Supporting Information for:

Mechanistic Analysis of Ammonium Cation Degradation for Anion Exchange Membrane Fuel Cells

Angela D. Mohanty and Chulsung Bae

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180

Table of Contents

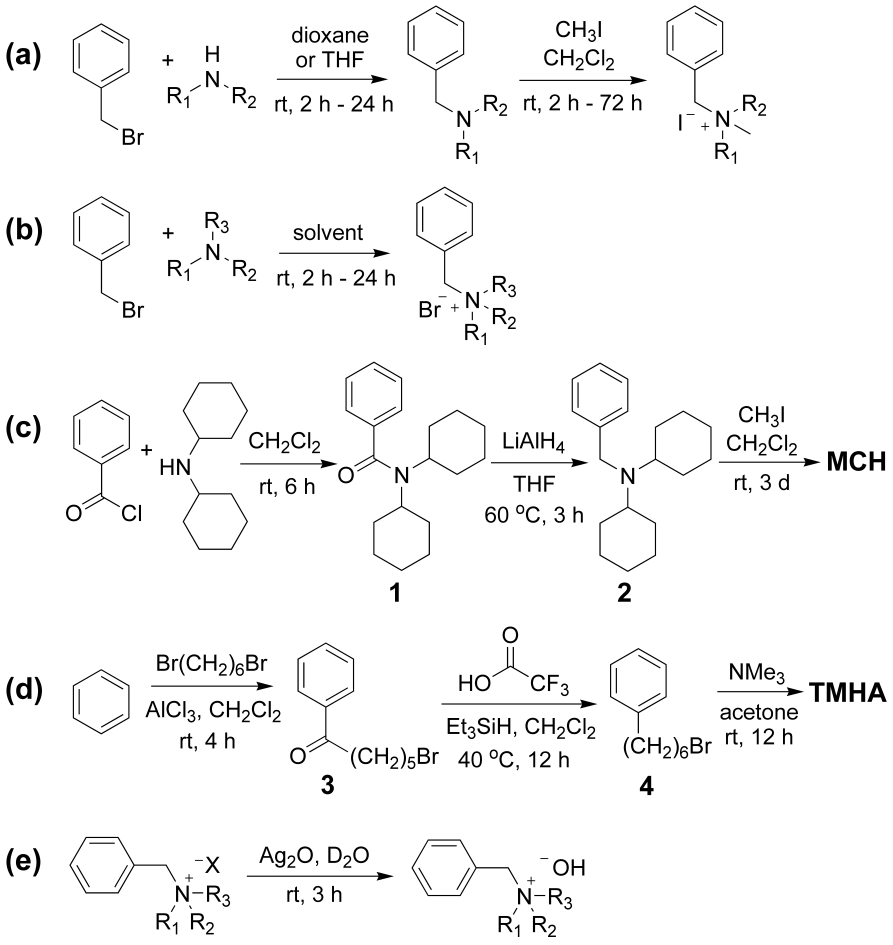


Figure S - 1: Preparation of model compounds from: (a) S_N2 reaction of secondary amine with benzyl bromide [for **TMA**, **MnPr**, **MiPr**, **TMG**], (b) Menshutkin reaction of tertiary amine with benzyl bromide [for **DABCO-1**, **MIm**, **Pyr**, **DMHA**], (c) nucleophilic addition/elimination reaction with benzoyl chloride [for **MCH**], (d) Friedel-Crafts acylation with benzene [for **TMHA**]. Scheme (e) shows Ag_2O-mediated ion exchange reaction from halide (where X = I or Br) to OH^- (or OD^-).

2. General experimental details

Unless otherwise noted, all reagents were purchased from Alfa Aesar, Acros Organics, or Sigma Aldrich and were used without further purification. Solvents (dioxane, dichloromethane, diethyl ether, chloroform, acetone, ethyl acetate, hexanes, toluene, and methanol) were reagent grade and used as received. Anhydrous tetrahydrofuran (THF) was obtained from Acros Organics and stored in a nitrogen-filled glovebox. Deuterated chloroform ($CDCl_3$) and deuterium oxide (D_2O) were purchased from Cambridge Isotope Laboratories, Inc.

All synthetic reactions were conducted in vials fitted with Teflon-lined screw cap under air unless otherwise noted. Reactions involving amine synthesis were monitored by thin-layer chromatography (TLC) using Baker-flex silica gel IB-F (2.5 x 7.5 cm) plates and were visualized by UV light. Flash column chromatography was performed with silica gel 60 (70-230 mesh ASTM).

^{1}H NMR spectra were obtained with a Varian Unity 500 MHz spectrometer. ^{13}C and 2D-NMR spectra were obtained with a Bruker 600 MHz (14.1 Tesla) spectrometer. All NMR spectra were recorded at 25 °C and chemical shifts were referenced to solvent residue peak $CDCl_3$ (at 7.26 ppm) or 18-crown-6 ether internal standard (at 3.71 ppm in D_2O) and were recorded using 5 second relaxation delay. NMR spectra were processed with MestReNova 8.1 (Mestrelab Research SL) software.

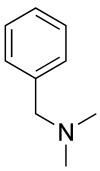
GC-MS analysis was conducted with a Shimadzu GC-2010 equipped with a ZB-XLB column (30 m x 0.25mm ID x 0.25 μm film) and a Shimadzu GC-MS-QP2010S detector. The temperature for each run was ramped from 40 to 250 °C at 20 °C/min, and held at 250 °C for 40 min.

3. QA-model compounds via 2° amine S_N2 reaction with benzyl bromide

General procedure for methylation of amines

Methylation was performed according to modified literature procedures.[1,2] To a 20 mL vial was added a synthetically prepared benzylamine (1 mmol, 1 equiv) and dichloromethane (1 mL per mmol of amine). Chilled methyl iodide (3 mmol, 3 equiv based on amine) was added all at once. The reaction was stirred at rt for a specified amount of time. After completion of the reaction, the resulting white precipitate was filtered and rinsed with cold dichloromethane (3 x 5 mL), unless otherwise noted. The resulting quaternized-benzylammonium iodide was collected and vacuum dried.

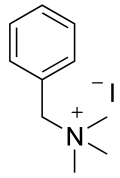
Preparation of *N*,*N*-dimethylbenzylamine



A 40 mL vial containing dioxane (10 mL) and benzyl bromide (5.00 g, 29.2 mmol) was cooled in an ice bath. Dimethylamine solution (40 wt% in H_2O, 5.90 mL, 117 mmol) was slowly added. After stirring in the ice bath for 2 h, the reaction was quenched with 0.5 M $NaHCO_3$ (10 mL)

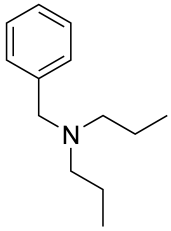
and water (10 mL), and extracted with diethyl ether (4 x 25 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator to yield a colorless liquid (0.61 g, 15 % yield). Spectral analysis (NMR Figure S2a) matched with literature reports.[3]

Preparation of *N*,*N*,*N*-trimethylbenzylammonium iodide (TMA)



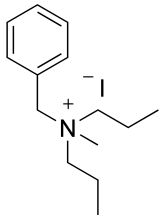
The reaction was performed according to the general procedure for methylation of amines on a 2.2 mmol scale (0.30 g of *N*,*N*-dimethylbenzylamine). The reaction was complete in 4 h, yielding **TMA** (0.34 g, 56 % yield). NMR Figure S2b.

Preparation of *N*,*N*-dipropylbenzylamine



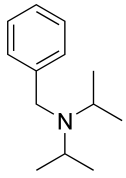
To a 40 mL vial was added THF (12 mL) and benzyl bromide (5.00 g, 29.2 mmol). Dipropylamine (6.01 mL, 43.8 mmol) was added all at once. After stirring at rt for 20 h, the reaction was quenched with 0.5 M $NaHCO_3$ (10 mL) and water (10 mL), and extracted with diethyl ether (4 x 25 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator to yield a yellow oil (5.19 g, 92 % yield). NMR Figure S3a.

Preparation of *N*-methyl-*N*,*N*-dipropylbenzylammonium iodide (MnPr)



The reaction was performed according to the general procedure for methylation of amines on a 8.8 mmol scale (1.70 g of *N*,*N*-dipropylbenzylamine). The reaction was complete in 2 h, yielding **MnPr** (1.17 g, 40 % yield). NMR Figure S3b.

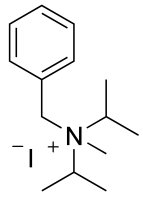
Preparation of *N*,*N*-diisopropylbenzylamine



The reaction was performed according to a modified literature procedure.[4] To a 40 mL vial was added dioxane (7 mL), benzyl bromide (3.00 g, 17.5 mmol), and potassium iodide (0.29 g, 1.75 mmol). Diisopropylamine (4.9 mL, 35 mmol) was added all at once. After stirring at rt for 5 days, the reaction was quenched with 0.5 M $NaHCO_3$ (10 mL) and water (10 mL), and extracted

with diethyl ether (4 x 20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator to yield a yellow liquid (2.40 g, 71 % yield). Spectral analysis (NMR Figure S4a) matched with literature reports.[4]

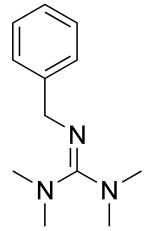
Preparation of *N*-methyl-*N*,*N*-diisopropylbenzylammonium iodide (MiPr)



The reaction was performed according to the general procedure for methylation of amines on a 7.28 mmol scale (1.40 g of *N*,*N*-diisopropylbenzylamine). The reaction was complete in 3 days, yielding **MiPr** (0.38 g, 16 % yield). NMR Figure S4b.

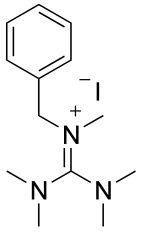
4. QA-model compounds via 3° amine Menshutkin reaction with benzyl bromide

Preparation of 2-benzyl-1,1,3,3-tetramethylguanidine



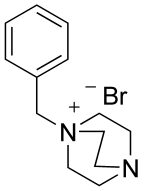
To a 40 mL vial was added THF (20 mL) and benzyl bromide (5.00 g, 29.2 mmol). 1,1,3,3-Tetramethylguanidine (7.3 mL, 58 mmol) was added all at once. After stirring at rt for 4 h, the reaction was quenched with 0.5 M $NaHCO_3$ (10 mL) and water (10 mL), and extracted with diethyl ether (4 x 20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator to yield a colorless liquid (1.31 g, 22 % yield). NMR Figure S5a.

Preparation of 2-benzyl-2-methyl-1,1,3,3-tetramethylguanidinium iodide (TMG)



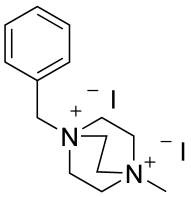
The reaction was performed according to the general procedure for methylation of amines on a 1.23 mmol scale (0.25 g of 2-benzyl-1,1,3,3-tetramethylguanidine). After 5 h, the reaction was poured into excess diethyl ether to precipitate a white solid, yielding **TMG** (0.43 g, 100 % yield). Spectral analysis (NMR Figure S5b) matched with literature reports.[5]

Preparation of 1-benzyl-1,4-diazabicyclo[2.2.2]octane (DABCO-1)



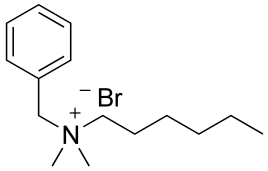
To a 40 mL vial was added dioxane (20 mL) and benzyl bromide (3.00 g, 17.5 mmol). 1,4-Diazabicyclo[2.2.2]octane (DABCO, 2.95 g, 26.3 mmol) was added all at once, resulting in the immediate formation of a white precipitate. After stirring at rt for 2 h, the reaction mixture was filtered and the white solid was rinsed with dioxane (3 x 15 mL). The white solid was collected and vacuum dried to yield **DABCO-1** (3.30 g, 67 % yield). NMR Figure S6a.

Preparation of 1-benzyl-4-methyl-1,4-diazabicyclo[2.2.2]octane (DABCO-2)



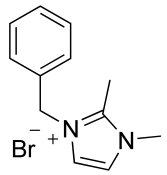
The reaction was performed according to the general procedure for methylation of amines on a 3.5 mmol scale (1.00 g of **DABCO-1**). The reaction was complete in 4 h, yielding **DABCO-2** (0.80 g, 48 % yield). NMR Figure S6b.

Preparation of *N*,*N*-dimethyl-*N*-hexylbenzylammonium bromide (DMHA)



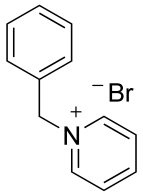
To a 20 mL vial was added THF (1 mL) and benzyl bromide (0.50 g, 2.92 mmol). *N*,*N*-dimethylhexylamine (0.76 mL, 4.38 mmol) was added all at once, resulting in formation of a white solution. After stirring at rt for 18 h, the reaction mixture was filtered and the white solid was rinsed with diethyl ether (3 x 5 mL). The white solid was collected and vacuum dried to yield **DMHA** (1.04 g, 100 % yield). NMR Figure S7.

Preparation of 1,2-dimethyl-3-benzylimidazolium bromide (1,2-DMIm)



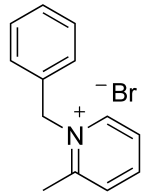
The reaction was performed according to a modified literature procedure.[6] A 20 mL vial containing chloroform (2 mL) and benzyl bromide (1.00 g, 5.85 mmol) was cooled in an ice bath. 1,2-Dimethylimidazole (0.52 mL, 5.85 mmol) was slowly added and the ice bath was removed. After stirring at rt for 12 h, the resulting white solid was filtered and washed with diethyl ether (3 x 5 mL). The white solid was collected and vacuum dried to yield **1,2-DMIm** (1.59 g, 100 % yield). Spectral analysis (NMR Figure S8) matched with literature reports.[6]

Preparation of *N*-benzylpyridinium bromide (Pyr)



The reaction was performed according to a modified literature procedure.[7] To a 20 mL vial was added toluene (3 mL) and benzyl bromide (1.00 g, 5.85 mmol). Pyridine (0.71 mL, 8.77 mmol) was added all at once. After stirring at rt for 24 h, the reaction mixture was filtered and the collected off-white solid was rinsed with diethyl ether (3 x 5 mL). The off-white solid was vacuum dried to yield **Pyr** (1.39 g, 95 % yield). Spectral analysis (NMR Figure S9) matched with literature reports.[7]

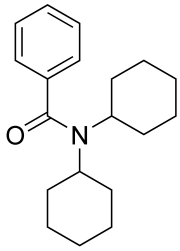
Preparation of 1-benzyl-2-methylpyridinium bromide (2MPyr)



The reaction was performed according to a modified literature procedure.[7] To a 20 mL vial was added toluene (3 mL) and benzyl bromide (1.00 g, 5.85 mmol). 2-Methylpyridine (0.87 mL, 8.77 mmol) was added all at once. After stirring at rt for 24 h, the reaction mixture was filtered and the collected off-white solid was rinsed with diethyl ether (3 x 5 mL). The pale yellow solid was vacuum dried to yield **2MPyr** (0.88 g, 57 % yield). NMR Figure S10.

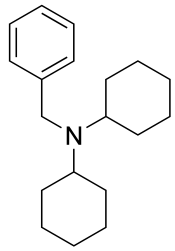
5. MCH and TMHA prepared via 3-step synthetic routes

Preparation of *N*,*N*-dicyclohexylbenzamide (1)



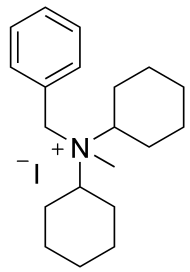
The reaction was followed according to a modified literature procedure.[8] In a two-neck 100 mL round bottom flask, dichloromethane (40 mL) and benzoyl chloride (6.00 g, 42.7 mmol) were added under nitrogen atmosphere. After cooling in an ice bath, dicyclohexylamine (11.0 mL, 55.0 mmol) was added dropwise. The ice bath was removed and the reaction was stirred at rt for 6 h. The reaction was then quenched with 1 M NaOH (10 mL) and water (20 mL), and extracted with dichloromethane (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator to yield a yellow oil. The crude product was purified with column chromatography by eluting with 15 % ethyl acetate in hexanes. The purified amide **1** was isolated as an off-white solid (12.70 g, 100 % yield). NMR Figure S11a.

Preparation of *N*,*N*-dicyclohexylbenzylamine (2)



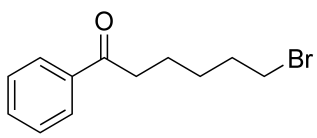
Reduction of the amide **1** was performed according to modified literature procedures.[8-10] In a nitrogen-filled glovebox, lithium aluminum hydride (3.02 g, 79.6 mmol), anhydrous THF (75 mL), and a magnetic stirring bar were added into a two-neck 250 mL round bottom flask. The flask was removed from the glovebox, fitted with a reflux condenser under nitrogen atmosphere, and cooled in an ice bath. A solution of *N*,*N*-dicyclohexylbenzamide (12.70 g, 44.2 mmol) in anhydrous THF (75 mL) was added to the reaction dropwise. The ice bath was removed and the reaction was stirred at 60 °C for 3 h, then at rt for 19 h. The reaction was then cooled in an ice bath and ethyl acetate (2 mL) followed by water (20 mL) were slowly added. After stirring at rt for 30 min the reaction was quenched with 0.5 M $NaHCO_3$ (10 mL), resulting in formation of insoluble inorganic solids. The solids were removed by filtration and extracted with diethyl ether (4 x 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator to yield **2** as a white sticky solid (11.06 g, 92 % yield). NMR Figure S11b.

Preparation of *N*-methyl-*N*,*N*-dicyclohexylbenzylammonium iodide (MCH)



The reaction was performed according to the general procedure for methylation of amines on a 7.3 mmol scale (2.0 g of *N*,*N*-dicyclohexylbenzylamine). The reaction was complete in 3 days, yielding **MCH** (0.83 g, 27 % yield) as a white solid. NMR Figure S11c.

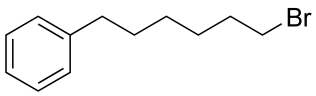
Preparation of 6-bromo-1-phenyl-1-hexanone (3)



The reaction was performed according to modified procedures.[11,12] A 100 mL round-bottom flask containing benzene (1.00 g, 12.8 mmol), 6-bromohexanoyl chloride (2.94 mL, 19.2 mmol) and dichloromethane (10 mL) under nitrogen atmosphere was cooled in an ice bath. Aluminum chloride ($AlCl_3$, 2.60 g, 19.2 mmol) was added all at once, causing the reaction to turn yellow. After removing the ice bath and stirring the reaction at rt for 4 h, the reaction was poured into ice water. The product was extracted with

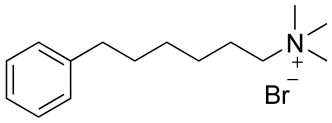
dichloromethane (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator to yield a viscous yellow liquid (4.61 g). Product **3** was used for the preparation of **4** without further purification. NMR Figure S12a.

