Graphical Abstract

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ABSTRACT

Synthesis, characterization and energetic properties of novel, nitrogen-rich 1-methyl-1,2,4-triazolium *N*-aryl/*N*-pyridinyl ylids **3a-m** are reported.

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1. Introduction

Synthetic energetic materials are widely used in military applications and numerous current research programs aim to develop new explosives and propellants with higher performance or reduced sensitivity to thermal shock or impact. Over the last several decades, the synthesis of energetic, heterocyclic compounds has made a substantial contribution to this area.^{1,2,3}

Energetic heterocycles such as pyridines,^{4,5} triazoles⁶⁻⁹ and tetrazoles^{2,10-12} generally have higher heats of formation, density, and oxygen balance than their carbocyclic analogues. Thus, formulations containing compounds of this type are potentially useful as novel explosives.¹⁻³ and this prompted us to synthesize novel 1-methyl-1,2,4-triazolium *N*-aryl / *N*-pyridinyl ylids in order to evaluate their properties as energetic materials.

2. Results and Discussion

1-Methyl-4-*H*-1,2,4-triazol-4-ium ylids **3a-m** were prepared in 34–90% yields by treatment of 4-amino-1-methyl-1*H*-1,2,4-triazol-4-ium iodide **1** with nitrobenzenes **2a-c**, nitropyridines **2d-l** and a pyridinium salt, **2m** in acetonitrile or ethanol in the presence of triethylamine or potassium carbonate (Table 1, Scheme 1).

Scheme 1. Synthesis of triazolium *N*-aryl / *N*-pyridinyl ylids.

All of the starting materials were commercially available except 1-chloro-2,4,6-trinitrobenzene (**2c**) which was synthesized from picric acid **4** using a modified literature procedure.¹³ (Scheme 2).

Scheme 2. Synthesis of 1-chloro-2,4,6-trinitrobenzene.

Table 1. Preparation of aryl/pyridinyl(1-methyl-4-*H*-1,2,4-triazol-4-ium-4-yl)amide **3a-m**

Base	Solvent	2	3	Mp (°C)	Yield (%)
Et ₃ N	MeCN	2a	3a	221–223	54
Et ₃ N	MeCN	2b	3b	143–145	52
Et ₃ N	EtOH	2c	3c	220–222	62
Et ₃ N	MeCN	2d	3d	234–236	34
Et ₃ N	EtOH	2e	3e	202–203	45
K ₂ CO ₃	MeCN	2f	3f	173–175	48
Et ₃ N	EtOH	2g	3g	211–213	60
K ₂ CO ₃	MeCN	2h	3h	182–184	42
Et ₃ N	MeCN	2i	3i	197–199	44 ^[a]
Et ₃ N	MeCN	2j	3j	195–197	16 ^[a]
Et ₃ N	MeCN	2k	3k	227–229	56
Et ₃ N	MeCN	2l	3l	212–213	59
Et ₃ N	MeCN	2m	3m	190–192	80
Et ₃ N	MeCN	2n	3n	211–213	90

^a Two regioisomers isolated in the same reaction.

Products **3a-l** were obtained in moderate yields after 1–3 days stirring at ambient temperature but **3m** required heating in acetonitrile. Compounds **2a-g** have only one replaceable halogen and give rise to compounds **3a-g** all of which were characterized by elemental analysis, mass spectrometry, ¹H, and ¹³C nmr. Substrates **2h**, **2i**, **2j** and **2k**, all have two non-equivalent chlorines and regioselectivity was a potential issue. NMR revealed that in substrates with chlorine *ortho* and *meta* to the nitro group (**2h**) or *meta* and *para* to the nitro group (**2j**) only the *ortho* or *para* chlorines were displaced to give **3h** and **3j** respectively. Comparison of the ¹H, ¹³C and ¹⁵N nmr data of **3h** with **3d** and of **3j** with **3e** reveals a striking similarity which serves to reinforce the structures assigned to **3h** and **3j**. Replacement of the chlorine *ortho* to the nitro group in **2h** and *para* to the nitro group in **2j** is, of course, expected of a S_NAr mechanism.

