Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of Reverse Glycosyl Fluorides *via* Organophotocatalytic Decarboxylative Fluorination of Uronic Acids

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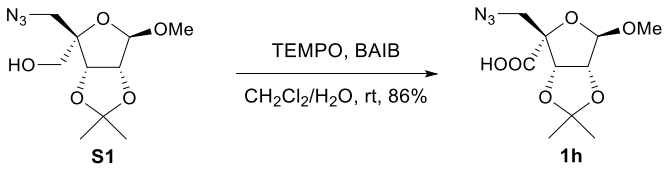
General Information

All reactions were carried out under argon with magnetic stirring unless otherwise indicated. The decarboxylative fluorination was carried out in a quartz tube under argon. All commercially obtained reagents were used as received, except where specified otherwise. Selectfluor was purchased from Energy Chemical; Mes-Acr·ClO_4 was purchased from TCI and used without further purification. Anhydrous dicholoromethane (CH_2Cl_2), *N*,*N*-dimethylformamide (DMF) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Tetrahydrofuran (THF) was distilled immediately before use from sodium-benzophenone ketyl. Pyridene and acetonitrile were refluxed over calcium hydride and distilled before use. Acetone was distilled from potassium permanganate and stored prior to use. Flash column chromatography was performed on Silica Gel H (300–400 mesh, Qingdao, China). Analytical thin layer chromatography was performed on Silicycle SiliaPlate glass-backed plates coated with silica gel (60 mesh pore size, F-254 indicator) and visualized by exposure to ultraviolet light and/or staining with 8% sulfuric acid in methanol. Optical rotations were determined with a JASCO P-1020 digital polarimeter. NMR spectra were recorded on a JEOL-ECP-600 MHZ spectrometer, an Agilent DD2 500 MHz NMR spectrometer and a Bruker AVENCE NEO 400 MHZ spectrometer. The ^{1}H NMR signal for residual non-deuterated solvent (δ 7.26 ppm for $CHCl_3$, 2.50 ppm for DMSO, 2.05 ppm for acetone, 3.31 ppm for methanol) was used as an internal reference. The ^{13}C NMR signal for $CDCl_3$ (δ 77.16 ppm), d_6-DMSO (δ 39.5 ppm), d_4-methanol (δ 49.0 ppm) or d_6-acetone (δ 29.8 ppm) was used as an internal reference. ^{19}FNMR signals were referenced against $PhCF_3$ (δ –63.2) as an external standard. ^{31}P NMR signals were reported relative to aqueous 85% H_3PO_4 (δ 0 ppm, external standard). The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, DEPT-Q = Distorsionless Enhancement by Polarization Transfer Including the Detection of Quaternary Nuclei.

Section 1. Synthesis of Uronic Acids

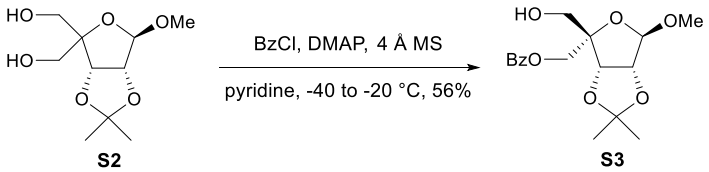
The required uronic acids **1a**,[1] **1b**,[2] **1c-d**,[3] **1e**,[4] **1f**,[1] **1g**,[1] **1n-o**[5], **1r**,[6] **1s**,[7] **1t**,[8] **1u**,[1] **1w**[9], were synthesized referred to the procedures in the literatures.

Methyl 2,3-*O*-isopropylidene-4-*C*-azidomethyl-α-L-lyxofuranuronic acid (1h)



To a solution of **S1**[10] (427 mg, 1.65 mmol, 1.0 equiv) in CH_2Cl_2/H_2O (v/v = 4:1, 10 mL) was added 2,2,6,6-tetramethylpiperidine-1-oxy1 (TEMPO, 52 mg, 0.33 mmol, 0.2 equiv) and (diacetoxyiodo)benzene (BAIB, 1.6 g, 4.95 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature overnight. The reaction was quenched with sat. NaS_2O_3 solution. The aqueous phase was extracted with ethyl acetate (EtOAc, 30 mL×5), the organic phase was dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 1:1) to afford **1h** (387 mg, 1.42 mmol, 86%) as a colorless syrup. $[\alpha]_D^{22}$ = -1.2 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.23 (s, 1H), 4.69 (d, *J* = 5.8 Hz, 1H), 4.65 (d, *J* = 5.8 Hz, 1H), 3.84 (d, *J* = 12.5 Hz, 1H), 3.59 (d, *J* = 12.5 Hz, 1H), 3.48 (s, 3H), 1.45 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 114.0, 110.4, 92.0, 84.9, 83.1, 56.4, 55.9, 25.9, 24.6; HRMS (ESI) *m/z* calcd for $C_{10}H_{15}N_3NaO_6$ $[M+Na]^+$ 296.0853, found 296.0853.

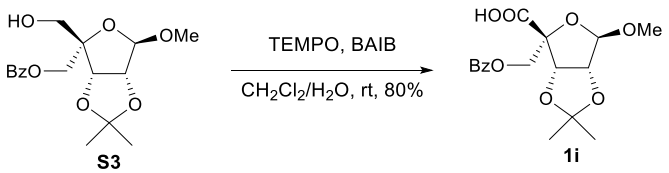
Methyl 2,3-*O*-isopropylidene-5-*O*-benzoyl-4-fluoro-α-L-lyxofuranoside (S3)



To a solution of **S2**[11] (1.0 g, 4.27 mmol, 1.0 equiv) and 4-dimethylaminopyridine (DMAP, 52 mg, 0.43 mmol, 0.1 equiv) in anhydrous pyridine (52 mL) was added benzoyl chloride (BzCl, 750 μL, 6.41 mmol, 1.5 equiv) drop-wise at -40 °C. The mixture was warm up to -20 °C and was stirred at this temperature for 2 h. After the

completion of the reaction, the mixture was quenched with MeOH (10 mL), and was concentrated in *vacuo*. The residue was dissolved in EtOAc (30 mL), and washed sequentially with 1 M HCl solution (50 mL), sat. $NaHCO_3$ solution (50 mL) and brine (50 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 5:1) to afford **S3** (809 mg, 2.39 mmol, 56%) as a white foam. $[\alpha]_D^{22}$ = -4.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.02 (s, 1H), 4.91−4.89 (m, 1H), 4.71 (d, *J* = 5.9 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 3.75 (s, 2H), 3.45 (s, 3H), 1.50 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 133.4, 129.9, 128.6, 112.9, 110.0, 90.1, 86.7, 82.1, 65.3, 64.8, 55.8, 26.3, 24.8; HRMS (ESI) *m/z* calcd for $C_{17}H_{23}O_7$ $[M+H]^+$ 339.1438, found 339.1439.

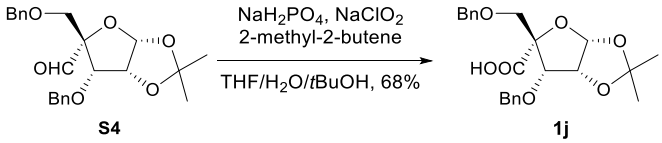
Methyl 2,3-*O*-isopropylidene-4-*C*-benzoyloxylmethyl-β-D-ribofuranuronic acid (1i)



S3 1i

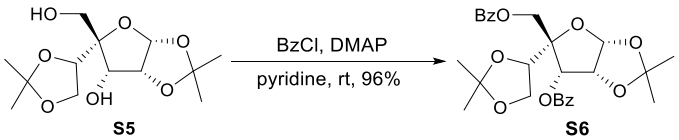
Following the procedure for **1h**, treatment of **S3** (1.57 g, 4.66 mmol, 1.0 equiv) with TEMPO (109 mg, 0.7 mmol, 0.15 equiv) and BAIB (3.0 g, 9.32 mmol, 2.0 equiv) in CH_2Cl_2/H_2O (v/v = 5:1, 24 mL) afford **1i** (1.32 g, 3.73 mmol, 80%) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 4:1, containing 7‰ trifluoroacetic acid). $[\alpha]_D^{22}$ = -43.3 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.5 Hz, 2H), 7.53 (t, *J* = 6.9 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 5.33 (d, *J* = 5.8 Hz, 1H), 5.05 (s, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.64 (d, *J* = 5.8 Hz, 1H), 4.60 (d, *J* = 11.1 Hz, 1H), 3.40 (s, 3H), 1.50 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 165.8, 133.4, 129.9, 129.6, 128.5, 113.4, 109.3, 87.4, 84.8, 81.7, 77.4, 76.9, 65.1, 56.1, 26.1, 24.8; HRMS (ESI) *m/z* calcd for $C_{17}H_{20}NaO_8$ $[M+Na]^+$ 375.1050, found 375.1048.

1,2-*O*-Isopropylidene-3-*O*-benzyl-4-*C*-benzyloxylmethyl-β-L-ribofuranuronic acid (1j)



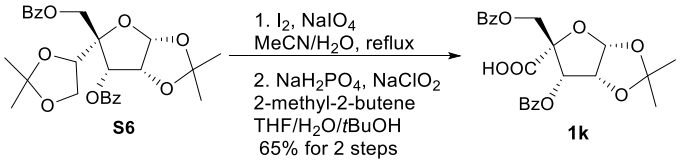
To a solution of aldehyde **S4**[12] (2.87 g, 7.2 mmol, 1.0 equiv) in a mixed solvent of THF/H_2O/*t*BuOH (v/v/v = 4:1:1, 42 mL) was added sequentially $NaH_2PO_4 \cdot 2H_2O$ (1.7 g, 10.8 mmol, 1.5 equiv), 2-methyl-2-butene (3.8 mL, 36.0 mmol, 5.0 equiv) and $NaClO_2$ (1.95 g, 21.6 mmol, 3.0 equiv) under an ice-bath. The mixture was warm up to room temperature and stirred overnight. The pH value of the mixture was adjusted to approximate 1 by addition of 1 M solution of HCl, and EtOAc (50 mL) was added. Two phases were separated and the aqueous phase was extracted with EtOAc (50 mL×5). The organic phase was dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (CH_2Cl_2:EtOAc = 2:1) to afford **1j** (2.03 g, 4.9 mmol, 68%) as a colorless syrup. $[\alpha]_D^{23}$ = +85.8 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.23 (m, 10H), 5.85 (d, *J* = 3.6 Hz, 1H), 4.81 (d, *J* = 11.9 Hz, 1H), 4.74−4.64 (m, 2H), 4.56 (d, *J* = 11.9 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.31 (d, *J* = 4.8 Hz, 1H), 3.83−3.69 (m, 2H), 1.60 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 137.4, 136.3, 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 114.6, 104.9, 87.3, 78.2, 78.0, 74.1, 73.4, 71.6, 26.3, 25.2; HRMS (ESI) *m/z* calcd for $C_{23}H_{26}NaO_7$ $[M+Na]^+$ 437.1571, found 437.1559.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzoyl-4-*C*-benzoyloxylmethyl-β-L-altrofuranoside (S6)



Followed the procedure for **S3**, **S5**[12] (40.0 g, 137.8 mmol, 1.0 equiv) was treated with BzCl (38.1 mL, 330.7 mmol, 2.4 equiv) and DMAP (3.37 g, 27.6 mmol, 0.2 equiv) in anhydrous pyridine (250 mL) to afford **S6** (65.0 g, 130.4 mmol, 95%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 7:1 to 6:1). $[\alpha]_D^{23}$ = +121.8 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.9 Hz, 2H), 6.04 (d, *J* = 4.1 Hz, 1H), 5.50 (d, *J* = 5.9 Hz, 1H), 5.08 (dd, *J* = 5.8, 4.2 Hz, 1H), 4.99 (dd, *J* = 7.3,6.5 Hz, 1H), 4.56 (s, 2H), 4.24 (dd, *J* = 9.0, 7.8 Hz, 1H), 3.98 (dd, *J* = 9.1, 6.4 Hz, 1H), 1.55 (s, 3H), 1.51 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 165.3, 133.8, 133.5, 129.8, 129.6, 129.5, 129.0, 128.8, 128.7, 114.8, 109.6, 105.6, 86.9, 80.1, 77.4, 74.4, 65.8, 65.5, 27.1, 27.0, 26.0, 24.2; HRMS (ESI) *m/z* calcd for $C_{27}H_{34}NO_9$ $[M+NH_4]^+$ 516.2228, found 516.2222.

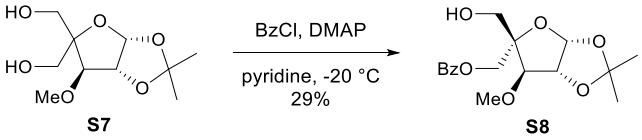
1,2-*O*-Isopropylidene-3-*O*-benzoyl-4-*C*-benzoyloxylmethyl-β-L-ribofuranuronic acid (1k)



To a solution of **S6** (11.9 g, 23.85 mmol, 1.0 equiv) in aqueous acetonitrile (v/v = 4:1, 220 mL) was sequentially added sodium periodate ($NaIO_4$, 20.4 g, 95.4 mmol, 4.0 equiv) and iodine (I_2, 3.6 g, 14.3 mmol, 0.6 equiv) under an ice-bath. The ice-bath was removed and the flask was evacuated and backfilled with argon 3 times before the mixture was heated to 80 °C and stirred vigorously at this temperature for 6 h. The mixture was cooled to room temperature. Sat. $Na_2S_2O_3$ solution (500 mL) was added to quench the reaction and the aqueous solution was taken up with EtOAc (200 mL×3). The combined organic phases were dried over Na_2SO_4, filtered. The filtrate was concentrated in *vacuo*. The resulting aldehyde was used directly without further

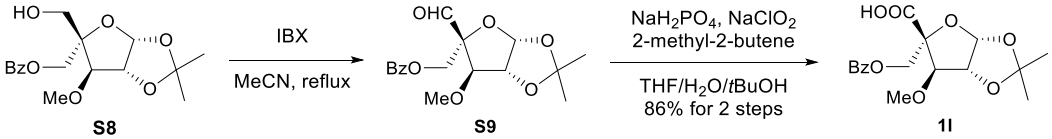
purification. Followed the procedure for **1j**, the above obtained aldehyde was transformed into uronic acid **1k** (6.87 g, 15.53 mmol, 65% over 2 steps) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 4:1, containing 5‰ of acetic acid). $[\alpha]_D^{23}$ = +11.4 (*c* 3.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.01 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.62−7.55 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 6.10 (d, *J* = 4.0 Hz, 1H), 5.50 (d, *J* = 5.6 Hz, 1H), 5.09 (dd, *J* = 5.6, 4.0 Hz, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 2.09 (s, 1H), 1.57 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 165.7, 165.4, 134.0, 133.6, 130.3, 129.9, 129.3, 128.8, 128.7, 128.6, 115.1, 105.9, 87.0, 78.3, 73.5, 66.5, 26.2, 25.3; HRMS (ESI) *m/z* calcd for $C_{23}H_{21}O_9$ $[M-H]^-$ 441.1191, found 441.1186.

1,2-*O*-Isopropylidene-3-*O*-methyl-5-*O*-benzoyl-4-*C*-hydroxylmethyl-β-L-arabinofuranoside (S8)



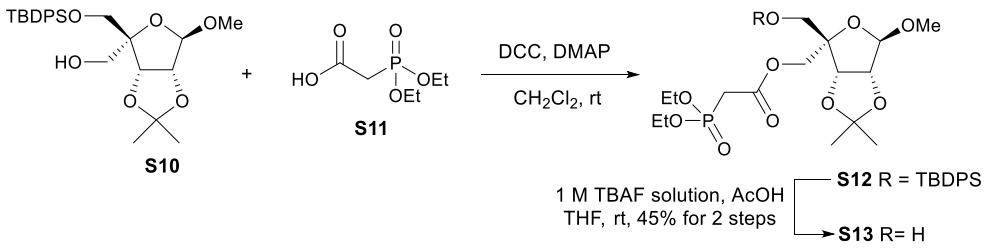
Following the procedure for **S3**, treatment of **S7**[13] (2.68 g, 11.43 mmol, 1.0 equiv) with BzCl (2.0 mL, 16.15 mmol, 1.5 equiv) and DMAP (140 mg, 1.14 mmol, 0.1 equiv) in anhydrous pyridine (100 mL) afford **S8** (1.13 g, 3.31 mmol, 29%) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 3:1). $[\alpha]_D^{23}$ = -4.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.01−5.97 (m, 1H), 4.70 (d, *J* = 4.3 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 3.95 (s, 1H), 3.80−3.72 (m, 2H), 3.43 (s, 3H), 1.56 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 133.3, 129.9, 129.8, 128.6, 113.2, 105.3, 88.6, 86.1, 85.2, 63.6, 62.6, 58.6, 27.3, 26.7; HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NaO_7$ $[M+Na]^+$ 361.1258, found 361.1249.

1,2-*O*-Isopropylidene-3-*O*-methyl-4-*C*-benzoyloxylmethyl-β-D-lyxofuranuronic acid (1l)



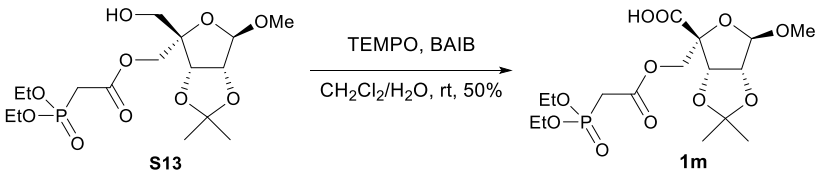
To a solution of **S8** (930 mg, 2.75 mmol, 1.0 equiv) in anhydrous MeCN (30 mL) was added 2-iodoxybenzoic acid (IBX, 1.54 g, 5.5 mmol, 2.0 equiv). The mixture was heated to reflux and stirred at this temperature for 2 h. After completion of the reaction, the mixture was cooled to room temperature, filtered, and the filtrate was concentrated in *vacuo* to obtain **S9** for the next conversion without further purification. Followed the procedure for **1j**, treatment of **S9** with $NaH_2PO_4 \cdot 2H_2O$ (644 mg, 4.13 mmol, 1.5 equiv), 2-methyl-2-butene (585 μL, 5.5 mmol, 2.0 equiv) and $NaClO_2$ (746 mg, 8.25 mmol, 3.0 equiv) in a mixed solvent of THF/H_2O/*t*BuOH (v/v/v = 4:1:1, 24 mL) afford **1l** (829 mg, 2.37 mmol, 86% over 2 steps) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 3:1 to CH_2Cl_2:MeOH = 9:1). $[\alpha]_D^{23}$ = -50.4 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 6.07 (d, *J* = 3.7 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.65 (d, *J* = 3.7 Hz, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.36 (s, 1H), 3.51 (s, 3H), 1.54 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 165.8, 133.5, 129.9, 129.4, 128.6, 113.6, 106.9, 90.1, 86.9, 82.0, 66.2, 59.0, 25.4, 25.2; HRMS (ESI) *m/z* calcd for $C_{17}H_{20}NaO_8$ $[M+Na]^+$ 375.1050, found 375.1041.

Methyl 2,3-*O*-isopropylidene-5-*O*-(2'-diethoxy)phosphorylacetyl-4-*C*-hydroxyl-methyl-α-L-lyxofuranoside (S13)



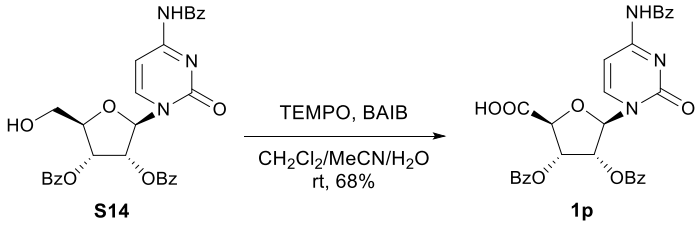
To a solution of methyl glucoside **S10**[14] (1.29 g, 2.73 mmol, 1.0 equiv) and phosphonoacetic acid **S11** (794 mg, 4.05 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (15 mL) was added DMAP (66 mg, 0.54 mmol, 0.2 equiv) and *N*,*N*′-dicyclohexylcarbodiimide (DCC, 835 mg, 4.05 mmol, 1.5 equiv) The mixture was stirred at room temperature for 1 h before the mixture was filtered, and concentrated in *vacuo*. The residue was dissolved in THF (5 mL), and this solution was added acetic acid (420 μL, 7.43 mmol, 2.75 equiv) and 1 M tetrabutylammonium fluoride (TBAF) solution in THF (4.8 mL, 4.80 mmol, 1.8 equiv). The mixture was stirred at room temperature overnight. After completion of the reaction, the mixture was concentrated in *vacuo* and the residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 2:1) to afford **S13** (506 mg, 1.22 mmol, 45% over 2 steps) as a colorless syrup. $[\alpha]_D^{21}$ = -24.2 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.93 (s, 1H), 4.78 (d, *J* = 6.0 Hz, 1H), 4.63 (d, *J* = 6.0 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 4.20−4.08 (m, 5H), 3.70 (d, *J* = 12.2 Hz, 1H), 3.57 (d, *J* = 12.2 Hz, 1H), 3.35 (s, 3H), 3.07−2.91 (m, 2H), 1.43 (s, 3H), 1.34−1.29 (m, 6H), 1.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 112.7, 109.5, 89.2, 86.3, 82.2, 65.8, 64.0, 63.2 ($J_{C\text{-}P}$ = 6.3 Hz), 62.9 ($J_{C\text{-}P}$ = 6.3 Hz), 55.5, 42.1, 34.6 ($J_{C\text{-}P}$ = 131.8 Hz), 26.2, 24.6, 16.44 ($J_{C\text{-}P}$ = 5.9 Hz), 16.39 ($J_{C\text{-}P}$ = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.06 (s, 1P); HRMS (ESI) *m/z* calcd for $C_{16}H_{30}O_{10}P$ $[M+H]^+$ 413.1571, found 413.1561.

Methyl 2,3-*O*-isopropylidene-4-*C*-(2'-diethoxy)phosphorylacetyloxylmethyl-β-D-ribofuranyronic acid (1m)



Following the procedure for **1h,** treatment of **S13** (410 mg, 0.99 mmol, 1.0 equiv) with TEMPO (31 mg, 0.2 mmol, 0.2 equiv) and BAIB (966 mg, 3.0 mmol, 3.0 equiv) in CH_2Cl_2/H_2O (v/v = 5:1, 10 mL) afford **1m** (213 mg, 0.5 mmol, 50%) as a colorless syrup after purification by silica gel column chromatography (CH_2Cl_2:EtOAc = 1:1). $[\alpha]_D^{21}$ = -16.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (d, *J* = 5.9 Hz, 1H), 4.97 (s, 1H), 4.92 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 5.9 Hz, 1H), 4.22−4.16 (m, 5H), 3.43 (s, 3H), 3.07−2.93 (m, 2H), 1.50 (s, 3H), 1.37−1.33 (m, 6H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 164.6, 113.2, 109.1, 87.6, 85.0, 82.5, 65.6, 63.7 (J_{C-P} = 6.5 Hz), 63.3 (J_{C-P} = 6.5 Hz), 56.2, 34.6 (J_{C-P} = 132.5 Hz), 26.1, 24.8, 16.44 (J_{C-P} = 6.2 Hz), 16.39 (J_{C-P} = 6.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.2 (s, 1P); HRMS (ESI) *m/z* calcd for $C_{16}H_{28}O_{11}P$ $[M+H]^+$ 427.1364, found 427.1355.

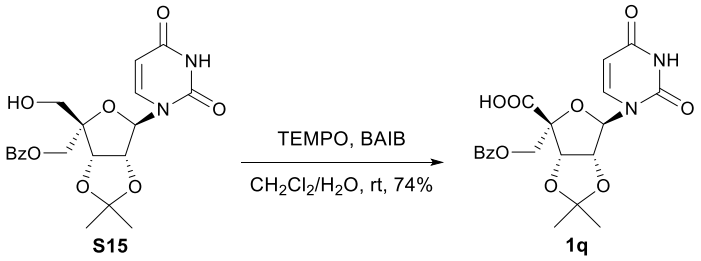
N$_4$-Benzoyl-2',3'-di-*O*-benzoyl-cytidinuronic acid (1p)



Following the procedure for **1h**, treatment of **S14**[14] (220 mg, 0.39 mmol, 1.0 equiv) with TEMPO (12 mg, 80.0 μmol, 0.2 equiv) and BAIB (387 mg, 1.2 mmol, 3.0 equiv) in MeCN/CH_2Cl_2/H_2O (v/v = 4:1:1, 6 mL) afford **1p** (151 mg, 0.27 mmol, 68%) as a white foam after purification by silica gel column chromatography (CH_2Cl_2:MeOH = 9:1). $[\alpha]_D^{20}$ = -34.1 (*c* 0.4, DMSO); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.54 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.66−7.61 (m, 2H), 7.56−7.46 (m, 4H), 7.41−7.47 (m, 3H), 6.38−6.31 (m, 1H), 6.14 (d, *J* = 4.7 Hz, 1H), 5.99−5.92 (m, 1H), 5.06 (d, *J* = 4.8 Hz,

1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.3, 164.6, 164.5, 134.1, 134.0, 132.9, 129.4, 128.9, 128.8, 128.61, 128.55, 128.5, 97.0, 91.4, 80.1, 74.3, 73.2; HRMS (ESI) *m/z* calcd for $C_{30}H_{24}N_3O_9$ $[M+H]^+$ 570.1507, found 570.1501.

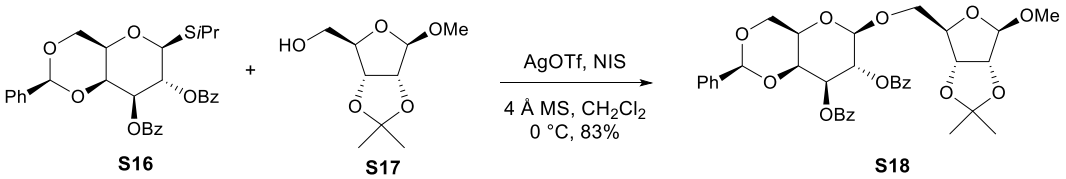
Uracil 2,3-*O*-isopropylidene-4-*C*-benzoyloxylmethyl-β-D-ribofuranuronic acid (1q)



S15 1q

Following the procedure for **1h**, treatment of **S15**[10] (416 mg, 0.99 mmol, 1.0 equiv) with TEMPO (31 mg, 0.22 mmol, 0.2 equiv) and BAIB (966 mg, 3.0 mmol, 3.0 equiv) in CH_2Cl_2/H_2O (v/v = 4:1, 10 mL) afford **1q** (320 mg, 0.73 mmol, 74%) as a colorless syrup after purification by silica gel column chromatography (CH_2Cl_2:EtOAc = 1:1). $[\alpha]_D^{23}$ = -109.3 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.06 (s, 1H), 11.38 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 5.86 (s, 1H), 5.63 (d, *J* = 7.6 Hz, 1H), 5.41–5.31 (m, 2H), 4.51 (d, *J* = 11.7 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 1.51 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.4, 165.1, 163.5, 151.0, 145.1, 133.6, 129.2, 128.8, 112.6, 101.5, 94.3, 90.4, 84.7, 84.0, 67.4, 25.6, 24.0; HRMS (ESI) *m/z* calcd for $C_{20}H_{20}N_2NaO_9$ $[M+Na]^+$ 455.1061, found 455.1058.

Methyl 5-*O*-(2',3'-di-*O*-benzoyl-4',6'-*O*-benzylidene-β-D-glactopyranosyl)-2,3-*O*-isopropylidene-β-D-ribofuranoside (S18)

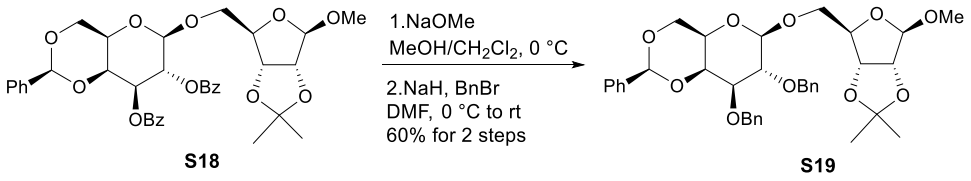


S16 S17 S18

To a solution of **S16**[15] (1.92 g, 3.62 mmol, 1.2 equiv) and **S17**[16] (613 mg, 3.0 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (30 mL) containing freshly activated 4 Å molecular sieve

(MS) were added silver trifluoromethanesulfonate (AgOTf, 116 mg, 0.45 mmol, 0.2 equiv) and *N*-iodosuccinimide (NIS, 1.35 g, 6.0 mmol, 2.0 equiv) at 0 °C. The mixture was stirred at 0 °C for 1 h before the reaction was quenched with sat. $Na_2S_2O_4$ solution (30 mL). Two phases were separated and the aqueous phase was extracted with CH_2Cl_2 (50 mL×3), the organic phase was combined, washed sequentially with sat. $NaHCO_3$ solution (30 mL) and brine (30 mL). The mixture was dried over Na_2SO_4, filtered. The filtrate was concentrated in *vacuo*, the residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 3:1) to afford disaccharide **S18** (1.81 g, 2.99 mmol, 83%) as a white foam. $[\alpha]_D^{23}$ = +62.2 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03–7.95 (m, 4H), 7.55–7.46 (m, 4H), 7.40–7.32 (m, 7H), 5.88 (dd, *J* = 10.3, 8.1 Hz, 1H), 5.55 (s, 1H), 5.36 (dd, *J* = 10.4, 3.5 Hz, 1H), 4.88 (s, 1H), 4.83 (d, *J* = 8.0 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 4.59 (d, *J* = 3.5 Hz, 1H), 4.50 (d, *J* = 5.9 Hz, 1H), 4.41 (d, *J* = 12.4 Hz, 1H), 4.29 (dd, *J* = 8.4, 6.3 Hz, 1H), 4.14 (d, *J* = 13.2 Hz,1H), 3.89 (t, *J* = 9.2 Hz, 1H), 3.72–3.67 (m, 2H), 3.22 (s, 3H), 1.37 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 165.3, 137.6, 133.5, 133.1, 130.1, 129.9, 129.8, 129.2, 129.1, 128.5, 128.4, 128.3, 126.4, 112.3, 109.5, 101.0, 100.7, 85.1, 84.6, 81.9, 73.7, 72.9, 69.0, 68.9, 68.8, 66.7, 54.8, 26.4, 24.8; HRMS (ESI) *m/z* calcd for $C_{36}H_{38}NaO_{12}$ $[M+Na]^+$ 685.2255, found 685.2250.

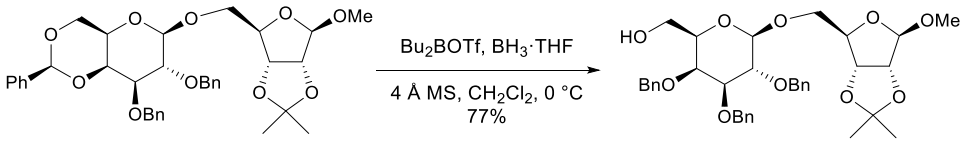
Methyl 5-*O*-(2',3',4'-tri-*O*-benzyl-β-D-glactopyranosyl)-2,3-*O*-isopropylidene-β-D-ribofuranoside (S20)



S18 **S19**

To a solution of **S18** (1.62 g, 2.45 mmol, 1.0 equiv) in MeOH/CH_2Cl_2 (v/v = 4:1, 25 mL) was added NaOMe solution in MeOH (0.5 mL, 0.49 mmol, 0.2 equiv) under an ice-bath. The mixture was stirred at this temperature for 30 min before the reaction was quenched with Dowex (H^+) resin. The mixture was filtered, and the filtrate was concentrated in *vacuo* to afford the product, which was used for the next transformation

without further purification. To a solution of the crude product in anhydrous DMF (8.0 mL) was added sodium hydride (NaH, 60% in mineral oil, 588 mg, 14.7 mmol, 6.0 equiv) under an ice-bath. The mixture was stirred for 30 min before benzyl bromide (BnBr, 1.3 mL, 11.0 mmol, 4.5 equiv) was added. The resulting mixture was warm up to room temperature and stirred overnight. The reaction was quenched with water (10 mL) at 0 °C, the mixture was concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc:CH_2Cl_2 = 4:1:1) to afford **S19** (930 mg, 1.47 mmol, 60% over 2 steps) as a white foam, which was directly exposed to selective ring-opening of benzylidene.

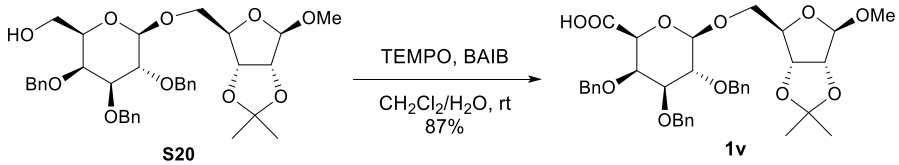


S19 **S20**

To a solution of **S19** (700 mg, 1.10 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (11 mL) containing freshly activated 4 Å MS was sequentially added borane tetrahydrofuran complex (1 M solution in THF, 11 mL, 11.0 mmol, 10.0 equiv), the mixture was stirred at room temperature for 30 min before dibutylboryl trifluoromethanesulfonate ($Bu_2B(OTf)_2$, 1 M solution in CH_2Cl_2, 550 µL, 0.55 mmol, 0.5 equiv) was added under an ice-bath. The mixture was stirred at 0 °C for 2 h before the reaction was quenched with MeOH (1 mL) and triethyl amine (TEA, 1 mL). The mixture was concentrated in *vacuo*, the residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 3:1 to 2:1) to afford **S20** (530 mg, 0.85 mmol, 77%) as a colorless syrup. $[\alpha]_D^{23}$ = -56.2 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.25 (m, 15H), 5.00−4.92 (m, 3H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.80−4.72 (m, 3H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.56 (d, *J* = 6.0 Hz, 1H), 4.41 (dd, *J* = 8.3, 5.7 Hz, 1H), 4.37 (d, *J* = 7.6 Hz, 1H), 3.88−3.75 (m, 4H), 3.66 (dd, *J* = 10.6, 5.6 Hz, 1H), 3.52 (dd, *J* = 9.8, 2.9 Hz, 1H), 3.45−3.36 (m, 2H), 3.27 (s, 3H), 2.06 (d, *J* = 5.9 Hz, 1H), 1.48 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 138.5, 138.3, 128.9, 128.6, 128.39, 128.37, 128.2, 127.9, 127.8, 127.7, 112.6, 109.2, 104.8, 85.7, 85.2, 82.5, 82.3, 79.7, 75.4, 75.2, 74.3,

73.6, 73.0, 71.6, 62.4, 55.1, 26.6, 25.1; HRMS (ESI) *m/z* calcd for $C_{36}H_{44}NaO_{10}$ $[M+Na]^+$ 659.2827, found 659.2813.

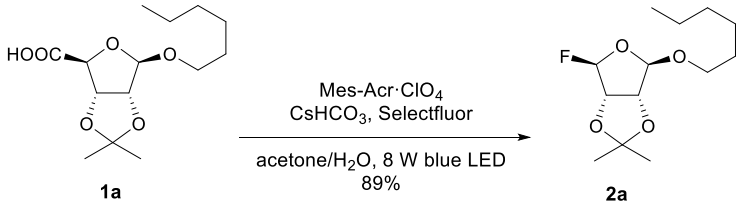
Methyl 5-*O*-[(5'*S*)-2',3',4'-tri-*O*-benzyl-5'-*C*-carboxyl-β-D-arabinopyranosyl]- 2,3-*O*-isopropylidene-β-D-ribofuranoside (1v)



Following the procedure for **1h**, treatment of **S20** (610 mg, 0.96 mmol, 1.0 equiv) with TEMPO (30 mg, 0.21 mmol, 0.2 equiv) and BAIB (928 mg, 2.88 mmol, 3.0 equiv) in CH_2Cl_2/H_2O (v/v = 4:1, 10 mL) afforded **1v** (542 mg, 0.84 mmol, 87%) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 3:1 to CH_2Cl_2:EtOAc = 1:2). $[\alpha]_D^{23}$ = -9.6 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.20 (m, 15H), 5.01−4.85 (m, 3H), 4.84−4.68 (m, 4H), 4.64 (d, *J* = 11.0 Hz, 1H), 4.58 (d, *J* = 5.6 Hz, 1H), 4.48 (d, *J* = 7.6 Hz, 1H), 4.40 (t, *J* = 7.1 Hz, 1H), 4.28 (s, 1H), 4.06 (s, 1H), 3.91−3.81 (m, 2H), 3.68 (dd, *J* = 10.1, 6.2 Hz, 1H), 3.59 (d, *J* = 8.9 Hz, 1H), 3.27 (s, 3H), 1.49 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 138.4, 138.0, 137.9, 128.6, 128.41, 128.35, 128.0, 127.9, 127.8, 127.7, 112.8, 109.2, 103.9, 85.3, 85.1, 82.1, 81.0, 78.1, 75.4, 75.3, 75.0, 74.0, 73.2, 71.4, 55.1, 26.5, 25.0; HRMS (ESI) *m/z* calcd for $C_{36}H_{42}NaO_{11}$ $[M+Na]^+$ 673.2619, found 673.2605.

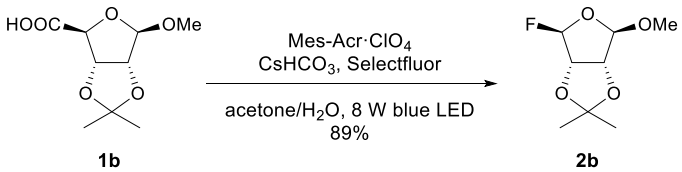
Section 2. Decarboxylative Fluorination of Uronic Acids

Hexyl (4*R*)-2,3-*O*-isopropylidene-4-fluoro-α-D-threoside (2a)



To a solution of **1a** (89 mg, 0.28 mmol, 1.0 equiv) in acetone/H_2O (v/v = 4:1, 3.0 mL) were added sequentially $CsHCO_3$ (81 mg, 0.42 mmol, 1.5 equiv), Selectfluor (198 mg, 0.56 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (5.8 mg, 14.0 μmol, 5 mol%). The reaction tube was evacuated and backfilled with argon 3 times. The mixture was stirred vigrously under the irradiation of 8 W blue LED belt at room temperature for 1h. After completion of the reaction, the acetone was removed in *vacuo*, the resulting water phase was diluted with CH_2Cl_2 (20 mL) and water (10 mL). Two phases were separated and the aqueous phase was ectracted with CH_2Cl_2 (10 mL×3). The combined organic phase was dried over Na_2SO_4, filtered, the filtrate was concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 50:1) to afford the titled compound **2a** (65 mg, 0.25 mmol, 89%) as a colorless syrup. ^{1}H NMR (500 MHz,$CDCl_3$) δ 5.77 (d, $J_{H\text{-}F}$ = 60.6 Hz, 1H), 5.25 (d, J = 2.8 Hz, 1H), 4.83 (t, J = 5.8 Hz, 1H), 4.67 (d, J = 5.7 Hz, 1H), 3.75 (m, 1H), 3.43 (m, 1H), 1.59–1.54 (m, 2H), 1.44 (s, 3H), 1.34–1.24 (m, 9H), 0.88 (t, J = 6.7 Hz, 3H). The data was identical to previous report.[10]

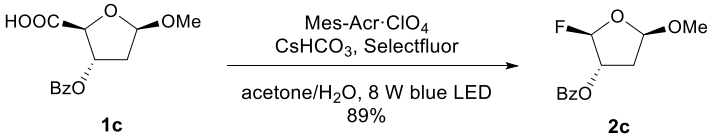
Methyl (4*R*)-2,3-*O*-isopropylidene-4-fluoro-α-D-threoside (2b)



Following the procedure for **2a**, uronic acid **1b** (65 mg, 0.3 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (87 mg, 0.45 mmol, 1.5 equiv), Selectfluor (213 mg, 0.6 mmol,

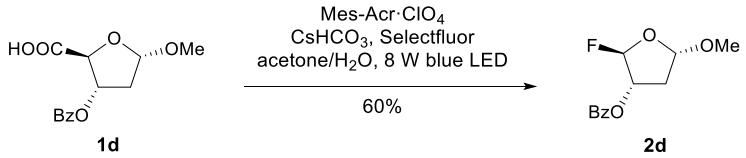
2.0 equiv) and Mes-Acr·ClO_4 (6.2 mg, 15.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 3.0 mL) to afford titled compound **2b** (51 mg, 0.27 mmol, 89%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 19:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (d, J = 60.5 Hz, 1H), 5.16 (d, J = 2.8 Hz, 1H), 4.81 (t, J = 6.0 Hz, 1H), 4.66 (d, J = 5.7 Hz, 1H), 3.42 (s, 2H), 1.44 (s, 3H), 1.31 (s, 3H). The data was identical to previous report.[10]

(1*R*, 3*S*, 4*R*)-1-Methyloxyl-3-benzoyloxyl-4-fluorotetrahydrofuran (2c)



Following the procedure for **2a**, uronic acid **1c** (80 mg, 0.3 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (87 mg, 0.45 mmol, 1.5 equiv), Selectfluor (213 mg, 0.6 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (6.2 mg, 15.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 3.0 mL) to afford titled compound **2c** (64 mg, 0.27 mmol, 89%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 15:1). $[\alpha]_D^{22}$ = +39.5 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 7.1 Hz, 2H), 7.58 (t, J = 8.1 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 5.89 (d, $J_{H\text{-}F}$ = 60.8 Hz, 1H), 5.59−5.53 (m, 1H), 5.48 (dd, J = 10.0, 5.0 Hz, 1H), 3.50 (s, 3H), 2.49−2.43 (m, 1H), 2.39−2.33 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 133.6, 129.8, 129.2, 128.6, 112.7 ($J_{C\text{-}F}$ = 226.8 Hz), 108.6, 77.6 ($J_{C\text{-}F}$ = 40.3 Hz), 56.5, 36.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ -117.69−-117.88 (m, 1F). HRMS (ESI): *m/z* calcd for $C_{12}H_{13}FNaO_4$ $[M+Na]^+$ 263.3202, found: 263.2595.

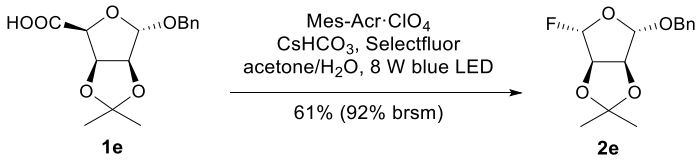
(1*S*, 3*S*, 4*R*)-1-Methyloxyl-3-benzoyloxyl-4-fluorotetrahydrofuran (2d)



Following the procedure for **2a**, uronic acid **1d** (83 mg, 0.31 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (91 mg, 0.47 mmol, 1.5 equiv), Selectfluor (167 mg, 0.47 mmol,

1.5 equiv) and Mes-Acr·ClO_4 (6.2 mg, 15.5 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 3.0 mL) to afford titled compound **2d** (45 mg, 0.19 mmol, 60%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 19:1). $[\alpha]_D^{20}$ = +90.6 (*c* 3.3, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 8.02−7.96 (m, 2H), 7.65−7.59 (m, 1H), 7.51−7.45 (m, 2H), 6.01 (d, $J_{C\text{-}F}$ = 62.2 Hz, 1H), 5.47−5.41 (m, 1H), 5.38−5.31 (m, 1H), 3.41 (s, 3H), 2.68−2.59 (m, 1H), 2.09 (d, *J* = 15.1 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 166.0, 134.3, 130.5, 130.4, 129.4, 113.5 ($J_{C\text{-}F}$ = 217 Hz), 108.9 ($J_{C\text{-}F}$ = 1.9 Hz), 76.7 ($J_{C\text{-}F}$ = 37.3 Hz), 56.4, 35.3; ^{19}F NMR (376 MHz, acetone-d_6) δ -117.8 (dd, *J* = 62.0 ,6.4 Hz). HRMS (ESI): *m/z* calcd for $C_{12}H_{14}FO_4$ $[M+H]^+$ 241.3284, found: 241.2597.

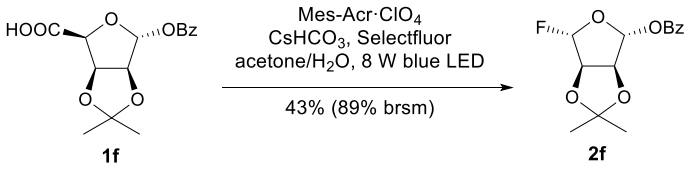
Benzyl (4*S*)-2,3-*O*-isopropylidene-4-fluoro-α-D-erythroside (2e)



1e **2e**

Following the procedure for **2a**, uronic acid **1e** (100 mg, 0.34 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (99 mg, 0.51 mmol, 1.5 equiv), Selectfluor (182 mg, 0.51 mmol, 1.5 equiv) and Mes-Acr·ClO_4 (10.6 mg, 26.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 3.5 mL) to afford titled compound **2e** (56 mg, 0.21 mmol, 61%) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 19:1) along with recovery of **1e** (28 mg, 95.2 μmol, 28%). $[\alpha]_D^{22}$ = +167.8 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.34 (m, 4H), 7.34−7.29 (m, 1H), 5.85 (d, $J_{H\text{-}F}$ = 60.4 Hz, 1H), 5.34 (d, *J* = 2.8 Hz, 1H), 4.88 (t, *J* = 6.0 Hz, 1H), 4.84 (d, *J* = 11.5 Hz, 1H), 4.76 (d, *J* = 5.7 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 1.45 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 128.6, 128.5, 128.1, 116.0 ($J_{C\text{-}F}$ = 227.6 Hz), 113.1, 109.2 ($J_{C\text{-}F}$ = 2.0 Hz), 84.2 ($J_{C\text{-}F}$ = 39.9 Hz), 83.6, 69.6, 26.3, 24.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.32 (m, 1F). HRMS (ESI): *m/z* calcd for $C_{14}H_{21}FNO_4$ $[M+NH_4]^+$ 286.3234, found: 286.1595.

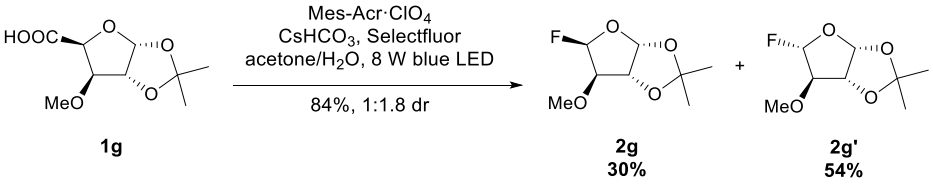
Benzoyl (4*S*)-2,3-*O*-isopropylidene-4-fluoro-α-D-erythroside (2f)



1f 2f

Following the procedure for **2a**, uronic acid **1f** (95 mg, 0.31 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (90 mg, 0.46 mmol, 1.5 equiv), Selectfluor (220 mg, 0.62 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (6.4 mg, 15.5 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 3.0 mL) to afford titled compound **2f** (38 mg, 0.13 mmol, 43%) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 19:1) along with recovery of **1f** (44 mg, 0.14 mmol, 46%). $[\alpha]_D^{20}$ = +51.2 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 6.60 (d, J = 2.6 Hz, 1H), 5.89 (d, $J_{H\text{-}F}$ = 59.2 Hz, 1H), 4.96−4.93 (m, 2H), 1.50 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 133.6, 130.0, 129.1, 128.5, 115.7 ($J_{C\text{-}F}$ = 227.4 Hz), 113.7, 103.36 ($J_{C\text{-}F}$ = 1.7 Hz), 83.6 ($J_{C\text{-}F}$ = 39.8 Hz), 83.1, 26.2, 24.9; ^{19}F NMR (470 MHz,$CDCl_3$) δ -120.7−-120.4 (m, 1F); HRMS (ESI): *m/z* calcd for $C_{14}H_{16}FO_5$ $[M+H]^+$ 283.0976, found: 283.0981.

1,2-*O*-Isopropylidene-3-*O*-methyl-(4*R*)-fluoro-β-L-threoside (2g) and 1,2-*O*-Isopropylidene-3-*O*-methyl-(4*S*)-fluoro-β-L-threoside (2g')

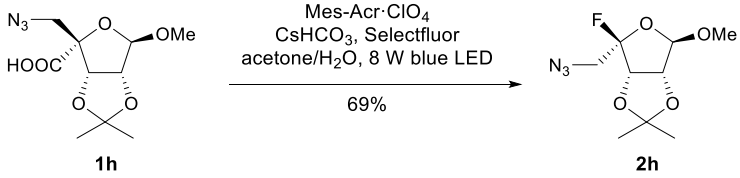


1g 2g 30% 2g' 54%

Following the procedure for **2a**, uronic acid **1g** (1.6 g, 7.33 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (2.13 g, 11.95 mmol, 1.5 equiv), Selectfluor (5.19 g, 14.66 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (30 mg, 73.0 μmol, 1 mol%) in acetone/H_2O (v/v = 4:1, 70.0 mL) to afford titled compound **2g/2g'** (1.19 g, 6.19 mmol, 84%, 1:1.8 *dr*) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 11:1). **2g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05 (d, *J* = 4.3 Hz, 1H), 5.91 (dd, $J_{H\text{-}F}$ = 61.9, *J* = 3.8 Hz, 1H), 4.64 (dd, *J* = 4.2, 2.6 Hz, 1H), 3.97−3.91 (m, 1H),

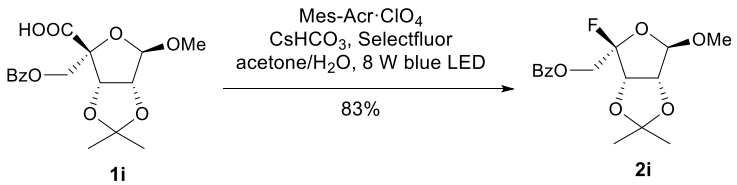
3.50 (s, 3H), 1.48 (s, 3H), 1.40 (s, 3H); **2g'**:^{1}H NMR (500 MHz, $CDCl_3$) δ 6.02 (t, J = 4.2 Hz, 1H), 5.72 (d, $J_{H\text{-}F}$ = 61.3 Hz, 1H), 4.56 (d, J = 3.8 Hz, 1H), 3.98 (d, J = 5.5 Hz, 1H), 3.44 (s, 3H), 1.53 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 114.6, 113.6 ($J_{C\text{-}F}$ = 230.9 Hz), 108.6 ($J_{C\text{-}F}$ = 2.5 Hz), 86.7 ($J_{C\text{-}F}$ = 30.7 Hz), 81.4, 58.2, 27.0, 26.7 ($J_{C\text{-}F}$ = 1.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.01− -119.23 (m, 1F); ^{13}C NMR (126 MHz, $CDCl_3$) δ115.4, 108.9 ($J_{C\text{-}F}$ = 230.5 Hz), 106.0 ($J_{C\text{-}F}$ = 1.1 Hz), 86.6 ($J_{C\text{-}F}$ = 19.7 Hz), 83.3, 58.7, 28.0, 27.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ -134.75−-134.96 (m, 1F). HRMS (ESI): *m/z* calcd for $C_8H_{14}FO_4$ $[M+H]^+$ 193.1944, found: 193.2014.

Methyl 2,3-*O*-isopropylidene-5-dexoy-5-azido-4-fluoro-α-L-lyxofuranoside (2h)



Following the procedure for **2a**, uronic acid **1h** (82 mg, 0.3 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (87 mg, 0.45 mmol, 1.5 equiv), Selectfluor (213 mg, 0.6 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (6.2 mg, 15.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 3.0 mL) to afford titled compound **2h** (51 mg, 0.21 mmol, 69%) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 19:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (d, J = 2.7 Hz, 1H), 4.83 (t, J = 6.1 Hz, 1H), 4.73 (d, J = 5.7 Hz, 1H), 3.65−3.49 (m, 2H), 3.43 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H). The data was identical to previous report.[10]

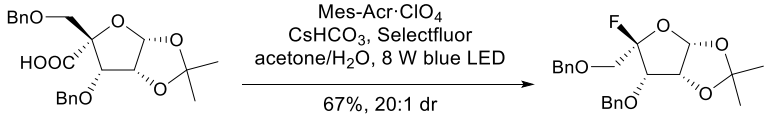
Methyl 2, 3-*O*-isopropylidene-5-*O*-benzoyl-4-fluoro-α-L-lyxofuranoside (2i)



Following the procedure for **2a**, uronic acid **1i** (88 mg, 0.25 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (73 mg, 0.38 mmol, 1.5 equiv), Selectfluor (177 mg, 0.5 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (5.1 mg, 12.5 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1,

2.5 mL) to afford titled compound **2i** (68 mg, 0.21 mmol, 83%) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 15:1). $[\alpha]_D^{22}$ = -59.9 (*c* 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.18 (d, *J* = 2.7 Hz, 1H), 4.89 (t, *J* = 6.0 Hz, 1H), 4.76 (d, *J* = 5.7 Hz, 1H), 4.67–4.55 (m, 2H), 3.44 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 133.3, 130.0, 129.8, 128.5, 119.8 ($J_{C\text{-}F}$ = 229.3 Hz), 113.7, 111.3, 84.1, 83.7 ($J_{C\text{-}F}$ = 46.6 Hz), 63.0 ($J_{C\text{-}F}$ = 26.5 Hz), 55.8, 26.3, 25.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ -107.9−-108.0 (m, 1F); HRMS (ESI) *m/z* calcd for $C_{16}H_{19}FNaO_6$ $[M+Na]^+$ 349.1058, found 349.1060.

