Supplementary Data

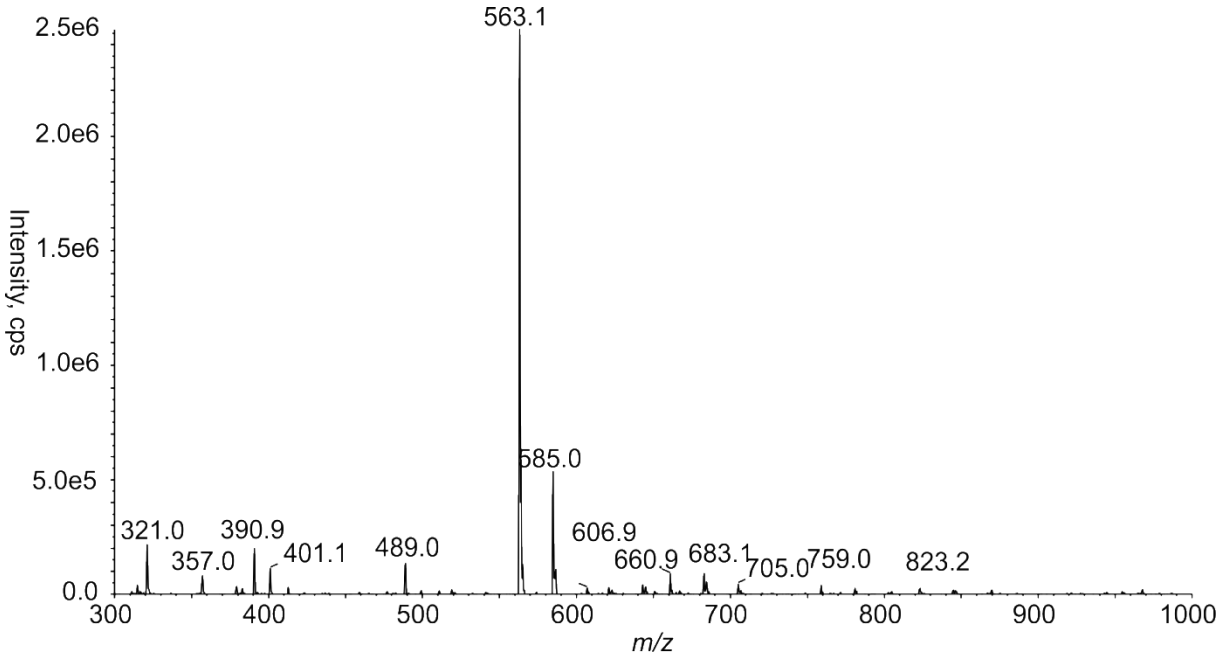


Figure S1: Capillary electrophoresis – mass spectrometry analysis of the RmlA product (construct CJV-11).

