

¹⁴N NMR and Two-Dimensional Suspension ¹H and ¹³C HRMAS NMR Spectroscopy of Ionic Liquids Immobilized on Silica

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Abstract: A variety of popular ionic liquids have been synthesized and characterized, including by optimized ¹⁴N NMR spectroscopy of the neat and dissolved ionic liquids. Ionic liquids incorporating Si(OEt)₃ groups have been immobilized on silica in a well-defined manner with the imidazolium moiety remaining intact. This has been proved by optimized one- and two-dimensional ¹H and ¹³C HRMAS NMR spectroscopy of the materials suspended in suitable solvents.

Keywords: ¹⁴N NMR spectroscopy • HRMAS spectroscopy • immobilization • ionic liquids • suspension NMR spectroscopy

Introduction

Ionic liquids are growing in importance as benign, nonvolatile solvents in organic chemistry and especially in “green” multiphase catalysis.^[1] Whole journal issues,^[2a,b] as well as conferences,^[2c] are nowadays dedicated to this medium and its various applications.

Our interest in ionic liquids arose from the quest for improved linkers^[3] for immobilizing catalysts^[4] and for modifying surfaces in a controllable manner.^[5] In catalysis, as well as in other applications, immobilized ionic liquids should have the advantage of easier solid–liquid phase separation as compared with liquid–liquid phase separation. Even in cases in which substrates and/or products are soluble in the ionic liquid, the solid support allows the latter to be removed from the mixture. Since the ionic liquid forms a monolayer on the porous high-surface-area supports, such as silica (used here is Merck silica: specific surface area 750 m² g^{−1}, average pore diameter 40 Å, particle size 0.063–0.2 mm), it should be easy for substrates to reach the catalyst as a result of its larger interface area. Also the distribution coefficients of the ionic liquid and the organic solvent used do not play a crucial role in the catalytic reaction. Furthermore, immobilized ionic liquids should be more widely applicable than

their neat precursors because their miscibility with the organic solvent used does not have to be taken into account in the later phase separation. In addition, only a small amount of the costly ionic liquid is needed to form the monolayer, while the support functions as the bulk material.

Taking a look at the literature, we were surprised to find only a few examples of immobilized ionic liquids^[6] and even fewer of catalysts immobilized by supported ionic liquids in academic^[7,8] or industrial^[8a] settings, although there are numerous and diverse industrial applications of neat ionic liquids.^[2c] This is especially astonishing since supported species are well-known and of growing importance in combinatorial chemistry,^[9] solid-phase synthesis,^[10] chromatography,^[11] and catalysis.^[4,12,13]

We assume that this is due to the lack of analytical methods available for checking the purity of neat or supported ionic liquids. Only a few publications mention, for example, the high-resolution NMR spectra^[1a,14–17] of ionic liquids, or substances dissolved therein or the solid-state NMR spectra^[6,7] of ionic liquids tethered to a support, although in surface chemistry solid-state NMR spectroscopy^[18] has always proved to be an indispensable and powerful analytical method.^[3–5] For catalysts immobilized via phosphine linkers we recently optimized the cross-polarization (CP) process at high magic-angle-spinning (MAS) frequencies^[19] to obtain better signal-to-noise ratios (S/N) and implemented stationary^[20a] and suspension HRMAS NMR spectroscopy^[20b] to study the mobility of surface species as well as their reactivity with oxidic surfaces and their structural nature.

¹⁴N NMR spectroscopy^[21] has been applied in many very different research areas. In some recent work, for example, it served to characterize metal complexes^[22] and main group

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compounds.^[23] It has also been used for analytical purposes in solution and in the solid state.^[24]

The importance of ionic liquids in catalysis is increasing rapidly and one of the key issues in the further development of this area will be the knowledge of the interaction of the metal center with the imidazole moiety. Therefore, it will be especially important to have a probe close to the metal center. This probe could be a ^{14}N nucleus, which would allow an insight into the catalytic systems to be gained through both its chemical shift and linewidth without the trouble of having to analyze a "crowded" ^1H NMR spectrum of a complex mixture. Thus, the ^{14}N nucleus could become as important for ionic liquid systems in catalysis as the ^{31}P nucleus is for homogeneous and immobilized catalysts with phosphine ligands.^[3,4]

In the following, we will demonstrate with the popular imidazolium-based species^[1,2,25] that ^{14}N NMR spectroscopy can be used to characterize neat and dissolved ionic liquids and that one- and two-dimensional suspension ^1H and ^{13}C HRMAS NMR spectroscopy can successfully be used to investigate immobilized ionic liquids.

Results and Discussion

^{14}N NMR spectroscopy of ionic liquids: The ionic liquids **1–8** have been synthesized and characterized (Scheme 1), in-

cluding by ^{14}N NMR spectroscopy. Examples of their ^{14}N NMR spectra are shown in Figure 1 and Figure 2 and all the ^{14}N NMR data are compiled in Table 1. The ^{14}N NMR signal assignments are based on a comparison of the chemical

