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Tin(IV)-Porphyrin Tetracarbonyl Cobaltate: An Efficient Catalyst for the Carbonylation of Epoxides

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Abstract: Cationic tin(IV) porphyrins with tetracarbonyl cobaltates were synthesized, exhibiting bifunctional catalytic reactivity. The Lewis acidic tin-porphyrin center activated epoxides; concurrently, cobalt carbonyl anions efficiently opened epoxides and delivered carbonyl moieties. Thus, a series of β-lactones with a high synthetic value were obtained. This catalytic system showed excellent efficiency exceeding a turnover number of one thousand with a broad substrate scope. In addition, the presented tin porphyrin-based catalyst exhibited exclusive chemoselectivity to terminal epoxides over internal ones. The selective carbonylation of di-epoxides demonstrated the usefulness of these catalysts in the synthesis of complex molecular structures.

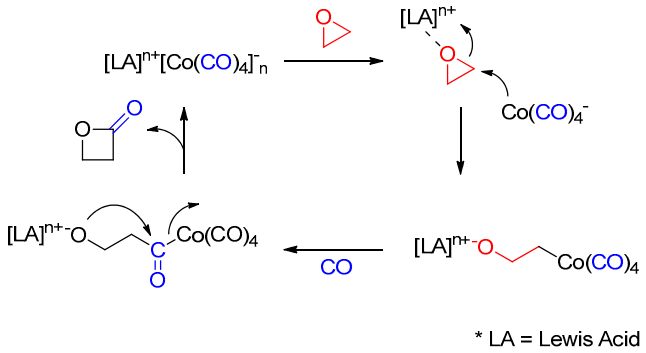
Keywords: tin-porphyrin; carbonylation; epoxide; β-lactone

1. Introduction

Porphyrins and metalloporphyrins are found in many living organisms and play an essential role in sustaining life [1–4]. Incorporation of various metals into the porphyrin, contraction or expansion of the ring, and desymmetrization or extension of the π-system can induce intriguing properties [5–14]. Thus, many natural and nonnatural porphyrins and their derivatives have been widely used in versatile applications such as medicine, materials, catalysis, supramolecular chemistry, and biomimetic models [15–21].

In the area of catalysis, numerous porphyrins, especially transition metal-based metalloporphyrins, promote many chemical transformations with high efficiency and reactivity; however, catalytic evaluation of main-group metal and semi-metal porphyrins has not received much attention despite the distinctive physical and chemical properties of such porphyrins [22–26]. Among those complexes, tin(IV) porphyrins have attracted our attention. Since the first synthesis of tin(IV) porphyrin in 1948 by Rothemund, a wide range of tin-based porphyrins have been developed [27–33]. As catalysts, they mediate hydrolysis [34], acetylation [30,31], alcoholysis [32], and epoxide ring-opening reactions [26], as well as polymerizations [26,28]. In general, the cationic porphyrin units with a +2 charge are balanced with non- or weakly coordinating anions such as ClO_4^-, BF_4^-, TfO^-, Br^-, F^-, Cl^-, and OH^-. In a continuous effort to expand tin-based catalytic systems, we investigated novel tin complexes with a noninnocent tetracarbonyl cobaltate anion, which produced β-lactones through the selective mono

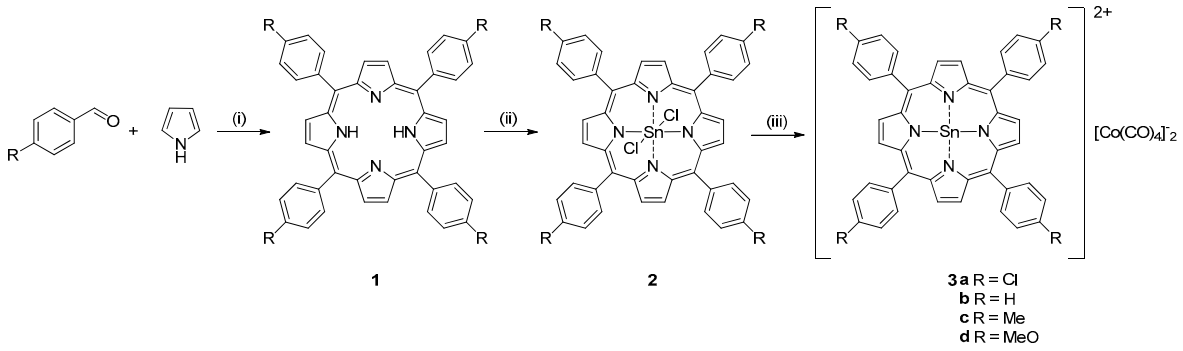
carbonylation of epoxides. The direct conversion of epoxides to the corresponding β-lactones is a clean, one carbon homologation method with a 100% atom-economy [35]. A list of catalytic systems has been developed based on the combination of Lewis acid and metal carbonyl for the carbonylative ring expansion of epoxides (Scheme 1) [36–39]. Compared to the previous examples, our catalytic system consisting of Sn(IV)-centered porphyrins exhibited comparable reactivity with a turnover number (TON) of over 1000 and exclusive selectivity to β-lactones, without any side products or double carbonylations. In addition, highly selective carbonylation of terminal epoxide over internal epoxide allowed chemoselective lactone formation. The details of our findings are presented herein.



Scheme 1. General reaction mechanism of epoxide carbonylation to form β-lactones.

