Expedient Synthesis of Symmetric Aryl Ketones and of Ambient-Temperature Molten Salts of Imidazole

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Abstract: A short procedure for the synthesis of 2,2-di(3-thienyl)-1,3-dioxolan is described. The route developed is convenient (only two synthetic and one chromatographic steps are required) and efficient (66% overall yield from 3-bromothiophene). This compound was transformed into the ketone, cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-one by a known process. Optimized syntheses of symmetric aryl ketones, 1-alkyl-3-methylimidazolium and 1-alkyl-2-methyl-3-methylimidazolium liquid salts are also reported.

Key words: ketones, thiophenes, imidazoles, heterocycles, sulfonamides

Electrochemical capacitors are energy conversion devices which consist of two active electrode materials that are in contact with an appropriate electrolyte.[1] First, electronically conducting polymers such as polythiophene derivatives, have recently received some attention as electrode materials due to their potentially high power densities which originate from fast redox switching (e.g. fast ionic transport).[2] Second, conventional liquid solvent-salt and polymer-salt were used as electrolyte (to insure ionic conduction between the two polymer electrodes) in these capacitors.[2]

Thiophene derivatives are among the most widely investigated model compounds for electrically conducting material since they give rise to polymers which may be both p- and n-type doped.[2-7] Within this family of polymers, poly(cyclopenta[2,1-b:3',4'-b']dithiophen-4-one, (CDT) **5**, introduced by Lambert and Ferraris,[8] stands out for its electrochemical properties, high stability in the conducting state and propensity to multiple redox cycling, making it a stable p- and n-dopable conductor suitable for application as supercapacitors composites as we have recently shown.[9] Roncali et al. have also reported that the polymer obtained from the 1,3-dioxolane derivative of the title compound **5** displayed similar electrochemical properties.[10] Since, many of the precursors of small band gap conducting polymers are substituted-4-methylidene derivatives of **5**,[4,9-16] ketone **5** is an important intermediate in the synthesis of a variety of low band gap conducting polymers.[17]

On the other hand, room-temperature ionic liquids have also attracted interest as solvents for synthesis and catalysis applications, which have recently been reviewed.[18] These liquid salts can replace classic organic solvents which may be volatile and/or hazardous. Much of the progress realized to date render these room-temperature molten salts more stable, chemically and thermally. These liquids are entirely composed of ions and in this state, they resemble the ionic melts which are generally produced by heating normal metallic salts such as sodium chloride to high temperature (e.g. NaCl to over 800 °C). Some other useful features of these ionic liquid systems include the greater solubilities of organic species, the prevalence of high coulombic forces resulting in the absence of any significant vapor pressure and the availability of air and moisture stable, water immiscible ionic liquids (e.g. imidazolium salts of PF_6^- or BF_4^-). Such systems are able media for the development of completely novel liquid-liquid extraction processes.[19] Some low melting salts have serve as models to modify the physical properties (melting points, conductivities, etc.);[20] more recently, they have been used as solvents for industrially important organic reactions such as regioselective alkylation,[21] Friedel-Crafts acetylations,[22] and biphasic hydrogenations.[23] Moreover, some imidazolium salts are excellent electrolytes for electrochemical devices, including supercapacitors since they are characterized by a fairly large window of electrochemical stability.[24-26] In addition to being liquids at room temperature, these electrolytes show higher conductivity, thermal stability and solubility than quaternary ammonium salts commonly used in these devices and are therefore potential candidates for application in electrochemical supercapacitors.

As part of a collaborative effort toward the development of an electrochemical supercapacitors constructed wholly with conducting polymers,[9] we wish to communicate an expedient synthesis of the title monomer cyclopenta[2,1-b:3',4'-b']dithiophen-4-one (CDT) **5**, and its 4-(1,3-dioxolane) derivative **4**. We would also like to describe the efficient synthesis of imidazolium liquid salts to be use as supporting electrolytes in such devices. We have also optimized a method for the preparation of symmetric ketones **2**.

