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DEVELOPMENTS IN THE REACTIVITY OF 2-METHYL IMIDAZOLIUM SALTS

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ABSTRACT: Unexpected and unusual reactivity of 2-methyl imidazolium salts towards aryl-*N*-sulfonylimines and aryl aldehydes is here reported. On reaction with aryl-*N*-sulfonylimines the addition product, arylethyl-2-imidazolium-1-tosylamides (**3**) is formed with moderate to good yields while on reaction with aldehydes, the initial addition product (**6**) observed in NMR and HPLC-MS experimental analysis is postulated by us as an intermediate to the final conversion to carboxylic acids. Studies in the presence and absence of molecular oxygen allow us to conclude that the imidazolium salts is crucial for the oxidation. A detailed mechanistic study was carried out to provide insights to this unexpected reactivity.

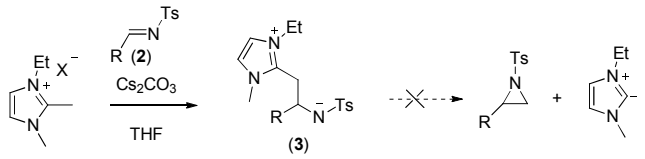
INTRODUCTION

The unique properties of ionic liquids are responsible for its numerous and potential applications.[1-3] Among several, they have been used successfully in many catalytic reactions, not only as the solvent but in some cases as the catalyst for N-heterocyclic carbene (NHC) catalyzed reactions.[4,5] Due to its characteristics, the NHC species has had an important role for the development of new synthetic methods. Transesterification, nucleophilic aromatic substitution, cycloaddition and C-C bond formation, are examples in which NHCs can play an important role.[6-11] These metal-free catalyzed processes are interesting alternatives to classical organic transformations since they are often more economical and environmentally friendly. The NHC-based reactive species is usually obtained by deprotonation of azolium salts, through a base (NaOH, NaH, DBU, K_2CO_3, MeONa, Et_3N, etc.). The benzoin condensation reaction, is a model reaction catalyzed by these NHC intermediate species. [12-16] For these and other important organic transformations imidazolium-based ionic liquids have been used often as catalyst, as solvent/catalyst, under microwave irradiation and ultrasonic activation,[13] in solventless conditions or in classical organic solvents.[16,17] In all these methodologies the presence of a base plays a key role in the generation of the NHC from the azolium salts but electrogenerated NHC[18] have also been reported.

Although the extensive work done with the frequently studied class of imidazolium-based ionic liquids very little has been published concerning the reactivity of these azolium salts when functionalized at the C2 position.[19] Nevertheless this is one of the most relevant substitution positions which is shown to be associated with the biological activities of azoles.[20,21] In the presence of a base the C2-substituted imidazolium salt forms a 1,3-dipolar specie that can act as a nucleophile reacting with aldehydes and the heteroarylvinyl imidazolium thus formed have interesting antitumoral activity.[22,23] This type of 1,3-dipolar specie have also been studied as captors and catalyst in reactions with CO_2.[24,25] These NHC–CO_2 adducts were found to catalyze the cyclization of CO_2 and propargylic alcohols at mild conditions giving α-alkylidene cyclic carbonates.[25] Interesting reactivity was also observed with alkyl imidazolium salts when *in-situ* generated. The so produced N-heterocyclic olefins (NHO) were involved in oxidative processes and coupling reactions.[26,27] Initially we had proposed ourselves to evaluate the application of 1,2-dimethyl-3-ethyl imidazolium salts (**1**) as a reagent for the condensation and/or methylene transfer reagent to electrophilic species such as imines and aldehydes. The interesting results obtained with the reactivity of **1** acting as an oxidant lead us to here present our results.

RESULTS AND DISCUSSION

Whereas the 1,2-dimethyl-3-ethyl imidazolium iodide (**1b**) was easily prepared through *N*-ethylation of 1,2-dimethylimidazole with ethyl iodide[28,29] the analogue (**1a**) was purchase from a commercial agent. From our previously experience with aryl-*N*-sulfonylimines (**2**),[30] we decide to test the reactivity of 1,2-dimethyl-3-ethyl imidazolium chloride (**1a**) with **2**. As expected, the 2-substituted methyl group is quite reactive in the presence of a base due to the strong electron withdrawing effect of the adjacent positively charged nitrogen atom on the imidazole ring. Our main purpose was a methylene group transfer from **1a** to the aryl-*N*-sulfonylimines (**2**) with concomitant by elimination of an imidazolium-based NHC to attain the aziridine ring (Scheme 1). However, it was only observed the formation of the zwiterrionic adduct, arylethyl-2-imidazolium-1-tosylamides (**3**) with low to moderate yields. The low yields observed for compounds **3c** and **3d** could be due to the high instability of the aryl-*N*-sulfonylimines **2c** and **2d**. Titration of **3b** with silver nitrate shows that the compound is present as an internal salt since the value of chloride detected is equal to the blank assay of MiliQ™ water. Although the few reports in literature concerning the reaction of 2-substituted imidazolium salts with electrophiles[22,31] this is the first report on the reaction with imines. Due to the high polar nature of the zwitterionic species **3**, its isolation could only be achieved through reverse phase chromatography using a water: methanol gradient. All the attempts using either acidic or basic conditions to transform **3** into the corresponding aziridine ring were unsuccessful. The NMR data including bidimensional experiments attest the proposed structure as also the mass spectra analysis. The rapid H/D exchange of the 2-methylene group could be observed on the NMR and MS spectra (see supporting information) with the corresponding isotopic pattern present. The ability of 2-substituted imidazolium ILs to endeavor in this H/D exchanged was very recently reported by others.[32] The compounds obtained were found to be quite stable and no special care was required with them. As these compound present himself as oils at room temperature, it is possible to infer that these adducts may have characteristics similar to ionic liquids. Studies are underway. Next we turn our attention to the reaction with aldehydes. From what we were able to observe and isolate in the reaction medium, here again, no methylene group transfer from the imidazolium salt to the aldehyde occur. We start our study with the reaction of 1,2-dimethyl-3-ethylimidazolium iodide (**1b**) with benzaldehyde (**4a**). Our first attempt with Cs_2CO_3 as base in dry THF allowed us to obtain the benzoic acid in 50% yield after 24h (Table 1, entry 1a). The work up of the reaction was performed the following way: the reaction mixture was evaporated to dryness and the residue washed out with ethyl ether to remove unreacted benzaldehyde and/or other products formed. To the residue was added water and after acidification with HCl 1M the mixture was extracted with CH_2Cl_2, dried with sodium sulfate and evaporated to dryness to leave pure benzoic acid.



	R	Yield (%)
3a	Ph	66
3b	p-$MeOC_6H_4$	71
3c	p-BrC_6H_4	22
3d	p-$NO_2C_6H_4$	33

Scheme 1. Reaction of 1,2-dimethyl-3-ethyl imidazolium chloride (**1a**) with aryl-*N*-sulfonylimines (**2**) to attain arylethyl-2-imidazolium-1-tosylamides (**3**).

