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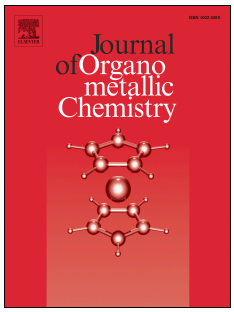

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Tuning acylthiourea ligands in Ru(II) catalysts for altering the reactivity and chemoselectivity of transfer hydrogenation reactions, and synthesis of 3-isopropoxy-1H-indole through a new synthetic approach

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Abstract

Ru(II)-*p*-cymene complexes (**1-3**) containing picolyl based pseudo-acylthiourea ligands (L_1-L_3) were synthesized and characterized. The crystallographic study confirmed the molecular structures of all the ligands (L_1-L_3) and complex **3.** The catalytic activity of the complexes was tested mainly towards TH of carbonyl compounds and nitroarenes. The influence of steric and electronic effects of the ligands on the chemoselectivity and reactivity were reported. The catalytic activity was enhanced and chemoselectivity was switched after tuning the ligands in the catalysts, compared to their corresponding unmodified Ru(II)-*p*-cymene complexes. The catalysis was extended to a broad range of substrates including some challenging systems like furfural, benzoylpyridine, benzoquinone, chromanone, etc. The strategy of tuning the bifunctional ligands in the catalysts for effective and selective catalysis worked nicely. Further, the catalysis was extended to one pot synthesis of 3-isopropoxyindole from 2-nitrocinnamaldehyde, the first synthetic route similar to Baeyer Emmerling indole synthesis. All the catalytic experiments exhibited high conversion and selectivity.

Keywords: Ruthenium-arene; Pseudo-acylthiourea ligands; Transfer hydrogenation; Chemoselectivity; Indole

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1. Introduction

Hydrogenation is the key step in many organic transformations. Many chemoselective homogeneous catalysts were reported for hydrogenation reactions so far.[1-4] Transfer hydrogenation (TH) reactions are preferred over hydrogenation using H_2 gas due to their mild and sustainable reaction conditions. Notably, TH reactions gained prominence after the milestone discovery of bifunctional catalysts by Noyori and his co-workers. They explained the importance of N–H moiety for the bifunctional mechanism which enhances the rate of the TH reactions. This metal-ligand cooperation effect (N–H effect) led to the discovery of many bifunctional catalysts for the effective catalytic TH reactions. However, there is an ongoing search for a universal catalyst which can comply the needs of TH reactions like phosphine free, inexpensive, active with cheaper hydrogen donors, chemoselective and compatible with a broad range of substrates.[5-7] Chemoselective reactions have inherent advantage as they facilitate single step reactions by avoiding protection and deprotection steps. The controlled chemoselectivity is achieved mostly in homogeneous catalysis due to the extraordinary variability in the structure of molecular catalysts. The change in bulkiness, chirality, coordination mode and electronic property of the ligands on the metal center of the catalysts will influence their reactivity, stereoselectivity, regioselectivity and chemoselectivity. Hence, ligands play an important role in tuning the behavior of the catalysts.[1,8–18] In some cases, even pH of the reaction medium influences the chemoselectivity.[19] Sommer *et al*. reported the influence of coordination mode of azocarboxamide ligands in Ru(II)-arene complexes on base-free TH catalysis.[20] Recently, Malan *et al*. reported picolyl based Ru(II)-NHC complexes as catalysts for TH of ketones and oxidation of alcohols.[21] Hintermair *et al*. reported the influence of ancillary ligands in Ir(III)-Cp* catalyst towards TH reaction using 2-propanol as hydrogen source and KOH as base.[22] Although the literature seems to offer a variety of tuned catalysts, scope of the substrates and chemoselectivity aspect remain limited.

Ruthenium-arene based catalysts with potential ligands are well known for TH reactions.[4-5,23] Acylthiourea ligands are one such ligands with a variety of coordination modes and having a huge space for tuning the electronic environment, which pave the way for the control of stereoselectivity, chemoselectivity and reactivity.[24–27] Picolylamine based compounds are also potential ligands for TH of carbonyl compounds.[28,29] Our group has previously reported various chiral acylthiourea based Ru(II)-arene complexes as bifunctional catalysts for asymmetric TH reactions. These ligands are bound to the ruthenium center *via* monodentate neutral sulphur coordination. Generally, high conversions and

excellent enantioselectivities were achieved, and mechanism was similar to Noyori's bifunctional outer sphere mechanism.[24,30–32] We have also reported Ru(II)-*p*-cymene catalysts containing picolyl based acylthiourea ligands for the TH of nitroarenes and carbonyl compounds, wherein the chemoselectivity was observed towards nitroarenes.[33] Srinivas *et al*. reported thiopseudourea (modified acylthiourea) based Pd(II) complexes as versatile and efficient catalysts for C–C coupling reactions.[34] Herein we report the change in chemoselectivity of TH by tuning the bulkiness and coordination mode of acylthiourea based ligands present in the Ru(II)-*p*-cymene complexes. Scope of the substrates was broadly explored. Some challenging substrates like furfural, benzoyl pyridine, benzoquinone and chromanone were successfully tested.

One pot synthesis of biologically active heterocyclic motifs like indoles, quinolines etc. *via* TH followed by cyclization is an important area of research. Achieving this through hydrogen borrowing strategy is an active field of current research.[35,36] Interestingly, we have devised a novel one pot method for the synthesis of 3-isopropoxy-1H-indole from 2-nitrocinnamaldehyde.

2. Experimental section

2.1 Synthesis of the ligands (L_1-L_3)

The pyridine based acylthiourea precursors were prepared by following our previously reported procedure. Benzyl bromide (1.5 mmol) was added to the solution of acylthiourea (1 mmol) and sodium hydride (3 mmol) in dry THF (20 mL). After stirring the reaction mixture under inert atmosphere for 5 h at 0 °C, it was neutralized with 10 % aqueous ammonium chloride solution. Then, THF was removed using rotary evaporator, and product was extracted with ethyl acetate, dried over anhydrous sodium sulphate and crystallized.[34]

Benzyl -N'-thiophene-2-carbonyl-N-(pyridin-2-ylmethyl)carbamimidothioate (L_1)

Yield: 353.3 mg, 96 %, m.p.: 114 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 11.60 (s, 1H), 8.62 (d, J = 4.0 Hz, 1H), 7.86 (d, J = 3.3 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.48 (d, J = 4.9 Hz, 1H), 7.44 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.28-7.24 (m, 2H), 7.23-7.20 (m, 1H), 7.09 (t, J = 4.3 Hz, 1H), 4.68 (d, J = 5.0 Hz, 2H), 4.59 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 172.59, 171.20, 154.75, 149.69, 143.69, 136.93, 131.58, 129.14, 128.71, 127.87, 127.56, 122.72, 121.30, 48.84, 35.49. FT-IR (KBr, cm^{-1}) 3181 (m; ν(thiourea N–H)), 1590 (m; ν(C=O)), 1545 (m; ν(pyridine C=N)), 1509 (m; ν(amidic C=N)), 707 (s, ν(C–S)).

UV-Vis (methanol, nm): λ 204, 263, 303. ESI-MS (m/z): found 368.08795 $[M+H]^+$ (calcd. 368.08310).

Benzyl N'-furan-2-carbonyl-N-(pyridin-2-ylmethyl)carbamimidothioate (L_2)

Yield: 306.3 mg, 87 %, m.p.: 92 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 11.58 (s, 1H), 8.60 (d, J = 3.8 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.57 (s, 1H), 7.43 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.26 (t, J = 5.7 Hz, 2H), 7.23-7.19 (m, 2H), 6.48 (s, 1H), 4.69 (d, J = 3.6 Hz, 2H), 4.56 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 172.98, 167.59, 154.75, 151.88, 149.58, 145.66, 137.09, 136.90, 129.09, 128.68, 127.54, 122.69, 121.21, 116.48, 111.73, 48.80, 35.49. FT-IR (KBr, cm^{-1}): 3158 (m; ν(thiourea N–H)), 1592 (m; ν(C=O)), 1573 (m; ν(pyridine C=N)), 1533 (s; ν(amidic C=N)), 707 (s; ν(C–S)). UV-Vis (methanol, nm): λ 203, 263, 303. ESI-MS (m/z): found 351.11284 $[M+H]^+$ (calcd. 351.11197).

