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Supplementary Material

Oxidative Damage of Pyrimidine Nucleosides by the Atmospheric Free-Radical Oxidant $NO_3^\bullet$ in the Absence and Presence of $NO_2^\bullet$ and other Radical and Non-Radical Oxidants

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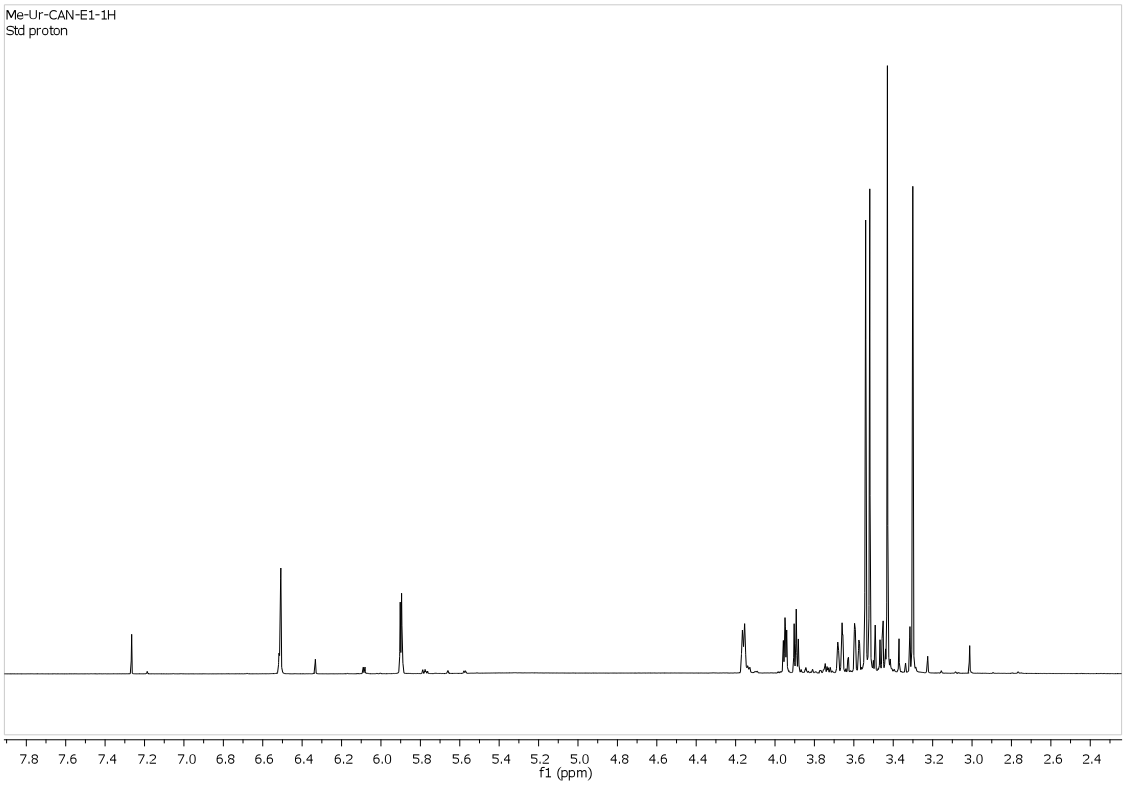
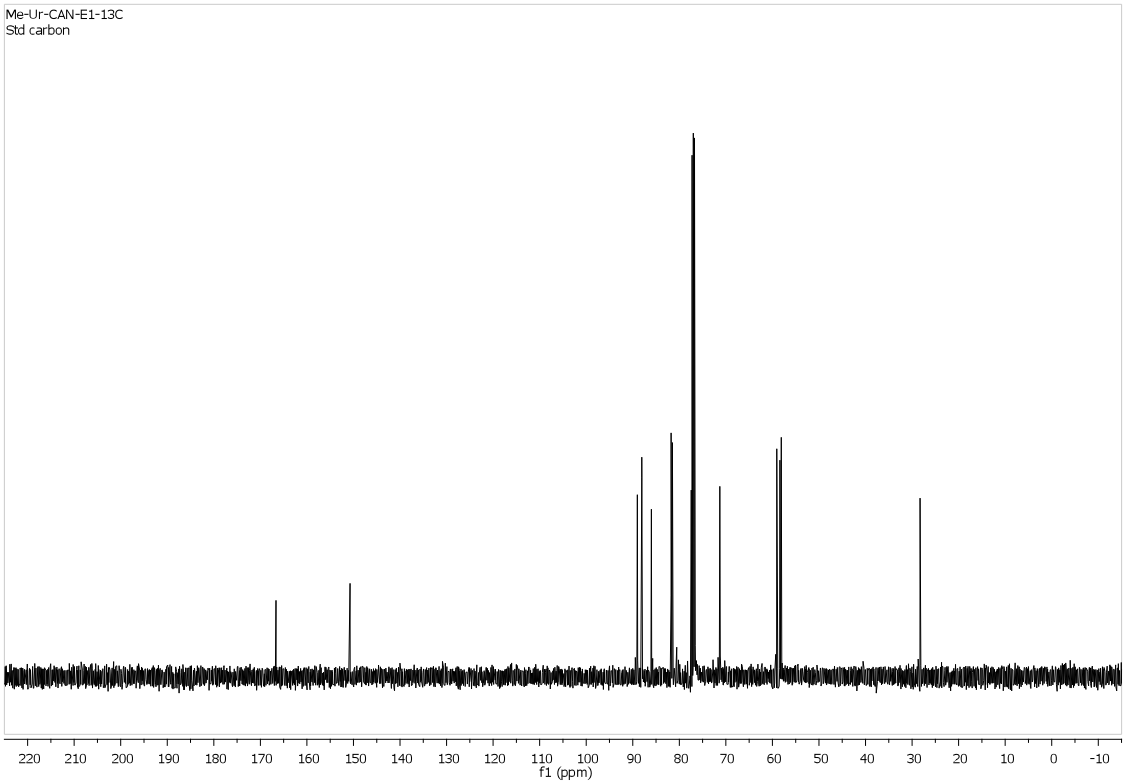
Contents:

1. NMR data

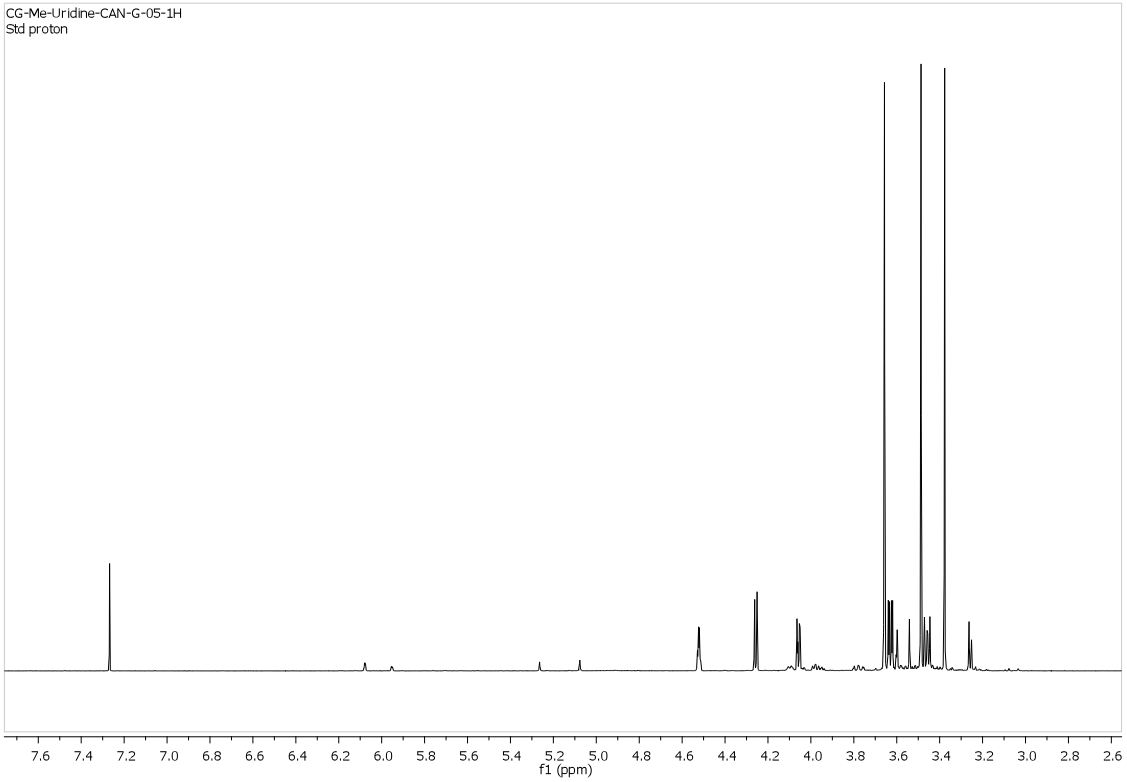
1.1 Reaction of uridine 1 with $NO_3^\bullet$ derived from CAN photolysis

