Synthesis of Pyridinium *N*-Aryl/*N*-Heteroarylcyclic Ylids as Potential Energetic Materials

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ABSTRACT

The synthesis, characterization and energetic properties of several types of nitrogen-rich pyridinium ylids are reported.

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1. Introduction

Energetic materials are the subject of considerable current interest^{1a-c} and novel compounds are being explored in order to ensure adequate replacements for existing explosives. Theoretical and experimental studies indicate that the presence of high concentrations of nitrogen species in the combustion products of propellants can reduce gun barrel erosion by promoting the formation of iron nitride rather than iron carbide on the interior surface of the barrel. Thus, synthesis of nitrogen-rich compounds has attracted considerable attention since the 1960s.²⁻⁷

Our continued interest in this field⁸ prompted us to synthesize a series of pyridinium *N*-arylylids and pyridinium *N*-heteroarylylids and evaluate their potential as energetic materials.

2. Result and Discussion

2.1. Synthesis

All the starting materials were commercially available except 1-chloro-2,4,6-trinitrobenzene **2f**, which was synthesized from picric acid and phosphorus oxychloride by a modified literature procedure.⁹

Pyridinium ylids **3a-u** were prepared in 82–99% yields by reaction of 1-aminopyridinium iodide **1** with

nitroaryl/nitroheteroaryl halides **2a-u** in either acetonitrile or ethanol in the presence of potassium carbonate or triethylamine (Scheme 1 and Table 1).⁸

Scheme 1

In most of the reactions in Table 1, halogen was displaced from the aromatic/heteroaromatic rings by a conventional S_NAr mechanism with the more reactive substrates containing two or three nitro groups (**2c**, **2d**, and **2f**) reacting much faster than **2a** or **2b**. The same was true in the pyridine series. In the case of **2q** and **2r** however, a 4- NO_2 group rather than Cl was displaced to generate **3q** and **3r** respectively presumably due to activation by heterocyclic nitrogen. This observation prompted us to investigate the use of **2e** as starting material. Reaction under reflux in acetonitrile for 5 h or at room temperature for 24h gave **3e** in 88–92% yield. The ^1H nmr and TLC of *crude* **3l** suggested the presence of a regioselective isomer (6-chloro-3-nitropyridin-2-yl)(pyridin-1-ium-1-yl)amide **3l'** in about 10% yield (Figure 1). The isolated material was assumed to be **3l** formed as the

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predominant isomer presumably due to a lower degree of steric hindrance at the 6-position of 2,6-dichloro-3-nitropyridine **2l**.

Table 1. Peptidyl and peptidomimetic P₁-argininal derivatives **2a-t** produced via Scheme 1

Entry	Time (h)	2	3^{a,b}	Mp (°C)	Yield %
1	18	a	a	151-153	99
2	15	b	b	196-197	99
3	3	c	c	251-253	95
4	3	d	d	160-162	98
5	5	e	e	189-191	92
6	3	f	f	238-239	98
7	8	g	g	237-239	95
8	7	h	h	219-221	90
9	6	i	i	266-268	90
10	4	j	j	233-235	94
11	3	k	k	273-275	85
12	4	l	l	251-253	82
13	4	m	m	175-177	95
14	10	n	n	189-191	90
15	8	o	o	226-228	88
16	4	p	p	227-229	90

17	10			186–187	95
18 ^c	4			197–199	98
19 ^c	3			391–392	99
20	3			195–197	99
21	24			212–214	95

^aSolvent: **3a–t**, MeCN; **3u**, EtOH.

^bTemperature: **3a–d**, **3f–u**, 23 °C; **3e**, 82 °C.

^cOnly mono-substituted products isolated even after heating under reflux

Figure 1. Regioisomers **3l** and **3l'**.

Triethylamine (4.5 molar excess over **2m** and **2n**) was also employed as a base at room temperature to give **3m** and **3n**, in 68% and 72% yields respectively, both lower than with the potassium carbonate method.

Figure 2. X-ray crystallography of **3f**, **3i** and **3u**.

The structures of ylids **3f**, **3i** and **3u** were unambiguously confirmed by X-ray crystallography (Figure 2). Crystals of **3u** contain two molecules in the asymmetric unit. In the structures of **3f** and **3i** the two rings are inclined at angles of 118.5 and 113.9°, respectively, whilst the values for **3u** are 71.1 and 101.2°, for the two independent cations.

2.2. Properties

Table 2 shows the heats of formation (ΔH_f) and densities of the pyridinium ylids as calculated by PM6. The table also reports the experimental densities of a selection of these compounds as determined by gas pycnometry together with the corresponding values of the detonation pressures (P_D), detonation velocities (V_D) and specific impulses (I_{SP}) calculated by the “Explo 5” program.

Examination of the data in Tables 3a and 3b indicates that in general, introduction of nitro groups, especially *ortho* to the ylid moiety, increases the calculated heats of formation (HOF). The calculated and experimental (by pycnometer) densities of the compounds also increase with the number of nitro groups present and there is a fair linear correlation between $\rho_{(calcd)}$ and $\rho_{(exp)}$ for the compounds of Table 3a. X-ray data on **3c**, **3f** and **3i** substantiate the pycnometer density values. Comparison of the data in Tables 3b and 3c shows that chlorine substituents in the heteroaromatic rings depress the calculated HOF values. The compounds in Table 3d (sans nitro groups) show high HOF value and densities (especially **3s**) but poor detonation parameters. In fact, none of these compounds give calculated detonation parameters close to those of commercial materials such as cyclotrimethylenetrinitramine (RDX)¹⁰ and therefore are unlikely to be useful as explosive materials.

Table 2. Heats of formation, densities and detonation parameters and specific impulses for pyridinium ylids

3a) Compounds of general formula:

Compound, ylid position in Py	Positions of (NO ₂) _n in Py	$\Delta H_{f(\text{calc})}^{\dagger}$ (kJ mol ⁻¹)	ρ			$P_{D(\text{calc})}$ (GPa)	$V_{D(\text{calc})}$ (m/s)	$I_{sp(\text{calc})}$ (s)
			calc	exp	X-ray			
3g , 2	3	408	1.124	1.49	–	12.42	6168	192.6
3h , 2	5	357	1.136	1.50	–	12.17	6135	187.2
3i , 2	3,5	356	1.259	1.56	1.598	15.45	6630	204.4
3m , 3	2	447	1.253	1.68	–	17.51	7150	196.7
3n , 3	6	412	1.275	1.44	–	11.38	5953	193.0
3o , 4	3	487	1.122	1.63	–	16.43	6849	200.9

[†] Determined by PM6

3b) Compounds of general formula:

Compound, ylid position in Py	Positions of (NO ₂) _n in Py	$\Delta H_{f(\text{calc})}^{\dagger}$ (kJ mol ⁻¹)	ρ			$P_{D(\text{calc})}$ (GPa)	$V_{D(\text{calc})}$ (m/s)	$I_{sp(\text{calc})}$ (s)
			calc	exp	X-ray			
3g , 2	3	408	1.124	1.49	–	12.42	6168	192.6
3h , 2	5	357	1.136	1.50	–	12.17	6135	187.2
3i , 2	3,5	356	1.259	1.56	1.598	15.45	6630	204.4
3m , 3	2	447	1.253	1.68	–	17.51	7150	196.7
3n , 3	6	412	1.275	1.44	–	11.38	5953	193.0
3o , 4	3	487	1.122	1.63	–	16.43	6849	200.9

[†] Determined by PM6

3c) Compounds of general formula:

Compound, ylid position in Py	Positions of Cl/NO ₂	$\Delta H_{f(\text{calc})}^{\dagger}$ (kJ mol ⁻¹)	ρ		$P_{D(\text{calc})}$ (GPa)	$V_{D(\text{calc})}$ (m/s)	$I_{sp(\text{calc})}$ (s)
			calc	exp			
3j , 2	3/5	372	1.210	1.548	11.21	5728	184.3
3k , 2	5/3	352	1.218	1.574	11.42	5778	182.3
3l , 2	6/5	336	1.209	1.545	10.78	5638	180.7
3p , 4	2/3	363	1.202	1.490	10.07	5478	183.4
3q , 4	2/–	357	1.077	–	–	–	–
3r , 4	2,6/–	331	1.265	–	–	–	–

[†] Determined by PM63d) Without NO₂ groups

Compound	Structure	$\Delta H_{f(\text{calc})}^{\dagger}$ (kJ mol ⁻¹)	ρ		$P_{D(\text{calc})}$ (GPa)	$V_{D(\text{calc})}$ (m/s)	$I_{sp(\text{calc})}$ (s)
			calc	exp			
3s		418	1.312	1.980	17.68	6720	170.7
3t		662	0.740	1.668	14.87	6449	193.2
3u		438	1.312	–	–	–	–

[†] Determined PM6

1. Experimental Section

Caution: in view of the potential explosive nature of the synthesized compounds, reactions were restricted to the millimolar scale and precautions were taken to avoid shock and friction in handling these materials.

1.1. General

Melting points were determined on a capillary tube melting point apparatus equipped with a digital thermometer and are uncorrected. NMR spectra were recorded in DMSO- d_6 and chemical shifts are reported with TMS or the residual solvent peak as the internal standard for ^1H (300 MHz) or in DMSO- d_6 with the residual solvent peak as internal standard for ^{13}C (75 MHz), unless otherwise specified. The multiplicity of individual peaks was reported s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet with coupling constants in Hertz (Hz). Elemental analyses were performed on a Carlo Erba EA 1108 elemental analyzer, Dept. of Chem., University of Florida. All reactions were carried out under a nitrogen atmosphere. All reagents were purchased from commercial sources and used without treatment unless otherwise indicated. Column chromatography was performed with S733-1 silica gel (200–425 mesh). Combustion analysis was performed using a Parr Oxygen

Densities were determined at room temperature by employing a Micromeritics AccuPyc 1330 gas pycnometer. The mass of the samples were determined on a METTLER TOLEDO AB104-S balance, and the volumes of the samples were measured by using the pycnometer - an average of 3 measured volumes was used to calculate the density. Sample density was calculated from the ratio of *mass* (m) to *volume* (V). ($d(\text{g}/\text{cm}^3) = m(\text{g})/V(\text{cm}^3)$).

The detonation velocity (V_D), detonation pressure (P_D) and specific impulse (I_{sp}) were calculated based on the experimental density and calculated heat of formation values using Explo 5 v.6.01.

1.2. Calculation of heats of formation and densities

The compounds were drawn in ChemDraw followed by 2D to 3D conversion using MM2¹² minimization in Chem3D.¹³ The 3D geometries were parameterized using PM6¹⁴ for further semi-empirical calculation. Geometry optimization followed by frequency calculation was performed using AMPAC software.¹⁵ The geometries were optimized to their energy minima using Trust algorithm which reduces the number of cycles and refines the precision of the calculation at each step. The optimized geometries were loaded to Codessa III¹⁶ software for the calculation of dipole moments, van der Waal's volume and densities.

1.3. General procedure for the preparation of nitroaryl/nitroheterocyclic (pyridin-1-ium-1-yl)amide **3a-u**

Potassium carbonate (9.0 mmol) for **3a-t** or triethylamine (9.0 mmol) for **3u** was added to a solution of 1-aminopyridinium iodide **1** (3.0 mmol) in acetonitrile (25 mL) for **3a-t** or EtOH (25 mL) for **3u**. The reaction mixtures were stirred vigorously for 10–20 min at room temperature to give a dark purple solution, to which electrophiles **2a-u** (3.0 mmol) were added in one portion. The mixtures were stirred at rt for 3–24 h except for **3e**, which was heated under reflux for 5 h. Mixtures **3a-t** were filtered to remove inorganic salts, which were washed with acetonitrile 3–5 times. The combined filtrates were concentrated in vacuo and the residues were purified either by gradient elution chromatography over silica gel and/or by recrystallization.

(2-Nitrophenyl)(pyridin-1-ium-1-yl)amide (**3a**) Catalyst: K_2CO_3 , 18 h, rt; column eluted with acetone and the product was recrystallized from acetone/hexanes. Yield 99%, red microcrystals, mp 151–153 °C [lit.⁸, mp 151–153 °C]; ^1H NMR (300 MHz, DMSO- d_6): δ 8.71 (d, J = 5.7 Hz, 2H), 8.14 (t, J = 7.7 Hz, 1H), 7.91 (t, J = 7.2 Hz, 2H), 7.85 (dd, J = 8.4, 1.2 Hz, 1H), 7.05 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 6.23 (t, J = 7.5 Hz, 1H), 6.04 (d, J = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 154.2, 142.9, 137.6, 134.5, 131.0, 128.6, 127.0, 112.4, 110.9.

(4-Nitrophenyl)(pyridin-1-ium-1-yl)amide (**3b**) Catalyst: K_2CO_3 , 15 h, rt; column eluted with acetone and the product was recrystallized from acetone/hexanes. Yield 99%, dark red microcrystals, mp 196–197 °C [lit.⁸, mp 197–197 °C]; ^1H NMR (300 MHz, DMSO- d_6): δ 8.79 (d, J = 5.7 Hz, 2H), 8.27 (t, J = 7.7 Hz, 1H), 7.99 (t, J = 7.1 Hz, 2H), 7.79 (d, J = 9.3 Hz, 2H), 6.04 (d, J = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 163.5, 143.3, 139.3, 131.4, 128.8, 127.4, 108.9.

