Scientific Research Publishing

International Journal of Organic Chemistry, 2024, 14, 1-19
https://www.scirp.org/journal/ijoc
ISSN Online: 2161-4695
ISSN Print: 2161-4687

# Operationally Simple Enantioselective Silane Reduction of Ketones by the $[Ir(OMe)(cod)]_2$/Azolium Catalytic System

**Satoshi Sakaguchi*, Chika Nagao, Ryo Ichihara, Shogo Matsuo**

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Japan
Email: *satoshi@kansai-u.ac.jp

**How to cite this paper:** Sakaguchi, S., Nagao, C., Ichihara, R. and Matsuo, S. (2024) Operationally Simple Enantioselective Silane Reduction of Ketones by the $[Ir(OMe)(cod)]_2$/Azolium Catalytic System. *International Journal of Organic Chemistry*, **14**, 1-19.
https://doi.org/10.4236/ijoc.2024.141001

**Received:** November 30, 2023
**Accepted:** February 25, 2024
**Published:** February 28, 2024



## Abstract

An operationally simple protocol was designed for the enantioselective silane reduction (ESR) of ketones using air- and moisture-stable $[Ir(OMe)(cod)]_2$ (cod = 1,5-cyclooctadiene) (**3**) as a metal catalyst precursor. This reaction was driven by chiral hydroxyamide-functionalized azolium salt **2**. The catalytic ESR reaction could be performed under benchtop conditions at room temperature. Treatment of **2** with **3** in THF yielded the monodentate IrCl(NHC)(cod) (NHC = *N*-heterocyclic carbene) complex **4** in 93% yield, herein the anionic methoxy ligand of **3** serves as an internal base that deprotonates the azolium ring of **2**. The well-defined Ir complex **4** catalyzed the ESR reaction of propiophenone (**6**) with $(EtO)_2MeSiH$ using the pre-mixing reaction procedure. Based on this success, the catalytic ESR reaction was designed and implemented using an *in situ*-generated NHC/Ir catalyst derived from **2** and **3**. Thus, a wide variety of aryl ketones could be reduced to the corresponding optically active alcohols in moderate to excellent stereoselectivities at room temperature without temperature control. Since the high catalytic activity of **3** was observed, we next evaluated several other transition metal catalyst precursors for the catalytic ESR reaction under the influence of **2**. This evaluation revealed that Ir(acac)(cod) (acac = acetylacetonate) (**28**) and $[IrCl(cod)]_2$ (**5**) can be successfully used as metal catalyst precursors in the ESR reaction.

## Keywords

Asymmetric Catalysis, Enantioselective Reduction, Hydrosilylation Reaction, *N*-Heterocyclic Carbene, Iridium

## 1. Introduction

Transition metal complexes of *N*-heterocyclic carbenes (NHCs) have been ex-

tensively researched in organometallic chemistry and homogeneous catalysis. Strong interactions between the metal and NHCs prevent the decomposition of the complex to free and inactive metal under catalytic conditions. Lin *et al.* achieved a decisive breakthrough in the synthesis of metal complexes bearing NHCs; they reported the preparation of silver NHCs by allowing azolium salts to react with $Ag_2O$ [1]. This strategy, known as the $Ag_2O$ method, offers a direct approach for synthesizing other metal/carbene systems *via* transmetalation. Thus far, a wide variety of transition metal complexes bearing NHCs have been developed [2]. Using the $Ag_2O$ method, Crabtree *et al.* prepared IrX(NHC)(cod)-type Ir complexes (cod = 1,5-cyclooctadiene, X = halogen) [3]. In 2004, Peris *et al.* reported the first catalytic application of metal complexes bearing NHCs; in this study, the hydrosilylation reaction of alkynes was catalyzed by bimetallic rhodium or iridium complexes bearing tripodal NHC ligands [4]. Liu *et al.* developed iridium pyridinyl NHC complexes for the catalytic transfer hydrogenation (TH) reaction [5]. Similarly, Herrmann and Kühn synthesized a series of IrX(NHC)(cod) complexes to study their catalytic activities in TH reactions. [6]. Currently, a large number of IrX(NHC)(cod)-type Ir complexes are continuously being investigated for homogeneous catalysis [7] [8] [9]. In 2006, Herrmann *et al.* developed well-defined chiral IrX(NHC)(cod) complexes using the $Ag_2O$ method [10]. The IrCl(NHC)(cod) complexes derived from chiral heterocyclic diamine 2,2'-bipiperidine were used to catalyze the asymmetric hydrosilylation and TH reactions of acetophenone. More recently, Yoshida and Yanagisawa demonstrated the highly enantioselective TH reaction of ketones, which was catalyzed by an Ir complex possessing a chiral bicyclic NHC ligand system [11] [12].

We developed a series of chiral IrCl(NHC)(cod) complexes *via* the transmetalation reaction of a hydroxyamide-functionalized NHC/Ag complex with $[IrCl(cod)]_2$ using the $Ag_2O$ method (**Figure 1**) [13]. Interestingly, the Ir-catalyzed enantioselective silane reduction (ESR) reaction of ketones was successfully carried out in the presence of a small amount of $AgBF_4$ at room temperature without temperature control [14]. Subsequently, we investigated the ESR reaction using $[Ir(cod)_2]BF_4$ (**1**) as an Ir catalyst precursor without $AgBF_4$ additive (**Figure 1**) [15]. Consequently, a simple combination of **1** and chiral hydroxyamide-functionalized benzimidazolium salt **2** promoted the catalytic ESR reaction of ketones. However, the complex **1** is unstable and sensitive toward air and moisture. These drawbacks limit the use of the **1**/**2** catalytic system for practical synthetic purposes. To overcome these limitations, we envisioned that $[Ir(OMe)(cod)]_2$ (**3**) could be used as an Ir catalyst precursor (**Figure 1**). We assumed that the reaction of **2** with **3** would furnish the corresponding NHC/Ir complex, in which the methoxy group of **3** could serve as an internal base that deprotonates the C-H bond of **2** at the C2 position. Importantly, the commercially available Ir complex **3** is relatively inexpensive and easy to manipulate because of its benchtop stability [16]. The ESR reaction of ketone using the **2**/**3** catalytic system can be performed at room temperature under benchtop conditions. Hence, the present protocol is suitable for the practical synthesis of optically active alcohols.

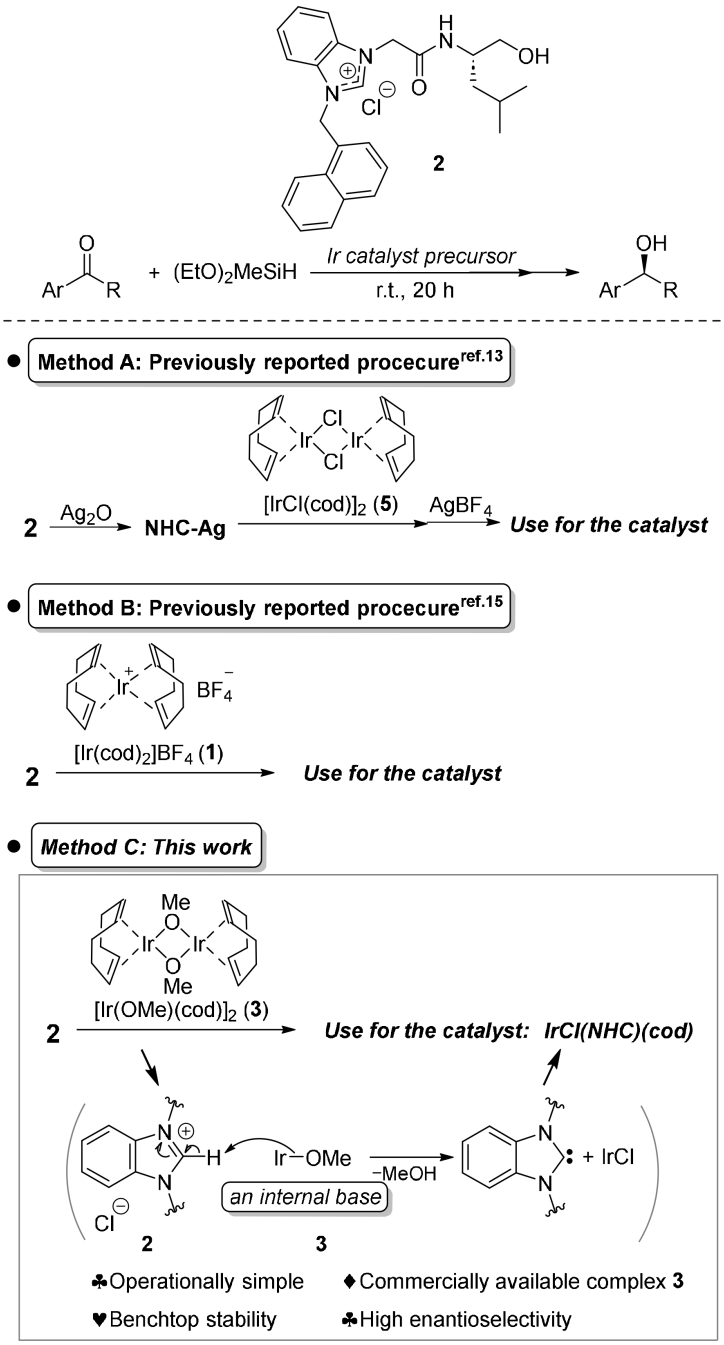



**Figure 1.** Development of enantioselective Ir-catalyzed silane reductions.

To the best of our knowledge, only three previous studies have synthesized IrX(NHC)(cod) complexes by reacting azolium halides with the dinuclear alkoxy complex of Ir; these representative examples are shown in Figure 2. Jiménez *et al.* demonstrated that the reaction of 1-(2-methoxybenzyl)-3-methyl-1H-benzimidazol-3-ium bromide with **3** yields the corresponding monodentate NHC/Ir complex. In addition, the catalytic TH reaction of cyclohexanone was successfully performed in the presence of KOH in 2-propanol at 80˚C [17]. Voutchkova-Kostal *et al.* reported that the reaction of 1-methyl-3-(4-sulfophenyl)-1H-imidazolium

