Electronic Supporting Information

The Role of the Fused Ring in Bicyclic Triazolium Organocatalysts: Kinetic, X-ray and DFT Insights

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S1. Experimental

S1.1 General Instrumentation

**NMR:** NMR samples were prepared in deuterated chloroform and deuterium oxide. NMR spectra were recorded on Oxford Varian Unity Inova 300 and 500 MHz, Varian Unity 300 MHz, and Bruker Ultrashield 400 MHz NMR spectrometers. $^1$H and $^{13}$C NMR chemical shifts in CDCl$_3$ are reported relative to CHCl$_3$ at 7.27 ppm and 77.0 ppm respectively. In D$_2$O, $^1$H NMR chemical shifts are reported relative to HOD at 4.67 ppm. 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 spectrometry:** ($m/z$) 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.

**Melting points:** Melting points were determined using an electrothermal 9100 melting point apparatus.
S1.2 Materials

Deuterium oxide-d$_2$ (99.9 atom % D), deuterium chloride (35 wt %, 99 atom % D) were purchased from Goss Scientific Instruments Ltd. Chloroform-d$_1$ (99.8 atom % D) was purchased from Apollo Scientific, and Euriso-top. Unless stated, all other chemicals were reagent grade and used without further purification. Reactions involving air or moisture sensitive reagents were performed under an argon atmosphere using oven-dried glassware. Solvents were dried prior to use using an Innovative Technology Inc. solvent purification system.

S1.3 Syntheses of Triazolium Tetrafluoroborate Salts

Triazolium tetrafluoroborate salts 7a-d, 7g, 7i-k, 8b, 8i, 8k, and 9b, 9k were synthesized according to literature procedures, with all physical and spectroscopic data in agreement with the literature$^{S1}$.

Triazolium tetrafluoroborate salts 7e, 7f, 7h, 8a, 8c, 9a, and 9c were not reported previously; the syntheses of these compounds were adapted from the same literature procedures used above$^{S1}$, with their physical and spectroscopic data presented in the following sections.
General procedure for the preparation of Triazolium tetrafluoroborate salts 7e, 7f, 7h, 8a, 8c, 9a, and 9c:

Scheme S1. General synthetic procedure for triazolium salts 7e, 7f, 7h, 8a, 8c, 9a, and 9c.

Trimethyloxonium tetrafluoroborate (1.1 equiv; S1) was added to a solution of the relevant lactam (1 equiv; S2 (n=1) for 7e, 7f, 7h; S2 (n=2) for 8a, 8c; S2 (n=3) for 9a, 9c) in dichloromethane (30 mL per 1.00g lactam) and stirred for 24 h at r.t. under an inert atmosphere. The appropriate aryl hydrazine (1 equiv; S3) was added to the reaction mixture and stirred for a further 48 h at r.t. under an inert atmosphere to form the corresponding amidrazone (S4). The solvent was removed under reduced pressure, and the residue dissolved in triethylorthoformate (5 mL per 1 g; S5), and the reaction mixture was refluxed for 24 to 48 hours. Solvent was removed and the triazolium salts (S6) were purified by recrystallisation from DCM/Diethyl ether or MeOH/Diethyl ether.

X-ray diffraction structural analysis was performed for all 20 triazolium salts 7a-k, 8a-c, j, k and 9a-c, k and is reported in Section S1.6. The crystal structures of 7a, 7b, 7g, and 7k were previously reported but were re-determined by us for consistency in structural analysis across the full series.
Synthesis of 2-(3-chlorophenyl)-6,7-dihydro-5H-pyrrolo[2,1-c]triazol-2-ium tetrafluoroborate 7e

Triazolium tetrafluoroborate 7e was obtained as a pale yellow solid (3.83 g, 83 %); mp = 188-190 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 10.76 (s, 1H), 8.10 – 8.00 (m, 1H), 7.92 – 7.86 (m, 1H), 7.76 – 7.69 (m, 2H), 4.49 – 4.31 (m, 2H), 3.22 (dd, J = 8.2, 7.1 Hz, 2H), 2.84 – 2.66 (m, 2H); ¹³C{¹H} NMR (101 MHz, DMSO-d₆) δ 163.6, 139.5, 137.1, 134.8, 132.5, 130.8, 121.1, 119.9, 47.5, 27.1, 21.7.; HRMS (ESI) m/z: [M–BF₄]⁺ Calculated for C₁₁H₁₁N₃Cl 220.0642; Found 220.0638.

Synthesis of 2-(4-trifluoromethylphenyl)-6,7-dihydro-5H-pyrrolo[2,1-c]triazol-2-ium tetrafluoroborate 7f

Triazolium tetrafluoroborate 7f was obtained as a white solid (1.02 g, 72 %); mp = 216-218 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 10.84 (s, 1H), 8.28 – 7.99 (m, 4H), 4.44 (dd, J = 8.1, 6.6 Hz, 2H), 3.24 (dd, J = 8.2, 7.2 Hz, 2H), 2.83 – 2.70 (m, 2H). ¹³C{¹H} NMR (101 MHz, DMSO) δ 163.8, 139.7, 138.9, 131.2, 130.9, 130.5, 130.2, 128.1, 128.1, 128.1, 128.0, 125.4, 122.7, 121.9, 47.6, 27.1, 21.7. HRMS (ES⁺): [M–BF₄]⁺ C₁₂H₁₁N₃F₃ requires: 254.0905, found: 254.0903.

Synthesis of 2-(2,4,6-triisopropylphenyl)-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium chloride 7h

Triazolium tetrafluoroborate 7h was obtained as a pale yellow powder (0.45 g, 29 %); mp = 142-145 °C; ¹H NMR (700 MHz, DMSO-d₆) δ 10.37 (s, 1H), 7.27 (s, 2H), 4.44 (t, J = 7.4 Hz, 2H), 3.18 (t, J = 7.7 Hz, 2H), 2.98 (p, J = 6.9 Hz, 1H), 2.73 (p, J = 7.6 Hz, 2H), 2.37 (h, J =
6.7 Hz, 2H), 1.23 (d, J = 6.9 Hz, 6H), 1.14 (d, J = 6.8 Hz, 6H), 1.08 (d, J = 6.8 Hz, 6H);

\(^{13}\text{C}\{1\text{H}\} \text{NMR (176 MHz, DMSO-d}_6\} \delta 163.6, 153.1, 146.0, 142.2, 129.8, 122.6, 47.8, 34.2, 28.1, 26.7, 24.4, 24.2, 24.1, 21.9.}; \text{HRMS (ESI) } m/z: [M–BF}_4]^+ \text{ Calculated for } C_{20}H_{30}N_3 312.2440; \text{ Found 312.2433.}

**Synthesis of 2-(4-methoxyphenyl)-5,6,7,8-tetrahydro-[1,2,4]triazolo[4,3-a]pyridin-2-ium tetrafluoroborate 8a**

Triazolium tetrafluoroborate 8a was obtained as a white solid (1.05 g, 65%). mp = 190-192 °C;

\(^1\text{H NMR (400 MHz, Chloroform-d) } \delta 10.07 (s, 1H), 7.82 – 7.74 (m, 2H), 7.06 – 6.99 (m, 2H), 4.55 (t, J = 5.8 Hz, 2H), 3.88 (s, 3H), 3.13 (t, J = 6.2 Hz, 2H), 2.20 – 2.06 (m, 4H); \text{; } \text{^{13}\text{C}\{1\text{H}\} \text{NMR (101 MHz, Chloroform-d) } \delta 161.3, 152.9, 138.8, 126.9, 122.3, 115.3, 55.7, 46.2, 21.4, 21.2, 18.8.}; m/z (ES+): 230 ([M–BF}_4]^+, 100%). \text{HRMS (ESI) } m/z: [M–BF}_4]^+ \text{ Calculated for } C_{13}H_{16}N_3O 230.1293; \text{ Found 230.1290.}

**Synthesis of 2-(4-fluorophenyl)-5,6,7,8-tetrahydro-[1,2,4]triazolo[4,3-a]pyridin-2-ium tetrafluoroborate 8c**

Triazolium tetrafluoroborate 8c was obtained as a white solid (0.90 g, 49%). mp = 108-109 °C;

\(^1\text{H NMR (400 MHz, Chloroform-d) } \delta 9.99 (s, 1H), 7.89 – 7.76 (m, 2H), 7.26 – 7.13 (m, 2H), 4.48 (t, J = 5.7 Hz, 2H), 3.10 (t, J = 6.0 Hz, 2H), 2.11 (qd, J = 6.8, 6.2, 3.8 Hz, 4H); \text{; } \text{^{13}\text{C}\{1\text{H}\} \text{NMR (101 MHz, Chloroform-d) } \delta 164.6, 162.1, 153.2, 139.7, 131.3, 131.2, 123.2, 123.1, 117.2, 117.0, 46.1, 21.4, 21.0, 18.6.}; m/z (ES+): 304 ([M–BF}_4]^+, 100%). \text{HRMS (ESI) } m/z: [M–BF}_4]^+ \text{ Calculated for } C_{13}H_{16}N_3F 218.1094; \text{ Found 218.1093.}
Synthesis of 2-(4-methoxyphenyl)-6,7,8,9-tetrahydro-5H-[1,2,4]triazolo[4,3-a]azepin-2-ium tetrafluoroborate 9a

Triazolium tetrafluoroborate 9a was obtained as an off-white powder (0.73 g, 22%). mp = 148-152 °C; $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 10.09 (s, 1H), 7.84 – 7.73 (m, 2H), 7.08 – 6.99 (m, 2H), 4.56 (s, 2H), 3.88 (s, 3H), 3.26 – 3.05 (m, 2H), 2.02 (s, 4H), 1.90 (s, 2H); $^{13}$C {$^1$H} NMR (101 MHz, Chloroform-d) $\delta$ 161.1, 158.4, 140.0, 127.9, 122.3, 115.2, 55.7, 49.6, 29.7, 27.4, 26.1, 24.5.; $m/z$ (ES+): 244 ([M–BF$_4]^+$, 100%). HRMS (ESI) $m/z$: [M–BF$_4]^+$ Calculated for C$_{14}$H$_{18}$N$_3$O 244.1437; Found 244.1442.

Synthesis of 2-(4-fluorophenyl)-6,7,8,9-tetrahydro-5H-[1,2,4]triazolo[4,3-a]azepin-2-ium tetrafluoroborate 9c

Triazolium tetrafluoroborate 9c was obtained as a white solid (0.342 g, 11%). mp = 118-122 °C; $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 10.03 (s, 1H), 7.96 – 7.77 (m, 2H), 7.27 – 7.10 (m, 2H), 4.52 (t, $J = 4.1$ Hz, 2H), 3.29 – 3.05 (m, 2H), 1.99 (dt, $J = 5.6$, 2.7 Hz, 6H); $^{13}$C {$^1$H} NMR (101 MHz, Chloroform-d) $\delta$ 164.6, 162.1, 158.6, 140.9, 131.1, 131.0, 123.1, 123.0, 117.3, 117.0, 49.8, 29.6, 27.2, 26.1, 24.4.; HRMS (ESI) $m/z$: [M–BF$_4]^+$ Calculated for C$_{13}$H$_{15}$N$_3$F 232.1250; Found 232.1252.
S1.4 Deuterium Exchange and pKₐ Measurements

S1.4.1 Preparation of Solutions

The deuterium exchange reactions were monitored by ¹H NMR spectroscopy in D₂O solution, with the pD values of all the experiment in between 0.59 – 3.50. The solution pD values were controlled by DCl or acetic acid buffer, and the internal standard, tetramethylammonium deuteriosulfate, were used to monitor the potential decomposition of the triazolium salts. KCl was used to control the ionic strength, I = 1.0.

S1.4.2 Measurement of pD in D₂O Solution and Determination of [DO⁻]

The pH values of buffer solutions were determined at 25 °C using a MeterLabTM PHM 290 pH-Stat Controller equipped with a radiometer (pH 1.68 - 4.00 @ 25 °C) combination electrode, that could be standardised between pH 1.68 – 4.00 to encompass the pH of the buffer solution. All the solutions were incubated in a thermostated water bath with temperature at 25 ± 0.1 °C.

The pD (± 0.03) was calculated by adding 0.4 to the observed reading of the pH meter in the D₂O solution. The concentration of deuteroxide, [DO⁻] (M), was calculated using Eq s1, where $K_w = 10^{-14.87}$ M² is the ion product of D₂O at 25 °C. The apparent activity coefficient of deuteroxide ion, $\gamma_{DO} = 0.73$, was determined from the measured pH of solutions of known [OH⁻] in water at I = 1.0 (KCl) at 25 °C, with the assumption that $\gamma_{DO} = \gamma_{HO}$. For these measurements, the pH apparatus was standardized at 7.00 and at 12.47 with calcium hydroxide that was saturated at 21 °C. The pD values for each experiment were recorded at the beginning and end of reactions, and were found to be constant within error (± 0.03).
\[ [DO^-] = \frac{(10^{pD-pKW})}{y_{DO}} \]  

\[(s1)\]

S1.4.3 NMR Parameters

\( ^1H \) NMR spectra of triazolium ions 7-9 were recorded on either Varian 400 or Oxford Varian Inova 500 MHz spectrometers. Spectra were run with 32 transients and a relaxation delay of 20 sec, sweep width of 8298.76 Hz, acquisition time of 4 sec and a 90° pulse angle. The total running time for each spectrum equals to 12 min 48 sec. The \( ^1H \) NMR spectral baselines were subject to a first-order drift correction before integration of the peak areas.

S1.4.4 Determination of Rate Constants for Deuteroxide-Catalyzed Exchange in Water

Deuterium exchange reactions were monitored in buffered D\(_2\)O solutions for triazolium salts 7a-c, 7k, 8a-c, 8k, 9a-c, 9k. A deuterium exchange study of 7a-c, 7k has been previously reported by us as part of a larger study,\(^{54}\) however, these experiments were repeated herein to demonstrate reproducibility and for consistency in analysis. Hydrogen-deuterium exchange of the C(3)-H results in a decrease of the singlet due to the C(3)-H of triazolium salts at ~10 ppm relative to the broad triplet at 3.3 ppm due to the methyl hydrogens of internal standard, tetramethylammonium deuterosulphate. Substrate and product peak areas were compared with the peak of internal standard to confirm that no parallel reactions including hydrolysis or decomposition of triazolium salt substrates were occurring under our conditions. Values for the fraction of remaining substrate could be calculated using Eq s2 by comparing the intergrated areas of the singlet due to the C(3)-H \((A_{C(3)-H})\) with those of the internal standard.
The observed first order rate constant for deuterium exchange, $k_{\text{ex}}$ (s$^{-1}$), at a given p$D$ could be obtained as the slope of a semilogarithmic plot of the fraction of remaining substrate against time according to Eq s3. For triazolium salts 7a-c, 8a-c, 9a-c, good linear fits of log $k_{\text{ex}}$ – p$D$ data to Eq 2 are observed whereas data for pentafluorophenyl triazolium salts 7k, 8k and 9k instead show excellent fits to Eq 3 (main manuscript).

\[
f(s) = \frac{(A_{C(3)-H}/A_{\text{std}})_{t}}{(A_{C(3)-H}/A_{\text{std}})_{0}}
\]

\[
\ln f(s) = -k_{\text{ex}}t
\]  

**S1.4.4.1 Representative $^1$H NMR Spectral Overlays of C(3)-H/D Exchange**

For triazolium salts 7-9a, 7-9b, 7-9c and 7-9k, representative $^1$H NMR spectral overlays are presented below showing the progress of C(3)-H/D exchange at one p$D$ value in each case. For a given N-aryl substituent (e.g. N-Ar = 4-methoxyphenyl for 7-9a), the closely similar p$D$ values are chosen for the representative spectral overlays to enable a comparison of the effect of fused ring size on the progress of C(3)-H/D exchange.
Figure S1. Representative $^1$H NMR spectra at 400MHz of triazolium salt 7a (10mM, pD 1.78), obtained during exchange of C(3)-H (s, 9.99 ppm) for deuterium in D$_2$O at 25 ºC and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S2. Representative $^1$H NMR spectra at 400MHz of triazolium salt 8a (10mM, pD 1.78), obtained during exchange of C(3)-H (s, 10 ppm) for deuterium in D$_2$O at 25 ºC and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S3. Representative $^1$H NMR spectra at 400MHz of triazolium salt $9a$ (10mM, $p$D 1.79), obtained during exchange of C(3)-H (s, 10 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S4. Representative $^1$H NMR spectra at 400MHz of triazolium salt 7b (10mM, pD 1.77), obtained during exchange of C(3)-H (s, 10.1 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S5. Representative $^1$H NMR spectra at 400MHz of triazolium salt 8b (10mM, pD 1.69), obtained during exchange of C(3)-H (s, 10.1 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S6. Representative $^1$H NMR spectra at 400MHz of triazolium salt 9b (10mM, pD 1.73), obtained during exchange of C(3)-H (s, 10.2 ppm) for deuterium in D$_2$O at 25 ºC and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S7. Representative $^1$H NMR spectra at 400MHz of triazolium salt 7c (10mM, pD 1.77), obtained during exchange of C(3)-H (s, 10.1 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S8. Representative $^1$H NMR spectra at 400MHz of triazolium salt 8c (10mM, pD 2.29), obtained during exchange of C(3)-H (s, 10.1 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S9. Representative $^1$H NMR spectra at 400MHz of triazolium salt 9c (10mM, pD 1.99), obtained during exchange of C(3)-H (s, 10.1 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S10. Representative $^1$H NMR spectra at 400MHz of triazolium salt 7k (10mM, pD 1.58), obtained during exchange of C(3)-H (s, 10 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S11. Representative $^1$H NMR spectra at 400MHz of triazolium salt $8k$ (10mM, pD 1.58), obtained during exchange of C(3)-H (s, 10 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]
Figure S12. Representative $^1$H NMR spectra at 400MHz of triazolium salt 9k (10mM, pD 1.56), obtained during exchange of C(3)-H (s, 10 ppm) for deuterium in D$_2$O at 25 °C and I = 1.0 M (KCl). [Internal standard, tetramethylammonium deuteriosulfate (s, 3.17 ppm)]

S1.4.4.2 Semilogarithmic Plots of $f(s)$ versus Time

For triazolium salts 7-9a, 7-9b, 7-9c and 7-9k, all semilogarithmic plots of the fraction of unexchanged substrate ($f(s)$) versus time at different pD values are included below. The observed first order rate constant for deuterium exchange, $k_{ex}$ (s$^{-1}$), at a given pD could be obtained as the slope of the semilogarithmic plot of the fraction of remaining substrate against time according to Eq s3.
Figure S13. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 7a in solutions of DCl in D$_2$O at 25 °C and I = 1.0 M (KCl).

Figure S14. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 8a in solutions of DCl in D$_2$O at 25 °C and I = 1.0 M (KCl).
Figure S15. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 9a in solutions of DCl in D2O at 25 ºC and I = 1.0 M (KCl).

\[ y = -1.37E-07x + 5.18E-04 \]
\[ R^2 = 0.999 \]
\[ y = -3.51E-07x + 1.20E-02 \]
\[ R^2 = 0.992 \]
\[ y = -8.66E-07x + 9.99E-03 \]
\[ R^2 = 0.988 \]
\[ y = -2.70E-06x - 5.17E-01 \]
\[ R^2 = 0.998 \]
\[ y = -7.62E-06x + 4.87E-03 \]
\[ R^2 = 0.997 \]
\[ y = -3.06E-05x + 6.75E-03 \]
\[ R^2 = 0.999 \]
\[ y = -9.70E-05x - 3.05E-03 \]
\[ R^2 = 0.999 \]

Figure S16. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 7b in solutions of DCl in D2O at 25 ºC and I = 1.0 M (KCl).

\[ y = -5.99E-07x - 1.94E-03 \]
\[ R^2 = 0.999 \]
\[ y = -1.31E-06x - 3.20E-04 \]
\[ R^2 = 0.982 \]
\[ y = -3.01E-06x + 1.35E-03 \]
\[ R^2 = 0.999 \]
\[ y = -6.68E-06x + 1.45E-03 \]
\[ R^2 = 0.999 \]
\[ y = -1.33E-05x - 9.72E-03 \]
\[ R^2 = 0.999 \]
\[ y = -2.36E-05x + 2.25E-02 \]
\[ R^2 = 0.999 \]
\[ y = -4.01E-05x + 5.65E-02 \]
\[ R^2 = 0.999 \]
\[ y = -5.14E-05x - 3.44E-02 \]
\[ R^2 = 0.999 \]
Figure S17. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 8b in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

Figure S18. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 9b in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).
Figure S19. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 7c in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

Figure S20. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 8c in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).
Figure S21. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 9c in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

Figure S22. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 7k in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).
Figure S23. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 8k in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

Figure S24. Semilogarithmic plots of the fraction of unexchanged substrate against time for the deuterium exchange reaction of 9k in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).
S1.4.4.3  Log $k_{ex} - pD$ Profiles for 7a-c, 8a-c and 9a-c

For triazolium salts 7a-c, 8a-c and 9a-c, good linear fits of log $k_{ex} - pD$ data to Eq 2 (main manuscript) are observed. The log $k_{ex} - pD$ profiles are included below for 7-9a, 7-9b and 7-9c showing fits to Eq 2 (Figures S25-27, respectively).

Figure S25. Plot of log $k_{ex}$ against pD for the C(3)-H/D exchange reaction of triazolium salt 7-9a in solutions of DCl in D$_2$O at 25 °C and I = 1.0 M (KCl).
Figure S26. Plot of $\log k_{ex}$ against $pD$ for the C(3)-H/D exchange reaction of triazolium salt 7-9b in solutions of DCl in D$_2$O at 25 °C and I = 1.0 M (KCl).

![Graph](image)

- Fitting with slope fixed = 1
  - $y = x - 6.90$ \( R^2 = 0.999 \)
  - $y = x - 7.15$ \( R^2 = 0.996 \)
  - $y = x - 7.18$ \( R^2 = 0.996 \)

- Fitting without restriction
  - $y = 0.99x - 6.89$ \( R^2 = 0.999 \)
  - $y = 1.03x - 7.20$ \( R^2 = 0.997 \)
  - $y = 1.02x - 7.21$ \( R^2 = 0.997 \)

Figure S27. Plot of $\log k_{ex}$ against $pD$ for the C(3)-H/D exchange reaction of triazolium salt 7-9c in solutions of DCl in D$_2$O at 25 °C and I = 1.0 M (KCl).

![Graph](image)

- Fitting with slope fixed = 1
  - $y = x - 6.80$ \( R^2 = 0.992 \)
  - $y = x - 7.04$ \( R^2 = 0.993 \)
  - $y = x - 7.04$ \( R^2 = 0.996 \)

- Fitting without restriction
  - $y = 1.06x - 6.89$ \( R^2 = 0.995 \)
  - $y = 1.05x - 7.12$ \( R^2 = 0.995 \)
  - $y = 1.06x - 7.13$ \( R^2 = 0.999 \)

**S1.4.4.4 Log $k_{ex}$ – pD Profiles for 7k, 8k and 9k**

Log $k_{ex}$ – pD data for pentafluorophenyl triazolium salts 7k, 8k and 9k do not fit to Eq 2 and instead show excellent fits to Eq 3 (main manuscript). The log $k_{ex}$ – pD profiles are included...
below for 7k, 8k and 9k showing fits to equation 3 (solid lines). The altered dependence of $k_{ex}$ on pD as the pD decreases is consistent with the onset of alternative pathways for deuterium exchange, which we have discussed in detail previously.\textsuperscript{54-55} The most likely mechanistic explanation, as discussed previously for 7k,\textsuperscript{54} is a pathway via N(1)-deuteration at lower pD values allowing for hydrogen-deuterium exchange of the N(1)-deuterated dicationic triazolium salt (Scheme S2).

Figure S28. Plot of log $k_{ex}$ against pD for the H/D exchange reaction of triazolium salt 7-9k in solutions of DCl in D\textsubscript{2}O at 25 °C and I = 1.0 M (KCl).

\begin{align*}
K_{aN1}^{Dk} &= 0.35 \text{ M} \\
K_{aN1}^{Dk} &= 7.37 \times 10^{8} \text{ M}^{-1}\text{s}^{-1} \\
k_{D0}^{k} &= 7.37 \times 10^{8} \text{ M}^{-1}\text{s}^{-1} \\
k_{D0}^{k} &= 4.04 \times 10^{9} \text{ M}^{-1}\text{s}^{-1} \\
K_{aN1}^{Dk} &= 0.55 \text{ M} \\
k_{D0}^{k} &= 7.87 \times 10^{9} \text{ M}^{-1}\text{s}^{-1} \\
k_{D0}^{k} &= 4.16 \times 10^{9} \text{ M}^{-1}\text{s}^{-1} \\
K_{aN1}^{Dk} &= 0.352 \text{ M} \\
k_{D0}^{k} &= 7.87 \times 10^{9} \text{ M}^{-1}\text{s}^{-1} \\
k_{D0}^{k} &= 4.16 \times 10^{9} \text{ M}^{-1}\text{s}^{-1}
\end{align*}
Scheme S2. Mechanisms of C(3)-H/D exchange for 7k, 8k and 9k (tetrafluorborate counterion excluded for clarity).

S1.4.4.5 Reaction Data, First Order Rate Constants for Exchange ($k_{ex}$, s$^{-1}$) and Second Order Rate Constants for Exchange ($k_{DO}$, M$^{-1}$s$^{-1}$)

Table S1. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 7a for deuterium in solutions of DCl in D$_2$O at 25 °C and I = 1.0 M (KCl).

| pD  | [DO$^-$], M  | $k_{ex}$, s$^{-1}$ | $k_{DO}$, M$^{-1}$s$^{-1}$ |
|-----|--------------|-------------------|--------------------------|
| 0.73| $9.92 \times 10^{-15}$ | $3.19 \times 10^{-7}$ |
| 1.00| $1.85 \times 10^{-14}$ | $8.72 \times 10^{-7}$ |
| 1.27| $3.44 \times 10^{-14}$ | $1.77 \times 10^{-6}$ |
| 1.78| $1.11 \times 10^{-13}$ | $4.65 \times 10^{-6}$ | $4.55 \times 10^{-7}$b |
| 2.20| $2.93 \times 10^{-13}$ | $1.50 \times 10^{-5}$ |
| 3.00| $1.85 \times 10^{-12}$ | $5.91 \times 10^{-5}$ |
| 3.43| $4.97 \times 10^{-12}$ | $1.89 \times 10^{-4}$ |

$^a$First order rate constants for C(3)-H/D exchange ($k_{ex}$, s$^{-1}$) were obtained as the slopes of plots shown in Figure S13. $^b$The second-order rate constant ($k_{DO}$, M$^{-1}$s$^{-1}$) was obtained from the fit of log $k_{ex}$ – pD data to Eq 2 (Figure S25).
Table S2. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 8a for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

| pD   | [DO⁻], M   | kex, s⁻¹<sup>a</sup> | kDO, M⁻¹s⁻¹<sup>b</sup> |
|------|------------|----------------------|--------------------------|
| 0.70 | 9.26 × 10⁻¹⁵ | 1.54 × 10⁻⁷          |                          |
| 1.00 | 1.85 × 10⁻¹⁴ | 3.72 × 10⁻⁷          |                          |
| 1.27 | 3.44 × 10⁻¹⁴ | 9.35 × 10⁻⁷          |                          |
| 1.78 | 1.11 × 10⁻¹³ | 2.52 × 10⁻⁶          | 2.11 × 10⁷               |
| 2.21 | 2.99 × 10⁻¹³ | 8.50 × 10⁻⁶          |                          |
| 3.02 | 1.93 × 10⁻¹² | 3.26 × 10⁻⁵          |                          |
| 3.40 | 4.64 × 10⁻¹² | 1.02 × 10⁻⁴          |                          |

<sup>a</sup>First order rate constants for C(3)-H/D exchange (kex, s⁻¹) were obtained as the slopes of plots shown in Figure S14. <sup>b</sup>The second-order rate constant (kDO, M⁻¹s⁻¹) was obtained from the fit of log kex – pD data to Eq 2 (Figure S25).

Table S3. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 9a for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

| pD   | [DO⁻], M   | kex, s⁻¹<sup>a</sup> | kDO, M⁻¹s⁻¹<sup>b</sup> |
|------|------------|----------------------|--------------------------|
| 0.72 | 9.70 × 10⁻¹⁵ | 1.37 × 10⁻⁷          |                          |
| 1.02 | 1.93 × 10⁻¹⁴ | 3.51 × 10⁻⁷          |                          |
| 1.27 | 3.44 × 10⁻¹⁴ | 8.66 × 10⁻⁷          |                          |
| 1.79 | 1.14 × 10⁻¹³ | 2.69 × 10⁻⁶          | 2.01 × 10⁷               |
| 2.20 | 2.93 × 10⁻¹³ | 7.62 × 10⁻⁶          |                          |
| 3.00 | 1.85 × 10⁻¹² | 3.06 × 10⁻⁵          |                          |
| 3.50 | 5.84 × 10⁻¹² | 9.70 × 10⁻⁵          |                          |

<sup>a</sup>First order rate constants for C(3)-H/D exchange (kex, s⁻¹) were obtained as the slopes of plots shown in Figure S15. <sup>b</sup>The second-order rate constant (kDO, M⁻¹s⁻¹) was obtained from the fit of log kex – pD data to Eq 2 (Figure S25).
Table S4. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 7b for deuterium in solutions of DC1 in D2O at 25 ºC and I = 1.0 M (KCl).

| pD  | [DO\textsuperscript{−}], M | $k_{ex}$, s\textsuperscript{-1}\textsuperscript{a} | $k_{DO}$, M\textsuperscript{-1}s\textsuperscript{-1} |
|-----|-----------------|-----------------|-----------------|
| 0.66| 8.45 \times 10\textsuperscript{-15} | 5.99 \times 10\textsuperscript{7} |                      |
| 1.01| 1.89 \times 10\textsuperscript{-14} | 1.31 \times 10\textsuperscript{6} |                      |
| 1.38| 4.43 \times 10\textsuperscript{-14} | 3.01 \times 10\textsuperscript{6} |                      |
| 1.77| 1.09 \times 10\textsuperscript{-13} | 6.68 \times 10\textsuperscript{6} | 6.99 \times 10\textsuperscript{7} \textsuperscript{b} |
| 2.05| 2.07 \times 10\textsuperscript{-13} | 1.33 \times 10\textsuperscript{5} |                      |
| 2.26| 3.36 \times 10\textsuperscript{-13} | 2.36 \times 10\textsuperscript{5} |                      |
| 2.50| 5.84 \times 10\textsuperscript{-13} | 4.01 \times 10\textsuperscript{5} |                      |
| 2.58| 7.03 \times 10\textsuperscript{-13} | 4.90 \times 10\textsuperscript{5} |                      |

\textsuperscript{a}First order rate constants for C(3)-H/D exchange ($k_{ex}$, s\textsuperscript{-1}) were obtained as the slopes of plots shown in Figure S16. \textsuperscript{b}The second-order rate constant ($k_{DO}$, M\textsuperscript{-1}s\textsuperscript{-1}) was obtained from the fit of log $k_{ex}$ – pD data to Eq 2 (Figure S26).

Table S5. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 8b for deuterium in solutions of DC1 in D2O at 25 ºC and I = 1.0 M (KCl).

| pD  | [DO\textsuperscript{−}], M | $k_{ex}$, s\textsuperscript{-1}\textsuperscript{a} | $k_{DO}$, M\textsuperscript{-1}s\textsuperscript{-1} |
|-----|-----------------|-----------------|-----------------|
| 0.61| 7.53 \times 10\textsuperscript{-15} | 2.78 \times 10\textsuperscript{7} |                      |
| 0.98| 1.76 \times 10\textsuperscript{-14} | 6.69 \times 10\textsuperscript{7} |                      |
| 1.41| 4.75 \times 10\textsuperscript{-14} | 1.57 \times 10\textsuperscript{6} |                      |
| 1.69| 9.05 \times 10\textsuperscript{-14} | 3.69 \times 10\textsuperscript{6} | 3.43 \times 10\textsuperscript{7} \textsuperscript{b} |
| 2.05| 2.07 \times 10\textsuperscript{-13} | 7.33 \times 10\textsuperscript{6} |                      |
| 2.21| 2.99 \times 10\textsuperscript{-13} | 1.29 \times 10\textsuperscript{5} |                      |
| 2.45| 5.21 \times 10\textsuperscript{-13} | 2.15 \times 10\textsuperscript{5} |                      |

\textsuperscript{a}First order rate constants for C(3)-H/D exchange ($k_{ex}$, s\textsuperscript{-1}) were obtained as the slopes of plots shown in Figure S17. \textsuperscript{b}The second-order rate constant ($k_{DO}$, M\textsuperscript{-1}s\textsuperscript{-1}) was obtained from the fit of log $k_{ex}$ – pD data to Eq 2 (Figure S26).
### Table S6. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 9b for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

| pD   | [DO⁻], M       |  \( k_{ex}, s^{-1} \) |  \( k_{DO}, M^{-1}s^{-1} \) |
|------|---------------|----------------|-----------------|
| 0.59 | \( 7.18 \times 10^{-15} \) | 2.61 \( \times 10^{-7} \) |  |
| 1.01 | \( 1.89 \times 10^{-14} \) | 6.52 \( \times 10^{-7} \) |  |
| 1.41 | \( 4.74 \times 10^{-14} \) | 1.55 \( \times 10^{6} \) |  |
| 1.73 | \( 9.92 \times 10^{-14} \) | 3.50 \( \times 10^{6} \) | 3.29 \( \times 10^{7} \)^b |
| 2.05 | \( 2.07 \times 10^{-13} \) | 6.74 \( \times 10^{6} \) |  |
| 2.29 | \( 3.60 \times 10^{-13} \) | 1.29 \( \times 10^{5} \) |  |
| 2.40 | \( 4.64 \times 10^{-13} \) | 2.02 \( \times 10^{5} \) |  |
| 2.58 | \( 7.03 \times 10^{-13} \) | 3.01 \( \times 10^{5} \) |  |

^a First order rate constants for C(3)-H/D exchange (\( k_{ex}, s^{-1} \)) were obtained as the slopes of plots shown in Figure S18. ^b The second-order rate constant (\( k_{DO}, M^{-1}s^{-1} \)) was obtained from the fit of log \( k_{ex} \) – pD data to Eq 2 (Figure S26).

### Table S7. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 7c for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

| pD   | [DO⁻], M       |  \( k_{ex}, s^{-1} \) |  \( k_{DO}, M^{-1}s^{-1} \) |
|------|---------------|----------------|-----------------|
| 0.77 | \( 1.09 \times 10^{-14} \) | 6.94 \( \times 10^{7} \) |  |
| 1.03 | \( 1.98 \times 10^{-14} \) | 1.70 \( \times 10^{6} \) |  |
| 1.34 | \( 4.04 \times 10^{-14} \) | 3.84 \( \times 10^{6} \) |  |
| 1.71 | \( 9.47 \times 10^{-14} \) | 8.75 \( \times 10^{6} \) | 8.97 \( \times 10^{7} \)^b |
| 2.00 | \( 1.85 \times 10^{-13} \) | 1.74 \( \times 10^{5} \) |  |
| 2.27 | \( 3.44 \times 10^{-13} \) | 3.03 \( \times 10^{5} \) |  |
| 2.44 | \( 5.09 \times 10^{-13} \) | 4.58 \( \times 10^{5} \) |  |

^a First order rate constants for C(3)-H/D exchange (\( k_{ex}, s^{-1} \)) were obtained as the slopes of plots shown in Figure S19. ^b The second-order rate constant (\( k_{DO}, M^{-1}s^{-1} \)) was obtained from the fit of log \( k_{ex} \) – pD data to Eq 2 (Figure S27).
Table S8. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 8c for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

| pD  | [DO⁻], M   | \(k_{\text{ex}}, \text{s}^{-1}\)^{a} | \(k_{\text{DO}}, \text{M}^{-1}\text{s}^{-1}\) |
|-----|-------------|----------------------------------------|----------------------------------------|
| 0.66| \(8.44 \times 10^{-15}\) | \(3.24 \times 10^{-7}\) | \(4.01 \times 10^{-7}\) |
| 1.01| \(1.89 \times 10^{-14}\) | \(8.82 \times 10^{-7}\) | \(2.10 \times 10^{-6}\) |
| 1.35| \(4.13 \times 10^{-14}\) | \(2.09 \times 10^{-6}\) | \(9.75 \times 10^{-6}\) |
| 1.67| \(8.64 \times 10^{-14}\) | \(4.93 \times 10^{-6}\) | \(5.00 \times 10^{-7}\)^{b} |
| 1.97| \(1.72 \times 10^{-13}\) | \(9.75 \times 10^{-6}\) | \(9.75 \times 10^{-6}\) |
| 2.29| \(3.60 \times 10^{-13}\) | \(1.74 \times 10^{-5}\) | \(2.10 \times 10^{-6}\) |
| 2.48| \(5.58 \times 10^{-13}\) | \(2.71 \times 10^{-5}\) | \(9.75 \times 10^{-6}\) |

\(^{a}\)First order rate constants for C(3)-H/D exchange (\(k_{\text{ex}}, \text{s}^{-1}\)) were obtained as the slopes of plots shown in Figure S20. \(^{b}\)The second-order rate constant (\(k_{\text{DO}}, \text{M}^{-1}\text{s}^{-1}\)) was obtained from the fit of log \(k_{\text{ex}} - pD\) data to Eq 2 (Figure S27).

