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# Remarkable Anion and Cation Effects on Stille Reactions in Functionalised Ionic Liquids

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**Abstract:** Task-specific ionic liquids bearing nitrile functional groups attached to the cation and nitrogen-donor-containing anions strongly affect the efficiency of the Stille cross-coupling, influencing the nature of the catalyst and its stability. The relative strengths of the coordinating power of the cations and anions are varied and compared, and under certain conditions nanoparticles are observed.

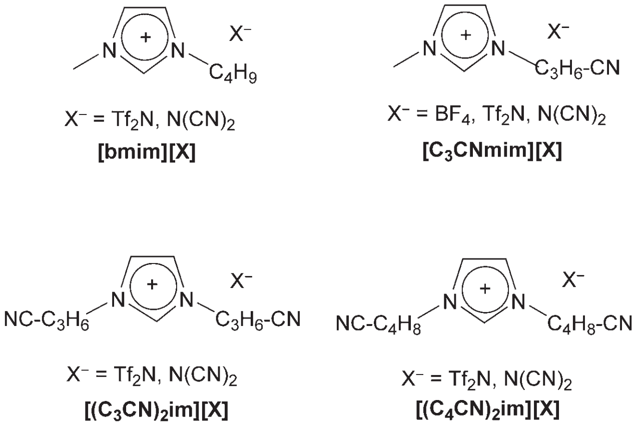
**Keywords:** catalysis; immobilization; ionic liquids; nanoparticles; palladium; Stille cross-coupling

Palladium-mediated cross-coupling reactions are among the most widely studied type of catalysed reactions in ionic liquids (ILs).[1] The reason for such interest may be ascribed to the ability of the ionic reaction media to overcome the drawbacks that generally accompany these reactions when performed in molecular solvents, limiting their applicability: namely, decomposition and leaching of expensive catalysts/co-catalysts, poor reagent and catalyst solubility and difficulties in catalyst recycling. In general, ionic transition metal catalysts tend to be well retained in ILs during work-up procedures, thus confirming their potential as the immobilising phase. By varying and combining the ions, approximately one trillion ILs are accessible,[2] at least in principle, which makes further optimisation of palladium cross-coupling reactions based on solvent selection a daunting task. Until now it has been difficult to predict which ILs are the best ones for certain applications, but with increased understanding on how the structure of an IL affects its physical and chemical properties the advantages of these solvents with respect to molecular ones should emerge.[3] Here, it is worth noting that even if the anions generally used to make ILs are formally defined as non-coordinating, recent work clearly indicates this is not the case,[4] so that differences between ILs may be apparent. Therefore, task-specific (or functionalised) ILs able to interact with a metal centre *via* a coordination group attached to the IL backbone (anion or cation) should further increase catalyst retention, thus avoiding the use of co-ligands and reducing leaching.[5] Numerous functional groups have been attached into imidazolium or pyridinium cations,[6] among which many have been found to be able to stabilise transition metal nanoparticle catalysts/catalyst reservoirs,[5] possibly *via* interaction of the functional group with the surface of the nanoparticles, thereby preventing aggregation.

While many efforts have been devoted to the functionalisation of IL cations, and the influence of functionalised ILs has been investigated in a few catalytic systems, there is little study of the influence of the anions.[7] Recently, it has been shown that Stille cross-coupling reactions are particularly sensitive to the structure of the IL.[8] Formally, nitrogen-containing anions like $[Tf_2N]^-$ ensure the highest reactivity, and facilitate a ligand-free reaction protocol. Despite high activity, the stability of the catalytic system is low, so that recycling procedures were ineffective. In contrast, the introduction of a nitrile-functionality onto pyridinium-based ILs not only reduces catalyst leaching, but improves catalyst stability.[5a]

Herein, we describe the synthesis of a series of symmetrical and asymmetrical nitrile-functionalised imidazolium-based ILs incorporating nitrogen-containing anions such as $[Tf_2N]^-$ and $[N(CN)_2]^-$ and assess their application as reaction media for the transfer of vinyl and methyl groups onto iodo- and bromobenzene.

