

Supplementary Information

Triazolium Salt Organocatalysis: Mechanistic Evaluation of Unusual *Ortho*-Substituent Effects on Deprotonation

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S1 – General Instrumentation

NMR samples were prepared in deuterated chloroform, deuterium oxide and d_6 -dimethyl sulfoxide (DMSO). NMR spectra were recorded on Oxford Varian Unity Inova 300 and 500 MHz, Varian Unity 300 MHz, Bruker Ultrashield 400 MHz, Bruker Avance 500 MHz, Bruker Avance 400 MHz and Bruker Avance 300 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts in CDCl_3 are reported relative to CDCl_3 at 7.27 ppm and 77.0 ppm respectively. In D_2O , ^1H NMR shifts are reported relative to HOD at 4.67 ppm. In d_6 -DMSO, ^1H NMR and ^{13}C NMR chemical shifts are reported relative to d_6 -DMSO at 2.50 ppm and 39.5 ppm respectively. Coupling constants (J) are reported in Hz. Multiplicities are indicated by br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet)

Mass spectrometric (m/z) data were acquired by electrospray ionisation (ESI). Low resolution ESI MS was carried out on a Waters Micromass ZQ4000 spectrometer and low resolution EI and CI MS was carried out on a Micromass Quattro II spectrometer. High resolution ESI and ESI MS was carried out on a Finnigan MAT 900 XLT or a Finnigan MAT 95 XP; a Thermofisher LTQ Orbitrap XL spectrometer was also used to obtain high resolution ESI MS for accurate mass determination but also provided fragmentation data for the characterisation of samples. Values are quoted as a ratio of mass to charge in Daltons.

Infrared spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer as KBr discs or thin films between NaCl plates

Melting points were determined using an electrothermal 9100 melting point apparatus and are uncorrected.

Analytical thin layer chromatography (tlc) was carried out on pre-coated 0.20 mm Machery-Nagel Polygram SIL G/UV₂₅₄ silica plates. Visualisation was carried out by absorption of ultraviolet light or thermal decomposition after dipping in either an ethanolic solution of phosphomolybdic acid or an aqueous solution of potassium permanganate/sodium hydroxide.

Chromatography was performed using Merck Ltd. Silica gel 40-63 μm , eluting with solvents under a positive pressure of compressed air.

Anhydrous solvents were obtained from the MBraun SPS-800 solvent purification system.

S2 – Materials

Deuterium oxide (99.9% D) was purchased from Cambridge Isotopes Inc. Deuterium chloride (35 wt %, 99.5 % D) and deuterated chloroform (99.8% D) were purchased from Sigma-Aldrich. All other chemicals were reagent grade and were used without further purification unless otherwise stated.

S3 – Preparation of Solutions

Stock solutions of deuterium chloride and potassium chloride were prepared by dilution and titration of the commercial concentrated solutions. Solutions of DCl were prepared by mixing stock solution of DCl in D₂O with addition of KCl to give various concentrations and *I* = 1.0 (KCl).

Stock solutions of formate buffers were prepared by mixing stock solutions of potassium formate and DCl with addition of KCl when needed to give buffer solutions of various acid/base ratios and *I*=1.0 (KCl).

S4 – Measurement of *pD* in D₂O solutions

Calibration: The *pH* values of buffered solutions were determined at 25 °C using a MeterLab™ PHM 210 *pH*-Stat Controller equipped with a radiometer (*pH* 4 – 7 – 10 @ 25 °C) combination electrode, that could be standardised between *pH* 4 – 7 or *pH* 7 – 10 to encompass the *pH* of the buffer solution.

Determination of [DO⁻]: The *pD* (± 0.05) was calculated by adding 0.4 to the observed reading of the *pH* meter in the D₂O solution.^{S1} The deuteroxide concentration (M) was calculated using eq. S1:

$$[\text{DO}^-] = (10^{\text{pD} - \text{pK}_w}) / \gamma_{\text{DO}} \quad (\text{S1})$$

Where $K_w = 10^{-14.87} \text{ M}^2$ is the ion product of D₂O at 25 °C^{S2} and γ_{DO} is the apparent activity coefficient of the deuteroxide ion under our experimental conditions. The apparent activity coefficient of deuteroxide, $\gamma_{\text{DO}} = 0.73$, was determined from the measured *pH* of solutions of known [HO⁻] in water at *I* = 1.0 M (KCl) and 25 °C, with the assumption that γ_{HO} is equal to γ_{DO} . *pD* values were recorded at the beginning and end of reaction, and were found to be constant within error (± 0.05).

S5 – NMR parameters

¹H NMR spectra of triazolium ions **6** and **7** were recorded on either Varian 400 or Oxford Varian Inova 500 MHz spectrometers. Spectra were run with 32 transients and a relaxation decay of 20 sec, sweep width of 8298.76 Hz, acquisition time of 4 sec and a 90° pulse angle (total running time approximately 13 min). ¹H NMR spectral baselines were subject to a first – order drift correction before integration of the peak areas. Substrate and product peak areas were compared with the peak of the internal standard (tetramethylammonium deuteriosulphate) that was set to an arbitrary figure of 1000; the integration was undertaken using MestreNova following a first order phase correction and baseline correction using a 6th order Bernstein polynomial.

S6 – Determination of rate constants for C(3)-H/D exchange and data fitting for *N*-pyrid-2-yl triazolium salts (6 and 7)

NMR spectroscopic data, kinetic data and fitting are included below for 2-(pyrid-2-yl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium tetrafluoroborate **6** and 2-(5-methoxypyrid-2-yl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium tetrafluoroborate **7**.

Figure S1: Representative ¹H NMR spectra between 11.2 and 6.8 ppm at 500 MHz of **6** (10 mM, p*D* 3.07) during exchange of C3-H (s, 10.3 ppm) for deuterium in formate buffer in D₂O at 25 °C and I = 1.0 (KCl). [internal standard, tetramethylammonium deuteriosulphate (s, 3.17 ppm)]

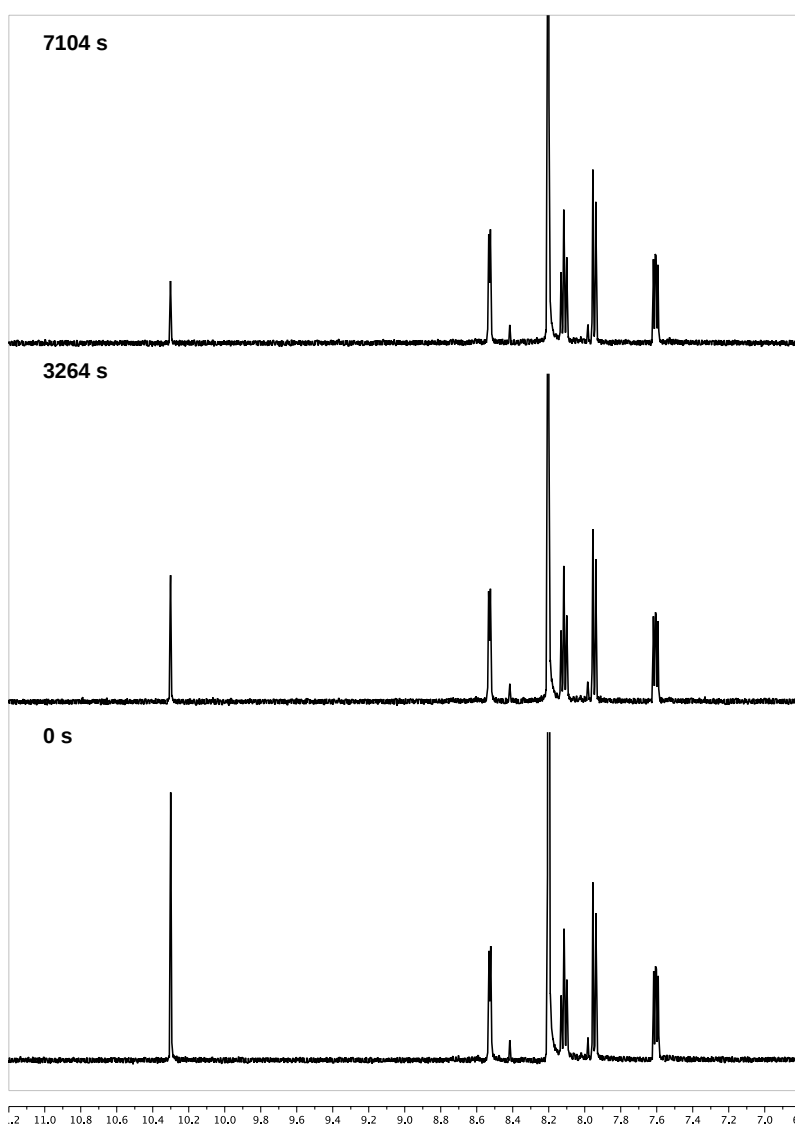


Figure S2: Representative ^1H NMR spectra between 11.2 and 6.8 ppm at 500 MHz of **7** (10 mM, pD 1.08) during exchange of C(3)-H (s, 10.4 ppm) for deuterium in DCl solution in D_2O at 25 °C and $I = 1.0$ (KCl). [internal standard, tetramethylammonium deuteriosulphate (s, 3.17 ppm)]

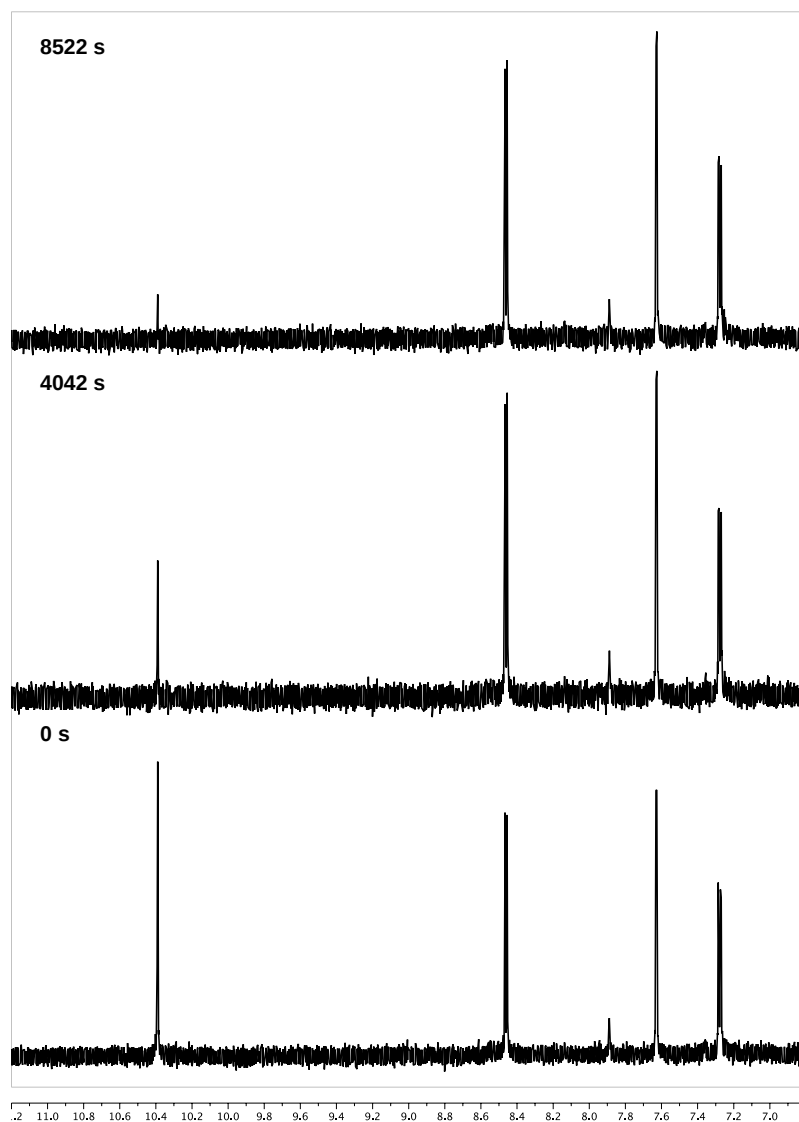


Figure S3: Semilogarithmic plots of the fraction of unexchanged substrate against time for the C(3)-H/D exchange reaction of **6** in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl). The majority of the data for **6** (at lower pD values) have been previously reported.^{S3}

