Supporting Information

Stereoselective Synthesis of 1'-α-Cyano Carbocyclic Pyrimidine Nucleoside Analogs via a Chelation-controlled 1'-α-Hydroxymethylation Strategy

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General Information:

Anhydrous solvents were purchased from Millipore Sigma (Milwaukee, WI, USA). All commercially available reagents were used without further purification. Reagents were purchased from commercial sources. All the reactions were carried out under nitrogen in oven-dried glassware unless otherwise noted. Thin layer chromatography was performed on Analtech GHLF silica gel plates. Column chromatography was accomplished on Combi- flash Rf200 or via reverse-phase high-performance liquid chromatography. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Ascend 400 spectrometer at rt (400, 101, and 377 MHz) and residual proton solvent signals were used as internal standards. Deuterium exchange and decoupling experiments were utilized to confirm proton assignments. NMR processing was performed with MestReNova (Mestrelab Research, Compostela, Spain) version 14.1.1 24571 or Topspin (Bruker, Berlin, Germany) version 3.5. Signal multiplicities are represented by s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quadru- plet), br (broad), bs (broad singlet), and m (multiplet). Coupling constants (*J*) are in hertz (Hz). Mass spectra were determined on a Waters Acquity

ultraperformance liquid chro- matography (UPLC) spectrometer using a SQ detector with electrospray ionization. The purity of final compounds was determined to be >95% using UPLC analyses performed on a Waters Acquity UPLC System with a Kinetex LC column (2.1 mm, 50 mm, 1.7 μm, C18, 100 Å) and further supported by clean NMR spectra. Mobile phase flow was 0.4 mL/min with a 1.20 min gradient from 95% aqueous media (0.05% formic acid) to 95% CH_3CN (0.05% formic acid) and a 4.5 min total acquisition time. Photodiode array detection was from 190 to 360 nm.

Synthesis of 1-((6a*R*,8*S*,9a*R*)-8-(hydroxymethyl)-2,2,4,4-tetraisopropyl-9-oxohexahydrocyclopenta[*f*][1,3,5,2,4]trioxadisilocin-8-yl)pyrimidine-2,4(1*H*,3*H*)-dione – 7. Under an inert atmosphere, compound **6** (1.31 g, 2.71 mmol) was dissolved in dry THF (30 mL) and cooled to -78 °C. LDA (2.5 M in hexanes, 2.28 mL, 5.7 mmol) was added dropwise, and the reaction mixture was allowed to warm to 0 °C and stirred for 10 min. The mixture was then cooled again to -78 °C, and paraformaldehyde (0.65 g, 21.68 mmol) was added. The reaction was allowed to gradually warm to room temperature and stirred for 6 h. Upon completion, the mixture was quenched with 1 M HCl, diluted with saturated $NaHCO_3$ (100 mL), and extracted with ethyl acetate (3 × 75 mL). The combined organic layers were washed with saturated brine (60 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (0-100% ethyl acetate in hexane) to afford the desired compound **7** (0.77 g, 50%) as a white foam. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.09 (s, 1H), 8.03 (d, 1H, J = 8.4 Hz), 5.64 (d, 1H, J = 8.3 Hz), 5.04 (t, 1H, J = 5.4 Hz,), 4.98 (d, 1H, J = 10.4 Hz), 4.10-3.84 (m, 4H), 2.45-2.41 (m, 1H), 2.19-1.96 (m, 2H), 1.14-0.92 (m, 28H).^{13}C NMR (101 MHz, Acetone-d_6) δ 171.8 164.2, 152.7, 144.7, 103.1, 76.4, 69.5, 63.4, 61.8, 61.4, 44.0, 28.4, 18.8, 18.7, 18.7, 18.6, 18.5, 18.3, 18.3, 15.1, 14.8, 14.3, 14.0. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 513.2374. for $C_{23}H_{41}N_2O_7Si_2$: found 513.2441.

Synthesis of 1-((6a*R*,8*S*,9a*R*)-8-(hydroxymethyl)-2,2,4,4-tetraisopropyl-9-oxohexahydrocyclopenta[*f*][1,3,5]trioxocin-8-yl)pyrimidine-2,4(1*H*,3*H*)-dione – 8. At 0 °C, a solution of compound **7** (0.54 g, 1.05 mmol) in dry pyridine (15 mL) was treated with acetic anhydride (0.16 mL, 1.68 mmol). The reaction mixture was stirred at room temperature for 4 h, then diluted with ethyl acetate (100 mL) and washed sequentially with 1 M HCl (25 mL), saturated

$NaHCO_3$ (40 mL), and saturated brine (30 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (0-50% ethyl acetate in hexane) to afford the desired compound **8** (0.42 g, 73%) as a white foam. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.15 (s, 1H), 7.81 (d, 1H, J = 8.2 Hz), 5.63 (d, 1H, J = 8.2 Hz), 5.01-4.95 (m, 1H), 4.60 (d, 1H, J = 13.4 Hz), 4.31 (d, 1H, J = 13.4 Hz), 4.08 (d, 1H, J = 14.1 Hz), 3.91 (d, 1H, J = 14.1 Hz), 2.29-2.21 (m, 3H), 2.12 (s, 3H), 1.29-0.86 (m, 28H).^{13}C NMR (101 MHz, Acetone-d_6) δ 206.1, 169.4 164.1, 150.9, 142.0, 101.8, 74.6, 66.0, 63.4, 61.7, 60.9, 42.2, 27.9, 19.7, 17.0, 16.9, 16.9, 16.8, 16.5, 16.4, 13.4, 13.3, 13.0, 12.6, 12.3. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 555.2480. for $C_{25}H_{43}N_2O_8Si_2$: found 555.2574.

Synthesis of ((6a*R*,8*S*,9a*R*)-8-(2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)-2,2,4,4-tetraisopropyl-9-oxohexahydrocyclopenta[*f*][1,3,5]trioxocin-8-yl)methyl acetate - 9. To a solution of compound **8** (1.01 g, 1.82 mmol) in methanol (52 mL) at 0 °C was added sodium borohydride (0.19 g, 5.18 mmol). After 1.5 h, the reaction mixture was diluted with saturated NH_4Cl (100 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with saturated brine (40 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (0-60% ethyl acetate in hexane) to afford the desired compound **9** (0.77 g, 76%) as a white foam. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.89 (s, 1H), 7.98 (d, 1H, J = 8.3 Hz), 5.56 (d, 1H, J = 8.4 Hz), 5.73 (d, 1H, J = 12.1 Hz), 4.53-4.49 (m, 2H), 4.40-4.37 (m, 1H), 4.14 (d, 1H, J = 7.5 Hz), 4.00 (dd, 1H, J = 11.6, 3.8 Hz), 3.84 (dd, 1H, J = 11.8, 1.9 Hz), 2.81-2.74 (m, 1H), 2.38-2.33 (m, 1H), 1.94 (s, 3H), 1.61-1.64 (m, 1H), 1.13-0.86 (m, 28H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 170.0, 162.6, 151.5, 143.6, 100.7, 76.9, 72.9, 70.6, 64.7, 63.0, 46.4, 32.4, 19.8, 17.8, 17.7, 17.7, 17.7, 17.6, 17.3, 14.3, 14.1, 13.6, 13.5. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 557.2636. for $C_{25}H_{45}N_2O_8Si_2$: found 557.2723.

Synthesis of ((6a*R*,8*S*,9*S*,9a*R*)-8-(2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)-9-hydroxy-2,2,4,4-tetraisopropylhexahydrocyclopenta[*f*][1,3,5]trioxocin-8-yl)methyl acetate - 10. 2,6-lutidine (0.12 mL, 1 mmol) and TBSOTf (0.12 mL, 0.5 mmol) were added to a solution of **9** (140 mg, 0.25 mmol) in THF (2.5 mL) at 0 °C. After 12 hours at room temperature, the reaction was diluted with water (20 mL), extracted with ethyl acetate (3 x 20 mL). Organic phases were combined, washed with sat. brine (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*

to dryness. The crude product was purified by flash chromatography (0-50% ethyl acetate in hexane) to give the compound **10** (140 mg, 86%) as a white foam. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.90 (s, 1H), 7.75 (d, 1H, J = 8.3 Hz), 5.53 (dt, 1H, J = 8.4, 1.2 Hz), 5.12 (d, 1H, J = 4.0 Hz), 4.68 (dd, 1H, J = 11.4, 1.3 Hz), 4.40 (d, 1H, J = 11.4 Hz), 4.02 (dd, 1H, J = 11.9, 2.7 Hz), 3.96 (dd, 1H, J = 10.2, 4.0 Hz), 3.84 (dd, 1H, J = 11.8, 1.9 Hz), 2.41-2.23 (m, 2H), 2.17-2.06 (m, 1H), 1.96 (s, 3H), 1.13-0.86 (m, 37H), 0.23 (s, 3H), 0.21 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 206.1, 170.7, 163.3, 152.2, 143.7, 101.7, 77.6, 73.3, 71.4, 65.3, 60.0, 42.4, 32.1, 26.5, 20.7, 19.0, 17.8, 17.7, 17.7, 17.7, 17.6, 17.3, 14.3, 14.1, 13.6, 13.5, -3.9, -4.1. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 671.3501. for $C_{31}H_{59}N_2O_8Si_3$: found 671.3593.

Synthesis of ((6a*R*,8*S*,9*S*,9a*R*)-9-((*tert*-butyldimethylsilyl)oxy)-8-(2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)-2,2,4,4-tetraisopropylhexahydrocyclopenta[*f*][1,3,5]trioxocin-8-yl)methyl acetate - 14. Ammonia gas was bubbled through a solution of compound **10** (0.43 g, 0.43 mmol) in methanol (13 mL) at 0 °C for 10 min. The reaction mixture was stirred at room temperature for 24 h, then concentrated in vacuo**.** The residue was purified by flash chromatography (0-50% ethyl acetate in hexane) to afford the desired compound **14** (0.37 g, 93%) as a white foam. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.76 (s, 1H), 7.65 (d, 1H, J = 8.4 Hz), 5.53-5.45 (m, 1H), 5.06 (d, 1H, J = 4.2 Hz), 4.20 (dd, 1H, J = 11.4, 5.6 Hz), 4.13-3.98 (m, 2H), 3.93 (dd, 1H, J = 10.3, 4.3 Hz), 3.84 (dd, 1H, J = 11.8, 2.2 Hz), 3.73 (dd, 1H, J = 11.4, 6.1 Hz), 2.33-2.24 (m, 1H), 2.15 (d, 2H, J = 9.0 Hz), 1.16-0.88 (m, 37H), 0.21 (s, 3H), 0.18 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 163.6, 152.3, 144.8, 101.0, 77.5, 73.6, 63.1, 60.3, 42.8, 31.7, 26.6, 19.1, 17.8, 17.8, 17.7, 17.7, 17.6, 17.3, 14.3, 14.1, 13.6, 13.5, -3.1, -3.2. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 629.3395. for $C_{29}H_{57}N_2O_7Si_3$: found 629.3485.

Synthesis of 1-((6a*R*,8*S*,9*S*,9a*R*)-9-((*tert*-butyldimethylsilyl)oxy)-8-(hydroxymethyl)-2,2,4,4-tetraisopropylhexahydrocyclopenta[*f*][1,3,5]trioxocin-8-yl)pyrimidine-2,4(1*H*,3*H*)-dione - 16. Under an argon atmosphere, Dess-Martin periodinane (0.88 g, 2.03 mmol) was added to a solution of compound **14** (1.03 g, 1.64 mmol) in dichloromethane (13 mL) and pyridine (1.06 mL, 13.1 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 16 h, then diluted with dichloromethane (20 mL) and saturated $NaHCO_3$ (40 mL). The resulting precipitate was filtered off, and the aqueous layer was extracted with dichloromethane (5 × 30 mL). The combined

organic extracts were washed with saturated brine (50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo**.** The crude product was purified by flash chromatography (0-50% ethyl acetate in hexane) to obtain intermediate **15** (0.88 g), which was dissolved in pyridine (7.4 mL), before addition of $NH_2OH{\cdot}HCl$ (0.42 g, 7.09 mmol). The reaction mixture was stirred at room temperature for 2 h, after which volatiles were removed in vacuo. The residue was dissolved in ethyl acetate (100 mL), washed with water (25 mL) and saturated brine (25 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to dryness. The resulting crude product was used directly in the next step without further purification. The crude intermediate (0.9 g) was dissolved in Ac_2O (12.6 mL), and NaOAc (0.7 g, 8.2 mmol) was added. The reaction mixture was heated at 130 °C for 2.5 h, then cooled to room temperature and quenched with saturated $NaHCO_3$ (200 mL) and stirred for 30 min. The aqueous layer was extracted with ethyl acetate (3 × 50 mL), and the combined organic extracts were washed with saturated $NaHCO_3$ (2 × 50 mL) and saturated brine (50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (0-60% ethyl acetate in hexane) to afford the desired compound **16** (0.51 g, 53% over three steps) as a white foam. ^{1}H NMR (400 MHz, Acetone-d_6) 7.89 (d, 1H, J = 8.4 Hz), 5.66 (d, 1H, J = 8.4 Hz), 4.77 (d, 1H, J = 3.6 Hz), 4.07 (ddd, 2H, J = 20.5, 11.3, 3.4 Hz), 3.97 (dd, 1H, J = 12.1, 1.9 Hz), 2.79 – 2.65 (m, 2H), 2.56 (tdd, 1H, J = 9.0, 3.4, 1.7 Hz), 1.19 – 0.88 (m, 37H), 0.29 (s, 3H), 0.21 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 162.8, 151.1, 140.8, 118.7, 103.0, 78.7, 72.4, 66.0, 60.1, 42.7, 34.9, 26.3, 18.8, 18.0, 17.8, 17.8, 17.7, 17.5, 17.5, 17.4, 17.3, 14.1, 14.1, 13.9, 13.5, -3.9, -3.9. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 624.3242. for $C_{29}H_{54}N_2O_6Si_3$: found 624.3331.

Synthesis of (6a*R*,8*S*,9*S*,9a*R*)-9-((*tert*-butyldimethylsilyl)oxy)-8-(2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)-2,2,4,4-tetraisopropylhexahydrocyclopenta[*f*][1,3,5]trioxocine-8-carbonitrile – (Carba-CNU-1). To a solution of compound **16** (0.61 g, 0.98 mmol) in THF (9.8 mL) was added TBAF (1 M in THF, 2.93 mL, 2.93 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. Volatiles were removed in vacuo, and the residue was purified by flash chromatography (0-15% methanol in dichloromethane) to afford the desired compound **1** (0.21 g, 80%) as a white foam. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.86 (d, 1H, J = 8.4 Hz), 5.62 (d, 1H, J = 8.3 Hz), 4.33 (d, 1H, J = 6.4 Hz), 3.93 (dd, 1H, J = 6.4, 3.6 Hz), 3.51 (m, 2H), 3.12 (dd, 1H, J = 14.0, 8.4 Hz), 2.24 (m, 1H,). 1.74 (dd, 1H, J = 14.0, 9.6 Hz). ^{13}C NMR (101 MHz,

Methanol-d_4) δ 165.7, 152.2, 142.9, 118.0, 102.8, 77.5, 72.3, 67.0, 63.2, 46.8, 36.7. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 268.0855. for $C_{11}H_{13}N_3O_5$: found 268.0929.

Synthesis of(1*R*,2*S*,3*S*,5*R*)-5-(acetoxymethyl)-3-cyano-3-(2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)cyclopentane-1,2-diyl diacetate - 17. To a suspension of Carba-CNU-**1** (0.21 g, 0.79 mmol) in anhydrous pyridine (7.8 mL) were added DMAP (19.1 mg, 0.15 mmol) and Ac_2O (0.3 mL, 3.1 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 8 h. Volatiles were removed in vacuo, and the residue was diluted with ethyl acetate (150 mL), washed with saturated $NaHCO_3$ (40 mL) and saturated brine (30 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to dryness. The crude product was purified by flash chromatography (0-60% ethyl acetate in hexane) to afford the compound **17** as a white foam. (0.24 g, 75%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.57 (d, 1H, *J* = 8.0 Hz), 5.82 (d, 1H, *J* = 6.8 Hz), 5.67 (d, 1H, *J* = 8.0 Hz), 5.34 (t, 1H, *J* = 6.4 Hz), 4.31-4.18 (m, 2H), 3.20 (dd, 1H, *J* = 14.0, 8.4 Hz), 2.84-2.74 (m, 1H), 2.45 (dd, 1H, *J* = 14.0, 10.4 Hz), 2.13 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 170.8, 170.2, 169.7 162.8, 151.1, 141.0, 116.4, 103.3, 74.7, 71.5, 65.8, 64.1, 41.4, 36.1, 20.8, 20.6, 20.5. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 394.1172. for $C_{17}H_{20}N_3O_8$: found 394.1246.

Synthesis of(1*S*,2*S*,3*R*,4*R*)-1-(4-amino-2-oxopyrimidin-1(2*H*)-yl)-2,3-dihydroxy-4-(hydroxymethyl)cyclopentane-1-carbonitrile – (Carba-CNC-3): To a solution of 1,2,4-triazole (1.20 g, 17.3 mmol) in acetonitrile (33 mL) were added Et_3N (2.6 mL, 18.7 mmol) and $POCl_3$ (0.27 mL, 2.91 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h. Then, a solution of compound **17** (0.22 g, 0.56 mmol) in acetonitrile (7 mL) was added dropwise at 0 °C, and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with ethyl acetate (50 mL), filtered, and the filtrate was washed with saturated $NaHCO_3$ (10 mL) and saturated brine (10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to dryness. The crude product was purified by quick flash chromatography (0-100% ethyl acetate in hexane) to afford the triazole intermediate **18** as a white solid (0.17 g). This material (0.09 g, 0.2 mmol) was dissolved in 1,4-dioxane (6 mL), and ammonia gas was bubbled at 5 °C for 10 min. The reaction mixture was then stirred at ambient temperature until complete consumption of the starting material, as monitored by TLC and LCMS (approximately

2 h). The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (0-10% methanol/dichloromethane) to afford the intermediate **18** as a white solid (0.05 g). To a solution of this intermediate (0.05 g, 0.14 mmol) in methanol (1.8 mL) was added NH_4OH (1.8 mL) at 0 °C. The reaction was maintained at the same temperature for 6 h, and then the solvents were evaporated. The residue was washed methanol (2 × 2 mL) to afford the desired compound Carba-CNC-**3** (34 mg, 63% over three steps) as a white solid. ^{1}H NMR (400 MHz, D_2O) δ 7.79 (d, 1H, *J* = 7.8 Hz), 6.01 (d, 1H, *J* = 7.7 Hz), 4.53 (d, 1H, *J* = 6.3 Hz), 4.08 (dd, 1H, *J* = 6.3, 4.5 Hz), 3.63 (d, 2H, *J* = 5.8 Hz), 3.15 (dd, 1H, *J* = 14.2, 8.6 Hz), 2.39 (td, 1H, *J* = 9.2, 4.4 Hz), 1.83 (dd, 1H, *J* = 14.2, 9.7 Hz). ^{13}C NMR (101 MHz, D_2O) δ 165.9, 157.4, 142.0, 117.8, 96.3, 75.3, 71.1, 65.6, 61.9, 44.2, 34.9. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 266.1015. for $C_{11}H_{15}N_4O_4$: found 267.1086.

Synthesis of isopropyl ((((1R,2R,3S,4S)-4-cyano-4-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-2,3-dihydroxycyclopentyl)methoxy)(phenoxy)phosphoryl)-L-alaninate - 2.

