Electronic Supplementary Information

Efficient synthesis of 5-hydroxymethyl-, 5-formyl-, and 5-carboxyl-2′-deoxycytidine and their triphosphates

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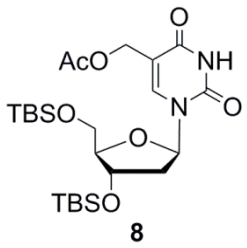
1. General Methods.

Chemical reagents and solvents were obtained from commercial suppliers. 3′,5′-diTBSdT (**7**) and tris(tetra-*n*-butylammonium) hydrogen pyrophosphate were prepared according to known procedures.[1,2] All reactions were performed under an atmosphere of dry argon and monitored by analytical thin-layer chromatography on plates coated with 0.25 mm silica gel 60 F_{254}. TLC plates were visualized by 254 nm UV light. Ion exchange chromatography employed DEAE A-25 exchanger. All NMR spectra were obtained on a 400 MHz instrument with chemical shifts reported in parts per million (ppm, δ) and referenced to $CDCl_3$, DMSO, or D_2O. IR spectra were recorded on a FT-IR spectrometer. High-resolution mass spectra were obtained with a TOFQ mass spectrometer and reported as *m/z*. HPLC traces were recorded on an analytical instrument equipped with a C18 analytical column (4.6 × 150 mm, 5 μm) [flow rate = 1.0 mL/min; linear gradient of 5% to 90% MeOH in TEAB buffer (10 mM, pH 8.5) over 20 min; UV detection at 254 nm for **1** and **2**/275 nm for **3**].

2. Synthetic procedures and characterization data for intermediates and products.

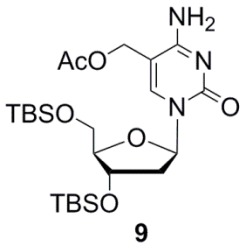
3′,5′-Di-*t*-butyldimethylsilyl-5-acetyloxymethyl-2′-deoxyuridine (8)



8

To a solution of **7** (12 g, 25.4 mmol) in dry CCl_4 (200 mL) were added recrystallized NBS (5.42 g, 30.4 mmol) and AIBN (100 mg, 0.61 mmol) at 60 °C. The reaction was refluxed for 30 min. Then, the second portion of recrystallized NBS (5.42 mg, 30.4 mmol) and AIBN (100 mg, 0.61 mmol) was added. After 1 h, the reaction mixture was cooled to room temperature and diluted with $CHCl_3$ (100 mL). The organic solution was washed with brine (200 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was dissolved in DMF (20 mL). To the solution was added CH_3COOK (4.98 g, 50.8 mmol). The resulting slurry was stirred at 40 °C for 30 min and diluted with EtOAc (200 mL). The organic solution was washed with H_2O (200 mL) and brine (200 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. Flash column chromatography (PE/EA 4:1) afforded the **8** (8.71 g, 65%) as a white solid.

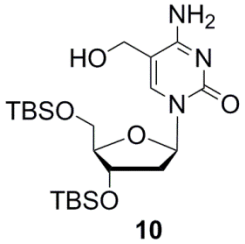
3′,5′-Di-*t*-butyldimethylsilyl-5-acetyloxymethyl-2′-deoxycytidine (9)



9

To a solution of **8** (4.22 g, 8.0 mmol), *N*-methylpiperidine (960 mg, 9.6 mmol), and Et_3N (2.44 mL, 17.6 mmol) in dry CH_3CN (80 mL) was added TsCl (3.36 g, 17.6 mmol) under an inert atmosphere at 0 °C. The reaction was stirred for 4 h. 28% NH_4OH (20 mL) was added at 0 °C, and the reaction mixture was stirred at 20 °C for 30 min and diluted with EtOAc(400 mL). The organic solution was washed with brine (400 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. Flash column chromatography (DCM/MeOH, 40:1) afforded the **9** (3.04 g, 72%) as a white solid. R_f = 0.34 (DCM/MeOH, 20:1); ^{1}H NMR (400 MHz, $CDCl_3$): 7.85 (s, 1H), 6.24 (t, J = 6.32 Hz, 1H), 4.81 (m, 2H), 4.33 (m, 1H), 3.94 (m, 1H), 3.76 (dd, 2H), 2.43 (m, 1H), 2.05 (s, 3H), 1.96 (m, 1H),0.87 (s, 18 H), 0.06 (s, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 164.8, 155.4, 142.7, 100.6, 87.9, 86.3, 71.8, 62.8, 60.6, 42.3, 25.9, 25.7, 20.8, 18.4, 18.0, –4.6. –4.9, –5.4 ppm; IR: ν_{max} 2958, 2937, 2846, 1692, 1682, 1483, 1361, 1207, 1085, 1039, 559, 457 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{24}H_{44}N_3O_6Si_2$ $[M+H]^+$ 528.2847; found 528.2859.

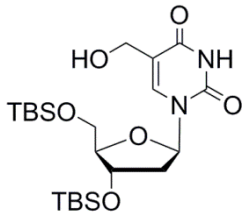
3′,5′-Di-*t*-butyldimethylsilyl-5-hydroxymethyl-2′-deoxycytidine (10)



10

To a solution of **9** (2.64 g, 5.0 mmol) in MeOH (20 mL) were added K_2CO_3 (1.38 g, 10.0 mmol) and H_2O (2 mL). The reaction was stirred at 20 °C for 2 h and concentrated in vacuo. The residue was dissolved in EtOAc (100 mL) and washed with H_2O (100 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash column chromatography (DCM/MeOH 30:1) afforded the **10** (2.23 g, 92%) as a white solid.

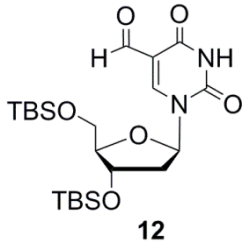
3′,5′-Di-*t*-butyldimethylsilyl-5-hydroxymethyl-2′-deoxyuridine (11)



11

To a solution of **8** (4.22 g, 8.0 mmol) in MeOH (40 mL) were added K_2CO_3 (2.20 g, 16.0 mmol) and H_2O (4 mL). The reaction was stirred at 20 °C for 2 h and concentrated in vacuo. The residue was dissolved in EtOAc (200 mL) and washed with H_2O (200 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash column chromatography (PE/EA 2:1) afforded the **11** (3.54 g, 91%) as a white solid.

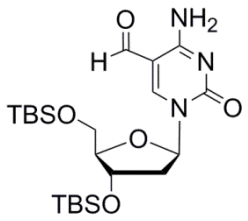
3′,5′-Di-*t*-butyldimethylsilyl-5-formyl-2′-deoxyuridine (12)



12

To a solution of **11** (2.92 g, 6.0 mmol) in DCM (40 mL) was added activated MnO_2 (10.44 g, 120.0 mmol). The reaction was stirred at 30 °C for 2 d. The reaction was cooled and filtered through a fritted funnel. The solid MnO_2 was washed with EtOAc (200 mL). The combined filtrate was concentrated in vacuo. Flash column chromatography (PE/EA 4:1) afforded the **12** (2.73 g, 94%) as a white solid.

3′,5′-Di-*t*-butyldimethylsilyl-5-formyl-2′-deoxycytidine (13)



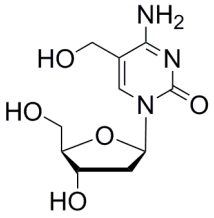
13

Method **A**：Compound **12** (2.42 g, 5 mmol) was used to synthesize **13** according to the procedure described for the preparation of **9**. Flash column chromatography (PE/EA 1:1) afforded the **13** (1.81 g, 75%) as a white solid.

Method **B**：To a solution of **10** (485 mg, 1.0 mmol) in DCM (6 mL) and H_2O (3 mL)

were added TEMPO (31 mg, 0.2 mmol) and BAIB (354 mg, 1.1 mmol). The reaction was stirred at 20 °C for 2 h and diluted with EtOAc (50 mL). The organic solution was washed with $Na_2S_2O_3$ aqueous solution (2 M, 50 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. Flash column chromatography (PE/EA 1:1) afforded the **13** (396 mg, 82%) as a white solid.

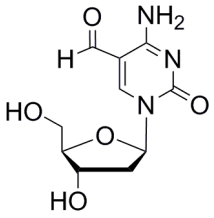
5-Hydroxymethyl-2′-deoxycytidine (4)



4

To a solution of **10** (2.9 g, 6 mmol) in THF (16 mL) were added 50% TFA aqueous solution (16 mL) at 20 °C. The reaction was stirred for 1 h and concentrated in vacuo. Flash column chromatography (DCM/MeOH 7:1) afforded the **4** (1.34 g, 87%) as a white solid.

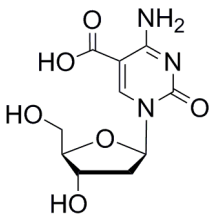
5-Formyl-2′-deoxycytidine (5)



5

To a solution of **13** (2.9 g, 6 mmol) in THF (16 mL) were added 50% TFA aqueous solution (16 mL) at 20 °C. The reaction was stirred for 1 h and concentrated in vacuo. Flash column chromatography (DCM/MeOH 7:1) afforded the **5** (1.32 g, 86%) as a white solid.

5-Carboxyl-2′-deoxycytidine (6)

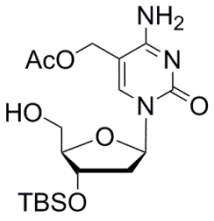


6

To a solution of **10** (2.91 g, 6.0 mmol) in DCM (50 mL) and H_2O (15 mL) were added TEMPO (187 mg, 1.2 mmol) and BAIB (4.83 g, 15 mmol). The reaction was stirred at 20 °C for 8 h and diluted with EtOAc(200 mL). The organic solution was washed with 2 M $Na_2S_2O_3$ (200 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo

to give the crude **14**. To a solution of crude **14** in THF (16 mL) were added 50% TFA aqueous solution (16 mL) at 20 °C. The reaction was stirred for 1 h and concentrated in vacuo. Flash column chromatography (DCM/MeOH 5:1 with 0.5% HOAc) afforded the **6** (1.10 g, 68%) as a white solid.

