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Anion-Dependent Imidazolium-Based Catalysts for Allylation of Aniline with Tunable Regioselectivity

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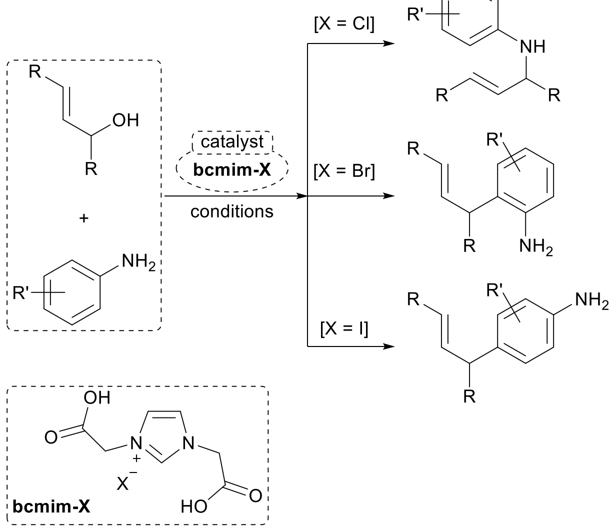
Abstract. Metal-free catalysts based on 1,3-bis(carboxymethyl)imidazolium halides mediate the reaction between allylic alcohols and anilines, providing the corresponding *N*-, 2- and 4-allylaniline isomers selectively. The imidazolium counterion plays a crucial role in the outcome of the reaction. Thus, while the imidazolium chloride selectively provides the *N*-substituted aniline, the bromide and iodide imidazolium salts produce the 2- and 4-allylaniline isomers, respectively, with excellent selectivities. A set of complementary catalysts, which are available by simple modulation, is here presented to conduct a highly regioselective allylation reaction of anilines. Not only the catalysts are synthesized in a straightforward and easily scalable manner, but they can be recycled and used under solvent-free reaction condition, due to the favorable interactions with the reactants.

Keywords: Allylic Substitution; Heterogeneous catalysis; Imidazolium salt; Metal-free; Regioselectivity; Sustainability

Introduction

The direct allylic substitution reaction of alcohols is a straightforward strategy to afford allylic derivatives avoiding the use of coupling agents or the necessity of derivatization (e.g. acetates, phosphates, carbonates, halides),[1] constituting an environmentally friendly alternative. When the nucleophile is an aniline derivative, three regioisomers are expected: 2-allylanilines, 4-allylanilines and *N*-allylanilines. Most of the reported catalytic systems for the allylic substitution of alcohols with anilines lead to the predominant generation of *N*-allylanilines,[2] and include metals such as palladium,[3] gold,[4] platinum,[3a,5] iron,[6] molybdenum[7] and cobalt,[8] amongst others. The formation of 2- and 4-allylanilines has been less studied. To the best of our knowledge, the formation of 2-allylanilines (*via* allylic substitution of alcohols with anilines) has been achieved using $Cu(OTf)_2$,[9] Re_2O_7,[10] a palladacycle[3d] and iron-based imidazolium salts (IBLAILs),[6a] while the synthesis of 4-allylanilines has only been reported using $Cu(OTf)_2$.[9] A carboxylic acid functionalized graphene oxide[11] and a cubane-type sulfido cluster incorporating palladium and molybdenum[12] have also been used for the synthesis of 4-allylanilines, starting from *N*,*N*-dialkyl substituted anilines, which rules out the possibility of the aniline acting as N-nucleophile.

We have proved that the imidazolium salt 1,3-bis(carboxymethyl)imidazolium chloride (**bcmim-Cl**), can be used as simple, efficient, regioselective and recyclable metal-free catalyst for the preparation of *N*-allylanilines by allylic substitution of alcohols with anilines.[13] Both the carboxyl and chloride moieties in the **bcmim-Cl** are responsible of the favorable interactions with the reactants and key in the effective preparation of quinoline and acridine derivatives.[14] We hypothesized that different counteranions in the imidazolium salt could result in a modification in the outcome of allylic substitution reaction of alcohols with anilines. Interestingly, the replacement of the anion for other halide (i.e. bromide and iodide) allowed the selective formation of both 2- and 4-allylanilines, respectively (Scheme 1). Herein, we report our finding in the development of metal-free catalytic systems for the regioselective allylic substitution of alcohols with anilines. The catalytic systems are based on 1,3-bis(carboxymethyl)imidazolium halides (**bcmim-X**), which are ionic organic solids (IOS). These organic salts can be easily separated from the reaction mixture.



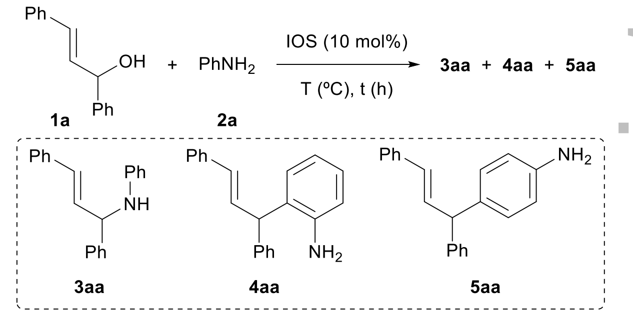
Scheme 1. Metal-free catalyzed substitution reaction of allylic alcohols with anilines: selective formation of the products by modulation of the catalytic system.

Results and Discussion

The different 1,3-bis(carboxymethyl)imidazolium halide catalysts were prepared by a simple procedure, starting from glyoxal, formaldehyde and glycine, and introducing the anion in the last step by treatment with the corresponding hydrogen halide.

