One-pot preparation of ternary and quaternary iminium salts from aldehydes and ketones

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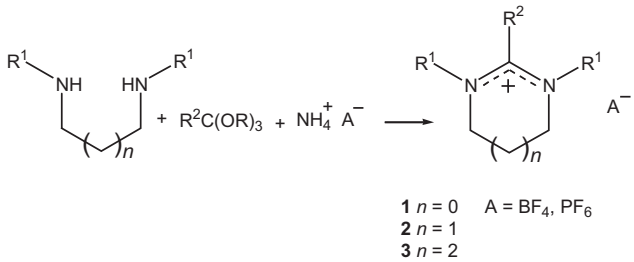
A facile, high-yielding, one-step procedure is described for the preparation of a wide range of stable iminium salts by direct combination of an aldehyde or a ketone with a secondary free amine in the presence of an ammonium salt. The broad scope of the method is illustrated by the preparation of iminium ions derived from aldehydes, cyclic/acyclic ketones, and cyclic/acyclic secondary amines.

Keywords: iminium salts, aldehydes, ketones, ammonium salts, amine salt

Previously, we reported a convenient one-pot procedure for the preparation of cyclic amidinium salts from orthoesters, primary or secondary α,ω-diamines and ammonium tetrafluoroborate or ammonium hexafluorophosphate. The resulting amidinium salts **1**, **2** and **3** were isolated in high yields and contained counterions with low nucleophilicity (Scheme 1).[1]

In the course of a related study on the preparation of acyclic amidinium salts[2] by application of the above procedure, we observed that treatment of primary or secondary monoamine free bases with ammonium tetrafluoroborate or hexafluorophosphate in refluxing toluene afforded nearly quantitative yields of 1° and 2° amine tetrafluoroborate and hexafluorophosphate salts within about 0.5 h. These findings led us to envision that synthetic transformations in which amine salts are requisite starting materials may well be accomplished using the corresponding amine free bases along with an added ammonium salt. Therefore, we decided to explore the preparation of iminium salts **4** by a direct, one-step procedure: heating a mixture of an aldehyde or a ketone with a 2° free amine in the presence of an ammonium salt (Scheme 2). The iminium function, $[R_2C{=}NR_2]^+$, is of enormous importance in organic chemistry[3-6] and preformed iminium salts **4** have been extensively used in various synthetic applications within the last three decades. In contrast to the existing methods that frequently start with an aldehyde or ketone derivative or require initial treatment of an amine with an acid and isolation of the formed salt in a previous step,[7] the procedure described here involves direct treatment of these compounds in the presence of an ammonium salt.

Herein we report the preparation and characterisation of a series of ternary and quaternary iminium perchlorates, tetrafluoroborates and hexafluorophosphates by this one-step procedure.



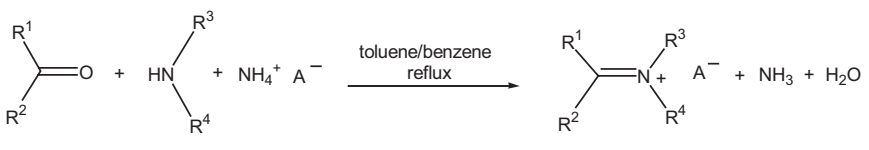
Scheme 1

Results and discussion

Typically, to prepare compound **4**, a mixture of an aldehyde or a ketone (**5**), a secondary amine (**6**) and an ammonium salt (**7**) was heated in toluene or benzene in a Dean–Stark apparatus. After cooling the mixture, the product precipitated and was separated by suction filtration, affording nearly pure iminium salts. A wide range of iminium salts was prepared and isolated in very high yields by this method (Table 1). This reaction worked well with substrates containing acid labile acetal groups (entries **4d** and **4m**) and was unaffected by the counterions (entries **4e** and **4f**; **4s** and **4t**; **4u** and **4v**; **4y** and **4z**; **4aa**, **4bb** and **4cc**).

All products were characterised by their ^{1}H and ^{13}C NMR spectra. The most diagnostic absorption in the ^{13}C NMR spectra of the salts prepared is a downfield signal representing the alkylidene carbon. For aliphatic ketones and aromatic aldehydes, this absorption appears in the range δ 184–201 and δ 161–166, respectively.

