3-Methylpiperidinium ionic liquids

Tayeb Belhocine, Stewart A. Forsyth, H. Q. Nimal Gunaratne, Mark Nieuwenhuyzen, Peter Nockemann, Alberto V. Puga,*
Kenneth R. Seddon, Geetha Srinivasan and Keith Whiston

Electronic Supplementary Information

Table S1-A. ^{1}H NMR (500 MHz) chemical shifts of ring hydrogen nuclei in 1-R-3-methylpiperidines ($Rm_\beta pip$) and $MeOC_2pip$[a]

	H^2_{eq}, H^6_{eq}	H^6_{ax}	H^3_{ax}, H^4_{eq}, H^5	H^2_{ax}	H^4_{ax}	3-Me
$C_4m_\beta pip$	2.82, 2.87 (2 × br m)	1.77 (td), J_{HH} 11.4, 3.0	1.56–1.74 (m)[b]	1.42–1.55 (m)[b]	0.82 (qd), J_{HH} 12.0, 4.4	0.85 (d), $^3J_{HH}$ 6.5
$C_6m_\beta pip$	2.82, 2.86 (2 × br m)	1.77 (td), J_{HH} 11.5, 3.1	1.56–1.75 (m)[b]	1.43–1.55 (m)[b]	0.82 (qd), J_{HH} 12.3, 4.4	0.85 (d), $^3J_{HH}$ 6.5
$MeOC_2m_\beta pip$	2.85, 2.90 (2 × br m)	1.85 (m)	1.59–1.73 (m)[b]	1.56 (t), J_{HH} 10.6	0.78–0.88 (m)[b]	0.85 (d), $^3J_{HH}$ 6.4
$MeOC_2OC_2m_\beta pip$	2.83, 2.88 (2 × br m)	1.88 (td), J_{HH} 11.2, 3.6	1.52–1.72 (m)[b]	1.52–1.72 (m)[b]	0.78–0.88 (m)[b]	0.84 (d), $^3J_{HH}$ 6.4
	NCH_2	NCH_2CH_2	$NCH_2CH_2CH_2$			
$MeOC_2pip$	2.41 (br m)	1.60 (quint), $^3J_{HH}$ 5.7	1.43 (2 H, m)			

[a] Chemical shifts (ppm relative to $SiMe_4$) and coupling constants (Hz) were recorded from solutions in $CDCl_3$; multiplicity is indicated in parentheses (br: broad, m: multiplet, d: doublet, t: triplet, q: quartet, quint: quintet); atom numbering as in Fig. 1; H^n_{eq} or H^n_{ax} represent nuclei in equatorial or axial positions bonded to the C^n atom, respectively. [b] Signals could not be distinguished due to overlapping.

Table S1-B. ^{1}H NMR (500 MHz) chemical shifts of side chain hydrogen nuclei in 1-R-3-methylpiperidines ($Rm_\beta pip$) and $MeOC_2pip$[a]

	NCH_2	NCH_2CH_2	$N(CH_2)_2(CH_2)_{n-3}$[b]	$N(CH_2)_{n-1}CH_3$[b]		
$C_4m_\beta pip$	2.27 (m)	1.43–1.49 (m)[d]	1.30 (sext), $^3J_{HH}$ 7.4	0.91 (t), $^3J_{HH}$ 7.4		
$C_6m_\beta pip$	2.27 (m)	1.43–1.50 (m)[d]	1.24–1.33 (m)	0.88 (t), $^3J_{HH}$ 6.8		
	NCH_2	NCH_2CH_2	$N(CH_2)_2OCH_2CH_2$	$N(CH_2)_2OCH_2CH_2$	$N((CH_2)_2O)_mCH_3$[c]	
$MeOC_2m_\beta pip$	2.53 (t), $^3J_{HH}$ 5.9	3.51 (t), $^3J_{HH}$ 5.9			3.35 (s)	
$MeOC_2OC_2m_\beta pip$	2.57 (t), $^3J_{HH}$ 6.3	3.60–3.64 (m)[d]	3.60–3.64 (m)[d]	3.54 (m)	3.38 (s)	
$MeOC_2pip$	2.53 (t), $^3J_{HH}$ 5.9	3.51 (t), $^3J_{HH}$ 5.9			3.35 (s)	

[a] Chemical shifts (ppm relative to $SiMe_4$) and coupling constants (Hz) recorded from solutions in $CDCl_3$; multiplicity is indicated in brackets (m: multiplet, s: singlet, t: triplet, sext: sextet). [b] n = 4 and 6 for $C_4m_\beta pip$ and $C_6m_\beta pip$, respectively. [c] m = 1 and 2 for $MeOC_2m_\beta pip$ and $MeOC_2OC_2m_\beta pip$, respectively. [d] Signals could not be distinguished due to overlapping.

