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Hydroxyl and Ester Functionalized *N*-Heterocyclic Carbene Complexes of Iridium(I): Efficient Catalysts for Transfer Hydrogenation Reactions

Derya Gülcemal[a], Aytaç Gürhan Gökçe[b], Süleyman Gülcemal[a]* and Bekir Çetinkaya[a]

[a] *Ege University, Department of Chemistry, TR-35100, Bornova, Izmir, Turkey.*

[b] *Dokuz Eylul University, Department of Physics, TR-35160, Buca, Izmir, Turkey*

ABSTRACT

Hydroxyl and ester-functionalized iridium(I) complexes of *N*-heterocyclic carbenes (**3a-e**) were obtained by transmetalation reactions from the in-situ prepared silver(I)-NHC complexes and characterized by IR, NMR, mass spectroscopies, and elemental analysis. X-ray diffraction studies on single crystals of **3a**, **3c** and **3d** verify the square planar geometry at the iridium center. Ester functionalized iridium(I)-NHC complexes were found to be highly active and selective catalysts for the transfer hydrogenation reactions of various aldehydes and ketones. The influence of different ester substituents on the reactivity of the complexes was studied and the complex with pivaloyl substituent (**3d**) showed the best activity (TON up to 10000).

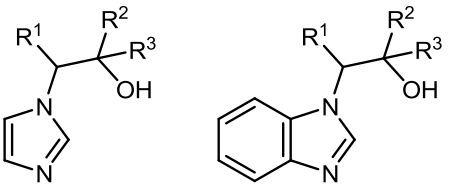
Keywords: N-heterocyclic carbene; iridium; homogeneous catalysis; transfer hydrogenation; ester functionalization

INTRODUCTION

Transfer hydrogenation is a metal-catalyzed process that consist of hydrogen transfer from a hydrogen donor, typically 2-propanol, to an acceptor molecule.[1] The reduction of aldehydes, ketones and imines into the corresponding primary and secondary alcohols and amines is one of the fundamental functional group transformations.[2] This environmentally friendly protocol is preferred for large-scale industrial use in the hope of avoiding or reducing the amount of waste production and developing a greener process by reducing energy use and lowering toxicity.[3] The transfer hydrogenation is a safer when compared with the conventional hydrogenation reaction using the potentially explosive H_2 gas.

There have been many reports of the use of iridium-catalyzed transfer hydrogenation of carbonyl compounds and imines.[4] In particular, iridium complexes bearing *N*-heterocyclic carbene (NHC) ligands have been successfully used as catalyst for transfer hydrogenation reactions.[5] NHCs have emerged as a versatile class of ligands since they often give stable organometallic complexes due to the strength of the metal-NHC bond.[6] Additionally, their tunable character allows for the control of the electronic and steric properties at the metal center.

Recently, Yus *et. al.* reported the preparation of 1-(β-hydroxyalkyl) substituted imidazole (**I**) and benzimidazole (**II**) derivatives by an epoxide ring opening with the free heterocycles under solvent-free conditions.[7] The method allows the synthesis of OH functionalized azole derivatives under very mild and simple reaction conditions. Furthermore, this methodology was also successfully applied to prepare chiral imidazolyl alcohols with high enantiomeric excess by using chiral epoxides[7] or in the presence of prochiral epoxides via chemoenzymatic resolution.[8]



I **II**

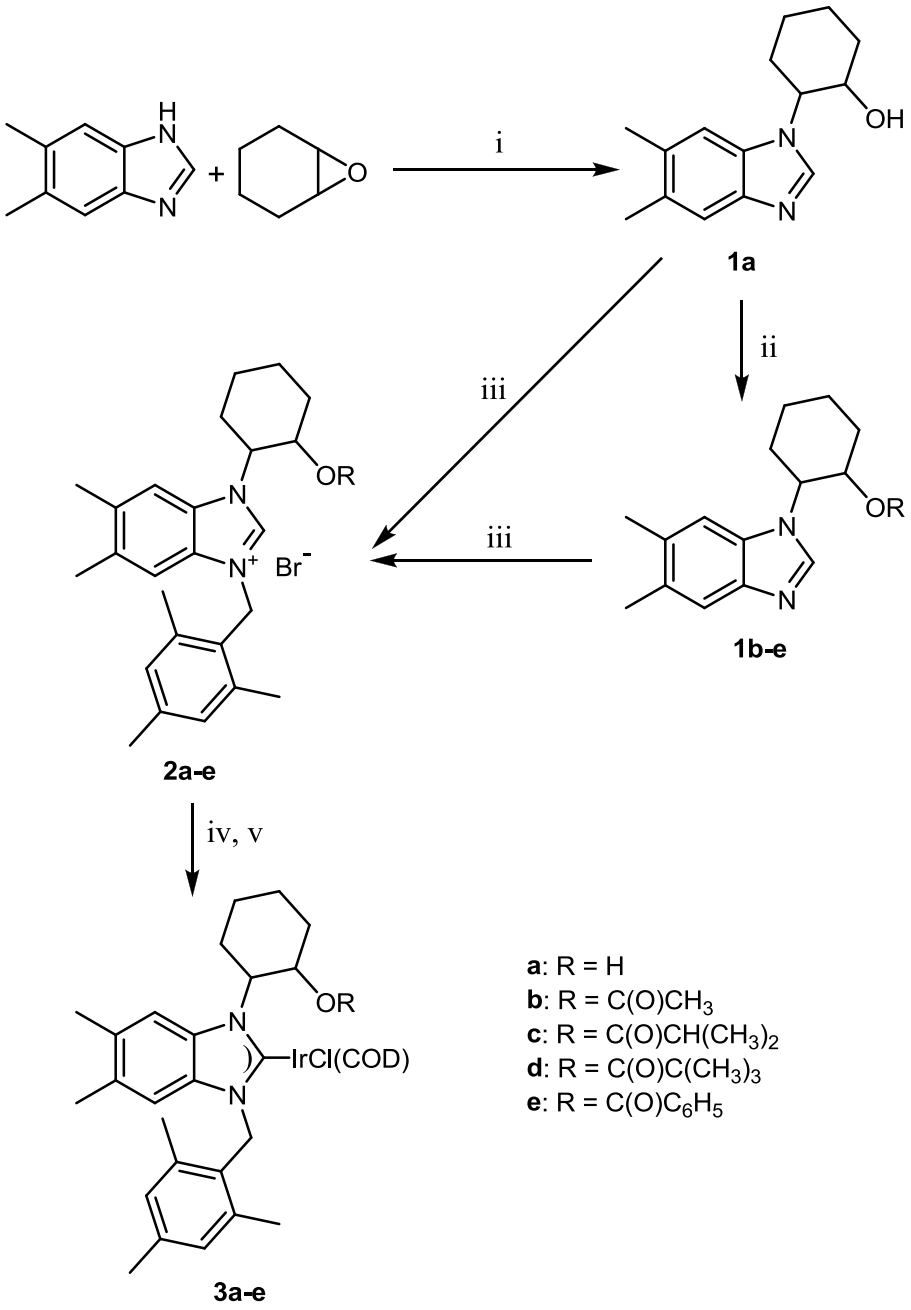
In view of the above information here we investigated the synthesis of hydroxyl and ester functionalized iridium(I)-NHC complexes and their application in the transfer hydrogenation reactions of aldehydes and ketones. Initially, 1-(2-hydroxycyclohexyl)-5,6-dimethylbenzimidazole was prepared by cyclohexene epoxide ring opening reaction with the 5,6-dimethylbenzimidazole under solvent-free conditions. 5,6-Dimethylbenzimidazole was used as the heterocyclic component since our previous studies showed that attachment of methyl groups on the 5,6-position of the benzene ring of benzimidazole has played an important role in rhodium(I)-NHC[9] and iridium(I)-NHC[5b] catalyzed reduction reactions. In the second step, ester functionalization of the corresponding alcohol is carried out by different anhydrides. Then, we obtained the corresponding 5,6-dimethylbenzimidazolium salts by simple quaternization of these 1-alkyl(5,6-dimethylbenzimidazole) derivatives with 2,4,6-trimethylbenzyl bromide. Finally, synthesized 5,6-dimethylbenzimidazolium salts were employed to generate the alcohol and ester functionalized iridium(I)-NHC complexes by transmetalation reaction from in-situ formed silver(I)-NHC complexes. The catalytic activity of the related complexes in the transfer hydrogenation of aldehydes and ketones was studied comparatively, and we observed that ester functionalization increased the catalytic activity considerably.

