



# Isothiuronium salts as useful and odorless intermediates for the synthesis of thiaalkylimidazolium ionic liquids

Gabriela I. Matiello<sup>a</sup>, Alessandra Pazini<sup>a,b</sup>, Kácris I.M. da Silva<sup>a</sup>, Rafaela G.M. da Costa<sup>b</sup>, Günter Ebeling<sup>a</sup>, Jairton Dupont<sup>a</sup>, Jones Limberger<sup>b,\*</sup>, Jackson D. Scholten<sup>a,\*</sup>

<sup>a</sup> Laboratory of Molecular Catalysis, Institute of Chemistry, UFRGS, Av. Bento Gonçalves, 9500, CEP 91501-970 Porto Alegre, RS, Brazil

<sup>b</sup> Department of Chemistry, Pontifical Catholic University of Rio de Janeiro, Rua Marquês de São Vicente, 225, Gávea, 22451-900 Rio de Janeiro, RJ, Brazil

## ARTICLE INFO

### Article history:

Received 23 January 2019

Revised 4 February 2019

Accepted 6 February 2019

Available online 7 February 2019

### Keywords:

Ionic liquids

Sulfur compounds

Isothiuronium salts

Cross-coupling

## ABSTRACT

A simple and odorless route for the synthesis of monocationic and dicationic thiaalkylimidazolium ionic liquids (ILs) is reported. Our approach starts with the selective monoalkylation of dihalogenated substrates by methylimidazole derivatives, followed by the synthesis of odorless isothiuronium salts *via* reaction with thiourea. The target ILs are obtained after sequential hydrolysis-alkylation of the isothiuronium salts followed by anion metathesis in water. After extraction, the novel thiaalkylimidazolium ILs are obtained with high purity, without the requirement of additional purification steps. In order to demonstrate their applicability, two of these task-specific ILs were employed as ligands in Ullmann and Suzuki couplings and also as charged probes to detect copper intermediates *via* ESI(+)-MS.

© 2019 Elsevier Ltd. All rights reserved.

Imidazolium-based ionic liquids (ILs) are among the most studied media for organic and inorganic reactions [1]. The facile modulation of the physical-chemical properties either by anion exchange or alkyl chain transformations has allowed a huge growth in the applications of these ionic fluids [2]. These compounds are widely applied for a plethora of purposes, as media for homogeneous and nanoparticle catalysis [3–6], CO<sub>2</sub> capture [7], electrochemistry [8], among others. Moreover, these features in combination with their very low vapor pressure, non-flammability, and recyclability render these materials ideal media for green chemistry transformations [9].

In recent years, the development of task-specific ILs has been reported [10–12]. These compounds can be used as task specific acidic [13] and basic [14] ILs, ionophilic ligands and/or reaction media for various catalytic transformations, including cross-coupling reactions [15,16], oxidation reactions [17], olefin metathesis [18,19], and hydrogenation reactions [20,21]. They also allow the detection of catalytic intermediates *via* electrospray ionization mass spectrometry (ESI-MS) experiments [22]. Besides their applications in homogeneous catalysis, N-, O-, P- and S-substituted imidazolium ILs have also been employed to modulate the stability and the reactivity of metallic nanoparticles [23].

In particular, thiaalkylimidazolium ILs have been applied in the extraction of heavy metal cations from water [24], in electrochemical studies [25], as recyclable and odorless Swern reagents [26] and as ligands for transition-metal complexes [27]. However, the synthesis of these compounds has some drawbacks, mainly related to the limited synthetic routes for their production and the toxicity and odor of the synthetic intermediates, thiols or haloalkylsulfides (Scheme 1) [24,25,28]. Taking into account these drawbacks, herein we describe a simple and odorless route to produce various monocationic and dicationic thiaalkylimidazolium ILs. Our approach is based on the selective monoalkylation of dihalogenated substrates (1,2-dibromoethane and 1,3-dibromopropane) by methylimidazole derivatives followed by the synthesis of odorless isothiuronium salts. These sulfur-based salts can be hydrolyzed and alkylated *in situ*, furnishing the corresponding thiaalkylimidazolium salts. Finally, after *in situ* anion metathesis and extraction, the target ILs can be obtained with reasonable to high yields and high purity, without additional purification steps.

