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Salicylaldoxime-functionalized poly (ethylene glycol)-bridged dicationic ionic liquid ([salox-PEG$_{1000}$-DIL][BF$_4$]) as a novel ligand for palladium-catalyzed Suzuki–Miyaura reaction in water

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Two novel salicylaldoxime-functionalized poly(ethylene glycol)-bridged dicationic ionic liquids ([salox-PEG$_{1000}$-DIL][BF$_4$] and [salox-PEG$_{1000}$-DIL][PF$_6$]) were prepared and characterized. [salox-PEG$_{1000}$-DIL][BF$_4$] was found to be an efficient and recyclable ligand for palladium-catalyzed Suzuki–Miyaura reaction in water. The catalytic system could be easily recovered and reused for at least five runs only with slight decrease in its activity. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: salicylaldoxime; poly(ethylene glycol); functionalized ionic liquid; Suzuki–Miyaura reaction; water

Introduction

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides with aryl boronic acids is one of the most important and powerful methods for the construction of C—C bonds in organic synthesis.[1] Traditionally, Suzuki–Miyaura reactions are catalyzed by palladium complexes with phosphine ligands in organic solvents under an inert atmosphere. However, phosphines are susceptible to oxidation during the reaction to yield phosphine oxides and 'palladium black', which is catalytically inactive. At the same time, another main drawback of such an approach is the difficulty in recovering and reusing the expensive palladium complex. More recently, many coupling reactions have been carried out with a phosphine-free catalytic system, and various ligands such as *N,N*-ligand,[2] *N,O*-ligand,[3] *O,O*-ligand[4] and *N*-heterocyclic carbenes (NHC)[5] have been employed in the palladium-catalyzed Suzuki–Miyaura reaction. A large number of strategies for the Suzuki–Miyaura reaction in water have also been developed, including the addition of organic co-solvents,[6] the use of water-soluble catalysts,[7] microwave heating[8] and ultrasonic irradiation.[9] In view of the increasing demand for economical and environmental benign processes in organic chemistry, it is highly desirable to develop a versatile, cost-efficient and non-phosphine ligand for palladium-catalyzed Suzuki–Miyaura reaction to make the catalyst recyclable.

Ionic liquids (ILs) have attracted considerable attention for application in organic transformation, owing to their favorable properties in relation to green chemistry, including high thermal and chemical stability, excellent electrical conductivity and negligible vapor pressure.[10] In recent years, functionalized ionic liquids (FILs), which incorporate functional groups as a part of the cation and/or anion, have been developed and applied in various fields.[11] FILs have been used not only as alternative solvents but also as reagents and/or catalysts in synthetic organic chemistry. Li and co-workers prepared a series of ionic liquid-supported Schiff bases and used them as ligands in the Suzuki–Miyaura reaction.[12] Wang and co-workers reported the use of palladium nanoparticles supported on amine functional ionic liquid modified magnetic nanoparticles as a recyclable catalyst for the Suzuki–Miyaura reaction.[13]

Currently, poly(ethylene glycol)s (PEGs) are employed as organic polymer-soluble supports for both synthesis and catalyst immobilization, owing to their main advantages such as low cost, non-volatility, non-toxicity, thermal stability and easy recyclability.[14] Owing to their special chemical and physical properties, various poly(ethylene glycol)-functionalized ionic liquids (PEG-ILs) have been designed, synthesized and applied in organic chemistry.[15] Bhanage and co-workers reported the use of PEG-functionalized phosphonium salt as an efficient and recyclable catalyst for the regioselective synthesis of 5-aryl-2-oxazolidinones from CO$_2$ and aziridines.[16] Liu and co-workers synthesized three PEG-functionalized imidazolium salts which served as *N*-heterocyclic carbine precursors for the palladium-catalyzed Suzuki–Miyaura reaction; however, the catalyst could not be recovered.[17]

Salicylaldoxime is a versatile ligand in coordination chemistry and is mainly used for analytical purposes and separation