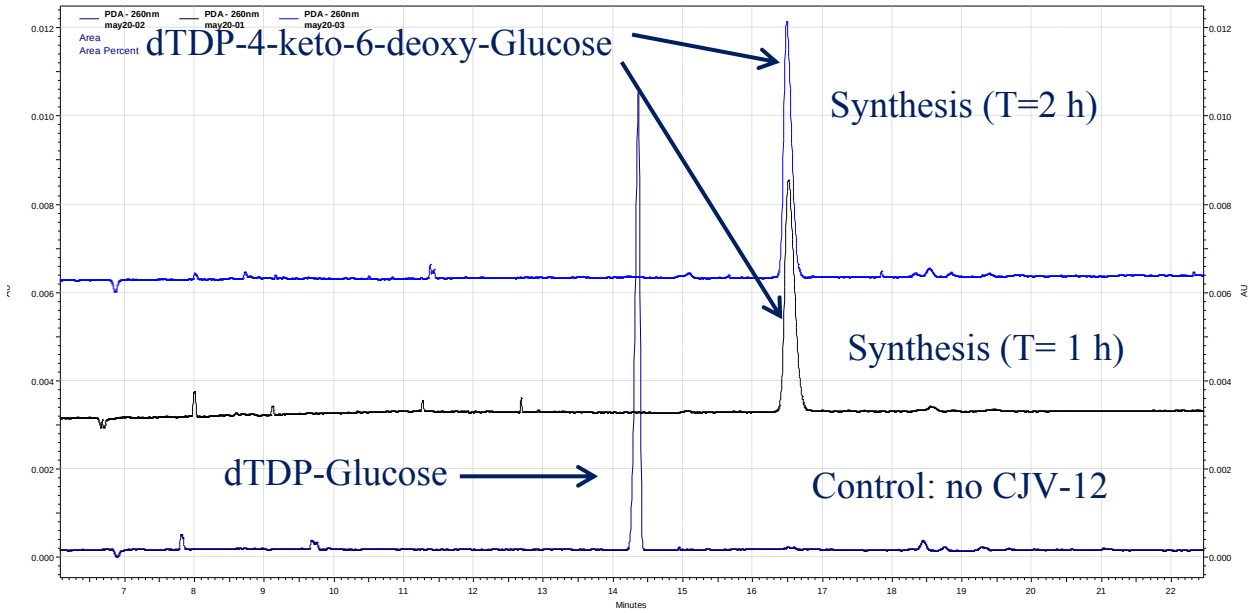


Figure S2: Capillary electrophoresis analysis (with PDA detector) of the reaction product of RmlB (construct CJV-12).

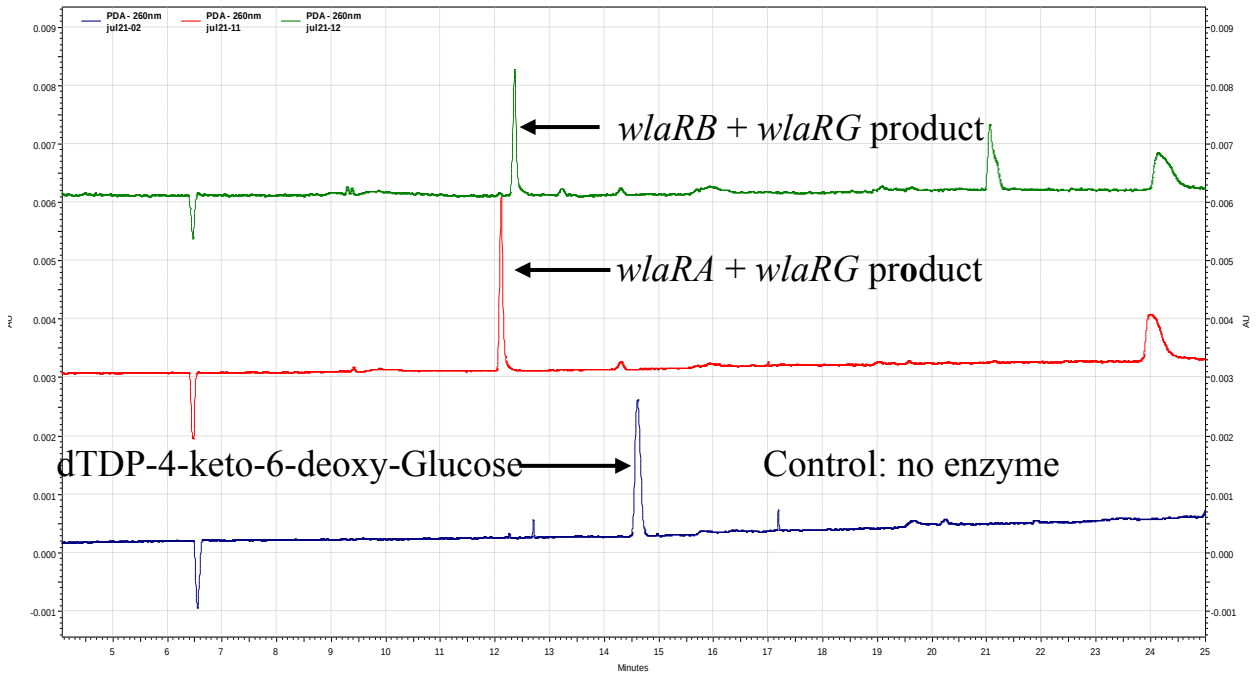


Figure S3: Capillary electrophoresis analysis (with PDA detector) of coupled reactions shows WlaRB+WlaRG products and WlaRA+WlaRG products are distinct. From top to bottom, WlaRB+WlaRG reaction, WlaRA+WlaRG reaction, and no enzyme control are shown respectively.