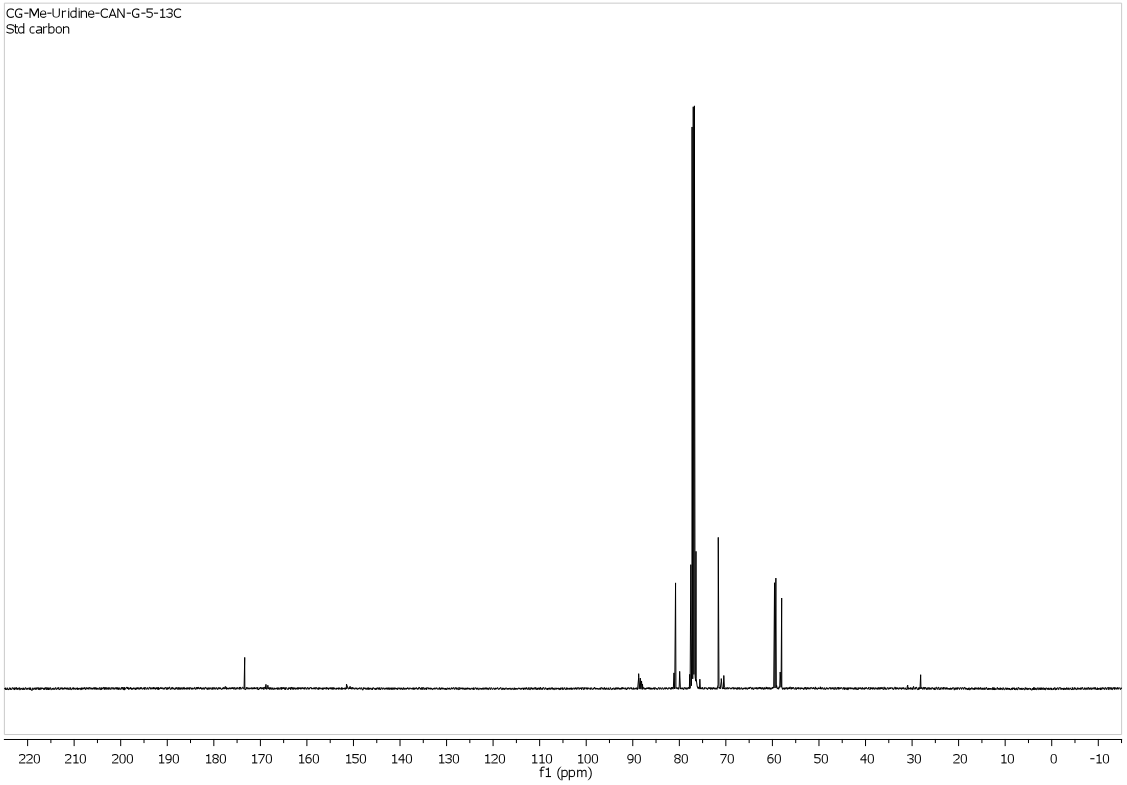
*5,5-Dihydroxy-2',3',5'-tri-O-methyl-N-methyl-6-nitrouridine (**4**)*



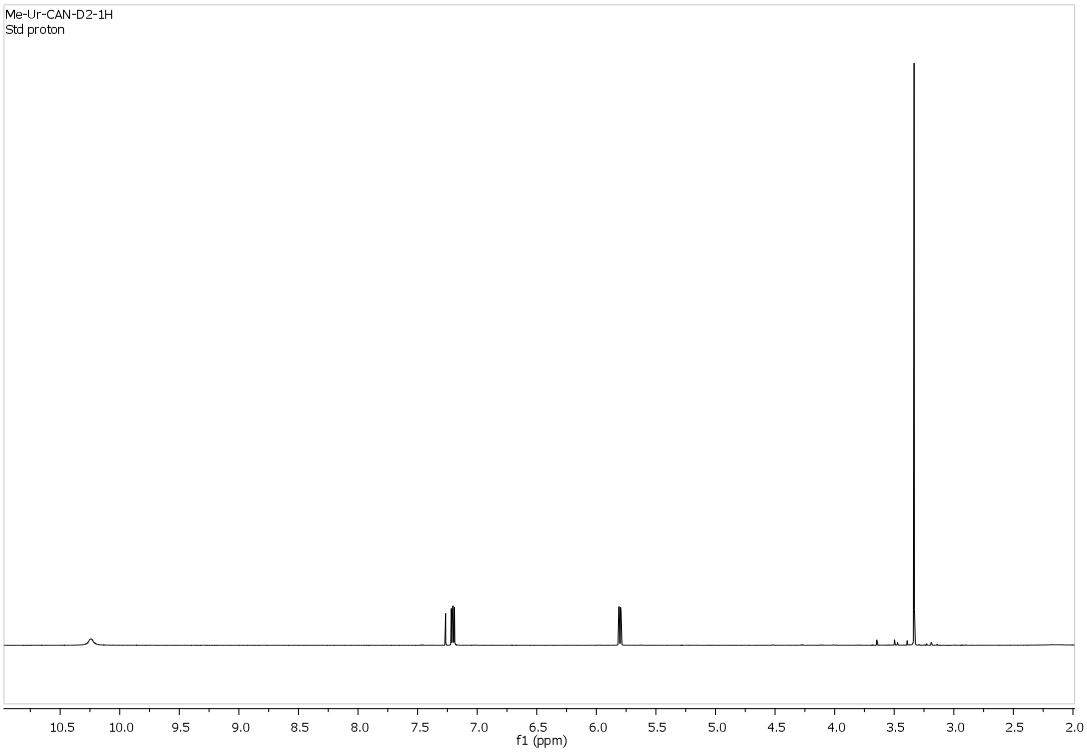


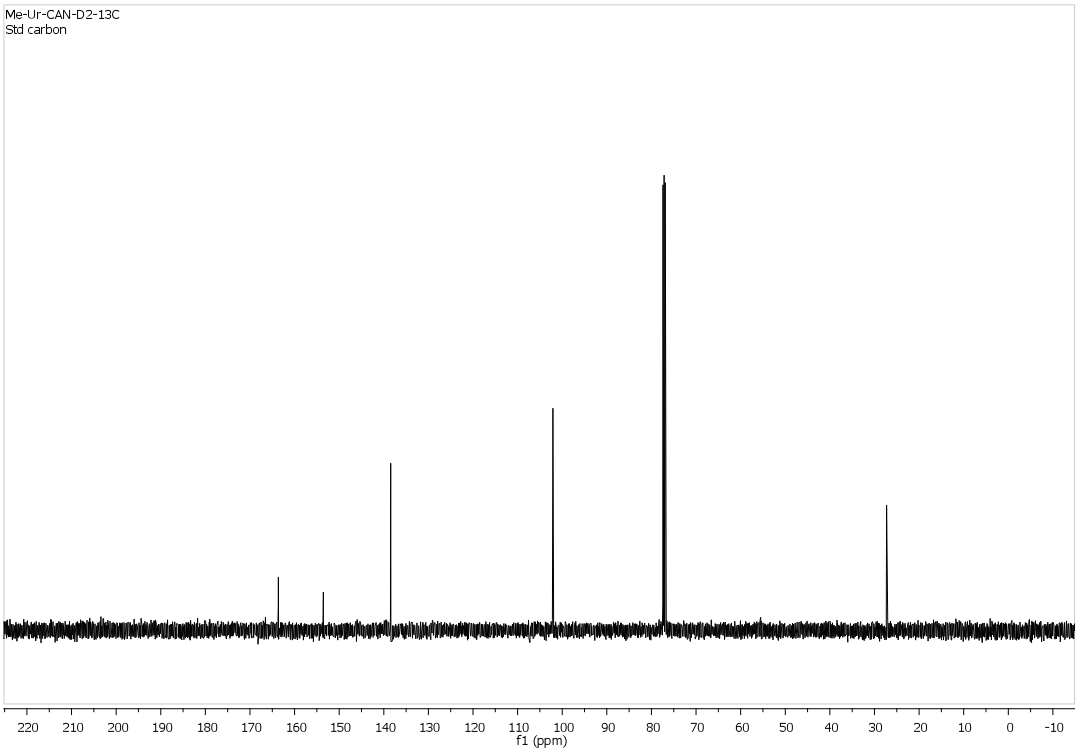
*(3S,4S,5R)-3,4-Dimethoxy-5-(methoxymethyl)-dihydrofuran-2(3H)-one (**5**)*





