While kinetic resolution (KR) processes of alcohols bearing point chirality has been widely explored, the acylative KR of alcohols bearing axial chirality remains surprisingly underdeveloped, with only 2 methods of organocatalytic acylative KR of biaryl alcohols reported to date.\cite{1,2} To address this limitation, we have developed an operationally-simple isothiourea-catalysed acylative kinetic resolution of unprotected 1,1′-biaryl-2,2′-diol derivatives that provides access to axially-chiral biaryl diols in highly enantioenriched form ($s$ values up to 190).\cite{3} Following extensive reaction optimization, investigation of reaction scope and limitations provided three key observations: i) the diol motif of the substrate was essential for obtaining good conversion and high $s$ values; ii) the use of an stable α,α-disubstituted mixed anhydride (2,2′-diphenylacetic pivalic anhydride) was critical to minimize diacylation and give high selectivity; iii) The presence of substituents in the 3,3′-positions of the diol hindered effective acylation. This observation led to the first highly regioselective acylative kinetic resolution of unsymmetrically-substituted biaryl diol substrates.