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Fluorine-Containing Ionic Liquids from *N*-Alkylpyrrolidine and *N*-Methylpiperidine and Fluorinated Acetylacetones: Low Melting Points and Low Viscosities

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A family of new fluorine-containing ionic liquids (**3**–**14**) was synthesized in high yield by the reaction of *N*-alkylpyrrolidine, *N*-methylpiperidine and fluorinated 1,3-diketones: 1,1,1,5,5,5-hexafluoroacetylacetone, 1,1,1-trifluoro-2,4-pentanedione and 4,4,4-trifluoro-1-phenyl-1,3-butanedione. Their properties, such as the phase-transition temperature, density, and viscosity, were determined. Most of them show relatively low melting points and low viscosities. The influence of fluorinated 1,3-diketonate anions and the structural variation in cyclic amine cations on the above physicochemical properties was examined. X-ray single-crystal diffraction analysis of compound **7** confirms the proton transfer from 4,4,4-trifluoro-1-phenyl-1,3-butanedione to *N*-butylpyrrolidine.

Introduction

Since the physical properties of ethylammonium nitrate [$(EtNH_3)NO_3$] (m.p. 13–14 °C)[1] were reported, considerable effort has been devoted to the study of ionic liquids[2–3] as well as to their green applications as solvents and advanced materials, and in separations.[4–7] Their unique physicochemical properties, such as nonvolatility, nonflammability, tunable polarity, water miscibility and wide liquid range, can be easily modified to optimize the materials for specific applications through variation and modification of their cationic and/or anionic components.[8] However, their relatively high viscosity, as compared with common organic solvents, is one of the major barriers restricting their practical applications, because high viscosity usually results in low diffusion coefficients, slow mass transfer, and low electric conductivity. Therefore, much interest has been focused on the syntheses of ionic liquids with low viscosity and low melting point or on methods to reduce their viscosity.[9]

The combination of the 1-ethyl-3-methylimidazolium (EMIM) cation and fluorine-containing anions produced many promising ionic liquids possessing low melting points and viscosities.[10–11] For example, the viscosities of [EMIM][$F(HF)_{2.3}$] and [EMIM][TSAC] [TSAC = 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide] are 4.85 cP[12] and 25 cP[13]at 25 °C, respectively. The combination of fluorine-containing anions with quaternary ammonium[14] and trialkylsulfonium cations[15] also led to numerous ionic liquids, which exhibit not only low melting points and low viscosity but also other interesting physical properties owing to the presence of fluorine.

Fluorinated 1,3-diketonates are promising anions in ionic liquids,[3b,16,17] in which the strong electron-withdrawing effect of the fluorinated moiety enhances the acidity of the acetylacetone proton and the delocalization of the negative charge which favors proton transfer to a Lewis base with concomitant stabilization of the conjugate base. 1,3-Diketones exist as enol/keto tautomers with the equilibrium skewed toward the enolic form when the substituents on the carbonyl carbon atoms are electron-withdrawing. Thus, fluorinated 1,3-diketones can act as Brønsted acids which offer an excellent choice for the anion of ionic liquids leading to low viscosities.[16,18] In fact, the viscosity of trioctylammonium hexafluoro-1,3-diketonate at 3.44 cP (25 °C) is among the lowest reported for any ionic liquid.[16] By taking advantage of 1,3-diketones as proton-transfer reagents to form quaternary salts with a variety of amines, it is possible to produce salts where an important feature of the anion, perfluoroalkyl 1,3-diketonate, is introduced. As is the case with the bis(trifluoromethanesulfonyl)amide anion, there is considerable delocalization of the electron cloud over the molecular backbone which may aid in reducing the degree of hydrogen bonding in these systems and thus have impact on melting points and other physical properties.[16,18] As a continuation of our research work in fluorine-containing ionic liquids, we were interested in the *N*-alkylpyrrolidines, which have generated some interesting slightly viscous and highly conductive ionic liquids owing to the existence of the related N-heterocyclic pyrrolidinium

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core.[19] We now report the preparation and characterization of a range of new fluorine-containing ionic liquids from fluorinated 1,3-diketones and *N*-alkylpyrrolidines with methyl, butyl, hexyl, and 4,4,4-trifluorobutyl substituents. In order to compare their physicochemical properties, ionic liquids formed from fluorinated 1,3-diketones and *N*-methylpiperidine were also synthesized.

