Journal of Molecular Structure 1216 (2020) 128351

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Reduction hydrogenation of imines by *in situ* generated rhodium NHC complexes

Emine Özge Karaca [a], Serpil Demir Düşünceli [a, b], Nevin Gürbüz [a, b], İsmail Özdemir [a, b, *]

[a] İnönü University, Catalysis Researcdsh, and Application Center, 44280, Malatya, Turkey
[b] Department of Chemistry, Faculty of Arts and Science, İnönü University, 44280, Malatya, Turkey

ARTICLE INFO

Article history:
Received 29 November 2019
Received in revised form
25 April 2020
Accepted 27 April 2020
Available online 30 April 2020

Keywords:
Rhodium
Bidentate azolium salt
N-heterocyclic carbene
Imine
Transfer hydrogenation

ABSTRACT

In this paper we examined the catalytic activity of *in situ* prepared bidentate azolium salt/$[RhCl(COD)]_2$ catalyst system in the transfer hydrogenation of imines with *i*-propanol to the corresponding amine. The first *in situ* transfer hydrogenation of imines to amines is described using $[RhCl(COD)]_2$ with bidentate azolium ligands. New bidentate azolium salts (**1a-c, 2a-c**) as NHC precursors have been synthesized and characterized. The *in situ* prepared three-component bidentate azolium salts (LHX)/$[RhCl(COD)]_2$ and t-BuOK catalyzes quantitatively the transfer hydrogenation of imines under mild reaction conditions in *i*-propanol. The results show that bidentate benzimidazolium salts were observed to be more active in reducing imines. Moreover, the method is simple and effective against various imines.

1. Introduction

Among all methods that can be used to reduce C = O and C = N, transfer hydrogenation is an important method that has emerged in recent years and is used as an alternative to the hydrogenation process [1,2]. Various catalytic systems including different metal centers and organocatalysts have been used for the transfer hydrogenation of imines. The most commonly used catalysts are those containing Ir [3–5], Rh [4–6] and Ru [4,5,7] metal. In metal-catalyzed transfer hydrogenation reactions, formic acid and *i*-propanol are commonly used as hydrogen servers.

Although the transfer hydrogenation process is widely applied in ketone reduction, the studies for transfer hydrogenation of imines are very limited [1,8–11]. Contrary to the reduction of ketones, the reduction of imines is thought to lead to some problems [12]. The most important are the; i) hydrolysis-susceptible occurrences; ii) the presence of the *cis*/*trans* and enamine isomers making it more difficult to control the enantioselectivity; iii) the significant effect of N-substituents on the activity and enantioselectivity, and iv) catalyst poisoning, resulting in imine or amine coordination of metal.

In recent years, *N*-heterocyclic carbenes have been used as an alternative to phosphine ligands used for homogeneous catalyst synthesis in organometallic chemistry [13]. Phosphine compounds are required to operate in an inert environment due to reasons such as being sensitive to air and moisture and breaking P–C bonds at high temperatures. In contrast to phosphine ligands, N-heterocyclic carbene ligands are more advantageous because of their strong σ donor properties, low toxicity, and easier synthesis. *N*-heterocyclic carbenes play a key role in both catalytic and catalytic stages of organic synthesis such as C–H activation, C–C, C–H, C–O, and C–N bond formation through selective coordination chemistry [14–22].

N-heterocyclic carbenes have used as ligands in transfer hydrogenation reactions of imines. Danopoulos's group in 2002 [23] synthesized a pincer type Ru complex that contains two NHC motifs and try it transfer hydrogenation of imines. After this, at the 2005 mono-NHC Ru complex prepared by William's group [24] was also tested with the same substrate and showed good reactivity. In 2002, Crabtree and Peris et al. [25] synthesized an air-stable chelating bis-carbene rhodium (III) complexes and reported their application in transfer hydrogenation of ketones and imines. Ir-based analogs of the above-mentioned chelating bis-carbene rhodium (III) complexes were also reported by Crabtree group in 2004 [26]. Besides the chelated bis-NHC Ir complexes, monodentate triazolylidene derived NHC Ir complexes were proved to be suitable for transfer hydrogenation of imines by the Crabtree group

* Corresponding author. İnönü University, Catalysis Researcdsh, and Application Center, 44280, Malatya, Turkey.
E-mail address: ismail.ozdemir@inonu.edu.tr (İ. Özdemir).

https://doi.org/10.1016/j.molstruc.2020.128351
0022-2860/

in 2007 as well [3]. Another example of NHC Ir complexes was reported by Li's group. They reported the first example of asymmetric transfer hydrogenation of cyclic *N*-sulfonylimines using a chiral metal carbene catalyst in 2017 [27]. The first example of Ni catalyzed transfer hydrogenation of imines was reported by Dchneider and Fort et al. [28] A series of Ni(0)/NHC complexes were synthesized and tested in 2003.

To the best of our knowledge, the catalytic *in situ* transfer hydrogenation reaction of imines using metal carbene catalysts has not been reported thus far. We have previously reported imidazolidine,benzimidazole-2-ylidene-ruthenium (II) complexes and *in situ* formed tetrahydropyrimidine ruthenium (II) system which exhibits high activity [29–34]. In order to find more efficient rhodium catalysts we have prepared a series of new bidentate azolium salts, **1a-c, 2a-c** (Scheme 1), and we now report the use of the *in situ* generated catalytic system composed of $[RhCl(COD)]_2$ as rhodium source, **1a-c, 2a-c** as carbene precursors and t-BuOK as a base for transfer hydrogenation of aryl ketones in *i*-propanol for 6 h. All synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis techniques the results of which support the proposed structures.

2. Results and discussion

2.1. Synthesis of bidentate azolium salts

Bisimidazolidinium (**1a**-**c**) and bisbenzimidazolium (**2a**-**c**) salts prepared according to the literature [35,36] by the reaction of 2,4-bischloromethyl-1,3,5-trimethylbenzene with 1-alkylimidazoline/benzimidazole. To a solution of 1-alkylimidazoline in DMF was added slowly 2,4-bischloromethyl-1,3,5-trimethylbenzene and the resulting mixture was stirred at 25 °C for 2 h. The heating of the resulting mixture (80 °C, 6 h) allows the formation of the imidazolidinium salts in excellent yields (Scheme 1). Bisbenzimidazolium (**2a**-**c**) salts prepared similarly from 1-alkylbenzimidazole and 2,4-bischloromethyl-1,3,5-trimethylbenzene (25 °C, 5 h, and 80 °C, 10 h) (Scheme 2).