Table S2-A. ^{13}C NMR (125 MHz) chemical shifts of ring carbon nuclei in 1-R-3-methylpiperidines ($Rm_\beta pip$)[a]

	C^6	C^2	C^5	C^3	C^4	3-Me
$C_4m_\beta pip$	54.3	62.4	25.8	31.3	33.3	20.0
$C_6m_\beta pip$	54.3	62.4	25.8	31.3	33.4	20.0
$MeOC_2m_\beta pip$	54.5	62.7	25.6	31.1	33.1	19.9
$MeOC_2OC_2m_\beta pip$	54.5	62.6	25.6	31.1	33.0	19.9

[a] Chemical shifts (ppm relative to $SiMe_4$) recorded from solutions in $CDCl_3$; atom numbering as in Fig. 1.

Table S2-B. ^{13}C NMR (125 MHz) chemical shifts of side chain carbon nuclei in 1-R-3-methylpiperidines ($Rm_\beta pip$)[a]

	NCH_2	NCH_2CH_2	$N(CH_2)_2(CH_2)_{n-3}$[b]	$N(CH_2)_{n-1}CH_3$[b]	
$C_4m_\beta pip$	59.2	29.3	21.1	14.2	
$C_6m_\beta pip$	59.6	32.0	27.6, 27.1, 22.7	14.2	
	NCH_2	NCH_2CH_2	$N(CH_2)_2OCH_2CH_2$	$N(CH_2)_2OCH_2CH_2$	$N((CH_2)_2O)_mCH_3$[c]
$MeOC_2m_\beta pip$	58.9	70.5			58.5
$MeOC_2OC_2m_\beta pip$	59.1	70.3	69.2	72.0	58.3

[a] Chemical shifts (ppm relative to $SiMe_4$) recorded from solutions in $CDCl_3$. [b] n = 4 and 6 for $C_4m_\beta pip$ and $C_6m_\beta pip$, respectively. [c] m = 1 and 2 for $MeOC_2m_\beta pip$ and $MeOC_2OC_2m_\beta pip$, respectively.

Table S3-A. ^{1}H NMR (500 MHz) chemical shifts of ring hydrogen nuclei in [Q]X ([Q] = [Rmm$_\beta$pip], [Rmpip] or [Rmpyrr])[a]