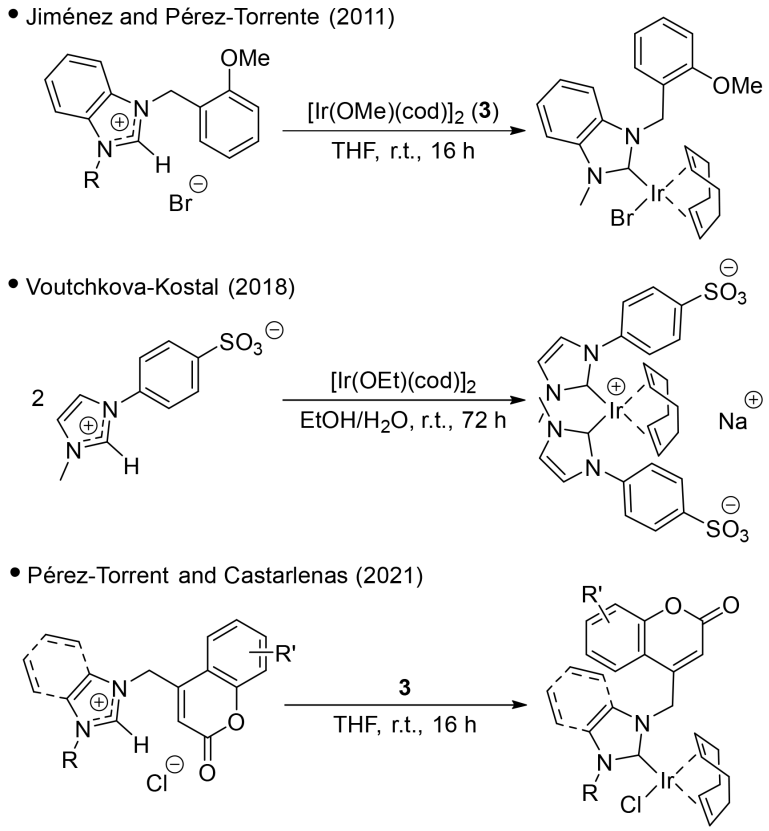



**Figure 2.** Previous studies that have reported the synthesis of IrX(NHC)(cod) complexes by reacting azolium salt with well-defined $[Ir(OMe)(cod)]_2$ or *in situ*-generated $[Ir(OEt)(cod)]_2$ from $[IrCl(cod)]_2$ and NaH in EtOH.

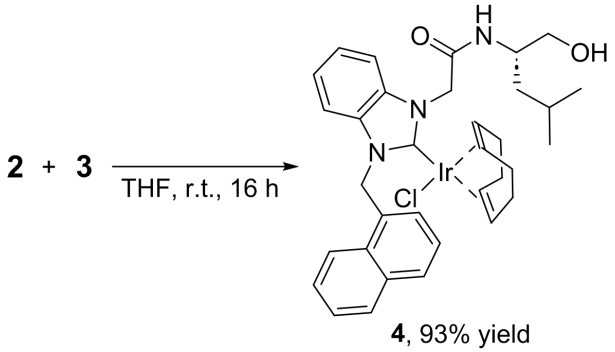
with $[Ir(OEt)(cod)]_2$, which was generated *in situ* from the reaction of $[IrCl(cod)]_2$ with NaH in EtOH, produced the corresponding water-soluble NHC/Ir complex with sulfonate-functionalized wingtips [18]. These Ir complexes promoted the conversion of glycerol into lactic acid in water in the presence of KOH under microwave conditions at 150˚C. More recently, Pérez-Torrent *et al.* synthesized a series of Ir complexes bearing a hemilabile NHC ligand by treating coumarin-functionalized azolium chlorides with **3** [19]. The Ir complex bearing hemilabile coumarin-functionalized NHC catalyzed the hydrosilylation reaction of terminal alkynes with $PhMe_2SiH$. However, to the best our knowledge, the synthesis of a chiral IrX(NHC)(cod) complex using **3** as an Ir precursor has not been reported so far.

Herein, we synthesized the IrCl(NHC)(cod) complex **4** by reacting **2** with **3**. The well-defined NHC/Ir complex **4** exhibited good catalytic activity for the ESR reaction of ketones at room temperature. In this reaction, we employed our previously developed pre-mixing reaction procedure [20]. Additionally, we designed and implemented an operationally simple protocol for the ESR reaction, which was catalyzed by an *in situ*-generated Ir species derived from **2** and **3**. This study reports an extremely useful method for synthesizing optically active alcohols, which can be performed on a benchtop under ambient conditions.

## 2. Results and Discussion

### 2.1. Preparation of 4 from the Reaction of 2 with 3 and Its Application in the ESR Reaction

Azolium salt **2** was reacted with **3** (0.5 equiv.) at room temperature for 16 h, to produce the corresponding IrCl(NHC)(cod) complex **4** as a yellow solid in 93% yield (Equation (1)). The formation of the carbene species strongly suggests that the OMe group of **3** acts as a base and deprotonates the C-H bond at azolium ring (Figure 1). Indeed, no reaction occurred when **2** was treated with $[IrCl(cod)]_2$ (**5**) under these reaction conditions. The use of **5** instead of **3** as an Ir catalyst precursor will be explained in Section 2.3.




(1)

Complex **4** was characterized using NMR spectroscopy and elemental analysis. Unfortunately, complex **4** failed to yield satisfactory crystals for an X-ray crystal structure. Notably, the $^{13}$C-NMR spectrum of **4** indicated that it exists as a mixture of two NHC/Ir complexes. Enders *et al.* observed the hindered rotation of the carbene-metal bond in an NHC/Rh complex, which contained a bulky cyclooctadiene ligand [21] [22]. As **4** contains a chiral carbon center on the side arm of the NHC ligand, the hindered rotation of carbene-Ir bond results in the formation of a mixture of two diastereotopic rotamers. These two rotamers could not be separated by conventional chromatographic techniques. In the $^{1}$H-NMR spectrum of **4**, the characteristic downfield signals for the $NCHN^{+}$ protons of **2** disappeared. Complex **4** also exhibits $^{13}$C chemical shifts at both $\delta$ 192.5 and 192.3 ppm, which are comparable to those of other reported NHC/Ir(I) complexes [23] [24]. The $^{13}$C chemical shifts indicate that $C_{carbene}$ is substantially deshielded. In addition to **4**, we synthesized two other IrCl(NHC)(cod) complexes, **4-Et** and **4-Me**, from benzimidazolium salts bearing both *N*-methyl and *N*-hydroxyamide wingtips derived from (*S*)-2-amino-1-butanol and (*S*)-alaninol, respectively. These complexes, **4-Et** and **4-Me**, also exist as a mixture of two NHC/Ir isomers, and characteristic carbene signals at approximately $\delta$ 191-192 ppm were observed in their $^{13}$C-NMR spectra. Notably, the obtained iridium complexes were completely stable in air and moisture environments.

The asymmetric catalytic property of **4** was examined by applying it in the reduction reaction of ketones with silanes at room temperature (Figure 3). The ESR reaction of propiophenone (**6**) with $(EtO)_2MeSiH$ was performed using our recently developed pre-mixing reaction procedure [20]. After stirring the mixture

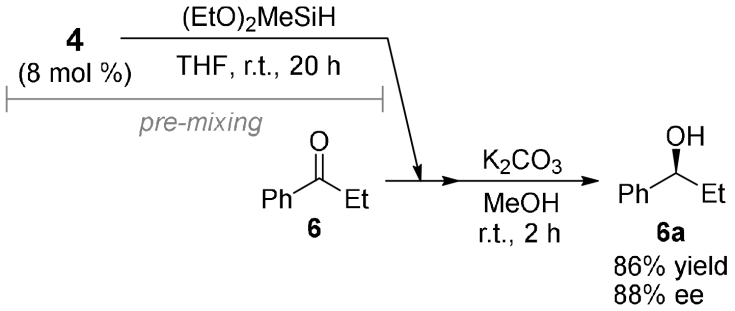



**Figure 3.** ESR reaction of **6** with $(EtO)_2MeSiH$ catalyzed by **4** using the pre-mixing reaction procedure.

of **4** (8 mol% wrt **6**) and $(EtO)_2MeSiH$ (4.5 equiv. wrt **6**) in THF at room temperature for 20 h, **6** was reduced in MeOH in the presence of a small amount of $K_2CO_3$. Consequently, (*S*)-1-phenyl-1-propanol (**6a**) was obtained in 86% yield with 88% ee. This result indicates that the newly prepared Ir complex **4** is very stable and is a suitable catalyst for the ESR reaction under ambient conditions.

