

Supplementary Materials: Direct Conversion of Propylene Oxide to 3-Hydroxy Butyric Acid Using a Cobalt Carbonyl Ionic Liquid Catalyst

Senkuttuvan Rajendiran, Gyoosoon Park* and Sungho Yoon *

Results and Discussion

General Consideration and Physical Measurements

All manipulations of air- and water-sensitive compounds were carried out using glovebox or standard Schlenk line techniques under an argon atmosphere. Chemicals 1-methyl-imidazole, anhydrous methanol, Tetrahydrofuran (THF), DME, Propylene oxide (PO) and 1-butylchloride were purchased from Sigma-Aldrich Co., (St, Louis, Missouri, USA). THF and DME were freshly distilled over sodium/benzoquinone, and methanol was distilled over Mg/I under a nitrogen atmosphere before use. PO was distilled over CaH_2 under a nitrogen atmosphere. $\text{KCo}(\text{CO})_4$ and $[\text{Bmim}][\text{Co}(\text{CO})_4]$ were synthesized according to a previously reported procedure [14]. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. (Andover, USA). Research-grade carbon monoxide was purchased from Sinyang Gas Company (Paju-si, Republic of Korea) with 99.995% purity and used as received. ^1H NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer (400 and 100 MHz) (ASCEND III HD; Bruker, Rheinstetten, Germany), and chemical shifts were referenced to TMS. FT-IR measurements were carried out on a Nicolet iS 50 (Thermo Fisher Scientific, Waltham, MA, USA) spectrometer. LC-MS measurements were performed on an Agilent 6130 Single Quadrupole LC/MS spectrometer (Santa clara, California, USA). All carbonylation reactions were performed in a 100 mL stainless steel tube reactor fitted with a pressure gauge and pressure release valve. All carbonylation reactions were set up and run in a well-ventilated fume hood equipped with a carbon monoxide detector (see MSDS for the proper handling of CO). PO conversion, 3-HBA, 2-hydroxypropyl-3-(2-hydroxypropyl)butanoate (2-HPHB), 1,2-propanediol (1,2-PD), and acetone were quantified by ^1H -NMR spectroscopy using naphthalene as an internal standard.

Synthesis of Potassium Cobalt Tetracarbonyl

To a solution of $\text{Co}_2(\text{CO})_8$ (0.974 g, 2.856 mmol) in 15 mL of THF was added excess KOH (0.413 g, 7.375 mmol). The brown solution was stirred at RT for 5 h and the resulting pale yellow solution was filtered and the volatiles in filtrate were removed under vacuum to afford off-white solid Yield = 0.572 g. IR = 1887 cm^{-1} (Figure S1).

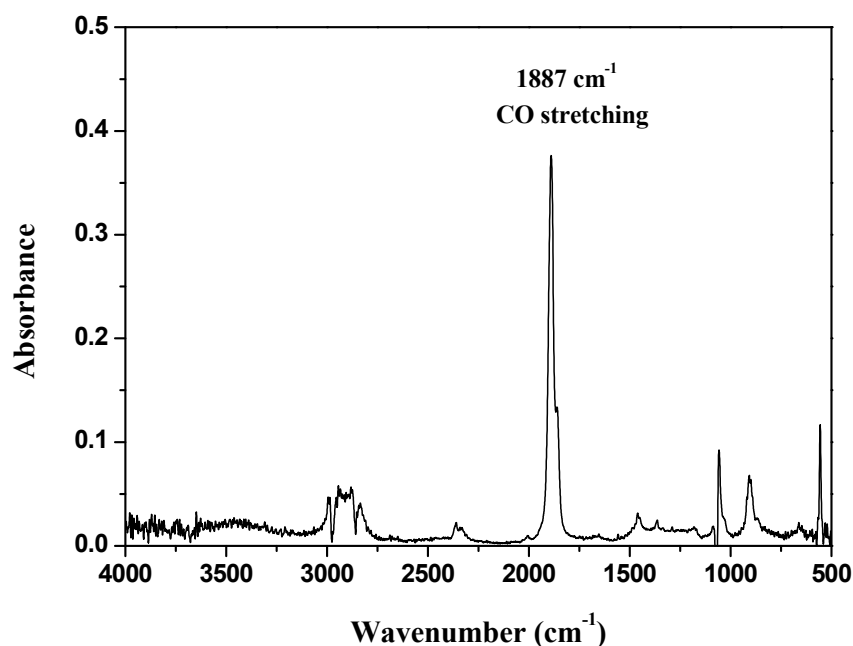


Figure S1. FT-IR spectrum of KCo(CO)_4 in THF solution.

