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Synthesis of *N*-heterocyclic carbene precursors bearing biphenyl units and their use in ruthenium-catalyzed ring-opening metathesis polymerization

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Abstract

A range of new imidazolium and imidazolinium chlorides bearing biphenyl units on their nitrogen atoms was synthesized. They differed by the electron-withdrawing or -donating nature and the steric bulk of the substituents on their aromatic rings. These various *N*-heterocyclic carbene (NHC) precursors were combined with the $[RuCl_2(p\text{-cymene})]_2$ dimer and potassium *tert*-butoxide to generate the corresponding ruthenium–arene complexes $[RuCl_2(p\text{-cymene})(NHC)]$ *in situ*. The catalytic activity of these species was investigated in the photoinduced ring-opening metathesis polymerization (ROMP) of cyclooctene. The results obtained confirmed the necessity of blocking the *ortho*-positions of the phenyl rings in the vicinity of the metal center in order to attain high catalytic efficiencies. They also showed that changing the steric and electronic properties of the substituents on the remote phenyl rings of the biphenyl units had no significant influence on the outcome of the polymerization.

Keywords: Arene ligands; Biaryls; Carbene ligands; Cyclooctene; Homogeneous catalysis; Substituent effects

1. Introduction

Stable *N*-heterocyclic carbenes (NHC) [1] have become ubiquitous species in organometallic synthesis and catalysis [2–10]. In particular, they have proved extremely valuable ligands for the development of highly active olefin metathesis catalysts [11–13]. Indeed, ruthenium–alkylidene complexes bearing NHC ligands have found numerous applications as promoters for ring-closing metathesis (RCM) [14–16], ring-opening metathesis polymerization (ROMP) [17–19], or cross-metathesis (CM) [20]. In the course of our investigations toward ruthenium–arene complexes as catalysts for the ROMP of strained and low-strain cycloolefins, we became interested in complexes of type **3** bearing a NHC ligand on the metal center [21]. Such species were obtained when the dichlororuthenium–(*p*-cymene) dimer **1** was reacted with a stoichiometric amount of free carbene, either preformed or generated *in situ* by deprotonation of a more stable ionic precursor (Scheme 1). Thus, a wide range of imidazolium and imidazolinium salts (with or without a formal double bond between C4 and C5 in structure **2**, respectively) were prepared, and the corresponding ruthenium complexes **3** were screened as catalyst precursors in the ROMP of cyclooctene. This preliminary study revealed the occurrence of a photochemical activation step due to visible light illumination during the polymerization process [22]. It also showed that complexes based on NHCs substituted by alkyl groups on both nitrogen atoms were devoid of any significant catalytic activity in the polymerization of cyclooctene. Aryl-substituted ligands, on the other hand, afforded much more active catalysts provided that all the available *ortho* positions of the phenyl rings were blocked by alkyl groups. Failure to do so most likely results

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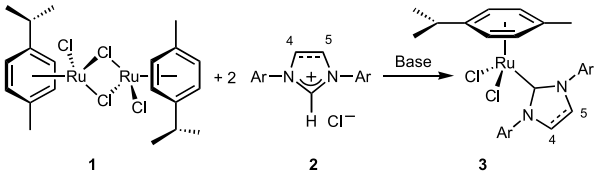


Scheme 1. Synthesis of ruthenium–arene complexes bearing NHC ligands.

in the *ortho*-metallation of the carbene ligand, thereby altering the coordination sphere of the ruthenium center [23].

Since the presence of highly conjugated substituents on the NHC ligand should favor the visible light absorption that triggers the photoinitiated polymerization process, we decided to direct our synthetic efforts toward the preparation of new imidazolium and imidazolinium salts bearing various biaryl groups on their nitrogen atoms. Structural motives derived from the biphenyl ring system are present in several types of organic compounds, including natural products, polymers, liquid crystals, advanced materials, and medicinal drugs [24,25]. The wide variety of physical and chemical properties available by changing the nature of the substituents on the two aromatic cycles makes them also very attractive ligand components for the fine-tuning of catalysts in organometallic chemistry. Hence, we focused on the synthesis of a small library of imidazolium and imidazolinium salts bearing biphenyl units that would differ by the electron-withdrawing or -donating nature and the steric bulk of substituents introduced on different *meta*- and *para*-positions of the remote phenyl rings. To avoid any *ortho*-metallation effect, we also chose to block both *ortho* positions of the aromatic rings in the vicinity of the metal center by methyl groups. In this contribution, we report on the synthesis of these new NHC precursors and their use in the visible-light induced ROMP of cyclooctene catalyzed by ruthenium complexes generated *in situ*.

2. Results and discussion

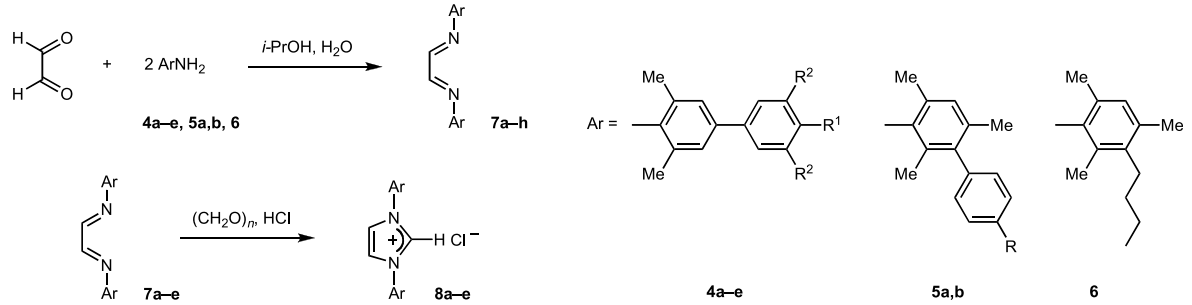
2.1. Synthesis of NHC precursors bearing biphenyl units on their nitrogen atoms

2.1.1. Preparation of imidazolium salts

The one-pot synthesis of 1,3-diarylimidazolium salts from glyoxal, an aromatic amine, and paraformaldehyde in the presence of an inorganic acid is often tedious and usually leads to highly colored ionomer by-products that are very difficult to separate from the desired heterocyclic compounds, particularly when working on a small laboratory scale. Thus, we have followed the more reliable "two reactions, two filtrations" approach first investigated by Arduengo [26] and Nolan [27]. This method involves the condensation of glyoxal with two equivalents of an arylamine to generate the corresponding Schiff base. This intermediate is isolated and subjected to cyclization with paraformaldehyde under acidic conditions in a second discrete step.

