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COMMUNICATION

Poly(ethylene glycol)-functionalized imidazolium salts–palladium-catalyzed Suzuki reaction in water†

Ning Liu, Chun Liu* and Zilin Jin

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Three water-soluble imidazolium salts bearing poly(ethylene glycol) moieties directly attached to an N-atom of imidazole have been synthesized *via* a simple synthetic method, which could be served as N-heterocyclic carbene precursors for the palladium-catalyzed Suzuki reaction. The catalytic system generated *in situ* from a source of $Pd(OAc)_2$, a precursor of imidazolium salt, and a base of triethylamine is able to smoothly perform the Suzuki reaction of a variety of substrates in water.

Introduction

Water is an attractive solvent for chemical reactions for reasons of low cost, non-flammability, non-toxicity, and environmental concerns.[1] Over the past decade, many organic reactions that were conventionally believed to occur only in organic solvents have been successfully performed using water as an environmentally-benign reaction medium.[2] Among the developed reactions, the Suzuki reaction is an excellent example and has strongly benefited from aqueous chemistry.[3] A large number of strategies for the Suzuki reaction in water have been developed, including the addition of organic co-solvents[4] or surfactants,[5] microwave-heating,[1a,6] ultrasonic-irradiation,[7] ligand-free methodology,[8] and the use of water-soluble catalysts.[9] Among them, the application of water-soluble ligands/palladium as catalysts in the aqueous Suzuki reaction has attracted increasing attention, not just for the sake of enhancing water solubility of the catalyst, but for facilitating the catalyst recovery by separating the water phase as well.[10] The typical strategy for obtaining a water-soluble catalyst is to modify a ligand with a water-soluble functional group, including carboxylate,[11] sulfonate,[4b,12] ammonium,[13] and polyoxyethylene groups.[14] Since Casalnuovo's[15] initial report of the palladium-catalyzed cross-coupling reactions in aqueous media catalyzed by TPPMS [sodium 3-(diphenylphosphino)benzenesulfonate]/$Pd(OAc)_2$, a lot of water-soluble palladium catalysts have been developed for a range of cross-coupling reactions.[3a,10a]

After being functionalized with PEG [poly(ethylene glycol)] moieties, a catalyst could possess a lot of advantages, such as enhanced water solubility, easy separation from the products by decantation, and so on.[16] The synthesis of a PEG-decorated phosphine ligand goes back to the earliest works reported by Schurig and Bayer in 1976.[17] Until the 1990s, Bergbreiter and co-workers synthesized PEG-bound phosphine and pincer-type SCS ligands for the rhodium-catalyzed hydrogenation and palladium-catalyzed cross-coupling reaction.[18] Since then, a variety of PEG-functionalized phosphine,[19] salen,[20] cinchona alkaloid,[21] diamino-oligothiophene,[22] diphenylethylenedi-amine,[23] dipyridyl,[14a,24] porphyrin,[25] tartrate ester,[26] and BINOL[27] ligands have been developed.[28] Recently, Uozumi *et al.* utilized a series of polystyrene–PEG-supported chiral phosphine ligands for an aqueous Suzuki reaction with high stereoselectivity.[29]

The nature of the strong electron-donating abilities of N-heterocyclic carbene (NHC) ligands facilitates the ligand tighter binding to the metal, which significantly enhances the catalyst lifetime and efficiency.[30] Thus, NHC ligands have been applied in versatile catalytic transformations due to their water or air stability, unique electron-donating abilities and the stability of the resulting metal complexes.[31] The groups of Herrmann,[32] Nolan,[33] Çetinkaya,[34] Y. S. Lee,[35] Organ,[36] Karimi,[37] Glorius,[38] Hagiwara,[39] H. M. Lee,[40] and Kirschning[41] have synthesized numerous NHC ligands for the Suzuki reaction. Since the report of the first water-soluble sulfonate-functionalized NHC ligand,[42] there have been a number of sulfonate-, carboxylate- and ammonium-functionalized NHC ligands used in the palladium-catalyzed cross-coupling reactions.[43]