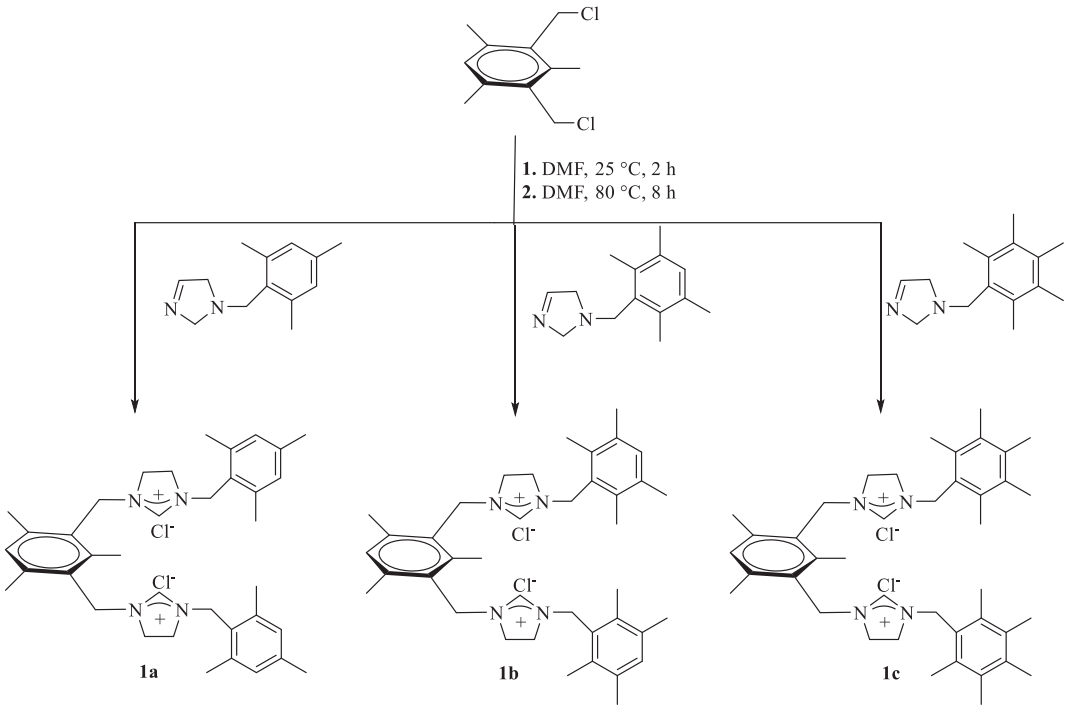
The bidentate azolium salts were isolated as white solids in very good yields and fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and elemental analyses (see Experimental section). The ^{1}H NMR spectra of the bidentate azolium salts further supported the assigned structures; the resonances for acidic C (2)-H were observed as a sharp singlet in the 9.03, 9.59, 9.63, 10.97, 10.02 and 10.39 ppm respectively for **1a-c, 2a-c**. ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode in the 157.1, 157.2, 157.1, 162.7, 163.0 and 163.1 ppm respectively for bidentate azolium salts (**1a-c, 2a-c**). The NMR values are similar to those found for other bidentate azolium salts [35,36]. The salts are air- and moisture stable both in the solid-state and in solution.

2.2. Catalytic transfer hydrogenation of imines

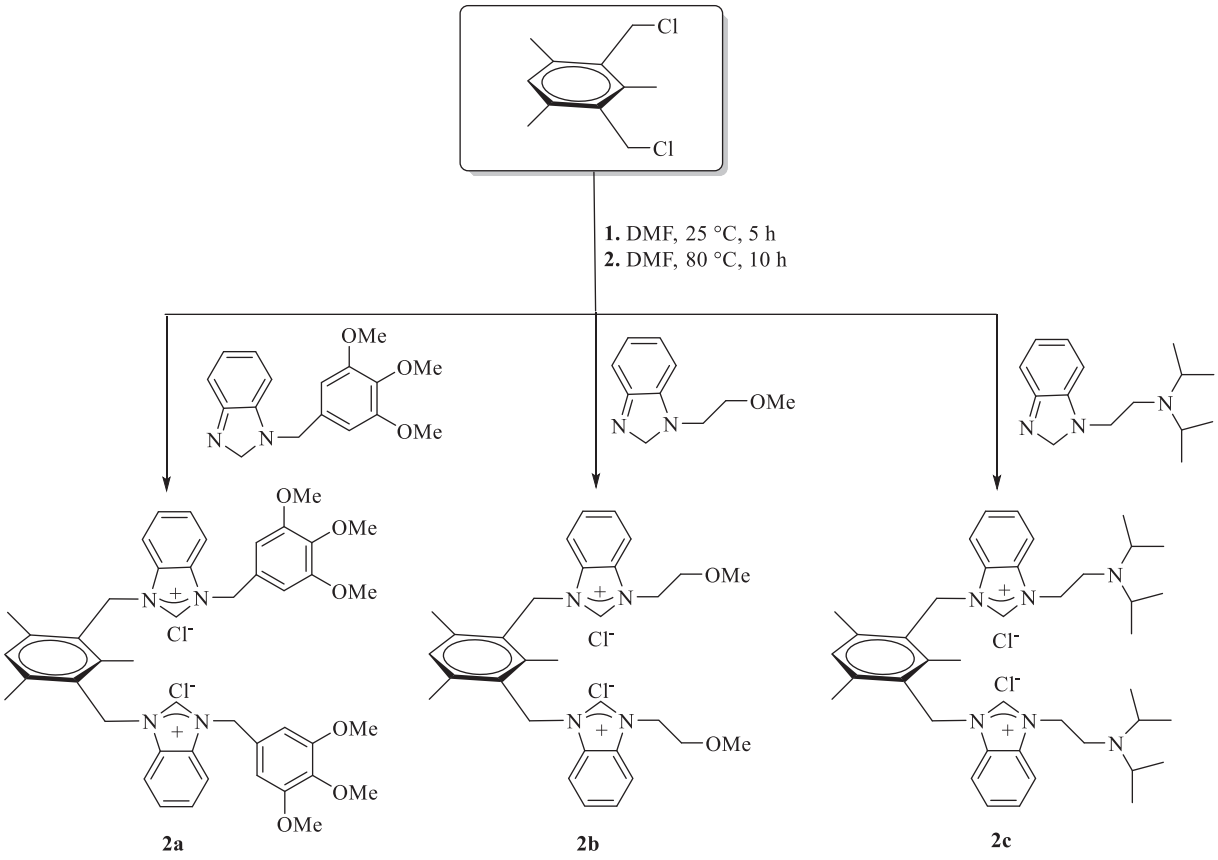
Hydrogen transfer reactions of functional groups have greatly contributed to the recent development of organic syntheses. During the transfer hydrogenation of ketones over the last two decades, the reaction of imines has been little studied.

