Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

One-pot Conversion of Lysine to Caprolactam over Ir/H-Beta Catalysts

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Experimental section

Materials: The zeolites (HB-124, HB-80, HB-50, HY-10, ZSM-5 (42)) were purchased from Nankai University Catalyst Co. Ltd., acidic Al_2O_3, anatase TiO_2, CeO_2, MoS_2, Nb_2O_5, La_2O_3 and Activated carbon were all commercial. The precursors for noble and non-metals are 21.06 wt% H_2IrCl_6 solution in H_2O, $RhCl_3.xH_2O$, $HAuCl_4.xH_2O$, $RuCl_3$, $H_2PtCl_6.6H_2O$, $PdCl_2$, $HReO_4$ and $Ni(NO_3)_2.6H_2O$.

Reagents: *L*-lysine, α-amino-ε-caprolactam (*L* and *DL*- ACPL) hydrochloride, anhydrous MeOH ($H_2O < 0.05\%$), THF, ethanol, 1,2-propanediol, γ-valerolactone, 37% HCHO solution. All the reagents were used as received.

Catalyst synthesis: All the catalysts were prepared by the incipient wetness impregnation method. A typical synthesis of 2Ir/HB-124 as follows, first the support was dried at 550°C for 6 hours. To 1.0 g of the dried support, 0.095 mL of H_2IrCl_6 precursor solution (21.06 wt% of Ir) along with 1.5 mL of deionized H_2O was added. It was then mixed well, covered and kept at room temperature for 6 hours followed by drying at 80°C for 12 hours. It was then ground and calcined at 550°C (2°C/min) for 4 hours. The catalyst was used for the experiments without any pretreatments. The same procedure was followed for other supports like Al_2O_3, TiO_2, CeO_2 and AC. The calcination step was avoided for AC.

Catalysts with other metals such as Rh, Pt, Ru, Au, Pd, Re and Ni were also prepared following the above procedure. These catalysts were reduced at a temperature of 300°C for Rh, Ru, Pd, Au, 350°C for Pt, 400°C for Ir/AC, 450°C for Ni and 500°C for Re for 3 hours (3°C/min) and then passivated in the O_2/N_2 mixture for 4 hours.

One-pot conversion of L-lysine to CPL: The reaction was performed in a high-pressure Parr-4848 Hastelloy autoclave (100 mL) equipped with a mechanical stirrer and an automatic temperature control system. The reactor was first charged with 0.200 g of *L*-lysine and 0.100 g of 2Ir/HB-124 catalyst. A volume of 20 mL of anhydrous methanol was then introduced. Then the reactor was purged with H_2 (10 bar) for at least five times and pressurized to 20 bar. The reactor temperature was slowly increased to 240°C (2.2°C/min) and maintained for a period of 6 hours. At the end of the reaction time, the reactor was cooled down to room temperature. It was then depressurized, the product mixture was filtered and analyzed by HPLC and GC. Recycle experiments were conducted as follows; after the reaction, the catalyst was separated by filtration and used for the next run without any pretreatments like drying or calcination.

ACPL to CPL: About 0.050 g of *L*-ACPL.HCl was charged into the reactor along with 0.025 g of 2Ir/HB-124 and 20 mL of anhydrous methanol. The reactor was purged with H_2 (10 bar) at least five times and pressurized to 20 bar. The temperature was slowly increased to 250°C (2°C/min) and maintained for a period of 1 hour. At the end of the reaction time, the reactor was cooled down, depressurized, filtered and analyzed by HPLC and GC.

DMAC to CPL: About 0.050 g of DMAC was introduced to the reactor along with 0.025 g of 2Ir/HB-124 and 20 mL of anhydrous methanol. It was then purged with H_2 and pressurized to 20 bar. The temperature was set to 250°C (2°C/min) and the reaction time to 1 hour. At the end of the reaction time, the reactor was cooled down, depressurized, the product was filtered and analyzed by GC. Recycle experiments were conducted as follows; after the reaction, the catalyst was separated by filtration and used for the next run without any pretreatments like drying or calcination.

