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The synthesis of oligoether-substituted benzimidazolium bromides and their use as ligand precursors for the Pd-catalyzed Heck coupling in water

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ABSTRACT

The oligoether-substituted ($CH_3(OCH_2CH_2)_n$–; $n = 1$, 2 or 3) benzimidazolium bromides (**3–7**) and oligoether-linked (–$CH_2(CH_2OCH_2)_nCH_2$–, $n = 1$, 2 or 3) bisbenzimidazolium dibromides (**8–13**) were prepared by quarternization of N-substituted benzimidazoles (**1** and **2**) with the bulky benzyl bromides ($ArCH_2Br$: Ar = $C_6H_2(CH_3)_3$-2,4,6 and $C_6(CH_3)_5$). *trans*-Bis(carbene) palladium(II) complexes **14** and **15** derived from **4** and **6** were synthesized by using Ag complexes as carbene-transfer agents in dichloromethane at ambient temperature. In addition, the reactions of **4** and **6** with $Pd(OAc)_2$ and NaBr gave the Pd(II) dimers **16** and **17** which can readily be cleaved by triphenylphosphine to afford the benzannulated monocarbene (NHC) monophosphine Pd(II) complexes [$PdBr_2$(NHC)(PPh_3)] (**18** and **19**). All compounds have been fully characterized by using elemental analysis, ^1H, ^{13}C and ^{31}P NMR spectroscopies. X-ray diffraction studies on single crystals of **19a** and **19b** confirm the *cis* square planar geometry. In situ formed complexes from $Pd(OAc)_2$ and benzimidazolium salts (**3–13**) and preformed Pd(II) complexes **14**, **15**, **18** and **19** were tested as catalyst for the Heck coupling reaction in water. The influence of the oligoether and benzyl substituents on N atoms and CH_3-substituents on the 5,6-positions of benzimidazole frame were investigated under the same conditions in the Heck coupling reaction. In situ formed catalysts showed better conversions than the isolated Pd(II) complexes. The length of the oligoether spacer significantly increases the activity. The salts with two benzimidazole moieties connected by an oligoether as the spacer **8–13** showed similar catalytic activities in the Heck coupling reaction with the mono salts **3–7** bearing corresponding oligoethers on the N atom.

1. Introduction

The transition metal complexes of *N*-heterocyclic carbenes (NHCs) based on imidazole, imidazoline and benzimidazole framework have been the focus of intense research in organometallic chemistry and homogeneous catalysis [1], for example, palladium–NHC complexes have been employed as catalysts for the Mizoroki–Heck and Suzuki–Miyaura C–C coupling reactions because of their facile preparation methods and better stability toward air and moisture [1f,2]. Even, benzannulated carbenes derived from benzimidazolium precursors exhibit interesting properties due to their intermediate position between saturated and unsaturated analogues [3], only a few groups reported the catalytic activities of Pd(II) benzimidazole-2-ylidene complexes [4].

Incorporation of alkoxyethyl substituents on N atom(s) of a variety of the NHC rings has shown enhanced activity over their hydrocarbon analogues [5]. Furthermore, highly active water-soluble ruthenium catalysts bearing oligoether-attached NHC ligands for olefin metathesis have been reported [6]. Some related imidazolium salts bearing oligoether substituents [7], and Hg(II)-and Ag(I)–NHC complexes of oligoether bridged benzimidazolin-2-ylidene [8] were reported while this work was in progress. Tsuji and co-workers reported that the NHC derivatives bearing hydrophilic tetraethylene glycol (TEG) chains on both sides of NHC ring enhance the catalytic activity considerably in the Suzuki–Miyaura coupling reaction [9]. Inspired by these reports, we decided to examine the influence of oligoether incorporated benzimidazolium salts as NHC precursors for the Pd(II) catalyzed C–C coupling reactions. We have also synthesized and characterized the bis(carbene) Pd(II) and mixed NHC–phosphine–Pd(II) complexes derived from the benzimidazolium salts. The Mizoroki–Heck reaction was used to compare the catalytic activities of both in situ formed and preformed carbene complexes of benzimidazolium salts with $Pd(OAc)_2$ and isolated NHC–Pd(II) complexes in water.

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2. Results and discussion

2.1. Synthesis and characterization of oligoether-substituted (5,6-dimethyl)benzimidazolium bromides (**3–7**) and oligoether-linked bis(5,6-dimethyl)benzimidazolium dibromides (**8–13**)

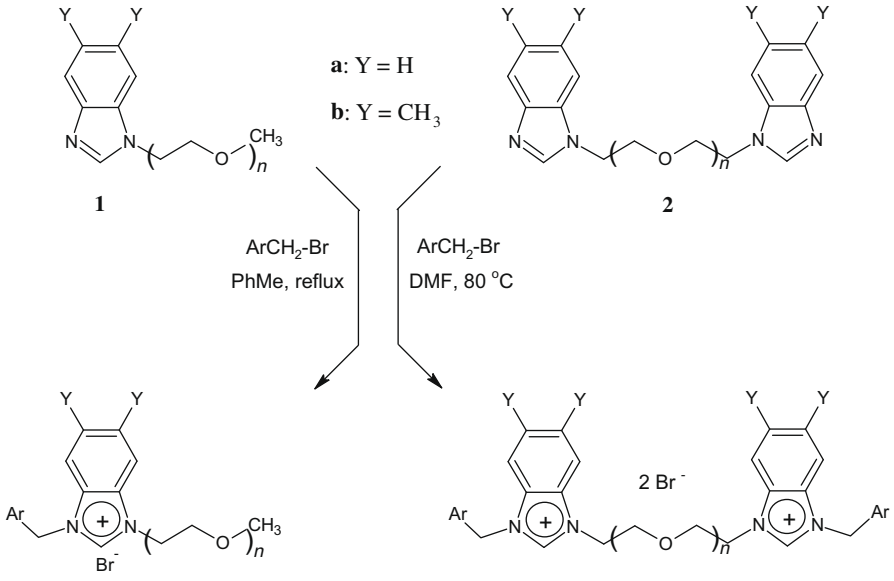
The (5,6-dimethyl)benzimidazolium bromides (**3–7**) were obtained in almost quantitative yield by quarternization of 1-oligoether-substituted (5,6-dimethyl)benzimidazole (**1**) in PhMe with the alkylated benzyl bromides (Scheme 1). In a similar manner, bis(5,6-dimethyl)benzimidazolium dibromide salts (**8–13**) were obtained in a moderate yield by quarternization of oligoether bridged (5,6-dimethyl)benzimidazole (**2**), in DMF with alkylated benzyl bromides. These salts are air-stable, colorless solids. The ^{1}H NMR spectra of these salts exhibit characteristic NC*H*N resonance at δ = 8.74–11.14 ppm. The formation of the salts was also supported by a resonance at δ = 139.5–143.4 ppm in the ^{13}C NMR spectrum for the NCHN carbon atom.

2.2. Synthesis and characterization of palladium complexes, **14–19**

In general, the bis(carbene) complexes of palladium(II) can be prepared by deprotonation of two equivalent azolium salts with $Pd(OAc)_2$ [4n,10]. The bis(carbene) Pd(II) complexes **14** and **15** bearing one oligoether substition on N^1 of (5,6-dimethyl)benzimidazole were synthesized by carbene-transfer reaction of in situ formed NHC–Ag species with $[PdCl_2(MeCN)_2]$ in dichloromethane at ambient temperature [11]. The complexes **14** and **15** were obtained in high yields as air-stable yellow solids, soluble in halogenated solvents (Scheme 2). The characteristics downfield signals for the NC*H*N proton of the benzimidazolium salts (**4** and **6**) were not observed in the ^{1}H NMR spectra of bis(carbene) Pd(II) complexes. ^{13}C NMR spectrum of bis(carbene) Pd(II) complexes (**14** and **15**) showed $C_{carbene}$ resonance between δ 180.8 and 182.4 ppm, which is consistent with the range for the reported *trans*-configurated benzimidazole-2-ylidene Pd(II) complexes [4f,j,l,11,12].

A synthetic pathway for the dimeric Pd(II) carbene complexes by reaction of benzimidazolium salt with $Pd(OAc)_2$ in the presence of NaBr in DMSO has been reported by Huynh [4i]. The dimeric Pd(II) carbene complexes of N^1-oligoether-substituted (5,6-dimethyl)benzimidazole-2-ylidenes (**16** and **17**) were obtained in about 80% yield by this procedure as air-stable orange solids soluble in halogenated solvents (Scheme 2). The formation of complexes was confirmed by the absence of the downfield signal for the NC*H*N proton in the ^{1}H NMR spectra. ^{13}C NMR spectrum of the dimeric Pd(II) carbene complexes **16** and **17** showed $C_{carbene}$ resonance between δ 156.9 and 159.5 ppm, which is in a good range for the previously reported dimeric benzimidazole-2-ylidene Pd(II) complexes [4c,d].