X	H^2_{eq}, H^6_{eq}	H^6_{ax}	H^3_{ax}, H^4_{eq}, H^5	H^2_{ax}	H^4_{ax}	3-Me
			[Q] = [$C_4mm_\beta pip$]			
I	3.52–3.63, 3.68–3.80 (2 × br m)[b]		1.87–2.12, 2.18 (2 × br m)	3.22, 3.46 (2 × m) J_{HH} 12.5, 12.5	1.37–1.50 (m)[b]	1.00–1.06 (m)[b]
[CF_3CO_2]	3.30–3.45, 3.50, 3.63 (3 × br m)[b]		1.82–2.03, 2.08 (2 × br m)	2.95, 3.17 (2 × t) J_{HH} 12.5, 12.5	1.27 (m)	0.96, 1.00 (2 × d) $^3J_{HH}$ 6.5, 6.5
[OTf]	3.22, 3.30–3.47, 3.49–3.60 (3 × br m)[b]		1.84–2.03, 2.07 (2 × br m)	2.89, 3.03 (2 × t) J_{HH} 12.6, 12.5	1.27 (m)	0.9**6**, 0.99 (2 × d) $^3J_{HH}$ 6.5, 6.5
[NTf_2]	3.23–3.33, 3.36–3.43, 3.49 (3 × br m)[b]	3.14 (m)	1.84–1.99, 2.04 (2 × br m)	2.74–2.83 (m)[b]	1.14–1.24 (m)[b]	0.95–1.00 (m)[b]
			[Q] = [$C_6mm_\beta pip$]			
I	3.48–3.62, 3.68–3.83 (2 × br m)[b]		1.87–2.09, 2.17 (2 × br m)	3.20, 3.46 (2 × m) J_{HH} 12.4, 12.5	1.28–1.52 (br m)[b]	1.04 (d) $^3J_{HH}$ 6.5
[CF_3CO_2]	3.29–3.41, 3.47, 3.60 (3 × br m)[b]		1.82–2.03, 2.08 (2 × br m)	2.95, 3.15 (2 × t) J_{HH} 12.5, 12.5	1.25 (m)	0.96, 1.00 (2 × d) $^3J_{HH}$ 6.5, 6.5
[OTf]	3.24, 3.30–3.44, 3.47–3.56 (3 × br m)[b]		1.84–2.03, 2.07 (2 × br m)	2.88, 3.03 (2 × t) J_{HH} 12.6, 12.5	1.26 (m)	1.00 (d) $^3J_{HH}$ 6.4
[NTf_2]	3.29–3.34, 3.36–3.44, 3.50 (3 × br m)[b]	3.15 (m)	1.84–2.00, 2.06 (2 × br m)	2.78, 2.82 (2 × t) J_{HH} 12.6, 12.5	1.21 (m)	0.99 (d) $^3J_{HH}$ 6.4
[BPh_4]	3.39–3.51, 3.51–3.66, 3.77 (3 × br m)[b]	3.17 (m)	1.95–2.15, 2.23 (2 × br m)	3.01, 3.32 (2 × t) J_{HH} 12.6, 12.5	1.20 (m)	0.97 (d) $^3J_{HH}$ 6.5
			[Q] = [$MeOC_2mm_\beta pip$]			
I	3.58–3.82, 3.84–3.96, 4.02 (3 × br m)[b]		1.85–2.12, 2.20 (2 × br m)	3.27–3.39 (m)[b]	1.35–1.48 (m)	1.01, 1.03 (2 × d) $^3J_{HH}$ 6.5, 6.5
[CF_3CO_2]	3.54, 3.66, 3.71–3.89 (3 × br m)[b]	3.28, 3.39 (2 × td) J_{HH} 13.2, 3.4; 12.9, 3.8	1.83–2.02, 2.08 (2 × br m)	2.91, 3.02 (2 × t) J_{HH} 12.5, 12.6	1.15–1.27 (m)	0.96, 0.99 (2 × d) $^3J_{HH}$ 6.5, 6.5
[OTf]	3.49, 3.59, 3.64–3.74, 3.79, 3.85 (5 × br m)[b]	3.25, 3.33 (2 × m)	1.83–2.02, 2.08 (2 × br m)	2.91, 2.98 (2 × t) J_{HH} 12.5, 12.6	1.19–1.29 (m)	0.97, 1.00 (2 × d) $^3J_{HH}$ 6.5, 6.5
[NTf_2]	3.32–3.43, 3.47–3.65 (2 × br m)[b]	3.16–3.26 (m)	1.81–2.02, 2.09 (2 × br m)	2.79, 2.85 (2 × t) J_{HH} 12.6, 12.6	1.13–1.25 (m)	0.96, 0.98 (2 × d) $^3J_{HH}$ 6.5, 6.5
			[Q] = [$MeOC_2OC_2mm_\beta pip$]			
I	3.59–3.82, 3.90, 3.94–4.07 (3 × br m)[b]		1.84–2.11, 2.18 (2 × br m)	3.27–3.40 (m)[b]	1.33–1.47 (m)	1.00, 1.03 (2 × d) $^3J_{HH}$ 6.6, 6.6
[CF_3CO_2]	3.57–3.62, 3.71, 3.77–3.95, 3.99 (5 × br m)[b]	3.31, 3.44 (2 × m)	1.82–2.02, 2.08 (2 × br m)	2.93, 3.08 (2 × t) J_{HH} 12.5, 12.5	1.17–1.27 (m)	0.96, 0.99 (2 × d) $^3J_{HH}$ 6.5, 6.5
[OTf]	3.48–3.54, 3.55–3.73, 3.90, 3.96 (4 × br m)[b]	3.25, 3.33 (2 × m)[b]	1.82–2.02, 2.08 (2 × br m)	2.89, 2.99 (2 × t) J_{HH} 12.5, 12.5	1.19–1.28 (m)	0.96, 0.99 (2 × d) $^3J_{HH}$ 6.5, 6.5
[NTf_2]	3.44, 3.50–3.69, 3.89, 3.95 (4 × br m)[b]	3.15, 3.25 (2 × m)	1.84–2.02, 2.08 (2 × br m)	2.77, 2.89 (2 × t) J_{HH} 12.5, 12.5	1.14–1.24 (m)	0.97, 0.99 (2 × d) $^3J_{HH}$ 6.6, 6.6

X	NCH_2	NCH_2CH_2	$NCH_2CH_2CH_2$
		[Q] = [$MeOC_2$mpip]	
Cl	3.61–3.84 (br m)	1.93 (br m)	1.77 (br m)
[CF_3CO_2]	3.51–3.59, 3.60–3.68 (2 × m)	1.90 (br m)	1.73 (m)
[OTf]	3.41–3.49, 3.49–3.57 (2 × br m)	1.90 (br m)	1.73 (m)
[NTf_2]	3.33–3.40, 3.43–3.49 (2 × br m)	1.90 (br m)	1.72 (br m)