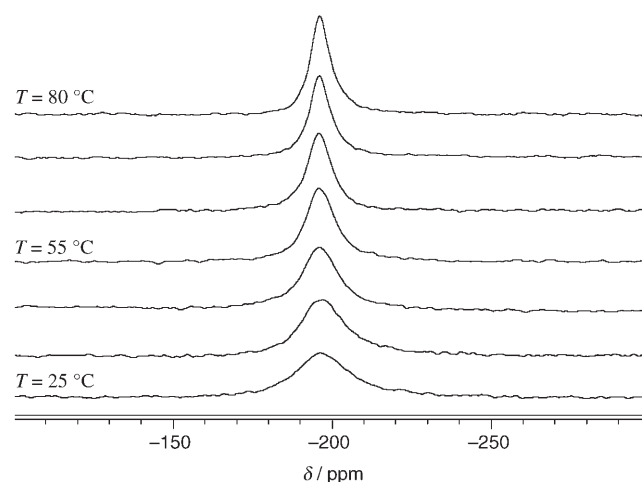
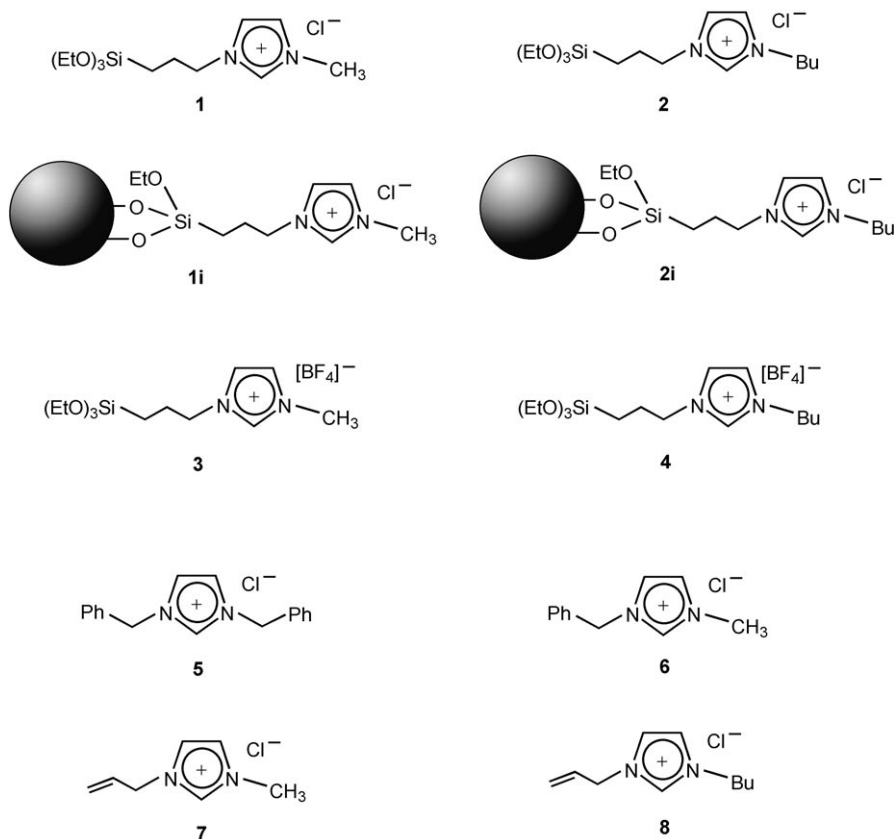


Figure 1. 36.1 MHz ^{14}N NMR spectra of **5** dissolved in EtOH. The temperature is increased in 10 °C steps, except for the last one (5 °C).



Scheme 1. Molecular (**1–8**) and silica-bound (**1i**, **2i**) ionic liquids.

shifts of the substances with different substituents at the nitrogen nuclei (Table 1). Longer alkyl chains bound to the ^{14}N nuclei lead to ^{14}N chemical shifts of around $\delta = -195$ to -200 ppm, while methyl groups shield the nitrogen nuclei, resulting in $\delta(^{14}\text{N})$ values of around $\delta = -210$ ppm.

While ^{15}N NMR spectroscopy suffers from the low natural abundance of this nucleus and needs special techniques for its measurement, ^{14}N NMR spectroscopy is comparatively easy to accomplish.^[21] It has a high natural abundance of 99.635 % and a receptivity of 5.69 relative to that of ^{13}C , while the nuclear quadrupole moment Q of this spin-1 nucleus is rather small ($0.0199 \times 10^{-28} \text{ m}^2$).^[21] Hence, unlike, for example, ^{61}Ni ,^[26] no special probehead is needed for the ^{14}N measurement and any conventional liquids NMR spectrometer equipped with a multinuclear probehead can be used. One can pulse quickly with 200 ms relaxation delays (relaxation of the electronics actually seems

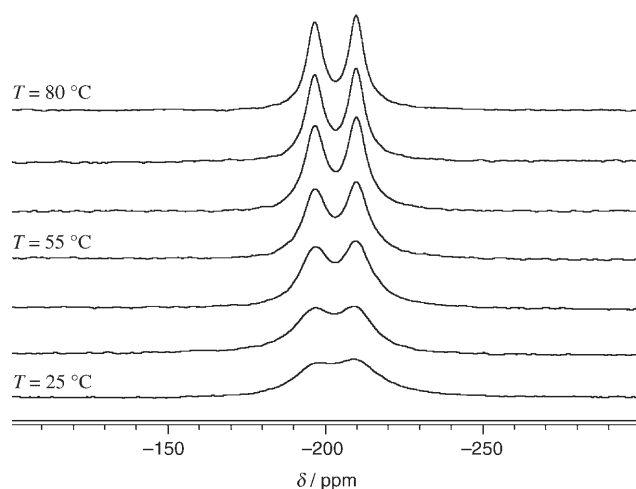


Figure 2. 36.1 MHz ^{14}N NMR spectra of **6** dissolved in EtOH. The temperature is increased in 10 °C steps, except for the last one (5 °C).

Table 1. 36.1 MHz ^{14}N NMR data for compounds **1–8** dissolved in EtOH (40 vol %; dilute: 80 vol %) unless stated otherwise.^[a]

Compound	$\delta(^{14}\text{N})$ [ppm] (80 °C)		$\Delta\nu_{1/2}$ [Hz]			
	N1	N2	N1 80 °C	N1 25 °C	N2 80 °C	N2 25 °C
1	–198	–210	140	480 ^[b]	140	480 ^[b]
1 (dilute)	–195	–207	110	470 ^[b]	125	470 ^[b]
1 ^[c] (neat)	–210	–210	1500	–	1500	–
2 ^[c]	–198	–198	256	500	256	500
3	–198	–210	130	520 ^[b]	140	520 ^[b]
4 ^[c]	–198	–198	380	980	380	980
5	–196	–196	180	530	180	530
6	–197	–210	140	400 ^[b]	145	450 ^[b]
7	–199	–209	90	140	90	145
7 ^[c] (neat)	–210	–210	2000	–	2000	–
8 ^[c]	–198	–198	215	310	215	310

[a] Chemical shifts are referenced with respect to neat liquid CH_3NO_2 [$\delta(^{14}\text{N}) = 0.0$ ppm].^[21] the chemical shifts $\delta(^{14}\text{N})$ and linewidths $\Delta\nu_{1/2}$ are accurate to within ± 1 ppm and ± 10 Hz, respectively. The chemical shifts are independent of the temperature. N1 corresponds to the nitrogen atom on the left-hand side of the formulae given in Scheme 1 and N2 to the one on the right-hand side. [b] $\Delta\nu_{1/2}$ after deconvolution. [c] The N1,N2 signals are unresolved.

to be the limiting factor) and spectra of neat organic liquids, such as the solvents CH_3NO_2 , CH_3CN , or pyridine, can be obtained within a few minutes.

