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# Hydroxyl and ester functionalized *N*-heterocyclic carbene complexes of iridium(I): efficient catalysts for transfer hydrogenation reactions<sup>†</sup>

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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 a pivaloyl substituent (**3d**) showed the best activity (TON up to 10 000).

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## Introduction

Transfer hydrogenation is a metal-catalyzed process that consists of hydrogen transfer from a hydrogen donor, typically 2-propanol, to an acceptor molecule.<sup>1</sup> The reduction of aldehydes, ketones and imines into the corresponding primary and secondary alcohols and amines is one of the fundamental functional group transformations.<sup>2</sup> 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.<sup>3</sup> The transfer hydrogenation is a safer when compared with the conventional hydrogenation reaction using the potentially explosive H<sub>2</sub> gas.

There have been many reports of the use of iridium-catalyzed transfer hydrogenation of carbonyl compounds and imines.<sup>4</sup> In particular, iridium complexes bearing *N*-heterocyclic carbene (NHC) ligands have been successfully used as catalyst for transfer hydrogenation reactions.<sup>5</sup> 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.<sup>6</sup> Additionally, their tunable character allows for the control of the electronic and steric properties at the metal center.

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Recently, Yus *et al.* reported the preparation of 1-( $\beta$ -hydroxyalkyl) substituted imidazole (I) and benzimidazole (II) derivatives by an epoxide ring opening with the free heterocycles under solvent-free conditions.<sup>7</sup> 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<sup>7</sup> or in the presence of prochiral epoxides *via* chemoenzymatic resolution.<sup>8</sup>



In view of the above information here we investigated the synthesis of hydroxyl and ester functionalized iridium(1)-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(1)-NHC<sup>9</sup> and iridium(I)-NHC<sup>5b</sup> catalyzed reduction reactions. In the second step, ester functionalization of the corresponding alcohol is carried out by different anhydrides. Then, we

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: 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**. CCDC 985402–985404. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ra02993c

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

Scheme 1 Synthetic pathway for the related compounds (1a-e, 2a-e and 3a-e): (i) neat, 70 °C, 12 h; (ii) anhydride, NEt<sub>3</sub>, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, rt, 24 h; (iii) MesCH<sub>2</sub>Br, PhMe, 80 °C, 4 h; (iv) Ag<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, rt, 1 h; (v) [IrCl(COD)]<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 12 h.

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 °C 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<sup>-1</sup>) of 1a disappeared and the corresponding C==O bands for 1b-e were observed at 1739, 1732, 1727 and 1716 cm<sup>-1</sup> respectively.

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 °C (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.<sup>5a,b</sup> In the <sup>1</sup>H NMR spectrum of 2a-e the NCHN<sup>+</sup> 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<sup>10</sup> 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)]<sub>2</sub> 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 NCHN<sup>+</sup> protons of the 5,6-dimethylbenzimidazolium salts 2a-e disappeared in the <sup>1</sup>H NMR spectra of



Fig. 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.

complexes **3a–e**, which confirms the deprotonation of the benzimidazolium fragment. The coordination of the NHC to the iridium center becomes evident in the <sup>13</sup>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.<sup>5</sup> The <sup>13</sup>C chemical shifts showed that C<sub>carbene</sub> 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.<sup>5a,b,g,m,n</sup> 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 ESI.<sup>†</sup>

#### **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 °C. 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(1)–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<sup>-1</sup>) and 15 min with catalyst 3e (final TOF 800 h<sup>-1</sup>). The OH-functionalized complex (3a) was found to

Table 1 Selecte	Selected bond lengths (Å) and angles (°) for <b>3a</b> , <b>3c</b> and <b>3d</b> <sup>a</sup>				
	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		

<sup>*a*</sup> M1 and M2 represent the midpoints of the olefinic bonds C11–C12 and C15–C16, respectively.



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

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.

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.<sup>3a</sup> 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	The effect of the catalyst loading <sup>a</sup>	

Entry	Cat.	% Cat.	Time [h]	Conv. <sup>b</sup> [%]	Yield <sup>c</sup> [%]
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

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

Table 3 Lifetime/stability studies with catalyst 3d<sup>a</sup>

Run	$1^{st}$	$2^{nd}$	3 <sup>rd</sup>	$4^{\mathrm{th}}$	$5^{\mathrm{th}}$
Time [h]	1	1	1	1	1.25
Conv. <sup><math>\tilde{b}</math></sup> [%]	>99	>99	>99	>99	>99

 $^a$  5 mmol of acetophenone, added in five separate stages; 1  $\times$  10<sup>-3</sup> 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.