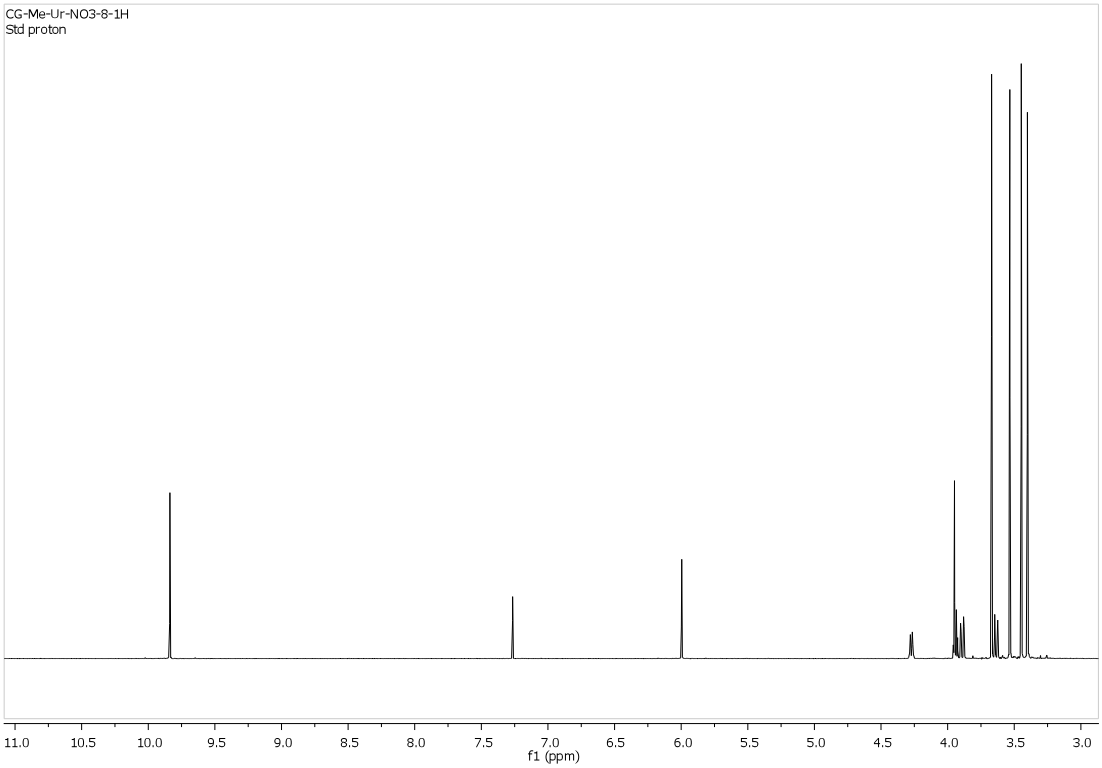
*3-Methyluracil (**6**)*

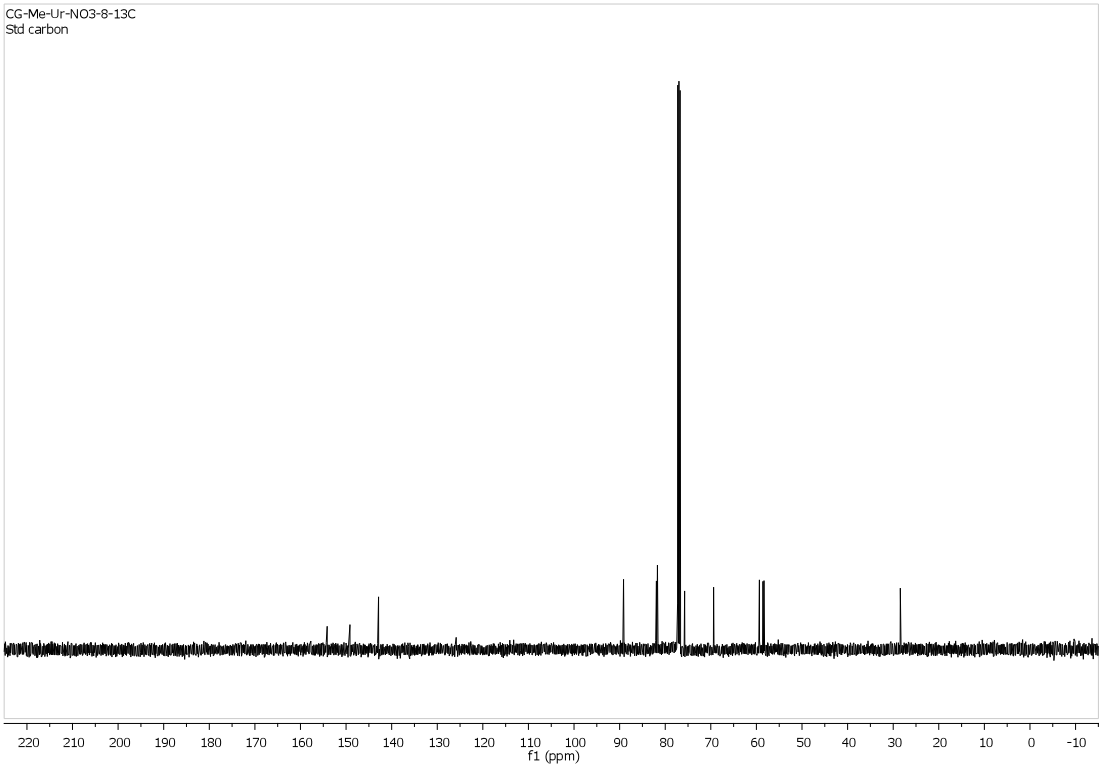




1.2 Reaction of uridine 1 with $NO_3^{\bullet}$ derived from $NO_2^{\bullet}/O_3$.

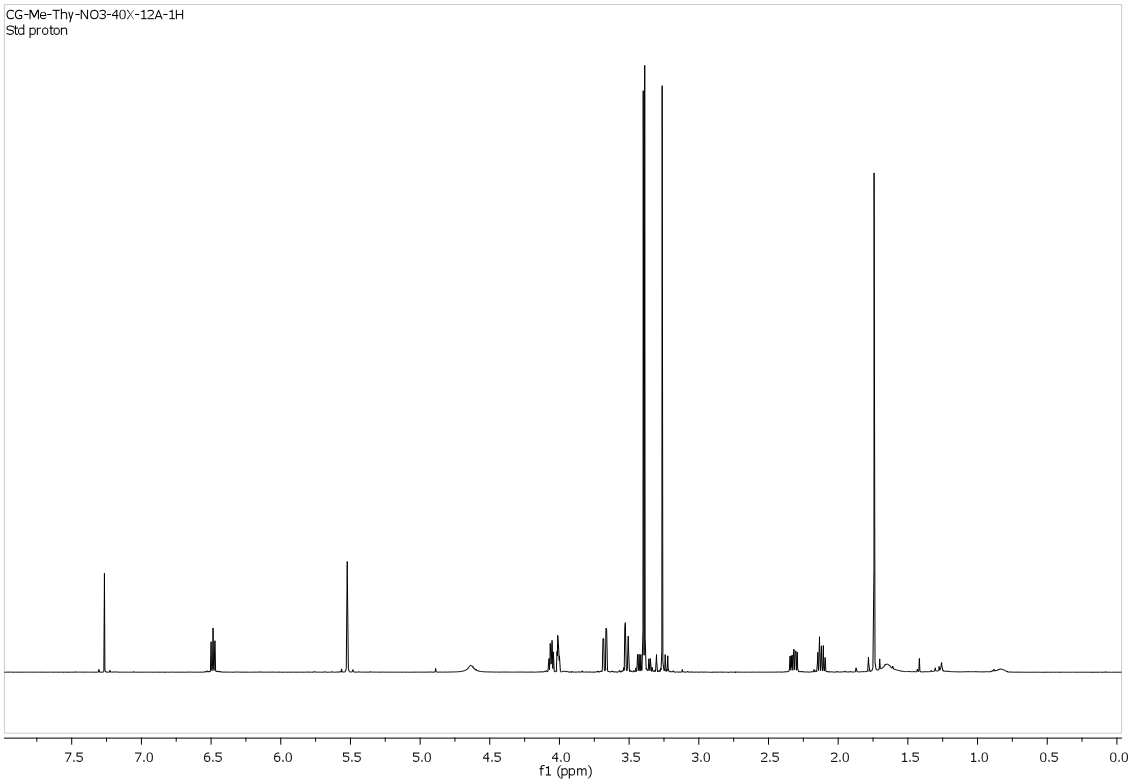
*2',3',5'-Tri-O-methyl-N-methyl-6-nitrouridine (**18**)*