Nitrogen is an ideal probe, especially for imidazole-based ionic liquids, because it allows one to check whether the imidazole unit is still intact, whether and how metal centers are bound, and it might also allow catalytic mechanisms to be studied in the future. Owing to the quadrupolar nature of the ^{14}N nucleus, in addition to the chemical shifts, numbers, and intensities of signals, the linewidths provide information on the whole system. As outlined in reference [21], the linewidth, which is determined by structural and motional factors, is given by Equation (1), where $\Delta\nu_{1/2}$ is the ^{14}N linewidth, $T_q = T_2 = T_1$ for mobile species in the extreme nar-

rowing limit, τ_q is the effective rotational correlation time of the nuclear quadrupole, $\chi = e^2qQ/h$ describes the nuclear quadrupolar coupling constant, where eq is the electric field gradient, and $\eta = (q_x - q_y)/q_z$ is the asymmetry parameter with values between 0 and 1.

$$\pi\Delta\nu_{1/2} = 1/T_q = \frac{3}{8}\chi^2(1+\eta^2/3)\tau_q \quad (1)$$

Thus, the linewidth depends, roughly, on the electronic symmetry around the ^{14}N nucleus and the mobility of the molecule. The more symmetric the immediate surroundings of the ^{14}N nucleus and the smaller the molecule it belongs to, the narrower the lines: The smaller the molecules or aggregates are, the narrower the halfwidths are due to the reduced correlation time, as shown in the case of amino acids and proteins^[27a] and in the interaction of acetonitrile with a C_{18} stationary phase.^[27b] With the given molecules, one can influence the linewidth by the choice of solvent used and by the temperature: Higher temperatures and less viscous solvents decrease the correlation time and therewith the linewidth. Even supercritical CO_2 has been used as a solvent for this purpose.^[28] In the case of the ionic liquids **1–8**, the addition of EtOH reduces the linewidths substantially (Table 1), although the EtOH concentration does not affect the linewidths within the range of 40–80 vol % EtOH, especially at ambient temperature. Only a small amount of solvent is probably needed to disrupt the “ionic liquid structure” and any additional EtOH makes no further difference.

In the case of the neat ionic liquids **1** and **7** the ^{14}N NMR signals are too broad to be visible at ambient temperature, but a slight rise in temperature, or dilution, results in decent signals.

The temperature effect is nicely illustrated by the spectra of the ionic liquid **5** dissolved in EtOH at different temperatures (Figure 1). While the spectrum at ambient temperature exhibits a rather broad signal at $\delta = -196.1$ ppm with a half-width of 530 Hz, the latter decreases to 180 Hz at 80 °C.

Next, we wanted to study the effect of the counteranion on the ^{14}N NMR signal linewidth. Therefore, we treated **1** and **2** in CH_2Cl_2 solutions with equimolar amounts of NaBF_4 . The immediate and quantitative anion exchange manifested itself by the precipitation of NaCl , which could easily be removed from the organic phase by filtration, while the resulting ionic liquids **3** and **4** are soluble in CH_2Cl_2 . The quantitative anion exchange can be proved, for example, in the change of the NCHN proton resonance in **1** (**2**) from $\delta = 10.64$ (10.90) to 8.90 (8.97) ppm in **3** (**4**). Further evidence comes from the ^{19}F NMR data (see the Experimental Section).

Changing the counterion from Cl^- to BF_4^- in **1** and **2** does not change the linewidth substantially, in accord with the reverse results described in the literature for cation exchange.^[23b] However, the lines of **4** are, especially at 25 °C, much broader (nearly double) than those of **3**. This difference in linewidth, and thus mobility, is a better reflection of the overall picture, taking into account the fact that the melting point of ionic liquids also depends very much on the nature

of the counterion.^[1c] To clarify this point, a more elaborate and systematic study will be needed in the future.

The unsymmetric ionic liquids, which have very different substituents on the two nitrogen atoms (**1**, **3**, **6**, and **7**), give two ¹⁴N signals that are nicely separated at higher temperatures, as one can see, for example, for **6** in Figure 2. In all the cases described herein, the two signals have very similar halfwidths. This nicely proves two assumptions that have always been taken as “generally granted”, but hardly proven. First, the two ¹⁴N nuclei have similar electronic surroundings. This is of course due to charge delocalization in the imidazole ring. But it also proves that the counteranions do not interact preferentially with any one moiety of the imidazole ring. Any potential specific interaction, such as possible hydrogen bonding of the NCHN proton with the fluorine atoms of the BF₄[−] ion, affect both ¹⁴N nuclei equally. Otherwise, owing to the different electric field gradients, different signal halfwidths would be obtained. This finding is true for the whole temperature range studied. Second, especially for the ionic liquids **1** and **3** with substituents of very different chain length and bulkiness on each side of the imidazole ring, the similarity of the halfwidths of the two signals shows that the linewidths depend on the correlation time of the whole molecule; the linewidth is not determined by any partial reorientation of the “lighter” moiety of the imidazole ring. This might also be the reason why at ambient temperature no signals from the suspensions of **1i** and **2i**, in which intrinsically only partial mobility is allowed owing to the immobile support, could be obtained.

As outlined in the review article by Wasserscheid and Keim,^[1b] the viscosity of ionic liquids is mainly determined by two factors, intermolecular van der Waals interactions due to alkyl substituents in the cations and potential hydrogen bridging between the imidazolium protons and the anions. These effects are important for characterizing the properties of ionic liquids and, as demonstrated in the first encouraging results described above, ¹⁴N NMR spectroscopy might help in later, more elaborate studies to disentangle and analyze both factors.