Results and Discussion

Synthesis and Properties

Cations and/or anions with varying substituents have an important effect on the chemical and physical properties of ionic liquids; therefore, we chose the *N*-alkylpyrrolidines **1a**–**1d** as proton acceptors and the three fluorinated 1,3-diketones 1,1,1,5,5,5-hexafluoroacetylacetone (**2a**), 1,1,1-trifluoro-2,4-pentanedione (**2b**), and 4,4,4-trifluoro-1-phenyl-1,3-butanedione (**2c**) as proton donors. The synthetic pathway leading to **3**–**11** is depicted in Scheme 1. The reactants **1b**, **1c** and **1d** were easily prepared by the alkylation reaction of pyrrolidine with 1-iodobutane, 1-bromohexane and 1,1,1-trifluoro-4-iodobutane, respectively, in the presence of dmf and aqueous NaOH solution. Subsequent reactions with **2a**–**2c** in acetonitrile gave rise to the target ionic liquids. According to similar procedures, the *N*-methylpiperidinium-based liquids **12**–**14** were synthesized by the reactions of *N*-methylpiperidine (**1e**) and **2a**–**2c**.

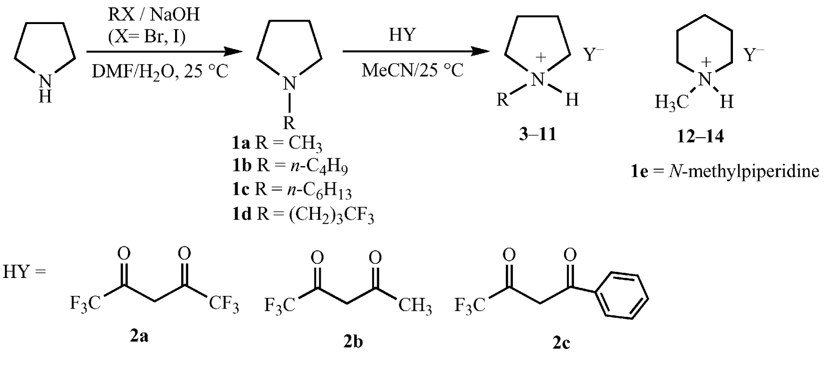
All of the newly synthesized ionic liquids are miscible with organic solvents ranging in polarity from hexane to methanol. They were characterized by ^{1}H and ^{19}F NMR spectroscopy and elemental analyses. For the ionic liquids with the same anion, the ^{1}H NMR spectroscopic data are routine with minimal or no change in the chemical shifts of the cationic pyrrolidine and piperidine parent rings. The chemical shifts of the protons of $–CH_2–N–$ in both the parent rings and the substituents were downfield compared to those of their corresponding precursors **1a**–**1d**; however, the trend decreases when changing the anion from 1,1,1,5,5,5-hexafluoroacetylacetone (**2a**) to 1,1,1-trifluoro-2,4-pentanedione (**2b**) to 4,4,4-trifluoro-1-phenyl-1,3-butanedione (**2c**).

Summarized in Table 1 are the physical properties (melting point, glass transition temperature, viscosity and density) of all the newly synthesized ionic liquids. Melting points or glass transition temperatures of **3**–**14** were determined by differential scanning calorimetry (DSC). The compounds **5**, **6**, **8**, **9**, and **14** are room-temperature ionic liquids with melting points below 0 °C, whereas **3**, **4**, **7**, and **10**–**13** can also be classified as falling into the ionic liquid class, because their melting points are below 100 °C. It should be pointed out that, although the phase-transition temperatures of the *N*-methylpyrrolidinium-based ionic liquids **3** (44 °C), **4** (36 °C) and **5** (–42 °C) are lower than those of the analogous *N*-methylpiperidinium-based salts **12** (95 °C), **13** (59 °C) and **14** (–31 °C), the decrease in both series is similar. The correlation between phase-transition temperatures and alkyl substituents of cations is also clearly observed in Table 1; e.g., with a constant fluorine-containing anion, an increase of length and flexibility of alkyl groups on the cations resulted in lower phase-transition temperatures in keeping with the alkyl-substituted imidazolium-based ionic liquids. For the **2a**-based *N*-alkylpyrrolidinium ionic liquids, **3**, **6** and **8**, variation of *N*-substituents from methyl to butyl to hexyl, the melting points de-

Table 1. Physicochemical properties of ionic liquids.