The procedure was applied to a set of *para*- (**4a–e**) and *meta*-substituted (**5a,b**) biphenylamines obtained by Suzuki–Miyaura cross-coupling reactions [28]. In all cases, the reactions with glyoxal afforded the corresponding diimines in moderate to good yields and high purities (Table 1). Conversely, the second step gave mixed results. With the 4-aminobiphenyl derivatives **7a–e**, cyclization proceeded cleanly and the imidazolium chlorides **8a–e** were

Table 1
Synthesis of biphenyl-substituted imidazolium chlorides



Substrate	R^1 (or R)	R^2	Schiff base		Imidazolium salt	
			Product	Isolated yield (%)	Product	Isolated yield (%)
4a	H	F	**7a**	35	**8a**	51
4b	H	CF_3	**7b**	36	**8b**	46
4c	OMe	H	**7c**	97	**8c**	75
4d	OPh	H	**7d**	73	**8d**	42
4e	*t*-Bu	H	**7e**	77	**8e**	65
5a	H	–	**7f**	36	**8f**	0[a]
5b	Cl	–	**7g**	26	**8g**	0[a]
6	–	–	**7h**	83	**8h**	15

[a] Only tarry materials were obtained.

isolated in satisfactory yields and purities by simple filtration and washing. Apparently, the presence of electron-donating substituents on the biphenyl units rendered the amino groups more nucleophilic and had a beneficial influence on the cyclization process, since the reaction of *para*-methoxy derivative **7c** occurred in 75% yield, whereas compounds **7a** and **7b** sporting fluorinated electron-withdrawing groups led to the imidazolium chlorides **8a** and **8b** in 51 and 46% yields, respectively.

Although the "two reactions, two filtrations" method with paraformaldehyde as the C1 building block gave better results than the other paths that we had investigated previously for the synthesis of imidazolium salts [23], it nevertheless had its own limitations. This was evidenced from our attempts to cyclize the 3-aminobiphenyl derivatives **7f** and **7g** using the same experimental conditions that proved successful for the 4-aminobiphenyl series (**7a**–**e**). Whereas members of the *para* family afforded off-white precipitates that could be easily separated by filtration, the *meta* isomers led only to dark molasses, out of which no pure products could be isolated. An additional experiment with diimine **7h** bearing alkyl chains instead of phenyl groups in *meta* position confirmed that this substitution pattern had an adverse effect on the outcome of the cyclization process.

2.1.2. Preparation of imidazolinium salts

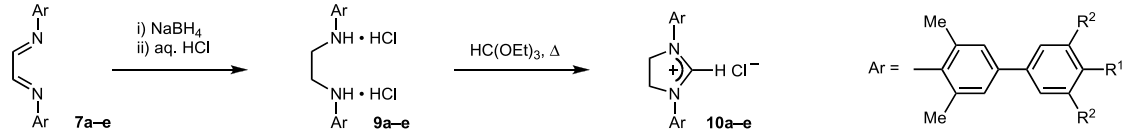
To further enlarge our set of NHC ligand precursors, we prepared the saturated imidazolinium chlorides **10a**–**e** bearing various substituted *para*-biphenyl units in parallel with the unsaturated imidazolium salts **8a**–**e**. To perform this transformation, we followed a reaction scheme first outlined by Arduengo [26] and later modified by Grubbs [29]. It involved the reduction of the biaryl diimines (**7a**–**e**) into the corresponding diamines dihydrochlorides **9a**–**e** using sodium borohydride in the presence of hydrochloric acid. The open-chain intermediates were then subjected to ring-closure with triethyl orthoformate in the presence of catalytic amounts of formic acid (Table 2) [30].

Compared to the cyclization of diimines into imidazolium salts (cf. Table 1), the reaction of diamines dihydrochlorides to give saturated rings usually proceeded with lower yields. Yet, the same trends were observed in both processes, since acceptable results were obtained with derivatives **9c**–**e** bearing electron-donating substituents, whereas compounds **9a** and **9b** bearing fluorinated electron-withdrawing groups afforded only traces of the corresponding imidazolinium salts (Table 2). Similar electronic effects also affected the reduction of the Schiff bases **7a**–**e** into the intermediate diamines dihydrochlorides **9a**–**e**. However, their influence was less critical and did not preclude the isolation of fluorinated compounds **9a** and **9b** in quantities large enough to carry on the synthesis.

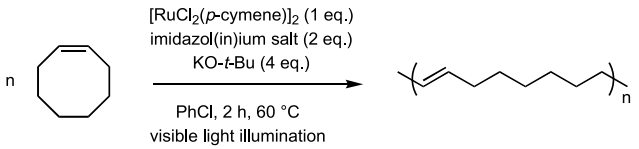
2.2. Polymerization of cyclooctene

In our laboratory, the ring-opening metathesis polymerization (ROMP) of cyclooctene serves as a standard test reaction to assess the metathetical activity of new catalyst precursors [21–23]. Unlike bicyclic olefins such as norbornene [31], cyclooctene displays only a low ring strain [32] and requires highly efficient catalysts to afford polyoctenamer within short periods of time under mild conditions. In the present study, NHC ligands bearing biphenyl units on their nitrogen atoms were generated *in situ* by deprotonation of the corresponding imidazol(in)ium salts with potassium *tert*-butoxide. The free carbenes were immediately trapped with ruthenium dimer **1** before cyclooctene was added and ROMP began. The whole sequence was carried out in chlorobenzene at 60 °C for 2 h under an inert atmosphere. The transition metal and the carbene precursors were in 1:1 stoichiometric proportions (albeit 2 equivalents of base were used), while the monomer-to-ruthenium ratio was 250. An ordinary 40 W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flasks complemented the experimental set-up and provided a constant and reproducible visible light source (Scheme 2). Although this procedure was less rigorous than the isolation of preformed ruthenium–NHC complexes prior to their use as catalysts for ROMP, it proved much more convenient to rapidly screen a large number of catalyst precursors. Furthermore, control experiments carried out with the mesityl-substituted imi-

Table 2
Synthesis of biphenyl-substituted imidazolinium chlorides



Substrate	R^1	R^2	Diamine dihydrochloride		Imidazolinium salt	
			Product	Isolated yield (%)	Product	Isolated yield (%)
7a	H	F	**9a**	22	**10a**	Traces
7b	H	CF_3	**9b**	47	**10b**	Traces
7c	OMe	H	**9c**	78	**10c**	60
7d	OPh	H	**9d**	91	**10d**	43
7e	*t*-Bu	H	**9e**	86	**10e**	60



Scheme 2. ROMP of cyclooctene with *in situ* generated catalysts.

dazolium salt **11** (shortened as IMes · HCl, see Fig. 1) confirmed that the catalyst generated *in situ* was almost as effective as the preformed complex [$RuCl_2$(*p*-cymene)(IMes)] [22,23].