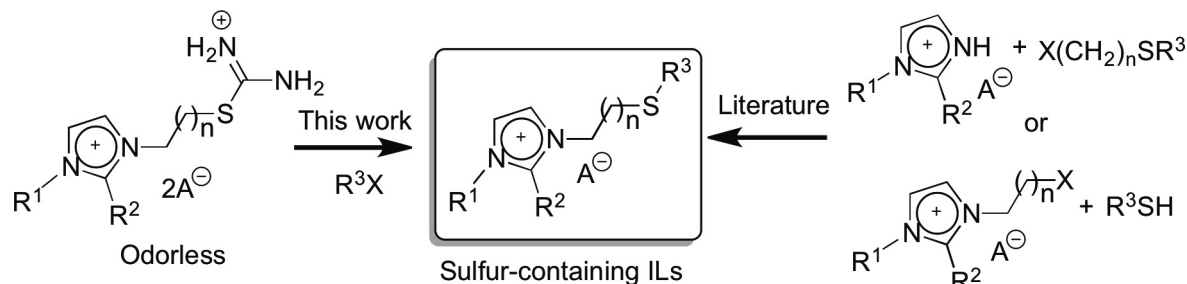
After preparation, in order to illustrate the applicability of these compounds, the thiaalkylimidazolium ILs were applied as ligands in Ullmann and Suzuki coupling reactions.

## Results and discussion

In our approach to prepare the thiaalkylimidazolium ILs, initially 1-methylimidazole or 1,2-dimethylimidazole were reacted with 1,2-dibromoethane or 1,3-dibromopropane in order to obtain

\* Corresponding authors.

E-mail addresses: [limberger@puc-rio.br](mailto:limberger@puc-rio.br) (J. Limberger), [jackson.scholten@ufrgs.br](mailto:jackson.scholten@ufrgs.br) (J.D. Scholten).



**Scheme 1.** Strategies used to synthesize thiaalkylimidazolium ILs: this work versus the literature.

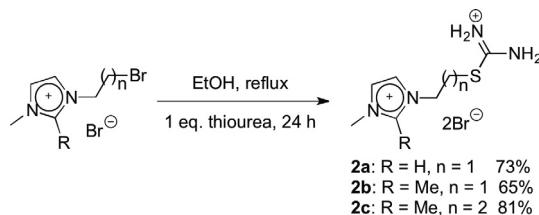
the monoalkylated products. Selective monoalkylation was only achieved using specific conditions for each imidazolium/alkyl bromide pair (Scheme 2).

In order to convert the brominated imidazolium salts into isothiouonium imidazolium salts **2**, intermediates **1** were reacted with thiourea in ethanol at reflux. Under these conditions, compounds **2a–c** were obtained in 65–81% yield (Scheme 3). It is noteworthy that the isothiouonium salts are odorless compounds and the work-up is very simple, since the addition of diethyl ether to the reaction mixture induces product crystallization.

For the synthesis of the desired thiaalkylimidazolium ILs, sequential hydrolysis-alkylation reactions were performed in water followed by *in situ* anion metathesis. With respect to dicationic ILs (Scheme 4), initially, **2a–c** were heated at reflux with KOH in water for 15 min. Afterwards, 1,2-dibromoethane, 1,3-dibromopropane or bis(2-chloroethyl)ammonium hydrochloride were added and the mixture was heated at reflux for an additional 15 min. For ILs **3a** and **3c**, the final solution was adjusted to pH = 6 and the water was evaporated before extraction of the ILs with methanol. For ILs **4a–c**, **5b**, **6b** and **7b**, LiNTf<sub>2</sub> (or KPF<sub>6</sub> for IL **5a**) was added to the reaction mixture and the ILs were extracted from water with ethyl acetate, affording the thiaalkylimidazolium ILs in 69–99% yield. Regarding the monocationic ILs (Scheme 5), after hydrolysis, monoalkylation and anion exchange afforded compounds **8b** and **9b** in 74% and 52% yield, respectively, after direct extraction.