(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).

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.

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.

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,  $5 \times 10^{-4}$  mmol (0.05 mol% for each substrate) of **3d**,  $2.5 \times 10^{-2}$  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

Table 4 Transfer hydrogenation of carbonyl compounds to alcohols with catalyst  $3d^{\alpha}$ 

	0	<b>3d</b> (0.1 mol%) KOH (5 mol%)	ОН	
	R R'	<i>i</i> -PrOH reflux	R R'	
Entry	Substrates	Time [h]	Conv. <sup>b</sup> [%]	Yield <sup>c</sup> [%]
1	Br	2.5	>99	98
2	MeO	3	>99	97
3	o I	2	>99	99
4	● ↓	1.5	>99	96
5	O Cl	1.5	>99	98
6 <sup><i>d</i></sup>	° C	2	>99	99
7	o	1.5	>99	98
8	° L	1.5	>99	97
9	O H	1.5	>99	98
10	MeO	`Н 3	>99	97
11	O OMe	6	>99	96

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

 Table 5
 Selectivity studies with catalyst 3d<sup>a</sup>



<sup>*a*</sup> 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. <sup>*b*</sup> Acetophenone was added right after benzaldehyde and determined by using GC from an average of at least two runs. <sup>*c*</sup> Benzaldehyde was added right after acetophenone and determined by using GC from an average of at least two runs.

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.

## 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)]<sub>2</sub> was prepared according to the published procedure.<sup>11</sup> 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). <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were acquired on a Varian AS 400 Mercury spectrometer with CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts ( $\delta$ ) were reported in units (ppm) by assigning TMS resonance in the <sup>1</sup>H spectrum as 0.00 ppm and CDCl<sub>3</sub> resonance in the <sup>13</sup>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 (30 m imes 320  $\mu$ m imes0.5 μm).

#### 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 °C 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 °C. IR:  $\nu$  (film) 3127 cm<sup>-1</sup> (OH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 1.46-1.58$ , 1.80–1.90, 2.00–2.03, 2.21–2.29 (8H, 4m, 4 × CH<sub>2</sub>), 2.23 (3H, s, Ar-CH<sub>3</sub>-BI), 2.35 (3H, s, Ar-CH<sub>3</sub>-BI), 3.94–3.97 (2H, m, 4 × CH ring), 5.37 (1H, s, OH), 7.08 (1H, s, ArH-BI), 7.19 (1H, s, ArH-BI), 7.48 (1H, s, NCHN). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 20.2$ , 20.6 (2 × Ar-CH<sub>3</sub>-BI), 24.6, 25.6, 32.2, 34.7 (4 × CH<sub>2</sub>), 62.8 (CHN ring), 72.5 (CHO ring), 110.7, 119.7, 130.8, 131.7, 132.6, 140.0, (ArC), 141.6 (NCHN). Anal. calc. for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O: C, 73.74; H, 8.25; N, 11.47. Found: C, 73.70; H, 8.28; N, 11.43. LC-MS (ESI<sup>+</sup>): *m*/z 245.0 [M + H]<sup>+</sup>.

# 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 4dimethylaminopyridine (61 mg, 0.5 mmol) in dichloromethane

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(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  $\times$  15 mL). Combined organic fractions were dried with MgSO<sub>4</sub> 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:  $\nu$  (film) 1739 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 1.45–1.57, 1.88–2.03, 2.16–2.23 (8H, 3m, 4 × CH<sub>2</sub>), 1.64 (3H, s, OCCH<sub>3</sub>), 2.35 (3H, s, Ar-CH<sub>3</sub>-BI), 2.39 (3H, s, Ar-CH<sub>3</sub>-BI), 4.16–4.24 (1H, m, NCH ring), 5.13–5.19 (1H, m, OCH ring), 7.23 (1H, s, ArH-BI), 7.52 (1H, s, ArH-BI), 7.82 (1H, s, NCHN). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 20.3, 20.7 (2 × Ar-CH<sub>3</sub>-BI), 20.8 (OCCH<sub>3</sub>), 24.2, 25.2, 31.8, 31.9 (4 × CH<sub>2</sub>), 58.8 (CHN ring), 74.3 (CHO ring), 110.7, 120.5, 131.0, 131.9, 132.5, 140.5, (ArC), 142.5 (NCHN), 169.9 (OCCH<sub>3</sub>). Anal. calc. for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.30; H, 7.74; N, 9.78. Found: C, 71.33; H, 7.69; N, 9.74. LC-MS (ESI<sup>+</sup>): m/z 287.1 [M + H]<sup>+</sup>.

