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NOVEL AZOLINIUM/RHODIUM SYSTEM CATALYZED ADDITION OF ARYLBORONIC ACIDS TO ALDEHYDES

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Abstract- There novel 1,3-dialkylperhydrobenzimidazolium (**2a-c**) and two 1,3-dialkylimidazolium salts (**4a,b**) as NHC precursors were synthesized from *N,N'*-dialkyl-1,2-cyclohexanediamine dihydrochloride and 1,2-dialkylpropanediamine dihydrochloride. The *in situ* prepared three component system [RhCl(COD)]₂ / imidazolium salts (**2**, **4**) and KOBu^t catalyses the addition of phenylboronic acid to sterically hindered aldehydes affording the corresponding arylated secondary alcohols in good yields.

INTRODUCTION

N-Heterocyclic carbenes (NHCs) have emerged as an important class of ligands for transition metals and are beginning to play a role in transition-metal catalysis.¹ Öfele and Wanzlick first pioneered the metalation of imidazol-2-ylidenes, better known as *N*-heterocyclic carbens, from imidazolium salts in 1968.^{2,3} Lappert and co-workers followed this work with the investigation of *N*-heterocyclic carbens complexes synthesized from electron-rich olefins.^{4,5} However, it was not until the isolation of the first free carbene by Arduengo, in 1991, that significant interest was given to the area.⁶ NHC ligands, predominantly regarded as σ -donors such as tertiary phosphines, are able to stabilize various oxidation states and coordinatively unsaturated intermediates occurring in catalytic cycles. In addition, ligand dissociation as experienced in the use of phosphines is less likely to appear in a considerable manner when NHCs are used. Employment of sterically demanding *N*-heterocyclic carbenes, which resemble bulky phosphines with respect to their bonding, has led to the synthesis of new robust ruthenium, rhodium and palladium catalysts, which are less oxygen sensitive in comparison to the phosphine analogues.⁷ Transition-metal complexes with these ligands have proven to be effective in the Heck reaction,⁸ Suzuki

and Sonogashira coupling,^{9,10} hydrosilylation,¹¹ Kumada coupling,¹² hydrogenation,¹³ olefin cyclopropanation,¹⁴ intramolecular cyclization of (Z)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran,^{15,16} cycloisomerisation,¹⁷ amination of aryl halides¹⁸ and, of course, olefin metathesis.¹⁹

Diarylmethanols are important intermediates for the synthesis of biologically and pharmaceutically active substances.^{20,21} The addition of organometallic reagents to aldehydes has been one of the general methods for the synthesis of diarylmethanols. Of those organometallic reagents, organolithium and organomagnesium compounds are most frequently used for this purpose, but tolerate only a few electrophilic groups on themselves.^{22,23} Examples of using other functionalized organometallic species^{24,25} such as organocopper, organochromium, organotin, especially organozinc, have been described. However, these organometallic reagents are usually toxic and sensitive to air and moisture.

Miyaura reported that rhodium catalyzes the addition of aryl and alkenylboronic acids to aldehydes giving secondary alcohols. The reactions were facilitated by the presence of an electron withdrawing group on the aldehyde and an electron donating group on the arylboronic acid, suggesting that the mechanism involves a nucleophilic attack of the aryl group on the aldehyde.²⁶ The finding that these reactions were run with sterically hindered and strongly basic ligands attracted the attention of Fürstner who subsequently applied *N*-heterocyclic carbene ligands. A *in-situ* generated catalytic system for the addition of phenylboronic acid to aldehydes is prepared combination of rhodium salt, 1,3-dialkylimidazolium chloride and base.²⁷⁻³¹ Buchmeiser reported rhodium- and iridium-tetrahydropyrimidin-2-ylidene complexes are effective of addition of phenylboronic acid to aldehydes,³² and also Rh(I) and nitrogen containing ligands are used for the aryl transferation to aldehydes.³³