In terms of physical-chemical properties, ILs **3a** and **3c** are highly hygroscopic, due the nature of bromine anion and also the NH group in the center of the structure, which enables hydrogen bonding between water and the ILs. The NH group also induces the hygroscopicity in ILs with anions such as NTf<sub>2</sub><sup>−</sup>, a classical anion of hydrophobic ILs.

Differential scanning calorimetry (DSC) analysis was performed to determine the influence of the ILs structure on their thermal behavior. The anion influence is observed when **4a** (NTf<sub>2</sub><sup>−</sup>) and **5a** (PF<sub>6</sub><sup>−</sup>) are compared, where the PF<sub>6</sub><sup>−</sup> anion confers a lower *T<sub>m</sub>* value to the IL than NTf<sub>2</sub><sup>−</sup>. The influence of a substituent at the C2 position

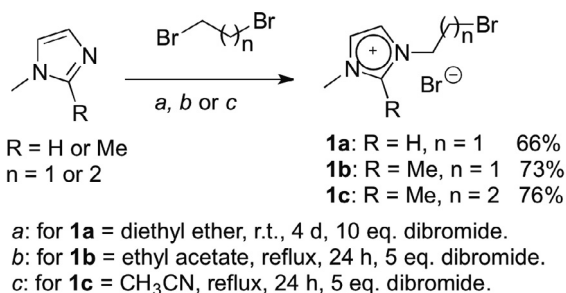


**Scheme 3.** Synthesis of isothiouonium imidazolium salts **2a–c**.

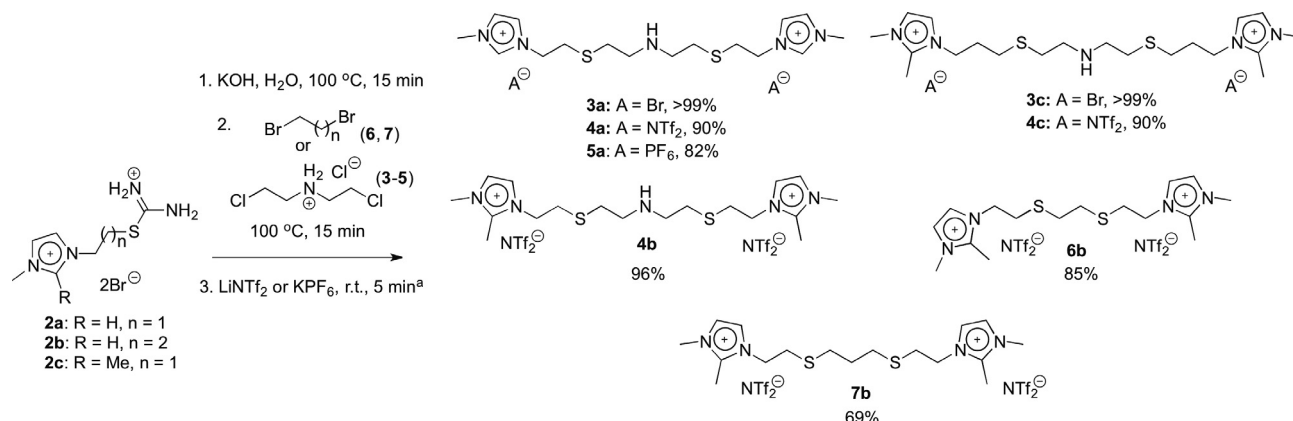
of the imidazolium ring was also evaluated by comparing **4a** (H) and **4b** (CH<sub>3</sub>), where compound **4b** has a lower *T<sub>m</sub>* temperature. This behavior can be regarded as being due to the methyl group, which hampers the formation of H-bonds between the cations and anions of the IL. The influence of chain length **4a** (2C) and **4c** (3C) cannot be verified because the *T<sub>m</sub>* and *T<sub>f</sub>* for **4c** were not obtained from DSC analysis.

