Supplementary Material (ESI) for New Journal of Chemistry

Influence of electron-withdrawing groups on the ionic liquid characteristics of 1-alkyl-*n*-cyanopyridinium and 1-alkyl-*n*-(trifluoromethyl)pyridinium salts

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Supplemental Data

IR spectra of selected Systems

$[C_2^4CNPy][EtSO_4]$ (**3**)
$[C_2^4CNPy][NTf_2]$ (**4**)
$[C_4^4CNPy][NTf_2]$ (**7**)
$[C_6^4CNPy][NTf_2]$ (**10**)
$[C_8^4CNPy][NTf_2]$ (**13**)
$[C_1^3CNPy][MeSO_4]$ (**21**)
$[C_2^3CNPy][EtSO_4]$ (**23**)
$[C_2^3CNPy][NTf_2]$ (**24**)
$[C_1^2CNPy][NTf_2]$ (**30**)
$[C_2^2CNPy][EtSO_4]$ (**31**)
$[C_2^2CNPy][NTf_2]$ (**32**)

Labelled plots of the crystallographic asymmetric units and principle cation-anion hydrogen-bonds in the crystal structures of 1, 2, 4, 22, 24, 32, (and closest contacts for 37)

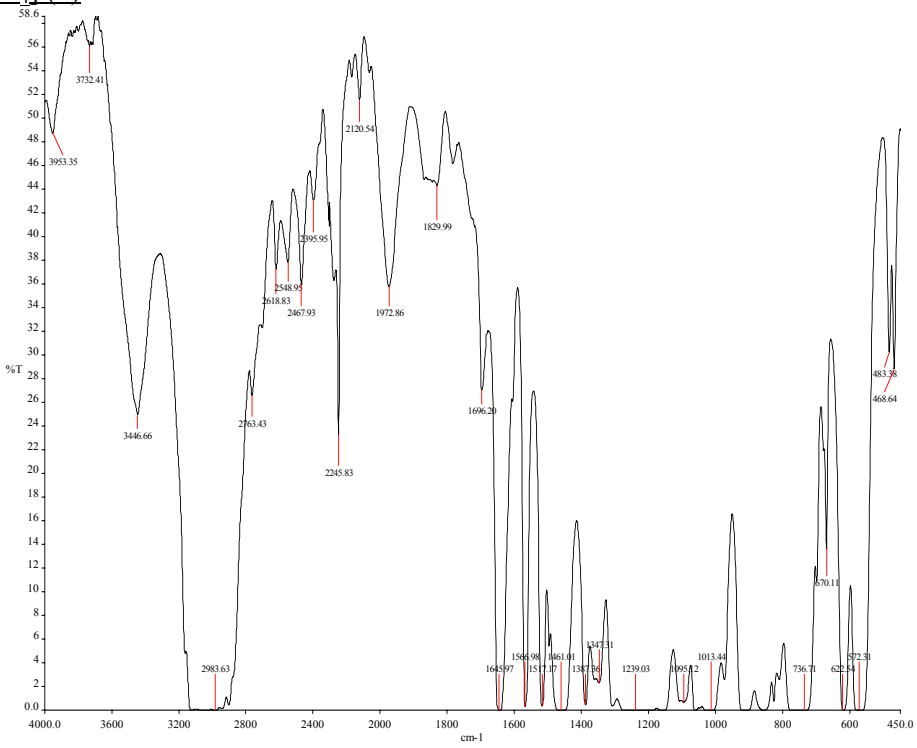
1-Methyl-4-cyanopyridinium methylsulfate (**1**)
1-Methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**2**)
1-Ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**4**)
1-Methyl-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**22**)
1-Ethyl-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**24**)
1-Ethyl-2-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**32**)
1-Ethyl-3-(trifluoromethyl)pyridinium bis{(trifluoromethyl)sulfonyl}imide (**37**)

IR spectra of selected Systems

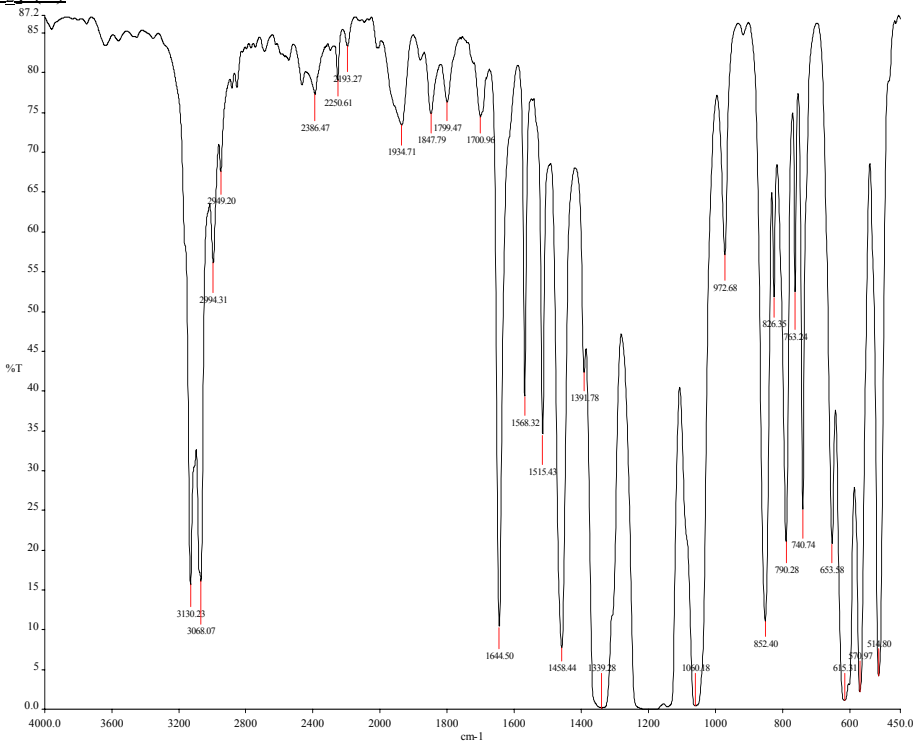
IR data were recorded for twelve of the ionic liquid salts (in the liquid state between KBr disks, on a Perkin-Elmer Spectrum 100 FT-IR) for eleven ionic liquids; **3**, **4**, **7**, **10**, **13**, **21**, **23**, **24**, **30**, **31**, **32**. The spectra showed a nitrile vibrational band at ~2249.5 cm^{-1} which had variable intensity between the different salts, but very little variation in position (shown in the table below).