Table S9. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 9c for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

| pD  | [DO⁻], M   | \(k_{\text{ex}}, \text{s}^{-1}\)^{a} | \(k_{\text{DO}}, \text{M}^{-1}\text{s}^{-1}\) |
|-----|-------------|----------------------------------------|----------------------------------------|
| 0.72| \(9.70 \times 10^{-15}\) | \(4.01 \times 10^{-7}\) | \(4.39 \times 10^{-7}\)^{b} |
| 1.00| \(1.85 \times 10^{-14}\) | \(8.40 \times 10^{-7}\) | \(2.10 \times 10^{-6}\) |
| 1.34| \(4.04 \times 10^{-14}\) | \(2.10 \times 10^{-6}\) | \(4.67 \times 10^{-6}\) |
| 1.68| \(8.84 \times 10^{-14}\) | \(4.67 \times 10^{-6}\) | \(4.67 \times 10^{-6}\) |
| 1.99| \(1.80 \times 10^{-13}\) | \(9.17 \times 10^{-6}\) | \(2.80 \times 10^{-5}\) |
| 2.45| \(5.20 \times 10^{-13}\) | \(2.80 \times 10^{-5}\) | \(2.80 \times 10^{-5}\) |

\(^{a}\)First order rate constants for C(3)-H/D exchange (\(k_{\text{ex}}, \text{s}^{-1}\)) were obtained as the slopes of plots shown in Figure S21. \(^{b}\)The second-order rate constant (\(k_{\text{DO}}, \text{M}^{-1}\text{s}^{-1}\)) was obtained from the fit of log \(k_{\text{ex}} - pD\) data to Eq 2 (Figure S27).
Table S10. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 7k for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

| pD    | [DO⁻], M  | kₑ, s⁻¹ | Results of Fitting to Eq 3 |
|-------|-----------|----------|----------------------------|
| 0.48  | 5.58 x 10⁻¹⁵ | 3.62 x 10⁻⁵   |                            |
| 0.67  | 8.64 x 10⁻¹⁵ | 5.16 x 10⁻⁵   |                            |
| 0.93  | 1.57 x 10⁻¹⁴ | 5.82 x 10⁻⁵   | k₉D = 3.52 x 10⁸ M⁻¹s⁻¹ b   |
| 1.32  | 3.86 x 10⁻¹⁴ | 7.34 x 10⁻⁵   | k′₉D = 1.38 x 10¹⁰ M⁻¹s⁻¹ c  |
| 1.58  | 7.03 x 10⁻¹⁴ | 8.83 x 10⁻⁵   | k₉N₁ = 0.35 M d             |
| 1.76  | 1.06 x 10⁻¹³ | 1.09 x 10⁻⁴   |                            |
| 2.39  | 4.53 x 10⁻¹³ | 2.29 x 10⁻⁴   |                            |

*a* First order rate constants for C(3)-H/D exchange (kₑ, s⁻¹) were obtained as the slopes of plots shown in Figure S22. *b* The second-order rate constant (k₉D, M⁻¹s⁻¹) was obtained from the fit of log kₑ - pD data to Eq 3 (Figure S28). *c* Values of k′₉D (M⁻¹s⁻¹) obtained by fitting log kₑ - pD data to equation 3 (Figure S28). *d* Values of KₙN₁ (M) obtained by fitting log kₑ - pD data to equation 3 (Figure S28).

Table S11. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 8k for deuterium in solutions of DCl in D₂O at 25 °C and I = 1.0 M (KCl).

| pD    | [DO⁻], M  | kₑ, s⁻¹ | Results of Fitting to Eq 3 |
|-------|-----------|----------|----------------------------|
| 0.45  | 5.21 x 10⁻¹⁵ | 1.69 x 10⁻⁵   |                            |
| 0.67  | 8.64 x 10⁻¹⁵ | 2.27 x 10⁻⁵   |                            |
| 0.99  | 1.81 x 10⁻¹⁴ | 2.85 x 10⁻⁵   | k₉D = 4.16 x 10⁸ M⁻¹s⁻¹ b   |
| 1.35  | 4.13 x 10⁻¹⁴ | 4.10 x 10⁻⁵   | k′₉D = 7.87 x 10⁹ M⁻¹s⁻¹ c  |
| 1.60  | 7.36 x 10⁻¹⁴ | 5.28 x 10⁻⁵   | KₙN₁ = 0.55 M d             |
| 1.78  | 1.11 x 10⁻¹³ | 6.91 x 10⁻⁵   |                            |
| 2.31  | 3.77 x 10⁻¹³ | 1.87 x 10⁻⁴   |                            |

*a* First order rate constants for C(3)-H/D exchange (kₑ, s⁻¹) were obtained as the slopes of plots shown in Figure S23. *b* The second-order rate constant (k₉D, M⁻¹s⁻¹) was obtained from the fit of log kₑ - pD data to Eq 3 (Figure S28). *c* Values of k′₉D (M⁻¹s⁻¹) obtained by fitting log kₑ - pD data to equation 3 (Figure S28). *d* Values of KₙN₁ (M) obtained by fitting log kₑ - pD data to equation 3 (Figure S28).
Table S12. First and second-order rate constants for exchange of the C(3)-H of triazolium salt 9k for deuterium in solutions of DCl in D$_2$O at 25 °C and I = 1.0 M (KCl).

| pD  | [DO$^-$], M  | \(k_{ex}, \text{s}^{-1}\) | Results of Fitting to Eq 3 |
|-----|--------------|-----------------|-----------------------------|
| 0.45| 5.21 x 10^{-15} | 1.75 x 10^{-5}  | \(k_{DO} = 4.04 \times 10^8 \text{M}^{-1}\text{s}^{-1}\) b |
| 0.66| 8.45 x 10^{-15} | 2.30 x 10^{-5}  | \(k_{DO}' = 7.37 \times 10^9 \text{M}^{-1}\text{s}^{-1}\) c |
| 0.94| 1.61 x 10^{-14} | 3.01 x 10^{-5}  | \(K_{aN1} = 0.46 \text{M}\) d |
| 1.35| 4.13 x 10^{-14} | 4.01 x 10^{-5}  |                                                 |
| 1.60| 7.36 x 10^{-14} | 5.61 x 10^{-5}  |                                                 |
| 1.78| 1.11 x 10^{-13} | 7.32 x 10^{-5}  |                                                 |
| 2.36| 4.23 x 10^{-13} | 2.00 x 10^{-4}  |                                                 |

*First order rate constants for C(3)-H/D exchange (\(k_{ex}, \text{s}^{-1}\)) were obtained as the slopes of plots shown in Figure S24. *The second-order rate constant (\(k_{DO}, \text{M}^{-1}\text{s}^{-1}\)) was obtained from the fit of log \(k_{ex} - pD\) data to Eq 3 (Figure S28). *Values of \(k_{DO}' (\text{M}^{-1}\text{s}^{-1})\) obtained by fitting log \(k_{ex} - pD\) data to equation 3 (Figure S28). *Values of \(K_{aN1} (\text{M})\) obtained by fitting log \(k_{ex} - pD\) data to equation 3 (Figure S28).

### S1.5 Hammett Analysis of Protofugalities (\(k_{DO}\)).

Figure S29. Semilogarithmic plots of log \(k_{DO}\) against Hammett substituent constant, \(\sigma\), for triazolium salts 7a-c, 7k (■); 8a-c, 8k (●); 9a-c, 9k (▲).

\[ y = 0.650x + 7.87 \]
\[ R^2 = 0.996 \]

\[ y = 0.653x + 7.66 \]
\[ R^2 = 0.997 \]

\[ y = 0.674x + 7.62 \]
\[ R^2 = 0.992 \]
Table S13. Hammett substituent constants, $\sigma$

| Substituent | $\sigma$ |
|-------------|----------|
| 4-MeO       | -0.27    |
| H           | 0        |
| 4-F         | 0.06     |
| 4-Br        | 0.23     |
| 3-Cl        | 0.37     |
| 4-CF$_3$    | 0.54     |
| 2,6-Di-MeO  | -0.54$^b$|
| 2,4,6-Tri-'Pr | -0.45$^b$|
| 2,4,6-Tri-Me | -0.51$^b$|
| 2,4,6-Tri-Cl | 0.69$^b$ |
| F$_5$       | 1.50$^c$ |

$^a$Taken from Hansch, Leo and Taft.$^{56, 60}$

$^b$For the purpose of ordering of ortho-substituted examples in Figure 3, we have assumed an additive substituent effect in the absence of available literature N-aryl substituent constants.$^{57}$

$^c$Based on Taft’s Hammett $\sigma$ value.$^{58}$
S1.6 Single-crystal X-ray Crystallography.

The crystal structures of 7a, 7b, 7g and 7k have been reported previously (the CCDC codes are ISOXEU [1], ISOXIY [1], LEBMIQ [2] and ISOXOE [1] respectively) but re-determination of these structures was deemed to be necessary for consistency in analysis. The X-ray single crystal data for compounds 7a, 7c, 7d, 7e, 7f, 7g, 7j, 7ja, 7k, 8a, 8b, 8c, 8i, 9a and 9k have been collected on a Bruker D8Venture (Photon100 CMOS detector, IμS-microsource, focusing mirrors) 3-circle diffractometer. The data for compounds 7h and 9c were collected on an Oxford Diffraction, Gemini-Ultra 4-circle diffractometer (Atlas CCD detector, fine-focus sealed tube, graphite monochromator). The data for compound 8k were collected on a Bruker D8Venture (Photon 2 CMOS detector, IμS-microsource, focusing mirrors) 3-circle diffractometer. The data for compound 7i were collected on an Agilent XCalibur 4-circle diffractometer (Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator); for compound 7b on a Bruker D8Venture (Photon III MM C7 CPAD detector, IμS microsource, focusing mirrors) 3-circle diffractometer; for compound 9b on a Bruker D8Venture (Photon III MM C14 CPAD detector, IμS III microsource, focusing mirrors) 3-circle diffractometer and for compound 8a on a Bruker D8Venture (Photon II CPAD detector, fine-focus sealed tube, focusing mirrors) 3-circle diffractometer.

The sources with λ CuKα = 1.54184 Å radiation were used for compounds 7h, 8k, 9b and 9c; in all other cases λMoKα radiation (λ = 0.71073Å) was used. The temperature on the crystals (150.0(2)K for compounds 7h, 8k and 9c; 120.0(2)K for all other compounds) was maintained by Oxford Cryosystems CryostreamPlus open-flow N2 cooling devices. Corresponding instrument’s software was used for cell refinement, data collection, data reduction and empirical absorption correction. All structures were solved by either direct or intrinsic phase methods and refined by full-matrix least squares on F² for all data using Olex2 [3] and
SHELXTL [4] software. All non-disordered non-hydrogen atoms were refined in anisotropic approximation, the hydrogen atoms in most of the structures were placed in the calculated positions and refined in riding mode. Several structures (7b, 7c, 7g, 7i, 7k, 8c and 9b) contain disordered fragments (usually BF₄⁻ anions). Various appropriate constrains and restrains were used in refinement of these fragments. Two polymorphs of the compound 7j were found in different available samples. Crystal data and parameters of refinement are listed in Tables S14-16. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2124937-2124950; 2124952-2124958.

S1.6.1 Analysis of Triazolium Salts 7h, 8k and 9c via Encapsulated Nanodroplet Crystallisation (ENaCt)/Single Crystal X-ray Diffraction

The growth of single crystals of 7h, 8k and 9c, suitable for single crystal X-ray diffraction analysis was performed via a modified high-throughput Encapsulated Nanodroplet Crystallisation (ENaCt) approach.¹⁹ Stock solutions of 7h, 8k and 9c were prepared in DMSO and DMF, droplets of which (50 nL) were then dispensed via an STP Labtech Mosquito liquid-handling robot into 96 well glass plates (SWISSCI LCP Modular, 100 µm spacer) containing an appropriate crystallization oil (50-300 nL of PDMSO, FC40, FYR or mineral oil). Experiments were performed with or without the addition of a secondary solvent (25-250 nL of H₂O, toluene, butanol, chlorobenzene or 2-methyl-2,4-pentanediol (MPD)). The plates were sealed with a glass cover slip, allowed to stand at room temperature in the dark and assessed visually and by cross-polarized light microscopy for crystal growth every few days. After 7 days, wells containing crystals were opened and suitable crystals of 7h, 8k and 9c selected for single crystal X-ray analysis. Specific ENaCt crystallisation conditions for each molecule are
given below: 7h 50 nL DMF (33 mg/mL) in 200 nL of FYR; 8k 50 nL DMSO (50 mg/mL), 100 nL 2-methyl-2,4-pentanediol (MPD) in 200 nL of FYR; 9c 50 nL DMSO (50 mg/mL) in 150 nL of FC40.
S1.6.2  Crystal Data and Structure Refinement Parameters

Table S14.  Crystal data and structure refinement parameters.

| Compound | 7a  | 7b  | 7c  | 7d  | 7e  | 7f  | 7g  |
|----------|-----|-----|-----|-----|-----|-----|-----|
| Empirical formula | $C_{12}H_{14}N_3OBF_4$ | $C_{11}H_{12}BF_4N_3$ | $C_{11}H_{11}FN_3BF_4$ | $C_{11}H_{11}BrN_3BF_4$ | $C_{11}H_{11}N_3ClBF_4$ | $C_{12}H_{11}F_3N_3BF_4$ | $C_{12}H_{16}N_3O_2BF_4$ |
| Formula weight | 303.07 | 273.05 | 291.04 | 351.95 | 307.49 | 341.05 | 333.10 |
| Temperature/K | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 |
| Crystal system | orthorhombic | orthorhombic | orthorhombic | monoclinic | monoclinic | monoclinic | orthorhombic |
| Space group | Iba2 | $P2_1_2_1$ | Pbca | $P2_1/n$ | $P2_1/c$ | $P2_1/n$ | Pbca |
| a/Å | 10.614(3) | 6.7732(3) | 7.8707(4) | 7.0877(3) | 9.0461(9) | 7.0168(4) | 10.5264(4) |
| b/Å | 34.391(11) | 10.5577(4) | 29.0299(14) | 12.1656(5) | 8.0475(8) | 12.7166(7) | 13.0742(4) |
| c/Å | 7.410(2) | 17.0417(7) | 29.0299(14) | 15.7597(7) | 9.3668(4) | 10.1332(2) | 21.4933(7) |
| α/° | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| β/° | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| γ/° | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| Volume/Å³ | 2704.8(15) | 1218.64(9) | 2498.4(2) | 1336.71(10) | 1279.1(2) | 1410.32(14) | 2958.00(17) |
| Z | 8 | 4 | 8 | 4 | 4 | 4 | 8 |
| $ρ_{calc}$/g/cm³ | 1.489 | 1.488 | 1.547 | 1.749 | 1.597 | 1.606 | 1.496 |
| μ/mm⁻¹ | 0.133 | 0.133 | 0.146 | 3.114 | 0.162 | 0.134 |
| F(000) | 1248.0 | 560.0 | 1184.0 | 696.0 | 624.0 | 688.0 | 1376.0 |
| Radiation | MoKα | MoKα | MoKα | MoKα | MoKα | MoKα | MoKα |
| Reflections collected | 17438 | 15661 | 35825 | 28802 | 25412 | 26012 | 43211 |
| Independent refl. R[int] | 2953, 0.1164, 0.0349 | 3538, 0.0439 | 3321, 0.0378 | 3866, 0.0287 | 3398, 0.0598 | 3236, 0.0633 | 3924, 0.0445 |
| Data/restraints/parameters | 2953/1/192 | 3538/10/185 | 3321/28/241 | 3866/0/181 | 3398/0/225 | 3236/15/248 | 3924/0/252 |
| Goodness-of-fit on F² | 1.003 | 1.031 | 1.035 | 1.036 | 1.025 | 1.045 | 1.025 |
| Final R₁ [I≥2σ (I)] | 0.0583 | 0.0514 | 0.0488 | 0.0213 | 0.0462 | 0.0618 | 0.0391 |
| Final wR₂ [all data] | 0.1317 | 0.1167 | 0.1272 | 0.0567 | 0.1213 | 0.1560 | 0.0997 |
| Largest diff. peak/hole,eÅ⁻³ | 0.27/-0.23 | 0.23/-0.21 | 0.43/-0.35 | 0.51/-0.36 | 0.51/-0.61 | 1.19/-0.63 | 0.28/-0.23 |
| Flack parameter | 0.2(8) | 0.0(4) | n/a | n/a | n/a | n/a | n/a |
| Compound | 7h | 7i | 7j | 7ja | 7k | 8a | 8b |
|-----------|----|----|----|------|----|----|----|
| Empirical formula | C_{20}H_{32}ClN_{3}O_{1.48} | C_{14}H_{18}N_{2}BF_{4} | C_{11}H_{8}Cl_{3}N_{3}BF_{4} | C_{11}H_{9}Cl_{3}N_{3}BF_{4} | C_{11}H_{9}Cl_{3}N_{3}BF_{4} | C_{13}H_{18}N_{2}OB_{4} | C_{12}H_{14}N_{2}BF_{4} |
| Formula weight | 374.58 | 315.12 | 376.37 | 376.37 | 363.01 | 317.10 | 287.07 |
| Temperature/K | 150.0 | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 |
| Crystal system | triclinic | monoclinic | monoclinic | orthorhombic | monoclinic | orthorhombic | orthorhombic |
| Space group | P-1 | P2/n | P2/n | Pca2_{1} | Pca2_{1} | Pca2_{1} | Pca2_{1} |
| a/Å | 8.0473(4) | 9.4928(6) | 9.6158(5) | 12.2618(8) | 12.0073(9) | 10.7585(10) | 11.0268(10) |
| b/Å | 8.4438(4) | 7.8963(3) | 7.9497(5) | 6.9776(5) | 7.6843(8) | 7.5490(7) | 7.5490(7) |
| c/Å | 16.4764(9) | 20.5873(12) | 19.1105(11) | 34.736(2) | 10.7857(11) | 7.4206(7) | 7.4206(7) |
| α/° | 77.912(4) | 90.00 | 90.00 | 90 | 90 | 90 | 90 |
| β/° | 83.956(4) | 94.597(5) | 91.871(2) | 90 | 90 | 90 | 90 |
| γ/° | 83.405(4) | 90.00 | 90.00 | 90 | 90 | 90 | 90 |
| Volume/Å³ | 1083.69(10) | 1538.22(14) | 1460.08(15) | 2971.9(3) | 665.93(12) | 1438.4(2) | 1313.5(2) |
| Z | 2 | 4 | 4 | 8 | 2 | 4 | 4 |
| \(\rho_{calculated}/g/cm^3\) | 1.148 | 1.361 | 1.712 | 1.682 | 1.810 | 1.464 | 1.452 |
| \(\mu/mm^{-1}\) | 1.666 | 0.115 | 0.668 | 0.656 | 0.198 | 0.129 | 0.127 |
| F(000) | 406.0 | 656.0 | 752.0 | 1504.0 | 360.0 | 656.0 | 592.0 |
| Radiation | CuKα | MoKα | MoKα | MoKα | MoKα | MoKα | MoKα |
| Reflections collected | 14921 | 20156 | 22432 | 30024 | 9298 | 18591 | 16998 |
| Independent refl. R_{int} | 3826, 0.0572 | 3525, 0.0931 | 4060, 0.0277 | 7055, 0.0712 | 3197, 0.0483 | 3141, 0.0767 | 2858, 0.0767 |
| Data/restraints/parameters | 3826/195/256 | 3525/28/214 | 4060/0/235 | 7055/1/397 | 3197/7/216 | 3141/1/200 | 2858/1/181 |
| Goodness-of-fit on F² | 1.028 | 1.047 | 1.050 | 1.039 | 1.031 | 1.029 | 1.007 |
| Final R_{1} [I≥2σ (I)] | 0.0447 | 0.0684 | 0.0259 | 0.0619 | 0.0485 | 0.0464 | 0.0430 |
| Final wR_{2} [all data] | 0.1170 | 0.2134 | 0.0668 | 0.1246 | 0.1174 | 0.1006 | 0.0937 |
| Largest diff. peak/hole, eÅ⁻³ | 0.25/-0.22 | 0.43/-0.28 | 0.39/-0.36 | 0.51/-0.42 | 0.35/-0.36 | 0.19/-0.23 | 0.17/-0.19 |
| Flack parameter | n/a | n/a | n/a | 0.05(5) | 0.2(4) | -0.4(6) | -0.1(6) |
Table S16. Crystal data and structure refinement parameters (cont.)

| Compound | 8c  | 8i  | 8k  | 9a  | 9b  | 9c  | 9k  |
|----------|-----|-----|-----|-----|-----|-----|-----|
| Empirical formula | C_{12}H_{13}FN_{3}BF_{4} | C_{15}H_{20}N_{3}BF_{4} | C_{12}H_{9}F_{2}N_{3}BF_{4} | C_{14}H_{16}N_{3}OBF_{4} | C_{13}H_{16}N_{3}BF_{4} | C_{13}H_{15}N_{3}BF_{5} | C_{13}H_{11}F_{3}N_{3}BF_{4} |
| Formula weight | 305.06 | 329.15 | 377.03 | 331.12 | 301.10 | 319.09 | 391.06 |
| Temperature/K | 120.0 | 120.0 | 150.0 | 120.0 | 120.0 | 120.0 | 120.0 |
| Crystal system | orthorhombic | orthorhombic | orthorhombic | orthorhombic | monoclinic | orthorhombic | monoclinic |
| Space group | Pca2\(_1\) | Pbca | Pca2\(_1\) | Pna2\(_1\) | C2/c | Pbca | P2\(_1\)/n |
| a/Å | 11.4598(16) | 10.6066(9) | 22.5508(6) | 14.4005(8) | 11.7102(7) | 11.2304(4) | 7.5945(3) |
| b/Å | 15.4396(19) | 7.7396(7) | 8.2325(2) | 11.7102(7) | 11.2304(4) | 7.5945(3) | 7.5945(3) |
| c/Å | 7.5533(10) | 39.222(3) | 7.8305(2) | 17.9974(10) | 7.7571(3) | 32.2135(9) | 23.1992(10) |
| α/° | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| β/° | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| γ/° | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| Volume/Å\(^3\) | 1336.4(3) | 3219.8(5) | 1453.73(6) | 3035.0(3) | 5689.8(4) | 2876.41(13) | 3025.4(2) |
| Z | 4 | 8 | 4 | 8 | 16 | 8 | 8 |
| \(\rho_{cak},g/cm^3\) | 1.516 | 1.358 | 1.723 | 1.449 | 1.406 | 1.474 | 1.717 |
| \(\mu,\text{mm}^{-1}\) | 0.140 | 0.113 | 1.686 | 0.126 | 1.049 | 1.176 | 0.181 |
| F(000) | 624.0 | 1376.0 | 752.0 | 1376.0 | 2496.0 | 1312.0 | 1568.0 |
| Radiation | MoK\(\alpha\) | MoK\(\alpha\) | CuK\(\alpha\) | MoK\(\alpha\) | CuK\(\alpha\) | CuK\(\alpha\) | MoK\(\alpha\) |
| Reflections collected | 15307 | 33230 | 12774 | 41084 | 38152 | 16278 | 45266 |
| Independent refl. R_int | 2914, 0.0542 | 3332, 0.1113 | 2631, 0.0304 | 6971, 0.0663 | 5466, 0.1207 | 2540, 0.0427 | 8048, 0.0506 |
| Data/restraints/parameters | 2914/29/187 | 3332/0/209 | 2631/1/227 | 6971/1/417 | 5466/39/407 | 2540/0/200 | 8048/0/557 |
| Goodness-of-fit on F^2 | 1.030 | 1.049 | 1.075 | 1.014 | 1.027 | 1.036 | 1.032 |
| Final R1 indexes | 0.0873 | 0.0672 | 0.0292 | 0.0508 | 0.0795 | 0.0335 | 0.0480 |
| Final wR2 [all data] | 0.2537 | 0.1434 | 0.0801 | 0.1221 | 0.2394 | 0.0880 | 0.1110 |
| Largest diff. peak/hole, e Å\(^{-3}\) | 0.60/-0.65 | 0.32/-0.30 | 0.28/-0.18 | 0.44/-0.26 | 0.30/-0.29 | 0.23/-0.22 | 0.45/-0.44 |
| Flack parameter | 0.5(4) | n/a | 0.45(16) | 0.4(3) | n/a | n/a | n/a |
S1.6.3 ORTEP Diagrams for X-ray Crystal Structures

Figure S30. ORTEP of 7a showing thermal ellipsoids at the 50% probability level.

Figure S31. ORTEP of 7b showing thermal ellipsoids at the 50% probability level.
Figure S32. ORTEP of 7c showing thermal ellipsoids at the 50% probability level.

Figure S33. ORTEP of 7d showing thermal ellipsoids at the 50% probability level.
Figure S34. ORTEP of 7e showing thermal ellipsoids at the 50% probability level.

Figure S35. ORTEP of 7f showing thermal ellipsoids at the 50% probability level.
Figure S36. ORTEP of 7g showing thermal ellipsoids at the 50% probability level.

Figure S37. ORTEP of 7h showing thermal ellipsoids at the 50% probability level.
Figure S38. ORTEP of 7i showing thermal ellipsoids at the 50% probability level.

Figure S39. ORTEP of 7j showing thermal ellipsoids at the 50% probability level.
Figure S40. ORTEP of 7ja showing thermal ellipsoids at the 50% probability level.

Figure S41. ORTEP of 7k showing thermal ellipsoids at the 50% probability level.
Figure S42. ORTEP of 8a showing thermal ellipsoids at the 50% probability level.

Figure S43. ORTEP of 8b showing thermal ellipsoids at the 50% probability level.
Figure S44. ORTEP of 8c showing thermal ellipsoids at the 50% probability level.

Figure S45. ORTEP of 8i showing thermal ellipsoids at the 50% probability level.
Figure S46. ORTEP of 8k showing thermal ellipsoids at the 50% probability level.

Figure S47. ORTEP of 9a showing thermal ellipsoids at the 50% probability level.
Figure S48. ORTEP of 9b showing thermal ellipsoids at the 50% probability level.

Figure S49. ORTEP of 9c showing thermal ellipsoids at the 50% probability level.
Figure S50. ORTEP of 9k showing thermal ellipsoids at the 50% probability level.
### S1.6.4 Summary of Bond Lengths, Bond Angles, and Dihedral Angles

Table S17. Structural data for individual triazolium salts 7a-k (n=1) obtained from single crystal X-ray diffraction measurements.

![Structure Diagram](image)

| Backbone Bond Length | 7a | 7b | 7c | 7d | 7e | 7f | 7g | 7h | 7i | 7j | 7k |
|----------------------|----|----|----|----|----|----|----|----|----|----|----|
| N1N2                 | 1.38 | 1.38 | 1.38 | 1.38 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.38 | 1.38 |
| N1C3                 | 1.32 | 1.33 | 1.33 | 1.33 | 1.32 | 1.32 | 1.31 | 1.32 | 1.32 | 1.31 | 1.31 |
| C1N4                 | 1.33 | 1.33 | 1.32 | 1.33 | 1.32 | 1.32 | 1.33 | 1.33 | 1.33 | 1.32 | 1.32 |
| N1C5                 | 1.36 | 1.37 | 1.36 | 1.37 | 1.37 | 1.35 | 1.36 | 1.35 | 1.35 | 1.35 | 1.36 |
| C1C1                 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.31 | 1.30 | 1.30 | 1.30 |
| C2C8                 | 1.47 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.50 |
| N1C1                 | 1.46 | 1.48 | 1.47 | 1.48 | 1.48 | 1.47 | 1.47 | 1.48 | 1.47 | 1.47 | 1.47 |
| N1C7                 | 1.43 | 1.43 | 1.43 | 1.43 | 1.43 | 1.45 | 1.44 | 1.43 | 1.43 | 1.43 | 1.43 |
| C1C6                 | 1.39 | 1.39 | 1.39 | 1.39 | 1.38 | 1.39 | 1.40 | 1.38 | 1.39 | 1.38 | 1.38 |
| C1C8                 | 1.37 | 1.39 | 1.39 | 1.39 | 1.39 | 1.40 | 1.39 | 1.39 | 1.38 | 1.38 | 1.38 |

| C-H Bond Length     |    |    |    |    |    |    |    |    |    |    |    |
|---------------------|----|----|----|----|----|----|----|----|----|----|----|
| C1H1                | 0.95 | 0.95 | 0.95 | 0.95 | 0.90 | 0.93 | 0.96 | 0.95 | 0.95 | 0.91 | 0.95 |
| C1H2                | 0.99 | 0.99 | 0.97 | 0.99 | 0.95 | 0.93 | 0.99 | 0.99 | 0.99 | 0.92 | 0.99 |
| C1H3                | 0.99 | 0.99 | 0.99 | 0.99 | 0.94 | 0.97 | 0.99 | 0.99 | 0.99 | 0.93 | 0.99 |

| H-H Distance        |    |    |    |    |    |    |    |    |    |    |    |
|---------------------|----|----|----|----|----|----|----|----|----|----|----|
| H1H2                | 3.06 | 3.09 | 3.04 | 3.08 | 3.02 | 2.99 | 3.12 | 3.12 | 3.08 | 3.04 | 3.07 |
| H1H3                | 3.30 | 3.33 | 3.23 | 3.34 | 3.24 | 3.24 | 3.32 | 3.28 | 3.34 | 3.22 | 3.32 |

| Bond Angles          |    |    |    |    |    |    |    |    |    |    |    |
|----------------------|----|----|----|----|----|----|----|----|----|----|----|
| C2N1N3               | 102.8  | 103.2  | 103.0  | 102.9  | 102.5  | 102.7  | 102.6  | 102.5  | 102.8  | 103.2  | 102.3  |
| N1N3C3               | 112.3  | 111.8  | 111.6  | 111.8  | 112.2  | 111.8  | 112.0  | 112.0  | 111.4  | 111.3  | 112.5  |
| N1C5N4               | 105.6  | 105.9  | 106.2  | 105.9  | 105.9  | 106.2  | 106.0  | 106.4  | 106.3  | 106.4  | 105.9  |
| C2N6C5               | 107.5  | 107.5  | 107.7  | 107.5  | 107.3  | 107.4  | 106.8  | 107.6  | 107.4  | 107.2  | 107.2  |
| N2C3N4               | 111.8  | 111.6  | 111.6  | 111.9  | 111.9  | 112.0  | 112.0  | 112.2  | 111.9  | 111.6  | 112.1  |
| C2C3N4               | 110.7  | 110.3  | 110.9  | 110.9  | 110.9  | 110.7  | 110.9  | 110.3  | 111.2  | 110.2  | 109.6  |
| C5N1C4               | 114.6  | 113.5  | 113.6  | 113.6  | 113.5  | 113.5  | 114.2  | 113.4  | 113.4  | 114.1  |        |

| Torsion Angles       |    |    |    |    |    |    |    |    |    |    |    |
|----------------------|----|----|----|----|----|----|----|----|----|----|----|
| H1C3*C4H2            | 44.4  | 41.7  | 46.3  | 42.3  | 46.0  | 40.7  | 43.6  | 45.5  | 41.9  | 43.9  | 42.9  |
| H1C3*C5H1            | 68.4  | 71.0  | 68.1  | 70.4  | 67.9  | 72.5  | 68.8  | 67.1  | 70.9  | 70.4  | 69.6  |
| N1N2*C3C3            | 16.1  | 19.9  | 25.2  | 3.8   | 73.7  | 4.1   | 76.6  | 91.2  | 79.9  | 2.8   | 62.1  |
| N1N2*C5C5            | 163.9 | 160.5 | 155.2 | 177.4 | 105.6 | 175.7 | 102.3 | 88.6  | 97.9  | 177.0 | 122.9 |

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Table S18. Structural data for individual triazolium salts 8a-c, i, k (n=2) and 9a-c, k (n=3) obtained from single crystal X-ray diffraction measurements.

| Backbone Bond Length | 8a  | 8b  | 8c  | 8i  | 8k  | 9a  | 9b  | 9c  | 9k  |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| N=N^2                | 1.38| 1.38| 1.37| 1.38| 1.38| 1.37| 1.38| 1.37| 1.38|
| N=C^3                | 1.32| 1.31| 1.31| 1.34| 1.32| 1.31| 1.32| 1.31| 1.32|
| C=N^4                | 1.34| 1.33| 1.33| 1.33| 1.33| 1.32| 1.33| 1.32| 1.33|
| N=C^5                | 1.36| 1.37| 1.37| 1.36| 1.37| 1.37| 1.38| 1.37| 1.37|
| C=N^1                | 1.31| 1.30| 1.32| 1.30| 1.31| 1.31| 1.31| 1.31| 1.31|
| C=O                 | 1.49| 1.49| 1.48| 1.49| 1.49| 1.48| 1.48| 1.48| 1.49|
| N=C^a                | 1.47| 1.47| 1.47| 1.47| 1.49| 1.48| 1.48| 1.47| 1.48|
| N=C^c                | 1.43| 1.44| 1.44| 1.44| 1.43| 1.43| 1.43| 1.43| 1.43|
| C=C^b                | 1.39| 1.38| 1.39| 1.39| 1.38| 1.38| 1.39| 1.39| 1.38|
| C=C^c                | 1.38| 1.39| 1.38| 1.39| 1.38| 1.38| 1.39| 1.39| 1.38|

| C-H Bond Length     |     |     |     |     |     |     |     |     |     |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C=H^1               | 0.95| 0.95| 0.95| 0.95| 0.95| 0.95| 0.95| 0.93| 0.93|
| C=H^2               | 0.99| 0.99| 0.99| 0.99| 0.99| 0.99| 0.99| 0.97| 0.95|
| C=H^3               | 0.99| 0.99| 0.99| 0.99| 0.99| 0.99| 0.99| 0.97| 0.99|

| H-H Distance        |     |     |     |     |     |     |     |     |     |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| H=H^2               | 2.72| 2.76| 2.77| 2.77| 2.76| 2.51| 2.51| 2.50| 2.45|
| H=H^3               | 3.14| 3.10| 3.10| 3.06| 3.07| 3.43| 3.40| 3.36| 3.31|

| Bond Angles         |     |     |     |     |     |     |     |     |     |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C=N=N^2             | 103.5| 103.5| 103.4| 103.2| 103.2| 104.3| 104.2| 104.3| 103.5|
| N=N^3=N^3           | 111.4| 111.4| 112.3| 111.4| 112.0| 111.1| 110.5| 110.0| 111.6|
| N=N=C^4             | 106.6| 107.1| 106.6| 107.2| 106.5| 107.4| 107.8| 107.4| 106.9|
| C=N=N^5             | 107.0| 106.2| 107.4| 106.7| 107.2| 106.8| 106.9| 106.5| 107.2|
| N=N^6=C^6           | 111.5| 111.7| 110.3| 111.5| 111.1| 110.4| 110.7| 110.8| 110.8|
| C=C=O^6             | 122.9| 121.8| 122.7| 121.8| 121.9| 123.5| 124.5| 124.5| 124.3|
| C=N=C^a             | 126.0| 125.8| 124.3| 126.1| 125.7| 127.6| 127.2| 127.9| 127.7|

| Torsion Angles       |     |     |     |     |     |     |     |     |     |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| H=3*C=H^2            | 35.1| 37.4| 38.4| 41.3| 39.0| 0.6 | 1.3 | 2.6 | 2.4 |
| H=3*C=H^3            | 74.1| 71.7| 70.4| 68.1| 70.1| 107.5| 105.6| 103.9| 104.3|
| N=2=C=3              | 21.7| 32.1| 21.0| 72.9| 65.0| 44.3| 21.0| 17.0| 73.8|
| N=N^2=C=3            | 157.3| 147.3| 158.4| 105.7| 119.3| 135.3| 159.5| 163.3| 105.9|
Table S19. Summary of average bond angles and distances of triazolium salts 7a-k (n=1); 8a-c, 8i, 8k (n=2); 9a-c, 9k (n=3) and corresponding standard deviations obtained from single crystal X-ray structural analysis. Data highlighted in purple is included in Table 2 in the main text.

| Backbone Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|----------------------|--------------|----------|--------------|----------|--------------|----------|-------------------------------|------------|------------|
| N^1N^2               | 1.38         | 0.00     | 1.38         | 0.00     | 1.38         | 0.01     | -0.01                         | 0.00       |            |
| N^2C^3               | 1.32         | 0.01     | 1.31         | 0.01     | 1.32         | 0.01     | -0.01                         | 0.00       |            |
| C^1N^4               | 1.33         | 0.00     | 1.33         | 0.00     | 1.33         | 0.00     | 0.01                          | 0.00       |            |
| N^4C^5               | 1.36         | 0.01     | 1.36         | 0.00     | 1.37         | 0.00     | 0.00                          | 0.00       |            |
| C^5N^1               | 1.30         | 0.00     | 1.31         | 0.01     | 1.31         | 0.00     | 0.01                          | 0.00       |            |
| C^5C^6               | 1.49         | 0.01     | 1.49         | 0.01     | 1.48         | 0.01     | 0.00                          | 0.00       |            |
| N^4C^9               | 1.47         | 0.01     | 1.47         | 0.01     | 1.48         | 0.00     | 0.00                          | 0.00       |            |
| N^7C^7               | 1.43         | 0.01     | 1.43         | 0.01     | 1.43         | 0.00     | 0.00                          | 0.00       |            |
| C^7C^8               | 1.39         | 0.01     | 1.39         | 0.01     | 1.38         | 0.01     | 0.00                          | -0.01      |            |
| C^7C^6               | 1.39         | 0.01     | 1.38         | 0.01     | 1.38         | 0.00     | 0.00                          | 0.00       |            |

| C-H Bond Length      |              |          |              |          |              |          |                              |            |            |
|----------------------|--------------|----------|--------------|----------|--------------|----------|-------------------------------|------------|------------|
| C^1H^1               | 0.94         | 0.02     | 0.95         | 0.00     | 0.94         | 0.01     | 0.01                          | -0.01      |            |
| C^4H^2               | 0.97         | 0.03     | 0.99         | 0.00     | 0.97         | 0.02     | 0.02                          | -0.02      |            |
| C^7H^3               | 0.98         | 0.02     | 0.99         | 0.00     | 0.99         | 0.01     | 0.01                          | 0.00       |            |

| H-H Distance         |              |          |              |          |              |          |                              |            |            |
|----------------------|--------------|----------|--------------|----------|--------------|----------|-------------------------------|------------|------------|
| H^1H^2               | 3.06         | 0.04     | 2.76         | 0.02     | 2.49         | 0.03     | -0.31                         | -0.26      |            |
| H^1H^3               | 3.29         | 0.05     | 3.09         | 0.03     | 3.37         | 0.05     | -0.19                         | 0.28       |            |

| Bond Angles          |              |          |              |          |              |          |                              |            |            |
|----------------------|--------------|----------|--------------|----------|--------------|----------|-------------------------------|------------|------------|
| C^3N^1N^2            | 102.8        | 0.3      | 103.3        | 0.1      | 104.1        | 0.4      | 0.6                           | 0.7        |            |
| N^1N^3C^3            | 111.9        | 0.4      | 111.7        | 0.4      | 110.8        | 0.7      | -0.2                          | -0.9       |            |
| N^2C^4N^4            | 106.1        | 0.3      | 106.8        | 0.3      | 107.4        | 0.3      | 0.8                           | 0.6        |            |
| C^5N^4C^5            | 107.4        | 0.2      | 106.9        | 0.5      | 106.9        | 0.3      | -0.5                          | 0.0        |            |
| N^4C^5N^1            | 111.9        | 0.2      | 111.3        | 0.6      | 110.7        | 0.2      | -0.6                          | -0.6       |            |
| C^6C^7N^4            | 110.6        | 0.5      | 122.2        | 0.5      | 124.2        | 0.5      | 11.6                          | 2.0        |            |
| C^3N^4C^6            | 113.7        | 0.4      | 125.6        | 0.7      | 127.6        | 0.3      | 11.8                          | 2.0        |            |

| Torsion Angles       |              |          |              |          |              |          |                              |            |            |
|----------------------|--------------|----------|--------------|----------|--------------|----------|-------------------------------|------------|------------|
| H^1C^3*C^6H^2        | 43.6         | 1.9      | 38.2         | 2.3      | 1.7          | 0.9      | -5.4                          | -36.5      |            |
| H^1C^3*C^6H^2        | 69.6         | 1.6      | 70.9         | 2.2      | 105.3        | 1.6      | 1.3                           | 34.4       |            |
| N^1N^2*C^7C^8        | 41.2         | 34.8     | 42.5         | 24.7     | 39.0         | 26.1     | 1.38                          | -3.54      |            |
| N^1N^2*C^7C^8        | 139.1        | 35.1     | 137.6        | 23.8     | 141.0        | 26.5     | -1.46                         | 3.39       |            |
Table S20. Summary of average* bond angles and distances of triazolium salts 7a-c, k (n=1); 8a-c, 8k (n=2); 9a-c, 9k (n=3) and corresponding standard deviations (SD) obtained from single crystal X-ray structural analysis.