X	NCH_2	NCH_2CH_2
	[Q] = [$MeOC_2$mpyrr]	
Br	3.81–4.02 (br m)	2.29 (m)
[NTf_2]	3.53–3.72 (br m)	2.28 (m)
	[Q] = [$MeOC_2OC_2$mpyrr]	
Br	3.81–4.01 (br m)	2.28 (m)
[NTf_2]	3.55–3.64 (br m)	2.26 (br m)

[a] Chemical shifts (ppm relative to $SiMe_4$) and coupling constants (Hz) recorded from solutions in $CDCl_3$; multiplicity is indicated in brackets (br: broad, m: multiplet, d: doublet, t: triplet); atom numbering as in Fig. 1 or equivalently. So for piperidinium and pyrrolidinium cationic cores; H^n_{eq} or H^n_{ax} represent nuclei in equatorial or axial positions bonded to the C^n atom, respectively. [b] Signals could not be distinguished due to overlapping.

Table S3-B. ^{1}H NMR (500 MHz) chemical shifts of side chain or anion hydrogen nuclei in [Q]X ([Q] = [Rmm$_\beta$pip], [Rmpip] or [Rmpyrr])[a]

X	NCH_3	NCH_2	NCH$_2$CH_2	N(CH$_2$)$_2$(CH_2)$_{n-3}$[b]	N(CH$_2$)$_{n-1}$CH_3[b]	BPh$_4$
			[Q] = [C$_4$mm$_\beta$pip]			
I	3.27, 3.43 (2 × s)	3.52–3.63, 3.68–3.80 (2 × br m)[d]	1.67–1.82 (2 × m)	1.47 (m)[d]	1.00–1.06 (m)[d]	
[CF_3CO_2]	3.16, 3.24 (2 × s)	3.54 (m)[d]	1.63, 1.77 (2 × m)	1.33 (m)	0.89 (m)	
[OTf]	3.10, 3.15 (2 × s)	3.41 (m)	1.63, 1.77 (2 × m)	1.34 (m)	0.89 (m)	
[NTf_2]	3.00, 3.04 (2 × s)	3.26 (m)[d]	1.60, 1.74 (2 × m)	1.38 (m)	0.95–1.00 (m)[d]	
			[Q] = [C$_6$mm$_\beta$pip]			
I	3.27, 3.44 (2 × s)	3.48–3.62, 3.68–3.83 (2 × br m)[d]	1.66–1.81 (2 × m)	1.28–1.52 (br m)[d]	0.90 (m)	
[CF_3CO_2]	3.16, 3.27 (2 × s)	3.52 (m)[d]	1.63, 1.77 (2 × m)	1.33 (m)	0.89 (m)	
[OTf]	3.09, 3.16 (2 × s)	3.40 (m)	1.63, 1.77 (2 × m)	1.34 (m)	0.89 (m)	
[NTf_2]	3.01, 3.05 (2 × s)	3.27 (m)	1.63, 1.76 (2 × m)	1.33 (m)	0.89 (m)	
[BPh$_4$]	2.83, 2.87 (2 × s)	3.47 (m)	1.82, 1.92 (2 × m)	1.35 (m)	0.88 (m)	6.78 (4 H, t, J_{HH} 7.2), 6.93 (8 H, t, J_{HH} 7.2), 7.33 (8 H, m)