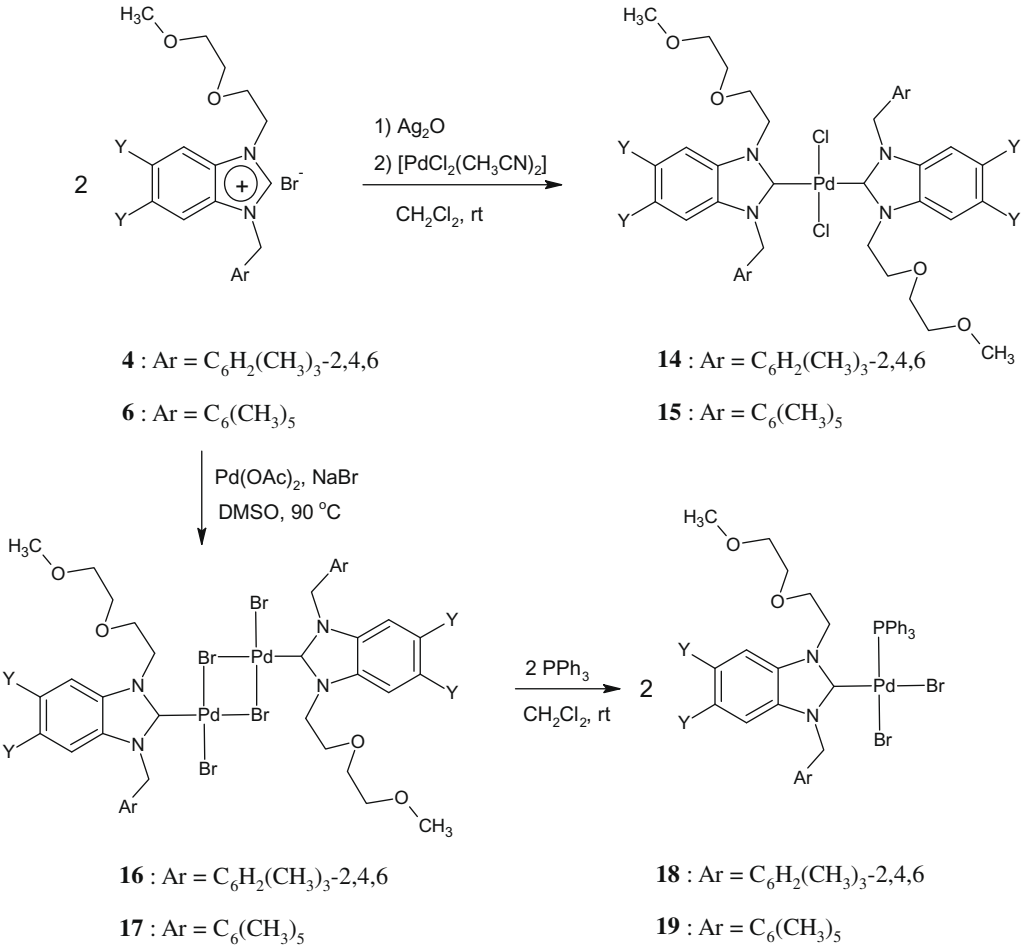
Dimeric Pd(II) carbene complexes are useful precursors for the preparation of neutral and mixed NHC–phosphine complexes of Pd(II) under mild conditions. Previously mixed NHC–phosphine complexes of Pd(II) derived from benzimidazolin-2-ylidene by cleavage of dimeric Pd(II) carbene complex with triphenylphosphine in dichloromethane have been reported [4c,i]. The dimeric Pd(II) carbene complexes **16** and **17** and triphenylphosphine reacted in dichloromethane to give mixed NHC–phosphine complexes of Pd(II) **18** and **19** as air-stable yellow solids soluble in halogenated solvents in about 90% yield (Scheme 2). NMR analyses of the complexes showed that the triphenylphosphine ligands coordinated the palladium center. ^{13}C NMR spectrum of the complexes **18** and **19** shown $C_{carbene}$ resonance between δ 173.1 and 175.6 ppm. The presence of triphenylphosphine is also demon-



3: n = 1; Ar = $C_6H_2(CH_3)_3$-2,4,6;
4: n = 2; Ar = $C_6H_2(CH_3)_3$-2,4,6;
5: n = 1; Ar = $C_6(CH_3)_5$;
6: n = 2; Ar = $C_6(CH_3)_5$;
7: n = 3; Ar = $C_6(CH_3)_5$;

8 : n = 1; Ar = $C_6H_2(CH_3)_3$-2,4,6;
9 : n = 2; Ar = $C_6H_2(CH_3)_3$-2,4,6;
10: n = 3; Ar = $C_6H_2(CH_3)_3$-2,4,6;
11: n = 1; Ar = $C_6(CH_3)_5$;
12: n = 2; Ar = $C_6(CH_3)_5$;
13: n = 3; Ar = $C_6(CH_3)_5$

Scheme 1. Synthesis of benzimidazolium salts.



Scheme 2. Synthesis of NHC–Pd(II) complexes.

strated by ^{31}P NMR spectroscopy, where one singlet between δ 26.99 and 27.20 ppm for the complexes **18** and **19** was observed.

2.3. Molecular structures of complexes *19a* and *19b*

The molecular view of compounds **19a** and **19b** are represented in Figs. 1 and 2. In both of them, the Pd atom is coordinated to two bromine, the phosphorus atom of a triphenyl phosphine ligand and the C atom of an *N*-heterocyclic carbene in a square planar geometry. The geometry of the square plane is very similar for the two compounds.

Expectedly, the Pd–Br bond lengths *trans* to carbene are slightly but significantly shorter than the Pd–Br bonds trans to phosphorus (Table 1). The heterocyclic carbene ring is oriented nearly perpendicular to the Pd square plane making a dihedral angle of 77.21(11)° and 86.03(8)°, respectively, for **19a** and **19b**.

2.4. Catalysis

The catalytic activities of compounds (with 1.5 mol% catalyst loading) were investigated in the Heck coupling reaction at 100 °C and Cs_2CO_3 was used as base. Reactions were performed in air and without any additive and the results are summarized in Table 2. The initial studies have been carried out using the in situ formed complexes with $Pd(OAc)_2$ and oligoether-substituted (5,6-dimethyl)benzimidazolium bromide salts (**3–7**, entries 1–10) and oligoether-linked bis(5,6-dimethyl)benzimidazolium dibromides (**8–13**, entries 11–22) under identical conditions. As

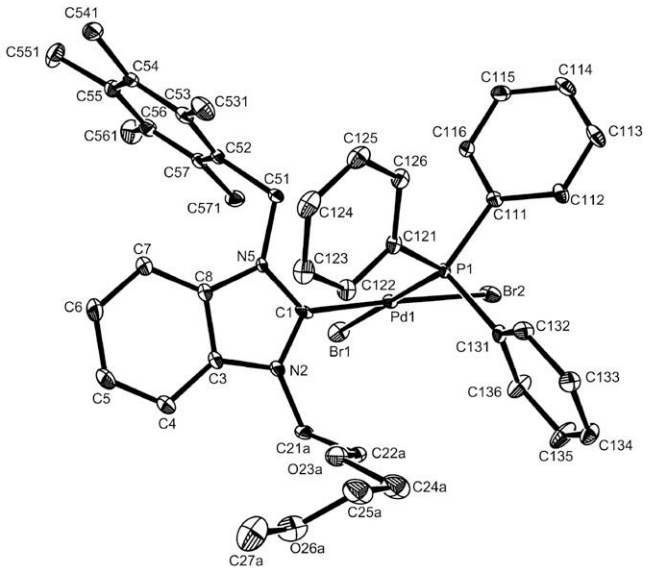


Fig. 1. Molecular view of complexes **19a** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. In compound **19a** only the major component of the disordered $(CH_2)_2O(CH_2)_2OCH_3$ chain is represented.

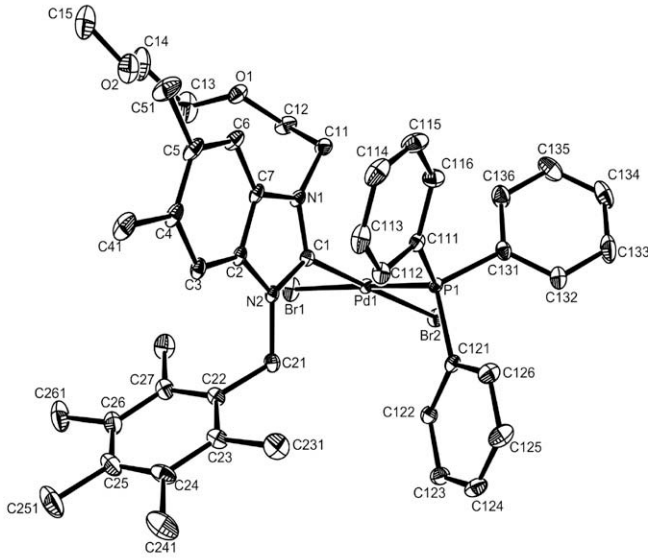


Fig. 2. Molecular view of complexes **19b** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. In compound **19a** only the major component of the disordered $(CH_2)_2O(CH_2)_2OCH_3$ chain is represented.

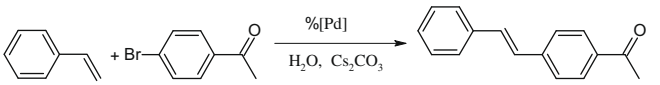
Table 1
Selected bond distances (Å) and angles (°) for **19a** and **19b**.

	19a	19b
Pd Br1	2.4606(5)	2.4627(8)
Pd Br2	2.4648(5)	2.4726(8)
Pd P	2.2667(9)	2.2620(9)
Pd C	2.001(4)	1.986(2)
Br1–Pd–Br2	91.173(18)	93.50(4)
Br1–Pd–P	178.62(3)	176.387(17)
Br1–Pd–C	86.57(10)	87.41(7)
Br2––Pd–P	87.46(3)	89.42(4)
Br2–Pd–C	177.00(10)	178.81(7)
P–Pd–C	94.81(10)	89.69(8)

the number of OCH_2CH_2 entities increase the catalytic activity slightly increases: $n = 3 > n = 2 > n = 1$. We also observed that both the pentamethylbenzyl substituent on N^3 position of benzimidazolium salts and the methyl groups on 5,6-position of benzimidazole ring increase the catalytic activity. These results are comparable with the previously reported studies [13]. Similarly, bis(carbene) Pd(II) complexes (**14** and **15**, entries 23–26) and mixed NHC–phosphine complexes of Pd(II) (**18** and **19**, entries 27–30) were tested for the same coupling reaction. The results showed that the mixed NHC–phosphine complexes have better activities (entires 27–30) than the classic bis(carbene) Pd(II) complexes (entries 23–26). However, it is worthy to note that the in situ formed complexes of the ligand by deprotonation of the (5,6-dimethyl)benzimidazolium bromides led to significantly better results (entries 3, 4 and 7, 8) than the use of the both bis(carbene) Pd(II) complexes and mixed NHC–phosphine complexes. Generally, in situ formed catalyst show better conversions than the isolated Pd(II) complexes. It is possible that the activity difference between $Pd(OAc)_2$/**4**, **6** system and preformed **14**, **15** or **18**, **19** is due to the additional species, such as AcO^-/AcOH in the in situ generated catalyst mixtures. In connection with this assumption, a recent report stated that weakly coordinating acetate counterions incorporated to NHC–Pd(II) complexes enhance the catalytic activity [14].

