Supporting Information for

A Visible-Light and Temperature Responsive Host-Guest System: Photoisomerization of a Ruthenium Complex and Inclusion Complex Formation with Cyclodextrins

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Supporting Information

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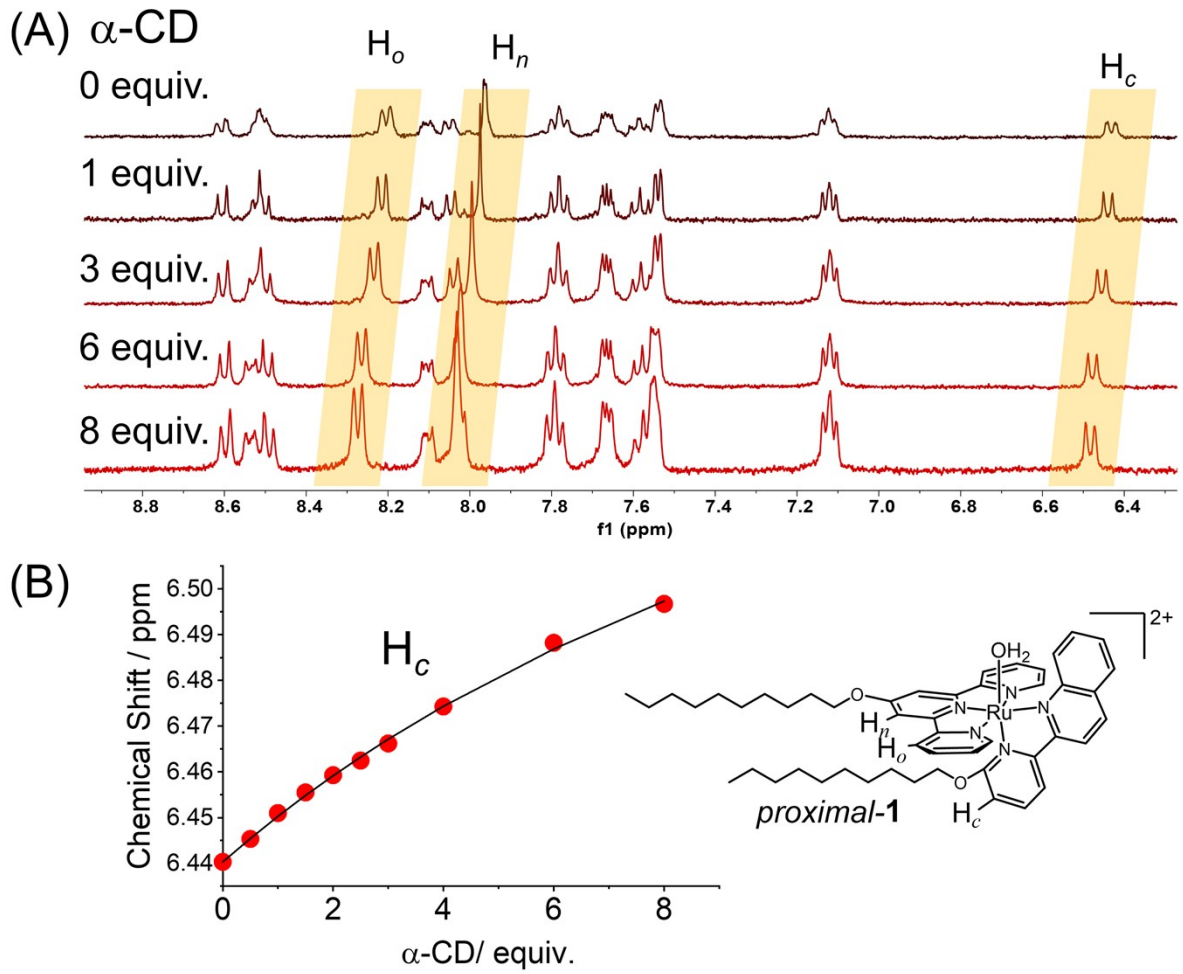

Figure S1. (A) ^{1}H NMR spectra of *proximal*-**1** (1.55 mM) during titration experiments with α-CD in D_2O, CD_3OD, and TFE mixed solvent (v/v/v = 70:40:2). Peaks of H_o, H_n, and H_c protons are highlighted. (B) Plots of chemical shifts of H_c proton verses equivalents of α-CD.