Compound	Alkyl	Nitrile position	Anion	CN stretch /cm^{-1}	Appearance
3	C_2H_5	4	$EtSO_4$	2246	s
4	C_2H_5	4	NTf_2	2249	w
7	C_4H_9	4	NTf_2	2248.5	w
10	C_6H_{13}	4	NTf_2	2247.5	w
13	C_8H_{17}	4	NTf_2	2247	w
21	CH_3	3	$MeSO_4$	2250.5	S
23	C_2H_5	3	$EtSO_4$	2250	S
24	C_2H_5	3	NTf_2	2255	S
30	CH_3	2	NTf_2	2250	w
31	C_2H_5	2	$EtSO_4$	2249	w
32	C_2H_5	2	NTf_2	2252.5	w
			Average	2249.5	
			Stdev	2.5	

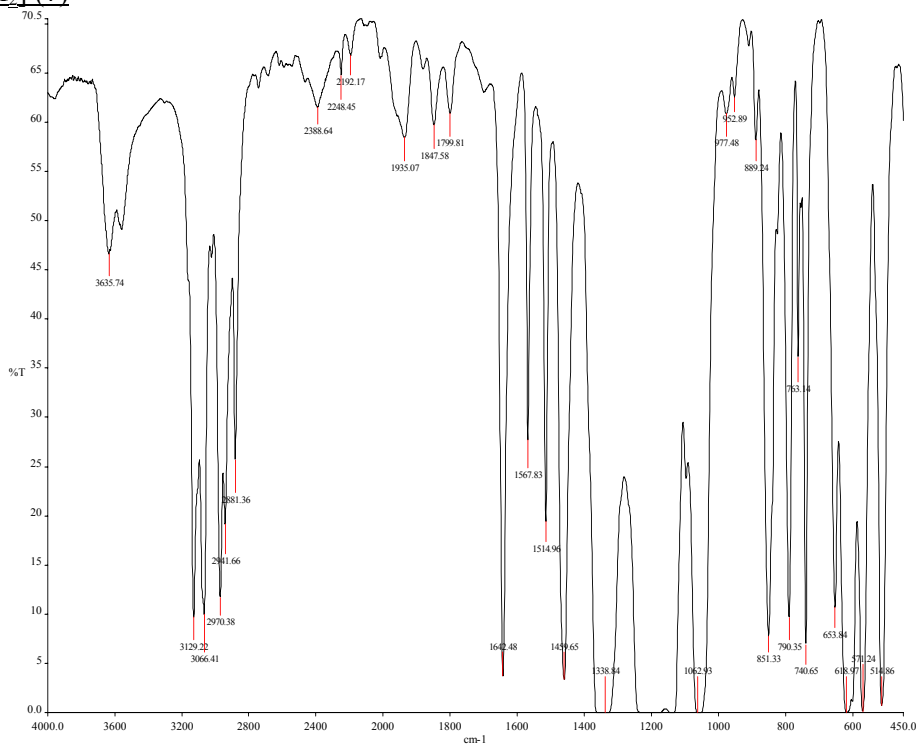
[C_2^4CNPy][$EtSO_4$] (**3**)



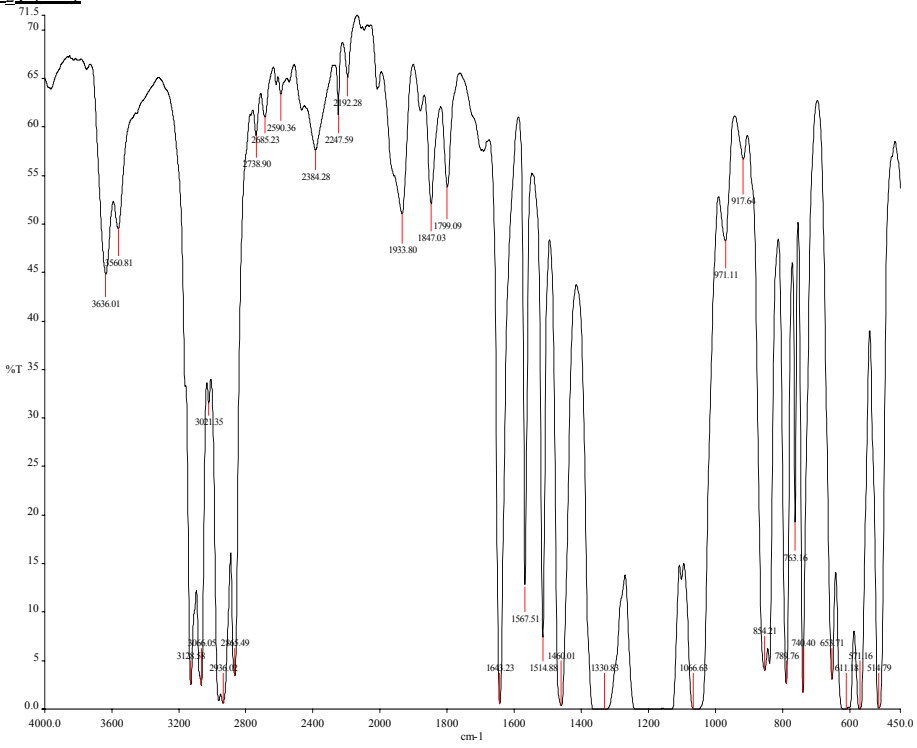
[C_2^4CNPy][NTf_2] (**4**)



