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Chiral Oxazolidine fused N-heterocyclic Carbene Complexes of Rhodium and Iridium and their Utility in Asymmetric Transfer Hydrogenation of Ketones

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Keywords: oxazolidine-fused imidazole based N−heterocyclic carbenes • chiral fused bicyclic NHC • rhodium • iridium • asymmetric transfer hydrogenation

Abstract: Catalytic potential of a new N–heterocyclic carbene ligand derived from a chiral fused bicyclic ring scaffold, having a restricted rotation along the C–N bond bearing the chiral auxiliary, have been explored in transition metal mediated asymmetric transfer hydrogenation reactions of ketones. In particular, the chiral oxazolidine fused N–heterocyclic carbene precursors namely, {(3*S*)-3-R-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-6-ium iodide (R= *sec*-butyl (**1f**), *i*-butyl (**2f**), *i*-propyl (**3f**)} were synthesized from commercially available optically pure amino acids in a multi-step sequence avoiding tedious chiral resolution protocol. The reaction of the chiral imidazolium iodide salts (**1**–**3**)**f** with Ag_2O yielded the corresponding silver complexes (**1**–**3**)**g**, which when treated with $\{(COD)MCl\}_2$ (M = Rh, Ir) gave the rhodium(I) (**1**–**3**)**h** and the iridium(I) (**1**–**3**)**i** complexes. The rhodium(I) (**1**–**3**)**h** and the iridium(I) (**1**–**3**)**i** complexes conveniently carried out the asymmetric transfer hydrogenation of acetophenones for a wide variety of substrates ranging from the electron rich ones namely, 4–methyl acetophenone, 3,4 dimethyl acetophenone, 4–*t*-butyl acetophenone, 4–methylthio acetophenone to the electron deficient ones namely, 4–bromo acetophenone, 4–chloro acetophenone, 4–fluoro acetophenone, 4–nitro acetophenone and 3–fluoro acetophenone in moderate to good yields (*ca*. 18–95 %) but low enantioselectivities (*ca*. 4–41 %).

Introduction

The development of new motifs as ligand platforms for catalysis remains an active area of research for the phenomenally successful N-heterocyclic carbenes (NHC's).[1-3] In this regard, the fusion of two immensely successful ligands in homogenous catalysis like that of the oxazolidines[4] and the imidazole based N-heterocyclic carbenes[5] has resulted in an interesting new breed of fused bicyclic N-heterocyclic ligand derived from a hybrid oxazolidine-imidazole motif.[6-9] In asymmetric catalysis, owing to its unique feature of having a restricted rotation along N−C bond housing the chiral substituent, this type of ligands exhibit promising enantioselectivities over conventional chiral ligands in many reactions namely, Micheal addition,[10] benzoin condensation,[11] α−arylation,[12] Stetter reaction,[13] Coates-Claisen rearrangement[14] and hydration of α−halo aldehydes.[15] For example, under Ligand Assisted Catalysis (LAC) conditions for the asymmetric Michael addition reaction of 1,3-diphenylpropane-1,3-dione and (*E*)-(2-nitrovinyl)benzene, a fused bicyclic N-heterocyclic carbene ligand namely, (5a*S*,10b*R*)-2-mesityl-4,5a,6,10b-tetrahydroindeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-2-ium tetrafluoroborate, having a restricted rotation around N–C bond, exhibited a higher enantiomeric excess (*ee*) of 76 %, whereas another chiral N-heterocyclic carbene ligand namely, (1,3-bis((*S*)-1-phenylethyl)-1*H*-imidazol-3-ium tetrafluoroborate, having a free rotation around the N–C bond, showed no chiral induction under analogous conditions.[16]

Despite the promise, the multi-step sequences required for synthesising these fused bicyclic oxazolidine N−heterocyclic carbene ligands has somewhat constricted a larger applicability of these ligands, and this has attracted our attention. Specifically, with our interest being in exploring the catalytic utility of different ring types of the N–heterocyclic carbene ligands,[17-20] spanning from the ubiquitous 5-membered cyclic imidazole[21-26] and triazole[27-29] based

ones to the less common variety like, the acyclic 6-membered N−heterocyclic carbenes,[30] the bicyclic imidazo[1,2-a]pyridine[31, 32] and the tricyclic triazolooxazine derived ones,[33] we became interested in exploring the catalytic exploits of one such less frequently encountered chiral bicyclic oxazolidine fused N-heterocyclic carbene ligands. Furthermore, as much of the catalysis reported for these bicyclic oxazolidine fused N−heterocyclic carbene based systems were performed under *in-situ* Ligand Assisted Catalysis (LAC) conditions,[8] with no examples known of well-defined transition metal complexes, we decided to employ structurally characterized molecular complexes for our study in asymmetric catalysis in order to obtain a better insight on the catalyst mode of action.

To begin with, we chose to study the asymmetric transfer hydrogenation of ketones for its scope for a larger applicability.[34, 35] Though the hydrogenation of ketones to the corresponding alcohols is achieved by conventional stoichiometric reducing agents like $NaBH_4$, $LiAlH_4$ and other hydrides, the subsequent economic considerations and the hazards involved in handling post–reaction wastes in scale up processes calls for cleaner methodologies for this simple reaction. In this scenario, the catalytic hydrogenation of ketones in both achiral and chiral fashion has gained prominence in recent times.[36] It is interesting to note that, though the transition metal complexes of N–heterocyclic carbenes have been extensively studied for the transfer hydrogenation of ketones to alcohols,[37, 38] the reports of the related chiral versions are surprisingly few.[39-43]

Here in this manuscript, we report the design and synthesis of a less explored chiral oxazolidine fused N-heterocyclic carbene ligand using a multi-step synthetic protocol avoiding tedious chiral resolution procedure by starting from cheap commercially available

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enantiopure amino acids. We further demonstrate the utility of the rhodium (**1**−**3**)**h** and the iridium (**1**−**3**)**i** complexes of these ligands in asymmetric transfer hydrogenation of ketones (Figure 1).

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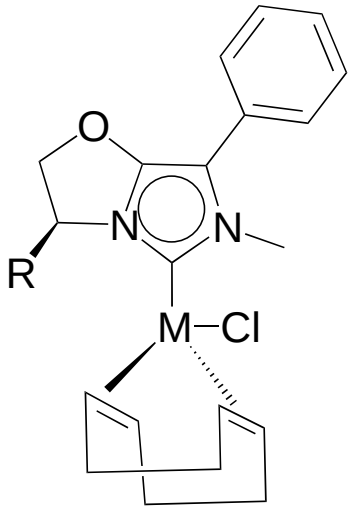
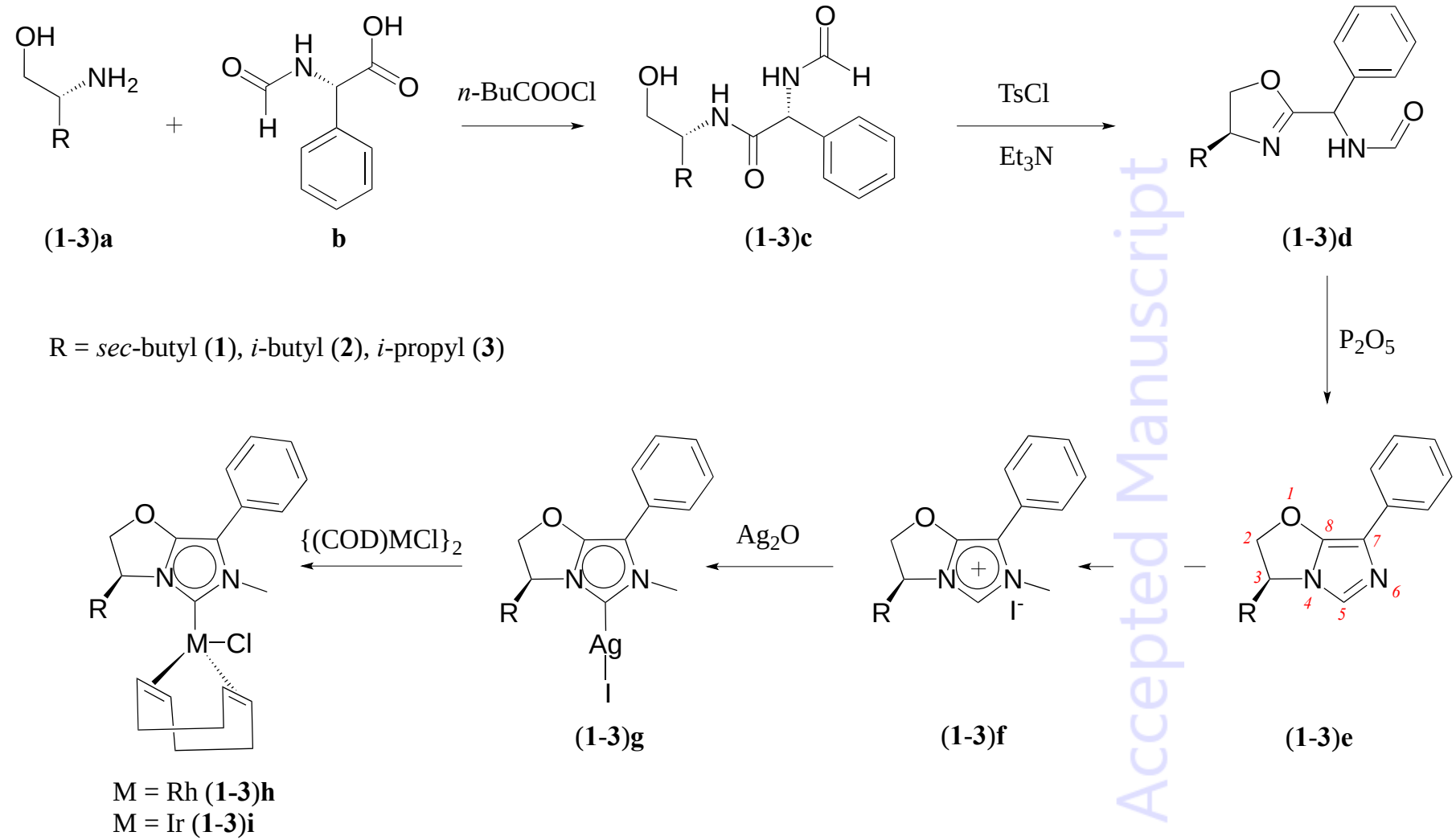


R = *sec*-butyl, M = Rh (**1h**), Ir (**1i**)
R = *i*-butyl, M = Rh (**2h**), Ir (**2i**)
R = *i*-propyl, M = Rh (**3h**), Ir (**3i**)

Figure 1. Rhodium(I) (**1**–**3**)**h** and iridium(I) (**1**−**3**)**i** complexes supported over NHC ligands derived from chiral oxazolidine-fused imidazole scaffolds synthesized from commercially available amino acids.



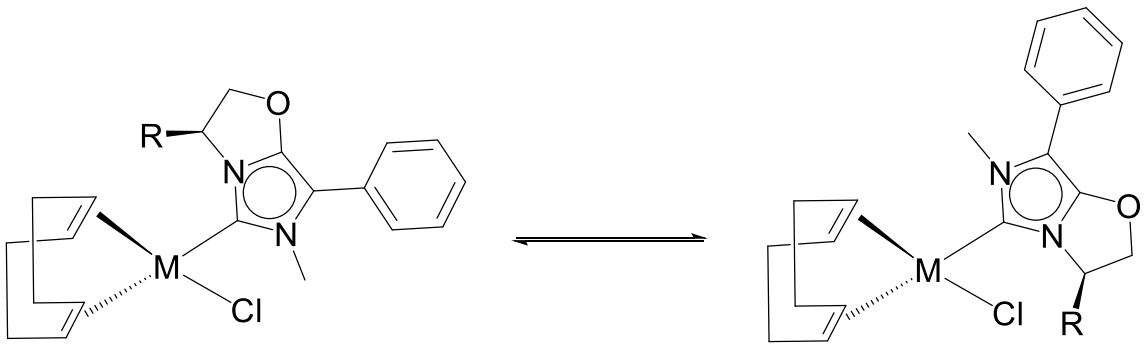
Scheme 1. Synthetic protocol for the chiral oxazolidine-fused imidazole derived N-heterocyclic carbene complexes of rhodium(I) (**1**−**3**)**h** and iridium(I) (**1**−**3**)**i**.

Results and discussion

A new class of chiral oxazolidine fused N–heterocyclic carbene ligand namely, {(3*S*)-3-R-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene} (R = *sec*-butyl, *i*-butyl, *i*-propyl), having a restricted rotation along the C–N bond containing the chiral centre, has been synthesized using a multi-step sequence (Scheme 1). The strategy successfully avoids tedious chiral resolution steps by making use of cheap and commercially available optically pure amino acids. In particular, the chiral oxazolidine fused imidazoles (**1**–**3**)**e** were constructed in four steps, starting from the reaction of amino alcohols (**1**–**3**)**a** with (*R*)-2-formamido-2-phenylacetic acid (**b**) in presence of *n*-butyl chloroformate and N-methyl morpholine as a base at –30 °C producing an amide intermediate (**1**–**3**)**c** in 20–49 % yield. The intramolecular cyclization of the amide intermediate (**1**–**3**)**c** in presence of *p*-toluene sulphonyl chloride (TsCl) at room temperature resulted in the formation of the formyl oxazole derivatives (**1**–**3**)**d** in 35–66 % yield. A second intramolecular cyclization leading to the chiral bicyclic oxazolidine fused imidazole compounds (**1**–**3**)**e** was affected by the dehydration of formyl oxazole (**1**–**3**)**d** in presence of anhydrous P_2O_5 in 46–66 % yield.

The alkylation of the oxazolidine fused imidazoles (**1**–**3**)**e** with methyl iodide gave the corresponding chiral bicyclic oxazolidine fused N–heterocyclic carbene precursors (**1**–**3**)**f** in 51–96 % yield. The formation of (**1**–**3**)**f** was evident by the appearance of a characteristic downfield NC*H*N peak at *ca* 9.74 – 9.89 ppm in the ^{1}H NMR spectrum. The treatment of chiral bicyclic oxazolidine fused imidazolium iodide salts (**1**–**3**)**f** with Ag_2O at room temperature yielded the corresponding silver complexes (**1**–**3**)**g** in

85–90 %. The formation of silver complexes (**1**–**3**)**g** was characterized by the disappearance of the NC*H*N peak of the reactant (**1**–**3**)**f** in ^{1}H NMR spectrum along with the appearance of the downfield shifted silver bound N*C*N (Ag–$C_{carbene}$) resonance at *ca.* 169.4 – 170.8 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum. The rhodium complexes (**1**–**3**)**h** were subsequently prepared by a transmetallation reaction from the silver complexes (**1**–**3**)**g** by the treatment with $\{(COD)RhCl\}_2$ at room temperature in 85–97 % yield. The ^{1}H NMR spectrum of (**1**−**3**)**h** revealed the presence of two isomers in a *ca.* 60 : 40 ratio at room temperature as observed from the N-C*H*$_3$ resonance at *ca* 4.03 – 4.05 ppm for the major isomer and at *ca*. 4.00 **–** 4.01 ppm for the minor isomer. The existence of these isomers in solution arise due to the rotation around the M−$C_{carbene}$ bond in these complexes (Scheme 2), which was further confirmed by variable temperature ^{1}H NMR experiment performed for a representative complex **1h**, where the coalescence of N-C*H*$_3$ resonance observed at 60°C (Supporting Information figures S300 and S301). The $^{13}C\{^{1}H\}$ NMR spectrum showed the expected Rh−$C_{carbene}$ coupling manifesting as a doublet at 176.3 ppm (J_{Rh-C} = 48 Hz) for **1h**, 171.7 ppm (J_{Rh-C} = 50 Hz) for **2h** and at 171.9 ppm (J_{Rh-C} = 50 Hz) for **3h**.



M = Rh, Ir

Scheme 2. Conformational exchange in complexes (**1**−**3**)**h** and (**1**−**3**)**i.**

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The iridium complexes (**1**–**3**)**i** were analogously obtained from the silver complexes (**1**–**3**)**g** by the transmetallation reaction with {(COD)IrCl}$_2$ in 45–96 % yield at room temperature. Both the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of iridium complexes (**1**−**3**)**i** were similar to that of the rhodium complexes (**1**−**3**)**h** in terms of the observation of two isomers in solution.

