

Supporting Information for

Exploring Borinane-Based Multi-Ammonium Salts for Epoxide (Co)Polymerization: Insights into Structure-Activity Relationship

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Experimental Section

1. Materials

All the chemicals and reagents used in this study were obtained commercially from Sigma-Aldrich and used without further purification unless otherwise specified. These chemicals include 9-borabicyclo[3.3.1]nonane (9-BBN, 0.4 M in hexane), borane dimethyl sulfide complex (BMS), boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$), 1,4-pentadiene, and 5-bromo-1-pentene. Bis(hexamethylene)triamine (BHMT) was dried over P_2O_5 under an inert atmosphere, while bis(3-aminopropyl)amine (BAPA) and tris(2-aminoethyl)amine (TREN) were used from a new bottle and dried over pre-dried molecular sieves prior to use. Butyl amine, propylene oxide (PO), epichlorohydrin (ECH), phenyl glycidyl ether (PGE), tetrahydrofuran (THF), and acetonitrile were purified by first distilling them over CaH_2 and then over n-butyl lithium for two cycles using standard Schlenk techniques. Glycidyl azide (GA) was prepared according to the literature protocol starting from ECH; dried over CaH_2 and distilled at temperature below $35\text{ }^\circ\text{C}$ under reduced pressure.¹ Hexane was distilled using sodium/benzophenone, and CO_2 was dried over TIBA immediately before being filled into a Parr reactor.²

2. Characterizations

^1H NMR, ^{13}C NMR and ^{11}B NMR spectra were obtained using a Bruker AVANCE III 400 MHz, 500 MHz and 900 MHz NMR spectrometers, with CDCl_3 as the deuterated solvent. Gel permeation chromatography (GPC) traces of polymer samples were collected using a VISCOTEK VE2001 system equipped with Styragel HR2 THF and Styragel HR4 THF columns, and THF was employed as the eluent with a flow rate of 1 mL/min. The relative molar masses and distributions were determined at $35\text{ }^\circ\text{C}$ using a refractive index (RI) detector calibrated with linear polystyrene standards as calibrants. Differential scanning calorimetry (DSC) measurements were performed at

a heating rate of 10 °C /min on a Mettler Toledo DSC1/TC100 system under nitrogen atmosphere. The curve of the second heating scan was adopted to determine the glass transition temperature (T_g) and the T_g was measured as a midpoint value of the graph after drawing two tangents.

3. Methods

3.1. Synthesis of Borinane

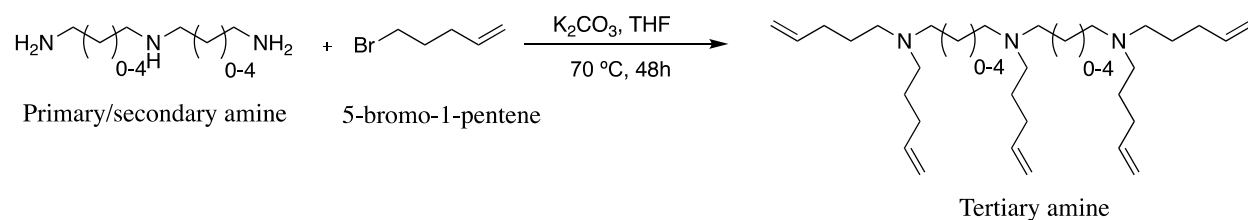
The six-membered cyclic borinane was synthesized as per reported literature procedures.³⁻⁴

3.2. General Procedure for the Synthesis of Catalysts A–D

In a typical procedure, Catalysts A–D were synthesized through a three-step process outlined as follows and their synthetic procedures were discussed in below in individual steps 1-3:

3.2.1. Step-1: General Procedure for Synthesis of Tertiary Amines of Catalysts A–D

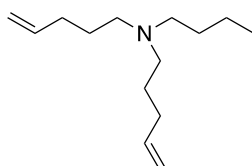
In a typical procedure, a flame-dried Schlenk flask equipped with a magnetic stir bar was employed. One equivalent of the amine starting material was added and dissolved in anhydrous THF. To this solution, an equal number of equivalents (one equivalent per each hydrogen present in the amine starting material) of 5-bromo-1-pentene and potassium carbonate were added. The reaction mixture was stirred at 70 °C for 48 hours or until complete amination was achieved as monitored by ¹H NMR. Subsequently, the solvent was removed via a rotary evaporation, and the crude product was subjected to purification through multiple washes with hexanes. The resulting material was then dissolved in either chloroform or ethanol. This solution was passed through a short column of neutral silica, followed by solvent removal via rotary evaporation to yield the pure product.



Scheme S1: General scheme for an amination reaction to convert primary/secondary amines to tertiary amines.

