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FULL PAPER

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Synthesis of Imines *via* Reactions of Benzyl Alcohol with Amines Using Half-Sandwich (η^6-*p*-cymene) Ruthenium(II) Complexes Stabilised by 2-aminofluorene Derivatives

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A new class of half-sandwich (η^6-*p*-cymene) ruthenium(II) complexes supported by 2-aminofluorene derivatives [Ru(η^6-*p*-cymene)(Cl)(L)] (**L** = 2-(((9H-fluoren-2-yl)imino)methyl)phenol (**L**^{1}), 2-(((9H-fluoren-2-yl)imino)methyl)-3-methoxyphenol (**L**^{2}), 1-(((9H-fluoren-2-yl)imino)methyl)naphthalene-2-ol (**L**^{3}) and N-((1H-pyrrol-2-yl)methylene)-9H-fluorene-2-amine (**L**^{4})) were synthesized. All compounds were fully characterized by analytical and spectroscopic techniques (IR, UV–Vis, NMR) and also by mass spectrometry. The solid state molecular structures of the complexes [Ru(η^6-*p*-cymene)(Cl)(L^2)], [Ru(η^6-*p*-cymene)(Cl)(L^3)] and [Ru(η^6-*p*-cymene)(Cl)(L^4)] revealed that the 2-aminofluorene and *p*-cymene moieties coordinate to ruthenium(II) in a three-legged piano-stool geometry. The synthesized complexes were used as catalysts for the dehydrogenative coupling of benzyl alcohol with a range of amines (aliphatic, aromatic and heterocyclic). The reactions were carried out under thermal heating, ultrasound and microwave assistance, using solvent or solvent free conditions, and the catalytic performance was optimized regarding the solvent, the type of base, the catalyst loading and the temperature. Moderately high to very high isolated yields were obtained using [Ru(η^6-*p*-cymene)(Cl)(L^4)] at 1 mol%. In general, microwave irradiation produced better yields than the other two techniques irrespective of the nature of the substituents.

KEYWORDS
imine synthesis, microwave energy, ruthenium catalysts, sonochemical energy, thermal energy

1 | INTRODUCTION

The development of efficient synthetic methods of imines is an important target owing to its widespread applications in pharmaceuticals, fungicides, agricultural and industrial products[1,2] (Figure 1). Furthermore, imines and their nitrogen containing derivatives are increasingly required for the production of a massive diversity of valuable biological active products.[3,4]

Imines may be obtained through several reactions such as addition, condensation, cycloaddition, asymmetric organo-catalysis, cross-dehydrogenative coupling and multicomponent reactions.[1] But still the imination reaction is a challenge, due to the formation of side-products

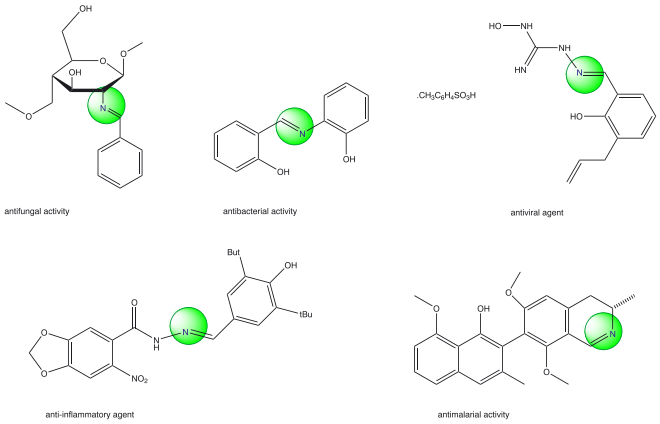


FIGURE 1 Biological active compounds containing imine functional groups

or wastes in several synthetic pathways. To overcome these drawbacks, acceptorless dehydrogenative methodologies involving the open-air oxidative coupling of an alcohol and an amine have been recently developed.[5] Through this procedure benzyl alcohol is converted into benzaldehyde that, in turn, reacts with amines leading to the formation of imines via an unstable hemiaminal intermediate (Scheme 1).

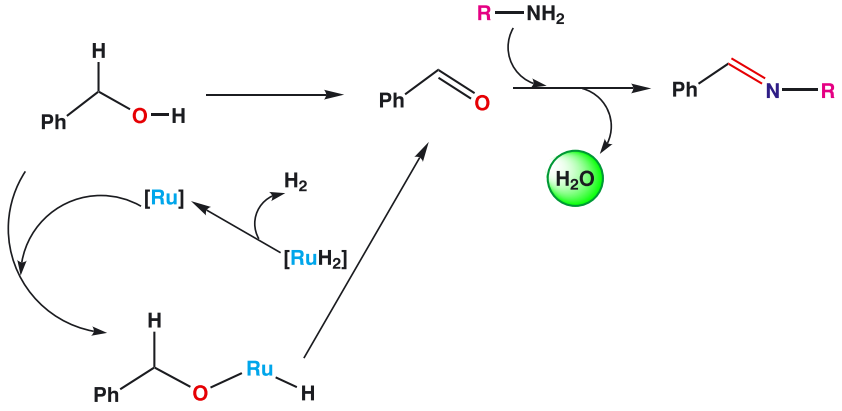
Several homogeneous and heterogeneous transition metal catalysts for the synthesis of imines, such as Ru,[6] Ir,[7] Fe,[8] Mn,[9] Os,[10] Co,[11] Cu,[12] Au/TiO_2,[13] Pd/DNA,[14] Pd/ZrO_2,[15] MOF[16] were reported. Ruthenium complexes, well known for their effective catalytic activity in huge assortment of organic transformation reactions,[17] are among the most useful catalysts for acceptorless dehydrogenative coupling of imines (see Figure 2). Milstein and co-workers reported an efficient Ru-PNP pincer catalyst that shows high turnover number and only generates hydrogen gas and water as co-products (**A**)[6a] Gelman *et. al* reported a bifunctional Ru-PCP pincer complex bearing a dibenzobarrelene-based ligand (**B**)[6b]; Bera *et. al* described a new type of direct metal–metal bonded diruthenium complex bridged by a naphthyridine functionalized *N*-heterocyclic carbene (NHC) ligand that was used in the presence of molecular sieves leading to imines as the only products (**C**)[6c]; Ramesh and co-workers reported the synergic catalytic activity of a bimetallic system bridged by two hydrazide nitrogens (**D**)[6d] and a mononuclear ruthenium (II) complex containing the benzhydrazone ligand (**E**).6e These studies showed that the catalytic activity is strongly influenced by the nature of the arene, the chelating ligands and the vacant coordination sites provided by leaving groups.[18,19]

This work describes new Schiff-base and pyrrolate-imine ruthenium complexes as catalysts for the synthesis of imines using benzyl alcohol and amines as starting materials. The effect of thermal heating, sonochemical and microwave irradiation on the catalytic activity is also discussed.