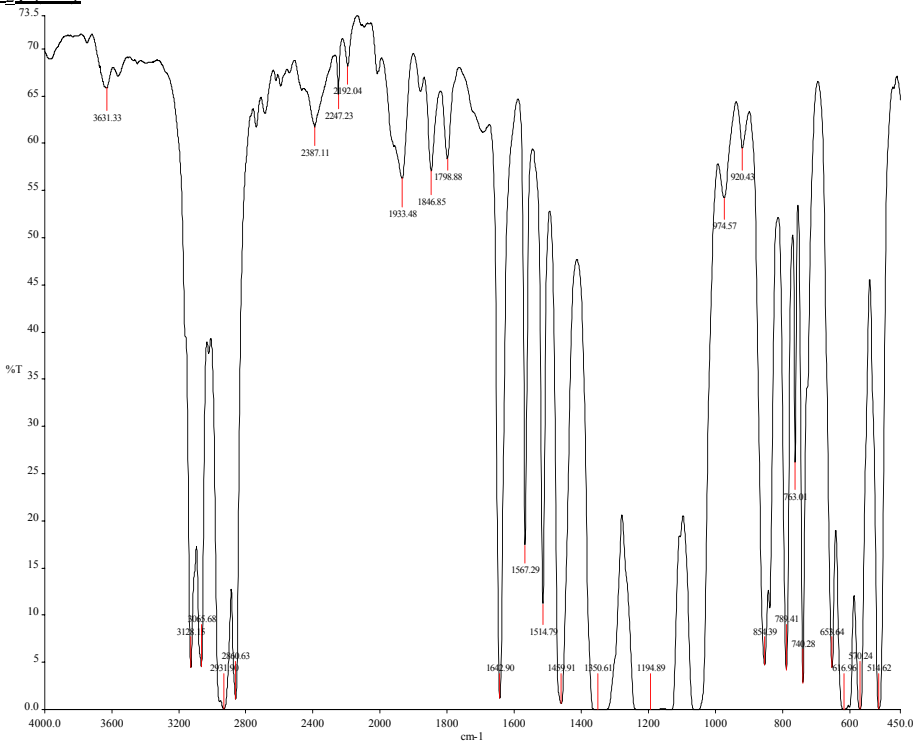
[$C_4{}^4$CNPy][NTf_2] (**7**)



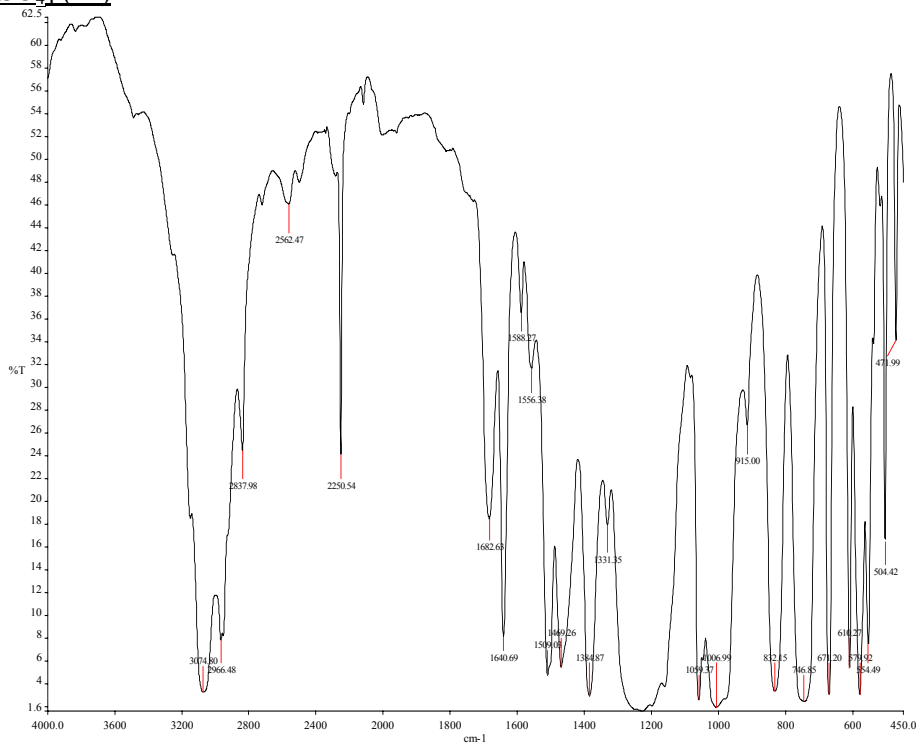
[$C_6{}^4$CNPy][NTf_2] (**10**)



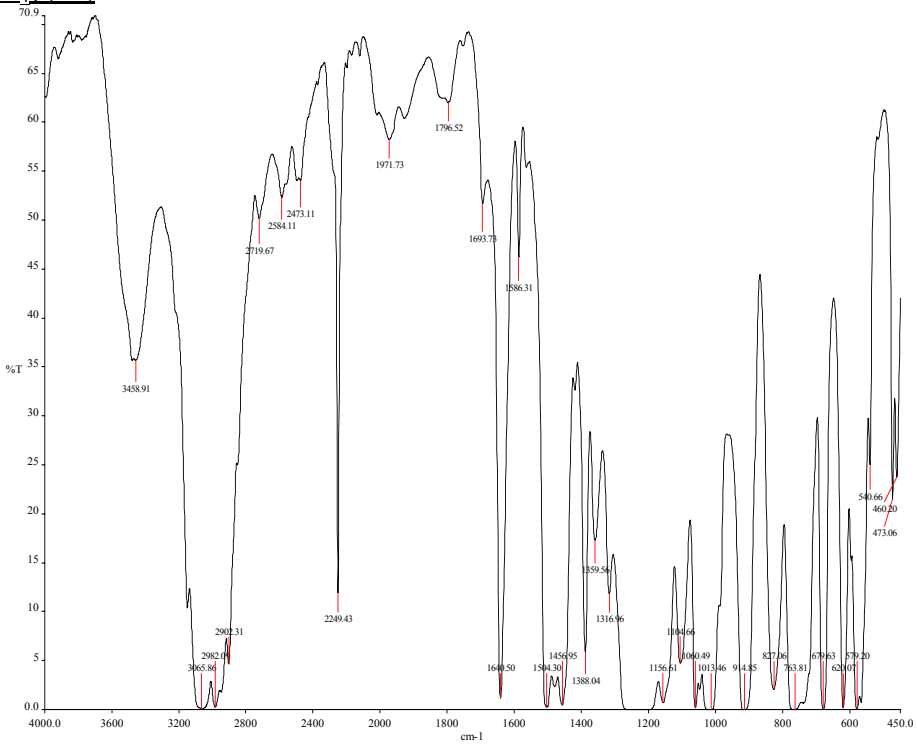
[C_8^4CNPy][NTf_2] (**13**)