ILs **4a–c** are liquids at room temperature, while **5a** exhibit wax aspect at the same temperature. As shown in Table 1, ILs **4a** and **5a** have a *T<sub>m</sub>* above 100 °C, although they are liquid and wax respectively at room temperature even after being dried at 100 °C under vacuum for several hours. This can be explained by the hygroscopicity of these ILs because of strong H-bonds involving water and both the NH of the side chain and the C2H on the imidazolium ring. This behavior allows the confinement of water molecules that are trapped inside the ionic network constituted of contact ion pairs on the IL and hampers the removal of water even under vacuum [29]. The *T<sub>m</sub>* for IL **4b** is lower than the *T<sub>m</sub>* for **4a** and **5a** due to the absence of H-bonds since the C2 position of the imidazolium ring of **4b** is protected by a CH<sub>3</sub> substituent. Thermogravimetric analysis (TGA) of the ILs were performed in order to determine the thermal stability of the compounds (Table 1). As depicted in Table 1, the thermal stability was **6b** > **4c** > **4b** > **7b** > **4a** > **8b** > **5a**. In general, monocationic ILs displayed lower *T<sub>onset</sub>* than dicationic ones. This result is in agreement with the literature since the observed higher thermal stability of dicationic ILs is attributed to the greater charge and intermolecular interactions, their higher molecular weight, higher density, smaller free volume and higher shear viscosity [30]. The reversibility of the breakdown reactions allows recombination of the fragments that do not move away due to this “cage effect”.

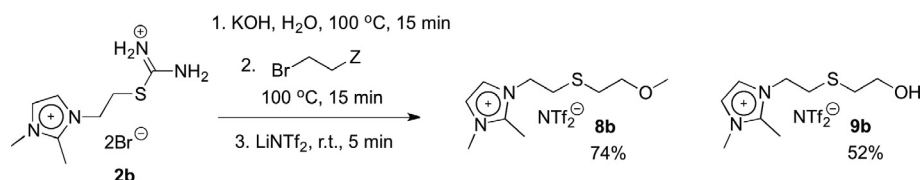
In order to evaluate the potential applicability of these thiaalkylimidazolium ILs, selected compounds were applied as ionophilic ligands for stabilizing the active species in copper-catalyzed Ullmann C–O coupling and as charged probes to detect copper intermediates in the same reaction. The coupling between 4-bromoacetophenone and 4-*tert*-butylphenol in the presence of CuI and ligand **8b** were used as a model (Table 2). Initially, conditions screening was performed and reasonable results were attained using Cs<sub>2</sub>CO<sub>3</sub> in toluene at 100 °C (Entry 3). Excellent conversion and selectivity were observed with ligand **6b** (Entry 5,



**Scheme 2.** Synthetic procedure for the preparation of bromo-substituted imidazolium salts **1a–c**.



**Scheme 4.** Isothiuronium salts as intermediates in the synthesis of dicationic thiaalkylimidazolium ILs. <sup>a</sup> Unless to **3a-c**.



**Scheme 5.** Isothiuronium salts as intermediates in the synthesis of monocationic thiaalkylimidazolium ILs.

**Table 1**  
Thermal properties of ILs obtained by DSC and TGA.

IL	T <sub>onset</sub> (°C) <sup>a</sup>	T <sub>f</sub> (°C) <sup>b</sup>	T <sub>m</sub> (°C) <sup>b</sup>
4a	286	133.5	168.5
5a	268	124.2	124.2
4b	305	89.6	53.7
4c	340	n.o.	n.o.
7b	289	–	–
6b	350	–	–
8b	<300	–	–

<sup>a</sup> TGA;

<sup>b</sup> DSC; n.o. = not observed.