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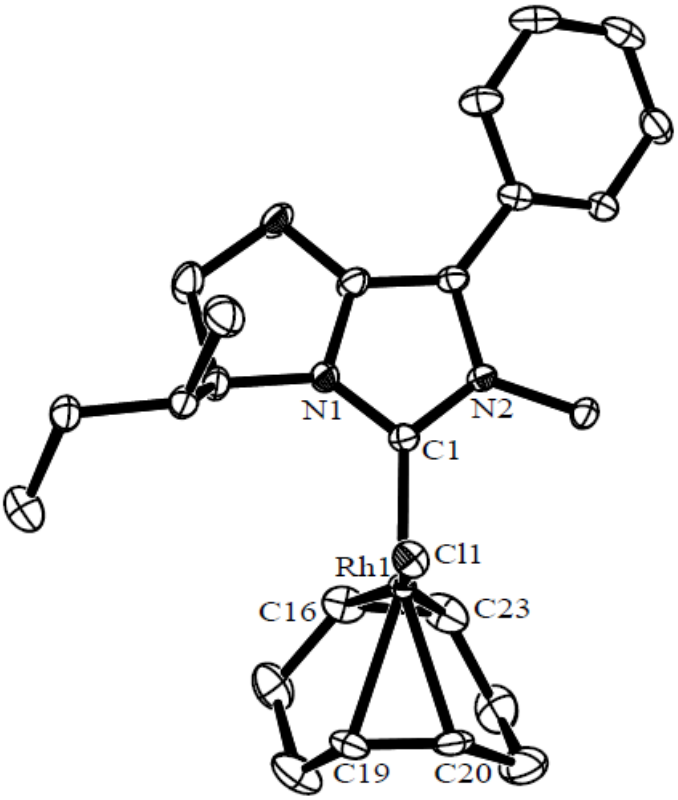

Figure 2. ORTEP of **1h** with thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Rh(1)−C(1) 2.0209(18), Rh(1)−Cl(1) 2.3823(5), Rh(1)−C(16) 2.100(2), Rh(1)−C(23) 2.1004(19), Rh(1)−C(20) 2.185(2), Rh(1)−C(19) 2.2102(18), C(1)−Rh(1)−Cl(1) 89.91(5), C(1)−Rh(1)−C(16) 89.49(7), C(1)−Rh(1)−C(23) 92.15(8), C(1)−Rh(1)−C(19) 162.16(8), C(1)−Rh(1)−C(20) 161.38(8).

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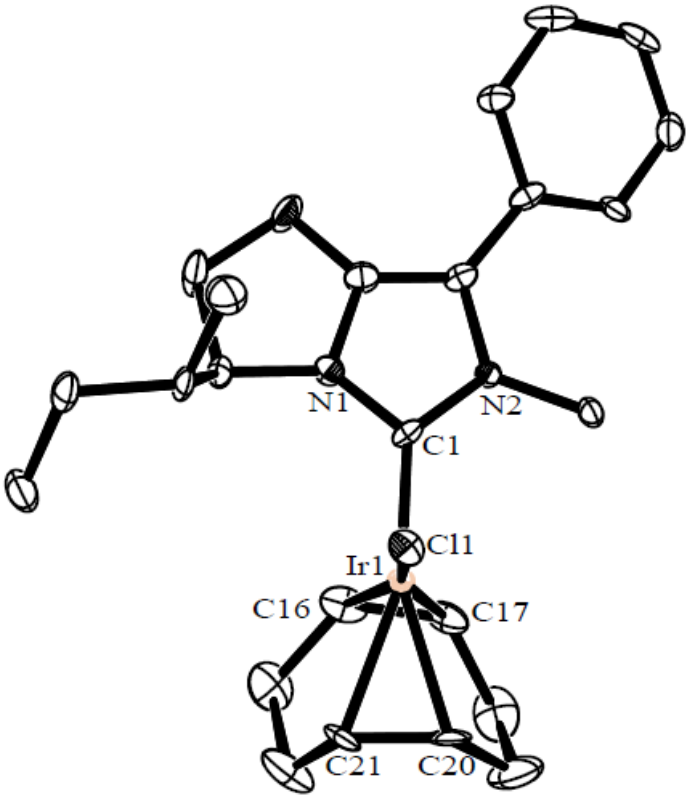

Figure 3. ORTEP of **1i** with thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Ir(1)−C(1) 2.018(5), Ir(1)−Cl(1) 2.3670(13), Ir(1)−C(17) 2.096(5), Ir(1)−C(16) 2.096(5), Ir(1)−C(20) 2.154(5), Ir(1)−C(21) 2.193(5), C(1)−Ir(1)−Cl(1) 90.68(14), C(1)−Ir(1)−C(16) 89.3(2), C(1)−Ir(1)−C(17) 92.4(2), C(1)−Ir(1) −C(20) 160.6(2), C(1)−Ir(1)−C(21) 161.89(19).

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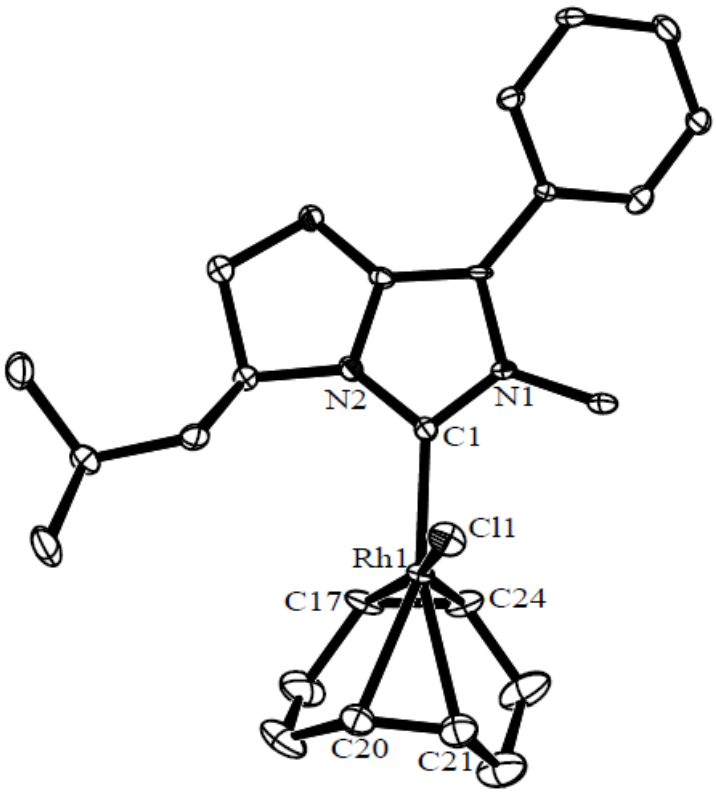

Figure 4. ORTEP of **2h** with thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Rh(1)−C(1) 2.023(4), Rh(1)−Cl(1) 2.376(10), Rh(1)−C(24) 2.091(4), Rh(1)−C(17) 2.104(4), Rh(1)−C(20) 2.187(4), Rh(1)−C(21) 2.200(4), C(1)−Rh(1)−Cl(1) 88.90(10), C(1)−Rh(1)−C(24) 91.55(15), C(1)−Rh(1)−C(17) 92.63(15), C(1)−Rh(1)−C(20) 159.25(14), C(1)−Rh(1)−C(21) 164.32(15).

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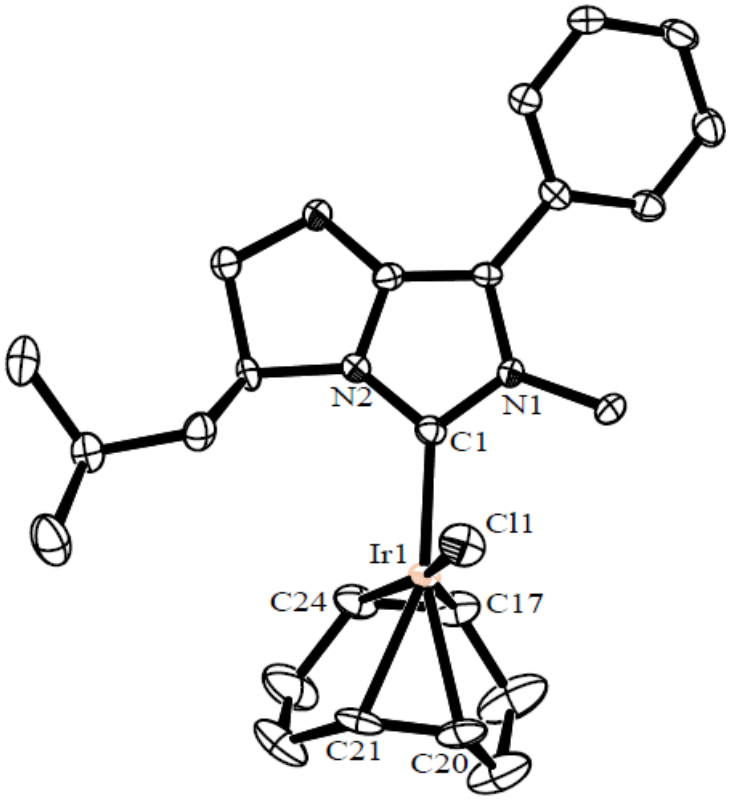

Figure 5. ORTEP of **2i** with thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Ir(1)−C(1) 2.026(3), Ir(1)−Cl(1) 2.3619(9), Ir(1)−C(17) 2.092(3), Ir(1)−C(20) 2.175(3), Ir(1)−C(21) 2.167(3), Ir(1)−C(24) 2.097(4), C(1)−Ir(1)−Cl(1) 89.52(9), C(1)−Ir(1)−C(17) 92.22(13), C(1)−Ir(1)−C(24) 91.95(13), C(1)−Ir(1)−C(20) 163.97(14), C(1)−Ir(1)−C(21) 158.83(13).

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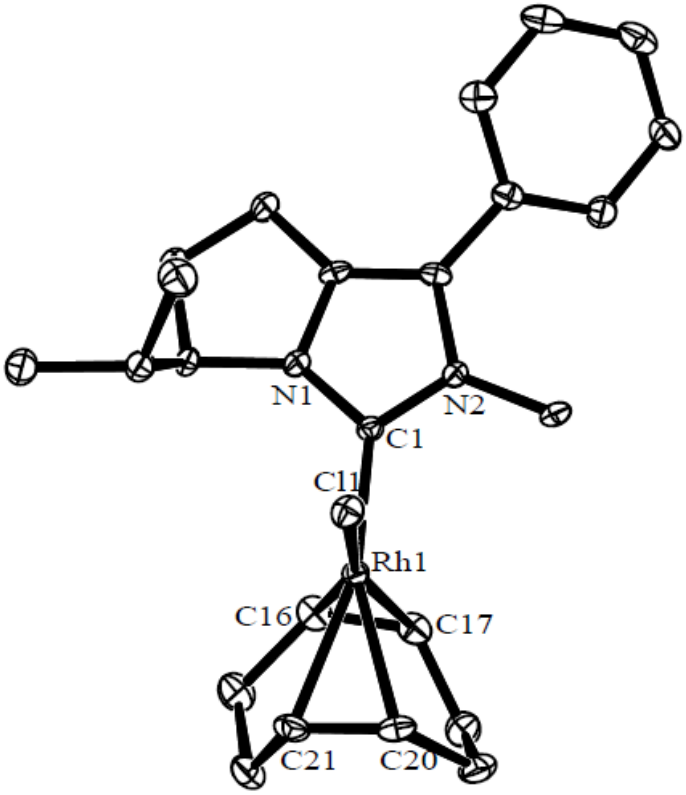

Figure 6. ORTEP of **3h** with thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Rh(1)−C(1) 2.019(3), Rh(1)−Cl(1) 2.3810(9), Rh(1)−C(16) 2.104(3), Rh(1)−C(17) 2.103(3), Rh(1)−C(20) 2.187(3), Rh(1)−C(21) 2.206(3), C(1)−Rh(1)−Cl(1) 87.97(8), C(1)−Rh(1)−C(16) 90.63(12), C(1)−Rh(1)−C(17) 93.75(11), C(1)−Rh(1)−C(20) 160.17(11), C(1)−Rh(1)−C(21) 163.16(11).

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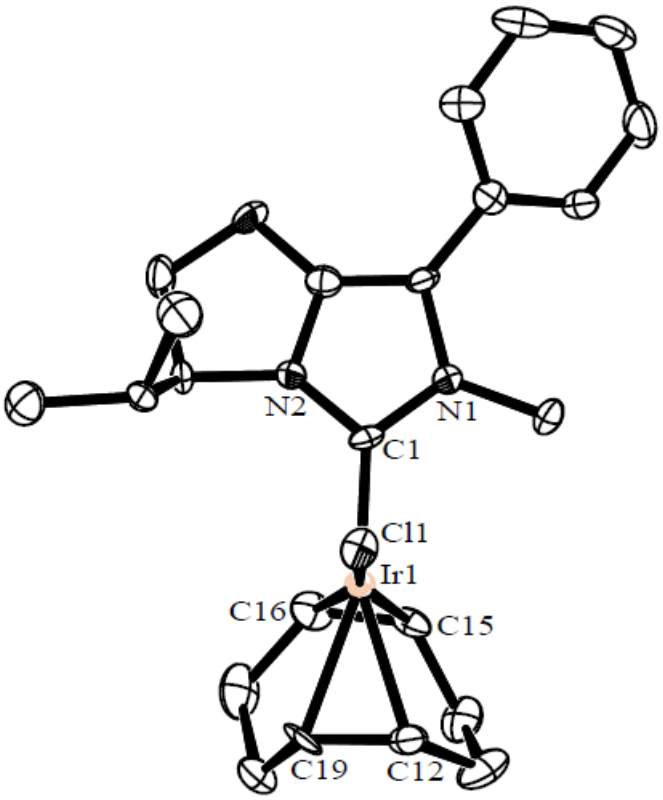

Figure 7. ORTEP of **3i** with thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Ir(1)−C(1) 2.029(5), Ir(1)−Cl(1) 2.3695(11), Ir(1)−C(12) 2.173(5), Ir(1)−C(15) 2.081(4), Ir(1)−C(16) 2.097(5), Ir(1)−C(19) 2.179(5), C(1)−Ir(1)−Cl(1) 88.66(12), C(1)−Ir(1)−C(15) 94.07(19), C(1)−Ir(1)−C(16) 91.1(2), C(1)−Ir(1)−C(12) 160.3(3), C(1)−Ir(1)−C(19) 162.0(2).

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Table 1. X-ray crystallographic data for the rhodium complexes (**1**−**3**)**h**

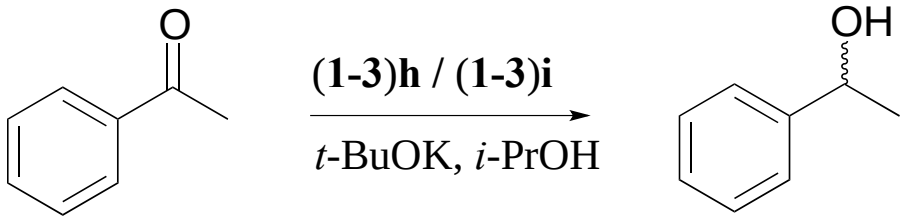
Compound	**1h**	**2h**	**3h**
Lattice	Orthorhombic	Orthorhombic	Orthorhombic
Formula	$C_{24}H_{32}N_2ORhCl$	$C_{24}H_{32}N_2ORhCl$	$C_{23}H_{30}N_2ORhCl$
Formula weight	502.88	502.88	488.85
Space group	$P2_1P2_1P2_1$	$P2_1P2_1P2_1$	$P2_1P2_1P2_1$
a/Å	8.2908(11)	8.2533(15)	8.4079(19)
b/Å	12.5399(16)	13.907(3)	12.317(3)
c/Å	21.613(3)	19.371(4)	20.926(5)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
V/Å^3	2247.0(5)	2223.4(8)	2167.1(9)
Z	4	4	4
Temperature (K)	100(2)	100(2)	100 (2)
Radiation (λ,Å)	0.71075	0.71070	0.71070
ρ (calcd.), g cm^{-3}	1.486	1.502	1.498
θ max, deg.	29.18	29.11	29.50
No. of data	26214	14202	28174
No. of parameters	262	262	257
R_1	0.0217	0.0377	0.0351
wR_2	0.0523	0.0740	0.0678
GOF	1.026	0.878	1.053
Crystal habit	Block	Block	Block
Crystal size mm^3	0.30 × 0.29 × 0.11	0.45 × 0.23 × 0.08	0.25 × 0.22 × 0.12
Absorption coefficient (μ)	0.896	0.906	0.927
No. of independent reflections	6057	5813	6262
No. of restraints	0	36	0
Rint	0.0311	0.0919	0.0534
CCDC number	1047074	1017714	990173
Extinction coefficient (μ)	none	none	None

Table 2. X-ray crystallographic data for the iridium complexes (**1**−**3**)**i**

Compound	**1i**	**2i**	**3i**
Lattice	Orthorhombic	Orthorhombic	Orthorhombic
Formula	$C_{24}H_{32}N_2OIrCl$	$C_{24}H_{32}N_2OIrCl$	$C_{23}H_{30}N_2OIrCl$
Formula weight	592.17	592.17	578.14
Space group	$P2_1P2_1P2_1$	$P2_1P2_1P2_1$	$P2_1P2_1P2_1$
a/Å	8.285(2))	8.2948(13)	8.4206(13)
b/Å	12.558(3)	13.914(2)	12.3709(18)
c/Å	21.674(6)	19.407(3)	20.986(3)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
V/Å^3	2255.0(10)	2239.8(6)	2186.1(6)
Z	4	4	4
Temperature (K)	100(2)	150(2)	150(2)
Radiation (λ,Å)	0.71070	0.71075	0.71070
ρ (calcd.), g cm^{-3}	1.744	1.756	1.757
θ max, deg.	29.21	25.00	25.00
No. of data	12620	16440	8606
No. of parameters	265	265	256
R_1	0.0314	0.0141	0.0215
wR_2	0.0525	0.0368	0.858
GOF	0.877	0.717	0.858
Crystal habit	Block	Block	Block
Crystal size mm^3	0.39 × 0.16 × 0.04	0.20 × 0.20 × 0.20	0.30 × 0.27 × 0.11
Absorption coefficient (μ)	6.057	6.098	6.245
No. of independent reflections	5632	3913	3794
No. of restraints	0	0	0
Rint	0.0489	0.0247	0.0312
CCDC number	1039096	1021593	1438249
Extinction coefficient (μ)	none	none	None

All of the rhodium (**1**–**3**)**h** and the iridium (**1**–**3**)**i** complexes, as structurally characterized by the X-ray single crystal diffraction studies (Figures 2-7 and Tables 1 and 2), were found to be monomeric in nature with the metal center adopting a tetrahedral geometry being surrounded by N–heterocyclic carbene, chloride and a η^4–bound 1, 5–cyclooctadiene (COD) ligands. Of particular interest is the M−$C_{carbene}$ bond distances in the rhodium (**1**−**3**)**h** and the iridium (**1**−**3**)**i** complexes. The Rh−$C_{carbene}$ bond distances of 2.020(18) Å (**1h**), 2.023(4) Å (**2h**) and 2.019(4) Å (**3h**) is slightly shorter than the sum of the covalent radii of the individual atoms [*d*/(Rh−C) = 2.182 Å][44] but are comparable to the structurally characterized examples namely, (1-*i*-propyl,3-phenyl-benzimidazol-2-ylidene)Rh(COD)Cl [*d*/Rh−$C_{carbene}$ = 2.015(9) Å][45] and (1,3-dicyclohexyl-1,3-dihydro-2H-imidazol-2-ylidene)Rh(COD)F [*d*/Rh−$C_{carbene}$ = 2.022(3) Å].[46]

Similarly, the Ir−$C_{carbene}$ bond distances of 2.018(5) Å (**1i**), 2.026(3) Å (**2i**) and 2.029(5) Å (**3i**) are shorter to the sum of the individual covalent radii of the iridium and carbon atoms [*d*/(Ir−C) = 2.172 Å][44] and are comparable with other structurally characterized examples like, (1,3-di-*i*-propylbenzimidazol-2-ylidene)Ir(COD)Cl [*d*/Ir−$C_{carbene}$ = 2.020(4) Å][47] and (1,3-di-*i*-propyl-1,3-dihydro-2H-imidazol-2-ylidene)Ir(COD)F [*d*/Ir−$C_{carbene}$ = 2.014(3) Å].[46]



(4)

Equation 1. Asymmetric transfer hydrogenation of acetophenone with chiral oxazolidine-fused imidazo ived N-heterocyclic carbene complexes of rhodium(I) (**1**−**3**)**h** and iridium(I) (**1**−**3**)**i**.