In the case of **2k**, one might have expected the formation of two products since both halogens are activated by hetero-N and the nitro group but in fact only one isomer was obtained (**3k**) analogous to **3f**.

Assignments of the ¹H, ¹³C and ¹⁵N chemical shifts of **3d**, **e**, **h**, **i**, **j** and **k** based on cross peaks in the ¹H-¹³C gHMBC and ¹H-¹⁵N gHMBC spectra, are given in Fig. 1. The proton at 6.12 in **3k** is β to the pyridine nitrogen (based on its chemical shift and that of the carbon attached to it) and a cross peak in the ¹H-¹⁵N gHMBC spectrum between this proton and ylid N at 186.9 ppm indicates that it is *ortho* to the ylid nitrogen consistent with structure **3k**. Confirmation of this conclusion is provided by a nOe between the signal at 6.12 and the protons of the triazole ring at 9.09 and 9.96 ppm. An analogous nOe was not however, detected in **3e**. A possible explanation for this observation is that

the triazole ring is *anti* to the nitro group in **3k** but *syn* to the pyridine N in **3e** due to lone pair repulsion in **3e** (Fig. 2)

Figure 1. ¹H, ¹³C and ¹⁵N chemical shifts in **3d**, **e**, **h**, **i**, **j** and **k**.

The crystal structure of **3k** confirms the proposed structure and stereochemistry (Fig. 3). It exists in the solid state as a trihydrate involving a complex hydrogen bonded network with all six water hydrogens strongly interacting with nitrogen acceptors or other water oxygens. The conformation of the molecule is as shown in Fig. 3 with the planes of the two

heterocyclic rings inclined at an angle of 96.3°.

Figure 2. Proposed stereochemistry of compounds **3k** and **3e**.

Figure 3. X-ray crystal structure of **3k** (CCDC 1431437).

In the case of substrate **2i**, the ylid nucleophile could, in principle, displace chlorine either at position 6 or position 2 of the pyridine ring to give **3i** or **3i'** respectively. In fact both were observed and the structures of **3i** and **3i'** were assigned on the basis of their ¹H-¹⁵N gHMBC spectra. In the major isomer (75%) the ylid nitrogen at 204.4 couples with protons at 6.23 and 8.15 over three and four bonds respectively. In the minor isomer the ylid nitrogen at 208.4 couples only with the proton at 7.93, para to pyridine nitrogen. Unfortunately attempts to form suitable crystals for X-ray confirmation of the proposed structures were unsuccessful.

The reaction of 4-amino-1-methyl-4*H*-1,2,4-triazole-1-ium iodide **1** with 2,6-dichloro-4-nitropyridine **2l** gave ylid **3l** in 80%

yield, in which the nitro group was substituted, an observation that has analogies in the literature.¹⁴⁻¹⁷

Reaction with 2-chloro-1-methylpyridin-1-ium iodide **2m** gave rise to the expected novel iodide **3m** in 90% yield, the structure of which was confirmed by single crystal X-ray crystallography (Fig. 4). In this case the planes of the two rings are inclined at an angle of 98.8°.

Figure 4. X-ray crystal structure of **3m** (CCDC 1429988).

2.1. Properties

Table 2 shows the heats of decomposition (ΔH_d) of a selection of the triazolium ylids as determined by differential scanning calorimetry. As expected, the heats of decomposition increase with the number of nitro groups present in the compounds.

Table 3 reports the heats of formation (ΔH_f) as calculated by PM6 together with calculated and experimental values of the densities of **3a,b,c,e,f,g,k**, and **m**.