In a first series of experiments, we investigated the catalytic activities of imidazolium salts **8a**–**e** toward the ruthenium-promoted ROMP of cyclooctene. In all cases, monomer conversion was essentially complete after 2 h at 60 °C and polyoctenamer was isolated in close to quantitative yields (Table 3, entries 1–5). These results are similar to those obtained previously with the mesityl-substituted imidazolium salt **11** (entry 6) [22]. However, the polymers formed in the presence of biphenyl-substituted derivatives **8a**–**e** resisted dissolution in THF or chloroform, thereby preventing their characterization, whereas the sample prepared with catalyst precursor **11** was more readily soluble in organic media. NMR and GPC analyses performed on this latter material had shown that it consisted mainly of *trans* polyoctenamer ($\sigma_{cis} = 0.20$) with a high molecular weight ($M_n = 659{,}000$) and a rather narrow polydispersity ($M_w/M_n = 2.02$) [22]. The polymers obtained with NHC precursors **8a**–**e** most likely possessed even higher molecular weights, thereby explaining their insolubility. Hence, contrary to our expectations, introduction of a second phenyl ring on the carbene nitrogen substituents did not increase the number of active species formed during the photocatalytic ROMP process.

Cross-examination of the results obtained with catalyst precursors **8a**–**e** and their unsubstituted parent 1,3-di(biphenyl-4-yl)imidazolium chloride (**12**) confirmed that

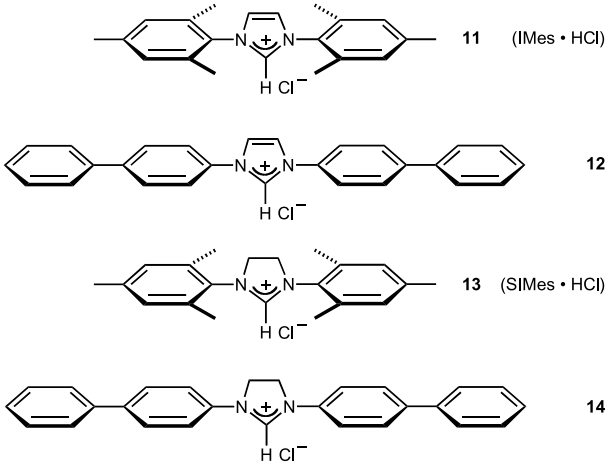


Fig. 1. Structure of imidazol(in)ium salts used for control experiments.

Table 3
ROMP of cyclooctene in PhCl at 60 °C catalyzed by various ruthenium–NHC complexes generated *in situ* from [$RuCl_2$(*p*-cymene)]$_2$, an imidazolium salt, and KO-*t*-Bu

Entry	Imidazolium salt	Monomer conversion (%)	Isolated polymer yield (%)
1	**8a**	97	83
2	**8b**	99	85
3	**8c**	99	88
4	**8d**	97	92
5	**8e**	99	89
6	**11**	99	92
7	**12**	24	0

the presence of methyl groups on all the *ortho* positions of the phenyl rings adjacent to the central heterocycle was mandatory to achieve high catalytic efficiencies. In the absence of any substituent on the biphenyl units, conversion stopped at a mere 24% after 2 h at 60 °C and no polymer was isolated (entry 7). This dissimilarity further supports the intervention of a deactivation process that is believed to take place via *ortho*-metallation when a phenyl C–H bond of the NHC ligand lies in the vicinity of the ruthenium center [23].

In a second series of experiments, we probed the catalytic activities of imidazolinium chlorides **10c**–**e** in the visible-light induced ROMP of cyclooctene (Table 4). The experimental conditions defined for the imidazolium salts **8a**–**e** were kept unchanged (cf. Scheme 2). Yet, a striking difference of behavior between the two types of NHC precursors was observed. Whereas the 4′-methoxy derivative **10c** was almost as efficient as its unsaturated analogue **8c** (entry 1), introduction of phenoxy or *tert*-butyl substituents on the remote *para*-positions of compounds **10d** and **10e**, respectively, led to significantly lower yields and conversions (entries 2 and 3). These results are in sharp contrast with those obtained for the imidazolium series, where the electron-withdrawing or -donating nature and the steric bulk of the terminal phenyl substituents did not affect the course of the polymerization (cf. Table 3). Moreover, the observed discrepancies go against previous results from our group showing that the removal of the C4–C5 double bond in the imidazole ring of various NHC precursors had only little influence on the outcome of the polymerization process [23]. As a matter of fact, recourse to

Table 4
ROMP of cyclooctene in PhCl at 60 °C catalyzed by various ruthenium–NHC complexes generated *in situ* from [$RuCl_2$(*p*-cymene)]$_2$, an imidazolinium salt, and KO-*t*-Bu

Entry	Imidazolinium salt	Monomer conversion (%)	Isolated polymer yield (%)
1	**10c**	97	83
2	**10d**	25	11
3	**10e**	24	0
4	**13**	99	93
5	**14**	23	0

the mesityl-substituted imidazolinium chloride **13** led to quantitative monomer conversion and polymer yield (entry 4). These results are almost identical to the ones obtained with the imidazolium salt **11**.

We suspect that the differences of reactivity between compounds **10c**, **10d**, and **10e** are more likely due to complications in generating active species *in situ* than to intrinsic steric or electronic effects. Indeed, attempts by Grubbs and co-workers to deprotonate imidazolinium salts with metal alkoxides afforded the corresponding NHC–alcohol adducts instead of the expected free carbenes [29,33]. There is also ample evidence in the literature that saturated imidazolidin-2-ylidenes are less stable than the corresponding aromatic imidazolin-2-ylidenes and easily dimerize [34–36] or form adducts with various classes of compounds [37–40]. Thus, it would be hazardous to infer any structure-activity relationship concerning imidazolinium salts from the limited data at hand, apart from the importance of *ortho*-substitution, as evidenced once again from the negative results obtained with the unprotected biphenyl derivative **14** (entry 5) [23].