The catalytic reduction is preferred to stoichiometric reduction for large scale industrial uses of ketones hydrogenation [37]. The use of a solvent that can donate hydrogen overcomes these difficulties. *i*-Propanol is a popular reactive solvent for the transfer hydrogenation since it is easy to handle (b.p. 82 °C) and is relatively non-toxic, environmentally benign, and inexpensive. The volatile acetone product can also be easily removed to shift an unfavorable equilibrium. Owing to its efficiency in the transfer hydrogenation of imine derivatives, *in situ* generated rhodium complexes were further investigated by transfer hydrogenation of various imines.

We examined the catalytic activity of *in situ* prepared bidentate azolium salt/$[RhCl(COD)]_2$ catalyst system in the transfer hydrogenation of imines with *i*-propanol to the corresponding amine. Wherein *i*-propanol is the hydrogen source and t-BuOK presumably enhances catalysis by promoting the formation of intermediates



Scheme 1. Preparation of bidentate imidazolidinium salts.



Scheme 2. Preparation of bidentate benzimidazolium salts.

and deprotonation of salts. The reduction of imine to amine was initially used as a model reaction with *in situ* prepared Rh(I) systems with **1a-c, 2a-c** as catalysts in the transfer hydrogenation. The Rh—NHC catalyst being generated *in situ* by mixing the corresponding rhodium complexes $[RhCl(COD)]_2$ with the bisazolium salts (**1** and **2**) (Fig. 1).

In order to ensure complete formation of the active catalyst a *i*-propanol solution of 0.5 mol% $[RhCl(COD)]_2$ and 0.5 mol% 1,1′-bis(*N*-(3,4,5-trimethoxybenzyl)-3,3'-(2,4-dimethylene-1,3,5-trimethylbenzene)benzimida-zolium chloride (**2a**) is stirred in the presence 4 mmol t-BuOK at room temperature for 0.5 h. Then *p*-methoxybenzilidene aniline (1.00 mmol) was added and was performed at 80 °C for 6 h. The reactions were conducted at a substrate/catalyst/base (S/C/base) molar ratio of 1:0.01:4.

Reaction conditions: **2a** (0.01 mmol), $[RhCl(COD)]_2$ (0.005 mmol) substrate (1 mmol), *i*-propanol (10 mL), base (4 mmol), 80 °C. The purity of the products was checked by GC and GC-MS and yields were calculated according to benzylidine aniline.

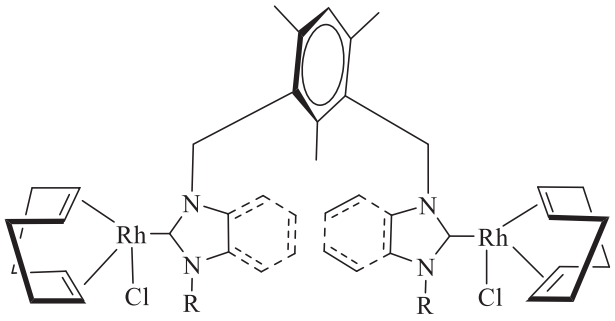


Fig. 1. Propose the structure of the *in situ* generated active Rh—NHC catalyst.

Since the base facilitates the formation of a rhodium alkoxide by abstracting the proton from *i*-propanol, different bases were used as promoters in the transfer hydrogenation of imines. İmine was kept as a test substrate and allowed it to react in *i*-propanol with $[RhCl(COD)]_2$/**2a** in the presence of different bases like NEt_3, Cs_2CO_3, K_2CO_3, NaOH, KOH, *t*-BuOK. With the organic base triethylamine and potassium carbonate, we observed only poor yields (Table 1 entry 1,2). Using the inorganic base the conversion showed a dependency upon the base strength. It has been observed that t-BuOK is shown to have good conversions when compared to the Cs_2CO_3, K_2CO_3, NaOH, and KOH in the hydrogenation reactions. When using DBU, a strong base, results similar to KOH were obtained (Table 1, entry 12). In the absence of a base no transfer hydrogenation of the imines was observed (Table 1, entry 11). Also, the catalytic system was used in the transfer hydrogenation of imine at room temperature but no appreciable formation of aniline. Under the reaction conditions $[RhCl(COD)]_2$/**2c** system proved to be most effective catalyst relative to **1a**, **1b, 1c, 2a** and **2b** (Table 2, entry 18).

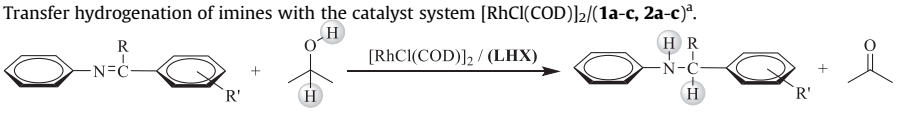
Reaction conditions: Bidentat azolium salts (**1a-c**, **2a-c**) (0.01 mmol), $[RhCl(COD)]_2$ (0.005 mmol) substrate (1 mmol), *i*-propanol (10 mL), t-BuOK (4 mmol), 80 °C, 6 h. The purity of the products was checked by GC and GC-MS and yields were calculated according to imine derivatives.

