

Supporting Information

A Readily Synthesized and Highly Active Epoxide Carbonylation Catalyst Based on a Chromium Porphyrin Framework: Expanding the Range of Available γ -Lactones

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General Considerations. Standard Schlenk-line and glovebox techniques were used in the synthesis and reactions of catalyst **1**. The product lactones were air-stable and could be handled under ambient atmosphere. THF was passed over activated alumina and degassed prior to use. (TPP)CrCl was purchased from Mid-Century Chemicals and used as received (see text). 1,2-Epoxybutane, 1,2-epoxyhexane, 1,2-epoxydodecane, 1,2-epoxy-5-hexene, n-butyl glycidyl ether, *tert*-butyldimethylsilyl glycidyl ether, *trans*-2,3-epoxybutane, cyclooctene oxide, 9-oxabicyclo[6.1.0]non-4-ene (cyclooctadiene monoxide), and cyclododecene oxide were purchased from Aldrich. *tert*-Butyl oxirane, *cis*-2,3-epoxybutane, and 13-oxabicyclo[10.1.0]trideca-4,8-diene (cyclododecatriene monoxide) were purchased from Lancaster. 1,2-Epoxyheptane,¹ NaCo(CO)₄,² and [(salph)Al][Co(CO)₄]³ were synthesized as previously reported. All liquid epoxides were dried over CaH₂ and vacuum distilled prior to use; solids were used as received. Carbon monoxide was purchased from Matheson and passed over a column of 3Å molecular sieves prior to use. NMR chemical shifts are given relative to residual CHCl₃ (¹H δ 7.26)

and CDCl₃ (¹³C δ 77.23). The ¹H NMR spectra of product lactones were identified by comparison with published spectra for γ -valerolactone,⁴ γ -heptanolactone,⁵ γ -octanolactone,⁶ γ -tridecalactone,⁵ 4-*tert*-butyl-2-propiolactone,⁷ 4-(but-3-enyl)-2-propiolactone,⁸ *cis*-3,4-dimethyl-2-propiolactone,⁹ *trans*-3,4-dimethyl-2-propiolactone,⁹ *trans*-9-oxa-bicyclo[6.2.0]decane-10-one,¹⁰ and *trans*-9-oxa-bicyclo[6.2.0]dec-4-ene-10-one.¹¹ ¹H and ¹³C NMR spectra for 4-(*n*-butoxymethyl)-2-propiolactone, 4-(*tert*-butyldimethylsiloxymethyl)-2-propiolactone, 13-oxa-bicyclo[10.2.0]tetradecan-14-one, and the lactones derived from cyclododecatriene monoxide are given below. High resolution mass spectra were obtained from the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, and in all cases employed electron impact conditions.

[(TPP)Cr(THF)₂][Co(CO)₄] (1). Under an atmosphere of nitrogen, a solution of NaCo(CO)₄ (148 mg, 0.76 mmol) in THF (40 ml) was added to a flask containing (TPP)CrCl (533 mg, 0.76 mmol) and THF (20 ml). The dark solution was stirred for 16 h and then allowed to stand and settle for 5 h. The resulting material was filtered through a Celite pad. The Celite pad was washed with several portions of THF to maximize product recovery. THF was removed under vacuum to yield a dark purple solid (515 mg, 81%); mp = 142 °C dec.; IR (nujol, KCl) ν_{CO} = 1877 cm⁻¹.

General Procedure for the Carbonylation of Epoxides. Reactions were performed on 100-300 mg of epoxide, measured out on a balance. Catalyst:substrate ratios are accurate to within 5%. Under nitrogen at room temperature, a 4-ml glass vial equipped with a stir bar was charged with catalyst followed by epoxide. This was immediately transferred to a custom-built, 6-well, high-pressure reactor and sealed (see

Figure S1). The reactor was pressurized to 900 psi with CO and heated to 60 °C with stirring. The temperature was held constant for 6 h, at which point the reactor was submerged in dry ice for 15 min. After careful venting of excess CO, the glass vial was removed and product yield determined by ^1H NMR. In general, pure lactones from most substrates could be isolated by careful vacuum distillation.



Figure S1. Six-well high pressure reactor.

