

Supporting Information for:

A Ring-Opening Metathesis Polymerization Route to Alkaline Anion Exchange Membranes: Development of Hydroxide-Conducting Thin Films from an Ammonium-Functionalized Monomer

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General Methods and Materials.

All reactions and manipulations of compounds were carried out in air unless otherwise specified. All solvents were used as received. Methacrolein, boron trichloride (1.0 M solution in dichloromethane), dimethylamine (2.0 M solution in tetrahydrofuran), sodium triacetoxyborohydride, potassium hydroxide flakes, and Grubbs 2nd Generation catalyst were purchased from Sigma-Aldrich and used as received. Dicyclopentadiene was also purchased from Sigma-Aldrich and was run through a plug of alumina prior to use. Methyl iodide and triethylamine were purchased from Acros Organics and Fisher Scientific, respectively, and used as received. Standardized hydrochloric acid (0.1014 N) and potassium hydroxide (0.1000 ± 0.0001 M) solutions were purchased from Sigma-Aldrich and Riedel-de Haën, respectively. Nafion 112 was purchased from Sigma-Aldrich and pretreated using a literature procedure.¹

Small Molecule Characterization.

¹H NMR spectra were recorded on Varian INOVA 400 (¹H, 400 MHz) or Varian INOVA 600 (¹H, 600 MHz) spectrometers and referenced to CHCl₃, 7.26 ppm or H₂O, 4.80 ppm. ¹³C NMR spectra were recorded on a Varian INOVA 600 (¹³C, 150 MHz)

spectrometer and referenced to CHCl_3 , 77.23 ppm.

The gradient selected HSQCAD, HMBCAD and ROESY spectra were recorded on a Varian Unity Inova (600 MHz) spectrometer operating at 599.757 MHz for ^1H observation using a Varian inverse $^1\text{H}-\{^{13}\text{C},^{15}\text{N}\}$ triple-resonance probehead with triple-axis gradients. NMR data were acquired with the pulse sequences supplied in Vnmrj 2.1B/Chempack 4.1 and were processed and analyzed using the MestReNova 5.3 software package (2008, Mestrelab Research S. L.). ROESY spectra were acquired using the ROESY sequence with a spectral width of 4.3 kHz. A total of 200 complex points were collected in the indirectly detected dimension with 4 scans and 0.15 s acquisition time per increment. The resulting matrices were zero filled to 1k x 1k complex data points and squared cosine window functions were applied in both dimensions prior to Fourier transformation. The multiplicity-edited adiabatic HSQC spectrum was acquired with the gHSQCAD sequence. Spectral widths were 4.3 kHz and 30 kHz in ^1H and ^{13}C dimensions, respectively. A total of 256 complex points were collected in the indirectly detected dimension with 2 scans and 0.15 s acquisition time per increment. The resulting matrices were zero filled to 2k x 2k complex data points and squared cosine window functions were applied in both dimensions prior to Fourier transformation. Gradient selected adiabatic HMBC spectra were acquired in phase sensitive mode with the gHMBCAD sequence optimized for 8 Hz couplings. Spectral widths were 4.3 kHz and 36.2 kHz in ^1H and ^{13}C dimensions, respectively. A total of 400 complex points were collected in the indirectly detected dimension with 4 scans and 1024 points per increment. The resulting matrices were zero filled to 2k x 2k complex data points and shifted sinebell window functions were applied in the ^1H dimension prior to Fourier

transformation.

Mass spectra were acquired using a JEOL GCMate II mass spectrometer operating at 3000 resolving power for high resolution measurements in positive ion mode and an electron ionization potential of 70 eV. Samples were introduced via a GC inlet using an Agilent HP 6890N GC equipped with a 30 m (0.25 μm i.d.) HP-5ms capillary GC column. The carrier gas was helium with a flow rate of 1 mL/min. Samples were introduced into the GC using a split/splitless injector at 230 °C with a split ratio of 10:1.

Elemental analysis was performed by Robertson Microlit Laboratories, Inc. Madison, New Jersey.

AAEM Characterization.