The ILs used as reaction media (see Scheme 1) were prepared by anion metathesis from their corresponding chlorides, following reported procedures.[9] All the compounds are liquid at room temperature and were characterised using electrospray ionisation-mass spectrometry (ESI-MS), IR and NMR spectroscopy (see Experimen-



**Scheme 1.** Ionic liquids employed.

tal Section). First, we evaluated the reaction of tributylvinylstannane using $Pd(OAc)_2$ as the catalyst source under ligand-free conditions, following a literature protocol.[8] For comparison, reactions with palladium catalyst/co-catalyst, $Pd(0)/AsPh_3$, have been also performed. The reduction of $Pd(OAc)_2$ to Pd(0) in $[Tf_2N]$-based ILs is immediate, the solutions rapidly turn black, indicative of nanoparticle formation (see below). In contrast, yellow solutions were obtained with $[N(CN)_2]^-$-based ILs (Figure 1).

Although $Pd(OAc)_2$ rapidly dissolved in the ionic media, reagents and products were only slightly soluble, affording a biphasic system, in principle enabling product recovery directly by decantation. Practically, considering the volume of IL used (1 mL), extraction with *n*-pentane was preferred.

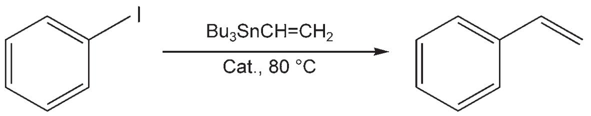
The degree of conversion, as well as the actual mass balance, which is related to the ease of extraction of products and unreacted materials from the ionic medium, were evaluated by GC analysis after the addition of an internal standard. The yields for the reactions involving the transfer of a vinyl group onto iodobenzene are generally high, considering that a relatively short reaction time was used; with the exception of $[C_3CNmim][Tf_2N]$, practically quantitative conversion can be obtained by increasing the reaction time. The results are summarised in Table 1 and show that the nature of the cation in the $[N(CN)_2]$-based ILs does not seem to have a major effect on the kinetics of the reaction, as the percentage of conversion is almost the same on going from $[bmim][N(CN)_2]$ to $[(C_4CN)_2im][N(CN)_2]$. It is, however, worth noting that, using the palladium-$AsPh_3$ system, the transfer of the vinyl group is almost quantitative: indicating that $[N(CN)_2]^-$ anions are not able to interact with the metal centre, if good ligands are employed.

Interestingly, visible increases in coupling yields characterise the reaction in $[C_3CNmim][Tf_2N]$ with respect to the non-functionalised IL. It has previously been proposed that the ability of the anion to interact with a metal centre in Stille cross-coupling reactions is affected by the nature of the cation, that is, by the strength of ion pairing through specific interactions,[8] and competition between the cation and the metal for the anion has been hypothesised. Moreover, Gordon et al. have shown that there is a correlation between the basicity of the anion in ILs with the rate of nickel-catalysed reactions.[10]

**Figure 1.** $Pd(OAc)_2$ solutions in $[bmim][N(CN_2)]$ (*left*) and in $[bmim][Tf_2N]$ (*right*).

Considering that microscopic properties of $[bmim][Tf_2N]$, determined through spectroscopic dyes (Table 2), are practically the same as those of $[C_3CNmim][Tf_2N]$ (i.e., the nucleophilicity of the anion is not modified by the cation structure), it is not unreasonable to conclude that the increased efficiency of the nitrile-functionalised IL is due to the interaction of the nitrile pendant group with the metal centre. IR analysis confirmed that the palladium coordinates to the nitrile group, since the $\nu_{CN}$ stretching frequency changes from 2251 $cm^{-1}$ to 2359 and 2341 $cm^{-1}$ (symmetric and asymmetric stretching). In addition, TEM images reveal that the near double conversion of the Stille reaction in the CN-IL than that of the normal IL may be ascribed to different states of the palladium nanoparticles in the different ILs (Figure 2). Nanoparticles have been implicated as catalysts/catalyst reservoirs for numerous reactions in ILs and in many cases they can be isolated and reused.[11] In $[bmim][Tf_2N]$, the palladium nanoparticles are small (2–4 nm), but highly aggregated, resulting in a low catalytically accessible area. Nanoparticle aggregation during a catalytic process in ILs has been observed previously,[12] but the CN group in the functionalised IL provides a stabilising effect. However, in spite of their larger size, the nanoparticles in the CN-IL are well dispersed and are open to activation. Such an observation