3.2.1.1. Step-1 of Catalyst-A: Synthesis of *N*-butyl-*N*-(pent-4-en-1-yl)pent-4-en-1-amine, $\text{C}_{14}\text{H}_{27}\text{N}$

Following the standard procedure for step-1, one equivalent of butyl amine (10 g, 0.137 moles, 1eq.), two equivalents of 5-bromo-1-pentene (40.8 g, 0.273 mol, 2eq.), and potassium carbonate (38 g, 274 mmol, 2eq.) were employed. This synthesis resulted in the desired pure product, obtained as a pale-yellow liquid through the process of distillation. Yield obtained is 90% (25.8 g, 0.123 moles).

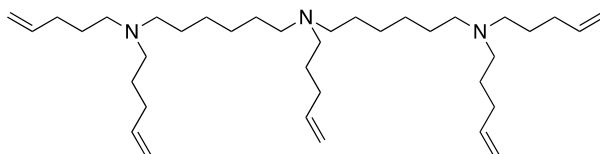


N-butyl-*N*-(pent-4-en-1-yl)pent-4-en-1-amine;
 $\text{C}_{14}\text{H}_{27}\text{N}$; molecular weight: 209.38 g/mol

3.2.1.2. Step-1 of Catalyst-B: Synthesis of *N*¹-(6-(di(pent-4-en-1-yl)amino)hexyl)-*N*¹,*N*⁶,*N*⁶-tri(pent-4-en-1-yl)hexane-1,6-diamine, $\text{C}_{37}\text{H}_{69}\text{N}_3$

Following the standard procedure for step-1, one equivalent of bis(hexamethylene)triamine (BHMT) (10 g, 0.0464 moles, 1eq.) was dissolved in 20 mL anhydrous THF. Subsequently, five equivalents of 5-bromo-1-pentene (34.6 g, 0.232 moles, 5eq.) and potassium carbonate (32.1 g, 0.232 moles, 5eq.) were added to the solution. This synthesis successfully yielded the desired pure

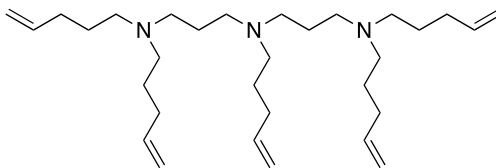
product, which was obtained in the form of a pale-yellow oily liquid after undergoing repeated passes through neutral silica. Yield obtained is 82% (21.1 g, 0.0380 moles).



*N*¹-(6-(di(pent-4-en-1-yl)amino)hexyl)-*N*¹,*N*⁶,*N*⁶-tri(pent-4-en-1-yl)hexane-1,6-diamine;
C₃₇H₆₉N₃; molecular weight: 555.98 g/mol

3.2.1.3. Step-1 of Catalyst-C: Synthesis of *N*¹-(3-(di(pent-4-en-1-yl)amino)propyl)-*N*¹,*N*³,*N*³-tri(pent-4-en-1-yl)propane-1,3-diamine, C₃₁H₅₇N

Following the standard procedure for step-1, one equivalent of bis(3-aminopropyl)amine (BAPA) (10 g, 0.0762 moles, 1eq.) was dissolved in 20 mL anhydrous THF, followed by the addition of five equivalents of 5-bromo-1-pentene (56.8 g, 0.381 moles, 5eq.) and potassium carbonate (52.6 g, 0.381 moles, 5eq.). This synthesis successfully yielded the desired pure product, which was obtained in the form of a pale-yellow oily liquid after undergoing repeated passes through neutral silica. Yield obtained is 78% (28 g, 0.059 moles).

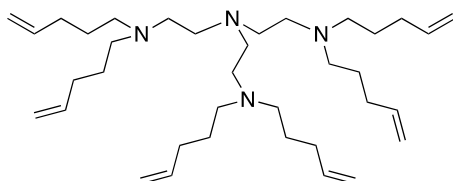


*N*¹-(3-(di(pent-4-en-1-yl)amino)propyl)-*N*¹,*N*³,*N*³-tri(pent-4-en-1-yl)propane-1,3-diamine;
C₃₁H₅₇N₃; molecular weight: 471.82 g/mol

3.2.1.4. Step-1 of Catalyst-D: Synthesis of *N*¹,*N*¹-bis(2-(di(pent-4-en-1-yl)amino)ethyl)-*N*²,*N*²-di(pent-4-en-1-yl)ethane-1,2-diamine, C₃₆H₆₆N₄

Following the standard procedure for step-1, one equivalent of tris(2-aminoethyl)amine (TREN) (10 g, 0.0684 moles, 1eq.) was dissolved in 20 mL anhydrous THF, followed by the addition of