The use of 1,3-bis(carboxymethyl)imidazolium chloride (**bcmim-Cl**) as heterogeneous catalyst in the reaction of *trans*-1,3-diphenylprop-2-en-1-ol (**1a**) and aniline (**2a**) at 80 ºC provided, after 90 minutes, the selective formation of product **3aa** in 82% conversion (Table 1, entry 1),[13] with less than 5% of each of the other isomers being detected. Longer reaction times resulted in the formation of larger amounts of isomers **4aa** and **5aa** (14-18% and 14% conversion, respectively, after 6-24 h, Table 1, entries 2, 3). The temperature has also an influence in the reaction selectivity. In our previous work,[13] we proved that both the *ortho*- and the *para*-allylanilines (i.e. **4aa** and **5aa**) can be formed, in low selectivity, from the *N*-allyl substituted product **3aa** by increasing the temperature and the reaction time (Table 1, entries 4 and 5), using **bcmim-Cl** as catalyst. Interestingly, the use of the imidazolium iodide analogue as catalyst (10 mol%) in our model reaction, resulted in a drastic change in the selectivity and product **5aa** was formed in 77% conversion after 6 h (Table 1, entry 11). Next, we explored the reaction using 1,3-bis(carboxymethyl)imidazolium bromide (**bcmim-Br**) as catalyst (Table 1, entries 6-10). Similar results to **bcmim-Cl** were obtained at low temperature (80 ºC), being the *N*-allylated aniline **3aa** the major product of the reaction (Table 1, compare entries 1-3 with entries 6-8). However, as also observed with catalysts **bcmim-Cl** (Table 1, entry 5), increasing the temperature to 100 ºC and extending the reaction time to 24 h, resulted in the selective formation of compound **4aa** (78% conversion, Table 1, entry 10) when **bcmim-Br** was employed as catalyst. Under these conditions, **bcmim-I** gave a mixture of isomers **4aa** and **5aa** with low selectivity (ratio 1:3, Table 1, entries 13 and 14), being remarkable that isomer **3aa** was not observed with this catalyst under any reaction conditions. Consequently, the modulation of the counteranion of this simple type of catalysts allows the selective preparation of *N*-allylaniline (using **bcmim-Cl**),[13] 2-allylaniline (using **bcmim-Br**) or 4-allylaniline derivatives (using **bcmim-I**).

Table 1. (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) and aniline (**2a**): Effect of the catalyst

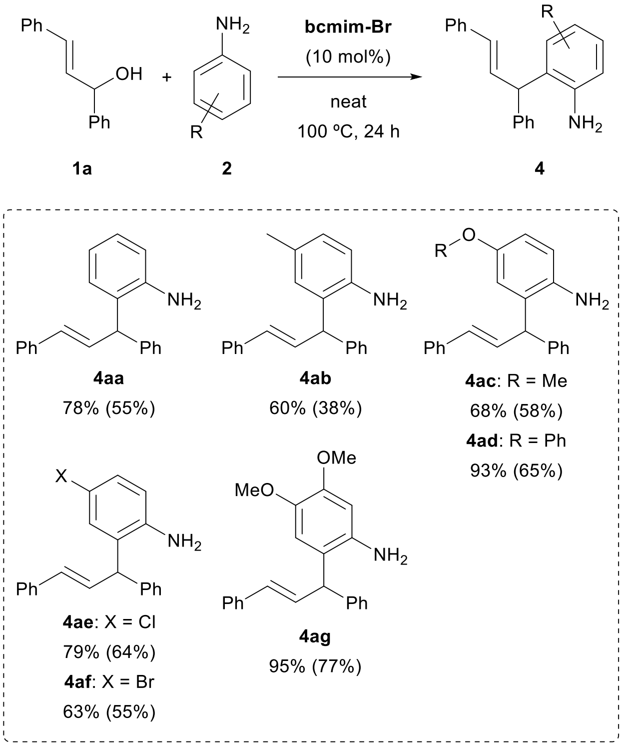


Entry	IOS	Temp (ºC)	Time (h)	Conv. (%)[a] **3aa**/**4aa**/**5aa**
1	**bcmim-Cl**	80	1.5	**82**/3/4
2	**bcmim-Cl**	80	6	60/14/14
3	**bcmim-Cl**	80	24	48/18/14
4	**bcmim-Cl**	100	1	80/9/6
5	**bcmim-Cl**	100	24	1/69/15
6	**bcmim-Br**	80	1.5	60/0/0
7	**bcmim-Br**	80	6	66/12/11
8	**bcmim-Br**	80	24	48/28/13
9	**bcmim-Br**	100	1	62/13/14
10	**bcmim-Br**	100	24	0/**78**/16
11	**bcmim-I**	80	6	0/1/**77**
12	**bcmim-I**	80	24	0/2/78
13	**bcmim-I**	100	1	0/23/67
14	**bcmim-I**	100	24	0/21/66

[a] Conversion determined by GC analysis for the compounds **3aa**, **4aa** and **5aa**.