RESULTS AND DISCUSSION

Synthesis and characterization of compounds

The reaction between 5,6-dimethylbenzimidazole and cyclohexene oxide under solvent-free conditions at 70 ºC produced the 1-(2-hydroxycyclohexyl)-5,6-dimethylbenzimidazole

(**1a**) in 97% yield (Scheme 1). Then, anhydrides were subsequently reacted with **1a** through its OH function to give corresponding ester functionalized 5,6-dimethylbenzimidazolyl ligands (**1b-e**) (Scheme 1). The IR spectra indicate that OH group was converted into ester. The OH stretching band (3127 cm^{-1}) of **1a** disappeared and the corresponding C=O bands for **1b-e** were observed at 1739, 1732, 1727 and 1716 cm^{-1} respectively.



Scheme 1. Synthetic pathway for the related compounds (**1a-e**, **2a-e** and **3a-e**): i) Neat, 70 ºC, 12 h; ii) Anhydride, NEt_3, DMAP, CH_2Cl_2, rt, 24 h; iii) $MesCH_2Br$, PhMe, 80 ºC, 4 h; iv) Ag_2O, CH_2Cl_2, rt, 1 h; v) $[IrCl(COD)]_2$, CH_2Cl_2, rt, 12 h.

The 5,6-dimethylbenzimidazolium salts (**2a-e**) were synthesized by the reaction of **1a-e** with 2,4,6-trimethylbenzyl bromide in toluene at 80 ºC (Scheme 1). These salts are white powders and were obtained in 94% to 98% yields. The spectral properties are similar to those of other reported 5,6-dimethylbenzimidazolium salts.[5a,b] In the ^{1}H NMR spectrum of **2a-e** the NC*H*N^{+} protons appear at 9.93, 10.67, 10.53, 10.59 and 10.77 ppm respectively, and these downfield signals indicate the formation of 5,6-dimethylbenzimidazolium salts.

The new OH and ester functionalized [IrCl(COD)(NHC)] (COD: 1,5-cyclooctadiene) complexes **3a-e** were prepared by transmetalation[10] from the in-situ formed silver-NHC derivatives by employing a two-step process (Scheme 1). The silver-NHC species were not isolated. In the second step, the addition of $[IrCl(COD)]_2$ to the mixture gave the yellow complexes in good yields (84% **3a**, 80% **3b**, 76% **3c**, 78% **3d** and 82% **3e)** as air and moisture stable solids.

The structure and the purity of complexes **3a-e** was clearly confirmed by IR, NMR, mass spectroscopies and elemental analysis. X-ray diffraction studies on single crystals of **3a**, **3c** and **3d** were also been achieved. The characteristic downfield signals for the NC*H*N^{+} protons of the 5,6-dimethylbenzimidazolium salts **2a-e** disappeared in the ^{1}H NMR spectra of complexes **3a-e**, which confirms the deprotonation of the benzimidazolium fragment. The coordination of the NHC to the iridium center becomes evident in the ^{13}C spectra. The chemical shifts were observed at 190.3, 191.3, 191.3, 191.7 and 191.1 ppm for the complexes **3a-e**, respectively, and are comparable to those of other reported Ir(I)-NHC complexes.[5] The ^{13}C chemical shifts showed that $C_{carbene}$ is substantially deshielded.

Molecular Structures

The crystal structures of the iridium complexes **3a**, **3c** and **3d** (Fig 1) were determined by single crystal X-ray diffraction studies. The structural studies showed that iridium centers are in slightly distorted square-planar coordination environments. The significant bond

distances and angles are tabulated in Table 1. The iridium−NHC distances of 2.030(6) (**3a**), 2.024(4) (**3c**) and 2.032(3) Å (**3d**) are consistent with previously characterized NHC-supported [Ir(COD)Cl] complexes.[5a,b,g,m,n] The planes of benzimidazole rings make dihedral angles of 85.9(3), 80.9(2) and 79.9(1)° with the least square planes of trimethylphenyl rings for **3a**, **3c** and **3d**, respectively. The six-membered cyclohexane ring in all three structures adopts a chair conformation. The details of intra- and intermolecular interactions are given in Supporting Information.

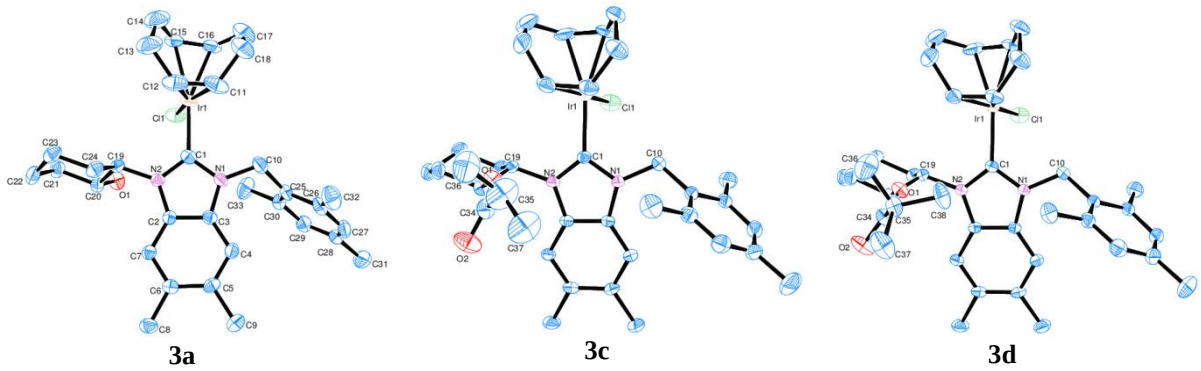


Figure 1. The molecular structures of **3a**, **3c** and **3d** with displacement ellipsoids drawn at the 30% probability level and hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **3a**, **3c** and **3d**.[a]

	3a	**3c**	**3d**
Ir1-C1	2.030(6)	2.024(4)	2.032(3)
Ir1-Cl1	2.359(16)	2.363(13)	2.364(8)
Ir1-M1	1.979	1.975	1.978
Ir1-M2	2.078	2.058	2.054
C1-N1	1.371(7)	1.369(5)	1.353(4)
C1-N2	1.354(7)	1.354(5)	1.361(4)
C1-Ir1-Cl1	91.65(15)	85.90(12)	85.82(8)
M1-Ir1-C1	91.48	96.71	96.84
M2-Ir1-Cl1	90.59	90.96	90.82
M1-Ir1-M2	86.62	86.63	86.79
M1-Ir1-Cl1	174.13	174.57	174.08
M2-Ir1-C1	175.64	176.17	175.45

[a] M1 and M2 represent the midpoints of the olefinic bonds C11-C12 and C15-C16, respectively.

