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PINENE-FUSED CHIRAL *N*-ETHYLPYRIDINIUM ROOM TEMPERATURE MOLTEN SALTS

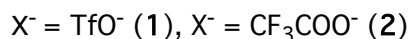
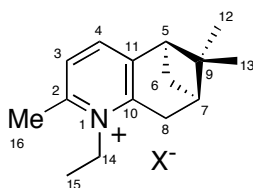
Dušan Drahoňovský,^a Gaël Charles Labat,^b Juraj Ševčík,^c and Alex von Zelewsky^{a,*}

^a Department of Chemistry, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland. E-mail: Alexander.vonZelewsky@unifr.ch; ^b Institute of Chemistry, University of Neuchâtel, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland; ^c Department of Analytical Chemistry, Palacky University, Tř. Svobody 8, 77146 Olomouc, Czech Republic

Abstract – New chiral room temperature molten salts (ionic liquids) based on the pinene-pyridinium unit associated with triflate or trifluoroacetate anions were prepared. The thermal behavior of these salts was observed by DSC and solventless ¹H NMR spectrum, whereas the diastereomeric interactions were studied by test asymmetric reactions, GC, CD spectroscopy, and ¹⁹F NMR spectra. X-Ray structure of iodide intermediate is presented.

INTRODUCTION

Room temperature molten salts, more frequently called "ionic liquids", represent today intensively studied systems in synthetic,¹ material,² and analytical chemistry^{3,4i} as alternative solvents, catalysts, and environment.



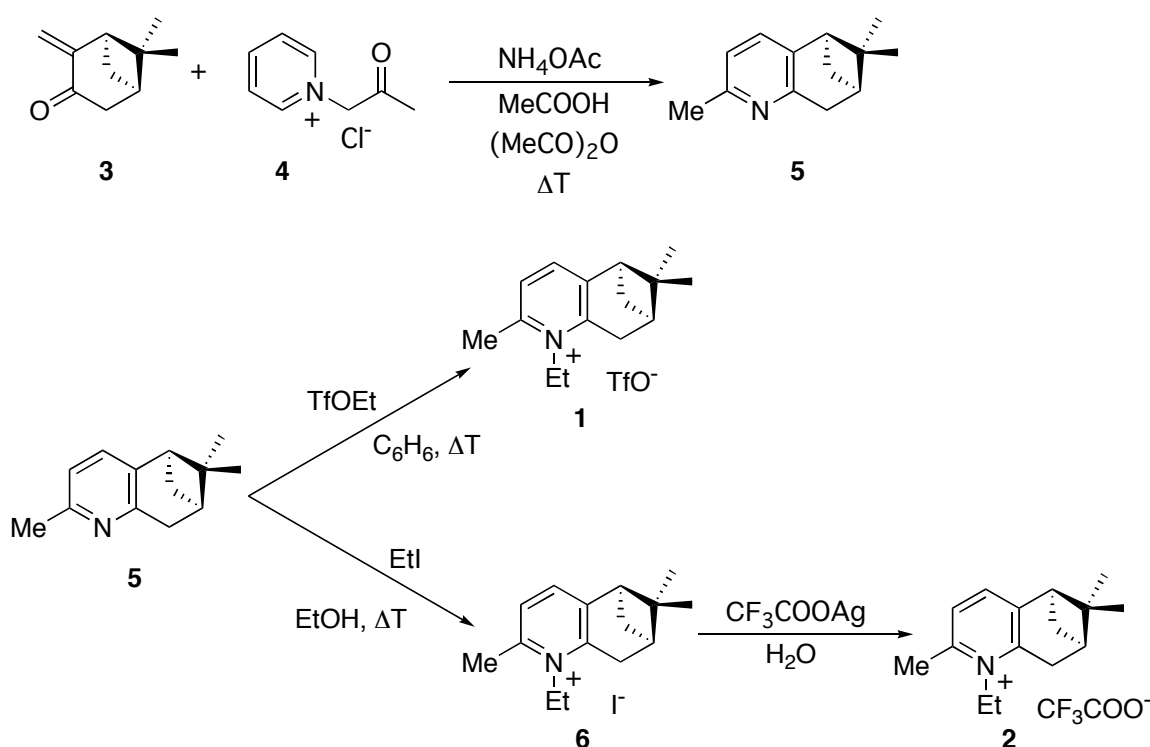
Scheme 1.

The ionic liquids are salts of organic cations, e.g. dialkylimidazolium, *N*-alkylpyridinium, tetraalkylammonium, tetraalkylphosphonium and trialkylsulfonium salts that are liquid at low

temperature ($< 100^{\circ}\text{C}$). A family of chiral ionic liquids⁴ has been studied over last 6 years with aim to apply a chiral discrimination to asymmetric synthesis, and separation of enantiomers. Herein, we would like to report the preparation and the properties of new chiral ionic liquids based on the *N*-ethyl-pinene-pyridinium cation combined with trifluoromethanesulfonate (triflate, TfO^-) (**1**) or trifluoroacetate (CF_3COO^-) (**2**) anions, respectively (*Scheme 1*).

RESULTS AND DISCUSSION

The synthesis of the chiral ionic liquids (**1**) and (**2**) consist in quarternarisation of the chiral base (**5**). First reported *Chelucci's* protocol⁵ gave the pyridine base (**5**) in yields up to 25% only. We applied a different approach starting from (+)-pinocarvone (**3**)⁶ and acetylpyridinium chloride (**4**)⁷ via Kröhnke condensation⁸ to obtain the base (**5**) in 70% yield (*Scheme 2*).