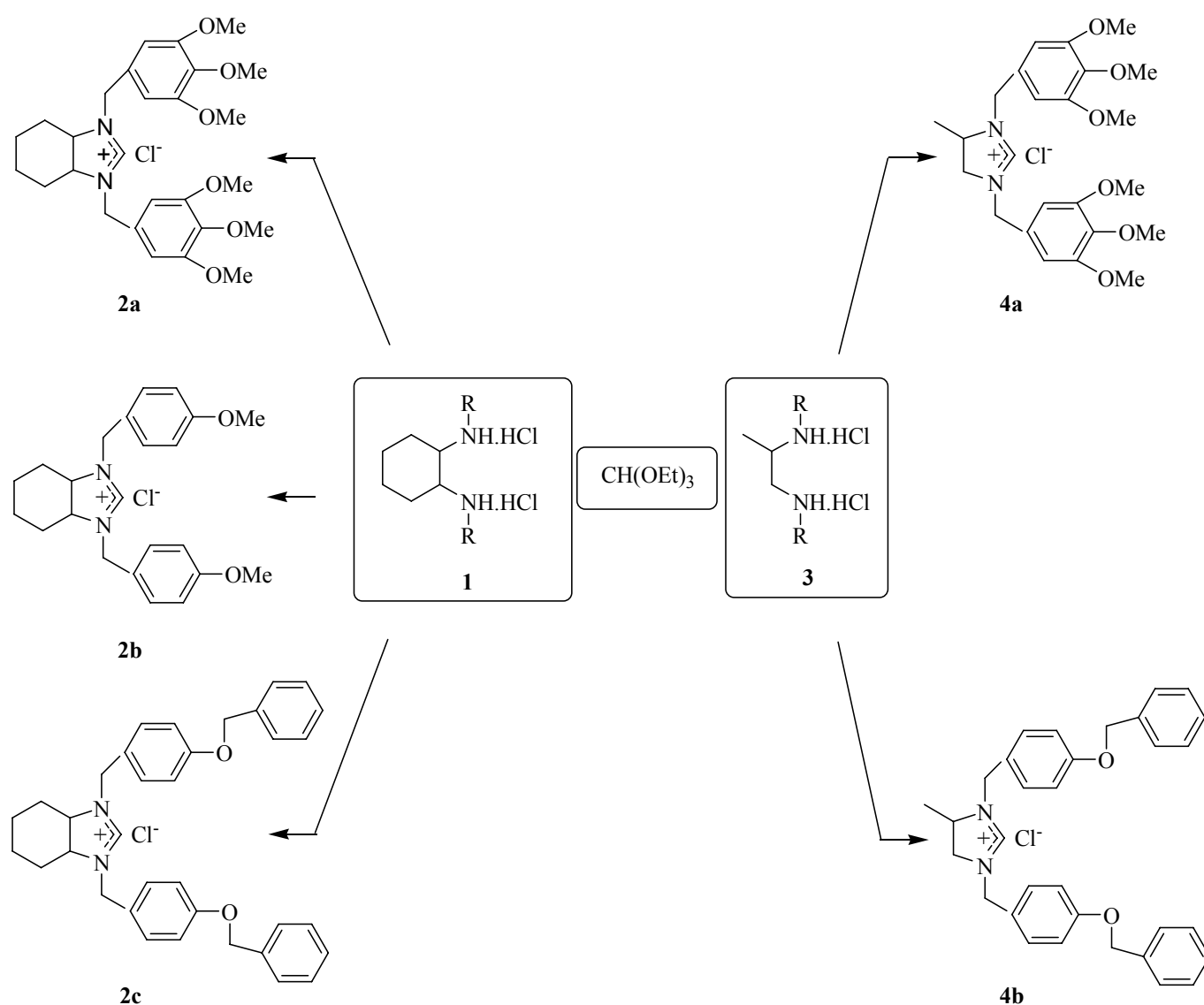
Although the nature of the NHC ligand on complexes has a tremendous influence on the rate of catalyzed reactions, the use of saturated NHC ligands in addition of phenylboronic acid to aldehydes reaction is a neglected area. In order to find more efficient rhodium catalysts we have prepared a series of new perhydrobenzimidazolium and imidazolium chlorides LHX, (**2a-c**) and (**4a,b**) (Scheme 1), containing a saturated imidazole ring and we report here *in-situ* rhodium-carbene based catalytic system for the addition of phenylboronic acid to aldehydes.