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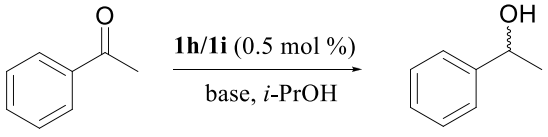
Table 3. Base variation study of the asymmetric transfer hydrogenation of acetophenone with the representative rhodium(I) (**1h)** and iridium(I) (**1i**) complexes.



(**4**)

S.No.	base	(**1h**)			(**1i**)		
		yield[a] (%)	*ee*[b] (%)	TON	yield[a] (%)	*ee*[b] (%)	TON
1	K_2CO_3	64	17	127	60	25	120
2	NaOH	56	15	111	61	20	121
3	KOH	54	21	109	40	14	80
4	CS_2CO_3	72	13	145	64	22	129
5	*t*-BuOK	73	16	146	85	14	170

Reaction conditions: Acetophenone (1.97 mmol), base (78.8 µmol), **1h** or **1i** (9.85 µmol, 0.5 mol %) in 8 mL of *i*-PrOH at 75 °C for 3 hours. *a*. yields are after isolation of the product. *b*. enantiomeric excess (*ee*) was determined by chiral HPLC with chiralpak-RJ chiral column.

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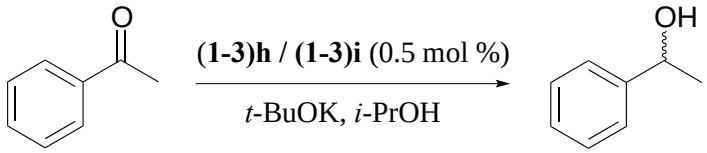
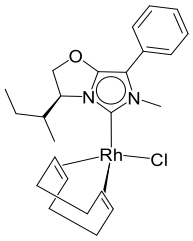
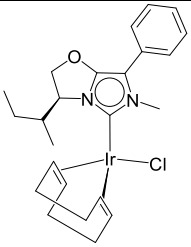
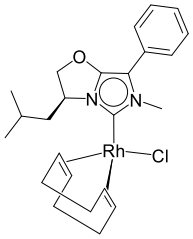
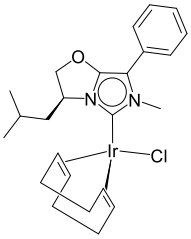
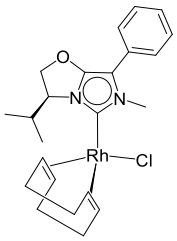
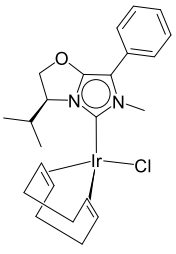
Table 4. Asymmetric transfer hydrogenation of acetophenone with various chiral oxazolidine-fused imidazole derived N-heterocyclic carbene complexes of rhodium(I) (**1**−**3)h** and iridium(I) (**1**−**3)i**.



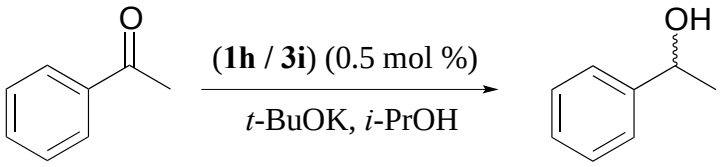
(**4**)

S.No.	Rh-NHC complex	yield[a] (%)	*ee*[b] (%)	TON	Ir-NHC complex	yield[a] (%)	*ee*[b] (%)	TON
1	 (**1h**)	73	16	146	 (**1i**)	85	14	170
2	 (**2h**)	73	2	146	 (**2i**)	76	6	152
3	 (**3h**)	65	14	130	 (**3i**)	95	18	190

Reaction conditions: Acetophenone (1.97 mmol), *t*-BuOK (78.8 µmol), **(1**−**3)h** or **(1**−**3)i** (9.85 µmol, 0.5 mol %) in 8 mL of *i*-PrOH at 75 °C for 3 hours. *a*. yields are after isolation of the product. *b*. enantiomeric excess (*ee*) was determined by chiral HPLC with chiralpak-RJ chiral column.

10.1002/ejic.201700303

Table 5. Time dependence study of the asymmetric transfer hydrogenation of acetophenone with chiral oxazolidine-fused imidazole derived N-heterocyclic carbene complexes of rhodium(I) (**1h)** and iridium(I) (**3i**) complexes.

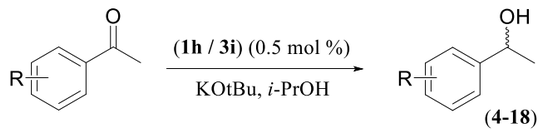


(**4**)

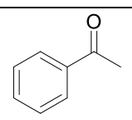
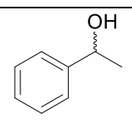
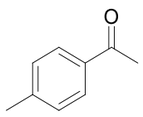
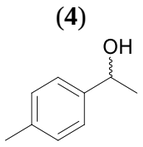
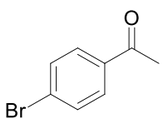
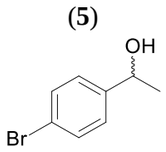
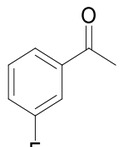
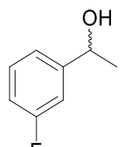
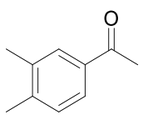
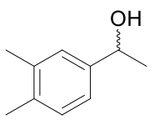
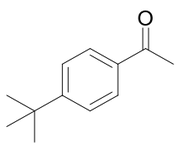
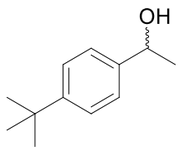
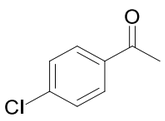
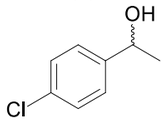
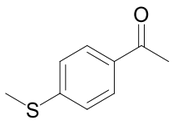
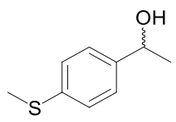
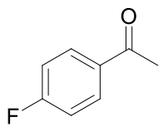
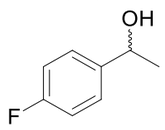
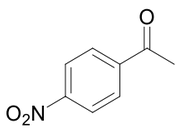
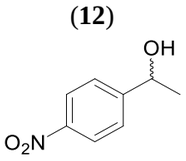
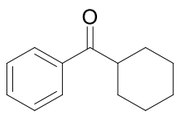
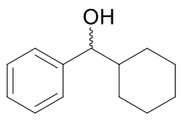
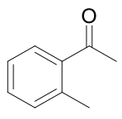
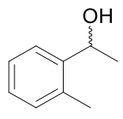
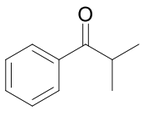
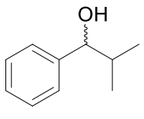
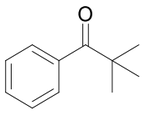
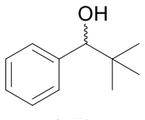
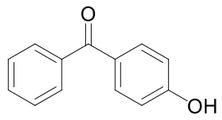
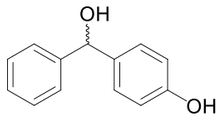
S.No.	time (min)	(**1h**)			(**3i**)		
		yield[a] (%)	*ee*[b] (%)	TON	yield[a] (%)	*ee*[b] (%)	TON
1	60	32	18	65	75	21	150
2	120	47	15	94	77	19	154
3	180	74	16	148	95	18	190
4	360	79	16	159	85	20	170
5	720	80	13	161	87	21	175

Reaction conditions: Acetophenone (1.97 mmol), *t*-BuOK (78.8 µmol), **1h** or **3i** (9.85 µmol, 0.5 mol %) in 8 mL of *i*-PrOH at 75 °C at various time intervals. *a*. yields are after isolation of the product. *b*. enantiomeric excess (*ee*) was determined by chiral HPLC with chiralpak-RJ chiral column.

Table 6. Asymmetric transfer hydrogenation of ketones with chiral oxazolidine-fused imidazole derived N-heterocyclic carbene complexes of rhodium(I) (**1h**) and iridium(I) (**3i**) complexes.



(**4-18**)

S.No.	substrate	Product	(**1h**)			(**3i**)		
			yield[a] (%)	*ee*[b]	TON	yield[a] (%)	*ee*[b]	TON
1		 (**4**)	73	16	146	95	18	190
2		 (**5**)	64	11	128	84	21	168
3		 (**6**)	55	25	110	72	16	144
4		 (**7**)	62	19	123	45	13	89
5		 (**8**)	70	13	139	66	24	131
6		 (**9**)	51	20	101	62	15	123
7		 (**10**)	58	22	116	73	15	146
8		 (**11**)	32	5	63	76	5	151
9		 (**12**)	50	19	99	80	21	159
10		 (**13**)	35	20	70	18	16	36
11		 (**14**)	21	4	42	38	20	76
12		 (**15**)	64	5	128	72	3	144
13		 (**16**)	47	11	93	54	41	107
14		 (**17**)	52	18	102	60	9	116
15		 (**18**)	0	0	0	0	0	0

Reaction conditions: Ketone (1.97 mmol), *t*-BuOK (78.8 µmol), **1h** or **3i** (9.85 µmol, 0.5 mol %) in 8 mL of *i*-PrOH at 75 °C for 3 hours. *a*. yields are after isolation of the product. *b*. enantiomeric excess (*ee*) was determined by chiral HPLC with chiralpak-RJ, chiralpak-OH and Chiralpak IA column.

The utility of chiral oxazolidine fused imidazole derived N–heterocyclic carbene ligand in the transfer hydrogenation reaction was explored with its rhodium (**1**−**3**)**h** and iridium (**1**−**3**)**i** complexes (Equation 1). Initial optimization study involving the variation of bases was attempted on the transfer hydrogenation of acetophenone in *i*−PrOH for the representative rhodium (**1h**) and iridium (**1i**) complexes, and which showed *t*-BuOK to be the most effective of all bases tried (Table 3, entry 5). Subsequently, the catalyst variation study performed for the rhodium (**1**–**3**)**h** and iridium (**1**–**3**)**i** complexes using *t*-BuOK as a base, showed the rhodium (**1h**) and the iridium (**3i**) complexes to be superior in performance displaying a maximum chiral induction of 16 % (*ee*) in case of rhodium complex (**1h**) (Table 4, entry 1) and of 18 % (*ee*) in case of the iridium complex (**3i**) for the transfer hydrogenation of acetophenone substrate (Table 4, entry 3).

Furthermore, the time dependent study was carried out for the two rhodium (**1h**) and the iridium (**3i**) complexes, and after careful analysis of the catalysis data (Table 5), the three hours of the reaction time was so chosen for the subsequent catalysis runs. The homogenous nature of the catalysis was evident form the transfer hydrogenation of acetophenone reaction performed in the presence and absence of Hg (Supporting Information Table S1) that showed comparable conversions in case of both of the rhodium (**1h**) [73 % with 16 % *ee* without Hg (Table 4) and 69 % with 22 % *ee* with Hg (Table S1)] and the iridium (**3i**) [95 % with 18 % *ee* without Hg (Table 4) and 75 % with 27 % *ee* with Hg (Table S1)] complexes, thereby upholding the homogenous nature of the catalysis. The influence of chiral oxazolidine fused imidazole based N–heterocyclic carbene ligand was very much evident from the fact that no conversion to product was observed in the case of the blank experiment as well as in the control experiment performed with $\{(COD)MCl\}_2$ (M = Rh, Ir) precursors (Supporting Information Table S1).

The substrate scope study was undertaken for a wide variety of acetophenone substrates bearing electron rich and electron deficient groups (Table 6). It is interesting to note that the iridium (**3i**) complex performed better than the rhodium (**1h**) complex both in terms of yield and enantioselectivity for the halogenated acetophenone (Table 6; entries 3, 7 and 9) and the alkylated acetophenone substrates (Table 6; entries 2, 5 and 6). Moderate to low yields (18–76 %) were obtained for the 4−methylthio acetophenone and 4-nitro acetophenone substrates both in case of the rhodium (**1h**) and iridium (**3i**) complexes. Furthermore, sterically demanding substrate like 2-methyl acetophenone, isobutyrophenone, 2,2 dimethyl propiophenone were reduced in good yields (47–82 %). The generally low enantioselectivites observed for the rhodium (**1h**) and the iridium (**3i**) complexes, for the catalysis runs performed at 75 °C, may be attributed to a rapid exchange between the two isomers under the catalysis conditions as seen in the variable temperature ^{1}H NMR experiment for a representative rhodium complex (**1h**).

Important is the comparison of the catalytic activities of the rhodium (**1h**) and the iridium (**3i**) complexes with the reported ones for the asymmetric transfer hydrogenation of acetophenone. In this regard it is worth noting that although, a lot of reports exist on the achiral version of the transfer hydrogenation reaction of ketones,[48-51] only a handful of examples have been reported for the chiral version of this reaction.[40, 42, 52, 53] We are aware of only two reports of iridium based N-heterocyclic carbene complexes exhibiting superior activity as compared to the iridium complex (**3i**). For example, for the transfer hydrogenation of acetophenone, the {[(*R*)-(2-bis(4-(trifluoromethyl)phenyl methyl)5-(2,4,6-tricyclohexylphenyl)6,7-dihydro,2H-pyrolo[1,2,-c]imidazol-5-ylidene)]Ir(COD)}Cl complex exhibited 78 % yield and 73 % *ee* at 0.05 mol % catalyst loading[39] and the {[(3-((1*R*,2*R*)-((*E*)-(3,5,di-*t*-butyl)2-hydroxybenzylidene)amino)cyclohexyl)1-*i*-propyl-4-phenyl-1-

imidazol-3-ylidene)]Ir(COD)}BAr_4 (Ar=3,5-$(CF_3)_2C_6H_3$) complex exhibited 98 % yield and 43 % *ee* at 0.5 mol % catalyst loading[43] while the iridium (**3i**) complex exhibited 95 % conversion with 18 % *ee* at 0.5 mol % catalyst loading for the same acetophenone substrate.

With regard to the utility of rhodium N−heterocyclic carbene complexes in asymmetric transfer hydrogenation reaction, we are aware of only one report of the transfer hydrogenation of ketones with a rhodium based N−heterocyclic carbene catalyst, and which showed only 40 % conversion with minimal chiral induction of 4 % in case of the transfer hydrogenation of acetophenone substrate at 0.1 mol % of catalyst loading.[52] In this backdrop the rhodium (**1h**) complex exhibiting 73 % yield and 16 % *ee* at 0.5 mol % catalyst loading for the same transfer hydrogenation of acetophenone is significant and it points towards possible entry of chiral oxazolidine fused N−heterocyclic carbene based rhodium complexes for the catalysis of this reaction.

Conclusions

In summary, a new class of chiral oxazolidine fused N−heterocyclic carbene ligand has been synthesized using a multi-step protocol starting from commercially available chiral amino acids without requiring any enantiomeric separation step. The utility of this class of ligand in the form of its rhodium (**1**−**3**)**h** and the iridium (**1**−**3**)**i** complexes have been demonstrated in asymmetric transfer hydrogenation reactions of ketones. The study paves way for exploring further applications of chiral oxazolidine fused N−heterocyclic carbenes as ligand platforms in homogenous catalysis.