Suspension ¹H and ¹³C HRMAS NMR spectroscopy of immobilized ionic liquids: As outlined above, ¹H, ¹³C, and ¹⁴N NMR spectra of neat or dilute ionic liquids can easily be obtained. However, ¹⁴N NMR spectroscopy in the solid state is hampered by the large quadrupolar interactions of this spin-1 nucleus, leading to a dispersion of the signal intensity in a broad Pake pattern. Therefore spectroscopic measurements of substances that are “dilute” on the surface of a bulk material, as is the case for **1i** and **2i**, would especially present difficulties. Even by considering the NMR of all other nuclei, there are only a few examples of solid-state NMR measurements of immobilized ionic liquids.^[6,17] These were accomplished by ²⁹Si CP/MAS or ²⁷Al MAS spectroscopy of the support material in order to prove the covalent bonding of the ionic liquids to the support. Problems were not to be expected here because the reactions of the ethoxysilane moiety with oxidic supports are already well-known^[5] and

therefore no surprises were found when anchoring the ethoxysilane group onto the support.^[6] However, previous investigations have shown that both phosphine-^[29] and nitrogen-containing^[20b] moieties of linker molecules can undergo massive side-reactions and even total decomposition during the immobilization step. They can be quaternized, as in the case of phosphines,^[29] or hydrolyzed, as happens with phosphinoamines on the wrong kind of support.^[20b] Especially with respect to the later coordination of metal complexes to the imidazole moieties, it is desirable to probe not only the bulk material, but also the heterocyclic moiety of the tethered ionic liquid.

Therefore, we immobilized compounds **1** and **2** according to the procedure given in reference [6] to give **1i** and **2i**. We took special care to remove all surplus ionic liquid that might have been merely adsorbed, but not covalently bound, by extraction with CH₂Cl₂. The modified silicas were then dried in vacuo for several hours. As displayed for **1i** in Figure 3, the ¹³C CP/MAS spectrum recorded at a moderate

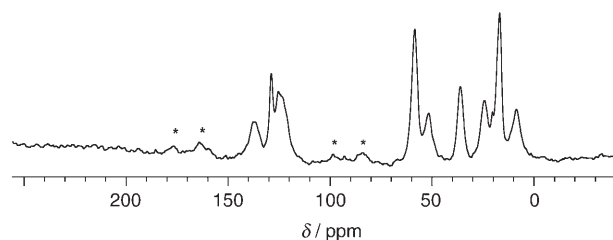


Figure 3. ¹³C CP/MAS NMR spectrum of **1i** at a rotational speed of 4 kHz. The asterisks denote rotational sidebands.

spinning speed shows that all the signals are rather well-resolved. Based on the ionic liquid's NMR data in solution, all resonances can be assigned in a straightforward manner and no serious overlapping occurs. Traces of toluene are visible at $\delta = 129$ and 21 ppm. The asterisks indicate rotational sidebands of the imidazole signals. The methyl and methylene carbon atoms of residual silane- and surface-bound^[5] ethoxy groups resonate at $\delta = 16.9$ and 58.4 ppm, respectively. The signals of the alkyl chain are visible at $\delta = 8.7$ (CH₂Si), 24.4 (CH₂CH₂CH₂), and 51.7 (NCH₂) ppm. The N-CH₃ signal appears at $\delta = 36.1$ ppm, the resonances for the NCHCHN (not resolved) and the NCHN carbon atoms of the imidazole moiety are visible at $\delta = 125.3$ and 137.1 ppm, respectively.

Encouraged by earlier results of suspension ³¹P HRMAS NMR spectroscopy of phosphines immobilized on inorganic oxides^[20b] and ¹H and ¹³C HRMAS NMR spectroscopy of proteins bound to swollen resins,^[30] we optimized the HRMAS conditions for analysis of the ionic liquids immobilized on silica. As in the case of ³¹P HRMAS NMR spectroscopy,^[19] cross polarization (CP)^[18,19] for ¹³C is not efficient and the best signal-to-noise ratios were obtained with simple high-power proton-decoupling. The optimal suspension medium for immobilized ionic liquids turns out to be DMSO, both with respect to the linewidth that can be ob-

tained and also to potential overlapping with solvent signals. Fortunately, suppression of the solvent signal with all the problems entailed is not necessary. Hence, measuring suspensions of **1i** and **2i** in DMSO even at the low rotational speed of 2 kHz leads to highly improved, nearly liquid-type resolution. For the unsymmetric **1i**, for example, even the signals of the imidazole NCHCHN moiety are now resolved (see Figure 4). Furthermore, the ethoxy resonances of adsorbed ethanol at $\delta = 57.0$ and 19.5 ppm can be distinguished from those of residual silane-bound ethoxy signals ($\delta = 58.8$ and 19.1 ppm), in accord with the literature.^[5] Fortunately, the newly appearing signals of grease ($\delta = 0.6$ ppm), DMSO ($\delta = 40.4$ ppm), and Teflon ($\delta = 111$ ppm), which stems from the rotor inserts, do not overlap with the resonances of **1i**.

Although ^1H MAS NMR spectroscopy of solid samples usually gives broad unstructured signals as a result of dipolar couplings,^[18] measuring the proton spectrum of a DMSO suspension even at the low rotational speed of 2 kHz led to a very high resolution, as demonstrated in Figure 5. Evidently the solvent mobilizes the surface-bound ionic liquid fragments sufficiently well to efficiently reduce chemical shift anisotropy and above all the homonuclear dipolar couplings. All the signals can be assigned, as shown in Figure 5.

Even $^1\text{H},^{13}\text{C}$ HMQC spectra can be easily recorded, as shown for example in Figure 6. This might become especially important later on, when more complicated scenarios, for example, catalytic reactions at ionic-liquid-bound metal centers, are investigated. The interactions of substrates with catalysts may be studied with two-dimensional transfer-NOE spectroscopy^[31] because NOESY spectra of immobilized ionic liquids can also be easily recorded (not shown here).

