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SYNTHESIS OF 1,3-DIALKYLPERHYDROBENZIMIDAZOLINIUM SALTS AND THEIR CATALYTIC PROPERTIES IN HECK REACTIONS

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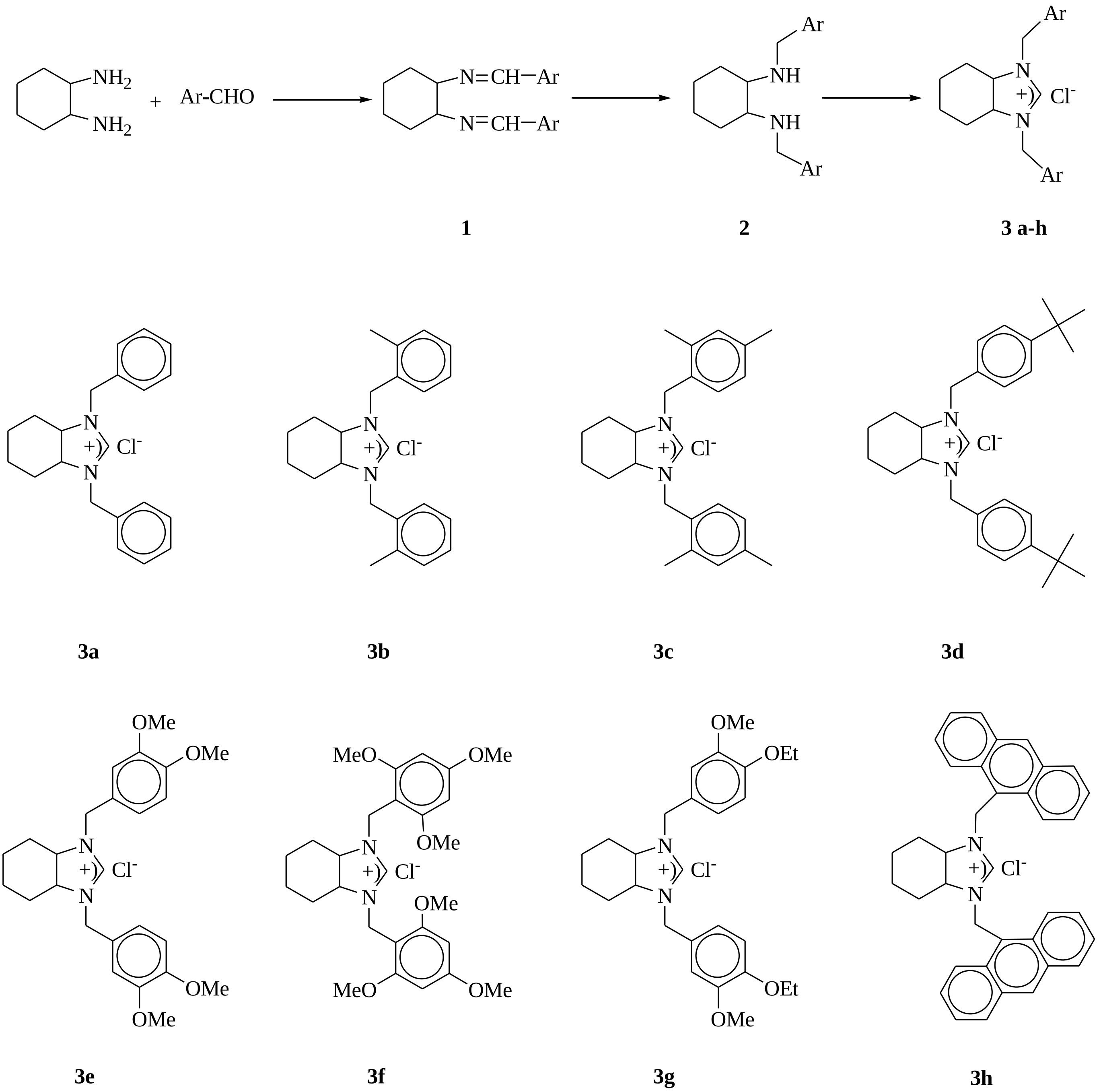
Abstract - Novel eight 1,3-dialkylperhydrobenzimidazolinium chloride salts **3a-h** were prepared as precursors of *N*-heterocyclic carbenes by reacting *N,N'*-dialkylcyclohexanediamine, triethyl orthoformate and ammonium chloride. The salts were characterized spectroscopically and the complexes formed *in situ* from Pd(OAc)$_2$ and **3** have been tested as catalysts in homogenous Heck coupling reactions.