Catalytic studies

Using the reduction of acetophenone to 1-phenylethanol as a benchmark reaction, all the synthesized complexes (**3a-e**) were screened as catalysts in 2-propanol as a hydrogen donor

and in the presence of base (KOH) at 85 ºC. Time depended conversions were given in Fig 2. The blank experiment was carried out without catalyst and less than 5% conversion was observed even after 24 h.

Within the iridium(I)-NHC complexes (**3a-e**) examined in this study, the complexes **3d** and **3e** were found to be more active than the others for the model reaction (Fig 2). The full conversion to 1-phenylethanol required only 10 min with catalyst **3d** (final TOF 1200 h^{-1}) and 15 min with catalyst **3e** (final TOF 800 h^{-1}). The OH-functionalized complex (**3a**) was found to be the least active catalyst under the same conditions. After 90 min, only a 27% conversion was achieved and it required 10 h for the total conversion. The activity for the tested complexes decreases in order **3d** > **3e** > **3c** > **3b** > **3a** indicating that increasing the steric bulk of the carbonyl group on NHC ligand, increase the catalytic activity considerably (Fig. 2). Another important observation during the catalytic process was the color change to black with catalysts **3a** and **3b**, which are resulted with lover activities. This color change was not observed with the other catalysts (**3c-e**) which have bulkier ester groups.

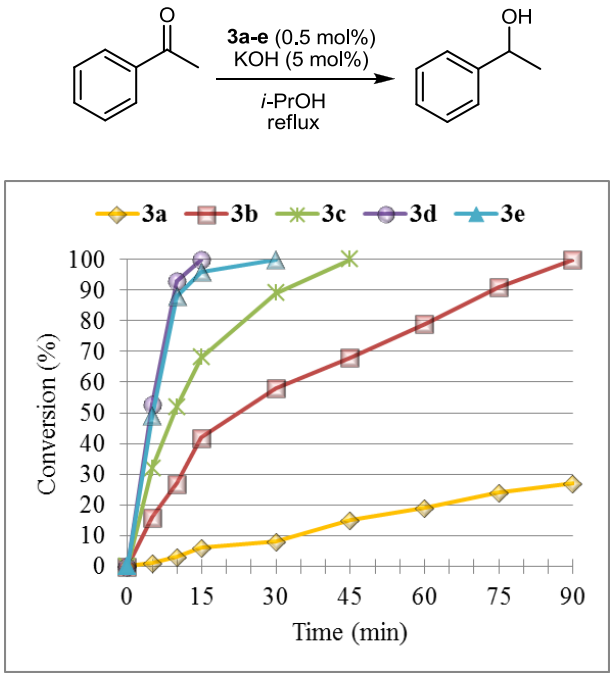


Figure 2. Time course of the catalytic transfer hydrogenation of acetophenone.

Next, we studied the effect of further catalyst loading (Table 2) since this is important for improving the environmental impact and cost of the process and also removal of residual iridium from the desired products.[3a] For this purpose, first 0.1 mol% catalyst loading investigated with the most active catalysts 3d and 3e. Complex 3d showed better activity, achieving complete reduction of acetophenone to 1-phenylethanol in 1 h, while complex 3e required 4 h with the same catalyst loading (Table 2, entries 1 and 2). Encouraged from these results, catalyst loading decreased to 0.05%, 0.025% and 0.01% and complete conversions was achieved with catalyst 3d in 2.5 h, 6 h and 9 h respectively (Table 2, entries 3-5). The catalyst 3d (0.05%) was also used for 20 mmol preparative scale synthesis of 1-phenylethanol and the reaction required 3 h for the total conversion (Table 2, entry 6).

Table 2. The effect of the catalyst loading.[a]

Entry	Cat.	% Cat.	Time [h]	Conv. [%][b]	Yield [%][c]
1	**3d**	0.1	1	>99	98
2	**3e**	0.1	4	>99	97
3	**3d**	0.05	2.5	>99	98
4	**3d**	0.025	6	>99	99
5	**3d**	0.01	9	>99	98
6[d]	**3d**	0.05	3	>99	98

[a] Substrate (0.5 mmol), KOH (5 mol%), IPA (2.5 mL), 85 °C.
[b] Determined by using GC from an average of at least two runs.
[c] Isolated yield.
[d] Scaled up by the factor 40.

The lifetime/stability of the catalyst **3d** was also examined by employing Cavell's previous method.[4i] A catalytic run was initiated using 1 mmol acetophenone, 0.1 mol% catalyst **3d**, 0.05 mmol of KOH and 5 mL of 2-propanol. After 1 h operating time 5 μL aliquot was taken for the analysis and an additional 1 mmol of substrate was added to the solution and the reaction monitored for an additional 1 h. Finally, a third (1 mmol), fourth (1 mmol) and fifth (1 mmol) aliquots of substrate was added and the reaction was again monitored. These results are shown in Table 3. In the first four runs, total conversions were observed after 1 h operating time. The fifth run required an additional 15 min (75 min in total)

for the complete conversion. It is clear that the catalyst maintained high activity during the entire experiment despite the decrease of the catalyst concentration (due to loss of small amounts of catalyst as aliquots were taken for GC analysis). Cavell's lifetime/stability experiments carried out in this study indicate that basic hydrolysis does not occur. Otherwise we could not repeat the subsequent cycles in high yields; though reaction time increases.

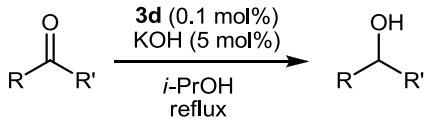
Table 3. Lifetime/stability studies with catalyst **3d**.[a]

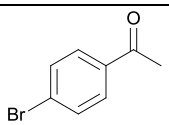
Run	1st	2nd	3rd	4th	5th
Time [h]	1	1	1	1	1.25
Conv. [%][b]	>99	>99	>99	>99	>99

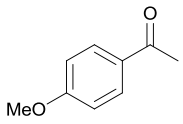
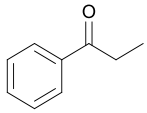
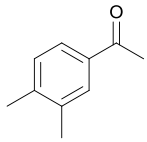
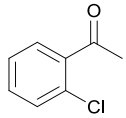
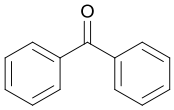
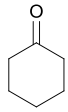
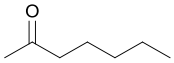
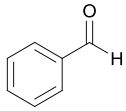
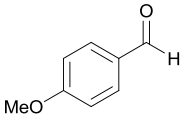
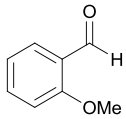
[a] 5 mmol of acetophenone, added in five separate stages; 1×10^{-3} mmol of **3d**; 0.05 mmol of KOH; IPA (5 mL); 85 °C.
[b] Determined by using GC from an average of at least two runs.

Encouraged by the results obtained with complexes **3d**, the study of catalyst substrate scope to different carbonyl compounds was examined and the results are presented in Table 4. The catalyst **3d** shows very high activity in the transfer hydrogenation of aromatic and aliphatic ketones (Table 4, entries 1-8) and aromatic aldehydes (Table 4, entries 9-11) with 0.1 mol% catalyst loading. It is worth nothing that, the **3d** is very tolerant to substrate variations. Complete conversions were obtained for transfer hydrogenation of aromatic and aliphatic ketones within only 1-3 h. Among the substrates examined, only the transformation of 2-methoxybenzaldehyde to 2-methoxybenzylalcohol (Table 4, entry 12) was disappointing, and in this case 6 h required for the complete conversion.

