Palladium NCN and CNC pincer complexes as exceptionally active catalysts for aerobic oxidation in sustainable media

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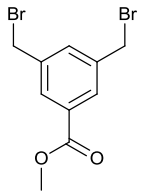
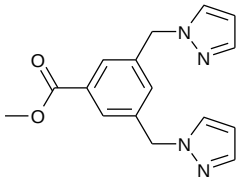
Electronic Supplementary Information

Experimental procedure for the synthesis of pincer 1.



Methyl 3,5-bis(bromomethyl)benzoate.[1] NBS (13 g, 73.08 mmol) was added in four equal portions during 31 h to a solution of methyl 3,5-dimethylbenzoate (1,5 g, 9.13 mmol) in refluxing CCl_4 (55.5 mL), each addition being followed by a few milligrams of benzoyl peroxide. The reaction outcome was monitored by ^{1}H-NMR. Upon completion, the mixture was cooled to room temperature and filtered. The filtrate was washed with a saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was redissolved in anhydrous THF (20 mL), and diethyl phosphate (13.8 mL, 1.07 mmol) and ^{i}Pr$_2$NEt (18.6 mL, 1.07 mmol) were added at 0ºC under Argon. The stirred mixture was allowed to warm to r.t and stirred for 2 d (the reaction was monitored by ^{1}H-NMR), and then poured onto ice/water (1:1) and extracted with Et_2O (4 x 30 mL). The organic layer was washed with 1M HCl (1 x 10 mL) and brine (1 x 10 mL), dried over anhydrous Na_2SO_4, and evaporated in vacuo to give a residue which was purified by flash chromatography on silicagel using Et_2O/Hexane (7:3) as eluent. Methyl 3,5-bis(bromomethyl)benzoate was obtained as a yellow powder (1.46 g, 68%). δ_H (300 MHz, $CDCl_3$): 3.93 (s, 3H), 4.49 (s, 4H), 7.61 (s, 1H), 7.99 (d, 2H, J= 1.6 Hz); δ_C (75 MHz, $CDCl_3$): 31.8 (CH_3); 52.4 (CH_2); 129.9 (C3-C5); 131.4 (C4); 133.8 (C1); 138.9 (C2-C6); 165.9 (C=O)



Methyl 3,5-Bis(pyrazol-1-ylmethyl)benzoate. A mixture of methyl 3,5-bis(bromomethyl)benzoate (600 mg, 1.86 mmol), pyrazole (2.79 mg, 4.09 mmol), and Cs_2CO_3 (2.37 g, 7.27 mmol) was refluxed in dry acetonitrile (45 mL) under argon for 2 h. After cooling, the resultant solution was filtered and water (30 mL) was added. The aqueous layer was extracted with EtOAc (2 x 40 mL). The combined organic extracts were dried with anhydrous Na_2SO_4 and the solvent was removed *in vacuo* to give a

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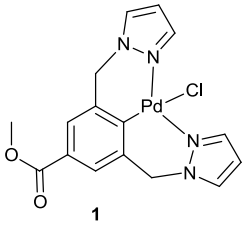
residue which was purified by gradient flash chromatography on silicagel (Hexane:EtOAc 7:3 → EtOAc → EtOAc:MeOH 9.5:0.5). Methyl 3,5-Bis(pyrazol-1-ylmethyl)benzoate was obtained as a white solid (570 mg, 99%). mp 62-63ºC (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 3.86 (3H, s, CH_3), 5.31 (4H, s, CH_2), 6.28 (2H, dd, *J* 2.1, 1.9 Hz, H4'), 7.18 (1H, s, H4), 7.38 (2H, d, *J* 2.1 Hz, H5'), 7.53 (2H, d, *J* 1.9 Hz, H3'), 7.80 (2H, s, H2, H6); ^{13}C NMR (63 MHz, $CDCl_3$) δ_C 52.19 (CH_3), 55.04 (CH_2), 106.17 (C4'), 128.12 (C2, C6), 129.40 (C5'), 130.97 (C4), 131.14 (C3, C5), 137.82 (C1), 139.88 (C3'), 166.14 (CO).