2 | EXPERIMENTAL SECTION

2.1 | General considerations

Elemental analyses were performed with a Vario EL CHN elemental analyser. The melting points were measured with the aid of Boetius micro-heating label. FT-IR spectra (4000–600 cm^{-1}) were accomplished on a Bruker



SCHEME 1 Direct synthesis of imines from benzyl alcohol and amines

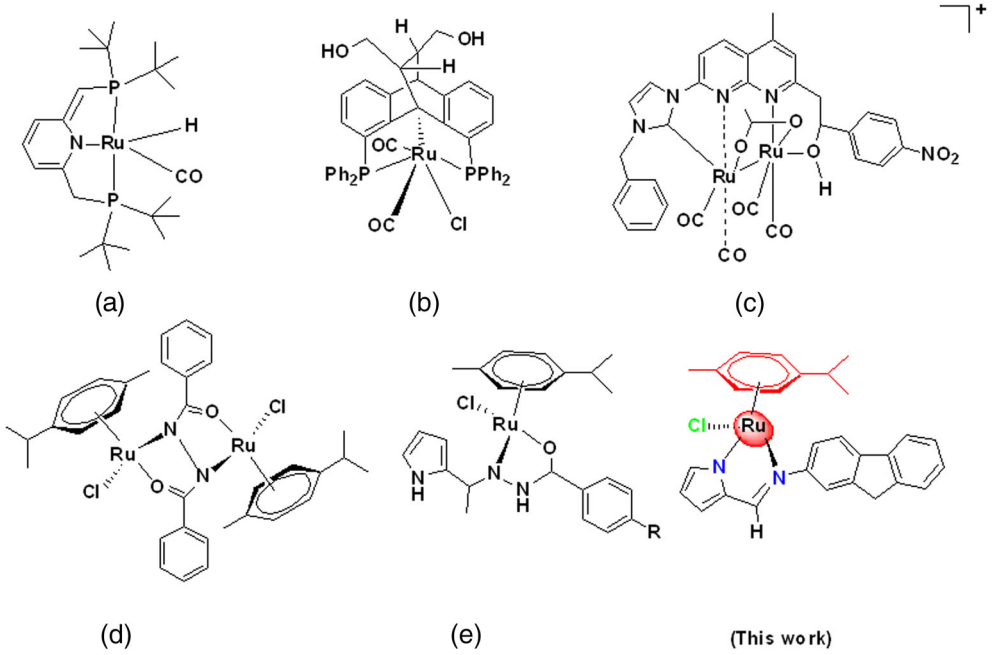


FIGURE 2 Ruthenium(II) catalysts for the synthesis of imines using benzyl alcohol and amines

783 spectrometer by direct utilization. Electronic spectra were obtained on a Cary 300 Bio UV–Vis Varian spectrophotometer from the solutions of chloroform, 10^{-3} M, in quartz cuvettes (1 cm optical path) in the range of 800–200 nm. NMR spectra were recorded using a Bruker Advances III HD Nanobay 400 MHz FT- NMR spectrometer at 295 K, referenced internally to the residual proton-solvent (^{1}H) or solvent (^{13}C) resonances, and reported in parts per million (ppm) relatively to tetramethylsilane (0 ppm). Sonication was performed using an Ultrasonic cleaner, sonica 2200 MHS^{3} (model no: 090.003.003). Convection microwave oven (MC2846SL, LG28L) was used to carry out the reactions.

Commercially available $RuCl_3.3H_2O$ was used as supplied from SRL Pvt. Ltd. All solvents and reagents were acquired from Merck or Aldrich. The starting precursor $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ was prepared according to literature.[20] (2-(((9H-fluoren-2-yl)imino)methyl)phenol (**HL^1**), 2-(((9H-fluoren-2-yl)imino)methyl)-3-methoxyphenol (**HL^2**) and 1-(((9H-fluoren-2-yl)imino)methyl)naphthalene-2-ol (**HL^3**) were synthesized by the reported procedure.[21]

2.2 | Synthesis of the 2-aminofluorene derivative HL^4

Pyrrole-2-carboxaldehyde (0.1 g, 1.0 mmol) was dissolved in ethanol (10 ml) and 2-aminofluorene (0.2 g, 1.0 mmol) was added to the solution. This mixture was stirred at room temperature for 3 hr. The solution turned yellow and the solvent partially evaporated. A yellow precipitate was obtained on standing. It was washed with cold ethanol and dried in a vacuum desiccator. Yield: 84%; m.p.: 240 °C; FT-IR: N-H, 3008 cm^{-1}, C=N, 1659 cm^{-1}. UV–Vis ($CHCl_3$, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}]): 408 (147), 274 (391). ^{1}H NMR (400 MHz, $CDCl_3$) (δ ppm): 10.62 (s, 1H, N*H*), 8.65 (s, 1H, *H*C=N), 7.90–6.82 (m, 10H, Ar*H*), 3.98 (s, 2H, CH_2). ESI-MS: m/z = 259.29 $[M + H]^+$ (Cald. 258.32).

2.3 | General procedure for the syntheses of half-Sandwich (^{6}-*p*-cymene) ruthenium(II) complexes (1–4)

To a solution of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ (0.1 g, 1 mmol) in dichloromethane (10 ml) was added a solution of the corresponding 2-aminofluorene derivative (**HL$^{1-4}$**) (2 mmol) in dichloromethane (5 ml) followed by a few drops of triethylamine. The reaction mixture was stirred at room temperature for 5 hr. A gradual color change from reddish orange to orange was observed. The solvent was evaporated to dryness under reduced pressure affording an orange solid. The complexes were crystallized from CH_2Cl_2/hexane solutions.

