Supporting Information

Ruthenium (II) Catalysed Transfer Hydrogenation of Aromatic and Heteroaromatic Aldehydes in Air

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Experimental procedures, characterization data and copies of ^1H and ^{13}C NMR spectra of selected alcohols

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General Information

Materials and General Procedures

All reactions were performed in Schlenk tubes under air unless otherwise specified. Solvents were commercially available and used as received. *p*-chlorobenzaldehyde, 3-methylthiophene-2-carboxaldehyde, *o*-chlorobenzaldehyde, *p*-nitrobenzaldehyde, *p*-anisaldehyde, 4-methoxynaphthaldehyde, 5-nitro-2-furfural, 5-(3-chlorophenyl)-2-furfuraldehyde, 5-(2-nitrophenyl)-2-furfuraldehyde, benzamide, N-methylbenzamide, acetophenone and 1-heptanal were purchased either from Sigma Aldrich or SD Fine. Infra-red spectra were recorded in a diffused reflection spectroscopy (DRS) assembly on a Shimadzu-8201PC spectrometer with sample prepared in KBr. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 300.13 (¹H), 75.47 MHz (¹³C) with SiMe₄ as internal references and coupling constants were given in Hertz. Mass spectral data were performed on QTOF-XL MS/MS Applied Biosystem mass spectrometer at the CSIR-National Institute of Oceanography, Dona Paula. The precursor complexes [RuCl₂(*p*-cymene)]₂ (**1**) [1], [RuCl(dpNmei)(*p*-cymene)]PF₆ (**2**) [2] (dpNmei = dipyridyl-N-methyl imine), [Ru(OAc)₂(*p*-cymene)] (**3**) [3,4] and [RuCl(KA)(*p*-cymene)] (**4**) [5] (KA= kojic acidate or 5-hydroxy-2-(hydroxymethyl)-4-pyronate), were prepared according to literature procedures.

General procedures for reduction of aldehydes catalysed by [RuCl₂(*p*-cymene)]₂

A dried Schlenk tube was loaded with [RuCl₂(*p*-cymene)]₂ (**1**) (0.0153g, 0.025 mmol, 5 mol%), aldehyde (0.5 mmol), benzamide or N-methyl benzamide (20 mol%). To this reaction mixture was added solvent (2-3 mL). Then the mixture was stirred at 80°C for 8-16 h, after which, the reaction mixture was rotary evaporated. The residue was purified over silica gel column using petroleum ether and ethyl acetate as eluant to give the compounds (**5a-5j**) in up to 80% isolated yield.

Representative procedure for reduction of aldehydes to alcohol using Ruthenium complexes (3 & 4)

A dried Schlenk tube was loaded with complex **3** or **4** (0.025 mmol, 5 mol%), *p*-nitro benzaldehyde aldehyde (0.5 mmol). To this reaction mixture was added 2-propanol (2-3 ml). Then the mixture was stirred at 80°C for 6 h. After which the reaction mixture was rotary evaporated and the residue was purified over silica gel column using petroleum ether and ethyl acetate as eluant to give the compounds **5a-5j** in up to 84% isolated yield.

Characterization data of alcohols (¹H, ¹³C & HRMS)

p-Nitrobenzylalcohol (**5a**)

Light yellow solid (0.064g 84%); FTIR (KBr, cm⁻¹): 3523, 3113, 1602, 1526, 1056, 736; ¹H NMR (CDCl₃, 300 MHz): δ 8.23 (d, 2H, *J* = 8.7), 7.54 (d, 2H, *J* = 8.7), 4.84 (s, 2H); ¹³C NMR (CDCl₃, 75.47 MHz): δ 148.08, 126.99, 123.73, 64.02; HRMS (ESI): Calculated for C₇H₇NO₃Na 176.0324 [M+Na]⁺; found: 176.0339.

p-Chlorobenzylalcohol (**5b**) [6]

White solid (0.057g, 81%); FTIR (KBr, cm⁻¹): 3332, 2922, 2852, 1597, 1450, 798; ¹H NMR (CDCl₃, 300 MHz): δ 8.05 (d, 1H, *J* = 8.1), 7.46 (d, 1H, *J* = 8.1), 7.33- 7.29 (m, 2H), 4.68 (s, 2H); ¹³C NMR (CDCl₃, 75.47 MHz): δ 139.24, 133.39, 131.56, 128.89, 128.67, 128.25, 64.57; HRMS (ESI): Calculated for C₇H₇ClONa: [M+Na]⁺ 165.0083; found: 165.0109.

***o*-Chlorobenzylalcohol (5c)** [6]

White solid (0.059 g, 85%); FTIR (KBr, cm^{-1}): 3300, 2916, 2864, 1571, 1062, 750; ^1H NMR (CDCl_3 , 300 MHz): δ 7.49 (s, 1H, $J = 7.2$), 7.38 (d, 1H, $J = 7.2$), 7.30-7.28 (m, 1H), 7.26-7.25 (m, 1H), 4.80 (d, 2H, $J = 5.7$); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 138.16, 132.75, 129.36, 128.85, 128.77, 127.02, 62.91; HRMS (ESI): Calculated for $\text{C}_7\text{H}_7\text{ClONa}$ $[\text{M}+\text{Na}]^+$ 165.0083; found: 165.0098.