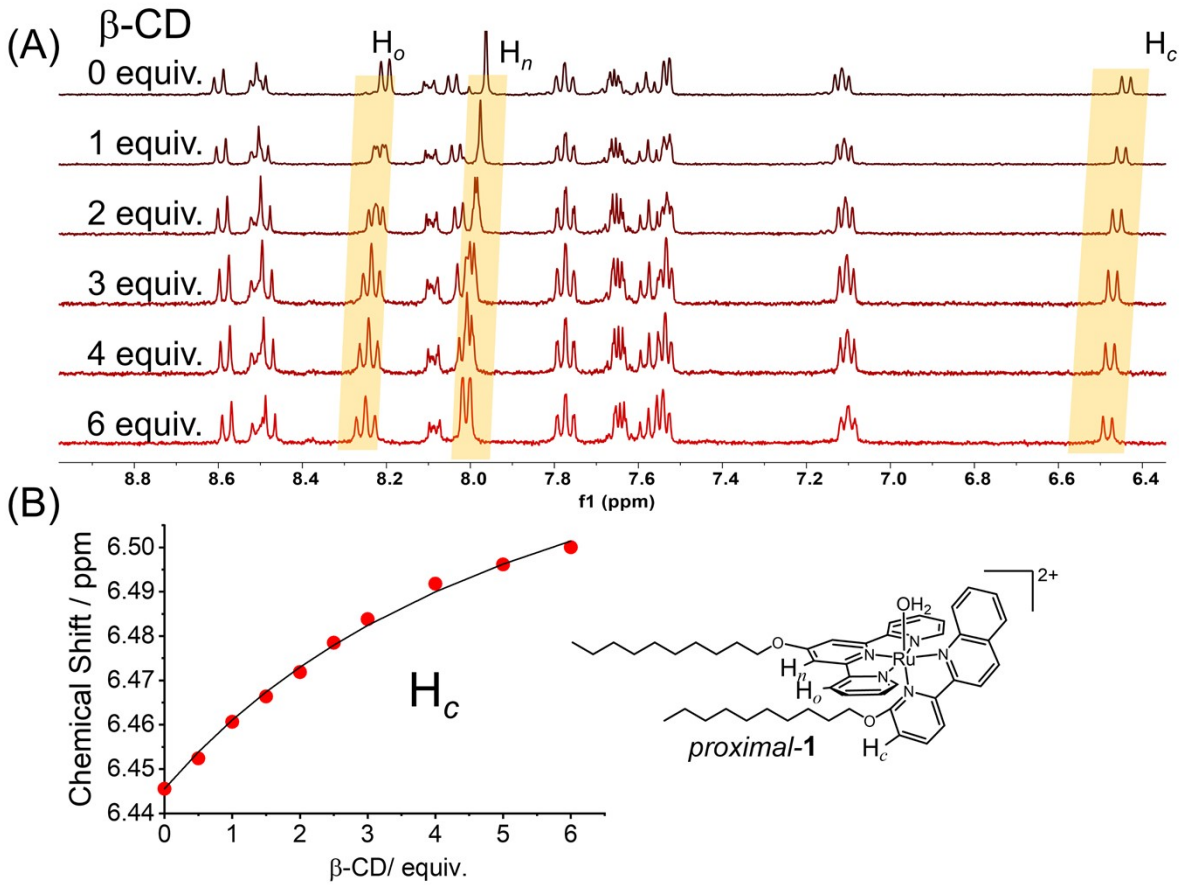

Figure S2. (A) ^{1}H NMR spectra of *proximal*-**1** (0.84 mM) during titration experiments with β-CD in D_2O, CD_3OD, and TFE mixed solvent (v/v/v = 70:40:2). Peaks of H_o, H_n, and H_c protons are highlighted. (B) Plots of chemical shifts of H_c proton verses equivalents of β-CD.

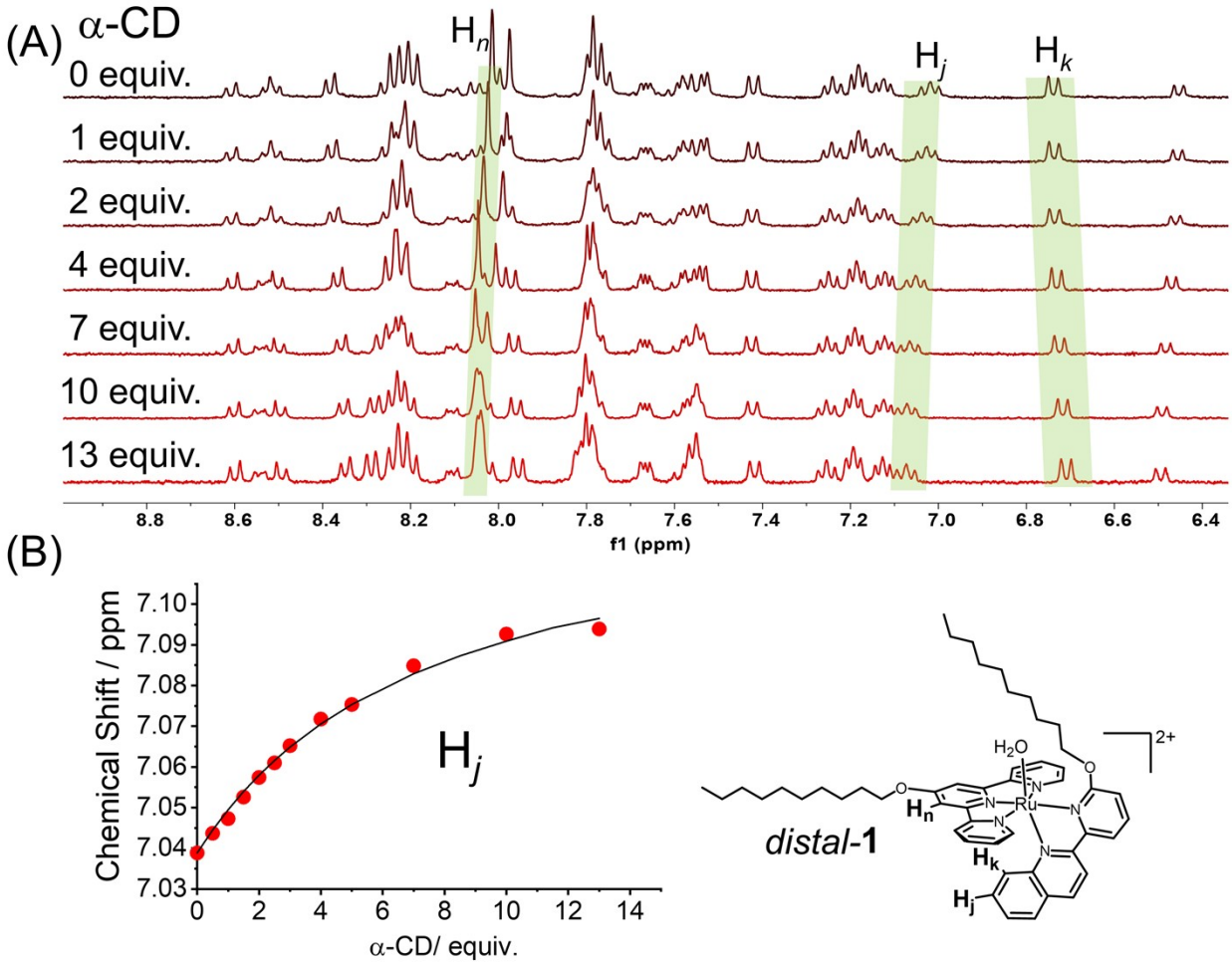

Figure S3. (A) ^{1}H NMR spectra of *proximal*-**1** and *distal*-**1** (total concentration: 1.36 mM, *proximal*-**1** : *distal*-**1** = 36 : 64) during titration experiments with α-CD in mixed aqueous solutions (D_2O : CD_3OD : TFE = 70 : 50 : 2). Peaks of H_n, H_j, and H_k protons for *distal*-**1** are highlighted. (B) Plots of chemical shifts of H_j proton verses equivalents of α-CD.