Benzyl N'-benzoyl-N-(pyridin-2-ylmethyl)carbamimidothioate (L_3)

Yield: 315.1 mg, 87 % , m.p.: 126 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 11.90 (s, 1H), 8.63 (d, J = 2.6 Hz, 1H), 8.30 (d, J = 7.3 Hz, 2H), 7.67 (td, J = 7.7, 1.5 Hz, 1H), 7.49 (dd, J = 10.4, 4.2 Hz, 1H), 7.42 (dd, J = 13.4, 7.0 Hz, 4H), 7.31 (t, J = 7.3 Hz, 2H), 7.29-7.24 (m, 2H), 7.24-7.19 (m, 1H), 4.71 (d, J = 2.8 Hz, 2H), 4.64 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 176.22, 173.06, 154.90, 149.71, 137.79, 136.97, 131.76, 129.68, 129.11, 128.76, 128.06, 127.61, 122.74, 121.36, 48.88, 35.61. FT-IR (KBr, cm^{-1}): 3151 (m; ν(thiourea N–H)), 1603 (m; ν(C=O)), 1568 (m; ν(pyridine C=N)), 1532 (s; ν(amidic C=N)), 705 (s; ν(C–S)). UV-Vis (methanol, nm): λ 205, 263, 301. ESI-MS (m/z): found 362.13271 $[M+H]^+$ (calcd. 362.13234).

2.2 Synthesis of the complexes

A mixture of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (0.5 mmol) and the ligand (L_1-L_3) (1 mmol) in toluene (20 mL) was stirred at room temperature for about 4-5 h. The completion of the reaction was verified by TLC. The product was precipitated by adding hexane, which was filtered, washed and dried in *vacuum*. It was then crystallized from its chloroform-acetonitrile solution.

*[RuCl(η^6-p-cymene)L_1]Cl (**1**)*

Yield: 529.6 mg, 83 % , m.p.: 178 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 12.13 (s, 1H), 8.99 (d, J = 5.1 Hz, 1H), 8.50 (s, 1H), 8.08 (d, J = 3.7 Hz, 1H), 7.97 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 6.6 Hz, 2H), 7.36 (dd, J = 15.9, 7.8 Hz, 6H), 5.70 (d, J = 5.7 Hz, 1H), 5.65-5.57 (m,

2H), 5.51 (d, *J* = 5.6 Hz, 1H), 5.11 (d, *J* = 19.5 Hz, 1H), 4.91 (d, *J* = 19.5 Hz, 1H), 4.40 (q, *J* = 13.3 Hz, 2H), 2.73 (dt, *J* = 13.3, 6.5 Hz, 1H), 2.15 (s, 3H), 1.15 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, ppm): δ 167.89, 159.90, 159.23, 155.06, 139.68, 137.48, 137.18, 135.13, 133.07, 129.53, 129.43, 129.22, 128.24, 125.50, 121.67, 106.42, 101.57, 85.98, 85.37, 85.02, 84.41, 64.26, 39.17, 30.88, 22.39, 22.36, 18.64. FT-IR (KBr, cm^{-1}): 3420 (b; ν(thiourea N–H)), 1648 (s; ν(C=O)), 1521 (m; ν(pyridine C=N)), 1607 (m; ν(thioamidic C=N)), 732 (s; ν(C–S)). UV-Vis (methanol, nm): λ 207, 252, 296, 417. ESI-MS (m/z): found 638.06344 $[RuCl(\eta^6\text{-}p\text{-cymene})L_1]^+$ (calcd. 638.06406).

*[RuCl(η^6-p-cymene)L_2]Cl (**2**)*

Yield: 547.4 mg, 88 % , m.p.: 154 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): *δ* 12.01 (s, 1H), 8.98 (d, *J* = 5.3 Hz, 1H), 8.08 (s, 1H), 7.96 (t, *J* = 7.6 Hz, 1H), 7.80 (s, 1H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.37 (s, 4H), 7.31 (d, *J* = 5.4 Hz, 1H), 6.81 (s, 1H), 5.68 (d, *J* = 5.5 Hz, 1H), 5.60 (d, *J* = 5.9 Hz, 1H), 5.56 (d, *J* = 5.8 Hz, 1H), 5.48 (d, *J* = 5.4 Hz, 1H), 5.04 (d, *J* = 19.4 Hz, 1H), 4.88 (d, *J* = 19.6 Hz, 1H), 4.39 (d, *J* = 13.3 Hz, 1H), 4.32 (d, *J* = 13.3 Hz, 1H), 2.73 (dt, *J* = 13.5, 6.7 Hz, 1H), 2.15 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J*= 6.9 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, ppm): δ 159.89, 155.00, 139.62, 129.58, 129.42, 129.34, 128.13, 125.42, 121.49, 113.05, 106.15, 101.66, 85.71, 85.33, 84.86, 84.53, 64.14, 38.98, 30.77, 22.40, 22.20, 18.58. FT-IR (KBr, cm^{-1}): 3424 (b; ν(thiourea N–H)), 1685 (s; ν(C=O)), 1556 (m; ν(pyridine C=N)), 1608 (m; ν(thioamidic C=N)), 711 (m; ν(C–S)). UV-Vis (methanol, nm): λ 203, 273, 294, 415. ESI-MS (m/z): found 622.08642 $[RuCl(\eta^6\text{-}p\text{-cymene})L_2]^+$ (calcd. 622.08690).

*[RuCl(η^6-p-cymene)L_3]Cl (**3**)*

Yield: 531.02 mg, 84 % , m.p.: 172 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): *δ* 11.91 (s, 1H), 8.99 (d, *J* = 5.4 Hz, 1H), 8.16 (d, *J* = 7.5 Hz, 2H), 7.98 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.3 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.39 (q, *J* = 7.3 Hz, 4H), 7.34 (d, *J* = 6.8 Hz, 1H), 5.71 (d, *J* = 5.8 Hz, 1H), 5.64-5.59 (m, 2H), 5.52 (d, *J* = 5.8 Hz, 1H), 5.13 (d, *J* = 19.5 Hz, 1H), 4.87 (d, *J* = 19.5 Hz, 1H), 4.36 (dd, *J* = 28.1, 13.3 Hz, 2H), 2.81-2.71 (m, 1H), 2.17 (s, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, ppm): *δ* 168.65, 165.13, 159.89, 155.03, 139.60, 137.46, 133.63, 132.15, 129.52, 129.37, 129.08, 128.17, 125.45, 121.64, 106.47, 101.42, 85.98, 85.48, 84.97, 84.22, 64.11, 38.99, 30.83, 22.35, 22.29, 18.58. FT-IR (KBr, cm^{-1}): 3484 (m; ν(thiourea N–H)), 1670 (s; ν(C=O)), 1563 (s; ν(pyridine C=N)), 1610 (m; ν(thioamidic C=N)), 707 (s; ν(C–S)).

UV-Vis (methanol, nm): λ 205, 257, 292, 416. ESI-MS (m/z): found 632.10806 [(RuClη^6-*p*-cymene)L_3]$^+$ (calcd. 632.10734).

2.3 Procedure for catalytic TH of nitroarenes and carbonyl compounds

Substrate (1 mmol) was added to 2-propanol (4 mL) solution of the catalyst (0.1 mol %) and KOH (1 mmol), and refluxed at 85 °C. The completion of the reaction was checked by TLC. Then, the reaction mixture was cooled to room temperature, eluted through short silica gel or alumina bed using 50 % hexane-ethyl acetate mixture and analyzed by GC or GC-MS. The products were isolated from the most of the reactions and confirmed by their ^{1}H NMR spectra.

2.4 Synthesis of 3-isopropoxy-1H-indole

When 2-nitrocinnamaldehyde (1 mmol) was used as a substrate in the above process, 3-isopropoxy-1H-indole was obtained. The product (yield 62 %) was isolated by column chromatography using 10 % hexane-ethyl acetate mixture as an eluent.

2.5 ^{1}H NMR data of TH products

*1-phenylethanol (**1a**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.20 (d, *J* = 4.1 Hz, 1H), 4.79-4.71 (m, 1H), 1.35 (d, *J* = 6.5 Hz, 3H).

*4'-chloro 1-phenylethanol (**1b**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.34 (d, *J* = 1.0 Hz, 4H), 5.23 (d, *J* = 4.0 Hz, 1H), 4.75-4.69 (m, 1H), 1.30 (d, *J* = 6.5 Hz, 3H).

*Diphenylmethanol (**1c**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.38 (d, *J* = 7.5 Hz, 4H), 7.30 (t, *J* = 7.5 Hz, 4H), 7.21 (t, *J* = 7.2 Hz, 2H), 5.88 (d, *J* = 3.8 Hz, 1H), 5.71 (d, *J* = 3.0 Hz, 1H).

*1-(p-tolyl)ethanol (**1e**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.21 (d, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 2H), 5.03 (d, *J* = 3.1 Hz, 1H), 4.66 (s, 1H), 2.26 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 3H).

*Cyclohexanol (**1g**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 4.42 (d, *J* = 4.2 Hz, 1H), 3.44-3.35 (m, 1H), 1.78-1.70 (m, 2H), 1.65 (dd, *J* = 9.0, 3.6 Hz, 2H), 1.51-1.43 (m, 1H), 1.25-1.08 (m, 5H).

*2-adamantanol (**1h**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 4.56 (d, J = 2.8 Hz, 1H), 3.71 (s, 1H), 2.12 (d, J = 11.9 Hz, 2H), 1.84-1.75 (m, 6H), 1.69 (d, J = 14.1 Hz, 4H), 1.43 (d, J = 11.9 Hz, 2H).