Scheme 1 depicts the synthesis of (CDT) **5**, as previously reported by Gronowitz et al.[27] and Jordens et al.[28] That is, bis-(3-thienyl) ketone **2a** was prepared from commercially available 3-bromothiophene via lithiation and subsequent reaction with 3-thiophenecarboxaldehyde followed by oxidation of the resulting *bis*-(3-thienyl)methanol **1**

with chromium (VI) oxide. (Scheme 1, route A). A modified procedure which did not require the use of 3-thiophenecarboxaldehyde has recently been reported by Beyer et al.[29] Thus, **2a** was prepared from the addition of two equivalents of 3-thienyllithium[30] to one equivalent of methylformate, immediately followed without purification by the oxidation of the resulting alcohol **1** with pyridinium chlorochromate (PCC).[12a] (Scheme 1, route B). The ketone **2a** was subsequently transformed into the 1,3-dioxolane **3**.[28] This reaction was carried out in refluxing benzene for 6 days, under which conditions some polymerization occurs due to the prolonged heating. Bis-deprotonation of compound **3** with two equivalents of *n*-butyllithium followed by iodine treatment afforded the corresponding 2,2'-diiodo derivative of **3**. An Ullmann ring closure, induced by activated copper powder in boiling dimethylformamide, afforded 2,2-di-(3-thienyl)-1,3-dioxolane **4**. Finally, the hydrolysis of the 1,3-dioxolane acetal under acidic conditions rendered CDT **5**.
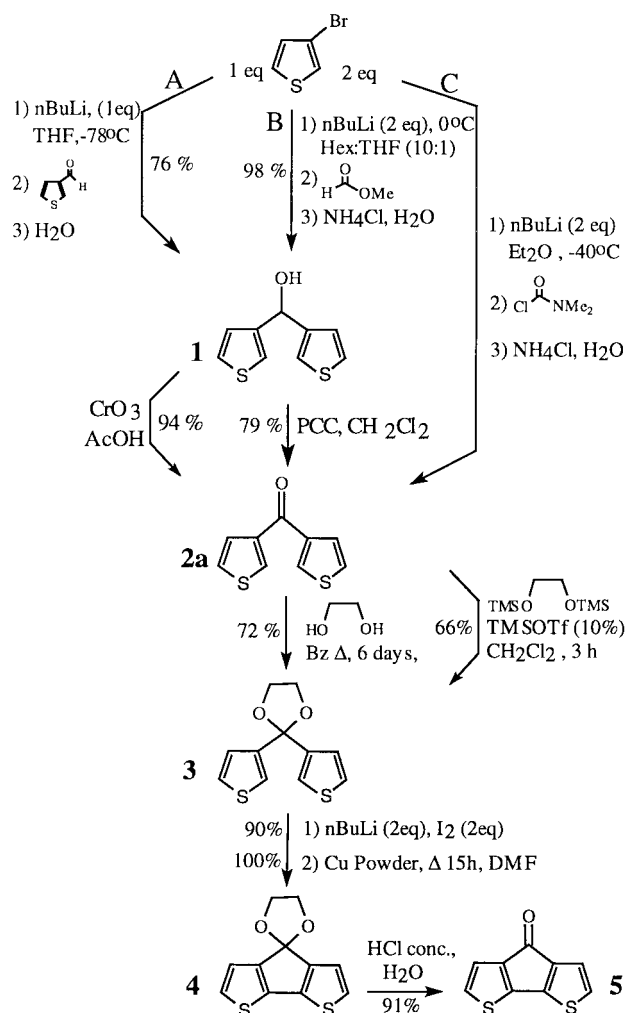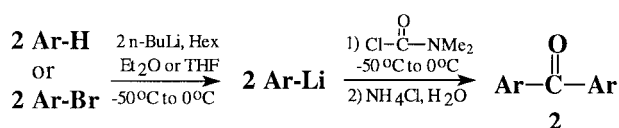
We devised a shorter synthetic route by modifying the preparation of bis-(3-thienyl) ketone **2a**, having adapted the procedure described by Michael et al.[31] (Scheme 1, route C) The first step was the reaction of 3-thienyl lithium with *N,N*-dimethylcarbamyl chloride (DMC) in diethyl ether, which was claimed to provide ketone **2a** in 89% yield.