Synthesis of 1-butyl-3-methylimidazolium Chloride (a)

To a solution of methyl imidazole (2.033 g, 24.7259 mmol) in 5 mL anhydrous CH_3CN was added 1-butylchloride slowly (2.961g, 31.3996 mmol). The colorless solution was refluxed for 48 h under N_2 atm and the resulting yellow solution was cooled to room temperature. All volatiles were removed under vacuum and dissolved with 3 mL CH_3CN to that 5 mL ethyl acetate was and cooled to $-40\text{ }^\circ\text{C}$ for 2 h. white precipitates were formed, decanned the mother liquid and washed with 10 mL ethyl acetate and dried under vacuum completely. Yield = 4386 g.

Procedure for Epoxide-ring Opening Carbonylation

In a glove box, a 100 mL stainless steel tube reactor was charged with (0.0267 g, 0.0861 mmol) $[\text{Bimm}][\text{Co(CO)}_4]$, imidazole (0.0127 g, 0.1867 mmol) and PO (0.5010 g, 8.6379 mmol) in 2.0 mL of dry DME, then removed from glove box. The reactor was cooled to $0\text{ }^\circ\text{C}$ and purged with 0.5 MPa of CO, (0.7655 g, 42.5277 mmol) nitrogen-bubbled water (oxygen-free) was added. Then reactor immediately pressurized with CO to the desired pressure at room temperature, followed by heated to the targeted temperature. After the appropriate time, the reactor was cooled to room temperature and CO gas was slowly released. The crude sample was weighed, filtered through celite and analyzed using $^1\text{H-NMR}$ spectroscopy in CDCl_3 .

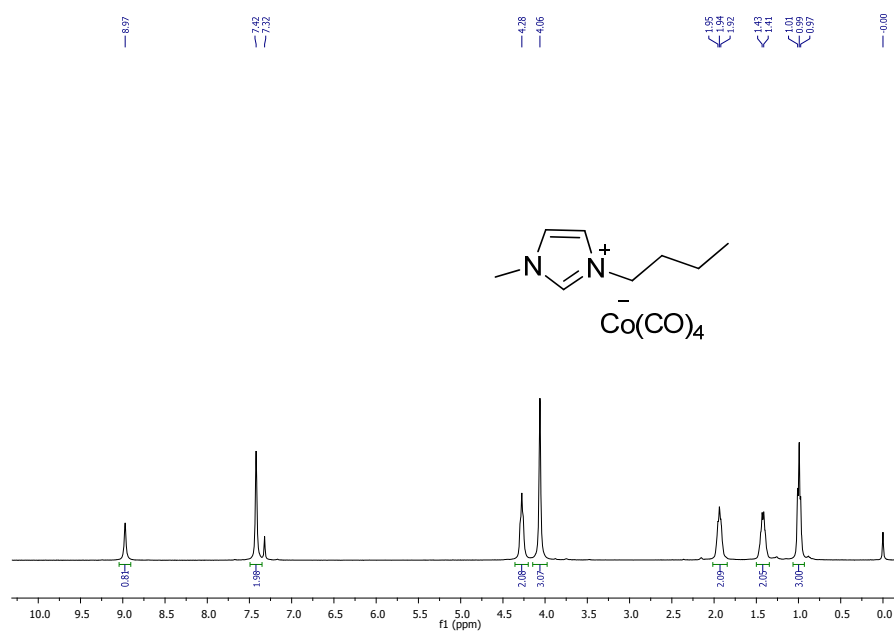


Figure S2. ^1H -NMR spectrum of C [Bmim][Co(CO)₄].