*Phenyl(pyridin-2-yl)methanol (**1j**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 8.42 (d, J = 4.1 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 7.7 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 6.6 Hz, 2H), 6.08 (d, J = 4.0 Hz, 1H), 5.72 (d, J = 7.2 Hz, 1H).

*Benzylalcohol (**2a**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.33 (d, J = 4.0 Hz, 4H), 7.22 (dd, J = 15.9, 12.1 Hz, 1H), 5.17 (t, J = 5.6 Hz, 1H), 4.51 (d, J = 5.6 Hz, 2H).

*4-methyl benzylalcohol (**2c**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.18 (d, J = 7.7 Hz, 2H), 7.10 (d, J = 7.7 Hz, 2H), 5.09 (s, 1H), 4.44 (s, 2H), 2.25 (s, 3H).

*4-methoxy benzylalcohol (**2d**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.16 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 4.97 (s, 1H), 4.35 (s, 2H), 3.66 (s, 3H).

*Furfuyl alcohol (**2f**) – Gram scale synthesis*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.57 (dd, J = 1.8, 0.9 Hz, 1H), 6.40 (dd, J = 3.2, 1.8 Hz, 1H), 6.30 (dd, J = 3.2, 0.7 Hz, 1H), 4.43 (s, 2H).

*Aniline (**3a**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.04 (t, J = 7.7 Hz, 2H), 6.60 (d, J = 8.3 Hz, 2H), 6.53 (t, J = 7.2 Hz, 1H), 4.99 (s, 2H).

*3-nitroaniline (**3f**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.39 (d, J = 1.7 Hz, 1H), 7.31 (dd, J = 8.1, 1.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 6.99-6.92 (m, 1H), 5.81 (s, 2H).

*4-amino acetophenone (**3i**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.67 (d, J = 8.7 Hz, 2H), 6.57 (d, J = 8.7 Hz, 2H), 6.02 (s, 2H), 2.39 (s, 3H).

*Benzamide (**5a**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.91 (s, 1H), 7.81 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.30 (s, 1H).

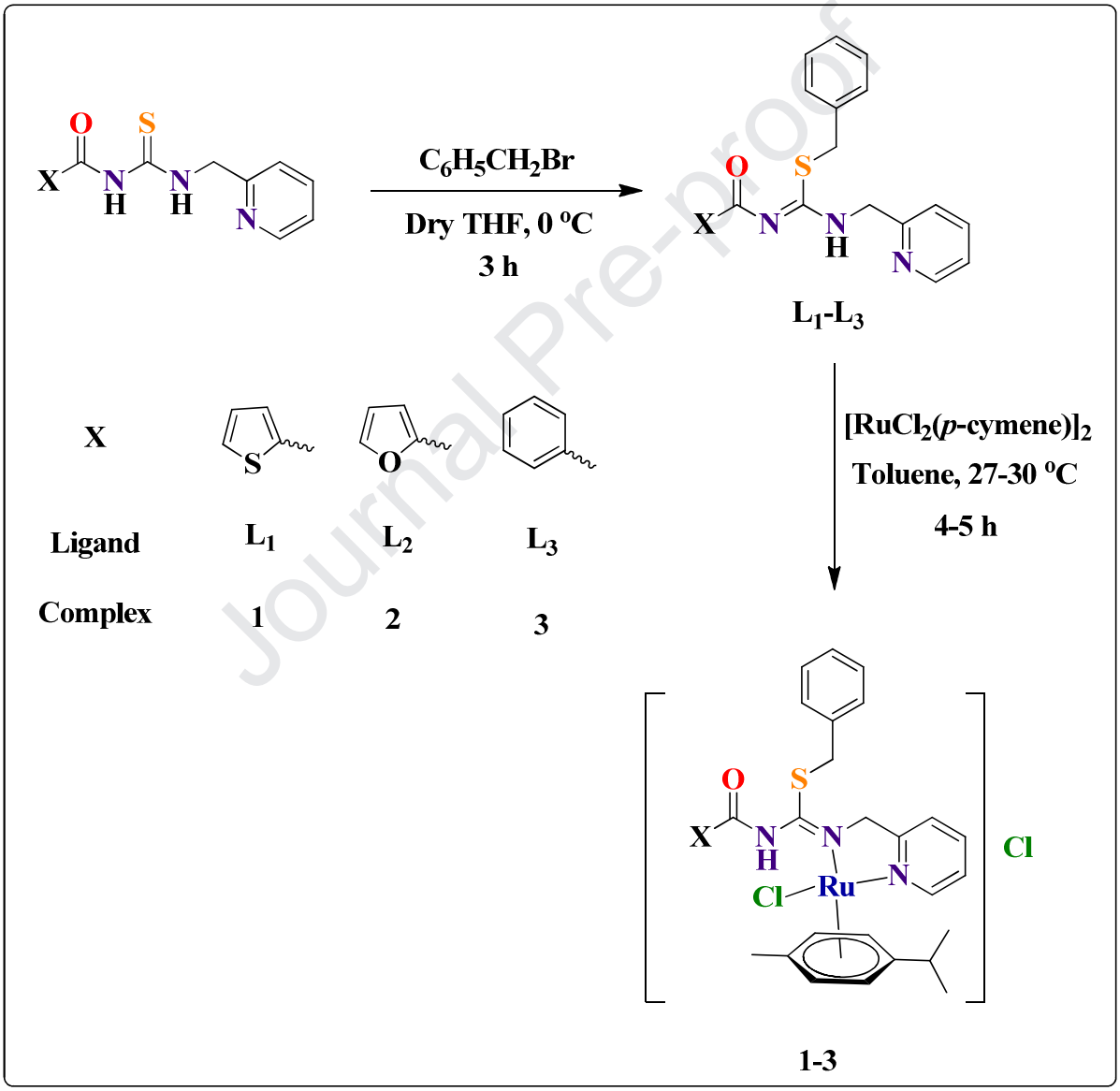
*4-chlorobenzamide (**5b**)*: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.87 (s, 1H), 7.58 (s, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.42 (ddd, J = 24.1, 11.1, 4.3 Hz, 3H).

3-isopropoxy-1H-indole: ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 10.49 (s, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.4 Hz, 2H), 4.46-4.32 (m, 1H), 1.37 (d, J = 6.1 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6, ppm): δ 137.92, 134.26, 121.82, 120.63, 118.26, 117.66, 111.96, 109.29, 73.40, 22.61.

3. Results and discussion

3.1 Synthesis of the ligands and complexes

The pyridine based acylthiourea precursors were synthesized as per our own literature.[32] The ligands (L_1-L_3) were synthesized by reacting the corresponding precursors with benzyl bromide and sodium hydride in dry THF at 0 °C. The complexes [RuCl(η^6-*p*-cymene)L]Cl were prepared from the reactions between [$RuCl_2$(η^6-*p*-cymene)]$_2$ and L in toluene (**Scheme 1**). All the ligands and complexes were stable in air and soluble in CH_3CN, $CHCl_3$, CH_3OH, CH_2Cl_2, C_2H_5OH, DMSO, DMF and DMAc.



Scheme 1 Synthesis of the pseudo-acylthiourea ligands and their Ru(II) complexes

3.2 Characterization of the ligands and complexes

Electronic spectra of the ligands (L_1-L_3) and their complexes (**1-3**) showed intense absorption bands in the ranges 252-273 and 292-303 nm, corresponding to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions respectively. The forbidden d→d transition was observed only at higher concentration in the range 415-420 nm. FT-IR spectra of the complexes were compared with those of the free ligands. The carbonyl stretching frequency (1590-1603 cm^{-1}) of the free ligands increased to 1648-1685 cm^{-1} upon complexation. This was due to the disappearance of intramolecular hydrogen bonding between thioamidic N–H and carbonyl oxygen during complex formation, which was also confirmed by the increase in the stretching frequency of N–H on complexation from 3151-3181 to 3420-3484 cm^{-1}. This was owing to the amine-imine tautomerism followed by hydrogen bonding with ionic chlorine present in the complexes. Further, increase in the stretching frequency of imine from 1509-1533 to 1607-1610 cm^{-1} was observed on complexation. This explains the shift of hydrogen atom from thioamidic N to amidic N, and imine from amidic to thioamidic position. The decrease in pyridyl C=N stretching frequency indicated that the nitrogen in the pyridine ring coordinated to Ru ion. These facts from the FT-IR analyses illustrated the complex formation.

