Supporting Information

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General: Melting points are uncorrected. ^{1}H NMR spectra were obtained at 400 MHz using DMSO-d_6 (unless otherwise noted) as the solvent. Column chromatography was performed on silica gel (Cica Merck No. 9385; silica gel 60; 230-400 mesh). For the thin-layer chromatographic (TLC) analyses, Merck precoated TLC plates (Merck No. 5715; silica gel 60-F_{254}) were used. According to a previously reported procedure, the $^{15}N^4$-labeled cytidine and $^{15}N^4$-labeled 2'-deoxycytidine were prepared using ^{15}N-enriched benzamide (99 atom% ^{15}N, Isotec, Inc.) and the appropriate unprotected uridines as the starting materials.[3] Unless otherwise noted, the materials obtained from commercial suppliers were used without further purification.

Acid-hydrolysis of $^{15}N_3$-Labeled Uridine 4-*O*-Benzyloxime ($^{15}N_3$-Labeled 2a). A solution of the labeled oxime ($^{15}N_3$-labeled **2a**) (17.5 mg, 0.05 mmol) in methanol-1N HCl (1/1) (2.0 mL) was stirred at 60^{o}C overnight. After being neutralized with 1N NaOH and subsequent removal of the solvent under reduced pressure, the resulting residue was subjected to a silica gel short column by eluting with chloroform-methanol (5/1) to isolate the $^{15}N_3$-labeled 1-(3,4-dihydroxy-5-hydroxymethyltetrahydrofuran-2-yl)-1*H*-pyrimidin-2,4-dione (uridine) [7] (triturated with acetone, 10.0 mg, 81%): UV (MeOH): 264 and 208 nm; ^{1}H NMR: identical to the data for uridine, except δ 11.31 (1H, br d, J= ~90) ppm; HR-FABMS *m/z*: 246.0753 [calcd for $C_9H_{13}N^{15}NO_6$ (MH^+): 246.0744].

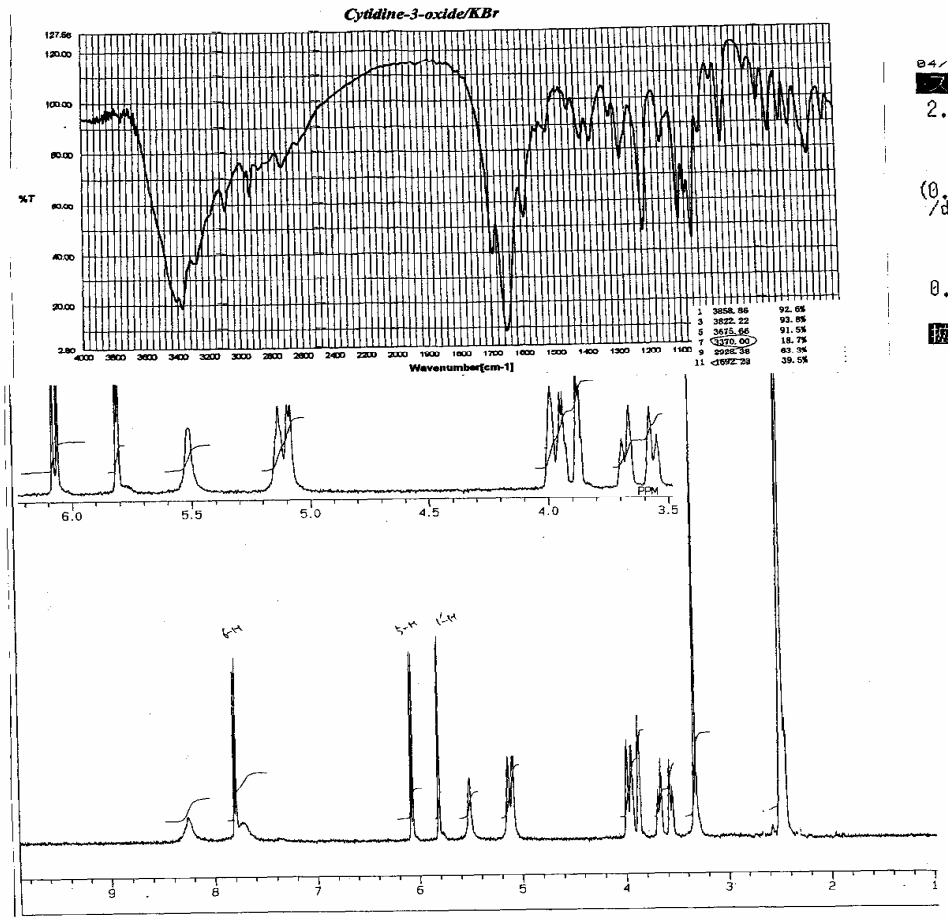
Conversion of the N_3-*O*-Benzylated 4-Iminouridine (3) to the Uridine 4-*O*-Benzyloxime (2a). A solution of the 4-iminouridine **3** (10.5 mg, 0.03 mmol) in dry methanol or acetonitrile (1.0 mL) containing lithium hydride (Aldrich, 95% purity) (1.0 mg, 0.12 mmol) was stirred at 37^{o}C

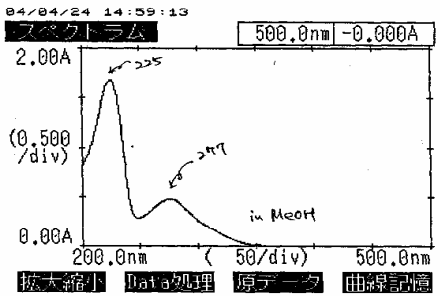
overnight under an argon atmosphere. TLC analyses of the reaction mixtures using chloroform-methanol (10/1 and 3/1) as the developing solvents showed the complete conversion of the starting **3** to the uridine 4-*O*-benzyloxime **2a** when using methanol as the solvent and the complete recovery of the starting **3** in the case of acetonitrile.