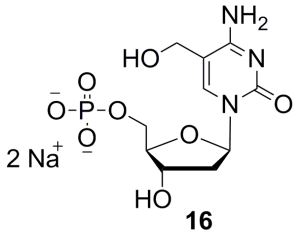
3′-*t*-Butyldimethylsilyl-5-formyl-2′-deoxycytidine (15)



15

To a solution of **9** (528 mg, 1.0 mmol) in THF (8 mL) were added 50% TFA aqueous solution (4 mL). The reaction was stirred for 2 h at 0 °C. The reaction mixture was diluted with EtOAc (100 mL). The organic solution was washed with H_2O (80 mL), saturated Na_2CO_3 aqueous solution (80 mL), and brine (80 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash column chromatography (DCM/MeOH 15:1) afforded the **15** (297 mg, 72%) as a white solid. R_f = 0.43 (DCM/MeOH 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (br, 1H), 7.97 (s, 1H), 6.12 (br, 1H), 6.08 (t, J = 6.2 Hz, 1H), 4.77 (s, 2H), 4.41 (m, 1H), 3.91 (m, 1H), 3.77 (dd, 2H), 2.26 (m, 2H), 1.98 (s, 3H), 0.82 (s, 9 H), 0.01 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 164.9, 155.6, 144.3, 101.1, 88.1, 87.8, 61.5, 60.5, 41.5, 25.7, 20.9, 17.9, –4.7, –4.9 ppm; IR: ν_{max} 2960, 1722, 1374, 1258, 1017, 763, 559, 457 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{18}H_{31}N_3O_6Si$ $[M+H]^+$ 414.1932; found 414.1917.

5-Hydroxymethyl-2′-deoxycytidine 5′-monophosphate, disodium salt (16)

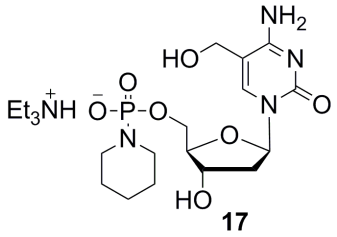


16

To a solution of **15** (515 mg, 1.25 mmol) in dry $PO(OCH_3)_3$ (10 mL) were added $POCl_3$ (380 mg, 2.5 mmol). The reaction was stirred at 0 °C for 2 h. The reaction mixture was then quenched by the slow addition of 0.1 M triethylammonium bicarbonate (TEAB) buffer (40 mL) followed by extraction with diethyl ether (40 mL×3). The aqueous layer was collected and concentrated in vacuo. To the residue were added TFA (5 mL) and H_2O (5 mL). The reaction was stirred at 20 °C for 1 h and concentrated in vacuo. MeOH (10 mL), K_2CO_3 (345 mg, 2.5 mmol), and H_2O (1 mL) were added to the solution. The reaction was stirred at 20 °C for 1 h and concentrated in vacuo. The crude product was dissolved in deionized H_2O (0.5 mL) and loaded on a DEAE Sephadex A-25 ion exchange column (1.6 × 25 cm). Elution

with NH_4HCO_3 buffer (linear gradient 0.1 to 0.4 M), combination of appropriate fractions, and lyophilization afforded the **16** in ammonium salt form. Passage of the solution of the ammonium salt in deionized H_2O through a bed of Dowex 50W-X8 ion exchange resin (Na^+ form) and lyophilization afforded the **16** (299 mg, 64%) as disodium salt, a white solid; ^{1}H NMR (400 MHz, D_2O): δ 7.90 (s, J = 6.6 Hz, 1H), 4.42 (m, 3H), 4.02 (m, 1H), 3.77 (dd, 2H), 2.40 (m, 1H), 2.29 (m, 1H) ppm; ^{13}C NMR (100 MHz, D_2O): δ 163.8, 155.7, 140.4, 106.2, 86.3, 85.8, 69.9, 60.7, 57.2, 38.9 ppm; ^{31}P NMR (162 MHz, D_2O): δ 0.13 ppm; IR: ν_{max} 3354, 2937, 2846, 2677, 1682, 1085, 1039, 932, 508, 455 cm^{-1}; HRMS (ESI–): *m/z* calcd for $C_{10}H_{16}N_3O_8P$ $[M–H]^–$ 336.0686; found 336.0656.

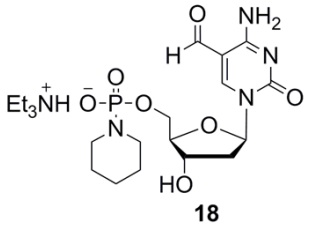
5-Hydroxymethyl-2′-deoxycytidine 5′-phosphoropiperidate, triethylammonium salt (17)



17

To a solution of **16** (175 mg, 0.4 mmol, triethylammonium salt) and piperidine (170 mg, 2.0 mmol) in DMSO (4 mL) were added 2,2′-dithiodianiline (300 mg, 1.2 mmol) and triphenylphosphine (260mg, 1 mmol). The solution was stirred at 20 °C for 8 h. A solution of NaI in acetone (0.5 M, 5 mL) was added dropwise to the reaction mixture. The resulting white precipitate was collected by centrifuge. Passage of the solution of the sodium salt in deionized H_2O through a bed of Dowex 50W-X8 ion exchange resin (Et_3NH^+ form) and lyophilization afforded **17** (190 mg, 94%) as white foam; ^{1}H NMR (400 MHz, D_2O): δ 7.94 (s, 1H), 6.25 (d, J = 6.6 Hz, 1H), 4.54 (m, 1H), 4.50 (s, 1H), 3.96 (dd, 2H), 3.17 (q, J = 7.2 Hz, 6H), 2.91 (m, 4H), 1.35 (m, 6H), 2.49 (m, 1H), 2.44 (m, 1H), 1.43 (m, 4H), 1.25 (t, J = 7.2 Hz, 9H) ppm; ^{13}C NMR (100 MHz, D_2O): δ 165.1, 157.4, 140.6, 106.7, 86.5, 86.2, 71.1, 64.0, 57.8, 45.8, 44.6, 40.0, 25.7, 24.1, 8.3 ppm; ^{31}P NMR (162 MHz, D_2O): δ 7.96 ppm; IR: ν_{max} 3459, 1660, 1561, 1453, 1332, 1123, 967, 754, 654 cm^{-1}; HRMS (ESI–): *m/z* calcd for $C_{15}H_{25}N_4O_7P$ $[M–H]^–$ 403.1461; found 403.1449.

5-Formyl-2′-deoxycytidine 5′-phosphoropiperidate, triethylammonium salt (18)

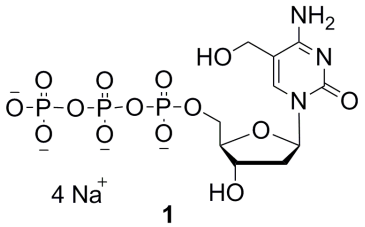


18

To a solution of **17** (101 mg, 0.2 mmol) in MeOH (5 mL) was added activated MnO_2 (174 mg, 2 mmol). The reaction was stirred at 50 °C for 24 h. The reaction solution was cooled and filtered through a fritted funnel. The MnO_2 was washed with MeOH

(50 mL). The combined filtrate was concentrated in vacuo. Flash column chromatography (DCM/MeOH 5:1 with 0.5% Et_3N) afforded **18** (85 mg, 84%) as a white foam. R_f = 0.35 (DCM/MeOH 4:1 with 0.5% Et_3N); ^{1}H NMR (400 MHz, D_2O): δ 9.52 (s, 1H), 8.60 (s, 1H), 5.87 (t, J = 6.0 Hz, 1H), 4.51 (m, 1H), 4.13 (m, 1H), 3.79 (dd, 2H), 3.00 (q, J = 7.2 Hz, 6H), 2.62 (m, 4H), 2.38 (m, 1H), 2.17 (m, 1H), 1.15 (m, 1H), 1.06 (t, J = 7.2 Hz, 9H) ppm; ^{13}C NMR (100 MHz, D_2O): δ 190.7, 162.7, 155.2, 154.5, 105.0, 81.8, 74.1, 64.5, 60.5, 60.4, 51.1, 46.7, 45.6, 25.6, 24.0, 8.3 ppm; IR: ν_{max} 3198, 2937, 2846, 2677, 1682, 1483, 1361, 1207, 1085, 1039, 932, 824 cm^{-1}; HRMS (ESI–): *m/z* calcd for $C_{15}H_{23}N_4O_7P$ $[M–H]^–$ 401.1310; found 401.1336.

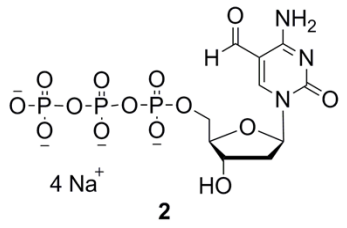
5-Hydroxymethyl-2′-deoxycytidine 5′-triphosphate, tetrasodium salt (1)



1

To a solution of **17** (50 mg, 0.1 mmol) in DMF (2 mL) were added tris(tetra-*n*-butylammonium) hydrogen pyrophosphate (180 mg, 0.2 mmol) and 4,5-dicyanoimidazole (71 mg, 0.6 mmol). The reaction was stirred at 20 °C for 6 h and concentrated in vacuo. The residue was dissolved in NaOAc aqueous solution (3 M, 0.5 mL). Then, EtOH (20 mL) was added. The resulting white precipitate was collected by centrifuge. The crude product was dissolved in deionized H_2O (0.5 mL) and loaded on a DEAE Sephadex A-25 ion exchange column (1.6 × 25 cm). Elution with NH_4HCO_3 buffer (linear gradient 0.2 to 0.6 M), combination of appropriate fractions, and lyophilization afforded **1** in ammonium salt form. Passage of the solution of the ammonium salt in deionized H_2O through a bed of Dowex 50W-X8 ion exchange resin (Na^+ form) and lyophilization afforded the **1** (42 mg, 72%) as tetrasodium salt, a white solid; ^{1}H NMR (400 MHz, D_2O): δ 7.92 (s, 1H), 6.21 (t, J = 6.4 Hz, 1H), 4.56 (m, 1H), 4.39 (s, 2H,), 4.13 (m, 3H), 2.31 (m, 1H), 2.24 (m, 1H) ppm; ^{13}C NMR (100 MHz, D_2O): δ 165.2, 157.4, 140.6, 107.1, 86.0, 85.7, 70.3, 65.1, 57.7, 39.5 ppm; ^{31}P NMR (162 MHz, D_2O): δ –8.2 (d, $J_{P\text{-}\gamma,P\text{-}\beta}$ = 18.1 Hz, 1P), –11.3 (d, $J_{P\text{-}\alpha,P\text{-}\beta}$ = 17.9 Hz, 1P), –22.4 (dd, $J_{P\text{-}\beta,P\text{-}\alpha}$ = $J_{P\text{-}\beta,P\text{-}\gamma}$ = 18.4 Hz, 1P) ppm; IR: ν_{max} 3346, 2986, 2856, 1694, 1413, 1226, 1080, 924, 813 cm^{-1}; HRMS (ESI–): *m/z* calcd for $C_{10}H_{18}N_3O_{14}P_3$ $[M–H]^–$ 495.9711; found 495.9733.