X	NCH_3	NCH_2	NCH$_2$CH_2	N(CH$_2$)$_2$OCH_2CH$_2$	N(CH$_2$)$_2$OCH$_2$CH_2	N((CH$_2$)$_2$O)$_m$CH_3[c]
			[Q] = [MeOC$_2$mm$_\beta$pip]			
I	3.35, 3.50 (2 × s)	3.58–3.82, 3.84–3.96, 4.02 (3 × br m)[d]				3.40, 3.42 (2 × s)
[CF_3CO_2]	3.21, 3.31 (2 × s)	3.54, 3.66, 3.71–3.89 (3 × br m)[d]				3.36, 3.37 (2 × s)
[OTf]	3.17, 3.24 (2 × s)	3.49, 3.59, 3.64–3.74, 3.79, 3.85 (5 × br m)[d]				3.37, 3.38 (2 × s)
[NTf_2]	3.10, 3.14 (2 × s)	3.52, 3.56 (2 × m)	3.75, 3.81 (2 × m)			3.36, 3.37 (2 × s)
			[Q] = [MeOC$_2$OC$_2$mm$_\beta$pip]			
I	3.35, 3.50 (2 × s)[d]	3.59–3.82, 3.90, 3.94–4.07 (3 × br m)[d]		3.71 (m)	3.54 (m)	3.35, 3.36 (2 × s)
[CF_3CO_2]	3.25, 3.35 (2 × s)	3.57–3.62, 3.71, 3.77–3.95, 3.99 (5 × br m)[d]		3.64 (m)[d]	3.52 (m)[d]	3.35, 3.36 (2 × s)
[OTf]	3.17, 3.24 (2 × s)	3.48–3.54, 3.55–3.73, 3.90, 3.96 (4 × br m)[d]				3.35, 3.35 (2 × s)
[NTf_2]	3.13, 3.17 (2 × s)	3.44, 3.50–3.69, 3.89, 3.95 (4 × br m)[d]		3.65 (m)[d]	3.53 (m)[d]	3.36, 3.36 (2 × s)
			[Q] = [MeOC$_2$mpip]			
Cl	3.42 (s)	4.01 (br m)	3.89 (br m)			3.38 (s)
[CF_3CO_2]	3.26 (s)	3.82 (br m)				3.36 (s)
[OTf]	3.18 (s)	3.82 (m)	3.65 (m)			3.37 (s)
[NTf_2]	3.12 (s)	3.55 (m)	3.79 (br m)			3.37 (s)
			[Q] = [MeOC$_2$mpyrr]			
Br	3.37 (s)	4.05 (m)	3.87 (m)			3.40 (s)
[NTf_2]	3.14 (s)	3.62 (m)	3.81 (m)			3.40 (s)
			[Q] = [MeOC$_2$OC$_2$mpyrr]			
Br	3.37 (s)	4.06 (m)	3.99 (m)	3.69 (m)	3.53 (m)	3.36 (s)
[NTf_2]	3.13 (s)	3.66 (m)	3.92 (m)	3.66 (m)	3.53 (m)	3.36 (s)

[a] Chemical shifts (ppm relative to $SiMe_4$) and coupling constants (Hz) recorded from solutions in $CDCl_3$; multiplicity is indicated in brackets (br: broad, m: multiplet, s: singlet). [b] n = 4 and 6 for [C$_4$mm$_\beta$pip] and [C$_6$mm$_\beta$pip], respectively. [c] m = 1 and 2 for [MeOC$_2$mm$_\beta$pip] and [MeOC$_2$OC$_2$mm$_\beta$pip], respectively. [d] Signals could not be distinguished due to overlapping.

Table S4-A ^{13}C NMR (125 MHz) chemical shifts of ring carbon nuclei in [Q]X ([Q] = [Rmm$_\beta$pip], [Rmpip] or [Rmpyrr])[a]

X	C^6	C^2	C^5	C^3	C^4	3-Me
			[Q] = [C_4mm$_\beta$pip]			
I	60.9, *60.6*	66.5, *66.3*	20.5, *20.4*	26.4, *26.3*	29.8, *29.1*	18.7, *18.5*
[CF_3CO_2]	60.7, *60.5*	66.4, *66.1*	20.2, *20.1*	26.2, *26.1*	30.0, *29.3*	18.5, *18.3*
[OTf]	60.8, *60.6*	66.7, *66.5*	20.4, *20.1*	26.3, *26.1*	30.0, *29.3*	18.4, *18.3*
[NTf_2]	60.9, *60.8*	66.8, *66.9*	20.2, *20.0*	26.2, *26.0*	29.9, *29.3*	18.3, *18.3*
			[Q] = [C_6mm$_\beta$pip]			
I	60.9, *60.6*	66.5, *66.3*	20.5, *20.4*	26.4, *26.3*	29.8, *29.1*	18.7, *18.5*
[CF_3CO_2]	60.6, *60.3*	66.4, *66.2*	20.3, *20.2*	26.3, *26.1*	30.1, *29.3*	18.6, *18.5*
[OTf]	60.8, *60.5*	66.6, *66.5*	20.4, *20.3*	26.3, *26.2*	30.0, *29.3*	18.6, *18.5*
[NTf_2]	61.0, *60.6*	66.9, *66.9*	20.2, *20.1*	26.2, *26.0*	29.9, *29.3*	18.5, *18.5*
			[Q] = [$MeOC_2$mm$_\beta$pip]			
I	61.5, *62.1*	66.0, *66.2*	20.4, *20.5*	26.1, *26.1*	29.5, *29.1*	18.5, *18.4*
[CF_3CO_2]	61.4, *62.2*	66.0, *66.2*	20.2, *20.3*	26.2	29.9, *29.5*	18.6, *18.4*
[OTf]	61.5, *62.2*	65.9, *66.1*	20.3, *20.4*	26.2	29.8, *29.3*	18.6, *18.4*
[NTf_2]	61.6, *62.2*	65.7, *66.0*	20.1, *20.2*	26.1	29.7, *29.3*	18.3, *18.2*
			[Q] = [$MeOC_2OC_2$mm$_\beta$pip]			
I	61.5, *62.3*	64.6, *64.8*	20.4, *20.5*	26.2, *26.2*	29.6, *29.1*	18.6, *18.3*
[CF_3CO_2]	61.3, *62.4*	64.7, *64.8*	20.3, *20.4*	26.2	29.9, *29.5*	18.7, *18.4*
[OTf]	61.5, *62.4*	64.5, *64.7*	20.3, *20.4*	26.2	29.8, *29.4*	18.9, *18.4*
[NTf_2]	61.8, *62.6*	64.3, *64.6*	20.2, *20.3*	26.2	29.8, *29.4*	18.5, *18.2*