Scheme 2. Preparation of the compounds (**1**) and (**2**).

One step direct alkylation of the base (**5**) with ethyl triflate in benzene under reflux gave the triflate (**1**) (*Scheme 2*) as colorless oily substance in almost quantitative yield, whereas the preparation of the trifluoroacetate (**2**) needed two steps – alkylation and anions metathesis. The alkylation step with iodoethane in ethanol yielded the iodide (**6**) as a brown-yellow solid which crystallized from water as monohydrate. Following anion metathesis replacing iodide by trifluoroacetate yielded the product (**2**) (*Scheme 2*). Finally, the ionic liquids were purified with activated charcoal and aluminium oxide, and dried under vacuo over several days (details see in EXPERIMENTAL). The prepared ionic liquids (**1**)

and (2) are high-viscous, colorless and odorless substances, immiscible 1 or slightly miscible 2 with water and well soluble in organic solvents such as tetrahydrofuran, acetonitrile or dichloromethane. On the other hand, they are insoluble in hexane or ether.

The thermal behavior of the compositions was observed both visually and by DSC. The differential scanning calorimetry showed stability of the compounds up to 160°C. Thermal decomposition started at 200°C for compound (1), 160°C for compound (2), and 180°C for the iodide (6). Glass transition temperatures of the ionic liquids (1) and (2) were below 0°C.

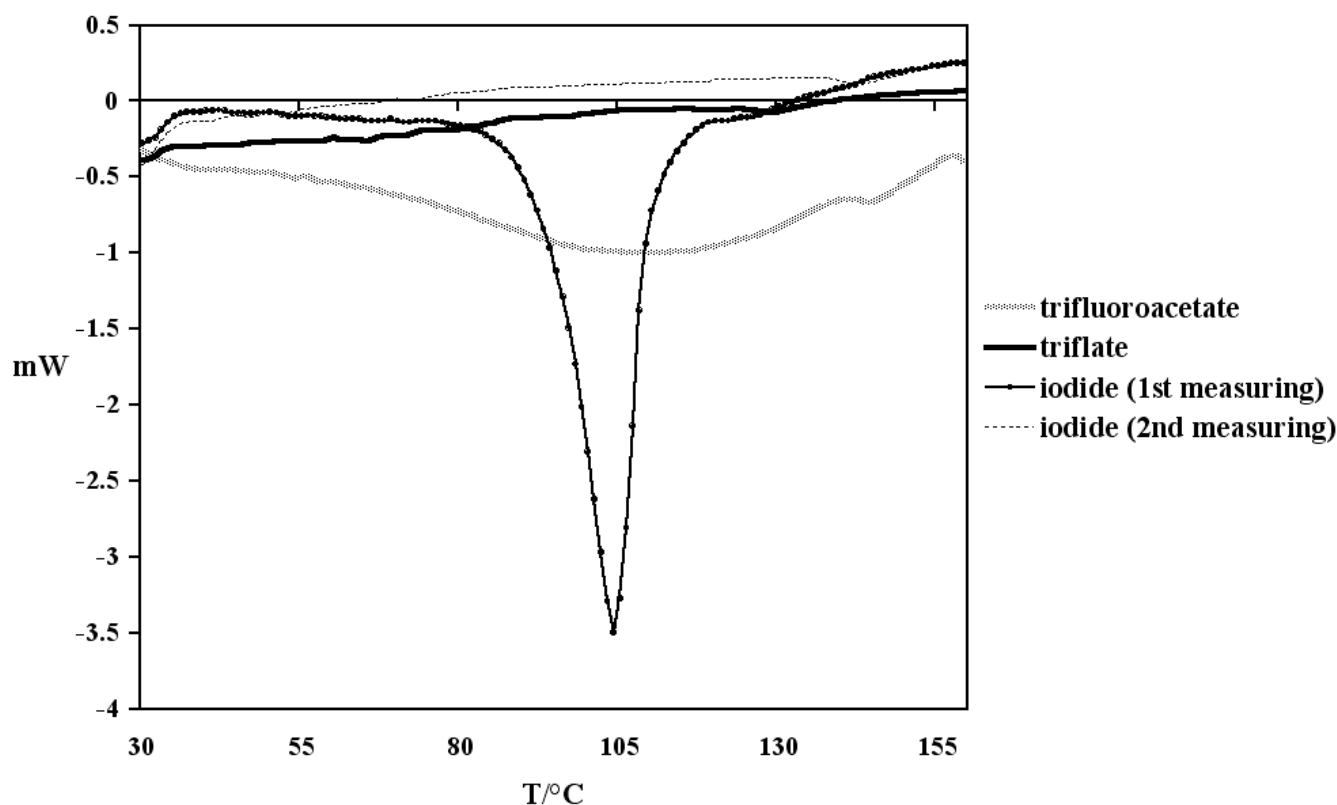


Figure 1. Differential scanning calorimetry: triflate (1), trifluoroacetate (2), iodide monohydrate (6) (1st measuring), and iodide anhydrous (2nd measuring).