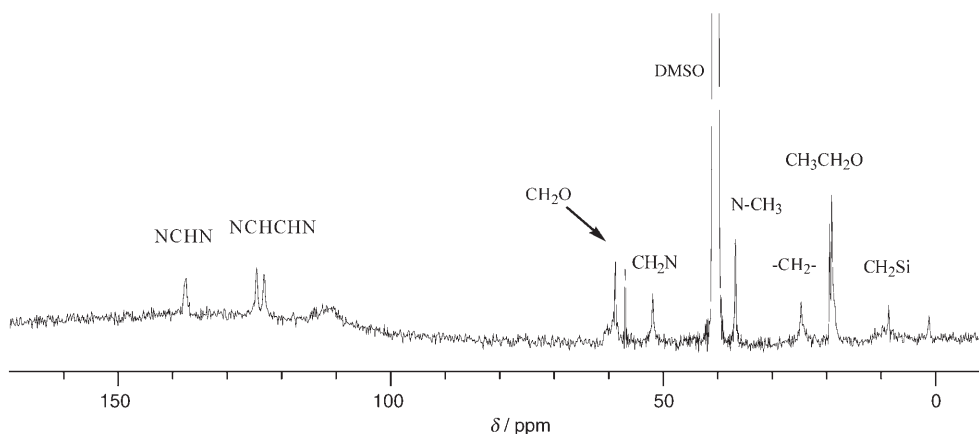


Figure 4. ^{13}C HRMAS NMR spectrum of **1i** suspended in DMSO at a rotational speed of 2 kHz.

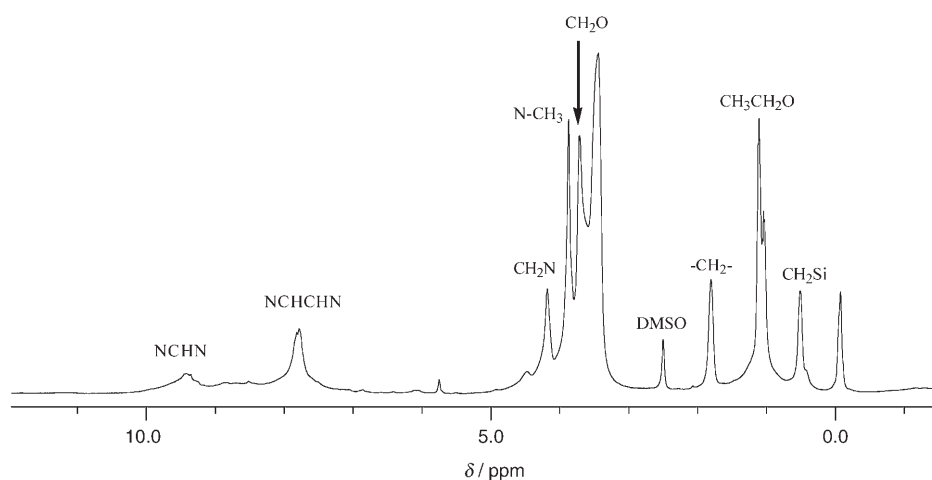


Figure 5. ^1H HRMAS NMR spectrum of **1i** suspended in DMSO at a rotational speed of 2 kHz.

Finally, besides TOCSY (not shown), $^1\text{H},^1\text{H}$ COSY spectra have been measured, although they needed some parameter optimization. The best results, with least pronounced blurring (“traces”), were obtained with double quantum filtered measurements, DQF-COSY, as displayed in Figure 7. The advantages of DQF-COSY compared with conventional COSY spectroscopy reside in the possibility of detecting only J -coupled spins so that intense signals (usually the solvent) are not detected. Furthermore, diagonal peaks are partially cancelled out so that it is easier to see cross peaks. Thus, it was, for example, possible to clearly recognize the correlations derived from the protons in the propyl chain, denoted by arrows in Figure 7.

Conclusion

We have demonstrated that ^{14}N NMR spectroscopy of neat and dissolved ionic liquids can routinely be used as an analytical tool. Ionic liquids immobilized on silica can successfully be studied by optimized multinuclear one- and two-dimensional ^1H and ^{13}C HRMAS NMR spectroscopy of their suspensions in a suitable solvent, such as DMSO. Thus, it

Experimental Section

All reactions were carried out in Schlenk flasks under purified nitrogen. The solvents were dried and distilled according to standard procedures prior to use. The ionic liquids **1–8** were prepared and immobilized (**1i**, **2i**) according to the standard procedures given in the literature.^[1,2,6] The NMR signal assignments were based on standard one- and two-dimensional ^1H and ^{13}C NMR measurements. Support material: Merck Silica gel 40 (specific surface area $750\text{ m}^2\text{ g}^{-1}$, average pore diameter $40\text{ \AA}$, particle size $0.063\text{--}0.2\text{ mm}$). The silica was dried rigorously at 600°C in vacuo prior to use. The surface coverage of the ionic liquid was typically between 30 and 55 molecules per 100 nm^2 , in accord with the formation of monolayers.^[3,4,8b] The solid-state and suspension NMR spectra were recorded with a fully digital Bruker Avance 400 NMR spectrometer equipped with a 4 mm MAS probehead. For the ^{13}C CP/MAS measurements a contact time of 5 ms and a pulse delay of 6 s were applied. Polycrystalline adamantane was used as

the Hartmann–Hahn and external chemical shift standard. The suspension HRMAS measurements were performed with simple high-power proton-decoupling for ^{13}C using a pulse delay of 2 s. The 2D HRMAS ^1H , ^1H DQF-COSY spectrum of compound **1i** was recorded using 1024 and 128 complex points, 64 scans, and a recycling delay of 1 s. The resulting total acquisition time was 3 h. The 2D HRMAS ^1H , ^{13}C HMQC spec-