***p*-Methoxybenzylalcohol (5d)**

Yellow liquid (0.055g, 80%); FTIR (KBr, cm^{-1}): 3356, 2935, 2835, 1612, 1508, 1033, 817; ^1H NMR (CDCl_3 , 300 MHz): δ 7.30 (d, 2H, $J = 8.1$), 6.90 (d, 2H, $J = 8.1$), 4.62 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 159.22, 133.13, 128.63, 113.96, 65.02, 55.29; HRMS (ESI): Calculated for $\text{C}_8\text{H}_{10}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 161.0578; found: 161.0532.

4-Methoxy(naphthalen-1-yl) methanol (5e)

Yellow oil (0.085g, 91%); FTIR (KBr, cm^{-1}): 3381, 3300, 2935, 1583, 1512; ^1H NMR (CDCl_3 , 300 MHz): δ 8.32 (d, 1H, $J = 8.4$), 8.13 (d, 1H, $J = 8.1$), 7.59-7.52 (m, 2H), 7.42 (d,

1H, $J = 7.8$), 6.78 (d, 1H, $J = 7.8$), 5.08 (s, 2H), 4.02 (s, 3H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 155.80, 132.34, 128.49, 126.92, 126.25, 125.26, 123.64, 122.59, 102.90, 63.80, 55.52; HRMS(ESI): Calculated for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 211.0735; found: 211.0754.

(5-nitrofuran-2-yl)methanol (**5f**)

White solid (0.042g, 59%); FTIR (KBr, cm^{-1}): 3163, 3122, 2985, 1716, 1529, 769; ^1H NMR (CDCl_3 , 300 MHz): δ 7.29 (d, 1H, $J = 9.6$), 6.57 (s, 1H), 4.73 (s, 2H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 157.38, 112.36, 110.57, 57.42; HRMS(ESI): Calculated for $\text{C}_5\text{H}_6\text{NO}_4$ $[\text{M}+\text{H}]^+$ 144.0297; found: 144.0322.

(5-nitrothiophen-2-yl)methanol (**5g**)

Brown liquid (0.04g, 50%); FTIR (KBr, cm^{-1}): 3361, 2924, 2852, 1610, 1500, 1280, 815; ^1H NMR (CDCl_3 , 300 MHz): δ 7.83 (d, 1H, $J = 4.2$), 6.95 (d, 1H, $J = 4.2$), 4.89 (s, 2H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 153.16, 128.65, 123.39, 60.29; HRMS (ESI): Calculated for $\text{C}_5\text{H}_5\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 181.9888; found: 181.9944.

(5-methylthiophen-2-yl)methanol (**5h**)

Colourless liquid (0.031g, 49%); FTIR (KBr, cm^{-1}): 3396, 2960, 2920, 1467, 1261, 800; ^1H NMR (CDCl_3 , 300 MHz): δ 7.18 (d, 1H, $J = 4.8$), 6.85 (d, 1H, $J = 4.8$), 4.77 (s, 2H), 2.26 (s,

3H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 136.55, 134.99, 130.30, 123.74, 57.86, 13.48;

HRMS: Calculated for $\text{C}_6\text{H}_8\text{OSNa}$ $[\text{M}+\text{Na}]^+$ 151.0194; found: 151.0427.

(5-(2-nitrophenyl)furfuran-2-yl)methanol (**5i**)

Brown oil (0.091g, 83%); FTIR (KBr, cm^{-1}): 3365, 2926, 2864, 1546, 1359, 748; ^1H NMR (CDCl_3 , 300 MHz): δ 7.71 (t, 2H, $J = 8.1$), 7.59 (t, 1H, $J = 7.5$), 7.42 (t, 1H, $J = 7.8$), 6.63 (d, 1H, $J = 3.3$), 6.42 (d, 1H, $J = 3$), 4.64 (s, 2H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 155.50, 148.18, 131.89, 128.88, 128.32, 124.04, 123.89, 110.51, 109.91, 57.44; HRMS (ESI): Calculated for $\text{C}_{11}\text{H}_9\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 242.0429; found: 242.0327.

(5-(3-chlorophenyl)furfuran-2-yl)methanol (**5j**)

Brown solid (0.091g, 88%); FTIR (KBr, cm^{-1}): 3275, 2958, 2941, 1687, 1591, 684; ^1H NMR (CDCl_3 , 300 MHz): δ 7.65-7.64 (m, 1H), 7.52 (d, 1H, $J = 7.8$), 7.29-7.23 (m, 2H), 6.62 (d, 1H, $J = 3.3$), 6.38 (d, 1H, $J = 3$), 4.60 (s, 2H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 154.15, 152.48, 134.70, 132.28, 129.95, 127.33, 123.76, 121.81, 110.05, 106.81, 57.53; HRMS (ESI): Calculated for $\text{C}_{11}\text{H}_9\text{ClO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 231.0189; found: 231.0150.

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¹H and ¹³C NMR spectra of alcohols