2. Results and Discussion

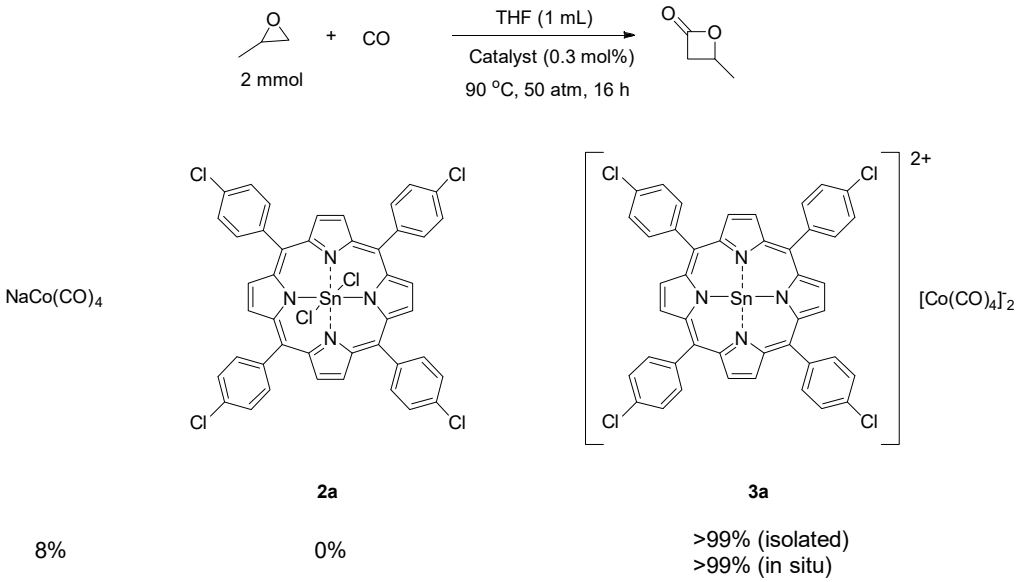
The syntheses of Sn(IV) porphyrins are outlined in Scheme 2. The conventional condensation reaction between benzaldehyde and pyrrole produced the porphyrins [40]. Subsequent reaction of porphyrins with Sn(II) chloride produced Sn(IV) porphyrin dichloride [41]. The X-ray crystal structure of **2a** shows a chloride anion tightly bound to the Sn center (Figure S1). Finally, sodium tetracarbonyl cobaltate, $NaCo(CO)_4$ reacted with Sn(IV) porphyrin dichloride precursors and produced the desired catalysts (**3a**–**3d**).



Scheme 2. Synthesis of Tin(IV) porphyrin catalysts. (**i**) Propionic acid, reflux, 1 h. (**ii**) $SnCl_2$, $2H_2O$, pyridine, reflux, 3 h. (**iii**) $NaCo(CO)_4$, THF, N_2, rt, 48 h.

First, catalyst **3a** (0.3 mol %) with electron withdrawing chlorine substituents was tested for carbonylation of propylene oxide (**4a**, 2 mmol) with carbon monoxide (50 atm) in tetrahydrofuran (THF, 1 mL) at 90 °C. After 16 h, the desired β-butyrolactone was formed quantitatively (Scheme 3). To elucidate the reactive catalytic species, we tested $NaCo(CO)_4$ and Sn(IV) porphyrin dichloride **2a** independently. Complex **2a** with the tightly bound chloride anions did not promote carbonylation, and epoxide **4a** remained unreacted. Interestingly, $NaCo(CO)_4$ was solely active under the same CO pressure, but the efficiency was relatively low (8%). The complex **3a** prepared in situ from the mixture of $NaCo(CO)_4$ (0.6 mol %) and **2a** (0.3 mol %) showed the same reactivity as isolated **3a**. These results imply that the reaction between $NaCo(CO)_4$ and **2a** produces a more reactive Lewis acidic species,

which is not exactly identified by analytical methods. However, currently, the formation of NaCl indicates that the Sn(IV) porphyrin cationic complex with an empty coordination site is the active catalytic species as a Lewis acid for epoxide activation.



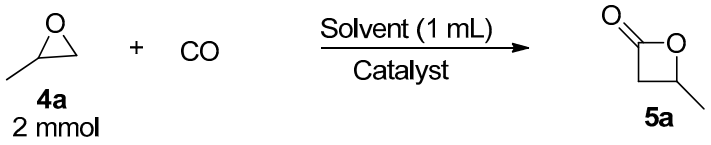
Scheme 3. Identification of reactive catalytic species.

Further optimizations were undertaken (Table 1), and the influence of the electronic nature of the catalyst was investigated. A shift to electron rich porphyrins by substitution of Cl (**3a**, entry 1) with H (**3b**, entry 2), methyl (**3c**, entry 3), and methoxy (**3d**, entry 4) groups exhibited a gradual decrease in catalytic turnover rates. The diminishing Lewis acid character was directly indicated by the catalytic efficiency. Additionally, the effect of reaction media was significant. THF and 2-methyl THF exhibited the same quantitative conversion with 0.3 mol % catalyst loading (entries 1 and 5), but another ethereal solvent 1,4-dioxane gave a lower conversion (entry 6). Another coordinating polar solvent, dimethyl formamide (DMF, entry 7) [42] and a protic polar solvent, methanol (MeOH, entry 8) showed complete catalyst inhibition. In noncoordinating and nonpolar solvents, **3a** showed poor performance (entries 9–11). In their study with Cr-porphyrin catalysts, Coates and coworkers noted that the coordination of solvents such as THF is very important for high efficiency [43]. The trans-addition of THF to a metal facilitates the alkoxide departure from the metal center allowing the alkoxide to attack the carbonyl group and form β-lactone (Scheme 1). We believe that a similar solvent effect is valid in the Sn-porphyrin system as well, thus the use of a noncoordinating solvent could not promote a β-lactone formation step.

Next, the variations in temperature and carbon monoxide pressure were evaluated. The catalytic efficiency of **3a** is sensitive to both temperature and CO pressure. Decreasing the reaction temperature to 70 °C gave 61% conversion under otherwise identical conditions (entry 12). At 50 °C, the conversion dropped to 20% (entry 13). The change in pressure to 30 atm maintained good reactivity with 95% conversion to β-lactone (entry 14), but a notable loss of conversion was observed at 10 atm of CO (63%, entry 15).

When the catalyst loading was decreased, higher temperature or pressure was required to maintain good β-lactone production. With 0.2 mol %, a longer reaction, 24 h, was needed to reach complete conversion (entries 16 and 17). When 0.1 mol % was used, changing the time and pressure to 36 h and 70 atm of CO, respectively, could achieve a TON of 1000 (entry 19). With the use of 0.05 mol %, **3a** exhibited 63% conversion at 110 °C, with a TON of 1260 [44].

Table 1. Optimization results [1,2].