Although we have not investigated the detailed mechanism of this reaction, it is most likely driven by initial proton transfer from the ammonium ion to the secondary amine free base with release of ammonia, leading to the secondary amine salt. Proton transfer from the secondary amine salt to the carbonyl oxygen and subsequent condensation affords iminium salts **4**. An alternative plausible mechanism involves initial formation of an enamine intermediate that, upon protonation by the ammonium ion, may yield the iminium species. To ascertain the possible involvement of enamines, several enamines were treated with ammonium salts. All attempts failed to afford the corresponding iminium salts and led to dark intractable materials. The likelihood of an enamine intermediate is further lessened since nonenolisable aromatic aldehydes, unable to form enamine intermediates, yielded iminium salts by direct combination with a secondary amine and an ammonium salt, as described here.



Scheme 2

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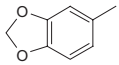
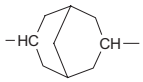
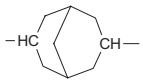
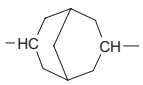
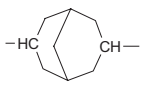
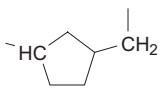
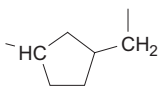
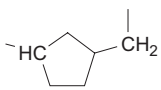
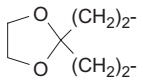
Table 1 One-pot preparation of iminium salts (**4**)

Entry	R^1	R^2	R^3 R^4	A^-	Yield/%[a]	Solvent	Reaction time/h
4a	4-$MeOC_6H_4$	H	$-(CH_2)_4-$	PF_6^-	88	Benzene	3
4b	4-$Me_2NC_6H_4$	H	$-(CH_2)_4-$	PF_6^-	90	Benzene	3
4c	1-naphthyl	H	$-(CH_2)_4-$	PF_6^-	81	Benzene	3
4d		H	$-(CH_2)_4-$	PF_6^-	84	Benzene	2
4e			$-(CH_2)_4-$	PF_6^-	89	Toluene	0.75
4f			$-(CH_2)_4-$	BF_4^-	92	Toluene	0.75
4g			$-(CH_2)_6-$	ClO_4^-	88	Toluene	0.75
4h			$-(CH_2)_3CH(CH_3)CH_2-$	PF_6^-	75	Toluene	3
4i			$-(CH_2)_3CH(CH_3)CH_2-$	PF_6^-	87	Toluene	3
4j			$-(CH_2)_4-$	PF_6^-	91	Toluene	2
4k			$-(CH_2)_6-$	ClO_4^-	90	Toluene	1.75
4l	$-CH_2CH(CH_3)(CH_2)_3-$		$-(CH_2)_4-$	PF_6^-	78	Toluene	2.75
4m			$-(CH_2)_4-$	PF_6^-	92	Toluene	2
4n	Me Me		$-(CH_2)_4-$	ClO_4^-	88	Benzene	0.25
4o	Et Et		$-(CH_2)_4-$	ClO_4^-	89	Toluene	2.75
4p	$-(CH_2)_4-$		$-(CH_2)_4-$	PF_6^-	89	Toluene	0.75
4q	$-(CH_2)_4-$		Et Et	ClO_4^-	89	Benzene	2
4r	$-(CH_2)_4-$		Pr Pr	ClO_4^-	94	Toluene	3
4s	$-(CH_2)_4-$		$-(CH_2)_4-$	ClO_4^-	88	Toluene	1
4t	$-(CH_2)_4-$		$-(CH_2)_4-$	BF_4^-	90	Toluene	0.75
4u	$-(CH_2)_4-$		$-(CH_2)_5-$	PF_6^-	91	Toluene	1.5
4v	$-(CH_2)_4-$		$-(CH_2)_5-$	ClO_4^-	93	Toluene	1.5
4w	$-(CH_2)_4-$		$-(CH_2)_6-$	ClO_4^-	91	Toluene	0.75
4x	$-(CH_2)_4-$		$-(CH_2)_3CH(CH_3)CH_2-$	PF_6^-	92	Benzene	2.5
4y	$-(CH_2)_5-$		$-(CH_2)_4-$	PF_6^-	91	Toluene	1.5
4z	$-(CH_2)_5-$		$-(CH_2)_4-$	ClO_4^-	88	Toluene	0.5
4aa	$-(CH_2)_6-$		$-(CH_2)_4-$	BF_4^-	90	Toluene	1.5
4bb	$-(CH_2)_6-$		$-(CH_2)_4-$	ClO_4^-	87	Toluene	0.5
4cc	$-(CH_2)_6-$		$-(CH_2)_4-$	PF_6^-	90	Toluene	1.5
4dd	$-(CH_2)_6-$		$-(CH_2)_6-$	ClO_4^-	80	Toluene	4