5-Formyl-2′-deoxycytidine 5′-triphosphate, tetrasodium salt (2)

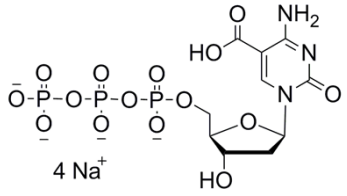


2

Compound **18** (50 mg, 0.1 mmol) was used to synthesize **2** according to the procedure

described for **1**. Passage of the solution of the ammonium salt in deionized H_2O through a bed of Dowex 50W-X8 ion exchange resin (Na^+ form) and lyophilization afforded **2** (44 mg, 76%) as tetrasodium salt, a white solid; ^{1}H NMR (400 MHz, D_2O): δ 9.58 (s, 1H), 8.81 (s, 1H), 6.16 (t, J = 5.9 Hz, 1H), 4.57 (m, 1H,), 4.22 (m, 3H), 2.40 (m, 2H) ppm; ^{13}C NMR (100 MHz, D_2O): δ 191.5, 162.8, 155.5, 154.6, 105.9, 87.2, 86.0, 69.5, 64.7, 40.0 ppm; ^{31}P NMR (162 MHz, D_2O): δ –6.7 (d, $J_{P\text{-}\gamma,P\text{-}\beta}$ = 19.7 Hz, 1P), –11.3 (d, $J_{P\text{-}\alpha,P\text{-}\beta}$ = 18.8 Hz, 1P), –22.2 (dd, $J_{P\text{-}\beta,P\text{-}\alpha}$ = $J_{P\text{-}\beta,P\text{-}\gamma}$ = 19.6 Hz, 1P) ppm; IR: ν_{max} 3338, 2947, 2570, 2311, 1889, 1176, 1087, 758, 508 cm^{-1}; HRMS (ESI–): *m/z* calcd for $C_{10}H_{16}N_3O_{14}P_3$ $[M–H]^–$ 493.9867; found 493.9888.

5-Carboxyl-2′-deoxycytidine 5′-triphosphate, tetrasodium salt (3)



3

To a solution of **1** (49 mg, 0.1 mmol, triethylammonium salt) in *t*BuOH/DCM/H_2O (2 /2/0.5 mL) were added TEMPO (6.2 mg, 0.04 mmol) and BAIB (81 mg, 0.25 mmol). The reaction was stirred at 20 °C for 48 h and diluted with H_2O (10 mL). The solution was washed with DCM (10 mL). The aqueous layer was collected and concentrated in vacuo. The residue was dissolved in deionized H_2O (0.5 mL) and loaded on a DEAE Sephadex A-25 ion exchange column (1.6 × 25 cm). Elution with NH_4HCO_3 buffer (linear gradient 0.2 to 0.7 M), combination of appropriate fractions, and lyophilization afforded **3** in ammonium salt form. Passage of the solution of the ammonium salt in deionized H_2O through a bed of Dowex 50W-X8 ion exchange resin (Na^+ form) and lyophilization afforded **3** (47 mg, 78%) as tetrasodium salt, a white solid; ^{1}H NMR (400 MHz, D_2O): δ 8.39 (s, 1H), 6.23 (t, J = 6.5 Hz, 1H), 4.56 (m, 1H), 4.18 (m, 3H), 2.36 (dd, 2H) ppm; ^{13}C NMR (100 MHz, D_2O): δ 170.1, 164.6, 156.3, 146.0, 103.0, 86.1, 85.0, 70.4, 65.2, 38.5 ppm; ^{31}P NMR (162 MHz, D_2O): δ –9.1 (d, $J_{P\text{-}\gamma,P\text{-}\beta}$ = 18.3 Hz, 1P), –10.8 (d, $J_{P\text{-}\alpha,P\text{-}\beta}$ = 17.9 Hz, 1P), –22.2 (dd, $J_{P\text{-}\beta,P\text{-}\alpha}$ = $J_{P\text{-}\beta,P\text{-}\gamma}$ = 18.4 Hz, 1P) ppm; IR: ν_{max} 3606, 1570, 2311, 1678, 931, 794, 621, 465 cm^{-1}; HRMS (ESI–): *m/z* calcd for $C_{10}H_{16}N_3O_{15}P_3$ $[M–H]^–$ 509.9816.; found 509.9843.

3. ^{1}H, ^{13}C, and ^{31}P NMR spectra of intermediates and products.