Crystalline iodide (6) monohydrate exhibited phase transition starting from 75°C (with top at 104°C) together with loss of crystalline water (*Figure 1, 1st measuring*). Second measuring of the same sample upon cooling (anhydrous iodide) (*Figure 1, 2nd measuring*) naturally did not show the phase transition because of melting point at about 22°C. The shape of the DSC curve of the trifluoroacetate (2) (*Figure 1*) also indicated presence of a trace amount of water because the substance is slightly hygroscopic. Furthermore, we also studied a temperature dependence of ¹H NMR spectra of the neat ionic liquids (1) and (2) without solvent (*Figure 2*) (assignment and details see in EXPERIMENTAL). The spectra were recorded at temperatures from 40°C to 100°C. Higher temperature and lower viscosity of the samples (1) and (2) correlates here with decrease in width of the NMR spectral signals.

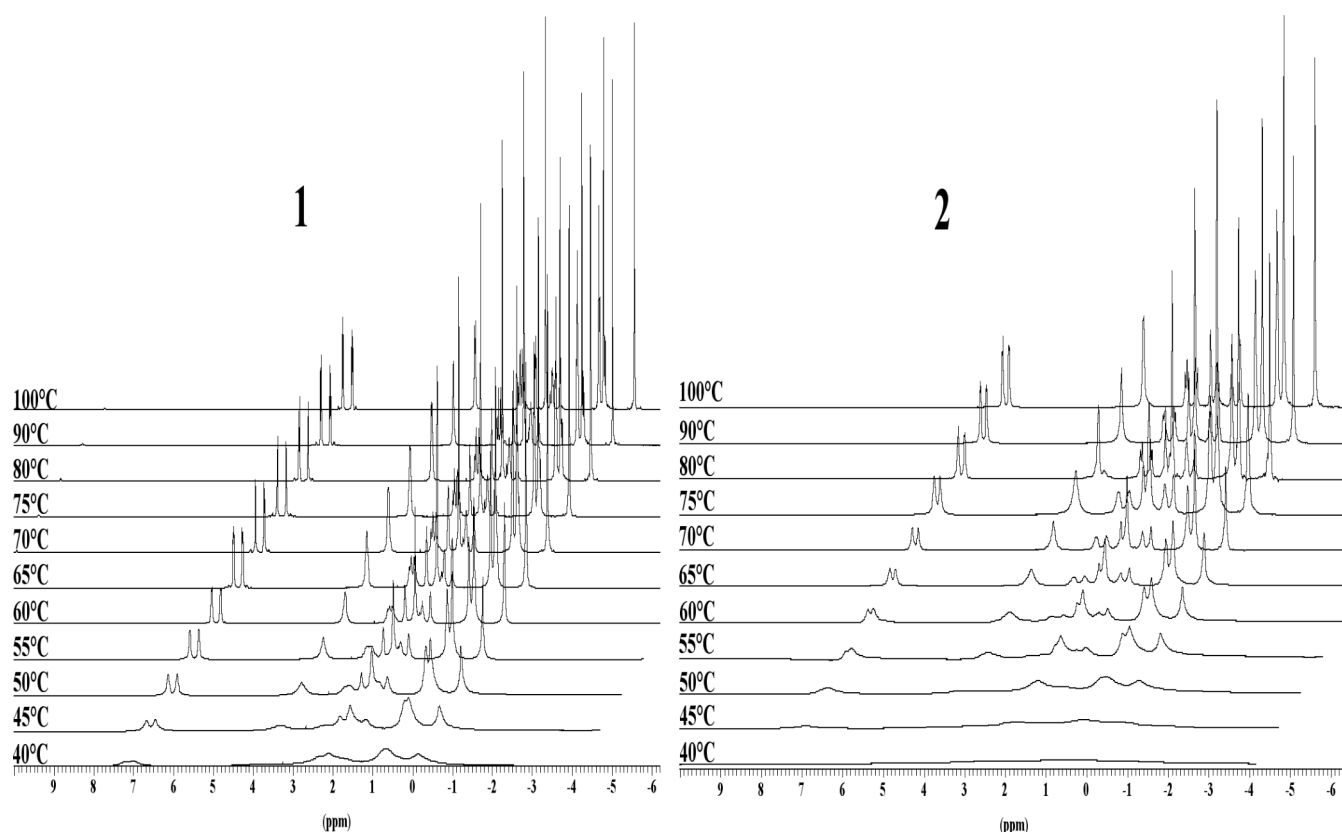
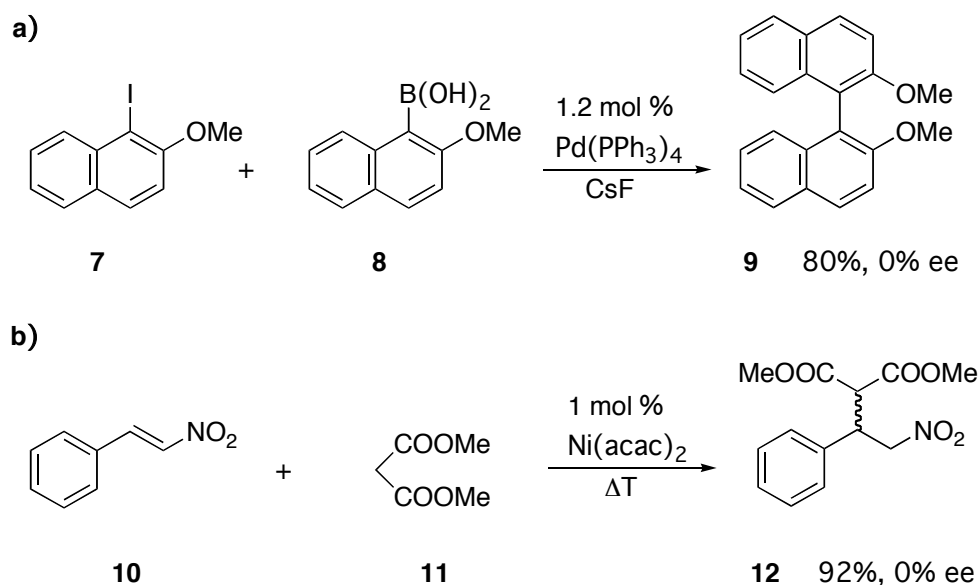


Figure 2. Solventless ^1H NMR spectra of **1** and **2**.