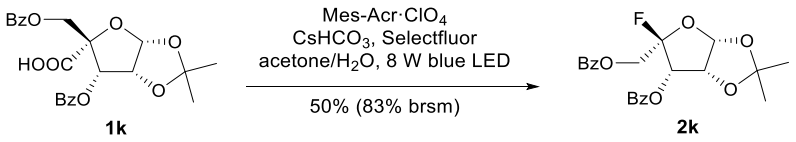
3,5-Di-*O*-benzyl-4-fluoro-1,2-*O*-isopropylidene-β-L-lyxofuranoside (2j)



1j **2j**

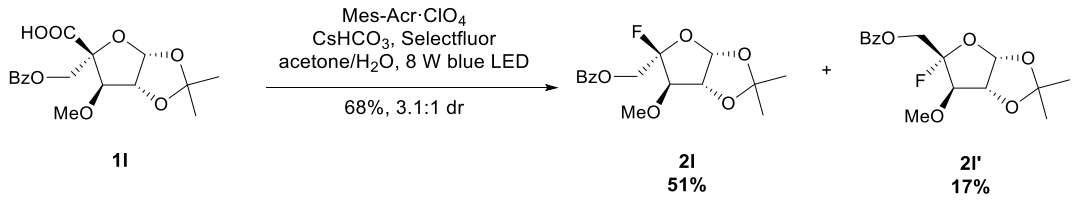
Following the procedure for **2a**, uronic acid **1j** (83 mg, 0.2 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (58 mg, 0.3 mmol, 1.5 equiv), Selectfluor (142 mg, 0.4 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (4.1 mg, 10.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 2.0 mL) to afford titled compound **2j** (52 mg, 0.13 mmol, 67%, 20:1 *dr*) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 9:1). $[\alpha]_D^{23}$ = +30.9 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42−7.19 (m, 10H), 5.77−5.70 (m, 1H), 4.80 (d, *J* = 12.5 Hz, 1H), 4.68 (s, 1H), 4.57 (t, *J* = 4.0 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 4.05 (dd, *J* = 18.8, 4.6 Hz, 1H), 3.61 (d, *J* = 3.0 Hz, 2H), 1.64 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 137.3, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 115.8 ($J_{C\text{-}F}$ = 236.4 Hz), 115.6, 104.7, 76.59, 76.2 ($J_{C\text{-}F}$ = 20.1 Hz), 73.7, 72.9, 67.8 ($J_{C\text{-}F}$ = 45.5 Hz), 27.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ -118.4 (d, *J* = 18.8, 4.7 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{22}H_{25}FNaO_5$ $[M+Na]^+$ 411.1578, found 411.1567.

3,5-Di-*O*-benzoyl-4-fluoro-1,2-*O*-isopropylidene-β-L-lyxofuranoside (2k)



Following the procedure for **2a**, uronic acid **1k** (121 mg, 0.27 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (77 mg, 0.4 mmol, 1.5 equiv), Selectfluor (186 mg, 0.53 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (5.4 mg, 14.0 mmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 2.5 mL) to afford titled compound **2k** (56 mg, 0.13 mmol, 50%) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 13:1) along with recovery of **1k** (52 mg, 0.12 mmol, 43%). $[\alpha]_D^{23}$ = +48.2 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03−7.93 (m, 4H), 7.59−7.49 (m, 2H), 7.43−7.34 (m, 4H), 6.15 (d, *J* = 3.8 Hz, 1H), 5.53 (dd, *J* = 11.7, 5.7 Hz, 1H), 5.16 (dd, *J* = 5.7, 3.9 Hz, 1H), 4.82 (d, *J* = 2.4 Hz, 1H), 4.79 (s, 1H), 1.47 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 164.9, 133.8, 133.5, 130.0, 129.9, 129.3, 128.7, 128.6, 128.5, 117.7 ($J_{C\text{-}F}$ = 222.6 Hz), 116.9, 107.0, 79.2, 75.8 ($J_{C\text{-}F}$ = 45.3 Hz), 63.1 ($J_{C\text{-}F}$ = 28.6 Hz), 27.7, 27.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -101.4−-101.6 (m, 1F); HRMS (ESI) *m/z* calcd for $C_{22}H_{21}FNaO_7$ $[M+Na]^+$ 439.1164, found 439.1155.

3-*O*-Methyl-5-*O*-benzoyl-4-fluoro-1,2-*O*-isopropylidene-β-L-*arabino*furanoside (2l) and 3-*O*-Methyl-5-*O*-benzoyl-4-fluoro-1,2-*O*-isopropylidene-α-D-xylofuranoside (2l')



Following the procedure for **2a**, uronic acid **1l** (164 mg, 0.47 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (135 mg, 0.7 mmol, 1.5 equiv), Selectfluor (329 mg, 0.93 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (9.0 mg, 23.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 5.4 mL) to afford titled compound **2l/2l'** (103 mg, 0.32 mmol, 68%, 3.1:1 *dr*) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 12:1). **2l**: $[\alpha]_D^{23}$ = +19.6 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ

8.04 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.07 (d, *J* = 4.2 Hz, 1H), 4.71 (dd, *J* = 4.1, 2.4 Hz, 1H), 4.61–4.52 (m, 2H), 4.03 (dd, *J* = 15.2, 2.3 Hz, 1H), 3.52 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 133.5, 129.9, 129.3, 128.5, 115.5, 115.0 ($J_{C\text{-}F}$ = 230.8 Hz), 105.8, 86.2 ($J_{C\text{-}F}$ = 20.5 Hz), 84.3, 62.9 ($J_{C\text{-}F}$ = 41.0 Hz), 59.0, 28.1, 27.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -118.9–-119.0 (m, 1F); HRMS (ESI) *m/z* calcd for $C_{16}H_{19}FNaO_6$ $[M+Na]^+$ 349.1058, found 349.1049. **2l'**: $[\alpha]_D^{23}$ = -33.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 6.06 (t, *J* = 3.9 Hz, 1H), 4.65 (d, *J* = 3.6 Hz, 1H), 4.61−4.49 (m, 2H), 4.10 (d, *J* = 6.2 Hz, 1H), 3.46 (s, 3H), 1.58 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 133.4, 129.9, 129.7, 128.6, 119.5 ($J_{C\text{-}F}$ = 233.4 Hz), 115.0, 108.4 ($J_{C\text{-}F}$ = 2.1 Hz), 86.4 ($J_{C\text{-}F}$ = 36.2 Hz), 81.5, 62.8 ($J_{C\text{-}F}$ = 27.6 Hz), 58.9, 27.1, 26.6 ($J_{C\text{-}F}$ = 1.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -105.9–-106.1 (m, 1F); HRMS (ESI) *m/z* calcd for $C_{16}H_{19}FNaO_6$ $[M+Na]^+$ 349.1058, found 349.1054.

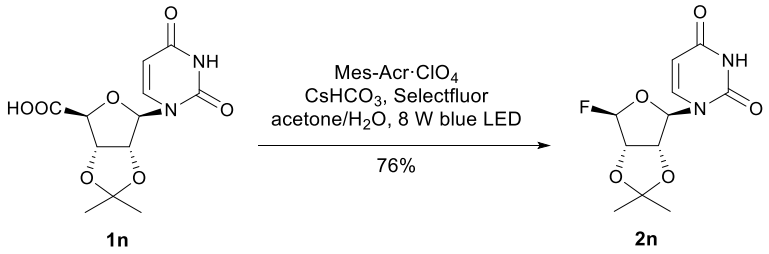
Methyl 2,3-*O*-isopropylidene-5-*O*-[(2''-diethoxy)-phosphoryl-2'-fluroacety]-4-fluoro-α-L-lyxofuanoside (2m)

1m **2m**

Following the procedure for **2a**, uronic acid **1m** (63 mg, 0.15 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (86 mg, 0.44 mmol, 3.0 equiv), Selectfluor (157 mg, 0.44 mmol, 3.0 equiv) and Mes-Acr·ClO_4 (3.0 mg, 7.4 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 3.0 mL) to afford titled compound **2m** (43 mg, 0.10 mmol, 69%, 1.15:1 *dr*) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 3:2). ^{1}H NMR (400 MHz,$CDCl_3$) δ 5.35 (dd, *J* = 12.8, 5.7 Hz, 1H), 5.24 (dd, *J* = 12.8, 5.7 Hz, 1H), 5.14 (dd, *J* = 2.8, 1.5 Hz, 2H), 4.86−4.78 (m, 2H), 4.72 (d, *J* = 5.7 Hz, 2H), 4.54 (s, 3H), 4.32−4.19 (m, 7H), 3.42 (d, *J* = 1.8 Hz, 5H), 1.45 (d, *J* = 2.7 Hz, 5H), 1.41−1.37 (m, 10H), 1.31 (d, *J* = 4.5 Hz, 7H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 164.3, 119.2 ($J_{C\text{-}F}$ = 229.8 Hz), 119.1 ($J_{C\text{-}F}$ = 229.8 Hz), 113.79, 113.76, 111.41, 111.39,

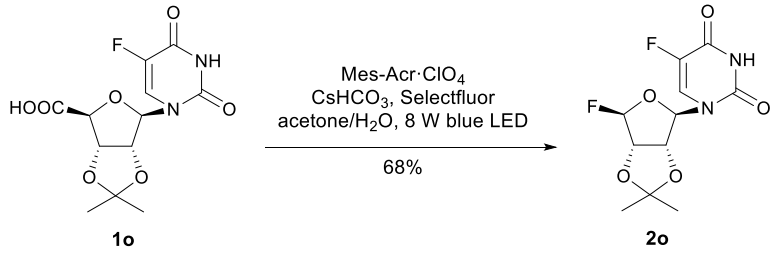
85.13 ($J_{C\text{-}F}$ = 196.5 Hz, $J_{C\text{-}P}$ = 158.6 Hz), 85.09 ($J_{C\text{-}F}$ = 195.8 Hz, $J_{C\text{-}P}$ = 158.7 Hz), 84.02, 83.99, 83.46 ($J_{C\text{-}F}$ = 45.9 Hz), 83.44 ($J_{C\text{-}F}$ = 46.2 Hz), 64.52, 64.49, 63.69 ($J_{C\text{-}F}$ = 26.3 Hz), 63.66 ($J_{C\text{-}F}$ = 26.2 Hz), 55.9, 26.3, 24.9, 16.52, 16.48; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.07 (s, 1F), -108.14 (s, 1F), -210.70 (d, $J_{F\text{-}P}$ = 72 Hz, 1F), -210.80 (d, $J_{F\text{-}P}$ = 72 Hz, 1F); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.64 (s, 1P), 9.20 (s, 1P); HRMS (ESI) *m/z* calcd for $C_{15}H_{25}O_9F_2NaP$ $[M+Na]^+$ 441.1096, found 441.1087.

Uracil (4*R*)-2,3-*O*-isopropylidene-4-fluoro-α-D-threoside (2n)



Following the procedure for **2a**, uronic acid **1n** (75 mg, 0.25 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (145 mg, 0.75 mmol, 3.0 equiv), Selectfluor (266 mg, 0.75 mmol, 3.0 equiv) and Mes-Acr·ClO_4 (5.2 mg, 12.5 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 5.0 mL) to afford titled compound **2n** (52 mg, 0.19 mmol, 76%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 1:1). $[\alpha]_D^{23}$ = -10.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d_6) δ 10.19 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 6.22 (d, *J* = 3.8 Hz, 1H), 5.94 (d, $J_{H\text{-}F}$ = 62.4 Hz, 1H), 5.66 (d, *J* = 8.1 Hz, 1H), 5.31 (d, *J* = 5.7 Hz, 1H), 5.11 (t, *J* = 6.3 Hz, 1H), 1.47 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (126 MHz, acetone-d_6) δ 163.2, 151.3, 142.2, 117.3 ($J_{C\text{-}F}$ = 225.8 Hz), 114.0, 103.2, 96.0 ($J_{C\text{-}F}$ = 2.4 Hz), 85.6 ($J_{C\text{-}F}$ = 38.0 Hz), 83.4, 26.5, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.95–-117.30 (m, 1F); HRMS (ESI) *m/z* calcd for $C_{11}H_{14}O_5FN_2$ $[M+H]^+$ 273.0881, found 273.0883.

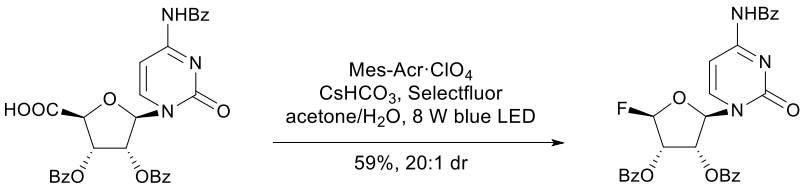
5-Fluorouracil (4*R*)-2,3-*O*-isopropylidene-4-fluoro-α-D-threoside (2o)



1o **2o**

Following the procedure for **2a**, uronic acid **1o** (94 mg, 0.3 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (175 mg, 0.9 mmol, 3.0 equiv), Selectfluor (319 mg, 0.9 mmol, 3.0 equiv) and Mes-Acr·ClO_4 (6.2 mg, 15.0 μmol, 5 mol%) in acetone/H_2O (*v*/*v* = 4:1, 6.0 mL) to afford titled compound **2o** (59 mg, 0.2 mmol, 68%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 2:1). $[\alpha]_D^{23}$ = -5.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.0 Hz, 1H), 6.09 (d, *J* = 4.2 Hz, 1H), 5.96 (d, $J_{H\text{-}F}$ = 61.5 Hz,1H), 5.04 (d, *J* = 5.7 Hz, 1H), 4.90 (t, *J* = 6.1 Hz, 1H), 1.53 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7 ($J_{C\text{-}F}$ = 26.8 Hz), 148.7, 140.5 ($J_{C\text{-}F}$ = 239.8 Hz), 124.5 ($J_{C\text{-}F}$ = 34.9, 7.5 Hz), 116.2 ($J_{C\text{-}F}$ = 227.5 Hz), 114.3, 96.3 ($J_{C\text{-}F}$ = 2.4 Hz), 83.8 ($J_{C\text{-}F}$ = 38.4 Hz), 83.3, 26.2, 24.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.65–-117.01 (m, 1F), -163.90 (d, *J* = 5.2 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{11}H_{13}F_2N_2O_5$ $[M+H]^+$ 291.0787, found 291.0792.

N$_4$-Benzoylcytosine 2,3-di-*O*-benzoyl-4-fluoro-α-D-threoside (2p)

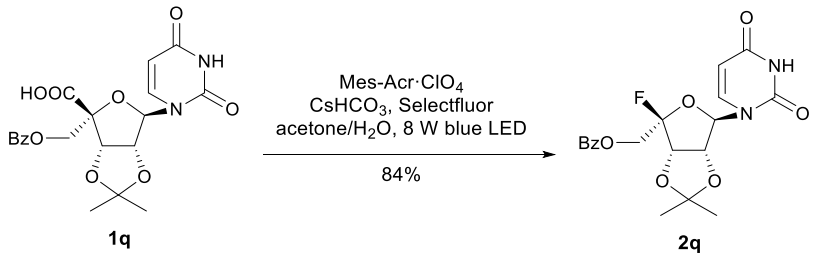


1p **2p**

Following the procedure for **2a**, uronic acid **1p** (114 mg, 0.2 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (116 mg, 0.6 mmol, 3.0 equiv), Selectfluor (213 mg, 0.6 mmol, 3.0 equiv) and Mes-Acr·ClO_4 (4.1 mg, 10.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 4.0 mL) to afford titled compound **2p** (64 mg, 0.12 mmol, 59%, 20:1 *dr*) as a white foam after purification by silica gel chromatography (CH_2Cl_2:EtOAc = 15:1). $[\alpha]_D^{23}$ = -154.7 (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (brs, 1H), 8.05–8.00 (m, 3H),

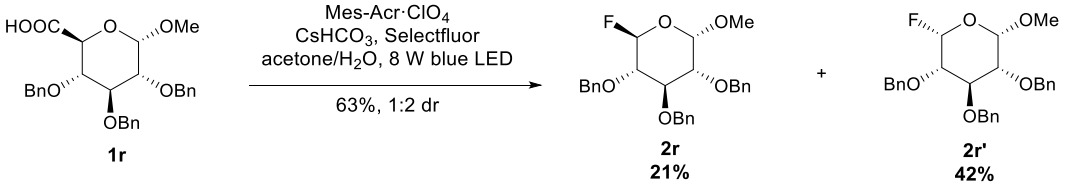
7.95–7.87 (m, 4H), 7.65–7.42 (m, 8H), 7.31 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 6.9 Hz, 1H), 6.06 (d, $J_{H\text{-}F}$ = 60.4 Hz, 1H), 5.91–5.88 (m, 1H), 5.83 (t, J = 5.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 164.9, 134.1, 133.8, 133.3, 130.1, 130.0, 129.0, 128.8, 128.5, 128.3, 128.2, 127.9, 112.0 ($J_{C\text{-}F}$ = 230.3 Hz), 88.9 ($J_{C\text{-}F}$ = 2.7 Hz), 74.2 ($J_{C\text{-}F}$ = 35.6 Hz), 74.2 ($J_{C\text{-}F}$ = 1.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.1 (dd, J = 60.5, 5.3 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{29}H_{23}FN_3O_7$ $[M+H]^+$ 544.1515, found 544.1502.

Uracil 2,3-*O*-isopropylidene-4-fluoro-5-*O*-benzoyl-α-L-lyxofuranoside (2q)



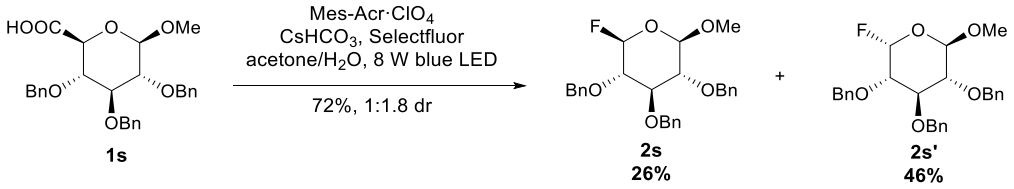
Following the procedure for **2a**, uronic acid **1q** (87 mg, 0.2 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (116 mg, 0.6 mmol, 3.0 equiv), Selectfluor (213 mg, 0.6 mmol, 3.0 equiv) and Mes-Acr·ClO_4 (4.1 mg, 10.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 4.0 mL) to afford titled compound **2q** (68 mg, 0.17 mmol, 84%) as a white foam after purification by silica gel column chromatography (CH_2Cl_2:EtOAc = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.06 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.40 (d, J = 8.2 Hz, 1H), 6.17 (d, J = 2.9 Hz, 1H), 5.76 (d, J = 8.2 Hz, 1H), 5.14 (d, J = 6.7 Hz, 1H), 4.98 (t, J = 6.2 Hz, 1H), 4.76−4.62 (m, 2H), 1.55 (s, 3H), 1.36 (s, 3H). The data is identical with previous report.[10]

Methyl (5*R*)-2,3,4-tri-*O*-benzyl-5-fluoro-α-D-xylopyranoside (2r) and Methyl (5*S*)-2,3,4-tri-*O*-benzyl-5-fluoro-α-D-xylopyranoside (2r')



Following the procedure for **2a**, uronic acid **1r** (107 mg, 0.22 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (65 mg, 0.34 mmol, 1.5 equiv), Selectfluor (158 mg, 0.45 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (4.6 mg, 11.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 2.0 mL) to afford titled compound **2r/2r'** (63 mg, 0.14 mmol, 63%, 1:2 *dr*) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 13:1). **2r**: $[\alpha]_D^{20}$ = -12.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42−7.30 (m, 15H), 5.49 (dd, *J* = 54.5, 7.1 Hz, 1H), 4.94−4.82 (m, 4H), 4.77 (d, *J* = 11.1 Hz, 1H), 4.70−4.66 (m, 2H), 3.99 (t, *J* = 9.3 Hz, 1H), 3.63 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.60−3.52 (m, 1H), 3.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$):δ 138.6, 137.9, 128.3, 128.5, 128.2, 128.1, 127.9, 127.8, 107.2 ($J_{C\text{-}F}$ = 210.8 Hz), 98.3 ($J_{C\text{-}F}$ = 7.6 Hz), 81.9 ($J_{C\text{-}F}$ = 20.1 Hz), 79.1 ($J_{C\text{-}F}$ = 11.9 Hz), 78.7, 74.8, 73.8, 56.2; ^{19}F NMR (470 MHz,$CDCl_3$): δ -150.2 (dd, *J* = 54.5, 14.9, 1F); HRMS (ESI): *m/z* calcd for $C_{27}H_{29}O_5FNa$ $[M+Na]^+$ 475.1891, found: 475.1880. **2r'**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.27 (m, 15H), 5.45 (dd, *J* = 54.1, 3.4 Hz, 1H), 4.96 (d, *J* = 10.7 Hz, 1H), 4.90 (d, *J* = 10.7 Hz, 1H), 4.83 (d, *J* = 12.1 Hz, 2H), 4.74−4.65 (m, 3H), 4.26 (t, *J* = 9.7 Hz, 1H), 3.52 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.49−3.45 (m, 4H). The data is identical with previous report.[10]

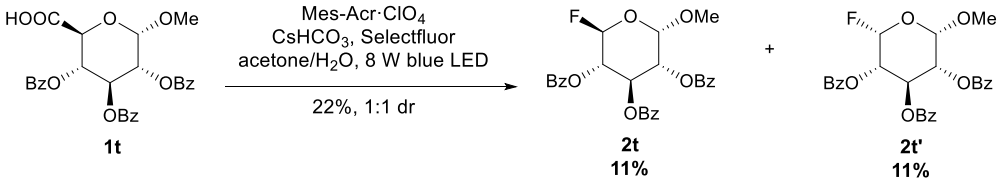
Methyl (5*R*)-2,3,4-tri-*O*-benzyl-5-fluoro-β-D-xylopyranoside (2s) and Methyl (5*S*)-2,3,4-tri-*O*-benzyl-5-fluoro-β-D-xylopyranoside (2s')



Following the procedure for **2a**, uronic acid **1s** (96 mg, 0.2 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (58 mg, 0.3 mmol, 1.5 equiv), Selectfluor (141 mg, 0.4 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (4.1 mg, 10.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 2.0 mL) to afford titled compound **2s/2s'** (65 mg, 0.144 mmol, 72%, 1:1.8 *dr*) as a white foam after purification by silica gel column chromatography (toluene:petroleum ether = 2:1). **2s**: $[\alpha]_D^{23}$ = -15.2 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43−7.27 (m, 15H), 5.52 (dd, $J_{H\text{-}F}$ = 57.2, *J* = 5.1 Hz, 1H), 4.83−4.71 (m, 6H), 4.65 (d, *J* = 11.5 Hz,

1H), 3.95−3.86 (m, 1H), 3.68 (dd, *J* = 7.3, 3.2 Hz, 1H), 3.66−3.60 (m, 1H), 3.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4, 137.91, 137.87, 128.6, 128.54, 128.46, 128.10, 128.07, 128.01, 128.00, 109.7 ($J_{C\text{-}F}$ = 225.1 Hz), 103.2, 82.6, 80.2 ($J_{C\text{-}F}$ = 36.1 Hz), 80.2, 74.9, 74.2, 73.5, 56.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ -122.9 (dd, *J* = 57.2, 14.2 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{27}H_{33}FNO_5$ $[M+NH_4]^+$ 470.2348, found 470.2339. **2s'**: $[\alpha]_D^{23}$ = +14.6 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.27 (m, 15H), 5.51 (dd, $J_{H\text{-}F}$ = 52.7, *J* = 2.1 Hz, 1H), 4.91−4.80 (m, 5H), 4.75−4.68 (m, 2H), 3.93 (t, *J* = 9.5 Hz, 1H), 3.61−3.51 (m, 4H), 3.44 (t, *J* = 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 138.4, 137.8, 128.7, 128.5, 128.2, 128.1, 127.8, 104.8 ($J_{C\text{-}F}$ = 226.3 Hz), 101.3 ($J_{C\text{-}F}$ = 4.5 Hz), 81.5, 79.1, 78.8 ($J_{C\text{-}F}$ = 24.4 Hz), 76.2, 75.1, 73.9, 57.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ -146.7 (dd, *J* = 52.7, 25.6 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{27}H_{33}FNO_5$ $[M+NH_4]^+$ 470.2337, found 470.2339.

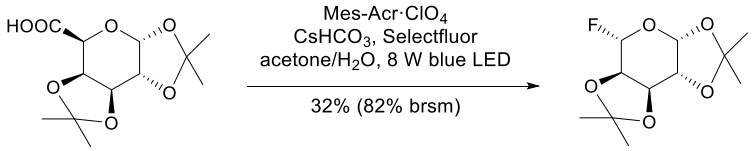
Methyl (5*R*)-2,3,4-tri-*O*-benzoyl-5-fluoro-α-D-xylopyranoside (2t) and Methyl (5*S*)-2,3,4-tri-*O*-benzoyl-5-fluoro-α-D-xylopyranoside (2t')



Following the procedure for **2a**, uronic acid **1t** (118 mg, 0.23 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (134 mg, 0.69 mmol, 3.0 equiv), Selectfluor (244 mg, 0.69 mmol, 3.0 equiv) and Mes-Acr·ClO_4 (14 mg, 35.0 μmol, 15 mol%) in acetone/H_2O (v/v = 4:1, 2.5 mL) to afford titled compound **2t/2t'** (25 mg, 51.0 μmol, 22%, 1:1 *dr*) as a colorless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 10:1). **2t**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02−7.09 (m, 4H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.54−7.47(m, 3H), 7.41−7.33 (m, 6H), 6.09 (t, *J* = 8.6 Hz, 1H), 5.82 (dd, *J* = 6.1 Hz, $J_{H\text{-}F}$ = 52.8 Hz, 1H), 5.65−5.58 (m, 1H), 5.42−5.38 (m, 2H), 3.60 (s, 3H). **2t'**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02−7.98 (m, 4H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.53−7,51 (m, 2H), 7.46−7,37 (m, 5H), 7.32 (t, *J* = 8.0 Hz, 2H), 6.47 (t, *J* = 10.2 Hz, 1H), 6.01 (dd, *J* = 3.4

Hz, $J_{H\text{-}F}$ = 54.1 Hz, 1H), 5.47−5.38 (m, 1H), 5.38−5.34 (m, 2H), 3.54 (s, 3H). These datas are identical with previous report.[10]

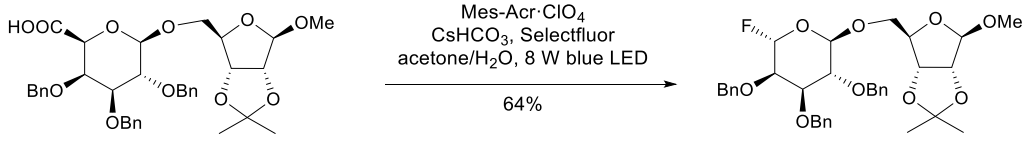
(5*S*)-1,2:3,4-Di-*O*-isopropylidene-5-fluoro-α-L-arabinopyranose (2u)



1u **2u**

Following the procedure for **2a**, uronic acid **1u** (82 mg, 0.3 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (87 mg, 0.45 mmol, 1.5 equiv), Selectfluor (320 mg, 0.9 mmol, 3.0 equiv) and Mes-Acr·ClO_4 (16.8 mg, 45.0 μmol, 15 mol%) in acetone/H_2O (v/v = 4:1, 3.0 mL) to afford titled compound **2u** (24 mg, 96.0 μmol, 32%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 30:1), along with recovery of **1u** (50 mg, 0.18 mmol, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (d, $J_{H\text{-}F}$ = 50.7 Hz, 1H), 5.51 (dd, J = 4.6, 1.5 Hz, 1H), 4.71 (dd, J = 7.2, 2.2 Hz, 1H), 4.41 (dd, J = 4.6, 2.2 Hz, 1H), 4.30 (dd, J = 7.1, 4.3 Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). The data is identical with previous report.[10]

Methyl 5-*O*-[(5'*R*)-2',3',4'-tri-*O*-benzyl-5'-fluoro-β-D-arabinopyranosyl]-2,3-*O*-isopropylidene-β-D-ribofuranoside (2v)

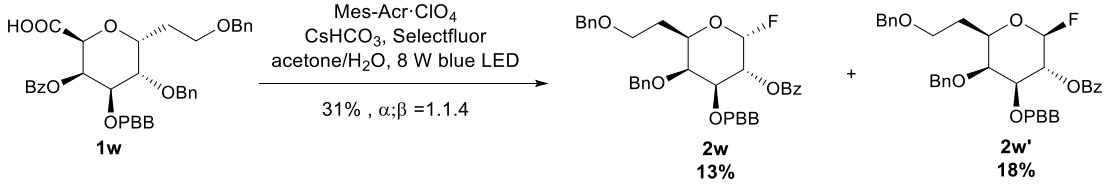


1v **2v**

Following the procedure for **2a**, uronic acid **1v** (106 mg, 0.16 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (48 mg, 0.25 mmol, 1.5 equiv), Selectfluor (115 mg, 0.33 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (3.4 mg, 8.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 1.6 mL) to afford titled compound **2v** (64 mg, 0.10 mmol, 64%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 11:1). $[\alpha]_D^{23}$ = -35.1 (*c* 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.4 Hz, 2H), 7.37−7.24 (m, 13H), 5.54 (d, $J_{H\text{-}F}$ = 50.5 Hz, 1H), 4.99 (s, 1H), 4.95 (d, J = 11.0 Hz,

1H), 4.86−4.75 (m, 5H), 4.69 (d, J = 12.2 Hz, 1H), 4.65 (d, J = 11.8 Hz, 1H), 4.60 (d, J = 5.9 Hz, 1H), 4.41 (t, J = 7.3 Hz, 1H), 3.96−3.87 (m, 2H), 3.85−3.78 (m, 2H), 3.62 (dd, J = 9.8, 6.6 Hz, 1H), 3.29 (s, 3H), 1.51 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 138.3, 137.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.83, 127.80, 127.7, 112.5, 109.4, 106.0 ($J_{C\text{-}F}$ = 221.6 Hz), 101.0 ($J_{C\text{-}F}$ = 1.8 Hz), 85.2 ($J_{C\text{-}F}$ = 8.1 Hz), 82.1, 78.6, 77.0, 75.3, 73.7, 73.6 ($J_{C\text{-}F}$ = 34.4 Hz), 73.5, 70.8, 55.0, 26.6, 25.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ -134.8 (d, J = 50.5 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{35}H_{41}FNaO_9$ $[M+Na]^+$ 647.2627, found 647.2615.

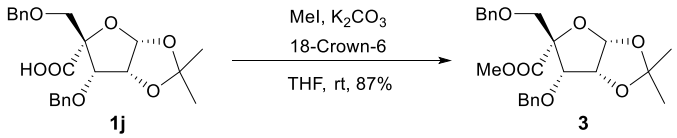
4,7-Di-*O*-benzyl-2-*O*-benzoyl-3-*O*-(4'-bromobenzyl)-6-deoxy-D-*gulo*-heptopyranosyl-α-fluoride (2w) and 4,7-Di-*O*-benzyl-2-*O*-benzoyl-3-*O*-(4'-bromobenzyl)- 6-deoxy-D-*gulo*-heptopyranosyl-β-fluoride (2w')



Following the procedure for **2a**, uronic acid **1w** (69 mg, 0.12 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (29 mg, 0.15 mmol, 1.25 equiv), Selectfluor (70 mg, 0.2 mmol, 1.64 equiv) and Mes-Acr·ClO_4 (2.1 mg, 5.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 1.0 mL) to afford titled compound **2w/2w'** (20 mg, 37.6 μmol, 31%, α:β = 1:1.4) as a clourless syrup after purification by silica gel column chromatography (petroleum ether:EtOAc = 11:1).**2w**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.7 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.38−7.25 (m, 12H), 7.09 (d, J = 8.0 Hz, 2H), 5.73 (dd, J = 3.1 Hz, $J_{H\text{-}F}$ = 54.7 Hz, 1H), 5.42−5.31(m, 1H), 4.64 (d, J = 11.9 Hz, 1H), 4.58 (dd, J = 8.9, 4.9 Hz, 1H), 4.55−4.45 (m, 5H), 4.07 (t, J = 3.8 Hz, 1H), 3.58−3.50 (m, 3H), 2.10−2.03 (m, 1H), 1.84−1.77 (m, 1H); **2w'**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.7 Hz, 2H), 7.70−7.25 (m, 15H), 7.01 (d, J = 7.9 Hz, 2H), 5.69 (dd, J = 6.9 Hz, $J_{H\text{-}F}$ = 54.2 Hz, 1H), 5.34−5.30 (m, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.55−4.45 (m, 3H), 4.42−4.38 (m, 2H), 4.34−4.31 (m, 1H), 4.17 (d, J = 4.6 Hz, 1H), 3.63−3.59 (m, 1H), 3.55–3.44 (m, 2H), 2.15−2.08 (m, 1H), 1.91−1.84 (m, 1H); The data is identical with previous report.[9]

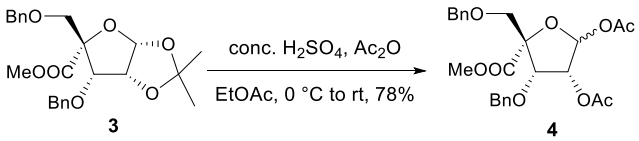
Section 3. Synthesis of 4' fluoro nucleoside

1,2-*O*-Isopropylidene-3,5-di-*O*-benzyl-4-*C*-methylester-α-D-ribofuranoside (3)



To a solution of **1j** (2.98 g, 7.19 mmol, 1.0 equiv) in anhydrous THF (50 mL) was added sequentially 18-crown-6 (95 mg, 0.36 mmol, 0.05 equiv), K_2CO_3 (3.0 g, 21.6 mmol, 3.0 equiv) and iodomethane (MeI, 1.4 mL, 21.6 mmol, 3.0 equiv) at 0 °C. The reaction mixture was warm up to room temperature and stirred overnight. The reaction was quenched by adding water (30 mL), THF was removed in *vacuo*. The aqueous phase was extracted with CH_2Cl_2 (30 mL×3). The combined organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 6:1) to afford the ester **3** (2.68 g, 6.26 mmol, 87%) as a colorless syrup. $[\alpha]_D^{23}$ = +29.9 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.22 (m, 10H), 5.89 (d, *J* = 3.9 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.68−4.65 (m, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.25 (d, *J* = 5.2 Hz, 1H), 3.82 (d, *J* = 10.2 Hz, 1H), 3.75 (s, 3H), 3.67 (d, *J* = 10.2 Hz, 1H), 1.64 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 137.8, 128.6, 128.5, 127.92, 127.86, 127.8, 127.7, 115.2, 106.1, 89.7, 80.6, 79.4, 73.9, 73.8, 73.1, 52.4, 27.4, 26.3; HRMS (ESI) *m/z* calcd for $C_{24}H_{32}NO_7$ $[M+NH_4]^+$ 446.2173, found 446.2166.

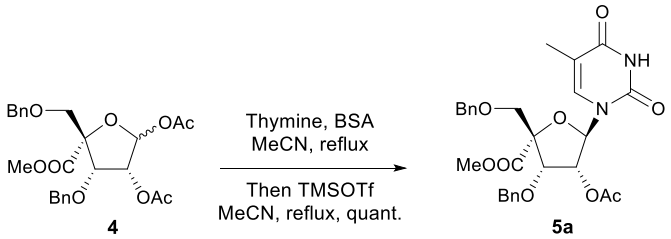
1,2-Di-*O*-acetyl-3-*O*-benzyl-4-*C*-benzyloxylmethyl-L-lyxofuranuronide methyl ester (4)



To a solution of acetonide **3** (1.3 g, 3.03 mmol, 1.0 equiv) in anhydrous EtOAc (15 mL) was added acetic anhydride (Ac_2O, 1.2 ml, 12.14 mmol, 4.0 equiv) and concentrated

sulfuric acid (32 μL, 0.61 mmol, 0.2 equiv) under an ice-bath. The reaction was warmed up to room temperature for 2 h before the mixture was poured into water (100 mL). The aqueous phase was extracted with EtOAc (50 mL×5). The combined organic phase was washed sequentially with water (200 mL×3) and sat. $NaHCO_3$ solution (100 mL). The mixture was dried over Na_2SO_4, filtered, and the filtrate was concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 4:1 to 3:1) to afford acetate **4** (1.28 g, 2.36 mmol, 78%, α:β = 3.3:1) as a colorless syrup. **α isomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.24 (m, 10H), 6.41 (d, J = 2.2 Hz, 1H), 5.24 (dd, J = 5.4, 2.3 Hz, 1H), 4.63−4.47 (m, 4H), 4.42−4.39 (m, 1H), 3.81 (d, J = 10.6 Hz, 1H), 3.77−3.73 (m, 4H), 2.04 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 169.3, 169.2, 137.8, 137.3, 128.5, 128.1, 127.9, 127.8, 127.7, 90.1, 89.8, 78.4, 74.8, 74.3, 73.7, 71.8, 52.6, 21.0, 20.7; HRMS (ESI) *m/z* calcd for $C_{25}H_{28}O_9Na$ $[M+Na]^+$ 495.1626, found 495.1613. **β isomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.24 (m, 10H), 6.50 (d, J = 4.8 Hz, 1H), 5.15 (t, J = 5.1 Hz, 1H), 4.63−4.47 (m, 4H), 4.42−4.39 (m, 1H), 3.92 (d, J = 10.4 Hz, 1H), 3.67−3.63 (m, 4H), 2.13 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 170.2, 168.9, 138.1, 137.5, 128.7, 128.3, 128.0, 127.8, 127.7, 127.2, 95.0, 92.1, 79.2, 77.4, 74.9, 74.0, 72.3, 52.6, 21.4, 20.6; HRMS (ESI) *m/z* calcd for $C_{25}H_{28}O_9Na$ $[M+Na]^+$ 495.1626, found 495.1613.

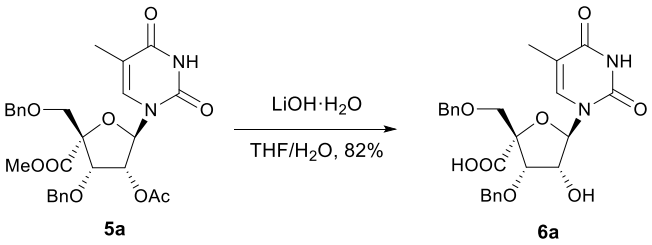
5-Methyluracil 2-*O*-acetyl-3-*O*-benzyl-4-*C*-benzyloxylmethyl-L-lyxofuranuronide methyl ester (5a)



To a solution of donor **4** (165 mg, 0.39 mmol, 1.0 equiv) in anhydrous acetonitrile (3 mL) was added thymine (93 mg, 0.74 mmol, 2.0 equiv) and *N*,*O*-bis(trimethylsilyl)acetamide (BSA, 475 μL, 1.95 mmol, 5.0 equiv). The suspension was heated to reflux and stirred vigorously for 1 h to obtain a clear solution before the

mixture was cooled to 0 °C. To this solution was added trimethylsilyl trifluoromethanesulfonate (TMSOTf, 145 μL, 1.17 mmol, 3.0 equiv). The mixture was heated to reflux for another 2.5 h before the mixture was cooled to room temperature and diluted with CH_2Cl_2 (20 mL). The solution was washed with sat. $NaHCO_3$ solution (20 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated in *vacuo*. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 3:2) to afford the titled nucleoside **5a** (210 mg, 0.39 mmol, quant.) as a white foam. $[\alpha]_D^{21}$ = -29.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.40−7.24 (m, 11H), 6.49 (d, *J* = 7.3 Hz, 1H), 5.24−5.19 (m, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.60−4.52 (m, 4H), 4.02 (d, *J* = 10.2 Hz, 1H), 3.80 (d, *J* = 10.2 Hz, 1H), 3.70 (s, 3H), 2.04 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 169.2, 163.4, 150.4, 137.1, 137.0, 135.7, 128.9, 128.6, 128.5, 128.2, 128.0, 127.9, 111.9, 89.8, 86.7, 79.4, 75.4, 74.5, 74.1, 71.8, 52.8, 20.7, 12.3; HRMS (ESI) *m/z* calcd for $C_{28}H_{31}N_2O_9$ $[M+H]^+$ 539.2000, found 539.2006.

5-Methyluracil 3-*O*-benzyl-4-*C*-benzyloxylmethyl-α-L-lyxofuranuronic acid (6a)

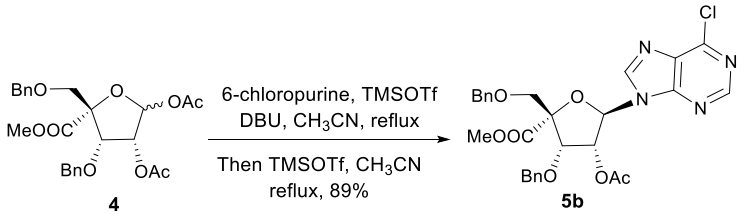


5a **6a**

To a solution of nucleoside **5a** (282 mg, 0.52 mmol, 1.0 equiv) in aqueous THF (v/v = 4:1, 6.5 mL) was added lithium hydroxide monohydrate ($LiOH·H_2O$, 88 mg, 2.09 mmol, 4.0 equiv) at room temperature. The mixture was stirred at room temperature for 2 h before the reaction was quenched with Dowex (H^+) resin. The resin was filtered and the filtrate was concentrated in *vacuo*. The residue was purified by silica gel column chromatography (CH_2Cl_2:MeOH = 15:1 to 9:1) to afford the uronic acid **6a** (201 mg, 0.43 mmol, 82%) as a white foam. $[\alpha]_D^{21}$ = -11.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.19 (m, 11H), 6.23 (s, 1H), 4.72−4.63 (m, 2H), 4.58−4.42 (m, 2H), 4.34−4.19 (m, 2H), 4.06 (d, *J* = 9.8 Hz, 1H), 3.78 (d, *J* = 8.9 Hz, 1H), 1.42 (s, 3H); ^{13}C

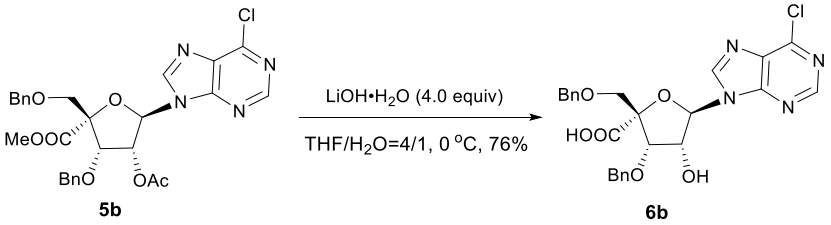
NMR (126 MHz, $CDCl_3$) δ 171.8, 164.0, 151.5, 137.1, 136.8, 135.8, 128.8, 128.6, 128.4, 127.8, 112.0, 89.6, 89.1, 75.2, 74.5, 74.0, 71.8, 12.1; HRMS (ESI) *m/z* calcd for $C_{25}H_{26}N_2NaO_8$ $[M+Na]^+$ 505.1581, found 505.1569.

6-Chloro-9-(2-*O*-acetyl-3-*O*-benzyl-4-*C*-benzyloxylmethyl-L-lyxofuran uronide methyl ester)-purine (5b)



To a solution of 6-chloropurine (327 mg, 2.12 mmol, 2.0 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 475 μL, 3.17 mmol, 3.0 equiv) in dry MeCN (5 mL) was added dropwise TMSOTf (960 μL, 5.29 mmol, 5.0 equiv) at 0 °C. The resulting solution was stirred for 2 h at 60 °C, after which it was cooled to room temperature and compound **4** (501 mg, 1.06 mmol, 1.0 equiv) in 5 mL MeCN and TMSOTf (960 μL, 5.29 mml, 5.0 equiv) were added. The resulting solution was stirred for 2 h at 60 °C. TEA (5 mL) was added. The residue evaporated under reduced pressure. The crude was purified by silica gel column chromatography (petroleum ether:EtOAc = 2:1) to afford the **5b** product as a white foam (534 mg, 0.94 mmol, 89%). $[\alpha]_D^{25}$ = -27.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.36 (s, 1H), 7.42−7.24 (m, 10H), 6.60 (d, *J* = 6.8 Hz, 1H), 5.79−5.70 (m, 1H), 4.71 (d, *J* = 5.6 Hz, 1H), 4.63−4.52 (m, 4H), 4.01 (d, *J* = 10.2 Hz, 1H), 3.84 (d, *J* = 10.2 Hz, 1H), 3.74 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.0, 152.3, 151.8, 151.4, 132.1, 144.1, 137.0, 136.9, 128.8, 128.6, 128.4, 128.3, 128.03, 128.01, 90.7, 86.7, 79.4, 75.4, 75.3, 74.1, 71.5, 52.8, 20.6; HRMS (ESI): *m/z* calcd for $C_{28}H_{28}ClN_4O_7$ $[M+H]^+$ 567.1641, found 567.1626.

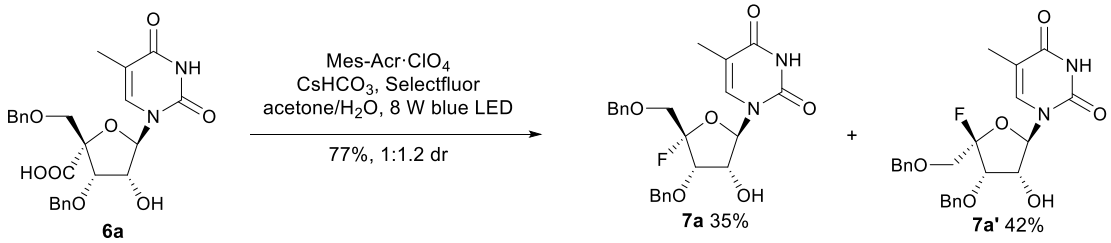
6-Chloro-9-(3-*O*-benzyl-4-*C*-benzyloxylmethyl-L-lyxofuranuronic acid)-purine (6b)



5b **6b**

Following the procedure for **6a**, **5b** (475 mg, 0.84 mmol, 1.0 equiv) was treated with LiOH·H_2O (141 mg, 3.35 mmol, 4.0 equiv) in THF/H_2O (v/v = 6:1, 5.6 mL) for 2 h at room temperature to give **6b** (325 mg, 0.64 mmol, 76%) as a white foam after purification by silica gel column chromatography (petroleum ether:EtOAc = 2:1 to DCM:MeOH = 20:1). $[\alpha]_D^{25}$ = +6.7 (*c* 0.3, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 8.63 (s, 2H), 7.45−7.21 (m, 10H), 6.37 (d, *J* = 6.9 Hz, 1H), 5.14 (dd, *J* = 6.8, 4.8 Hz, 1H), 4.89 (overlap, 1H), 4.90 (d, *J* = 11.1 Hz, 1H) 4.71 (d, *J* = 11.1 Hz, 1H), 4.58−4.47 (m, 2H), 4.43 (d, *J* = 4.9 Hz, 1H), 4.09 (d, *J* = 10.1 Hz, 1H), 3.89 (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (101 MHz, CD_3OD) δ 153.14, 153.09, 151.4, 147.1, 139.2, 138.9, 132.7, 129.5, 129.23, 129.19, 128.98, 128.96, 128.8, 90.6, 81.4, 75.8, 75.7, 74.6, 73.2; HRMS (ESI): *m/z* calcd for $C_{25}H_{24}ClN_4O_6$ $[M+H]^+$ 511.1379, found 511.1364.

5-Methyluracil 3,5-di-*O*-benzyl-4-fluoro-β-D-ribofuranoside(7a) and 5-Methyluracil 3,5-di-*O*-benzyl-4-fluoro-α-L-lyxofuranoside (7a')

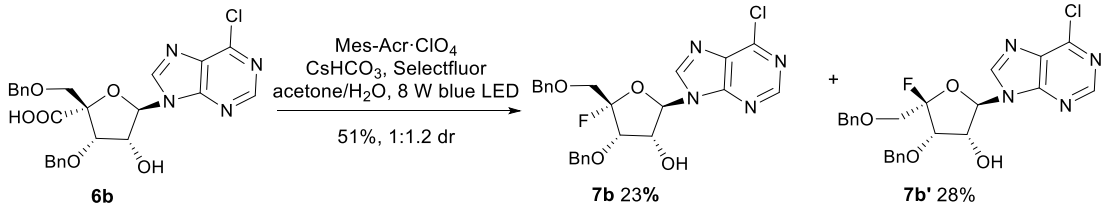


6a **7a** 35% **7a'** 42%

Following the procedure for **2a**, uronic acid **6a** (28 mg, 58.0 μmol, 1.0 equiv) was reacted with $CsHCO_3$ (35 mg, 0.2 mmol, 3.0 equiv), Selectfluor (43 mg, 0.12 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (1.2 mg, 3.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 1.2 mL) to afford titled compound **7a** (9.3 mg, 20.4 μmol, 35%) and **7a'** (11.1 mg, 24.3 μmol, 42%) as white foams after purification by silica gel column chromatography (petroleum ether:EtOAc = 3:2). **7a**: $[\alpha]_D^{21}$ = -37.7 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.42−7.27 (m, 10H), 7.20 (s, 1H), 6.28 (t, *J* = 7.0 Hz, 1H), 4.85

(d, J = 11.2 Hz, 1H), 4.75 (d, J = 11.2 Hz, 1H), 4.68 (d, J = 11.8 Hz, 1H), 4.62 (d, J = 11.8 Hz, 1H), 4.43 (s, 1H), 4.25−4.19 (m, 1H), 3.91 (dd, $J_{C\text{-}F}$ = 27.0, J = 11.2 Hz, 1H), 3.72 (t, J = 10.9 Hz, 1H), 3.31 (d, J = 11.3 Hz, 1H), 1.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 151.0, 137.1, 136.7, 134.59, 134.56, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 119.9 ($J_{C\text{-}F}$ = 232.1 Hz), 112.6, 107.8, 89.8 ($J_{C\text{-}F}$ = 2.1 Hz), 80.0, 79.8 ($J_{C\text{-}F}$ = 37.4 Hz), 75.0, 74.2, 68.0 ($J_{C\text{-}F}$ = 27.9 Hz), 12.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ -102.7 (d, J = 26.6 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{24}H_{25}O_6FN_2Na$ $[M+Na]^+$ 479.1589, found 479.1576. **7a'**: $[\alpha]_D^{21}$ = -2.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.43−7.16 (m, 11H), 6.07 (s, 1H), 4.75 (d, J = 11.7 Hz, 1H), 4.67 (d, J = 11.7 Hz, 1H), 4.53 (d, J = 11.4 Hz, 1H), 4.47 (d, J = 11.4 Hz, 1H), 4.42−4.32 (m, 2H), 3.78 (dd, J = 10.3, 4.9 Hz, 1H), 3.71 (dd, J = 10.4, 3.5 Hz, 1H), 3.54 (s, 1H), 1.57 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 150.3, 137.0, 136.7, 136.2, 128.8, 128.7, 128.6, 128.4, 128.3, 128.0, 116.4 ($J_{C\text{-}F}$ = 232.7 Hz), 111.4, 93.8, 75.6 ($J_{C\text{-}F}$ = 18.4 Hz), 73.9, 73.5, 71.8, 68.5 ($J_{C\text{-}F}$ = 43.4 Hz), 12.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ -118.0 (d, J = 15.3 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{24}H_{25}O_6FN_2Na$ $[M+Na]^+$ 479.1589, found 479.1575.

6-Chloro-9-(3′, 5′-di-*O*-benzyl-4′-fluoro-β-D-ribofuranoside)-purine (7b) and 6-Chloro-9-(3′, 5′-di-*O*-benzyl-4′-fluoro-α-L-lyxoribofuranoside)-purine (7b')



6b **7b** 23% **7b'** 28%

Following the procedure for **2a**, uronic acid **6b** (104 mg, 0.2 mmol, 1.0 equiv) was reacted with $CsHCO_3$ (59 mg, 0.3 mmol, 1.5 equiv), Selectfluor (144 mg, 0.4 mmol, 2.0 equiv) and Mes-Acr·ClO_4 (4.2 mg, 100.0 μmol, 5 mol%) in acetone/H_2O (v/v = 4:1, 7.5 mL) to afford titled compound **7b** (23 mg, 46.8 μmol, 23%) and **7b'** (28 mg, 57.0 μmol, 28%) as white foams after purification by silica gel column chromatography (petroleum ether:EtOAc = 3:2). **7b**: $[\alpha]_D^{25}$ = -49.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.30 (s, 1H), 7.50−7.22 (m, 11H), 6.31 (t, J = 5.5 Hz, 1H),

4.96−4.89 (m, 1H), 4.88 (d, *J* = 11.2 Hz, 1H), 4.77 (d, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 11.8 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.44 (t, *J* = 5.0 Hz, 1H), 3.95 (dd, $J_{F\text{-}H}$ = 24.3, 11.1 Hz, 1H), 3.80 (dd, *J* = 11.1, 9.2 Hz, 1H), 3.63 (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 151.65, 151.62, 143.12, 143.08, 136.9, 136.6, 128.9, 128.8, 128.4, 128.2, 120.6 ($J_{C\text{-}F}$ = 233.1 Hz), 90.4, 80.1 ($J_{C\text{-}F}$ = 37.0 Hz), 75.0, 74.8, 74.4, 67.8 ($J_{C\text{-}F}$ = 30.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.2 (s, 1F); HRMS (ESI): *m/z* calcd for $C_{24}H_{23}ClFN_4O_4$ $[M+H]^+$ 485.1386, found 485.1376. **7b'**: $[\alpha]_D^{25}$ = -31.1 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.26 (s, 1H), 7.43–7.23 (m, 9H), 7.21−7.11 (m, 2H), 6.37 (s, 1H), 4.89 (dd, *J* = 16.3, 6.0 Hz, 1H), 4.74 (s, 2H), 4.67−4.61 (m, 1H), 4.51−4.42 (m, 2H), 3.78−3.69 (m, 2H), 3.25 (dd, *J* = 5.1, 1.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 151.7, 150.9, 144.2, 136.9, 136.4, 132.4, 128.9, 128.7, 128.6, 128.3, 127.8, 116.9 ($J_{C\text{-}F}$ = 234.7 Hz), 91.7, 75.5 ($J_{C\text{-}F}$ = 18.6 Hz), 73.9, 73.8, 71.8, 68.1 ($J_{C\text{-}F}$ = 42.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.8 (s, 1F); HRMS (ESI): *m/z* calcd for $C_{24}H_{23}O_4N_4ClF$ $[M+H]^+$ 485.1386, found 485.1373.