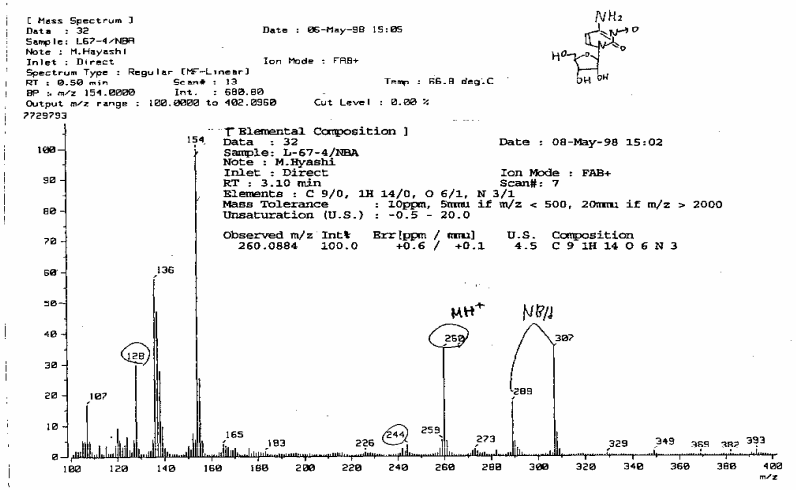
Pd/C-Reduction of the Uridine 4-*O*-Benzyloxime (2a). To a suspension of the uridine oxime (**2a**) (25 mg, 0.07 mmol) in dry methanol (1.0 mL) was added 10% Pd/C (2.5 mg), and the mixture was stirred vigorously at 60^{o}C for 1 h under a hydrogen atmosphere. TLC analyses of the reaction mixture using chloroform-methanol-acetic acid (16/6/3) and chloroform-methanol (10/1) as the developing solvents showed the complete conversion of the starting **2a** to two polar products. After removal of the solvent under reduced pressure, the resulting residue was subjected to silica gel column by eluting with chloroform-methanol (5/1 to 3/1) to isolate cytidine and uridine 4-oxime in 77% and 22% yields, respectively. The structure of the uridine 4-oxime was confirmed by spectral comparison with the authentic compound which was independently prepared by the reaction of cytidine with hydroxylamine.[Ref.]

[Ref.] Brown, D. M.; Shell, P. *J. Chem. Soc*. **1965**, 208-215.

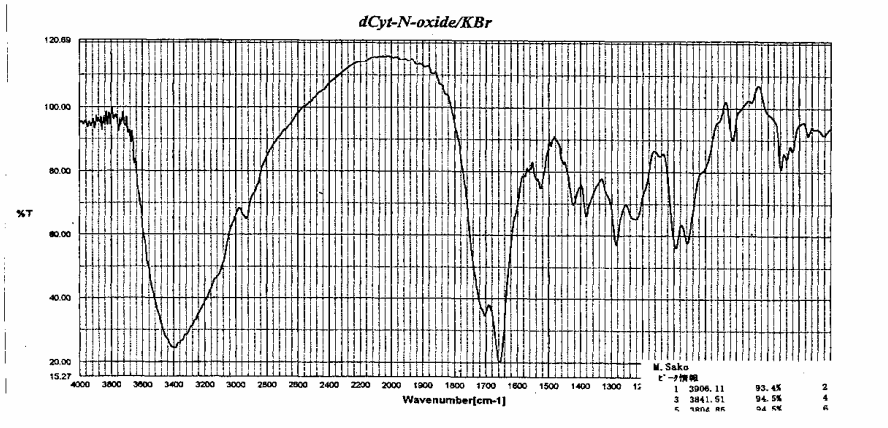
S-2: IR, UV, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of Cytidine N_3-Oxide (**1a**).