Preparation of 1-bromo-6-phenylhexane (4)



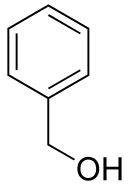
The reaction was performed according to a modified procedure.[12] In a nitrogen-filled glovebox, **3** (4.50 g, 17.7 mmol), anhydrous dichloromethane (85 mL), anhydrous trifluoroacetic acid (13.5 mL, 177 mmol), and a magnetic stirring bar were added into a two-neck 250 mL round bottom flask. The flask was removed from the glovebox and fitted with a reflux condenser under nitrogen atmosphere. Triethylsilane (14.1 mL, 88.6 mmol) was then added using a syringe in 5 mL portions. After stirring at 40 °C for 12 h, the reaction was quenched with 0.5 M $NaHCO_3$ (10 mL) followed by 0.5 M NaOH (10 mL), and extracted with dichloromethane (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude product was purified with column chromatography by eluting with 9 % dichloromethane in hexanes, and then dried under reduced pressure (150 mtorr, 70 °C) to remove silane byproducts. Purified **4** was isolated as a colorless liquid (2.26 g, 74 % yield). NMR Figure S12b.

Preparation of *N*,*N*,*N*-trimethyl-6-phenylhexylaminium bromide (TMHA)



To a 5 mL vial was added acetone (0.5 mL) and compound **4** (0.45 g, 1.88 mmol). Trimethylamine 45 % w/w aqueous solution (0.48 g, 5.63 mmol) was added all at once, resulting in formation of a white precipitate. After stirring at rt for 12 h, the reaction mixture was filtered and the collected white solid was rinsed with acetone (3 x 5 mL). The white solid was vacuum dried to yield **TMHA** (0.16 g, 29 % yield). NMR Figure S12c.

6. Preparation of benzyl alcohol



In a nitrogen-filled glovebox, lithium aluminum hydride (0.860 g, 21.0 mmol), anhydrous THF (10 mL), and a magnetic stirring bar were added into a 50 mL round bottom flask. The flask was sealed with a rubber septum, removed from the glovebox, and cooled in an ice bath. Benzaldehyde (1.00 g, 9.40 mmol) was slowly added using a syringe under nitrogen atmosphere. After 10 min, the ice bath was removed and the reaction was stirred at rt for 3 h. The reaction was then cooled in an ice bath and water (5 mL) followed by 1 M HCl (2 mL) were slowly added. After stirring at rt for 15 min the reaction was quenched with diethyl ether (10 mL), resulting in formation of insoluble inorganic solids. The solids were collected by filtration and extracted with diethyl ether (4 x 20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator to yield a colorless liquid (1.10 g, 100 % yield). Spectral analysis Figure S13.

7. General procedure for stability analysis via Ag_2O ion exchange

To a 5 mL vial was added synthetically prepared benzylammonium iodide or bromide (0.10 g, 1 equiv) and D_2O (1.5 mL). To this vial was added silver oxide (Ag_2O, 0.13 g, 1.5 equiv). After stirring at rt for 3 h, the reaction mixture was centrifuged for 10 min to precipitate down silver halide solids. The top solution was then filtered through a tightly packed cotton plug into a vial. To this vial was added 1 drop of 18-crown-6-ether (0.45 M in D_2O), then 0.45 mL of this solution was transferred to a NMR tube which was capped and sealed with parafilm. ^1H NMR spectrum was immediately recorded (labeled as 0 h) and then the NMR tube was placed in an oil bath set at a specified temperature (40, 60, 90, or 120 °C). NMR spectra were recorded at the specified time intervals of 24, 144, 264, 432, and 672 h. Percentage of degradation was estimated based on the change in the relative intensity of the benzylic $–CH_2–$ resonance of the quaternary ammonium structure (unless otherwise stated) and the methylene resonance of 18-crown-6 internal standard (at 3.70 ppm, set to an integral ratio of 1).

8. General procedure for byproduct analysis

At the end of the stability study (i.e., after 672 h), NMR solution was transferred to a 5 mL vial. Neutral organic byproducts were extracted with $CDCl_3$ (1 mL). The $CDCl_3$ layer was separated from the D_2O layer and the organic extracts were analyzed with GC-MS, ^{1}H-, ^{13}C-, and 2D-NMR spectroscopies.

9. General procedure for stability analysis in 2 M NaOD/CD_3OD

A 2 M solution of NaOD in D_2O was prepared by diluting 1.02 mL of 40 wt% NaOD/D_2O with 4 mL CD_3OD. To a 5 mL vial was added synthetically prepared benzylammonium iodide or bromide (50 mg), 2 M NaOD/CD_3OD solution (0.5 mL), and 1 drop of 18-crown-6-ether solution (0.45 M in D_2O). After stirring the solution by vortex, 0.45 mL of the solution was transferred to a NMR tube which was subsequently capped and sealed with parafilm. ^{1}H NMR spectrum was immediately recorded (labeled as 0 h) and then the NMR tube was placed in a 90 °C oil bath. Subsequent NMR spectra were recorded at specified time intervals of 24, 144, 264, 432, and 672 h. Percentage of degradation was estimated based on the change in the relative intensity of the benzylic –CH_2– resonance of the quaternary ammonium structure and the methylene resonance of 18-crown-6 internal standard (at 3.70 ppm, set to an integral ratio of 1).

10. References

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11. NMR spectra for QA model compounds and their precursors

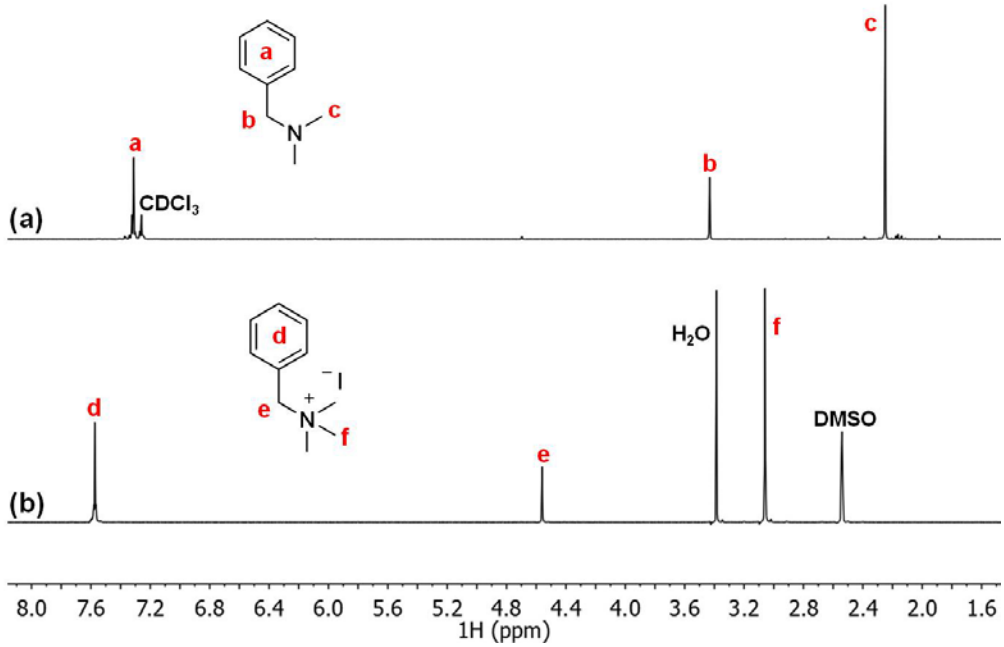

Figure S - 2: ^{1}H NMR spectra of (a) *N*,*N*-dimethylbenzylamine and (b) **TMA** in iodide form.

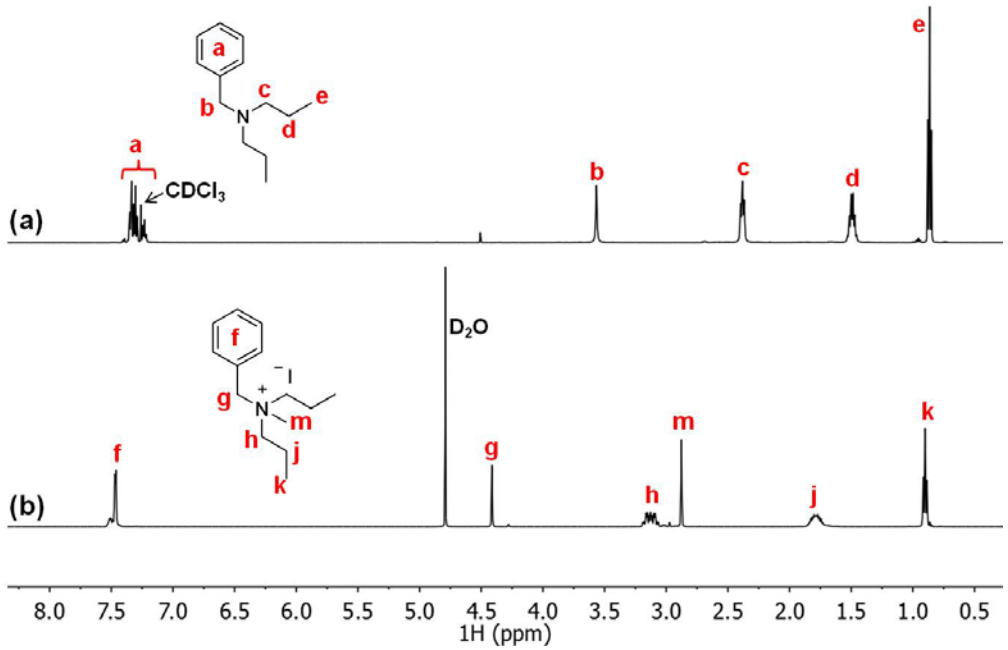

Figure S - 3: ^{1}H NMR spectra of (a) *N*,*N*-dipropylbenzylamine and (b) **MnPr** in iodide form.

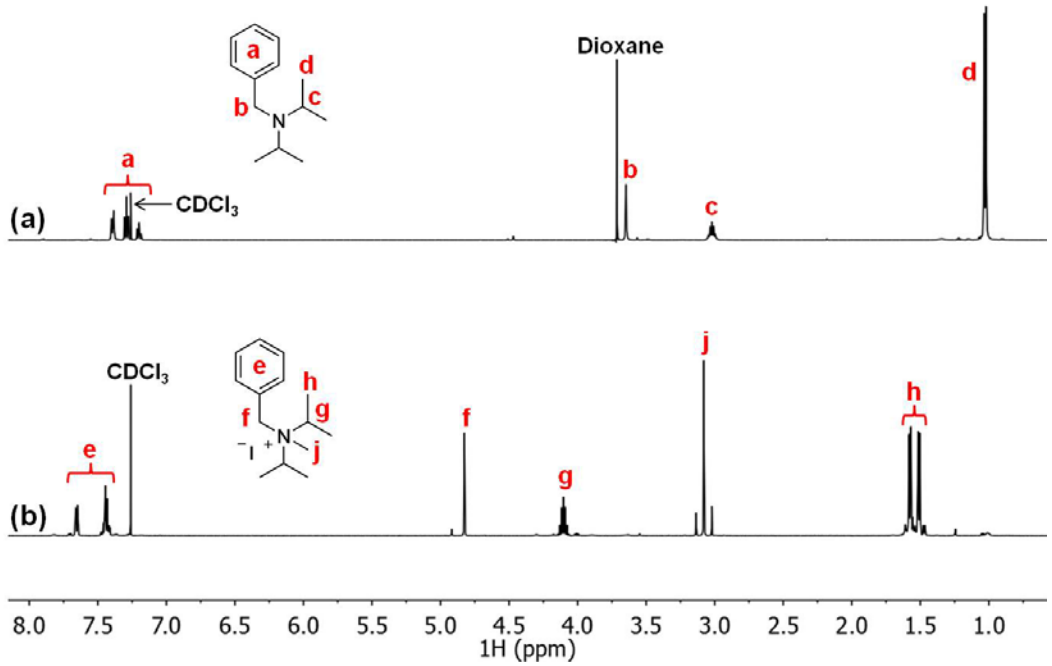

Figure S - 4: ^{1}H NMR spectra of (a) *N*,*N*-diisopropylbenzylamine and (b) **MiPr** in iodide form.

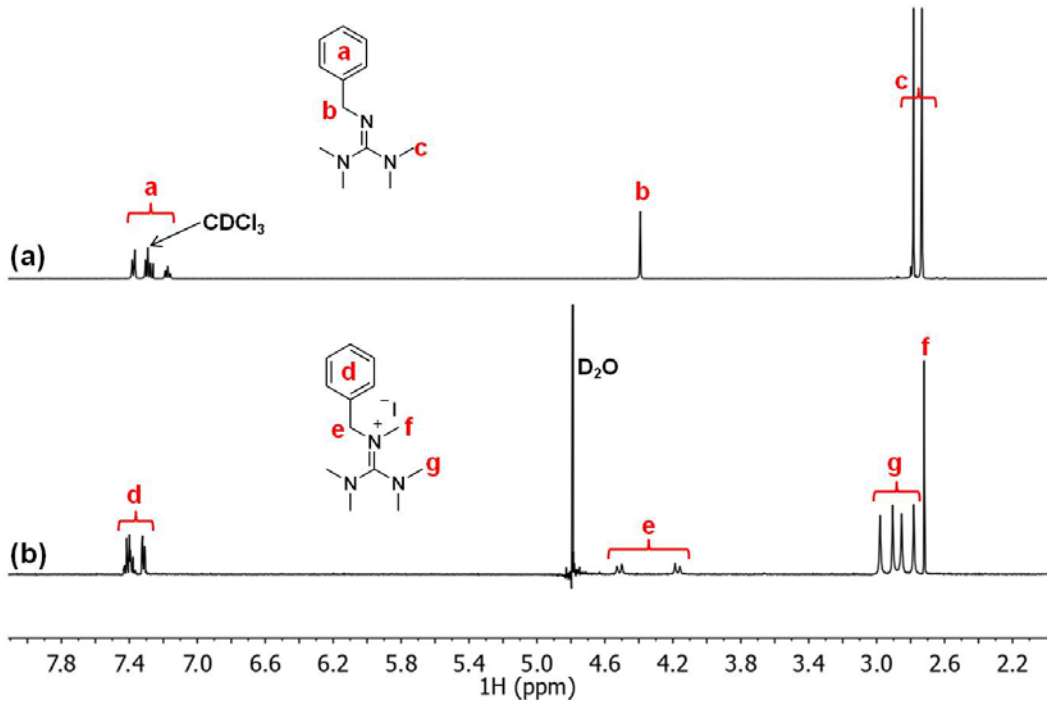

Figure S - 5: ^{1}H NMR spectra of (a) 2-benzyl-1,1,3,3-tetramethylguanidine and (b) **TMG** in iodide form.

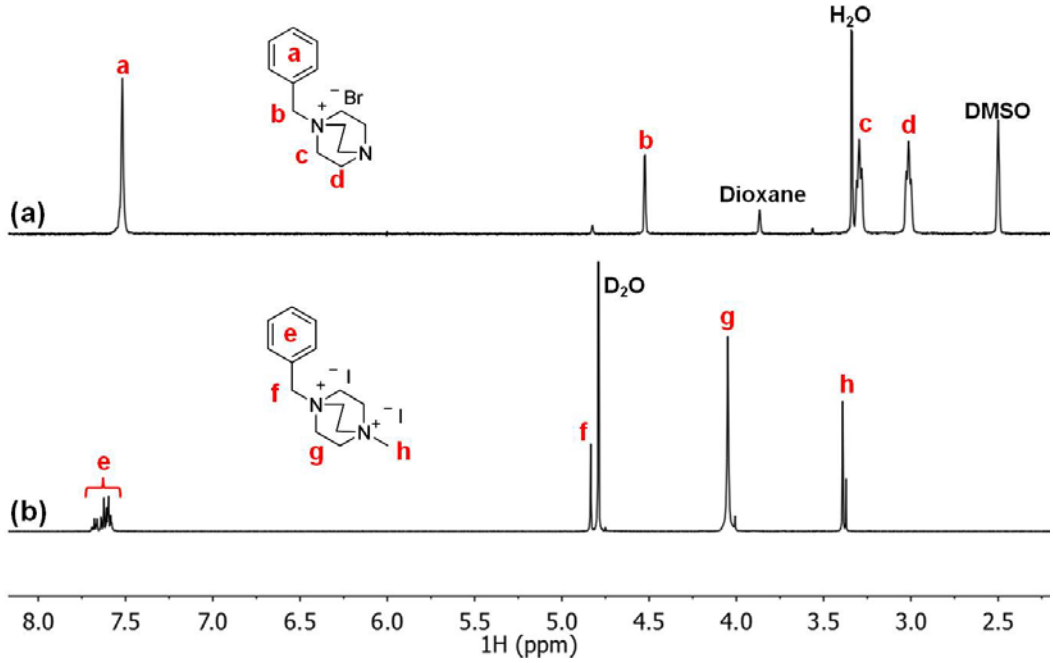

Figure S - 6: ^{1}H NMR spectra of (a) **DABCO-1** in bromide form and (b) **DABCO-2** in iodide form.

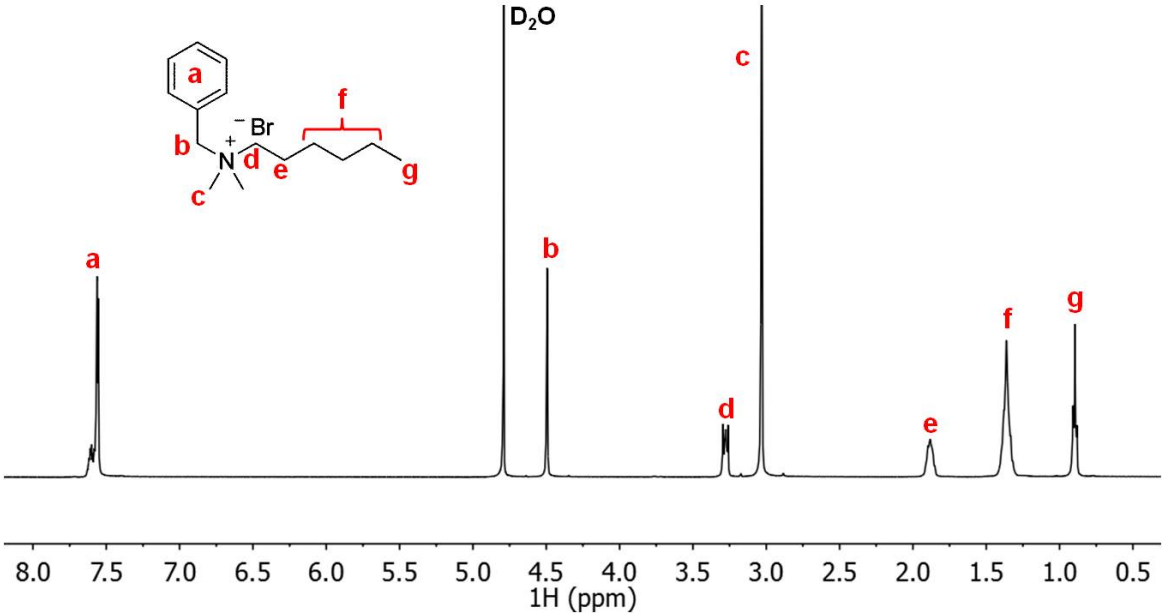

Figure S - 7: ^{1}H NMR spectrum of **DMHA** in bromide form.