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techniques.[18] More recently, salicylaldoxime has been used as an efficient *N,O*-ligand for transition-metal-catalyzed reactions such as *N*-arylation,[19] *C*-arylation reaction[20] and *O*-arylation.[21] However, one drawback of those reactions is that the catalyst could not be efficiently recovered. Recently, Naik and co-workers prepared metal complexes of salicylaldoxime and salen containing imidazolium ionic liquids with copper and manganese, and then used these for biphasic catalysis and metal extraction.[22]

In continuation of our studies on the synthesis and applications of PEG-bridged dicationic ionic liquids in synthetic organic chemistry,[23] herein we report the preparation and characterization of salicylaldoxime-functionalized PEG-bridged dicationic ionic liquids ([salox-PEG_{1000}-DIL][X]) (Scheme 1), which have also been tested as ligands in the palladium-catalyzed Suzuki–Miyaura reaction.

Experimental

General Remarks

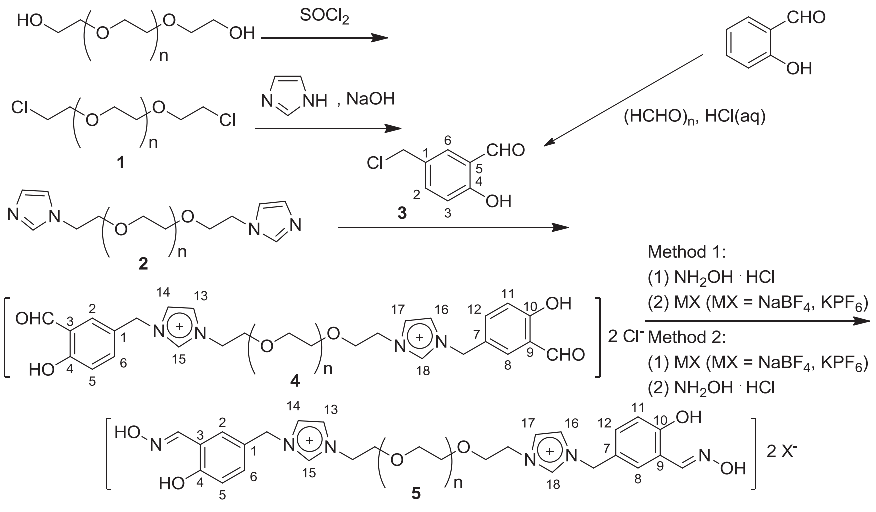
All of the reagents and solvents are commercially available and were used without further purification. ^1H NMR and ^{13}C NMR were recorded on Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference. IR spectra were recorded in KBr disks with a Shimadzu IR Prestige-21 FT-IR spectrometer. Mass spectra were taken on an Agilent LC-MS 1100 series instrument in the electrospray ionization (positive ESI) mode. TGA was performed on a TGA/SDTA851e thermal analyzer (Mettler Toledo). Samples were loaded into an aluminium oxide crucible and heated at a rate of 20 °C min^{-1} from 50 to 600 °C under N_2.

Synthesis of [salox-PEG_{1000}-DIL][BF_4] and [salox-PEG_{1000}-DIL][PF_6]

To the solution of compound **4** in CH_2Cl_2 (100 ml) was added $NaBF_4$ (2.4 equiv., 2.9 g) or KPF_6 (2.4 equiv., 4.9 g) and the reaction mixture was stirred at room temperature for 48 h. After completion, the resulting mixture was filtered. After removal of the filtrate under vacuum, methanol (30 ml) was added and hydroxylamine hydrochloride (2.4 equiv., 1.8 g) in methanol (30 ml) was added dropwise with constant stirring at 40 °C for 12 h. Subsequently, $NaHCO_3$ (2.4 equiv., 2.2 g) in water (20 ml) was added dropwise and stirred for another 12 h. After removal of the solvent in vacuum, the residue was dissolved in CH_2Cl_2 and the inorganic salts were filtered. The [salox-PEG_{1000}-DIL][X] was finally obtained after removal of the filtrate under vacuum.