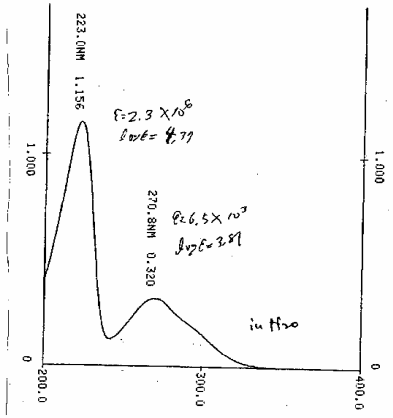


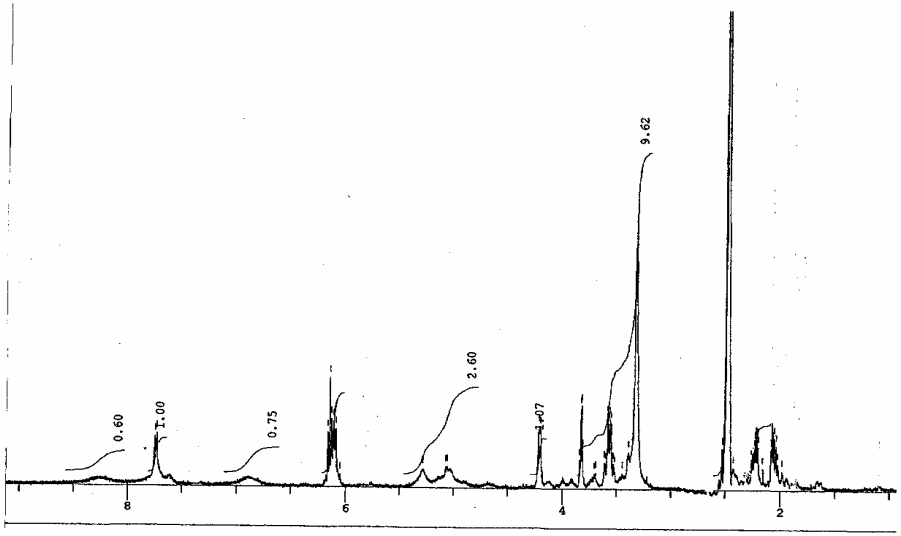


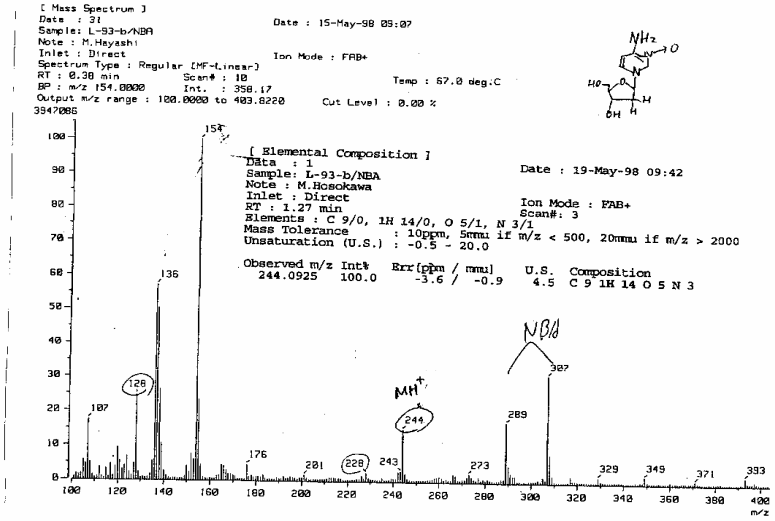


S-3: IR, UV, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of 2'-Deoxycytidine N_3-Oxide (**1b**).

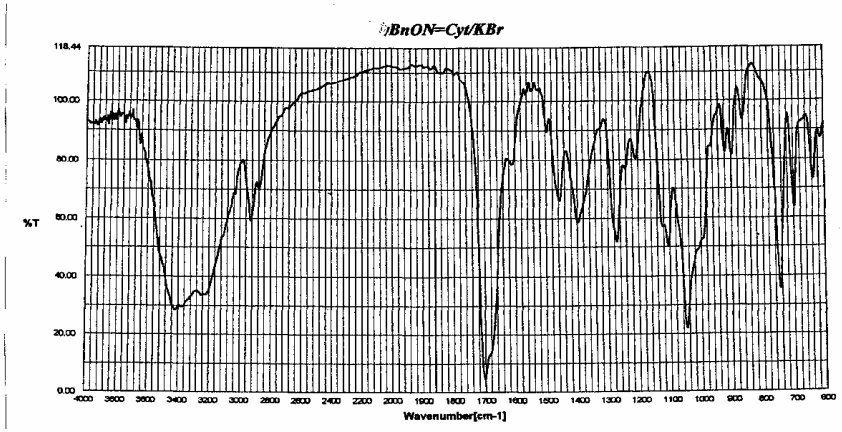


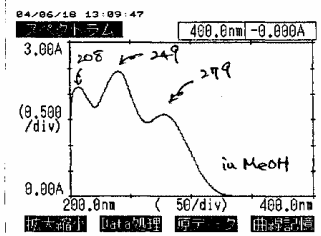


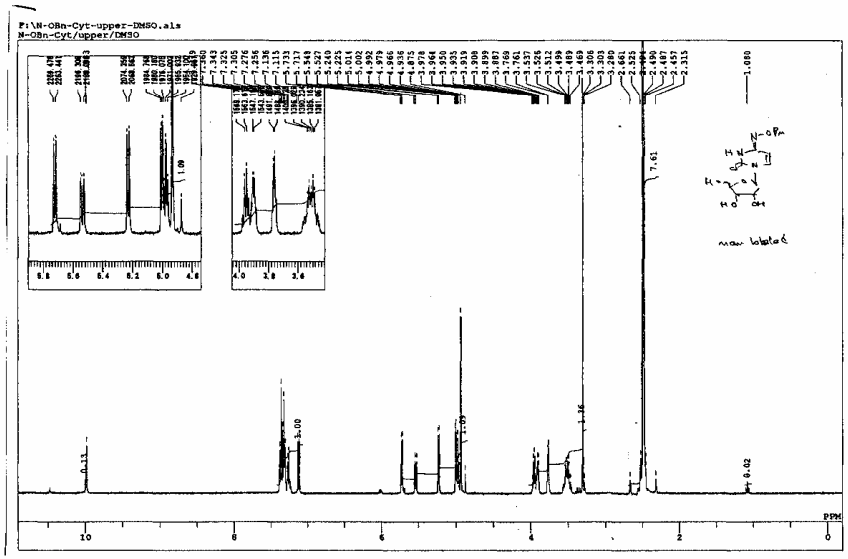


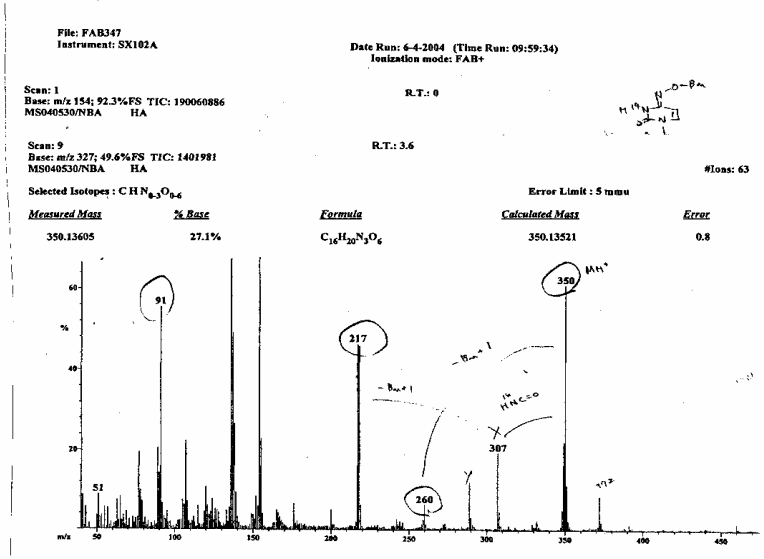


S-4: IR, UV, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of Uridine 4-*O*-Benzyloxime (**2a**).