(2,4-Dinitrophenyl)(pyridin-1-ium-1-yl)amide (**3c**) Catalyst: K_2CO_3 , 3 h, rt; column eluted with acetone and the product was recrystallized from acetone/hexanes. Yield 95%, orange needles, mp 251–253 °C [lit.⁸, mp 251–253 °C]; 1H NMR (300 MHz, DMSO- d_6): δ 8.86 (d, J = 6.0 Hz, 2H), 8.70 (d, J = 2.7 Hz, 1H), 8.40 (t, J = 7.7 Hz, 1H), 8.10 (t, J = 7.1 Hz, 2H), 7.79 (dd, J = 9.6, 2.7 Hz, 1H), 5.90 (d, J = 9.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 156.6, 143.0, 141.0, 130.6, 130.2, 129.3, 128.6, 124.8, 111.2.

(2,6-Dinitrophenyl)(pyridin-1-ium-1-yl)amide (**3d**) Catalyst: K_2CO_3 , 3 h, rt; inorganic salts were filtered off and the filtrate was concentrated and the product was recrystallized from MeCN/EtOH (1/1, v/v). Yield 98%, red solids, mp 160–162 °C; 1H NMR (300 MHz, DMSO- d_6): δ 8.59 (dd, J = 6.0, 0.6 Hz, 2H), 7.93 (t, J = 7.7 Hz, 1H), 7.86 (dd, J = 8.1, 0.6 Hz, 2H), 7.76 (t, J = 7.2 Hz, 2H), 6.50 (t, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 143.6, 139.2, 138.3, 136.0, 129.9, 127.9, 111.1. Anal. Calcd. for $C_{11}H_8N_4O_4$: C, 50.77; H, 3.10; N, 21.53. Found: C, 51.15; H, 2.74; N, 21.17.

(3,5-Dinitrophenyl)(pyridin-1-ium-1-yl)amide (**3e**) Catalyst: K_2CO_3 , 5 h, 82 °C; column eluted with AcOEt/hexanes (1/4–1/1, v/v) first and then acetone, and the product was recrystallized from acetone/hexanes. Yield 92%, dark red brown solids, mp 189–191 °C; 1H NMR (300 MHz, DMSO- d_6): δ 9.02 (d, J = 6.6 Hz, 2H), 8.46 (t, J = 7.1 Hz, 1H), 8.14 (t, J = 6.9 Hz, 2H), 7.92 (d, J = 2.1 Hz, 1H), 7.49 (d, J = 2.1 Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 154.1, 149.3, 144.5, 142.1, 129.4, 111.0, 104.2. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{11}H_8N_4O_4$ 261.0618; Found, 261.0626.

Pyridin-1-ium-1-yl(2,4,6-trinitrophenyl)amide (**3f**) Catalyst: K_2CO_3 , 3 h, rt. The mixture was filtered, the cake washed with MeCN 3 times, filtrates concentrated to dryness and the residue was recrystallized from acetone/hexanes. Yield 98%, coral red crystals, mp 238–239 °C [lit.¹⁷, mp 239.0 °C]; 1H NMR (300 MHz, DMSO- d_6): δ 8.88 (dd, J = 5.7, 0.6 Hz, 2H), 8.62 (d, J = 0.9 Hz, 2H), 8.25 (td, J = 7.8, 0.6 Hz, 1H), 7.98 (t, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 147.0, 140.4, 139.8, 136.8, 128.6, 125.7.

(3-Nitropyridin-2-yl)(pyridin-1-ium-1-yl)amide (**3g**) Catalyst: K_2CO_3 , 8 h, rt; The mixture was filtered, filtrate was concentrated to dryness and the residue was recrystallized from MeCN. Yield 95%, dark red solids, mp 237–239 °C [lit.^{7a}, mp 257–258 °C]; 1H NMR (300 MHz, DMSO- d_6): δ 8.70 (d, J = 6.3 Hz, 2H), 8.19 (td, J = 7.8, 1.2 Hz, 1H), 8.25 (dd, J = 8.0, 1.7 Hz, 1H), 7.95–7.88 (m, 3H), 6.40 (dd, J = 8.1, 4.5 Hz, 1H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 158.2, 154.0, 143.9, 138.7, 135.1, 127.4, 127.0, 107.5.

(5-Nitropyridin-2-yl)(pyridin-1-ium-1-yl)amide (**3h**) Catalyst: K_2CO_3 , 7 h, rt; column eluted with acetone and the product was recrystallized from acetone/hexanes. Yield 90%, yellow fibrous solids, mp 219–221 °C [lit.^{7a}, mp 220–222 °C]; 1H NMR (300 MHz, DMSO- d_6): δ 8.78 (dd, J = 6.2, 0.9 Hz, 2H), 8.58 (d, J = 2.7 Hz, 1H), 8.25 (t, J = 7.8 Hz, 1H), 7.95 (t, J = 7.1 Hz, 2H), 7.86 (dd, J = 9.5, 2.9 Hz, 1H), 6.30 (d, J = 9.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 165.7, 148.1, 143.5, 139.6, 131.4, 130.6, 127.5, 109.5.

(3,5-Dinitropyridin-2-yl)(pyridin-1-ium-1-yl)amide (**3i**) Catalyst: K_2CO_3 , 6 h, rt; column eluted with a mixture of MeCN and MeOH and the product was recrystallized from MeCN. Yield 90%, yellow solids, mp 266–268 °C; 1H NMR (300 MHz, DMSO- d_6): δ 8.81 (dd, J = 6.9, 1.2 Hz, 2H), 8.75 (d, J = 2.7 Hz, 1H), 8.72 (d, J = 2.7 Hz, 1H), 8.36 (t, J = 7.8 Hz, 1H), 8.05 (t, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 158.1, 149.9, 143.2, 141.0, 130.0, 129.7, 127.9, 127.3. Anal. Calcd. for $C_{10}H_7N_5O_4$: C, 45.98; H, 2.70; N, 26.81. Found: C, 46.21; H, 2.37; N, 26.51.

(3-Chloro-5-nitropyridin-2-yl)(pyridin-1-ium-1-yl)amide (**3j**) Catalyst: K_2CO_3 , 4 h, rt; The mixture was filtered, filtrate was concentrated to dryness and the residue was recrystallized from MeCN. Yield 94%, orange needles, mp 233–235 °C; 1H NMR (300 MHz, DMSO- d_6): δ 8.78 (d, J = 5.7 Hz, 2H), 8.52 (d, J = 2.7 Hz, 1H), 8.31 (t, J = 7.8 Hz, 1H), 8.06 (d, J = 2.4 Hz, 1H), 8.00 (t, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 162.1, 145.6, 143.5, 140.3, 131.2, 129.7, 127.7, 113.7. Anal. Calcd. for $C_{10}H_7ClN_4O_2$: C, 47.92; H, 2.81; N, 22.35. Found: C, 48.13; H, 2.51; N, 22.15.