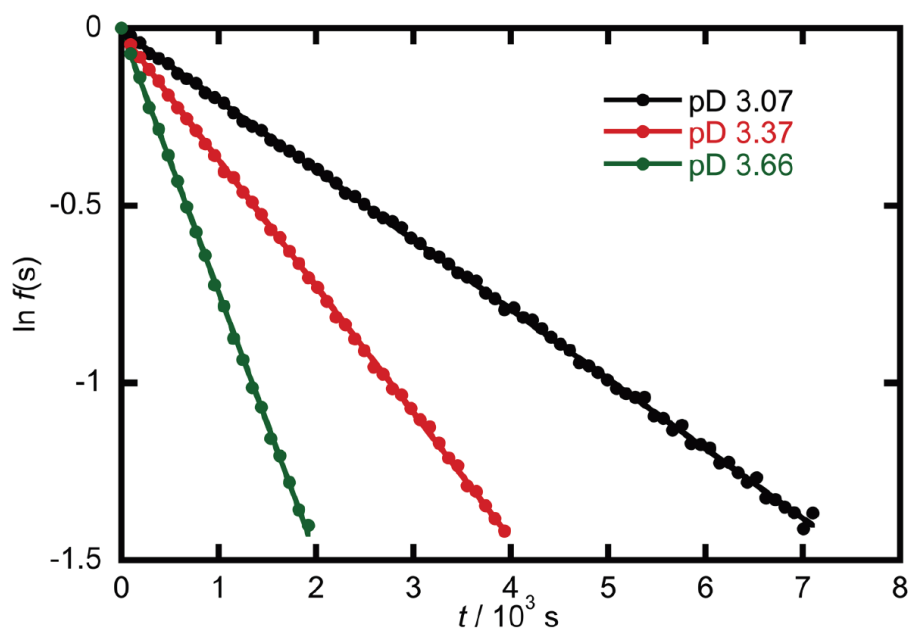


Figure S4: Semilogarithmic plots between pD = 0.42 and pD = 1.73 of the fraction of unexchanged substrate against time for the C(3)-H/D exchange reaction of **7** in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl).

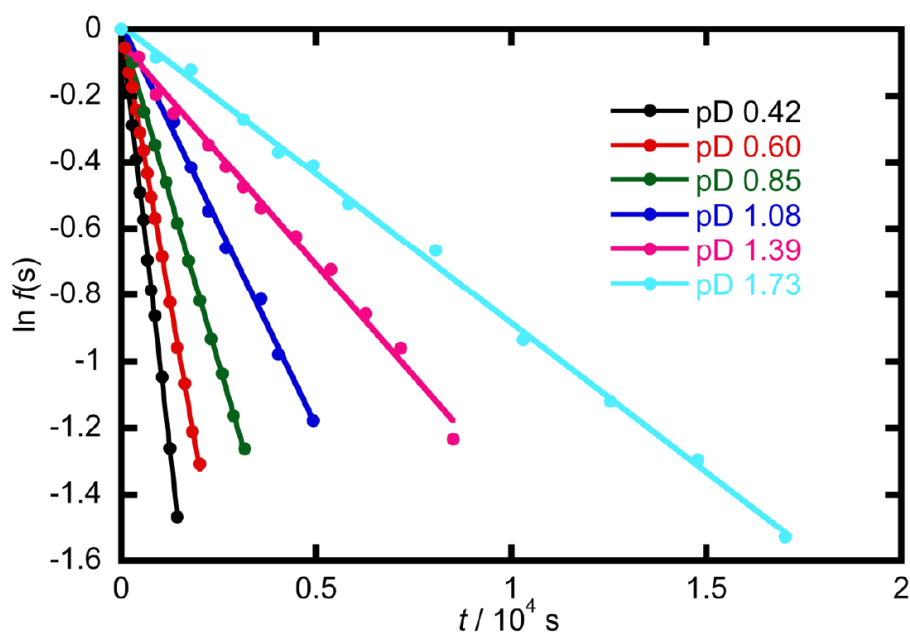


Figure S5: Semilogarithmic plots between $pD = 2.03$ and $pD = 3.66$ of the fraction of unexchanged substrate against time for the C(3)-H/D exchange reaction of **7** in solutions of DCl in D_2O at $25\text{ }^{\circ}C$ and $I = 1.0$ (KCl).

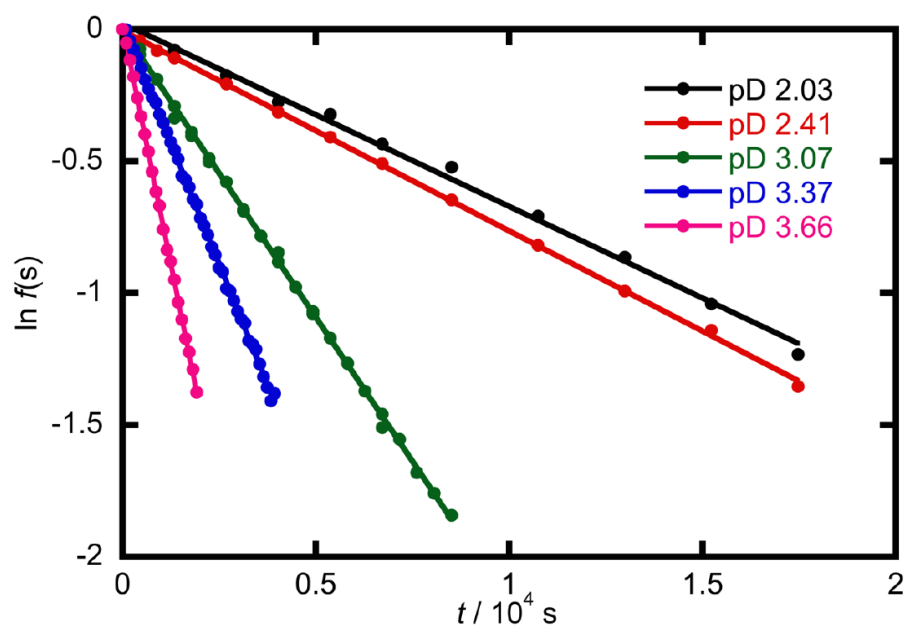


Table S1: First order rate constants for exchange of the C3-H of triazolium salt **6** for deuterium, in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl). Data for pD values of 3.07 – 3.66 were obtained as part of this work.

[DCl], M	pD	[DO-], M	$k_{\text{ex}}, \text{s}^{-1}$	$\text{Log } k_{\text{ex}}$	
8.51×10^{-4}	3.07	1.17×10^{-11}	$1.96 (\pm 0.01) \times 10^{-4}$	-3.71	
4.27×10^{-4}	3.37	2.34×10^{-11}	$3.56 (\pm 0.01) \times 10^{-4}$	-3.45	This work
2.19×10^{-4}	3.66	4.57×10^{-11}	$7.41 (\pm 0.04) \times 10^{-4}$	-3.13	
8.32×10^{-1}	0.08	1.20×10^{-14}	6.92×10^{-4}	-4.16	
4.27×10^{-1}	0.37	2.34×10^{-14}	4.27×10^{-4}	-4.37	
1.74×10^{-1}	0.76	5.75×10^{-14}	2.22×10^{-4}	-4.65	
9.33×10^{-2}	1.03	1.07×10^{-13}	1.40×10^{-4}	-4.85	
4.57×10^{-2}	1.34	2.19×10^{-13}	1.11×10^{-4}	-4.95	Previous work ^{S3}
2.19×10^{-2}	1.66	4.57×10^{-13}	1.39×10^{-4}	-4.86	
1.78×10^{-2}	1.75	5.62×10^{-13}	1.57×10^{-4}	-4.80	
1.32×10^{-2}	1.88	7.59×10^{-13}	1.83×10^{-4}	-4.74	
8.91×10^{-3}	2.05	1.12×10^{-12}	2.47×10^{-4}	-4.61	
4.90×10^{-3}	2.31	2.04×10^{-12}	4.20×10^{-4}	-4.38	

Table S2: First order rate constants for exchange of the C3-H of triazolium salt **7** for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl).

[DCl], M	pD	[DO-], M	$k_{\text{ex}}, \text{s}^{-1}$	Log k_{ex}
3.80×10^{-1}	0.42	2.63×10^{-14}	$1.01 (\pm 0.08) \times 10^{-3}$	-3.00
2.51×10^{-1}	0.60	3.98×10^{-14}	$6.60 (\pm 0.04) \times 10^{-4}$	-3.18
1.41×10^{-1}	0.85	7.08×10^{-14}	$4.02 (\pm 0.03) \times 10^{-4}$	-3.40
8.32×10^{-2}	1.08	1.20×10^{-13}	$2.42 (\pm 0.05) \times 10^{-4}$	-3.62
4.07×10^{-2}	1.39	2.45×10^{-13}	$1.34 (\pm 0.04) \times 10^{-4}$	-3.87
1.86×10^{-2}	1.73	5.37×10^{-13}	$8.96 (\pm 0.01) \times 10^{-5}$	-4.05
9.33×10^{-3}	2.03	1.07×10^{-12}	$6.77 (\pm 0.01) \times 10^{-5}$	-4.17
3.89×10^{-3}	2.41	2.57×10^{-12}	$7.60 (\pm 0.01) \times 10^{-5}$	-4.12
8.51×10^{-4}	3.07	1.17×10^{-11}	$2.18 (\pm 0.01) \times 10^{-4}$	-3.66
4.27×10^{-4}	3.37	2.34×10^{-11}	$3.66 (\pm 0.02) \times 10^{-4}$	-3.44
2.19×10^{-4}	3.66	4.57×10^{-11}	$7.23 (\pm 0.04) \times 10^{-4}$	-3.14

Figure S6: Linear plot of log k_{ex} against pD for the C(3)-H/D exchange of triazolium salt **6** (●) and **7** (●) at pD values ≤ 1.1 , 25 °C and I = 1.0 (KCl).