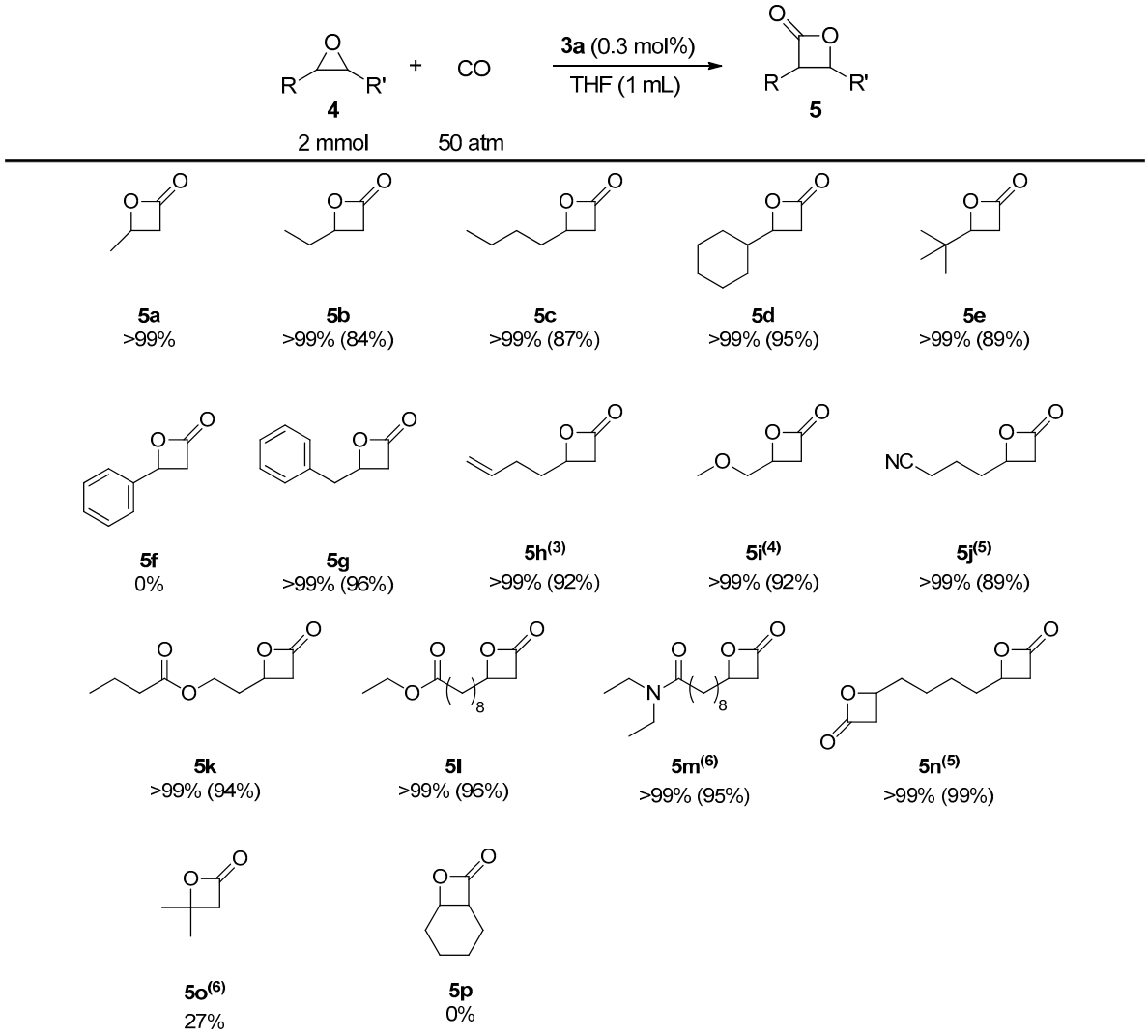
Entry	Catalyst	mol %	Temp (°C)	CO (atm)	Solvent	Yield (%)[3]	TON [4]
1	3a	0.3	90	50	THF	>99	333
2	3b	0.3	90	50	THF	94	313
3	3c	0.3	90	50	THF	83	277
4	3d	0.3	90	50	THF	57	190
5	3a	0.3	90	50	2-Me-THF	>99	333
6	3a	0.3	90	50	1,4-dioxane	89	297
7	3a	0.3	90	50	DMF	0	-
8	3a	0.3	90	50	MeOH	0	-
9	3a	0.3	90	50	o-xylene	35	117
10	3a	0.3	90	50	toluene	13	43
11	3a	0.3	90	50	n-hexane	3	10
12	3a	0.3	70	50	THF	61	203
13	3a	0.3	50	50	THF	20	67
14	3a	0.3	90	30	THF	95	317
15	3a	0.3	90	10	THF	63	210
16	3a	0.2	90	50	THF	91	455
17	3a (24 h)	0.2	90	50	THF	>99	500
18	3a (24 h)	0.1	90	50	THF	80	800
19	3a (36 h)	0.1	90	70	THF	>99	1000
21	3a (36 h)	0.05	110	70	THF	63	1260

[1] Unless otherwise indicated, the reaction was carried out for 16 h. [2] Single experiment was performed on each entry. [3] Yields were determined by ^{1}H NMR. [4] TON (turnover number) = Moles of product formed/moles of catalyst.