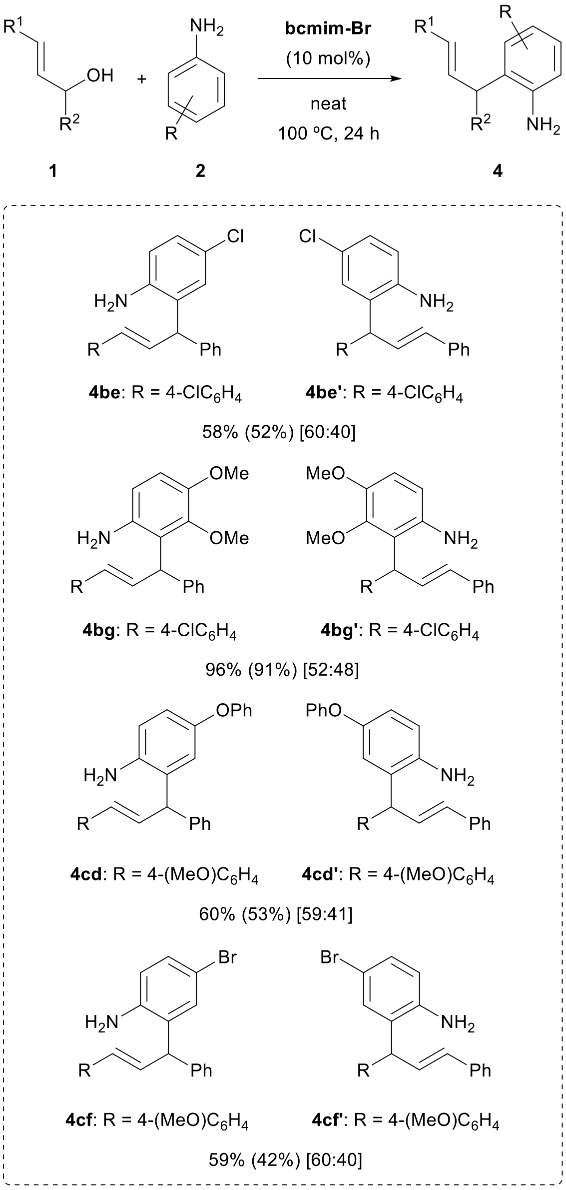
Under the optimised reaction conditions – **bcmim-Br** (10 mol%), 100 ºC, 24 h for the synthesis of 2-allylanilines and **bcmim-I** (10 mol%), 80 ºC, 6 h for the preparation of 4-allylanilines – the scope of the reaction was explored.

The 2-allylation reaction of *trans*-1,3-diphenyl-2-propen-1-ol, catalysed by **bcmim-Br**, was carried out with different anilines (Scheme 2). Aniline, 4-toluidine, 4-anisidine and 4-phenoxyaniline afforded the corresponding compounds **4aa-4ad** with conversions between 60 and 93% (Scheme 2). Halogen substituted anilines provided also the expected 2-allylanilines in moderate conversions (Scheme 2, compounds **4ae** and **4af**). Products **4** were isolated with lower yields due to the purification process (Scheme 2, isolated yields in brackets). 3,4-Dimethoxyaniline gave the desired compound **4ag** in excellent conversion and good isolated yield (Scheme 2).



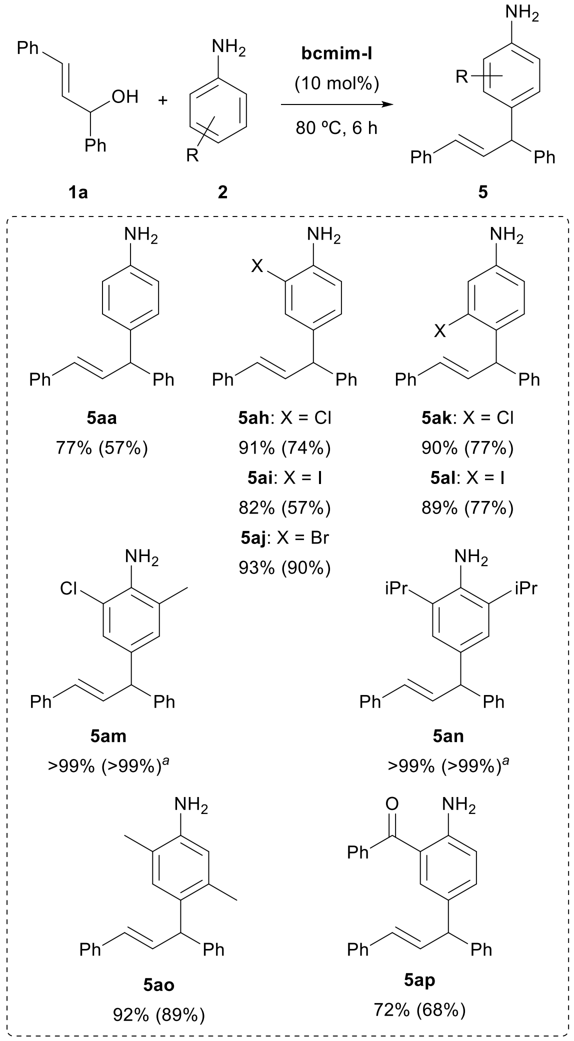
Scheme 2. Evaluation of anilines for the formation of 2-allyl-anilines using **bcmim-Br** as catalyst. Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), **bcmim-Br** (10 mol%), 100 ºC, 24 h. Conversion determined by ^{1}H-NMR analysis (in brackets, isolated yield of pure product after column chromatography).

Next, we studied the effect of substituents in aromatic rings of the 1,3-diaryl-2-propen-1-ol. As previously reported for *N*-allylanilines,[13] non-symmetrically substituted alcohols led to the formation of two 2-allylaniline regioisomers. The regioisomers ratio was *ca.* 1:1 for different anilines and alcohols, regardless of the electron properties of the substituents. This agrees with the fact that 2-allylanilines are formed from *N*-allylanilines, which are formed *via* a carbocation intermediate. Thus, alcohols and anilines bearing both electron-donating and electron-withdrawing groups were evaluated in the reaction leading to the formation of the corresponding 2-allylanilines in moderate conversions and yields (Scheme 3, compounds **4be**, **4cd**, **4cf** and their corresponding regioisomers). Using 3,4-dimethoxyaniline in combination with *trans*-1-(4-chlorophenyl)-3-phenyl-2-propen-1-ol produced the expected compound **4bg** in excellent conversion and yield (Scheme 3, compound **4bg** and regioisomer **4bg'**).

