Supporting Information for:

Synthesis of Alkaline Anion Exchange Membranes with Chemically Stable Imidazolium Cations: Unexpected Crosslinked Macrocycles from Ring-Fused ROMP Monomers

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General Methods and Materials

^{1}H and ^{13}C NMR spectra were collected in deuterated solvents on Varian INOVA 300, Varian INOVA 400, Bruker 500, or Varian INOVA 600 NMR spectrometers at 22 °C with shifts reported relative to the residual solvent peaks ($CDCl_3$ (7.26 ppm (^{1}H) and 77.16 ppm (^{13}C); or CD_3OD or CD_3OH); 3.31 ppm (^{1}H) and 49.00 ppm (^{13}C)). High resolution mass spectrometry analyses were performed on a Thermo Scientific Exactive Orbitrap MS system equipped with an electrospray ionization source (ESI-HRMS) or with an Ion Sense DART ion source (DART-HRMS). Thermogravimetric analysis (TGA) were performed on a TA Instruments Q500 Thermogravimetric Analyzer (heat rate: 10 °C/min.; air flow rate: 60 ml/min).

All reactions and manipulations of air or water sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk techniques unless otherwise specified. Benzaldehyde, L-proline, 1-iodobutane, 1-bromobutane, terephthalaldehyde, Grubbs' 2nd Generation catalyst ($Cl_2Ru(IMes)(PCy_3)CHPh$), and Crabtree's catalyst $[(COD)Ir(py)(PCy_3)]PF_6$, were purchased from Aldrich and used as received. Diacetyl, benzil, ammonium acetate, triethylamine, and trifluoroacetic anhydride (TFAA) were purchased from Alfa Aesar and used as received. Methanol-d_3 (CD_3OH) and iodoethane were purchased from Acros and used as received. 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt was purchased from TCI and used as received.

Cis-cyclooctene (95%) was purchased from Aldrich and distilled from 4Å sieves prior to use. Sodium hydroxide, sodium bicarbonate, sodium chloride and potassium hydroxide were purchased from Mallinckrodt and used as received. All solvents (methylene chloride, diethyl ether, tetrahydrofuran, acetonitrile, and methanol) were purchased from Sigma-Aldrich or Mallinckrodt. Methylene chloride and tetrahydrofuran were dried over an alumina column and

degassed by three freeze-pump-thaw cycles before use. Chloroform was dried over P_2O_5 and distilled prior to use. Hydrogen (99.99%) was purchased from Airgas. NMR solvents ($CDCl_3$, CD_3OD, DMSO–d_6) were purchased from Cambridge Isotope Laboratories (CIL) and used as received. Standardized hydrochloric acid (0.1014 M) and potassium hydroxide (0.1000 ± 0.0001 M) solutions were purchased from Sigma-Aldrich.

Cyclooct-4-en-1-ylmethanamine was prepared according to a literature procedure.[1] Cyclooct-5-ene-1,2-*trans*-diol was prepared according to a literature procedure.[2]

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 BekkTeck LLC (Loveland, CO), and a helpful schematic and description of a similar experimental setup has been reported.[3] A strip of the thin film in iodide form (ca. 4 cm long x 0.5 cm wide) was converted to the hydroxide form by immersing it in a stirring 30 mL portion of 1 M potassium hydroxide for a minimum of 2 h and the 1 M KOH solution was replaced twice with fresh solution during that time. Residual potassium hydroxide was washed away by immersing the membrane in 3 x 60 mL portions of deionized water for 20 minutes each. The AAEM was then clamped into the cell using a Proto 6104 torque screwdriver set to 1 inch ounce and completely immersed in deionized water at either 22 °C or 50 °C during the measurement time. 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. A Bode plot was used to assess the frequency range over which the impedance approached a constant and the phase angle approached zero. In a Nyquist plot of the data, the high frequency intercept on the real

impedance axis was taken to be the 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 x 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 a minimum of three separate AAEMs (per composition).

Water uptake and percentage dimensional change were measured by the change between the fully hydrated and dried AAEMs. Conversion to the hydroxide form was achieved by immersing it in a stirring 30 mL portion of 1 M potassium hydroxide for a minimum of 2 h and the 1 M KOH solution was replaced twice with fresh solution during that time. Residual potassium hydroxide was washed away by immersing the membrane in 3 x 60 mL portions of deionized water for 20 minutes each. Immediately following hydroxide ion exchange, a sample was dried with a paper towel, measured by length, and weighed on the balance with a piece a weighing paper. The thin film (in the hydroxide form) was dried under full vacuum at 60 °C in order to completely dehydrate it and then weighed and measured. The water uptake percentage value was calculated by: $WU = [(Mass_{wet} - Mass_{dry})/Mass_{dry}]*100$. The dimensional change percentage was calculated by: $\Delta L = [(L_{wet} - L_{dry})/L_{dry}]*100$.

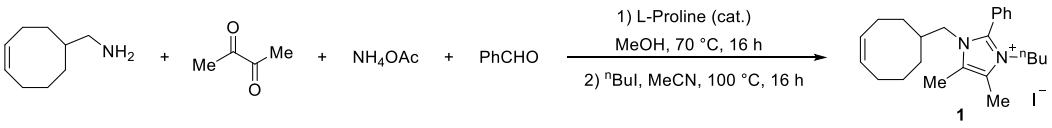
Ion exchange capacities (IECs) were determined using standard back titration methods. The thin film as synthesized (in the iodide form) was converted to the hydroxide form by immersing the film in a stirring 30 mL portion of 1 M potassium hydroxide for a minimum of 2 hours with the 1 M KOH solution being replaced twice with fresh 1 M KOH during that time. Residual potassium hydroxide was washed away by immersing the membrane in 3 x 60 mL

portions of deionized water for 20 minutes each. The AAEM was then stirred in 20 mL standardized 0.1 M HCl (aq) solution for 48 hours followed by titration with standardized 0.1 M KOH (aq) to determine the equivalence point. Control acid samples (with no AAEM present) were also titrated with standardized 0.1 M KOH (aq), and the difference between the volumes required to titrate the control and the sample was used to calculate the amount of hydroxide ions in the membrane. The resulting thin film (in the chloride form) was dried under full vacuum at 60 °C in order to completely dehydrate it and then weighed. The amount of hydroxide ions was divided by the dried mass of the membrane (*vide supra*) to give an IEC value with the units mmol OH^-/g Cl^-.

The mechanical properties of the film samples in the iodide form were characterized using a Zwick/Roell Z010 testing system equipped with a 10 kN load cell and analyzed using Zwick/Roell TestXpert II v.3.5 software. Measurements were taken on samples immediately removed from water after being soaked for at least 24 hours to ensure complete hydration.

Synthesis of Imidazolium Monomers

3-Butyl-1-(cyclooct-4-en-1-ylmethyl)-4,5-dimethyl-2-phenyl-1*H*-imidazol-3-ium (1)



1

A modified literature procedure was used.[4] To a pre-dried 100 ml round bottom flask, diacetyl (5.00 mmol, 1.00 equiv), NH_4OAc (5.00 mmol, 1.00 equiv), cyclooct-4-en-1-ylmethanamine (5.00 mmol, 1.00 equiv), L-proline (0.750 mmol, 0.150 equiv), benzaldehyde (5.00 mmol, 1.00 equiv), and 15 mL MeOH were added sequentially. The mixture was stirred at 70 ^oC for 16 hours. After cooling to 22 ^oC, the solvent was removed under reduced pressure. The

residue was dissolved in Et_2O, washed with H_2O, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude dark brown oil was purified by column chromatography (EtOAc : NEt_3 = 3:1) to obtain 1-(cyclooct-4-en-1-ylmethyl)-4,5-dimethyl-2-phenyl-1*H*-imidazole (580 mg) as dark orange oil. The imidazole was dissolved in 10 mL MeCN in a 50 mL round bottom flask and 1-iodobutane (4.00 mmol) was added while stirring. The mixture was stirred at 100 ^oC for 16 hours. After cooling to 22 ^oC, the solvent was removed under reduced pressure and was then washed with Et_2O. The resulting dark brown oil was viscous, but further purification was difficult (566 mg, 24% yield over two steps). Due to its high polarity, compound **1** cannot be purified by traditional methods such as column chromatography, distillation, or crystallization. The impurities in monomer **1** did not affect the sequential ROMP.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.55 (m, 5H), 5.61-5.40 (m, 2H), 4.01-3.82 (m, 3H), 3.77 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.26-2.14 (m, 1H), 2.02-1.87 (m, 3H), 1.69-1.59 (m, 1H), 1.59-1.49 (m, 3H), 1.29-1.10 (m, 5H), 1.05-0.93 (m, 1H), 0.89 (dddd, *J* = 12.7, 10.6, 6.3, 4.5 Hz, 1H), 0.73 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 142.9, 132.3, 130.6, 130.5, 130.2, 129.7, 129.7, 128.9, 127.0, 126.5, 122.1, 52.6, 46.3, 36.5, 31.6, 31.5, 29.8, 27.2, 25.6, 23.7, 19.4, 13.1, 9.8, 9.4; **HRMS (ESI+):** Calculated for $C_{24}H_{35}N_2$ ($[M - I]^+$): 351.2795, Found 351.2779.

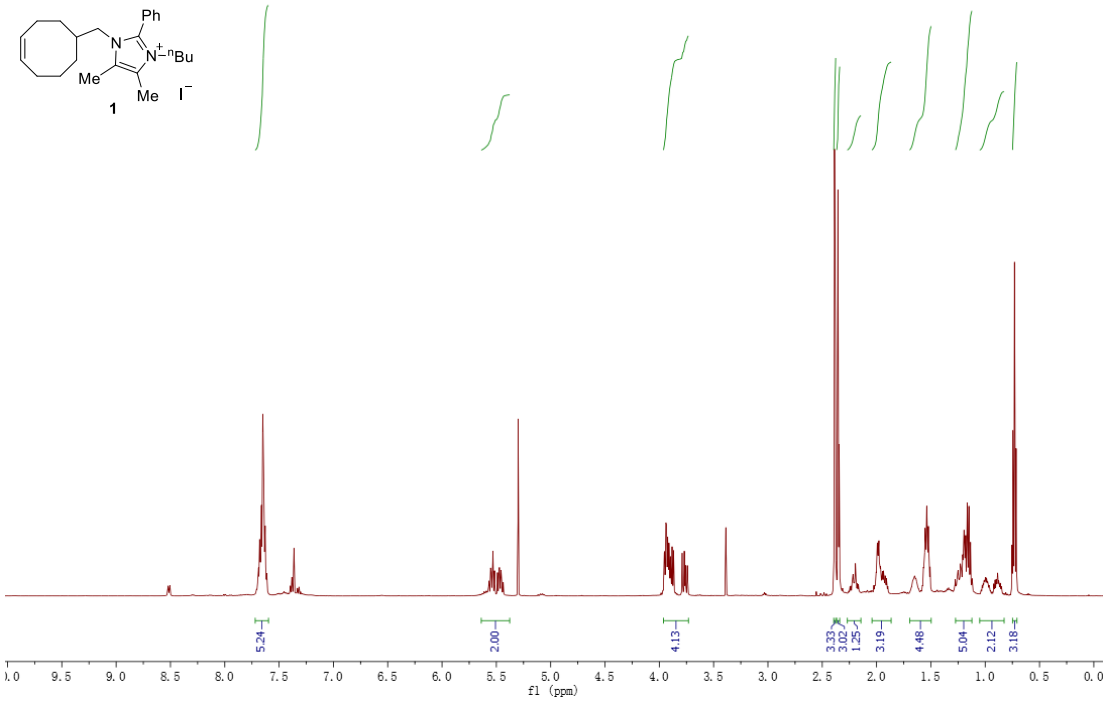


Figure S1. ^{1}H NMR Spectrum of **1** in $CDCl_3$.

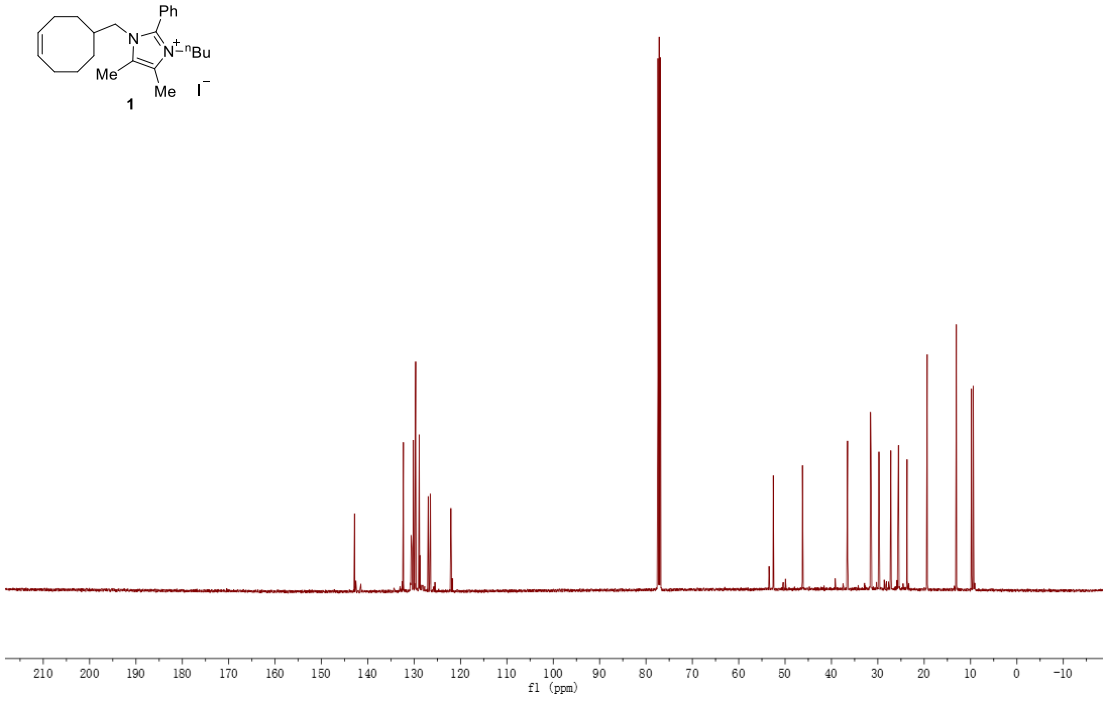
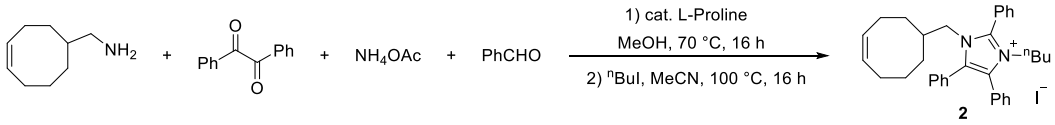


Figure S2. ^{13}C NMR Spectrum of **1** in $CDCl_3$.

3-Butyl-1-(cyclooct-4-en-1-ylmethyl)-2,4,5-triphenyl-1*H*-imidazol-3-ium (2)



A modified literature procedure was used.[4] To a pre-dried 100 ml round bottom flask, benzil (15.0 mmol, 1.00 equiv), NH_4OAc (15.0 mmol, 1.00 equiv), cyclooct-4-en-1-ylmethanamine (15.0 mmol, 1.00 equiv), L-proline (2.25 mmol, 0.150 equiv), PhCHO (15.0 mmol, 1.00 equiv), and 20 mL MeOH were added sequentially. The mixture was stirred at 70 °C for 16 hours. After cooling to 22 °C, the solvent was removed under reduced pressure. The residue was dissolved in Et_2O, washed with H_2O, dried with $MgSO_4$, filtered and concentrated. The crude solid (1-(cyclooct-4-en-1-ylmethyl)-2,4,5-triphenyl-1*H*-imidazole, 4.2 g) was used without further purification. The crude imidazole was dissolved in 10 mL MeCN in a 50 mL round bottom flask and 1-iodobutane (20.0 mmol, 1.30 equiv) was added while stirring. The mixture was stirred at 100 °C for 16 hours. After cooling to room temperature, the residue was dissolved in CH_2Cl_2, washed with H_2O, dried with $MgSO_4$, filtered, concentrated and precipitated in Et_2O. The orange precipitate was then recrystallized from EtOAc to give the desired imidazolium product **2** as yellow solid (1.62 g, 18% yield over two steps).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.3 Hz, 1H), 8.12 (d, *J* = 7.0 Hz, 1H), 7.73-7.64 (m, 7H), 7.39-7.33 (m, 6H), 5.42-5.31 (m 2H), 4.00 (dd, *J* = 14.1, 6.3 Hz, 1H), 3.94 (t, *J* = 8.0 Hz, 2H), 3.78 (dd, *J* = 14.2, 9.6 Hz, 1H), 2.15-2.06 (m, 1H), 1.90-1.73 (m, 3H), 1.47-1.36 (m, 3H), 1.33-1.19 (m, 2H), 1.05-0.91 (m, 4H), 0.74-0.63 (m, 2H), 0.52 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 144.1, 132.5, 132.4, 132.0, 131.6, 131.6, 131.5, 130.3, 130.2, 130.1, 129.8, 129.1, 129.0, 129.0, 126.2, 125.7, 122.7, 53.7, 47.1, 35.6, 31.8, 31.7, 30.1, 27.3, 25.8, 24.0, 19.5, 13.0; **HRMS (DART):** Calculated for $C_{34}H_{39}N_2$ ($[M - I]^+$): 475.3108, Found 475.3097.

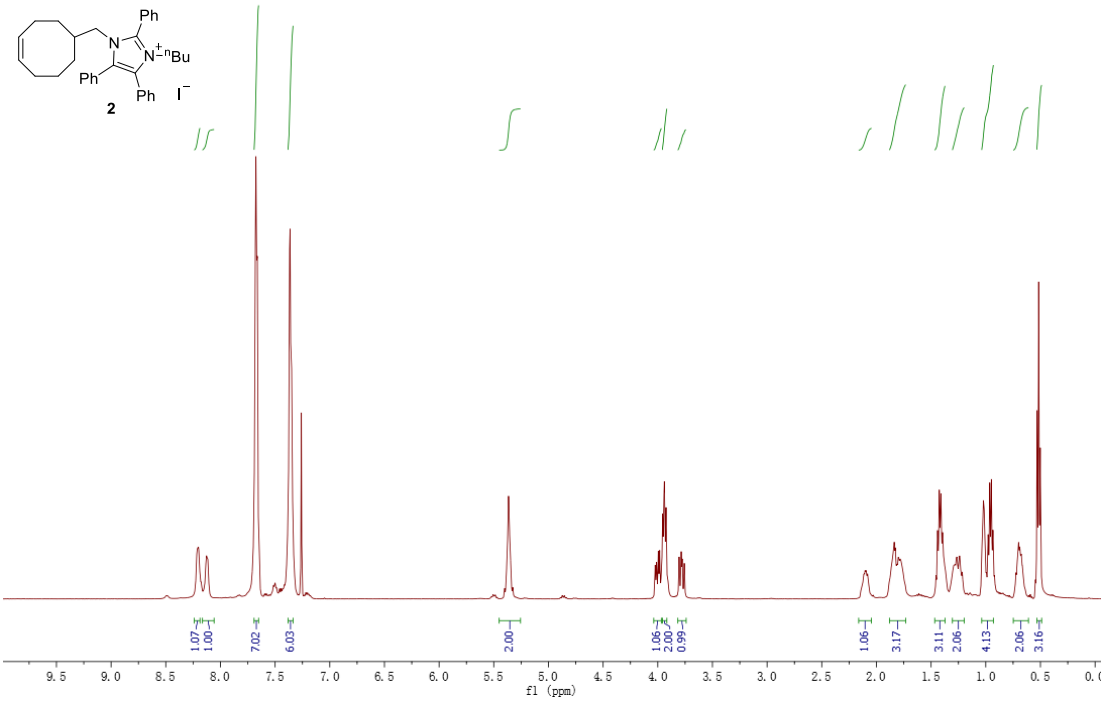


Figure S3. ^{1}H NMR Spectrum of **2** in $CDCl_3$.