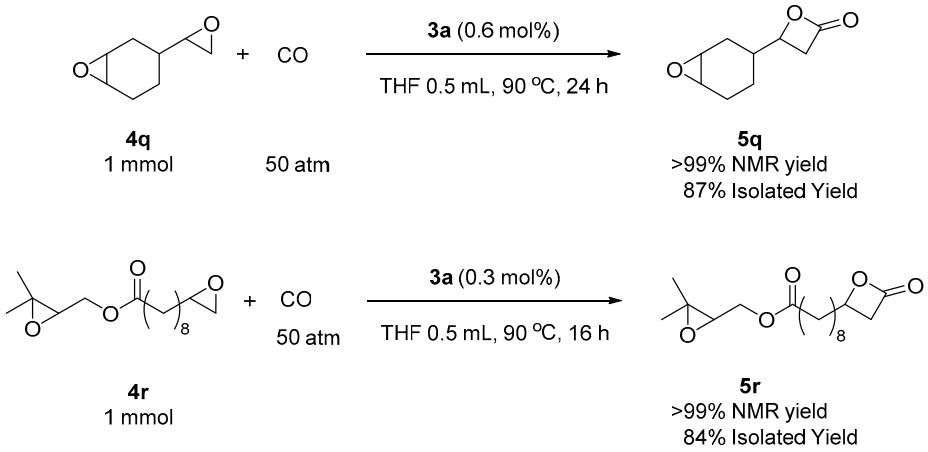
The direct carbonylation of epoxides provided a series of β-lactones with high efficiencies (Table 2). A substituent on the terminal epoxides did not hamper the carbonylation performance of **3a**. Variations in the chain length (**5a**–**c**) and size (**5d** and **e**) of substituents showed no influence and quantitative β-lactones were obtained. Interestingly, the aromatic substituent exhibited positional sensitivity. Styrene oxide, surprisingly, did not react with catalyst **3a** at all (**5f**); however, adding a methylene bridge restored its reactivity (**5g**). Various kinds of coordinating functional groups were introduced that could behave as potential catalyst inhibitors. Epoxides with alkene (**5h**), ether (**5i**), and nitrile (**5j**) groups were smoothly converted to the corresponding β-lactones with a slight increase in catalyst loadings. Moreover, ester and amide functionalities were well tolerated (**5k**–**m**). Dual carbonylations of di-epoxide were also successful (**5n**).

Next, sterically more congested epoxides with 1,1- and 1,2-substitution were investigated. 1,2-Epoxy-2-methylpropane (**4o**) gave only 27% of NMR yield under a high amount of catalyst loading. In the case of 1,2-substitution, such as with cyclohexene oxide (**4p**), carbon monoxide insertion did not occur and the starting material remained intact. This dramatic reactivity dependence on substitution patterns allowed for chemoselective carbonylation (Scheme 4). The di-epoxide (**4q**) has two distinctive epoxides: one has a single substitution and the other epoxide is internal and di-substituted. Catalyst **3a** successfully discriminated the difference and only the terminal epoxide was converted to the corresponding β-lactone (**5q**). The other di-epoxide **4r** also exhibited the same terminal selectivity to produce **5r** with both epoxide and β-lactone. The use of these products in selective polymerization is currently under investigation.

Table 2. Scope of substrates [1,2].



[1] Single experiment was performed on each entry.[2] Yields were determined by ^{1}H NMR. Numbers in parentheses are isolation yields. [3] Catalyst loading = 0.4 mol %; [4] Catalyst loading = 0.5 mol %; [5] Catalyst loading = 0.6 mol %; [6] Catalyst loading = 1 mol %.



Scheme 4. Chemoselective carbonylations of di-epoxides.

3. Materials and Methods

3.1. General Considerations

All manipulations for air and moisture sensitive compounds were carried out under dry nitrogen using either a glove box (MBRAUN UNIlab, Garching, Germany) or standard Schlenk line technique. Carbonylations of epoxides were carried out in stainless steel reactors (Uto Engineering, Namyangju, Korea). Flash column chromatography was performed on silica gel 60 (230–400 mesh) (ZEOCHEM, Ruti, Switzerland). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD Fourier transform 400 MHz NMR spectrometer (Billerica, MA, USA). Chemical shifts are reported in parts per million relative to residual solvent ($CDCl_3$, ^{1}H δ 7.26 ppm, and ^{13}C δ 77.0 ppm), and coupling (J) constants are expressed in hertz (Hz). The multiplicities of ^{1}H NMR are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet. Infrared (IR) spectra were recorded on an ABB FT-IR spectrometer MB3000 (Zurich, Switzerland) and are reported in wavenumbers (cm^{-1}). High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu, Korea) on a JEOL JMS 700 high resolution spectrometer (Tokyo, Japan). Carbon monoxide (99.999%) was purchased from Korea specialty gas (Iksan, Korea) and used without further purification. Unless otherwise stated, all reagents were purchased from Sigma-Aldrich (Seoul, Korea), Alfa Aesar (Seoul, Korea), or Acros Organics (Seoul, Korea) and used as received. 1,4-Dioxane, tetrahydrofuran, 2-methyltetrahydrofuran, toluene, o-xylene, and hexane were dried using activated 3 Å molecular sieves and degassed by repeated freeze-pump-thaw cycles before use. All epoxides were stirred for a few days over CaH_2, vacuum distilled, and degassed by freeze-pump-thaw prior to use. $NaCo(CO)_4$ [45], 5,6-epoxyhexanenitrile, 3,4-epoxybutyl butyrate [46], cyclohexyl oxirane [47], 2-(*tert*-butyl)oxirane [48], and 2-benzyl oxirane [49] were synthesized following previously reported methods.

3.2. Syntheses of Substrates

Synthesis of Ethyl 9-(oxiran-2-yl)nonanoate (**4l**). First, 10-Undecenoyl chloride (2.6 mL, 12 mmol) was mixed with ethanol (5.0 mL). The mixture was stirred at room temperature for 2 h. Removal of excess ethanol and vacuum drying gave a colorless liquid of ethyl undec-10-enoate which was directly used for the epoxidation using a modified previous report [37]. The ethyl undec-10-enoate was dissolved in 100 mL of CH_2Cl_2 and cooled at 0 °C. *m*-Chloroperoxybenzoic acid (70–75% purity, Acros Organics) (3.7 g, 15 mmol) was gradually added to the solution. The resulting mixture was stirred at 0 °C for 2 h and then at room temperature for 14 h. The excess peroxide was quenched by the addition of a 10% solution of $NaHSO_3$ at 0 °C. A saturated solution of $NaHCO_3$ was added until gas evolution ceased. Then, the aqueous layer was extracted with CH_2Cl_2. The separated organic layer was washed with $NaHCO_3$ and dried with anhydrous $MgSO_4$. The removal of solvent in the rotary evaporator and subsequent vacuum distillation gave the epoxide product **4l** (0.80 g, 72%). The NMR data is identical to reported that reported previously [50]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (q, J = 7.2 Hz, 2H), 2.88–2. 91 (m, 1H), 2.73 (dd, J = 5.1, 4.0 Hz, 1H), 2.45 (dd, J = 5.1, 2.8 Hz, 1H), 2.27 (t, J = 7.8 Hz, 2H), 1.66–1.55 (m, 2H), 1.56–1.48 (m, 2H), 1.49–1.37 (m, 2H), 1.29–1.35 (m, 8H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 60.1, 52.3, 47.1, 34.3, 32.4, 29.3, 29.3, 29.1, 29.0, 25.9, 24.9, 14.2.