Compound	Tertiary amine	Brønsted acid (HY)	T_m[a] [°C]	T_g[a] [°C]	Viscosity [cP][b] 25 °C	50 °C	60 °C	Density[c] [g/cm^3]
3	**1a**	**2a**	44					1.45
4	**1a**	**2b**	36					1.31
5	**1a**	**2c**		–42	592.0	66.8	37.4	1.22
6	**1b**	**2a**	–5		11.8	7.1	4.2	1.25
7	**1b**	**2c**	67					1.08
8	**1c**	**2a**		–16	26.8			1.21
9	**1c**	**2c**		–53	346.3	52.7	29.8	1.16
10	**1d**	**2a**	30					1.48
11	**1d**	**2c**	102					1.35
12	**1e**[d]	**2a**	95					1.44
13	**1e**[d]	**2b**	59					1.23
14	**1e**[d]	**2c**		–31		149.8	68.3	1.21

[a] T_m (melting point) and T_g (glass transformation temperature) determined by DSC. [b] Viscosity for room-temperature ionic liquids, determined by MINIVIS II. [c] Density determined by Micromeritics Accupyc 1330 gas pycnometer. [d] **1e**, *N*-methylpiperidine.



Scheme 1.

crease from 44 (**3**) to –5 (**6**) to –16 °C (**8**). This suggests decreased packing efficiency in the crystal lattice as the alkyl groups are elongated. In the case of trifluorobutyl-substituted liquids higher melting points are observed for **10** (30 °C) and **11** (102 °C) than those of butyl-substituted **6** (–5 °C) and **7** (67 °C).

The densities of **3**–**14** fall in the range from 1.08 to 1.48 $\mathrm{g\,cm^{-3}}$ (Table 1). Changing of the anion precursors from 1,1,1,5,5,5-hexafluoroacetylacetone to 1,1,1-trifluoro-2,4-pentanedione to 4,4,4-trifluoro-1-phenyl-1,3-butanedione results in the decrease of density in both pyrrolidinium-based and piperidinium-based ionic liquids. Not surprisingly, the densities of ionic liquids bearing fluoroalkyl chains (**10** and **11**) are higher than those of their congeners with non-fluoroalkyl chains (**6** and **7**). Thus, the presence of alkyl and fluoroalkyl substituents has an important impact on the physicochemical properties of these materials.

As expected, the viscosities of the room-temperature ionic liquids **5**, **6**, **9** and **14** remarkably decrease with increasing temperature. Ionic liquid **6**, 1-butylpyrrolidinium 1,1,1,5,5,5-hexafluoroacetylacetonate has an interestingly low viscosity (11.8 cP at 25 °C), which is considerably lower than that of the *N*-methoxymethyl-*N*-methylpyrrolidinium trifluoro(perfluoroethyl)borate (37 cP) reported earlier.[19] Of the quaternary ammonium cations, *N*-alkyl-*N*-methylpyrrolidinium salts have been shown to produce slightly viscous ionic liquids due to the quasi-flat shape of the pyrrolidinium core.[20] This fact must arise because of the proclivity of the 1,3-diketonate to delocalize the electron cloud along the anion backbone. The viscosity of the pyrrolidinium-based ionic liquid **5** (66.9 cP at 50 °C, 37.4 cP at 60 °C) is also lower than that of the piperidinium-based analogue **14** (149.8 cP at 50 °C, 68.3 cP at 60 °C).

Table 2. Crystal data and structure refinement for compound **7**.