Reusability of the catalyst **6b** showed only 5% difference at three reaction cycles (Table 3).

Table 2
The Heck coupling reaction of styrene with aryl bromide.



Entry	Catalyst	Yield (%)
1	**3a**	71
2	**3b**	76
3	**4a**	84
4	**4b**	88
5	**5a**	86
6	**5b**	91
7	**6a**	92
8	**6b**	95
9	**7a**	93
10	**7b**	95
11	**8a**	73
12	**8b**	75
13	**9a**	83
14	**9b**	85
15	**10a**	89
16	**10b**	90
17	**11a**	87
18	**11b**	88
19	**12a**	90
20	**12b**	93
21	**13a**	92
22	**13b**	96
23	**14a**	56
24	**14b**	59
25	**15a**	61
26	**15b**	63
27	**18a**	73
28	**18b**	80
29	**19a**	77
30	**19b**	81

Reaction conditions: 1.0 mmol *p*-$BrC_6H_4COCH_3$, 1.5 mmol styrene, 2.0 mmol Cs_2CO_3, 1. 5 mmol% $Pd(OAc)_2$, 3.0 mmol% **3**–**7** or 1.5 mmol% **8**–**13**, water (3.0 mL), diethyleneglycol-di-*n*-butyl ether as the internal standard. Purity of compound was checked by ^1H NMR and yields are based on aryl bromide, 100 °C, 4 h. GC yields.

Table 3
Reusability of the benzimidazolium salt (**6b**) in Heck coupling.

Recycles	1st	2nd	3rd
Yield (%)	95	92	90

3. Conclusions

Benzimidazolium bromides (**3**–**7**) bearing oligoether side chains $–(CH_2CH_2O)_n–$ ($n = 1$, 2 or 3) and oligoether-linked bis-benzimidazolium dibromides (**8**–**13**) were synthesized, characterized and used with $Pd(OAc)_2$ as in situ formed Heck coupling catalyst. The former series were converted to synthesize bis, dimeric and mixed Pd–NHC complexes **14** and **15**, **16** and **17** and **18** and **19**, respectively. The identity of **19a** and **19b** as *cis*-complexes has been confirmed by X-ray diffraction studies. Both the longer oligoether and bulky benzyl substituents on N atoms and the methyl groups on 5,6-position of benzimidazole ring gave an enhanced reaction rate. On the basis of such results, it is not unreasonable to assume that the interactions between the O atoms of the oligoether and the palladium center could play an important role.

4. Experimental

Unless otherwise noted all manipulations were performed in air. All solvents used as received. 2,4,6-Trimethylbenzyl bromide, 2,3,4,5,6-pentamethylbenzyl bromide were synthesized according to methods previously known [15]. Substituted- or linled- oligoether functionalized (5,6-dimethyl)benzimidazoles and (5,6-dimethyl)bisbenzimidazoles (**1** and **2**) were prepared according to a slightly modified procedure from Refs. [5,16]. All reagents were purchased from Merck, Fluka, Alfa Aesar and Acros Organics. Melting points were recorded with Gallenkamp electrothermal melting point apparatus. ^{1}H NMR, ^{13}C NMR and ^{31}P spectra were recorded with a Varian AS 400 Mercury instrument. As solvents $CDCl_3$, were employed. Chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer.

4.1. Preparation of oligoether-substituted (5,6-dimethyl)benzimidazolium bromides (**3–7**)

1-Alkyl-(5,6-dimethyl)benzimidazole (5.0 mmol) was dissolved in toluene (20 mL) and then 2,4,6-trimethylbenzyl bromide or 2,3,4,5,6-pentamethylbenzyl bromide (5.0 mmol) was added. The mixture was refluxed for 6 h. The solid that separated out after cooling was filtered off and washed with diethyl ether (20 mL). The product was recrystallized from CH_2Cl_2/Et_2O. The following salts **3**–**7** were synthesized according to this procedure.

4.1.1. Synthesis of 1-(2-methoxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazolium bromide (**3a**)

Yield: 97%, m.p. = 205 °C. Anal. Calc. for $C_{20}H_{25}BrN_2O$ (389.3): C, 61.70; H, 6.47; N, 7.20. Found: C, 61.58; H, 6.54; N, 7.12%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.22 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.23 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.23 (s, 3H, OCH_3), 3.82 (t, J = 4.0 Hz, 2H, CH_2), 4.84 (t, J = 4.0 Hz, 2H, CH_2), 5.75 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.88 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.36 (d, J = 8.0 Hz, 1H, Ar–H), 7.44 (t, J = 7.6 Hz, 1H, Ar–H), 7.53 (t, J = 7.6 Hz, 1H, Ar–H), 7.53 (d, J = 8.0 Hz, 1H, Ar–H), 10.33 (s, 1H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.2, 21.2, 47.2, 48.0, 59.0, 69.8, 113.7, 114.4, 125.1, 127.4, 130.3, 131.3, 132.1, 138.1, 139.9, 142.1 (NCN) ppm.

4.1.2. Synthesis of 1-(2-methoxyethyl)-3-(2,4,6-trimethylbenzyl)-5,6-dimethylbenzimidazolium bromide (**3b**)

Yield: 93%, m.p. = 203 °C. Anal. Calc. for $C_{22}H_{29}BrN_2O$ (417.4): C, 63.31; H, 7.00; N, 6.71. Found: C, 63.44; H, 7.09; N, 6.74%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.21 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.23 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.27 (s, 3H, CH_3–Ar), 2.34 (s, 3H, CH_3–Ar), 3.21 (s, 3H, OCH_3), 3.79 (t, J = 4.2 Hz, 2H, CH_2), 4.75 (t, J = 4.2 Hz, 2H, CH_2), 5.64 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.87 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.14 (s, 1 H, Ar–H), 7.61 (s, 1H, Ar–H), 9.98 (s, 1H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.2, 20.7, 20.8, 21.2, 46.8, 47.8, 59.1, 69.8, 113.3, 113.8, 125.2, 129.9, 130.2, 130.6, 137.6, 138.1, 139.9, 140.8 (NCN) ppm.

4.1.3. Synthesis of 1-[2-(2-methoxyethoxy)ethyl]-3-(2,4,6-trimethylbenzyl)benzimidazolium bromide (**4a**)

Yield: 93%. m.p. = 147 °C. Anal. Calc. for $C_{22}H_{29}BrN_2O_2$ (433.4): C, 60.97; H, 6.74; N, 6.46. Found: C, 61.01; H, 6.71; N, 6.43%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.26 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.28 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.21 (s, 3H, OCH_3), 3.37 (t, J = 4.4 Hz, 2H, CH_2), 3.60 (t, J = 4.4 Hz, 2H, CH_2), 4.00 (t, J = 4.4 Hz, 2H, CH_2), 4.87 (t, J = 4.4 Hz, 2H, CH_2), 5.74 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.91 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.35 (d, J = 8.4 Hz, 1H, Ar–H), 7.45 (t, J = 7.2 Hz, 1H, Ar–H), 7.55 (t, J = 7.2 Hz, 1H, Ar–H), 7.92 (d, J = 8.2 Hz, 1H, Ar–H), 10.44 (s, 1H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.4, 21.3, 47.2, 48.1, 59.1, 68.7, 70.6, 71.9, 113.5, 114.5, 125.1, 127.2, 127.4, 130.4, 131.4, 132.4, 138.3, 140.1, 142.7 (NCN) ppm.

4.1.4. Synthesis of 1-[2-(2-methoxyethoxy)ethyl]-3-(2,4,6-trimethylbenzyl)-5,6-dimethylbenzimidazolium bromide (**4b**)

Yield: 91%. m.p. = 138 °C. Anal. Calc. for $C_{24}H_{33}BrN_2O_2$ (461.4): C, 62.47; H, 7.21; N, 6.07. Found: C, 62.49; H, 7.24; N, 6.10%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.27 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.28 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.31 (s, 3H, CH_3–Ar), 2.38 (s, 3H, CH_3–Ar), 3.23 (s, 3H, OCH_3), 3.37 (t, J = 4.8 Hz, 2H, CH_2), 3.59 (t, J = 4.8 Hz, 2H, CH_2), 3.97 (t, J = 4.8 Hz, 2H, CH_2), 4.80 (t, J = 4.8 Hz, 2H, CH_2), 5.72 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.92 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.15 (s, 1H, Ar–H), 7.66 (s, 1H, Ar–H), 10.05 (s, 1H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.2, 20.7, 20.9, 21.2, 46.7, 47.9, 59.0, 68.6, 70.5, 71.8, 113.2, 114.0, 125.2, 130.0, 130.2, 137.5, 138.2, 140.5 (NCN) ppm.