References

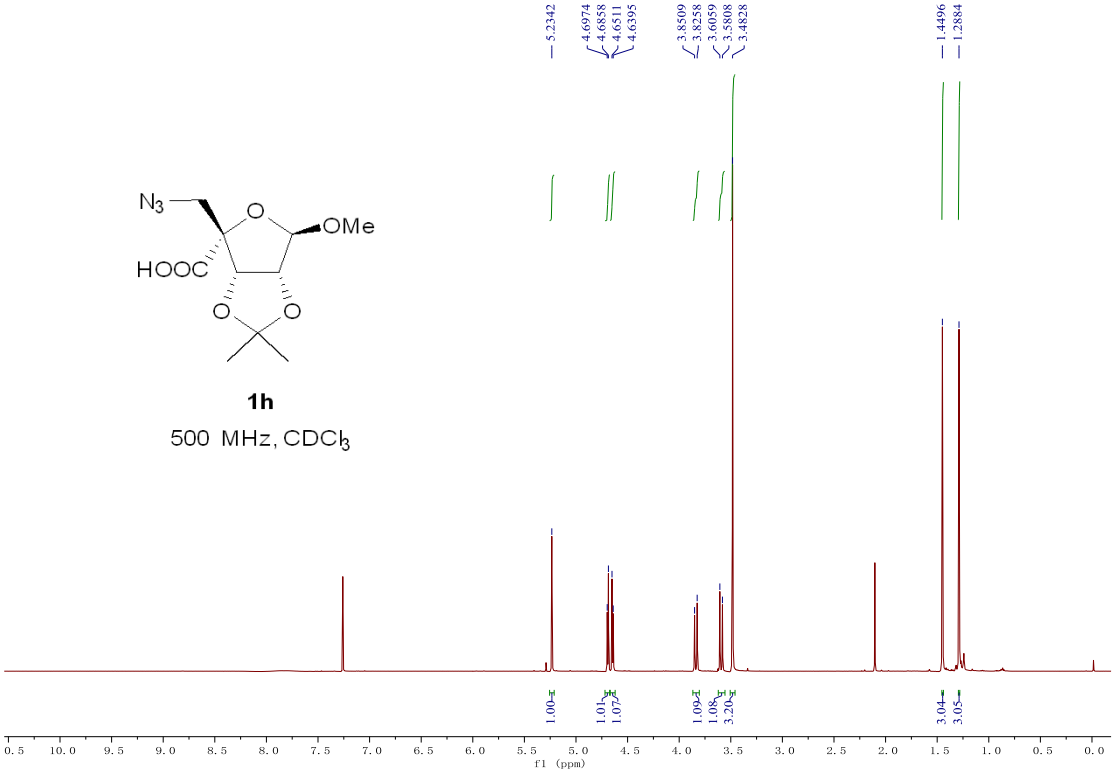
1. X. Zhou, P. Wang, L. Zhang, P. Chen, M. Ma, N. Song, S. Ren, M. Li, Transition-Metal-Free Synthesis of C-Glycosylated Phenanthridines via $K_2S_2O_8$-Mediated Oxidative Radical Decarboxylation of Uronic Acids, *J. Org. Chem.* 2018, **83**, 588–603.
2. S. Ventre, F. R. Petronijević, D. W. C. MacMillan, Decarboxylative Fluorination of Aliphatic Carboxylic Acids via Photoredox Catalysis, *J. Am. Chem. Soc.* 2015, **137**, 5654–5657.
3. M.-Y. Jang, X.-P. Song, M. Froeyen, P. Marlière, E. Lescrinier, J. Rozenski, P. Herdewijn. A Synthetic Substrate of DNA Polymerase Deviating from the Bases, Sugar, and Leaving Group of Canonical Deoxynucleoside Triphosphates, *Chem. Bio.* 2013, **20**, 416–423.
4. R. E. Ireland, D. W. Norbeck, *J. Am. Chem. Soc.* 1985, **107**, 3279–3285.
5. H. Fujino, M. Nagatomo, A. Paudel, S. Panthee, H. Hamamoto, K. Sekimizu, M. Inoue, Unified Total Synthesis of Polyoxins J, L, and Fluorinated Analogues on the Basis of Decarbonylative Radical Coupling Reactions, *Angew. Chem. Int. Ed.* 2017, **56**, 11865–11869.
6. Z. Guan, L.-H. Zhang, P. Sinaÿ, Y.-M. Zhang, Study on Metal-Induced Reactions of α-Diazocarbonyl Glucosides, *J. Org. Chem.* 2012, **77**, 8888-8895.
7. N. Pravdić, D. Keglević, Glucuronic Esters—III: The synthesis of the fully benzylated C-1 hydroxyl free glucuronic acid, *Tetrahedron* 1965, **21**, 1897–1901.
8. D. Crich, K. Sasaki, *Org. Lett.* 2009, **11**, 3514–3517.
9. T. Li, S, Sun, P. Wang, M. Li, Synthesis of 6-deoxy-D-guloheptopyranosyl fluoride. *J. Ocean Univ. China*. 2020, **50**, 70–75.
10. X. Zhou, H. Ding, P. Chen, L. Liu, Q. Sun, X. Wang, P. Wang, Z. Lv, M. Li, Radical Dehydroxymethylative Fluorination of Carbohydrates and Divergent Transformations of the Resulting Reverse Glycosyl Fluorides, *Angew. Chem. Int. Ed.* 2020, **59**, 4138–4144.
11. G. H. Jones, M. Taniguchi, D. Tegg, J. G. Moffatt, 4'-Substituted nucleosides. 5.

Hydroxymethylation of nucleoside 5'-aldehydes, *J. Org. Chem.* 1979, 44, 1309–1317.

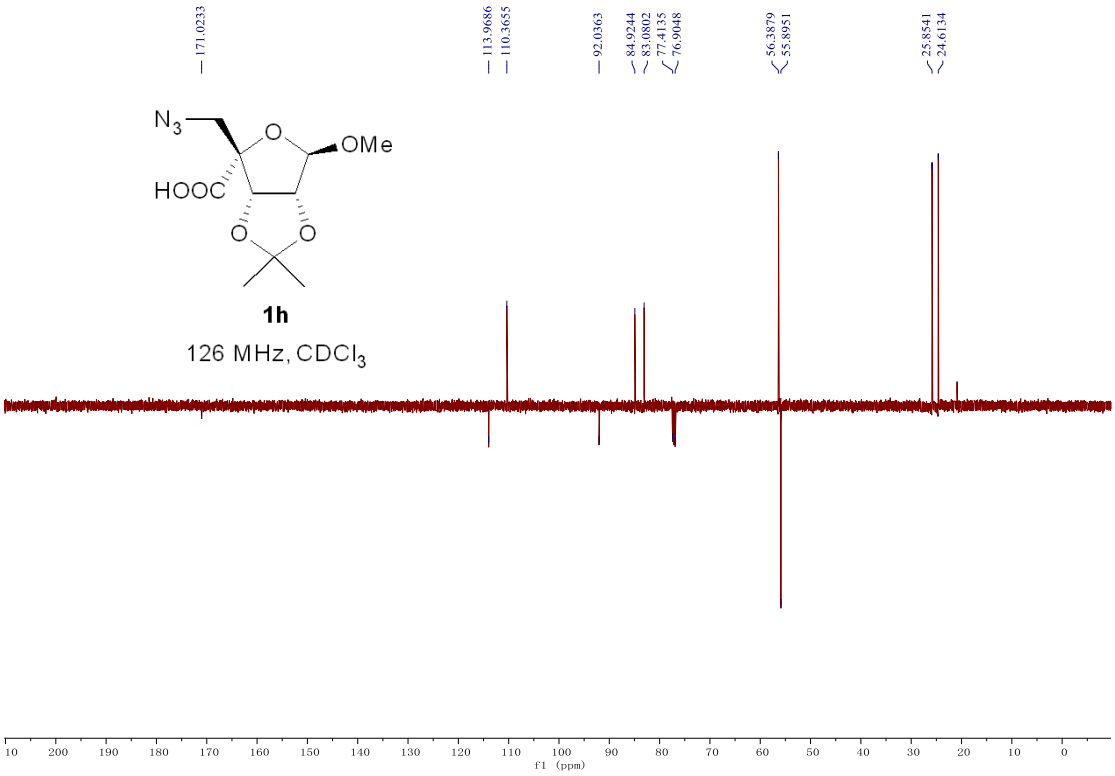
12. K. Fukuyama, H. Ohrui, S. Kuwahara, Synthesis of EFdA via a Diastereoselective Aldol Reaction of a Protected 3-Keto Furanose, *Org. Lett.* 2015, **17**, 828–831.
13. G. V. M. Sharma, P. S. Reddy, D. Chatterjee, A. C. Kunwar, Synthesis and Structural Studies of Homooligomers of Geminally Disubstituted β 2,2-Amino Acids with Carbohydrate Side Chain, *J. Org. Chem.* 2011, **76**, 1562–1571.
14. Y. Hari, S. Obika, M. Sakaki, K. Morio, Y. Yamagata, T. Imanishi, Effective synthesis of C-nucleosides with 2′,4′-BNA modification, *Tetrohedron* 2002, **58**, 3051–3063.
15. L. Chen, F. Kong, Unusual α-glycosylation with galactosyl donors with a C2 ester capable of neighboring group participation, *Tetrahedron Lett.* 2003, **44**, 3691–3695.
16. P. Ji, Y. Zhang, Y. Wei, H. Huang, W. Hu, P. A. Mariano, W. Wang, Visible-Light-Mediated, Chemo- and Stereoselective Radical Process for the Synthesis of C-Glycoamino Acids, *Org. Lett.* 2019, **21**, 3086–3092.