2.3.1 | Synthesis of [Ru(η^6-*p*-cymene)(cl)(L^1)] (1)

Yield: 78%; m.p.: 190 °C; Anal. calcd. For $C_{30}H_{28}NOClRu$: C, 64.86; H, 5.01; N, 2.29. Found: C, 64.91; H, 5.08; N,

2.52. FT-IR: C=N, 1602 cm^{-1}; C-O, 1386 cm^{-1}. UV–Vis ($CHCl_3$, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}]): 439 (713), 334 (6034), 262 (2154). ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 8.79 (s, 1H, *H*C=N), 7.92 (s, 1H, Ar*H*), 7.83 (t, J = 4.0 Hz, 1H, Ar*H*), 7.61–7.60 (overlapping, 2H, Ar*H*), 7.43 (t, J = 7.6 Hz, 1H, Ar*H*), 7.35 (t, J = 7.2 Hz, 1H, Ar*H*), 7.22 (d, J = 8.0 Hz, 1H, Ar*H*), 7.03–7.00 (overlapping, 2H, Ar*H*), 6.99 (d, J = 8.0 Hz, 1H, Ar*H*), 6.43 (t, J = 7.2 Hz, 1H, Ar*H*), 5.37 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 5.26 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 5.02 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 4.23 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 3.99 (s, 2H, CH_2), 2.67 (sept, J = 6.7 Hz, 1H, *p*-cym ArC*H*(CH_3)$_2$), 2.13 (s, 3H, *p*-cym Ar(CH_3)), 1.19 (d, J = 6.8 Hz, 3H, *p*-cym ArCH(CH_3)$_2$), 1.13 (d, J = 6.8 Hz, 3H, *p*-cym ArCH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 165.2 164.0, 162.7 (L^1 C_qPhO, *C*H=N and $C_qN_{Fluorene}$), 157.7, 150.3, 144.2, 143.9, 140.8, 137.2, 135.4, 129.2, 127.1, 125.2, 123.8, 122.7, 120.9, 119.8, 118.2, 114.3 (L^1 $C_{q,Fluorene}$, $C_qAr_{CCH=N}$ and C_HAr), 101.7, 97.5 (*p*-cym C_qAr), 86.3, 84.1, 83.9, 80.1 (*p*-cym C_HAr), 37.1 (CH_2), 22.8, 21.6 (*p*-cym ArCH(CH_3)$_2$ and Ar(CH_3)), 8.8, 8.7 (*p*-cym ArCH(CH_3)$_2$). ESI-MS: m/z = 554.5210 $[M + H]^+$ (Cald. 555.08).

2.3.2 | Synthesis of [Ru(η^6-*p*-cymene)(cl)(L^2)] (2)

Yield: 84%; m.p.: 174 °C; Anal. calcd. For $C_{31}H_{30}NO_2ClRu$: C, 63.38; H, 5.11; N, 2.23. Found: C, 63.63; H, 5.16; N, 2.39. FT-IR: C=N, 1596 cm^{-1}; C-O, 1383 cm^{-1}. UV–Vis ($CHCl_3$, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}]): 446 (483), 331 (6008), 264 (2079). ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 8.14 (s, 1H, *H*C=N), 7.92 (s, 1H, Ar*H*), 7.85–7.81 (overlapping, 4H, Ar*H*), 7.43 (t, J = 7.6 Hz, 1H, Ar*H*), 7.36 (t, J = 7.6 Hz, 1H, Ar*H*), 6.76 (d, J = 7.6 Hz, 1H, Ar*H*), 6.62 (d, J = 8.0 Hz, 1H, Ar*H*), 6.36 (t, J = 7.2 Hz, 1H, Ar*H*), 5.38 (d, J = 6.0 Hz, 1H, *p*-cym Ar*H*), 5.31 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 5.03 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 4.30 (d, J = 5.2 Hz, 1H, *p*-cym Ar*H*), 3.97 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 2.68 (sept, J = 6.9 Hz, 1H, *p*-cym ArC*H*(CH_3)$_2$), 2.12 (s, 3H, *p*-cym Ar(CH_3)), 1.42 (d, J = 7.2 Hz, 3H, *p*-cym ArCH(CH_3)$_2$), 1.41 (d, J = 7.2 Hz, 3H, *p*-cym ArCH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 168.3, 165.1, 163.8 (L^2 C_qPhO, *C*H=N and $C_qN_{Fluorene}$), 157.7, 156.6, 152.5, 144.9, 143.5, 141.8, 140.4, 127.1, 126.9, 125.2, 123.9, 120.0, 119.8, 118.0, 115.0, 113.2 (L^2 $C_{q,Fluorene}$, $C_qAr_{CCH=N}$ and C_HAr), 101.9, 97.5 (*p*-cym C_qAr), 86.2, 84.1, 83.9, 80.2 (*p*-cym C_HAr), 56.1 (OCH_3), 37.1 (CH_2), 22.8, 21.6 (*p*-cym ArCH(CH_3)$_2$ and Ar(CH_3)), 8.7, 8.5 (*p*-cym ArCH(CH_3)$_2$. HR-MS: m/z = 586.1019 $[M + H]^+$ (Cald. 586.108).

2.3.3 | Synthesis of [Ru(η^6-*p*-cymene)(cl)(L^3)] (3)

Yield: 85%; m.p.: 210 °C; Anal. calcd. For $C_{34}H_{30}NOClRu$: C, 67.37; H, 4.95; N, 2.30. Found: C, 67.47; H, 4.99; N, 2.31. FT-IR: C=N, 1616 cm^{-1}; C-O, 1383 cm^{-1}. UV–Vis ($CHCl_3$, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}]): 458 (827), 334 (6006), 264 (2126). ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 8.66 (s, 1H, *H*C=N), 7.94 (s, 1H, Ar*H*), 7.86 (d, J = 8.0 Hz, 1H, Ar*H*), 7.72 (d, J = 8.0 Hz, 1H, Ar*H*), 7.63 (d, J = 8.8 Hz, 1H, Ar*H*), 7.57 (d, J = 8.0 Hz, 1H, Ar*H*), 7.45–7.43 (overlapping 2H, ArH), 7.32–7.30 (overlapping, 2H, Ar*H*), 7.18–7.12 (overlapping, 4H, Ar*H*), 5.42 (d, J = 5.2 Hz, 1H, *p*-cym Ar*H*), 5.31 (d, J = 3.2 Hz, 1H, *p*-cym Ar*H*), 5.02 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 4.25 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 4.01 (s, 2H, CH_2), 2.67 (sept, J = 6.8 Hz, 1H, *p*-cym ArC*H*(CH_3)$_2$), 2.15 (s, 3H, *p*-cym Ar(CH_3)), 1.20 (d, J = 6.8 Hz, 3H, *p*-cym ArCH(CH_3)$_2$), 1.12 (d, J = 6.8 Hz, 3H, *p*-cym ArCH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 168.8, 167.9, 166.0 (L^3 C_qPhO, *C*H=N and $C_qN_{Fluorene}$), 158.8, 157.6, 147.0, 145.1, 143.5, 141.6, 140.2, 135.3, 134.8, 128.9, 127.0, 126.6, 125.4, 124.0, 122.8, 121.9, 120.0, 119.8, 118.6, 108.2 (L^3 $C_{q,Fluorene}$, $C_qAr_{CCH=N}$, C_qAr and C_HAr), 101.6, 97.5 (*p*-cym C_qAr), 86.4, 84.7, 84.3, 80.2 (*p*-cym C_HAr), 37.1 (CH_2), 22.8, 21.6 (*p*-cym ArCH(CH_3)$_2$ and Ar(CH_3)), 8.8, 8.7 (*p*-cym ArCH(CH_3)$_2$). HR-MS: m/z = 606.1110 $[M + H]^+$ (Cald. 606.1132).