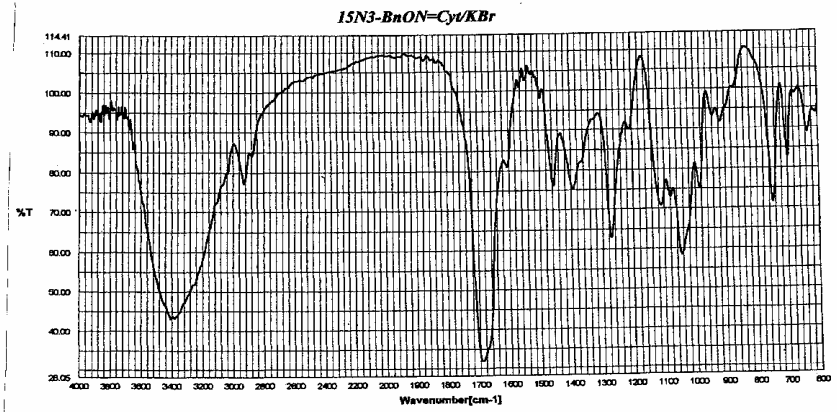


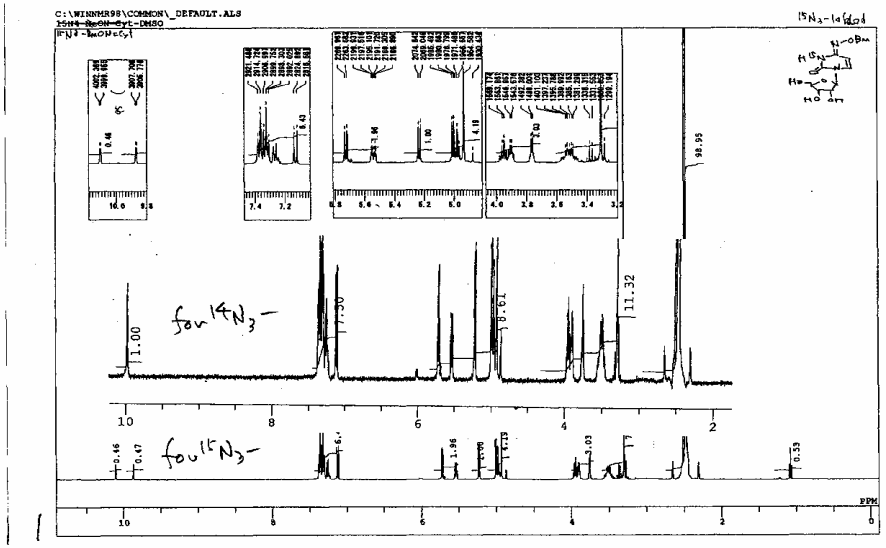






S-5: IR, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of $^{15}N_3$-Labeled Uridine 4-*O*-Benzyloxime ($^{15}N_3$-Labeled **2a**).





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R.T.: 0

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Error Limit : 5 mmu

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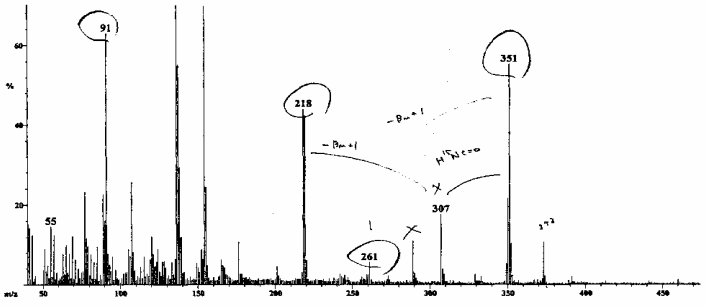
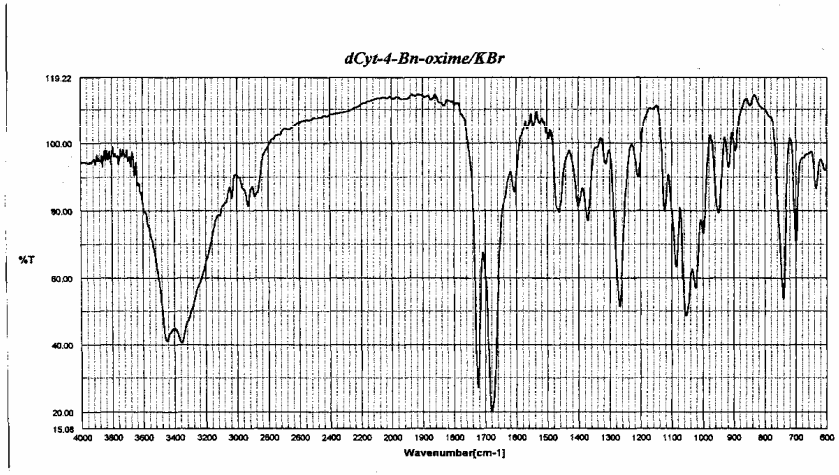
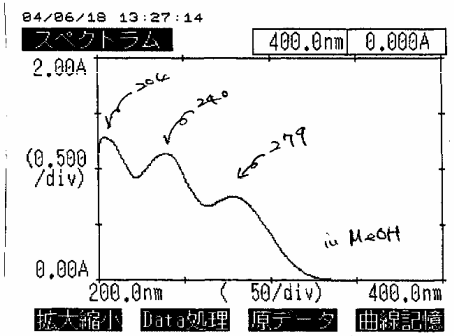
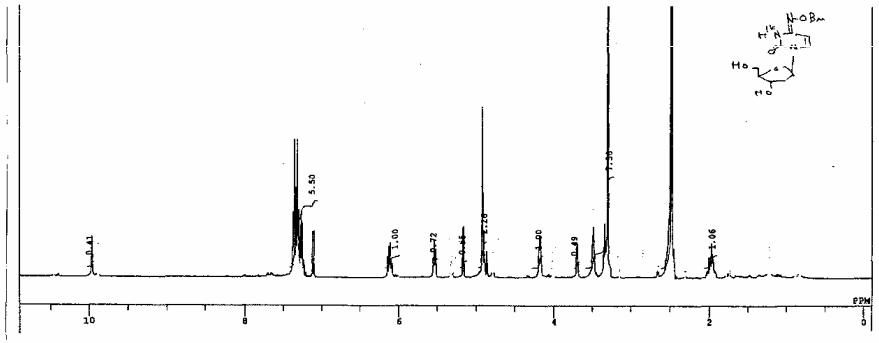
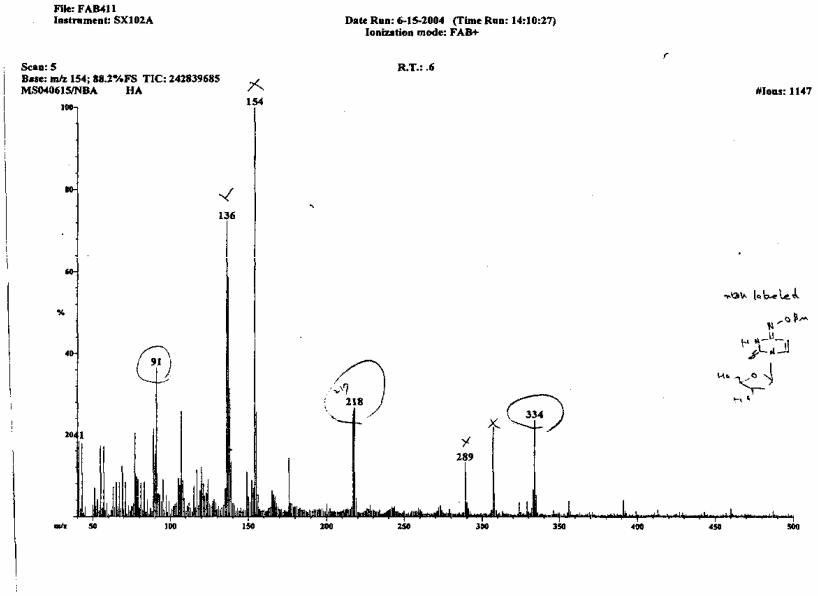