NMR Spectra

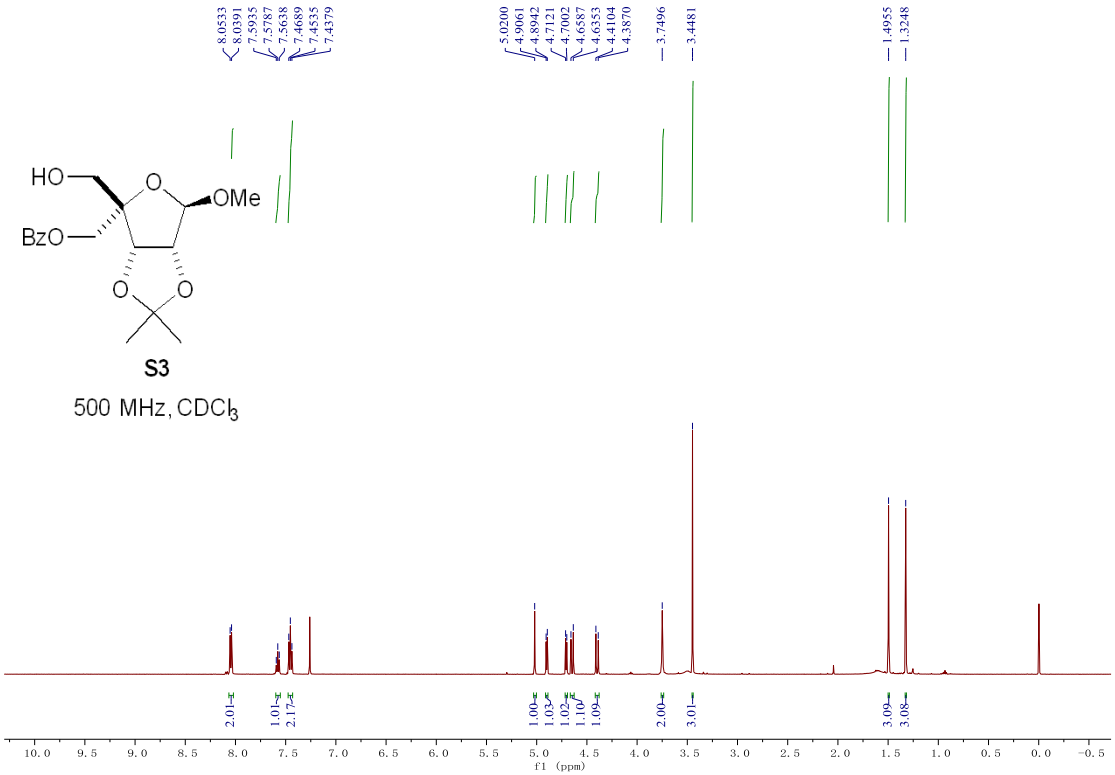
^{1}H NMR Spectrum of **1h**



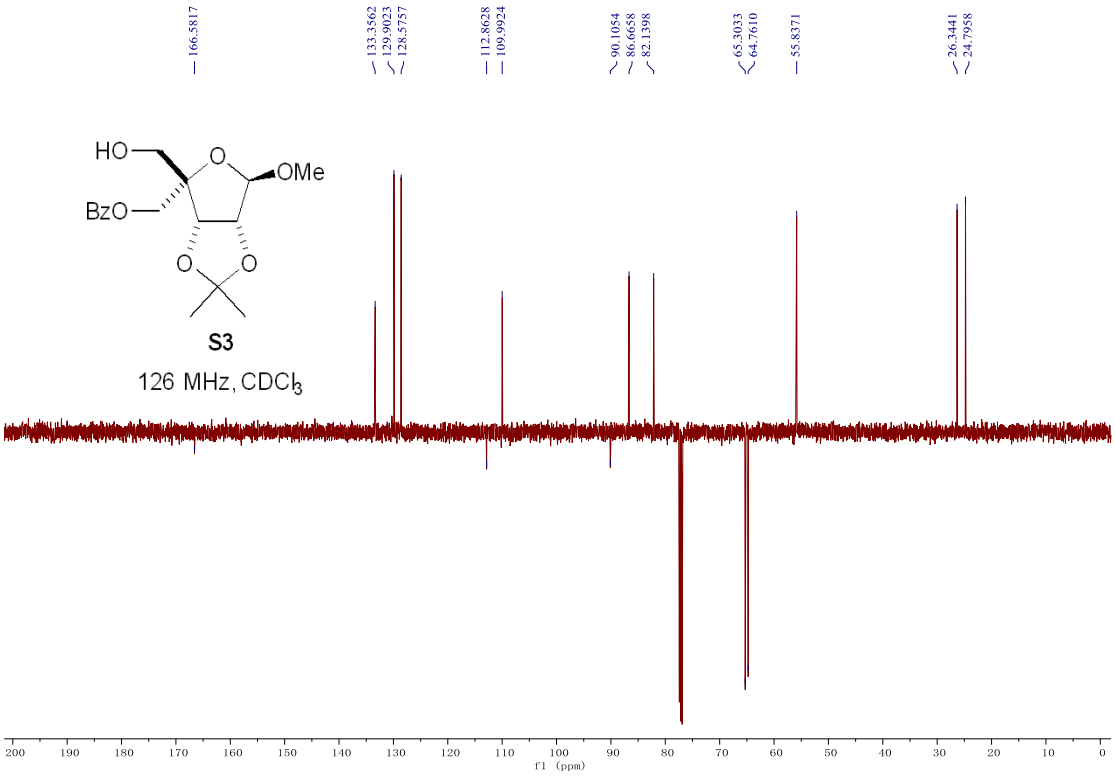
DEPT-Q NMR Spectrum of **1h**



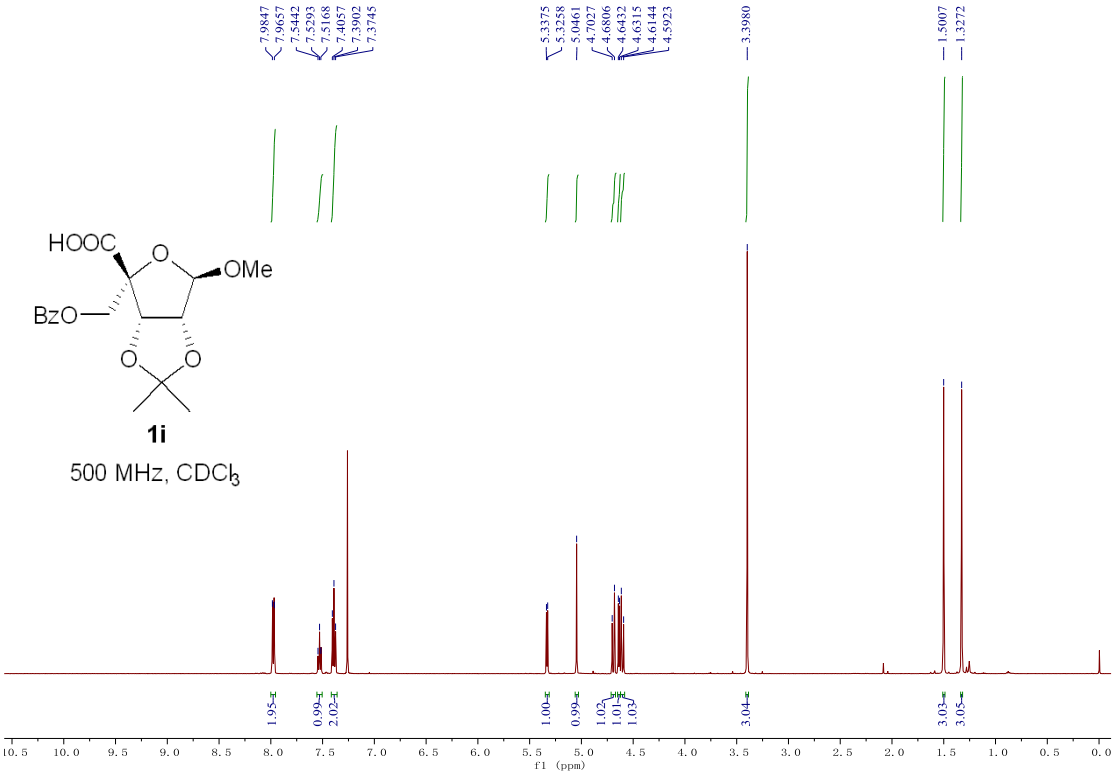
^{1}H NMR Spectrum of **S3**



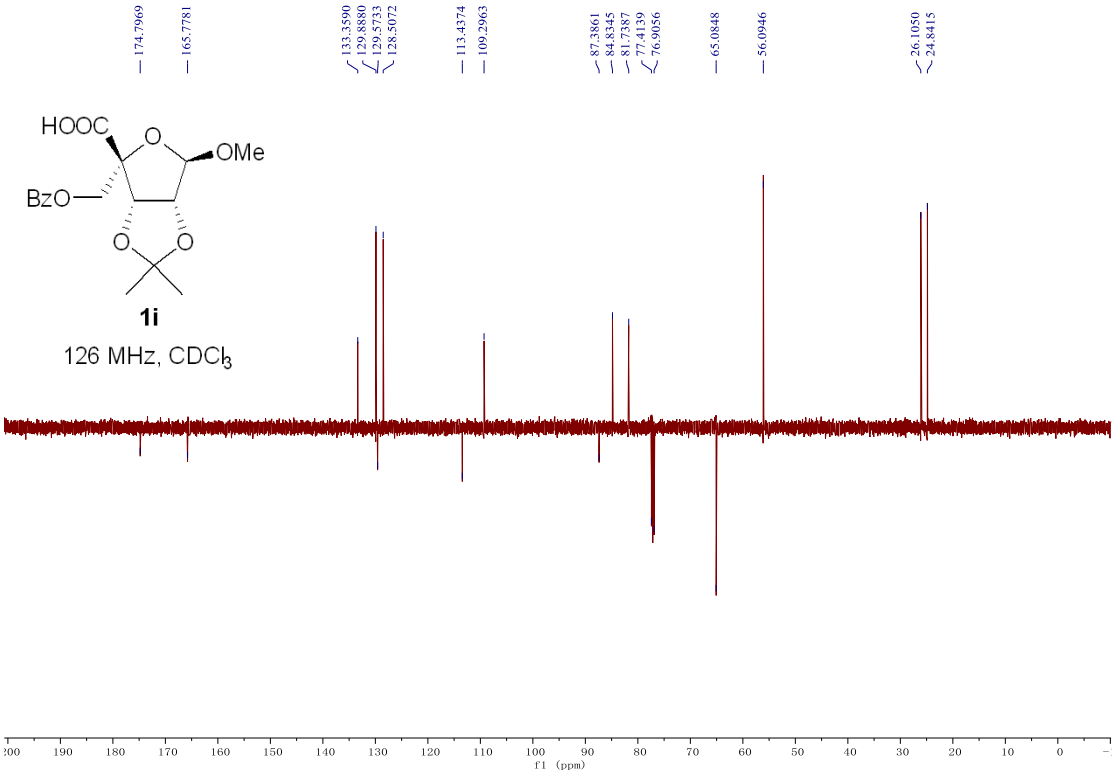
DEPT-Q NMR Spectrum of **S3**



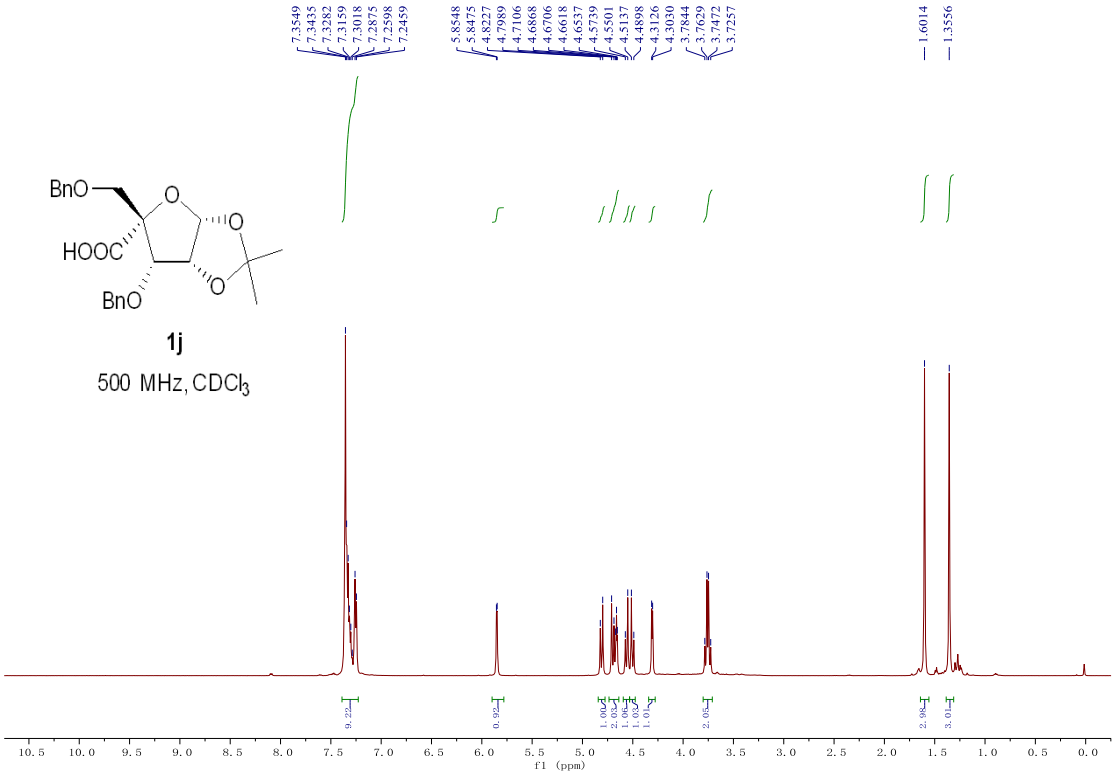
^{1}H NMR Spectrum of **1i**



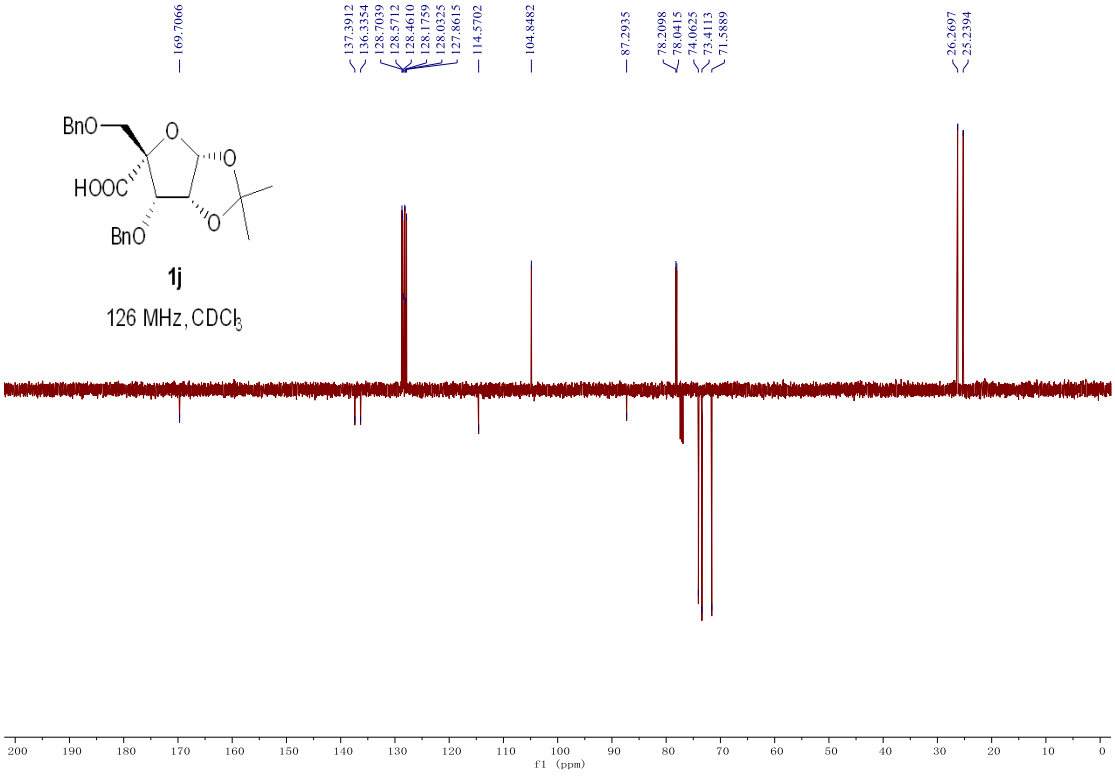
DEPT-Q NMR Spectrum of **1i**



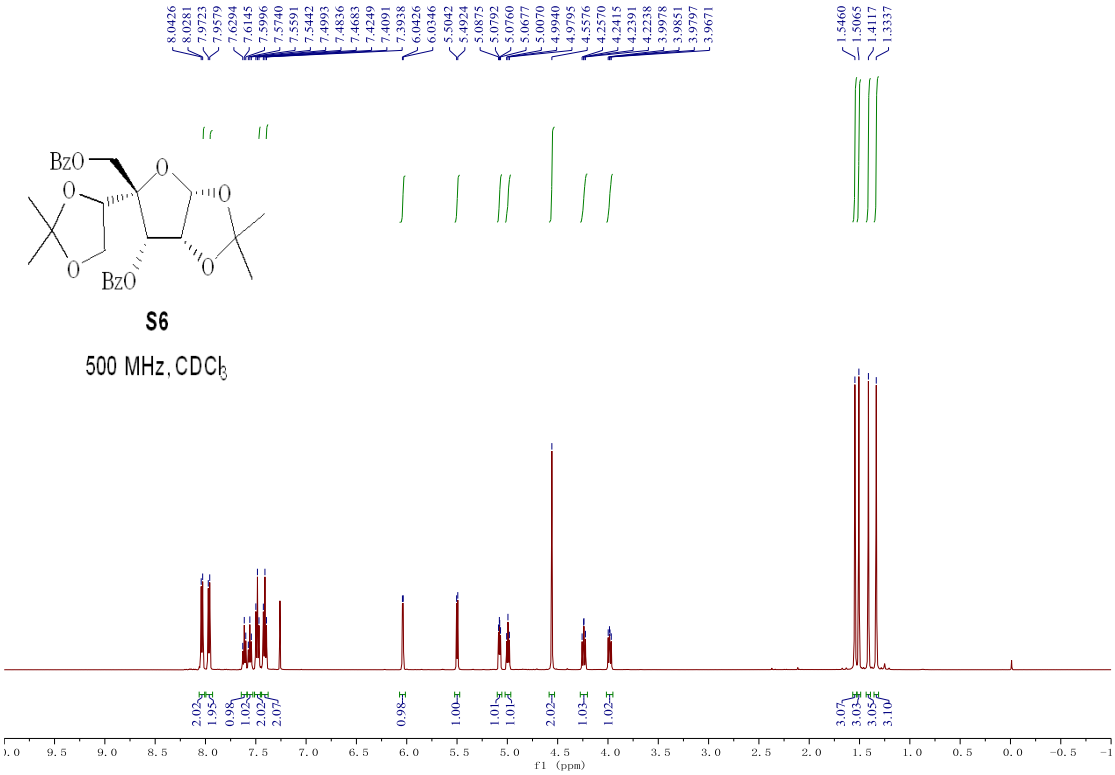
^{1}H NMR Spectrum of **1j**



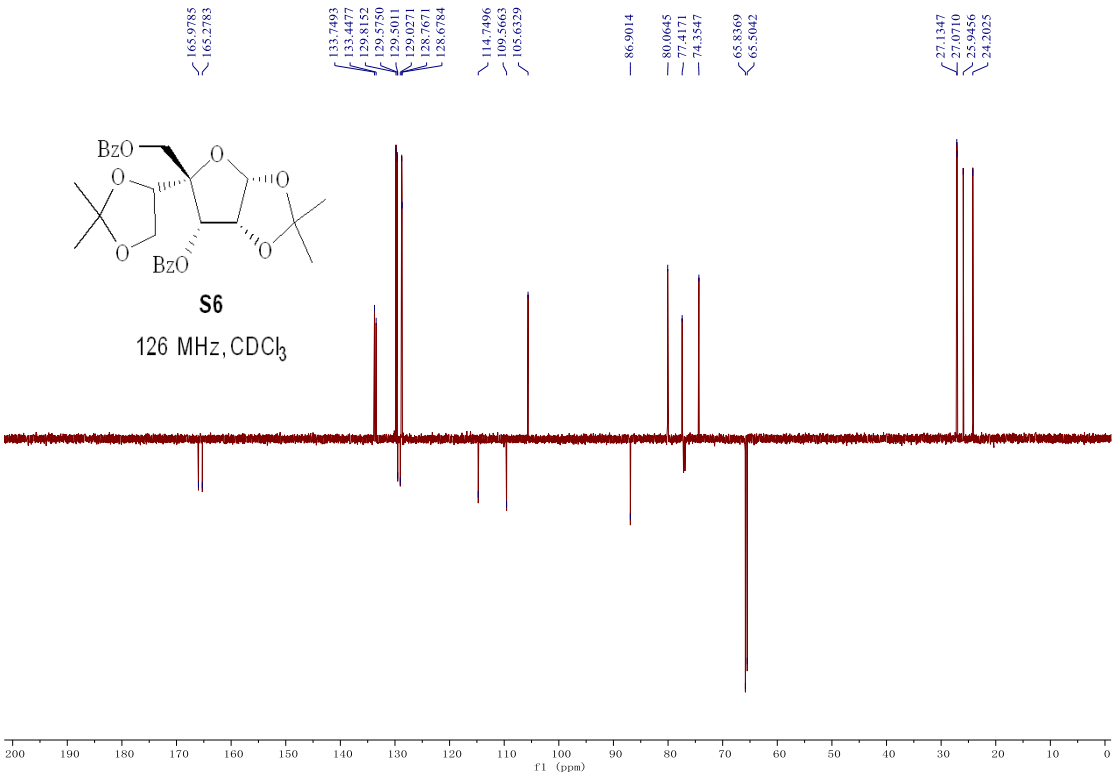
DEPT-Q NMR Spectrum of **1j**



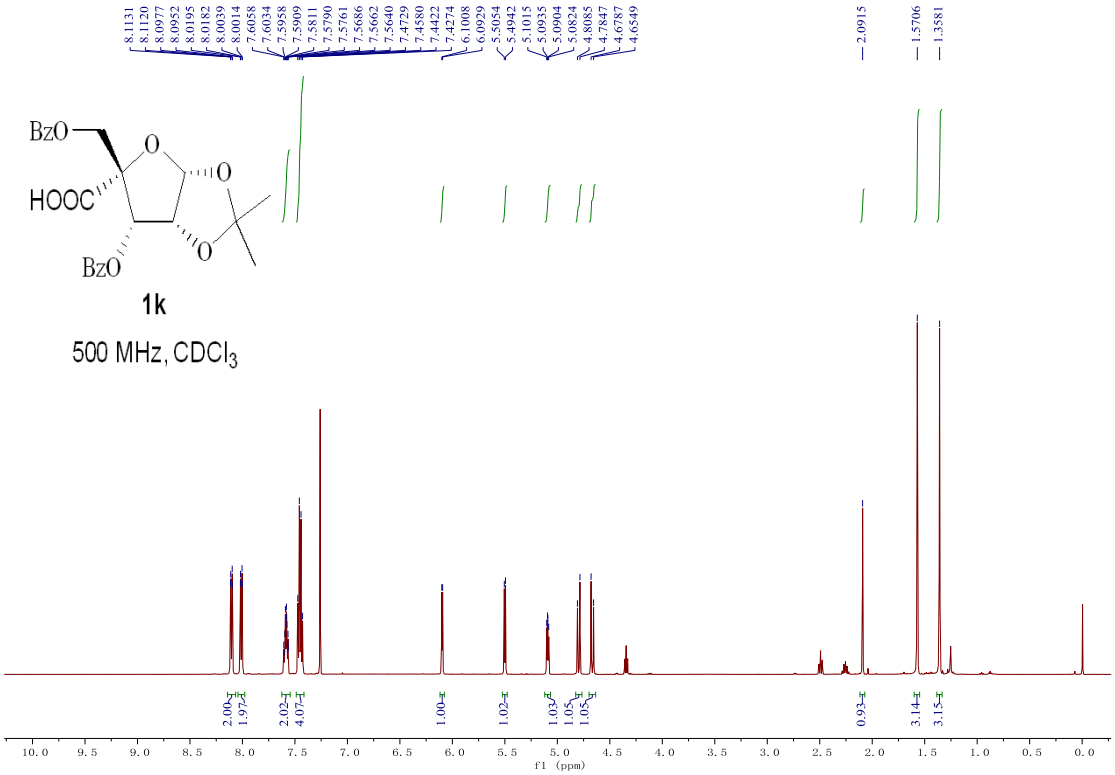
^{1}H NMR Spectrum of **S6**



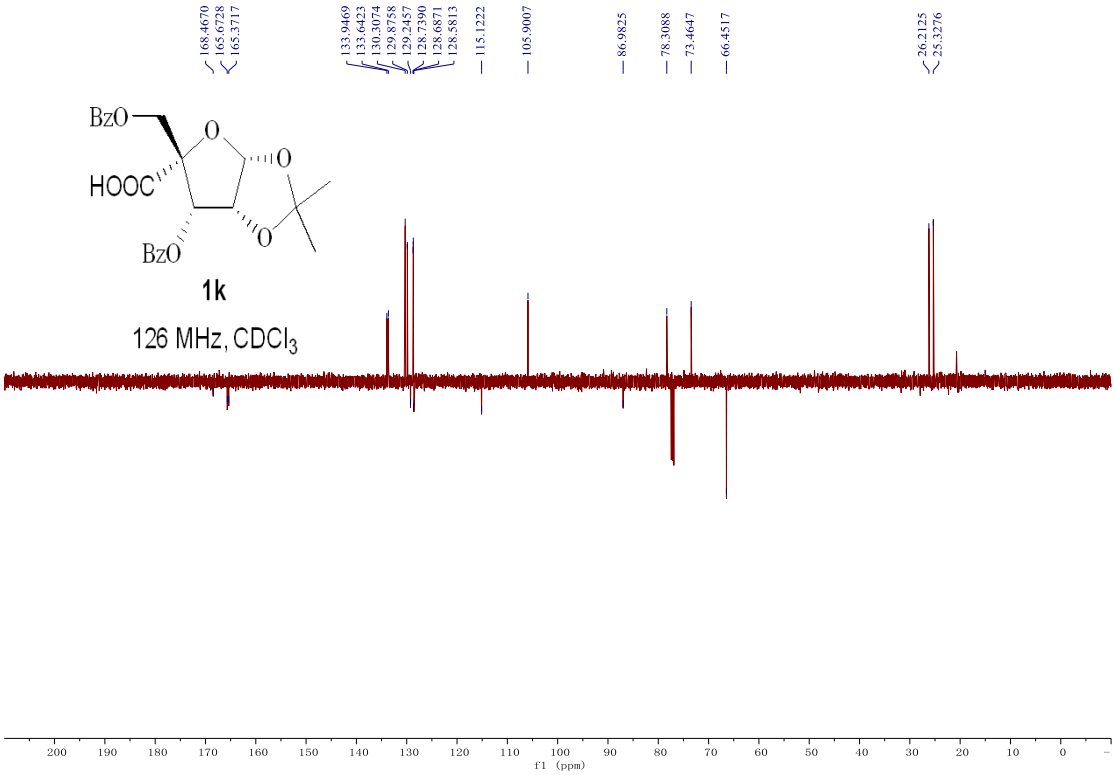
DEPT-Q NMR Spectrum of **S6**



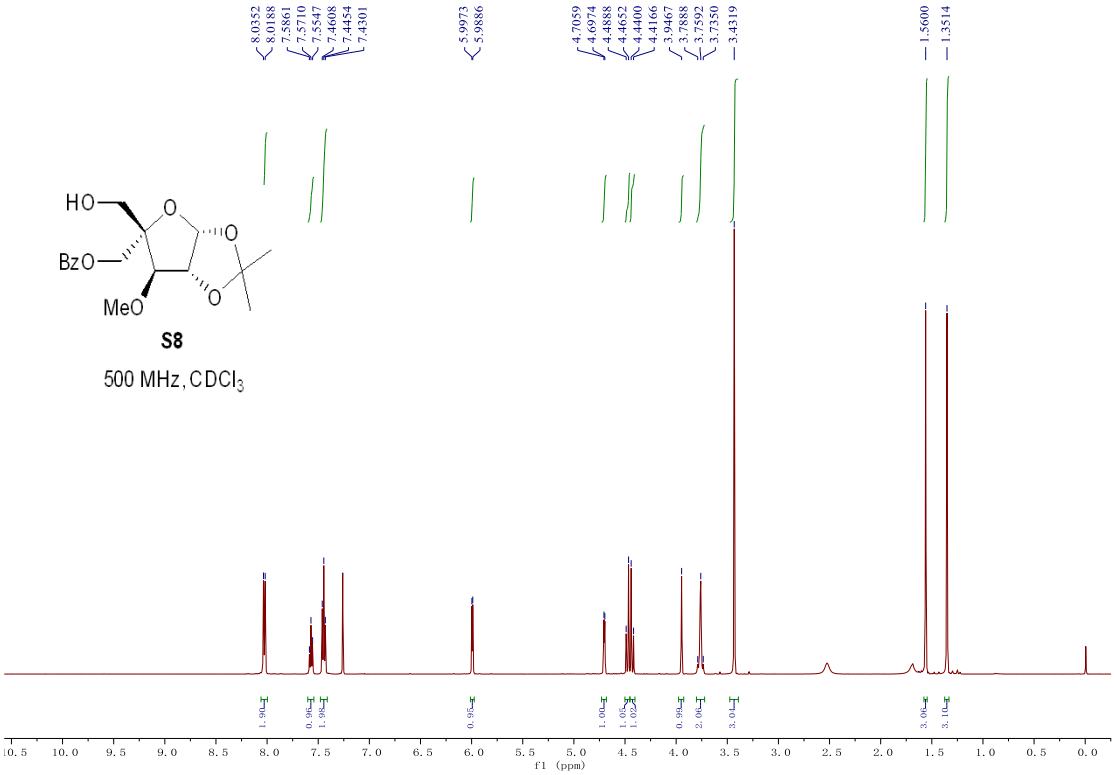
^{1}H NMR Spectrum of **1k**



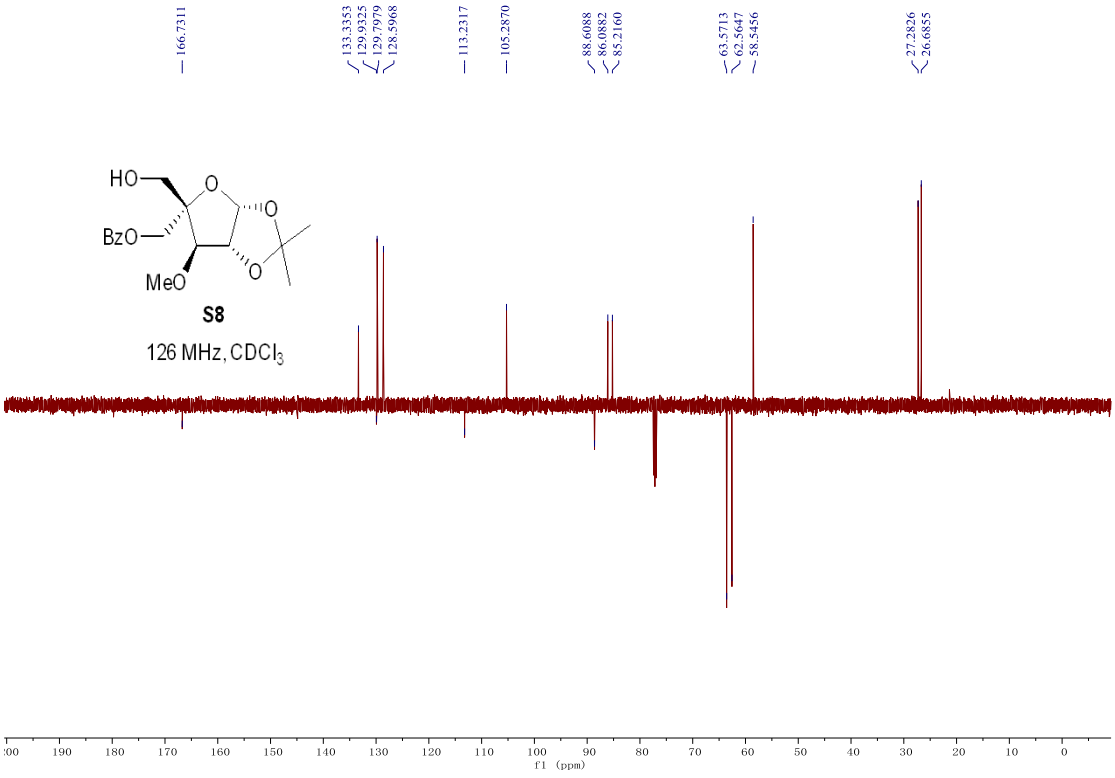
DEPT-Q NMR Spectrum of **1k**



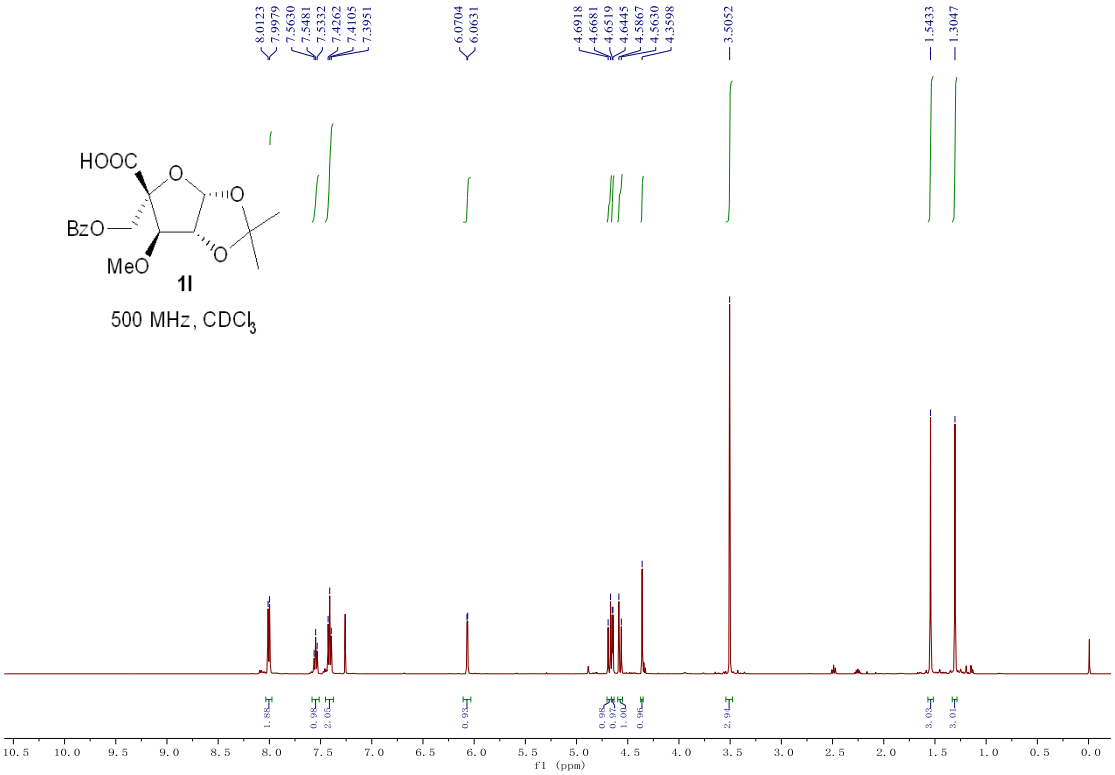
^{1}H NMR Spectrum of **S8**



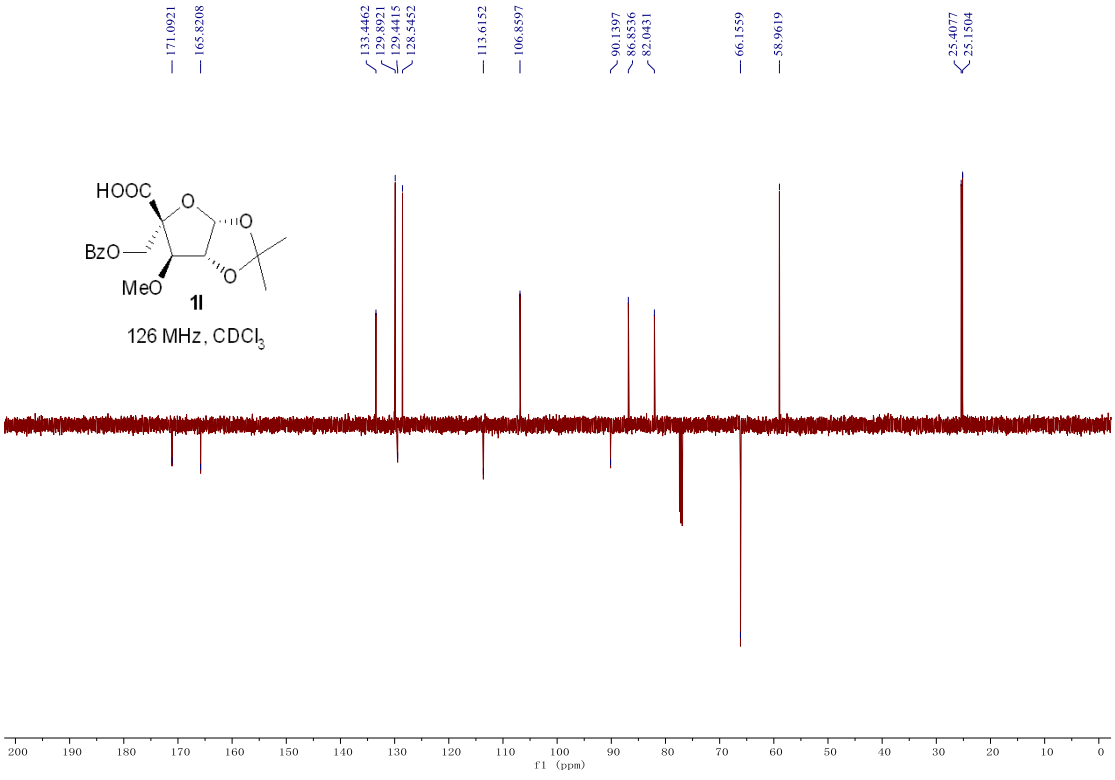
DEPT-Q NMR Spectrum of **S8**



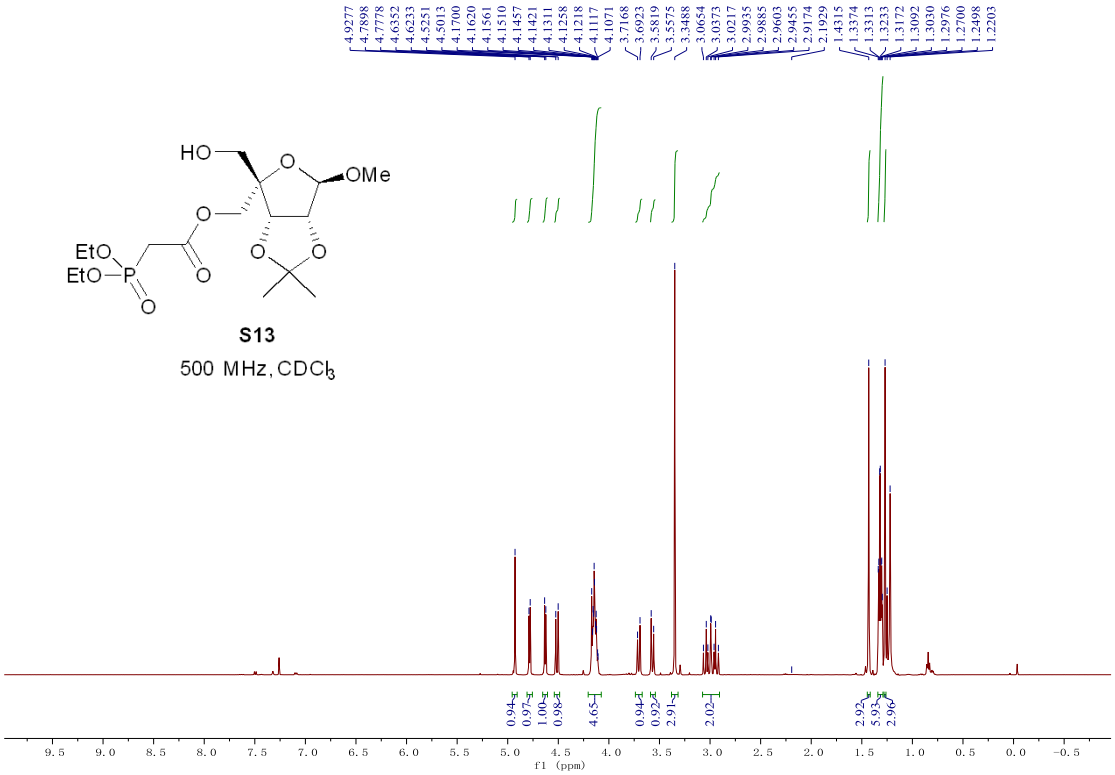
^{1}H NMR Spectrum of **1l**



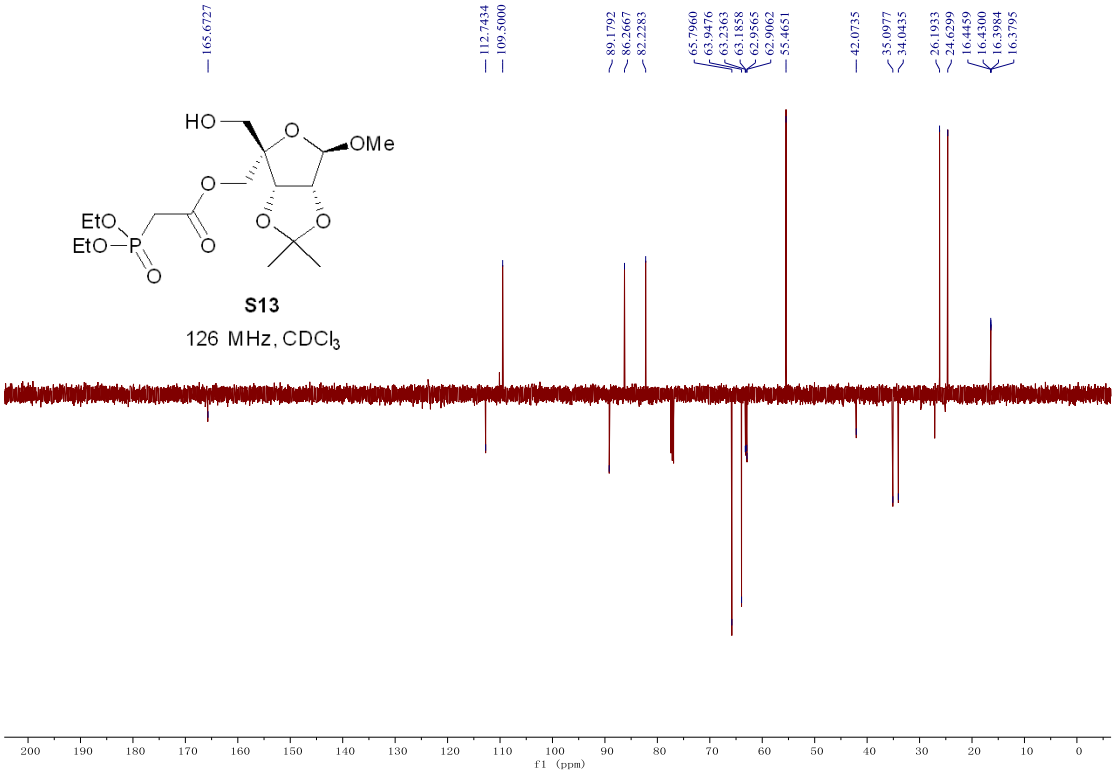
DEPT-Q NMR Spectrum of **1l**



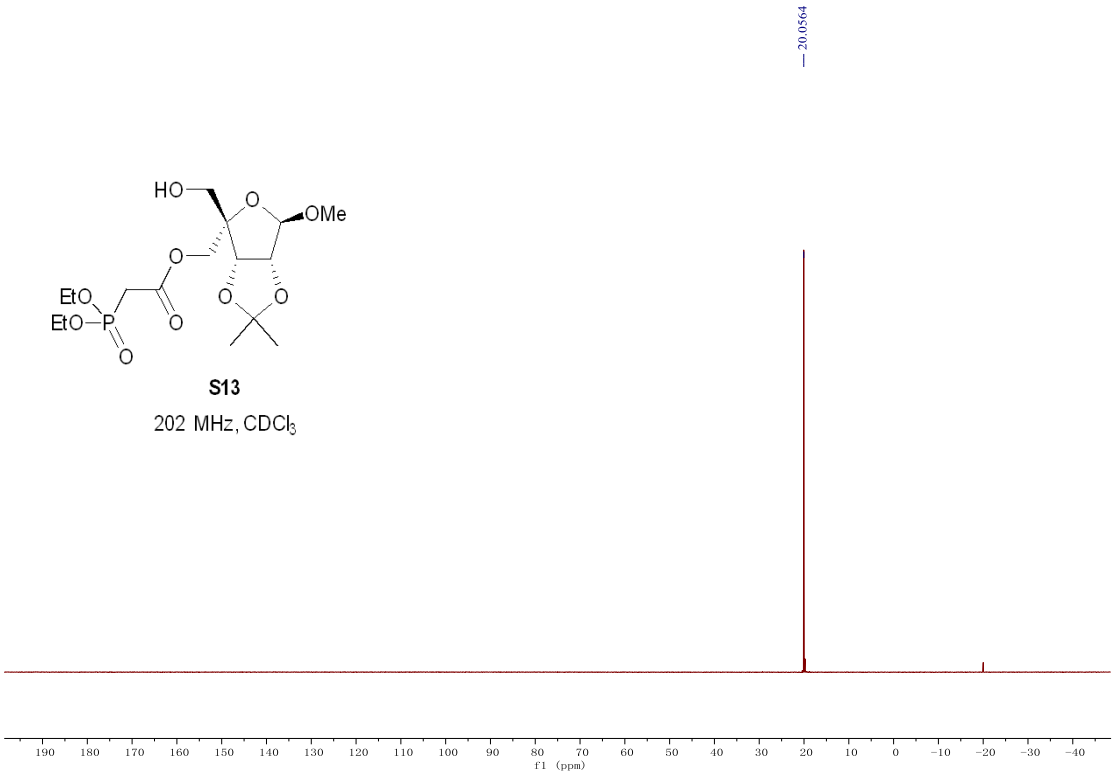
^{1}H NMR Spectrum of **S13**



DEPT-Q NMR Spectrum of **S13**



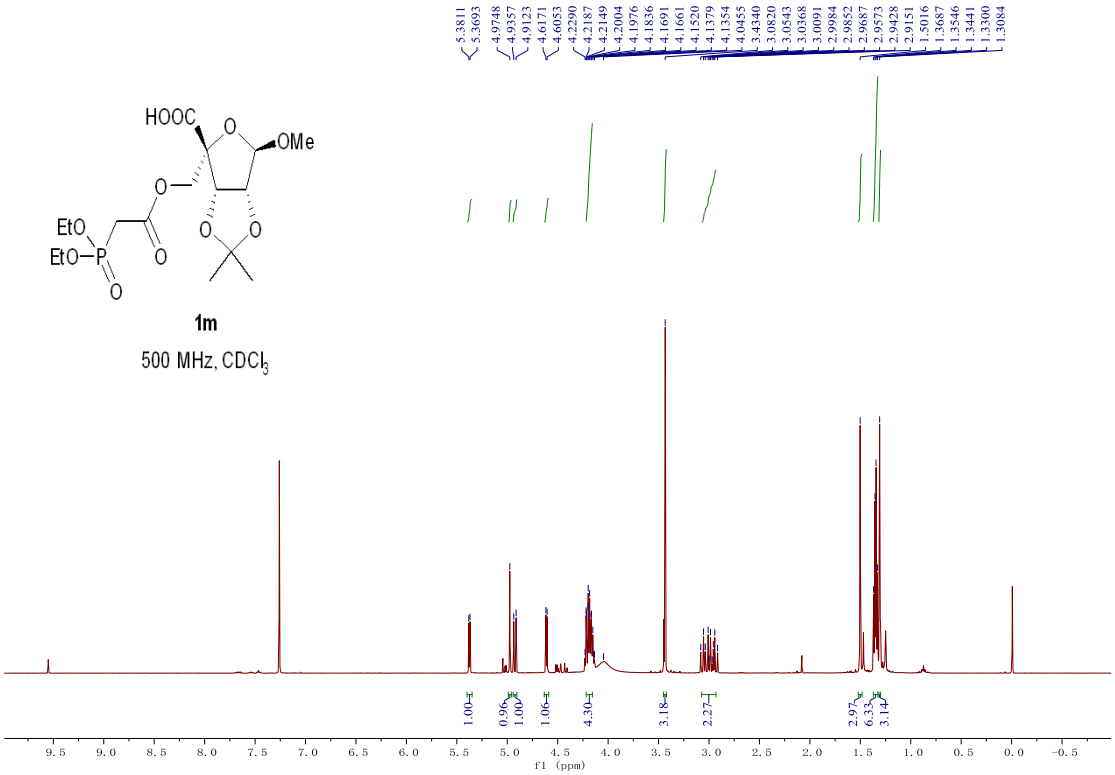
^{31}P NMR Spectrum of **S13**



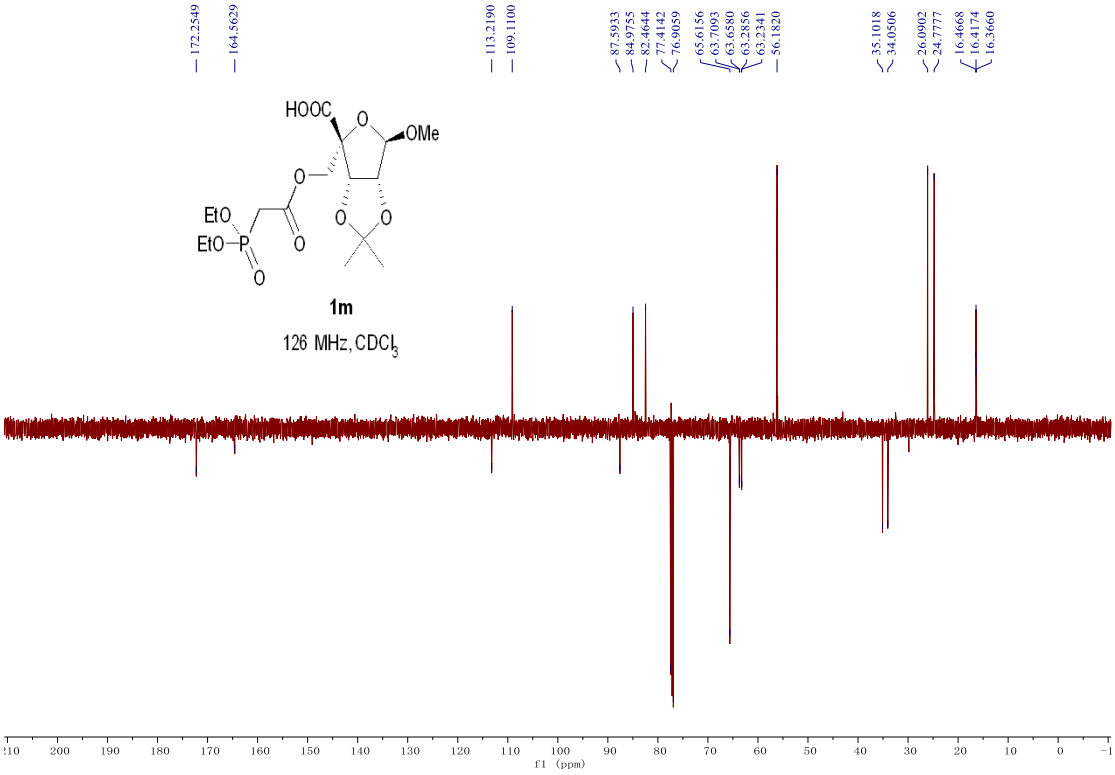
S13

202 MHz, $CDCl_3$

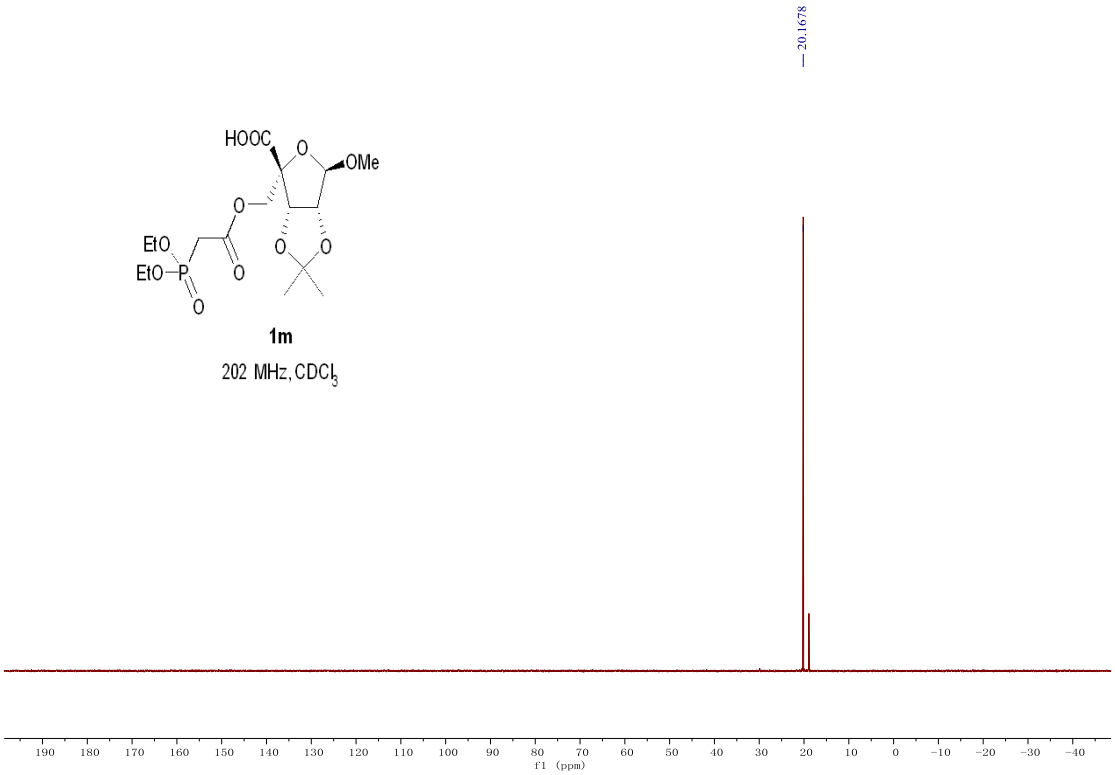
^{1}H NMR Spectrum of **1m**



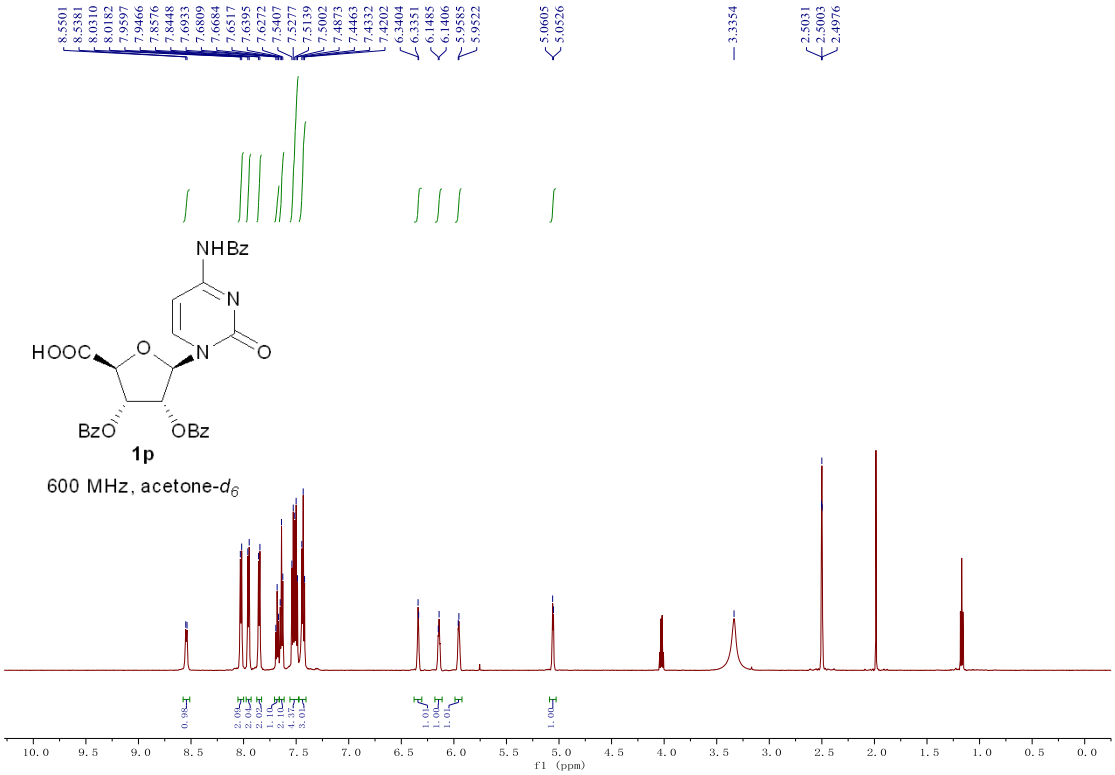
DEPT-Q NMR Spectrum of **1m**



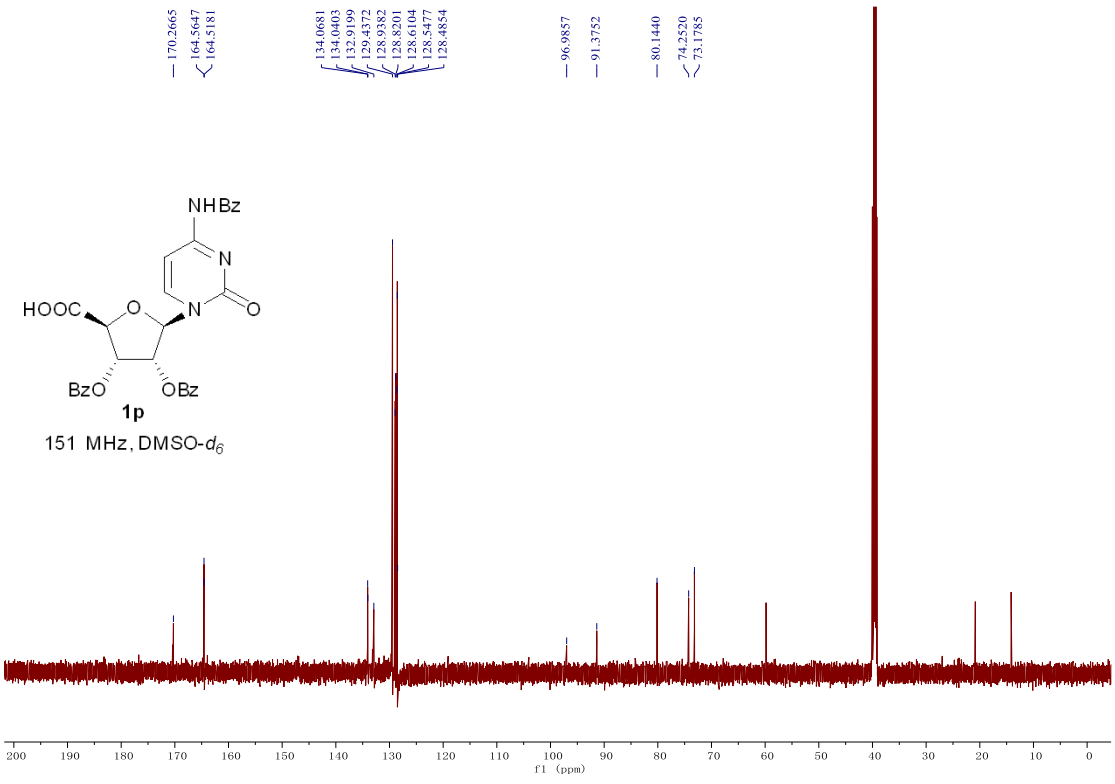
^{31}P NMR Spectrum of **1m**



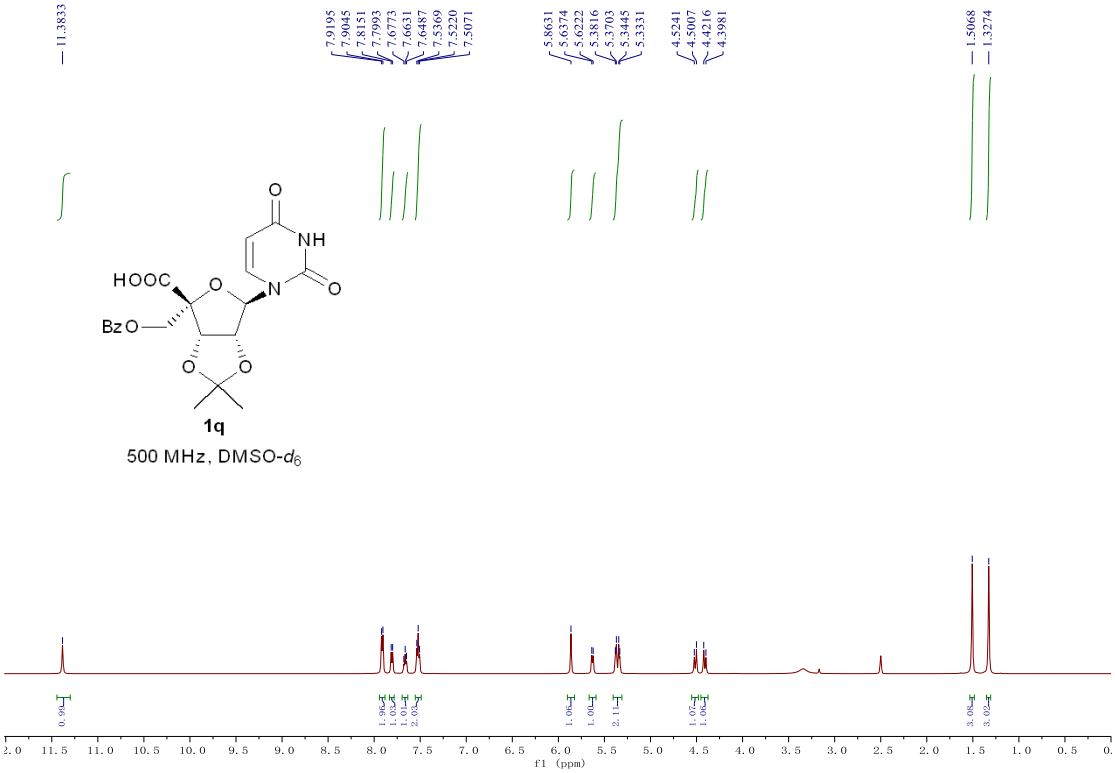
^{1}H NMR Spectrum of **1p**