Figure S1. ^{1}H NMR Spectrum of **9**

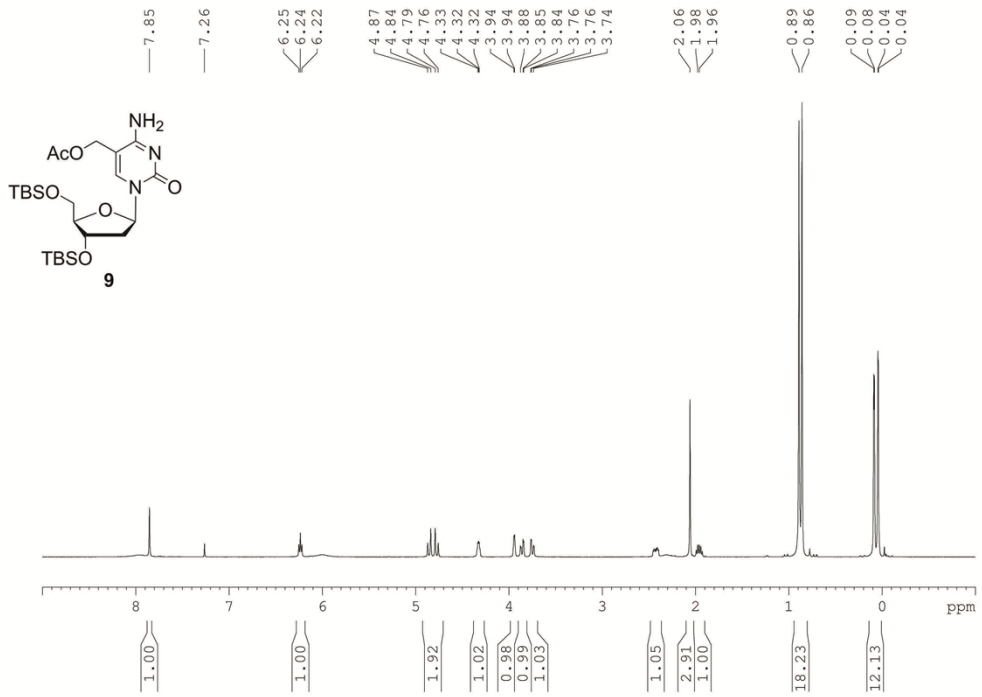


Figure S2. ^{13}C NMR Spectrum of **9**

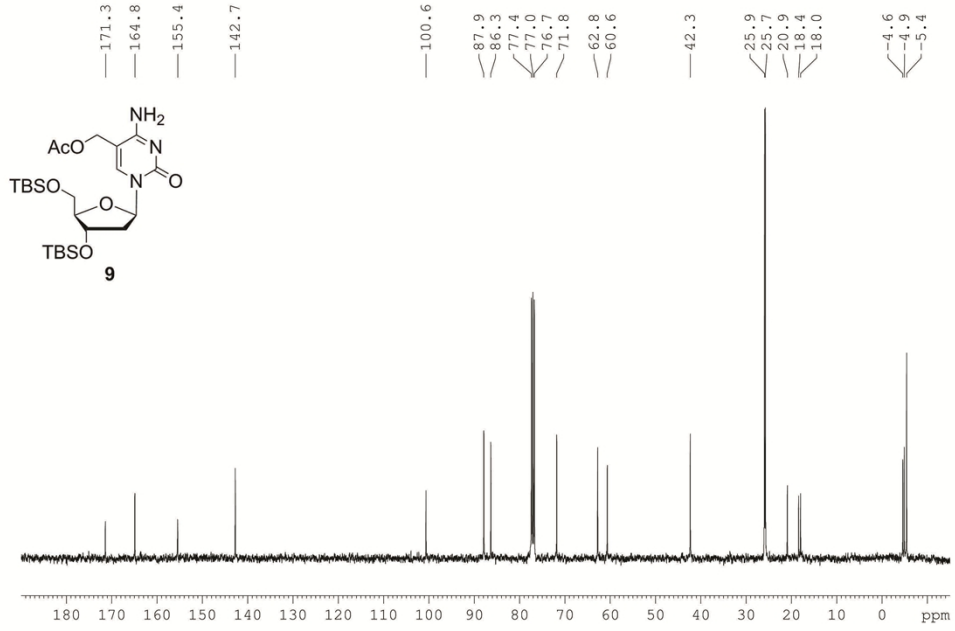


Figure S3. ^{1}H NMR Spectrum of **15**

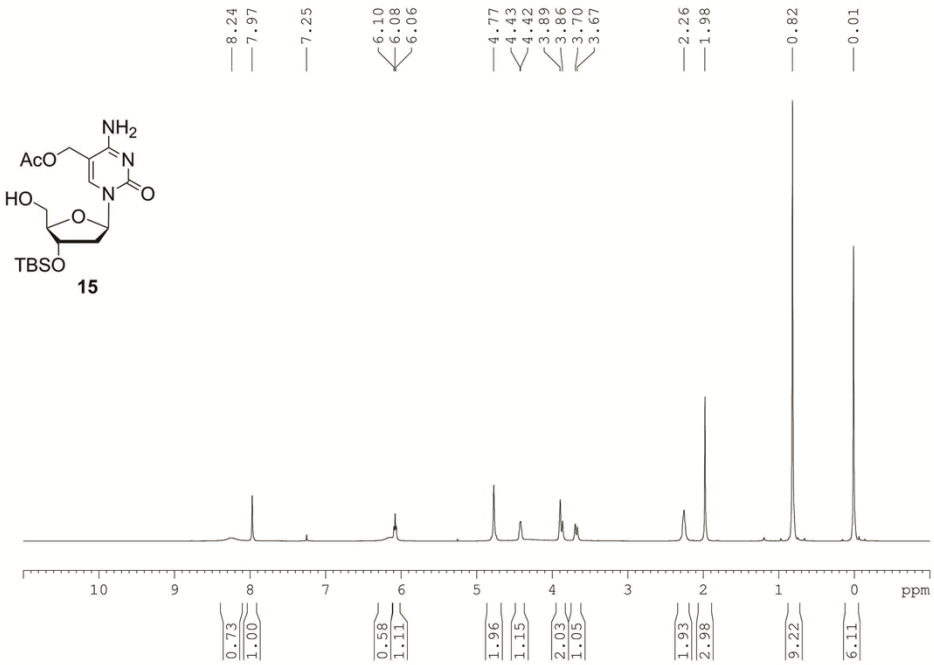


Figure S4. ^{13}C NMR Spectrum of **15**

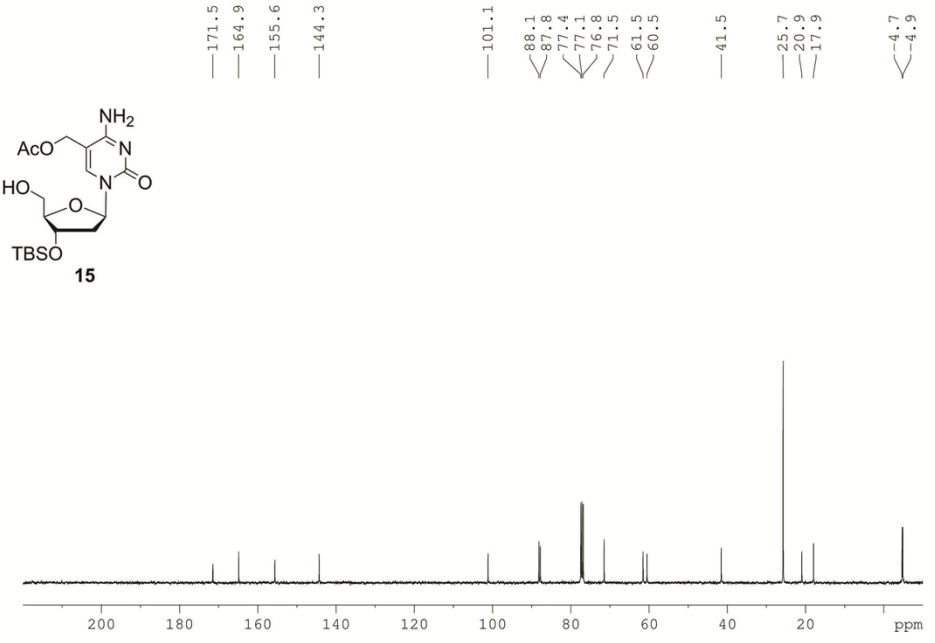


Figure S5. ^{1}H NMR Spectrum of **16**

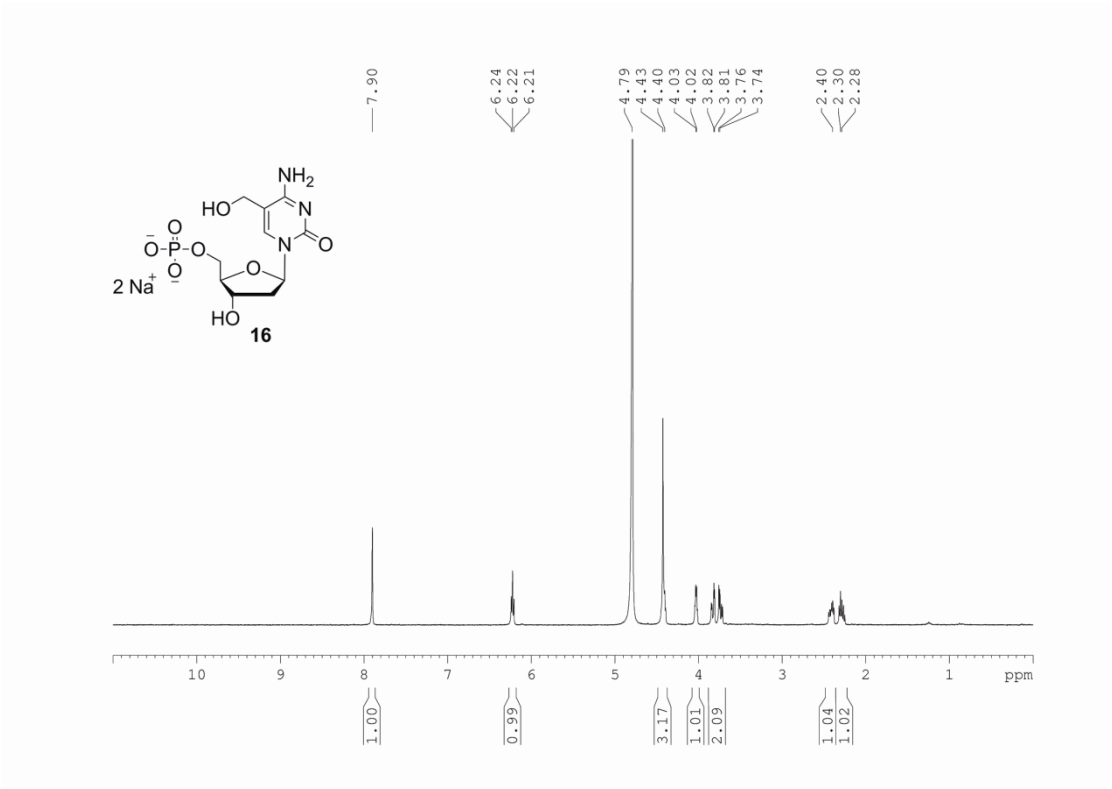