To date, there are only a few examples of PEG-modified NHC ligands,[11a,43a] although PEG moieties are widely used to functionalize phosphine ligands. In 2006, Grubbs and co-workers reported the first example of a PEG-decorated ruthenium NHC complex for aqueous olefin metathesis.[44] PEG-decorated NHC ligands have also been used as organocatalysts in the Stetter reaction and redox esterification.[45] Tsuji and co-workers reported a series of palladium-catalysts bearing tetraethylene glycol and/or long-chain alkyl groups for the Suzuki reaction.[46] As a result, the palladium-catalysts bearing tetraethylene glycol groups were apparently more effective than the catalysts with long-chain alkyl groups. However, to the best of our knowledge, the palladium-catalyzed aqueous Suzuki reaction promoted by the PEG-bound NHC ligand has not been reported.

We have a long-standing interest in developing efficient aqueous catalytic systems for palladium-catalyzed cross-coupling reactions.[47] Encouraged by previous results, we report herein a new and simple synthetic method for the preparation of three

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Linggong Road 2, 116024 Dalian, China. E-mail: chunliu70@yahoo.com; Tel: + 86 411 84986182

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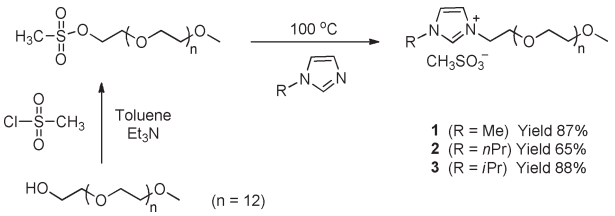


Scheme 1 The synthetic path of imidazolium salts **1–3**.

new water soluble imidazolium salts containing PEG moieties, which have been successfully employed in the palladium-catalyzed Suzuki reaction in water. This study gives an opportunity to disclose the catalytic performance differences of imidazolium salts containing PEG moieties from other water-soluble groups functionalized NHC ligand precursors described in the literature for the palladium-catalyzed Suzuki reaction.

Results and discussion

The synthetic path for the imidazolium salts **1–3** is depicted in Scheme 1. The $MeOPEG_{550}OSO_2CH_3$ was firstly prepared *via* a reaction of $MeOPEG_{550}OH$ with methanesulfonyl chloride using Et_3N as a base in toluene. The key step in the synthesis was a nucleophilic substitution between $MeOPEG_{550}OSO_2CH_3$ and substituted imidazoles to generate the desired imidazolium salts **1–3** under solvent-free conditions.

All imidazolium salts are water-soluble and air-stable. The imidazolium salts, **1–3**, were characterized by means of NMR spectroscopy and high-resolution mass spectrometry. Fig. 1 shows the mass assignments for the imidazolium cations of **1–3**. As illustrated in Fig. 1, the average separation between the peaks in the distribution is 44.03 *m*/*z*, which is in exact agreement with the theoretical value of 44.03 *m*/*z* for the ethoxyl group repeat unit. In Fig. 1a, the peaks of imidazolium cation of **1** correspond very well to the masses expected for polyoxyethylene chains with an imidazole end group, where the corresponding theoretical values are 449.2857, 493.3120, 537.3382, 581.3644, 625.3906, 669.4168, 713.4430, 757.4692, 801.4955 and 845.5217 *m*/*z*, consistent with polymerization degrees of 8, 9, 10, 11, 12, 13, 14, 15, 16 and 17, respectively.

The next investigation is to study the catalytic performance of the synthesized imidazolium salts as NHC precursors in the palladium-catalyzed Suzuki reaction in water. It is known that the nature of the base is an important factor for determining the efficiency of the Suzuki cross-coupling reaction. Therefore, the influence of various bases was firstly investigated for the $Pd(OAc)_2$/**1** catalyzed Suzuki coupling reaction of 4-bromoanisole with phenylboronic acid in water. The results in Table 1 show that Et_3N (Table 1, entry 5) is the best choice as compared to the other bases. The activity towards cross-coupled product was decreased when Et_3N was replaced with morpholine, CH_3CH_2ONa, piperidine, 1,2-diaminocyclohexane, DMEDA (*N*,*N*′-dimethylethanediamine), and TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethanediamine) (Table 1, entries 7, 8, 9, 11, 12, and 13). Interestingly, $(nPr)_3N$ (Table 1, entry 10) was inefficient as well, although it is more sterically hindered, indicating that the steric effect of the base does not play a significant role in this system. Only DABCO (1,4-diazabicyclo[2.2.2]octane) showed relatively