2.3.4 | Synthesis of [Ru(η^6-*p*-cymene)(cl)(L^4)] (4)

Yield: 88%; m.p.: 182 °C; Anal. calcd for $C_{28}H_{27}N_2ClRu$: C, 63.55; H, 5.11; N, 5.25. Found: C, 63.67; H, 5.15; N, 5.30. FT-IR: C=N, 1563 cm^{-1}. UV–Vis ($CHCl_3$, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}]): 427 (739), 365 (1293), 267 (1043). ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 8.64 (s, 1H, *H*C=N), 7.82–7.77 (overlapping, 2H, Ar*H*), 7.67 (s, 1H, Ar*H*), 7.62–7.57 (overlapping, 2H, Ar*H*), 7.40 (t, J = 7.6 Hz, 1H, Ar*H*), 7.33–7.31 (overlapping, 2H, Ar*H*), 6.82 (d, J = 3.6 Hz, 1H, Ar*H*), 6.37 (d, J = 2.4 Hz, 1H, Ar*H*), 5.45 (d, J = 6.0 Hz, 1H, *p*-cym Ar*H*), 5.19 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 5.12 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 4.97 (d, J = 5.6 Hz, 1H, *p*-cym Ar*H*), 3.96 (s, 2H, CH_2), 2.39 (sept, J = 6.8 Hz, 1H, *p*-cym ArC*H*(CH_3)$_2$), 2.20 (s, 3H, *p*-cym Ar(CH_3)), 1.07 (d, J = 6.8 Hz, 3H, *p*-cym ArCH(CH_3)$_2$), 0.99 (d, J = 6.8 Hz, 3H, *p*-cym ArCH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 161.2, 159.6, 156.3, 153.6 (L^4 $C_qN_{Pyrrole}$, $C_HN_{Pyrrole}$, *C*H=N and $C_qN_{Fluorene}$), 144.2, 143.3, 141.1, 140.9, 139.6, 127.0, 126.7, 125.1, 121.8, 120.0, 119.8, 118.1, 114.0 (L^4 $C_{q,Fluorene}$ and C_HAr), 100.8, 99.9 (*p*-cym C_qAr), 84.4,

82.4, 81.7, 79.8 (*p*-cym C_HAr), 37.0 (CH_2), 22.6, 21.6 (*p*-cym Ar$CH(CH_3)_2$ and Ar(CH_3)), 8.6, 8.2 (*p*-cym ArCH(CH_3)$_2$). HR-MS: m/z = 551.0807 $[M + Na]^+$ (Cald. 551.0798).

2.4 | Synthesis of imines via benzyl alcohol with amines exploitation of various methods

i. Conventional thermal heating method

A mixture of benzyl alcohol (1 mmol), mono amine/diamine (1 mmol/0.5 mmol), complex **4** (0.01 mmol), Cs_2CO_3 (0.2 mmol) in toluene (5 ml) was refluxed at 110 °C with constant stirring for 12 hr. The reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate (10 ml). Two layers were formed upon the addition of water (5 ml) and the organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The product was purified by column chromatography on a silica gel of 100–200 mesh using a hexane/ethyl acetate (3:1) mixture as eluent. The product was analysed by a proton NMR spectrum and the isolated yield was calculated.

ii. Ultrasonic irradiation

A mixture of benzyl alcohol (1 mmol), mono- or diamine (1 mmol or 0.5 mmol, respectively), complex **4** (0.01 mmol) and Cs_2CO_3 (0.2 mmol) was sonicated at a frequency of 50 kHz and an input power of 170 W using an US bath at 90 °C. The progress of the reaction was monitored by TLC. The solution was filtered and concentrated under reduced pressure and the product was purified by the column chromatography on a silica gel of 100–200 mesh using a mixture of hexane/ethyl acetate (3:1) as eluent.

iii. Microwave irradiation

Catalyst **4** (1 mol%), benzyl alcohol (1 mmol), mono- or diamine (1 mmol/0.5 mmol) and Cs_2CO_3 (0.2 mmol) were placed in a microwave vial containing a stirrer bar. The mixture was irradiated at 115 °C for 120 min. The crude product was purified by column chromatography on silica gel 100–200 mesh using a mixture of hexane/EtOAc (3:1) as eluent.

2.5 | General procedures for X-ray crystallography

Suitable crystals of compounds **2**, **3** and **4** were coated and selected in Fomblin® oil, mounted on a loop and data collected using the graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using the Bruker SMART software and refined using Bruker SAINT on all observed reflections.[22] Absorption corrections were applied using SADABS.[23] The structures were solved by direct methods using SIR97.[24] Structure refinement was done using SHELXL.[25] These programs are part of the WinGX software package version 1.80.05.[26] The hydrogen atoms were inserted in fixed positions and allowed to refine riding on the parent carbon atom except on the NH groups that were located in the electron density map. Torsion angles, mean square planes and other geometrical parameters were calculated using SHELX.[25] Crystallographic and experimental details of data collection and crystal structure determinations are available in Table 1. Illustrations of the molecular structures were made with ORTEP-3 for Windows.[27] The poor diffracting power and crystal quality of **2** (as attested by the R_{int} value obtained) precluded the final refinement to lower the *R* values.

Data for structures **2**, **3** and **4** were deposited in CCDC under the deposit numbers 1858584, 1858585 and 1858586, respectively, and can be obtained by free of charge from The Cambridge Crystallographic Data Centre.

3 | RESULTS AND DISCUSSION

A collection of 2-aminofluorene imine derivatives were synthesised by the reactions of 2-aminofluorene with salicylaldehyde (**HL^1**), o-vanillin (**HL^2**), 2-hydroxy-1-naphthaldehyde (**HL^3**) and pyrrole-2-carboxaldehyde (**HL^4**). The compounds **HL$^{1–3}$** were previously described.[21] Using a similar methodology, N-((1H-pyrrol-2-yl)methylene)-9H-fluorene-2-amine, **HL^4**, was isolated in 84% yield. The treatment of [Ru(η^6-*p*-cymene)Cl_2]$_2$ with **HL^i** (***i*** = 1–4) in a 1:2 molar ratio led to the formation of complexes of general formula [Ru(η^6-*p*-cymene)(Cl)(L^i)] (**1**–**4**) in high yields (Scheme 2).