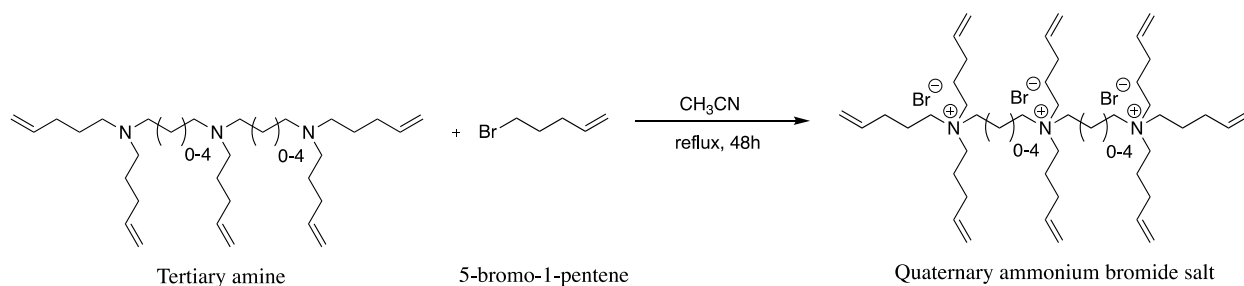
six equivalents of 5-bromo-1-pentene (61.1 g, 0.410 moles, 6eq.) and potassium carbonate (56.7 g, 0.410 moles, 6eq.). This synthesis successfully yielded the desired pure product, which was obtained in the form of a pale-yellow oily liquid after undergoing repeated passes through neutral silica. Yield obtained is 79% (30 g, 0.054 moles).



*N*¹,*N*¹-bis(2-(di(pent-4-en-1-yl)amino)ethyl)-*N*²,*N*²-di(pent-4-en-1-yl)ethane-1,2-diamine;
C₃₆H₆₆N₄; molecular weight: 554.95 g/mol

3.2.2. Step-2: General Procedure for Synthesis of Quaternary Ammonium Bromide Salts of Catalysts A–D

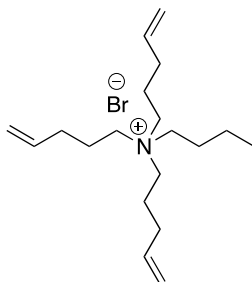
In a standard procedure, a flame-dried Schlenk flask equipped with a magnetic stir bar is utilized. One equivalent of tertiary amine obtained from step-1 was dissolved in the minimum amount of anhydrous acetonitrile to facilitate an efficient quaternization reaction. To this mixture, one equivalent of 5-bromo-1-pentene per nitrogen atom in the tertiary amine is added. The resulting solution was refluxed for 48 hours or until complete quaternization is confirmed by ¹H NMR monitoring. Subsequently, the crude product was re-dissolved in dichloromethane and subjected to purification via column chromatography, employing a chloroform/methanol elution system. The resulting pure product, obtained after rotary evaporation, was isolated and stored in a flask under an inert gas atmosphere.



Scheme S2: General scheme for a Menshutkin quaternization reaction to convert tertiary amines to quaternary ammonium salts.

3.2.2.1. Step-2 of Catalyst-A: Synthesis of *N*-butyl-*N,N*-di(pent-4-en-1-yl)pent-4-en-1-aminium bromide; $C_{19}H_{36}NBr$

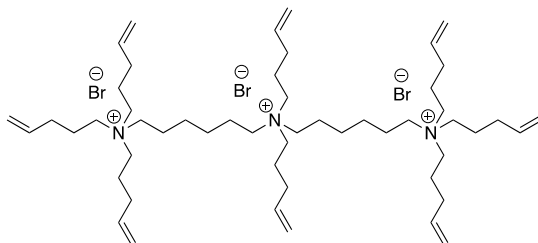
Following the standard procedure for step-2, one equivalent of the tertiary amine (10 g, 0.0478 moles, 1eq.) obtained in step-1 was dissolved in 15 mL anhydrous acetonitrile and one equivalent of 5-bromo-1-pentene (7.12 g, 0.0478 moles, 1eq.) was subsequently added to the mixture. This results in a solid white powder, which is dried over P_2O_5 under an inert atmosphere until complete drying was achieved. The resulting product is the quaternary ammonium bromide salt, prepared and ready for use in the next step. Yield obtained is 87% (14.9 g, 0.0416 moles).



