Nucleoside Analogues from Push-Pull Functionalized Branched-Chain Pyranosides*

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The reaction of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose (**1**) with ethynylmagnesium bromide in tetrahydrofuran and subsequent trimethylsilylation yielded the methyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-ethynyl-3-*O*-trimethylsilyl-α-D-*ribo*-hexopyranoside (**3**). Push-pull functionalization of **3** with *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylguanidinium chloride under basic conditions and following deprotection afforded the spiro{2,5-dihydro-3-dimethylamino-furan-2,8'-4',4'a,6',7',8',8'a-hexahydro-6'-methoxy-2'-phenyl-pyrano[3,2-*d*][1.3]dioxine}-5-ylidenemalononitrile (**9**). Furthermore, compound **1** reacted with *N*,*N*-dimethylformamide dimethylacetal to furnish methyl (*E*)-4,6-*O*-benzylidene-2-deoxy-2-dimethylaminomethylene-α-D-*erythro*-hexopyranosid-3-ulose (**10**). Treatment of **10** with methylhydrazine and amidines yielded (4*S*,5a*R*,8*R*,9a*S*)-2,5a,6,9a-tetrahydro-4-methoxy-2-methyl-8-phenyl-4*H*-[1,3]dioxino[4',5':5,6]-pyrano[4,3-*c*]pyrazole (**11a**) and (2*R*,4a*R*,6*S*,10b*S*)-4,4a,6,10b-tetrahydro-6-methoxy-2-phenyl-[1,3]dioxino[4',5':5,6]pyrano[4,3-*d*]pyrimidines **12**, respectively.

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