1c. Colorless oil. Yield: 1.52 g, 97%. IR:  $\nu$  (film) 1732 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 0.63 (3H, d, J = 7.2 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.83 (3H, d, J = 7.2 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.45–1.57, 1.89–2.06, 2.20–2.22 (8H, 3m, 4 × CH<sub>2</sub>), 2.10–2.17 (1H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 2.34 (3H, s, Ar-CH<sub>3</sub>-BI), 2.38 (3H, s, Ar-CH<sub>3</sub>-BI), 4.18–4.25 (1H, m, NCH ring), 5.13–5.21 (1H, m, OCH ring), 7.22 (1H, s, ArH-BI), 7.51 (1H, s, ArH-BI), 7.81 (1H, s, NCHN). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 18.5, 18.7 (2 × CH(CH<sub>3</sub>)<sub>2</sub>), 20.3, 20.7 (2 × Ar-CH<sub>3</sub>-BI), 24.2, 25.3, 31.8, 32.0 (4 × CH<sub>2</sub>), 33.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 58.7 (CHN ring), 74.0 (CHO ring), 110.7, 120.5, 130.9, 131.8, 132.5, 140.4, (ArC), 142.6 (NCHN), 176.1 (OCCH(CH<sub>3</sub>)<sub>2</sub>). Anal. calc. for C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.58; H, 8.33; N, 8.91. Found: C, 72.63; H, 8.30; N, 8.96. LC-MS (ESI<sup>+</sup>): *m*/*z* 315.1 [M + H]<sup>+</sup>.

1d. White solid, Mp: 110–111 °C. Yield: 1.50 g, 92%. IR:  $\nu$  (film) 1727 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 0.79$  (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.46–1.55, 1.90–2.06, 2.18–2.24 (8H, 3m, 4 × CH<sub>2</sub>), 2.35 (3H, s, Ar-CH<sub>3</sub>-BI), 2.39 (3H, s, Ar-CH<sub>3</sub>-BI), 4.19–4.27 (1H, m, NCH ring), 5.11–5.15 (1H, m, OCH ring), 7.21 (1H, s, ArH-BI), 7.53 (1H, s, ArH-BI), 7.87 (1H, s, NCHN). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 20.3$ , 20.7 (2 × Ar-CH<sub>3</sub>-BI), 24.2, 25.3 (2 × CH<sub>2</sub>), 26.8 (C(CH<sub>3</sub>)<sub>3</sub>), 31.8, 32.1 (2 × CH<sub>2</sub>), 38.6 (C(CH<sub>3</sub>)<sub>3</sub>), 58.8 (CHN ring), 74.2 (CHO ring), 110.8, 120.2, 131.3, 132.1, 132.3, 140.6, (ArC), 141.7 (NCHN), 177.6 (OCC(CH<sub>3</sub>)<sub>3</sub>). Anal. calc. for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.14; H, 8.59; N, 8.53. Found: C, 73.08; H, 8.61; N, 8.55. LC-MS (ESI<sup>+</sup>): *m*/*z* 329.2 [M + H]<sup>+</sup>.