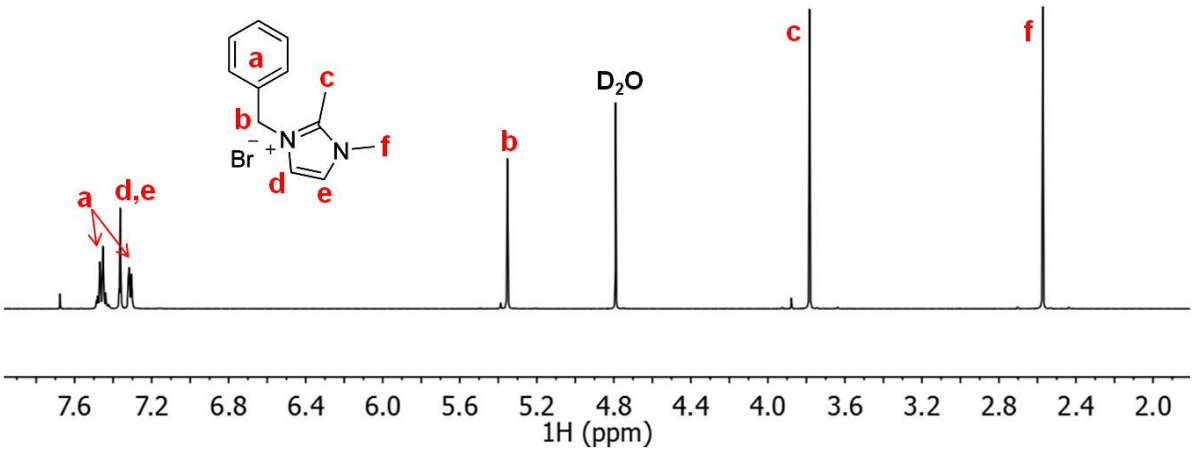

Figure S - 8: ^{1}H NMR spectrum of **1,2-DMIm** in bromide form.

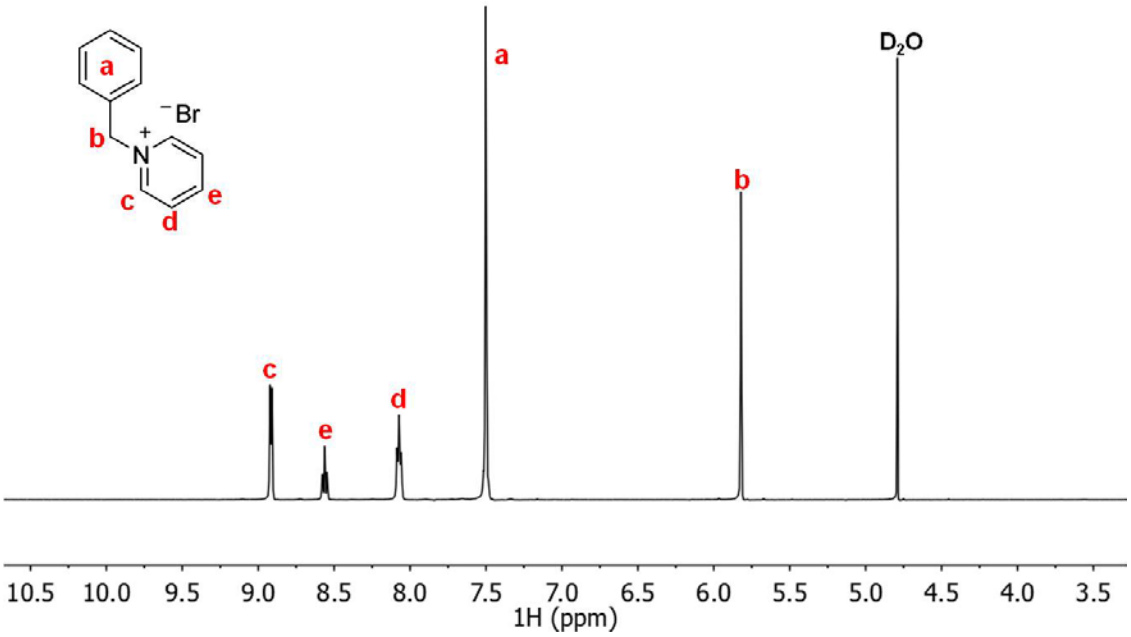

Figure S - 9: ^{1}H NMR spectrum of **Pyr** in bromide form.

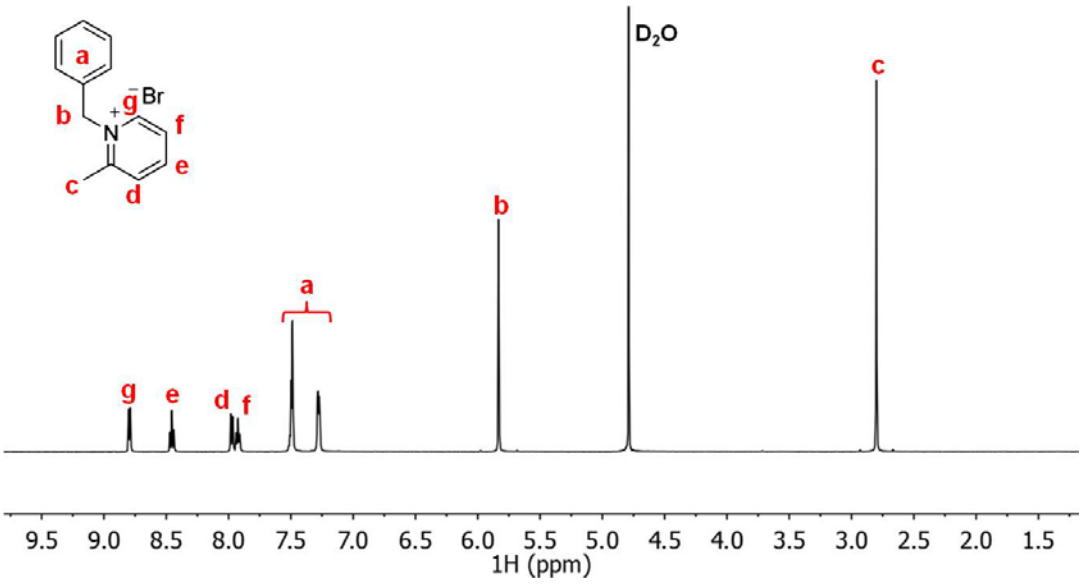

Figure S - 10: ^{1}H NMR spectrum of **2MPyr** in bromide form.

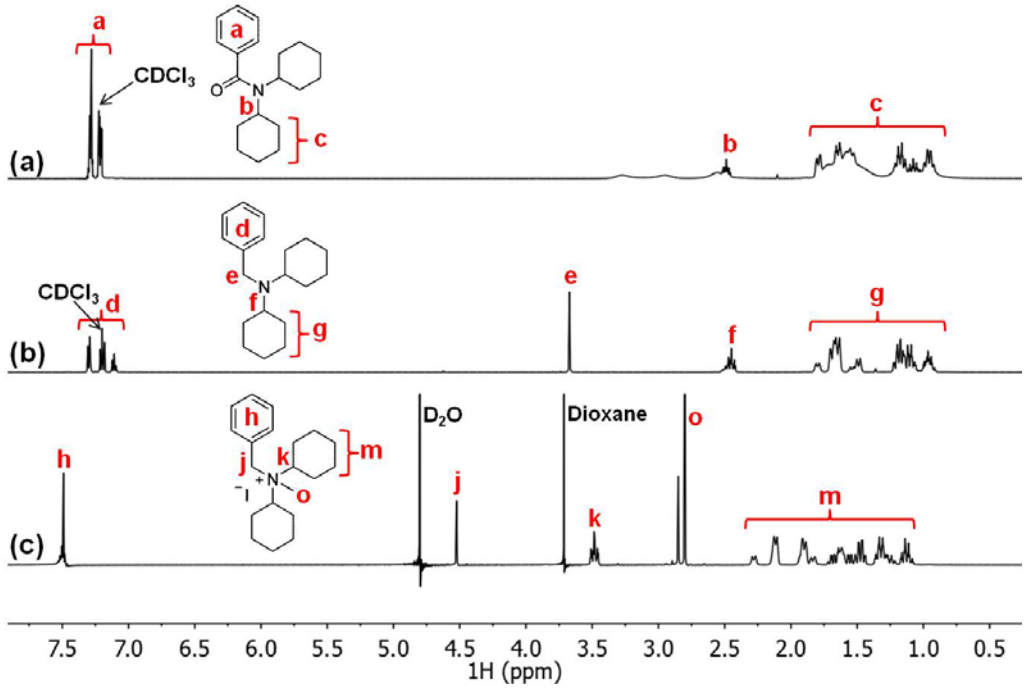

Figure S - 11: ^{1}H NMR spectra of (a) *N*,*N*-dicyclohexylbenzamide **(1)**, (b) *N*,*N*-dicyclohexylbenzylamine **(2)**, and (c) **MCH** in iodide form.

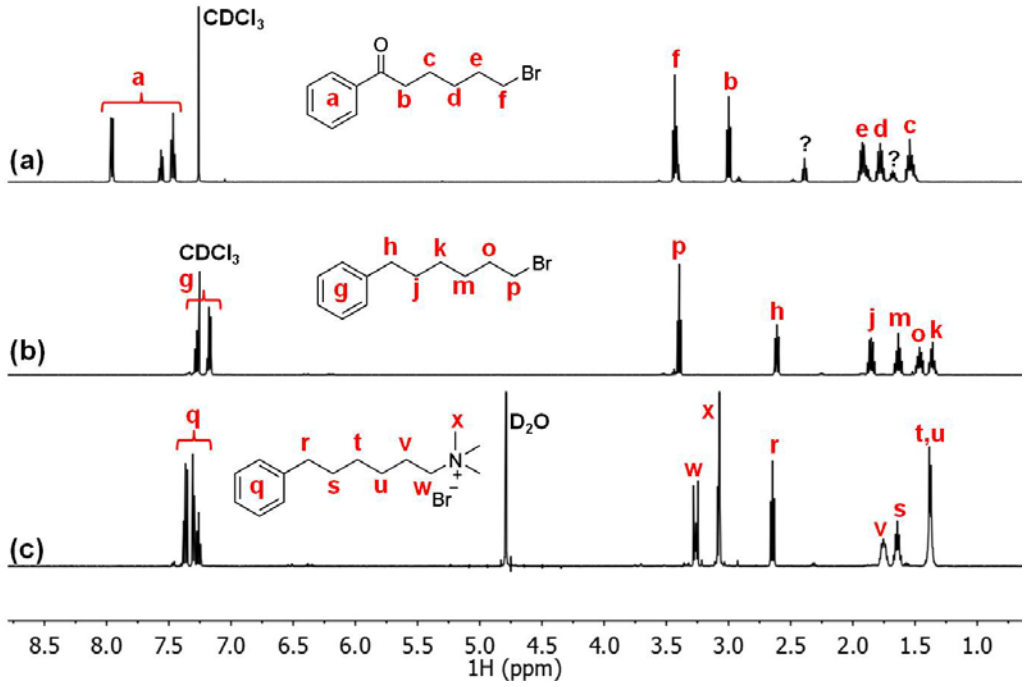

Figure S - 12: ^{1}H NMR spectra of (a) 6-bromo-1-phenyl-1-hexanone **(3)**, (b) 1-bromo-6-phenylhexane **(4)**, and (c) **TMHA** in bromide form.

12. GC-MS and NMR spectra for benzyl alcohol

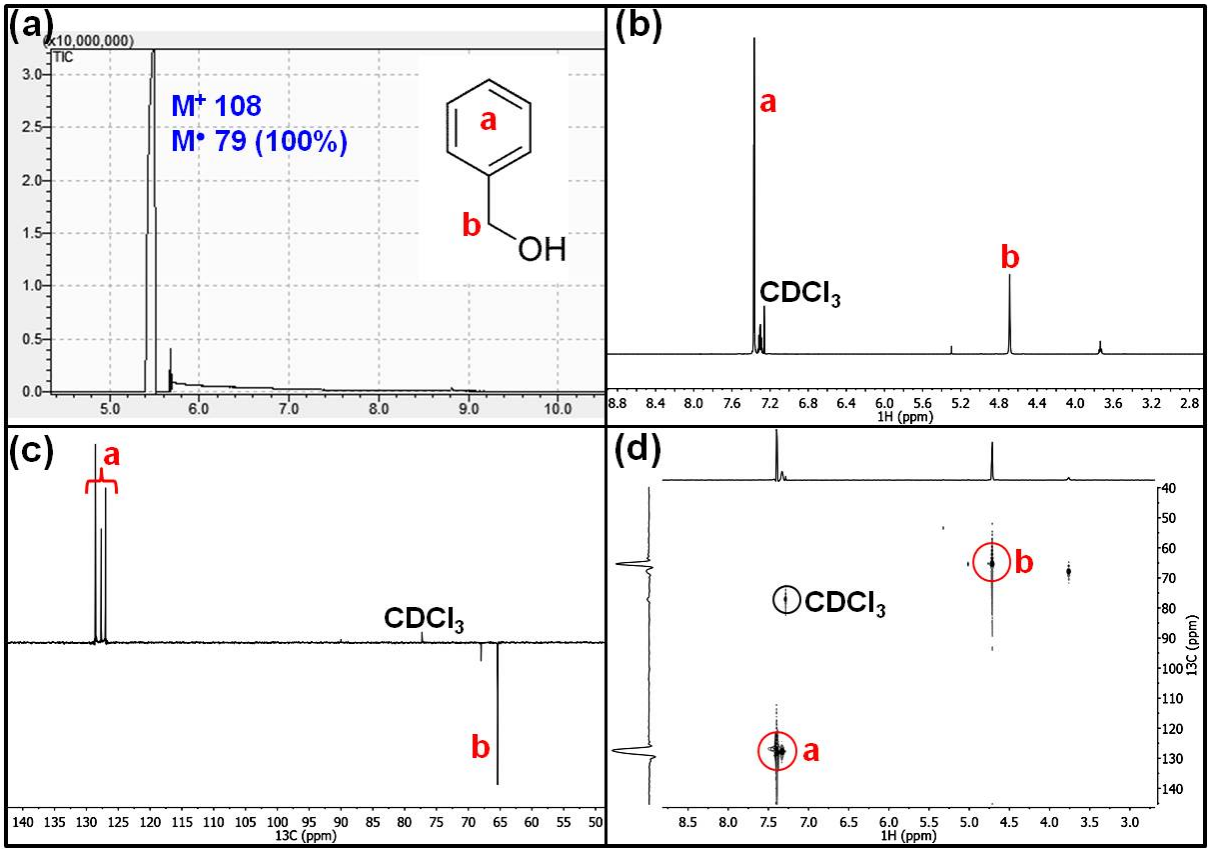

Figure S - 13: Spectral analysis of benzyl alcohol: (a) gas chromatogram from GC-MS, (b) ^{1}H NMR, (c) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. See Figure S49a and S49b for mass spectrum of benzyl alcohol.

13. Stacked NMR spectra for degradation studies

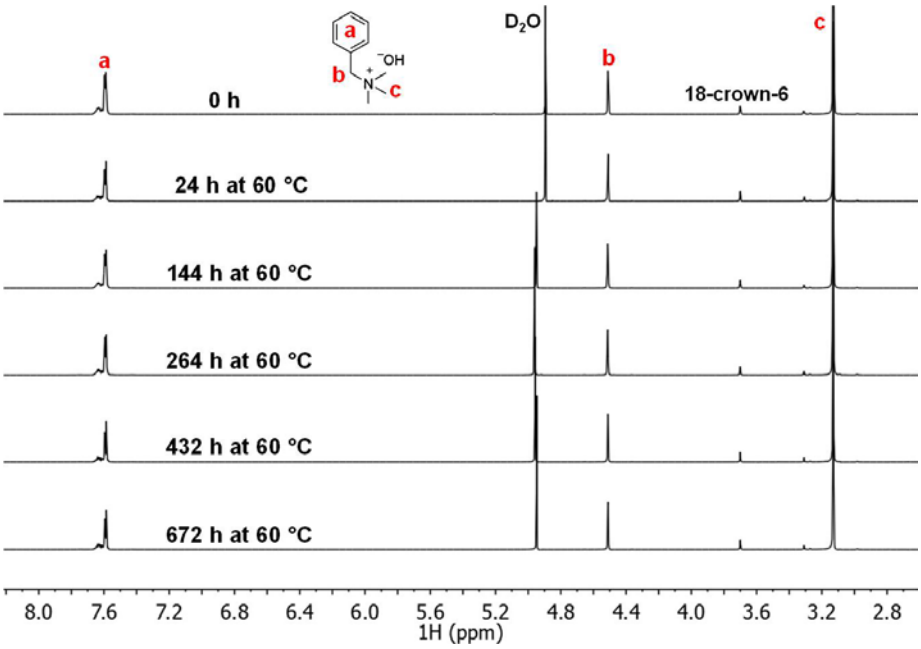

Figure S - 14: ^{1}H NMR spectra for degradation study of **TMA** from 0 to 672 h at 60 °C. No changes were observed in any of the spectra. Percentage of degradation was estimated based on the change in the relative intensity of peak c relative to 18-crown-6.

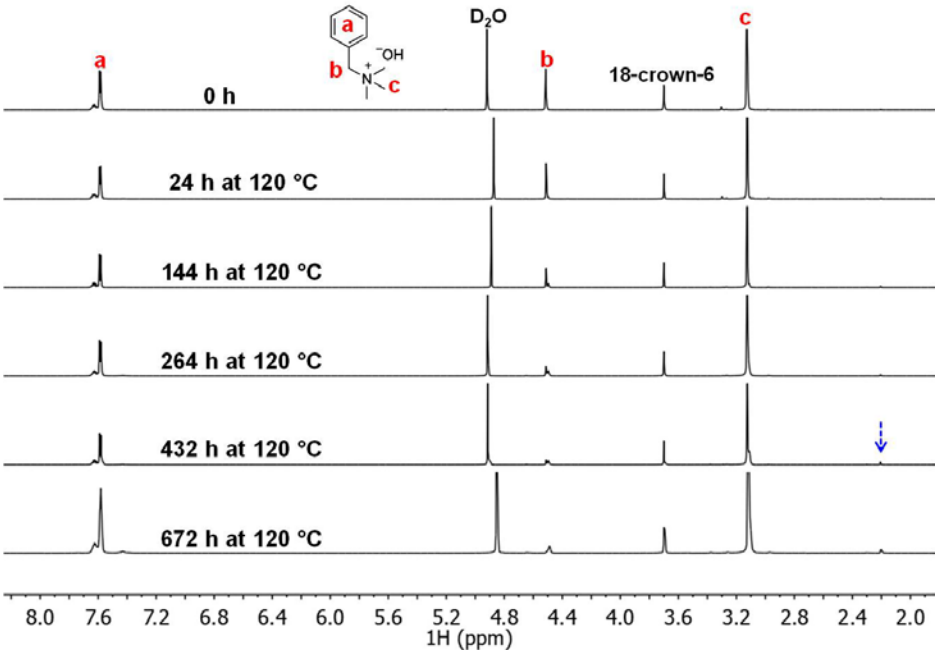

Figure S - 15: ^{1}H NMR spectra for degradation study of **TMA** from 0 to 672 h at 120 °C. The blue dotted arrow indicates appearance of byproducts formed as a result of alkaline degradation. Note the decrease in intensity of peak b as a result of H/D exchange from ylide formation. Percentage of degradation was estimated based on the change in the relative intensity of peak c relative to 18-crown-6.