	7
Empirical formula	$C_{18}H_{24}F_3NO_2$
Formula mass	343.38
Crystal size [mm]	0.40 × 0.32 × 0.21
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	10.7435(7)
b [Å]	16.2935(10)
c [Å]	11.1612(7)
β [°]	112.808(1)
V [Å^3]	1801.0(2)
Z	4
$D_{\text{calcd.}}$ [$\mathrm{g\,cm^{-3}}$]	1.266
μ [$\mathrm{mm^{-1}}$]	0.102
T [K]	90(2)
λ(Mo-K_α) [Å]	0.71073
Reflections collected	26763
Unique reflections	4132
R_{int}	0.0332
Parameters	221
S on F^2	1.035
R_1 [$I > 2\sigma(I)$][a]	0.0418
wR_2 [$I > 2\sigma(I)$][b]	0.1051
R_1 (all data)[a]	0.0524
wR_2 (all data)[b]	0.1125
$\Delta\rho_{\text{min/max}}$ [e/Å^3]	0.334/–0.175

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Molecular Structure

Compound **7** is solid at room temperature. Crystals suitable for X-ray single crystal diffraction were obtained by slow concentration of a hexane solution. The crystal data and structural information are summarized in Table 2. The asymmetric unit of **7** consists of one 1-butylpyrrolidinium cation and one 4,4,4-trifluoro-1-phenyl-1,3-butanedionate anion. One hydrogen atom of 4,4,4-trifluoro-1-phenyl-1,3-butanedione was transferred to N(5) of 1-butyl-pyrrolidine forming a six-membered hydrogen-bonded ring, which confirms that the fluorinated diketone can serve as a Brønsted acid when reacting with cyclic tertiary amines. The hydrogen-bonding distances of N(5)–H(5)···O(2) and N(5)–H(5)···O(1) are 2.759(1) Å and 2.767(1) Å, respectively (Figure 1).

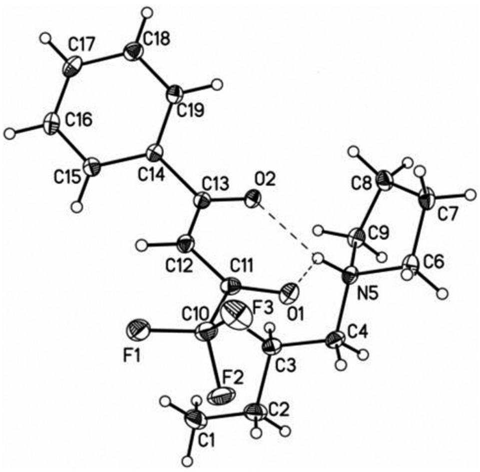


Figure 1. Asymmetric unit of **7** with the thermal ellipsoids at a 30% probability level; hydrogen bonding is indicated by dashed lines.

Conclusions

A series of new *N*-alkylpyrrolidinium-based and piperidinium-based ionic liquids with fluorine-containing 1,3-diketonates as anions has been synthesized and characterized successfully. The relationship between their structures, phase-transition temperatures, densities and viscosities was determined. Most of them have low melting points and low viscosities. Fluorinated 1,3-diketonate anions are excellent choices for the formation of slightly viscous ionic liquids and provide a promising route for the design and synthesis of new types of ionic liquids.

Experimental Section

General Methods: All the reagents were available commercially and were used as purchased. ^1H and ^{19}F NMR spectra were recorded in $CDCl_3$ with a 300 MHz spectrometer (Bruker AMX 300) operating at 300 and 282 MHz, respectively by using $CDCl_3$ as locking solvent. Chemical shifts are reported in ppm relative to $CFCl_3$ for ^{19}F and TMS for ^{1}H NMR spectra. IR spectra were recorded using KBr plates for neat liquids and KBr pellets for solids with a BIORAD model 3000 FTS spectrometer. Differential scanning calorimetry (DSC) measurements were performed by using a calorimeter equipped with an Autocool accessory and calibrated with indium. The following procedure was used in experiments for each sample: cooling from 40 to –80 °C and heating to 400 °C at 10 °C/min. The transition temperature, T_m, was taken at the onset of the event. Density was measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Viscosity was obtained with a MINIVIS II (Grabner Instruments). Elemental analyses were determined with an Exeter CE-440 Elemental Analyzer.