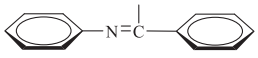
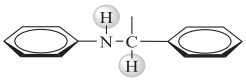
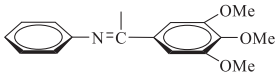
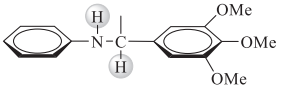
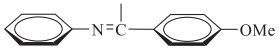
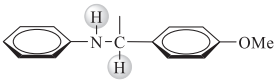
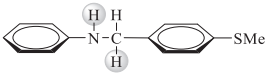
Encouraged by the obtained in these catalytic systems we extended our investigations to include transfer hydrogenation of aldimine and ketimine derivatives. A variety of imines were transformed into the corresponding amines. Typical results are shown in Table 2. Under those conditions *N*-(1-diphenylethan-1-imine) and 1-(3,4,5-trimethoxyphenyl)-*N*-phenylethan-1-imine

Table 1
Screening of transfer hydrogenation reaction conditions.

Entry	Base	Time (h)	Yield (%)
1	NEt_3	6	<3
2	K_2CO_3	6	5
3	Cs_2CO_3	6	10
4	KOH	2	6
5	KOH	4	23
6	KOH	6	46
7	NaOH	6	44
8	t-BuOK	2	14
9	t-BuOK	4	57
10	t-BuOK	6	82
11	–	6	–
12	DBU	6	74

Table 2
Transfer hydrogenation of imines with the catalyst system [RhCl(COD)]$_2$/(**1a-c, 2a-c**)[a].



Entry	Substrate	Product	LHX	Yield (%)
1			**1a**	51
2			**1b**	53
3			**1c**	50
4			**2a**	82
5			**2b**	87
6			**2c**	88
7			**1a**	28
8			**1b**	50
9			**1c**	42
10			**2a**	90
11			**2b**	91
12			**2c**	98
13			**1a**	33
14			**1b**	56
15			**1c**	32
16			**2a**	92
17			**2b**	90
18			**2c**	96
19			**1a**	30
20			**1b**	44
21			**1c**	40
22			**2a**	48
23			**2b**	50
24			**2c**	58

react very cleanly and in goods yields with *i*-propanol (Table 2, entries 5, 6, 10–12). The presence of electron-donating (OCH_3) substituent on phenyl (Table 2, entries 10–12 and 16–18) has a significant effect on the reduction of imines to their corresponding amine. The maximum conversion of 1-(3,4,5-trimethoxyphenyl)-*N*-phenylethan-1-imine to the corresponding amine was achieved over a period of 6 h (Table 2, entry 12). Finally, we also investigated to reduce of an aldimine such as a 1-(4-methylthio)phenyl-N-phenylmethamine was also reduced under optimal conditions (Table 2, entries 19–24). The best catalytic activity was achieved with ligant **2c** (Table 2, entry 2).

Peris et al. reported the chelating bis-carbene rhodium (II) complexes in the transfer hydrogenation of imines. Imine derivatives were reduced at reflux temperature for 10 h [25]. In 2005 Williams et al. reported dihydrideruthenium *N*-heterocyclic carbene complexes as a catalyst for the transfer hydrogenation of imines in *i*-propanol at 70 °C for 16 h [24]. Also, Fort et al. reported the application of *in situ* generated nickel (0) carbene complexes in the reduction of imines to the corresponding amines used Et_2CH-ONa [28]. Using catalyst system a variety of imines were reduced at 100 °C in dioxane. Compared with the litherature [25] *in situ* prepared three-component bidentate azolium salts (LHX)/[RhCl(COD)]$_2$/t-BuOK are active in the reduction of imines under mild conditions with almost quantitative conversions. Under the reaction conditions, benzimidazolium salts proved to be the most effective catalyst relative to imidazolidinium salts. The reduction of the imine with bidentate azolium salts was completed within 6 h in high yields. It is evident that the NHC precursors that contain electron-donating isopropylaminoethyl substituent (**1f**) are the most effective of the salts examined.

3. Conclusions

In this paper, we have synthesized new bidentate azolium salts as precursors of *N*-heterocyclic carbenes. They were associated with [RhCl(COD)]$_2$ to generate catalytic species. This concept for

making catalysts *in situ* opens the way for the discovery of many new catalysts via the interaction of metal complexes and suitable ligands. The catalytic advantages of this *in situ* prepared catalyst system were investigated in the reduction of imine using *i*-propanol and t-BuOK under mild reaction conditions. The study results show that bidentate benzimidazolium salts are much more active than bidentate imidazolidinium salts in reducing imines. Moreover, the procedure is simple and effective against various imines. Detailed investigations focusing on new metal-NHC complexes and other applications are underway.

4. Experimental section

4.1. Materials

All reactions for the prepared compounds were carried out under argon in flame-dried glassware using standard Schlenk techniques. Chemicals and solvents were purchased from Sigma−Aldrich, and Merck. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na).

4.1.1. NMR spectroscopy

^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 300 Merkur spectrometer operating at 300 MHz (^1H), 75 MHz (^{13}C) in $CDCl_3$ and DMSO-d_6 with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal.

4.1.2. Elemental analyse

Elemental analyses were performed by LECO CHNS-932 elementary chemical analyser.

4.1.3. Gas chromatography

All reactions were monitored on an Agilent 6890 N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness.

4.1.4. Gas chromatography-mass spectroscopy

All catalytic reactions were monitored on a Shimadzu 2010 Plus GC-MS system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness.

4.1.5. Column chromatography

Column chromatography was performed using silica gel 60 (70−230 mesh). Solvent ratios are given as v/v.

4.2. Synthesis of bidentate imidazolidinium salts

4.2.1. General synthesis method for bisimidazolidinium salts (1a-c)

To the solution of 1-alkylimidazolidine (10 mmol) in DMF was slowly added 2,4-bischloromethyl-1,3,5-trimethylbenzene (5 mmol) and stirred at 25 °C for 2 h. The resulting mixture was heated at 80 °C for 8 h. When diethyl ether (15 mL) was added, the resulting white crystals were filtered, washed with diethyl ether (3 × 15 mL) and dried in vacuum. The crude product was recrystallized from EtOH/Et_2O.