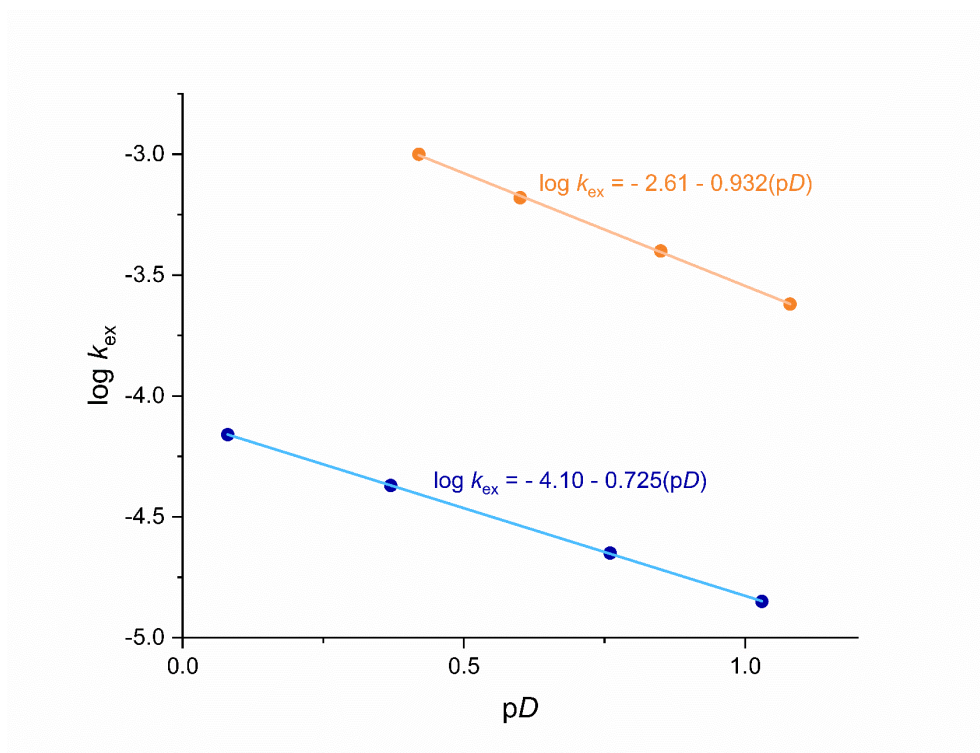
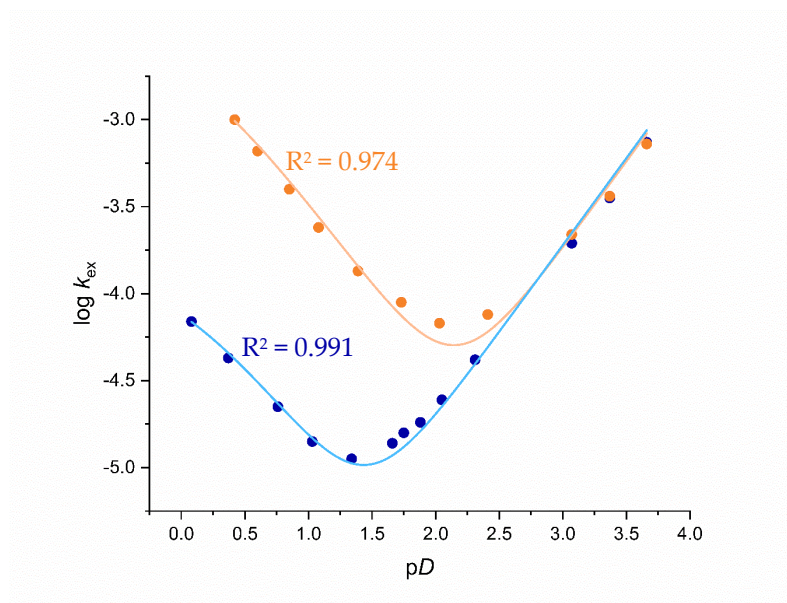
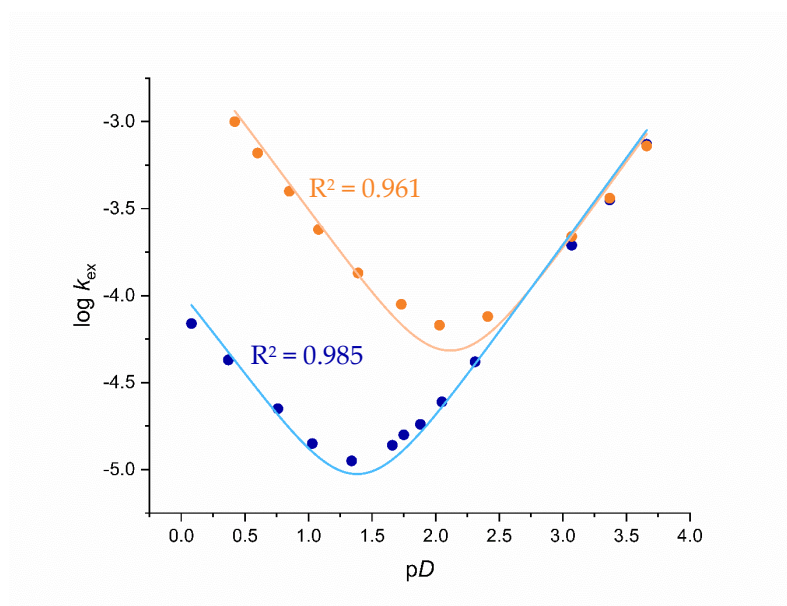


Figure S7: Plots of $\log k_{\text{ex}}$ versus pD for the C(3)-H/D exchange of **6** (●) and **7** (●) using eqn. 3 (main text), with K_{a}^{N} fixed to different values:

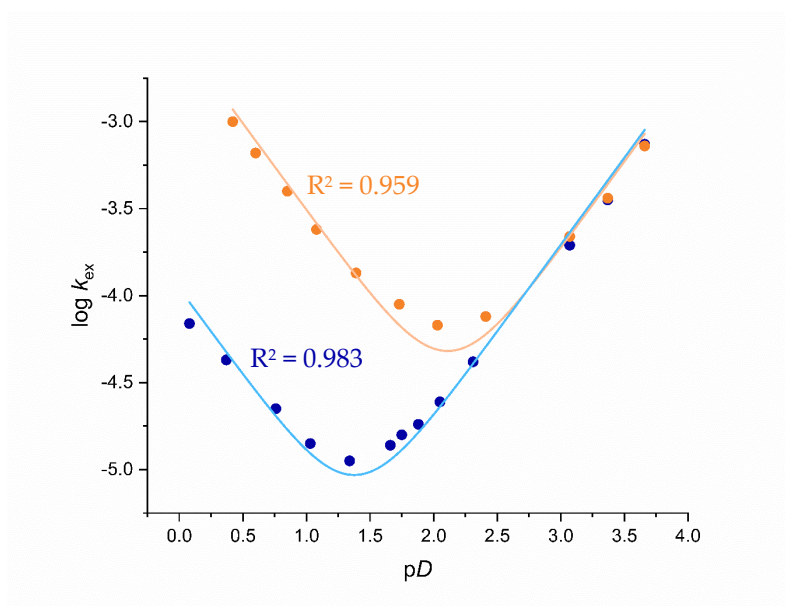
$$K_{\text{a}}^{\text{N}} = 1$$



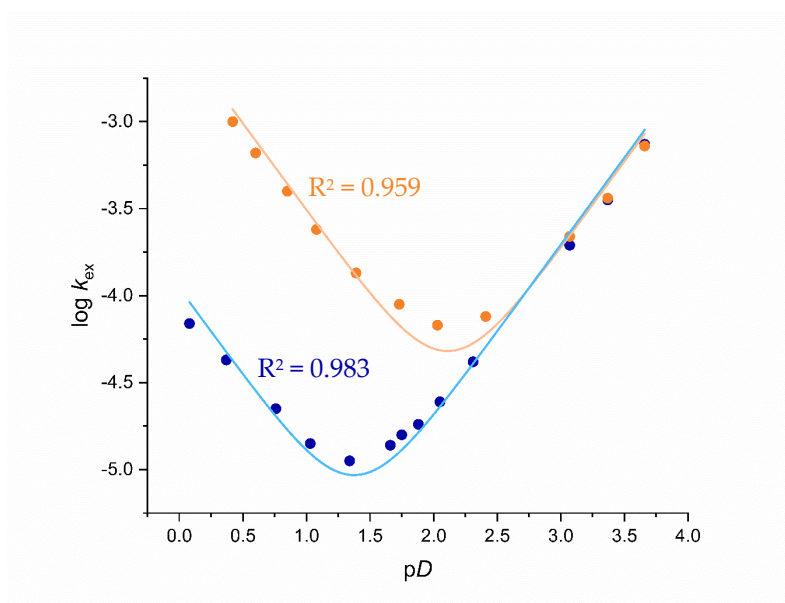
$$K_{\text{a}}^{\text{N}} = 10$$



$K_a^N = 100$



$K_a^N = 1000$



S7 – Determination of rate constants for C(3)-H/D exchange and data fitting for the *N*-di-*ortho*-alkoxyphenyl triazolium salts (8 and 9)

NMR spectroscopic data, kinetic data and fitting are included below for 2-(2,6-dimethoxyphenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium tetrafluoroborate **8** and 2-(2,6-diisopropoxyphenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium tetrafluoroborate **9**.

Figure S8: Representative ^1H NMR at 400 MHz of **8** (10 mM, pD 1.08) during exchange of C3-H (s, 9.76 ppm) for deuterium in DCl solution in D_2O at 25 °C and I = 1.0 (KCl). [internal standard, tetramethylammonium deuteriosulphate (s, 3.17 ppm)]

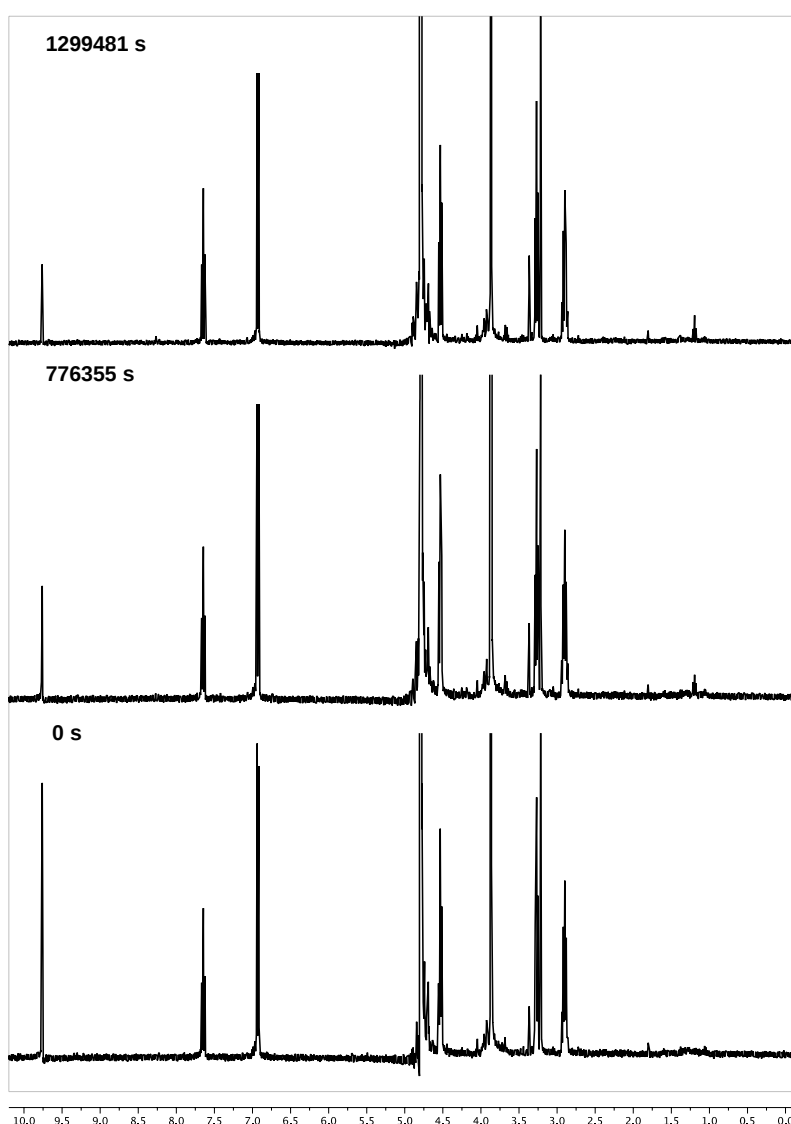


Figure S9: Representative ^1H NMR at 400 MHz of **9** (10 mM, pD 1.08) during exchange of C3-H (s, 9.82 ppm) for deuterium in DCl solution in D_2O at 25 $^\circ\text{C}$ and $I = 1.0$ (KCl). [internal standard, tetramethylammonium deuteriosulphate (s, 3.17 ppm)]

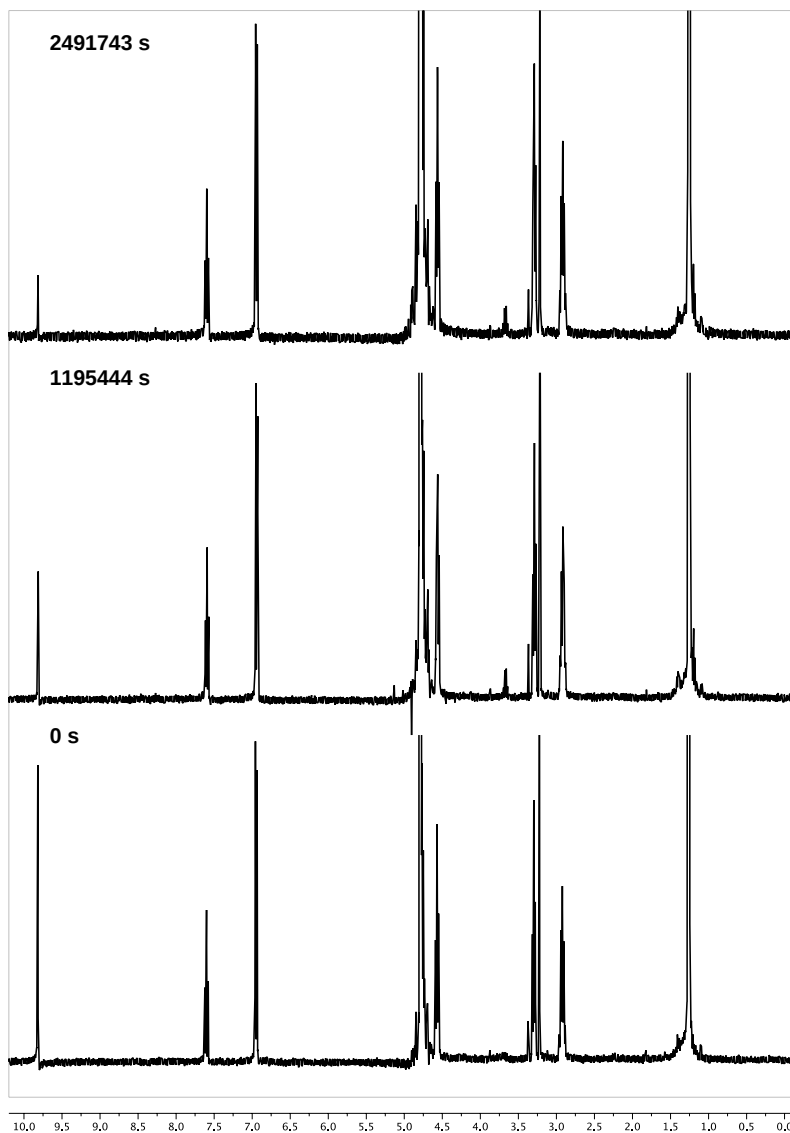


Figure S10: Semilogarithmic plot of the fraction of unexchanged substrate against time for the deuterium exchange reaction of **8** in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl).