RESULTS AND DISCUSSION

Dialkylperhydrobenzimidazolium and imidazolium salts, (**2a-c** and **4a,b**) are conventional NHC precursors. The reaction of **1** and **3**^{34,35} with triethyl orthoformate yielded the symmetrical perhydrobenzimidazolium (**2a-c**) and imidazolium (**4a,b**) salts (Scheme 1). The salts are air- and moisture stable both in the solid state and in solution. The structures of **2** and **4** were determined by their characteristic spectroscopic data and elemental analyses.

¹³C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a

typical singlet in the ^1H -decoupled mode in the 162.63, 162.4, 162.04, 158.74 and 159.16 ppm respectively for imidazolium salts (**2a-c**) and (**4a,b**). The ^1H NMR spectra of the perhydrobenzimidazolium and imidazolium salts further supported the assigned structures; the resonances for C(2)-H were observed as sharp singlets in the 10.42, 10.75, 10.56, 10.23 and 9.00 ppm respectively for **2a-c** and **4a,b**. The IR data for perhydrobenzimidazolium and imidazolium salts (**2a-c**) and (**4a,b**) clearly indicate the presence of the $-\text{C}=\text{N}-$ group with a $\nu(\text{C}=\text{N})$ vibration at 1665, 1585, 1603, 1654, and 1644 cm^{-1} respectively for **2a-c** and **4a,b**. The NMR and IR values are similar to those found for other 1,3-dialkylimidazolium salts.^{34,35}



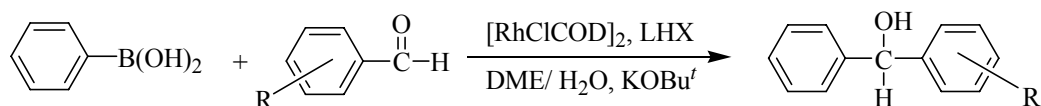
Scheme 1. Synthesis of 1,3-dialkylperhydrobenzimidazolium and 1,3-dialkylimidazolium salts

Although the addition of carbon nucleophiles to aldehydes is usually a facile process, limits are encountered that functionalized organometallic reagents required. Recent publications describing the

addition of arylboronic acid derivatives to aldehydes in the presence of the catalytic amounts of Rh(I) and phosphine derivatives deserve particular mention.^{26,27} Originally $[\text{Rh}(\text{acac})(\text{CO})_2]$ in combination with bidentate phosphine ligand such as dppf [1,1'-bis(diphenylphosphino)ferrocene] has been recommended for the *in situ* preparation of the yet elusive catalyst.³⁶

Here, various perhydrobenzimidazolium and imidazolidinium salts (**2a-c** and **4a,b**) were compared as ligand precursors under the same reaction conditions. To survey the reaction parameters for the addition of phenylboronic acid to aldehydes, we chose to examine Cs_2CO_3 , K_2CO_3 , and KOBU^t as base and DME/ H_2O (3:1) as solvent. We found that the reactions performed in DME/ H_2O (3:1) with Cs_2CO_3 or KOBU^t as the base at 25 °C and 60 °C appeared to be best. We started our investigation with the addition of phenylboronic acid to *p*-chlorobenzaldehyde, in the presence of $[\text{RhCl}(\text{COD})]_2$ /**2-4**. Table 1 summarizes the results obtained in the presence of **2a-c** and **4a,b** (Table 1, Entries 1-5).

Table 1. Rhodium-carbene catalyzed addition of phenylboronic acid to aldehydes.