[salox-PEG_{1000}-DIL][BF_4] (15.1 g, 87%) ^1H NMR (500 MHz, DMSO-d_6) δ: 11.35 (s, 2H, —N—O*H*), 10.30 (s, 2H, Ph—O*H*), 9.16 (s, 2H, Im—$H^{15,18}$), 8.29 (s, 2H, Ph—C*H*—N—OH), 7.77 (t, $J = 1.6$ Hz, 2H, *Im*—$H^{13,17}$), 7.74 (t, $J = 1.6$ Hz, 2H, *Im*—$H^{14,16}$), 7.61 (d, $J = 2.1$ Hz, 2H, Ph—$H^{2,8}$), 7.30 (dd, $J = 8.4$, 2.1 Hz, 2H, Ph—$H^{6,12}$), 6.93 (d, $J = 8.4$ Hz, 2H, Ph—$H^{5,11}$), 5.33 (s, 4H, Ph—CH_2—Im), 4.38–4.32 (m, 4H, Im—CH_2CH_2), 3.79–3.75 (m, 4H, Im—CH_2CH_2), 3.59–3.42 (m, 91H, $(OCH_2CH_2)_n$); ^{13}C NMR (126 MHz, DMSO-d_6) δ: 156.65 (Ph—$C^{4,10}$), 146.45 (Ph—CH—N—OH), 136.71 (Im—$C^{15,18}$), 131.27 (Ph—$C^{6,12}$), 128.10 (Ph—$C^{2,8}$), 126.02 (Ph—$C^{1,7}$), 123.59 (Im—$C^{13,17}$), 122.60 (Im—$C^{14,16}$), 119.37 (Ph—$C^{3,9}$), 117.08 (Ph—$C^{5,11}$), 70.23 ($(OCH_2CH_2)_n$), 70.07 ($(OCH_2CH_2)_n$), 69.99 ($(OCH_2CH_2)_n$), 68.52 (Im—CH_2CH_2), 51.95 (Ph—CH_2—Im), 49.38 (Im—CH_2CH_2); IR (KBr, cm^{-1}): 3147.14, 2870.11, 1624.59, 1562.68, 1497.71, 1452.84, 1349.07, 1271.78, 1054.67, 947.00, 840.64, 804.42, 756.05, 726.25, 672.04, 643.00, 579.79, 541.58; ESI-MS, *m/z*: 693.4 ($M^{++}/2$, $n = 20$), 715.6 ($M^{++}/2$, $n = 21$), 737.8 ($M^{++}/2$, $n = 22$); Anal. Calcd (%) for $C_{66}H_{110}O_{25}N_6B_2F_8$ (1560.06, $n = 21$): C 50.77, H 7.10, N 5.38; Found: C 51.08, H 7.54, N 4.97.

[salox-PEG_{1000}-DIL][PF_6] (15.6 g, 84%) ^1H NMR (500 MHz, DMSO-d_6) δ: 11.37 (s, 2H, —N—O*H*), 10.32 (s, 2H, Ph—O*H*), 9.16 (s, 2H, Im—$H^{15,18}$), 8.29 (s, 2H, Ph—C*H*—N—OH), 7.77 (s, 2H, *Im*—$H^{13,17}$), 7.74 (s, 2H, *Im*—$H^{14,16}$), 7.75 (d, $J = 13.9$ Hz, 4H, Im—$H^{13,14,16,17}$), 7.61 (d, $J = 2.1$ Hz, 2H, Ph—$H^{2,8}$), 7.31 (dd, $J = 8.4$, 2.1 Hz, 2H, Ph—$H^{6,12}$), 6.93 (d, $J = 8.4$ Hz, 2H, Ph—$H^{5,11}$), 5.33 (s, 4H, Ph—CH_2—Im), 4.38–4.31 (m, 4H, Im—CH_2CH_2), 3.78–3.74 (m, 4H, Im—CH_2CH_2), 3.68–3.36 (m, 104H, $(OCH_2CH_2)_n$); ^{13}C NMR (126 MHz, DMSO-d_6) δ: 156.67 (Ph—$C^{4,10}$), 146.48 (Ph—CH—N—OH), 136.71 (Im—$C^{15,18}$), 131.27 (Ph—$C^{6,12}$), 128.12 (Ph—$C^{2,8}$), 126.01 (Ph—$C^{1,7}$), 123.59 (Im—$C^{13,17}$), 122.58 (Im—$C^{14,16}$), 119.36 (Ph—$C^{3,9}$), 117.07 (Ph—$C^{5,11}$), 70.23 ($(OCH_2CH_2)_n$), 70.07 ($(OCH_2CH_2)_n$), 69.99 ($(OCH_2CH_2)_n$), 68.52 (Im—CH_2CH_2), 51.94 (Ph—CH_2—Im), 49.38 (Im—CH_2CH_2); IR (KBr, cm^{-1}): 3144.79, 3073.17, 2870.60, 1623.91, 1588.26, 1562.34, 1497.25, 1452.34, 1397.00, 1349.67, 1299.09, 1271.51, 1249.25, 1188.81, 1089.65, 1036.28, 950.15, 833.30, 754.78, 739.67, 672.36, 643.37, 616.52, 589.88, 580.54, 556.53, 541.47, 534.93, 526.10; ESI-MS, *m/z*: 693.6 ($M^{++}/2$, $n = 20$), 715.8 ($M^{++}/2$, $n = 21$), 737.6