1e. White solid, Mp: 95–96 °C. Yield: 1.69 g, 97%. IR:  $\nu$  (film) 1716 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 1.50–1.63, 1.93–2.00, 2.06–2.16, 2.29–2.43 (8H, 4m, 4 × CH<sub>2</sub>), 2.23 (3H, s, Ar-CH<sub>3</sub>-BI), 2.29 (3H, s, Ar-CH<sub>3</sub>-BI), 4.36– 4.43 (1H, m, NCH ring), 5.32–5.39 (1H, m, OCH ring), 7.24 (2H, t, J = 8.0 Hz, ArH), 7.30 (1H, s, ArH-BI), 7.38–7.45 (1H, m, ArH), 7.49 (1H, s, ArH-BI), 7.66 (2H, d, J = 7.2 Hz, ArH), 7.98 (1H, s, NCHN). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 20.1, 20.5 (2 × Ar-CH<sub>3</sub>-BI), 24.0, 25.1, 31.7, 31.8 (4 × CH<sub>2</sub>), 58.6 (CHN ring), 75.1 (CHO 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*( $C_6H_5$ )). 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<sup>+</sup>): *m*/*z* 349.2 [M + H]<sup>+</sup>.

#### General procedure for the synthesis of 5,6dimethylbenzimidazolium 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 °C 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 5,6dimethylbenzimidazolium salts (**2a–e**).

**2a.** White solid, Mp: 241–242 °C. Yield: 900 mg, 98%. IR:  $\nu$  (film) 3302 cm<sup>-1</sup> (OH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 1.40$ –1.51, 1.60–1.69, 1.79–1.85, 2.10–2.43 (8H, 4m, 4 × CH<sub>2</sub>), 2.26, 2.27, 2.35 (15H, 3s, CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 4.20–4.28 (1H, m, NCH ring), 4.45–4.50 (1H, m, OCH ring), 4.89 (1H, d, J = 5.6 Hz, OH), 5.79 (2H, dd, J = 14.8, NCH<sub>2</sub>-Mes), 6.89 (2H, s, ArH-Mes), 6.99 (1H, s, ArH-BI), 7.55 (1H, s, ArH-BI), 9.93 (1H, s, NCHN<sup>+</sup>). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 20.3$ , 20.5 (CH<sub>3</sub>-Mes), 20.7, 21.0 (2 × Ar-CH<sub>3</sub>-BI), 24.1, 24.9, 31.9, 34.5 (4 × CH<sub>2</sub>), 46.8 (NCH<sub>2</sub>-Mes), 64.2 (CHN ring), 70.8 (CHO ring), 113.0, 113.7, 125.3, 129.9, 130.0, 130.6, 136.8, 136.9, 138.1, 139.5 (ArC), 139.7 (NCHN<sup>+</sup>). Anal. calc. for C<sub>25</sub>H<sub>33</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 65.64; H, 7.27; N, 6.12. Found: C, 64.67; H, 7.26; N, 6.10. LC-MS (ESI<sup>+</sup>): m/z 377.2 [M – Br]<sup>+</sup>.

2b. White solid, Mp: 252–253 °C. Yield: 950 mg, 95%. IR:  $\nu$  (film) 1738 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 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 × CH<sub>2</sub>), 1.53 (3H, s, OCCH<sub>3</sub>), 2.21, 2.22, 2.23, 2.36 (15H, 4s, CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 4.67–4.74 (1H, m, NCH ring), 5.11–5.17 (1H, m, OCH ring), 5.79 (2H, s, NCH<sub>2</sub>-Mes), 6.84 (2H, s, ArH-Mes), 6.91 (1H, s, ArH-BI), 7.56 (1H, s, ArH-BI), 10.67 (1H, s, NCHN<sup>+</sup>). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 20.2, (OCCH<sub>3</sub>), 20.5, 20.6 (CH<sub>3</sub>-Mes), 20.8, 21.1 (2 × Ar-CH<sub>3</sub>-BI), 23.6, 24.5, 31.0, 31.3 (4 × CH<sub>2</sub>), 47.3 (NCH<sub>2</sub>-Mes), 61.2 (CHN ring), 74.7 (CHO 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 (ArC), 140.3 (NCHN<sup>+</sup>), 169.5 (OCCH<sub>3</sub>). Anal. calc. for C<sub>27</sub>H<sub>35</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 64.92; H, 7.06; N, 5.61. Found: C, 64.98; H, 7.04; N, 5.59. LC-MS (ESI<sup>+</sup>): *m/z* 419.2 [M – Br]<sup>+</sup>.