Several examples of asymmetric reactions in chiral ionic liquids have been published in literature.^{4a,d,f,g} In our hands, the ionic liquids (**1**) and (**2**) were practically applicable as solvents at temperatures above 60°C due to high viscosity.



Scheme 3. Asymmetric test reactions: a) Suzuki coupling reaction, b) Ni-catalysed Michael addition.

Suzuki cross-coupling reaction⁹ of 1-iodo-2-methoxynaphthalene (**7**) with 2-methoxy-1-naphthylboronic acid (**8**) and nickel-catalysed Michael addition¹⁰ of dimethyl malonate (**11**) to *trans*- β -nitrostyrene (**10**)

were chosen as test reactions (Scheme 3). The Suzuki reaction performed in the ionic liquids in presence of cesium fluoride gave 2,2'-dimethoxy-1,1'-dinaphthalene (**9**) in 80% preparative yields. The stereochemical outcome of the reaction detected by ^1H NMR spectrum in presence of a chiral solvating agent ((*R*)-trifluoroanthrylethanol) in CDCl_3 indicated no asymmetric induction. Similar results have been achieved for the Michael addition, where a lanthanide chiral shift reagent $\text{Eu}(\text{hfc})_3$ was used for the NMR spectral determination of the enantiomeric excess of the product (**12**). Thus, good preparative yields (92%) and no asymmetric inductions were confirmed here.

The chiral ionic liquids were further studied by CD spectroscopy with the aim to observe a possible Pfeiffer effect¹¹ of a dissolved stereochemically labile complex. Thus, the CD spectrum of a solution of iron(II) complex $\text{rac-}[\text{Fe}(\text{bpy})_3](\text{TfO})_2$ in triflate (**1**) ($c = 3.573 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) was recorded in the range of MLCT bands at about 400-600 nm. The Pfeiffer effect did not appear here in the experiment which indicates practically no mutual diastereomeric interactions between the ionic liquid (**1**) and the complex $\text{rac-}[\text{Fe}(\text{bpy})_3](\text{TfO})_2$.

Evidence for only very weak diastereomeric interactions we finally confirmed by ^{19}F NMR spectral experiments (Figure 3).

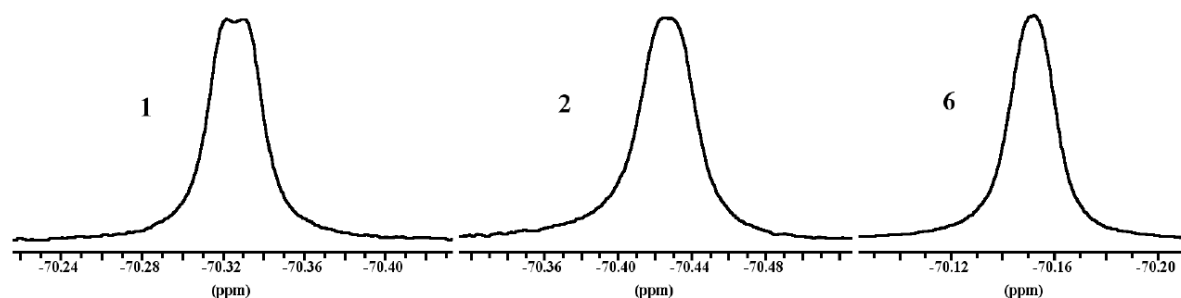


Figure 3. $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of Mosher's acid Bu_4N^+ salt in presence of **1**, **2**, and **6**.

Mixtures of the ionic liquids (**1**), (**2**) and iodide (**6**) with *rac*-Mosher's acid tetrabutylammonium salt in 0.4 ml of CD_2Cl_2 , respectively were studied by $^{19}\text{F}\{^1\text{H}\}$ NMR spectra, and the signal of the trifluoromethyl group of the Mosher's acid salt was probed (Figure 3). The molar ratio 10 : 1 (ionic liquid : Mosher's acid salt) was applied for all experiments. The split of the signals related to the CF_3 group clearly show either weak (**1**) $J = 4.10 \text{ Hz}$, weaker (**2**) $J = 2.35 \text{ Hz}$ or no diastereomeric interactions (**6**). The strength of the interactions demonstrates also the stability of the ion pairs of the salts (**1**), (**2**) and (**6**), which increases in this order.