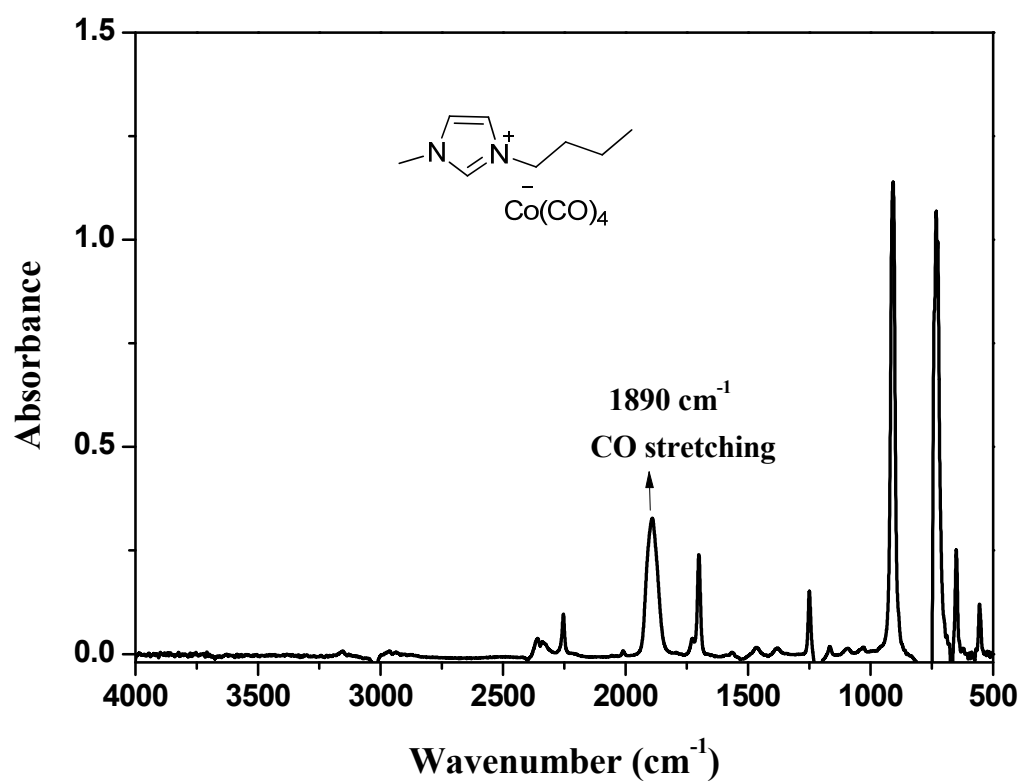
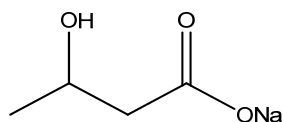
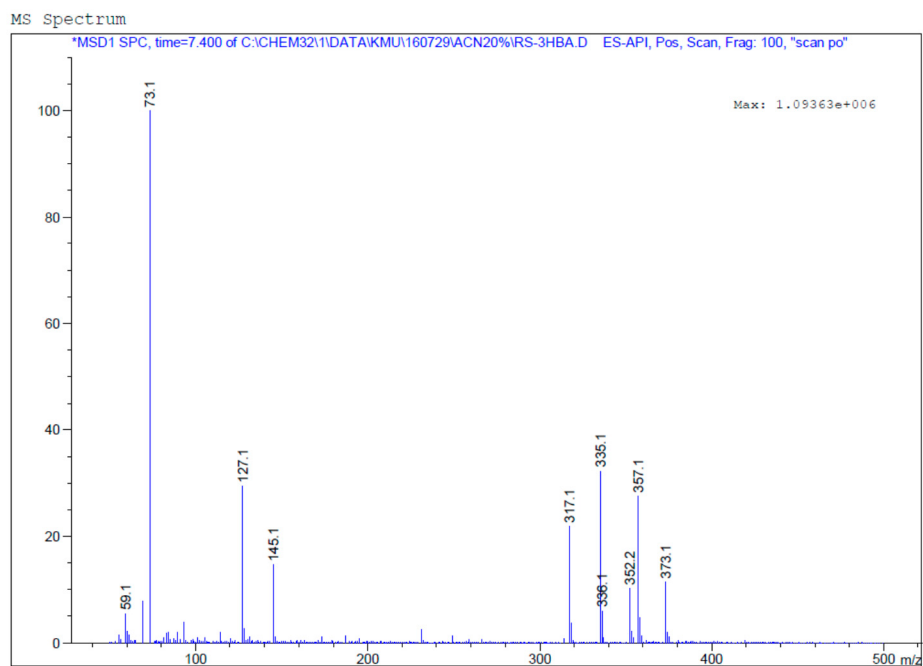