2c. White solid, Mp: 185–186 °C. Yield: 990 mg, 94%. IR:  $\nu$  (film) 1732 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 0.41$  (3H, d, J = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.68 (3H, d, J = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.49–1.57, 1.75–1.77, 1.85–1.87, 2.00–2.04, 2.33–2.37, (8H, 5m, 4 × CH<sub>2</sub>), 1.88–1.94 (1H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 2.15, 2.17, 2.28, (15H, 3s, CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 4.65–4.71 (1H, m, NCH ring), 5.01–5.08 (1H, m, OCH ring), 5.73 (2H, dd, J = 14.8 Hz, NCH<sub>2</sub>-Mes), 6.78 (2H, s, ArH-Mes), 6.87 (1H, s, ArH-BI), 7.55 (1H, s, ArH-BI), 10.53 (1H, s, NCHN<sup>+</sup>). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 18.2$ , 18.8 (2 × CH(CH<sub>3</sub>)<sub>2</sub>), 20.3, 20.7 (CH<sub>3</sub>-Mes), 20.9, 21.2 (2 × Ar-CH<sub>3</sub>-BI), 23.6, 24.7, 31.3, 31.4 (4 × CH<sub>2</sub>), 33.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 47.4 (NCH<sub>2</sub>-Mes), 61.3 (CHN ring), 74.8 (CHO 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<sup>+</sup>), 175.8 (O*C*CH(CH<sub>3</sub>)<sub>2</sub>). 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<sup>+</sup>): *m/z* 447.3 [M - Br]<sup>+</sup>.

2d. White solid, Mp: 199–200 °C. Yield: 1.02 g, 94%. IR:  $\nu$  (film) 1727 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 0.74$  (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.59–1.73, 1.85–1.89, 1.99–2.05, 2.14–2.42, (8H, 4m, 4 × CH<sub>2</sub>), 2.05, 2.14, 2.31, 2.42 (15H, 4s, CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 4.80–4.89 (1H, m, NCH ring), 5.15–5.21 (1H, m, OCH ring), 5.86 (2H, dd, J = 14.8 Hz, NCH<sub>2</sub>-Mes), 6.92 (2H, s, ArH-Mes), 7.05 (1H, s, ArH-BI), 7.71 (1H, s, ArH-BI), 10.59 (1H, s, NCHN<sup>+</sup>). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 19.7$ , 20.0 (CH<sub>3</sub>-Mes), 20.2, 20.5 (2 × Ar-CH<sub>3</sub>-BI), 22.9, 24.0 (2 × CH<sub>2</sub>), 26.1 (C(CH<sub>3</sub>)<sub>3</sub>), 30.7, 30.8 (2 × CH<sub>2</sub>), 37.8 (C(CH<sub>3</sub>)<sub>3</sub>), 46.7 (NCH<sub>2</sub>-Mes), 60.4 (CHN ring), 74.5 (CHO ring), 112.8, 113.2, 124.7, 129.0, 129.4, 129.8, 136.6, 136.8, 137.5, 139.0 (ArC), 139.8 (NCHN<sup>+</sup>), 176.4 (OCC(CH<sub>3</sub>)<sub>3</sub>). Anal. calc. for C<sub>30</sub>H<sub>41</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 66.53; H, 7.63; N, 5.17. Found: C, 66.50; H, 7.66; N, 5.14. LC-MS (ESI<sup>+</sup>): m/z 461.3 [M – Br]<sup>+</sup>.