Experimental section

General procedures

All manipulations were carried out using standard Schlenk techniques. $RhCl_3•3H_2O$, $IrCl_3•3H_2O$, D-phenyl glycine, L-Valine, L-Leucine, L-Isoleucine were purchased from Sigma Aldrich. $\{(COD)RhCl\}_2$,[54] $\{(COD)IrCl\}_2$,[55] (2R)-2-amino-3-methylpentan-1-ol (**1a**),[56] (R)-2-amino-4-methylpentan-1-ol (**2a**),[56] (R)-2-amino-3-methylbutan-1-ol (**3a**)[56] and (R)-2-formamido-2-phenylacetic acid (**1b**)[57] were synthesised by literature procedures. ^{1}H NMR, $^{13}C\{^1H\}$ NMR, spectrum were recorded on Bruker 300 MHz spectrometer. ^{1}H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), broad (br), triplet of triplet (tt), doublet of doublet (dd), multiplet (m) and septet (sept). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer and Bruker maxis impact spectrometer. Elemental Analysis was carried out on ThermoFinnigan FLASH EA 1112 SERIES (CHNS) Elemental Analyzer. The enantiomeric excess were determined by HPLC with a Chiralpak-1A, Chiralpak-1C, Chiralpak-OH and Chiralpak-RJ chiral column on a Shimadzu LC-2010. The X-ray diffraction data for compounds (**1**−**3**)**h**, (**1**−**3**)**i** were collected on Rigaku Hg 724+ diffractometer. The structures were solved using direct method and standard difference map techniques, and refined by full-matrix least-squares procedures on F^2.[58, 59] CCDC-1047074 (for **1h**), CCDC-1039096 (for **1i**), CCDC-1017714 (for **2h**), CCDC-1021593 (for **2i**), CCDC-990173 (for **3h**) and CCDC-1438249 (for **3i**) contain the supplementary crystallographic data related to this article. These data can be obtained free of charge from the Cambridge Crystallographic Data center *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of (2*S*)-2-formamido-N-((2*S*)-1-hydroxy-3-methylpentan-2-yl)-2-phenylacetamide (1c)

N-methyl morpholine (12.7 g, 124 mmol) was added to a solution of (R)-2-formamido-2-phenylacetic acid (**1b**) (15.0 g, 83.7 mmol) in THF (*ca*. 150 mL) at -20 °C under nitrogen atmosphere. This was followed by the addition of *n*-butylchloroformate (13.7 g, 100 mmol) and the reaction mixture stirred at this temperature for 15 minutes, after which (2S)-2-amino-3-methylpentan-1-ol (**1a**) (9.80 g, 83.6 mmol) was added. The reaction mixture was then stirred at room temperature for 1 hour. The progress of the reaction was monitored by thin layer chromatography (TLC) and upon observing the complete conversion of the starting material to product, the solvent was removed in *vaccuo*, followed by the addition of water (*ca* 300 mL). The resulting the product was filtered, washed with *n*-heptane (*ca*. 200 mL) and dried in *vaccuo* to give the desired compound **1c** as white solid (11.1 g, 48 %). ^{1}H NMR (DMSO-d_6, 300 MHz, 25 °C): δ 8.81 (t, 1H, $^{3}J_{HH}$ = 9 Hz, N*H*), 8.13–8.10 (m, 2H, N*H* & C*H*O), 7.45–7.28 (m, 5H, C_6H_5), 5.63 (d, 1H, $^{3}J_{HH}$ = 6 Hz, COC*H*NH), 4.68–4.51 (m, 1H, CH_2OH), 3.64–3.29 (m, 2H, CH_2OH), 1.68–1.56 (m, 2H, CH_2CH_3), 1.38–1.13 (m, 1H, $CHCH_3$), 0.85 (d, 3H, $^{3}J_{HH}$ = 9 Hz, $CHCH_3$), 0.65 (t, 3H, $^{3}J_{HH}$ = 9 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz, 25 °C): (Diasteriomer-1) δ 169.1 (*C*ONH), 160.4 (N*C*HO), 139.3 (C_6H_5), 128.1(C_6H_5) , 127.8(C_6H_5) , 127.2 (C_6H_5), 60.6 (CH_2OH), 54.8 (*C*HNHCHO), 54.5 (*C*HNH), 34.8 ($CHCH_3$), 24.5 (CH_2CH_3), 15.4 ($CHCH_3$), 11.2 (CH_2CH_3). (Diasteriomer-2) δ 169.0 (*C*ONH), 160.3 (N*C*HO), 138.8 (C_6H_5), 128.0 (C_6H_5), 127.8 (C_6H_5), 127.2 (C_6H_5), 60.7 (CH_2OH), 54.6 (*C*HNHCHO), 54.5 (*C*HNH), 34.6 ($CHCH_3$), 24.1 (CH_2CH_3), 15.3 ($CHCH_3$), 10.8 (CH_2CH_3). IR data (KBr pellet) cm^{-1}: 3276 (m), 3087 (w), 2971 (m), 2882 (m), 1650 (s), 1567 (m), 1384 (m), 1234 (m), 707 (m). HRMS (ES): *m/z* 301.1517 $[M+Na]^+$, calcd: *m/z* 301.1523. Anal. Calcd. for $C_{15}H_{22}N_2O_3$•CH_3OH: C, 61.91; H, 8.44; N, 9.03. Found: C, 62.67; H, 7.63; N, 9.43.

Synthesis of N-((*R*)-((*S*)-4-*sec*-butyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl)formamide (1d)

A solution of *p*-toluene sulphonyl chloride (18.8 g, 98.6 mmol) in 1,2 dichloroethane (*ca*. 250 mL) was added to a mixture containing (2S)-2-formamido-N-((2S)-1-hydroxy-3-methylpentan-2-yl)-2-phenylacetamide (**1c**) (11.0 g, 39.5 mmol), 4-dimethylaminopyridine (0.482 g, 3.94 mmol) and Et_3N (17.9 g, 177 mmol) in 1,2 dichloroethane (*ca*. 200 mL) at room temperature. After which, the reaction mixture was stirred for 12 hours at room temperature and during which the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture quenched with saturated $NaHCO_3$ solution (*ca*. 200 mL). The resulting organic layer was collected, dried over anhydrous Na_2SO_4 and filtered. The volatiles were then removed in *vaccuo* and the crude product thus obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of $CHCl_3$ and MeOH (9:1, *v/v*) to give the desired compound **1d** as an yellow liquid (3.61 g, 35 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.12 (s, 1H, C*H*O), 7.35–7.22 (m, 5H, C_6H_5), 5.67–5.54 (m, C*H*NH), 4.27–4.22 (m, 1H, C_3H_3NO), 4.04–3.96 (m, 1H, C_3H_3NO), 3.91–3.84 (m, 1H, C_3H_3NO), 1.59–1.47 (m, 1H, C*H*CH_3), 1.45–1.36 (m, 1H, C*H*$_2CH_3$), 1.14–1.00 (m, 1H, C*H*$_2CH_3$), 0.83 (t, 3H, $^3J_{HH}$ = 7 Hz, CHC*H*$_3$), 0.71 (d, 3H, $^3J_{HH}$ = 8 Hz, CH_2C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 ^{o}C): δ 165.4 (*C*$_3H_3NO$), 160.1 (N*C*HO), 137.3 (*C*$_6H_5$), 128.8 (*C*$_6H_5$), 128.4 (*C*$_6H_5$), 127.2 (*C*$_6H_5$), 70.8 (CH_2 of *C*$_3H_3NO$), 70.2 (*C*HNHCHO), 50.4 (*C*H of *C*$_3H_3NO$), 38.7 (*C*HCH_3), 26.1 (*C*H$_2CH_3$), 14.2 (CH*C*H$_3$), 11.5 (CH_2*C*H$_3$). IR data (NaCl pellet) cm^{-1}: 3270 (m), 3193 (m), 2965 (m), 2887 (m), 2749 (w), 1965 (w), 1678 (m), 1532 (m), 1384 (m), 1234 (m), 985 (m), 702 (m), 630 (w). HRMS (ES): *m/z* 261.1590 [M+H]$^+$, calcd: *m/z* 261.1598.

Synthesis of (*S*)-3-*sec*-butyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazole (1e)

P_2O_5 (7.60 g, 26.7 mmol) was added to a solution of N-((R)-((S)-4-sec-butyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl)formamide (**1d**) (3.50 g, 13.5 mmol) in toluene (*ca*. 200 mL) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 30 minutes at room temperature and then refluxed for 12 hours. The progress of the reaction was monitored by thin layer chromatography (TLC) and upon observing the complete conversion of the starting material to product, the reaction mixture was cooled to room temperature and filtered. The isolated solid was dissolved using a 1N HCl (*ca*. 50 mL) solution and then the pH was adjusted to 12 using saturated KOH solution. The aqueous solution was extracted with CH_2Cl_2 (2 × 50 mL), combined organic layers were dried over anhydrous Na_2SO_4, filtered and finally the filtrate was reduced in *vaccuo*. The crude product so obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of $CHCl_3$ and MeOH (*v/v*. 9:1). The desired compound **1e** was thus isolated as an yellow solid (2.15 g, 66 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.73 (d, 2H, $^3J_{HH}$ = 6 Hz, $C_6\underline{H}_5$), 7.37 (t, 2H, $^3J_{HH}$ = 6 Hz, $C_6\underline{H}_5$), 7.15 (s, 1H, NC$\underline{H}$N of $C_5H_4N_2O$), 7.12–7.10 (m, 1H, $C_6\underline{H}_5$), 5.11 (t, 1H, $^3J_{HH}$ = 9 Hz, $C_5\underline{H}_4N_2O$), 4.88–4.83 (m, 1H, $C_5\underline{H}_4N_2O$), 4.40–4.34 (m, 1H,$C_5\underline{H}_4N_2O$), 1.95-1.80 (m, 1H, C$\underline{H}$$CH_3$), 1.61-1.45 (m, 1H, C$\underline{H}_2$$CH_3$), 1.25–1.08 (m, 1H, C$\underline{H}_2$$CH_3$), 0.95 (t, 3H, $^3J_{HH}$ = 8Hz, $CH_2C\underline{H}_3$), 0.93 (d, 3H, $^3J_{HH}$ = 7Hz, CHC$\underline{H}_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 149.8 ($\underline{C}_6H_5$), 133.5 (N$\underline{C}$HN of $\underline{C}_5H_4N_2O$), 128.4 ($\underline{C}_6H_5$), 124.9 ($\underline{C}_6H_5$), 123.6 ($\underline{C}_6H_5$), 122.9 ($C_5H_4N_2O$), 111.1 ($\underline{C}_5H_4N_2O$), 80.0 ($\underline{C}H_2$ of $C_5H_3N_2O$), 59.7 ($\underline{C}$H of $C_5H_4N_2O$), 38.0 ($\underline{C}$HCH_3), 25.0 ($\underline{C}H_2CH_3$), 14.0 (CH$\underline{C}H_3$), 11.2 ($CH_2\underline{C}H_3$). IR data (NaCl pellet) cm^{-1}: 3115 (m), 2976 (m), 2876 (w), 1617 (m), 1506 (m), 1434 (m), 1362 (m), 1140 (m), 1007 (m), 763 (m), 691 (w). HRMS (ES): *m/z* 243.1488 $[M+H]^+$, calcd: *m/z* 243.1492. Anal. Calcd. for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56. Found: C, 74.17; H, 7.15; N, 11.34.

Synthesis of (*S*)-3-*sec*-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-6-ium iodide (1f)

A solution of methyl iodide (7.32 g, 51.6 mmol) and (S)-3-sec-butyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazole (**1e**) (0.500 g, 2.06 mmol) was refluxed in CH_3CN (*ca.*30 mL) for 6 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was cooled to room temperature and volatiles were removed in *vaccuo*. The crude product thus obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of $CHCl_3$ and MeOH (*v/v*, 8:2). The desired product **1f** isolated as an yellow liquid (0.401 g, 51 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.89 (s, 1H, NC*H*N of $C_5H_4N_2O$), 7.47–7.35 (m, 5H, C_6H_5), 5.32–5.17 (m, 2H, $C_5H_4N_2O$), 4.90–4.80 (m, 1H, $C_5H_4N_2O$), 3.94 (s, 3H, NCH_3), 2.33–2.19 (m, 1H, $CHCH_3$), 1.64–1.48 (m, 1H, CH_2CH_3), 1.27–1.10 (m, 1H, CH_2CH_3), 0.96 (t, 3H, $^3J_{HH}$ = 8Hz, CH_2CH_3), 0.95 (d, 3H, $^3J_{HH}$ = 8Hz, $CHCH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 147.8 (C_6H_5), 129.7 (N*C*HN of $C_5H_4N_2O$), 129.4 (C_6H_5), 129.0 (C_6H_5), 126.9 (C_6H_5), 123.6 ($C_5H_4N_2O$), 108.0 ($C_5H_4N_2O$), 79.0 (CH_2 of $C_5H_3N_2O$), 62.5 (*C*H of $C_5H_4N_2O$), 37.2 ($CHCH_3$), 36.7 (NCH_3), 25.1 (CH_2CH_3), 13.7 ($CHCH_3$), 11.2 (CH_2CH_3). IR data (NaCl pellet) cm^{-1}: 3455 (m), 2963 (s), 2941 (w), 2880 (w), 1663 (s), 1547 (m), 1448 (m), 1188 (w), 983 (w), 762 (w), 696 (w). HRMS (ES): *m/z* 257.1646 $[M-I]^+$, calcd: *m/z* 257.1648.

Synthesis of ((*S*)-3-*sec*-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene)silver(I) iodide (1g)

A mixture of (S)-3-sec-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-6-ium iodide (**1f**) (0.990 g, 2.57 mmol) and Ag_2O (0.298 g, 1.28 mmol) was stirred in CH_2Cl_2 (*ca.*

100 mL) for 1 hour at room temperature and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, solvent was removed from the filtrate, and the residue thus obtained was crystalized using CH_2Cl_2 and *i*-Pr_2O (*v/v*, 1:9, 10 mL) as a mixed solvent to give **1g** as off-white solid (1.13 g, 90 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.42–7.27 (m, 5H, $C_6\underline{H}_5$), 4.98–4.90 (m, 1H, $C_5\underline{H}_3N_2O$), 4.86–4.77 (m, 1H, $C_5\underline{H}_3N_2O$), 4.75–4.68 (m, 1H, $C_5\underline{H}_3N_2O$), 3.79 (s, 3H, $C\underline{H}_3$), 2.48–2.27 (m, 1H, $C\underline{H}(CH_3)$, 1.63–1.36 (m, 1H, $C\underline{H}_2CH_3$), 1.25–1.09 (m, 1H, $C\underline{H}_2CH_3$), 0.94 (t, 3H, $^3J_{HH}$ = 8 Hz, $CH_2C\underline{H}_3$), 0.79 (d, 3H, $^3J_{HH}$ = 9 Hz, $CH_2C\underline{H}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 169.4 (N$\underline{C}$N of $\underline{C}_5H_4N_2O$), 148.8 ($\underline{C}_6H_5$), 129.5 ($\underline{C}_6H_5$), 129.3 ($\underline{C}_6H_5$), 128.9 ($\underline{C}_6H_5$), 128.8 ($C_5H_3N_2O$), 106.9 ($\underline{C}_5H_3N_2O$), 77.4 ($\underline{C}H_2$ of $C_5H_3N_2O$), 60.3 ($\underline{C}H$ of $C_5H_3N_2O$), 39.5 ($\underline{C}HCH_3$), 37.6 (N$\underline{C}H_3$), 25.8 ($\underline{C}H_2CH_3$), 12.0 (CH$\underline{C}H_3$), 11.4 ($CH_2\underline{C}H_3$). IR data (KBr pellet) cm^{-1}: 2965 (s), 2932 (w), 2882 (w), 1694 (s), 1451 (s), 1384 (m), 1357 (w), 907 (w), 763 (w), 696 (w). Anal. Calcd. for $C_{16}H_{20}AgIN_2O•H_2O$: C, 37.74; H, 4.36; N, 5.50. Found: C, 37.78; H, 3.43; N, 5.36.