The Palladium-catalyzed Mizoroki-Heck cross-coupling reaction of an olefin with aryl halides under basic conditions is one of the highly efficient tools for the carbon–carbon bond formation in organic synthesis.[1-3] Phosphines generally have been used as ligands for the palladium-catalyzed Heck and Suzuki coupling reactions. However, the phosphine ligands are expensive, toxic and sensitive to air and the moisture.[4-7] The strong electron donating property of *N*-heterocyclic carbene ligands leads to metal complexes with high stability against heat, air and moisture. These properties of *N*-heterocyclic carbene ligands make them alternatives to tertiary phosphines used in different transition metal-catalyzed reactions such as C-C and C-N arylation, olefin metathesis, hydrogenation, hydrosilylation and CO-ethylene co-polymerization reactions.[8-19] Apart from phosphine and *N*-heterocyclic carbene ligands, Schiff bases, amines, oxazolines, pyridines, hydroxyquinolines, hydrazones, tetrazoles, *N*-phenylurea have been used as ligands in Heck and Suzuki coupling reactions.[20-27] Use of ligand free palladium salts for Heck reactions has been reported.[28] However, ligandless catalysts such as palladium acetate are not good catalysts for the Heck reactions of unactivated aryl chlorides. Recently, Gibson *et al* and Jones *et al* showed that palladium complexes with chiral ligands are well suited as catalysts for the asymmetric Heck reactions.[29,30] Saturated imidazolinium salts as precursors for *N*-heterocyclic carbenes are generally prepared by alkylation of dihydroimidazole and by cyclization reactions of a secondary bisamine with triethyl orthoformate in the presence of ammonium salt or *N*,*N*'-dialkyl-1,2-diaminoethane dihydrohalides with triethyl orthoformate.[31-33] The imidazolinium and benzimidazolium salts are an effective ligand precursor for the coupling of unactivated, activated and deactivated chlorides. In situ prepared catalysts from these salts and palladium acetate gave effective catalysts for Suzuki coupling of aryl chlorides and Heck coupling of aryl bromides in aqueous DMF at 80 °C. Both class *N*-heterocyclic carbene precursor appeared to give similar activities.[34-37]

We recently reported the synthesis of *N*-heterocyclic carbene derivative ligands and their palladium(II) carbene complexes and investigated for catalytic activity in Heck and Suzuki reactions.[38-43] In this article we wish to report the synthesis of new 1,3-dialkylperhydrobenzimidazolinium chloride salts **3a-h** (scheme 1), and their application to Heck cross-coupling with aryl halides.

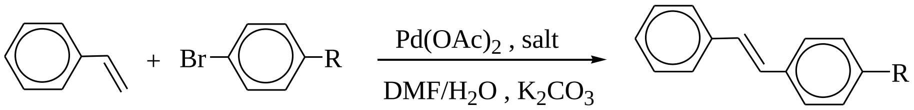
The synthesis of 1,3-dialkylperhydrobenzimidazolinium salts is shown in Scheme 1. The Schiff bases **1** were prepared by the condensation of 1,2-diaminocyclohexane with aromatic aldehydes in ethanol. Reduction of these Schiff bases with sodium borohydride in methanol gave the *N,N'*-dialkylcyclohexane-1,2-diamines **2**. The symmetrical 1,3-dialkylperhydrobenzimidazolinium salts **3** were easily synthesized in high yields from the *N,N'*-dialkylcyclohexane-1,2-diamines, triethyl ortoformate and ammonium chloride. After purification, the 1,3-dialkylperhydrobenzimidazolinium salts **3a-h** were isolated as colorless solids except for **3h** in good yields (78-89%). The salts are soluble in the common polar solvents and are air- and moisture stable both in the solid state and in solution. The structures of 1,3-dialkylperhydrobenzimidazolinium salts were determined by their spectroscopic data and elemental analyses (see Experimental section). The ^{13}C- NMR spectra of **3a-h** show only sharp high field signals [162.35 (**3a**), 162.57 (**3b**), 162.44 (**3c**), 162.02 (**3d**), 162.18 (**3e**), 162.28 (**3f**), 162.11 (**3g**), 161.55 ppm (**3h**)] for the imino carbon and for a benzylic carbon [67.40 (**3a**), 68.28 (**3b**), 67.82 (**3c**), 66.08 (**3d**), 66.75 (**3e**), 66.74 (**3f**), 66.70 (**3g**), 68.93 ppm (**3h**)]. The ^{1}H-NMR spectra of the perhydrobenzimidazolinium salts further supported the assigned structures. The resonances of the C(2)-H were observed as sharp singlets at δ = 10.56, 9.89, 10.37, 10.74, 10.82, 8.63, 10.81, 9.36 ppm for **3a-h**, respectively. While the benzylic protons for **3c** appeared as a singlet at 4.90 ppm, others appeared as a doublet in the range 4.62-5.84 ppm. The IR data for perhydrobenzimidazolinium **3a-h** salts clearly indicate the presence of the –C=N– group with a $\nu_{(C=N)}$ vibration at 1512-1619 cm^{-1}. These NMR and IR values were similar to those reproted for other 1,3-dialkylperhydrobenzimidazolinium and 1,3-dialkylimidazolinium salts.[38,44]