All ligand precursors and ruthenium complexes are air and moisture stable and readily soluble in organic solvents like acetonitrile, benzene, chloroform, dichloromethane, dimethylformaide, dimethylsulfoxide, ethanol and methanol. The new compounds were characterised by elemental analysis and spectroscopic methods (IR, UV–Vis and NMR). Ruthenium(II) complexes **2**–**4** were further characterised by the single crystal X-ray diffraction.

The IR spectra of the ligand precursors and of the ruthenium(II) complexes display sharp bands at 1659 cm^{-1} and 1314 cm^{-1} that are assigned to the

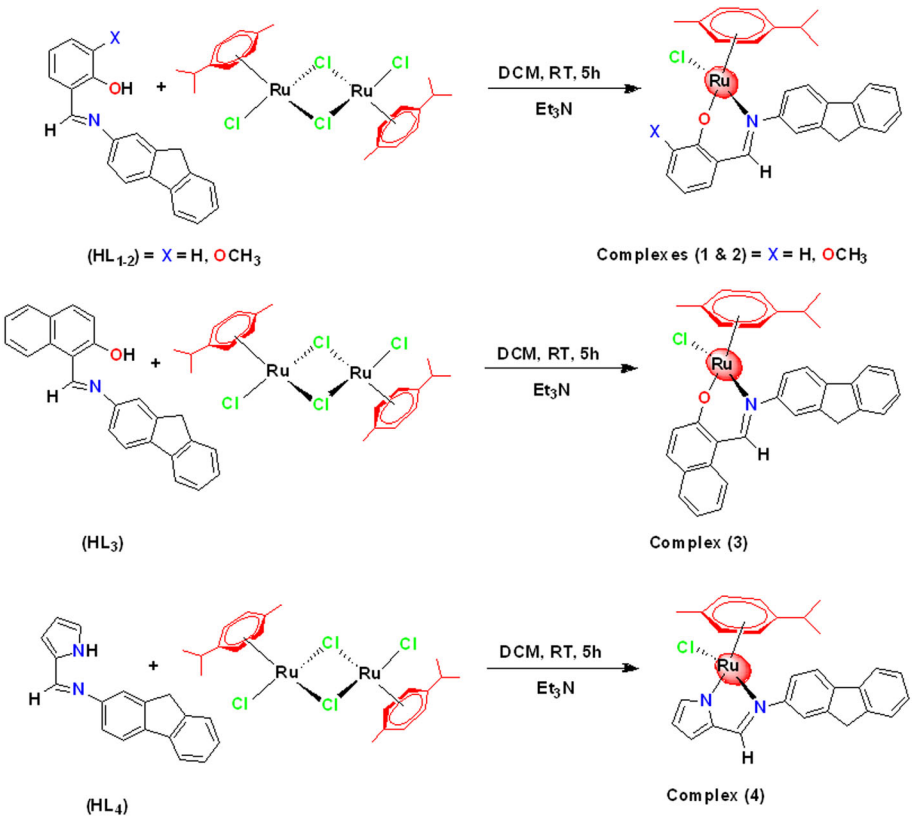
TABLE 1 Crystal data and structure refinement for compounds **2–4**

Compound	2	3	4
Empirical formula	C_{31} H_{30} Cl N O_2 Ru	C_{34} H_{30} Cl N O Ru	C_{28} H_{27} Cl N_2 Ru
Formula weight	585.08	605.11	528.04
Temperature (K)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	$P2_1/c$	$P2_1/c$
Unit Cell Dimensions:			
a (Å)	15.113(1)	19.461(2)	13.949(1)
b (Å)	14.323(1)	7.6151(6)	8.0893(6)
c (Å)	23.844(2)	19.054(2)	21.084(1)
α(°)	90	90	90
β(°)	90	106.447(5)	105.454(3)
γ(°)	90	90	90
Volume ($Å^3$)	5161.4(7)	2708.2(5)	2293.1(3)
Z	8	4	4
Calculated density (g m^{-3})	1.506	1.484	1.530
Absorption coefficient (mm^{-1})	0.741	0.706	0.819
F (000)	2400	1240	1080
Crystal size (mm)	0.06 x 0.08 x 0.14	0.20 x 0.22 x 0.30	0.04 x 0.10 x 0.22
Theta range for data collection (°)	2.599–25.752	3.206–29.643	2.939–25.735
Limiting indices	$-16 \le h \le 18$, $-17 \le k \le 17$, $-29 \le l \le 29$	$-27 \le h \le 21$, $-10 \le k \le 9$, $-23 \le l \le 26$	$-16 \le h \le 17$, $-9 \le k \le 9$, $-25 \le l \le 23$
Reflections collected/unique [R_{int}]	39481/4913 [0.1776]	28171/7620 [0.0588]	21036/4360 [0.0670]
Completeness to θ (%)	99.9 (θ = 25.242)	99.8 (θ = 25.242)	99.9 (θ = 25.242)
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	4913/0/329	7620/0/346	4360/0/292
Goodness-of-fit on F^2	0.928	1.021	0991
Final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0519$, $wR_2 = 0.0995$	$R_1 = 0.0352$, $wR_2 = 0.0769$	$R_1 = 0.0346$, $wR_2 = 0.0776$
R indices (all data)[a]	$R_1 = 0.1233$, $wR_2 = 0.1160$	$R_1 = 0.0500$, $wR_2 = 0.0815$	$R_1 = 0.0494$, $wR_2 = 0.0823$
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Largest diff. Peak/hole (e $Å^{-3}$)	0.584 and − 0.832	0.472 and − 0.439	0.991 and − 0.684

[a]$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $wR_2 = \{\Sigma[w(F^2_0 - F^2_c)^2]/\Sigma[w(F^2_0)^2]\}^{1/2}$.

stretching of azomethine ($\nu_{C=N}$) and phenolic ($\nu_{C\text{-}O}$) bonds, respectively. A broad band at 3453 cm^{-1} and a sharp band at 3008 cm^{-1} are due to the vibrations of the $\nu_{O\text{-}H}$ and $\nu_{N\text{-}H}$ bonds of the ligand precursors, respectively. The disappearance of the latter bands and the simultaneous increase in the C-O stretching band in the region of 1386–1383 cm^{-1} indicate the coordination to the metal through the oxygen of the phenolate or naphtholate moieties in the case of complexes **1–3** and through the nitrogen of the pyrrolate fragment in complex **4**. Moreover, the azomethine stretching band ($\nu_{C=N}$) is shifted to lower wavenumber, in the region of 1616–1563 cm^{-1}, attesting the coordination of the imine nitrogen to ruthenium(II).[28]