Synthesis of [(3*S*)-6-methyl-7-phenyl-3-*sec*-butyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene] rhodium (1,5-cyclooctadiene) chloride (1h)

A mixture of ((S)-3-sec-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5(6H)-ylidene)silver(I) iodide (**1g**) (0.485 g, 0.989 mmol) and $\{(COD)RhCl\}_2$ (0.243 g, 0.494 mmol) was stirred in CH_2Cl_2 (*ca*. 50 mL) at room temperature for 2 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, and the solvent was removed in *vaccuo*. The crude product so obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed

medium of heptane and EtOAc (*v/v*, 8:2). The desired product **1h** was isolated as an yellow solid (0.435 g, 87 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): Major isomer: δ 7.34–7.29 (m, 2H, $C_6\underline{H}_5$), 7.25–7.19 (m, 3H, $C_6\underline{H}_5$), 4.88–4.80 (m, 1H, $C_5\underline{H}_3N_2O$), 4.76–4.63 (m, 4H, $C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.04 (s, 3H, $NC\underline{H}_3$), 3.62–3.39 (m, 2H, $C_8\underline{H}_{12}$), 2.53–2.33 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}CH_3$), 2.10–1.71 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}_2CH_3$), 1.71–1.49 (m, 1H, $C\underline{H}_2CH_3$), 1.09 (t, 3H, $^{3}J_{HH}$ = 9Hz, $CH_2C\underline{H}_3$), 0.88 (d, 3H, $^{3}J_{HH}$ = 6Hz, $CHC\underline{H}_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 176.3 (d, J_{Rh-C} = 48 Hz, N$\underline{C}$N of $\underline{C}_5H_3N_2O$), 153.5 ($\underline{C}_6H_5$), 133.4 ($\underline{C}_6H_5$), 132.3 (2 $\underline{C}_6H_5$), 131.9 ($\underline{C}_5H_3N_2O$), 111.5 ($\underline{C}_5H_3N_2O$), 103.2 ($\underline{C}_8H_{12}$), 80.7 ($\underline{C}H_2$ of $C_5H_3N_2O$), 73.8 ($\underline{C}_8H_{12}$), 72.8 ($\underline{C}_8H_{12}$), 70.8 ($\underline{C}H$ of $C_5H_3N_2O$), 64.6 ($\underline{C}_8H_{12}$), 43.1 ($\underline{C}HCH_3$), 42.4 ($\underline{C}_8H_{12}$), 38.9 ($\underline{C}_8H_{12}$), 36.7 ($\underline{C}_8H_{12}$), 34.7 ($\underline{C}_8H_{12}$), 32.6 (N$\underline{C}H_3$), 31.2 ($\underline{C}HCH_3$), 17.1 (CH$\underline{C}H_3$), 16.8 ($CH_2\underline{C}H_3$). Minor isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.34–7.29 (m, 2H, $C_6\underline{H}_5$), 7.25–7.19 (m, 3H, $C_6\underline{H}_5$), 5.07–4.98 (m, 1H, $C_8\underline{H}_{12}$), 4.98–4.88 (m, 4H, $C_5\underline{H}_3N_2O$), 4.00 (s, 3H, $NC\underline{H}_3$), 3.35–3.15 (m, 2H, $C_8\underline{H}_{12}$), 2.53–2.33 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}CH_3$), 2.10–1.71 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}_2CH_3$), 1.71–1.49 (m, 1H, $C\underline{H}_2CH_3$), 1.43 (t, 3H, $^{3}J_{HH}$ = 9Hz, $CH_2C\underline{H}_3$), 0.84 (d, 3H, $^{3}J_{HH}$ = 7Hz, $CHC\underline{H}_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 176.3 (d, J_{Rh-C} = 48 Hz, N$\underline{C}$N of $\underline{C}_5H_3N_2O$), 153.5 ($\underline{C}_6H_5$), 133.4 ($\underline{C}_6H_5$), 132.3 (2 $\underline{C}_6H_5$), 131.9 ($\underline{C}_5H_3N_2O$), 111.5 ($\underline{C}_5H_3N_2O$), 102.7 ($\underline{C}_8H_{12}$), 80.7 ($\underline{C}H_2$ of $C_5H_3N_2O$), 73.4 ($\underline{C}_8H_{12}$), 72.5 ($\underline{C}_8H_{12}$), 70.5 ($\underline{C}H$ of $C_5H_3N_2O$), 64.8 ($\underline{C}_8H_{12}$), 43.8 ($\underline{C}HCH_3$), 41.2 ($\underline{C}_8H_{12}$), 37.7 ($\underline{C}_8H_{12}$), 37.3 ($\underline{C}_8H_{12}$), 33.7 ($\underline{C}_8H_{12}$), 33.2 (N$\underline{C}H_3$), 31.3 ($\underline{C}HCH_3$), 16.9 (CH$\underline{C}H_3$), 16.4 ($CH_2\underline{C}H_3$). IR data (KBr pellet) cm^{-1}: 2998 (w), 2960 (s), 2932 (w), 2882 (w), 2826 (w), 1667 (s), 1606 (w), 1434 (w), 1384 (w), 1151 (w), 763 (w), 707 (w), 630 (w). HRMS (ES): *m/z* 467.1564 $[M\text{-}Cl]^{+}$, calcd: *m/z* 467.1564. Anal. Calcd. for $C_{24}H_{32}ClN_2ORh$: C, 57.32; H, 6.41; N, 5.57. Found: C, 57.61; H, 5.58; N, 5.62.

Synthesis of [(3*S*)-6-methyl-7-phenyl-3-*sec*-butyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene] iridium (1,5-cyclooctadiene) chloride (1i)

A mixture of ((S)-3-sec-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5(6H)-ylidene)silver(I) iodide (**1g**) (0.250 g, 0.510 mmol) and {(COD)IrCl}$_2$ (0.171 g, 0.254 mmol) was stirred in CH_2Cl_2 (*ca*. 50 mL) at room temperature for 2 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, and the solvent was removed in *vaccuo*. The crude product so obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of heptane and EtOAc (*v/v*, 8:2). The desired product **1i** was isolated as an yellow solid (0.138 g, 46 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): Major isomer : δ 7.35–7.19 (m, 5H, $C_6\underline{H}_5$), 4.94–4.87 (m, 1H, $C_5\underline{H}_3N_2O$), 4.80–4.46 (m, 4H, $C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 3.92 (s, 3H, $NC\underline{H}_3$), 3.35–3.18 (m, 2H, $C_8\underline{H}_{12}$), 2.32–1.97 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}CH_3$), 1.76–1.42 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}_2CH_3$), 1.40–1.25 (m, 1H, $C\underline{H}_2CH_3$), 1.03 (t, 3H, $^3J_{HH}$ = 7Hz, $CH_2C\underline{H}_3$), 0.82 (d, 3H, $^3J_{HH}$ = 7Hz, $CHC\underline{H}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 170.2 ($N\underline{C}N$ of $\underline{C}_5H_3N_2O$), 148.4 ($\underline{C}_6H_5$), 128.7 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$), 127.3 ($\underline{C}_5H_3N_2O$), 106.2 ($\underline{C}_5H_3N_2O$), 84.9 ($\underline{C}_8H_{12}$), 84.0 ($\underline{C}_8H_{12}$) , 75.8 ($\underline{C}H_2$ of $C_5H_3N_2O$), 59.5 ($\underline{C}_8H_{12}$), 51.9 ($\underline{C}H$ of $C_5H_3N_2O$), 49.5 ($\underline{C}_8H_{12}$), 38.0 ($\underline{C}HCH_3$), 37.4 ($\underline{C}_8H_{12}$), 34.9 ($\underline{C}_8H_{12}$), 32.7 ($\underline{C}_8H_{12}$), 30.7 ($\underline{C}_8H_{12}$), 28.5 ($N\underline{C}H_3$), 26.5 ($CH_2\underline{C}H_3$), 12.1 ($CH\underline{C}H_3$), 12.0 ($CH_2\underline{C}H_3$). Minor isomer: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 170.0 ($N\underline{C}N$ of $\underline{C}_5H_3N_2O$), 148.5 ($\underline{C}_6H_5$), 128.7 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$), 127.3 ($\underline{C}_5H_3N_2O$), 106.3 ($\underline{C}_5H_3N_2O$), 84.8 ($\underline{C}_8H_{12}$), 84.2 ($\underline{C}_8H_{12}$), 75.8 ($\underline{C}H_2$ of $C_5H_3N_2O$), 59.8 ($\underline{C}_8H_{12}$), 52.4 ($\underline{C}H$ of $C_5H_3N_2O$), 51.4 ($\underline{C}_8H_{12}$), 38.3 ($\underline{C}HCH_3$), 36.3 ($\underline{C}_8H_{12}$), 33.8 ($\underline{C}_8H_{12}$), 33.1 ($\underline{C}_8H_{12}$), 29.0 ($N\underline{C}H_3$), 28.5 ($\underline{C}_8H_{12}$), 26.6 ($CH_2\underline{C}H_3$), 12.1 ($CH\underline{C}H_3$), 12.0 ($CH_2\underline{C}H_3$). IR data (KBr pellet) cm^{-1}: 2971 (s), 2871 (w), 2832 (w), 1673 (s), 1603 (w), 1440 (m), 1395 (m), 1357 (m), 1157 (m), 907 (m), 768 (m). HRMS (ES): *m/z* 592.1830 $[M]^+$, calcd. *m/z* 592.1819. Anal. Calcd. for $C_{24}H_{32}ClN_2OIr•H_2O$: C, 47.24; H, 5.62; N, 4.59. Found: C, 47.15; H, 4.67; N, 4.50.

Synthesis of (*S*)-2-formamido-N-((i)-1-hydroxy-4-methylpentan-2-yl)-2-phenylacetamide (2c)

N-methyl morpholine (8.08 g, 79.9 mmol) was added to a solution of (R)-2-formamido-2-phenylacetic acid (**2b**) (9.50 g, 53.1 mmol) in THF (*ca*. 150 mL) at -20 °C under nitrogen atmosphere. This was followed by the addition of *n*-butylchloroformate (8.68 g, 63.6 mmol) and the reaction mixture stirred at this temperature for 15 minutes, after which (S)-2-amino-4-methylpentan-1-ol (**2a**) (6.21 g, 53.0 mmol) was added. The reaction mixture was then stirred at room temperature for 1 hour. The progress of the reaction was monitored by thin layer chromatography (TLC) and upon observing the complete conversion of the starting material to product, the solvent was removed in *vaccuo*, followed by the addition of water (*ca* 300 mL) resulting the product, which is filtered and washed with *n*-heptane (*ca*. 200 mL) and dried in *vaccuo* to give the desired compound **2c** as an white solid (2.93 g, 20 %). ^{1}H NMR (DMSO-d_6, 300 MHz, 25 °C): δ 8.85–8.77 (m, 1H, N*H*), 8.07 (bs, 2H, N*H* & C*H*O), 7.47–7.17 (m, 5H, C_6H_5), 5.59–5.51 (m, 1H, COC*H*NH), 4.77–4.52 (m, 1H, CH_2OH), 3.87–3.66 (m, 1H,CH_2CHNH), 3.43–3.04 (m, 2H, CH_2OH), 1.69–1.46 (m, 1H, C*H*$(CH_3)_2$), 1.41–1.16 (m, 2H, $CH_2CH(CH_3)_2$), 0.89 (d, 3H, $^{3}J_{HH}$ = 8 Hz, CH(CH_3)$_2$), 0.85 (d, 3H, $^{3}J_{HH}$ = 6 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz, 25 °C): (Diastereomer-1): δ 168.9 (*C*ONH), 160.4 (N*C*HO), 139.1 (C_6H_5), 128.1(C_6H_5), 127.3(C_6H_5), 126.9 (C_6H_5), 63.5 (CH_2OH), 54.5 (*C*HNHCHO), 48.9 (*C*HNH), 24.1 (*C*H$(CH_3)_2$), 23.3 ($CH_2CH(CH_3)_2$), 21.7 ($CH_2CH(CH_3)_2$). (Diastereomer-2): δ 168.9 (*C*ONH), 160.3 (N*C*HO), 138.8 (C_6H_5), 128.0 (C_6H_5), 127.3 (C_6H_5), 126.7 (C_6H_5), 63.6 (CH_2OH), 54.6 (*C*HNHCHO), 48.9 (*C*HNH), 23.9 (*C*H$(CH_3)_2$), 23.2 ($CH_2CH(CH_3)_2$), 21.6 ($CH_2CH(CH_3)_2$). IR data (KBr pellet) cm^{-1}: 3326 (s), 3281 (s), 3087 (w), 2954 (m), 2871 (m), 1684 (m), 1650 (m), 1573 (m), 1523 (m), 1379 (w), 1063 (w), 1040 (m), 741 (m). HRMS (ES): *m/z* 301.1517 [M+Na]$^{+}$, calcd: *m/z*

301.1523. Anal. Calcd. for $C_{15}H_{22}N_2O_3$: C, 64.73; H, 7.97; N, 10.06. Found: C, 64.25; H, 7.62; N, 9.33.

Synthesis of N-((*R*)-((*S*)-4-*i*-butyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl)formamide (2d)

A solution of *p*-toluene sulphonyl chloride (9.93 g, 52.3 mmol) in 1,2 dichloroethane (*ca*. 150 mL) was added to a mixture containing (S)-2-formamido-N-((S)-1-hydroxy-4-methylpentan-2-yl)-2-phenylacetamide (**2c**) (5.81 g, 20.9 mmol), 4-dimethylaminopyridine (0.250 g, 2.04 mmol) and Et_3N (9.47 g, 93.6 mmol) in 1,2 dichloroethane (*ca*. 150 mL) at room temperature. After which, the reaction mixture was stirred for 12 hours at room temperature and during which the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture quenched with saturated $NaHCO_3$ solution (*ca*. 200 mL). The resulting organic layer was collected, dried over anhydrous Na_2SO_4 and filtered. The volatiles were then removed in *vaccuo* and the crude product thus obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of $CHCl_3$ and MeOH (9:1, *v/v*) to give the desired compound **2d** as an yellow liquid (3.01 g, 56 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.17 (s, 1H, C*H*O), 7.51–7.24 (m, 5H, C_6H_5), 5.79–5.74 (m, 1H, C*H*NH), 4.45–4.33 (m, 1H, C_3H_3NO), 4.29–4.02 (m, 1H, C_3H_3NO), 3.93–3.79 (m, 1H, C_3H_3NO), 1.75–1.64 (m, 1H, C*H*$(CH_3)_2$), 1.57–1.47 (m, 1H, $CH_2CH(CH_3)_2$), 1.34–1.19 (m, 1H, $CH_2CH(CH_3)_2$), 0.93–0.88 (m, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ δ 165.4 (C_3H_3NO), 160.1 (N*C*HO), 137.3 (C_6H_5), 128.9 (C_6H_5), 128.5(C_6H_5), 127.2 (C_6H_5), 74.1 (CH_2 of C_3H_3NO), 64.1 (*C*HNHCHO), 50.4 (*C*H of C_3H_3NO), 45.2 (*C*H$(CH_3)_2$), 25.3 ($CH_2CH(CH_3)_2$), 22.6 ($CH_2CH(CH_3)_2$), 22.6 ($CH_2CH(CH_3)_2$). IR data (NaCl pellet) cm^{-1}: 3261 (w), 2963 (m), 2869 (m), 1669 (s), 1503

(m), 1381 (m), 1193 (m), 983 (w), 707 (m). HRMS (ES): *m/z* 261.1598 $[M+]^+$, calcd: *m/z* 261.1598.

Synthesis of (*S*)-3-*i*-butyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazole (2e)

P_2O_5 (6.51 g, 22.9 mmol) was added to a solution of N-((R)-((S)-4-*i*-butyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl)formamide (**2d**) (3.00 g, 11.5 mmol) in toluene (*ca*. 150 mL) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 30 minutes at room temperature and then refluxed for 12 hours. The progress of the reaction was monitored by thin layer chromatography (TLC) and upon observing the complete conversion of the starting material to product, the reaction mixture was cooled to room temperature and filtered. The isolated solid was dissolved using a 1N HCl (*ca*. 50 mL) solution and then the pH was adjusted to 12 using saturated KOH solution. The aqueous solution was extracted with CH_2Cl_2 (2 × 50 mL), combined organic layers were dried over anhydrous Na_2SO_4, filtered and finally the filtrate was reduced in *vaccuo*. The crude product thus obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of $CHCl_3$ and MeOH (*v/v*. 9:1). The desired compound **2e** was thus isolated as an yellow solid (1.81 g, 65 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.74 (d, 2H, $^3J_{HH}$ = 11Hz, $C_6\underline{H}_5$), 7.38 (t, 2H, $^3J_{HH}$ = 9Hz, $C_6\underline{H}_5$), 7.17–7.12 (m, 2H, NC$\underline{H}$N of $C_5H_4N_2O$ & $C_6\underline{H}_5$), 5.18–5.13 (m, 1H, $C_5\underline{H}_4N_2O$), 4.72–4.67 (m, 1H, $C_5\underline{H}_4N_2O$), 4.49–4.44 (m, 1H, $C_5\underline{H}_4N_2O$), 1.93-1.90 (m, 1H, C$\underline{H}$$(CH_3)_2$), 1.86–1.79 (m, 1H, C$\underline{H}_2CH(CH_3)_2$), 1.62–1.50 (m, 1H, C$\underline{H}_2CH(CH_3)_2$), 1.02 (d, 3H, $^3J_{HH}$ = 7 Hz, CH(C$\underline{H}_3)_2$), 1.00 (d, 3H, $^3J_{HH}$ = 7 Hz, CH(C$\underline{H}_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 149.2 ($\underline{C}_6H_5$), 133.5 (N$\underline{C}$HN), 128.4 ($\underline{C}_6H_5$), 124.9 ($\underline{C}_6H_5$), 123.6 ($\underline{C}_6H_5$), 122.7 ($\underline{C}_5H_4N_2O$), 111.4 ($\underline{C}_5H_4N_2O$), 83.1 ($\underline{C}H_2$ of $\underline{C}_5H_4N_2O$), 53.9 ($\underline{C}$H of $\underline{C}_5H_4N_2O$), 42.9 ($\underline{C}$H$(CH_3)_2$), 25.4 ($\underline{C}H_2$CH$(CH_3)_2$), 22.7 (CH_2CH($\underline{C}H_3)_2$), 22.0 (CH_2CH($\underline{C}H_3)_2$). IR data (NaCl pellet) cm^{-1}: 3261 (m), 3065 (w),

3026 (w), 2960 (m), 2876 (w), 2388 (w), 1944 (w), 1878 (w), 1612 (m), 1429 (m), 1362 (m), 1223 (w), 1129 (m), 996 (m), 757 (m), 702 (w). HRMS (ES): *m/z* 243.1482 $[M+H]^+$, calcd: *m/z* 243.1492. Anal. Calcd. for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56. Found: C, 73.34; H, 6.91; N, 11.11.

