Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Kinetic analysis of hydrolytic reaction of homo- and heterochiral adenylyl(3'-5')adenosine isomers: breaking homochirality reduces hydrolytic stability of RNA

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Experimental

The synthesis of the diastereomeric isomers of adenylyl(3'-5')adenosine (ApA) was reported previously.[1] Each dimer (D-(ApA), ADpAL, ALpAD and L-(ApA); 1 OD unit each) and deoxyadenosine (1 OD unit) as the internal standard were lyophilized in a 1.5 mL microtube. After the samples were dissolved in an aqueous buffer solution (1 mL) containing 0.2 M NaCl, 75 mM $MgCl_2$, and 0.1 M HEPES (pH 8.0), silicone oil (400 μL) was layered on the solution to prevent evaporation. The reactions were started by heating the microtubes to an appropriate temperature (40-80°C). Aliquots (90 μL) of the solutions were withdrawn periodically and analyzed with reversed phase HPLC. The HPLC analysis was performed on a Shimadzu LC-6A system equipped with a Cosmosil 3C18 column (Nacalai Tesque, Kyoto, Japan; 4.6 x 50 mm, 3 μm particle size) with a linear gradient of acetonitrile (0-10 % during 15 min) in 50 mM potassium phosphate, pH 4.0.

Rate constants for the hydrolysis of the dimers were obtained by using the slope of the pseudo-first order rate plots. Half-lives for the hydrolysis of the dimers at 0 °C and 100 °C were calculated by the extrapolation of the Arrhenius plots (1/T vs. ln k_{obs}). Activation parameters for the hydrolysis of the dimers were calculated by using the slopes and the y-intercepts of the Eyring plots [1/T vs. ln (k_{obs}/T)].

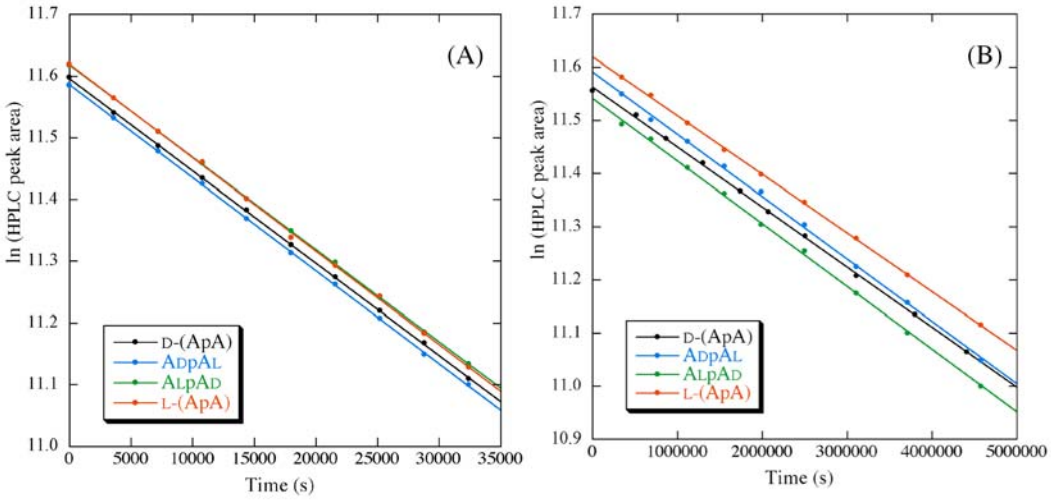

Figure S1. Kinetics of the hydrolysis of the diastereomeric ApAs at 80°C (A) and 40°C (B). Black, blue, green and red lines represent D-(ApA), ADpAL, ALpAD and L-(ApA), respectively.

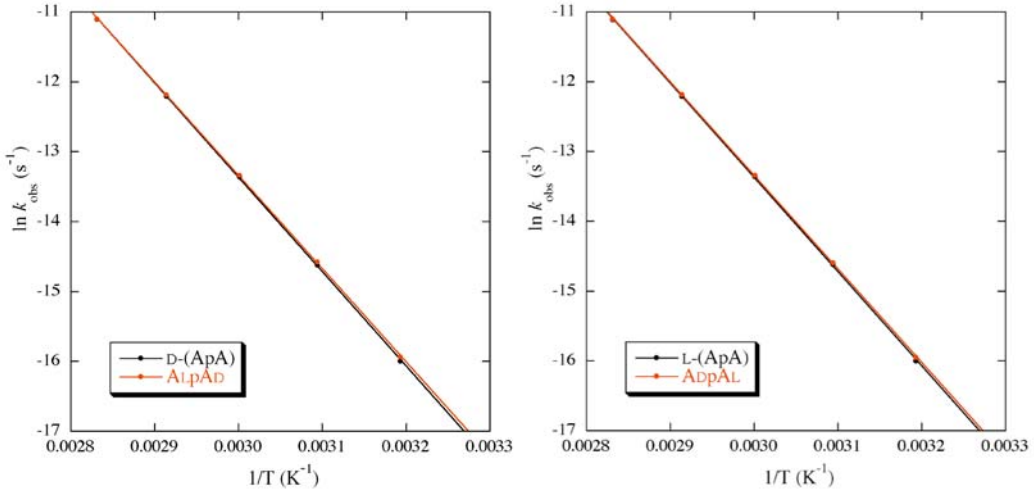

Figure S2. Arrhenius plots for the hydrolysis of the homochiral- (black) and heterochiral (red) ApAs.

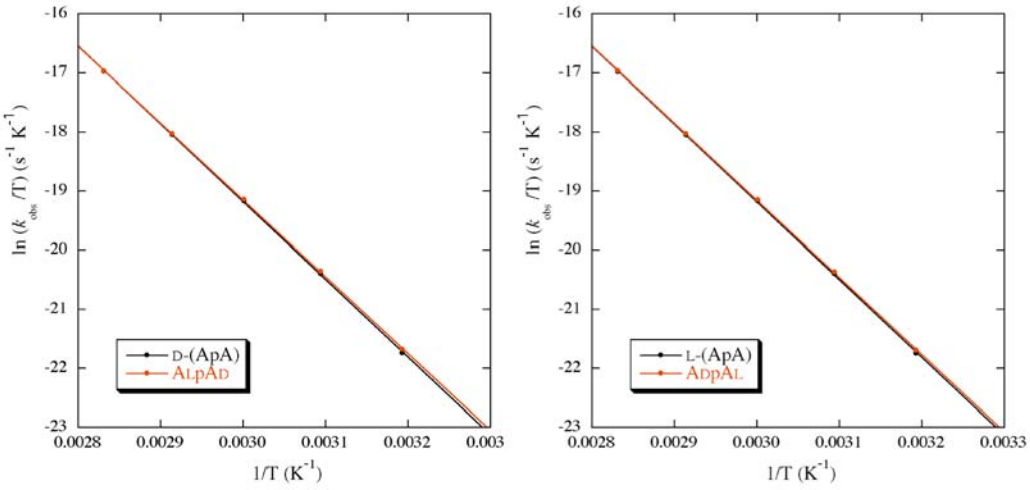

***Figure S3*.** Eyring plots for the hydrolysis of the homochiral- (black) and heterochiral (red) ApAs.

References

1. H. Urata, M. Go, N. Ohmoto, K. Minoura and M. Akagi, *Chem. Commun*. **2002**, 544–545.