The aqueous phase was also evaporated and analyzed. The products profile changed according to the reaction time. After 24 h no benzaldehyde was recovered, the benzoic acid was obtained as mention above in 50% and the aqueous phase shows only the adduct **6** in nearly 50% yield taking into account the recovered benzaldehyde and benzoic acid (Table 1, entry 1a). Although the reaction was performed with equimolar amounts of benzaldehyde and imidazolium salt (**1b**) no traces of the later one could be observed after 24h. Using the same procedure the outcome of the reaction was analyzed after 48, 72 and 192h in independent reactions. The results are presented in table 1 (entries 1a to 1d). Repeatedly, the yield of formation of benzoic acid decreased in the following days but attain the highest yield (82%) after 192h with the benzaldehyde being identified in vestigial amounts. We proposed that the benzaldehyde appeared from the reverse reaction of formation of **6** to the starting materials. The phenylvinyl imidazolium iodide **7a** results from water elimination of **6**. Analogs of the arylvinyl imidazolium salts **7** were also observed by others on reaction of imidazolium salts with aldehydes.[22,23] Compounds **1b**, **6** and **7** were identified by ^{1}H NMR and HPLC-ESI analysis of the crude of the aqueous polar fractions (see supporting information). In order to clarify the outcome of this reaction, the experimental conditions were reproduced in an NMR tube. To the initial mixture of 1,2-dimethyl-3-ethylimidazolium iodide (**1b**) and base in CD_3OD, 1.0 equivalents of benzaldehyde were added. Diffusion-ordered spectroscopy (DOSY) allows the separation of the NMR signals of different species according to their diffusion coefficients.[33,34] In figure 1 it´s possible to observe the DOSY spectra of the initial mixture (I) and after benzaldehyde addition (II). Before benzaldehyde (I) addition only the imidazolium and methanol diffusion pattern were distinguished, whereas after benzaldehyde addition, the immediate formation of adduct **6**, takes place as can be seen by the respective diffusion coefficient with ^{1}H signals. This adduct presents chemical shifts between and 7.26-7.42 ppm, as well as the imidazolium side chains (figure 1.II). The reaction was followed throughout 24 h and it was possible to identify in the ^{1}H, ^{13}C HMBC NMR spectra correlations between the benzylic signal at 5.2 ppm and C2 (144 ppm) from the imidazolium, as well as with the aromatic carbon from benzaldehyde addition (125 ppm) (see SI).

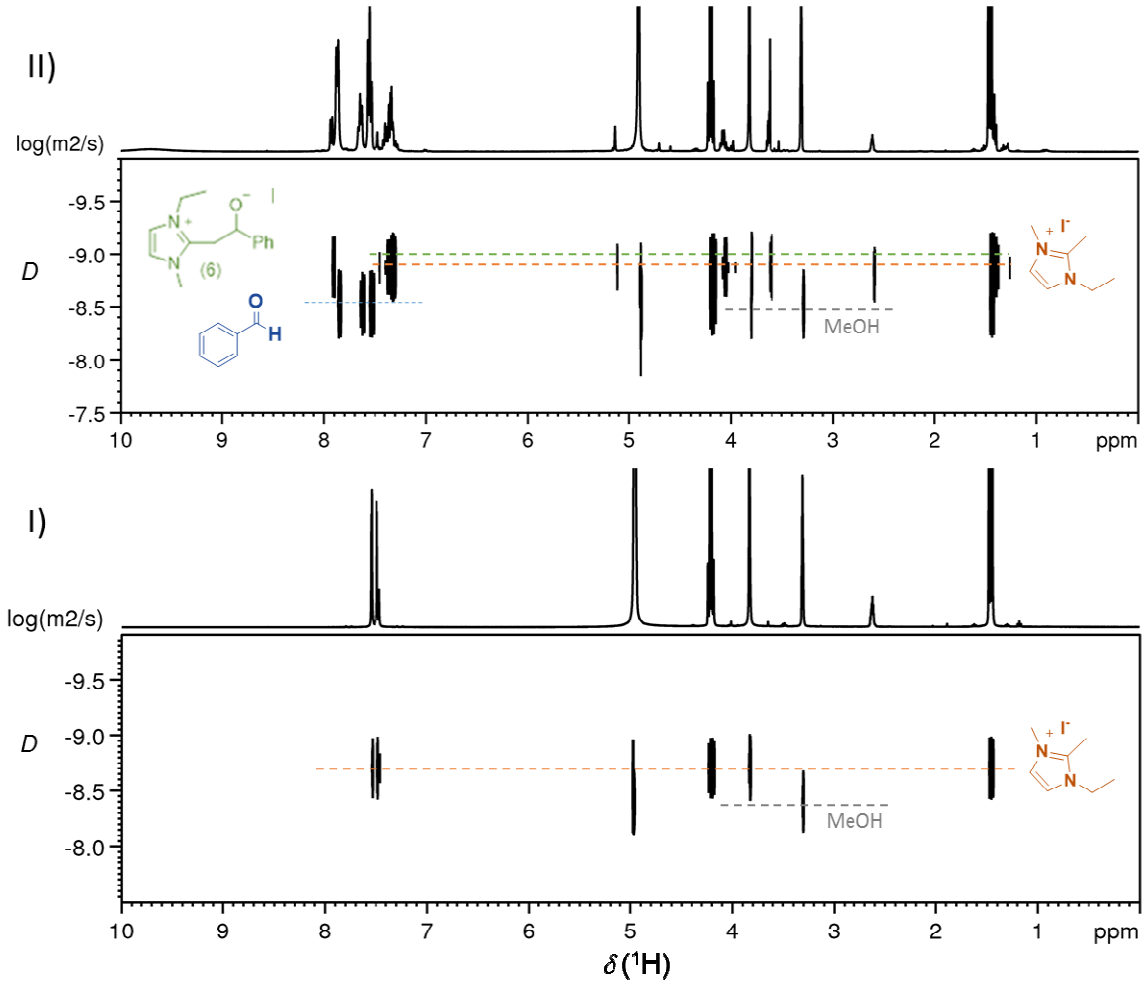
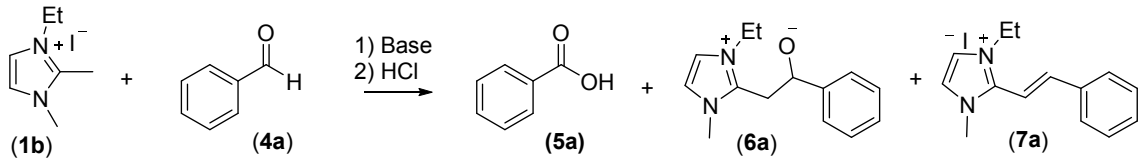


Figure 1. ^{1}H DOSY spectra (400 MHz, CD_3OD) of 1,2-dimethyl-3-ethylimidazolium iodide (**1b**) and base mixture in CD_3OD (I), and immediately after the addition of 1.0 equivalents of benzaldehyde (II) acquired with bipolar LED pulse sequence

Formation of benzoic acid in this conditions is residual and not observed on the NMR spectra after 24h. Also observed in this spectra is a correlation between a signal at 7.95 ppm and a carbonyl group at 174 ppm which is compatible with another intermediate species (see mechanism further ahead). The reaction was tested with other solvents and the formation of benzoic acid was observed to be residual in methylene chloride (4%) and very low in methanol (9%) and water (22%) (Table 1, entries 7-9). In the absence of **1b**, benzoic acid was obtained in vestigial amounts so that we can´t exclude an ordinary oxidation reaction of benzaldehyde % (Table 1, entries 17). No benzyl alcohol has ever been observed and as so, the Cannizarro reaction was not involved in the oxidation process. Since the best results were observed in THF, other bases were tested. The yields are reported in Table 1. Using NaH as base (Table 1, entries 2a to 2d) the yield of benzoic acid range from 42 to 47%. With NaOH (Table 1, entries 3a to 3d) a very good yield was obtained after 192h while with Na_2CO_3 (Table 1, entries 4a to 4d) and K_2CO_3 (Table 1, entries 5a to 5d) only moderate yields were observed. Using an organic base as NEt_3 the highest yield was obtained after 24h (85%) although decreased substantially in the assays preformed with more time of reaction (Table 1, entries 6a to 6d). The reaction was extended to other aromatic, heteroaromatic and aliphatic aldehydes. With aliphatic aldehydes as phenylacetic aldehyde the expected aldol condensation product was formed (5%) together with recovered aldehyde. With *p*-cyanobenzaldehyde (**4b**) the respective acid **5b** was obtained in 59 and 44% yield after 24h and 192h respectively (Table 2, entry 1a and 1b). It was also identified the elimination product **7b** in 14% after 192h (Table 2, entry 1b). As for the *p*-bromobenzaldehyde (**4c**), the amount of *p*-bromobenzoic acid **5c** found was 27% (Table 2 entry 2a). After 192h it was obtained the adduct **7c** in 36% yield (Table 2, entry 2b). As for *p*-metoxybenzaldehyde (**4d**) the formation of the corresponding carboxylic acid (**5d**) was obtained in 13 and 43% yield after 24h and 192h respectively (Table 2, entry 3a and 3b).