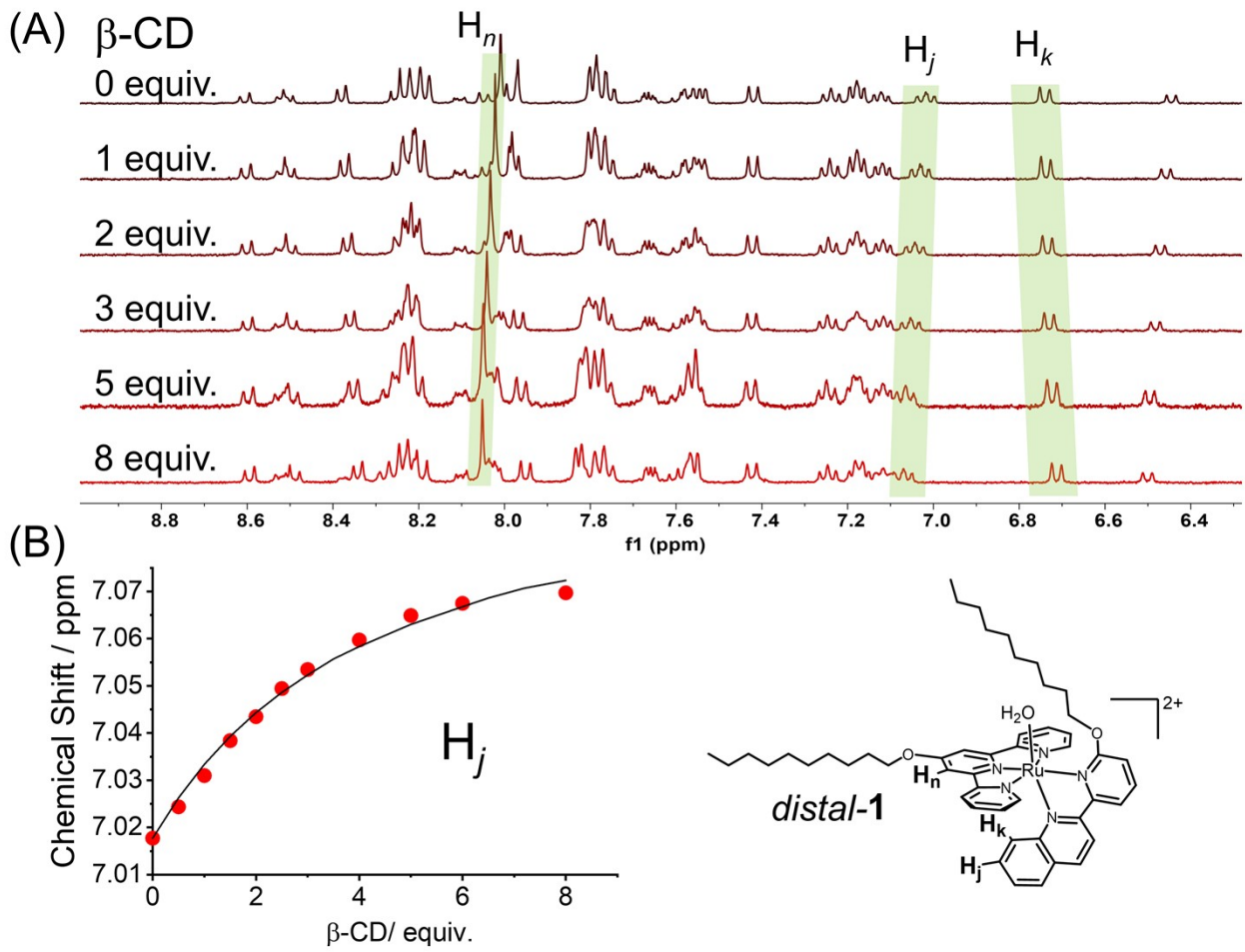

Figure S4. (A) ^{1}H NMR spectra of *proximal*-**1** and *distal*-**1** (total concentration: 0.88 mM, *proximal*-**1** : *distal*-**1** = 36 : 64) during titration experiments with β-CD in mixed aqueous solutions (D_2O : CD_3OD : TFE = 70 : 40 : 2). Peaks of H_n, H_j, and H_k protons for *distal*-**1** are highlighted. (B) Plots of chemical shifts of H_j proton verses equivalents of β-CD, respectively.