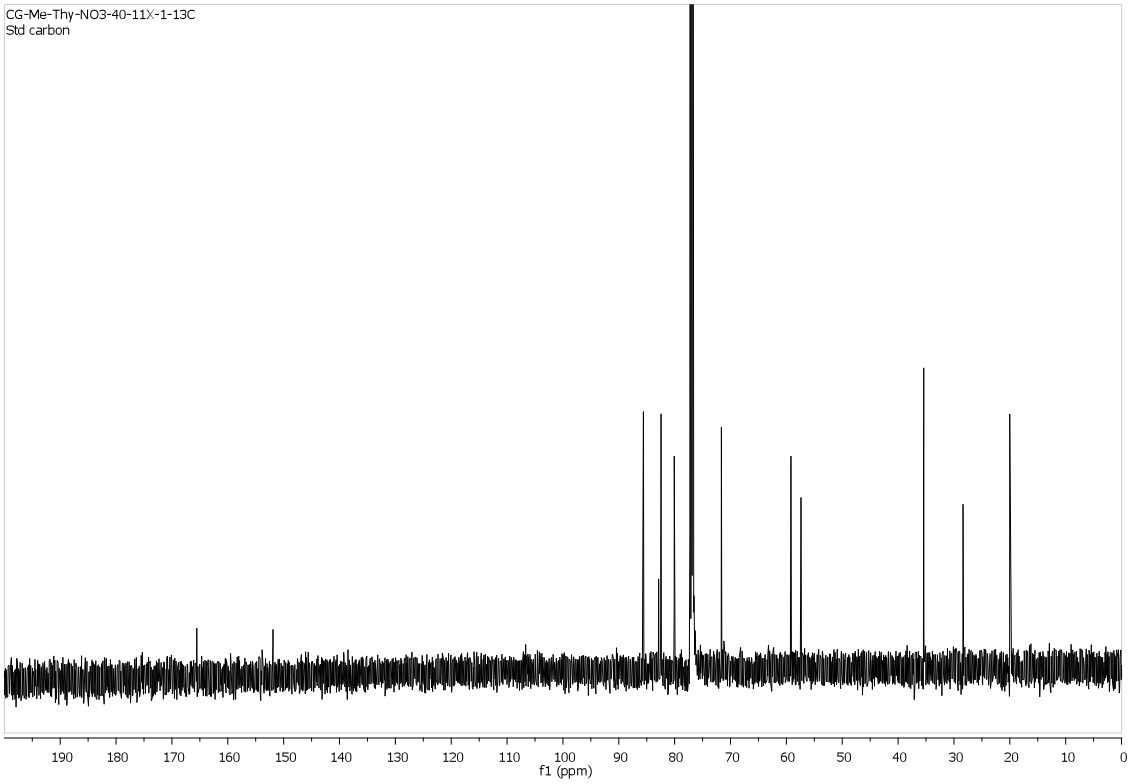




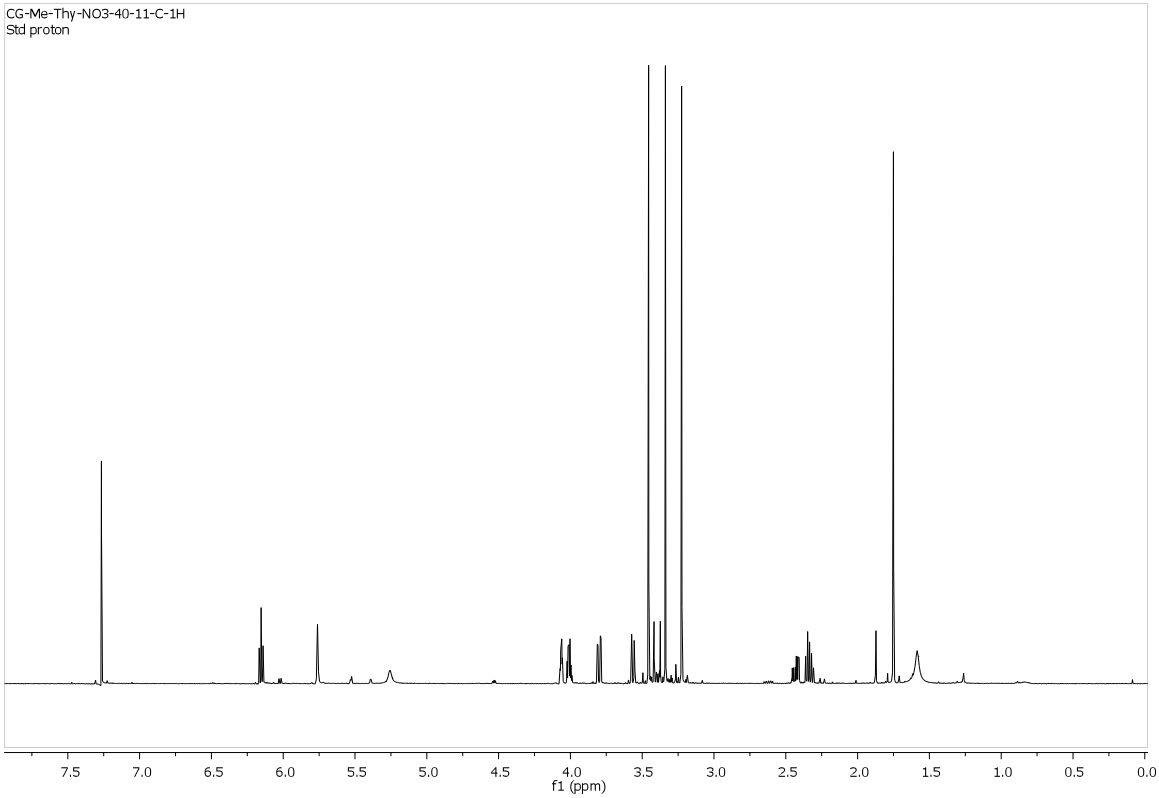
1.3 Reaction of thymidine 2 with $NO_3^{\bullet}$ derived from $NO_2^{\bullet}/O_3$.