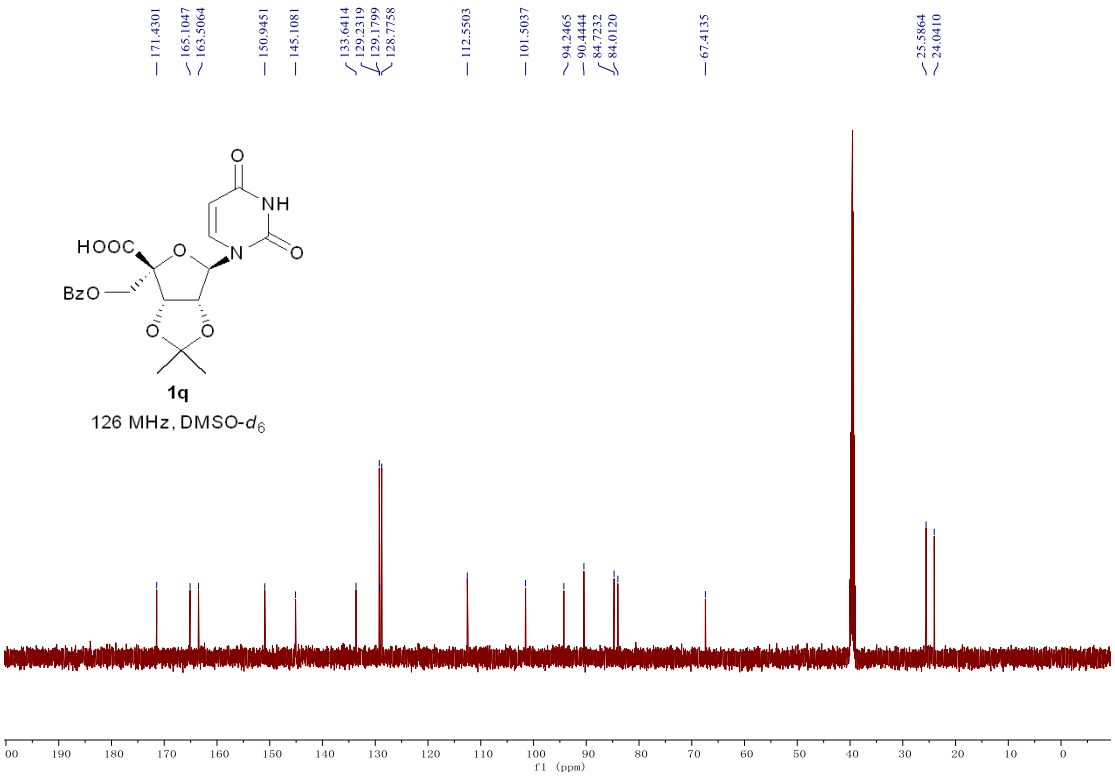
^{1}H NMR Spectrum of **1p**



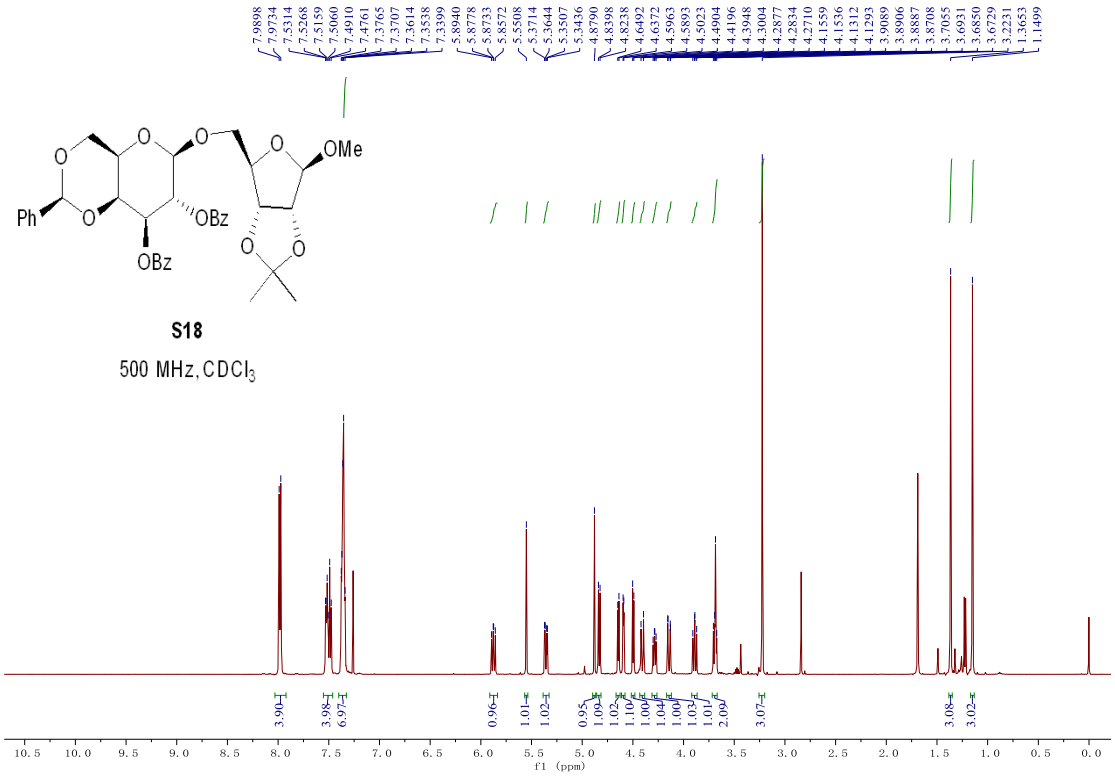
^{1}H NMR Spectrum of **1q**



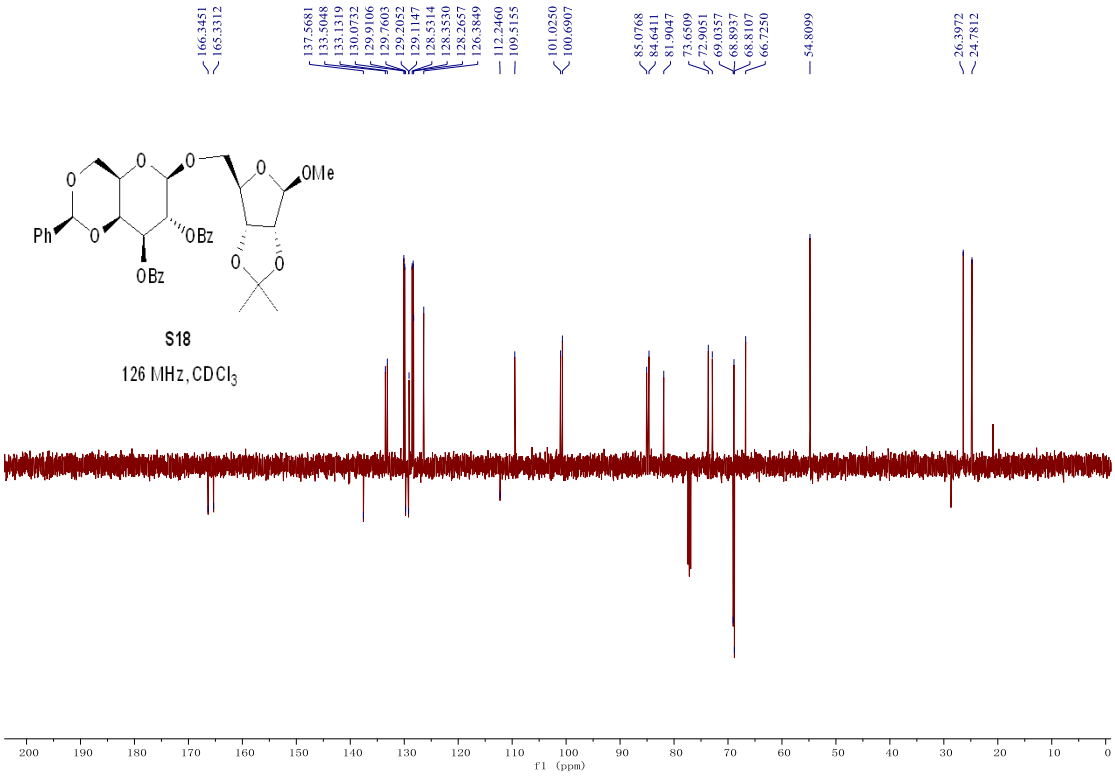
^{13}C NMR Spectrum of **1q**



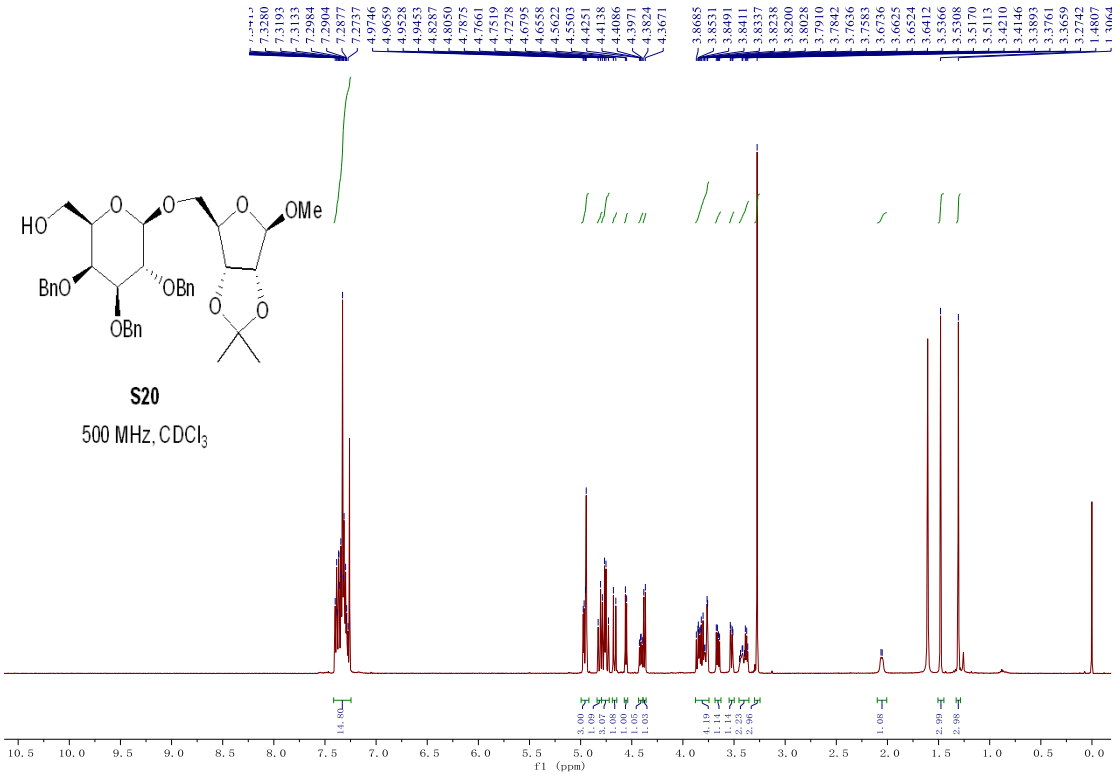
^{1}H NMR Spectrum of **S18**



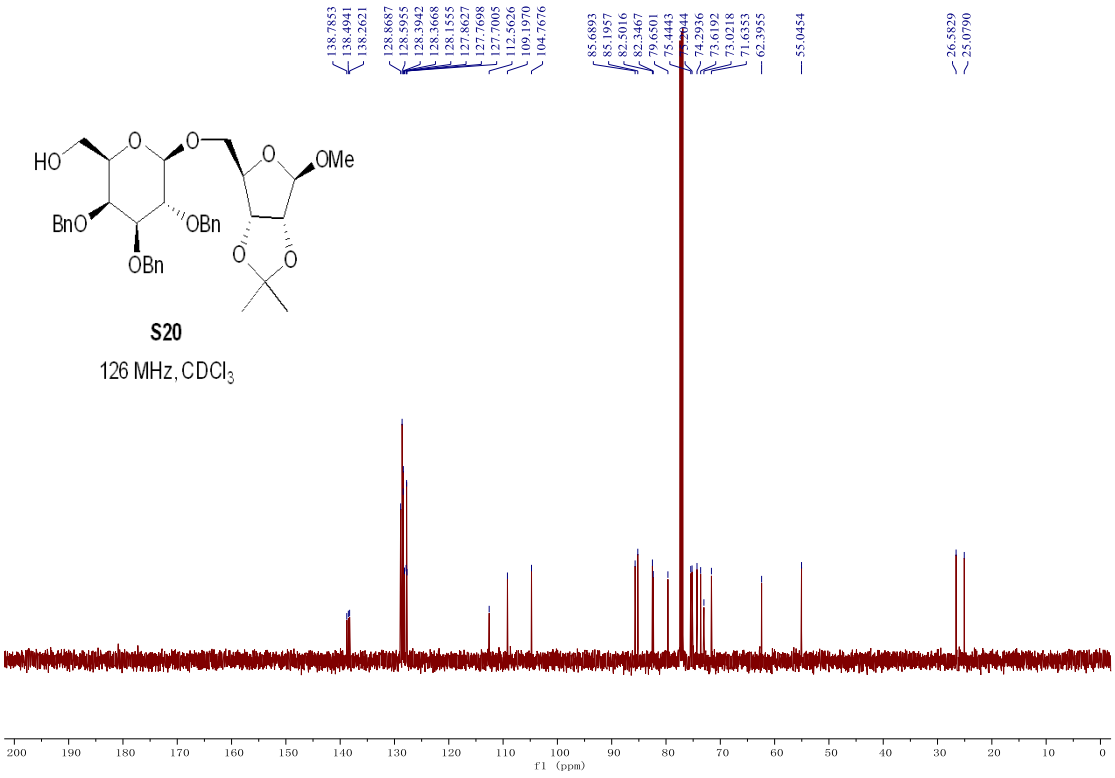
DEPT-Q NMR Spectrum of **S18**



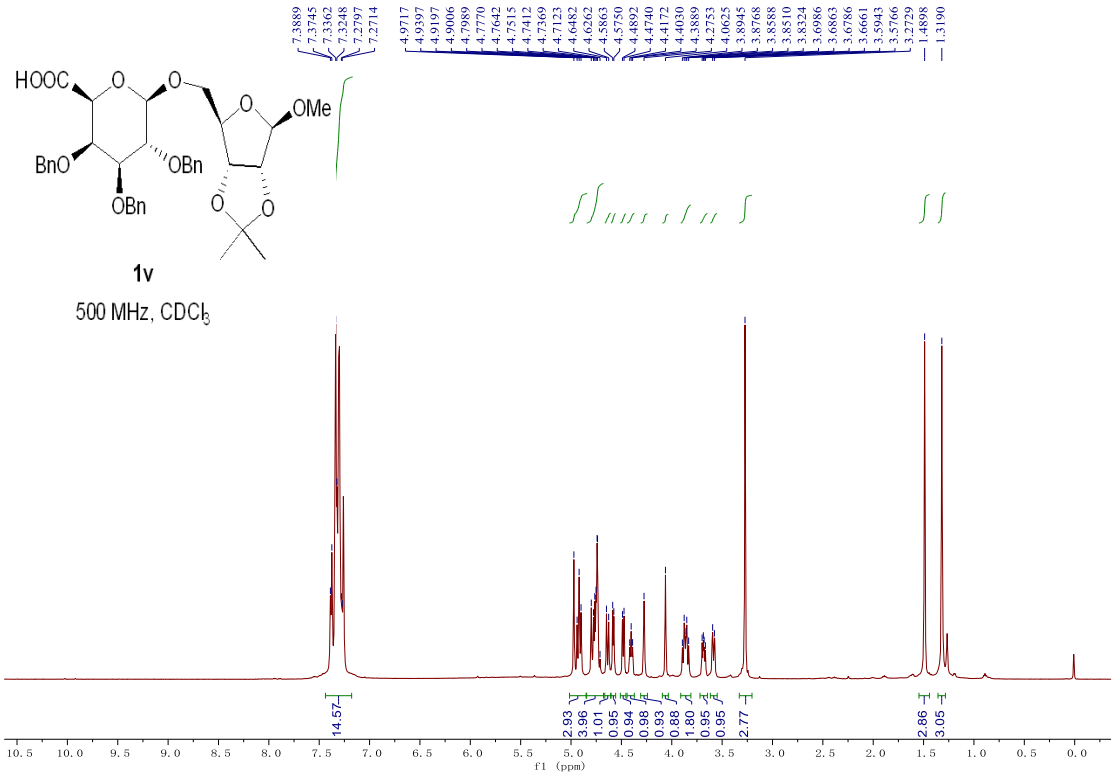
^{1}H NMR Spectrum of **S20**



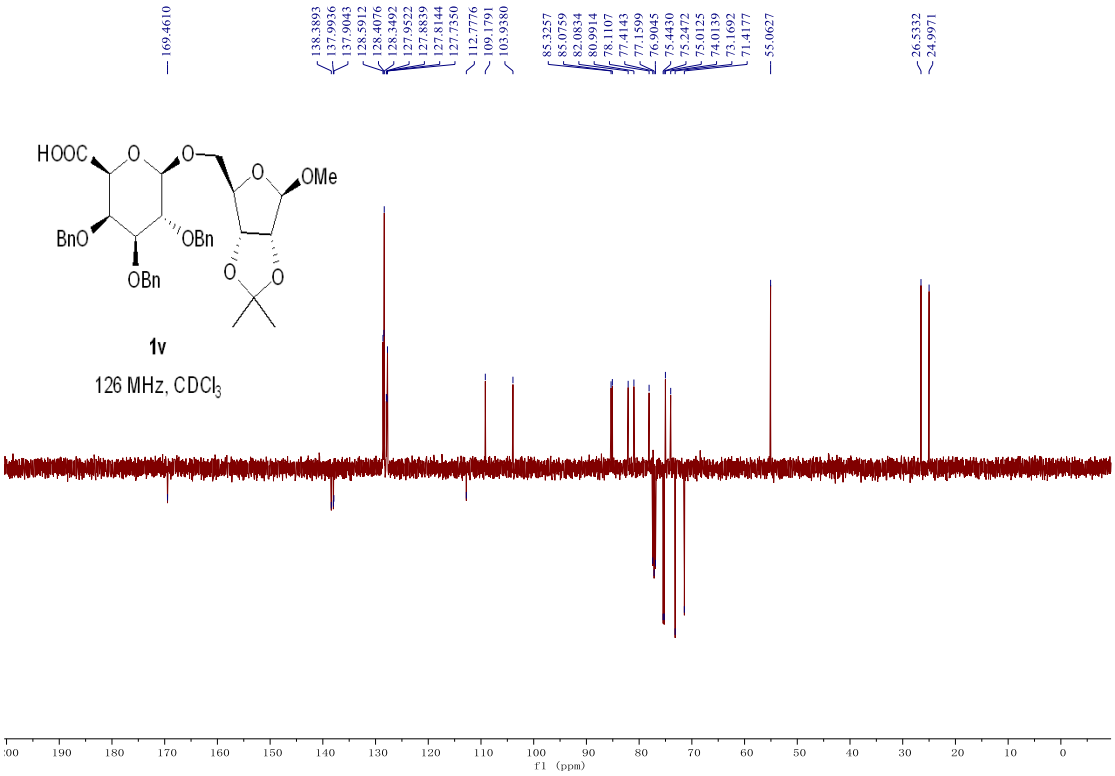
^{13}C NMR Spectrum of **S20**



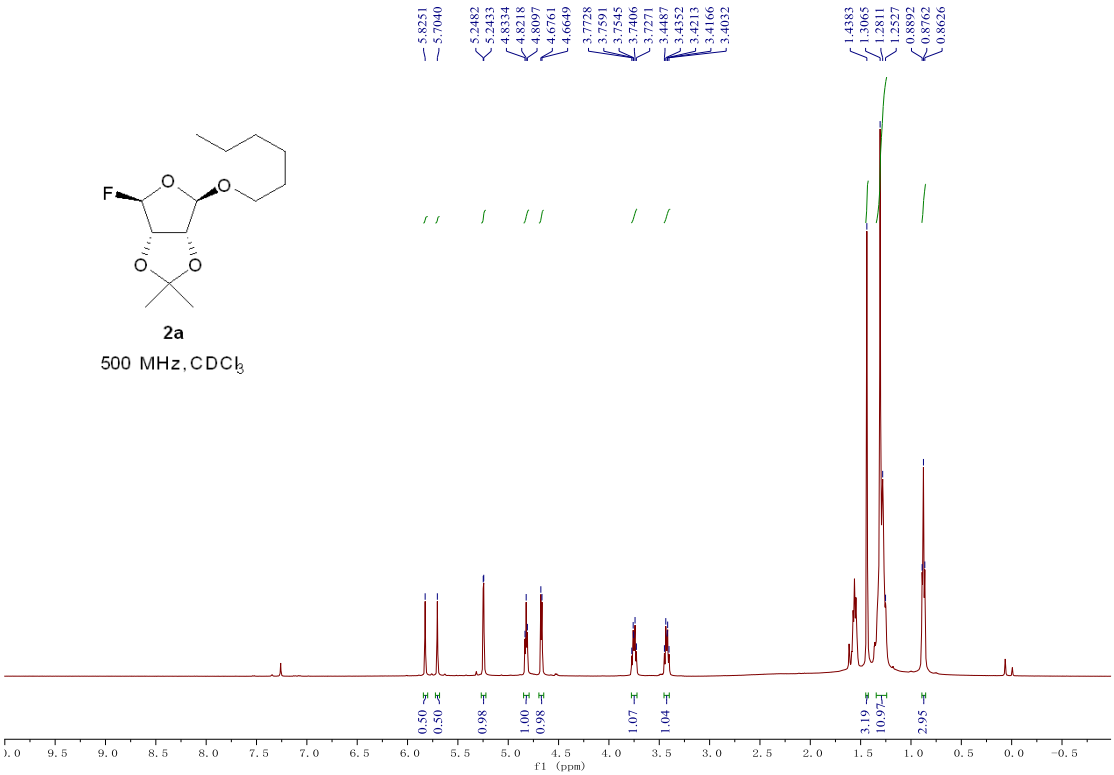
^{1}H NMR Spectrum of **1v**



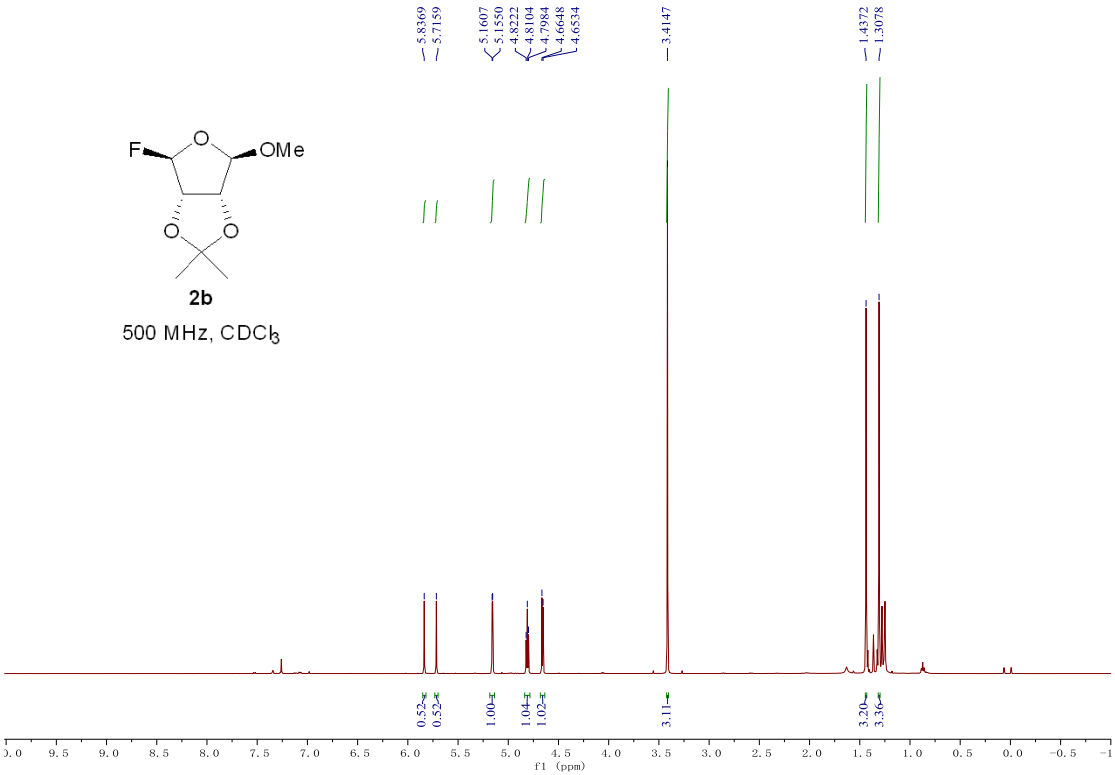
DEPT-Q NMR Spectrum of **1v**



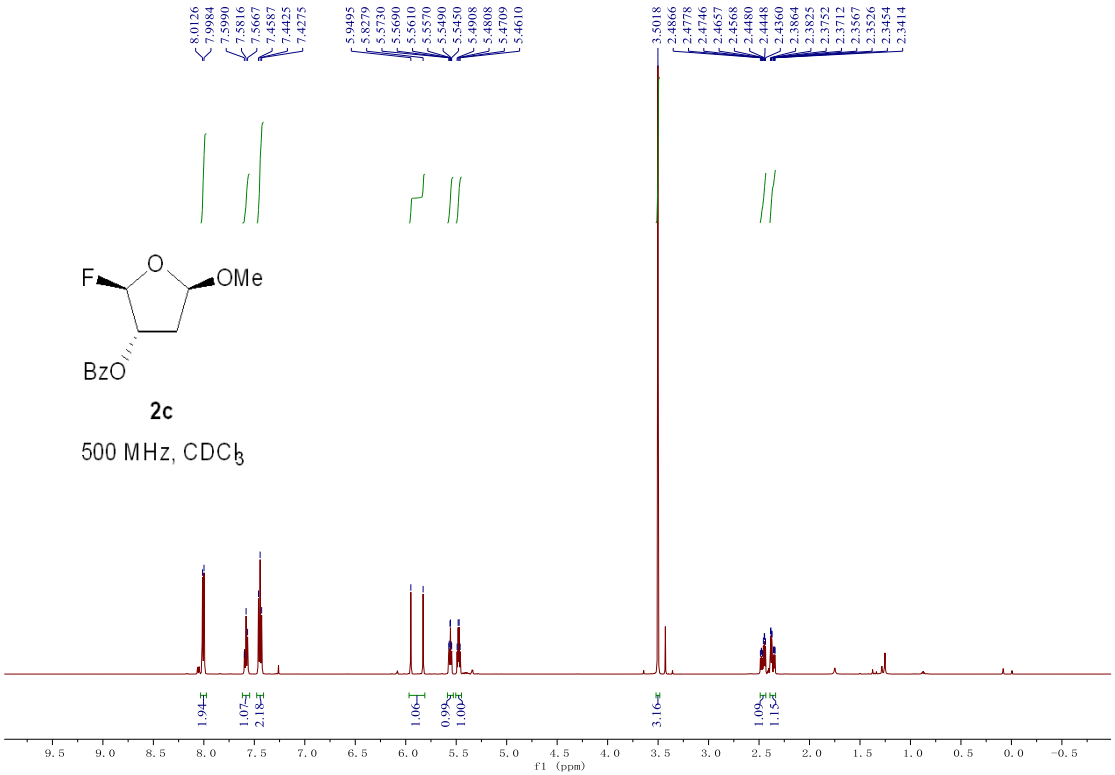
^{1}H NMR Spectrum of **2a**



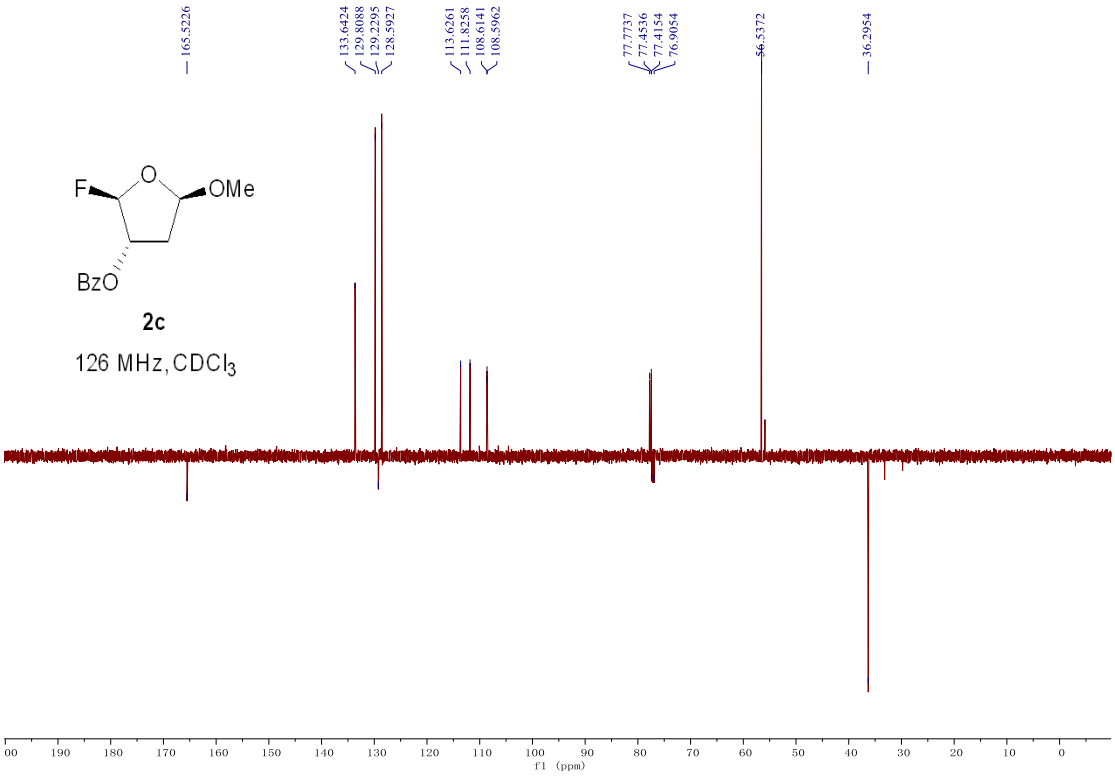
^{1}H NMR Spectrum of **2b**



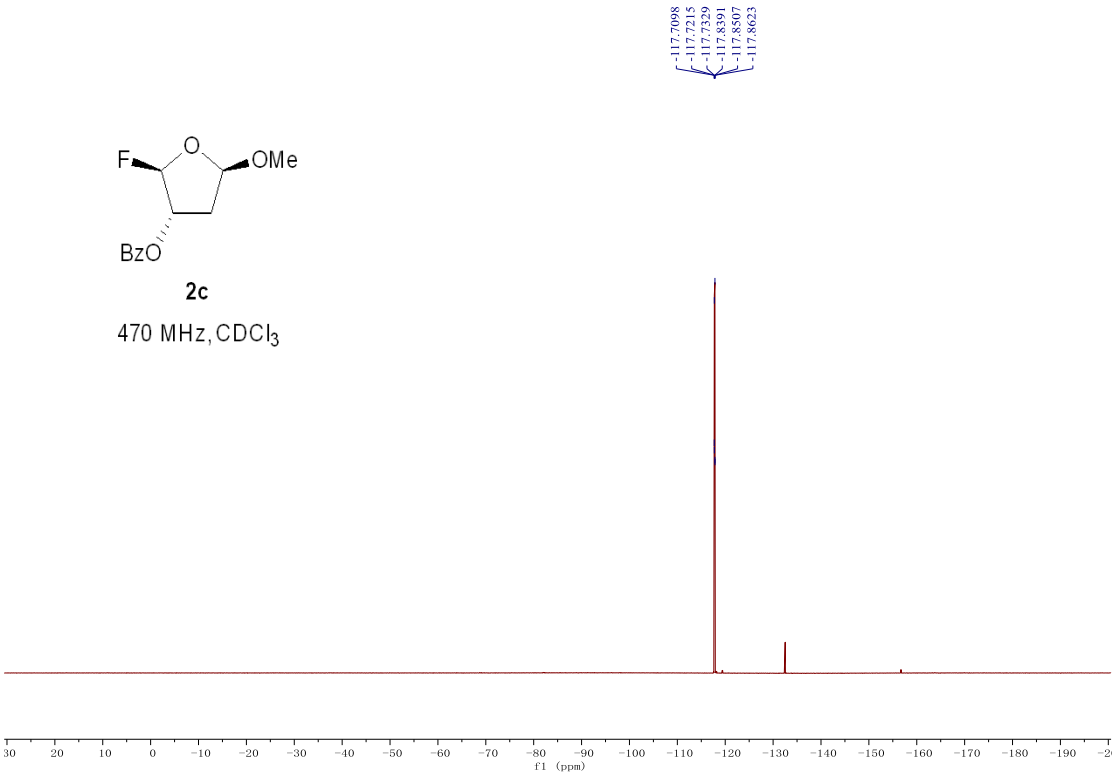
^{1}H NMR Spectrum of **2c**



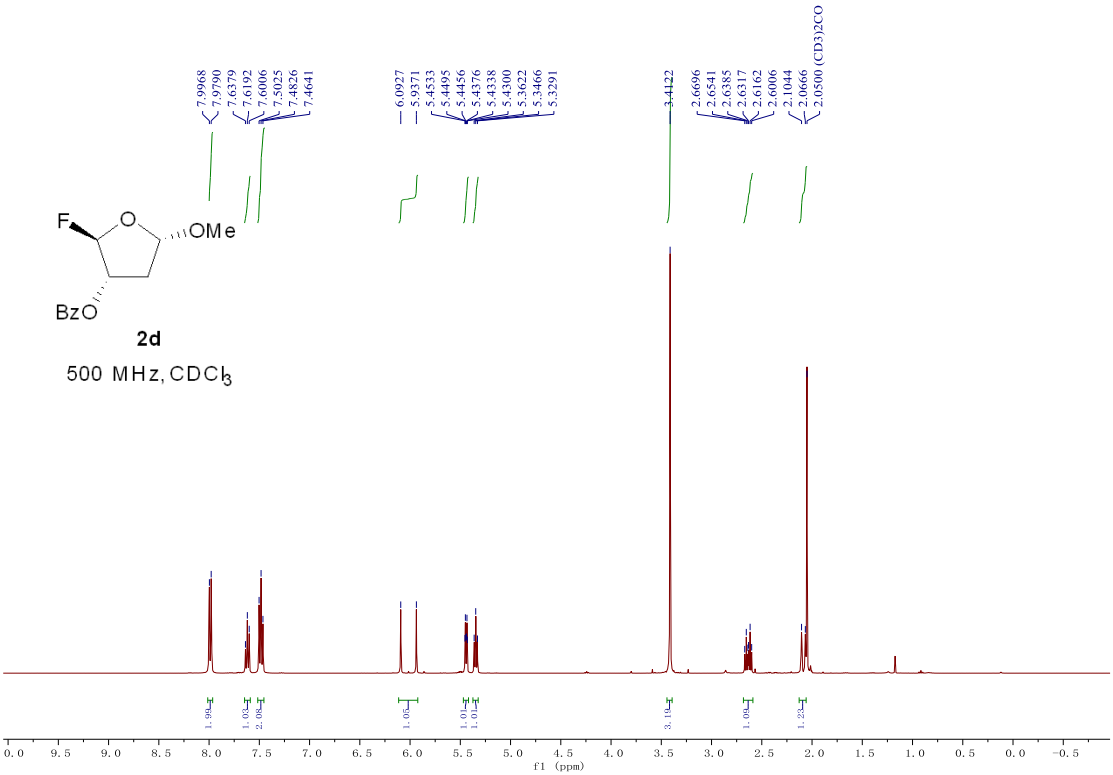
DEPT-Q NMR Spectrum of **2c**



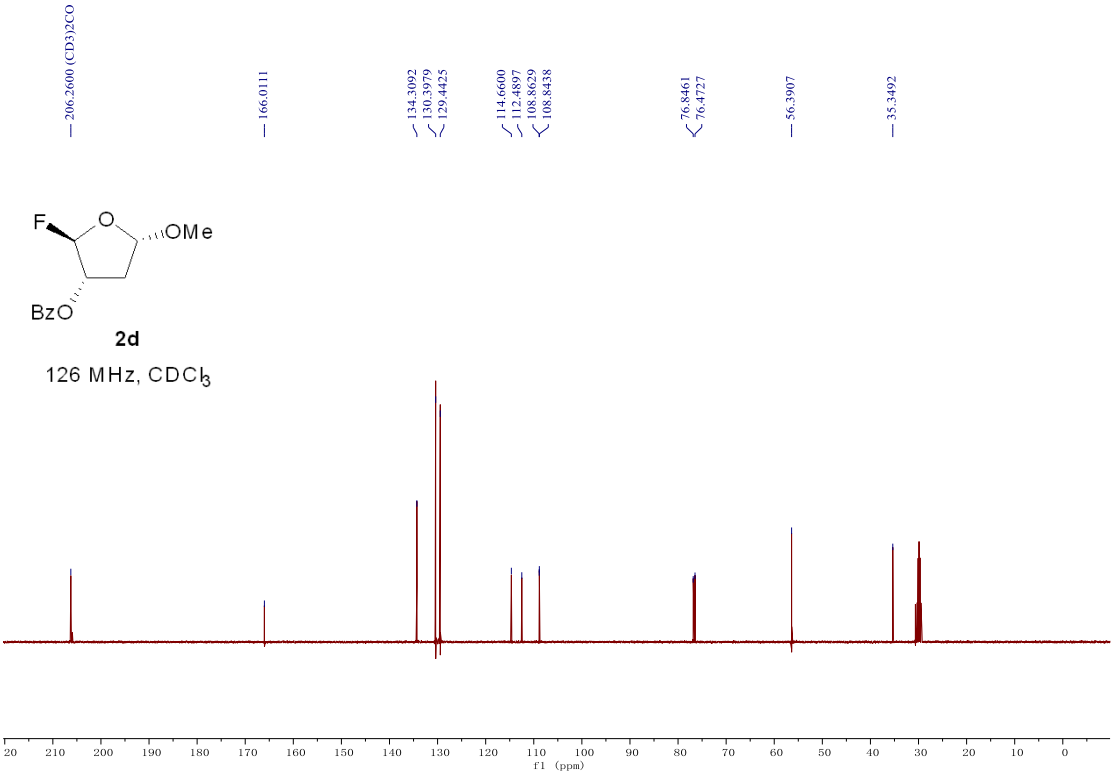
^{19}F NMR Spectrum of **2c**



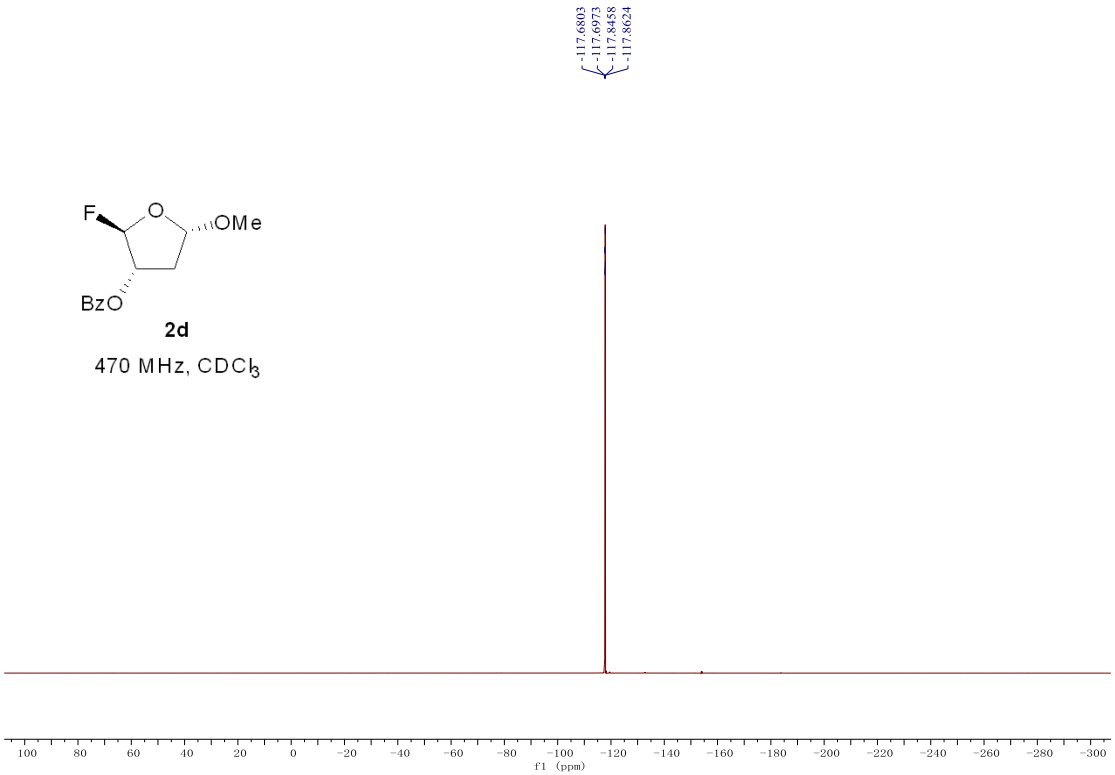
^{1}H NMR Spectrum of **2d**



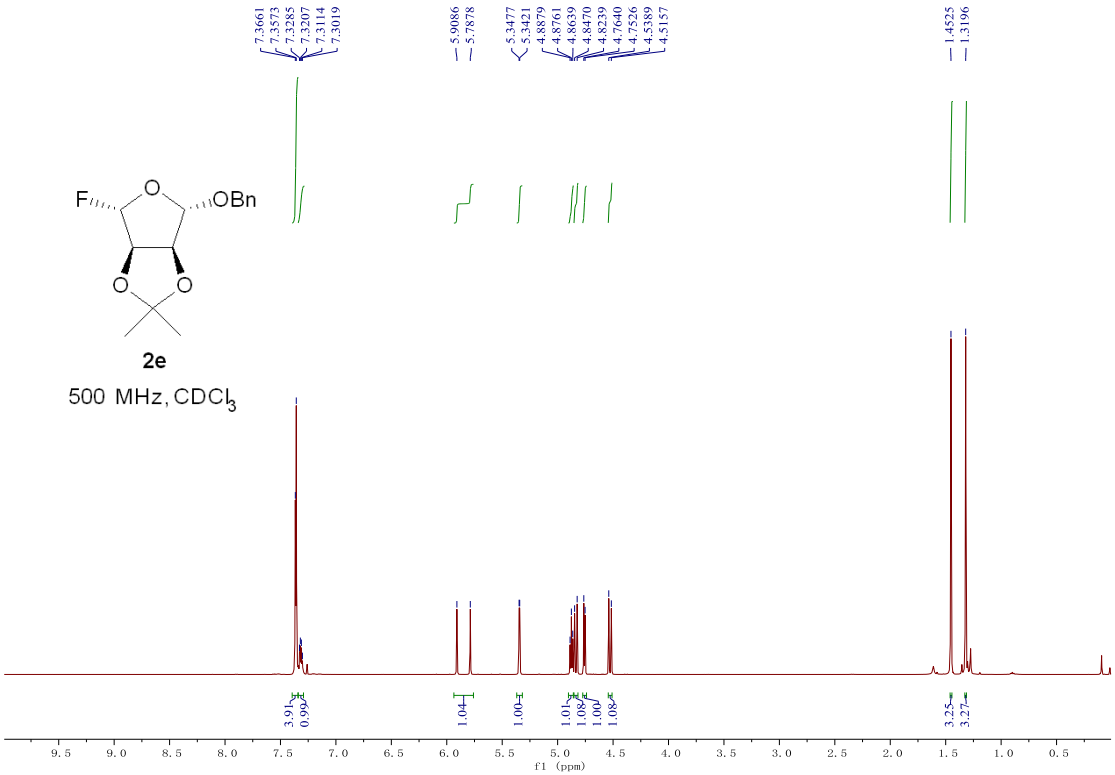
^{13}C NMR Spectrum of **2d**



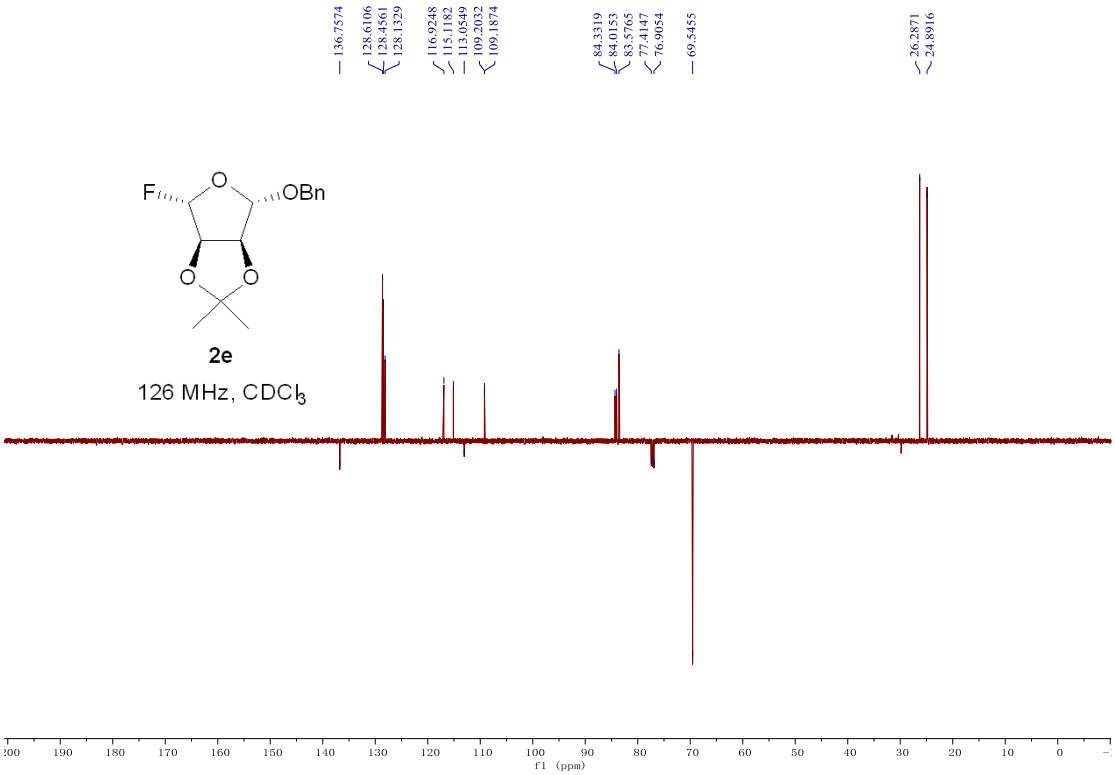
^{19}F NMR Spectrum of **2d**



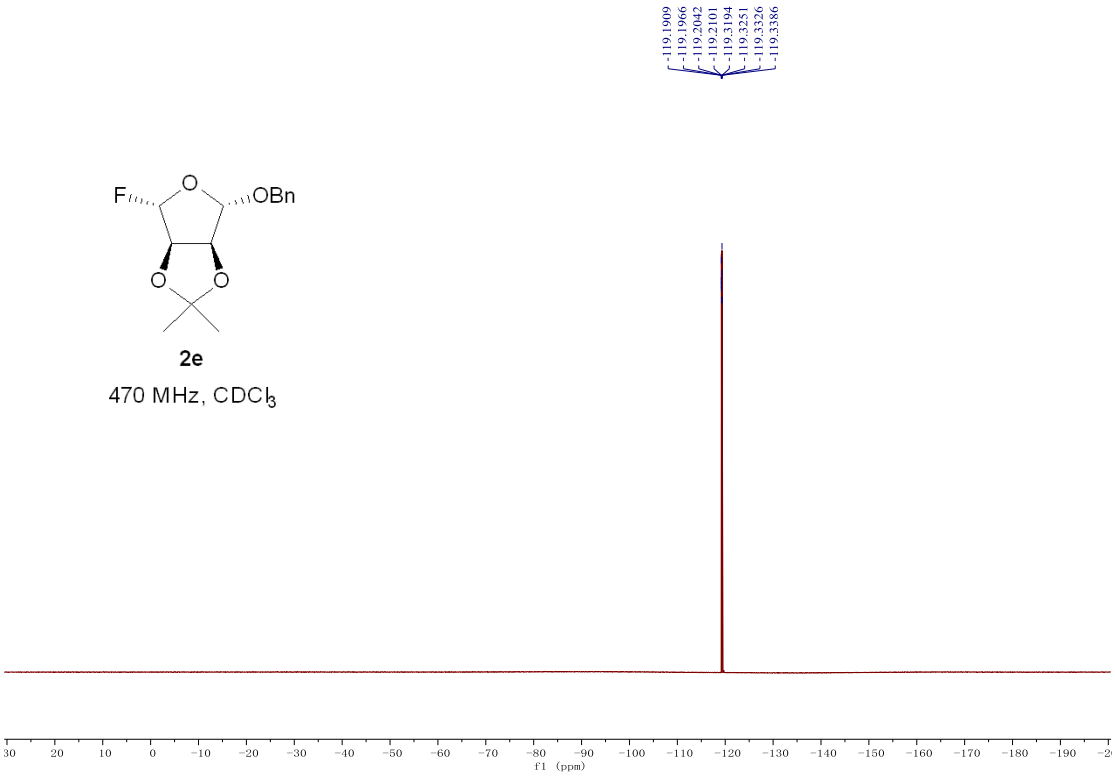
^{1}H NMR Spectrum of **2e**



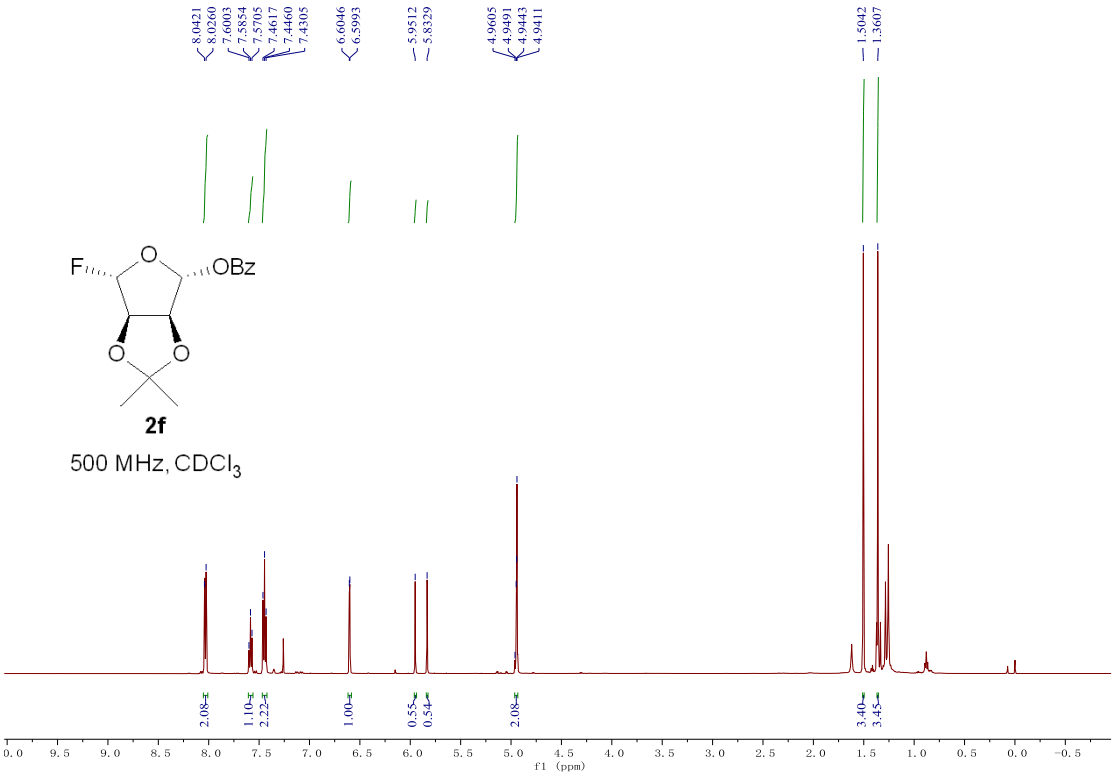
DEPT-Q NMR Spectrum of **2e**



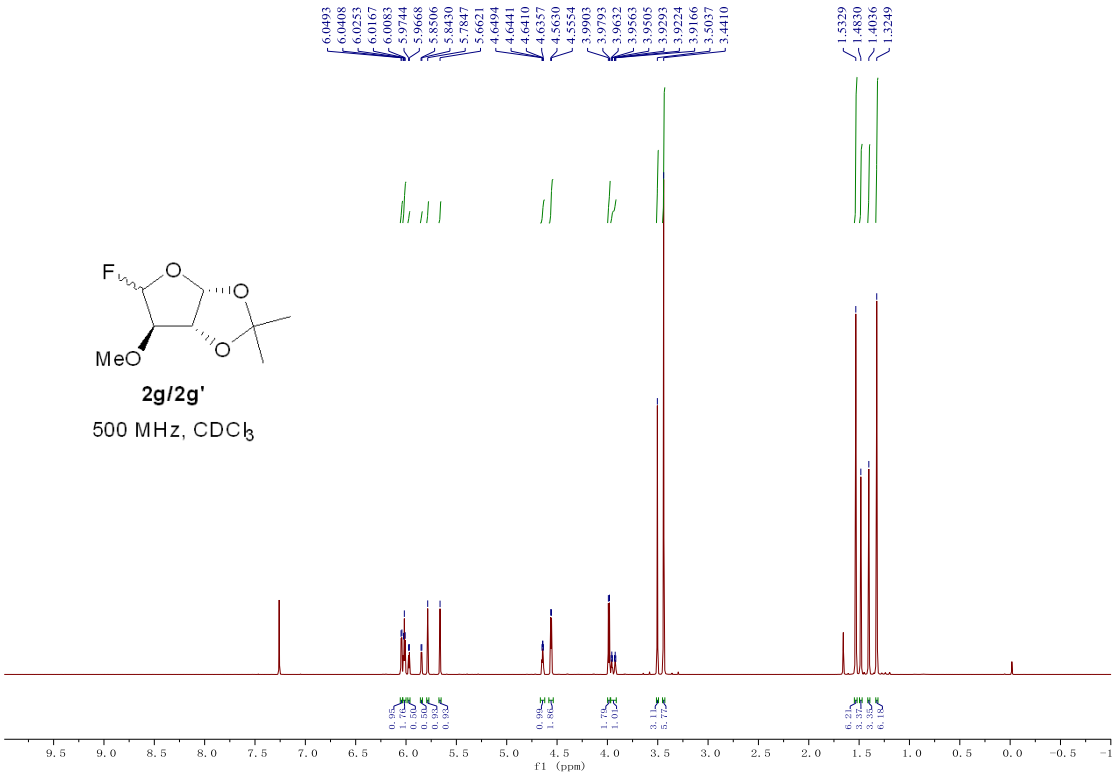
^{19}F NMR Spectrum of **2e**



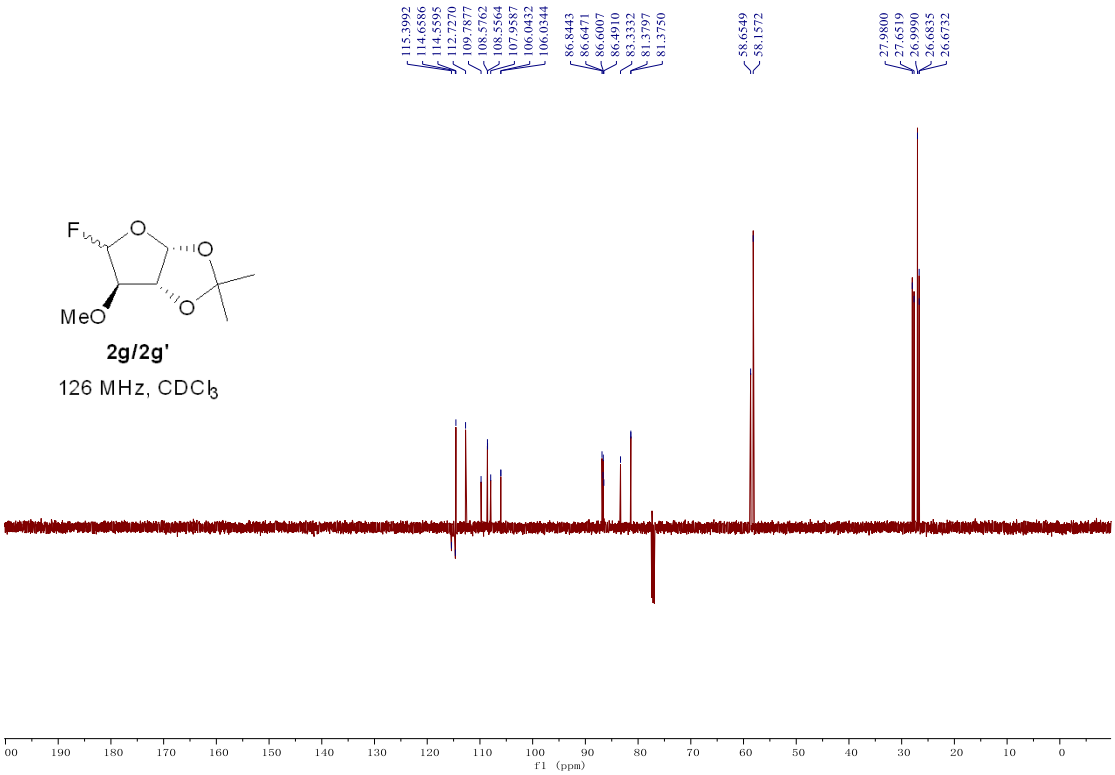
^{1}H NMR Spectrum of **2f**



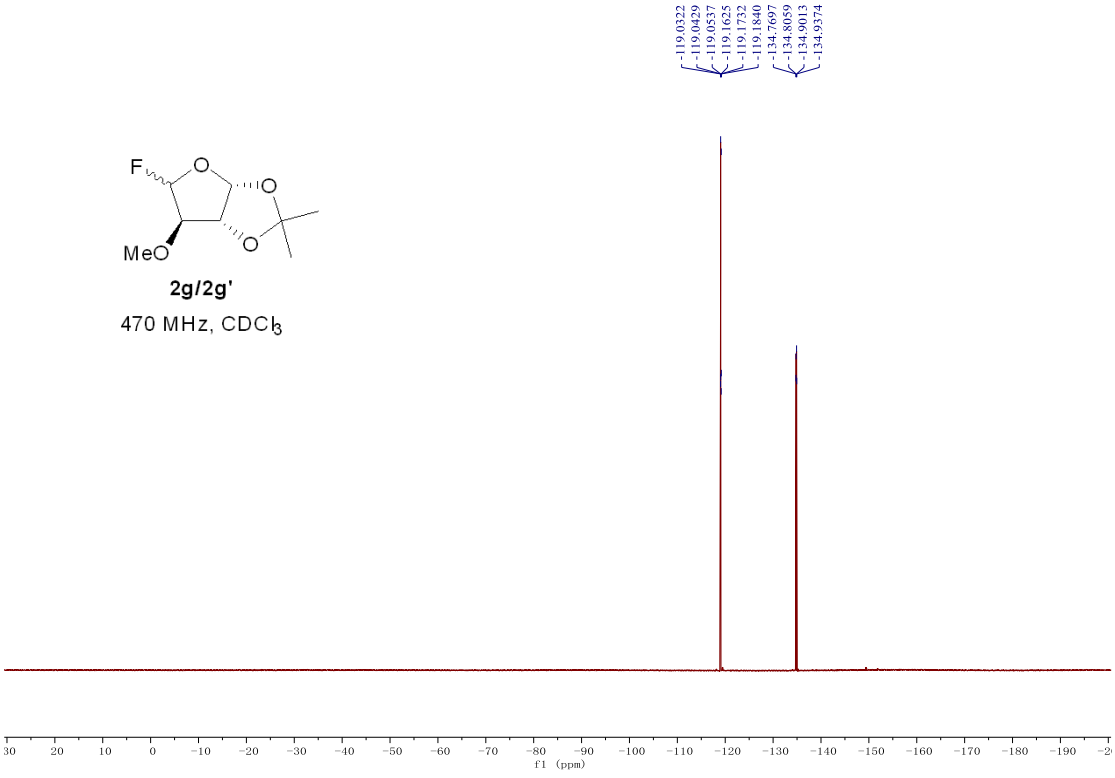
^{1}H NMR Spectrum of **2g/2g'**



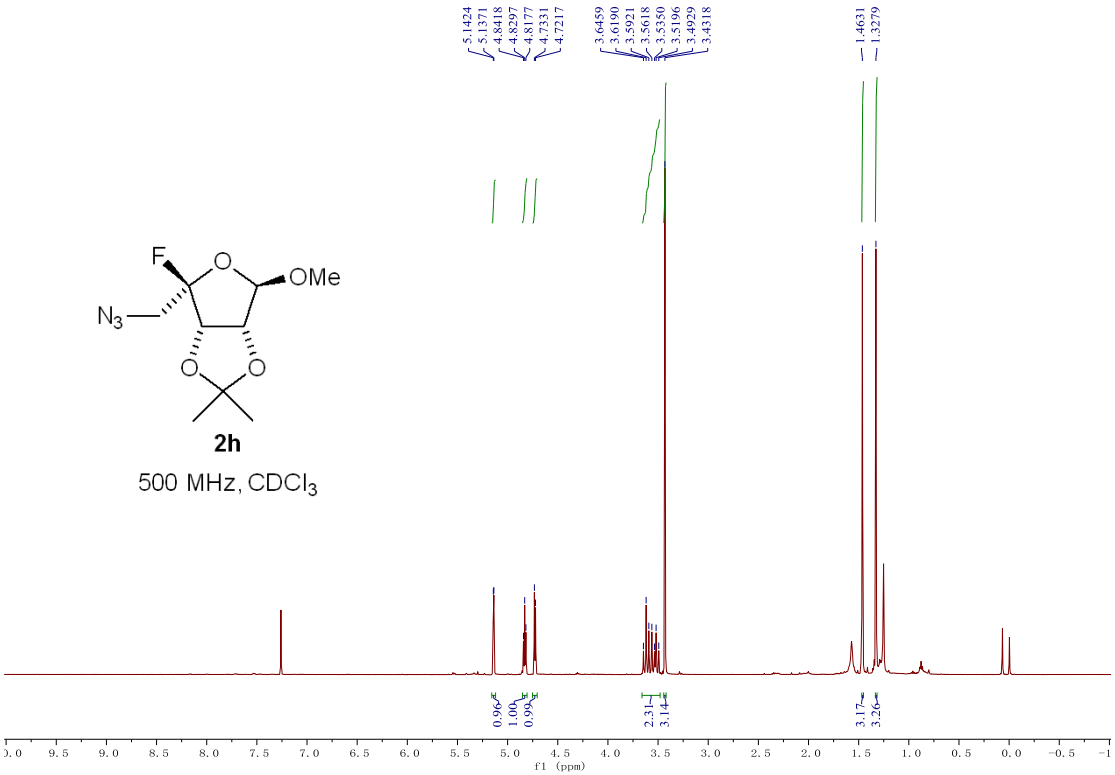
DEPT-Q NMR Spectrum of **2g/2g'**