Ion exchange capacities (IECs) were determined using standard back titration methods. The thin film as synthesized (in iodide form) was dried under full vacuum overnight at 50 °C in order to completely dehydrate it and then weighed. Conversion to the hydroxide form was achieved by immersing the film in 3-60 mL portions of 1 M potassium hydroxide for 20 minutes each. Residual potassium hydroxide was washed away by immersing the membrane in 3-500 mL portions of deionized water for 20 minutes each. The AAEM was then stirred in 20 mL standardized 0.1 M $\text{HCl}_{(\text{aq})}$ solution for 24 hours followed by titration with standardized 0.1 M $\text{KOH}_{(\text{aq})}$ to determine the equivalence point. Control acid samples (with no AAEM present) were also titrated with standardized 0.1 M $\text{KOH}_{(\text{aq})}$, and the difference between the volume required to titrate the control and the sample was used to calculate the amount of hydroxide ions in the

membrane. This was divided by the dried mass of the membrane (*vide supra*) to give an IEC value with the units mmol OH⁻/g I⁻.

The in-plane hydroxide conductivity of the AAEM sample was measured by four probe electrochemical impedance spectroscopy (EIS) using a Solartron 1280B electrochemical workstation along with ZPlot and ZView software. The conductivity cell was purchased from BekkTech LLC (Loveland, CO), and a helpful schematic and description of a similar experimental setup has been reported.² A strip of the thin film in iodide form (ca. 4 cm long x 0.5 mm wide) was converted to the hydroxide form by immersing it in 3-30 mL portions of 1 M potassium hydroxide for 20 minutes each. Residual potassium hydroxide was washed away by immersing the membrane in 3-60 mL portions of deionized water for 20 minutes each. Aliquots of each of these water washings were removed and analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) for potassium ions. ICP-AES was performed by the Cornell Nutrient Analysis Laboratories, Department of Crop and Soil Sciences, Cornell University using a CIROS model from Spectro Analytical Instruments, Inc. and the EPA 6010B method. Negligible potassium ions were detected in the aqueous sample (0.047 mg/L) by the third water washing; approximately equal to that detected in deionized water (0.055 mg/L) verifying complete removal of base and preventing falsely high hydroxide conductivities. The AAEM was then clamped into the cell using a Proto 6104 torque screwdriver set to 1 inch ounce and completely immersed in Millipore water (> 18 MΩ·cm), at either 20 °C or 50 °C, during the measurement time. In the case of the 50 °C measurement, the sample was allowed to equilibrate at that temperature for 1 hour. EIS was performed by imposing a small sinusoidal (AC signal) voltage, 10 mV, across the

membrane sample at frequencies between 20,000 Hz and 0.1 Hz (scanning from high to low frequencies) and measuring the resultant current response. Using a Bode plot, the frequency region over which the impedance had a constant value was checked, and the highest frequency measurement in the Nyquist plot was taken as the effective resistance of the membrane. This was then used to calculate the hydroxide conductivity by employing the following formula: $\sigma = L / Z' \cdot A$ where L is the length between sense electrodes (0.425 cm), Z' is the real impedance response at high frequency, and A is the membrane area available for hydroxide conduction (width·thickness). The dimensional measurements were performed using a digital micrometer (± 0.001 mm) purchased from Marathon Watch Company Ltd. (Richmond Hill, ON).

The hydroxide conductivity was measured for four separate AAEMs (per composition) and the precision of these measurements was evaluated. All errors are determined from sample standard deviations. Confidence intervals are at the 95 % confidence level based on the sample deviations and using the relevant student- t distribution ($N-1$ degrees of freedom, N is the number of samples tested for each membrane).

Dimensional swelling measurements were carried out in either deionized water (10 mL) or 2 M aqueous methanol solution (0.81 mL methanol in 10 mL deionized water) pre-heated to 60 °C. Two stamp-sized pieces were cut out of an AAEM sample and their length, width and thickness measurements were recorded followed by placement of the samples in either one of the above solutions for 2 hours. At this time, the measurements were repeated and the dimensional swelling expressed as the percent difference between the two volumes.

