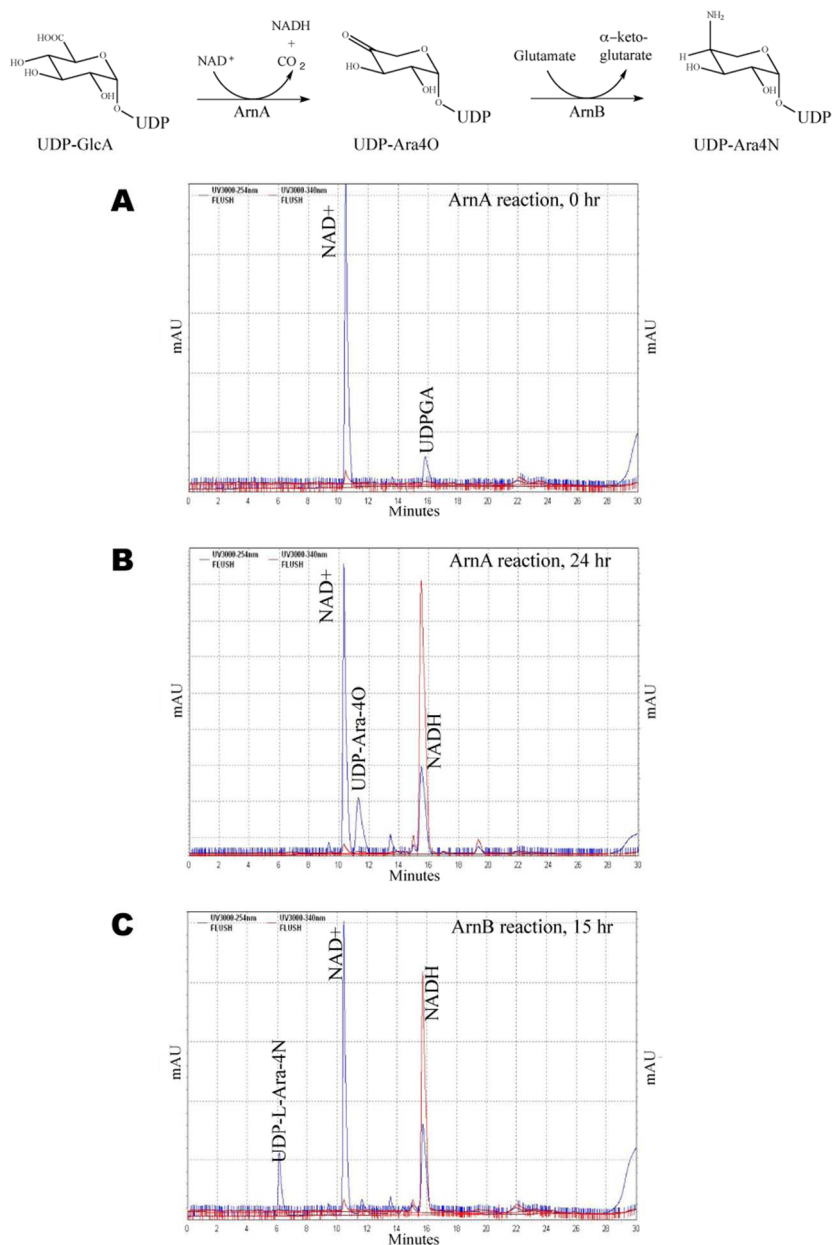