Table 2), while low conversion was attained without the ligand (Entry 6, Table 2). Therefore, the presence of an IL as ligand provides a significant positive effect on the catalytic process.

A reaction under the optimized conditions (Entry 5, Table 2) was monitored by ESI-MS experiments in positive mode for the detection of intermediates with ligand **6b** as an ionophilic probe. First, the solution of CuI and ligand **6b** was analyzed and the free

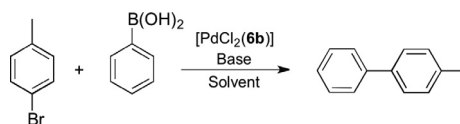
ligand with one counter-anion unit ( $m/z = 621$ ), the doubly charged free ligand ( $m/z = 170$ ) and the ligand coordinated at the Cu metal center ( $m/z = 964$ ) were detected (ESI, Fig. S31). Continuing the experiment, the base, 4-bromoacetophenone and *tert*-butylphenol were added and the solution was analyzed by ESI-MS after two hours (ESI, Fig. S32). One peak was observed related to a structure with the characteristic isotope distribution of a copper species ( $m/z = 340$ ). This peak was attributed to the copper-nucleophile species [Cu(**6b**)OAr]<sup>+</sup>I<sup>-</sup>, which has a double positive charge due to the ionophilic probe. Copper-nucleophile species have been reported as being capable of reacting with aryl halides under mild conditions [31–37]. This finding suggests that the formation of copper-nucleophilic species precedes activation of the aryl halide, as observed in the literature [38].

Taking into account that various organosulfur ligands have been synthesized and applied in Suzuki cross-coupling reactions [39] with advantages (thermal stability and air/moisture insensitivity) over classic phosphines or *N*-heterocyclic carbenes (NHCs), the applicability of the thiaalkylimidazolium ILs was extended to the Suzuki reaction. Initially, the Pd precursor [PdCl<sub>2</sub>(**6b**)] was

**Table 2**  
Coupling reaction between 4-bromoacetophenone and 4-*tert*-butylphenol in the presence of CuI employing thiaalkylimidazolium ILs as ligands.

Entry	Ligand	Base	Solvent	Conv. (%)	Sel. <sup>a</sup> (%)
1	<b>8b</b>	K <sub>3</sub> PO <sub>4</sub>	Dioxane	10	>99
2	<b>8b</b>	K <sub>3</sub> PO <sub>4</sub>	Toluene	31	>99
3	<b>8b</b>	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	64	>99
4 <sup>b</sup>	<b>8b</b>	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	71	94
5	<b>6b</b>	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	90	>99
6	–	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	11	>99

Reagents and conditions: 4-bromoacetophenone (0.5 mmol), 4-*tert*-butylphenol (0.6 mmol), base (1 mmol), ligand (10 mol%), CuI (10 mol%), solvent (2 mL), 100 °C, 24 h. Conversion and selectivity determined by GC. <sup>a</sup>By-products: homocoupling and aryl halide reduction. <sup>b</sup>Reaction performed at 125 °C in a resealable Schlenk tube.

**Table 3**Suzuki coupling reaction between 4-bromotoluene and phenylboronic acid promoted by [PdCl<sub>2</sub>(**6b**)] as the catalyst precursor.