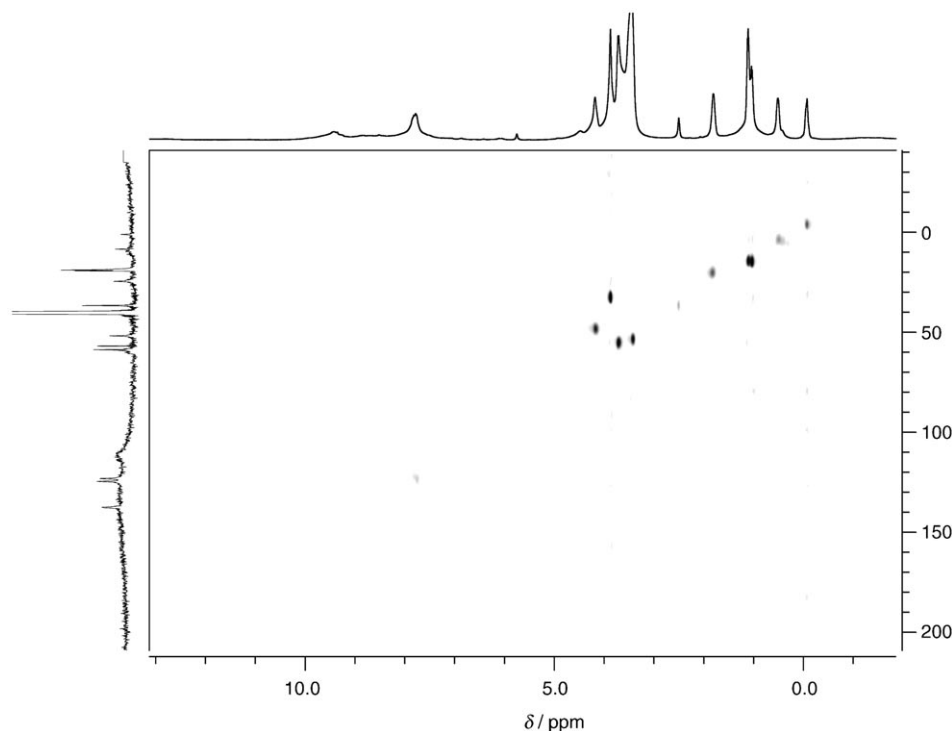


Figure 6. ^1H , ^{13}C HMQC spectrum of **1i** suspended in DMSO at a rotational speed of 2 kHz.

has been shown that ionic liquids are immobilized in a well-defined, clean manner and especially that the imidazolium moiety of the immobilized cations stays intact. In current studies we are exploring the potential of ionic liquids as linkers for immobilizing molecular catalysts.

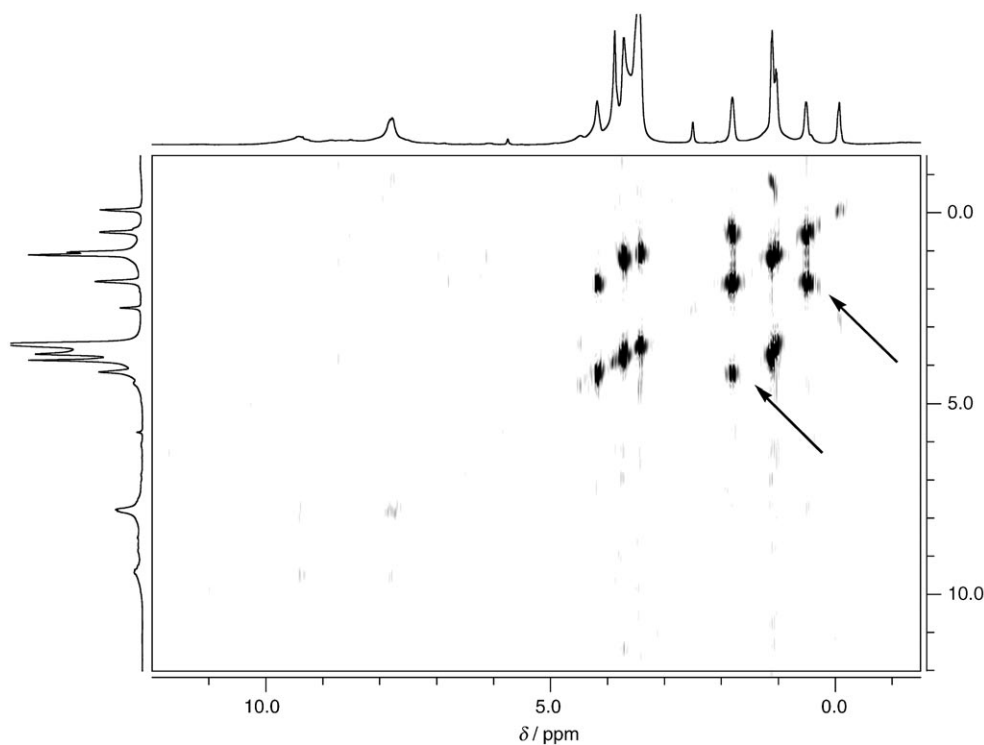


Figure 7. ^1H , ^1H DQF-COSY spectrum of **1i** suspended in DMSO at a rotational speed of 2 kHz.

trum of compound **1i** was recorded by using 1024 and 128 complex points, 128 scans, and a recycling delay of 1 s. The resulting total acquisition time was 6 h. For ^1H MAS NMR spectroscopy, a single-pulse sequence with a 1 s pulse delay was applied. All samples for suspension NMR analysis were packed into commercial Bruker HRMAS NMR rotors with ZrO_2 bottoms and Teflon/Kel-F inserts at the top. For the CP/MAS spectra a line-broadening factor (LB) of 50 Hz was applied, for ^{13}C suspension NMR spectra the LB factor was 10 Hz, and for ^1H suspension NMR spectra, it was 0 Hz. The rotational speed used for all suspension NMR spectra was 2 kHz. The signal assignments are based on comparisons with previously characterized phosphine linkers,^[3,4,20b] ^{31}P -decoupled, and two-dimensional correlation spectra. All ^{14}N NMR spectra were measured with a 500 MHz Bruker DRX spectrometer using neat liquid CH_3NO_2 [$\delta(^{14}\text{N})=0.0$ ppm] as the external reference. The 90° pulse length was 30 μs , the dead time 20 μs , and the pulse repetition rate 200 ms. For neat liquids, 16 scans were accumulated. The line-broadening factor used was maximally 50 Hz.