4.2.1.1. 1,1′-Bis{(N-2,4,6-trimethylbenzyl)-3,3'-(2,4-dimethylene-1,3,5-trimethylbenzene)-imidazolidinium chloride, 1a. Yield: 2.45 g; 80%. ^1H NMR (δ, $CDCl_3$): 9.03 (s, 2H, NC*H*N); 7.05 (s, 1H, $-CH_2C_6H(CH_3)_3CH_2$-); 6.88 (s, 4H, $CH_2C_6H_2(CH_3)_3$−2,4,6); 4.77 (s, 4H, -$CH_2C_6H(CH_3)_3CH_2$-); 4.65 (s, 4H, $CH_2C_6H_2(CH_3)_3$−2,4,6); 3.80 and 3.65 (t, *J* = 9.4 Hz, 8H, NCH_2CH_2N); 2.50 and 2.29 (s, 9H, $-CH_2C_6H(CH_3)_3CH_2$-); 2.26 and 2.21 (s, 18H, $CH_2C_6H_2(CH_3)_3$−2,4,6). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 157.1 (NCHN), 138.7, 138.5, 131.8 and 128.7 (-$CH_2C_6H(CH_3)_3CH_2$-); 139.6, 139.4, 130.1 and 127.3 ($CH_2C_6H_2(CH_3)_3$−2,4,6); 49.1 (-$CH_2C_6H(CH_3)_3CH_2$-); 48.2 and 46.6 (NCH_2CH_2N); 45.9 ($CH_2C_6H_2(CH_3)_3$−2,4,6); 21.4 and 20.3 ($CH_2C_6H_2(CH_3)_3$−2,4,6); 20.1 and 16.3 (-$CH_2C_6H(CH_3)_3CH_2$-). Anal. Calc. For $C_{37}H_{50}N_4Cl_2$: C, 71.48; H, 8.10; N, 9.01. Found C, 71.50; H, 8.08; N, 9.00.

4.2.1.2. 1,1′-Bis{(N-2,3,5,6-tetramethylbenzyl)-3,3'-(2,4-dimethylene-1,3,5-trimethylbenzene)-imidazolidinium chloride, 1b. Yield: 2.66 g; 82%. ^1H NMR (δ, $CDCl_3$): 9.59 (s, 2H, NC*H*N); 7.03 (s, 1H, $-CH_2C_6H(CH_3)_3CH_2$-); 6.94 (s, 2H, $CH_2C_6H(CH_3)_4$−2,3,5,6); 5.07 (s, 4H, -$CH_2C_6H(CH_3)_3CH_2$-); 4.72 (s, 4H, $CH_2C_6H(CH_3)_4$−2,3,5,6); 4.05 and 3.73 (t, *J* = 9.9 Hz, 8H, NCH_2CH_2N); 2.55 and 2.31 and (s, 9H, $-CH_2C_6H(CH_3)_3CH_2$-); 2.21 and 2.19 (s, 24H, $CH_2C_6H(CH_3)_4$−2,3,5,6). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 157.2 (NCHN), 139.6, 139.1, 131.5 and 128.7 (-$CH_2C_6H(CH_3)_3CH_2$-); 134.5, 133.9, 132.4 and 127.6 ($CH_2C_6H(CH_3)_4$−2,3,5,6); 49.1 (-$CH_2C_6H(CH_3)_3CH_2$-); 47.5 and 46.9 (NCH_2CH_2N); 46.7 ($CH_2C_6H(CH_3)_4$−2,3,5,6); 20.5 and 15.9 ($CH_2C_6H(CH_3)_4$−2,3,5,6); 19.9 and 16.7 (-$CH_2C_6H(CH_3)_3CH_2$-). Anal. Calc. For $C_{39}H_{54}N_4Cl_2$: C, 72.09; H, 8.38; N, 8.62. Found C, 72.15; H, 8.42; N, 8.59.

4.2.1.3. 1,1′-Bis{(N-2,3,4,5,6-pentamethylbenzyl)-3,3'-(2,4-dimethylene-1,3,5-trimethylbenzene)-imidazolidinium chloride, 1c. Yield: 2.94 g; 87%. ^1H NMR (δ, $CDCl_3$): 9.63 (s, 2H, NC*H*N); 7.03 (s, 1H, $-CH_2C_6H(CH_3)_3CH_2$-); 5.06 (s, 4H, -$CH_2C_6H(CH_3)_3CH_2$-); 4.71 (s, 4H, $CH_2C_6(CH_3)_5$−2,3,4,5,6); 4.05 and 3.71 (t, *J* = 9.9 Hz, 8H, NCH_2CH_2N); 2.51 and 2.32 (s, 9H, $-CH_2C_6H(CH_3)_3CH_2$-); 2.25, 2.21 and 2.19 (s, 30H, $CH_2C_6(CH_3)_5$−2,3,4,5,6). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 157.1 (NCHN), 139.4, 139.2, 131.7 and 127.6 (-$CH_2C_6H(CH_3)_3CH_2$-); 136.1, 133.4, 133.3 and 125.9 ($CH_2C_6(CH_3)_5$−2,3,4,5,6); 49.1 (-$CH_2C_6H(CH_3)_3CH_2$-); 47.5 and 47.2 (NCH_2CH_2N); 46.9 ($CH_2C_6(CH_3)_5$−2,3,4,5,6); 20.0 and 18.4 (-$CH_2C_6H(CH_3)_3CH_2$-), 17.2, 16.9 and 16.7 ($CH_2C_6(CH_3)_5$−2,3,4,5,6). Anal. Calc. For $C_{41}H_{58}N_4Cl_2$: C, 72.65; H, 8.62; N, 8.27. Found C, 72.69; H, 8.65; N, 8.31.

4.2.2. Synthesis of bidentate benzimidazolium salts

4.2.2.1. General synthesis method for bisbenzimidazolidinium salts (2a-c). To a solution of 1-alkylbenzimidazole (10 mmol) in DMF was slowly added 2,4-bischloromethyl-1,3,5-trimethylbenzene (5 mmol) and stirred at 25 °C for 5 h. The resulting mixture was heated at 80 °C for 10 h. Diethylether (10 mL) was added to the cooled solution to precipitate the white solid. The crude product was filtered, washed with diethylether (3 × 5 mL) and dried in vacuum. Recrystallized in ethanol/diethyl ether solvent mixture.