In conclusion, we presented the synthetic pathway to the new chiral ionic liquids based on pinene-pyridinium unit, and we studied their characteristics, behaviour and interactions towards chiral discrimination and asymmetric induction. The crystal structure of the iodide (**6**) intermediate is reported in Experimental. Furthermore, the molten salt (**1**) was also tested as a chiral stationary phase in gas

chromatography. The experiments indicated no separation of enantiomers (selected terpenes and amino alcohols). The stationary phase further showed rather low stability under experimental conditions, and separation capability equaled to empty column (details see in EXPERIMENTAL). Finally, we assume, in accordance with literature,^{4b,g,i} that the presence of a free polar auxiliary group (-OH, -NH, etc.) in molecule of a chiral ionic liquid seems to be crucial to achieve more significant diastereomeric interactions. The structures presented in this article do not contain any such group, which may explain the existence of the weak diastereomeric interactions only.

EXPERIMENTAL

Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. NMR spectra were measured on a Bruker DRX 500 or Bruker Avance 400 in acetonitrile-D₃ (D, 99.8%), dichloromethane-D₂ (D, 99.9%), chloroform-D (D, 99.8%), or dimethyl sulfoxide-D₆ (D, 99.8%) (all deuterated solvents were purchased from Cambridge Isotope Laboratories). Bruker Avance 400 (¹H: 400.13 MHz, ¹³C: 100.62 MHz), Bruker DRX 500 (¹H: 500.13 MHz, ¹³C: 125.76 MHz, ¹⁹F: 470.59 MHz). Chemical shifts (δ-scale, ppm) are given relative to internal Me₄Si (¹H, ¹³C) or external Me₄Si (¹H) and BF₃-etherate (¹⁹F) standards. Assignment of the NMR signals is based on ¹H, ¹³C{¹H}, ¹³C APT, COSY, ¹³C HMQC, and ¹⁹F{¹H} spectra. Temperature dependent solventless ¹H NMR spectral experiments of the ionic liquids (**1**) and (**2**) were measured in temperature range from 40°C to 100°C, dimethyl sulfoxide-D₆ sealed in glass capillary in the samples was used for NMR locking. UV/VIS spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer. CD spectra were recorded on a JASCO J-715 spectropolarimeter. Optical rotations were measured on an automatic polarimeter Autopol III (Rudolph Research, New Jersey) and are given in deg.cm³.g⁻¹.dm⁻¹. MS spectra were recorded on a Bruker Bio Apex II. A diffractometer STOE IPDS-2 was used to record X-Ray diffractions. GC experiments were performed on a CHROM V gas chromatograph (Laboratorní přístroje, Praha, ČR). The Ecole d'ingénieurs et d'architectes de Fribourg accomplished the elemental analysis. Differential Scanning Calorimetry experiments were performed on a Mettler Toledo TC15 apparatus. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. (+)-Pinocarvone (**3**),⁶ *N*-acetylpyridinium chloride (**4**),⁷ 1-iodo-2-methoxynaphthalene (**7**),⁹ 2-methoxy-1-naphthylboronic acid (**8**),⁹ and *rac*-[Fe(bpy)₃](TfO)₂¹² were synthesized by literature procedures.

(-)-2-Methyl-(5*R*,7*R*)-5,6,7,8-tetrahydro-5,7-(9,9-dimethylmethano)quinoline (**5**)

A mixture of (+)-pinocarvone (**3**) (15 g, 100 mmol), *N*-acetylpyridinium chloride (**4**) (20.6 g, 120 mmol), dried ammonium acetate (58 g, 752 mmol), glacial acetic acid (150 mL), and acetic anhydride (15 mL) was heated at 120°C with stirring under condenser equipped with calcium chloride drying tube for 18 h. The resulting dark reaction mixture was diluted with 100 mL of water, and NaOH (15% H₂O solution)

was added slowly to achieve alkaline reaction. The product was isolated from the mixture by steam distillation. Collected emulsion was saturated with NaCl, extracted with ether (5 x 100 mL), and organic phase was dried over anhydrous Na₂SO₄. The solvent was evaporated, and remaining crude product was distilled under reduced pressure (105°C/1 Torr) to give the product (**5**) (13 g, 70%) as a colorless oily substance. $[\alpha]_D^{25} = -36.10^\circ$ (25°C, c = 1.2, hexane). ¹H NMR (CD₃CN): 0.56 (s, 3H-13, *endo* CH₃); 1.14 (d, 1H-6, *endo* CH₂, *J* = 9.3 Hz); 1.35 (s, 3H-12, *exo* CH₃); 2.28 (m, 1H-7, -CH₂-CH-); 2.39 (s, 3H, Ar-CH₃); 2.63 (dt, 1H-6, *exo* CH₂, *J* = 9.3 Hz, *J* = 5.4 Hz); 2.67 (t, 1H-5, CH, *J* = 5.6 Hz); 2.96 (d, 2H-8, CH₂, *J* = 3.0 Hz); 6.82 (d, 1H-4, CH aromatic, *J* = 7.6 Hz); 7.08 (d, 1H-3, CH aromatic, *J* = 7.6 Hz). ¹³C NMR (CD₃CN): 21.50 (*endo* CH₃); 24.22 (Ar-CH₃); 26.32 (*exo* CH₃); 32.78 (C-6, CH₂); 37.15 (C-8, CH₂); 39.98 (C-9, -CMe₂); 41.06 (C-7, CH); 46.74 (C-5, CH); 120.17 (C-4, CH aromatic); 133.92 (C-3, CH aromatic); 139.16, 155.73, 156.63 (C-q, aromatic). *Anal.* Calcd for C₁₃H₁₇N: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.30; H, 9.05; N, 7.36.