Synthesis of *N*,*N*-Diethyl-10,11-epoxyundecylamide (**4m**). Diethyl amine (1.0 mL, 10.0 mmol) and triethyl amine (2.8 mL, 20.0 mmol) were mixed in CH_2Cl_2 (100 mL) at 0 °C. Then, 10-Undecenoyl chloride (2.6 mL, 12 mmol) was added dropwise. The mixture was stirred at room temperature for 14 h. A saturated solution of $NaHCO_3$ was added and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed using a rotary evaporator and the product was purified by flash column chromatography using hexane/ethyl acetate as the eluent. The resulting *N*,*N*-diethylunde-10-enamide (1.7 g, 7.1 mmol) was dissolved in 100 mL of CH_2Cl_2 and cooled at 0 °C. *m*-Chloroperoxybenzoic acid (70–75% purity, Acros Organics) (2.8 g, 9.2 mmol) was gradually added to the solution. The resulting mixture was stirred at 0 °C for 2 h and then at room

temperature for 14 h. The excess peroxide was quenched by addition of a 10% solution of $NaHSO_3$ at 0 °C. A saturated solution of $NaHCO_3$ was added until gas evolution ceased. Then, the aqueous layer was extracted with CH_2Cl_2. The separated organic layer was washed with $NaHCO_3$ and dried over anhydrous $MgSO_4$. The removal of solvent in the rotary evaporator and subsequent vacuum distillation gave the epoxide product **4m** (1.0 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (q, J = 7.2 Hz, 2H), 3.28 (q, J = 7.2 Hz, 2H), 2.86–2.90 (m, 1H), 2.73 (dd, J = 5.0, 4.0 Hz, 1H), 2.44 (dd, J = 5.0, 2.7 Hz, 1H), 2.34–2.18 (m, 2H), 1.68–1.58 (m, 2H), 1.56–1.47 (m, 2H), 1.47–1.37 (m, 2H), 1.37–1.26 (m, 8H), 1.15 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 52.3, 47.1, 41.9, 39.9, 33.1, 32.4, 29.4, 29.4, 29.3 (2C), 25.9, 25.4, 14.4, 13.1; IR (ATR) 1639 (amide) cm^{-1}; HRMS *m*/*z* (ESI) calcd for $C_{15}H_{29}NO_2$ [M^+] 255.2198, found: 255.2200.

Synthesis of 3-(Oxiran-2-yl)-7-oxabicyclo[4.1.0]heptane (**4q**). First, 4-Vinylcyclohex-1-ene (3.0 g, 28 mmol) was dissolved in 100 mL of CH_2Cl_2 and cooled at 0 °C. *m*-Chloroperoxybenzoic acid (70–75% purity, Acros Organics) (12.0 g, 72.0 mmol) was gradually added to the solution. The resulting mixture was stirred at 0 °C for 2 h and then at room temperature for 14 h. The excess peroxide was quenched by the addition of a 10% solution of $NaHSO_3$ at 0 °C. A saturated solution of $NaHCO_3$ was added until gas evolution ceased. Then, the aqueous layer was extracted with CH_2Cl_2. The separated organic layer was washed with $NaHCO_3$ and dried over anhydrous $MgSO_4$. The removal of solvent in the rotary evaporator and subsequent vacuum distillation gave the epoxide product **4q** (2.8 g, 72%) as the mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.24–3.09 (m, 2H), 2.77–2.60 (m, 2H), 2.51–2.46 (m, 1H), 2.26–2.09 (m, 1H), 2.08–1.92 (m, 1H), 1.90–1.80 (m, 1H), 1.78–1.64 (m, 1H), 1.63–1.45 (m, 1H), 1.43–1.22 (m, 1H), 1.22–1.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 55.65, 55.63, 52.5, 52.4, 52.3, 52.2, 51.6, 51.5, 50.9, 50.8, 46.2, 46.1, 45.6, 45.4, 35.8, 353, 32.7, 31.9, 27.5, 27.3, 27.0, 25.8, 24.4, 24.1, 23.6, 23.3, 22.9, 22.7, 21.4, 20.2; IR (ATR) 2927, 1434, 257, 929, 925, 856, 790 cm^{-1}. HRMS *m*/*z* (ESI) calcd for $C_{15}H_{29}NO_2$ [M^+] 255.2198, found: 255.2200.

Synthesis of (3,3-Dimethyloxiran-2-yl)methyl 9-(oxiran-2-yl)nonanoate (**4r**). A 50 mL round-bottom flask was charged with 3-methylbut-2-en-1-ol (1.4 g, 16 mmol), toluene (15 mL), and triethyl amine (2.5 mL) at 0 °C. At 0 °C, 10-undecenoyl chloride (3.2 g, 16 mmol) was added dropwise. The mixture was stirred at 0 °C for 2 h and then at room temperature for 12 h. The toluene was evaporated after filtration. The resulting liquid was dissolved in 100 mL of CH_2Cl_2. After cooling at 0 °C, *m*-Chloroperoxybenzoic acid (70–75% purity, Acros Organics) (9.5 g, 41 mmol) was gradually added to the solution. The resulting mixture was stirred at 0 °C for 2 h and then at room temperature for 14 h. The excess peroxide was quenched by the addition of a 10% solution of $NaHSO_3$ at 0 °C. The saturated solution of $NaHCO_3$ was added until gas evolution ceased. Then, the aqueous layer was extracted with CH_2Cl_2. The separated organic layer was washed with $NaHCO_3$ and dried over anhydrous $MgSO_4$. The removal of solvent in the rotary evaporator and subsequent flash column chromatography gave the epoxide product **4r** (3.5 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (dd, J = 12.1, 4.3 Hz, 1H), 4.01 (dd, J = 12.1, 6.9 Hz, 1H), 2.98 (dd, J = 6.9, 4.3 Hz, 1H), 2.93–2.84 (m, 1H), 2.74 (dd, J = 4.9, 4.1 Hz, 1H), 2.45 (dd, J = 5.0, 2.7 Hz, 1H), 2.34 (t, J = 7.5 Hz, 2H), 1.71–1.58 (m, 2H), 1.513–1.50 (m, 2H), 1.47–1.41 (m, 2H), 1.36–1.27 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 63.2, 60.5, 58.1, 52.3, 47.1, 34.1, 32.4, 29.3, 29.2, 29.1, 29.0, 25.9, 24.8, 24.5, 18.9; IR (ATR) 1737 (ester) cm^{-1}. HRMS *m*/*z* (ESI) calcd for $C_8H_{12}O_2$ [M^+] 140.0837, found: 140.0834.