Table 4. Transfer hydrogenation of carbonyl compounds to alcohols with catalyst **3d**.[a]



Entry	Substrates	Time [h]	Conv. [%][b]	Yield [%][c]
1		2.5	>99	98

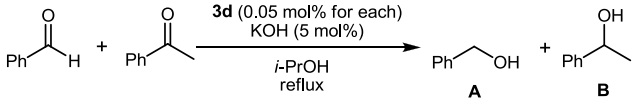
2		3	>99	97
3		2	>99	99
4		1.5	>99	96
5		1.5	>99	98
6[d]		2	>99	99
7		1.5	>99	98
8		1.5	>99	97
9		1.5	>99	98
10		3	>99	97
11		6	>99	96

[a] Substrate (0.5 mmol), KOH (5 mol%), **3d** (0.1 mol%), IPA (2.5 mL), 85 °C.
[b] Determined by using GC from an average of at least two runs.
[c] Isolated yield.
[d] Conversion determined by ^{1}H NMR.

Finally, selectivity of the catalytic system to ketone or aldehyde was investigated. The catalytic experiment was carried using 0.5 mmol of benzaldehyde, 0.5 mmol of acetophenone, 5×10^{-4} mmol (0.05 mol% for each substrate) of **3d**, 2.5×10^{-2} mmol of KOH and 2.5 mL of 2-propanol and the results are presented in Table 5. In our initial study, benzaldehyde was added first and acetophenone was added right after to the solution including catalyst, base and 2-propanol. Under these conditions, benzaldehyde was completely reduced to benzyl alcohol (**A**) within 1.5 h while there was no conversion of acetophenone to 1-phenylethanol (**B**)

(Table 5, entries 1-3). Reduction of acetophenone was started after 2.5 h 3% conversion, and full conversion to 1-phenylethanol was achieved within 6 h (Table 5, entries 5-12). In the next attempt, acetophenone was added first and benzaldehyde was added right after. In this case, first analysis after 0.5 h showed that the conversion to **A** and **B** is 28% and 15% respectively (Table 5, entry 1). There was no change for conversion to **B** until complete conversion to **A** was achieved (Table 5, entries 2 and 3). Then, reduction of acetophenone was continued after benzaldehyde was fully reduced to benzyl alcohol (Table 5, entry 4-10). As a result, in both case reduction of benzaldehyde was found to be more favorable to acetophenone.

Table 5. Selectivity studies with catalyst **3d**.[a]



Entry	Time [h]	Conv. to **A**/**B** [%][b]	Conv. to **A**/**B** [%][c]
1	0.5	35/0	28/15
2	1.0	81/0	79/15
3	1.5	100/0	100/15
4	2.0	100/0	100/16
5	2.5	100/3	100/24
6	3.0	100/15	100/41
7	3.5	100/34	100/62
8	4.0	100/51	100/79
9	4.5	100/67	100/91
10	5.0	100/84	100/100
11	5.5	100/93	-
12	6.0	100/100	-

[a] Substrate; benzaldehyde (0.5 mmol) and acetophenone (0.5 mmol), KOH (2.5 mol% for each substrate), **3d** (0.05 mol% for each substrate), IPA (2.5 mL), 85 °C.
[b] Acetophenone was added right after benzaldehyde and determined by using GC from an average of at least two runs.
[c] Benzaldehyde was added right after acetophenone and determined by using GC from an average of at least two runs.

CONCLUSIONS

In this report, 1-(2-hydroxycyclohexyl)-5,6-dimethylbenzimidazole (**1a**), obtained by the ring opening reaction of cyclohexene oxide with 5,6-dimethylbenzimidazole, was converted to the NHC precursors (**2a-e**) by quaternization with 2,4,6-trimethylbenzyl bromide directly (**1a**) or after esterification of OH group by various anhydrides (**1b-e**) to see the

influence of structural modularity. Iridium complexes of NHC ligands were studied for transfer hydrogenation reactions. The efficiency of NHC-ester ligands in transfer hydrogenation reaction is greater in comparison to the NHC-alcohol ligands. Therefore, we may conclude that strong coordinative O atom in NHC-alcohol serves as chelating ligand. The reaction rate strongly depends on the bulk of the carbonyl entity. A 1:1 mixture of benzaldehyde and acetophenone substrates towards transfer hydrogenation showed a clear preference of the aldehyde reduction. The applications of this methodology to the asymmetric synthesis of chiral iridium(I)-NHC complexes by using chiral epoxides such as (R)-(+)-styrene oxide or in the presence of prochiral epoxides via chemoenzymatic resolution are underway in our laboratory.

EXPERIMENTAL

General Considerations

The reagents and solvents were purchased from Sigma-Aldrich, Merck and Alfa Aesar and were used as received. $[IrCl(COD)]_2$ was prepared according to the published procedure.[11] The synthesis of metal complexes was carried out using standard Schlenk techniques under an argon atmosphere. Column chromatography was performed on silica gel 60 (230-400 mesh). ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were acquired on a Varian AS 400 Mercury spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) were reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Melting points were recorded with Gallenkamp electrothermal melting point apparatus. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer. FTIR spectra were recorded on a Perkin Elmer Spectrum 100 series. Mass spectra were acquired using a Bruker HCT Ultra Ion Trap Mass Spectrometer. The chromatographic analyses (GC) were performed with an

Agilent 7820A instrument equipped with a flame ionization detector and an Agilent 19091J-413 column (30m×320μm×0.5μm).

Syntheses

1a: A mixture of 5,6-dimethylbenzimidazole (7.30 g, 50 mmol) and cyclohexene oxide (4.90 g, 50 mmol) was placed in a 100 mL round bottom flask and stirred at 70 ºC for 12 h. The resulting mixture was purified by recrystallization with acetone/hexane to give a white solid (11.80 g, 97%). Mp: 232-233 ºC. IR: *v* (film) 3127 cm^{-1} (OH). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 1.46-1.58, 1.80-1.90, 2.00-2.03, 2.21-2.29 (8H, 4m, 4×C*H*$_2$), 2.23 (3H, s, Ar-C*H*$_3$-BI), 2.35 (3H, s, Ar-C*H*$_3$-BI), 3.94-3.97 (2H, m, 4×C*H* ring), 5.37 (1H, s, O*H*), 7.08 (1H, s, Ar*H*-BI), 7.19 (1H, s, Ar*H*-BI), 7.48 (1H, s, NC*H*N). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.2, 20.6 (2×Ar-*C*H$_3$-BI), 24.6, 25.6, 32.2, 34.7 (4×*C*H$_2$), 62.8 (*C*HN ring), 72.5 (*C*HO ring), 110.7, 119.7, 130.8, 131.7, 132.6, 140.0, (Ar*C*), 141.6 (N*C*HN). Anal. Calc. for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25; N, 11.47. Found: C, 73.70; H, 8.28; N, 11.43. LC-MS (ESI^+): *m/z* 245.0 $[M+H]^+$.