X-ray Crystallography: Crystals of compound **7** were removed from the flask, a suitable crystal was selected, attached to a glass fiber, and data were collected at 90(2) K with a Bruker/Siemens SMART APEX instrument (Mo-K_α radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω-scans 0.3° per frame for 5 s, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.77 Å. Cell parameters were retrieved by using SMART[21] software and refined by using SAINTPlus[22] on all observed reflections. Data reduction and correction for Lp and decay were performed by using the SAINTPlus software. Absorption corrections were applied by using SADABS.[23] The structure was solved by direct methods and refined by least-squares methods on F^2 with the SHELXTL program package.[24] The structure was solved in the space group $P2_1/n$ (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were refined by using a mixture of constrained and independent [i.e. H(5)] parameters. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 2. CCDC-684761 for compound **7** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedures for the Preparation of 1-Butyl-, 1-Hexyl-, and 1-(3,3,3-Trifluorobutyl)pyrrolidine (1b–1d): A mixture of pyrrolidine (1.4 g, 20 mmol) and 35% aqueous NaOH (3.0 mL) in dmf (15 mL) was stirred at 25 °C for 1 h. Then 1-iodobutane (4.8 g, 26 mmol) for **1b**, 1-bromohexane (4.3 g, 26 mmol) for **1c**, and 1,1,1-trifluoro-4-iodobutane for **1d** (6.2 g, 26 mmol) was added slowly. The mixture was stirred at 25 °C overnight. The resulting solution was poured into H_2O (15 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with H_2O (3 × 10 mL), and dried with Na_2SO_4. After the solvents were removed, the residue was purified by flash chromatography on silica gel (70–230 mesh) to give **1b**–**1d**.

1-Butylpyrrolidine (1b): Yellow liquid (1.58 g), yield 62%. ^{1}H NMR: δ = 2.49 (m, 4 H), 2.43 (t, J = 10.7 Hz, 2 H), 1.76 (m, 4 H), 1.48 (m, 2 H), 1.33 (m, 2 H), 0.90 (t, J = 14.55 Hz, 3 H) ppm.

1-Hexylpyrrolidine (1c): Yellow liquid (2.14 g), yield 69%. ^{1}H NMR: δ = 2.48 (m, 4 H), 2.41 (t, J = 15.6 Hz, 2 H), 1.77 (m, 4 H), 1.34 (m, 8 H), 0.88 (t, J = 24.5 Hz, 3 H) ppm.

1-(4,4,4-Trifluorobutyl)pyrrolidine (1d): Yellow liquid (2.83 g), yield 78%. ^{1}H NMR: δ = 2.48 (t, J = 11.9 Hz, 4 H), 2.16 (m, 2 H), 2.02 (m, 2 H), 1.76 (m, 4 H), 1.24 (t, J = 14.3 Hz, 2 H) ppm. ^{19}F NMR: δ = –66.9 (t, J = 23.1 Hz, 3 F) ppm.

General Procedure for the Preparation of 3–14: A mixture of *N*-alkylpyrrolidine (1.0 mmol) or *N*-methylpiperidinium (0.10 g, 1.0 mmol), a fluorinated 1,3-diketone (1.0 mmol), and acetonitrile (15 mL) were placed in a round flask and stirred at 25 °C for 24 h. Then the solvent was removed, the residue was washed three times with hexane (3 × 5 mL), and dried under vacuum to give the pure products **3**–**14**.

1-Methylpyrrolidinium 1,1,1,5,5,5-Hexafluoroacetylacetonate (3): White solid (0.28 g), yield 95%. IR: $\tilde{\nu}$ = 3048 (br.), 2835 (br.), 1668 (vs), 1554 (vs), 1460 (s), 1254 (vs), 1192 (s), 1130 (s), 1009 (s), 942 (ms), 902 (w), 858 (w), 788 (s), 755 (m), 659 (ms), 572 (ms), 524 (w) cm^{-1}. ^{1}H NMR: δ = 11.37 (b, 1 H), 5.75 (s, 1 H), 3.93 (s, 2 H), 2.92 (s, 3 H), 2.79 (s, 2 H), 2.10 (m, 4 H) ppm. ^{19}F NMR: δ = –76.9 (s, 6 F) ppm. $C_{10}H_{13}F_6NO_2$ (293.21): calcd. C 40.96, H 4.47, N 4.78; found C 40.74, H 4.42, N 4.71.

