## Supporting Information to accompany

## High pressure combinatorial screening of homogeneous catalysts: hydrogenation of carbon dioxide

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## **Experimental**

**Safety Warning.** Operators of high-pressure equipment such as that required for these experiments should take proper precautions, including but not limited to the use of blast shields and pressure relief mechanisms, to minimise the risk of personal injury.

**General.** DMSO, DBU(1,8-diazabicyclo[5.4.0]-undec-7-ene) were degassed by repeated freeze-vacuum-thaw cycles before use. Carbon dioxide gas (Airgas, research grade, 99.995 % purity) was passed through an oxygen trap before use. Metal salts, complexes, phosphines, hydrogen gas (99.99% purity) and bromothymol blue were used as received from commercial sources.

**Apparatus for high pressure experiments.** The high pressure, high-throughput apparatus (Figure 1) contains four components, a 160 ml high pressure vessel from Parr Inc. (model 4772, 4773 or 4774), a removable round metallic disc, a removable handle to fit into that disc, and a square plastic plate with a  $6 \times 6$  array of holes to hold the vials. The last three items are easily prepared in a machine shop; diagrams with dimensions are in the supplementary material. The removable round metallic disc (2.4 cm high, 6.3 cm diameter) contains one threaded hole in the centre to take the removable handle and 36 unthreaded holes (8 mm dia.) to hold 36 vials (Kimble # 60820-740, 7 × 40 mm standard opening glass vials). The disk fits into the reaction vessel as shown in the figure. The T-shaped handle can be screwed into the disc to pull it out from the vessel. The square plastic plate ( $7.4 \times 7.4 \times 1.8$  cm) contains 36 holes (8 mm diameter for top 1.6 cm, 6 mm dia for bottom 2 mm) in a  $6 \times 6$  array. The holes in the plate are narrower at the bottom to prevent the vials from falling through while still allowing light to enter from below.

The vessel temperature was maintained during experiments by a constant-temperature water bath. The contents of each vial in the vessel was stirred by a micro-stirbar (7 mm long, 2 mm dia.) driven by a magnetic stir plate underneath the water bath. Stir plates containing sufficiently powerful magnets are available from IKA. That the stir plate used was capable of coupling to all 36 of the stir bars inside the vessel was confirmed visually in a blank experiment at 1 bar with the cover of the vessel removed. Note that the stir bars do not sit flat against the bottom of the vials.



Figure S1. Cross-sectional views of the metallic disk (above) and the plastic plate (below).

**First tier screening of catalysts.** All preparations before the pressurization were performed under dry and inert gas atmosphere in a glove box. DMSO stock solutions of the metal salts (0.030 M), the ligands (0.090 M if monodentate, 0.045 M if bidentate), DBU (6.0 M) and bromothymol blue (6 mg in 25 mL) were prepared. Into each of the 36 vials in the square plate were placed a microstir bar, 100 µL of metal salt solution, 200 µL of ligand solution, and 50 µL of DBU solution. The desired metal salt solution were injected into the vials in columns on the square plastic plate, and ligands solution were injected into the vials in rows. DBU solution was injected into all the vials. The vials were then transferred onto the round metallic disc, which contains markings to correlate the positions on the disc to those on the plate. The steel vessel was sealed, flushed with hydrogen, and then pressurized with hydrogen to 40 bar. The vessel was placed in 50 °C water bath. After 20 minutes for the attainment of thermal equilibrium, CO<sub>2</sub> was added to 100 bar. After 21 h, the reaction was stopped by putting the vessel into water/ice bath. After the pressure dropped to a constant value, the gases were slowly released and the vessel warmed to room temperature. The vials were transferred from the vessel to the square plastic plate. Several drops of bromothymol blue solution were added to each vial. The extent of conversion was determined visually from the color of the solution. Photographs were taken of the vials in the plate will illumination from below (using a light table).

Second tier screening of catalysts. The concentration of the DBU stock solution in DMSO was changed to 1.5 M and the amount of the DBU solution added to each vial was increased to 100  $\mu$ L. All other concentrations and volumes were unchanged.

**Individual testing of catalyst precursors.** A 160 mL high pressure vessel equipped with 13 glass vials was adopted. Nine of the vials have a micro-stir bar with 15  $\mu$ mol of various metal salts, 45  $\mu$ mol of PPh<sub>3</sub> or 22.5  $\mu$ mol of dppe or dcpe, 1.0 mL DMSO, 3.34 mmole DBU. After the vessel was sealed in the dry grove box, the vessel was flushed 3 times with 5 bar H<sub>2</sub>, and then 40 bar of H<sub>2</sub> were introduced. When the vessel was heated up in 50 °C water bath for 10 minutes, CO<sub>2</sub> was added to 100 bar total for 7.5 h reaction time. After the reaction finished, the vessel was put into an ice/water bath to terminate the reaction. When the gas pressure had dropped to a constant level, the gases were slowly vented. CH<sub>2</sub>Cl<sub>2</sub> (100  $\mu$ L) was added into each vial as an internal standard to determine the yield by NMR spectroscopy. The sample for NMR analysis was using CD<sub>3</sub>OD as solvent. The detection of formic acid was confirmed by adding a drop of commercially obtained formic acid and finding that the formyl proton peak exactly overlapped the peak from the experimental sample.

Testing of NiCl<sub>2</sub>(dcpe) as a catalyst precursor. A 31 ml high pressure vessel was

filled with a stir bar, 15  $\mu$ mol of NiCl<sub>2</sub>(dcpe), 1.0 mL DMSO, and 6.0 mmol DBU under N<sub>2</sub>, flushed 3 times with 5 bar H<sub>2</sub>, and then pressurized with 40 bar of H<sub>2</sub>. The vessel was placed in a 50 °C water bath for 1 h and then CO<sub>2</sub> was added to 200 bar total pressure. After 21 h, the vessel was put into an ice/water bath to terminate the reaction. When the gas pressure dropped to a constant level, the gases were slowly vented. CH<sub>2</sub>Cl<sub>2</sub> (100  $\mu$ L) and CD<sub>3</sub>OD were added into the vessel as an internal standard and as the solvent to determine the yield by NMR spectroscopy.