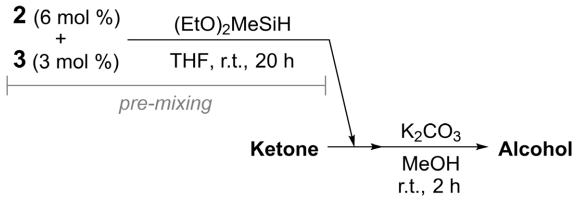
## 2.2. ESR Reaction Catalyzed by the *in Situ*-Generated Ir Species Derived from 2 and 3

Encouraged by the success of the well-defined IrX(NHC)(cod) complex **4**, we continued our investigation on the ESR reaction of ketones. Next, we used the *in situ*-generated Ir species derived from **2** and **3** as a catalyst precursor. The *in situ*-generated metal complexes offer several distinct advantages over well-defined metal complexes [25]. In this approach, there was no need to prepare the NHC/metal catalyst in advance.

The catalytic ESR reaction was performed using the **2**/**3** combined catalytic system and the pre-mixing reaction procedure. The operational simplicity of this protocol enables the synthesis of various optically active alcohols (Table 1). All alcohol products listed in Table 1 have the (*S*)-configuration. First, **2**, **3**, and $(EtO)_2MeSiH$ were premixed, and **6** was reacted with the resulting mixture in MeOH in the presence of a small amount of $K_2CO_3$ at room temperature for 2 h. This reaction produced **6a** in 86% yield with 92% ee (Entry 1). Similarly, butyrophenone (**7**), valerophenone (**8**), and benzyl phenyl ketone (**9**) were successfully reduced to the corresponding optically active alcohols **7a**-**9a** with excellent enantioselectivities (Entries 2-4). Alkyl aryl ketones with branched alkyl groups can also be reduced using this reaction. The reduction of isobutyrophenone (**11**) and cyclohexyl phenyl ketone (**12**) yielded **11a** and **12a**, respectively, with 90% ee (Entries 6 and 7).

Although *p*-methoxypropiophenone (**13**), which contained an electron-donating substituent, was reduced to produce the alcohol **13a** in 53% yield, higher product yield (85%) was obtained in the reduction of *p*-chloropropiophenone (**14**), which contained an electron-withdrawing substituent (Table 1, Entry 8 vs. Entry 9). These results suggest that the electrophilicity of the ketone affected the catalytic activity of the **2**/**3** catalytic system. Similar results were obtained in the

**Table 1.** Enantioselective reduction of various ketones with $(EtO)_2MeSiH$ catalyzed by an *in situ*-generated NHC/Ir species[a].




| Entry | Ketone [ArCOR] | | | Yield [%][b] | Ee [%][c] |
|---|---|---|---|---|---|
| | Ar | R | | | |
| 1 | Ph | Et | (**6**) | 86 | 92 |
| 2[d] | Ph | $^n$Pr | (**7**) | 90 | 92 |
| 3 | Ph | $^n$Bu | (**8**) | 98 | 90 |
| 4[d] | Ph | Bn | (**9**) | 88 | 90 |
| 5 | Ph | Me | (**10**) | 62 | 86 |
| 6 | Ph | $^i$Pr | (**11**) | 54 | 90 |
| 7[d] | Ph | Cy | (**12**) | 67 | 90 |
| 8 | (4-MeO)$C_6H_4$ | Et | (**13**) | 53 | 82 |
| 9 | (4-Cl)$C_6H_4$ | Et | (**14**) | 85 | 82 |
| 10 | (4-$^n$Bu)$C_6H_4$ | Me | (**15**) | 90 | 80 |
| 11 | (4-MeO)$C_6H_4$ | Me | (**16**) | 61 | 80 |
| 12 | (3-MeO)$C_6H_4$ | Me | (**17**) | 90 | 85 |
| 13 | (4-Cl)$C_6H_4$ | Me | (**18**) | 80 | 88 |
| 14 | (2-Cl)$C_6H_4$ | Me | (**19**) | 61 | 41 |
| 15 | (4-$Me_2N$)$C_6H_4$ | Me | (**20**) | 24 | 75 |
| 16 | 2-Naphthyl | Me | (**21**) | 96 | 83 |
| 17[d] | 1-Naphthyl | Me | (**22**) | 56 | 66 |
| 18[d] | 2-Thiophenyl | Me | (**23**) | 54 | 85 |
| 19 | Ph | $CH_2Cl$ | (**24**) | 84 | 42 |
| 20[d] | Ph | $(CH_2)_2Cl$ | (**25**) | 76 | 42 |
| 21 | (4-Cl)$C_6H_4$ | (2-Cl)$C_6H_4$ | (**26**) | 47 | 60 |
| 22 | 4-Chromanone | | (**27**) | 67 | 23 |

[a]**2** (0.03 mmol), **3** (0.015 mmol), and $(EtO)_2MeSiH$ (2.25 mmol) were added to THF (2 mL). After stirring the mixture at room temperature for 20 h, ketone (0.5 mmol), $K_2CO_3$ (5 mg) and MeOH (2 mL) were added. Then, the resulting mixture was reacted at room temperature for 2 h. [b]Isolated yield. [c]Determined by GC or LC using a chiral stationary phase. [d]Ketone was reacted with $(EtO)_2MeSiH$ for 6 h.

reduction reactions of *p*-methoxyacetophenone (**16**) and *p*-chloroacetophenone (**18**), which formed the corresponding alcohols **16a** and **18a** in 61% and 80%

yields, respectively (Entry 11 vs. Entry 13). The product **16a** was obtained in moderate yield (61%) when *p*-methoxyacetophenone (**16**) was reacted with $(EtO)_2MeSiH$. However, *m*-methoxyacetophenone (**17**) was reduced smoothly to furnish **17a** in good yield (90%) with 85% ee (Entry 11 vs. Entry 12). In general, the *meta*-OMe group acts as an electron-withdrawing group, whereas the *para*-OMe group acts as an electron-donating group. Therefore, the higher yield of **17a** may have been caused by the higher electrophilicity of the carbonyl group in **17** (Entry 12). In contrast to the reduction of *p*-chloroacetophenone (**18**) to form **18a** in 80% yield with 88% ee under the standard conditions, *o*-chloroacetophenone (**19**) was converted into **19a** in moderate yield (61%) with low enantioselectivity (41% ee); this probably occurred because of the steric effect (Entry 13 vs. Entry 14). A poor product yield (24%) was observed in the reduction reaction of *p*-(dimethylamino)acetophenone (**20**) (Entry 15). This may have occurred because the dimethylamino group acts as a catalyst poison for the **2**/**3** catalytic system.

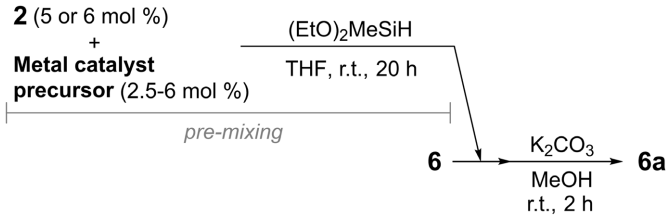
The *in situ*-generated **2**/**3** catalytic system was also suitable for the ESR reduction of 2-acetylnaphthalene (**21**), which afforded (*S*)-1-(2-naphthyl)ethanol (**21a**) in 96% yield with 83% ee (Table 1, Entry 16). However, the reduction of 1-acetylnaphthalene (**22**) furnished the alcohol **22a** in a moderate yield and enantioselectivity (Entry 17). These results indicate that the reactivity of the NHC/Ir catalyst was sterically affected by the arene moiety on the substrate (Entry 16 vs. Entry 17). A satisfactory ee value (85%) was obtained in the reduction of 2-acetylthiophene (**23**); however, the product yield was slightly lower (Entry 18). Diaryl ketones such as 2,4'-dichlorobenzophenone (**26**) produced the corresponding diarylmethanol derivative **26a** with moderate yield (47%) and enantioselectivity (60% ee) (Entry 21). However, 4-chromanone (**27**) was reduced to 4-chromanol (**27a**) with poor stereoselectivity (Entry 22).

### 2.3. ESR Reaction Catalyzed by *in Situ*-Generated Ir Species Derived from 2 and 26 or 5

The good performance of the **2**/**3** catalytic system prompted us to investigate the ability of other metal catalyst precursors for the ESR reaction of **6** using the pre-mixing reaction procedure (Table 2). To compare the relative abilities of the catalysts, the results of the ESR reaction catalyzed by the **2**/**3** catalytic system are also listed in Table 2 as Entries 1 and 2.