N-butyl-*N,N*-di(pent-4-en-1-yl)pent-4-en-1-aminium bromide;
 $C_{19}H_{36}NBr$; molecular weight: 358.40 g/mol

3.2.2.2. Step-2 of Catalyst-B: Synthesis of N^1,N^1,N^1,N^6,N^6 -penta(pent-4-en-1-yl)- N^6 -(6-(tri(pent-4-en-1-yl)ammonio)hexyl)hexane-1,6-diaminium bromide; $C_{52}H_{96}N_3Br_3$

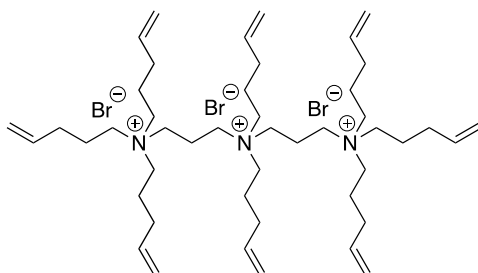
Following the standard procedure for step-2, one equivalent of the tertiary amine (10 g, 0.0179 moles, 1eq.) obtained in step-1 was dissolved in 15 mL anhydrous acetonitrile and three equivalents of 5-bromo-1-pentene (8 g, 0.0537 moles, 3eq.) was subsequently added to the mixture. The resulting pure product appears to be a pale-yellow oily liquid. Yield obtained is 74% (13.29 g, 0.0132 moles).



N^1,N^1,N^1,N^6,N^6 -penta(pent-4-en-1-yl)- N^6 -(6-(tri(pent-4-en-1-yl)ammonio)hexyl)hexane-1,6-diaminium bromide; $C_{52}H_{96}N_3Br_3$; molecular weight: 1003.06 g/mol

3.2.2.3. Step-2 of Catalyst-C: Synthesis of N^1,N^1,N^1,N^3,N^3 -penta(pent-4-en-1-yl)- N^3 -(3-(tri(pent-4-en-1-yl)ammonio)propyl)propane-1,3-diaminium bromide; $C_{46}H_{84}N_3Br_3$

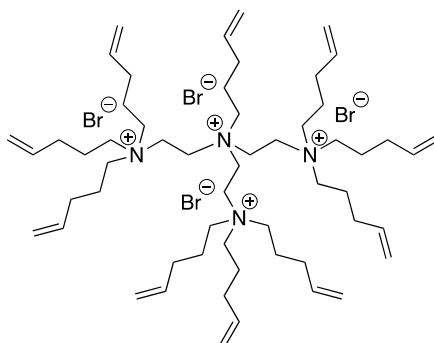
Following the standard procedure for step-2, one equivalent of the tertiary amine (10 g, 0.0212 moles, 1eq.) obtained in step-1 was dissolved in 15 mL anhydrous acetonitrile and three equivalents of 5-bromo-1-pentene (9.47 g, 0.0636 moles, 3eq.) was subsequently added to the mixture. The resulting pure product appears to be a pale-yellow oily liquid. Yield obtained is 76% (14.80 g, 0.0161 moles).



*N*¹,*N*¹,*N*¹,*N*³,*N*³-penta(pent-4-en-1-yl)-*N*³-(3-(tri(pent-4-en-1-yl)ammonio)propyl)propane-1,3-diaminium bromide; C₄₆H₈₄N₃Br₃; molecular weight: 918.90 g/mol

3.2.2.4. Step-2 of Catalyst-D: Synthesis of *N*¹,*N*¹,*N*¹,*N*²-tetra(pent-4-en-1-yl)-*N*²,*N*²-bis(2-(tri(pent-4-en-1-yl)ammonio)ethyl)ethane-1,2-diaminium bromide; C₅₆H₁₀₂N₄Br₄

Following the standard procedure for step-2, one equivalent of the tertiary amine (10 g, 0.0180 moles, 1eq.) obtained in step-1 was dissolved in 15 mL anhydrous acetonitrile and four equivalents of 5-bromo-1-pentene (10.70 g, 0.0720 moles, 4eq.) was subsequently added to the mixture. The resulting pure product appears to be a pale-yellow oily liquid. Yield obtained is 72% (14.96 g, 0.0130 moles).