[salox-PEG_{1000}-DIL][X]

Scheme 1. Synthesis of salicylaldoxime-functionalized PEG-bridged dicationic ionic liquid ([salox-PEG_{1000}-DIL][X]).

($M^{++}/2$, $n=22$); Anal. Calcd (%) for $C_{66}H_{110}O_{25}N_6P_2F_{12}$ (1677.58, $n=21$): C 47.25, H 6.61, N 5.01; Found: C 47.85, H 6.83, N 4.78.

General Procedure for the Suzuki–Miyaura Reaction

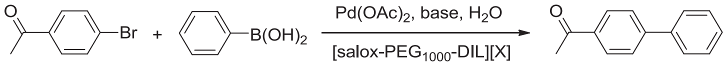
Aryl halide (1.0 mmol), aryl boronic acid (1.2 mmol), $Pd(OAc)_2$ (0.005 mmol), Et_3N (2 mmol), [salox-PEG$_{1000}$-DIL][BF$_4$] (0.1 mmol) and H_2O (2 ml) were placed in a tube and sealed. The reaction mixture was stirred at 100 °C for a certain time. After cooling to room temperature, the reaction mixture was extracted with diethyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated to give the crude product, which was purified by column chromatography on silica gel (200–300 mesh) using ethyl acetate–petroleum ether as eluent. The products were identified by NMR; all data were compared with those that reported in the literature.

Results and Discussion

The synthetic pathway for the salicylaldoxime-functionalized PEG-bridged dicationic ionic liquids are described in Scheme 1. They are readily prepared through a five-step procedure from commercially available starting materials and reagents with good yields. The PEG-1000 dichloride (**1**) and PEG-1000-bridged diimidazolium compound (**2**) were prepared according to our previous reported method.[23a] 5-Chloromethyl-2-hydroxybenzaldehyde (**3**) was synthesized by a modified synthetic procedure described in the literature.[24] The quaternization of compounds **2** and **3** was conducted in toluene to afford the compound **4**. Two methods for preparing [salox-PEG$_{1000}$-DIL][X] were studied. The first method was the classical approach with anion exchange as the last step. However, this method suffered from tedious workup and it was almost impossible to purify the ILs. Alternatively, when the Cl^- of compound **4** was exchanged with BF_4^- or PF_6^- first, and then reacted with hydroxylamine hydrochloride in the presence of $NaHCO_3$, the target salicylaldoxime-functionalized PEG-bridged dicationic ionic liquids could be obtained in high purity and were characterized by ^1H NMR, ^{13}C NMR, infrared and mass spectrometry. The thermal properties of these dicationic ionic liquids were determined by TGA. As shown in the TGA figure (see supporting information), the salicylaldoxime-functionalized PEG-bridged dicationic ionic liquid with BF_4^- as anion is more stable than that with PF_6^- anion. In addition, the solubility of [salox-PEG$_{1000}$-DIL][X] was determined at room temperature. In general, these liquids are immiscible with hexane, cyclohexane, petroleum ether, diethyl ether, toluene, but miscible with dichloromethane, acetone, methanol, ethanol, DMF and DMSO.