First, we selected the commercially available Ir(acac)(cod) (acac = acetylacetonate) (**28**) complex by assuming that the $CH_3C(O)CHC(O)CH_3^-$ (acac) moiety of **28** may serve as an internal base to deprotonate the C-H bond of **2** [26] [27] [28]. Notably, complex **28** exhibited a high catalytic activity for the ESR reaction of **6**. When **6** was treated with $(EtO)_2MeSiH$ in the presence of the **2**/**28** catalytic system in MeOH at room temperature, **6a** was obtained in 90% yield with 85% ee (Table 2, Entry 4). To our surprise, the combination of **2** and $[IrCl(cod)]_2$ (**5**) unexpectedly promoted the ESR reaction of **6** to produce **6a** in 99% yield with 93% ee (Entry 6). The p*K*a values of the bases in DMSO are as follows: $CH_3OH$ 29.0; $CH_3C(O)CH_2C(O)CH_3$ (acac-H) 13.3; HCl 1.8 [29] [30] [31]. These values

**Table 2.** Catalytic performances of various metal catalyst precursors for the enantioselective reduction of **6** with $(EtO)_2MeSiH$ under the influence of **2**[a].




| Entry | Metal catalyst precursor [mol %] | Yield [%][b] | Ee [%][c] |
|---|---|---|---|
| 1 | $[Ir(OMe)(cod)]_2$ (**3**) [3] | 86 | 92 |
| 2 | **3** [2.5] | 72 | 85 |
| 3 | Ir(acac)(cod) (**28**) [6] | 96 | 80 |
| 4 | **28** [5] | 90 | 85 |
| 5 | $[IrCl(cod)]_2$ (**5**) [3] | 97 | 92 |
| 6 | **5** [2.5] | 99 | 93 |
| 7 | $[IrCl(cyclooctene)_2]_2$ (**29**) [2.5] | 20 | 76 |
| 8 | $[Ir(cod)_2]^+\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}^-$ (**30**) [5] | 17 | 86 |
| 9 | $[IrCp^*Cl_2]_2$ (**31**) [2.5] | <5 | - |
| 10 | $[RhCl(cod)]_2$ (**32**) [2.5] | <5 | - |
| 11 | [Rh(cod)2]+$BF4^-$ (33) [5] | 11 | 15 |
| 12 | $PdCl_2(cod)$ (**34**) [5] | 18 | <1 |
| 13 | $PtCl_2(cod)$ (**35**) [5] | <1 | - |
| 14 | $[RuCl_2(cod)]_n$ (**36**) [5] | <5 | - |
| 15 | $[CuCl(cod)]_2$ (**37**) [5] | <1 | - |

[a]**2** (0.025 - 0.03 mmol), metal catalyst precursor (0.0125 - 0.03 mmol), and $(EtO)_2MeSiH$ (2.25 mmol) were added to THF (2 mL). After stirring the resulting mixture at room temperature for 20 h, ketone (0.5 mmol), $K_2CO_3$ (5 mg), and MeOH (2 mL) were added to it. Subsequently, the resulting mixture was reacted at room temperature for 2 h. [b]GC yield using internal standard method. [c]Determined by GC using a chiral stationary phase.

indicate that the chloride ion in **5** could not act as an internal base. Indeed, as described above, no reaction was observed between **2** and **5**. The use of the Ir catalyst precursors **28** and **5** will be discussed later.

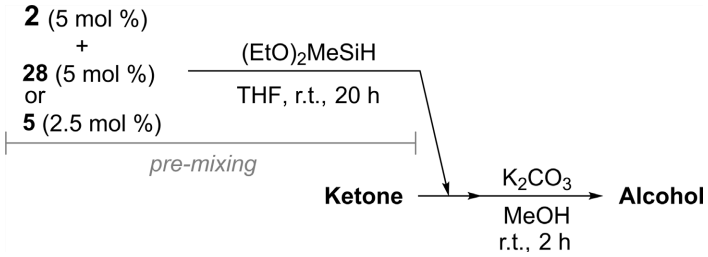
Although good product yield and stereoselectivity were observed in the ESR reaction of **6** using **5** (Table 2, Entry 6), a lower yield was obtained when $[IrCl(cyclooctene)_2]_2$ (**29**) was used instead of **5**; this reaction afforded **6a** in 20% yield (Entry 7). Furthermore, cationic Ir(I) complexes, such as $[Ir(cod)_2]^+\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}^-$ (**30**), and Ir(III) complexes, such as $[IrCp^*Cl_2]_2$ (**31**), were found to be inert (Entries 8 and 9). In addition, the execution of the ESR reac-

tion was difficult when Rh catalyst precursors, such as $[RhCl(cod)]_2$ (**32**) and [Rh(cod)2]+BF4$^-$ (**33**), were used under typical reaction conditions (Entries 10 and 11). However, several well-defined chiral NHC/Rh complexes have been developed to date for the catalytic ESR reaction of ketones with $Ph_2SiH_2$ [32] [33] [34].

Encouraged by our success with **5** as an Ir catalyst precursor, we continued to explore the use of Pd, Pt, Ru and Cu complexes in the ESR reaction. In the literature, the ESR reaction of ketone has been achieved using the well-defined NHC/Cu complex catalyst or an *in situ*-generated NHC/Ru catalyst derived from $RuCl_2(PPh_3)_2$ and a chiral azolium salt [35] [36]. However, as shown in Table 2 (Entries 12-15), the metal catalyst precursors **34**-**37**, which possess both anionic chloride and neutral cod ligands, could not be applied in the ESR reaction. These results showed that only Ir complexes promoted the catalytic ESR reaction using the pre-mixing reaction procedure.

Table 3 summarizes the results of the ESR reactions of several ketones catalyzed by the **2**/**28** and **2**/**5** catalytic system. These data show that **28** and **5** could be successfully used as Ir catalyst precursors. The use of the pre-mixing

**Table 3.** Enantioselective reduction of several ketones with $(EtO)_2MeSiH$ using the **2**/**28** or **2**/**5** catalytic system[a].

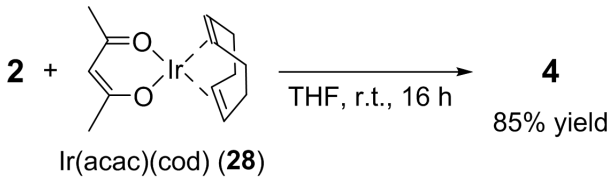



| Entry | Ir catalyst precursor [mol %] | Ketone | Yield [%][b] | Ee [%][c] |
|---|---|---|---|---|
| 1 | Ir(acac)(cod) (**28**) [5] | **6** | 90 | 85 |
| 2 | **28** [5] | **7** | 80 | 90 |
| 3 | **28** [5] | **12** | 65 | 92 |
| 4 | $[IrCl(cod)]_2$ (**5**) [2.5] | **6** | 99 | 93 |
| 5[d] | **5** [2.5] | **7** | 79 | 91 |
| 6[d] | **5** [2.5] | **9** | 88 | 86 |
| 7 | **5** [2.5] | **10** | 61 | 84 |
| 8[d] | **5** [2.5] | **12** | 74 | 91 |

[a]**2** (0.025 mmol), Ir catalyst precursor (0.0125 or 0.025 mmol), and $(EtO)_2MeSiH$ (2.25 mmol) were added to THF (2 mL). After stirring the resulting mixture at room temperature for 20 h, the ketone (0.5 mmol), $K_2CO_3$ (5 mg), and MeOH (2 mL) were added. Then, the mixture was reacted at room temperature for 2 h. [b]Isolated yield. [c]Determined by GC or LC using a chiral stationary phase. [d]Ketone was reacted with $(EtO)_2MeSiH$ for 6 h.

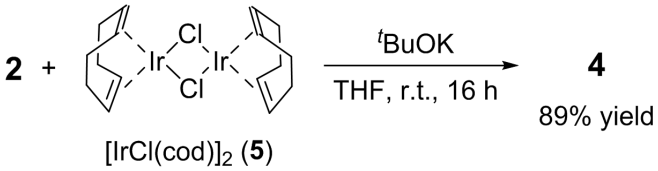
reaction procedure was essential. Indeed, almost no reaction was observed when ketone, $(EtO)_2MeSiH$, $K_2CO_3$ and MeOH were added at once to the reaction vessel after stirring a mixture of **2** and **28** (or **5**) in THF for 20 h. Notably, the experiments could be performed under benchtop conditions at ambient temperature.

Finally, we investigated the independent reactions of **2** with **28** and **5**. We assumed that the anionic acac ligand of **28** would serve as an internal base to deprotonate the C-H bond of **2**. As expected, the reaction of **2** with **28** in THF at room temperature afforded **4** in 85% yield (Equation (2)). This result strongly suggests that the formation of the NHC species from **2** is promoted by the acac ligand of **28** in a manner similar to the reaction between **2** and **3** (Figure 1).