Fixed-bed reactions of DMAC to CPL: The reactions were carried out in a stainless steel tube reactor (6 mm i.d. and 31 cm length). 2Ir/HB-124 was sieved into a 20-40 mesh size and loaded (0.30 g) into the reactor. The reactor was heated to 250°C (2°C/min) under a H_2 flow of 50 mL/min. The hydrogen pressure in the reactor was maintained at 65 bar throughout the reaction and the flow was maintained at 50 mL/min. A 0.25 wt% of DMAC in anhydrous methanol was used as the feed (0.5 mL/min, WHSV = 100). Product samples were collected at regular time intervals and were analyzed by GC.

Synthesis of DMAC: About 1.0 g of *L*-ACPL.HCl, 0.720 g of 5Pd/AC, 1.7 mL of 37% HCHO and 20 mL of anhydrous methanol were charged into the reactor. The reactor was then flushed five times with 10 bar H_2 and pressurized to 40 bar. The reactor temperature was set to 50°C and time to 4 hours. In the end, the reactor was cooled down to room temperature and depressurized. The solvent methanol and unreacted HCHO were removed by rota-evaporation and the solid product obtained was double recrystallized from methanol-ethyl acetate mixtures. The final product, DMAC was obtained through decantation and drying at 60°C overnight. The purity of the product was analyzed by ^1H

& ^{13}C NMR spectroscopy (Figure S4). It was found that the purity of DMAC as-prepared is >98%.

Product analysis: L-lysine and L-ACPL conversions were analyzed by using an HPLC instrument (Column: ACE Excel 5 AQ, 250 x 4.6 mm id, UV-detector 210 nm, 35^{o}C, solvent A = H_2O containing 10 mmol of $HCOONH_4$, solvent B = 90% CH_3CN and 10% H_2O, flow = 0.6 mL of 80% A & 20% B). DMAC conversion and CPL yield were quantified using a GC instrument fitted with an FFAP column (30m x 0.32 mm). Identification of the products was done using a GC-MS instrument fitted with a DB-5 column (30 m x 0.25 mm x 0.25 μm). The conversion, yield and selectivity of different compounds were calculated using the following equations with the calibrated values (benzyl alcohol as the standard).

$$Conversion\ (\%) = \frac{Input\ lysine\ (mol) - Output\ lysine (mol)}{Input\ lysine\ (mol)} \times 100$$

$$Product\ yield\ (\%) = \frac{Moles\ of\ CPL\ (\ or\ DMAC)}{Input\ lysine\ (mol)} \times 100$$

$$CPL\ selectivity\ (\%) = \frac{Moles\ of\ CPL}{Moles\ of\ DMAC\ converted} \times 100$$

Nitrogen balance of the reaction: The amount of nitrogen in the reaction can be partially balanced to DMAC formation. On the other hand, dimethylamine and trimethylamine[15] might be formed *via* C-N$(CH_3)_2$ bond hydrogenolysis of DMAC in methanol, and will contribute to the nitrogen balance. Figure S5 shows the GC-MS spectra of the product mixture. Notable amount of trimethylamine was found in the products but without dimethylamine observation. Because of the high volatility and the difficulty in the accurate quantification, the byproduct trimethylamine was not quantified. Thus, it can be confirmed that besides DMAC, trimethylamine is the major co-product which contributes to the nitrogen balance.

The molecular dimensions of *L*-lysine, ACPL, DMAC and CPL were calculated using Materials Studio software.

ICP-OES analysis: The amount of Ir leached in to the product mixture was analyzed on a PerkinElmer ICP-OES 7300DV instrument after removing the organic phase.

Table S1: Effect of solvent on CPL production from *L*-lysine and DMAC.