Table 1. Conditions for the reaction of 1,2-dimethyl-3-ethyl imidazolium iodide mediated oxidation with benzaldehyde

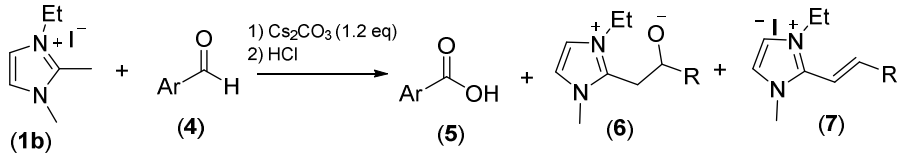


Entry	(**4a**), 1eq	Base (1.2 eq)	Solvent	Reaction time (h)	(**5a**) η %	(**7a**) η %
1a	**4a**	Cs_2CO_3	THF	24	50	-
1b	**4a**	Cs_2CO_3	THF	48	17	-
1c	**4a**	Cs_2CO_3	THF	72	23	-
1d	**4a**	Cs_2CO_3	THF	192	82	[i]
2a	**4a**	NaH	THF	24	42	-
2b	**4a**	NaH	THF	48	43	-
2c	**4a**	NaH	THF	72	47	-
2d	**4a**	NaH	THF	192	42	-
3a	**4a**	NaOH	THF	24	40	-
3b	**4a**	NaOH	THF	48	19	-
3c	**4a**	NaOH	THF	72	37	-
3d	**4a**	NaOH	THF	192	81	-
4a	**4a**	Na_2CO_3	THF	24	30	-
4b	**4a**	Na_2CO_3	THF	48	21	-
4c	**4a**	Na_2CO_3	THF	72	12	-
4d	**4a**	Na_2CO_3	THF	192	24	-
5a	**4a**	K_2CO_3	THF	24	43	-
5b	**4a**	K_2CO_3	THF	48	20	-
5c	**4a**	K_2CO_3	THF	72	21	-
5d	**4a**	K_2CO_3	THF	192	35	-
6a	**4a**	NEt_3	THF	24	85	-
6b	**4a**	NEt_3	THF	48	5	-
6c	**4a**	NEt_3	THF	72	6	-
6d	**4a**	NEt_3	THF	192	47	-
7	**4a**	Cs_2CO_3	CH_2Cl_2	192	4	-
8	**4a**	Cs_2CO_3	MeOH	192	9	-
9	**4a**	Cs_2CO_3	H_2O	192	22	-
10	**4a**	Cs_2CO_3	THF	192	20[iii]	
11	**4a**	NaH	THF	192	20[iii]	
12	**4a**	NaH	THF / O_2	24	93	
13	**4a**	Cs_2CO_3	THF degassed	24	40	
14	**4a**	Cs_2CO_3	THF / O_2	24	70	
15	**4a**	Cs_2CO_3	THF	24	57[iv]	
16	**4a**	Cs_2CO_3	THF	192	72[iv]	
17	**4a**	Cs_2CO_3	THF	24	-[v]	

[i] identified by NMR in the crude mixture of the aqueous phase; [ii] identified in the 24h reaction, [iii] general procedure with 20 mol% of **1b**; [iv] general procedure with 2 equivalents of benzaldehyde; [v] without **1b**, vestigial amounts of **5a**.

Mainly it was recovered the aldehyde **4d** and in the crude of the aqueous phase the compound **6d** , was identified by ^{1}H NMR which is not a surprise taking into consideration the formation of a fully conjugated system assisted by the methoxyl substituent (Table 2, entry 3b). With *p*-nitrobenzaldehyde (**4e**) the corresponding oxidation product (**5e**) was obtained in yields ranging from 21 to 48% (Table 2, entry 4a and 4b) as also the elimination adduct **7e**. As for the *m*-hydroxybenzaldehyde (**4f**), no carboxylic acid was observed (Table 2, entries 5), instead, a 1:1 mixture of **6f** and starting material **1b** was identified. The *m*-hydroxybenzaldehyde (**4f**) was recovered in 50% yield. As for the *m*-chlorobenzaldehyde (**4g**) the formation of the corresponding carboxylic acid **5g** was obtained in 87% yield (Table 2, entries 6). The elimination compound **7g** was also identified but on the 24h reaction (Table 2, entries 6). With heteroaromatic aldehydes as 2-furaldehyde (**4h**) the corresponding carboxylic acid (**5h**) was obtained in 46 and 52% yield after 24h and 192h respectively (Table 2, entry 7a and 7b). The elimination compound **7h** was also identified. In the presence of a catalytic amount (20%) of **1b** the formation of benzoic acid never exceed the 20% either with Cs_2CO_3 or NaH as base, which point to a stoichiometric role for this reagent (Table 1, entry 10 and 11). When the reaction was conducted with a degassed solution (free of oxygen) only a slightly reduction on the yield from 50 to 40% was observed (Table 1, entry 1a *vs* 13).

Table 2. 1,2-Dimethyl-3-ethyl imidazolium iodide mediated oxidation of aromatic aldehydes



4b, Ar = *p*-NCC_6H_4 **4d**, Ar = *p*-$MeOC_6H_4$ **4f**, Ar = *m*-HOC_6H_4
4c, Ar = *p*-BrC_6H_4 **4e**, Ar = *p*-$NO_2C_6H_4$ **4g**, Ar = *m*-ClC_6H_4
4h, Ar = 2-furan

Entry	(4), 1eq	Solvent	Reaction time (h)	(5) η %	(7) η %
1a	**4b**	THF	24	59	-
1b	**4b**	THF	192	44	14
2a	**4c**	THF	24	27	-
2b	**4c**	THF	192	-	36
3a	**4d**	THF	24	13	
3b	**4d**	THF	192	43	
4a	**4e**	THF	24	21	27
4b	**4e**	THF	192	48	3
5	**4f**	THF	192	-	
6	**4g**	THF	192	87	11[i)]
7a	**4h**	THF	24	46	14
7b	**4h**	THF	192	52	8
8	**4c**	THF/O_2	24	37.5	18
9	**4d**	THF/O_2	24	12	
10	**4e**	THF/O_2	24	27	27

[i)] identified in the 24h reaction.