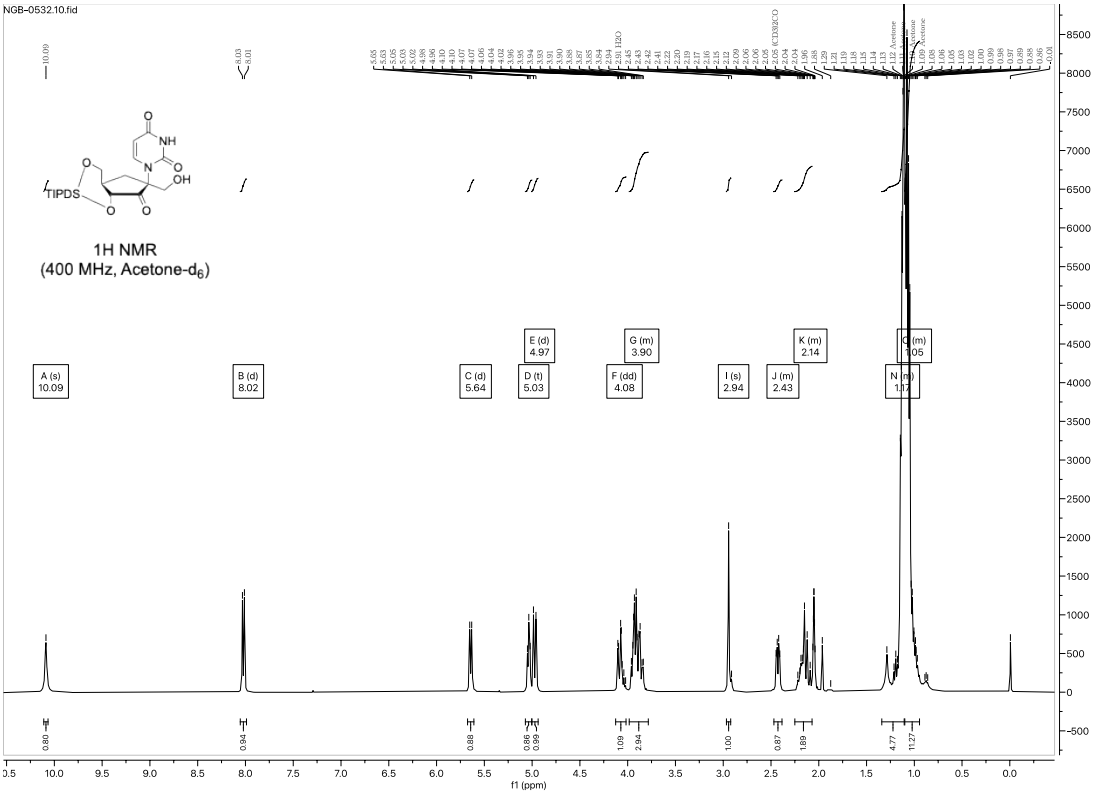
To a solution of Carba-CNU - **1** (40.5 mg, 0.15 mmol) in anhydrous THF (2.5 mL) and anhydrous DMF (1.5 mL) containing 4 Å molecular sieves, ^{t}BuMgCl (1.0 M in THF, 0.3 mL, 0.30 mmol) was added dropwise at -10 °C and the reaction mixture was stirred for 30 min. A solution of isopropyl ((R)-(perfluorophenoxy)(phenoxy)phosphoryl)-L-alaninate (Reagent A, 66.2 mg, 0.14 mmol) in THF (0.6 mL) was then added dropwise at –10 °C. The reaction mixture was stirred overnight at 0 °C, then diluted with saturated $NaHCO_3$ (25 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with saturated brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to dryness. The crude product was purified by flash chromatography (0-10% methanol/dichloromethane) to afford the desired compound **2** (23.4 mg, 29%) as a white foam. ^{1}H NMR (400 MHz, Methanol -d_4) δ 7.90 (d, 1H, *J* = 8.4 Hz), 7.34 (t, 2H, *J* = 8.0 Hz), 7.22-7.15 (m, 3H), 5.73 (d,1H, *J* = 8.4 Hz), 4.95 (hep, 1H, *J* = 6.0 Hz), 4.29 (d, 1H, *J* = 6.4 Hz), 4.24-4.19 (m, 1H), 4.14-4.09 (m, 1H), 4.08-4.05 (m, 1H), 3.21 (dd, 1H, *J* = 14.0, 8.4 Hz), 2.49-2.46 (m, 1H), 1.72 (dd, 1H, *J* = 14.0, 10.0 Hz), 1.33 (d, *J* = 6.8 Hz, 3H), 1.22 (dd, *J* = 6.4, 4.8 Hz, 6H). ^{13}C NMR (101 MHz, Methanol -d_4) δ 174.4 (d, *J* = 4.0 Hz), 165.6, 152.2, 151.1 (d, *J* = 2.0 Hz), 142.8, 130.8, 126.2, 121.4 (d, *J* = 4.0 Hz), 117.7 103.0, 77.3, 71.6, 70.1, 67.9 (d, *J* = 6.0 Hz), 66.7, 51.6, 45.2 (d, *J* = 8.0 Hz), 36.0, 21.8 (d, *J* = 10.1 Hz), 21.4 (d, *J*

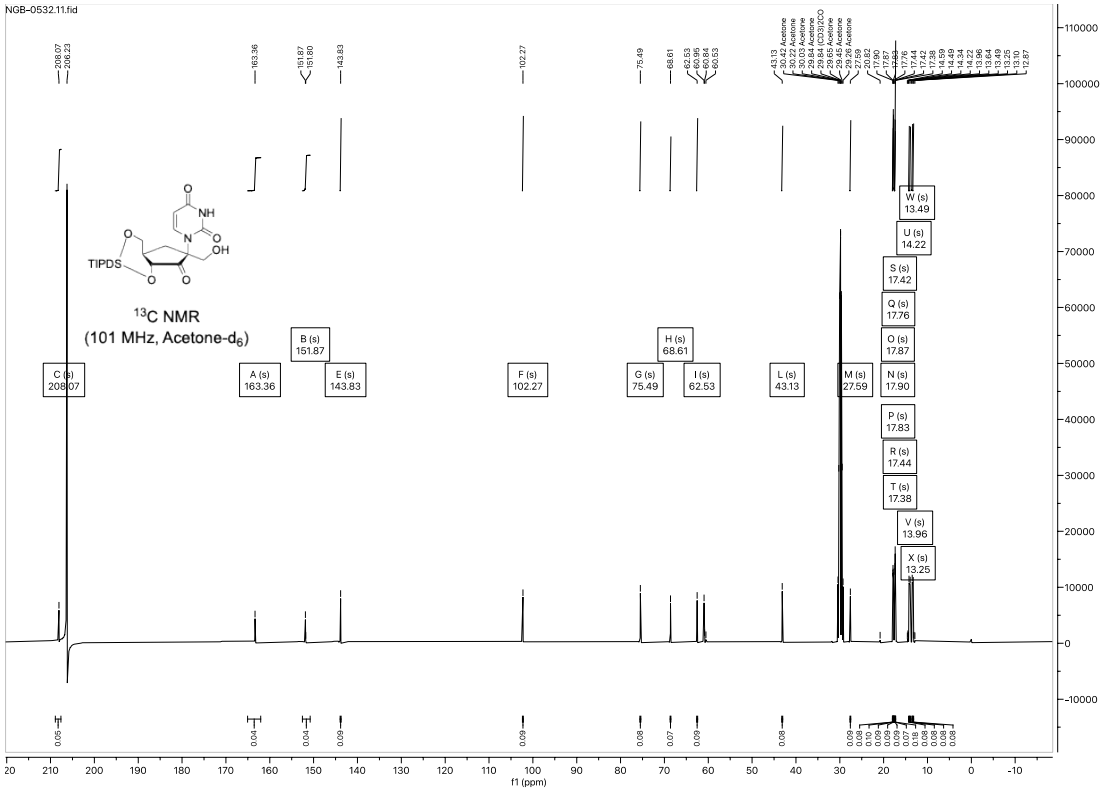
= 7.0 Hz). ^{31}P NMR (162 MHz, Methanol -d_4) δ 3.53. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 537.1372. for $C_{23}H_{30}N_4O_9P$: found 537.1756.

Synthesis of isopropyl ((((1R,2R,3S,4S)-4-(4-amino-2-oxopyrimidin-1(2H)-yl)-4-cyano-2,3-dihydroxycyclopentyl)methoxy)(phenoxy)phosphoryl)-L-alaninate - 4.

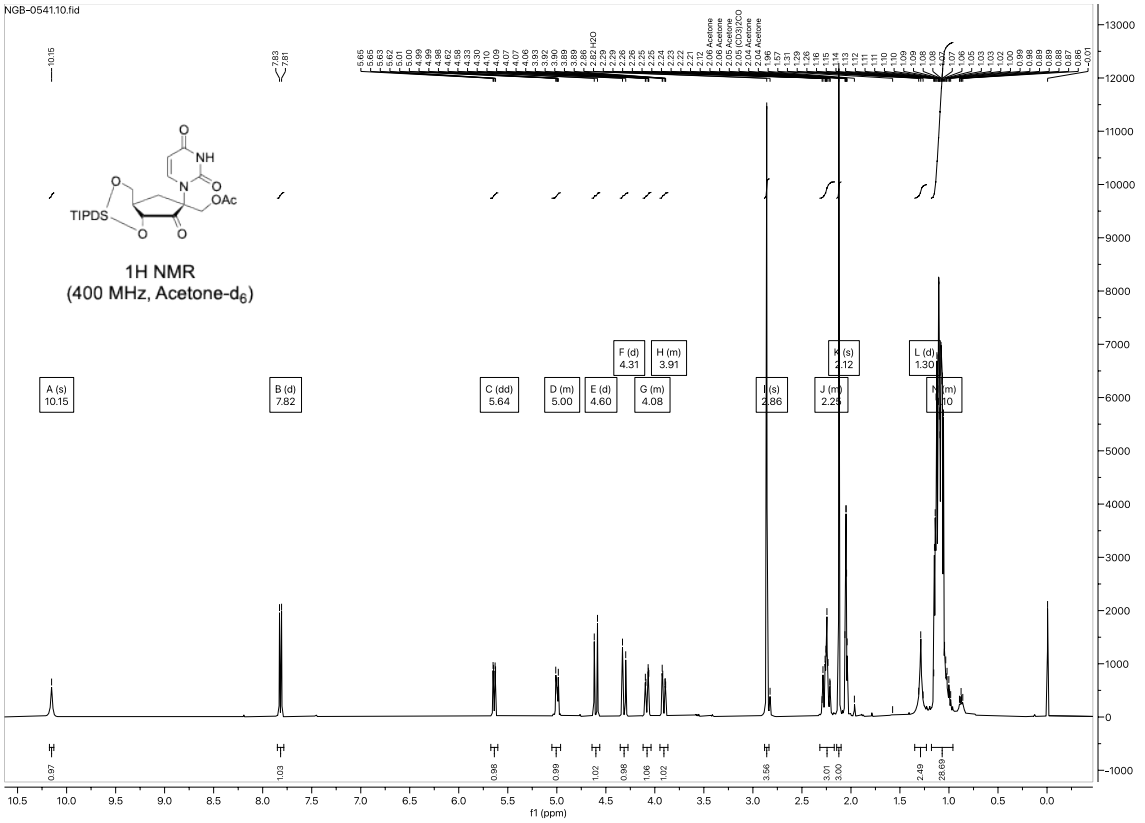
To a solution of compound **3** (34 mg, 0.12 mmol) in anhydrous DMF (1.5 mL) containing 4 Å molecular sieves, ^{t}BuMgCl (1.0 M in THF, 0.26 mL, 0.26 mmol) was added dropwise at -10 °C, and the reaction mixture was stirred for 30 min. A solution of isopropyl ((R)-(perfluorophenoxy)(phenoxy)phosphoryl)-L-alaninate (Reagent A, 55 mg, 0.11 mmol) in THF (0.5 mL) was then added dropwise at –10 °C. The mixture was stirred overnight at 0 °C, diluted with saturated $NaHCO_3$ (25 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with saturated brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to dryness. The crude product was purified by flash chromatography (0-10% methanol/dichloromethane) to afford the title compound **4** (8.4 mg, 13%) as a white foam. ^{1}H NMR (400 MHz, Methanol -d_4) δ 7.87 (d, 1H, *J* = 7.7 Hz), 7.35 (t, 2H, *J* = 7.9 Hz), 7.26-7.14 (m, 3H), 5.94 (d, 1H, *J* = 7.7 Hz), 4.99-4.91 (m, 1H), 4.29 (d, 1H, *J* = 6.7 Hz), 4.29-4.20 (m, 1H), 4.14 (ddd, 1H, *J* = 10.4, 6.0, 4.3 Hz), 4.08 (dd, 1H, *J* = 6.7, 4.2 Hz), 3.89 (dq, 1H, *J* = 9.5, 7.1 Hz), 3.24 (dd, 1H, *J* = 13.9, 8.5 Hz), 2.56-2.46 (m, 1H), 1.72 (dd, 1H, *J* = 14.0, 10.4 Hz), 1.35 (dd, 3H *J* = 7.2, 1.1 Hz), 1.24 (dd, 6H *J* = 6.3, 2.5 Hz). ^{13}C NMR (101 MHz, Methanol -d_4) δ 174.4 (d, *J* = 4.5 Hz), 167.4, 158.0, 152.1, 143.4, 130.8, 126.2, 121.4 (d, *J* = 4.7 Hz), 118.1, 77.2, 71.7, 70.1, 67.9 (d, *J* = 5.6 Hz), 67.4, 51.6, 45.2 (d, *J* = 7.7 Hz), 35.9, 21.9 (d, *J* = 11.2 Hz), 20.4 (d, *J* = 7.3 Hz).^{31}P NMR (162 MHz, Methanol -d_4) δ 3.52. HRMS-ESI (*m/z*) $[M+H]^+$ calcd. 536.1832. for $C_{23}H_{31}N_5O_8P$: found 536.1912.

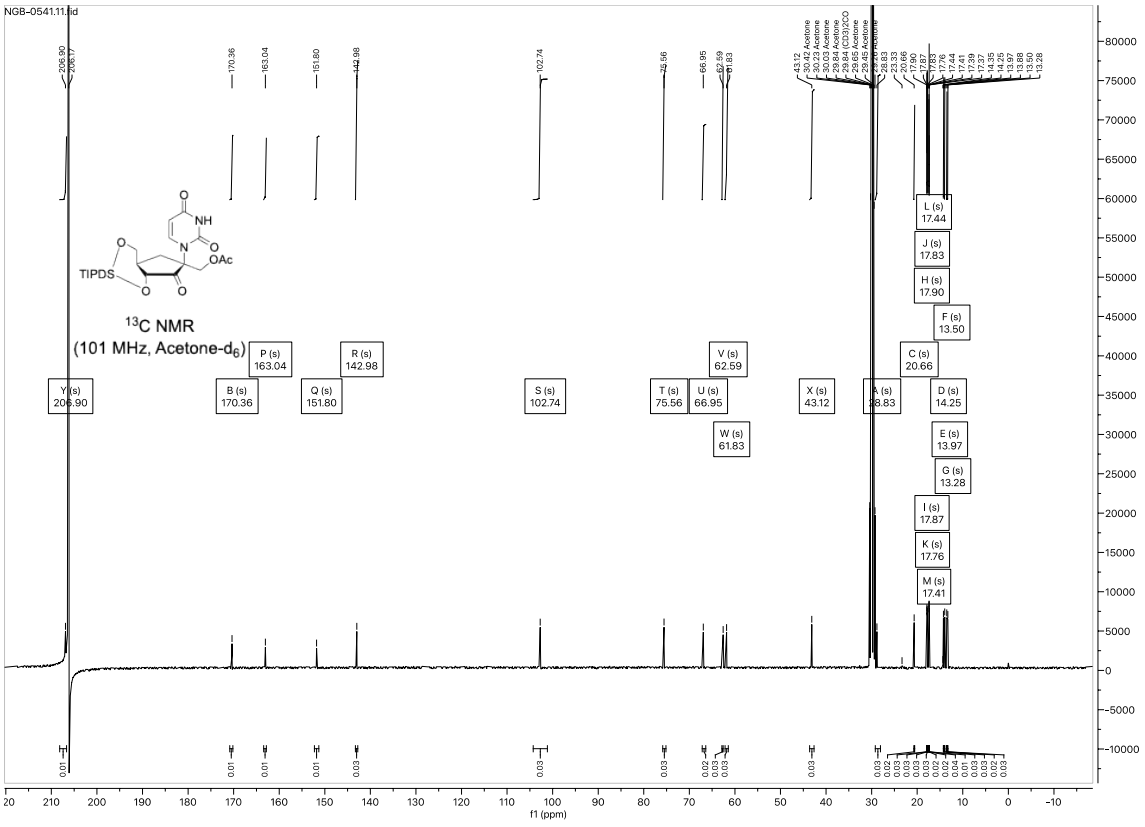
NMR Spectral data of compound-**7**:



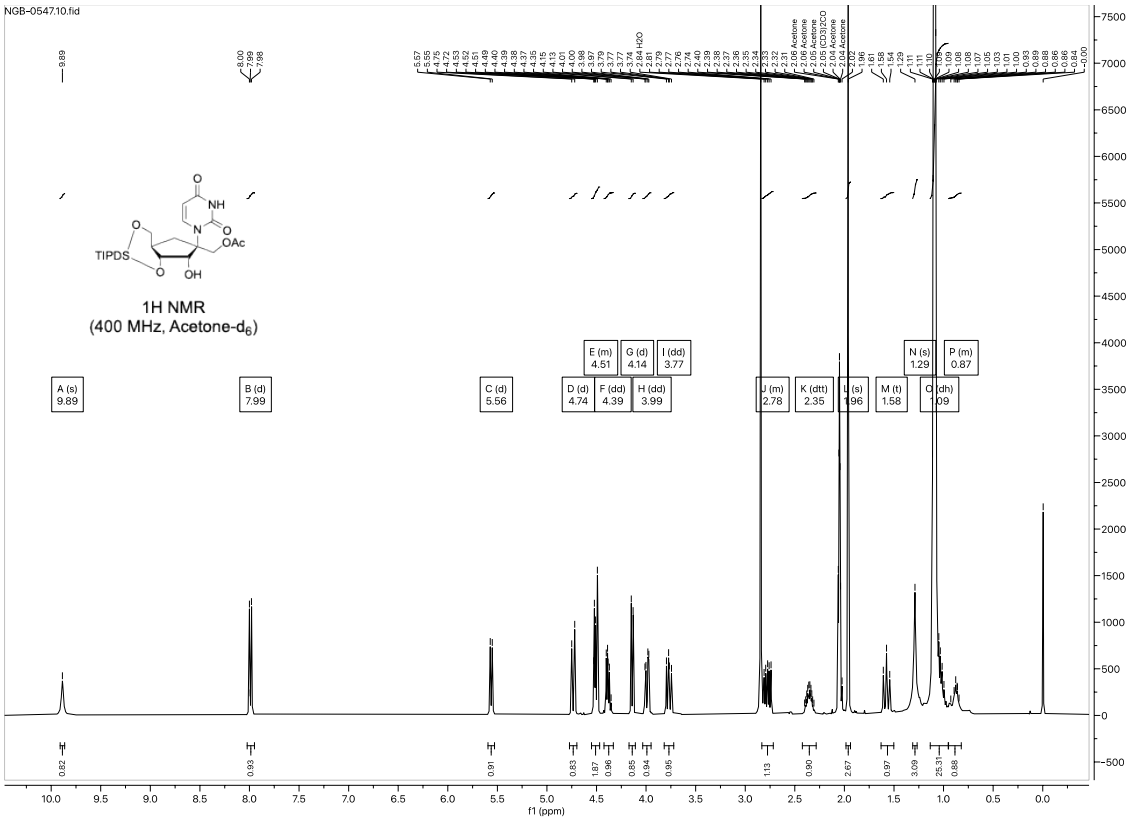


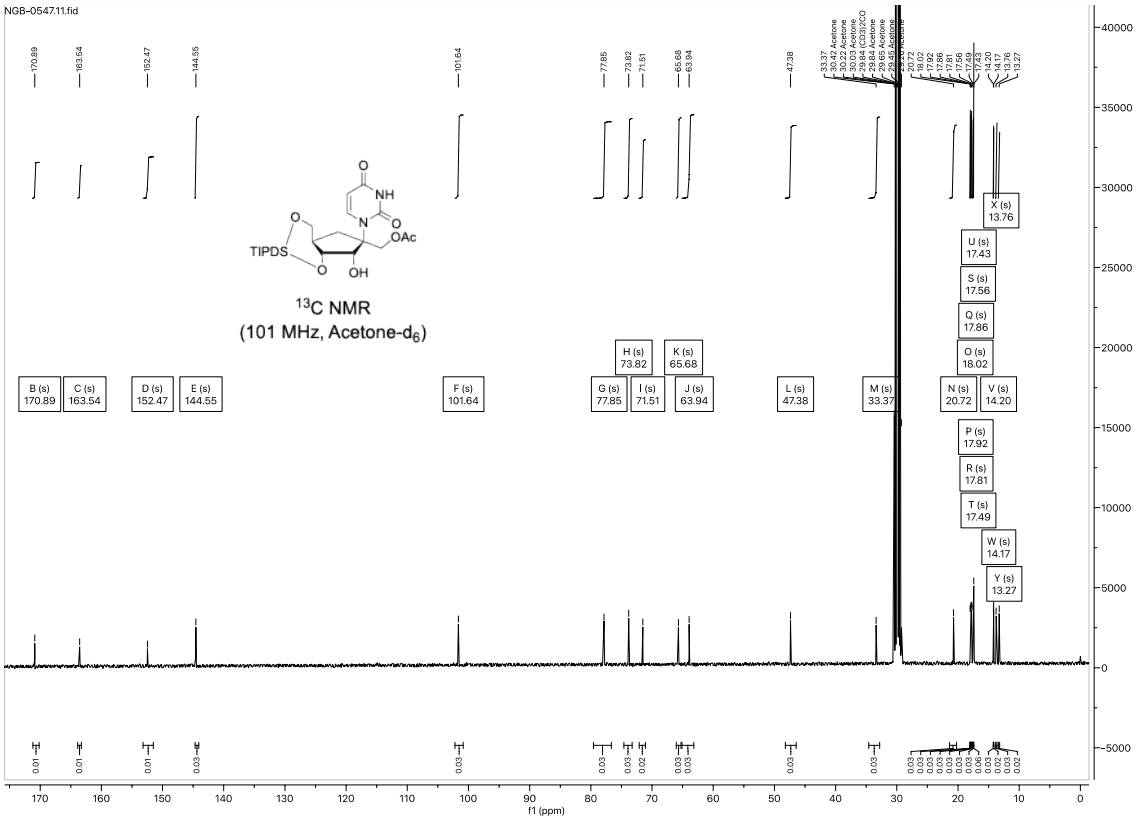
NMR Spectral data of compound-8:



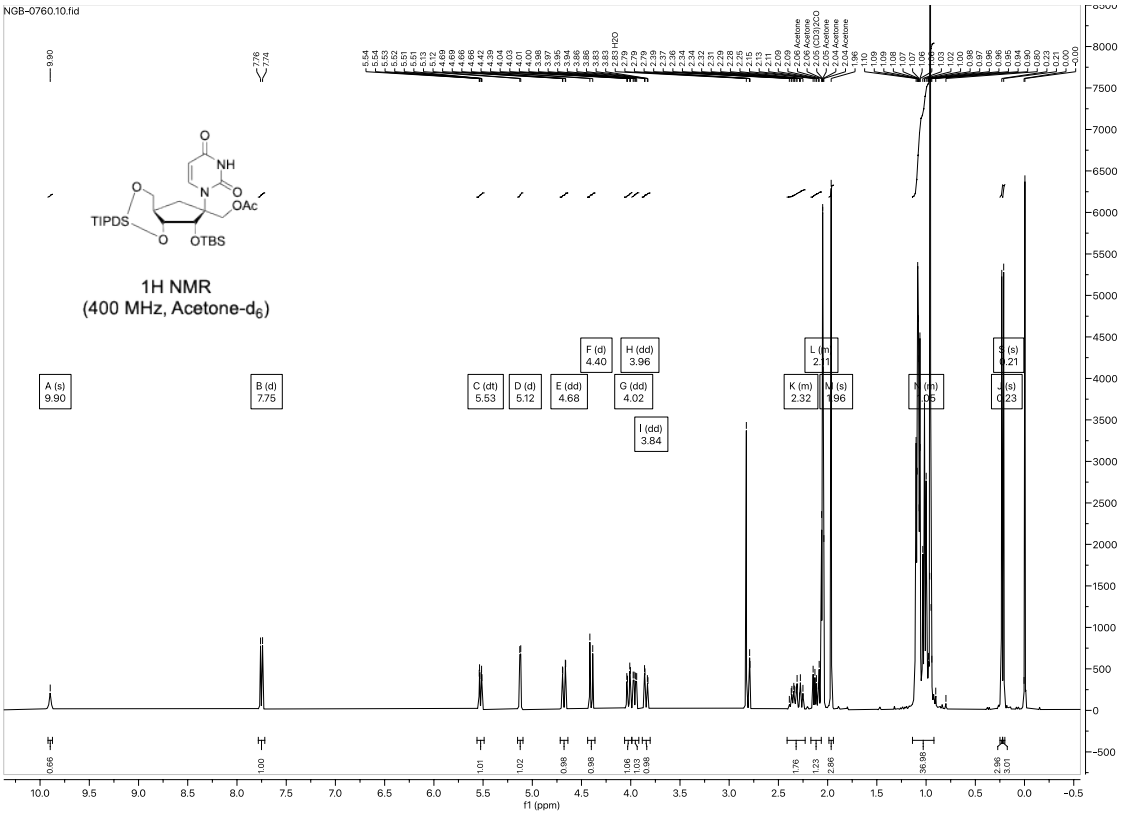


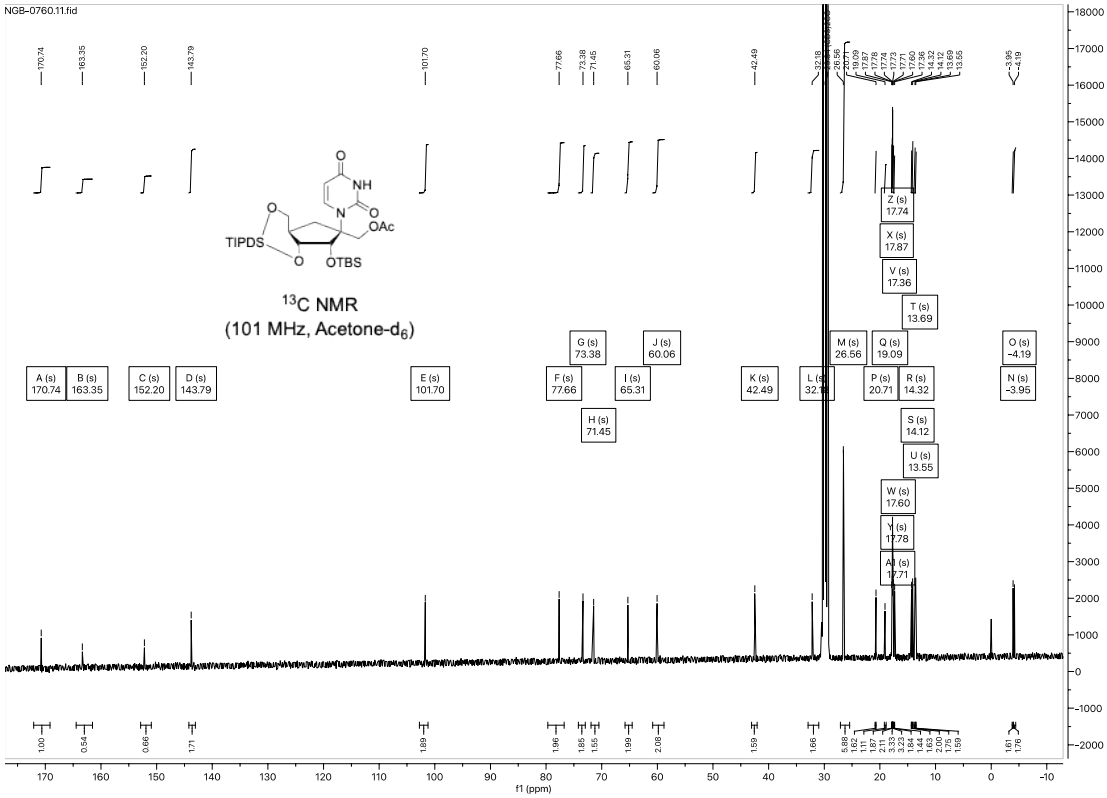
NMR Spectral data of compound-9:



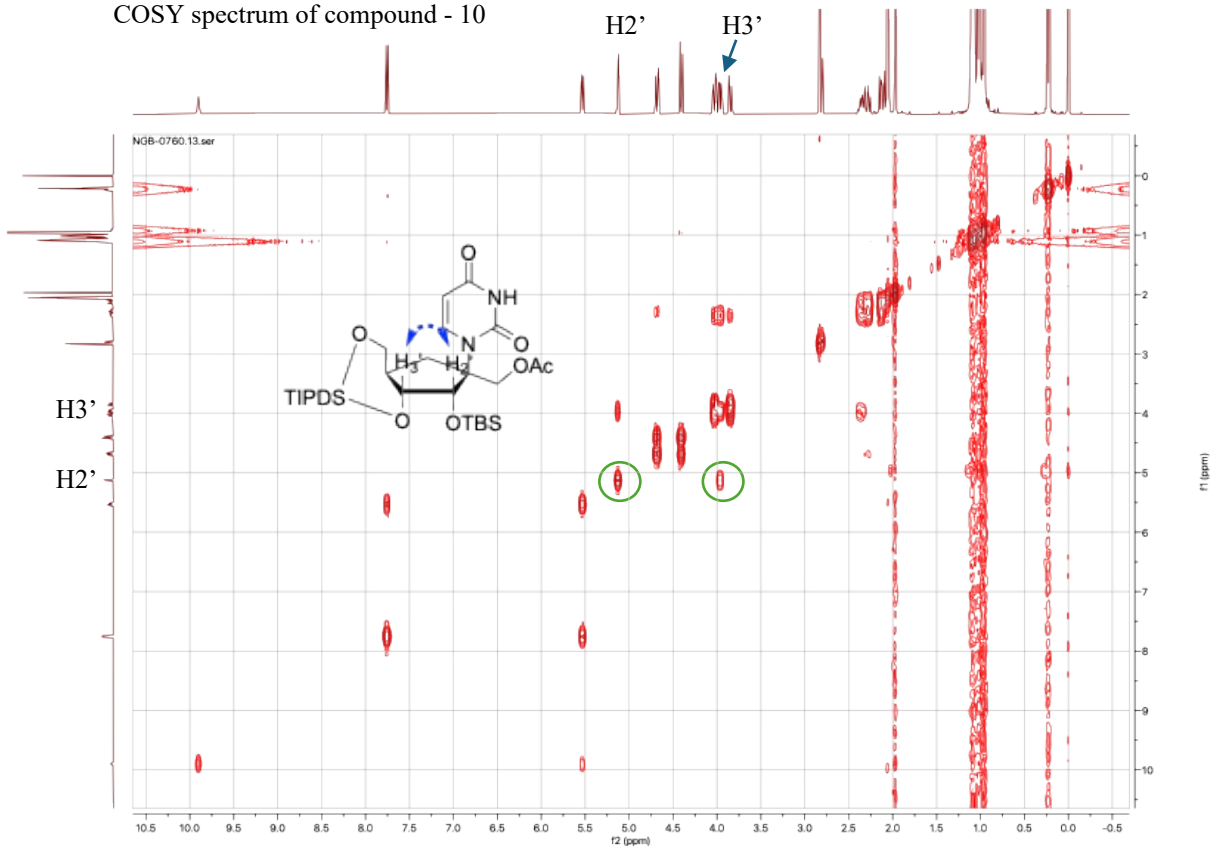


NMR Spectral data of compound-10:

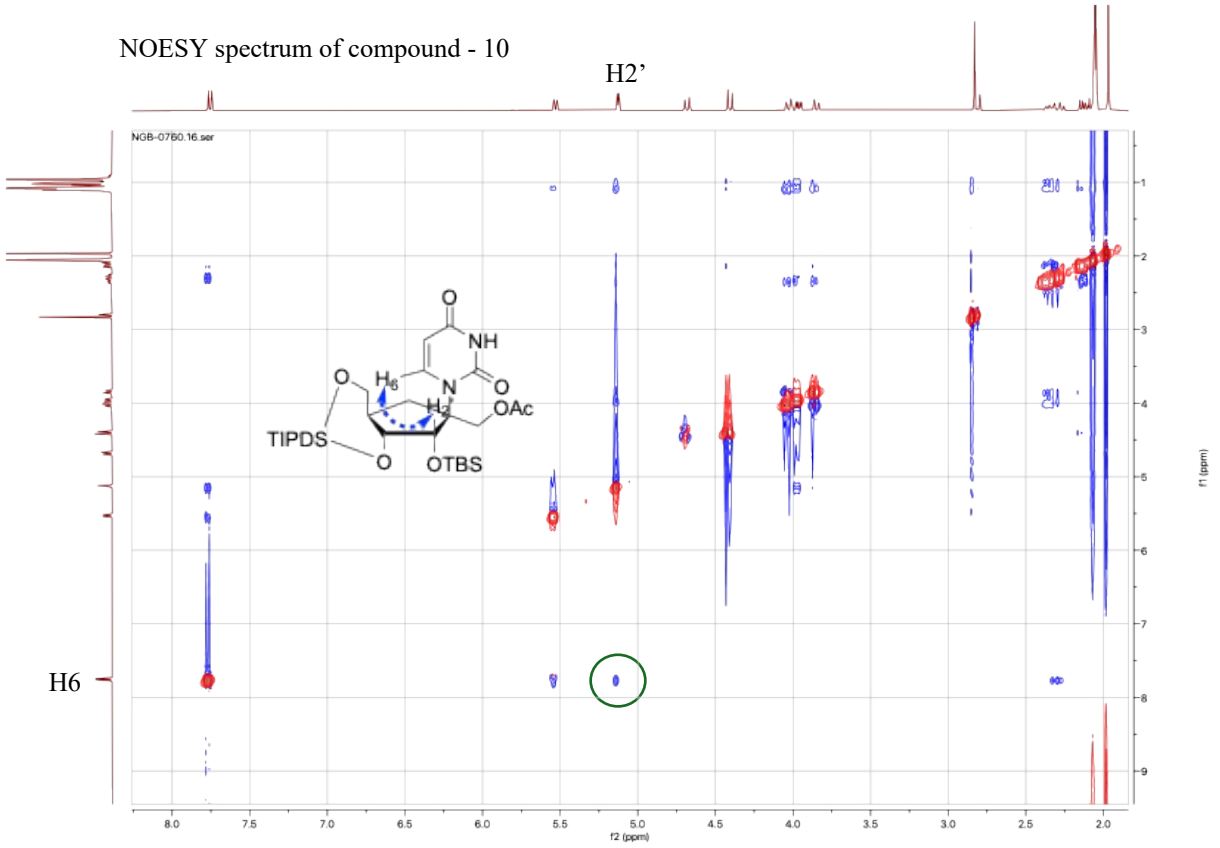




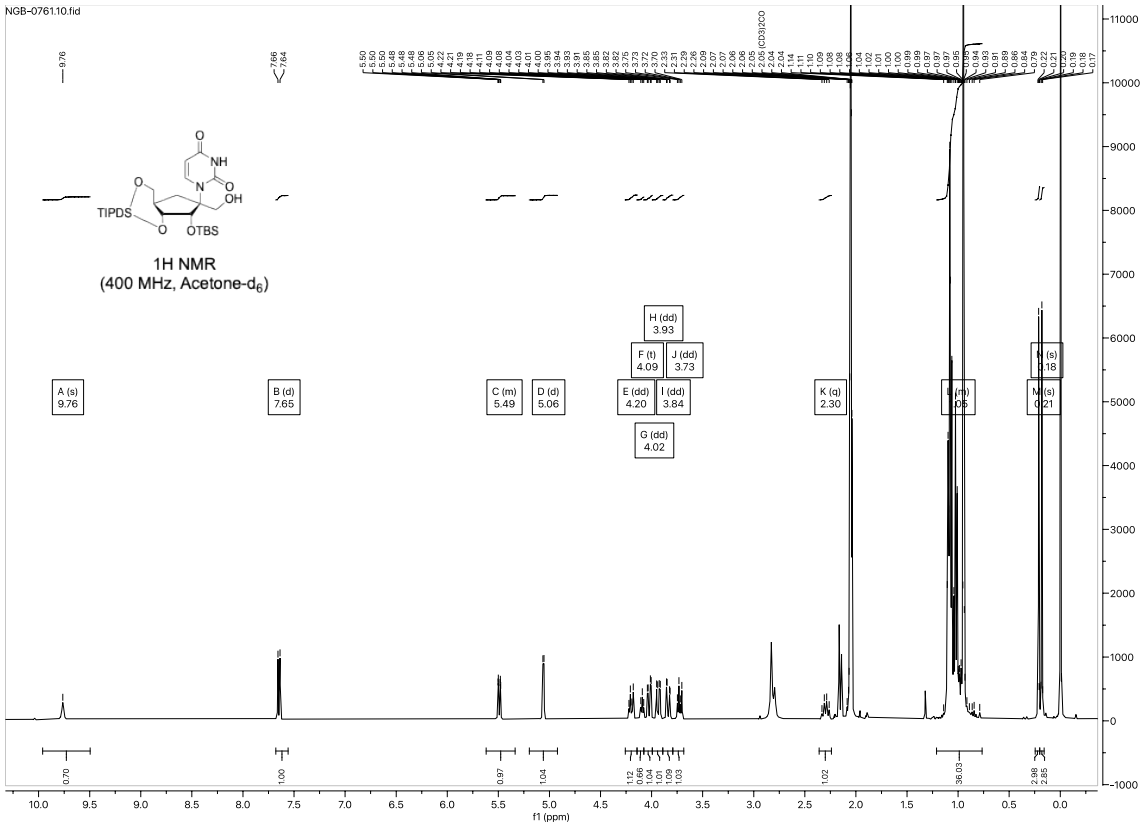
COSY spectrum of compound - 10

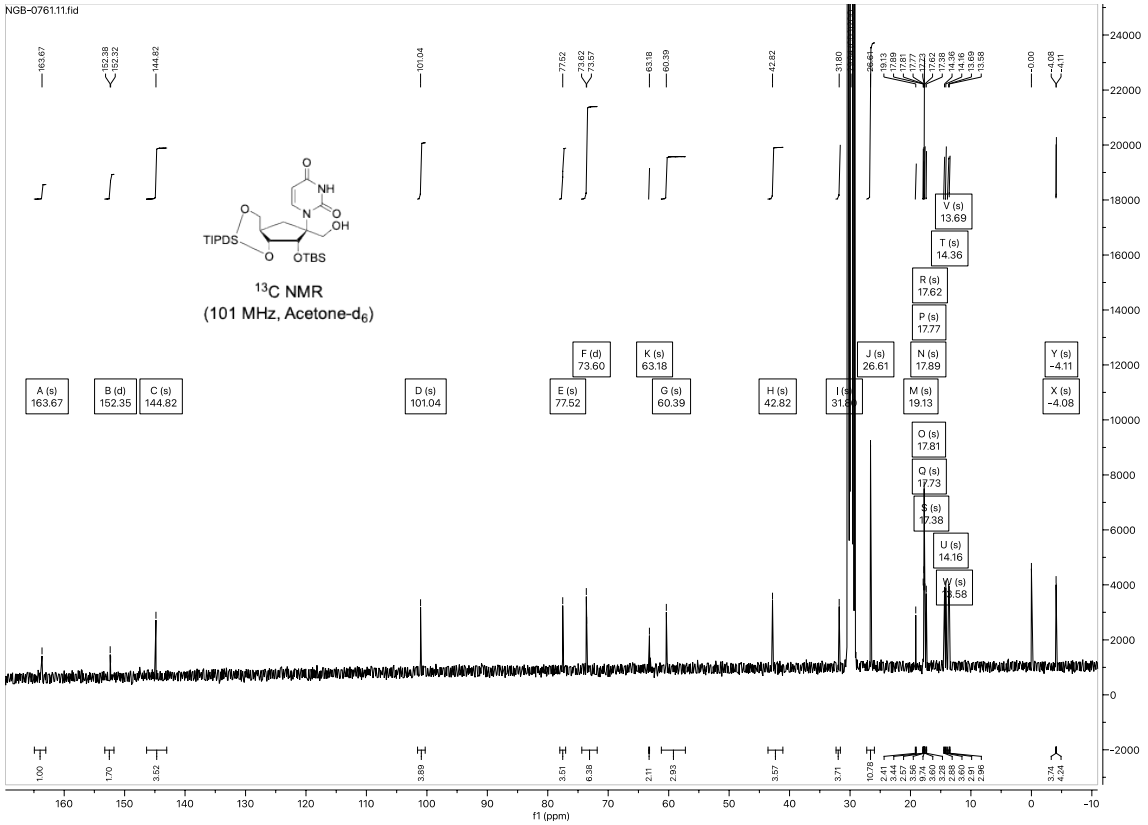


NOESY spectrum of compound - 10

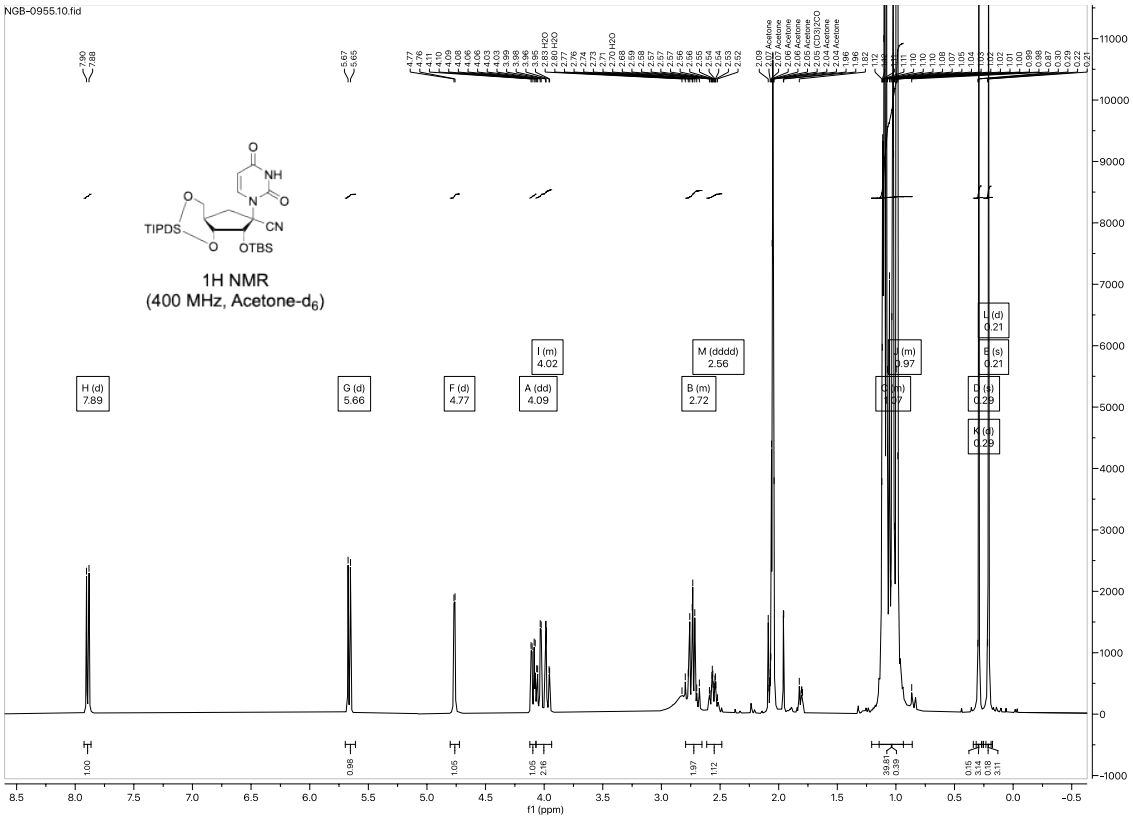


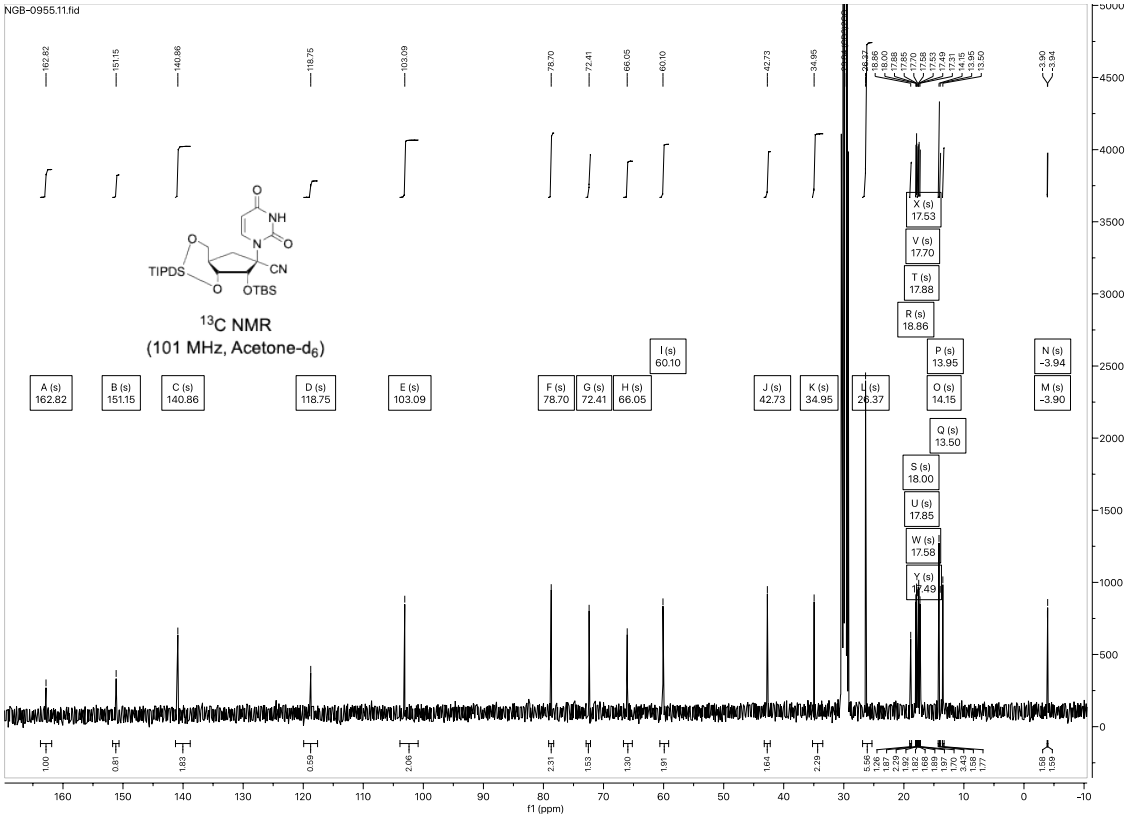
NMR Spectral data of compound-14:



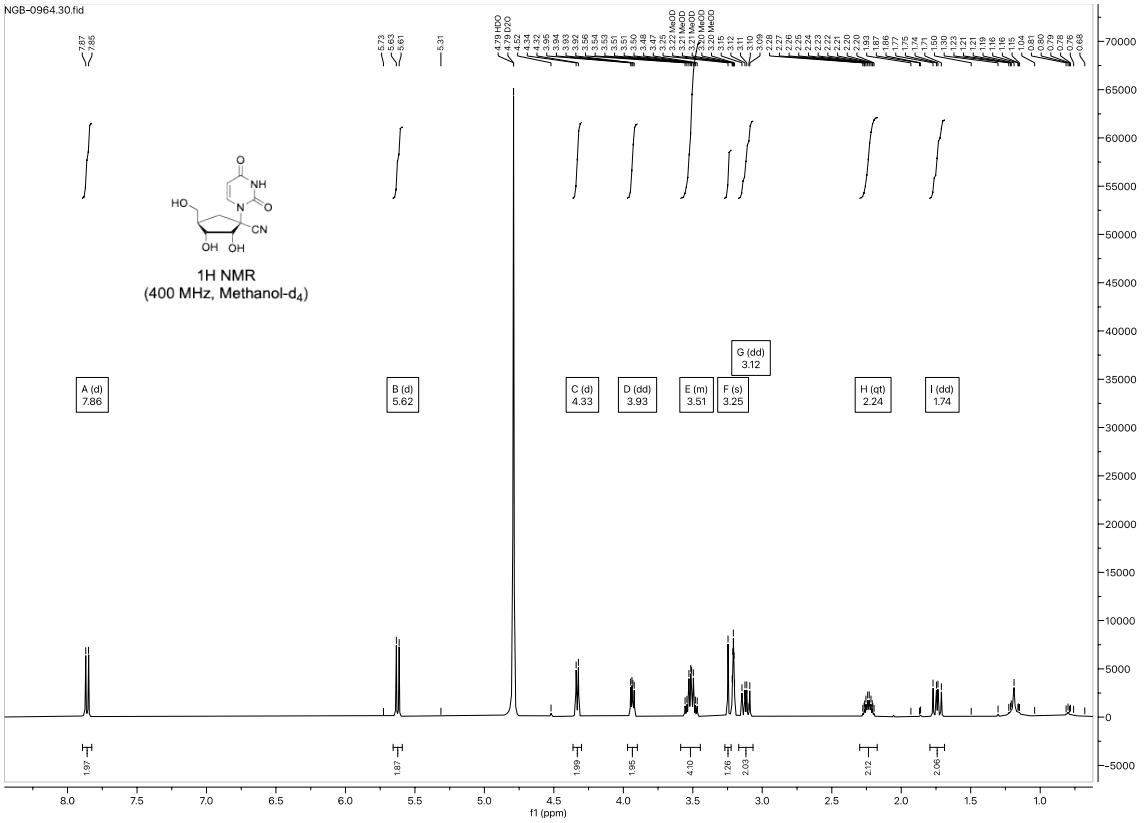


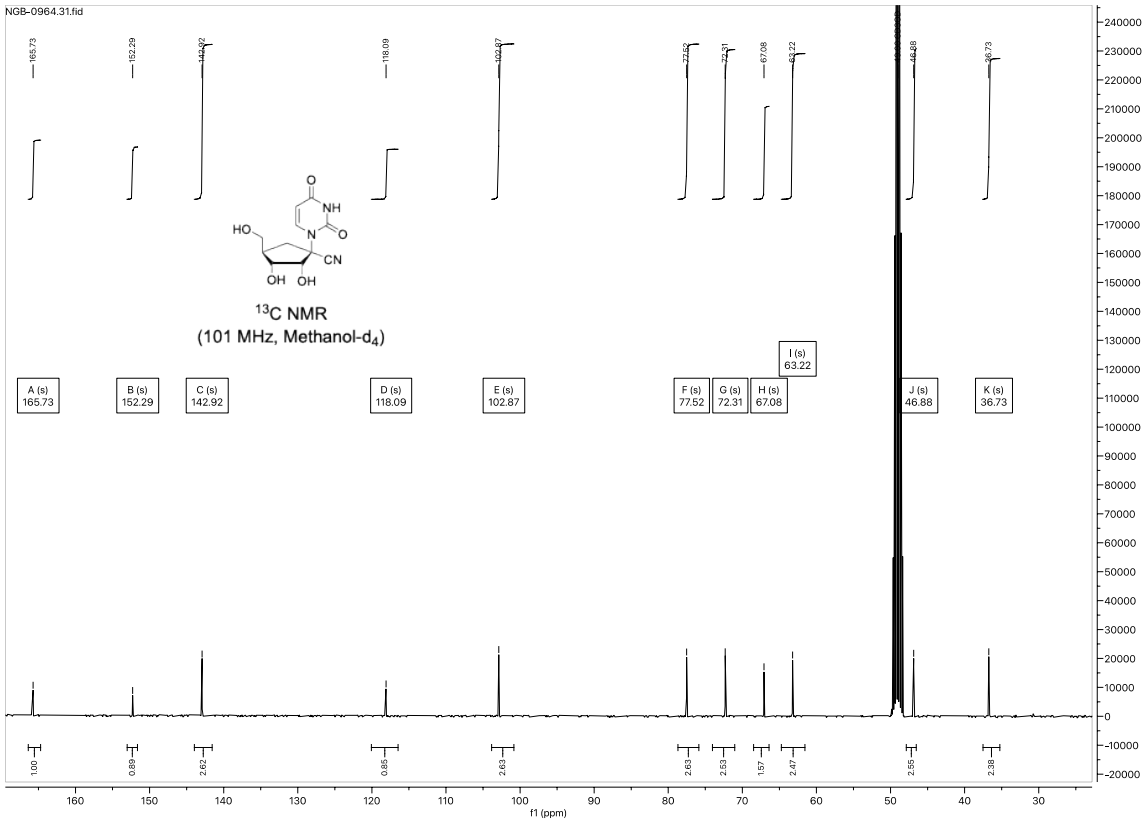
NMR Spectral data of compound-16:



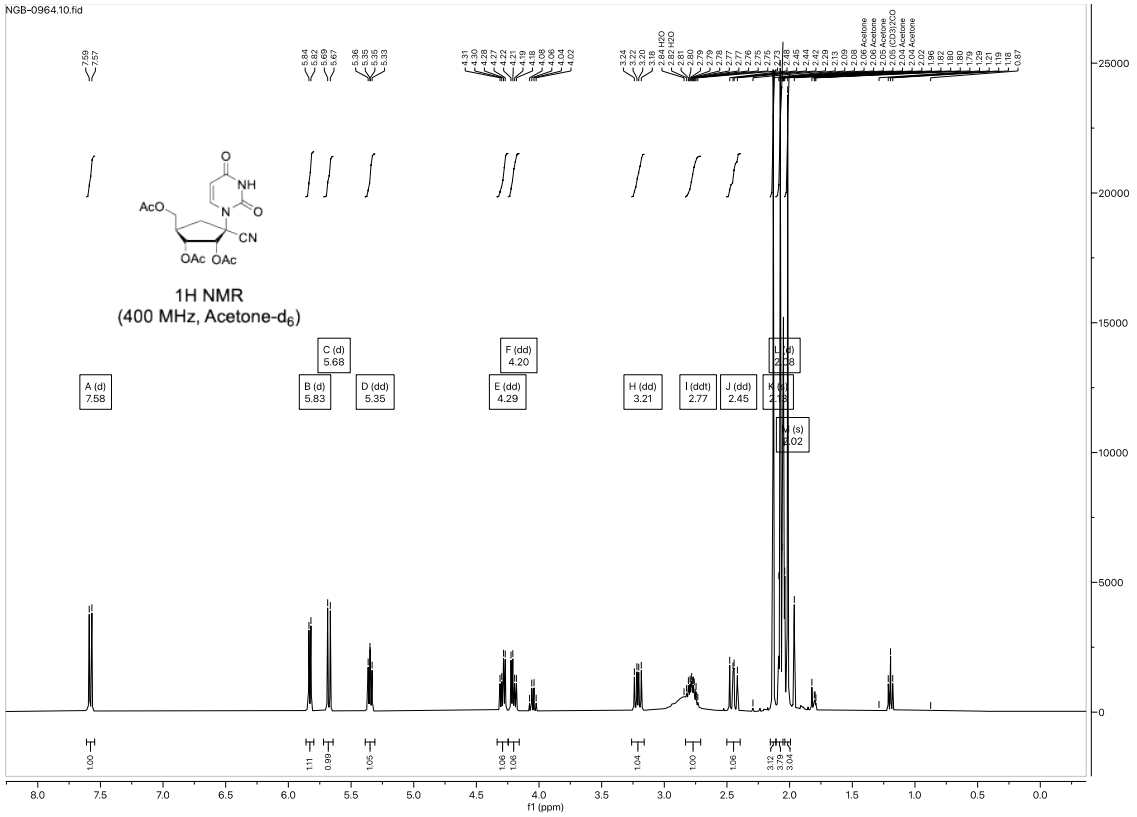


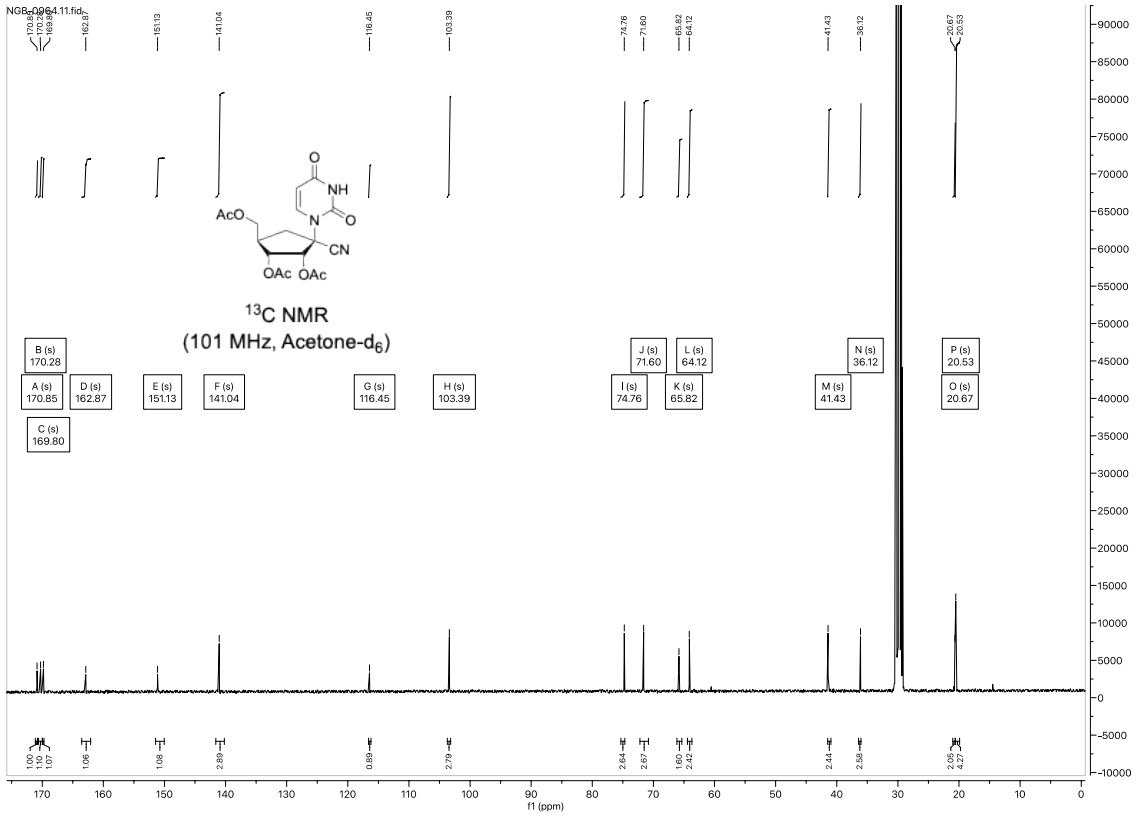
NMR Spectral data of Carba-CNU-1:



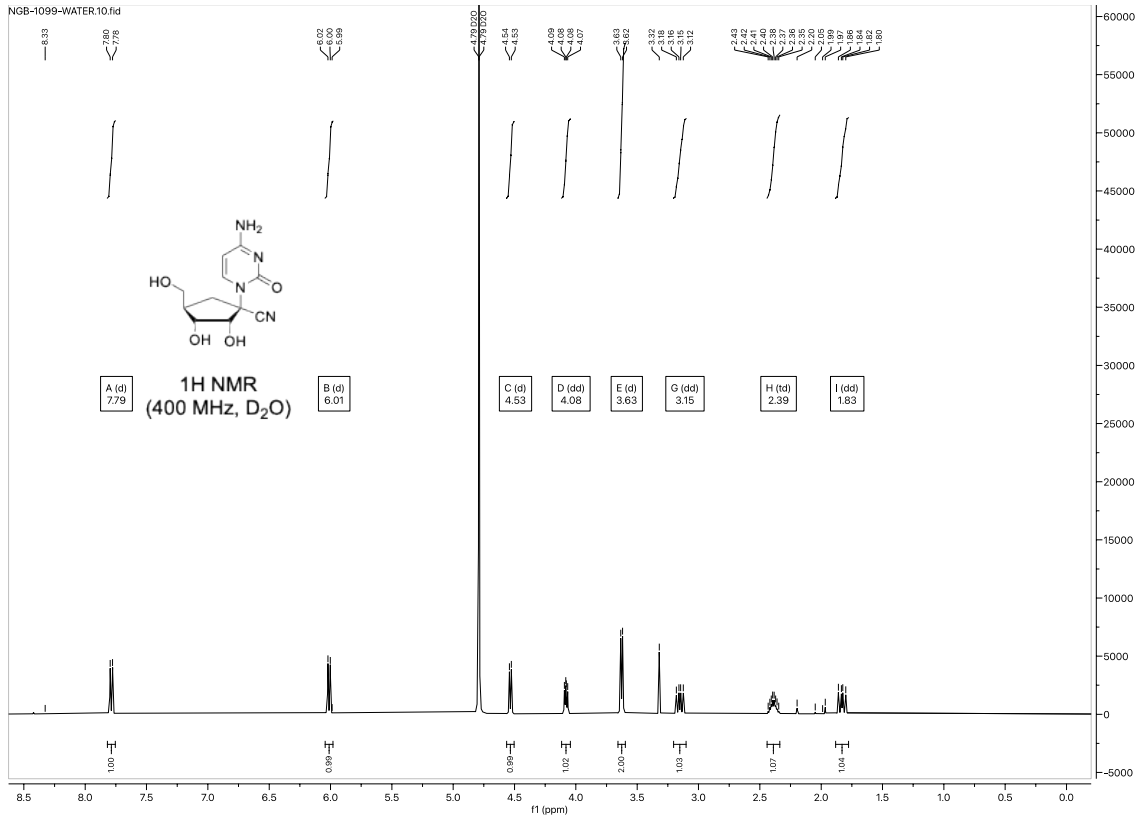


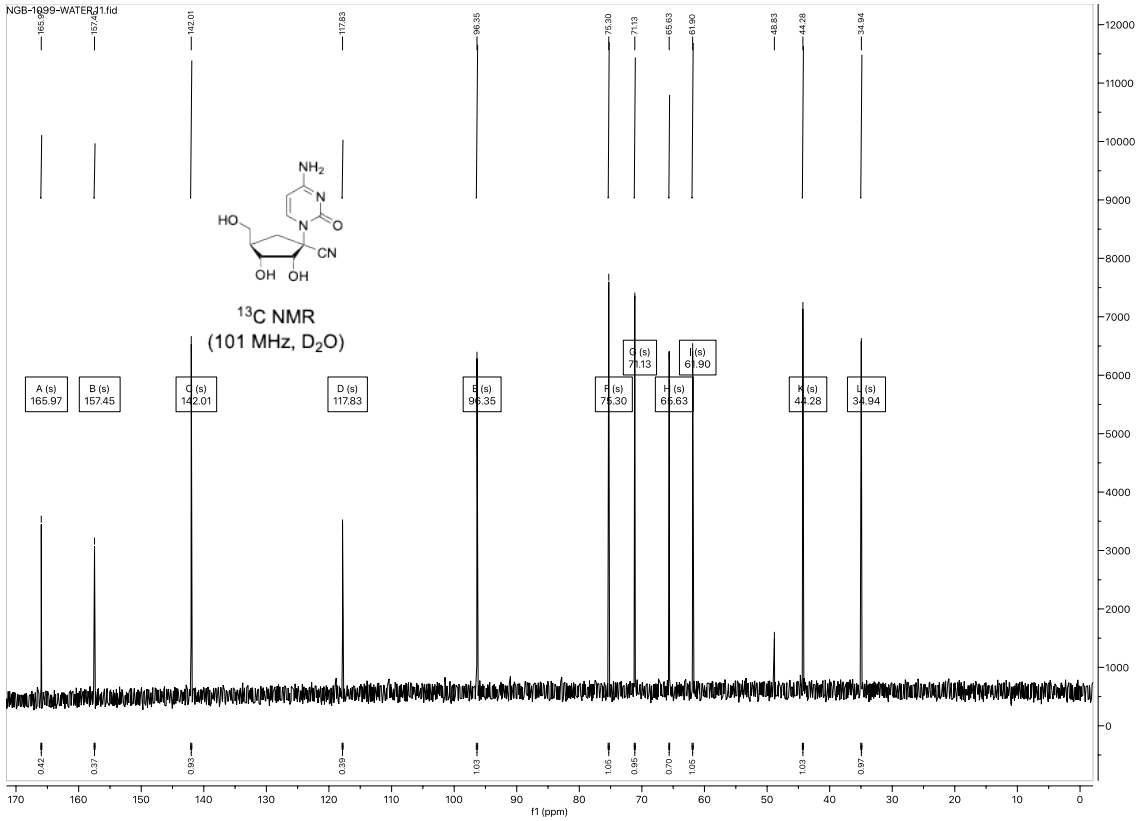
NMR Spectral data of compound-17:



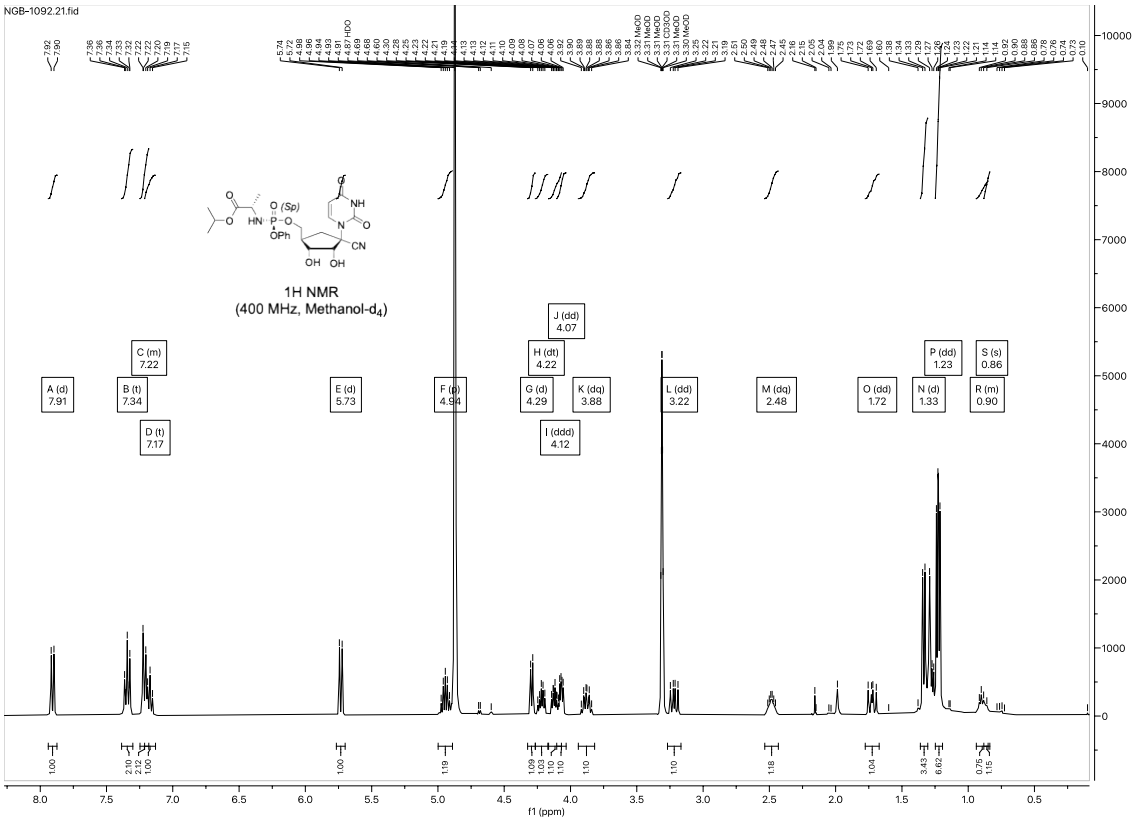


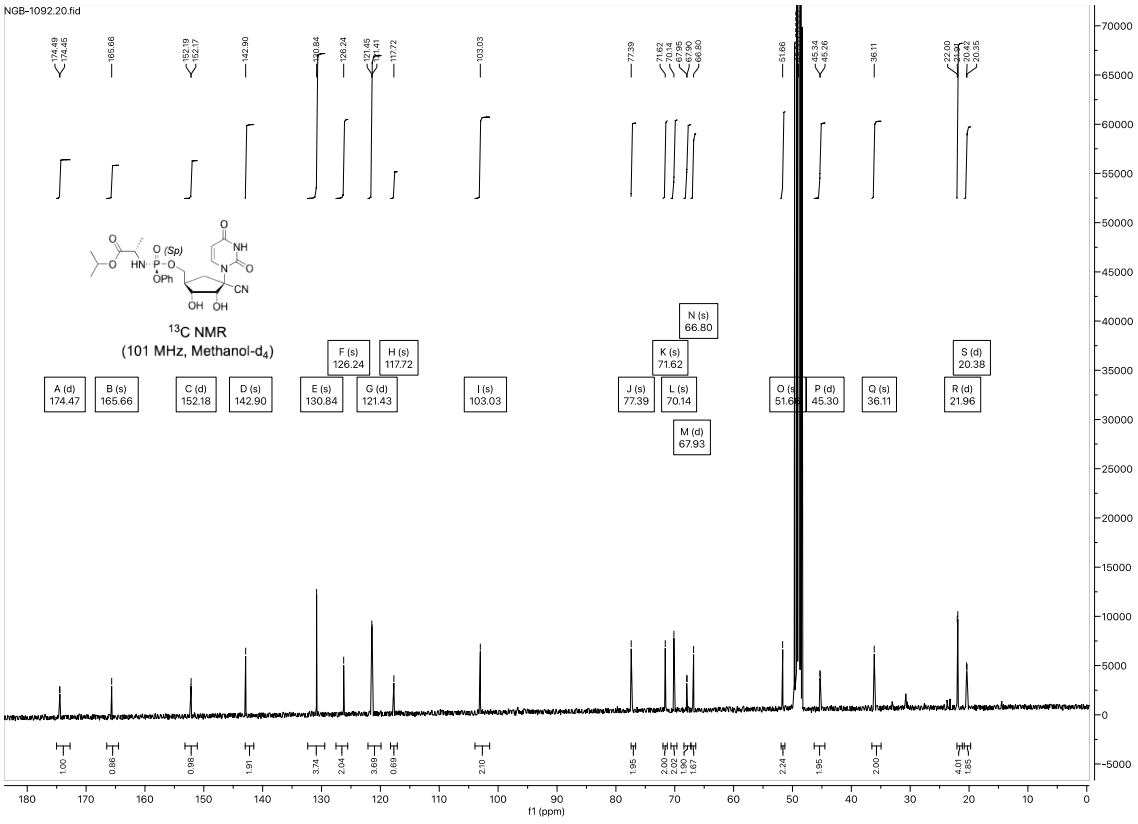
NMR Spectral data of Carba-CNC-3:

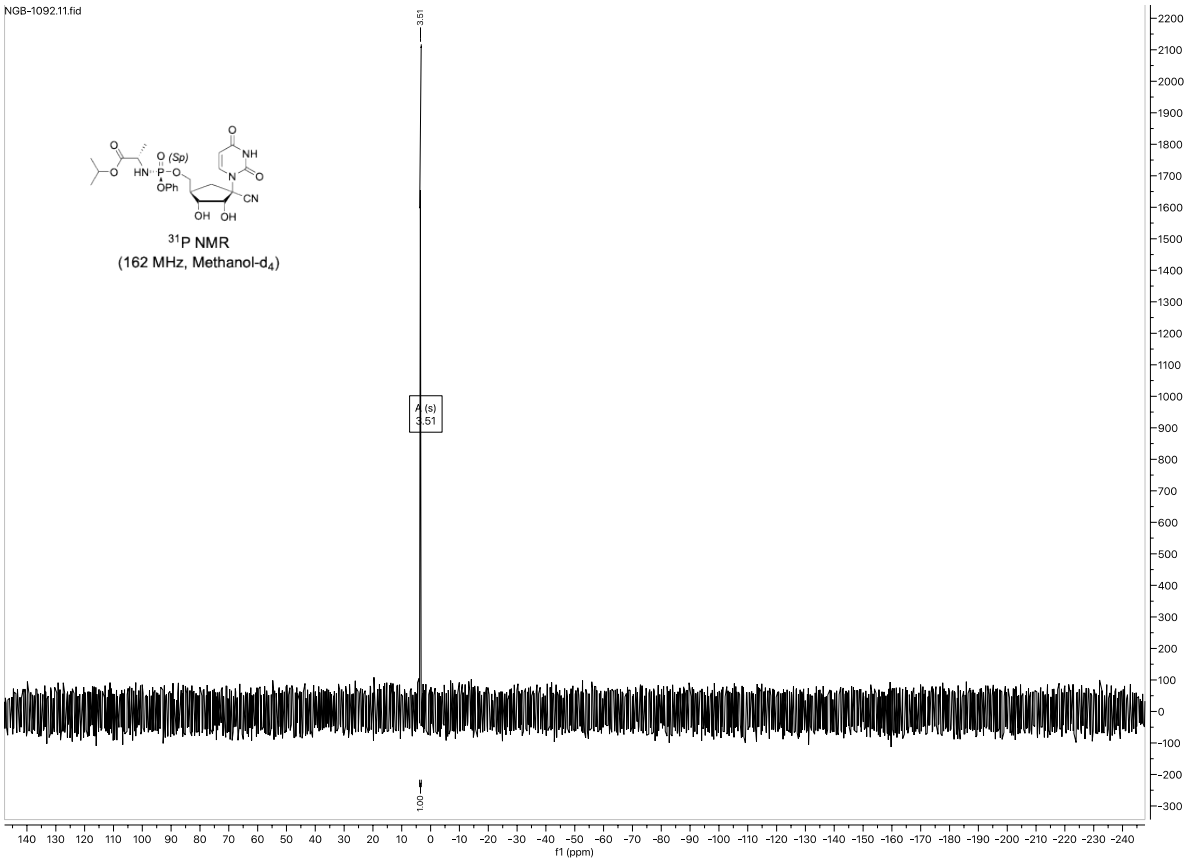




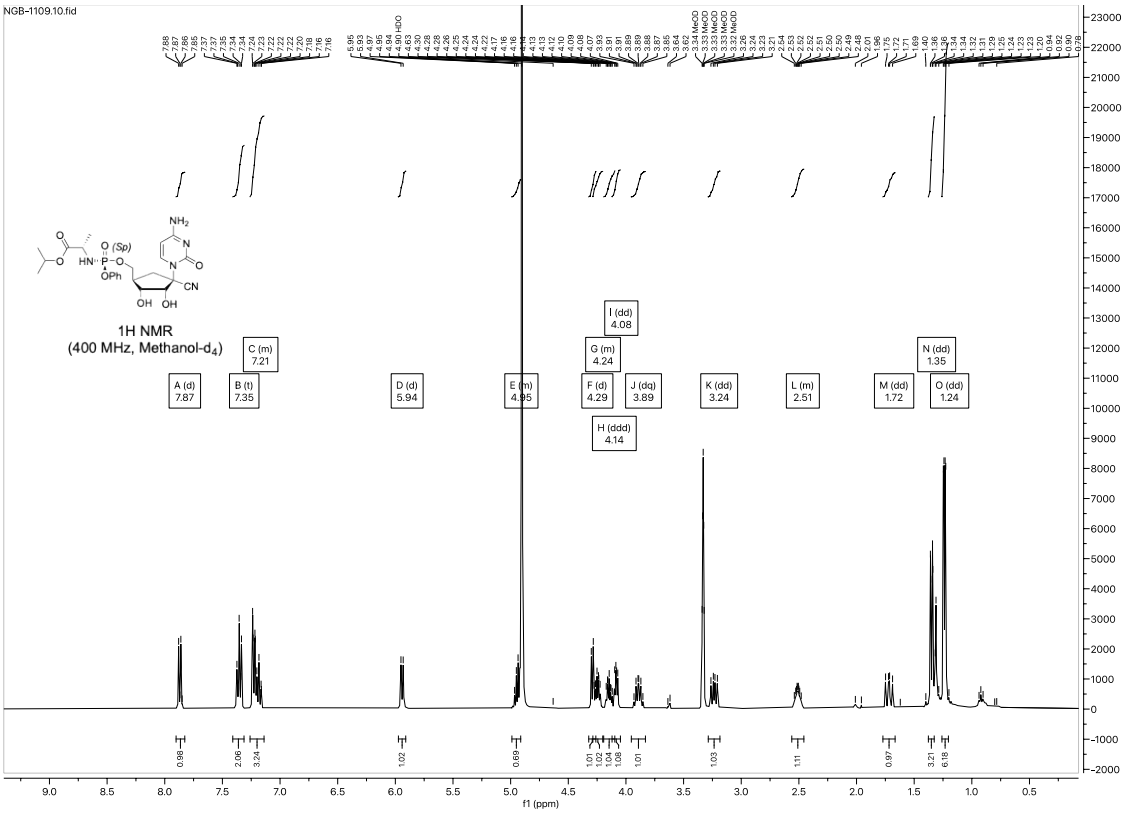
NMR Spectral data of compound-2:

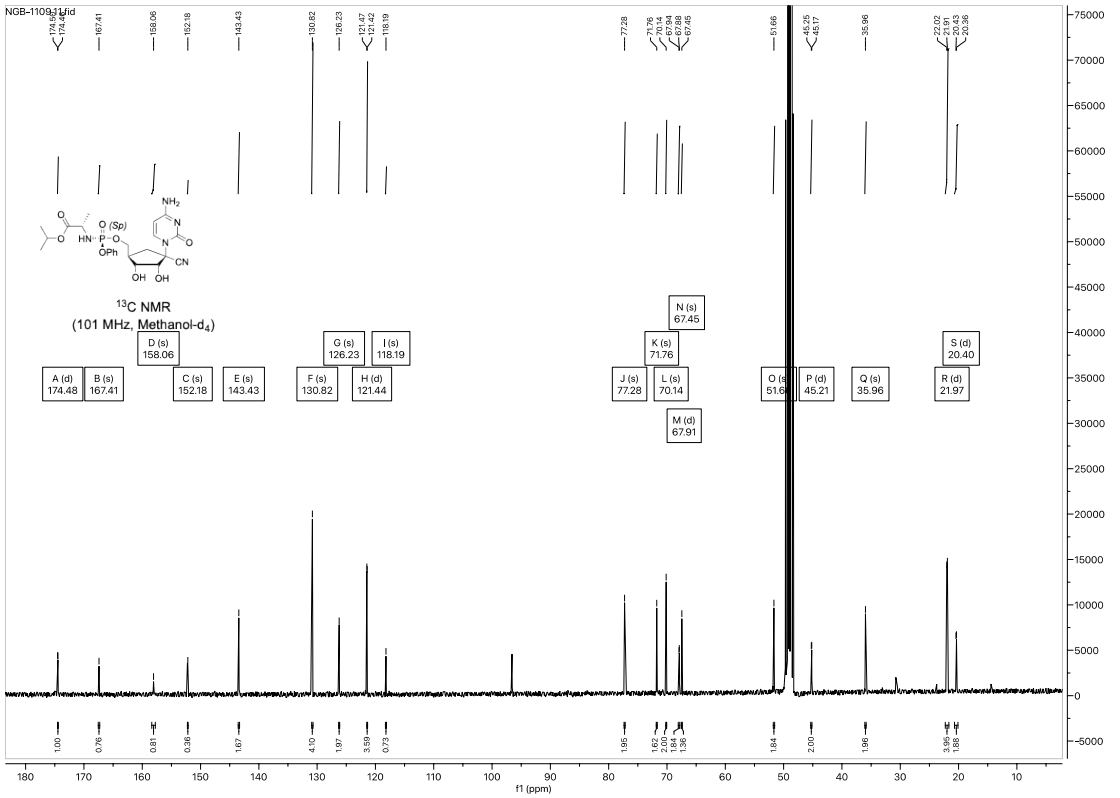


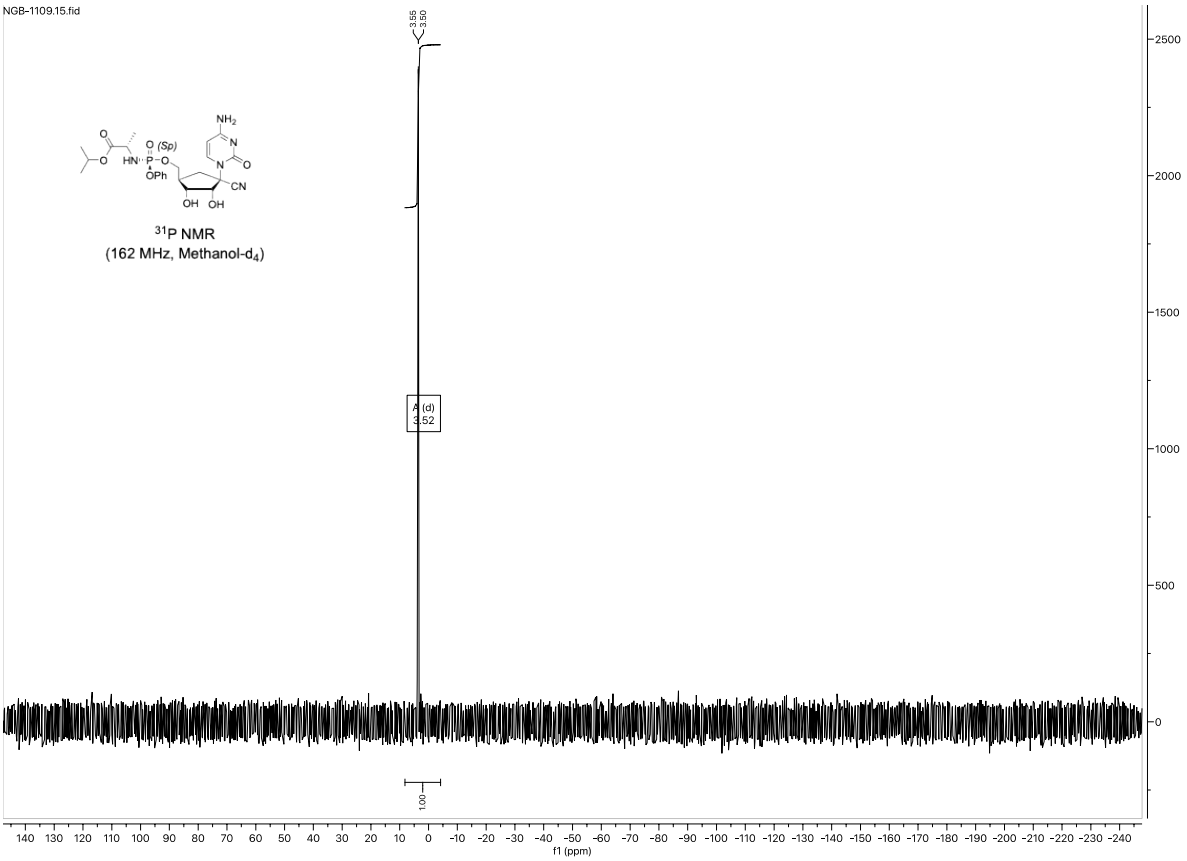



NGB-1092.11.fid
(Sp)
^{31}P NMR
(162 MHz, Methanol-d$_4$)
A (s)
3.51
f1 (ppm)

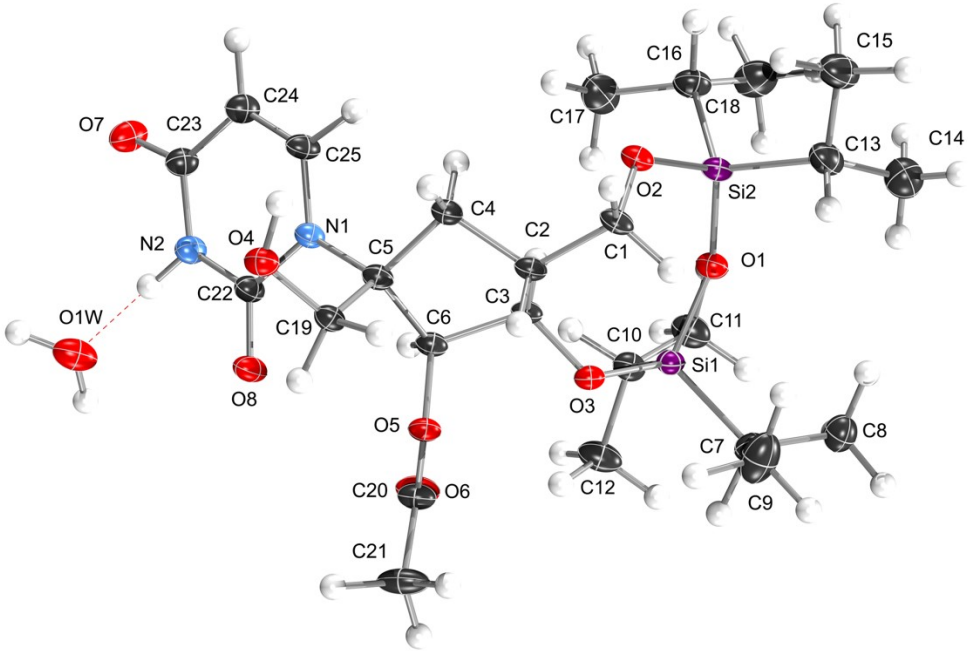
NMR Spectral data of compound-4:







X-ray crystallographic data of intermediate – 9A.[1a-e]



Experimental. Single colorless prism-shaped crystals of **9A** were recrystallised from methanol by slow evaporation. A suitable crystal with dimensions 0.25 × 0.17 × 0.07 mm^3 was selected and mounted on a loop on a XtaLAB Synergy-S diffractometer. The crystal was kept at a steady T = 99.9(2) K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 1.5-alpha (Dolomanov et al., 2009) as the graphical interface. The model was refined with olex2.refine 1.5-alpha (Bourhis et al., 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{51}H_{96}N_4O_{19}Si_4$, M_r = 1181.688, triclinic, $P\bar{1}$ (No. 1), a = 9.4118(3) Å, b = 9.4411(3) Å, c = 19.4473(6) Å, α = 93.921(2)°, β = 94.270(2)°, γ = 115.720(3)°, V = 1542.74(9) Å^3, T = 99.9(2) K, Z = 1, Z' = 1, μ(Cu K$_\alpha$) = 1.490, 22437 reflections measured, 7868 unique (R_{int} = 0.0756) which were used in all calculations. The final wR_2 was 0.1260 (all data) and R_1 was 0.0573 (I≥2 σ(I)).

Compound	**9A**
Formula	$C_{51}H_{96}N_4O_{19}Si_4$
$D_{calc.}$/ g cm^{-3}	1.272
μ/mm^{-1}	1.490
Formula Weight	1181.688
Color	colorless
Shape	prism-shaped
Size/mm^3	0.25×0.17×0.07
T/K	99.9(2)
Crystal System	triclinic
Flack Parameter	0.05(4)
Hooft Parameter	0.05(4)
Space Group	$P1$
a/Å	9.4118(3)
b/Å	9.4411(3)
c/Å	19.4473(6)
α/°	93.921(2)
β/°	94.270(2)
γ/°	115.720(3)
V/Å^3	1542.74(9)
Z	1
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	2.29
Θ_{max}/°	73.19
Measured Refl's.	22437
Indep't Refl's	7868
Refl's I≥2 σ(I)	7024
R_{int}	0.0756
Parameters	1318
Restraints	2522
Largest Peak	0.2500
Deepest Hole	-0.2563
GooF	1.1210
wR_2 (all data)	0.1260
wR_2	0.1223
R_1 (all data)	0.0650
R_1	0.0573

Structure Quality Indicators

Reflections: d min (Cu\a) 2Θ=146.4° 0.81 | I/σ(I) 13.7 | Rint m=2.85 7.56% | Full 135.4° 94% to 146.4° 98.8

Refinement: Shift -0.082 | Max Peak 0.2 | Min Peak -0.3 | GooF 1.121 | Hooft .05(4)

A colourless prism-shaped-shaped crystal with dimensions 0.25 × 0.17 × 0.07 mm^3 was mounted on a loop. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer operating at T = 99.9(2) K. Data were measured using ω scans with Cu K$_\alpha$ radiation. The diffraction pattern was indexed

and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.42.74a (Rigaku OD, 2022). The maximum resolution that was achieved was Θ = 73.19° (0.81 Å).

The unit cell was refined using CrysAlisPro 1.171.42.74a (Rigaku OD, 2022) on 8300 reflections, 37% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.42.74a (Rigaku OD, 2022). The final completeness is 98.88 % out to 73.19° in Θ. A numerical absorption correction based on gaussian integration over a multifaceted crystal model was performed using CrysAlisPro 1.171.42.74a (Rigaku Oxford Diffraction, 2022). An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was also applied. The absorption coefficient μ of this material is 1.490 mm^{-1} at this wavelength (λ = 1.54184Å) and the minimum and maximum transmissions are 0.628 and 1.000.

The structure was solved and the space group *P*1 (# 1) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version of olex2.refine 1.5-alpha (Bourhis et al., 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

Hydrogen atom positions were located from the electron densities and freely refined using Hirshfeld scattering factors. Refinement was by using NoSpherA2, an implementation of non-spherical atom-form-factors (F. Kleemiss, H. Puschmann, O. Dolomanov, S.Grabowsky - https://doi.org/10.1039/D0SC05526C – 2020). NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated from a Hirshfeld-partitioned electron density (ED) not from spherical-atom form factors. The ED was calculated from a Gaussian basis set single determinant SCF wavefunction from DFT using selected functionals for a fragment of this crystal. The following options were used: SOFTWARE: ORCA PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: PBE BASIS SET: def2-SVP CHARGE: 0 MULTIPLICITY: 1 SOLVATION: Ethanol DATE: 2023-03-06_18-51-20

The crystal structure shows the presence of an additional methanol molecule and two water molecules in the crystal lattice. The methanol shows long range disorder with the hydroxyl and methyl groups switching positions (head to tail disorder). Because there is only one whole methanol for two formula units of the target molecule, the formula unit is $2(C_{25}\ H_{44}\ N_2\ O_8\ Si_2)$, $2(H_2O)$, $(CH_3\ OH)$. There is a single formula unit in the asymmetric unit (and the unit cell), which is represented by the reported sum formula. In other words: Z is 1 and Z' is 1.

The Flack parameter was refined to 0.1(1). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.1(4). The chiral atoms in this structure are: C2(R), C2B(R), C3(R), C3B(R), C5(S), C5B(S), C6(S), C6B(S). It's important to note that the Flack parameter is a crucial parameter for determining the chirality of the crystal under study. Ideally, its value should be close to 0. A value of 1 indicates that the stereochemistry is incorrect and the model should be inverted. A value of 0.5 signifies that the crystal is a racemic mixture of both enantiomers.