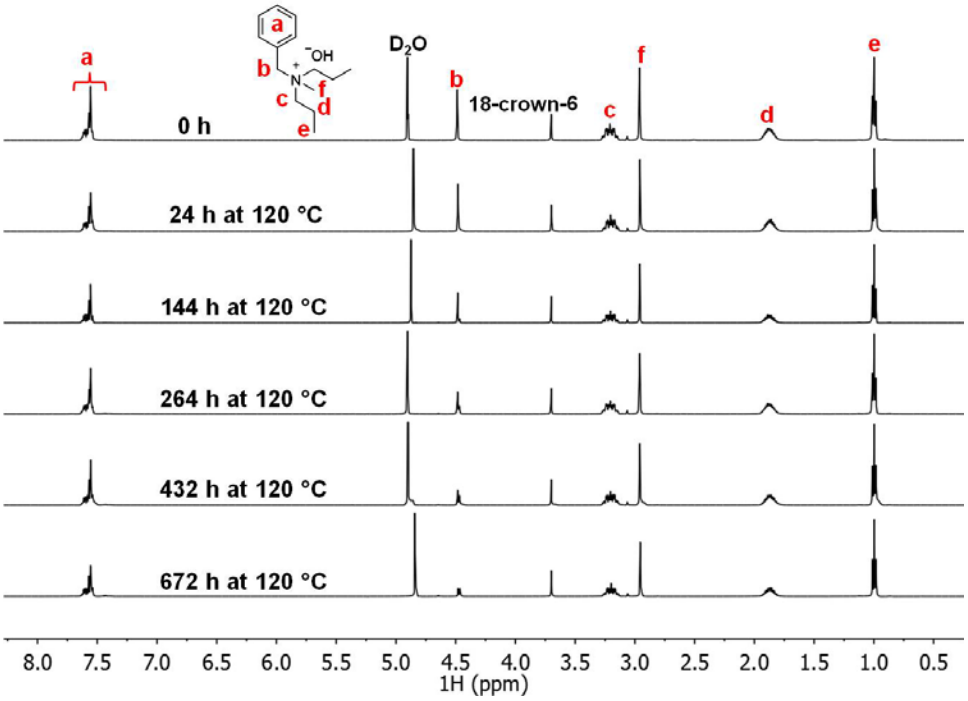

Figure S - 16: ^{1}H NMR spectra for degradation study of **MnPr** from 0 to 672 h at 120 °C. Note the decrease in intensity of peak b as a result of H/D exchange from ylide formation. Percentage of degradation was estimated based on the change in the relative intensity of peak c relative to 18-crown-6.

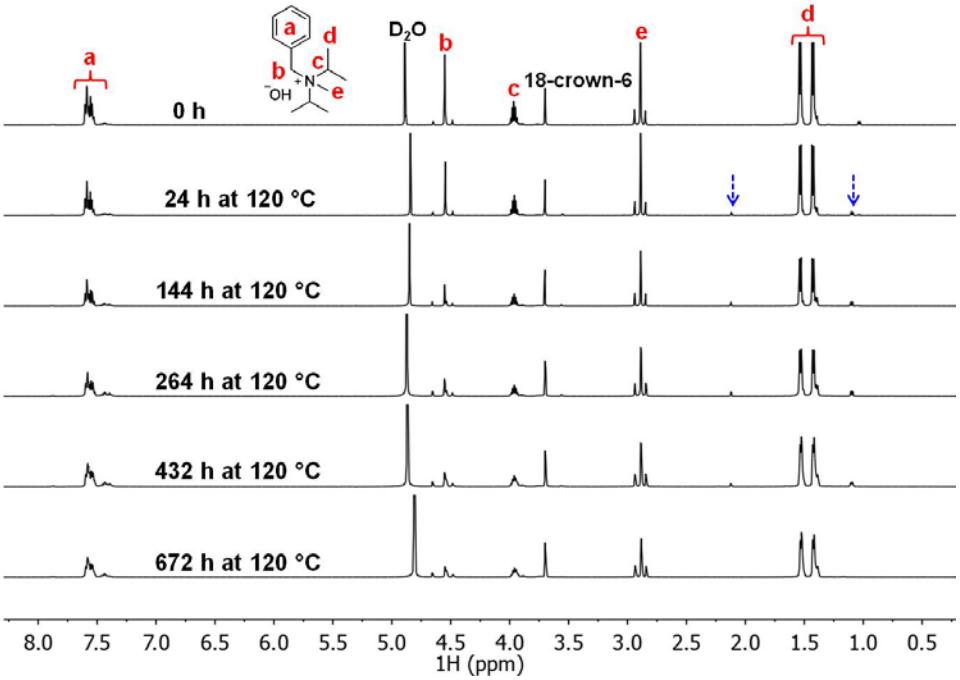

Figure S - 17: ^{1}H NMR spectra for degradation study of **MiPr** from 0 to 672 h at 120 °C. The blue dotted arrows indicate appearance of byproducts formed as a result of alkaline degradation. Note the decrease in intensity of peaks b, d, and e. Percentage of degradation was estimated based on the change in the relative intensity of peak d relative to 18-crown-6.

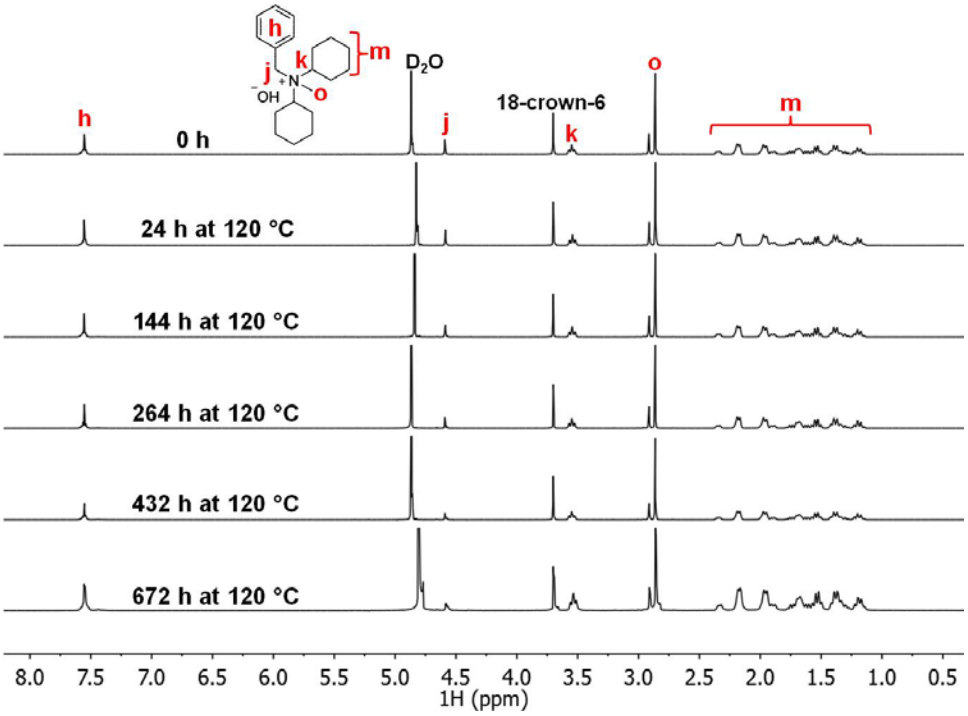

Figure S - 18: ^{1}H NMR spectra for degradation study of **MCH** from 0 to 672 h at 120 °C. Percentage of degradation was estimated based on the change in the relative intensity of peak o relative to 18-crown-6.

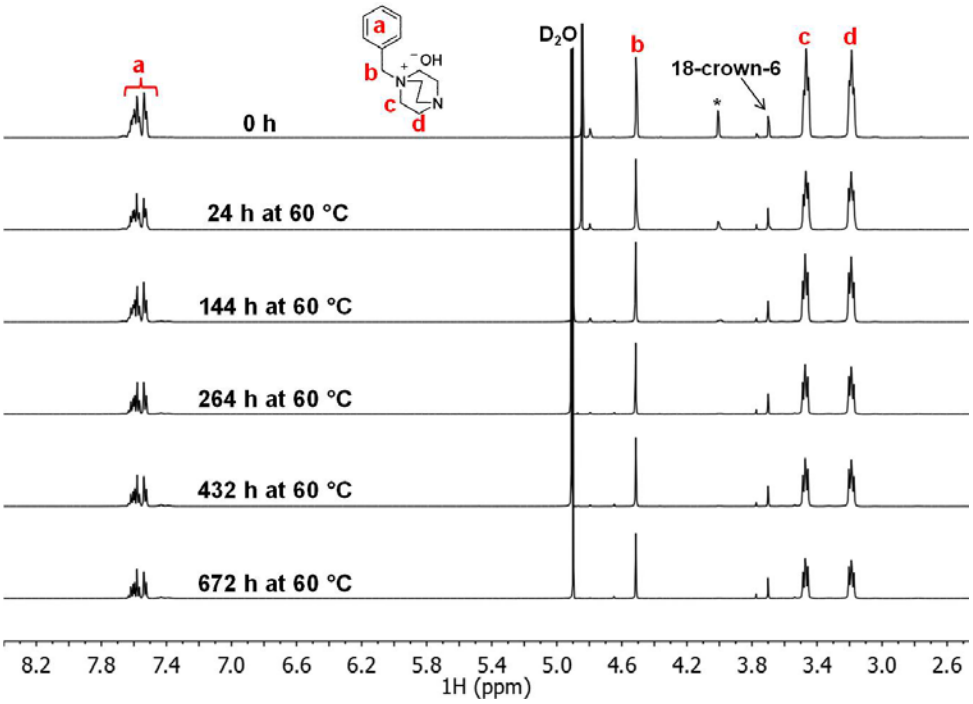

Figure S - 19: ^{1}H NMR spectra for degradation study of **DABCO-1** from 0 to 672 h at 60 °C. No changes were observed in any of the spectra. The asterisk indicates the presence of dioxane. Percentage of degradation was estimated based on the change in the relative intensity of peak c relative to 18-crown-6.

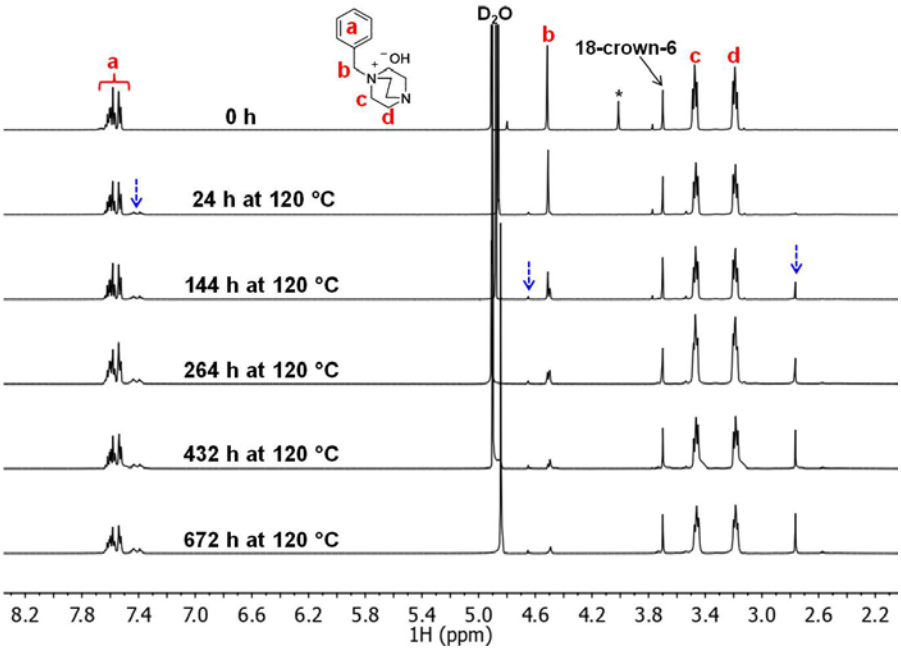

Figure S - 20: ^{1}H NMR spectra for degradation study of **DABCO-1** from 0 to 672 h at 120 °C. The blue dotted arrows indicate the appearance of byproducts formed. The asterisk indicates the presence of dioxane. Note the decrease in intensity of peak b as a result of H/D exchange from ylide formation. Percentage of degradation was estimated based on the change in the relative intensity of peak c relative to 18-crown-6.

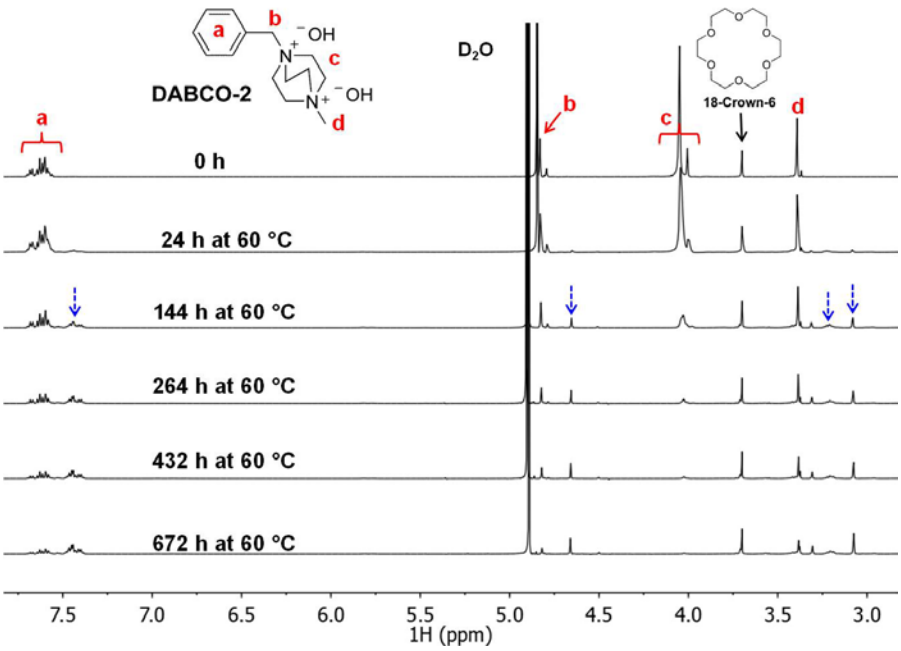

Figure S - 21: ^{1}H NMR spectra for degradation study of **DABCO-2** from 0 to 672 h at 60 °C. The blue dotted arrows indicate the appearance of byproducts formed. Note the decrease in intensity of peaks b, c, and d as a result of alkaline degradation. No H/D exchange was observed from MS (see Figure S49g). Percentage of degradation was estimated based on the change in the relative intensity of peak c relative to 18-crown-6.

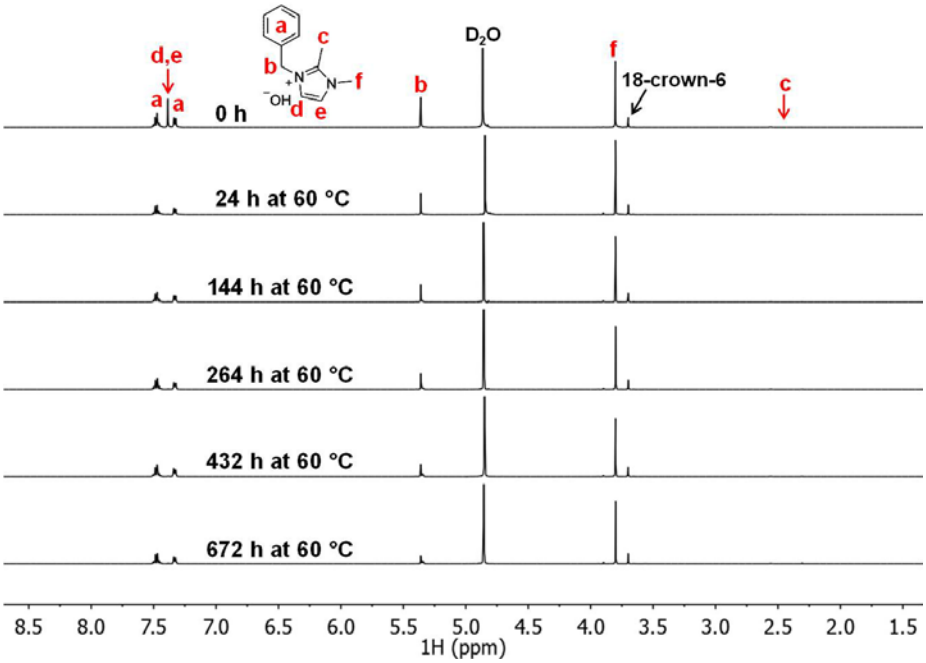

Figure S - 22: ^{1}H NMR spectra for degradation study of **1,2-DMIm** from 0 to 672 h at 60 °C. Peak c is not visible and peaks d and e quickly disappear within 24 h due to H/D exchange. Percentage of degradation was estimated based on the change in the relative intensity of peak a (and confirmed with peak f) relative to 18-crown-6.

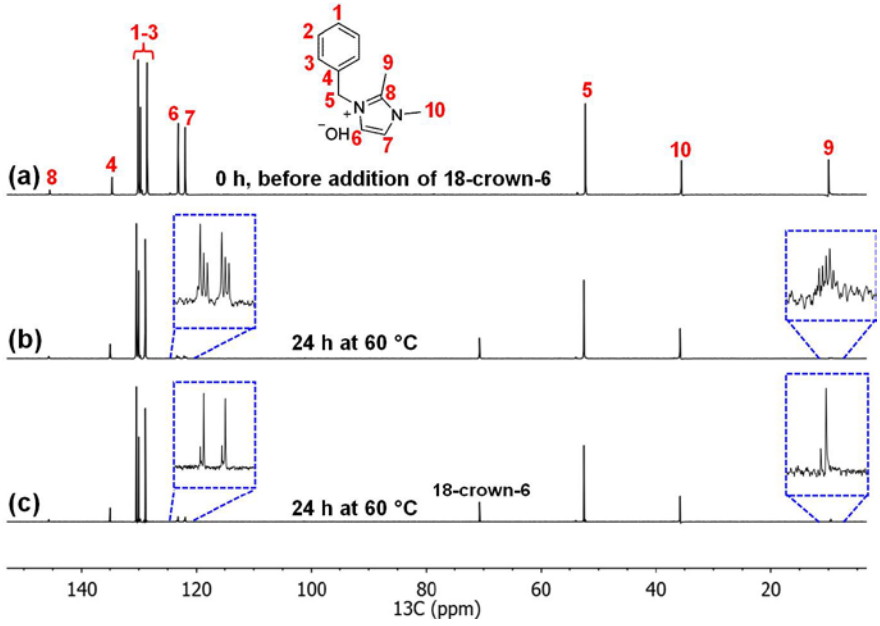

Figure S - 23: Proton decoupled ^{13}C NMR spectra for **1,2-DMIm** (a) at 0 h before addition of 18-crown-6 and (b) after 24 h at 60 °C with 18-crown-6 peak referenced to 70.7 ppm. (c) Deuterium decoupled ^{13}C NMR for **1,2-DMIm** after 24 h at 60 °C. The blue dotted boxes are zoomed-in images of peaks 6, 7, and 9. Peaks 6 and 7 appear as 1:1:1 triplets since carbons 6 and 7 are coupled with one deuterium. These peaks merge to two singlets in (c) as a result of deuterium-decoupled ^{13}C NMR. Peak 9 should appear as a septet if coupled to three deuterium, but is difficult to distinguish in this NMR spectra.