Synthesis of (*S*)-3-*i*-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-6-ium iodide (2f)

A solution of methyl iodide (7.32 g, 51.6 mmol) and (S)-3-*i*-butyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazole (**2e**) (0.500 g, 2.06 mmol) was refluxed in CH_3CN (*ca.* 30 mL) for 6 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was cooled to room temperature and volatiles were removed in *vaccuo*. The crude product thus obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of chloroform and MeOH (*v/v*, 8:2) as a mixed solvent. The desired product **2f** isolated as a thick yellow liquid (0.713 g, 90 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.74 (s, 1H, NC*H*N of $C_5H_4N_2O$), 7.51–7.35 (m, 5H, C_6H_5), 5.38–5.24 (m, 2H, $C_5H_4N_2O$), 4.84–4.72 (m, 1H, $C_5H_4N_2O$), 3.95 (s, 3H, NCH_3), 2.27–2.14 (m, 2H, $CH(CH_3)_2$ & $CH_2CH(CH_3)_2$), 1.90–1.71 (m, 1H, $CH_2CH(CH_3)_2$), 1.05 (d, 3H, $^3J_{HH}$ = 3 Hz, $CH(CH_3)_2$), 1.03 (d, 3H, $^3J_{HH}$ = 3 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 147.2 (C_6H_5), 129.8 (NCHN), 129.3 (C_6H_5), 129.1 (C_6H_5), 126.6 (C_6H_5), 123.7 ($C_5H_4N_2O$), 108.5 ($C_5H_4N_2O$), 82.3 (CH_2 of $C_5H_4N_2O$), 57.5 (CH of $C_5H_4N_2O$), 42.3 ($CH(CH_3)_2$), 37.1 ($CH_2CH(CH_3)_2$), 25.7 (NCH_3), 22.4 ($CH_2CH(CH_3)_2$). IR data (NaCl pellet) cm^{-1}: 3449 (w), 2963 (s), 2880 (w), 1713 (m), 1656 (s), 1553 (w), 1453 (m), 1204 (m), 762 (m), 701 (m). HRMS (ES): *m/z* 257.1649 $[M-I]^+$, calcd: *m/z* 257.1648.

Synthesis of ((*S*)-3-*i*-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene)silver(I) iodide (2g)

A mixture of (S)-3-*i*-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-6-ium iodide (**2f**) (0.990 g, 2.57 mmol) and Ag_2O (0.298 g, 1.29 mmol) was stirred in CH_2Cl_2 (*ca*. 100 mL) for 1 hours at room temperature and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, solvent was removed from the filtrate, and the residue thus obtained was crystallized using CH_2Cl_2 and *i*-Pr_2O (*v/v*, 1:9, 10 mL) as a mixed solvent to give **2g** as an off-white solid (1.13 g, 90 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.45–7.21 (m, 5H, $C_6\underline{H}_5$), 5.17 (t, 1H, $^3J_{HH}$ = 9Hz, $C_5\underline{H}_3N_2O$), 5.05–4.92 (m, 1H, $C_5\underline{H}_3N_2O$), 4.60 (dd, 1H, $^3J_{HH}$ = 6Hz, $C_5\underline{H}_3N_2O$), 3.82 (s, 3H, $C\underline{H}_3$), 2.34–2.15 (m, 1H, $C\underline{H}(CH_3)_2$), 1.83–1.71 (m, 1H, $C\underline{H}_2CH(CH_3)_2$), 1.71–1.50 (m, 1H, $C\underline{H}_2CH(CH_3)_2$), 0.97 (d, 3H, $^3J_{HH}$ = 9 Hz, $CH(C\underline{H}_3)_2$), 0.91 (d, 3H, $^3J_{HH}$ = 5 Hz, $CH(C\underline{H}_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 169.8 (N$\underline{C}$N of $\underline{C}_5H_3N_2O$), 148.7 ($\underline{C}_6H_5$), 128.8 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$) 127.5 ($\underline{C}_5H_3N_2O$), 107.5 ($\underline{C}_5H_3N_2O$), 81.8 ($\underline{C}H_2$ of $C_5H_3N_2O$), 55.5 ($\underline{C}H$ of $C_5H_3N_2O$), 43.8 ($\underline{C}H(CH_3)_2$), 40.0 ($\underline{C}H_2CH(CH_3)_2$), 25.3 ($N\underline{C}H_3$), 23.5 ($CH(\underline{C}H_3)_2$), 22.7 ($CH(\underline{C}H_3)_2$). IR data (KBr pellet) cm^{-1}: 3065 (w), 2954 (s), 2876 (w), 1956 (w), 1889 (w), 1678 (m), 1606 (m), 1440 (m), 1362 (m), 1151 (w), 924 (m), 757 (w), 702 (m), 624 (w). Anal. Calcd. for $C_{16}H_{20}AgIN_2O{\bullet}H_2O$: C, 37.74; H, 4.36; N, 5.50. Found: C, 38.02; H, 3.62; N, 5.60.

Synthesis of [(3*S*)-6-methyl-7-phenyl-3-*i*-butyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene]rhodium (1,5-cyclooctadiene) chloride (2h)

A mixture of ((S)-3-*i*-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5(6H)-ylidene)silver(I) iodide (**2g**) (0.500 g, 1.01 mmol) and $\{(COD)RhCl\}_2$ (0.250 g, 0.509 mmol)

was stirred in CH_2Cl_2 (*ca*. 50 mL) at room temperature for 2 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, and the solvent was removed in *vaccuo*. The crude product so obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of heptane and EtOAc (*v/v*, 8:2). The desired product **2h** was isolated as an yellow solid (0.483 g, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): Major isomer: δ 7.34–7.29 (m, 2H, $C_6\underline{H}_5$), 7.24–7.20 (m, 3H, $C_6\underline{H}_5$) 5.10–4.81 (m, 3H,$C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.61–4.41 (m, 2H,$C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.03 (s, 3H, $NC\underline{H}_3$), 3.47–3.31 (m, 2H, $C_8\underline{H}_{12}$), 2.52–2.08 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}(CH_3)_2$), 2.08–1.65 (m, 6H, $C_8\underline{H}_{12}$, $C\underline{H}_2CH(CH_3)_2$), 1.13 (d, 3H, $^3J_{HH}$ = 5 Hz, $CH(C\underline{H}_3)_2$), 1.10 (d, 3H, $^3J_{HH}$ = 8 Hz, $CH(C\underline{H}_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 171.7 (d, $J_{Rh\text{-}C}$ = 50 Hz, $N\underline{C}N$ of $C_5\underline{H}_3N_2O$), 148.1 ($\underline{C}_6H_5$), 128.7 ($\underline{C}_6H_5$), 127.8 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$) 127.3 ($\underline{C}_5H_3N_2O$), 107.5 ($\underline{C}_5H_3N_2O$), 98.5 ($\underline{C}_8H_{12}$), 81.4 ($\underline{C}H_2$ of $C_5H_3N_2O$), 68.9 ($\underline{C}_8H_{12}$), 65.9 ($\underline{C}_8H_{12}$), 55.6 ($\underline{C}H$ of $C_5H_3N_2O$), 43.7 ($\underline{C}H(CH_3)_2$), 38.3 ($\underline{C}_8H_{12}$), 34.3 ($\underline{C}_8H_{12}$), 32.9 ($\underline{C}_8H_{12}$), 29.9 ($\underline{C}_8H_{12}$), 29.0 ($\underline{C}H_2CH(CH_3)_2$), 27.8 ($\underline{C}_8H_{12}$), 26.0 ($N\underline{C}H_3$), 23.9 ($CH(\underline{C}H_3)_2$), 21.9 ($CH(\underline{C}H_3)_2$). Minor isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.34–7.29 (m, 2H, $C_6\underline{H}_5$), 7.24–7.20 (m, 3H, $C_6\underline{H}_5$) 5.10–4.81 (m, 3H,$C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.61–4.41 (m, 2H,$C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.00 (s, 3H, $NC\underline{H}_3$), 3.25–3.16 (m, 2H, $C_8\underline{H}_{12}$), 2.52–2.08 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}(CH_3)_2$), 2.08–1.65 (m, 6H, $C_8\underline{H}_{12}$, $C\underline{H}_2CH(CH_3)_2$), 1.13 (d, 3H, $^3J_{HH}$ = 5 Hz, $CH(C\underline{H}_3)_2$), 1.10 (d, 3H, $^3J_{HH}$ = 8 Hz, $CH(C\underline{H}_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 171.9 (d, $J_{Rh\text{-}C}$ = 51 Hz, $N\underline{C}N$ of $C_5\underline{H}_3N_2O$), 148.4 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 127.8 ($\underline{C}_6H_5$), 127.6 ($\underline{C}_6H_5$) 127.2 ($\underline{C}_5H_3N_2O$), 107.4 ($\underline{C}_5H_3N_2O$), 98.4 ($\underline{C}_8H_{12}$), 81.2 ($\underline{C}H_2$ of $C_5H_3N_2O$), 68.8 ($\underline{C}_8H_{12}$), 65.7 ($\underline{C}_8H_{12}$), 55.8 ($\underline{C}H$ of $C_5H_3N_2O$), 42.9 ($\underline{C}H(CH_3)_2$), 38.5 ($\underline{C}_8H_{12}$), 32.9 ($\underline{C}_8H_{12}$), 31.9 ($\underline{C}_8H_{12}$), 29.9 ($\underline{C}H_2CH(CH_3)_2$), 29.0 ($\underline{C}_8H_{12}$), 28.6 ($\underline{C}_8H_{12}$), 25.8 ($N\underline{C}H_3$), 23.5 ($CH(\underline{C}H_3)_2$), 22.0 ($CH(\underline{C}H_3)_2$). IR data (KBr pellet) cm^{-1}: 3048 (w), 2954 (m), 2876 (m),

2826 (m), 1667 (s), 1606 (m), 1506 (m), 1429 (m), 1390 (m), 1140 (m), 996 (m), 913 (m), 757 (m), 702 (m), 630 (w). HRMS (ES): *m/z* 503.1305 $[M+H]^+$, calcd: *m/z* 503.1331. Anal. Calcd. for $C_{24}H_{32}ClRhN_2O$: C, 57.32; H, 6.41; N, 5.57. Found: C, 57.38; H, 5.55; N, 5.55.

Synthesis of [(3*S*)-6-methyl-7-phenyl-3-*i*-butyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene] iridium (1,5-cyclooctadiene) chloride (2i)

A mixture of ((S)-3-*i*-butyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5(6H)-ylidene)silver(I) iodide (**2g**) (0.400 g, 0.764 mmol) and $\{(COD)IrCl\}_2$ (0.256 g, 0.381 mmol) was stirred in CH_2Cl_2 (*ca*. 50 mL) at room temperature for 2 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, and the solvent was removed in *vaccuo*. The crude product so obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of heptane and EtOAc (*v/v*, 8:2). The desired product **2i** was isolated as an yellow solid (0.202 g, 45 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): Major isomer: δ 7.34–7.29 (m, 2H, $C_6\underline{H}_5$), 7.25–7.20 (m, 3H, $C_6\underline{H}_5$) 5.10–4.83 (m, 3H, $C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.59–4.46 (m, 2H, $C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.04 (s, 3H, $NC\underline{H}_3$), 3.48–3.30 (m, 2H, $C_8\underline{H}_{12}$), 2.54–2.15 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}(CH_3)_2$), 2.07–1.69 (m, 6H, $C_8\underline{H}_{12}$, $C\underline{H}_2CH(CH_3)_2$), 1.13 (d, 3H, $^3J_{HH}$ = 4 Hz, $CH(C\underline{H}_3)_2$), 1.10 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH(C\underline{H}_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 171.0 ($N\underline{C}N$ of $C_5\underline{H}_3N_2O$), 148.1 ($\underline{C}_6H_5$), 128.7 ($\underline{C}_6H_5$), 127.8 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$) 127.3 ($\underline{C}_5H_3N_2O$), 107.4 ($\underline{C}_5H_3N_2O$), 98.5 ($\underline{C}_8H_{12}$), 81.2 ($\underline{C}H_2$ of $C_5H_3N_2O$), 68.9 ($\underline{C}_8H_{12}$), 65.9 ($\underline{C}_8H_{12}$), 55.8 ($\underline{C}H$ of $C_5H_3N_2O$), 43.7 ($\underline{C}H(CH_3)_2$), 38.3 ($\underline{C}_8H_{12}$), 34.3 ($\underline{C}_8H_{12}$), 29.0 ($\underline{C}_8H_{12}$), 29.9 ($\underline{C}H_2CH(CH_3)_2$), 28.6 ($\underline{C}_8H_{12}$), 27.8 ($\underline{C}_8H_{12}$), 26.0 ($N\underline{C}H_3$), 23.5 ($CH(\underline{C}H_3)_2$), 21.9 ($CH(\underline{C}H_3)_2$). Minor isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.34–7.29 (m, 2H, $C_6\underline{H}_5$), 7.25–7.20 (m, 3H, $C_6\underline{H}_5$) 5.10–4.83 (m, 3H, $C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.59–4.46 (m, 2H, $C_5\underline{H}_3N_2O$

& $C_8\underline{H}_{12}$), 4.00 (s, 3H, NC$\underline{H}_3$), 3.26–3.17 (m, 2H, $C_8\underline{H}_{12}$), 2.54–2.15 (m, 5H, $C_8\underline{H}_{12}$ & C$\underline{H}$(CH_3)$_2$), 2.07–1.69 (m, 6H, $C_8\underline{H}_{12}$, C$\underline{H}_2$CH(CH_3)$_2$), 1.13 (d, 3H, $^3J_{HH}$ = 4 Hz, CH(C$\underline{H}_3$)$_2$), 1.10 (d, 3H, $^3J_{HH}$ = 7 Hz, CH(C$\underline{H}_3$)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 171.7 (N$\underline{C}$N of $C_5\underline{H}_3N_2O$), 148.5 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 127.8 ($\underline{C}_6H_5$), 127.6 ($\underline{C}_6H_5$) 127.2 ($\underline{C}_5H_3N_2O$), 107.3 ($\underline{C}_5H_3N_2O$), 98.2 ($\underline{C}_8H_{12}$), 81.4 ($\underline{C}H_2$ of $C_5H_3N_2O$), 68.9 ($\underline{C}_8H_{12}$), 65.9 ($\underline{C}_8H_{12}$), 55.6 ($\underline{C}$H of $C_5H_3N_2O$), 42.9 ($\underline{C}$H(CH_3)$_2$), 38.5 ($\underline{C}_8H_{12}$), 32.9 ($\underline{C}_8H_{12}$), 32.9 ($\underline{C}_8H_{12}$), 29.0 ($\underline{C}H_2$CH(CH_3)$_2$), 31.9 ($\underline{C}_8H_{12}$), 29.9 ($\underline{C}_8H_{12}$), 28.6 ($\underline{C}_8H_{12}$), 23.9 (N$\underline{C}H_3$), 23.5 (CH($\underline{C}H_3$)$_2$), 22.0 (CH($\underline{C}H_3$)$_2$). IR data (KBr pellet) cm^{-1}: 3054 (m), 2971 (m), 2921 (m), 2876 (m), 2826(m), 2355 (w), 1926 (w), 1656 (m), 1601 (m), 1434 (m), 1140 (m), 1002 (m), 913 (m), 757 (m), 696 (w), 630 (w). HRMS (ES): *m/z* 557.2138 $[M\text{-}Cl]^+$, calcd: *m/z* 557.2139. Anal. Calcd. for $C_{24}H_{32}ClN_2OIr{\bullet}CHCl_3{\bullet}H_2O$: C, 41.16; H, 4.84; N, 3.84. Found: C, 40.47; H, 4.27; N, 3.94.

Synthesis of (*R*)-2-formamido-N-((*S*)-1-hydroxy-3-methylbutan-2-yl)-2-phenylacetamide (3c)

N-methyl morpholine (18.5 g, 182 mmol) was added to a solution of (R)-2-formamido-2-phenylacetic acid (**3b**) (21.7 g, 121 mmol) in THF (*ca*. 350 mL) at -20 °C under nitrogen atmosphere. This was followed by the addition of *n*-butylchloroformate (18.2 g, 133 mmol) and the reaction mixture stirred at this temperature for 15 minutes, after which (R)-2-amino-3-methylbutan-1-ol (**3a**) (12.4 g, 120 mmol) was added. The reaction mixture was then stirred at room temperature for 1 hour. The progress of the reaction was monitored by thin layer chromatography (TLC) and upon observing the complete conversion of the starting material to product, the solvent was removed in *vaccuo*, followed by the addition of water (*ca* 300 mL) resulting the product, which is filtered and washed with *n*-heptane (*ca*. 200 mL) and dried under *vaccuo* to give the desired compound **3c** as white solid (15.4 g, 49 %). ^1H NMR

(DMSO-d_6, 300 MHz, 25 °C): δ 8.80–8.03 (m, 1H, N*H*), 8.07–8.03 (m, 2H, N*H* & C*H*O), 7.48–7.39 (m, 2H, C_6H_5), 7.37–7.20 (m, 3H, C_6H_5), 5.65–5.62 (m, 1H, COC*H*NH), 4.65–4.48 (m, 1H, CH_2OH), 3.60–3.42 (m, 1H, CH_2CHNH), 3.36–3.27 (m, 2H, CH_2), 1.90–1.65 (m, 1H, $CH(CH_3)_2$), 0.87–0.82 (m, 3H, $CH(CH_3)_2$, 0.64–0.59 (m, 3H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz, 25 °C): (Diasteriomer-1): δ 169.2 (*C*ONH), 160.4 (N*C*HO), 138.7 (C_6H_5), 128.2 (C_6H_5), 128.1 (C_6H_5), 126.6 (C_6H_5), 60.9 (CH_2OH), 55.7 (*C*HNHCHO), 54.4 (*C*HNH), 28.0 ($CH(CH_3)_2$), 19.5 ($CH(CH_3)_2$), 18.1 ($CH(CH_3)_2$). (Diasteriomer-2): δ 169.3 (*C*ONH), 160.3 (N*C*HO), 139.3 (C_6H_5), 128.2 (C_6H_5), 127.3 (C_6H_5), 126.9 (C_6H_5), 61.0 (CH_2OH), 55.6 (*C*HNHCHO), 54.5 (*C*HNH), 28.2 ($CH(CH_3)_2$), 19.3 ($CH(CH_3)_2$), 17.9 ($CH(CH_3)_2$). IR data (KBr pellet) cm^{-1}: 3270 (m), 3093 (m), 2976 (m), 2882 (m), 1956 (w), 1645 (m), 1573 (m), 1534 (m), 1390 (m), 1234 (m), 702 (m). HRMS (ES): *m/z* 287.1356 $[M+Na]^+$, calcd: *m/z* 287.1366. Anal. Calcd. for $C_{14}H_{20}N_2O_3$: C, 63.62; H, 7.63; N, 10.60. Found: C, 62.64; H, 7.24; N, 11.26.