[a]Isolated yields.

Other ammonium salts such as ammonium triflate also afforded the corresponding iminium salts, but we report here a sampling of those that could easily be purified by crystallisation, affording nonhygroscopic crystalline products. In conclusion, a one-pot high-yielding, facile, and direct procedure for the preparation of iminium salts was developed using commercially available and inexpensive bulk chemicals.

Experimental

All solvents and reagents were obtained from commercial suppliers and were used without further purification. Benzene and toluene which are used as solvents in this work are both flammable and toxic with benzene being a carcinogen. Melting points are uncorrected and were determined using a Mel-Temp capillary melting point apparatus. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer in DMSO-d_6 with TMS as the internal standard. Chemical shifts are reported in ppm (δ) and *J* values are in Hz. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ, USA.

General procedure for one-pot preparation of iminium salts (**4a–4dd**) To a solution of an aldehyde or a ketone (13 mmol) and a 2° amine (13 mmol) in benzene or toluene (20 ml) was added an ammonium salt (10 mmol). The magnetically stirred mixture was heated at reflux with continuous removal of the water formed (Dean–Stark trap). The mixture was then cooled in an ice-water bath and the precipitated product was collected by suction filtration, washed with ether (3×10 ml), and air dried. Alternatively, the separated oily product was rapidly stirred while cooling until it solidified prior to isolation by suction filtration. The product was crystallised using the solvent system below.

1-(4-Methoxybenzylidene)pyrrolidinium hexafluorophosphate (**4a**): Pale yellow plates (ethanol–acetonitrile), m.p. 146–147°C. ^1H NMR (300 MHz, DMSO-d_6): δ 1.99–2.08 (m, 2H), 2.14–2.23 (m, 2H), 3.95 (s, 3H, OCH_3), 4.17–4.25 (m, 4H, NCH_2), 7.29 (d, *J* = 9.0 Hz, 2H, ArH), 8.04 (d, *J* = 9.0 Hz, 2H, ArH), 9.09 (s, 1H, N=CH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.2, 25.4, 53.1, 56.2, 59.5, 115.5, 120.3, 136.7, 164.7, 165.6. Anal. Calcd for $C_{12}H_{16}F_6NOP$: C, 42.99; H, 4.81, N, 4.18. Found: C, 43.1; H, 4.8; N, 4.2%.

1-(4-Dimethylaminobenzylidene)pyrrolidinium hexafluorophosphate (**4b**): Orange needles (ethanol–acetonitrile), m.p. 169–171°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.93–2.02 (m, 2H), 2.11–2.20 (m, 2H), 3.16 (s, 6H, NCH_3), 4.01–4.11 (m, 4H, NCH_2), 6.93 (d, J = 9.2 Hz, 2H, ArH), 7.82 (d, J = 9.2 Hz, 2H, ArH), 8.67 (s, 1H, N=CH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.4, 25.6, 39.7, 52.1, 58.3, 112.1, 113.8, 136.5, 154.9, 161.2. Anal. Calcd for $C_{13}H_{19}F_6N_2P$: C, 44.83; H, 5.50; N, 8.04. Found: C, 44.5; H, 5.3; N, 7.9%.