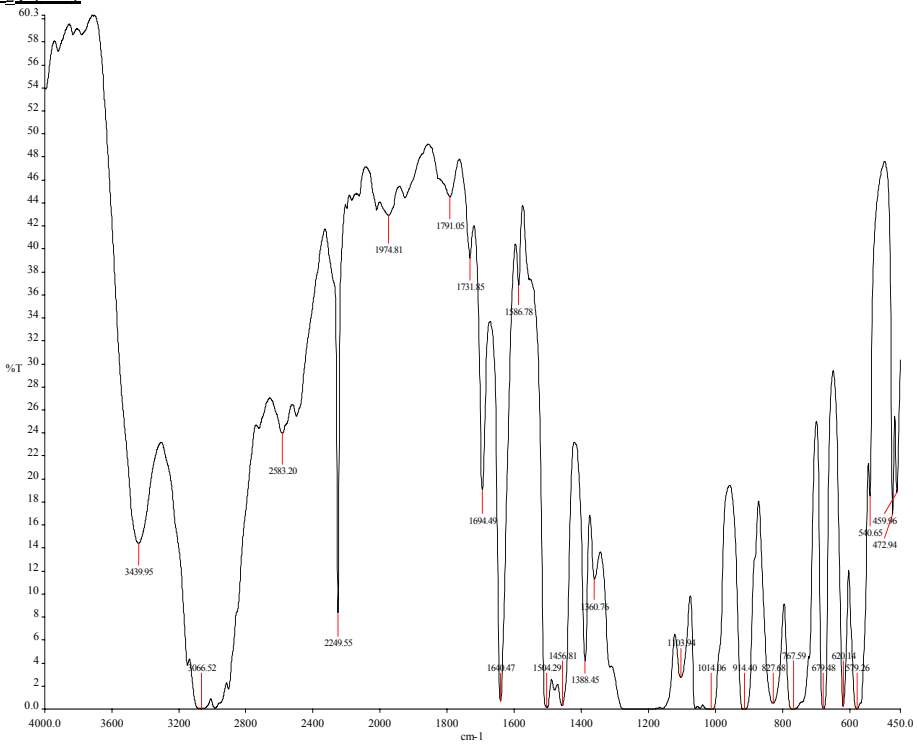
[C_1^3CNPy][$MeSO_4$] (**21**)



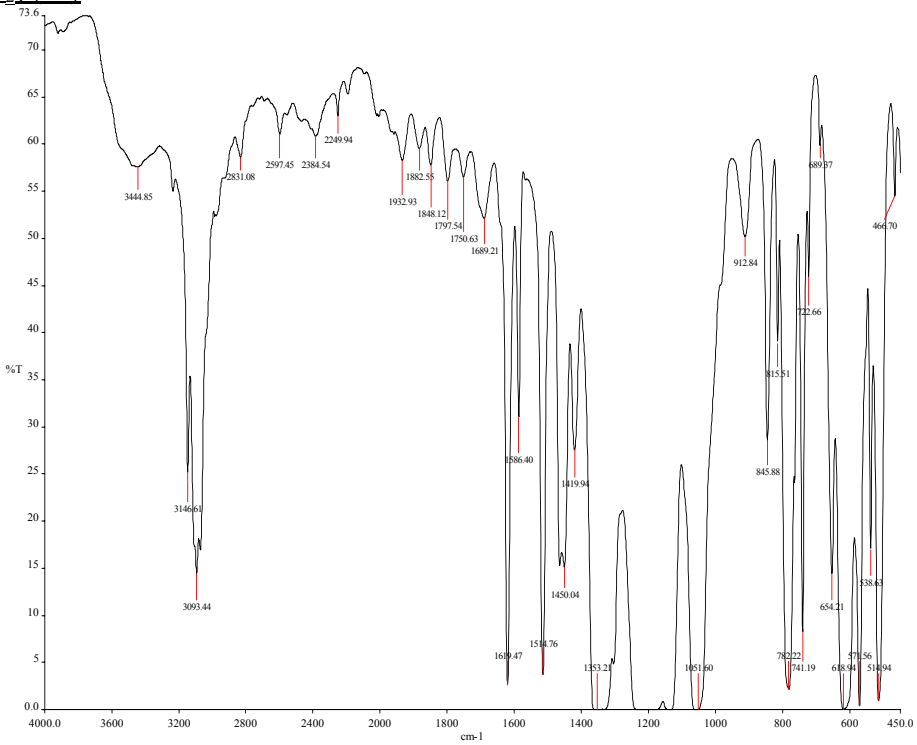
$[C_2{}^3CNPy][EtSO_4]$ (**23**)



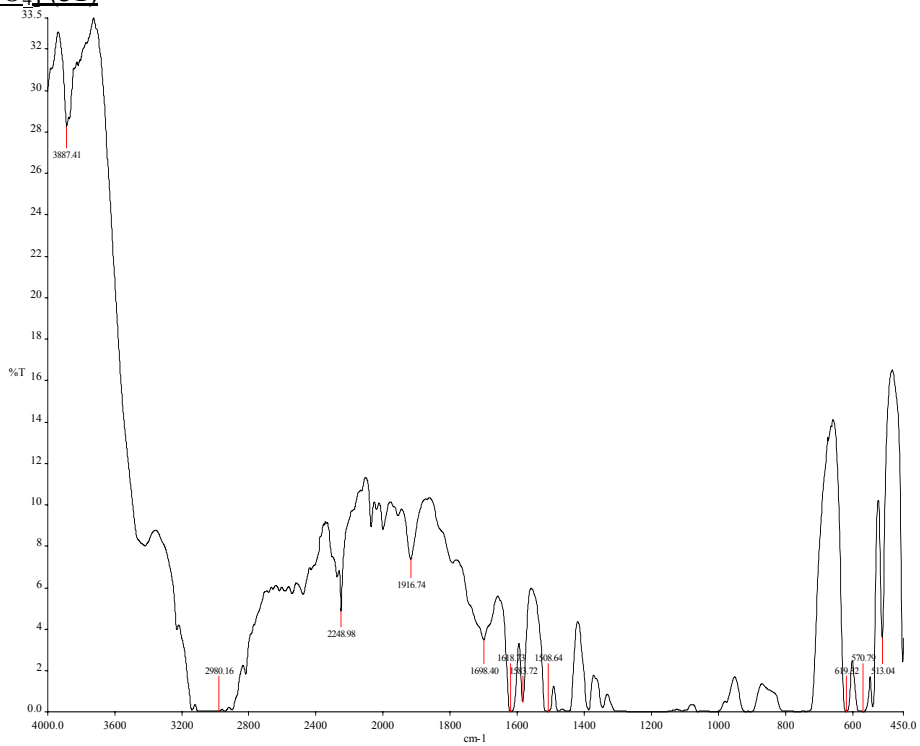
$[C_2{}^3CNPy][NTf_2]$ (**24**)