To evaluate the catalytic efficiency of the catalyst, 4-bromoacetophenone and phenylboronic acid were first chosen as the model substrates for Suzuki–Miyaura reaction. Selected results from our screening experiments are summarized in Table 1. The salicylaldoxime-functionalized PEG-bridged dicationic ionic liquid with different anion was first investigated. It was observed that [salox-PEG$_{1000}$-DIL][BF$_4$] exhibited much higher catalytic activity than [salox-PEG$_{1000}$-DIL][PF$_6$] (Table 1, entries 1 and 2). Pd black precipitated and low yield was obtained in the absence of ionic liquid (Table 1, entry 3). The amount of catalyst loading was then studied. It was observed that 0.5 mol%

Table 1. Screening reaction conditions for Pd-catalyzed Suzuki–Miyaura coupling reaction between 4-bromoacetophenone and phenylboronic acid [a]



Entry	[salox-PEG$_{1000}$-DIL][X]	$Pd(OAc)_2$ (mol%)	Base	*t* (h)	*T* (°C)	Yield (%)[b]
1	[salox-PEG$_{1000}$-DIL][BF$_4$]	1.0	Et_3N	12	100	94
2	[salox-PEG$_{1000}$-DIL][PF$_6$]	1.0	Et_3N	12	100	90
3	—	1.0	Et_3N	12	100	29
4	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Et_3N	12	100	94
5	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.25	Et_3N	12	100	67
6	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	—	12	100	Trace
7	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	K_2CO_3	12	100	56
8	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Na_2CO_3	12	100	49
9	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Cs_2CO_3	12	100	65
10	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	K_3PO_4	12	100	33
11	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	NaOAc	12	100	74
12	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Bu_3N	12	100	90
13	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	DIPEA	12	100	91
14	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Pyridine	12	100	21
15	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Et_3N	12	90	62
16	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Et_3N	12	80	48
17	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Et_3N	9	100	71
18	[salox-PEG$_{1000}$-DIL][BF$_4$]	0.5	Et_3N	6	100	28

[a] Reaction conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.2 mmol), base (2 mmol), [salox-PEG$_{1000}$-DIL][X] (0.1 mmol), H_2O (2 ml).

[b] Gas chromatographic yield.

$Pd(OAc)_2$ could afford 4-acetylbiphenyl in high yield (Table 1, entries 4 and 5). Base was an important factor for the coupling reaction. Only a trace amount of product was detected in the absence of base (Table 1, entry 6). Among various bases examined, some organic bases such as triethylamine, tributylamine and diisopropylethylamine (DIPEA) were all effective for the catalysis, but pyridine and inorganic bases such as K_2CO_3, Na_2CO_3, Cs_2CO_3, K_3PO_4 and NaOAc resulted in lower yields (Table 1, entries 7–14). Furthermore, low temperature or short time led to lower yields (Table 1, entries 15–18).

One of the main aims of our study was to investigate the recyclability of the catalyst. For this purpose, the recycling of $Pd(OAc)_2$/[salox-PEG_{1000}-DIL][BF_4] was studied using the above model reaction under optimized conditions. After completion of the reaction, the reaction mixture was cooled to room temperature and the product was extracted with diethyl ether. The resultant residues were reused directly without further treatment for the next run after being charged with fresh starting materials (4-bromoacetophenone, 1.0 mmol; phenylboronic acid, 1.2 mmol; triethylamine, 2.0 mmol). It was found that the $Pd(OAc)_2$/[salox-PEG_{1000}-DIL][BF_4] system could be recycled five times with a slight decrease in its activity (Fig. 1).