^1H and ^{13}C NMR spectra of the ligands and complexes are shown in **Figs. S1**-**S12**. In **t**he ^1H NMR spectra of the ligands, the most deshielded singlet in the range 11.58-11.90 ppm corresponded to N–H proton. The most shielded singlet in the range 4.56-4.64 ppm corresponded to benzyl CH_2 protons. A doublet in the range 4.68-4.71 ppm corresponded to pyridyl CH_2 protons. All other aromatic protons were observed in the region 7.09-8.63 ppm. In the spectra of the complexes, a signal due to thioamidic NH disappeared and newly formed amidic NH was observed in the range 11.91-12.13 ppm. This confirmed the resonance of proton between amidic and thioamidic nitrogen. A doublet observed for two equivalent pyridyl CH_2 protons in the spectra of the ligands would become two distinct doublets (4.87-4.91 and 5.04-5.13 ppm) in the spectra of the complexes. This may be due to the bidentate coordination of the ligands to Ru ion through thioamidic imine nitrogen and pyridine nitrogen. No significant change was observed in the signals due to aromatic protons on complexation. Generally, isopropyl methyl protons present in the *p*-cymene ring are equivalent and would give a doublet (6 protons) when Ru-*p*-cymene complexes contain monodentate acylthiourea ligand. But in the present case, two doublets were seen at 1.07-1.16 ppm. These protons become inequivalent due to the bidentate coordination of the modified ligands. Here, one methyl is nearby the coordinated pyridine N and other methyl is away from it. Further, 2D ^1H-^1H COSY NMR spectrum (**Fig. S13**) revealed the interaction between

protons of one methyl group and neighboring CH proton, which also made them inequivalent. In addition, aromatic protons of *p*-cymene ring were observed at 5.48-5.71 ppm as doublets. The protons of methyl group directly attached to *p*-cymene ring showed a singlet at 2.15-2.17 ppm. The multiplet at 2.71-2.73 ppm was due to isopropyl CH proton in the *p*-cymene ring.

In the ^{13}C NMR spectra of the ligands, a peak in the range 172.59-176.22 ppm corresponded to carbonyl carbon and a peak in the range 167.59-173.06 ppm corresponded to imine carbon. The peaks in the ranges 35.49-35.61 and 48.80-48.88 ppm corresponded to benzyl and pyridyl CH_2 carbons respectively. The aromatic carbons showed peaks in the range 111.73-154.75 ppm. In the spectra of the complexes, amidic imine carbon signal disappeared and newly formed thioamidic imine carbon was observed in the range 155.00-165.13 ppm. Due to the absence of neighbouring imine group, carbonyl carbon was shielded (159.89-168.65 ppm) in the complexes. The signals at 38.98-39.13 and 64.11-64.26 ppm corresponded to benzyl and pyridyl CH_2 carbons respectively. The significant increase in the chemical shift of pyridyl CH_2 carbon was due to the coordination of pyridine N and thioimidic N. The most shielded peaks corresponded to aliphatic carbons in the *p*-cymene ring. The aromatic carbons in the *p*-cymene ring were observed in the ranges 84.22-85.98 and 101.42-106.47 ppm. All other aromatic carbons of the complexes were detected in the range 113.05-159.89 ppm. Through ^{1}H and ^{13}C NMR studies, formation of the pseudo-acylthiourea based Ru(II)-*p*-cymene complexes was confirmed, in which the ligand was coordinated to Ru(II) ion *via* neutral bidentate fashion.

The calculated $[M+H]^+$ mass of ligands L_1, L_2 and L_3 (368.08310, 351.11197 and 363.13271) was exactly matching with the found mass (368.08795, 351.11284 and 363.13234) (**Figs. S14**-**S16**). Similarly, the calculated mass of the complexes (**1**-**3**), $[(\eta^6$-*p*-cymene)RuLCl$]^+$ (638.06406, 622.08690 and 632.10764**)** was accurately matching with the found mass (638.06344, 622.08642 and 632.10806) (**Figs. S17**-**S19**).

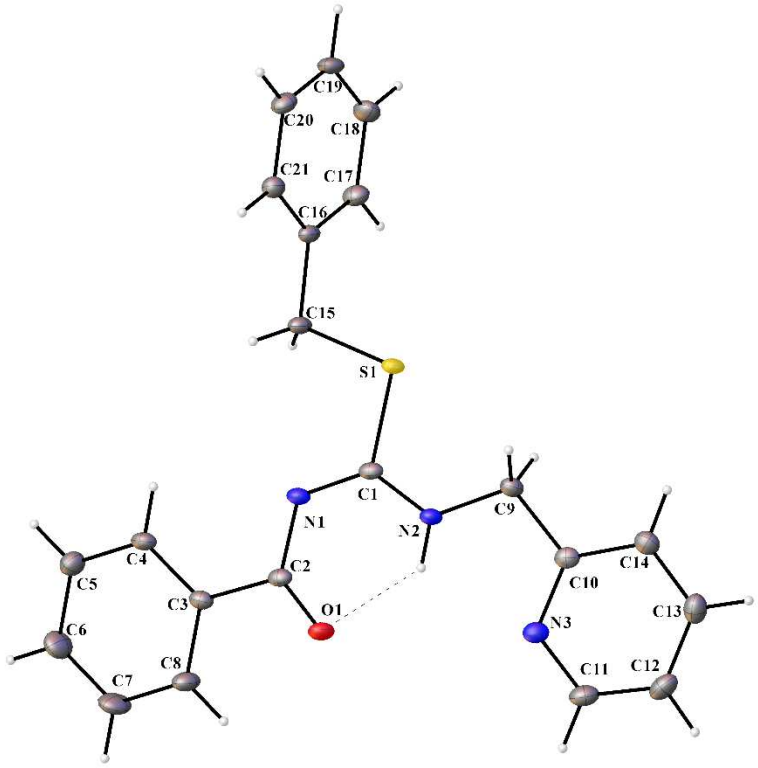


Fig. 1 Molecular structure of L_3 [Important bond lengths (Å) and angles (°): S(1)–C(1) 1.7558(14), N(2)–C(1) 1.3255(16), N(2)–H(2) 0.88, N(2)–C(9) 1.4481(17), N(1)–C(2) 1.3699(16), N(1)–C(1) 1.3226(17), O(1)–C(2) 1.2369(15), C(9)–C(10) 1.5091(18), N(3)–C(10) 1.3297(17), O(1)–C(2)–N(1) 127.08(11), C(2)–N(1)–C(1) 118.81(11), N(2)–C(1)–N(1) 126.77(11), N(1)–C(1)–S(1) 118.42(10), N(2)–C(1)–S(1) 114.81(10), N(2)–C(9)–C(10) 110.24(10), N(3)–C(10)–C(9) 117.21(11)]. CCDC No. 1869570.

Molecular structures of the ligands (L_1-L_3) and complex **3** were confirmed by single crystal XRD (**Figs. S20**, **S21**, **1** and **2**). The ligand crystals were grown from the respective saturated ethyl acetate solution by slow evaporation technique. Ligand L_1 cystallized in monoclinic fashion with space group $P12_1/n1$ whereas ligands L_2 and L_3 crystallized in triclinic fashion with space group P-1. Complex **3** crystallized in monoclinic system with space group $P12_1/n1$. Crystal data and structure refinement parameters of the ligands and complex **3** are given in **Table S1**. The intramolecular hydrogen bonding (1.961-2.030 Å) between N–H and carbonyl oxygen in the ligands was confirmed. This hydrogen bonding disappeared and a new hydrogen bonding (N–H···Cl···H_2O) was seen in complex **3**. While comparing the bond lengths of L_3 and **3**, it was found that the bond length of thioamidic N–C decreased from 1.3255 to 1.287 Å whereas that of amidic N–C increased from 1.3226 to 1.398 Å on complexation. This revealed amine-imine tautomerism of the ligand prior to coordination. In complex **3**, the distance between Ru and centroid of *p*-cymene was found to be 1.681 Å. Ru–C and Ru–Cl bond lengths, and N–Ru–Cl bond angles were in accordance

with the literature values.[37,38] Further, the neutral bidentate coordination of the ligand to Ru ion, and presence of ionic chlorine outside the coordination sphere were confirmed. In addition, from the bond angles, the geometry of complex **3** was found to be pseudo-octahedral.