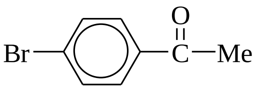
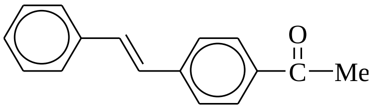
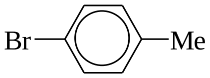
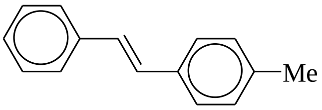


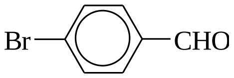
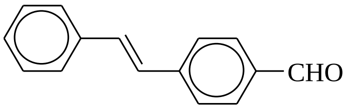
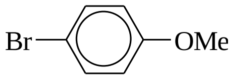
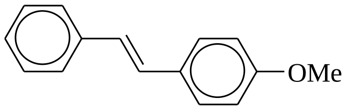
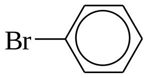
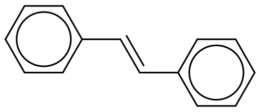
Scheme 1. Synthesis of 1,3-dialkylperhydrobenzimidazolinium salts

Pd-Catalyzed Heck reaction between aryl halides and alkenes is very useful methods to prepare styrene derivatives, which are important chemicals for many applications. A variety of parameters such as base, solvent, time, temperature, ligands and nature of the catalyst can influence the reactivity of Heck coupling reactions. The published results showed that *N*-heterocyclic carbenes were efficient ligands for the Pd-catalyzed Heck coupling reactions. The choice of bases and solvents are usually important in achieving an efficient cross coupling reaction. For optimal reaction conditions, the $Pd(OAc)_2$-catalyzed cross coupling of bromobenzene with styrene was employed as the model reaction using ligand **3a** at 80 °C; Cs_2CO_3, K_2CO_3, K_3PO_4 and *t*-BuOK were tested as the base. We chose K_2CO_3 as a base and DMF-water as a solvent that the most commonly used in the Heck reaction. Under these reaction conditions, the coupling reactions of aryl bromides and styrene were carried out in DMF/H_2O (3:3 mL) with 1 mol% $Pd(OAc)_2$, 2 mol% **3** and 2 equiv. K_2CO_3 for 2 h at 80 °C. Reaction of *p*-bromoacetophenone, *p*-bromotoluene, *p*-bromobenzaldehyde, *p*-bromoanisol and bromobenzene with styrene gave a high yield using this catalytic system. Control experiments showed that palladium acetate in the absence of 1,3-dialkylperhydrobenzimidazolinium salts was inactive under these conditions for Heck reaction. However, the activated (electron-poor) and deactivated (electron-rich) aryl chlorides do not react under these reaction conditions, and yields are typically <5%. The results are summarized in Table 1.