In the presence of oxygen, the yield of the reaction after 24h increase from 50 to 70% with Cs_2CO_3 as base and from 42 to 93% with NaH (Table 1, entries 1a *vs* 14 and 2a *vs* 12). With other aryl aldehydes a possible role of O_2 was not as conclusive nor did it support the results with benzaldehyde (Table 2 entries 2a vs 8, 3a vs 9 and 4a vs 10). The yields were more or less in the same order of magnitude when no O_2 was present. To elucidate the mechanism, the reaction was performed in the presence of 2 equivalents of benzaldehyde. The benzoic acid was obtained in 57% and in 72% yield after 24h and 192h of reaction respectively (Table 1, entry 15 and 16). These results are in the same order of magnitude as those with a 1:1 proportion of reagents (Table 1, entry 1a and 1d). As expected, in these conditions with two equivalents, 50% of benzaldehyde was recovered after 24h. Although the formation of benzoic acid was consistently observed though with different outcome, it wasn't possible to see such a reproducibility with other minor products isolated from the organic phase. It was possible in some instances to proceed to the isolation and characterization of some of these compounds whose structures were postulated by comparison with spectroscopic data in the literature while others were identified by GC-MS and evaluation with data bases. Those compounds that we were able to identify (**8-12**)[35-39] are presented below in Figure 2. Our proposed mechanism is presented in Scheme 2. Taking as example the benzaldehyde we proposed the formation of the intermediate (**6**) based on NMR experimental and HPLC-ESI analysis as mentioned above. Every attempt to purify this intermediate by reverse phase column chromatography lead to the aryl-vinyl imidazolium (**7**) as also the imidazolium (**1b**). Since after 24h only the benzoic acid (**5a**) and the intermediate **6** were identified points us to establish an oxidative role for **1b** that lead to the formation of the acyl derivative (**14,** corresponding signals observed on the diffusion experiments – Figure 1) and the reduce form of **1b**, the specie (**15**).

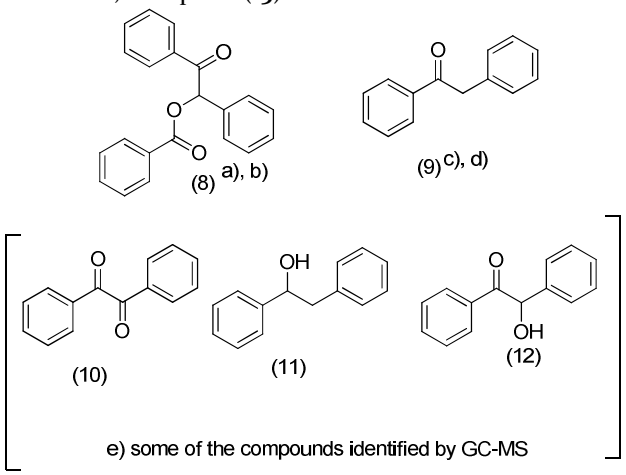
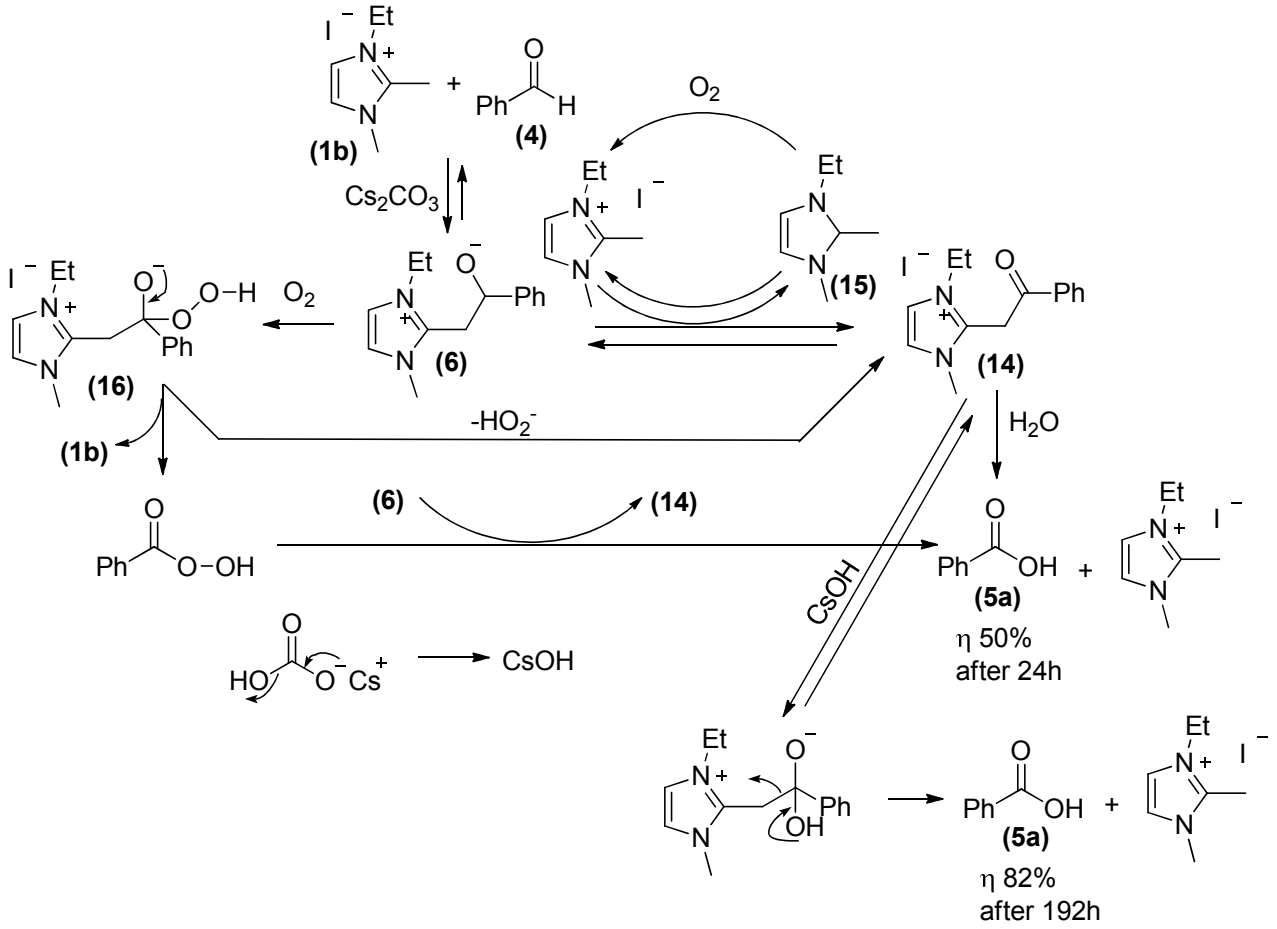


Figure 2. Minor compounds isolated on the 1,2-dimethyl-3-ethyl imidazolium iodide mediated oxidation of benzaldehyde. Unless otherwise mention the base reaction conditions were: **1b** (1.0 equiv.), benzaldehyde (1.0 equiv.), Cs_2CO_3 (1.2 equiv.), r.t., THF; [a)]base reaction conditions 12 days; [b)]$CDCl_3$ 15 days; [c)]24h; [d)]r.t., CD_3OD; e) THF-d_8.

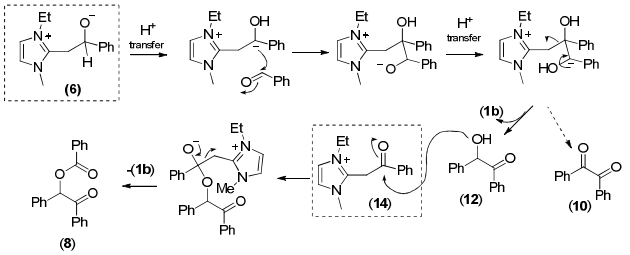


Scheme 2. Proposed mechanism for the oxidation reaction promoted by 1,2-dimethyl-3-ethyl imidazolium iodide (**1b**).

