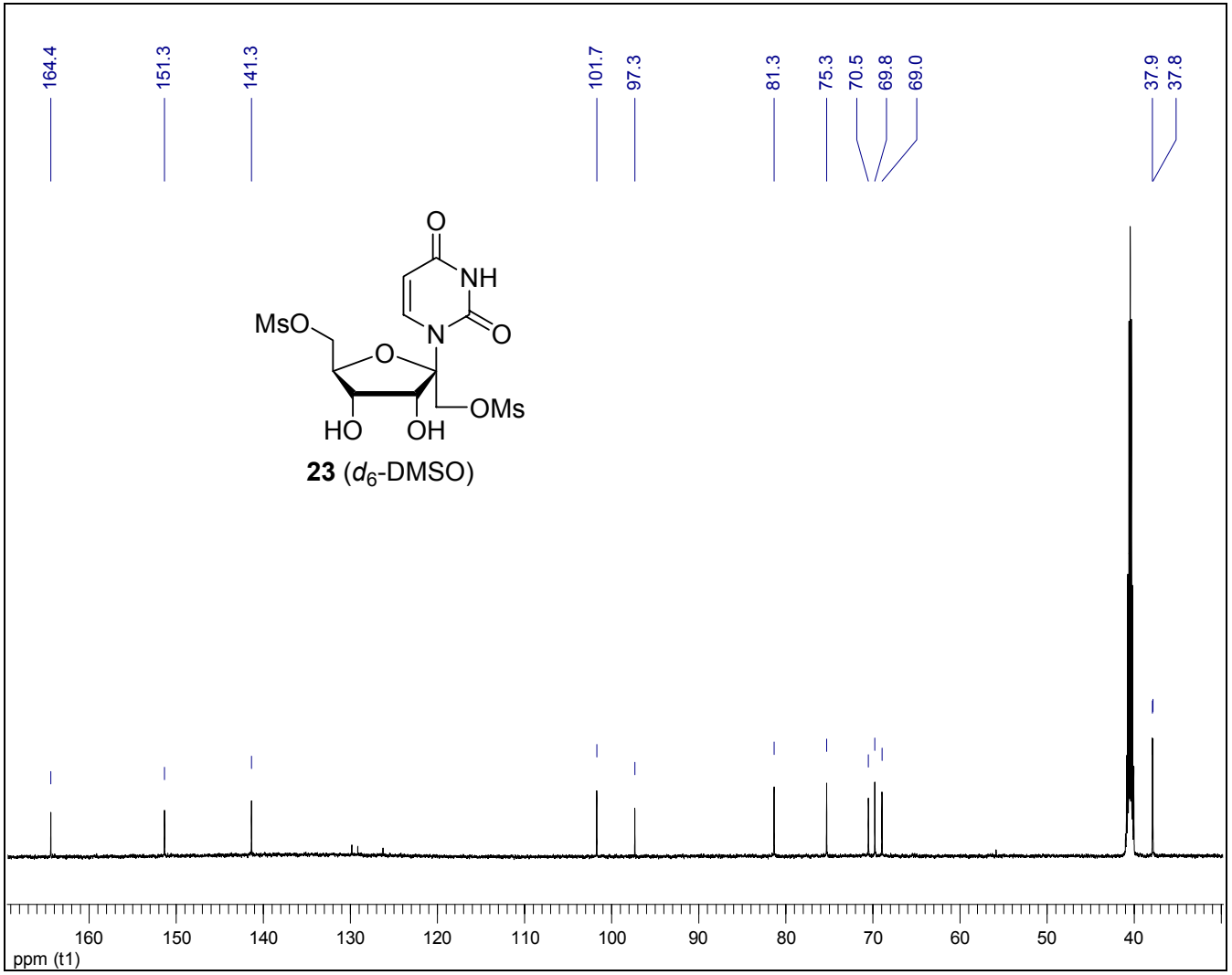
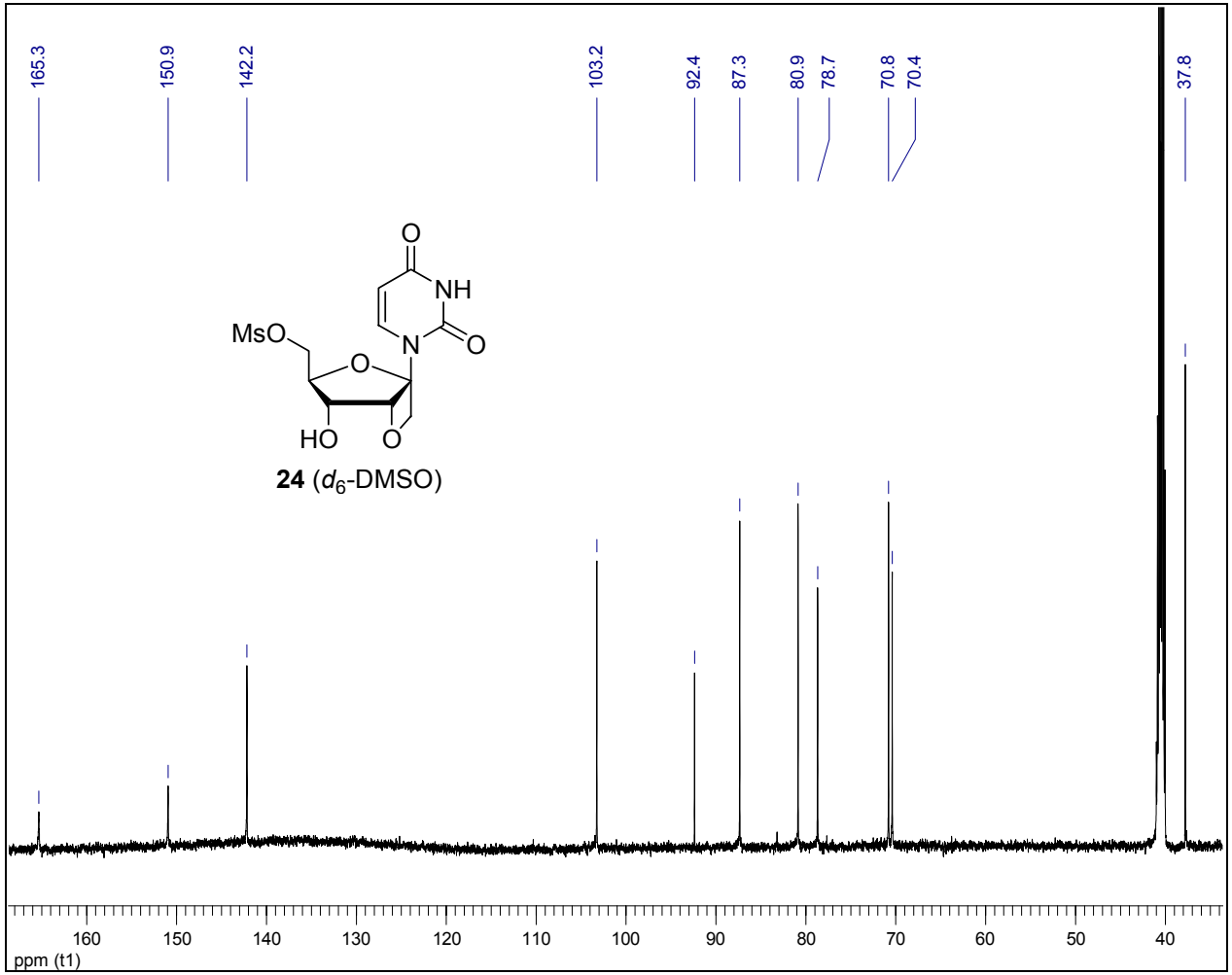