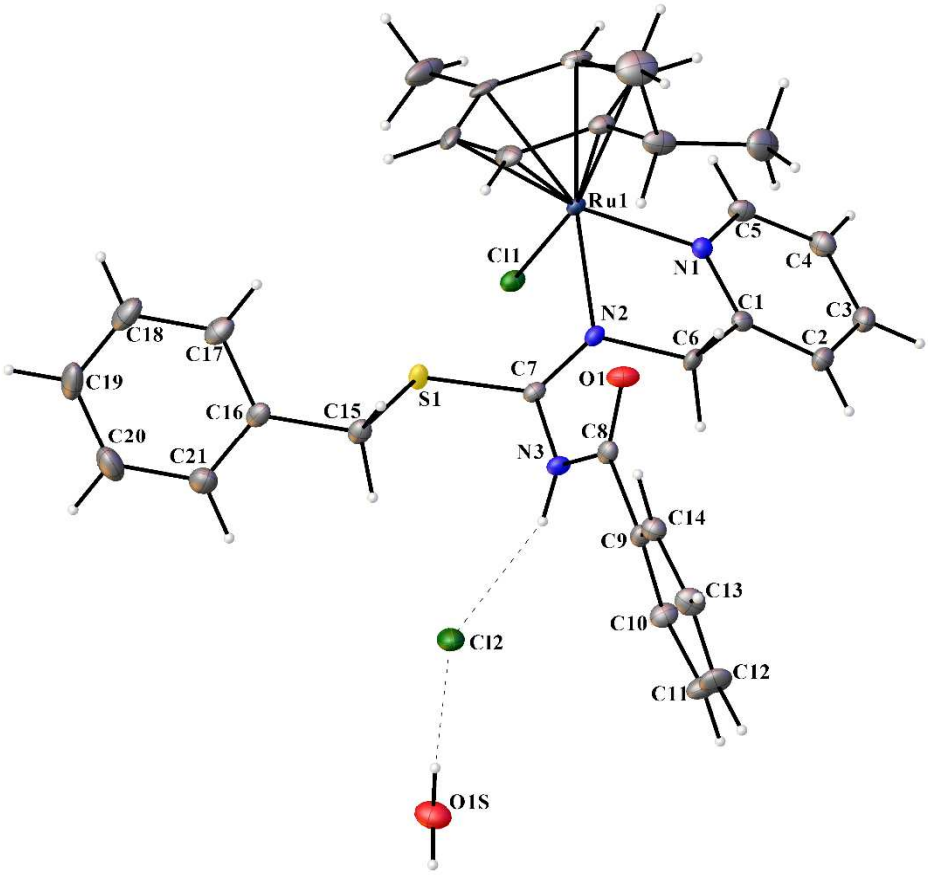


Fig. 2 Molecular structure of **3** [Important bond lengths (Å) and angles (°): S(1)–C(7) 1.753(2), N(2)–C(7) 1.287(3), N(3)–C(8) 1.393(3), N(3)–H(3) 0.88, N(3)–C(7) 1.398(3), O(1)–C(8) 1.219(3), N(2)–Ru(1) 2.1003(18), N(2)–C(6) 1.475(3), C(6)–C(1) 1.501(3), N(1)–C(1) 1.349(3), N(1)–Ru(1) 2.008873(18), Ru(1)–Cl(1) 2.3930(5), Ru(1)–C(24) 2.207(2), Cl(2)···H(3) 2.32 N(2)–Ru(1)–N(1) 77.19(7), N(2)–Ru(1)–Cl(1) 87.82(5), Cl(1)–Ru(1)–C(24) 107.03(6), C(6)–N(2)–Ru(1) 111.66(13), C(1)–N(1)–Ru(1) 116.61(14), N(2)–C(6)–C(1) 108.06(17)]. CCDC No. 1869571.

3.3 Transfer hydrogenation (TH) reactions

The complexes (**1**-**3**) were found to be excellent catalysts for the TH of aldehydes, ketones and nitro compounds with 2-propanol as hydrogen source and KOH as base. The molar ratio of substrate, base and catalyst was maintained as 1:1:0.001 for the purpose of comparison of the catalytic activity of the pseudo-acylthiourea Ru(II)-*p*-cymene complexes (**1**-**3**) with that of corresponding previously reported unprotected acylthiourea Ru(II)-*p*-

cymene complexes. In the absence of base, only 3 % conversion was observed. When the base amount was less than 1 mmol, significant decrease in the conversion was noted (**Fig. S22**). The conversion was only 34 % in the absence of the catalyst (**Fig. S23**). Though no variation was observed in the catalytic activity of the three Ru(II) complexes (**1**-**3**), **1** was chosen for scope extension (**Table S2**). The scope of TH was extended to various substituted ketones, aldehydes and nitro compounds. All the substrates showed an excellent conversion and selectivity, which were analyzed by GC / GC-MS (**Figs. S24**-**S57**). Some of the catalytic products were isolated and characterized by ^{1}H NMR spectra (**Figs. S58**-**S72**). The main advantages of the present system are chemoselectivity and functional group tolerance. The catalysts are chemoselective in the order aldehyde > nitro > ketone > nitrile > alkene. The electronic effect of the substituents in the substrates play a predominant role in TH.

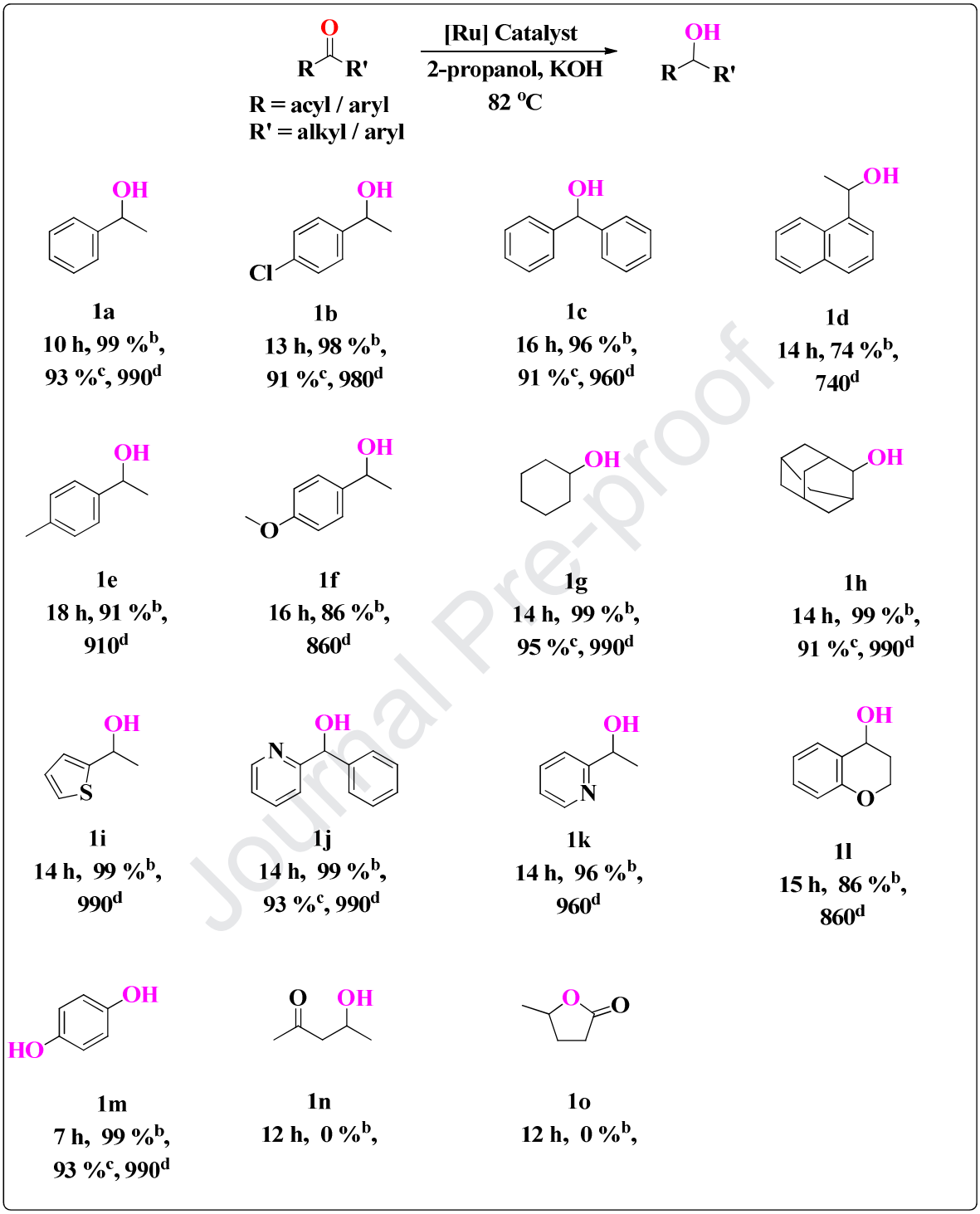
*3.4 Catalytic activity of the Ru(II)-p-cymene complexes containing bidentate pseudo-acylthiourea ligands (**1**)*

Generally, electron withdrawing substituents increase the electron deficiency at carbonyl carbon, which leads to enhanced reaction rate, and *vice versa* for electron donating groups. This catalytic system also followed the same trend. Initially, the scope of substrates was extended to ketones (**Table 1**). Acetophenone took 10 h for the complete conversion to form 1-phenylethanol (**1a**), whereas benzophenone took 16 h to yield 96 % of benzhydrol (**1c**). This was due to the greater influence of steric effect over –I effect of the phenyl ring since the catalyst as well as benzophenone are bulky. This was further confirmed in the formation of **1d**, where the yield was only 74 % after 14 h. In the case of 4-chloroacetophenone, the time taken to yield 98 % of respective alcohol (**1b**) was 13 h. The dominating +R effect over –I effect of chloro substituent decreases the electron deficiency of carbonyl carbon and hence it takes more time than acetophenone. The time taken for the conversion of the substrates with electron donating group to their respective alcohols (**1e** and **1f**) was still higher. The alicyclic systems like cyclohexanone and 2-adamantanone showed good yields after 14 h (**1g** and **1h**). This revealed the efficiency of the catalytic system towards TH of alicyclic ketones. In homogeneous catalysis, the major drawback is the non-compatibility of catalysts with heterocyclic substrates since there is a possibility for poisoning the catalysts by the hetero atoms. At the same time, heterocyclic compounds have tremendous importance in various fields including pharmaceuticals. The present catalytic system possessed superb compatibility with heterocyclic ketones, which was evident from the appreciable yields of heterocyclic alcohols (**1i**-**1l**). Among them, preparation of

phenyl(pyridin-2-yl)methanol is a challenging one. Conventionally, pyridine nitrogen was protected and then the ketone was hydroborated to yield the respective alcohol followed by deprotection. Hence, the direct TH of 2-benzoylpyridine to form its corresponding alcohol has significant importance. Moreover, histamine H_1 antagonists like bepotastine besilate and carbinoxamine contain phenyl(pyridin-2-yl)methanol as their basic core.[16,39-40]