Solvent	CPL yield (mol%)
Methanol	23.0
Ethanol	2.8
Tetrahydrofuran	--
1,2-Propanediol	--
γ-valerolactone	--
H_2O	--
Methanol + H_2O[a]	13.8
Ethanol[b]	< 1
Tetrahydofuran[b]	< 1

Reaction conditions: *L*-lysine = 0.200g, 2Ir/HB-124 = 0.100g, solvent = 20 mL, P_{H2} = 30 bar, T = 240°C, t = 6 h. [a]MeOH = 19.5 mL and H_2O = 0.5 mL, t = 4 h. [b]DMAC as the feedstock.

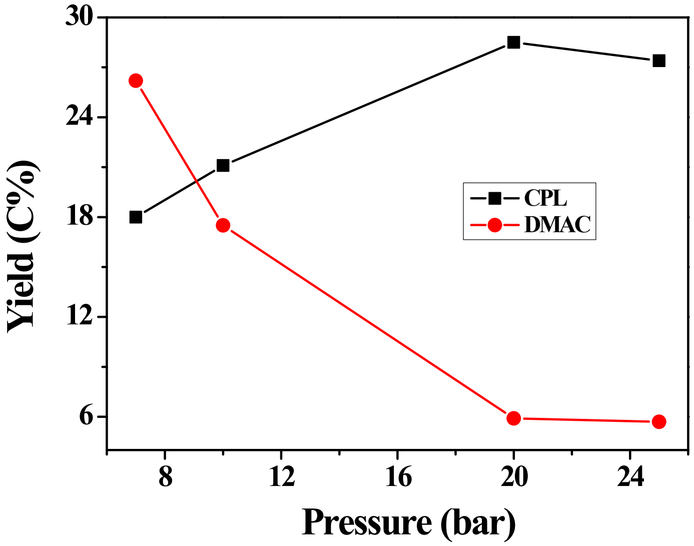

Figure S1: Effect of reaction pressure on DMAC and CPL yield. R*eaction conditions: L*-lysine = 0.200g, 2Ir/HB-124 = 0.100g, MeOH = 20 mL, T = 250°C, t = 4 h.

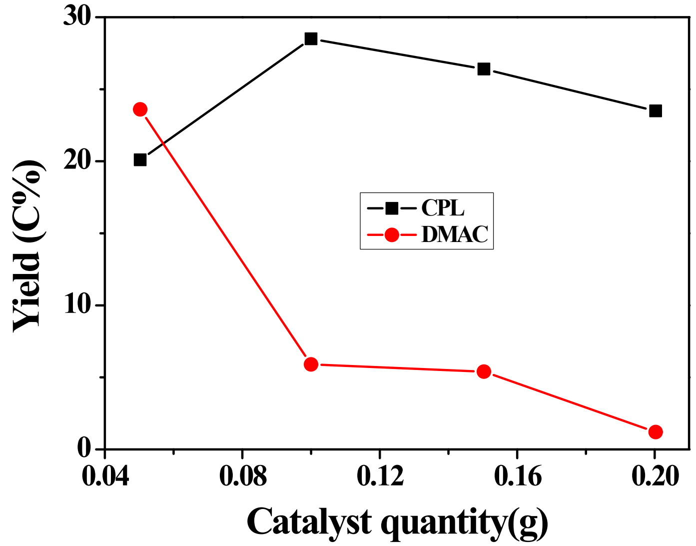

Figure S2: Effect of catalyst quantity on DMAC and CPL yield. *Reaction conditions: L*-lysine = 0.200g, MeOH = 20 mL, T = 250°C, P_{H2} = 20 bar, t = 4 h.