1-Methylpyrrolidinium 1,1,1-Trifluoro-2,4-pentanedionate (4): Semisolid (0.22 g), yield 93%. IR: $\tilde{\nu}$ = 1643 (vs), 1460 (s), 1356 (s), 1273 (vs), 1175 (m), 1124 (m), 999 (s), 932 (m), 878 (s), 837 (vs), 762 (s), 721 (s), 606 (w), 545 (vs), 449 (w) cm^{-1}. ^{1}H NMR: δ = 9.4 (br. s, 1 H), 5.53 (s, 1 H), 3.14 (t, J = 13.5 Hz, 4 H), 2.75 (s, 3 H), 1.93 (m, 7 H) ppm. ^{19}F NMR: δ = –76.3 (s, 3 F) ppm. $C_{10}H_{16}NO_2F_3$ (239.23): Elemental analysis was not possible because of the hygroscopic nature of the salt.

1-Methylpyrrolidinium 4,4,4-Trifluoro-1-phenyl-1,3-butanedionate (5): Yellow liquid (0.28 g); yield 93%. IR: $\tilde{\nu}$ = 2966 (br., s), 1970 (w), 1681 (s), 1635 (vs), 1577 (m), 1522 (vs), 1274 (vs), 1176 (s), 1122 (s), 1072 (m), 935 (m), 758 (s), 709 (s), 626 (s), 569 (s), 407 (m) cm^{-1}. ^{1}H NMR: δ = 7.89 (d, J = 7.2 Hz, 2 H), 7.47–7.42 (m, 3 H), 6.33 (s, 1 H), 3.06–3.05 (m, 4 H), 2.73 (s, 3 H), 2.01–1.96 (m, 4 H) ppm. ^{19}F NMR: δ = –76.2 (s, 3 F) ppm. $C_{15}H_{18}F_3NO_2$ (301.30): calcd. C 59.79, H 6.02, N 4.65; found C 58.92, H 5.81, N 4.34.

1-Butylpyrrolidinium 1,1,1,5,5,5-Hexafluoroacetylacetonate (6): Yellow liquid (0.30 g); yield 90%. IR: $\tilde{\nu}$ = 2968 (br., s), 2877 (s), 1668 (vs), 1553 (vs), 1459 (s), 1386 (m), 1252 (vs), 1188 (s), 1079 (m), 941 (s), 906 (w), 825 (m), 787 (s), 748 (m), 659 (vs), 617 (w), 518 (vs), 504 (m) cm^{-1}. ^{1}H NMR: δ = 11.32 (br. s, 1 H), 5.74 (s, 1 H), 3.90 (s, 2 H), 3.10–3.04 (t, J = 18.0 Hz, 2 H), 2.75 (s, 2 H), 2.05 (m, 4 H), 1.67 (m, 2 H), 1.36 (m, 2 H), 0.92–0.88 (t, J = 15.0 Hz, 3 H) ppm. ^{19}F NMR: δ = –76.2 (s, 3 F) ppm. $C_{13}H_{19}F_6NO_2$ (335.29): calcd. C 46.57, H 5.71, N 4.18; found C 45.68, H 5.62, N 4.33.

1-Buthylpyrrolidinium 4,4,4-Trifluoro-1-phenyl-1,3-butanedionate (7): White solid (0.32 g); yield 92%. IR: $\tilde{\nu}$ = 3049 (br., s), 2962 (s), 1637 (vs), 1577 (m), 1509 (vs), 1354 (m), 1278 (s), 1238 (m), 1172 (s), 1126 (s), 1072 (m), 980 (w), 761 (vs), 854 (m), 713 (s), 624 (s), 579 (s), 519 (m), 478 (w) cm^{-1}. ^{1}H NMR: δ = 7.89 (d, J = 9.6 Hz, 2 H), 7.45 (m, 3 H), 6.43 (s, 3 H), 2.98 (s, 4 H), 2.81 (t, J = 58.5 Hz, 2 H), 1.94 (s, 4 H), 1.63 (m, 2 H), 1.35 (m, 2 H),092 (t, J = 14.7 Hz, 3 H) ppm. ^{19}F NMR: δ = –76.1 (s, 3 F) ppm. $C_{18}H_{24}F_3NO_2$ (343.18): calcd. C 62.96, H 7.04, N 4.08; found C 62.58, H 7.16, N 4.15.