2e. White solid, Mp: 226-227 °C. Yield: 1.06 g, 95%. IR: v (film) 1716 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 1.67 - 1.69, 1.74 - 1.80, 1.95 - 1.98, 2.04 - 2.07, 2.53 - 2.56,$ (8H, 5m,  $4 \times CH_2$ ), 2.13, (6H, s,  $CH_3$ -Mes), 2.20 (3H, s, Ar- $CH_3$ -BI), 2.27 (6H, s, CH<sub>3</sub>-Mes), 2.29 (3H, s, Ar-CH<sub>3</sub>-BI), 5.02–5.08 (1H, m, NCH ring), 5.50–5.56 (1H, m, OCH ring), 5.73 (2H, dd, J = 14.8 Hz, NCH<sub>2</sub>-Mes), 6.81 (2H, s, ArH-Mes), 6.88 (1H, s, ArH-BI), 7.32 (2H, t, J = 8.4 Hz, ArH), 7.48-7.52 (1H, m, ArH), 7.58 (1H, s, ArH-BI), 7.72 (2H, d, I = 7.2 Hz, ArH), 10.77 (1H, s, NCHN<sup>+</sup>). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 20.2, 20.8$  (*C*H<sub>3</sub>-Mes), 20.7, 21.2,  $(2 \times \text{Ar-}CH_3\text{-BI})$ , 23.9, 24.7, 30.8, 31.6  $(4 \times$ CH<sub>2</sub>), 47.2 (NCH<sub>2</sub>-Mes), 62.2 (CHN ring), 74.5 (CHO 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 (ArC), 141.3 (NCHN<sup>+</sup>), 165.3 (OC(C<sub>6</sub>H<sub>5</sub>)). Anal. calc. for C<sub>32</sub>H<sub>37</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 68.44; H, 6.64; N, 4.99. Found: C, 68.39; H, 6.62; N, 5.02. LC-MS (ESI<sup>+</sup>): m/z 481.2  $[M - Br]^+$ .

# General procedure for the synthesis of iridium(1)-NHC complexes (3a-e)

Under an argon atmosphere, a mixture of 2a-e (0.2 mmol) and Ag<sub>2</sub>O (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)]<sub>2</sub> (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:  $\nu$  (film) 3418 cm<sup>-1</sup> (OH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta$  = 1.47–1.79, 1.88–2.01, 2.17–2.37 (16H, 3m, 8 × CH<sub>2</sub>), 2.04, 2.25, 2.26, 2.29 (15H, 4s, CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 3.01–3.08 (2H, m, COD-CH), 3.56 (1H, d, *J* = 10.4 Hz, OH), 4.11–4.14 (1H, m, NCH ring), 4.65–4.70 (1H, m, COD-CH), 4.75–4.80 (1H, m, COD-CH), 5.55 (1H, d, *J* = 14.8 Hz,

$$\begin{split} & \text{NC}H_2\text{-Mes}), 5.87\text{-}5.94 \text{ (1H, m, OC}H \text{ ring)}, 6.21 \text{ (1H, s, Ar}H\text{-BI)}, \\ & 6.41 \text{ (1H, d, }J = 14.8 \text{ Hz}, \text{NC}H_2\text{-Mes}), 6.86 \text{ (2H, s, Ar}H\text{-Mes}), 7.23 \\ & (1\text{H, s, Ar}H\text{-BI}). \\ ^{13}\text{C} \text{ NMR} \text{ (100.6 MHz, CDCl}_3, \text{TMS, 25 °C, ppm)}: \\ & \delta = 20.4, 20.5, 21.1, 21.2 \text{ (CH}_3\text{-Mes} + \text{Ar}\text{-CH}_3\text{-BI}), 25.3, 26.3, 28.7, \\ & 30.6, 32.0, 32.8, 35.0, 36.8 \text{ (8 } \times \text{CH}_2), 49.1 \text{ (NC}H_2\text{-Mes}), 51.8, \\ & 53.0 \text{ (2 } \times \text{COD-CH}), 68.0 \text{ (CHN ring)}, 70.5 \text{ (CHO ring)}, 85.6, 86.6 \\ & (2 \times \text{COD-CH}), 112.2, 112.5, 128.3, 129.8, 131.2, 131.3, 132.2, \\ & 134.7, 138.2, 138.6 \text{ (ArC)}, 190.3 \text{ (Ir-}C_{\text{carbene}}). \text{ Anal. calc. for} \\ & C_{33}\text{H}_{44}\text{ClIrN}_2\text{O: C, 55.64; H, 6.23; N, 3.93. Found: C, 55.57; H, \\ & 6.18; \text{ N, } 3.90. \text{ LC-MS} \text{ (ESI}^+): m/z \text{ 675.0 (}^{191}\text{Ir}), \text{ 677.0 (}^{193}\text{Ir}) \\ & [\text{M} - \text{Cl}]^+. \end{split}$$