This postulated intermediate **15** must be quite unstable since whenever in the mixture of an organic fraction, were identified in the NMR signals that could correspond to **15**, its isolation was impossible. Nevertheless in one case it was possible to obtain an organic phase (from the ethyl ether extraction) which analysis by NMR presented signals at higher filed than the imidazolium ring and could be attributed to the structure of **15**. This was further confirmed by the CG-MS with a molecular ion of m/z of 126 (see supporting information). As expected after 48h the NMR spectrum showed an intractable mixture which was also confirmed by the GC-MS with the absence of the peak corresponding for the previously identified and postulated compound **15**. The nucleophilic attack of the hydroxide ion or water onto **14** maybe the responsible for the benzoic acid formation. The conversion of **6** to **14** is an equilibrium as also from **6** to **1b** since in the following days the yield of benzoic acid decrease and **1b** was identified. The highest yield obtained for benzoic acid after 1 week (192h) can in our view be justified by the nucleophilic attack of the hydroxide ion as presented in scheme. When the reaction is conducted in the presence of molecular oxygen the yield is 70% after 24h which is the result of the shift of the equilibrium of **6** / **14** to the last one. As for the good yield when NEt_3 is used as base we can postulate an attack of NEt_3 to **14**, thus shifting the equilibrium **6** / **14** to the right, that upon **1b** elimination gives a very reactive and highly electrophilic acylium cation intermediate that on work up with water give the benzoic acid. The low yields obtained in the following days (Table 1 entry 7b to 7c) should result from the instability if this acylium cation intermediate in the reaction medium. Our proposed mechanism involving as key step a redox reaction between the species **6** and **14** was reinforced by the result obtained when the reaction was run in the presence of oxygen (table 1, entry 21) which could favor this transition step. Even so, we can't exclude that the intermediate **6** reacts with dioxygen to form the peroxy-species (**16**) which has already been postulated by others when NHC is involved[40] although radical species reported by others[41] cannot be excluded. We have also previously detected radical species in the redox reaction involving aromatic nitroso compounds and thiazolium salts.[42] The decomposition of this unstable compound as presented in scheme 2 may be happening in two ways leading to two different compounds. It can decompose to form the activated ketone **14** by abstraction of HO_2^- or in a second possible pathway the formation of the peroxy acid by abstraction of **1b**. This peroxy acid is a

strong oxidant agent itself and thereby able to shift the equilibrium of **6** / **14** to the right under formation of benzoic acid and **14**. Here we can't roll out the possible reaction of the peroxy acid with the aldehyde to give benzoic acid. To support this equilibrium, the reaction of crude **6** with benzaldehyde in the presence of cesium carbonate allowed benzoic acid to be obtained in 44% yield after 72h which means that **6** is in the reaction conditions, in equilibrium with **1b**. The formation of the acyl intermediate (**14**) was postulated in similarly to the NHC-based azolium salts which catalyze the oxidation of unactivated aldehydes to esters or acids.[40] The authors reported the reaction proceeding through a transient activated alcohol which is then converted to the NHC-acyl intermediate by manganese(IV) oxidation[43] or by oxygen.[40,44]

The benzoin condensation product **12** and the derivatives **10** and **8** can be justified by the mechanism presented in scheme 3 where **1b** has a catalytic role similar to that reported for NHC.[45] Here again, the formation of **8** may reinforce the postulated intermediate **14** as represented in scheme 3. The fact that we have observed by HPLC-ESI a compound whose m/z of 217 u.m.a. may correspond to the Breslow intermediate (see supporting information) does not allow us to exclude a possible role of this intermediate in the formation of the minor benzoin condensation product **12**.



Scheme 3. Proposed mechanism for the formation of benzaldehyde oxidation products.

CONCLUSIONS

While the use of ILs may offer superior physical properties relative to more traditional and volatile aprotic solvents, their potential reactivity must not be overlooked. Here we have demonstrated that 2-methyl imidazolium salts may in the presence of a base react with electrodeficient species such as aryl-*N*-sulfonylimines and aldehydes. On reaction with imines, arylethyl-2-imidazolium-1-tosylamides (**3**) are formed with moderate to good yields. The reaction with aldehydes had an unexpected result with the oxidation to the corresponding carboxylic acid taking place. Although the conversion of aldehydes to carboxylic acids can happen rather spontaneously, efficient methods to achieve this transformation without hazardous oxidants or harmful solvents are still scarce. Here we have demonstrated that 2-methyl imidazolium salts can promote the oxidation of aromatic aldehydes in the presence of a mild base, in good to excellent yields. A detailed mechanistic study was carried out to provide insights to this unexpected reactivity.

EXPERIMENTAL SECTION

General methods and materials: All the reagents and solvents were obtained commercially and these were used without further purification. The solvents used were dried using current laboratory techniques. Thin layer chromatography (t.l.c.) was carried out on aluminium backed Kieselgel 60 F254 silica gel plates (Merck). Plates were visualized either by UV light (254 and/or 366nm). Preparative layer chromatography (PLC) was performed on Merck Kieselgel GF 254 silica gel plates with a thickness of 0.5 mm or 1 mm. Column chromatography were carried out silica gel Kieselgel 60 (Merck), 70 - 230 mesh particle size as stationary phase, in normal phase chromatography or Li-Chroprep RP-18 (Merck) silica, with a particle size of 40-63 µm as the stationary phase in reverse phase chromatography. The reverse phase columns were eluted using water-methanol mixtures in order to decrease the polarity of the mixture (from 0% methanol, 10%, 20% and successively up to 100% methanol). Ultraviolet spectroscopy (UV) was recorded on a Thermo Corporation spectrophotometer, Helius γ, on quartz cell support. Absorption spectrum measurements were made in the range of 190 to 320 nm. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker ARX400 at 400 and 100 MHz, respectively. Mass spectrum (MALDI-TOF) were run on a Voyager-DE ™ PRO Workstation mass spectrometer, in positive reflector mode (unless otherwise noted), with 2,5-dihydroxybenzoic acid (DHB) as matrix. HPLC-MS-ESI was acquired on a Agilent 1200 Series LC with quaternary pump, ALS, TCC, DAD and Agilent G6130B LC/MSD with API-ES source. HRMS was acquired on a G6545A Q-TOF with Agilent JetStream technology source (ESI) LC is 1290 Infinity II LC system (UHPLC) with High Speed Pump, Multisampler and Multicolumn Thermostat. Chromatographic conditions (see supporting information). Mass spectra (MS) using the EI-TOF technique were obtained from Unidade de Masas e Proteómica, the University of Santiago de Compostela, Spain. Infrared (IR) spectroscopy was performed on a Perkin Elmer spectrophotometer, Spectrum 1000FT-IR, in support of KBr pellets. Melting points (m.p.) (uncorrected) were measured on the Reichert Thermovar. Gas chromatography-mass spectrometry (GC-MS) was done on an Agilent 6890N chromatograph coupled to a Thermo DSQ electronic impact detector (EI). Chromatographic conditions: VF5-ms column, 0.25mm ID, 0.25µm film; 250 ° C-injector temperature; Temperature program: 50ºC (1min), 10ºC / min up to 300ºC; Split ratio 1:20; 1mL / min of drag gas flow; 1µL of sample injected; 5min of solvent delay. DIONEX ion chromatography was acquired on a DIONEX ion chromatograph, ICS3000, with IonPack® AS15 4x250mm column, coupled with pre-column. The analysis was done at 30 °C with 38 mM NaOH.

Synthesis of the 3-ethyl-1,2-dimethyl imidazolium iodide (1b): In a flask equipped with a magnetic stir bar and a reflux condenser, equimolar amounts of 1,2-dimethylimidazole and iodoethane (11 x 10^{-3} mol) were added in 20 mL of dry THF. The mixture was stirred and refluxed under a nitrogen atmosphere for 15h. The solid obtained was washed with dry ethyl ether, dissolved in

methanol and recrystallized by addition of dry ethyl ether in an ice-salt bath (-20 °C). The white solid obtained was filtered and dried under vacuum. 74.6 %; UV-Vis λ_{max} 223,50 nm; ^{1}H NMR (D_2O, 400 MHz) δ: 7.38 (d, *J* = 2.0 Hz, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.60 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (D_2O, 100 MHz): δ 143.9 (C), 122.1 (CH), 121.7 (C), 119.9 (CH), 43.3 (CH_2), 34.5 (CH_3), 14.1 (CH_3), 8.7 (CH_3) ppm; IR υ_{max} (cm^{-1}): 3095 (aromatic C-H), 1586 (C=N). HRMS-CI(+) calcd for $C_7H_{13}N_2$ $[M]^+$ 125.1073 found 125.1083.