(5-Chloro-3-nitropyridin-2-yl)(pyridin-1-ium-1-yl)amide (**3k**) Catalyst: K_2CO_3 , 3 h, rt; column eluted with MeCN + EtOH (1/1, v/v) and the product was recrystallized from MeCN. Yield 85%, coral solids, mp 273–275 °C (dec); 1H NMR (499 MHz, DMSO- d_6 at 75 °C): δ 8.70 (d, J = 6.0 Hz, 2H), 8.19 (t, J = 7.7 Hz, 1H), 8.12 (d, J = 2.0 Hz, 1H), 7.93–7.87 (m, 3H); ^{13}C NMR (126 MHz, DMSO- d_6 , at 75 °C): 156.1, 151.1, 143.3, 138.4, 133.0, 127.0, 111.1. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{10}H_8ClN_4O_2$ 251.0330; Found, 251.0342.

(6-Chloro-5-nitropyridin-2-yl)(pyridin-1-ium-1-yl)amide (**3l**) Catalyst: K_2CO_3 , 4 h, rt; column eluted with AcOEt/hexanes and the product was recrystallized from either acetone or MeCN. Yield 82%, yellow microcrystals, mp

251–253 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.75 (d, *J* = 5.7 Hz, 2H), 8.27 (t, *J* = 7.7 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.98 (t, *J* = 7.1 Hz, 2H), 6.25 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 157.4, 153.3, 143.7, 139.7, 138.5, 127.6, 126.1, 106.3. Anal. Calcd. for C₁₀H₇ClN₄O₂: C, 47.92; H, 2.81; N, 22.35. Found: C, 48.00; H, 2.51; N, 22.04.

(2-Nitropyridin-3-yl)(pyridin-1-ium-1-yl)amide (**3m**) Catalyst: K₂CO₃, 4 h, rt; column eluted with AcOEt/hexanes and the product was recrystallized from acetone/hexanes. Yield 95%; dark red solids, mp 175–177 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.75 (d, *J* = 5.7 Hz, 2H), 8.12 (t, *J* = 7.7 Hz, 1H), 7.89 (t, *J* = 6.6 Hz, 2H), 7.31–7.28 (m, 1H), 7.10 (dd, *J* = 8.6, 4.1 Hz, 1H), 6.68 (dd, *J* = 8.6, 1.4 Hz, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 147.1, 143.5, 142.5, 137.4, 129.5, 128.6, 119.3. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₀H₉N₄O₂ 217.0720; Found, 217.0722.

(6-Nitropyridin-3-yl)(pyridin-1-ium-1-yl)amide (**3n**) Catalyst: K₂CO₃, 10 h, rt, yield 90%, red solid, mp 189–191 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.85 (d, *J* = 6.0 Hz, 2H), 8.28 (t, *J* = 7.7 Hz, 1H), 8.02 (t, *J* = 6.6 Hz, 2H), 7.87 (d, *J* = 9.3 Hz, 1H), 7.53 (d, *J* = 3.0 Hz, 1H), 6.21 (dd, *J* = 9.2, 2.9 Hz, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 158.3, 143.0, 142.2, 139.6, 133.9, 128.9, 122.3, 111.0. Anal. Calcd. for C₁₀H₈N₄O₂: C, 55.56; H, 3.73; N, 25.91. Found: C, 55.49; H, 3.44; N, 25.54.

(3-Nitropyridin-4-yl)(pyridin-1-ium-1-yl)amide (**3o**) Catalyst: K₂CO₃, 8 h, rt; column eluted with a mixture of MeCN and MeOH and the product was recrystallized from MeCN. Yield 88%, orange prisms, mp 226–228 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.80 (d, *J* = 6.3 Hz, 2H), 8.75 (s, 1H), 8.35 (td, *J* = 7.6, 0.8 Hz, 1H), 8.05 (t, *J* = 7.1 Hz, 2H), 7.69 (d, *J* = 6.3 Hz, 1H), 5.69 (d, *J* = 6.3 Hz, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 155.8, 146.2, 145.1, 142.9, 141.1, 129.9, 129.2, 106.2. Anal. Calcd. for C₁₀H₈N₄O₂: C, 55.56; H, 3.73; N, 25.91. Found: C, 55.26; H, 3.44; N, 25.78.

(2-Chloro-3-nitropyridin-4-yl)(pyridin-1-ium-1-yl)amide (**3p**) Catalyst: K₂CO₃, 4 h, rt; the mixture was filtered, the filtrate concentrated in vacuo to give the crude, which was recrystallized from MeCN. Yield 90%, yellow microcrystals, mp 227–229 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.78 (dd, *J* = 6.9, 1.2 Hz, 2H), 8.31 (tt, *J* = 7.8, 1.2 Hz, 1H), 8.0 (t, *J* = 6.9 Hz, 2H), 7.53 (d, *J* = 6.3 Hz, 1H), 5.84 (d, *J* = 6.0 Hz, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 155.6, 148.5, 143.6, 140.3, 140.1, 131.5, 128.9, 103.6. Anal. Calcd. for C₁₀H₇ClN₄O₂: C, 47.92; H, 2.81; N, 22.35. Found: C, 47.69; H, 2.42; N, 22.38.

(2-Chloropyridin-4-yl)(pyridin-1-ium-1-yl)amide (**3q**) Catalyst: K₂CO₃, 10 h, rt; the mixture was filtered, filtrate concentrated in vacuo and residue recrystallized from acetonitrile. Yield 95%, yellow-brown solid, mp 186–187 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.72 (dd, *J* = 6.6, 0.6 Hz, 2H), 8.18 (td, *J* = 7.7, 1.0 Hz, 1H), 7.92 (t, *J* = 6.9 Hz, 2H), 7.52 (d, *J* = 6.0 Hz, 1H), 5.99 (dd, *J* = 6.0, 2.1 Hz, 1H), 5.75 (d, *J* = 2.1 Hz, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 163.6, 151.5, 148.3, 143.4, 138.3, 128.6, 105.8, 101.3. Anal. Calcd. for C₁₀H₈ClN₃: C, 58.41; H, 3.92; N, 20.43. Found: C, 58.49; H, 3.69; N, 20.19.

(2,6-Dichloropyridin-4-yl)(pyridin-1-ium-1-yl)amide (**3r**) Catalyst: K₂CO₃, 4 h, rt; the mixture was filtered, filtrate concentrated in vacuo, the product was purified by column chromatography eluted with acetonitrile/methanol (10/1, v/v). The product was recrystallized from acetonitrile. Yield 98%, yellow solids, mp 197–199 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.74 (dd, *J* = 5.7, 1.2 Hz, 2H), 8.26 (tt, *J* = 7.7, 1.2 Hz, 1H), 7.97 (t, *J* = 7.1 Hz, 2H), 5.83 (s, 2H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 164.9, 149.3, 143.4, 139.5, 128.8, 102.3. Anal. Calcd. for C₁₀H₇Cl₂N₃: C, 50.03; H, 2.94; N, 17.50. Found: C, 50.15; H, 2.64; N, 17.28.