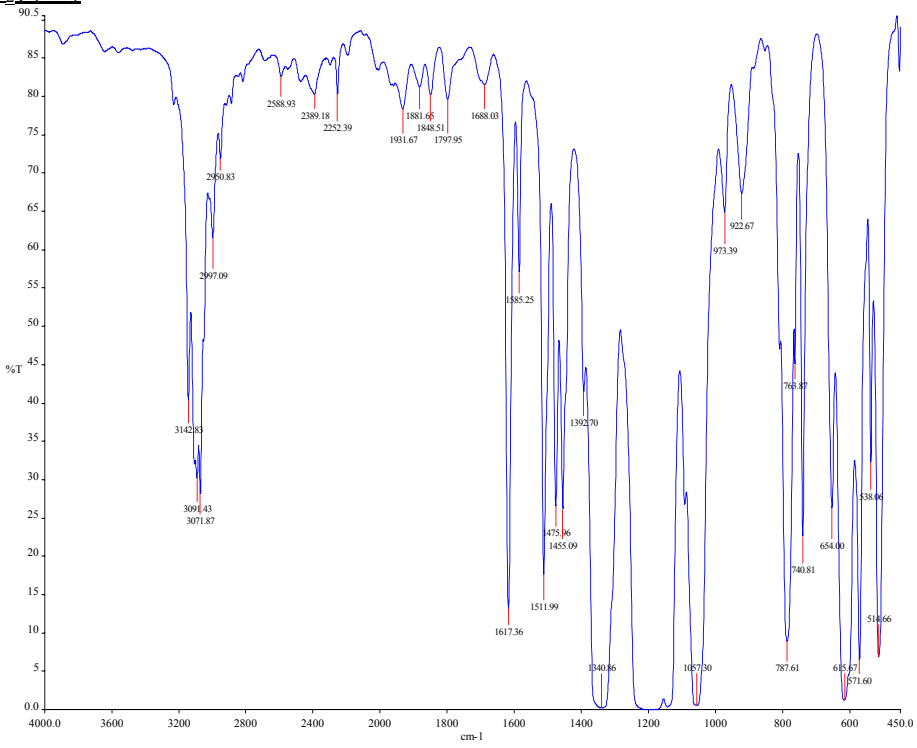
[C_1^2CNPy][NTf_2] (**30**)



[C_2^2CNPy][$EtSO_4$] (**31**)



$[C_2{}^2CNPy][NTf_2]$ (**32**)



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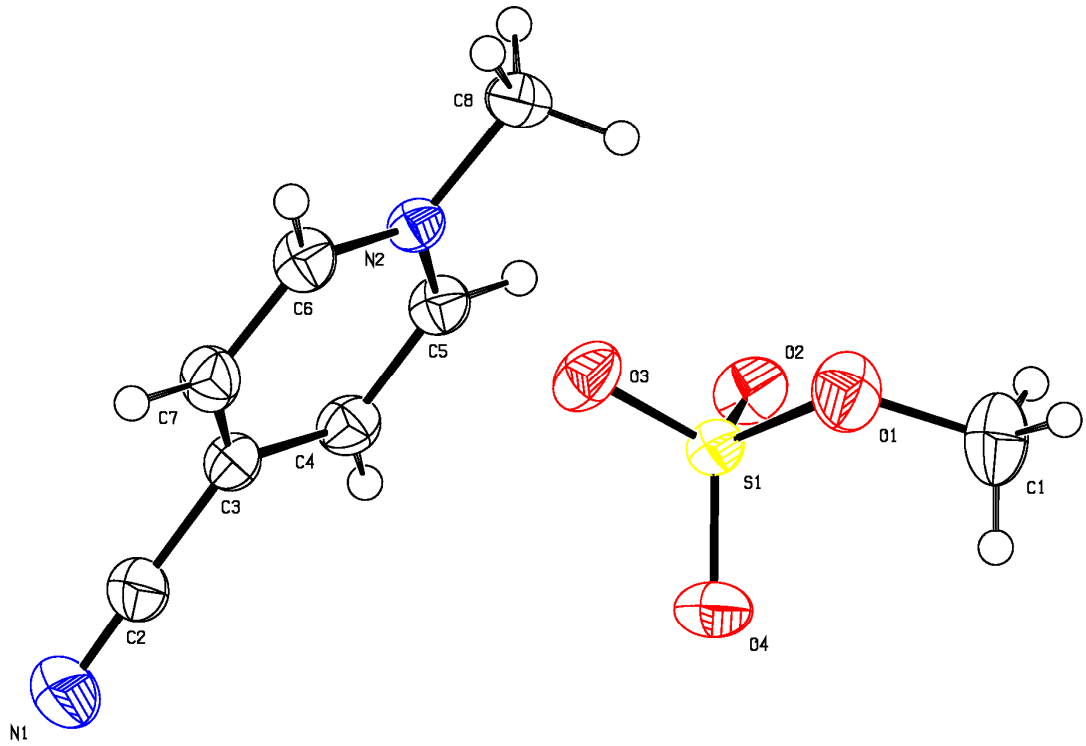
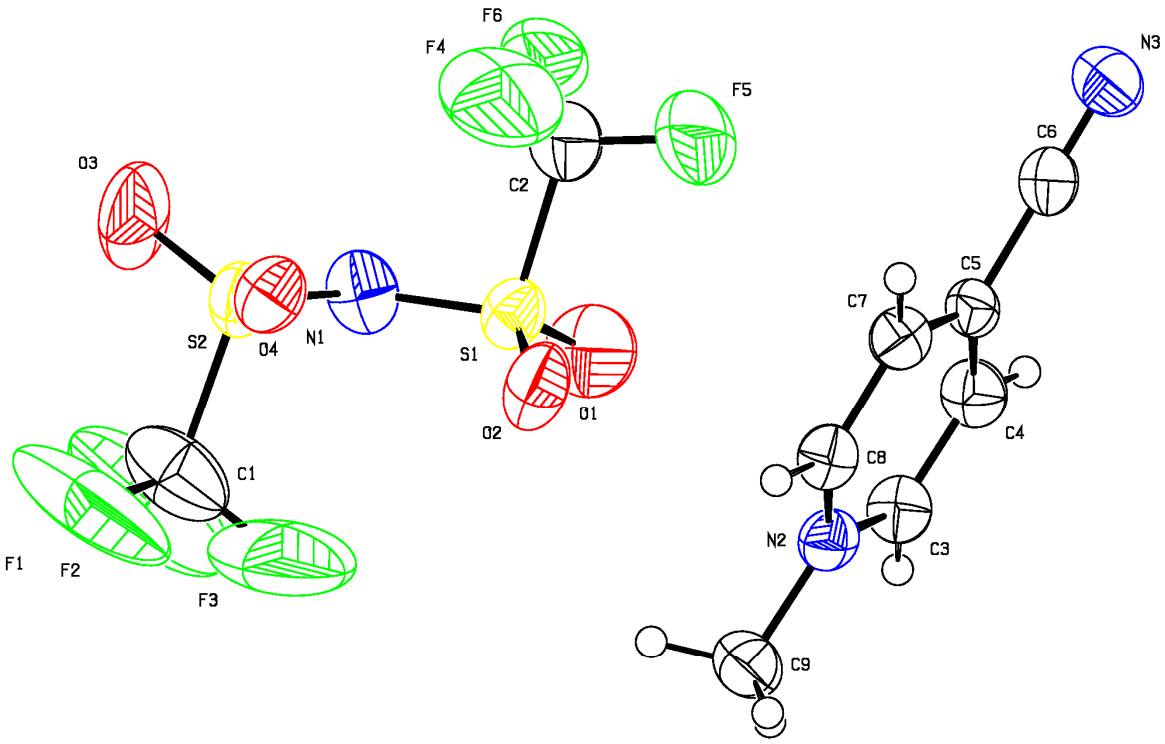
Labelled plots of the crystallographic asymmetric units and principle cation-anion hydrogen-bonds in the crystal structures of 1, 2, 4, 22, 24, 32, (and closest contacts for 37)