(2)

In the **2**/**5** catalytic system, we assumed that $(EtO)_2MeSiH$ would act as a base that deprotonates the C-H bond of **2** during the pre-mixing reaction process. Therefore, we next attempted to prepare an NHC/Ir complex by reacting **2** with **5** in the presence of $(EtO)_2MeSiH$. However, we could not confirm the formation of the IrCl(NHC)(cod) complex in a pure form by analyzing the NMR spectra of the crude mixture, which was obtained after reacting **2**, **5**, and $(EtO)_2MeSiH$. Meanwhile, we succeeded in synthesizing **4** by reacting **2** with **5** in the presence of *t*BuOK [37]. After stirring a mixture of **5** and *t*BuOK in THF for 10 min, **2** was added to the reaction vessel. The resulting mixture was then stirred at room temperature for 16 h, producing **4** in 89% yield (Equation (3)). Although the reaction mechanism of the **2**/**5** catalytic system is still unclear at this stage, we believe that **4** would be generated *in situ* during the catalytic cycle of the ESR reaction.




(3)

## 3. Conclusion

In summary, we investigated the use of a commercially available and air- and moisture stable Ir complex **3** in the ESR reaction of ketones. The complex **3** contains an OMe group, which acts as an internal base and deprotonates the C-H bond of the azolium ring of **2**. The reaction of **2** with **3** furnished the well-defined IrCl(NHC)(cod) complex **4** in an almost quantitative yield. The ESR reaction of **6** with $(EtO)_2MeSiH$ was catalyzed by **4** and was performed using the pre-mixing reaction procedure. Additionally, we demonstrated that the *in situ*-generated NHC-Ir species derived from **2** and **3** promoted the catalytic ESR reaction of various ketones, which afforded the corresponding alcohols with

moderate to excellent stereoselectivities. Throughout the course of this study, experiments were performed under benchtop conditions at room temperature. Hence, this study reports a useful and operationally simple method for the synthesis of optically active alcohols. Moreover, several transition metal complexes were evaluated as metal catalyst precursors; the evaluation revealed that **28** and **5** facilitated the catalytic ESR reaction using the pre-mixing reaction procedure. We believe that this protocol can be used for the practical and efficient synthesis of optically active alcohols from ketones.

## 4. Experimental

All other chemical reagents and solvents were obtained from commercial sources. Column chromatography was performed with silica gel 60 (63 - 210 μm) purchased from Kanto Chemical Co., Inc. $^{1}$H-NMR spectra were recorded on a JEOL ECA400 (400 MHz for $^{1}$H-NMR and 100 MHz for $^{13}$C-NMR) spectrometer. Chemical shifts were reported downfield from TMS ($\delta$ = 0 ppm) for $^{1}$H-NMR. For $^{13}$C-NMR, chemical shifts were reported on the scale relative to the solvent used as an internal reference. Elemental analyses were performed at Osaka University.

### 4.1. Procedure for Preparation of 4 from the Reaction of 2 with 3 or 28

**2** (0.21 mmol, 95 mg) and **3** (0.1 mmol, 66 mg) were stirred in THF (2 mL) at room temperature for 16 h under Ar. After passing through a short silica gel column using THF as a solvent, the filtrate was dried in a rotary evaporator to afford **4** as a yellow solid (139 mg, 92% yield). **28** (0.2 mmol, 80 mg) could be used instead of **3** to obtain **4** (127 mg, 85% yield). **4** was very stable under air and could be stored as a solid for a minimum of one month at room temperature.

**4:** $^{1}$H-NMR ($CDCl_3$, 400 MHz): Major isomer: $\delta$ 8.27 (d, $J$ = 8.2 Hz, 1H, NH), 8.01 - 6.78 (m, 12H), 6.36 (d, $J$ = 15.4 Hz, 1H, $CH_2CO$), 6.29 (d, $J$ = 15.4 Hz, 1H, $NCH_2Ar$), 4.85 (d, $J$ = 15.4 Hz, 1H, $CH_2CO$), 4.76 (br, 1H, cod), 4.76 (br, 1H, NHC*H*), 4.10 (br, 1H, cod), 3.66 (br, 1H, cod), 3.53 - 3.48 (m, 1H, C$H_2$OH), 3.08 - 3.01 (m, 1H, cod), 2.96 - 2.93 (m, 1H, C$H_2$OH), 2.78 (t, $J$ = 6.8 Hz, 1H, OH), 2.30 - 2.24 (m, 2H, cod), 1.99 - 1.97 (m, 1H, cod), 1.74 - 1.59 (m, 4H, cod), 1.41 (br, 1H, cod), 1.25-1.01 (m, 2H, $CH_{2tBu}$), 0.93-0.86 (m, 1H, $CH_{tBu}$), 0.61 (d, $J$ = 6.8 Hz, 3H, $CH_{3tBu}$), 0.56 (d, $J$ = 6.8 Hz, 3H, $CH_{3tBu}$). The following signals were attributed to minor isomer: $\delta$ 8.26 (d, $J$ = 8.2 Hz, 1H, NH), 6.27 (d, $J$ = 16.8 Hz, 1H, $NCH_2Ar$), 6.21 (d, $J$ = 16.8 Hz, 1H, $NCH_2Ar$), 0.90 (d, $J$ = 6.3 Hz, 3H, $CH_{3tBu}$), 0.87 (d, $J$ = 6.3 Hz, 3H, $CH_{3tBu}$). $^{13}$C-NMR ($CDCl_3$, 100 MHz): Major isomer: $\delta$ 192.4 ($C_{carbene}$), 167.0 (C=O), 134.9, 134.3, 133.5, 130.8, 130.4, 129.0, 128.3, 126.8, 126.1, 125.2, 123.6, 123.5, 123.3, 122.3, 111.1, 110.4, 89.0 ($CH_{cod}$), 88.6 ($CH_{cod}$), 65.6 ($CH_2OH$), 54.0 ($CH_{cod}$), 53.6 ($CH_{cod}$), 52.5 (NHCH), 50.4 ($CH_2CO$), 49.6 ($NCH_2Ar$), 39.2 ($CH_{2tBu}$), 33.8 ($CH_{2cod}$), 32.6 ($CH_{2cod}$), 29.1 ($CH_{2cod}$), 28.7 ($CH_{2cod}$), 24.4 ($CH_{tBu}$), 22.8 ($CH_{3tBu}$), 21.4 ($CH_{3tBu}$). Minor isomer: $\delta$ 192.3 ($C_{carbene}$), 167.2 (C=O), 134.9, 134.4, 133.6, 130.9, 130.3, 128.9, 128.2, 126.7,

126.1, 125.2, 123.6, 123.4, 123.4, 122.4, 111.1, 110.6, 88.5 ($CH_{cod}$), 85.0 ($CH_{cod}$), 65.4 ($CH_2OH$), 53.9 ($CH_{cod}$), 53.7 ($CH_{cod}$), 51.0 (NHCH), 50.5 ($CH_2CO$), 49.5 ($NCH_2Ar$), 39.2 ($CH_{2tBu}$), 33.5 ($CH_{2cod}$), 32.9 ($CH_{2cod}$), 30.8 ($CH_{2cod}$), 28.9 ($CH_{2cod}$), 24.7 ($CH_{tBu}$), 22.8 ($CH_{3tBu}$), 22.1 ($CH_{3tBu}$). Anal. Calc. for $C_{34}H_{41}ClIrN_3O_2 \cdot 0.5H_2O$: C, 53.71; H, 5.57; N, 5.53. Found: C, 53.74; H, 5.60; N, 5.50%.

**4-Et**: $^1$H NMR ($CDCl_3$, 400 MHz): Major isomer: $\delta$ 7.49 - 7.26 (m, 4H), 6.60 (d, $J$ = 8.4 Hz, 1H, NH), 6.26 (d, $J$ = 15.2 Hz, 1H, $CH_2CO$), 4.76 (d, $J$ = 15.2 Hz, 1H, $CH_2CO$), 4.84 - 4.76 (br, 1H, cod), 4.84 - 4.76 (br, 1H, NHC*H*), 4.20 (s, 3H, $NCH_3$), 3.88 - 3.83 (m, 1H, cod), 3.64 - 3.60 (m, 1H, cod), 3.49-3.46 (m, 1H, C$H_2$OH) 3.15 - 3.10 (m, 1H, cod), 2.98 - 2.90 (m, 1H, C$H_2$OH), 2.77 (t, $J$ = 7.0 Hz, 1H, OH), 2.38 - 2.22 (m, 4H, cod), 1.94 - 1.83 (m, 2H, cod), 1.80 - 1.66 (m, 2H, cod), 1.38 - 1.25 (m, 1H, C$H_2$CH$_3$), 1.25 - 1.10 (m, 1H, C$H_2$CH$_3$), 0.53 (t, $J$ = 7.2 Hz, 3H, $CH_2CH_3$). The following signals were attributed to minor isomer: $\delta$ 7.14 (d, $J$ = 8.4 Hz, 1H, NH), 6.22 (d, $J$ = 15.2 Hz, 1H, $CH_2CO$), 4.80 (d, $J$ = 15.2 Hz, 1H, $CH_2CO$), 4.17 (s, 3H, $NCH_3$), 1.54 - 1.47 (m, 2H, C$H_2$CH$_3$), 0.88 (t, $J$ = 7.2 Hz, 3H, $CH_2CH_3$). $^{13}$C-NMR ($CDCl_3$, 100 MHz): Major isomer: $\delta$ 191.5 ($C_{carbene}$), 166.9 (C=O), 135.4, 134.0, 123.4, 123.3, 110.1, 109.8, 88.8 ($CH_{cod}$), 88.2 ($CH_{cod}$), 64.3 ($CH_2OH$), 53.8 ($CH_{cod}$), 53.4 ($CH_{cod}$), 53.1 (CHNH), 52.3 ($CH_2CO$), 34.3 ($CH_{2cod}$), 33.4 ($CH_{2cod}$), 33.2 ($CH_3N$), 29.3 ($CH_{2cod}$), 29.0 ($CH_{2cod}$), 23.5 ($CH_{2Et}$), 10.0 ($CH_{3Et}$); Minor isomer: $\delta$ 167.4 (C=O), 135.3, 134.1, 123.4, 123.3, 110.9, 110.4, 88.6 ($CH_{cod}$), 87.4 ($CH_{cod}$), 64.7 ($CH_2OH$), 54.5 ($CH_{cod}$), 53.5 ($CH_{cod}$), 53.0 (CHNH), 52.8 ($CH_2CO$), 34.2 ($CH_{2cod}$), 33.6 ($CH_{2cod}$), 33.1 ($CH_3N$), 29.6 ($CH_{2cod}$), 28.9 ($CH_{2cod}$), 23.4 ($CH_{2Et}$), 10.5 ($CH_{3Et}$); The carbene $^{13}$C-NMR resonance of the minor isomer was not observed. Anal. Calc. for $C_{22}H_{31}ClIrN_3O_2$: C, 44.25; H, 5.23; N, 7.04%. Found: C, 44.48; H, 5.56; N, 6.76%.