**Table 1.** Stille coupling of iodobenzene with tributylvinylstannane in ILs.



| Entry | Ionic liquid | Time [h] | Catalyst | Mass Balance[a] [%] | Conversion[b] [%] |
|---|---|---|---|---|---|
| 1 | [bmim][$N(CN)_2$] | 1 | $Pd(OAc)_2$ | 65 | 52 |
| 2 | [bmim][$N(CN)_2$][c] | 1 | $Pd(OAc)_2$ | 70 | 36 |
| 3 | [bmim][$N(CN)_2$] | 1 | $Pd_2(dba)_3$ | 79 | 97 |
| 4 | [bmim][$Tf_2N$] | 1 | $Pd(OAc)_2$ | >99 | 40 |
| 5 | [bmim][$Tf_2N$][c] | 1 | $Pd(OAc)_2$ | >99 | 40 |
| 6 | [bmim][$Tf_2N$] | 1 | $Pd_2(dba)_3$ | >99 | 73 |
| 7 | [bmim][$BF_4$] | 1 | $Pd(OAc)_2$ | 90 | 30 |
| 8 | [$C_3CNmim$][$BF_4$] | 1 | $Pd(OAc)_2$ | 70 | 80 |
| 9 | [$C_3CNmim$][$BF_4$][c] | 1 | $Pd(OAc)_2$ | 70 | 48 |
| 10 | [$C_3CNmim$][$BF_4$] | 2 | $Pd(OAc)_2$ | 70 | 85 |
| 11 | [$C_3CNmim$][$BF_4$] | 1 | $Pd_2(dba)_3$ | 75 | 65 |
| 12 | [$C_3CNmim$][$N(CN)_2$] | 1 | $Pd(OAc)_2$ | 90 | 55 |
| 13 | [$C_3CNmim$][$N(CN)_2$] | 2 | $Pd(OAc)_2$ | 90 | 83 |
| 14 | [$C_3CNmim$][$Tf_2N$] | 1 | $Pd(OAc)_2$ | 90 | 72 |
| 15 | [$C_3CNmim$][$Tf_2N$] | 2 | $Pd(OAc)_2$ | 87 | 75 |
| 16 | [$C_3CNmim$][$Tf_2N$] | 1 | $Pd_2(dba)_3$ | 90 | 72 |
| 17 | [$(C_3CN)_2im$][$N(CN)_2$] | 1 | $Pd(OAc)_2$ | 64 | 57 |
| 18 | [$(C_3CN)_2im$][$Tf_2N$] | 1 | $Pd(OAc)_2$ | 90 | 90 |
| 19 | [$(C_4CN)_2im$][$N(CN)_2$] | 1 | $Pd(OAc)_2$ | 54 | 60 |
| 20 | [$(C_4CN)_2im$][$Tf_2N$] | 1 | $Pd(OAc)_2$ | 70 | 60 |

[a] Determined using benzonitrile as external standard.
[b] Determined by GC analysis.
[c] Water equilibrated.

**Table 2.** $E_N^T$ and Kamlet–Taft values for nitrile-functionalised ionic liquids.

| Solvent | $E_N^T$ | $\pi^*$ | $\alpha$ | $\beta$ |
|---|---|---|---|---|
| [bmim][$BF_4$] | 0.667 | 0.984 | 0.665 | 0.451 |
| [bmim][$Tf_2N$] | 0.645 | 0.971 | 0.635 | 0.248 |
| [bmim][$N(CN)_2$] | 0.629 | 1.129 | 0.464 | 0.708 |
| [$C_3CNmim$][$BF_4$] | 0.695 | 1.078 | 0.638 | 0.337 |
| [$C_3CNmim$][$N(CN)_2$] | 0.653 | 1.124 | 0.516 | 0.508 |
| [$C_3CNmim$][$Tf_2N$] | 0.677 | 1.029 | 0.646 | 0.219 |

