Functionalised ionic liquids: synthesis of ionic liquids with tethered basic groups and their use in Heck and Knoevenagel reactions

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A simple and efficient synthesis of a novel series of ionic liquids bearing nucleophilic (Me_2N) and non-nucleophilic base ($^iPr_2N$) functionalities is described. The non-nucleophilic base functionality resembles the structure of the Hünig's base (*N*,*N*-diisopropylethylamine), which has been used widely in organic synthesis. A qualitative measure of the basicity of these ionic liquids is presented by utilising their interaction with universal indicator. The basicity of these ionic liquids was found to be dependent on the amine tether and choice of linker between the two nitrogen centres. The relative base strength of these ionic liquids was also probed by using them as catalysts in the Heck and Knoevenagel reactions.

Introduction

Recently, there has been considerable interest in using room temperature ionic liquids as environmentally benign reaction media. There are numerous examples of all classes of organic reactions that have been successfully carried out in such media.[1] However, in many of these reactions, the ionic liquids were just a media to facilitate the reaction. Ionic liquids are often referred to as designer solvents[2] due to the fact that choice of combination of anion, cation and cation chain length can be used to obtain specific properties such as viscosity, solubility or melting point. The concept of functional ionic liquids extends this idea by covalently tethering a functional group to the cation or anion which can interact with dissolved substrates.[3]

Functionalised ionic liquids (previously referred to as task specific ionic liquids) have been used in an analogous way to supported (polymer, silica or other solids) reagents and catalysts.[4] Although the latter have been in use in organic synthesis for a number of years, and provide a simplified procedure for isolation of products from a reaction mixture, mass transport within a solid can often result in decreased reaction rates. This effect would be much reduced in the case of a 'liquid-support' by using ionic liquid-supported reagents. This could be achieved where one of the reactants is an integral part of the ionic liquid.[5–8] This methodological approach in organic synthesis has been the subject of a recent review.[9]

Functionalisation of ionic liquids with acidic groups has been reported. The zwitterionic imidazolium compounds originally developed by Yoshizawa *et al.* for electrochemical purposes[10] have been converted into the Brønsted-acidic ionic liquids and have been shown to act as effective solvent catalysts for the Fischer esterification,[11] the esterification of aliphatic acids with alkenes[12] and the oligomerisation of alkenes.[13] More recently, carboxylic acids have been attached to a range of cations by Nockemann *et al.* designed for the solubilisation of metal oxides and hydroxides.[14] Basic groups have also been tethered to ionic liquids. Davis *et al.* described the synthesis of an imidazolium tetrafluoroborate with an amine group in the cation side chain.[3] Developed for gas separation, the amine-tethered ionic liquid is able to capture carbon dioxide by carbamate formation.[4] A range of nitrile functionalised ionic liquids have been synthesised and characterised and have been utilised in Heck, Suzuki and Stille coupling reactions as well as shown to be capable of forming charge transfer complexes.[15] Guanidine-based ionic liquids have also been developed and employed as base catalysts for the aldol condensation,[16] Henry[17] and Knoevenagel reactions.[18] Furthermore, asymmetric aldol condensations have been performed with L-proline tagged imidazolium-based ionic liquids giving >99% ee.[19]

A range of hydrophobic functionalised ionic liquids designed to aid the extraction of mercury(II) and cadmium(II) from water have been reported by Rogers and co-workers.[20] These were prepared by appending urea-, thiourea- or thioether groups to an imidazolium cation. Park *et al.* have also synthesised an imidazolium polyoxyethylene-based crown ether ionic liquid for the selective extraction of the radioactive strontium(II) from aqueous solutions.[21]

Herein, we report the synthesis and utility of a new class of ionic liquids with a tethered base functionality with tuneable basicity.[22] The ionic liquids prepared and characterised utilise a non-nucleophilic, sterically-hindered tertiary amine functionality which is linked to a quaternary ammonium molecular segment by an alkyl chain or by a tether containing ethereal segments of differing lengths.

Results and discussion

The general synthetic strategy for the preparation of $[^iPr_2N(CH_2)_2mim][NTf_2]$, $[^iPr_2N(CH_2)_2N_{112}][NTf_2]$ and $[Me_2N(CH_2)_2N_{112}][NTf_2]$ is simple and versatile (see Scheme 1). The synthetic strategy makes use of the synthesis of a diamine

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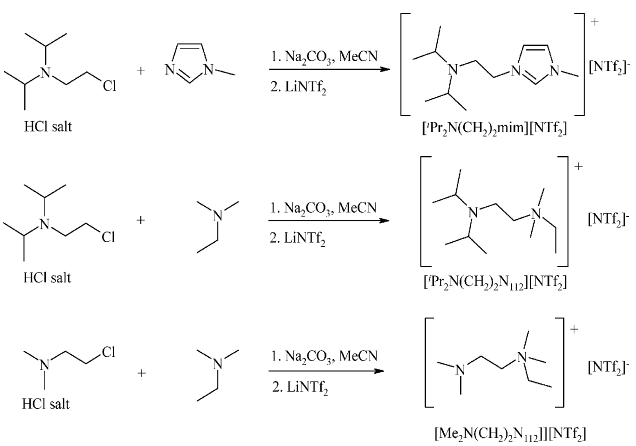
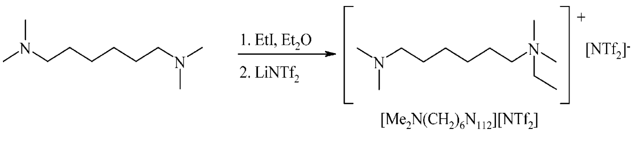


Scheme 1 Synthesis of $[^i Pr_2N(CH_2)_2mim][NTf_2]$, $[^i Pr_2N(CH_2)_2N_{112}][NTf_2]$ and $[Me_2N(CH_2)_2N_{112}][NTf_2]$.

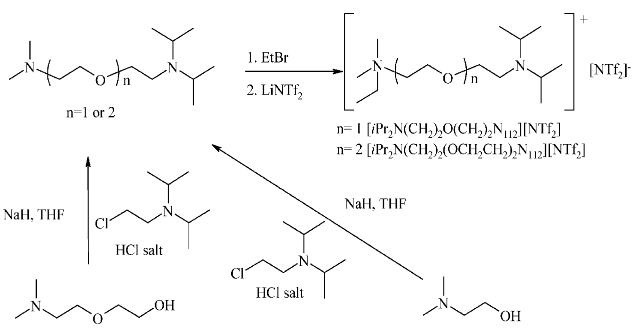
intermediate where one amine group is readily quaternised compared with the other. A vital part of the synthesis of the base-tethered ionic liquids involves the use of 2-diisopropylaminoethyl chloride reacting with a chosen nucleophilic reagent, which is facilitated by the neighbouring group participation from the diisopropylamino moiety. The synthesis of an ionic liquid with an extended linker is not entirely straightforward, because long chain haloalkylamines are not commercially available. These amines can undergo self-alkylation or hydrodehalogenation and are, therefore, very difficult to prepare. The alternative is to start from a longer chain diamine, and carry out a monoalkylation utilising a large excess of the diamine.

The synthetic strategy for the preparation of $[Me_2N(CH_2)_6N_{112}][NTf_2]$ makes use of the insolubility of the mono-quaternised diamine which precipitates out of the diethyl ether solvent thereby preventing dialkylation with the haloalkane, Scheme 2.