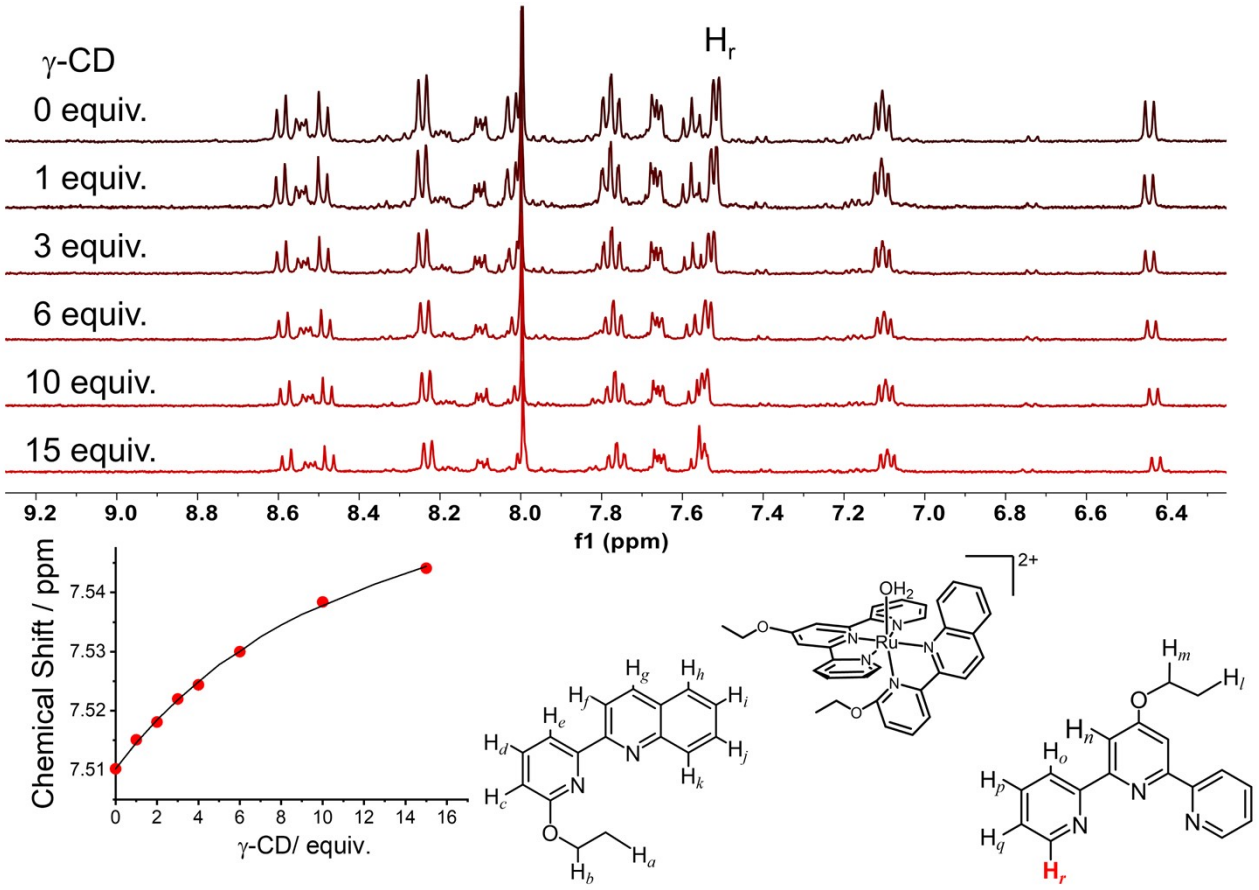

Figure S5. (A) ^{1}H NMR spectra of *proximal*-[Ru(C_2tpy)(C_2pyqu)OH_2]$^{2+}$ (1.63 mM) during titration experiments with γ-CD in D_2O, CD_3OD, and TFE mixed solvent (v/v/v = 70:40:2). (B) Plots of chemical shifts of H_r proton verses equivalents of γ-CD. Small peaks correspond to *distal*-[Ru(C_2tpy)(C_2pyqu)OH_2]$^{2+}$.[1]

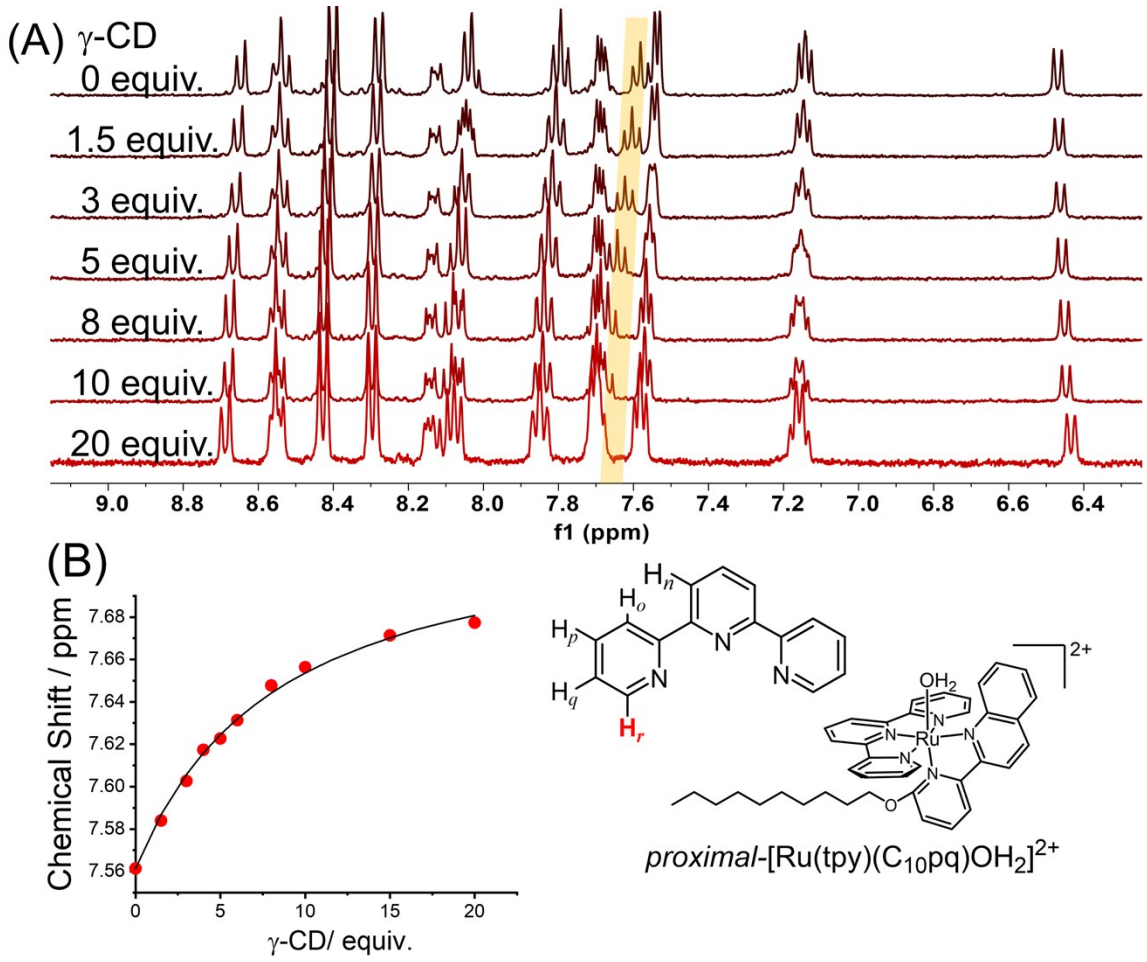

Figure S6. (A) ^{1}H NMR spectra of *proximal*-[Ru(tpy)(C_{10}pyqu)OH_2]$^{2+}$ (1.58 mM) during titration experiments with γ-CD in D_2O, CD_3OD, and TFE mixed solvent (v/v/v = 70:40:2). (B) Plots of chemical shifts of H_r proton verses equivalents of γ-CD.