Another very challenging reaction is the reduction of quinone to hydroquinone, which involves aromatization of ring by two electron transfer. The current catalytic system produced excellent yield of hydroquinone within 7 h (**1m**). Hydroquinone has a wide variety of applications such as reducing agent, cosmetics, etc. Liu *et al*. reported Ir-catalyzed reduction of quinone using NADH as hydrogen source to mimick the action of reductase. This reaction favoured semiquinones rather than dihydroquinones.[41] Pande *et al*. reported the catalytic TH of quinone to yield hydroquinone using Pd/C as catalyst and ammonium formate as hydrogen source.[42] Wang *et al*. reported the conversion of quinone to hydroquinone using Pt/C as catalyst and cyclohexanone as hydrogen source.[43] Compared to the literature, yield and selectivity of hydroquinone were excellent in the present work. Unfortunately, complex **1** failed to catalyze the hydrogenation of aliphatic substrates (**1n** and **1o**).

Table 1 Transfer hydrogenation of ketones[a]

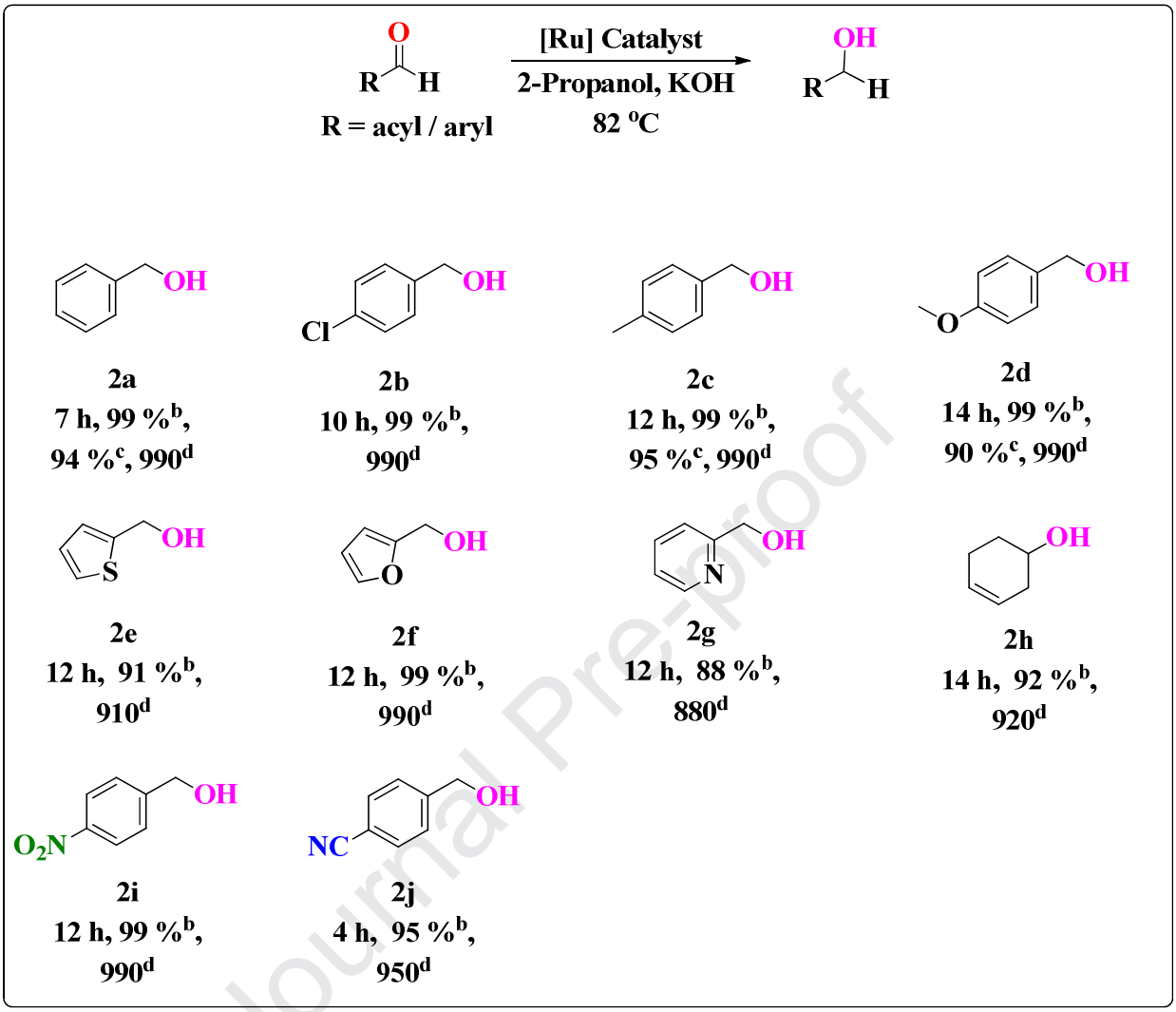


[a] 1 mmol of substrate, 0.1 mol % catalyst **1** in 4 mL of 2-propanol and 1 mmol of KOH were used

[b] Yield was analyzed by GCMS [c] Isolated yield

[d] Turn over number (TON) = No. of moles of product / No. of moles of catalyst

Table 2 Transfer hydrogenation of aldehydes[a]

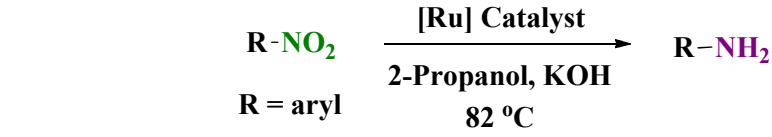


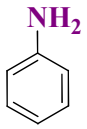
[a] 1 mmol of substrate, 0.1 mol % catalyst **1** in 4 mL of 2-propanol and 1 mmol of KOH were used

[b] Yield was analyzed by GCMS [c] Isolated yield

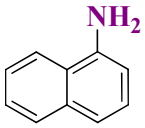
[d] Turn over number (TON) = No. of moles of product / No. of moles of catalyst

Table 3 Transfer hydrogenation of nitroarenes[a]

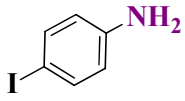




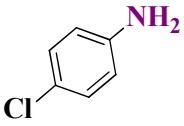
3a
7 h, 99 %[b], 89 %[c], 990[d]



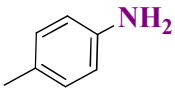
3b
14 h, 96 %[b], 960[d]



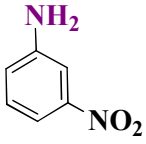
3c
14 h, 99 %[b], 90 %[c], 990[d]



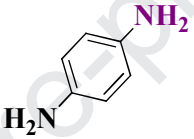
3d
16 h, 44 %[b], 440[d]



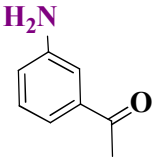
3e
12 h, 97 %[b], 970[d]



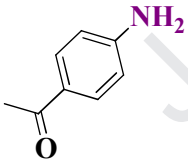
3f
12 h, 99 %[b], 94 %[c], 990[d]



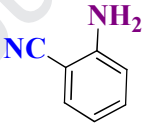
3g
8 h, 99 %[b], 95 %[c], 990[d]



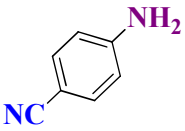
3h
10 h, 99 %[b], 93 %[c], 990[d]



3i
8 h, 99 %[b], 92 %[c], 990[d]



3j
4 h, 99 %[b], 990[d]



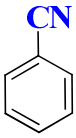
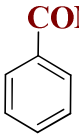
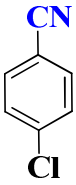
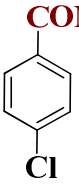
3k
4 h, 69 %[b], 690[d]

[a] 1 mmol of substrate, 0.1 mol % catalyst **1** in 4 mL of 2-propanol and 1 mmol of KOH were used

[b] Yield was analyzed by GCMS [c] Isolated yield

[d] Turn over number (TON) = No. of moles of product / No. of moles of catalyst

Table 4 Hydration of nitriles to amides[a]

Entry	Substrates	Products	Isolated yield (%)	TON[b]
5a			97	970
5b			94	940

[a] 1 mmol of substrate, 0.1 mol % catalyst **1** in 4 mL of 2-propanol and 1 mmol of KOH were used

