Excited-state proton transfer and ion pair formation in a
Cinchona organocatalyst

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Fig. S1 The decay associated spectra of BnCPD ($c = 50 \, \mu\text{M}$) in MeCN. The inset shows the individual $\chi^2$-values. The relative amplitude of $\tau_1$ is divided by a factor of 50. Excitation wavelength was 295 nm.

Fig. S2 The decay associated spectra of BnCPD ($c = 40 \, \mu\text{M}$) in toluene. The inset shows the individual $\chi^2$-values. Excitation wavelength was 315 nm.
Fig. S3 The decay associated spectra of BnCPD \((c = 10 \mu M)\) in THF in the presence of \(p\)TsOH \((c = 110 \mu M)\). The inset shows the individual \(\chi^2\)-values. Excitation wavelength was 315 nm.

Fig. S4 The decay associated spectra of 6HQ \((c = 40 \mu M)\) in THF in the presence of \(p\)TsOH \((c = 30 \mu M)\). The inset shows the individual \(\chi^2\)-values. Excitation wavelength was 315 nm.
Fig. S5 Absorption and emission spectra of 6HQ (c = 20 μM) in THF upon addition of water.
Fig. S6 Absorption spectra of BnCPD (c = 20 µM) in THF upon addition of water.
Fig. S7 Examples of decays and fittings of BnCPD in THF in the presence of 1.2 v-% of a) H$_2$O and b) D$_2$O. The data points are indicated by markers and fits by solid lines. The instrument response function is indicated by the dashed grey line. Excitation wavelength was 315 nm.
Fig. S8 The decay associated spectra of BnCPD ($c = 50 \, \mu\text{M}$) in THF in the presence of 0.4 v-% of a) H$_2$O and b) D$_2$O. The inset shows the individual $\chi^2$-values. Excitation wavelength was 315 nm.
Fig. S9 The decay associated spectra of BnCPD (c = 50 µM) in THF in the presence of 0.8 v-% of a) H$_2$O and b) D$_2$O. The inset shows the individual $\chi^2$-values. Excitation wavelength was 315 nm.
Fig. S10 The decay associated spectra of the long-wavelength region of BuCPD (c = 50 µM) in THF in the presence of 1.2 v-% of a) H₂O and b) D₂O. The inset shows the individual χ²-values. Excitation wavelength was 315 nm.
Fig. S11 The decay associated spectra of BnCPD (c = 50 µM) in THF in the presence of 1.6 v-% of a) H₂O and b) D₂O. The inset shows the individual χ²-values. Excitation wavelength was 315 nm.
Fig. S12 Absorption spectra of BnCPD ($c = 20 \, \mu\text{M}$) in THF upon addition of a base (DBU). Absorption of DBU has been subtracted ($< 300 \, \text{nm}$).