S-6: IR, UV, ^{1}H NMR, and FAB-Mass of 2'-Deoxyuridine 4-*O*-Benzyloxime (**2b**).

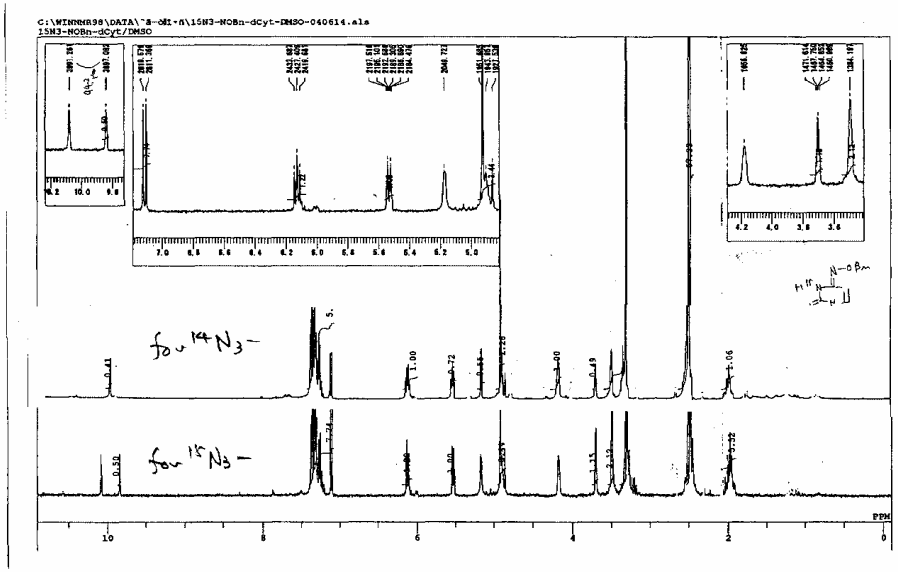


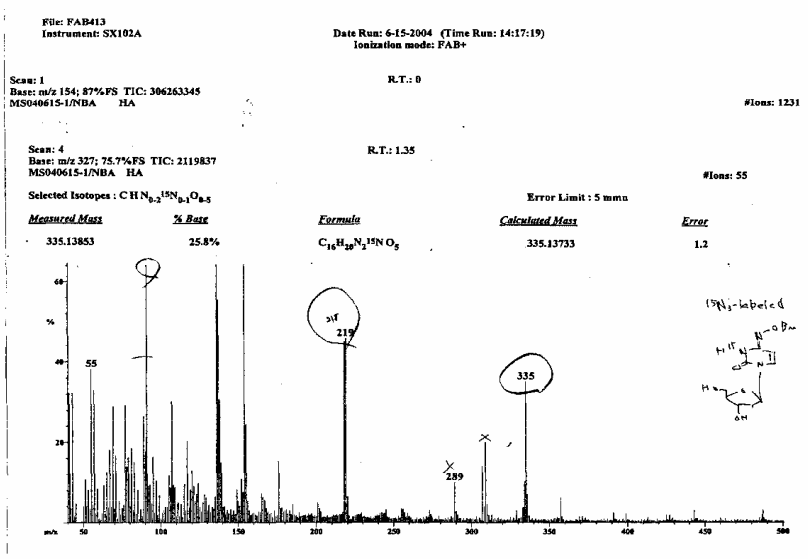




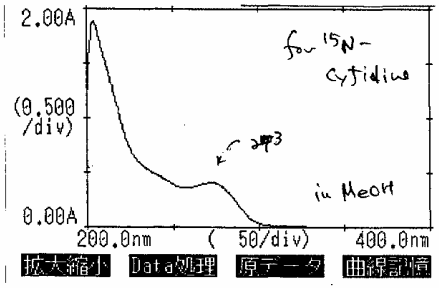


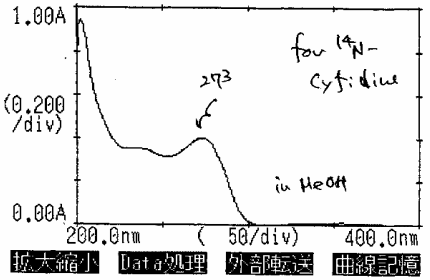
S-7: ^{1}H NMR, FAB-Mass, and HRFAB-Mass of $^{15}N_3$-Labeled 2'-Deoxyuridine 4-*O*-Benzyloxime ($^{15}N_3$-Labeled **2b**).

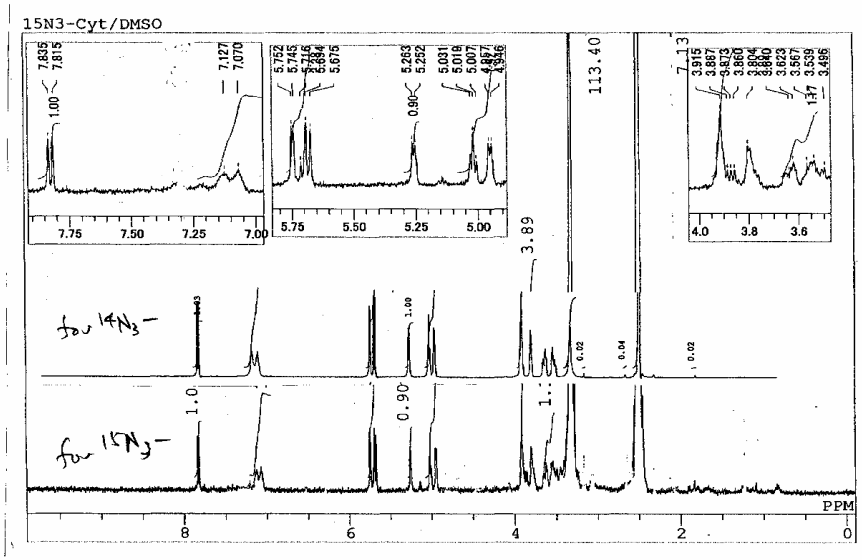


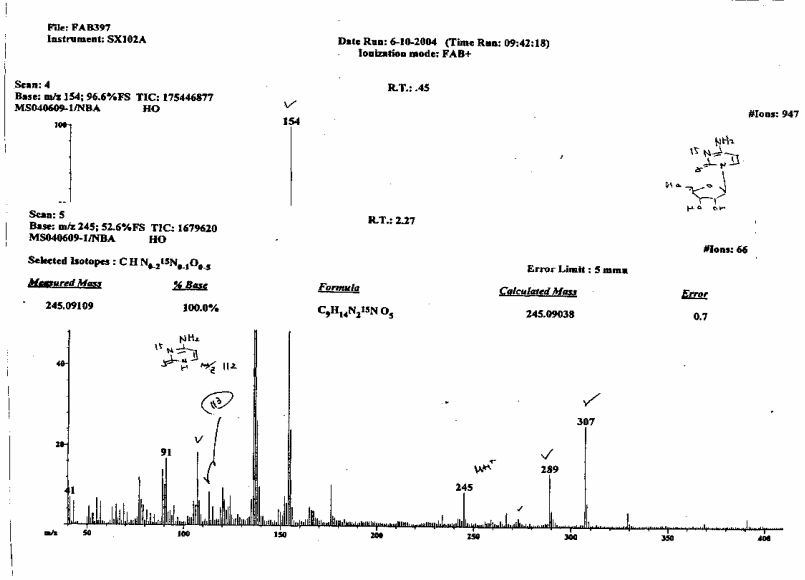


S-8: UV, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of $^{15}N_3$-Labeled Cytidine.