Unfortunately, we were unable to reproduce these results as described. The use of etheral ethyllithium or methyllithium up to −60 °C, in diethyl ether as solvent, to generate 3-thienyl lithium rendered only the starting 3-bromothiophene. The same reaction in THF as solvent at −60 °C, for 45 minutes, and treatment with DMC furnished many side products along with 3-bromothiophene. Higher temperatures were avoided since it is known that the 3-lithiothiophene converts into the 2-lithiothiophene upon warm-up in polar solvents. However, it was recently shown that 3-lithiothiophene was stable in hexane at room temperature.[30] We are pleased to report that the use of *n*-butyllithium in hexane with a limited amount of diethyl ether allow the exchange reaction to occur without isomerization at temperatures up to −40 °C. Subsequent treatment of the 3-thienyllithium thus generated with DMC afforded good yield of the ketone **2a** in a reproducible fashion. This transformation bypasses the usually required oxidation step. Therefore, we report this as a general method for the facile preparation of symmetric aryl ketones (see below).

The following acetalization step, leading to **3**, was found to be time-consuming but necessary to achieve optimal conversion. We reasoned that this reaction did not proceed sufficiently fast due to inefficient cyclization and therefore some decomposition and other undesired reactions occur. This problem was effectively solved by adapting the Noyori et al. procedure for acetalization under aprotic conditions.[32,33] That is, the crude ketone **2a** was efficiently acetalyzed under mild conditions mixing with 1,2-bis(trimethylsilyloxy)ethane and a catalytic amount of trimethylsilyl trifluoromethane-sulfonate (TMSOTf) at room temperature for three hours. This procedure provided us with an extremely facile and fast pathway to the relatively advanced precursor acetal **3**, which, in turn, was transformed into compound **4** in nearly quantitative yields by the Cu-catalyzed Ulmann coupling reaction, when freshly prepared activated copper powder was used as previously mentioned.[34] Finally, the deprotection step was carried out as reported.[28]

The synthesis of asymmetric ketones has recently attracted interest. The methods developed include the samarium (II) mediated addition of alkyliodides to alkyl nitriles[35] and the cross-coupling reactions of acid chlorides with arylboronic acids.[36] However, the synthesis of symmetric ketones directly from organometallic reagents and acid chlorides or esters often proceeds in low yield because of the possibility of subsequent addition of the organometallic reagent to the in situ generated ketone to form a tertiary alcohol.[37] We have optimized a complementary method for the preparation of symmetric aryl ketones which sim-

Synthesis of Cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-one **5**.
Route A: Gronowitz et al.[27] and Jorden et al.[28]
Route B: Beyer et al.[29]
Route C: This work

Scheme1

ply involves the addition of an aryllithium to DMC as shown in Scheme 2.

Synthesis of symmetric aryl ketones

Scheme 2

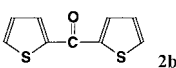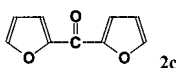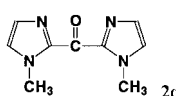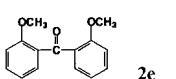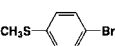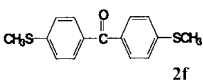The results for various aryl ketones **2b−h** derived from their corresponding aromatic and heteroaromatic precursors are summarized in Tables 1 and 2. In general, generation of the carbanion from the corresponding bromide, by a metal-halogen exchange with *n*-butyllithium, were carried out in diethyl ether by allowing the reaction to warm from −50 °C up to −10 °C over 3 hours, while deprotonation at the 2-position of the various heterocycles was achieved in THF at higher temperatures. TMEDA was essential for the *ortho*-metallation of anisole[38] and 1-methylimidazole. Ketones **2** were obtained in yields rang-
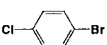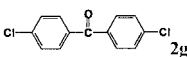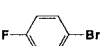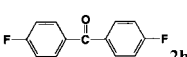
ing from 70% to as high of 92%. This method provides heterocyclic aryl ketones which may be useful for the preparation of conducting polymers and also represents a new one-pot synthesis of the industrially important monomer 4,4'-dichlorobenzophenone, a precursor to 4,4'-difluorobenzophenone, the key intermediate in the manufacture of poly(ether ether ketone), PEEK, a speciality polymer.[39]