General procedure for the synthesis of aryl-N-sulfonylimines (2):[46] In a round bottom flask equipped with a magnetic stirrer and reflux condenser, equimolar amounts (3 x 10^{-3} mol) of *p*-toluenesulfonamide and the corresponding aldehyde, 0.05 g of Amberlyst 15 and about 0.5 g of the Molecular Sieves 4Å in dry toluene. The reaction mixture was stirred and heated under reflux under a nitrogen atmosphere until the total consumption of the aldehyde was verified. This monitoring was by TLC, in an eluent of hexane: ethyl acetate (6: 4). Subsequently, the mixture was removed from the heat and decanted into a new flask, thereby removing the Molecular Sieves. The mixture was then allowed to cool to room temperature to give precipitation of the imine. To assist precipitation, petroleum ether was added, and the sample was filtered and dried in vacuum.

***N*-Benzylidene-4-methylbenzenesulfonamide (2a):** From benzaldehyde (0.318g) and *p*-toluenesulfonamide (0,513g) according to the general procedure, compound **2a** was obtained as a white solid (0,358g, 46%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.03 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.2 (HC=N), 144.6 (C), 139.1 (C), 134.5 (C), 132.4 (CH), 129.8 (2xCH), 129.2 (2xCH), 128.1 (2xCH), 126.4 (2xCH), 21.5 (CH_3) ppm.

***N*-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide (2b):** From 4-methoxybenzaldehyde (0.408g) and *p*-toluenesulfonamide (0,513g) according to the general procedure, compound **2b** was obtained as a white solid (0.443,51%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.94 (s, 1H), 7.89-7.89 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.3 (HC=N), 164.7 (C), 144.3 (C), 139.1 (C'), 129.7 (2xCH), 127.9 (2xCH), 126.5 (C), 125.2 (2xCH), 114.3 (2xCH), 55.6 (OMe), 21.5 (CH_3) ppm.

***N*-(4-Bromobenzylidene)-4-methylbenzenesulfonamide (2c):** From 4-bromobenzaldehyde (0.555g) and *p*-toluenesulfonamide (0,513g) according to the general procedure, compound **2c** was obtained as a white solid (0.517g, 51%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.98 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H) ppm.

4-Methyl-*N*-(4-nitrobenzylidene)benzenesulfonamide (2d): From 4-bromobenzaldehyde (0.453g) and *p*-toluenesulfonamide (0,513g) according to the general procedure, compound **2d** was obtained as a yellow solid (0.420, 46%); ^{1}H NMR ($CDCl_3$, 400MHz) δ: 9.11 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H) ppm.

General procedure for the synthesis of arylethyl-2-imidazolium-1-tosylamides (3): In a round bottom flask equipped with magnetic stir bar was added 1,2-dimethyl-3-ethylimidazolium chloride (**1a**) (0.0257 g, 0.16 x 10^{-3} mol) and cesium carbonate (1.2 equiv.) in dry THF. The reaction mixture was stirred at room temperature under nitrogen for 1 h. Subsequently, under a nitrogen atmosphere, the corresponding imine (**2a-d**) (see supporting information) (1 equiv.) was added, and the reaction proceeded under the same conditions until consumption of the imine (approximately 1-2 h). The reaction was followed by t.l.c., eluting with a mixture of hexane: ethyl acetate (8: 2). The reaction mixture was evaporated to dryness, and the crude product was washed with ethyl ether. The mixture was diluted in water (either dissolved in acetone and adsorbed onto celite) and applied to a reverse phase column (RP-18) for purification. Elution was done using water-methanol mixtures, in order to decrease the polarity of the blend (from 0% methanol, 10%, 20% to 100% methanol - 20 ml of each mixture). The collected fractions were analyzed by UV-Vis spectroscopy, with scanning between 190 and 320 nm. The fractions exhibiting identical absorption maxima were pooled and evaporated to dryness to give the product **3a-d**.

(2-(3-Ethyl-1-methyl-1*H*-imidazol-3-ium-2-yl)-1-phenylethyl)(tosyl)amide (3a): From compound **1a** (0.0257g) and **2a** (0,041 g) according to the general procedure, compound **3a** was obtained as a white oil (0,040g, 66%); UV-Vis λ_{max} 223 nm; ^{1}H NMR (MeOD, 400 MHz) δ: 7.45 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.18 – 7.13 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.44-4.41 (m, 1H), 4.03 – 3.96 (m, 2H), 3.58 (s, 3H), 3.37 (dd, *J* = 15.2 and 8.4 Hz, 1H), 3.23 (dd, *J* = 15.2 and 6.0 Hz, 1H), 2.25 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H') ppm; ^{13}C NMR (MeOD, 100 MHz) δ: 145.3 (C), 143.1 (C), 142.7 (C), 142.3 (C), 130.1 (2xCH), 129.6 (2xCH), 128.6 (CH), 127.7 (2xCH), 127.6 (2xCH), 124.2 (CH), 121.5 (CH), 58.7 (CH), 44.4 (CH_2), 35.7 (CH_3), 34.3 (CH_2), 21.3 (CH_3), 15.2 (CH_3) ppm; IR υ_{max} (cm^{-1}): 3053 (aromatic C-H), 1329 (symmetric stretching SO_2), 1265 (C-N), 1158 (symmetric stretching SO_2); MS (MALDI-TOF) ($[M+H]^+$) m/z: $C_{21}H_{26}N_3O_2S$ 384.1703; $C_{21}H_{25}DN_3O_2S$ 385.1660; $C_{21}H_{24}D_2N_3O_2S$ 386.1564. FIA-HRMS calcd for $C_{21}H_{26}N_3O_2S$ $[M+H]^+$ 384.17457 found 384.17444.

(2-(3-Ethyl-1-methyl-1H-imidazol-3-ium-2-yl)-1-(4-methoxyphenyl)ethyl)(tosyl)amide (3b): From compound **1a** (0.0257g) and **2b** (0,047 g) according to the general procedure, compound **3a** was obtained as a colorless oil (0.047g, 71%); UV-Vis λ_{max} 227 nm; ^{1}H NMR (MeOD, 400 MHz) δ: 7.44 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* =2.0 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.34 (t, *J* = 7.2 Hz, 1H), 4.03-3.99 (m, 2H), 3.69 (s, 3H), 3.56 (s, 3H), 3.28 (dd, *J* = 15.2 and 8.0 Hz, 1H), 3.14 (dd, *J* = 15.0 and 6.4 Hz, 1H), 2.26 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (MeOD, 100 MHz) δ: 160.1 (C), 146.1 (C), 144.4 (C), 141.2 (C), 137.4 (C), 129.7 (2xCH), 128.9 (2xCH), 127.5 (2xCH), 123.9 (CH), 121.2 (CH), 114.6 (2xCH), 59.0 (CH), 55.7 (O<u>Me</u>), 44.4 (CH_2), 35.6 (CH_3), 35.3 (CH_2), 21.3 (CH_3), 15.2 (CH_3) ppm; IR υ_{max} (cm^{-1}): 3053 (aromatic C-H), 1421 (methyl C-H), 1327 (symmetric stretching SO_2), 1265 (C-N), 1159 (symmetric stretching SO_2); MS (MALDI-TOF) ($[M+H]^+$) m/z: $C_{22}H_{28}N_3O_3S$ 414.1884; $C_{22}H_{27}DN_3O_3S$ 415.1979; $C_{22}H_{26}D_2N_3O_3S$ 416.2016; Determination of the chloride ion by ion chromatography

DIONEX (mg/Kg): 10.55. FIA-HRMS calcd for $C_{22}H_{27}DN_3O_3S$ $[M+H]^+$ 415.19141 found 415.19043.