Ionic liquid 1: 1-Methylimidazole (2.060 g, 25.085 mmol) and (3-chloropropyl)triethoxysilane (6.042 g, 25.091 mmol) were dissolved in toluene (20 mL) and refluxed for three days. Without stirring, two phases rapidly formed, with **1** as a viscous oil at the bottom and toluene at the top. The phases were separated and the oil was washed with toluene (6 $\times$ 10 mL). After drying the oil under vacuum at 60°C for one day, **1** (4.686 g, 14.548 mmol, 58 % yield) was obtained with a honey-like consistency at room temperature. ^1H NMR (500 MHz, CDCl_3): $\delta=10.64$ (s, 1H, NCHN), 7.49 (s, 1H, NCHCH), 7.28 (s, 1H, NCHCH), 4.29 (t, $J=7.3$ Hz, 2H, CH_2N), 4.05 (s, 3H, NCH_3), 3.74 (q, $J=7.0$ Hz, 6H, OCH_2), 1.95 (quint., $J=7.3$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.13 (t, $J=7.0$ Hz, 9H, CH_3CH_2), 0.55 ppm (t, $J=7.7$ Hz, 2H, SiCH_2); ^{13}C NMR (125.8 MHz, CDCl_3): $\delta=138.3$ (NCN), 123.3 (NCH), 121.6 (CHN), 58.5 (OCH_2), 51.7 (NCH_2), 36.5 (NCH_3), 24.3 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 18.2 (CH_3CH_2), 7.1 ppm (SiCH_2); HRMS (FAB^+): m/z : calcd for $[\text{C}_{13}\text{H}_{27}\text{N}_2\text{O}_3\text{Si}]^+$: 287.1791; found: 287.1805.

Ionic liquid 2: Ionic liquid **2** was synthesized in 73 % yield from 1-butylimidazole and (3-chloropropyl)triethoxysilane according to the procedure given above for **1**. ^1H NMR (500.1 MHz, CDCl_3): $\delta=10.90$ (s, 1H, NCHN), 7.38 (s, 1H, NCHCH), 7.30 (s, 1H, NCHCH), 4.35 (t, $J=7.4$ Hz, 2H, CH_2N), 4.35 (t, $J=7.2$, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.79 (q, $J=7.0$ Hz, 6H, OCH_2), 1.99 (quint., $J=7.7$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.88 (quint., $J=7.5$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.36 (sext., $J=7.5$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.18 (t, $J=7.0$ Hz, 9H, CH_3CH_2), 0.94 (t, $J=7.4$ Hz, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.58 ppm (t, $J=7.7$ Hz, 2H, SiCH_2); ^{13}C NMR (125.8 MHz, CDCl_3): $\delta=138.2$ (NCN), 121.5 (NCH), 121.5 (CHN), 58.5 (OCH_2), 49.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 32.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 24.3 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 19.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.2 ($\text{CH}_3\text{CH}_2\text{O}$), 13.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.1 ppm (SiCH_2); HRMS (FAB^+): m/z : calcd for $[\text{C}_{16}\text{H}_{33}\text{N}_2\text{O}_3\text{Si}]^+$: 329.2260; found: 329.2281.

Immobilized ionic liquids 1i and 2i: The ionic liquids **1i** and **2i** were synthesized according to procedures described in reference [6] and as described for **1i** as a representative case. Silica (1.016 g) was suspended in CH_2Cl_2 (5 mL) and **1** (300 mg, 0.929 mmol) dissolved in CH_2Cl_2 was then added. After stirring the mixture for 3 days at ambient temperature, the silica was allowed to settle. The supernatant solution was decanted and the modified silica was extracted with CH_2Cl_2 prior to being dried for several hours in vacuo. Removal of the solvent from the combined CH_2Cl_2 solutions gave residual **1** (80 mg). The amount of **1** (220 mg, 0.681 mmol) bound to silica corresponds to a surface coverage of 0.671 mmol of **1i** per g of SiO_2 or 54 particles per 100 nm^2 of silica.

Ionic liquid 3: Ionic liquid **3** was synthesized by stirring an equimolar amount of **1** with NaBF_4 in CH_2Cl_2 at room temperature. A white precipitate of NaCl formed immediately. Ionic liquid **3** was obtained typically in 85 % yield as an oil after filtration and removal of the solvent in vacuo. ^1H NMR (500.1 MHz, CDCl_3): $\delta=8.90$ (s, 1H, NCHN), 7.37 (s, 1H, NCHCH), 7.29 (s, 1H, NCHCH), 4.18 (t, $J=7.2$ Hz, 2H, CH_2N), 3.94 (s, 3H, NCH_3), 3.78 (q, $J=7.0$ Hz, 6H, OCH_2), 1.95 (quint., $J=7.3$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.18 (t, $J=7.0$ Hz, 9H, CH_3CH_2), 0.56 ppm (t, $J=7.7$ Hz, 2H, SiCH_2); ^{13}C NMR (125.8 MHz, CDCl_3): $\delta=136.6$ (NCN), 123.6 (NCH), 122.0 (CHN), 58.5 (OCH_2), 51.8 (NCH_2), 36.3 (NCH_3),

24.1 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 18.2 (CH_3CH_2), 7.0 ppm (SiCH_2); ^{19}F NMR (470.6 MHz, CDCl_3): $\delta=-151.9$ ppm. HRMS (FAB^+): m/z : calcd for $[\text{C}_{13}\text{H}_{27}\text{N}_2\text{O}_3\text{Si}]^+$: 287.1791; found: 287.1782.