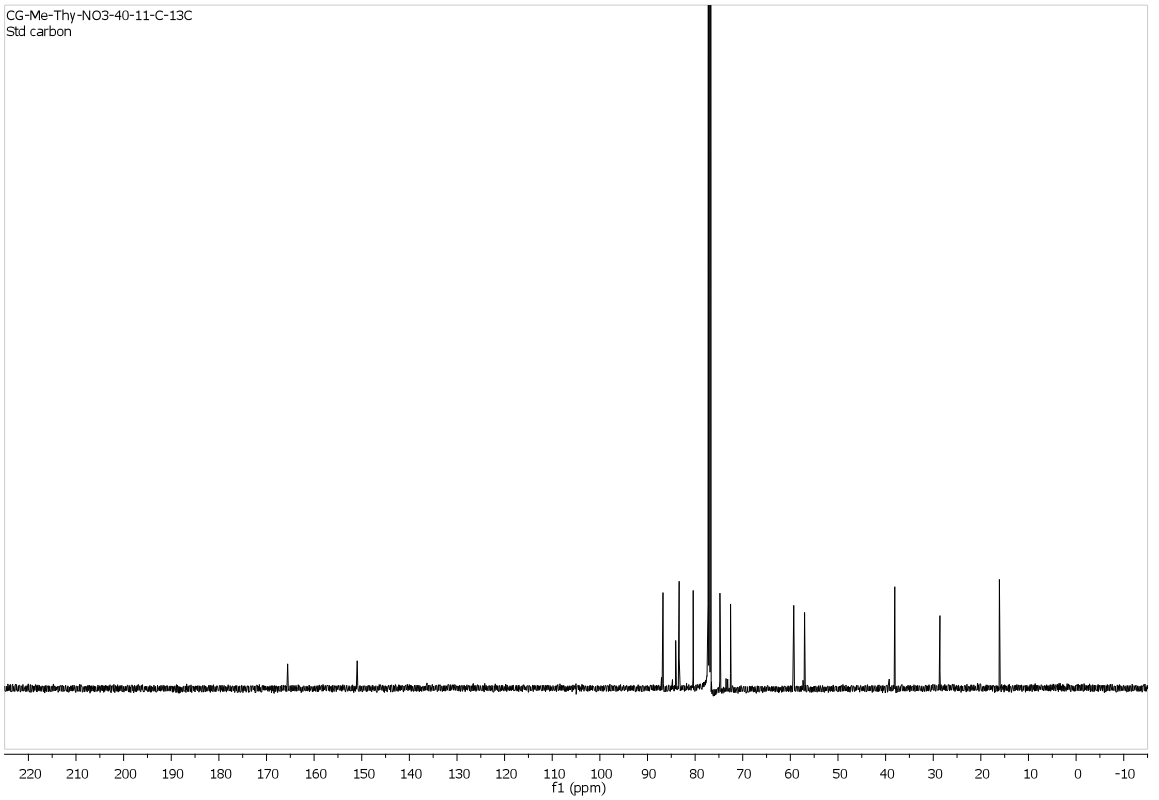
*(5S,6R)-6-Hydroxy-3',5'-di-O-methyl-N-methyl-5-nitrato-2'-desoxythymidine (**20a**)*



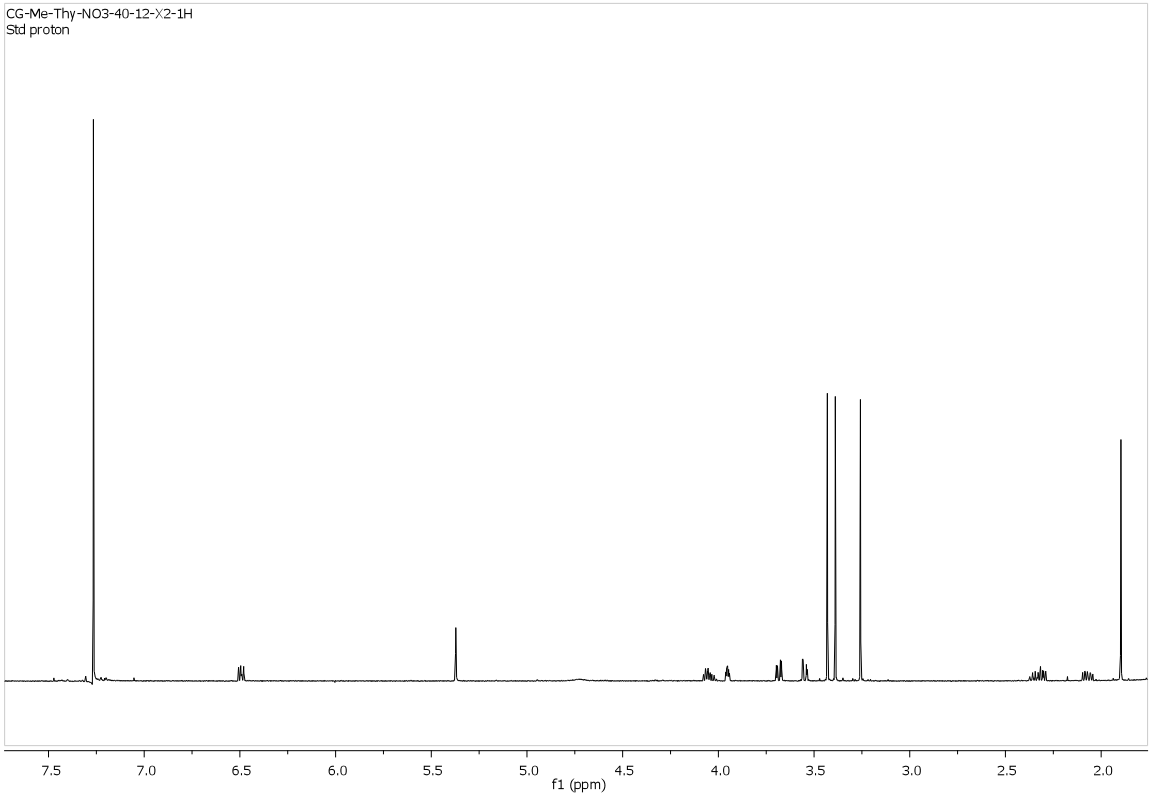


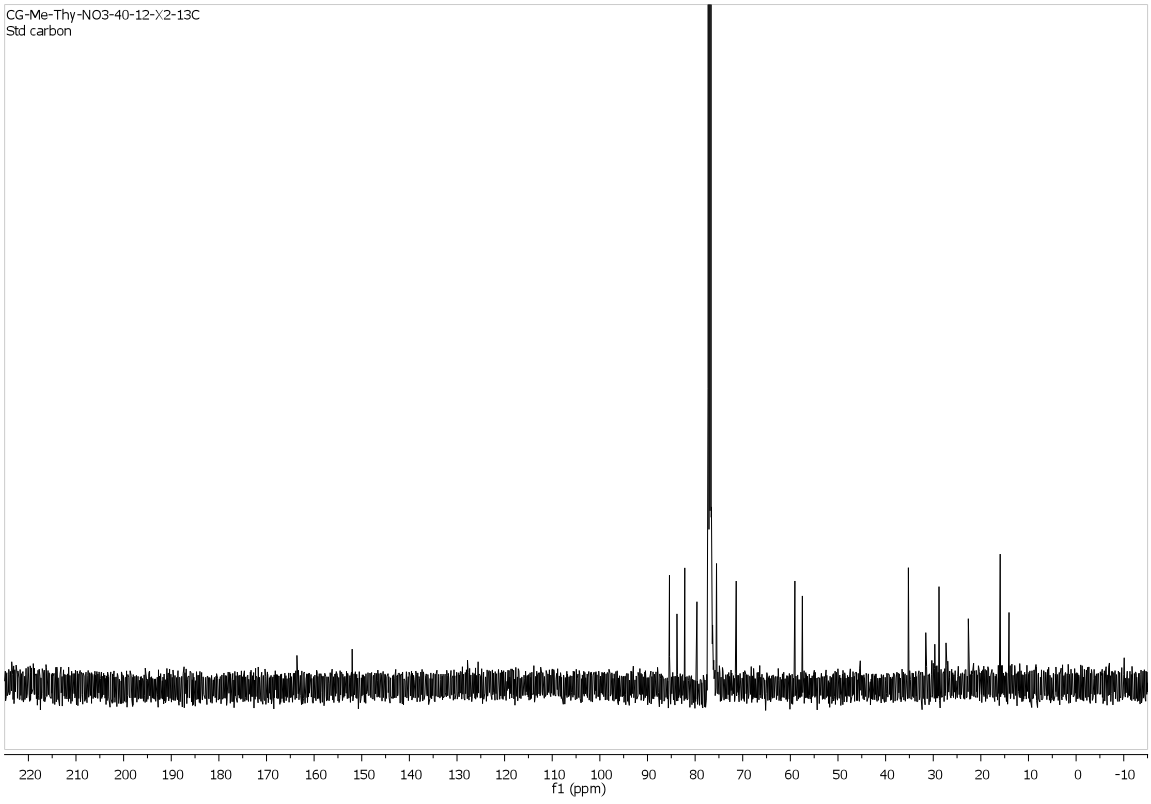
*(5S,6S)-6-Hydroxy-3',5'-di-O-methyl-N-methyl-5-nitrato-2'-desoxythymidine (**20b**)*