*Averages calculated using only data for the 12 triazolium salts used for C(3)-H/D exchange studies. These average values and trends are in excellent agreement with data in Table S19 as expected given the small standard deviations.

| Backbone Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) |
|----------------------|--------------|---------|--------------|---------|--------------|---------|
| N1N2                 | 1.38         | 0.00    | 1.38         | 0.00    | 1.38         | 0.01    |
| N2C3                 | 1.32         | 0.01    | 1.31         | 0.01    | 1.32         | 0.01    |
| C3N4                 | 1.33         | 0.01    | 1.33         | 0.00    | 1.33         | 0.00    |
| N4C5                 | 1.36         | 0.00    | 1.36         | 0.01    | 1.37         | 0.00    |
| C5N1                 | 1.30         | 0.00    | 1.31         | 0.01    | 1.31         | 0.00    |
| C5C6                 | 1.49         | 0.01    | 1.49         | 0.01    | 1.48         | 0.01    |
| N5C7                 | 1.47         | 0.01    | 1.47         | 0.01    | 1.48         | 0.00    |
| N5C8                 | 1.43         | 0.00    | 1.43         | 0.01    | 1.43         | 0.00    |
| C5C8                 | 1.39         | 0.01    | 1.39         | 0.01    | 1.38         | 0.01    |
| C5C9                 | 1.38         | 0.01    | 1.38         | 0.00    | 1.38         | 0.00    |
| C-H Bond Length      |              |         |              |         |              |         |
| C3H1                 | 0.95         | 0.00    | 0.95         | 0.00    | 0.94         | 0.01    |
| C3H2                 | 0.98         | 0.01    | 0.99         | 0.00    | 0.97         | 0.02    |
| C3H3                 | 0.99         | 0.00    | 0.99         | 0.00    | 0.99         | 0.01    |
| H-H Distance         |              |         |              |         |              |         |
| H3H2                 | 3.07         | 0.02    | 2.75         | 0.02    | 2.49         | 0.03    |
| H3H3                 | 3.29         | 0.04    | 3.10         | 0.03    | 3.37         | 0.05    |
| Bond Angles          |              |         |              |         |              |         |
| C3N3N2               | 102.8        | 0.4     | 103.4        | 0.1     | 104.1        | 0.4     |
| N3N2C3               | 112.1        | 0.4     | 111.8        | 0.4     | 110.8        | 0.7     |
| N2C3N4               | 105.9        | 0.2     | 106.7        | 0.3     | 107.4        | 0.3     |
| C3N4C5               | 107.5        | 0.2     | 106.9        | 0.5     | 106.9        | 0.3     |
| N4C5N1               | 111.8        | 0.3     | 111.2        | 0.6     | 110.7        | 0.2     |
| C5C5N4               | 110.4        | 0.6     | 122.3        | 0.5     | 124.2        | 0.5     |
| C5N4C6               | 114.0        | 0.5     | 125.4        | 0.8     | 127.6        | 0.3     |
### Torsion Angles

|                  | H1C3*C6H2 | H1C3*C6H1 | N1N2*C6C5 | N1N2*C6C6 |
|------------------|-----------|-----------|-----------|-----------|
|                  | 43.8      | 2.0       | 37.5      | 1.7       |
|                  | 69.3      | 1.3       | 71.6      | 1.8       |
|                  | 150.6     | 18.8      | 145.6     | 18.2      |
|                  | 30.8      | 21.2      | 35.0      | 20.7      |
|                  |           |           | 39.0      | 26.1      |
|                  |           |           |           |           |
|                  |           |           | 141.0     | 26.5      |
S1.7  Synthetic \(^1\)H and \(^{13}\)C\{H\} NMR Spectra for New Triazolium Salts

7e
DMSO-d$_6$
$^1$H  700 MHz

DMSO-d$_6$
$^{13}$C{1H} 176 MHz
CDCl$_3$-$d_1$
$^1$H 400 MHz

CDCl$_3$-$d_1$
$^{13}$C{1H} 101 MHz
S1.8  Synthetic $^1$H NMR Spectra for Known Triazolium Salts

7a

D$_2$O-$_d_2$

$^1$H 400 MHz

7b

D$_2$O-$_d_2$

$^1$H 400 MHz
D$_2$O-$d_2$
$^1$H 400 MHz

D$_2$O-$d_2$
$^1$H 400 MHz
9k

CDCl₃-d₆

$^1$H 400 MHz

BF₄⁻
S2. DFT Calculations

All the DFT calculations were performed using Gaussian 09 on the Durham University Hamilton HPC.\textsuperscript{S10} The level of theory used for determining conformations for each molecule was B3LYP/6-31+g(d,p) for initial global minimima searches with subsequent structural refinement by B3LYP and M062X/6-311++g (d,p) unless stated otherwise, using redundant internal coordinates, with solvent water being modelled using an implicit polarisable continuum model (PCM).\textsuperscript{S11} Gaussian NBO version 3.1 (within the Gaussian 09 package) was used for natural bond analysis (NBO) calculations.\textsuperscript{S12} The imaginary frequencies of all the molecules were observed to be zero.

S2.1 Conformation Search and Total Energies

The conformations of molecules were obtained by optimizing structures with different dihedral angles between N\textsuperscript{1}N\textsuperscript{2} and C\textsuperscript{1}C\textsuperscript{e}. The resulting structures and the corresponding energies (Hartrees) for different conformers are listed below. Only one structure is presented for conformations of the same energy. The structural differences between conformers are small.
S2.1.1 Triazolium Salts

7a

7b

7c

7d

7e
7f

-927.578205

7g

-819.580078

7h

-944.381175

7i

-708.483613
-708.483616
S2.1.2  Carbene

7’a

7’b

7’c

7’d
$8'$b

$8'$c

$8'$i

$8'$k

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S2.2 Coordinates of Triazolium salts

7a (B3LYP)

```
O                  4.77379700    0.41104900    -0.10491600
N                  -0.77315800    0.00387600    -0.06778400
N                 -1.54293200    1.03797600    0.41556400
N                 -2.79399200   -0.63793700    -0.29134900
C                 -1.52909000   -1.00402800   -0.50582100
H                 -1.17725800   -1.91805800    -0.95262600
C                 -2.76843100    0.61378000    0.25838500
C                 -4.14932100    1.12716500    0.48785800
H                 -4.38901300    1.87664600   -0.27122000
H                 -4.26307900    1.59030400    1.46693700
C                 -5.00282600   -0.16532800    0.32324300
H                 -5.96336200    0.03675800   -0.14636700
H                 -5.18797500   -0.60686500    1.30287300
C                 -4.16064100   -1.14768100   -0.53126200
H                 -4.23891400   -2.18365900   -0.20998000
H                 -4.37296700   -1.07685800   -1.59818400
C                 0.65729300    0.08157600   -0.05533700
C                 1.40668600   -1.01083100    0.36413500
H                 0.91979000   -1.91239400    0.71543400
C                 2.79820700   -0.94046400    0.35285300
```
|   |    X    |    Y    |    Z    |
|---|---------|---------|---------|
| H | 3.36822000 | -1.79652600 | 0.68433100 |
| C | 3.43074700 | 0.23652800  | -0.06360200 |
| C | 2.65884300 | 1.33729000  | -0.47027300 |
| H | 3.16236800 | 2.24058800  | -0.79129800 |
| C | 1.27756400 | 1.26214400  | -0.47104600 |
| H | 0.68149200 | 2.10530100  | -0.79518600 |
| C | 5.62588900 | -0.67089800 | 0.29117900  |
| H | 5.47250100 | -1.54413200 | -0.34819600 |
| H | 5.45693600 | -0.93948200 | 1.33718800  |
| H | 6.64193400 | -0.30294300 | 0.16873900  |

**M062X**

|   |    X    |    Y    |    Z    |
|---|---------|---------|---------|
| O | 4.75436900 | 0.41668300  | -0.09537400 |
| N | -0.77146900 | 0.00283500  | -0.06518700 |
| N | -1.53285800 | 1.04363800  | 0.37850200  |
| N | -2.77998100 | -0.64346200 | -0.28297300 |
| C | -1.51860300 | -1.01490800 | -0.47769500 |
| H | -1.15839900 | -1.94188000 | -0.89347700 |
| C | -2.75473900 | 0.62069600  | 0.22941800  |
| C | -4.13785600 | 1.13684500  | 0.43714300  |
| H | -4.38461500 | 1.83010900  | -0.36997100 |
| H | -4.24847000 | 1.65426700  | 1.38740100  |
| C | -4.96800700 | -0.16977100 | 0.35342800  |
| H | -5.95365300 | -0.00409200 | -0.07433600 |
| H | -5.08791300 | -0.58675600 | 1.35319100  |
|    |        |        |        |
|----|--------|--------|--------|
| C  | -4.14539000 | -1.15230900 | -0.50849400 |
| H  | -4.21952700 | -2.18708600 | -0.18527400 |
| H  | -4.36705800 | -1.07438400 | -1.57236700 |
| C  | 0.65760900  | 0.08119700  | -0.05154800 |
| C  | 1.40272100  | -1.01937700 | 0.33586700  |
| H  | 0.91443900  | -1.92942100 | 0.66350600  |
| C  | 2.79239100  | -0.94680900 | 0.32385900  |
| H  | 3.36463900  | -1.81181400 | 0.62782500  |
| C  | 3.41715700  | 0.24136800  | -0.05819200 |
| C  | 2.64597200  | 1.35109700  | -0.43069200 |
| H  | 3.15231200  | 2.26243800  | -0.72270700 |
| C  | 1.26791700  | 1.27360000  | -0.43403500 |
| H  | 0.66410300  | 2.12190900  | -0.73061400 |
| C  | 5.58338100  | -0.67826800 | 0.27588600  |
| H  | 5.42011900  | -1.53101700 | -0.38764600 |
| H  | 5.39798700  | -0.97162000 | 1.31202200  |
| H  | 6.60592000  | -0.32535600 | 0.17336700  |

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### 7b (B3LYP)

![Structure of 7b](image-url)

| Atom | X | Y | Z |
|------|---|---|---|
| N    | 0.08613000 | 0.06190100 | 0.02057800 |
| N    | -0.65230700 | -1.02355400 | 0.43186400 |
| N    | -1.95113200 | 0.65032000 | -0.18821800 |
| C    | -0.69869500 | 1.07265200 | -0.35799200 |
| H    | -0.37429000 | 2.02224700 | -0.74802100 |
| C    | -1.88953900 | -0.62882000 | 0.29321200 |
| C    | -3.25499000 | -1.17578700 | 0.53554200 |
| H    | -3.46309700 | -1.17535000 | 1.60888200 |
| H    | -3.36334200 | -2.19617900 | 0.17093100 |
| C    | -4.14794800 | -0.15631100 | -0.23294800 |
| H    | -5.09895000 | 0.01213200 | 0.26818700 |
| H    | -4.35221000 | -0.53431100 | -1.23514400 |
| C    | -3.33174400 | 1.15805400 | -0.33652900 |
| H    | -3.44455300 | 1.66998600 | -1.28936000 |
| H    | -3.53214400 | 1.85220300 | 0.47980100 |
| C    | 1.52058400 | 0.01840600 | 0.00995600 |
| C    | 2.24022700 | 1.13516000 | 0.42889100 |
| H    | 1.72961500 | 2.01730900 | 0.79481300 |
| C    | 3.63194800 | 1.08800900 | 0.39198000 |
| H    | 4.20223000 | 1.94989900 | 0.71603400 |
| C    | 4.28470800 | -0.06588700 | -0.03980300 |
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| C       | 3.54592600 | -1.17953400 | -0.44127100 |
| H       | 4.05123700 | -2.07665800 | -0.77755800 |
| C       | 2.15458400 | -1.14383200 | -0.42352000 |
| H       | 1.56888200 | -1.99539300 | -0.74377200 |
| H       | 5.36741100 | -0.09922900 | -0.05946900 |

**M062X**

| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| N       | 0.08247600 | 0.06673000 | 0.03663200 |
| N       | -0.64632600 | -1.02524500 | 0.40410400 |
| N       | -1.94404300 | 0.66061100 | -0.15526000 |
| C       | -0.69610600 | 1.08799000 | -0.30609500 |
| H       | -0.36596600 | 2.05022400 | -0.66233700 |
| C       | -1.88035600 | -0.63224900 | 0.27890400 |
| C       | -3.24714500 | -1.18518200 | 0.49702700 |
| H       | -3.46905300 | -1.18030100 | 1.56642800 |
| H       | -3.34541700 | -2.20228200 | 0.12475100 |
| C       | -4.11666900 | -0.16340100 | -0.28003900 |
| H       | -5.09759600 | -0.03238800 | 0.16997300 |
| H       | -4.24680300 | -0.50706900 | -1.30614200 |
| C       | -3.32462200 | 1.16219300 | -0.28658800 |
| H       | -3.43099900 | 1.73396600 | -1.20445600 |
| H       | -3.54153400 | 1.79141500 | 0.57611500 |
| C       | 1.51497500 | 0.02144600 | 0.01598100 |
| C       | 2.23512100 | 1.15161500 | 0.38081900 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| H       | 1.72875400 | 2.04880700 | 0.71531400 |
| C       | 3.62357600 | 1.09799700 | 0.33308400 |
| H       | 4.19936900 | 1.97090600 | 0.61398200 |
| C       | 4.26712400 | -0.07353500| -0.05371500|
| C       | 3.52388200 | -1.19937900| -0.39992900|
| H       | 4.02428000 | -2.11149400| -0.70003300|
| C       | 2.13551400 | -1.15861700| -0.37302500|
| H       | 1.53938200 | -2.01862800| -0.64958500|
| H       | 5.34907800 | -0.11110600| -0.08088700|
7c (B3LYP)

N  0.33370600 -0.04402800  0.04626000
N  1.06509400  1.04031400 -0.38172100
N  2.37410600 -0.60812800  0.28442500
C  1.12456200 -1.03635600  0.45906700
H  0.80531900 -1.98234800  0.86221600
C  2.30458400  0.66234300 -0.21909500
C  3.66623700  1.23924800 -0.40726900
H  3.86427800  1.96795000  0.38338300
H  3.77419500  1.74401800 -1.36620700
C  4.56954300 -0.02347700 -0.27864100
H  5.51495400  0.19967300  0.21155300
H  4.78446000 -0.42028700 -1.27123700
C  3.75748000 -1.07024000  0.52728900
H  3.88167900 -2.08990600  0.17054400
H  3.95080600 -1.02888200  1.59928300
C -1.09917100 -0.02488800  0.01256000
C -1.78916400 -1.13807500 -0.46200300
H -1.25632700 -2.00283400 -0.83645200
C -3.18056300 -1.12147200 -0.47155900
H -3.74839900 -1.96779500 -0.83503800
C -3.83112500  0.01730900 -0.02339300

SI-94
|   | X           | Y           | Z           |
|---|-------------|-------------|-------------|
| C | -3.15581500 | 1.13846000  | 0.43686900  |
| H | -3.70719700 | 2.00472400  | 0.77833100  |
| C | -1.76621400 | 1.11436800  | 0.45894500  |
| H | -1.20761200 | 1.96627200  | 0.82292500  |
| F | -5.18540300 | 0.03877700  | -0.03985300 |

**M062X**

|   | X           | Y           | Z           |
|---|-------------|-------------|-------------|
| N | 0.33512500  | -0.04486300 | 0.04539400  |
| N | 1.05674600  | 1.04452100  | -0.34406800 |
| N | 2.36439000  | -0.61277800 | 0.27560800  |
| C | 1.11903200  | -1.04567900 | 0.43235900  |
| H | 0.79307100  | -2.00291200 | 0.80620500  |
| C | 2.29296500  | 0.66860600  | -0.18998900 |
| C | 3.65578000  | 1.24842000  | -0.35752200 |
| H | 3.86341500  | 1.91876600  | 0.47940700  |
| H | 3.75617000  | 1.80707300  | -1.28520600 |
| C | 4.53810000  | -0.02577500 | -0.31258000 |
| H | 5.51162100  | 0.16366000  | 0.13262700  |
| H | 4.68499600  | -0.40006600 | -1.32555600 |
| C | 3.74727400  | -1.07234000 | 0.50279900  |
| H | 3.86787000  | -2.09091700 | 0.14429100  |
| H | 3.95111600  | -1.02256300 | 1.57183300  |
| C | -1.09586300 | -0.02645500 | 0.01084100  |
| C | -1.78104200 | -1.15288600 | -0.42527300 |
|   |   |   |   |
|---|---|---|---|
| H | -1.24578800 | -2.02811200 | -0.77225700 |
| C | -3.16950000 | -1.13468800 | -0.43281600 |
| H | -3.74309800 | -1.99028200 | -0.76407800 |
| C | -3.81583000 | 0.01839200  | -0.02455300 |
| C | -3.14068800 | 1.15266600  | 0.39494600  |
| H | -3.69512000 | 2.02956900  | 0.70259700  |
| C | -1.75413700 | 1.12757500  | 0.41770000  |
| H | -1.18743300 | 1.98851200  | 0.74785500  |
| F | -5.15857700 | 0.04134500  | -0.04130200 |
7d (B3LYP)

N  -1.50113000  0.08407000  0.03221400
N  -2.22537300  -1.01486000  0.43353200
N  -3.54508900  0.64167300  -0.18951000
C  -2.29912500  1.08458300  -0.34863800
H  -1.98751200  2.04093900  -0.73298100
C  -3.46723400  -0.63883300  0.28735400
C  -4.82562200  -1.20797300  0.51674800
H  -5.04230400  -1.21312600  1.58839900
H  -4.91442800  -2.22911700  0.14902900
C  -5.72791500  -0.20060400  -0.25673000
H  -6.68641800  -0.05008200  0.23563900
H  -5.91578900  -0.57800900  -1.2623400
C  -4.93288400  1.12752300  -0.34714200
H  -5.04566000  1.64242900  -1.29835400
H  -5.15113200  1.81401000  0.47105400
C  -0.06857700  0.05765700  0.03005500
C  0.58216800  -1.10014700  -0.38865400
H  0.01237800  -1.96328500  -0.70583900
C  1.97245400  -1.13102500  -0.40038500
H  2.48974300  -2.02351300  -0.72551200
C  2.68238400  -0.00067900  -0.00178500

SI-97
C    2.03213500  1.15595100  0.41844000
H    2.59361600  2.02316500  0.73848500
C    0.64059000  1.18213800  0.44369200
H    0.12630700  2.06541600  0.80071700
Br   4.59691700  -0.04218800  -0.02599100

M062X

N    -1.49531600  0.08831300  0.04944700
N    -2.20947000 -1.01732300  0.40529300
N    -3.52861400  0.65017100 -0.15958200
C    -2.28739900  1.09890500 -0.29683400
H    -1.97071700  2.06830900 -0.64613300
C    -3.44822200 -0.64382900  0.26994600
C    -4.80771400 -1.21931000  0.47365700
H    -5.03839700 -1.22200900  1.54123200
H    -4.88623700 -2.23642600  0.09677500
C    -5.68676900 -0.20835000 -0.30683600
H    -6.67305800 -0.09426000  0.13594400
H    -5.80348100 -0.55013400 -1.33511900
C    -4.91623900  1.12977700 -0.30186800
H    -5.02304700  1.70321500 -1.21865500
H    -5.15065100  1.75216300  0.56115000
C    -0.06456300  0.06210300  0.04186000
C    0.57573900  -1.11260600 -0.32970600

SI-98
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | -0.00272700 | -1.98517600 | -0.60374300 |
| C       | 1.96307200  | -1.14564900 | -0.34625900 |
| H       | 2.48198000  | -2.05083200 | -0.63213300 |
| C       | 2.67380100  | -0.00125900 | -0.00173700 |
| C       | 2.02977600  | 1.17173300  | 0.37118400  |
| H       | 2.59792300  | 2.04926900  | 0.64953000  |
| C       | 0.64142900  | 1.20150100  | 0.40324600  |
| H       | 0.12800100  | 2.09870400  | 0.72579200  |
| Br      | 4.56962100  | -0.04511500 | -0.03430500 |
7e (B3LYP)

\[
\begin{align*}
    &N &-0.59942900 & 0.35076300 & 0.05761900 \\
    &N &-1.14202500 & -0.79585700 & 0.58992100 \\
    &N &-2.69616800 & 0.50757300 & -0.28147400 \\
    &C &-1.53894900 & 1.13763200 & -0.47309700 \\
    &H &-1.37841100 & 2.07522600 & -0.97706100 \\
    &C &-2.42203500 & -0.66596900 & 0.36785900 \\
    &C &-3.67232200 & -1.42670800 & 0.64952800 \\
    &H &-3.92669900 & -1.32875200 & 1.70833900 \\
    &H &-3.57198300 & -2.48703700 & 0.42268000 \\
    &C &-4.70110600 & -0.70117700 & -0.26798700 \\
    &H &-5.68904600 & -0.65308000 & 0.18524300 \\
    &H &-4.78491500 & -1.23543400 & -1.21479000 \\
    &C &-4.13850800 & 0.71977900 & -0.52870400 \\
    &H &-4.29811800 & 1.07503600 & -1.54386000 \\
    &H &-4.50265600 & 1.46158800 & 0.18225600 \\
    &C &0.81464900 & 0.58033000 & 0.09413700 \\
    &C &1.29754600 & 1.86670000 & 0.31731800 \\
    &H &0.62105400 & 2.69195100 & 0.49818800 \\
    &C &2.67519600 & 2.06841100 & 0.33000700 \\
    &H &3.06853200 & 3.06206100 & 0.50344200 \\
\end{align*}
\]
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 3.55352600| 1.00383100| 0.14334700|
| C    | 3.03381300| -0.27148500| -0.06271600|
| C    | 1.66507900| -0.50608000| -0.09683600|
| H    | 1.26745800| -1.49621500| -0.26864000|
| Cl   | 4.13134700| -1.62322000| -0.29757200|
| H    | 4.62390200| 1.16047000| 0.16333100|

**M062X**

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| N    | -0.59968100| 0.35599300| 0.06918800|
| N    | -1.12820500| -0.79825600| 0.56566000|
| N    | -2.68783200| 0.51983100| -0.25277100|
| C    | -1.53738400| 1.15634900| -0.42998800|
| H    | -1.37696100| 2.11169300| -0.90271400|
| C    | -2.40573800| -0.66915500| 0.35794000|
| C    | -3.65432300| -1.43876700| 0.62060600|
| H    | -3.92236900| -1.33440300| 1.67430300|
| H    | -3.54330900| -2.49619700| 0.39206400|
| C    | -4.66127600| -0.71335000| -0.30826100|
| H    | -5.66890600| -0.71252500| 0.09950700|
| H    | -4.67891300| -1.20817200| -1.27922500|
| C    | -4.13048700| 0.72594800| -0.48252100|
| H    | -4.29772600| 1.14027600| -1.47285800|
| H    | -4.50060700| 1.41151100| 0.27905000|
| C    | 0.81319400| 0.58347200| 0.09446100|

SI-101
C  1.29537300  1.86912200  0.29595100
H  0.61833200  2.69597100  0.46897400
C  2.67135700  2.06603000  0.29796200
H  3.06961900  3.06035500  0.45352200
C  3.54193000  0.99716800  0.12189700
C  3.01851500  -0.27718300  -0.06235100
C  1.65176700  -0.50823500  -0.08549100
H  1.24661500  -1.49947400  -0.23854800
Cl  4.10194700  -1.62394000  -0.28250800
H  4.61358900  1.14657000  0.13278300
7f (B3LYP)

N  -1.43454200  0.09553100  0.03368300
N  -2.15040700  -1.02485600  0.38779700
N  -3.48229900  0.64983800  -0.15534800
C  -2.24123300  1.10795100  -0.29839700
H  -1.93956900  2.08280900  -0.64180900
C  -3.39464400  -0.65081400  0.26410300
C  -4.74867400  -1.23749700  0.47309100
H  -4.96261400  -1.28565900  1.54426400
H  -4.83151100  -2.24398700  0.06589000
C  -5.65823200  -0.20567400  -0.25817500
H  -6.61923900  -0.08513400  0.23744100
H  -5.83954600  -0.54028500  -1.28005500
C  -4.87439200  1.13157800  -0.28770900
H  -4.99290300  1.69025100  -1.21306700
H  -5.09572400  1.77642400  0.56296500
C  -0.00250200  0.07177500  0.01921600
C  0.64265400  -1.10403600  -0.35640200
H  0.06806500  -1.97767100  -0.63110000
C  2.03115300  -1.13159100  -0.37796100
H  2.54227900  -2.03852500  -0.67289000
C  2.75634500  0.01138900  -0.03761200
C  2.09828900  1.18195800  0.33841600
H  2.65952400  2.06557200  0.61170000
C  0.70886400  1.21445700  0.37596200
H  0.19963200  2.11372100  0.69654500
C  4.25995500 -0.04073500 -0.02032100
F  4.73662200 -0.46647400  1.18024300
F  4.82115900  1.16760200 -0.24732100
F  4.75520300 -0.88931300 -0.94937600

M062X

N  -1.42878500  0.09396800  0.04403500
N  -2.13765600 -1.01888400  0.38844500
N  -3.46423600  0.65281700 -0.14637800
C  -2.22631400  1.10743700 -0.28394300
H  -1.91565200  2.08286800 -0.62189300
C  -3.37776800 -0.64713300  0.26623200
C  -4.73443500 -1.22869400  0.47052800
H  -4.95899800 -1.24391400  1.53930400
H  -4.81197800 -2.24172800  0.08266600
C  -5.62042600 -0.21142200 -0.29362300
H  -6.60483400 -0.10568500  0.15532700
H  -5.74117700 -0.54120200 -1.32534100
C  -4.85440800  1.12914100 -0.27633000
H  -4.96714600  1.71326400 -1.18559800
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -5.08634800 | 1.74035800 | 0.59526900 |
| C    | 0.00171600  | 0.06891400  | 0.02557300  |
| C    | 0.63558300  | -1.11163700 | -0.33869000 |
| H    | 0.05221700  | -1.98409700 | -0.60064900 |
| C    | 2.02208700  | -1.14098200 | -0.36454200 |
| H    | 2.53762300  | -2.04922200 | -0.64939000 |
| C    | 2.74108300  | 0.00480800  | -0.04012200 |
| C    | 2.09398000  | 1.18023000  | 0.32461800  |
| H    | 2.66344500  | 2.06368100  | 0.58449300  |
| C    | 0.70747100  | 1.21519400  | 0.36780600  |
| H    | 0.19480900  | 2.11560000  | 0.68116600  |
| C    | 4.24188500  | -0.04196800 | -0.02362700 |
| F    | 4.71549000  | -0.35481700 | 1.19663400  |
| F    | 4.78649400  | 1.13702900  | -0.35445200 |
| F    | 4.72802200  | -0.95871900 | -0.87122100 |
7g (B3LYP)

\[ \text{N} \quad -0.35075300 \quad -0.03309100 \quad 0.04184500 \\
\text{N} \quad -1.09160500 \quad -0.02664900 \quad -1.12347000 \\
\text{N} \quad -2.38594900 \quad -0.08594500 \quad 0.66695900 \\
\text{C} \quad -1.13353600 \quad -0.07216700 \quad 1.11782800 \\
\text{H} \quad -0.80064200 \quad -0.08268100 \quad 2.14201800 \\
\text{C} \quad -2.32640500 \quad -0.06179500 \quad -0.70227200 \\
\text{C} \quad -3.69412100 \quad -0.10819500 \quad -1.29577400 \\
\text{H} \quad -3.88616600 \quad -1.10969100 \quad -1.68999800 \\
\text{H} \quad -3.81781900 \quad 0.60464800 \quad -2.10968400 \\
\text{C} \quad -4.58965100 \quad 0.21433100 \quad -0.06270900 \\
\text{H} \quad -5.53236600 \quad -0.32838400 \quad -0.08929500 \\
\text{H} \quad -4.81053800 \quad 1.28202600 \quad -0.04214800 \\
\text{C} \quad -3.76454300 \quad -0.16299200 \quad 1.19452000 \\
\text{H} \quad -3.88979700 \quad 0.52827900 \quad 2.02450200 \\
\text{H} \quad -3.94671400 \quad -1.18264200 \quad 1.53449700 \\
\text{C} \quad 1.07823400 \quad 0.00772200 \quad 0.01877600 \\
\text{C} \quad 1.79462400 \quad -1.19980800 \quad -0.00621000 \\
\text{C} \quad 3.19167900 \quad -1.15467300 \quad -0.04034000 \\
\text{H} \quad 3.77616000 \quad -2.06296600 \quad -0.05793500 \\
\text{C} \quad 3.82721800 \quad 0.08435900 \quad -0.05295000 \\
\text{C} \quad 3.12362500 \quad 1.28593400 \quad -0.03148400 \\
\]
|   |   |   |   |
|---|---|---|---|
| C | -4.56043200 | 0.23904300 | -0.05834200 |
| H | -5.52586100 | -0.25973100 | -0.09172900 |
| H | -4.72595000 | 1.31558700 | -0.01896300 |
| C | -3.75158500 | -0.19443500 | 1.18377900 |
| H | -3.87392200 | 0.46397000 | 2.03947800 |
| H | -3.93988400 | -1.22747800 | 1.47437000 |
| C | 1.07422600 | 0.00843100 | 0.01882300 |
| C | 1.78603100 | -1.19461900 | -0.00876500 |
| C | 3.18019300 | -1.14792300 | -0.04053600 |
| H | 3.76875700 | -2.05374000 | -0.05907300 |
| C | 3.80830900 | 0.09233000 | -0.04981100 |
| C | 3.10524400 | 1.29168400 | -0.02755700 |
| H | 3.63730100 | 2.23174500 | -0.03632600 |
| C | 1.71091200 | 1.25267700 | 0.00510300 |
| H | 4.89091500 | 0.12571900 | -0.07506200 |
| O | 1.04272500 | -2.31475900 | 0.00223600 |
| O | 0.90086900 | 2.32536600 | 0.03032500 |
| C | 1.72665400 | -3.56588700 | -0.01126800 |
| H | 2.36291900 | -3.66548000 | 0.87050400 |
| H | 0.95065200 | -4.32602900 | 0.00650600 |
| H | 2.32390600 | -3.66739500 | -0.91971000 |
| C | 1.50786100 | 3.61562900 | 0.02764900 |
| H | 2.09532700 | 3.76212500 | -0.88106800 |
| H | 0.68735300 | 4.32706200 | 0.05443200 |
| H | 2.13946500 | 3.74546800 | 0.90890500 |
### 7h (B3LYP)

![Chemical Structure](image)

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| N    | -1.27531800 | -0.04804900 | 0.04704300 |
| N    | -2.00925300 | -0.1191200 | -1.11845300 |
| N    | -3.31258200 | -0.16844600 | 0.66369200 |
| C    | -2.06351400 | -0.08108100 | 1.11993900 |
| H    | -1.73812300 | -0.03794400 | 2.14571300 |
| C    | -3.24568900 | -0.19470600 | -0.70370800 |
| C    | -4.60551300 | -0.32665800 | -1.30207200 |
| H    | -4.74937600 | -1.35166800 | -1.65430800 |
| H    | -4.75494200 | 0.34487100 | -2.14613700 |
| C    | -5.52229000 | 0.00657200 | -0.08775400 |
| H    | -6.44101100 | -0.57635500 | -0.09731100 |
| H    | -5.78814900 | 1.06389500 | -0.11138400 |
| C    | -4.69024500 | -0.28472800 | 1.18752800 |
| H    | -4.85066100 | 0.43297400 | 1.98848300 |
| H    | -4.83012400 | -1.29702000 | 1.56700400 |
| C    | 0.16802100 | 0.06161800 | 0.02421100 |
| C    | 0.92771700 | -1.12101000 | 0.00906100 |
| C    | 2.31589500 | -0.98108600 | -0.00471000 |
| H    | 2.92637100 | -1.87645900 | -0.01221700 |
| C    | 2.93913500 | 0.27018800 | -0.00973100 |
|   | X       | Y       | Z       |
|---|---------|---------|---------|
| C | 5.07051000 | -0.21230200 | -1.29517900 |
| H | 6.15172300 | -0.04823200 | -1.30814400 |
| H | 4.89626400 | -1.29110400 | -1.34647400 |
| H | 4.64739800 | 0.24170900  | -2.19513300 |
| C | 5.08877700 | -0.21107300 | 1.24473400  |
| H | 6.17004100 | -0.04676000 | 1.24230200  |
| H | 4.67843800 | 0.24351600  | 2.15031500  |
| H | 4.91554600 | -1.28987500 | 1.29931600  |

**M062X**

|   | X       | Y       | Z       |
|---|---------|---------|---------|
| N | -1.26729600 | -0.06340600 | 0.04074000 |
| N | -1.99164900 | -0.10412300 | -1.11553700 |
| N | -3.29093900 | -0.20570300 | 0.65808400  |
| C | -2.04495000 | -0.12714500 | 1.11300600  |
| H | -1.70921000 | -0.10962000 | 2.13782900  |
| C | -3.22485000 | -0.19408800 | -0.70597200 |
| C | -4.58635000 | -0.31354700 | -1.30199500 |
| H | -4.73573200 | -1.33872500 | -1.64772100 |
| H | -4.73080400 | 0.36233000  | -2.14166900 |
| C | -5.48483700 | 0.02411800  | -0.08448600 |
| H | -6.42844400 | -0.51509900 | -0.10849200 |
| H | -5.69457700 | 1.09363100  | -0.07553800 |
| C | -4.66613600 | -0.34144300 | 1.17276900  |
| H | -4.82238200 | 0.33317400  | 2.01003700  |

SI-111
H  -4.81070500  -1.37380600  1.48947300
C   0.16988800   0.05898900   0.01907200
C   0.93394000  -1.11339000  -0.00267800
C   2.31732000  -0.96189200  -0.01194800
H   2.93851900  -1.85187300  -0.02150300
C   2.92292900   0.29575300  -0.00933700
C   2.11304400   1.42880200  -0.00434100
H   2.58012300   2.40859400  -0.00796500
C   0.72094000   1.34183700   0.00539100
C   0.31664700  -2.49996900  -0.00917600
H  -0.77006700  -2.40146200  -0.06025400
C  -0.12518600   2.60187400   0.00316400
H  -1.17958600   2.31682800  -0.02672900
C   4.43267100   0.42534800  -0.01588400
H   4.66610400   1.49435400  -0.01177600
C   0.65808100  -3.25146600   1.28310000
H   1.73631500  -3.41188500   1.36525800
H   0.32851900  -2.69452200   2.16317100
H   0.16931400  -4.22815000   1.28848300
C   0.76009600  -3.29368500  -1.24349600
H   0.51125200  -2.76077000  -2.16354500
H   1.83828000  -3.47137700  -1.23087200
H   0.26004300  -4.26448000  -1.26002400
C   0.10314000   3.41283900   1.28400000
H  -0.12203700   2.81846100   2.17239300
|  |  |  |  |  |
|---|---|---|---|---|
| H | 1.14089100 | 3.74915300 | 1.35167700 |  |
| H | -0.53903200 | 4.29633900 | 1.28726400 |  |
| C | 0.15545400 | 3.44650500 | -1.24499800 |  |
| H | 1.19090100 | 3.79575300 | -1.25798800 |  |
| H | -0.02374600 | 2.87228600 | -2.15647600 |  |
| H | -0.49530400 | 4.32360000 | -1.25510700 |  |
| C | 5.03704800 | -0.18903400 | -1.28369100 |  |
| H | 6.11812000 | -0.03310200 | -1.29887400 |  |
| H | 4.85248400 | -1.26617500 | -1.32052400 |  |
| H | 4.61067900 | 0.26081900 | -2.18278500 |  |
| C | 5.04856200 | -0.20147100 | 1.24023200 |  |
| H | 6.12971300 | -0.04547300 | 1.24729900 |  |
| H | 4.63031700 | 0.23919000 | 2.14768200 |  |
| H | 4.86453700 | -1.27899000 | 1.26787200 |  |
7i (B3LYP)

![Chemical Structure Image]

N 0.48241800 0.03273600 0.05075900
N 1.21936300 -0.00626800 -1.11526200
N 2.52332700 0.07253400 0.66533500
C 1.27191800 0.08330000 1.12209800
H 0.94575400 0.11882500 2.14809200
C 2.45757000 0.02218700 -0.70161000
C 3.82265900 0.04073700 -1.30242400
H 4.02370000 1.03174500 -1.71811700
H 3.93405700 -0.68991600 -2.10221600
C 4.72052400 -0.26692700 -0.06720800
H 5.66856400 0.26551900 -2.10842300
H 4.93063900 -1.33620100 -0.02687600
C 3.90504400 0.14291000 1.18616100
H 4.02536000 -0.53462600 2.02810000
H 4.10011500 1.16634100 1.50708200
C -0.96284600 0.00951100 0.02823600
C -1.64761700 1.23111500 -0.01191700
C -3.04251700 1.17819500 -0.04133600
H -3.59774200 2.10953800 -0.07631700
C -3.73665000 -0.03485600 -0.03389300
C -3.00456200 -1.22554300 -0.00665100