**4-Me**: $^{13}$C-NMR ($CDCl_3$, 100 MHz): Major isomer: $\delta$ 191.5 ($C_{carbene}$), 166.6 (C=O), 135.4, 134.0, 123.4, 123.4, 110.0, 109.8, 89.0 ($CH_{cod}$), 88.2 ($CH_{cod}$), 65.5 ($CH_2OH$), 53.5 ($CH_{cod}$), 53.1 ($CH_{cod}$), 52.4 (CHNH), 48.4 ($CH_2CO$), 34.3 ($CH_{2cod}$), 33.4 ($CH_{2cod}$), 33.2 ($CH_3N$), 29.4 ($CH_{2cod}$), 29.0 ($CH_{2cod}$), 16.3 ($CH_{3Me}$); Minor isomer: $\delta$ 191.3 ($C_{carbene}$), 167.3 (C=O), 135.3, 134.0 123.4, 123.3, 110.4, 109.7, 88.5 ($CH_{cod}$), 88.0 ($CH_{cod}$), 66.7 ($CH_2OH$), 53.3 ($CH_{cod}$), 53.2 ($CH_{cod}$), 52.7 (CHNH), 48.9 ($CH_2CO$), 34.2 ($CH_{2cod}$), 33.4 ($CH_{2cod}$), 33.2 ($CH_3N$), 29.4 ($CH_{2cod}$), 29.2 ($CH_{2cod}$), 16.2 ($CH_{3Me}$). Anal. Calc. for $C_{21}H_{29}ClIrN_3O_2$: C, 43.25; H, 5.01; N, 7.21%. Found: C, 43.18; H, 5.31; N, 7.01%. Identity is known from $^{13}$C-NMR and elemental analysis, but our efforts to obtain the clean $^1$H-NMR spectra proved to be unsuccessful because of the broad signal.

### 4.2. Procedure for Preparation of 4 from the Reaction of 2 with 5 in the Presence of $^t$BuOK

A mixture of **5** (0.07 mmol, 47 mg) and $^t$BuOK (0.12 mmol, 14 mg) was stirred in THF (2 mL) at room temperature. After stirring for 10 min, **2** (0.12 mmol, 54 mg) was added to the reaction vessel. Then, the reaction mixture was stirred at room temperature for 16 h. After passing through a short silica gel using THF as a solvent, the filtrate was dried in a rotary evaporator to afford **4** as a yellow solid

(80 mg, 89% yield).

### 4.3. General Procedure for ESR Reaction of Ketone with $(EtO)_2MeSiH$

A mixture of **3** (0.015 mmol, 10 mg) and **2** (0.03 mmol, 14 mg) were stirred in THF (2 mL) at room temperature. After stirring for 3 h, $(EtO)_2MeSiH$ (2.25 mmol, 302 mg) was added to the reaction vessel. After further stirring at room temperature for 20 h, ketone (0.50 mmol), $K_2CO_3$ (5 mg) and MeOH (2 mL) were added. Then, the resulting mixture was stirred at room temperature for 2 h. After evaporation of the solvents, the corresponding alcohol product from the residue was purified by column chromatography on silica gel. The ee was measured by chiral GC or chiral LC according to our previously reported procedure.

**1-Phenyl-1-propanol (6a):** $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.35 - 7.26 (m, 5H), 4.59 (t, $J$ = 6.4 Hz, 1H), 3.53 (br, 1H), 1.84 - 1.71 (m, 2H), 0.92 (t, $J$ = 6.4 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 144.6, 128.4, 127.5, 125.9, 76.0, 31.9, 10.1.

**1-Phenyl-1-butanol (7a):** $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.18 - 7.10 (m, 5H), 4.48 (t, $J$ = 6.4 Hz, 1H), 1.64 - 1.58 (m, 1H), 1.55 - 1.46 (m, 1H), 1.32 - 1.21 (m, 1H), 1.19 - 1.08 (m, 2H), 0.77 (t, $J$ = 7.2 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 144.9, 128.3, 127.3, 125.8, 74.3, 41.2, 18.9, 13.9.

**1-Phenyl-1-pentanol (8a):** $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.33 - 7.24 (m, 5H), 4.64 - 4.60 (m, 1H), 1.83 - 1.64 (m, 3H), 1.43 - 1.34 (m, 2H), 1.28 - 1.19 (m, 2H), 0.88 (t, $J$ = 7.2 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 144.9, 128.4, 127.4, 125.9, 74.6, 38.8, 27.9, 22.6, 14.0.

**1,2-Diphenylethanol (9a):** $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.36 - 7.18 (m, 10H), 4.89 (dd, $J$ = 8.2 and 5.2 Hz, 1H), 3.45 (br, 1H), 3.06 - 2.95 (m, 2H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 143.8, 138.0, 129.5, 128.5, 128.4, 127.6, 126.6, 125.9, 75.3, 46.1.

**1-Phenylethanol (10a):** $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.40 - 7.25 (m, 5H), 4.90 (q, $J$ = 6.4 Hz, 1H), 3.53 (br, 1H), 1.50 (d, $J$ = 6.4 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 145.8, 128.5, 127.4, 125.4, 70.4, 25.1.

**1-Phenyl-2-methyl-1-propanol (11a):** $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.22 - 7.11 (m, 5H), 4.21 (d, $J$ = 6.8 Hz, 1H), 3.67 (br, 1H), 1.86 - 1.78 (m, 1H), 0.86 (d, $J$ = 6.8 Hz, 3H), 0.66 (d, $J$ = 6.8 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 143.6, 128.2, 127.4, 126.5, 80.0, 35.2, 19.0, 18.2.

**Cyclohexyl(phenyl)methanol (12a):** $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.35 - 7.26 (m, 5H), 4.36 (dd, $J$ = 7.2 and 3.2 Hz, 1H), 1.98 (d, $J$ = 12.8 Hz, 1H), 1.83 - 1.75 (m, 2H), 1.65 - 1.57 (m, 4H), 1.40 - 1.35 (m, 1H), 1.24 - 0.91 (m, 4H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 143.6, 128.2, 127.4, 126.6, 79.4, 44.9, 29.3, 28.8, 26.4, 26.1, 26.0.

**1-(4-Methoxyphenyl)propanol (13a):** $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.28 - 7.24 (m, 2H), 6.90 - 6.86 (m, 2H), 4.53 (t, $J$ = 6.4 Hz, 1H), 3.80 (br, 3H), 1.87 - 1.66 (m, 3H), 0.89 (t, $J$ = 7.6 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 158.9, 136.7, 127.2, 113.8, 75.6, 55.2, 31.7, 10.2.

**1-(4-Chlorophenyl)propanol (14a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.32 - 7.25 (m, 4H), 4.57 (t, $J$ = 6.4 Hz, 3H), 1.94 (br, 1H), 1.82 - 1.67 (m, 2H), 0.90 (t, $J$ = 7.2 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 142.9, 133.0, 128.5, 127.3, 75.2, 31.9, 9.9.

**1-(4-Butylphenyl)ethanol (15a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.27 (d, $J$ = 7.6 Hz, 2H), 7.16 (d, $J$ = 7.6 Hz, 2H), 4.86 (q, $J$ = 6.4 Hz, 1H), 2.60 (t, $J$ = 7.6 Hz, 2H), 1.91 (br, 1H), 1.63 - 1.55 (m, 2H), 1.48 (d, $J$ = 6.4 Hz, 3H), 1.40 - 1.31 (m, 2H), 0.92 (t, $J$ = 7.6 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 143.0, 142.2, 128.5, 125.3, 70.2, 35.2, 33.6, 25.0, 22.3, 13.9.

