Supporting Information

**Productive Utilization of Chlorobenzene:
Palladium-Catalyzed Selective Oxidation of Alcohols**

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Experimental Section:

General Comments. All reactions were performed under argon atmosphere in oven-dried glass Schlenk tubes using standard Schlenk techniques. All alcohols, bases (K_2CO_3 , K_3PO_4 , $NaOtBu$), chlorobenzene, bis(dibenzylideneacetone)palladium, diethyl ether, toluene were purchased from commercial sources and used as such. The phosphine ligand **1** was synthesized using the previously described procedure of Buchwald (reference 2a of the communication). All solvents were of the anhydrous, sure-seal grade. The detailed procedure described for the synthesis and isolation of 4,4'-Diflourobenzophenone was generally followed for all Pd/ligand **1**-catalyzed alcohol oxidation reactions using chlorobenzene. All reactions were performed until complete consumption of the starting alcohols; but the reaction times and conditions have not been minimized. Column chromatography was performed using commercially available Silica Gel 60 (particle size: 0.063 - 0.100 mm), hexanes and ethyl acetate. Details and results are summarized in Table 1 and 2 of the communication. The aldehyde and ketone products are known compounds.

4,4'-Diflourobenzophenone: A mixture of 4,4'-diflourobenzhydrol (220 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol),

$\text{Pd}(\text{dba})_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) was loaded into a Schlenk reaction tube. The mixture was thoroughly degassed using vacuum and argon purge cycles. Chlorobenzene (0.15 mL) and toluene (4 mL) were added and the mixture was heated at 105 °C for 12 h. The reaction mixture was taken up in ether (100 mL) and washed with H_2O (30 mL) and brine (30 mL). The organic phase was dried over MgSO_4 , filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to afford 4,4'-difluorobenzophenone as an off-white solid (215 mg, 98 %) after drying under vacuum.

Acetophenone: This compound was obtained as an oil (82 mg, 68 %) from the reaction of sec-phenethyl alcohol (0.12 mL, 1.0 mmol), chlorobenzene (0.15 mL), K_2CO_3 (276 mg, 2.0 mmol), $\text{Pd}(\text{dba})_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in toluene at 80 °C for 24 h.

2-Naphthaldehyde: This compound was obtained as a yellowish solid (149 mg, 96 %) from the reaction of 2-naphthalenemethanol (158 mg, 1.0 mmol), chlorobenzene (0.15 mL), K_2CO_3 (276 mg, 2.0 mmol), $\text{Pd}(\text{dba})_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in toluene at 105 °C for 6 h.

Piperonal: This compound was obtained as a pale yellow solid (138 mg, 92 %) from the reaction of piperonyl alcohol (152 mg, 1.0 mmol), chlorobenzene (0.15 mL), K_3PO_4 (425 mg, 2.0 mmol), $\text{Pd}(\text{dba})_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in toluene at 105 °C for 14 h.

9-Fluorenone: This compound was obtained as yellow solid (179 mg, 100 %) from the reaction of 9-hydroxyfluorene (182 mg,

1.0 mmol), chlorobenzene (0.15 mL), K_2CO_3 (284 mg, 2.0 mmol), $Pd(dba)_2$ (6 mg, 10 mol) and ligand **1** (11 mg, 30 mol) in toluene at 105 °C for 12 h.

9-Anthraldehyde: This compound was formed (99 % yield) from the reaction of 9-anthracenemethanol (208 mg, 1.0 mmol), chlorobenzene (0.15 mL), K_2CO_3 (276 mg, 2.0 mmol), $Pd(dba)_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in toluene at 105 °C for 24 h.

p-Methylthiobenzaldehyde: This compound was obtained as a yellow oil (125 mg, 82 %) from the reaction of p-methylthiobenzyl alcohol (154 mg, 1.0 mmol), chlorobenzene (0.15 mL), K_3PO_4 (425 mg, 2.0 mmol), $Pd(dba)_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in o-xylene at 130 °C for 4 h.

Dibenzosuberone: This compound was obtained as a yellow oil (197 mg, 95 %) from the reaction of dibenzosuberol (210 mg, 1.0 mmol), chlorobenzene (0.15 mL), K_3PO_4 (425 mg, 2.0 mmol), $Pd(dba)_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in toluene at 105 °C for 48 h.

trans-4-Stilbenecarboxaldehyde: This compound was obtained as an off-white solid (196 mg, 94 %) from the reaction of trans-stilbenemethanol (210 mg, 1.0 mmol), chlorobenzene (0.15 mL, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(dba)_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in toluene at 110 °C for 14 h.

4,4'-Bis(dimethylamino)benzophenone: This compound was obtained as an off-white solid (255 mg, 95 %) from the reaction of 4,4'-Bis(dimethylamino)benzhydrol (270 mg, 1.0 mmol),

chlorobenzene (0.15 mL, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(dba)_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in toluene at 110 °C for 18 h.

Dibenz (C,E) oxepin-5 (7H) -one: This compound was obtained as an off-white solid (202 mg, 96 %) from the reaction of 2,2'-biphenyldimethanol (214 mg, 1.0 mmol), chlorobenzene (0.15 mL), K_2CO_3 (276 mg, 2.0 mmol), $Pd(dba)_2$ (6 mg, 10 mol) and ligand **1** (10 mg, 30 mol) in toluene at 105 °C for 11.5 h.

1,5-Dimethyl-bicyclo-[3,2,1]-octane-8-on: This compound was formed (quantitative yield, calibrated GC) from the reaction of 1,5-dimethyl-bicyclo-[3,2,1]-octane-8-ol (154 mg, 1.0 mmol), chlorobenzene (0.10 mL, 1.0 mmol), NaO^tBu (192 mg, 2.0 mmol), $Pd(dba)_2$ (0.29 mg, 2.0 mol) and ligand **1** (10 mg, 6.0 mol) in toluene at 105 °C for 2 h.

(1S) - (-) -Camphor: This compound was formed (quantitative yield, calibrated GC) from the reaction of [(1S)-endo]-(-)-borneol (171 mg, 1.1 mmol), chlorobenzene (0.11 mL, 1.1 mmol), NaO^tBu (192 mg, 2.0 mmol), $Pd(dba)_2$ (0.29 mg, 2.0 mol) and ligand **1** (10 mg, 6.0 mol) in toluene at 105 °C for 2 h.