Table 1. The Heck coupling reaction of aryl bromides with styrene



Entry	Aryl bromide	Product	Catalyst	Yield[a,b,c] (%)
1			**3a**	93
2			**3b**	95
3			**3c**	98
4			**3d**	97
5			**3e**	98
6			**3f**	99
7			**3g**	98
8			**3h**	97
9			**3a**	80
10			**3b**	84
11			**3c**	86
12			**3d**	85
13			**3e**	87
14			**3f**	88
15			**3g**	86
16			**3h**	85

17			**3a**	92
18			**3b**	94
19			**3c**	97
20			**3d**	95
21			**3e**	96
22			**3f**	98
23			**3g**	93
24			**3h**	95
25			**3a**	81
26			**3b**	88
27			**3c**	89
28			**3d**	85
29			**3e**	87
30			**3f**	89
31			**3g**	84
32			**3h**	86
33			**3a**	94
34			**3b**	92
35			**3c**	96
36			**3d**	95
37			**3e**	94
38			**3f**	97
39			**3g**	93
40			**3h**	95

[a] *Reaction conditions*: 1.0 mmol of R-C_6H_4Br-*p*, 1.5 mmol of styrene, 2.0 mmol K_2CO_3, 1.0 mmol $Pd(OAc)_2$, 2.0 mol% **3a-h**. [b] Purity of compounds is checked by NMR and isolated yields are based on aryl bromide. [c] All reactions were monitered by GC.

Of the five different aryl bromides, aryl bromides bearing electron-withdrawing groups react with styrene affording the coupled products in excellent yields (Table 1, entries 6, 14, 22, 30 and 38). We observed that the perhydrobenzimidazolinium salts bearing methyl groups (**3b**, **3c**), *tert*-butyl group (**3d**) and methoxy groups (**3e**, **3f**, **3g**) were the most effective of the salts than nonsubstituted counterparts (**3a**) for the Heck reactions. It can be show these salts are an effective ligand precursor for the coupling of unactivated, activated and deactivated aryl bromides with styrene. These results are in agreement with other reports.[34,38]

In summary, eight 1,3-dialkylperhydrobenzimidazolinium chloride salts **3a-h** were prepared by reacting *N,N'*-dialkylcyclohexanediamine, triethyl orthoformate and ammonium chloride, and their catalytic activities in the Heck coupling reactions were investigated. This catalytic system provides good conditions for the coupling of aryl bromides without additives such as tetrabutylammonium bromide in air. All *in situ* prepared palladium complexes demonstrated good catalytic activity in Heck coupling reactions. Particularly, the **3f** catalyst system is seen to be the most effective in the Heck reactions of aryl bromides with styrene.

EXPERIMENTAL

All reactions for the preparation of 1,3-dialkylperhydrobenzimidazolinium salts **3a-h** were carried out under argon using standard Schlenk-type flasks. Heck coupling reactions were carried out in air. 1,2-Diaminocyclohexane (mixture of *cis* and *trans*), aldehydes and other reagents were purchased from Aldrich Chemical Co. (Turkey). All ^{1}H- and ^{13}C-NMR were recorded in $CDCI_3$ using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) or 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in hertz. FT-IR spectra were recorded as KBr pellets in the range 400-4000 cm^{-1} on a Mattson 1000 spectrophotometer (wavenumbers, cm^{-1}). GC were measured by GC-FID on a Agilent 6890N gas chromatograph equipped with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed at Inönü University research center.

General synthesis of Schiff bases

A solution of the aldehydes (10 mmol) and 1,2-diaminocyclohexane (5 mmol) in EtOH (30 mL) was heated under reflux 3 h, then volatiles were removed in vacuum to dryness. The crude product was crystallized from toluene/hexane.

General synthesis of diamines

Sodium borohydride (15 mmol) was added portionwise over 30 min to a solution of diimine (10 mmol) in MeOH (30 mL) at room temperature and reaction mixture was stirred for 12 h and then heated under reflux for 1 h. Upon cooling to room temperature, the mixture was treated with 1 N HCl, and organic phase was extracted with CH_2Cl_2 (3 x 30 mL). After drying over $MgSO_4$ and evaporation, The crude product was crystallized from toluene/hexane.

Synthesis of 1,3-dibenzylperhydrobenzimidazolinium chloride (3a).