4.2.2.2. 1,1′-Bis(N-(3,4,5-trimethoxybenzyl)-3,3'-(2,4-dimethylene-1,3,5-trimethylbenzene)-benzimidazolium chloride, 2a. Yield: 3.35 g; 85%. ^1H NMR (δ, $CDCl_3$): 10.97 (s, 2H, NC*H*N); 8.25 (d, *J* = 8.4 Hz, 2H, NC_6H_4N); 7.69−7.53 (m, 6H, NC_6H_4N); 7.14 (s, 1H, $-CH_2C_6H(CH_3)_3CH_2$-); 6.74 (s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5); 5.84 and 5.80 (s, 8H, -$CH_2C_6H(CH_3)_3CH_2$- and $CH_2C_6H_2(OCH_3)_3$-3,4,5); 3.74 and 3.73 (s, 18H, $CH_2C_6H_2(OCH_3)_3$-3,4,5); 2.31 and 2.24 (s, 9H, $CH_2C_6H(CH_3)_3CH_2$). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 162.7 (NCHN), 142.2, 140.9, 140.3, 129.3, and 127.2 (-$CH_2C_6H(CH_3)_3CH_2$-), 132.0, 131.8, 127.7, 127.6, 114.4 and 114.0 (NC_6H_4N); 153.9, 138.6, 132.6 and 106.1 ($CH_2C_6H_2(OCH_3)_3$-3,4,5); 60.9 and 56.7 ($CH_2C_6H_2(OCH_3)_3$-3,4,5); 53.6, 51.5 and 46.8 ($CH_2C_6H_2(OCH_3)_3$-3,4,5 and -$CH_2C_6H(CH_3)_3CH_2$-); 20.2 and 17.2 (-$CH_2C_6H(CH_3)_3CH_2$-). Anal. Calc. For. $C_{45}H_{50}N_4O_6Cl_2$: C, 66.41; H, 6.19; N, 6.88. Found C, 66.45; H, 6.23; N, 6.85.

4.2.2.3. 3,3′-(2,4-Dimethylene-1,3,5-trimethylbenzene)-1,1′-bis(N-methoxyethyl)-benzimidazolium chloride, 2b. Yield: 2.56 g; 90%. ^{1}H NMR (δ, DMSO-d_6):10.02 (s, 2H, NC*H*N); 8.24–8.21 (m, 2H, NC_6H_4N); 8.12–8.09 (m, 2H, NC_6H_4N); 7.72–7.69 (m, 4H, NC_6H_4N); 7.24 (s, 1H, $-CH_2C_6H(CH_3)_3CH_2$-); 5.79 (s, 4H, -$CH_2C_6H(CH_3)_3CH_2$-); 4.83 (s, 4H, $CH_2CH_2OCH_3$); 3.12 (s, 6H, $CH_2CH_2OCH_3$); 3.72 (t, J = 4.8 Hz, 4H, $CH_2CH_2OCH_3$); 2.29 and 2.26 (s, 9H, $-CH_2C_6H(CH_3)_3CH_2$-). ^{13}C{H}NMR (δ, DMSO-d_6): 163.0 (NCHN), 142.7, 140.9, 140.4, 132.3 and 128.2 (-$CH_2C_6H(CH_3)_3CH_2$-), 132.2, 132.0, 127.4, 127.2, 114.8 and 114.7 (NC_6H_4N); 70.2 ($CH_2CH_2OCH_3$); 58.8 ($CH_2CH_2OCH_3$); 47.0 ($CH_2CH_2OCH_3$); 46.2 (-$CH_2C_6H(CH_3)_3CH_2$-); 20.2 and 16.3 (-$CH_2C_6H(CH_3)_3CH_2$-). Anal. Calc. For $C_{31}H_{38}N_4O_2Cl_2$: C, 65.37; H, 6.72; N, 9.84. Found C, 65.33; H, 6.73; N, 9.90.

4.2.2.4. 1,1′-bis(N-diisopropylaminoethyl)-3,3′-(2,4-Dimethylene-1,3,5-trimethylbenzene)-benzimidazolium chloride, 2c. Yield: 2.96 g; 84%. ^{1}H NMR (δ, $CDCl_3$): 10.39 (s, 2H, NC*H*N); 8.38 (d, J = 8.1 Hz, 2H, NC_6H_4N); 7.76–7.63 (m, 6H, NC_6H_4N); 7.14 (s, 1H, $-CH_2C_6H(CH_3)_3CH_2$-); 5.77 (s, 4H, -$CH_2C_6H(CH_3)_3CH_2$-); 4.76 (t, J = 5.1 Hz, 4H, $CH_2CH_2N(CH(CH_3)_2)_2$); 3.02 (hept, J = 6.3 Hz, 4H, $CH_2CH_2N(CH(CH_3)_2)_2$); 2.85 (t, J = 5.1 Hz, 4H, $CH_2CH_2N(CH(CH_3)_2)_2$); 2.31 and 2.22 (s, 9H, $-CH_2C_6H(CH_3)_3CH_2$-); 0.67 (d, J = 6.3 Hz, 24H, $CH_2CH_2N(CH(CH_3)_2)_2$). ^{13}C{H}NMR (δ, $CDCl_3$): 163.1 (NCHN), 142.2, 140.6, 140.5, 1131.9 and 127.3 (-$CH_2C_6H(CH_3)_3CH_2$-), 131.8, 131.4, 127.1, 126.8, 114.3 and 112.9 (NC_6H_4N); 47.0 (-$CH_2C_6H(CH_3)_3CH_2$-); 46.6 ($CH_2CH_2N(CH(CH_3)_2)_2$); 46.3 ($CH_2CH_2N(CH(CH_3)_2)_2$); 43.8 ($CH_2CH_2N(CH(CH_3)_2)_2$); 20.6 ($CH_2CH_2N(CH(CH_3)_2)_2$); 20.1 and 17.0 ($CH_2C_6H(CH_3)_3CH_2$). Anal. Calc. For $C_{41}H_{60}N_6Cl_2$: C, 69.57; H, 8.54; N, 11.87. Found C, 69.62; H, 8.59, N, 11.80.