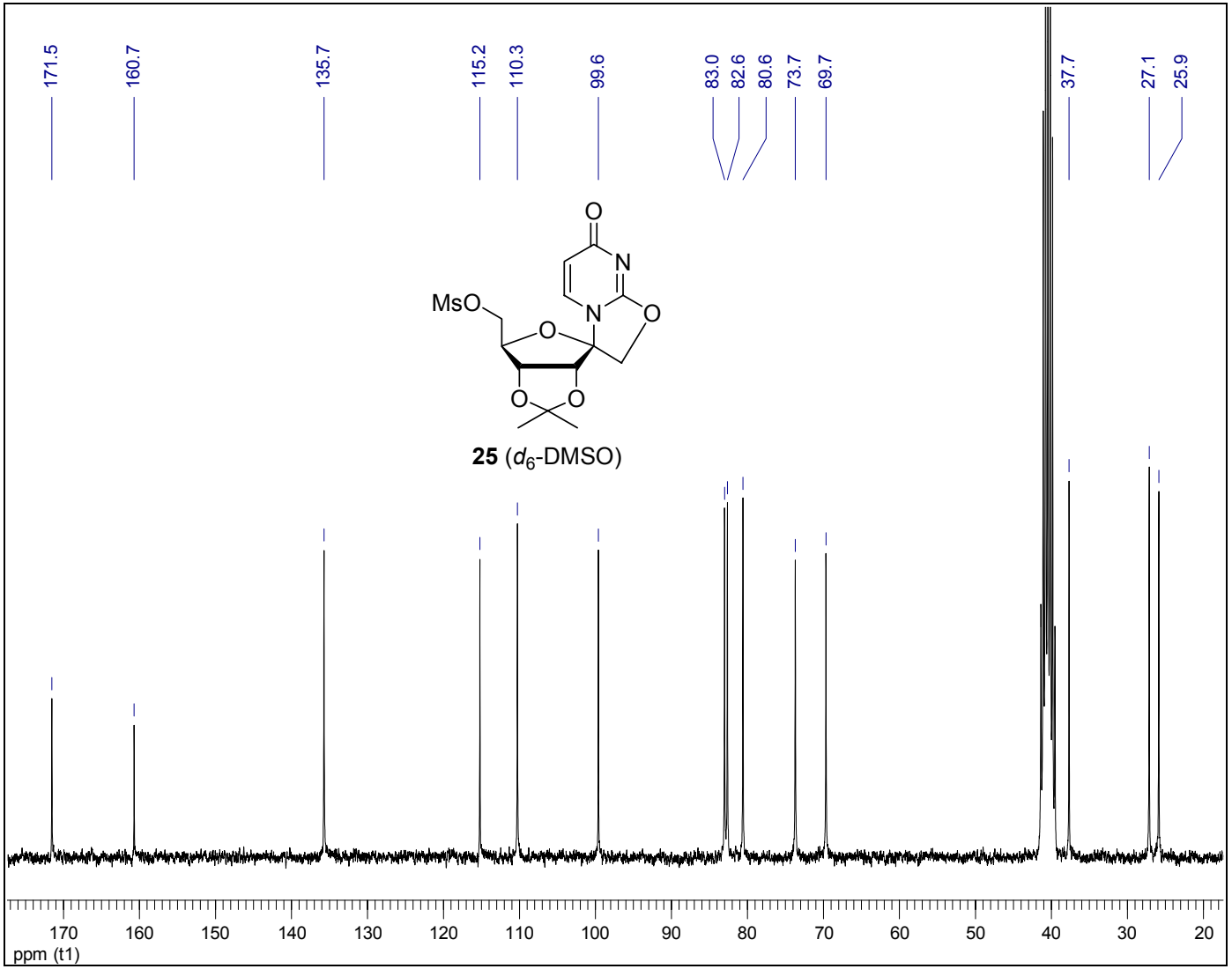
23 (d_6-DMSO)

Figure S 15



24 (d_6-DMSO)