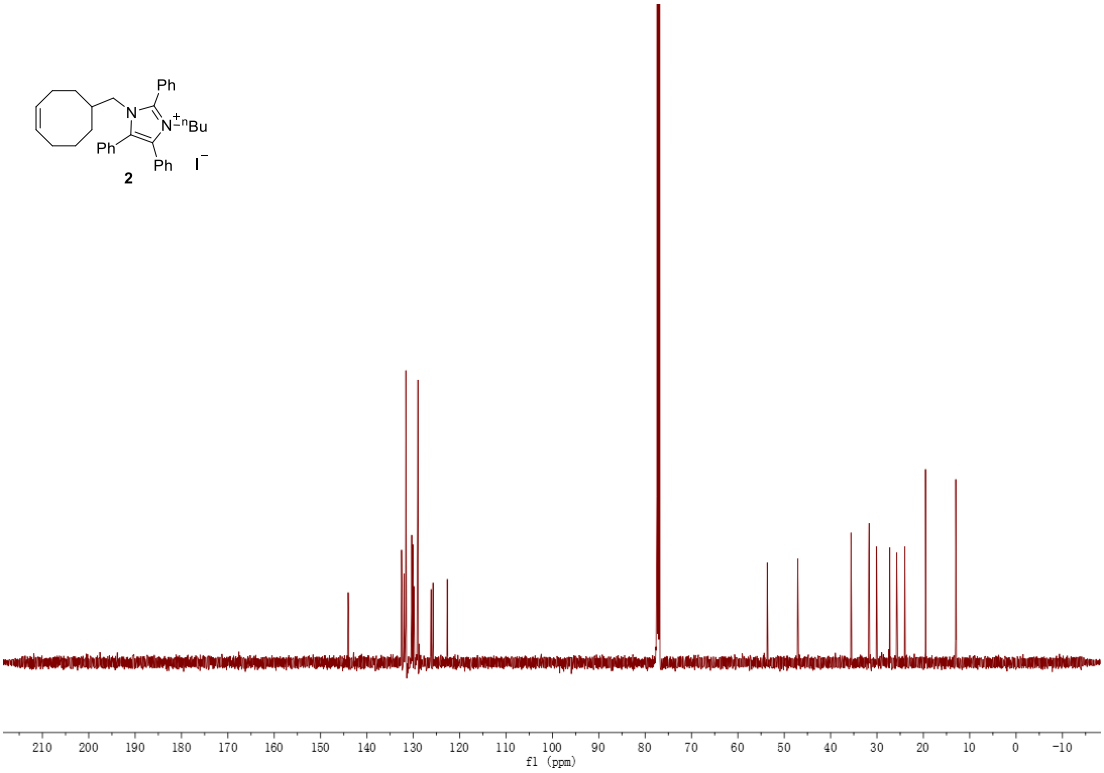
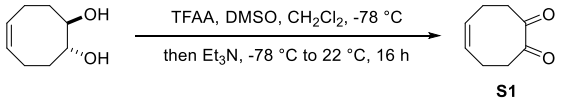


Figure S4. ^{13}C NMR Spectrum of **2** in $CDCl_3$.

Cyclooct-5-ene-1,2-dione (S1)



S1

A modified literature procedure was used (Swern oxidation).[5] To a pre-dried, N_2 filled 500 ml three-neck flask, 28.6 mL DMSO (403 mmol, 3.10 equiv) and 150 mL CH_2Cl_2 were added. The flask was then cooled down to -78 °C, followed by adding trifluoroacetic anhydride (TFAA, 377 mmol, 2.90 equiv) dropwise over 30 minutes. The mixture was stirred at -78 °C for 1 hour, then a solution of cyclooct-5-ene-1,2-trans-diol (130 mmol, 1.00 equiv) in 30 mL CH_2Cl_2 was added into the reaction. The mixture was then stirred at -78 °C for another 2 hours, followed by adding triethylamine (676 mmol, 5.20 equiv). The reaction was then allowed to warm up slowly to 22 °C and was stirred at 22°C for 16 hours. The reaction was quenched by 2 M HCl (aq, 300 mL) and was extracted with CH_2Cl_2 (100 mL x3). The combined organic layers were dried with magnesium sulfate, filtered and concentrated to obtain dark orange oil. Vacuum distillation was then performed and the light yellow distillate between 60-70 °C was collected as the desired product **S1** (17.8 g, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.86-5.74 (m, 2H), 2.62-2.55 (m, 4H), 2.34 (q, *J* = 6.6 Hz, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 207.7, 130.4, 38.5, 21.6. The result is consistent with previous literature.[5b]

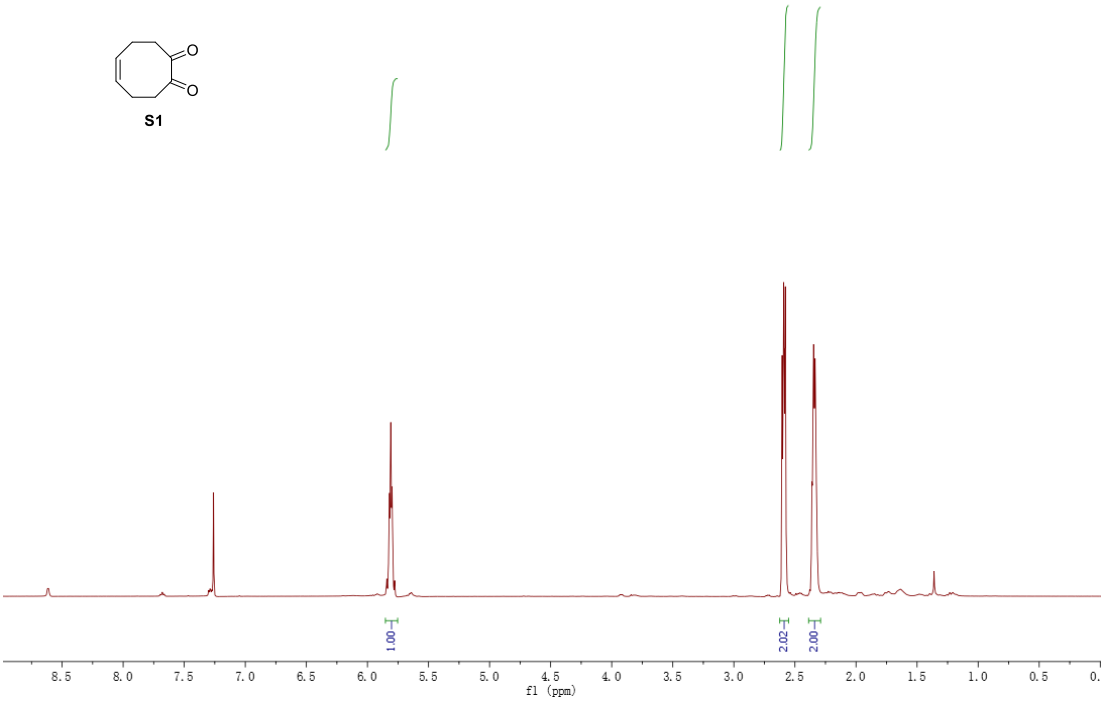


Figure S5. ^{1}H NMR Spectrum of **S1** in $CDCl_3$.

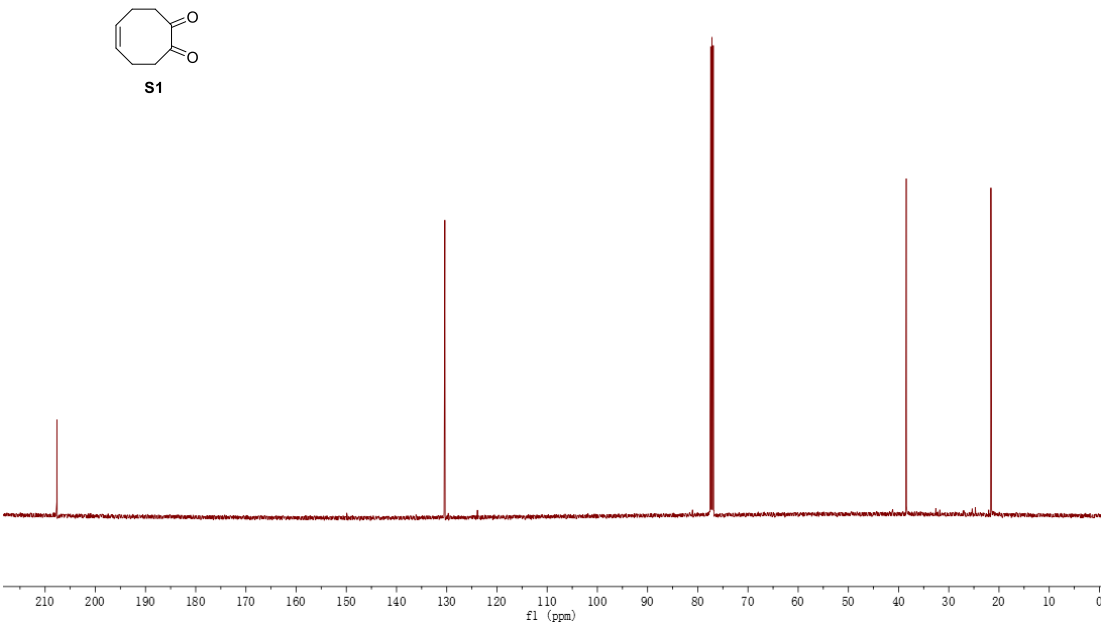
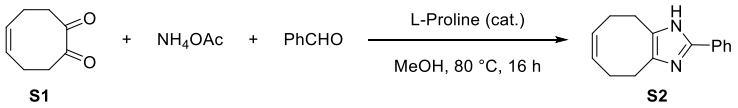


Figure S6. ^{13}C NMR Spectrum of **S1** in $CDCl_3$.

2-Phenyl-4,5,8,9-tetrahydro-1*H*-cycloocta[*d*]imidazole (S2)



S1 **S2**

A modified literature procedure was used.[4] To a pre-dried 100 ml round bottom flask, **S1** (15.0 mmol, 1.00 equiv), ammonium acetate (37.5 mmol, 2.50 equiv), L-proline (4.5 mmol, 0.300 equiv), benzaldehyde (15.0 mmol, 1.00 equiv), and 20 mL MeOH were added sequentially. The flask was then sealed and the mixture was stirred at 80 °C for 16 hours. After cooling to 22 °C, the solvent was removed under reduced pressure. After adding 20 mL H_2O and 10 mL Et_2O to the reaction mixture, a large amount of solid was formed. The solid product was then collected by vacuum filtration, washed with 1 M KOH (aqueous, 20 mL x 3), and dried under vacuum at 60 °C. The crude pale white solid (2.67 g, 79% yield) was used for imidazolium **3** synthesis without further purification.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.99-7.87 (m, 2H), 7.65-7.51 (m, 3H), 5.63-5.47 (m, 2H), 3.03-2.90 (m, 4H), 2.57-2.43 (m, 4H); **^{13}C NMR (125 MHz, DMSO-d_6):** δ 140.5, 131.4, 129.3, 129.3, 128.3, 126.3, 123.1, 25.6, 23.4; **HRMS (DART):** Calculated for $C_{15}H_{17}N_2$ (M^++H): 225.1386, Found 225.1394.

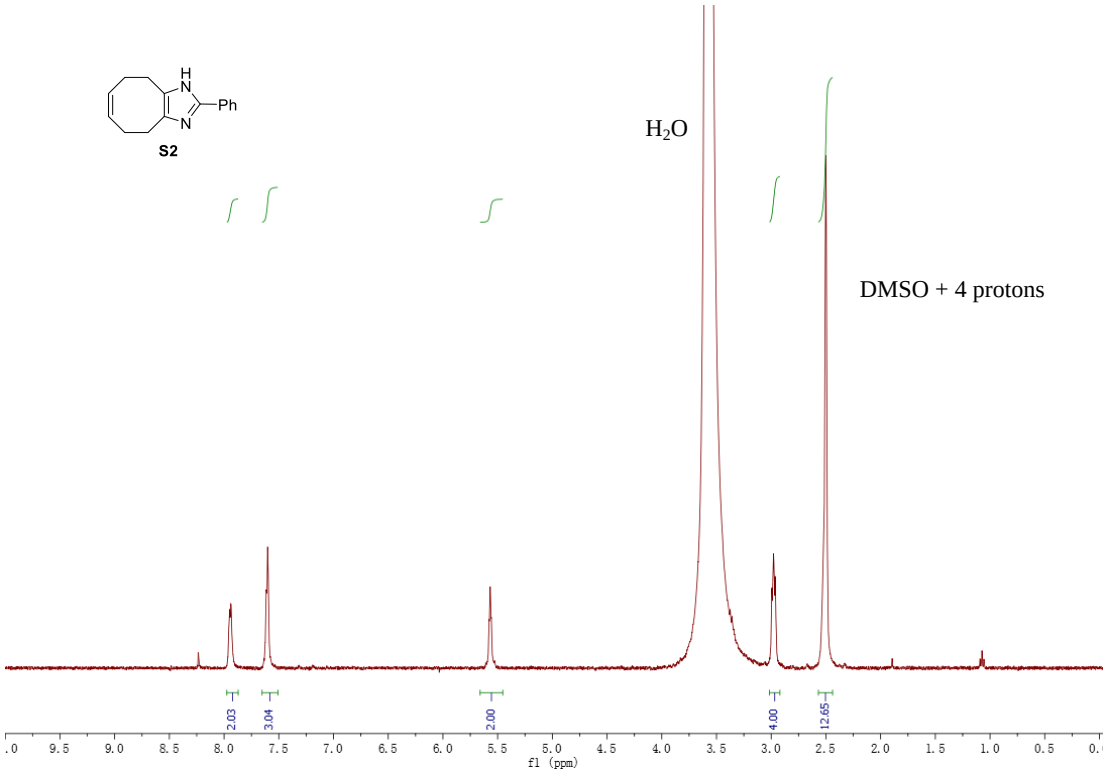


Figure S7. ^{1}H NMR Spectrum of **S2** in DMSO-d_6.

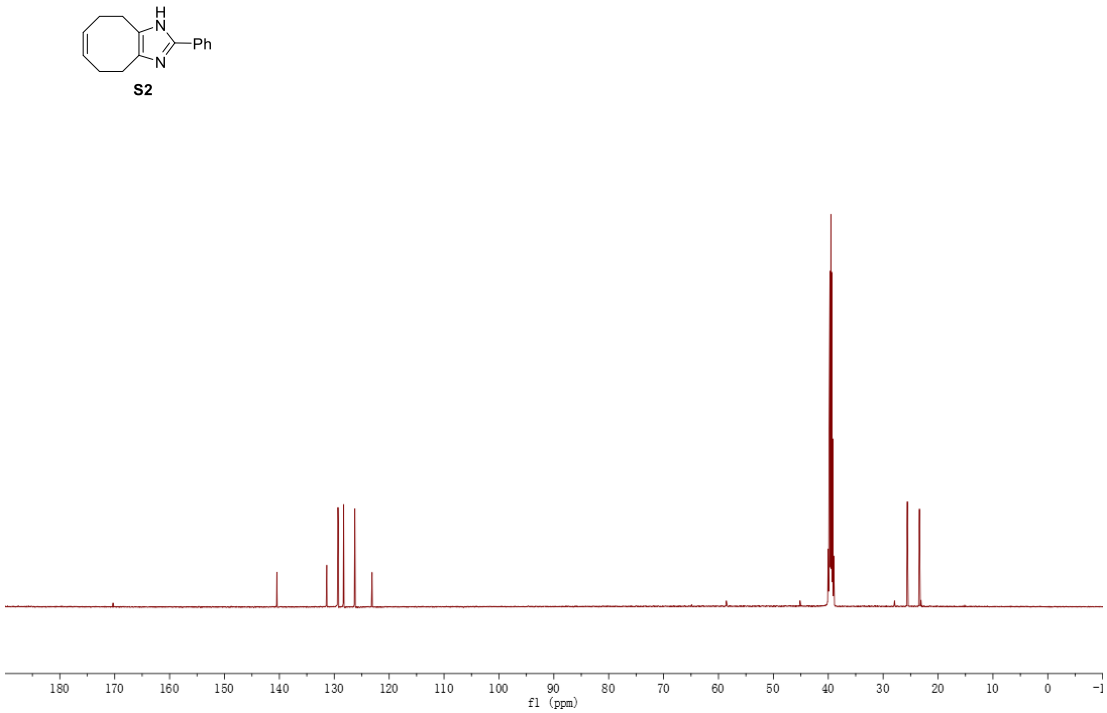
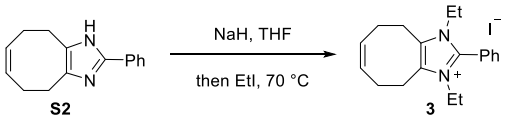


Figure S8. ^{13}C NMR Spectrum of **S2** in DMSO-d_6.

1,3-Diethyl-2-phenyl-4,5,8,9-tetrahydro-1*H*-cycloocta[*d*]imidazol-3-ium iodide (3)



A modified literature procedure was used.[6] To a pre-dried 100 ml round bottom Schlenk flask was added NaH (60% in oil, 16.0 mmol, 1.60 equiv). The flask was left under vacuum for 10 min, then refilled with N_2. This process was repeated for three times, followed by addition of 30 mL THF. Then imidazole **S2** (10.0 mmol, 1.00 equiv) was added into the mixture at 22 °C under nitrogen. A pale white slurry formed after stirring under N_2 at 22 °C for 2 hours. Iodoethane (40.0 mmol, 4.00 equiv) was then added. The reaction was warmed up to 70 °C, and was allowed to stir at 70 °C for 16 hours. After cooling to 22 °C, the reaction was quenched by the addition of H_2O (10 mL). The aqueous layer was washed with Et_2O (10 mL x 3), and was then extracted with CH_2Cl_2 (10 mL x 3). The combined CH_2Cl_2 layers were dried with magnesium sulfate, filtered and concentrated to obtain a pale yellow solid. The desired product **3** was afforded as light yellow solid (2.88 g, 71% yield) after washing with Et_2O (10 mL) and hexanes (10 mL).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.60 (m, 5H), 5.68-5.57 (m, 2H), 3.96 (q, *J* = 7.3 Hz, 4H), 3.13-3.07 (m, 4H), 2.69-2.59 (m, 4H), 1.26 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 142.7, 132.7, 130.7, 130.1, 130.0, 128.2, 122.2, 41.9, 26.1, 23.5, 16.0; **HRMS (ESI+):** Calculated for $C_{19}H_{25}N_2$ ($[M - I]^+$): 281.2012, Found 281.2014.