The influence of steric and electronic variations within the series of imidazolium chlorides **8a**–**e** was also examined. Changing the steric bulkiness and the electron-donating or -withdrawing properties of the R^1 and R^2 substituents within these NHC precursors did not have any significant impact on the catalytic system under investigation (cf. Table 3). The absence of steric effects did not come as a surprise. Due to the rigidity of the biphenyl units, the remote phenyl rings and their *meta* or *para* substituents are too distant from the ruthenium coordination sphere to interact with the active site (Fig. 2). They have no influence on the value of % V_{Bur}, a parameter first introduced by Nolan and co-workers to measure the fraction of volume of a sphere centered on the metal, buried by overlap with atoms of the NHC ligand [41,42]. We were more disconcerted to note that the ROMP of cyclooctene proceeded equally well, whether strongly electron-attracting groups (like CF_3 in **8b**) or electron-donating groups (like OMe in **8c**) were present on the biphenyl units. Through-bond transmission of their electronic effects to the ruthenium center was not expected. It is most likely hampered by the orthogonal arrangement of the aryl substituents relative to the central imidazole ring, as evidenced by X-ray crystallography for the mesityl-substituted salt **11** [43] and the free carbene derived thereof [44]. Indeed, a careful examination of the NMR data recorded for compounds **8a**–**e** (see Section 4) revealed that the chemical shifts of the imidazolium protons H^2 and $H^{4,5}$ were not correlated with the σ (or σ^+) constants [45] of the *meta* or *para* substituents on the remote phenyl rings. Yet, variations in the substituents on the phenyl rings of NHCs were shown to significantly influence the redox behavior and the metathetical activity of second-generation Grubbs and Hoveyda–Grubbs catalysts. This was rationalized by invoking a through-space transfer of π-electron density between the Ru=CHR alkylidene fragment and the NHC aryl substituents [46].

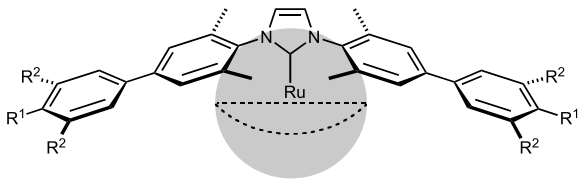


Fig. 2. Coordination sphere of a ruthenium atom bearing a NHC ligand with biphenyl substituents.

3. Conclusion

A range of new imidazolium and imidazolinium chlorides bearing biphenyl units on their nitrogen atoms was synthesized by a multi-step pathway. These NHC ligand precursors differed by the electron-withdrawing or -donating nature and the steric bulk of the substituents on their aromatic rings. They were combined with the $[RuCl_2(p\text{-cymene})]_2$ dimer and potassium *tert*-butoxide to generate the corresponding ruthenium–arene complexes $[RuCl_2(p\text{-cymene})(NHC)]$ *in situ*. The catalytic activity of these species was investigated in the photoinduced ROMP of cyclooctene. The results obtained confirmed the necessity of blocking the *ortho*-positions of the phenyl rings in the vicinity of the metal center in order to attain high catalytic efficiencies. They also showed that structural variations on the remote phenyl rings of the biphenyl units had only very limited influence on the outcome of the polymerization. Furthermore, none of the new imidazol(in)ium salts bearing biphenyl units on their nitrogen atoms outperformed the mesityl-based ligand precursors IMes · HCl (**11**) or SIMes · HCl (**13**) in the test reaction under scrutiny. Thus, further attempts at improving the metathetical activity of ruthenium–arene complexes bearing NHC ligands should focus on structural elements within the metal coordination sphere.

4. Experimental

4.1. General information

Solvents were freshly distilled from standard drying agents and kept under argon. GLC analyses were performed on a Perkin–Elmer 8500 gas chromatograph equipped with a RSLM-150 capillary column and a flame ionization detector (FID) or a Varian 3900 gas chromatograph with a WCOT capillary column and FID. Melting points were recorded on a Electrothermal 9100 apparatus and are not corrected. ^1H and ^{13}C NMR spectra (400 and 100 MHz, respectively) were recorded at 298 K on a Bruker DRX 400 spectrometer in $CDCl_3$ with TMS as internal standard or in DMSO-d_6 using the solvent peaks as reference. All assignments are tentative, based on additivity rules [47] and comparison between related structures. Mass spectra were recorded on a Bruker APEX-Qe 9.4 T hybrid quad-

rupole-FTICR (Fourier transform ion cyclotron resonance) mass spectrometer. $[RuCl_2(p\text{-cymene})]_2$ was purchased from Strem. Substituted biphenylamines **4a**–**e**, **5a,b**, and **6** were prepared according to literature [28]. All the other starting materials were obtained from Aldrich.

4.2. Preparation of N,N′-diarylethane-1,2-diimines (7)

A mixture of glyoxal (0.307 g of a 40% aqueous solution, 2.1 mmol), 2-propanol (5 mL), and water (2.5 mL) was slowly added to a solution of biphenylamine (4.3 mmol) in 2-propanol (15 mL). The reaction mixture was stirred for 3 days at room temperature. The resulting suspension was filtered with suction and the precipitate was rinsed with water (5 mL). It was dried under an IR lamp.

4.2.1. N,N′-Bis(3′,5′-difluoro-3,5-dimethylbiphenyl-4-yl)-ethane-1,2-diimine (7a)

Yellow powder; yield: 35%; mp: 239–241 °C (dec.). ^{1}H NMR ($CDCl_3$): $\delta = 2.28$ (s, 12H, *ortho*-CH_3), 6.19–6.24 (m, 2H, CH_{ar}), 7.72 (m, 4H, CH_{ar}), 8.01 (s, 4H, CH_{ar}), 8.12 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.2$ (*ortho*-CH_3), 103.0 (*para*-CH_{ar}), 109.9 (CH_{ar}), 128.1 (CH_{ar}), 132.9 (C_{ar}), 133.3 (C_{ar}), 135.7 (C_{ar}), 143.9 (C_{ar}), 161.4 (CH=N), 164.4 (C_{ar}F) ppm.