(2-(3-Ethyl-1-methyl-1H-imidazol-3-ium-2-yl)-1-(4-bromophenyl)ethyl)(tosyl)amide (3c): From compound **1a** (0.0257g) and **2c** (0,054 g) according to the general procedure, compound **3a** was obtained as a colorless oil (0.016, 22%); UV-Vis λ_{max} 228 nm; ^{1}H NMR (MeOD, 400 MHz) δ: 7.45 (br s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.36-7.33 (m, 3H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.41 (dd, *J* = 9.2 and 5.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 3.33-3.29 (m, 1H), 3.19 (dd, *J* = 14.8 and 5,2 Hz, 1H), 2.30 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (MeOD, 100 MHz) δ: 146.0 (C), 144.7 (C), 144.3 (C), 141.4 (C), 132.3 (2xCH), 129.9 (2xCH), 129.8 (2xCH), 127.3 (2xCH), 124.0 (CH), 121.6 (C), 121.3 (CH), 59.0 (CH), 44.5 (CH_2), 35.8 (CH_3), 35,1 (CH_2), 21.2 (CH_3), 15.1 (CH_3) ppm; IR υ_{max} (cm^{-1}): 3131 (Aromatic C-H), 1331 (symmetric stretching SO_2), 1265 (C-N), 1148 (symmetric stretching SO_2), 739 (C-Br); MS (MALDI-TOF) ($[M+H]^+$) m/z: $C_{21}H_{25}{}^{79}BrN_3O_2S$ 462.0362; $C_{21}H_{25}{}^{81}BrN_3O_2S$ 464.0954 ; $C_{21}H_{24}D^{79}BrN_3O_2S$ 463.0571; $C_{21}H_{24}D^{81}BrN_3O_2S$ 465.0500; $C_{21}H_{23}D_2{}^{79}BrN_3O_2S$ 464.0954; $C_{21}H_{24}D_2{}^{81}BrN_3O_2S$ 466.0550. FIA-HRMS calcd for $C_{21}H_{22}D_2BrN_3O_2S$ $[M+H]^+$ 464.09764 found. 464.09509.

(2-(3-Ethyl-1-methyl-1H-imidazol-3-ium-2-yl)-1-(4-nitrophenyl)ethyl)(tosyl)amide (3d): From compound **1a** (0.0257g) and **2d** (0,049 g) according to the general procedure, compound **3a** was obtained as a yellow oil (0.023g, 33%); UV-VIS λ_{max} 220 and 269 nm; ^{1}H NMR (MeOD, 400 MHz) δ: 8.07 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.50 (m, 3H), 7.44-7.42 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.65 – 4.61 (m, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 3.70 – 3.57 (m, 1H), 3.41-3.36 (m, 1H), 2.31 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (MeOD, 100 MHz) δ: 151.8 (C), 148.4 (C), 145.4 (C), 143.1 (C), 142.3 (’), 130.0 (2xCH), 129.1 (2xCH), 127.4 (2xCH), 124.4 (2xCH), 124.3 (CH), 121.5 (CH), 58.5 (CH), 44.7 (CH_2), 35.9 (CH_3), 34.0 (CH_2), 21.2 (CH_3), 15.2 (CH_3) ppm; MS (MALDI-TOF) ($[M+H]^+$) m/z: $C_{21}H_{25}N_4O_4S$ 429.1864; $C_{21}H_{24}DN_4O_4S$ 430.1786; $C_{21}H_{23}D_2N_4O_4S$ 431.1869. FIA-HRMS calcd for $C_{21}H_{24}DN_4O_4S$ $[M+H]^+$ 430.16593 found. 430.16501.

General procedure for the synthesis of the compounds 5-12: In a round bottom flask equipped with magnetic stir bar was added 1,2-dimethyl-3-ethylimidazolium iodium (**1b**) (0,050 g, 0.20 x 10^{-3} mol) and cesium carbonate (1.2 equiv.) in dry THF. The flask was kept closed with a stopper and the reaction mixture was stirred at room temperature for 1 h and then the corresponding aldehyde (**4a-h**) (1 equiv) was added. Following and depending the reaction conditions used the following procedure were applied: i) To the reaction under oxygen atmosphere, we used a take-off and an oxygen balloon. Ii) For degassed reactions, they were conducted using degassed solvent and under a nitrogen atmosphere. In both cases and upon completion of the reaction, the mixture was evaporated under reduced pressure and the crude was washed with ethyl ether. The reaction mixture was diluted with water, acidified with HCl (1M) and extracted with dichloromethane. The organic phase was dried (Na_2SO_4) and filtered. The organic and aqueous phase were evaporated under reduced pressure to dryness to give the following products.

Benzoic acid (5a): Yields in accordance with table 1; white solid; m.p. 121-122 °C (Lit[47] 121-125 °C); ^{1}H NMR (CDCl3, 400 MHz) δ: 8.13 (br d, *J* = 8.4 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 171.7 (C=O), 133.9 (CH), 130.4 (2xCH), 129.4 (C), 128.6 (2xCH) ppm.

4-Cyanobenzoic acid (5b): From compound **1b** (0.050g) and **4b** (0,026 g) according to the general procedure, compound **5b** was obtained as a white solid (0.017g, 59% after 24h; 0.013g, 44% after 192h); m.p. 215.216 °C (Lit[47] 215-217 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.21 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H) ppm.

4-Bromobenzoic acid (5c): From compound **1b** (0.050g) and **4c** (0,037 g) according to the general procedure, compound **5c** was obtained as a yellow solid (0.011g, 27% after 24h); m.p. 248-249 °C (Lit[47] 248-250 °C); ^{1}H NMR (Acetone-d_6, 400 MHz) δ: 7.95 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.40 Hz, 2H) ppm; ^{13}C NMR (Acetone-d_6, 100 MHz) δ: 166.9 (C=O), 132.6 (2xCH), 132.3 (2xCH), 130.7 (C), 128.1 (C) ppm. MS (M^+) m/z: $C_7H_5{}^{79}BrO_2$ 199.9; $C_7H_5{}^{81}BrO_2$ 201.8.

4-Methoxybenzoic acid (5d): From compound **1b** (0.050g) and **4d** (0,027 g) according to the general procedure, compound **5d** was obtained as a yellow solid (0.004g, 13% after 24h; 0.013g, 43% after 192h); m.p. 181-182 °C (Lit[47] 180-182 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.06 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H) ppm.

4-Nitrobenzoic acid (5e): From compound **1b** (0.050g) and **4e** (0,030 g) according to the general procedure, compound **5e** was obtained as a yellow solid (0.007g, 21% after 24h; 0.016g, 48% after 192h); m.p. 232-233 °C (Lit[47] 232-234 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.32 (d, *J* = 8.4 Hz, 2H), 8.27 (d, *J* = 8.8 Hz, 2H) ppm.

3-Chlorobenzoic acid (5g): From compound **1b** (0.050g) and **4g** (0,028 g) according to the general procedure, compound **5g** was obtained as a white solid (0.027g, 87% after 192h); m.p. 155-157 °C (Lit[48,49] 154-158 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.32 (br s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz) ppm.