1-Hexylpyrrolidinium 1,1,1,5,5,5-Hexafluoroacetylacetonate (8): Yellow liquid (0.33 g); yield 91%. IR: $\tilde{\nu}$ = 2936 (br., s), 2863 (bs), 1668 (vs), 1553 (vs), 1459 (s), 1382 (m), 1251 (vs), 1188 (m), 1131 (m), 1080 (s), 941 (s), 788 (vs), 750 (s), 659 (vs), 574 (s), 524 (m) cm^{-1}. ^{1}H NMR: δ = 5.73 (s, 1 H), 3.93 (s, 2 H), 3.11–3.06 (t, J = 16.2 Hz, 2 H), 2.76 (s, 2 H), 2.06 (m, 4 H), 1.64 (m, 2 H), 1.26 (m, 6 H), 0.85 (t, J = 13.2 Hz, 3 H) ppm. ^{19}F NMR: δ = –76.1 (s, 6 F) ppm. $C_{15}H_{23}F_6NO_2$ (363.34): calcd. C 49.58, H 6.38, N 3.85; found C 48.30, H 6.05, N 3.75.

1-Hexylpyrrolidinium 4,4,4-Trifluoro-1-phenyl-1,3-butanedionate (9): Yellow liquid (0.32 g); yield 86%. IR: $\tilde{\nu}$ = 3264 (br., s), 1963 (m), 1905 (m), 1818 (s), 1678 (m), 1634 (s), 1562 (s), 1273 (w), 1072 (s), 1020 (s), 935 (vs), 787 (s), 756 (vs), 705 (m), 629 (s), 569 (s) cm^{-1}. ^{1}H NMR: δ = 7.87 (d, J = 9.6 Hz, 2 H), 7.46 (m, 3 H), 6.32 (s, 1 H), 3.89 (s, 2 H), 3.10 (t, J = 16.2 Hz, 2 H), 2.47 (s, 2 H), 1.99 (m, 4 H), 1.62 (m, 2 H), 1.28 (m, 6 H), 0.84 (t, J = 18.9 Hz) ppm. ^{19}F NMR: δ = –76.2 (s, 3 F) ppm. $C_{20}H_{28}F_3NO_2$ (371.44): calcd. C 64.67, H 7.60, N 3.77; found C 63.15, H 7.40, N 4.48.

1-Butyl-1-(4,4,4-trifluorobutyl)pyrrolidinium 1,1,1,5,5,5-Hexafluoroacetylacetonate (10): White solid (0.37 g); yield 95%. IR: $\tilde{\nu}$ = 1669 (vs), 1549 (vs), 1456 (s), 1038 (m), 940 (ms), 838 (ms), 788 (s), 754 (s), 659 (vs), 574 (vs), 525 (m), 447 (m) cm^{-1}. ^{1}H NMR: δ = 11.34 (br. s, 1 H), 5.76 (s, 1 H), 3.94 (s, 2 H), 3.24 (t, J = 15.6 Hz, 2 H), 2.79 (s, 2 H), 2.12 (m, 8 H) ppm. ^{19}F NMR: δ = –66.1 (t, J = 21.2 Hz, 3 F), –77.0 (s, 3 F) ppm. $C_{13}H_{16}F_9NO_2$ (389.26): calcd. C 40.11, H 4.14, N 3.60; found C 40.33, H 4.14, N 3.54.