X	NCH_2	NCH_2CH_2	$NCH_2CH_2CH_2$
			[Q] = [$MeOC_2$mpip]
[CF_3CO_2]	62.0	20.1	20.6
[OTf]	62.2	20.1	20.6

X	NCH_2	NCH_2CH_2
		[Q] = [$MeOC_2$mpyrr]
[NTf_2]	63.8	21.8
		[Q] = [$MeOC_2OC_2$mpyrr]
[NTf_2]	63.8	21.7

[a] Chemical shifts (ppm relative to $SiMe_4$) recorded from solutions in $CDCl_3$; atom numbering as in Fig. 1, or equivalently so for piperidinium and pyrrolidinium cationic cores; signals in italics are for minor diastereomers.

Table S4-B ^{13}C NMR (125 MHz) chemical shifts of either side chain or anion carbon nuclei in [Q]X ([Q] = [Rmm$_\beta$pip], [Rmpip] or [Rmpyrr])[a]

X	N*C*H$_3$[b]	N*C*H$_2$[c]	NCH$_2$*C*H$_2$	N(CH$_2$)$_2$(*C*H$_2$)$_{n-3}$[d]	N(CH$_2$)$_{n-1}$*C*H$_3$[d]		*C*F$_3$	*C*O$_2$
	[Q] = [C$_4$mm$_\beta$pip]							
I	45.8, *53.2*	68.5, *57.9*	24.2, *24.2*	19.8, *19.9*	13.9, *13.9*			
[CF$_3$CO$_2$]	44.7, *52.9*	69.0, *57.5*	23.8, *24.1*	19.5, *19. 5*	13.6, *13.5*		117.5 (q), $^1J_{CF}$ 297	161.0 (q), $^2J_{CF}$ 33
[OTf]	44.9, *53.1*	69.2, *57.8*	23.8, *24.0*	19.5, *19. 6*	13.6, *13.5*		120.8 (q), $^1J_{CF}$ 321	
[NTf$_2$]	44.8, *53.2*	69.3, *57.8*	23.7, *24.0*	19.6, *19. 6*	13.5, *13.5*		120.0 (q), $^1J_{CF}$ 321	
	[Q] = [C$_6$mm$_\beta$pip]							
I	45.7, *53.2*	68.8, *58.1*	31.5,*31.4*	26.0, *26.1*; 22.2; 22.5	14.1, *14.0*			
[CF$_3$CO$_2$]	44.7, *52.9*	69.0, *57.5*	31.3, *31.3*	26.0, *26.1*; 22.5; 22.0, *22.0*	13.9		117.5 (q), $^1J_{CF}$ 297	161.0 (q), $^2J_{CF}$ 33
[OTf]	44.9, *53.1*	69.3, *57.8*	31.3	26.0, *26.1*; 22.5; 22.0, *22.1*	14.0		120.8 (q), $^1J_{CF}$ 321	
[NTf$_2$]	44.8, *53.2*	69.6, *58.0*	31.1,*31.2*	25.8, *25.9*; 22.4, *22.4*; 21.8, *22.0*	13.8		120.0 (q), $^1J_{CF}$ 321	
X	N*C*H$_3$[b]	N*C*H$_2$[c]	NCH$_2$*C*H$_2$	N(CH$_2$)$_2$O*C*H$_2$CH$_2$	N(CH$_2$)$_2$OCH$_2$*C*H$_2$	N((CH$_2$)$_2$O)$_m$*C*H$_3$[e]	*C*F$_3$	*C*O$_2$
	[Q] = [MeOC$_2$mm$_\beta$pip]							
I	46.3, *53.9*	67.2, *57.6*	67.4, *67.7*[c]			59.2, *59.3*		
[CF$_3$CO$_2$]	45.4, *53.6*	67.4, *57.2*	67.9, *68.0*[c]			59.0, *59.1*	117.4 (q), $^1J_{CF}$ 297	160.9 (q), $^2J_{CF}$ 32
[OTf]	45.5, *53.7*	67.4, *57.4*	68.0, *68.0*[c]			59.1, *59.2*	120.8 (q), $^1J_{CF}$ 320	
[NTf$_2$]	45.5, *53.9*	67.6, *57.5*	68.2, *68.3*[c]			58.9, *59.0*	119.9 (q), $^1J_{CF}$ 322	
	[Q] = [MeOC$_2$OC$_2$mm$_\beta$pip]							
I	46.4, *53.9*	67.2, *57.8*	67.5, *67.6*[c]	70.4, *70.5*	71.5, *71.6*	59.0, *59.0*		
[CF$_3$CO$_2$]	45.4, *53.5*	67.3, *57.1*	67.8, *67.9*[c]	70.3, *70.5*	71.5, *71.7*	59.0	117.4 (q), $^1J_{CF}$ 297	161.0 (q), $^2J_{CF}$ 32
[OTf]	45.7, *53.8*	67.4, *57.5*	68.0, *67.9*[c]	70.4, *70.5*	71.6, *71.7*	59.0	120.8 (q), $^1J_{CF}$ 320	
[NTf$_2$]	45.8, *54.1*	67.7, *57.7*	68.4, *68.2*[c]	70.5, *70.6*	71.6, *71.7*	59.0	119.9 (q), $^1J_{CF}$ 321	
	[Q] = [MeOC$_2$mpip]							
[CF$_3$CO$_2$]	48.6	62.3	65.9			58.9	117.4 (q), $^1J_{CF}$ 297	160.5 (q), $^2J_{CF}$ 32
[OTf]	49.0	62.4	65.8			59.0	120.7 (q), $^1J_{CF}$ 320	
	[Q] = [MeOC$_2$mpyrr]							
[NTf$_2$]	49.3	66.1	66.8			59.5	122.4 (q), $^1J_{CF}$ 322	
	[Q] = [MeOC$_2$OC$_2$mpyrr]							
[NTf$_2$]	49.2	65.4	66.0	70.8	71.9	59.2	122.3 (q), $^1J_{CF}$ 322	