Characterization of Lactones:

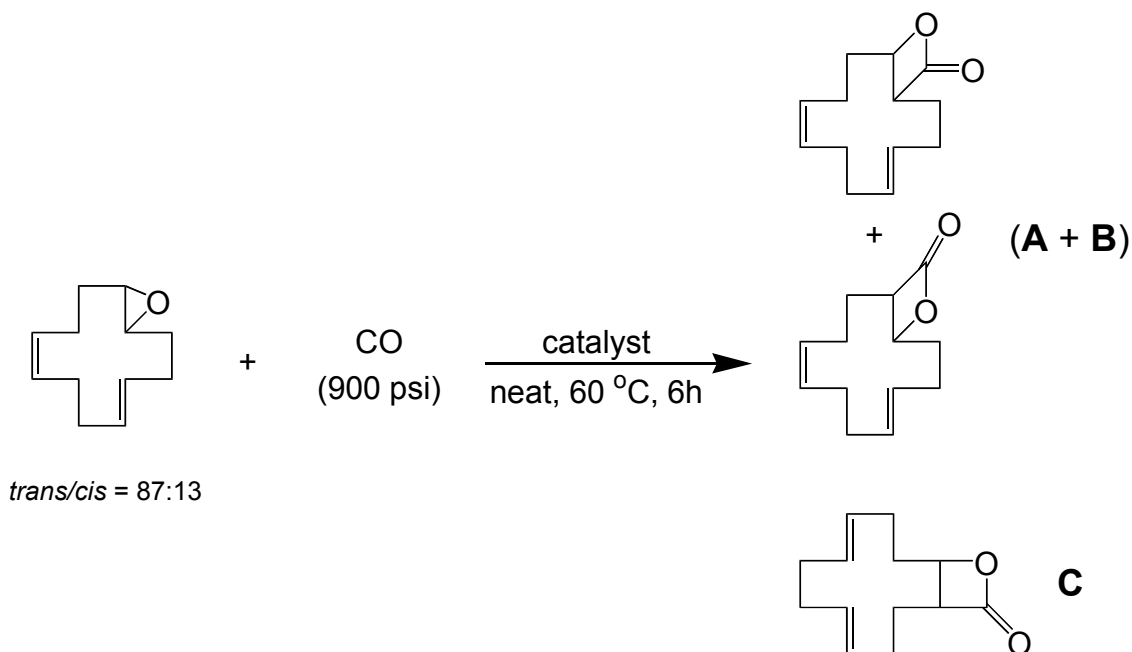
4-(n-Butoxymethyl)-2-propiolactone: ^1H NMR (CDCl_3 , 300 MHz) δ 4.63 (m, 1H), 3.76 (dd, 1H, $^2J = 12$ Hz, $^3J = 3$ Hz), 3.67 (dd, 1H, $^2J = 12$ Hz, $^3J = 4$ Hz), 3.51 (t, 2H, $^3J = 6$ Hz), 3.42 (t, 2H, $^3J = 5$ Hz), 1.55 (m, 2H), 1.35 (m, 2H), 0.90 (t, 3H, $^3J = 8$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.1, 19.4, 31.8, 39.8, 69.8, 70.2, 72.1, 168.0; IR (neat, KCl) $\nu_{\text{CO}} = 1832$ cm^{-1} ; HRMS (EI) m/z calcd ($\text{C}_8\text{H}_{14}\text{O}_3 + \text{H}^+$) 159.1021, found 159.1029.

4-(tert-Butyldimethylsiloxymethyl)-2-propiolactone: ^1H NMR (CDCl_3 , 300 MHz) δ 4.57 (m, 1H), 4.01 (dd, 1H, $^2J = 12$ Hz, $^3J = 3$ Hz), 3.81 (dd, 1H, $^2J = 12$ Hz, $^3J = 3$ Hz), 3.42 (m, 2H), 0.87 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ -5.3, 18.5,

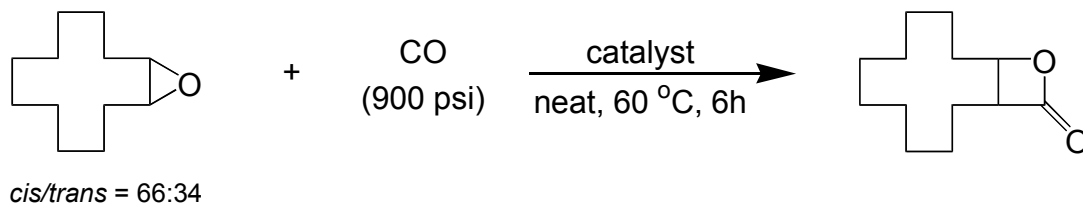
26.0, 38.8, 62.5, 70.8, 168.1; IR (neat, KCl) $\nu_{\text{CO}} = 1839 \text{ cm}^{-1}$; HRMS (EI) m/z calcd ($\text{C}_{10}\text{H}_{20}\text{O}_3\text{Si} + \text{H}^+$) 217.1260, found 217.1256.