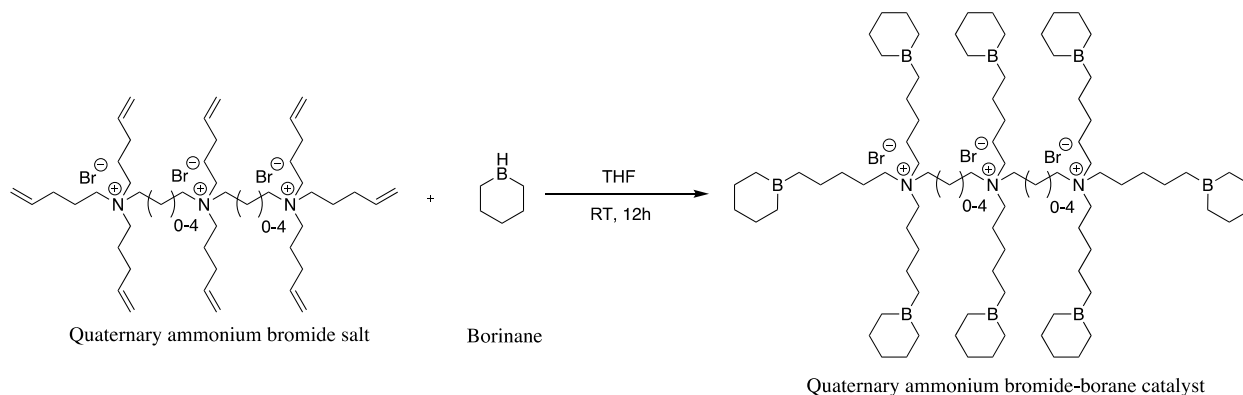


*N*¹,*N*¹,*N*¹,*N*²-tetra(pent-4-en-1-yl)-*N*²,*N*²-bis(2-(tri(pent-4-en-1-yl)ammonio)ethyl)ethane-1,2-diaminium bromide; C₅₆H₁₀₂N₄Br₄; molecular weight: 1151.06 g/mol

3.2.3. Step-3: General Procedure for Synthesis of Quaternary Ammonium-Borinane Catalysts A–D

In the standard procedure, a flame-dried Schlenk flask equipped with a magnetic stir bar was employed. The flask was charged with one equivalent of the quaternary ammonium bromide salt

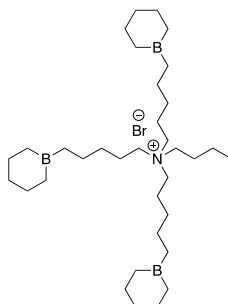
obtained from step-2, and it was dissolved in anhydrous THF. One equivalent of six-membered cyclic borinane, corresponding to each double bond present in the structure, was added to the mixture. The resulting mixture was stirred at room temperature for 12 hours. Completion of the hydroboration reaction was monitored using ^{11}B NMR, and the final mixture can be used directly for polymerization reactions without the need for further purification.



Scheme S3: General scheme for a hydroboration reaction to convert quaternary ammonium salts to quaternary ammonium-borane catalysts.

3.2.3.1. Step-3 of Catalyst-A: Synthesis of 5-(borinan-1-yl)-*N,N*-bis(5-(borinan-1-yl)pentyl)-*N*-butylpentan-1-aminium bromide; $\text{C}_{34}\text{H}_{69}\text{B}_3\text{NBr}$

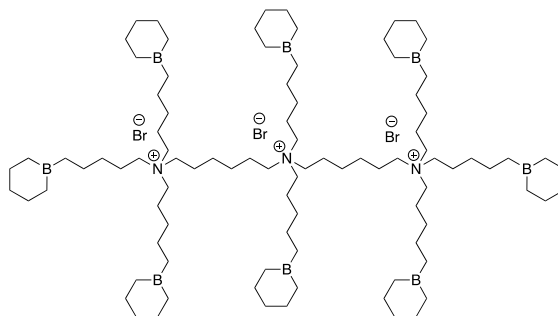
Following the standard procedure for step-3, one equivalent of quaternary ammonium bromide salt (3.58 g, 0.01 moles, 1eq.) was dissolved in 10 mL anhydrous THF and three equivalents of the borinane (2.46 g, 0.03 moles, 3eq.) was added to the mixture. Yield obtained is 100% (6.04 g, 0.01 moles).



5-(borinan-1-yl)-*N,N*-bis(5-(borinan-1-yl)pentyl)-*N*-butylpentan-1-aminium bromide;
 $C_{34}H_{69}B_3NBr$; molecular weight: 604.26 g/mol

3.2.3.2. Step-3 of Catalyst-B: Synthesis of *N*¹,*N*¹,*N*¹,*N*⁶,*N*⁶-pentakis(5-(borinan-1-yl)pentyl)-*N*⁶-(6-(tris(5-(borinan-1-yl)pentyl)ammonio)hexyl)hexane-1,6-diaminium bromide;
 $C_{92}H_{184}B_8N_3Br_3$

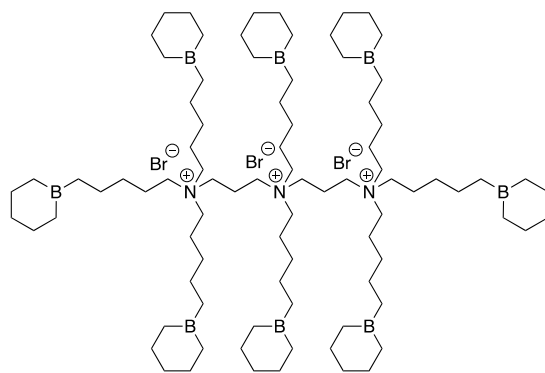
Following the standard procedure for step-3, one equivalent of quaternary ammonium bromide salt (5.00 g, 0.005 moles, 1eq.) was dissolved in 5 mL anhydrous THF and eight equivalents of the borinane (3.28 g, 0.04 moles, 8eq.) was added to the mixture. Yield obtained is 100% (8.28 g, 0.005 moles).