1-(Naphthalen-1-ylmethylene)pyrrolidinium hexafluorophosphate (**4c**): Yellow prisms (precipitation by addition of anhydrous ether from methylene chloride-acetonitrile solution), m.p. 206–208°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.11–2.18 (m, 4H), 4.27 (bs, 2H, NCH_2), 4.47–4.51 (m, 2H, NCH_2), 7.73–8.42 (m, 7H, ArH), 10.06 (s, 1H, N=CH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.9, 24.7, 54.3, 59.2, 124.0, 124.7, 125.2, 127.5, 128.6, 129.2, 130.3, 131.2, 132.9, 135.7, 166.8. Anal. Calcd for $C_{15}H_{16}F_6NP$: C, 50.71; H, 4.54; N, 3.94. Found: C, 50.5; H, 4.4; N, 4.0%.

1-(1,3-Benzodioxol-5-ylmethylene)pyrrolidinium hexafluorophosphate (**4d**): Pale yellow prisms (ethanol–acetonitrile), m.p. 169–172°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.98–2.20 (m, 4H), 4.18–4.24 (m, 4H, NCH_2), 6.30 (s, 2H, OCH_2), 7.32 (d, J = 8.2 Hz, 1H, ArH), 7.62–7.67 (m, 2H, ArH), 9.04 (s, 1H, N=CH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.2, 25.3, 53.1, 59.6, 103.4, 109.5, 110.3, 121.7, 134.2, 148.8, 154.4, 164.9. Anal. Calcd for $C_{12}H_{14}F_6NO_2P$: C, 41.27; H, 4.04; N, 4.01. Found: C, 41.1; H, 3.9; N, 4.1%.

1-(Adamantan-2-ylidene)pyrrolidinium hexafluorophosphate (**4e**): White needles (ethanol), m.p. 214–218°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.86–2.12 (m, 16H), 3.17 (bs, 2H), 3.94–3.98 (m, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.8, 25.9, 34.6, 38.0, 38.2, 53.0, 193.5. Anal. Calcd for $C_{14}H_{22}F_6NP$: C, 48.14; H, 6.35; N, 4.01. Found: C, 48.1; H, 6.3; N, 4.0%.

1-(Adamantan-2-ylidene)pyrrolidinium tetrafluoroborate (**4f**): Light tan plates (ethanol), m.p. 233–235°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.86–2.12 (m, 16H), 3.17 (bs, 2H), 3.94–3.98 (m, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.8, 25.9, 34.6, 38.0, 38.2, 53.0, 193.4. Anal. Calcd for $C_{14}H_{22}BF_4N$: C, 57.76; H, 7.62; N, 4.81. Found: C, 57.6; H, 7.8; N, 4.8%.

1-(Adamantan-2-ylidene)azepanium perchlorate (**4g**): White plates (ethanol), m.p. 350–354°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.58–2.19 (m, 20H), 3.46 (bs, 2H), 4.14 (t, J = 6.2 Hz, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.6, 25.7, 26.3, 34.4, 36.4, 39.0, 55.6, 197.9. Anal. Calcd for $C_{16}H_{26}ClNO_4$: C, 57.91; H, 7.90; N, 4.22. Found: C, 57.9; H, 7.9; N, 4.1%.

1-(Adamantan-2-ylidiene)-3-methylpiperidinium hexafluorophosphate (**4h**): White plates (ethanol–acetonitrile), m.p. 299–305°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.97 (d, J = 6.5 Hz, 3H), 1.37–2.20 (m, 17H), 3.32–3.44 (m, 1H), 3.59–3.68 (m, 3H), 4.42–4.51 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 18.1, 25.7, 25.9, 26.1, 31.1, 33.1, 34.5, 36.1, 36.3, 38.3, 38.4, 39.4, 53.0, 58.4, 195.4. Anal. Calcd for $C_{16}H_{26}F_6NP$: C, 50.93; H, 6.94; N, 3.71. Found: C, 51.0; H, 7.15; N, 3.7%.