To examine the scope of this method, we investigated the coupling reaction using a variety of aryl halides and aryl boronic acids under the optimized conditions. The results are summarized in Table 2. The aryl bromides bearing either electron-withdrawing or electron-donating groups could couple with phenylboronic acid efficiently to afford the corresponding products in good to excellent yields (Table 2, entries 1–12). Furthermore, the catalytic system could tolerate a wide range of functional groups, including acetyl, halide, aldehyde, nitro and cyano. The *ortho*-substituted aryl bromide generated the corresponding product in lower yield than the *meta*- and *para*-substituted ones due to steric hindrance (Table 2, entries 10–12). Meanwhile, some substituted aryl boronic acids reacted smoothly with aryl halides and generated the desired products in high yields (Table 2, entries 13–16). Then, in order to test the feasibility of this protocol for challenging substrates, we conducted the coupling of aryl chlorides with phenylboronic acid. However, poor yields were obtained, even when prolonging the time to 48 h and elevating the temperature to 120 °C (Table 2, entries 17 and 18). When tetrabutylammonium bromide (TBAB) was added, the coupling between 4-chloronitrobenzene and phenylboronic acid could give a high yield. Here, the TBAB may play the role of phase transfer catalyst or halogen exchange reagent.[25]

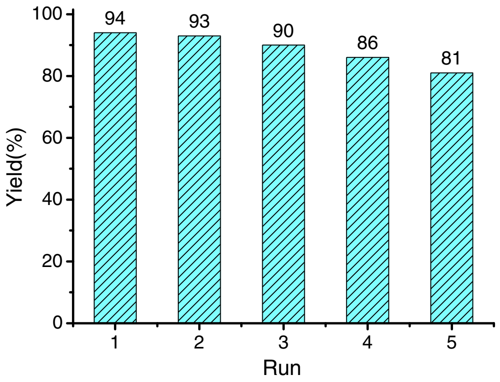
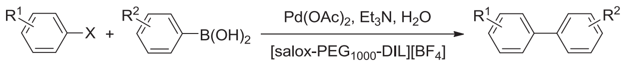


Figure 1. Recycling of $Pd(OAc)_2$/[salox-PEG_{1000}-DIL][BF_4] in the Suzuki–Miyaura coupling reaction of 4-bromoacetophenone and phenylboronic acid.

Table 2. Suzuki–Miyaura coupling reaction of aryl halide with aryl boronic acids catalyzed by $Pd(OAc)_2$/[salox-PEG_{1000}-DIL][BF_4] in water[a]



Entry	X	R^1	R^2	Product	Yield (%)[b]
1	Br	4-CH_3CO	H	**9a**	92
2	Br	4-Cl	H	**9b**	93
3	Br	4-CHO	H	**9c**	94
4	Br	3-CHO	H	**9d**	93
5	Br	4-NO_2	H	**9e**	96
6	Br	4-CN	H	**9f**	91
7	Br	4-CF_3	H	**9g**	94
8	Br	H	H	**9h**	90
9	Br	4-CH_3	H	**9i**	89
10	Br	4-CH_3O	H	**9j**	88
11	Br	3-CH_3O	H	**9k**	86
12	Br	2-CH_3O	H	**9l**	80
13	Br	H	4-Cl	**9b**	91
14	Br	H	4-CH_3	**9i**	89
15	Br	4-CH_3CO	4-CH_3	**9m**	86
16	Br	4-CH_3	4-CH_3O	**9n**	85
17	Cl	H	H	**9h**	7[c]
18	Cl	4-NO_2	H	**9e**	18[c] 83[d]

[a] Reaction conditions: aryl halide (1.0 mmol), aryl boronic acid (1.2 mmol), Et_3N (2 mmol), $Pd(OAc)_2$ (0.005 mmol), [salox-PEG_{1000}-DIL][BF_4] (0.1 mmol), H_2O (2 ml), 12 h, 100 °C.

[b] Isolated yield.

[c] 48 h, 120 °C.

[d] 48 h, 120 °C, 1 mmol TBAB.

Conclusion

In summary, we have prepared two novel salicylaldoxime functionalized PEG-bridged dicationic ionic liquids ([salox-PEG_{1000}-DIL][BF_4] and [salox-PEG_{1000}-DIL][PF_6]), which could be used as ligands for the palladium-catalyzed Suzuki–Miyaura reaction. Using the $Pd(OAc)_2$/[salox-PEG_{1000}-DIL][BF_4] system, a series of substituted aryl halides could couple with aryl boronic acids to afford the corresponding products in water with good to excellent yields. Furthermore, the catalytic system could be easily recycled at least five times without significant loss in activity.

Supporting information

Supporting information may be found in the online version of this article.

Acknowledgments

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