Furan-2-carboxylic acid (5h): From compound **1b** (0.050g) and **4h** (0,019 g) according to the general procedure, compound **5h** was obtained as a beige solid (0.010g, 46% after 24h; 0.012g, 52% after 192h); m.p. 128-129 °C (Lit[50] 128-132 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.64 (br s, 1H), 7.31 (d, *J* = 3.2 Hz, 1H), 6.56 (br s, 1H) ppm; ^{13}C ($CDCl_3$, 100MHz) δ: 163.0 (C=O), 147.5 (CH), 143.9 (C), 120.2 (CH), 112.4 (CH) ppm.

3-Ethyl-2-(2-hydroxy-2-phenylethyl)-1-methyl-1H-imidazol-3-ium (6a): identified on the crude aqueous fraction. ^{1}H NMR (D_2O, 400 MHz) δ: 7.42-7.40 (m, 4H), 7.33-7.26 (m, 3H), 5.17 (t, *J* = 6.0 Hz, 1H), 3.94 (q, *J* = 7.6 Hz, 2H), 3.54 (s, 3H), 3.48 (t, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (D_2O, 100 MHz) δ: 142.8 (C), 141.0 (C), 129.0 (2xCH), 128.7 (CH), 125.5 (2xCH), 123.1 (CH), 120.4 (CH), 71.0 (CH), 43.3 (CH_2), 34.8 (CH_3), 32.3 (CH_2), 14.1 (CH_3) ppm.

3-Ethyl-2-(2-hydroxy-2-(4-methoxyphenyl)ethyl)-1-methyl-1H-imidazol-3-ium (6d): identified on the crude aqueous fraction. ^{1}H NMR (D_2O, 400 MHz) δ: 7.47 (d, *J* = 2.0 Hz, 1H), 7.33 (br s, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.23 (t, *J* = 6.4 Hz, 1H), 4.054 (q, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 3.67 (s, 3H), 3.61-3.49 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm.

3-Ethyl-2-(2-hydroxy-2-(3-hydroxyphenyl)ethyl)-1-methyl-1H-imidazol-3-ium (6f): identified on the crude aqueous fraction. ^{1}H NMR (D_2O, 400 MHz) δ: 7.49 (br s,

1H), 7.39-7.32 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.80 (brs, 1H), 5.19 (t, *J* = 6.4 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.62 (s, 3H), 3.53 (t, *J* = 6.0 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H) ppm.

3-Ethyl-1-methyl-2-styryl-1H-imidazol-3-ium (7a): identified on the crude aqueous fraction. ^{1}H NMR (D_2O, 400 MHz) δ: 7.73-7.72 (m, 2H), 7.52-7.49 (m, 4H), 7.37 (br s, 1H), 7.30 (br s, 1H), 7.04 (d, *J* = 16.8 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H) ppm.

2-(4-Cyanostyryl)-3-ethyl-1-methyl-1H-imidazol-3-ium (7b): 14% calculated by NMR; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.94 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.69 (br s, 1H), 7.59 (br s, 1H), 7.54 (d, *J* = 16.4 Hz, 1H), 7.41 (d, *J* = 16.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 4.12 (s, 3H), 1.57 (t, *J* = 7.2 Hz, 3H) ppm.

(2-(4-Bromostyryl)-3-ethyl-1-methyl-1H-imidazol-3-ium (7c): beige solid (0.030g, 36% after 192h); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.69-7.68 (m, 3H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 16.8 Hz, 1H), 7.20 (d, *J* = 16.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.04 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ: 143.5 (HC=CH), 142.1 (C), 132.7 (C), 132.3 (2xCH), 130.0 (2xCH), 125.3 (C), 124.7 (CH), 121.6 (CH), 107.9 (HC=CH), 45.0 (CH_2), 37.8 (CH_3), 15.6 (CH_3) ppm. HRMS-CI(+) calcd for $C_{14}H_{16}{}^{79}BrN_2$ $[M]^+$ 291.0491 found 291.0497.

3-Ethyl-1-methyl-2-(4-nitrostyryl)-1H-imidazol-3-ium (7e): 27 and 3% yield after 24h and 192h, calculated by NMR; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.28 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.62 (d, *J* = 16.8 Hz, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 16.8 Hz, 1H), 4.43 (q, *J* = 7.6 Hz, 2H), 4.14 (s, 3H), 1.61 (t, *J* = 7.2 Hz, 3H) ppm.

(2-(3-Chlorostyryl)-3-ethyl-1-methyl-1H-imidazol-3-ium (7g): beige solid (0.008g, 11% after 24h); ^{1}H NMR (MeOD, 400 MHz) δ: 7.85 (br s, 1H), 7.70-7.68 (m, 2H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.48-7.44 (m, 3H), 7.22 (d, *J* = 16.4 Hz, 2H), 3.97 (s, 3H), 1.52 (t, *J* = 7.2 Hz, 3H) ppm. 13C NMR (MeOD, 100 MHz) δ: 144.1 (CH). 143.5 (C), 137.8 (C), 136.2 (C), 131.7 (CH), 131.6 (CH), 128.7 (CH), 127.5 (CH), 125.2 (CH). 122.6 (CH), 109.9 (CH), 45.3 (CH_2), 36.9 (CH_3), 15.4 (CH_3). HRMS-CI(+) calcd for $C_{14}H_{16}{}^{35}ClN_2$ $[M]^+$ 247.0997 found 247.1006.

3-Ethyl-2-(2-(furan-2-yl)vinyl)-1-methyl-1H-imidazol-3-ium (7h): 14 and 8% yield after 24h and 192h, calculated by NMR; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.70 (d, *J* = 2.4 Hz, 1H), 7.63 (br s, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 3.6 Hz, 1H), 6.70 (d, *J* = 16.4 Hz, 1H), 6.51-6.50 (m, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.05 (s, 3H), 1.53 (t, *J* = 7.2 Hz, 3H) ppm.

2-Oxo-1,2-diphenylethyl benzoate (8)[51]: yellow oil (0.014g, 21.8%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.02 (d, *J* = 7.6 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.49-7.39 (m, 4H), 7.34-7.25 (m, 7H), 7.01 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 193.8 (C=O), 166.1 (C=O), 134.8 (C), 133.6 (2xCH), 133.4 (2xCH), 130.0 (2xCH), 129.5 (C), 129.4 (C), 129.2 (2xCH), 128.9 (2xCH), 128.8 (3xCH), 128.5 (2xCH), 78.0 (C-OH) ppm; GC-MS rt= 28.22 min: 105 m/z $[C_7H_5O]^+$, 107 m/z $[C_7H_8O]^+$. According to the literature.

1,2-Diphenylethan-1-one (9)[52]: white oil (0.010g, 26.7%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.02 (d, *J* = 7,6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.2 Hz 2H), 7.29 – 7.26 (m, 3H), 4,30 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 197.7 (C=O), 136.8 (C), 134.7 (C), 133.3 (CH), 129.6 (2xCH), 128.8 (2xCH), 128.8 (2xCH), 128.7 (2xCH), 127.0 (CH), 45.6 (CH_2). According to the literature.

Benzil (10): GC-MS: rt = 17.23 min :105 m/z $[C_7H_5O]^+$, 210 m/z $([M+H]^+)$.

1,2-Diphenylethan-1-ol (11): GC-MS: rt = 18.76 min: 197 $([M+H]^+)$.

2-Hydroxy-1,2-diphenylethan-1-one (12): GC-MS: rt = 28.46 min: 105 m/z $[C_7H_5O]^+$, 107 m/z $[C_7H_7O]^+$, 212 m/z $[M+H]^+$.

1-Ethyl-2,3-dimethyl-2,3-dihydro-1H-imidazole (15): GC-MS: rt = 8.96 min: 126 m/z $[C_7H_{14}N_2]^+$.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org

NMR experiments; NMR spectra of the compounds; Mass spectra and GC-MS.

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