1-Butyl-1-(4,4,4-trifluorobutyl)pyrrolidinium 4,4,4-Trifluoro-1-phenyl-1,3-butanedionate (11): Colorless crystals (0.36 g); yield 92%. IR: $\tilde{\nu}$ = 3047 (br.), 1630 (br.), 1513 (s), 1280 (w), 1035 (s), 978 (w), 850 (s), 800 (ms), 763 (vs), 713 (vs), 660 (ms), 569 (s), 524 (m), 465 (s) cm^{-1}. ^{1}H NMR: δ = 7.88 (d, J = 7.2 Hz, 2 H), 7.45 (m, 3 H), 6.41 (s, 1 H), 2.76 (m, 4 H), 2.18 (m, 6 H), 1.89 (m, 4 H) ppm. ^{19}F NMR: δ = –76.3 (s, 3 F), –66.2 (t, J = 22.0 Hz, 3 F) ppm. $C_{18}H_{21}F_6NO_2$ (397.36): calcd. C 54.41, H 5.33, N 3.52; found C 53.91, H 5.26, N 3.90.

1-Methylpiperidinium 1,1,1,5,5,5-Hexafluoroacetylacetonate (12): White solid (0.29 g); yield 96%. IR: $\tilde{\nu}$ = 3024 (br., s), 2966 (s), 1666 (vs), 1550 (vs), 1493 (m), 1458 (s), 1188 (s), 1130 (m), 997 (s), 974 (m), 860 (s), 788 (vs), 750 (s), 660 (vs), 572 (s), 524 (m), 461 (w), 414 (w) cm^{-1}. ^{1}H NMR: δ = 5.74 (s, 1 H), 3.66 (d, J = 11.4 Hz, 2 H), 2.77 (s, 3 H), 2.58 (s, 2 H), 1.89 (m, 2 H) ppm. ^{19}F NMR: δ = –76.9 (s, 6 F) ppm. ^{13}C NMR: δ = 85.9, 55.6, 44.3, 22.8, 22.6, 21.5, 14.0 ppm. $C_{11}H_{15}F_6NO_2$ (307.23): calcd. C 43.00, H 4.92, N 4.56; found C 42.80, H 4.87, N 4.55.

1-Methylpiperidinium 1,1,1-Trifluoro-2,4-pentanedionate (13): White solid (0.23 g); yield 92%. IR: $\tilde{\nu}$ = 1688 (s), 1354 (s), 994 (s), 983 (s), 938 (m), 836 (vs), 720 (vs), 605 (s), 563 (m), 547 (s), 515 (s), 461 (s), 441 (m), 413 (m) cm^{-1}. ^{1}H NMR: δ = 5.69 (s, 1 H), 2.94–2.87 (m, 4 H), 2.64 (s, 3 H), 1.97 (s, 3 H), 1.76 (m, J = 23.1 Hz, 4 H), 1.54–1.50 (m, J = 11.7 Hz, 2 H) ppm. ^{19}F NMR: δ = –76.1 (s, 3 F) ppm. $C_{11}H_{18}F_3NO_2$ (253.26): calcd. C 52.17, H 7.16, N 5.53; found C 52.09, H 7.18, N 5.60.

1-Methylpiperidinium 4,4,4-Trifluoro-1-phenyl-1,3-butanedionate (14): Yellow liquid (0.26 g); yield 84%. IR: $\tilde{\nu}$ = 3441 (br., s), 3264 (s), 1909 (m), 1824 (m), 1676 (s), 1636 (vs), 1456 (m), 1278 (s), 1070 (s), 986 (m), 976 (s), 938 (s), 855 (vs), 783 (vs), 758 (s), 707 (s), 629 (vs), 563 (m) cm^{-1}. ^{1}H NMR: δ = 7.83 (d, J = 6.0 Hz, 2 H), 7.41–7.35 (m, 3 H), 6.16 (s, 1 H), 3.04 (s, 4 H), 2.74 (s, 3 H), 1.82–1.77 (m, 2 H) ppm. ^{19}F NMR: δ = –75.8 (s, 3 F) ppm. ^{13}C NMR: δ = 187.3, 171.2 (q, J = 166.1 Hz), 140.8, 128.1, 126.9, 121.2 (q, J = 377.5 Hz), 89.2, 55.3, 44.2, 22.9, 21.6 ppm. $C_{16}H_{20}F_3NO_2$ (315.33): calcd. C 60.94, H 6.39, N 4.44; found C 58.94, H 6.03, N 4.24.

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