1-(Bicyclo[2.2.1]hept-2-ylidene)-3-methylpiperidinium hexafluorophosphate (**4i**): Colourless plates (ethanol–acetonitrile), m.p. 255–260°C (dec). Complex NMR spectra due to mixture of diastereomers. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92–0.98 (m), 1.27–1.47 (m), 1.56–2.00 (m), 2.45–2.79 (m), 3.20–3.91 (m), 4.19–4.34 (m). ^{13}C NMR (75 MHz, DMSO-d_6): δ 17.90, 18.01, 18.05, 18.08, 24.15, 24.19, 24.42, 24.55, 24.65, 25.04, 25.66, 30.31, 30.36, 30.45, 31.32, 31.54, 31.63, 32.14, 35.36, 38.54, 38.59, 40.45, 40.60, 40.62, 40.85, 44.33, 44.44, 44.50, 44.60, 53.51, 53.56, 53.88, 54.07, 59.14, 59.19, 59.48, 59.62, 195.24 and 195.37. Anal. Calcd for $C_{13}H_{22}F_6NP$: C, 46.29; H, 6.57; N, 4.15. Found: C, 46.3; H, 6.6; N, 4.1%.

1-(Bicyclo[2.2.1]hept-2-ylidene)pyrrolidinium hexafluorophosphate (**4j**): White plates (ethanol), m.p. 213–217°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.26–2.69 (m, 13H), 3.38–3.40 (m, 1H), 3.68–4.05 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.6, 24.0, 24.3, 25.5, 35.5, 39.1, 41.1, 45.8, 53.4, 54.0, 193.6. Anal. Calcd for $C_{11}H_{18}F_6NP$: C, 42.72; H, 5.87; N, 4.53. Found: C, 42.7; H, 5.7; N, 4.5%.

1-(Bicyclo[2.2.1]hept-2-ylidene)azepanium perchlorate (**4k**): White plates (ethanol), m.p. 300–302°C (dec). (lit.[8] m.p. 301.5–302.5°C (dec)). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.33–2.05 (m, 14H), 2.46–2.81 (m, 3H), 3.62–3.63 (m, 1H), 3.79–3.83 (m, 2H, NCH_2), 3.99–4.06 (m, 2H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.5, 25.3, 25.5, 25.6, 26.1, 26.2, 35.4, 38.7, 40.6, 44.8, 55.28, 55.31, 198.2. Anal. Calcd for $C_{13}H_{22}ClNO_4$: C, 53.51; H, 7.60; N, 4.80. Found: C, 53.6; H, 7.7; N, 4.7%.

1-(3-Methylcyclohexylidene)pyrrolidinium hexafluorophosphate (**4l**): White needles (ethanol), m.p. 221–224°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.02 (d, J = 6.6 Hz, 3H, CH_3), 1.18–1.30 (m, 1H), 1.59–2.08 (m, 8H), 2.21–2.30 (m, 1H), 2.45–2.57 (m, 1H), 2.83, 2.92 (m, 2H), 3.87–4.00 (m, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.4, 23.6, 23.9, 31.2, 32.0, 32.9, 40.8, 53.4, 53.5, 188.3. Anal. Calcd for $C_{11}H_{20}F_6NP$: C, 42.45; H, 6.48; N, 4.50. Found: C, 42.4; H, 6.6; N, 4.3%.

1-(1,4-Dioxaspiro[4.5]dec-8-ylidene)pyrrolidinium hexafluorophosphate (**4m**): White needles (ethanol–acetonitrile), m.p. 211–213°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.92 (t, J = 6.7 Hz, 4H), 2.00–2.05 (m, 4H), 2.83–2.88 (m, 4H), 3.85–3.93 (m, 4H, NCH_2), 3.95 (s, 4H, OCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.0, 30.8, 31.1, 53.7, 64.1, 105.9, 186.3. Anal. Calcd for $C_{12}H_{20}F_6NO_2P$: C, 40.57; H, 5.67; N, 3.94. Found: C, 40.7; H, 5.5; N, 3.9%.

1-Isopropylidenepyrrolidinium perchlorate (**4n**): Off white plates (ethanol–acetonitrile), m.p. 228–230°C (lit.[9] m.p. 232–233°C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.00–2.05 (m, 4H), 2.42–2.43 (m, 6H), 3.85–3.90 (m, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.2, 25.1, 53.8, 184.8.