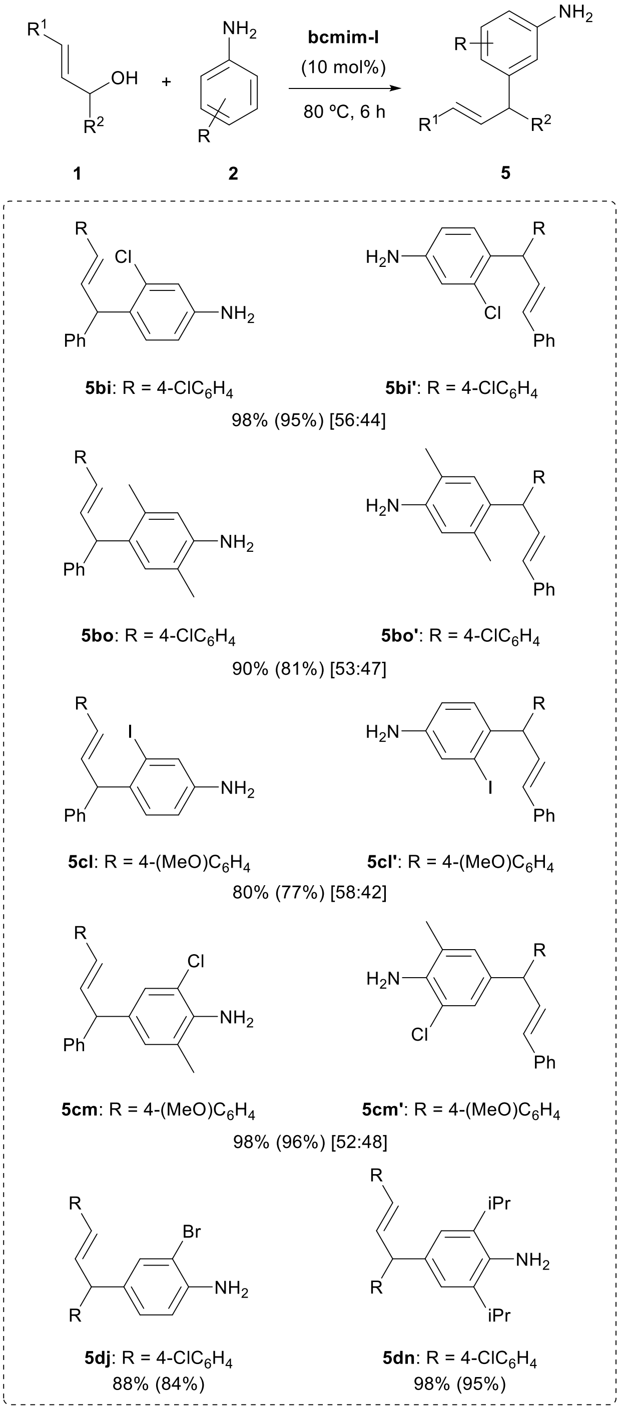


Scheme 3. Evaluation of alcohols for the formation of 2-allyl-anilines using **bcmim-Br** as catalyst. Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), **bcmim-Br** (10 mol%), 100 ºC, 24 h. Conversion determined by ^{1}H-NMR analysis (in brackets, isolated yield of pure product after column chromatography), [in square brackets, ratio of the regioisomers determined by ^{1}H-NMR].

Next, we explored the reaction of *trans*-1,3-diphenylprop-2-en-1-ol (**1a**) with **bcmim-I** in the presence of different substituted anilines, under the optimized reaction conditions, for the synthesis of the corresponding 4-allylaniline adducts. Thus, anilines with electron-withdrawing groups afforded the corresponding 4-allylanilines in excellent conversions, compounds **5ah**, **5ai**, **5aj**, **5ak** and **5al** being isolated with good yields (Scheme 4). Substituted anilines in both *ortho*-positions, such as 2-chloro-6-methylaniline and 2,6-diisopropylaniline, led to the quantitative formation of the desired compounds **5am** and **5an** respectively (Scheme 4) without any further purification, apart from separation of the catalyst by filtration. 2,5-Dimethylaniline afforded the desired product **5ao** in excellent conversion and yield (Scheme 4). Finally, 2-benzoylaniline gave rise to the formation of the desired product **5ap** in good conversion and yield (Scheme 4).



Scheme 4. Evaluation of anilines for the formation of 4-allylanilines using **bcmim-I** as catalyst. Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), **bcmim-I** (10 mol%), 80 ºC, 6 h. Conversion determined by ^{1}H-NMR analysis (in brackets, isolated yield of pure product after column chromatography). [a]Pure product isolated after simple filtration.



Scheme 5. Evaluation of alcohols for the formation of 4-allyl-anilines using **bcmim-I** as catalyst. Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), **bcmim-I** (10 mol%), 80 ºC, 6 h. Conversion determined by ^{1}H-NMR analysis (in brackets, isolated yield of pure product after column chromatography), [in square brackets, ratio of the regioisomers determined by ^{1}H-NMR].