13-Oxa-bicyclo[10.2.0]tetradecan-14-one: ^1H NMR (CDCl_3 , 300 MHz) (*trans*) δ 4.39 (m, 1H), 3.30 (m, 1H), 2.18 (m, 1H), 1.92 (m, 2H), 1.69 (m, 1H), 1.6-1.1 (m, 16H); (*cis*) δ 4.55 (m, 1H), 3.59 (m, 1H), 2.21 (m, 1H), 1.90 (m, 2H), 1.67 (m, 1H), 1.6-1.1 (m, 16H); ^{13}C NMR (CDCl_3 , 125 MHz) (*trans*) δ 22.8, 22.9, 23.6, 23.8, 24.9, 25.1, 27.5, 27.7, 27.8, 33.5, 54.3, 77.7, 172.7; IR (neat, KCl) $\nu_{\text{CO}} = 1823 \text{ cm}^{-1}$; HRMS (EI) m/z calcd ($\text{C}_{13}\text{H}_{22}\text{O}_2 + \text{H}^+$) 211.1698, found 211.1698.

Lactones from cyclododecatriene monoxide: ^1H NMR (CDCl_3 , 300 MHz) **A** δ 5.55-5.15 (m, 4H), 4.68 (m, 1H), 3.60 (m, 1H), 2.4-1.8 (m, 11H), 1.72 (m, 1H); **B** δ 5.55-5.15 (m, 4H), 4.54 (m, 1H), 3.53 (m, 1H), 2.4-1.8 (m, 11H), 1.69 (m, 1H); **C** δ 5.55-5.15 (m, 4H), 4.43 (m, 1H), 3.48 (m, 1H), 2.4-1.8 (m, 11H), 1.63 (m, 1H); IR (neat, KCl) $\nu_{\text{CO}} = 1822 \text{ cm}^{-1}$; HRMS (EI) m/z calcd ($\text{C}_{13}\text{H}_{18}\text{O}_2$) 206.1307, found 206.1301.



Observed and Selectivity for Carbonylation of Cyclododecene Oxide:



Substrate:Catalyst	Yield	% <i>trans</i> -Lactone
200:1	75%	89%
300:1	70%	93%
400:1	67%	96%
450:1	66%	97%
500:1	57%	98%

References

- (1) Weijers, C.; Botes, A. L.; van Dyk, M. S.; de Bont, J. A. M. *Tetrahedron: Asymmetry* **1998**, *9*, 467-473.
- (2) Edgell, W. F.; Lyford, J. *Inorg. Chem.* **1970**, *9*, 1932-1933.
- (3) Getzler, Y. D. Y. L.; Mahadevan, V.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1174-1175.
- (4) Noels, A. F.; Herman, J. J.; Teyssie, P. *J. Org. Chem.* **1976**, *41*, 2527-2531.
- (5) Romo, D.; Harrison, P. H. M.; Jenkins, S. I.; Riddoch, R. W.; Park, K.; Yang, H. W.; Zhao, C.; Wright, G. D. *Bioorg. Med. Chem.* **1998**, *6*, 1255-1272.
- (6) Peres, R.; Lenz, R. W. *Macromolecules* **1993**, *26*, 6697-6701.
- (7) Sakai, N.; Ageishi, S.; Isobe, H.; Hayashi, Y.; Yamamoto, Y. *J. Chem. Soc.-Perkin Trans. 1* **2000**, 71-77.
- (8) Lee, J. T.; Thomas, P. J.; Alper, H. *J. Org. Chem.* **2001**, *66*, 5424-5426.
- (9) Mahadevan, V.; Getzler, Y. D. Y. L.; Coates, G. W. *Angew. Chem.* **2002**, *114*, 2905-2908; *Angew. Chem. Int. Ed.* **2002**, *41*, 2781-2784.
- (10) Crandall, J. K.; Machlede, W. H.; Sojka, S. A. *J. Org. Chem.* **1973**, *38*, 1149-1154.
- (11) Stille, J. K.; James, D. E. *J. Organomet. Chem.* **1976**, *108*, 401-408.