

## **Supporting Information**

### **Kinetic Study on the Coupling of CO<sub>2</sub> and Epoxides Catalyzed by Co(III)**

#### **Complex with an Inter- or Intra-Molecular Nucleophilic Cocatalyst**

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*Scheme S1*: Binary and one-component catalysts for CO<sub>2</sub>/epoxides coupling

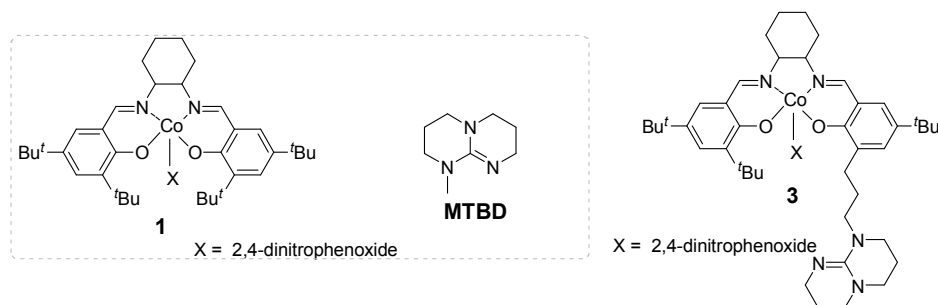


Table S1 Effects of catalyst loading on the initial rate and induction period<sup>a</sup>

Run	Catal./Cocatal. (molar ratio)	Epoxide/Catal. (molar ratio)	Catalyst concn. <sup>b</sup> (mol/L)	Initial rate <sup>c</sup> (Abs.×10 <sup>6</sup> /s)	Induction period <sup>d</sup> (seconds)
1	<b>1</b> /MTBD (1/1)	1000	0.0142	281.8	0
2	<b>1</b> /MTBD (1/1)	2000	0.0071	79.6	200
3	<b>1</b> /MTBD (1/1)	5000	0.0028	21.0	1200
4	<b>1</b> /MTBD (1/1)	10000	0.0014	7.5	2000
5	<b>3</b>	2000	0.0071	210.7	0
6	<b>3</b>	5000	0.0028	89.3	0
7	<b>3</b>	10000	0.0014	43.3	0

<sup>a</sup> All reactions were performed in 20 mL neat propylene oxide at 25 °C and 20 bar CO<sub>2</sub> pressure. <sup>b</sup> Based on cobalt complex concentration. <sup>c</sup> Slope of absorption vs time curves calculated for the linear part. <sup>d</sup> Time for initial rate at zero, corresponding to the intersection of the linear part at the time axis.

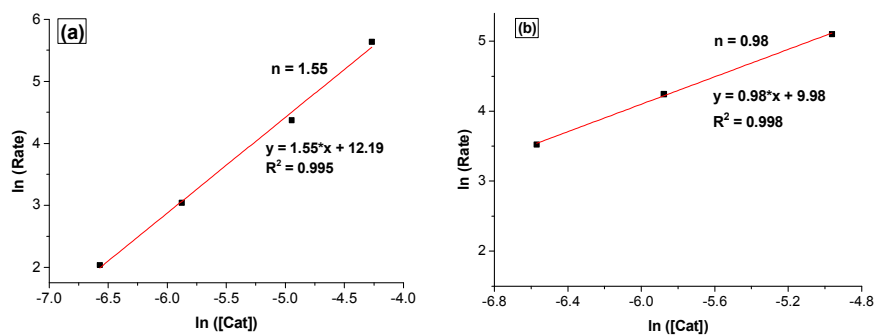


Figure S1: Logarithmic plots of initial rate *versus* catalyst concentration. (a) binary catalyst system of complex **1** and equivalent MTBD, and (b) catalyst **3**.