[a] Chemical shifts (ppm relative to SiMe$_4$) recorded from solutions in CDCl$_3$; signals in italics are for minor diastereomers. [b] Most intense signals (non-italics) are for nuclei in axial positions. [c] Most intense signals (non-italics) are for nuclei in equatorial positions. [d] n = 4 and 6 for [C$_4$mm$_\beta$pip] and [C$_6$mm$_\beta$pip], respectively. [e] m = 1 and 2 for [MeOC$_2$mm$_\beta$pip] and [MeOC$_2$OC$_2$mm$_\beta$pip], respectively.

Table S5 Experimental density (ρ) data for the 3-methylpiperidinium-, piperidinium- and pyrrolidinium-based room temperature ionic liquids and correlation parameters for the linear fit of their variation with temperature.[a]

	ρ/g cm^{-3}						
	[$C_4mm_\beta pip$]	[$C_6mm_\beta pip$]	[$MeOC_2mm_\beta pip$]	[$MeOC_2OC_2mm_\beta pip$]	[$MeOC_2mpip$]	[$MeOC_2mpyrr$]	[$MeOC_2OC_2mpyrr$]
T/K	X = [NTf_2]						
293.1			1.403	1.369	1.440	1.463	1.417
298.1	1.348	1.298	1.398	1.365	1.435	1.458	1.413
303.1			1.394	1.361	1.431	1.453	1.408
313.1			1.384	1.352	1.421	1.444	1.399
323.1			1.375	1.343	1.411	1.434	1.390
333.1			1.366	1.334	1.402	1.425	1.381
343.1			1.358	1.326	1.392	1.416	1.372
353.1			1.349	1.317	1.381	1.407	1.363
363.1			1.340	1.309	1.371	1.398	1.354
a/g cm^{-3}			1.665	1.624	1.728	1.735	1.683
10^4b/g cm^{-3} K^{-1}			8.966	8.679	9.795	9.301	9.073
R^2			0.99996	0.99994	0.9996	0.99994	0.99994
T/K	X = [OTf]						
293.1			1.275	1.254	1.314		
298.1			1.271	1.251	1.310		
303.1			1.268	1.247	1.307		
313.1			1.260	1.239	1.299		
323.1			1.252	1.232	1.292		
333.1			1.245	1.224	1.284		
343.1			1.238	1.217	1.277		
353.1			1.230	1.210	1.269		
363.1			1.222	1.202	1.262		
a/g cm^{-3}			1.495	1.473	1.534		
10^4b/g cm^{-3} K^{-1}			7.493	7.453	7.513		
R^2			0.99995	0.9998	0.99998		
T/K	X = [CF_3CO_2]						
293.1			1.200	1.185	1.236		
298.1			1.197	1.182	1.232		
303.1			1.193	1.178	1.229		
313.1			1.186	1.171	1.222		
323.1			1.179	1.164	1.214		
333.1			1.172	1.156	1.207		
343.1			1.164	1.149	1.200		
353.1			1.158	1.142	1.193		
363.1			1.150	1.135	1.186		
a/g cm^{-3}			1.408	1.395	1.447		
10^4b/g cm^{-3} K^{-1}			7.103	7.150	7.190		
R^2			0.99997	0.99990	0.99991		