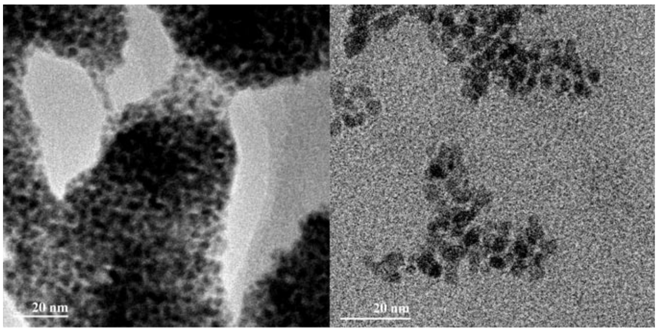


**Figure 2.** Comparison of TEM images of the palladium nanoparticles isolated after the Stille reaction from [bmim][$Tf_2N$] (*left*) and [$C_3CNmim$][$Tf_2N$] (*right*).

can only be explained by the stabilisation effect from the CN functionality incorporated into the IL, and may be connected to the higher catalytic activity in the CN-ILs.

Further evidence that the nitrile pendant group is chiefly responsible for the increased reaction rate in the CN-IL with the $[Tf_2N]^-$ anion arises from similar results obtained with respect to [$C_3CNmim$][$BF_4$]: given its symmetrical shape and low charge density, the tetrafluoroborate anion possesses a low nucleophilicity, and therefore, it is generally considered as being effectively non-coordinating.

The low sensitivity of cross-coupling rates when [$N(CN)_2$]-based ILs are used may be rationalised in terms of coordination of the palladium only involving the anion. Unfortunately, it is not possible to confirm this hypothesis by IR, due to overlap of the stretching bands of the anion and cation counterparts. Moreover, it was not possible to isolate palladium nanoparticles from these media, suggesting the involvement of another catalyst state.

It is reasonably to propose that when ILs possessing nucleophilic anions are used as solvents for palladium-

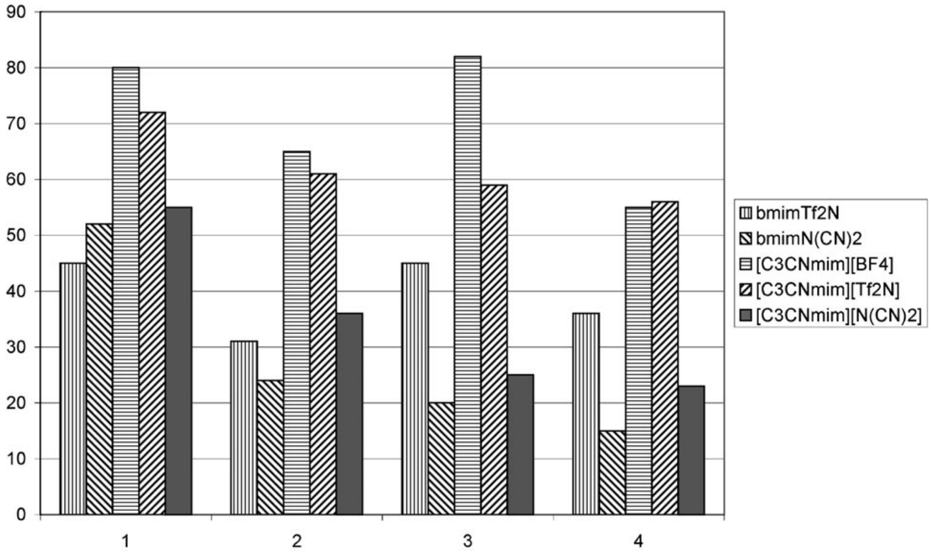


**Figure 3.** Recyclability of the Stille reaction between vinyltributylstannane and iodobenzene.

mediated cross-couplings, the stabilisation of the metal centre involves mainly the anion and therefore is insensitive to variation on the cation structure; however, when non-nucleophilic anions are used a positive effect of the nitrile pendant group may be envisaged, as in [$C_3$CNmim][$BF_4$]. $Tf_2$N-based ILs represent an intermediate case as, in principle, both the anion and the cation are able to stabilise a metal centre.