The synthesis of ambient temperature ionic liquids is relatively straightforward, as shown in Scheme 3. The first step is the reaction of 1-methylimidazole or 1-methyl-2-methylimidazole and the appropriate bromoalkyl, which provides the corresponding imidazolium bromide. The bromide reacts with $Li^+(CF_3SO_2)_2N^-$ (anion exchange and phase separation) to give the corresponding methylimidazolium bis[(trifluoromethyl)sulfonyl]amide.

For the N-alkylation step, the Grätzel's method[40] works well for reactions involving small electrophiles and monosubstituted *N*-alkyl imidazole. However, a significant drop in conversion yield was observed when bulkier electrophiles (i.e. butyl) and/or when sterically more hindered 1,2-imidazole were used. 1,1,1-Trichloroethane was used as solvent. The utilization of other solvents was

Table 1   Prepared Symmetric Aryl Ketones **2**

Substrates	Conditions[a]	Aryl ketone **2**	Yield (%)[b]	Mp (°C)	IR (KBr) ν (cm^{-1})
	Ether −50 °C to 0 °C	**2b**	77[c]	87−88	3097, 1650, 1614, 1413, 1350,1286, 1224, 1118, 1079, 1047, 860, 780
	THF −50 °C to 0 °C	**2c**	87[c]	bp 98−99 (03 mmHg)	3138, 1634, 1572, 1468, 1394,1310, 1031, 1013, 884, 838, 758
	THF + TMEDA 0 °C (30 min)	**2d**	92[d]	148−149	3110, 2949, 1625, 1426, 1146, 938, 886, 787
	Ether + TMEDA −55 °C to r.t.	**2e**	77[c]	97−98	2945, 1626, 1421, 1314, 793, 745
	Ether −30 °C to −10 °C	**2f**	78[d]	115−116	2978, 2917, 1637,1589, 1397, 1291, 1089, 848, 750, 671
	Ether −50 °C to −30 °C	**2g**	70[c]	131−132	3020, 1652, 1587, 1399,1307, 1286, 1088, 1013, 928, 851, 832, 753
	Ether −50 °C to −30 °C	**2h**	75[c]	99−100	3080, 1648, 1598, 1506, 1409, 1306, 1298, 1281, 1244, 1228, 1160, 1155, 1145, 1106
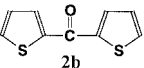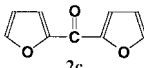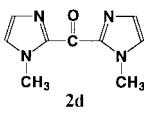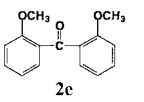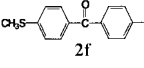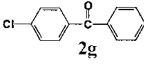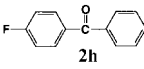
[a] Reaction conditions: The reactions were carried out on a 0.50 g scale for aromatic substrates and on a 1.00 g scale for bromoaromatic species, in the specified solvent (10 mL). TMEDA (1.0 equiv) was added where indicated. *n*-BuLi in hexanes (1.0 equiv) was added at the initial temperature and gradually warmed to the specified temperature over 3 h, unless otherwise indicated. DMC (0.5 equiv.) was added to the aryllithium solution, cooled to –50 °C, gradually warm to 0 °C over 3 h and then quenched with sat. NH$_4$Cl.
[b] Isolated yields.
[c] Et$_2$O extraction.
[d] CH$_2$Cl$_2$ extraction.