Chiral form of **3a** was reported by Smith *et al*.[45] A mixture of *N,N'*-dibenzyl-1,2-cyclohexanediamine (1.82 g, 6.2 mmol), NH_4Cl (0.33 g, 6.2 mmol) and triethyl orthoformate (10 mL) was heated for 12 h at 110 °C. Upon cooling to room temperature, colorless crystals of **3a** were obtained. The crystals were filtered, washed with diethyl ether (3 x 15 mL) and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O. Yield: 1.70 g, 81%, mp 155 °C. IR (cm^{-1}) ν: 1606 (NCN), ^1H NMR ($CDCl_3$) δ: 10.56 (s, 1H, C-2*H*); 1.05-1.27 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 1.69-1.95 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 3.19-3.21 (m, 2H, $NCHCH_2CH_2CH_2CH_2CHN$); 4.77 and 5.48 (d, 4H, J = 11.1 Hz, $CH_2C_6H_5$); 7.25-7.36 (m, 10H, $CH_2C_6H_5$). ^{13}C-NMR ($CDCl_3$) δ: 162.35 (*C*-2); 23.77 ($NCHCH_2CH_2CH_2CH_2CHN$); 27.74 ($NCHCH_2CH_2CH_2CH_2CHN$); 51.22 ($NCHCH_2CH_2CH_2CH_2CHN$); 67.40 ($CH_2C_6H_5$); 128.71, 128.98, 129.38, 133.48 ($CH_2C_6H_5$). Anal. Calcd for $C_{21}H_{25}N_2Cl$: C, 74.00; H, 7.34; N, 8.22. Found: C, 74.12; H, 7.39; N, 8.27.

Synthesis of 1,3-bis(2-methylbenzyl)perhydrobenzimidazolinium chloride (3b).

This compound was prepared in same way as **3a** from *N,N'*-bis(2-methylbenzyl)-1,2-cyclohexanediamine (2.12 g, 6.54 mmol), NH_4Cl (0.35 g, 6.54 mmol) and triethyl orthoformate (10 mL) to give colorless crystals of **3b**. Yield: 2.15 g, 89%, mp 128 °C. IR(cm^{-1}) ν: 1600 (NCN), ^1H NMR ($CDCl_3$) δ: 9.89 (s, 1H, C-2*H*); 1.11-1.33 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 1.68-1.93 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 3.35-3.38 (m, 2H, $NCHCH_2CH_2CH_2CH_2CHN$); 2.30 (s, 6H, $CH_2C_6H_5CH_3$-2); 4.89 and 4.97 (d, 4H, J = 11.7 Hz, $CH_2C_6H_4CH_3$-2); 7.11-7.26 (m, 8H, $CH_2C_6H_4CH_3$-2). ^{13}C-NMR ($CDCl_3$) δ: 162.57 (*C*-2); 23.83 ($NCHCH_2CH_2CH_2CH_2CHN$); 27.95 ($NCHCH_2CH_2CH_2CH_2CHN$); 49.53 ($NCHCH_2CH_2CH_2CH_2CHN$); 19.67 ($CH_2C_6H_4CH_3$-2); 68.27 ($CH_2C_6H_4CH_3$-2), 126.73, 129.02, 129.38, 131.26, 131.49, 136.82 ($CH_2C_6H_4CH_3$-2). Anal. Calcd for $C_{23}H_{29}N_2Cl$: C, 74.89; H, 7.86; N, 7.59. Found: C, 74.96; H, 7.81; N, 7.63.

Synthesis of 1,3-bis(2,4-dimethylbenzyl)perhydrobenzimidazolinium chloride (3c).

This compound was prepared in same way as **3a** from *N,N'*-bis(2,4-dimethylbenzyl)-1,2-cyclohexanediamine (1.84 g, 5.23 mmol), NH_4Cl (0.28 g, 5.23 mmol) and triethyl orthoformate (10 mL) to give colorless crystals of **3c**. Yield: 1.78 g, 86%, mp 157 °C. IR (cm^{-1}) ν: 1619 (NCN), ^1H NMR ($CDCl_3$) δ: 10.37 (s, 1H, C-2*H*); 1.19-1.34 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 1.73-2.02 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 3.25-3.28 (m, 2H, $NCHCH_2CH_2CH_2CH_2CHN$); 2.28 and 2.31 (s, 12H, $CH_2C_6H_3(CH_3)_2$-2,4); 4.90 (s, 4H, $CH_2C_6H_3(CH_3)_2$-2,4); 6.99-7.28 (m, 6H, $CH_2C_6H_3(CH_3)_2$-2,4). ^{13}C-NMR ($CDCl_3$) δ: 162.44 (*C*-2); 23.63

($\mathrm{NCHCH_2\mathit{C}H_2\mathit{C}H_2CH_2CHN}$); 27.78 ($\mathrm{NCH\mathit{C}H_2CH_2CH_2\mathit{C}H_2CHN}$); 49.14 ($\mathrm{N\mathit{C}HCH_2CH_2CH_2CH_2\mathit{C}HN}$); 19.48 and 21.05 ($\mathrm{CH_2C_6H_3(\mathit{C}H_3)_2}$-2,4); 67.82 ($\mathrm{\mathit{C}H_2C_6H_3(CH_3)_2}$-2,4); 127.21, 127.89, 129.29, 131.92, 136.45, 139.79 ($\mathrm{CH_2\mathit{C}_6H_3(CH_3)_2}$-2,4). Anal. Calcd for $\mathrm{C_{25}H_{33}N_2Cl}$: C, 75.66; H, 8.32; N, 7.06. Found: C, 75.61; H, 8.37; N, 7.12.