1-(Pent-3-ylidene)pyrrolidinium perchlorate (**4o**): White plates (ethanol), m.p. 210–212°C (lit.[9] m.p. 213–214°C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.18 (t, J = 7.6 Hz, 6H, CH_3), 2.00–2.05 (m, 4H), 2.70 (q, J = 7.6 Hz, 4H), 3.93–3.97 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 8.8, 24.0, 28.5, 53.5, 191.0.

1-Cyclopentylidenepyrrolidinium hexafluorophosphate (**4p**): Off white needles (ethanol), m.p. 236–239°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.89–1.93 (m, 4H), 2.02–2.07 (m, 4H), 2.78 (bs, 4H), 3.82 (bs, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.3, 35.4, 54.3, 195.8. Anal. Calcd for $C_9H_{16}F_6NP$: C, 38.17; H, 5.69; N, 4.95. Found: C, 38.3; H, 5.6; N, 5.0%.

N-Cyclopentylidenediethylaminium perchlorate (**4q**): White needles (ethanol), m.p. 203–204°C (lit.[10] m.p. 200–202°C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.29 (t, J = 7.3 Hz, 6H, CH_3), 1.88–1.93 (m, 4H), 2.87–2.92 (m, 4H), 3.79 (q, J = 7.3 Hz 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 11.9, 24.6, 35.0, 50.6, 200.5.

N-Cyclopentylidenedipropylaminium perchlorate (**4r**): White needles (ethanol), m.p. 251–253°C (dec). (lit.[10] m.p. 255–256°C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.93 (t, J = 7.4 Hz, 6H, CH_3), 1.67–1.80 (m, 4H), 1.88–1.93 (m, 4H), 2.90–2.95 (m, 4H), 3.71 (t, J = 8.0 Hz, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 10.8, 19.6, 24.2, 35.0, 56.8, 201.0.

1-Cyclopentylidenepyrrolidinium perchlorate (**4s**): Off white plates (ethanol–acetonitrile), m.p. 229–231°C (dec). (lit.[11] m.p. 231–233°C (dec.)). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.89–1.93 (m, 4H), 2.03–2.07 (m, 4H), 2.78 (bs, 4H), 3.83 (bs, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.3, 35.5, 54.4, 195.8.

1-Cyclopentylidenepyrrolidinium tetrafluoroborate (**4t**): White plates (ethyl acetate–acetonitrile), m.p. 206–208°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.88–1.93 (m, 4H), 2.02–2.07 (m, 4H), 2.78 (bs, 4H), 3.82 (bs, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.3, 35.4, 54.3, 195.8. Anal. Calcd for $C_9H_{16}BF_4N$: C, 48.04; H, 7.17; N, 6.22. Found: C, 48.1; H, 7.1; N, 6.2%.

1-Cyclopentylidenepiperidinium hexafluorophosphate (**4u**): White prisms (ethanol–acetonitrile), m.p. 225–227°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.67–1.92 (m, 10H), 2.84–2.89 (m, 4H), 3.82–3.86 (m, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.0, 24.2, 25.4, 34.6, 54.8, 197.3. Anal. Calcd for $C_{10}H_{18}F_6NP$: C, 40.41; H, 6.10; N, 4.71. Found: C, 40.5; H, 6.1; N, 4.7%.

1-Cyclopentylidenepiperidinium perchlorate (**4v**): White plates (ethanol–acetonitrile), m.p. 231–233°C (dec). (lit.[8] m.p. 232.5–235.5°C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.67–1.92 (m, 10H), 2.84–2.89 (m, 4H), 3.82–3.86 (m, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.0, 24.2, 25.4, 34.6, 54.8, 197.3.

1-Cyclopentylideneazepanium perchlorate (**4w**): White plates (ethanol), m.p. 218–221°C (dec). (lit.[12] m.p. 212–213°C dec.). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.56–1.63 (m, 4H), 1.84–1.93 (m, 8H), 2.86–2.91 (m, 4H), 3.90 (t, J = 5.8 Hz, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.1, 25.3, 26.0.0, 35.0, 55.8, 200.5.