4.2.2. N,N′-Bis(3,5-dimethyl-3′,5′-bis(trifluoromethyl)-biphenyl-4-yl)ethane-1,2-diimine (7b)

Yellow powder; yield: 36%. ^{1}H NMR ($CDCl_3$): $\delta = 2.28$ (s, 12H, *ortho*-CH_3), 7.24–7.34 (m, 4H, CH_{ar}), 7.82 (s, 2H, CH_{ar}), 8.01 (s, 4H, CH_{ar}), 8.18 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.2$ (*ortho*-CH_3), 122.0 (CH_{ar}), 127.8 (CF_3), 127.9 (CH_{ar}), 128.1 (CH_{ar}), 128.5 (C_{ar}), 132.9 (C_{ar}), 135.7 (C_{ar}), 143.9 (C_{ar}), 151.4 (C_{ar}N), 164.4 (CH=N) ppm.

4.2.3. N,N′-Bis(4′-methoxy-3,5-dimethylbiphenyl-4-yl)-ethane-1,2-diimine(7c)

Yellow powder; yield: 97%; mp: 194–196 °C. ^{1}H NMR ($CDCl_3$): $\delta = 2.26$ (s, 12H, *ortho*-CH_3), 3.86 (s, 6H, OCH_3), 6.97 (d, $J = 12$ Hz, 4H, CH_{ar}), 7.27 (d, $J = 12$ Hz, 4H, CH_{ar}), 7.54 (d, $J = 8$ Hz, 4H, CH_{ar}), 8.18 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.6$ (*ortho*-CH_3), 55.5 (OCH_3), 114.3 (CH_{ar}), 126.8 (CH_{ar}), 127.3 (C_{ar}), 127.6 (C_{ar}), 128.1 (CH_{ar}), 133.5 (C_{ar}), 148.8 (C_{ar}N), 159.2 (C_{ar}O), 163.6 (CH=N) ppm.

4.2.4. N,N′-Bis(3,5-dimethyl-4′-phenoxybiphenyl-4-yl)-ethane-1,2-diimine (7d)

Yellow powder; yield: 73%; mp: 212–213 °C (dec.). ^{1}H NMR ($CDCl_3$): $\delta = 2.27$ (s, 12 H, *ortho*-CH_3), 7.05–7.14 (m, 10H, CH_{ar}), 7.31–7.37 (m, 8H, CH_{ar}), 7.56 (d, $J = 8$ Hz, 4H, CH_{ar}), 8.19 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.6$ (*ortho*-CH_3), 119.1 (CH_{ar}), 119.3 (CH_{ar}), 123.4 (C_{ar}), 127.0 (CH_{ar}), 127.3 (C_{ar}), 128.3 (CH_{ar}), 129.9 (CH_{ar}), 136.1 (CH_{ar}), 137.3 (C_{ar}), 149.1 (C_{ar}N), 156.8 (C_{ar}O), 158.0 (C_{ar}O), 163.6 (CH=N) ppm.

4.2.5. N,N′-Bis(4′-tert-butyl-3,5-dimethylbiphenyl-4-yl)-ethane-1,2-diimine (7e)

Yellow powder; yield: 77%; mp: 226–227 °C (dec.). ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (s, 18H, $C(CH_3)_3$), 2.26 (s, 12H, *ortho*-CH_3), 7.33 (s, 4H, CH_{ar}), 7.46 (d, $J = 8$ Hz, 4H, CH_{ar}), 7.54 (d, $J = 8$ Hz, 4H, CH_{ar}), 8.19 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.6$ (*ortho*-CH_3), 31.5 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 125.8 (CH_{ar}), 126.7 (CH_{ar}), 127.1 (CH_{ar}), 131.1 (C_{ar}), 137.8 (C_{ar}), 138.1 (C_{ar}), 149.1 (C_{ar}N), 150.2 (C_{ar}), 163.6 (CH=N) ppm.

4.2.6. N,N′-Bis(2,4,6-trimethylbiphenyl-3-yl)ethane-1,2-diimine (7f)

Yellow powder; yield: 36%.^{1}H NMR ($CDCl_3$): $\delta = 1.84$ (s, 6H, CH_3), 1.99 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 7.01 (s, 2H, 5-CH_{ar}), 7.14 (d, $J = 8$ Hz, 2H, CH_{ar}), 7.23–7.30 (m, 2H, CH_{ar}), 7.34–7.41 (m, 6H, CH_{ar}), 8.15 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 17.1$ (CH_3), 19.2 (CH_3), 21.5 (CH_3), 125.7 (CH_{ar}), 126.2 (CH_{ar}), 127.6 (CH_{ar}), 129.4 (CH_{ar}), 130.3 (C_{ar}), 130.4 (C_{ar}), 133.5 (C_{ar}), 141.4 (C_{ar}), 142.0 (C_{ar}), 148.9 (C_{ar}N), 164.7 (CH=N) ppm.

4.2.7. N,N′-Bis(4′-chloro-2,4,6-trimethylbiphenyl-3-yl)-ethane-1,2-diimine (7g)

Yellow powder; yield: 26%; mp: 161–163 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.83$ (s, 6H, CH_3), 1.98 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 7.01 (s, 2H, 5-CH_{ar}), 7.06 (d, $J = 12$ Hz, 4H, CH_{ar}), 7.40 (d, $J = 12$ Hz, 4H, CH_{ar}), 8.13 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 17.1$ (CH_3), 19.0 (CH_3), 21.4 (CH_3), 126.1 (CH_{ar}), 129.7 (C_{ar}), 130.5 (CH_{ar}), 131.7 (CH_{ar}), 133.4 (C_{ar}), 133.7 (C_{ar}), 140.1 (C_{ar}), 140.4 (C_{ar}), 144.6 (C_{ar}), 148.9 (C_{ar}N), 164.7 (CH=N) ppm.

4.2.8. N,N′-Bis(3-butyl-2,4,6-trimethylphenyl)ethane-1,2-imine (7h)

Yellow powder; yield: 83%. ^{1}H NMR ($CDCl_3$): $\delta = 0.93$ (m, 6H, CH_3), 1.41 (m, 8H, CH_2), 2.07 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 2.26 (s, 6H, CH_3), 2.59–2.61 (m, 4H, CH_2), 6.87 (s, 2H, CH_{ar}), 8.03 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3), 14.5 (CH_3), 18.3 (CH_2), 19.8 (CH_3), 23.4 (CH_3), 29.7 (CH_2), 31.7 (CH_2), 122.9 (C_{ar}), 125.3 (C_{ar}), 130.1 (CH_{ar}), 132.5 (C_{ar}), 138.2 (C_{ar}), 148.6 (C_{ar}N), 163.6 (CH=N) ppm.