Synthesis of 1,3-bis(4-tert-butylbenzyl)perhydrobenzimidazolinium chloride (3d).

This compound was prepared in same way as **3a** from *N,N'*-bis(4-*tert*-butylbenzyl)-1,2-cyclohexanediamine (2.36 g, 5.79 mmol), $\mathrm{NH_4Cl}$ (0.31 g, 5.79 mmol) and triethyl orthoformate (10 mL) to give colorless crystals of **3d**. Yield: 2.12 g, 81%, mp 245 °C. IR ($\mathrm{cm^{-1}}$) ν: 1512 (NCN), ^{1}H-NMR ($\mathrm{CDCl_3}$) δ: 10.74 (s, 1H, 2-C*H*); 1.18-1.23 (m, 4H, $\mathrm{NCHCH_2C\mathit{H_2}C\mathit{H_2}CH_2CHN}$); 1.78-2.10 (m, 4H, $\mathrm{NCHC\mathit{H_2}CH_2CH_2C\mathit{H_2}CHN}$); 3.15-3.21 (m, 2H, $\mathrm{NC\mathit{H}CH_2CH_2CH_2CH_2C\mathit{H}N}$); 1.27 (s, 18H, $\mathrm{CH_2C_6H_4C(C\mathit{H_3})_3}$-*p*); 4.66 and 5.02 (d, 4H, *J* = 15.0 Hz, $\mathrm{C\mathit{H_2}C_6H_4C(CH_3)_3}$-*p*); 7.32 and 7.36 (m, 8H, *J* = 8.3 Hz, and *J* = 8.5 Hz, $\mathrm{CH_2C_6\mathit{H_4}C(CH_3)_3}$-*p*). ^{13}C-NMR ($\mathrm{CDCl_3}$) δ: 162.02 (2-*C*H); 23.58 ($\mathrm{NCHCH_2\mathit{C}H_2\mathit{C}H_2CH_2CHN}$); 27.37 ($\mathrm{NCH\mathit{C}H_2CH_2CH_2\mathit{C}H_2CHN}$); 50.45 ($\mathrm{N\mathit{C}HCH_2CH_2CH_2CH_2\mathit{C}HN}$); 31.22 ($\mathrm{CH_2C_6H_4C(\mathit{C}H_3)_3}$-*p*); 34.61 ($\mathrm{CH_2C_6H_4\mathit{C}(CH_3)_3}$-*p*); 66.83 ($\mathrm{\mathit{C}H_2C_6H_4C(CH_3)_3}$-*p*); 126.10, 128.23, 129.96, 151.87 ($\mathrm{CH_2\mathit{C}_6H_4C(OCH_3)_3}$-p). Anal. Calcd for $\mathrm{C_{29}H_{41}N_2Cl}$: C, 76.90; H, 9.06; N, 6.19. Found: C, 76.24; H, 9.27; N, 6.02.

Synthesis of 1,3-bis(3,4-dimethoxybenzyl)perhydrobenzimidazolinium chloride (3e).