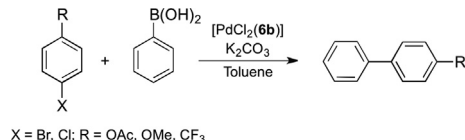
Entry	Solvent	Base	Temp. (°C)	time (h)	Conv. (%)
1	H <sub>2</sub> O	KOH	80	2	0
2	THF	KOH	80	2	0
3	THF	K <sub>2</sub> CO <sub>3</sub>	100	18	>99
4	Toluene	KOH	80	2	99
5	Toluene	K <sub>2</sub> CO <sub>3</sub>	100	2	99
6	Toluene	K <sub>2</sub> CO <sub>3</sub>	100	18	>99
7	Toluene	KF·2H <sub>2</sub> O	100	2	99
8 <sup>a</sup>	Toluene	K <sub>2</sub> CO <sub>3</sub>	100	18	77

Reagents and conditions: bromotoluene (0.25 mmol), phenylboronic acid (0.275 mmol), base (1.0 mmol), [PdCl<sub>2</sub>(**6b**)] (0.5 mol%), degassed solvent, anisole as an internal standard. Conversion determined by GC. <sup>a</sup>Pd(OAc)<sub>2</sub> without ligand and diphenylether as an internal standard.

prepared by reacting PdCl<sub>2</sub> with LiCl to generate the [PdCl<sub>4</sub>]<sup>2-</sup> anion, and then the dicationic ligand was added to form the desired complex (ESI, Fig. S34). The [PdCl<sub>2</sub>(**6b**)] complex was applied as the catalyst precursor to promote the C–C coupling between bromotoluene and phenylboronic acid (Table 3).

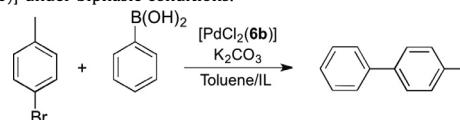
As observed in Table 3, except for the reactions in THF and water at 80 °C (Entries 1 and 2), all experiments showed satisfactory conversion. In addition, a control experiment using Pd(OAc)<sub>2</sub> showed lower conversion (Entry 8) when compared to the reactions employing the IL ligand (see Entries 5 and 6). Indeed, by comparing entries 5 and 8 it is clear that the complex [PdCl<sub>2</sub>(**6b**)] allowed almost full conversion in only 2 h whereas Pd(OAc)<sub>2</sub> led to only 77% conversion over 18 h. These results indicate that the sulfur-based IL ligand has an important role for the efficiency of the reaction. This is probably related to the stabilizing effect provided by the IL ligand avoiding the aggregation of Pd particles in the reaction medium. Further substrates were evaluated with the intention to widen the scope of the reaction. Indeed, the catalytic system produced the coupling products with high conversions and, in particular, could activate the C–Cl bond in chloroacetophenone (Table 4).

Due to these promising results, imidazolium-based ILs were used as media for the Suzuki coupling reaction. In these tests, the system from entry 6 (Table 3) was employed under biphasic conditions (toluene/IL). Among the ILs tested, the best conversion was achieved using BMI-BF<sub>4</sub>, but it was less active when compared to the homogeneous reaction conducted in toluene (compare Tables 3 and 5). Unfortunately, attempts to recycle the biphasic

**Table 4**Suzuki coupling reaction of different substrates and phenylboronic acid promoted by [PdCl<sub>2</sub>(**6b**)] in toluene.

Entry	Substrate	Conv. (%) <sup>a</sup>
1	Bromoacetophenone	99
2	Bromoanisole	99
3	Bromobenzotrifluoride	97
4	Chloroacetophenone	99
5	Chloroanisole	16

Reagents and conditions: aryl halide (0.25 mmol), phenylboronic acid (0.275 mmol), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol), [PdCl<sub>2</sub>(**6b**)] (0.5 mol%), 100 °C, 18 h, degassed solvent (2 mL), anisole as an internal standard. Conversion determined by GC.

**Table 5**Suzuki coupling reaction between 4-bromotoluene and phenylboronic acid promoted by [PdCl<sub>2</sub>(**6b**)] under biphasic conditions.