The diamines $^i Pr_2N(CH_2)_2O(CH_2)_2NMe_2$ and $^i Pr_2N(CH_2)_2(OCH_2CH_2)_2NMe_2$ with five and eight atoms in the chain connecting the nitrogen centres, respectively, were prepared as ionic liquid precursors from dimethylaminoethanol with sodium hydride in a Williamson ether synthesis, Scheme 3. The diamine $^i Pr_2N(CH_2)_2O(CH_2)_2NMe_2$ was prepared in good yield 89% and high purity (through distillation) after workup from the reaction between dimethylaminoethanol and diisopropylaminoethyl chloride hydrochloride. Diamine $^i Pr_2N(CH_2)_2(OCH_2CH_2)_2NMe_2$ with a diether functionality was prepared in a similar manner and also purified by distillation. Another crucial advantage in using a sterically-hindered amine tether becomes clear in the subsequent quaternisation reactions. In the case of both these diamine compounds, the alkylation is 100% selective with only the dimethylamino group reacted due to the fact that the diisopropylamino group is non-nucleophilic.



Scheme 2 Synthesis of $[Me_2N(CH_2)_6N_{112}][NTf_2]$.



Scheme 3 Synthesis of $[^i Pr_2N(CH_2)_2O(CH_2)_2N_{112}][NTf_2]$ and $[^i Pr_2N(CH_2)_2(OCH_2)_2N_{112}][NTf_2]$.

An overview of the synthesised basic ionic liquids and their physical properties is shown in Table 1. All of the materials synthesised are liquids at room temperature and show relatively low viscosities. The structurally related compounds $[^i Pr_2N(CH_2)_2mim][NTf_2]$ and $[^i Pr_2N(CH_2)_2N_{112}][NTf_2]$ show how the type of cationic centre greatly influences the melting point. The choice of an Me_2N group instead of an $^i Pr_2N$ group in the case of $[R_2N(CH_2)_2N_{112}][NTf_2]$ shows how the structure of the base tether greatly effects the viscosity. A pronounced decrease in viscosity is also noted between $[^i Pr_2N(CH_2)_2O(CH_2)_2N_{112}][NTf_2]$ and $[^i Pr_2N(CH_2)_2(OCH_2CH_2)_2N_{112}][NTf_2]$ when increasing linker length between the cationic centre and tethered amine. This is uncommon for ionic liquids where increasing the chain length normally leads to an increase in viscosity.[1,23]

Table 2 shows the proton shifts of the methylene groups in the linker adjacent to the ionic centre (α) and the pendant amino group (ω). The structurally similar compounds $[^i Pr_2N(CH_2)_2mim][NTf_2]$ and $[^i Pr_2N(CH_2)_2N_{112}][NTf_2]$ show how the choice of cationic centre greatly influences the chemical shift of the α-methylene protons, 4.11 and 3.24 ppm, respectively, as expected from the relative electron densities on the ammonium and the imidazolium nitrogen centres. Despite this large change in chemical shift for the α-methylene protons little change is observed for the corresponding ω-methylene groups adjacent to the diisopropylamino moiety. Similarly, substitution of the $^i Pr_2N$ pendant amino group in $[^i Pr_2N(CH_2)_2N_{112}][NTf_2]$ with an Me_2N resulted in an increase in chemical shift of the corresponding ω methylene protons from 2.86 to 3.56 ppm due to the increased inductive effect. Increasing the linker chain length from two to six carbons in the case of $[Me_2N(CH_2)_6N_{112}][NTf_2]$ resulted in a significant decrease in ω chemical shift from 3.56 to 2.26 ppm. In contrast, little change in chemical shift was observed for α and ω methylene protons with both the ethereal linker type ionic liquids $[^i Pr_2N(CH_2)_2O(CH_2)_2N_{112}][NTf_2]$ and $[^i Pr_2N(CH_2)_2(OCH_2CH_2)_2N_{112}][NTf_2]$, however, in both these ionic liquids the ω methylene protons were found to overlap with the corresponding methylene protons in the linker.

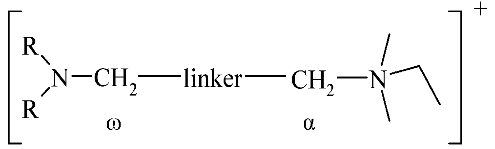
The non-nucleophilicity of the Hünig's base ($^i Pr_2N$) unit was demonstrated by the inability to form complexes with transition metal ions such as cobalt(II) and copper(II), as seen by lack of visual colouration. In contrast, the Me_2N unit formed a coloured complex with copper(II), demonstrating the nucleophilic nature of this amino moiety.

Table 1 Viscosity and density data at 25 °C and melting point as a function of the type of base-tethered ionic liquid

Ionic liquid	Melting point/°C	Viscosity/cP	Density/g cm^{-3}
$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{mim}][\mathrm{NTf}_2]$	33[a]	417	1.354
$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$	−73	540	1.300
$[\mathrm{Me}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$	23	129[b]	1.320[b]
$[\mathrm{Me}_2\mathrm{N}(\mathrm{CH}_2)_6\mathrm{N}_{112}][\mathrm{NTf}_2]$	−59	475	1.319
$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{O}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$	−77	389	1.277
$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2(\mathrm{OCH}_2\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$	−82	195	1.247

[a] Supercooled with a freezing point of −10 °C. [b] Measured at 35 °C.

Table 2 Effect of ionic liquid cation structure on the methylene proton shift for the α and ω species



Ionic liquid	δ_ω/ppm	δ_α/ppm
$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{mim}][\mathrm{NTf}_2]$	2.78	4.11
$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$	2.86	3.24
$[\mathrm{Me}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$	3.56	3.56
$[\mathrm{Me}_2\mathrm{N}(\mathrm{CH}_2)_6\mathrm{N}_{112}][\mathrm{NTf}_2]$	2.26	3.37
$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{O}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$	2.62	3.39–3.53[a]
$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2(\mathrm{OCH}_2\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$	2.64	3.49–3.53[a]

[a] Overlap with the methylene protons in the linker.

The relative base strength of these ionic liquids was measured using universal indicator.[24] It should be noted that universal indicator is a mixture of acids and bases and that the ionic liquid competes with the proton with these compounds. Therefore, the changes are relative and cannot be related to pK_a values. Whilst the change in alkyl chain length in a series of imidazolium, ammonium, pyrrolidinium and pyridinium ionic liquids had little effect on the change in polarity,[25] a significant change in the response to the indicator was found for the ionic liquids reported herein. Fig. 1 shows the electronic absorption spectra of the universal indicator as a function of the base-tethered ionic liquid structure. The electronic absorption spectra give an indication of how the base strength of the pendant amino group varies with chain length and the type of chain, alkyl or ethereal, employed. In the spectra, two absorption bands are observed; one at 400–460 nm corresponding to the protonated state of indicator dye and one at 620–640 nm corresponding to the free base form of the dye.[26] No significant change in the electronic absorption spectra is observed between the equivalent ammonium and imidazolium ionic liquids studied, *i.e.* $[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$ (Fig. 1b) and $[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{mim}][\mathrm{NTf}_2]$ (Fig. 1c), with both ionic liquids showing similar spectra to that found for $[\mathrm{C}_4\mathrm{mim}][\mathrm{NTf}_2]$, see Fig. 1a. However, in general, with increasing chain length the proportion of the longer wavelength band increases showing increasing proton transfer from the dye to the ionic liquid, Fig. 1d–1f. This can be explained by the fact that when the tethered amine is protonated, electronic repulsion between two positive centres within the cation decreases with increasing chain length leading to a stabilisation of the dication. Furthermore, a solvatochromic shift in the longer wavelength band[27] is also observed associated with the type of ionic liquid showing that the basicity of the ionic liquids studied follows the trend:

$$[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2(\mathrm{OCH}_2\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2] > [^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{O}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2] \approx [\mathrm{Me}_2\mathrm{N}(\mathrm{CH}_2)_6\mathrm{N}_{112}][\mathrm{NTf}_2] > [^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2] \approx [^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{mim}][\mathrm{NTf}_2]$$

As well as the basicity of an ionic liquid increasing with the number of atoms separating the two nitrogen atoms, changing the separator from an alkyl chain to one containing ether linkages also increases the basicity of the ionic liquid. In this case, it is thought that the ether groups stabilise the protonated tethered amine base *via* an intramolecular hydrogen bonded complex as shown in Scheme 4.