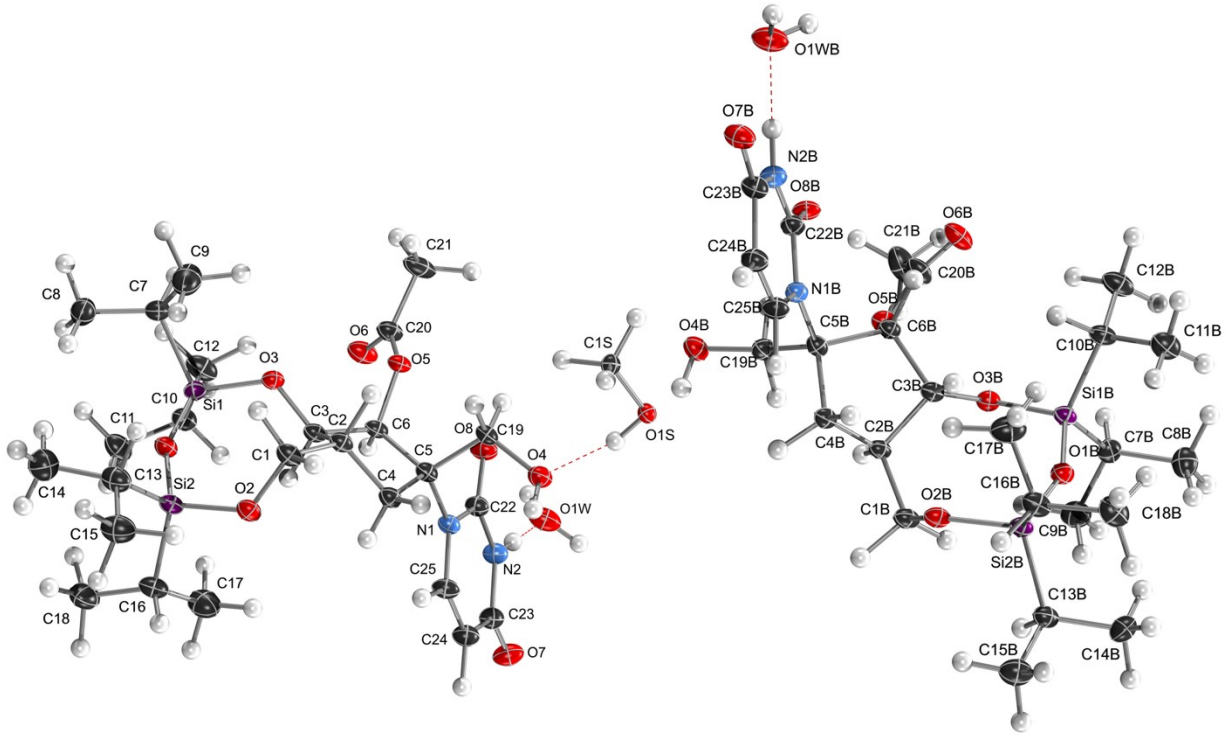


Figure 1: The repeating unit of the crystal structure of the sample. There is only one whole methanol for two formula units of the target molecule, the formula unit is $2(C_{25}\ H_{44}\ N_2\ O_8\ Si_2)$, $2(H_2O)$, $(CH_3\ OH)$. There is a single formula unit in the asymmetric unit (and the unit cell), which is represented by the reported sum formula The methanol shows long range disorder with the hydroxyl and methyl groups switching positions (head to tail disorder).

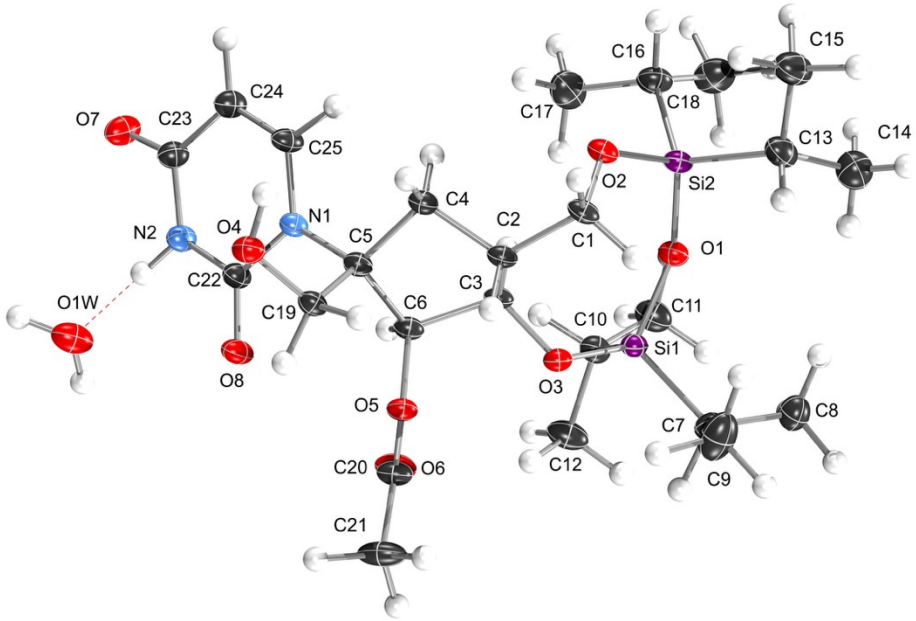
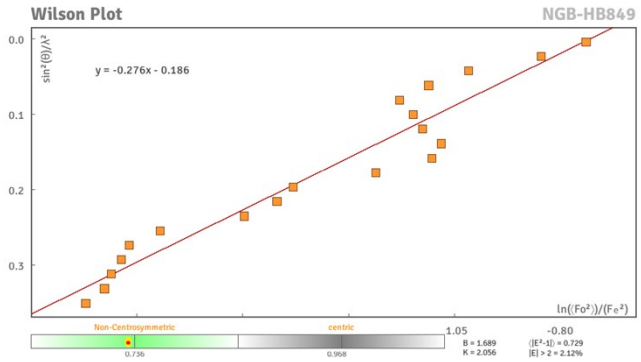
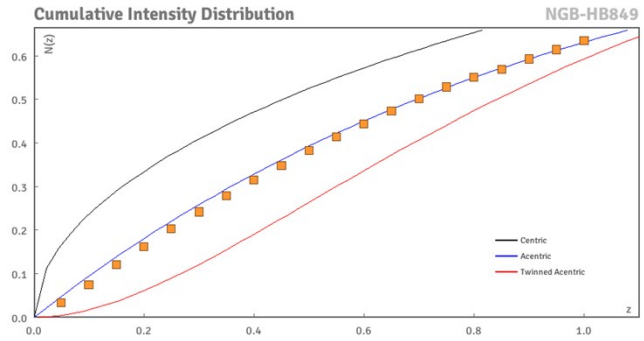
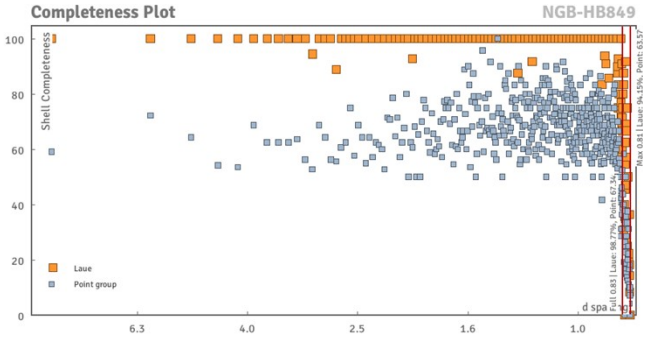


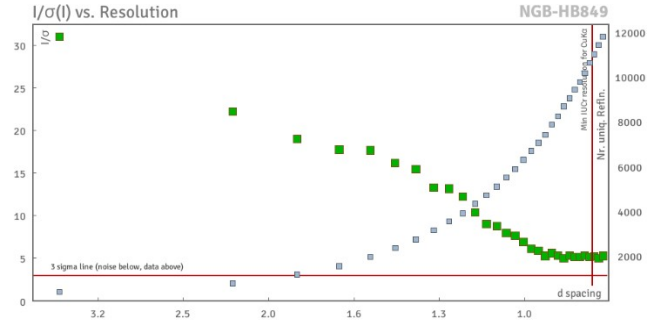
Figure 2: The molecular structure. The chiral atoms in this structure are: C2(R), C3(R), C5(S), C6(S).

Data Plots: Diffraction Data

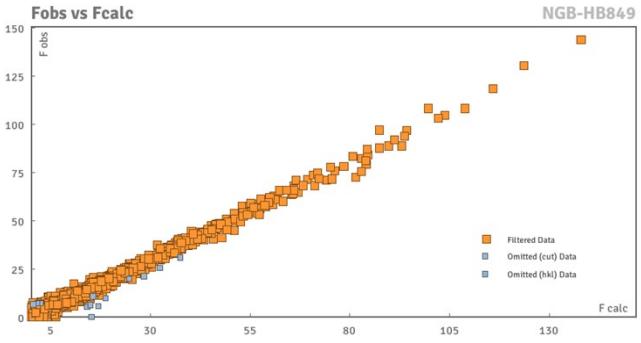


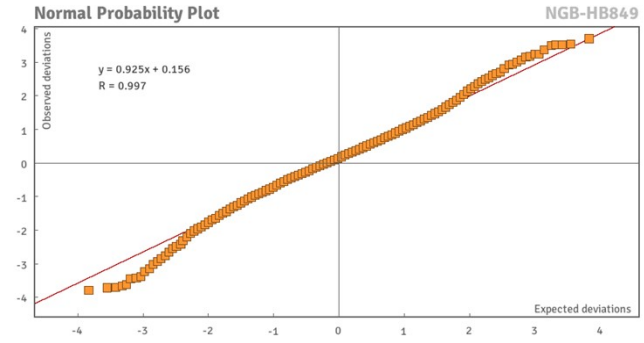






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	22437	Unique reflections	7868
Completeness	0.636	Mean I/σ	10.41
hkl_{max} collected	(11, 10, 24)	hkl_{min} collected	(-11, -11, -24)
hkl_{max} used	(11, 10, 24)	hkl_{min} used	(-11, -11, -23)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	19.27	d_{min} used	0.81
Friedel pairs	2042	Friedel pairs merged	0

Inconsistent equivalents	10	R_{int}	0.0756
R_{sigma}	0.073	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	23
Multiplicity	(2548, 1825, 1138, 920, 613, 353, 213, 113, 92, 35, 15, 9, 4, 1, 0, 1, 2)	Maximum multiplicity	17
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **9A**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Si1B	-1093.9(11)	7784.8(11)	1610.1(5)	17.2(2)
Si2B	2232.1(11)	10847.5(11)	1790.0(5)	17.5(2)
O3B	-607(3)	6840(3)	2197.0(13)	19.1(6)
O1B	424(3)	9478(3)	1554.7(14)	20.9(6)
O2B	3031(3)	10345(3)	2459.7(15)	20.9(6)
O8B	-1634(3)	5906(3)	4775.3(15)	22.9(6)
O7B	-628(3)	10133(3)	6318.6(15)	29.5(7)
O5B	-1059(3)	5122(3)	3317.4(14)	19.3(6)
O6B	-3590(3)	4794(3)	3173.2(16)	30.1(7)
O4B	2357(3)	6632(3)	4953.3(15)	24.4(6)
N1B	552(3)	8204(3)	4673.7(17)	18.4(7)
N2B	-1075(4)	8042(4)	5540.0(18)	23.9(7)
C19B	1327(4)	6118(4)	4309(2)	22.1(8)
C5B	933(4)	7430(4)	4065(2)	17.2(8)
C6B	-499(4)	6791(4)	3469(2)	17.1(8)
C3B	232(4)	7641(4)	2848(2)	17.0(7)
C1B	3031(4)	8850(4)	2464(2)	21.9(8)
C2B	1949(4)	7857(4)	2962(2)	17.5(7)
C4B	2354(4)	8570(4)	3720(2)	18.6(8)
C25B	1536(5)	9713(5)	4958(2)	22.4(8)
C24B	1250(5)	10451(5)	5514(2)	23.6(9)
C23B	-182(4)	9592(5)	5832(2)	23.0(8)
C22B	-766(4)	7295(4)	4986(2)	20.0(8)
C7B	-1518(5)	6456(5)	787(2)	23.5(9)
C8B	-2159(5)	7007(5)	166(2)	31.3(10)
C9B	-56(5)	6255(5)	627(2)	33.1(11)
C10B	-2766(4)	8199(4)	1871(2)	22.5(9)
C12B	-4316(5)	6680(5)	1814(3)	29.8(10)
C11B	-3003(5)	9469(5)	1497(2)	29.2(10)
C13B	3424(4)	10960(5)	1049(2)	22.2(9)
C15B	5099(5)	12333(5)	1192(3)	33.3(11)
C14B	2626(5)	10993(5)	342(2)	33.9(11)
C16B	2244(5)	12751(4)	2130(2)	23.6(9)
C17B	1347(5)	12540(5)	2776(3)	34.2(11)
C18B	1594(5)	13486(5)	1591(2)	30.4(10)
C20B	-2651(5)	4251(5)	3206(2)	25.4(9)
C21B	-3088(5)	2520(5)	3143(3)	40.0(12)
Si1	8607.2(11)	1447.7(11)	8379.4(6)	18.7(2)
Si2	11624.5(11)	4665.6(12)	8217.9(6)	20.3(2)
O3	7379(3)	1642(3)	7784.0(13)	19.3(6)
O1	10344(3)	3000(3)	8442.8(14)	22.6(6)