SI-114
H  -3.53033800  -2.17445900  -0.01338100
C  -1.60909200  -1.23375100  0.02346800
C  -0.92373000  2.55456200  -0.02167800
H  -0.42278200  2.74360100  0.93257500
H  -0.16200400  2.59252600  -0.80421600
H  -1.62699700  3.36947700  -0.19354100
C  -0.84250300  -2.53254000  0.04687200
H  -0.13533200  -2.59608500  -0.78412900
H  -0.26957100  -2.64470800  0.97203700
H  -1.52680300  -3.37790800  -0.02506700
C  -5.24481900  -0.05896000  -0.03260000
H  -5.62860900  -0.95118400  -0.53129600
H  -5.62690700  -0.06675800  0.99378800
H  -5.65712900  0.82161200  -0.52903000

M062X

N   0.47751900  0.05676300  0.04133900
N   1.20467300  -0.14587700  -1.09743500
N   2.50629200  0.18012600  0.64719700
C   1.25841200  0.25632700  1.09492500
H   0.92290900  0.43099600  2.10504700
C   2.43978800  -0.06271800  -0.69555100
C   3.80656300  -0.13302600  -1.28718100
H   4.02326000  0.80840600  -1.79685600

SI-115
| H   | -5.59701100 | -0.01952800 | 1.00698300 |
|-----|-------------|-------------|------------|
| H   | -5.64346200 | 0.73286100  | -0.58708700 |
### 7j (B3LYP)

![Chemical Structure](image)

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| N    | 0.87186   | 0.03821   | 0.05898   |
| N    | 1.59446   | 0.02737   | -1.11679  |
| N    | 2.91154   | 0.06020   | 0.65822   |
| C    | 1.66987   | 0.06052   | 1.12925   |
| H    | 1.35109   | 0.06965   | 2.15852   |
| C    | 2.83428   | 0.04394   | -0.71186  |
| C    | 4.19365   | 0.07182   | -1.32295  |
| H    | 4.39487   | 1.07318   | -1.71280  |
| H    | 4.29296   | -0.63703  | -2.14348  |
| C    | 5.10016   | -0.27366  | -0.10421  |
| H    | 6.05137   | 0.25308   | -0.14139  |
| H    | 5.30230   | -1.34507  | -0.09271  |
| C    | 4.30045   | 0.11156   | 1.16661   |
| H    | 4.42356   | -0.58542  | 1.99185   |
| H    | 4.50148   | 1.12704   | 1.50778   |
| C    | -0.55505  | 0.01345   | 0.04189   |
| C    | -1.28272  | 1.20897   | 0.01596   |
| C    | -2.67115  | 1.19544   | -0.01477  |
| H    | -3.22659  | 2.12212   | -0.03072  |
| C    | -3.32348  | -0.03294  | -0.02525  |
| C    | -2.63049  | -1.23882  | -0.00743  |
|   | X   | Y   | Z      |
|---|-----|-----|--------|
| H | -3.15449500 | -2.18375200 | -0.01764400 |
| C | -1.24237000 | -1.20579200 | 0.02412800 |
| Cl | -0.45001100 | 2.73904300 | 0.02446000 |
| Cl | -5.07010000 | -0.06179500 | -0.06159000 |
| Cl | -0.35875000 | -2.70674400 | 0.04475000 |

**M062X**

|   | X   | Y   | Z      |
|---|-----|-----|--------|
| N | 0.86324300 | 0.06437500 | 0.06017700 |
| N | 1.57396400 | 0.05823100 | -1.10716500 |
| N | 2.89188200 | 0.06922300 | 0.65815000 |
| C | 1.65481100 | 0.07295100 | 1.12898000 |
| H | 1.32948600 | 0.07396400 | 2.15777300 |
| C | 2.81119000 | 0.06436300 | -0.70901200 |
| C | 4.17156300 | 0.08630900 | -1.31735000 |
| H | 4.39128600 | 1.09969500 | -1.66033700 |
| H | 4.25637200 | -0.59448000 | -2.16109600 |
| C | 5.05487700 | -0.32124900 | -0.11005400 |
| H | 6.03624300 | 0.14513500 | -0.14468600 |
| H | 5.18310100 | -1.40351700 | -0.10467100 |
| C | 4.28084600 | 0.10364700 | 1.15655500 |
| H | 4.39459900 | -0.58005700 | 1.99312600 |
| H | 4.50204600 | 1.12345700 | 1.46935000 |
| C | -0.55976400 | 0.02672500 | 0.04485100 |
| C | -1.29218000 | 1.21210700 | 0.01784900 |
|  | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| C | -2.67744300 | 1.18217600 | -0.01418200 |
| H | -3.24635800 | 2.10156000 | -0.03044300 |
| C | -3.31092500 | -0.05347600 | -0.02573800 |
| C | -2.60698600 | -1.25066000 | -0.00915500 |
| H | -3.12141700 | -2.20166300 | -0.02205500 |
| C | -1.22257300 | -1.19917700 | 0.02366800 |
| Cl | -0.46476200 | 2.72894600 | 0.02705500 |
| Cl | -5.04329300 | -0.10327900 | -0.06266400 |
| Cl | -0.30661900 | -2.66385600 | 0.04187000 |
### 7k (B3LYP)

```
N  -0.91321700  -0.03901700  0.06481800
N  -1.63543900  -0.01031900  -1.11283600
N  -2.95131800  -0.07275900  0.66400800
C  -1.71243000  -0.07907600  1.13650800
H  -1.39310400  -0.10429900  2.16558000
C  -2.87413000  -0.03456500  -0.70710500
C  -4.23358300  -0.05371900  -1.31780400
H  -4.43295000  -1.04888600  -1.72408400
H  -4.33323500  0.66842100  -2.12661600
C  -5.14058500  0.27062000  -0.09363400
H  -6.09066300  -0.25742500  -0.13965500
H  -5.34466300  1.34125800  -0.06453500
C  -4.34113800  -0.13406900  1.17097300
H  -4.46442200  0.54894600  2.00768300
H  -4.53933300  -1.15564600  1.49500700
C  0.50873700  -0.01504700  0.04838100
C  1.19240400  1.19959500  0.03437300
C  2.57902800  1.22605300  -0.00154100
C  3.28869200  0.03064600  -0.02921500
C  2.61849800  -1.18757200  -0.02050300
```
|  |  |  |  |  |
|---|---|---|---|---|
| C | 1.23171700 | -1.20654600 | 0.01516600 |
| F | 4.61734900 | 0.05290100 | -0.06183900 |
| F | 3.23095600 | 2.38875100 | -0.00912600 |
| F | 0.51677300 | 2.34699900 | 0.05994300 |
| F | 0.59335700 | -2.37542200 | 0.02077200 |
| F | 3.30766700 | -2.32829700 | -0.04740600 |

**M062X**

|  |  |  |  |  |
|---|---|---|---|---|
| N | -0.90998000 | -0.04560900 | 0.06229000 |
| N | -1.62353400 | -0.01724900 | -1.10512500 |
| N | -2.93668400 | -0.07752900 | 0.66347500 |
| C | -1.70170300 | -0.08443700 | 1.13343600 |
| H | -1.37518800 | -0.10796600 | 2.16157100 |
| C | -2.85894600 | -0.04062000 | -0.70447200 |
| C | -4.22000000 | -0.06304600 | -1.31094700 |
| H | -4.42499800 | -1.06758900 | -1.68675900 |
| H | -4.31507400 | 0.64339500 | -2.13230200 |
| C | -5.10862800 | 0.29574500 | -0.09188600 |
| H | -6.07913000 | -0.19186300 | -0.13612300 |
| H | -5.26160500 | 1.37417700 | -0.06077000 |
| C | -4.32420000 | -0.14163100 | 1.16427400 |
| H | -4.44447800 | 0.52444800 | 2.01402000 |
| H | -4.52782700 | -1.17048700 | 1.45834500 |
| C | 0.50941100 | -0.01894500 | 0.04706600 |

SI-122
| Element | Distance1  | Distance2  | Distance3  |
|---------|-----------|------------|------------|
| C       | 1.18128100| 1.19598500 | 0.03236000 |
| C       | 2.56398500| 1.22720000 | -0.00082200|
| C       | 3.27365600| 0.03602500 | -0.02734400|
| C       | 2.61142300| -1.18231000| -0.01973000|
| C       | 1.22846000| -1.20656800| 0.01344900 |
| F       | 4.59302500| 0.06216100 | -0.05925100|
| F       | 3.20877500| 2.38306100 | -0.00830000|
| F       | 0.50134700| 2.32938900 | 0.05553200 |
| F       | 0.59400000| -2.36619900| 0.01714400 |
| F       | 3.30188100| -2.31127800| -0.04676500|
8a (B3LYP)

\[
\begin{array}{c}
\text{N} & 0.43202900 & -0.00941200 & -0.03428800 \\
\text{N} & 1.20274900 & 1.05127400 & 0.35848000 \\
\text{N} & 2.46373300 & -0.67103600 & -0.20289000 \\
\text{C} & 1.18952400 & -1.04144800 & -0.38204800 \\
\text{H} & 0.84697900 & -1.98963600 & -0.76004900 \\
\text{C} & 2.43891600 & 0.62964900 & 0.24657500 \\
\text{C} & -0.99804000 & 0.07458100 & -0.03916100 \\
\text{C} & -1.75657600 & -1.00722100 & 0.39134000 \\
\text{C} & -3.14744100 & -0.93122200 & 0.36408600 \\
\text{C} & -3.77082300 & 0.24050200 & -0.08008400 \\
\text{C} & -2.98980900 & 1.33027300 & -0.49800600 \\
\text{C} & -1.60874600 & 1.24966100 & -0.48281600 \\
\text{C} & 3.68842500 & -1.45281900 & -0.50834400 \\
\text{H} & 3.80060400 & -1.46293600 & -1.59385300 \\
\text{H} & 3.52724000 & -2.47203700 & -0.16070000 \\
\text{C} & 3.68386300 & 1.38358700 & 0.57393800 \\
\text{H} & 3.56555000 & 2.41847300 & 0.24887500 \\
\text{H} & 3.79007900 & 1.40056100 & 1.66381800 \\
\text{C} & 4.91311300 & 0.71641000 & -0.06608700 \\
\text{H} & 4.93333600 & 0.92751400 & -1.14010600 \\
\text{H} & 5.81666000 & 1.15119100 & 0.36349200 \\
\end{array}
\]
| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| C       | 4.89350800 | -0.79971400 | 0.16626400 |
| H       | 4.87706600 | -1.01390100 | 1.23942500 |
| H       | 5.79279300 | -1.26440700 | -0.24211900 |
| H       | -1.27911800 | -1.90493300 | 0.76464600 |
| H       | -3.72425700 | -1.77895500 | 0.70503400 |
| H       | -3.48576000 | 2.22997200 | -0.84021000 |
| H       | -1.00575800 | 2.08447700 | -0.81513200 |
| O       | -5.11280800 | 0.41966800 | -0.13805400 |
| C       | -5.97314000 | -0.65175200 | 0.26858500 |
| H       | -6.98645600 | -0.28217800 | 0.12951800 |
| H       | -5.81694000 | -1.53680700 | -0.35363300 |
| H       | -5.81577300 | -0.90243600 | 1.32085100 |

**M062X**

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| N       | 0.43251800 | -0.01093400 | -0.02242200 |
| N       | 1.19505500 | 1.04628700 | 0.35356100 |
| N       | 2.45199000 | -0.67179500 | -0.19612200 |
| C       | 1.18228100 | -1.04387500 | -0.36380300 |
| H       | 0.83384700 | -1.99626400 | -0.73015900 |
| C       | 2.42745400 | 0.62863200 | 0.24118600 |
| C       | -0.99626200 | 0.07369300 | -0.03086100 |
| C       | -1.75124600 | -1.01360300 | 0.37428000 |
| C       | -3.14022700 | -0.93545600 | 0.34151200 |
| C       | -3.75469000 | 0.24461400 | -0.08042600 |

SI-125
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -2.97355400 | 1.34078400 | -0.47110600 |
| C       | -1.59579500 | 1.25804600 | -0.45277300 |
| C       | 3.67082800  | -1.45557300 | -0.49368800 |
| H       | 3.78708900  | -1.46904900 | -1.57814100 |
| H       | 3.50581500  | -2.47018100 | -0.13605600 |
| C       | 3.67185300  | 1.38737900  | 0.55276600  |
| H       | 3.54475000  | 2.41708500  | 0.21847300  |
| H       | 3.78979400  | 1.40508000  | 1.64008900  |
| C       | 4.88340100  | 0.71123000  | -0.09781700 |
| H       | 4.87380500  | 0.88866200  | -1.17727900 |
| H       | 5.79493600  | 1.15744400  | 0.29864200  |
| C       | 4.86524200  | -0.79279400 | 0.17952800  |
| H       | 4.82853200  | -0.97376200 | 1.25756200  |
| H       | 5.76777400  | -1.26886500 | -0.20432700 |
| H       | -1.27323700 | -1.91748100 | 0.73267600  |
| H       | -3.72026100 | -1.78993500 | 0.66005600  |
| H       | -3.47144400 | 2.24633400  | -0.79414100 |
| H       | -0.98413200 | 2.09593100  | -0.76221800 |
| O       | -5.09066100 | 0.42401800  | -0.14101400 |
| C       | -5.92931100 | -0.65540400 | 0.25320200  |
| H       | -6.94887700 | -0.30148100 | 0.12714200  |
| H       | -5.76188500 | -1.52911600 | -0.38144200 |
| H       | -5.75801600 | -0.91749100 | 1.30011500  |
8b (B3LYP)

\[
\text{N} & -0.41365400 & -0.05554900 & -0.00990800 \\
\text{N} & 0.32623900 & 1.04474100 & 0.32695000 \\
\text{N} & 1.63456700 & -0.65615600 & -0.19043600 \\
\text{C} & 0.37222900 & -1.07585000 & -0.32981200 \\
\text{H} & 0.05560800 & -2.04950600 & -0.66343800 \\
\text{C} & 1.57361900 & 0.66003700 & 0.21117400 \\
\text{C} & -1.84820100 & 0.01893700 & 0.00246800 \\
\text{C} & -2.55613900 & -1.12904400 & 0.45737300 \\
\text{C} & -3.94842000 & -1.08760200 & 0.44254500 \\
\text{C} & -4.61305200 & 0.05411700 & -0.00335100 \\
\text{C} & -3.88539300 & 1.16132000 & -0.44105300 \\
\text{C} & -2.49378300 & 1.13128000 & -0.44525000 \\
\text{C} & 2.88047800 & -1.40788300 & -0.48674200 \\
\text{H} & 2.98235300 & -1.44459200 & -1.57268500 \\
\text{H} & 2.75339900 & -2.42125800 & -0.10935100 \\
\text{C} & 2.79782100 & 1.46272000 & 0.49819300 \\
\text{H} & 2.64600100 & 2.48078900 & 0.13614300 \\
\text{H} & 2.91047200 & 1.52341700 & 1.58591600 \\
\text{C} & 4.04278200 & 0.80955500 & -0.12604700 \\
\text{H} & 4.05181600 & 0.98418100 & -1.20655300 \\
\text{H} & 4.93501600 & 1.28512700 & 0.28338200
\]
| Atom | X         | Y         | Z        |
|------|-----------|-----------|----------|
| C    | 4.06954800| -0.69781200| 0.15738600|
| H    | 4.06588100| -0.87662200| 1.23704000|
| H    | 4.97969400| -1.14897700| -0.24196200|
| H    | -2.03712000| -2.00134000| 0.83505200|
| H    | -4.50971100| -1.94425900| 0.79489400|
| H    | -4.39964800| 2.04932000| -0.78782600|
| H    | -1.91671900| 1.97799500| -0.79259700|
| H    | -5.69604600| 0.08308600| -0.00554500|

M062X

| Atom | X         | Y         | Z        |
|------|-----------|-----------|----------|
| N    | -0.40785000| -0.05889900| -0.00079400|
| N    | 0.32272600| 1.03817100| 0.31918700|
| N    | 1.62944000| -0.65841700| -0.17989000|
| C    | 0.37218900| -1.08018500| -0.31052100|
| H    | 0.05207700| -2.05848200| -0.63185900|
| C    | 1.56663400| 0.65812900| 0.20586700|
| C    | -1.84067200| -0.02151500| 0.00601500|
| C    | -2.54687900| -1.14170500| 0.42391500|
| C    | -3.93632300| -1.09531200| 0.40319900|
| C    | -4.59313600| 0.05970600| -0.01015900|
| C    | -3.86283600| 1.17631100| -0.40967300|
| C    | -2.47407100| 1.14256900| -0.40910200|
| C    | 2.87097900| -1.41206200| -0.46230700|
| H    | 2.97756400| -1.46006400| -1.54680500|

SI-128
|   | X      | Y      | Z      |
|---|--------|--------|--------|
| H | 2.74165800 | -2.41790900 | -0.06743000 |
| C | 2.78853900  | 1.46824700  | 0.47369200  |
| H | 2.62570800  | 2.47897100  | 0.09940300  |
| H | 2.91434500  | 1.53365100  | 1.55840500  |
| C | 4.01612000  | 0.80540500  | -0.16019700 |
| H | 3.99319500  | 0.93948400  | -1.24560900 |
| H | 4.91561100  | 1.29563200  | 0.21081500  |
| C | 4.04790700  | -0.68640300 | 0.17552600  |
| H | 4.02388000  | -0.82649300 | 1.25996200  |
| H | 4.96261800  | -1.14804100 | -0.19698700 |
| H | -2.02875200 | -2.02443000 | 0.77852500  |
| H | -4.50242500 | -1.96033700 | 0.72511100  |
| H | -4.37386200 | 2.07566700  | -0.72978200 |
| H | -1.88696200 | 1.99543500  | -0.72448700 |
| H | -5.67556200 | 0.09183500  | -0.01632000 |
8c (B3LYP)

\[
\begin{align*}
\text{N} & \quad 0.00026000 \quad 0.06341700 \quad -0.01339300 \\
\text{N} & \quad -0.73400400 \quad -1.03661700 \quad 0.33705800 \\
\text{N} & \quad -2.05025600 \quad 0.65259300 \quad -0.19885900 \\
\text{C} & \quad -0.79032900 \quad 1.07646800 \quad -0.34504500 \\
\text{H} & \quad -0.47817200 \quad 2.04759400 \quad -0.69042400 \\
\text{C} & \quad -1.98321000 \quad -0.65886500 \quad 0.21741200 \\
\text{C} & \quad 1.43298000 \quad 0.03250000 \quad 0.00058700 \\
\text{C} & \quad 2.13825100 \quad 1.13669300 \quad 0.47397200 \\
\text{C} & \quad 3.52933200 \quad 1.10870000 \quad 0.46457300 \\
\text{C} & \quad 4.16487800 \quad -0.03187700 \quad -0.00040600 \\
\text{C} & \quad 3.47426400 \quad -1.14397200 \quad -0.45928800 \\
\text{C} & \quad 2.08461400 \quad -1.10860300 \quad -0.46279900 \\
\text{C} & \quad -3.30005600 \quad 1.39635400 \quad -0.49992600 \\
\text{H} & \quad -3.40405200 \quad 1.42205100 \quad -1.58594500 \\
\text{H} & \quad -3.17619500 \quad 2.41378800 \quad -0.13253100 \\
\text{C} & \quad -3.20350300 \quad -1.46410600 \quad 0.51351700 \\
\text{H} & \quad -3.04755700 \quad -2.48483000 \quad 0.16080800 \\
\text{H} & \quad -3.31423000 \quad -1.51507400 \quad 1.60192700 \\
\text{C} & \quad -4.45216600 \quad -0.82230000 \quad -0.11511200 \\
\text{H} & \quad -4.46232000 \quad -1.00775900 \quad -1.19381200 \\
\text{H} & \quad -5.34164000 \quad -1.29754100 \quad 0.30063000
\end{align*}
\]
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -4.48477700 | 0.68761400 | 0.15351000 |
| H       | -4.47984800 | 0.87721500 | 1.23132800 |
| H       | -5.39752900 | 1.13101300 | -0.24855900 |
| F       | 5.51915000  | -0.06431300 | -0.00167700 |
| H       | 1.61899300  | 2.00320900 | 0.86335600 |
| H       | 4.10864300  | 1.94780300 | 0.82664000 |
| H       | 4.01372200  | -2.01261700 | -0.81348100 |
| H       | 1.51417900  | -1.95342300 | -0.82448800 |

**M062X**

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| N       | -0.00331800 | 0.06694900 | -0.00366100 |
| N       | -0.72818400 | -1.02973100 | 0.33085100 |
| N       | -2.04291700 | 0.65430300 | -0.18988100 |
| C       | -0.78801000 | 1.08043000 | -0.32707800 |
| H       | -0.47213600 | 2.05591900 | -0.66128600 |
| C       | -1.97392700 | -0.65701300 | 0.21248500 |
| C       | 1.42776500  | 0.03587200 | 0.00578200 |
| C       | 2.13033500  | 1.14987300 | 0.44607800 |
| C       | 3.51841900  | 1.11818900 | 0.43103900 |
| C       | 4.14738200  | -0.03476300 | -0.00410900 |
| C       | 3.45464900  | -1.15634100 | -0.42849600 |
| C       | 2.06813200  | -1.11804000 | -0.42838200 |
| C       | -3.28830700 | 1.39919500 | -0.47953800 |
| H       | -3.39656300 | 1.43345000 | -1.56433600 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | -3.16248200 | 2.41025400 | -0.09708100 |
| C       | -3.19191700 | -1.46935000 | 0.49110500 |
| H       | -3.02498000 | -2.48366800 | 0.12853400 |
| H       | -3.31572500 | -1.52255000 | 1.57670100 |
| C       | -4.42340900 | -0.81937700 | -0.14853700 |
| H       | -4.40224900 | -0.96684300 | -1.23223000 |
| H       | -5.32001700 | -1.30876400 | 0.23043900 |
| C       | -4.46102200 | 0.67625500  | 0.16900000 |
| H       | -4.43609700 | 0.82994800  | 1.25156900 |
| H       | -5.37823900 | 1.12934700  | -0.20782000 |
| F       | 5.48996300  | -0.07037200 | -0.00932300 |
| H       | 1.61067100  | 2.02546700  | 0.81503900 |
| H       | 4.10529000  | 1.96360700  | 0.76512200 |
| H       | 3.99538600  | -2.03410000 | -0.75737300 |
| H       | 1.48787200  | -1.96894300 | -0.76063800 |
8i (B3LYP)

\[
\begin{array}{cccc}
\text{N} & 0.18034000 & 0.01431800 & 0.05749400 \\
\text{N} & 0.91853600 & -0.20506500 & -1.07734000 \\
\text{N} & 2.23208000 & 0.13575100 & 0.66502900 \\
\text{C} & 0.97014800 & 0.21587900 & 1.10136500 \\
\text{H} & 0.64990200 & 0.40291600 & 2.11315600 \\
\text{C} & 2.16682900 & -0.12736700 & -0.68679800 \\
\text{C} & -1.26553400 & 0.00830800 & 0.03183300 \\
\text{C} & -1.93545900 & 1.22940300 & -0.11102600 \\
\text{C} & -3.33155400 & 1.18951400 & -0.14171000 \\
\text{C} & -4.03908500 & -0.01066800 & -0.03931700 \\
\text{C} & -3.32020100 & -1.20348500 & 0.08934900 \\
\text{C} & -1.92564300 & -1.22444600 & 0.12746100 \\
\text{C} & 3.48197900 & 0.23238300 & 1.46180300 \\
\text{H} & 3.58999700 & -0.70819500 & 2.00450700 \\
\text{H} & 3.35716300 & 1.04211300 & 2.17901100 \\
\text{C} & 3.38937400 & -0.25691100 & -1.53303500 \\
\text{H} & 3.23503200 & -1.05923500 & -2.25630100 \\
\text{H} & 3.50076300 & 0.67110200 & -2.10372100 \\
\text{C} & 4.63714500 & -0.49554100 & -0.66587900 \\
\text{H} & 4.64852200 & -1.52933500 & -0.30623600 \\
\text{H} & 5.52760800 & -0.36011300 & -1.28118900 \\
\end{array}
\]
C  4.66546100  0.46918500  0.52574600
H  4.65449100  1.50425000  0.17016600
H  5.57928400  0.33658600  1.10766100
C  -1.17296100 -2.52440100  0.26339600
H  -0.51072400 -2.69396700 -0.58966700
H  -0.55291200 -2.53815900  1.16437500
H  -1.86908600 -3.36094200  0.32368100
C  -1.19776500  2.54048300 -0.22499700
H  -0.71183500  2.80923400  0.71784200
H  -0.42256500  2.50383200 -0.99435500
H  -1.89021900  3.34276500 -0.48002900
C  -5.54747400 -0.02162900 -0.04489600
H  -5.93585600 -0.89734700 -0.56941500
H  -5.93465100 -0.05651100  0.97891900
H  -5.95043700  0.87460500 -0.51986300
H  -3.85649000 -2.14397400  0.16008700
H  -3.87573000  2.12109800 -0.25467800

M062X

N  0.17755000  0.00954000  0.06042600
N  0.90407200 -0.21754400 -1.06556700
N  2.21859800  0.13642300  0.66297700
C  0.96212400  0.22019800  1.10014300
H  0.63771100  0.41818000  2.11027200
C  2.14982000 -0.13604800 -0.68231800
|   |   |   |   |   |
|---|---|---|---|---|
| C | -1.26419600 | 0.00755200 | 0.03676700 |
| C | -1.92191300 | 1.22686800 | -0.11212600 |
| C | -3.31517700 | 1.19314100 | -0.14499400 |
| C | -4.02040600 | -0.00469100 | -0.03966500 |
| C | -3.30944500 | -1.19940200 | 0.09443200 |
| C | -1.91898800 | -1.22126000 | 0.13469700 |
| C | 3.46560400 | 0.24464700 | 1.45257000 |
| H | 3.58706800 | -0.69677300 | 1.98999900 |
| H | 3.33468600 | 1.05416200 | 2.16809000 |
| C | 3.36908400 | -0.27200500 | -1.52981500 |
| H | 3.20868100 | -1.07709900 | -2.24687000 |
| H | 3.48366900 | 0.65659800 | -2.09660100 |
| C | 4.60428500 | -0.50840300 | -0.65452900 |
| H | 4.59344900 | -1.52961900 | -0.26232400 |
| H | 5.49930500 | -0.40332000 | -1.26700400 |
| C | 4.63140200 | 0.48848400 | 0.50443300 |
| H | 4.58662300 | 1.51139100 | 0.11949900 |
| H | 5.55286100 | 0.39164500 | 1.07892000 |
| C | -1.14782400 | -2.50567800 | 0.27473500 |
| H | -0.47476200 | -2.65290000 | -0.57301900 |
| H | -0.53812300 | -2.50139700 | 1.18186500 |
| H | -1.82938400 | -3.35336000 | 0.32613000 |
| C | -1.15940700 | 2.51902700 | -0.23175500 |
| H | -0.67820300 | 2.77991700 | 0.71438900 |
| H | -0.37868400 | 2.44752600 | -0.99243000 |
|  | x   | y   | z   |
|---|-----|-----|-----|
| H | -1.83189000 | 3.33161800 | -0.50242700 |
| C | -5.52588300 | -0.01729900 | -0.05405400 |
| H | -5.90267600 | -0.84673500 | -0.65456400 |
| H | -5.91338600 | -0.14241900 | 0.96046200 |
| H | -5.92451800 | 0.91497300 | -0.45443900 |
| H | -3.85069200 | -2.13738700 | 0.16676300 |
| H | -3.85775700 | 2.12527500 | -0.26268900 |
### 8k (B3LYP)

![Chemical Structure](image)

| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| N    | -0.62053500  | -0.00957700  | 0.07415500   |
| N    | -1.34547600  | 0.21755200   | -1.06959500  |
| N    | -2.66872200  | -0.13728300  | 0.66715100   |
| C    | -1.41814900  | -0.22017400  | 1.11709100   |
| H    | -1.10234300  | -0.41346800  | 2.12973400   |
| C    | -2.59380300  | 0.13568400   | -0.68675300  |
| C    | 0.80165800   | -0.00688100  | 0.05251000   |
| C    | 1.50751300   | -1.20325500  | -0.05875000  |
| C    | 2.89451500   | -1.20119200  | -0.09666600  |
| C    | 3.58139700   | 0.00581000   | -0.03363900  |
| C    | 2.88816800   | 1.20671200   | 0.06990800   |
| C    | 1.50152900   | 1.19676100   | 0.11179100   |
| C    | -3.92980700  | -0.24089000  | 1.45133000   |
| H    | -4.04266100  | 0.69894900   | 1.99377700   |
| H    | -3.80811200  | -1.05243400  | 2.16666300   |
| C    | -3.80925600  | 0.26705700   | -1.54127600  |
| H    | -3.64984000  | 1.07387000   | -2.25821000  |
| H    | -3.90942800  | -0.65864500  | -2.11769400  |
| C    | -5.06568300  | 0.49490400   | -0.68396200  |
| H    | -5.08570200  | 1.52655200   | -0.31920400  |
| Element | X    | Y    | Z    |
|---------|------|------|------|
| H       | -5.94854900 | 0.35815500 | -1.30950800 |
| C       | -5.10118200 | -0.47751200 | 0.50094500 |
| H       | -5.08258600 | -1.51052500 | 0.14027200 |
| H       | -6.02056800 | -0.35156500 | 1.07533300 |
| F       | 4.91026800  | 0.01187900  | -0.07062000 |
| F       | 3.56756300  | -2.34739400 | -0.19739300 |
| F       | 0.85282700  | -2.36133600 | -0.12747700 |
| F       | 0.84126100  | 2.34842100  | 0.21660100  |
| F       | 3.55602700  | 2.35866700  | 0.13240900  |

**M062X**

| Element | X    | Y    | Z    |
|---------|------|------|------|
| N       | -0.61954700 | -0.03231800 | 0.06750400 |
| N       | -1.33541200 | 0.58032200  | -0.91499100 |
| N       | -2.65669200 | -0.37017300 | 0.56944900 |
| C       | -1.41179200 | -0.60275600 | 0.96369700 |
| H       | -1.09801600 | -1.14314200 | 1.84374600 |
| C       | -2.58036100 | 0.36610400  | -0.59367500 |
| C       | 0.79861300  | -0.02100200 | 0.04893400 |
| C       | 1.50855200  | -1.19742900 | -0.14949300 |
| C       | 2.89179600  | -1.18035300 | -0.18422900 |
| C       | 3.56464800  | 0.02158300  | -0.03137300 |
| C       | 2.86381700  | 1.20281900  | 0.16058100 |
| C       | 1.48163000  | 1.17859100  | 0.20267900 |
| C       | -3.91099100 | -0.75005500 | 1.26234500 |

SI-138
| Atoms | X         | Y         | Z         |
|-------|-----------|-----------|-----------|
| H     | -4.03018600 | -0.06127400 | 2.09936400 |
| H     | -3.78248100 | -1.76258500 | 1.63984600 |
| C     | -3.79469700 | 0.78896800  | -1.34659400|
| H     | -3.63044100 | 1.79318500  | -1.73708300|
| H     | -3.90242900 | 0.11497700  | -2.20150400|
| C     | -5.03470000 | 0.70612500  | -0.45029100|
| H     | -5.02683700 | 1.52588200  | 0.27375900 |
| H     | -5.92485900 | 0.82341000  | -1.06743900|
| C     | -5.07156200 | -0.63457400 | 0.28411000 |
| H     | -5.03208000 | -1.45768800 | -0.43478000|
| H     | -5.99460100 | -0.73861700 | 0.85474300 |
| F     | 4.88431100  | 0.04241000  | -0.06759200|
| F     | 3.57076100  | -2.30116500 | -0.37082200|
| F     | 0.86501600  | -2.34274200 | -0.30928900|
| F     | 0.81353700  | 2.30218400  | 0.39969900 |
| F     | 3.51901600  | 2.34296900  | 0.31194400 |
9a (B3LYP)

N  -0.12376500  0.07485700  -0.17074700
N  -0.89371900  -0.98040900  -0.57814100
N  -2.14669000  0.79063900  -0.17169400
C  -0.87867600  1.13493600  0.08327800
H  -0.53952500  2.09010800  0.44700200
C  -2.12491800  -0.52880700  -0.57381500
C   1.29974100  -0.04186700  -0.05593500
C   2.11646700  0.98402000  -0.51530300
C   3.49952300  0.87881800  -0.38353500
C   4.05716000  -0.26762100  0.19388700
C   3.21854100  -1.30204900  0.64016000
C   1.84452800  -1.19118300  0.52088000
C  -3.33459300  1.66269600  -0.02508400
H  -3.75578700  1.80882200  -1.02181500
H  -2.96079700  2.62326300  0.32499200
C  -3.33105900  -1.32152000  -0.93832600
H  -3.77413600  -0.89425200  -1.84522800
H  -2.97947300  -2.32130200  -1.19569000
C  -4.39408600  -1.39869100  0.17782100
H  -3.92020200  -1.73207500  1.10711000
H  -5.10052800  -2.18172500  -0.10895400
C       2.10286800    0.98971300    -0.50090200
C       3.48262500    0.88614800    -0.35303100
C       4.03170100    -0.27466400    0.19416900
C       3.19476300    -1.32572500    0.59314600
C       1.82507000    -1.21639700    0.46068100
C      -3.32382100    1.65412500    -0.05428100
H      -3.78193400    1.75304600    -1.04052400
H      -2.95172700    2.63105200    0.24879200
C      -3.34031800    -1.30405200    -0.93329400
H      -3.81904800    -0.85143600    -1.80805000
H      -3.00000000    -2.29787200    -1.22359900
C      -4.34101200    -1.39024600    0.23095100
H      -3.81311000    -1.69760700    1.13919600
H      -5.04802600    -2.18662300   -0.00880200
C      -4.30453600    1.09455000    0.96988000
H      -3.75881100    0.84625600    1.88548200
H      -4.98758400    1.91001300    1.21796200
C      -5.12690500    -0.10250800    0.48605100
H      -5.89089800    -0.31095200    1.23858500
H      -5.66008400    0.17923400    -0.42907100
H       1.17005100    -2.01777000    0.77811400
H       3.64223200    -2.21667200    1.01519500
H       4.10703100    1.70497800    -0.68082800
H       1.67554000    1.87662600    -0.95353600
O       5.35372600    -0.47636000    0.37387800
|  | C     | 6.24778300 | 0.55953500 | -0.01523400 |
|---|---|---|---|---|
| H | 7.24481000 | 0.19588700 | 0.21831700 |
| H | 6.17034800 | 0.75685300 | -1.08721200 |
| H | 6.04945500 | 1.47530600 | 0.54684700 |
**9b (B3LYP)**

|      | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| N    | -0.70596300 | -0.02346800 | -0.17686600 |
| N    | 0.02942100  | 1.11237000  | 0.02189400   |
| N    | 1.33478600  | -0.57796800  | -0.53690100  |
| C    | 0.07900900  | -1.03752900  | -0.51652900  |
| H    | -0.23565600  | -2.04054600  | -0.74971900  |
| C    | 1.27165500  | 0.76076000  | -0.20481700  |
| C    | -2.13267000  | -0.02298800  | -0.01876300  |
| C    | -2.85649400  | 1.07746000  | -0.47215900  |
| C    | -4.24083500  | 1.07338900  | -0.32647300  |
| C    | -4.88511900  | -0.01880800  | 0.25569800   |
| C    | -4.14301700  | -1.11041600  | 0.70465000   |
| C    | -2.75568600  | -1.11616100  | 0.57859400   |
| C    | 2.54835100  | -1.36082100  | -0.86979500  |
| H    | 2.95435300  | -0.95027200  | -1.79679900  |
| H    | 2.20787400  | -2.37493500  | -1.07171200  |
| C    | 2.45191700  | 1.66126100  | -0.09845900  |
| H    | 2.89652200  | 1.77929900  | -1.09332200  |
| H    | 2.07100500  | 2.63900200  | 0.19860200   |
| C    | 3.52270600  | 1.17614300  | 0.90031500   |
| H    | 3.04857400  | 0.95809100  | 1.86313800   |
| H    | 4.20189100  | 2.01504100  | 1.07182900   |
C          3.58614500  -1.34816200  0.25340500
H          3.10412400  -1.64557400  1.19053100
H          4.30427900  -2.13586100  0.00899300
C          4.35060500  -0.02807800  0.43021700
H          5.14763600  -0.19770300  1.15974300
H          4.84837300  0.22489600  -0.51373800
H          -2.17440800  -1.94780400  0.95684400
H          -4.63824800  -1.95465600  1.16841300
H          -4.81537100  1.92250600  -0.67604000
H          -2.34489500  1.91253800  -0.93208200
H          -5.96316300  -0.01684700  0.36312200

M062X

N          -0.69378000  -0.01598800  -0.19503800
N           0.03253000  1.11446500  -0.00735300
N          1.33302400  -0.56832700  -0.56514300
C          0.08375800  -1.02939700  -0.53499100
H          -0.23525300  -2.03417600  -0.76249600
C          1.26966700  0.76557400  -0.23754500
C          -2.11704900  -0.02073400  -0.02531000
C          -2.83875200  1.09057200  -0.44086300
C          -4.21881800  1.08115400  -0.28018100
C          -4.85433400  -0.02620600  0.27612300
C          -4.11004600  -1.12817100  0.68605300