This compound was prepared in same way as **3a** from *N,N'*-bis(3,4-dimethoxybenzyl)-1,2-cyclohexanediamine (3.11 g, 7.48 mmol), $\mathrm{NH_4Cl}$ (0.40 g, 7.48 mmol) and triethyl orthoformate (10 mL) to give colorless crystals of **3e**. Yield: 2.92 g, 85%, mp 103 °C. IR ($\mathrm{cm^{-1}}$) ν: 1588 (NCN), ^{1}H-NMR ($\mathrm{CDCl_3}$) δ: 10.82 (s, 1H, 2-C*H*); 1.17-1.23 (m, 4H, $\mathrm{NCHCH_2C\mathit{H_2}C\mathit{H_2}CH_2CHN}$); 1.74-2.12 (m, 4H, $\mathrm{NCHC\mathit{H_2}CH_2CH_2C\mathit{H_2}CHN}$); 3.09-3.17 (m, 2H, $\mathrm{NC\mathit{H}CH_2CH_2CH_2CH_2C\mathit{H}N}$); 3.84 and 3.92 (s, 12H, $\mathrm{CH_2C_6H_3(OC\mathit{H_3})_2}$-2,4); 4.63 and 4.95 (d, 4H, *J* = 14.6 Hz, $\mathrm{C\mathit{H_2}C_6H_3(OCH_3)_2}$-2,4); 6.77-6.88 (m, 4H, $\mathrm{CH_2C_6\mathit{H_3}(OCH_3)_2}$-2,4) and 7.17 (s, 2H, $\mathrm{CH_2C_6\mathit{H_3}(OCH_3)_2}$-2,4). ^{13}C-NMR ($\mathrm{CDCl_3}$) δ: 162.18 (2-*C*H); 23.62 ($\mathrm{NCHCH_2\mathit{C}H_2\mathit{C}H_2CH_2CHN}$); 27.51 ($\mathrm{NCH\mathit{C}H_2CH_2CH_2\mathit{C}H_2CHN}$); 50.74 ($\mathrm{N\mathit{C}HCH_2CH_2CH_2CH_2\mathit{C}HN}$); 55.87 and 56.62 ($\mathrm{CH_2C_6H_3(O\mathit{C}H_3)_2}$-2,4); 66.75 ($\mathrm{\mathit{C}H_2C_6H_3(OCH_3)_2}$-2,4); 111.05, 111.87, 121.08, 125.53, 149.40, 149.68 ($\mathrm{CH_2\mathit{C}_6H_3(OCH_3)_2}$-2,4). Anal. Calcd for $\mathrm{C_{25}H_{33}N_2O_4Cl}$: C, 65.14; H, 7.16; N, 6.08. Found: C, 65.26; H, 7.34; N, 6.28.

Synthesis of 1,3-bis(2,4,6-trimethoxybenzyl)perhydrobenzimidazolinium chloride (3f).

This compound was prepared in same way as **3a** from *N,N'*-bis(2,4,6-trimethoxybenzyl)-1,2-

cyclohexanediamine (2.22 g, 4.67 mmol), NH_4Cl (0.25 g, 4.67 mmol) and triethyl orthoformate (10 mL) to give colorless crystals of **3f**. Yield: 1.89 g, 78%, mp 214-216 °C. IR (cm^{-1}) ν: 1591 (NCN), ^1H NMR ($CDCl_3$) *δ*: 8.63 (s, 1H, C-2*H*); 1.16-1.43 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 1.80-2.28 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 2.82-3.03 (m, 2H, $NCHCH_2CH_2CH_2CH_2CHN$); 3.78 and 3.79 (s, 18H, $CH_2C_6H_2(OCH_3)_2$-2,4,6); 4.42 and 4.45 (d, 4H, J = 14.4 Hz, $CH_2C_6H_2(OCH_3)_2$-2,4,6); 6.08 (s, 4H, $CH_2C_6H_2(OCH_3)_2$-2,4,6). ^{13}C-NMR ($CDCl_3$) *δ*: 162.28 (*C*-2); 22.35 ($NCHCH_2CH_2CH_2CH_2CHN$); 27.33 ($NCHCH_2CH_2CH_2CH_2CHN$); 39.30 ($NCHCH_2CH_2CH_2CH_2CHN$); 55.90 and 55.95 ($CH_2C_6H_2(OCH_3)_2$-2,4,6); 66.74 ($CH_2C_6H_2(OCH_3)_2$-2,4,6); 90.58, 101.67, 159.61, 161.86 ($CH_2C_6H_2(OCH_3)_2$-2,4,6). Anal. Calcd for $C_{27}H_{37}N_2O_6Cl$: C, 62.24; H, 7.10; N, 5.34. Found: C, 62.30; H, 7.19; N, 5.41.

Synthesis of 1,3-bis(4-ethoxy-3-methoxybenzyl)perhydrobenzimidazolinium chloride (3g).