Table 2 ¹H, ¹³C NMR and EI-MS Data of Symmetric Aryl Ketones **2** Prepared

| Product	¹H NMR (CDCl₃/TMS); δ, *J* (Hz)	¹³C NMR (CDCl₃/TMS)	EI-MS (70 eV) *m/z* (%)
2b	7.15 (dd, 2 H, *J* = 5.1, 3.9 H-4+4'), 7.67 (dd, 2 H, *J* = 5.1, 1.2, H-5+5'), 7.87 (dd, 2 H, *J* = 3.9, 1.2, H-3+3')	128.16, 133.35, 133.68, 143.14, 178.50	194 (45), 111 (100), 83 (12)
2c	6.58 (dd, 2 H, *J* = 3.6, 1.8, H-4+4'), 7.53 (dd, 2 H, *J* = 3.6, 0.8, H-3+3'), 7.66 (dd, 2 H, *J* = 1.8, 0.8, H-5+5')	112.58, 119.79, 147.01, 151.39, 168.68	162 (66), 95 (100), 67 (6)
2d	3.98 (s, 6 H, N-CH₃), 7.05 (s, 2 H, H-5+5'), 7.27 (s, 2 H, H-4+4')	35.74, 126.53, 130.21, 143.60, 174.20	190 (50), 162 (50), 161 (60), 109 (100), 95 (42), 82 (70), 54 (40)
2e	3.64 (s, 6 H, 2 x OCH₃), 6.89 (d, 2 H, *J* = 8.2, H-6+6'), 6.96 (dt, 2 H, *J* = 8.2, 0.9, H-4+4'), 7.41 (ddd, 2 H, *J* = 8.2, 7.5, 1.8, H-5+5'), 7.49 (dd, 2 H, *J* = 7.5, 1.8, H-3+3')	55.89, 111.64, 120.54, 130.42, 130.62, 132.80, 158.50, 195.56	242 (25), 211 (10), 135 (100), 121, (30), 92 (22), 77 (17)
2f	2.10 (s, 6 H, 2 x SCH₃), 7.24 (d, 4 H, *J* = 8.4, H-3+3'), 7.69 (d, 4 H, *J* = 8.4, H-2+2')	15.08, 96.52, 125.07, 130.66, 134.10, 144.85	274 (37), 227 (10), 151 (100)
2g	7.45 (d, 4 H, *J* = 8.8, H-3+3'), 7.71 (d, 4 H, *J* = 8.8, H-2+2')	128.96, 129.67, 131.52, 135.70, 139.36	252 (12), 250 (15), 141 (32), 139, (100), 111 (35), 75 (17)
2h	7.15 (t, 4 H, *J* = 8.6, H-3+3'), 7.78 (dd, 4 H, *J* = 8.6, 5.4, H 2+2')	115.75 (d, J_{C-F} = 22), 132.69 (d, J_{C-F} = 8), 148.90 (d, J_{C-F} = 254), 193.99	218 (30), 123 (100), 95 (19), 75, (15)

explored and it was found that replacing trichloroethane with toluene increased the yield up to 90–100% and facilitated the process (see experimental). Toluene is also a solvent of choice when scale-up production is considered.
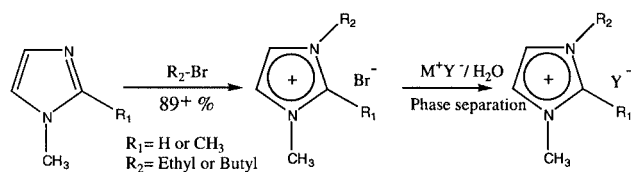
Synthesis of the ambient temperature imidazolium salts