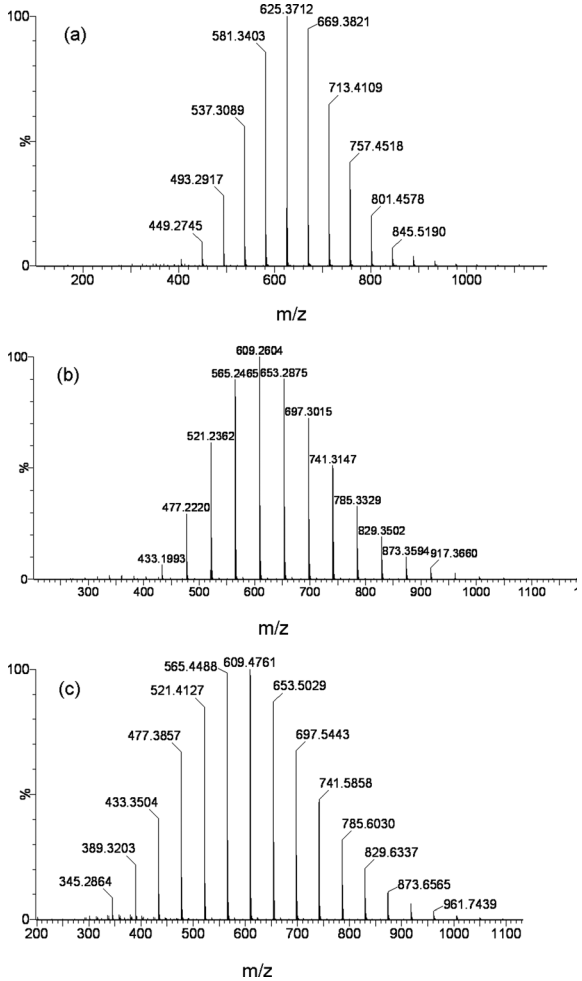
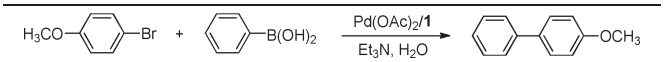


Fig. 1 Q-TOF mass spectra of imidazolium cations of **1** (a), **2** (b), and **3** (c).

Table 1 The effect of base on the Suzuki reaction[a]



Entry	Base	Yield (%)[b]
1	KOH	30
2	Na_2CO_3	21
3	$K_3PO_4 \cdot 7H_2O$	19
4	K_2CO_3	10
5	Et_3N	71
6	DABCO	37
7	Morpholine	7
8	CH_3CH_2ONa	6
9	Piperidine	trace
10	$(nPr)_3N$	trace
11	1,2-Diaminocyclohexane	no reaction
12	DMEDA	no reaction
13	TMEDA	no reaction

[a] Reaction conditions: 0.5 mmol of 4-bromoanisole, 0.75 mmol of phenylboronic acid, 1 mmol of Et_3N, 0.25 mol% $Pd(OAc)_2$, ligand **1**/Pd = 4 : 1 (molar ratio), 100 °C, 5 min, 1 mL H_2O. [b] Isolated yield.

high activity (Table 1, entry 6), which is known as a typical organic base used in the palladium-catalyzed cross-coupling reactions. The excellent performance of Et_3N (Table 1, entry 5)