The mechanical properties of the thin films in the iodide form were characterized using an Instron system (model 5566) (Instron Co.,Canton, MA) using a 100 N static Lodge cell and Blue Hill software. The tensile strength of two strips from each of two wet samples were measured in the iodide form (ie four measurements total).

Preparation of 2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde: This compound was prepared using a modified literature procedure.³ To a solution of freshly cracked cyclopentadiene (14.0 mL, 172 mmol) in 125 mL dichloromethane at -50 °C, methacrolein (18.5 mL, 224 mmol) and boron trichloride solution (17.0 mL, 17.0 mmol) were added sequentially under nitrogen. After these additions, stirring was commenced and the reaction allowed to proceed at -50 °C for 90 minutes. Triethylamine (10.0 mL, 71.7 mmol) was then added *via* syringe and the reaction allowed to warm to room temperature. 125 mL of water were then added resulting in a biphasic yellow mixture, which was separated. The aqueous fraction was then extracted with 2x100 mL portions of dichloromethane, combined with the separated organic fraction and dried with magnesium sulfate. The clear, yellow solution was then dried by rotary evaporation affording 2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (21.7 g, 159 mmol), as 85% *exo* aldehyde diastereomer, in 92% yield as an orange liquid which partially solidified upon standing at room temperature. The compound was generally used as is, but further purification could be carried out by distilling under full vacuum at 65 °C resulting in the isolation of the pure aldehyde as a colorless liquid/solid. The NMR shifts closely match those in the aforementioned literature procedure for the *exo* isomer.³ ¹H NMR (400 MHz, CDCl₃) δ 9.65 (1H, CHO), 6.25 (1H, dd, ³J = 5.6 Hz,



3.2 Hz, $CH=CH$), 6.06 (1H, dd, $^3J = 5.6$ Hz, 2.8 Hz, $CH=CH$), 2.85 (1H, b, Bridgehead CH), 2.77 (1H, b, Bridgehead CH), 2.20 (1H, dd, $^2J = 12$ Hz, $^3J = 4.0$ Hz, CH_2), 1.35 (1H, m, Bridge CH), 1.25 (1H, m, Bridge CH), 0.96 (3H, s, CH_3), 0.72 (1H, d, $^2J = 12$ Hz, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.9, 139.7, 133.2, 54.0, 50.9, 48.6, 43.4, 34.8, 20.2.

Preparation of *N,N*-dimethyl-1-(2-methylbicyclo[2.2.1]hept-5-en-2-yl)methanamine:

To a solution of 2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (14.3 g, 105 mmol) in 150 mL of tetrahydrofuran, dimethylamine solution (68.0 mL, 136 mmol) was added and stirred at 20 °C for 2 hours. At this time, $Na[BH(OAc)_3]$ (28.9 g, 136 mmol) was slowly added, diluted with a further 100 mL of tetrahydrofuran to loosen the slurry and stirred overnight. The reductant was quenched with 1 M aqueous potassium hydroxide (150 mL, 150 mmol) causing the reaction mixture to turn clear yellow. After 15 minutes, the solution was extracted with 3x100 mL portions of diethyl ether and dried with magnesium sulfate. The clear, yellow solution was then dried by rotary evaporation affording *N,N*-dimethyl-1-(2-methylbicyclo[2.2.1]hept-5-en-2-yl)methanamine (14.4 g, 87.1 mmol) in 83% yield as a yellow-orange liquid. The compound was generally used as is, but further purification could be carried out by distilling under full vacuum at 50 °C resulting in the isolation of the pure amine as a colorless liquid. The resonances for the *exo* and *endo* isomers (*ca.* 4:1, respectively) were assigned with the aid of gHMBC, gHSQC, and ROESY experiments.