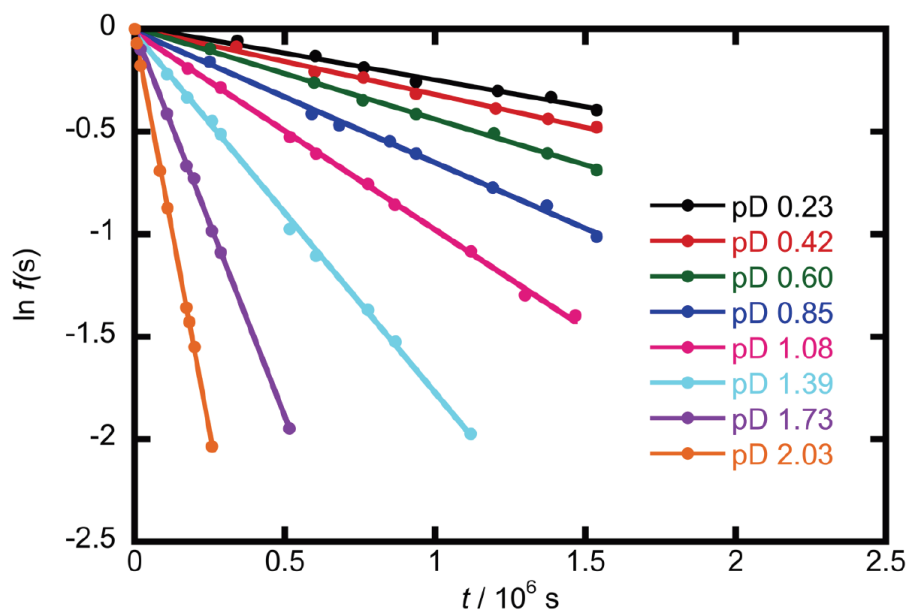


Figure S11: Semilogarithmic plot of the fraction of unexchanged substrate against time for the deuterium exchange reaction of **8** in solutions of varying formate buffer concentration in D₂O at 25 °C and I = 1.0 (KCl).

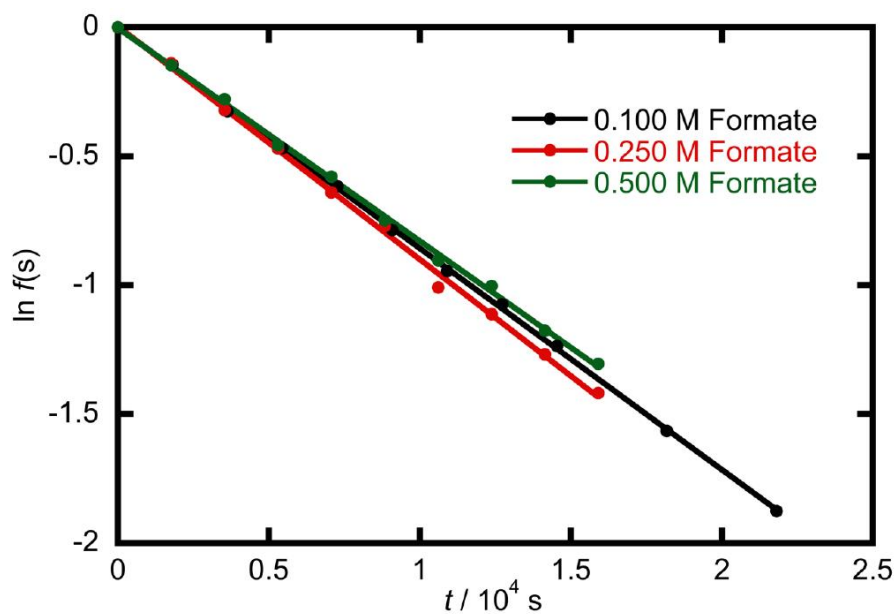


Figure S12: Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of **9** in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl).

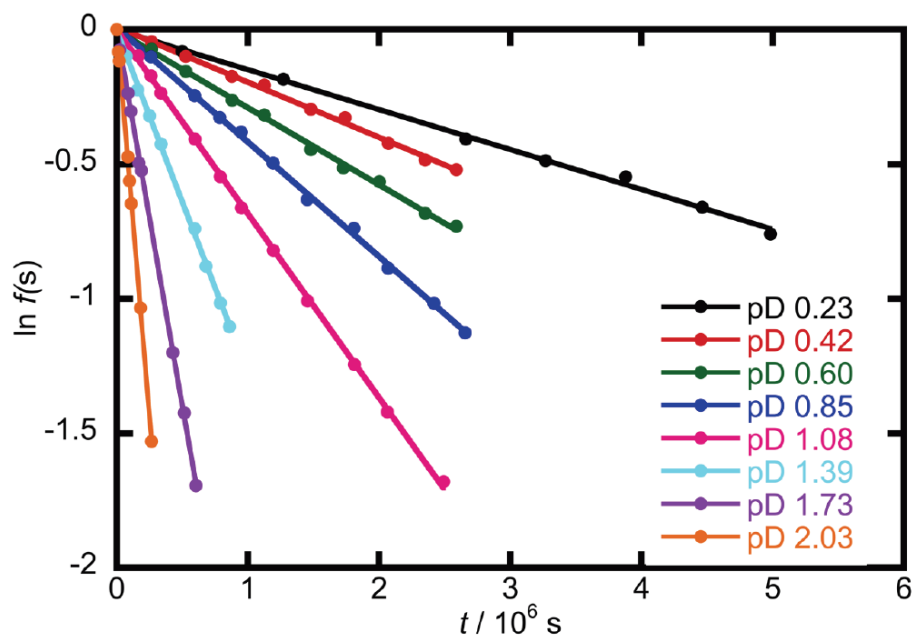


Figure S13: Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of **9** in solutions of varying formate buffer concentration in D₂O at 25 °C and I = 1.0 (KCl).

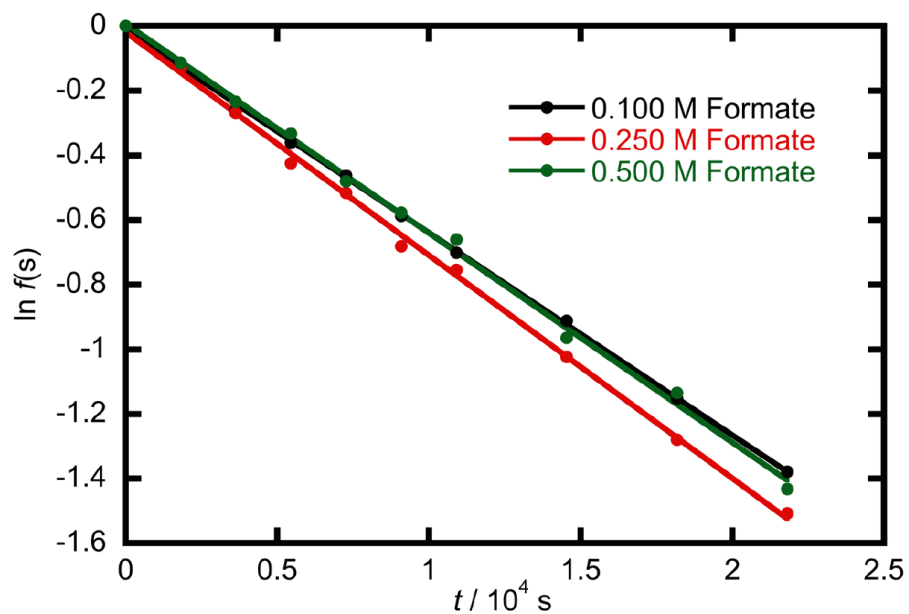


Table S3: First order rate constants for exchange of the C3-H of triazolium salt **8** for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl).

[DCl], M	pD	[DO ⁻], M	k_{ex} , s ⁻¹	Log k_{ex}
5.89×10^{-1}	0.23	1.70×10^{-14}	$2.61 (\pm 0.01) \times 10^{-7}$	-6.58
3.80×10^{-1}	0.42	2.63×10^{-14}	$3.21 (\pm 0.01) \times 10^{-7}$	-6.49
2.51×10^{-1}	0.60	3.98×10^{-14}	$4.45 (\pm 0.01) \times 10^{-7}$	-6.35
1.41×10^{-1}	0.85	7.08×10^{-14}	$6.41 (\pm 0.01) \times 10^{-7}$	-6.19
8.32×10^{-2}	1.08	1.20×10^{-13}	$9.62 (\pm 0.01) \times 10^{-7}$	-6.02
4.07×10^{-2}	1.39	2.45×10^{-13}	$1.75 (\pm 0.02) \times 10^{-6}$	-5.76
1.86×10^{-2}	1.73	5.37×10^{-13}	$3.76 (\pm 0.03) \times 10^{-6}$	-5.42
9.33×10^{-3}	2.03	1.07×10^{-12}	$7.80 (\pm 0.05) \times 10^{-6}$	-5.11

Table S4: First order rate constants for exchange of the C3-H of triazolium salt **9** for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl).

[DCl], M	pD	[DO ⁻], M	k_{ex} , s ⁻¹	Log (k_{ex} , s ⁻¹)
5.89×10^{-1}	0.23	1.70×10^{-14}	$1.48 (\pm 0.00) \times 10^{-7}$	-6.83
3.80×10^{-1}	0.42	2.63×10^{-14}	$2.05 (\pm 0.00) \times 10^{-7}$	-6.69
2.51×10^{-1}	0.60	3.98×10^{-14}	$2.86 (\pm 0.00) \times 10^{-7}$	-6.54
1.41×10^{-1}	0.85	7.08×10^{-14}	$4.25 (\pm 0.01) \times 10^{-7}$	-6.37
8.32×10^{-2}	1.08	1.20×10^{-13}	$6.84 (\pm 0.00) \times 10^{-7}$	-6.16
4.07×10^{-2}	1.39	2.45×10^{-13}	$1.28 (\pm 0.01) \times 10^{-6}$	-5.90
1.86×10^{-2}	1.73	5.37×10^{-13}	$2.78 (\pm 0.02) \times 10^{-6}$	-5.56
9.33×10^{-3}	2.03	1.07×10^{-12}	$5.72 (\pm 0.04) \times 10^{-6}$	-5.24

Table S5: First order rate constants for exchange of the C3-H of triazolium salt **8** for deuterium, with varying formate buffer concentration, in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl).

pD	[A + HA], M	k_{ex} , s ⁻¹	averaged k_{ex} , s ⁻¹	Log k_{ex}
3.07	0.100	$8.58 (\pm 0.05) \times 10^{-5}$		
3.09	0.250	$9.04 (\pm 0.14) \times 10^{-5}$	8.62×10^{-5}	-4.06
3.07	0.500	$8.25 (\pm 0.01) \times 10^{-5}$		

Table S6: First order rate constants for exchange of the C3-H of triazolium salt **9** for deuterium, with varying formate buffer concentration, in solutions of DCl in D₂O at 25 °C and I = 1.0 (KCl).