SI-145
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -2.726743 | -1.129602 | 0.546344  |
| C    | 2.550986  | -1.339232 | -0.879908 |
| H    | 2.990253  | -0.898260 | -1.777234 |
| H    | 2.217276  | -2.346835 | -1.121463 |
| C    | 2.457708  | 1.651336  | -0.128166 |
| H    | 2.937011  | 1.724180  | -1.110242 |
| H    | 2.082785  | 2.642101  | 0.128014  |
| C    | 3.470302  | 1.164355  | 0.920773  |
| H    | 2.944970  | 0.941868  | 1.854881  |
| H    | 4.145571  | 1.996462  | 1.128610  |
| C    | 3.535424  | -1.347623 | 0.284553  |
| H    | 3.001968  | -1.626328 | 1.198635  |
| H    | 4.250320  | -2.146978 | 0.077146  |
| C    | 4.305833  | -0.040387 | 0.483289  |
| H    | 5.074936  | -0.214149 | 1.239393  |
| H    | 4.832624  | 0.207003  | -0.445285 |
| H    | -2.136818 | -1.968851 | 0.894388  |
| H    | -4.600501 | -1.984591 | 1.131183  |
| H    | -4.797966 | 1.939406  | -0.597336 |
| H    | -2.326526 | 1.935847  | -0.882086 |
| H    | -5.930694 | -0.027590 | 0.395598  |
9c (B3LYP)

\[
\begin{array}{cccc}
N & -0.29922000 & -0.02198900 & -0.20997700 \\
N & 0.43219000 & 1.11205100 & 0.01425700 \\
N & 1.74626900 & -0.57059400 & -0.54816400 \\
C & 0.49103200 & -1.03132000 & -0.55191500 \\
H & 0.18016100 & -2.03131300 & -0.80297400 \\
C & 1.67763700 & 0.76393400 & -0.19997200 \\
C & -1.72602900 & -0.02281300 & -0.07065400 \\
C & -2.44809200 & 1.06368900 & -0.56044200 \\
C & -3.83257700 & 1.06951300 & -0.43516300 \\
C & -4.44848800 & -0.01713600 & 0.16824100 \\
C & -3.74256100 & -1.10334500 & 0.66084100 \\
C & -2.35567300 & -1.10059800 & 0.54754600 \\
C & 2.96543300 & -1.34839600 & -0.87345300 \\
H & 3.38518200 & -0.92442400 & -1.78821500 \\
H & 2.62841600 & -2.35959100 & -1.09495200 \\
C & 2.85615400 & 1.66251100 & -0.06305500 \\
H & 3.31753600 & 1.79238200 & -1.04867000 \\
H & 2.47072300 & 2.63667100 & 0.23982000 \\
C & 3.90936400 & 1.16340200 & 0.94759000 \\
H & 3.41841700 & 0.93179300 & 1.89874100 \\
H & 4.58514400 & 1.99989000 & 1.14263500
\end{array}
\]
C     3.98511800  -1.35161000  0.26624100
H     3.48807600  -1.66298000  1.19088500
H     4.70757600  -2.13536500  0.02192300
C     4.74575600  -0.03397800  0.47507700
H     5.52983900  -0.21381600  1.21610400
H     5.26015700  0.23244900  -0.45613100
F     -5.79805900  -0.01381500  0.28586000
H     -1.78057000  -1.92237300  0.95444000
H     -4.26365900  -1.92342200  1.13703300
H     -4.42541900  1.89560200  -0.80550600
H     -1.93616700  1.88943500  -1.03597500

M062X

N     -0.28950000  -0.01358700  -0.22968200
N     0.43296800  1.11448300  -0.01369600
N     1.74261400  -0.56001700  -0.57569300
C     0.49352600  -1.02198700  -0.57216200
H     0.17854200  -2.02355300  -0.81891300
C     1.67366000  0.76922500  -0.23010000
C     -1.71340000  -0.01915500  -0.08108300
C     -2.43295800  1.07886400  -0.53546200
C     -3.81331600  1.08003900  -0.39744000
C     -4.42162700  -0.02215300  0.17987200
C     -3.71350100  -1.11961200  0.63600100
|  | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| C | -2.33055600 | -1.11282400 | 0.51173300 |
| C | 2.96577800  | -1.32604300 | -0.88334800 |
| H | 3.41873500  | -0.87109700 | -1.76677500 |
| H | 2.63608000  | -2.32970100 | -1.14592900 |
| C | 2.85954300  | 1.65296800  | -0.08706400 |
| H | 3.35543400  | 1.74091900  | -1.05951600 |
| H | 2.48023300  | 2.63960100  | 0.17839100  |
| C | 3.85355400  | 1.14860700  | 0.97153500  |
| H | 3.31145100  | 0.90941800  | 1.89183200  |
| H | 4.52383000  | 1.97767200  | 1.20580400  |
| C | 3.93200200  | -1.35244400 | 0.29599600  |
| H | 3.38468600  | -1.64631000 | 1.19705800  |
| H | 4.65080200  | -2.14781000 | 0.08675800  |
| C | 4.69774400  | -0.04791200 | 0.52824800  |
| H | 5.45461000  | -0.23323700 | 1.29389000  |
| H | 5.23953400  | 0.21513600  | -0.38729800 |
| F | -5.75836900 | -0.02217300 | 0.30890900  |
| H | -1.74666900 | -1.94233100 | 0.89062800  |
| H | -4.23380500 | -1.95003900 | 1.09470200  |
| H | -4.41383600 | 1.91419600  | -0.73579900 |
| H | -1.91956900 | 1.91511100  | -0.99186900 |
9k (B3LYP)

N  -0.34688500  -0.22488200  -0.05750700
N  -1.07547600  -0.18199500  1.10528300
N  -2.38557200  -0.48316900  -0.65163400
C  -1.13866900  -0.40262800  -1.11039500
H  -0.82259800  -0.46633800  -2.13894400
C  -2.31771600  -0.34303800  0.72620900
C   1.06848200  -0.08299000  -0.04475200
C   1.88803000  -1.20802500  0.02855400
C   3.26857100  -1.07241300  0.05592600
C   3.83444700   0.19695400  0.01871500
C   3.02741400  1.32732500  -0.04653700
C   1.64775100  1.18420900  -0.07510900
C  -3.60631900  -0.68076400  -1.47319800
H  -4.01913300  -1.65544100  -1.20635000
H  -3.26694400  -0.73111700  -2.50622100
C  -3.49430400  -0.35799600  1.63714600
H  -3.94284700  -1.35765400  1.61532800
H  -3.10646200  -0.20434900  2.64474400
C  -4.56163600   0.70619200  1.30479200
H  -4.08351900  1.68838100  1.22912700
H  -5.23705700  0.75438600  2.16243900
C  -4.63002500  0.43881700 -1.28592900
H  -4.13797000  1.40491800 -1.43897500
H  -5.35028600  0.32418700 -2.10078000
C  -5.39281800  0.42149700  0.04680600
H  -6.18545100  1.17264900 -0.01317400
H  -5.89618900 -0.54633800  0.15879100
F   3.58086800  2.53958400 -0.08175600
F   0.87820600  2.26929900 -0.13841300
F   5.15673400  0.33153400  0.04463800
F   4.05076000 -2.15000700  0.12065000
F   1.34951400 -2.42550100  0.06906300

M062X

N  -0.34938000 -0.22876100  0.04803200
N  -1.07605800  0.29982100  1.07080600
N  -2.36985700 -0.73972200 -0.37784300
C  -1.12716900 -0.85115200 -0.82624900
H  -0.80361100 -1.34722100 -1.72869100
C  -2.31029600 -0.01936700  0.79844700
C   1.06094200 -0.08942400  0.00498800
C   1.88103200 -1.19560700  0.18081600
C   3.25721900 -1.05615800  0.14617400
C   3.81259000  0.19848300 -0.05145100
|     | x        | y        | z        |
|-----|----------|----------|----------|
| C   | 3.00136300 | 1.31096500 | -0.21684900 |
| C   | 1.62637700 | 1.16412700 | -0.19033700 |
| C   | -3.59056800 | -1.26448100 | -1.02321300 |
| H   | -4.02964200 | -1.98853700 | -0.33401400 |
| H   | -3.25595500 | -1.79531300 | -1.91255800 |
| C   | -3.50100100 | 0.34417300 | 1.60934500 |
| H   | -3.97474800 | -0.57652200 | 1.96632300 |
| H   | -3.12845100 | 0.88173100 | 2.48103600 |
| C   | -4.51880400 | 1.19860900 | 0.83528400 |
| H   | -3.99959900 | 2.03070600 | 0.34965300 |
| H   | -5.19663900 | 1.63475700 | 1.57128600 |
| C   | -4.56938600 | -0.15054800 | -1.37523700 |
| H   | -4.03237400 | 0.64154900 | -1.90608800 |
| H   | -5.27974100 | -0.58166100 | -2.08425800 |
| C   | -5.34736500 | 0.42159800 | -0.18839700 |
| H   | -6.11609900 | 1.09025200 | -0.58222700 |
| H   | -5.87406100 | -0.39419600 | 0.31956700 |
| F   | 3.54415900  | 2.50257100 | -0.41100400 |
| F   | 0.85160800  | 2.22130300 | -0.36173800 |
| F   | 5.12534900  | 0.33479200 | -0.08695100 |
| F   | 4.04123600  | -2.11041800 | 0.30586800 |
| F   | 1.34969000  | -2.39071600 | 0.38194400 |
S2.3 Coordinates of Carbenes

7a (B3LYP)

```
\begin{align*}
\text{O} & \quad -4.75960800 \quad 0.46185500 \quad -0.11844500 \\
\text{N} & \quad 0.80000900 \quad -0.07760100 \quad 0.00518900 \\
\text{N} & \quad 1.56136100 \quad 1.05231100 \quad 0.34494200 \\
\text{N} & \quad 2.78115600 \quad -0.71466300 \quad -0.13502300 \\
\text{C} & \quad 1.51728200 \quad -1.19192900 \quad -0.30128200 \\
\text{C} & \quad 2.77512600 \quad 0.60216600 \quad 0.24466600 \\
\text{C} & \quad 4.16268400 \quad 1.11424900 \quad 0.45170800 \\
\text{H} & \quad 4.38013900 \quad 1.17925500 \quad 1.52209500 \\
\text{H} & \quad 4.32075800 \quad 2.10182300 \quad 0.01869100 \\
\text{C} & \quad 5.01123400 \quad 0.00584100 \quad -0.24025100 \\
\text{H} & \quad 5.96513700 \quad -0.15661800 \quad 0.25959500 \\
\text{H} & \quad 5.21614100 \quad 0.29834200 \quad -1.27178700 \\
\text{C} & \quad 4.13427500 \quad -1.27333300 \quad -0.23306000 \\
\text{H} & \quad 4.24096800 \quad -1.87079900 \quad -1.13705100 \\
\text{H} & \quad 4.33148000 \quad -1.90583000 \quad 0.63536700 \\
\text{C} & \quad -0.62163200 \quad 0.03735600 \quad -0.01186100 \\
\text{C} & \quad -1.41745600 \quad -1.07349700 \quad 0.25428700 \\
\text{H} & \quad -0.95151100 \quad -2.02110700 \quad 0.48968700 \\
\text{C} & \quad -2.80856400 \quad -0.97307100 \quad 0.21943100 \\
\text{H} & \quad -3.40132300 \quad -1.85248300 \quad 0.42997400 \\
\end{align*}
```
C  -3.41178300  0.25495500  -0.06784300
C  -2.60745900  1.37330500  -0.32241700
H  -3.08194600  2.32163600  -0.54493300
C  -1.22452100  1.26592000  -0.29996300
H  -0.60906000  2.13155900  -0.50487400
C  -5.63030500  -0.64358700  0.13360000
H  -5.48469200  -1.03910100  1.14296100
H  -5.47929600  -1.44076000  -0.60010500
H  -6.64089700  -0.25134200  0.04008800

M062X

O  -4.74043100  0.46468300  -0.11198500
N  0.79860700  -0.07415400  0.02005300
N  1.55139700  1.05158800  0.32141800
N  2.76607600  -0.71960000  -0.10846600
C  1.50480600  -1.19926700  -0.25676500
C  2.76204300  0.60346900  0.23197300
C  4.15225000  1.11576300  0.41618800
H  4.38215000  1.17400300  1.48295700
H  4.30243700  2.10036300  -0.02252500
C  4.97662600  0.00413200  -0.28456700
H  5.95595200  -0.13439300  0.16879100
H  5.11715800  0.26901300  -1.33340400
C  4.11587500  -1.27591000  -0.19627800

SI-154
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | 4.20947200 | -1.91933300 | -1.06853500 |
| H       | 4.32878100 | -1.85413000 | 0.70454900  |
| C       | -0.62111500 | 0.04184900  | -0.00053300 |
| C       | -1.41201000 | -1.07374200 | 0.23493300  |
| H       | -0.94198100 | -2.02502100 | 0.44732800  |
| C       | -2.80074700 | -0.97282800 | 0.19776200  |
| H       | -3.39382000 | -1.85734600 | 0.38529800  |
| C       | -3.39869300 | 0.26001100  | -0.06194100 |
| C       | -2.59665000 | 1.38227900  | -0.28716000 |
| H       | -3.07504800 | 2.33316600  | -0.48836100 |
| C       | -1.21677000 | 1.27559300  | -0.26243600 |
| H       | -0.59673300 | 2.14303300  | -0.44618400 |
| C       | -5.58640600 | -0.65539700 | 0.09938200  |
| H       | -5.43599900 | -1.07810700 | 1.09630900  |
| H       | -5.41238000 | -1.42565600 | -0.65677800 |
| H       | -6.60420500 | -0.28361100 | 0.01206100  |
### 7b (B3LYP)

```
N  0.065377  -0.108851  -0.022624
N -0.659667  1.071396  -0.254975
N -1.935287 -0.689546  0.083326
C -0.689934 -1.221896  0.192498
C -1.886343  0.655419  -0.182755
C -3.256609  1.229383  -0.333052
H  3.476030  1.396273  -1.391856
H  3.378342  2.179369  0.186906
C -4.139903  0.093503  0.264863
H  5.098885  0.006165  -0.243824
H  4.334467  0.302929  1.318295
C  3.306329 -1.208957  0.144612
H  3.428187 -1.875658  0.996708
H  3.527905 -1.760453  -0.771707
C  1.489445 -0.046135  -0.004103
C  2.238156 -1.207837  -0.213593
H  1.728755 -2.143978  -0.397531
C  3.628881 -1.144995  -0.183231
H  4.204162 -2.049209  -0.346189
C  4.280119  0.068568  0.042075
C  3.525344  1.223718  0.241265
```
H  4.01870800  2.17262200  0.41826600
C  2.13241800  1.17284400  0.22279200
H  1.54535400  2.06648200  0.38319300
H  5.36278700  0.11277400  0.05942900

M062X

N  0.06104300  -0.10817800  -0.02889800
N  -0.65241100  1.05866300  -0.26435600
N  -1.92791600  -0.68917200  0.07812300
C  -0.68620600  -1.22170600  0.19072300
C  -1.87717600  0.65005400  -0.19268500
C  -3.24833800  1.21973700  -0.34595000
H  -3.47595900  1.34037500  -1.40799300
H  -3.36355700  2.18550200  0.14221000
C  -4.11077500  0.10330500  0.29861900
H  -5.09537600  0.02378700  -0.15733800
H  -4.23928500  0.31731500  1.36054400
C  -3.29735600  -1.20028000  0.13941100
H  -3.41387800  -1.88636200  0.97549300
H  -3.53012500  -1.72086700  -0.79105800
C  1.48320700  -0.04568800  -0.00529300
C  2.22705500  -1.20578700  -0.21284100
H  1.71531600  -2.14050600  -0.39897300
C  3.61491200  -1.14133600  -0.17972800
| element | x      | y      | z      |
|---------|--------|--------|--------|
| H       | 4.19109300 | -2.04442300 | -0.34255100 |
| C       | 4.26250300 | 0.07073800 | 0.04710200 |
| C       | 3.50893000 | 1.22327500 | 0.24531200 |
| H       | 4.00155500 | 2.17174200 | 0.42363400 |
| C       | 2.11874300 | 1.17191200 | 0.22386500 |
| H       | 1.52768200 | 2.06327500 | 0.38430100 |
| H       | 5.34452500 | 0.11562400 | 0.06644000 |
7c (B3LYP)

\[
\begin{array}{ccc}
\text{N} & 0.35890500 & 0.11632800 -0.02519100 \\
\text{N} & 1.07669500 & -1.06719900 -0.26123800 \\
\text{N} & 2.36163400 & 0.68514900 0.08749400 \\
\text{C} & 1.11913400 & 1.22437300 0.19649500 \\
\text{C} & 2.30579300 & -0.65839500 -0.18399500 \\
\text{C} & 3.67298200 & -1.23970400 -0.33299600 \\
\text{H} & 3.89372200 & -1.40428100 -1.39187800 \\
\text{H} & 3.78779800 & -2.19216200 0.18400100 \\
\text{C} & 4.56140400 & -0.11100600 0.27091000 \\
\text{H} & 5.52185600 & -0.02721900 -0.23558600 \\
\text{H} & 4.75263200 & -0.32543000 1.32394100 \\
\text{C} & 3.73555000 & 1.19659700 0.15379600 \\
\text{H} & 3.85914400 & 1.85930900 1.00873100 \\
\text{H} & 3.96204200 & 1.75032500 -0.75994900 \\
\text{C} & -1.06424300 & 0.06157500 -0.01121800 \\
\text{C} & -1.80621800 & 1.22635700 -0.22570000 \\
\text{H} & -1.29418100 & 2.16045900 -0.41046300 \\
\text{C} & -3.19697400 & 1.18080600 -0.20025600 \\
\text{H} & -3.78810100 & 2.07288600 -0.36483300 \\
\text{C} & -3.81923500 & -0.03649100 0.02642400 \\
\text{C} & -3.10704500 & -1.20571700 0.23187700 \\
\end{array}
\]
| Element | X   | Y       | Z       |
|---------|-----|---------|---------|
| H       | -3.62842100 | -2.13828100 | 0.40729600 |
| C       | -1.71486000 | -1.15288100 | 0.21655300 |
| H       | -1.13603100 | -2.05068000 | 0.38105700 |
| F       | -5.18098100 | -0.08421500 | 0.04432100 |

**M062X**

| Element | X   | Y       | Z       |
|---------|-----|---------|---------|
| N       | 0.36088500 | 0.11705500 | -0.03464000 |
| N       | 1.06716900 | -1.05085200 | -0.28401700 |
| N       | 2.35189500 | 0.68428500 | 0.08830200 |
| C       | 1.11274800 | 1.22267500 | 0.20459800 |
| C       | 2.29430300 | -0.65062100 | -0.20142100 |
| C       | 3.66253100 | -1.22676900 | -0.35640900 |
| H       | 3.89427700 | -1.33383700 | -1.41899700 |
| H       | 3.76924900 | -2.19998600 | 0.11874100 |
| C       | 4.52877700 | -0.12502200 | 0.30795200 |
| H       | 5.51585500 | -0.04505600 | -0.14250600 |
| H       | 4.65118500 | -0.35503800 | 1.36722900 |
| C       | 3.72425000 | 1.18587800 | 0.16404000 |
| H       | 3.84045100 | 1.85830000 | 1.01120700 |
| H       | 3.96500200 | 1.71915200 | -0.75709700 |
| C       | -1.06061600 | 0.06195800 | -0.01637000 |
| C       | -1.79810800 | 1.22279000 | -0.23943300 |
| H       | -1.28342600 | 2.15363600 | -0.43531800 |
| C       | -3.18584300 | 1.17552900 | -0.20914400 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| H       | -3.78218400| 2.06254000 | -0.38114100|
| C       | -3.80387300| -0.03865200| 0.03123900 |
| C       | -3.09160600| -1.20354400| 0.24497100 |
| H       | -3.61533000| -2.13241600| 0.43105400 |
| C       | -1.70259900| -1.14956400| 0.22469700 |
| H       | -1.11816600| -2.04287600| 0.39686700 |
| F       | -5.15292700| -0.08730900| 0.05490300 |
7d (B3LYP)

| Atoms | X          | Y          | Z          |
|-------|------------|------------|------------|
| N     | 1.53476600 | 0.11563700 | -0.04084900|
| N     | 2.24470900 | -1.09577900| -0.03896400|
| N     | 3.54216500 | 0.68172800 | -0.04471600|
| C     | 2.30579900 | 1.24088300 | -0.04738800|
| C     | 3.47613100 | -0.68907300| -0.04477100|
| C     | 4.83897600 | -1.29789500| -0.07344000|
| H     | 5.05765700 | -1.67032900| -1.07871900|
| H     | 4.94725300 | -2.13022600| 0.62157400|
| C     | 5.73555700 | -0.07805800| 0.29525400|
| H     | 6.69757700 | -0.10449500| -0.21438800|
| H     | 5.92272400 | -0.07847400| 1.37060600|
| C     | 4.92039100 | 1.18535400 | -0.08462500|
| H     | 5.05048900 | 2.00728600 | 0.61732100|
| H     | 5.14865600 | 1.53908700 | -1.09232600|
| C     | 0.11268400 | 0.07702100 | -0.02466000|
| C     | -0.61778400| 1.26927400 | -0.00876900|
| H     | -0.09687000| 2.21645300 | -0.00702600|
| C     | -2.00839700| 1.23635300 | 0.00488400|
| H     | -2.56804400| 2.16262200 | 0.01733900|
| C     | -2.66386500| 0.00820700 | 0.00301600|
| C     | -1.94994200 | -1.18409100| -0.01251100|

SI-162
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -2.46285500 | -2.13703000 | -0.01398100 |
| C    | -0.55706000  | -1.14847100 | -0.02675400 |
| H    | 0.00588100   | -2.07052200 | -0.03924800 |
| Br   | -4.58596800  | -0.03892900 | 0.02311800  |

**M062X**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| N    | 1.52918100  | 0.11474500 | -0.04521600 |
| N    | 2.22817800   | -1.08392400 | -0.07145100 |
| N    | 3.52522200   | 0.68128000  | -0.03648200 |
| C    | 2.29293300   | 1.24092300  | -0.02509900 |
| C    | 3.45727800   | -0.68479100 | -0.06840600 |
| C    | 4.82093000   | -1.28974600 | -0.11042300 |
| H    | 5.04878200   | -1.60240500 | -1.13245700 |
| H    | 4.92097700   | -2.15310000 | 0.54437900 |
| C    | 5.69775700   | -0.08707000 | 0.32692200 |
| H    | 6.68268900   | -0.10324100 | -0.13477500 |
| H    | 5.82465900   | -0.11088900 | 1.41006400 |
| C    | 4.90134500   | 1.17832900  | -0.06235000 |
| H    | 5.02554100   | 1.99850000  | 0.64127500 |
| H    | 5.14097600   | 1.52388300  | -1.06929400 |
| C    | 0.10872800   | 0.07639300  | -0.02653200 |
| C    | -0.61606200  | 1.26775100  | -0.03573300 |
| H    | -0.09258900  | 2.21352700  | -0.05623000 |
| C    | -2.00357900  | 1.23345700  | -0.01934800 |
|  | x     | y     | z     |
|---|-------|-------|-------|
| H | -2.56826500 | 2.15677600 | -0.02660300 |
| C | -2.65610600 | 0.00698600 | 0.00496300 |
| C | -1.94397400 | -1.18342700 | 0.01414500 |
| H | -2.46063600 | -2.13424800 | 0.03407500 |
| C | -0.55400800 | -1.14791000 | -0.00119900 |
| H | 0.01274000  | -2.06798100 | 0.00639500 |
| Br| -4.55841100 | -0.03916900 | 0.02495900 |
7e (B3LYP)

N  0.63065200  0.38495400  -0.03559600  
N  1.10755100  -0.93567200  -0.04426700  
N  2.70713300  0.57574800  -0.04584700  
C  1.59416600  1.35124100  -0.03937300  
C  2.39224400  -0.76030200  -0.05359100  
C  3.62097400  -1.60733500  -0.09027000  
H  3.76505200  -2.00820700  -1.09804500  
H  3.57676600  -2.44890300  0.60057900  
C  4.72635900  -0.57381500  0.28102800  
H  5.66518400  -0.77203900  -0.23398800  
H  4.91501400  -0.61580900  1.35524700  
C  4.15407300  0.81997100  -0.08682800  
H  4.43299900  1.59862800  0.62102800  
H  4.44092800  1.13447800  -1.09257600  
C  -0.77411400  0.60711100  -0.01116100  
C  -1.27781500  1.91157500  0.01186900  
H  -0.59295500  2.74729800  0.01282000  
C  -2.65321300  2.11451100  0.03360600  
H  -3.04167700  3.12586900  0.05142100  
C  -3.54292500  1.03968200  0.03355900  

SI-165
C  -3.01387200  -0.24469800  0.01070500
C  -1.64503900  -0.48532600  -0.01184500
H  -1.25663400  -1.49232000  -0.02933600
Cl -4.11141500  -1.62812700  0.01033400
H  -4.61300000  1.19825400  0.05094500

M062X

N    0.63058700  0.37337300  -0.02732000
N    1.10317600  -0.92490300  0.10410800
N    2.69316600   0.56279300  -0.13955000
C    1.58144200   1.33390800  -0.18661900
C    2.38270900  -0.75925800  0.02689400
C    3.61428800  -1.60179200  0.04927200
H    3.73833500  -2.08946600  -0.92078700
H    3.58753400  -2.36964100  0.81991600
C    4.70867400  -0.52974000  0.29245100
H    5.65399400  -0.78851700  -0.17957600
H    4.87639500  -0.42481200  1.36520200
C    4.13326300   0.79251000  -0.26231500
H    4.43164600   1.66691200  0.31184400
H    4.38553900   0.94465600  -1.31299400
C   -0.77138900   0.59800800  0.01288200
C   -1.26526300   1.89900200  0.10238900
H   -0.57489000   2.72931300  0.14891700

SI-166
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -2.63774700 | 2.10478400 | 0.13124900 |
| H       | -3.02364300 | 3.11435800 | 0.20117200 |
| C       | -3.52724600 | 1.03525500 | 0.07942100 |
| C       | -3.00446500 | -0.24645200 | -0.00391100 |
| C       | -1.63892300 | -0.49001000 | -0.04027800 |
| H       | -1.25405800 | -1.49708500 | -0.10963800 |
| Cl      | -4.09788100 | -1.61023300 | -0.07048600 |
| H       | -4.59742600 | 1.19210800 | 0.10492400 |
7f (B3LYP)

N  1.46476000  -0.11304300  0.02960300
N  2.17765600  1.09754100  0.04681400
N  3.47027400  -0.68468000  0.04129900
C  2.23479500  -1.24145400  0.02812300
C  3.40723900  0.68757600  0.05688900
C  4.77132700  1.29206000  0.10172900
H  4.98401400  1.65080400  1.11322800
H  4.88559400  2.13312000  -0.58164500
C  5.66724500  0.07487200  -0.27678300
H  6.62653600  0.09338300  0.23824200
H  5.85999500  0.08760300  -1.35104900
C  4.84774600  -1.19109000  0.08415100
H  4.98035700  -2.00570800  -0.62569700
H  5.06853500  -1.55577900  1.08952700
C  0.04651500  -0.07278500  0.00505100
C  -0.62019700  1.15506400  -0.01399000
H  -0.05352800  2.07443800  -0.01328300
C  -2.01019300  1.18744600  -0.03581200
H  -2.51901100  2.14263000  -0.05286700
C  -2.74076800  -0.00002200  -0.04327700
C  -2.07132300  -1.22688600  -0.02316700
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -2.62879100 | -2.15527400 | -0.03045900 |
| C    | -0.68474100  | -1.26658300 | -0.00024700  |
| H    | -0.16237400  | -2.21240700 | 0.01169800   |
| C    | -4.23822700  | 0.03211200  | -0.01381600  |
| F    | -4.73456300  | -0.08781900 | 1.25172800   |
| F    | -4.79446700  | -0.97898600 | -0.72618500  |
| F    | -4.74726500  | 1.18531600  | -0.50718800  |

**M062X**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| N    | -1.46030700 | 0.11191000 | 0.04047300 |
| N    | -2.16173400 | -1.08602900 | 0.06935800 |
| N    | -3.45491800 | 0.68309500  | 0.04100300  |
| C    | -2.22351300 | 1.24082100  | 0.02395600  |
| C    | -3.38937600 | -0.68427500 | 0.07221900  |
| C    | -4.75412600 | -1.28590500 | 0.11937700  |
| H    | -4.97860700 | -1.59689100 | 1.14267400  |
| H    | -4.85811500 | -2.14977200 | -0.53406600 |
| C    | -5.62995600 | -0.08172600 | -0.31573300 |
| H    | -6.61359000 | -0.09625900 | 0.14869800  |
| H    | -5.75977700 | -0.10523100 | -1.39851700 |
| C    | -4.83050900 | 1.18216000  | 0.07172900  |
| H    | -4.95533100 | 2.00313200  | -0.63077000 |
| H    | -5.06575700 | 1.52708600  | 1.07986000  |
| C    | -0.04299500 | 0.07303900  | 0.01457000  |

SI-169
|  | X          | Y          | Z          |
|---|------------|------------|------------|
| C | 0.61694200 | -1.15399600| -0.01764300|
| H | 0.04662000 | -2.07142400| -0.02500400|
| C | 2.00461400 | -1.18502200| -0.04390100|
| H | 2.51964900 | -2.13737300| -0.07377900|
| C | 2.72611800 | 0.00286500 | -0.04223500|
| C | 2.06472100 | 1.22775500 | -0.00786600|
| H | 2.62814500 | 2.15294800 | -0.00861700|
| C | 0.68010200 | 1.26717900 | 0.01964800 |
| H | 0.15345700 | 2.21069600 | 0.04244200 |
| C | 4.22175200 | -0.03146400| -0.01801000|
| F | 4.71168600 | -0.02350000| 1.23921600 |
| F | 4.76542200 | 1.02872300 | -0.63786900|
| F | 4.71837700 | -1.13059400| -0.60750600|
7g (B3LYP)
H  -3.63067500  2.22951200  0.05971100
C  -1.70368700  1.24693100  -0.01406000
H  -4.89614700  0.12449500  0.10389500
O  -1.04985600  -2.33503000  -0.03732000
O  -0.90724900  2.34498700  -0.03801400
C  -1.74106600  -3.58843600  -0.01417600
H  -2.39006800  -3.69597300  -0.88718800
H  -0.96492000  -4.35021900  -0.04144000
H  -2.32828300  -3.69730700  0.90139400
C  -1.51951700  3.63878700  -0.01319200
H  -2.09905900  3.78261600  0.90248200
H  -0.69761300  4.35100900  -0.03935000
H  -2.16040300  3.78767900  -0.88612800

M062X

N   0.37945400  -0.04537800  -0.09641300
N   1.08752100  -0.06528400  1.09918900
N   2.36707900  -0.08899300  -0.68035000
C   1.12247800  -0.06124400  -1.22641500
C   2.31328800  -0.09549500  0.68575000
C   3.68382000  -0.15939000  1.27637300
H   3.89246000  -1.18001900  1.60643800
H   3.81117500  0.50969500  2.12511600
C   4.55675800  0.23408500  0.05604600
H
5.53085200 -0.25045700  0.06918300
H
4.70960600  1.31421300  0.05792700
C
3.73541000 -0.15896500 -1.19207900
H
3.86902800  0.52545600 -2.02712100
H
3.94816500 -1.17767100 -1.52106400
C
-1.03952600  0.00739000 -0.04490500
C
-1.77377100 -1.18283100 -0.01254800
C
-3.16901200 -1.13140700  0.03806400
H
-3.76184900 -2.03450100  0.06031300
C
-3.79413400  0.10941200  0.06155500
C
-3.07868500  1.30057900  0.03714100
H
-3.60297300  2.24494900  0.05935700
C
-1.68352800  1.24849200 -0.01306300
H
-4.87625200  0.14963800  0.10115100
O
-1.05076500 -2.32255200 -0.03605300
O
-0.87852000  2.33195800 -0.03610400
C
-1.75867000 -3.55595300 -0.01236400
H
-2.41328600 -3.64545300 -0.88249300
H
-1.00047400 -4.33411500 -0.04409500
H
-2.34471800 -3.65057500  0.90490300
C
-1.49359800  3.61412600 -0.01394200
H
-2.07206900  3.75254900  0.90261900
H
-0.67994700  4.33403400 -0.04477800
H
-2.13879900  3.75178300 -0.88486000
7h (B3LYP)

N  1.29816600  -0.04780500  -0.10594300
N  2.00493500  -0.10231100  1.10959500
N  3.30274700  -0.17850000  -0.66630200
C  2.06091000  -0.09549600  -1.22494300
C  3.23598800  -0.18569300  0.70229000
C  4.59536700  -0.31001000  1.31079200
H  4.74925100  -1.33093700  1.67301700
H  4.74986000  0.36837400  2.14965200
C  5.51337300  0.01158000  0.09399900
H  6.44257800  -0.55624800  0.11540700
H  5.76630400  1.07354000  0.10246900
C  4.67457800  -0.30665500  -1.17092000
H  4.85226100  0.38939500  -1.98921900
H  4.83804400  -1.32512700  -1.53042300
C  -0.13580700  0.06114700  -0.06207500
C  -0.90881900  -1.11443000  -0.03933500
C  -2.29846400  -0.98060600  0.00143900
H  -2.90704900  -1.87808200  0.01545300
C  -2.92511100  0.26841200  0.02657000
C  -2.12033700  1.40776800  0.01080600

SI-174
|   | X     | Y     | Z     |
|---|-------|-------|-------|
| H | -2.59739700 | 2.38228800 | 0.03094300 |
| C | -0.72372100  | 1.33618500  | -0.03001000 |
| C | -0.28155600  | -2.50444000 | -0.05872700 |
| H | 0.80220700   | -2.38182000 | -0.08000800 |
| C | 0.10159500   | 2.61793100  | -0.04269800 |
| H | 1.15552100   | 2.33622900  | -0.06007900 |
| C | -4.44191400  | 0.39371600  | 0.06937100 |
| H | -4.67108900  | 1.46450300  | 0.09953700 |
| C | -0.67514700  | -3.28811600 | -1.32505100 |
| H | -1.75187800  | -3.47772900 | -1.36115800 |
| H | -0.39783900  | -2.74219100 | -2.23061000 |
| H | -0.16555100  | -4.25599500 | -1.34299200 |
| C | -0.62591700  | -3.30115300 | 1.21371900 |
| H | -0.31521900  | -2.76416700 | 2.11380300 |
| H | -1.70017000  | -3.49298900 | 1.28896900 |
| H | -0.11490500  | -4.26838900 | 1.20253000 |
| C | -0.16945400  | 3.45162400  | -1.30910200 |
| H | 0.02827300   | 2.87109100  | -2.21401900 |
| H | -1.20779600  | 3.79365300  | -1.34776500 |
| H | 0.47438500   | 4.33596600  | -1.32552100 |
| C | -0.12655200  | 3.45389300  | 1.23070500 |
| H | -1.16004700  | 3.80523900  | 1.30105200 |
| H | 0.09380500   | 2.87275700  | 2.13001800 |
| H | 0.52441200   | 4.33311400  | 1.22679400 |
| C | -5.03673800  | -0.24121100 | 1.33974300 |

SI-175
| Atom | x      | y      | z      |
|------|--------|--------|--------|
| H    | -6.11772800 | -0.07747500 | 1.37656000 |
| H    | -4.86238400 | -1.32105900 | 1.36424000 |
| H    | -4.59689000 | 0.19188800  | 2.24216000 |
| C    | -5.10176000 | -0.18363800 | -1.19687300 |
| H    | -6.18274100 | -0.02113000 | -1.17116600 |
| H    | -4.70814200 | 0.29148200  | -2.09971800 |
| H    | -4.92759300 | -1.26072100 | -1.27956000 |

**M062X**

| Atom | x      | y      | z      |
|------|--------|--------|--------|
| N    | -1.28995800 | -0.06240200 | 0.08912500 |
| N    | -1.98843800 | -0.08415700 | -1.11033000 |
| N    | -3.27856500 | -0.21712300 | 0.65574800 |
| C    | -2.03789700 | -0.14400300 | 1.21171800 |
| C    | -3.21629500 | -0.18428200 | -0.70788900 |
| C    | -4.57827700 | -0.29506400 | -1.31117300 |
| H    | -4.73751900 | -1.31489200 | -1.66984000 |
| H    | -4.72989200 | 0.38990500  | -2.14307600 |
| C    | -5.47584000 | 0.02636700  | -0.08773600 |
| H    | -6.42729700 | -0.50025600 | -0.12088200 |
| H    | -5.67601600 | 1.09845400  | -0.06221600 |
| C    | -4.64555700 | -0.36322800 | 1.15552000 |
| H    | -4.81532800 | 0.29064400  | 2.00830300 |
| H    | -4.81320800 | -1.39936600 | 1.45477000 |
| C    | 0.13749500  | 0.05912600  | 0.04387400  |

SI-176
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| C       | 0.913861 | -1.106769 | 0.012343 |
| C       | 2.298981 | -0.962517 | -0.015925 |
| H       | 2.917714 | -1.854911 | -0.030839 |
| C       | 2.909510 | 0.292444  | -0.023811 |
| C       | 2.099101 | 1.424641  | -0.006650 |
| H       | 2.567120 | 2.404676  | -0.015366 |
| C       | 0.706035 | 1.335593  | 0.024306  |
| C       | 0.293025 | -2.491887 | 0.023869  |
| H       | -0.791714| -2.379306 | -0.026730 |
| C       | -0.137677| 2.597260  | 0.045104  |
| H       | -1.189444| 2.303404  | 0.037960  |
| C       | 4.420009 | 0.419866  | -0.050700 |
| H       | 4.654908 | 1.488930  | -0.055482 |
| C       | 0.627889 | -3.224871 | 1.328325  |
| H       | 1.706124 | -3.384543 | 1.418397  |
| H       | 0.294602 | -2.651800 | 2.196595  |
| H       | 0.138641 | -4.201678 | 1.350071  |
| C       | 0.733212 | -3.311577 | -1.194277 |
| H       | 0.490732 | -2.793567 | -2.124842 |
| H       | 1.810264 | -3.497812 | -1.178052 |
| H       | 0.226709 | -4.279685 | -1.196770 |
| C       | 0.115512 | 3.401785  | 1.325241  |
| H       | -0.093051| 2.800770  | 2.213321  |
| H       | 1.155060 | 3.737131  | 1.376181  |
| H       | -0.525466| 4.286474  | 1.348433  |
C  0.11641600  3.45289100  -1.20110300
H  1.15150900  3.80325000  -1.23417300
H  -0.08045300  2.88536700  -2.11348500
H  -0.53426400  4.33065100  -1.19404500
C  5.01057300  -0.20165700  -1.32142600
H  6.09226200  -0.05013800  -1.35020400
H  4.82136500  -1.27833000  -1.35106800
H  4.57556500  0.24483000  -2.21821000
C  5.05336800  -0.19994000  1.20020000
H  6.13519400  -0.04672000  1.19350400
H  4.64722300  0.24610800  2.11063600
H  4.86677300  -1.27688400  1.23644300
### 7i (B3LYP)

![Chemical Structure of 7i](Image)