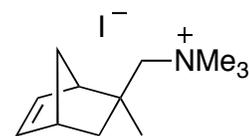
For the *exo*-isomer: 1H NMR (600 MHz, $CDCl_3$) δ 6.07 (1H, dd, $^3J = 5.7$ Hz, 2.9

Hz, CH=CH), 6.04 (1H, dd, $^3J = 5.7$ Hz, 3.1 Hz, CH=CH), 2.71 (1H, m, Bridgehead CH), 2.47 (1H, m, Bridgehead CH), 2.39 (1H, d, $^2J = 13.2$ Hz, CH₂N(CH₃)₂), 2.28 (1H, d, $^2J = 13.2$ Hz, CH₂NMe₂), 2.26 (6H, s, N(CH₃)₂), 1.55 (1H, ddd, $^2J = 8.4$ Hz, $^3J = 1.5$ Hz, $^3J = 1.5$ Hz, Bridge CH), 1.49 (1H, dd, $^2J = 11.5$ Hz, $^3J = 3.8$ Hz, CH₂), 1.30 (1H, ddd, $^2J = 8.4$ Hz, $^3J = 2.7$ Hz, $^3J = 1.8$ Hz, Bridge CH), 0.89 (3H, s, CH₃), 0.78 (1H, dd, $^2J = 11.5$ Hz, $^3J = 2.6$ Hz, CH₂). ¹³C NMR (150 MHz, CDCl₃) δ 136.9, 136.0, 71.6, 50.6, 48.4, 47.7, 43.5, 42.8, 39.7, 24.6.

For the *endo*-isomer: ¹H NMR (600 MHz, CDCl₃) δ 6.09 (1H, dd, $^3J = 5.6$ Hz, 2.9 Hz, CH=CH), 6.05 (1H, m, CH=CH), 2.69 (1H, m, Bridgehead CH), 2.43 (1H, m, Bridgehead CH), 2.18 (6H, s, N(CH₃)₂), 2.13 (1H, d, $^2J = 12.8$ Hz, CH₂N(CH₃)₂), 1.91 (1H, d, $^2J = 12.8$ Hz, CH₂NMe₂), 1.58 (1H, ddd, $^2J = 8.4$ Hz, $^3J = 1.5$ Hz, $^3J = 1.5$ Hz, Bridge CH), 1.41 (1H, dd, $^2J = 11.5$ Hz, $^3J = 3.8$ Hz, CH₂), 1.32 (1H, m, Bridge CH), 1.21 (3H, s, CH₃), 0.86 (1H, dd, $^2J = 11.5$ Hz, $^3J = 2.6$ Hz, CH₂). ¹³C NMR (150 MHz, CDCl₃) δ 136.3, 135.5, 69.7, 52.4, 47.8, 47.5, 42.9, 42.1, 40.6, 26.3.

HRMS EI (*m/z*): calc. for C₁₁H₁₉N, 165.1517; found, 165.1522.

Preparation of *N,N,N*-trimethyl-1-(2-methylbicyclo[2.2.1]hept-5-en-2-yl)methanaminium iodide (1): To a solution of *N,N*-dimethyl-1-(2-methylbicyclo[2.2.1]hept-5-en-2-yl)methanamine (12.5 g, 75.6 mmol) in 125 mL acetone, methyl iodide (7.1 mL, 114 mmol) was added dropwise and stirred at 20 °C with the formation of a white precipitate occurring after 2 minutes. After stirring for 16 hours to ensure complete reaction, 100 mL *n*-pentane was added to the reaction mixture and filtered. The white



powder was washed with 3-100 mL portions of *n*-pentane, isolated and dried under vacuum affording **1** (18.5 g, 60.2 mmol) in 80% yield. Compound **1** can be recrystallized from hot dichloromethane, chloroform, or acetonitrile, at 4 °C yielding single crystals as the *exo* isomer exclusively. ¹H NMR (600 MHz, CDCl₃) δ 6.19 (1H, dd, ³J = 6.0 Hz, 3.0 Hz, CH=CH), 6.05 (1H, dd, ³J = 6.0 Hz, 3.0 Hz, CH=CH), 3.88 (2H, m, CH₂N(CH₃)₂), 3.55 (9H, s, N(CH₃)₃), 2.90 (1H, b, Bridgehead CH), 2.67 (1H, b, Bridgehead CH), 2.09 (1H, dd, ²J = 12.0 Hz, ³J = 4.2 Hz, CH₂), 1.85 (1H, d, ²J = 9.0 Hz, Bridge CH), 1.43 (1H, d, ²J = 9.0 Hz, Bridge CH), 1.17 (3H, s, CH₃), 0.96 (1H, dd, ²J = 12.0 Hz, ³J = 3.0 Hz, CH₂). ¹³C NMR (150 MHz, CDCl₃) δ 138.2, 134.8, 77.6, 56.2, 52.4, 48.4, 44.4, 43.3, 40.4, 25.8. Anal. calc. for C₁₂H₂₂Ni: C, 46.92; H, 7.22; N, 4.56. Anal. found: C, 47.18; H, 7.33; N, 4.55.