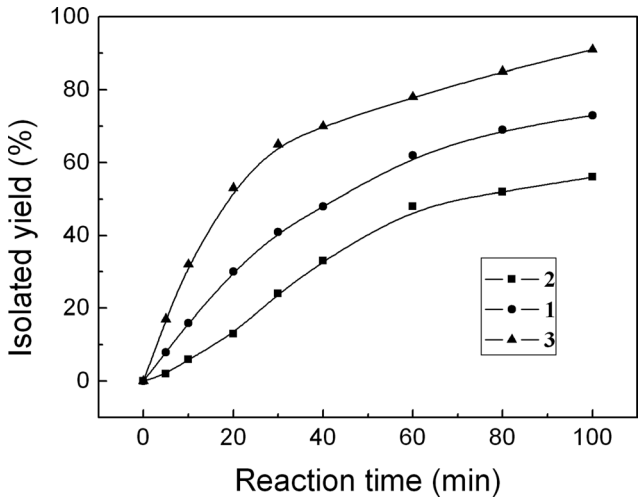


Fig. 2 Kinetic profile of $Pd(OAc)_2$/**1** (round), **2** (square), and **3** (triangle) catalyzed Suzuki reaction in water. Reaction conditions: 0.5 mmol of 4-bromoanisole, 0.75 mmol of phenylboronic acid, 1 mmol of Et_3N, 0.2 mol% $Pd(OAc)_2$, Ligand/Pd = 4 : 1 (molar ratio), 80 °C, 1 mL H_2O.

is supposedly due to Et_3N having a much higher tendency to re-coordinate to the active NHC-Pd species, elongating the lifetime of active species in solution.[48] Among inorganic bases, the stronger base KOH (Table 1, entry 1) gave better results than the weaker bases (Table 1, entries 2–4).

To evaluate the catalytic performance of the NHC precursors **1–3**, a kinetic study of the Suzuki reaction between 4-bromoanisole and phenylboronic acid was performed in the presence of $Pd(OAc)_2$ and Et_3N at 80 °C in water. Fig. 2 demonstrates the kinetic curves of the reaction time *vs.* the isolated yield using *in situ*-generated catalysts from $Pd(OAc)_2$ and imidazolium salts **1–3**. As shown in Fig. 2, $Pd(OAc)_2$/**3** has a relatively shorter induction period and a higher catalytic activity than those of $Pd(OAc)_2$/**1** and $Pd(OAc)_2$/**2**. These results indicate that the enhancement of the "steric-bulk" of the ligand attached to the metal center is crucial to the success of the palladium-catalyzed Suzuki reaction.

The scope of the catalytic system was explored with a range of aryl halides and arylboronic acids in the presence of 0.5 mol % $Pd(OAc)_2$ at 100 °C in 1 mL H_2O. As illustrated in Table 2, the results showed that the Suzuki coupling of aryl bromides with arylboronic acids took place smoothly to give a nearly quantitative yield of biaryls (Table 2, entries 1–6). The electronic nature of substituents bearing aryl bromides is initially investigated. Various 4-substituted aryl bromides bearing either electron-donating groups or electron-withdrawing groups such as methoxy, nitro, cyano and acetyl groups, provided the corresponding products in excellent yields in short reaction times (Table 2, entries 1–5). Furthermore, sterically hindered aryl bromide was also highly reactive in the reaction system, affording the desired cross-coupling product in a high yield (Table 2, entry 6). The hydrophilic aryl bromides with hydroxyl or carboxyl groups were successfully coupled with 4-methylphenylboronic acid in excellent yields (Table 2, entries 7 and 8). It is noteworthy that trace amounts of homocoupling by-product was observed, although cross-coupling reactions were carried out without an inert atmosphere. As aryl-substituted pyridines are the most common N-heteroaryl units in pharmaceutically active compounds, we further investigated the Suzuki reaction of 3-pyridyl bromides with arylboronic acids. As shown in Table 2 (entries 9 and 10), this protocol is applicable to the couplings between 3-pyridyl bromides and phenylboronic acid. Encouraged by such promising results, we next turned our attention to the Suzuki coupling of aryl chlorides. The activation of 4-chloronitrobenzene required the addition of tetrabutylammoniumbromide (TBAB) as a phase transfer catalyst, an 88% isolated yield was obtained (Table 2, entry 11). These results showed that the activity of $Pd(OAc)_2$/**3** in the coupling of 4-chloronitrobenzene is similar with the results recently reported by Godoy and coworkers.[43a] However, the Suzuki coupling of 4-chloronitrobenzene was difficult to proceed in the absence of TBAB under the same reaction conditions.