Figure S6. ^{13}C NMR Spectrum of **16**

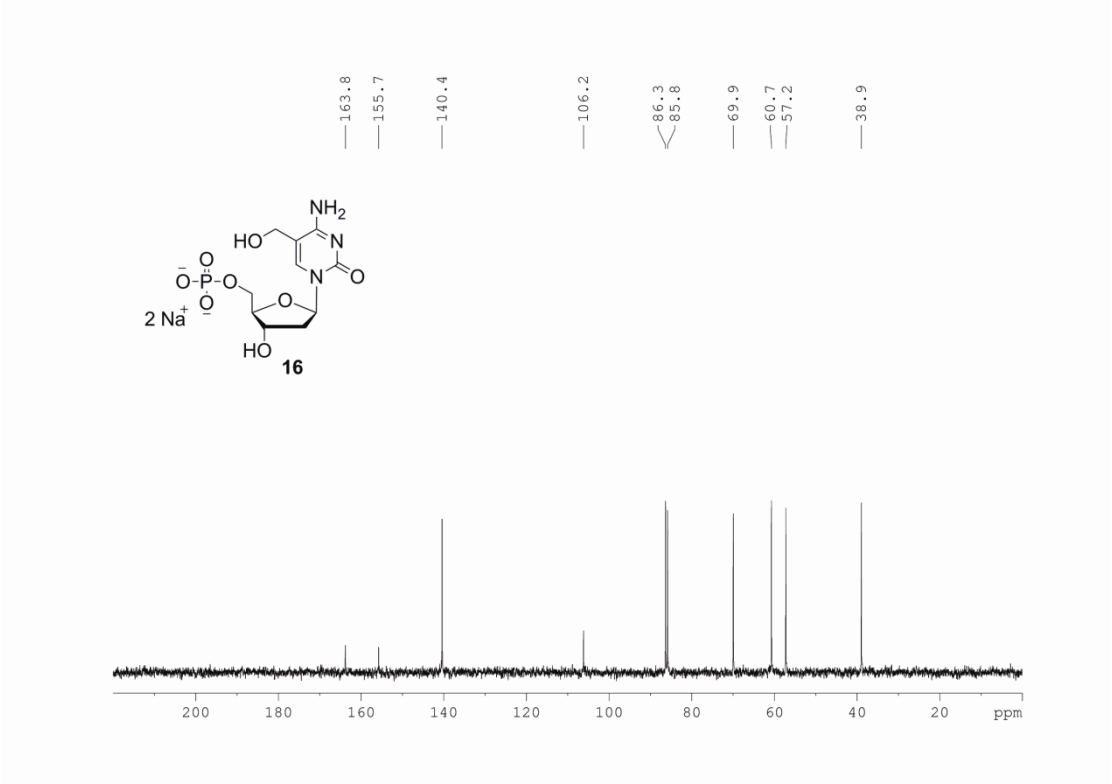


Figure S7. ^{31}P NMR Spectrum of **16**

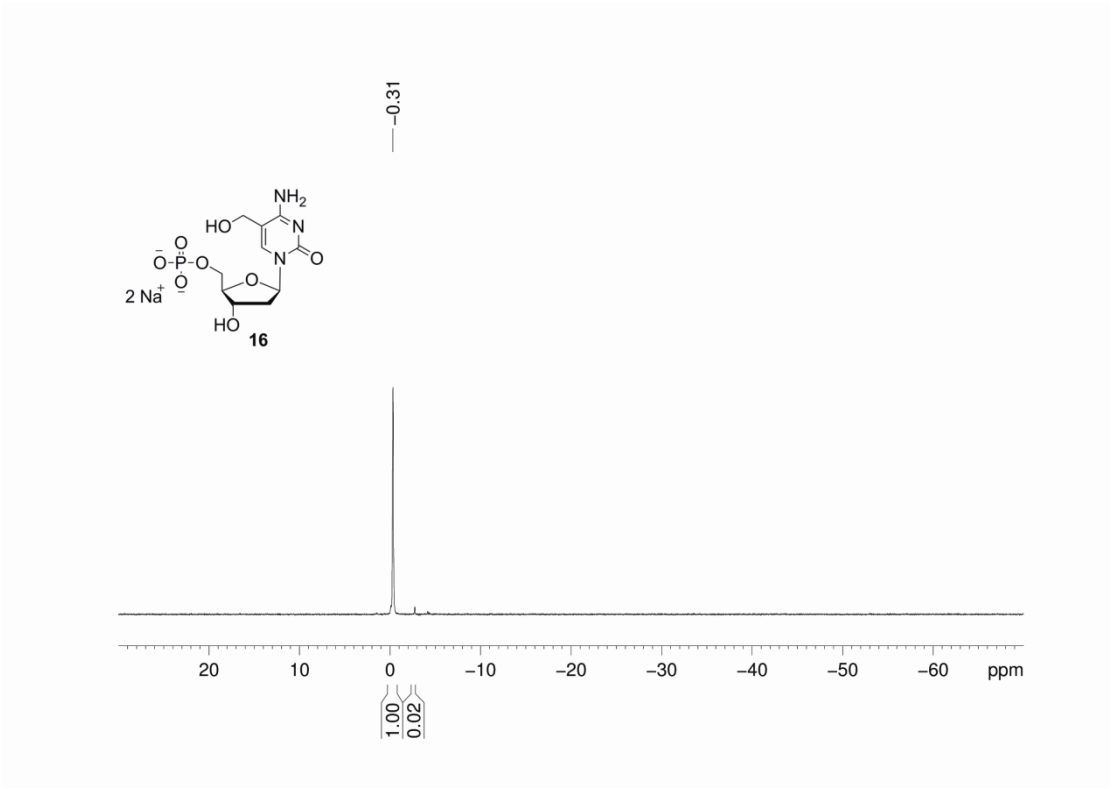


Figure S8. ^{1}H NMR Spectrum of **17**

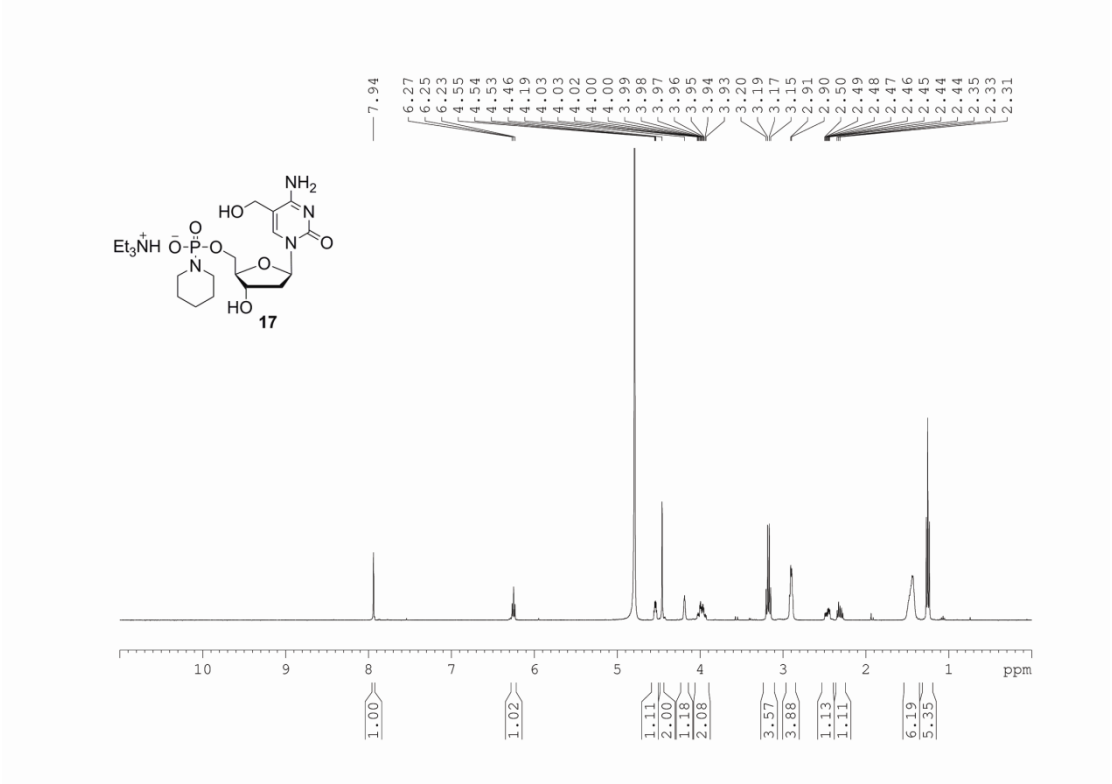


Figure S9. ^{13}C NMR Spectrum of **17**

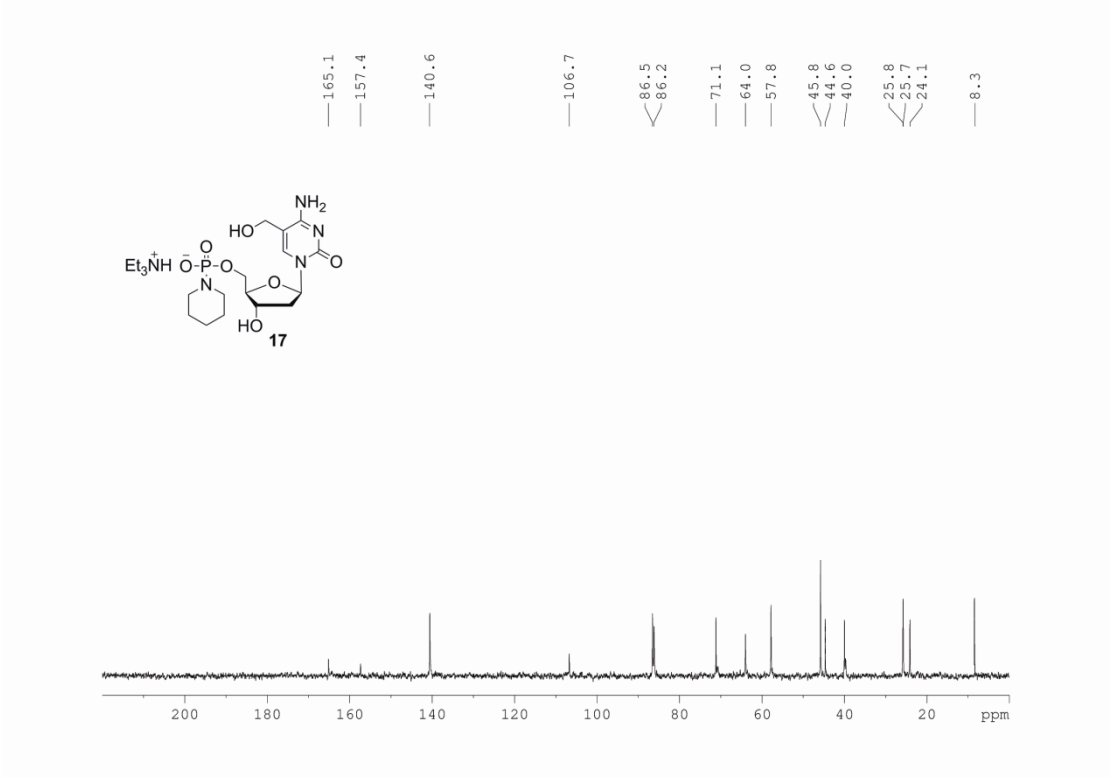


Figure S10. ^{31}P NMR Spectrum of **17**

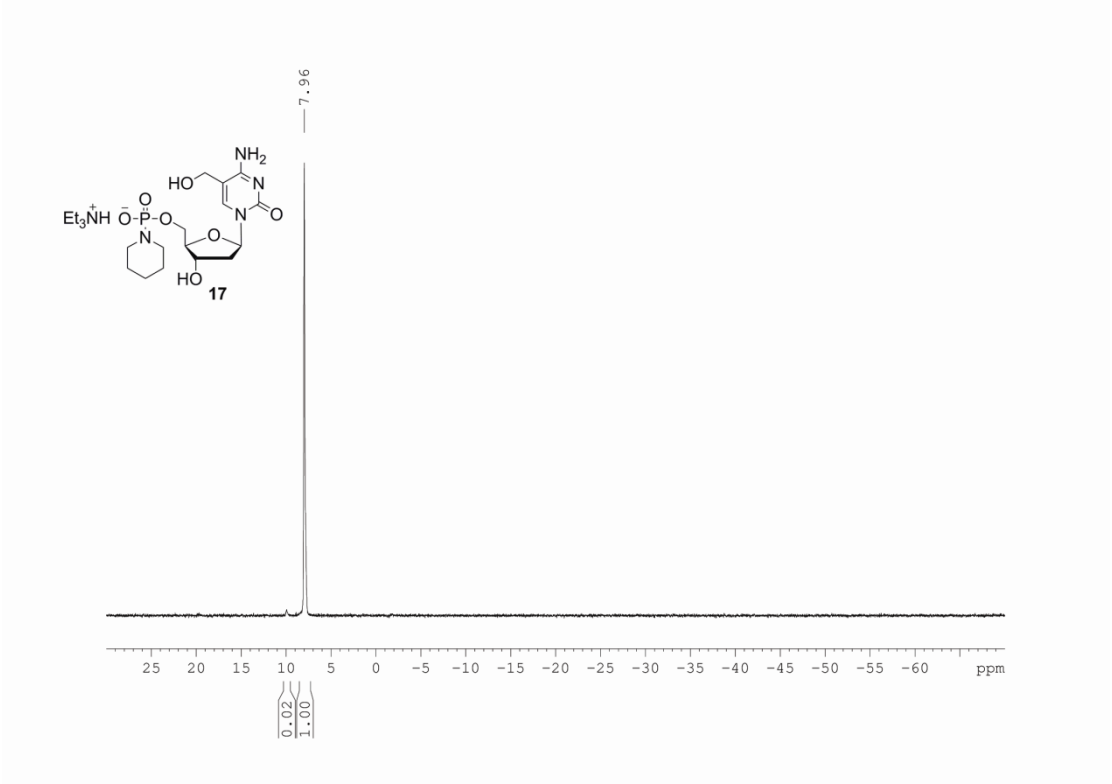