The variation in basicity of the ionic liquids for reactions was examined using the Heck and Knoevenagel reactions, Scheme 5. The Heck reaction between 2-methylprop-2-en-1-ol and 4-*tert*-butyliodobenzene was examined at 95 °C using

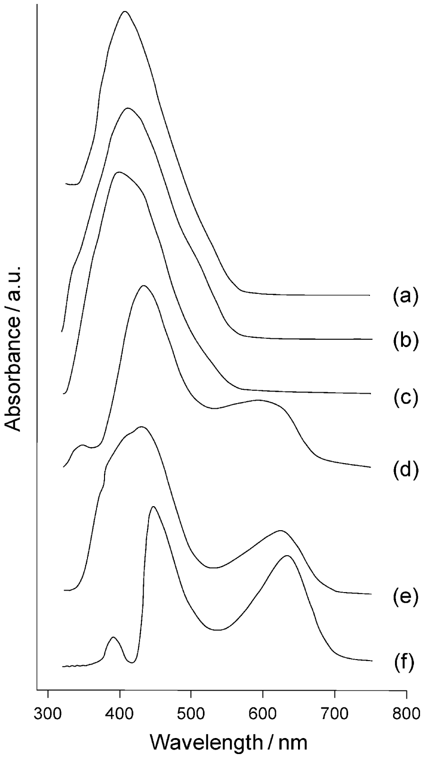
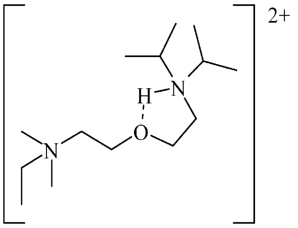


Fig. 1 UV/vis spectra of the universal indicator in (a) $[\mathrm{C}_4\mathrm{mim}][\mathrm{NTf}_2]$, (b) $[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$, (c) $[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{mim}][\mathrm{NTf}_2]$, (d) $[\mathrm{Me}_2\mathrm{N}(\mathrm{CH}_2)_6\mathrm{N}_{112}][\mathrm{NTf}_2]$, (e) $[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{O}(\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$ and (f) $[^i\mathrm{Pr}_2\mathrm{N}(\mathrm{CH}_2)_2(\mathrm{OCH}_2\mathrm{CH}_2)_2\mathrm{N}_{112}][\mathrm{NTf}_2]$.



Scheme 4 Stabilisation of the tethered protonated tethered amine *via* the formation of a intramolecular hydrogen bonded complex $[^i\mathrm{Pr_2N(CH_2)_2O(CH_2)_2N_{112}}][\mathrm{NTf_2}]$.

palladium(II) ethanoate as the catalyst using $[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}]$ and $[^i\mathrm{Pr_2N(CH_2)_2O(CH_2)_2N_{112}}][\mathrm{NTf_2}]$. The conversion to 3-(4-*tert*-butylphenyl)-2-methylpropanal (β-Lilial®) was ~32% after 10 h using $[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}]$ as the reaction medium compared with 84% in $[^i\mathrm{Pr_2N(CH_2)_2O(CH_2)_2N_{112}}][\mathrm{NTf_2}]$. These results match the relative basicity of the ionic liquids using universal indicator. A direct comparison of the Heck reaction using the free Hünig's base under solventless conditions, maintaining the same substrate to base ratio as used for the ionic liquid systems, showed a conversion of 39% demonstrating the greater catalytic activity of the functionalised ionic liquids.[28] The selectivity between 3-(4-*tert*-butylphenyl)-2-methylpropanal and 2-(4-*tert*-butylphenyl)-3-methylpropanal (α-Lilial®) was found to be >95% with respect to β-Lilial® and was invariant with the basicity of the ionic liquid-base used.

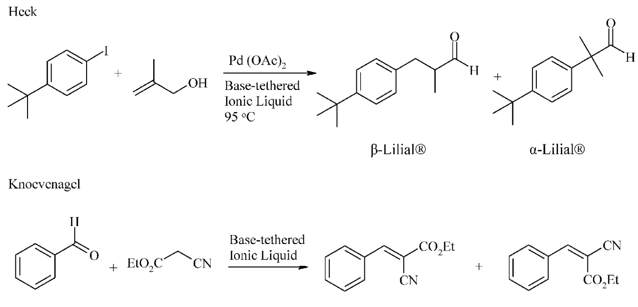
Similarly the Knoevenagel reaction was carried out in the base-tethered ionic liquids and compared with free Hünig's base dissolved in $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ obtaining near quantitative yields (Table 3). Interestingly, although $[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}]$, $[^i\mathrm{Pr_2N(CH_2)_2N_{112}}][\mathrm{NTf_2}]$ and $[\mathrm{Me_2N(CH_2)_2N_{112}}][\mathrm{NTf_2}]$ were too weakly basic to deprotonate the dye present in the universal indicator, the basicity was sufficient to catalyse the Knoevenagel reaction, albeit slowly. Again the rate of reaction was found to follow the basicity of the ionic liquid with $[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}] < [^i\mathrm{Pr_2N(CH_2)_2N_{112}}][\mathrm{NTf_2}] < [\mathrm{Me_2N(CH_2)_2N_{112}}][\mathrm{NTf_2}] < [\mathrm{Me_2N(CH_2)_6N_{112}}][\mathrm{NTf_2}] < [^i\mathrm{Pr_2N(CH_2)_2O(CH_2)_2N_{112}}][\mathrm{NTf_2}] < [^i\mathrm{Pr_2N(CH_2)_2(OCH_2CH_2)_2N_{112}}][\mathrm{NTf_2}]$. Importantly, although the universal indicator shows the general trends, the Knoevenagel reaction is a more sensitive probe of the basicity and shows that $[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}]$ is less basic than $[^i\mathrm{Pr_2N(CH_2)_2N_{112}}][\mathrm{NTf_2}]$, for example. This may be understood as the proton at the C(2) position on the imidazolium ring in $[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}]$ is much more acidic than the protons of the methyl or methylene groups on the ammonium centre. Therefore, as the rest of the structure is invariant the basicity of the $[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}]$ ionic liquid is expected to be weaker than that found for $[^i\mathrm{Pr_2N(CH_2)_2N_{112}}][\mathrm{NTf_2}]$. While none of the ionic liquids tested were more active than free Hünig's base in $[\mathrm{C_4mim}][\mathrm{NTf_2}]$, both $[^i\mathrm{Pr_2N(CH_2)_2O(CH_2)_2N_{112}}][\mathrm{NTf_2}]$ and $[^i\mathrm{Pr_2N(CH_2)_2(OCH_2CH_2)_2N_{112}}][\mathrm{NTf_2}]$ did show comparable reactivity and, importantly, the base-tethered ionic liquid allowed facile recycle of the base by solvent extraction.[29] In comparison, the workup of the reaction mixture when using the free Hünig's base dissolved in $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ by extraction or distillation leads to significant loss of the amine and loss of activity. A more detailed study of the base catalysed Knoevenagel condensation reaction using $[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}]$, $[^i\mathrm{Pr_2N(CH_2)_2O(CH_2)_2N_{112}}][\mathrm{NTf_2}]$ and $[^i\mathrm{Pr_2N(CH_2)_2(OCH_2CH_2)_2N_{112}}][\mathrm{NTf_2}]$ shows that the relative activities shown for the reaction between benzaldehyde and ethyl cyanoethanoate are found for a wide range of substrates.[29]