Conclusion

In conclusion, three new NHC precursors bearing PEG moieties have been synthesized, which are readily accessible from inexpensive and commercial materials. The *in situ*-generated catalysts from palladium acetate and water-soluble imidazolium salts **1–3** demonstrated excellent catalytic activities towards the Suzuki reaction of aryl halides bearing a wide range of functional groups, which were varied in their electronic, steric and dissolution properties, while using water as the sole medium. Further work to explore the real catalytic species in this reaction system and to develop more efficient ligands is currently under investigation in our laboratory.

Experimental

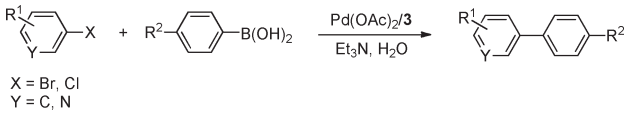
General

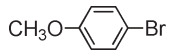
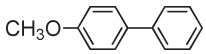
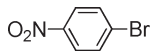
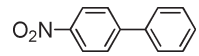
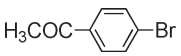
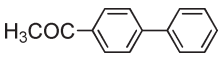
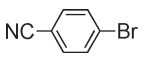
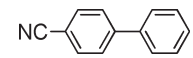
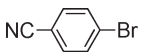
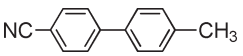
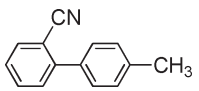
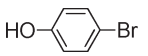
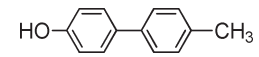
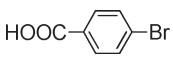
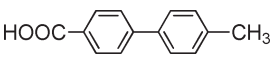
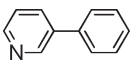
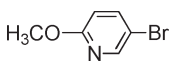
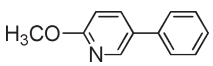
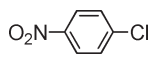
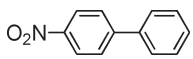
Aryl halides and arylboronic acids were purchased from Alfa Aesar. Other chemicals were obtained commercially and used without any prior purification. NMR spectra were recorded on a Brucker Advance II 400 spectrometer using TMS as internal standard (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR). Mass spectroscopy data (ESI-MS) of the compounds were collected on a UPLC/Q-TOF mass spectrometer. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. Compounds described in the literature were characterized by ^1H NMR spectra compared to reported data.

Synthesis of $MeOPEG_{550}OSO_2CH_3$

A solution of methanesulfonyl chloride (4.6 g, 0.04 mol) in dry toluene (50 mL) was added dropwise to a mixture of $MeOPEG_{550}OH$ (22 g, 0.04 mol), Et_3N (4.1 g, 0.04 mol) in dry toluene (100 mL) under N_2. The mixture was stirred at 0 °C for 24 h and then the white solid by-product was removed by filtration. The filtrate was evaporated under vacuum to afford $MeOPEG_{550}OSO_2CH_3$ (22.9 g, yield 89%) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 4.39–4.36 (m, 2H, CH_2OSO_2), 3.78–3.53 (m, 49H, PEG-H), 3.37 (s, 3H, PEG-OCH_3), 3.09 (s, 3H, OSO_2CH_3) ppm.

Table 2 Suzuki reaction between aryl halides and aryl boronic acids[a]



Entry	Aryl halide	Product	Time (min)	Yield (%)[b]
1			5	97
2			5	96
3			5	95
4			10	97
5			10	96
6			20	98
7			10	96
8			10	93
9			30	95
10			30	98
11[c]			480	88

[a] Reaction conditions: 0.5 mmol of aryl halide, 0.75 mmol of arylboronic acid, 1 mmol of Et_3N, 0.5 mol% $Pd(OAc)_2$, ligand **3**/Pd = 4 : 1 (molar ratio), 100 °C, 1 mL H_2O. [b] Isolated yield. [c] 0.75 mmol TBAB, 1 mol% $Pd(OAc)_2$.

Synthesis of imidazolium salts 1, 2, and 3

A mixture of $MeOPEG_{550}OSO_2CH_3$ (1.6 g, 2.5 mmol) and the respective substituted imidazole (3.0 mmol) was heated in a sealed tube at 100 °C for 24 h. The resulting solution was isolated by short chromatography on a silica gel (200–300 mesh) column using CH_2Cl_2 and CH_3OH.