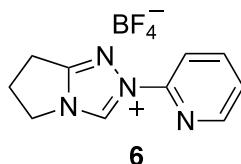
pD	[A + HA], M	$k_{\text{ex}}, \text{s}^{-1}$	averaged $k_{\text{ex}}, \text{s}^{-1}$	Log k_{ex}
3.07	0.100	$6.26 (\pm 0.01) \times 10^{-5}$		
3.09	0.250	$6.90 (\pm 0.09) \times 10^{-5}$	6.55×10^{-5}	-4.18
3.07	0.500	$6.48 (\pm 0.12) \times 10^{-5}$		

S8 – Determination of Error

The maximum percentage error in the first order rate constant for C(3)-H/D exchange, k_{ex} (s^{-1}), is estimated as 6% based on our previous work.^{S4} In general, errors in the range 2 – 3% were obtained. We have assumed that the error in the k_{DO} value is equal to the standard error in the value of $(k_{\text{DO}} \times K_{\text{w}} / \gamma_{\text{DO}})$ obtained from the fits of $\log k_{\text{ex}} - \text{pD}$ data to eq (3) or (5). As discussed in the main text, C(3)-H pK_{a} values for all triazolium salts were calculated using equation (6) and a discussion of pK_{a} error was included in our previous work.^{S4} As mentioned in the main text, the largest source of error can be attributed to the use of $k_{\text{HOH}} = 1 \times 10^{11} \pm 1 \times 10^{10} \text{ s}^{-1}$ for the reverse rate constant for protonation of the NHC assuming that this step is limited by the physical transport process of solvent reorganisation. As discussed previously,^{S4} there is good evidence that the protonation is limited by solvent reorganisation.

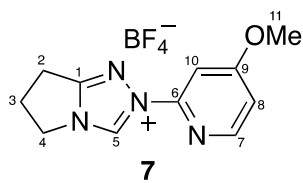
S9 – Synthesis of Substrates

2-(Pyrid-2-yl)-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate (**6**)



The title compound **6** was prepared as described in our previous work^{S3} using a modification of a procedure from Glorius *et al.*^{S5} All physical and spectroscopic characterisation data were in accordance with the literature.^{S3}

2-(5-Methoxypyrid-2-yl)-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate (**7**)



The synthetic route employed in the preparation of the title compound **7** is shown in the main text (Scheme 1).

Based on a procedure by Glorius and others,¹³ 2-pyrrolidone (321 μ L, 4.23 mmol) was dissolved in dry DCM (20 mL, 0.2 M) and Me₃OBF₄ (646 mg, 4.37 mmol, 1.2 equiv.) was added. The mixture was stirred at RT overnight to afford 5-methoxy-3,4-dihydro-2H-pyrrol-1-ium tetrafluoroborate, which was used in the next step without further purification still within the dry DCM.

Based on a procedure by Buckwald and others,^{S6} benzophenone hydrazine **10** (719 mg, 3.67 mmol), 2-chloro-4-methoxypyridine **11** (398 μ L, 3.48 mmol), Pd(OAc)₂ (10.9 mg, 0.049 mmol) and *rac*-BINAP (22.5 mg, 0.036 mmol) were dissolved in dry toluene (7 mL). The mixture was stirred at 80 °C overnight. The reaction mixture was cooled, diluted with Et₂O (35 mL) and filtered through a celite pad. The celite pad was rinsed with Et₂O (70 mL), concentrated under reduced pressure, and purified by column flash chromatography (hexane:EtOAc 8:2) to give *N*-(5-methoxypyrid-2-yl)benzophenone hydrazone **12** (1.05 g, 99%) as a white solid.

Melting point: 117.0 – 118.6 °C (No literature mp); δ_{H} (700 MHz, CDCl₃) 3.91 (3H, s, OMe), 6.34 (1H, dd, *J* = 5.8, 2.4, *ArH*), 7.00 (1H, d, *J* = 2.4, *ArH*), 7.29 – 7.35 (5H, m, *Ph*), 7.48 (1H, t, *J* = 8.4, 0.7, *Ph*), 7.52 – 7.60

(4H, m, *Ph*), 7.87 (1H, d, *J* = 5.8, *ArH*), 8.14 (1H, br s, *NH*); δ_c (176 MHz, $CDCl_3$) 55.2, 91.5, 104.2, 126.8, 128.2, 128.5, 128.9, 129.4, 129.7, 132.5, 138.0, 146.3, 148.6, 158.4, 167.6; LCMS (ESI+) *m/z* 304 [*M*+*H*]⁺; HRMS (ESI+) *m/z* 304.1454 [*M*+*H*]⁺ ($C_{19}H_{18}N_3O$ requires 304.1454).

N-(5-Methoxypyrid-2-yl)benzophenone hydrazone **12** (933 mg, 3.08 mmol) was suspended in toluene (6.2 mL) and 2.4 M HCl (15.5 mL) then heated to 90 °C overnight. The reaction mixture was cooled and toluene (10 mL) was added. The aqueous phase was separated and added to diethyl ether (100 mL). 1.0 M NaOH (62.2 mL) was added slowly with stirring. The ether layer was separated and the aqueous phase was extracted with diethyl ether (3 x 90 mL). The organic layers were combined, washed with brine (100 mL) and concentrated under reduced pressure to give crude *N*-(5-methoxypyrid-2-yl)hydrazine **13** as a yellow oil, which was used directly in the next step.

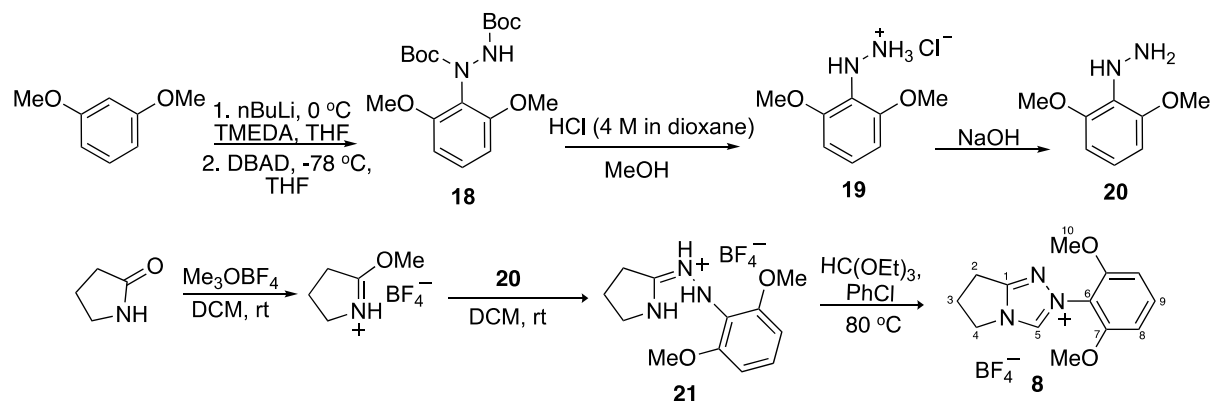
Based on a procedure by *Glorius* and others,⁵⁷ crude *N*-(5-methoxypyrid-2-yl)hydrazine **13** ($\leq$ 3.08 mmol, 1.0 equiv.) and 5-methoxy-3,4-dihydro-2H-pyrrol-1-ium tetrafluoroborate ($\leq$ 3.08 mmol, 1.0 equiv.) were dissolved in dry DCM (15 mL). The resulting solution was stirred (RT, 72 h) before concentration in vacuo to afford *N*-(5-methoxypyrid-2-yl)amidrazonium tetrafluoroborate **14**, which was used directly without further purification.

Crude *N*-(5-methoxypyrid-2-yl)amidrazonium tetrafluoroborate **14** was suspended in triethylorthoformate (10.2 mL, 61.5 mmol, 8.0 equiv.) under an atmosphere of argon. The resulting mixture was heated to 120 °C overnight then concentrated under reduced pressure. The resulting brown oil was purified by flash column chromatography (DCM:MeOH 90:1, *R_f* = 0.23) on silica gel to afford the title compound, 2-(5-methoxypyrid-2-yl)-6,7-dihydro-5H-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium tetrafluoroborate **7** (51.8 mg, 6%) as a yellow solid, which could be crystallised by slow evaporation of methanol.

δ_H (700 MHz, CD_3CN) 2.83 (2H, app quin, CH_2 , H^3), 3.21 (2H, t, *J* = 7.7, CH_2 , H^2), 3.99 (3H, s, *OMe*, H^{11}), 4.44 (2H, t, *J* = 7.4, CH_2 , H^4), 7.14 (1H, dd, *J* = 5.6, 2.3, *ArH*, H^8), 7.47 (1H, d, *J* = 2.3, *ArH*, H^{10}), 8.39 (1H, d, *J* = 5.6, *ArH*, H^7), 10.00 (1H, s, *NCHN*, H^5); δ_c (176 MHz, CD_3CN) 21.5 (C^2), 26.6 (C^3), 47.5 (C^4), 56.3 (C^{11}), 99.7 (C^{10}), 112.1 (C^8), 137.0 (C^5), 149.1 (C^6), 150.3 (C^7) 164.0 (C^1), 168.8 (C^9); LCMS (ESI+) *m/z* 217 [*M*- BF_4]⁺; HRMS (ESI+) *m/z* 217.1096 [*M*- BF_4]⁺ ($C_{11}H_{13}N_4O$ requires 217.1089).

2-(2,6-Dimethoxyphenyl)-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate (8)

The title compound **8** was prepared as shown in the scheme below using a modification of a procedure reported by Glorius *et al*⁵⁷ for the preparation of the analogous chloride salt of **8**.



n-Butyllithium (1.6 M solution in hexanes, 6.9 mL, 11.0 mmol, 1.1 equiv.) was added dropwise to an ice cold solution of 1,3-dimethoxybenzene (1.31 mL, 10.0 mmol, 1.0 equiv.) and tetramethylethylenediamine (TMEDA, 1.64 mL, 11.0 mmol, 1.1 equiv.) in THF (80 mL) at 0 °C. After 1 h, the reaction mixture was cooled to -78 °C. A solution of di-*tert*-butyl diazene-1,2-dicarboxylate (DBAD, 2.30 g, 10.0 mmol, 1.0 equiv.) in THF (20 mL) was added dropwise via cannula. After 20 min, the reaction mixture was quenched by the addition of AcOH (575 µL, 10.0 mmol, 1.0 equiv.) at -78 °C. The resulting solution was warmed to room temperature, diluted with EtOAc (200 mL) and poured over distilled water (300 mL). The aqueous layer was extracted with EtOAc (3 x 200 mL), washed with brine (200 mL), dried over anhydrous Na₂SO₄, filtered, and was concentrated under reduced pressure. The oil was purified by flash column chromatography (hexane:EtOAc 3:1) to give a sticky, foamy residue. The residue was dissolved in a small amount of eluent, transferred to a glass vial, and placed inside a Schlenk tube. Rotary evaporation afforded di-*tert*-butyl-1-(2,6-dimethoxyphenyl)hydrazine-1,2-dicarboxylate **18**, (2.27 g, 62%) as a white powder. The product exists as a ~1.8:1 mixture of carbamate rotamers.

Melting point: 97 – 99 °C (No lit. value)*; ν_{max} / cm⁻¹ 3295w (C-H stretch), 2976m, 1723m, 1709m (C=O carbamate), 1706m (C=O carbamate), 1704m, 1591m, 1481m (C-H stretch); δ_{H} (400 MHz, d⁶-DMSO) Major rotamer: 1.30 (9H, s, C(CH₃)₃), 1.37 (9H, s, C(CH₃)₃), 3.75 (6H, s, (CH₃)₂), 6.62 (2H, d, *J* = 8.4, *ArH*), 7.18 (1H, t, *J* = 8.4, *ArH*), 8.80 (1H, br s, *NH*). Minor rotamer: 1.41 (9H, s, C(CH₃)₃), 1.43 (9H, s, C(CH₃)₃), 3.72 (6H, s, (CH₃)₂), 6.63 (2H, d, *J* = 8.4, *ArH*), 7.21 (1H, t, *J* = 8.4, *ArH*), 8.46 (1H, br s, *NH*); δ_{C} (100 MHz,

* No literature value exists for the melting point as this product was obtained as a sticky yellow foam in the literature procedure.

d⁶-DMSO) Major rotamer: 28.2, 28.5, 56.0, 79.2, 80.2, 104.7, 119.8, 128.7, 154.2, 156.6. Minor rotamer: 28.3, 28.5, 56.3, 79.4, 80.2, 105.2, 119.8, 129.0, 153.7, 155.7.