(-)-N-Ethyl-2-methyl-(5*R*,7*R*)-5,6,7,8-tetrahydro-5,7-(9,9-dimethylmethano)quinolinium trifluoromethanesulfonate (1**)**

Chiral base (**5**) (7 g, 37.5 mmol) was combined with ethyl triflate (6.7 g, 37.5 mmol) in dry benzene (40 mL), and the resulting solution was heated to reflux with stirring under argon for 18 h. Two organic layers were separated, and the lower one (product) was washed with benzene (2 x 10 mL) and hexane (2 x 10 mL) to remove organic impurities. The crude product was dissolved in acetonitrile (200 mL), activated charcoal and neutral aluminium oxide were added, and the mixture was allowed to stir at rt for 24 h. The mixture was further filtered through silica pad, the solvent was evaporated from the filtrate, and the remaining stuff was dried at 70°C under deep vacuo over 2 days to give the final product (**1**) as a colorless oily substance (12.6 g, 92%). $[\alpha]_D^{22} = -37.8^\circ$ (22°C, c = 1.05, CHCl₃). UV-VIS (λ_{\max} (ε), CH₂Cl₂, c = 2.1 · 10⁻⁵ mol·dm⁻³, L = 1 cm): 288 (2.2 · 10⁴). ¹H NMR (CD₃CN): 0.64 (s, 3H-13, *endo* CH₃); 1.28 (d, 1H-6, *endo* CH₂, *J* = 10.1 Hz); 1.42 (s, 3H-12, *exo* CH₃); 1.45 (t, 3H-15, CH₃-CH₂-N, *J* = 7.3 Hz); 2.49 (m, 1H-7, -CH₂-CH-); 2.75 (dt, 1H-6, *exo* CH₂, *J* = 9.3 Hz, *J* = 5.3 Hz); 2.76 (s, 3H-16, Ar-CH₃); 3.04 (t, 1H-5, CH, *J* = 5.6 Hz); 3.35 (dd, 2H-8, CH₂, *J* = 20.7 Hz, *J* = 3.3 Hz); 4.48 (q, 2H-14, CH₃-CH₂-N, *J* = 7.3 Hz); 7.58 (d, 1H-4, CH aromatic, *J* = 7.8 Hz); 7.85 (d, 1H-3, CH aromatic, *J* = 7.8 Hz). ¹³C NMR (CD₃CN): 13.70 (CH₃-CH₂-N); 20.70 (Ar-CH₃); 21.16 (*endo* CH₃); 25.39 (*exo* CH₃); 31.14 (C-6, CH₂); 33.71 (C-8, CH₂); 39.42 (C-9, -CMe₂); 40.21 (C-7, CH); 46.90 (C-5, CH); 48.76 (CH₃-CH₂-N); 128.14 (C-4, CH aromatic); 142.04 (C-3, CH aromatic); 147.11, 152.94, 154.21 (C-q, aromatic). ¹H NMR (neat compound, 100°C): -0.10 (s, 3H-13, *endo* CH₃); 0.62 (d, 1H-6, *endo* CH₂, *J* = 10.1 Hz); 0.67 (s, 3H-12, *exo* CH₃); 0.78 (t, 3H-15, CH₃-CH₂-N, *J* = 6.8 Hz); 1.76 (m, 1H-7, -CH₂-CH-); 1.95 (m, 1H-6, *exo* CH₂); 2.11 (s, 3H-16, Ar-CH₃); 2.38 (t, 1H-5, CH, *J* = 5.6 Hz); 2.73 (dd, 2H-8, CH₂, *J* = 24.8 Hz, *J* = 3.4 Hz); 3.90 (q, 2H-14, CH₃-CH₂-N, *J* = 7.1 Hz); 6.98 (d, 1H-4, CH aromatic, *J* = 8.1 Hz); 7.21 (d, 1H-3, CH

aromatic, $J = 8.1$ Hz). MS (ESI): 216 (cation); negative 149 (TfO⁻). *Anal.* Calcd for C₁₆H₂₂NO₃F₃S: C, 52.59; H, 6.07; N, 3.83. Found: C, 52.47; H, 6.19; N, 3.84.

GC experiments: A solution of triflate (**1**) in chloroform was mixed with analytical column support (Chromaton N-AW 0.16-0.20 mm), the solvent was evaporated under careful stirring, and the resulting coated particles were placed into a packed GC column. Chromatographic experiments were carried out at 120°C (nitrogen flow 10 mL/min) with series of terpenes and aminoalcohols (limonene, citronellal, leucinol, 1-amino-2-propanol), and separation of enantiomers was not occurred for all tested samples. Further experiments towards application of chiral ionic liquids in chiral GC and CE are still under investigation.