Conclusions

A versatile synthesis for a series of base-tethered ionic liquids has been reported which can be used as effective catalysts for the Heck and the Knoevenagel reactions. By changing the structure of the cation and length/type of spacer between the pendant amino group and the cation centre, the basicity may be varied systematically. Both increasing the spacer length as well as incorporating ether linkages into the spacer resulted in higher basicity. This was due to a stabilisation of the protonated amine *via* decreased coulombic repulsion and the formation of intramolecular hydrogen bonded complexes.

Experimental

All reagents and solvents (*ex* Aldrich) were used as received except for 1-methylimidazole which was distilled from calcium hydride prior to use. ^{1}H- and ^{13}C-NMR spectra were measured using a Bruker Avance AVX 300 at ambient temperature or a Bruker Avance DRX 500 spectrometer at 27 °C. All samples were run with tetramethylsilane added as an internal standard. The phase transition temperatures were determined by DSC measurements with a Perkin-Elmer Pyris 1 DSC equipped with a liquid nitrogen cryostatic cooler. The heating and cooling rates were both 10 °C $\mathrm{min^{-1}}$ and the melting point and glass



Scheme 5 Homogeneous Heck coupling and Knoevenagel condensations carried out in the base-tethered ionic liquids.

Table 3 Comparison of the conversion for the Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate at room temperature under homogeneous reaction conditions as a function of the ionic liquid catalyst used at 10 mol% with respect to carbonyl compound

Ionic liquid catalyst	Time	% Conversion
$[\mathrm{C_4mim}][\mathrm{NTf_2}]$/Hünig's base	20 min	100
$[^i\mathrm{Pr_2N(CH_2)_2mim}][\mathrm{NTf_2}]$	24 h	12
$[^i\mathrm{Pr_2N(CH_2)_2N_{112}}][\mathrm{NTf_2}]$	60 min	50
$[\mathrm{Me_2N(CH_2)_2N_{112}}][\mathrm{NTf_2}]$	60 min	63
$[\mathrm{Me_2N(CH_2)_6N_{112}}][\mathrm{NTf_2}]$	60 min	87
$[^i\mathrm{Pr_2N(CH_2)_2O(CH_2)_2N_{112}}][\mathrm{NTf_2}]$	20 min	82
$[^i\mathrm{Pr_2N(CH_2)_2(OCH_2)_2N_{112}}][\mathrm{NTf_2}]$	20 min	91

transitions are defined as peak maxima. Calibration of the DSC was carried out with iridium samples. Mass spectrometry was carried out on a Micromass Autopsec X Series spectrometer. Microanalyses were carried out by A.S.E.P. (The Queen's University of Belfast) on a Perkin Elmer Series II CHNS/O Analyzer 2400. The densities were measured using an Anton Paar DMA density meter and the viscosities measured using a Brookfield DV-II + cone and plate viscometer. GC analysis was conducted on an Agilent 1320 using a RTX-5 (5% diphenyl–95% dimethyl polysiloxane) column.

Synthesis of the ionic liquids

1-Butyl-3-methylimidazolium bromide. 1-Methylimidazole (20.50 g, 0.25 mol) and 1-bromobutane (41.10 g, 0.3 mol) were heated under reflux for 24 h. The reaction mixture was washed with cold dry propanone (3 × 50 cm^3) and the solvent was removed *in vacuo* at 50 °C and further dried overnight at 65 °C under high vacuum yielding a white solid (50.37 g, 0.23 mmol, 93% yield).

^{1}H-NMR (300 MHz, d_3-ethanenitrile): δ/ppm = 0.89 (t, J = 7.3 Hz, 3H, Bu-CH$_3$); 1.28 (sextet, J = 7.5 Hz, 2H, CH$_2$); 1.80 (p, J = 7.4 Hz, 2H, CH$_2$); 3.91 (s, 3H, N$^+$-CH$_3$); 4.20 (q, J = 7.2 Hz, 2H, N-CH$_2$); 7.45 (t, J = 1.8 Hz, 1H), 7.53 (t, J = 1.7 Hz, 1H) (4-H and 5-H); 9.38 (s, 1H, 2-H).

1-Butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}-amide ([C$_4$mim][NTf$_2$]). 1-Butyl-3-methylimidazolium bromide (50.37 g, 0.23 mol) was dissolved in dichloromethane (100 cm^3) and a solution of lithium bis{(trifluoromethyl)sulfonyl}amide (73.12 g, 0.253 mol) in water (100 cm^3) was added. The organic phase was washed with water (6 × 100 cm^3) and the organic solvent was removed *in vacuo* at 40 °C. The ionic liquid was then dried overnight at 65 °C under high vacuum to obtain as a colourless liquid (92.50 g, 0.22 mol, 96% yield).

^{1}H-NMR (300 MHz, d_3-ethanenitrile): δ/ppm = 0.90 (t, J = 7.3 Hz, 3H, Bu-CH$_3$); 1.29 (sextet, J = 7.5 Hz, 2H, CH$_2$); 1.77 (p, J = 7.3 Hz, 2H, CH$_2$); 3.84 (s, 3H, N$^+$-CH$_3$); 4.11 (q, J = 7.2 Hz, 2H, N-CH$_2$); 7.35 (t, J = 1.8 Hz, 1H), 7.39 (t, J = 1.7 Hz, 1H) (4-H and 5-H); 8.44 (s, 1H, 2-H).

1-(2-Diisopropylaminoethyl)-3-methylimidazolium chloride. 1-Methylimidazole (3.99 g, 48.6 mmol) and 2-diisopropylaminoethyl chloride hydrochloride (10.21 g, 51.0 mmol) were dissolved in ethanenitrile (50 cm^3) and sodium carbonate (14.00 g, 132.1 mmol) was added. After heating under reflux for 24 h the mixture was filtered through Celite. The solvent was removed *in vacuo* at 50 °C and the residue was washed with diethyl ether (30 cm^3) and recrystallised from ethanenitrile (10 cm^3). After drying under high vacuum a white solid was obtained (11.62 g, 47.3 mmol, 97% yield).

^{1}H-NMR (300 MHz, d_3-ethanenitrile): δ/ppm = 0.89 (d, J = 6.6 Hz, 12H, ^{i}Pr-CH$_3$); 2.81 (t, J = 5.6 Hz, 2H, N-CH$_2$); 3.02 (q, J = 6.6 Hz, 2H, ^{i}Pr-CH); 3.91 (s, 3H, N$^+$-CH$_3$); 4.16 (t, J = 5.7 Hz, 2H, N$^+$-CH$_2$); 7.45 (t, J = 1.8 Hz, 1H), 7.53 (t, J = 1.7 Hz, 1H) (4-H and 5-H); 9.38 (s, 1H, 2-H).