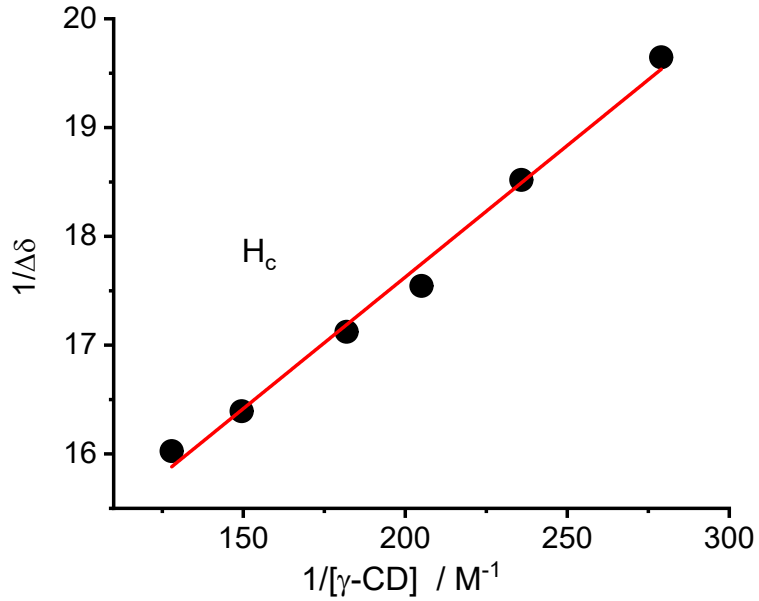

Figure S7. Benesi–Hildebrand plots from ^{1}H NMR titration between *proximal*-**1** and γ-CD.

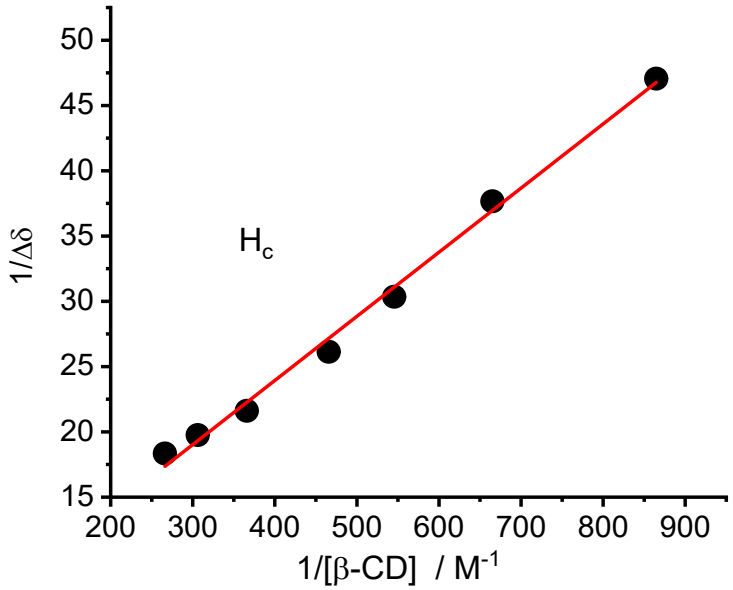

Figure S8. Benesi–Hildebrand plots from ^{1}H NMR titration between *proximal*-**1** and β-CD.

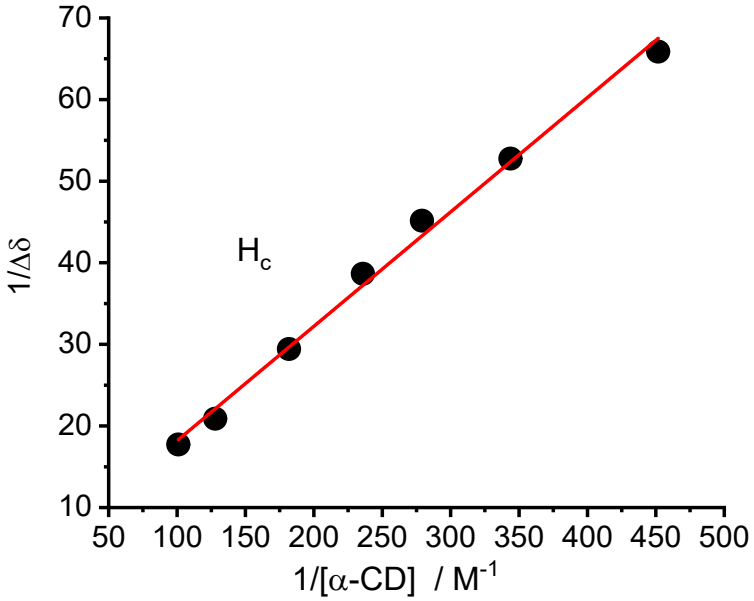

Figure S9. Benesi–Hildebrand plots from ^{1}H NMR titration between *proximal*-**1** and α-CD.

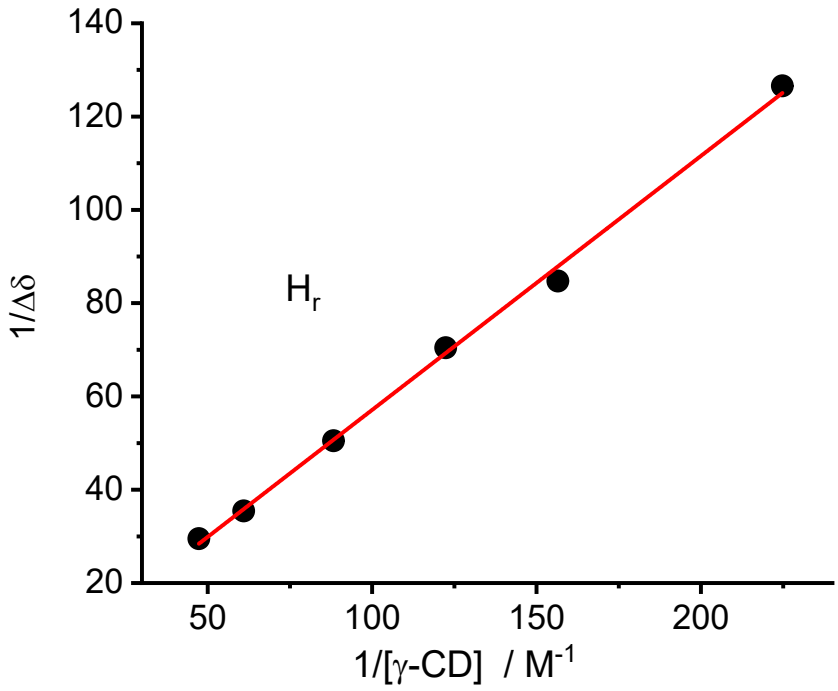

Figure S10. Benesi–Hildebrand plots from ^{1}H NMR titration between *proximal*-$[Ru(C_2tpy)(C_2pyqu)OH_2]^{2+}$ and γ-CD.