Ionic liquid 4: Ionic liquid **4** was synthesized by stirring an equimolar amount of **2** with NaBF_4 in CH_2Cl_2 at room temperature. A white precipitate of NaCl formed immediately. Ionic liquid **4** was obtained typically in 98 % yield as an oil after filtration and removal of the solvent in vacuo. ^1H NMR (500.1 MHz, CDCl_3): $\delta=8.97$ (s, 1H, NCHN), 7.35 (s, 1H, NCHCH), 7.31 (s, 1H, NCHCH), 4.20 (t, $J=7.4$ Hz, 2H, CH_2N), 4.20 (t, $J=7.4$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.79 (q, $J=7.0$ Hz, 6H, OCH_2), 1.95 (quint., $J=7.3$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.83 (quint., $J=7.4$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.33 (sext., $J=7.4$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.19 (t, $J=7.0$ Hz, 9H, CH_3CH_2), 0.92 (t, $J=7.4$ Hz, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.57 ppm (t, $J=7.4$ Hz, 2H, SiCH_2); ^{13}C NMR (125.8 MHz, CDCl_3): $\delta=136.1$ (NCN), 122.2 (NCH), 122.2 (CHN), 58.6 (OCH_2), 52.0 (NCH_2), 49.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 31.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 24.2 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 19.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.2 (CH_3CH_2), 13.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.0 ppm (SiCH_2); ^{19}F NMR (470.6 MHz, CDCl_3): $\delta=-151.6$ ppm. HRMS (FAB^+): m/z : calcd for $[\text{C}_{16}\text{H}_{33}\text{N}_2\text{O}_3\text{Si}]^+$: 329.2260; found: 329.2273.

Ionic liquid 5: Ionic liquid **5** was synthesized in 79 % yield from 1-benzylimidazole and benzyl chloride according to the procedure given above for **1**. The NMR data are in good agreement with those obtained previously in toluene.^[32] ^1H NMR (500.1 MHz, CDCl_3): $\delta=10.81$ (s, 1H, NCHN), 7.42 (d, $J=1.5$ Hz, 2H, NCHCHN), 7.37 (m, 4H, CH_m), 7.20 (m, 6H, CH_o), 5.44 ppm (s, 4H, NCH_2); ^{13}C NMR (125.8 MHz, CDCl_3): $\delta=136.7$ (NCN), 132.9 (C_i), 129.0 (C_o), 128.6 (C_m), 121.9 (NCH), 121.9 (CHN), 52.8 ppm (NCH_2); HRMS (FAB^+): m/z : calcd for $[\text{C}_{17}\text{H}_{17}\text{N}_2]^+$: 249.1392; found: 249.1408.

Ionic liquid 6: Ionic liquid **6** was synthesized in 95 % yield from 1-methylimidazole and benzyl chloride according to the procedure given above for **1**. The ^1H NMR data are in good agreement with those obtained previously in D_2O .^[33] For the sake of completeness, here we include the ^{13}C NMR data. ^1H NMR (500.1 MHz, CDCl_3): $\delta=10.51$ (s, 1H, NCHN), 7.56 (s, 1H, NCHCH), 7.38 (s, 1H, NCHCH), 7.32 (m, 2H, CH_m), 7.18 (m, 3H, CH_o), 5.44 (s, 2H, NCH_2), 3.90 ppm (s, 3H, NCH_3); ^{13}C NMR (125.8 MHz, CDCl_3): $\delta=137.2$ (NCN), 133.1 (C_i), 129.0 (C_o), 128.5 (C_m), 123.6 (NCH), 121.7 (CHN), 52.7 (NCH_2), 36.2 ppm (NCH_3); HRMS (FAB^+): m/z : calcd for $[\text{C}_{11}\text{H}_{13}\text{N}_2]^+$: 173.1079; found: 173.1074.

Ionic liquid 7: Ionic liquid **7** was synthesized in 76 % yield from 1-methylimidazole and allyl chloride according to the procedure given above for **1** in toluene at a temperature of 105°C . ^1H NMR (500.1 MHz, CDCl_3): $\delta=10.79$ (s, 1H, NCHN), 7.49 (s, 1H, NCHCH), 7.34 (s, 1H, NCHCH), 6.00 (ddt, $J_{\text{trans}}=17.0$, $J_{\text{cis}}=10.1$, $J=6.4$ Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{N}$), 5.46 (m, $\text{CH}_2=\text{CHCH}_2\text{N}$), 5.00 (d, $J=6.4$ Hz, 2H, CH_2N), 4.10 ppm (s, 3H, NCH_3); ^{13}C NMR (125.8 MHz, CDCl_3): $\delta=138.4$ (NCN), 129.8 ($\text{CH}_2=\text{CHCH}_2\text{N}$), 123.4 (NCH), 122.6 ($\text{CH}_2=\text{CHCH}_2\text{N}$), 121.5 (CHN), 52.0 (NCH_2), 36.6 ppm (NCH_3); HRMS (FAB^+): m/z : calcd for $[\text{C}_7\text{H}_{11}\text{N}_2]^+$: 123.0922; found: 123.0927.

Ionic liquid 8: Ionic liquid **8** was synthesized in 46 % yield from 1-butylimidazole and allyl chloride according to the procedure given above for **1** in toluene at a temperature of 105°C . ^1H NMR (500.1 MHz, CDCl_3): $\delta=10.99$ (s, 1H, NCHN), 7.35 (s, 2H, NCHCHN), 6.05 (ddt, $J_{\text{trans}}=17.1$, $J_{\text{cis}}=10.2$, $J=6.4$ Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{N}$), 5.45 (m, 2H, $\text{CH}_2=\text{CHCH}_2\text{N}$), 5.06 (d, $J=6.3$ Hz, 2H, CH_2N), 4.32 (t, $J=7.4$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.90 (quint., $J=7.5$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.38 (quint., $J=7.5$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.97 ppm (t, $J=7.4$ Hz, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (125.8 MHz, CDCl_3): $\delta=138.7$ (NCN), 130.8 ($\text{CH}_2=\text{CHCH}_2\text{N}$), 122.1 ($\text{CH}_2=\text{CHCH}_2\text{N}$), 122.0 (NCH), 121.8 (CHN), 50.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 32.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.5 ppm ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). HRMS (FAB^+): m/z : calcd for $[\text{C}_{10}\text{H}_{17}\text{N}_2]^+$: 165.1392; found: 165.1389.

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