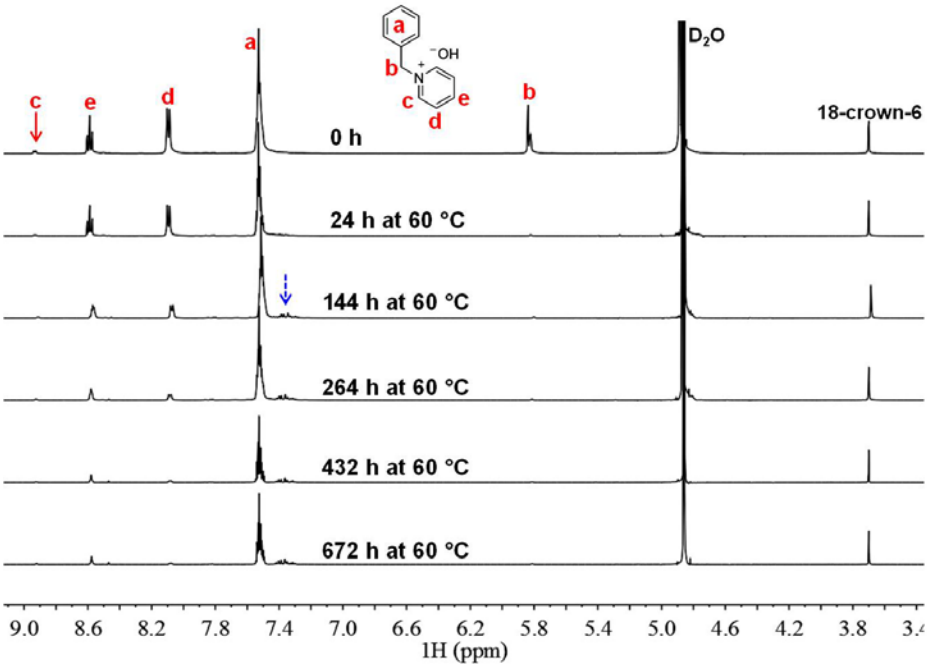

Figure S - 24: ^{1}H NMR spectra for degradation study of **Pyr** from 0 to 672 h at 60 °C. Peaks b and c quickly disappear within 24 h due to H/D exchange. The blue dotted arrow indicates the appearance of byproducts formed. Percentage of degradation was estimated based on the change in the relative intensity of peak a relative to 18-crown-6.

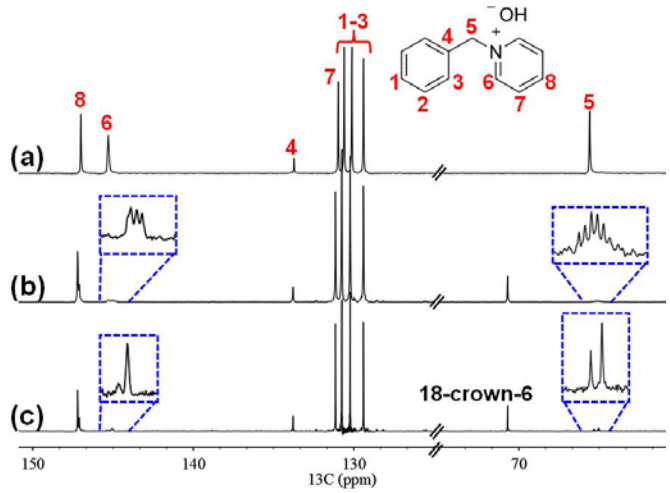

Figure S - 25: Proton decoupled ^{13}C NMR spectra for **Pyr** (a) at 0 h before addition of 18-crown-6 and (b) after 24 h at 60 °C with 18-crown-6 peak referenced to 70.7 ppm. (c) Deuterium decoupled ^{13}C NMR for **Pyr** after 24 h at 60 °C. The blue dotted boxes are zoomed-in images of peaks 6 and 7. C-6 (centered at 145.0 ppm with a coupling constant $J_{C\text{-}D}$ = 30.1 Hz) appears as a 1:1:1 triplet because it is coupled with one deuterium. The ^{13}C NMR resonance of C-5 (centered at 65.2 ppm with $J_{C\text{-}D}$ = 21.4 Hz) also appears as a quintet due to its coupling with two benzylic deuterium. C-5 and C-6 merge back to singlets as a result of deuterium-decoupled ^{13}C NMR (c). However, it was noticed that the signal of C-5 in (b) was not a perfect 1:2:3:2:1 quintet and merged to two singlets in (c) instead of one, indicating that degradation may have already occurred at this position. This is consistent with the data plotted in Figure 2a in the manuscript in which approximately 17% of Pyr cation degradation was observed within 24 h.

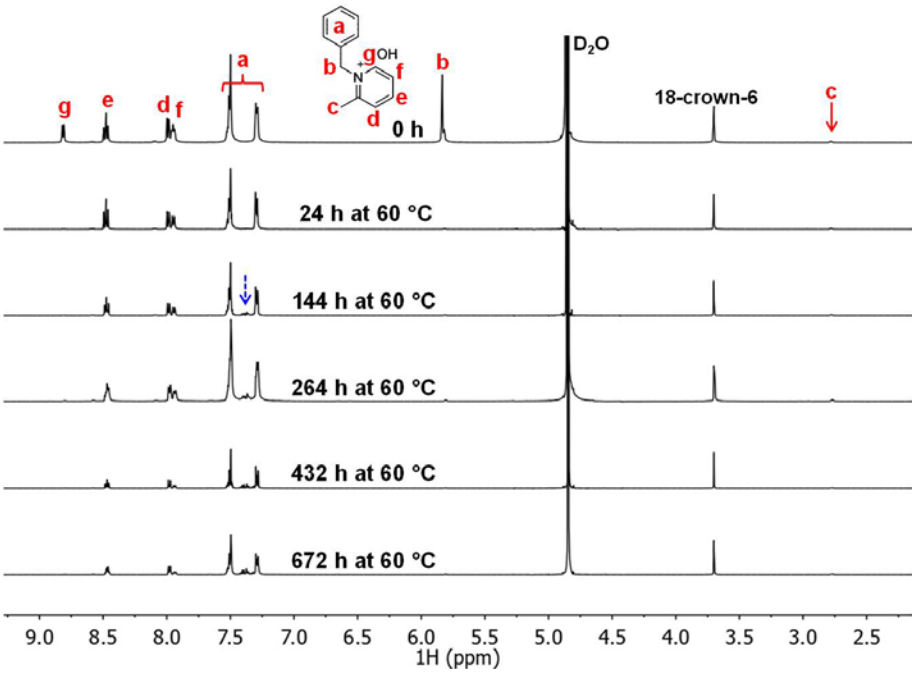

Figure S - 26: ^{1}H NMR spectra for degradation study of **2MPyr** from 0 to 672 h at 60 °C. Peaks b, c, and g disappear within 24 h due to H/D exchange. The blue dotted arrow indicates byproducts formed. Percentage of degradation was estimated based on the change in the relative intensity of peak a relative to 18-crown-6.

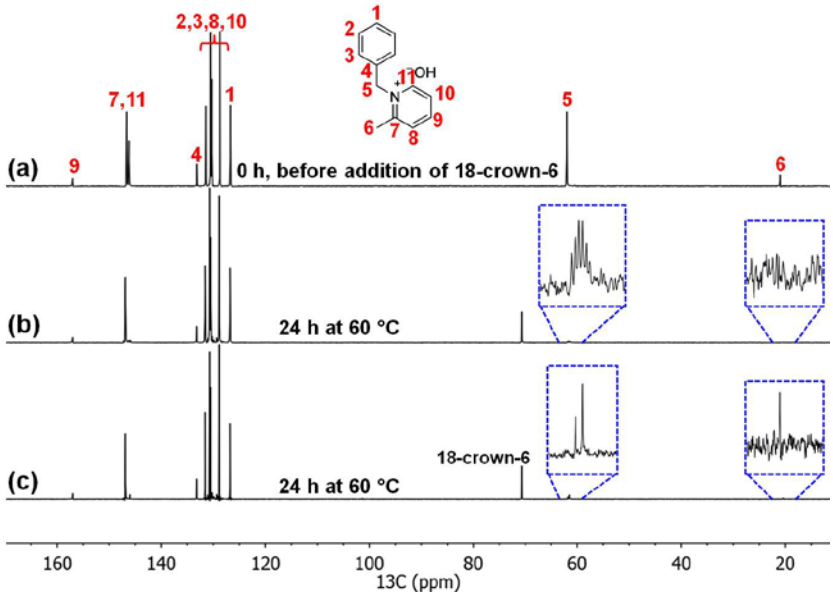

Figure S - 27: Proton decoupled ^{13}C NMR spectra for **2MPyr** (a) at 0 h before addition of 18-crown-6 and (b) after 24 h at 60 °C with 18-crown-6 peak referenced to 70.7 ppm. (c) Deuterium decoupled ^{13}C NMR for **2MPyr** after 24 h at 60 °C. The blue dotted boxes are zoomed-in images of peaks 5 and 6. Peak 5 appears as a quintet due to its coupling with two benzylic deuterium. Peak 6 is difficult to see in (b) because of its splitting from deuterium, but is clearly identified as a singlet in (c) after deuterium-decoupling. Also note the decrease in intensity of peak 11 as a result of H/D exchange (zoomed-in image not shown).

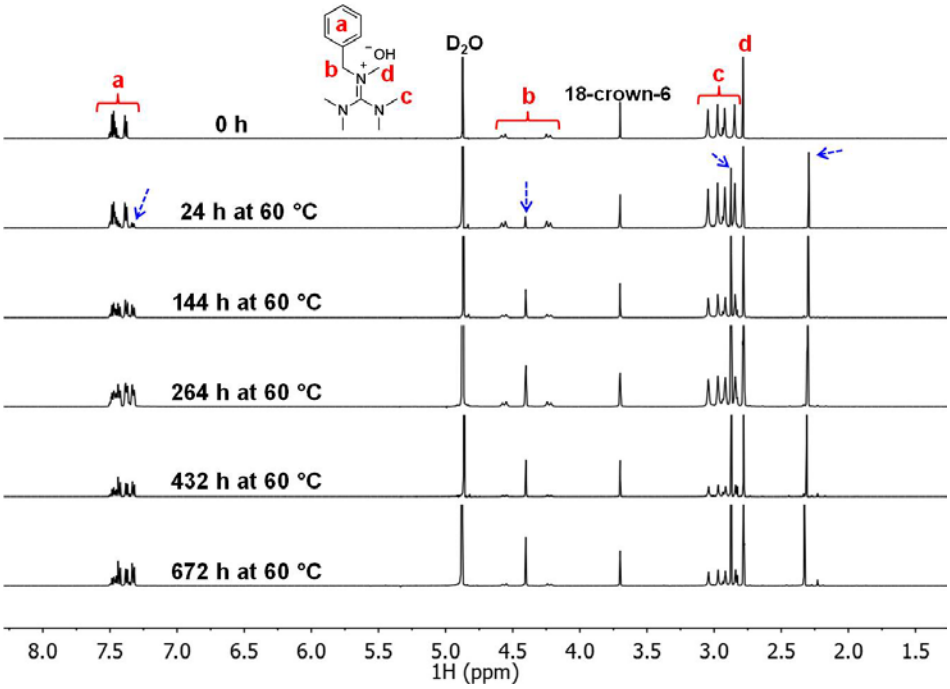

Figure S - 28: ^{1}H NMR spectra for degradation study of **TMG** from 0 to 672 h at 60 °C. The blue dotted arrows indicate appearance of byproducts formed. Note the decrease in intensity of peaks b and c as a result of alkaline degradation. Percentage of degradation was estimated based on the change in the relative intensity of peak b relative to 18-crown-6.

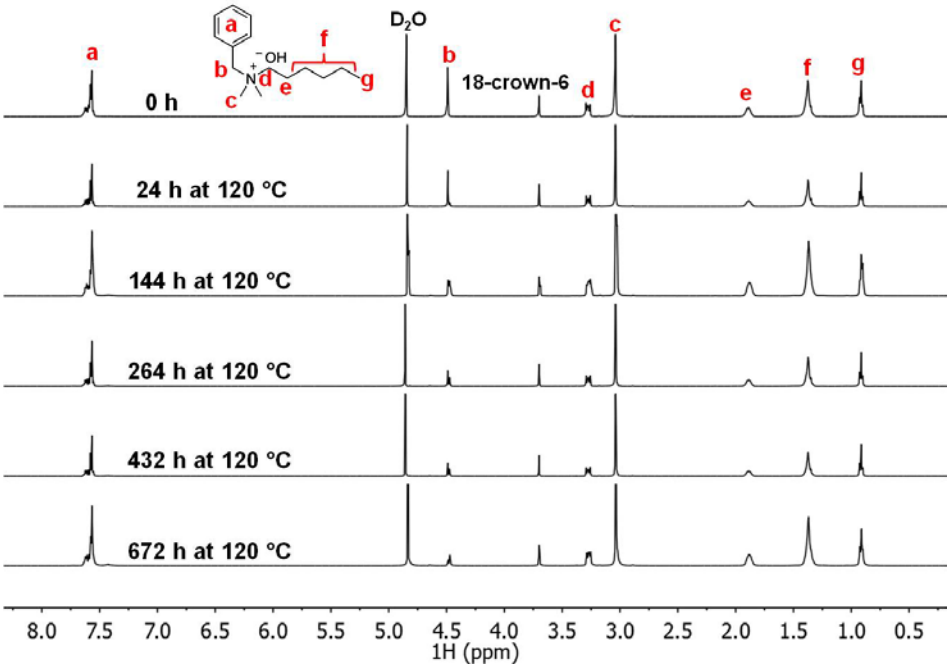

Figure S - 29: ^{1}H NMR spectra for degradation study of **DMHA** from 0 to 672 h at 120 °C. Note the decrease in intensity of peak b as a result of H/D exchange from ylide formation. Percentage of degradation was estimated based on the change in the relative intensity of peak c relative to 18-crown-6.

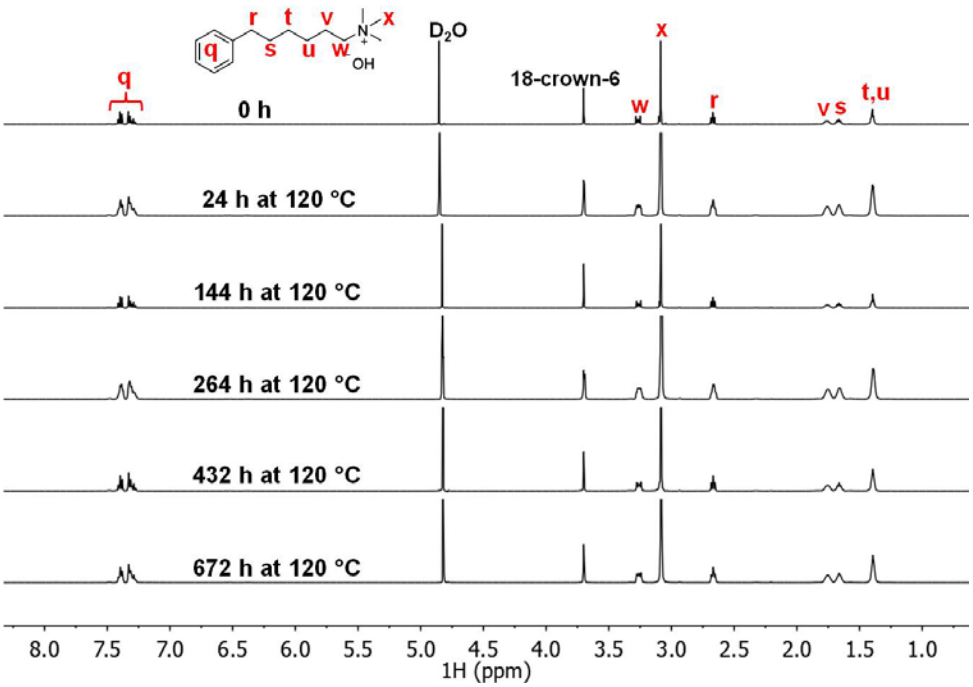

Figure S - 30: ^{1}H NMR spectra for degradation study of **TMHA** from 0 to 672 h at 120 °C. Percentage of degradation was estimated based on the change in the relative intensity of peak x relative to 18-crown-6.

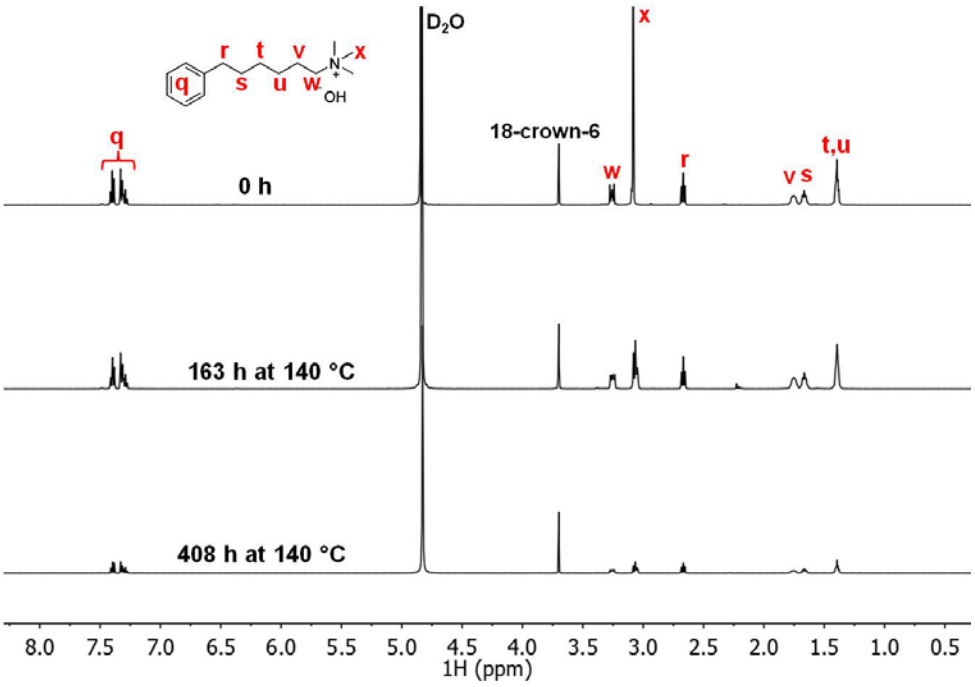

Figure S - 31: ^{1}H NMR spectra for degradation study of **TMHA** from 0 to 408 h at 140 °C. Note the decrease in intensity of all peaks relative to the internal standard 18-crown-6. Formation of white precipitates was also observed. Percentage of degradation was estimated based on the change in the relative intensity of peak x relative to 18-crown-6.