4.1.5. Synthesis of 1-(2-methoxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium bromide (**5a**)

This salt was synthesized according to published procedure [4c]

4.1.6. Synthesis of 1-(2-methoxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazolium bromide (**5b**)

Yield: 95%, m.p. = 166 °C. Anal. Calc. for $C_{24}H_{33}BrN_2O$ (445.4): C, 64.71; H, 7.47; N, 6.29. Found: C, 64.65; H, 7.39; N, 6.31%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.23 (s, 6H, $CH_2C_6(CH_3)_5$), 2.25 (s, 6H, $CH_2C_6(CH_3)_5$), 2.27 (s, 3H, $CH_2C_6(CH_3)_5$), 2.37 (s, 3H, CH_3–Ar), 2.41 (s, 3H, CH_3–Ar), 3.24 (s, 3H, OCH_3), 3.80 (t, J = 4.0 Hz, 2H, CH_2), 4.84 (t, J = 4.0 Hz, 2H, CH_2), 5.62 (s, 2H, $CH_2C_6(CH_3)_5$), 7.33 (s, 1H, Ar–H), 7.66 (s, 1H, Ar–H), 9.54 (s, 1H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.0, 17.1, 17.4, 20.8, 20.9, 47.6, 48.0, 59.1, 70.1, 113.1, 114.0, 124.9, 129.9, 130.8, 133.7, 134.1, 137.5, 137.7, 140.2 (NCN) ppm.

4.1.7. Synthesis of 1-[2-(2-methoxyethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium bromide (**6a**)

Yield: 98%. m.p. = 164 °C. Anal. Calc. for $C_{24}H_{33}BrN_2O_2$ (461.4): C, 62.47; H, 7.21; N, 6.07. Found: C, 62.42; H, 7.19; N, 6.11%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.17 (s, 3H, $CH_2C_6(CH_3)_5$), 2.19 (s, 6H, $CH_2C_6(CH_3)_5$), 2.25 (s, 6H, $CH_2C_6(CH_3)_5$), 3.20 (s, 3H, OCH_3), 3.36 (t, J = 4.6 Hz, 2H, CH_2), 3.59 (t, J = 4.6 Hz, 2H, CH_2), 3.98 (t, J = 4.4 Hz, 2H, CH_2), 4.94 (t, J = 4.4 Hz, 2H, CH_2), 5.73 (s, 2H, $CH_2C_6(CH_3)_5$), 7.54–760 (m, 3H, Ar–H), 7.99 (d, J = 8.0 Hz, 1H, Ar–H), 9.93 (s, 1H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.2, 17.3, 17.5, 48.0, 48.3, 59.0, 68.9, 70.6, 71.8, 113.4, 114.8, 124.8, 127.4, 127.4, 131.4, 132.5, 133.8, 134.3, 137.7, 142.0 (NCN) ppm.

4.1.8. Synthesis of 1-[2-(2-methoxyethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazolium bromide (**6b**)

Yield: 95%, m.p. = 198 °C. Anal. Calc. for $C_{26}H_{37}BrN_2O_2$ (489.5): C, 63.80; H, 7.62; N, 5.72. Found: C, 63.77; H, 7.58; N, 5.74%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.20 (s, 6H, $CH_2C_6(CH_3)_5$), 2.21 (s, 6H, $CH_2C_6(CH_3)_5$), 2.23 (s, 3H, $CH_2C_6(CH_3)_5$), 2.36 (s, 3H, CH_3–Ar), 2.38 (s, 3H, CH_3–Ar), 3.17 (s, 3H, OCH_3), 3.31 (t, J = 4.6 Hz, 2H, CH_2), 3.52 (t, J = 4.6 Hz, 2H, CH_2), 3.89 (t, J = 4.6 Hz, 2H, CH_2), 4.82 (t, J = 4.6 Hz, 2H, CH_2), 5.59 (s, 2H, $CH_2C_6(CH_3)_5$), 7.39 (s, 1H, Ar–H), 7.74 (s, 1H, Ar–H), 9.37 (s, 1H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 16.9, 17.0, 17.3, 20.6, 20.7, 47.0, 47.7, 58.7, 68.3, 70.3, 71.5, 113.0, 113.9, 124.7, 129.9, 130.5, 133.6, 133.9, 137.6, 139.5 (NCN) ppm.

*4.1.9. Synthesis of 1-[2-(2-(2-methoxyethoxy)ethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium bromide (**7a**)*

Yield: 89%, m.p. = 118 °C. Anal. Calc. for $C_{26}H_{37}BrN_2O_3$ (505.5): C, 61.78; H, 7.38; N, 5.54. Found: C, 61.75; H, 7.48; N, 5.61%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.26 (s, 6H, $CH_2C_6(CH_3)_5$), 2.28 (s, 6H, $CH_2C_6(CH_3)_5$), 2.29 (s, 3H, $CH_2C_6(CH_3)_5$), 3.30 (s, 3H, OCH_3), 3.42 (t, J = 4.2 Hz, 2H, CH_2), 3.46–3.49 (m, 4H, CH_2), 3.62 (t, J = 4.2 Hz, 2H, CH_2), 3.99 (t, J = 4.8 Hz, 2H, CH_2), 4.96 (t, J = 4.4 Hz, 2H, CH_2), 5.77 (s, 2H, $CH_2C_6(CH_3)_5$), 7.58–7.65 (m, 3H, Ar–*H*), 8.07 (d, J = 8.8 Hz, 1H, Ar–*H*), 9.84 (s, 1H, NC*H*N) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.1, 17.2, 17.4, 40.0, 48.2, 59.0, 68.8, 70.3, 70.7, 71.8, 113.6, 114.7, 124.9, 127.5, 131.4, 132.3, 133.8, 134.1, 137.5, 141.6 (N*C*N) ppm.

*4.1.10. Synthesis of 1-[2-(2-(2-methoxyethoxy)ethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazolium bromide (**7b**)*

Yield: 92%, m.p. = 135 °C. Anal. Calc. for $C_{28}H_{41}BrN_2O_3$ (533.6): C, 63.03; H, 7.75; N, 5.25. Found: C, 63.12; H, 7.67; N, 5.17%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.16 (s, 3H, $CH_2C_6(CH_3)_5$), 2.21 (s, 6H, $CH_2C_6(CH_3)_5$), 2.24 (s, 6H, $CH_2C_6(CH_3)_5$), 2.34 (s, 3H, CH_3–Ar), 2.37 (s, 3H, CH_3–Ar), 3.25 (s, 3H, OCH_3), 3.35 (t, J = 4.8 Hz, 2H, CH_2), 3.40–3.46 (m, 4H, CH_2), 3.56 (t, J = 4.4 Hz, 2H, CH_2), 3.93 (t, J = 4.4 Hz, 2H, CH_2), 4.82 (t, J = 4.6 Hz, 2H, CH_2), 5.65 (s, 2H, $CH_2C_6(CH_3)_5$), 7.30 (s, 1H, Ar–*H*), 7.77 (s, 1H, Ar–*H*), 9.73 (s, 1H, NC*H*N$^+$) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.0, 17.2, 17.4, 20.7, 20.9, 47.5, 59.0, 68.9, 70.4, 70.7, 71.8, 113.0, 114.2, 124.9, 130.0, 130.8, 133.8, 134.1, 137.6, 137.7, 140.2 (N*C*N) ppm.

*4.2. Preparation of linked-oligoether functionalized (5,6-dimethyl)benzimidazolium dibromides (**8–13**)*

The linked-oligoether functionalized benzimidazole (2.5 mmol) was dissolved in DMF (20 mL) and 2,4,6-trimethylbenzyl bromide or 2,3,4,5,6-pentamethylbenzyl bromide was added. The mixture was heated at 80 °C for 24 h. After completion of the reaction, the volume of DMF was reduced to *ca.* 2 mL and diethyl ether added (20 mL) then the products were obtained with crystallization from CH_2Cl_2/Et_2O. The following salts (**8–13**) were synthesized according to this procedure.

*4.2.1. Synthesis of 1,1′-di(2,4,6-trimethylbenzyl)-3,3′-oxapentanebibenzimidazolium dibromide (**8a**)*

Yield: 51%, m.p. = 220 °C. Anal. Calc. for $C_{38}H_{44}Br_2N_4O$ (752.6): C, 62.30; H, 6.05; N, 7.65. Found: C, 62.58; H, 5.95; N, 7.58%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.25 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.29 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.11 (t, J = 4.8 Hz, 4H, CH_2), 4.95 (t, J = 4.4 Hz, 4H, CH_2), 5.99 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.88 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.06 (d, J = 8.8 Hz, 2H, Ar–*H*), 7.37 (t, J = 8.6 Hz, 2H, Ar–*H*), 7.53 (t, J = 8.0 Hz, 2H, Ar–*H*), 8.03 (d, J = 8.4 Hz, 2H, Ar–*H*), 11.14 (s, 2H, NC*H*N) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.6, 21.2, 47.7, 48.0, 68.4, 114.0, 114.1, 125.7, 127.5, 130.4, 131.8, 138.1, 139.7, 143.4 (N*C*N) ppm.

*4.2.2. Synthesis of 1,1′-di(2,4,6-trimethylbenzyl)-3,3′-oxapentane-5,6-dimethylbibenzimidazolium dibromide (**8b**)*

Yield: 73%, m.p. = 234 °C. Anal. Calc. for $C_{42}H_{52}Br_2N_4O$ (788.7): C, 63.96; H, 6.65; N, 7.10. Found: C, 63.74; H, 6.60; N, 7.17%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.26 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.33 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.41 (s, 12H, CH_3–Ar), 4.08 (t, J = 4.0 Hz, 4H, CH_2), 4.84 (t, J = 4.4 Hz, 4H, CH_2), 5.92 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.85 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.90 (s, 4H, Ar–*H*), 10.93 (s, 2H, NC*H*N) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.1, 20.6, 21.3, 45.8, 47.0, 68.2, 113.9, 114.2, 126.8, 130.2, 130.5, 130.5, 136.9, 137.1, 138.8, 139.3, 141.2 (N*C*N) ppm.