**3b.** Yield: 121 mg, 80%. IR:  $\nu$  (film) 1739 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 1.52-1.74$ , 1.85-1.99, 2.35–2.42 (16H, 3m,  $8 \times CH_2$ ), 1.81 (3H, s, OCCH<sub>3</sub>), 2.04, 2.22, 2.26, 2.31 (15H, 4s, CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 3.11-3.15 (1H, m, COD-CH), 3.71-3.74 (1H, m, COD-CH), 4.64-4.71 (2H, m, COD-CH), 5.69–5.75 (1H, m, NCH ring), 5.90 (2H, dd, J = 14.8 Hz, NCH2-Mes), 5.99-6.02 (1H, m, OCH ring), 6.18 (1H, s, ArH-BI), 6.88 (2H, s, ArH-Mes), 7.25 (1H, s, ArH-BI). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 20.3$ , 20.6, 20.7, 21.0 (*C*H<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 21.1 (OCCH<sub>3</sub>), 24.4, 25.1, 28.9, 29.8, 30.2, 32.5,  $32.9, 34.1 (8 \times CH_2), 49.0 (NCH_2-Mes), 51.8, 53.2 (2 \times COD-CH),$ 64.4 (CHN ring), 71.9 (CHO ring), 84.9, 85.0 (2 × COD-CH), 111.8, 112.1, 128.5, 129.6, 130.9, 131.0, 131.6, 134.6, 137.9 (ArC), 169.8  $(OCCH_3)$ , 191.3  $(Ir-C_{carbene})$ . Anal. calc. for C35H46ClIrN2O2: C, 55.72; H, 6.15; N, 3.71. Found: C, 55.78; H, 6.17; N, 3.73. LC-MS (ESI<sup>+</sup>): *m*/*z* 717.2 (<sup>191</sup>Ir), 719.2 (<sup>193</sup>Ir)  $[M - Cl]^+$ .

**3c.** Yield: 118 mg, 76%. IR:  $\nu$  (film) 1734 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 0.70$  (3H, d, J =7.2 Hz,  $CH(CH_3)_2$ , 0.91 (3H, d, J = 7.2 Hz,  $CH(CH_3)_2$ ), 1.52–1.64, 1.74–1.86, 1.88–1.95, 2.08–2.17, 2.20–2.45 (17H, 5m, 8  $\times$  CH<sub>2</sub> +  $CH(CH_3)_2$ , 2.02, 2.23, 2.24, 2.32 (15H, 4s,  $CH_3$ -Mes + Ar- $CH_3$ -BI), 3.13-3.17 (1H, m, COD-CH), 3.75-3.80 (1H, m, COD-CH), 4.66-4.71 (2H, m, COD-CH), 5.65-5.71 (1H, m, NCH ring), 5.86 (2H, dd, J = 14.8 Hz, NCH<sub>2</sub>-Mes), 6.00–6.07 (1H, m, OCH ring), 6.09 (1H, s, ArH-BI), 6.89 (2H, s, ArH-Mes), 7.22 (1H, s, ArH-BI). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 18.4$ , 18.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.2, 20.3, 20.6, 20.9 (CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 24.4, 25.3, 29.0, 29.6  $(4 \times CH_2)$ , 30.3  $(CH(CH_3)_2)$ , 32.5, 33.1, 33.9, 34.0  $(4 \times CH_2)$ , 49.0 (NCH<sub>2</sub>-Mes), 51.6, 53.0 (2 × COD-CH), 64.5 (CHN ring), 71.6 (CHO ring), 84.8, 84.9 (2 × COD-CH), 111.6, 111.8, 128.5, 129.5, 130.8, 13.9, 131.5, 134.6, 138.0 (ArC), 176.0  $(OCH(CH_3)_2)$ , 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<sup>+</sup>): m/z 745.1 (<sup>191</sup>Ir), 747.1 (<sup>193</sup>Ir) [M - Cl]<sup>+</sup>.