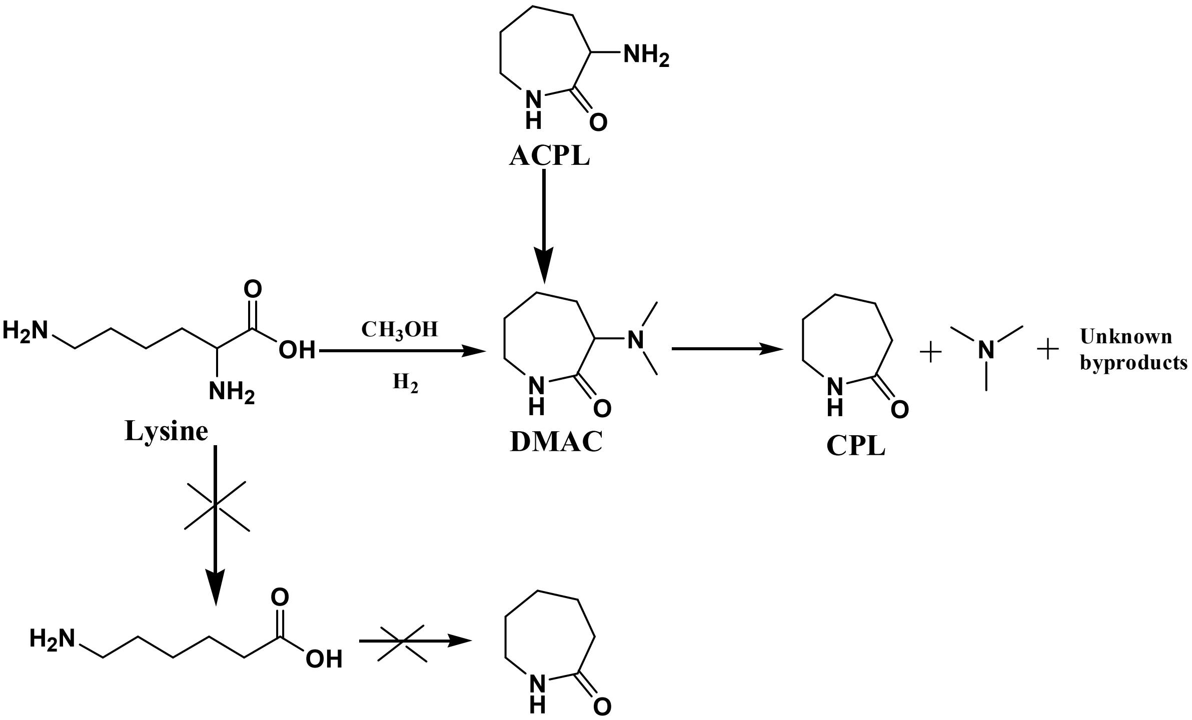

Figure S3: Summary of the *L*-lysine to CPL reaction route observed over Ir/HB-124 catalysts.