3.3. Catalyst Synthesis

General procedure for synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin dichlorotin(IV) (**2a**): 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin (1.00 g, 1.33 mmol) synthesized from pyrrole and 4-chlorobenzaldehyde by a reported procedure was dissolved in 200 mL of pyridine, and tin(II) chloride dihydrate (0.805 g, 3.57 mmol) was added, after which the mixture was refluxed for 3 h. The product was precipitated by adding excess water. The precipitate was filter-washed sequentially with water, 1.0 M hydrochloric acid solution, and then again with water. The collected product was dried to give 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin dichlorotin(IV) **2a** (1.00 g, 80%) as a purple solid. An

X-ray quality crystal was obtained from THF/benzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 8H, $^{4}J_{H-Sn}$ = 15.6 Hz), 8.25 (d, J = 8.3 Hz, 8H), 7.84 (d, J = 8.3 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2 (8C), 138.7 (4C), 135.8 (8C), 135.4 (4C), 132.7 (8C), 127.5 (8C), 120.0 (4C).

5,10,15,20-Tetraphenylporphyrin dichlorotin(IV) $TPPSnCl_2$ (**2b**) [51] was prepared from 5,10,15, 20-tetraphenylporphyrin (1.00 g, 1.64 mmol) and tin(II) chloride dihydrate (0.993 g, 4.40 mmol) following the general procedure (1.12 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 8H, $^{4}J_{H-Sn}$ = 15.6 Hz), 8.43–8.23 (m, 8H), 7.9–7.72 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3 (8C), 140.5 (4C), 134.9 (8C), 132.7 (8C), 128.5 (4C), 127.1 (8C), 121.2 (4C).

5,10,15,20-tetrakis(p-tolyl)porphyrin dichlorotin(IV) $MeTPPSnCl_2$ (**2c**) was prepared from 5,10,15,20-tetrakis(*p*-tolyl)porphyrin (1.00 g, 1.49 mmol) and tin(II) chloride dihydrate (0.902 g, 4.00 mmol) following the procedure of **2a** (1.0 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 8H, $^{4}J_{H-Sn}$ = 15.6 Hz), 8.20 (d, J = 7.9 Hz, 8H), 7.62 (d, J = 7.7 Hz, 8H), 2.74 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4 (8C), 138.3 (4C), 137.7 (4), 134.9 (8), 132.6 (8C), 127.8 (8), 121.2 (4C), 21.6 (4C).

5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin dichlorotin(IV) $MeOTPPSnCl_2$ (2d) was prepared from 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin (1.00 g, 1.36 mmol) and tin(II) chloride dihydrate (0.821 g, 3.64 mmol) following a similar procedure to $ClTPPSnCl_2$ (0.90 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 8H, $^{4}J_{H-Sn}$ = 15.6 Hz), 8.24 (d, J = 8.6 Hz, 8H), 7.36 (d, J = 8.6 Hz, 8H), 4.13 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (4C), 146.6 (8C), 136.1 (8C), 133.0 (4C), 132.6 (8C), 120. 9 (4C), 112.6 (8C), 55.6 (4C).

Synthesis of Bimetallic Catalysts: [(ClTPP)Sn] $[Co(CO)_4]_2$ (**3a**). $ClTPPSnCl_2$ (0.20 g, 0.21 mmol) and $NaCo(CO)_4$ (81 mg, 0.42 mmol) were mixed in THF (20 mL) in a nitrogen atmosphere. The solution was stirred at room temperature, wrapped with aluminum foil for 48 h, and then allowed to settle. The resulting mixture was filtered and the solid was washed with additional THF. The filtrate was concentrated to 7–8 mL and was layered with hexane. The solid was filtered and washed with hexane and vacuum dried. Purple-greenish solid was obtained (0.18 g, 64%).

Similarly, the bimetallic catalysts [(TPP)Sn] $[Co(CO)_4]_2$ (**3b**), [(MeTPP)Sn] $[Co(CO)_4]_2$ (**3c**), and [(MeOTPP)Sn] $[Co(CO)_4]_2$ (**3d**) were synthesized in the same way as **3a** from $TPPSnCl_2$ (**2b**), $MeTPPSnCl_2$ (**2c**), and $MeOTPPSnCl_2$ (**2d**), respectively.

3.4. General Procedure for the Carbonylation of Epoxides

In a nitrogen glove box at room temperature, the appropriate amount of catalyst (**3a**) was added into a stainless-steel reactor. The solvent THF was added, followed by the addition of epoxide. The reactor was sealed properly and removed from the glove box. Then, the reactor was immediately pressurized to 50 atm pressure and stirred at 90 °C in a preheated heat bath. After the indicated time, the reactor was cooled at room temperature and with ice to a temperature of 0 °C. The excess CO gas was slowly vented. The lactone formed was determined by ^{1}H NMR spectroscopy. The mixture was filtered through a short column packed with silica gel using diethyl ether. The lactones were further purified by flash column chromatography using hexane/ethyl acetate (4/1) as the eluent.

β-Butyrolactone (**5a**) [52]: The compound **5a** was obtained as a colorless liquid by following a general procedure and only the ^{1}H-NMR yield (99%) was recorded due to its low boiling point (71 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75–4.70 (m, 1H), 3.59 (dd, J = 16.3, 5.6 Hz, 1H), 3.09 (dd, J = 16.3, 4.0 Hz, 1H), 1.60 (d, J = 6.0, 3H).