General procedure for the synthesis of ester functionalized 5,6-dimethylbenzimidazoles (1b-e):

Corresponding anhydride (6.0 mmol) was added to a solution of **1a** (1.22 g, 5.0 mmol), triethylamine (0.7 mL, 5.0 mmol) and 4-dimethylaminopyridine (61 mg, 0.5 mmol) in dichloromethane (20 mL), and the mixture was stirred at room temperature for 24 h. Water (30 mL) was added to the resulting mixture and extracted with dichloromethane (3×15 mL). Combined organic fractions were dried with $MgSO_4$ and the solvent was evaporated. The resulting crude product was purified by column chromatography (silica gel, dichloromethane/methanol 95:5) to yield the corresponding ester functionalized 5,6-dimethylbenzimidazole derivatives.

1b: Beige oil. Yield: 1.37 g, 96%. IR: *v* (film) 1739 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 1.45-1.57, 1.88-2.03, 2.16-2.23 (8H, 3m, 4×C*H*$_2$), 1.64 (3H, s, OCC*H*$_3$), 2.35 (3H, s, Ar-C*H*$_3$-BI), 2.39 (3H, s, Ar-C*H*$_3$-BI), 4.16-4.24 (1H, m, NC*H* ring), 5.13-5.19 (1H, m, OC*H* ring), 7.23 (1H, s, Ar*H*-BI), 7.52 (1H, s, Ar*H*-BI), 7.82 (1H, s, NC*H*N). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.3, 20.7 (2×Ar-*C*H$_3$-BI), 20.8 (OC*C*H$_3$), 24.2, 25.2, 31.8, 31.9 (4×*C*H$_2$), 58.8 (*C*HN ring), 74.3 (*C*HO ring), 110.7, 120.5, 131.0, 131.9, 132.5, 140.5, (Ar*C*), 142.5 (N*C*HN), 169.9 (O*C*CH$_3$). Anal. Calc. for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.74; N, 9.78. Found: C, 71.33; H, 7.69; N, 9.74. LC-MS (ESI^+): *m/z* 287.1 $[M+H]^+$.

1c: Colorless oil. Yield: 1.52 g, 97%. IR: *v* (film) 1732 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 0.63 (3H, d, J = 7.2 Hz, CH(C*H*$_3$)$_2$), 0.83 (3H, d, J = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.45-1.57, 1.89-2.06, 2.20-2.22 (8H, 3m, 4×C*H*$_2$), 2.10-2.17 (1H, m, C*H*(CH$_3$)$_2$), 2.34 (3H, s, Ar-C*H*$_3$-BI), 2.38 (3H, s, Ar-C*H*$_3$-BI), 4.18-4.25 (1H, m, NC*H* ring), 5.13-5.21 (1H, m, OC*H* ring), 7.22 (1H, s, Ar*H*-BI), 7.51 (1H, s, Ar*H*-BI), 7.81 (1H, s, NC*H*N). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 18.5, 18.7 (2×CH(*C*H$_3$)$_2$), 20.3, 20.7 (2×Ar-*C*H$_3$-BI), 24.2, 25.3, 31.8, 32.0 (4×*C*H$_2$), 33.9 (*C*H(CH$_3$)$_2$), 58.7 (*C*HN ring), 74.0 (*C*HO ring), 110.7, 120.5, 130.9, 131.8, 132.5, 140.4, (Ar*C*), 142.6 (N*C*HN), 176.1 (O*C*CH(CH$_3$)$_2$). Anal. Calc. for $C_{19}H_{26}N_2O_2$: C, 72.58; H, 8.33; N, 8.91. Found: C, 72.63; H, 8.30; N, 8.96. LC-MS (ESI^+): *m/z* 315.1 $[M+H]^+$.

1d: White solid, mp: 110-111 ºC. Yield: 1.50 g, 92%. IR: *v* (film) 1727 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 0.79 (9H, s, C(C*H*$_3$)$_3$), 1.46-1.55, 1.90-2.06, 2.18-2.24 (8H, 3m, 4×C*H*$_2$), 2.35 (3H, s, Ar-C*H*$_3$-BI), 2.39 (3H, s, Ar-C*H*$_3$-BI), 4.19-4.27 (1H, m, NC*H* ring), 5.11-5.15 (1H, m, OC*H* ring), 7.21 (1H, s, Ar*H*-BI), 7.53 (1H, s, Ar*H*-BI), 7.87 (1H, s, NC*H*N). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.3, 20.7 (2×Ar-*C*H$_3$-BI), 24.2, 25.3 (2×*C*H$_2$), 26.8 (C(*C*H$_3$)$_3$), 31.8, 32.1 (2×*C*H$_2$), 38.6 (*C*(CH$_3$)$_3$), 58.8

(*C*HN ring), 74.2 (*C*HO ring), 110.8, 120.2, 131.3, 132.1, 132.3, 140.6, (Ar*C*), 141.7 (N*C*HN), 177.6 (O*C*C(CH$_3$)$_3$). Anal. Calc. for $C_{20}H_{28}N_2O_2$: C, 73.14; H, 8.59; N, 8.53. Found: C, 73.08; H, 8.61; N, 8.55. LC-MS (ESI$^+$): *m/z* 329.2 [M+H]$^+$.

1e: White solid, mp: 95-96 ºC. Yield: 1.69 g, 97%. IR: *v* (film) 1716 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 1.50-1.63, 1.93-2.00, 2.06-2.16, 2.29-2.43 (8H, 4m, 4×C*H*$_2$), 2.23 (3H, s, Ar-C*H*$_3$-BI), 2.29 (3H, s, Ar-C*H*$_3$-BI), 4.36-4.43 (1H, m, NC*H* ring), 5.32-5.39 (1H, m, OC*H* ring), 7.24 (2H, t, J = 8.0 Hz, Ar*H*), 7.30 (1H, s, Ar*H*-BI), 7.38-7.45 (1H, m, Ar*H*), 7.49 (1H, s, Ar*H*-BI), 7.66 (2H, d, J = 7.2 Hz, Ar*H*), 7.98 (1H, s, NC*H*N). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.1, 20.5 (2×Ar-*C*H$_3$-BI), 24.0, 25.1, 31.7, 31.8 (4×*C*H$_2$), 58.6 (*C*HN ring), 75.1 (*C*HO ring), 110.7, 120.1, 128.1, 129.4, 129.6, 131.0, 131.9, 132.8, 140.3, (Ar*C*), 141.8 (N*C*HN), 165.5 (O*C*(C$_6$H$_5$)). Anal. Calc. for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.77; H, 6.96; N, 7.99. LC-MS (ESI$^+$): *m/z* 349.2 [M+H]$^+$.

General procedure for the synthesis of 5,6-dimethylbenzimidazolium bromide salts (2a-e):

2,4,6-Trimethylbenzyl bromide (426 mg, 2.0 mmol) was added to a solution of **1a-e** (2.0 mmol) in toluene (10 mL), and the mixture was stirred at 80 ºC for 4 h. The solid that separated out after cooling to room temperature was filtered off and washed with diethyl ether (20 mL). The product was recrystallized from dichloromethane/diethyl ether to give the corresponding 5,6-dimethylbenzimidazolium salts (**2a-e**).