1-(2-Diisopropylaminoethyl)-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([^{i}Pr$_2$N(CH$_2$)$_2$mim][NTf$_2$]). 1-(2-Diisopropylaminoethyl)-3-methylimidazolium chloride (7.58 g, 30.84 mmol) was dissolved in dichloromethane (50 cm^3) and a solution of lithium bis{(trifluoromethyl)sulfonyl}amide (9.71 g, 33.92 mmol) in water (10 cm^3) was added. The organic phase was washed with water (6 × 15 cm^3) and the solvent was removed *in vacuo* at 40 °C. The ionic liquid was then dried overnight at 65 °C under high vacuum to obtain a colourless liquid (14.19 g, 29.0 mmol, 94% yield).

Mp (DSC): 33 °C (supercooled, glass transition at −61 °C). ^{1}H-NMR (300 MHz, d-trichloromethane): δ/ppm = 0.88 (d, J = 6.6 Hz, 12H, ^{i}Pr-CH$_3$); 2.78 (t, J = 5.6 Hz, 2H, N-CH$_2$); 2.98 (q, J = 6.7 Hz, 2H, ^{i}Pr-CH); 3.92 (s, 3H, N$^+$-CH$_3$); 4.11 (t, J = 5.6 Hz, 2H, N$^+$-CH$_2$); 7.29 (t, J = 1.8 Hz, 1H), 7.37 (t, J = 1.7 Hz, 1H) (4-H and 5-H); 8.62 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d-trichloromethane): δ/ppm = 20.52 (^{i}Pr-CH$_3$); 36.20 (N-CH$_3$); 44.98, 47.86, 49.83 (NCH$_2$ and NCH); 118.89 (q, J_{CF} = 320 Hz, CF$_3$), 122.95, 123.35 (C$_4$ and C$_5$); 136.32 (C$_2$). Elemental analysis % calc. (% found): C 34.28 (34.37), H 4.93 (4.75), N 11.42 (11.17). MS FAB$^+$ m/z (% rel. intensity): 128 [^{i}Pr$_2$NEt]$^+$ (100), 210 [^{i}Pr$_2$N(CH$_2$)$_2$mim]$^+$ (68), 700 [(^{i}Pr$_2$N(CH$_2$)$_2$mim)$_2$NTf$_2$]$^+$ (<1). Viscosity at 25 °C: 417 cP. Density at 25 °C: 1.354 g cm^{-3}.

1-(2-Diisopropylaminoethyl)dimethylethylammonium chloride. Dimethylethylamine (3.51 g, 48.0 mmol) and 2-diisopropylaminoethyl chloride hydrochloride (10.06 g, 50.3 mmol) were dissolved in ethanenitrile (50 cm^3) and sodium carbonate (14.0 g, 132.1 mmol) was added. After heating under reflux for 24 h the mixture was filtered through Celite. The solvent was removed *in vacuo* at 50 °C and the residue was washed with diethyl ether (50 cm^3) and recrystallised from ethanenitrile (10 cm^3). After drying overnight under high vacuum at 60 °C a white solid was obtained (11.16 g, 46.9 mmol, 98% yield).

^{1}H-NMR (300 MHz, d_3-ethanenitrile): δ/ppm = 0.97 (d, J = 7.1 Hz, 12H, ^{i}Pr-CH$_3$); 1.37 (t, J = 7.2 Hz, 3H, Et-CH$_3$); 2.87 (t, J = 6.9 Hz, 2H, N-CH$_2$); 3.03 (q, J = 7.1 Hz, 2H, ^{i}Pr-CH); 3.14 (s, 6H, N$^+$-CH$_3$); 3.26 (t, J = 6.7 Hz, 2H, N$^+$-CH$_2$); 3.39 (q, J = 7.1 Hz, 2H, CH$_2$-Me).

1-(2-Diisopropylaminoethyl)dimethylethylammonium bis{(trifluoromethyl)sulfonyl}amide ([^{i}Pr$_2$N(CH$_2$)$_2$N$_{112}$][NTf$_2$]). 1-(2-Diisopropylaminoethyl)dimethylethylammonium chloride (7.68 g, 32.3 mmol) was dissolved in dichloromethane (50 cm^3) and a solution of lithium bis{(trifluoromethyl)sulfonyl}amide (9.71 g, 33.9 mmol) in water (10 cm^3) was added. The organic phase was washed with water (6 × 15 cm^3) and the solvent was removed *in vacuo* at 40 °C. The ionic liquid was then dried overnight at 65 °C under high vacuum to obtain a colourless liquid (14.66 g, 30.4 mmol, 94% yield).

Mp (DSC): −73 °C. ^{1}H-NMR (300 MHz, d-trichloromethane): δ/ppm = 0.99 (d, J = 7.2 Hz, 12H, ^{i}Pr-CH$_3$); 1.38 (t, J = 7.3 Hz, 3H, Et-CH$_3$); 2.86 (t, J = 7.0 Hz, 2H, N-CH$_2$); 3.01 (q, J = 7.1 Hz, 2H, ^{i}Pr-CH); 3.11 (s, 6H, N$^+$-CH$_3$); 3.24 (t, J = 6.5 Hz, 2H, N$^+$-CH$_2$); 3.39 (q, J = 7.2 Hz, 2H, CH$_2$-Me). ^{13}C-NMR (75 MHz, d-trichloromethane): δ/ppm = 20.52 (^{i}Pr-CH$_3$); 36.20 (N-CH$_3$); 44.98, 47.86, 49.83 (NCH$_2$ and NCH); 119.88 (q, J_{CF} = 320 Hz, CF$_3$), 122.95, 123.35 (C_4 and C_5); 136.32 (C_2). Elemental analysis % calc. (% found): C 34.92 (34.94), H 6.07 (6.06), N 8.73 (8.76). MS FAB$^+$ m/z (% rel. intensity): 128 $[{}^i\mathrm{Pr_2NEt}]^+$ (100), 201 $[{}^i\mathrm{Pr_2N(CH_2)_2N_{112}}]^+$ (19), 682 $[({}^i\mathrm{Pr_2N(CH_2)_2N_{112}})_2\mathrm{NTf_2}]^+$ (<1). Viscosity at 25 °C: 540 cP. Density at 25 °C: 1.300 g cm^{-3}.

1-(2-Dimethylaminoethyl)dimethylethylammonium chloride. 2-(Dimethylaminoethyl) chloride hydrochloride (14.4 g, 0.1 mol) and dimethylethylamine (24.9 g, 0.3 mol) were dissolved in ethanenitrile (100 cm^3) and sodium carbonate (21.6 g, 0.20 mol) was added. After heating under reflux for 24 h the mixture was filtered through Celite. The solvent was removed *in vacuo* at 50 °C and the residue was washed with diethyl ether (70 cm^3) and recrystallised from ethanenitrile (10 cm^3). After drying overnight at 60 °C under high vacuum, a white solid was obtained (16.96 g, 94.0 mmol, 94% yield).

^{1}H-NMR (300 MHz, d_3-ethanenitrile): δ/ppm = 1.32 (m, 3H, $\mathrm{CH_2\text{-}CH_3}$); 2.26 (s, 6H, $\mathrm{N\text{-}CH_3}$); 2.67 (m, 2H, $\mathrm{CH_2\text{-}CH_3}$); 3.18 (s, 6H, $\mathrm{N^+\text{-}CH_3}$); 3.55 (m, 4H, $\mathrm{N^+\text{-}CH_2CH_2N}$).