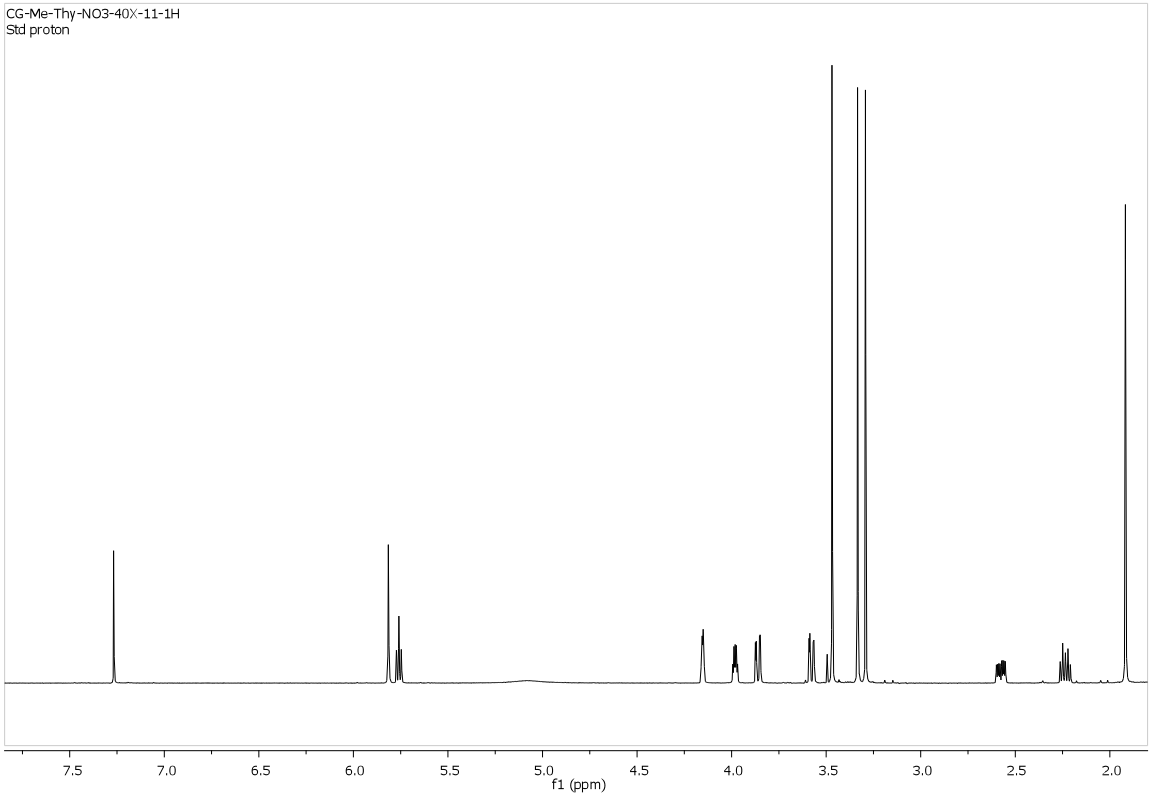


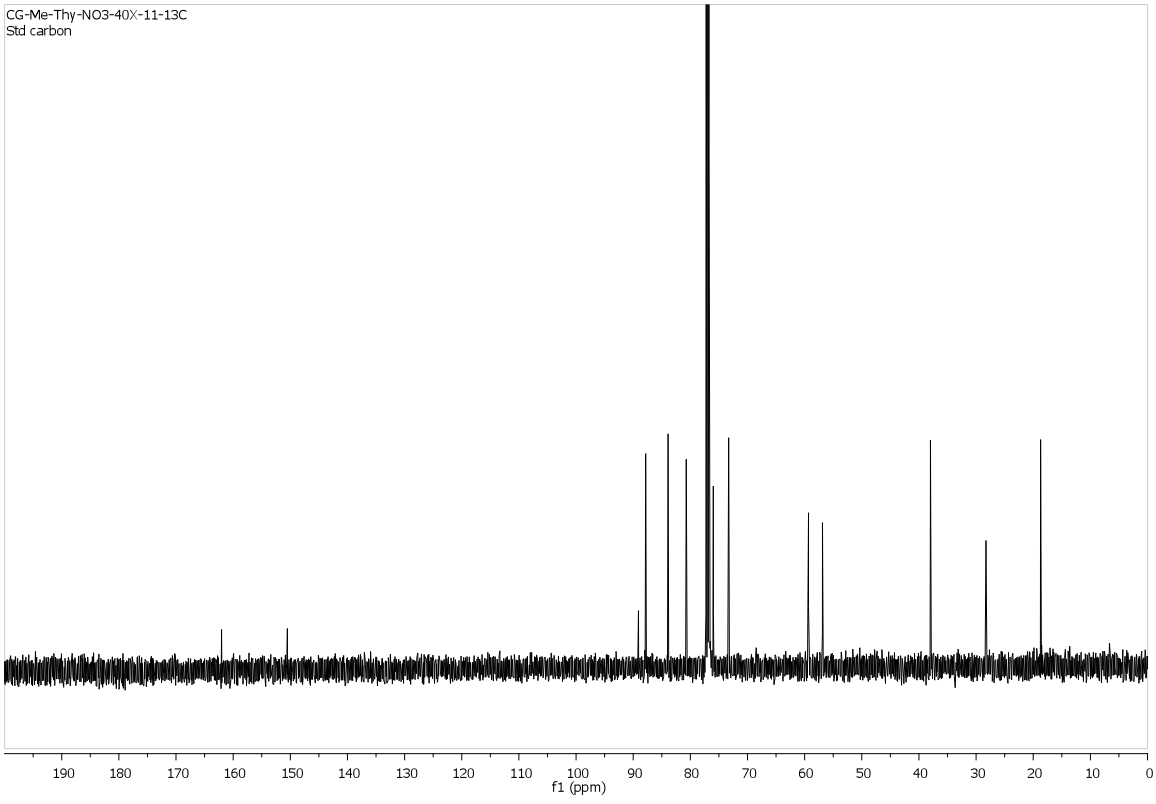
*6-Hydroxy-3',5'-di-O-methyl-N-methyl-5-nitrato- 2'-desoxythymidine (**20c**)*