3d. Yield: 124 mg, 78%. IR:  $\nu$  (film) 1728 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 0.74$  (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 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<sub>2</sub>), 1.94, 2.16, 2.17, 2.25 (15H, 4s, CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 3.05–3.10 (1H, m, COD-CH), 3.68–3.71 (1H, m, COD-CH), 4.57–4.63 (2H, m, COD-CH), 5.57–5.64 (1H, m, NCH ring), 5.73 (2H, dd, J = 14.8 Hz, NCH<sub>2</sub>-Mes), 5.99 (1H, s, ArH-BI), 6.01–6.05 (1H, m, OCH ring), 6.83 (2H, s, ArH-Mes), 7.19 (1H, s, ArH-BI). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 20.3$ , 20.4, 20.8, 21.1 (CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 24.6, 25.7 (2 × CH<sub>2</sub>), 26.7 (C(CH<sub>3</sub>)<sub>3</sub>), 29.4, 29.5, 30.8, 32.9, 33.5, 33.8

(6 × CH<sub>2</sub>), 38.6 (*C*(CH<sub>3</sub>)<sub>3</sub>), 49.1 (NCH<sub>2</sub>-Mes), 51.6, 52.9 (2 × COD-CH), 64.7 (CHN ring), 72.3 (CHO ring), 84.9, 85.2 (2 × COD-CH), 111.7, 111.8, 128.8, 129.6, 131.0, 131.1, 131.8, 135.0, 138.2, 138.5 (ArC), 177.5 (OC(CH<sub>3</sub>)<sub>3</sub>), 191.7 (Ir- $C_{carbene}$ ). Anal. calc. for C<sub>38</sub>H<sub>52</sub>ClIrN<sub>2</sub>O<sub>2</sub>: C, 57.30; H, 6.58; N, 3.52. Found: C, 57.25; H, 6.54; N, 3.53. LC-MS (ESI<sup>+</sup>): *m/z* 759.1 (<sup>191</sup>Ir), 761.1 (<sup>193</sup>Ir) [M - Cl]<sup>+</sup>.

**3e.** Yield: 134 mg, 82%. IR:  $\nu$  (film) 1727 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta = 0.84-0.94$ , 1.26-1.35, 1.50–1.57, 1.66–1.72, 2.03–2.23, 2.37–2.53 (16H, 6m, 8  $\times$ CH<sub>2</sub>), 2.01, 2.11, 2.26, 2.29 (15H, 4s, CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 3.11-3.16 (1H, m, COD-CH), 3.83-3.86 (1H, m, COD-CH), 4.68-4.72 (2H, m, COD-CH), 5.83 (2H, dd, J = 14.8 Hz, NCH<sub>2</sub>-Mes), 5.98-6.04 (1H, m, NCH ring), 6.13 (1H, s, ArH-BI), 6.16-6.19 (1H, m, OCH ring), 6.83 (2H, s, ArH-Mes), 7.29-7.33 (2H, m, ArH), 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, ArH). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, TMS, 25 °C, ppm):  $\delta =$ 20.2, 20.3, 20.6, 20.9 (CH<sub>3</sub>-Mes + Ar-CH<sub>3</sub>-BI), 24.5, 25.4, 28.9, 29.6, 30.5, 32.8, 33.0, 34.2 (8  $\times$  CH<sub>2</sub>), 48.8 (NCH<sub>2</sub>-Mes), 51.5, 52.9 (2 × COD-CH), 64.5 (CHN ring), 72.8 (CHO ring), 84.7, 85.0  $(2 \times \text{COD-}CH)$ , 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 (ArC), 165.6 (OCCH<sub>3</sub>), 191.1 (Ir-C<sub>carbene</sub>). Anal. calc. for C<sub>40</sub>H<sub>48</sub>ClIrN<sub>2</sub>O<sub>2</sub>: C, 58.84; H, 5.93; N, 3.43. Found: C, 58.77; H, 5.97; N, 3.41. LC-MS (ESI<sup>+</sup>): *m/z* 779.0 (<sup>191</sup>Ir), 781.0 (<sup>193</sup>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 2propanol (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

Single crystal X-ray diffraction data were collected with an Agilent XCalibur X-ray diffractometer with EOS CCD detector using Mo-K $\alpha$  radiation (graphite crystal monochromator  $\lambda = 0.7107$  Å) at room temperature. The data collection, cell refinement and data reduction was executed using CrysAlisPro<sup>12</sup> program. For **3a** and **3c**, the absorption corrections were done analytically using a multifaceted crystal model.<sup>13</sup> The absorption correction was based on multiple scans for **3d**.<sup>12</sup> The structures were solved by direct methods (SHELXS-97<sup>14</sup>) and refined (on F<sup>2</sup>) by full-matrix least-squares (SHELXL-97<sup>14</sup>). 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.<sup>15</sup>

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