Figure S11. ^{1}H NMR Spectrum of **18**

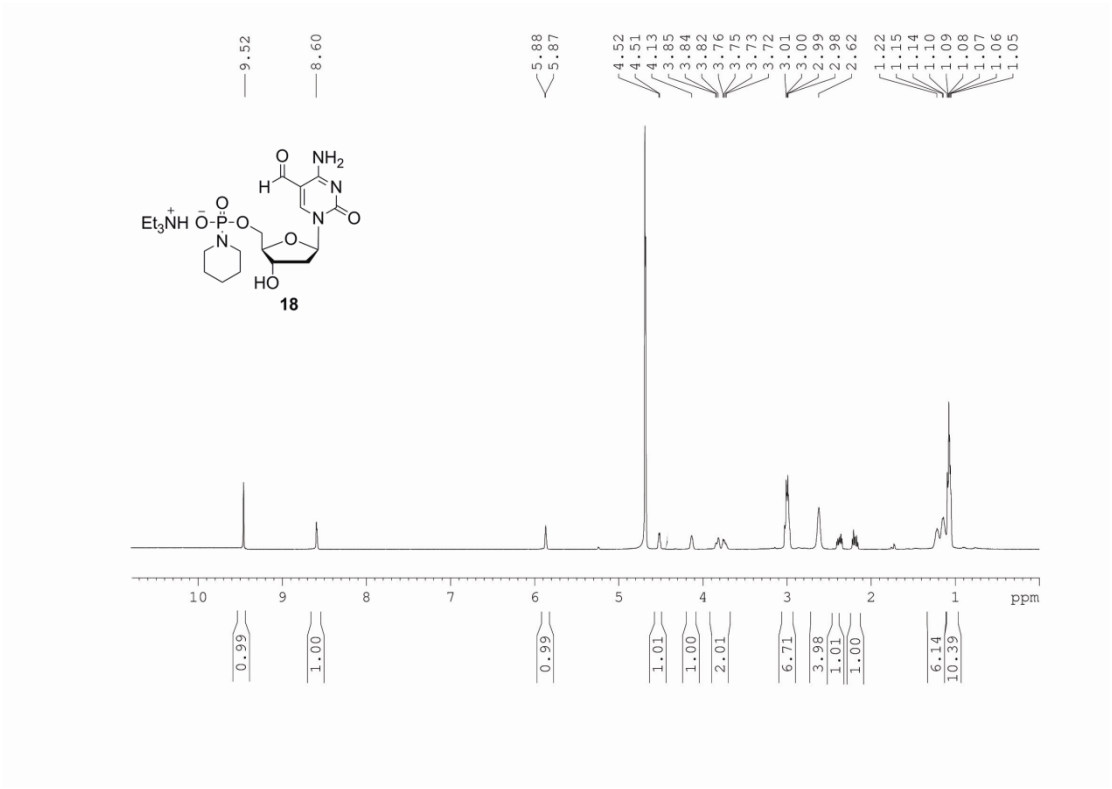


Figure S12. ^{13}C NMR Spectrum of **18**

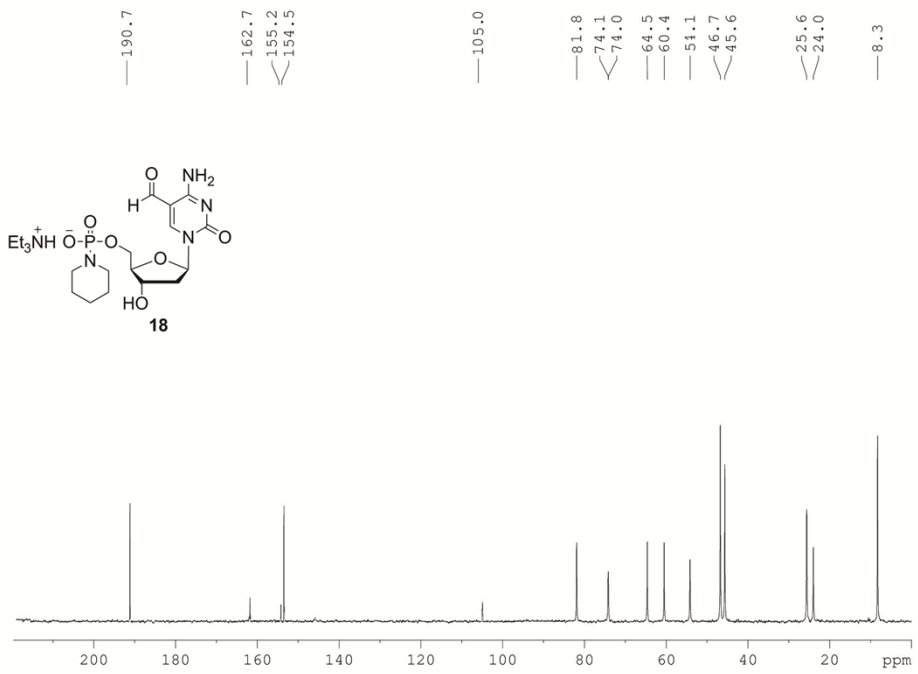


Figure S13. ^{31}P NMR Spectrum of **18**

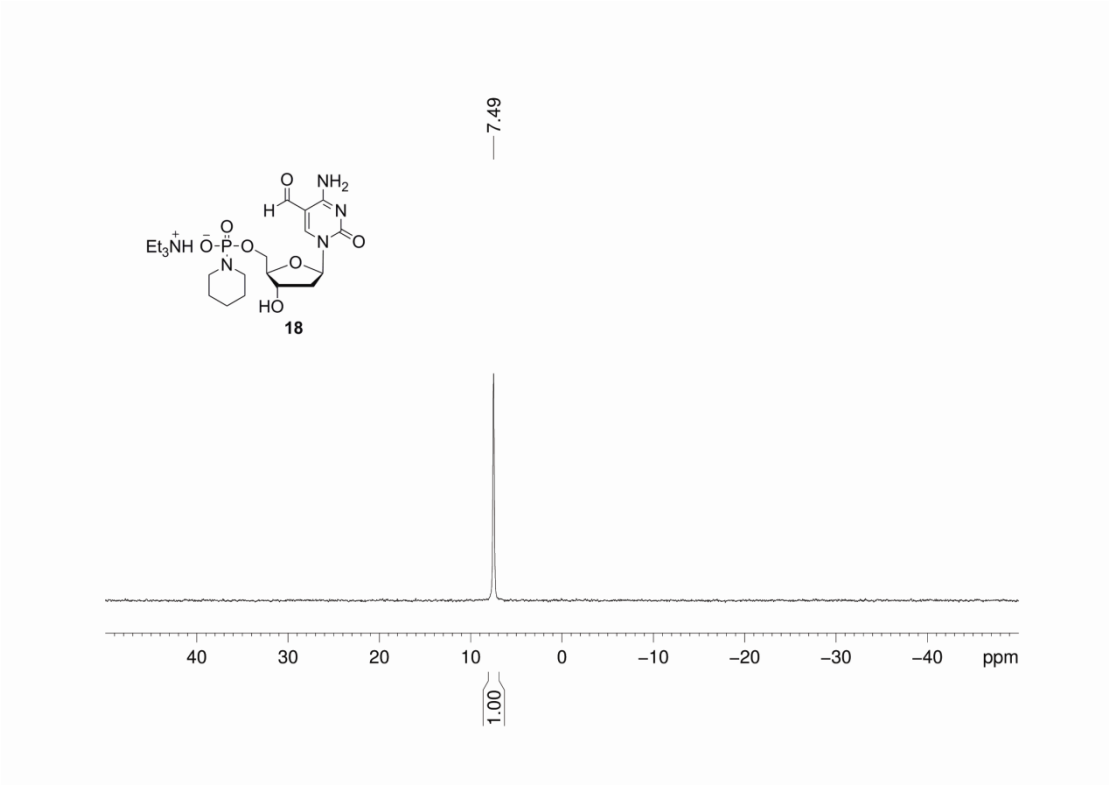


Figure S14. ^{1}H NMR Spectrum of **1**

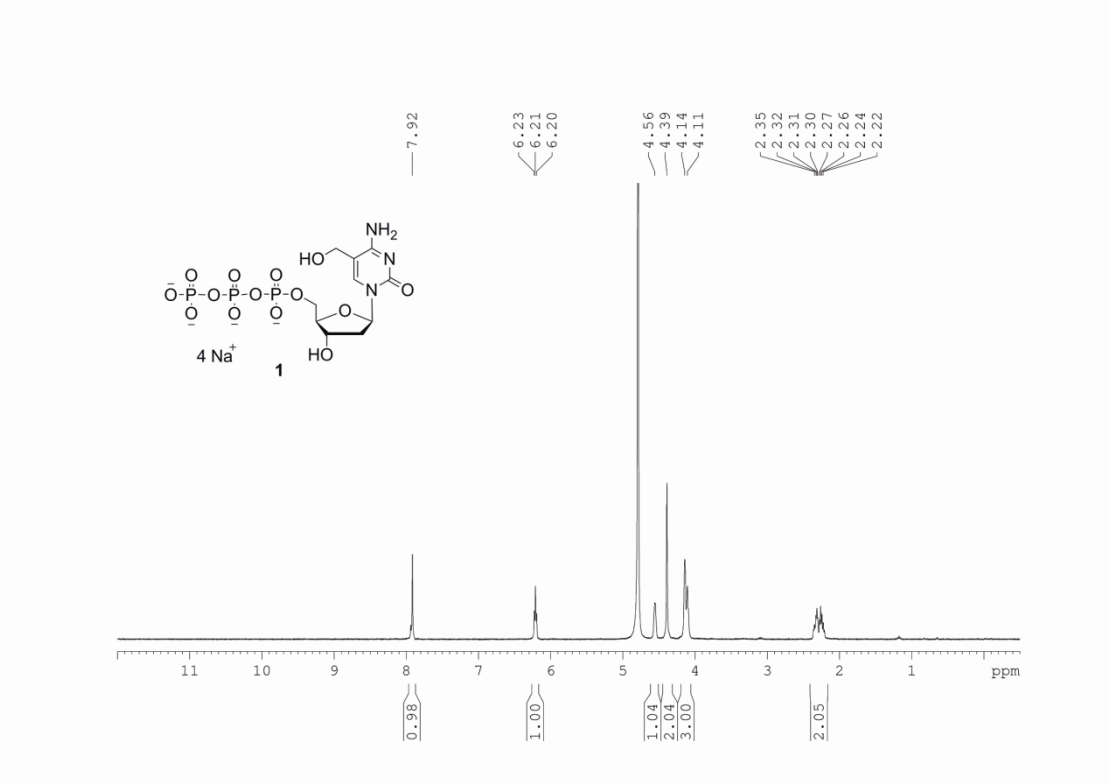


Figure S15. ^{13}C NMR Spectrum of **1**

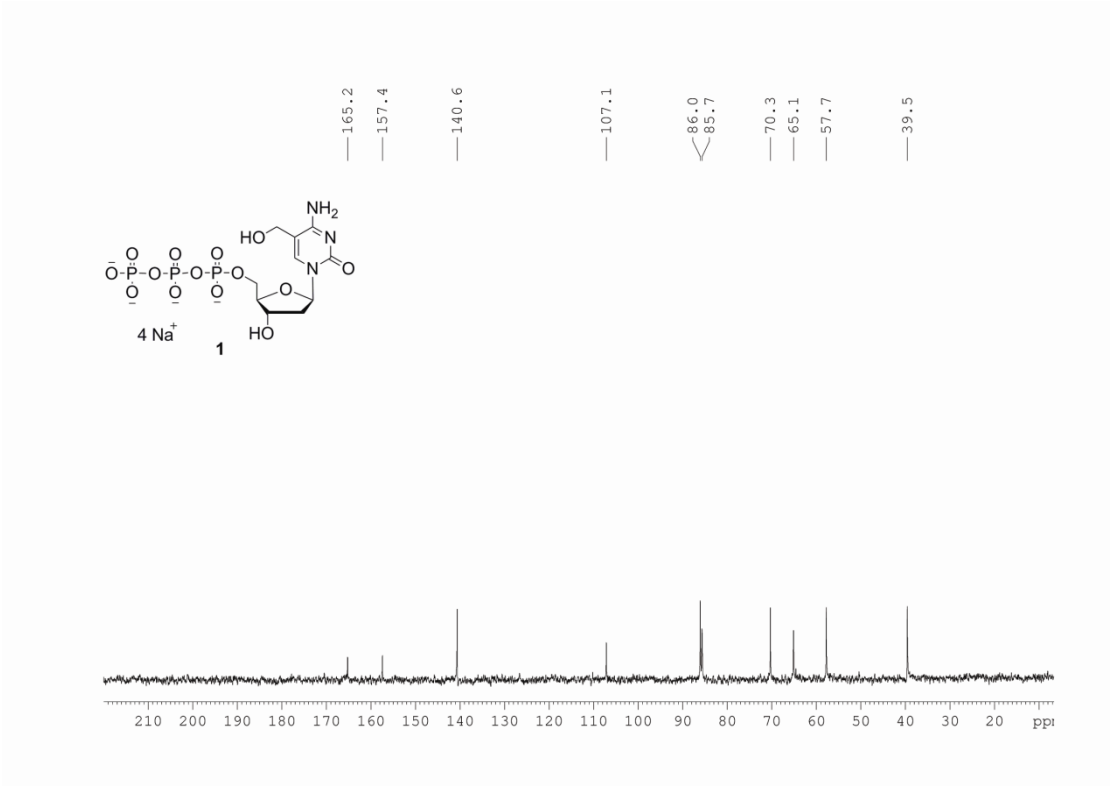