To a Schlenk flask containing di-*tert*-butyl-1-(2,6-dimethoxyphenyl)hydrazine-1,2-dicarboxylate **18** (1.56 g, 4.23 mmol, 1.0 equiv.) anhydrous MeOH (10 mL) was introduced. HCl (4.0 M solution in 1,4-dioxane, 10.5 mL, 41.8 mmol, 10 equiv.) was then added dropwise via syringe with the resultant solution stirred at room temperature. After 4 h, the solution was concentrated *in vacuo* to afford crude (2,6-dimethoxyphenyl)hydrazine hydrochloride **19** as an orange solid, which was used without purification. LCMS (ESI+) m/z = 169 [M-Cl]⁺

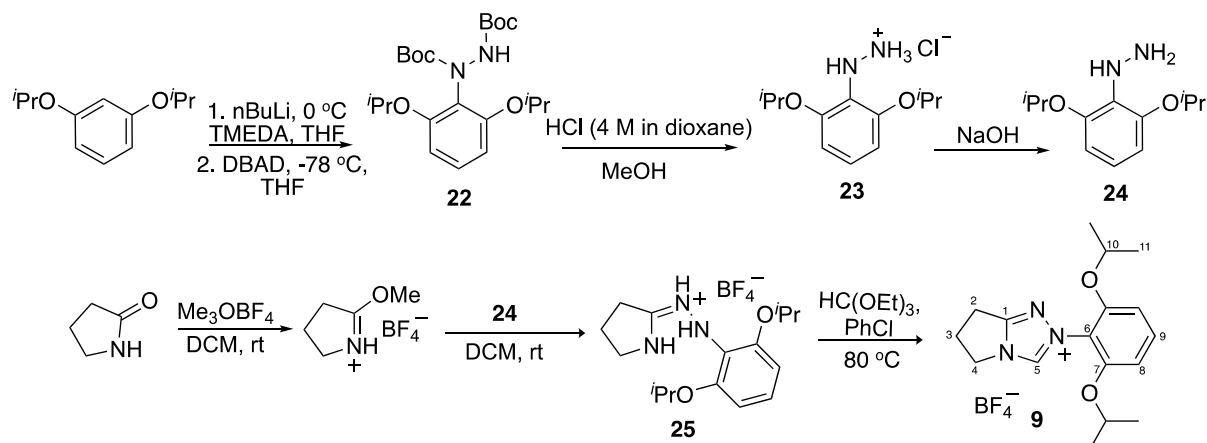
2-Pyrrolidinone (321 μ L, 4.23 mmol) was dissolved in anhydrous DCM (20 mL) under argon. Trimethyloxonium tetrafluoroborate (646 mg, 4.37 mmol) was added in one portion and the reaction mixture stirred at room temperature under argon overnight to afford 5-methoxy-3,4-dihydro-2H-pyrrol-1-ium tetrafluoroborate, which was used in the next step without further purification still within the dry DCM.

Diethyl ether (20 mL) and 1 M NaOH (20 mL) were cooled in an ice bath. 2,6-Dimethoxyphenyl)hydrazine hydrochloride **19** was added to this cooled mixture and stirred for ~ 10 minutes. The ether layer was separated and the aqueous phase was washed with diethyl ether (3 $\times$ 20 mL). The combined organics were washed with brine (20 mL), dried over Na₂SO₄, filtered and concentrated to give **20** as an orange residue, which was dissolved in anhydrous DCM (10 mL) and combined with the DCM solution of 5-methoxy-3,4-dihydro-2H-pyrrol-1-ium tetrafluoroborate.

The mixture was stirred at room temperature under argon overnight. The solvent was removed to give **21** as a brown oil, which was then dissolved in chlorobenzene (4 mL). Triethyl orthoformate (5.63 mL, 33.8 mmol) was added and the mixture heated at 80 °C overnight. The reaction was allowed to cool and the solvent was removed *in vacuo* to give a brown oil. Flash column chromatography (DCM:MeOH 95:5) gave the desired compound **8** as a brown oil (151 mg, 11% from 2-pyrrolidinone). **8** could be crystallised by slow evaporation from MeOH; δ_{H} (600 MHz, CDCl₃) 2.89 (2H, apparent quintet, CH₂, H³), 3.24 (2H, t, J 7.8, CH₂, H²), 3.83 (6H, s, 2 $\times$ CH₃, H¹⁰), 4.70 (2H, t, J 7.8, CH₂, H⁴), 6.69 (2H, d, J 8.4, 2 $\times$ ArH, H⁸), 7.48 (1H, t, J 8.4, ArH, H⁹), 9.60 (1H, s, NCHN, H⁵); δ_{C} (151 MHz, CDCl₃) 22.0 (C²), 26.7 (C³), 48.0 (C⁴), 56.4 (C¹⁰), 104.3 (C⁸), 113.2 (ArC), 133.5 (C⁹), 142.6 (C⁵), 155.5 (ArC), 161.9 (C¹); LCMS (ESI+) m/z 246 [M-BF₄]⁺; HRMS (ESI+) m/z 246.1249 [M-BF₄]⁺ (C₁₃H₁₆N₃O₂⁺ requires 246.1243).

2-(2,6-Diisopropoxyphenyl)-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate (9)

The title compound **9** was prepared as shown in the scheme below using a modification of a procedure reported by Glorius *et al*⁵⁷ for the preparation of the chloride salt of **8**.



n-Butyllithium (2.5 M solution in hexanes, 2.64 mL, 6.6 mmol, 1.1 equiv.) was added dropwise to an ice cold solution of 1,3-diisopropoxybenzene (1.21 mL, 6 mmol, 1.0 equiv.) and tetramethylethylenediamine (TMEDA, 0.99 mL, 6.6 mmol, 1.1 equiv.) in THF (50 mL) at 0 °C. After 1 h, the reaction mixture was cooled to -78 °C. A solution of di-*tert*-butyl diazene-1,2-dicarboxylate (DBAD, 11.39 g, 6 mmol, 1.0 equiv.) in THF (12 mL) was added dropwise via cannula. After 20 min, the reaction mixture was quenched by the addition of AcOH (360 µL, 6 mmol, 1.0 equiv.) at -78 °C. The resulting solution was warmed to room temperature, diluted with EtOAc (100 mL) and poured over distilled water (150 mL). The aqueous layer was extracted with EtOAc (3 x 100 mL), washed with brine (100 mL), dried over anhydrous Na₂SO₄, filtered, and was concentrated under reduced pressure to give a yellow oil. The resulting oil was purified by flash column chromatography (hexane:EtOAc 9:1 R_f= 0.16) to afford di-*tert*-butyl-1-(2,6-diisopropoxyphenyl)hydrazine-1,2-dicarboxylate **22** (982 mg, 39 %) as a yellow oil.

ν_{max} / cm⁻¹ 2978m, 2933w, 2933w, 1759m, 1718m (C=O carbamate), 1590m, 1472m (C-H stretch); δ_{H} (600 MHz, CDCl₃) 1.27 – 1.54 (30 H, m, 10 x CH₃), 4.52 – 4.62 (2H, m, CH), 6.48 – 6.54 (2H, m, ArH), 6.72 (1H, br s, NH), 7.11 (1H, t, *J* = 8.4, ArH); δ_{C} (151 MHz, CDCl₃) 22.2, 22.3, 28.06, 28.14, 28.18, 28.3, 28.4, 70.9, 71.2, 80.6, 80.8, 128.2, 128.5, 155.2, 154.8.

To a Schlenk flask containing di-*tert*-butyl-1-(2,6-diisopropoxyphenyl)hydrazine-1,2-dicarboxylate **22** (2.68 g, 6.31 mmol, 1.0 equiv.) anhydrous MeOH (16 mL) was introduced. HCl (4.0 M solution in 1,4-dioxane, 15.8 mL, 10 equiv.) was then added dropwise via syringe with the resultant solution stirred at room temperature. After 4 h, the solution was concentrated in vacuo to afford crude (2,6-

diisopropoxyphenyl)hydrazine hydrochloride **23** which was used in the next step without purification.
LCMS (ESI+) $m/z = 247$ $[M+Na]^+$

2-Pyrrolidinone (479 μ L, 6.31 mmol) was dissolved in anhydrous DCM (30 mL) under argon. Trimethyloxonium tetrafluoroborate (948 mg, 6.41 mmol) was added in one portion and the reaction mixture stirred at room temperature under argon overnight to afford 5-methoxy-3,4-dihydro-2H-pyrrol-1-ium tetrafluoroborate, which was used in the next step without further purification still within the dry DCM.

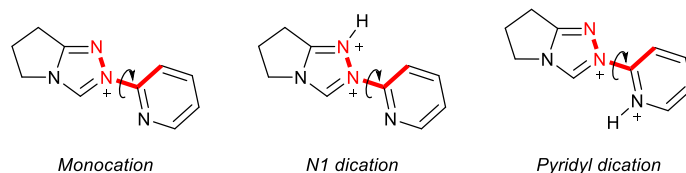
Diethyl ether (30 mL) and 1 M NaOH (30 mL) were cooled in an ice bath. 2,6-Diisopropoxyphenyl)hydrazine hydrochloride **23** was added to this cooled mixture and stirred for ~ 10 minutes. The ether layer was separated and the aqueous phase was washed with diethyl ether (3 $\times$ 30 mL). The combined organics were washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated to give **24** as an orange residue, which was dissolved in anhydrous DCM (15 mL) and combined with the DCM solution of 5-methoxy-3,4-dihydro-2H-pyrrol-1-ium tetrafluoroborate. The mixture was stirred at room temperature under argon overnight. The solvent was removed to give **25** as a brown oil (LCMS (ESI+) m/z 292 $[M+H-BF_4]^+$), which was then dissolved in chlorobenzene (6 mL). Triethyl orthoformate (8.40 mL, 50.5 mmol, 8 equiv.) was added and the mixture heated at 80 °C overnight. The reaction was allowed to cool and the solvent was removed *in vacuo* to give a brown oil (LCMS (ESI+) m/z 302 $[M-BF_4]^+$). Flash column chromatography (DCM:MeOH 95:5) gave the desired compound **9** as a brown oil (312 mg, 13% from 2-pyrrolidinone); δ_H (700 MHz, CDCl₃) 1.24 (12H, d, J 6.3, CH₃, H¹¹), 2.87 (2H, app quin, CH₂, H³), 3.22 (2H, t, J 7.7, CH₂, H²), 4.56 (2H, septet, J 6.3, CH(CH₃)₂, H¹⁰), 4.67 (2H, t, J 7.7, CH₂, H⁴), 6.59 (2H, d, J 8.4, ArH, H⁸), 7.37 (1H, t, J 8.4, ArH, H⁹), 9.48 (1H, s, NCHN, H⁵); δ_C (151 MHz, CDCl₃) 21.6 (C¹¹), 21.8 (C²), 26.6 (C³), 47.9 (C⁴), 72.1 (C¹⁰), 105.5 (C⁸), 114.7 (C⁶), 132.9 (C⁹), 142.2 (C⁵), 154.1 (C⁷), 161.7 (C¹); LCMS (ESI+) m/z 302 $[M-BF_4]^+$; HRMS (ESI+) m/z 302.1862 $[M-BF_4]^+$ (C₁₇H₂₄N₃O₂⁺ requires 302.1869).

S10 – DFT Calculations

The energy as a function of dihedral angle N(1)-N(2)-C_{ipso}-C_{ortho} within the triazolium salt of interest was studied using Gaussian 09⁵⁸ on the Durham University Hamilton HPC.⁵⁹ The level of theory used was B3LYP/6-311++g (d,p) unless stated otherwise, using redundant internal coordinates, with solvent methanol and water being modelled using an implicit polarisable continuum model (PCM). Calculations were run using 5° steps starting from a dihedral angle of -180° towards +180°.