Figure S 16



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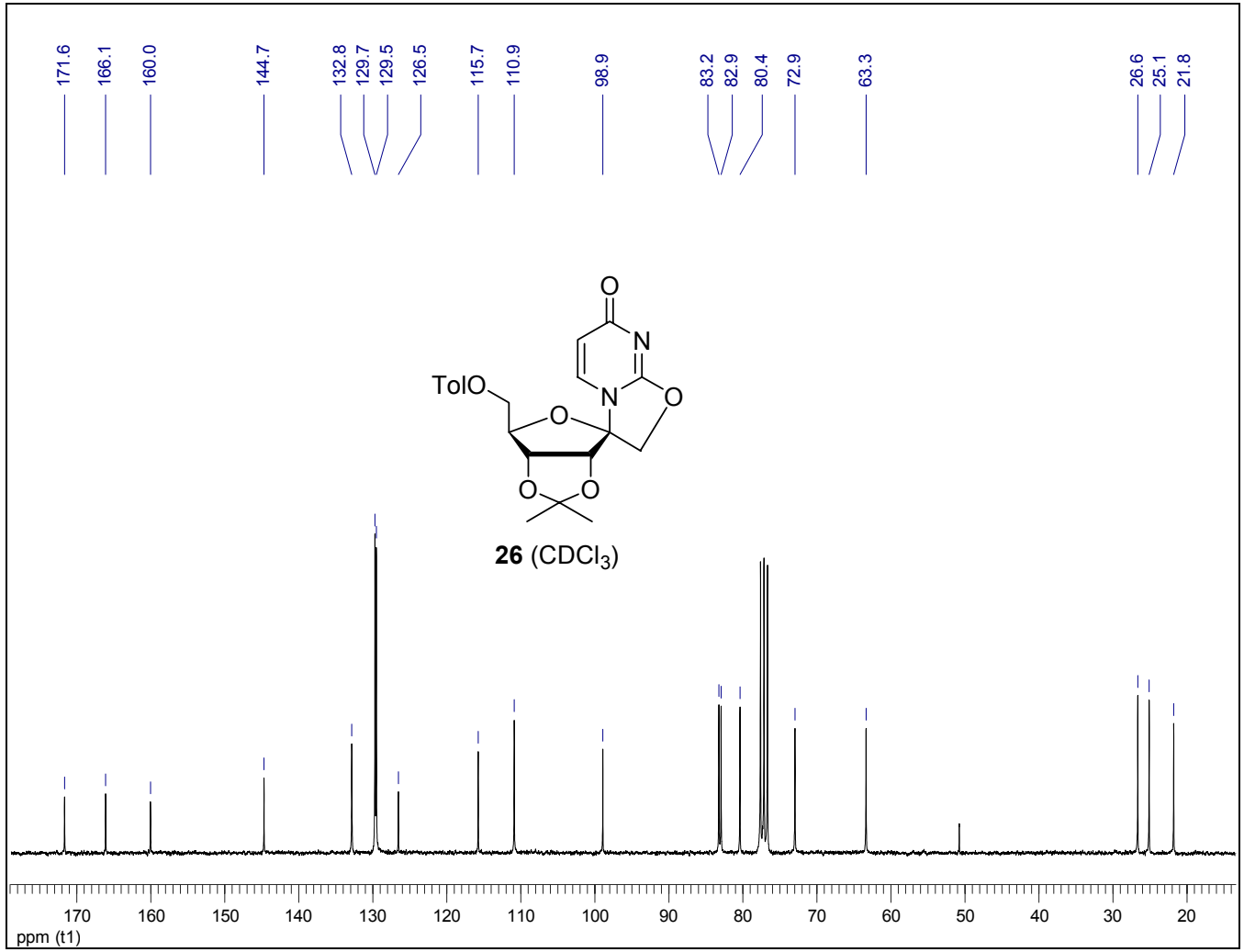

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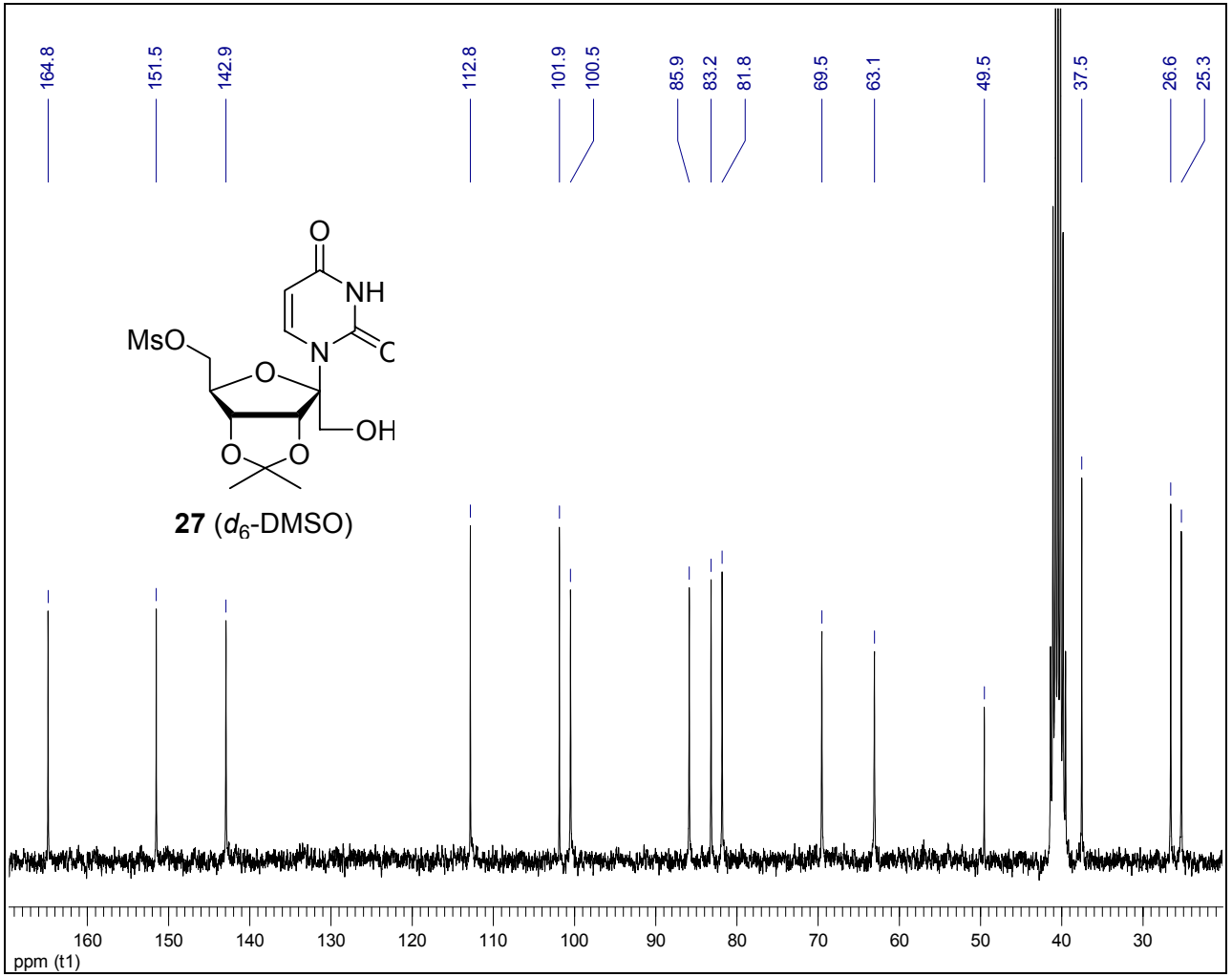