(4,6-Dichloro-1,3,5-triazin-2-yl)(pyridin-1-ium-1-yl)amide (**3s**) Catalyst: K₂CO₃, 3 h, rt; the mixture was filtered, washed with MeCN, the combined filtrates concentrated and the residue was purified by column chromatography eluted with MeOH/MeCN (1/10, v/v) and the residue was recrystallized from MeCN/hexanes. Yield 99%, colorless needles, mp 391–392 °C (dec); ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.78 (d, *J* = 6.0 Hz, 2H), 8.35 (t, *J* = 7.7 Hz, 1H), 8.03 (t, *J* = 6.9 Hz, 2H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 168.7, 168.0, 143.2, 141.1, 127.9. Anal. Calcd. for C₈H₅Cl₂N₅: C, 39.69; H, 2.08; N, 28.93. Found: C, 40.07; H, 2.14; N, 29.02.

(6-Chloro-1,2,4,5-tetrazin-3-yl)(pyridin-1-ium-1-yl)amide (**3t**) Catalyst: K₂CO₃, 3 h, rt; the mixture was filtered, the filtrate concentrated and the product was recrystallized from MeCN. Yield 99%, dark red solids, mp 195–197 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.90 (d, *J* = 6.9 Hz, 2H), 8.32 (td, *J* = 7.7, 1.4 Hz, 1H), 8.03 (t, *J* = 7.1 Hz, 2H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 165.7, 155.1, 143.4, 140.5, 128.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₇H₆ClN₆ 209.0337; Found, 209.0340.

(1-Methylpyridin-1-ium-2-yl)(pyridin-1-ium-1-yl)amide iodide (**3u**) Catalyst: Et₃N, 24 h, rt in EtOH; the mixture was concentrated and the residue was purified by column chromatography eluted with acetone and the product recrystallized from acetone/hexanes. Yield 95%, yellowish solids, mp 212–214 °C[lit.¹⁸, mp 215–216 °C]; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.87 (d, J = 5.7 Hz, 2H), 8.47 (t, J = 7.8 Hz, 1H), 8.15 (t, J = 7.2 Hz, 2H), 7.97 (d, J = 6.0 Hz, 1H), 7.49 (ddd, J = 9.0, 7.1, 1.8 Hz, 1H), 6.47 (td, J = 6.7, 1.0 Hz, 1H), 6.08 (d, J = 9.0 Hz, 1H), 3.68 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 159.9, 143.6, 141.9, 140.8, 140.7, 129.5, 108.3, 107.7. Anal. Calcd. for C₁₁H₁₂IN₃: C, 42.19; H, 3.86; N, 13.42. Found: C, 42.54; H, 3.73; N, 13.05.

INDEX	FREQUENCY	PPM	HEIGHT
1	2641.6	8.803	56.4
2	2635.9	8.784	59.6
3	2487.9	8.281	14.1
4	2480.1	8.265	32.7
5	2472.5	8.240	20.2
6	2405.0	8.015	39.0
7	2398.2	7.992	52.0
8	2390.9	7.968	31.4
9	2344.8	7.814	9.2
10	2341.4	7.803	80.5
11	2332.0	7.772	85.8
12	2328.6	7.760	10.8
13	1820.7	6.068	9.2
14	1817.3	6.056	79.9
15	1815.4	6.050	29.1
16	1808.0	6.025	80.0
17	1804.6	6.014	11.3
18	1001.4	3.337	138.6
19	751.9	2.506	50.9
20	750.2	2.500	69.7
21	748.4	2.494	54.7
22	-1.1	-0.004	51.8

3b

INDEX	FREQUENCY	PPM	HEIGHT
1	2580.694	8.604	15.2
2	2580.110	8.602	16.0
3	2574.706	8.584	15.8
4	2574.121	8.582	16.3
5	2384.979	7.951	3.5
6	2377.384	7.926	9.5
7	2369.643	7.900	6.5
8	2362.341	7.876	25.8
9	2361.756	7.874	33.9
10	2354.307	7.849	27.1
11	2353.723	7.847	34.8
12	2332.691	7.777	12.5
13	2326.119	7.755	15.6
14	2320.130	7.735	4.0
15	2318.378	7.729	8.8
16	1958.935	6.531	9.1
17	1950.902	6.504	17.0
18	1943.453	6.479	6.6
19	1942.868	6.477	8.5
20	1005.191	3.351	148.5
21	751.638	2.506	7.4
22	749.885	2.500	9.4
23	747.987	2.494	6.6

INDEX	FREQUENCY	PPM	HEIGHT
1	10830.270	143.593	5.4
2	10498.200	139.190	11.1
3	10427.761	138.256	30.3
4	10255.635	135.974	16.3
5	9789.635	129.928	33.9
6	9647.635	127.913	32.4
7	8580.792	111.116	16.6
8	3042.255	40.336	16.8
9	3021.070	40.055	49.2
10	3000.415	39.781	97.3
11	2979.230	39.500	112.1
12	2958.575	39.226	95.4
13	2937.391	38.945	47.5
14	2916.736	38.671	16.1

EAGER 200 Stripchart

Sample Ident. : 10 HZ-3 Filename : 290510
 Analysed : 11-20-14 10:20:10 Printed : 11-20-2014 15:32:31

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 32.2
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 11-20-14 10:20:10 Printed : 11-20-2014 15:32:32
 Sample Ident. : 10 HZ-3 Filename : 290510
 Sample Weight : 2.125 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	102	82	6900.1	95573	11.58	Nitrogen
2	FU	102	265	112	42347.6	643531	77.96	Carbon
3	RS	292	597	312	1381.7	86327	10.46	Hydrogen
							825432	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 32.2
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 11-20-14 10:20:10 Printed : 11-20-2014 15:32:32
 Sample Ident. : 10 HZ-3 Filename : 290510
 Sample Weight : 2.125 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	82	95573	21.171	.673338E+01	Nitrogen
2	112	643531	51.150	.100000E+01	Carbon
3	312	86327	2.737	.745458E+01	Hydrogen

INDEX	FREQUENCY	PPM	HEIGHT
1	2711.7	9.035	51.2
2	2705.3	9.013	42.1
3	2546.2	8.483	15.4
4	2538.6	8.458	23.2
5	2531.9	8.436	12.5
6	2449.2	8.160	39.0
7	2442.6	8.138	43.6
8	2435.3	8.114	20.9
9	2376.8	7.919	28.9
10	2374.7	7.912	32.6
11	2249.4	7.495	83.1
12	2247.5	7.488	62.3
13	1105.1	3.682	7.7
14	752.1	2.506	31.9
15	750.4	2.500	32.1