The electronic spectra of the ligand precursors (**HL^i**) display two absorption bands observed at 274–262 nm and 408–348 nm that are due to π-π* and n-π* charge transfer transitions, respectively. Analogously to the previously reported ruthenium(II) *p*-cymene complexes,[29] the spectra of complexes **1–4** show three characteristic peaks, namely high-intensity π-π* bands at 267–262 nm, medium-intensity n-π* bands at 365–331 nm and also



SCHEME 2 Synthesis of ruthenium(II) *p*-cymene complexes **1–4**

bands at 458–427 nm that are assigned to the Ru(dπ)-to-(Lπ*) charge transfer transitions (MLCT).[23]

The proton NMR spectra of the ligand precursors display several resonances in the range δ 9.38–6.37 ppm assigned to the aromatic protons and singlets in the region of δ 9.40–8.59 ppm that are attributed to the azomethine protons (*H*C=N). The methylene protons of fluorene moiety and the methoxy group of **HL^2** give rise to singlets at δ 3.98–3.94 ppm and δ 3.85 ppm, respectively. The O*H* and N*H* resonances of the phenol, naphthol or pyrrole groups appear at low field (δ 15.70–13.43 ppm and δ 10.62 ppm), in accordance with its acidic properties. As expected, the latter protons are not observed in the proton NMR spectra of the ruthenium complexes. The down field shift to δ 8.79–8.14 ppm registered for the azomethine protons also confirms the coordination to ruthenium. The resonances assigned to the other protons of the ligands **L$^{1–4}$** are similar to those of the ligand precursors. In agreement with the structures proposed for complexes **1–4**, the *p*-cymene protons gave rise to 4 doublets in the range δ 5.42–4.22 ppm and the ^{1}H NMR spectra of Figure S1-S8 see the supporting information.

The ^{13}C NMR spectra of complexes **1–4** further support the proposed structures. The peaks assigned to the carbons of the azomethine (H***C***=N) and the phenolate/naphtholate groups of the ligands[21] are shifted downfield and appeared at δ 168.8–165.1 ppm and δ 157.6 ppm, respectively. The two isopropyl methyl carbons (C (***C***H$_3$)$_2$) of *p*-cymene are observed at δ 8.8–8.1 ppm and the methine carbons (***C***H (CH$_3$)$_2$) appear at δ 22.8–22.6 ppm. In the complexes, the methoxy (O***C***H$_3$), methylene (***C***H$_2$), and *p*-cymene methyl (***C***H$_3$) carbons are observed close to δ 56 ppm, δ 37 ppm, and δ 21 ppm, respectively.The ^{13}C NMR and mass spectra of Figure S9-S17 see the supporting information.

The solid-state molecular structures of complexes **2–4** were determined by single crystal X-ray diffraction. Compound **2** crystalizes in the orthorhombic space group Pbca while both **3** and **4** crystalize in the monoclinic space group P2$_1$/c. ORTEP depictions of the molecular structures of **2–4** are displayed in Figures 3–5, respectively, and relevant distances and angles are shown in Table 2.

All complexes display a typical three-legged piano-stool geometry with distances between ruthenium and the ring centroids (Ru-Ph$_{CT}$) ranging from 1.666(2) to 1.6688(8) Å. The distances between the metal centre and the chloride and the bidentate ligands are with the usual ranges observed for this type of bonds.[30] These values reveal that no steric or electronic effects were perceived in the bidentate N,O- and N,N-ligand moieties. In general, the structural parameters obtained for **2–4** agree with those reported for other [Ru(η^6-*p*-cymene)(Cl)(L)] complexes.[31]

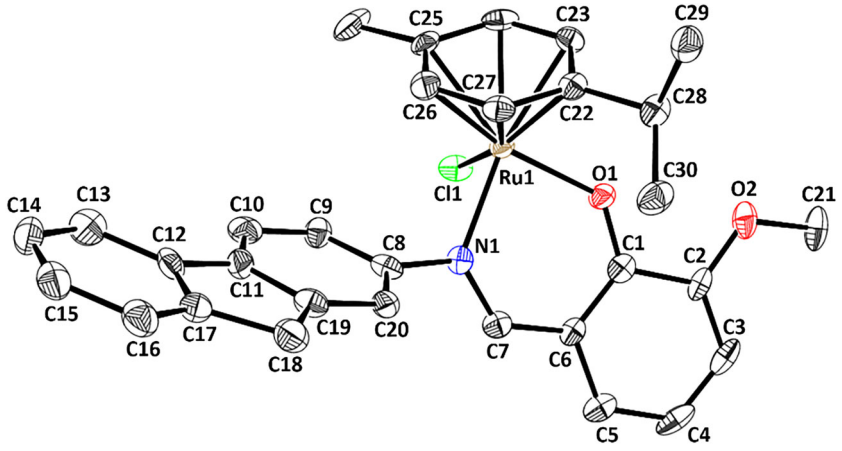


FIGURE 3 ORTEP diagram of **2** with thermal ellipsoids at 40% probability level. Hydrogen atoms are omitted for clarity

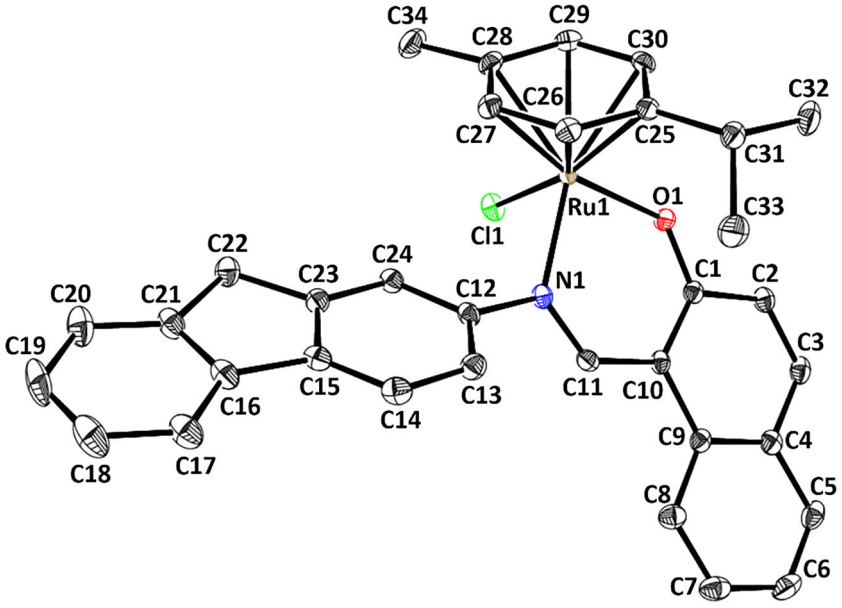


FIGURE 4 ORTEP diagram of **3** with thermal ellipsoids at 40% probability level. Hydrogen atoms are omitted for clarity