Atom	x	y	z	U_{eq}
O2	10786(3)	5183(3)	7571.9(15)	22.3(6)
O8	5154(3)	-641(3)	5208.6(15)	25.9(7)
O7	8640(3)	-393(3)	3675.1(16)	30.3(7)
O5	5100(3)	662(3)	6669.4(14)	19.9(6)
O6	4821(3)	-1800(3)	6792.1(17)	31.2(7)
O4	5788(3)	3237(3)	5035.8(15)	25.1(6)
N2	6933(4)	-461(3)	4452.9(17)	23.0(7)
C5	7043(4)	2281(4)	5934(2)	18.9(7)
C6	6705(4)	1144(4)	6513(2)	18.3(7)
C3	7866(4)	2172(4)	7146(2)	17.8(7)
C1	9260(4)	5159(4)	7561(2)	21.3(8)
C2	8042(4)	3842(4)	7046(2)	19.0(7)
C4	8356(4)	3875(4)	6285(2)	20.3(8)
C23	8342(5)	290(4)	4161(2)	22.6(8)
C24	9362(5)	1866(5)	4488(2)	24.9(9)
C25	8910(5)	2443(4)	5045(2)	22.8(8)
N1	7518(4)	1610(3)	5321.7(17)	19.0(7)
C22	6456(4)	133(4)	5002(2)	21.3(8)
C7	7675(5)	1395(5)	9193(2)	28.2(9)
C8	8775(5)	1619(5)	9854(2)	32.8(10)
C9	7004(6)	2617(6)	9240(3)	47.6(13)
C10	8899(5)	-343(5)	8116(2)	23.7(8)
C12	7379(5)	-1871(5)	8133(3)	33.5(11)
C11	10328(5)	-404(5)	8525(2)	31.6(10)
C13	12215(5)	6189(5)	8990(2)	31.3(9)
C15	13360(5)	7825(5)	8842(3)	38.7(11)
C14	12850(6)	5739(6)	9648(3)	44.3(13)
C16	13307(5)	4468(5)	7840(2)	29.2(9)
C18	14328(6)	4007(6)	8336(3)	40.9(12)
C17	12700(5)	3318(6)	7174(3)	42.1(12)
C20	4285(5)	-841(5)	6789(2)	25.4(9)
C21	2608(5)	-1235(5)	6893(3)	39.5(12)
C19	5613(4)	2554(4)	5676(2)	19.8(8)
O1W	4879(3)	-3522(3)	3824.2(19)	36.6(8)
O1WB	-3812(3)	6328(3)	6168.7(18)	34.0(8)
O1S_1	3359(5)	3837(5)	4590(3)	16.2(8)
C1S_1	3140(8)	4312(8)	5269(4)	17.0(8)
O1SB_2	3201(5)	4446(5)	5381(3)	17.0(8)
C1SB_2	3357(8)	3935(8)	4697(4)	16.2(8)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) for **NGB-HB849**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1B	14.8(5)	14.1(5)	21.4(5)	4.7(4)	3.3(4)	2.7(4)
Si2B	15.6(5)	14.6(5)	20.8(5)	4.8(4)	3.7(4)	3.0(4)
O3B	18.9(13)	14.5(13)	22.6(13)	5.9(10)	3.8(9)	1.7(9)
O1B	19.4(15)	20.0(15)	24.2(15)	8.4(12)	5.2(12)	6.4(12)
O2B	17.4(14)	14.5(12)	29.3(16)	4.5(9)	7.3(12)	5.5(10)
O8B	18.9(14)	17.6(12)	28.2(16)	3.1(9)	9.6(11)	4.9(9)
O7B	22.8(15)	30.7(17)	33.0(16)	11.0(12)	5.3(11)	-5.3(11)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O5B	19.2(14)	11.6(13)	25.3(15)	5.2(11)	3.7(11)	1.1(11)
O6B	17.0(16)	23.6(16)	48.1(19)	8.0(13)	0.8(13)	3.2(14)
O4B	20.4(15)	21.7(15)	32.9(15)	10.4(12)	3.0(11)	6.2(12)
N1B	17.0(14)	15.4(13)	21.4(16)	5.4(10)	3.9(10)	4.3(10)
N2B	22.9(16)	21.8(14)	26.1(16)	8.3(10)	6.6(10)	3.7(9)
C19B	20.0(19)	19.3(19)	26.9(18)	7.2(14)	6.0(13)	9.5(14)
H2B	42(15)	27(7)	49(17)	0(4)	27(8)	-4(5)
C5B	14.8(16)	13.2(16)	21.8(17)	4.8(11)	0.5(10)	1.8(11)
C6B	15.4(16)	14.5(16)	20.6(17)	5.7(12)	2.9(10)	2.6(11)
C3B	15.8(15)	12.4(15)	23.4(15)	6.4(10)	4.9(9)	2.7(10)
H3B	18(9)	13(3)	18(8)	8(2)	3(3)	2(2)
C1B	17.8(17)	19.2(15)	30(2)	7.3(10)	8.0(12)	7.3(11)
C2B	14.6(15)	15.0(16)	23.9(16)	6.6(9)	5.2(9)	5.3(10)
H2Ba	17(8)	15(3)	28(9)	8(2)	7(3)	5.8(19)
C4B	16.9(16)	15.9(16)	24.2(17)	7.7(12)	4.3(10)	5.0(11)
C25B	19.9(18)	19.3(16)	25.8(18)	6.1(11)	5.3(11)	3.4(11)
H25B	23(8)	24(9)	29(14)	2(4)	8(5)	-2(5)
C24B	19.3(17)	22.3(18)	25.8(18)	6.3(12)	3.6(11)	0.3(12)
H24B	37(13)	27(4)	50(18)	-2(4)	22(8)	-10(4)
C23B	20.5(17)	21.9(16)	27.5(18)	9.8(10)	4.8(10)	2.3(10)
C22B	16.1(15)	17.6(14)	24.0(17)	4.6(9)	4.3(10)	5.2(9)
C7B	23(2)	17(2)	27(2)	6.2(17)	2.4(17)	6.3(17)
C8B	36(3)	31(2)	28(2)	17(2)	-1(2)	-1.3(19)
C9B	32(3)	34(3)	32(3)	14(2)	5(2)	-3(2)
C10B	16.4(18)	19.0(17)	31(2)	5.8(12)	6.2(14)	2.5(13)
C12B	19.0(19)	20.3(18)	48(3)	6.2(14)	6.7(16)	3.9(15)
H12a	20(9)	22(6)	51(8)	7(3)	8(3)	6(3)
H12b	22(5)	27(9)	54(9)	10(3)	9(3)	4(4)
H12c	25(9)	24(8)	48(3)	9(4)	5(2)	3(2)
C11B	25(2)	20.3(19)	40(3)	8.1(14)	3.5(17)	3.9(15)
H11a	22(8)	16(8)	40(3)	7(3)	4(2)	5.1(19)
H11b	30(5)	27(8)	47(8)	13(3)	8(3)	5(3)
H11c	27(4)	22(4)	45(9)	6.9(19)	4(3)	4(2)
C13B	19(2)	20(2)	29(2)	8.7(17)	6.7(17)	5.8(18)
C15B	29(2)	26(2)	42(3)	7.5(19)	10(2)	5(2)
C14B	34(3)	45(3)	23(2)	16(2)	7.2(19)	9(2)
C16B	20.7(19)	15.8(18)	35(2)	8.2(13)	5.3(13)	2.2(13)
C17B	38(2)	27(2)	41(2)	15.1(18)	15.3(16)	5.5(16)
H17a	37(10)	27(4)	48(9)	15(3)	16(4)	5(3)
H17b	38(3)	30(6)	50(10)	14(2)	14(2)	6(3)
H17c	39(8)	28(9)	41(6)	16(4)	15(3)	6(3)
C18B	28(2)	20(2)	44(2)	11.7(15)	2.9(15)	4.6(15)
H18a	29(3)	25(6)	46(9)	11(2)	2(2)	4(3)
H18b	38(10)	23(4)	49(9)	16(3)	3(4)	3(2)
H18c	32(7)	28(9)	45(5)	15(4)	5(3)	7(3)
C20B	15(2)	17(2)	38(2)	2.0(16)	-2.7(17)	1.0(18)
C21B	31(3)	23(2)	60(3)	9(2)	-9(2)	5(2)
H1Ba	22(9)	23(8)	30(3)	10(3)	7.0(18)	6.1(18)
H1Bb	19(3)	24(9)	34(9)	9(2)	7(2)	7(4)
H4Ba	21(9)	17(3)	36(9)	10(2)	6(4)	7(2)
H4Bb	18(3)	17(9)	27(9)	8(2)	2(2)	2(4)
H10B	31(11)	23(8)	32(3)	11(4)	3(2)	1.2(19)
H16B	22(3)	30(11)	36(9)	6.4(19)	5.0(19)	4(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H19a	28(9)	21(13)	33(6)	7(4)	12(3)	9(4)
H19b	24(5)	25(7)	29(9)	3(3)	6(3)	10(3)
H4B	26(4)	60(30)	41(13)	-3(5)	1(3)	15(6)
Si1	17.0(5)	17.4(5)	20.2(5)	5.6(4)	3.5(4)	4.1(4)
Si2	14.4(5)	20.4(5)	24.2(5)	5.5(4)	4.3(4)	3.4(4)
O3	17.3(13)	17.8(13)	22.2(12)	6.5(9)	5.3(8)	4.4(8)
O1	17.2(12)	22.4(12)	27.1(15)	7.5(8)	3.1(9)	4.8(9)
O2	17.0(12)	17.8(13)	28.0(15)	3.9(8)	2.6(9)	3.0(10)
O8	19.4(12)	20.8(14)	30.9(16)	2.9(9)	6.0(9)	-1.5(11)
O7	36.1(17)	22.2(15)	33.4(15)	12.2(11)	14.1(10)	2.1(10)
O5	14.2(11)	20.1(12)	26.0(15)	7.3(8)	6.1(9)	3.8(9)
O6	23.1(15)	22.3(14)	48.9(19)	8.8(9)	10.1(13)	10.2(12)
O4	19.8(15)	25.7(15)	29.7(14)	9.2(12)	4.8(10)	6.1(11)
N2	22.7(14)	18.1(15)	26.0(15)	7.0(10)	5.5(9)	-0.4(10)
C5	15.1(15)	16.9(15)	24.9(15)	7.3(9)	2.7(8)	2.9(9)
C6	14.7(14)	15.6(15)	25.8(17)	7.3(9)	4.6(9)	3.1(9)
H6	18(9)	16(4)	29(9)	8(3)	7(3)	4(2)
C3	14.7(16)	13.6(14)	24.3(15)	4.9(9)	4.2(9)	4.4(8)
H3	17(3)	24(9)	28(9)	10(2)	6(2)	7(3)
C1	17.0(15)	12.5(15)	30.5(19)	3.0(9)	1.6(10)	1.5(12)
H1a	28(9)	16(3)	40(9)	8(2)	5(3)	6(2)
H1b	20(8)	12(9)	31(3)	4(4)	3(2)	2(2)
C2	15.3(16)	14.5(14)	25.9(16)	4.9(9)	3.7(10)	3.4(9)
H2a	16(3)	16(9)	31(9)	6(2)	5(2)	5(4)
C4	16.5(17)	17.3(16)	25.7(17)	5.7(11)	3.0(10)	4.5(9)
H4a	25(8)	22(4)	30(8)	11(3)	6(3)	8(2)
H4c	18(3)	21(9)	32(9)	7(2)	4.4(19)	5(3)
C23	23.3(15)	18.7(15)	26.8(17)	9.5(9)	6.0(9)	3.5(9)
C24	23.9(17)	21.0(15)	30.1(18)	9.7(10)	7.1(10)	2.1(10)
C25	19.1(15)	15.1(16)	30.9(18)	3.9(10)	6.8(9)	0.8(10)
N1	16.5(12)	15.3(12)	23.8(14)	5.7(8)	3.1(8)	1.8(8)
C22	18.8(13)	17.7(13)	24.3(16)	5.4(8)	3.2(8)	-0.2(9)
C7	22.1(19)	38(2)	25.2(17)	12.9(13)	7.7(10)	5.7(12)
C8	36(2)	37(2)	27(2)	17.5(17)	2.5(14)	5.3(15)
H8a	38(9)	38(5)	33(10)	19(3)	3(4)	5(3)
H8b	36(5)	37(4)	27(10)	18(2)	2(3)	6(2)
H8c	43(8)	42(10)	30(5)	21(4)	7(3)	7(3)
C9	58(3)	71(3)	34(3)	46.7(18)	8(2)	5(2)
H9a	64(9)	78(11)	36(5)	51(4)	12(3)	7(3)
H9b	63(6)	71(4)	38(11)	44(2)	9(3)	6(3)
H9c	61(7)	78(10)	36(5)	49(4)	7(3)	5(3)
C10	22.4(17)	20.5(16)	29(2)	9.8(10)	3.8(12)	1.9(11)
C12	24.8(19)	20.1(18)	54(3)	8.2(13)	6.0(16)	4.6(15)
H12d	27(10)	22(5)	56(8)	10(3)	5(4)	3(3)
H12e	32(10)	27(10)	55(4)	13(4)	8(2)	7(2)
H12f	27(5)	24(10)	57(9)	11(3)	5(3)	4(4)
C11	26(2)	28(2)	43(3)	14.0(13)	2.2(15)	4.7(17)
H11d	30(9)	36(9)	43(3)	17(4)	3(2)	6(2)
H11e	29(9)	29(5)	49(9)	16(3)	5(4)	4(3)
H11f	27(4)	30(4)	47(10)	13.0(19)	3(3)	5(3)
C13	25(2)	28.0(19)	34.6(19)	7.2(12)	3.8(12)	-5.7(11)
H13	26(4)	32(9)	33(9)	9(3)	4(2)	-6(3)
C15	33(2)	30(2)	45(3)	7.7(15)	8.3(17)	-3.2(14)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H15d	34(9)	25(9)	46(6)	5(4)	6(3)	-4(3)
H15e	33(10)	37(7)	49(5)	9(3)	7(3)	-8(3)
H15f	34(4)	30(10)	49(10)	8(3)	10(3)	-1(4)
C14	39(3)	50(3)	40(2)	16.7(19)	2.4(16)	1.4(16)
H14d	42(6)	51(4)	49(9)	17(2)	5(3)	4(3)
H14e	42(4)	57(10)	48(9)	21(3)	4(3)	2(4)
H14f	46(9)	53(6)	43(5)	19(3)	2(3)	-1(3)
C16	20.4(18)	30(2)	37(2)	10.3(11)	8.8(11)	3.8(13)
H16	24(6)	31(3)	35(9)	9.2(18)	8(3)	3(2)
C18	32(2)	53(3)	46(3)	24.6(17)	10.1(16)	12.1(19)
C17	36(3)	47(3)	42(2)	19.3(17)	5.5(16)	-8.0(16)
H17d	40(9)	52(9)	46(6)	22(4)	4(3)	-5(3)
H17e	39(5)	53(10)	47(9)	23(3)	8(3)	-6(4)
H17f	40(6)	50(4)	55(10)	18(2)	9(3)	-4(3)
C20	18.3(15)	22.0(14)	35(2)	6.6(8)	7.2(11)	8.3(10)
C21	21.1(17)	39(2)	63(3)	13.5(11)	16.6(13)	24.8(19)
H21d	25(6)	39(4)	63(7)	13.2(19)	16(3)	25(3)
H21e	27(7)	40(4)	65(6)	15(2)	19(3)	25(3)
H21f	27(6)	44(8)	65(4)	14(3)	13.2(19)	25(2)
C19	13.8(16)	20.6(18)	24.8(16)	7.6(10)	1.9(10)	1.5(11)
H19c	19(8)	22(5)	27(4)	9(3)	4(2)	1(2)
H19d	15(4)	21(3)	29(7)	7.3(15)	2.3(19)	1.4(17)
H24	22(6)	19(7)	27(12)	12(3)	5(4)	6(4)
H25	34(9)	31(8)	59(15)	-11(4)	27(6)	-20(6)
H2	23(8)	18(6)	25(14)	8(3)	4(5)	1(4)
H7	25(5)	41(4)	29(10)	12(2)	9(3)	5(2)
H10	23(9)	21(9)	29(3)	9(4)	3.7(18)	1.2(16)
H18d	32(7)	54(5)	50(8)	26(3)	12(3)	14(3)
H18e	34(7)	58(12)	49(9)	27(4)	12(4)	12(4)
H18f	34(8)	56(6)	47(4)	26(3)	9(2)	10(3)
H4	40(14)	44(12)	39(10)	-10(6)	-7(5)	18(4)
O1W	27.1(18)	27.2(17)	54(2)	10.6(14)	10.1(17)	1.4(16)
H1Wa	50(40)	33(14)	55(3)	-12(16)	13(2)	-1(2)
H1Wb	100(40)	27(5)	59(12)	21(8)	38(15)	2(4)
O1WB	27.8(18)	23.2(17)	49(2)	8.8(14)	14.1(16)	1.4(15)
H1Wc	48(18)	53(16)	90(30)	33(8)	-12(9)	-31(10)
H1Wd	27(9)	40(20)	50(20)	13(5)	14(7)	-9(9)
O1S_1	15.8(12)	16.6(12)	17.1(15)	8.0(7)	1.0(7)	1.3(7)
H1S_1	38(15)	37(15)	38(15)	16(3)	4.4(12)	4.2(12)
C1S_1	18.1(12)	16.0(12)	17.6(15)	8.2(7)	1.4(7)	2.0(7)
H1Sa_1	20(2)	26(10)	35(19)	11.0(16)	5(2)	10(6)
H1Sb_1	27(9)	30(9)	33(12)	13(4)	0(4)	13(5)
H1Sc_1	21(8)	17(2)	17(17)	8.5(12)	3(5)	2.4(13)
O1SB_2	18.1(12)	16.0(12)	17.6(15)	8.2(7)	1.4(7)	2.0(7)
H1SB_2	36(15)	36(15)	36(15)	16(3)	4.2(12)	4.1(12)
C1SB_2	15.8(12)	16.6(12)	17.1(15)	8.0(7)	1.0(7)	1.3(7)
H1Sa_2	17(3)	22(9)	28(18)	9.4(17)	4(2)	6(6)
H1Sc_2	23(9)	18(2)	23(18)	9.6(13)	3(5)	1.9(14)
H1Sd_2	24(7)	27(10)	28(12)	13(4)	-3(4)	6(5)

Table 3: Bond Lengths in Å for **9A**.

Atom	Atom	Length/Å
Si1B	O3B	1.651(3)
Si1B	O1B	1.635(3)
Si1B	C7B	1.869(4)
Si1B	C10B	1.875(4)
Si2B	O1B	1.634(3)
Si2B	O2B	1.653(3)
Si2B	C13B	1.872(4)
Si2B	C16B	1.867(4)
O3B	C3B	1.414(4)
O2B	C1B	1.412(4)
O8B	C22B	1.226(4)
O7B	C23B	1.230(5)
O5B	C6B	1.428(4)
O5B	C20B	1.352(4)
O6B	C20B	1.198(5)
O4B	C19B	1.439(5)
O4B	H4B	0.9550(17)
N1B	C5B	1.496(5)
N1B	C25B	1.366(5)
N1B	C22B	1.379(5)
N2B	H2B	0.982(3)
N2B	C23B	1.384(5)
N2B	C22B	1.366(5)
C19B	C5B	1.533(5)
C19B	H19a	1.14(4)
C19B	H19b	1.10(4)
C5B	C6B	1.578(5)
C5B	C4B	1.542(5)
C6B	C3B	1.534(5)
C6B	H6B	1.16(6)
C3B	H3B	1.11(4)
C3B	C2B	1.535(5)
C1B	C2B	1.515(5)
C1B	H1Ba	1.11(5)
C1B	H1Bb	1.19(4)
C2B	H2Ba	1.03(4)
C2B	C4B	1.526(6)
C4B	H4Ba	1.14(4)
C4B	H4Bb	1.12(4)
C25B	H25B	1.11(4)
C25B	C24B	1.352(6)
C24B	H24B	1.01(5)
C24B	C23B	1.449(6)
C7B	H7B	1.0000
C7B	C8B	1.530(6)
C7B	C9B	1.519(6)
C8B	H8Ba	1.08(3)
C8B	H8Bb	1.08(3)
C8B	H8Bc	1.08(3)
C9B	H9Ba	1.10(3)
C9B	H9Bb	1.10(3)
C9B	H9Bc	1.10(3)
C10B	C12B	1.529(5)

Atom	Atom	Length/Å
C10B	C11B	1.530(6)
C10B	H10B	1.16(5)
C12B	H12a	1.06(3)
C12B	H12b	1.06(3)
C12B	H12c	1.06(3)
C11B	H11a	0.9800
C11B	H11b	0.9800
C11B	H11c	0.9800
C13B	C15B	1.535(5)
C13B	C14B	1.525(6)
C13B	H13B	1.07(5)
C15B	H15a	1.06(3)
C15B	H15b	1.06(3)
C15B	H15c	1.06(3)
C14B	H14a	1.08(3)
C14B	H14b	1.08(3)
C14B	H14c	1.08(3)
C16B	C17B	1.542(6)
C16B	C18B	1.526(6)
C16B	H16B	1.09(5)
C17B	H17a	1.08(3)
C17B	H17b	1.08(3)
C17B	H17c	1.08(3)
C18B	H18a	1.08(3)
C18B	H18b	1.08(3)
C18B	H18c	1.08(3)
C20B	C21B	1.496(6)
C21B	H21a	1.06(3)
C21B	H21b	1.06(3)
C21B	H21c	1.06(3)
Si1	O3	1.650(3)
Si1	O1	1.644(3)
Si1	C7	1.858(4)
Si1	C10	1.871(4)
Si2	O1	1.626(3)
Si2	O2	1.646(3)
Si2	C13	1.876(4)
Si2	C16	1.870(4)
O3	C3	1.404(4)
O2	C1	1.425(5)
O8	C22	1.238(5)
O7	C23	1.225(5)
O5	C6	1.440(4)
O5	C20	1.335(5)
O6	C20	1.213(5)
O4	C19	1.429(5)
O4	H4	0.9550(17)
N2	C23	1.391(5)
N2	C22	1.365(5)
N2	H2	0.9819(15)
C5	C6	1.563(5)
C5	C4	1.542(5)
C5	N1	1.497(5)

Atom	Atom	Length/Å
C5	C19	1.532(5)
C6	H6	1.11(4)
C6	C3	1.539(5)
C3	H3	1.12(4)
C3	C2	1.540(5)
C1	H1a	1.09(3)
C1	H1b	1.09(3)
C1	C2	1.511(5)
C2	H2a	1.19(4)
C2	C4	1.531(6)
C4	H4a	0.9900
C4	H4c	0.9900
C23	C24	1.442(6)
C24	C25	1.356(6)
C24	H24	1.08(4)
C25	N1	1.376(5)
C25	H25	1.07(5)
N1	C22	1.382(5)
C7	C8	1.532(6)
C7	C9	1.538(6)
C7	H7	1.20(5)
C8	H8a	1.07(3)
C8	H8b	1.07(3)
C8	H8c	1.07(3)
C9	H9a	1.11(3)
C9	H9b	1.11(3)
C9	H9c	1.11(3)
C10	C12	1.533(5)
C10	C11	1.536(6)
C10	H10	1.09(5)
C12	H12d	1.11(3)
C12	H12e	1.11(3)
C12	H12f	1.11(3)
C11	H11d	1.06(3)
C11	H11e	1.06(3)
C11	H11f	1.06(3)
C13	H13	1.09(5)
C13	C15	1.514(6)
C13	C14	1.535(7)
C15	H15d	1.15(3)
C15	H15e	1.15(3)
C15	H15f	1.15(3)
C14	H14d	0.9800
C14	H14e	0.9800
C14	H14f	0.9800
C16	H16	1.08(5)
C16	C18	1.525(7)
C16	C17	1.531(6)
C18	H18d	1.09(6)
C18	H18e	1.21(5)
C18	H18f	1.00(6)
C17	H17d	1.09(3)
C17	H17e	1.09(3)

Atom	Atom	Length/Å
C17	H17f	1.09(3)
C20	C21	1.489(6)
C21	H21d	1.12(3)
C21	H21e	1.12(3)
C21	H21f	1.12(3)
C19	H19c	1.09(3)
C19	H19d	1.09(3)
O1W	H1Wa	0.952(16)
O1W	H1Wb	0.948(16)
O1WB	H1Wc	0.960(16)
O1WB	H1Wd	0.955(16)
O1S_1	H1S_1	0.9751(17)
O1S_1	C1S_1	1.424(3)
C1S_1	H1Sa_1	1.0830
C1S_1	H1Sb_1	1.0830
C1S_1	H1Sc_1	1.0830
O1SB_2	H1SB_2	0.9752(17)
O1SB_2	C1SB_2	1.423(3)
C1SB_2	H1Sa_2	1.0830
C1SB_2	H1Sc_2	1.0830
C1SB_2	H1Sd_2	1.0830

Table 4: Bond Angles in ° for **9A**.

Atom	Atom	Atom	Angle/°
O1B	Si1B	O3B	109.68(13)
C7B	Si1B	O3B	103.25(16)
C7B	Si1B	O1B	109.42(16)
C10B	Si1B	O3B	110.07(16)
C10B	Si1B	O1B	108.00(15)
C10B	Si1B	C7B	116.28(18)
O2B	Si2B	O1B	109.46(13)
C13B	Si2B	O1B	108.04(16)
C13B	Si2B	O2B	108.31(16)
C16B	Si2B	O1B	111.38(16)
C16B	Si2B	O2B	103.92(17)
C16B	Si2B	C13B	115.54(18)
C3B	O3B	Si1B	120.8(2)
Si2B	O1B	Si1B	153.50(18)
C1B	O2B	Si2B	122.8(3)
C20B	O5B	C6B	116.2(3)
H4B	O4B	C19B	116(4)
C25B	N1B	C5B	122.0(3)
C22B	N1B	C5B	117.7(3)
C22B	N1B	C25B	120.0(3)
C23B	N2B	H2B	120(3)
C22B	N2B	H2B	113(3)
C22B	N2B	C23B	126.9(3)
C5B	C19B	O4B	111.7(3)
H19a	C19B	O4B	114(2)

Atom	Atom	Atom	Angle/°
H19a	C19B	C5B	103(2)
H19b	C19B	O4B	108(2)
H19b	C19B	C5B	111(2)
H19b	C19B	H19a	109(3)
C19B	C5B	N1B	108.6(3)
C6B	C5B	N1B	109.8(3)
C6B	C5B	C19B	112.6(3)
C4B	C5B	N1B	113.9(3)
C4B	C5B	C19B	108.0(3)
C4B	C5B	C6B	104.0(3)
C5B	C6B	O5B	108.9(3)
C3B	C6B	O5B	110.4(3)
C3B	C6B	C5B	104.1(3)
H6B	C6B	O5B	110(3)
H6B	C6B	C5B	112(3)
H6B	C6B	C3B	111(3)
C6B	C3B	O3B	113.9(3)
H3B	C3B	O3B	108(2)
H3B	C3B	C6B	105(2)
C2B	C3B	O3B	115.0(3)
C2B	C3B	C6B	102.8(3)
C2B	C3B	H3B	112(2)
C2B	C1B	O2B	112.0(3)
H1Ba	C1B	O2B	104(2)
H1Ba	C1B	C2B	115(2)
H1Bb	C1B	O2B	108(2)
H1Bb	C1B	C2B	109(2)
H1Bb	C1B	H1Ba	108(3)
C1B	C2B	C3B	114.7(3)
H2Ba	C2B	C3B	109(2)
H2Ba	C2B	C1B	107(2)
C4B	C2B	C3B	98.8(3)
C4B	C2B	C1B	115.5(3)
C4B	C2B	H2Ba	111(2)
C2B	C4B	C5B	103.0(3)
H4Ba	C4B	C5B	110(2)
H4Ba	C4B	C2B	104(2)
H4Bb	C4B	C5B	114(2)
H4Bb	C4B	C2B	110(2)
H4Bb	C4B	H4Ba	114(3)
H25B	C25B	N1B	114(2)
C24B	C25B	N1B	124.0(4)
C24B	C25B	H25B	122(2)
H24B	C24B	C25B	118(3)
C23B	C24B	C25B	118.3(4)
C23B	C24B	H24B	123(3)
N2B	C23B	O7B	120.2(4)
C24B	C23B	O7B	125.4(4)
C24B	C23B	N2B	114.4(4)
N1B	C22B	O8B	122.6(4)
N2B	C22B	O8B	121.3(3)
N2B	C22B	N1B	116.1(3)
H7B	C7B	Si1B	107.36(12)

Atom	Atom	Atom	Angle/°
C8B	C7B	Si1B	113.2(3)
C8B	C7B	H7B	107.4(2)
C9B	C7B	Si1B	110.9(3)
C9B	C7B	H7B	107.4(2)
C9B	C7B	C8B	110.4(4)
H8Ba	C8B	C7B	109.5
H8Bb	C8B	C7B	109.5
H8Bb	C8B	H8Ba	109.5
H8Bc	C8B	C7B	109.5
H8Bc	C8B	H8Ba	109.5
H8Bc	C8B	H8Bb	109.5
H9Ba	C9B	C7B	109.5
H9Bb	C9B	C7B	109.5
H9Bb	C9B	H9Ba	109.5
H9Bc	C9B	C7B	109.5
H9Bc	C9B	H9Ba	109.5
H9Bc	C9B	H9Bb	109.5
C12B	C10B	Si1B	111.3(3)
C11B	C10B	Si1B	114.9(3)
C11B	C10B	C12B	111.0(3)
H10B	C10B	Si1B	101(2)
H10B	C10B	C12B	109(2)
H10B	C10B	C11B	110(2)
H12a	C12B	C10B	109.5
H12b	C12B	C10B	109.5
H12b	C12B	H12a	109.5
H12c	C12B	C10B	109.5
H12c	C12B	H12a	109.5
H12c	C12B	H12b	109.5
H11a	C11B	C10B	109.5
H11b	C11B	C10B	109.5
H11b	C11B	H11a	109.5
H11c	C11B	C10B	109.5
H11c	C11B	H11a	109.5
H11c	C11B	H11b	109.5
C15B	C13B	Si2B	111.9(3)
C14B	C13B	Si2B	115.0(3)
C14B	C13B	C15B	110.7(3)
H13B	C13B	Si2B	110(3)
H13B	C13B	C15B	103(3)
H13B	C13B	C14B	105(3)
H15a	C15B	C13B	109.5
H15b	C15B	C13B	109.5
H15b	C15B	H15a	109.5
H15c	C15B	C13B	109.5
H15c	C15B	H15a	109.5
H15c	C15B	H15b	109.5
H14a	C14B	C13B	109.5
H14b	C14B	C13B	109.5
H14b	C14B	H14a	109.5
H14c	C14B	C13B	109.5
H14c	C14B	H14a	109.5
H14c	C14B	H14b	109.5