4.3. Typical procedure for catalytic transfer hydrogenation of imines

Under an inert atmosphere $[RhCl(COD)]_2$ (0.05 mmol), bidentate azolium salts (**1a-c**, **2a-c**), (0.05 mmol), t-BuOK (4 mmol) and 5 mL of *i*-propanol were added to a small Schlenk tube and the mixture was stirred at room temperature for 0.5 h. Then imine (1 mmol) was added to the mixture and was heated at 80 °C for 6 h. The solvent was then removed under reduced pressure and the product was determined by GC and GC-MS using undecane as an internal standard. The yield calculations were based on the relative areas of signal peaks of chromatograms.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Emine Özge Karaca: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Serpil Demir Düşünceli:** Conceptualization, Methodology, Investigation. **Nevin Gürbüz:** Conceptualization, Methodology, Investigation, Resources, Writing - original draft, Writing - original draft, Writing - review & editing, Supervision, Funding acquisition. **İsmail Özdemir:** Conceptualization, Investigation, Writing - original draft, Writing - review & editing.

Acknowledgments

This work was financially supported by the Technological and Scientific Research Council of Turkey TÜBİTAK [TBAG (107T098)].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2020.128351.

References

[1] R. Noyori, S. Hashiguchi, Asymmetric transfer hydrogenation catalyzed by chiral ruthenium complexes, Acc. Chem. Res. 30 (1997) 97–102, https://doi.org/10.1021/ar9502341.
[2] H.U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, Selective hydrogenation for fine chemicals: recent trends and new developments, Adv. Synth. Catal. 345 (2003) 103–151, https://doi.org/10.1002/adsc.200390000.
[3] D. Gnanamgari, A. Moores, E. Rajaseelan, R.H. Crabtree, Transfer hydrogenation of imines and alkenes and direct reductive amination of aldehydes catalyzed by triazole-derived iridium(I) carbene complexes, Organometallics 26 (2007) 1226–1230, https://doi.org/10.1021/om060938m.
[4] J. Blum, Y. Sasson, S. Iflah, Hydrogen transfer from formyl compounds to α,β-unsaturated ketones catalyzed by Ru, Rh and Ir complexes, Tetrahedron Lett. 13 (1972) 1015–1018, https://doi.org/10.1016/S0040-4039(01)84497-X.
[5] G. Brieger, T.J. Nestrick, Catalytic transfer hydrogenation, Chem. Rev. 74 (1974) 567–580, https://doi.org/10.1021/cr60291a003.
[6] H.-A. Brune, J. Unsin, R. Hemmer, M. Reichhardt, Untersuchungen zum Mechanismus der Rhodium(I)-katalysierten Hydrogen-Transfer-Reaktion von sekundären Alkoholen auf Imine, J. Organomet. Chem. 369 (1989) 335–342, https://doi.org/10.1016/0022-328X(89)85184-8.
[7] Y. Sasson, J. Blum, Dichlorotris(triphenylphosphine)ruthenium-catalyzed hydrogen transfer from alcohols to saturated and .alpha.,.beta.-unsaturated ketones, J. Org. Chem. 40 (1975) 1887–1896, https://doi.org/10.1021/jo00901a004.
[8] M.J. Palmer, M. Wills, Asymmetric transfer hydrogenation of C=O and C=N bonds, Tetrahedron Asymmetry 10 (1999) 2045–2061, https://doi.org/10.1016/S0957-4166(99)00216-5.
[9] T. Ikariya, K. Murata, R. Noyori, Bifunctional transition metal-based molecular catalysts for asymmetric syntheses, Org. Biomol. Chem. 4 (2006) 393–406, https://doi.org/10.1039/B513564H.
[10] T. Ikariya, A.J. Blacker, Asymmetric transfer hydrogenation of ketones with bifunctional transition metal-based molecular catalysts, Acc. Chem. Res. 40 (2007) 1300–1308, https://doi.org/10.1021/ar700134q.
[11] D. Wang, D. Astruc, The golden age of transfer hydrogenation, Chem. Rev. 115 (2015) 6621–6686, https://doi.org/10.1021/acs.chemrev.5b00203.
[12] A.A. Mikhailine, M.I. Maishan, R.H. Morris, Asymmetric transfer hydrogenation of ketimines using well-defined iron(II)-Based precatalysts containing a PNNP ligand, Org. Lett. 14 (2012) 4638–4641, https://doi.org/10.1021/ol302079q.
[13] M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, An overview of N-heterocyclic carbenes, Nature 510 (2014) 485–496, https://doi.org/10.1038/nature13384.
[14] a) N. Gürbüz, E.Ö. Karaca, İ. Özdemir, B. Çetinkaya, Cross coupling reactions catalyzed by (NHC)Pd(II) complexes, Turk. J. Chem. 39 (2015) 1115–1157, https://doi.org/10.3906/kim-1510-31;
b) E.Ö. Karaca, N. Gürbüz, İ. Özdemir, H. Doucet, O. Şahin, O. Büyükgüngör, B. Çetinkaya, Palladium complexes with tetrahydropyrimidin-2-ylidene ligands: catalytic activity for the direct arylation of furan, thiophene, and thiazole derivatives, Organometallics 34 (2015) 2487–2493, https://doi.org/10.1021/om501201r.
[15] N. Şahin, S.D. Düşünceli, İ. Özdemir, Arylation of aniline and amines by Pd-(N-heterocyclic carbene) complexes, Heterocycles 94 (2017) 1506–1517, https://doi.org/10.3987/COM-17-13737.
[16] H. Clavier, C.A. Urbina-Blanco, S.P. Nolan, Indenylidene ruthenium complex bearing a sterically demanding NHC ligand: an efficient catalyst for olefin metathesis at room temperature, Organometallics 28 (2009) 2848–2854, https://doi.org/10.1021/om900071t.
[17] A. Hryniewicka, I. Misztalewska, D. Czajkowska-Szczykowska, D. Urbanczyk-Lipkowska, J.W. Morzycki, S. Witkowski, New olefin metathesis catalysts bearing polyether clamp in *N*-heterocyclic carbenes ligands, Tetrahedron 70 (2014) 6810–6816, https://doi.org/10.1016/j.tet.2014.07.056.
[18] S. Demir, M. Yiğit, İ. Özdemir, Synthesis of rhodium complexes derived from benzimidazolin-2-ylidene ligands and first used for the addition of arylboron to benzonitriles, J. Organomet. Chem. 732 (2013) 21–26, https://doi.org/10.1016/j.jorganchem.2013.01.025.
[19] C. Song, C. Ma, Y. Ma, Y. Feng, S. Ma, Q. Chai, M.B. Andrus, "Bis-paracyclophane *N*-heterocyclic carbene–ruthenium catalyzed asymmetric ketone hydrosilylation", Tetrahedron Lett. 46 (2005) 3241–3244, https://doi.org/10.1016/j.tetlet.2005.03.026.
[20] S.V. Maifeld, M.N. Tran, D. Lee, Hydrosilylation of alkynes catalyzed by ruthenium carbene complexes, Tetrahedron Lett. 46 (2005) 105–108, https://doi.org/10.1016/j.tetlet.2004.11.025.
[21] B. Çetinkaya, İ. Özdemir, P.H. Dixneuf, Synthesis and catalytic properties of *N*-functionalized carbene complexes of rhodium(I) and ruthenium(II),