14. Percent cation remaining for additional TMHA and Pyr studies

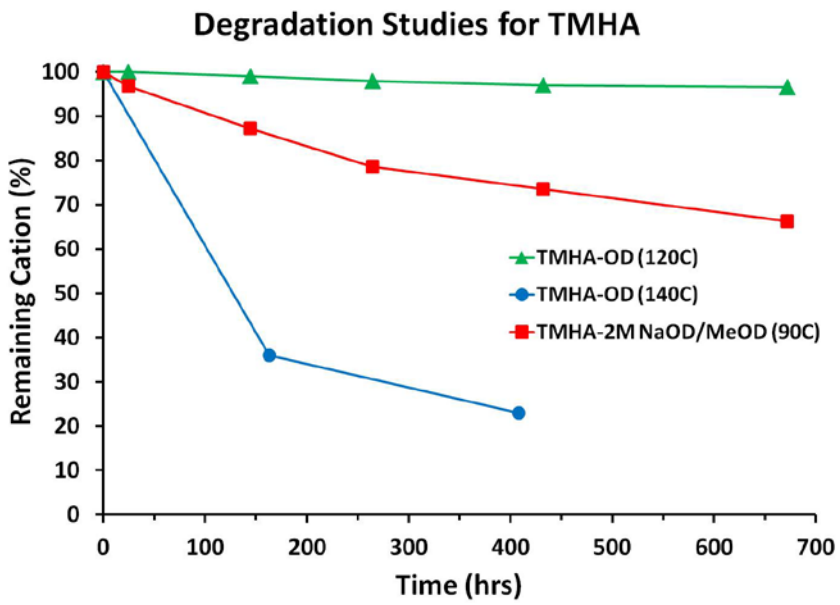

Figure S - 32: Percentage of **TMHA** remaining cation over time in OD^- form at 140 °C and in 2M $NaOD/CD_3OD$ aqueous solution at 90 °C. Significant precipitate formation was observed at 140 °C.

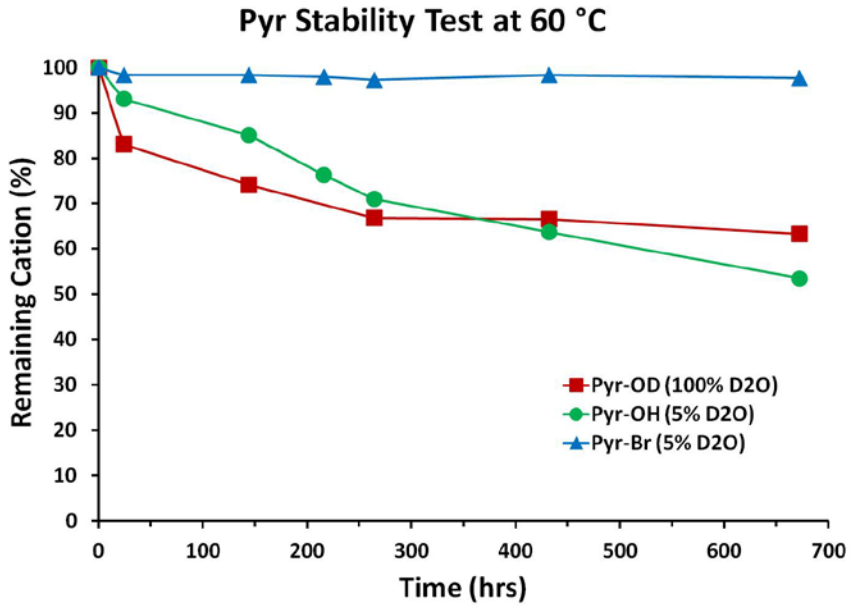

Figure S - 33: Percentage of **Pyr** remaining cation over time at 60 °C. **Pyr** was studied with Br^- and OH^- counter anion in 5 % D_2O/H_2O solution and compared with OD^- form in 100% D_2O. See Figures S35 and S36 for photos of observed color changes.

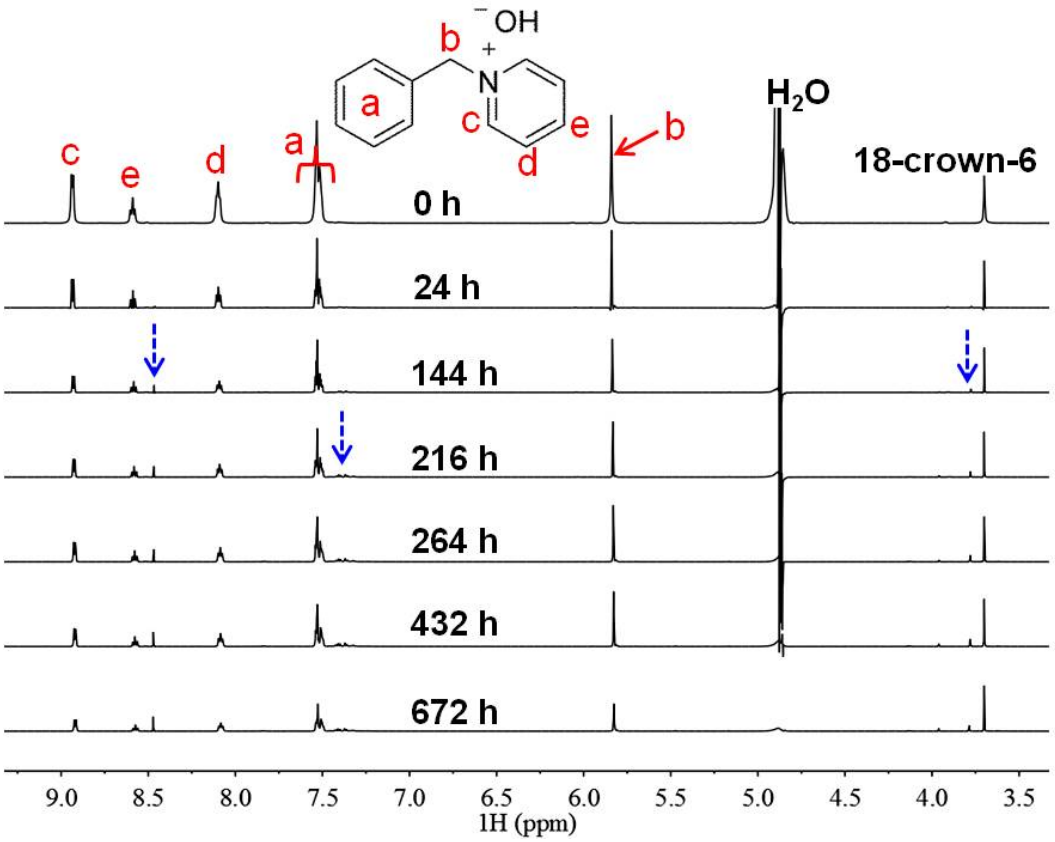

Figure S - 34: Pyr degradation study in 5% D_2O/H_2O from 0 to 672 h at 60 °C. Water suppression used in NMR data collection. The blue dotted arrows indicate appearance of byproducts formed as a result of alkaline degradation. Percentage of degradation was estimated based on the change in the relative intensity of peak a relative to 18-crown-6.

15. Photos of pyridinium and imidazolium color changes during degradation studes

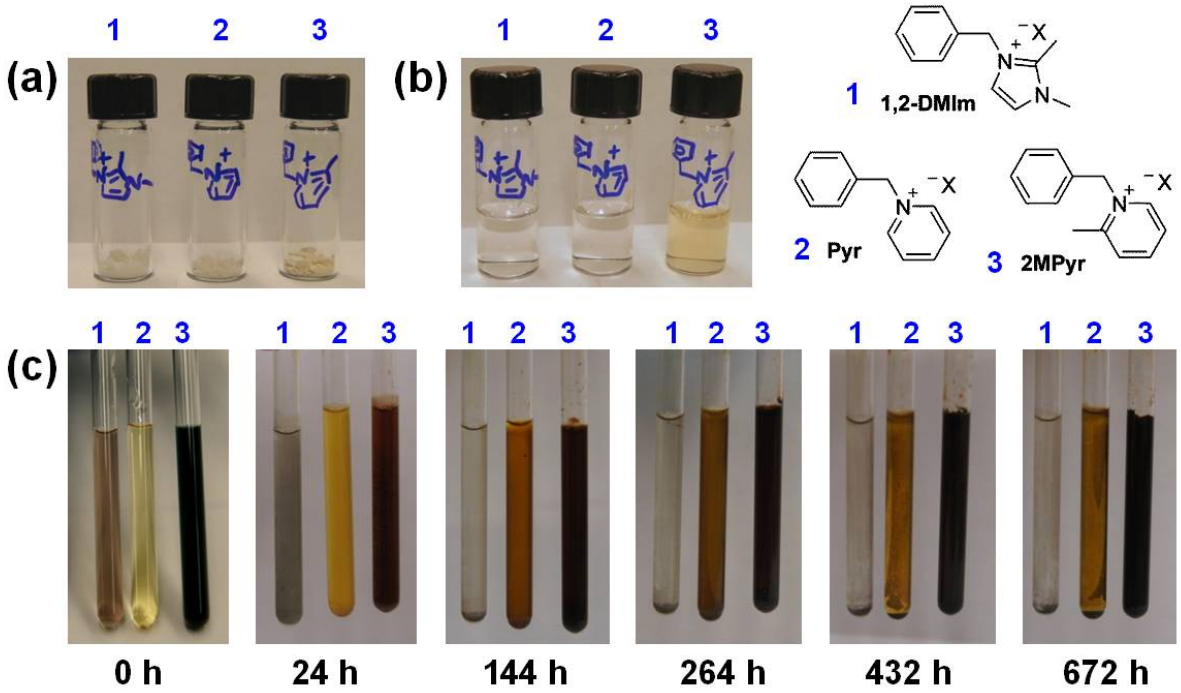

Figure S - 35: Color changes observed for imidazolium and pyridinium model compounds during the 60 °C degradation study. Image (a) shows the dry model compounds in Br^- anion form, while image (b) shows the model compounds in Br^- form dissolved in D_2O. Image (c) shows the model compounds in OD^- form after conducting Ag_2O-mediated ion exchange reaction in their respective NMR tubes. At 0 hour **1,2-DMIm** (1) is light pink/red, **Pyr** (2) is light yellow, and **2MPyr** (3) is dark blue. Over time all compounds darken or changed in color and resulted in some precipitate formation.

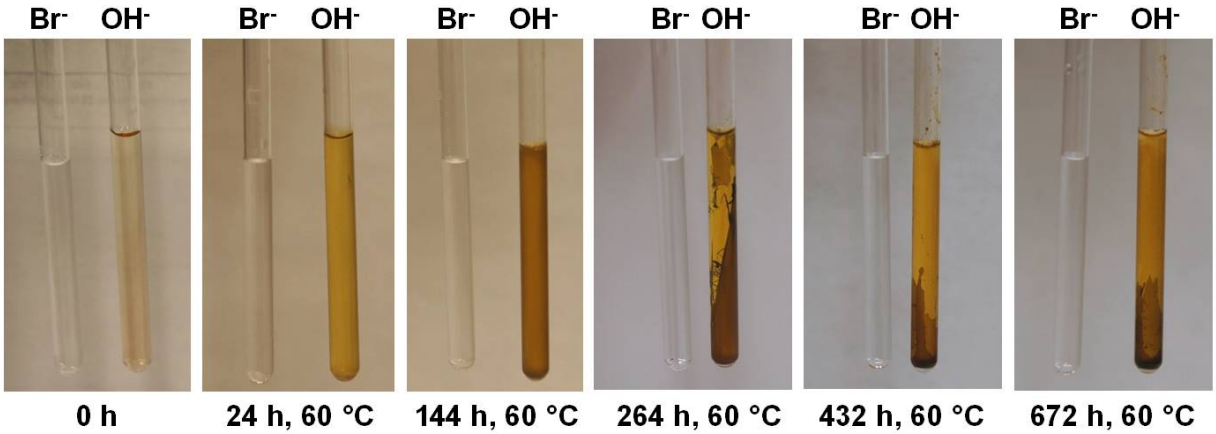

Figure S - 36: Color changes observed for **Pyr** during the 60 °C degradation study in 5% D_2O/H_2O. **Pyr** in OH^- form (after Ag_2O reaction) exhibited the same color changes and precipitate formation as observed in Figure S35c (NMR tubes labeled with number 2). **Pyr** in Br^- form remained colorless throughout the study since no degradation occurred.

16. GC-MS and NMR spectra for analysis of byproduct formation

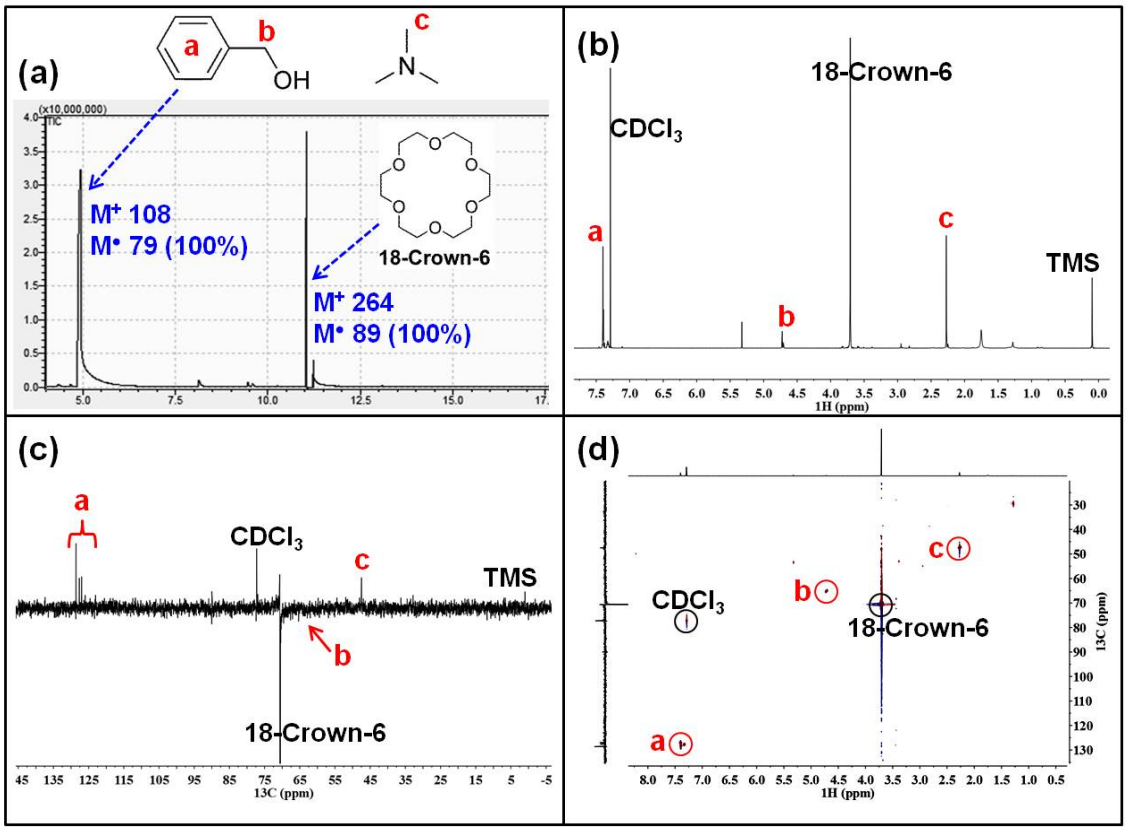

Figure S - 37: Byproduct analysis from **TMA** after degradation study at 120 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly.

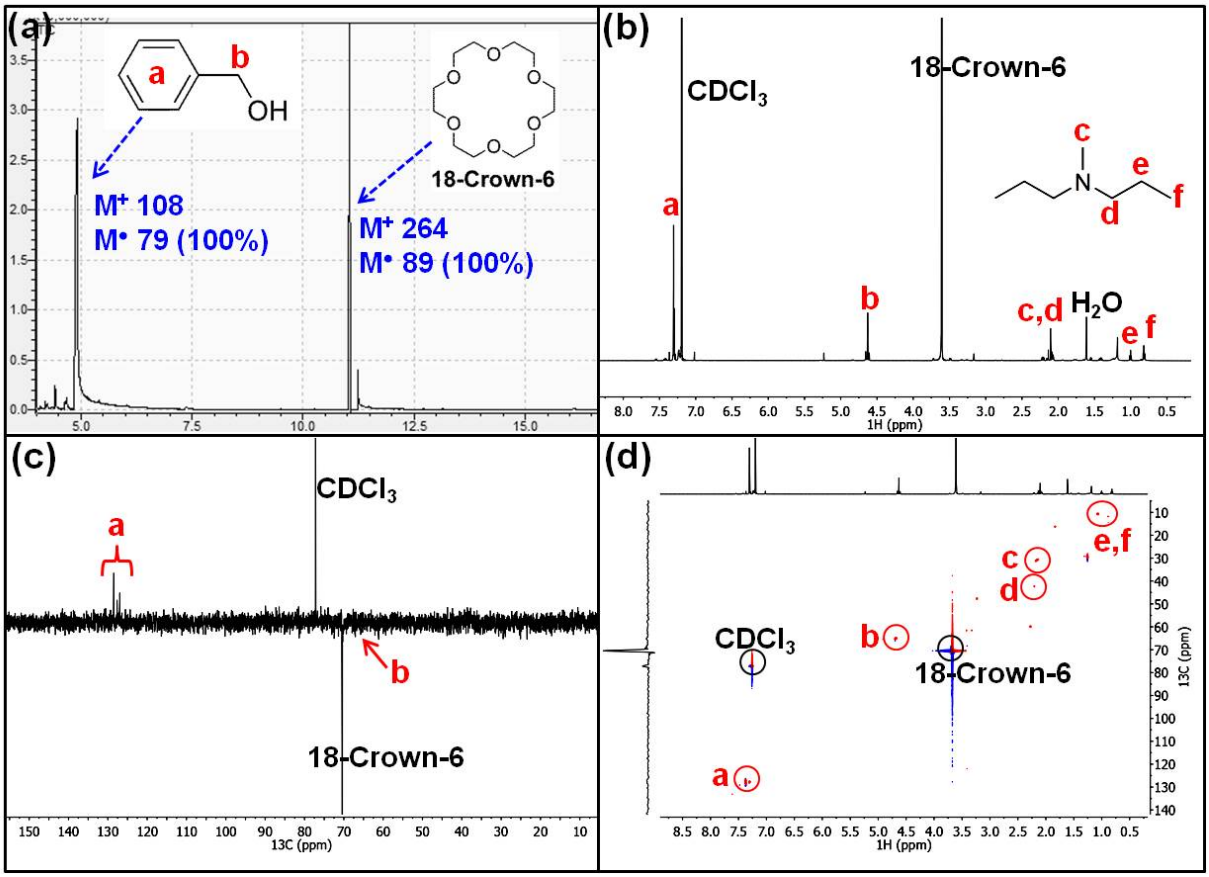

Figure S - 38: Byproduct analysis from **MnPr** after degradation study at 120 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly. The methyldipropylamine byproduct was not seen in GC-MS or ^{13}C DEPT-135 NMR, but is suggested in the ^{1}H and 2D-NMR.

