Supporting Information

Synthesis of Methylene- and Difluoromethylenephosphonate Analogues of Uridine-4-Phosphate and 3-Deazauridine-4- Phosphate

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General. All starting materials and reagents were obtained from commercially available sources and were used without further purification with the exception of NFSi which was recrystallized from methanol before use and TMSBr which was distilled under Ar and stored under Ar in a Schlenk tube. Tetrahydrofuran (THF) was distilled from sodium metal in the presence of benzophenone under argon. CH₂Cl₂ was distilled from calcium hydride under nitrogen. Chloroform was distilled from calcium chloride and stored over Ar. DMF was distilled under aspirator pressure from CaH and stored under Ar. Silica gel flash chromatography (FC) was performed using silica gel 60 Å (230-400 mesh). All NMR spectra were run in CDCl₃ unless stated otherwise. For ¹H NMR in CDCl₃, chemical shifts (δ) are reported in ppm relative to tetramethylsilane (δ 0.0, internal standard). For ¹H NMR in CD₃OD, chemical shifts are reported in ppm relative to the solvent residual peak (δ 3.31, central peak). For ¹H NMR in D₂O, chemical shifts are reported in ppm relative to the solvent residual peak (δ 4.79). For ¹H NMR in DMSO-*d*₆, chemical shifts are reported in ppm relative to the solvent residual peak (δ 2.49). For ¹³C NMR in CDCl₃, chemical shifts are reported in ppm relative to CDCl₃ (δ 77.0 for the central peak). For ¹³C NMR spectra run in CD₃OD, chemical shifts are reported in ppm relative to the solvent residual peak (δ 49.00, central peak). For ¹³C NMR in DMSO-*d*₆, chemical shifts are reported in ppm relative to DMSO-*d*₆, (δ 39.5 for the central peak). For ¹³C NMR spectra run in D₂O, chemical shifts are reported in ppm relative to CH₃OH in D₂O (δ 49.5, external standard). All ³¹P NMR spectra chemical shifts are reported in ppm relative to 85% H₃PO₄ (δ 0.0, external standard). All ¹⁹F spectra chemical shifts are reported in ppm relative to an external fluoroform standard (δ 0.0, CFCl₃). Melting points are uncorrected.

5 (CDCl₃)

¹H

5 (CDCl₃)

¹³C

¹H

¹³C

³¹P

¹³C

³¹P

¹H

¹³C

³¹P

1 (D₂O)

1 (D₂O)

³¹P

13 (CDCl₃)

¹H

13 (CDCl₃)

¹³C

13 (CDCl₃)

³¹P

13 (CDCl₃)

¹⁹F

¹H

³¹P

21 (CDCl₃)

¹H

21 (CDCl₃)

¹³C

¹H

¹H

25 (DMSO- d_6)

^1H

25 (DMSO-*d*₆)

¹³C

¹H

¹H

8.270
8.253

7.259
7.243
7.072

4.355

3.454

¹³C

¹H

¹³C

157.403
157.364
147.736
147.702
146.017
145.903
123.890
123.816
116.196
116.114

77.415
76.996
76.570

52.928
52.837
40.426
32.949
31.128

³¹P

¹H

¹³C

³¹P

¹³C

³¹P

3 (D₂O)

¹H

3 (D₂O)

¹³C

3 (D₂O)

³¹P

31 (CDCl₃)

¹H

31 (CDCl₃)

¹³C

31 (CDCl₃)

³¹P

¹H

¹³C

³¹P

¹⁹F

¹H

¹³C

³¹P

¹⁹F

34 (CDCl₃)

¹H

¹³C

³¹P

4 (D₂O)

¹H

4 (D₂O)

¹³C

4 (D₂O)

³¹P

4 (D₂O)

¹⁹F