1-Methyl-4-cyanopyridinium methylsulfate (**1**)



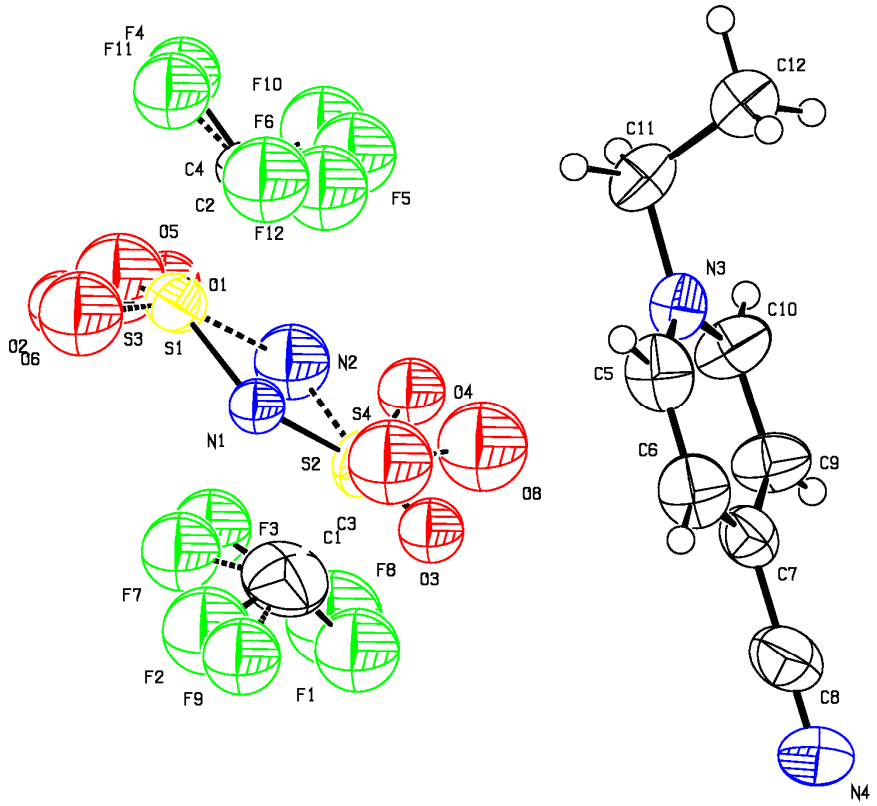
D	H	A	D-H	H...A	D...A	D-H...A	symm(A)
C6	H5	O2	0.9500	2.4200	3.2412	144.00	1/2-x, 1/2+y, 1/2+z
C6	H5	O4	0.9500	2.3900	3.1953	142.00	1/2-x, 1/2+y, 1/2+z
C8	H7	O2	0.9800	2.5300	3.3104	137.00	
C8	H8	O3	0.9800	2.5700	3.2631	128.00	1/2-x, -1/2+y, 1/2+z
C5	H9	O3	0.9500	2.4200	3.1780	136.00	1/2-x, -1/2+y, 1/2+z
C5	H9	O4	0.9500	2.5600	3.2586	131.00	1/2-x, -1/2+y, 1/2+z

1-Methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**2**)



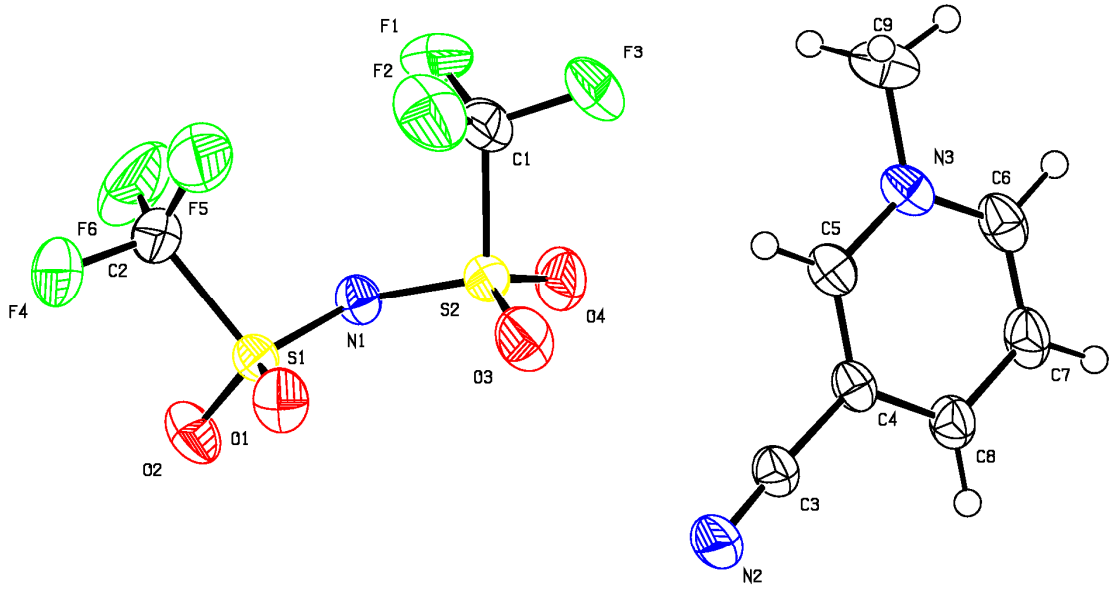
D	H	A	D-H	H...A	D...A	D-H...A	symm(A)
C8	H1	O2	0.9500	2.3400	3.2721	167.00	1-x,-y, 1-z
C7	H2	O1	0.9500	2.3200	3.2689	172.00	1/2+x, 1/2-y, 1/2+z
C4	H3	O4	0.9500	2.4600	3.3929	167.00	-1/2+x, 1/2-y, -1/2+z