4.3. Preparation of imidazolium chlorides (8)

A two-neck 25 mL round-bottom flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with paraformaldehyde (145 mg, 4.8 mmol). The reactor was purged of air by applying three vacuum/argon cycles before 1.4 mL of a 4 N HCl solution in dioxane (5.6 mmol) was added. The mixture was stirred and gently warmed until complete dissolution of the solid. A second, similarly equipped flask was charged with a *N*,*N*′-diarylethane-1,2-diimine (**7**) (4 mmol) and dry THF (16 mL).

The two mixtures were cooled to 0 °C in an ice-water bath and the acidic paraformaldehyde solution was added dropwise to the diimine solution. A precipitate appeared within 1 h. The resulting suspension was stirred 4 h at room temperature. It was filtered with suction. The precipitate was rinsed with AcOEt (20 mL) and dried under vacuum.

4.3.1. 1,3-Bis(3′,5′-difluoro-3,5-dimethylbiphenyl-4-yl)-imidazolium chloride (**8a**)

White grey powder; yield: 51%. ^{1}H NMR (DMSO-d_6): $\delta = 2.17$ (s, 12H, *ortho*-CH_3), 7.69–7.71 (m, 6H, CH_{ar}), 8.01–8.03 (m, 2H, CH_{ar}), 8.36–8.38 (m, 2H, CH_{ar}), 8.47–8.49 (m, 2H, im-$H^{4,5}$), 9.92 (s, 1H, im-H^2) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 16.7$ (*ortho*-CH_3), 123.7 (im-$CH^{4,5}$), 124.6 (CH_{ar}), 127.7 (C_{ar}), 131.3 (CH_{ar}), 132.7 (C_{ar}), 133.9 (C_{ar}), 135.7 (C_{ar}), 137.3 (CH_{ar}), 138.7 (im-CH^2), 141.1 (C_{ar}) ppm. HRMS (ESI): calcd for $C_{31}H_{25}F_4N_2^+$ ([M−Cl]$^+$): 501.19484; found: 501.19531.

4.3.2. 1,3-Bis(3,5-dimethyl-3′,5′-bis(trifluoromethyl)-biphenyl-4-yl)imidazolium chloride (**8b**)

Beige powder; yield: 46%. ^{1}H NMR (DMSO-d_6): $\delta = 2.20$ (s, 12H, *ortho*-CH_3), 7.58 (d, $J = 8$ Hz, 2H, CH_{ar}), 7.68–7.86 (m, 8H, CH_{ar}), 8.36–8.37 (m, 2H, im-$H^{4,5}$), 9.91 (s, 1H, im-H^2) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 17.4$ (*ortho*-CH_3), 103.5 (im-$CH^{4,5}$), 110.2 (C_{ar}), 123.7 (CH_{ar}), 124.7 (CH_{ar}), 127.2 (CF_3), 130.3 (C_{ar}), 131.3 (CH_{ar}), 132.6 (C_{ar}), 135.4 (C_{ar}), 137.3 (C_{ar}), 138.6 (im-CH^2) ppm. HRMS (ESI): calcd for $C_{35}H_{25}F_{12}N_2^+$ ([M−Cl]$^+$): 701.18206; found: 701.18410.

4.3.3. 1,3-Bis(4′-methoxy-3,5-dimethylbiphenyl-4-yl)-imidazolium chloride (**8c**)

Beige powder; yield: 75%. ^{1}H NMR (DMSO-d_6): $\delta = 2.25$ (s, 12H, *ortho*-CH_3), 3.83 (s, 6H, OCH_3), 7.09 (d, $J = 8$ Hz, 4H, CH_{ar}), 7,67 (s, 4H, CH_{ar}), 7.72 (d, $J = 8$ Hz, 2H, CH_{ar}), 8.37 (s, 2H, im-$H^{4,5}$), 9.82 (s, 1H, im-H^2) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 17.2$ (*ortho*-CH_3), 55.4 (OCH_3), 114.6 (CH_{ar}), 124.9 (im-$CH^{4,5}$), 126.5 (C_{ar}), 127.5 (CH_{ar}), 129.3 (CH_{ar}), 132.1 (C_{ar}), 135.2 (C_{ar}), 138.6 (im-CH^2), 142.2 (C_{ar}), 159.6 (C_{ar}O) ppm. HRMS (ESI): calcd for $C_{33}H_{33}N_2O_2^+$ ([M−Cl]$^+$): 489.25365; found: 489.25374.

4.3.4. 1,3-Bis(3,5-dimethyl-4′-phenoxybiphenyl-4-yl)-imidazolium chloride (**8d**)

White pinkish powder; yield: 42%. ^{1}H NMR (DMSO-d_6): $\delta = 2.27$ (s, 12H, *ortho*-CH_3), 7.09–7.15 (m, 8H, CH_{ar}), 7.20–7.22 (m, 2H, CH_{ar}), 7.43–7.47 (m, 4H, CH_{ar}), 7.71 (s, 4H, CH_{ar}), 7.79 (d, $J = 8$ Hz, 4H, CH_{ar}), 8.42–8.43 (m, 2H, im-$H^{4,5}$), 9.92 (s, 1H, im-H^2) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 17.1$ (*ortho*-CH_3), 118.7 (CH_{ar}), 119.0 (CH_{ar}), 123.8 (C_{ar}), 124.8 (im-$CH^{4,5}$), 126.8 (CH_{ar}), 128.6 (CH_{ar}), 130.1 (CH_{ar}), 132.4 (C_{ar}), 133.7 (C_{ar}), 135.2 (CH_{ar}), 138.6 (im-CH^2), 141.7 (C_{ar}), 156.2 (C_{ar}O), 157.1 (C_{ar}O) ppm. HRMS (ESI): calcd for $C_{43}H_{37}N_2O_2^+$ ([M−Cl]$^+$): 613.28495; found: 613.28617.