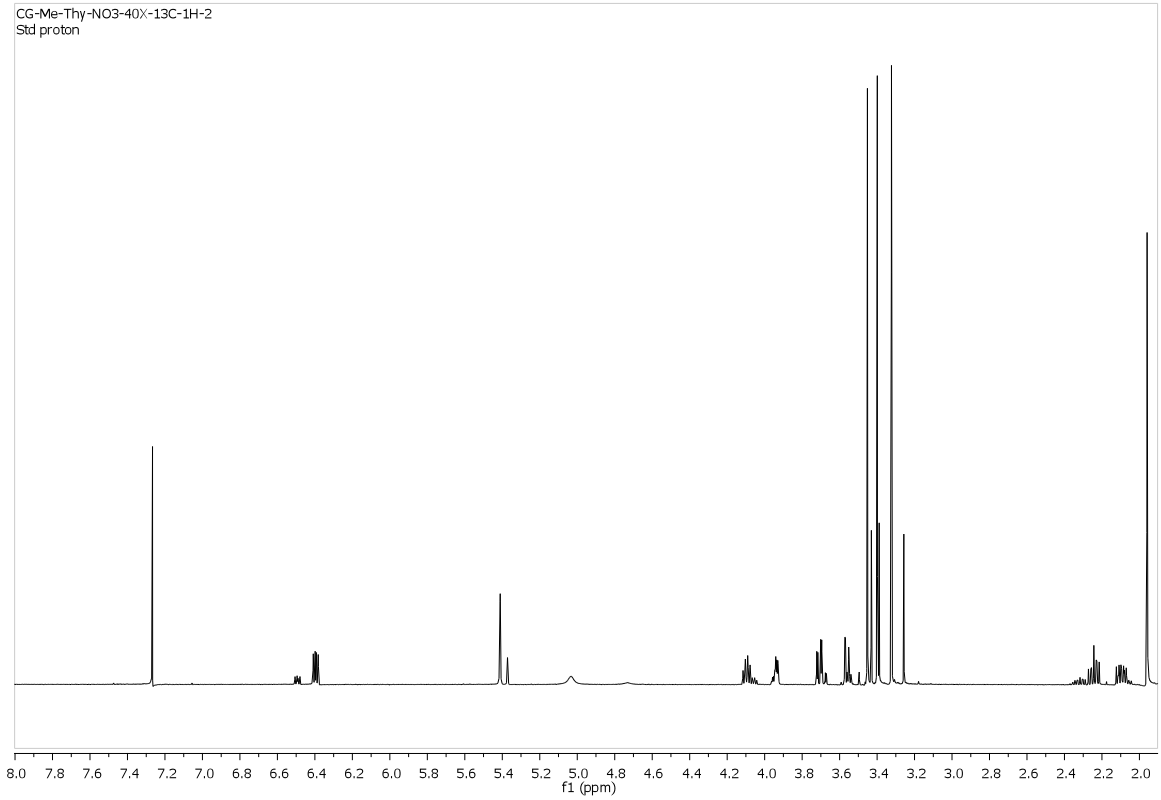


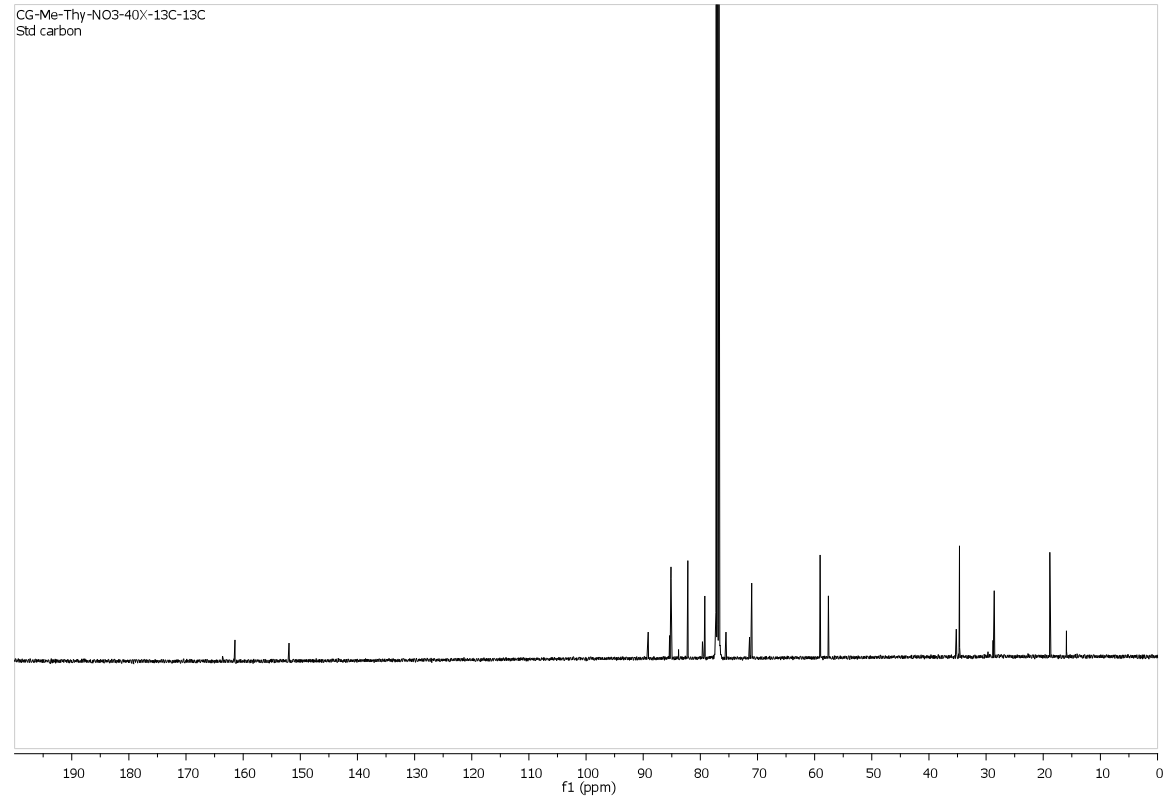
*6-Hydroxy- -3',5'-Di-O-methyl-N-methyl-5-nitro-2'-desoxythymidine (**21a**)*





*6-Hydroxy- -3',5'-Di-O-methyl-N-methyl-5-nitro-2'-desoxythymidine (**21b**)*



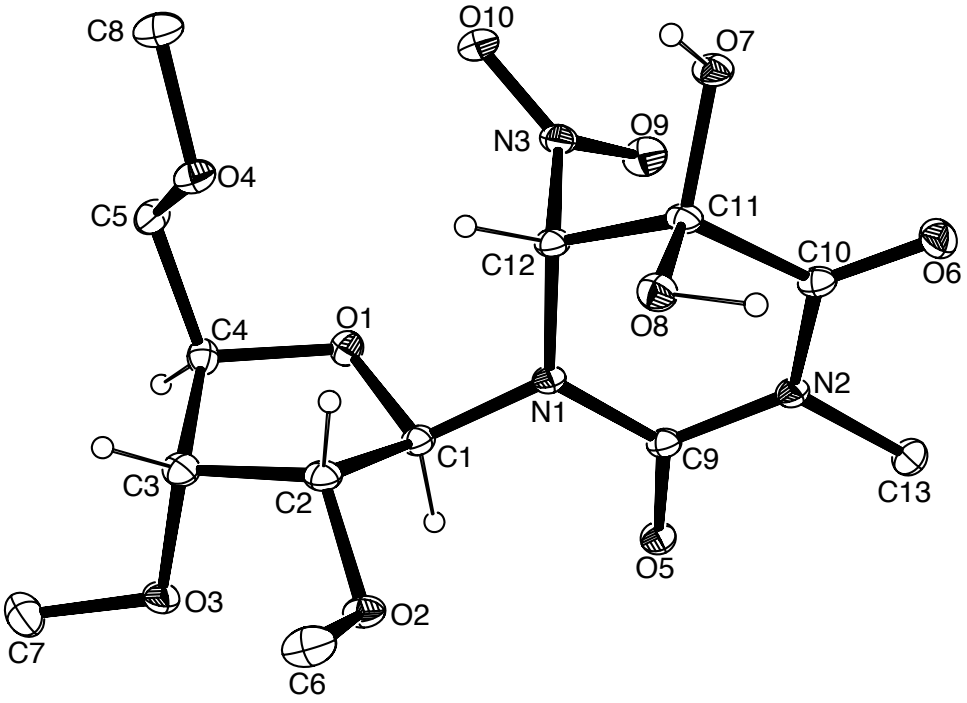


2. Chrystallographic data

Crystallography. Intensity data were collected with an Oxford Diffraction SuperNova CCD diffractometer using Cu-Kα microsource radiation (graphite crystal monochromator λ = 1.54184). The temperature during the data collections was maintained at 130.0(1) (except for rwg_2011_3: 180.0(1). Structure solution,[1] and refinement were implemented within the WingX suite of programs.[2]

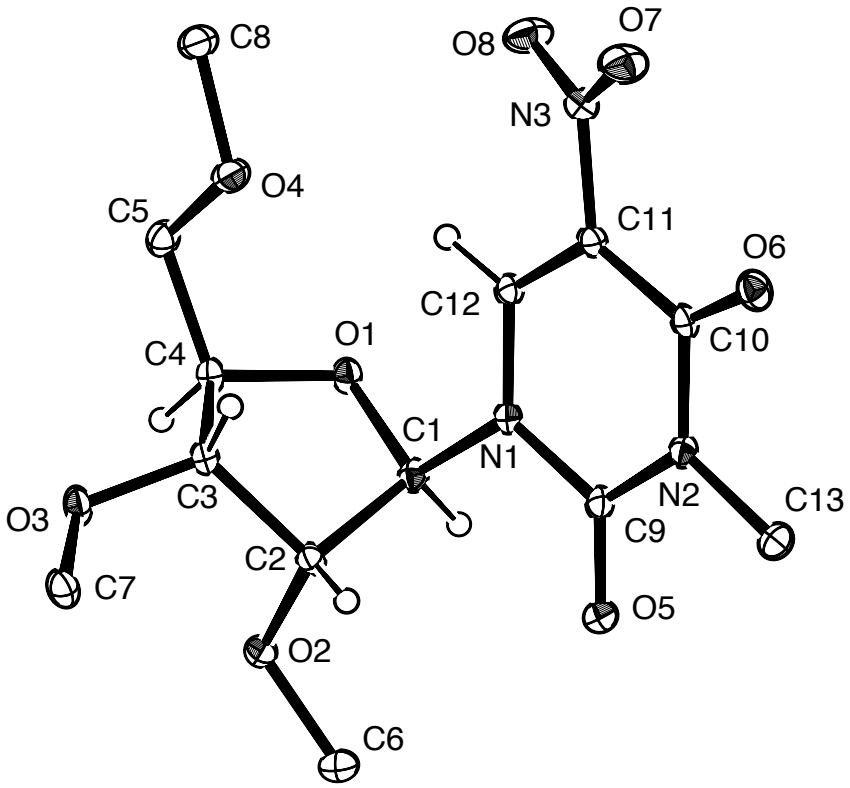
2.1 5,5-Dihydroxy-2',3',5'-tri-*O*-methyl-*N*-methyl-6-nitrouridine (4)

$C_{13}H_{21}N_3O_{10}.2(H_2O)$, M = 415.36, T = 130.0(2) K, λ= 1.5418 Å, Orthorhombic, space group $P2_12_12_1$ a = 9.5940(6), b = 11.2963(5) c =17.1360(11), *Å* , V 1857.14(19) $Å^3$, Z = 4, D_c = 1.486 Mg M^{-3} μ(Cu-Kα) 1.153 mm^{-1}, F(000) = 880, crystal size 0.16 x 0.08 x 0.04 mm. 4314 reflections measured, 2876 independent reflections (R_{int} = 0. 034) the final R was 0.0426 [I > 2σ(I)] and $wR(F^2)$ was 0.0971 (all data).