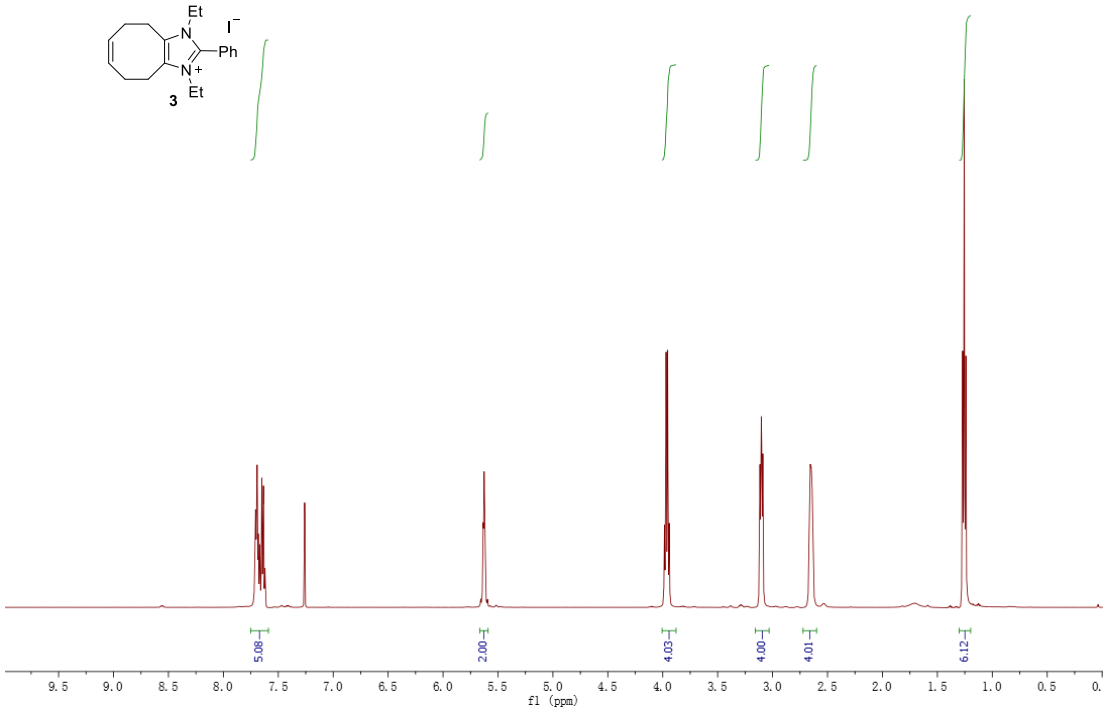


Figure S9. ^{1}H NMR Spectrum of **3** in $CDCl_3$.

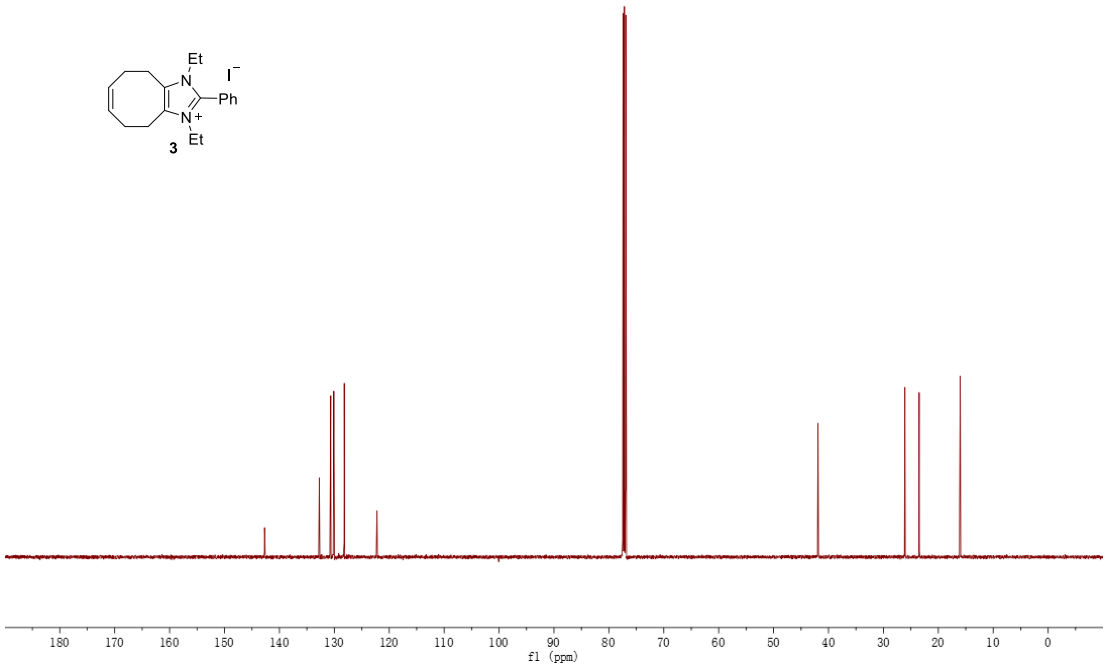
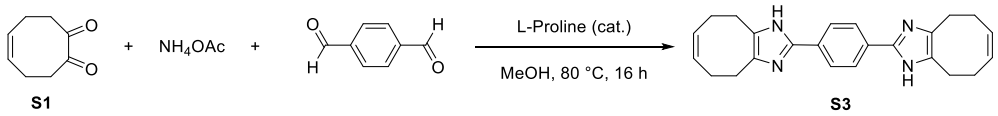


Figure S10. ^{13}C NMR Spectrum of **3** in $CDCl_3$.

1,4-Bis(4,5,8,9-tetrahydro-1*H*-cycloocta[*d*]imidazol-2-yl)benzene (S3)



A modified literature procedure was used.[4] To a pre-dried 100 ml round bottom flask, **S1** (15.0 mmol, 2.00 equiv), ammonium acetate (37.5 mmol, 5.00 equiv), L-proline (4.50 mmol, 0.600 equiv), terephthalaldehyde (7.50 mmol, 1.00 equiv), and 25 mL MeOH were added sequentially. The flask was then sealed and the mixture was stirred at 80 °C for 16 hours. After cooling to 22 °C, the orange precipitate was collected by vacuum filtration, washed with 1 M KOH (aqueous, 20 mL x 3), and dried under vacuum at 60 °C. The crude orange solid (2.37 g, 85% yield) was used for diimidazolium **4** synthesis without further purification. Note: The desired diimidazole product **S3** has very poor solubility in common organic solvents at room temperature. The NMR spectroscopy were recorded in DMSO-d_6, but the NMR sample was dilute and slurry.

^{1}H NMR (500 MHz, DMSO-d_6): δ 11.99 (broad s, 2H), 7.83 (s, 4H), 5.62-5.46 (m, 4H), 2.85 (t, J = 6.5 Hz, 8H), 2.47-2.38 (m, 8H); **^{13}C NMR (125 MHz, DMSO-d_6):** δ 172.1, 142.3, 129.6, 128.6 (broad), 124.3, 26.9, 21.3; **HRMS (DART):** Calculated for $C_{24}H_{27}N_4$ (M^++H): 371.2230, Found 371.2233.

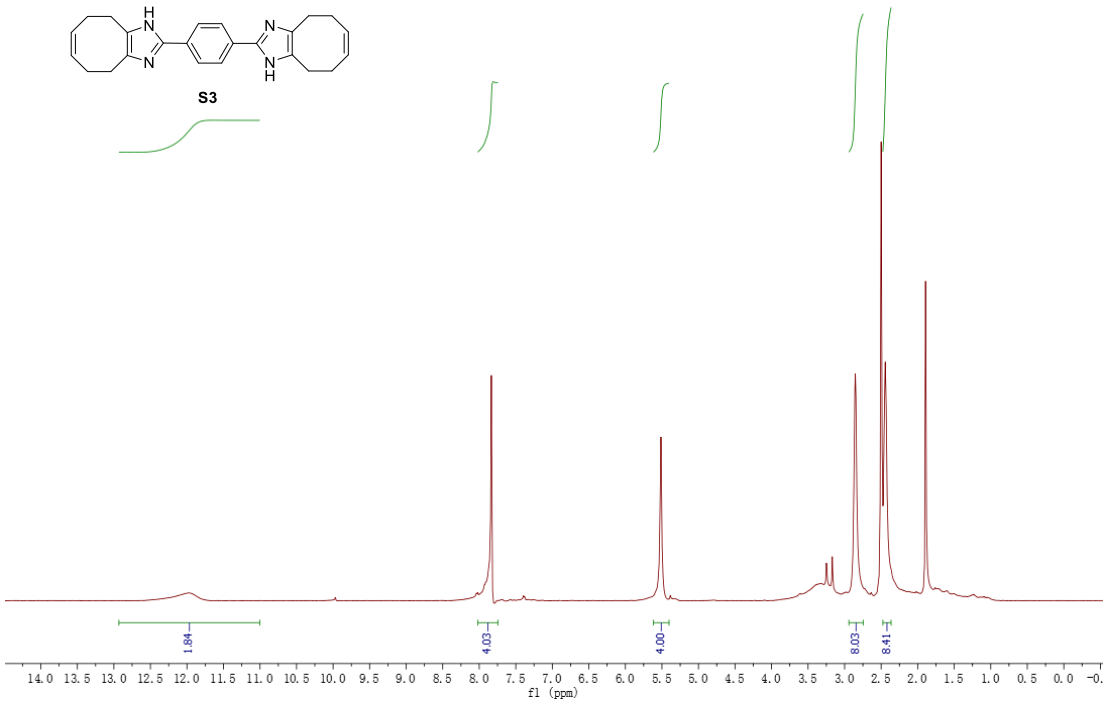


Figure S11. ^{1}H NMR Spectrum of **S3** in DMSO-d_6.

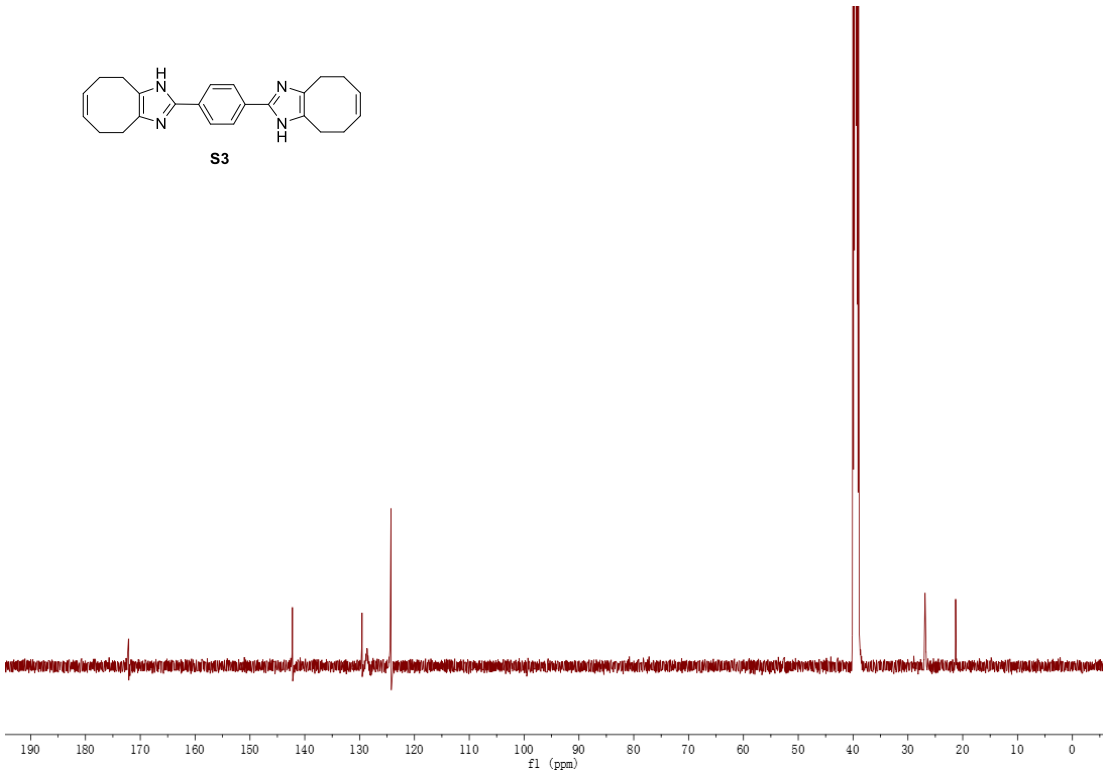
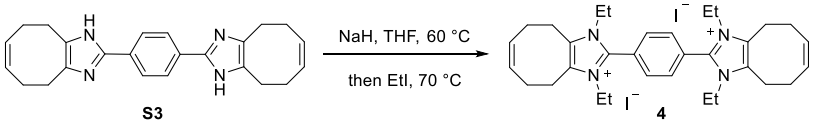


Figure S12. ^{13}C NMR Spectrum of **S3** in DMSO-d_6.

2,2'-(1,4-Phenylene)bis(1,3-diethyl-4,5,8,9-tetrahydro-1*H*-cycloocta[*d*]imidazol-3-ium) iodide (4)



S3 **4**

A modified literature procedure was used.[6] To a pre-dried 100 ml round bottom Schlenk flask was added NaH (60% in oil, 19.2 mmol, 3.20 equiv). The flask was left under vacuum for 10 min, then refilled with N_2. This process was repeated three times, followed by addition of 30 mL THF. Then diimidazole **S3** (6.00 mmol, 1.00 equiv) was added into the mixture at 22 °C under nitrogen. A dark orange slurry formed after stirring under N_2 at 60 °C for 24 hours. Iodoethane (48.0 mmol, 8.00 equiv) was then added at 60 °C. The reaction was warmed up to 70 °C, and was allowed to stir at 70 °C for 48 hours. After cooling to 22 °C, the reaction was quenched by the addition of H_2O (10 mL). The aqueous layer was washed with Et_2O (10 mL x 3) and the orange insoluble solids were removed by filtration. The aqueous layer was then extracted with CH_2Cl_2 (10 mL x 3). The combined CH_2Cl_2 layers were dried with magnesium sulfate, filtered and concentrated to afford the desired product **4** as an orange solid (2.42 g, 55% yield). The diimidazolium product **4** is soluble in CH_2Cl_2 and methanol, but almost insoluble in $CHCl_3$.

^{1}H NMR (500 MHz, CD_3OD): δ 8.10 (s, 4H), 5.74-5.63 (t, *J* = 4.1 Hz, 4H), 4.07 (q, *J* = 7.3 Hz, 8H), 3.22-3.14 (m, 8H), 2.72 (dt, *J* = 9.5, 4.8 Hz, 8H), 1.33 (t, *J* = 7.3 Hz, 12H); **^{13}C NMR (125 MHz, CD_3OD):** δ 142.5, 133.5, 131.9, 129.3, 128.1, 42.6, 26.9, 23.9, 16.1; **HRMS (ESI+):** Calculated for $C_{32}H_{44}N_4I$ ($[M - I]^+$): 611.2605, Found 611.2602.

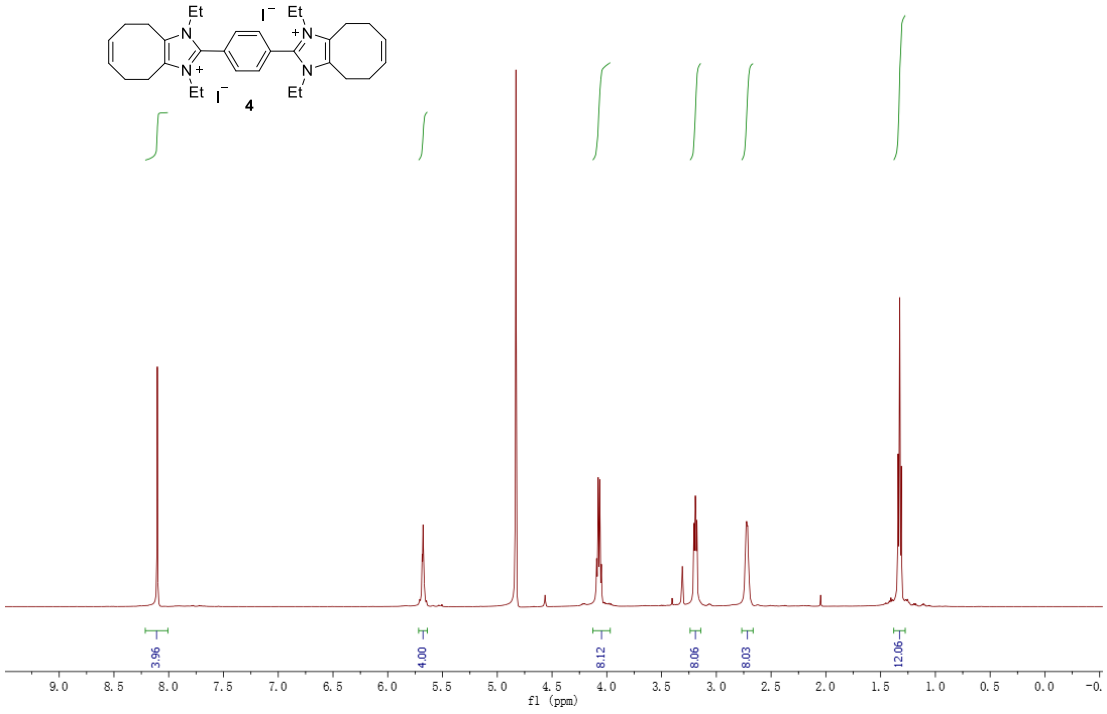


Figure S13. ^{1}H NMR Spectrum of **4** in CD_3OD.