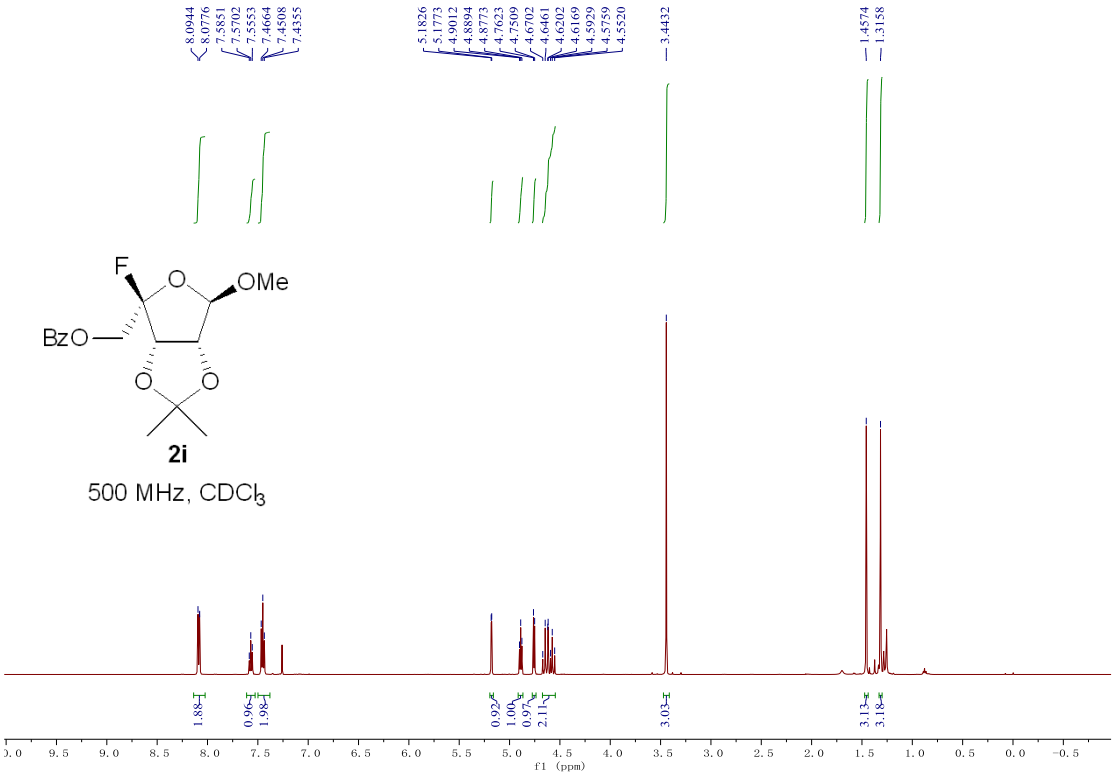
^{19}F NMR Spectrum of **2g/2g'**



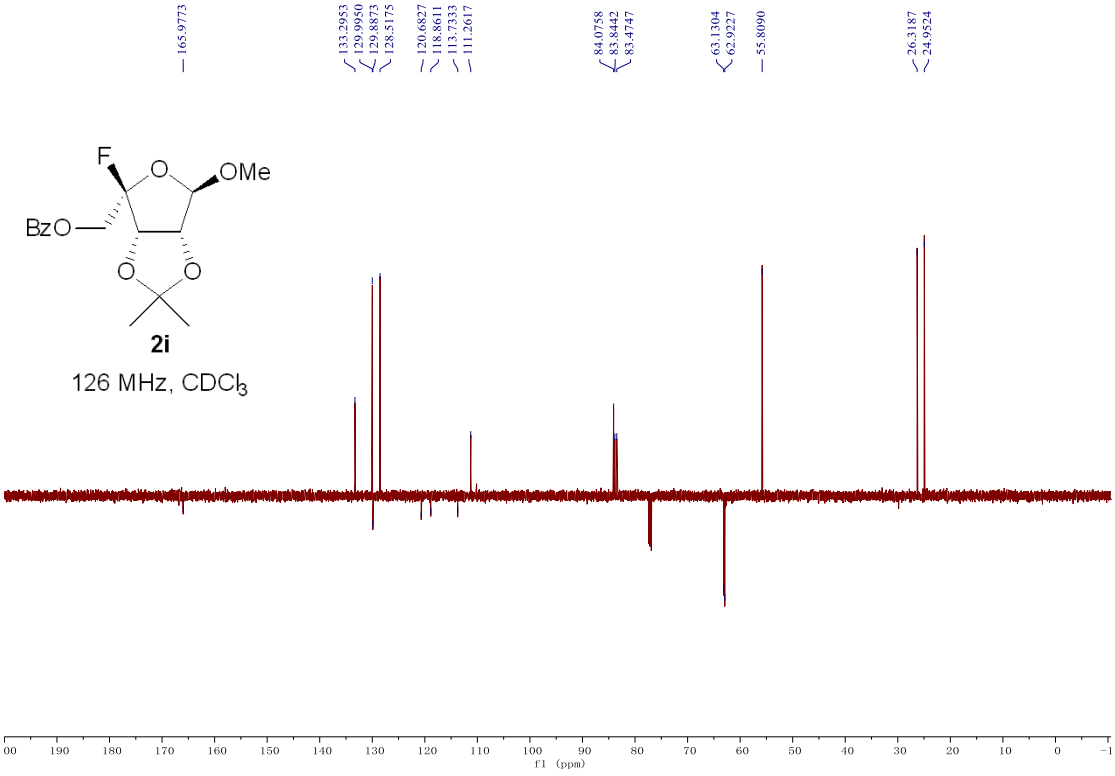
^{1}H NMR Spectrum of **2h**



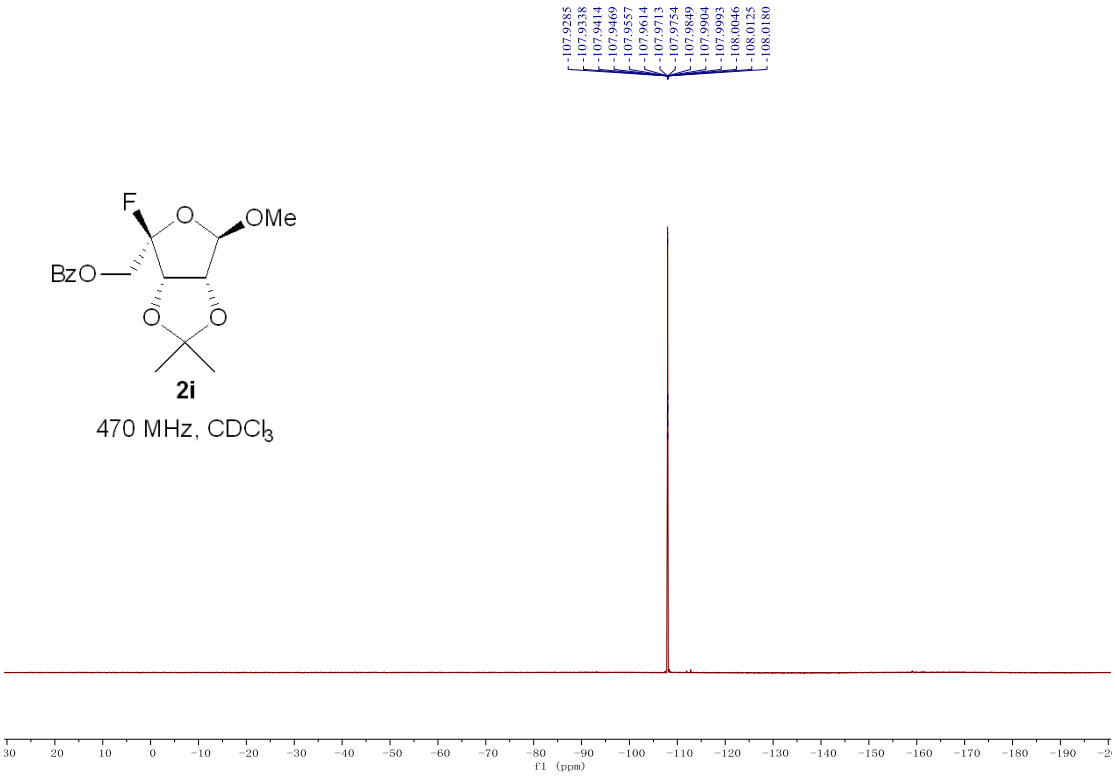
^{1}H NMR Spectrum of **2i**



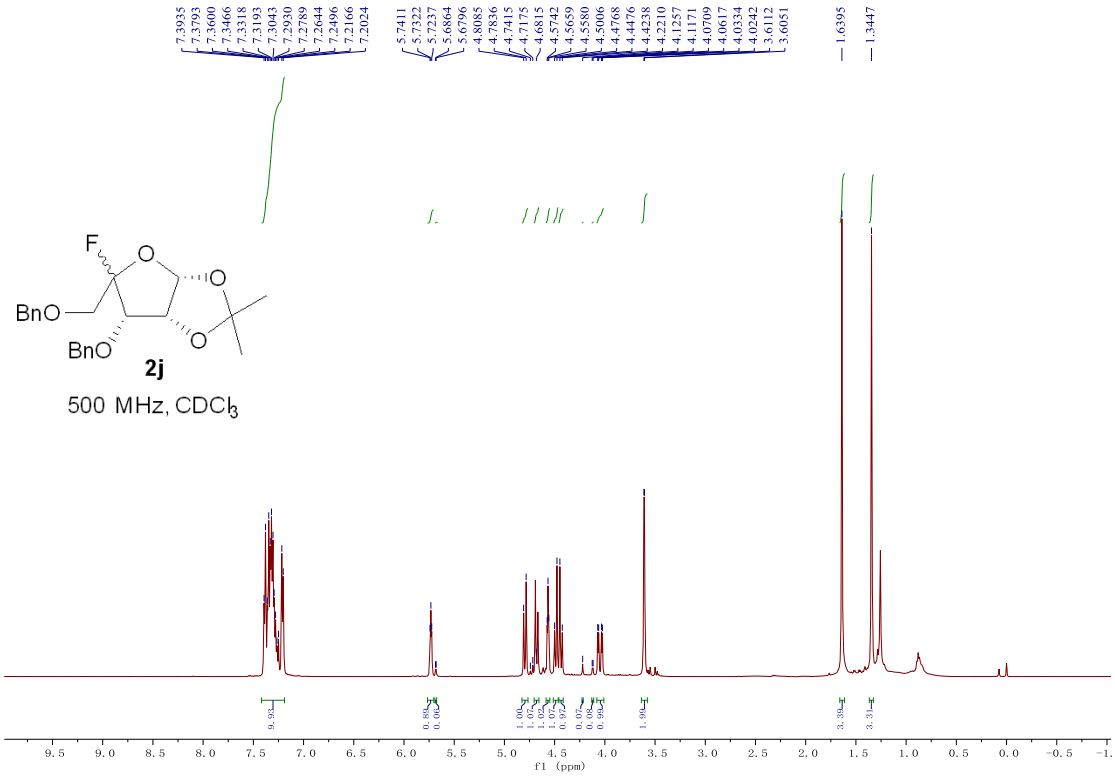
DEPT-Q NMR Spectrum of **2i**



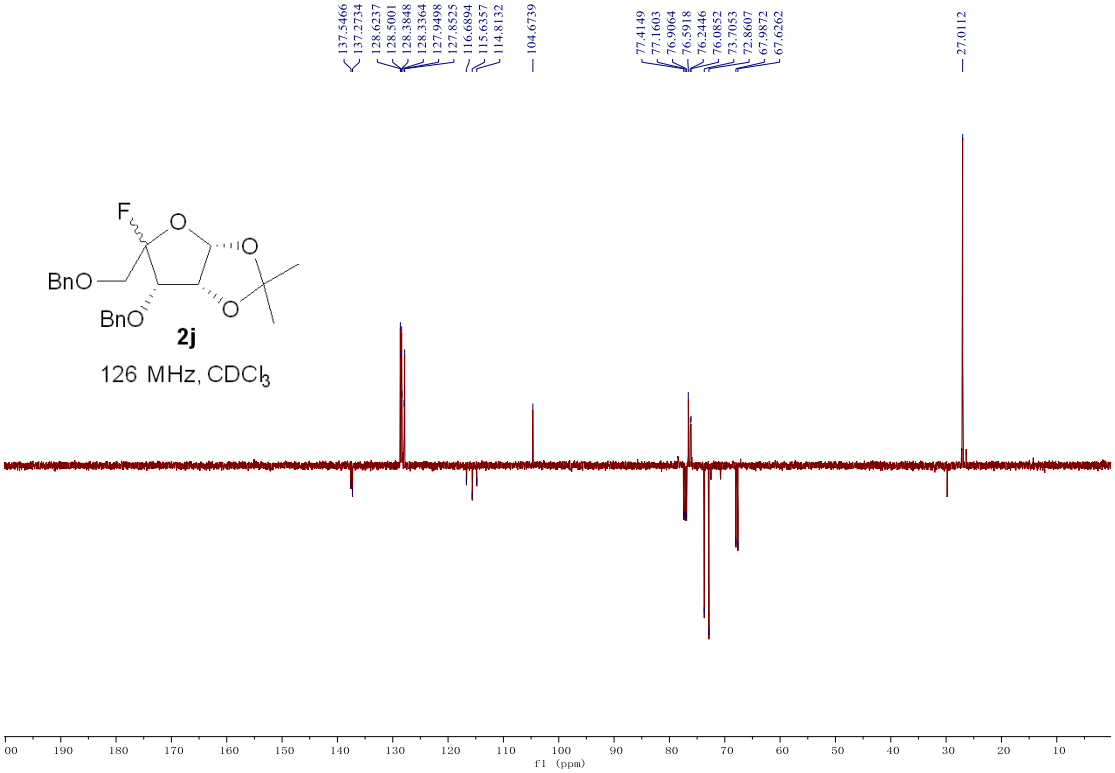
^{19}F NMR Spectrum of **2i**



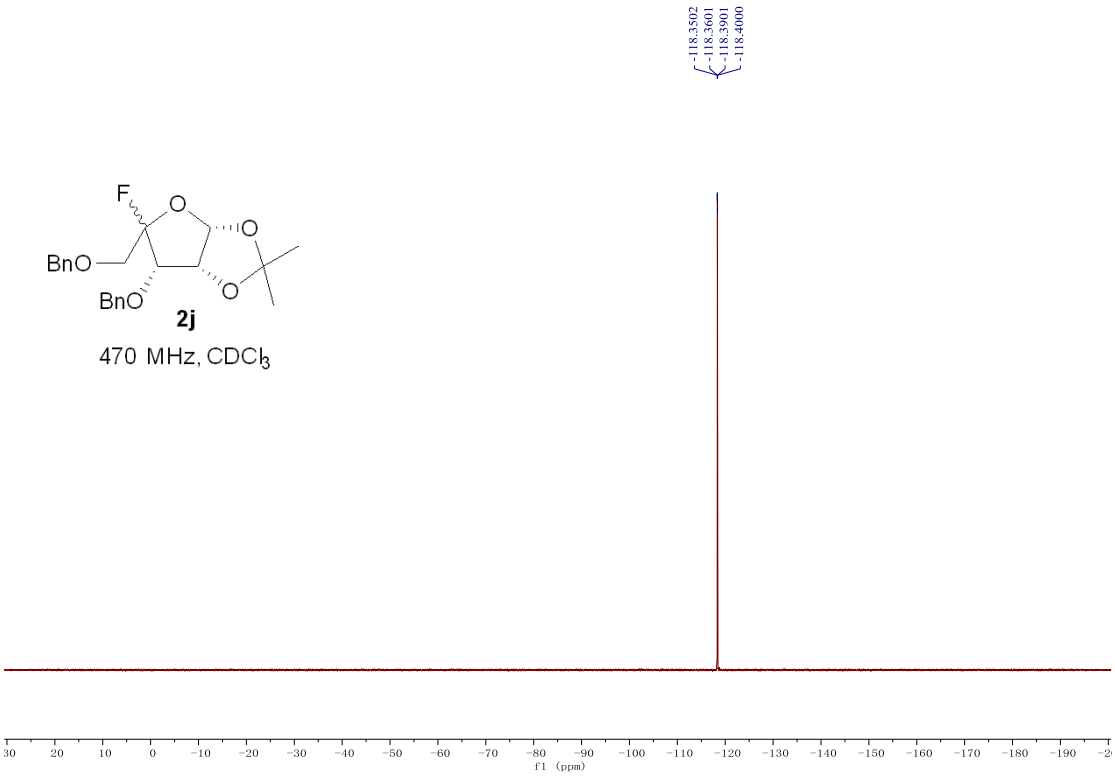
^{1}H NMR Spectrum of **2j**



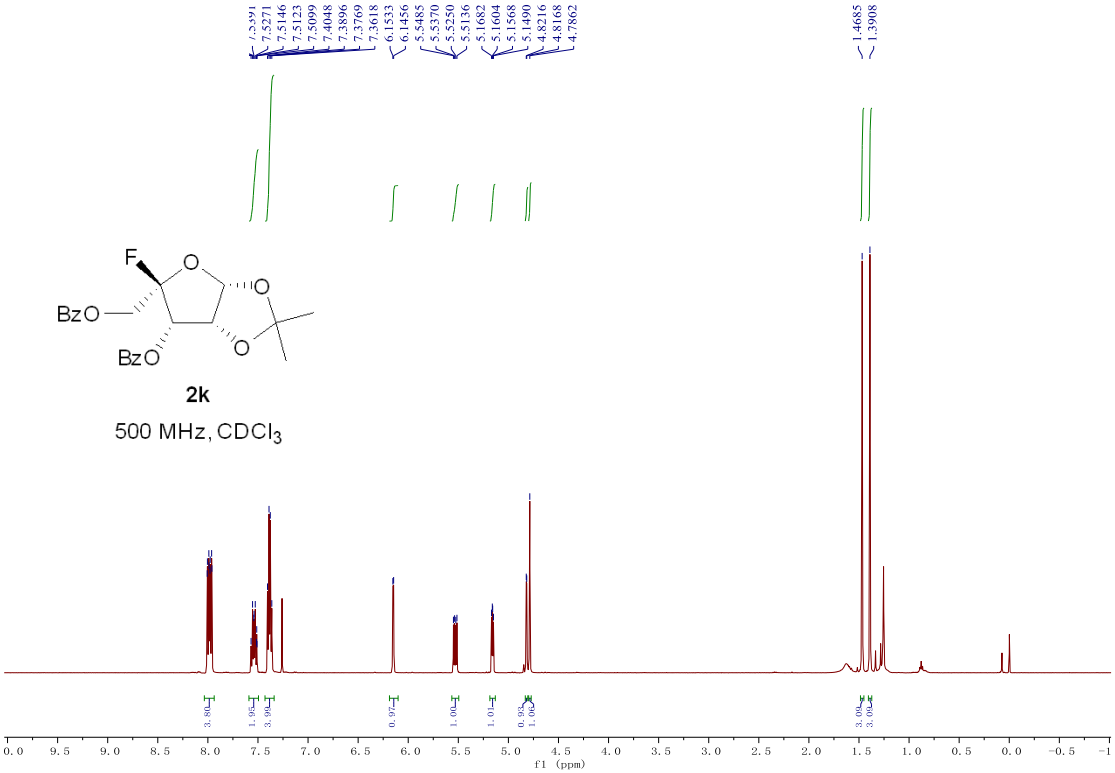
DEPT-Q NMR Spectrum of **2j**



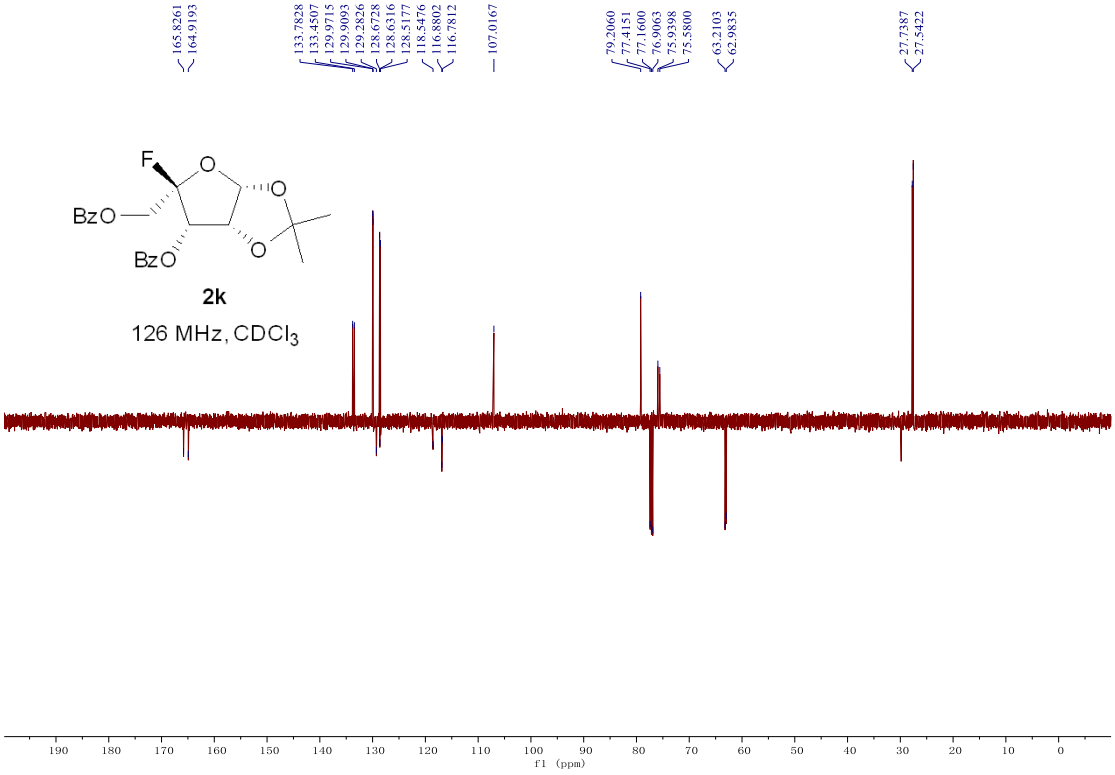
^{19}F NMR Spectrum of **2j**



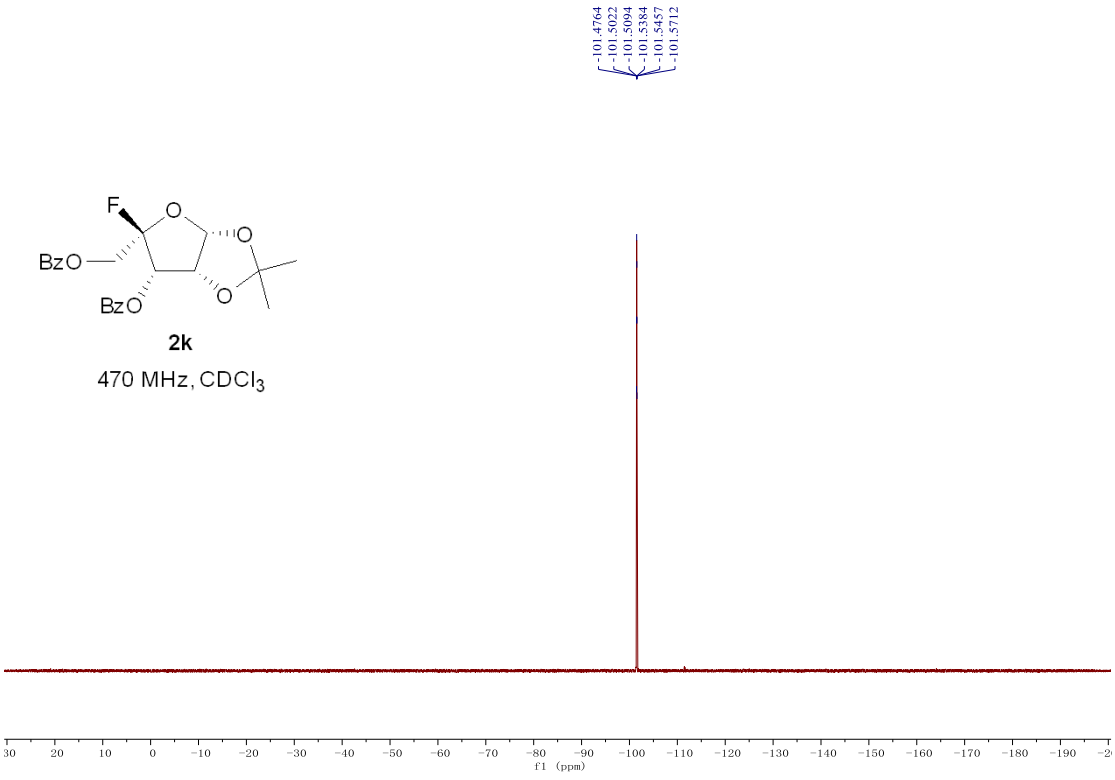
^{1}H NMR Spectrum of **2k**



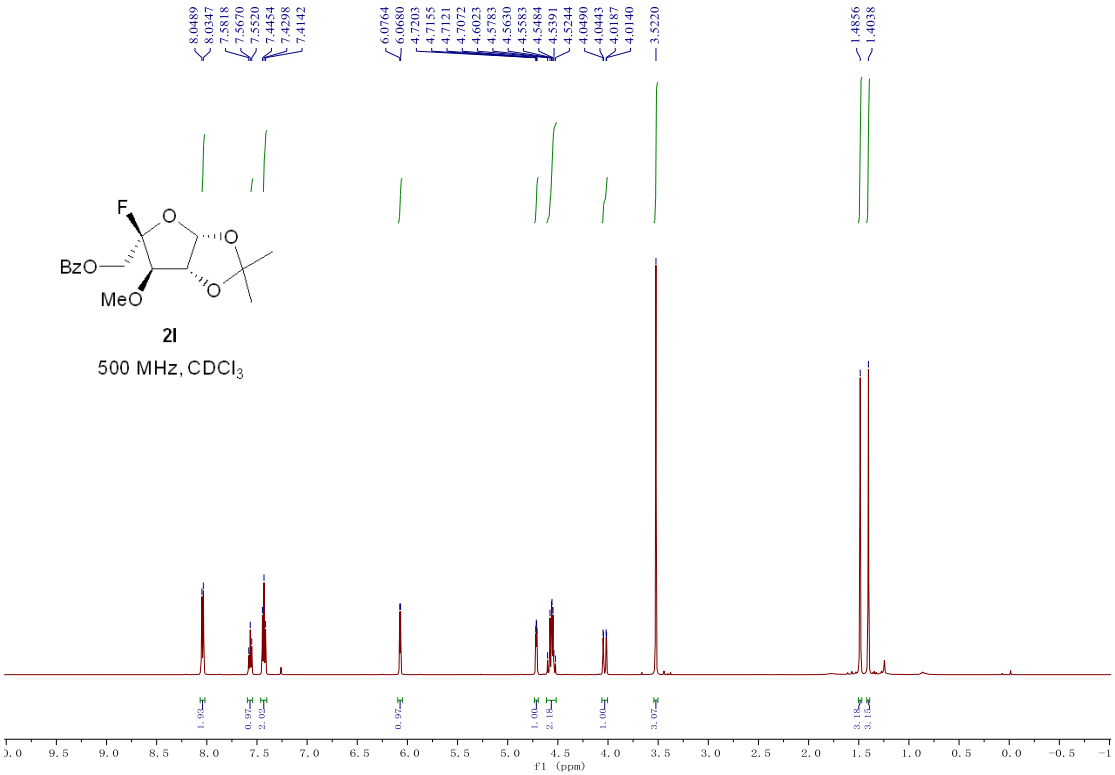
DEPT-Q NMR Spectrum of **2k**



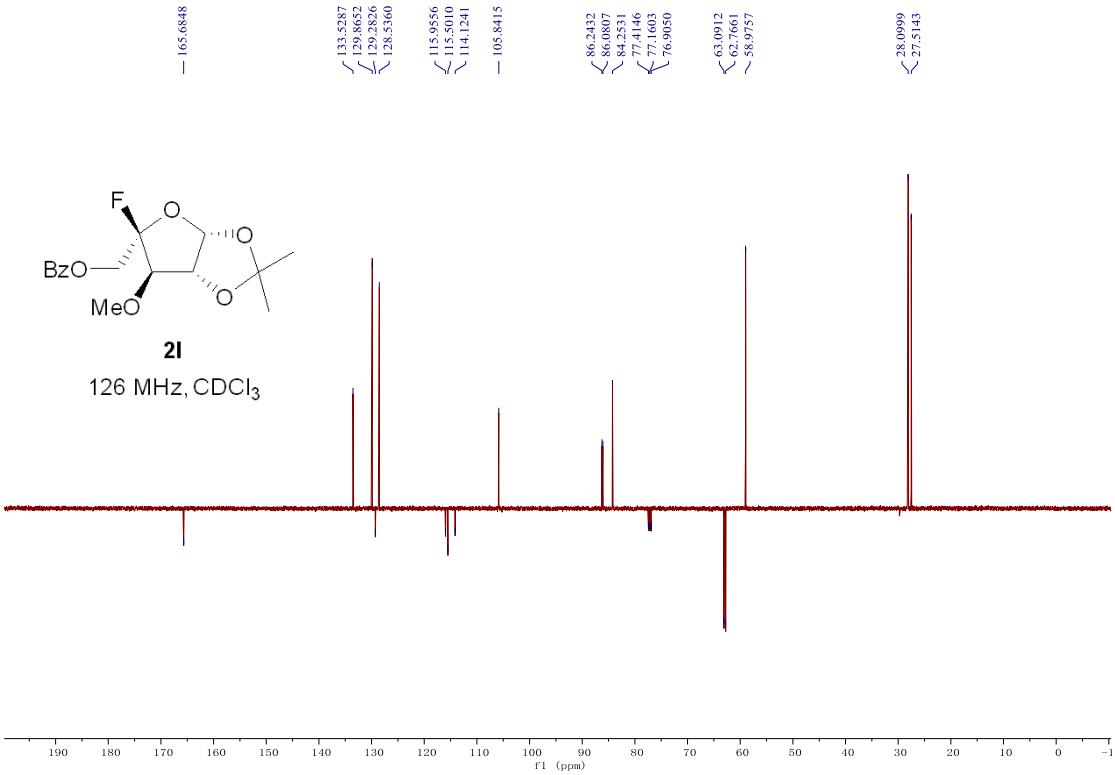
^{19}F NMR Spectrum of **2k**



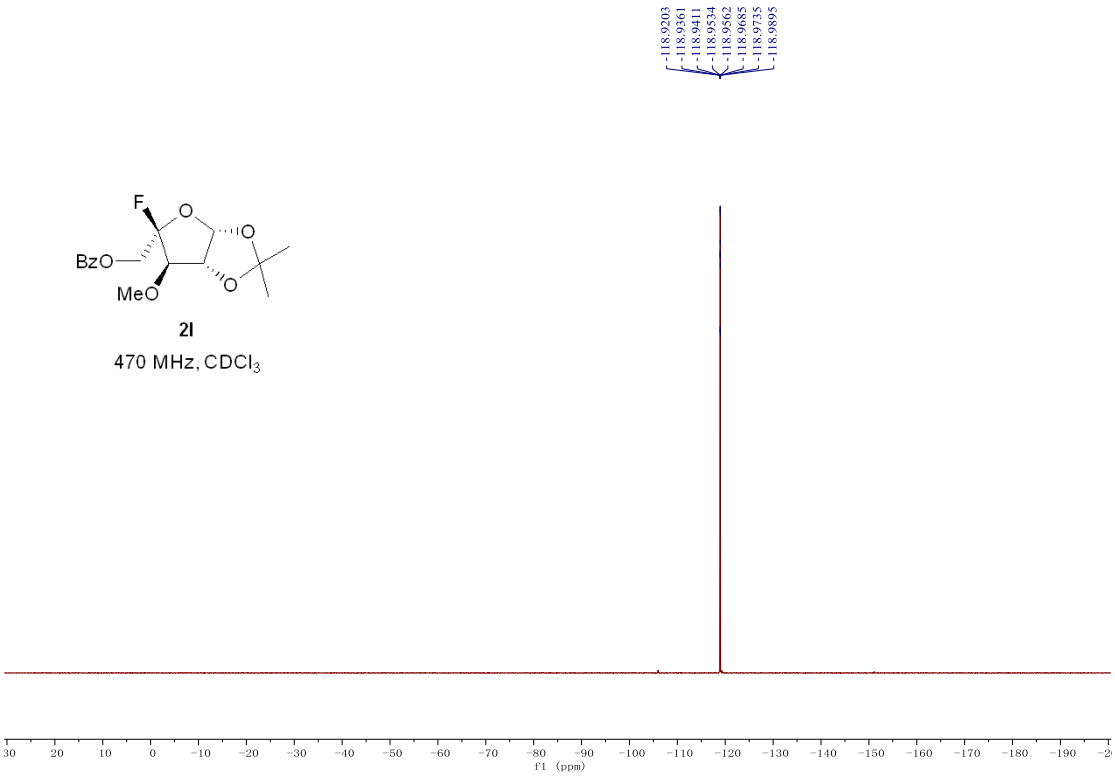
^{1}H NMR Spectrum of **2l**



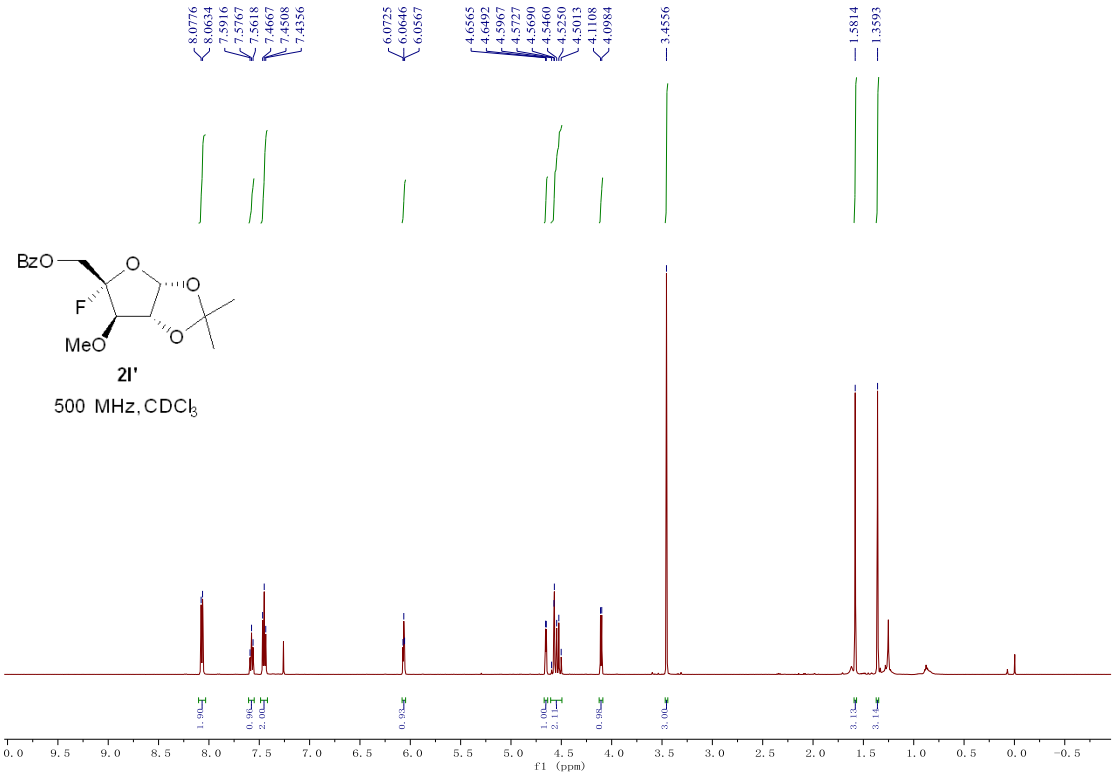
DEPT-Q NMR Spectrum of **2l**



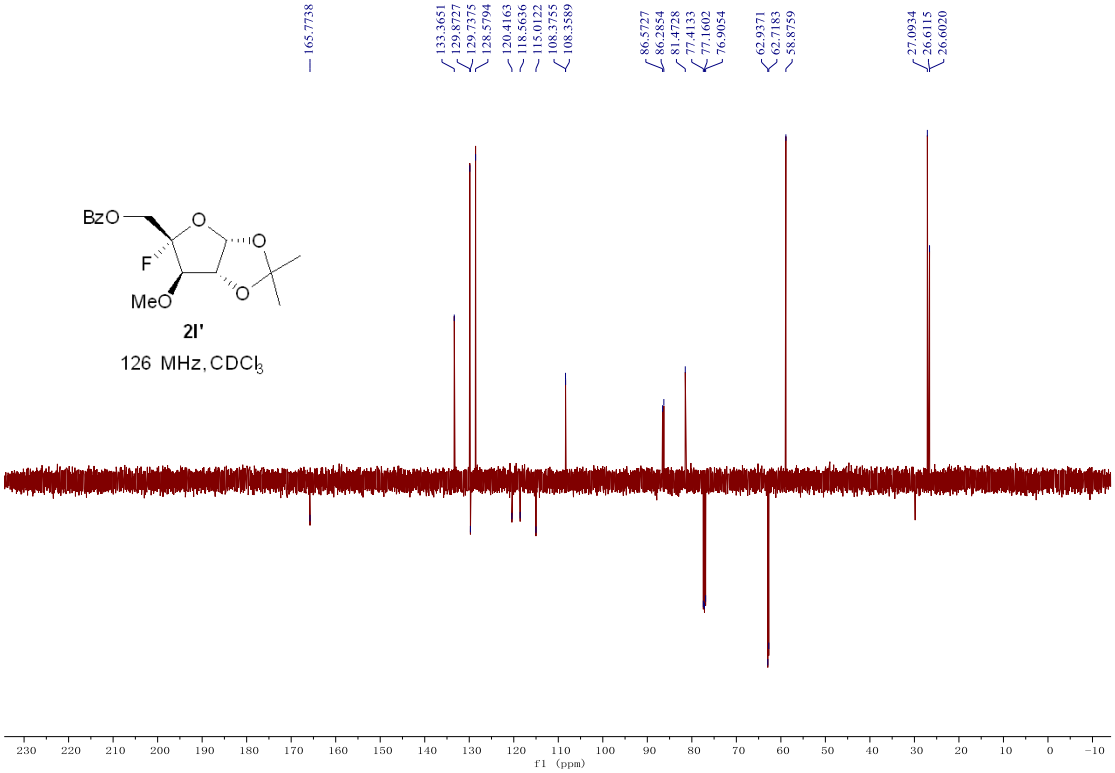
^{19}F NMR Spectrum of **2l**



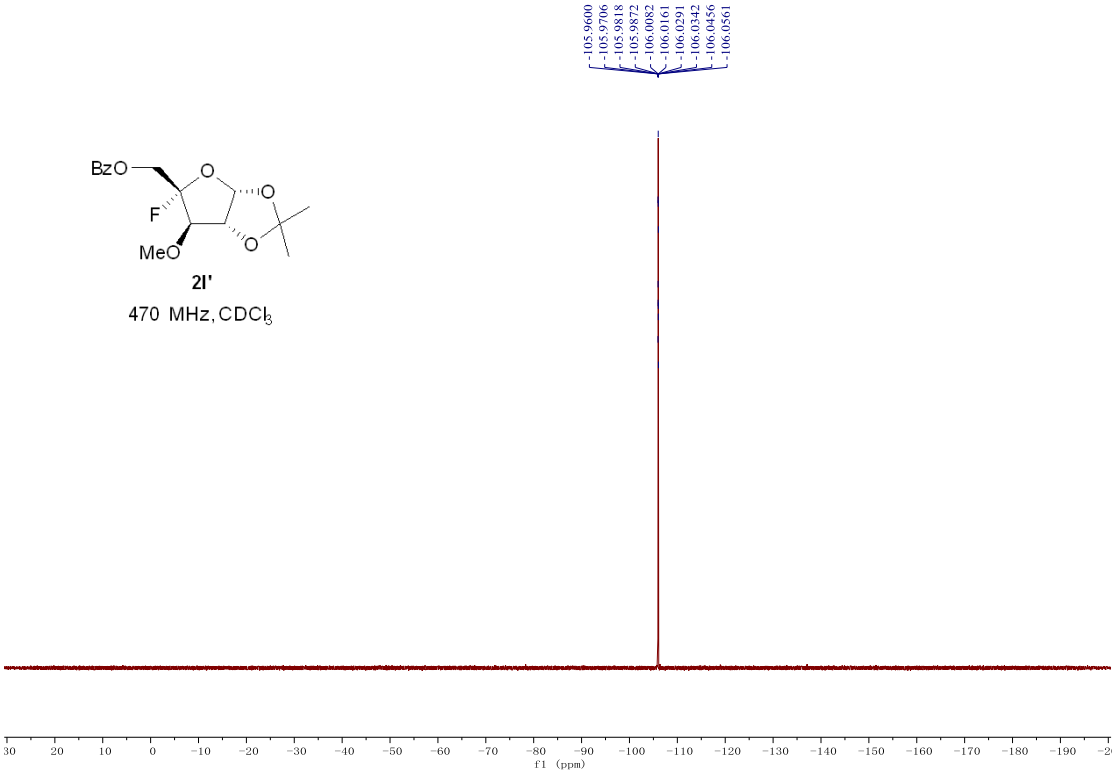
^{1}H NMR Spectrum of **2l'**



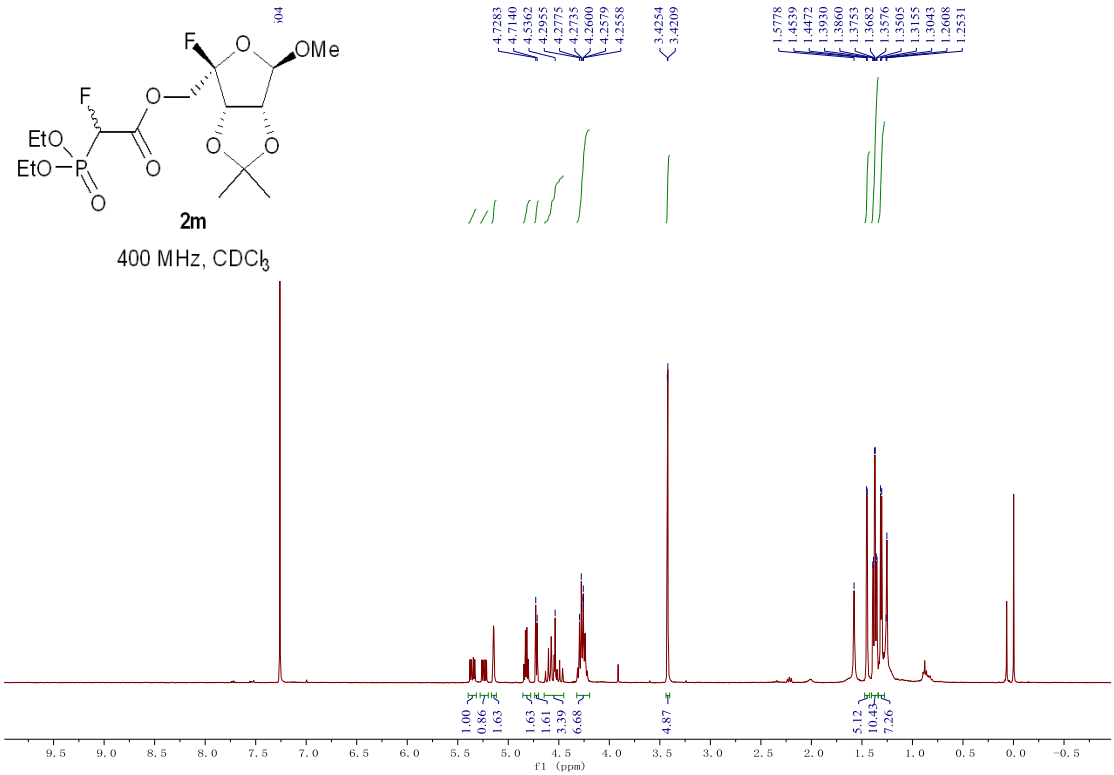
DEPT-Q NMR Spectrum of **2l'**



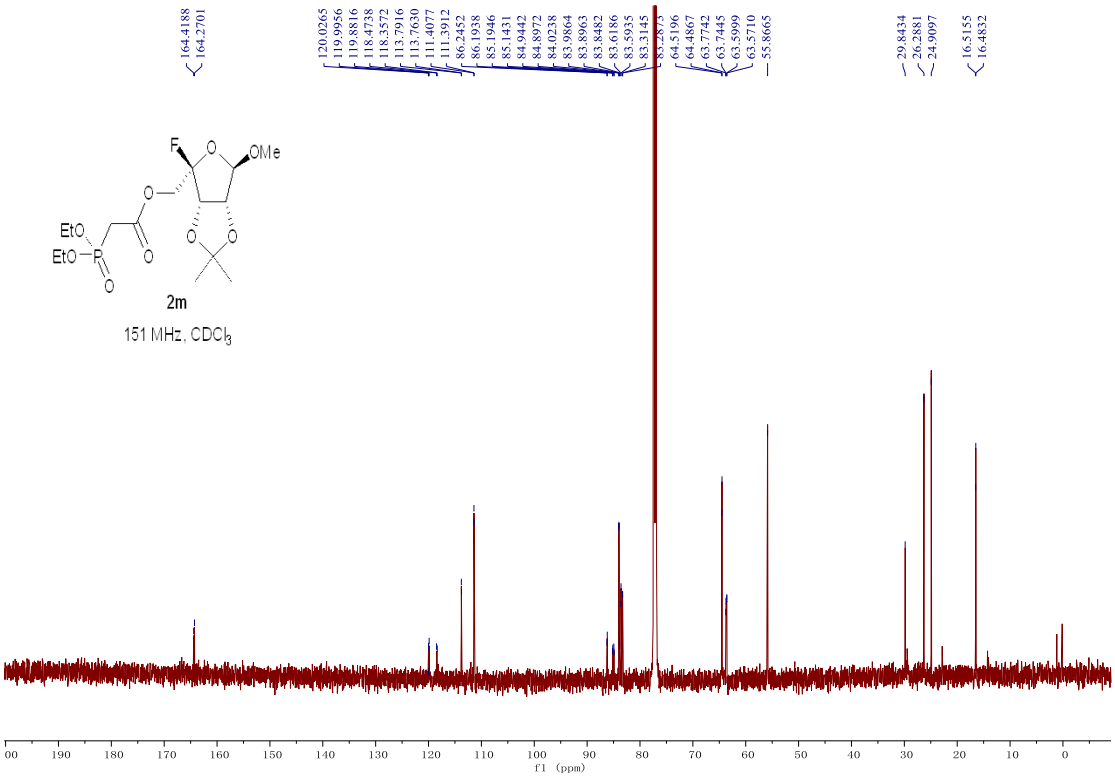
^{19}F NMR Spectrum of **2l'**



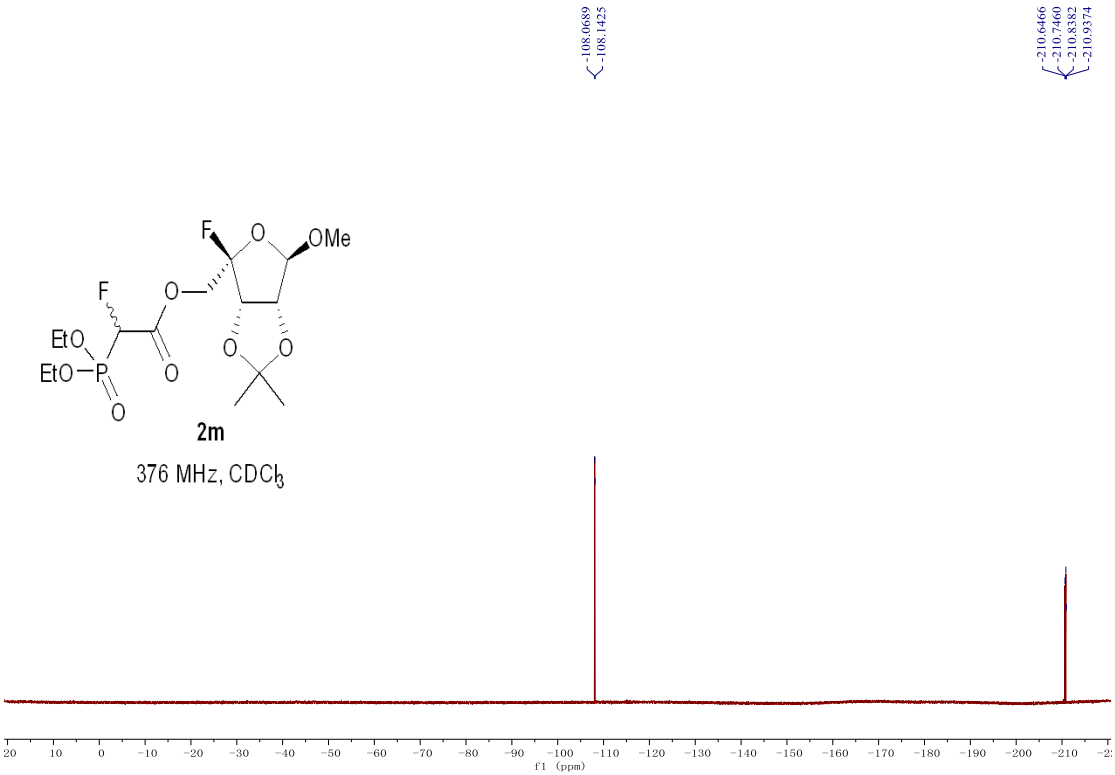
^{1}H NMR Spectrum of **2m**



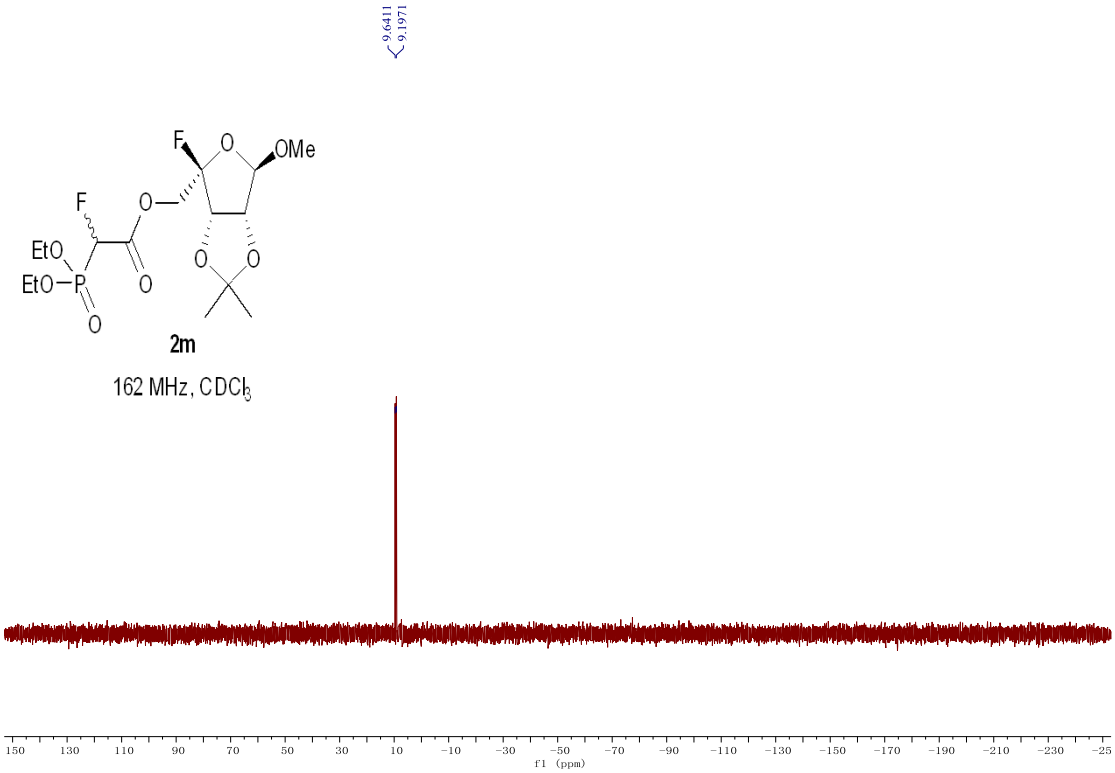
DEPT-Q NMR Spectrum of **2m**



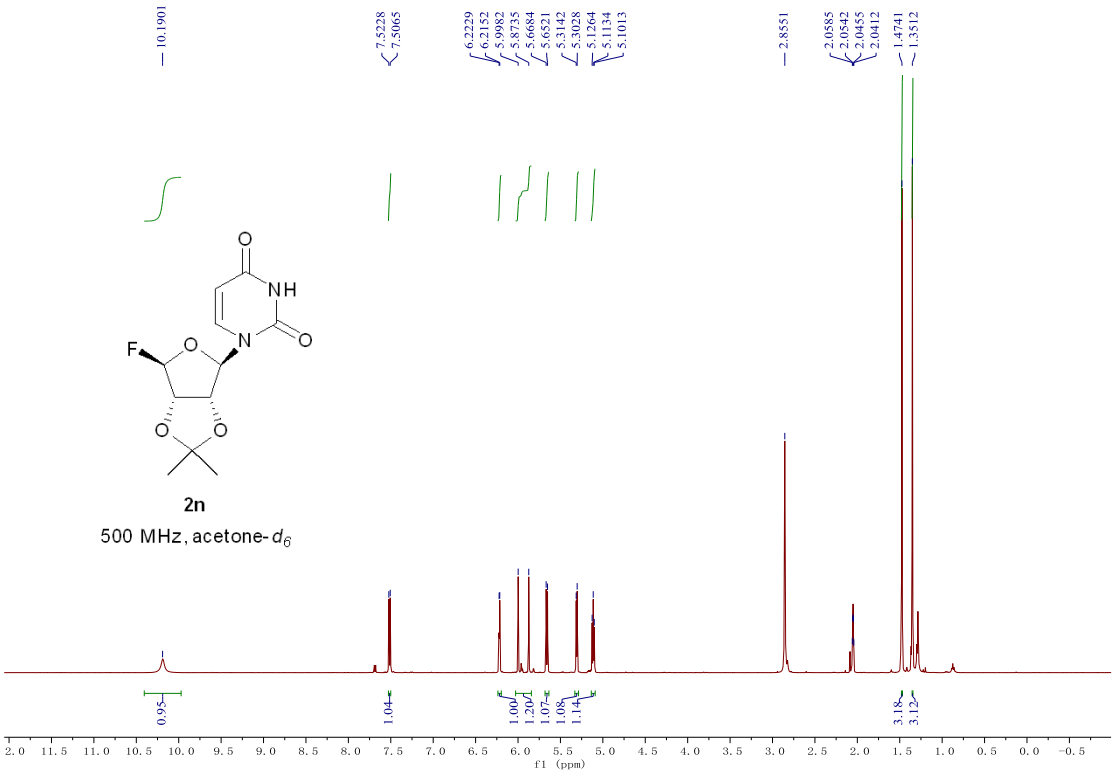
^{19}F NMR Spectrum of **2m**



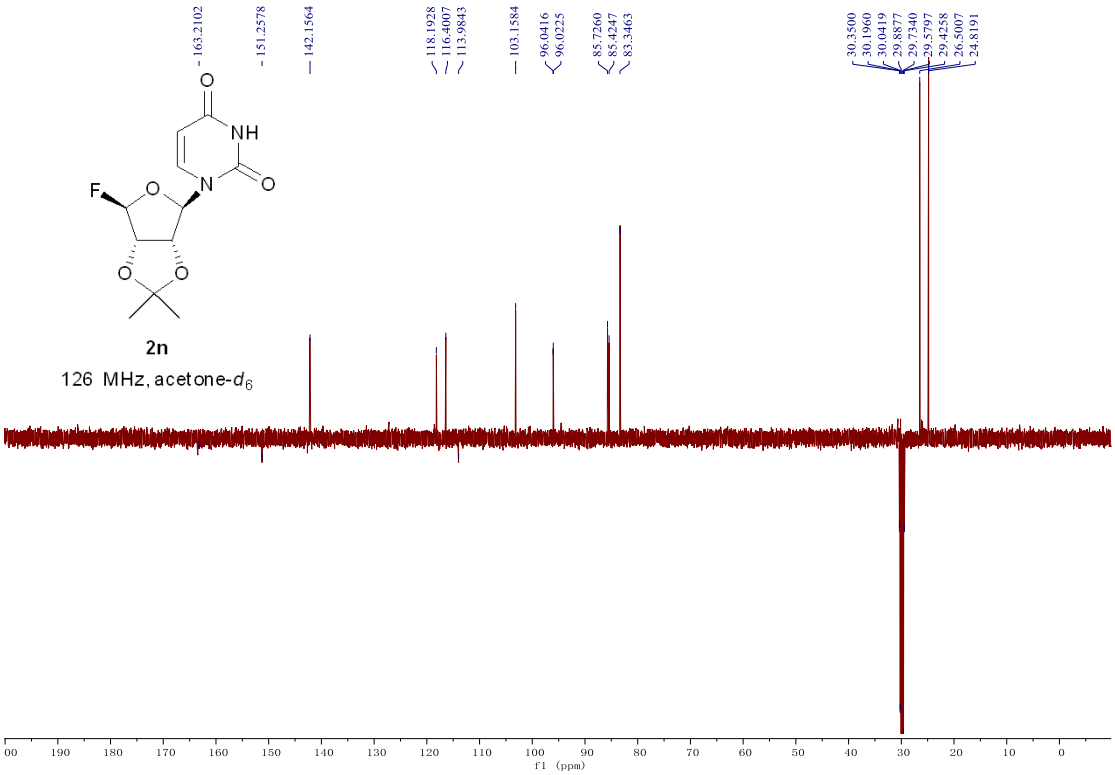
^{31}P NMR Spectrum of **2m**



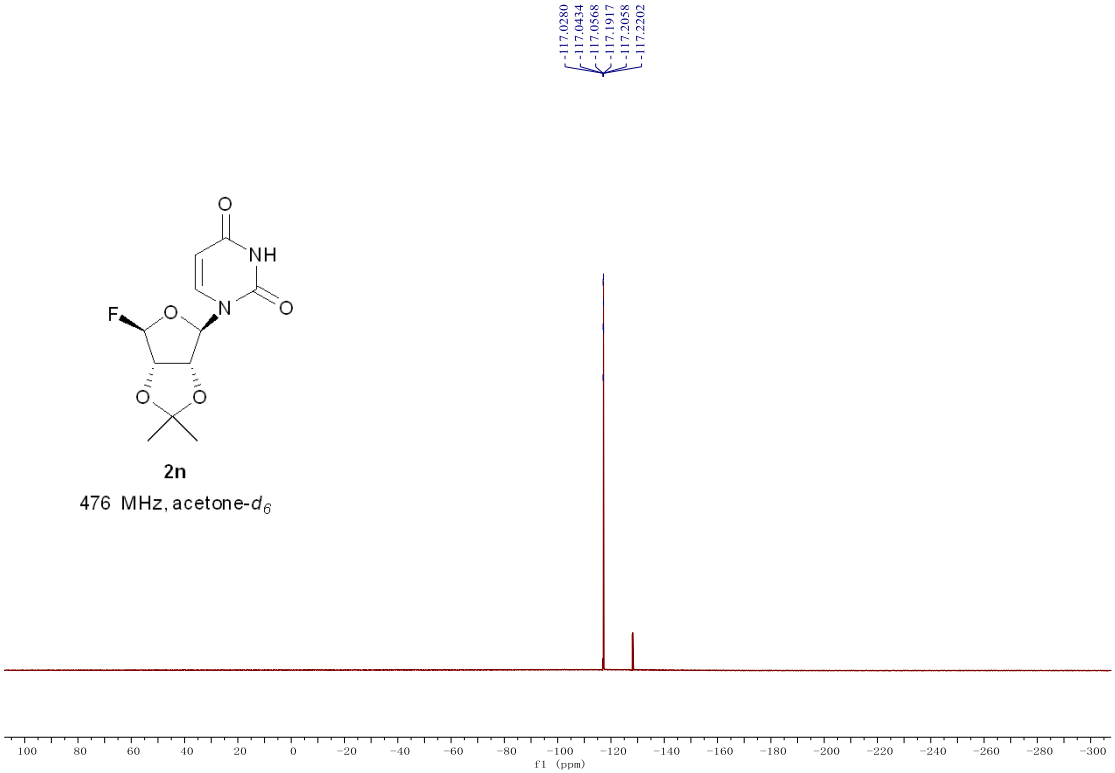
^{1}H NMR Spectrum of **2n**



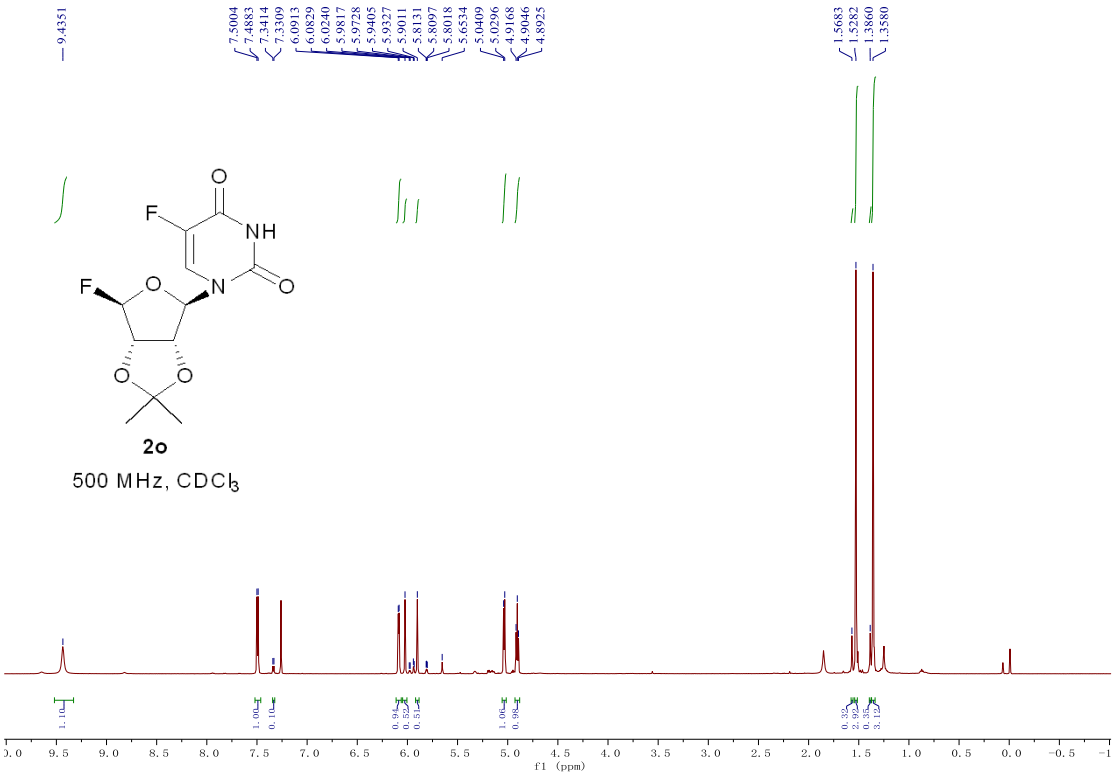
DEPT-Q NMR Spectrum of **2n**



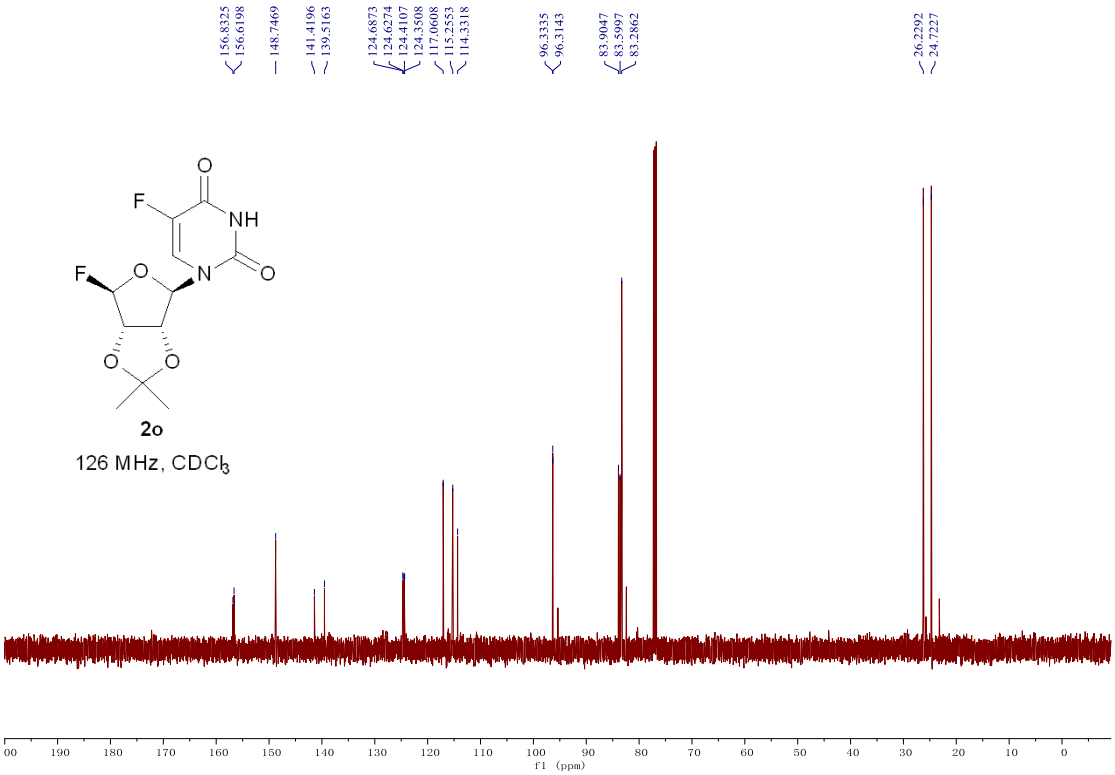