2a: White solid, mp: 241-242 ºC. Yield: 900 mg, 98%. IR: *v* (film) 3302 cm^{-1} (OH). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 1.40-1.51, 1.60-1.69, 1.79-1.85, 2.10-2.43 (8H, 4m, 4×C*H*$_2$), 2.26, 2.27, 2.35 (15H, 3s, C*H*$_3$-Mes + Ar-C*H*$_3$-BI), 4.20-4.28 (1H, m, NC*H* ring), 4.45-4.50 (1H, m, OC*H* ring), 4.89 (1H, d, J = 5.6 Hz, O*H*), 5.79 (2H, dd, J = 14.8, NC*H*$_2$-Mes), 6.89 (2H, s, Ar*H*-Mes), 6.99 (1H, s, Ar*H*-BI), 7.55 (1H, s, Ar*H*-BI), 9.93 (1H, s,

NC*H*N$^+$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.3, 20.5 (*C*H_3-Mes), 20.7, 21.0 (2×Ar-*C*H_3-BI), 24.1, 24.9, 31.9, 34.5 (4×*C*H_2), 46.8 (N*C*H_2-Mes), 64.2 (*C*HN ring), 70.8 (*C*HO ring), 113.0, 113.7, 125.3, 129.9, 130.0, 130.6, 136.8, 136.9, 138.1, 139.5 (Ar*C*), 139.7 (N*C*HN$^+$). Anal. Calc. for $C_{25}H_{33}BrN_2O_2$: C, 65.64; H, 7.27; N, 6.12. Found: C, 64.67; H, 7.26; N, 6.10. LC-MS (ESI$^+$): *m/z* 377.2 [M-Br]$^+$.

2b: White solid, mp: 252-253 ºC. Yield: 950 mg, 95%. IR: *v* (film) 1738 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 1.52-1.60, 1.81-1.85, 1.91-1.95, 2.02-2.08, 2.21-2.31, 2.38-2.44 (8H, 6m, 4×C*H*$_2$), 1.53 (3H, s, OCC*H*$_3$), 2.21, 2.22, 2.23, 2.36 (15H, 4s, C*H*$_3$-Mes + Ar-C*H*$_3$-BI), 4.67-4.74 (1H, m, NC*H* ring), 5.11-5.17 (1H, m, OC*H* ring), 5.79 (2H, s, NC*H*$_2$-Mes), 6.84 (2H, s, Ar*H*-Mes), 6.91 (1H, s, Ar*H*-BI), 7.56 (1H, s, Ar*H*-BI), 10.67 (1H, s, NC*H*N$^+$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.2, (OC*C*H$_3$), 20.5, 20.6 (*C*H$_3$-Mes), 20.8, 21.1 (2×Ar-*C*H$_3$-BI), 23.6, 24.5, 31.0, 31.3 (4×*C*H$_2$), 47.3 (N*C*H$_2$-Mes), 61.2 (*C*HN ring), 74.7 (*C*HO ring), 113.5, 113.8, 125.3, 125.5, 128.2, 129.0, 129.8, 130.1, 130.3, 137.3, 137.4, 138.0, 139.5 (Ar*C*), 140.3 (N*C*HN$^+$), 169.5 (O*C*CH$_3$). Anal. Calc. for $C_{27}H_{35}BrN_2O_2$: C, 64.92; H, 7.06; N, 5.61. Found: C, 64.98; H, 7.04; N, 5.59. LC-MS (ESI$^+$): *m/z* 419.2 [M-Br]$^+$.

2c: White solid, mp: 185-186 ºC. Yield: 990 mg, 94%. IR: *v* (film) 1732 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 0.41 (3H, d, J = 6.8 Hz, CH(C*H*$_3$)$_2$), 0.68 (3H, d, J = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.49-1.57, 1.75-1.77, 1.85-1.87, 2.00-2.04, 2.33-2.37, (8H, 5m, 4×C*H*$_2$), 1.88-1.94 (1H, m, C*H*(CH$_3$)$_2$), 2.15, 2.17, 2.28, (15H, 3s, C*H*$_3$-Mes + Ar-C*H*$_3$-BI), 4.65-4.71 (1H, m, NC*H* ring), 5.01-5.08 (1H, m, OC*H* ring), 5.73 (2H, dd, J = 14.8 Hz, NC*H*$_2$-Mes), 6.78 (2H, s, Ar*H*-Mes), 6.87 (1H, s, Ar*H*-BI), 7.55 (1H, s, Ar*H*-BI), 10.53 (1H, s, NC*H*N$^+$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 18.2, 18.8 (2×CH(*C*H$_3$)$_2$), 20.3, 20.7 (*C*H$_3$-Mes), 20.9, 21.2 (2×Ar-*C*H$_3$-BI), 23.6, 24.7, 31.3, 31.4 (4×*C*H$_2$), 33.7 (*C*H(CH$_3$)$_2$), 47.4 (N*C*H$_2$-Mes), 61.3 (*C*HN ring), 74.8 (*C*HO ring), 113.5, 113.9, 125.4,

125.5, 128.3, 129.1, 129.8, 130.1, 130.5, 137.3, 137.4, 137.9, 139.7 (Ar*C*), 140.6 (N*C*HN$^+$), 175.8 (O*C*CH(CH$_3$)$_2$). Anal. Calc. for $C_{29}H_{39}BrN_2O_2$: C, 66.03; H, 7.45; N, 5.31. Found: C, 65.97; H, 7.44; N, 5.29. LC-MS (ESI$^+$): *m/z* 447.3 [M-Br]$^+$.

2d: White solid, mp: 199-200 ºC. Yield: 1.02 g, 94%. IR: *v* (film) 1727 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 0.74 (9H, s, C(C*H*$_3$)$_3$), 1.59-1.73, 1.85-1.89, 1.99-2.05, 2.14-2.42, (8H, 4m, 4×C*H*$_2$), 2.05, 2.14, 2.31, 2.42 (15H, 4s, C*H*$_3$-Mes + Ar-C*H*$_3$-BI), 4.80-4.89 (1H, m, NC*H* ring), 5.15-5.21 (1H, m, OC*H* ring), 5.86 (2H, dd, J = 14.8 Hz, NC*H*$_2$-Mes), 6.92 (2H, s, Ar*H*-Mes), 7.05 (1H, s, Ar*H*-BI), 7.71 (1H, s, Ar*H*-BI), 10.59 (1H, s, NC*H*N$^+$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 19.7, 20.0 (*C*H$_3$-Mes), 20.2, 20.5 (2×Ar-*C*H$_3$-BI), 22.9, 24.0 (2×*C*H$_2$), 26.1 (C(*C*H$_3$)$_3$), 30.7, 30.8 (2×*C*H$_2$), 37.8 (*C*(CH$_3$)$_3$), 46.7 (N*C*H$_2$-Mes), 60.4 (*C*HN ring), 74.5 (*C*HO ring), 112.8, 113.2, 124.7, 129.0, 129.4, 129.8, 136.6, 136.8, 137.5, 139.0 (Ar*C*), 139.8 (N*C*HN$^+$), 176.4 (O*C*C(CH$_3$)$_3$). Anal. Calc. for $C_{30}H_{41}BrN_2O_2$: C, 66.53; H, 7.63; N, 5.17. Found: C, 66.50; H, 7.66; N, 5.14. LC-MS (ESI$^+$): *m/z* 461.3 [M-Br]$^+$.