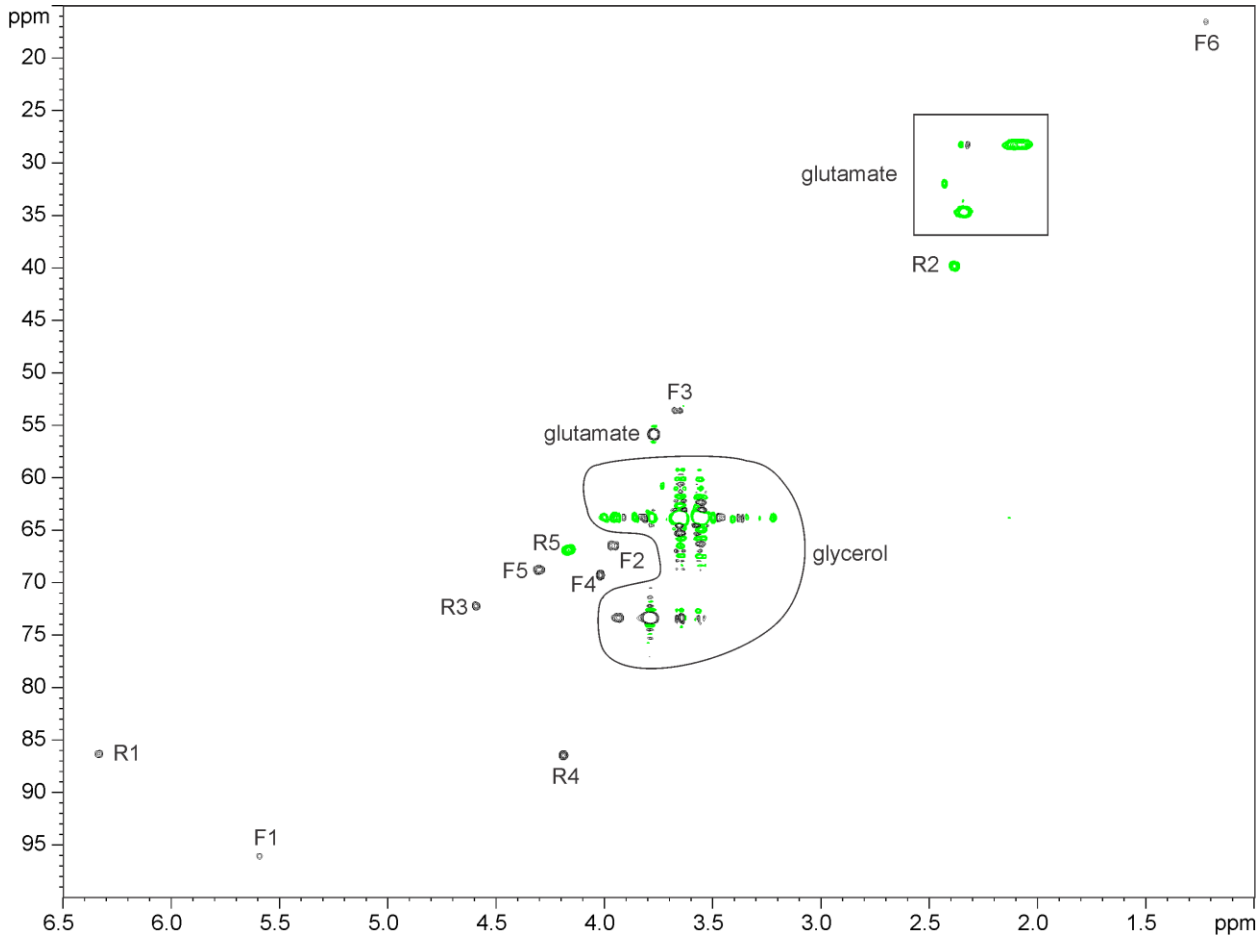


Figure S4: Part of the $^{1}H - ^{13}C$ HSQC NMR spectrum of the product from RmlB-WlaRA-WlaRG (dTDP-Fuc3N). Cross-peaks are labeled using "R" for 2-deoxyribose and "F" for Fuc3N, and by the atom number as in Table II.