Other allylic alcohol derivatives were tested in the reaction mediated by **bcmim-I** in combination with a variety of anilines. Likewise, both regioisomers (in *ca.* 1:1 ratio) were obtained with non-symmetrically substituted allylic alcohols. Alcohols bearing electron-withdrawing and donating groups in the aromatic ring were tested in combination with different anilines, obtaining good to excellent conversions and yields in all cases (Scheme 5, compounds **5bi**, **5bo**, **5cl** and **5cm**, and their isomers). Moreover, compounds **5dj** and **5dn** were isolated in 84% and 95% yield when *trans*-1,3-di(4-chlorophenyl)-2-propen-1-ol was reacted with 2-bromoaniline and 2,6-diisopropylaniline, respectively (Scheme 5).

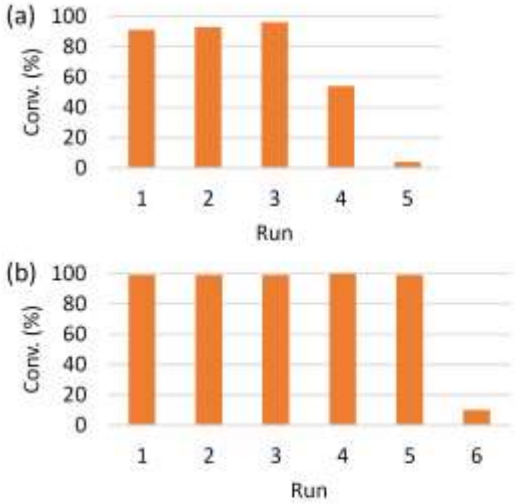
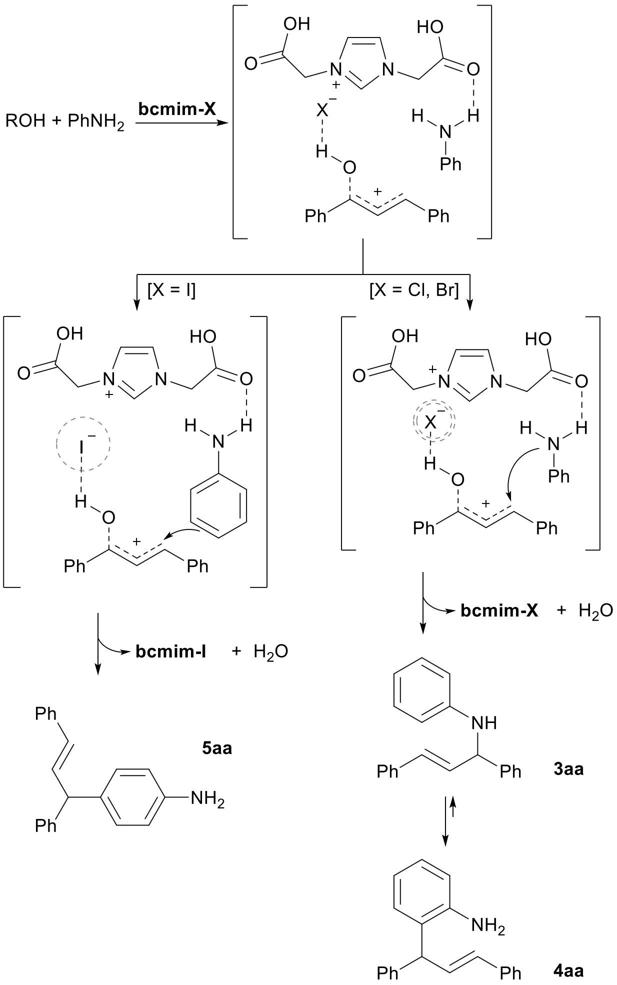


Figure 1. Recycling of catalysts: (a) reaction of **1a** and **2g** catalyzed by **bcmim-Br**; (b) reaction of **1a** and **2m** catalyzed by **bcmim-I**.

The recyclability of both **bcmim-Br** and **bcmim-I** catalysts was also studied. Due to their non-solubility in organic solvents, such as ethyl acetate, the same protocol employed for recycling **bcmim-Cl**[13] was also applied here. The reaction mixture, after adding a small portion of ethyl acetate, was centrifuged to separate the catalyst; this protocol allowed the complete recovery of the catalyst (no traces were observed in the filtrate, ^{1}H-NMR). The recovered **bcmim-Br** catalyst could be recycled up to 3 times without loss of activity in the synthesis of compound **4ag**, observing a decrease in activity in the fourth cycle (Figure 1a). Whereas, **bcmim-I** could be recycled up to 5 times providing full conversion in the synthesis of compound **5am**, with a drastic reduction in the conversion in the sixth cycle (Figure 1b). This catalysts deactivation could be attributed to their degradation. It has been proven that the effectiveness of the catalyst depends, in part, on the halide, bearing in mind that the zwitterion [1,3-bis(carboxymethyl)imidazole, **bcmim**] is inactive for this type of transformation.[13] We pondered the premise that the amount of halide could decrease during the reaction and/or the work-up, the less bound the halide is to the cation, the easier the dissociation. Based on that idea, recycled **bcmim-I** (after the sixth cycle) was analyzed by ionic chromatography observing that the amount of iodide had been reduced to less than 0.1% compared with a fresh sample. Likewise, the amount of bromide in **bcmim-Br** was reduced to less than 11%, compared with a fresh sample, after the fifth cycle. For comparison, a recycled sample of **bcmim-Cl**, which holds its activity for 15 cycles, contains 16% of the initial amount of chloride after fifteen cycles.[13] Although, the higher robustness of the chloride salt is vindicated, it should be noted that the reactivation of all three different catalysts can be easily performed by treatment in the corresponding acid medium.



Scheme 6. Proposed mechanism for the formation of the different regioisomers by allylic substitution of alcohols with anilines.