*4.2.3. Synthesis of 1,1′-di(2,4,6-trimethylbenzyl)-3,3′-dioxaoctanebibenzimidazolium dibromide (**9a**)*

Yield: 50%, m.p. = 201 °C. Anal. Calc. for $C_{40}H_{48}Br_2N_4O_2$ (776.6): C, 61.86; H, 6.23; N, 7.21. Found: C. 61.92; H. 6.32; N, 7.08%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.25 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.27 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.57 (s, 4H, CH_2), 4.00 (t, J = 4.0 Hz, 4H, CH_2), 4.87 (t, J = 4.4 Hz, 4H, CH_2), 5.87 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.90 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.26 (d, J = 8.0 Hz, 2H, Ar–*H*), 7.43 (t, J = 8.0 Hz, 2H, Ar–*H*), 7.58 (t, J = 7.6 Hz, 2H, Ar–*H*), 8.00 (d, J = 8.4 Hz, 2H, Ar–*H*), 10.57 (s, 2H, NC*H*N) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.5, 21.3, 47.5, 48.1, 68.4, 70.9, 113.8, 114.4, 125.5, 127.4, 127.4, 130.4, 131.4, 132.0, 138.9, 139.7, 142.8 (N*C*N) ppm.

*4.2.4. Synthesis of 1,1′-di(2,4,6-trimethylbenzyl)-3,3′-dioxaoctane-5,6-dimethylbibenzimidazolium dibromide (**9b**)*

Yield: 78%, m.p. = 231 °C. Anal. Calc. for $C_{44}H_{56}Br_2N_4O_2$ (832.8): C, 63.46; H, 6.78; N, 6.73. Found: C, 63.77; H, 6.70; N, 6.61%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.15 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.23 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.26 (s, 6H, CH_3–Ar), 2.41 (s, 6H, CH_3–Ar), 3.55 (s, 4H, CH_2), 3.98 (t, J = 4.8 Hz, 4H, CH_2), 4.78 (t, J = 4.8 Hz, 4H, CH_2), 5.77 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.90 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.02 (s, 2H, Ar–*H*), 7.72 (s, 2H, Ar–*H*), 10.30 (s, 2H, NC*H*N) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.4, 20.7, 20.9, 21.2, 47.0, 47.9, 68.4, 70.9, 113.4, 113.8, 125.6, 129.9, 130.2, 130.4, 137.4, 137.6, 138.2, 139.7, 141.3 (N*C*N) ppm.

*4.2.5. Synthesis of 1,1′-di(2,4,6-trimethylbenzyl)-3,3′-trioxaundecanebibenzimidazolium dibromide (**10a**)*

Yield: 42%, m.p. = 91 °C. Anal. Calc. for $C_{42}H_{52}Br_2N_4O_3$ (820.7): C, 61.47; H, 6.39; N, 6.83. Found: C, 61.19; H, 6.26; N, 7.01%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 8 2.41 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.65 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.40–3.55 (m, 8H, CH_2), 3.99 (t, J = 4.4 Hz, 4H, CH_2), 4.87 (t, J = 4.4 Hz, 4H, CH_2), 5.79 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.88 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.30 (d, J = 8.4 Hz, 2H, Ar–*H*), 7.42 (t, J = 8.0 Hz, 2H, Ar–*H*), 7.53 (t, J = 7.6 Hz, 2H, Ar–*H*), 8.02 (d, J = 8.0 Hz, 2H, Ar–*H*), 10.30 (s, 2H, NC*H*N) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.4, 21.3, 47.4, 48.2, 68.5, 70.7, 70.8, 113.7, 114.5, 125.3, 127.3, 130.4, 131.4, 132.1, 138.2, 139.9, 142.7 (N*C*N) ppm.

*4.2.6. Synthesis of 1,1′-di(2,4,6-trimethylbenzyl)-3,3′-trioxaundecane-5,6-dimethylbibenzimidazolium dibromide (**10b**)*

Yield: 65%, m.p. = 163 °C. Anal. Calc. for $C_{46}H_{60}Br_2N_4O_3$ (876.8): C, 63.01; H, 6.90; N, 6.39. Found: C, 63.17; H, 6.82; N, 6.34%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.25 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.26 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.28 (s, 6H, CH_3–Ar), 2.34 (s, 6H, CH_3–Ar), 3.48 (t, J = 4.4 Hz, 4H, CH_2), 3.58 (t, J = 4.8 Hz, 4H, CH_2), 4.01 (t, J = 4.8 Hz, 4H, CH_2), 4.84 (t, J = 4.8 Hz, 4H, CH_2), 5.76 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.86 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.02 (s, 2H, Ar–*H*), 7.79 (s, 2H, Ar–*H*), 10.18 (s, 2H, NC*H*N) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.5, 20.7, 20.9, 21.3, 47.1, 48.1, 68.4, 70.6, 70.8, 113.3, 114.1, 125.9, 130.0, 130.2, 130.6, 136.9, 137.2, 138.3, 139.5, 141.9 (N*C*N) ppm.

*4.2.7. Synthesis of 1,1′-di(2,3,4,5,6-pentamethylbenzyl)-3,3′-oxapentanebibenzimidazolium dibromide (**11a**)*

Yield: 53%, m.p. = 223 °C. Anal. Calc. for $C_{42}H_{52}Br_2N_4O$ (788.7): C, 63.96; H, 6.65; N, 7.10. Found: C, 63.91; H, 6.55; N, 7.02%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.19 (s, 6H, $CH_2C_6(CH_3)_5$), 2.23 (s, 12H, $CH_2C_6(CH_3)_5$), 2.28 (s, 12H, $CH_2C_6(CH_3)_5$), 4.12 (t,

J = 4.8 Hz, 4H, CH_2), 4.93 (t, J = 4.4 Hz, 4H, CH_2), 6.00 (s, 4H, CH_2C$_6$(CH$_3$)$_5$), 7.13 (d, J = 8.4 Hz, 2H, Ar–H), 7.40 (t, J = 8.8 Hz, 2H, Ar–H), 7.55 (t, J = 8.4 Hz, 2H, Ar–H–), 7.99 (d, J = 8.0 Hz, 2H, Ar–H), 10.84 (s, 2H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$, TMS, 25 °C): δ = 17.2, 17.4, 17.5, 47.6, 48.9, 68.4, 113.9, 114.1, 125.7, 127.4, 131.5, 131.9, 133.8, 134.0, 137.2, 142.9 (N*C*N) ppm.

*4.2.8. Synthesis of 1,1′-di(2,3,4,5,6-pentamethylbenzyl)-3,3′-oxapentane-5,6-dimethylbibenzimidazolium dibromide (**11b**)*

Yield: 75%, m.p. = 187 °C. Anal. Calc. $C_{46}H_{60}Br_2N_4O$ (844.8): C, 65.40; H, 7.16; N, 6.63. Found: C, 65.63; H, 7.10; N, 6.68%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C): δ = 2.16 (s, 6H, CH$_2$C$_6$(CH_3)$_5$), 2.19 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 2.24 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 2.34 (s, 6H, CH_3–Ar), 2.48 (s, 6H, CH_3–Ar), 4.02 (t, J = 4.8 Hz, 4H, CH_2), 4.78 (t, J = 4.8 Hz, 4H, CH_2), 5.84 (s, 4H, CH_2C$_6$(CH$_3$)$_5$), 6.95 (s, 2H, Ar–H), 7.71 (s, 2H, Ar–H), 10.41 (s, 2H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$, TMS, 25 °C): δ = 17.1, 17.3, 17.4, 20.7, 21.0, 47.2, 48.3, 68.2, 110.0, 113.5, 125.8, 129.9, 130.3, 133.1, 133.7, 137.3, 137.7, 141.5 (N*C*N) ppm.

*4.2.9. Synthesis of 1,1′-di(2,3,4,5,6-pentamethylbenzyl)-3,3′-dioxaoctanebibenzimidazolium dibromide (**12a**)*

Yield: 55%, m.p. = 140 °C. Anal. Calc. for $C_{44}H_{56}Br_2N_4O_2$ (832.8): C, 63.46; H, 6.78; N, 6.73. Found: C, 63.42; H, 6.77; N, 6.42%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C): δ = 2.17 (s, 6H, CH$_2$C$_6$(CH_3)$_5$), 2.22 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 2.26 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 3.52 (s, 4H, CH_2), 3.95 (s, 4H, CH_2), 4.85 (t, J = 4.8 Hz, 4H, CH_2), 5.85 (s, 4H, CH_2C$_6$(CH$_3$)$_5$), 7.38 (d, J = 8.0 Hz, 2H, Ar–H), 7.48 (t, J = 8.4 Hz, 2H, Ar–H), 7.60 (t, J = 8.0 Hz, 2H, Ar–H), 7.90 (d, J = 7.6 Hz, 2H, Ar–H), 10.15 (s, 2H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$, TMS, 25 °C): δ = 17.2, 17.4, 17.5, 48.4, 68.7, 70.9, 113.7, 114.5, 125.3, 127.4, 127.5, 131.5, 132.2, 133.8, 134.1, 137.4, 142.3 (N*C*N) ppm.

*4.2.10. Synthesis of 1,1′-di(2,3,4,5,6-pentamethylbenzyl)-3,3′-dioxaoctane-5,6-dimethylbibenzimidazolium dibromide (**12b**)*

Yield: 80%, m.p. = 202 °C. Anal. Calc. for $C_{48}H_{64}Br_2N_4O_2$ (888.9): C, 64.86; H, 7.26; N, 6.30. Found: C, 64.93; H, 7.18; N, 6.31%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C): δ = 2.11 (s, 6H, CH$_2$C$_6$(CH_3)$_5$), 2.17 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 2.34 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 2.41 (s, 6H, CH_3–Ar), 2.45 (s, 6H, CH_3–Ar), 3.23 (s, 4H, CH_2), 3.62 (s, 4H, CH_2), 4.53 (s, 4H, CH_2), 5.63 (s, 4H, CH_2C$_6$(CH$_3$)$_5$), 7.86 (s, 2H, Ar–H), 8.00 (s, 2H, Ar–H), 8.74 (s, 2H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$, TMS, 25 °C): δ = 16.9, 17.3, 17.6, 20.7, 20.8, 46.8, 47.0, 68.2, 69.9, 114.1, 114.2, 126.4, 130.5, 130.6, 133.6, 134.4, 136.9, 137.0, 137.2, 140.7 (N*C*N) ppm.