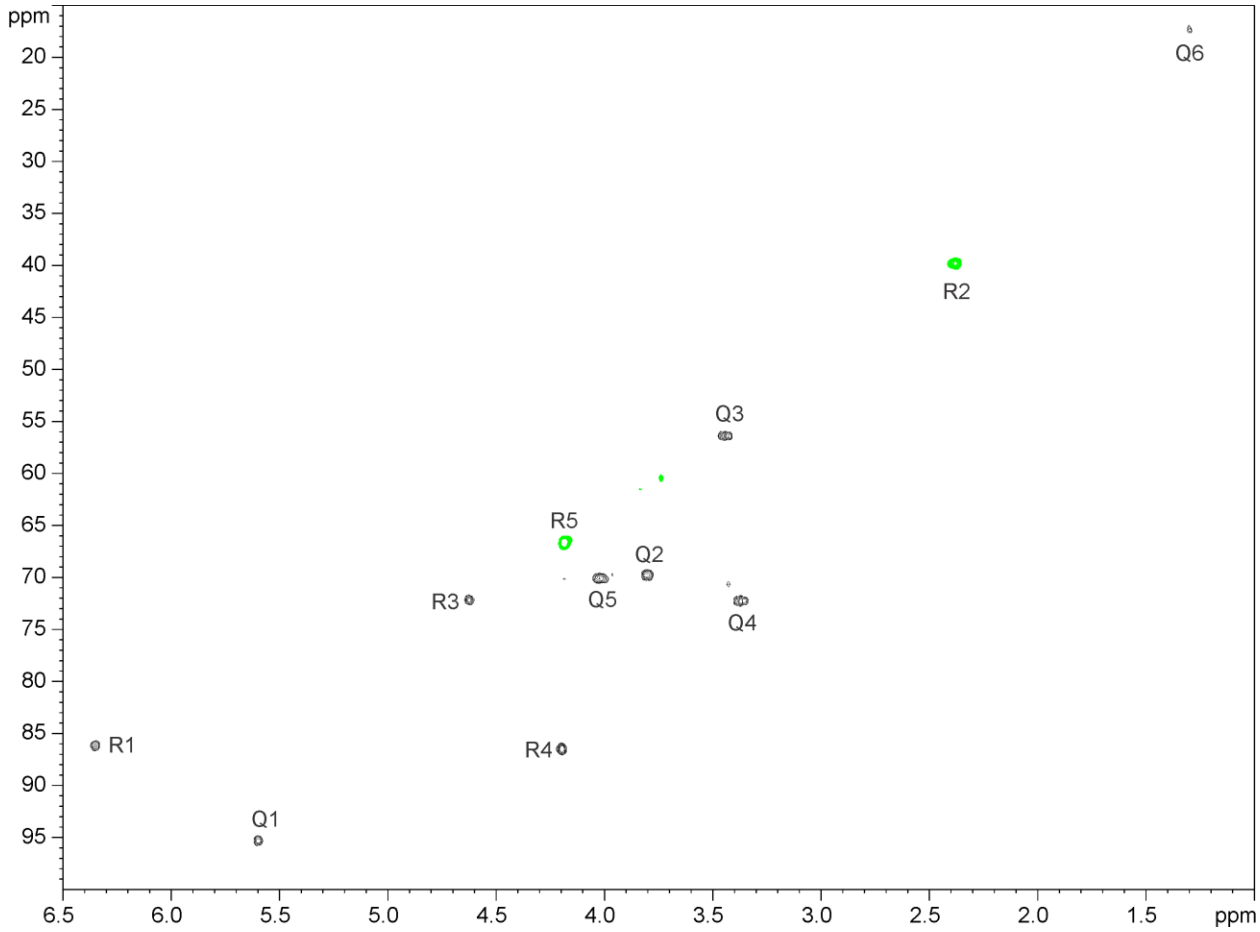
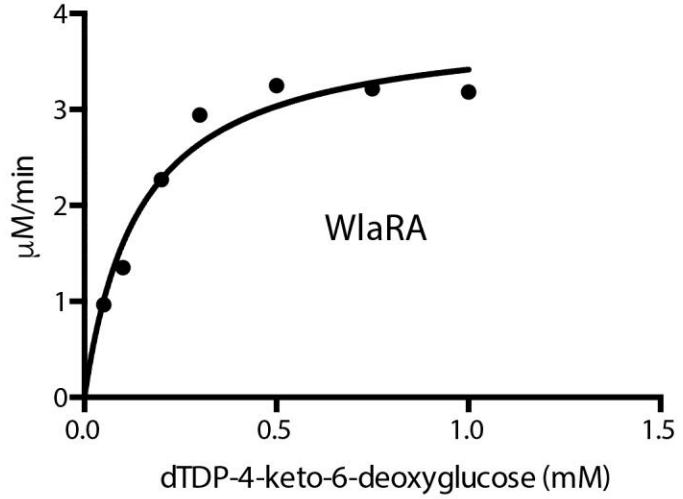
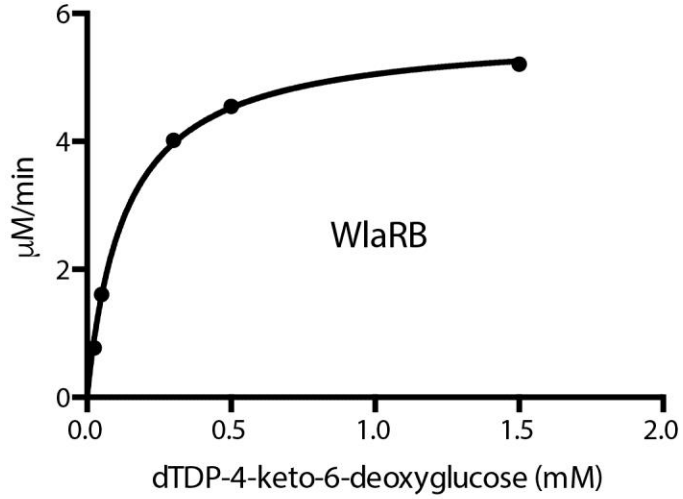


