Supporting Information

Toward Transition Metal-Catalyzed Carbonylation of Methanol without HI as Co-Promoter – Catalytic Exocyclic Carbonylation of Cylcoimino esters

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Experimental

All manipulations were performed in a Vacuum Atmosphere DRI-LAB-08/85 dry box under a nitrogen atmosphere or using standard Schlenk line techniques. Diethyl ether, hexane and tetrahydrofuran (THF) were dried by refluxing over sodium/benzophenone under nitrogen. Toluene was dried by refluxing over sodium under nitrogen. DME was dried over ally of potassium and sodium. 2-Ethoxyl-4,5-dihydro-2-oxaoline^{S1} and 2-ethoxy-4,5-dihydro-4-isopropyl-2-oxaoline^{S1, S2} were prepared following slightly modified literature procedures. 1-Aza-2-methoxycycloheptene and 2-methoxypyridine were purchased from Aldrich Chemicals. 1-Aza-2-methoxycyclohexene and 1-aza-2-methoxycyclopentene were purchased from Oakwood Products, Inc. 1-Aza-2-ethoxyl-cycloheptene and 1-aza-2-isopropylcycloheptene were prepared following slightly modified literature procedures.^{S3} The above compounds were further purified by reduced-pressure distillation from calcium hydride and then were stored in Schlenk tubes over activated molecular sieves (4 Å) under nitrogen. The Co₂(CO)₈ catalyst was purchased from Alfa Aesar Chemicals and used as received.

The ¹H NMR spectra and ¹³C NMR spectra were recorded with an AMX 360 MHz or a DRX 500 MHz NMR spectrometer. Both the ¹H and ¹³C chemical shifts were measured using the solvent resonances as internal references. GC/MS were obtained with a SHIMADZU GC-17A gas chromatography instrument or Hewlett Packard 5890 series instrument.

General procedure of carbonylation. A 125 mL or 160 mL or 300mL Parr bomb reactor was evacuated on a Schlenk line and backfilled with CO (1 atm). The substrate (3.8 mmol), the dicobalt catalyst (0.19 mmol), and DME (25 mL) were transferred into

the reactor with syringes under a gentle flow of CO. The reactor was immediately closed, and the pressure of CO was raised to 1000 psi. The reactor was heated in 100 °C oil bath while being magnetically stirred for 48 h and then cooled to the ambient temperature. The CO pressure was slowly released in a hood, and the reactor was opened. The DME solution was transferred into a flask with a CaCl₂-drying tube attached to it and stirred for 2 h to allow aerobic decomposition and precipitation of the decomposed Co species. The crude carbonylation product was obtained after removal of DME. The product was then extracted from diethyl ether by filtration. All carbonylation products are known compounds. Their identities are confirmed by comparison of the ¹H and ¹³C spectroscopic data with the data in the literature.^{S4}

Reference

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