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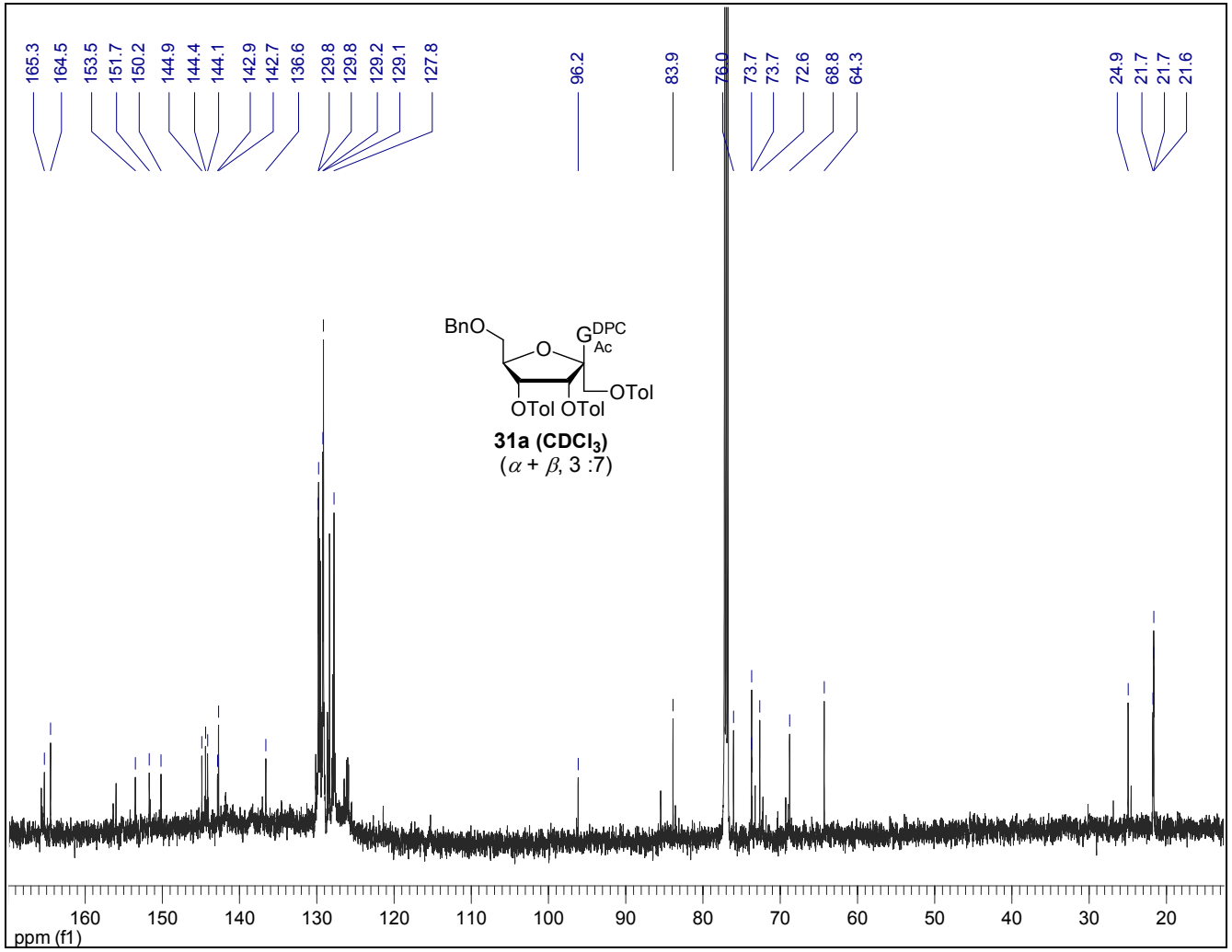

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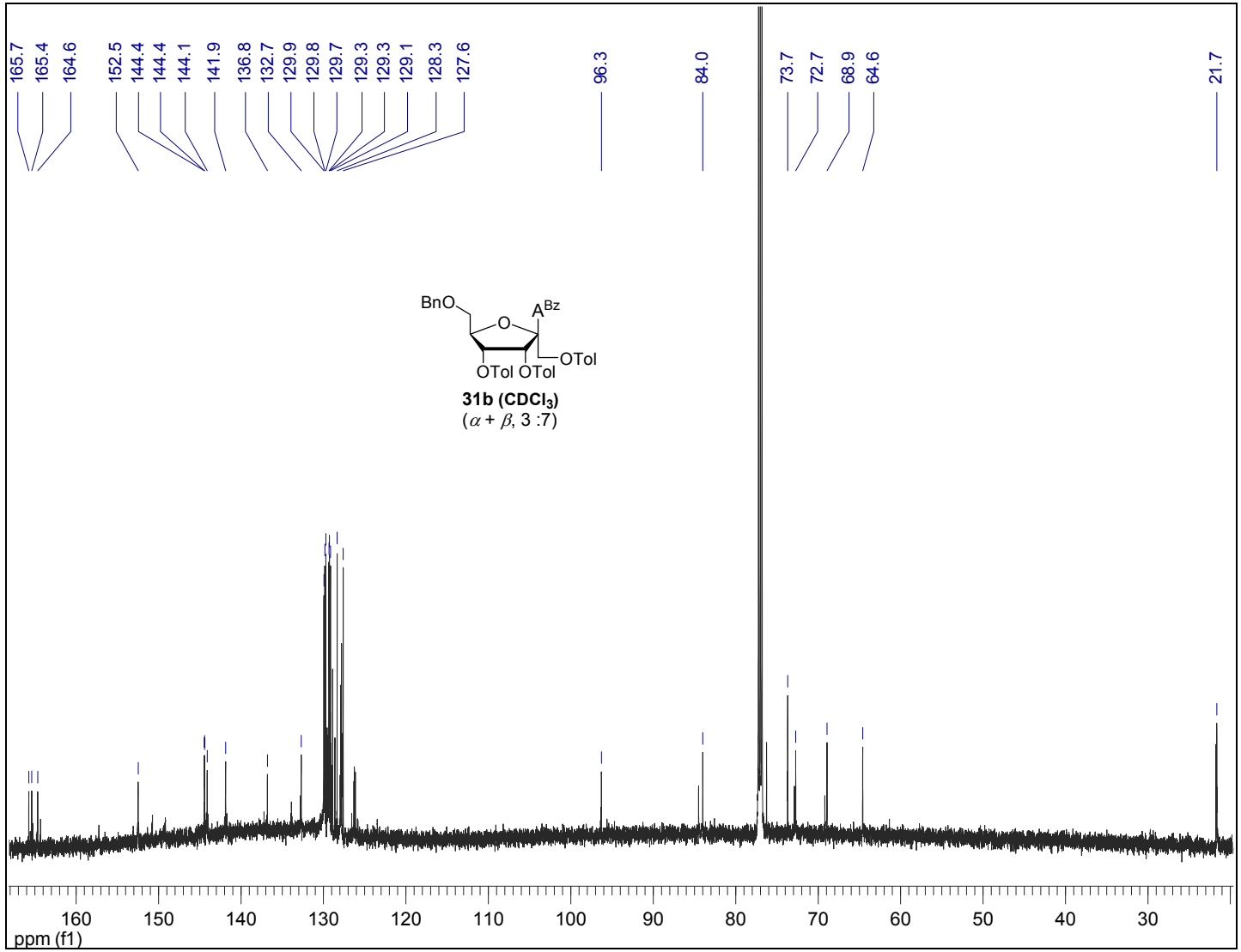