Control Measurements of Nafion 112: The average proton conductivity values measured for four samples at 20 °C and 50 °C were 75 ± 2 mS/cm and 112 ± 3 mS/cm, respectively. The average tensile stress and strain at maximum loads measured for two samples were 31.5 MPa at 194%. The percent dimensional swelling measurements of two stamp-sized samples in 60 °C deionized water and 2 M aqueous methanol were 1.0 % and 2.2 %, respectively.

Preparation of AAEM with 2:1 Molar Ratio of Dicyclopentadiene:Compound 1: To a solution of **1** (0.053 g, 0.17 mmol) and dicyclopentadiene (0.046 g, 0.35 mmol) in 2.0 mL chloroform, a solution of Grubbs' 2nd Generation catalyst (0.0030 g, 0.0035 mmol) in 0.6 mL chloroform was added and stirred for 1 minute at 20 °C. At this time, the orange

reaction mixture was deposited onto a flat glass Petri dish sitting on a hot plate pre-heated to a surface temperature of ca. 30 °C with a thin metal plate separating the two in order to ensure uniform heating. Within a fumehood, a round glass cover with a volume of 550 mL and a diameter of 7 cm and a Kontes valve affixed at the top to control the rate of solvent evaporation was placed over the Petri dish to prevent drafts yielding even films (Figure S1). The reaction mixture solidified after 120-150 minutes, at which time the cover was removed and the surface temperature increased to ca. 75 °C for 1 hour to ensure all volatiles were removed. The sample was then cooled, and deionized water added to the Petri dish in order to ease removal of the film.



Figure S1. Photograph depicting the experimental setup for AAEM preparation.

The measured IEC for two separate AAEMs was 0.96 and 1.04 mmol OH/g giving an average value of 1.0 mmol OH/g. The average hydroxide conductivity values measured for four separate AAEMs at 20 °C and 50 °C were 14 ± 2 mS/cm and 21 ± 4 mS/cm, respectively.

The percent dimensional swelling measurements were:

Sample 1 (2 M methanol): 2.2 %

Sample 1 (deionized water): 0 %

Sample 2 (2 M methanol): 1.1 %

Sample 2 (deionized water): 1.1 %

Average: 1.7 % (methanol), 0.55 % (deionized water)

A single dimensional swelling experiment employing four stamp-sized pieces from the same AAEM sample was also performed as a means of determining the maximum concentration of aqueous methanol the membrane could tolerate (e.g. percent swelling less than 10 %) at 60 °C. The four pieces, in the hydroxide form, were measured as above and immersed in pre-heated solutions of 4 M, 6 M, 8M and 10 M aqueous methanol. After two hours, the samples' dimensions were re-measured giving percent swelling values of 3.7 %, 3.7 %, 5.4 % and 20.7 %, respectively.

The average tensile stress and strain at break measurements for four thin films were 16 ± 6 MPa and 7.2 ± 3 %, respectively.

Preparation of AAEM with 1:1 Molar Ratio of Dicyclopentadiene:Compound 1: To a solution of **1** (0.070 g, 0.23 mmol) and dicyclopentadiene (0.030 g, 0.23 mmol) in 2.0 mL chloroform, a solution of Grubbs' 2nd Generation catalyst (0.0019 g, 0.0022 mmol) in 0.3 mL chloroform was added and stirred for 1 minute at 20 °C. At this time, the orange reaction mixture was deposited onto a flat glass dish, and the AAEM generated as above.

The measured IEC for two separate AAEMs was 1.39 and 1.31 mmol OH⁻/g giving an average value of 1.35 mmol OH⁻/g. The average hydroxide conductivity values measured for four separate AAEMs at 20 °C and 50 °C were 18.2 ± 2.1 mS/cm and 27.9 ± 3.4 mS/cm, respectively.