Scheme 3

Mps were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR instrument. ¹³C NMR spectra were recorded at 75 MHz. ¹H NMR spectra were recorded using a Varian 300 MHz spectrometer. Chemical shifts (δ) are reported in ppm. Mass spectra were obtained using a GC-MS (GCD plus gas chromatography-electron ionization detector, HPG 1800A GCD system) equipped

with a 5% crosslinked Ph Me silicone HP 19091 J-433 column. Elemental analyses were carried out at the chemistry department of the Université de Montréal, Montréal, P.Q., Canada; on a Fisons Instrument SPA, model EA1108. Separations were carried out on silica gel (7749 Merck) using circular chromatography (chromatotron®, model 7924, Harrison Research). Li⁺(CF₃SO₂)₂N⁻ was obtained from 3M company and was used as received. All other chemicals were obtained from Aldrich Chemical Co. and were used without further purification. THF Et₂O were dried over sodium benzophenone ketyl anion radical and distilled under a dry N₂ atm immediately prior to use. All reactions involving organometallic reagents and liquid salt syntheses were carried out under N₂. All liquids involved in the liquid salt preparations were freshly distilled before use.

Bis(3-thienyl) Ketone 2a

3-Bromothiophene (10.00 g, 61.3 mmol) was dissolved in dry Et₂O (Et₂O, 50 mL) and cooled to −78 °C; *n*-BuLi (25.5 mL of a 2.4 M solution in hexane, 61.3 mmol) was then added dropwise. The resulting mixture was stirred for 1 h during which time, the temperature was allowed to warm to −40 °C. The pale yellow suspension of 3-thienyllithium thus obtained was cooled to −50 °C and *N,N*-dimethylcarbamyl chloride (3.3 g, 31 mmol) was added dropwise over 1 to 2 min. The mixture was allowed to warm to −40 °C, then stirred for 3 h at temperatures between −40 to −30 °C, and treated with aq

HCl (1 N, 50 mL) at 0 °C. The reaction vessel was allowed to warm to r.t., the layers were separated, and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), the solvent was evaporated and the residue was dried under vacuum to yield 4.64 g of a dark colored mass (78%). The product thus obtained was then used without further purification. An analytical sample was obtained by chromatography (dissolved in CCl_4 and eluted with petroleum ether/Et_2O, 3:1) and recrystallized from Et_2O/petroleum ether.

Mp: 73 °C (Lit.[27] 72–73 °C).

IR (KBr): ν = 3113, 1700, 1695, 1629, 1511, 1426, 1266, 1136, 847, 826, 740, 696 cm^{-1}.

^{1}H NMR: δ = 7.38 (dd, J = 5.1, 3.0 Hz, 2H, H-5+5'), 7.60 (dd, J = 5.1, 1.3 Hz, 2H, H-4+4'), 8.01 (dd, J = 3.0, 1.3 Hz, 2H, H-2+2').

These spectroscopic data were similar to those reported in the literature.[29]

^{13}C NMR (CDCl$_3$): δ = 126.30 (2 CH), 128.23 (2 CH), 132.64 (2 CH), 142.02 (2C), 183.24 (C).

GC-MS (70 eV): m/z (%) = 194 (M$^+$, 61), 111 (M$^+$–Th, 100), 83 (Th$^+$, 15).

Anal. Calcd for $C_9H_6OS_2$: C, 55.64; H, 3.11; S, 33.01. Found: C, 55.48; H, 3.08; S, 33.01.

2,2-Di(3-thienyl)-1,3-dioxolane 3

To a cooled stirred CH_2Cl_2 solution (25 mL) containing the crude ketone **2** (5.83 g, 30 mmol), were successively added 1,2-bis(trimethylsilyloxy)ethane (12.8 g, 62 mmol) and trimethylsilyl trifluoromethanesulfonate (0.56 mL, 3 mmol, 10% mol) at 0 °C. The mixture was stirred at r.t. for an additional 3 h, quenched by the addition of dry pyridine (1 mL), poured into sat. $NaHCO_3$ (25 mL) and extracted with Et_2O (3 × 25 mL). The combined extracts were dried (1:1 mixture of Na_2CO_3 and Na_2SO_4) and evaporated. The crude product was purified by chromatography (petroleum ether/CH_2Cl_2, 1:1). The product was thus crystallized from light petroleum as colorless plates (4.72g, 66%), mp: 111 °C (Lit.[28] 113–114 °C).