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| N    | -0.50531800 | 0.03898800 | -0.10695100 |
| N    | -1.21660000 | 0.01945100 | 1.10788800  |
| N    | -2.51224700 | 0.06270700 | -0.67120200 |
| C    | -1.26652800 | 0.06884100 | -1.22650700 |
| C    | -2.44880000 | 0.03874900 | 0.69788000  |
| C    | -3.81456500 | 0.06673700 | 1.30417600  |
| H    | -4.02891800 | 1.06645200 | 1.69376400  |
| H    | -3.93107300 | -0.64240400 | 2.12355300  |
| C    | -4.71004800 | -0.27461500 | 0.07597000  |
| H    | -5.66978500 | 0.23936000 | 0.10838600  |
| H    | -4.90308700 | -1.34891600 | 0.05633700  |
| C    | -3.88790500 | 0.12267500 | -1.17756100 |
| H    | -4.02283600 | -0.56263600 | -2.01295100 |
| H    | -4.10997800 | 1.13817000 | -1.51338600 |
| C    | 0.93082900  | 0.01203500 | -0.06400800 |
| C    | 1.58874500  | -1.22573300 | -0.04897000 |
| C    | 2.98572200  | -1.22506700 | -0.00473200 |
| H    | 3.50893600  | -2.17621400 | 0.00211400  |
| C    | 3.72236100  | -0.03807000 | 0.02917300  |
| C    | 3.02826500  | 1.17486600 | 0.01251800  |
| H    | 3.58487800  | 2.10669300 | 0.03317400  |
C     1.63235400  1.22550100 -0.03053300
C     0.82058000 -2.52355900 -0.08781800
H     0.13604200 -2.60671700  0.76070400
H     0.21531900 -2.59838700 -0.99561800
H     1.50245900 -3.37454400 -0.06071300
C     5.22989400  0.06489000  0.10952600
H     5.56351400  0.05666700  1.15291000
H     5.63725400 -0.96463100 -0.35656700
H     5.67001500  0.80657800 -0.38015200
C     0.91037000  2.55009200 -0.04867300
H     0.31823300  2.66571500 -0.96079700
H     0.21953700  2.63879200  0.79414900
H     1.62099900  3.37595900  0.00431200

M062X

N     -0.50054600  0.06644300 -0.09643000
N     -1.19971800 -0.10259000  1.09261300
N     -2.49493000  0.15762500 -0.65596400
C     -1.25282800  0.23373000 -1.20634800
C     -2.43023900 -0.03498100  0.69510700
C     -3.79681400 -0.08405600  1.29617600
H     -4.02198300  0.87477300  1.76962000
H     -3.90500700 -0.86927500  2.04188200
C     -4.67079700 -0.31656200  0.03634600

SI-180
|   | X       | Y       | Z       |
|---|---------|---------|---------|
| H | -5.65623900 | 0.13611900 | 0.12507900 |
| H | -4.79737100 | -1.38902300 | -0.11915900 |
| C | -3.86884300 | 0.27438700 | -1.14426600 |
| H | -3.99591000 | -0.28020600 | -2.07155500 |
| H | -4.10409000 | 1.32607700 | -1.31732300 |
| C | 0.93111400 | 0.02545600 | -0.05829800 |
| C | 1.56647300 | -1.21645100 | -0.08967400 |
| C | 2.96006000 | -1.23638900 | -0.04884500 |
| H | 3.47420700 | -2.19220900 | -0.07811000 |
| C | 3.70535100 | -0.05974900 | 0.02359100 |
| C | 3.03013500 | 1.16098500 | 0.05123600 |
| H | 3.59988800 | 2.08395200 | 0.10351000 |
| C | 1.63834200 | 1.22704200 | 0.01591200 |
| C | 0.76181000 | -2.48518800 | -0.17827300 |
| H | 0.08270000 | -2.57559500 | 0.67265900 |
| H | 0.14773600 | -2.48952500 | -1.08247200 |
| H | 1.41633600 | -3.35611700 | -0.19685600 |
| C | 5.20978900 | -0.10327500 | 0.09833100 |
| H | 5.54212000 | -0.04826400 | 1.13873300 |
| H | 5.59871400 | -1.02947900 | -0.32644900 |
| H | 5.65464100 | 0.73879500 | -0.43415600 |
| C | 0.91174500 | 2.54489400 | 0.04758400 |
| H | 0.37720700 | 2.71411000 | -0.89026500 |
| H | 0.16969400 | 2.56116200 | 0.84935800 |
| H | 1.61192900 | 3.36530300 | 0.20249500 |

SI-181
7j (B3LYP)

\[
\begin{array}{cccc}
N & -0.89825800 & 0.04415000 & -0.10010600 \\
N & -1.60484000 & 0.04013900 & 1.11827100 \\
N & -2.89676900 & 0.05781900 & -0.66807800 \\
C & -1.65678900 & 0.05697100 & -1.22594900 \\
C & -2.83453000 & 0.05256500 & 0.70406600 \\
C & -4.20045300 & 0.08365100 & 1.30771300 \\
H & -4.41763600 & 1.08892600 & 1.68066300 \\
H & -4.31293400 & -0.61257600 & 2.13835500 \\
C & -5.09312900 & -0.28095100 & 0.08421800 \\
H & -6.05560800 & 0.22788900 & 0.10966700 \\
H & -5.27931800 & -1.35650300 & 0.07992100 \\
C & -4.27428900 & 0.10421300 & -1.17481100 \\
H & -4.40395600 & -0.59261200 & -2.00010700 \\
H & -4.49920700 & 1.11456200 & -1.52283500 \\
C & 0.51960500 & 0.01649400 & -0.06163500 \\
C & 1.26487400 & 1.20177600 & -0.03193500 \\
C & 2.65454800 & 1.19131600 & 0.00784000 \\
H & 3.21020300 & 2.11794600 & 0.02593000 \\
C & 3.30546300 & -0.03628900 & 0.02435400 \\
C & 2.60866600 & -1.23844400 & 0.00387200 \\
H & 3.12879600 & -2.18556200 & 0.01881000 \\
\end{array}
\]
C                  1.21964400 -1.19619000 -0.03657600
Cl                 0.44497000  2.74505500 -0.04777400
Cl                 5.05741300 -0.06918900  0.07261200
Cl                 0.34156200 -2.70689500 -0.05936700

M062X

N                  -0.88983400  0.07536500 -0.09634900
N                  -1.58431400  0.04555800  1.10736700
N                 -2.87608700  0.08507800 -0.66642600
C                  -1.64001100  0.10028500 -1.22455100
C                 -2.81241800  0.05679200  0.70101700
C                 -4.17939400  0.06478800  1.30122000
H                 -4.41586100  1.07146300  1.65422600
H                 -4.27792600 -0.62590700  2.13616400
C                 -5.04754100 -0.32940600  0.07778600
H                 -6.03822300  0.11887300  0.11108600
H                 -5.16064300 -1.41414300  0.05313300
C                 -4.25180000  0.12535700 -1.16543900
H                 -4.36837200 -0.53872100 -2.01898000
H                 -4.49765300  1.14617700 -1.46228400
C                  0.52385800  0.03263500 -0.05852600
C                  1.27651000  1.20608800 -0.02647900
C                  2.66301500  1.17588600  0.01066500
H                  3.23415800  2.09390700  0.03034700
|   |         |         |         |         |
|---|---------|---------|---------|---------|
| C | 3.29295500 | -0.06012200 | 0.02311800 |
| C | 2.58232600 | -1.25184300 | 0.00168300 |
| H | 3.09106300 | -2.20594700 | 0.01458700 |
| C | 1.19727000 | -1.18839800 | -0.03719200 |
| Cl | 0.46597500 | 2.73788600 | -0.03463500 |
| Cl | 5.02985000 | -0.11755700 | 0.06706000 |
| Cl | 0.28396800 | -2.66033400 | -0.06479200 |
7k (B3LYP)

N  0.93789200  -0.08694300  -0.07610000
N  1.65059600  0.44353400  1.01905300
N  2.93274800 -0.35844000 -0.58724400
C  1.69371300 -0.59456900 -1.08876600
C  2.87707800  0.24525700  0.64680600
C  4.24530500  0.47366700  1.19925500
H  4.46028700 -0.26988700  1.97226000
H  4.36241200  1.46175400  1.64329800
C  5.13357600  0.26452100 -0.06305600
H  6.09430700 -0.18699300  0.17961500
H  5.32302000  1.22964800 -0.53626200
C  4.30882300 -0.62748300 -1.02597600
H  4.43673700 -0.36163500 -2.07368500
H  4.52793500 -1.68947800 -0.89812200
C  -0.47407600 -0.04239600 -0.04923000
C  -1.15295300  1.17303700 -0.13091700
C  -2.53907600  1.22729000 -0.09552200
C  -3.27130700  0.05213300  0.01348700
C  -2.61568200 -1.16919600  0.09289700
C  -1.22797700 -1.20920700  0.07024300

SI-185
F   -4.60476700  0.09740200  0.04132200
F   -3.17247400  2.40213800 -0.18008900
F   -0.46943100  2.31429700 -0.26317800
F   -0.62189200 -2.39568600  0.17437300
F   -3.32231300 -2.29912700  0.20619500

M062X

N   0.93567000 -0.11809300 -0.04729300
N   1.63922500  0.55947000  0.94485100
N   2.91759000 -0.45662200 -0.52355000
C   1.68219500 -0.76545200 -0.98204400
C   2.86282800  0.31685500  0.60700600
C   4.23304600  0.62756600  1.11010300
H   4.46720400 -0.02642500  1.95356500
H   4.33882300  1.66057200  1.43483200
C   5.09450700  0.28592300 -0.13321400
H   6.08453200 -0.07559200  0.13572200
H   5.20792200  1.18056500 -0.74706200
C   4.29143200 -0.77095500 -0.92243300
H   4.40558400 -0.68358500 -2.00056400
H   4.53147700 -1.78917800 -0.61252500
C   -0.47218300 -0.05964200 -0.03171300
C   -1.12897000  1.16089500 -0.13752700
C   -2.51053100  1.23315700 -0.11522100

SI-186
|   |       |       |       |
|---|-------|-------|-------|
| C | -3.25614600  | 0.07180900  | 0.00179700  |
| C | -2.61957700  | -1.15352200  | 0.10296400  |
| C | -1.23604800  | -1.21330200  | 0.09560900  |
| F | -4.57979500  | 0.13331600  | 0.01613100  |
| F | -3.12360400  | 2.40609900  | -0.22069700  |
| F | -0.43284500  | 2.28124500  | -0.28348900  |
| F | -0.65116500  | -2.39698200  | 0.22405200  |
| F | -3.33773000  | -2.26363800  | 0.22467100  |
8a (B3LYP)

N  0.45610500 -0.06478100 -0.03238800
N  1.21543000  1.06232700  0.26723700
N  2.45007800 -0.70887400 -0.15757800
C  1.17347500 -1.17674600 -0.31025400
C  2.44123500  0.62880700  0.18007000
C  -0.96654000  0.04312600 -0.03277400
C  -1.75360400 -1.06542800  0.26569400
C  -3.14552000 -0.97142000  0.24637800
C  -3.75774700  0.24778600 -0.05898200
C  -2.96151100  1.36407100 -0.34648600
C  -1.57796800  1.26313400 -0.33805300
C  3.67327900 -1.48591900 -0.41666800
H  3.80074600 -1.56909900 -1.49968000
H  3.52360700 -2.48828900 -0.01611500
C  3.69008800  1.40843900  0.44737600
H  3.58075900  2.41799500  0.04612200
H  3.80596700  1.50961500  1.53248700
C  4.91945100  0.69368100 -0.13717400
H  4.93874000  0.81726300 -1.22553500
H  5.82747700  1.15755200  0.25355900
C  4.88783100 -0.80044300  0.20952400
H      4.86387300 -0.92566600  1.29770200
H      5.78901400 -1.30082000 -0.15213900
H      -1.28043300 -2.00591300  0.51484900
H      -3.73168400 -1.84863800  0.48284000
H      -3.44293500  2.30559700 -0.58260400
H      -0.96862500  2.12696500 -0.56753600
O      -5.10681300  0.44804900 -0.09714700
C      -5.96994900 -0.65521400  0.18812200
H      -6.98318800 -0.26865800  0.09962000
H      -5.82514500 -1.46648500 -0.53123200
H      -5.81008200 -1.02976600  1.20330100

M062X

N      0.45680800 -0.06165300 -0.02540000
N      1.20782200  1.05830400  0.25226700
N      2.43775600 -0.70975400 -0.14657000
C      1.16457400 -1.17933500 -0.28829700
C      2.43012900  0.62739500  0.16948300
C      -0.96378000  0.04693400 -0.02598100
C      -1.74578600 -1.06743300  0.24147700
C      -3.13542200 -0.97239000  0.22357100
C      -3.74200100  0.25323200 -0.04967100
C      -2.94815100  1.37454900 -0.30762100
C      -1.56775700  1.27360800 -0.30089600
| Symbol | X    | Y    | Z    |
|--------|------|------|------|
| C      | 3.65475400 | -1.49277400 | -0.38546400 |
| H      | 3.78699900 | -1.59465700 | -1.46555500 |
| H      | 3.49990000 | -2.48417000 |  0.03825200 |
| C      | 3.67789800 |  1.41296600 |  0.41264100 |
| H      | 3.55855600 |  2.41292100 | -0.00600100 |
| H      | 3.80663700 |  1.52468800 |  1.49385000 |
| C      | 4.88904600 |  0.68305700 | -0.17615500 |
| H      | 4.87549900 |  0.76059800 | -1.26809300 |
| H      | 5.80537300 |  1.15966000 |  0.17369600 |
| C      | 4.85883400 | -0.79118700 |  0.23070800 |
| H      | 4.81320500 | -0.86973000 |  1.32189400 |
| H      | 5.76307700 | -1.30525300 | -0.09833800 |
| H      | -1.26838300 | -2.01253900 |  0.46477700 |
| H      | -3.72231500 | -1.85521800 |  0.43683200 |
| H      | -3.43367700 |  2.31950500 | -0.51921600 |
| H      | -0.95357000 |  2.13972400 | -0.50935700 |
| O      | -5.08498800 |  0.45224200 | -0.08241300 |
| C      | -5.92378100 | -0.66799900 |  0.15534100 |
| H      | -6.94406700 | -0.30144100 |  0.07527100 |
| H      | -5.75571800 | -1.44821600 | -0.59189400 |
| H      | -5.75966200 | -1.07582500 |  1.15630200 |
8b (B3LYP)

\[
\begin{align*}
\text{N} & : 0.39609600, -0.10808500, -0.00207300 \\
\text{N} & : -0.33087900, 1.06772300, 0.15847800 \\
\text{N} & : -1.61535700, -0.70065200, -0.09895900 \\
\text{C} & : -0.35489600, -1.22326600, -0.16383500 \\
\text{C} & : -1.56802700, 0.66540500, 0.09558700 \\
\text{C} & : 1.82076100, -0.04669100, 0.00037800 \\
\text{C} & : 2.46741400, 1.15829000, -0.28259400 \\
\text{C} & : 3.86048500, 1.20831700, -0.28275100 \\
\text{C} & : 4.61105600, 0.06575000, -0.00885500 \\
\text{C} & : 3.95570400, -1.13375600, 0.27291900 \\
\text{C} & : 2.56464200, -1.19504200, 0.28496200 \\
\text{C} & : -2.86112200, -1.48415100, -0.14999800 \\
\text{H} & : -2.99364500, -1.97451300, 0.81845900 \\
\text{H} & : -2.73779700, -2.25828800, -0.90697600 \\
\text{C} & : -2.79434300, 1.51935900, 0.17154000 \\
\text{H} & : -2.65445000, 2.28905800, 0.93320900 \\
\text{H} & : -2.90853900, 2.03905800, -0.78654100 \\
\text{C} & : -4.04338400, 0.66574600, 0.44639800 \\
\text{H} & : -4.05976800, 0.35775000, 1.49758900 \\
\text{H} & : -4.93771100, 1.26841900, 0.27571200 \\
\text{C} & : -4.05354300, -0.57661500, -0.45264700
\end{align*}
\]
M062X

N   0.38970800  -0.10824800  -0.00137100
N   -0.32636500  1.05716300   0.15895800
N   -1.61062200 -0.69868900   -0.10101700
C   -0.35457900  -1.22293900  -0.16627700
C   -1.56072300   0.66162300   0.09533100
C    1.81242200  -0.04737800  -0.00002000
C    2.45163900   1.15437100  -0.29242500
C    3.84192800   1.20552800  -0.29180600
C    4.59089600   0.06768100   -0.00803800
C    3.93923200  -1.12856300   0.28234600
C    2.55091300  -1.19201100   0.29351900
C   -2.85253900  -1.47740100  -0.16470800
H   -2.99316300  -1.97016600   0.80049300
H   -2.72424500  -2.24334500  -0.92826500
C   -2.78374500   1.51611200   0.18174600
|  | H                | H                | C                | H                | H                | C                | H                | H                | H                | H                | H                | H                | H                |
|---|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|   | -2.63333000     | 2.28217900       | 0.94320600       | -2.90875200     | 2.02851800       | -0.77729300      | -4.01697900     | 0.65316500       | 0.46653800       | -4.00238000     | 0.31397400       | 1.50734400       | -4.91803200     | 1.25237000       | 0.33140700      |
|   | -2.90875200     | 2.02851800       | -0.77729300      | -4.00238000     | 0.31397400       | 1.50734400       | -4.91803200     | 1.25237000       | 0.33140700       | -4.03106200     | -0.55935800      | -0.46491500      | -3.98264500     | -0.22347700     | -1.50592100      |
|   | -4.01697900     | 0.65316500       | 0.46653800       | -4.00238000     | 0.31397400       | 1.50734400       | -4.91803200     | 1.25237000       | 0.33140700       | -4.03106200     | -0.55935800      | -0.46491500      | -3.98264500     | -0.22347700     | -1.50592100      |
|   | -4.00238000     | 0.31397400       | 1.50734400       | -4.91803200     | 1.25237000       | 0.33140700       | -3.98264500     | -0.22347700      | -1.50592100      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      |
|   | -4.91803200     | 1.25237000       | 0.33140700       | -3.98264500     | -0.22347700      | -1.50592100      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      |
|   | -4.03106200     | -0.55935800      | -0.46491500      | -3.98264500     | -0.22347700      | -1.50592100      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      |
|   | -3.98264500     | -0.22347700      | -1.50592100      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      |
|   | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      | -4.95269300     | -1.13087500      | -0.34645300      |
|   | 1.86259800      | 2.03287800       | -0.51885700      | 4.33888700      | 2.14095000       | -0.51969800      | 4.51276900      | -2.01866900      | 0.51232900      | 2.03440400      | -2.11305000      | 0.52834300       | 5.67311000      | 0.11215700      | -0.01036900      |
8c (B3LYP)

```
N  0.02152000  -0.11655300  -0.00789300
N  0.74161500  1.05578100   0.19977200
N  2.03514200  -0.69690000  -0.11512100
C  0.77737800  -1.22058300  -0.21491400
C  1.98083400  0.66117500   0.12731900
C  -1.40209500  -0.06236100  -0.00172700
C  -2.14046800  -1.22506700   0.23350100
C  -3.53150600  -1.17962400   0.22651200
C  -4.15631700  0.03562700  -0.00364300
C  -3.44737700  1.20296200  -0.22982000
C  -2.05511300  1.15014400  -0.23188000
C  3.28430800  -1.44614100  -0.33112400
H  3.40582400  -1.60025400  -1.40689000
H  3.17374900  -2.42234200   0.14027300
C  3.20271700  1.50200900   0.32302900
H  3.05313400  2.47463900  -0.14992800
H  3.32224600  1.68671300   1.39657500
C  4.45295900   0.79046100  -0.21987700
H  4.46069100   0.83586200  -1.31442500
H  5.34604100  1.31323000   0.12833500
C  4.47714700  -0.67480800   0.23342000
```

SI-194
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | 4.46452500 | -0.72250300 | 1.32795300 |
| H    | 5.39322700 | -1.16777300 | -0.09966200 |
| F    | -5.51853000 | 0.08339100  | -0.00368700 |
| H    | -1.62548900 | -2.15717300 | 0.42023900  |
| H    | -4.12057000 | -2.06983700 | 0.40755600  |
| H    | -3.97129000 | 2.13373800  | -0.40697300 |
| H    | -1.47807000 | 2.04612700  | -0.41195700 |

**M062X**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| N    | -0.02548600 | -0.11862100 | 0.00391700 |
| N    | -0.73415700 | 1.03909100  | -0.22622000 |
| N    | -2.02806500 | -0.69358600 | 0.12651400 |
| C    | -0.77460100 | -1.21744000 | 0.23671600 |
| C    | -1.97080700 | 0.65325600  | -0.14505900 |
| C    | 1.39626000  | -0.06450200 | -0.00003300 |
| C    | 2.12985000  | -1.21993100 | -0.25906400 |
| C    | 3.51797100  | -1.17185500 | -0.25013500 |
| C    | 4.13867200  | 0.03767600  | 0.00611000 |
| C    | 3.42955500  | 1.19745000  | 0.25611700 |
| C    | 2.04057000  | 1.14249400  | 0.25614600 |
| C    | -3.27360600 | -1.43466700 | 0.35424400 |
| H    | -3.39918000 | -1.56319000 | 1.43225500 |
| H    | -3.16138800 | -2.41828400 | -0.09976500 |
| C    | -3.18883500 | 1.49359200  | -0.35154900 |
| Atom | X-Position | Y-Position | Z-Position |
|------|------------|------------|------------|
| H    | -3.02709000 | 2.47508000 | 0.09554400 |
| H    | -3.32156500 | 1.64272500 | -1.42770100 |
| C    | -4.42252500 | 0.79326100 | 0.22596000 |
| H    | -4.39617500 | 0.83525600 | 1.31962900 |
| H    | -5.32208900 | 1.31696800 | -0.09902500 |
| C    | -4.45421300 | -0.66719000 | -0.22749700 |
| H    | -4.42213700 | -0.71328200 | -1.32093500 |
| H    | -5.37480300 | -1.15543500 | 0.09540700 |
| F    | 5.48785300  | 0.08732400 | 0.00805600 |
| H    | 1.61207500  | -2.14645900 | -0.46711900 |
| H    | 4.11244300  | -2.05395200 | -0.45143700 |
| H    | 3.95593400  | 2.12251700 | 0.45336000 |
| H    | 1.45750500  | 2.03108700 | 0.45585800 |
8i (B3LYP)

N  -0.20046000  0.01692800  -0.11398000
N  -0.91734600  -0.13726700  1.07243200
N  -2.21665100  0.09814100  -0.68901500
C  -0.95434700  0.16007200  -1.22059900
C  -2.15864000  -0.08305300  0.67732300
C   1.23608700  0.00950700  -0.06385900
C   1.91916200  1.22750300  0.05046800
C   3.31606400  1.19314200  0.10348500
C   4.02708800  -0.00796400  0.04956200
C   3.30692200  -1.20175200  -0.05495300
C   1.91134100  -1.21864300  -0.11367100
C  -3.46674500  0.12946200  -1.46539500
H  -3.59567100  -0.84529300  -1.94450300
H  -3.35532600  0.87837500  -2.24930900
C  -3.37999900  -0.15186800  1.54057800
H  -3.23144500  -0.90076700  2.32116700
H  -3.49826200  0.81331300  2.04601400
C  -4.63224000  -0.44834200  0.69907700
H  -4.64199100  -1.50374900  0.40518500
H  -5.52457600  -0.27692500  1.30470600
C  -4.65703500  0.43369100  -0.55527100
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | -4.64010300| 1.48972600 | -0.26345600|
| H    | -5.57538700| 0.27188600 | -1.12433900|
| C    | 1.16080500 | -2.52223900| -0.22891300|
| H    | 0.48744500 | -2.67063000| 0.61962400 |
| H    | 0.54579200 | -2.54610000| -1.13290500|
| H    | 1.85465200 | -3.36311400| -0.26530500|
| C    | 1.17948400 | 2.54094500 | 0.11426800 |
| H    | 0.62119300 | 2.72531200 | -0.80785100|
| H    | 0.45560600 | 2.55196500 | 0.93351000 |
| H    | 1.87600500 | 3.36721700 | 0.26247500 |
| C    | 5.53662300 | -0.01870400| 0.07924300 |
| H    | 5.91716400 | -0.87516900| 0.64085200 |
| H    | 5.94487700 | -0.08784000| -0.93482500|
| H    | 5.93240100 | 0.89292400 | 0.53140700 |
| H    | 3.84285000 | -2.14525100| -0.09090200|
| H    | 3.85854300 | 2.12897000 | 0.19433600 |

**M062X**

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| N    | -0.19803800| 0.02127600 | -0.11398400|
| N    | -0.90168400| -0.18831100| 1.05318400 |
| N    | -2.20298200| 0.12935500 | -0.68146300|
| C    | -0.94591800| 0.21843900 | -1.21245200|
| C    | -2.14109900| -0.11557500| 0.66925300 |
| C    | 1.23408900 | 0.01299900 | -0.06562600|
|  | C      | H      | H      | H      | H      |
|---|--------|--------|--------|--------|--------|
|   | 5.51452000 | -0.02605900 | 0.08677500 | 5.88102700 | -0.85064500 | 0.70070000 | 5.92113200 | -0.15945200 | -0.91936500 | 5.90989100 | 0.90821700 | 0.48684400 | 3.82973500 | -2.14202100 | -0.13329200 | 3.84744300 | 2.12422900 | 0.23708700 |
8k (B3LYP)

N  -0.64330200  0.05129900  -0.09935900
N  -1.35725100  -0.48597400   0.97424300
N  -2.64900600   0.32640600  -0.61912300
C  -1.39462500   0.55917800  -1.10391100
C  -2.59441200  -0.29752700   0.61443500
C   0.76949700   0.02884400  -0.05962700
C   1.50245300  1.20174200   0.11441200
C   2.89035000  1.18293100   0.15022800
C   3.56637500  -0.02356800   0.02670800
C   2.85470000  -1.20491600  -0.13817400
C   1.46813000  -1.17139600  -0.18354200
C  -3.90114600   0.61353600  -1.34248300
H  -4.02752000  -0.15107000  -2.11356700
H  -3.78623200   1.57797700  -1.83597700
C  -3.81728900  -0.64183500   1.40489100
H  -3.67001100  -1.60501400   1.89701400
H  -3.93087000   0.10602100   2.19760500
C  -5.06899600  -0.64175300   0.51240800
H  -5.08243300  -1.54266600  -0.11048700
H  -5.96010400  -0.67505100   1.14232500
C  -5.09054400  0.60369400 -0.38260200
H  -5.07283600  1.50563300  0.23902900
H  -6.00770600  0.63906600 -0.97470600
F   4.90003800 -0.04839200  0.06543600
F   3.57746100  2.31825900  0.31612900
F   0.87519900  2.37291700  0.25915200
F   0.80341300 -2.31688500 -0.36561900
F   3.50807400 -2.36485100 -0.26488000

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N   -0.64310400  0.07830000 -0.07883000
N   -1.34857400 -0.60298400  0.89381700
N   -2.63627500  0.41918500 -0.56211800
C   -1.38639800  0.72298700 -1.00511000
C   -2.58224300 -0.37147900  0.56583600
C    0.76577300  0.04386800 -0.04591900
C    1.50630600  1.20400300  0.14198200
C    2.89052100  1.16809000  0.16651500
C    3.54989200 -0.04039100  0.01856300
C    2.82705900 -1.20834600 -0.16048800
C    1.44468700 -1.15930900 -0.19644800
C    -3.88257000  0.80443500 -1.23732300
H   -4.00999800  0.15296700 -2.10510700
H   -3.76530900  1.82900500 -1.58679200
| Element | X       | Y       | Z       |\(d\)   |
|---------|---------|---------|---------|---------|
| C       | -3.80378400 | -0.83252100 | 1.29256300 |
| H       | -3.64540300 | -1.85182600 | 1.64593000 |
| H       | -3.93276300 | -0.19669800 | 2.17394200 |
| C       | -5.03580100 | -0.71773300 | 0.38997100 |
| H       | -5.01092000 | -1.50120100 | -0.37424800 |
| H       | -5.93611900 | -0.87141400 | 0.98558900 |
| C       | -5.06208700 | 0.65425000 | -0.28515700 |
| H       | -5.02474000 | 1.44035700 | 0.47599200 |
| H       | -5.98273300 | 0.79101500 | -0.85404400 |
| F       | 4.87396900  | -0.07976600 | 0.04841200 |
| F       | 3.58699100  | 2.28400700  | 0.34642200 |
| F       | 0.89746800  | 2.36989700  | 0.31433900 |
| F       | 0.76917500  | -2.28369800 | -0.39739900 |
| F       | 3.46301100  | -2.36386500 | -0.31191400 |
9a (B3LYP)

N  0.15038300 -0.15706700 -0.20786200
N  0.82135800  1.05070200 -0.07040300
N  2.17867900 -0.62727700 -0.49985600
C  0.94464400 -1.21938500 -0.47461000
C  2.07121700  0.72865600 -0.25908000
C -1.26993700 -0.17965800 -0.07514100
C -2.02150700  0.95374200 -0.37011700
C -3.41226600  0.93308900 -0.24915200
C -4.05853300 -0.23548800  0.16170000
C -3.29733100 -1.37450000  0.45817700
C -1.91550800 -1.34624900  0.34834800
C  3.43061600 -1.34922200 -0.76260700
H  3.85467500 -0.98547000 -1.70396800
H  3.14086000 -2.38838000 -0.90969200
C  3.21522000  1.68564400 -0.20283600
H  3.67894100  1.75146000 -1.19477100
H  2.79730400  2.66950900  0.01635100
C  4.29184300  1.32442300  0.84141600
H  3.81152700  1.15516700  1.81177200
H  4.93689300  2.19947500  0.96281400
C  4.45572000 -1.23273800  0.36885300
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | 3.96797300 | -1.48048000| 1.31845700 |
| H    | 5.20921900 | -2.00722100| 0.19408900 |
| C    | 5.17165900 | 0.12208000 | 0.47273000 |
| H    | 5.96245100 | 0.03294300 | 1.22437700 |
| H    | 5.67727800 | 0.32951200 | -0.47905200|
| H    | -1.33074800| -2.22397100| 0.58921100 |
| H    | -3.80455400| -2.27413200| 0.78591500 |
| H    | -3.97022200| 1.82851200 | -0.48553300|
| H    | -1.52479200| 1.85759000 | -0.69646000|
| O    | -5.40946500| -0.36408600| 0.30660700 |
| C    | -6.23737700| 0.76643100 | 0.02378400 |
| H    | -7.25856600| 0.43865800 | 0.20723800 |
| H    | -5.99951500| 1.60536600 | 0.68419600 |
| H    | -6.13671700| 1.07870000 | -1.01974800|

\textbf{M062X}

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| N    | 0.15673800 | -0.15847400| -0.21858100|
| N    | 0.81653700 | 1.04315300 | -0.11369600|
| N    | 2.17186900 | -0.63188500| -0.50769400|
| C    | 0.94499200 | -1.22698200| -0.46330700|
| C    | 2.06217200 | 0.72225600 | -0.29758500|
| C    | -1.26146000| -0.18171900| -0.08499300|
| C    | -2.00531200| 0.96050800 | -0.34032300|
| C    | -3.39410800| 0.93902900 | -0.21721200|

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C   -4.03753300  -0.23953500  0.15470700
C   -3.28111700  -1.38807200  0.41075200
C   -1.90295000  -1.36021900  0.29937900
C    3.43005300  -1.33839900  -0.74404800
H    3.88077800  -0.95048700  -1.66274200
H    3.15449100  -2.37750200  -0.91534700
C    3.21279600  1.66729600  -0.25967300
H    3.71086700  1.66549700  -1.23592100
H    2.80000700  2.66478100  -0.1065600
C    4.23464400  1.33326100  0.83893600
H    3.70814500  1.17561000  1.78614400
H    4.87381300  2.20882900  0.97475800
C    4.40558700  -1.21985100  0.42438200
H    3.87059700  -1.43993500  1.35431800
H    5.15775600  -2.00268300  0.29663300
C    5.12393400  0.12813700  0.52604900
H    5.88759200  0.05127000  1.3045100
H    5.65615700  0.31538900  -0.41434100
H   -1.31585100  -2.24438400  0.50995400
H   -3.79461800  -2.29437500  0.70824600
H   -3.95045700  1.84324900  -0.42234500
H   -1.50361700  1.87207200  -0.63678300
O   -5.38219100  -0.36713100  0.29803500
C   -6.18080700  0.78408000  0.07040000
H   -7.20885800  0.47695500  0.24545800
|   | H           |         |         |         |
|---|-------------|---------|---------|---------|
| H | -5.91579300 | 1.58704700 | 0.76352300 |         |
| H | -6.07484800 | 1.13743200 | -0.95880100 |         |
9b (B3LYP)

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| N       | -0.690749 | -0.093669 | -0.177242 |
| N       | 0.033617  | 1.09007   | -0.123826 |
| N       | 1.31148   | -0.66978  | -0.460923 |
| C       | 0.056545  | -1.20508  | -0.383938 |
| C       | 1.26505   | 0.70309   | -0.303862 |
| C       | -2.10812  | -0.04819  | -0.027124 |
| C       | -2.78956  | 1.15936   | -0.195127 |
| C       | -4.17584  | 1.19343   | -0.051948 |
| C       | -4.88673  | 0.03329   | 0.251592  |
| C       | -4.19689  | -1.16851  | 0.417742  |
| C       | -2.81159  | -1.21491  | 0.285571  |
| C       | 2.52890   | -1.46067  | -0.686985 |
| H       | 2.95826   | -1.17522  | -1.652511 |
| H       | 2.19292   | -2.49327  | -0.765824 |
| C       | 2.44982   | 1.61018   | -0.319776 |
| H       | 2.90419   | 1.59052   | -1.317909 |
| H       | 2.07746   | 2.62357   | -0.161665 |
| C       | 3.52096   | 1.26947   | 0.736950  |
| H       | 3.04441   | 1.18335   | 1.719834  |
| H       | 4.20462   | 2.12159   | 0.796638  |
| C       | 3.56906   | -1.31730  | 0.427506  |
|   |      |      |      |
|---|------|------|------|
| H | 3.08023900 | -1.48236600 | 1.39437000 |
| H | 4.28631700 | -2.13379000 | 0.29745600 |
| C | 4.34424000 | 0.00869200 | 0.43936200 |
| H | 5.13758900 | -0.06723200 | 1.18971500 |
| H | 4.84908600 | 0.13283600 | -0.52718800 |
| H | -2.27172000 | -2.14199700 | 0.42152800 |
| H | -4.73689400 | -2.07685700 | 0.65964000 |
| H | -4.69909300 | 2.13360600 | -0.18414600 |
| H | -2.23747600 | 2.05730400 | -0.43531000 |
| H | -5.96459600 | 0.06445300 | 0.35951300 |

**M062X**

|   |      |      |      |
|---|------|------|------|
| N | -0.67908600 | -0.09395700 | -0.18371600 |
| N | 0.03383700 | 1.08152700 | -0.13716900 |
| N | 1.30968000 | -0.66544700 | -0.48166400 |
| C | 0.06148900 | -1.20514300 | -0.39522200 |
| C | 1.26073200 | 0.70033900 | -0.32418400 |
| C | -2.09383400 | -0.04973900 | -0.02864500 |
| C | -2.76884000 | 1.15725200 | -0.19202300 |
| C | -4.15174200 | 1.19236000 | -0.04270000 |
| C | -4.86010300 | 0.03420600 | 0.26148600 |
| C | -4.17322300 | -1.16676600 | 0.42198500 |
| C | -2.79124800 | -1.21554800 | 0.28344500 |
| C | 2.53302400 | -1.43539600 | -0.70612700 |
$9c$ (B3LYP)

\begin{align*}
\text{N} & \quad -0.28053300 \quad -0.09690200 \quad -0.20587900 \\
\text{N} & \quad 0.43844900 \quad 1.08835000 \quad -0.12588600 \\
\text{N} & \quad 1.72609100 \quad -0.66328500 \quad -0.47009400 \\
\text{C} & \quad 0.47171700 \quad -1.20333900 \quad -0.41811800 \\
\text{C} & \quad 1.67351700 \quad 0.70715500 \quad -0.29493100 \\
\text{C} & \quad -1.69859900 \quad -0.05705900 \quad -0.07484400 \\
\text{C} & \quad -2.38501700 \quad 1.14136200 \quad -0.28098700 \\
\text{C} & \quad -3.77243400 \quad 1.17979100 \quad -0.15844200 \\
\text{C} & \quad -4.44409100 \quad 0.01243600 \quad 0.16141400 \\
\text{C} & \quad -3.78583100 \quad -1.18894200 \quad 0.37015600 \\
\text{C} & \quad -2.39902000 \quad -1.21989600 \quad 0.25677000 \\
\text{C} & \quad 2.94870700 \quad 1.44760300 \quad -0.69215700 \\
\text{H} & \quad 3.38820700 \quad -1.14803100 \quad -1.64877700 \\
\text{H} & \quad 2.61680500 \quad -2.48001200 \quad -0.78864300 \\
\text{C} & \quad 2.85526200 \quad 1.61815400 \quad -0.28319200 \\
\text{H} & \quad 3.32147100 \quad 1.61460900 \quad -1.27602700 \\
\text{H} & \quad 2.47747400 \quad 2.62789000 \quad -0.11492600 \\
\text{C} & \quad 3.91488900 \quad 1.26566600 \quad 0.78117000 \\
\text{H} & \quad 3.42687600 \quad 1.16403800 \quad 1.75703900 \\
\text{H} & \quad 4.59439800 \quad 2.11905800 \quad 0.86112000 \\
\text{C} & \quad 3.97530700 \quad -1.31615300 \quad 0.43624100
\end{align*}
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | 3.47604300| -1.49625300| 1.39504200|
| H       | 4.69670400| -2.12846800| 0.30312100|
| C       | 4.74582200| 0.01196800 | 0.47531400|
| H       | 5.53087300| -0.07185800| 1.23350000|
| H       | 5.26115000| 0.15128400 | -0.48359400|
| F       | -5.80184400| 0.04585600 | 0.27847600|
| H       | -1.85815100| -2.14097400| 0.42352800|
| H       | -4.34528500| -2.07986800| 0.62620500|
| H       | -4.32154100| 2.09964300 | -0.31519300|
| H       | -1.83783700| 2.03785500 | -0.53602100|

**M062X**

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| N       | -0.27113100| -0.09643600| -0.21442900|
| N       | 0.43622000 | 1.08055400 | -0.13984800|
| N       | 1.72239300 | -0.65757700| -0.49228200|
| C       | 0.47461700 | -1.20238100| -0.43189700|
| C       | 1.66714500 | 0.70549800 | -0.31515600|
| C       | -1.68703800| -0.05847200| -0.07925500|
| C       | -2.36772800| 1.13883700 | -0.28226300|
| C       | -3.75156400| 1.17774100 | -0.15385100|
| C       | -4.42082500| 0.01224100 | 0.16800300 |
| C       | -3.76372100| -1.18804900| 0.37210500 |
| C       | -2.38045200| -1.22060400| 0.25286500 |
| C       | 2.95120700 | -1.42028500| -0.71244500|

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| X          | Y          | Z          |
|------------|------------|------------|
| 3.41405300 | -1.07422900| -1.64163400|
| 2.63277900 | -2.45119000| -0.85637400|
| 2.85406800 | 1.60483300 | -0.29978100|
| 3.35027400 | 1.55996000 | -1.27586200|
| 2.48093000 | 2.62091000 | -0.16962300|
| 3.86235400 | 1.25529600 | 0.80633400 |
| 3.33084200 | 1.13883100 | 1.75666300 |
| 4.53514900 | 2.10809000 | 0.92308000 |
| 3.93394000 | -1.31122200| 0.45071700 |
| 3.39459500 | -1.48932200| 1.38710000 |
| 4.65531600 | -2.12487300| 0.33928800 |
| 4.70375500 | 0.01020700 | 0.51918100 |
| 5.46665700 | -0.07804900| 1.29714500 |
| 5.23906600 | 0.15550000 | -0.42679200|
| -5.76476700| 0.04606800 | 0.29162500 |
| -1.83624600| -2.14057800| 0.41686000 |
| -4.32677900| -2.07607300| 0.62991700 |
| -4.30412100| 2.09588200 | -0.30706500|
| -1.81652200| 2.03298300 | -0.53876800|
9k (B3LYP)

N  0.36854000  -0.15558200  0.19776200
N  1.07756100  -0.71780600  -0.86271500
N  2.36936700  -0.08092300  0.80890600
C  1.12003900  0.25452100  1.24648900
C  2.31177700  -0.65918400  -0.44883700
C  -1.03777300  -0.04749000  0.10168400
C  -1.84762400  -1.17899100  0.18887800
C  -3.22866800  -1.08525000  0.08985200
C  -3.82162500  0.15739400  -0.09363900
C  -3.03359200  1.29734800  -0.18166300
C  -1.65231300  1.18858700  -0.09177000
C  3.59654200  0.14258600  1.58864200
H  4.03434500  -0.82953700  1.83520700
H  3.26779900  0.60430500  2.51809000
C  3.49281400  -1.12913000  -1.23123900
H  3.95996800  -1.96999700  -0.70447900
H  3.11283500  -1.51941000  -2.17658000
C  4.54734600  -0.03539000  -1.49516600
H  4.05471300  0.84746600  -1.91772300
H  5.22248000  -0.41349400  -2.26818400
C  4.62197800  1.03161000  0.87915100
H  4.12297100  1.94246500  0.52963500
H  5.34592600  1.34392200  1.63810000
C  5.38575400  0.36364300 -0.27325100
H  6.16982300  1.05070000 -0.60669800
H  5.90163200 -0.52549900  0.11092000
F  -3.60747100  2.49127900 -0.36501600
F  -0.91459900  2.29752500 -0.20165600
F  -5.14915700  0.25601500 -0.18435100
F  -3.99017300 -2.18066300  0.18209000
F  -1.29734300 -2.38107500  0.38662700

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N  0.37328300 -0.14442400  0.24494300
N  1.06790200 -0.88321500 -0.69081500
N  2.36385000  0.03485600  0.82581200
C  1.12322900  0.44787700  1.20233000
C  2.29979500 -0.75444600 -0.30285200
C  -1.02727300 -0.04188000  0.12659400
C  -1.83176700 -1.17055000  0.22837100
C  -3.20660600 -1.08089600  0.09916900
C  -3.79552300  0.15281100 -0.12462800
C  -3.01023400  1.28874600 -0.22416000
C  -1.63440200  1.18578200 -0.10707100
### S2.4 Summary of Bond Lengths, Bond Angles, and Dihedral Angles from Computational Analysis

#### S2.4.1 Summary for Triazolium Computational Analysis
Table S21. Computational structural data for individual triazolium salts 7a-k (n=1) obtained from DFT optimized structures (B3LYP, n=1).