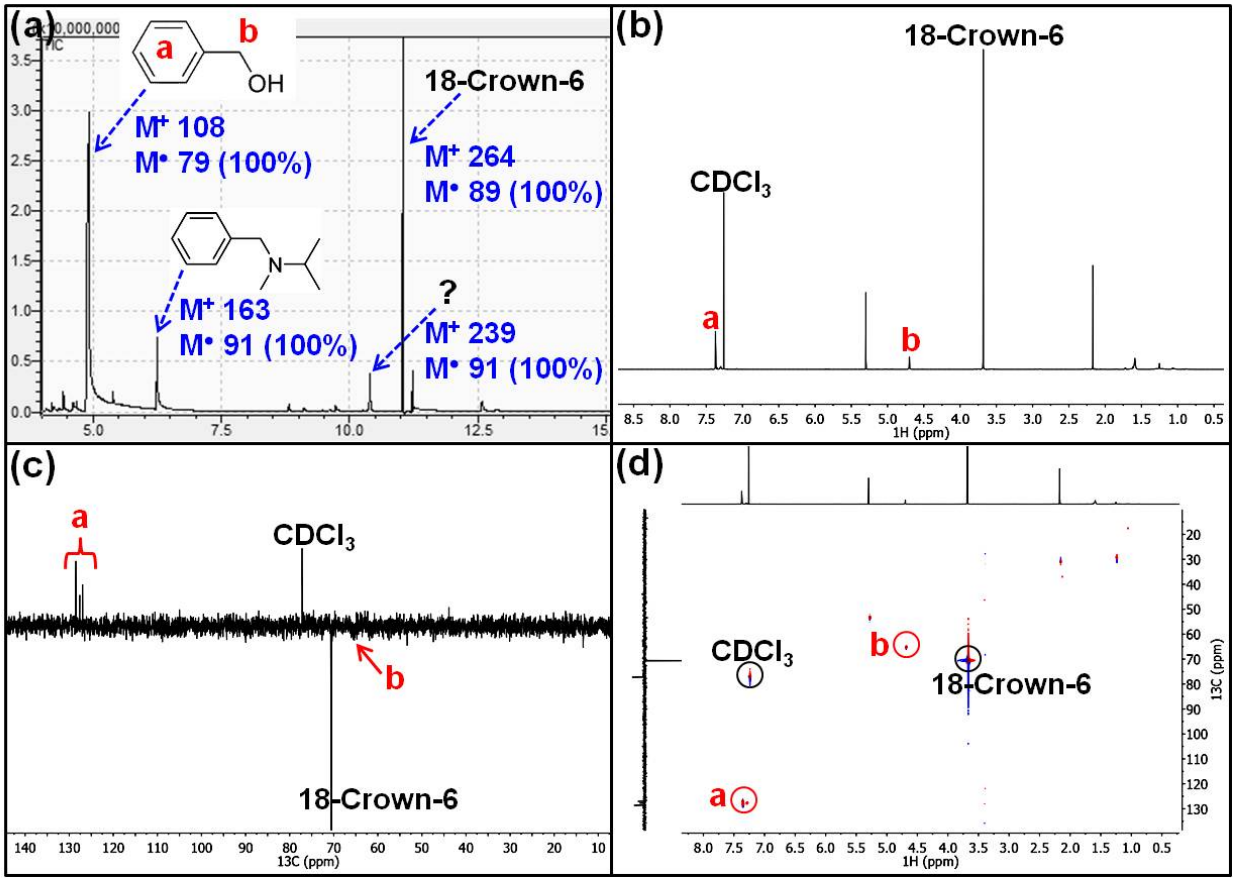

Figure S - 39: Byproduct analysis from **MiPr** after degradation study at 120 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly. The amine Hofmann elimination byproduct was seen in GC-MS, but was difficult to assign in NMR.

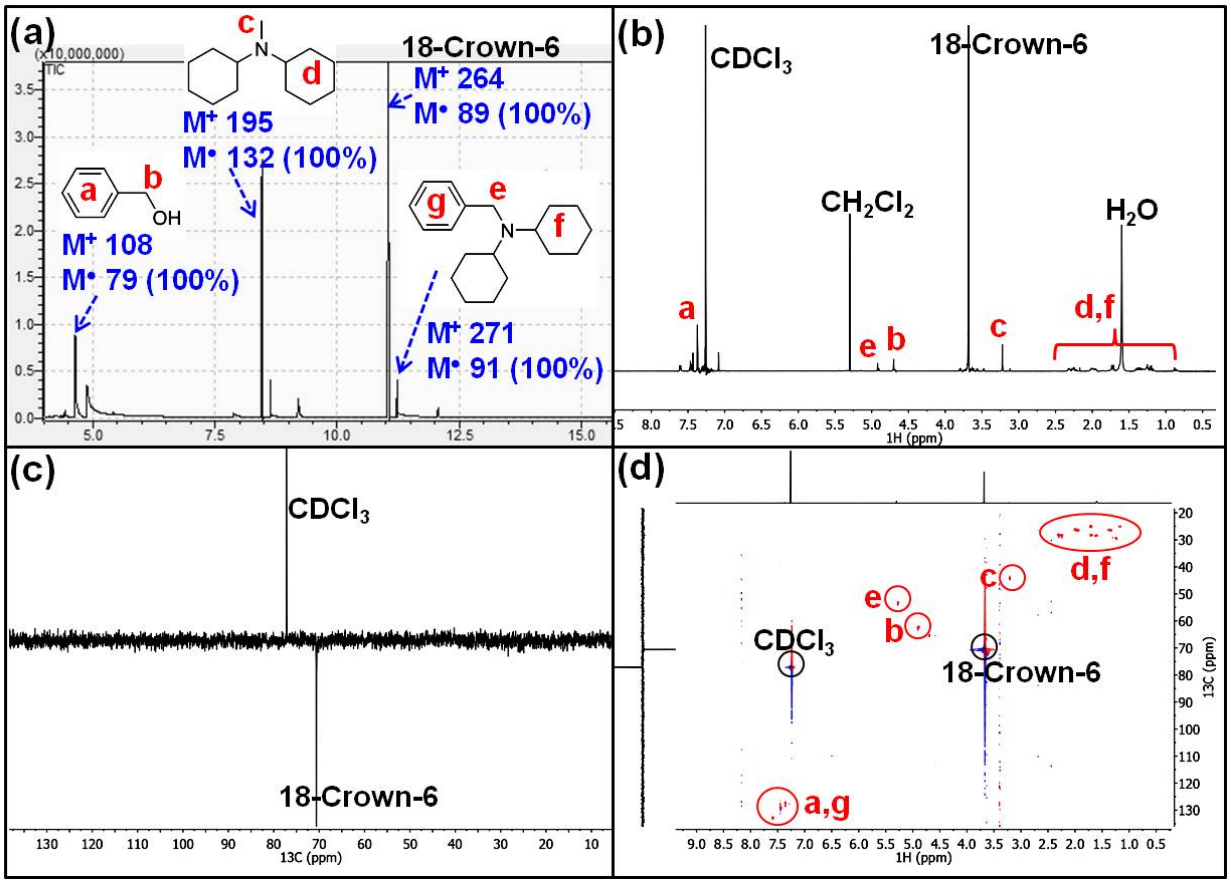

Figure S - 40: Byproduct analysis from **MCH** after degradation study at 120 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly. No peaks were observed in ^{13}C DEPT-135 NMR due to low concentration of byproducts. From ^{1}H NMR analysis, the ratio of byproducts seem consistent with 1:1:0.7 for peaks b:c:e, respectively.

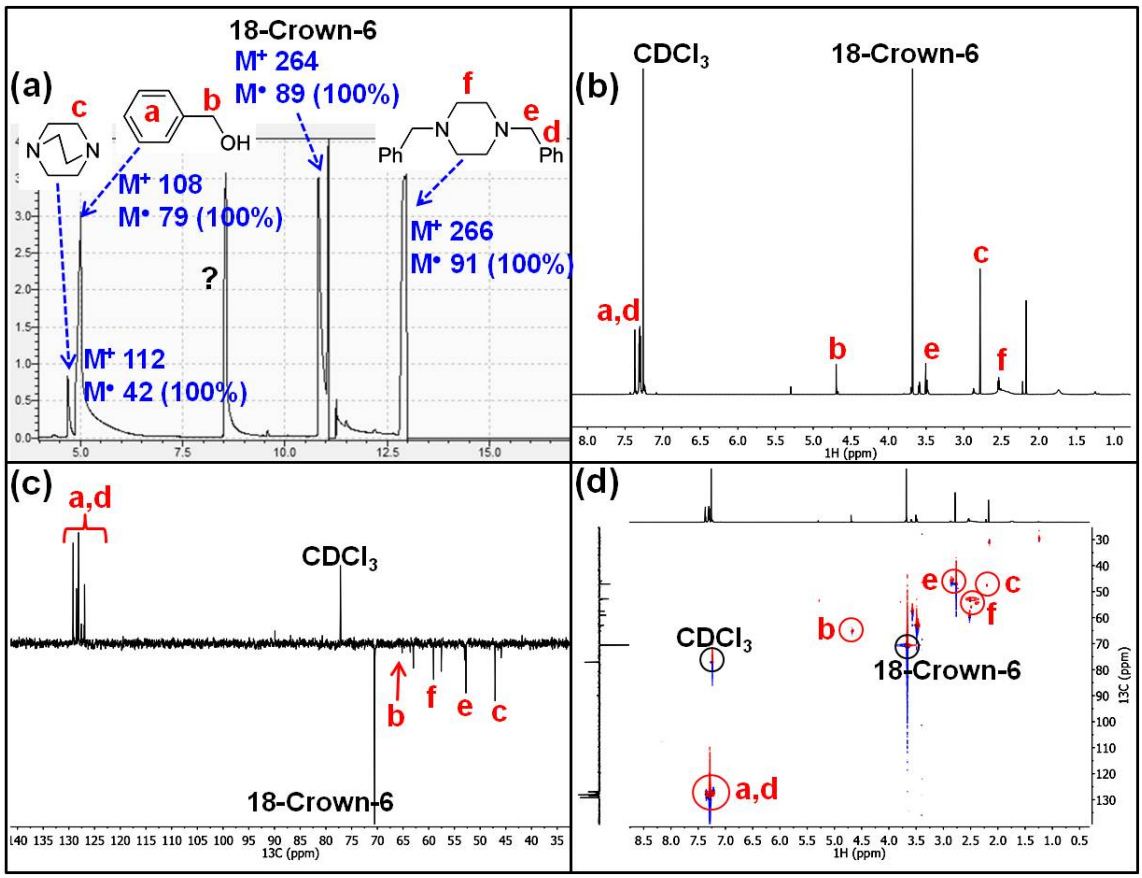

Figure S - 41: Byproduct analysis from **DABCO-1** after degradation study at 120 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly. The peak with question mark in (a) indicates an unidentified compound with a molecular ion peak of M^+ 138 and base peak of 91.

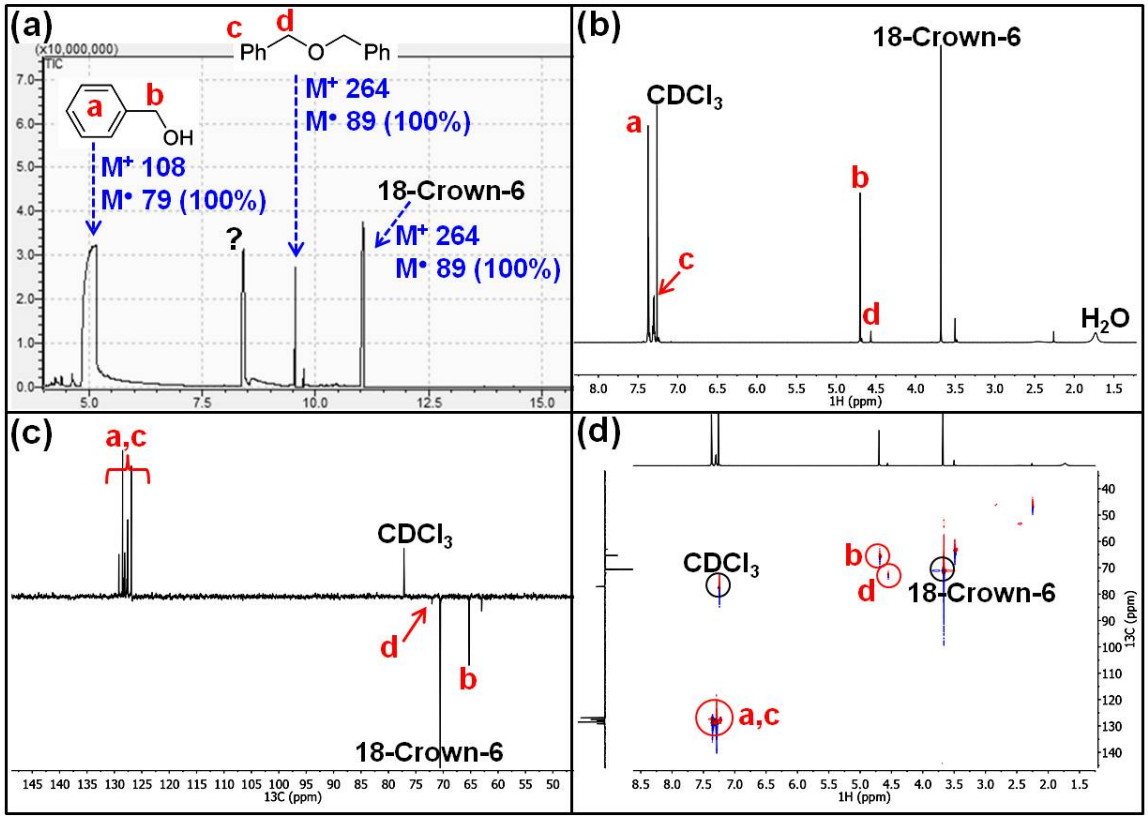

Figure S - 42: Byproduct analysis from **DABCO-2** after degradation study at 60 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly. The peak with question mark in (a) indicates an unidentified compound with a molecular ion peak of M^+ 194 and base peak of 91.

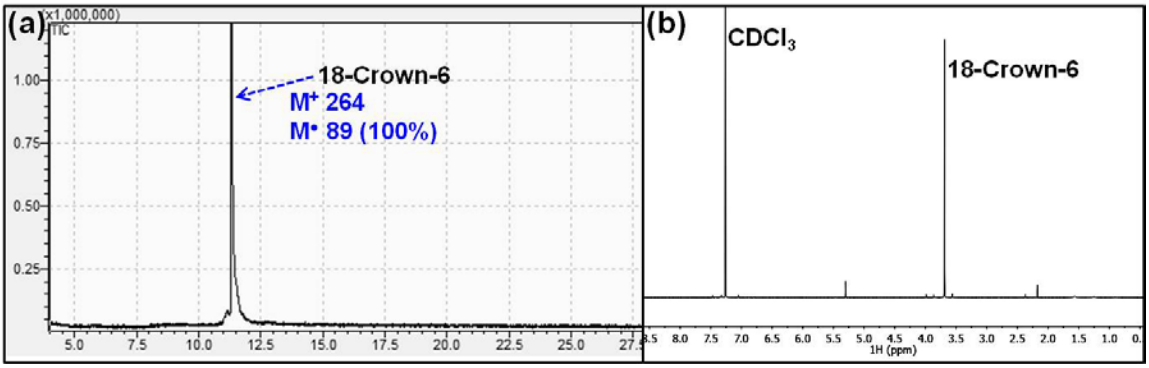

Figure S - 43: Byproduct analysis from **1,2-DMIm** after degradation study at 60 °C for 672 h in 100 % D_2O. $CDCl_3$ extracts were analyzed with (a) GC-MS and (b) ^{1}H NMR. ^{13}C DEPT-135 NMR and HSQC 2D-NMR were not taken since no information was obtained from GC-MS and ^{1}H NMR. Byproducts were unable to be clearly identified.

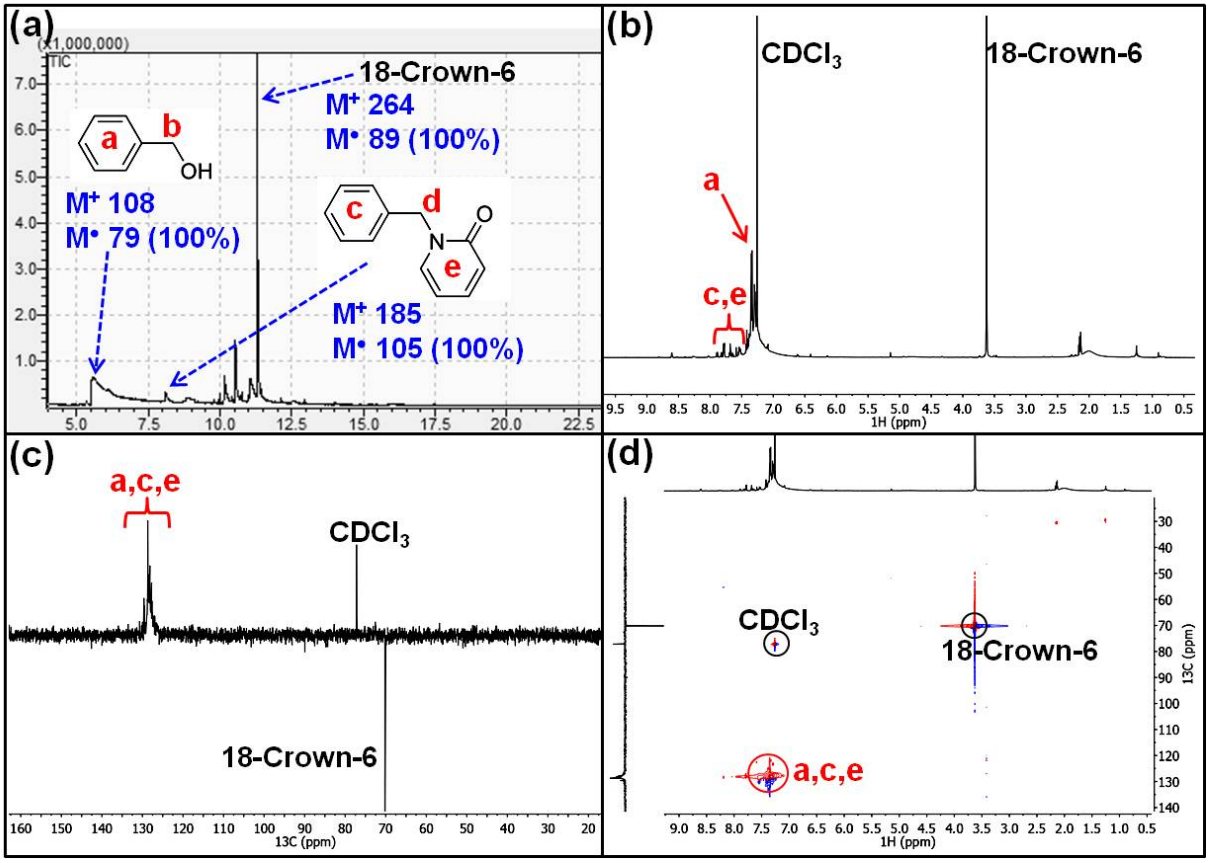

Figure S - 44: Byproduct analysis from **Pyr** after degradation study at 60 °C for 672 h in 100 % D_2O. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly. The benzylic $–CH_2–$ resonance peaks (b and d) are not visible in ^{1}H NMR spectrum since a high degree of H/D exchange occurred at this position. The mass spectrum of benzyl alcohol byproduct suggests the incorporation of multiple deuteriums (see Figure S49i).