Figure S5: Part of the ^{1}H – ^{13}C HSQC NMR spectrum of the product from RmlB-WlaRB-WlaRG (dTDP-Qui3N). Cross-peaks are labeled using "R" for 2-deoxyribose and "Q" for Qui3N, and by the atom number as in Table II.



(a)



(b)

Figure S6: Initial velocities of the WlaRA and WlaRB reactions. Shown in (a) is the initial velocity of the WlaRA reaction versus substrate concentration. Shown in (b) is the initial velocity of the WlaRB reaction versus substrate concentration.

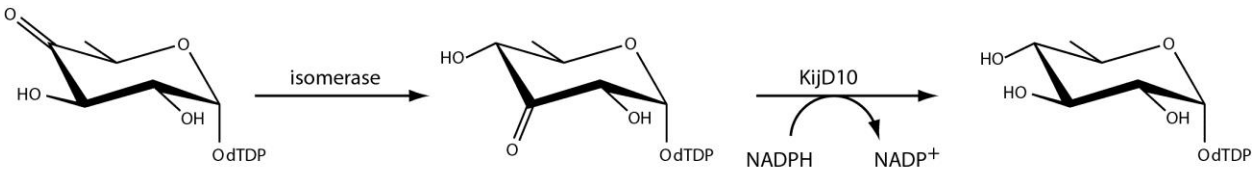


Figure S7: The kinetic constants for WlaRA, WlaRB, and the WlaRB mutant variant were determined via this coupled assay using KijD10 from *Actinomadura kijaniata* as an NADPH-dependent C-3' ketoreductase.