The average tensile stress and strain at break measurements for four thin films were 2.3 ± 0.5 MPa and 26 ± 3 %, respectively.

Single-Crystal X-Ray Crystallography.

Crystals of **1** were transferred from a crystallization vessel onto a microscope slide in a drop of viscous organic oil. Using a nylon loop, a suitable single crystal was chosen and mounted on a Bruker X8 APEX II diffractometer (MoK_α radiation) and cooled to 0 °C. Data collection and reduction were done using Bruker APEX2⁴ and SAINT+⁵ software packages. An empirical absorption correction was applied with SADABS.⁶ Structure was solved by direct methods and refined on F² by full matrix least-squares techniques using SHELXTL⁷ software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to the model in their geometrically ideal positions. Colorless plate like crystals belong to a monoclinic P2(1)/c space group. The sample size was 0.30x0.20x0.05 mm³. Overall 16041 reflections were collected, 4203 of which were unique (R_{int} = 0.0264); with 3393 ‘strong’ reflections (F_o > 4σF_o). Final R₁ = 3.22 %. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax:

(+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

References

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Table S1. Crystal data and structure refinement for **1**.

| | | |
|-----------------------------------|--|--|
| Identification code | tjc2 | |
| Empirical formula | C ₁₃ H ₂₄ Cl ₂ I N | |
| Formula weight | 392.13 | |
| Temperature | 273(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 11.1922(6) Å b = 7.8529(4) Å c = 19.6551(10) Å | α = 90°. β = 103.138(3)°. γ = 90°. |
| Volume | 1682.29(15) Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.548 Mg/m ³ | |
| Absorption coefficient | 2.204 mm ⁻¹ | |
| F(000) | 784 | |
| Crystal size | 0.30 x 0.20 x 0.05 mm ³ | |
| Theta range for data collection | 1.87 to 28.44°. | |
| Index ranges | -14 ≤ h ≤ 15, -10 ≤ k ≤ 6, -26 ≤ l ≤ 25 | |
| Reflections collected | 15249 | |
| Independent reflections | 4203 [R(int) = 0.0264] | |
| Completeness to theta = 28.44° | 99.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8978 and 0.5577 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 4203 / 0 / 166 | |
| Goodness-of-fit on F ² | 0.999 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0322, wR2 = 0.0822 | |
| R indices (all data) | R1 = 0.0429, wR2 = 0.0893 | |
| Largest diff. peak and hole | 0.910 and -0.597 e.Å ⁻³ | |