Entry	R	LHX	Yield ^{a-d} (%)
1	<i>p</i> -Cl	2a	95
2	<i>p</i> -Cl	2b	82
3	<i>p</i> -Cl	2c	90
4	<i>p</i> -Cl	4a	92
5	<i>p</i> -Cl	4b	88
6	H	2a	94
7	H	2b	84
8	H	2c	92
9	H	4a	93
10	H	4b	90
11	2,4,6(CH ₃) ₃	2a	89
12	2,4,6(CH ₃) ₃	2b	77
13	2,4,6(CH ₃) ₃	2c	85
14	2,4,6(CH ₃) ₃	4a	87
15	2,4,6(CH ₃) ₃	4b	82

16	<i>p</i> -C(CH ₃) ₃	2a	91
17	<i>p</i> -C(CH ₃) ₃	2b	79
18	<i>p</i> -C(CH ₃) ₃	2c	84
19	<i>p</i> -C(CH ₃) ₃	4a	88
20	<i>p</i> -C(CH ₃) ₃	4b	82
21	2,5(OCH ₃) ₂	2a	80
22	2,5(OCH ₃) ₂	2b	71
23	2,5(OCH ₃) ₂	2c	76
24	2,5(OCH ₃) ₂	4a	77
25	2,5(OCH ₃) ₂	4b	73
26	3,4,5(OCH ₃) ₃	2a	75
27	3,4,5(OCH ₃) ₃	2b	65
28	3,4,5(OCH ₃) ₃	2c	73
29	3,4,5(OCH ₃) ₃	4a	74
30	3,4,5(OCH ₃) ₃	4b	69

^aIsolated yield (purity of yield checked by NMR and GC), ^b Yields are based on aldehydes, ^cAll reactions were monitored by TLC, ^d60°C, 5h.

Control experiment indicated that the addition of phenylboronic acid to *p*-chlorobenzaldehyde reaction did not occur in the absence of **2a**. Under the determined reaction conditions, a wide range of aryl aldehydes bearing electron-donating or electron-withdrawing groups can react with phenylboronic acid affording the addition products in excellent yields (Table 1 Entries 1, 6, 9, 11, 16, 21 and 26). A systematic study on the substituent effect in the imidazolidinium salts (**2a**, **4a**) indicated that the introduction of 3,4,5-trimethoxybenzyl substituent on the N-atoms notably increased the reaction rate and the yield of the product. In summary, we have demonstrated that *in situ* generated imidazolidin-2-ylidene complexes of rhodium are very effective for the addition of phenylboronic acid to aldehydes.

Although the chemistry of NHC is limited as compare to phosphine chemistry. The NHCs ligands are more stable than corresponding phosphine ligands. Furthermore milder experimental conditions exist for preparation of secondary alcohols by NHCs ligands.

In conclusion, we are pleased to find that among the various NHC precursors, perhydrobenzimidazolium and imidazolidinium salts (**2**, **4**) are excellent ligand precursors for the addition of phenylboronic acid to aldehydes reaction. Also a convenient and highly user-friendly method

for the addition of phenylboronic acid to aldehydes is presented. The procedure is simple and efficient towards various aryl aldehydes and does not require induction periods.

EXPERIMENTAL

All reactions for the preparation of perhydrobenzimidazolium and imidazolium salts (**2a,c** and **4a,b**) were carried out under argon using standart Schlenk-type flasks. Test reactions for the catalytic activity of catalysts in the addition of phenylboronic acid to aldehydes reactions were carried out in air. The complex $[\text{RhCl}(\text{COD})]_2$ ³⁷ and **1** and **3** were prepared according to known methods.^{34,35} All reagents were purchased from Aldrich Chemical Co. All ¹H and ¹³C-NMR were performed in DMSO-*d*₆. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (¹H), 75.47 MHz (¹³C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. Infrared spectra were recorded as KBr pellets in the range 400-4000 cm⁻¹ on a ATI UNICAM 1000 spectrometer. Melting points were measures in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

Preparation of 1,3-bis(3,4,5-trimethoxybenzyl)perhydrobenzimidazolium chloride (**2a**).