The experimental densities of the compounds were determined by gas pycnometry and these values, coupled with the ΔH_f values, were used to calculate the explosion parameters (Table 3) by the Explo 5 program. In parallel with the ΔH_d data, the ΔH_f values increase with the number of nitro groups in each type of molecule. Experimental densities also increase in line with the calculated values with one notable exception, - compound **3e**, which had an experimental density of 2.01, far in excess of the expected value based on PM6 calculations. Duplicate measurements on a second sample arrived at the same figure and gave rise to a set of explosion parameters close to those of RDX. There is no obvious explanation for this anomalous result. The HRMS and nmr data were exactly as expected and the only unusual feature of **3e** was its extremely dark red color. This suggests the compound may have adopted an unusual crystal form but unfortunately we were unable to obtain crystals suitable for X-ray analysis.

Table 2. Heats of decomposition (ΔH_d) of triazolium ylids

2a) Compounds of general formula:				
Compound	(NO ₂) _n	T _{exo} (°C)	ΔH_d (kJ/mol)	ΔH_d (J/g)
3a	2,4-di-NO ₂	229.2	-101	-384
3b	2,6-di-NO ₂	152.9	-67.4	-255
3c	2,4,6-tri-NO ₂	227.7	-173	-560
2b) Compounds of general formula:				
Compound	2-ylid, (NO ₂) _n	T _{exo} (°C)	ΔH_d (kJ/mol)	ΔH_d (J/g)
3e	5-NO ₂	203.2	-41.6	-189
3g	3,5-di-NO ₂	186.1	-86.7	-327
2c) Compounds of general formula:				
Compound	4-ylid, NO ₂	T _{exo} (°C)	ΔH_d (kJ/mol)	ΔH_d (J/g)
3f	3-NO ₂	220.5	-46.2	-210

Table 3. Calculated heats of formation (ΔH_f), densities (ρ_{calc}), experimental densities (ρ_{pyc}) and calculated detonation parameters (P_D , V_D and I_{sp})

3a) Compounds of general formula:

Compound (NO_2) _n	$\Delta H_f(\text{calc})^{[a]}$ (kJ mol ⁻¹)	ρ calc	P pyc	$P_{D(\text{calc})}$ (GPa)	$V_{D(\text{calc})}$ (m/s)	$I_{\text{sp}(\text{calc})}$ (s)
3a , 2,4-di- NO_2	397	1.246	1.56	17.02	6959	212.9
3b , 2,6-di- NO_2	423	1.231	1.56	17.25	6990	215.3
3c , 2,4,6-tri- NO_2	404	1.340	1.63	21.38	7460	225.3

^a Determined by PM6

3b) Compounds of general formula:

Compound, ylid position in Py_n	Positions of (NO_2) _n in Py	$\Delta H_f(\text{calc})^{[a]}$ (kJ mol ⁻¹)	ρ		$P_{D(\text{calc})}$ (GPa)	$V_{D(\text{calc})}$ (m/s)	$I_{\text{sp}(\text{calc})}$ (s)
			calc	exp			
3e , 2	5	438	1.178	2.01	34.83	9498	208.3
3f , 4	3	460	1.171	1.56	16.47	6986	205.7
3g , 2	3,5	437	1.268	1.64	20.44	7438	218.1

^a Determined by PM6

3c) Compounds of general formula:

Compound, ylid position in Py_n	Positions of Cl/NO_2	$\Delta H_f(\text{calc})^{[a]}$ (kJ mol ⁻¹)	ρ		$P_{D(\text{calc})}$ (GPa)	$V_{D(\text{calc})}$ (m/s)	$I_{\text{sp}(\text{calc})}$ (s)
			calc	exp			
3k , 2	3/5	424	1.271	1.68	16.53	6732	196.8
3m , 4	2,6-di-Cl	430	1.235	1.57	10.18	5411	173.6

3. Conclusions

In summary we have developed a practical synthesis of novel, nitrogen-rich 1-methyl-1,2,4-triazolium *N*-aryl/*N*-pyridinyl ylids **3a-n** from readily available precursors and evaluated their properties as potential energetic materials.