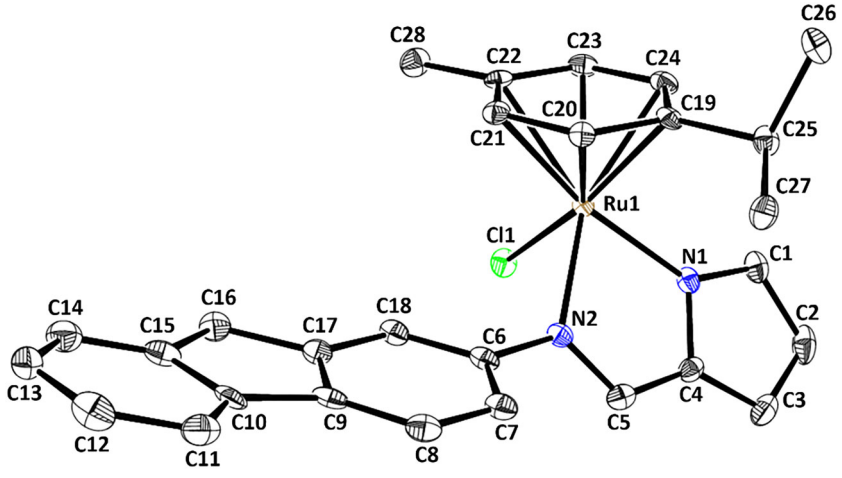


FIGURE 5 ORTEP diagram of **4** with thermal ellipsoids at 40% probability level. Hydrogen atoms are omitted for clarity

TABLE 2 Selected bond lengths (Å) and angles (°) for compounds **2–4**

	Ru-N	Ru-Cl	Ru-X	Ru-[C_6Plane]
2	2.081(4)	2.431(1)	2.043(3)	1.666(2)
3	2.083(2)	2.4255(5)	2.055(1)	1.6688(8)
4	2.104(2)	2.4095(8)	2.052(2)	1.676(1)
	Cl-Ru-N	N-Ru-X		X-Ru-Cl
2	84.5(1)	87.6(2)		85.8(1)
3	85.15(5)	87.70(6)		84.24(4)
4	85.35(7)	76.7(1)		86.67(8)

3.1 | Catalytic studies for the synthesis of imines via reactions of benzyl alcohol and amines

Complexes **1–4** were used as catalysts for the syntheses of imines from reactions of benzyl alcohol with amines. These reactions were carried out using different energy supply methods, namely, thermal heating, sonochemical and microwave irradiation. The suitability and effectiveness of the three methods are compared. The catalytic reactions were optimised having in consideration the catalyst, the catalysts loading, the temperature, the solvent and the base.

In order to evaluate the role of the solvent on the imination reaction, benzyl alcohol and aniline were used as model substrates and the reactions were carried out in the presence of Cs_2CO_3 and the ruthenium catalyst **4**. The results are listed in Table 3. Among the various solvents tested, the best solvent to perform the reaction is toluene (entry 4), which led to an excellent conversion of 95%. Highly polar solvents as acetonitrile, dichloromethane, DMSO and chloroform (entries 6, 2, 5 and 7, respectively) led to low conversions, in the range 43–57%. Methanol and benzene also led to high conversions of 80% and 78%, respectively (entries 3, 1).

The comparison of catalysts **1–4** was carried out in toluene at 110 °C for 12 h, using benzyl alcohol, aniline and Cs_2CO_3 as reference reagents. In these conditions, all catalysts are active within the range 73–95% yield of imine (see Table 4). The higher activity is shown by

TABLE 4 Screening of half-sandwich ruthenium complexes 1–4 for imines formation via benzyl alcohol and aniline[a]

Entry	Catalyst	Yield[b] (%)
1	[Ru(*p*-cymene)(Cl)(L^1)] **(1)**	73
2	[Ru(*p*-cymene)(Cl)(L^2)] **(2)**	85
3	[Ru(*p*-cymene)(Cl)(L^3)] **(3)**	88
4	[Ru(*p*-cymene)(Cl)(L^4)] **(4)**	95

[a]Conditions: benzyl alcohol (1 mmol), aniline (1 mmol), catalyst **1–4** (1.0 mol%), Cs_2CO_3 (0.2 mmol) in the presence of toluene (5 ml) at 110 °C for 12 hr.

[b]Isolated yield.

TABLE 5 Effect of the catalyst loading[a]

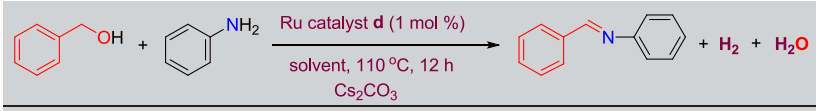
Entry	Ruthenium catalyst (mol %)	Yield[2](%)[a]
1[c]	-	05
2	0.5	89
3	1.0	95
4	1.5	91
5	2.0	72
6	2.5	57

[a]Conditions: benzyl alcohol (1 mmol), aniline (1 mmol), catalyst **4** (0.5–2.5 mol%), Cs_2CO_3 (0.2 mmol) in the presence of toluene (5 ml) at 110 °C for 12 hr.

[b]Isolated yield.

[c]Absence of catalyst.

TABLE 3 Screening of different solvents for the synthesis of imines[a]



Entry	Solvent	Yield[b] (%)
1	Benzene	78
2	Dichloromethane	48
3	Methanol	80
4	Toluene	95
5	Dimethyl sulfoxide	57
6	Acetonitrile	42
7	Chloroform	56

[a]Conditions: benzyl alcohol (1 mmol), aniline (1 mmol), catalyst **4** (1.0 mol%), Cs_2CO_3 (0.2 mmol) in the presence of solvent (5 ml) at 110 °C for 12 hr.

[b]Isolated yield.

complex **4** that displays the best ligand donor set. This result suggests that the oxidative addition of the benzyl alcohol, which is the first step for the formation of the aldehyde is also the limiting step of the imination reaction. Complexes **2** and **3** display essentially the same activity and are better catalysts than **1**. The better performance of complex **2** in comparison with **1** is in line with the requirement of good electron donor sets already justified, but the possibility of a stereochemical protection of the *ortho*-methoxy group may not be excluded, as the bulkiness of the *o*-OMe group may avoid dimerization thought phenolate bridges. This process may also be restricted by the naphthoic moiety of complex **3** and is likely the reason for the similar activity of complexes **2** and **3**.

The effect of the concentration of the catalyst (see Table 5) was assessed using complex **4** between 0.5 and 2.5 mol%. A maximum activity was obtained at 1 mol% catalyst. The observation of a decrease in the reaction yield for the higher ruthenium concentration is consistent with the assumption that the most active catalysts are monomeric species.