Entry	Ionic liquid	Conv. (%) <sup>a</sup>
1	BMI-BF <sub>4</sub>	1) 88; 2) 0
2	BMI-NTf <sub>2</sub>	1) 58; 2) 41; 3) 18
3	BMI-PF <sub>6</sub>	1) 34; 2) 32; 3) 29

Reagents and conditions: bromotoluene (0.25 mmol), phenylboronic acid (0.275 mmol), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol), [PdCl<sub>2</sub>(**6b**)] (0.5 mol%), toluene (1.0 mL), IL (0.5 mL), 100 °C, 18 h, degassed solvent, anisole as an internal standard; <sup>a</sup>Conversion determined by GC after each run.

catalytic system failed, since the conversion dropped in the second run (Table 5).

In summary, we have described a practical, useful and odorless synthesis of mono and dicationic sulfur-containing imidazolium-based ILs. Our strategy based on a key isothiuronium salt intermediate allowed the generation of ten new ILs with yields ranging from 52% to 99%, which represents an excellent alternative to the protocols already described in literature for the synthesis of thi-alkylimidazolium ILs. Moreover, these compounds were applied as ligands and ionic tags for the detection of reaction intermediates in Ullmann and Suzuki coupling reactions, opening new possibilities to apply these ILs in several catalytic transformations. A more comprehensive scope evaluation as well as the application of these ILs in other metal-catalyzed reactions are underway in our groups and it will be published in due course.

## Acknowledgments

We thank the CNPq (449758/2014-1, J.D.S.), FAPERGS (16/2551-0000373-4, J.D.S.), PRONEX-FAPERGS, VRAC-PUC-Rio (J.L.), and INCT-Catálise for financial support. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. We also thank the CAPES (G.I.M.) and the CNPq (A.P., R.G.M.C.) for scholarships.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tetlet.2019.02.013>.