Calculations were performed on **6**, the monocationic pyrid-2-yl triazolium salt, alongside the proposed dications formed as a result of N(1) protonation (N1-dication) or pyrid-2-yl nitrogen protonation (pyridyl dication) (Figure S14).

Figure S14. Structures of pyrid-2-yl triazolium salts for which DFT calculations were undertaken of energies as a function of dihedral angle of the monocation, dication from N1 protonation (N1 dication) and dication from protonation of the pyrid-2-yl nitrogen (pyridyl dication).



The results from the calculations using PCM water are provided in the main paper. Figure S15 shows the equivalent calculations using PCM solvent methanol. M062X was used to quantify the barrier to rotation by an equivalent level functional to verify that all possible conformations are accessible and rapidly interchangeable, with the results in Figure S16.

Figure S15. Conformational profiles of monocationic *N*-5-methoxypyrid-2-yl **7** (—) and the two dicationic forms afforded from *N*-protonation of the triazolyl N(1) (—) or the pyridyl nitrogen (—) obtained by DFT calculations using B3LYP (6-311G++(d,p) basis set, PCM methanol).

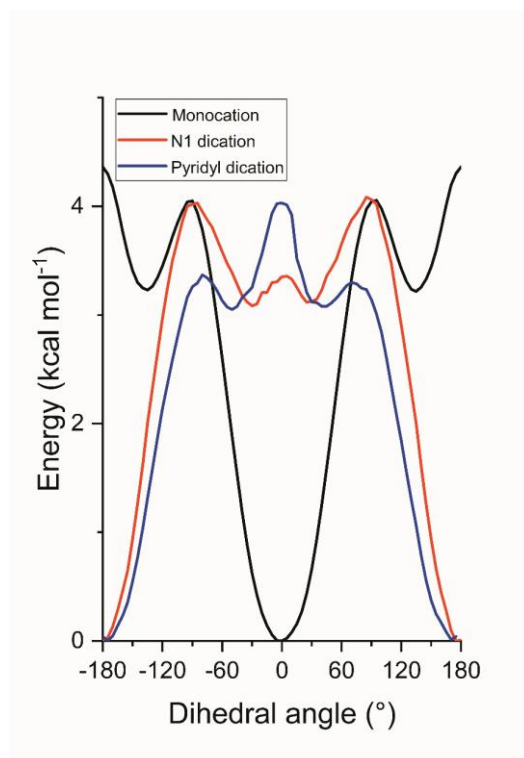
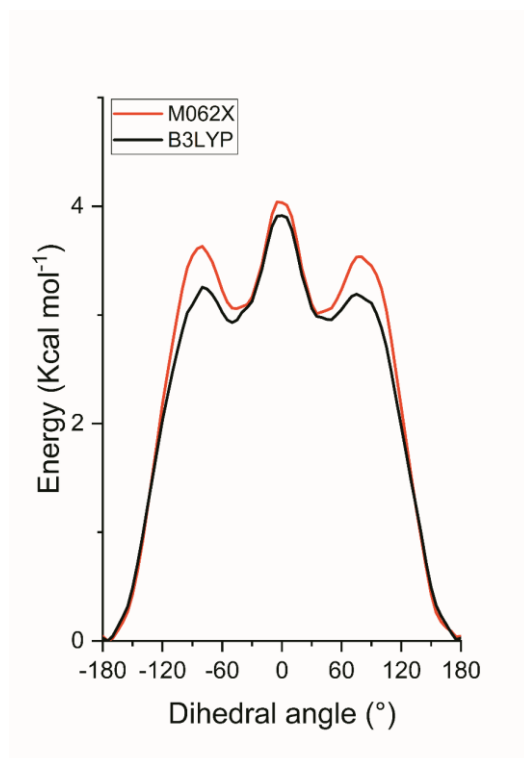


Figure S16. The effect of dihedral angle between *N*-aryl and triazolium ring on the calculated energy of the dication of **6** resulting from pyrid-2-yl nitrogen protonation obtained using B3LYP/6-311g++ (d,p) or M062X/6-311g++ (d,p) with PCM (water). Points are calculated energies with the solid curve an interpolation between the data points.

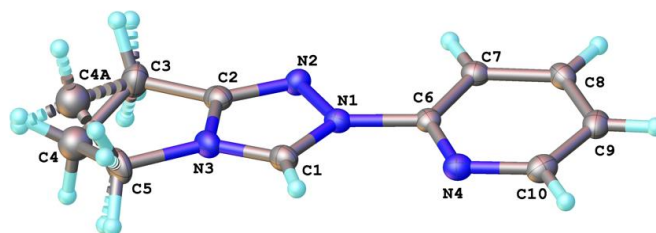


S11 – Single Crystal X-ray Crystallography

The X-ray single crystal data have been collected using $\lambda\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) on a Bruker D8Venture (Photon100 CMOS detector, I μ S-microsource, focusing mirrors; compound **6**) and Agilent XCalibur (Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator, compound **7**) diffractometers equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 120.0(2)K. Both structures were solved by direct method (ShelXS) and refined by full-matrix least squares on F^2 for all data using Olex2^{S10} and SHELXTL software^{S11}. All non-disordered non-hydrogen atoms were refined in anisotropic approximation, hydrogen atoms in structure **7** were refined isotropically. Hydrogen atoms in structure **6** were placed in calculated positions and refined in riding mode. Disordered atoms in structure **6** were refined isotropically with fixed SOFs 0.45 and 0.55. Crystal data and parameters of refinement are listed in Section S11.1 for **6** and S11.2 for **7**. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2100846-2100847.

S11.1 Crystal data and parameters of refinement for

N-(Pyrid-2-yl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium tetrafluoroborate (6)



Crystal data and structure refinement for 6.	
Empirical formula	C ₁₀ H ₁₁ BF ₄ N ₄ × BF ₄
Formula weight	274.04
Temperature/K	120.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	14.4010(7)
b/Å	6.6195(4)
c/Å	14.0719(7)
α/°	90
β/°	117.315(2)
γ/°	90
Volume/Å ³	1191.86(11)
Z	4
ρ _{calc} /g/cm ³	1.527
μ/mm ⁻¹	0.139
F(000)	560.0
Crystal size/mm ³	0.25 × 0.22 × 0.04
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.368 to 57.994
Index ranges	-19 ≤ h ≤ 19, -9 ≤ k ≤ 9, -18 ≤ l ≤ 19
Reflections collected	17743
Independent reflections	3160 [R _{int} = 0.0442, R _{sigma} = 0.0385]
Data/restraints/parameters	3160/6/171
Goodness-of-fit on F ²	1.039
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0508, wR ₂ = 0.1148
Final R indexes [all data]	R ₁ = 0.0787, wR ₂ = 0.1257
Largest diff. peak/hole / e Å ⁻³	0.88/-0.74

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 6 . U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(eq)$
F1	1224.9(8)	-599.0(16)	1970.8(9)	31.2(3)
F2	2825.9(8)	707.7(17)	3049.4(9)	29.8(3)
F3	1545.2(9)	2721.1(18)	1869(1)	43.8(4)
F4	1445.0(9)	1497(2)	3327.3(10)	45.5(4)
B1	1753.9(15)	1080(3)	2548.4(16)	22.5(4)
N1	3613.5(10)	6833(2)	4102.7(11)	17.3(3)
N2	3644.8(11)	7645(2)	5016.5(11)	19.2(3)
N3	2080.1(11)	6493(2)	3913.8(12)	21.9(3)
N4	4339.9(11)	6204(2)	2969.4(11)	20.3(3)
C1	2668.6(13)	6141(3)	3435.8(14)	20.8(4)
C2	2687.5(13)	7405(3)	4865.8(14)	21.3(4)
C3	2073.3(14)	7863(3)	5448.2(16)	29.5(4)
C4	932(2)	7622(5)	4565(2)	32.2(8)
C4A	1092(3)	6513(7)	4831(2)	32.5(10)
C5	980.4(13)	6237(3)	3694.2(16)	30.2(4)
C6	4518.3(12)	6849(2)	3930.3(13)	16.6(3)
C7	5464.8(13)	7503(2)	4734.1(13)	18.9(3)
C8	6302.4(13)	7473(2)	4503.8(14)	20.2(4)
C9	6152.8(14)	6809(3)	3512.4(14)	22.2(4)
C10	5164.5(14)	6198(3)	2774.0(14)	22.9(4)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 17srv371. The Anisotropic displacement factor exponent takes the form: - $2\pi^2[h^2a^2U_{11}+2hka^*b^*U_{12}+\dots]$.						
Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
F1	29.5(6)	26.2(6)	35.0(6)	-7.2(5)	12.2(5)	-4.9(4)
F2	18.1(5)	40.5(7)	28.0(6)	6.6(5)	8.3(4)	2.8(4)
F3	38.8(7)	27.4(6)	38.5(7)	9.4(5)	-5.2(6)	-2.5(5)
F4	27.7(6)	73.5(10)	35.4(7)	-20.2(7)	14.6(5)	2.5(6)
B1	18.0(9)	23.8(10)	23.5(10)	0.0(8)	7.7(8)	1.2(8)
N1	17.4(7)	14.5(7)	17.4(7)	0.1(5)	5.7(6)	-1.1(5)
N2	19.8(7)	20.0(7)	17.9(7)	-0.2(6)	8.7(6)	-2.3(5)
N3	15.9(7)	23.0(7)	23.5(7)	2.2(6)	6.3(6)	-2.6(6)
N4	22.6(7)	17.0(7)	20.0(7)	-0.5(6)	8.5(6)	-0.6(6)
C1	18.3(8)	19.9(8)	20.2(8)	0.6(7)	5.4(7)	-1.9(6)
C2	20.0(8)	19.3(8)	21.7(8)	3.7(7)	7.0(7)	-0.8(7)
C3	24.8(9)	37.4(11)	29.5(10)	0.5(8)	15.2(8)	-3.1(8)
C5	14.3(8)	33.8(10)	38.4(11)	0.2(9)	8.6(8)	-5.0(7)
C6	17.9(8)	12.3(7)	19.4(8)	1.8(6)	8.3(7)	0.1(6)
C7	20.3(8)	15.6(8)	18.7(8)	1.0(7)	7.1(7)	1.0(6)
C8	16.9(8)	16.6(8)	24.4(9)	1.5(7)	7.0(7)	-0.4(6)
C9	23.8(9)	17.5(8)	28.4(9)	3.4(7)	14.6(8)	2.5(7)
C10	29.4(9)	18.2(8)	22.7(9)	-0.4(7)	13.2(8)	0.6(7)

Bond Lengths for 6.						
Atom	Atom	Length/ $\text{\AA}$		Atom	Atom	Length/ $\text{\AA}$
F1	B1	1.381(2)		N4	C6	1.326(2)
F2	B1	1.394(2)		N4	C10	1.336(2)
F3	B1	1.386(2)		C2	C3	1.487(3)
F4	B1	1.387(2)		C3	C4	1.548(2)
N1	N2	1.3752(19)		C3	C4A	1.556(2)
N1	C1	1.330(2)		C4	C5	1.557(2)
N1	C6	1.431(2)		C4A	C5	1.544(2)
N2	C2	1.305(2)		C6	C7	1.382(2)
N3	C1	1.322(2)		C7	C8	1.385(2)
N3	C2	1.359(2)		C8	C9	1.382(2)
N3	C5	1.478(2)		C9	C10	1.383(2)