Next, the synthetic utility of our methodology was showcased by the ease of upscaling of the reaction, allowing access to 1 g of **5am** employing only 10 mol% of **bcmim-I**. Product **5am** was isolated in quantitative yield after filtration, using ethyl acetate (4 mL) to wash the catalyst. Interestingly, this reaction presented an *E-factor* of 3.4, verifying the sustainability of the protocol.[15]

Considering that the reactions are performed in the absence of any solvent, it is postulated that the catalysts facilitate the interactions between the reactants. The presence of the carboxy groups in the imidazolium catalyst, that enables the formation of hydrogen bonds with the reagents, is key to the catalytic process, although the interaction of the halide with the reagents appears to be also crucial.[13-14] Thus, it can be proposed that these **bcmim-X** salts, which are ionic organic solids (IOS), establish favorable interactions by acting both as hydrogen donors and hydrogen acceptors. These interactions would favor the formation of the allylic carbocation, which is involved in the reaction mechanism, bringing the amine closer to facilitate the nucleophilic attack (Scheme 6). The measurement of the heat flow by Differential Scanning Calorimetry (DSC) of mixtures of the alcohol **1a** and the different catalysts **bcmim-X** (X = Cl, Br, I) showed differences compared with a sample of pure alcohol **1a** (Figure 2). The alcohol **1a** melting thermal event is modified by the presence of the ionic organic salts (IOS), due to the favorable interactions between the components in a similar way as occurs between the components of a low transition temperature mixtures (LTTM) or deep eutectic solvents (DES).[16] Interestingly, in the presence of both chloride and bromide salt, a similar decrease in melting temperature is observed (Figure 2b and 2c), but in the case of the iodide salt, the mixture shows a greater variation (Figure 2d). Iodide has larger ionic radius and higher polarizability than the other halides, which may facilitate interactions with alcohol **1a**. In addition, the presence of an iodide would stabilize the allyl carbocation generated during the reaction, making the nucleophilic attack selective towards the *para* position of the aromatic ring (Scheme 6). In the cases of chloride and bromide the reaction occurs, preferably, with the nitrogen acting as nucleophile, forming the *N*-allyl product, which can equilibrate to the more stable 2-allyl derivative (Scheme 6). Moreover, the **bcmim-I** catalyst, apart from being selective towards the 4-allyl product, is more effective than the chloro and bromo imidazolium salts. It was observed that the heat release in the reaction of alcohol **1a** and aniline **2a** in the presence of **bcmim-I** occurs at lower temperature compared to the reactions catalyzed by **bcmim-Cl** or **bcmim-Br** (Figure 3). Furthermore, reactions catalyzed by **bcmim-Cl** and **bcmim-Br** present similar DSC spectra, which agrees with the observed experimental results. At this point, it is worth mentioning that the selectivity in phenol *tert*-butylation has been reported based on the acidic sites of different catalysts,[17] so we cannot rule out certain likeness with our case.

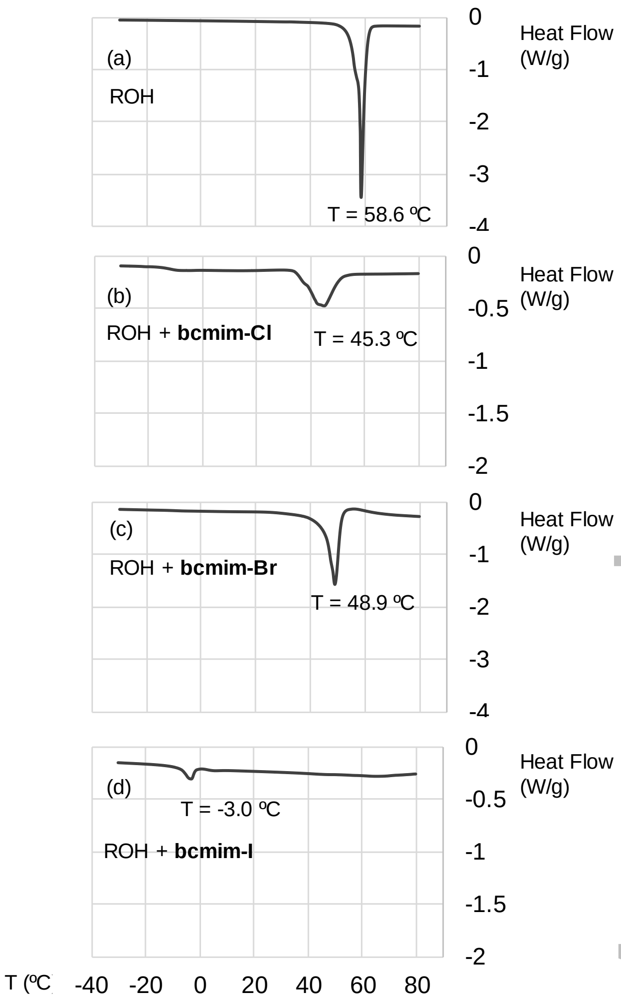


Figure 2. Differential Scanning Calorimetry (DSC) spectra: (a) alcohol **1a**, (b) mixture of alcohol **1a** and **bcmim-Cl**, (c) mixture of alcohol **1a** and **bcmim-Br** and (d) mixture of alcohol **1a** and **bcmim-I**.