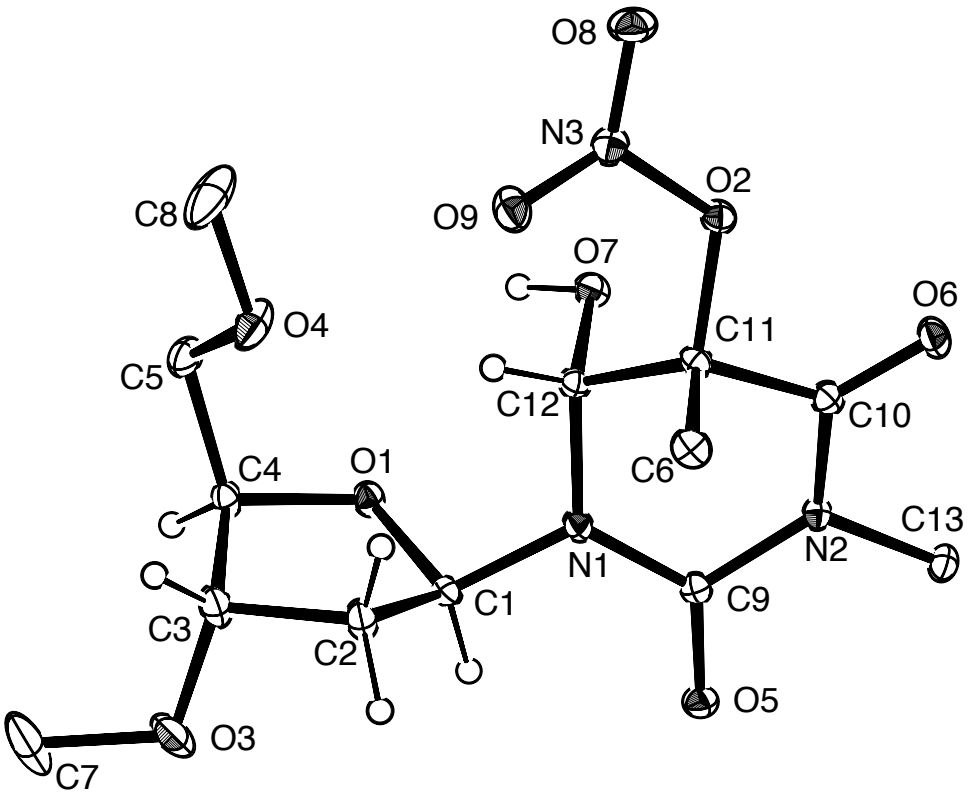
2.2 2',3',5'-Tri-*O*-methyl-*N*-methyl-6-nitrouridine (18)

$C_{13}H_{19}N_3O_8$, M = 345.31, T = 130.0 K, λ = 1.5418, Orthorhombic, space group P $2_12_12_1$, a = 5.04889(3), b = 16.43708(11), c =18.43712(13) Å, V 1530.078(13) Å^3, Z = 4, D_c = 1.499 mg M^{-3} μ(Cu-Kα) 1.080 mm^{-1}, F(000) = 728, crystal size 0.34 x 0.16 x 0.06 mm^3, 70761 reflections measured, 3250 independent reflections [R(int) = 0.0362], the final R was 0.0226 [I > 2σ(I)] and wR(F^2) was 0.0559 (all data).



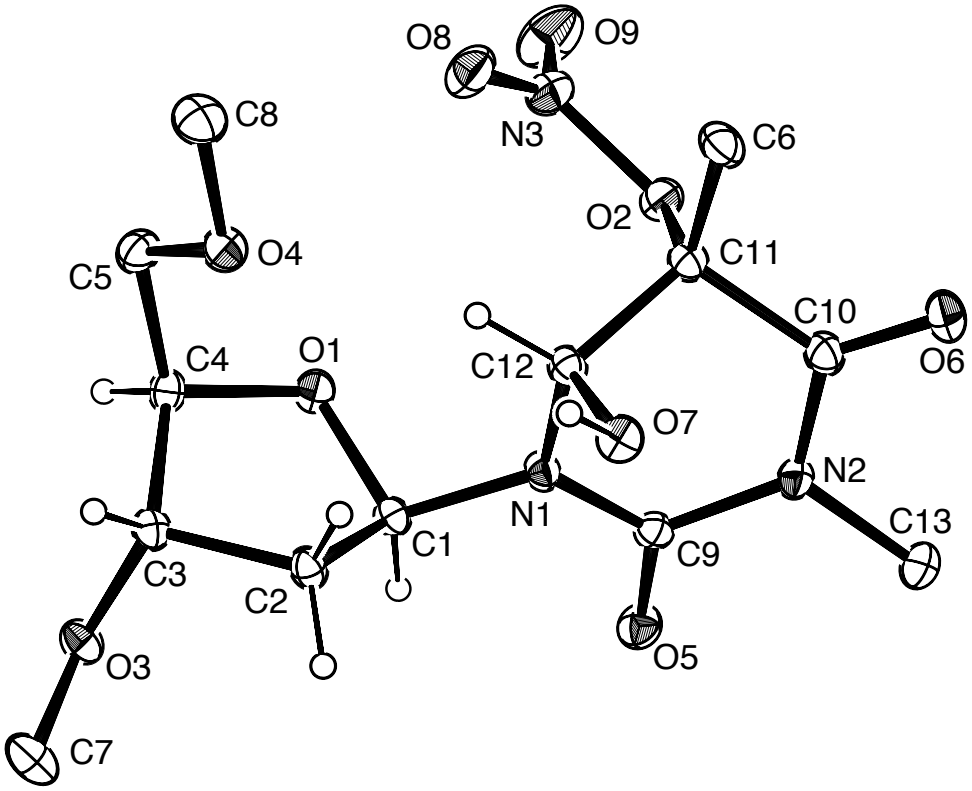
2.3 (5*S*,6*R*)-6-Hydroxy-3',5'-di-*O*-methyl-*N*-methyl-5-nitrato-2'-desoxythymidine (20a).

$C_{13}H_{21}N_3O_9$, M = 363.33, T = 130.0 K, λ= 1.5418, Orthorhombic, space group P $2_12_12_1$, a = 9.120390(6), b = 9.82523(3), c =18.52958(11) Å, V 1660.435(18) $Å^3$, Z = 4, D_c = 1.453 mg M^{-3} μ(Cu-Kα) 1.069 mm^{-1}, F(000) = 768, crystal size 0.40 x 0.18 x 0.14 mm^3, 65375 reflections measured, 3501 independent reflections [R(int) = 0.0238], the final R was 0.0224 [I > 2σ(I)] and *w*R(F^2) was 0.0592 (all data).



2.4 (5*S*,6*S*)-6-Hydroxy-3',5'-di-*O*-methyl-*N*-methyl-5-nitrato-2'-desoxythymidine (20b).

$C_{13}H_{21}N_3O_9$, M = 363.33, T = 180.0 K, λ= 1.5418, Orthorhombic, space group P $2_12_12_1$, a = 9.4820(2), b = 12.2108(3), c =14.5377(4) Å, V 1683.22(7) $Å^3$, Z = 4, D_c = 1.434 mg M^{-3} μ(Cu-Kα) 1.055 mm^{-1}, F(000) = 768, crystal size 0.26 x 0.19 x 0.16 mm^3, 19316 reflections measured, 3387 independent reflections [R(int) = 0.0370], the final R was 0.0316 [I > 2σ(I)] and $wR(F^2)$ was 0.0815 (all data).



References:

[1] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
[2] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.