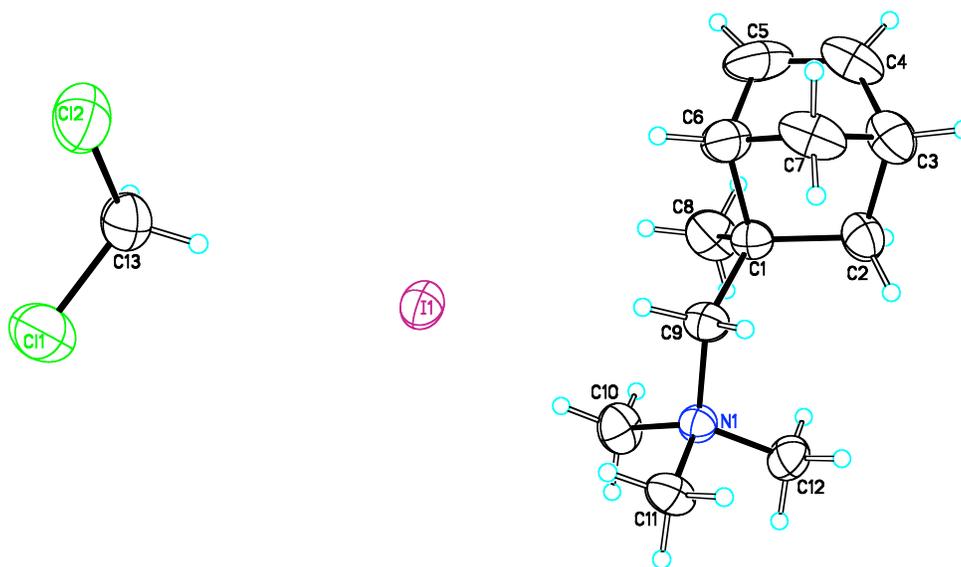


Figure S2. ORTEP drawing of **1** with thermal ellipsoids drawn at the 40% probability level.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|---------|----------|---------|-------|
| I(1) | 5719(1) | 7211(1) | 1226(1) | 48(1) |
| Cl(1) | 8612(1) | 4247(2) | 183(1) | 98(1) |
| Cl(2) | 7288(1) | 1548(1) | 717(1) | 84(1) |
| N(1) | 3773(2) | 12228(2) | 1455(1) | 37(1) |
| C(1) | 1813(2) | 10307(3) | 1464(1) | 40(1) |
| C(2) | 1132(2) | 11125(4) | 1966(2) | 54(1) |
| C(3) | 630(3) | 9586(4) | 2320(2) | 65(1) |
| C(4) | -265(3) | 8677(5) | 1778(2) | 73(1) |
| C(5) | 317(4) | 7926(5) | 1358(2) | 85(1) |
| C(6) | 1665(3) | 8325(4) | 1622(2) | 63(1) |
| C(7) | 1720(3) | 8399(5) | 2396(2) | 71(1) |
| C(8) | 1217(3) | 10701(5) | 694(1) | 68(1) |

| | | | | |
|-------|---------|----------|---------|-------|
| C(9) | 3208(2) | 10590(3) | 1654(1) | 42(1) |
| C(10) | 3807(3) | 12275(4) | 698(1) | 57(1) |
| C(11) | 5082(2) | 12222(4) | 1858(1) | 50(1) |
| C(12) | 3178(3) | 13790(3) | 1644(2) | 52(1) |
| C(13) | 7221(3) | 3577(4) | 354(2) | 70(1) |

Table S3. Bond lengths [Å] and angles [°] for **1**.

| | |
|------------------|------------|
| Cl(1)-C(13) | 1.747(3) |
| Cl(2)-C(13) | 1.741(4) |
| N(1)-C(12) | 1.483(3) |
| N(1)-C(10) | 1.498(3) |
| N(1)-C(11) | 1.499(3) |
| N(1)-C(9) | 1.523(3) |
| C(1)-C(2) | 1.520(4) |
| C(1)-C(9) | 1.537(3) |
| C(1)-C(8) | 1.540(3) |
| C(1)-C(6) | 1.603(4) |
| C(2)-C(3) | 1.561(4) |
| C(3)-C(4) | 1.470(5) |
| C(3)-C(7) | 1.516(5) |
| C(4)-C(5) | 1.303(6) |
| C(5)-C(6) | 1.512(5) |
| C(6)-C(7) | 1.509(5) |
| C(12)-N(1)-C(10) | 110.1(2) |
| C(12)-N(1)-C(11) | 108.1(2) |
| C(10)-N(1)-C(11) | 106.4(2) |
| C(12)-N(1)-C(9) | 113.4(2) |
| C(10)-N(1)-C(9) | 112.5(2) |
| C(11)-N(1)-C(9) | 105.94(18) |
| C(2)-C(1)-C(9) | 114.3(2) |
| C(2)-C(1)-C(8) | 112.6(2) |

| | |
|-------------------|------------|
| C(9)-C(1)-C(8) | 113.5(2) |
| C(2)-C(1)-C(6) | 101.3(2) |
| C(9)-C(1)-C(6) | 103.75(19) |
| C(8)-C(1)-C(6) | 110.2(2) |
| C(1)-C(2)-C(3) | 104.2(2) |
| C(4)-C(3)-C(7) | 100.0(3) |
| C(4)-C(3)-C(2) | 108.0(3) |
| C(7)-C(3)-C(2) | 99.0(2) |
| C(5)-C(4)-C(3) | 108.8(3) |
| C(4)-C(5)-C(6) | 107.0(3) |
| C(5)-C(6)-C(7) | 99.4(3) |
| C(5)-C(6)-C(1) | 105.9(3) |
| C(7)-C(6)-C(1) | 100.1(3) |
| C(3)-C(7)-C(6) | 94.4(2) |
| N(1)-C(9)-C(1) | 121.21(19) |
| Cl(1)-C(13)-Cl(2) | 113.44(18) |