**1-(4-Methoxyphenyl)ethanol (16a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.31 - 7.26 (m, 2H), 6.89 - 6.86 (m, 2H), 4.84 (q, $J$ = 6.4 Hz, 1H), 3.80 (s, 3H), 1.94 (br, 1H), 1.47 (d, $J$ = 6.8 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 158.9, 138.0, 126.6, 113.8, 69.9, 55.2, 25.0.

**1-(3-Methoxyphenyl)ethanol (17a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.28 - 7.24 (m, 1H), 6.95 - 6.93 (m, 2H), 6.82 - 6.79 (m, 1H), 4.86 (q, $J$ = 6.4 Hz, 1H), 3.81 (s, 3H), 2.00 (br, 1H), 1.48 (d, $J$ = 6.4 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 159.7, 147.6, 129.5, 117.6, 112.8, 110.8, 70.3, 55.2, 25.1.

**1-(4-Chlorophenyl)ethanol (18a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.32 - 7.26 (m, 4H), 4.86 (q, $J$ = 6.4 Hz, 1H), 2.14 (br, 1H), 1.46 (dd, $J$ = 6.4 and 1.2 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 144.2, 133.0, 128.5, 126.8, 69.7, 25.2.

**1-(2-Chlorophenyl)ethanol (19a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.60 - 7.58 (m, 1H), 7.33 - 7.17 (m, 3H), 5.29 (q, $J$ = 6.4 Hz, 1H), 2.15 (br, 1H), 1.48 (d, $J$ = 6.4 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 143.0, 131.6, 129.4, 128.4, 127.2, 126.4, 66.9, 23.5.

**1-(4-Dimethylaminophenyl)ethanol (20a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.26 - 7.24 (m, 2H), 6.74 - 6.71 (m, 2H), 4.81 (q, $J$ = 6.4 Hz, 1H), 2.94 (s, 6H), 1.74 (br, 1H), 1.48 (d, $J$ = 6.4 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 150.2, 133.7, 126.4, 112.6, 70.1, 40.7, 24.6.

**1-(2-Naphthyl)ethanol (21a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.80 - 7.74 (m, 4H), 7.46 - 7.41 (m, 3H), 4.98 (q, $J$ = 6.4 Hz, 1H), 1.87 (br, 1H), 1.53 (d, $J$ = 6.4 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 143.2, 133.3, 132.8, 128.2, 127.9, 127.6, 126.1, 125.7, 123.8, 123.7, 70.4, 25.0.

**1-(1-Naphthyl)ethanol (22a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.32 - 7.26 (m, 4H), 4.86 (q, $J$ = 6.4 Hz, 1H), 2.14 (br, 1H), 1.46 (dd, $J$ = 6.4 and 1.2 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 141.3, 133.8, 130.2, 128.8, 127.9, 126.0, 125.5, 123.1, 122.0, 67.1, 24.3.

**1-(2-Thiophenyl)ethanol (23a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.26 - 7.23 (m, 1H), 6.98 - 6.95 (m, 2H), 5.12 (q, $J$ = 6.4 Hz, 1H), 2.06 (br, 1H), 1.60 (d, $J$ = 6.4 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 149.8, 126.6, 124.4, 123.2, 66.2, 25.2.

**2-Chloro-1-phenylethanol (24a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.38 - 7.25 (m, 4H), 4.89 (dd, $J$ = 8.8 and 3.2 Hz, 1H), 3.73 (dd, $J$ = 11.0 and 3.2 Hz, 1H), 3.64 (dd, $J$ = 11.0 and 8.8 Hz, 1H), 2.77 (br, 1H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 139.9, 128.6, 128.4, 126.0, 74.0, 50.8.

**3-Chloro-1-phenylpropanol (25a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.38 - 7.26 (m, 5H), 4.97 - 4.94 (m, 1H), 3.77 - 3.71 (m, 1H), 3.61 - 3.53 (m, 1H), 2.29 - 2.20 (m, 1H), 2.14 - 2.05 (m, 1H), 2.01 (br, 1H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 143.7, 128.6, 127.9, 125.8, 71.3, 41.7, 41.4.

**(2-Chlorophenyl)(4-chlorophenyl)methanol (26a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.56 - 7.54 (m, 1H), 7.35 - 7.21 (m, 7H), 6.20 (d, $J$ = 3.2 Hz, 1H), 2.42 (d, $J$ = 3.6 Hz, 1H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 140.7, 140.6, 133.5, 132.4, 129.6, 129.0, 128.6, 128.3, 127.9, 127.2, 72.0.

**3,4-Dihydro-2H-chromen-4-ol (27a):** $^{1}$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 7.30 - 7.26 (m, 1H), 7.22 - 7.17 (m, 1H), 6.93 - 6.82 (m, 2H), 4.75 (t, $J$ = 4.0 Hz, 1H), 4.26 - 4.23 (m, 1H), 2.15 - 2.06 (m, 2H), 2.04 - 1.97 (m, 2H); $^{13}$C-NMR ($CDCl_3$, 100 MHz) $\delta$ 154.6, 129.7, 129.6, 124.3, 120.6, 117.1, 63.2, 61.9, 30.8.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

## References

[1] Wang, H.M.J. and Lin, I.J.B. (1998) Facile Synthesis of Silver(I)-Carbene Complexes. Useful Carbene Transfer Agents. *Organometallics*, **17**, 972-975. https://doi.org/10.1021/om9709704

[2] Garrison, J.C. and Youngs, W.J. (2005) Ag(I) *N*-Heterocyclic Carbene Complexes: Synthesis, Structure, and Application. *Chemical Reviews*, **105**, 3978-4008. https://doi.org/10.1021/cr050004s

[3] Chianese, A.R., Li, X., Janzen, M.C., Faller, J.W. and Crabtree, R.H. (2003) Rhodium and Iridium Complexes of *N*-Heterocyclic Carbenes via Transmetalation: Structure and Dynamics. *Organometallics*, **22**, 1663-1667. https://doi.org/10.1021/om021029+

[4] Mas-Marza, E., Poyatos, M., SanaÚ, M. and Peris, E. (2004) Carbene Complexes of Rhodium and Iridium from Tripodal *N*-Heterocyclic Carbene Ligands: Synthesis and Catalytic Properties. *Inorganic Chemistry*, **43**, 2213-2219. https://doi.org/10.1021/ic035317p

[5] Wang, C.-Y., Fu, C.-F., Liu, Y.-H., Peng, S.-M. and Liu, S.-T. (2007) Synthesis of Iridium Pyridinyl *N*-Heterocyclic Carbene Complexes and Their Catalytic Activities on Reduction of Nitroarenes. *Inorganic Chemistry*, **46**, 5779-5786. https://doi.org/10.1021/ic070330l

[6] Zinner, S.C., Rentzsch, C.F., Herdtweck, E., Herrmann, W.A. and KÜHn, F.E. (2009) *N*-Heterocyclic Carbenes of Iridium(I): Ligand Effects on the Catalytic Activity in Transfer Hydrogenation. *Dalton Transactions*, **35**, 7055-7062. https://doi.org/10.1039/b906855d

[7] Zhao, Q., Meng, G., Nolan, S.P. and Szostak, M. (2020) *N*-Heterocyclic Carbene Complexes in C-H Activation Reactions. *Chemical Reviews*, **120**, 1981-2048. https://doi.org/10.1021/acs.chemrev.9b00634

[8] Sipos, G. and Dorta, R. (2018) Iridium Complexes with Monodentate *N*-Heterocyclic Carbene Ligands. *Coordination Chemistry Reviews*, **375**, 13-68. https://doi.org/10.1016/j.ccr.2017.10.019

[9] Van Vuuren, E., Malan, F.P. and Landman, M. (2021) Multidentate NHC Complexes of Group IX Metals Featuring Carbon-Based Tethers: Synthesis and Applications. *Coordination Chemistry Reviews*, **430**, Article ID: 213731. https://doi.org/10.1016/j.ccr.2020.213731

[10] Herrmann, W.A., Baskakov, D., Herdtweck, E., Hoffmann, S.D., Bunlaksananusorn, T., Rampf, F. and Rodefeld, L. (2006) Chiral *N*-Heterocyclic Carbene Ligands Derived from 2,2'-Bipiperidine and Partially Reduced Biisoquinoline: Rhodium and Iridium Complexes in Asymmetric Catalysis. *Organometallics*, **25**, 2449-2456. https://doi.org/10.1021/om060098b

[11] Yoshida, K., Kamimura, T., Kuwabara, H. and Yanagisawa, A. (2015) Chiral Bicyclic NHC/Ir Complexes for Catalytic Asymmetric Transfer Hydrogenation of Ketones. *Chemical Communications*, **51**, 15442-15445. https://doi.org/10.1039/C5CC05318H

[12] Mukherje, N., Mondal, B., Saha, T.N. and Maity, R. (2022) Palladium, Iridium, and Rhodium Complexes Bearing Chiral *N*-Heterocyclic Carbene Ligands Applied in Asymmetric Catalysis. *Applied Organometallic Chemistry*, e6794. https://doi.org/10.1002/aoc.6794