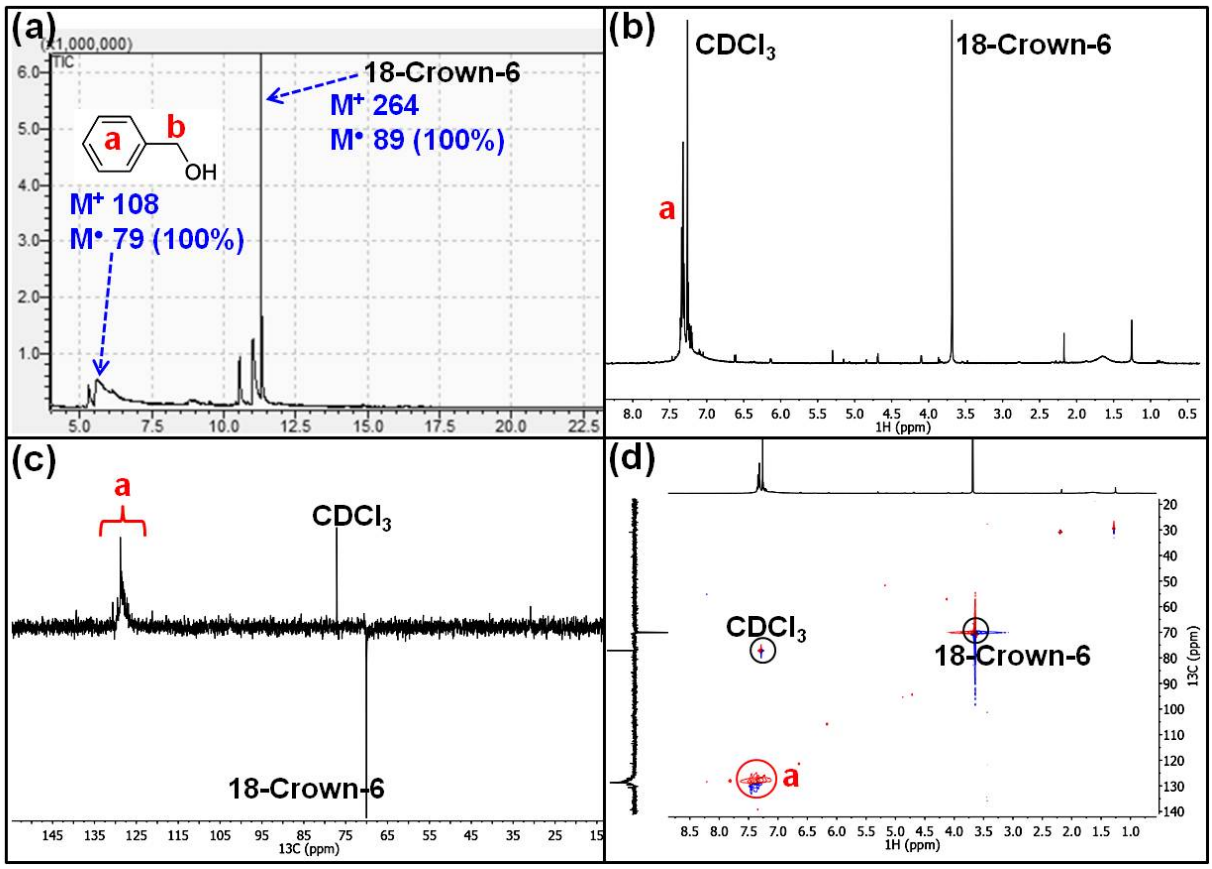

Figure S - 45: Byproduct analysis from **2MPyr** after degradation study at 60 °C for 672 h in 100 % D_2O. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly. The benzylic $–CH_2–$ resonance peak (labeled b) is not visible in ^{1}H NMR since a high degree of H/D exchange occurred at this position. The mass spectrum of benzyl alcohol byproduct suggests the incorporation of multiple deuteriums (see Figure S49j).

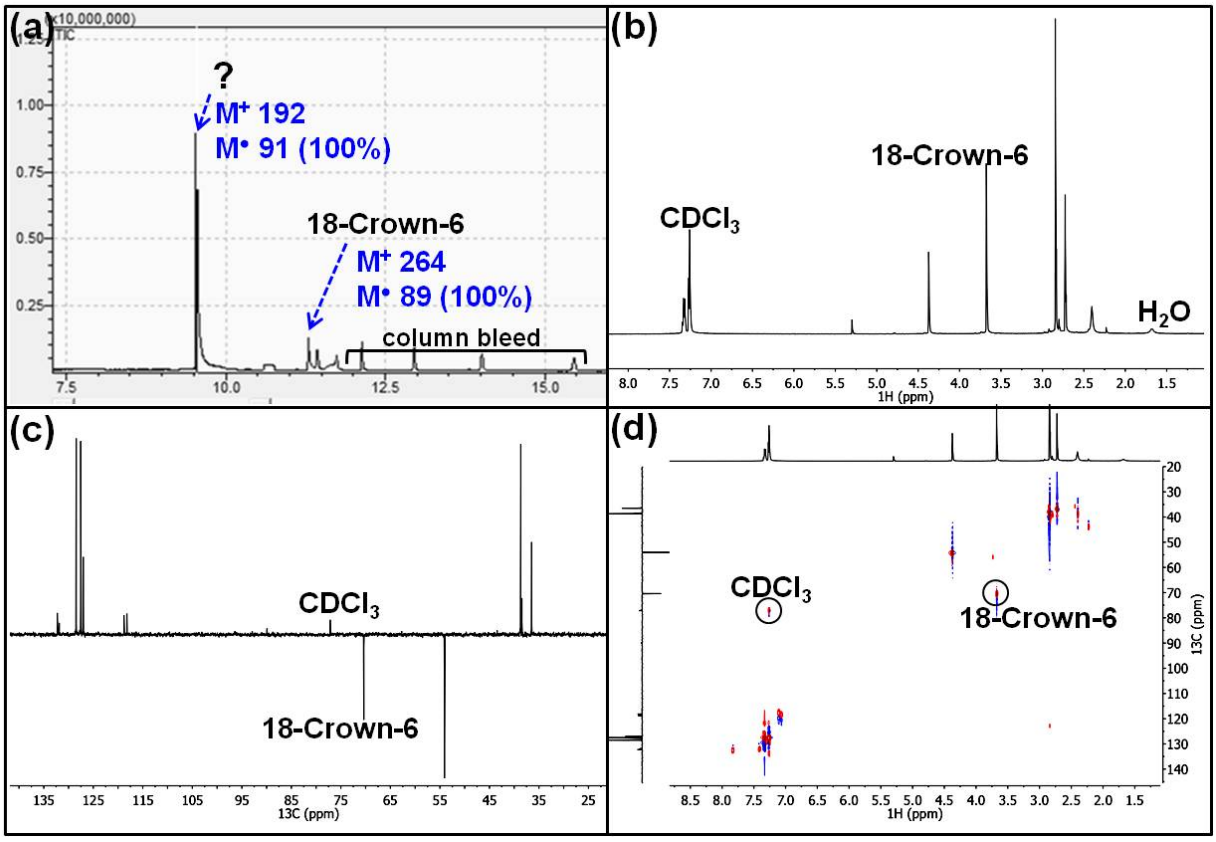

Figure S - 46: Byproduct analysis from **TMG** after degradation study at 60 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. The peak with question mark in (a) indicates an unidentified compound with a molecular ion peak of M^+ 192 and base peak of 91.

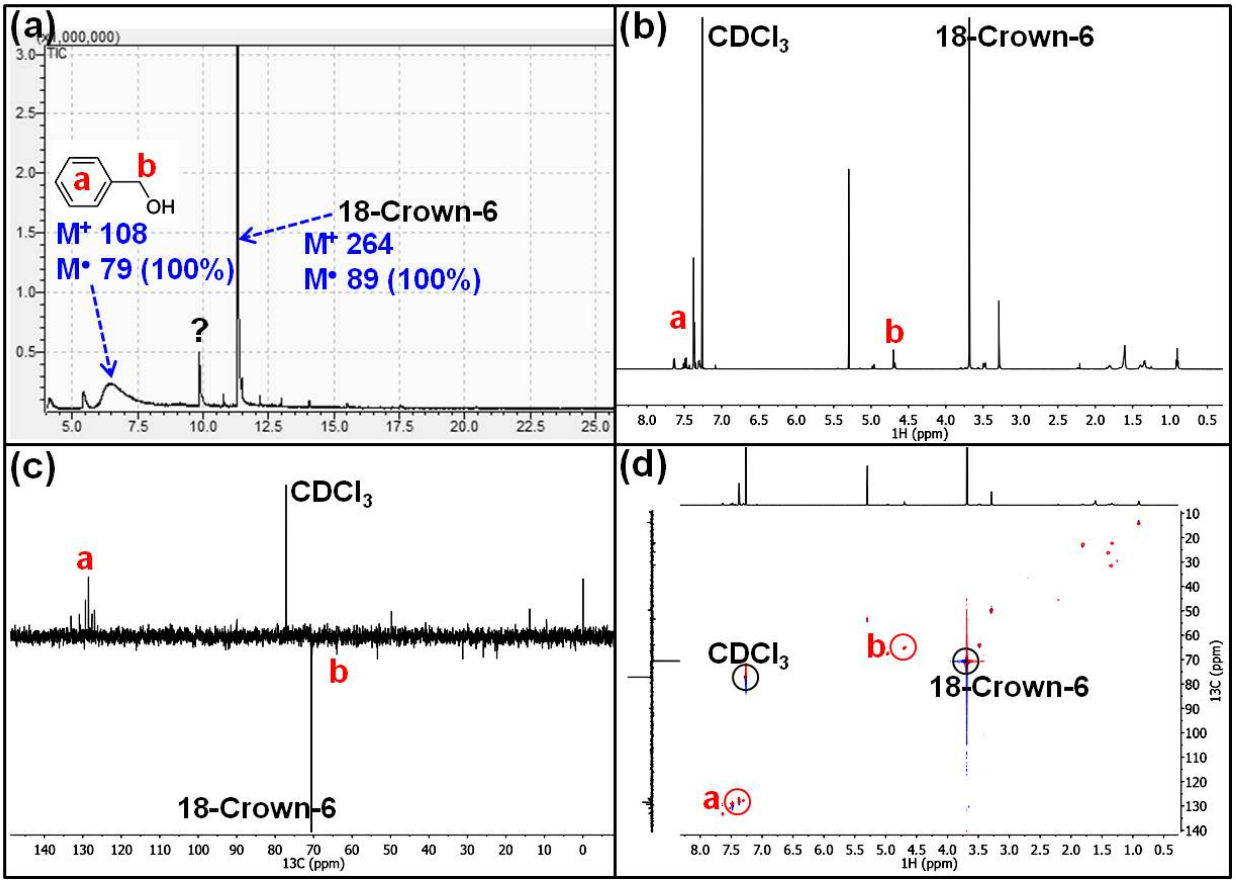

Figure S - 47: Byproduct analysis from **DMHA** after degradation study at 120 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Byproducts were unable to be clearly identified except benzyl alcohol. The peak with question mark in (a) indicates an unidentified compound with a molecular ion peak of M^+ 207 and base peak of 178.

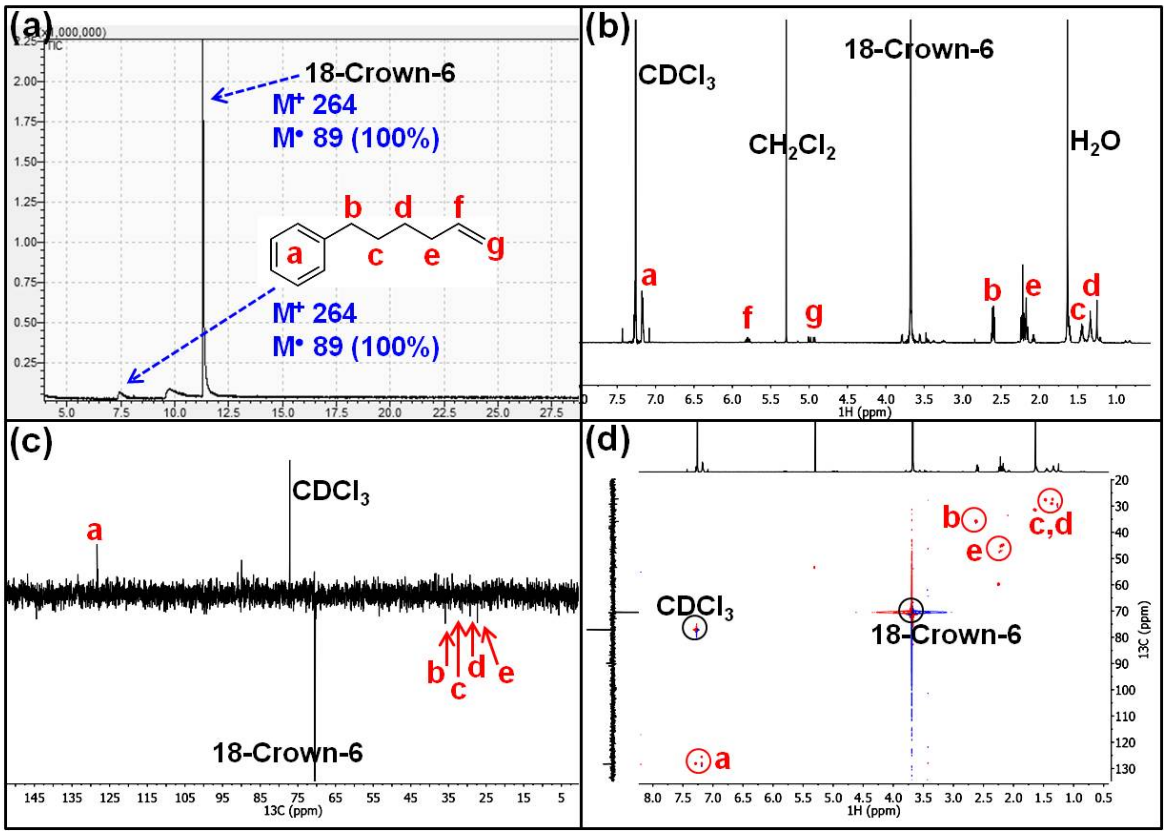

Figure S - 48: Byproduct analysis from **TMHA** after degradation study at 140 °C for 672 h. $CDCl_3$ extracts were analyzed with (a) GC-MS (b) ^{1}H NMR, (b) ^{13}C DEPT-135 NMR, and (d) HSQC 2D-NMR. Suggested byproducts formed are drawn and labeled accordingly. Suggested peaks correlate with hexa-5-enylbenzene reported in: T. J. A. Graham, T. H. Poole, C. N. Reese, B. C. Goess, *J. Org. Chem*., **2011**, *76*, 4132-4138.

17. Mass spectra of benzyl alcohol byproducts

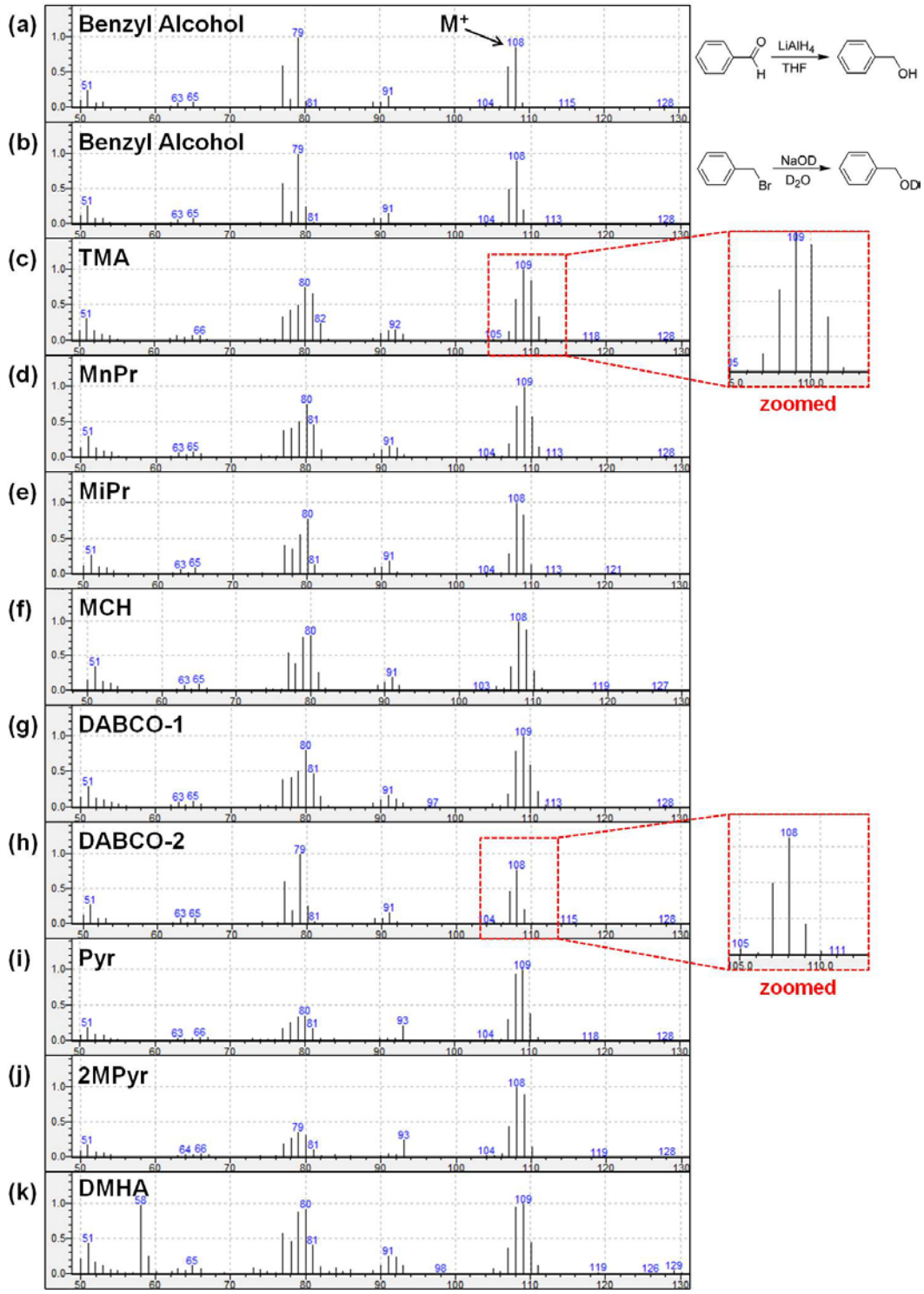

Figure S - 49: Mass spectra from benzyl alcohol byproducts extracted after QA degradation studies. Benzyl alcohol extracts from specified QAs are labeled accordingly. The top show MS spectra of authentic samples of benzyl alcohol as prepared from benzaldehyde (a) and from benzyl bromide (b) shown for reference. The additional isotope peaks indicate the incorporation of deuterium.