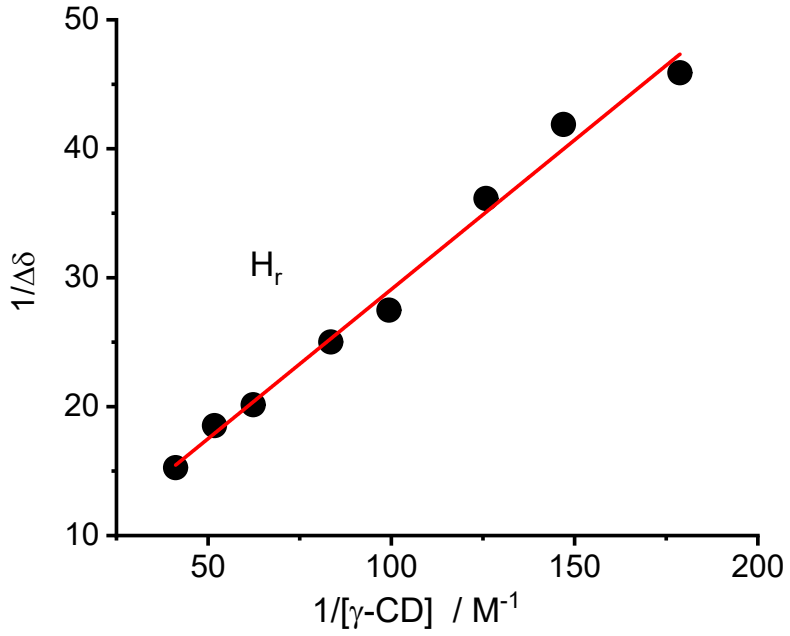

Figure S11. Benesi–Hildebrand plots from ^{1}H NMR titration between *proximal*-$[Ru(tpy)(C_{10}pyqu)OH_2]^{2+}$ and γ-CD.

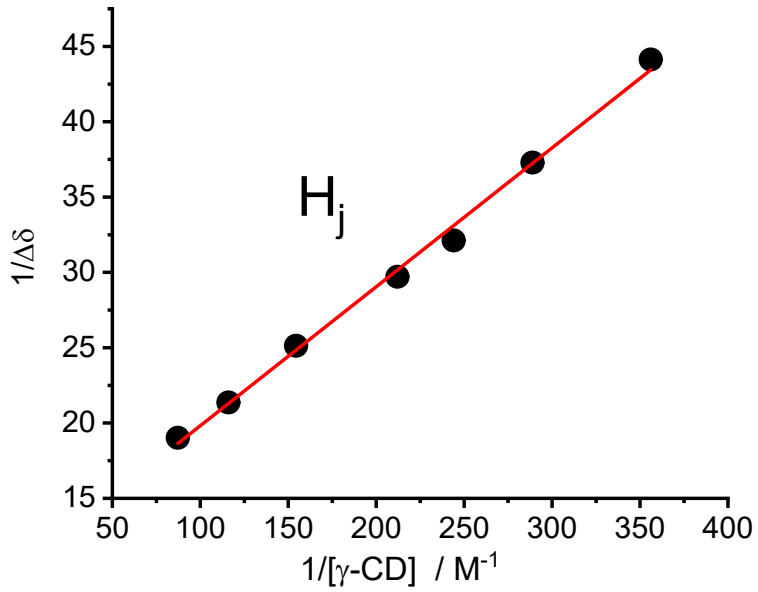

Figure S12. Benesi–Hildebrand plots from ^{1}H NMR titration between *distal*-**1** and γ-CD.

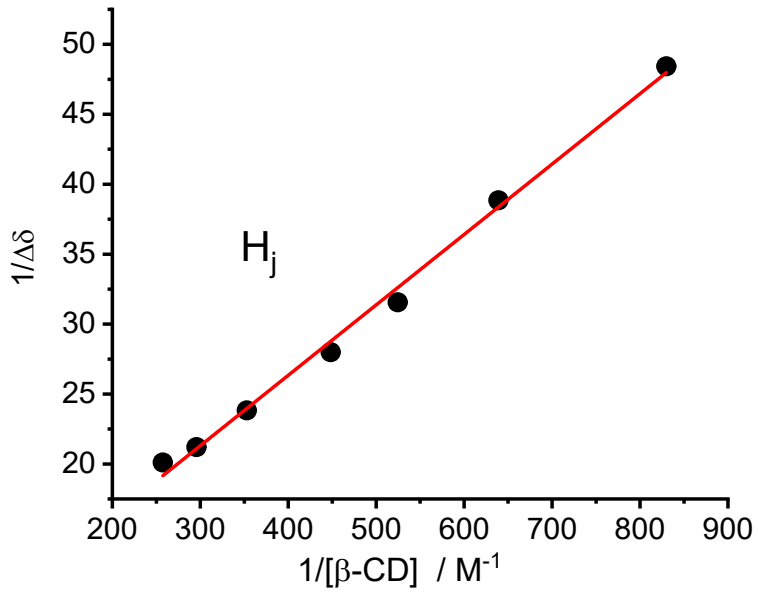

Figure S13. Benesi–Hildebrand plots from ^{1}H NMR titration between *distal*-**1** and β-CD.

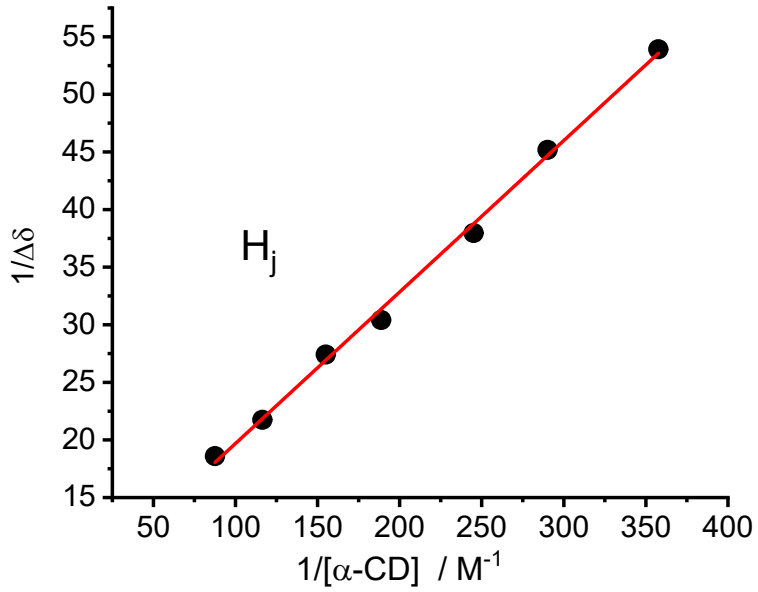

Figure S14. Benesi–Hildebrand plots from ^{1}H NMR titration between *distal*-**1** and α-CD.