^{19}F NMR Spectrum of **2n**



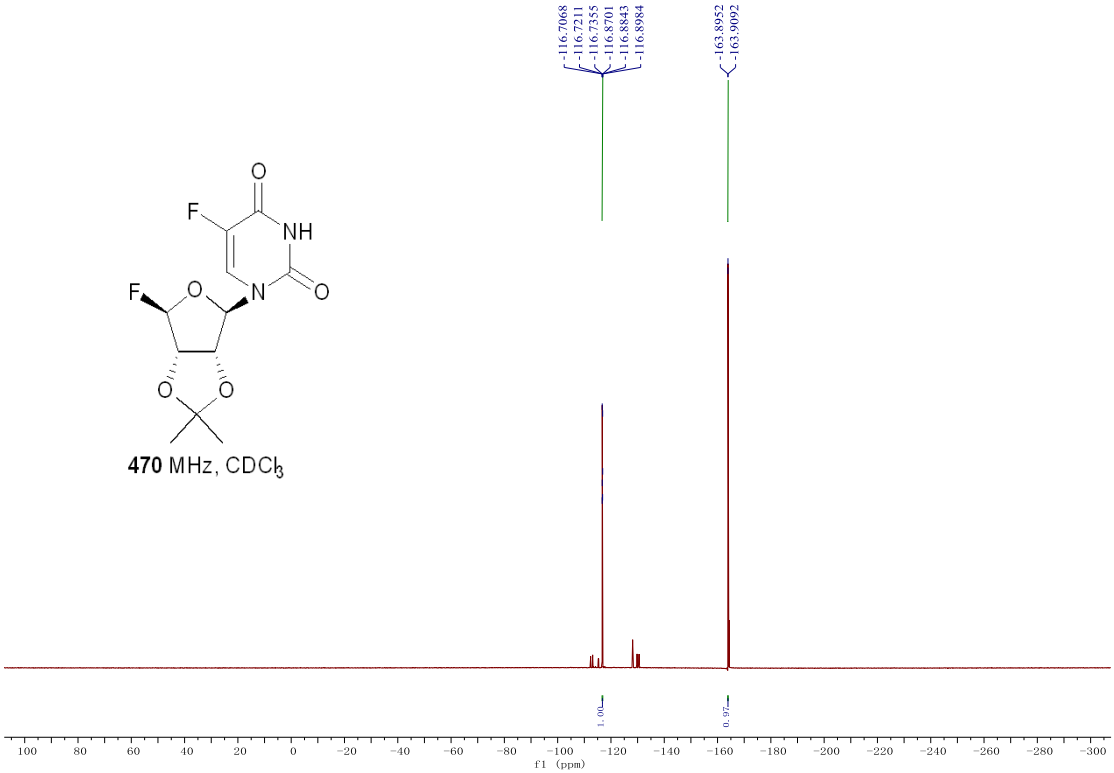
^{1}H NMR Spectrum of **2o**



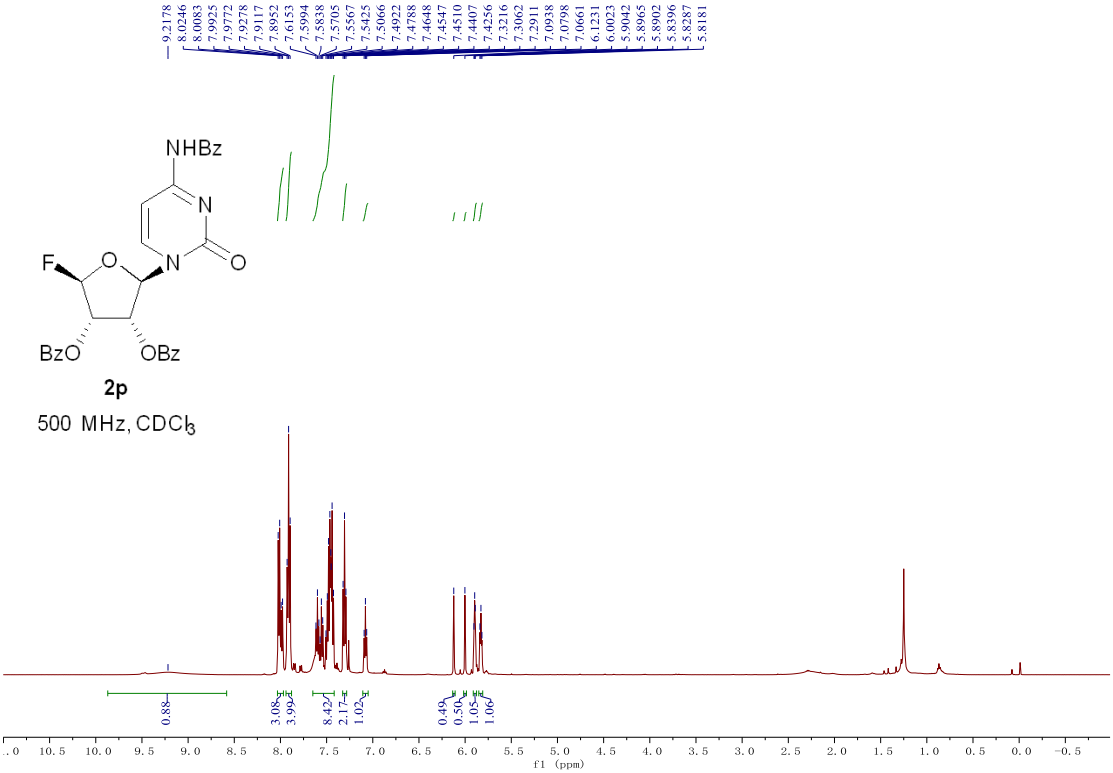
^{13}C NMR Spectrum of **2o**



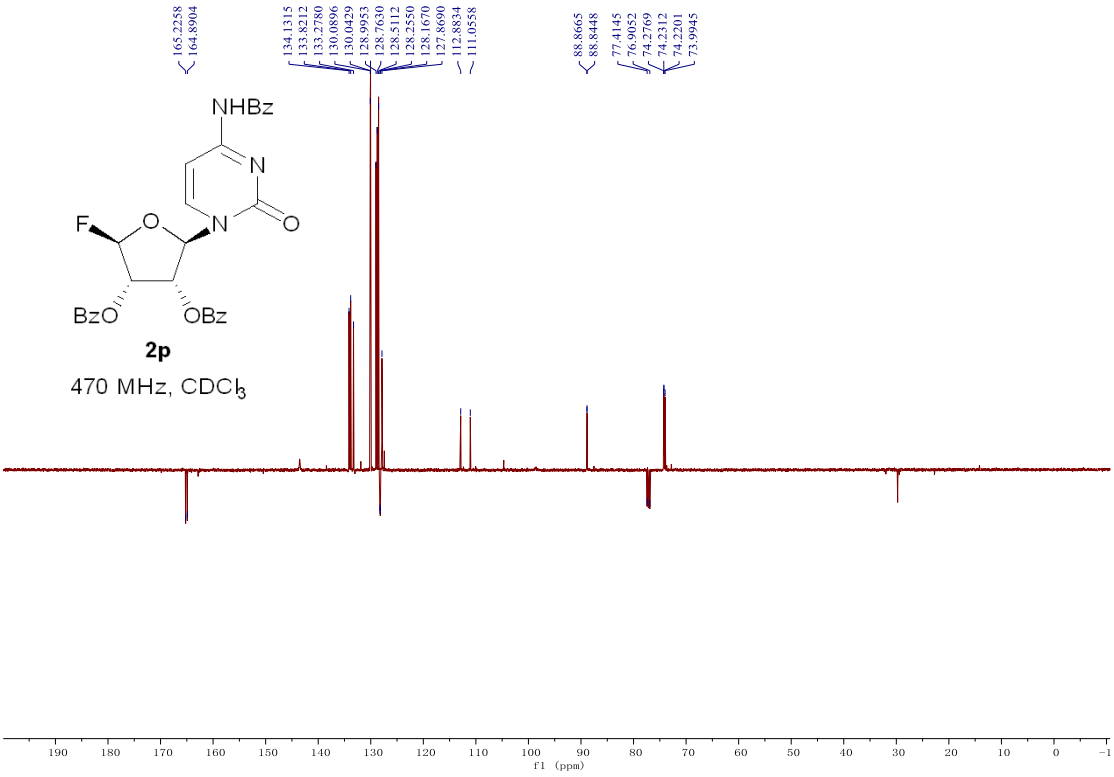
^{19}F NMR Spectrum of **2o**



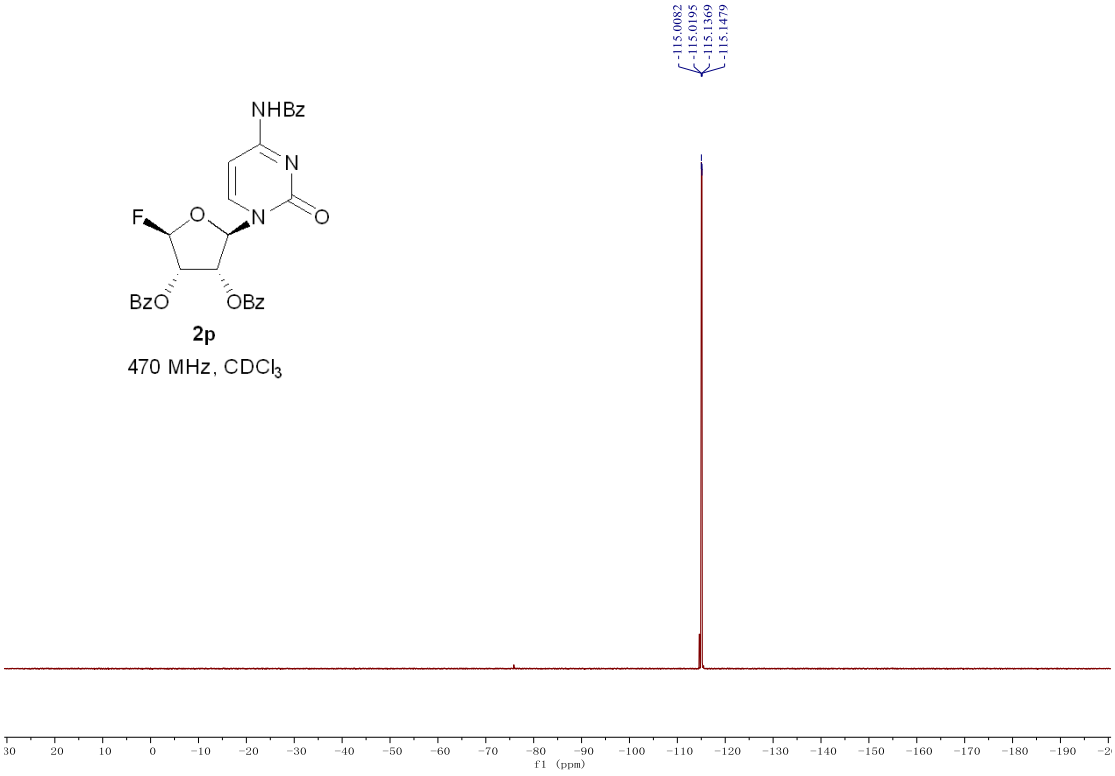
^{1}H NMR Spectrum of **2p**



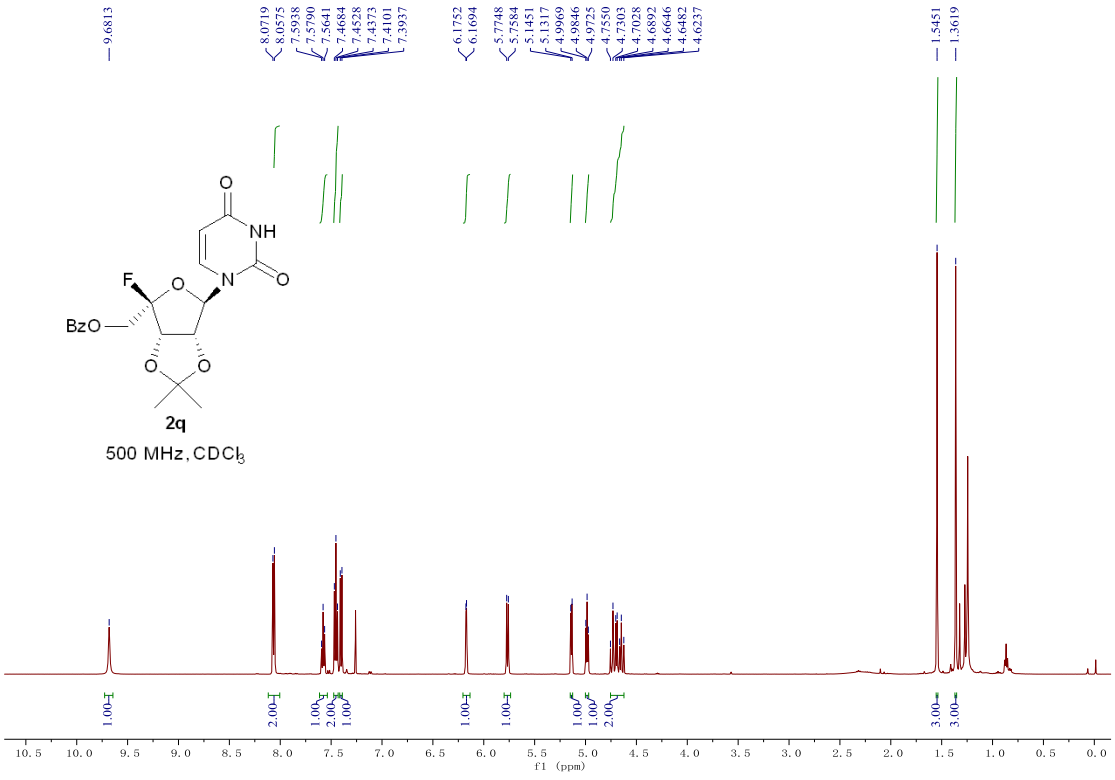
^{13}C NMR Spectrum of **2p**



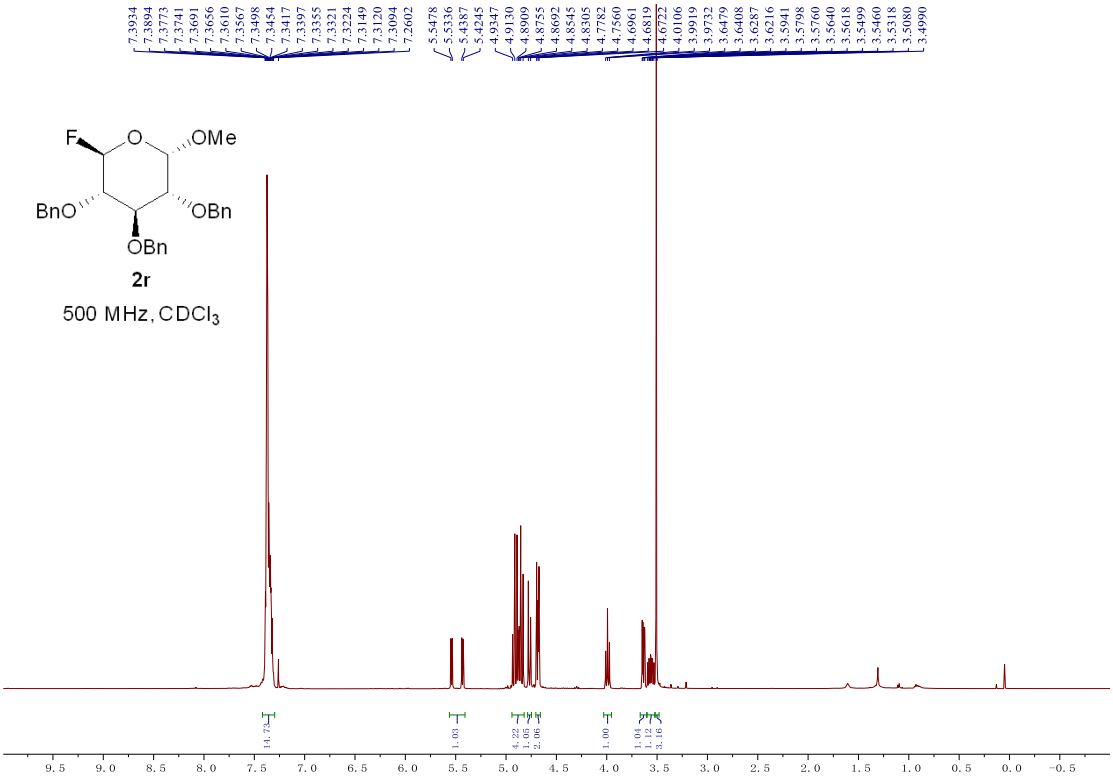
^{19}F NMR Spectrum of **2p**



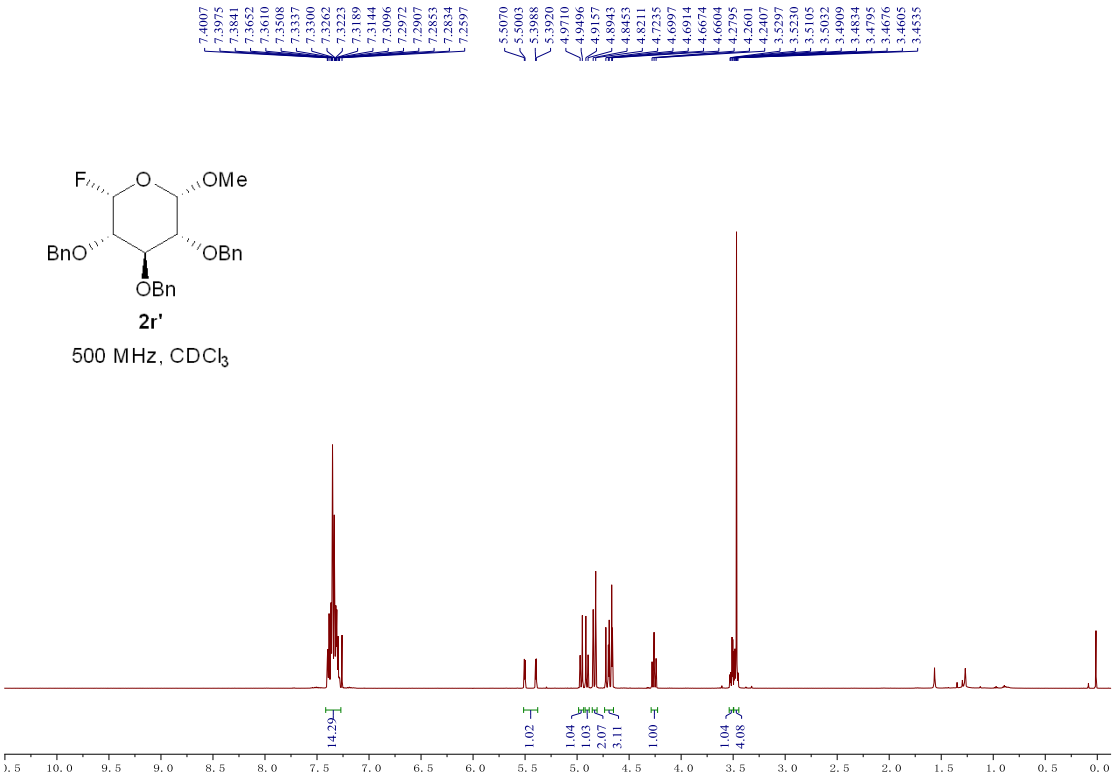
^{1}H NMR Spectrum of **2q**



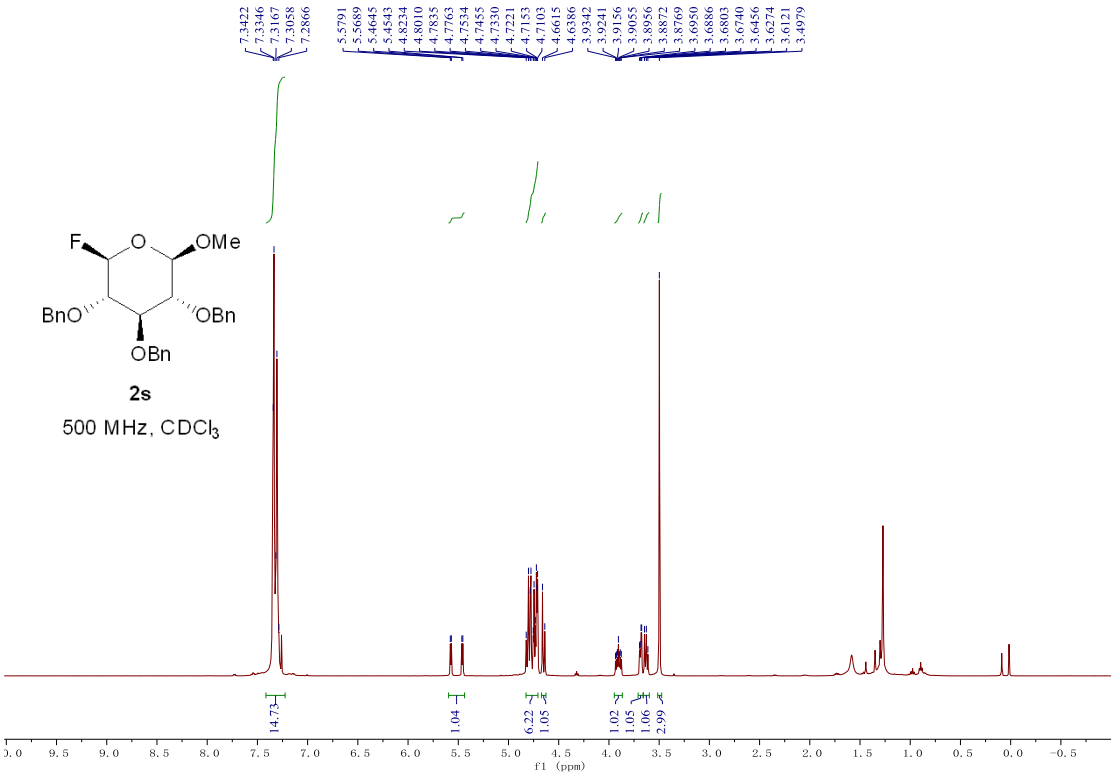
^{1}H NMR Spectrum of **2r**



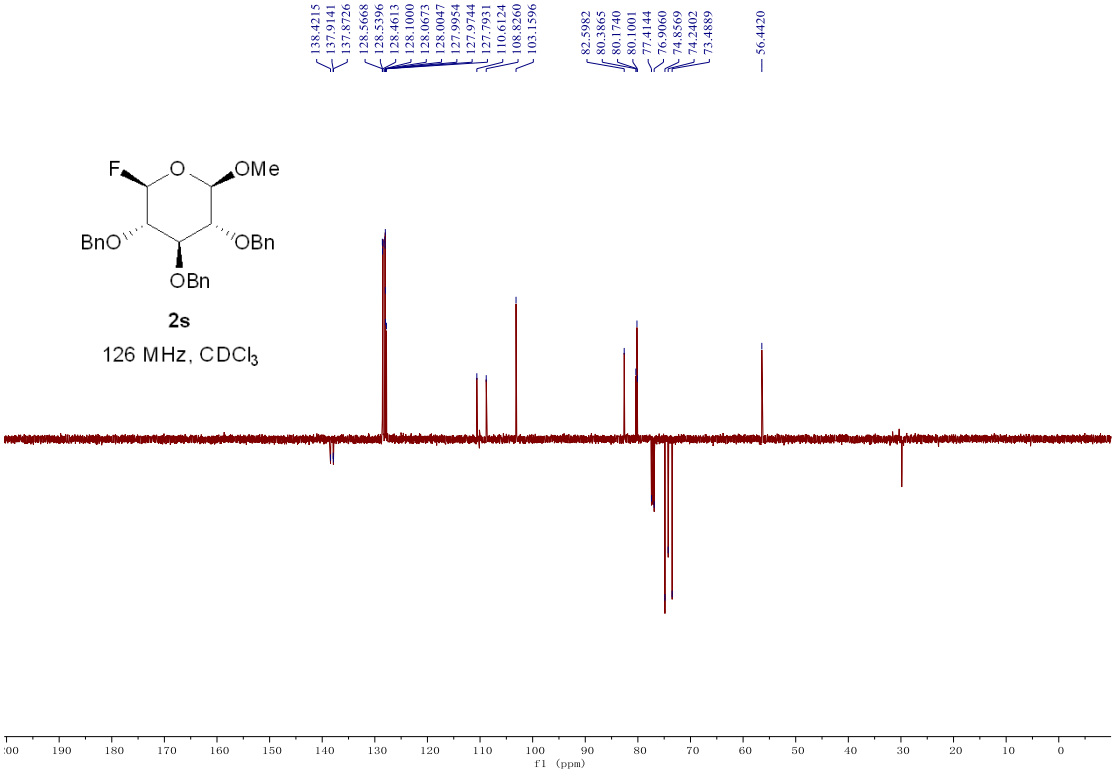
^{1}H NMR Spectrum of **2r'**



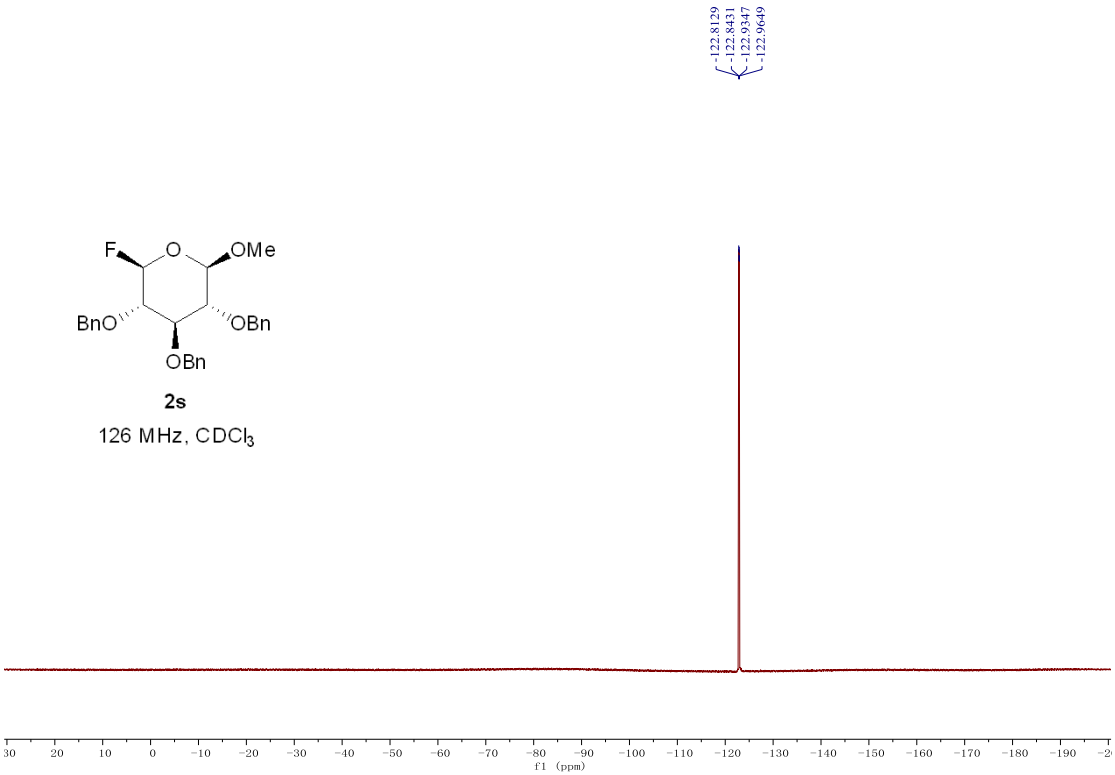
^{1}H NMR Spectrum of **2s**



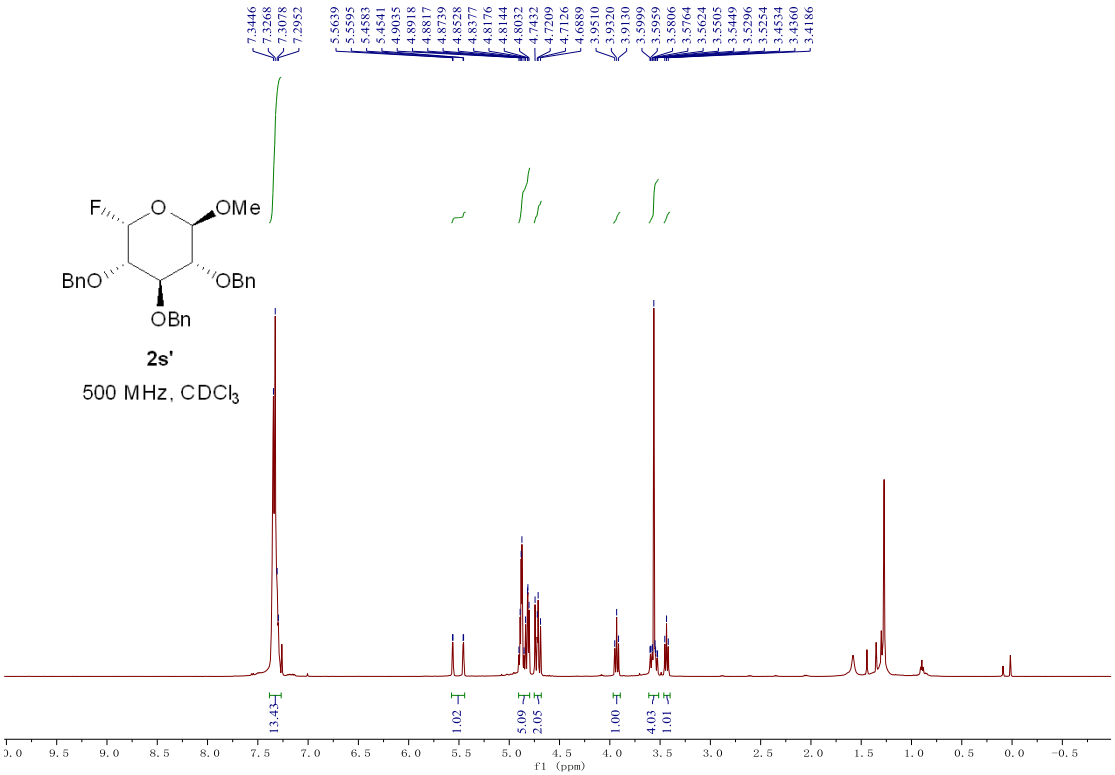
DEPT-Q NMR Spectrum of **2s**



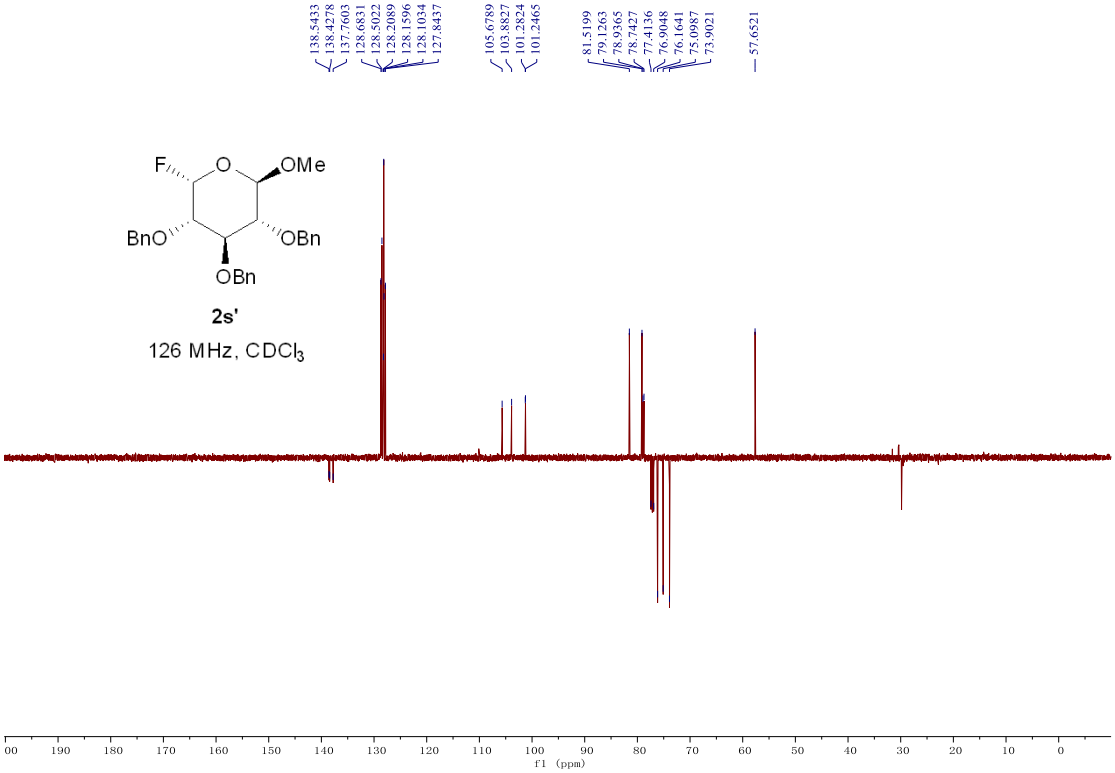
^{19}F NMR Spectrum of **2s**



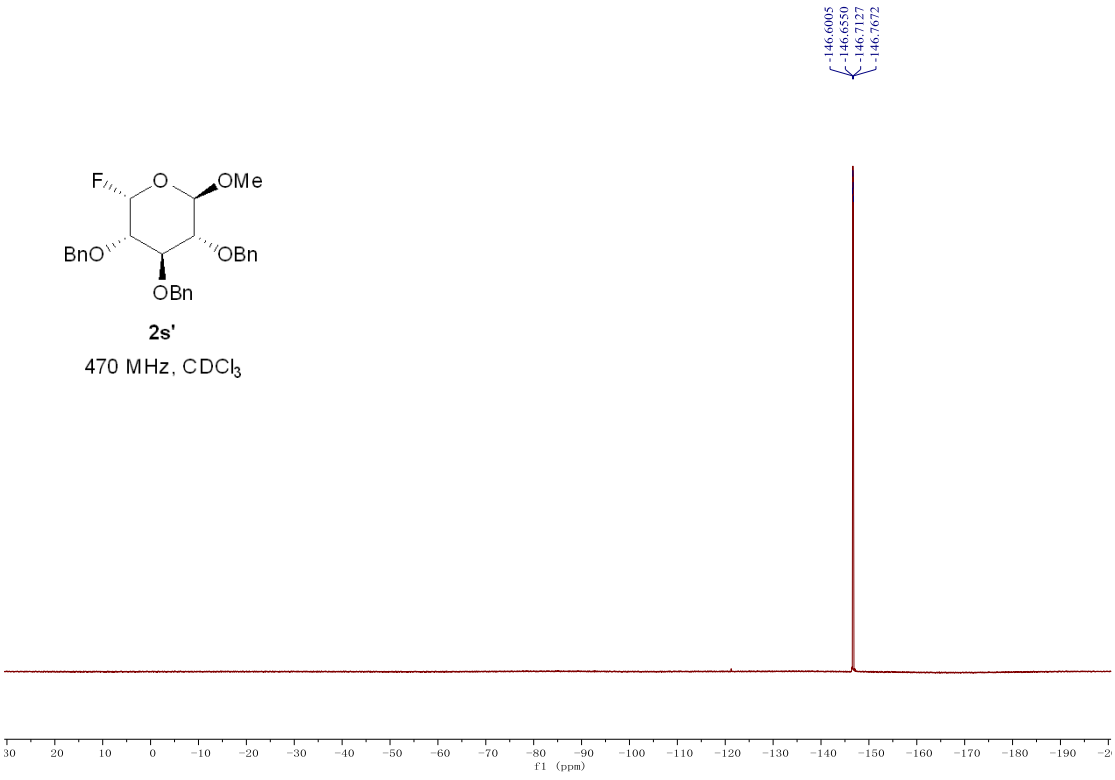
^{1}H NMR Spectrum of **2s'**



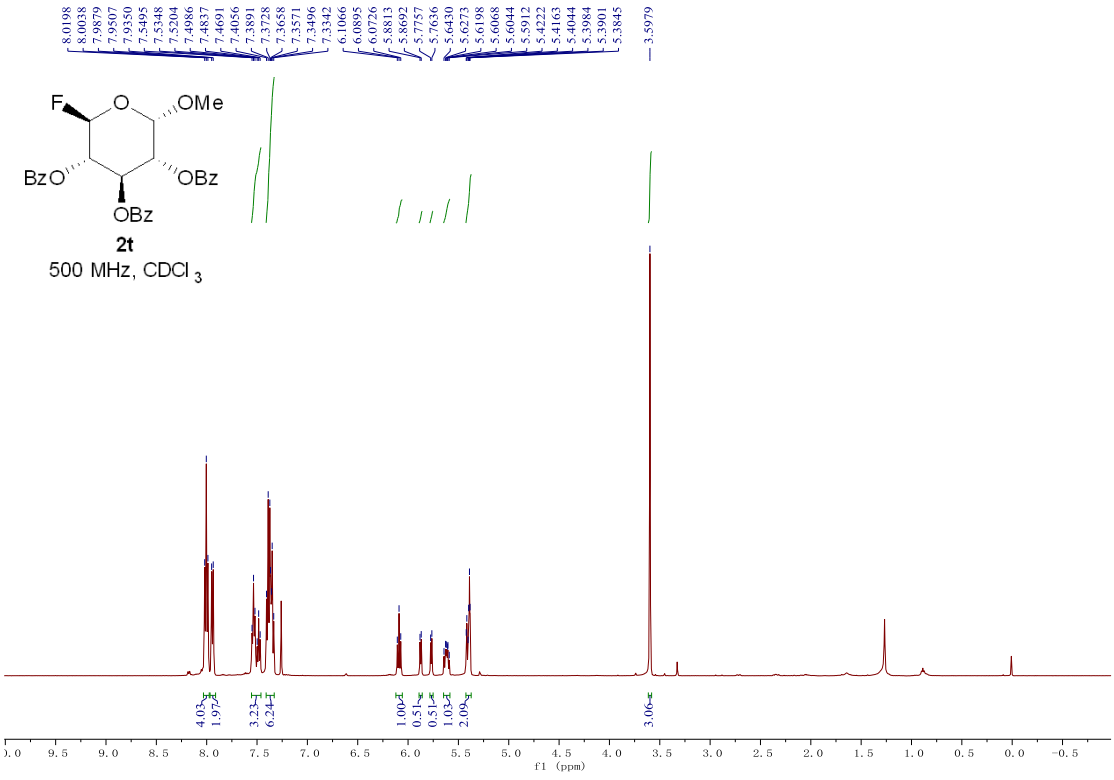
DEPT-Q NMR Spectrum of **2s'**



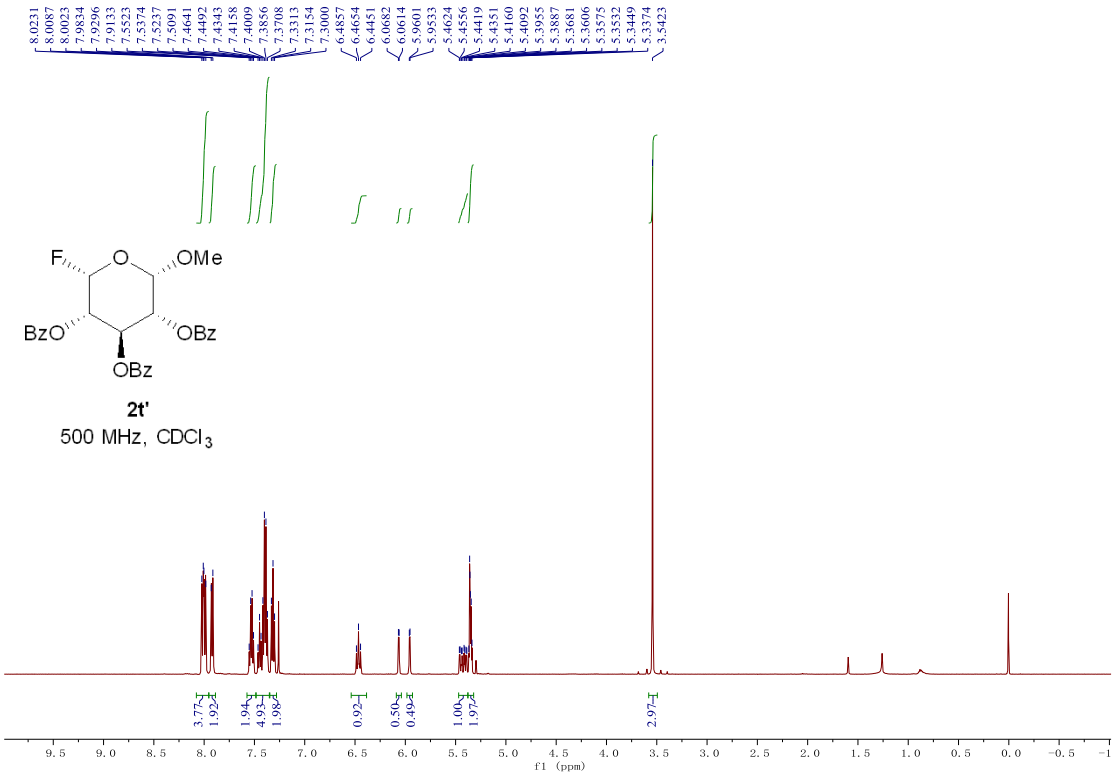
^{19}F NMR Spectrum of **2s'**



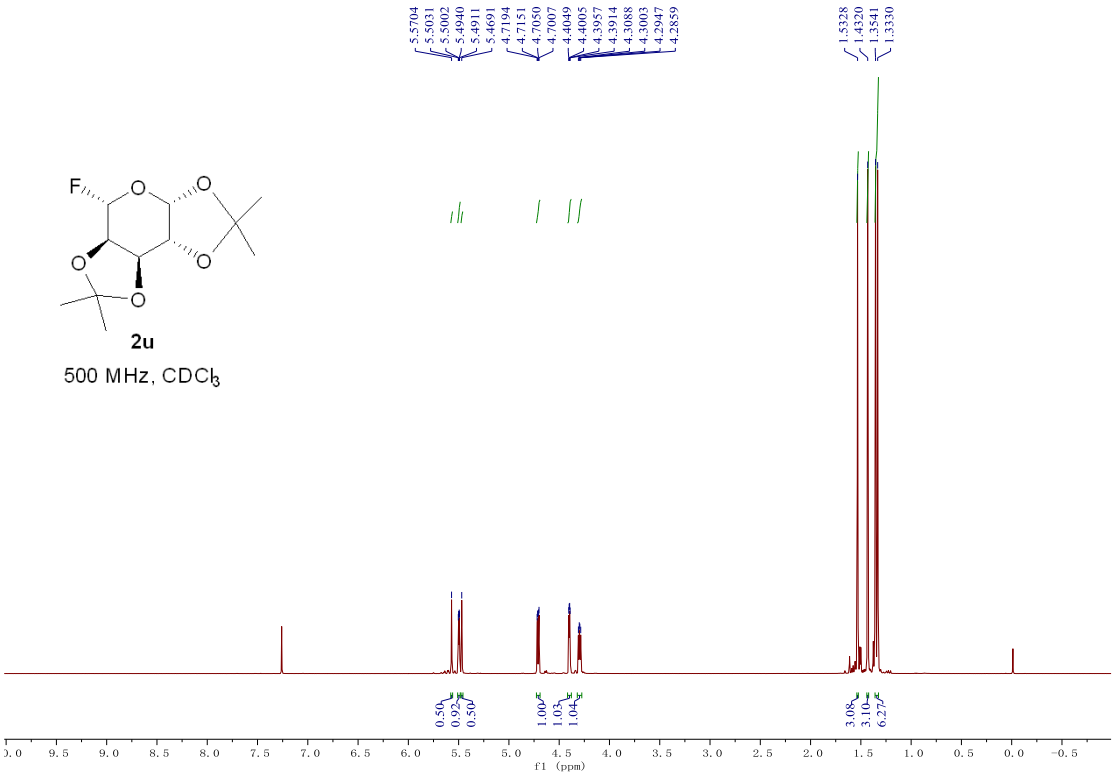
^{1}H NMR Spectrum of **2t**



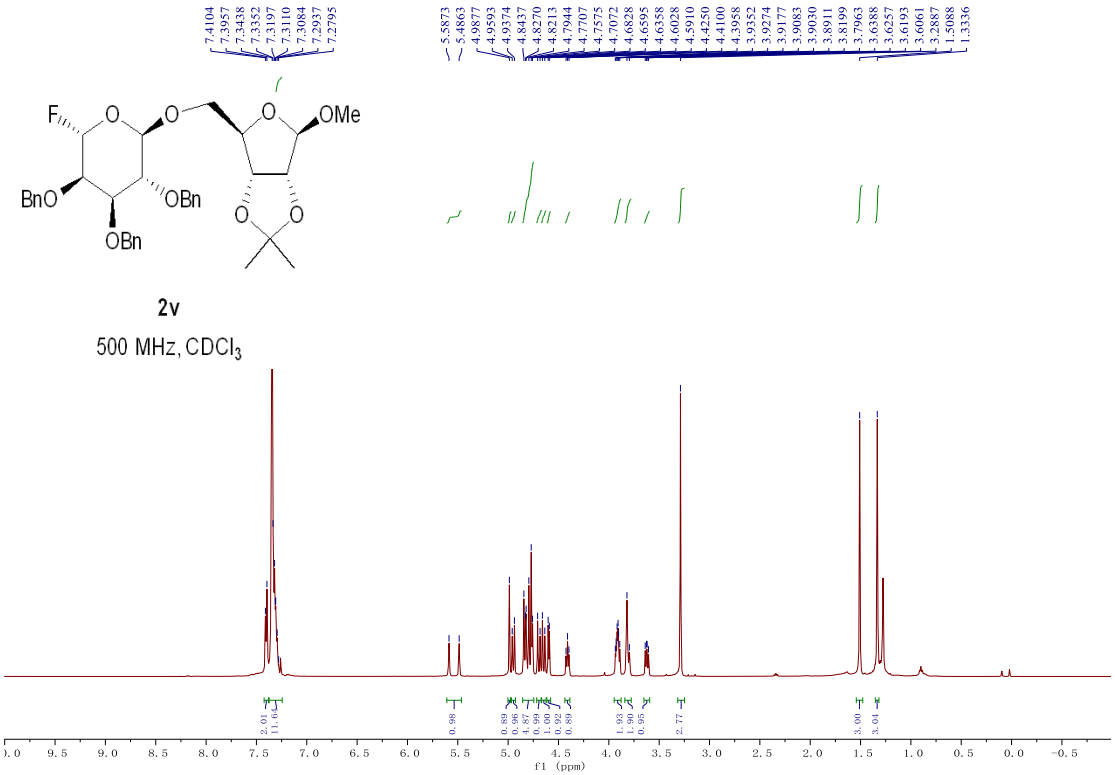
^{1}H NMR Spectrum of **2t'**



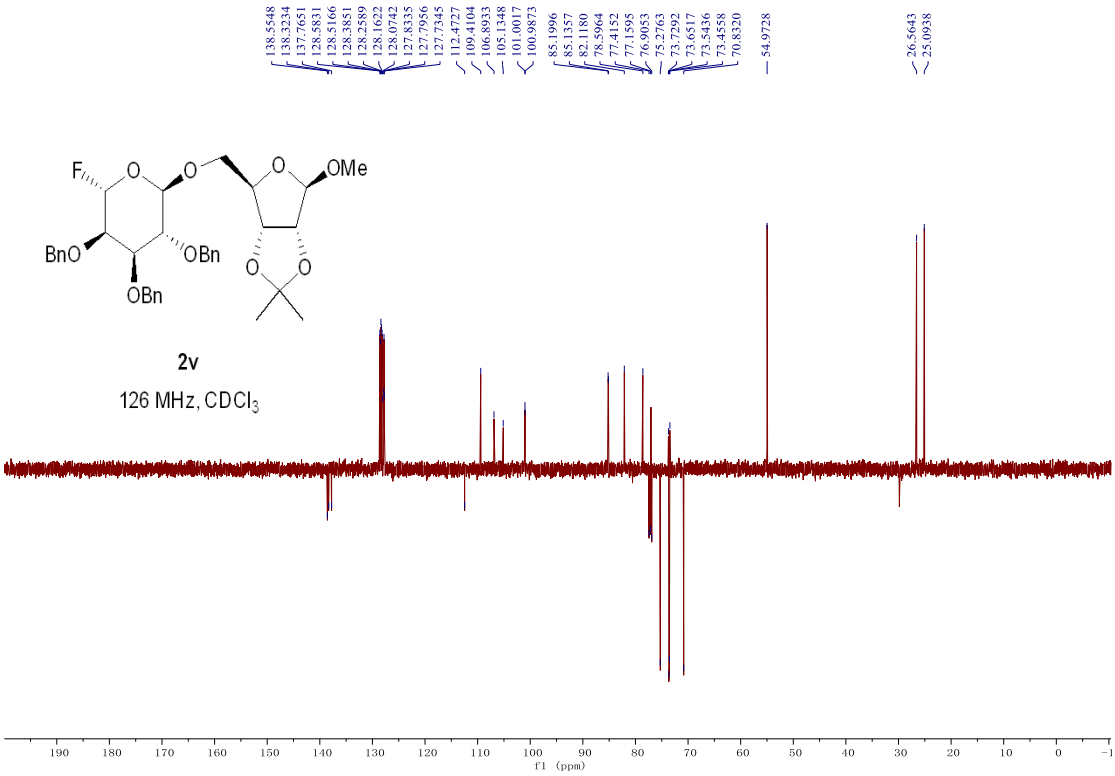
^{1}H NMR Spectrum of **2u**



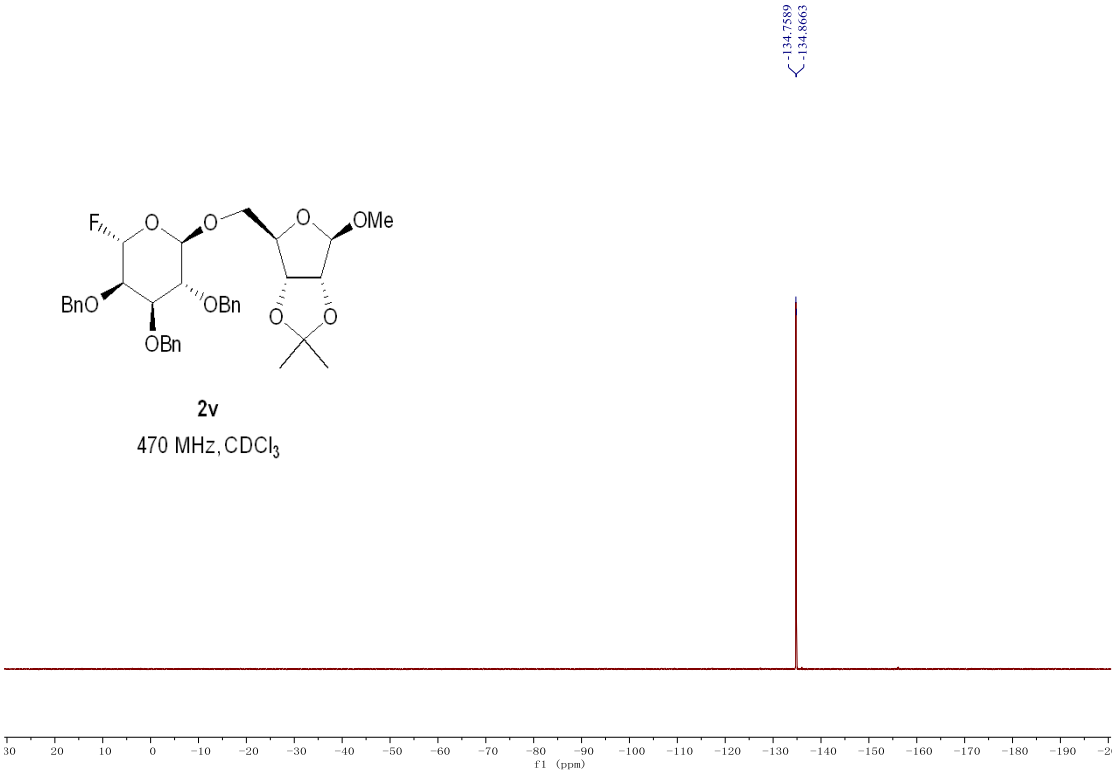
^{1}H NMR Spectrum of **2v**



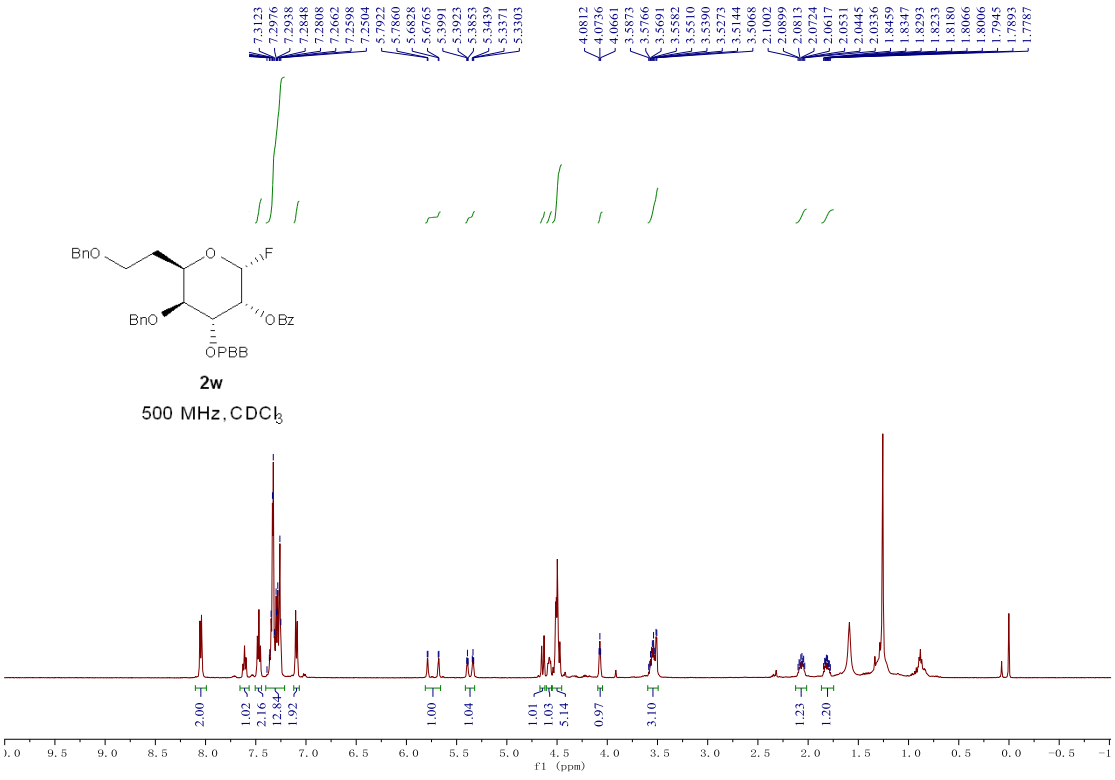
DEPT-Q NMR Spectrum of **2v**



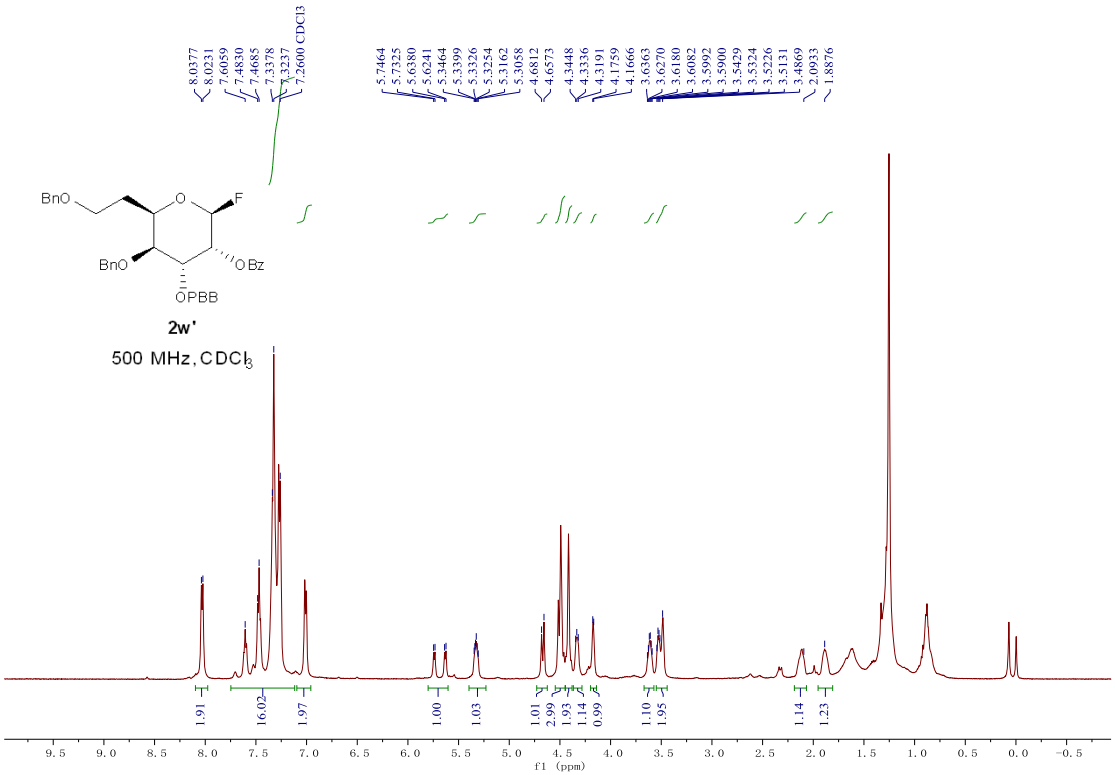
^{19}F NMR Spectrum of **2v**



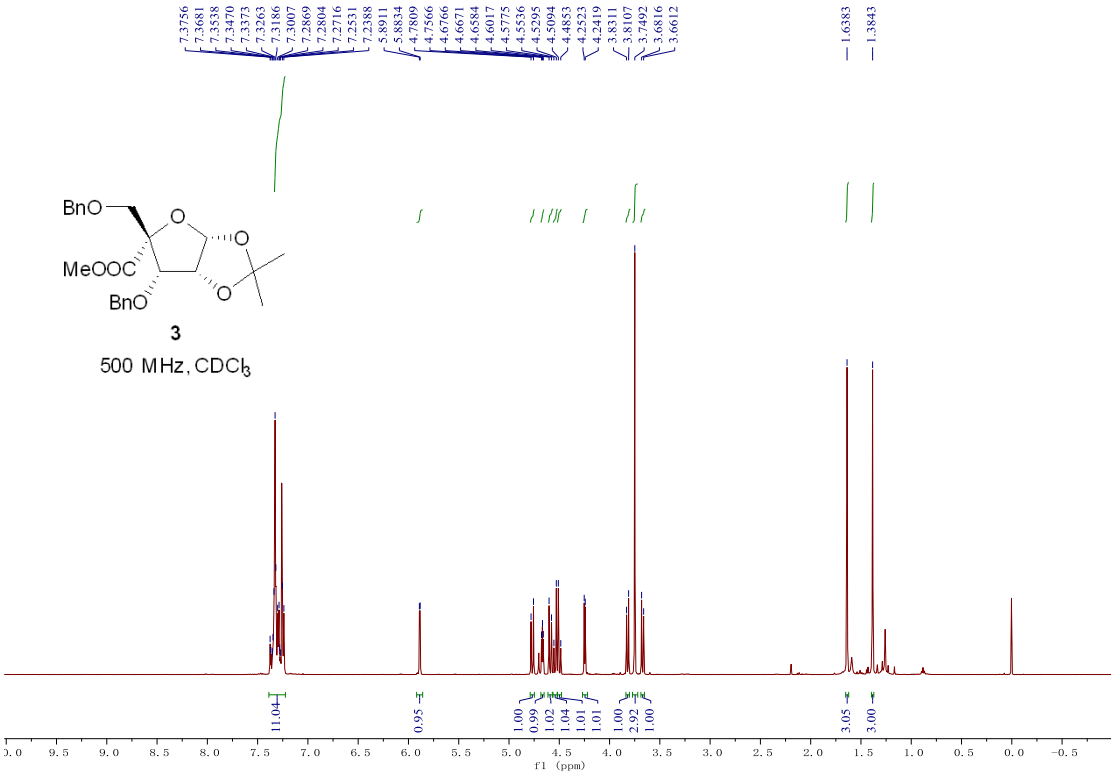
^{1}H NMR Spectrum of **2w**



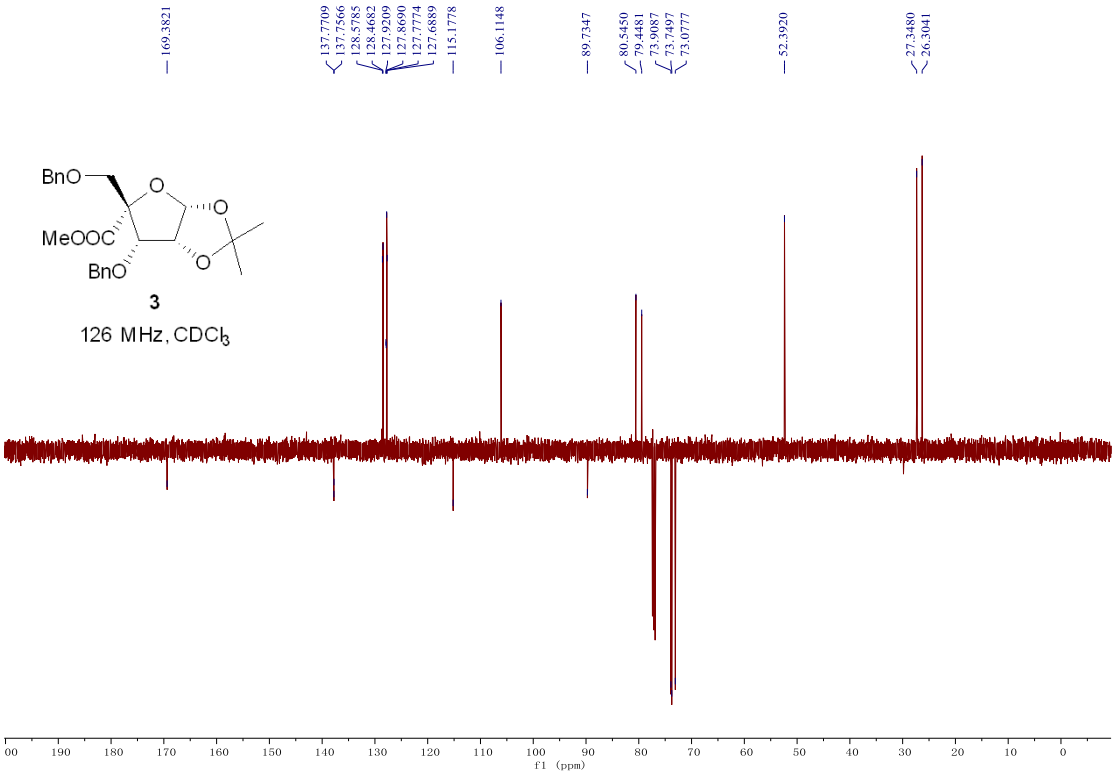
^{1}H NMR Spectrum of **2w'**