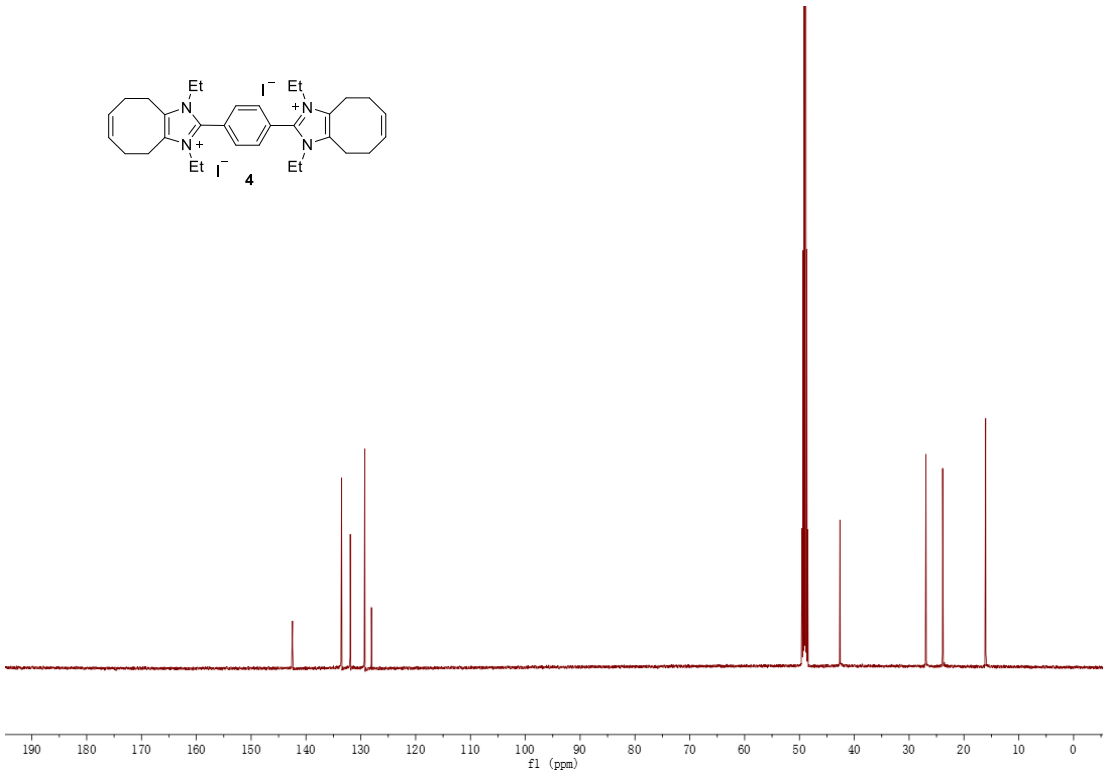


Figure S14. ^{13}C NMR Spectrum of **4** in CD_3OD.

Alkaline Stabilities of Imidazolium Monomers

General procedure:[7]

A solution of the basic methanol were prepared by dissolving KOH (2 M or 5 M) and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (0.03 M) in CD_3OH. The imidazolium monomers (**2**-**4**, 0.03 M) was dissolved in the methanol solution (0.5 mL) and passed through a glass wool plug into an NMR tube. The NMR tube was flame sealed and analyzed by ^1H NMR spectroscopy for the initial time point. Integration of a selected signal in the model compound relative to a signal related to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt provided the initial quantity of model compound. The tube was heated in an oil bath at 80 °C. At specified time points, every 5 days, the tubes were removed, cooled to room temperature and analyzed by ^1H NMR spectroscopy in order to determine the quantity of imidazolium monomer remaining (^1H NMR spectra are provided in Figures S15-S19).

Solvent suppression procedure:[7]

Quantitative ^1H NMR spectra for imidazolium monomer stability studies were acquired in CD_3OH. The OH signal in CD_3OH was suppressed by prestauration with a 2 second presaturation delay and continuous wave irradiation with decoupler field strength ($\gamma B1$) of 195 Hz (equivalent to a presaturation power of 15). Spectra were acquired over a spectral width of -2 to 14 ppm with 20 second relaxation delay and nominal 90° excitation pulse. 32 scans were averaged for each analysis. Residual signals between 6.0-7.1 ppm derive from solvent suppression.

The imidazolium monomer stability data (Figure S15-S19) was summarized in Table S1 (data plots for Figure 1 in the text).

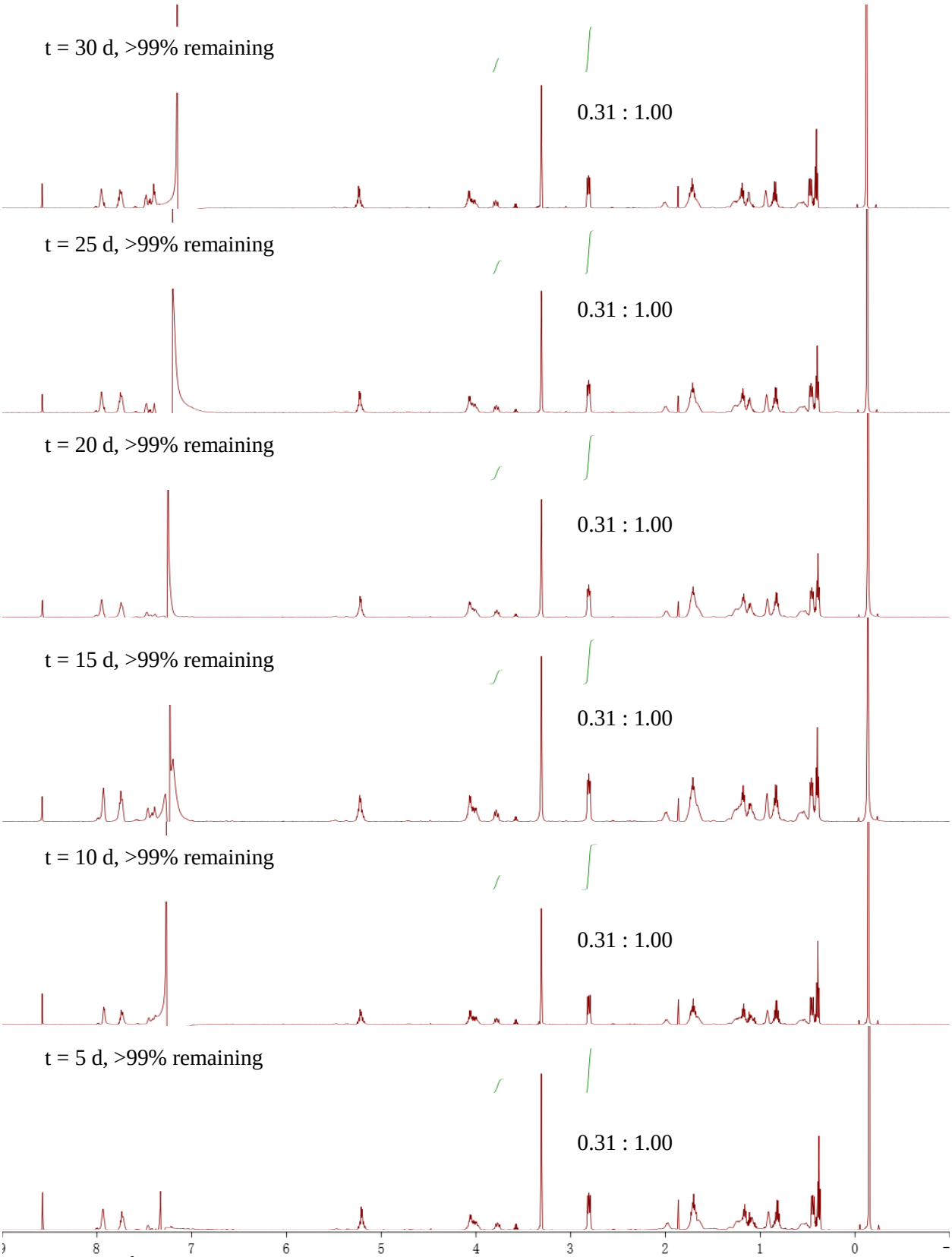


Figure S15. ^{1}H NMR spectra of **2** over 30 days dissolved in a basic CD_3OH solution at 80 °C (5 M KOH, [KOH]/[**2**] = 167) with an internal standard ($TMS(CH_2)_3SO_3Na$).

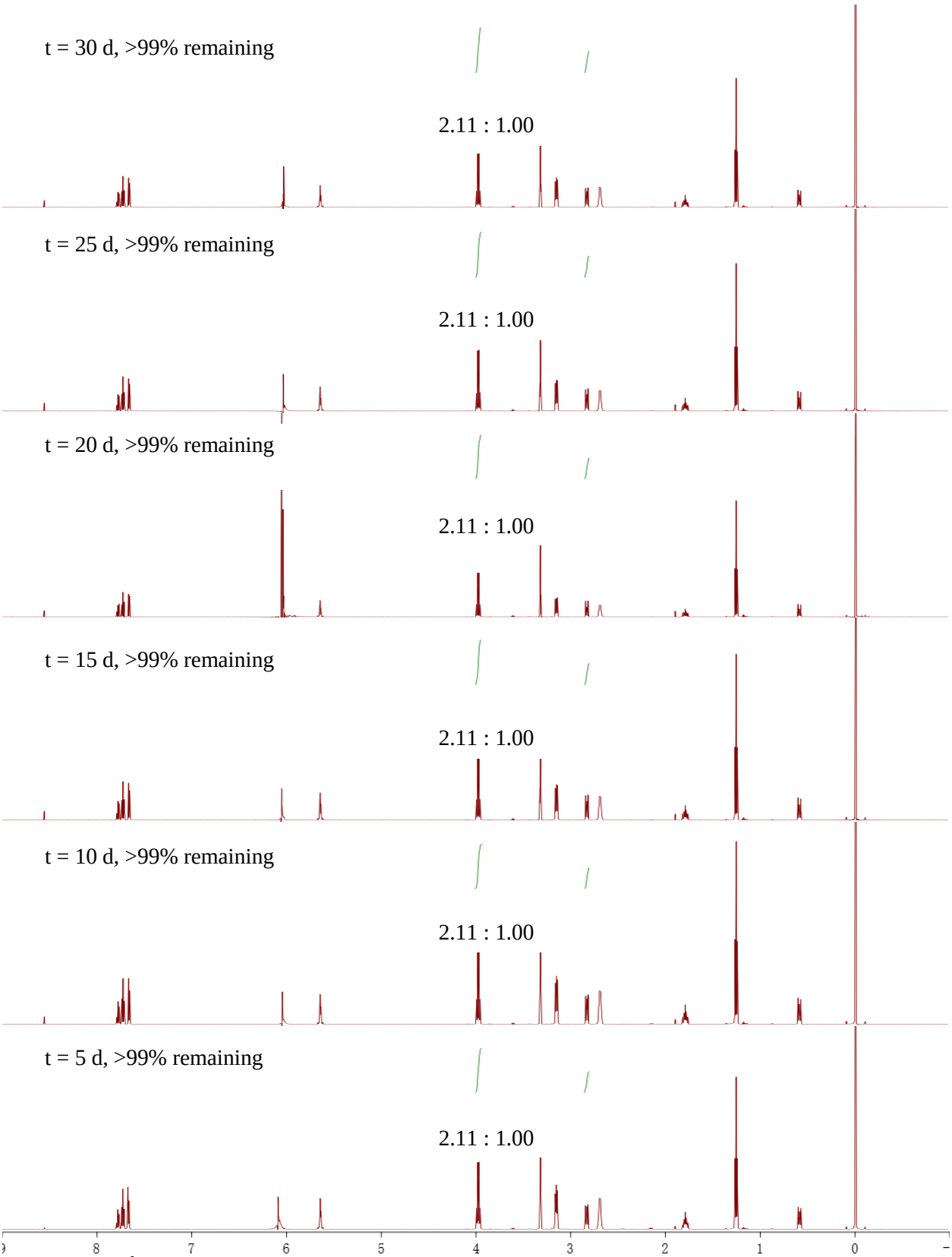


Figure S16. ^{1}H NMR spectra of **3** over 30 days dissolved in a basic CD_3OH solution at 80 °C (2 M KOH, [KOH]/[**3**] = 67) with an internal standard ($TMS(CH_2)_3SO_3Na$).

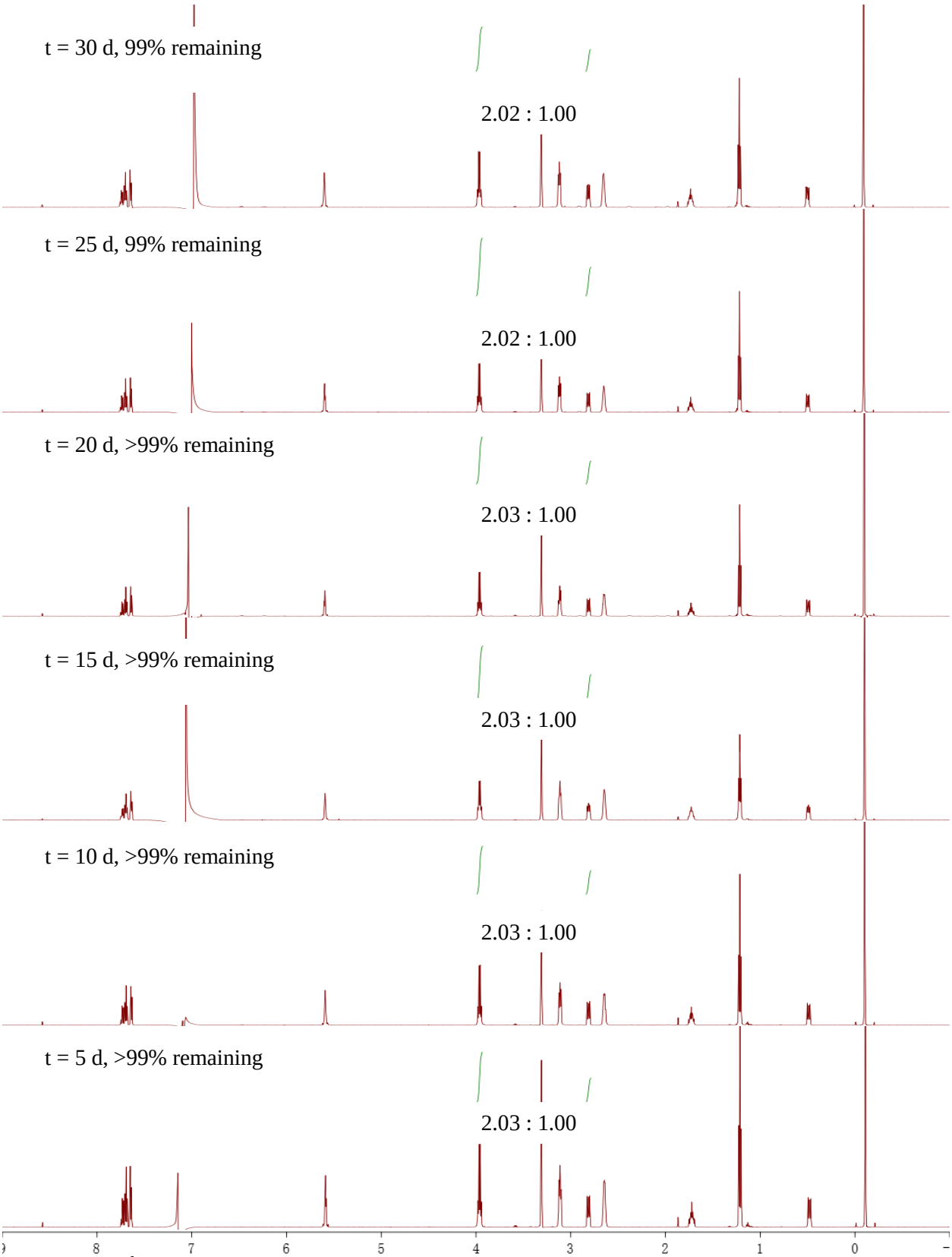


Figure S17. ^{1}H NMR spectra of **3** over 30 days dissolved in a basic CD_3OH solution at 80 °C (5 M KOH, [KOH]/[**3**] = 167) with an internal standard ($TMS(CH_2)_3SO_3Na$).

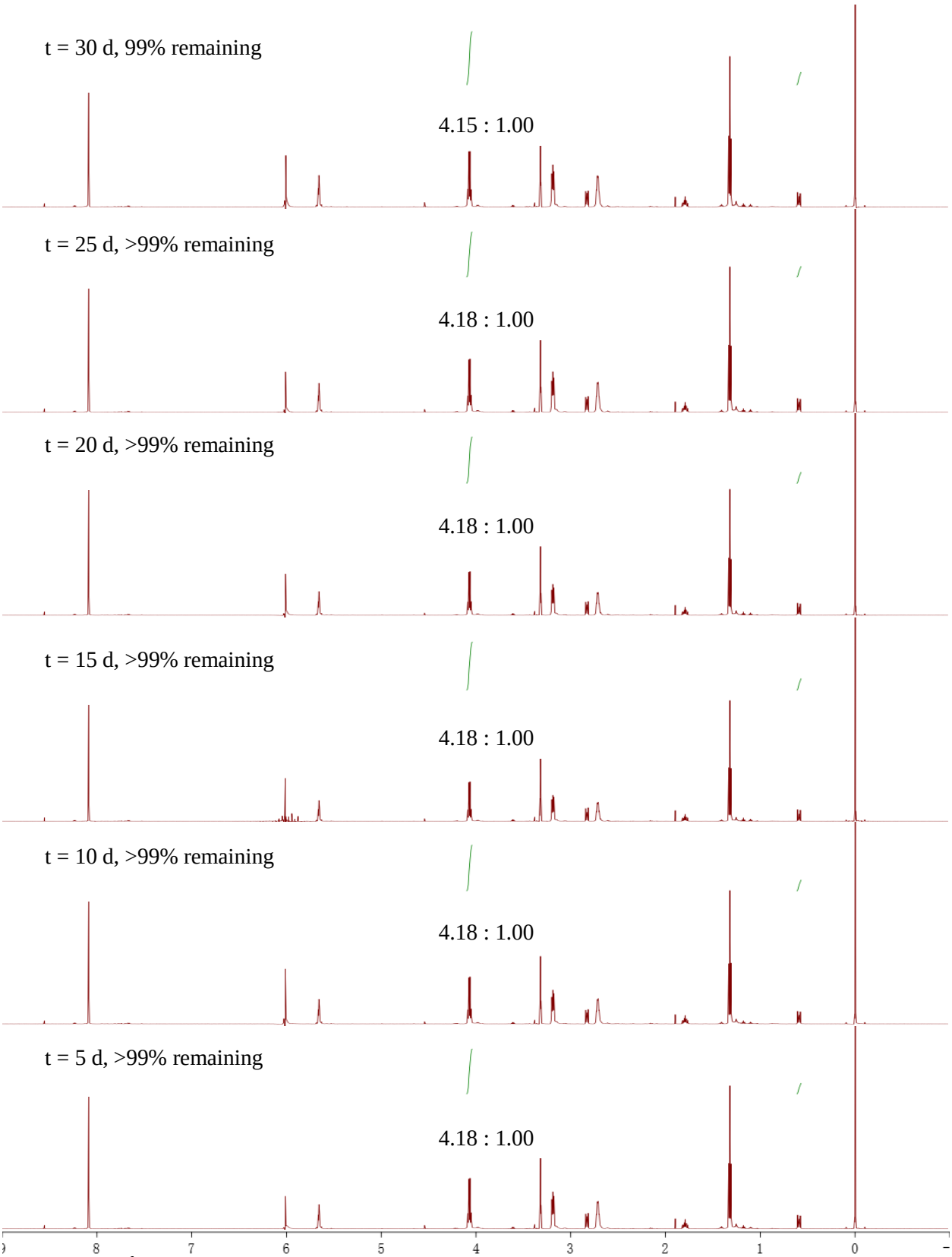


Figure S18. ^{1}H NMR spectra of **4** over 30 days dissolved in a basic CD_3OH solution at 80 °C (2 M KOH, [KOH]/[**4**] = 67) with an internal standard ($TMS(CH_2)_3SO_3Na$).