[b] Turn over number (TON) = No. of moles of product / No. of moles of catalyst

The scope of TH was extended to aldehydes (**Table 2**) and the influence of electronic effect was found to be similar to ketones. Good compatibility of the catalyst was observed with heterocyclic aldehydes. Among them, conversion of furfural to furfuryl alcohol (**2f**) was significant due to its importance in bio-fuel synthesis and green chemistry. Many homogeneous and heterogeneous catalysts were used for the selective synthesis of furfuryl alcohol from furfural.[44–48] But in most of the cases, the selectivity was poor even at very high temperature. But the present catalytic system excelled in the selective synthesis of furfuryl alcohol. Puthiaraj *et al*. reported Pd nanoparticles supported on nitrogen functionalized carbon as an active catalyst for the selective TH of furfural to furfuryl alcohol using 2-butanol as hydrogen source and K*t*OBu as base.[49] Panagiotopoulou *et al*. reported Lewis acid catalyzed selective TH reaction of furfural to form furfuryl alcohol at 180 °C in 3 h. The synergistic effect of Ru/C and Lewis acid led to an increased furfural conversion to methyl furan.[50] Meng *et al*. reported heterogeneous Ni catalyst supported on mixed metal oxides (MMO) for the selective hydrogenation of furfural, where the selectivity was switched by changing the MMO.[51] Remarkably, 4-nitrobenzaldehyde and 4-formylbenzonitrile were selectively reduced to their respective alcohol (**2i** and **2j**) without affecting nitro or cyano group in basic medium (**Fig. 3**).

Usually, nitroarenes are reduced using H_2 gas or reducing agents in presence of heterogeneous catalyst. The reports on this reduction using homogeneous catalyst were limited. Moreover, TH of nitroarenes is difficult compared to that of carbonyl compounds.

So, there is a need for the design of functionalized molecular architectures for nitro reduction with high chemoselectivity by tolerating diverse array of functional moieties.[11,52–54] Hohloch *et al*. reported Ru(II) catalysts containing click based triazoles and carbene ligands for the TH of nitrobenzene. By tuning the catalysts and reaction conditions, selectivity of the TH product was controlled. The significance of ligand variation on the product selectivity was clearly explained.[55] Jia *et al*. reported the phenolate-oxazoline ligand based half-sandwich Ru(II) catalyst for the TH of nitroarenes using 2-propanol as hydrogen donor and KOH as initiator.[56] The present catalytic system worked well for the TH of nitroarenes too (**Table 3**). The complete conversion of nitrobenzene to aniline (**3a**) took only 7 h. The present catalyst was compatible with nitroarenes containing electron donating or electron withdrawing substituent. Mostly, molecular catalysis in basic medium is challenging for halogenated nitroarenes since dehalogenated amines are formed as a major product. But, no such dehalogenated amines were observed when catalyst **1** was used (**3c** and **3d**). Except **3d** and **3k**, all other amines were formed in excellent yields and selectivities. Notably, 1,3-dinitrobenzene, 2-nitrobenzonitrile and nitroacetophenone were reduced to 3-nitroaniline, 2-aminobenzonitrile and aminoacetophenone respectively with complete selectivity (**3f**, **3h**-**3j**). But, 4-nitrobenzonitrile to 4-aminobenzontrile had moderate selectivity due to the substitution of amine by acetoxy group (**3k**) (**Fig. 3**). The present catalyst was inactive towards TH of alkene, which was evident from **2h**. To understand this further, styrene was tested, and no reaction was observed. This paved the way for the selective TH of unsaturated carbonyl compounds and nitroarenes. The catalyst was also effective for the hydration of nitriles to give amides (**Table 4**). Thus, the current catalytic system was compatible with a broad range of substrates (39 examples) including ketones, aldehydes, nitroarenes, nitriles and alkenes. Further, the homogeneity of the catalyst was tested by mercury drop test. No significant loss in the conversion was observed, which confirmed the absence of Ru nanoparticles, and the catalytic pathway was truly homogeneous (**Fig. S73**).[33]

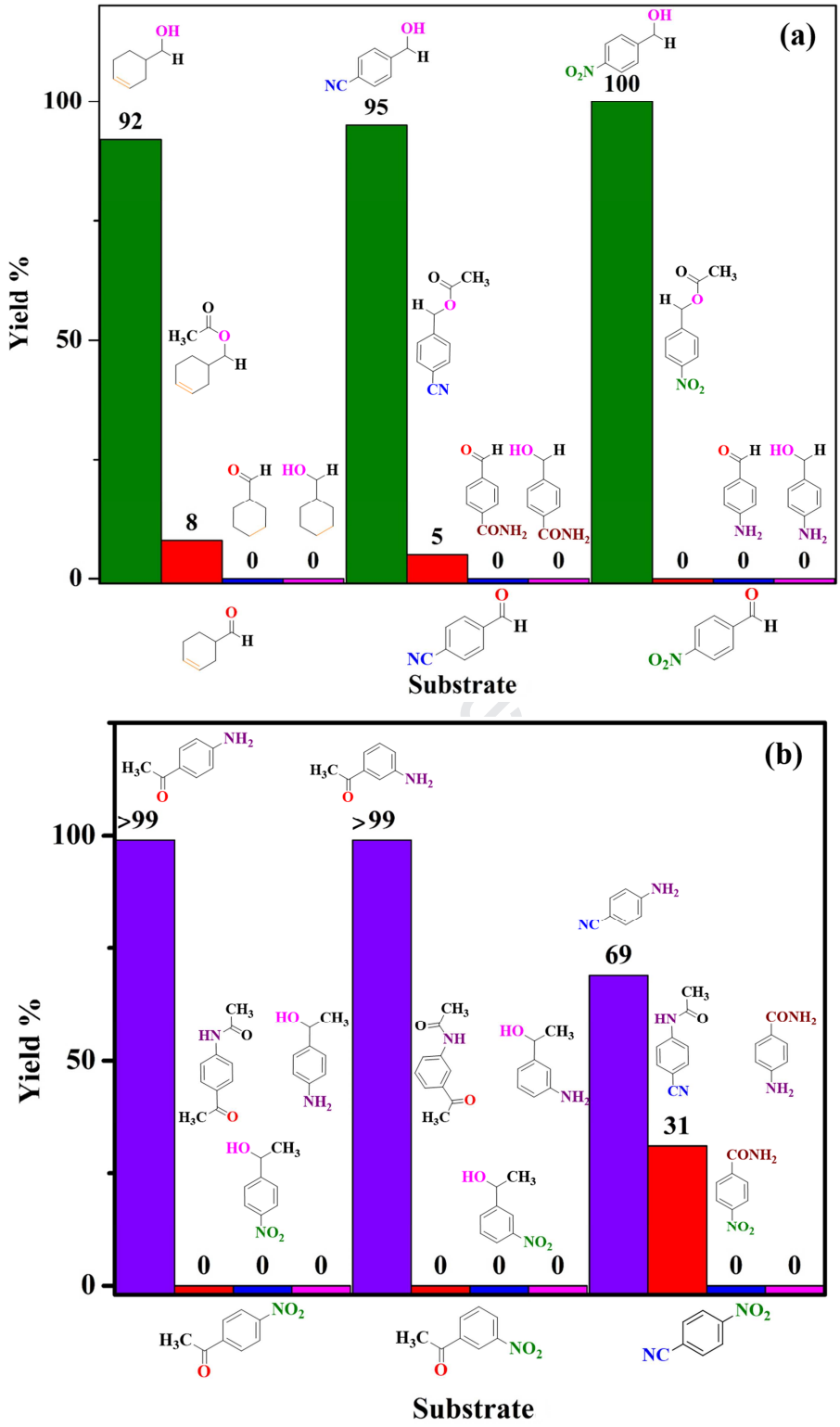
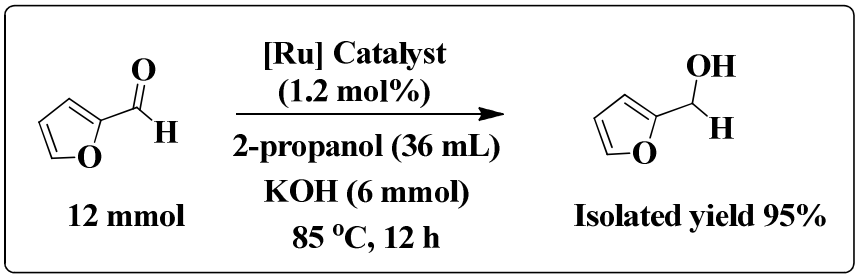


Fig. 3 Selectivity profile for challenging (a) aldehydes and (b) nitroarenes



Scheme 2 Gram scale synthesis of furfuryl alcohol from furfural

Most of the catalysis is compatible only in the smaller scale but scale up to larger extent is highly needed for industrial applications. Hence, we tested the gram scale synthesis of 2-furfuryl alcohol under the optimized conditions (**Scheme 2**). The complete conversion with absolute selectivity was achieved. The product was analyzed by GC and confirmed by ^{1}H NMR (**Figs. S74** and **S75**). Thus, the present catalytic system is compatible in larger scale, which paved the way for its industrial application.