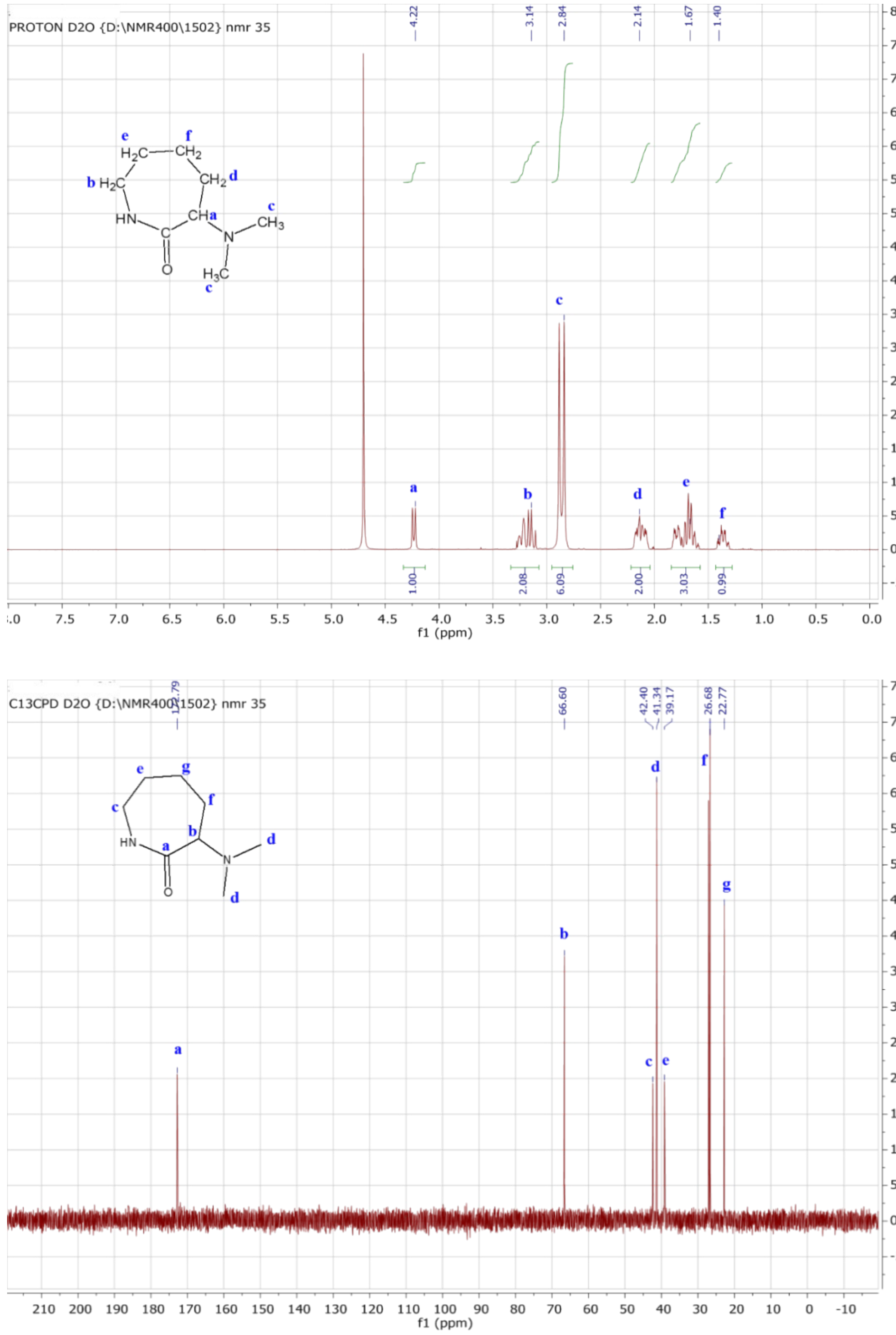

Figure S4: ^{1}H and ^{13}C-NMR spectra of purified DMAC in D_2O synthesized from *L*-ACPL.HCl.

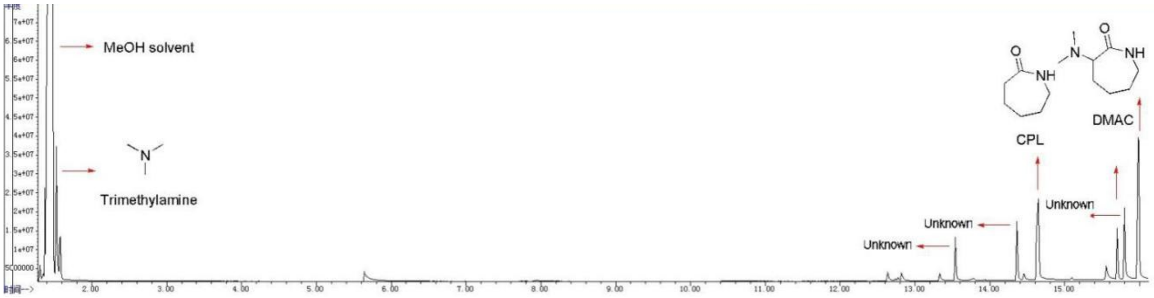

Figure S5: GC-MS spectra of product mixture showing the presence of trimethylamine. *Reaction conditions: L*-lysine = 0.200g, 2Ir/HB-124 = 0.100 g, MeOH = 20 mL, P_{H2} = 30 bar, T = 240 ^{o}C, t = 6 h.