Data collated in Table 1 also suggest that the introduction of a second nitrile group on the cation determines, in the case of [$Tf_2$N]-based ILs, a further increase in the activity of the catalyst, even if the magnitude is not the same as when passing from non-functionalised to mono-functionalised ILs. Moreover, a substantial drop in catalytic activity is evidenced in [($C_4$CN)$_2$im][$Tf_2$N]: the high viscosity of this IL might well account for a reduced mass transfer, determining a lower reaction rate.

The effect of water has been also taken into consideration: as we might expect, water has detrimental effect on conversion for hydrophilic ILs, whereas it effects no appreciable variation of the rate of conversion when [bmim][$Tf_2$N] is used.

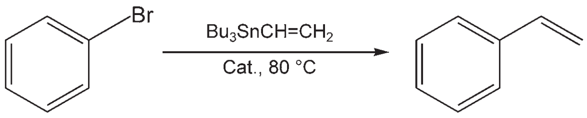
The difference between reactions conducted in [N(CN)$_2$]-based ILs with respect to the others is also apparent in the recycling tests (see Figure 3). Although palladium solutions in [N(CN)$_2$]-based ILs generally yield colourless organic phases during extraction, indicating less pronounced leaching, they are generally less stable. Moreover, the catalyst immobilised in [$C_3$CNmim][$Tf_2$N] is much more stable than the non-functionalised analogue (after three cycles, there is no significant decrease in activity). It is noteworthy that the fourth cycle was conducted seven days after the preceding one.

Nitrile-functionalised ILs of the type [$C_3$CNmim][X] have also been tested as solvents for the transfer of the vinyl group from tributylvinyltin to bromobenzene. Data reported in Table 3 clearly reveal that [$C_3$CNmim][$Tf_2$N] is far superior to the [$BF_4$] analogue, even if the reaction rates are markedly lower to those characterising the reaction of iodobenzene (only 32% of product is recovered). Moreover, product yields are practically doubled on changing from [bmim][$Tf_2$N] to [$C_3$CNmim][$Tf_2$N]. The [N(CN)$_2$]-based ILs are the least active for the ligandless Stille cross-coupling involving bromobenzene as substrate, even though a difference was observed on passing from the non-functionalised to the nitrile containing IL.

Completely different behaviour was observed for the transfer of a methyl group (see Table 4). In this case, both cross-coupling and homocoupling are sensitive to the structure of the solvent. For example, nitrile-functionalised ILs do not improve the yields of the methyl transfer reaction with respect to the non-functionalised derivatives in the presence of a ligand. [bmim][$Tf_2$N] and [bmim][N(CN)$_2$] ensure the highest conversion together with the lowest percentage of homocoupling. The situation deteriorates on application of the ligandless protocol: in this case, only [$C_3$CNmim][N(CN)$_2$] ensured a conversion comparable to that obtained in the presence of $AsPh_3$.

In conclusion, nitrile-functionalized ILs are considerably more-effective for the immobilisation of palladium catalysts for the transfer of a vinyl group in Stille reactions with respect to 1-butyl-3-methylimidazolium derivatives. TEM analysis of nanoparticles extracted from [$Tf_2$N]-based ILs provides evidence for the stabilising effect exerted by the nitrile pendant group on the metal centre. Although such task-specific ILs may well prove to be decisive in vinyl transfer, they do not appear to be as effective in transferring a methyl group.

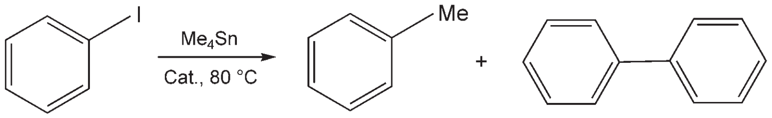
**Table 3.** Stille coupling of bromobenzene and tributylvinylstannane in ILs.



| Solvent | Time [h] | Catalyst | Mass Balance[a] [%] | Conversion[b] [%] |
|---|---|---|---|---|
| [bmim][$N(CN)_2$] | 24 | $Pd(OAc)_2$ | 65 | 2 |
| [bmim][$Tf_2N$] | 24 | $Pd(OAc)_2$ | 81 | 16.3 |
| [$C_3$CNmim][$BF_4$] | 24 | $Pd(OAc)_2$ | 86.2 | 12 |
| [$C_3$CNmim][$Tf_2N$] | 24 | $Pd(OAc)_2$ | 80 | 32.5 |
| [$C_3$CNmim][$N(CN)_2$] | 24 | $Pd(OAc)_2$ | 62 | 14 |

[a] Determined using benzonitrile as external standard.
[b] Determined by GC analysis.