Synthesis of N-((*R*)-((*S*)-4-*i*-propyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl)formamide (3d)

A solution of *p*-toluene sulphonyl chloride (27.0 g, 142 mmol) in 1,2 dichloroethane (*ca*. 200 mL) was added to a mixture containing (R)-2-formamido-N-((S)-1-hydroxy-3-methylbutan-2-yl)-2-phenylacetamide (**3c**) (15.0 g, 56.7 mmol), 4-dimethylaminopyridine (0.692 g, 5.66 mmol) and Et_3N (25.8 g, 255 mmol) in 1,2 dichloroethane (*ca*. 200 mL) at room temperature. After which, the reaction mixture was stirred for 12 hours at room temperature and during which the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture quenched with saturated $NaHCO_3$ solution (*ca*. 200 mL). The resulting organic layer was collected, dried over anhydrous Na_2SO_4 and filtered. The volatiles were then removed in

vaccuo and the crude product thus obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of $CHCl_3$ and MeOH (9:1, *v/v*) to give the desired compound **3d** as an yellow liquid (9.22 g, 66 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.20 (s, 1H, C*H*O), 7.48–7.26 (m, 5H, C_6H_5), 5.84–5.71 (m, 1H, C*H*NH), 4.45–4.21 (m, 1H, C_3H_3NO), 4.21–3.92 (m, 2H, C_3H_3NO), 1.88–1.64 (m, 1H, C*H*$(CH_3)_2$), 1.03–0.87 (m, 3H, CH(C*H*$_3$)$_2$), 0.86–0.81 (m, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 165.5 (C_3H_3NO), 160.4 (N*C*HO), 137.3 (C_6H_5), 128.8 (C_6H_5), 128.3 (C_6H_5), 127.2 (C_6H_5), 71.5 (*C*H$_2$ of C_3H_3NO), 71.2 (*C*HNHCHO), 50.2 (*C*H of C_3H_3NO), 32.7 (*C*H$(CH_3)_2$), 18.8 (CH(*C*H$_3$)$_2$), 17.8 (CH(*C*H$_3$)$_2$). IR data (NaCl pellet) cm^{-1}: 3289 (m), 2968 (m), 2880 (w), 1663 (s), 1525 (m), 1497 (m), 1361 (m), 1232 (m), 696 (m). LRMS (ES): *m/z* 247.1386 $[M+H]^+$, calcd: *m/z* 247.1441.

Synthesis of (*S*)-3-*i*-propyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazole (3e)

P_2O_5 (4.65 g, 32.9 mmol) was added to a solution of N-((R)-((S)-4-*i*-propyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl)formamide (**3d**) (2.03 g, 8.24 mmol) in toluene (*ca*. 150 mL) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 30 minutes at room temperature and then refluxed for 12 hours. The progress of the reaction was monitored by thin layer chromatography (TLC) and upon observing the complete conversion of the starting material to product, the reaction mixture was cooled to room temperature and filtered. The isolated solid was dissolved using a 1N HCl (*ca*. 50 mL) solution and then the pH was adjusted to 12 using saturated KOH solution. The aqueous solution was extracted with CH_2Cl_2 (*ca*.2 × 50 mL), combined organic layers were dried over anhydrous Na_2SO_4, filtered and finally the filtrate was reduced in *vaccuo*. The crude product so obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of $CHCl_3$ and MeOH (*v/v*. 9:1). The desired compound **3e**

was thus isolated as an yellow solid (0.851 g, 46 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.64 (d, 2H, $^{3}J_{HH}$ = 9 Hz, $C_6\underline{H}_5$), 7.29–7.24 (m, 2H, $C_6\underline{H}_5$), 7.07 (s, 1H, NC$\underline{H}$N of $C_5H_4N_2O$), 7.04–7.01 (m, 1H, $C_6\underline{H}_5$), 5.05 (t, 1H, $^{3}J_{HH}$ = 9Hz, $C_5\underline{H}_4N_2O$), 4.78–4.74 (m, 1H, $C_5\underline{H}_4N_2O$), 4.23–4.17 (m, 1H,$C_5\underline{H}_4N_2O$), 2.05–1.86 (m, 1H, C$\underline{H}$(CH_3)$_2$), 0.91 (d, 3H, $^{3}J_{HH}$ = 3 Hz, CH(C$\underline{H}_3$)$_2$), 0.89 (d, 3H, $^{3}J_{HH}$ = 4 Hz, CH(C$\underline{H}_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 149.8 ($\underline{C}_6H_5$), 133.3 (N$\underline{C}$HN), 128.9 ($\underline{C}_6H_5$), 125.0 ($\underline{C}_6H_5$), 123.6 ($\underline{C}_6H_5$) 123.2 ($C_5H_4N_2O$), 110.9 ($C_5H_4N_2O$), 80.6 ($\underline{C}H_2$ of $C_5H_4N_2O$), 61.0 ($\underline{C}$H of $C_5H_4N_2O$), 31.8 ($\underline{C}$H(CH_3)$_2$), 18.1 (CH($\underline{C}H_3$)$_2$), 17.7 (CH($\underline{C}H_3$)$_2$). IR data (NaCl pellet) cm^{-1}: 3239 (m), 2963 (m), 2869 (w), 1724 (m), 1619 (s), 1437 (m), 1370 (m), 989 (m), 762 (m). HRMS (ES): *m/z* 229.1343 $[M+H]^+$, calcd: *m/z* 229.1335. Anal. Calcd. for $C_{14}H_{16}N_2O$•CH_3OH: C, 69.20; H, 7.70; N, 10.76. Found: C, 69.88; H, 6.33; N, 10.77.

Synthesis of (*S*)-3-*i*-propyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-6-ium iodide (3f)

A solution of methyl iodide (14.7 g, 104 mmol) and (S)-3-*i*-propyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazole (**3e**) (0.950 g, 4.16 mmol) was refluxed in CH_3CN (*ca*.30 mL) for 6 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was cooled to room temperature and volatiles were removed in *vaccuo*. The crude product thus obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of chloroform and MeOH (*v/v*, 8:2). The desired product **3f** isolated as an yellow liquid (1.48 g, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.87 (s, 1H, NC$\underline{H}$N), 7.46–7.34 (m, 5H, $C_6\underline{H}_5$), 5.31–5.17 (m, 2H, $C_5\underline{H}_4N_2O$), 4.92–4.81 (m, 1H, $C_5\underline{H}_4N_2O$), 3.95 (s, 3H, NC$\underline{H}_3$), 2.51–2.35 (m, 1H, C$\underline{H}$(CH_3)$_2$), 1.07 (d, 3H, $^{3}J_{HH}$ = 7Hz, CH(C$\underline{H}_3$)$_2$), 1.02 (d, 3H, $^{3}J_{HH}$ = 6Hz, CH(C$\underline{H}_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75

MHz, 25 °C): δ 147.9 ($\underline{C}_6H_5$), 129.7 (N$\underline{C}$HN), 129.4 ($\underline{C}_6H_5$), 129.0 ($\underline{C}_6H_5$), 127.3 ($\underline{C}_6H_5$), 123.8 ($C_5H_4N_2O$), 108.0 ($C_5H_4N_2O$), 79.6 ($\underline{C}H_2$ of $C_5H_4N_2O$), 63.7 ($\underline{C}$H of $C_5H_4N_2O$), 36.9 (N$\underline{C}H_3$), 31.2 ($\underline{C}$H(CH_3)$_2$), 18.0 (CH($\underline{C}H_3$)$_2$), 17.3 (CH($\underline{C}H_3$)$_2$). IR data (NaCl pellet) cm^{-1}: 3355 (m), 3289 (m), 2968 (m), 2874 (m), 2343 (m), 1591 (m), 1470 (m), 1387 (m), 1066 (m), 878 (m). HRMS (ES): *m/z* 243.1495 $[M-I]^+$, calcd: *m/z* 243.1492.

Synthesis of (*S*)-(3-*i*-propyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene)silver(I) iodide (3g)

A mixture of (S)-3-*i*-propyl-6-methyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-6-ium iodide (**3f**) (1.00 g, 2.70 mmol) and Ag_2O (0.313 g, 1.35 mmol) was stirred in CH_2Cl_2 (*ca.* 100 mL) for 1 hour at room temperature and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, solvent was removed from the filtrate, and the residue thus obtained was crystalized using CH_2Cl_2 and *i*-Pr_2O (*v/v*, 1:9, 10 mL) as a mixed solvent to give **3g** as an off-white solid (1.10 g, 85 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): 7.36–7.21 (m, 5H, $C_6\underline{H}_5$), 5.02–4.93 (m, 2H, $C_5\underline{H}_3N_2O$), 4.71–4.62 (m, 1H, $C_5\underline{H}_3N_2O$), 3.80 (s, 3H, C$\underline{H}_3$), 2.66–2.50 (m, 1H, C$\underline{H}$(CH_3)$_2$), 0.96 (d, 3H, $^3J_{HH}$ = 7 Hz, CH(C$\underline{H}_3$)$_2$), 0.83 (d, 3H, $^3J_{HH}$ = 6 Hz, CH(C$\underline{H}_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 170.8 (N$\underline{C}$N), 149.0 ($\underline{C}_6H_5$), 128.8 ($\underline{C}_6H_5$), 128.5 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$) 127.5 ($C_5H_3N_2O$), 106.7 ($C_5H_3N_2O$), 61.0 ($\underline{C}H_2$ of $C_5H_3N_2O$), 61.0 ($\underline{C}$H of $C_5H_3N_2O$), 39.7 (N$\underline{C}H_3$), 31.3 ($\underline{C}$H(CH_3)$_2$), 18.5 (CH($\underline{C}H_3$)$_2$), 15.4 (CH($\underline{C}H_3$)$_2$). IR data (KBr pellet) cm^{-1}: 3059 (m), 2973(m), 2871 (w), 2183 (w), 1972 (w), 1895 (w), 1728 (m), 1678 (s), 1440 (m), 1390 (m), 1074 (m), 924 (m), 763 (m), 702 (m). Anal. Calcd. for $C_{15}H_{18}AgIN_2O$•H_2O: C, 36.39; H, 4.07; N, 5.66. Found: C, 36.99; H, 3.20; N, 5.89.

Synthesis of [(3*S*)-6-methyl-7-phenyl-3-*i*-propyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene] rhodium (1,5-cyclooctadiene) chloride (3h)

A mixture of ((S)-6-methyl-3-*i*-propyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5(6H)-ylidene)silver(I) iodide (**3g**) (0.500 g, 1.05 mmol) and{(COD)RhCl}$_2$ (0.258 g, 0.523 mmol) was stirred in CH_2Cl_2 (*ca*. 50 mL) at room temperature for 4 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, and the solvent was removed in *vaccuo*. The crude product so obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of heptane and EtOAc (*v/v*, 8:2). The desired product **3h** was isolated as an yellow solid (0.438 g, 85 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): Major isomer: δ 7.34–7.29 (m, 2H, $C_6\underline{H}_5$), 7.25–7.19 (m, 3H, $C_6\underline{H}_5$), 5.05–4.88 (m, 2H, $C_5\underline{H}_3N_2O$), 4.85–4.81 (m, 3H, $C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.05 (s, 3H, $NC\underline{H}_3$), 3.64–3.50 (m, 2H, $C_8\underline{H}_{12}$), 2.50–2.19 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}(CH_3)_2$), 2.04–1.73 (m, 4H, $C_8\underline{H}_{12}$), 1.08 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH(C\underline{H}_3)_2$), 0.93 (d, 3H, $^3J_{HH}$ = 8 Hz, $CH(C\underline{H}_3)_2$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 171.9 (d, $J_{Rh\text{-}C}$ = 50 Hz, N$\underline{C}$N of $\underline{C}_5H_3N_2O$), 148.8 ($\underline{C}_6H_5$), 128.7 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$), 127.2 ($C_5H_3N_2O$), 106.8 ($C_5H_3N_2O$), 98.4 ($\underline{C}_8H_{12}$), 75.7 ($\underline{C}H_2$ of $C_5H_3N_2O$), 68.3 ($\underline{C}_8H_{12}$), 66.4 ($\underline{C}_8H_{12}$), 61.6 ($\underline{C}H$ of $C_5H_3N_2O$), 38.4 ($\underline{C}H(CH_3)_2$), 33.9 ($\underline{C}_8H_{12}$), 32.4 ($\underline{C}_8H_{12}$), 31.2 ($\underline{C}_8H_{12}$), 29.6 ((N$\underline{C}H_3$), 28.2 ($\underline{C}_8H_{12}$), 28.0 ($\underline{C}_8H_{12}$), 18.9 ($CH(\underline{C}H_3)_2$), 14.6 ($CH(\underline{C}H_3)_2$). Minor isomer : ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.34–7.29 (m, 2H, $C_6\underline{H}_5$), 7.25–7.19 (m, 3H, $C_6\underline{H}_5$), 4.78–4.65 (m, 2H, $C_5\underline{H}_3N_2O$), 4.78–4.65 (m, 3H, $C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 4.01 (s, 3H, $NC\underline{H}_3$), 3.30–3.19 (m, 2H, $C_8\underline{H}_{12}$), 2.50–2.19 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}(CH_3)_2$), 2.04–1.73 (m, 4H, $C_8\underline{H}_{12}$), 1.10 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH(C\underline{H}_3)_2$), 0.85 (d, 3H, $^3J_{HH}$ = 8 Hz, $CH(C\underline{H}_3)_2$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 171.9 (d, $J_{Rh\text{-}C}$ = 50 Hz, N$\underline{C}$N of $\underline{C}_5H_3N_2O$), 148.8 ($\underline{C}_5H_3N_2O$), 128.7 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$), 127.2 ($\underline{C}_6H_5$), 106.8 ($C_5H_3N_2O$), 98.6 ($\underline{C}_8H_{12}$),

76.1 (<u>C</u>H$_2$ of $C_5H_3N_2O$), 68.5 (<u>C</u>$_8$H$_{12}$), 66.2 (<u>C</u>$_8$H$_{12}$), 60.9 (<u>C</u>H of $C_5H_3N_2O$), 38.5 (<u>C</u>H(CH$_3$)$_2$), 32.9 (<u>C</u>$_8$H$_{12}$), 32.8 (<u>C</u>$_8$H$_{12}$), 32.4 (N<u>C</u>H$_3$), 29.6 (<u>C</u>$_8$H$_{12}$), 28.2 (<u>C</u>$_8$H$_{12}$), 28.0 (<u>C</u>$_8$H$_{12}$), 19.0 (CH(<u>C</u>H$_3$)$_2$), 14.2 (CH(<u>C</u>H$_3$)$_2$). IR data (KBr pellet) cm^{-1}: 3453 (w), 2960 (m), 2882 (m), 2826 (m), 1673 (s), 1606 (m), 1434 (m), 1390 (m), 1151 (m), 1112 (m), 763 (m), 702 (m). HRMS (ES): *m/z* 453.1406 [M-Cl]$^+$, calcd: *m/z* 453.1408. Anal. Calcd. for $C_{23}H_{30}ClN_2ORh$: C, 56.51; H, 6.19; N, 5.73. Found: C, 56.52; H, 4.62; N, 6.20.