A mixture of *N,N'*-bis(3,4,5-trimethoxybenzyl) 1,2-cyclohexanediamine dihydrochloride (5 g; 9.14 mmol), in triethyl orthoformate (50 mL) was heated in a distillation apparatus until the distillation ethanol ceased. The temperature of the reaction mixture reached 110 °C. Upon cooling to rt a colorless solid precipitated which was collected by filtratiton, and dried in vacuum. The crude product was recrystallized from absolute ethanol to give colourless needles, and the solid was washed with ether (2x10 mL), dried under vacuum. Yield: 4.42 g, 93%. mp 161°C, IR (KBr) $\nu = 1665 \text{ cm}^{-1}$ (-CH=N-). ¹H-NMR(CDCl₃) δ : 1.18, 2.07, 3.25 (m, 10 H, NCH(CH₂)₄CHN); 3.80, 3.87 (s, 18H, CH₂C₆H₂(OCH₃)₃); 4.71, 4.87 (d, *J* 14.8 Hz, 4H, CH₂C₆H₂(OCH₃)₃); 6.68 (s, 4H, CH₂C₆H₂(OCH₃)₃); 10.42 (s, 1H, 2-CH). ¹³C- NMR(CDCl₃): 23.85, 27.88, 51.55 (NCH(CH₂)₄CHN); 56.68, 61.02 (CH₂C₆H₂(OCH₃)₃); 67.44 (CH₂C₆H₂(OCH₃)₃); 106.16, 129.14, 138.55, 153.94 (CH₂C₆H₂(OCH₃)₃); 162.63 (2-CH). Anal. Calcd for C₂₇H₃₇N₂O₆Cl: C, 62.24; H, 7.10; N, 5.37. Found: C, 62.52; H, 7.28; N, 5.12.

Preparation of 1,3-bis(*p*-methoxybenzyl)perhydrobenzimidazolium chloride (**2b**).

Compound (**2b**) was prepared in the same way as **2a** from *N,N'*-bis(*p*-methoxybenzyl) 1,2-cyclohexanediamine dihydrochloride (5.5 g; 12.88 mmol), in triethyl orthoformate (50 mL) to give white crystals of **2b**. Yield: 4.64 g, 90%. mp 186°C. IR $\nu = 1585 \text{ cm}^{-1}$ (-CH=N-). ¹H-NMR(CDCl₃) δ : 1.11, 1.74, 3.13 (m, 10 H, NCH(CH₂)₄CHN); 3.65 (s, 6H, CH₂C₆H₄OCH₃); 4.64, 4.89 (d, *J* 14.8 Hz, 4H,

$\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_3$); 6.55, 7.28 (d, J 8.4 Hz, 8H, $\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_3$); 10.75 (s, 1H, 2-CH). ^{13}C -NMR(CDCl_3): 23.81, 27.76, 50.58 (NCH(CH_2) $_4$ CHN); 55.30 ($\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_3$); 67.07 ($\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_3$); 96.28, 114.60, 125.51, 130.15, 159.95 ($\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_3$); 162.40 (2-CH). Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_2\text{Cl}$: C, 68.91; H, 7.24; N, 6.99. Found C, 68.72; H, 7.38; N, 6.84.

Preparation of 1,3-bis(*p*-benzyloxybenzyl)perhydrobenzimidazolium chloride (2c).

Compound (2c) was prepared in the same way as 2a from *N,N'*-bis(*p*-benzyloxybenzyl) 1,2-cyclohexanediamine dihydrochloride (6 g; 8.85 mmol), in triethylorthoformate (50 mL) to give white crystals of 2c. Yield: 5.22 g, 87%. mp 164°C. IR $\nu = 1603\text{ cm}^{-1}$ (-CH=N-). ^1H -NMR(CDCl_3) δ : 1.18, 1.85, 2.76 (m, 10 H, NCH(CH_2) $_4$ CHN); 4.64, 4.89 (d, J 11.2 Hz, 4H, $\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 5.04 (s, 4H, $\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 6.91, 7.32 (m, 18H, $\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 10.56 (s, 1H, 2-CH). ^{13}C -NMR(CDCl_3): 23.82, 27.70, 50.57 (NCH(CH_2) $_4$ CHN); 67.04, 70.29 ($\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 115.67, 125.63, 127.71, 128.26, 128.79, 130.26, 136.83, 159.32 ($\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 162.04 (2-CH). Anal. Calcd for $\text{C}_{35}\text{H}_{37}\text{N}_2\text{O}_2\text{Cl}$: C, 76.01; H, 6.69; N, 5.06. Found C, 76.32; H, 6.53; N, 5.21.

Preparation of 1,3-bis(3,4,5-trimethoxybenzyl)-4-methylimidazolium chloride (4a).