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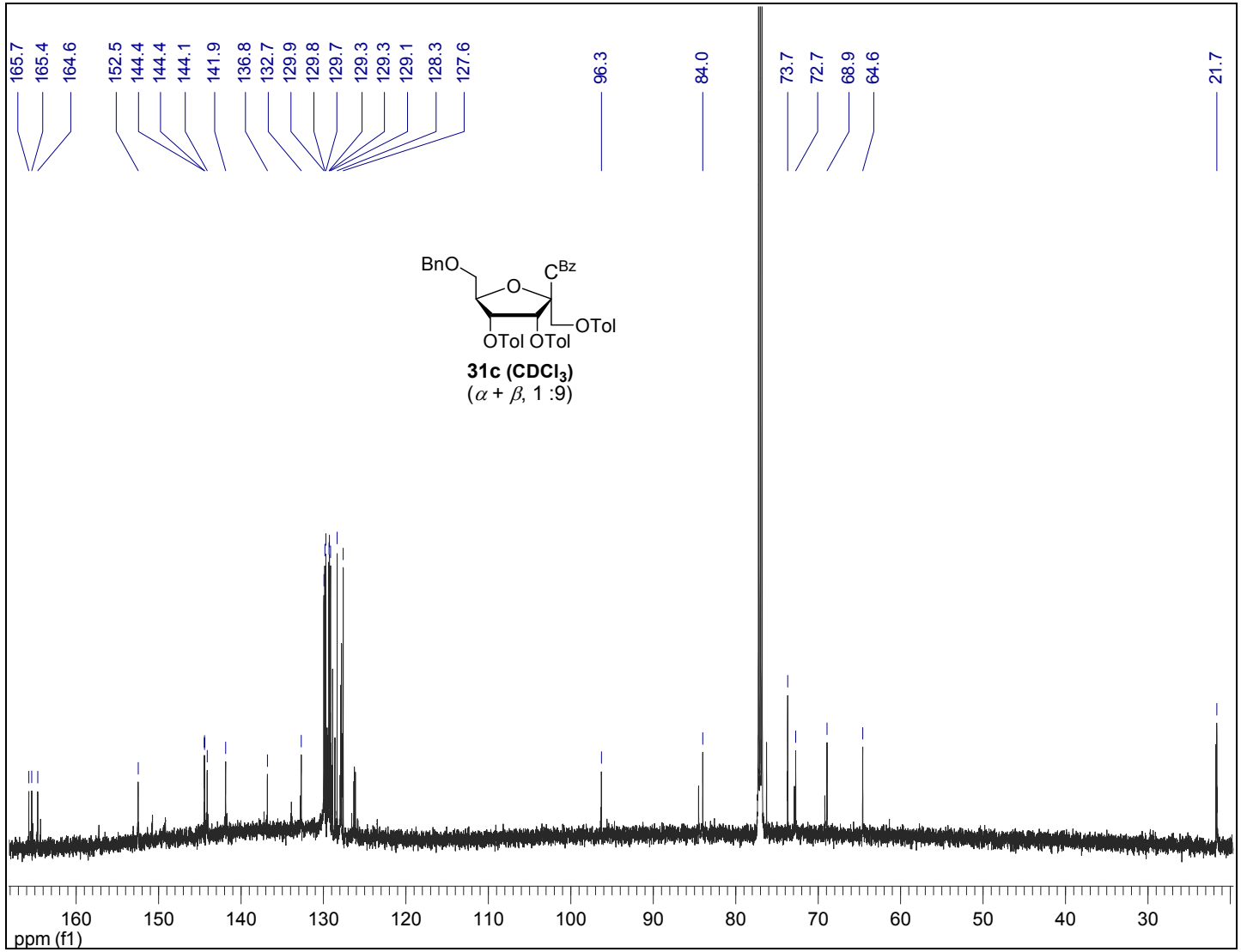

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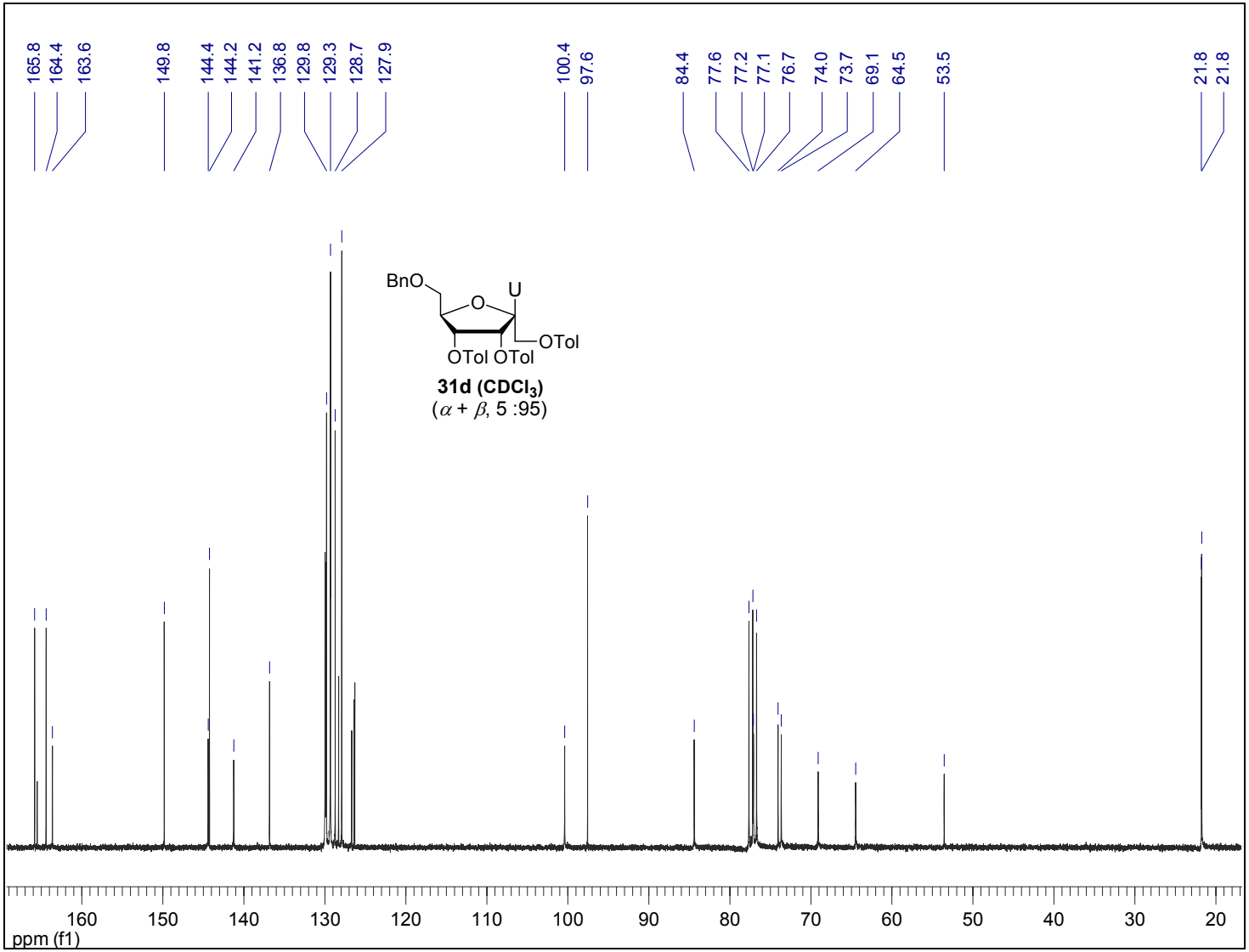