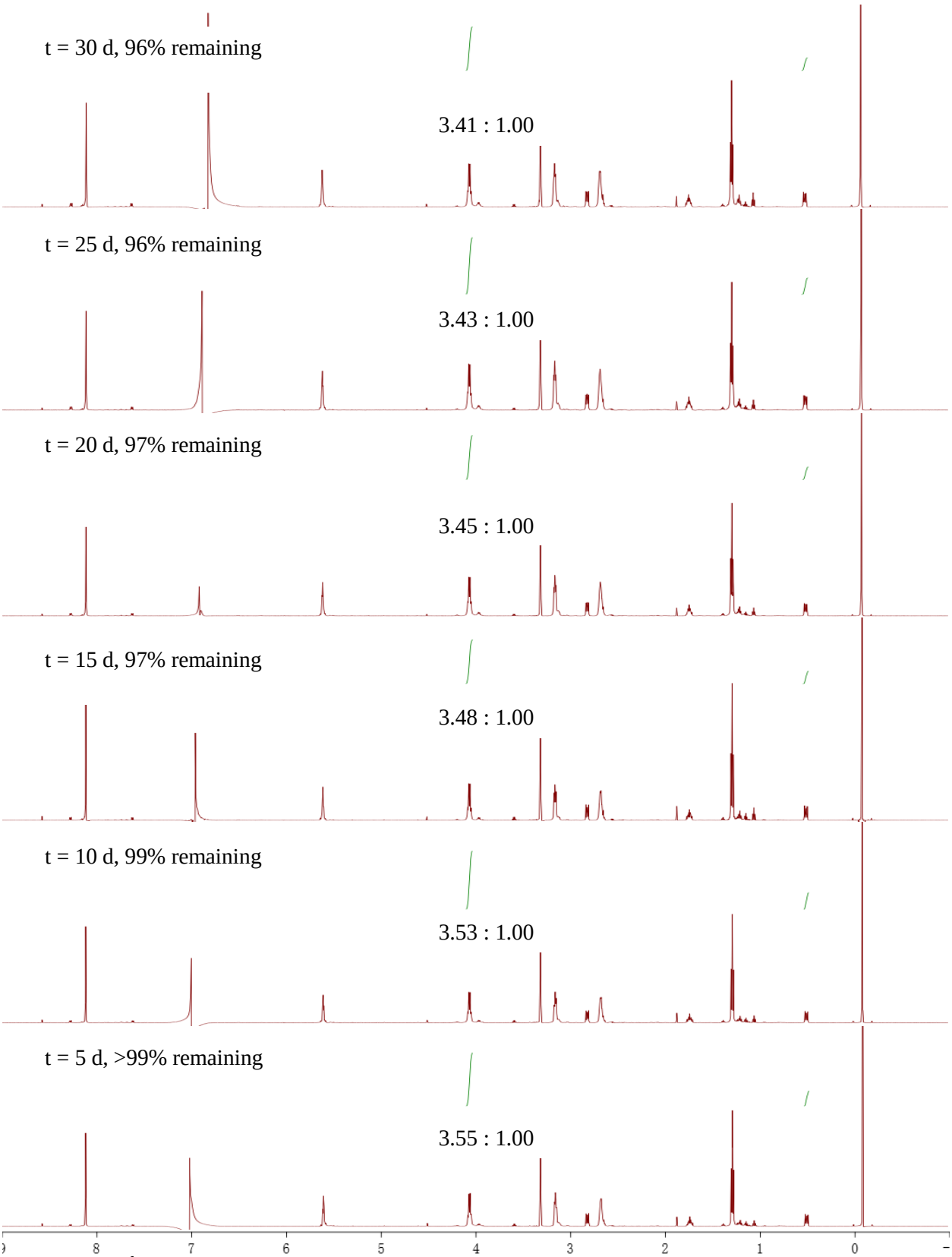
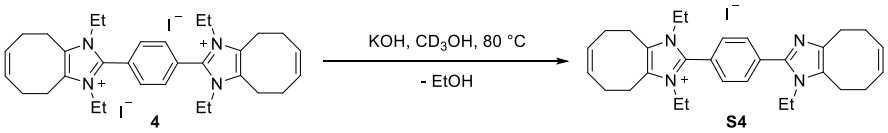


Figure S19. ^{1}H NMR spectra of **4** over 30 days dissolved in a basic CD_3OH solution at 80 °C (5 M KOH, [KOH]/[**4**] = 167) with an internal standard ($TMS(CH_2)_3SO_3Na$).

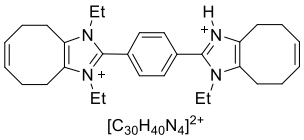
Table S1. Summary of imidazolium monomer stability studies.[a]

Imidazolium Monomer	[KOH]	Cation Remaining (%)[b]					
		5 d	10 d	15 d	20 d	25 d	30 d
2	5 M	>99	>99	>99	>99	>99	>99
3	2 M	>99	>99	>99	>99	>99	>99
	5 M	>99	>99	>99	>99	99	99
4	2 M	>99	>99	>99	>99	>99	99
	5 M	>99	99	97	97	96	96

[a] Reaction Conditions: [ImI]:[KOH] = 1:67 and 1:167 for 2 M and 5 M KOH experiments, respectively, 80 °C. [b] Percent of cation remaining, determined by ^{1}H NMR spectroscopy relative to an internal standard, 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt.



The decomposed product of diimidazolium monomer **4** was identified to be **S4**, in which one of the four ethyl groups was lost (^{1}H NMR spectrum shown in Figure S20). The new aromatic peaks are observed at 8.27 (d, J = 8.3 Hz, 2H) and 7.63 (d, J = 8.3 Hz, 2H), which are significantly different than the aromatic peak in monomer **4** (8.10 (s, 4H)). It was also identified by ESI-HRMS: Calculated for $C_{30}H_{40}N_4$ ($[M+H-2I]^{2+}$): 228.1621, Found 228.1625. Peaks at 3.59 (q, J = 7.0 Hz, 2H) and 1.21 (t, J = 7.0 Hz, 3H) matched well with ethanol protons in CD_3OD.[8]



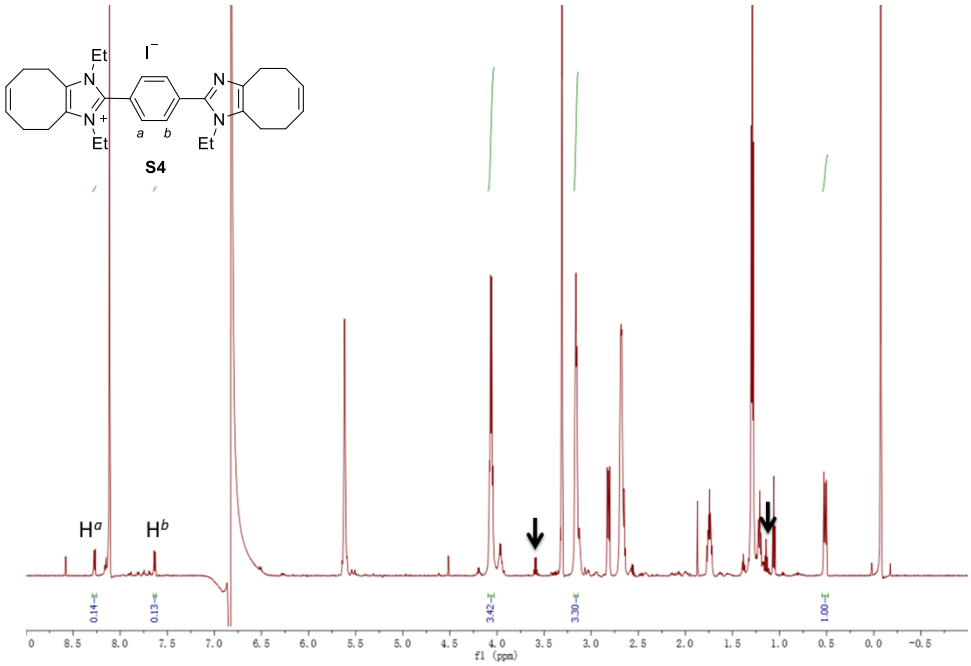
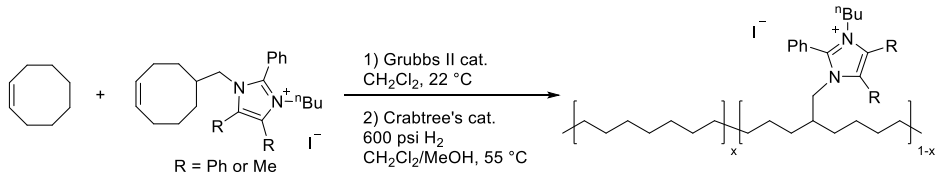


Figure S20. ^{1}H NMR spectra of **4** in 5 M KOH/CD_3OH for 30 days (byproduct **S4** highlighted**)**

Preparation of the First Generation Imidazolium-Contained Copolymer[9]



Under a nitrogen atmosphere monomer **1** or **2** (0.200 mmol) and COE (0.800 mmol) were combined and dissolved in chloroform (1.00 mL). To the reaction mixture, Grubbs 2nd generation catalyst (0.00100 mmol) dissolved in 0.500 mL of chloroform was added and the solution was stirred vigorously. The reaction was conducted for a minimum of 17 hours. The resulting copolymer was characterized by ^{1}H NMR spectrocopy(Figure S21 and S22). The unsaturated copolymer was then dissolved in a 1:1 chloroform/methanol cosolvent (20 mL) forming a yellow solution. The slurry polymer solution and Crabtree's catalyst (0.0040 mmol) were combined in a Parr reactor and sealed. It was pressurized to 600 psig hydrogen and then vented down to 50 psig. This process was repeated twice more to purge the reactor of air, then pressurized to 600 psig and heated to 55 °C with stirring. After 17 hours, it was cooled, vented and the slurry polymer mixture was dried under vacuum at 90 °C furnishing a yellow solid.

The resulting copolymer showed very poor solubility in common organic solvents. For this reason, solvent-evaporation casting could not be performed. The membranes were prepared in a Carver-Press (4120 Hydraulic Unit Carver press and stainless steel die molds, Teflon protective sheets from American Durafilm, 150 °C with 500 psig pressure for 5 min), but the resulting membranes were very hydrophobic. No water or methanol uptake was observed even at 80 °C. There was no evidence to support that the anions can be exchanged by immersing the membranes in 1 M KOH aqueous solution, and the ionic conductivities were determined to be <1 mS/cm. The TGA trace of the copolymer was shown in Figure S23.

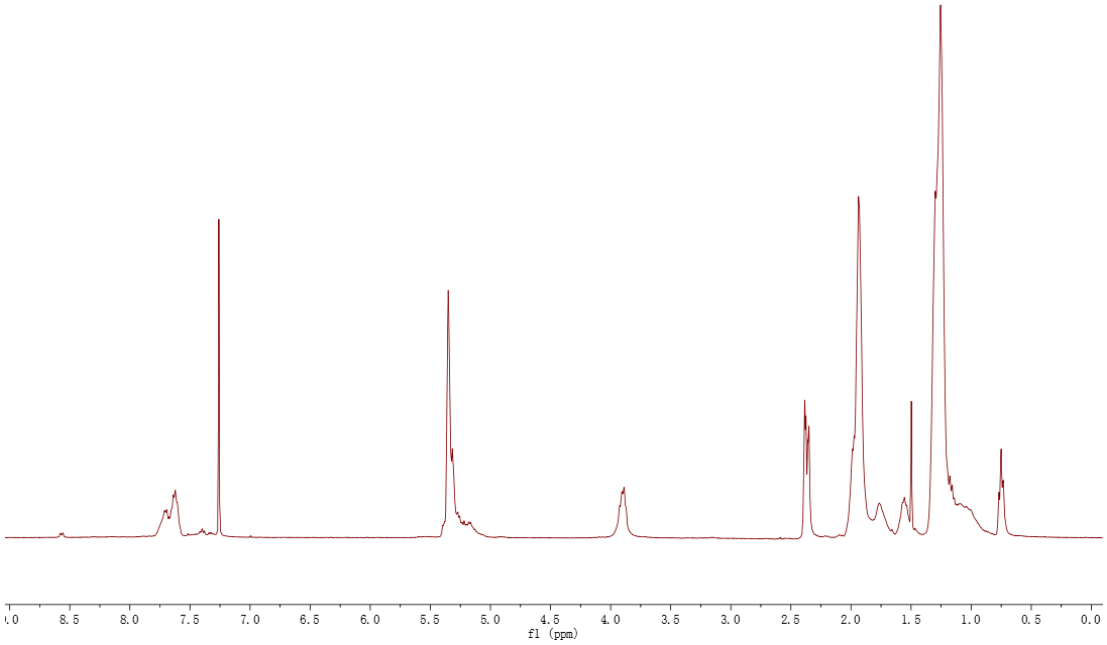


Figure S21. ^{1}H NMR spectra of COE and **1** copolymerization

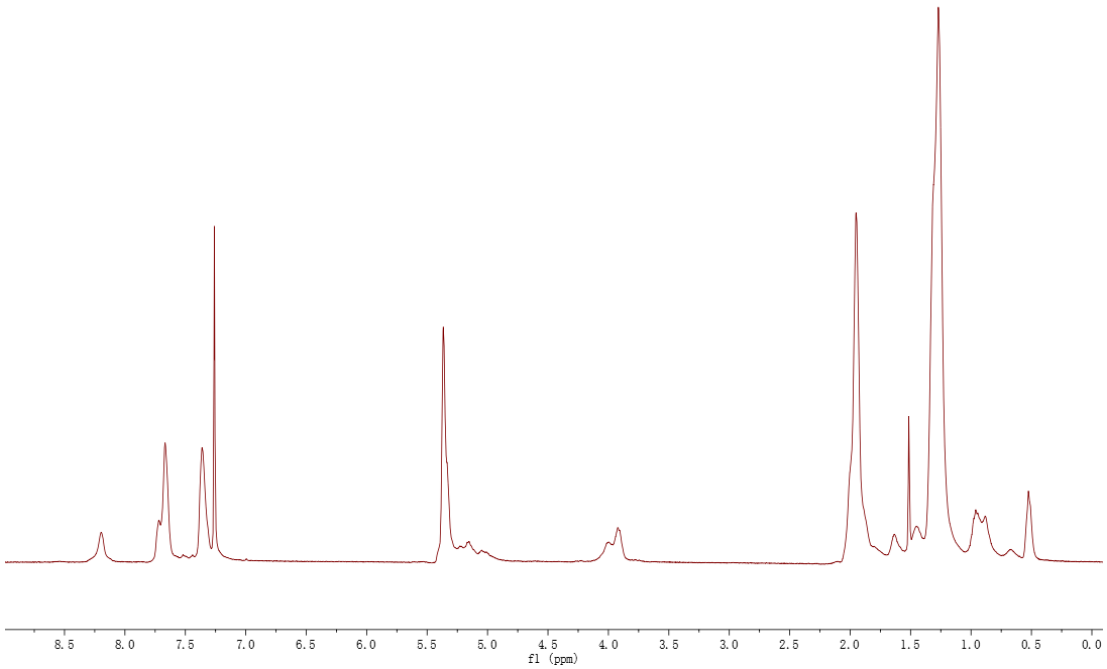


Figure S22. ^{1}H NMR spectra of COE and **2** copolymerization

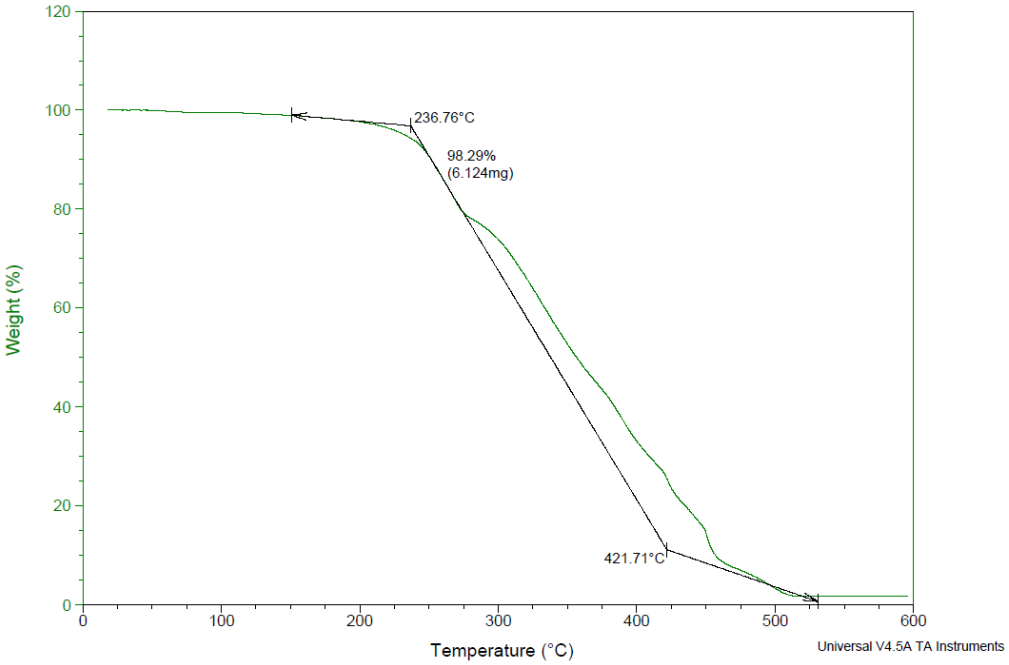


Figure S23. TGA trace of COE and **2** copolymer

^{1}H NMR Study of Imidazolium Monomer 3/COE Copolymerization

Under a nitrogen atmosphere monomer **3** (0.0250 mmol) and COE (0.0500 mmol, or polyCOE with 0.0500 mmol alkenes) were combined and dissolved in $CDCl_3$ (0.400 mL). The reaction mixture was transferred into a screw-capped NMR tube. To the NMR tube, Grubbs 2nd generation catalyst (0.00100 mmol) dissolved in 0.100 mL of $CDCl_3$ was added and the tube was sealed under N_2. At specified time points, the reactions were analyzed by ^{1}H NMR spectroscopy in order to determine the monomer conversion percentage (^{1}H NMR spectra are provided in Figures S24-S26). The monomer **3** conversion was determined by integration of 3.13-3.07 ppm (CH_2 protons in imidazolium-fused COE rings, **3** residue peak) divided by integration of 4.17-3.83 ppm (ethyl CH_2 protons in all forms of imidazolium products). The conversion data (Figure S24-S26) was summarized in Table S2 (data plots for Figure 2 in the text).