Atom	Atom	Atom	Angle/°
C17B	C16B	Si2B	110.7(3)
C18B	C16B	Si2B	113.8(3)
C18B	C16B	C17B	110.4(3)
H16B	C16B	Si2B	102(2)
H16B	C16B	C17B	107(3)
H16B	C16B	C18B	113(3)
H17a	C17B	C16B	109.5
H17b	C17B	C16B	109.5
H17b	C17B	H17a	109.5
H17c	C17B	C16B	109.5
H17c	C17B	H17a	109.5
H17c	C17B	H17b	109.5
H18a	C18B	C16B	109.5
H18b	C18B	C16B	109.5
H18b	C18B	H18a	109.5
H18c	C18B	C16B	109.5
H18c	C18B	H18a	109.5
H18c	C18B	H18b	109.5
O6B	C20B	O5B	124.5(3)
C21B	C20B	O5B	111.0(3)
C21B	C20B	O6B	124.5(4)
H21a	C21B	C20B	109.5
H21b	C21B	C20B	109.5
H21b	C21B	H21a	109.5
H21c	C21B	C20B	109.5
H21c	C21B	H21a	109.5
H21c	C21B	H21b	109.5
O1	Si1	O3	109.20(13)
C7	Si1	O3	104.06(17)
C7	Si1	O1	110.34(17)
C10	Si1	O3	109.90(17)
C10	Si1	O1	107.84(16)
C10	Si1	C7	115.4(2)
O2	Si2	O1	109.34(13)
C13	Si2	O1	107.33(17)
C13	Si2	O2	109.57(18)
C16	Si2	O1	112.11(17)
C16	Si2	O2	103.21(18)
C16	Si2	C13	115.1(2)
C3	O3	Si1	121.3(2)
Si2	O1	Si1	154.47(18)
C1	O2	Si2	123.9(3)
C20	O5	C6	117.0(3)
H4	O4	C19	117(4)
C22	N2	C23	127.0(3)
H2	N2	C23	114(3)
H2	N2	C22	119(3)
C4	C5	C6	104.7(3)
N1	C5	C6	109.6(3)
N1	C5	C4	113.7(3)
C19	C5	C6	113.6(3)
C19	C5	C4	107.8(3)
C19	C5	N1	107.5(3)

Atom	Atom	Atom	Angle/°
C5	C6	O5	109.1(3)
H6	C6	O5	111.29(18)
H6	C6	C5	111.3(2)
C3	C6	O5	109.3(3)
C3	C6	C5	104.3(3)
C3	C6	H6	111.3(2)
C6	C3	O3	113.8(3)
H3	C3	O3	108.15(19)
H3	C3	C6	108.1(2)
C2	C3	O3	115.1(3)
C2	C3	C6	103.1(3)
C2	C3	H3	108.15(19)
H1a	C1	O2	109.26(18)
H1b	C1	O2	109.3(2)
H1b	C1	H1a	107.9
C2	C1	O2	111.8(3)
C2	C1	H1a	109.3(2)
C2	C1	H1b	109.3(2)
C1	C2	C3	115.3(3)
H2a	C2	C3	108.35(19)
H2a	C2	C1	108.4(2)
C4	C2	C3	98.8(3)
C4	C2	C1	117.0(3)
C4	C2	H2a	108.4(2)
C2	C4	C5	103.1(3)
H4a	C4	C5	111.1(2)
H4a	C4	C2	111.1(2)
H4c	C4	C5	111.1(2)
H4c	C4	C2	111.1(2)
H4c	C4	H4a	109.1
N2	C23	O7	120.4(3)
C24	C23	O7	125.5(4)
C24	C23	N2	114.1(4)
C25	C24	C23	119.0(4)
H24	C24	C23	115(2)
H24	C24	C25	126(2)
N1	C25	C24	123.8(4)
H25	C25	C24	123(2)
H25	C25	N1	113(3)
C25	N1	C5	122.6(3)
C22	N1	C5	117.8(3)
C22	N1	C25	119.4(3)
N2	C22	O8	121.1(3)
N1	C22	O8	122.4(4)
N1	C22	N2	116.5(3)
C8	C7	Si1	114.1(3)
C9	C7	Si1	111.0(3)
C9	C7	C8	109.9(4)
H7	C7	Si1	106(2)
H7	C7	C8	111(2)
H7	C7	C9	105(2)
H8a	C8	C7	109.5
H8b	C8	C7	109.5

Atom	Atom	Atom	Angle/°
H8b	C8	H8a	109.5
H8c	C8	C7	109.5
H8c	C8	H8a	109.5
H8c	C8	H8b	109.5
H9a	C9	C7	109.5
H9b	C9	C7	109.5
H9b	C9	H9a	109.5
H9c	C9	C7	109.5
H9c	C9	H9a	109.5
H9c	C9	H9b	109.5
C12	C10	Si1	111.5(3)
C11	C10	Si1	114.2(3)
C11	C10	C12	111.1(3)
H10	C10	Si1	106(2)
H10	C10	C12	104(2)
H10	C10	C11	110(2)
H12d	C12	C10	109.5
H12e	C12	C10	109.5
H12e	C12	H12d	109.5
H12f	C12	C10	109.5
H12f	C12	H12d	109.5
H12f	C12	H12e	109.5
H11d	C11	C10	109.5
H11e	C11	C10	109.5
H11e	C11	H11d	109.5
H11f	C11	C10	109.5
H11f	C11	H11d	109.5
H11f	C11	H11e	109.5
H13	C13	Si2	106.25(14)
C15	C13	Si2	112.9(3)
C15	C13	H13	106.2(3)
C14	C13	Si2	114.0(3)
C14	C13	H13	106.2(3)
C14	C13	C15	110.5(4)
H15d	C15	C13	109.5
H15e	C15	C13	109.5
H15e	C15	H15d	109.5
H15f	C15	C13	109.5
H15f	C15	H15d	109.5
H15f	C15	H15e	109.5
H14d	C14	C13	109.5
H14e	C14	C13	109.5
H14e	C14	H14d	109.5
H14f	C14	C13	109.5
H14f	C14	H14d	109.5
H14f	C14	H14e	109.5
H16	C16	Si2	106.87(13)
C18	C16	Si2	114.9(3)
C18	C16	H16	106.9(2)
C17	C16	Si2	110.5(3)
C17	C16	H16	106.9(3)
C17	C16	C18	110.4(4)
H18d	C18	C16	109(3)

Atom	Atom	Atom	Angle/˚
H18e	C18	C16	110(3)
H18e	C18	H18d	112(4)
H18f	C18	C16	113(3)
H18f	C18	H18d	98(4)
H18f	C18	H18e	115(4)
H17d	C17	C16	109.5
H17e	C17	C16	109.5
H17e	C17	H17d	109.5
H17f	C17	C16	109.5
H17f	C17	H17d	109.5
H17f	C17	H17e	109.5
O6	C20	O5	124.4(4)
C21	C20	O5	112.3(3)
C21	C20	O6	123.3(4)
H21d	C21	C20	109.5
H21e	C21	C20	109.5
H21e	C21	H21d	109.5
H21f	C21	C20	109.5
H21f	C21	H21d	109.5
H21f	C21	H21e	109.5
C5	C19	O4	112.9(3)
H19c	C19	O4	109.00(19)
H19c	C19	C5	109.0(2)
H19d	C19	O4	109.00(18)
H19d	C19	C5	109.00(19)
H19d	C19	H19c	107.787076690(16)
H1Wb	O1W	H1Wa	115(4)
H1Wd	O1WB	H1Wc	106(3)
C1S_1	O1S_1	H1S_1	107.5(7)
H1Sa_1	C1S_1	O1S_1	109.5
H1Sb_1	C1S_1	O1S_1	109.5
H1Sb_1	C1S_1	H1Sa_1	109.5
H1Sc_1	C1S_1	O1S_1	109.5
H1Sc_1	C1S_1	H1Sa_1	109.5
H1Sc_1	C1S_1	H1Sb_1	109.5
C1SB_2	O1SB_2	H1SB_2	107.7(7)
H1Sa_2	C1SB_2	O1SB_2	109.5
H1Sc_2	C1SB_2	O1SB_2	109.5
H1Sc_2	C1SB_2	H1Sa_2	109.5
H1Sd_2	C1SB_2	O1SB_2	109.5
H1Sd_2	C1SB_2	H1Sa_2	109.5
H1Sd_2	C1SB_2	H1Sc_2	109.5

Table 5: Torsion Angles in ˚ for **9A**.

Atom	Atom	Atom	Atom	Angle/˚
Si1B	O3B	C3B	C6B	130.8(3)
Si1B	O3B	C3B	C2B	-110.8(3)
Si1B	O1B	Si2B	O2B	-2.4(4)
Si1B	O1B	Si2B	C13B	115.3(4)
Si1B	O1B	Si2B	C16B	-116.8(4)
Si2B	O2B	C1B	C2B	-110.6(3)
O3B	C3B	C6B	O5B	39.5(3)

Atom	Atom	Atom	Atom	Angle/°
O3B	C3B	C6B	C5B	156.3(3)
O3B	C3B	C2B	C1B	62.5(3)
O3B	C3B	C2B	C4B	-174.1(3)
O2B	C1B	C2B	C3B	54.3(4)
O2B	C1B	C2B	C4B	-59.7(4)
O8B	C22B	N1B	C5B	-1.3(5)
O8B	C22B	N1B	C25B	-175.5(4)
O8B	C22B	N2B	C23B	179.1(4)
O7B	C23B	N2B	C22B	177.5(4)
O7B	C23B	C24B	C25B	-176.7(4)
O5B	C6B	C5B	N1B	-120.8(3)
O5B	C6B	C5B	C19B	0.3(3)
O5B	C6B	C5B	C4B	116.9(3)
O5B	C6B	C3B	C2B	-85.5(3)
O4B	C19B	C5B	N1B	-44.3(3)
O4B	C19B	C5B	C6B	-166.1(3)
O4B	C19B	C5B	C4B	79.7(3)
N1B	C5B	C6B	C3B	121.4(3)
N1B	C5B	C4B	C2B	-149.6(3)
N1B	C25B	C24B	C23B	0.4(5)
N1B	C22B	N2B	C23B	-2.1(5)
N2B	C23B	C24B	C25B	3.1(4)
C19B	C5B	C6B	C3B	-117.5(3)
C19B	C5B	C4B	C2B	89.8(3)
C5B	C6B	C3B	C2B	31.2(3)
C5B	C4B	C2B	C3B	49.1(3)
C5B	C4B	C2B	C1B	172.0(3)
C6B	C3B	C2B	C1B	-173.2(3)
C6B	C3B	C2B	C4B	-49.7(3)
Si1	O3	C3	C6	131.6(3)
Si1	O3	C3	C2	-109.7(3)
Si1	O1	Si2	O2	2.0(5)
Si1	O1	Si2	C13	120.8(5)
Si1	O1	Si2	C16	-111.8(5)
Si2	O2	C1	C2	-108.8(3)
O3	C3	C6	O5	39.4(3)
O3	C3	C6	C5	156.0(3)
O3	C3	C2	C1	61.3(3)
O3	C3	C2	C4	-173.1(3)
O2	C1	C2	C3	55.4(4)
O2	C1	C2	C4	-60.2(4)
O8	C22	N2	C23	178.7(4)
O8	C22	N1	C5	-0.6(5)
O8	C22	N1	C25	-176.7(4)
O7	C23	N2	C22	178.5(4)
O7	C23	C24	C25	-176.9(4)
O5	C6	C5	C4	116.0(3)
O5	C6	C5	N1	-121.7(3)
O5	C6	C5	C19	-1.4(3)
O5	C6	C3	C2	-86.0(3)
O4	C19	C5	C6	-164.5(3)
O4	C19	C5	C4	79.9(3)
O4	C19	C5	N1	-43.0(3)

Atom	Atom	Atom	Atom	Angle/°
N2	C23	C24	C25	2.2(4)
N2	C22	N1	C5	-178.9(3)
N2	C22	N1	C25	5.1(4)
C5	C6	C3	C2	30.6(3)
C5	C4	C2	C3	47.9(3)
C5	C4	C2	C1	172.4(3)
C5	N1	C25	C24	-179.6(4)
C6	C3	C2	C1	-174.1(3)
C6	C3	C2	C4	-48.5(3)
C23	C24	C25	N1	-0.1(5)
C24	C25	N1	C22	-3.8(5)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **9A**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2B	-2010(40)	7330(40)	5750(30)	44(14)
H3B	170(50)	8800(50)	2910(20)	16(5)
H2Ba	1950(50)	6770(50)	2910(20)	20(5)
H25B	2620(50)	10290(50)	4700(20)	28(10)
H24B	2010(60)	11600(60)	5670(30)	44(13)
H7B	-2354(5)	5391(5)	860(2)	35.2(13)
H8Ba	-1320(20)	8190(30)	95(3)	47.0(15)
H8Bb	-2331(7)	6220(20)	-296(14)	47.0(15)
H8Bc	-3280(30)	6997(5)	262(3)	47.0(15)
H9Ba	387(14)	5853(13)	1077(13)	49.6(16)
H9Bb	-369(10)	5370(30)	172(13)	49.6(16)
H9Bc	870(30)	7390(30)	516(4)	49.6(16)
H12a	-4132(6)	5840(20)	2096(7)	32(5)
H12b	-5200(20)	6932(7)	2023(6)	34(5)
H12c	-4691(11)	6214(13)	1285(13)	33(5)
H11a	-3340(30)	9092(14)	1003(4)	27(4)
H11b	-3820(20)	9690(20)	1698(10)	34(5)
H11c	-2002(10)	10439(11)	1551(13)	33(4)
H15a	5810(20)	12208(6)	818(11)	50.0(16)
H15b	5032(5)	13420(30)	1163(3)	50.0(16)
H15c	5611(16)	12320(5)	1694(15)	50.0(16)
H14a	2549(6)	12100(30)	331(2)	50.9(16)
H14b	3320(20)	10879(6)	-57(12)	50.9(16)
H14c	1450(40)	10030(30)	254(4)	50.9(16)
H17a	1372(5)	13650(30)	2964(6)	36(5)
H17b	130(30)	11670(20)	2640(4)	39(4)
H17c	1909(15)	12152(11)	3175(11)	35(5)
H18a	380(30)	12680(20)	1404(5)	34(4)
H18b	1643(5)	14580(30)	1825(6)	36(5)
H18c	2301(18)	13723(8)	1163(11)	35(5)
H21a	-2300(30)	2293(9)	2845(10)	60.0(18)
H21b	-3012(6)	2164(13)	3644(16)	60.0(18)
H21c	-4260(40)	1880(20)	2896(8)	60.0(18)
H6B	-1530(70)	7070(70)	3620(30)	60.0(18)
H1Ba	2720(50)	8330(50)	1910(20)	24(5)
H1Bb	4350(50)	9060(50)	2640(20)	25(5)

Atom	x	y	z	U_{eq}
H4Ba	2330(50)	9760(50)	3710(20)	24(5)
H4Bb	3530(50)	8640(50)	3930(20)	20(5)
H10B	-2330(60)	8660(60)	2450(30)	30(5)
H13B	3640(60)	9940(60)	990(30)	44(8)
H16B	3500(60)	13480(60)	2310(20)	31(6)
H19a	1870(50)	5800(50)	3850(20)	28(6)
H19b	240(50)	5070(50)	4390(20)	28(6)
H4B	3420(30)	7400(60)	4940(30)	48(15)
H6	6917(9)	100(40)	6355(6)	20(5)
H3	9040(40)	2166(4)	7097(3)	22(5)
H1a	9341(5)	6290(30)	7424(4)	28(5)
H1b	8877(12)	5005(6)	8079(15)	22(5)
H2a	6790(40)	3846(4)	7084(2)	21(5)
H4a	8265(4)	4775(4)	6088(2)	25(5)
H4c	9424(4)	3950(4)	6233(2)	24(5)
H8a	9152(11)	700(20)	9838(2)	36(5)
H8b	9790(30)	2740(30)	9890(3)	33(4)
H8c	8151(16)	1568(5)	10296(11)	37(5)
H9a	6444(17)	2551(6)	9726(14)	52(6)
H9b	7980(30)	3820(30)	9240(3)	52(5)
H9c	6100(30)	2362(9)	8789(13)	52(5)
H12d	7483(5)	-2870(30)	7845(8)	35(5)
H12e	7207(7)	-2108(8)	8679(15)	38(5)
H12f	6350(30)	-1740(6)	7886(7)	36(5)
H11d	10136(7)	-499(6)	9053(14)	35(5)
H11e	10468(6)	-1400(30)	8318(6)	35(5)
H11f	11370(30)	640(30)	8486(3)	35(4)
H13	11130(50)	6267(6)	9107(6)	32(5)
H15d	12803(15)	8196(11)	8381(12)	38(6)
H15e	13622(9)	8720(20)	9327(13)	42(5)
H15f	14530(30)	7813(5)	8707(4)	40(5)
H14d	12047(16)	4730(20)	9764(10)	49(4)
H14e	13820(20)	5640(40)	9568(6)	49(5)
H14f	13090(40)	6560(20)	10033(5)	49(5)
H16	14080(30)	5620(50)	7694(7)	31(5)
H17d	12204(15)	3806(14)	6780(11)	46(6)
H17e	13680(30)	3144(8)	6982(6)	46(6)
H17f	11780(30)	2180(30)	7282(4)	49(5)
H21d	2095(15)	-2340(30)	7156(8)	41(4)
H21e	2569(5)	-230(30)	7223(9)	42(4)
H21f	1900(20)	-1427(7)	6376(14)	44(4)
H19c	5448(6)	3340(20)	6070(11)	23(4)
H19d	4550(30)	1420(30)	5608(3)	22(3)
H24	10480(50)	2450(50)	4270(20)	21(8)
H25	9650(60)	3560(60)	5340(30)	51(13)
H2	6230(40)	-1530(20)	4220(20)	22(10)
H7	6530(60)	130(60)	9130(20)	32(4)
H10	9060(50)	-310(50)	7570(20)	24(5)
H18d	13560(60)	2970(70)	8570(30)	41(5)
H18e	15290(60)	3780(70)	8030(30)	44(6)
H18f	14790(60)	4760(70)	8770(30)	43(4)
H4	6690(50)	4230(40)	5020(30)	51(14)
H1Wa	4830(90)	-3640(70)	3332(9)	58(16)

Atom	x	y	z	U_{eq}
H1Wb	4430(100)	-4480(40)	4030(30)	65(17)
H1Wc	-3960(70)	7180(60)	6400(40)	61(16)
H1Wd	-4780(40)	5710(60)	5880(30)	40(14)
H1S_1	4180(30)	3470(50)	4639(7)	38(16)
H1Sa_1	1891(8)	3974(8)	5297(4)	26(7)
H1Sb_1	3557(8)	3740(8)	5644(4)	29(7)
H1Sc_1	3805(8)	5584(8)	5383(4)	18(7)
H1SB_2	2770(40)	5210(30)	5344(8)	36(16)
H1Sa_2	4587(8)	4531(8)	4601(4)	22(7)
H1Sc_2	2973(8)	2669(8)	4644(4)	21(7)
H1Sd_2	2630(8)	4216(8)	4325(4)	26(7)

Table 7: Hydrogen Bond information for **9A**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N2B	H2B	O1WB	0.982(3)	1.833(6)	2.805(4)	170(3)
O4B	H4B	O8[1]	0.9550(17)	1.86(3)	2.748(4)	153(6)
N2	H2	O1W	0.9819(15)	1.829(4)	2.811(4)	178(4)
O4	H4	O8B[2]	0.9550(17)	1.811(17)	2.747(4)	166(6)
O1W	H1Wb	O1S_1[3]	0.948(16)	1.93(2)	2.865(6)	167(6)
O1WB	H1Wc	O6[4]	0.960(16)	1.96(3)	2.857(4)	155(5)
O1WB	H1Wd	O1SB_2[5]	0.955(16)	1.888(19)	2.839(6)	174(6)
O1S_1	H1S_1	O4	0.9751(17)	1.753(3)	2.682(5)	158.0(12)
O1SB_2	H1SB_2	O4B	0.9752(17)	1.753(3)	2.672(5)	155.6(12)

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[1]+x,1+y,+z; [2]1+x,+y,+z; [3]+x,-1+y,+z; [4]-1+x,1+y,+z; [5]-1+x,+y,+z

Table 8: Atomic Occupancies for all atoms that are not fully occupied in **9A**.

Atom	Occupancy
O1S_1	0.500000
H1S_1	0.500000
C1S_1	0.500000
H1Sa_1	0.500000
H1Sb_1	0.500000
H1Sc_1	0.500000
O1SB_2	0.500000
H1SB_2	0.500000
C1SB_2	0.500000
H1Sa_2	0.500000
H1Sc_2	0.500000
H1Sd_2	0.500000

Table 9. Antiviral activity of compounds 1-4.

Compound	SARS CoV-2 activity[2] in			Influenza A[3]	Influenza B[3]	Norwalk[4]	RSV[5]
	Vero (EC_{50} µM)	Calu-3 (EC_{50} µM)	Caco-2 (EC_{50} µM)	A549 (EC_{50} µM)	A549 (EC_{50} µM)	Huh7 (EC_{50} µM)	Hep-2 (EC_{50} µM)
1	>10	>10	>10	>40	>40	>10	>10
2	>10	>10	>10	>40	>40	>10	>10
3	>10	>10	>10	>40	>40	>10	>10
4	>10	>10	>10	>40	>40	>10	>10
CNC	2.1	0.7	0.02	NA	NA	NA	NA
Remdesivir[a]	1.8	0.2	0.02	NA	NA	NA	0.2
VX-787[a]	NA	NA	NA	0.051	NA	NA	NA
Baloxavir acid[a]	NA	NA	NA	NA	0.15	NA	NA
2'Me-C[a]	NA	NA	NA	NA	NA	2.8	NA

[a] Positive controls, 2'Me-C: 2′-C-methylcytidine, CNC: 1'-Cyanocytidine, NA: Not applicable

Table 10. Cytotoxicity profile of compounds 1-4

Compound	Cytotoxicity - CC_{50} (µM)			
	PBM	CEM	Vero	Huh-7
1	>100	>100	>100	>100
2	>100	>100	>100	>100
3	>100	>100	>100	>100
4	>100	>100	>100	>100

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