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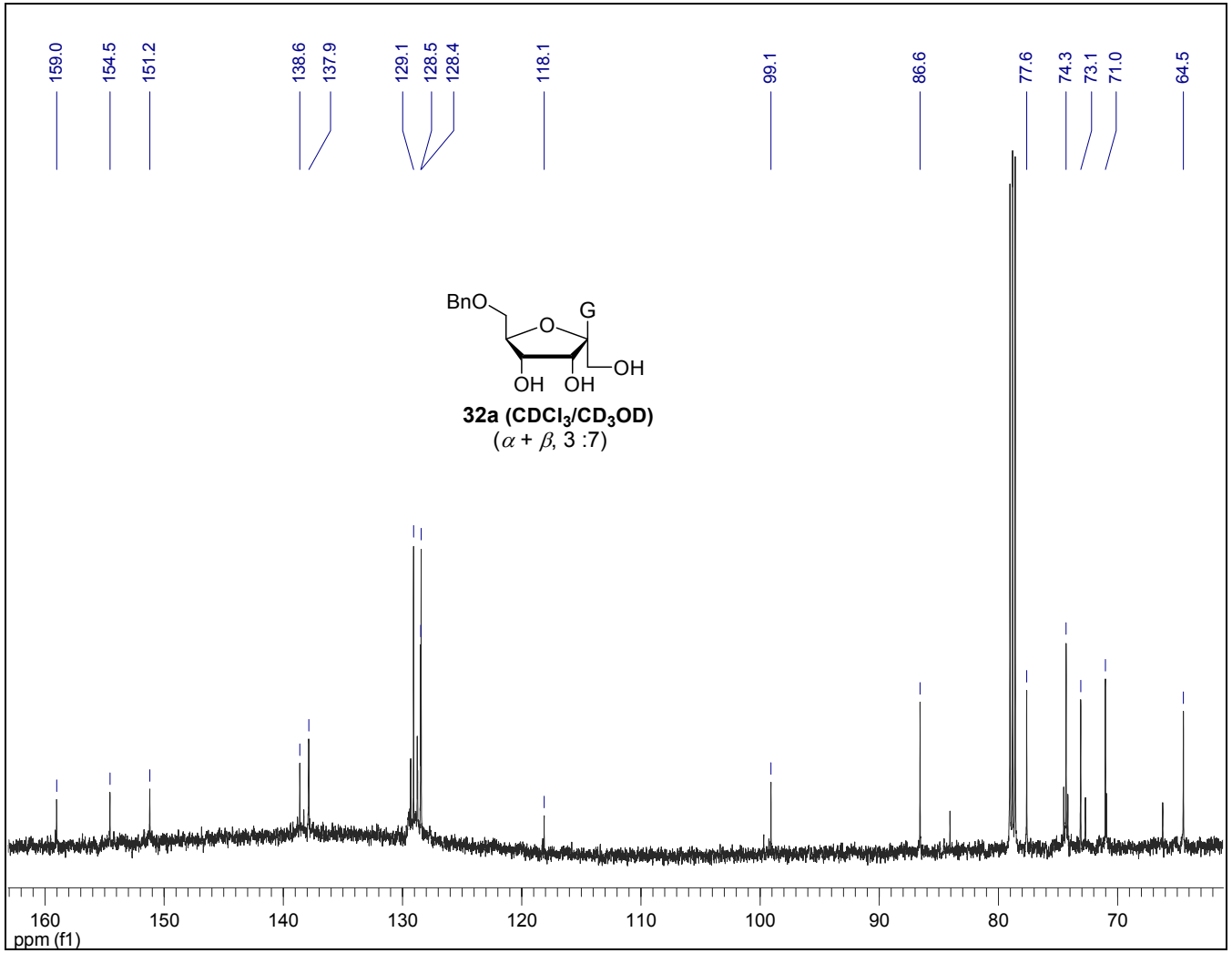

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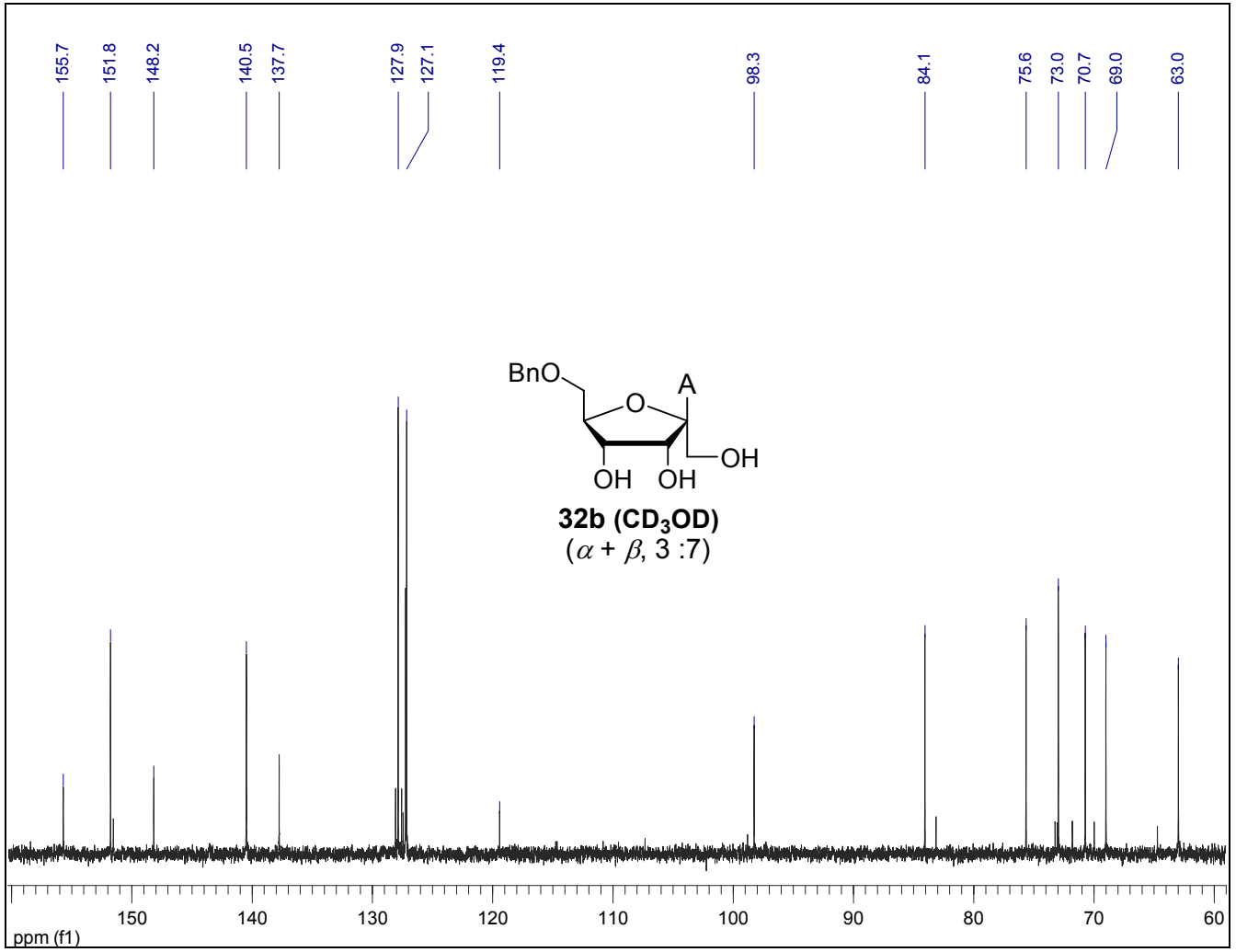