Figure S16. ^{31}P NMR Spectrum of **1**

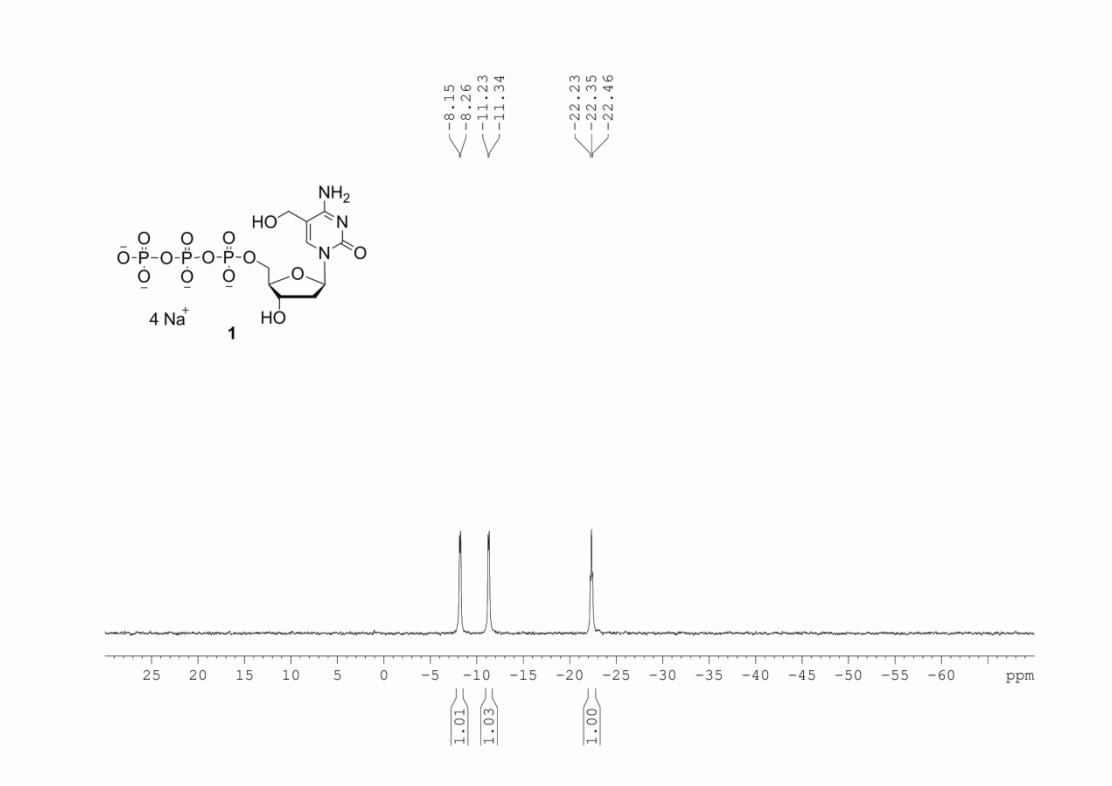


Figure S17. ^{1}H NMR Spectrum of **2**

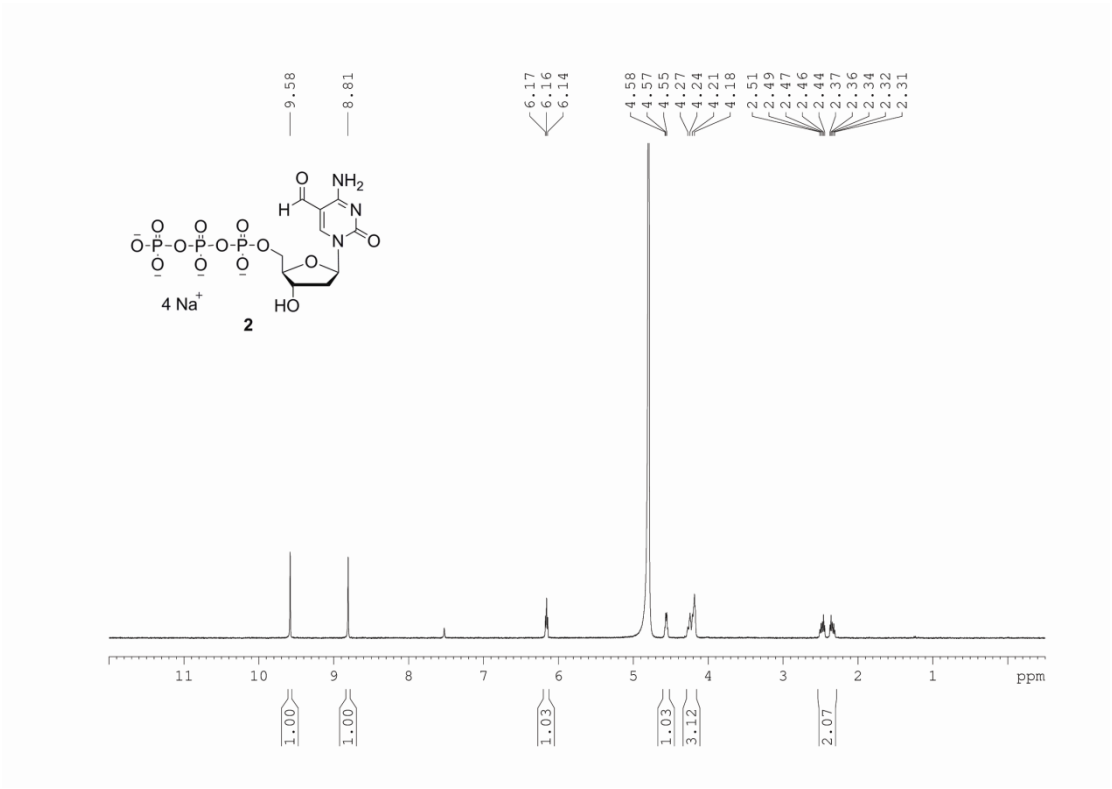


Figure S18. ^{13}C NMR Spectrum of **2**

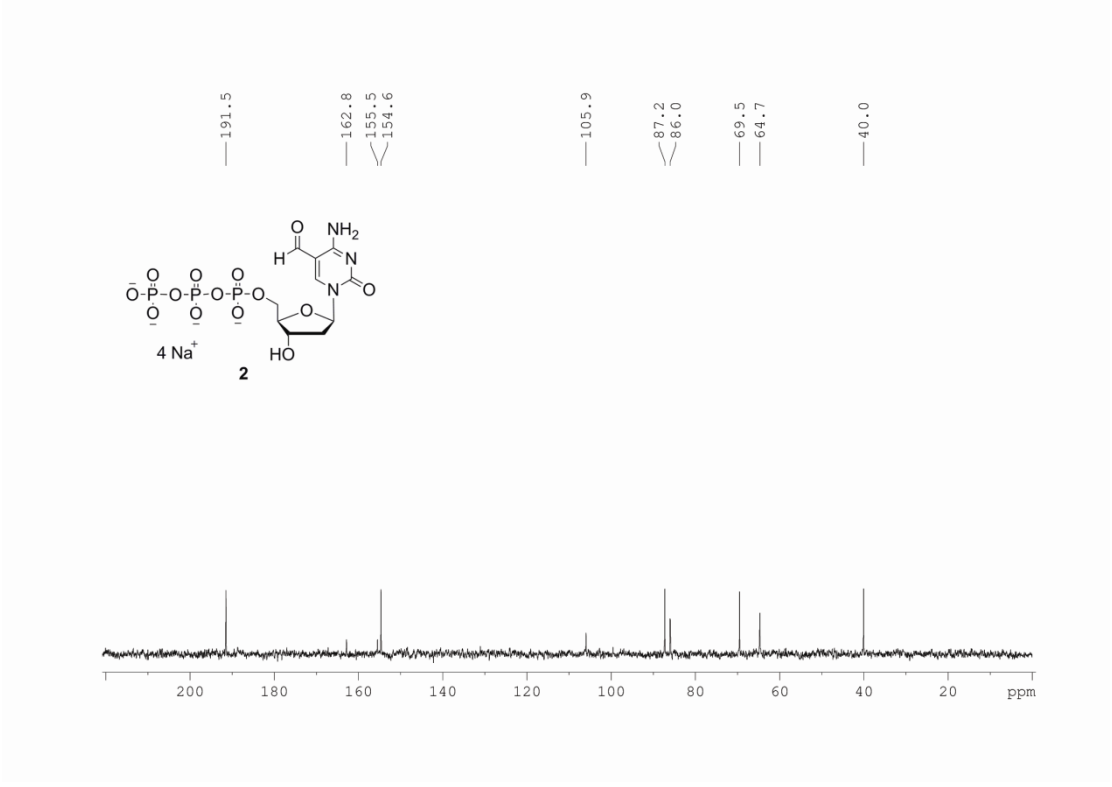


Figure S19. ^{31}P NMR Spectrum of **2**

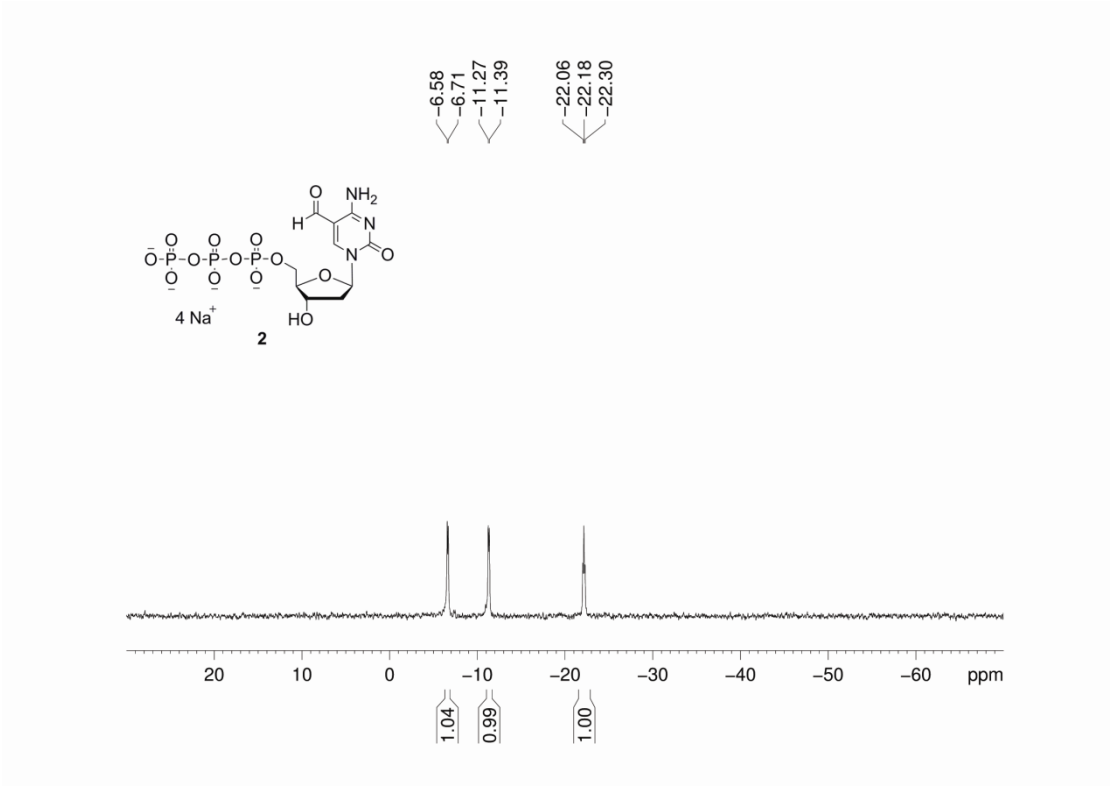


Figure S20. ^{1}H NMR Spectrum of **3**

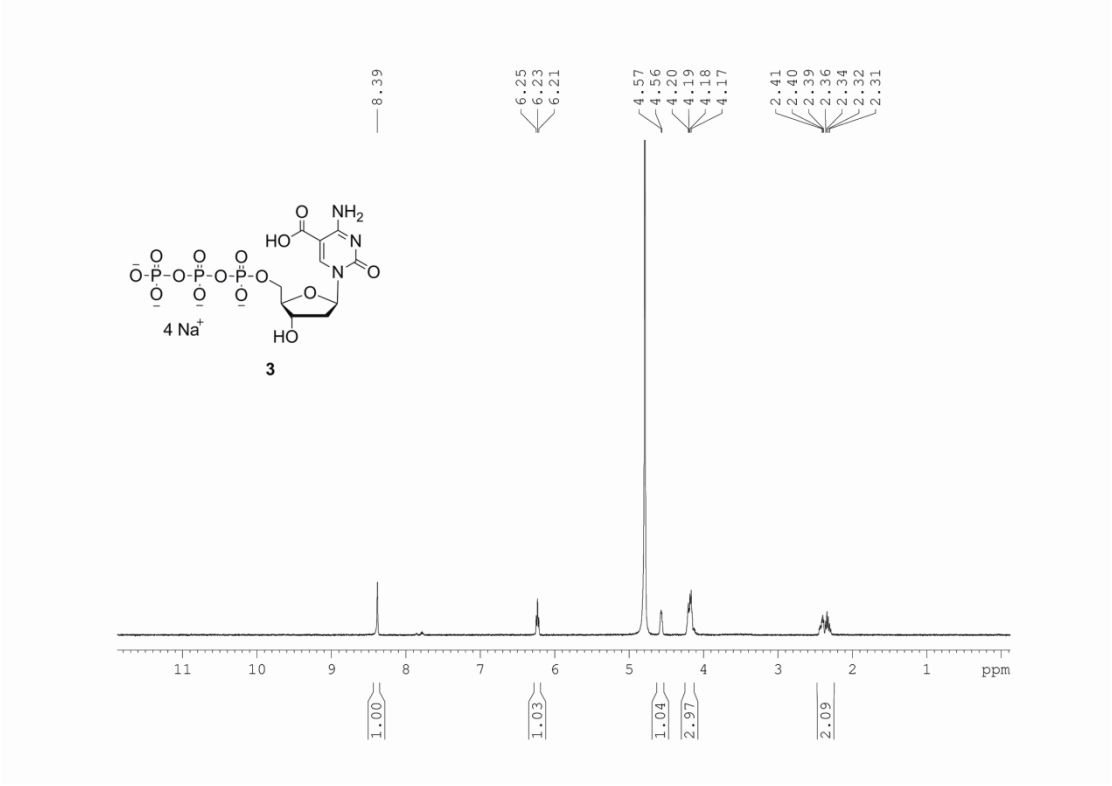


Figure S21. ^{13}C NMR Spectrum of **3**