4. Experimental

General Methods and Materials. Melting points were determined on a capillary tube melting point apparatus equipped with a digital thermometer and are uncorrected. NMR spectra were recorded for most compounds on a Varian Mercury spectrometer operating at 300 MHz for ¹H. The ¹H and ¹³C chemical shifts are reported on the TMS scale and were referenced to the residual peak of the solvent (DMSO, 2.50 ppm for ¹H and 39.5 ppm for ¹³C). For compounds **3d**, **3e**, **3h**, **3i**, **3j**, **3k**, **3l** and **5** the spectra were recorded on a Varian Inova operating at 500 MHz for protons. The ¹⁵N chemical shifts are given on the ammonia scale, and were referenced with the frequency ratio, $\Xi = 10.1329120$. Elemental analyses were performed on a Carlo Erba EA 1108 elemental analyzer, Dept. of Chem., University of Florida. All reactions were carried out under nitrogen atmosphere. All reagents were purchased from commercial sources and used as received unless otherwise indicated. Column chromatography was performed with S733-1 silica gel (200–425 mesh). Heats of decomposition were determined using a DuPont Instruments DSC 2910 differential scanning calorimeter. Samples were heated from 100 °C–500 °C in hermetic aluminum pans, with helium as the purge gas. All sample pan lids were perforated to allow venting of gaseous products.

Densities were determined at room temperature by employing a Micromeritics AccuPyc 1330 gas pycnometer. The masses of the samples were determined on a METTLER TOLEDO AB104-S balance, and the volumes of the samples were measured 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 velocities (V_D), detonation pressures (P_D) and specific impulses (I_{sp}) were calculated based on the experimental densities and calculated heats of formation using Explo5 v.6.01 (OZN Research, Czechoslovakia).

Calculation of heats of formation and densities

The compounds were drawn in ChemDraw followed by 2D to 3D conversion using MM2¹⁹ minimization in Chem3D.²⁰ The 3D geometries were parameterized using PM6²¹ for further semi-empirical calculation. Geometry optimization followed by frequency calculation, was performed using AMPAC software.²² The geometries were optimized to their energy minima using Trust algorithm which reduces the number of cycles and refines the precision of the calculations at each step. The optimized geometries were loaded to Codessa III²³ software for the calculation of heats of formation, van der Waal's volume and densities.

X-Ray Crystallography

The X-ray single crystal diffraction data for **3k** (CCDC1431437) and **3m** (CCDC 1429988) were collected at 120 K on an Agilent SuperNova instrument with focussed microsource Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and ATLAS CCD area detector. The structures were solved using direct methods with SHELXS and refined on F^2 using all data by full-matrix least square procedures with SHELXL-97.²⁴ Multiscan absorption corrections were done using SCALE3 ABSPACK. The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms.

General procedure for the preparation of 1-methyl-1,2,4-triazolium *N*-aryl/*N*-pyridinyl ylids **3a-m.** Potassium carbonate or trimethylamine (9.0 mmol) was added to a solution of 4-amino-1-methyl-1*H*-1,2,4-triazol-4-ium iodide, **1** (3.0 mmol) in acetonitrile or ethanol (25 mL) and each reaction mixture was vigorously stirred at room temperature for 20 min to give a purple solution, to which nitrophenyl halides **2a-c** nitropyridinyl halides **2d-l** or pyridinium iodide **2m** (3.0 mmol) were added in

one portion. Each mixture was stirred at rt for 72 h except for **2l** (rt for 24 h) and **2m** (82 °C for 72 h). The mixtures were concentrated in vacuo and the residues purified either by gradient elution chromatography over silica gel or by recrystallization.

(2,4-Dinitrophenyl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3a). Base: Et₃N (3/1 molar ratio to **2a**), 72 h, rt, in MeCN; product recrystallized from acetone/hexanes. Yield 54%, golden solid, mp 221–223 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.06 (s, 1H), 9.19 (s, 1H), 8.62 (d, *J* = 2.7 Hz, 1H), 7.77 (dd, *J* = 9.9, 2.7 Hz, 1H), 6.32 (d, *J* = 9.9 Hz, 1H), 4.04 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 158.6, 143.2, 140.9, 131.2, 129.8, 127.9, 124.5, 112.1, 39.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₉H₉N₆O₄ 265.0680; Found, 265.0678.