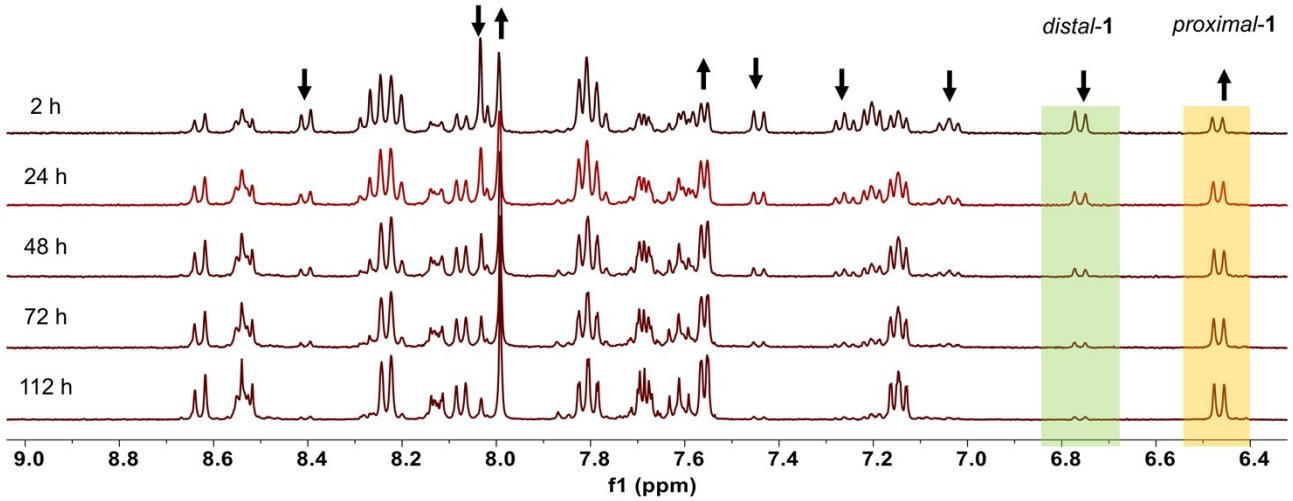

Figure S15. ^{1}H NMR spectra during thermal back isomerization from *distal*-**1** to *proximal*-**1** at 293 K. The sample solution was prepared by light irradiation to an aqueous solution of *proximal*-**1** (1.5 mM) in mixed aqueous solution (D_2O : CD_3OD : TFE = 70 : 50 : 2). H_k proton of *distal*-**1** and H_c proton of *proximal*-**1** were highlighted with green and orange, respectively. The progress of the reaction was monitored in the dark.

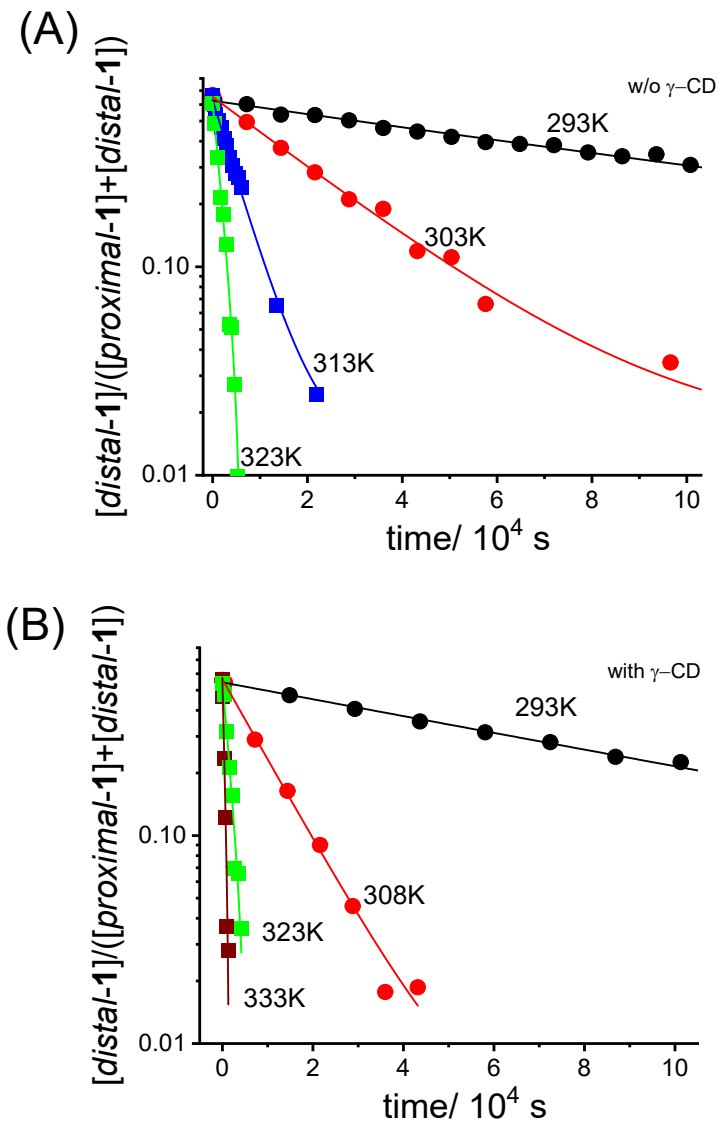

Figure S16. Kinetic traces for thermal back isomerization from *distal*-**1** to *proximal*-**1** at various temperatures. (A) Traces at 293, 303, 313, and 323 K in the absence of a host molecule. (B) Traces at 293, 308, 323, and 333 K in the presence of 5 equiv. of γ-CD. The concentration of distal-1 was estimated based on the integration of an Hc proton for *proximal*-**1** and an H_k proton for *distal*-**1**, respectively.