*4.2.11. Synthesis of 1,1′-di(2,3,4,5,6-pentamethylbenzyl)-3,3′-trioxaundecanebibenzimidazolium dibromide (**13a**)*

Yield: 45%, m.p. = 120 °C. Anal. Calc. for $C_{46}H_{60}Br_2N_4O_3$ (876.8): C, 63.01; H, 6.90; N, 6.39. Found: C, 62.94; H, 6.78; N, 6.15%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C): δ = 2.15 (s, 6H, CH$_2$C$_6$(CH_3)$_5$), 2.19 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 2.21 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 3.35 (d, J = 4.4 Hz, 4H, CH_2), 3.49 (t, J = 4.0 Hz, 4H, CH_2), 3.93 (t, J = 4.0 Hz, 4H, CH_2), 4.89 (t, J = 4.0 Hz, 4H, CH_2), 5.83 (s, 4H, CH_2C$_6$(CH$_3$)$_5$), 7.42 (t, J = 7.6 Hz, 4H, Ar–H), 7.48 (t, J = 7.6 Hz, 2H, Ar–H), 8.05 (d, J = 8.0 Hz, 2H, Ar–H), 9.94 (s, 2H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$, TMS, 25 °C): δ = 17.2, 17.4, 17.5, 48.2, 48.4, 68.6, 70.5, 70.6, 113.7, 114.8, 125.7, 127.0, 127.1, 131.5, 132.2, 133.8, 133.9, 137.0, 142.5 (N*C*N) ppm.

*4.2.12. Synthesis of 1,1′-di(2,3,4,5,6-pentamethylbenzyl)-3,3′-trioxaundecane-5,6-dimethylbibenzimidazolium dibromide (**13b**)*

Yield: 71%, m.p. = 74 °C. Anal. Calc. for $C_{50}H_{68}Br_2N_4O_3$ (932.9): C, 64.37; H, 7.35; N 6.01. Found: C, 64.54; H, 7.24; N, 5.87%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C): δ = 2.24 (s, 6H, CH$_2$C$_6$(CH_3)$_5$), 2.26 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 2.27 (s, 12H, CH$_2$C$_6$(CH_3)$_5$), 2.38 (s, 6H, CH_3–Ar), 2.42 (s, 6H, CH_3–Ar), 3.38–3.53 (m, 8H, CH_2), 3.97 (t, J 8 4.0 Hz, 4H, CH_2), 4.84 (t, J = 4.4 Hz, 4H, CH_2), 5.69 (s, 4H, CH_2C$_6$(CH$_3$)$_5$), 7.30 (s, 2H, Ar–H), 7.75 (s, 2H, Ar–H), 9.63 (s, 2H, NCHN) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$, TMS, 25 °C): δ = 17.2, 17.3, 17.5, 20.8, 20.9, 47.7, 48.1, 68.7, 70.6, 70.7, 113.1, 114.1, 125.2, 130.0, 130.8, 133.8, 134.2, 137.4, 137.5, 137.6, 140.7 (N*C*N) ppm.

*4.3. Preparation of bis(NHC)–Pd(II) complexes (**14** and **15**)*

Ag_2O (0.5 mmol) was added to a solution of salt **4** and **6** (1.0 mmol) in CH_2Cl_2 (15 mL). The suspension became clear after stirring for 24 h at room temperature. [Pd(CH$_3$CN)$_2$Cl$_2$] (0.5 mmol) was added to the suspension. After the mixture was stirred for 2 h at room temperature, the solid AgBr was filtered off and the volume of the clear yellow solution was reduced to 3 mL. The yellow solid, formed after the addition of 15 mL of Et_2O, was filtered and dried under vacuum to give *trans*-bis(NHC)–Pd(II) complex. The following complexes **14** and **15** were synthesized according to this procedure.

*4.3.1. Synthesis of trans-bis{1-[2-(2-methoxyethoxy)ethyl]-3-(2,4,6-trimethylbenzyl)benzimidazolin-2-ylidene}palladium(II) dichloride (**14a**)*

Yield: 81%, m.p. = 213 °C. Anal. Calc. for $C_{44}H_{56}Cl_2N_4O_4Pd$ (882.3): C, 59.90; H, 6.40; N, 6.35. Found: C, 60.13; H, 6.23; N, 6.17%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C): δ = 2.32 (s, 12H, CH$_2$C$_6$H$_2$(CH_3)$_3$-2,4,6), 2.39 (s, 6H, CH$_2$C$_6$H$_2$(CH_3)$_3$-2,4,6), 3.22 (s, 3H, OCH_3), 3.26 (t, J = 4.0 Hz, 2H, CH_2), 3.33 (s, 3H, OCH_3), 3.46 (t, J = 4.0 Hz, 2H, CH_2), 3.54 (t, J = 4.0 Hz, 2H, CH_2), 3.63 (t, J = 4.0 Hz, 2H, CH_2), 4.33 (t, J = 8.0 Hz, 4H, CH_2), 5.14 (t, J = 8.0 Hz, 4H, CH_2), 6.03–6.27 (m, 4H, CH_2C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 6.46–6.57 (m, 2H, Ar–H), 6.86 (s, 2H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 6.92 (d, J = 8.0 Hz, 2H, Ar–H), 6.95 (s, 2H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 7.14 (d, J = 8.0 Hz, 2H, Ar–H), 7.51–7.57 (m, 2H, Ar–H). ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$, TMS, 25 °C): δ = 21.2, 21.3, 48.4, 49.7, 50.1, 50.6, 59.1, 59.2, 70.6, 70.9, 71.0, 71.1, 71.9, 72.1, 111.5, 111.7, 122.7, 123.1, 128.3, 128.4, 129.8, 134.4, 134.5, 135.8, 138.5, 138.7, 138.9, 182.3 (N*C*N) ppm.

*4.3.2. Synthesis of trans-bis{1-[2-(2-methoxyethoxy)ethyl]-3-(2,4,6-trimethylbenzyl)-5,6-dimethylbenzimidazolin-2-ylidene}palladium(II) dichloride (**14b**)*

Yield: 78%, m.p. = 223 °C. Anal. Calc. for $C_{48}H_{64}Cl_2N_4O_4Pd$ (938.4): C, 61.44; H, 6.87; N, 5.97. Found: C, 61.31; H, 6.72; N, 6.08%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C): δ = 2.09, 2.26, 2.28, 2.30, 2.34, 2.39 (s, 30H, CH$_2$C$_6$H$_2$(CH_3)$_3$-2,4,6, CH_3–Ar), 3.24 (s, 3H, OCH_3), 3.27 (t, J = 4.2 Hz, 2H, CH_2), 3.35 (s, 3H, OCH_3), 3.47 (t, J = 4.2 Hz, 2H, CH_2), 3.54 (t, J = 4.2 Hz, 2H, CH_2), 3.64 (t, J = 4.2 Hz, 2H, CH_2), 4.31 (t, J = 8.0 Hz, 4H, CH_2), 5.07 (t, J = 8.0 Hz, 4H, CH_2), 5.99–6.30 (m, 6H, CH_2C$_6$H$_2$(CH$_3$)$_3$-2,4,6, Ar–H), 6.85, 6.94 (s, 4H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 7.26 (s, 1H, Ar–H), 7.30 (s, 1H, Ar–H). ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$, TMS, 25 °C): δ = 20.3, 20.5, 20.6, 21.1, 21.3, 21.4, 48.1, 48.4, 49.5, 50.3, 59.1, 59.2, 70.7, 70.9, 71.0, 71.1, 71.9, 72.2, 111.7, 111.9, 128.5, 128.7, 129.7, 131.7, 133.1, 133.2, 134.3, 134.4, 138.3, 138.7, 138.9, 180.8 (NCN) ppm.

*4.3.3. Synthesis of trans-bis{1-[2-(2-methoxyethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolin-2-ylidene}palladium(II) dichloride (**15a**)*

Yield: 84%, m.p. = 220 °C. Anal. Calc. for $C_{48}H_{64}Cl_2N_4O_4Pd$ (938.4): C, 61.44; H, 6.87; N, 5.97. Found: C, 61.59; H, 6.69; N, 5.75%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C): δ = 2.14 (s, 6H, CH$_2$C$_6$(CH_3)$_5$), 2.21 (s, 9H, CH$_2$C$_6$(CH_3)$_5$), 2.27 (s, 9H, CH$_2$C$_6$(CH_3)$_5$), 2.32 (s, 6H, CH$_2$C$_6$(CH_3)$_5$), 3.13 (s, 3H, OCH_3), 3.18 (t, J = 4.0 Hz, 2H, CH_2), 3.27 (s, 3H, OCH_3), 3.41 (t, J = 4.0 Hz, 2H, CH_2), 3.47 (t, J = 4.0 Hz, 2H, CH_2), 3.59 (t, J = 4.0 Hz, 2H, CH_2), 4.28 (t, J = 8.0 Hz,

4H, CH_2), 5.07 (t, J = 8.0 Hz, 4H, CH_2), 6.14–6.35 (m, 6H, $CH_2C_6(CH_3)_5$, Ar–*H*), 6.80 (t, J = 8.0 Hz, 2H, Ar–*H*), 7.05 (t, J = 8.0 Hz, 2H, Ar–*H*), 7.45 (d, J = 8.4 Hz, 2H, Ar–*H*) ppm. ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.1, 17.4, 17.5, 17.9, 48.4, 51.5, 51.6, 51.9, 59.0, 59.2, 70.7, 70.8, 70.9, 71.1, 71.9, 72.1, 111.4, 112.0, 122.5, 122.9, 128.5, 133.3, 134.6, 134.7, 135.9, 182.4 (NCN) ppm.

4.3.4. Synthesis of trans-bis{1-[2-(2-methoxyethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazolin-2-ylidene}palladium(II) dichloride (**15b**)

Yield: 86%, m.p. = 234 °C. Anal. Calc. for $C_{52}H_{72}Cl_2N_4O_4Pd$ (994.5): C, 62.80; H, 7.30; N, 5.63. Found: C, 63.01; H, 7.46; N, 5.69%. ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.02, 2.21, 2.26, 2.28, 2.35, 2.41 (s, 42H, $CH_2C_6(CH_3)_5$, CH_3–Ar), 3.23 (s, 3H, OCH_3), 3.27 (t, J = 4.0 Hz, 2H, CH_2), 3.37 (s, 3H, OCH_3), 3.49 (t, J = 4.0 Hz, 2H, CH_2), 3.55 (t, J = 4.0 Hz, 2H, CH_2), 3.66 (t, J = 4.0 Hz, 2H, CH_2), 4.32 (t, J = 8.0 Hz, 4H, CH_2), 5.07 (t, J = 8.0 Hz, 4H, CH_2), 6.08–6.31 (m, 6H, $CH_2C_6(CH_3)_5$, Ar–*H*), 7.26 (s, 1H, Ar–*H*), 7.29 (s, 1H, Ar–*H*). ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.1, 17.4, 17.5, 17.9, 48.1, 48.2, 51.1, 51.3, 51.5, 51.7, 59.1, 59.3, 70.8, 70.9, 71.1, 72.0, 72.2, 111.6, 112.5, 128.9, 131.5, 133.1, 133.2, 133.4, 134.4, 134.6, 134.7, 134.8, 181.0 (NCN) ppm.

4.4. Preparation of dimeric NHC–Pd(II) complexes (**16** and **17**)

A mixture of salt **4** and **6** (0.5 mmol), $Pd(OAc)_2$ (0.5 mmol) and NaBr (2 mmol) in DMSO (10 mL) was stirred at 90 °C for 24 h. The reaction mixture was filtered over Celite®, and the solvent of filtrate was removed by vacuum distillation. The resulting residue was suspended in CH_2Cl_2 (20 mL) and then extracted with H_2O (3 × 20 mL). Drying of the organic phase over $MgSO_4$ followed by removal of the solvent by vacuum afforded the solid as an orange solid. The following complexes **16** and **17** were synthesized according to this procedure.

4.4.1. Synthesis of di-μ-bromobis{1-[2-(2-methoxyethoxy)ethyl]-3-(2,4,6-trimethylbenzyl)benzimidazolin-2-ylidene}dibromodipalladium-(II) (**16a**)

Yield: 82%, m.p. = 230 °C. Anal. Calc. for $C_{44}H_{56}Br_4N_4O_4Pd_2$ (1237.4): C, 42.71; H, 4.56; N, 4.53. Found: C, 42.84; H, 4.47; N, 4.58%. ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.29 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.35 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.30 (s, 6H, OCH_3), 3.42 (t, J = 4.0 Hz, 4H, CH_2), 3.61 (t, J = 4.0 Hz, 4H, CH_2), 4.31 (t, J = 4.4 Hz, 4H, CH_2), 5.13 (br, 4H, CH_2), 6.21 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.35 (d, J = 8.0 Hz, 2H, Ar–*H*), 6.93 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.95 (t, J = 7.6 Hz, 2H, Ar–*H*), 7.16 (t, J = 7.6 Hz, 2H, Ar–*H*), 7.59 (d, J = 8.0 Hz, 2H, Ar–*H*) ppm. ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 21.2, 21.4, 49.4, 51.4, 59.2, 70.3, 70.9, 71.9, 111.4, 112.2, 123.2, 123.7, 127.2, 129.9, 134.62, 135.9, 139.2, 159.5 (NCN) ppm.

4.4.2. Synthesis of di-μ-bromobis{1-[2-(2-methoxyethoxy)ethyl]-3-(2,4,6-trimethylbenzyl)-5,6-dimethylbenzimidazolin-2-ylidene}dibromodipalladium(II) (**16b**)

Yield: 78%, m.p. = 227 °C. Anal. Calc. for $C_{48}H_{64}Br_4N_4O_4Pd_2$ (1293.5): C, 44.57; H, 4.99; N, 4.33. Found: C, 44.51; H, 4.91; N, 4.36%. ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.07, 2.28, 2.30, 2.36 (s, 30H, $CH_2C_6H_2(CH_3)_3$-2,4,6, CH_3–Ar), 3.21 (s, 6H, OCH_3), 3.37 (t, J = 4.2 Hz, 4H, CH_2), 3.55 (t, J = 4.4 Hz, 4H, CH_2), 4.28 (t, J = 4.4 Hz, 4H, CH_2), 5.06 (br, 4H, CH_2), 6.12 (s, 2H, Ar–*H*), 6.13 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.94 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.35 (s, 2H, Ar–*H*) ppm. ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.1, 20.5, 21.0, 21.1, 49.1, 51.0, 59.2, 70.2, 70.9, 72.0, 111.7, 112.1, 127.6, 129.7, 132.5, 133.3, 134.4, 139.1, 157.1 (NCN) ppm.

4.4.3. Synthesis of di-μ-bromobis{1-[2-(2-methoxyethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolin-2-ylidene}dibromodipalladium(II) (**17a**)

Yield: 85%, m.p. = 267 °C. Anal. Calc. for $C_{48}H_{64}Br_4N_4O_4Pd_2$ (1293.5): C, 44.57; H, 4.99; N, 4.33. Found: C, 44.48; H, 5.06; N, 4.26%. ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 2.23 (s, 24H, $CH_2C_6(CH_3)_5$), 2.33 (s, 6H, $CH_2C_6(CH_3)_5$), 3.30 (s, 6H, OCH_3), 3.42 (t, J = 4.2 Hz, 4H, CH_2), 3.61 (t, J = 4.2 Hz, 4H, CH_2), 4.31 (t, J = 4.4 Hz, 4H, CH_2), 5.11 (br, 4H, CH_2), 6.26 (d, J = 8.0 Hz, 2H, Ar–*H*), 6.33 (s, 4H, $CH_2C_6(CH_3)_5$), 6.90 (t, J = 8.0 Hz, 2H, Ar–*H*), 7.14 (t, J = 8.0 Hz, 2H, Ar–*H*), 7.58 (d, J = 8.8 Hz, 2H, Ar–*H*) ppm. ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.1, 17.8, 49.4, 52.0, 59.2, 70.3, 70.9, 71.9, 111.7, 112.0, 123.0, 123.6, 127.3, 133.4, 134.8, 134.9, 135.9, 159.2 (NCN) ppm.

4.4.4. Synthesis of di-μ-bromobis{1-[2-(2-methoxyethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazolin-2-ylidene}-dibromodipalladium(II) (**17b**)

Yield: 83%, m.p. = 274 °C. Anal. Calc. for $C_{52}H_{72}Br_4N_4O_4Pd_2$ (1349.6): C, 46.28; H, 5.38; N, 4.15. Found: C, 46.17; H, 5.32; N, 4.19%. ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 1.95, 2.08, 2.16, 2.24, 2.32 (s, 42H, $CH_2C_6(CH_3)_5$, CH_3–Ar), 3.26 (s, 6H, OCH_3), 3.41 (t, J = 4.6 Hz, 4H, CH_2), 3.56 (t, J = 4.4 Hz, 4H, CH_2), 4.28 (t, J = 4.4 Hz, 4H, CH_2), 4.98 (br, 4H, CH_2), 5.93 (s, 2H, Ar–*H*), 6.14 (s, 4H, $CH_2C_6(CH_3)_5$), 7.25 (s, 2H, Ar–*H*) ppm. ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.1, 17.5, 17.9, 49.2, 52.2, 59.2, 70.3, 70.9, 72.0, 112.0, 112.1, 127.7, 132.3, 132.4, 133.3, 133.5, 134.4, 134.8, 136.3, 156.9 (NCN) ppm.

4.5. Preparation of mixed NHC–phosphine Pd(II) complexes (**18** and **19**)

A mixture of complex **16** and **17** (0.2 mmol) and triphenylphosphine (0.4 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 1 h. Solution was reduced to 1 mL. The yellow solid, formed after the addition of 10 mL of pentane, was filtered and dried under vacuum to give *cis*-NHC–phosphine Pd(II) complexes as yellow solid. The following complexes **18** and **19** were synthesized according to this procedure. Slow evaporation of a CH_2Cl_2/hexane mixture afforded the yellow crystals for the complexes **19a** and **19b.**

4.5.1. Synthesis of cis-dibromo{1-[2-(2-methoxyethoxy)ethyl]-3-(2,4,6-trimethylbenzyl)benzimidazolin-2-ylidene}(triphenylphosphine)palladium(II) (**18a**)

Yield: 93%, m.p. = 223 °C. Anal. Calc. for $C_{40}H_{43}Br_2N_2O_2PPd$ (881.0): C, 54.53; H, 4.92; N, 3.18. Found: C, 54.48; H, 5.01; N, 3.16%. ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 1.99 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.31 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.29 (s, 3H, OCH_3), 3.31–3.37 (m, 1H, CH_2), 3.41–3.45 (m, 3H, CH_2), 3.98–4.16 (m, 3H, CH_2), 4.72–4.79 (m, 1H, CH_2), 4.95 (d, J = 14.0 Hz, 1H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.79 (d, J = 8.0 Hz, 1H, Ar–*H*), 6.42 (d, J = 14.0 Hz, 1H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.78 (t, J = 8.0 Hz, 1H, Ar–*H*), 6.86 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.04 (t, J = 8.0 Hz, 1H, Ar–*H*), 7.20 (br, 8H, Ar–*H*–PPh_3), 7.28 (d, J = 8.0 Hz, 1H, Ar–*H*) 7.35 (br, 3H, Ar–*H*–PPh_3), 7.58 (br, 4H, Ar–*H*–PPh_3), ppm. ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 21.0, 21.3, 48.9, 50.5, 59.1, 69.1, 70.6, 71.8, 111.1, 111.8, 122.7, 123.3, 126.6, 128.6, 128.7, 129.7, 131.4, 134.5, 134.8, 135.6, 139.4, 175.6 (NCN) ppm. ^{31}P {^1H} NMR (161.9 MHz, $CDCl_3$, 25 °C): δ = 26.99 ppm.

Table 4
Crystal data and structure refinement.

Identification code	**19a**	**19b**
Empirical formula	$C_{42}H_{47}Br_2N_2O_2PPd$	$C_{44}H_{51}Br_2N_2O_2PPd$
Formula weight	909.01	937.06
Temperature (K)	110(2)	180(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.7736(4)	12.043(5)
b (Å)	12.2100(5)	12.804(5)
c (Å)	14.0081(6)	15.010(5)
α (°)	94.377(4)	85.593(5)
β (°)	106.357(3)	84.969(5)
γ (°)	90.343(3)	64.379(5)
Volume (Å^3)	1925.81(13)	2077.0(14)
Z	2	2
D_{calc} (Mg/m^3)	1.568	1.498
Absorption coefficient (mm^{-1})	2.636	2.447
F(0 0 0)	920	952
Crystal size (mm)	0.59 × 0.39 × 0.10	0.48 × 0.36 × 0.29
θ Range (°)	3.04–30.03°	3.19–30.51
Reflections collected	18 046	29 154
Independent reflections (R_{int})	10 770 (0.0438)	12 460 (0.0874)
Completeness (%)	95.7	98.3
Absorption correction	Multi-scan	Multi-scan
Maximum/minimum transmission	1.0/0.513	1.0/0.7605
Refinement method	F^2	F^2
Data/restraints/parameters	10 770/13/467	12 460/0/476
Goodness-of-fit (GOF) on F^2	1.032	0.946
R_1, wR_2 [$I > 2\sigma(I)$]	0.0509, 0.1241	0.0386, 0.0881
R_1, wR_2 (all data)	0.0787, 0.1396	0.0653, 0.0947
Residual density (e Å^{-3})	2.201/−2.535	1.255/−1.051

*4.5.2. Synthesis of cis-dibromo{1-[2-(2-methoxyethoxy)ethyl]-3-(2,4,6-trimethylbenzyl)-5,6-dimethylbenzimidazolin-2-ylidene}(triphenylphosphine)palladium(II) (**18b**)*

Yield: 87%, m.p. = 226 °C. Anal. Calc. for $C_{42}H_{47}Br_2N_2O_2PPd$ (909.0): C, 55.49; H, 5.21; N, 3.08. Found: C, 55.51; H, 5.25; N, 3.04%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 1.93 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 1.97 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.20 (s, 3H, CH_3–Ar), 2.31 (s, 3H, CH_3–Ar), 3.32 (s, 3H, OCH_3), 3.34–3.40 (m, 1H, CH_2), 3.43–3.49 (m, 3H, CH_2), 3.93–4.06 (m, 3H, CH_2), 4.65–4.71 (m, 1H, CH_2), 4.91 (d, J = 14.0 Hz, 1H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.45 (s, 1H, Ar–H), 6.33 (d, J = 14.0 Hz, 1H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.85 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.02 (s, 1H, Ar–H), 7.21 (br, 8H, Ar–H–PPh_3), 7.35 (br, 3H, Ar–H–PPh_3), 7.56 (br, 4H, Ar–H–PPh_3), ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.2, 20.6, 20.9, 21.2, 48.6, 50.3, 59.2, 69.0, 70.6, 71.9, 111.5, 111.8, 126.9, 128.6, 128.7, 129.5, 131.3, 131.9, 132.1, 133.5, 134.2, 134.5, 139.2, 173.2 (NCN) ppm. ^{31}P {^{1}H} NMR (161.9 MHz, $CDCl_3$, 25 °C): δ = 27.07 ppm.

*4.5.3. Synthesis of cis-dibromo{1-[2-(2-methoxyethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolin-2-ylidene}(triphenylphosphine)palladium(II) (**19a**)*

Yield: 92%, m.p. = 232 °C. Anal. Calc. for $C_{42}H_{47}Br_2N_2O_2PPd$ (909.0): C, 55.49; H, 5.21; N, 3.08. Found: C, 55.42; H, 5.16; N, 3.13%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 1.93 (s, 6H, $CH_2C_6(CH_3)_5$), 2.19 (s, 6H, $CH_2C_6(CH_3)_5$), 2.29 (s, 3H, $CH_2C_6(CH_3)_5$), 3.30 (s, 3H, OCH_3), 3.34–3.39 (m, 1H, CH_2), 3.43–3.48 (m, 3H, CH_2), 3.96–4.09 (m, 3H, CH_2), 4.70–4.78 (m, 1H, CH_2), 5.15 (d, J = 14.0 Hz, 1H, $CH_2C_6(CH_3)_5$), 5.75 (d, J = 8.0 Hz, 1H, Ar–H), 6.43 (d, J = 14.0 Hz, 1H, $CH_2C_6(CH_3)_5$), 6.75 (t, J = 8.0 Hz, 1H, Ar–H), 7.02 (t, J = 8.0 Hz, 1H, Ar–H), 7.20 (br, 8H, Ar–H–PPh_3), 7.25 (d, J = 8.0 Hz, 1H, Ar–H) 7.34 (br, 3H, Ar–H–PPh_3), 7.57 (br, 4H, Ar–H–PPh_3), ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.2, 17.6, 48.9, 52.2, 59.3, 69.1, 70.7, 71.9, 111.6, 111.8, 122.6, 123.4, 127.1, 128.7, 128.8, 131.5, 133.4, 134.6, 135.0, 135.3, 135.6, 136.8, 175.6 (NCN) ppm. ^{31}P {^{1}H} NMR (161.9 MHz, $CDCl_3$, 25 °C): δ = 27.13 ppm.

*4.5.4. Synthesis of cis-dibromo{1-[2-(2-methoxyethoxy)ethyl]-3-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazolin-2-ylidene}(triphenylphosphine)palladium(II) (**19b**)*

Yield: 91%, m.p. = 245 °C. Anal. Calc. for $C_{44}H_{51}Br_2N_2O_2PPd$ (937.1): C, 56.39; H, 5.49; N, 2.99. Found: C, 56.42; H, 5.54; N, 2.96%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 1.89, 1.92, 2.20, 2.31 (s, 21H, $CH_2C_6(CH_3)_5$, CH_3–Ar), 3.34 (s, 3H, OCH_3), 3.37–3.42 (m, 1H, CH_2), 3.46–3.48 (m, 3H, CH_2), 3.89–4.07 (m, 3H, CH_2), 4.63–4.69 (m, 1H, CH_2), 5.09 (d, J = 14.0 Hz, 1H, $CH_2C_6(CH_3)_5$), 5.38 (s, 1H, Ar–H), 6.37 (d, J = 14.0 Hz, 1H, $CH_2C_6(CH_3)_5$), 6.99 (s, 1H, Ar–H), 7.21 (br, 8H, Ar–H–PPh_3), 7.36 (br, 3H, Ar–H–PPh_3), 7.55 (br, 4H, Ar–H–PPh_3), ppm. ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C): δ = 17.0, 17.2, 20.2, 20.6, 48.6, 50.1, 59.2, 68.9, 70.6, 71.9, 111.6, 111.9, 127.0, 127.3, 128.6, 128.7, 131.3, 131.7, 131.9, 133.8, 134.1, 134.6, 136.6, 173.1 (NCN) ppm. ^{31}P {^{1}H} NMR (161.9 MHz, $CDCl_3$, 25 °C): δ = 27.20 ppm.

4.6. General procedure for the Heck coupling reactions

In a typical run, a reaction vessel was charged with 4-bromoacetophenone (1.0 mmol), styrene (1.5 mmol), Cs_2CO_3 (2 mmol), diethyleneglycol-di-*n*-butyl ether and catalyst (1.5 mmol%). About 3 mL water was added. The reaction mixture was vigorously stirred at 100 °C for 4 h. At the conclusion the solution was allowed to cool, extracted with Et_2O and the organic phase separated. Yields were determined by gas chromatography for an average of two runs.

4.7. X-ray diffraction studies

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR or a Bruker APEX-II CCD diffractometer. Data were collected using the monochromatic Mo Kα radiation (λ = 0.71073). The structures were solved by direct methods (SIR97) [17] and refined by least-squares procedures on F^2 using SHELXL-97 [18]. All H atoms attached to carbon were introduced in idealized positions and treated as riding on their parent atoms in the calculations. In the ligand structure the H atoms attached to nitrogen and oxygen atoms were located in difference Fourier synthesis but were treated as riding on their parent atoms. In compound **19b**, some residual electron density were difficult to modelize and therefore, the SQUEEZE function of PLATON [19] was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. There is one cavity of 39 Å^3 per unit cell. PLATON estimated that the cavity contains 14 electrons which may correspond to a 1/3 of ether molecule as suggested by the synthetic procedure. In compound 6d, the long methoxyethoxy chain is disordered over two positions with occupancy factors in the ratio 0.53/0.47. This disorder was treated using the tools (PART and SAME) available in SHELXL-97. The drawing of the molecules was realized with the help of ORTEP3 [20]. Crystal data and refinement parameters are shown in Table 4. Bond distances and angles are given in Table 1.

Supplementary material

CCDC 733626 and 733625 contain the supplementary crystallographic data for **19a and 19b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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