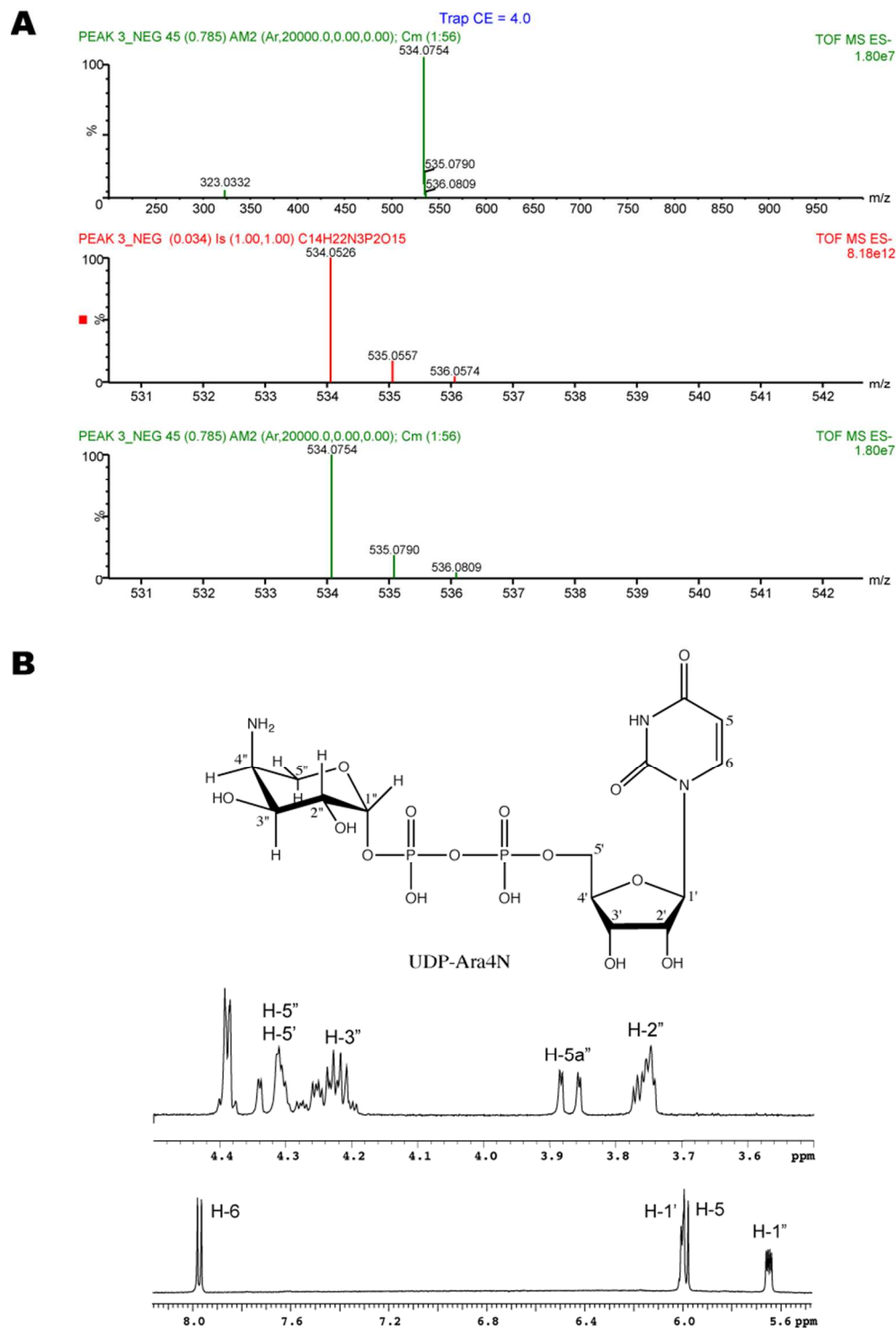