1-(2-Dimethylaminoethyl)dimethylethylammonium bis{(trifluoromethyl)sulfonyl}amide ($[\mathbf{Me_2N(CH_2)_2N_{112}}][\mathbf{NTf_2}]$). 1-(2-Dimethylaminoethyl)dimethylethylammonium chloride (6.50 g, 36.0 mmol) was dissolved in dichloromethane (50 cm^3) and a solution of lithium bis{(trifluoromethyl)sulfonyl}amide (11.26 g, 39.3 mmol) in water (40 cm^3) was added. The organic phase was washed with water (6 × 15 cm^3) and the solvent was removed *in vacuo* at 40 °C. The ionic liquid was then dried overnight at 65 °C under high vacuum to obtain a colourless liquid (14.39 g, 33.9 mmol, 94% yield).

Mp (DSC): 23 °C. ^{1}H-NMR (300 MHz, *d*-trichloromethane): δ/ppm = 1.34 (m, 3H, $\mathrm{CH_2\text{-}CH_3}$); 2.26 (s, 6H, $\mathrm{N\text{-}CH_3}$); 2.69 (m, 2H, $\mathrm{CH_2\text{-}CH_3}$); 3.20 (s, 6H, $\mathrm{N^+\text{-}CH_3}$); 3.56 (m, 4H, $\mathrm{N^+\text{-}CH_2CH_2N}$). ^{13}C-NMR (75 MHz, *d*-trichloromethane): δ/ppm = 8.23 (Et-$\mathrm{CH_3}$); 45.62 ($\mathrm{N\text{-}CH_3}$); 51.46 ($\mathrm{N\text{-}CH_2}$); 53.21 ($\mathrm{N^+\text{-}CH_3}$); 60.89 ($\mathrm{N^+\text{-}CH_2CH_3}$); 61.76 ($\mathrm{N^+\text{-}CH_2CH_2}$); 119.93 (q, J_{CF} = 321 Hz, $\mathrm{CF_3}$). Elemental analysis % calc. (% found): C 28.24 (28.65), H 4.94 (4.81), N 9.88 (9.37). MS FAB$^+$ m/z (% rel. intensity): 72 $[\mathrm{Me_2N(CH_2)_2}]^+$ (29), 145 $[\mathrm{Me_2N(CH_2)_2N_{112}}]^+$ (100). MS ES$^-$ m/z (% rel. intensity): 147 $[\mathrm{NTf^-}]$ (11), 280 $[\mathrm{NTf_2^-}]$ (100). Viscosity at 35 °C: 129 cP. Density at 35 °C: 1.320 g cm^{-3}.

1-(6-Dimethylaminohexyl)dimethylethylammonium iodide. *N*,*N*,*N*′,*N*′-Tetramethyl-1,6-hexanediamine (17.89 g, 103.8 mmol) was dissolved in diethyl ether (400 cm^3) and iodoethane (16.19 g, 103.8 mmol) was added dropwise. The solution was stirred in the dark at room temperature for two days, during which the formation of a white precipitate was observed. The precipitate was collected by filtration, washed with diethyl ether (50 cm^3) and dried under high vacuum. It then was suspended in trichloromethane (200 cm^3) and filtered again to remove traces of the dialkylated side product. The filtrate contained only monoalkylated product. After drying under high vacuum at 60 °C, an off-white powder was obtained (8.94 g, 27.2 mmol, 26% yield).

^{1}H-NMR (300 MHz, *d*-trichloromethane): δ/ppm = 1.20–1.46 (m, 9H, $\gamma,\delta,\varepsilon$-$\mathrm{CH_2}$ and $\mathrm{N^+\text{-}CH_2}CH_3$); 1.59–1.75 (m, 2H, $\mathrm{N^+\text{-}CH_2}CH_2$); 2.12 (s, 6H, $\mathrm{N\text{-}CH_3}$); 2.16 (t, J = 7.3 Hz, 2H, $\mathrm{N\text{-}CH_2}$); 3.27 (s, 6H, $\mathrm{N^+\text{-}CH_3}$); 3.39–3.52 (m, 2H, $\mathrm{N^+}$-$CH_2\mathrm{CH_3}$), 3.61 (q, J = 7.2 Hz, 2H, $\mathrm{N^+}$-$CH_2\mathrm{CH_2}$).

1-(6-Dimethylaminohexyl)dimethylethylammonium bis{(trifluoromethyl)sulfonyl}amide ($[\mathbf{Me_2N(CH_2)_6N_{112}}][\mathbf{NTf_2}]$). 1-(6-Dimethylaminohexyl)dimethylethylammonium iodide (4.67 g, 12.2 mmol) was dissolved in dichloromethane (50 cm^3) and a solution of lithium bis{(trifluoromethyl)sulfonyl}amide (3.85 g, 13.4 mmol) in water (10 cm^3) was added. The organic phase was washed with water (5 × 10 cm^3), dried with sodium sulfate (2 g) and the solvent was removed *in vacuo* at 40 °C. The ionic liquid was then dried overnight at 65 °C under high vacuum to obtain a pale yellow liquid (5.28 g, 11.0 mmol, 90% yield).

Mp (DSC): −59 °C. ^{1}H-NMR (300 MHz, *d*-trichloromethane): δ/ppm = 1.27–1.55 (m, 9H, $\gamma,\delta,\varepsilon$-$\mathrm{CH_2}$ and $\mathrm{N^+\text{-}CH_2}CH_3$); 1.62–1.80 (m, 2H, $\mathrm{N^+\text{-}CH_2}CH_2$); 2.22 (s, 6H, $\mathrm{N\text{-}CH_3}$); 2.26 (t, J = 7.3 Hz, 2H, $\mathrm{N\text{-}CH_2}$); 3.02 (s, 6H, $\mathrm{N^+\text{-}CH_3}$); 3.15–3.26 (m, 2H, $\mathrm{N^+\text{-}CH_2CH_3}$), 3.37 (q, J = 7.3 Hz, 2H, $\mathrm{N^+}$-$CH_2\mathrm{CH_2}$). ^{13}C-NMR (75 MHz, *d*-trichloromethane): δ/ppm = 8.22 (Et-$\mathrm{CH_3}$); 22.61, 26.00, 26.83, 27.33 ($\beta,\gamma,\delta,\varepsilon$-$\mathrm{CH_2}$); 45.49 ($\mathrm{N\text{-}CH_3}$); 50.46 ($\mathrm{N\text{-}CH_2}$); 59.41 ($\mathrm{N^+\text{-}CH_3}$); 60.03 ($\mathrm{N^+\text{-}CH_2CH_3}$); 64.15 ($\mathrm{N^+\text{-}CH_2CH_2}$); 119.93 (q, J_{CF} = 321 Hz, $\mathrm{CF_3}$). Elemental analysis % calc. (% found): C 34.92 (32.35), H 6.07 (5.54), N 8.73 (8.07). MS ES$^+$ m/z (% rel. intensity): 128 $[\mathrm{Me_2N(CH_2)_6}]^+$ (37), 201 $[\mathrm{Me_2N(CH_2)_6N_{112}}]^+$ (100). MS ES$^-$ m/z (% rel. intensity): 147 $[\mathrm{NTf^-}]$ (9), 280 $[\mathrm{NTf_2^-}]$ (100). Viscosity at 25 °C: 475 cP. Density at 25 °C: 1.319 g cm^{-3}.