2e: White solid, mp: 226-227 ºC. Yield: 1.06 g, 95%. IR: *v* (film) 1716 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 1.67-1.69, 1.74-1.80, 1.95-1.98, 2.04-2.07, 2.53-2.56, (8H, 5m, 4×C*H*$_2$), 2.13, (6H, s, C*H*$_3$-Mes), 2.20 (3H, s, Ar-C*H*$_3$-BI), 2.27 (6H, s, C*H*$_3$-Mes), 2.29 (3H, s, Ar-C*H*$_3$-BI), 5.02-5.08 (1H, m, NC*H* ring), 5.50-5.56 (1H, m, OC*H* ring), 5.73 (2H, dd, J = 14.8 Hz, NC*H*$_2$-Mes), 6.81 (2H, s, Ar*H*-Mes), 6.88 (1H, s, Ar*H*-BI), 7.32 (2H, t, J = 8.4 Hz, Ar*H*), 7.48-7.52 (1H, m, Ar*H*), 7.58 (1H, s, Ar*H*-BI), 7.72 (2H, d, J = 7.2 Hz, Ar*H*), 10.77 (1H, s, NC*H*N$^+$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.2, 20.8 (*C*H$_3$-Mes), 20.7, 21.2, (2×Ar-*C*H$_3$-BI), 23.9, 24.7, 30.8, 31.6 (4×*C*H$_2$), 47.2 (N*C*H$_2$-Mes), 62.2 (*C*HN ring), 74.5 (*C*HO ring), 113.4, 114.2, 125.4, 128.4, 129.1, 129.7, 129.9, 130.1, 130.2, 133.4, 137.2, 137.3, 138.2, 139.6 (Ar*C*), 141.3 (N*C*HN$^+$), 165.3

(O*C*(C_6H_5)). Anal. Calc. for $C_{32}H_{37}BrN_2O_2$: C, 68.44; H, 6.64; N, 4.99. Found: C, 68.39; H, 6.62; N, 5.02. LC-MS (ESI^+): *m/z* 481.2 $[M\text{-}Br]^+$.

General procedure for the synthesis of iridium(I)-NHC complexes (3a-e):

Under an argon atmosphere, a mixture of **2a-e** (0.2 mmol) and Ag_2O (23 mg, 0.1 mmol) was suspended in degassed dichloromethane (5 mL) and stirred at ambient temperature for 1 h shielded from light. $[IrCl(COD)]_2$ (67 mg, 0.1 mmol) was then added to the suspension and the reaction mixture was stirred at ambient temperature for more 12 h. The resulting suspension was filtered over Celite®. The remaining solid was washed with dichloromethane (2×5 mL) and the solvent of the filtrate was evaporated. The residue was purified by column chromatography on silica gel (eluent: dichloromethane) to give pure complex as a yellow solid.

3a: Yield: 119 mg, 84%. IR: *v* (film) 3418 cm^{-1} (OH). ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 1.47-1.79, 1.88-2.01, 2.17-2.37 (16H, 3m, 8×C*H*$_2$), 2.04, 2.25, 2.26, 2.29 (15H, 4s, C*H*$_3$-Mes + Ar-C*H*$_3$-BI), 3.01-3.08 (2H, m, COD-C*H*), 3.56 (1H, d, J = 10.4 Hz, O*H*), 4.11-4.14 (1H, m, NC*H* ring), 4.65-4.70 (1H, m, COD-C*H*), 4.75-4.80 (1H, m, COD-C*H*), 5.55 (1H, d, J = 14.8 Hz, NC*H*$_2$-Mes), 5.87-5.94 (1H, m, OC*H* ring), 6.21 (1H, s, Ar*H*-BI), 6.41 (1H, d, J = 14.8 Hz, NC*H*$_2$-Mes), 6.86 (2H, s, Ar*H*-Mes), 7.23 (1H, s, Ar*H*-BI). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.4, 20.5, 21.1, 21.2 (*C*H$_3$-Mes + Ar-*C*H$_3$-BI), 25.3, 26.3, 28.7, 30.6, 32.0, 32.8, 35.0, 36.8 (8×*C*H$_2$), 49.1 (N*C*H$_2$-Mes), 51.8, 53.0 (2×COD-*C*H), 68.0 (*C*HN ring), 70.5 (*C*HO ring), 85.6, 86.6 (2×COD-*C*H), 112.2, 112.5, 128.3, 129.8, 131.2, 131.3, 132.2, 134.7, 138.2, 138.6 (Ar*C*), 190.3 (Ir-$C_{carbene}$). Anal. Calc. for $C_{33}H_{44}ClIrN_2O$: C, 55.64; H, 6.23; N, 3.93. Found: C, 55.57; H, 6.18; N, 3.90. LC-MS (ESI^+): *m/z* 675.0 (^{191}Ir), 677.0 (^{193}Ir) $[M\text{-}Cl]^+$.

3b: Yield: 121 mg, 80%. IR: *v* (film) 1739 cm^{-1} (C=O). ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 1.52-1.74, 1.85-1.99, 2.35-2.42 (16H, 3m, 8×C*H*$_2$), 1.81 (3H, s, OCC*H*$_3$), 2.04,

2.22, 2.26, 2.31 (15H, 4s, C*H*$_3$-Mes + Ar-C*H*$_3$-BI), 3.11-3.15 (1H, m, COD-C*H*), 3.71-3.74 (1H, m, COD-C*H*), 4.64-4.71 (2H, m, COD-C*H*), 5.69-5.75 (1H, m, NC*H* ring), 5.90 (2H, dd, J = 14.8 Hz, NC*H*$_2$-Mes), 5.99-6.02 (1H, m, OC*H* ring), 6.18 (1H, s, Ar*H*-BI), 6.88 (2H, s, Ar*H*-Mes), 7.25 (1H, s, Ar*H*-BI). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.3, 20.6, 20.7, 21.0 (*C*H$_3$-Mes + Ar-*C*H$_3$-BI), 21.1 (OC*C*H$_3$), 24.4, 25.1, 28.9, 29.8, 30.2, 32.5, 32.9, 34.1 (8×*C*H$_2$), 49.0 (N*C*H$_2$-Mes), 51.8, 53.2 (2×COD-*C*H), 64.4 (*C*HN ring), 71.9 (*C*HO ring), 84.9, 85.0 (2×COD-*C*H), 111.8, 112.1, 128.5, 129.6, 130.9, 131.0, 131.6, 134.6, 137.9 (Ar*C*), 169.8 (O*C*CH$_3$), 191.3 (Ir-$C_{carbene}$). Anal. Calc. for $C_{35}H_{46}ClIrN_2O_2$: C, 55.72; H, 6.15; N, 3.71. Found: C, 55.78; H, 6.17; N, 3.73. LC-MS (ESI$^+$): *m/z* 717.2 (^{191}Ir), 719.2 (^{193}Ir) [M-Cl]$^+$.

3c: Yield: 118 mg, 76%. IR: *v* (film) 1734 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 0.70 (3H, d, J = 7.2 Hz, CH(C*H*$_3$)$_2$), 0.91 (3H, d, J = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.52-1.64, 1.74-1.86, 1.88-1.95, 2.08-2.17, 2.20-2.45 (17H, 5m, 8×C*H*$_2$ + C*H*(CH$_3$)$_2$), 2.02, 2.23, 2.24, 2.32 (15H, 4s, C*H*$_3$-Mes + Ar-C*H*$_3$-BI), 3.13-3.17 (1H, m, COD-C*H*), 3.75-3.80 (1H, m, COD-C*H*), 4.66-4.71 (2H, m, COD-C*H*), 5.65-5.71 (1H, m, NC*H* ring), 5.86 (2H, dd, J = 14.8 Hz, NC*H*$_2$-Mes), 6.00-6.07 (1H, m, OC*H* ring), 6.09 (1H, s, Ar*H*-BI), 6.89 (2H, s, Ar*H*-Mes), 7.22 (1H, s, Ar*H*-BI). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 18.4, 18.6 (CH(*C*H$_3$)$_2$), 20.2, 20.3, 20.6, 20.9 (*C*H$_3$-Mes + Ar-*C*H$_3$-BI), 24.4, 25.3, 29.0, 29.6 (4×*C*H$_2$), 30.3 (*C*H(CH$_3$)$_2$), 32.5, 33.1, 33.9, 34.0 (4×*C*H$_2$), 49.0 (N*C*H$_2$-Mes), 51.6, 53.0 (2×COD-*C*H), 64.5 (*C*HN ring), 71.6 (*C*HO ring), 84.8, 84.9 (2×COD-*C*H), 111.6, 111.8, 128.5, 129.5, 130.8, 13.9, 131.5, 134.6, 138.0 (Ar*C*), 176.0 (O*C*H(CH$_3$)$_2$), 191.3 (Ir-$C_{carbene}$). Anal. Calc. for $C_{37}H_{50}ClIrN_2O_2$: C, 56.79; H, 6.44; N, 3.58. Found: C, 56.84; H, 6.47; N, 3.61. LC-MS (ESI$^+$): *m/z* 745.1 (^{191}Ir), 747.1 (^{193}Ir) [M-Cl]$^+$.