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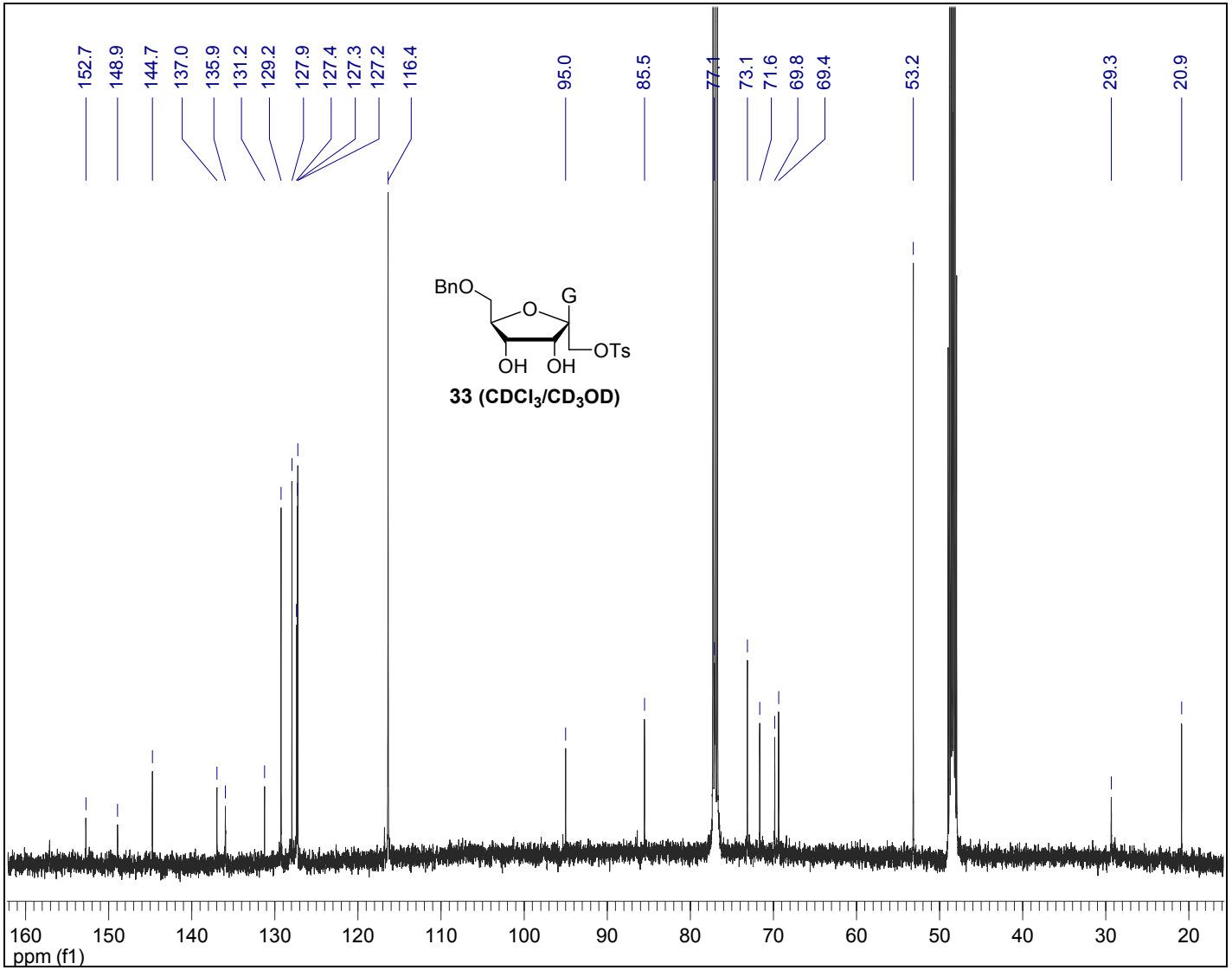
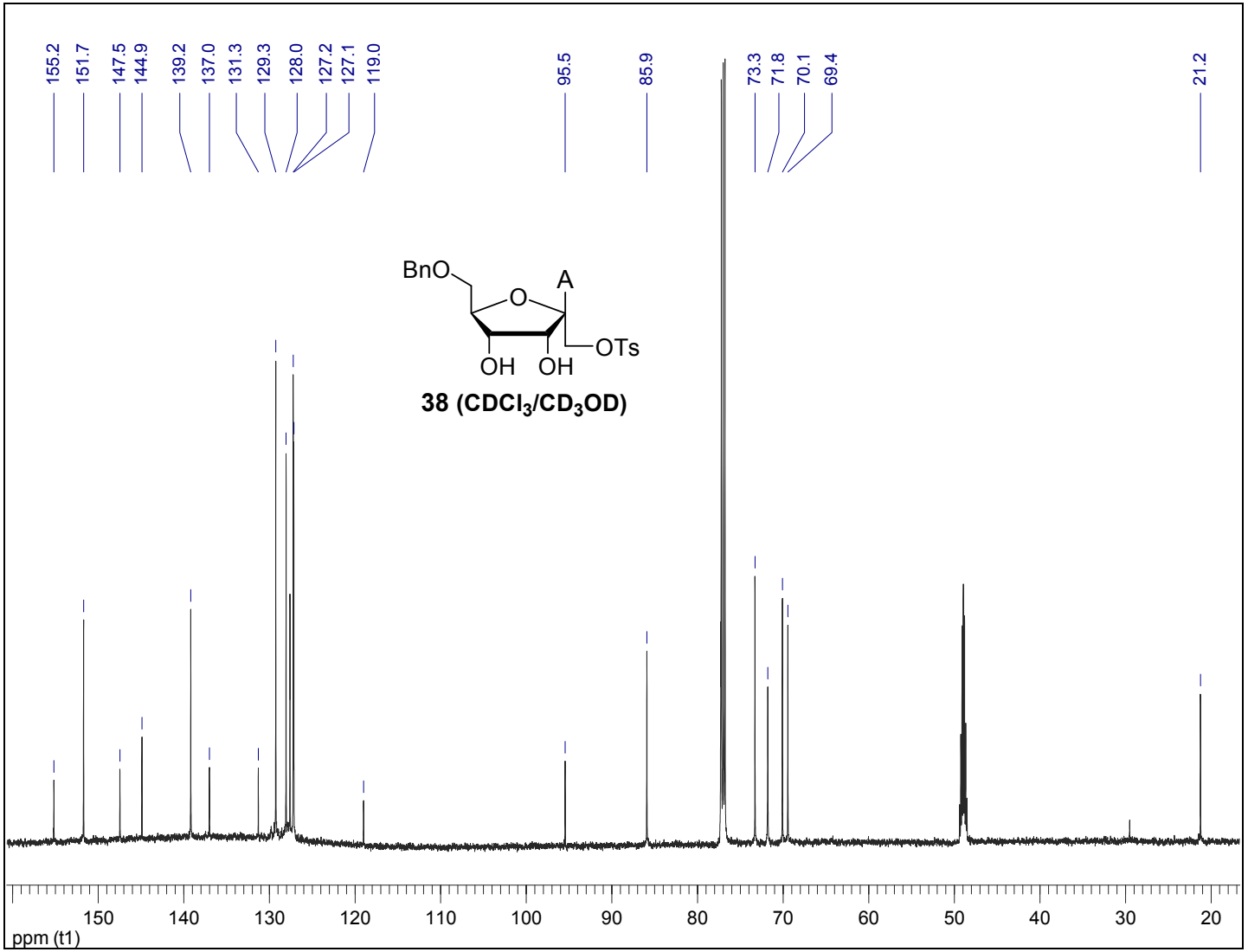