**Table 4.** Methyl transfer from tetramethyltin to iodobenzene in ionic liquids.



| Entry | Solvent | Catalyst | Ligand | Time [h] | Mass balance[a] [%] | Ph-Me[b] [%] | Tol/Biphenyl[b] [%] |
|---|---|---|---|---|---|---|---|
| 1 | [bmim][$N(CN)_2$] | $Pd_2(dba)_3$ | $AsPh_3$ | 24 | 60 | 52.6[c] | 1.40 |
| 2 | [bmim] [$N(CN)_2$] | $Pd(OAc)_2$ | – | 24 | 100 | – | – |
| 3 | [bmim][$Tf_2N$] | $Pd_2(dba)_3$ | $AsPh_3$ | 24 | 90 | 62[c] | 2.29 |
| 4 | [bmim][$Tf_2N$] | $Pd(OAc)_2$ | – | 24 | 70 | 12[c] | 0.617 |
| 5 | [$C_3$CNmim][$BF_4$] | $Pd_2(dba)_3$ | $AsPh_3$ | 24 | 64 | 23.4[c] | 1.45 |
| 6 | [$C_3$CNmim][$BF_4$] | $Pd(OAc)_2$ | – | 24 | 80 | 8[c] | – |
| 7 | [$C_3$CNmim][$N(CN)_2$] | $Pd_2(dba)_3$ | $AsPh_3$ | 24 | 77 | 33[c] | 0.993 |
| 8 | [$C_3$CNmim][$N(CN)_2$] | $Pd(OAc)_2$ | – | 24 | 47 | 26[c] | 1.77 |
| 9 | [$C_3$CNmim][$Tf_2N$] | $Pd_2(dba)_3$ | $AsPh_3$ | 24 | 77 | 9[c] | 0.303 |
| 10 | [$C_3$CNmim][$Tf_2N$] | $Pd(OAc)_2$ | – | 24 | 92 | 7[c] | 0.786 |

[a] Determined using benzonitrile as external standard.
[b] Determined by GC and GM analysis.
[c] The unreacted material is iodobenzene.

## Experimental Section

### General Remarks

GC-MS were carried out on a 30 m DB5 capillary column using an instrument equipped with an ion trap detector. GC analyses were carried out using an ECONOCAP EC-5 column (30 m). ESI-MS analyses were performed on a Finnigan LCQ Advantage (Thermo Finnigan, San Jose, CA, USA) ion trap instrument equipped with an Excalibur software (capillary temperature 493.15 K, flow rate 3 mL/min) as described previously.[13] The UV-VIS spectroscopic measurements were performed using a Cary 2200 spectrometer at temperature of 25 ± 0.2 °C. $\lambda_{max}$ was measured by taking the middle point between the two positions of the band where the absorbance is equal to 0.90 $A_{max}$. Individual stock solutions of Reichardt's betaine dye, 4-nitroaniline and *N,N*-diethyl-4-nitroaniline were prepared in dichloromethane. To prepare a given dye/ionic liquid solution, the appropriate amount of the dye stock solution was micropipetted into a clean dry quartz cuvette. Residual dichloromethane was evaporated under gentle stream of argon gas. The ionic liquid was then added to the cuvette, the cuvette was capped and sealed, and the sample was mixed for an appropriate time prior to experimental measurements. The dye concentration in the ionic liquid was such that it had an absorbance under 1 for aniline dyes and between 0.1 and 0.3 for Reichardt dye. 4-Nitroaniline (Fluka), *N,N*-diethyl-4-nitroaniline (Frinton), Reichardt's betaine dye (Aldrich), iodobenzene (99%), tributylvinylstannane, tetramethylstannane were used without purification. [bmim][$Tf_2N$], [bmim][$N(CN)_2$], [$C_3$CNmim][$BF_4$], [$C_3$CNmim][$Tf_2N$], [$C_3$CNmim][$N(CN)_2$], [$(C_3CN)_2$im][$Tf_2N$], [$(C_3CN)_2$im][$N(CN)_2$], [$(C_4CN)_2$im][$Tf_2N$], [$(C_4CN)_2$im][$N(CN)_2$] were prepared from the corresponding chlorides, following the reported procedures.[9]