β-Valerorolactone (**5b**) [53]: The compound **5b** was obtained by using **4b** (144 mg, 2.00 mmol), **3a** (8.2 mg, 0.3 mol %), and CO (50 atm) in THF (1.0 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (168 mg, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49–4.43 (m, 1H), 3.49 (dd, J = 16.3, 5.7 Hz, 1H), 3.06 (dd, J = 16.3, 4.2 Hz, 1H), 1.94–184 (m, 1H), 1.84–1.73 (m, 1H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 72.3, 42.3, 27.7, 8.9.

β-Heptanolactone (**5c**) [54]: The compound **5c** was obtained by using **4c** (200 mg, 2.00 mmol), **3a** (8.2 mg, 0.3 mol %), and CO (50 atm) in THF (1.0 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (223 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53–4.47 (m, 1H), 3.50 (dd,

J = 16.3, 5.8 Hz, 1H), 3.05 (dd, J = 16.3, 4.3 Hz, 1H), 1. 90–1.83 (m, 1H), 1.81–1.64 (m, 1H), 1.37 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 71.3, 42.8, 34.3, 26.9, 22.2, 13.8.

4-Cyclohexyl-2-propiolactone (**5d**) [55]: The compound **5d** was obtained by using **4d** (126 mg, 1.00 mmol), **3a** (4.1 mg, 0.3 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (146 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20–4.17 (m, 1H), 3.42 (dd, J = 16.3, 5.8 Hz, 1H), 3.10 (dd, J = 16.3, 4.3 Hz, 1H), 1.98–1.91 (m, 1H), 1.87–1.51 (m, 5H), 1.36–1.10 (m, 3H), 1.07–0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 74. 9, 41.9, 41.0, 28.1, 27.0, 25. 9, 25.3, 25.1.

4-(*tert*-Butyl)oxetan-2-one (**5e**) [56]: The compound **5e** was obtained by using **4e** (100 mg, 1.00 mmol), **3a** (4.1 mg, 0.3 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (114 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25–4.22 (m, 1H), 3.31 (dd, J = 16.5, 6.0 Hz, 1H), 3.14 (dd, J = 16.5, 4.5 Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 77.9, 38.1, 32.8, 23.95.

4-Benzyloxetan-2-one (**5g**) [57]: The compound **5g** was obtained by using **4g** (134 mg, 1.00 mmol), **3a** (4.1 mg, 0.3 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure. White solid (155 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.18 (m, 3H), 7.18–7.12 (m, 2H), 4.67–4.63 (m, 1H), 3.40 (dd, J = 16.4, 5.7 Hz, 1H), 3.17–2.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 134.9, 129.2 (2C), 128.8 (2C), 127.3, 70.8, 42.4, 40.4.

4-(But-3-enyl)-2-propiolactone (**5h**) [35]: The compound **5h** was obtained by using **4h** (196 mg, 2.00 mmol), **3a** (10.8 mg, 0.4 mol %), and CO (50 atm) in THF (1.0 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (232 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85–5.74 (m, 1H), 5.10–4.99 (m, 2H), 4.55–4.49 (m, 1H), 3.51 (dd, J = 16.3, 5.8 Hz, 1H), 3.08 (dd, J = 16.3, 4.3 Hz, 1H), 2.31–2.09 (m, 2H), 2.01–1.93 (m, 1H), 1.89–1.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 136.3, 116.0, 70.6, 42.8, 33.8, 29.1.

4-(Methoxymethyl)-2-propiolactone (**5i**) [37]: The compound **5i** was obtained by using **4i** (176 mg, 2.00 mmol), **3a** (13.5 mg, 0.5 mol %), and CO (50 atm) in THF (1.0 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (214 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66–4.62 (m, 1H), 3.73 (dd, J = 11.7, 2.9 Hz, 1H), 3.63 (dd, J = 11.7, 4.5 Hz, 1H), 3.51–3.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 71.8, 69.3, 59.5, 39.4.

4-(4-oxooxetan-2-yl)butanenitrile (**5j**): The compound **5j** was obtained by using **4j** (222 mg, 2.00 mmol), **3a** (16.4 mg, 0.6 mol %), and CO (50 atm) in THF (1.0 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (248 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57–4.49 (m, 1H), 3.56 (dd, J = 16.4, 5.8 Hz, 1H), 3.10 (dd, J = 16.4, 4.3 Hz, 1H), 2.45–2.41 (m, 2H), 2.03–1.70 (m, 4H); ^{13}C NMR (100 MHz $CDCl_3$) δ 167.5, 118.9, 70.0, 43.0, 33.3, 21.2, 16.6; IR (ATR) 1820 (lactone), 2248 (nitrile) cm^{-1}; HRMS *m*/*z* (FAB) calcd for $C_7H_9O_2$ $[M+H]^+$ 140.0712, found: 140.0714.

4-(2-Butyroxyethyl)-2-propiolactone (**5k**) [37]: The compound **5k** was obtained by using **4k** (158 mg, 1.00 mmol), **3a** (4.1 mg, 0.3 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (174 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69–4.57 (m, 1H), 4.32–4.14 (m, 2H), 3.59 (dd, J = 16.4, 5.8 Hz, 1H), 3.17 (dd, J = 16.4, 4.3 Hz, 1H), 2.29 (t, J = 7.4 Hz, 2H), 2.25–2.07 (m, 2H), 1.70–1.60 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 167.5, 68.4, 59.9, 43.3, 36.0, 33.0, 18.3, 13.6.

Ethyl 9-(4-oxooxetan-2-yl)nonanoate (**5l**): The compound **5l** was obtained by using **4l** (228 mg, 1.00 mmol), **3a** (4.1 mg, 0.3 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (246 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51–4.45 (m, 1H), 4.09 (q, J = 7.2 Hz, 2H), 3.48 (dd, J = 16.3, 5.8 Hz, 1H), 3.03 (dd, J = 16.3, 4.3 Hz, 1H), 2.26 (t, J = 7.5 Hz, 2H), 1.88–1.79 (m, 1H), 1.78–1.66 (m, 1H), 1.62–1.55 (m, 2H), 1.47–1.25 (m, 10H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 168.2, 71.1, 60.0, 42.7, 34.5, 34.1, 29.0, 28.9 (2C), 28. 8, 24.74, 24.71, 14.1; IR (ATR) 1822 (lactone), 1731 (ester) cm^{-1}; HRMS *m*/*z* (FAB) calcd for $C_{14}H_{24}O_4$ $[M+H]^+$ 257.1755, found: 257.1755.