*N*¹,*N*¹,*N*¹,*N*⁶,*N*⁶-pentakis(5-(borinan-1-yl)pentyl)-*N*⁶-(6-(tris(5-(borinan-1-yl)pentyl)ammonio)hexyl)hexane-1,6-diaminium bromide; $C_{92}H_{184}B_8N_3Br_3$; molecular weight: 1658.68 g/mol

3.2.3.3. Step-3 of Catalyst-C: Synthesis of *N*¹,*N*¹,*N*¹,*N*³,*N*³-pentakis(5-(borinan-1-yl)pentyl)-*N*³-(3-(tris(5-(borinan-1-yl)pentyl)ammonio)propyl)propane-1,3-diaminium bromide;
 $C_{86}H_{172}B_8N_3Br_3$

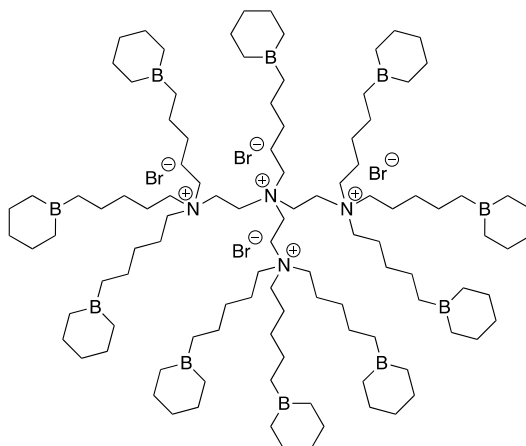
Following the standard procedure for step-3, one equivalent of quaternary ammonium bromide salt (4.59 g, 0.005 moles, 1eq.) was dissolved in 5 mL anhydrous THF and eight equivalents of the borinane (3.28 g, 0.04 moles, 8eq.) was added to the mixture. Yield obtained is 100% (7.87 g, 0.005 moles).



*N*¹,*N*¹,*N*¹,*N*³,*N*³-pentakis(5-(borinan-1-yl)pentyl)-*N*³-(3-(tris(5-(borinan-1-yl)pentyl)ammonio)propyl)propane-1,3-diaminium bromide; C₈₆H₁₇₂B₈N₃Br₃; molecular weight: 1574.52 g/mol

3.2.3.4. Step-3 of Catalyst-D: Synthesis of *N*¹,*N*¹,*N*¹,*N*²-tetrakis(5-(borinan-1-yl)pentyl)-*N*²,*N*²-bis(2-(tris(5-(borinan-1-yl)pentyl)ammonio)ethyl)ethane-1,2-diaminium bromide; C₁₀₆H₂₁₂B₁₀N₄Br₄

Following the standard procedure for step-3, one equivalent of quaternary ammonium bromide salt (5.75 g, 0.005 moles, 1eq.) was dissolved in 5 mL anhydrous THF and ten equivalents of the borinane (4.09 g, 0.05 moles, 10eq.) was added to the above solution. Yield obtained is 100% (9.84 g, 0.005 moles).



*N*¹,*N*¹,*N*¹,*N*²-tetrakis(5-(borinan-1-yl)pentyl)-*N*²,*N*²-bis(2-(tris(5-(borinan-1-yl)pentyl)ammonio)ethyl)ethane-1,2-diaminium bromide; C₁₀₆H₂₁₂B₁₀N₄Br₄; molecular weight: 1970.59 g/mol