(5-Diisopropylamino-3-oxapentyl)dimethylamine. Into a solution of 2-dimethylaminoethanol (19.61 g, 220 mmol) in dry tetrahydrofuran (100 cm^3) at 0 °C was added sodium hydride (60% dispersion in mineral oil, 10.0 g, 250 mmol) under a dinitrogen atmosphere. After stirring for 10 min at 0 °C 2-diisopropylaminoethyl chloride hydrochloride (20.0 g, 100 mmol) was added slowly. The reaction mixture was heated under reflux for 4 h and then quenched by dropwise addition of water (20 cm^3) at 0 °C. After evaporation of tetrahydrofuran *in vacuo* at 50 °C, the reaction mixture was diluted with water (30 cm^3) and extracted with dichloromethane (3 × 50 cm^3). The combined organic extracts were dried with sodium sulfate (5 g) and the solvent was removed *in vacuo* at 40 °C. The crude product was purified by Kugelrohr distillation; 19.19 g (89 mmol, 89% yield) of a colourless liquid were obtained.

^{1}H-NMR (300 MHz, *d*-trichloromethane): δ/ppm = 1.00 (d, J = 6.6 Hz, 12H, ${}^i\mathrm{Pr\text{-}CH_3}$); 2.27 (s, 6H, $\mathrm{NCH_3}$); 2.49 (t, J = 5.8 Hz, 2H, $\mathrm{NCH_2}$); 2.62 (t, J = 7.6 Hz, 2H, $\mathrm{NCH_2}$); 2.98 (t, J = 6.5 Hz, 2H, ${}^i\mathrm{Pr\text{-}CH}$); 3.39 (t, J = 8.0 Hz, 2H, $\mathrm{OCH_2}$); 3.54 (t, J = 5.8 Hz, 2H, $\mathrm{OCH_2}$). ^{13}C-NMR (75 MHz, *d*-trichloromethane): δ/ppm = 20.81 (${}^i\mathrm{Pr\text{-}CH_3}$); 44.79 ($\mathrm{NCH_2}$); 46.1 ($\mathrm{NCH_3}$); 49.54 ($\mathrm{NCH_2}$); 50.06 ($\mathrm{Me_2NCH_2}$); 69.28, 72.88 ($\mathrm{OCH_2}$). MS EI$^+$ m/z (% rel. intensity): 149 $[{}^i\mathrm{Pr_2NCH_2CH_2O\text{-}CH_2CH_2NH_2} + \mathrm{H_2O}]$ (100); 188 $[{}^i\mathrm{Pr_2NCH_2CH_2OCH_2CH}]$ (53); 215 $[\mathrm{M^+} - \mathrm{H}]$ (52).

(5-Diisopropylamino-3-oxapentyl)dimethylethylammonium bromide. (5-Diisopropylamino-3-oxapentyl)dimethylamine (14.85 g, 68.6 mmol) was heated under reflux with bromoethane (18.35 g, 0.172 mol) in ethanenitrile (20 cm^3) for 30 h. After evaporation of the solvent and excess bromoethane *in vacuo* at 60 °C, the product was recrystallised from ethanenitrile (10 cm^3). After filtration and drying under high vacuum a pale yellow powder was obtained (19.87 g, 61.1 mmol, 89% yield).

^{1}H-NMR (300 MHz, d_4-methanol): δ/ppm = 1.04 (d, J = 6.6 Hz, 12H, ^{i}Pr-CH$_3$); 1.38 (t, J = 7.2 Hz, 3H, Et-CH$_3$); 2.67 (t, J = 6.7 Hz, 2H, N-CH$_2$); 3.04 (p, J = 6.6 Hz, 2H, ^{i}Pr-CH); 3.15 (s, 6H, N$^+$-CH$_3$); 3.42–3.61 (m, 6H, O-CH$_2$ and N$^+$-CH$_2$) 3.83–3.93 (m, 2H, O-CH$_2$).

(5-Diisopropylamino-3-oxapentyl)dimethylethylammonium bis{(trifluoromethyl)sulfonyl}amide ([^{i}Pr$_2$N(CH$_2$)$_2$O(CH$_2$)$_2$N$_{112}$][NTf$_2$]). Lithium bis{(trifluoromethyl)sulfonyl}amide (7.3 g, 25.5 mmol) in water (10 cm^3) was added to a solution of (5-diisopropylamino-3-oxapentyl)dimethylethylammonium bromide (7.55 g, 23.3 mmol) in dichloromethane (100 cm^3). After extraction of the organic phase with water (5 × 20 cm^3), dichloromethane was removed *in vacuo* at 40 °C. The product was further purified by filtration through charcoal as a solution in ethanenitrile (30 cm^3). After removal of the solvent and drying overnight in high vacuum at 60 °C, the product was obtained as a pale yellow liquid (11.35 g, 21.6 mmol, 93% yield).

Mp (DSC): −77 °C. ^{1}H-NMR (300 MHz, *d*-trichloromethane): δ/ppm = 0.99 (d, J = 6.6 Hz, 12H, ^{i}Pr-CH$_3$); 1.38 (t, J = 7.4 Hz, 3H, Et-CH$_3$); 2.62 (t, J = 6.5 Hz, 2H, N-CH$_2$); 3.01 (p, J = 6.6 Hz, 2H, ^{i}Pr-CH); 3.09 (s, 6H, N$^+$-CH$_3$); 3.39–3.53 (m, 6H, O-CH$_2$ and N$^+$CH$_2$); 3.79–3.88 (m, 2H, O-CH$_2$). ^{13}C-NMR (75 MHz, *d*-trichloromethane): δ/ppm = 8.33 (Et-CH$_3$); 20.68 (^{i}Pr-CH$_3$); 44.65 (^{i}Pr-CH); 49.47 (N$^+$-CH$_3$); 51.28 (N-CH$_2$); 62.78, 63.26 (N$^+$-CH$_2$); 64.56, 72.41 (O-CH$_2$); 119.92 (q, J_{CF} = 321 Hz, CF$_3$). Elemental analysis % calc. (% found): C 36.56 (35.81), H 6.33 (6.18), N 8.00 (8.10). MS ES$^+$ *m*/*z* (% rel. intensity): 172 [^{i}Pr$_2$N(CH$_2$)$_2$-O(CH$_2$)$_2$]$^+$ (37), 245 [^{i}Pr$_2$N(CH$_2$)$_2$O(CH$_2$)$_2$N$_{112}$]$^+$ (100). MS ES$^-$ *m*/*z* (% rel. intensity): 147 NTf$^-$ (9), 280 NTf$_2^-$ (100). Viscosity at 25 °C: 389 cP. Density at 25 °C: 1.277 g cm^{-3}.

(8-Diisopropylamino-3,6-dioxaoctyl)dimethylamine. Into a solution of 2-[2-(dimethylamino)ethoxy]ethanol (42.60 g, 0.4 mol) in dry tetrahydrofuran (300 cm^3) at 0 °C was slowly added sodium hydride (60% dispersion in mineral oil, 20.0 g, 0.5 mol) and the mixture was stirred for one hour. 2-Diisopropylaminoethyl chloride hydrochloride (60.0 g, 0.36 mol) was slowly added. The reaction mixture was heated under reflux for 24 h and then quenched by dropwise addition of water (40 cm^3) at 0 °C. After evaporation of tetrahydrofuran *in vacuo* at 50 °C, the reaction mixture was diluted with water (30 cm^3) and extracted with dichloromethane (3 × 50 cm^3). The combined organic extracts were dried with sodium sulfate (5 g) and the solvent was removed *in vacuo* at 40 °C. The crude product was purified by Kugelrohr distillation at 140 °C at 0.01 bar; (52.08 g, 0.2 mol, 50% yield) of a colourless liquid was obtained.