Polycyclooctene (polyCOE) was prepared according to the literature procedure.[10] Under a nitrogen atmosphere monomer COE (2.50 mmol) were mixed with Grubbs 2nd generation catalyst (0.00250 mmol) and CH_2Cl_2 (5.00 mL). The reaction was conducted for one hour at 22 °C and was quenched by the addition of 50 mL methanol. The white precipitate was collected by vacuum filtration and was dried under vacuum at 80 °C to isolate polyCOE as white solid (yield 198 mg, M_n = 54.4 kDa, $Đ$ = 1.91). Molecular weights (M_n and M_w) and molecular weight distributions ($Đ$) were determined by gel permeation chromatography (GPC). Analyses were performed using an Agilent PL-220 equipped with a RI detector. The column set (three Agilent PL-Gel Mixed B columns and one PL-Gel Mixed B guard column) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt% 3,5-di-tert-butyl-4-hydroxytoluene (BHT) at 1.0 mL/min at 150 °C. Data were measured relative to a polyethylene calibration curve (Varian and Polymer Standards Service). The GPC trace was shown in Figure S27.

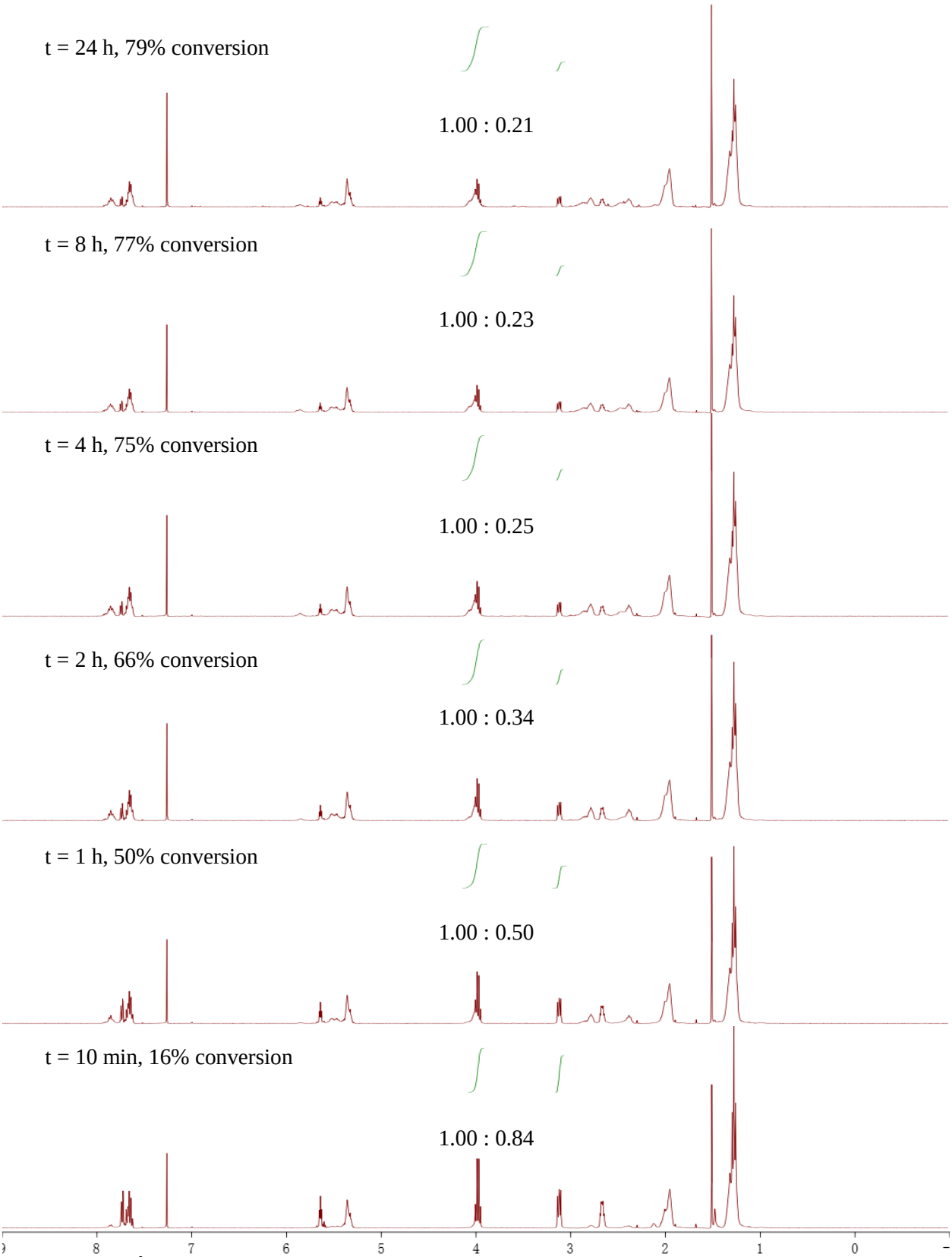


Figure S24. ^{1}H NMR spectra of **3**/COE copolymerization with Grubbs II catalyst in $CDCl_3$ solution at 22 °C ([Ru] = 0.002 M).

Figure S25. ^{1}H NMR spectra of **3** reactions with polyCOE and Grubbs II catalyst in $CDCl_3$ solution at 22 °C ([Ru] = 0.002 M).

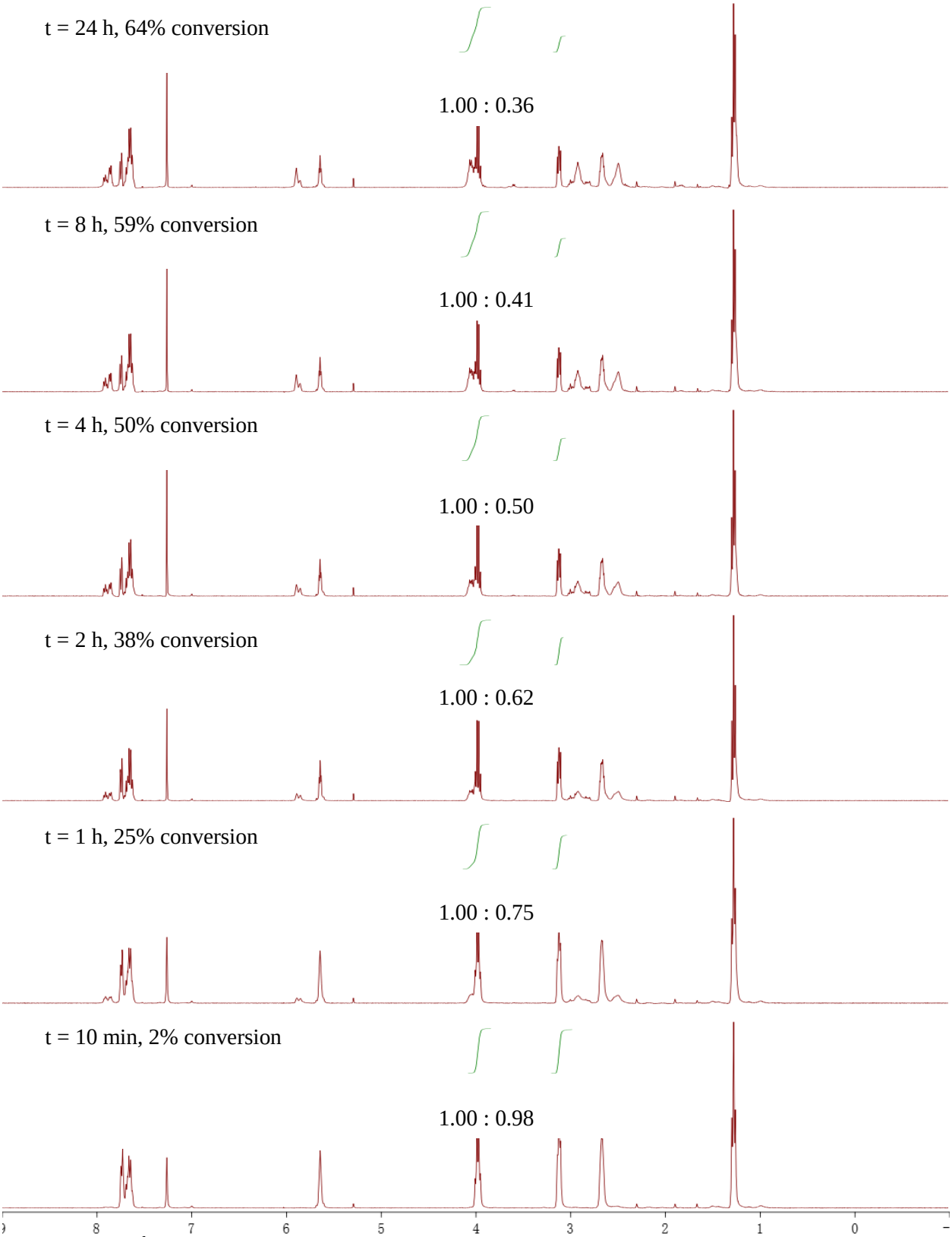


Figure S26. ^{1}H NMR spectra of **3** homopolymerization with Grubbs II catalyst in $CDCl_3$ solution at 22 °C ([Ru] = 0.002 M).

Table S2. Summary of imidazolium monomer **3** percentage conversion (^{1}H NMR study).[a]

Monomer	Monomer Conversion (%)[b]								
	10 min	20 min	30 min	1 h	2 h	4 h	6 h	8 h	24 h
COE (with **3**)	96				>99				
3 (with COE)	16	27	33	50	66	75	77	77	79
3 (with polyCOE)	11	18	27	40	69	79	80	81	82
3 (homopolymerization)	2	n.d.[c]	n.d.[c]	25	38	50	55	59	64

[a] Reaction Conditions: [Ru] = 0.002 M, [**3**] = 0.05 M, [COE] = 0.1 M or polyCOE with [alkene] = 0.1 M in $CDCl_3$ at 22 °C. [b] Percent of cation remaining, determined by ^{1}H NMR spectroscopy. [c] Not determined.

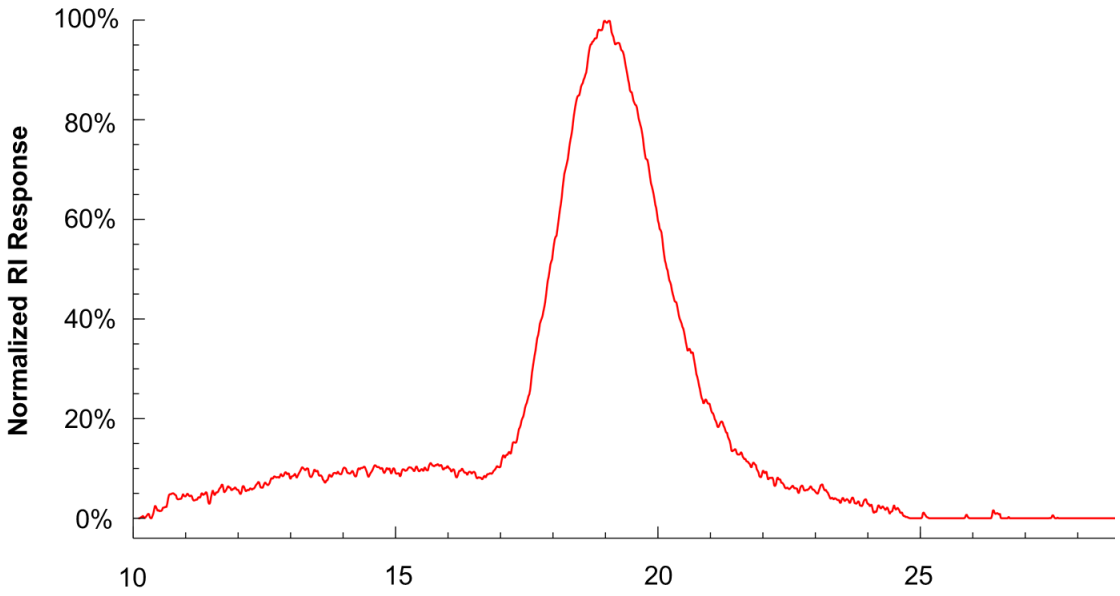


Figure S27. GPC Trace of polyCOE in 1,2,4-Trichlorobenzene at 150 °C.

The detailed ^{1}H NMR was shown and assigned in Figure S28, which is a zoom-in spectrum of "8 hour" in Figure S26. As shown in Figure S28, the monomer residue **3** was marked as black while the red arrow was pointing at all the ethyl CH_2 protons of imidazolium cations. The ratio of the two integration values designated the monomer conversion percentage. It was also proposed that the alkene protons between two imidazolium cations have higher chemical shift than the alkene protons between one imidazolium and one ring-opened COE.

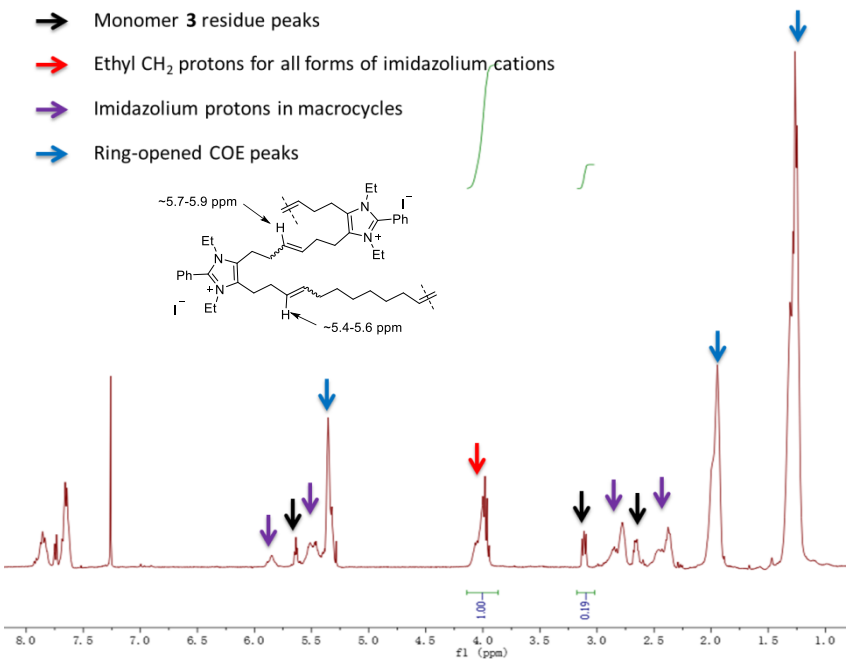


Figure S28. ^{1}H NMR spectra and proposed assignment of **3**/COE copolymerization products.

ESI-HRMS and GPC Characterization of 3/COE Copolymerization Products

The resultant reaction mixture (as NMR-tube reactions described above) was diluted in MeOH and was subjected to ESI-HRMS directly for analysis. Mass spectra were recorded in centroid mode on an Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific) equipped with a HESI II probe. The instrument was calibrated in the m/z range 100-2000 using Pierce LTQ ESI Calibration Solution (Thermo Scientific). All spectra were recorded in the positive-ion mode, using methanol in a concentration of 0.1 mg/mL as solvent. A capillary temperature of 320 °C, and ESI spray voltage of 3.9 kV, and a sheath gas flow rate of 10.00 were used. The samples were introduced into the ESI source using a syringe pump and Rheodyne valve with a 5 µL sample loop. The mobile phase used was methanol and the flow rate was set to 100 µL/min. Spectra were analyzed with Mestrenova processing software (Mestrelab Resarch; Santiago de Compostela, Spain) and reported HRMS data are within 5 ppm of the theoretical values.

Figure S29 and Figure S30 showed the ESI-HRMS results for COE/**3** copolymerization (^{1}H NMR reaction in Figure S24 after 24 h) and **3**/polyCOE reaction (^{1}H NMR reaction in Figure S25 after 24 h), respectively. The two reactions showed very similar ^{1}H NMR and ESI-HRMS results. The HRMS result of **3** homopolymerization was shown in Figure S31 with a zoomed-in spectrum of *m*/*z* 281.2-282.2. Imidazolium tetramer (n=4) was identified by HRMS, while the signals for bigger rings are much smaller.