Figure S3. FT-IR spectrum of C in THF solution.



Chemical Formula: $C_4H_7NaO_3$

Exact Mass: 126.03

Figure S4. LC-MS spectrum of 3-HBA.

NMR Spectra

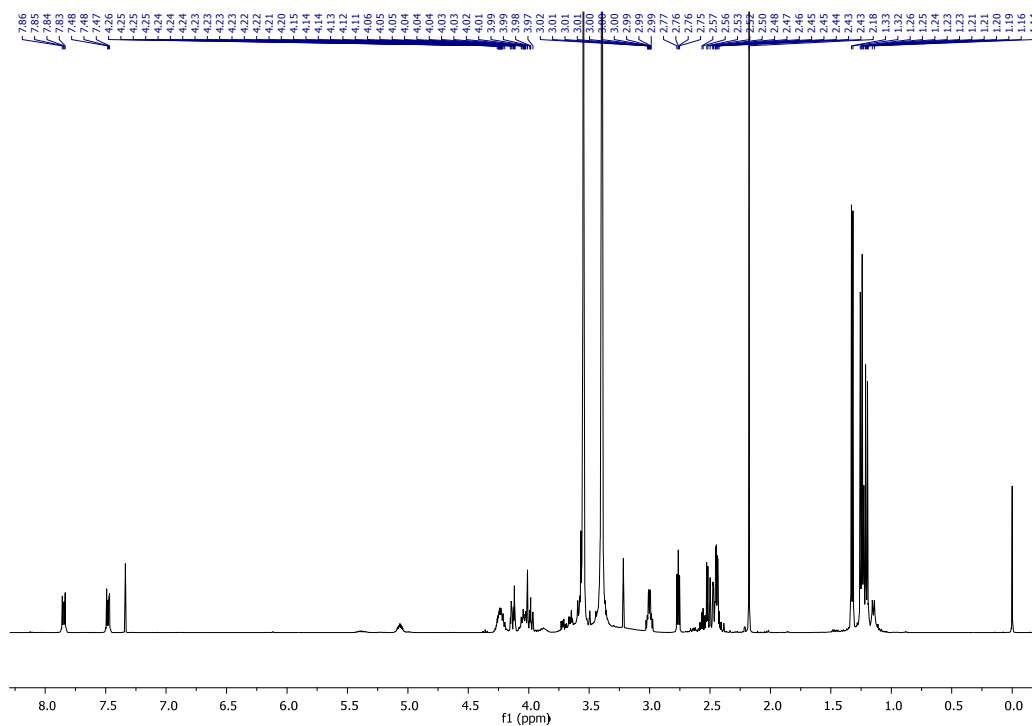


Figure S5. 1H -NMR spectrum of entry 2.

References

Guo, Z.M.; Wang, H.S.; Lv, Z.G.; Wang, Z.H.; Nie, T.; Zhang, W.W. Catalytic performance of [Bmim][Co(CO)₄] functional ionic liquids for preparation of 1,3-propanediol by coupling of hydroesterification-hydrogenation from ethylene oxide. *J. Organomet. Chem.* **2011**, *696*, 3668–3672.