INDEX	FREQUENCY	PPM	HEIGHT
1	11627.4	154.064	7.8
2	11268.1	149.304	28.4
3	10908.8	144.543	44.1
4	10721.0	142.056	19.7
5	9765.2	129.391	40.8
6	8377.5	111.004	39.9
7	7866.2	104.229	15.8
8	3044.4	40.339	12.3
9	3023.7	40.065	37.5
10	3001.8	39.775	68.5
11	2981.1	39.500	84.1
12	2960.4	39.225	74.1
13	2939.6	38.951	35.1
14	2918.9	38.676	11.5

INDEX	FREQUENCY	PPM	HEIGHT
1	2666.429	8.889	14.4
2	2665.698	8.887	14.9
3	2660.586	8.870	14.9
4	2659.856	8.868	14.9
5	2586.536	8.623	2.9
6	2586.244	8.622	3.7
7	2585.514	8.620	61.8
8	2584.783	8.617	61.7
9	2482.983	8.278	3.3
10	2473.242	8.252	8.0
11	2474.511	8.250	8.1
12	2467.501	8.226	4.8
13	2399.877	8.001	11.1
14	2392.720	7.977	13.9
15	2385.563	7.953	9.0
16	1003.292	3.345	215.7
17	1002.562	3.342	222.9
18	983.720	3.280	2.9
19	751.638	2.506	13.7
20	749.885	2.500	18.7
21	748.425	2.495	14.6

INDEX	FREQUENCY	PPM	HEIGHT
1	11088.193	147.012	5.6
2	10589.824	140.405	13.6
3	10542.158	139.773	26.3
4	10319.719	136.824	9.6
5	9697.419	128.573	28.9
6	9477.099	125.652	25.6
7	3042.255	40.336	31.2
8	3021.600	40.062	88.2
9	3000.415	39.781	171.7
10	2979.230	39.500	197.0
11	2958.575	39.226	165.7
12	2937.391	38.945	81.8
13	2916.736	38.671	27.0

FREQUENCY	PPM	HEIGHT
12501.210	165.747	5.1
11167.106	148.059	18.5
10820.736	143.466	32.8
10527.858	139.583	17.2
9911.384	131.410	7.3
9851.538	130.616	17.7
9614.799	127.477	36.3
8258.450	109.494	9.2
3042.255	40.336	10.0
3021.070	40.055	28.3
3000.415	39.781	54.4
2979.230	39.500	63.5
2958.575	39.226	53.5
2937.391	38.945	27.0
2916.736	38.671	9.1

INDEX	FREQUENCY	PPM	HEIGHT
1	2647.879	8.828	15.3
2	2646.711	8.824	18.1
3	2641.015	8.805	18.3
4	2639.846	8.801	14.1
5	2624.657	8.750	14.7
6	2622.028	8.741	29.7
7	2618.376	8.729	27.0
8	2615.747	8.720	12.6
9	2514.823	8.384	4.8
10	2507.082	8.358	9.7
11	2500.509	8.336	4.4
12	2499.341	8.332	6.0
13	2420.325	8.069	12.4
14	2413.314	8.046	15.9
15	2405.865	8.021	9.3
16	1004.752	3.350	81.1
17	751.638	2.506	11.1
18	749.885	2.500	13.5
19	746.133	2.494	9.9

INDEX	FREQUENCY	PPM	HEIGHT
1	11924.458	158.100	3.1
2	11307.984	149.926	11.5
3	10797.963	143.164	20.2
4	10633.252	140.981	9.6
5	9808.639	130.047	10.7
6	9784.806	129.731	5.8
7	9649.224	127.934	23.3
8	9598.911	127.267	4.6
9	3784.248	50.173	-2.4
10	3042.255	40.336	11.7
11	3021.070	40.055	32.3
12	3000.415	39.781	64.6
13	2979.230	39.500	74.3
14	2958.046	39.219	62.2
15	2937.391	38.945	32.1
16	2916.206	38.664	11.3

EAGER 200 Stripchart

Sample Ident. : 12 HZ-6 Filename : 288112
 Analysed : 06-19-14 09:44:30 Printed : 06-19-2014 09:54:32

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-18.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 06-19-14 09:44:30 Printed : 06-19-2014 09:54:3
 Sample Ident. : 12 HZ-6 Filename : 288112
 Sample Weight : 2.103 Calc.method: using 'K. Factors'

No. (#)	Type (#)	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	102	82	8449.7	116831	15.17	Nitroge
2	FU	102	288	112	38255.1	571443	74.19	Carbon
3	TL	288	597	303	1463.0	81898	10.63	Hydroge
4	CR	509	549	511	5.5	88	0.01	
						770260	100.00	

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-18.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 06-19-14 09:44:30 Printed : 06-19-2014 09:54:3
 Sample Ident. : 12 HZ-6 Filename : 288112
 Sample Weight : 2.103 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	82	116831	26.505	.489120E+01	Nitrogen
2	112	571443	46.213	.100000E+01	Carbon
3	303	81898	2.366	.697747E+01	Hydrogen

INDEX	FREQUENCY	PPM	HEIGHT
1	1228.988	162.138	3.9
2	10978.562	145.559	13.9
3	10825.503	143.529	24.3
4	10578.702	140.257	13.5
5	9892.848	131.164	8.0
6	9784.806	129.731	14.3
7	9631.217	127.695	26.8
8	8577.280	113.722	6.4
9	3042.255	40.336	19.5
10	3021.070	40.055	51.5
11	3000.415	39.781	95.4
12	2979.230	39.500	108.2
13	2958.575	39.226	87.9
14	2937.391	38.945	43.7
15	2916.206	38.664	13.2

EAGER 200 Stripchart

Sample Ident. : 12 HZ-4 Filename : 287912
 Analysed : 06-16-14 10:04:03 Printed : 06-16-2014 10:14:04

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-3.2
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 06-16-14 10:04:03 Printed : 06-16-2014 10:14:05
 Sample Ident. : 12 HZ-4 Filename : 287912
 Sample Weight : 2.148 Calc.method: using 'K. Factors'

No. (#)	Type (#)	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	102	83	7192.2	99225	12.53	Nitrogen
2	FU	102	285	112	40400.4	604334	76.33	Carbon
3	RS	285	597	301	1659.5	88164	11.14	Hydrogen
						791722	100.00	

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-3.2
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 06-16-14 10:04:03 Printed : 06-16-2014 10:14:05
 Sample Ident. : 12 HZ-4 Filename : 287912
 Sample Weight : 2.148 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	83	99225	22.145	.609056E+01	Nitrogen
2	112	604334	48.133	.100000E+01	Carbon
3	301	88164	2.509	.685469E+01	Hydrogen