IR (KBr): 3097, 2968, 2876, 1609, 1411, 1264, 1071, 809 and 736 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 4.09 (s, 4H, H-4+5), 7.09 (dd, J = 5.0, 1.3 Hz, 2H, H-4'+4"), 7.26 (dd, J = 5.0, 3.1 Hz, 2H, H-5'+5") and 7.30 (dd, J = 3.1, 1.3 Hz, 2H, H-2'+2").

These spectroscopic data were similar to those reported in the literature.[28]

^{13}C NMR (CDCl$_3$): δ65.06 (2 CH$_2$), 106.06 (C), 123.03 (2 CH), 125.94 (2 CH), 126.32 (2 CH) and 143.59 (2C).

GC-MS (70 eV): m/z (%) = 238 (M$^+$, 9), 166 (20), 155 (100), 111 (73), 83 (13).

Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.44; H, 4.23; S, 26.90. Found: C, 55.18; H, 4.16; S, 26.79.

1-Butyl-3-methylimidazolium Bromide (BuMeIm$^+$Br$^-$)

Bromobutane (9.76 g, 71.23 mmol) was added dropwise with vigorous stirring to a solution of 1-methylimidazole (5.8 g, 70.63 mmol) in toluene (30 mL), and the mixture was refluxed for 3 h. The melt was decanted from the hot solution and the toluene phase was removed via canula. The ionic liquid was washed 4 times with EtOAc and dried under reduced pressure.

Viscous colorless liquid, yield: 15.48 g (100%).

^{1}H NMR (CDCl$_3$): δ = 0.94 (t, 3H, J = 7.4 Hz), 1.38 (m, 2H), 1.91 (m, 2H), 4.12 (s, 3H), 4.35 (t, 2H, J = 7.4 Hz), 7.61 (t, 1H, J = 1.8 Hz), 7.74 (t, 1H, J = 1.8 Hz), 10.26 (s, 1H).

^{13}C NMR (CDCl$_3$): δ = 13.07, 19.05, 31.78, 36.33, 49.41, 121.94, 123.49, 136.74.

1-Butyl-3-methylimidazolium Bis((trifluoromethyl)sulfonyl)-amide (BuMeIm$^+$Tf$_2$N$^-$)

A solution of lithium bis((trifluoromethyl)sulfonyl)amide (LiTf$_2$N, 20.27 g, 70.63 mmol) in deionised H$_2$O (60 mL) was added to a solution of 1-butyl-3-methylimidazolium bromide (15.48 g, 70.63 mmol) in deionised H$_2$O (20 mL). The mixture was heated for over 2 h at 70 °C. The solution was extracted with CH$_2$Cl$_2$ and the extract was washed with deionised H$_2$O and then dried under reduced pressure to afford 27.62 g (93%) of BuMeIm$^+$Tf$_2$N$^-$ as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ = 0.96 (t, 3H, J = 7.4 Hz), 1.36 (m, 2H), 1.85 (m, 2H), 3.94 (s, 3H), 4.17 (t, 2H, J = 7.4 Hz), 7.31 (m, 2H), 8.76 (s, 1H).

^{13}C NMR (CDCl$_3$): δ = 13.15, 19.31, 31.89, 36.30, 49.95, 120.00 (q, 2C, J_{C-F} = 322 Hz), 122.23, 123.66, 136.08.

Anal. Calcd for $C_{10}H_{15}F_6N_3O_4S_2$: C, 28.64; H, 3.61; N, 10.02; S, 15.29. Found: C, 28.67; H, 3.63; N, 9.98; S, 15.19.

1-Ethyl-3-methylimidazolium Bromide (EtMeIm$^+$Br$^-$)

Same procedure as for BuMeIm$^+$Br$^-$: From 1-methylimidazole (5.8 g, 70.63 mmol) and bromoethane (23.1 g, 211.9 mmol), EtMeIm$^+$Br$^-$ was obtained as a white solid, yield: 13.49 g (95%).