![Chemical structure](image)

| Backbone Bond Length | 7a  | 7b  | 7c  | 7d  | 7e  | 7f  | 7g  | 7h  | 7i  | 7j  | 7k  |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| N°N²                | 1.38| 1.38| 1.38| 1.38| 1.38| 1.38| 1.38| 1.38| 1.38| 1.38| 1.38|
| N²C³                | 1.33| 1.33| 1.33| 1.34| 1.34| 1.33| 1.33| 1.33| 1.33| 1.33| 1.34|
| C°N⁴                | 1.33| 1.33| 1.33| 1.33| 1.33| 1.33| 1.33| 1.33| 1.33| 1.33| 1.33|
| N⁴C⁵                | 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37|
| C°N⁶                | 1.31| 1.31| 1.31| 1.31| 1.31| 1.31| 1.31| 1.31| 1.31| 1.31| 1.30|
| C°C⁷                | 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49|
| N²C⁸                | 1.48| 1.48| 1.48| 1.48| 1.48| 1.48| 1.48| 1.48| 1.48| 1.48| 1.48|
| C⁹C⁹                | 1.43| 1.44| 1.43| 1.43| 1.43| 1.43| 1.43| 1.45| 1.45| 1.43| 1.42|
| C°C¹⁰               | 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.40| 1.40| 1.40| 1.40| 1.39|
| C²C¹¹               | 1.40| 1.39| 1.39| 1.39| 1.39| 1.39| 1.40| 1.40| 1.40| 1.40| 1.39|

| C-H Bond Length | 7a  | 7b  | 7c  | 7d  | 7e  | 7f  | 7g  | 7h  | 7i  | 7j  | 7k  |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C°H¹            | 1.08| 1.08| 1.08| 1.08| 1.08| 1.08| 1.08| 1.08| 1.08| 1.08| 1.08|
| C²H²            | 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09|
| C³H³            | 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09|

| H-H Distance | 7a  | 7b  | 7c  | 7d  | 7e  | 7f  | 7g  | 7h  | 7i  | 7j  | 7k  |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| H°H¹         | 3.16| 3.14| 3.16| 3.14| 3.14| 3.13| 3.15| 3.15| 3.15| 3.15| 3.14|
| H²H²         | 3.37| 3.39| 3.37| 3.39| 3.39| 3.39| 3.39| 3.39| 3.39| 3.39| 3.38|

| Bond Angles | 7a  | 7b  | 7c  | 7d  | 7e  | 7f  | 7g  | 7h  | 7i  | 7j  | 7k  |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C°N²N²      | 103.8| 103.8| 103.7| 103.8| 103.8| 103.7| 103.8| 103.8| 103.5| 103.4| 103.4|
| N²N²C²      | 111.5| 111.5| 111.5| 111.5| 111.6| 111.5| 111.5| 111.4| 111.4| 111.7| 111.8|
| N²C⁴N⁴      | 106.1| 106.0| 106.0| 106.0| 106.0| 106.0| 106.0| 106.0| 106.3| 106.3| 106.3|
| C°N⁴C⁵      | 107.3| 107.4| 107.4| 107.4| 107.4| 107.5| 107.3| 107.3| 107.6| 107.6| 107.7|
| N⁴C⁶N¹      | 111.3| 111.3| 111.3| 111.3| 111.2| 111.2| 111.3| 111.2| 111.3| 111.3| 111.4|
| C⁶C⁷N⁴      | 111.1| 111.0| 111.1| 111.0| 111.0| 110.9| 111.0| 111.0| 111.0| 110.9| 110.9|
| C⁷N⁸C⁹      | 113.5| 113.5| 113.5| 113.4| 113.4| 113.4| 113.4| 113.4| 113.5| 113.3| 113.3|

| Torsion Angles | 7a  | 7b  | 7c  | 7d  | 7e  | 7f  | 7g  | 7h  | 7i  | 7j  | 7k  |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| H°C¹*C¹*H²    | 43.1| 40.0| 42.9| 39.9| 40.1| 39.6| 41.3| 41.4| 41.4| 41.2| 41.1|
| H²C²*C²*H¹    | 68.7| 71.8| 69.0| 71.9| 71.7| 72.2| 70.6| 70.5| 70.4| 70.7| 70.7|
| N²N²*C²*C³    | 44.7| 40.7| 44.4| 39.8| 37.5| 34.6| 38.4| 39.0| 38.7| 38.4| 37.7|
| N²N²*C²*C³    | 135.4| 139.4| 135.7| 140.2| 142.4| 145.5| 90.7| 90.4| 91.1| 90.3| 90.8|
Table S22. Computational structural data for individual triazolium salts 8a-c, i, k (n=2) and 9a-c, k (n=3) obtained from DFT optimized structures (B3LYP, n=2 and 3).

![Diagram of triazolium salt]

| Backbone Bond Length | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|----------------------|----|----|----|----|----|----|----|----|----|
| N²N³                | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 |
| N²C³                | 1.33 | 1.33 | 1.33 | 1.32 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 |
| C³N⁴                | 1.34 | 1.34 | 1.34 | 1.34 | 1.33 | 1.34 | 1.34 | 1.34 | 1.33 |
| N²C⁵                | 1.38 | 1.38 | 1.38 | 1.38 | 1.38 | 1.38 | 1.38 | 1.38 | 1.39 |
| C³N¹                | 1.31 | 1.31 | 1.31 | 1.31 | 1.31 | 1.31 | 1.31 | 1.31 | 1.31 |
| C⁴C⁶                | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 |
| N³C⁶                | 1.48 | 1.48 | 1.49 | 1.49 | 1.48 | 1.48 | 1.48 | 1.48 | 1.48 |
| N²C⁷                | 1.43 | 1.44 | 1.43 | 1.45 | 1.42 | 1.43 | 1.44 | 1.43 | 1.42 |
| C⁵C⁸                | 1.40 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 |
| C⁶C⁹                | 1.39 | 1.39 | 1.39 | 1.40 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 |

| C-H Bond Length | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|----------------|----|----|----|----|----|----|----|----|----|
| C²H¹            | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 |
| C²H²            | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |
| C³H¹            | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |

| H-H Distance | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|--------------|----|----|----|----|----|----|----|----|----|
| H¹H²         | 3.11 | 3.12 | 3.12 | 3.14 | 3.15 | 3.55 | 3.53 | 3.53 | 3.54 |
| H¹H¹         | 2.79 | 2.78 | 2.78 | 2.78 | 2.78 | 2.48 | 2.49 | 2.49 | 2.49 |

| Bond Angles | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|------------|----|----|----|----|----|----|----|----|----|
| C²N²N³     | 104.9 | 104.9 | 104.9 | 104.9 | 104.5 | 105.2 | 105.2 | 105.1 | 104.7 |
| N²N²C³     | 110.9 | 110.9 | 111.0 | 110.8 | 111.3 | 110.7 | 110.7 | 110.8 | 111.0 |
| N²C²N⁴     | 107.0 | 107.0 | 107.0 | 107.2 | 106.8 | 107.3 | 107.3 | 107.2 | 107.0 |
| C²N²C⁵     | 106.7 | 106.8 | 106.8 | 106.7 | 107.0 | 106.7 | 106.7 | 106.7 | 106.9 |
| N²C²N¹     | 110.4 | 110.4 | 110.4 | 110.4 | 110.5 | 110.2 | 110.2 | 110.2 | 110.3 |
| C⁴C⁶N⁴     | 122.3 | 122.3 | 122.3 | 122.3 | 122.3 | 124.6 | 124.6 | 124.6 | 124.6 |
| C⁵N²C⁹     | 125.4 | 125.4 | 125.4 | 125.3 | 125.1 | 127.2 | 127.1 | 127.1 | 127.1 |

| Torsion Angles | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|---------------|----|----|----|----|----|----|----|----|----|
| H¹C²*C²H²     | 39.9 | 39.1 | 39.3 | 37.9 | 37.7 | 1.0 | 1.6 | 1.5 | 0.6 |
| H¹C²*C²H¹     | 69.1 | 69.9 | 69.8 | 71.2 | 71.5 | 106.4 | 104.0 | 104.0 | 104.9 |
| N²N²*C³C⁵     | 40.7 | 38.9 | 40.4 | 84.0 | 82.1 | 43.0 | 39.5 | 41.7 | 86.1 |
| N²N²*C³C⁹     | 139.5 | 141.2 | 139.6 | 94.9 | 96.4 | 137.1 | 140.6 | 138.2 | 92.4 |

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Table S23. Computational structural data for individual triazolium salts 7a-k (n=1) obtained from DFT optimized structures (M062X, n=1).

![Diagram of triazolium salt structure]

| Backbone Bond Length | 7a | 7b | 7c | 7d | 7e | 7f | 7g | 7h | 7i | 7j | 7k |
|----------------------|----|----|----|----|----|----|----|----|----|----|----|
| N1N2^2               | 1.36 | 1.36 | 1.36 | 1.36 | 1.36 | 1.36 | 1.37 | 1.36 | 1.37 | 1.37 | 1.37 |
| N1C3                  | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 |
| C3N4                  | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.32 | 1.32 |
| N1C5                  | 1.36 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 | 1.37 |
| C5N1                  | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 |
| C5C6                  | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 |
| N1C8                  | 1.47 | 1.47 | 1.47 | 1.48 | 1.48 | 1.48 | 1.47 | 1.47 | 1.48 | 1.48 | 1.48 |
| N1C7                  | 1.43 | 1.43 | 1.43 | 1.43 | 1.43 | 1.43 | 1.43 | 1.44 | 1.44 | 1.42 | 1.42 |
| C7C8                  | 1.38 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.40 | 1.39 | 1.39 | 1.39 | 1.39 |
| C7C9                  | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.40 | 1.39 | 1.39 | 1.39 | 1.39 |

| C-H Bond Length | 7a | 7b | 7c | 7d | 7e | 7f | 7g | 7h | 7i | 7j | 7k |
|----------------|----|----|----|----|----|----|----|----|----|----|----|
| C1H1           | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 |
| C4H2           | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |
| C6H3           | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |

| H-H Distance | 7a | 7b | 7c | 7d | 7e | 7f | 7g | 7h | 7i | 7j | 7k |
|--------------|----|----|----|----|----|----|----|----|----|----|----|
| H1-H2        | 3.15 | 3.13 | 3.15 | 3.13 | 3.13 | 3.12 | 3.14 | 3.15 | 3.14 | 3.14 | 3.14 |
| H1-H3        | 3.39 | 3.42 | 3.39 | 3.42 | 3.41 | 3.41 | 3.41 | 3.42 | 3.41 | 3.41 | 3.40 |

| Bond Angles | 7a | 7b | 7c | 7d | 7e | 7f | 7g | 7h | 7i | 7j | 7k |
|-------------|----|----|----|----|----|----|----|----|----|----|----|
| C1N1N2^2    | 103.8 | 103.8 | 103.8 | 103.8 | 103.8 | 103.7 | 103.8 | 103.8 | 103.5 | 103.4 |
| N1N2C3      | 111.8 | 111.8 | 111.9 | 111.9 | 111.9 | 111.9 | 111.9 | 111.9 | 111.8 | 112.1 | 112.1 |
| N2C3N4      | 105.9 | 105.9 | 105.9 | 105.9 | 105.8 | 105.8 | 106.0 | 106.0 | 106.1 | 105.7 | 105.6 |
| C3N4C5      | 107.2 | 107.3 | 107.3 | 107.3 | 107.4 | 107.4 | 107.2 | 107.2 | 107.5 | 107.6 |
| N4C4N1      | 111.2 | 111.2 | 111.2 | 111.2 | 111.1 | 111.1 | 111.2 | 111.1 | 111.2 | 111.2 | 111.2 |
| C6N4C7      | 110.8 | 110.8 | 110.8 | 110.8 | 110.8 | 110.7 | 110.8 | 110.7 | 110.7 | 110.7 | 110.7 |
| C7N4N5      | 113.2 | 113.2 | 113.2 | 113.2 | 113.1 | 113.2 | 113.3 | 113.2 | 113.2 | 113.1 | 113.1 |

| Torsion Angles | 7a | 7b | 7c | 7d | 7e | 7f | 7g | 7h | 7i | 7j | 7k |
|----------------|----|----|----|----|----|----|----|----|----|----|----|
| H1C3*C4H2      | 41.4 | 38.2 | 41.3 | 38.3 | 38.6 | 38.3 | 40.0 | 39.9 | 39.4 | 39.6 | 39.9 |
| H1C3*C6H3      | 70.9 | 74.1 | 71.1 | 74.1 | 73.7 | 74.0 | 72.4 | 72.4 | 73.0 | 72.8 | 72.4 |
| N1N2*C7C3      | 41.2 | 35.9 | 40.6 | 35.0 | 34.7 | 33.5 | 87.6 | 88.8 | 81.8 | 88.1 | 87.6 |
| N1N2*C7C5      | 138.9 | 144.2 | 139.4 | 144.9 | 145.2 | 146.5 | 91.4 | 90.5 | 97.0 | 90.3 | 90.8 |
Table S24. Computational structural data for individual triazolium salts 8a-c, i, k (n=2) and 9a-c, k (n=3) obtained from DFT optimized structures (M062X, n=2 and 3).

![Triazolium salt structure](image)

| Backbone Bond Length | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|----------------------|----|----|----|----|----|----|----|----|----|
| N1N2 | 1.36 | 1.36 | 1.36 | 1.36 | 1.36 | 1.36 | 1.36 | 1.36 | 1.36 |
| N2C3 | 1.32 | 1.32 | 1.32 | 1.32 | 1.33 | 1.32 | 1.32 | 1.32 | 1.33 |
| C3N4 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 |
| N3C5 | 1.37 | 1.37 | 1.37 | 1.37 | 1.38 | 1.37 | 1.38 | 1.38 | 1.38 |
| C5N1 | 1.31 | 1.31 | 1.31 | 1.31 | 1.30 | 1.31 | 1.31 | 1.31 | 1.30 |
| C6C8 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 |
| N4C6 | 1.48 | 1.48 | 1.48 | 1.48 | 1.48 | 1.47 | 1.48 | 1.48 | 1.48 |
| N5C7 | 1.43 | 1.43 | 1.43 | 1.44 | 1.42 | 1.43 | 1.43 | 1.43 | 1.42 |
| C7C8 | 1.39 | 1.39 | 1.39 | 1.40 | 1.39 | 1.38 | 1.39 | 1.39 | 1.39 |
| C8C9 | 1.38 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 |

| C-H Bond Length | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|-----------------|----|----|----|----|----|----|----|----|----|
| C5H1 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 |
| C6H2 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |
| C7H3 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |

| H-H Distance | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|---------------|----|----|----|----|----|----|----|----|----|
| H0H1 | 2.78 | 2.77 | 2.77 | 2.77 | 2.76 | 2.50 | 2.50 | 2.50 | 2.50 |
| H0H2 | 3.12 | 3.12 | 3.12 | 3.16 | 3.14 | 3.58 | 3.57 | 3.57 | 3.57 |

| Bond Angles | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|-------------|----|----|----|----|----|----|----|----|----|
| C5N1N2 | 104.9 | 104.9 | 104.9 | 104.9 | 104.5 | 105.1 | 105.1 | 105.1 | 104.7 |
| N1N2C3 | 111.2 | 111.2 | 111.3 | 111.2 | 111.6 | 111.1 | 111.1 | 111.1 | 111.4 |
| N2C3N4 | 106.8 | 106.8 | 106.8 | 107.0 | 106.5 | 107.0 | 107.0 | 107.0 | 106.7 |
| C3N4C5 | 106.7 | 106.7 | 106.8 | 106.6 | 107.0 | 106.7 | 106.7 | 106.7 | 107.0 |
| N4C5N1 | 110.3 | 110.3 | 110.3 | 110.3 | 110.4 | 110.2 | 110.2 | 110.2 | 110.3 |
| C5C7N1 | 122.3 | 122.3 | 122.3 | 122.2 | 122.2 | 124.1 | 124.0 | 124.0 | 123.9 |
| C7C8N9 | 125.5 | 125.5 | 125.5 | 125.4 | 125.3 | 126.6 | 126.6 | 126.6 | 126.4 |

| Torsion Angles | 8a | 8b | 8c | 8i | 8k | 9a | 9b | 9c | 9k |
|----------------|----|----|----|----|----|----|----|----|----|
| H0C5*C0H2 | 39.8 | 39.4 | 39.5 | 37.3 | 37.8 | 3.0 | 0.8 | 0.9 | 2.0 |
| H0C5*C0H3 | 69.7 | 70.0 | 70.0 | 72.2 | 71.8 | 108.9 | 106.8 | 106.9 | 108.1 |
| N1N2C0C8 | 38.7 | 36.2 | 38.0 | 83.7 | 65.8 | 40.4 | 37.7 | 40.0 | 67.5 |
| N1N2C0C8 | 141.4 | 143.8 | 141.9 | 94.9 | 112.8 | 140.0 | 142.3 | 139.8 | 111.3 |
Table S25. Summary of average bond angles and distances of triazolium salts 7a-k (n=1); 8a-c, 8i, 8k (n=2); 9a-c, 9k (n=3) and corresponding standard deviations obtained from from DFT calculation (B3LYP).

![Diagram of molecule]

| Backbone Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|----------------------|--------------|----------|--------------|----------|--------------|----------|-------------------------------|-----------|-----------|
| N1N2                | 1.38         | 0.00     | 1.37         | 0.00     | 1.37         | 0.00     | -0.01                         | 0         |           |
| N2C3                | 1.33         | 0.00     | 1.33         | 0.00     | 1.33         | 0.00     | -0.01                         | 0         |           |
| C4N4                | 1.33         | 0.00     | 1.34         | 0.00     | 1.34         | 0.00     | 0.01                          | 0         |           |
| N4C5                | 1.37         | 0.00     | 1.38         | 0.00     | 1.38         | 0.00     | 0.01                          | 0         |           |
| C6N4                | 1.31         | 0.00     | 1.31         | 0.00     | 1.31         | 0.00     | 0.00                          | 0         |           |
| C6C8                | 1.49         | 0.00     | 1.49         | 0.00     | 1.49         | 0.00     | 0.00                          | 0         |           |
| N8C8                | 1.48         | 0.00     | 1.49         | 0.00     | 1.48         | 0.00     | 0.01                          | 0         |           |
| N8C7                | 1.43         | 0.01     | 1.43         | 0.01     | 1.43         | 0.01     | 0.00                          | 0         |           |
| C6C8                | 1.40         | 0.01     | 1.40         | 0.00     | 1.39         | 0.00     | 0.00                          | 0         |           |
| C6C8                | 1.40         | 0.01     | 1.39         | 0.00     | 1.39         | 0.00     | 0.00                          | 0         |           |

| C-H Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|----------------|--------------|----------|--------------|----------|--------------|----------|-------------------------------|-----------|-----------|
| C1H1           | 1.08         | 0.00     | 1.08         | 0.00     | 1.08         | 0.00     | 0.00                          | 0         | 0.00      |
| C2H1           | 1.09         | 0.00     | 1.09         | 0.00     | 1.09         | 0.00     | 0.00                          | 0         | 0.00      |
| C3H1           | 1.09         | 0.00     | 1.09         | 0.00     | 1.09         | 0.00     | 0.00                          | 0         | 0.00      |

| H-H Distance | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|--------------|--------------|----------|-------------------------------|-----------|-----------|
| H1H2         | 3.15         | 0.01     | 3.13                          | 0.01     | 3.54       | 0.01     | -0.02                          | 0.41      |
| H1H3         | 3.38         | 0.01     | 2.78                          | 0.00     | 2.49       | 0.00     | -0.60                          | -0.30     |

| Bond Angles | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|-------------|--------------|----------|-------------------------------|-----------|-----------|
| C5N1N2      | 103.7        | 0.1      | 104.8                         | 0.2       | 105.1      | 0.2       | 1.1                            | 0.25      |
| N3N1C3      | 111.5        | 0.1      | 111.0                         | 0.2       | 110.8      | 0.2       | -0.55                          | -0.18     |
| N3C2N4      | 106.1        | 0.2      | 107.0                         | 0.2       | 107.2      | 0.1       | 0.94                           | 0.2       |
| C3N4C5      | 107.4        | 0.1      | 106.8                         | 0.1       | 106.7      | 0.1       | -0.63                          | -0.07     |
| N3C4N1      | 111.3        | 0.0      | 110.4                         | 0.1       | 110.2      | 0.1       | -0.86                          | -0.21     |
| C6C2N4      | 111.0        | 0.1      | 122.3                         | 0.0       | 124.6      | 0.0       | 11.27                          | 2.32      |
| C5N4C6      | 113.4        | 0.1      | 125.3                         | 0.1       | 127.1      | 0.0       | 11.9                           | 1.82      |

| Torsion Angles | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|---------------|--------------|----------|-------------------------------|-----------|-----------|
| H1C1C4H2      | 41.1         | 1.2      | 38.8                          | 1.0       | 1.2        | 0.5       | -2.31                          | -37.59    |
| H1C1C4C6      | 70.7         | 1.2      | 70.3                          | 1.0       | 104.8      | 1.1       | -0.44                          | 34.53     |
| N1N2C2C3      | 62.1         | 25.2     | 57.2                          | 23.6      | 52.6       | 22.4      | -4.89                          | -4.65     |
| N1N2C2C6      | 117.4        | 25.8     | 122.3                         | 24.4      | 127.1      | 23.1      | 4.88                           | 4.78      |
Table S26. Summary of average bond angles and distances of triazolium salts 7a-k (n=1); 8a-c, 8i, 8k (n=2); 9a-c, 9k (n=3) and corresponding standard deviations obtained from from DFT calculation (M062X).

![Diagram of triazolium salt]

| Backbone Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|----------------------|--------------|----------|--------------|----------|--------------|----------|--------------------------------|-----------|-----------|
| N N² | 1.36 | 0.00 | 1.36 | 0.00 | 1.36 | 0.00 | -0.01 | 0 |
| N C³ | 1.33 | 0.00 | 1.33 | 0.00 | 1.33 | 0.00 | 0 | 0 |
| C² N⁴ | 1.33 | 0.00 | 1.33 | 0.00 | 1.33 | 0.00 | 0.01 | 0 |
| N C⁵ | 1.37 | 0.00 | 1.37 | 0.00 | 1.37 | 0.00 | 0 | 0 |
| C² N⁶ | 1.37 | 0.00 | 1.37 | 0.00 | 1.37 | 0.00 | 0.01 | 0 |
| C² C⁶ | 1.49 | 0.00 | 1.49 | 0.00 | 1.49 | 0.00 | 0 | 0 |
| N C⁷ | 1.47 | 0.00 | 1.47 | 0.00 | 1.47 | 0.00 | 0.01 | 0 |
| N C⁸ | 1.47 | 0.00 | 1.47 | 0.00 | 1.47 | 0.00 | 0 | 0 |
| C² C⁸ | 1.39 | 0.00 | 1.39 | 0.00 | 1.39 | 0.00 | 0 | 0 |

| C-H Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|-----------------|--------------|----------|--------------|----------|--------------|----------|--------------------------------|-----------|-----------|
| C¹ H¹ | 1.08 | 0.00 | 1.08 | 0.00 | 1.08 | 0.00 | 0.00 | 0.00 |
| C² H² | 1.09 | 0.00 | 1.09 | 0.00 | 1.09 | 0.00 | 0.00 | 0.00 |
| C² H³ | 1.09 | 0.00 | 1.09 | 0.00 | 1.09 | 0.00 | 0.00 | 0.00 |

| H-H Distance | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|---------------|--------------|----------|--------------|----------|--------------|----------|--------------------------------|-----------|-----------|
| H¹ H² | 3.14 | 0.01 | 2.77 | 0.01 | 2.50 | 0.00 | -0.37 | -0.27 |
| H¹ H³ | 3.41 | 0.01 | 3.13 | 0.02 | 3.57 | 0.01 | -0.28 | 0.44 |

| Bond Angles | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|-------------|--------------|----------|--------------|----------|--------------|----------|--------------------------------|-----------|-----------|
| C⁴ N⁵ N² | 103.7 | 1.0 | 104.8 | 0.2 | 105.0 | 0.2 | 1.08 | 0.16 |
| N² N⁶ C³ | 111.9 | 0.1 | 111.3 | 0.1 | 111.2 | 0.2 | -0.6 | -0.14 |
| N² C⁴ N⁵ | 105.9 | 0.1 | 106.8 | 0.2 | 106.9 | 0.1 | 0.92 | 0.12 |
| C⁴ N⁶ C⁵ | 107.3 | 0.1 | 106.8 | 0.1 | 106.8 | 0.1 | -0.56 | 0 |
| N² C⁵ N¹ | 111.2 | 0.0 | 110.3 | 0.0 | 110.2 | 0.1 | -0.84 | -0.13 |
| C⁶ N⁷ C⁴ | 110.8 | 0.1 | 122.3 | 0.0 | 124.0 | 0.1 | 11.49 | 1.73 |
| C⁷ N⁸ C¹⁰ | 113.2 | 0.0 | 125.4 | 0.1 | 126.5 | 0.1 | 12.24 | 1.1 |

| Torsion Angles | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|---------------|--------------|----------|--------------|----------|--------------|----------|--------------------------------|-----------|-----------|
| H¹ C² C⁶ H² | 39.5 | 1.1 | 38.8 | 1.1 | 1.6 | 1.0 | -0.78 | -37.11 |
| H¹ C² C⁶ H³ | 72.8 | 1.1 | 70.7 | 1.2 | 107.7 | 1.0 | -2.07 | 36.96 |
| N² N⁶ C⁴ C⁵ | 59.5 | 26.3 | 52.5 | 21.3 | 46.4 | 14.1 | -7.05 | -6.08 |
| N² N⁶ C⁴ C⁵ | 119.9 | 26.9 | 127.0 | 22.1 | 133.4 | 14.7 | 7.05 | 6.4 |
Table S27. Summary of average* bond angles and distances of triazolium salts 7a-c, k (n=1); 8a-c, 8k (n=2); 9a-c, 9k (n=3) and corresponding standard deviations (SD) obtained from DFT calculation (M062X).

*Averages calculated using only data for the 12 triazolium salts related to C(3)-H/D exchange studies. These average values and trends are in excellent agreement with data in Table S30 as expected given the small standard deviations.

| Backbone Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) |
|----------------------|--------------|----------|--------------|----------|--------------|----------|
| N1N2                 | 1.36         | 0.00     | 1.36         | 0.00     | 1.36         | 0.00     |
| N2C3                 | 1.33         | 0.00     | 1.32         | 0.00     | 1.32         | 0.00     |
| CN4                  | 1.33         | 0.01     | 1.33         | 0.00     | 1.33         | 0.00     |
| N2C3                 | 1.37         | 0.00     | 1.37         | 0.00     | 1.38         | 0.00     |
| CN4                  | 1.30         | 0.00     | 1.31         | 0.00     | 1.31         | 0.00     |
| C3C0                 | 1.49         | 0.00     | 1.49         | 0.00     | 1.49         | 0.00     |
| N2C6                 | 1.47         | 0.00     | 1.48         | 0.00     | 1.48         | 0.00     |
| N2C7                 | 1.43         | 0.01     | 1.43         | 0.01     | 1.43         | 0.01     |
| C5C0                 | 1.39         | 0.00     | 1.39         | 0.00     | 1.39         | 0.00     |
| C5C8                 | 1.39         | 0.00     | 1.39         | 0.00     | 1.39         | 0.00     |

| C-H Bond Length  |
|------------------|
| C3H1             | 1.08         | 0.00     | 1.08         | 0.00     | 1.08         | 0.00     |
| C5H2             | 1.09         | 0.00     | 1.09         | 0.00     | 1.09         | 0.00     |
| C5H3             | 1.09         | 0.00     | 1.09         | 0.00     | 1.09         | 0.00     |

| H-H Distance |
|---------------|
| H1H2          | 3.14         | 0.01     | 2.77         | 0.01     | 2.50         | 0.00     |
| H1H3          | 3.40         | 0.01     | 3.12         | 0.01     | 3.57         | 0.01     |

| Bond Angles |
|-------------|
| C3N1N2      | 103.69       | 0.20     | 104.80       | 0.20     | 104.97       | 0.20     |
| N1N2C3      | 111.90       | 0.14     | 111.31       | 0.17     | 111.16       | 0.15     |
| N2C3N4      | 105.82       | 0.15     | 106.73       | 0.13     | 106.91       | 0.14     |
| C3N4C3      | 107.36       | 0.16     | 106.80       | 0.14     | 106.76       | 0.13     |
| N2C3N1      | 111.19       | 0.01     | 110.32       | 0.05     | 110.20       | 0.06     |
| C5C3N4      | 110.79       | 0.07     | 122.27       | 0.05     | 123.99       | 0.06     |
| C5N4C0      | 113.18       | 0.06     | 125.45       | 0.10     | 126.53       | 0.10     |
| Torsion Angles |  |  |  |  |  |  |
|---------------|---|---|---|---|---|---|
| H1C3*C0H2     | 40.21 | 1.51 | 39.13 | 0.90 | 1.65 | 1.05 |
| H1C3*C0H3     | 72.12 | 1.49 | 70.37 | 0.96 | 107.69 | 1.00 |
| N1N2*C3C6     | 51.32 | 24.30 | 44.68 | 14.14 | 46.41 | 14.12 |
| N1N2*C3C6     | 128.33 | 25.13 | 134.99 | 14.80 | 133.37 | 14.74 |
### Summary for Triazolylidene Computational Analysis

Table S28. Computational structural data for individual triazolylidenes 7'a-k (n=1) obtained from DFT optimized structures (B3LYP, n=1).

![Diagram of triazolylidene structure](image)

| Backbone Bond Length | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| N1N2                 | 1.40| 1.40| 1.40| 1.40| 1.40| 1.41| 1.41| 1.41| 1.41| 1.41| 1.41|
| N2C3                 | 1.36| 1.36| 1.36| 1.36| 1.37| 1.37| 1.35| 1.36| 1.36| 1.36| 1.36|
| C1N4                 | 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36|
| N2C5                 | 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37|
| C1N1                 | 1.30| 1.30| 1.30| 1.30| 1.30| 1.30| 1.30| 1.30| 1.30| 1.30| 1.30|
| C2C6                 | 1.47| 1.47| 1.47| 1.47| 1.47| 1.47| 1.47| 1.47| 1.47| 1.47| 1.47|
| N2C7                 | 1.43| 1.43| 1.42| 1.42| 1.42| 1.42| 1.44| 1.44| 1.42| 1.42| 1.41|
| C1C8                 | 1.40| 1.40| 1.40| 1.40| 1.40| 1.40| 1.40| 1.40| 1.40| 1.40| 1.39|
| C1C9                 | 1.39| 1.40| 1.40| 1.40| 1.40| 1.40| 1.41| 1.40| 1.40| 1.40| 1.39|

| C-H Bond Length | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C1H2            | 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09|
| C1H3            | 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09|

| C-H Distance | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C1H2         | 2.93| 2.93| 2.93| 2.93| 2.93| 2.92| 2.93| 2.93| 2.94| 2.93| 2.92|
| C1H3         | 3.05| 3.05| 3.05| 3.04| 3.04| 3.04| 3.05| 3.05| 3.05| 3.05| 3.04|

| Bond Angles | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C1N2N2      | 102.1| 102.1| 102.0| 102.1| 102.1| 102.1| 101.9| 102.0| 101.9| 101.5| 101.4|
| N2C3N3      | 115.3| 115.2| 115.3| 115.2| 115.2| 115.2| 115.5| 115.4| 115.4| 115.9| 115.9|
| N2C4N4      | 100.1| 100.1| 100.0| 100.1| 100.1| 100.0| 100.1| 100.2| 100.2| 99.7| 99.6|
| C1N5C5      | 111.5| 111.5| 111.6| 111.6| 111.6| 111.6| 111.4| 111.4| 111.4| 111.6| 111.8|
| N2C6N6      | 111.0| 111.0| 111.0| 111.0| 111.0| 111.0| 111.1| 111.1| 111.1| 111.2| 111.3|
| C6C7N7      | 111.3| 111.3| 111.3| 111.3| 111.3| 111.2| 111.3| 111.3| 111.2| 111.2| 111.2|
| C1N8C9      | 112.9| 112.9| 112.9| 112.8| 112.8| 112.8| 112.9| 112.9| 112.9| 112.8| 112.7|

| Torsion Angles | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C1N2C4H2      | 52.3| 52.6| 52.6| 52.3| 52.4| 52.2| 52.3| 52.2| 52.3| 52.2| 52.1|
| C1N2C4H3      | 83.6| 83.3| 83.3| 83.5| 83.4| 83.6| 83.7| 83.6| 83.7| 83.8| 83.8|
| N2C5C6       | 29.0| 20.8| 21.3| 0.9| 0.7| 0.6| 89.5| 89.5| 88.7| 88.9| 68.1|
| N1N2C4C5     | 151.2| 159.2| 158.8| 179.2| 179.3| 179.4| 89.8| 89.9| 90.9| 90.3| 111.4|
Table S29. Computational structural data for individual triazolylidenes 8'a-c, i, k (n=2) and 9'a-c, k (n=3) obtained from DFT optimized structures (B3LYP, n=2 and 3).