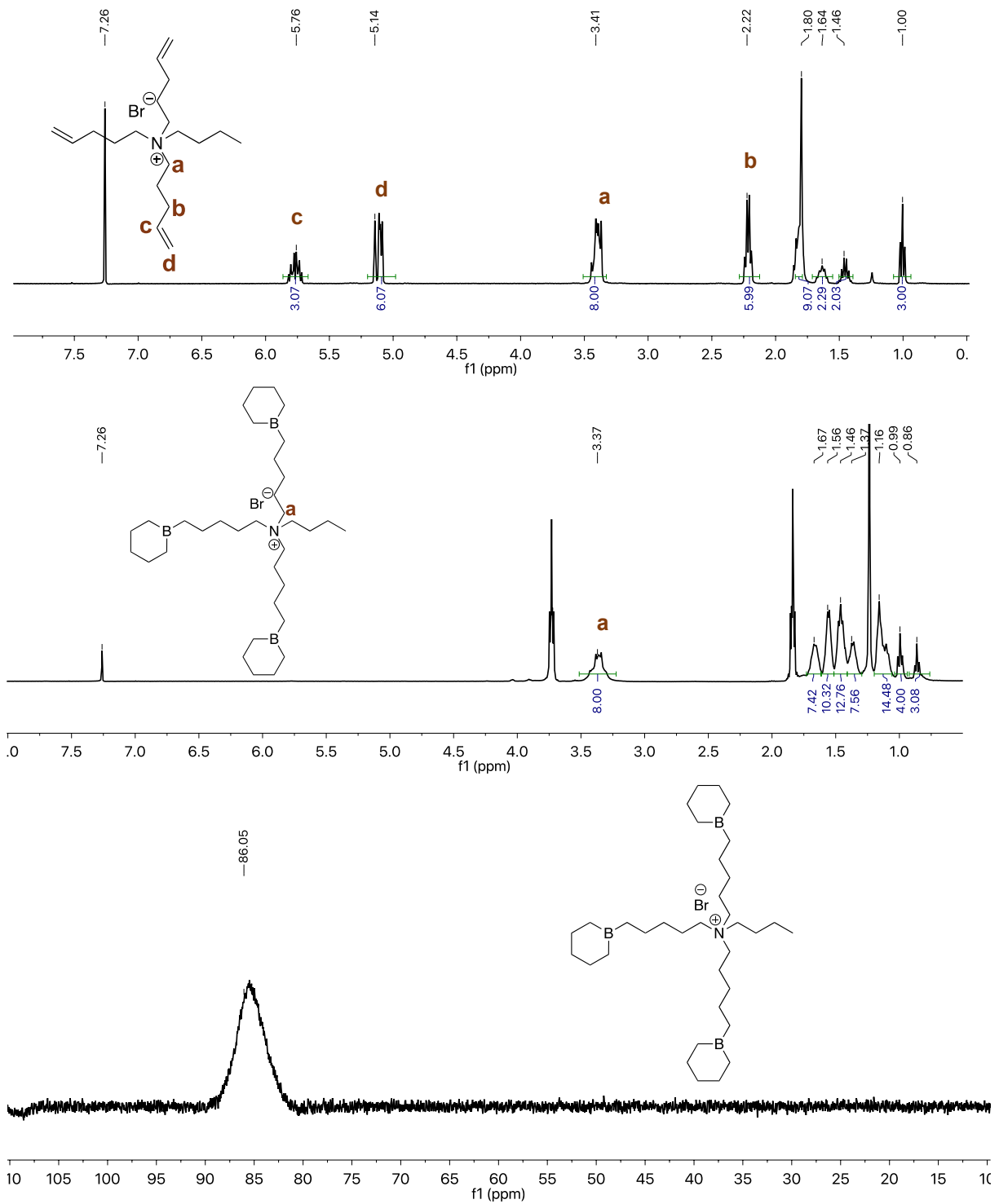


Figure S1: ^1H NMR of quaternary ammonium salt from step-2 of Catalyst-A in CDCl_3 (top); ^1H NMR of quaternary ammonium salt-Borane from step-3 of Catalyst-A in CDCl_3 (middle); ^{11}B NMR of quaternary ammonium salt-Borane from step-3 of Catalyst-A (bottom) in CDCl_3 .