Compound (4a) was prepared in the same way as 2a from 1,2-bis(3,4,5-trimethoxybenzylamino)propane dihydrochloride (5.8 g, 11.43 mmol), in triethyl orthoformate (50 mL) to give white crystals of 4a. Yield: 4.83 g, 88%. mp 111°C. IR $\nu = 1654\text{ cm}^{-1}$ (-CH=N-). ^1H -NMR(CDCl_3) δ : 4.06 (m, 1H, NCH(CH_3) CH_2N); 3.24, 3.88 (t, J 8.4 Hz, 2H, NCH(CH_3) CH_2N); 1.30 (d, J 6.4 Hz, 3H, NCH(CH_3) CH_2N); 3.76, 3.82, 3.83 (s, 18H, $\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3$); 4.35, 5.07 (d, J 14.8 Hz, 2H, $\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3$); 4.71, 4.75 (d, J 14.4 Hz, 2H, $\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3$); 6.66, 6.68 (s, 4H, $\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3$); 10.23 (s, 1H, 2-CH). ^{13}C -NMR(CDCl_3): 18.49, 50.19, 52.84 (NCH(CH_3) CH_2N); 54.73, 55.71, 56.75, 56.85 ($\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3$); 60.97 ($\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3$); 106.43, 128.53, 138.62, 138.65, 153.96, 153.99 ($\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3$); 158.74 (2-CH). Anal. Calcd for $\text{C}_{24}\text{H}_{33}\text{N}_2\text{O}_6\text{Cl}$: C, 59.93; H, 6.86; N, 5.82. Found C, 59.71; H, 6.97; N, 5.92.

Preparation of 1,3-bis(*p*-benzyloxybenzyl)-4-methylimidazolium chloride (4b).

Compound (4b) was prepared in the same way as 2a from 1,2-bis(*p*-benzyloxybenzylamino)propane dihydrochloride (5.3 g, 9.83 mmol), in triethyl orthoformate (50 mL) to give white crystals of 4b. Yield: 4.28 g, 85%. mp 158°C. IR $\nu = 1644\text{ cm}^{-1}$ (-CH=N-). ^1H -NMR(CDCl_3) δ : 4.02 (m, 1H, NCH(CH_3) CH_2N); 3.25, 3.82 (t, J 11.2 Hz, 2H, NCH(CH_3) CH_2N); 1.20 (d, J 6.4 Hz, 3H, NCH(CH_3) CH_2N); 4.46, 4.75 (d, J 14.8 Hz, 2H, $\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 4.60 (s, 2H, $\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 5.09 (s, 4H, $\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 7.04, 7.36 (m, 18H, $\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 9.00 (s, 1H, 2-CH). ^{13}C -NMR(CDCl_3): 18.49, 48.42, 50.99 (NCH(CH_3) CH_2N); 54.98, 56.37, 70.00 ($\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 115.80, 126.56, 126.82, 128.39, 128.56, 129.13, 130.72, 130.76, 137.62, 157.84 ($\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5$); 159.16 (2-CH). Anal. Calcd for $\text{C}_{35}\text{H}_{37}\text{N}_2\text{O}_2\text{Cl}$: C, 76.01; H, 6.69; N, 5.06. Found C, 76.32; H, 6.53; N, 5.21.

74.92; H, 6.43; N, 5.46. Found C, 74.79; H, 6.64; N, 5.62.

General Procedure for Rhodium-Carbene Catalyzed Addition of Phenylboronic Acid to Aldehydes.

Phenylboronic Acid (1.20 g, 9.8 mmol), KOBu^t (4.9 mmol), substituted aldehydes (4.9 mmol), [RhCl(COD)]₂ (1 mol%), imidazolium salts (**2-4**) (2 mol), dimethoxyethane (15 mL) were introduced in to Schlenk tube and then water (5 mL) was added. The resulting mixture was heated for 5 h at 60 °C, cooled to ambient temperature, extracted with ethyl acetate (30 mL). After drying over MgSO₄ the organic phase was evaporated and the residue was purified by flash chromatography. Isolated yield (yields based on aldehydes) is checked by NMR and GC, all reactions were monitored by TLC.

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