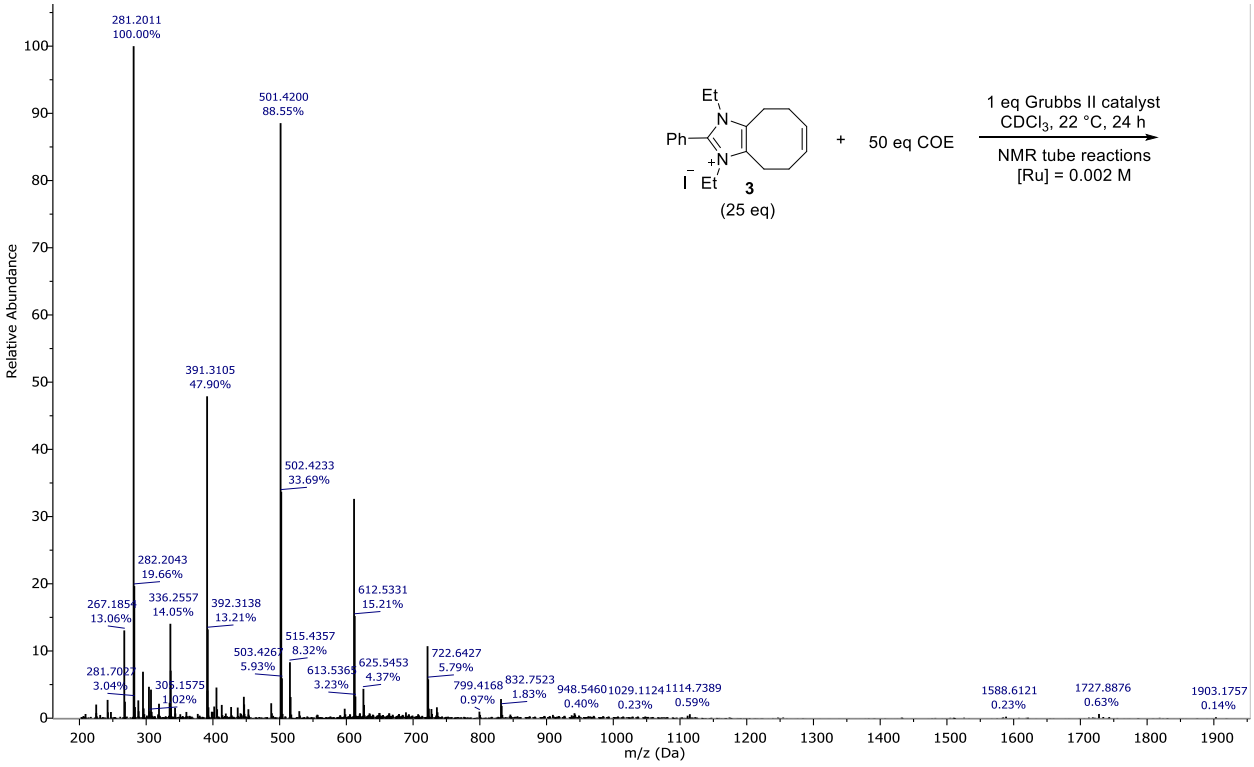


Figure S29. ESI-HRMS of **3**/COE Copolymerization

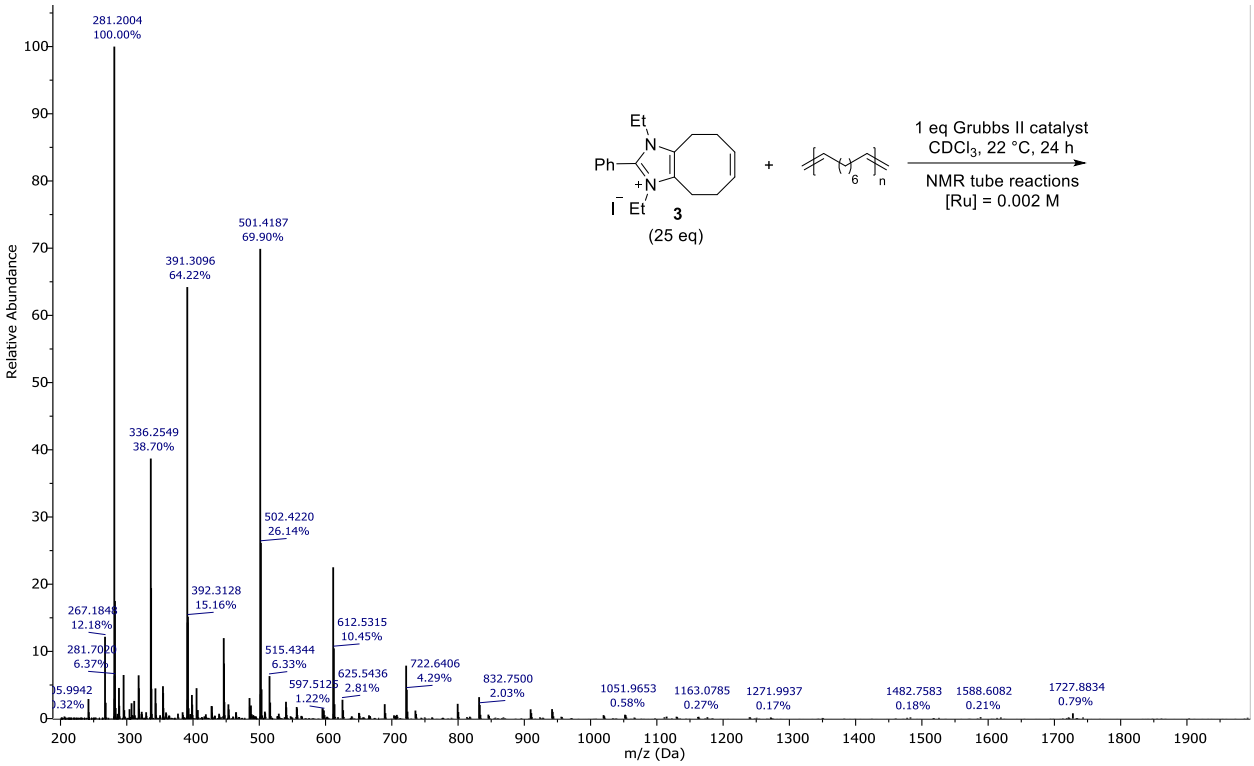


Figure S30. ESI-HRMS of **3**/polyCOE Reaction

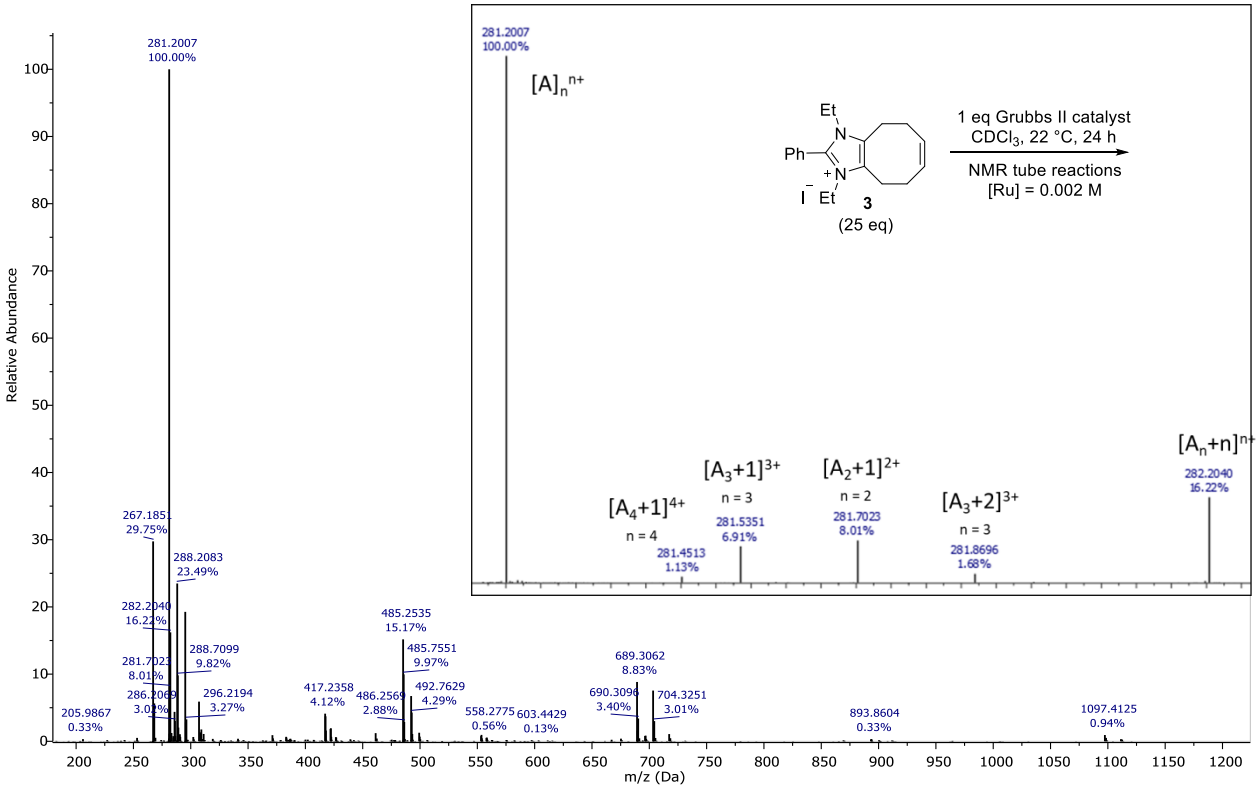
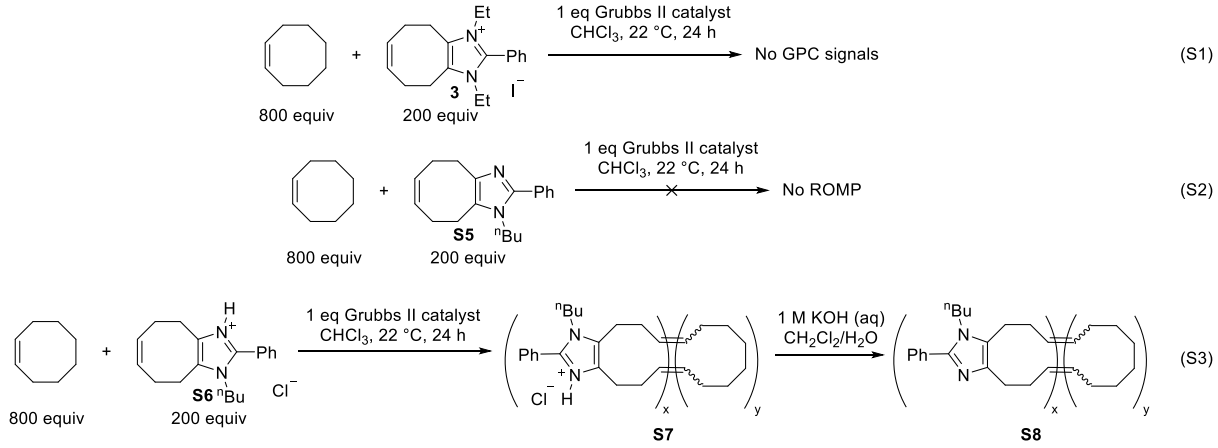
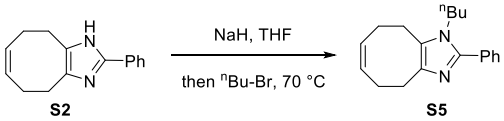


Figure S31. ESI-HRMS of **3** Homopolymerization (with 281.2-282.2 zoomed in)

Gel permeation chromatography (GPC) analyses were carried out using an Agilent 1260 Infinity GPC System equipped with a UV detector as well as an Agilent 1260 Infinity autosampler. The Agilent GPC system was equipped with two Agilent PolyPore columns (5 micron, 4.6 mm ID which were eluted with THF at 30 °C at 0.3 mL/min and calibrated using monodisperse polystyrene standards. However, the charged macromolecules showed no signals during the GPC analysis (eq S1). It was also noticed that unprotected imidazole **S5** can poison the Ru-catalyst, and the ROMP of COE did not occur (eq S2).[11] As a consequence, protonated imidazolium **S6** was used to make the macrocyclic oligomer **S7**, which was then deprotonated by base to generated the neutral product **S8** (eq S3). **S8** was determined to have M_n = 570 Da with $Đ$ = 4.54, even though its $M_{n,theo}$ = 144 kDa. The GPC trace was shown in Figure S36. This is consistent with the ESI-HRMS results.



1-Butyl-2-phenyl-4,5,8,9-tetrahydro-1*H*-cycloocta[*d*]imidazole (S5)



A modified literature procedure was used.[6] To a pre-dried 100 ml round bottom Schlenk flask was added NaH (60% in oil, 8.00 mmol, 1.60 equiv). The flask was left under vacuum for 10 min, then refilled with N_2. This process was repeated for three times, followed by addition of

15 mL THF. Then imidazole **S2** (5.00 mmol, 1.00 equiv) was added into the mixture at 22 °C under nitrogen. A pale white slurry formed after stirring under N_2 at 22 °C for 2 hours. 1-Bromobutane (8.00 mmol, 1.60 equiv) was then added. The reaction was warmed up to 70 °C, and was allowed to stir at 70 °C for 16 hours. After cooling to 22 °C, the reaction was quenched by the addition of H_2O (10 mL). The aqueous layer was extracted with Et_2O (10 mL x 3). The combined organic layers were dried with magnesium sulfate, filtered and concentrated to obtain pale yellow oil. The oil was then mixed with hexanes (10 mL) to afford white solid. The desired product **S5** was collected by vacuum filtration (1.75 g, 78% yield). Impurities such as THF and 1-bromobutane do not affect the subsequent reaction.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.49 (m, 2H), 7.45-7.32 (m, 3H), 5.65-5.53 (m, 2H), 3.3 (t, *J* = 7.8 Hz,, 2H), 3.11-3.01 (m, 2H), 2.88-2.77 (m, 2H), 2.67 (t, *J* = 6.1 Hz, 2H), 2.56-2.45 (m, 2H), 1.60 (pent, *J* = 7.7 Hz, 2H), 1.25-1.17 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

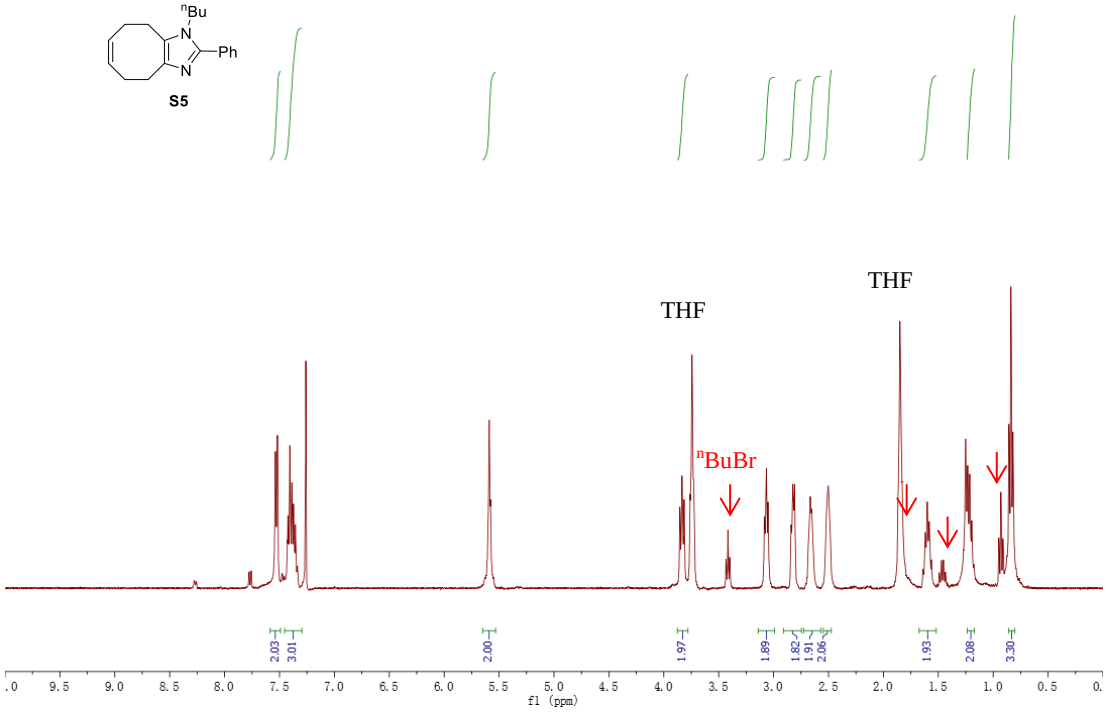
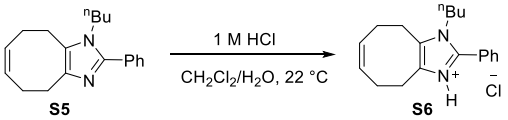


Figure S32. ^{1}H NMR Spectrum of **S5** in $CDCl_3$.

1-Butyl-2-phenyl-4,5,8,9-tetrahydro-1*H*-cycloocta[*d*]imidazol-3-ium chloride (S6)



To a pre-dried 10 ml round bottom flask was added imidazole **S5** (2.00 mmol, 1.00 equiv), CH_2Cl_2 (2.00 mL), and 1 M HCl (aq, 2.00 mL, 2.00 equiv) sequentially. The mixture was stirred vigorously at 22 °C for 4 hours, which was then dried under vacuum at 40 °C for 24 hours to afford the desired product **S6** as white solid (602 mg, 95% yield). Impurities (at 3.2 ppm, 2.5 ppm, and 1.9 ppm) do not affect the subsequent reaction.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79-7.47 (m, 5H), 5.69-5.48 (m, 2H), 3.99 (t, *J* = 7.3 Hz,, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.92-2.78 (m, 2H), 2.78-2.53 (m, 4H), 1.68 (pent, *J* = 7.8 Hz, 2H), 1.27 (hex, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

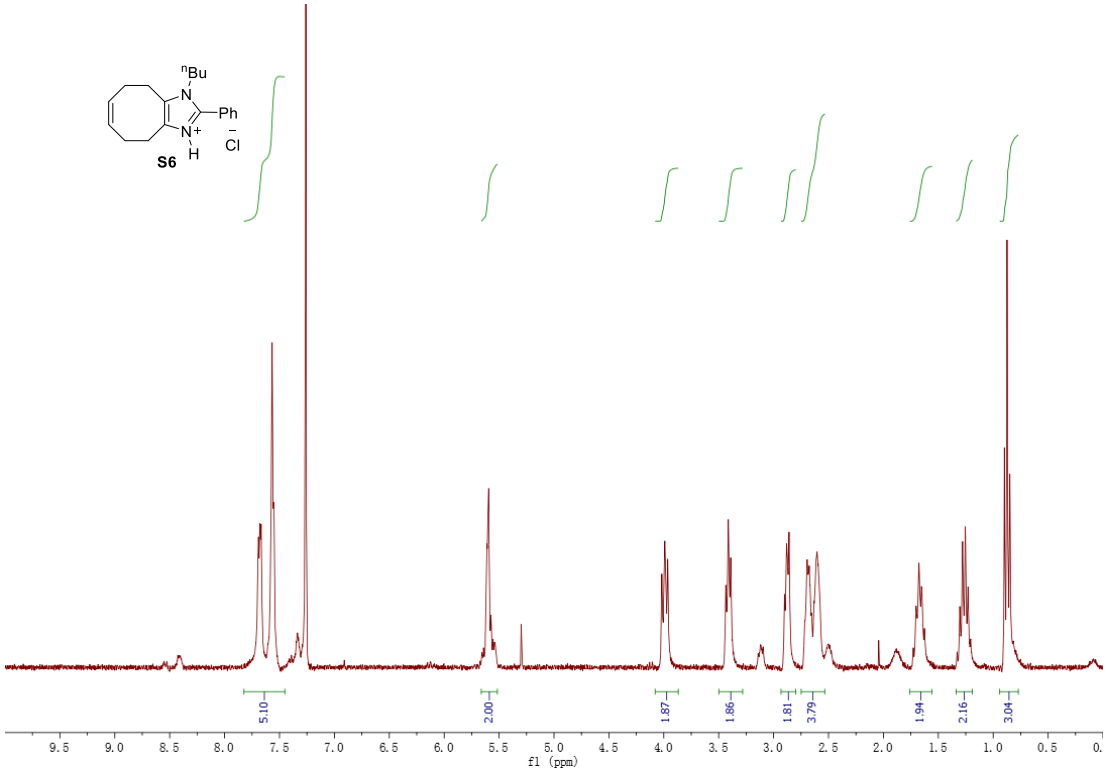
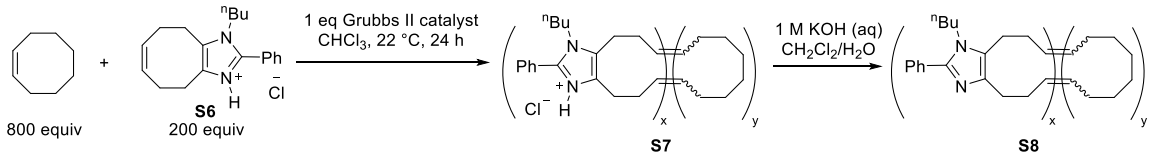


Figure S33. ^{1}H NMR Spectrum of **S6** in $CDCl_3$.