Synthesis of [(3*S*)-6-methyl-7-phenyl-3-*i*-propyl-2,3-dihydroimidazo[5,1-b]oxazol-5-ylidene] iridium (1,5-cyclooctadiene) chloride (3i)

A mixture of ((S)-6-methyl-3-*i*-propyl-7-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-5(6H)-ylidene)silver(I) iodide (**3g**) (0.608 g, 1.27 mmol) and{(COD)IrCl}$_2$ (0.423 g, 0.629 mmol) was stirred in CH_2Cl_2 (*ca*. 50 mL) at room temperature for 4 hours and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon observing the complete conversion of the starting material to product, the reaction mixture was then filtered, and the solvent was removed in *vaccuo*. The crude product so obtained was purified by column chromatography using silica gel as a stationary phase and eluting it with a mixed medium of heptane and EtOAc (*v/v*, 8:2). The desired product (**3i**) was isolated as an yellow solid (0.708 g, 96 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): Major isomer: δ 7.35–7.20 (m, 5H, C$_6$<u>H</u>$_5$), 4.88–4.81 (m, 2H, C$_5$<u>H</u>$_3$N$_2$O), 4.56–4.54 (m, 3H, C$_5$<u>H</u>$_3$N$_2$O & C$_8$<u>H</u>$_{12}$), 3.91 (s, 3H, NC<u>H</u>$_3$), 3.27–3.23 (m, 2H, C$_8$<u>H</u>$_{12}$), 2.26–2.00 (m, 5H, C$_8$<u>H</u>$_{12}$ & C<u>H</u>(CH$_3$)$_2$), 1.67–1.44 (m, 4H, C$_8$<u>H</u>$_{12}$), 1.04 (d, 3H, $^3J_{HH}$ = 9 Hz, CH(C<u>H</u>$_3$)$_2$), 0.85 (d, 3H, $^3J_{HH}$ = 7 Hz, CH(C<u>H</u>$_3$)$_2$. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 170.3 (N<u>C</u>N of <u>C</u>$_5$H$_3$N$_2$O), 148.3 (<u>C</u>$_6$H$_5$), 128.8 (<u>C</u>$_6$H$_5$), 128.6 (<u>C</u>$_6$H$_5$), 127.7 (<u>C</u>$_6$H$_5$), 127.3 ($C_5H_3N_2O$), 106.2 ($C_5H_3N_2O$), 84.7 (<u>C</u>$_8$H$_{12}$), 75.9 (<u>C</u>H$_2$ of $C_5H_3N_2O$), 61.4 (<u>C</u>$_8$H$_{12}$), 51.7 (<u>C</u>$_8$H$_{12}$), 50.0 (<u>C</u>H of $C_5H_3N_2O$), 38.0 (<u>C</u>H(CH$_3$)$_2$), 34.4 (<u>C</u>$_8$H$_{12}$), 33.1 (<u>C</u>$_8$H$_{12}$), 30.9 (N<u>C</u>H$_3$), 30.4 (<u>C</u>$_8$H$_{12}$), 29.5 (<u>C</u>$_8$H$_{12}$), 29.3 (<u>C</u>$_8$H$_{12}$), 19.0

($CH(\underline{C}H_3)_2$), 14.2 ($CH(\underline{C}H_3)_2$). Minor isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.35–7.20 (m, 5H, $C_6\underline{H}_5$), 4.56–4.54 (m, 2H, $C_5\underline{H}_3N_2O$), 4.54–4.43 (m, 2H, $C_5\underline{H}_3N_2O$ & $C_8\underline{H}_{12}$), 3.93 (s, 3H, $NC\underline{H}_3$), 3.15–3.02 (m, 2H, $C_8\underline{H}_{12}$), 2.26–2.00 (m, 5H, $C_8\underline{H}_{12}$ & $C\underline{H}(CH_3)_2$), 1.67–1.44 (m, 4H, $C_8\underline{H}_{12}$), 1.04 (d, 3H, $^3J_{HH}$ = 9 Hz, $CH(C\underline{H}_3)_2$), 0.85 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH(C\underline{H}_3)_2$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 170.1 ($N\underline{C}N$ of $\underline{C}_5H_3N_2O$), 148.3 ($\underline{C}_6H_5$), 128.8 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 127.7 ($\underline{C}_6H_5$), 127.3 ($C_5H_3N_2O$), 106.2 ($C_5H_3N_2O$), 84.4 ($\underline{C}_8H_{12}$), 75.8 ($\underline{C}H_2$ of $C_5H_3N_2O$), 60.4 ($\underline{C}_8H_{12}$), 52.3 ($\underline{C}_8H_{12}$), 50.0 ($\underline{C}H$ of $C_5H_3N_2O$), 38.3 ($\underline{C}H(CH_3)_2$), 33.5 ($\underline{C}_8H_{12}$), 33.4 ($\underline{C}_8H_{12}$), 30.9 ($N\underline{C}H_3$), 30.4 ($\underline{C}_8H_{12}$), 28.9 ($\underline{C}_8H_{12}$), 28.0 (2 $\underline{C}_8H_{12}$), 19.0 ($CH(\underline{C}H_3)_2$), 14.2 ($CH(\underline{C}H_3)_2$). IR data (KBr pellet) cm^{-1}: 3448 (w), 2960 (m), 2937 (m), 2887 (m), 2826 (m), 1673 (m), 1606 (m), 1434 (m), 1384 (m), 1157 (m), 768 (m), 707 (m). HRMS (ES): *m/z* 578.1680 $[M]^+$, calcd: *m/z* 578.1663. Anal. Calcd. for $C_{23}H_{30}ClN_2OIr$: C, 47.78; H, 5.23; N, 4.85. Found: C, 47.04; H, 4.83; N, 4.62.

General procedure for asymmetric transfer hydrogenation

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing ketone (1.97 mmol), base (78.8 µmol), **1h** or **3i** (9.85 µmol, 0.5 mol %) in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired products (**4**–**14**). The *ee* was determined by chiral HPLC with Chiralpak-RJ and Chiralpak-IC column.

General procedure for Hg drop test.

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing acetophenone (1.97 mmol), *t*-BuOK (78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), and Hg(0) (0.152 g, 0.758 mmol) in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product (**4**). The *ee* was determined by chiral HPLC with Chiralpak-RJ and Chiralpak-IC column.

General procedure for the control experiment

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing acetophenone (1.97 mmol), *t*-BuOK (78.8 µmol), {(COD)RhCl} or {(COD)IrCl} (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was analyzed by ^{1}H NMR, GC−MS and the *ee* was determined by chiral HPLC with Chiralpak-RJ and Chiralpak-IC column.

General procedure for the blank experiment

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing acetophenone (1.97 mmol), *t*-BuOK (78.8 µmol) in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was analyzed by ^{1}H NMR, GC−MS and the *ee* was determined by chiral HPLC with Chiralpak-RJ and Chiralpak-IC column.

1-Phenylethanol (4)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing acetophenone (0.237 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **4** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.31−7.29 (m, 5H, $C_6\underline{H}_5$), 4.91 (q, 1H, $^{3}J_{HH}$ = 7 Hz, C$\underline{H}$$CH_3$), 2.36 (bs, 1H, O$\underline{H}$), 1.52 (d, 3H, $^{3}J_{HH}$ = 7 Hz, CH_3). GCMS (ESI): *m/z* 122 $[M]^+$, calcd: 122.

4-Methyl-phenylethanol (5)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 4−methyl acetophenone (0.264 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **5** as a colorless liquid. H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.18 (d, 2H, $^{3}J_{HH}$ = 8 Hz, $C_6\underline{H}_4$), 7.08 (d, 2H, $^{3}J_{HH}$ = 8 Hz, $C_6\underline{H}_4$), 4.76 (q, 1H, $^{3}J_{HH}$ = 9 Hz, C$\underline{H}$$CH_3$), 2.55(s, 3H, C$\underline{H}_3$), 1.39 (d, 3H, $^{3}J_{HH}$ = 6 Hz, CHC$\underline{H}_3$). GCMS (ESI): *m/z* 136 $[M]^+$, calcd: 136.

4-Bromo-phenylethanol (6)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 4−bromo acetophenone (0.390 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **6** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.40 (d, 2H, $^{3}J_{HH}$ = 9 Hz, $C_6\underline{H}_4$), 7.17 (d, 2H, $^{3}J_{HH}$ = 9 Hz, $C_6\underline{H}_4$), 4.78 (q, 1H, $^{3}J_{HH}$ = 6 Hz, $C\underline{H}CH_3$), 1.98 (bs, 1H, O*H*), 1.39 (d, 3H, $^{3}J_{HH}$ = 6 Hz, $CHCH_3$). GCMS (ESI): *m/z* 200 $[M]^+$, calcd: 200.

3-Fluoro-phenylethanol (7)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 3−fluoro acetophenone (0.271 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **7** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.26−7.18 (m, 1H, $C_6\underline{H}_4$), 7.06−7.00 (m, 2H, $C_6\underline{H}_4$), 6.91-6.84 (m, 1H, $C_6\underline{H}_4$), 4.85 (q, 1H, $^{3}J_{HH}$ = 9 Hz, $C\underline{H}CH_3$), 1.86 (bs, 1H, O*H*), 1.41 (d, 3H, $^{3}J_{HH}$ = 6 Hz, $CHC\underline{H}_3$). GCMS (ESI): *m/z* 140 $[M]^+$, calcd: 140.

3,4–Dimethyl–phenylethanol (8)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 4, 5−dimethyl acetophenone (0.291 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **8** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.08−7.05 (m, 1H, $C_6\underline{H}_3$), 7.04−7.00 (m, 2H, $C_6\underline{H}_3$), 4.78 (q, 1H, $^{3}J_{HH}$ = 6 Hz, C$\underline{H}$CH$_3$), 1.80 (bs, 1H, O$\underline{H}$), 2.19 (s, 3H, C$\underline{H}_3$), 2.17 (s, 3H, C$\underline{H}_3$), 1.41 (d, 3H, $^{3}J_{HH}$ = 7 Hz, CHC$\underline{H}_3$). GCMS (ESI): *m/z* 150 $[M]^+$, calcd: 150.

4-*t*-Butyl-phenylethanol (9)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 4−*t*-butyl acetophenone (0.346 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **9** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.31−7.29 (m, 2H, $C_6\underline{H}_4$), 7.21−7.12 (m, 2H, $C_6\underline{H}_4$), 4.82 (q, 1H, $^{3}J_{HH}$ = 6 Hz, C$\underline{H}$CH$_3$), 1.83 (bs, 1H, O$\underline{H}$), 1.42 (d, 3H, $^{3}J_{HH}$ = 6 Hz, CHC$\underline{H}_3$), 1.24 (s, 9H, C$\underline{H}_3$). GCMS (ESI): *m/z* 178 $[M]^+$, calcd: 178.

4-Chloro-phenylethanol (10)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 4−chloro acetophenone (0.303 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **10** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.26−7.18 (m, 4H, $C_6\underline{H}_4$), 4.83 (q, 1H, $^{3}J_{HH}$ = 6 Hz, C$\underline{H}$CH$_3$), 1.76 (bs, 1H, O$\underline{H}$), 1.40 (d, 3H, $^{3}J_{HH}$ = 6 Hz, CHC$\underline{H}_3$). GCMS (ESI): *m/z* 156 $[M]^+$, calcd: 156.

4-Thio methyl-phenylethanol (11)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 4−thio methyl acetophenone (0.327 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **11** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.17−7.10 (m, 4H, $C_6\underline{H}_4$), 4.80 (q, 1H, $^{3}J_{HH}$ = 6 Hz, C$\underline{H}$CH$_3$), 2.40 (s, 3H, SC$\underline{H}_3$), 1.45 (d, 3H, $^{3}J_{HH}$ = 6 Hz, $CHCH_3$). GCMS (ESI): *m/z* 168 $[M]^+$, calcd: 168.

4-Fluoro-phenylethanol (12)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 4−fluoro acetophenone (0.271 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85

μmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **12** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.34−7.19 (m, 2H, $C_6\underline{H}_4$), 7.03-6.83 (m, 2H, $C_6\underline{H}_4$) 4.83 (q, 1H, $^{3}J_{HH}$ = 6 Hz, C$\underline{H}$CH$_3$), 1.39 (d, 3H, $^{3}J_{HH}$ = 5 Hz, CHCH$_3$). GCMS (ESI): *m/z* 140 $[M]^+$, calcd: 140.

4-Nitro-phenylethanol (13)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 4−nitro acetophenone (0.325 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 μmol), catalyst **1h** or **3i** (9.85 μmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **13** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.15 (d, 2H, $^{3}J_{HH}$ = 10 Hz, $C_6\underline{H}_4$), 7.49 (d, 2H, $^{3}J_{HH}$ = 8 Hz, $C_6\underline{H}_4$), 4.99 (q, 1H, $^{3}J_{HH}$ = 6 Hz, C$\underline{H}$CH$_3$), 1.46 (d, 3H, $^{3}J_{HH}$ = 6 Hz, CHCH$_3$). GCMS (ESI): *m/z* 166 $[M]^+$, calcd: 167.

Cyclohexyl(phenyl)MeOH (14)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing cyclohexyl benzophenone (0.370 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 μmol), catalyst **1h** or **3i** (9.85 μmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The

reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **14** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.26−7.12 (m, 5H, $C_6\underline{H}_5$), 4.25 (d, 1H, $^{3}J_{HH}$ = 10 Hz, C$\underline{H}$CH), 2.03 (s, 1H, O$\underline{H}$), 1.95−1.63 (m, 5H, CH & C$\underline{H}_2$ of C_6H_{11}), 1.44−0.75 (m, 6H, C$\underline{H}_2$ of C_6H_{11}). GCMS (ESI): *m/z* 190 $[M]^+$, calcd: 190.

1-(o-tolyl)ethan-1-ol (15)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 2-methyl acetophenone (0.264 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85 µmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **15** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.43 (d, 1H, $^{3}J_{HH}$ = 8 Hz, $C_6\underline{H}_4$), 7.17 (d, 1H, $^{3}J_{HH}$ = 9 Hz, $C_6\underline{H}_4$), 7.14−7.04 (m, 2H, $C_6\underline{H}_4$), 5.05 (q, 1H, $^{3}J_{HH}$ = 7 Hz, C$\underline{H}$CH), 2.26 (s, 3H, C$\underline{H}_3$), 1.39 (d, 1H, $^{3}J_{HH}$ = 7 Hz, $C_6\underline{H}_4$). GCMS (ESI): *m/z* 136 $[M]^+$, calcd: 136.

2-methyl-1-phenylpropan-1-ol (16)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing isopropiophenone(0.291 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 µmol), catalyst **1h** or **3i** (9.85

μmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **16** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.27−7.18 (m, 5H, $C_6\underline{H}_4$), 4.28 (d, 1H, $^{3}J_{HH}$ = 5 Hz, C$\underline{H}$OH), 1.90 (q, 1H, $^{3}J_{HH}$ = 7 Hz, C$\underline{H}(CH_3)_2$), 0.93 (d, 1H, $^{3}J_{HH}$ = 7 Hz, C$\underline{H}(CH_3)_2$), 0.72 (d, 1H, $^{3}J_{HH}$ = 7 Hz, C$\underline{H}(CH_3)_2$). GCMS (ESI): *m/z* 148 $[M]^+$, calcd: 148.

2,2-dimethyl-1-phenylpropan-1-ol (17)

In a typical catalysis run, performed under nitrogen atmosphere, a flask containing 2,2 dimethyl propiophenone(0.319 g, 1.97 mmol), *t*-BuOK (0.008 g, 78.8 μmol), catalyst **1h** or **3i** (9.85 μmol, 0.5 mol %), in *i*-PrOH (*ca*. 8 mL) are refluxed for 3 hours at 75 °C. The reaction mixture was then cooled to room temperature and volatiles were evaporated to dryness. The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of heptane and EtOAc to give the desired product **17** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.20−7.16 (m, 5H, $C_6\underline{H}_4$), 4.28 (s, 1H, C$\underline{H}$OH), 0.83 (s, 9H, CH($C\underline{H}_3)_3$). GCMS (ESI): *m/z* 164 $[M]^+$, calcd: 164.

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Supporting information available

The ^{1}H NMR, ^{13}C{^{1}H} NMR, IR, HRMS and CHN data of the compounds (**1**−**3**)**c,** (**1**−**3**)**d,** (**1**−**3**)**e,** (**1**−**3**)**f,** (**1**−**3**)**g,** (**1**−**3**)**h,** (**1**−**3**)**i**; CIF file giving X-ray crystallographic data; including ^{1}H NMR, GCMS and Chiral HPLC data of the catalysis product (**4**−**14**) associated with this article can be found in the journal webpage. This material is available free of charge via the journal webpage.

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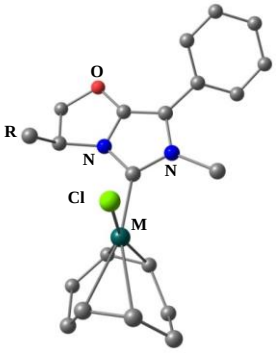
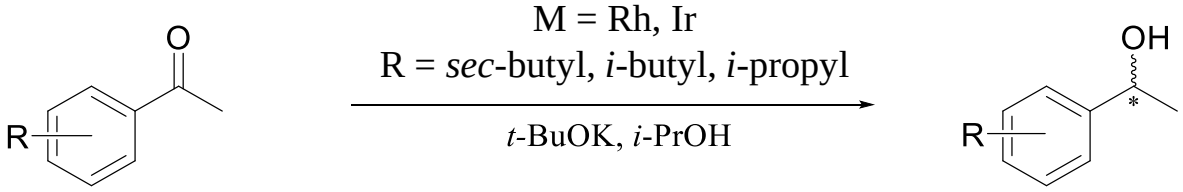
Chiral Oxazolidine fused N-heterocyclic Carbene Complexes of Rhodium and Iridium and their Utility in Asymmetric Transfer Hydrogenation of Ketones

*Balasubramaniyam Ramasamy, Manoj Kumar Gangwar and Prasenjit Ghosh**





The iridium and rhodium complexes of a new chiral oxazolidine fused N−heterocyclic carbene ligands effectively catalyzed transfer hydrogenation of ketones displaying turnover number (TON) of up to 190 and enantiomeric excess of up to 41 %.

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