## References

- [1] J.P. Hallett, T. Welton, *Chem. Rev.* 111 (2011) 3508–3576.
- [2] J. Dupont, R.F. de Souza, P.A.Z. Suarez, *Chem. Rev.* 102 (2002) 3667–3691.
- [3] J. Dupont, J.D. Scholten, *Chem. Soc. Rev.* 39 (2010) 1780–1804.
- [4] J.D. Scholten, *Curr. Org. Chem.* 17 (2013) 348–363.
- [5] P. Migowski, J. Dupont, *Chem. Eur. J.* 13 (2007) 32–39.
- [6] M.H.G. Prechtl, J.D. Scholten, J. Dupont, *Molecules* 15 (2010) 3441–3461.
- [7] M.C. Corvo, J. Sardinha, T. Casimiro, G. Marin, M. Seferin, S. Einloft, S.C. Menezes, J. Dupont, E.J. Cabrita, *ChemSusChem* 8 (2015) 1935–1946.
- [8] G.B. Appetecchi, A. D'Annibale, C. Santilli, E. Genova, L. Lombardo, M.A. Navarra, S. Panero, *Electrochem. Commun.* 63 (2016) 26–29.
- [9] T. Welton, *Coord. Chem. Rev.* 248 (2004) 2459–2477.
- [10] S.G. Lee, *Chem. Commun.* (2006) 1049–1063.
- [11] R. Giernoth, *Angew. Chem. Int. Ed.* 49 (2010) 2834–2839.
- [12] C.B. Yue, D. Fang, L. Liu, T.F. Yi, *J. Mol. Liquid.* 163 (2011) 99–121.
- [13] B.C. Ranu, S. Banerjee, *J. Org. Chem.* 70 (2005) 4517–4519.
- [14] B.C. Ranu, S. Banerjee, *Org. Lett.* 7 (2005) 3049–3052.
- [15] R. Wang, J.C. Xiao, B. Twamley, J.M. Shreeve, *Org. Biomol. Chem.* 5 (2007) 671–678.
- [16] J.C. Xiao, J.M. Shreeve, *J. Org. Chem.* 70 (2005) 3072–3078.
- [17] M.R. dos Santos, J.R. Diniz, A.M. Arouca, A.F. Gomes, F.C. Gozzo, S.M. Tamborim, A.L. Parize, P.A.Z. Suarez, B.A.D. Neto, *ChemSusChem* 5 (2012) 716–726.
- [18] C.S. Consorti, G.L.P. Aydos, G. Ebeling, J. Dupont, *Org. Lett.* 10 (2008) 237–240.
- [19] C.S. Consorti, G.L.P. Aydos, G. Ebeling, *Organometallics* 28 (2009) 4527–4533.
- [20] X.D. Feng, B. Pugin, E. Kuesters, G. Sedelmeier, H.U. Blaser, *Adv. Synth. Catal.* 349 (2007) 1803–1807.
- [21] Y.W. Zhao, H.M. Huang, J.P. Shao, C.G. Xia, *Tetrahedron: Asymmetry* 22 (2011) 769–774.
- [22] J. Limberger, B.C. Leal, A.L. Monteiro, J. Dupont, *Chem. Sci.* 6 (2015) 77–94.
- [23] J.D. Scholten, B.C. Leal, J. Dupont, *ACS Catal.* 2 (2012) 184–200.
- [24] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davis, R.D. Rogers, *Environ. Sci. Technol.* 36 (2002) 2523–2529.
- [25] A.A.J. Torriero, A.I. Siriwardana, A.M. Bond, I.M. Bugar, N.F. Dunlop, G.B. Deacon, D.R. MacFarlane, *J. Phys. Chem. B* 113 (2009) 11222–11231.
- [26] X. He, T.H. Chan, *Tetrahedron* 62 (2006) 3389–3394.
- [27] C. Flidel, P. Braunstein, *J. Organomet. Chem.* 751 (2014) 286–300.
- [28] A. Bhadani, S. Singh, *Langmuir* 27 (2011) 14033–14044.
- [29] M. Zanatta, A.L. Girard, G. Marin, G. Ebeling, F.P. dos Santos, C. Valsecchi, H. Stassen, P.R. Livotto, W. Lewis, J. Dupont, *Phys. Chem. Chem. Phys.* 18 (2016) 18297–18304.
- [30] H. Shirota, T. Mandai, H. Fukazawa, T. Kato, *J. Chem. Eng. Data* 56 (2011) 2453–2459.
- [31] B.M. Choudary, C. Sridhar, M.L. Kantam, G.T. Venkanna, B. Sreedhar, *J. Am. Chem. Soc.* 127 (2005) 9948–9949.
- [32] E.R. Strieter, D.G. Blackmond, S.L. Buchwald, *J. Am. Chem. Soc.* 127 (2005) 4120–4121.
- [33] A. Shafir, P.A. Lichter, S.L. Buchwald, *J. Am. Chem. Soc.* 129 (2007) 3490–3491.
- [34] J.W. Tye, Z. Weng, A.M. Johns, C.D. Incarvito, J.F. Hartwig, *J. Am. Chem. Soc.* 130 (2008) 9971–9983.
- [35] S.L. Zhang, Y.Q. Ding, *Organometallics* 30 (2011) 633–641.
- [36] G. Franc, Q. Cacciuttolo, G. Lefevre, C. Adamo, I. Ciofini, A. Jutand, *ChemCatChem* 3 (2011) 305–309.
- [37] J.W. Tye, Z.Q. Weng, R. Giri, J.F. Hartwig, *Angew. Chem. Int. Ed.* 49 (2010) 2185–2189.
- [38] J. Limberger, B.C. Leal, D.F. Back, J. Dupont, A.L. Monteiro, *Adv. Synth. Catal.* 354 (2012) 1429–1436.
- [39] A. Kumar, G.K. Rao, S. Kumar, A.K. Singh, *Dalton Trans.* 42 (2013) 5200–5223.