N,*N*-Diethyl 9-(4-oxooxetan-2-yl)nonamide (**5m**): The compound **5m** was obtained by using **4m** (255 mg, 1.00 mmol), **3a** (13.5 mg, 1.0 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (269 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46–4.41 (m, 1H), 3.43 (dd, J = 16.3, 5.8 Hz, 1H), 3.27 (q, J = 7.2 Hz, 2H), 3.27 (q, J = 7.2 Hz, 2H), 2.97 (dd, J = 16.3, 4.3 Hz, 1H), 2.25–2.12 (m, 2H), 1.82–1.72 (m, 1H), 1.69–1.64 (m, 1H), 1.59–1.49 (m, 2H), 1.33–1.19 (m, 10 H), 1.08 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 168.2, 71.1, 42.6, 41.7, 39.7, 34.4, 32.8, 29.1, 29.0, 28.9, 28.8, 25.1, 24.6, 14.1, 12.9; IR (ATR) 1824 (lactone) cm^{-1}, 1635 (amide) cm^{-1}; HRMS *m*/*z* (ESI) calcd for $C_{16}H_{29}NO_3$ [M^+] 283.2147, found: 283.2150.

4,4′-(Butane-1,4-diyl)bis(oxetan-2-one) (**5n**): The compound **5n** was obtained by using **4n** (142 mg, 1.00 mmol), **3a** (8.2 mg, 0.6 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure. White solid (196 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54–4.48 (m, 2H), 3.53 (dd, J = 16.3, 5.8 Hz, 2H), 3.07 (dd, J = 16.3, 4.3 Hz, 2H), 1.94–1.73 (m, 4H), 1.66–1.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0 (2C), 70. 9 (2C), 42.93, 42.91, 34.5, 34.4, 24.6, 24.6; IR (ATR) 1816 cm^{-1}; HRMS *m*/*z* (FAB) calcd for $C_{10}H_{14}O_4$ [M+H]$^+$ 199.0972, found: 199.0972.

4,4-Dimethyloxetan-2-one (5o) [58]: The compound **5o** was obtained by using **4o** (72.11 mg, 1.00 mmol), **3a** (13.5 mg, 1.0 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure (27% NMR yield). ^{1}H NMR (400 MHz, $CDCl_3$, crude NMR) δ 3.19 (s, 2H), 1.62 (s, 6H); IR (ATR) 1811 cm^{-1}.

4-(7-Oxabicyclo[4.1.0]heptan-3-yl)oxetan-2-one (**5q**): The compound **5q** was obtained by using **4q** (140 mg, 1.00 mmol), **3a** (8.2 mg, 0.6 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 24 h by following the general procedure. Colorless liquid (146 mg, 87%) as the mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25–4.16 (m, 1H), 3.50–3.36 (m, 1H), 3.29–3.00 (m, 3H), 2.40–2.17 (m, 1H), 2.16–1.99 (m, 1H), 1.98–1.70 (m, 2H), 1.68–1.51 (m, 1H), 1.50–1.36 (m, 1H), 1.34–1.18 (m, 1H), 1.14–0.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 73.9, 73.8, 62.1, 62.06, 62.00, 61.4, 60.4, 41.1, 41.07, 41.03, 37.1, 34.5, 34.2, 26.5, 26.1, 24.2, 22.6, 22.5, 22.1, 1.8, 18.6; IR (ATR) 1816 cm^{-1}; HRMS *m*/*z* (ESI) calcd for $C_9H_{12}O_3$ [M^+] 168.0786, found: 168.0788.

(3,3-Dimethyloxiran-2-yl)methyl 9-(4-oxooxetan-2-yl)nonanoate (**5r**): The compound **5r** was obtained by using **4r** (284 mg, 1.00 mmol), **3a** (4.1 mg 0.3 mol %), and CO (50 atm) in THF (0.5 mL) at 90 °C for 16 h by following the general procedure. Colorless liquid (262 mg, 84%). ^{1}H NMR (400 MHz) δ 4.52–4.47 (m, 1H), 4.33 (dd, J = 12.1, 4.2 Hz, 1H), 4.01 (dd, J = 12.1, 7.0 Hz, 1H), 3.50 (dd, J = 16.3, 5.8 Hz, 1H), 3.05 (dd, J = 16.3, 4.3 Hz, 1H), 2.98 (dd, J = 6.9, 4.2 Hz, 1H), 2.35 (t, J = 7.5 Hz, 2H), 1.90–1.81 (m, 1H), 1.79–1.68 (m, 1H), 1.65–1.59 (m, 2H), 1.34–1.30 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 168.3, 71.3, 63.3, 60.5, 58.1, 42. 9, 34.6, 34.0, 29.1, 29.0 (2C), 28. 9, 24.8, 24.8, 24.6, 18.9; IR (ATR) 1824 (lactone), 1734 (ester) cm^{-1}; HRMS *m*/*z* (ESI) calcd for $C_{17}H_{28}O_5$ [M^+] 312.1937, found: 312.1939.

4. Conclusions

A new highly reactive Sn(IV) porphyrin-mediated epoxide carbonylation was developed, producing synthetically valuable β-lactones. The Lewis acidic Sn(IV)-centered porphyrin activated an epoxide, and cobalt tetracarbonyl anions delivered carbon monoxide with high efficiencies. In particular, TONs up to 1260 were achieved. Furthermore, a variation of the porphyrin structure revealed the importance of high Lewis acidity and a broad substrate scope was disclosed. This new catalyst also exhibited interesting chemical selectivity on epoxide substitution patterns; thus, the synthesis of molecules with both epoxide and β-lactone has been realized, and its further utilization is currently in progress.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/4/311/s1, Figure S1: ORTEP of **2a**.

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