^{1}H NMR (CDCl$_3$): δ = 1.34 (t, 3H, J = 7.4 Hz), 3.87 (s, 3H), 4.18 (q, 2H, J = 7.4 Hz), 7.48 (d, 2H, J = 1.7 Hz), 9.98 (s, 1H).

^{13}C NMR (CDCl$_3$): δ = 15.05, 35.96, 44.51, 121.50, 123.13, 135.95.

1-Ethyl-3-methylimidazolium Bis((trifluoromethyl)sulfonyl) amide (EtMeIm$^+$Tf$_2$N$^-$)

Same procedure as for BuMeIm$^+$Tf$_2$N$^-$: From 1-Ethyl-3-methylimidazolium bromide (13.49 g, 70.63 mmol) and LiTf$_2$N (20.28 g, 70.63 mmol), EtMeIm$^+$Tf$_2$N$^-$ was obtained as a colorless liquid, yield: 23.64 g (90%).

^{1}H NMR (DMSO-d_6): δ = 1.41 (t, 3H, J = 7.4 Hz), 3.84 (s, 3H), 4.19 (q, 2H, J = 7.4 Hz), 7.66 (t, 1H, J = 1.7 Hz), 7.75 (t, 1H, J = 1.7 Hz), 9.1 (s, 1H).

^{13}C NMR (DMSO-d_6): δ = 15.17, 35.85, 44.38, 120.00 (q, 2C, J_{C-F} = 322 Hz), 122.16, 123.77, 136.47.

Anal. Calcd for $C_8H_{11}F_6N_3O_4S_2$: C, 24.56; H, 2.83; N, 10.74; S, 16.39. Found: C, 24.37; H, 3.05; N, 10.72; S, 16.24.

1-Ethyl-2-methyl-3-methylimidazolium Bromide (EtMeMeIm$^+$Br$^-$)

Same procedure as for BuMeIm$^+$Br$^-$: From 1-methy-2-methyl imidazole (6.0 g, 62.42 mmol) and bromoethane (20.4 g, 187.24 mmol), EtMeMeIm$^+$Br$^-$ was obtained as a white solid, yield: 11.40 g (89%).

^{1}H NMR (CDCl$_3$): δ = 1.47 (t, 3H, J = 7.4 Hz), 2.80 (s, 3H), 3.98 (s, 3H), 4.28 (q, 2H, J = 7.4 Hz), 7.61 (d, 1H, J = 1.9 Hz), 7.69 (d, 1H, J = 1.9 Hz).

^{13}C NMR (CDCl$_3$): δ = 10.83, 15.19, 36.01, 44.02, 120.64, 122.97, 143.46.

1-Ethyl-2-methyl-3-methylimidazolium Bis((trifluoromethyl)-sulfonyl) amide (EtMeMeIm$^+$Tf$_2$N$^-$)

Same procedure as for BuMeIm$^+$Tf$_2$N$^-$: From 1-Ethyl-2-methyl-3-methylimidazolium bromide (10.0 g, 48.75 mmol) and LiTf$_2$N (14.00 g, 48.75 mmol), EtMeMeIm$^+$Tf$_2$N$^-$ was obtained as a colorless liquid, yield: 19.76 g (89%).

^{1}H NMR (DMSO-d_6): δ = 1.28 (t, 3H, J = 7.4 Hz), 2.52 (s, 3H), 3.69 (s, 3H), 4.07 (q, 2H, J = 7.4 Hz), 7.52 (d, 1H, J = 2.1 Hz), 7.57 (d, 1H, J = 2.1 Hz).

^{13}C NMR (DMSO-d_6): δ = 9.39, 15.16, 35.08, 43.43, 120.00 (q, 2C, J_{C-F} = 322 Hz), 120.75, 122.84, 144.50.

Anal. Calcd for $C_9H_{13}F_6N_3O_4S_2$: C, 26.67; H, 3.23; N, 10.37; S, 15.82. Found: C, 26.63; H, 3.08; N, 10.31; S, 15.82.

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