Imidazolium salt **1**. Yield: 1.57 g, 87%, a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.76 (s, 1H, CH_{imid}), 7.68 (s, 1H, CH_{imid}), 7.41 (s, 1H, CH_{imid}), 4.52 (t, J = 4.0 Hz, 2H, NCH_2), 4.01 (s, 3H, NCH_3), 3.88–3.54 (m, 52H, PEG–H), 3.38 (s, 3H, PEG–OCH_3), 2.79 (s, 3H, OSO_2CH_3) ppm; ^{13}C NMR: δ 137.95 (C_{imid}), 123.55 (C_{imid}), 122.92 (C_{imid}), 71.86–69.06 (C_{PEG}), 58.96 (OCH_3), 49.51 (CH_2), 39.53 (OSO_2CH_3), 36.24 (NCH_3) ppm; MS (ESI) m/z $[M]^+$: 449.2745, 493.2917, 537.3089, 581.3403, 625.3712, 669.3821, 713.4109, 757.4518, 801.4578, 845.5190, 889.5416.

Imidazolium salt **2**. Yield: 1.22 g, 65%, a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.86 (s, 1H, CH_{imid}), 7.69 (s, 1H, CH_{imid}), 7.42 (s, 1H, CH_{imid}), 4.55 (t, J = 4.4 Hz, 2H, NCH_2), 4.24 (t, J = 8.0 Hz, 2H, NCH_2), 3.89–3.54 (m, 49H, PEG–H), 3.38 (s, 3H, PEG–OCH_3), 2.77 (s, 3H, OSO_2CH_3), 1.95 (sextet, J = 8.0 Hz, 2H, CH_2), 0.99 (t, J = 8.0 Hz, 3H, CH_3) ppm; ^{13}C NMR: δ 137.66 (C_{imid}), 123.67 (C_{imid}), 121.31 (C_{imid}), 71.87–69.17 (C_{PEG}), 58.97 (OCH_3), 51.27 (NCH_2), 49.51 (NCH_2), 39.55 (OSO_2CH_3), 23.49 (CH_2), 10.71 (CH_3) ppm; MS (ESI) m/z $[M]^+$: 433.1993, 477.2220, 521.2362, 565.2465, 609.2604, 653.2875, 697.3015, 741.3147, 785.3329, 829.3502, 873.3594, 917.3660.

Imidazolium salt **3**. Yield: 1.69 g, 88%, a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.13 (s, 1H, CH_{imid}), 7.64 (s, 1H, CH_{imid}), 7.25 (s, 1H, CH_{imid}), 4.75 (heptet, J = 8.0 Hz, 1H, NCH), 4.60 (t, J = 4.4 Hz, 2H, NCH_2), 3.90-3.53 (m, 47H, PEG–H), 3.38 (s, 3H, PEG–OCH_3), 2.80 (s, 3H, OSO_2CH_3), 1.61 (d, J = 8.0 Hz, 6H, $2CH_3$) ppm; ^{13}C NMR: δ 136.51 (C_{imid}), 123.79 (C_{imid}), 118.99 (C_{imid}), 71.86–69.21 (C_{PEG}), 58.96 (OCH_3), 53.03 (NCH), 49.54 (NCH_2), 39.51 (OSO_2CH_3), 22.95 ($2CH_3$) ppm; MS (ESI) m/z $[M]^+$: 345.2864, 389.3203, 433.3504, 477.3857, 521.4127, 565.4488, 609.4761, 653.5029, 697.5443, 741.5858, 785.6030, 829.6337, 873.6565, 917.7091, 961.7439.

General procedure for the Suzuki reactions

All Suzuki reactions were carried out without an inert atmosphere. A mixture of aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), Et_3N (101 mg, 1 mmol), $Pd(OAc)_2$ (0.56 mg, 0.0025 mmol), and imidazolium salts (7.2 mg, 0.01 mmol) in H_2O (1 mL) was allowed to react in a sealed tube at 100 °C. The

activation of 4-chloronitrobenzene required the addition of TBAB (0.75 mmol) as a phase transfer catalyst. The reaction mixtures was added to brine (15 mL) and extracted three times with ethyl acetate (3 × 15 mL). The solvent was concentrated under vacuum and the product was isolated by short chromatography on a silica gel (200–300 mesh) column.

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