3d: Yield: 124 mg, 78%. IR: *v* (film) 1728 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 0.74 (9H, s, C(C*H*$_3$)$_3$), 1.44-1.58, 1.66-1.73, 1.82-1.90, 1.99-2.09, 2.13-2.27,

2.38-2.41, (16H, 6m, 8×CH_2), 1.94, 2.16, 2.17, 2.25 (15H, 4s, CH_3-Mes + Ar-CH_3-BI), 3.05-3.10 (1H, m, COD-C*H*), 3.68-3.71 (1H, m, COD-C*H*), 4.57-4.63 (2H, m, COD-C*H*), 5.57-5.64 (1H, m, NC*H* ring), 5.73 (2H, dd, J = 14.8 Hz, NCH_2-Mes), 5.99 (1H, s, Ar*H*-BI), 6.01-6.05 (1H, m, OC*H* ring), 6.83 (2H, s, Ar*H*-Mes), 7.19 (1H, s, Ar*H*-BI). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.3, 20.4, 20.8, 21.1 (*C*H_3-Mes + Ar-*C*H_3-BI), 24.6, 25.7 (2×*C*H_2), 26.7 (C(*C*H_3)$_3$), 29.4, 29.5, 30.8, 32.9, 33.5, 33.8 (6×*C*H_2), 38.6 (*C*(CH_3)$_3$), 49.1 (N*C*H_2-Mes), 51.6, 52.9 (2×COD-*C*H), 64.7 (*C*HN ring), 72.3 (*C*HO ring), 84.9, 85.2 (2×COD-*C*H), 111.7, 111.8, 128.8, 129.6, 131.0, 131.1, 131.8, 135.0, 138.2, 138.5 (Ar*C*), 177.5 (O*C*(CH_3)$_3$), 191.7 (Ir-$C_{carbene}$). Anal. Calc. for $C_{38}H_{52}ClIrN_2O_2$: C, 57.30; H, 6.58; N, 3.52. Found: C, 57.25; H, 6.54; N, 3.53. LC-MS (ESI$^+$): *m/z* 759.1 (^{191}Ir), 761.1 (^{193}Ir) [M-Cl]$^+$.

3e: Yield: 134 mg, 82%. IR: *v* (film) 1727 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 0.84-0.94, 1.26-1.35, 1.50-1.57, 1.66-1.72, 2.03-2.23, 2.37-2.53 (16H, 6m, 8×CH_2), 2.01, 2.11, 2.26, 2.29 (15H, 4s, CH_3-Mes + Ar-CH_3-BI), 3.11-3.16 (1H, m, COD-C*H*), 3.83-3.86 (1H, m, COD-C*H*), 4.68-4.72 (2H, m, COD-C*H*), 5.83 (2H, dd, J = 14.8 Hz, NCH_2-Mes), 5.98-6.04 (1H, m, NC*H* ring), 6.13 (1H, s, Ar*H*-BI), 6.16-6.19 (1H, m, OC*H* ring), 6.83 (2H, s, Ar*H*-Mes), 7.29-7.33 (2H, m, Ar*H*), 7.32 (1H, s, Ar*H*-BI), 7.48 (1H, t, J = 7.6 Hz, Ar*H*), 7.74 (2H, d, J = 8.4 Hz, Ar*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 ºC, ppm): δ = 20.2, 20.3, 20.6, 20.9 (*C*H_3-Mes + Ar-*C*H_3-BI), 24.5, 25.4, 28.9, 29.6, 30.5, 32.8, 33.0, 34.2 (8×*C*H_2), 48.8 (N*C*H_2-Mes), 51.5, 52.9 (2×COD-*C*H), 64.5 (*C*HN ring), 72.8 (*C*HO ring), 84.7, 85.0 (2×COD-*C*H), 111.6, 112.0, 128.1, 128.7, 129.4, 129.5, 129.9, 130.9, 131.0, 131.6, 132.8, 134.7, 137.8 (Ar*C*), 165.6 (O*C*CH$_3$), 191.1 (Ir-$C_{carbene}$). Anal. Calc. for $C_{40}H_{48}ClIrN_2O_2$: C, 58.84; H, 5.93; N, 3.43. Found: C, 58.77; H, 5.97; N, 3.41. LC-MS (ESI$^+$): *m/z* 779.0 (^{191}Ir), 781.0 (^{193}Ir) [M-Cl]$^+$.

General procedure for the transfer hydrogenation of aldehydes and ketones:

Under inert atmosphere, in a vial fitted with a screw cap, an aliquot of the tested complex (the proper amount), from a stock solution in dichloromethane was added. The solvent was removed under vacuum and solution of KOH (0.25 mmol) in 2-propanol (2.5 mL) was added. Mesitylene (0.1 mmol) was added to the solution as internal standard. The solution was heated to 85 °C for 5 min. Subsequently, corresponding ketone or aldehyde (0.5 mmol) was added. After the desired reaction time an aliquot (10 μL) of the mixture was taken and quenched with 2 mL of dichloromethane. The resulting solution was filtered to remove insoluble inorganic material and the reaction progress was monitored by GC. The results for each experiment are averages over two runs. All the resulting crude products were purified by column chromatography (silica gel, dichloromethane/hexane 9:1) to yield the corresponding primary and secondary alcohols.

X- ray diffraction studies

CCDC 985402 (for **3a**), 985403 (for **3c**) and 985404 (for **3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

Single crystal X-ray diffraction data were collected with an Agilent XCalibur X-ray diffractometer with EOS CCD detector using Mo-Kα radiation (graphite crystal monochromator λ = 0.7107 Å) at room temperature. The data collection, cell refinement and data reduction was executed using CrysAlisPro[12] program. For **3a** and **3c**, the absorption corrections were done analytically using a multifaceted crystal model.[13] The absorption correction was based on multiple scans for **3d**.[12] The structures were solved by direct methods (SHELXS-97[14]) and refined (on F^2) by full-matrix least-squares (SHELXL-97[14]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding atoms (C-H = 0.95 to 0.99 Å). Equal Uij constraints (EADP) were used for C13/C14 and C17/C18 atom pairs in **3a**. Similar Uij (SIMU) restraint was also applied to C12/C13,

C14/C15, C34/C35 and C35/C37 atoms in **3c**. Thermal ellipsoid plots were generated using the program ORTEP-3.[15]

Supporting Information

See the Supporting Information for further details as well as copies of NMR and mass spectra of ligands, iridium(I) complexes and corresponding alcohols obtained from catalytic reactions. CIF files are giving crystallographic information for **3a**, **3c** and **3d**.

Corresponding Author:

E-mail: suleyman.gulcemal@ege.edu.tr

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