1-Cyclopentylidene-3-methylpiperidinium hexafluorophosphate (**4x**): Light tan plates (ethanol), m.p. 220–223°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (d, J = 6.7 Hz, 3H, CH_3), 1.29–1.40 (m, 1H), 1.65–1.92 (m, 8H), 2.80–2.96 (m, 4H), 3.29 (t, J = 11.8 Hz, 1H), 3.54 (t, J = 11.8 Hz, 1H), 4.05 (t, J = 11.7 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 18.1, 24.1, 24.4, 30.3, 31.5, 34.6, 34.7, 54.3, 59.9, 197.5. Anal. Calcd for $C_{11}H_{20}F_6NP$: C, 42.45; H, 6.48; N, 4.50. Found: C, 42.4; H, 6.4; N, 4.5%.

1-Cyclohexylidenepyrrolidinium hexafluorophosphate (**4y**): White needles (ethanol–acetonitrile), m.p. 233–234°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.56–1.64 (m, 2H), 1.75–1.84 (m, 4H), 1.99–2.04 (m, 4H), 2.71 (t, J = 6.4 Hz, 4H), 3.90 (bs, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.7, 23.9, 24.2, 33.2, 53.3, 188.3. Anal. Calcd for $C_{10}H_{18}F_6NP$: C, 40.41; H, 6.10; N, 4.71. Found: C, 40.3; H, 6.2; N, 4.7%.

1-Cyclohexylidenepyrrolidinium perchlorate (**4z**): White prisms (ethanol) m.p. 231–233°C (dec). (lit.[11] m.p. 230–231°C (dec.)). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.56–1.64 (m, 2H), 1.76–1.86 (m, 4H), 2.00–2.06 (m, 4H), 2.71 (t, J = 6.4 Hz, 4H), 3.91 (bs, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.7, 24.0, 24.2, 33.2, 53.3, 188.3.

1-Cycloheptylidenepyrrolidinium tetrafluoroborate (**4aa**): Colourless plates (ethanol), m.p. 210–213°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.57–1.77 (m, 8H), 2.00–2.05 (m, 4H), 2.84 (t, J = 5.0 Hz, 4H, N=CCH_2), 3.89 (bs, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.6, 24.3, 29.0, 36.4, 54.0, 191.3. Anal. Calcd for $C_{11}H_{20}BF_4N$: C, 52.20; H, 7.97; N, 5.53. Found: C, 52.2; H, 8.1; N, 5.5%.

1-Cycloheptylidenepyrrolidinium perchlorate (**4bb**): Off white plates (ethanol), m.p. 234–236°C (dec). (lit.[11] m.p. 234–235°C (dec)). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.57–1.84 (m, 8H), 2.00–2.05 (m, 4H), 2.84 (t, J = 5.0 Hz, 4H, N=CCH_2), 3.89 (bs, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.3, 24.0, 28.7, 36.1, 53.7, 191.0.

1-Cycloheptylidenepyrrolidinium hexafluorophosphate (**4cc**): White plates (ethanol–acetonitrile), m.p. 233–236°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.59–1.77 (m, 8H), 2.00–2.05 (m, 4H), 2.84 (t, J = 5.0 Hz, 4H, N=CCH_2), 3.89 (bs, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.3, 24.0, 28.7, 36.1, 53.7, 191.0. Anal. Calcd for $C_{11}H_{20}F_6NP$: C, 42.45; H, 6.48; N, 4.50. Found: C, 42.5; H, 6.4; N, 4.5%.

1-Cycloheptylideneazepanium perchlorate (**4dd**): Off white prisms (ethanol–acetnitrile), m.p. 284–288°C (dec). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.56–1.81 (m, 16H), 2.92–2.96 (m, 4H, N=CCH_2), 4.02 (t, J = 6 Hz, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.5, 25.0, 25.7, 28.0, 34.3, 54.9, 195.1. Anal. Calcd for $C_{13}H_{24}ClNO_4$: C, 53.15; H, 8.23; N, 4.77. Found: C, 53.2; H, 8.4; N, 4.8%.

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