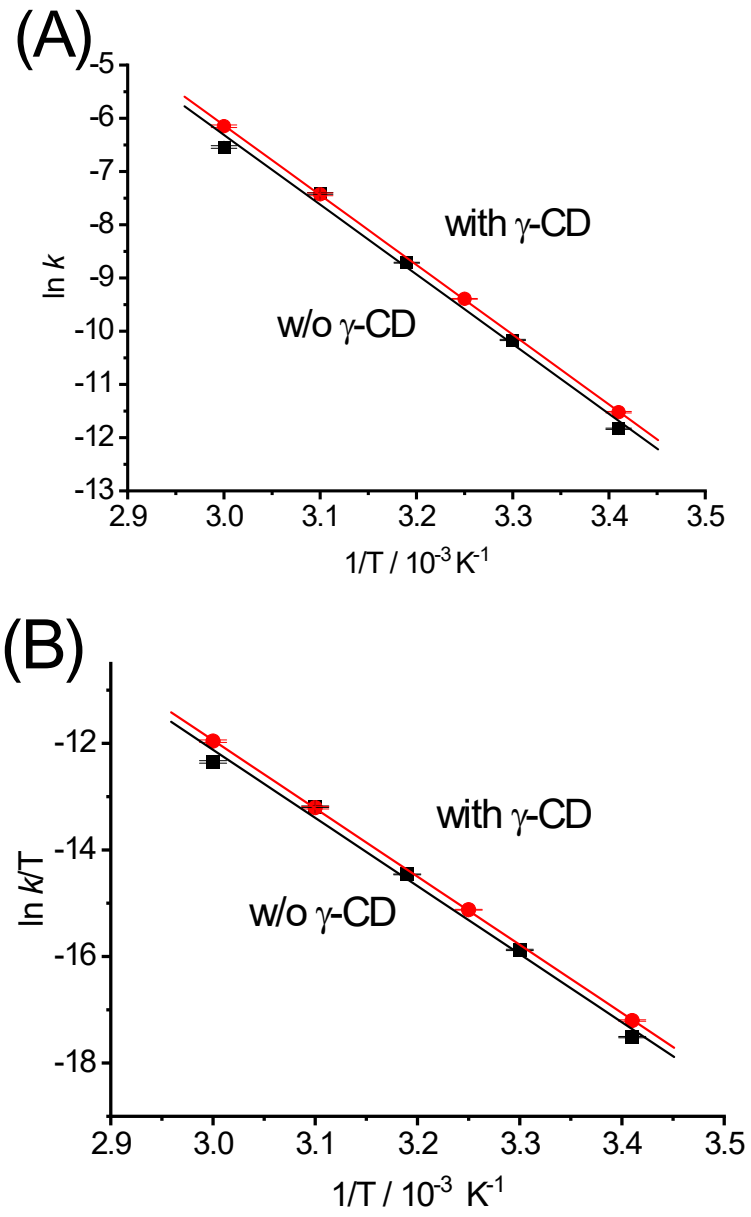

Figure S17. (A) Arrhenius and (B) Eyring plots for the thermal-back-isomerization from *distal*-**1** to *proximal*-**1**. Plots for the isomerization in the absence and presence of γ-CD are plotted with black square and red circle, respectively.

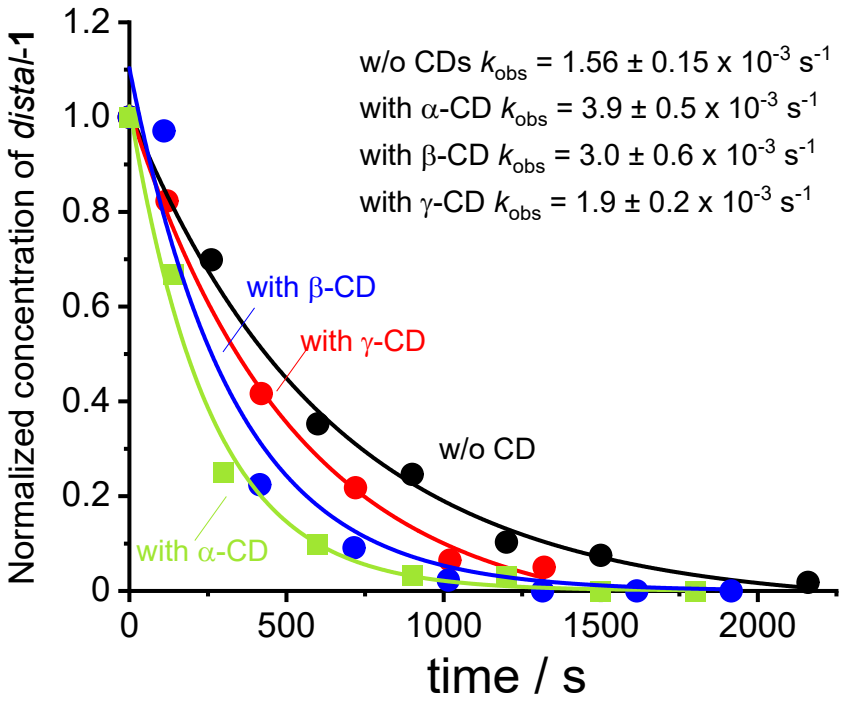

Figure S18. Kinetic traces for thermal back isomerization from *distal*-**1** to *proximal*-**1** at 333K in the absence or presence of cyclodextrins. The sample solution of *distal*-**1** and *proximal*-**1** in the photostationary state was prepared by light irradiation to an aqueous solution of *proximal*-**1** in the mixed aqueous solution (D_2O : CD_3OD : TFE = 70 : 50 : 2) prior to the measurements. Black: in the absence of cyclodextrins (c_{Ru} = 1.52 mM), red: in the presence of γ-CD (c_{Ru} = 1.38 mM, [γ-CD] = 7.1 mM), blue; in the presence of β-CD (c_{Ru} = 0.70 mM, [β-CD] = 3.5 mM), and green; in the presence of α-CD (c_{Ru} = 1.35 mM, [α-CD] = 6.35 mM). The initial concentration was normalized for comparison. c_{Ru} = [*proximal*-**1**] + [*distal*-**1**].

Table S1. Summary of thermodynamic parameters for thermal-back-isomerization from *distal*-**1** to *proximal*-**1** in the absence and presence of γ-CD (5 equiv.)

	E_{act} / kJ mol^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}
With γ-CD	109 ± 1	106 ± 1	22 ± 2	99 ± 1
w/o γ-CD	109 ± 5	106 ± 5	21±17	100 ± 7

References

1. Hirahara, M.; Goto, H.; Yagi, M.; Umemura, Y., A multi-stimuli responsive ruthenium complex for catalytic water oxidation. *Chem. Commun.* **2020,** *56* (84), 12825-12828.