3.5 Comparison of the catalysts containing bidendate pseudo-acylthiourea or monodendate acylthiourea ligand

In our previously reported catalysts, the acylthiourea (unprotected) ligands coordinated to Ru ion *via* neutral sulphur atom (monodentate). In addition, two labile chlorine ligands and *p*-cymene were present. The catalysts adopted half-sandwich piano stool structure with pseudo-octahedral geometry. The catalysts have sufficient space to interact with the substrates due to the presence of two labile chlorine ligands.[34] Now, sulphur was protected by benzyl group, which led to the N, N' bidentate coordination of the ligands to Ru ion. Hence, only one chlorine ligand was present along with *p*-cymene around Ru(II) ion. This favoured single active site on Ru ion, which accounted selective and effective catalysis (**Fig. 4**). Overall, the present catalytic system was efficient and exhibited enhanced reaction rate compared to the previously reported catalytic system.[33]

The complete conversion of acetophenone to 1-phenylethanol happened in 10 h in presence of catalyst **1**, whereas analogous catalyst containing monodentate acylthiourea ligand (**1'**) required 14 h. The same reaction was carried out for 10 h using **1'** and the conversion was found to be 88 % only. Similarly, many substrates have enhanced their reactivity with catalyst **1**. Notably, the complete conversion of benzaldehyde to benzyl alcohol, and nitrobenzene to aniline took only 7 h. Catalyst **1'** was not effective in the selective conversion of nitrobenzene to aniline. Even after 16 h, it yielded only 46 % of aniline, and remaining were the intermediates azoxybenzene and azobenzene. But in the case

of bulkier substrate benzophenone or non-planar substrates like adamantanone and cyclohexanone, the reaction rate was not enhanced. This may be due to the steric hindrance between catalyst **1** and the incoming substrate. Interestingly, chemoselectivity was altered by tuning the ligand. The chemoselectivity order exhibited by catalyst **1'** was nitro > aldehyde > ketone > alkene, whereas for catalyst **1**, it was aldehyde > nitro > ketone > nitrile > alkene. To give an example, TH reaction of 4-nitrobenzaldehyde yielded 4-aminobenzaldehyde with catalyst **1'** whereas 4'-nitro(1-phenylethanol) was formed with catalyst **1**. This may be due to the presence of many lone pair of electrons on the nitro group, which made it sterically hindered to interact with the Ru center of catalyst **1** since the latter was already bulky and had narrow catalytic site.

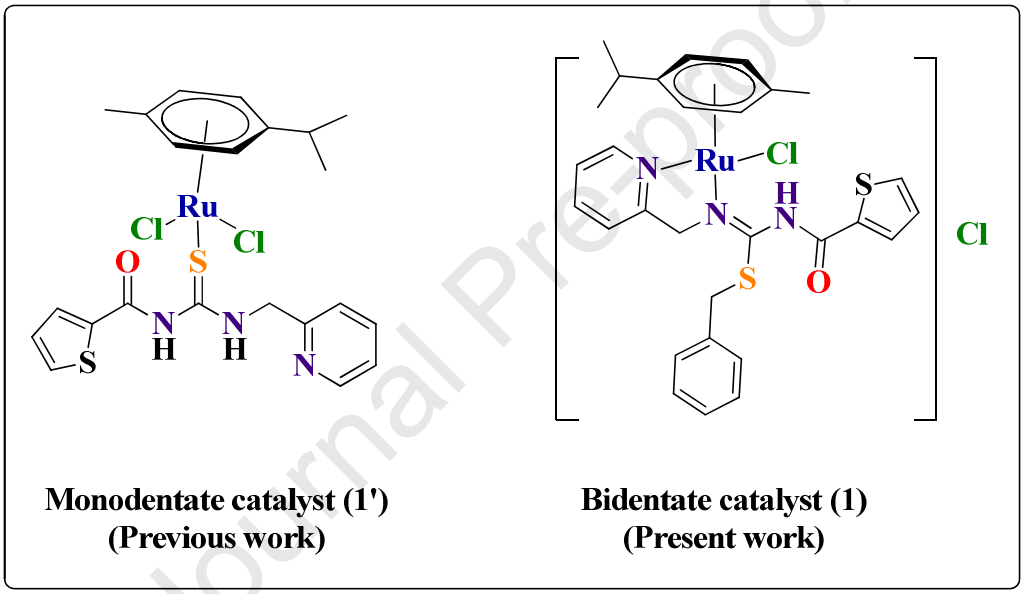
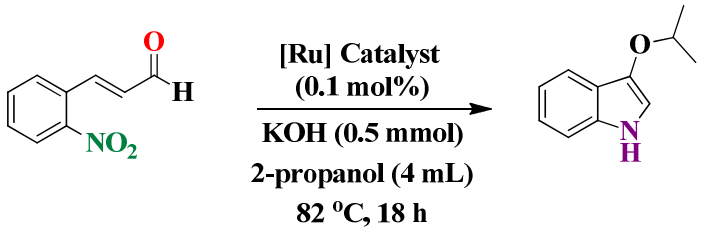


Fig. 4 Molecular structures of our previous and present catalysts

3.6 Synthesis of 3-isopropoxy-1H-indole

2'-nitrocinnamaldehyde was used to check the chemoselectivity among nitro, alkene and aldehyde groups under optimized conditions. Surprisingly, the product obtained was 3-isopropoxy-1H-indole (**Scheme 3**). The product was characterized by ^{1}H and ^{13}C NMR (**Figs. S76** and **S77**) and GC-MS techniques. From the literature survey, it was realized that this was the first synthetic route to prepare 3-isopropoxy-1H-indole from 2-nitrocinnamladehyde. Marchetti *et al*. reported the synthesis of indole derivatives from 2-nitrocinamaldehyde by hydroformylation route using gaseous CO and H_2.[57] Indole derivatives have tremendous applications in pharmaceuticals. This 3-isopropoxy-1H-indole may be a useful intermediate for the preparation of indole based drug molecules. The reaction

mechanism was expected to be similar to Baeyer-Emmerling indole synthesis. The suggested reaction mechanism followed intramolecular hydrogen borrowing strategy followed by cyclization along with the nucleophilic attack of isopropoxide to yield 3-isopropoxy-1H-indole (**Fig. S78**).



Scheme 3 Synthesis of 3-isopropoxy-1H-indole from 2-nitrocinnamaldehyde

4. Conclusions

The objective of the work was to tune the chemoselectivity and reaction rate by engineering the ligand in the catalyst. Hence, our previous Ru(II)-*p*-cymene catalyst containing monodentate acylthiourea ligand was tuned by protecting S atom of the ligand. This made bidentate coordination of resulting pseudo-acylthiourea feasible with ruthenium ion. Thus, the first Ru(II)-*p*-cymene complexes containing pseudo-acylthiourea ligand were synthesized and characterized by spectral techniques. The molecular structures of all the ligands and complex **3** were confirmed by single crystal XRD technique. The coordination of the ligands to Ru ion *via* N, N' neutral bidentate fashion and the pseudo-octahedral geometry were proved. The complexes were used as pre-catalysts towards TH reaction of carbonyl compounds and nitroarenes using 2-propanol as hydrogen donor and KOH as base. The scope of TH reaction was extended to a broad range of substrates including different ketones, aldehydes and nitroarenes using catalyst **1**. The efficiency of the present catalyst in TH reaction was compared with that of previously reported catalyst containing monodentate acylthiourea ligand. The current catalytic system showed enhanced reaction rate compared to the previous one. The previous catalytic system showed chemoselectivity towards the nitro group in presence of carbonyl. After tuning the ligand, the current catalytic system showed chemoselectivity in the order aldehyde > nitro > ketone. Thus, the catalysts with the monodentate ligands can be used for the chemoselective TH of nitroarenes even in the presence of carbonyl group and alkene, whereas the catalysts (**1**-**3**) with the bidentate ligands can be used for the chemoselective TH of aldehydes even in the presence of ketone, nitro group and alkene. Remarkably, the first and novel synthetic route for the synthesis of 3-

isopropoxy-1H-indole from 2-nitrocinnamaldehyde is reported. The scope of this new one pot reaction will be extended in future.

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Highlights

- ✓ A new series of Ru(II)-*p*-cymene complexes containing picolyl based pseudo-acylthiourea ligands was synthesized and characterized
- ✓ The molecular structure of the ligands and one of the complexes was confirmed by XRD technique
- ✓ The chemoselectivity and reactivity of transfer hydrogenation reaction was altered by tuning the acylthiourea ligands in the Ru(II) catalyst
- ✓ The catalyst was compatible with broad range of substrates which include many heterocycles, and gram-scale synthesis was also achieved for the bio-fuel
- ✓ One pot synthesis of 3-isopropoxy indole from 2-nitrocinnamaldehyde was achieved *via* a new synthetic route

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

N.A.