J. Organomet. Chem. 534 (1997) 153–158, https://doi.org/10.1016/S0022-328X(96)06927-6.
[22] L. Delaude, A. Demonceau, A.F. Noels, Synthesis and application of new N-heterocyclic carbene ruthenium complexes in catalysis: a case study, Curr. Org. Chem. 10 (2006) 203–215, https://doi.org/10.2174/138527206775192924.
[23] A.A. Danopoulos, S. Winston, W.B. Motherwell, Chelating bis-carbene rhodium(iii) complexes in transfer hydrogenation of ketones and imines, Chem. Commun. (2002) 1376–1377, https://doi.org/10.1039/B109491B.
[24] S. Burling, M.K. Whittlesey, J.M.J. Williams, Direct and transfer hydrogenation of ketones and imines with a ruthenium N-heterocyclic carbene complex, Adv. Synth. Catal. 347 (2005) 591–594, https://doi.org/10.1002/adsc.200404308.
[25] M. Albrecht, R.H. Crabtree, J. Mata, E. Peris, Chelating bis-carbene rhodium(iii) complexes in transfer hydrogenation of ketones and imines, Chem. Commun. (2002) 32–33, https://doi.org/10.1039/B109491B.
[26] J.R. Miecznikowski, R.H. Crabtree, Transfer hydrogenation reduction of ketones, aldehydes and imines using chelated iridium(III) *N*-heterocyclic bis-carbene complexes, Polyhedron 23 (2004) 2857–2872, https://doi.org/10.1016/j.poly.2004.07.001.
[27] Y. Li, M. Lei, W. Yuan, E. Meggers, L. Gong, An N-heterocyclic carbene iridium catalyst with metal-centered chirality for enantioselective transfer hydrogenation of imines, Chem. Commun. 53 (2017) 8089–8092, https://doi.org/10.1039/C7CC04691J.
[28] S. Kuhl, R. Schneider, Y. Fort, Transfer hydrogenation of imines catalyzed by a nickel(0)/NHC complex, Organometallics 22 (2003) 4184–4186, https://doi.org/10.1021/om034046n.
[29] N. Gürbüz, S. Yaşar, E.Ö. Özcan, İ. Özdemir, B. Çetinkaya, "Transfer hydrogenation of ketones by ruthenium complexes bearing benzimidazol-2-ylidene ligands", Eur. J. Inorg. Chem. 19 (2010) 3051–3056, https://doi.org/10.1002/ejic.201000181.
[30] N. Gürbüz, E.Ö. Özcan, İ. Özdemir, B. Çetinkaya, O. Şahin, O. Büyükgüngör, Preparation of a series of Ru(ii) complexes with N-heterocyclic carbene ligands for the catalytic transfer hydrogenation of aromatic ketones, Dalton Trans. 41 (2012) 2330–2339, https://doi.org/10.1039/C1DT11203A.
[31] S. Yaşar, E.Ö. Karaca, Ç. Şahin, İ. Özdemir, O. Şahin, O. Büyükgüngör, "Novel ruthenium(II)–*N*-heterocyclic carbene complexes; synthesis, characterization and catalytic application", J. Organomet. Chem. 789 (2015) 1–7, https://doi.org/10.1016/j.jorganchem.2015.04.012.
[32] S. Yaşar, S. Çekirdek, N.A. Tan, S. Yıldırım, İ. Özdemir, An efficient ligand-free method for the transfer hydrogenation of ketones and aldehydes catalyzed by different complexes, Turk. J. Chem. 37 (2013) 292–298, https://doi.org/10.3906/kim-1211-29.
[33] E.Ö. Özcan, D. Mercan, N. Gürbüz, E. Çetinkaya, B. Çetinkaya, İ. Özdemir, In situ catalytic activities of1,3-dialkyltetrahydropyrimidiniumsalts/[RuCl2(p-cymene)]2system for transferhydrogenation reactions, Turk. J. Chem. 35 (2011) 699–709, https://doi.org/10.3906/kim-1104-4.
[34] E.Ö. Karaca, N. Gürbüz, H. Arslan, D. VanDerveer, İ. Özdemir, Catalytic activity of Ru/tetrahydropyrimidinium salts system for transfer hydrogenation reactions, Appl. Organomet. Chem. 29 (2015) 475–480, https://doi.org/10.1002/aoc.3322.
[35] İ. Özdemir, S. Demir, O. Şahin, O. Büyükgüngör, B. Çetinkaya, Synthesis of novel rhodium-xylyl linked *N*-heterocyclic carbene complexes as hydrosilylation catalysts, Appl. Organomet. Chem. 22 (2008) 59–66, https://doi.org/10.1002/aoc.1353.
[36] S. Demir, İ. Özdemir, B. Çetinkaya, Synthesis and catalytic activity of novel xylyl-linked benzimidazolium salts, Appl. Organomet. Chem. 23 (2009) 520–523, https://doi.org/10.1002/aoc.1558.
[37] J.P. Genet, Asymmetric catalytic hydrogenation. Design of new Ru catalysts and chiral Ligands: from laboratory to industrial applications, Acc. Chem. Res. 36 (2003) 908–918, https://doi.org/10.1021/ar020152u.