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|----------|----------|----------|----------|----------|----------|
| I(1) | 59(1) | 43(1) | 44(1) | -1(1) | 17(1) | 3(1) |
| Cl(1) | 72(1) | 85(1) | 141(1) | 10(1) | 33(1) | -6(1) |
| Cl(2) | 109(1) | 73(1) | 83(1) | 15(1) | 48(1) | 17(1) |
| N(1) | 39(1) | 34(1) | 37(1) | 1(1) | 10(1) | -1(1) |
| C(1) | 35(1) | 40(1) | 43(1) | 3(1) | 4(1) | 1(1) |
| C(2) | 48(1) | 59(2) | 60(2) | 1(1) | 20(1) | 6(1) |
| C(3) | 64(2) | 71(2) | 63(2) | 12(2) | 25(1) | 2(2) |
| C(4) | 45(1) | 88(2) | 85(2) | 28(2) | 15(1) | -11(2) |
| C(5) | 101(3) | 67(2) | 77(2) | -5(2) | -1(2) | -42(2) |
| C(6) | 54(1) | 49(2) | 89(2) | -12(2) | 21(1) | -8(1) |

| | | | | | | |
|-------|-------|-------|-------|-------|-------|--------|
| C(7) | 51(2) | 78(2) | 80(2) | 27(2) | 7(1) | -12(2) |
| C(8) | 54(2) | 99(3) | 45(1) | -1(2) | 0(1) | -11(2) |
| C(9) | 37(1) | 37(1) | 50(1) | 8(1) | 7(1) | 1(1) |
| C(10) | 63(2) | 72(2) | 37(1) | 4(1) | 12(1) | 2(1) |
| C(11) | 39(1) | 61(2) | 48(1) | 5(1) | 7(1) | -9(1) |
| C(12) | 63(2) | 38(1) | 60(2) | -2(1) | 21(1) | 4(1) |
| C(13) | 63(2) | 62(2) | 88(2) | 2(2) | 24(2) | 10(2) |

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**.

| | x | y | z | U(eq) |
|--------|----------|-----------|----------|--------|
| H(2A) | 466 | 11836 | 1717 | 65 |
| H(2B) | 1682 | 11814 | 2311 | 65 |
| H(3A) | 365 | 9842 | 2751 | 77 |
| H(4A) | -1108 | 8643 | 1741 | 87 |
| H(5A) | -31 | 7270 | 970 | 102 |
| H(6A) | 2243 | 7548 | 1474 | 76 |
| H(7A) | 1582 | 7300 | 2590 | 85 |
| H(7B) | 2476 | 8899 | 2661 | 85 |
| H(8A) | 359 | 10432 | 601 | 102 |
| H(8B) | 1604 | 10030 | 397 | 102 |
| H(8C) | 1318 | 11888 | 604 | 102 |
| H(9B) | 3450(20) | 10540(30) | 2131(13) | 40(7) |
| H(9A) | 3630(30) | 9740(40) | 1484(16) | 74(10) |
| H(10A) | 2986 | 12354 | 418 | 86 |
| H(10B) | 4186 | 11254 | 579 | 86 |
| H(10C) | 4272 | 13246 | 611 | 86 |
| H(11A) | 5494 | 13212 | 1737 | 75 |
| H(11B) | 5484 | 11216 | 1744 | 75 |
| H(11C) | 5108 | 12234 | 2349 | 75 |

| | | | | |
|--------|------|-------|------|----|
| H(12A) | 3609 | 14774 | 1535 | 79 |
| H(12B) | 3200 | 13777 | 2135 | 79 |
| H(12C) | 2341 | 13831 | 1384 | 79 |
| H(13A) | 6598 | 3588 | -79 | 84 |
| H(13B) | 6974 | 4380 | 671 | 84 |