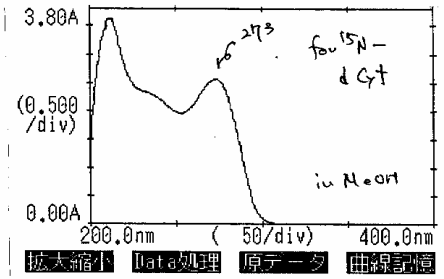


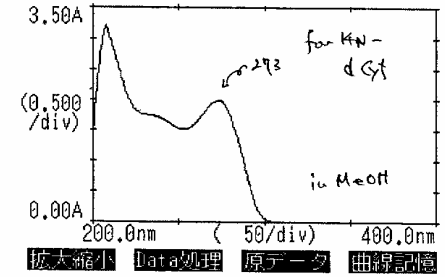


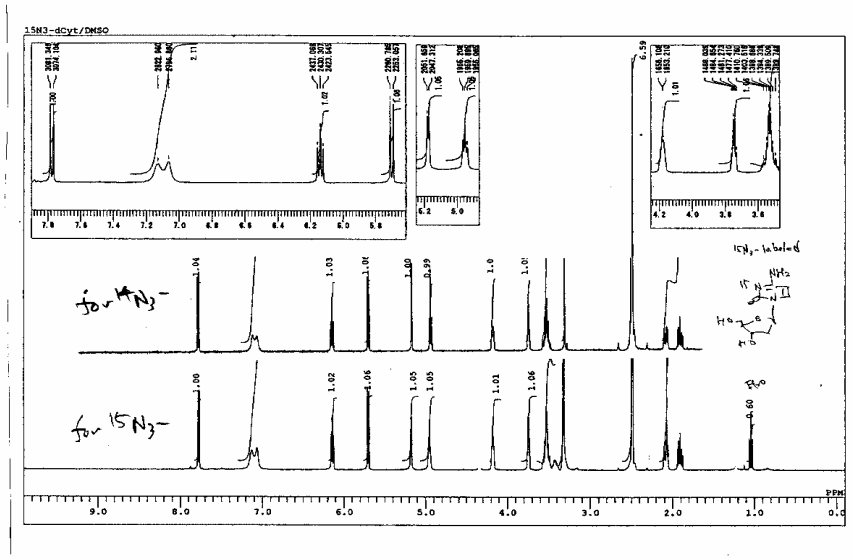


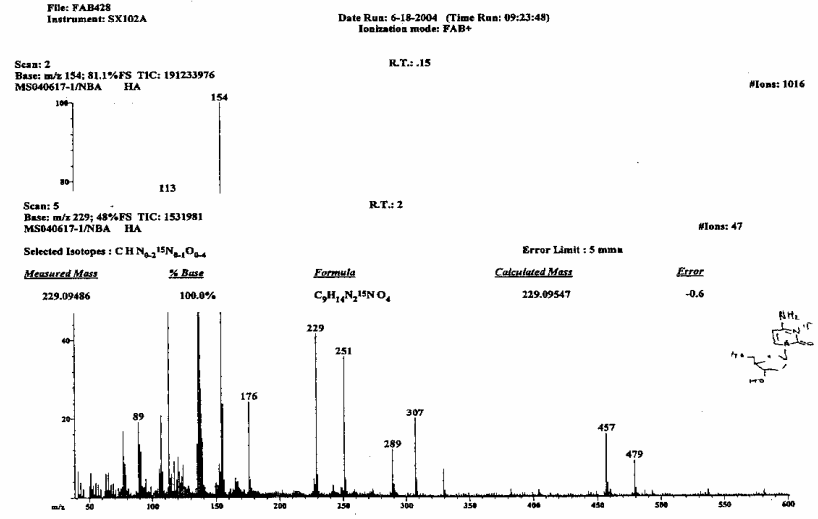


S-9: UV, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of $^{15}N_3$-Labeled 2'-Deoxycytidine.