![Diagram of a triazolylidene molecule]

| Backbone Bond Length | 8'a | 8'b | 8'c | 8'i | 8'k | 9'a | 9'b | 9'c | 9'k |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| N3N2                 | 1.39| 1.39| 1.39| 1.39| 1.40| 1.39| 1.39| 1.39| 1.39|
| N3C3                 | 1.35| 1.35| 1.35| 1.35| 1.35| 1.35| 1.36| 1.35| 1.35|
| C3N4                 | 1.37| 1.37| 1.37| 1.37| 1.36| 1.37| 1.37| 1.37| 1.37|
| N3C5                 | 1.38| 1.38| 1.38| 1.38| 1.38| 1.38| 1.38| 1.38| 1.38|
| C3N4                 | 1.30| 1.30| 1.30| 1.30| 1.30| 1.30| 1.30| 1.30| 1.30|
| C3C6                 | 1.50| 1.50| 1.50| 1.50| 1.50| 1.49| 1.49| 1.49| 1.49|
| N4C6                 | 1.47| 1.47| 1.47| 1.47| 1.47| 1.47| 1.47| 1.47| 1.47|
| N3C6                 | 1.43| 1.43| 1.42| 1.44| 1.41| 1.43| 1.43| 1.42| 1.41|
| C3C6                 | 1.40| 1.40| 1.40| 1.39| 1.39| 1.40| 1.40| 1.39| 1.39|
| C3C6                 | 1.39| 1.40| 1.40| 1.39| 1.40| 1.40| 1.40| 1.39| 1.39|

| C-H Bond Length | 8'a | 8'b | 8'c | 8'i | 8'k | 9'a | 9'b | 9'c | 9'k |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C3H2            | 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09|
| C3H3            | 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09|

| C-H Distance |
|---------------|
| 8'a | 8'b | 8'c | 8'i | 8'k | 9'a | 9'b | 9'c | 9'k |
| 2.91 | 2.91 | 2.91 | 2.92 | 2.91 | 3.17 | 3.17 | 3.17 | 3.16 |
| 2.71 | 2.70 | 2.70 | 2.71 | 2.70 | 2.53 | 2.52 | 2.52 | 2.52 |

| Bond Angles |
|-------------|
| 8'a | 8'b | 8'c | 8'i | 8'k | 9'a | 9'b | 9'c | 9'k |
| 103.3 | 103.3 | 103.2 | 103.1 | 102.6 | 103.5 | 103.6 | 103.5 | 102.8 |
| 114.9 | 114.8 | 114.9 | 115.0 | 115.5 | 114.8 | 114.7 | 114.8 | 115.4 |
| 101.0 | 101.0 | 101.0 | 101.1 | 100.5 | 101.1 | 101.2 | 101.1 | 100.7 |
| 110.7 | 110.7 | 110.7 | 110.6 | 110.9 | 110.6 | 110.6 | 110.6 | 110.8 |
| 110.2 | 110.2 | 110.2 | 110.4 | 110.0 | 110.0 | 110.0 | 110.0 | 110.3 |
| 122.9 | 122.9 | 122.9 | 122.9 | 122.9 | 125.2 | 125.2 | 125.2 | 125.1 |
| 124.1 | 124.1 | 124.0 | 124.1 | 124.0 | 125.4 | 125.4 | 125.4 | 125.4 |

| Torsion Angles |
|---------------|
| 8'a | 8'b | 8'c | 8'i | 8'k | 9'a | 9'b | 9'c | 9'k |
| 82.3 | 82.4 | 82.5 | 82.3 | 82.4 | 0.1 | 0.0 | 0.1 | 0.3 |
| 42.0 | 42.0 | 41.8 | 42.1 | 42.0 | 118.3 | 118.4 | 118.3 | 118.5 |
| 28.8 | 21.2 | 21.1 | 86.0 | 70.3 | 27.1 | 17.5 | 19.7 | 72.0 |
| 151.4 | 158.8 | 159.0 | 93.2 | 109.3 | 153.2 | 162.6 | 160.4 | 107.6 |

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Table S30. Computational structural data for individual triazolylidenes 7'a-k (n=1) obtained from DFT optimized structures (M062X, n=1).

![Diagram of triazolylidene structure]

| Backbone Bond Length | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| N=N^2                | 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39|
| N=C^3                | 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36| 1.36|
| C=N^4                | 1.36| 1.36| 1.36| 1.35| 1.35| 1.35| 1.36| 1.36| 1.36| 1.36| 1.35|
| N=C^5                | 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37| 1.37|
| C=N^1                | 1.29| 1.29| 1.29| 1.29| 1.29| 1.29| 1.29| 1.30| 1.29| 1.29| 1.29|
| C=C^6                | 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49| 1.49|
| N=C^7                | 1.46| 1.46| 1.46| 1.46| 1.46| 1.46| 1.46| 1.46| 1.46| 1.46| 1.46|
| C=C^8                | 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39|
| C=C^9                | 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39| 1.39|

| C-H Bond Length | Bond Length | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|-----------------|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C-H^1           | 1.09        | 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09|
| C-H^2           | 1.09        | 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09| 1.09|

| C-H Distance | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C-H^1         | 2.91| 2.92| 2.91| 2.91| 2.91| 2.92| 2.92| 2.92| 2.91| 2.91| 2.91|
| C-H^2         | 3.05| 3.05| 3.05| 3.05| 3.05| 3.05| 3.05| 3.06| 3.05| 3.05| 3.05|

| Bond Angles | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C=N^2       | 102.2| 102.2| 102.2| 102.3| 102.2| 102.2| 102.0| 102.1| 102.1| 101.7| 101.6|
| N=N^2       | 115.8| 115.7| 115.8| 115.6| 115.7| 115.6| 116.0| 116.0| 116.0| 116.4| 116.4|
| N=C^3       | 99.7| 99.7| 99.6| 99.7| 99.7| 99.7| 99.7| 99.7| 99.7| 99.3| 99.2|
| C=N^4       | 111.5| 111.5| 111.6| 111.6| 111.6| 111.6| 111.4| 111.4| 111.4| 111.6| 111.8|
| N=C^5       | 110.8| 110.8| 110.8| 110.8| 110.8| 110.9| 110.9| 110.9| 110.9| 111.0| 111.1|
| C^6=C^7     | 111.1| 111.1| 111.1| 111.1| 111.1| 111.1| 111.1| 111.1| 111.1| 111.0| 111.0|
| C=N^8       | 112.7| 112.7| 112.7| 112.7| 112.7| 112.6| 112.7| 112.7| 112.7| 112.6| 112.5|

| Torsion Angles | 7'a | 7'b | 7'c | 7'd | 7'e | 7'f | 7'g | 7'h | 7'i | 7'j | 7'k |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C=N^2*C-H^1   | 50.6| 50.6| 50.7| 50.7| 50.6| 50.7| 50.7| 50.6| 50.5| 50.4| 50.4|
| C,N^2*C=H^2   | 85.4| 85.3| 85.3| 85.2| 85.3| 85.3| 85.3| 85.4| 85.4| 85.6| 85.7|
| N=N^2*C=C^5   | 25.9| 21.0| 22.5| 1.6| 10.5| 1.7| 89.4| 88.3| 83.4| 87.5| 60.2|
| N=N^2*C=C^8   | 154.4| 159.0| 157.6| 178.3| 169.6| 178.4| 90.0| 91.3| 96.3| 91.8| 119.5|

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Table S31.  
Computational structural data for individual triazolyldenes 8'a-c, i, k (n=2) and 9'a-c, k (n=3) obtained from DFT optimized structures (M062X, n=2 and 3).

![Image of a chemical structure](image)

| Backbone Bond Length | 8'a  | 8'b  | 8'c  | 8'i  | 8'k  | 9'a  | 9'b  | 9'c  | 9'k  |
|----------------------|------|------|------|------|------|------|------|------|------|
| N'N2                 | 1.38 | 1.38 | 1.38 | 1.38 | 1.37 | 1.38 | 1.38 | 1.38 | 1.38 |
| N2C3                 | 1.35 | 1.35 | 1.35 | 1.35 | 1.35 | 1.35 | 1.35 | 1.35 | 1.35 |
| C'N4                 | 1.36 | 1.36 | 1.36 | 1.37 | 1.36 | 1.36 | 1.36 | 1.36 | 1.36 |
| N4C5                 | 1.37 | 1.38 | 1.38 | 1.37 | 1.38 | 1.38 | 1.38 | 1.38 | 1.38 |
| C'N1                 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 |
| C'C6                 | 1.49 | 1.49 | 1.49 | 1.50 | 1.49 | 1.49 | 1.49 | 1.49 | 1.49 |
| N4C6                 | 1.47 | 1.47 | 1.47 | 1.47 | 1.47 | 1.47 | 1.46 | 1.46 | 1.46 |
| N3C                 | 1.42 | 1.42 | 1.42 | 1.43 | 1.41 | 1.42 | 1.42 | 1.42 | 1.42 |
| C'C5                 | 1.39 | 1.39 | 1.39 | 1.40 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 |
| C'C                 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 | 1.39 |

| C-H Bond Length | 8'a  | 8'b  | 8'c  | 8'i  | 8'k  | 9'a  | 9'b  | 9'c  | 9'k  |
|----------------|------|------|------|------|------|------|------|------|------|
| C'H2           | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |
| C'H3           | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |

| C-H Distance | 8'a  | 8'b  | 8'c  | 8'i  | 8'k  | 9'a  | 9'b  | 9'c  | 9'k  |
|--------------|------|------|------|------|------|------|------|------|------|
| C'H2         | 2.70 | 2.69 | 2.69 | 2.69 | 2.69 | 2.53 | 2.53 | 2.53 | 2.53 |
| C'H3         | 2.90 | 2.91 | 2.90 | 2.91 | 2.90 | 3.18 | 3.18 | 3.18 | 3.18 |

| Bond Angles | 8'a  | 8'b  | 8'c  | 8'i  | 8'k  | 9'a  | 9'b  | 9'c  | 9'k  |
|-------------|------|------|------|------|------|------|------|------|------|
| C'N1N2      | 103.3| 103.3| 103.3| 103.2| 102.7| 103.5| 103.5| 103.5| 102.8|
| N2N3C4      | 115.3| 115.2| 115.3| 115.5| 115.9| 115.2| 115.1| 115.2| 115.8|
| N3C5N4      | 100.6| 100.6| 100.6| 100.6| 100.1| 100.7| 100.7| 100.7| 100.2|
| C'N4C5      | 110.7| 110.7| 110.7| 110.6| 111.0| 110.7| 110.7| 110.7| 111.0|
| N4C6N1      | 110.0| 110.1| 110.1| 110.3| 110.0| 110.0| 110.0| 110.0| 110.2|
| C'C5N4      | 123.0| 123.0| 123.0| 122.9| 122.9| 124.6| 124.6| 124.6| 124.4|
| C'N5C6      | 124.2| 124.2| 124.1| 124.2| 124.0| 124.7| 124.7| 124.7| 124.5|

| Torsion Angles | 8'a  | 8'b  | 8'c  | 8'i  | 8'k  | 9'a  | 9'b  | 9'c  | 9'k  |
|---------------|------|------|------|------|------|------|------|------|------|
| C'N1*C'H2     | 42.4 | 42.4 | 42.0 | 41.8 | 41.8 | 2.8  | 2.7  | 2.7  | 3.2 |
| C'N1*C'H3     | 82.4 | 82.4 | 82.7 | 82.9 | 82.9 | 121.4| 121.3| 121.3| 121.9|
| N2*C'C6      | 26.4 | 21.7 | 23.4 | 84.3 | 62.8 | 23.6 | 17.2 | 19.5 | 63.2|
| N3*N*C'C     | 153.8| 158.3| 156.6| 94.7 | 117.0| 156.6| 162.9| 160.6| 116.2|

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Table S32. Summary of average bond angles and distances of triazolylidenes 7′a-k (n=1); 8′a-c, i, k (n=2); 9′a-c, k (n=3) and corresponding standard deviations obtained from DFT calculation (B3LYP).

![Triazolylidene diagram]

| Backbone Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|----------------------|---------------|----------|---------------|----------|---------------|----------|-------------------------------|------------|------------|
| N′N2                 | 1.41          | 0.00     | 1.39          | 0.00     | 1.39          | 0.00     | -0.01                         | 0          | 0          |
| N′C3                 | 1.36          | 0.00     | 1.35          | 0.00     | 1.35          | 0.00     | -0.01                         | 0          | 0          |
| C′N4                 | 1.36          | 0.00     | 1.37          | 0.00     | 1.37          | 0.00     | 0.01                          | 0          | 0          |
| N′C5                 | 1.37          | 0.00     | 1.38          | 0.00     | 1.38          | 0.00     | 0.01                          | 0          | 0          |
| C′N6                 | 1.30          | 0.00     | 1.30          | 0.00     | 1.30          | 0.00     | 0.01                          | 0          | 0          |
| C′C8                 | 1.49          | 0.00     | 1.50          | 0.00     | 1.49          | 0.00     | 0                             | 0          | 0          |
| N′C9                 | 1.47          | 0.00     | 1.47          | 0.00     | 1.47          | 0.00     | 0                             | 0          | 0          |
| N′C7                 | 1.42          | 0.01     | 1.43          | 0.01     | 1.42          | 0.01     | 0                             | 0          | 0          |
| C′C6                 | 1.40          | 0.00     | 1.40          | 0.00     | 1.39          | 0.00     | 0                             | 0          | 0          |
| C′C4                 | 1.40          | 0.00     | 1.40          | 0.00     | 1.40          | 0.00     | 0                             | 0          | 0          |

| C-H Bond Length | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|-----------------|---------------|----------|---------------|----------|---------------|----------|-------------------------------|------------|------------|
| C′H2            | 1.09          | 0.00     | 1.09          | 0.00     | 1.09          | 0.00     | 0                             | 0.00       | 0.00       |
| C′H3            | 1.09          | 0.00     | 1.09          | 0.00     | 1.09          | 0.00     | 0                             | 0.00       | 0.00       |

| C-H Distance | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|--------------|---------------|----------|---------------|----------|---------------|----------|-------------------------------|------------|------------|
| C′H2         | 2.93          | 0.00     | 2.91          | 0.00     | 3.17          | 0.00     | -0.02                         | 0.25       |            |
| C′H3         | 3.05          | 0.00     | 2.70          | 0.00     | 2.52          | 0.00     | -0.34                         | -0.18      |            |

| Bond Angles | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|-------------|---------------|----------|---------------|----------|---------------|----------|-------------------------------|------------|------------|
| C′N2′N3′    | 101.9         | 0.2      | 103.1         | 0.3      | 103.4         | 0.4      | 1.2                           | 0.3        |            |
| N′N3′C3′    | 115.4         | 0.3      | 115.0         | 0.3      | 114.9         | 0.3      | -0.4                          | -0.1       |            |
| N′C3′N4′    | 100.0         | 0.2      | 100.9         | 0.2      | 101.0         | 0.2      | 0.9                           | 0.1        |            |
| C′N4′C5′    | 111.5         | 0.1      | 110.7         | 0.1      | 110.6         | 0.1      | -0.8                          | -0.1       |            |
| N′C5′N6′    | 111.1         | 0.1      | 110.2         | 0.1      | 110.1         | 0.1      | -0.8                          | -0.2       |            |
| C′C6′N4′    | 111.3         | 0.0      | 122.9         | 0.0      | 125.1         | 0.1      | 11.6                          | 2.2        |            |
| C′N4′C6′    | 112.8         | 0.0      | 124.1         | 0.1      | 125.4         | 0.0      | 11.2                          | 1.4        |            |

| Torsion Angles | Average (n=1) | SD (n=1) | Average (n=2) | SD (n=2) | Average (n=3) | SD (n=3) | Differences of averaged values | n=1 vs n=2 | n=2 vs n=3 |
|----------------|---------------|----------|---------------|----------|---------------|----------|-------------------------------|------------|------------|
| C′N4′C′H2′    | 52.3          | 0.2      | 82.4          | 0.1      | 0.1           | 0.1      | 30.1                          | -82.3      |            |
| C′N4′C′H3′    | 83.6          | 0.2      | 42.0          | 0.1      | 118.4         | 0.1      | -41.6                         | 76.4       |            |
| N′N2′C′C′8′   | 45.3          | 39.5     | 45.5          | 30.5     | 34.1          | 25.6     | 0.2                           | -11.4      |            |
| N′N2′C′C′6′   | 134.5         | 39.8     | 134.3         | 30.9     | 145.9         | 25.9     | -0.2                          | 11.6       |            |
Table S33. Summary of average bond angles and distances of triazolylidenes 7\textsuperscript{a-k} (n=1); 8\textsuperscript{a-c}, i, k (n=2); 9\textsuperscript{a-c}, k (n=3) and corresponding standard deviations obtained from DFT calculation (M062X). Data highlighted in purple is included in Table 3 in the main text.

![Diagram](image)

| Backbone Bond Length | Average \( (n=1) \) | SD \( (n=1) \) | Average \( (n=2) \) | SD \( (n=2) \) | Average \( (n=3) \) | SD \( (n=3) \) | Differences of averaged values | \( n=1 \) vs \( n=2 \) | \( n=2 \) vs \( n=3 \) |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|-----------------------------|----------------|----------------|
| N\textsuperscript{1}N\textsuperscript{2} | 1.39 | 0.00 | 1.38 | 0.00 | 1.38 | 0.00 | -0.01 | 0 | 0 |
| N\textsuperscript{2}C\textsuperscript{3} | 1.36 | 0.00 | 1.35 | 0.00 | 1.35 | 0.00 | -0.01 | 0 | 0 |
| C\textsuperscript{3}N\textsuperscript{4} | 1.36 | 0.00 | 1.36 | 0.00 | 1.36 | 0.00 | 0.01 | 0 | 0 |
| N\textsuperscript{4}C\textsuperscript{5} | 1.37 | 0.00 | 1.38 | 0.00 | 1.38 | 0.00 | 0.01 | 0 | 0 |
| C\textsuperscript{5}N\textsuperscript{1} | 1.29 | 0.00 | 1.30 | 0.00 | 1.30 | 0.00 | 0 | 0 | 0 |
| C\textsuperscript{4}C\textsuperscript{6} | 1.49 | 0.00 | 1.49 | 0.00 | 1.49 | 0.00 | 0 | -0.01 | 0 |
| N\textsuperscript{6}C\textsuperscript{7} | 1.46 | 0.00 | 1.47 | 0.00 | 1.46 | 0.00 | 0 | 0 | 0 |
| N\textsuperscript{7}C\textsuperscript{8} | 1.42 | 0.01 | 1.42 | 0.01 | 1.42 | 0.01 | 0 | 0 | 0 |
| C\textsuperscript{8}C\textsuperscript{9} | 1.39 | 0.00 | 1.39 | 0.00 | 1.39 | 0.00 | 0 | 0 | 0 |
| C\textsuperscript{9}C\textsuperscript{10} | 1.39 | 0.00 | 1.39 | 0.00 | 1.39 | 0.00 | 0 | 0 | 0 |
| C-H Bond Length | | | | | | | | |
| C\textsuperscript{9}H\textsuperscript{2} | 1.09 | 0.00 | 1.09 | 0.00 | 1.09 | 0.00 | 0.01 | 0.00 | 0.00 |
| C\textsuperscript{9}H\textsuperscript{3} | 1.09 | 0.00 | 1.09 | 0.00 | 1.09 | 0.00 | 0.00 | 0.00 | 0.00 |
| C-H Distance | | | | | | | | |
| C\textsuperscript{9}H\textsuperscript{2} | 2.92 | 0.00 | 2.69 | 0.00 | 2.53 | 0.00 | -0.22 | -0.16 | -0.28 |
| C\textsuperscript{9}H\textsuperscript{3} | 3.05 | 0.00 | 2.91 | 0.00 | 3.18 | 0.00 | -0.14 | 0.28 | -0.14 |
| Bond Angles | | | | | | | | |
| C\textsuperscript{3}N\textsuperscript{1}N\textsuperscript{2} | 102.1 | 0.2 | 103.2 | 0.3 | 103.3 | 0.3 | 1.1 | 0.2 | 0.1 |
| N\textsuperscript{1}N\textsuperscript{2}C\textsuperscript{3} | 115.9 | 0.3 | 115.4 | 0.3 | 115.3 | 0.3 | -0.5 | 0.1 | -0.1 |
| N\textsuperscript{2}C\textsuperscript{3}N\textsuperscript{4} | 99.6 | 0.2 | 100.5 | 0.2 | 100.6 | 0.3 | 0.9 | 0.1 | 0.1 |
| C\textsuperscript{3}N\textsuperscript{4}C\textsuperscript{5} | 111.6 | 0.1 | 110.8 | 0.2 | 110.8 | 0.1 | -0.8 | 0 | 0.1 |
| N\textsuperscript{4}C\textsuperscript{5}N\textsuperscript{1} | 110.9 | 0.1 | 110.1 | 0.1 | 110.0 | 0.1 | -0.8 | 0 | 0.1 |
| C\textsuperscript{5}C\textsuperscript{6}N\textsuperscript{4} | 111.1 | 0.0 | 122.9 | 0.0 | 124.5 | 0.1 | 11.9 | 1.6 | 1.6 |
| C\textsuperscript{9}N\textsuperscript{1}C\textsuperscript{8}C\textsuperscript{9} | 112.7 | 0.1 | 124.1 | 0.1 | 124.7 | 0.1 | 11.5 | 0.5 | 0.5 |
| Torsion Angles | | | | | | | | |
| N\textsuperscript{1}C\textsuperscript{3}C\textsuperscript{9}H\textsuperscript{2} | 50.6 | 0.1 | 42.1 | 0.3 | 29.0 | 0.3 | -8.5 | -39.2 | -39.2 |
| N\textsuperscript{1}C\textsuperscript{3}C\textsuperscript{9}H\textsuperscript{3} | 85.4 | 0.1 | 82.6 | 0.2 | 121.5 | 0.3 | -2.7 | 38.8 | 38.8 |
| N\textsuperscript{1}N\textsuperscript{2}C\textsuperscript{3}C\textsuperscript{4} | 44.7 | 37.1 | 43.7 | 28.3 | 30.9 | 21.7 | -1.0 | -12.9 | -12.9 |
| N\textsuperscript{1}N\textsuperscript{2}C\textsuperscript{3}C\textsuperscript{4} | 135.1 | 37.4 | 136.1 | 28.8 | 149.1 | 22.1 | 1.0 | 13.0 | 13.0 |
Table S34. Summary of average* bond angles and distances of triazolylidenes 7'a-c, k (n=1); 8'a-c, k (n=2); 9'a-c, k (n=3) and corresponding standard deviations (SD) obtained from DFT calculation (M062X).

*Averages calculated using only data for the 12 triazolylidenes related to C(3)-H/D exchange studies. These average values and trends are in excellent agreement with data in Table S32 as expected given the small standard deviations.

| Backbone Bond Length | Average (n=1) | SD  (n=1) | Average (n=2) | SD  (n=2) | Average (n=3) | SD  (n=3) |
|----------------------|--------------|-----------|--------------|-----------|--------------|-----------|
| N1N2                 | 1.39         | 0.00      | 1.38         | 0.00      | 1.38         | 0.00      |
| N1C3                 | 1.36         | 0.00      | 1.35         | 0.00      | 1.35         | 0.00      |
| C3N4                 | 1.36         | 0.00      | 1.36         | 0.00      | 1.36         | 0.00      |
| N4C5                 | 1.37         | 0.00      | 1.38         | 0.00      | 1.38         | 0.00      |
| C5N1                 | 1.29         | 0.00      | 1.30         | 0.00      | 1.30         | 0.00      |
| C5C6                 | 1.49         | 0.00      | 1.49         | 0.00      | 1.49         | 0.00      |
| N4C6                 | 1.46         | 0.00      | 1.47         | 0.00      | 1.46         | 0.00      |
| N5C7                 | 1.42         | 0.01      | 1.42         | 0.01      | 1.42         | 0.01      |
| C5C8                 | 1.39         | 0.00      | 1.39         | 0.00      | 1.39         | 0.00      |
| C5C9                 | 1.39         | 0.00      | 1.39         | 0.00      | 1.39         | 0.00      |

| C-H Bond Length      |              |           |              |           |              |           |
|----------------------|--------------|-----------|--------------|-----------|--------------|-----------|
| C1H2                 | 1.09         | 0.00      | 1.09         | 0.00      | 1.09         | 0.00      |
| C1H3                 | 1.09         | 0.00      | 1.09         | 0.00      | 1.09         | 0.00      |

| C-H Distance         |              |           |              |           |              |           |
|----------------------|--------------|-----------|--------------|-----------|--------------|-----------|
| C1H2                 | 2.91         | 0.00      | 2.69         | 0.00      | 2.53         | 0.00      |
| C1H3                 | 3.05         | 0.00      | 2.90         | 0.00      | 3.18         | 0.00      |

| Bond Angles          |              |           |              |           |              |           |
|----------------------|--------------|-----------|--------------|-----------|--------------|-----------|
| C5N1N2               | 102.1        | 0.3       | 103.2        | 0.3       | 103.3        | 0.3       |
| N1N2C3               | 115.9        | 0.3       | 115.4        | 0.3       | 115.3        | 0.3       |
| N2C3N4               | 99.6         | 0.2       | 100.5        | 0.3       | 100.6        | 0.3       |
| C3N4C5               | 111.6        | 0.1       | 110.8        | 0.1       | 110.8        | 0.1       |
| N4C5N1               | 110.9        | 0.1       | 110.1        | 0.1       | 110.0        | 0.1       |
| C5C8N4               | 111.1        | 0.0       | 122.9        | 0.0       | 124.5        | 0.1       |
| C5N7C6               | 112.6        | 0.1       | 124.1        | 0.1       | 124.7        | 0.1       |
| Torsion Angles |  |  |  |  |  |
|---------------|---|---|---|---|---|
| C\(^3\)N\(^1\)C\(^\alpha\)H\(^2\) | 50.6 | 0.1 | 42.1 | 0.3 | 2.9 | 0.3 |
| C\(^3\)N\(^1\)C\(^\alpha\)H\(^3\) | 85.4 | 0.2 | 82.6 | 0.2 | 121.5 | 0.3 |
| N\(^3\)N\(^2\)C\(^\beta\) | 32.4 | 18.7 | 33.6 | 19.6 | 30.9 | 21.7 |
| N\(^3\)N\(^2\)C\(^e\) | 147.6 | 18.8 | 146.4 | 19.7 | 149.1 | 22.1 |
S2.5  Computational Analysis of Conformational Changes in Fused Ring

By fixing the torsion angle between H²Cα relative to C³H¹ for 7-9b and between H²Cα relative to C³N¹ for 7'-9'b, the energy increments caused by conformational changes in the fused ring in the vicinity of the carbenic position could be evaluated.

Table S35.  Energy and conformer distribution of triazolium 7b obtained from DFT calculation (M062X).

| Torsion Angle (°) | Eᵢ (a.u.)ᵃ | Torsion Angle Difference (°)ᵇ | Eᵅdiff (a.u.)ᶜ | Populational Ratio (%)ᵈ |
|------------------|------------|-------------------------------|----------------|------------------------|
| 26.0             | -590.384464 | -12.0                         | -0.000843      | 26.10                  |
| 28.0             | -590.384718 | -10.0                         | -0.000589      | 39.12                  |
| 30.0             | -590.384926 | -8.0                          | -0.000381      | 54.49                  |
| 32.0             | -590.385089 | -6.0                          | -0.000218      | 70.65                  |
| 34.0             | -590.385207 | -4.0                          | -1E-04         | 85.27                  |
| 36.0             | -590.385279 | -2.0                          | -2.8E-05       | 95.64                  |
| 38.0ᵃ            | -590.385307 | 0.0                           | 0              | 100.00                 |
| 40.0             | -590.38529  | 2.0                           | -1.7E-05       | 97.33                  |
| 42.0             | -590.385232 | 4.0                           | -7.5E-05       | 88.73                  |
| 44.0             | -590.385136 | 6.0                           | -0.000171      | 76.15                  |
| 46.0             | -590.385006 | 8.0                           | -0.000301      | 61.90                  |
| 48.0             | -590.384845 | 10.0                          | -0.000462      | 47.89                  |
| 50.0             | -590.384654 | 12.0                          | -0.000653      | 35.32                  |
| 52.0             | -590.384438 | 14.0                          | -0.000869      | 25.04                  |

ᵃReference taken as torsion angle associated with minimum energy value. ᵇEnergy for each individual conformation obtained from DFT calculation (M062X). ᶜAngle Difference = Torsion angle – Reference. ᵈEᵅdiff = Eᵢ – Eᵞ. ⁵Populational ratio calculated using Boltzmann distribution.
# Table S36

Energy and conformer distribution of triazolium 8b obtained from DFT calculation (M062X).

| Torsion Angle (°) | $E_i$ (a.u.)$^b$ | Torsion Angle Difference (°)$^c$ | $E_{\text{diff}}$ (a.u.)$^d$ | Populational Ratio (%)$^f$ |
|------------------|-----------------|-------------------------------|----------------------------|-------------------------|
| 26.0             | -629.702606     | -13.4                         | -0.000808                  | 27.59                   |
| 28.0             | -629.702826     | -11.4                         | -0.000588                  | 39.18                   |
| 30.0             | -629.703013     | -9.4                          | -0.000401                  | 52.78                   |
| 32.0             | -629.703165     | -7.4                          | -0.000249                  | 67.25                   |
| 34.0             | -629.703282     | -5.4                          | -0.00132                   | 81.03                   |
| 36.0             | -629.703362     | -3.4                          | -5.2E-05                   | 92.05                   |
| 38.0             | -629.703405     | -1.4                          | -9E-06                     | 98.58                   |
| 39.4$^a$         | -629.703414     | 0                             | 0                          | 100.00                  |
| 40.0             | -629.703412     | 0.6                           | -2E-06                     | 99.68                   |
| 42.0             | -629.703383     | 2.6                           | -3.1E-05                   | 95.18                   |
| 44.0             | -629.703317     | 4.6                           | -9.7E-05                   | 85.68                   |
| 46.0             | -629.703215     | 6.6                           | -0.000199                  | 72.82                   |
| 48.0             | -629.703081     | 8.6                           | -0.000333                  | 58.82                   |
| 50.0             | -629.702913     | 10.6                          | -0.000501                  | 45.00                   |
| 52.0             | -629.702717     | 12.6                          | -0.000697                  | 32.93                   |

$^a$Reference taken as torsion angle associated with minimum energy value. $^b$Energy for each individual conformation obtained from DFT calculation (M062X). $^c$Angle Difference = Torsion angle – Reference. $^dE_{\text{diff}} = E_i - E_{\text{ref}}$. $^f$Populational ratio calculated using Boltzmann distribution.
Table S37. Energy and conformer distribution of triazolium 9b obtained from DFT calculation (M062X).

| Torsion Angle (°) | $E_i$ (a.u.) | Torsion Angle Difference (°) | $E_{diff}$ (a.u.) | Populational Ratio (%) |
|-------------------|--------------|-------------------------------|-------------------|------------------------|
| -14.0             | -669.007195  | -14.8                         | -0.000935         | 22.54                  |
| -12.0             | -669.007425  | -12.8                         | -0.000705         | 32.51                  |
| -10.0             | -669.007622  | -10.8                         | -0.000508         | 44.51                  |
| -8.0              | -669.007789  | -8.8                          | -0.000341         | 58.08                  |
| -6.0              | -669.007923  | -6.8                          | -0.000207         | 71.90                  |
| -4.0              | -669.008025  | -4.8                          | -0.000105         | 84.59                  |
| -2.0              | -669.008094  | -2.8                          | -3.6E-05          | 94.42                  |
| 0.0               | -669.008127  | -0.8                          | -3E-06            | 99.52                  |
| 0.8               | -669.00813   | 0.0                           | 0                 | 100.00                 |
| 2.0               | -669.008122  | 1.2                           | -8E-06            | 98.73                  |
| 4.0               | -669.008076  | 3.2                           | -5.4E-05          | 91.75                  |
| 6.0               | -669.007987  | 5.2                           | -0.000143         | 79.62                  |
| 8.0               | -669.007856  | 7.2                           | -0.000274         | 64.62                  |
| 10.0              | -669.007684  | 9.2                           | -0.000446         | 49.13                  |
| 12.0              | -669.007469  | 11.2                          | -0.000661         | 34.88                  |

*Reference taken as torsion angle associated with minimum energy value. *aEnergy for each individual conformation obtained from DFT calculation (M062X). *bAngle Difference = Torsion angle – Reference. *c$E_{diff}$ = $E_i – E_{ref}$. *dPopulational ratio calculated using Boltzmann distribution.
Table S38. Energy and conformer distribution of carbene 7b obtained from DFT calculation (M062X).

| Torsion Angle (°) | $E_i$ (a.u.) | Torsion Angle Difference (°) | $E_{diff}$ (a.u.) | Populational Ratio (%) |
|-------------------|--------------|-------------------------------|------------------|------------------------|
| 26.0              | -589.912786  | -15.5                         | -0.001309        | 12.42                  |
| 28.0              | -589.913112  | -13.5                         | -0.000983        | 20.88                  |
| 30.0              | -589.91339   | -11.5                         | -0.000705        | 32.51                  |
| 32.0              | -589.913621  | -9.5                          | -0.000474        | 46.98                  |
| 34.0              | -589.913805  | -7.5                          | -0.00029         | 62.99                  |
| 36.0              | -589.913942  | -5.5                          | -0.000153        | 78.36                  |
| 38.0              | -589.914034  | -3.5                          | -6.1E-05         | 90.74                  |
| 40.0              | -589.914084  | -1.5                          | -1.1E-05         | 98.26                  |
| 41.5a             | -589.914095  | 0.0                           | 0                | 100.00                 |
| 42.0              | -589.914094  | 0.5                           | -1E-06           | 99.84                  |
| 44.0              | -589.914065  | 2.5                           | -3E-05           | 95.33                  |
| 46.0              | -589.913998  | 4.5                           | -9.7E-05         | 85.68                  |
| 48.0              | -589.913894  | 6.5                           | -0.000201        | 72.59                  |
| 50.0              | -589.913754  | 8.5                           | -0.000341        | 58.08                  |
| 52.0              | -589.913579  | 10.5                          | -0.000516        | 43.94                  |

*a*Reference taken as torsion angle associated with minimum energy value. *b*Energy for each individual conformation obtained from DFT calculation (M062X). *c*Angle Difference = Torsion angle – Reference. *d*$E_{diff} = E_i - E_{ref}$. *e*Populational ratio calculated using Boltzmann distribution.
Table S39. Energy and conformer distribution of carbene 8\textsuperscript{b}obtained from DFT calculation (M062X).

| Torsion Angle (°) | $E_i$ (a.u.)\textsuperscript{b} | Torsion Angle Difference (°)\textsuperscript{c} | $E_{diff}$ (a.u.)\textsuperscript{d} | Populational Ratio (%)\textsuperscript{e} |
|------------------|-------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 22.0             | -629.230307                   | -14.3                           | -0.000862                       | 25.32                           |
| 24.0             | -629.230528                   | -12.3                           | -0.000641                       | 36.01                           |
| 26.0             | -629.230717                   | -10.3                           | -0.000452                       | 48.66                           |
| 28.0             | -629.230875                   | -8.3                            | -0.000294                       | 62.59                           |
| 30.0             | -629.231                     | -6.3                            | -0.000169                       | 76.39                           |
| 32.0             | -629.231091                   | -4.3                            | -7.8E-05                        | 88.31                           |
| 34.0             | -629.231147                   | -2.3                            | -2.2E-05                        | 96.55                           |
| 36.0             | -629.231169                   | -0.3                            | 0                               | 100.00                          |
| 36.3             | -629.231169                   | 0                               | 0                               | 100.00                          |
| 38.0             | -629.231157                   | 1.7                             | -1.2E-05                        | 98.11                           |
| 40.0             | -629.231113                   | 3.7                             | -5.6E-05                        | 91.46                           |
| 42.0             | -629.231037                   | 5.7                             | -0.000132                       | 81.03                           |
| 44.0             | -629.230933                   | 7.7                             | -0.000236                       | 68.65                           |
| 46.0             | -629.230802                   | 9.7                             | -0.000367                       | 55.72                           |
| 48.0             | -629.230644                   | 11.7                            | -0.000525                       | 43.32                           |

\textsuperscript{a}Reference taken as torsion angle associated with minimum energy value. \textsuperscript{b}Energy for each individual conformation obtained from DFT calculation (M062X). \textsuperscript{c}Angle Difference = Torsion angle – Reference. \textsuperscript{d}$E_{diff} = E_i – E_{ref}$. \textsuperscript{e}Populational ratio calculated using Boltzmann distribution.
Table S40. Energy and conformer distribution of carbene $9'b$ obtained from DFT calculation (M062X).

| Torsion Angle (°) | $E_i$ (a.u.)$^b$ | Torsion Angle Difference (°)$^c$ | $E_{\text{diff}}$ (a.u.)$^d$ | Populational Ratio (%)$^e$ |
|------------------|-----------------|-------------------------------|-------------------------------|-------------------------|
| -12.0            | -668.535105     | -14.3                         | -0.000942                     | 22.29                   |
| -10.0            | -668.535348     | -12.3                         | -0.000699                     | 32.83                   |
| -8.0             | -668.535556     | -10.3                         | -0.000491                     | 45.73                   |
| -6.0             | -668.535729     | -8.3                          | -0.000318                     | 60.24                   |
| -2.0             | -668.535966     | -4.3                          | -8.1E-05                      | 87.89                   |
| 0.0              | -668.536026     | -2.3                          | -2.1E-05                      | 96.71                   |
| 2.3              | -668.536047     | -1.7                          | 0                             | 100.00                  |
| 4.0              | -668.53603      | 1.7                           | -1.7E-05                      | 97.33                   |
| 6.0              | -668.535974     | 3.7                           | -7.3E-05                      | 89.02                   |
| 8.0              | -668.535878     | 5.7                           | -0.000169                     | 76.39                   |
| 10.0             | -668.535742     | 7.7                           | -0.000305                     | 61.50                   |
| 12.0             | -668.535564     | 9.7                           | -0.000483                     | 46.31                   |
| 14.0             | -668.535343     | 11.7                          | -0.000704                     | 32.57                   |

$^a$Reference taken as torsion angle associated with minimum energy value. $^b$Energy for each individual conformation obtained from DFT calculation (M062X). $^c$Angle Difference = Torsion angle – Reference. $^d$\(E_{\text{diff}} = E_i – E_{\text{ref}}\). $^e$Populational ratio calculated using Boltzmann distribution.
Figure S51. Plots of populational ratio of triazolium salts 7-9b against torsion angle between CαH2 relative to C3H1.

Figure S52. Plots of populational ratio of carbenes 7'-9'b against torsion angle between CαH2 relative to C3N1.
Figure S53. Superimposed populational ratio of triazolium salts 7-9b and carbenes 7’-9’b against torsion angle differences using the data from Tables S35-S40.

S2.6 NBO analysis

For the para-fluorophenyl triazolium ion 7c (n=1), NBO analyses suggest that the C(3)-H bond contains 38.9% s-character and 61.0% p-character. The s-character occupancy changed to 38.7% in both 8c and 9c, and the p-character occupancy changed to 61.2% in both cases.
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