(-)-N-Ethyl-2-methyl-(5R,7R)-5,6,7,8-tetrahydro-5,7-(9,9-dimethylmethano)quinolinium iodide (6)

A solution of chiral base (**5**) (3.51 g, 18.74 mmol) and iodoethane (3.22 g, 20.61 mmol) in ethanol (20 mL) was heated under reflux for 24 h. The solvent was evaporated, and remaining solid was recrystallized from water to give the product (**6**) (6.4 g, 94%) as a brown-yellow crystalline monohydrate, mp 98-100°C. $[\alpha]_D^{25} = -49.5^\circ$ (22°C, $c = 1.1$, CHCl₃). ¹H NMR (CD₃CN): 0.64 (s, 3H-13, *endo* CH₃); 1.29 (d, 1H-6, *endo* CH₂, $J = 10.1$ Hz); 1.42 (s, 3H-12, *exo* CH₃); 1.45 (t, 3H-15, CH₃-CH₂-N, $J = 7.3$ Hz); 2.50 (m, 1H-7, -CH₂-CH-); 2.75 (dt, 1H-6, *exo* CH₂, $J = 9.3$ Hz, $J = 5.3$ Hz); 2.77 (s, 3H-16, Ar-CH₃); 3.05 (t, 1H-5, CH, $J = 5.6$ Hz); 3.36 (dd, 2H-8, CH₂, $J = 20.7$ Hz, $J = 3.3$ Hz); 4.48 (q, 2H, CH₃-CH₂-N, $J = 7.3$ Hz); 7.60 (d, 1H-4, CH aromatic, $J = 7.8$ Hz); 7.87 (d, 1H-3, CH aromatic, $J = 7.8$ Hz). ¹³C NMR (CD₃CN): 13.64 (CH₃-CH₂-N); 20.87 (Ar-CH₃); 21.11 (*endo* CH₃); 25.22 (*exo* CH₃); 30.95 (C-6, CH₂); 33.75 (C-8, CH₂); 39.22 (C-9, -CMe₂); 40.00 (C-7, CH); 46.66 (C-5, CH); 48.91 (CH₃-CH₂-N); 128.00 (C-4, CH aromatic); 141.85 (C-3, CH aromatic); 146.84, 152.72, 153.89 (C-q, aromatic). MS (ESI): 216 (cation); negative 126.9 (I⁻). *Anal.* Calcd for C₁₅H₂₄NOI: C, 49.88; H, 6.70; N, 3.88. Found: C, 50.23; H, 6.76; N, 3.68.

A colorless block crystal of the compound (**6**) (crystallized from water) (Figure 4) was mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite-monochromator. Data collection was performed at -120°C using Mo-K α radiation ($\lambda = 0.71073$ Å). 150 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 150^\circ$ and with the crystal oscillating through 1° in φ . The resolution was $D_{\min} - D_{\max} 12.45 - 0.81$ Å. This compound crystallised in the non-centrosymmetric orthorhombic space group P 2₁ 2₁ 2₁ [Flack parameter $x = -0.03(2)$]. The molecular formula of this compound is $\{(C_{15}H_{22}N)I\}(H_2O)$. The structure was solved by direct methods using the program SHELXS-97¹³ and refined by full matrix least squares on F^2 with SHELXL-97¹⁴. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms, were refined anisotropically. A semi-empirical absorption correction was applied using MULABS (PLATON03¹⁵, $T_{\min} = 0.442$, $T_{\max} = 0.519$). Crystal and data collection parameters, relevant structure refinement parameters, atomic

coordinates for the non-hydrogen atoms, positional and isotropic displacement coefficients for hydrogen atoms, a list of anisotropic displacement coefficients for the non-hydrogen atoms and a full list of bond distances and bond angles have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-266192. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; www.ccdc.cam.ac.uk).

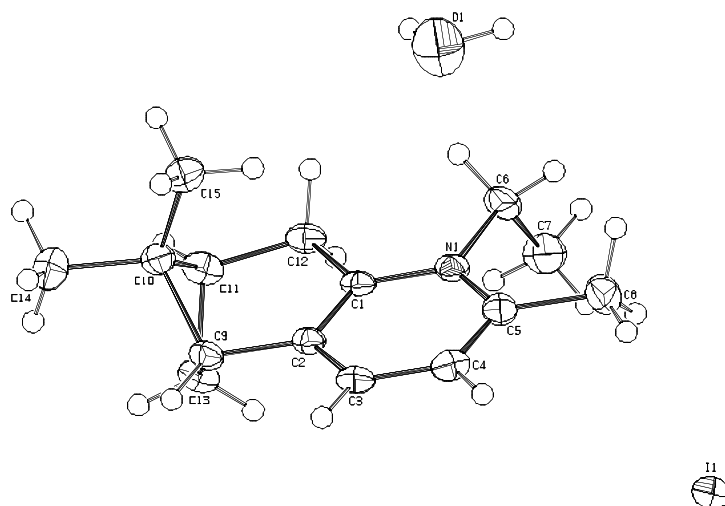


Figure 4. ORTEP of iodide monohydrate (**6**).

(-)-N-Ethyl-2-methyl-(5*R*,7*R*)-5,6,7,8-tetrahydro-5,7-(9,9-dimethylmethano)quinolinium trifluoroacetate (2**)**