1-Ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**4**)



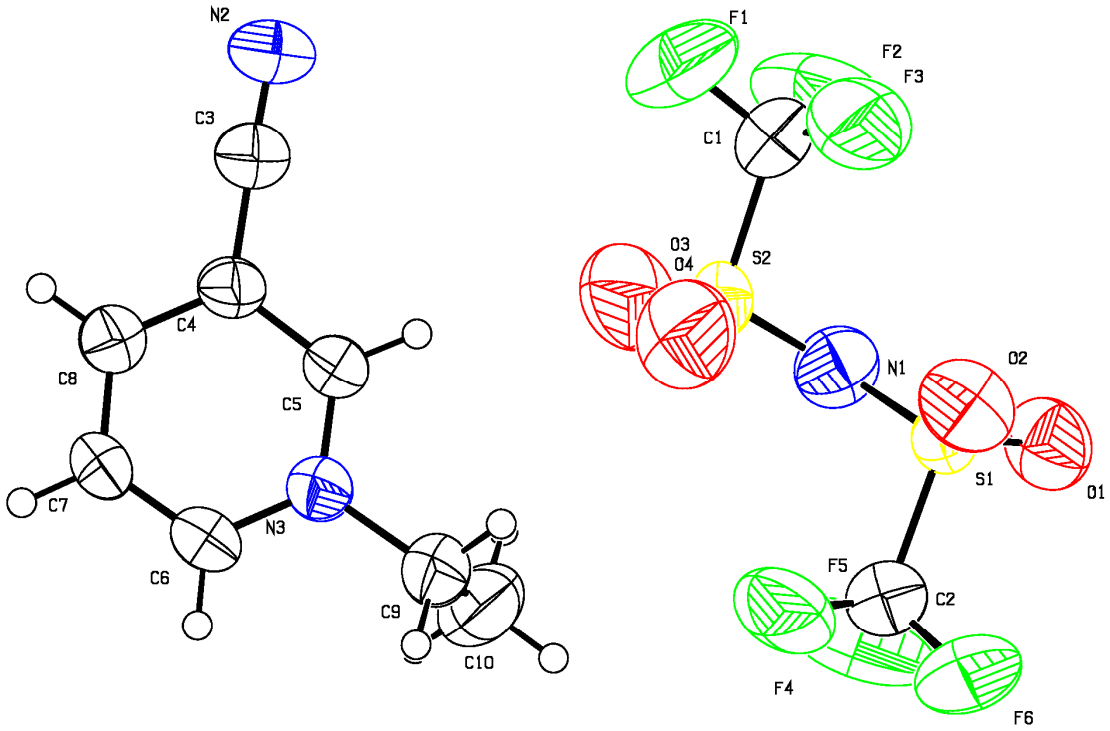
D	H	A	D-H	H...A	D...A	D-H...A	symm(A)
C10	H1	N1	0.9500	2.3100	3.2559	171.00	-1/2+x, -1/2+y, z
C6	H3	O1	0.9500	2.4900	3.2082	132.00	-1/2+x, 1/2+y,z
C6	H3	O4	0.9500	2.4400	3.2583	144.00	-1/2+x, 1/2+y,z
C11	H9	N4	0.9900	2.5000	3.3400	143.00	1/2+x, 1/2-y, 1/2+z

1-Methyl-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**22**)



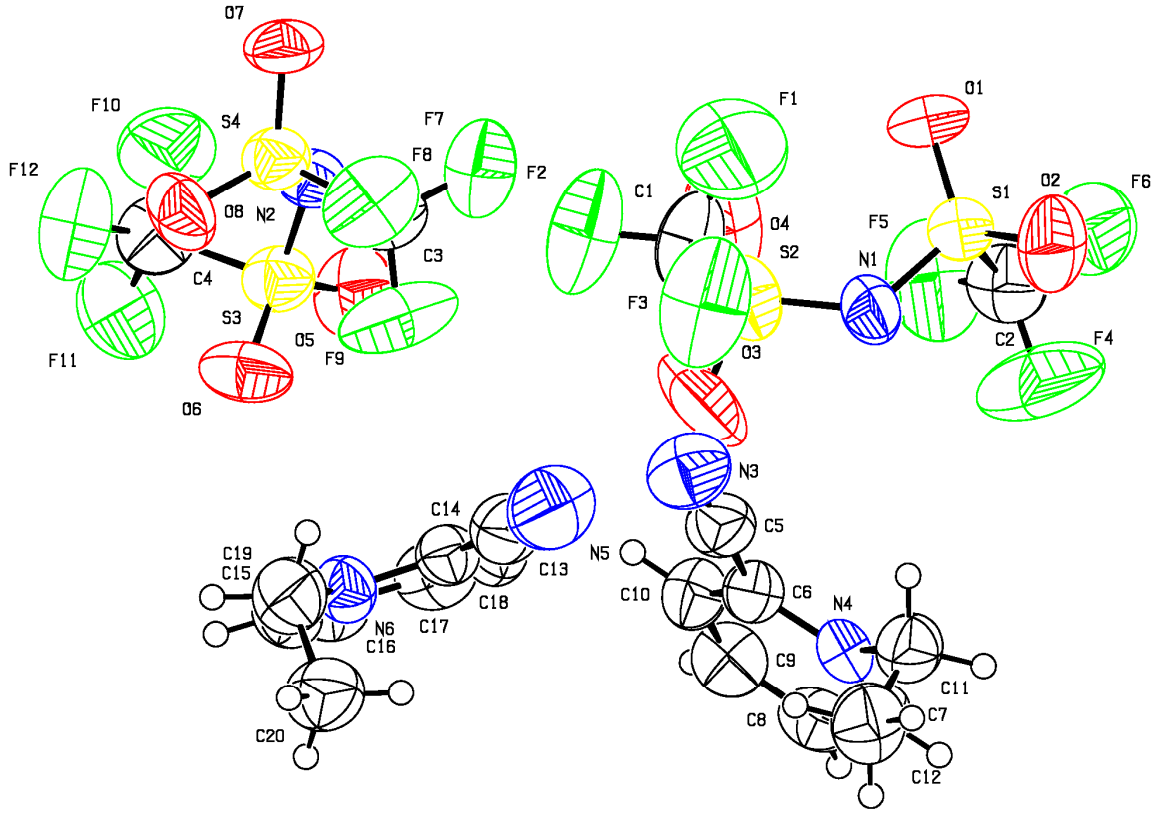
D	H	A	D-H	H...A	D...A	D-H...A	symm(A)
C7	H2	N2	0.9500	2.3800	3.1648	140.00	x, y, -1+z
C6	H3	O3	0.9500	2.4200	3.1379	132.00	x, y, -1+z
C9	H6	F3	0.9800	2.5300	3.3471	141.00	
C5	H7	O2	0.9500	2.5700	3.2681	130.00	1+x, y, z