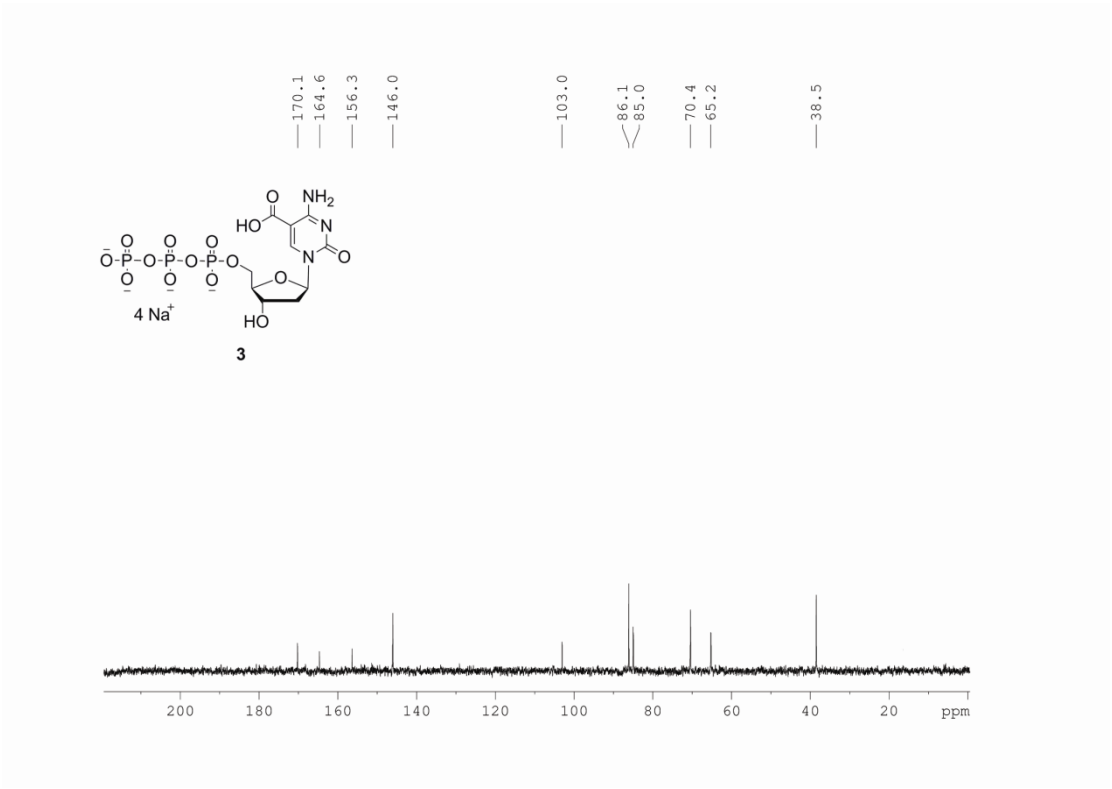
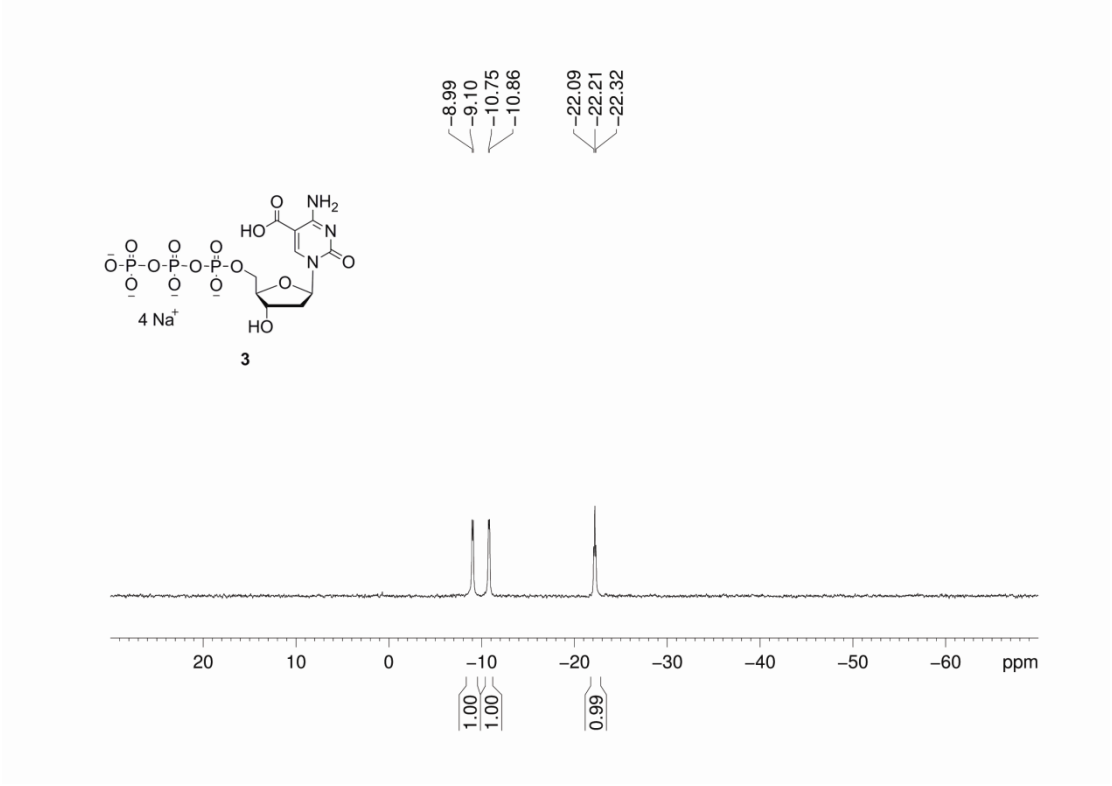


Figure S22. ^{31}P NMR Spectrum of **3**



4. References.

1. M. D. Bartholomä, A. R. Vortherms, S. Hillier, J. Joyal, J. Vabich, R. P. Doyle and J. Zubieta, *Dalton Trans.,* 2011, **40**, 6216.
2. V. J. Davisson, A. B. Woodside, T. R. Neal, K. E. Stremler, M. Muehlbacher, C. D. Poulter, *J. Org. Chem.,* 1986, **51**, 4768.