INDEX	FREQUENCY	PPM	HEIGHT
1	2628.016	8.761	31.5
2	2627.320	8.742	31.1
3	2488.825	8.297	7.9
4	2481.084	8.272	16.9
5	2473.343	8.246	10.9
6	2461.951	8.208	31.2
7	2453.625	8.180	30.8
8	2399.147	7.998	22.7
9	2392.136	7.975	29.1
10	2384.979	7.951	17.3
11	1880.064	6.268	32.1
12	1871.739	6.240	30.4
13	1000.809	3.337	72.9
14	751.638	2.506	34.4
15	749.885	2.500	44.4

INDEX	FREQUENCY	PPM	HEIGHT
1	11868.848	157.363	3.8
2	11564.848	153.332	6.5
3	10837.155	143.684	29.6
4	10539.510	139.738	14.6
5	10446.827	138.509	14.4
6	9627.510	127.646	31.3
7	9513.642	126.136	7.1
8	8019.593	106.327	16.2
9	3041.725	40.329	20.1
10	3021.070	40.055	57.0
11	2999.885	39.774	111.7
12	2979.230	39.500	127.4
13	2958.046	39.219	108.6
14	2937.391	38.945	53.6
15	2916.206	38.664	18.5

EAGER 200 Stripchart

Sample Ident. : 13 HZ-12 Filename : 288413
 Analysed : 07-24-14 09:47:54 Printed : 07-24-2014 09:57:55

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-7.7
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 07-24-14 09:47:54 Printed : 07-24-2014 09:57:55
 Sample Ident. : 13 HZ-12 Filename : 288413
 Sample Weight : 2.106 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	101	82	7134.2	97815	12.49	Nitroge
2	FU	101	288	112	40120.2	597768	76.34	Carbon
3	TL	288	597	303	1613.6	87398	11.16	Hydroge
4	CR	552	597	555	3.9	78	0.01	
783059							100.00	

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-7.7
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 07-24-14 09:47:54 Printed : 07-24-2014 09:57:55
 Sample Ident. : 13 HZ-12 Filename : 288413
 Sample Weight : 2.106 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	82	97815	22.044	.611122E+01	Nitrogen
2	112	597768	48.000	.100000E+01	Carbon
3	303	87398	2.513	.683957E+01	Hydrogen

FREQUENCY	PPM	HEIGHT
2656.643	8.857	62.9
2650.655	8.837	61.6
2492.768	8.310	14.5
2484.881	8.284	31.7
2477.286	8.259	18.9
2410.831	8.037	40.8
2404.258	8.015	57.5
2396.810	7.991	28.9
2364.970	7.884	42.2
2355.622	7.853	43.4
2261.416	7.539	43.1
2258.495	7.529	40.6
1869.402	6.232	24.9
1866.481	6.223	23.9
1860.201	6.202	24.0
1857.280	6.192	22.3
1005.775	3.353	31.9
749.885	2.500	21.2

EAGER 200 Stripchart

Sample Ident. : 21 HZ-29 Filename : 289421
 Analysed : 09-10-14 11:32:37 Printed : 09-10-2014 11:42:4

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 10.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 09-10-14 11:32:37 Printed : 09-10-2014 11:42:
 Sample Ident. : 21 HZ-29 Filename : 289421
 Sample Weight : 2.153 Calc.method: using 'K. Factors'

No. (#)	Type (#)	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	102	83	8185.8	114994	12.26	Nitrog
2	FU	102	292	112	45005.0	703180	74.96	Carbon
3	RS	292	598	311	2129.1	119928	12.78	Hydrog
							938102	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 10.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 09-10-14 11:32:37 Printed : 09-10-2014 11:42:
 Sample Ident. : 21 HZ-29 Filename : 289421
 Sample Weight : 2.153 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	83	114994	25.540	.611494E+01	Nitrogen
2	112	703180	55.485	.100000E+01	Carbon
3	311	119928	3.444	.586335E+01	Hydrogen

INDEX	FREQUENCY	PPM	HEIGHT
1	2643.206	8.812	22.0
2	2636.925	8.791	22.5
3	2623.488	8.746	31.4
4	2511.463	8.373	5.4
5	2504.453	8.349	11.5
6	2503.722	8.347	11.6
7	2496.858	8.324	6.8
8	2495.835	8.321	6.7
9	2421.201	8.072	16.1
10	2414.336	8.049	20.7
11	2407.034	8.025	11.9
12	2311.075	7.705	16.9
13	2304.795	7.684	17.0
14	1709.617	5.700	17.9
15	1703.337	5.679	17.2
16	1009.280	3.365	37.0
17	749.885	2.500	36.0

FREQUENCY	PPM	HEIGHT
11751.273	155.804	11.1
11030.465	146.247	16.6
10940.430	145.053	18.9
10776.778	142.883	45.9
10642.785	141.107	22.7
9799.106	129.921	9.8
9744.555	129.198	48.4
8011.119	106.215	21.4
3042.255	40.336	47.6
3021.070	40.055	143.4
3000.415	39.781	283.2
2979.230	39.500	331.0
2958.575	39.226	281.5
2937.391	38.945	143.1
2916.206	38.664	48.4

EAGER 200 Stripchart

Sample Ident. : 13 HZ-7 Filename : 288113
 Analysed : 06-19-14 09:54:33 Printed : 06-19-2014 16:10:25

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 5.7
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 06-19-14 09:54:33 Printed : 06-19-2014 16:10:2
 Sample Ident. : 13 HZ-7 Filename : 288113
 Sample Weight : 2.127 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	102	82	8414.7	114938	12.41	Nitroge
2	FU	102	234	111	45947.6	691106	74.60	Carbon
3	RS	234	285	238	2.6	40	0.00	
4	TL	285	597	303	2399.1	120345	12.99	Hydroge
5	CR	463	472	465	2.1	15	0.00	
							926443	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 5.7
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 06-19-14 09:54:33 Printed : 06-19-2014 16:10:2
 Sample Ident. : 13 HZ-7 Filename : 288113
 Sample Weight : 2.127 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	82	114938	25.781	.601287E+01	Nitrogen
2	111	691106	55.262	.100000E+01	Carbon
4	303	120345	3.438	.574270E+01	Hydrogen

8.730
8.728
8.707

8.204
8.200

8.178
8.175
8.152
8.149
7.942
7.919
7.896

7.534
7.514

6.006
5.999

5.986
5.979
5.753
5.746

3.351

2.500
2.495

EAGER 200 Stripchart

Sample Ident. : 13 HZ-17 Filename : 288913
 Analysed : 08-11-14 09:47:30 Printed : 08-11-2014 09:57:32