This compound was prepared in same way as **3a** from *N,N'*-bis(4-ethoxy-3-methoxybenzyl)-1,2-cyclohexanediamine (2.49 g, 5.61 mmol), NH_4Cl (0.30 g, 5.61 mmol) and triethyl orthoformate (10 mL) to give colorless crystals of **3g**. Yield: 2.25 g, 82%, mp 85-86 °C. ^1H-NMR ($CDCl_3$) *δ*: 10.81 (s, 1H, 2-C*H*); 1.09-1.23 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 1.72-2.12 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 3.08-3.20 (m, 2H, $NCHCH_2CH_2CH_2CH_2CHN$); 3.92 (s, 6H, $CH_2C_6H_3(OCH_3)$-3); 1.44 (t, 6H, J = 6.9 Hz $CH_2C_6H_3(OCH_2CH_3)$-*p*); 4.06 (q, 4H, J = 6.9 Hz, $CH_2C_6H_3(OCH_2CH_3)$-*p*); 4.62 and 4.96 (d, 4H, J = 14.7 Hz, $CH_2C_6H_3(OCH_3)$-3); 6.77-6.86 and 7.12-7.15 (m, 6H, $CH_2C_6H_3(OCH_3)$-3). ^{13}C-NMR ($CDCl_3$) *δ*: 162.11 (2-*C*H); 23.62 ($NCHCH_2CH_2CH_2CH_2CHN$); 27.51 ($NCHCH_2CH_2CH_2CH_2CHN$); 50.76 ($NCHCH_2CH_2CH_2CH_2CHN$); 56.64 ($CH_2C_6H_3(OCH_3)$-3); 64.30 ($CH_2C_6H_3(OCH_2CH_3)$-*p*); 14.73 ($CH_2C_6H_3(OCH_2CH_3)$-*p*); 66.70 ($CH_2C_6H_3(OCH_3)$-3); 112.10, 112.37, 121.07, 125.36, 148.75, 149.91 ($CH_2C_6H_3(OCH_3)$-3). Anal. Calcd for $C_{27}H_{37}N_2O_4Cl$: C, 66.32; H, 7.57; N, 5.73. Found: C, 66.45; H, 7.68; N, 5.61.

Synthesis of 1,3-bis(9-anthracenylmethyl)perhydrobenzimidazolinium chloride (3h).

This compound was prepared in same way as **3a** from *N,N'*-bis(9-anhtracenylmethyl)-1,2-cyclohexanediamine (3.52 g, 7.10 mmol), NH_4Cl (0.38 g, 7.10 mmol) and triethyl orthoformate (10 mL) to give orange crystals of **3h**. Yield: 3.22 g, 84%, mp 223-225 °C. IR (cm^{-1}) ν: 1612 (NCN), ^1H NMR ($CDCl_3$) *δ*: 9.36 (s, 1H, C-2 *H*); 0.85-1.14 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 1.44-1.71 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$); 3.41-3.43 (m, 2H, $NCHCH_2CH_2CH_2CH_2CHN$); 5.76 and 5.84 (d, 4H, J = 11.4 Hz, CH_2An); 7.41 and 7.50 (t, 8H, J = 6.3 Hz, An*H*) (An: anthracene); 7.89 and 8.21 (d, 8H, J = 6.0 Hz, J = 6.6 Hz, An*H*); 8.37 (s, 2H, An*H*). ^{13}C-NMR ($CDCl_3$) *δ*: 161.51 (*C*-2); 23.75

(NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CH$_2$CHN); 27.94 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN); 44.16 (N*C*HCH$_2$CH$_2$CH$_2$CH$_2$*C*HN); 68.93 (*C*H$_2$An); 122.72, 123.36, 123.76, 125.50, 125.90, 127.95, 129.32, 129.49, 129.56, 130.02, 130.90, 131.31, 132.35, 135.41 (An*C*). Anal. Calcd for $C_{37}H_{33}N_2Cl$: C, 82.14; H, 6.10; N, 5.18. Found: C, 82.21; H, 6.19; N, 5.25.

General procedure for the Heck coupling reactions

Pd(OAc)$_2$ (1.0 mmol%), the appropriate 1,3-dialkylperhydrobenzimidazolinium salt **3a-h** (2 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol), water (3 mL) and DMF (3 mL) were added to a small Schlenk tube and the mixture was heated at 80 °C for 2 h. At the conclusion of the reaction, the mixture was cooled, extracted with EtOAc–hexane (1 : 5), filtered through a pad of silica gel with copious washing, concentrated and purified by flash chromatography on silica gel. All reactions were monitored by GC. The purity of the compounds was checked by NMR and yields are based on aryl bromide.

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