4.3.5. 1,3-Bis(4′-tert-butyl-3,5-dimethylbiphenyl-4-yl)-imidazolium chloride (**8e**)

Beige powder; yield: 65%. ^{1}H NMR (DMSO-d_6): $\delta = 1.34$ (s, 18H, $C(CH_3)_3$), 2.28 (s, 12H, *ortho*-CH_3), 7.54 (d, $J = 8$ Hz, 4H, CH_{ar}), 7.70 (d, $J = 8$ Hz, 8H, CH_{ar}), 8.40 (s, 2H, im-$H^{4,5}$), 10.11 (s, 1H, im-H^2) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 17.2$ (*ortho*-CH_3), 31.0 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 124.8 (im-$CH^{4,5}$), 125.8 (C_{ar}), 126.6 (CH_{ar}), 126.8 (CH_{ar}), 132.4 (C_{ar}), 135.1 (CH_{ar}), 135.8 (C_{ar}), 138.7 (im-CH^2), 142.3 (C_{ar}), 150.7 (C_{ar}) ppm. HRMS (ESI): calcd for $C_{39}H_{45}N_2^+$ ([M−Cl]$^+$): 541.35773; found: 541.35863.

4.3.6. 1,3-Bis(3-butyl-2,4,6-trimethylphenyl)imidazolium chloride (**8h**)

White powder; yield: 15%. ^{1}H NMR ($CDCl_3$): $\delta = 0.97$ (t, 6H, CH_3), 1.44 (m, 8H, $(CH_2)_2$), 2.11 (s, 6H, CH_3), 2.14 (s, 6H, CH_3), 2.34 (s, 6H, CH_3), 2.63 (s, 4H, CH_2), 7.03 (s, 2H, CH_{ar}), 7.70 (s, 2H, im-$H^{4,5}$), 10.38 (d, $J = 8$ Hz, 1H, im-H^2) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.0$ (CH_3), 14.5 (CH_3), 17.7 (CH_3), 20.1 (CH_2), 23.3 (CH_2), 29.9 (CH_3), 31.2 (CH_2), 125.0 (im-$CH^{4,5}$), 130.9 (CH_{ar}), 131.1 (C_{ar}), 131.2 (C_{ar}), 131.5 (C_{ar}), 132.2 (C_{ar}), 139.2 (im-CH^2), 139.7 (C_{ar}) ppm.

4.4. Preparation of N,N′-diarylethane-1,2-diamines dihydrochlorides (**9**)

A solution of *N*,*N*′-diarylethane-1,2-diimine (**7**) (1 mmol) in dry THF (25 mL) was cooled to 0 °C before sodium borohydride (0.15 g, 4 mmol) was added in one portion. Next, concentrated hydrochloric acid (0.17 mL, 2 mmol) was added dropwise in 15 min. The reaction mixture was stirred at 0 °C for 20 min. A 3 M aqueous HCl solution (40 mL) was then carefully added to the flask, still at 0 °C, and the reaction mixture was further stirred for 1 h at room temperature. The resulting suspension was filtered with suction and the precipitate was rinsed with water (20 mL). It was dried under high vacuum.

4.4.1. N,N′-Bis(3′,5′-difluoro-3,5-dimethylbiphenyl-4-yl)-ethane-1,2-diamine dihydrochloride (**9a**)

White beige powder; yield: 22%. ^{1}H NMR (DMSO-d_6): $\delta = 2.46$ (s, 12H, *ortho*-CH_3), 3.52 (s, 4H, CH_2), 7.38 (s, 4H, CH_{ar}), 7.45 (s, 2H, CH_{ar}), 7.55–7.59 (m, 4H, CH_{ar}) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 19.2$ (*ortho*-CH_3), 41.2 (CH_2), 127.1 (CH_{ar}), 127.6 (CH_{ar}), 127.8 (CH_{ar}), 128.8 (C_{ar}), 129.2 (C_{ar}), 132.8 (C_{ar}), 137.7 (C_{ar}), 151.4 (C_{ar}F) ppm.

4.4.2. N,N′-Bis(3,5-dimethyl-3′,5′- bis(trifluoromethyl)-biphenyl-4-yl)ethane-1,2-diamine dihydrochloride (**9b**)

White beige powder; yield: 47%. ^{1}H NMR (DMSO-d_6): $\delta = 2.48$ (s, 12H, *ortho*-CH_3), 3.52 (s, 4H, CH_2), 7.53–7.60 (m, 4H, CH_{ar}), 7.93–7.99 (m, 2H, CH_{ar}), 8.24–8.27 (m, 4H, CH_{ar}) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 17.6$

(*ortho*-CH_3), 46.9 (CH_2), 119.5 (C_{ar}), 126.2 (CH_{ar}), 126.6 (CH_{ar}), 127.0 (CH_{ar}), 127.9 (CF_3), 130.5 (C_{ar}), 130.8 (C_{ar}), 131.1 (C_{ar}), 142.3 (C_{ar}) ppm.

4.4.3. N,N′-Bis(4′-methoxy-3,5-dimethylbiphenyl-4-yl)-ethane-1,2-diamine dihydrochloride (**9c**)

White yellowish powder; yield: 78%. ^{1}H NMR (DMSO-d_6): $\delta = 2.52$ (s, 12H, *ortho*-CH_3), 3.63 (s, 4H, CH_2), 3.80 (s, 6H, OCH_3), 7.01 (d, $J = 8.4$ Hz, 4H, CH_{ar}), 7.40 (s, 4H, CH_{ar}), 7.60 (d, $J = 8.4$ Hz, 4H, CH_{ar}) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 18.4$ (*ortho*-CH_3), 46.7 (CH_2), 55.2 (OCH_3), 114.3 (CH_{ar}), 126.6 (C_{ar}), 127.1 (CH_{ar}), 127.6 (CH_{ar}), 131.7 (C_{ar}), 136.4 (C_{ar}), 137.7 (C_{ar}), 141.2 (C_{ar}N), 158.9 (C_{ar}O) ppm.

4.4.4. N,N′-Bis(3,5-dimethyl-4′-phenoxybiphenyl-4-yl)-ethane-1,2-diamine dihydrochloride (**9d**)

White yellowish powder; yield: 91%. ^{1}H NMR (DMSO-d_6): $\delta = 2.57$ (s, 12H, *ortho*-CH_3), 3.74 (s, 4H, CH_2), 7.08 (d, $J = 4$ Hz, 8H, CH_{ar}), 7.16–7.19 (m, 2H, CH_{ar}), 7.40–7.44 (m, 8H, CH_{ar}), 7.67 (d, $J = 4$ Hz, 4H, CH_{ar}) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 18.5$ (*ortho*-CH_3), 39.5 (CH_2), 119.1 (CH_{ar}), 118.8 (CH_{ar}), 123.6 (C_{ar}), 126.9 (CH_{ar}), 127.5 (C_{ar}), 128.2 (CH_{ar}), 128.9 (CH_{ar}), 130.1 (CH_{ar}), 136.6 (C_{ar}), 137.7 (C_{ar}), 138.3 (C_{ar}), 156.6 (C_{ar}O) ppm.