(2,6-Dinitrophenyl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3b). Base: Et₃N (3/1 molar ratio to **2b**), 72 h, rt, in MeCN; residue purified by column chromatography, eluted first with AcOEt/hexanes and then AcOEt/acetone; product recrystallized from acetone/hexanes. Yield 52%, dark red solid, mp 143–145 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.03 (s, 1H), 9.12 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 6.25 (t, *J* = 8.1 Hz, 1H), 3.97 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 147.7, 141.4, 139.1, 138.2, 130.0, 108.0, 38.6. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₉H₉N₆O₄ 265.0680; Found, 265.0675.

(2,4,6-Trinitrophenyl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3c). Base: Et₃N (3/1 molar ratio to **2c**), 72 h, rt, in MeCN; residue purified by column chromatography, eluted first with AcOEt/hexanes and then acetone; product recrystallized from acetone/hexanes. Yield 62%, yellow solid, mp 220–222 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.24 (s, 1H), 9.31 (s, 1H), 8.58 (s, 2H), 4.02 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 149.3, 140.9, 139.4, 127.8, 38.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₉H₈N₇O₆ 310.0531; Found, 310.0542.

(3-Nitropyridin-2-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3d). Base: Et₃N (3/1 molar ratio to **2d**), 72 h, rt, in MeCN; purified by column chromatography, eluted first with AcOEt/hexanes and then acetone; product recrystallized from acetone/hexanes. Yield 34%, yellow solid, mp 234–236 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.62 (s, 1H), 9.51 (s, 1H), 8.67 (m, 1H), 8.49 (m, 1H), 7.29 (m, 1H), 4.20 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 154.7, 149.8, 146.7, 140.9, 135.4, 131.1, 118.7, 40.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₉N₆O₂ 221.0781; Found, 221.0790.

(5-Nitropyridin-2-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3e). Base: Et₃N (3/1 molar ratio to **2e**), 72 h, rt, in EtOH; purified by column chromatography, eluted with MeOH/MeCN and MeCN/MeOH; product recrystallized from MeCN/AcOEt. Yield 45%, dark brown solid, mp 202–203 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.21 (s, 1H), 9.64 (s, 1H), 9.09 (s, 1H), 7.77 (d, 1H), 6.24 (d, 1H), 4.01 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 165.7, 143.9, 148.5, 140.6, 131.3, 130.5, 110.1, 39.1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₉N₆O₂ 221.0781; Found, 221.0778.

(3-Nitropyridin-4-yl)(1-methyl-1H-1,2,4-triazol-4-ium-4-yl)amide (3f). Base: K₂CO₃ (3/1 molar ratio to **2f**), 72 h, rt, in MeCN; purified by column chromatography eluted with AcOEt/hexanes and MeCN/MeOH; product recrystallized from MeCN. Yield 48%, yellow solid, mp 173–175 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.98 (s, 1H), 9.11 (s, 1H), 8.68 (s, 1H), 7.68 (d, *J* = 6.3 Hz, 1H), 6.07 (d, *J* = 6.3 Hz, 1H), 4.03 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 157.9, 150.2, 148.2, 143.7, 141.1, 130.0, 106.7, 38.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₉N₆O₂ 221.0781; Found, 221.0782.

(3,5-Dinitropyridin-2-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3g). Base: Et₃N (3/1 molar ratio to **2g**), 72 h, rt, in EtOH; mixture cooled in fridge, precipitate filtered, washed with EtOH/AcOEt and dried. Yield 60%, orange solid, mp 211–213 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.23 (s, 1H), 9.26 (s, 1H), 8.80 (dd, *J* = 2.4, 0.6 Hz, 1H), 8.66 (d, *J* = 2.7 Hz, 1H), 4.06 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 157.6, 149.5, 143.5, 140.5, 129.4, 129.3, 128.3, 38.8. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₈N₇O₄ 266.0632; Found, 266.0643.