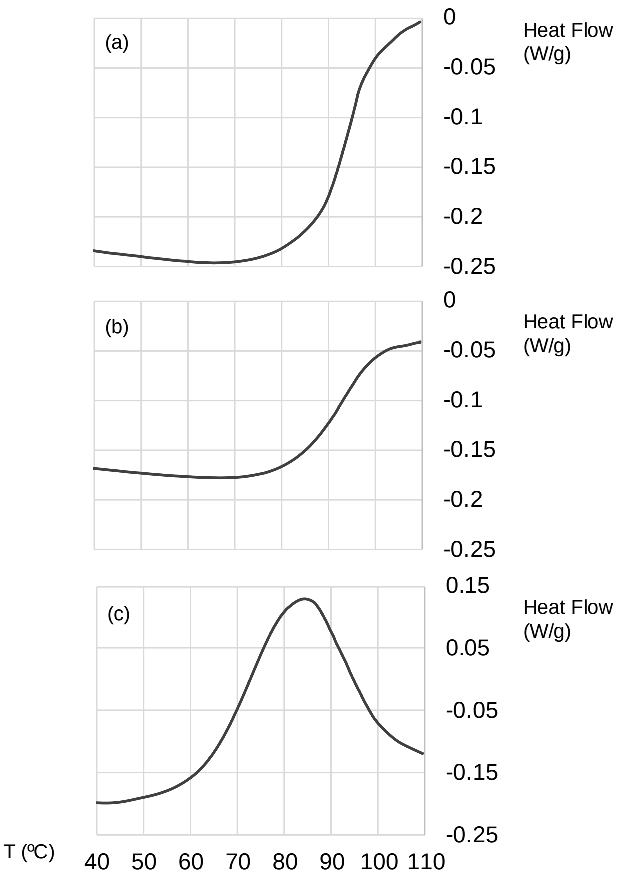
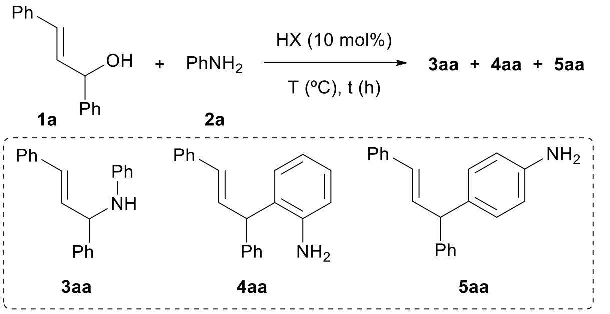


Figure 3. Differential Scanning Calorimetry (DSC) spectra of the reaction mixture: alcohol **1a**, aniline (**2a**) and (a) **bcmim-Cl** (10 mol%), (b) **bcmim-Br** (10 mol%) and (c) **bcmim-I** (10 mo%).

Finally, different experiments were conducted in the presence of HCl, HBr and HI, instead of the imidazolium halides. The reactions were performed under the optimized reaction conditions for each halide. Thus, the reaction between alcohol **1a** and aniline **2a**, using HCl (10 mol%) at 80 ºC, provided compounds **3aa** and **4aa** in 51% and 4% conversion, respectively, after 6 h (Table 2, entry 1). The reaction of **1a** and **2a**, employing HBr (10 mol%) as catalyst, afforded, after 1 h, products **3aa**, **4aa** and **5aa** in 58%, 24% and 16% conversion, respectively (Table 2, entry 2), although after 24 h, only products **4aa** and **5aa** were observed in 3:2 ratio (Table 2, entry 3). Similarly, the reaction catalyzed by HI (10 mol%) gave, initially, all three isomers **3aa**, **4aa** and **5aa** (Table 2, entry 4), but provided, after 6 h, the products **4aa** and **5aa** in 2:3 ratio (Table 2, entry 5). The results obtained with hydrogen halides are in clear contrast with the ones obtained employing **bcmim-X** catalysts (Table 1). Indeed, the **bcmim-X** catalyzed reactions provide higher regioselectivities than the corresponding hydrogen halides; especially in the synthesis of the 4-allylaniline isomers.

Table 2. (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) and aniline (**2a**) catalyzed by hydrogen halides



Entry	HX	Temp (ºC)	Time (h)	Conv. (%)[a] **3aa**/**4aa**/**5aa**
1	HCl	80	6	51/4/0
2	HBr	100	1	58/24/16
3	HBr	100	24	0/59/40
4	HI	80	1	38/22/34
5	HI	80	6	0/42/58

[a] Conversion determined by GC analysis for the compounds **3aa**, **4aa** and **5aa**.

Conclusion

To conclude, we have described three simple, effective and robust metal-free catalysts based on solid imidazolium halides, which are complementary in terms of regioselectivity for the allylic substitution of alcohols with anilines. The counterion in the 1,3-bis(carboxymethyl)imidazolium salt catalysts plays a crucial role and determines the regioselectivity of the process. Thus, the chloride catalyst selectively produces *N*-allylanilines, the imidazolium bromide generates 2-allylaniline isomers and the corresponding iodide catalyst mediates the selective formation of 4-allylanilines. Although **bcmim-Cl** catalyst proved to be more robust than the others, with less degradation during the successive cycles, **bcmim-I** catalyst resulted more effective, allowing lower reaction temperatures and providing unprecedented selectivities for the synthesis of 4-allylanilines. The synthesis of all three catalysts is straightforward and easily scalable. The catalytic allylation reaction is carried out under solvent-free conditions, being the catalysts responsible for the favorable interactions in the absence of any solvent. Moreover, the catalysts are easily separated from the reaction mixture and recycled, which makes this methodology a sustainable process. These protocols represent a significant improvement compare with the previously reported ones (most of them based on metals), particularly for the 4-allylaniline isomers.