## Supplementary Figure S1



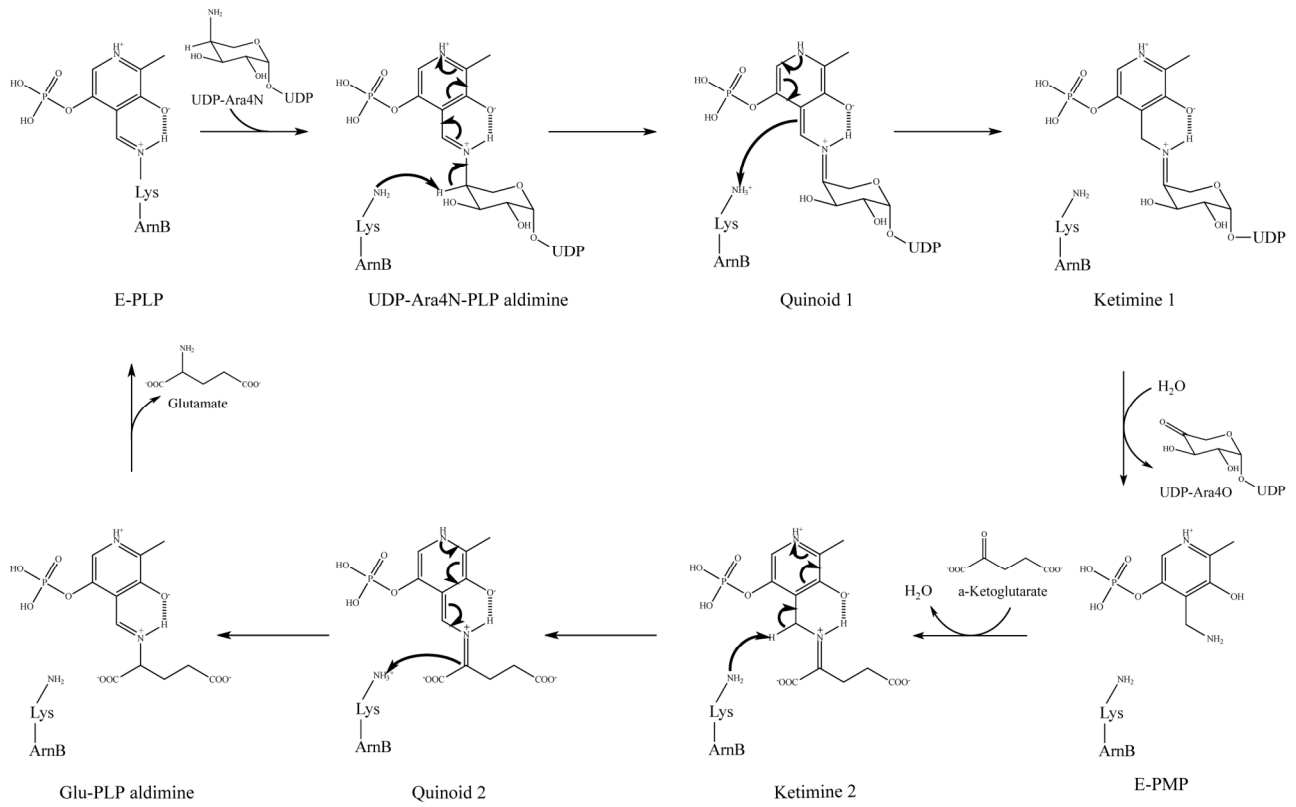
**Figure S1: Production and separation of reactants and products of the ArnA and ArnB reactions by optimized ion-pair reversed-phase HPLC.** Reaction mixtures were diluted 50 times in 25mM Tris-HCl (pH 8.0) and an aliquot (20  $\mu$ l) of the diluted samples was injected onto the column and then eluted as described in the “Materials and methods”. The eluted compounds were detected by their absorbance at 254 nm (blue line) for nucleotide and at 340 nm (red line) for NADH. A scheme showing the substrates and products of each reaction is included for reference. (A) ArnA substrates at time = 0; (B) ArnA reaction products after 24 hr incubation; (c) ArnB products after 15 hr. incubation.

## Supplementary Figure S2:



**Figure S2: Identification of the purified UDP-Ara4N.** (A) Mass-spectrometric analysis shows that the observed mass (bottom panel) is identical to the calculated mass (middle panel): Top panel is the entire spectra showing purity of the purified UDP-Ara4N. (B) NMR analysis of the purified UDP-Ara4N.

**Supplementary Figure S3:**



**Figure S3: Proposed catalytic mechanism of ArnB.** The lysine residue is the "catalytic" Lys188.