4.4.5. N,N′-Bis(4′-tert-butyl-3,5-dimethylbiphenyl-4-yl)-ethane-1,2-diamine dihydrochloride (**9e**)

White yellowish powder; yield: 86%. ^{1}H NMR (DMSO-d_6): $\delta = 1.31$ (s, 18H, $C(CH_3)_3$), 2.57 (s, 12H, *ortho*-CH_3), 3.76 (s, 4H, CH_2), 7.46 (d, $J = 16$ Hz, 8H, CH_{ar}), 7.59 (d, $J = 8$ Hz, 4H, CH_{ar}) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 18.4$ (*ortho*-CH_3), 31.0 ($C(CH_3)_3$), 34.1 ($C(CH_3)_3$), 46.2 (CH_2), 125.6 (CH_{ar}), 126.2 (CH_{ar}), 127.6 (CH_{ar}), 131.9 (C_{ar}), 135.5 (C_{ar}), 136.1(C_{ar}), 138.6 (C_{ar}), 150.0 (C_{ar}) ppm.

4.5. Preparation of imidazolinium chlorides (**10**)

A *N*,*N*′-diarylethane-1,2-diamine dihydrochloride (**9**) (3 mmol) was suspended in triethyl orthoformate (50 mL) containing 2 drops of formic acid. The mixture was refluxed for 2 days in an oil bath at 130 °C. It was then cooled to 0 °C and the resulting suspension was filtered with suction. The precipitate was rinsed with small portions of Et_2O and dried under vacuum.

4.5.1. 1,3-Bis(4′-methoxy-3,5-dimethylbiphenyl-4-yl)-imidazolinium chloride (**10c**)

Beige powder; yield: 60%. ^{1}H NMR (DMSO-d_6): $\delta = 2.48$ (s, 12H, *ortho*-CH_3), 3.81 (s, 6H, OCH_3), 4.56 (s, 4H, CH_2), 7.05 (d, $J = 8$ Hz, 4H, CH_{ar}), 7.55 (s, 4H, CH_{ar}), 7.66 (d, $J = 8$ Hz, 4H, CH_{ar}), 9.26 (s, 1H, im-H^2) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 17.4$ (*ortho*-CH_3), 51.0 (CH_2), 55.2 (OCH_3), 114.4 (CH_{ar}), 126.5 (CH_{ar}), 127.9 (CH_{ar}), 131.1 (C_{ar}), 131.9 (C_{ar}), 136.1 (C_{ar}), 141.2 (C_{ar}N), 159.3 (C_{ar}O), 160.3 (im-CH^2) ppm. HRMS (ESI): calcd for $C_{33}H_{35}N_2O_2^+$ ($[M-Cl]^+$): 491.26930; found: 491.26991.

4.5.2. 1,3-Bis(3,5-dimethyl-4′-phenoxybiphenyl-4-yl)-imidazolinium chloride (**10d**)

Beige powder; yield: 43%. ^{1}H NMR (DMSO-d_6): $\delta = 2.26$ (s, 12H, *ortho*-CH_3), 3.88 (s, 4H, CH_2), 7.04–7.24 (m, 12H, CH_{ar}), 7.35–7.47 (m, 10H, CH_{ar}), 8.44 (s, 1H, im-H^2) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 17.6$ (*ortho*-CH_3), 51.0 (CH_2), 120.1 (CH_{ar}), 125.2 (C_{ar}), 128.3 (CH_{ar}), 130.3 (CH_{ar}), 131.8 (CH_{ar}), 134.0 (C_{ar}), 135.0 (C_{ar}), 137.8 (CH_{ar}), 143.2 (C_{ar}), 146.2 (C_{ar}), 157.5 (C_{ar}O), 158.8 (im-CH^2) ppm. HRMS (ESI): calcd for $C_{43}H_{39}N_2O_2^+$ ($[M-Cl]^+$): 615.30060; found: 615.30173.

4.5.3. 1,3-Bis(4′-tert-butyl-3,5-dimethylbiphenyl-4-yl)-imidazolinium chloride (**10e**)

Beige powder; yield: 60%. ^{1}H NMR (DMSO-d_6): $\delta = 1.30$ (s, 18H, $C(CH_3)_3$), 2.22 (s, 12H, *ortho*-CH_3), 3.82 (s, 4H, CH_2), 7.29–7.34 (m, 2H, CH_{ar}), 7.42–7.52 (m, 10H, CH_{ar}), 7.95 (s, 1H, im-H^2) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 18.7$ (*ortho*-CH_3), 31.3 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 59.2 (CH_2), 126.3 (CH_{ar}), 126.8 (CH_{ar}), 127.7 (CH_{ar}), 135.7 (C_{ar}), 136.5 (C_{ar}), 137.2 (C_{ar}), 141.5 (C_{ar}), 150.7 (C_{ar}), 163.7 (im-CH^2) ppm. HRMS (ESI): calcd for $C_{39}H_{47}N_2^+$ ($[M-Cl]^+$): 543.37338; found: 543.37229.

4.6. Polymerization of cyclooctene

A 25 mL round-bottom flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 1.5×10^{-5} mol), an imidazol(in)ium salt (3×10^{-5} mol), and potassium *tert*-butoxide (6.7 mg, 6×10^{-5} mol). The reactor was purged of air by applying three vacuum/argon cycles before dry chlorobenzene (5 mL) was added. The solution was warmed to 60 °C in a thermostated oil bath and irradiated by a 40 W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flask. Cyclooctene (1 mL, 7.5×10^{-3} mol) was added with a syringe and the reaction mixture was stirred for 2 h at 60 °C. The conversion was monitored by gas chromatography using the cyclooctane impurity of cyclooctene as an internal standard. The resulting gel was diluted with $CHCl_3$ (20 mL) and slowly poured into CH_3OH (500 mL) under vigorous stirring. The precipitated polyoctenamer was filtered and dried under dynamic vacuum.

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