[13] Kawabata, S., Tokura, H., Chiyojima, H., Okamoto, M. and Sakaguchi, S. (2012) Asymmetric Hydrosilane Reduction of Ketones Catalyzed by an Iridium Complex Bearing a Hydroxyamide-Functionalized NHC Ligand. *Advanced Synthesis & Catalysis*, **354**, 807-812. https://doi.org/10.1002/adsc.201100897

[14] Shinohara, K., Kawabata, S., Nakamura, H., Manabe, Y. and Sakaguchi, S. (2014) Enantioselective Hydrosilylation of Ketones Catalyzed by a Readily Accessible *N*-Heterocyclic Carbene-Ir Complex at Room Temperature. *European Journal of Organic Chemistry*, **2014**, 5532-5539. https://doi.org/10.1002/ejoc.201402279

[15] Teramoto, H. and Sakaguchi, S. (2018) Enantioselective Catalytic Hydrosilylation of Propiophenone with a Simple Combination of a Cationic Iridium Complex and a Chiral Azolium Salt. *Journal of Organometallic Chemistry*, **875**, 52-58. https://doi.org/10.1016/j.jorganchem.2018.09.001

[16] Uson, R., Oro, L.A., Cabeza, J.A., Bryndza, H.E. and Stepro, M.P. (1985) Dinuclear Methoxy, Cyclooctadiene, and Barrelene Complexes of Rhodium(I) and Iridium(I). In: Kirschner, S., Ed., *Inorganic Syntheses* 23, Wiley-VCH, Weinheim, 126-130. https://doi.org/10.1002/9780470132548.ch25

[17] JimÉNez, M.V., FernÁNdez-Tornos, J., PÉRez-Torrente, J.J., Modrego, F.J., Winterle, S., Cunchillos, C., Lahoz, F.J. and Oro, L.A. (2011) Iridium(I) Complexes with Hemilabile *N*-Heterocyclic Carbenes: Efficient and Versatile Transfer Hydrogenation Catalysts. *Organometallics*, **30**, 5493-5508. https://doi.org/10.1021/om200747k

[18] Finn, M., Ridenour, J.A., Heltzel, J., Cahill, C. and Voutchkova-Kostal, A. (2018) Next-Generation Water-Soluble Homogeneous Catalysts for Conversion of Glycerol to Lactic Acid. *Organometallics*, **37**, 1400-1409. https://doi.org/10.1021/acs.organomet.8b00081

[19] Karataş, M.O., Alıcı, B., Passarelli, V., Özdemir, I., PÉRez-Torrent, J.J. and Castarlenas, R. (2021) Iridium(I) Complexes Bearing Hemilabile Coumarin Functionalised *N*-Heterocyclic Carbene Ligands with Application as Alkyne Hydrosilylation Catalysts. *Dalton Transactions*, **50**, 11206-11215. https://doi.org/10.1039/D1DT01946E

[20] Matsuki, T., Teramoto, H., Ichihara, R., Inui, K. and Sakaguchi, S. (2022) Asymmetric Silane Reduction of Ketones and *β*-Keto Esters Catalyzed by a Chiral Azolium/Iridium System in the Presence of a Base in Methanol at Room Temperature. *Results in Chemistry*, **4**, Article ID: 100364. https://doi.org/10.1016/j.rechem.2022.100364

[21] Enders, D. and Gielen, H. (2001) Synthesis of Chiral Triazolinylidene and Imidazolinylidene Transition Metal Complexes and First Application in Asymmetric Catalysis. *Journal of Organometallic Chemistry*, **617**, 70-80. https://doi.org/10.1016/S0022-328X(00)00600-8

[22] Enders, D., Gielen, H., Runsink, J., Breuer, K., Brode, S. and Boehn, K. (1998) Diastereoselective Synthesis of Chiral (Triazolinylidene)rhodium Complexes Containing an Axis of Chirality. *European Journal of Inorganic Chemistry*, **1998**, 913-919. https://doi.org/10.1002/(SICI)1099-0682(199807)1998:7<913::AID-EJIC913>3.0.CO;2-1

[23] Zanardi, A., Peris, E. and Mata, J.A. (2008) Alkenyl-Functionalized NHC Iridium-Based Catalysts for Hydrosilylation. *New Journal of Chemistry*, **32**, 120-126. https://doi.org/10.1039/B707280E

[24] GÜLcemal, S., Gökçe, A.G. and Çetinkaya, B. (2013) Iridium(I) *N*-Heterocyclic Carbene Complexes of Benzimidazol-2-Ylidene: Effect of Electron Donating Groups on the Catalytic Transfer Hydrogenation Reaction. *Dalton Transactions*, **42**, 7305-7311. https://doi.org/10.1039/C2DT32482B

[25] Mullick, A.B., Jeletic, A.S., Powers, A.R., Ghiviriga, I., Abboud, I.K.A. and Veige, A.S. (2013) Convenient *in Situ* Generation of a Chiral Bis-*N*-Heterocyclic Carbene Palladium Catalyst and Its Application in Enantioselective Synthesis. *Polyhedron*, **52**, 810-819. https://doi.org/10.1016/j.poly.2012.07.046

[26] Riener, K., Bitzer, M.J., PöThig, A., Raba, A., Cokoja, M., Herrmann, W.A. and KüHn, F.E. (2014) On the Concept of Hemilability: Insights into a Donor-Functionalized Iridium(I) NHC Motif and Its Impact on Reactivity. *Inorganic Chemistry*, **53**, 12767-12777. https://doi.org/10.1021/ic5016324

[27] Jeletic, M.S., Jan, M.T., Ghiviriga, I., Abboud, K.A. and Veige, A.S. (2009) New Iridium and Rhodium Chiral Di-*N*-Heterocyclic Carbene (NHC) Complexes and Their Application in Enantioselective Catalysis. *Dalton Transactions*, No. 15, 2764-2776. https://doi.org/10.1039/b819524b

[28] Ortega-Lepe, I., Rossin, A., Sánchez, P., Santos, L.L., Rendón, N., Álvarez, E., López-Serrano, J. and Suárez, A. (2021) Ammonia-Borane Dehydrogenation Catalyzed by Dual-Mode Proton-Responsive Ir-$C^{NNH}$ Complexes. *Inorganic Chemistry*, **60**, 18490-18502. https://doi.org/10.1021/acs.inorgchem.1c03056

[29] Olmstead, W.N., Margolin, Z. and Bordwel, F.G. (1980) Acidities of Water and Simple Alcohols in Dimethyl Sulfoxide Solution. *Journal of Organic Chemistry*, **45**, 3295-3299. https://doi.org/10.1021/jo01304a032

[30] Olmstead, W.N. and Bordwel, F.G. (1980) Ion-Pair Association Constants in Dimethyl Sulfoxide. *Journal of Organic Chemistry*, **45**, 3299-3305. https://doi.org/10.1021/jo01304a033

[31] Bordwel, F.G. (1988) Equilibrium Acidities in Dimethyl Sulfoxide Solution. *Accounts of Chemical Research*, **21**, 456-463. https://doi.org/10.1021/ar00156a004

[32] Duan, W.-L., Shi, M. and Rong, G.-B. (2003) Synthesis of Novel Axially Chiral Rh-NHC Complexes Derived from BINAM and Application in the Enantioselective Hydrosilylation of Methyl Ketones. *Chemical Communications*, No. 23, 2916-2917. https://doi.org/10.1039/B309185F

[33] Xu, Q., Gu, X., Liu, S., Dou, Q. and Shi, M. (2007) The Use of Chiral BINAM NHC-Rh(III) Complexes in Enantioselective Hydrosilylation of 3-Oxo-3-Arylpropionic Acid Methyl or Ethyl Esters. *Journal of Organic Chemistry*, **72**, 2240-2242. https://doi.org/10.1021/jo062453d

[34] Gade, L.H., CÉSar, V. and Bellemin-Laponnaz, S. (2004) A Modular Assembly of

Chiral Oxazolinylcarbene-Rhodium Complexes: Efficient Phosphane-Free Catalysts for the Asymmetric Hydrosilylation of Dialkyl Ketones. *Angewandte Chemie International Edition*, **43**, 1014-1017. https://doi.org/10.1002/anie.200353133

[35] Albright, A. and Gawley, R.E. (2011) Application of a C2-Symmetric Copper Carbenoid in the Enantioselective Hydrosilylation of Dialkyl and Aryl-Alkyl Ketones. *Journal of the American Chemical Society*, **133**, 19680-19683. https://doi.org/10.1021/ja209187a

[36] Song, C., Ma, C., Ma, Y., Feng, W., Ma, S., Chaia, Q. and Andrus, M.B. (2005) Bis-Paracyclophane *N*-Heterocyclic Carbene-Ruthenium Catalyzed Asymmetric Ketone Hydrosilylation. *Tetrahedron Letters*, **46**, 3241-3244. https://doi.org/10.1016/j.tetlet.2005.03.026

[37] Hafedh, N., Favereau, L., Caytan, E., Roisnel, T., Jean, M., Vanthuyne, N., Aloui, F. and Crassous, J. (2019) Synthesis and Chiroptical Properties of Organometallic Complexes of Helicenic *N*-Heterocyclic Carbenes. *Chirality*, **31**, 1005-1013. https://doi.org/10.1002/chir.23143