Supplementary Material for:

The Base and Co(II) Catalyzed Ring-Opening Reactions of Perhydrooxireno[2,3-*d*][1,2]dioxines: An Efficient Route to 4-Hydroxy-2,3-epoxy-ketones.

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General Experimental. ^1H NMR and ^{13}C NMR were recorded in CDCl_3 solution on either a 300 MHz or 600 MHz instrument, with TMS (0 ppm) and CDCl_3 (77.0 ppm) as internal standards unless stated otherwise. Thin-layer chromatography (TLC) used aluminum sheets silica gel 60 F₂₅₄.

X-ray crystallography

Intensity data for a colorless crystal were measured at 183(2) K on a Bruker AXS SMART CCD using Mo K α radiation so that $\theta_{\text{max}} = 30.1^\circ$. The structure was solved by direct-methods and refined (anisotropic displacement parameters, H atoms in their calculated positions and a weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.0834P^2 + 0.1066P]$ where $P = (F_o^2 + 2F_c^2)/3$ on F^2 with SHELXL-97. The molecular structure (ORTEP, 50% displacement parameters) is shown in Fig. 1 of the Supplementary Material.

Crystal data: $\text{C}_{11}\text{H}_{12}\text{O}_3$, $M = 192.21$, monoclinic, $P2_1/c$, $a = 10.9197(12)$, $b = 11.1051(12)$, $c = 8.7057(9)$ Å, $\beta = 112.301(2)^\circ$, $V = 976.73(18)$ Å³, $Z = 4$, $D_x = 1.307$, $F(000) = 408$, $\mu = 0.095$ mm⁻¹, no. of unique data = 2850, no. of parameters = 128, R (all data) = 0.055, wR (all data) = 0.149, $\rho = 0.41$ e Å⁻³.

Molecular Structure of **4b** showing crystallographic numbering scheme employed: