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Journal of Organometallic Chemistry 693 (2008) 425–434
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and use of mono- or bisxylyl linked bis(benzimidazolium) bromides as carbene precursors for C–C bond formation reactions

Hayati Türkmen [a], Serpil Denizaltı [a], Ismail Özdemir [b], Engin Çetinkaya [a,*], Bekir Çetinkaya [a]

[a] Department of Chemistry, Ege University, 35100 Bornova-Izmir, Turkey
[b] Department of Chemistry, Inönü University, 44069 Malatya, Turkey

Received 23 October 2007; received in revised form 7 November 2007; accepted 8 November 2007
Available online 17 November 2007

Abstract

Two benzimidazolium moieties linked by one or two xylyls (*m*- and *p*-) have been synthesized, characterized and then they were used for Heck coupling reactions as in situ formed catalysts. Mono bridged salts are more efficient as compared to bisbridged salts. In addition, mono bridged salts were converted to Rh–NHC complexes which were tested as catalysts for the arylation of aldehydes.
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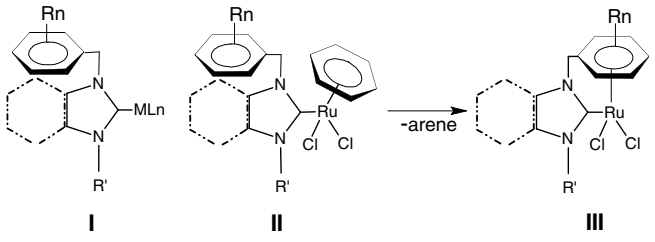
Keywords: Bridged bisbenzimidazolium salts; Catalytic activities; C–C coupling; Rhodium complexes

1. Introduction

Recent studies have shown that *N*-heterocyclic carbenes (NHC's) are important ligands in metal catalyzed reactions and the electronic and steric effects of the NHC have a great influence on the performance of the reaction which occurs at the metal center [1]. Thus, a number of new NHC ligands are reported every year. The main body of information has been accumulated on imidazol-2-ylidene based NHC's, whereas their corresponding benzannulated counterpart are relatively unexplored [2]. As a matter of fact, benzimidazol-2-ylidenes have structures reminiscent of imidazol-2-ylidenes, but spectroscopic properties and reactivity which are close to saturated imidazol-2-ylidenes [3,4].

The transition metal complexes of NHC ligands bearing alkylated benzyl substituents on the N atom(s) of hetero rings (**I**) are found to be more efficient catalysts than the simple benzyl substituted ones in C–C bond formation reactions [5]. In addition, the aryl part of such NHC ligands attached to the Ru atom (**II**) are prone to displace the other arene groups to form an intramolecular arene (**III**) [6].



Therefore, the main objective of this study is to investigate the influence of polymethylated benzyls in the form of *m*- and *o*-xylyls in bimetallic systems bearing benzimidazole framework. The bisbridged salts are known as cyclophanes, and many related cyclophanes have been studied by Baker et al. [7] and others [8].

* Corresponding author. Tel.: +90 2323881092; fax: +90 2323881036.
E-mail address: engin.cetinkaya@ege.edu.tr (E. Çetinkaya).

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doi:10.1016/j.jorganchem.2007.11.015

2. Results and discussion

2.1. Preparation of the 3,3′- and 1,1′,3,3′-bridged bibenzimidazolium precursors

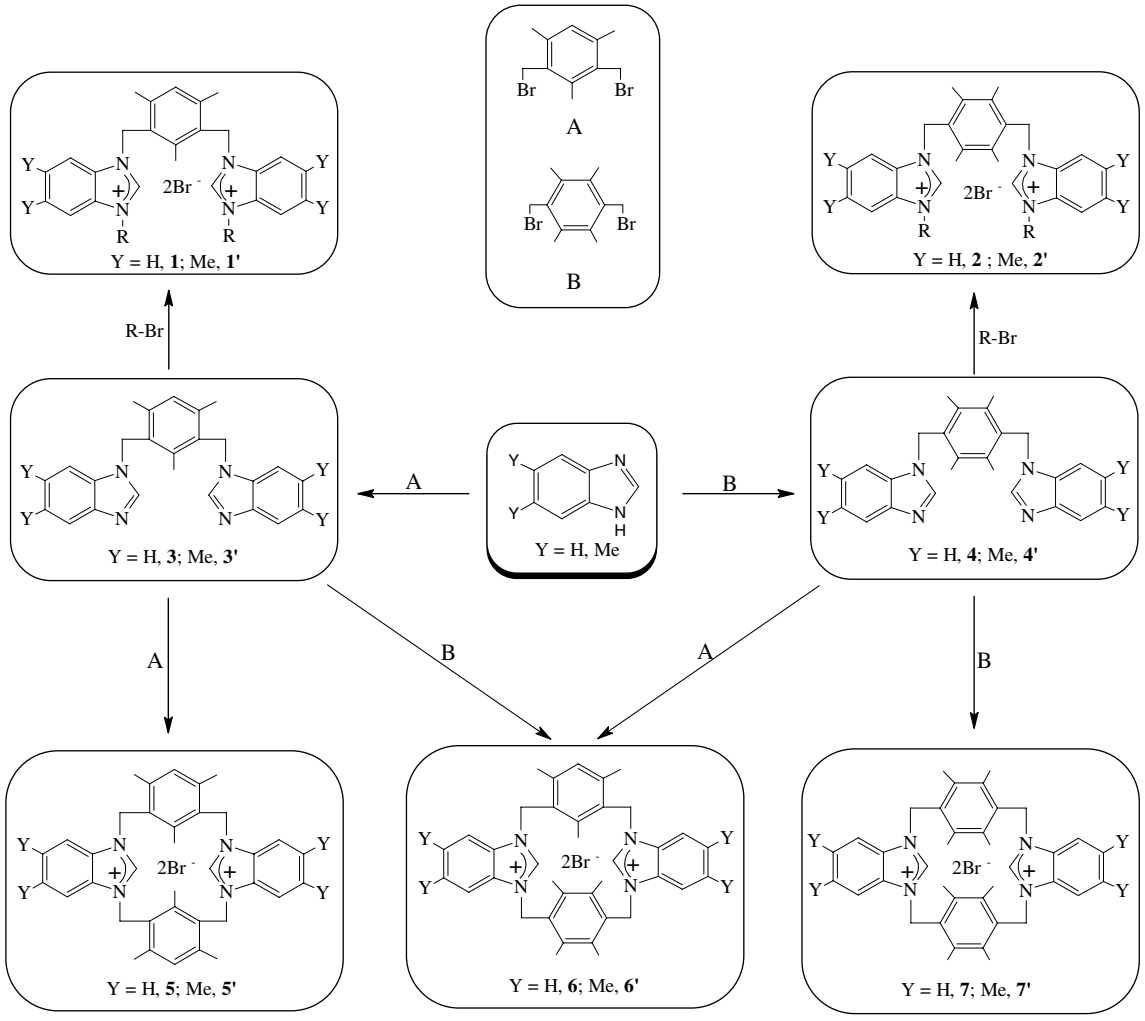
As mentioned in the introduction, the main aim of this study was the attachment of sterically bulky *m*- or *p*-xylyl groups between two benzimidazoles via the N atom(s). The salts of general structure **1/1′**, **2/2′**, **5/5′**, **6/6′**, and **7/7′** were synthesized according to Scheme 1. The introduction of the xylyl substituents into the benzimidazole system was achieved by direct alkylation in toluene. The resulting 1,1′-bridged bibenzimidazoles (**3** and **4**) can be alkylated to give **1/1′** and **2/2′**, respectively. The salts with two bridges (**5/5′** and **7/7′**) are also easily accessible and can be obtained by the usual quaternization of 1,1′-bridged bibenzimidazoles. In the case of **6/6′** the cross quaternization method was employed. There was no significant difference in total yield in connection with the method.

The IR data for benzimidazolium salts (**1**–**2**; **1′**–**2′**) clearly indicate the presence of the –C=N– group with a υ(C=N) vibration between 1558 and 1562 cm^{-1} [9] (Scheme 2).

These benzimidazolium salts have been characterized by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR chemical shifts were consistent with the proposed structures; the resonances for C_2-hydrogens were observed as sharp singlets between 9.51 and 10.86 ppm. ^{13}C NMR of these salts showed the C_2 carbon at 140.4–142.2 ppm.

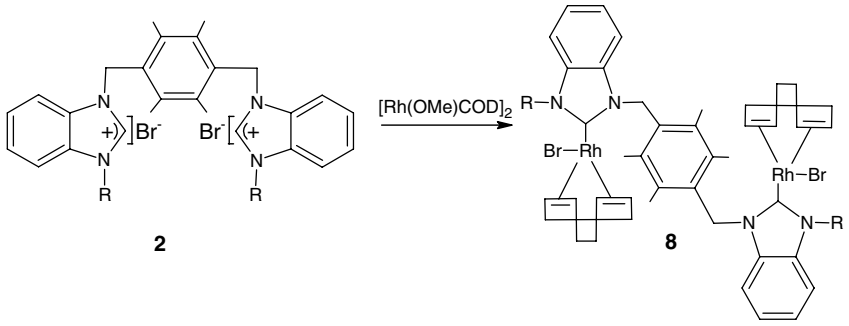
2.2. Synthesis of di-bridged bibenzimidazolium salts, II (5–7′)

The di-bridged benzimidazoles were synthesized by *N*-alkylation of mono-bridged (5,6-dimethyl)benzimidazole with the corresponding *m*- or *p*-dibromides in toluene at reflux. These salts were purified by recrystallization from methanol.



R	-$CH_2CH_2OCH_3$	-$CH_2C_6H_2(CH_3)_3$-2,4,6	-$CH_2C_6H(CH_3)_4$-2,3,5,6	-$CH_2C_6(CH_3)_5$
	a	**b**	**c**	**d**

Scheme 1. Alkylation and quaternization of benzimidazoles with A, B or R–Br.



Scheme 2.

The IR data for symmetrical di-bridged benzimidazoles (**5**,**5′**,**7**,**7′**) clearly indicate the presence of the –C=N– group with a υ(C=N) vibration between 1546 and 1573 cm^{-1}.

The ^1H NMR spectrum of the metacyclophanes displayed the methyl protons as an 18 proton singlet at about $\delta = 1.54$; 2.43 ppm. The *N*-methylene protons appeared as doublets at about $\delta = 5.49$; 5.80 ppm. The C_2–H signals were observed at approximately $\delta = 7.20$ ppm. The ^{13}C NMR showed the C_2 carbon at 140.9 ppm.

The ^1H NMR spectrum of the paracyclophanes showed the methyl protons as a singlet at 2.10 ppm. The benzylic protons appeared as a singlet at 5.73–5.81 ppm. The resonances for the C_2–hydrogens were observed as singlets between 6.22 and 7.23 ppm. The ^{13}C NMR of paracyclophanes showed the C_2 carbon at 136.7, 137.9 ppm.

The ^1H and ^{13}C NMR spectra of the unsymmetrical di-bridged benzimidazoles were recorded in CD_3OD. The C_2–H signals were observed at very high field (6.45–6.67 ppm) as singlets. It is proposed that these protons are directed towards cyclophane cavity. However, in spite of their high field signals, these hydrogens are reactive enough to react with basic metal salts such as [Rh(μ-OMe)(COD)]$_2$. The benzylic protons appeared as multiplet between 5.44 and 6.05 ppm. In the ^{13}C NMR the C_2 carbon appeared between 141.8 and 141.9 ppm. The IR data show the presence of the –C=N– group with a υ(C=N) vibration between 1563 and 1569 cm^{-1}.

2.3. The Heck C–C coupling reaction

The coupling reactions of aryl halides with olefins are usually carried out homogenously in the presence of a base under inert atmosphere. It was noted that in situ formation of the azolium salt led to significantly better results than the use of the preformed complex.

We found that use of 3% $Pd(OAc)_2$, 3% ligand and 1.5 mmol Cs_2CO_3 in DMA at 100 °C led to the best conversion within 3 h. Under the optimised reaction conditions, we investigated the reaction of aryl halides with *n*-butyl acrylate and observed that the reactions at 100 °C gave coupling products in good yields (62–100%). The results obtained are summarized in Table 1.

We noted that the NHC precursors bearing methoxyethyl groups (**1a**, **1′a**, **2a**, **2′a**) were the most effective of the salts examined. We expected that activities of these salts would increase in the following order: pentamethylbenzyl (i) (**1d**, **1′d**, **2d**, **2′d**) > tetramethylbenzyl (ii) (**1c**, **1′c**, **2c**, **2′c**) > trimethylbenzyl substituent (iii) (**1b**, **1′b**, **2b**, **2′b**). However, the catalytic activity increases in the sequence i > iii > ii, indicating the influence of the *p*-substituent. In addition, benzimidazolium salts bearing methyl groups on the 5,6-positions of the benzene ring have also shown better catalytic activity than nonsubstituted counterparts. These observations are consistent with the previous reports [1c,10].

2.4. Synthesis of rhodium–carbene complexes and their catalytic activity for arylation of aldehydes

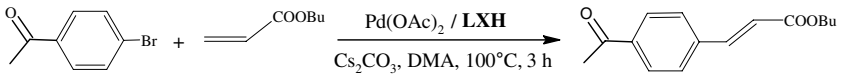
Rhodium–carbene complexes and their catalytic activity have been studied by various researchers [11,12]. In the rhodium catalyzed addition of aryl boronic acids to aldehydes to give secondary alcohols, the reactions were facilitated by the presence of an electron-withdrawing group on the aldehyde and an electron donating group on the arylboronic acid. This observation indicates that the mechanism involves a nucleophilic attack of the aryl group on the aldehyde [13–15].

The Rh(I)–NHC complexes synthesized in this study showed differences in their behaviour as catalyst for arylation of various aromatic aldehydes. Of the four complexes, the complex **8a**, containing 2-methoxyethyl substituent on N^1 atom, was the most efficient. As was observed in the Heck reactions (Table 1).

2.4.1. 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), the substituted aldehyde (4.9 mmol), diethyleneglycol-di-*n*-butyl ether (0.6 mmol, internal standard) rhodium-carbene catalyst (1 mol%) and dimethoxyethane (15 mL) were introduced in to a two-necked 25 mL flask and then H_2O (5 mL) was added. The resulting mixture was heated for 1 h at 80 °C under an argon atmosphere. The conversion was monitored by gas chromatography (Table 2).

Table 1
The Heck reaction catalyzed by in situ formed (LHX + $Pd(OAc)_2$)



Entry	LXH	Aryl Halide	Olefin	Yield (%)
1	**1a**	4-Bromoacetophenone	*n*-Butyl acrylate	98
2	**1b**	4-Bromoacetophenone	*n*-Butyl acrylate	90
3	**1c**	4-Bromoacetophenone	*n*-Butyl acrylate	80
4	**1d**	4-Bromoacetophenone	*n*-Butyl acrylate	94
5	**2a**	4-Bromoacetophenone	*n*-Butyl acrylate	96
6	**2b**	4-Bromoacetophenone	*n*-Butyl acrylate	88
7	**2c**	4-Bromoacetophenone	*n*-Butyl acrylate	82
8	**2d**	4-Bromoacetophenone	*n*-Butyl acrylate	91
9	**1′a**	4-Bromoacetophenone	*n*-Butyl acrylate	100
10	**1′b**	4-Bromoacetophenone	*n*-Butyl acrylate	92
11	**1′c**	4-Bromoacetophenone	*n*-Butyl acrylate	88
12	**1′d**	4-Bromoacetophenone	*n*-Butyl acrylate	96
13	**2′a**	4-Bromoacetophenone	*n*-Butyl acrylate	100
14	**2′b**	4-Bromoacetophenone	*n*-Butyl acrylate	91
15	**2′c**	4-Bromoacetophenone	*n*-Butyl acrylate	83
16	**2′d**	4-Bromoacetophenone	*n*-Butyl acrylate	92
17	**5**	4-Bromoacetophenone	*n*-Butyl acrylate	70
18	**7**	4-Bromoacetophenone	*n*-Butyl acrylate	67
19	**5′**	4-Bromoacetophenone	*n*-Butyl acrylate	73
20	**7′**	4-Bromoacetophenone	*n*-Butyl acrylate	67
21	**6**	4-Bromoacetophenone	*n*-Butyl acrylate	75
22	**6′**	4-Bromoacetophenone	*n*-Butyl acrylate	83
23	**1a**	4-Bromoanisole	*n*-Butyl acrylate	78
24	**1b**	4-Bromoanisole	*n*-Butyl acrylate	68
25	**1c**	4-Bromoanisole	*n*-Butyl acrylate	62
26	**1d**	4-Bromoanisole	*n*-Butyl acrylate	75
27	**2a**	4-Bromoanisole	*n*-Butyl acrylate	77
28	**2a**	4-Bromoacetophenone	Styrene	88
29	**2′a**	Bromobenzene	*n*-Butyl acrylate	80

Abbreviation: LXH = benzimidazolium salts; DMA = *N*,*N*-dimethylacetamide.

Reaction conditions: 9.8 mmol of phenylboronic acid, 4.9 mmol aldehydes, 1.0 mmol% rhodium-carbene, 4.9 mmol $KOBu^t$, dimethoxyethane (15 mL), H_2O (5 mL); GC-yield using diethyleneglycol-di-*n*-butyl ether as the internal standard; temperature 80 °C, 1 h.

3. Conclusions

In conclusion, in this study, mono- and bis-xylyl-bridged bibenzimidazolium bromides (**1**, **7**) were synthesized and their in situ catalytic activities were tested for Heck reactions. The Heck coupling reactions were performed between aryl halides with *n*-butyl acrylate in the presence of the salts and $Pd(OAc)_2$ in DMA at 100 °C.

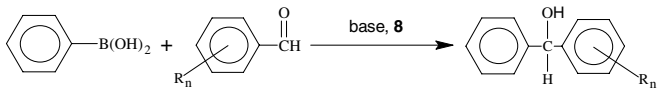
The mono-bridged bisbenzimidazolium salts bearing a methoxyethyl substituent on the N atom (**1′a**, **2′a**) are the most effective of the salts examined. Catalytic activity increased in the sequence: (i) > (iii) > (ii). Benzimidazolium salts bearing methyl groups on the 5,6-positions have also shown a better activity as compared to nonsubstituted ones. On the other hand, meta bridged bisbenzimidazolium salts showed better catalytic activity in comparison to para bridged bisbenzimidazolium salts. In addition, unsymmetrical cyclophanes gave better results than symmetrical ones.

The complexes **8** displayed differences in their behaviour as catalysts for arylation of aldehydes.The complexes with *N*-(2-methoxyethyl) substitution showed higher activities then the complexes with *N*-benzyls. The general activity trend is as follows: **a** > **d** > **c** > **b**.

4. Experimental

2,4,6-Trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide, 2,3,4,5,6-pentamethylbenzyl bromide, 1,3-bis-(bromomethyl)-2,4,6-trimethylbenzene, 1,4-bis(bromethyl)-2,3,5,6-tetramethylbenzene [13], 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene and 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene [14], 1-alkyl-5,6-dimethylbenzimidazoles [15] were synthesized according to the methods previously known. All reagents were purchased from Merck, Fluka, Alfa Aesar and Acros Organics. Melting points were recorded with Gallenkamp electrothermal melting point apparatus.

Table 2
Rhodium–carbene catalyzed addition of phenylboronic acid to aldehydes



Entry	8	R_n	Yield %
1	**a**	3,4,5-$(OCH_3)_3$	93
2	**b**	3,4,5-$(OCH_3)_3$	90
3	**c**	3,4,5-$(OCH_3)_3$	90
4	**d**	3,4,5-$(OCH_3)_3$	91
5	**a**	2,4,6-$(CH_3)_3$	97
6	**b**	2,4,6-$(CH_3)_3$	92
7	**c**	2,4,6-$(CH_3)_3$	94
8	**d**	2,4,6-$(CH_3)_3$	93
9	**a**	4-Cl	96
10	**b**	4-Cl	88
11	**c**	4-Cl	94
12	**d**	4-Cl	95
13	**a**	4-OCH_3	96
14	**b**	4-OCH_3	88
15	**c**	4-OCH_3	91
16	**d**	4-OCH_3	94

^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian AS 400 Mercury instrument. As solvents $CDCl_3$, CD_3OD and d_6-DMSO were employed. Chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. FTIR Spectra were recorded on a Perkin Elmer Spectrum 100 series.

4.1. General procedure

4.1.1. Preparation of monoxylyl linked bis(benzimidazolium) bromides *1, 2*

1-Alkyl-(5,6-dimethyl)benzimidazole (2.0 mmol) was dissolved in toluene and then 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene or 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (1.0 mmol) was added. The mixture was refluxed for 4 h. The solid that separated out after cooling was filtered off and washed with diethyl ether (5 mL). The product was recrystallized from CH_2Cl_2/Et_2O.

Meta bridged bibenzimidazolium salts (**1a**–**d**) were synthesized by a similar method but with stirring at room temperature for 24 h.

4.1.2. Preparation of bisxylyl linked bis(benzimidazolium) bromides (*5, 6, 7*)

1,3-Bis(5,6-dimethyl)benzimidazol-1-ylmethyl-2,4,6-trimethylbenzene or 1,4-bis(5,6-dimethyl)benzimidazol-1-ylmethyl- 2,3,5,6,-tetramethylbenzene (2.6 mmol) was dissolved in toluene and then 1,3-bis(bromomethyl)-2, 4,6-trimethylbenzene or 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (2.6 mmol) was added. The mixture was refluxed overnight. The solid that separated out after cooling was filtered off and washed with diethyl ether (5 mL).

4.1.3. 1,1′-Di(methoxyethyl)-3,3′-(2,4,6-trimethyl-1,3-xylylene)bibenzimidazolium dibromide (*1a*)

Yield: 90%; m.p. = 171–174 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1562. Anal. Calc. for $C_{31}H_{38}Br_2N_4O_2$: C, 56,55; H, 5.82; N, 8.51. Found: C, 56.51; H, 5.81; N, 8.59%. ^{1}H NMR (δ, $CDCI_3$): 2.30, 2.48 (s, 9H, $NCH_2C_6H(CH_3)_3CH_2N$), 3.22 (s, 6H, $-OCH_3$), 3.80 (t, 4H, $J = 1.2$ Hz, $NCH_2CH_2OCH_3$), 4.97 (t, 4H, $J = 1.2$ Hz, $NCH_2CH_2OCH_3$), 5.80 (s, 4H, $NCH_2C_6H(CH_3)_3CH_2N$), 7,15 (s, 1H, $NCH_2C_6H(CH_3)_3$-CH_2N), 7.62, 7.67 (t, 4H, $J = 2$ Hz, C_6H_4), 7.83, 8.24 (d, 4H, $J = 2.1$ Hz, C_6H_4), 10.27 (s, 2H, H_2). ^{13}C NMR (δ, $CDCI_3$): 17.6, 20.3 (-$NCH_2C_6H(CH_3)_3CH_2N$), 46.9 ($NCH_2C_6H_1(CH_3)_3CH_2N$), 48.1, 59.2 ($NCH_2CH_2OCH_3$), 71.2 ($NCH_2CH_2OCH_3$), 113.9, 114.4, 126.9, 127.6, 127.7, 131.6, 132.8, 132.8, 140.5, 140.9 ($NCH_2C_6H_1(CH_3)_3$-CH_2N,C_6H_4), 141.7 (C_2).

4.1.4. 1,1′-Di(2,4,6-trimethylbenzyl)-3,3′-(2,4,6-trimethyl-1,3-xylylene)bibenzimidazolium dibromide (*1b*)

Yield: 80%; m.p. = 199–201 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1560. Anal. Calc. for $C_{45}H_{50}Br_2N_4$: C, 67,00; H, 6.25; N, 6.95. Found: C, 67.11; H, 6.21; N, 6.89%. ^{1}H NMR (δ, $CDCI_3$): 2.23, 2.25, 2.32, 2.57 (s, 18H, $NCH_2C_6H(CH_3)_3CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 6.09 (s, 4H, 2,4,6-$CH_2C_6H_2$-$(CH_3)_3$), 7.26 (s, 4H, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 5.84 (s, 4H, $NCH_2C_6H_1(CH_3)_3CH_2N$), 6,84 (s, 1H, $NCH_2C_6H_1$-$(CH_3)_3CH_2N$), 6.89, 8.27 (d, 4H, $J = 2.1$ Hz, C_6H_4), 7.39, 7.62 (t, 4H, $J = 2.0$ Hz, C_6H_4), 10.86 (s, 2H, H_2). ^{13}C NMR(δ, $CDCI_3$): 17.1, 17.3, 17.5, 17.7, 20.3, (2,4,6-$CH_2C_6H_2(CH_3)_3$, $NCH_2C_6H(CH_3)_3CH_2N$), 47.3, 49.8 (2,4,6-$CH_2C_6H_2(CH_3)_3$, $NCH_2C_6H(CH_3)_3CH_2N$), 114.3, 114.4, 126.2, 126.9, 127.5, 127.6, 132.1, 132.0, 132.9, 133.6, 133.8, 136.9, 140.5, 140.9 (C_6H_4, NCH_2C_6H-$(CH_3)_3CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 141.9 (C_2).

4.1.5. 1,1′-Di(2,3,5,6-tetramethylbenzyl)-3,3′-(2,4,6-trimethyl-1,3-xylylene)bibenzimidazolium dibromide (*1c*)

Yield: 60%; m.p. = 200–202 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1559. Anal. Calc. for $C_{47}H_{54}Br_2N_4$: C, 67,62; H, 6.52; N, 6.71. Found: C, 67.70; H, 6.61; N, 6.80%. ^{1}H NMR (δ, $CDCI_3$): 2.17, 2.20 (s, 24H, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 2.33, 2.58 (s, 9H, $NCH_2C_6H(CH_3)_3CH_2N$), 5,86 (s, 4H, NCH_2C_6H-$(CH_3)_3CH_2N$), 6.15 (s, 4H, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 7,00 (s, 1H, $NCH_2C_6H(CH_3)_3CH_2N$), 7.32 (s, 2H, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 6.82, 8.22 (d, 4H, $J = 2.2$ Hz, C_6H_4), 7.34, 7.60 (m, 4H, C_6H_4), 10.83 (s, 2H, H_2). ^{13}C NMR (δ, $CDCI_3$): 16.3, 20.7 (2,3,5,6-$CH_2C_6H(CH_3)_4$), 17.7, 20.3 ($NCH_2C_6H(CH_3)_3CH_2N$), 47.3, 49.3 (NCH_2C_6H-$(CH_3)_3CH_2N$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 126.9, 127.5, 127.7, 128.9, 132.1, 132.9, 133.4, 134.1, 134.9, 140.5, 141.0 (C_6H_4, $NCH_2C_6H(CH_3)_3CH_2N$, 2,3,5,6-CH_2C_6H-$(CH_3)_4$), 141.9 (C_2).

4.1.6. 1,1′-Di(2,3,4,5,6-pentamethylbenzyl)-3,3′-(2,4,6-trimethyl-1,3-xylylene)bibenzimidazolium dibromide (*1d*)

Yield: 65%; m.p. = 217–221 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1560. Anal. Calc. for $C_{49}H_{58}Br_2N_4$: C, 68,21; H, 6.78; N, 6.49.

Found: C, 68.28; H, 6.81; N, 6.49%. ^{1}H NMR (δ, $CDCl_3$): 2.05–2.54 (m, 39H, $NCH_2C_6H(CH_3)_3CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 6.11 (s, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 6.10 (s, 1H, $NCH_2C_6H(CH_3)_3CH_2N$), 7,23 (s, 1H, $NCH_2C_6H(CH_3)_3CH_2N$), 6.84, 8.18 (d, 4H, $J = 2.1$ Hz, C_6H_4), 7.33, 7.58 (t, 4H, $J = 2.1$ Hz, C_6H_4), 10,75 (s, 2H, H_2). ^{13}C NMR(δ, $CDCl_3$): 17.6, 20.2, 20.5, 21.2 ($NCH_2C_6H(CH_3)_3CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 47.3, 48.5 (–$NCH_2C_6H(CH_3)_3CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 114.2, 114.5, 125.9, 126.8, 127.6, 127.7, 130.3, 131.9, 132.1, 132.9, 137.9, 139.4, 140.5, 141.1 (C_6H_4, $NCH_2C_6H(CH_3)_3CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 141.97 (C_2).

4.1.7. 1,1′-Di(methoxyethyl)-3,3′-(2,4,6-trimethyl-1,3-xylylene)5,6-dimethylbibenzimidazolium dibromide (**1′a**)

Yield: 59%, m.p. = 250–253 °C $\upsilon_{(NCN)}$ (cm^{-1}) = 1561. Anal. Calc. for $C_{35}H_{46}Br_2N_4O_2$: C, 58,83; H, 6.49; N, 7.84. Found: C, 58.91; H, 6.55; N, 7.89%.^{1}H NMR (δ, $CDCl_3$): 2.26, 2.45, 2.49, 2.50 (s, 21H $NCH_2C_6H(CH_3)_3CH_2N$, $C_6H_2(CH_3)_2$), 3.24 (s, 6H, –OCH_3), 3.79, 4.88 (t, 8H, $J = 1.2$ Hz; $NCH_2CH_2OCH_3$), 5.68 (s, 4H, $NCH_2C_6H(CH_3)_3CH_2N$), 7.16 (s, 1H, –$NCH_2C_6H(CH_3)_3CH_2N$), 7.52, 7.94 (s, 4H, $C_6H_2(CH_3)_2$), 10.09 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 17.6, 20.2, 20.8, 20.94 ($NCH_2C_6H(CH_3)_3CH_2N$, $C_6H_2(CH_3)_2$), 46.7, ($NCH_2C_6H(CH_3)_3CH_2N$), 47.7, 59.2 (–$NCH_2CH_2OCH_3$), 71.2 (-OCH_3), 113.5, 113.8, 127.0, 130.1, 131.2, 132.6, 137.7, 137.9, 140.4 ($NCH_2C_6H(CH_3)_3CH_2N$, $C_6H_2(CH_3)_2$), 140.7 (C_2).

4.1.8. 1,1′-Di(2,4,6-trimethylbenzyl)-3,3′-(2,4,6-trimethyl-1,3-xylylene)5,6-dimethylbibenzimidazolium dibromide (**1′b**)

Yield: 34%; m.p. = 172–175 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1560. Anal. Calc. for $C_{49}H_{58}Br_2N_4$: C, 68,21; H, 6.78; N, 6.49. Found: C, 68.23; H, 6.72; N, 6.52%. ^{1}H NMR (δ, $CDCl_3$): 2.15, 2.16, 2.20, 2.21, 2.38, 2.44 (s, 39H, 2,4,6-$CH_2C_6H_2(CH_3)_3$, $C_6H_2(CH_3)_2$, $NCH_2C_6H(CH_3)_3CH_2N$), 5.94 (s, 4H, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 6.78 (s, 4H, 2,4,6-$CH_2C_6H_2(CH_3)_3$); 5.69 (s, 4H, $NCH_2C_6H(CH_3)_3CH_2N$), 7.21 (s, 1H, $NCH_2C_6H(CH_3)_3CH_2N$), 6.56, 8.00 (s, 4H, $C_6H_2(CH_3)_2$), 10.58 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 17.4, 20.1, 20.4, 20.7, 21.1, 21.2 ($NCH_2C_6H(CH_3)_3CH_2N$, $C_6H_2(CH_3)_2$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 46.9, 48.2 ($NCH_2C_6H(CH_3)_3CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 113.8, 113.9, 126.1, 126.9, 130.2, 130.4, 130.7, 132.7, 137.8, 137.8, 137.9, 139.3, 140.1, 140.7 ($NCH_2C_6H(CH_3)_3CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$,$C_6H_2(CH_3)_2$), 140.9 (C_2).

4.1.9. 1,1′-Di(2,3,5,6-tetramethylbenzyl)-3,3′-(2,4,6-trimethyl-1,3-xylylene)5,6-dimethylbibenzimidazolium dibromide (**1′c**)

Yield: 46%; m.p. = 192–194 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1561. Anal. Calc. for $C_{51}H_{62}Br_2N_4$: C, 68.76; H, 7.01; N, 6.29. Found: C, 68.79; H, 7.11; N, 6.23%. ^{1}H NMR (δ, $CDCl_3$): 2.17, 2.22 (s, 24H, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 2.20, 2.31 (s, 12H, $C_6H_2(CH_3)_2$), 2.41, 2.53 (s, 9H, $NCH_2C_6H(CH_3)_3CH_2N$), 6.05, 6.56 (s, 4H, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 5.74 (s, 4H, $NCH_2C_6H(CH_3)_3CH_2N$), 7.23 (s, 1H, $NCH_2C_6H(CH_3)_3CH_2N$), 7.00, 7.82 (s, 4H, $C_6H_2(CH_3)_2$), 10.52 (s, 2H, H_2). ^{13}C NMR(δ, $CDCl_3$): 16.3, 17.6, 20.2, 20.7, 20.8, 21.1 ($NCH_2C_6H(CH_3)_3CH_2N$, $C_6H_2(CH_3)_2$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 46.9, 48.9 ($NCH_2C_6H(CH_3)_3CH_2N$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 113.7, 113.9, 127.1, 129.0, 130.5, 130.6, 132.7, 133.2, 134.1, 134.9, 137.5, 137.7, 140.5 ($NCH_2C_6H(CH_3)_3CH_2N$, $C_6H_2(CH_3)_2$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 140.7 (C_2).

4.1.10. 1,1′-Di(2,3,4,5,6-pentamethylbenzyl)-3,3′-(2,3,5,6-tetramethyl-1,3-xylylene)5,6-dimethylbibenzimidazolium dibromide (**1′d**)

Yield: 40%; m.p. = 197–199 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1561. Anal. Calc. for $C_{53}H_{66}Br_2N_4$: C, 69.27; H, 7.24; N, 6.10. Found: C, 69.25; H, 7.25; N, 6.19%. ^{1}H NMR (δ, $CDCl_3$): 2.19, 2.22, 2.26, 2.29, 2.31, 2.35, 2.39 (s, 51H, $C_6H_2(CH_3)_2$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), $NCH_2C_6H(CH_3)_3CH_2N$, 5.69 (s, 4H, $NCH_2C_6H(CH_3)_3CH_2N$), 7.09 (s, $NCH_2C_6H(CH_3)_3CH_2N$), 6.93, 7.21 (s, 4H, $C_6H_2(CH_3)_2$), 9.56 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 15.9, 17.2, 17.3, 19.7, 20.6, 20.9 ($NCH_2C_6H(CH_3)_3CH_2N$, $C_6H_2(CH_3)_2$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 47.8, 48.0 ($NCH_2C_6H(CH_3)_3CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 113.3, 113.2, 125.2, 127.2, 130.5, 131.7, 133.6, 133.9, 134.2, 137.5, 137.7, 138.0, 138.9, 139.3 ($NCH_2C_6H(CH_3)_3CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$, $C_6H_2(CH_3)_2$), 140.6 (C_2).

4.1.11. 1,1′-Di(methoxyethyl)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)bibenzimidazolium dibromide (**2a**)

Yield: 82%; m.p. = 265–267 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1560. Anal. Calc. for $C_{32}H_{40}Br_2N_4O_2$: C, 57.15; H, 6.00; N, 8.33. Found: C, 57.11; H, 6.05; N, 8.29%. ^{1}H NMR (δ, $CDCl_3$): 2.24 (s, 12H, $NCH_2C_6(CH_3)_4CH_2N$), 3.18 (s, 6H, –OCH_3), 3.72 (t, 4H, $J = 1.3$ Hz, $NCH_2CH_2OCH_3$), 4.77 (t, 4H, $J = 1.3$ Hz, $NCH_2CH_2OCH_3$), 5,84 (s, 4H, $NCH_2C_6(CH_3)_4CH_2N$), 7.72–8.21 (m, 8H, C_6H_4), 9,51 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 17.2 ($NCH_2C_6(CH_3)_4CH_2N$), 40.9, 58.8 ($NCH_2CH_2OCH_3$), 56.7 ($NCH_2C_6(CH_3)_4CH_2N$), 70.1 ($NCH_2CH_2OCH_3$), 127.4, 127.5, 130.6, 132.0, 132.3, 136.5 (C_6H_4, $NCH_2C_6(CH_3)_4CH_2N$), 142.2 (C_2).

4.1.12. 1,1′-Di(2,4,6-trimethylbenzyl)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)bibenzimidazolium dibromide (**2b**)

Yield: 80%; m.p. = 308–310 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1559. Anal. Calc. for $C_{46}H_{52}Br_2N_4$: C, 67,32; H, 6.39; N, 6.83. Found: C, 67.31; H, 6.44; N, 6.80%. ^{1}H NMR (δ, $CDCl_3$): 1.95, 2.22, 2.34 (s, 30H, $NCH_2C_6(CH_3)_4CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 6.07 (s, 4H, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 6.83 (s, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 5,93 (s, 4H, $NCH_2C_6(CH_3)_4CH_2N$), 6.87, 8.53 (d, 4H, $J = 2.2$ Hz, C_6H_4), 7.37, 7.66 (t, 4H, $J = 2.0$ Hz, C_6H_4), 10,77 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 17.4, 20.4, 21.2 ($NCH_2C_6(CH_3)_4CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 47.1, 48.2 ($NCH_2C_6(CH_3)_4CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 113.9, 115.1, 125.9, 127.7, 127.7,

129.5, 130.3, 131.9, 132.1, 136.7, 137.8, 139.4 (C_6H_4, $NCH_2C_6(CH_3)_4CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 142.1 (C_2).

*4.1.13. 1,1′-Di(2,3,5,6-tetramethylbenzyl)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)bibenzimidazolium dibromide (**2c**)*

Yield: 89%; m.p. = 250–251 °C (dec.); $\upsilon_{(NCN)}$ (cm^{-1}) = 1561. Anal. Calc. for $C_{48}H_{56}Br_2N_4$: C, 67,92; H, 6.65; N, 6.60. Found: C, 67.91; H, 6.71; N, 6.59%. ^1H NMR (δ, $CDCl_3$): 2.16, 2.19, 2.32 (s, 36H, $NCH_2C_6(CH_3)_4CH_2N$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 6.14 (s, 4H, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 5.93 (s, 4H, $NCH_2C_6(CH_3)_4CH_2N$), 6.77, 8.49 (d, 4H, $J = 2.2$ Hz, C_6H_4), 7.34, 7.65 (t, 4H, $J = 2.1$ Hz, C_6H_4), 10.78 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 16.2, 17.4, 20.7 (–$NCH_2C_6(CH_3)_4CH_2N$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 47.9, 49.1 ($NCH_2C_6(CH_3)_4CH_2N$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 114.1, 114.9, 127.6, 128.9, 129.2, 129.4, 132.0, 132.1, 133.3, 134.9, 136.6 (C_6H_4, $NCH_2C_6(CH_3)_4CH_2N$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 142.1 (C_2).

*4.1.14. 1,1′-Di(2,3,4,5,6-pentamethylbenzyl)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene) bibenzimidazolium dibromide (**2d**)*

Yield: 77%; m.p. = 220–221 °C (dec.) $\upsilon_{(NCN)}$ (cm^{-1}) = 1560. Anal. Calc. for $C_{50}H_{60}Br_2N_4$: C, 68.49; H, 6.90; N, 6.39. Found: C, 68.54; H, 6.92; N, 6.29%. ^1H NMR (δ, $CDCl_3$): 2.16–2.33 (m, 42H, $NCH_2C_6(CH_3)_4CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 6.13 (s, 4H, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 5.91 (s, $NCH_2C_6(CH_3)_4CH_2N$), 6.77, 8.47 (d, 4H, $J = 2.1$ Hz, C_6H_4), 7.32, 7.63 (t, 2H,$J = 1.9$ Hz, C_6H_4), 10,78 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 17.2, 17.4, 17.5, 20.7, ($NCH_2C_6(CH_3)_4CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 47.9, 49.6 ($NCH_2C_6(CH_3)_4CH_2N$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 114.2, 114.9, 126.3, 127.6, 127.7, 129.5, 132.0, 132.1, 133.5, 133.7, 136.7, 136.9 (C_6H_4, $NCH_2C_6(CH_3)_4CH_2N$, 2,3,5,6-$CH_2C_6(CH_3)_5$), 141.9 (C_2).

*4.1.15. 1,1′-Di(methoxyethyl)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)5,6- dimethylbibenzimidazolium dibromide (**2′a**)*

Yield: 70%, m.p. = 268–269 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1560. Anal. Calc. for $C_{36}H_{48}Br_2N_4O_2$: C, 59,34; H, 6.64; N, 7.69. Found: C, 59.31; H, 6.61; N, 7.77%. ^1H NMR (δ, $CDCl_3$): 2.28 (s, 12H, $NCH_2C_6(CH_3)_4CH_2N$), 2.43, 2.50 (s, 12H, $C_6H_2(CH_3)_2$); 3.26 (s, 6H, –OCH_3), 3.79, 4.84 (t, 4H, $J = 1.2$ Hz, $CH_2CH_2OCH_3$), 5,71 (s, 4H, $NCH_2C_6(CH_3)_4CH_2N$), 7.56, 8.05 (s, 4H, $C_6H_2(CH_3)_2$), 10.02 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 17.3 ($NCH_2C_6(CH_3)_4CH_2N$), 20.9, 20.96 ($C_6H_2(CH_3)_2$), 47.2 ($NCH_2C_6(CH_3)_4CH_2N$), 47.7, 59.3 ($NCH_2CH_2OCH_3$), 71.8 (OCH_3), 113.6, 113.9, 129.4, 130.1, 131.3, 136.5, 137.9, 138.0 ($C_6H_2(CH_3)_2$, $NCH_2C_6(CH_3)_4CH_2N$), 140.4 (C_2).

*4.1.16. 1,1′-Di(2,4,6-trimethylbenzyl)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)5, 6-dimethylbibenzimidazolium dibromide (**2′b**)*

Yield: 57%; m.p. = 226–228 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1559. Anal. Calc. for $C_{50}H_{60}Br_2N_4$: C, 68.49; H, 6.90; N, 6.39. Found: C, 68.45; H, 6.82; N, 6.42%. ^1H NMR (δ, $CDCl_3$): 2.21, 2.22 (s, 18H, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 2.25, 2.50 (s, 12H, $C_6H_2(CH_3)_2$), 2.33 (s, 12H, $NCH_2C_6(CH_3)_4CH_2N$), 6.84 (s, 4H, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 5,79 (s, $NCH_2C_6(CH_3)_4CH_2N$), 6.61, 8.16 (s, 4H, $C_6H_2(CH_3)_2$); 10,60 (s, 2H, H_2). ^{13}C NMR(δ, $CDCl_3$): 17.3, 20.4, 20.7 (2,4,6-$CH_2C_6H_2(CH_3)_3$, $NCH_2C_6(CH_3)_4CH_2N$), 21.1, 21.2 ($C_6H_2(CH_3)_2$), 47.4, 47.9 (2,4,6-$CH_2C_6H_2(CH_3)_3$, $NCH_2C_6(CH_3)_4CH_2N$), 113.7, 114.1, 126.1, 129.5, 130.2, 130.4, 130.6, 136.5, 137.7, 137.8, 137.9, 139.3 ($C_6H_2(CH_3)_2$, $NCH_2C_6(CH_3)_4CH_2N$, 2,4,6-$CH_2C_6H_2(CH_3)_3$), 141.0 (C_2).

*4.1.17. 1,1′-Di(2,3,5,6-tetramethylbenzyl)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)5,6-dimethylbibenzimidazolium dibromide (**2′c**)*

Yield: 75%; m.p. = 220–222 °C $\upsilon_{(NCN)}$ (cm^{-1}) = 1558. Anal. Calc. for $C_{52}H_{64}Br_2N_4$: C, 69,02; H, 7.13; N, 6.19. Found: C, 69.01; H, 7.11; N, 6.12%.^1H NMR (δ, $CDCl_3$): 2.15, 2.17, 2.20, 2.33, 2.45 (s, 48H, 2,3,5,6-$CH_2C_6H(CH_3)_4$, $NCH_2C_6(CH_3)_4CH_2N$, $C_6H_2(CH_3)_2$), 6.07 (s, 4H, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 6.51 (s, 2H, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 5,78 (s, 4H, $NCH_2C_6(CH_3)_4CH_2N$), 6.99, 8.13 (s, 4H, $C_6H_2(CH_3)_2$), 10,63 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 16.2, 17.3 (2,3,5,6-$CH_2C_6H(CH_3)_4$), 20.7 ($NCH_2C_6(CH_3)_4CH_2N$), 20.7, 21.1 ($C_6H_2(CH_3)_2$), 47.4, 48.8 (2,3,5,6-$CH_2C_6H(CH_3)_4$, $NCH_2C_6(CH_3)_4CH_2N$), 113.9, 129.1, 129.5, 130.5, 130.6, 133.2, 134.1, 134.8, 136.6, 137.6, 137.8 ($C_6H_2(CH_3)_2$, $NCH_2C_6(CH_3)_4CH_2N$, 2,3,5,6-$CH_2C_6H(CH_3)_4$), 140.9 (C_2).

*4.1.18. 1,1′-Di(2,3,4,5,6-pentamethylbenzyl)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)5,6-dimethylbibenzimidazolium dibromide (**2′d**)*

Yield: 59%; m.p. = 218–220 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1559. Anal. Calc. for $C_{45}H_{50}Br_2N_4$: C, 67.00; H, 6.25; N, 6.95. Found: C, 67.11; H, 6.21; N, 6.89%. ^1H NMR (δ, $CDCl_3$): 2.17, 2.18, 2.22, 2.23, 2.33, 2.44 (s, 54H, $NCH_2C_6(CH_3)_4CH_2N$, $C_6H_2(CH_3)_2$, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 6.53 (s, 2,3,4,5,6-$CH_2C_6(CH_3)_5$), 5,76 (s, 4H, $NCH_2C_6(CH_3)_4CH_2N$), 6.53; 8.06 (s, 4H, $C_6H_2(CH_3)_2$), 10,57 (s, 2H, H_2). ^{13}C NMR (δ, $CDCl_3$): 17.1, 17.2, 17.3, 17.5 (2,3,4,5,6-$CH_2C_6(CH_3)_5$, $NCH_2C_6(CH_3)_4CH_2N$), 20.8, 21.1 ($C_6H_2(CH_3)_2$), 47.4, 49.3 (2,3,4,5,6-$CH_2C_6(CH_3)_5$, $NCH_2C_6H_0(CH_3)_4CH_2N$), 113.9, 114.1, 126.5, 129.5, 130.5, 130.6, 133.5, 133.6, 136.5, 136.7, 137.5, 137.7 ($C_6H_2(CH_3)_2$, $NCH_2C_6(CH_3)_4CH_2N$, 2,3,4,5,6-CH_2C_6 $(CH_3)_5$), 140.9 (C_2).

*4.1.19. 1,1′-(2,4,6-Trimethylbenzyl-1,3-xylylene)-3,3′-(2,4,6- trimethyl-1,3-xylylene)bibenzimidazolium dibromide (**5**)*

Yield: 65%; m.p. = 294–295 °C (dec.) $\upsilon_{(NCN)}$ (cm^{-1}) = 1553. Anal. Calc. for $C_{36}H_{38}Br_2N_4$: C, 62.98; H, 5.58; N, 8.16. Found: C, 63.01; H, 5.61; N, 8.09%.^1H NMR (δ, DMSO): 1.59, 2.43 (s, 18H, $NCH_2C_6H(CH_3)_3CH_2N$), 5.56; 5.80 (d, 8H, $J = 3.7$ Hz, $NCH_2C_6H(CH_3)_3CH_2N$), 7.78 (s, 2H, $NCH_2C_6H(CH_3)_3CH_2N$), 7.80–8.30 (m, 8H, C_6H_4), 7,22 (s, 2H, H_2). ^{13}C NMR (δ, DMSO): 15.6, 20.6 ($NCH_2C_6H(CH_3)_3CH_2N$), 46.3 ($NCH_2C_6H(CH_3)_3CH_2N$);

114.7, 127.9, 128.1 132.5, 133.0, 138.5, 138.7 (C_6H_4, $NCH_2C_6H(CH_3)_3CH_2N$), 140.9 (C_2).

4.1.20. 1,1′-(2,4,6-Trimethylbenzyl-1,3-xylylene)-3,3′-(2,4,6-trimethyl-1,3-xylylene)5,6-dimethylbibenzimidazolium dibromide (5′)

Yield: 60%; m.p. = 295 °C (dec.) $\upsilon_{(NCN)}$ (cm^{-1}) = 1573. Anal. Calc. for $C_{40}H_{46}Br_2N_4$: C, 64,69; H, 6.24; N, 7.54. Found: C, 64.71; H, 6.21; N, 6.58%. ^1H NMR (δ, DMSO): 1.54, 2.41 (s, 18H, $NCH_2C_6H(CH_3)_3CH_2N$), 3.31 (s, 12H, $C_6H_2(CH_3)_2$), 5.49; 5.72 (d, 8H, $J = 3.7$ Hz, $NCH_2C_6H(CH_3)_3CH_2N$), 7.62 (s, 2H, $NCH_2C_6H(CH_3)_3CH_2N$), 8.08 (s, 4H, $C_6H_2(CH_3)_2$), 7.20 (s, 2H, H_2). ^{13}C NMR (δ, DMSO): 15.9, 20.7 ($NCH_2C_6H(CH_3)_3CH_2N$), 20.9 ($C_6H_2(CH_3)_2$), 46.2 ($NCH_2C_6H(CH_3)_3CH_2N$), 114.2, 128.3, 131.0, 137.7, 138.4 ($C_6H_2(CH_3)_2$, $NCH_2C_6H(CH_3)_3CH_2N$), 140.8 (C_2).

4.1.21. 1,1′-(2,4,6-Trimethylbenzyl-1,3-xylylene)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)bibenzimidazolium dibromide (6)

Yield: 66%; m.p. = 291 °C (dec.) $\upsilon_{(NCN)}$ (cm^{-1}) = 1563. Anal. Calc. for $C_{37}H_{40}Br_2N_4$: C, 63,44; H, 5.76; N, 8.00. Found: C, 63.41; H, 5.82; N, 8.09%. ^1H NMR (δ, CD_3OD): 2.15; 2.23 (s, 9H, $NCH_2C_6H(CH_3)_3CH_2N$), 2.31 (s, 12H, $NCH_2C_6(CH_3)_4CH_2N$), 5.61–6.05 (m, 8H, $NCH_2C_6H(CH_3)_3CH_2N$, $NCH_2C_6(CH_3)_4CH_2N$), 7.29 (s, 1H, $NCH_2C_6H(CH_3)_3CH_2N$), 7.89–8.35 (m, 8H, C_6H_4), 6,67 (s, 2H, H_2). ^{13}C NMR (δ, CD_3OD): 14.6, 15.6, 18.6 ($NCH_2C_6H(CH_3)_3CH_2N$, $NCH_2C_6(CH_3)_4CH_2N$), 45.7, 46.3 ($NCH_2C_6H(CH_3)_3CH_2N$, $NCH_2C_6(CH_3)_4CH_2N$), 113.8, 113.9, 127.9, 128.1, 128.1, 131.2, 132.5, 132.7, 132.8 (C_6H_4,$NCH_2C_6H(CH_3)_3CH_2N$, $NCH_2C_6(CH_3)_4CH_2N$), 141.9 (C_2).

4.1.22. 1,1′-(2,4,6-Trimethylbenzyl-1,3-xylylene)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)5,6-dimethylbibenzimidazolium dibromide (6′)

Yield: 47%; m.p. = 327–330 °C (dec.) $\upsilon_{(NCN)}$ (cm^{-1}) = 1569. Anal. Calc. for $C_{41}H_{48}Br_2N_4$: C, 65,08; H, 6.39; N, 7.40. Found: C, 65.11; H, 6.33; N, 7.28%. ^1H NMR (δ, CD_3OD): 2.29 (s, 12H, $NCH_2C_6(CH_3)_4CH_2N$), 2.17, 2.22 (s, 9H, $NCH_2C_6H(CH_3)_3CH_2N$), 2.57 (s, 4H, $C_6H_2(CH_3)_2$), 5.44–5.97 (m, 8H, $NCH_2C_6(CH_3)_4CH_2N$, $NCH_2C_6H(CH_3)_3CH_2N$), 7.27 (s, 1H, $NCH_2C_6H(CH_3)_3CH_2N$), 8.07, 8.10 (s, 4H, $C_6H_2(CH_3)_2$), 6,45 (s, 2H, H_2). ^{13}C NMR(δ, CD_3OD): 14.6, 15.5, 18.6, 19.6 ($NCH_2C_6H(CH_3)_3CH_2N$, $NCH_2C_6(CH_3)_4CH_2N$, $C_6H_2(CH_3)_2$), 45.6, 46.2 ($NCH_2C_6H(CH_3)_3CH_2N$, $NCH_2C_6(CH_3)_4CH_2N$), 113.3, 127.7, 131.2, 131.3, 131.4, 132.4, 135.2, 135.9, 136.5, 138.7, 138.7, 138.9 ($C_6H_2(CH_3)_2$, $NCH_2C_6H(CH_3)_3CH_2N$, $NCH_2C_6(CH_3)_4CH_2N$), 141.8 (C_2).

4.1.23. 1,1′-(2,3,5,6-Tetramethylbenzyl-1,4-xylylene)-3,3′-(2,3,5, 6-tetramethyl-1,4-xylylene) bibenzimidazolium dibromide (7)

Yield: 70%; m.p. = 348–350 °C (dec.) $\upsilon_{(NCN)}$ (cm^{-1}) = 1551. Anal. Calc. for $C_{38}H_{42}Br_2N_4$: C, 63,87; H, 5.92; N, 7.84. Found: C, 63.80; H, 5.91; N, 7.89 %.^1H NMR (δ, DMSO): 2.10 (s, 24H, $NCH_2C_6(CH_3)_4CH_2N$), 5.81 (s, 8H, $NCH_2C_6(CH_3)_4CH_2N$), 7.90–8.37 (m, 8H, C_6H_4), 7,23 (s, 2H, H_2). ^{13}C NMR (δ, DMSO): 16.8 ($NCH_2C_6(CH_3)_4CH_2N$), 46.8 ($NCH_2C_6(CH_3)_4CH_2N$), 114.9, 128.2, 130.9, 132.9, 136.4 (C_6H_4,$NCH_2C_6(CH_3)_4CH_2N$), 136.7 (C_2).

4.1.24. 1,1′-(2,3,5,6-Tetramethylbenzyl-1,4-xylylene)-3,3′-(2,3,5,6-tetramethyl-1,4-xylylene)5,6-dimethylbibenzimidazolium dibromide (7′)

Yield: 66%; m.p. = 329 (dec.); $\upsilon_{(NCN)}$ (cm^{-1}) = 1546. Anal. Calc. for $C_{42}H_{50}Br_2N_4$: C, 65,46; H, 6.54; N, 7.27. Found: C, 65.48; H, 6.51; N, 6.29 %. ^1H NMR (δ, DMSO): 2.07 (s, 24H, $NCH_2C_6(CH_3)_4CH_2N$), 2.53 (s, 12H, $C_6H_2(CH_3)_2$), 5.73 (s, $NCH_2C_6(CH_3)_4CH_2N$), 6,22 (s, 2H, H_2), 8.14 (s, 4H, $C_6H_2(CH_3)_2$). ^{13}C NMR (δ, DMSO): 16.7 ($NCH_2C_6H(CH_3)_4CH_2N$), 20.9 ($C_6H_2(CH_3)_2$), 46.6 ($NCH_2C_6(CH_3)_4CH_2N$), 114.4, 131.0, 131.3, 135.2, 136.3 ($C_6H_2(CH_3)_2$, $NCH_2C_6(CH_3)_4CH_2N$), 137.9 (C_2).

4.1.25. General procedure for the preparation of [RhBr(η⁴-COD)(NHC)] (8)

Complex **2** (0.32 mmol) and $[Rh(OMe)COD]_2$ (0.32 mmol) were added in a SCHLENK tube. The mixture stirred in toluene (8 mL) and refluxed overnight. The product was filtered off and the filtrate was concentrated under vacuum, then crystallized from CH_2Cl_2/EtOH.

4.1.26. [Di(cyclopentadiene){1,1′-di(2-methoxyethyll)-3,3′-2,3,5,6-tetramethyl-1,4-xylylene bibenzimidazole-2,2′-diylidene}]dirhodium(I) dibromide (8a)

Yield: 72%; m.p. = 290–291 °C. Anal. Calc. for $C_{48}H_{62}Rh_2Br_2N_4$: C, 52,76; H, 5.72; N, 5.13. Found: C, 52.51; H, 5.91; N, 4.99 %. ^1H NMR ($CDCl_3$): 1.89–1.99 (m, 8H, COD–CH_2), 2.24 (s, 12H, $NCH_2C_6(CH_3)_4CH_2N$), 2.34–2.48 (m, 8H, COD-CH_2), 3.34 (s, 6H, –OCH_3), 3.41 (s, 2H, COD–CH=CH), 3.55 (s, 2H, COD–CH=CH), 4.01, 4.85 (m, 4H, $NCH_2CH_2OCH_3$), 5.21 (s, 4H, COD–CH=CH), 5.92, 6.48 (d,$J = 3.7$ Hz, 4H, $NCH_2C_6(CH_3)_4CH_2N$), 6.10, 6.78, 7.03, 7.38 (m, 8H, C_6H_4). ^{13}C NMR ($CDCl_3$, δ, ppm): 17.9 ($NCH_2C_6(CH_3)_4CH_2N$), 28.8, 29.7, 32.7, 33.8 (COD-CH_2), 46.7 ($NCH_2CH_2OCH_3$), 52.0 ($NCH_2C_6(CH_3)_4CH_2N$), 59.8 ($NCH_2CH_2OCH_3$), 70.2 (d, $J = 14.5$ Hz, COD–CH=CH), 70.4 (d, $J = 13.7$ Hz, COD–CH=CH), 72.5 ($NCH_2CH_2OCH_3$), 99.6; 99.9 (d, $J = 6.1$ Hz, COD–CH=CH), 110.6, 112.0, 123.2, 124.3, 131.9, 134.3, 135.1, 136.9 (C_6H_4, $NCH_2C_6(CH_3)_4CH_2N$), 198.6 (d, $J = 50.3$ Hz, Rh–C).

4.1.27. [Di(cyclopentadiene){1,1′-Di(2,4,6-trimethylbenzyl)-3,3′-2,3,5,6-tetramethyl-1,4-xylylenebibenzimidazole-2,2′-diylidene}]dirhodium(I) dibromide (8b)

Yield: 75%; m.p. = 308–309 °C. Anal. Calc. for $C_{62}H_{74}Rh_2Br_2N_4$: C, 60.01; H, 6.01; 4.52. Found: C, 60.11; H, 6.13; N, 4.43%. ^1H NMR ($CDCl_3$): 1.97–2.08 (m, 8H, COD–CH_2), 2.33 (s, 30H, $NCH_2C_6(CH_3)_4CH_2N$,

$NCH_2C_6H_2(CH_3)_3$), 2.38–2.55 (m, 8H, COD–CH_2), 3.56 (s, 2H, COD–CH=CH), 3.62 (s, 2H, COD–CH=CH), 5.28 (s, 4H, COD–CH=CH), 5.91 (d, 2H, $J = 3.7$ Hz, $NCH_2C_6(CH_3)_4CH_2N$), 6.01, 6.03 (s, 4H, $NCH_2C_6(CH_3)_4CH_2N$), 6.54 (s, 2H, $NCH_2C_6H_2(CH_3)_3$), 6.71–6.78 (m, 6H, $NCH_2C_6H_2(CH_3)_3$, C_6H_4), 6.18, 6.28 (m, 4H, C_6H_4), 6.92 (s, 4H, $NCH_2C_6H_2(CH_3)_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 17.9, 21.2, 22.5 ($NCH_2C_6H(CH_3)_3$, $NCH_2C_6(CH_3)_4CH_2N$), 28.9, 29.5, 32.7, 33.4 (COD–CH_2), 50.4 ($NCH_2C_6H(CH_3)_3$), 52.0 ($NCH_2C_6(CH_3)_4CH_2N$), 70.2 (d, $J = 14.5$ Hz, COD–CH=CH), 70.4 (d, $J = 13.7$ Hz, COD–CH=CH), 99.6; 99.9 (d, $J = 6.1$ Hz, COD–CH=CH), 110.9, 122.0, 122.2, 128.3, 129.9, 132.3, 135.5, 135.9, 137.7, 138.5, 138.6 (C_6H_4, $NCH_2C_6(CH_3)_4CH_2N$, $NCH_2C_6H_2(CH_3)_3$), 198.6 (d, $J = 50.3$ Hz, Rh–C).

4.1.28. [Di(cyclopentadiene){1,1′-Di(2,3,5,6-tetramethylbenzyl)-3,3′-2,3,5,6-tetramethyl-1,4-xylylenebibenzimidazole-2,2′-diylidene}]dirhodium(I) dibromide (**8c**)

Yield: 68%; m.p. = 305–306 °C. Anal. Calc. for $C_{64}H_{78}Rh_2Br_2N_4$: C, 60.58; H, 6.20; 4.42. Found: C, 60.61; H, 6.18; N, 4.41%. ^{1}H NMR ($CDCl_3$): 1.98–2.04 (m, 8H, COD–CH_2), 2.26; 2.33 (s, 36H, $NCH_2C_6(CH_3)_4CH_2N$, $NCH_2C_6H(CH_3)_4$) 2.43–2.55 (m, 8H, COD–CH_2), 3.65 (m, 4H, COD–CH=CH), 5.30 (m, 4H, COD–CH=CH), 6.04, 5.99 (d, 4H, $J = 3.8$ Hz, $NCH_2C_6(CH_3)_4CH_2N$), 6.63 (d, 2H, $J = 3.7$ Hz, $NCH_2C_6H(CH_3)_4$), 6.10, 6.18, 6.73 (m, 12H, $NCH_2C_6H(CH_3)_4$, C_6H_4) 7.07 (s, 2H, $NC_6H(CH_3)_4$). ^{13}C NMR ($CDCl_3$, δ, ppm): 16.8, 17.9, 20.8 ($NCH_2C_6H(CH_3)_4$, $NCH_2C_6(CH_3)_4CH_2N$), 28.9, 29.5, 32.7, 33.4 (COD-CH_2), 51.4 ($NCH_2C_6H(CH_3)_4$), 51.9 ($NCH_2C_6(CH_3)_4CH_2N$), 69.9, 70.5 (d, $J = 15.2$ Hz, COD–CH=CH), 99.4 (d, $J = 6.1$ Hz, COD–CH=CH), 110.7, 111.0, 121.9, 128.9, 131.1, 132.2, 132.6, 134.5, 134.9, 135.5, 135.6 (C_6H_4, $NCH_2C_6(CH_3)_4CH_2N$, $NCH_2C_6H(CH_3)_4$), 198.1 (d, $J = 48.8$ Hz, Rh–C).

4.1.29. [Di(cyclopentadiene){1,1′-di(pentamethylbenzyl)-3,3′-2,3,5,6-tetramethyl-1,4-xylylenebibenzimidazole-2,2′-diylidene}]dirhodium(I) dibromide (**8d**)

Yield: 82%; m.p. = 301–302 °C. Anal. Calc. for $C_{66}H_{82}Rh_2Br_2N_4$: C, 61.12; H, 6.37; N, 4.32. Found: C, 61.21; H, 6.32; N, 4.41%. ^{1}H NMR ($CDCl_3$): 1.96–2.07 (m, 8H, COD–CH_2), 2.11, 2.20, 2.27 (s, 30H, $NCH_2C_6(CH_3)_5$), 2.36 (s, 12H, $NCH_2(CH_3)_4C_6CH_2N$), 2.38 (m, 8H, COD–CH_2), 3.60 (s, 2H, COD–CH=CH), 3.62 (s, 2H, COD–CH=CH), 5.24 (s, 4H, COD–CH=CH), 5.91, 5.93, 5.96, 6.01, (s, 4H, $NCH_2C_6(CH_3)_5$), 6.20 (m, 2H, C_6H_4), 6.28 (m, 2H, C_6H_4), 6.53, 6.57 (s, 4H, $NCH_2C_6(CH_3)_5$), 6.64 (m, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$, δ, ppm): 16.4, 20.8, 21.2, 21.3 ($NCH_2C_6(CH_3)_4CH_2N$, $NCH_2C_6(CH_3)_5$), 29.1, 33.1 (COD–CH_2), 51.2, 51.8 ($NCH_2C_6(CH_3)_4CH_2N$, $NCH_2C_6(CH_3)_5$), 70.0 (d, $J = 14.5$ Hz, COD–CH=CH), 99.4 (d, $J = 6.1$ Hz, COD–CH=CH), 111.7, 117.9, 120.8, 125.7, 131.0, 128.3, 132.2, 134.0, 134.1, 135.1, 135.3 (C_6H_4, $NCH_2C_6(CH_3)_4CH_2N$, $NCH_2C_6(CH_3)_5$), 198.0 (d, $J = 50.0$ Hz, Rh–C).

Acknowledgement

Financial support from Ege University (Project 05 FEN-020) is gratefully acknowledged.

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