^{1}H-NMR (300 MHz, *d*-trichloromethane): δ/ppm = 0.99 (d, J = 6.7 Hz, 12H, ^{i}Pr-CH$_3$); 2.26 (s, 6H, NCH$_3$); 2.82 (t, J = 2.6 Hz, 2H, (CH$_3$)$_2$N*CH*$_2$); 2.88 (h, J = 6.7 Hz, 2H, ^{i}Pr-CH); 3.01 (t, J = 2.7 Hz, 2H, ^{i}Pr$_2$N*CH*$_2$); 3.61 (t, J = 2.6 Hz, 2H, OCH$_2$); 3.64 (t, J = 4.8 Hz, 2H, OCH$_2$); 3.66–3.68 (m, 4H, OCH$_2$CH$_2$O)

Ethyl(8-diisopropylamino-3,6-dioxaoctyl)dimethylammonium bromide. (8-Diisopropylamino-3,6-dioxaoctyl)dimethylamine (10.0 g, 40 mmol) was heated under reflux with bromoethane (10.8 g, 0.1 mol) in ethanenitrile (20 cm^3) for 30 h. After evaporation of the solvent and excess bromoethane *in vacuo* at 60 °C, the product was recrystallised from ethanenitrile (10 cm^3). After drying under high vacuum at 60 °C overnight a yellow powder was obtained (12.31 g, 33.5 mmol, 84% yield).

^{1}H-NMR (300 MHz, d_4-methanol): δ/ppm = 1.04 (d, J = 6.6 Hz, 12H, ^{i}Pr-CH$_3$); 1.38 (t, J = 7.2 Hz, 3H, Et-CH$_3$); 2.67 (t, J = 6.7 Hz, 2H, N-CH$_2$); 3.04 (p, J = 6.6 Hz, 2H, ^{i}Pr-CH); 3.15 (s, 6H, N$^+$-CH$_3$); 3.42–3.61 (m, 6H, O-CH$_2$ and N$^+$-CH$_2$); 3.83–3.93 (s, 4H, OCH$_2$CH$_2$O).

Ethyl(8-diisopropylamino-3,6-dioxaoctyl)dimethylammonium bis{(trifluoromethyl)sulfonyl}imide ([^{i}Pr$_2$N(CH$_2$)$_2$(OCH$_2$CH$_2$)$_2$N$_{112}$]-[NTf$_2$]). Lithium bis{(trifluoromethyl)sulfonyl}amide (6.42 g, 22.4 mmol) in water (10 cm^3) was added to a solution of ethyl(8-diisopropylamino-3,6-dioxaoctyl)dimethylammonium bromide (7.55 g, 21.3 mmol) in dichloromethane (100 cm^3). After extraction of the organic phase with water (5 × 20 cm^3), dichloromethane was removed *in vacuo* at 40 °C. The product was further purified by filtration through charcoal as a solution in ethanenitrile (30 cm^3). After removal of the solvent *in vacuo* and drying in high vacuum at 60 °C overnight, the product was obtained as a pale yellow liquid (11.85 g, 19.8 mmol, 93% yield).

Mp (DSC): −82 °C. ^{1}H-NMR (300 MHz, *d*-trichloromethane): δ/ppm = 1.04 (d, J = 6.6 Hz, 12H, ^{i}Pr-CH$_3$); 1.38 (t, J = 7.5 Hz, 3H, Et-CH$_3$); 2.64 (t, J = 7.5 Hz, 2H, N-CH$_2$); 3.01 (p, J = 6.6 Hz, 2H, ^{i}Pr-CH); 3.13 (s, 6H, N$^+$-CH$_3$); 3.43 (t, 2H, J = 7.0 Hz, N-CH$_2$-*CH*$_2$); 3.49–3.53 (m, 4H, O-CH$_2$ and N$^+$-CH$_2$); 3.60 (t, 2H, J = 7.0 Hz, N$^+$-CH$_2$*CH*$_2$), 3.91 (s, 4H, O-CH$_2$-CH$_2$-O). ^{13}C-NMR (75 MHz, *d*-trichloromethane): δ/ppm = 7.44 (Et-CH$_3$); 19.67 (^{i}Pr-CH$_3$); 44.15 (N-CH$_2$) 49.30 (^{i}Pr-CH); 49.30 (N$^+$-CH$_3$); 50.43 (N-CH$_2$); 60.93, 62.33 (N$^+$-CH$_2$); 64.56, 72.41 (O-CH$_2$); 119.92 (q, J_{CF} = 321 Hz, CF$_3$). Elemental analysis % calc. (% found): C 37.74 (37.95), H 6.45 (6.25), N 7.43 (7.38). MS ES$^+$ *m*/*z* (% rel. intensity): 172 [M − NEtMe$_2$]$^+$ (37), 245 [^{i}Pr$_2$N(CH$_2$)$_2$-(OCH$_2$)$_2$N$_{112}$]$^+$ (100). MS ES$^-$ *m*/*z* (% rel. intensity): 147 NTf$^-$ (9), 280 NTf$_2^-$ (100). Viscosity at 25 °C: 195 cP. Density at 25 °C: 1.247 g cm^{-3}.

Procedure used to probe the ionic liquid basicity using universal indicator

An ethanolic solution (0.040 g) of universal indicator (Merck-BDH) was dissolved in ionic liquid (1 cm^3) and the alcohol solvent removed *in vacuo*. The electronic absorption spectrum of the pure ionic liquid was subtracted as a background in the measurement of each ionic liquid/indicator solution. It should be noted that the presence of water can have a significant effect on the spectra observed, as shown by MacFarlane *et al.* and therefore careful drying of the ionic liquid/indicator solution must be performed.[30]

Typical procedure for the Heck reaction catalysed by Hünig's base

To a suspension of $Pd(O_2CMe)_2$ (0.011 g, 0.05 mmol) in 4-*tert*-butyliodobenzene (1.241 g, 5 mmol) were added 2-methylprop-2-en-1-ol (0.367 g, 5.1 mmol) and Hünig's base (0.37 cm^3, 10 mmol) in a Schlenk tube. The sealed reaction vessel was heated at 95 °C for 10 h with stirring. The cooled reaction mixture was concentrated *in vacuo* at 60 °C and extracted with cyclohexane (2 × 5 cm^3) to remove products. Evaporation of the solvent from combined cyclohexane extracts yielded the products. The extracted product was analysed by GC.

Typical procedure for the Heck reaction catalysed by ionic liquids

4-*tert*-Butyliodobenzene (1.241 g, 5 mmol) and 2-methylprop-2-en-1-ol (0.367 g, 5.1 mmol) and $Pd(O_2CMe)_2$ (0.011 g, 0.05 mmol) were added to the base-tethered ionic liquid (~3.7 cm^3, 10 mmol) in a Schlenk tube. The sealed reaction vessel was heated at 95 °C for 10 h with stirring. The cooled reaction mixture was extracted with cyclohexane (4 × 5 cm^3) to remove products from the ionic liquid. Evaporation of the solvent from combined cyclohexane extracts yielded the products. The extracted product was analysed by GC.

Typical procedure for the Knoevenagel reaction

Benzaldehyde (0.424 g, 4 mmol) and ethyl cyanoethanoate (0.464 g, 4.1 mmol) were added to the base-tethered ionic liquid (0.15 cm^3, 0.4 mmol) into a sealed Schlenk tube and stirred at room temperature. The products were extracted into cyclohexene (4 × 4 cm^3) and evaporation of the solvent from combined cyclohexene extracts yielded the products. The extracted product was analysed by GC.

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