[a] Correlation parameters for the equation $\rho = a + bT$.

Table 6 Experimental viscosity (η) data for the studied 3-methylpiperidinium-, piperidinium- and pyrrolidinium-based room temperature ionic liquids and correlation parameters for the Vogel-Fülcher-Tammann (VFT) fit of their variation with temperature.[a]

	η/cP						
	$[C_4mm_\beta pip]$	$[C_6mm_\beta pip]$	$[MeOC_2mm_\beta pip]$	$[MeOC_2OC_2mm_\beta pip]$	$[MeOC_2mpip]$	$[MeOC_2mpyrr]$	$[MeOC_2OC_2mpyrr]$
T/K	X = $[NTf_2]$						
298.1	315	392	136	129	103	58.6	49.8
303.1	239	288	103	99.1	81.2	47.9	40.6
308.1	182	212	78.8	77.1	64.2	39.8	33.3
313.1	140	159	61.3	60.9	51.6	33.0	27.6
318.1	110	121	48.4	48.8	42.0	27.9	23.2
323.1	88.2	93.8	39.0	39.6	34.8	23.7	19.6
328.1	72.0	73.6	31.8	32.7	29.0	20.2	16.8
333.1	59.6	58.8	26.3	27.3	24.6	17.6	14.6
338.1	50.4	47.7	21.9	23.0	21.0	15.4	12.9
343.1	43.1	39.2	18.4	19.7	18.2	13.7	11.4
348.1	37.2	32.4	15.7	17.0	15.9	12.2	10.2
353.1	32.3	27.1	13.4	14.9	14.0	10.9	9.2
358.1	28.6	23.0	11.6	13.1	12.3	9.8	8.2
363.1	26.0	19.4	10.2	11.5	11.0	8.7	7.4
368.1	23.9	16.6	9.0	10.2	10.0	7.9	6.6
η_o/cP	0.6972	0.0283	0.0553	0.1224	0.1706	0.1360	0.1810
B/K	569	1343	1021	848	774	862	708
T_o/K	205	157	167	176	178	156	172
R^2	0.9996	0.99997	0.99997	0.99996	0.99995	0.99991	0.9998
T/K			X = [OTf]				
298.1			654	409	401		
303.1			454	295	296		
308.1			319	215	221		
313.1			228	160	167		
318.1			167	122	128		
323.1			125	94.1	100		
328.1			95.8	74.0	79.4		
333.1			74.8	59.0	63.6		
338.1			59.1	47.9	51.8		
343.1			47.4	39.3	42.8		
348.1			38.5	32.8	35.9		
353.1			31.7	27.6	30.4		
358.1			26.4	23.4	26.0		
363.1			22.2	20.1	22.3		
368.1			19.0	17.3	19.2		
η_o/cP			0.0401	0.0662	0.0595		
B/K			1174	1071	1168		
T_o/K			177	176	166		
R^2			0.99997	0.99997	0.99994		
T/K			X = $[CF_3CO_2]$				
298.1			453	325	288		
303.1			320	233	213		
308.1			226	169	158		
313.1			162	126	119		
318.1			119	95.4	91.0		
323.1			89.0	73.9	70.9		
328.1			67.9	58.1	56.1		
333.1			52.9	46.3	45.1		
338.1			41.9	37.7	36.8		
343.1			33.8	31.0	30.4		
348.1			27.7	25.7	25.6		
353.1			23.0	21.5	21.7		
358.1			19.3	18.2	18.6		
363.1			16.4	15.6	15.9		
368.1			13.9	13.5	13.7		
η_o/cP			0.0383	0.0509	0.0552		
B/K			1101	1072	1082		
T_o/K			181	176	172		
R^2			0.99990	0.99999	0.99993		

[a] Correlation parameters for the VFT equation $\ln(\eta) = \ln(\eta_o) + B/(T - T_o)$.