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 1.5
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 08-11-14 09:47:30 Printed : 08-11-2014 09:57:32
 Sample Ident. : 13 HZ-17 Filename : 288913
 Sample Weight : 2.165 Calc.method: using 'K. Factors'

No. (#)	Type	Start (#)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	101	83	6291.6	89953	9.35	Nitroge
2	FU	101	278	111	46789.0	742348	77.14	Carbon
3	TL	289	597	308	2516.0	129940	13.50	Hydroge
4	CR	509	531	511	4.0	43	0.00	
							962284	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 1.5
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 08-11-14 09:47:30 Printed : 08-11-2014 09:57:32
 Sample Ident. : 13 HZ-17 Filename : 288913
 Sample Weight : 2.165 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	83	89953	20.189	.825263E+01	Nitrogen
2	111	742348	58.494	.100000E+01	Carbon
3	308	129940	3.687	.571301E+01	Hydrogen

FREQUENCY	PPM	HEIGHT
2624.657	8.750	33.5
2621.443	8.739	13.1
2619.399	8.733	33.4
2618.230	8.729	33.8
2484.443	8.283	8.1
2483.275	8.279	6.8
2476.702	8.257	18.9
2469.107	8.232	11.7
2467.939	8.228	9.0
2398.124	7.995	22.6
2390.675	7.970	30.4
2383.957	7.948	19.2
1748.760	5.830	77.2
1010.157	3.368	103.8
751.638	2.506	12.2
749.885	2.500	17.7
748.133	2.494	14.7

FREQUENCY	PPM	HEIGHT
12438.716	164.918	4.4
11258.730	149.273	7.9
10819.148	143.445	18.9
10525.210	139.548	9.3
9714.897	128.805	21.3
7716.123	102.304	8.3
3042.255	40.336	6.9
3021.070	40.055	19.6
3000.415	39.781	38.6
2979.230	39.500	44.8
2958.575	39.226	38.5
2937.391	38.945	18.3
2916.736	38.671	6.3

EAGER 200 Stripchart

Sample Ident. : 13 HZ-5 Filename : 287913
 Analysed : 06-16-14 10:14:05 Printed : 06-16-2014 10:24:07

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): .3
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 06-16-14 10:14:05 Printed : 06-16-2014 10:24:08
 Sample Ident. : 13 HZ-5 Filename : 287913
 Sample Weight : 2.138 Calc.method: using 'K. Factors'

No. (#)	Type (#)	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	101	83	5459.5	77082	9.68	Nitrogen
2	FU	101	284	112	40867.3	626702	78.73	Carbon
3	RS	284	597	299	1779.7	92275	11.59	Hydrogen
							796059	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): .3
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 06-16-14 10:14:05 Printed : 06-16-2014 10:24:08
 Sample Ident. : 13 HZ-5 Filename : 287913
 Sample Weight : 2.138 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	83	77082	17.282	.813029E+01	Nitrogen
2	112	626702	50.149	.100000E+01	Carbon
3	299	92275	2.638	.679166E+01	Hydrogen

FREQUENCY	PPM	HEIGHT
2637.358	8.789	19.0
2631.370	8.769	19.4
2514.233	8.379	4.5
2506.784	8.354	9.7
2498.897	8.328	6.0
2416.522	8.053	12.4
2409.803	8.031	18.3
2402.646	8.007	9.8
1002.264	3.340	146.8
750.172	2.500	26.8
621.497	2.071	16.3

FREQUENCY	PPM	HEIGHT
12732.203	168.745	6.5
12679.242	168.043	6.4
10803.869	143.188	34.7
10648.161	141.124	17.8
9652.482	127.928	38.3
3042.864	40.328	43.3
3022.209	40.055	126.1
3001.025	39.774	240.1
2980.369	39.500	278.4
2959.185	39.219	237.5
2938.530	38.945	119.3
2917.345	38.665	40.6

EAGER 200 Stripchart

Sample Ident. : 32 HZ-1 Filename : 284432
 Analysed : 12-18-13 14:10:02 Printed : 12-18-2013 14:20:0

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-15.3
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-18-13 14:10:02 Printed : 12-18-2013 14:20:
 Sample Ident. : 32 HZ-1 Filename : 284432
 Sample Weight : 2.158 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	99	80	8805.6	118175	17.63	Nitrog
2	FU	99	275	110	33107.7	483105	72.07	Carbon
3	RS	275	598	290	1284.8	69080	10.30	Hydrog
							670360	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-15.3
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-18-13 14:10:02 Printed : 12-18-2013 14:20:
 Sample Ident. : 32 HZ-1 Filename : 284432
 Sample Weight : 2.158 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	80	118175	29.022	.408806E+01	Nitrogen
2	110	483105	40.070	.100000E+01	Carbon
3	290	69080	2.141	.699342E+01	Hydrogen

FREQUENCY	PPM	HEIGHT
2671.687	8.907	24.6
2664.822	8.884	26.7
2504.453	8.349	5.4
2503.138	8.345	6.2
2495.397	8.319	13.2
2488.971	8.298	7.9
2487.656	8.293	8.4
2415.213	8.052	16.3
2408.348	8.029	23.8
2401.191	8.005	11.9
1013.516	3.379	240.9
1012.201	3.375	327.8
993.944	3.314	3.7
992.630	3.309	3.8
751.346	2.505	10.7
749.885	2.500	11.2

FREQUENCY	PPM	HEIGHT
12500.151	165.733	7.3
11696.723	155.081	7.0
10819.148	143.445	62.1
10595.649	140.482	32.4
9669.879	128.208	70.4
3042.255	40.336	28.1
3021.070	40.055	80.1
2999.885	39.774	152.8
2979.230	39.500	181.3
2958.046	39.219	150.6
2937.391	38.945	77.1
2916.206	38.664	25.1

EAGER 200 Stripchart

Sample Ident. : 14 HZ-39 Filename : 291014
 Analysed : 12-17-14 11:27:17 Printed : 12-17-2014 12:34:54

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-13.2
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-17-14 11:27:17 Printed : 12-17-2014 12:34:5
 Sample Ident. : 14 HZ-39 Filename : 291014
 Sample Weight : 2.116 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	101	82	4194.3	60398	8.28	Nitroge
2	FU	101	290	113	35744.5	550632	75.45	Carbon
3	RS	290	597	312	2196.3	118791	16.28	Hydroge
							729822	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-13.2
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-17-14 11:27:17 Printed : 12-17-2014 12:34:5
 Sample Ident. : 14 HZ-39 Filename : 291014
 Sample Weight : 2.116 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	82	60398	13.047	.911666E+01	Nitrogen
2	113	550632	42.539	.100000E+01	Carbon
3	312	118791	3.727	.463529E+01	Hydrogen

Graphical Abstract

Synthesis of pyridinium *N*-aryl/*N*-heteroaryl cyclic ylids as potential energetic materials

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