Reactions were carried out in a screw cup with Teflon-faced rubber septum vials under magnetic stirring. To a suspension of $Pd_2(dba)_3$ (0.025 mmol) and $Ph_3As$ (0.05 mmol) or $Pd(OAc)_2$ (0.025 mmol) in 1 mL of ionic liquid were added iodobenzene

(0.5 mmol) and the organostannane (0.6 mmol). The mixture was stirred at 80 °C for the times reported in Tables 1, 3 and 4. The products were extracted with diethyl ether (10 × 1 mL), the organic layers were dried over $MgSO_4$ and diluted to an exactly known volume. A portion of this solution, exactly measured, was analysed by GC-MS, the remainder by GC, after the addition of an appropriate amount of an internal standard (benzonitrile).

### $[C_3CNmim][Tf_2N]$

The product was obtained as a colourless liquid; yield: 85%. ESI-MS ($CH_3OH$): positive ion, 150 [$C_3CNmim$]; negative ion, 280 [$Tf_2N$]; $^1H$ NMR ($CD_3CN$): $\delta = 8.43$ (s, 1H), 7.38 (s, 1H), 7.35 (s, 1H), 4.21 (t, 2H, $NCH_2$, $J = 7.11$ Hz), 3.82 (s, 3H, $NCH_3$), 2.46 (t, 2H, $CH_2CN$, $J = 7.08$ Hz), 2.16 (m, 2H, $CH_2$); $^{13}C$ NMR ($CD_3CN$): $\delta = 137.11$, 124.88, 123.28, 117.67, 48.96, 36.84, 26.46, 14.63; IR: $\nu = 3159$, 3122 ($\nu_{C\text{-}H}$ aromatic); 2251 ($\nu_{C\equiv N}$); 1577 cm$^{-1}$ ($\nu_{C=N}$).

### $[C_3CNmim][N(CN)_2]$

The product was obtained as a colourless liquid; yield: 78%. ESI-MS ($CH_3OH$): positive ion, 150 [$C_3CNmim$], 82 [mim]; negative ion, 66 [$N(CN)_2$], 282 [anion-cation-anion]; $^1H$ NMR ($CD_3CN$): $\delta = 8.64$ (s, 1H), 7.44 (s, 1H), 7.40 (s, 1H), 4.20 (t, 2H, $NCH_2$, $J = 7.08$ Hz), 3.83 (s, 3H, $NCH_3$), 2.48 (t, 2H, $CH_2CN$, $J = 7.12$ Hz), 2.17 (m, 2H, $CH_2$); $^{13}C$ NMR ($CD_3CN$): $\delta = 137.32$, 124.75, 123.21, 120.42, 119.85, 48.87, 36.78, 26.44, 14.59; IR: $\nu = 3153$, 3107 ($\nu_{C\text{–}H}$ aromatic) 2233, 2197, 2139 cm$^{-1}$ ($\nu_{C\equiv N}$).

### $[(C_3CN)_2im][Tf_2N]$

The product was obtained as a yellow liquid; yield: 80%. ESI-MS ($CH_3OH$): positive ion, 203 [$(C_3CN)_2im$], 137 [$C_3CNim$]; negative ion, 280 [$Tf_2N$], 211[$CF_3$ loss], 147 [$NSO_2CF_3$]; $^1H$ NMR ($CD_3CN$): $\delta = 8.53$ (s, 1H), 7.44 (s, 2H), 4.23 (t, 4H, $2NCH_2$, $J = 7.05$ Hz), 2.47 (t, 4H, $2CH_2CN$, $J = 7.12$ Hz), 2.19 (m, 4H, $2CH_2$); $^{13}C$ NMR ($CDCl_3$): $\delta = 136.78$, 123.74, 117.63, 49.16, 26.31, 14.68; IR: $\nu = 3151$, 3119, 3095 ($\nu_{C\text{-}H}$ aromatic), 2964 ($\nu_{C\text{-}H}$ aliphatic), 2251 ($\nu_{C\equiv N}$), 1616, 1566 cm$^{-1}$ ($\nu_{C=N}$).