Copolymerization and Deprotonation of COE/S6



Under a nitrogen atmosphere, monomer **S6** (0.100 mmol) and COE (0.400 mmol) were dissolved in $CHCl_3$ (1.00 mL). To the reaction mixture, Grubbs' 2nd generation catalyst (0.000500 mmol) dissolved in 0.500 mL of $CHCl_3$ was added and the solution was stirred vigorously. The reaction was conducted for 24 hours and was characterized by ^{1}H NMR (**S7**, Figure S34). Polymer **S7** was dissolved in CH_2Cl_2 (2.0 mL) and was mixed with 1 M KOH (aq, 2.0 mL, excess). The mixture was stirred vigorously at 22 °C for 4 hours. After extraction with CH_2Cl_2, the combined organic layers were concentrated and dried under vacuum at 40 °C for 24 hours to afford **S8**, which was characterized by ^{1}H NMR (Figure S35) and GPC (Figure S36).

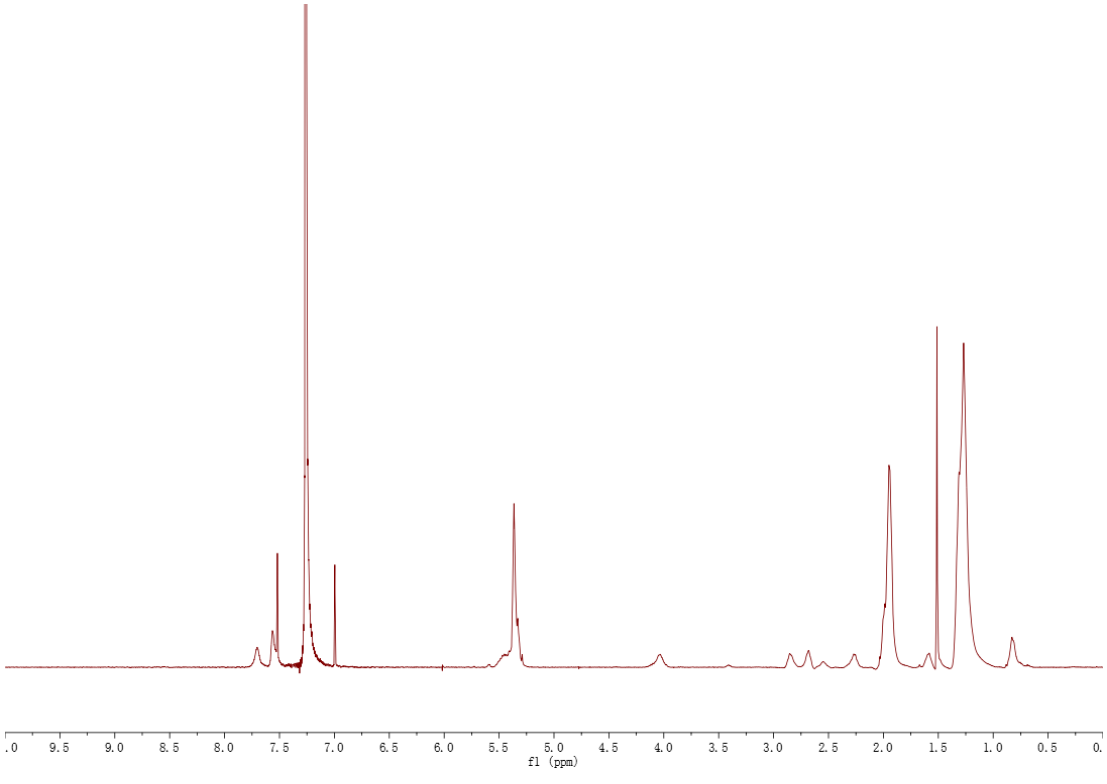


Figure S34. ^{1}H NMR Spectrum of **S7** in $CDCl_3$.

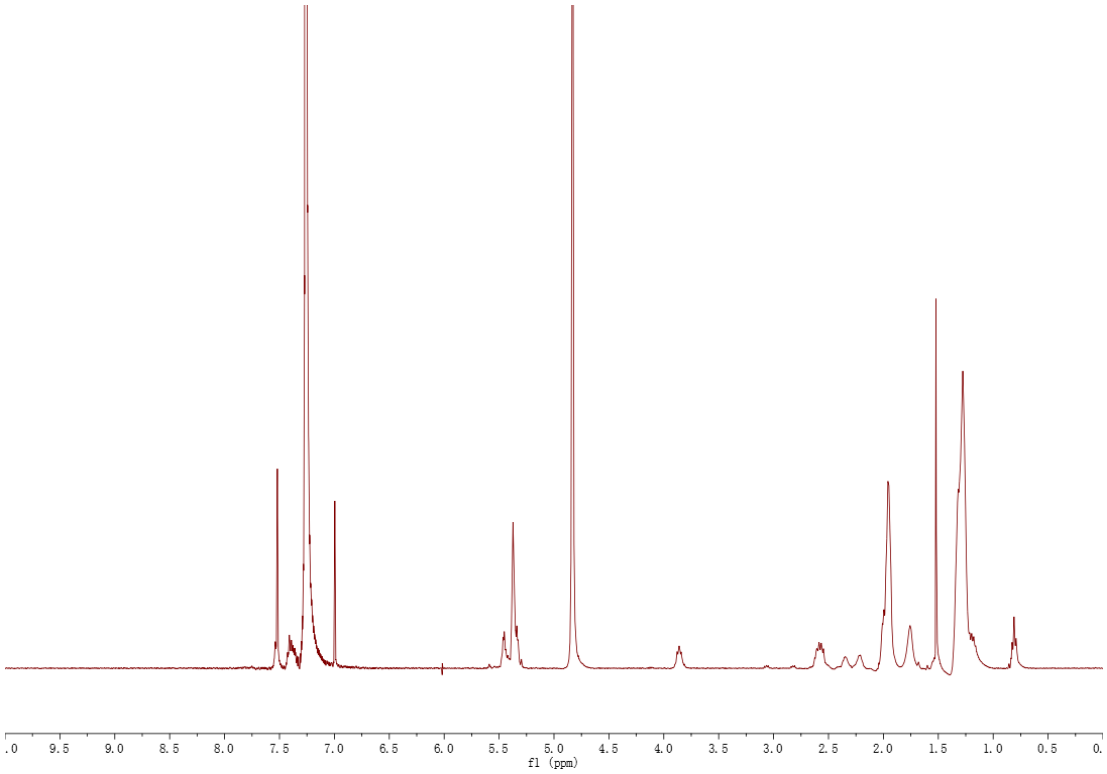


Figure S35. ^{1}H NMR Spectrum of **S8** in $CDCl_3$.

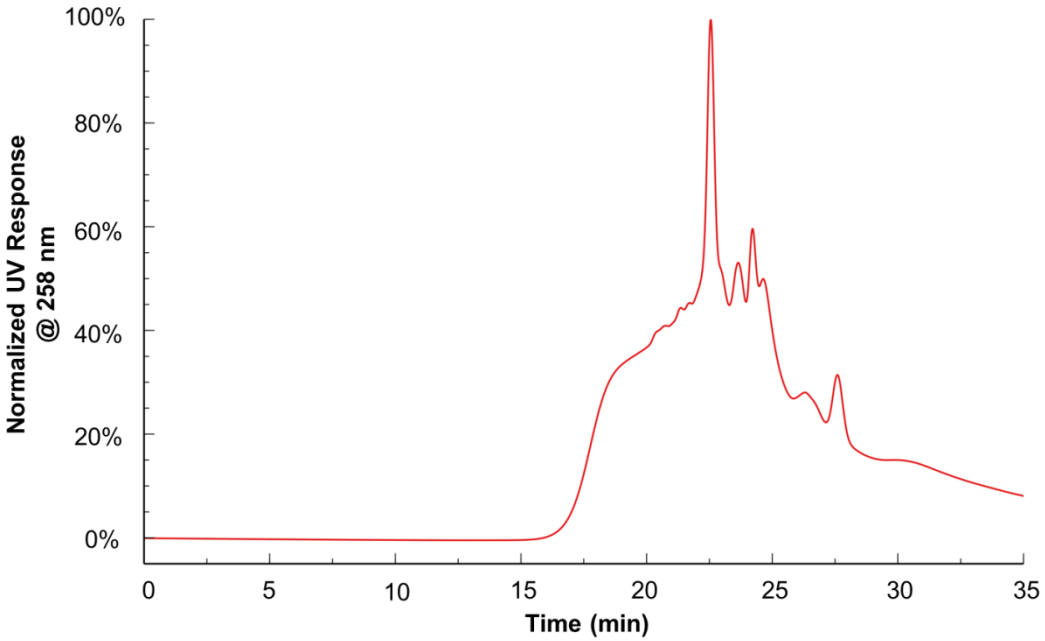


Figure S36. GPC Trace of **S8** in THF.

In Figure S34, the imidazolium butyl CH_2 peak was observed at *ca.* 4.0 ppm. After deprotonation, the chemical shift of butyl CH_2 was observed at 3.8 ppm (Figure S35), indicative a successful deprotonation reaction.

Synthesis of Crosslinked Imidazolium-Contained AAEM (AAEM-2)

In a N_2 filled glovebox, COE (0.800 mmol), **3** (0.100 mmol) and **4** (0.160 mmol) were combined and dissolved in 2 mL CH_2Cl_2. (Note: Monomer **4** has poor solubility in $CHCl_3$, so CH_2Cl_2 was used.) Grubbs' 2nd generation catalyst (0.800 mg, 0.00100 mmol) and Crabtree's catalyst (3.20 mg, 0.00400 mmol) were dissolved in 0.500 mL CH_2Cl_2 and the catalyst solution was added to the monomer solution. The mixture was stirred vigorously for five minutes to ensure homogeneity (gel was formed if stirred longer than 10 minutes), and then transferred to a flat-bottom glass dish (diameter of 5.25 cm and depth of 3.0 cm) in the glovebox. The metal dish was then sealed in a glass chamber and carefully removed from the glovebox. The glass chamber was placed on a metal plate to evaporate CH_2Cl_2 slowly at 22 °C. The pressure in the sealed chamber would build up with the evaporation of CH_2Cl_2, so the pressure was released after 2 hours and every hour afterwards. After 6 hours, the membrane was formed and it was left under N_2 at 22 °C for another 16 hours, after which the glass chamber was removed. The membrane was then removed from the dish and was heated at 60 °C for one hour to remove residue CH_2Cl_2. **AAEM-1** was prepared using similar strategies without adding monomer **3**. The ratio of COE/**3**/**4** was carefully tuned to ensure the best performance of the crosslinked membrane. The higher COE content resulted in lower conductivity, while the membranes became more fragile when ionomer content (especially crosslinker **4**) was increased.

The membrane prepared above (with the Crabtree's catalyst in the film) was placed into a Parr reactor and sealed. It was pressurized to 1000 psig hydrogen and then vented down to 600

psig. This process was repeated twice to purge the reactor of air, and then pressurized to 1000 psig. The reactor was kept at 22 °C for 2 hours and was then heated to 55 °C. After 20 hours, it was cooled, vented and the yellow membrane was obtained. The membrane was then dried at 60 °C and was soaked in deionized water for at least 24 hours prior to hydroxide ion exchange.

Table S3. Hydroxide Conductivities of **AAEM-2** at Various Temperatures [a]

Temperature (°C)	22	30	40	50	60	70	80	90
Hydroxide Conductivity (mS/cm)	37	42	51	59	64	70	71	73

[a] All samples are equilibrated for 20 min at a given temperature.

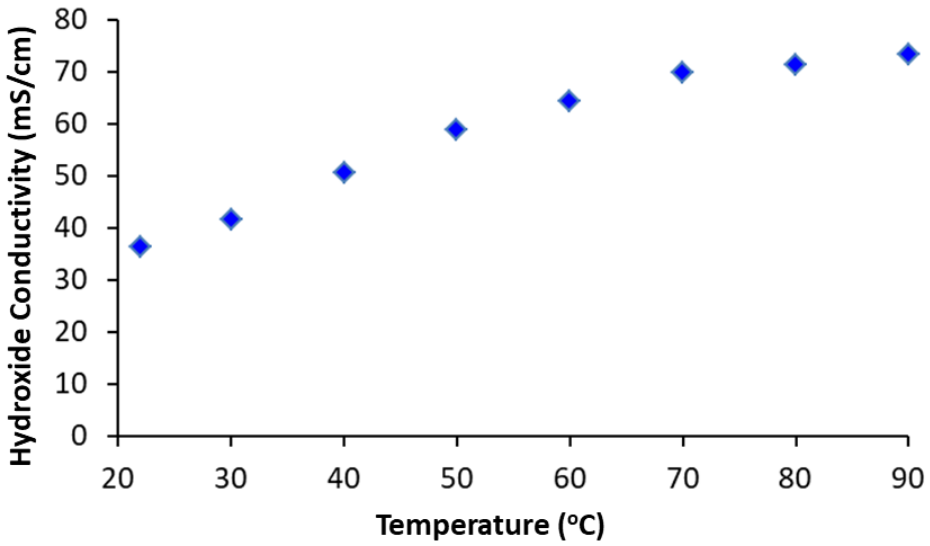


Figure S37. Hydroxide Conductivities of **AAEM-2** at Various Temperatures.

Table S4. Membrane Stability in 1 M KOH (aq) at 80 °C (data plots for Figure 4 in the text) [a]

Time (days)	0	3	7	14	21	30
Hydroxide Conductivity (mS/cm)	37	29	30	31	29	27

[a] Strips of the thin film in the chloride form (ca. 4 cm long × 0.5 cm wide) were placed in a flask containing 1 M KOH at 80 °C. The flask was maintained under N_2 to ensure the alkaline concentration unchanged. At specified time intervals, membrane strips were re-exchanged with 1 M KOH (typical procedure with a 2 h exchange), washed with water to remove any residual base and the in-plane hydroxide conductivity measured at 22 °C.

Polymer melting points (T_m) were measured by differential scanning calorimetry (DSC) using a Mettler Polymer DSC. **AAEM-2** sample (hydroxide form) was heated under nitrogen from -70 °C to 200 °C at a rate of 10 °C per minute and then cooled to -70 °C at a rate of 10 °C per minute, followed heating to 200 °C at a rate of 10 °C per minute. The T_m was recorded from the second heating run (95 °C). Glass transition temperatures were not observed for **AAEM-2**. The DSC traces (first cool and second heat) of **AAEM-2** (hydroxide form) were shown in Figure **S38**. The TGA trace of **AAEM-2** (chloride form, fully hydrated) was shown in Figure **S39**.

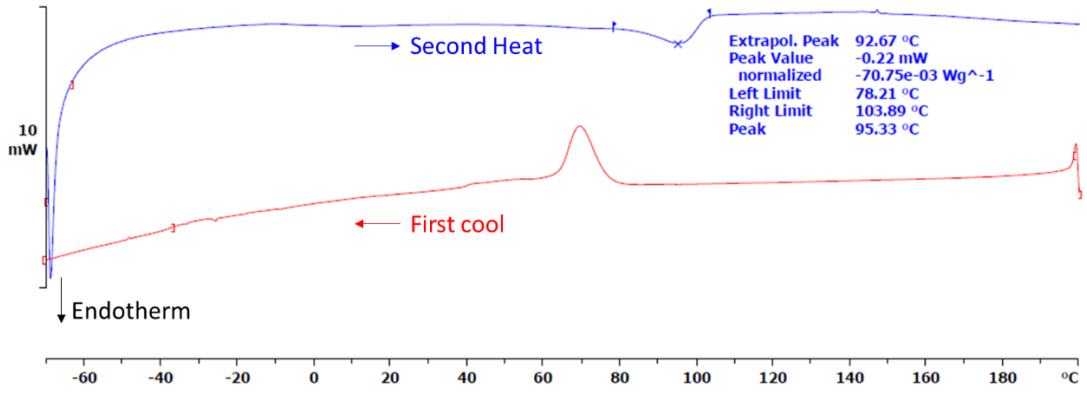


Figure S38. DSC traces (first cool and second heat) of **AAEM-2** (hydroxide form).

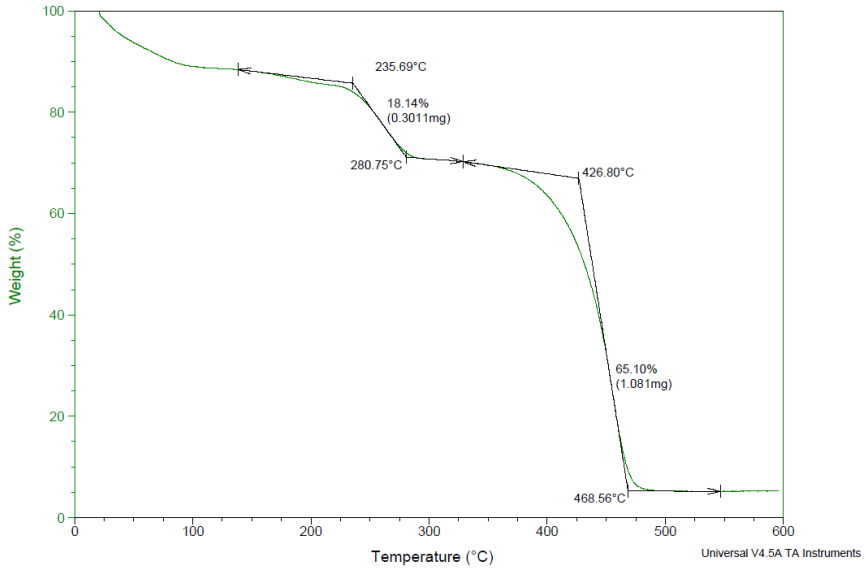


Figure S39. TGA trace of **AAEM-2** (chloride form, fully hydrated).

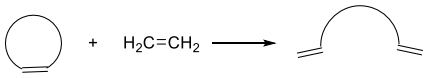
DFT Calculation of the Ring-Opening Energy

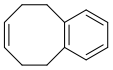
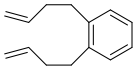
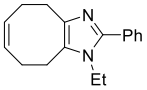
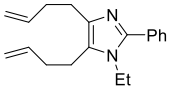
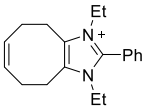
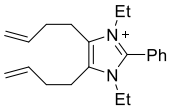
Theoretical calculations were carried out using the ORCA program package.[12] Molecular geometry optimizations were performed using the B3LYP density functional method with the def2-SVP basis set. The single point energy (SPE) was achieved after the geometry optimization, and it was used directly to calculate the ΔE for the ring-opening reaction using the equation below:

$$\Delta E = E_{open} - (E_{ring} + E_{ethylene}) \quad \text{(S4)}$$

in which the E_{open} represents the optimized SPE for the ring-opened alkenes; E_{ring} represents the optimized SPE for the cyclic alkenes; and $E_{ethylene}$ represents the optimized SPE for ethylene. It is noteworthy that this method is a very preliminary calculation of the ring stain energies.[13] It is only used as a semi-quantitative method to estimate the ring strain difference of ring-fused COE and simple cyclic alkenes.

Table S5. DFT Calculation of Ring-Opening Energy[a]



Cyclic Monomer	Ring-Opened Diene	ΔE (kcal/mol)
		-6.9
		-1.6
		-11.5
		-6.7
		-6.0
		-7.5

[a] DFT calculation was performed with the ORCA program package and the molecular geometry were optimized using the B3LYP density functional method. The energy was calculated according to equation S4.

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