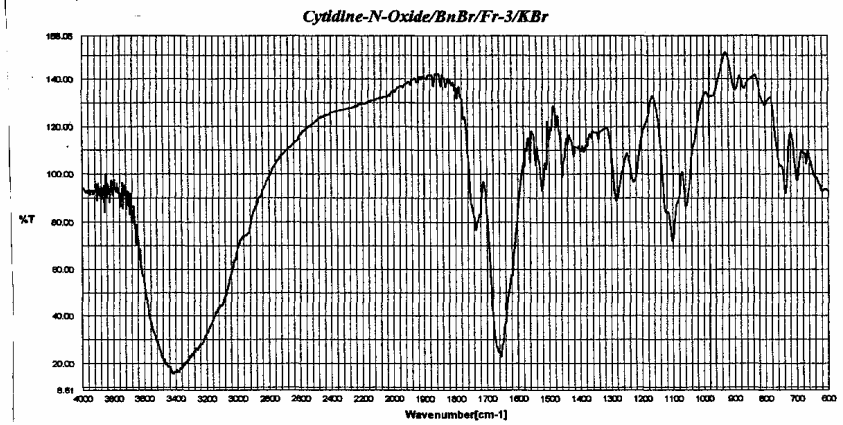


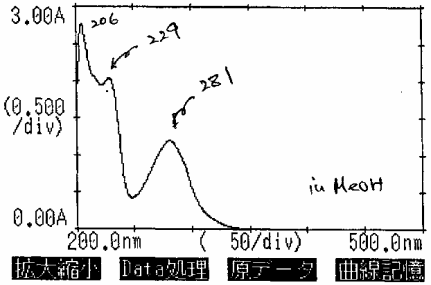


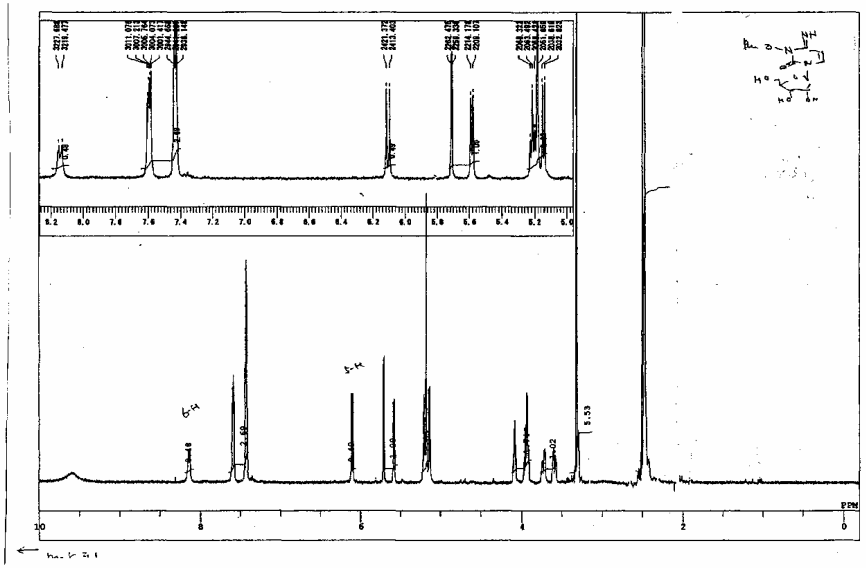


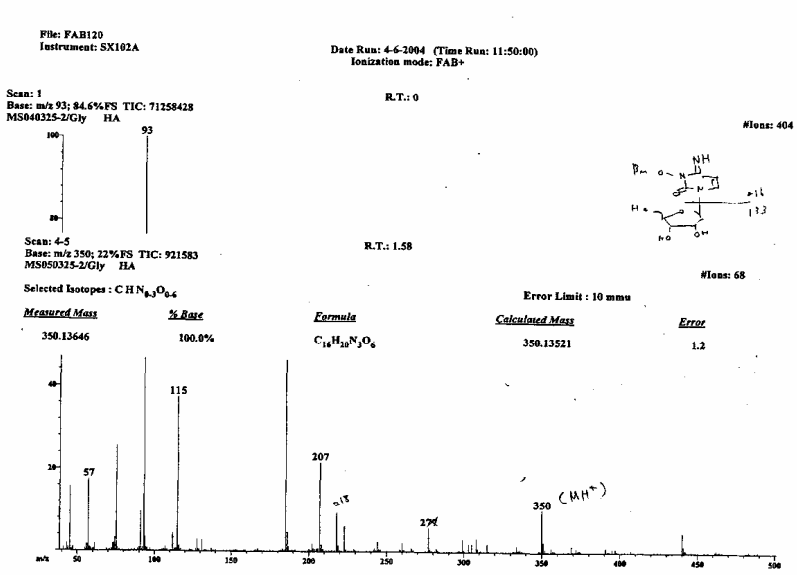


S-10: IR, UV, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of N_3-*O*-Benzylated 4-Iminouridine (**3**).

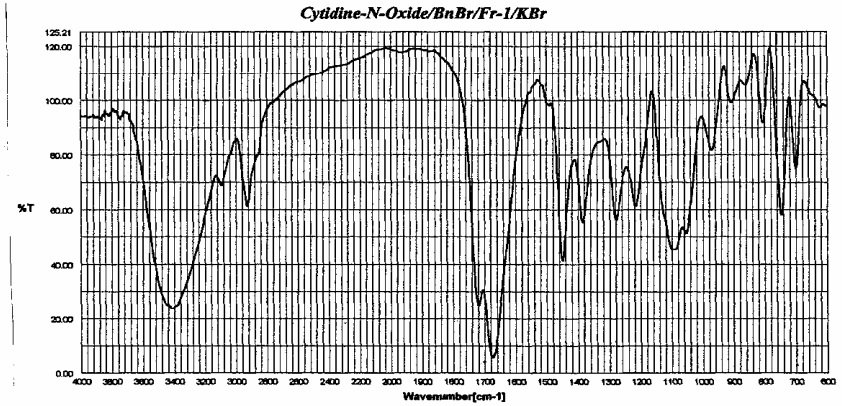