TABLE 6 Screening of different bases for the synthesis of imines[a]

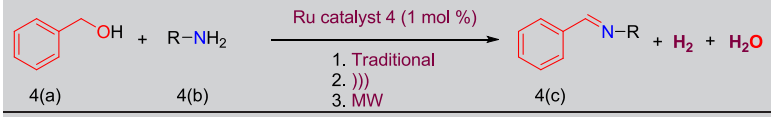
Entry	Base	Yield[b] (%)
1	Na_2CO_3	83
2	NaH	78
3	NaOH	67
4	KOH	77
5[c]	-	13
6	Cs_2CO_3	95
7	K_2CO_3	86

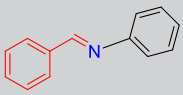
[a]Conditions: benzyl alcohol (1 mmol), aniline (1 mmol), catalyst **4** (1.0 mol%), base (0.2 mmol) in the presence of toluene (5 ml) at 110 °C for 12 hr.

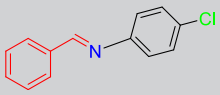
[b]Isolated yield.

[c]Absence of base.

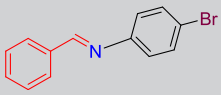
TABLE 7 Assessment of substrate scope for the synthesis of imines using catalyst 4[a]



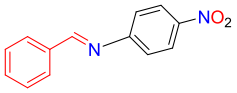

4c1, (e95, f92, g99)%



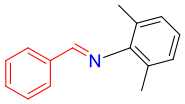
4c2, (e83, f82, g84)%

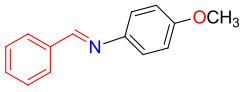


4c3, (e89, f82, g85)%

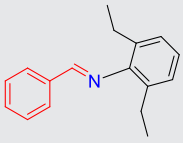


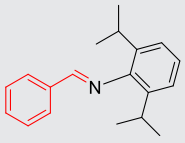
4c4, (e88, f86, g85)%

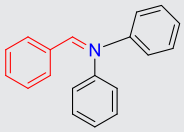

4c5, (e89, f91, g89)%

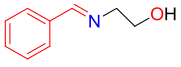


4c6, (e90, f90, g91)%

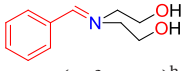

4c7, (e71, f77, g71)%


4c8, (e95, f74, g76)%

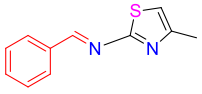

4c9, (e67, f66, g69)%



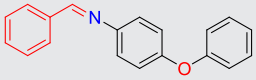
4c10, (e60, f57, g69)%

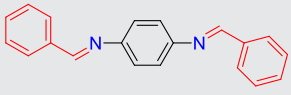


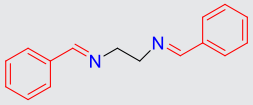
4c11, (e, f, g NR)[h] %

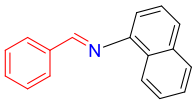


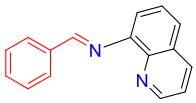
4c12, (e83, f83, g95)%

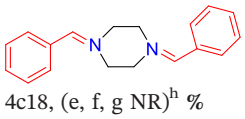

4c13, (e65, f65, g88)%


4c14, (e75, f64, g90)%


4c15, (e83, f62, g64)%


4c16, (e72, f87, g90)%


4c17, (e74, f52, g80)%


4c18, (e, f, g NR)[h] %

[**a**] **Conventional method 1:** toluene (5 ml), 110 °C, 12 hr.; **Ultrasonic method 2:** solvent-free, 90 °C, 6.5 hr.; **Microwave method 3:** solvent-free, 115 °C, 2 h.; the total amount of substrates (benzyl alcohol and amine), catalyst **4** and Cs_2CO_3 for all the three methods is the same. Isolated yield [%] for conventional method (**e**), ultrasonic method (**f**) and microwave method (**g**). [**h**] no reaction.

The requirement of a base to initiate an efficient imination reaction was confirmed by the low yield of 13% obtained in the absence of base when benzyl alcohol, aniline and catalyst **4** were reacted for 12 h, in toluene at 110 °C (see Table 6, entry 5). The efficiency of several bases, as metal carbonates (K_2CO_3, Na_2CO_3 and Cs_2CO_3), hydroxides (NaOH and KOH) and sodium hydride was made from the comparison of reactions carried out in the same experimental conditions. Strong bases, such as potassium hydroxide, sodium hydroxide and sodium hydride gave moderate conversions (entries 2, 3 and 4 respectively), but lower than the ones obtained for reaction using metal carbonates. From the latter, caesium carbonate proved being the most useful base leading to an excellent yield, 95% (entry 6).

Having established an optimised protocol for the catalytic synthesis of imines we tested the reaction using several amines to evaluate the scope of application of our procedure using 3 different energy supply methodologies, namely traditional heating, sonochemical and microwave irradiation. The results are listed in Table 7 and the ^{1}H NMR spectra of Figure S18-S24 see the supporting information. The first aspect that is worth noting is that in general the reactions display moderately high to very high yields, the only exceptions being the secondary aliphatic amines diethanolamine (4c11) and piperazine (4c18). Electron attractor *p*-substituted anilines (4c2-4c4) react with lower yields than electron donor *para*- or *ortho*-substituted ones (4c5-4c8), which in turn are slightly less reactive than aniline. For these reactions, there are no significant differences between thermal heating, sonication or microwave irradiation, except in the case of 2,6-diisopropylaniline that displays *ortho* bulky groups and shows a clear beneficial effect of thermal heating. The same preference is observed for the reaction of ethylenediamine (4c15). All other reactions (4c12–14, 4c16, 4c17) show a beneficial effect when carried out under microwave irradiation. This result is important not only because the substrates are either functionalised or more extended aromatic amines but also because the reactions are carried out without solvent addition and require short reaction times.[6b, d, 13, 32]

4 | CONCLUDING REMARKS

This work describes the synthesis, characterization, molecular structures and catalytic activity of Ru(II) complexes in the dehydrogenative coupling of benzyl alcohol with amines. The reactions proceed with moderately high to excellent yields for a large variety of mono- and diamines. While aromatic amines give, in general, better results, ethylene diamine and piperazine led to very good yields. Microwave irradiation revealed an excellent method to perform the generality of the catalytic reactions having in account these reactions are faster than the ones thermally activated, lead to better or the same yields and are carried out in solvent-free conditions.

There are several positive points that should be mentioned about the study carried out in this work, namely, the use of an easily prepared and easily to handle catalyst, the use of solvent-free conditions, a simple workup procedure, a catalytic process that only produces water as by-product and does not require the use of molecular sieves and good to high conversion for a wide range of amines.

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