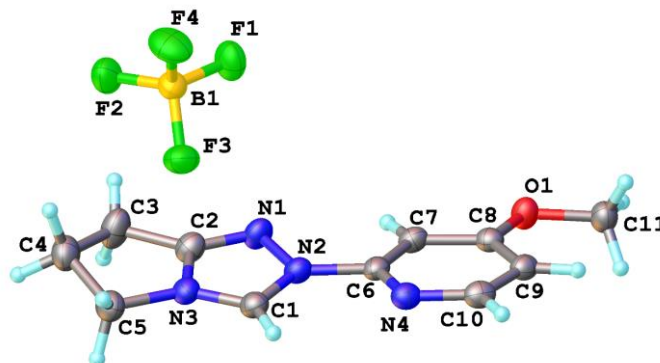
Bond Angles for 6.								
Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
F1	B1	F2	109.83(15)		N2	C2	C3	137.47(17)
F1	B1	F3	109.77(15)		N3	C2	C3	110.92(15)
F1	B1	F4	109.58(16)		C2	C3	C4	102.52(16)
F3	B1	F2	109.07(15)		C2	C3	C4A	101.11(18)
F3	B1	F4	110.03(16)		C3	C4	C5	106.19(19)
F4	B1	F2	108.54(15)		C5	C4A	C3	106.4(2)
N2	N1	C6	120.93(13)		N3	C5	C4	101.43(15)
C1	N1	N2	112.22(14)		N3	C5	C4A	100.22(17)
C1	N1	C6	126.81(14)		N4	C6	N1	113.91(14)
C2	N2	N1	102.80(14)		N4	C6	C7	126.33(16)
C1	N3	C2	107.87(14)		C7	C6	N1	119.77(15)
C1	N3	C5	138.51(16)		C6	C7	C8	116.21(16)
C2	N3	C5	113.59(15)		C9	C8	C7	119.44(16)
C6	N4	C10	115.87(15)		C8	C9	C10	118.79(16)
N3	C1	N1	105.50(15)		N4	C10	C9	123.36(16)
N2	C2	N3	111.61(16)					

Selected Torsion Angles for 6.										
A	B	C	D	Angle/°		A	B	C	D	Angle/°
N4	C6	N1	N2	-173.41(14)		C7	C6	N1	N2	6.5(2)
C1	N1	C6	N4	4.3(2)		C7	C6	N1	C1	-175.79(16)

Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 6 .				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H1	2460.49	5524.22	2758.68	25
H3AA	2208.73	9254.32	5738.41	35
H3AB	2234.98	6896.26	6040.47	35
H3BC	1885.45	9311.72	5395.4	35
H3BD	2457	7472.57	6211.09	35
H4A	631.01	8954.04	4257.71	39
H4B	495.93	6996.1	4860.2	39
H4AA	1184.21	5188.45	5189.66	39
H4AB	462.59	7174.99	4800.43	39
H5AA	824.56	4813.77	3783.39	36
H5AB	490.98	6699.74	2964.7	36
H5BC	710.74	4879.64	3403.56	36
H5BD	522.19	7281.39	3195.8	36
H7	5537.01	7947.5	5406.51	23
H8	6973.9	7905.89	5022.88	24
H9	6718.72	6772.22	3341.53	27
H10	5066.66	5750.88	2092.71	28

Atomic Occupancy for 6.							
Atom	Occupancy		Atom	Occupancy		Atom	Occupancy
H3AA	0.5		H3AB	0.5		H3BC	0.5
H3BD	0.5		C4	0.55		H4A	0.55
H4B	0.55		C4A	0.45		H4AA	0.45
H4AB	0.45		H5AA	0.5		H5AB	0.5
H5BC	0.5		H5BD	0.5			

S11.2 Crystal data and parameters of refinement for *N*-(5-methoxypyrid-2-yl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium tetrafluoroborate (7)



Crystal data and structure refinement for 7.	
Identification code	17srv192
Empirical formula	C ₁₁ H ₁₃ N ₄ O × BF ₄
Formula weight	304.06
Temperature/K	120.0
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> /Å	15.8326(8)
<i>b</i> /Å	6.1322(2)
<i>c</i> /Å	13.5284(5)
α /°	90
β /°	94.315(4)
γ /°	90
Volume/Å ³	1309.72(9)
<i>Z</i>	4
ρ_{calc} /cm ³	1.542
μ /mm ⁻¹	0.140
<i>F</i> (000)	624.0
Crystal size/mm ³	0.45 × 0.27 × 0.03
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.16 to 55.994
Index ranges	-18 ≤ <i>h</i> ≤ 20, -8 ≤ <i>k</i> ≤ 6, -17 ≤ <i>l</i> ≤ 15
Reflections collected	11121
Independent reflections	3157 [<i>R</i> _{int} = 0.0501, <i>R</i> _{sigma} = 0.0601]
Data/restraints/parameters	3157/0/242
Goodness-of-fit on <i>F</i> ²	1.036
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0469, <i>wR</i> ₂ = 0.0912
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0892, <i>wR</i> ₂ = 0.1111
Largest diff. peak/hole / e Å ⁻³	0.20/-0.20

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 7. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(eq)$
F1	7426.9(8)	1353(2)	6664.4(9)	47.4(4)
F2	5999.8(8)	1729(2)	6535.2(8)	48.3(4)
F3	6620.4(8)	-635.0(19)	5526.2(7)	43.3(4)
F4	6595.0(9)	-1382(2)	7158.0(8)	54.2(4)
B1	6662.5(16)	274(4)	6465.9(15)	32.4(5)
O1	10793.7(9)	3870(2)	4108.3(9)	31.8(3)
N1	7646.8(11)	3315(3)	4106.5(11)	32.8(4)
N2	7948.1(11)	1395(2)	3732.6(10)	27.1(4)
N3	6610.2(11)	1105(3)	3573.4(10)	28.9(4)
N4	9025.6(11)	-1039(3)	3496.3(10)	28.7(4)
C1	7321.0(13)	65(3)	3411.9(13)	28.9(5)
C2	6827.3(14)	3058(3)	3998.1(13)	31.9(5)
C3	6057.0(16)	4308(4)	4215(2)	44.9(6)
C4	5353.0(16)	2616(4)	4064.3(17)	40.0(6)
C5	5689.6(14)	727(4)	3464.2(15)	35.8(5)
C6	8837.3(13)	1007(3)	3725.4(12)	25.5(4)
C7	9395.4(14)	2673(3)	3945.1(13)	27.5(5)
C8	10252.7(13)	2191(3)	3918.7(12)	25.9(4)
C9	10495.2(14)	78(3)	3693.1(12)	27.6(4)
C10	9857.8(14)	-1435(3)	3487.8(13)	30.2(5)
C11	11680.4(14)	3454(4)	4025.3(16)	34.4(5)

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 7. The Anisotropic displacement factor exponent takes the form: - $2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.						
Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
F1	32.6(9)	48.3(8)	61.1(8)	-7.3(6)	1.8(6)	-7.1(6)
F2	37.7(9)	55.5(8)	51.0(7)	-9.9(6)	-0.3(6)	11.7(6)
F3	49.2(9)	49.0(8)	31.3(6)	-4.6(5)	1.2(5)	3.8(6)
F4	65.2(11)	56.4(9)	39.8(7)	19.0(6)	-5.0(6)	-9.6(7)
B1	31.0(15)	37.3(14)	28.8(11)	3.2(10)	1.2(10)	2.9(11)
O1	27.1(9)	29.1(8)	39.7(7)	-5.5(6)	5.2(6)	-1.9(6)
N1	32.3(12)	30.1(10)	36.9(9)	-7.7(7)	8.1(8)	0.6(8)
N2	28.9(11)	26.9(9)	25.7(7)	-3.4(7)	4.7(7)	-1.1(7)
N3	27.8(11)	33.3(9)	26.2(8)	1.0(7)	5.2(7)	-1.0(8)
N4	33.5(11)	26.0(9)	26.5(8)	0.4(7)	1.9(7)	0.5(7)
C1	30.1(13)	31.5(11)	25.5(9)	-1.1(8)	4.1(8)	-2.5(9)
C2	33.5(14)	28.9(11)	34.1(10)	-0.5(8)	8.0(9)	-2.3(9)
C3	36.0(16)	39.5(14)	60.9(16)	-8.6(12)	15.0(12)	1.4(11)
C4	31.4(15)	43.7(14)	45.1(13)	3.3(10)	4.5(10)	5.7(11)
C5	29.8(14)	42.8(14)	35.1(11)	1.1(10)	4.4(9)	-3.8(10)
C6	27.3(12)	29.3(11)	20.3(8)	0.7(7)	3.8(7)	1.4(8)
C7	32.7(13)	25.0(11)	25.3(9)	-1.9(8)	5.8(8)	-0.2(9)
C8	29.1(12)	27.3(11)	21.4(8)	0.5(7)	2.0(8)	-2.5(9)
C9	30.4(13)	28.4(11)	24.1(9)	0.4(8)	2.0(8)	4.5(9)
C10	38.2(14)	25.2(11)	27.4(9)	0.8(8)	2.9(8)	1.8(9)
C11	26.9(13)	38.8(13)	37.6(11)	-5(1)	3.1(9)	-1.6(10)

Bond Lengths for 7.						
Atom	Atom	Length/ $\text{\AA}$		Atom	Atom	Length/ $\text{\AA}$
F1	B1	1.388(3)		N3	C2	1.361(2)
F2	B1	1.386(3)		N3	C5	1.472(3)
F3	B1	1.385(2)		N4	C6	1.332(2)
F4	B1	1.391(2)		N4	C10	1.341(3)
O1	C8	1.351(2)		C2	C3	1.488(3)
O1	C11	1.440(3)		C3	C4	1.525(3)
N1	N2	1.381(2)		C4	C5	1.533(3)
N1	C2	1.304(3)		C6	C7	1.368(3)
N2	C1	1.332(2)		C7	C8	1.392(3)
N2	C6	1.428(3)		C8	C9	1.391(3)
N3	C1	1.326(2)		C9	C10	1.384(3)

Bond Angles for 7.								
Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
F1	B1	F4	109.14(18)		N1	C2	N3	111.78(18)
F2	B1	F1	109.50(19)		N1	C2	C3	137.7(2)
F2	B1	F4	109.13(17)		N3	C2	C3	110.6(2)
F3	B1	F1	110.51(17)		C2	C3	C4	103.02(19)
F3	B1	F2	109.68(18)		C3	C4	C5	107.76(19)
F3	B1	F4	108.86(18)		N3	C5	C4	102.04(17)
C8	O1	C11	117.27(15)		N4	C6	N2	113.34(17)
C2	N1	N2	102.97(16)		N4	C6	C7	126.98(19)
N1	N2	C6	120.81(16)		C7	C6	N2	119.68(17)
C1	N2	N1	111.82(17)		C6	C7	C8	116.81(18)
C1	N2	C6	127.37(16)		O1	C8	C7	116.01(17)
C1	N3	C2	107.59(18)		O1	C8	C9	124.72(19)
C1	N3	C5	138.91(18)		C9	C8	C7	119.26(19)
C2	N3	C5	113.44(17)		C10	C9	C8	117.4(2)
C6	N4	C10	114.21(17)		N4	C10	C9	125.38(19)
N3	C1	N2	105.85(17)					

Selected Torsion Angles for 7.									
A	B	C	D	Angle/°	A	B	C	D	Angle/°
N4	C6	N2	N1	169.55(14)	C4	C3	C2	N3	11.8(2)
C1	N2	C6	N4	-10.0(2)	C4	C5	N3	C1	167.2(2)
C1	N3	C2	N1	0.5(2)	C4	C5	N3	C2	-9.7(2)
C2	C3	C4	C5	-17.5(3)	C5	N3	C2	N1	178.36(16)
C3	C2	N3	C1	-179.18(17)	C7	C6	N2	N1	-10.3(2)
C3	C2	N3	C5	-1.4(2)	C7	C6	N2	C1	170.22(17)
C3	C4	C5	N3	16.6(2)	C7	C8	O1	C11	-176.20(16)
C4	C3	C2	N1	-167.8(2)	C9	C8	O1	C11	3.0(2)

Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for 7.				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H1	7419(13)	-1410(30)	3136(13)	41(6)
H3A	6140(15)	4880(40)	4822(15)	49(7)
H3B	5959(17)	5610(40)	3711(17)	76(8)
H4A	5185(16)	1990(40)	4716(16)	61(7)
H4B	4809(17)	3240(40)	3758(16)	64(8)
H5A	5476(15)	820(30)	2746(15)	52(6)
H5B	5525(15)	-800(40)	3692(14)	49(6)
H7	9199(12)	4030(30)	4088(12)	28(5)
H9	11087(14)	-340(30)	3644(13)	34(5)
H10	10003(13)	-2900(30)	3324(13)	37(6)
H11A	11768(14)	2760(30)	3371(14)	42(6)
H11B	11914(14)	2460(40)	4565(14)	44(6)
H11C	11990(14)	4890(40)	4096(14)	48(6)

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