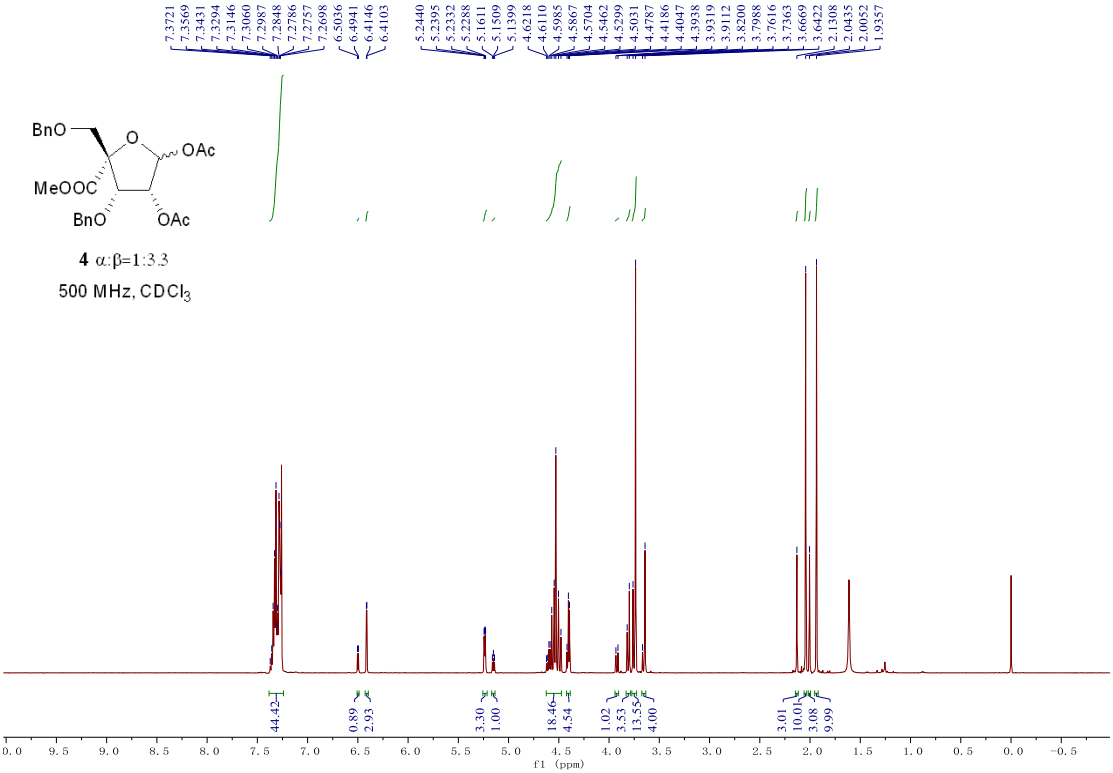
^{1}H NMR Spectrum of **3**



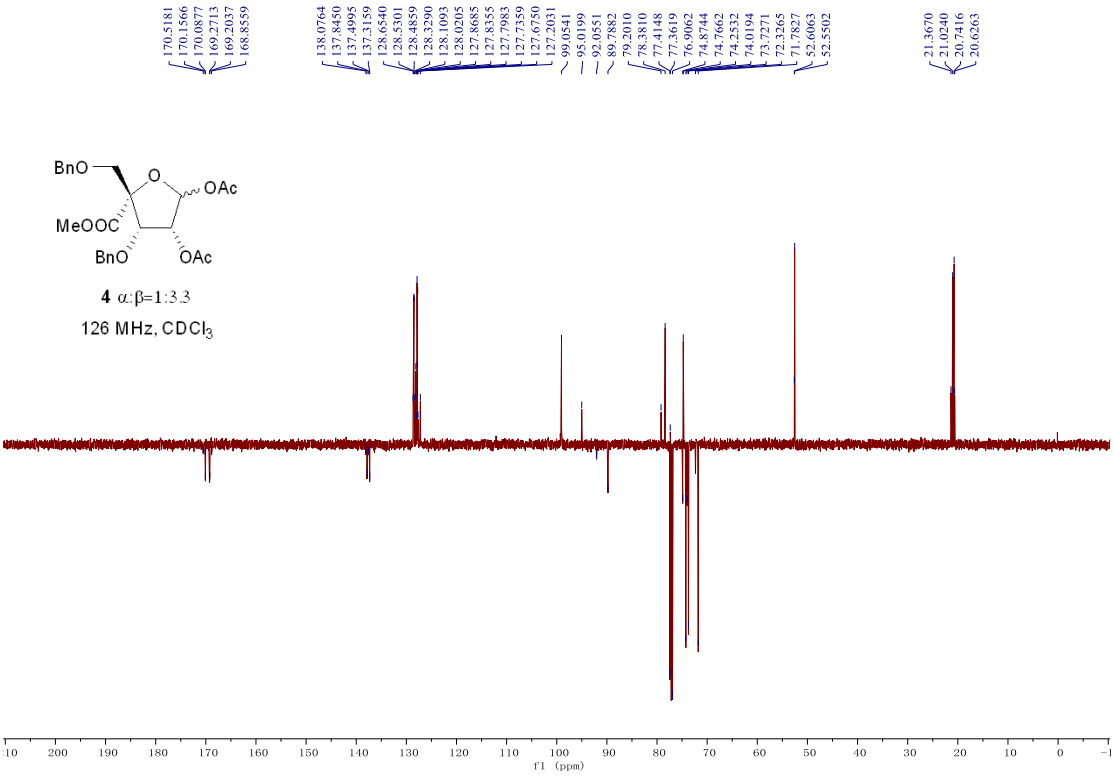
DEPT-Q NMR Spectrum of **3**



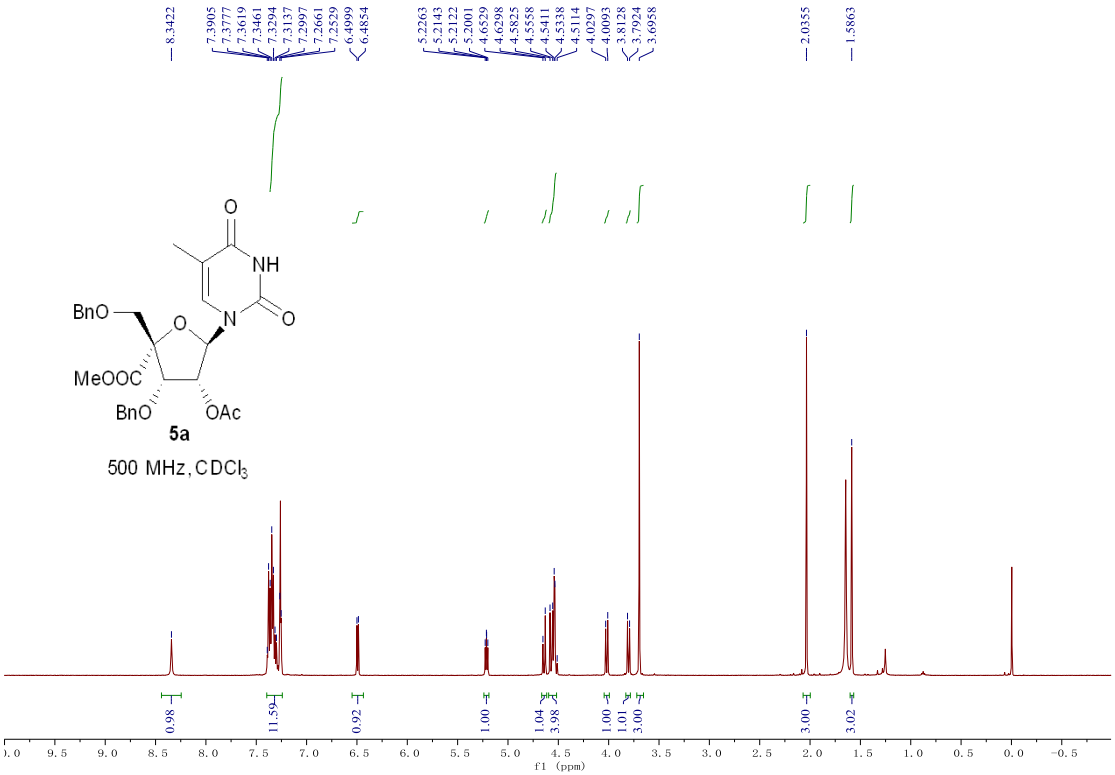
^{1}H NMR Spectrum of **4**



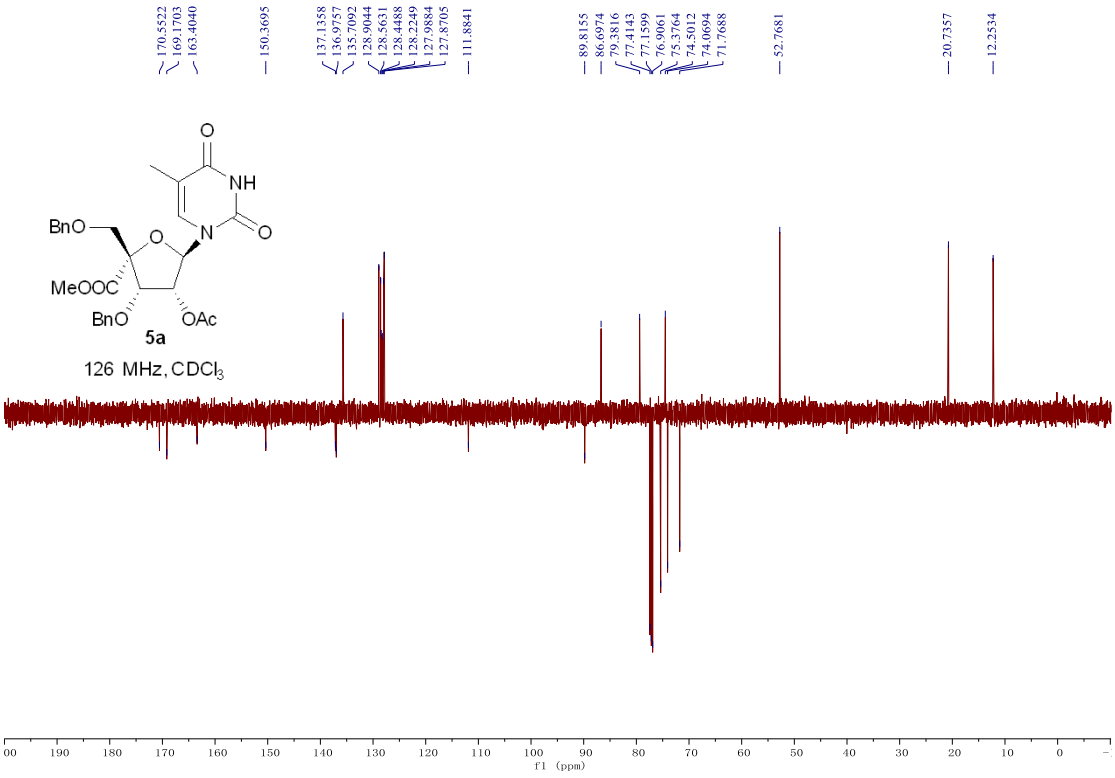
DEPT-Q NMR Spectrum of **4**



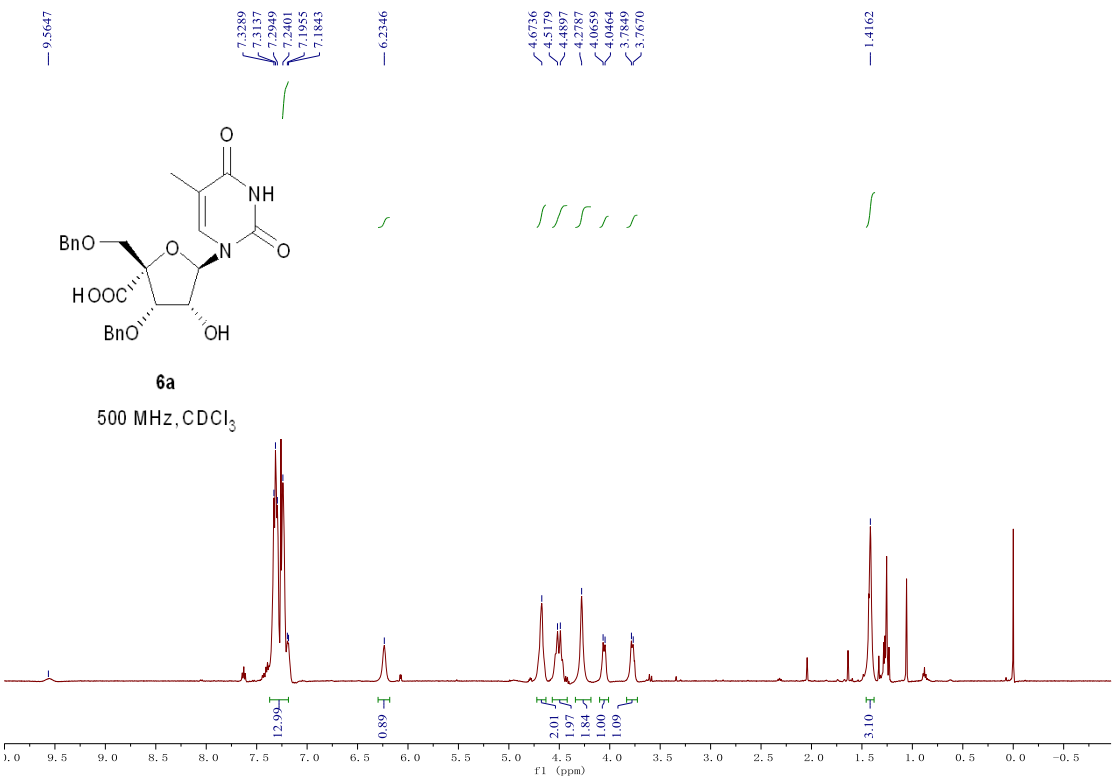
^{1}H NMR Spectrum of **5a**



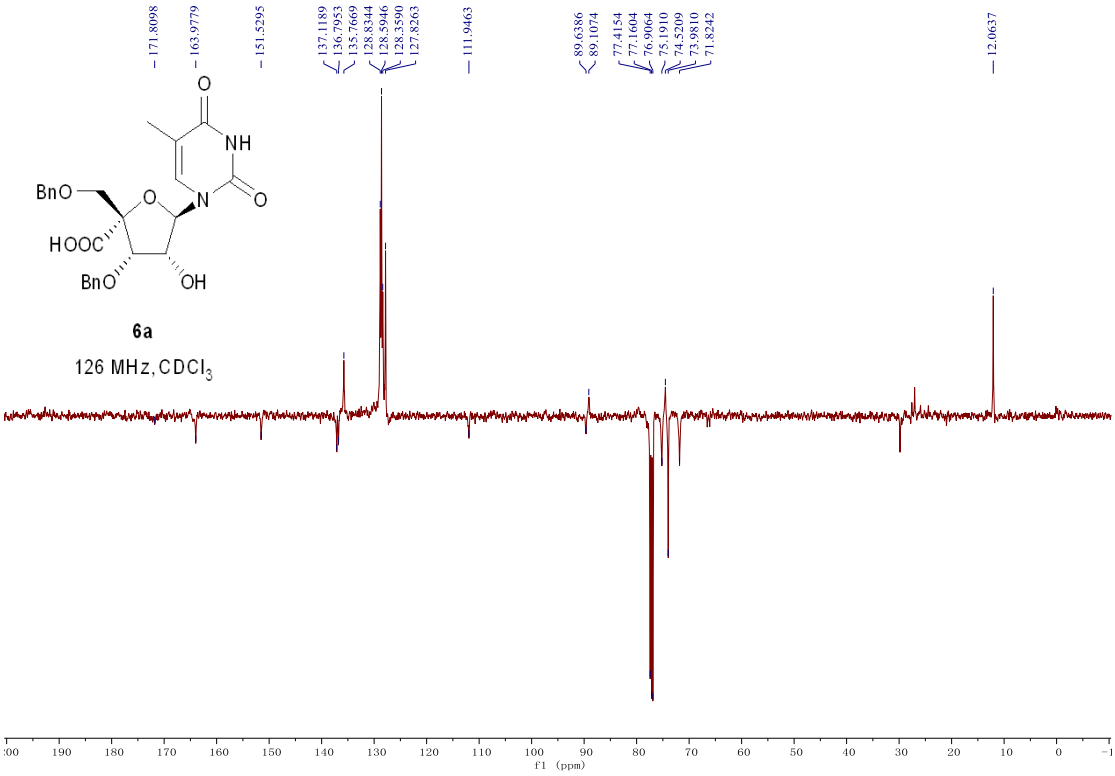
DEPT-Q NMR Spectrum of **5a**



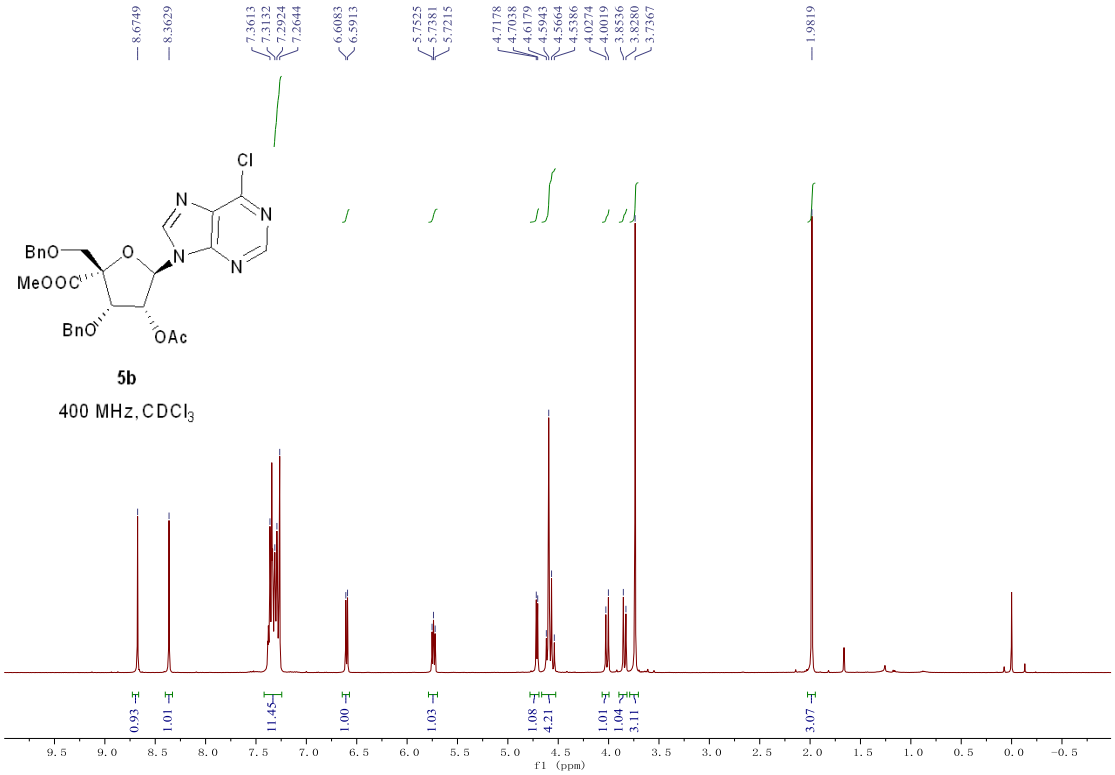
^{1}H NMR Spectrum of **6a**



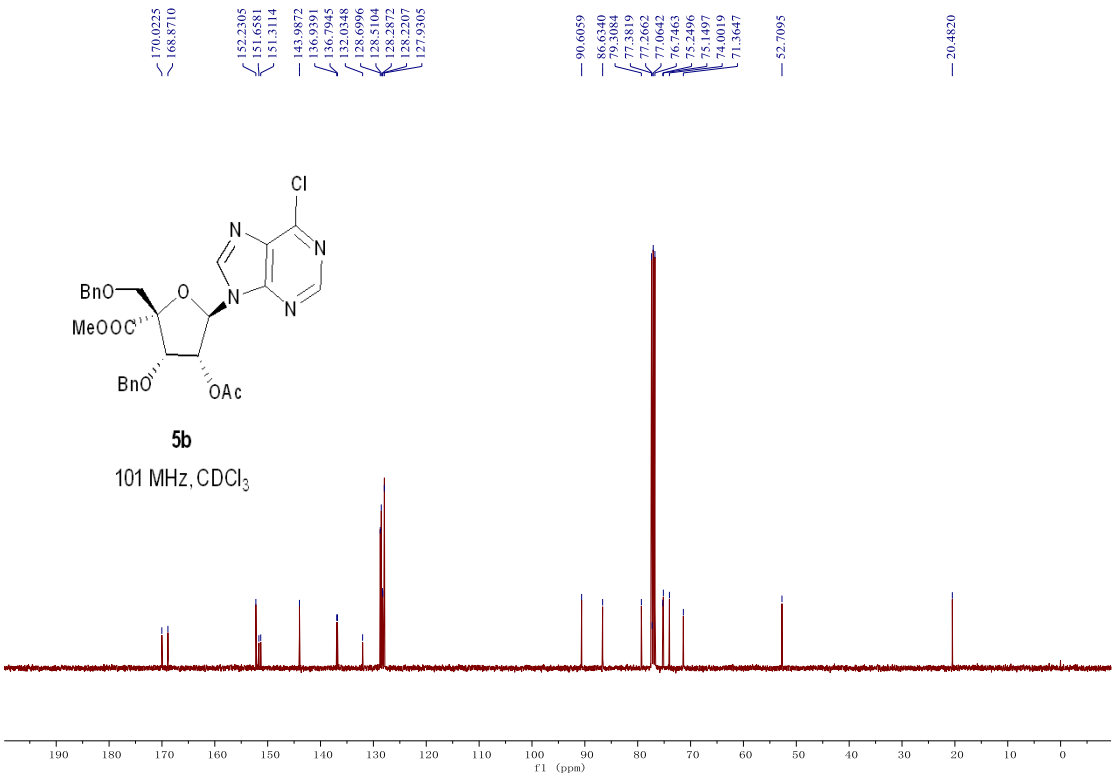
DEPT-Q NMR Spectrum of **6a**



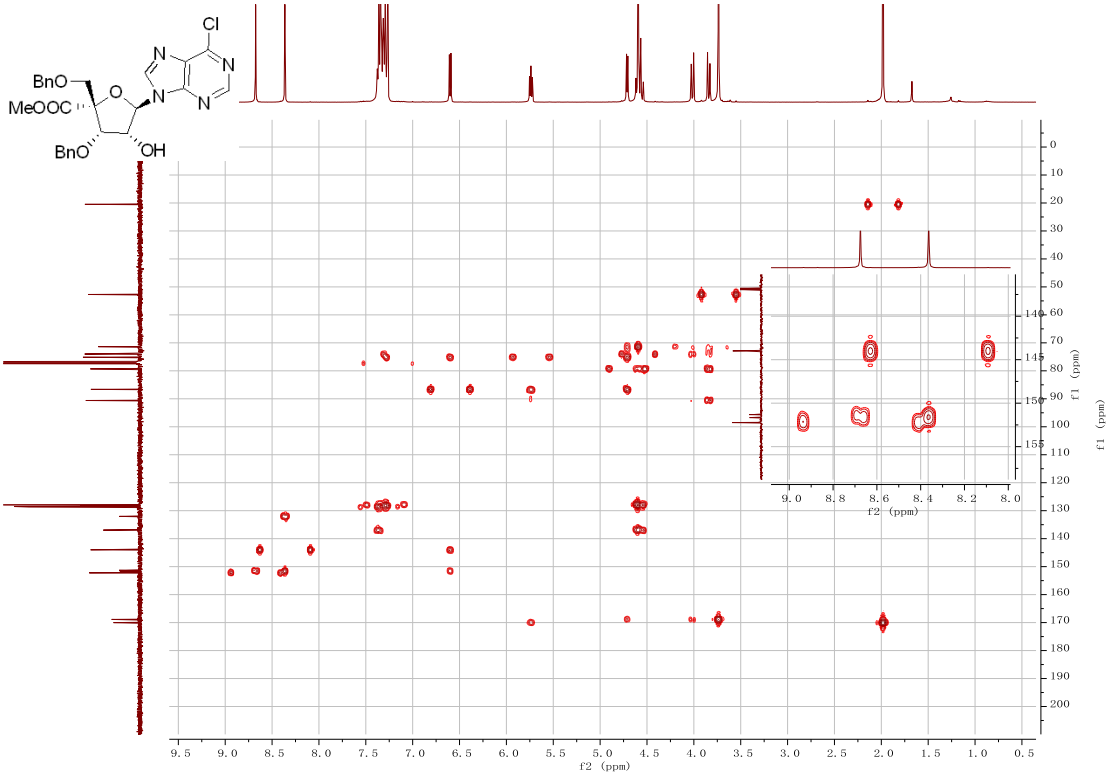
^{1}H NMR Spectrum of **5b**



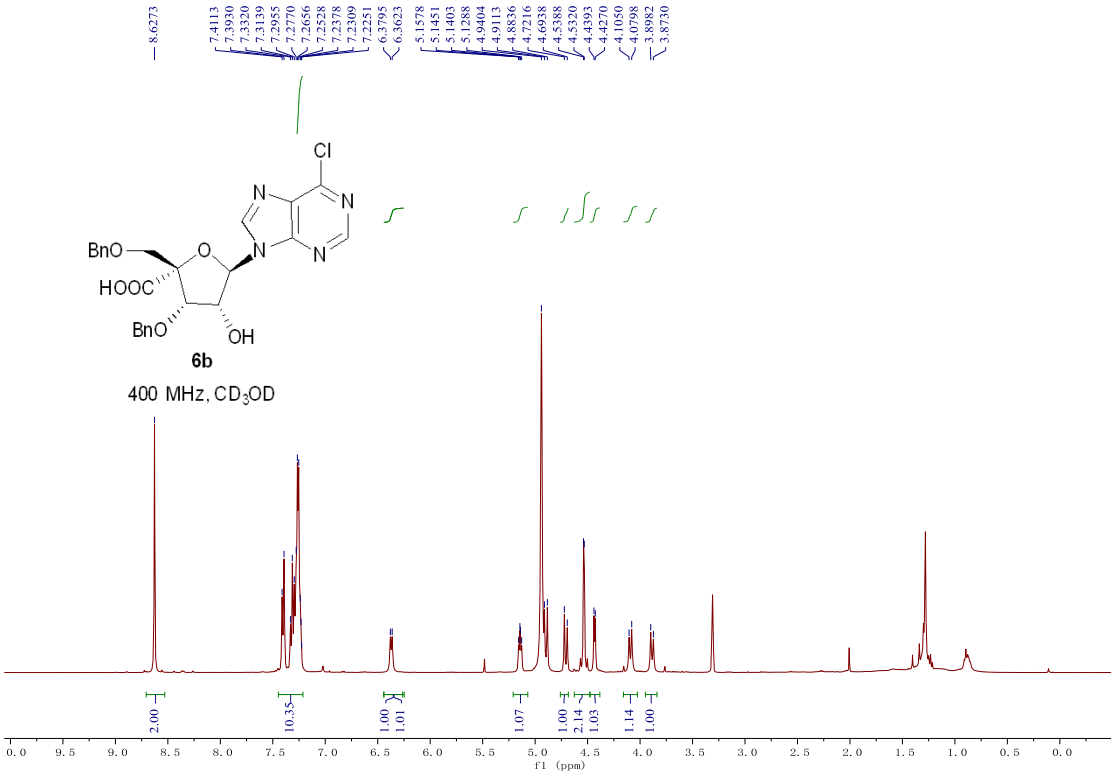
^{13}CNMR Spectrum of **5b**



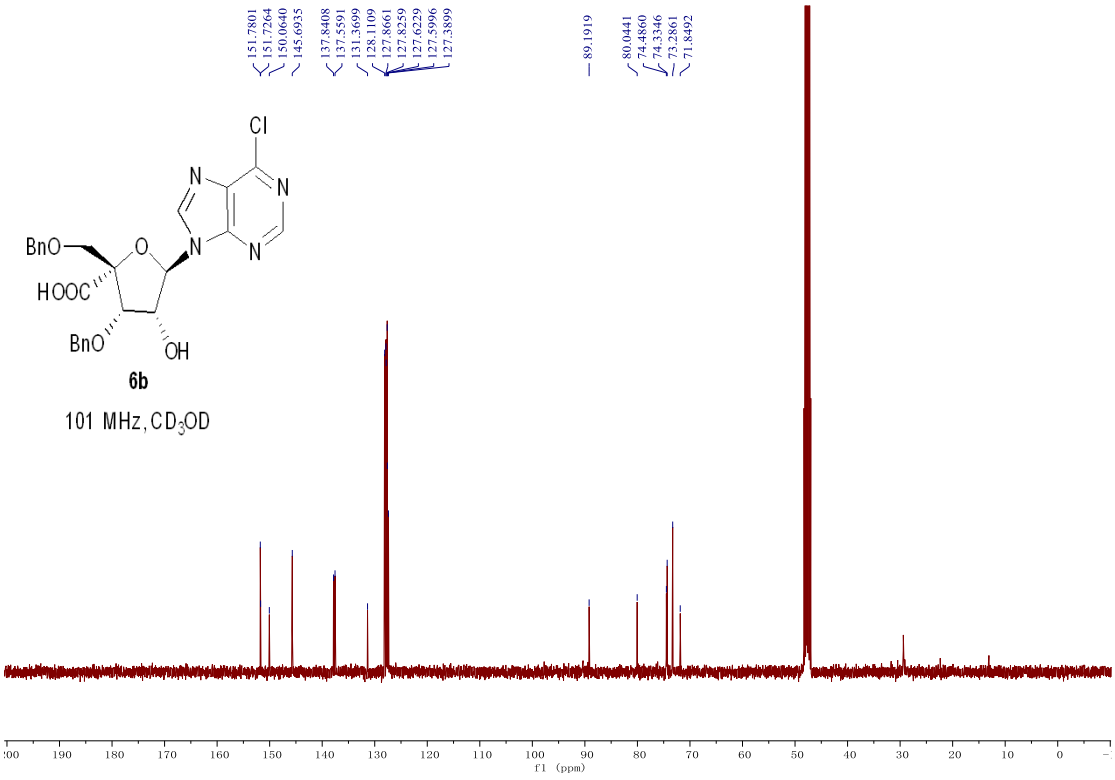
HMBC Spectrum of **5b**



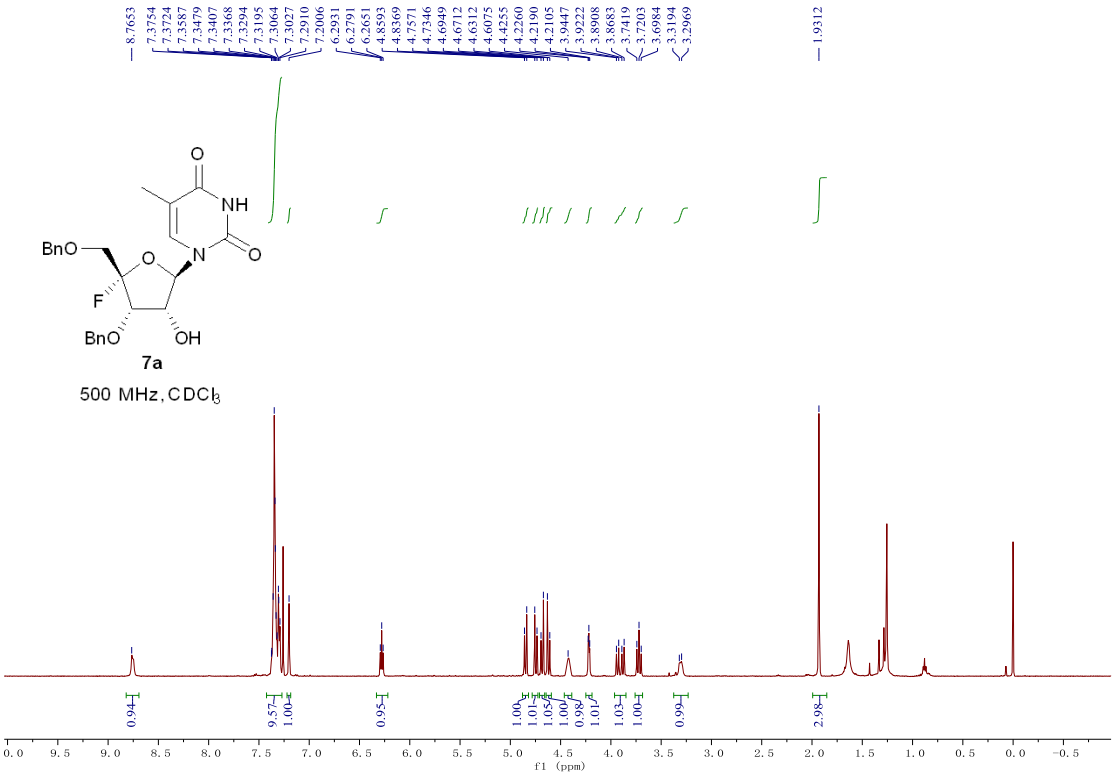
^{1}H NMR Spectrum of **6b**



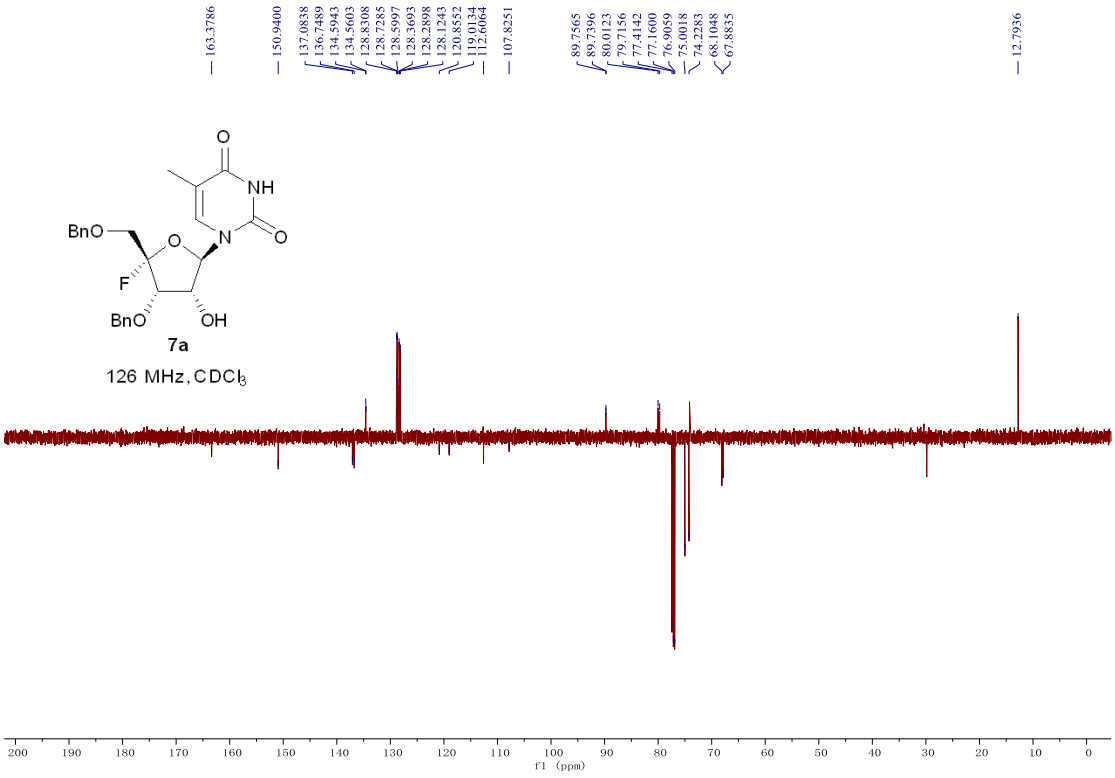
^{13}C NMR Spectrum of **6b**



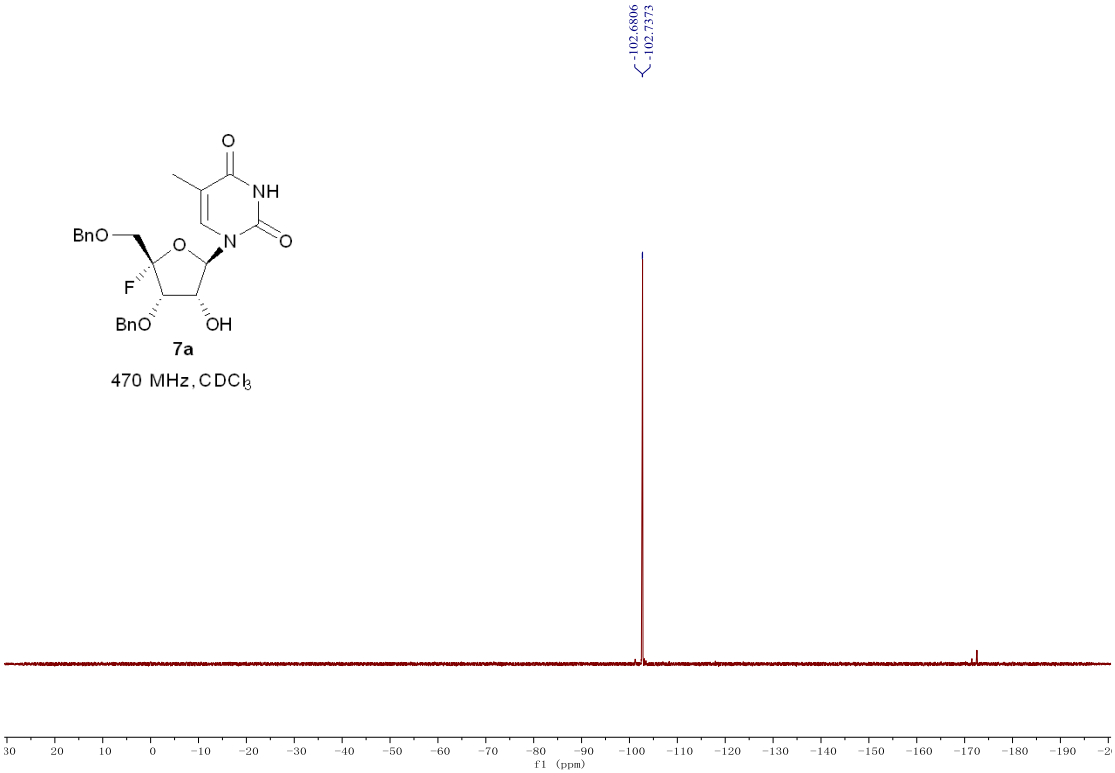
^{1}H NMR Spectrum of **7a**



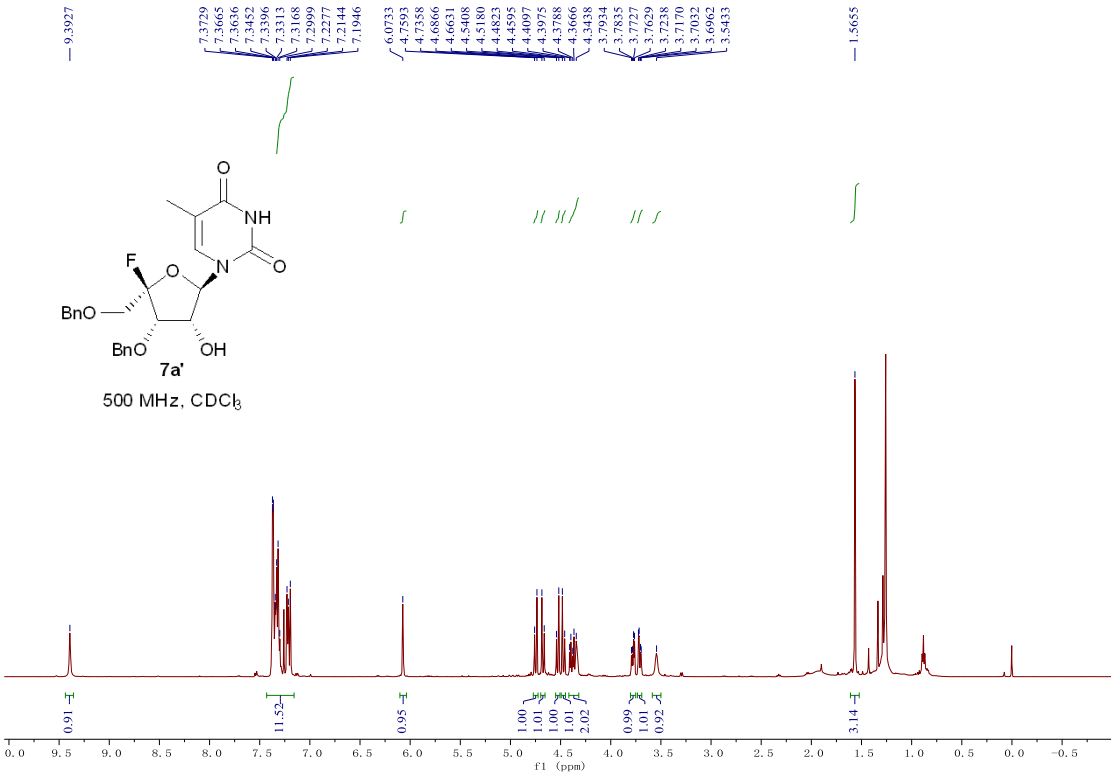
DEPT-Q NMR Spectrum of **7a**



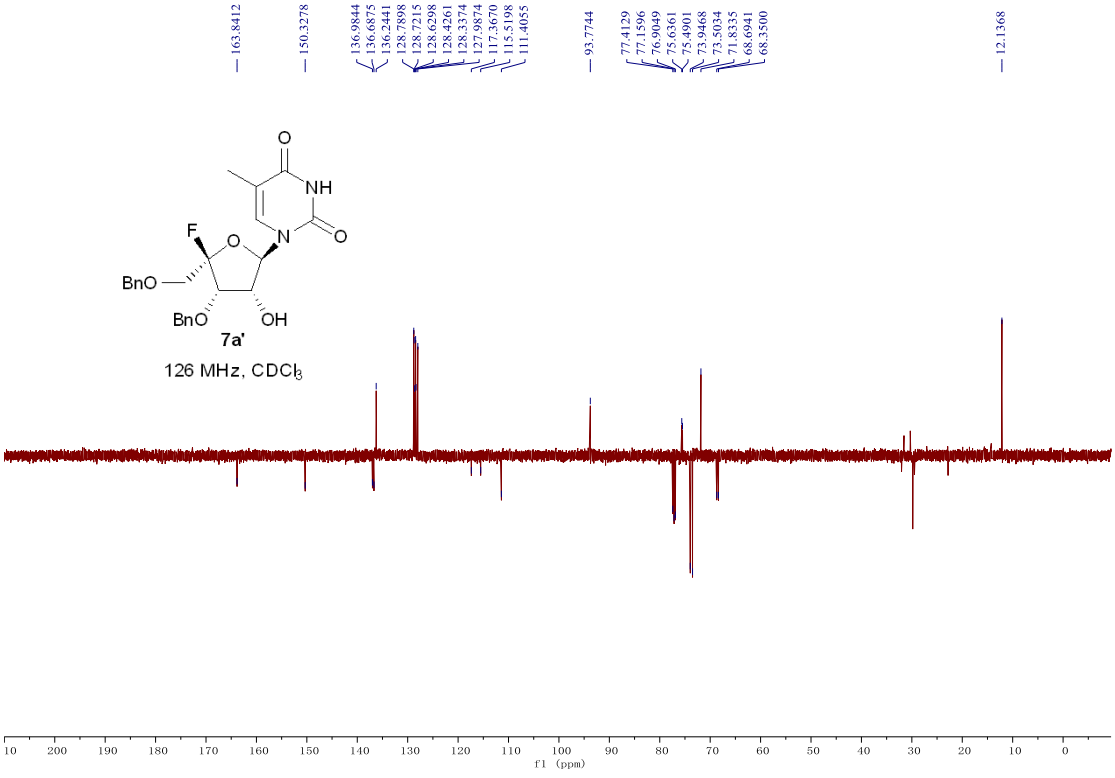
^{19}F NMR Spectrum of **7a**



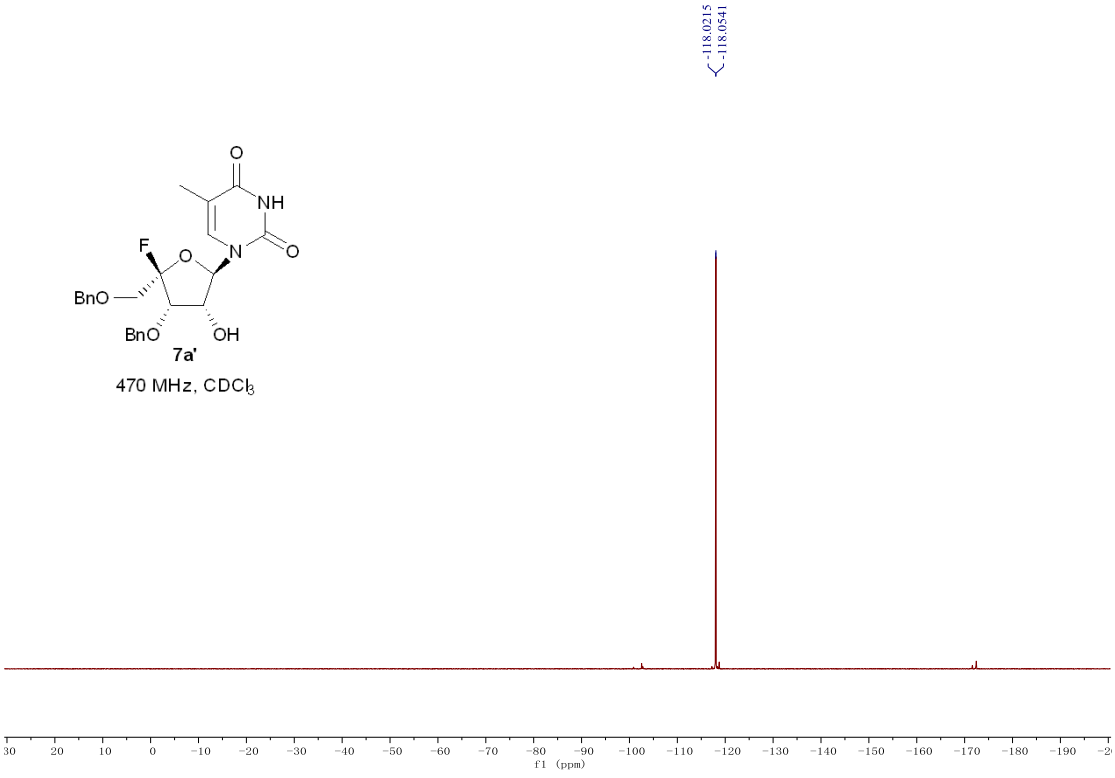
^{1}H NMR Spectrum of **7a'**



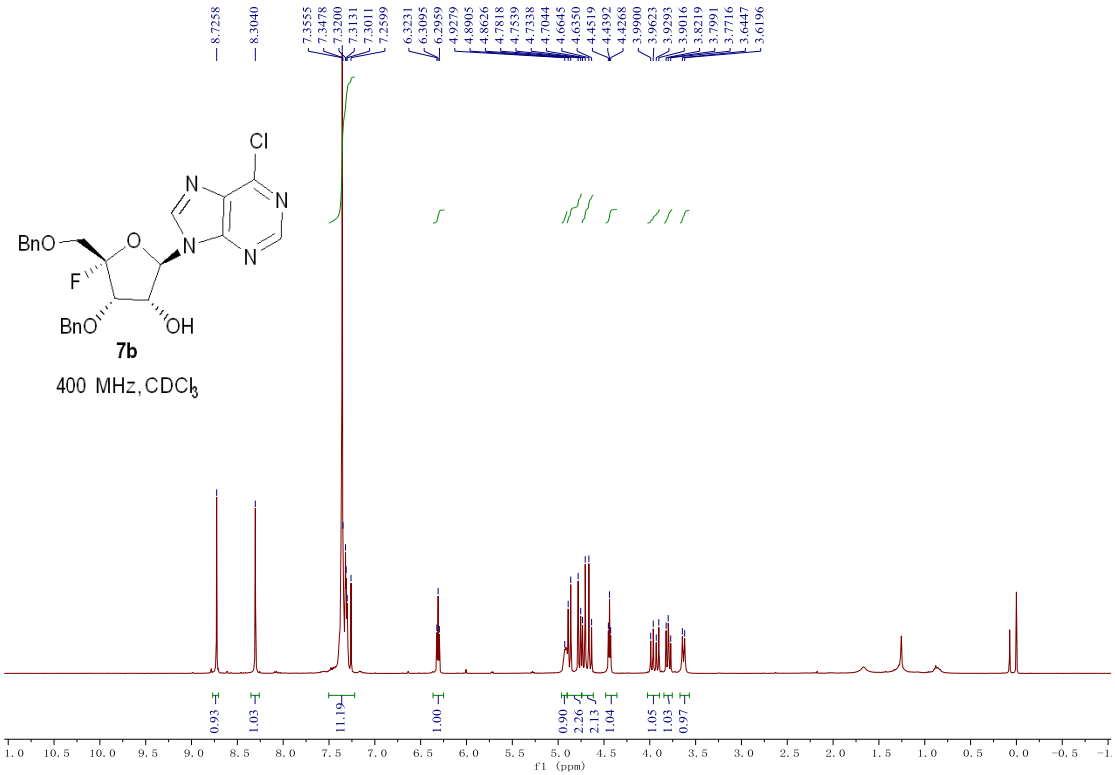
DEPT-Q NMR Spectrum of **7a'**



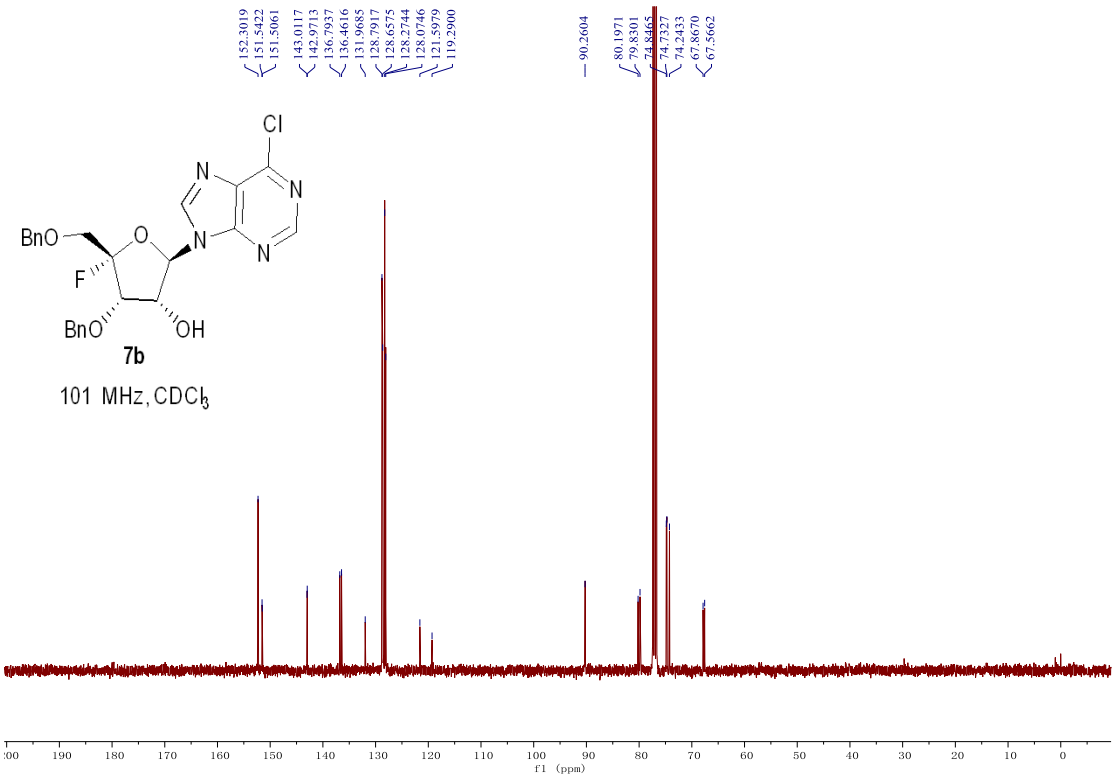
^{19}F NMR Spectrum of **7a'**



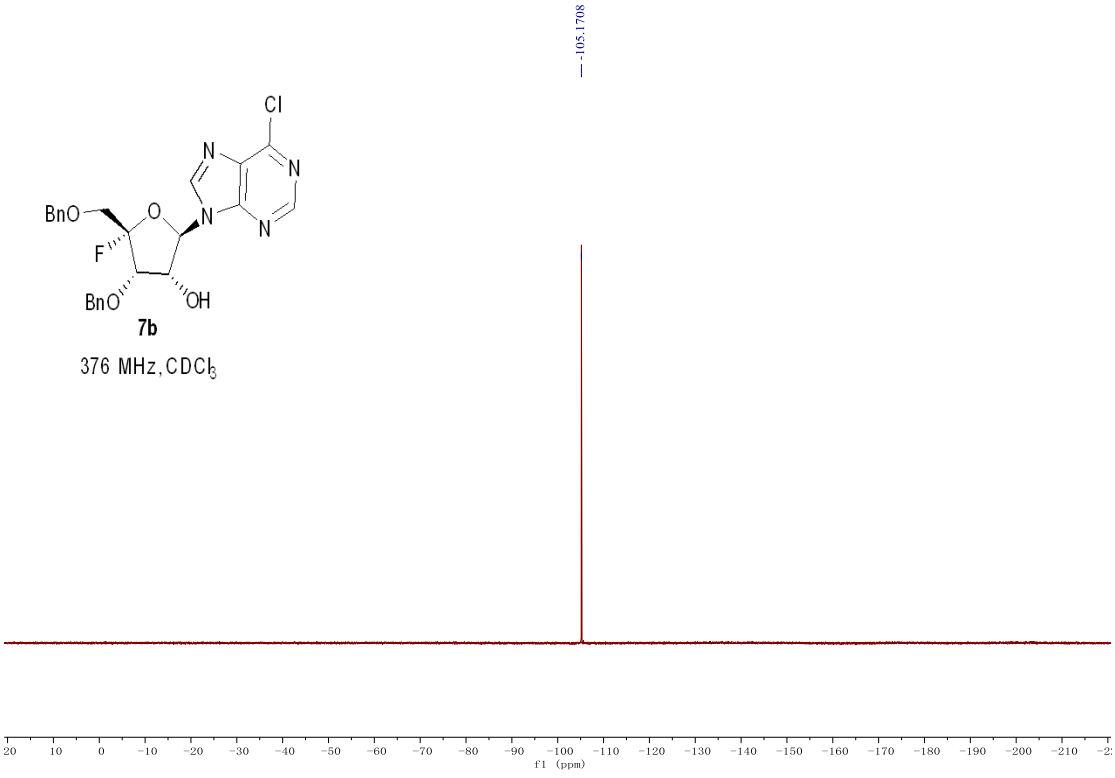
^{1}H NMR Spectrum of **7b**



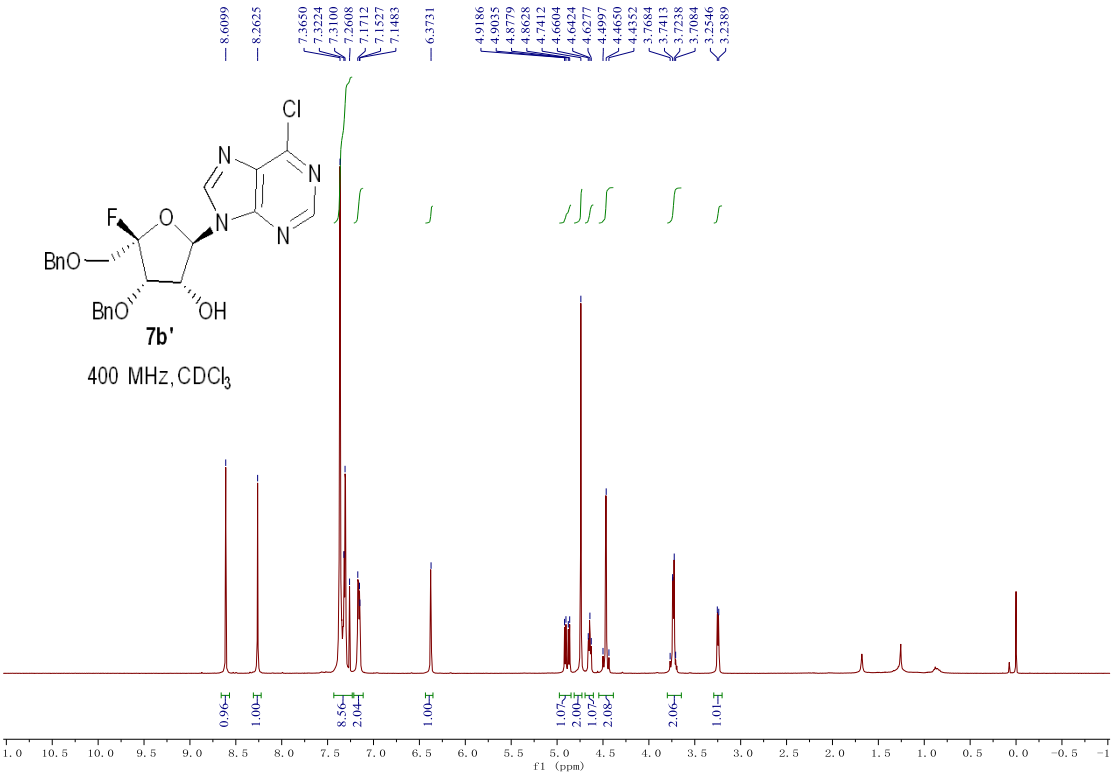
^{13}C NMR Spectrum of **7b**



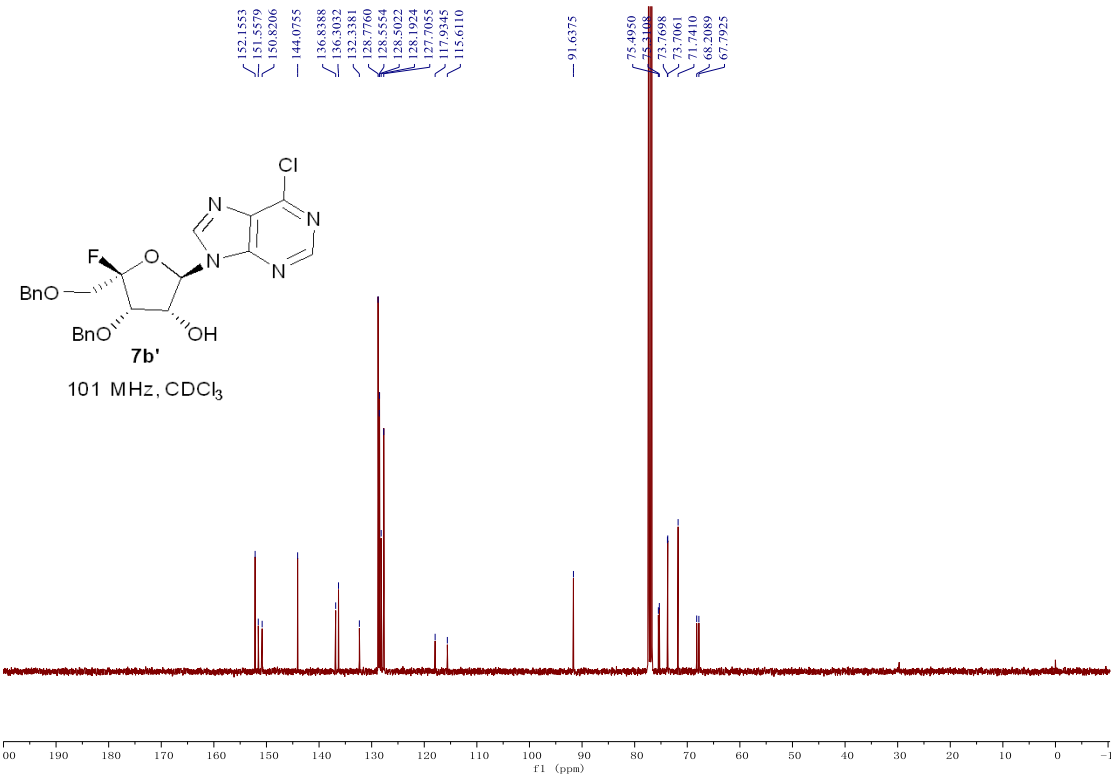
^{19}F NMR Spectrum of **7b**



^{1}H NMR Spectrum of **7b'**



^{13}C NMR Spectrum of **7b'**



^{19}F NMR Spectrum of **7b'**