33 ($CDCl_3/CD_3OD$)



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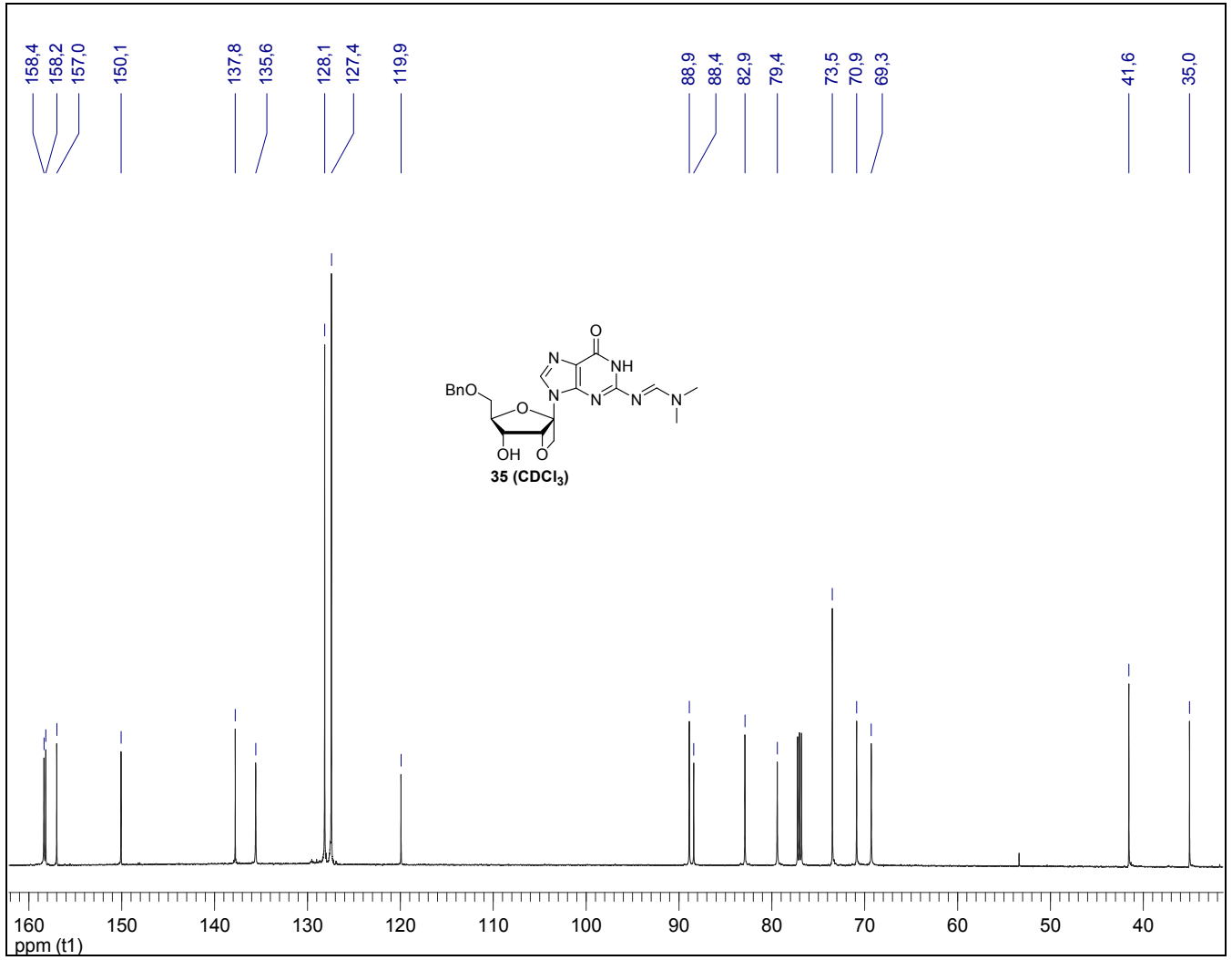

Figure S28