A solution of silver trifluoroacetate (1.94 g, 8.80 mmol) in water (5 mL) was added to a solution of iodide (**6**) (3.18 g, 8.80 mmol) in water (5 mL) at rt under stirring. The precipitated silver iodide was filtered off, and the filtrate was concentrated in vacuo to give crude product. The substance was diluted with acetonitrile (100 mL), activated charcoal and neutral aluminium oxide were added, and the mixture was allowed to stir at rt for 24 h. The mixture was filtered through silica pad, and the solvent was evaporated from filtrate, and remaining stuff was dried at 70°C under deep vacuo over 2 days to give the final product (**2**) as a colorless oily substance (2.75 g, 95%). $[\alpha]_D = -44.5^\circ$ (22°C, $c = 1.2$, CHCl_3). ^1H NMR (CD_3CN): 0.63 (s, 3H-13, *endo* CH_3); 1.27 (d, 1H-6, *endo* CH_2 , $J = 10.1$ Hz); 1.42 (s, 3H-12, *exo* CH_3); 1.45 (t, 3H-15, $\text{CH}_3\text{-CH}_2\text{-N}$, $J = 7.3$ Hz); 2.49 (m, 1H-7, $\text{-CH}_2\text{-CH-}$); 2.75 (dt, 1H-6, *exo* CH_2 , $J = 9.3$ Hz, $J = 5.3$ Hz); 2.77 (s, 3H-16, Ar- CH_3); 3.03 (t, 1H-5, CH, $J = 5.6$ Hz); 3.35 (dd, 2H-8, CH_2 , $J = 20.7$ Hz, $J = 3.3$ Hz); 4.48 (q, 2H-14, $\text{CH}_3\text{-CH}_2\text{-N}$, $J = 7.3$ Hz); 7.60 (d, 1H-4, CH aromatic, $J = 7.8$ Hz); 7.86 (d, 1H-3, CH aromatic, $J = 7.8$ Hz). ^{13}C NMR (CD_3CN): 13.70 ($\text{CH}_3\text{-CH}_2\text{-N}$); 20.70 (Ar- CH_3); 21.18 (*endo* CH_3); 25.40 (*exo* CH_3); 31.15 (C-6, CH_2); 33.72 (C-8, CH_2); 39.43 (C-9, -CMe_2); 40.22 (C-7, CH); 46.90 (C-5, CH); 48.77 ($\text{CH}_3\text{-CH}_2\text{-N}$); 128.18 (C-4, CH aromatic); 142.08 (C-3, CH aromatic); 147.10, 152.97,

154.08 (C-q, aromatic). ^1H NMR (neat compound, 100°C): - 0.17 (s, 3H-13, *endo* CH_3); 0.59 (br s, 4H, 1H-6 *endo* CH_2 + *exo* CH_3); 0.76 (br s, 3H-15, $\text{CH}_3\text{-CH}_2\text{-N}$); 1.67 (m, 1H-7, $-\text{CH}_2\text{-CH-}$); 1.87 (m, 1H-6, *exo* CH_2); 2.25 (s, 3H-16, Ar- CH_3); 2.40 (br s, 1H-5, CH); 2.88 (m, 2H-8, CH_2); 4.05 (m, 2H-14, $\text{CH}_3\text{-CH}_2\text{-N}$); 7.37 (d, 1H-4, CH aromatic, $J = 6.3$ Hz); 7.52 (d, 1H-3, CH aromatic, $J = 6.3$ Hz). MS (ESI): 216 (cation); negative 113 (CF_3COO^-), dimer 226 (2 x CF_3COO^-). *Anal.* Calcd for $\text{C}_{17}\text{H}_{22}\text{F}_3\text{NO}_2$: C, 62.00; H, 6.73; N, 4.25. Found: C, 61.71; H, 7.02; N, 4.01.

2,2'-Dimethoxy-1,1'-dinaphthalene (9)

Tetrakis(triphenylphosphine)palladium (5 mg, 4.33 μmol) was added to the ionic liquids (1) or (2) (2 g), respectively, and the mixture was stirred for 5 min at 70°C under argon. 1-Iodo-2-methoxynaphthalene (7) (100 mg, 0.352 mmol), 2-methoxy-1-naphthylboronic acid (8) (107 mg, 0.528 mmol) and cesium fluoride (267 mg, 1.76 mmol) were then added, and the reaction mixture was stirred intensively for 12 h at 70°C . The product was extracted in several portions of ether, and the extract was purified by column chromatography (silica gel, hexane/ethyl acetate, 5:1) to give pure product (9) (88.5 mg, 80%) as a white crystalline solid. Analytical data are in accordance with those reported in ref.⁹ ^1H NMR (CDCl_3): 3.76 (s, 6H, CH_3); 7.09-7.35 (m, 6H, CH aromatic); 7.46 (d, 2H, CH aromatic, $J = 9.3$ Hz); 7.88 (d, 2H, CH aromatic, $J = 7.3$ Hz); 7.99 (d, 2H, CH aromatic, $J = 8.8$ Hz).

Methyl 2-carbomethoxy-4-nitro-3-phenylbutyrate (12)

Dimethyl malonate (11) (350 mg, 2.65 mmol) and nickel(II) acetylacetonate (6 mg, 23.35 μmol) were added to the ionic liquids (1) or (2) (2 g), respectively, and the mixture was stirred for 10 min at 70°C . *trans*- β -Nitrostyrene (10) (395 mg, 2.65 mmol) was then added, and the reaction mixture was stirred intensively for 4 h at 70°C . The product was extracted in several portions of ether, and the extract was purified by column chromatography (silica gel, hexane/ethyl acetate, 4:1) to give pure product (12) (685 mg, 92%). Analytical data are in accordance with those reported in ref.¹⁰ ^1H NMR (CDCl_3): 3.55 (s, 3H); 3.76 (s, 3H); 3.89 (d, 1H, $J = 8.7$ Hz); 4.25 (td, 1H, $J = 8.7$ Hz, $J = 5.4$ Hz); 4.86 (dd, 1H, $J = 13.1$ Hz, $J = 8.5$ Hz); 4.93 (dd, 1H, $J = 13.1$ Hz, $J = 8.5$ Hz); 7.21-7.35 (m, 5H).

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