1-Ethyl-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**24**)



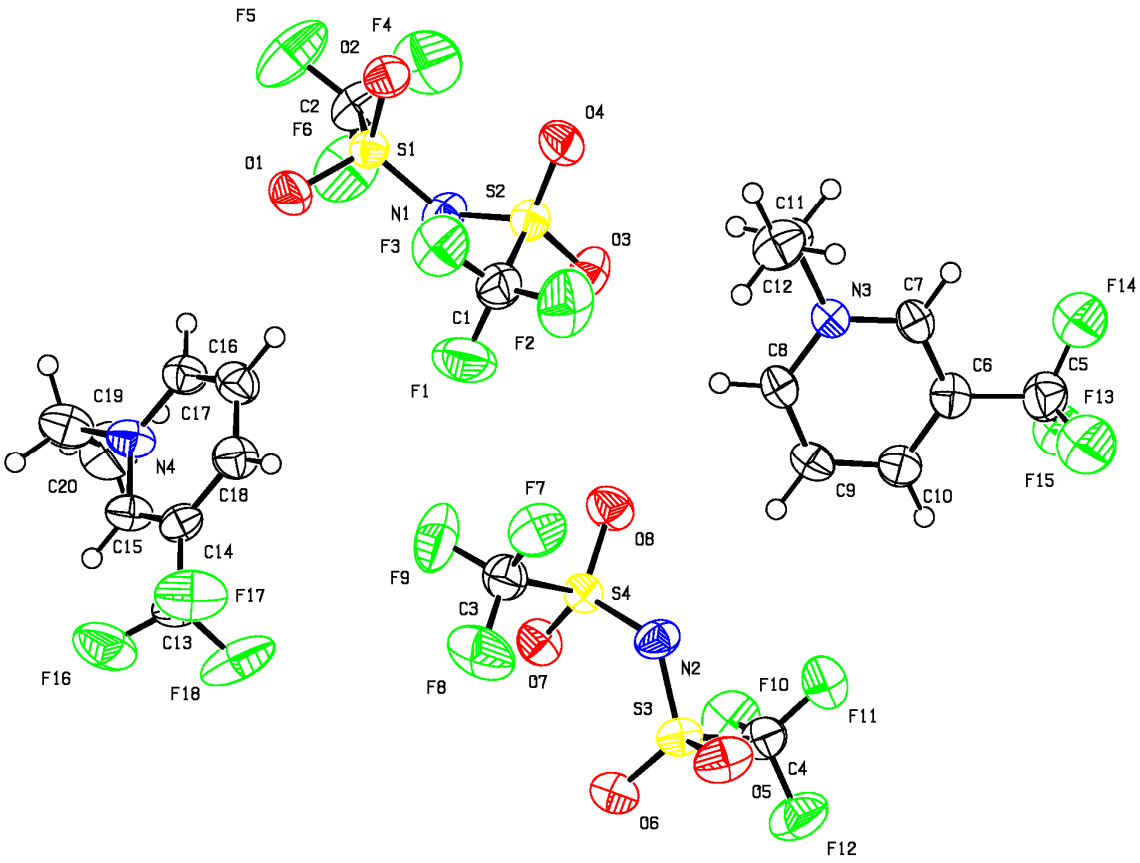
D	H	A	D-H	H...A	D...A	D-H...A	symm(A)
C9	H7	O1	0.9700	2.5700	3.4577	152.00	1/2-x, -1/2+y, 1/2-z
C5	H9	O3	0.9300	2.5000	3.3742	157.00	

1-Ethyl-2-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (**32**)



D	H	A	D-H	H...A	D...A	D-H...A	symm(A)
C9	H2	O1	0.9300	2.4800	3.3007	147.00	1-x, -1/2+y, 1/2-z
C8	H3	O4	0.9300	2.6000	3.4451	152.00	1-x, -1/2+y, 1/2-z
C7	H4	O2	0.9300	2.3100	3.2270	167.00	-1/2+x, 1/2-y, 1-z
C18	H10	O3	0.9300	2.3300	3.1910	154.00	
C17	H11	O6	0.9300	2.5000	3.4098	166.00	1/2+x, 1/2-y, -z
C15	H13	O4	0.9300	2.5200	3.1608	126.00	-1/2+x, 1/2-y, -z

1-Ethyl-3-(trifluoromethyl)pyridinium bis{(trifluoromethyl)sulfonyl}imide (**37**)



D	H	A	D-H	H...A	D...A	D-H...A	symm(A)
C9	H2	O8	0.9500	2.5900	3.2263	125.00	
C11	H7	O7	0.9900	2.4100	3.3058	150.00	1+x, y, z
C11	H8	O3	0.9900	2.4200	3.2892	146.00	
C7	H9	O6	0.9500	2.5700	3.1855	123.00	1+x, y, z
C17	H11	O1	0.9500	2.4900	3.1641	128.00	
C16	H12	O5	0.9500	2.5700	3.4251	149.00	x, y, -1+z
C19	H16	O5	0.9900	2.5600	3.3631	139.00	x, y, -1+z
C19	H17	O2	0.9900	2.5400	3.3360	137.00	-1+x, y, z
C15	H18	O2	0.9500	2.5600	3.4295	152.00	-1+x, y, z
C15	H18	O4	0.9500	2.5400	3.1294	121.00	-1+x, y, z