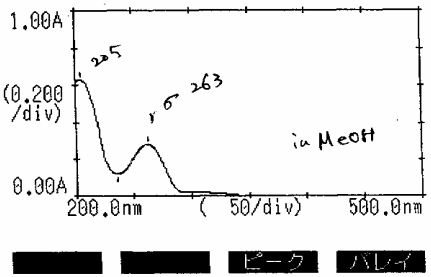


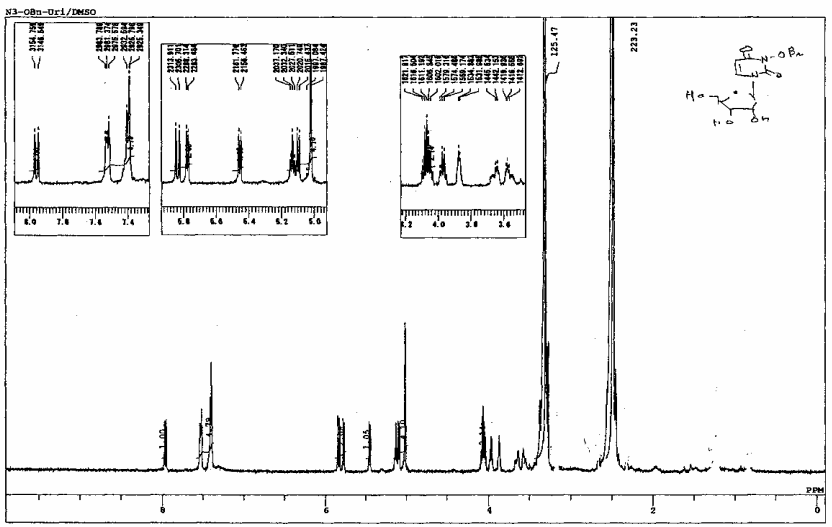


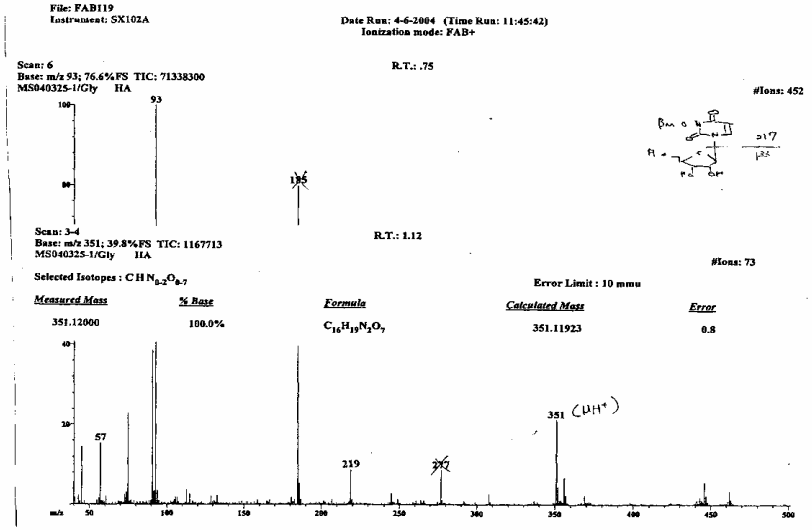


S-11: IR, UV, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of N_3-*O*-Benzylated Uridine (**4**).









S-12: UV, ^{1}H NMR, FAB-Mass, and HRFAB-Mass of $^{15}N_3$-Labeled Uridine