Supporting Information

**The Ring-Opening of Unsymmetrical 1,2-Dioxines Using Cobalt (II) Salen
Complexes.**

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General Experimental

^1H NMR and ^{13}C NMR were recorded in CDCl_3 solution using a 200 MHz, 300 MHz or 600 MHz instrument, with TMS (0 ppm, ^1H) and CDCl_3 (77.0 ppm, ^{13}C) as internal standard. Thin-layer chromatography was performed using aluminium sheets silica gel 60 F₂₅₄. THF was distilled from benzophenone ketyl.

300 MHz VT NMR of **1a** at a) 0°C, b) -65°C and c) -97°C.

300 MHz VT NMR of **1d** in CD₂Cl₂ at a) 25°C, b) -65°C and c) -97°C.

300 MHz VT NMR of **1d** in CD₂Cl₂ at a) 25°C, b) -65°C and c) -97°C.

300 MHz ^1H NMR of 1e.

300 MHz ^1H NMR of **13e**.

600 MHz ^1H NMR of 13h.

50 MHz ^{13}C NMR of **15a**.

75 MHz ^{13}C NMR of 15e.

300 MHz ^1H NMR of diene **15g**.

150 MHz ^{13}C NMR of lactone 17.