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NCN palladium pincer 1. A mixture of the methyl 3,5-bis(pyrazol-1-ylmethyl)benzoate (300 mg, 1.01 mmol) and palladium(II) acetate (230 mg, 1.01 mmol) was refluxed in glacial acetic acid (5 mL) under argon for 20 h. After cooling, the solvent was removed *in vacuo,* and to the resulting residue excess LiCl (5.5 mmol) and a mixture of acetone/water (3:2, 5 mL) were added. The resulting mixture was stirred at r.t. for 2 days. The reaction outcome was monitored by ^{1}H-NMR. Upon completion, the mixture was filtered to provide a grey solid (400mg, 92%). mp >300ºC (EtOAc); ^{1}H NMR (300 MHz, DMSO) δ_H 3.83 (3H, s, CH_3), 5.55 (4H, s, CH_2), 6.46 (2H, dd, *J* 2.0, 1.6 Hz, H4'), 7.70 (2H, s, H2, H6), 7.92 (2H, d, *J* 1.6 Hz, H5'), 8.14 (2H, d, *J* 2.1 Hz, H3'); ^{13}C NMR (63 MHz, DMSO) δ_C 52.10 (CH_3), 56.72 (CH_2), 106.62 (C4'), 125.91 (C2, C6), 126.40 (C1), 133.08 (C5'), 137.16 (C3, C5), 143.18 (C3'), 150.69 (C4), 166.25 (CO).

Spectroscopic data of known aromatic ketones prepared by aerobic oxidation of benzylic substrates (alcohols and methylene compounds)

Acetophenone[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.61 (3H, s), 7.42-7.63 (3H, m), 7.96 (2H, d, J 8 Hz)

Benzoyl cyanide[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.59 (m, 1H), 8.13 (m, 2H)

9*H*-Fluorenone[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-8.34 (m, 8H)

Benzophenone[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (m, 4H), 7.59 (m, 2H), 7.81 (m, 4H)

Indanone[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.67 (t, 2H, J 7.6 Hz), 3.13 (t, 2H, 7.6 Hz), 7.35 (t, 1H, J 7.6 Hz), 7.46 (d, 1H, J 8 Hz), 7.57 (t, 1H, J 7.6 Hz), 7.74 (d, 1H, J 8 Hz)

2-oxo-2-Phenylacetic acid[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, 2H, J 7.6 Hz), 7.72 (d, 1H, J 7.6 Hz), 7.55 (t, 2H, J 7.8 Hz)

9*H*-Xanthenone[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–8.34 (m, 8H)

3,4-Dihydro-1(2H)-naphthalenone[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.11 (m, 2H), 2.63 (m, 2H), 2.94 (m, 2H), 7.21-8.11 (m, 4H)

1-(*p*-Tolyl)ethanone[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.50 (s, 3H), 6.75 (d, 2H, J 8 Hz), 7.34 (d, 2H, J 8 Hz).

1-Phenyl-1-propanone[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (m, 3H), 2.94 (m, 2H), 7.40-7.51 (m, 3H).

1-(2-Methoxyphenyl)ethanone[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57, (s, 3H), 3.87 (s, 3H), 6.97 (d, 2H, J 8 Hz), 7.93 (d, 2H, J 8 Hz)

2,2-Dimethyl-1-phenylpropanone.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, 2H, J 7.3 Hz), 6.44 (dd, 1H), 7.16 (dd, 1H), 7.43-7.51 (m, 2H), 7.54-7.60 (m, 1H), 7.91-7.98 (m, 2H).

Benzil[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, 4H, J 8 Hz), 7.6-7.68 (m, 2H), 7.5-7.54 (m, 2H).

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Deoxybenzoin[9] ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (s, 2H), 7.24-7.29 (m, 3H), 77.32-7.36 (m, 2H), 7.45-7.49 (m, 2H), 7.55-7.59 (m, 2H), 8.02-8.05 (m, 2H).

2-Methylbenzophenone[10] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.22-7.32 (m, 3H), 7.32-7.41 (m, 2H), 7.56-7.60 (m, 1H), 7.79-7.82 (m, 2H), 7.43-7.47 (m, 2H).

4'-Chloroacetophenone[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.90 (d, 2H, J 8.4 Hz), 7.44 (d, 2H, J 8.4 Hz).

Methyl phenylglyoxylate[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.54-7.50 (m, 2H), 7.69-7.65 (m, 1H), 8.01-8.04 (m, 2H).

Anthraquinone[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (m, 4H), 8.33 (m, 4H)

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