### $[(C_3CN)_2im][N(CN)_2]$

The product was obtained as a light yellow liquid; yield: 82%. ESI-MS ($CH_3OH$): positive ion, 203 [$(C_3CN)_2im$], 137 [$C_3$ CNim]; negative ion, 66 [$N(CN)_2$], 335 [anion-cation-anion]; $^1H$ NMR ($CD_3CN$): $\delta = 8.65$ (s, 1H), 7.46 (s, 2H), 4.24 (t, 4H, $2NCH_2$, $J = 7.05$ Hz), 2.49 (t, 4H, $2CH_2CN$, $J = 7.07$ Hz), 2.18 (m, 4H, $2CH_2$); $^{13}C$ NMR ($CD_3CN$): $\delta = 136.96$, 123.74, 119.82, 49.17, 26.34, 14.71; IR: $\nu = 3499$, 3425, 3144, 3107 ($\nu_{C\text{-}H}$ aromatic), 2958 ($\nu_{C\text{-}H}$ aliphatic), 2235, 2195, 2135 ($\nu_{C\equiv N}$), 1624, 1566 cm$^{-1}$ ($\nu_{C=N}$).

### $[(C_4CN)_2im][Tf_2N]$

The product was obtained as a deep yellow liquid; yield: 82%. ESI-MS ($CH_3OH$): positive ion, 231 [$(C_4CN)_2im$], 149 [$C_4CNim$]; negative ion, 280 [$Tf_2N$], 211 [$CF_3$ loss], 147 [$NSO_2CF_3$]; $^1H$ NMR ($CD_3CN$): $\delta = 8.48$ (s, 1H), 7.40 (s, 2H), 4.15 (t, 4H, $2NCH_2$, $J = 7.18$ Hz), 2.45 (t, 4H, $2CH_2CN$, $J = 7.03$ Hz), 1.95 (m, 4H, $2CH_2$), 1.65 (m, 4H, $2CH_2$); $^{13}C$ NMR ($CD_3CN$): $\delta = 136.88$, 123.85, 121.13, 50.08, 29.94, 23.20, 17.42; IR: $\nu = 3149$, 3115, ($\nu_{C\text{-}H}$ aromatic), 2945, 2877 ($\nu_{C\text{-}H}$ aliphatic), 2249 ($\nu_{C\equiv N}$), 1618, 1566 cm$^{-1}$ ($\nu_{C=N}$).

### $[(C_4CN)_2im][N(CN)_2]$

The product was obtained as a deep yellow liquid; yield: 75%. ESI-MS ($CH_3OH$): positive ion, 231 [$(C_4CN)_2im$], 149 [$C_4CNim$]; negative ion, 66 [$N(CN)_2$]; $^1H$ NMR ($CD_3CN$): $\delta = 8.58$ (s, 1H), 7.42 (s, 2H), 4.16 (t, 4H, $2NCH_2$, $J = 7.05$ Hz), 2.45 (t, 4H, $2CH_2CN$, $J = 7.04$ Hz), 1.95 (m, 4H, $2CH_2$), 1.65 (m, 4H, $CH_2$); $^{13}C$ NMR ($CD_3CN$): $\delta = 136.48$, 123.45, 120.74, 49.68, 29.53, 22.78, 17.02; IR: $\nu = 3144$, 3103 ($\nu_{C\text{–}H}$ aromatic), 2943, 2874 ($\nu_{C\text{–}H}$ aliphatic), 2231, 2193, 2135 ($\nu_{C\equiv N}$), 1566 cm$^{-1}$ ($\nu_{C=N}$).

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