(5-Chloro-3-nitropyridin-2-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3h). Base: K₂CO₃ (3/1 molar ratio to **2h**), 72 h, rt, in MeCN; purified by column chromatography eluted with acetone/hexanes, then acetone; product recrystallized from MeCN/AcOEt. Yield 42%, red solid, mp 182–184 °C; NMR data in figure 1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₈ClN₆O₂ 255.0392; Found, 255.0404.

(6-Chloro-5-nitropyridin-2-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3i). Base: Et₃N (3/1 molar ratio to **2i**), 72 h, rt, in MeCN. The solution was cooled to 0 °C, the mixture of **3i** and **3i'** filtered off and the filter cake washed with cold AcOEt. The mixture was recrystallized twice from acetone/hexanes to give the first crop of pure **3i**. After evaporation of the mother liquor, the resultant mixture of orange and yellow crystals was separated by hand. Recrystallization of the separated crystals (from acetone/hexane) gave a second crop of **3i** and pure **3i'**. Yield of **3i**, 44%, yellow fibers, mp 195–197 °C (dec); NMR data in Figure 1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₈ClN₆O₂ 255.0392; Found, 255.0402.

(6-Chloro-3-nitropyridin-2-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3i'). Yield 16%, coral red prisms, mp 197–199 °C (dec); NMR data in Figure 1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₈ClN₆O₂ 255.0392; Found, 255.0403.

(3-Chloro-5-nitropyridin-2-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3j). Base: Et₃N (3/1 molar ratio to **2j**), 72 h, rt, in MeCN, mixture concentrated to dryness, residue washed with MeCN/AcOEt and recrystallized from acetone. Yield 56%, yellow solid, mp 227–229 °C; NMR data in figure 1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₈ClN₆O₂ 255.0392; Found, 255.0388.

(2-Chloro-3-nitropyridin-4-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3k). Base: Et₃N (3/1 molar ratio to **2k**), 72 h, rt, in MeCN; purified by column chromatography eluted with AcOEt/hexanes and acetone, then recrystallized from acetone/hexanes. Yield 59%, yellow solid, mp 212–213 °C; NMR data in figure 1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₈ClN₆O₂ 255.0392; Found, 255.0380.

(2,6-Dichloropyridin-4-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide (3l). Base: Et₃N (3/1 molar ratio to **4l**), 24 h, rt, in MeCN; purified by column chromatography eluted with hexanes/AcOEt and acetone/AcOEt, then recrystallized from acetone/hexanes. Yield 80%, colorless solid, mp 190–192 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.88 (s, 1H), 9.02 (s, 1H), 6.14 (d, *J* = 2.1 Hz, 1H), 5.69 (d, *J* = 1.5 Hz, 1H), 3.99 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 167.1, 149.0, 144.0, 141.3, 103.0–101.9 (m). HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₈Cl₂N₅ 244.0151; Found, 244.0143.

(1-Methylpyridin-1-ium-2-yl)(1-methyl-4H-1,2,4-triazol-1-ium-4-yl)amide iodide (3m). Base: Et₃N (3/1 molar ratio to **2m**), 72 h, 82 °C, in MeCN; mixture concentrated to dryness, residue washed with MeOH/MeCN and recrystallized from MeCN/AcOEt. Yield 90%, colorless prisms, mp 211–213 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.08 (s, 1H), 9.17 (s, 1H), 7.93 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.51 (ddd, *J* = 9.0, 6.9, 1.7 Hz, 1H),

6.52 (d, $J = 9.0$ Hz, 1H), 6.45 (td, $J = 6.8, 1.2$ Hz, 1H), 4.05 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 161.3, 143.3, 141.4, 140.6, 140.0, 109.4, 107.5, 39.9, 39.1. HRMS (ESI-TOF) m/z : $[\text{M} - \text{I}]^+$ Calcd for $\text{C}_9\text{H}_{12}\text{N}_5$ 190.1087; Found, 190.1082.

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