Experimental Section

Reagents and instruments. All commercially available reagents and solvents were purchased (Acros, Aldrich, Fluka) and used without further purification. Melting points were determined using a Gallenkamp capillary melting point apparatus (model MPD 350 BM 2.5) and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at the research technical service of the University of Alicante (SSTTI–UA), employing a Bruker AC-300 or a Bruker Advance-400.§ Chemical shifts (δ) are given in ppm and the coupling constants (*J*) in Hz. The conversion of the reactions and purity of the products were determined by GC analysis using an Agilent 7820A apparatus, equipped with a flame ionization detector and a Phenomenex ZB-5MS column (5% PH-ME siloxane): 30 m (length), 0.25 mm (inner diameter) and 0.25 μm (film). Low-resolution mass spectra (EI) were obtained at 70 eV with an Agilent 5973 Network spectrometer, with fragment ions *m/z* reported with relative intensities (%) in parentheses. Low-resolution HPLC with electrospray ionization (HPLC-ESI) mass spectra were recorded at the research technical service of the University of Alicante (SSTTI–UA), employing an Agilent 1100 series apparatus with the possibility of MS/MS.§ High resolution mass spectra (IE) were recorded at the research technical service of the University of Alicante (SSTTI–UA) with an Agilent 7200 Network spectrometer (Q-TOF).§ Ion chromatography (IC) anions were measured at the research technical service of the University of Alicante (SSTTI–UA) with an Ion Chromatograph, with chemical suppression, conductometric, amp and Spectrophotometric UV-VIS, Metrohm, 850 detection ProfIC Acuma - MCS, with derivatization post-column reactor.§ Differential Scanning Calorimetry (DSC) spectra were recorded at the research technical service of the University of Alicante (SSTTI–UA) with a Heat Flow Q100 TA Instruments DSC equipped with temperature modulation. § Infrared spectra were recorded with an FT-IR 4100 LE (JASCO, Pike Miracle ATR) spectrometer. Spectra were recorded from neat samples and results are given in cm^{-1}. Analytical TLC was performed on Merck aluminum sheets with silica gel 60 F254, 0.2 mm thick. Silica gel 60 (0.04-0.06 mm) was employed for column chromatography. P/UV$_{254}$ silica gel with $CaSO_4$ supported on glass plates was employed for preparative TLC. Centrifugation was carried out with a Nahita Model 2610 apparatus (4000 rpm).

Synthesis of 1,3-bis(carboxymethyl)imidazole (bcmim).[18] A mixture of glycine (100 mmol, 7.5 g), glyoxal (40% in water, 50 mmol, 5.7 mL) and formaldehyde (36% in water, 100 mmol, 3.9 mL) was stirred at 95 °C for 2 h. The mixture was cooled down to room temperature and the resulting brown solid was filtered, washed with cold water and dried at room temperature to afford the corresponding product as a white solid in 89% yield.

Synthesis of 1,3-bis(carboxymethyl)imidazolium halide (bcmim-X).[18a,19] A mixture of **bcmim** (920 mg, 5 mmol) and concentrated HCl (37% in water, 0.9 mL, 11.0 mmol), HBr (48% in water, 0.9 mL, 16.5 mmol) or HI (57% in water, 1.2 mL, 16.5 mmol) was stirred and refluxed for 30 minutes. Then, the corresponding hydrogen halide was removed under reduced pressure and the resultant solid was filtered and washed with acetone and diethyl ether to afford **bcmim-Cl** and **bcmim-Br** as white solids in 93% and 91% yield respectively, and **bcmim-I** as a reddish solid in 83% yield.

General procedure for the synthesis of 2-allylanilines (4). The corresponding allylic alcohol (**1**, 0.5 mmol), the corresponding aniline (**2**, 0.5 mmol) and **bcmim-Br** (10 mol%, 13.3 mg) were placed in a tube provided with a stirring bar. The mixture was stirred at 100 °C for 24 h. Then, ethyl acetate (3 mL) was added, and the mixture was filtered to separate the catalyst. After evaporating the solvent under vacuum, the corresponding crude was purified by column chromatography using mixtures of hexane/ethyl acetate. In the recycling experiments, the catalyst was separated by centrifugation and washed with ethyl acetate (2×3 mL) and with diethyl ether (1×3 mL).

General procedure for the synthesis of 4-allylanilines (5). The corresponding allylic alcohol (**1**, 0.5 mmol), the corresponding aniline (**2**, 0.5 mmol) and **bcmim-I** (10 mol%, 15.6 mg) were placed in a tube provided with a stirring bar. The mixture was stirred at 80 °C for 6 h. Then, ethyl acetate (3 mL) was added, and the mixture was filtered to separate the catalyst. After evaporating the solvent under vacuum, the corresponding crude was purified by column chromatography using mixtures of hexane/ethyl acetate. In the recycling experiments, the catalyst was separated by centrifugation and washed with ethyl acetate (2×3 mL) and with diethyl ether (1×3 mL).

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FULL PAPER

Anion-dependent imidazolium-based catalysts for allylation of aniline with tunable regioselectivity

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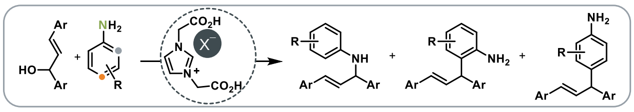
María Albert-Soriano, Isidro M. Pastor*



Complementary catalysts

- ✓ No derivatisation
- ✓ Use of catalyst
  - ✓ Recoverable
  - ✓ Reusable
- ✓ No solvent nor additives
- ✓ Atom economy

Cl$^-$	Br$^-$	I$^-$
80 °C, 2 h	100 °C, 24 h	80 °C, 6 h
21 products	11 products	16 products
Up to 99% yield	Up to 91% yield	Up to 99% yield
Up to 15 runs	Up to 4 runs	Up to 5 runs
Up to 3.3 g		Up to 1 g