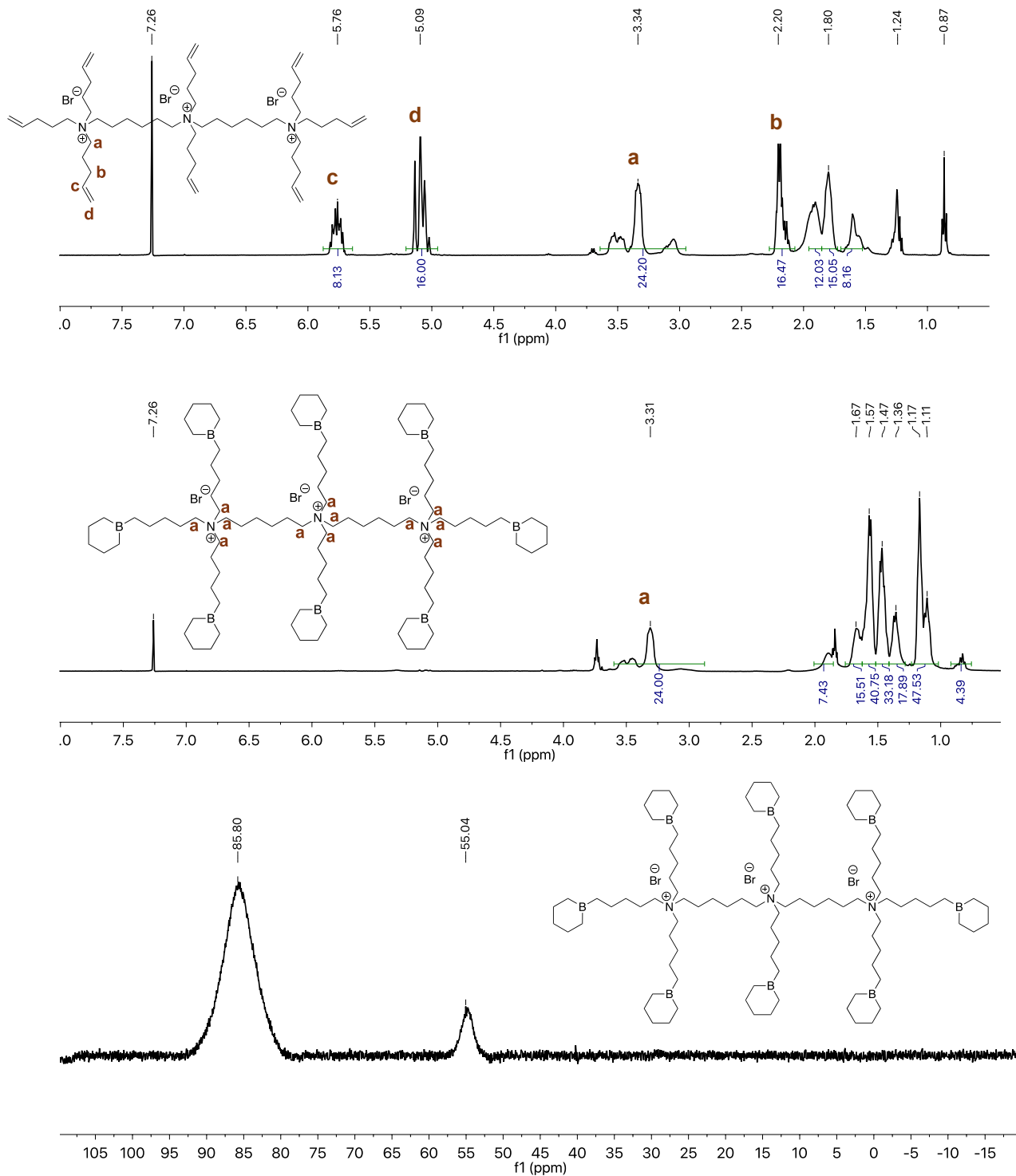
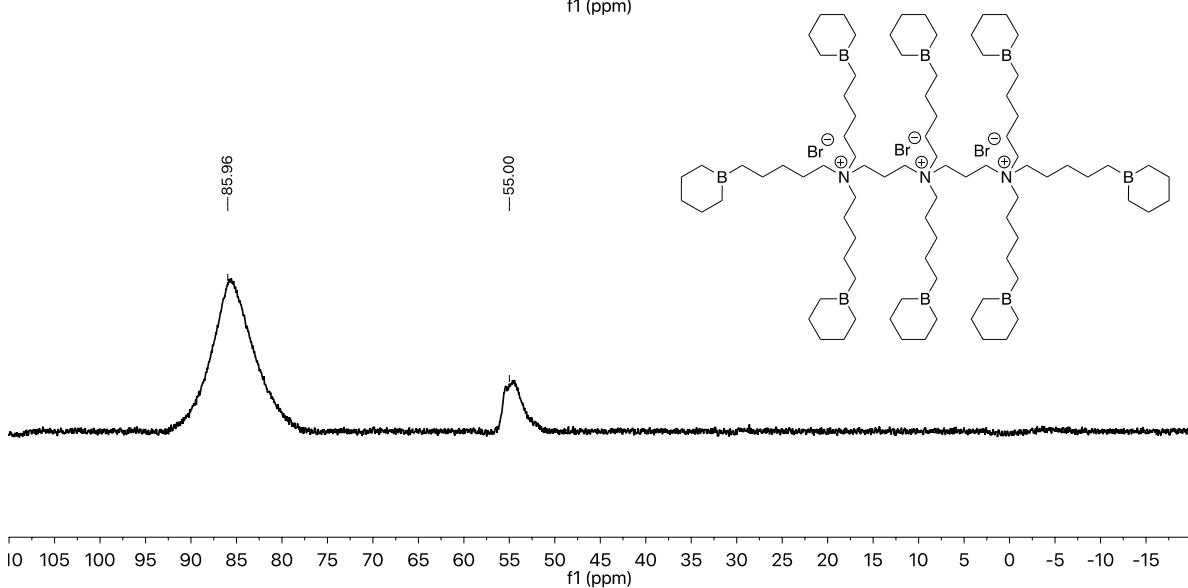
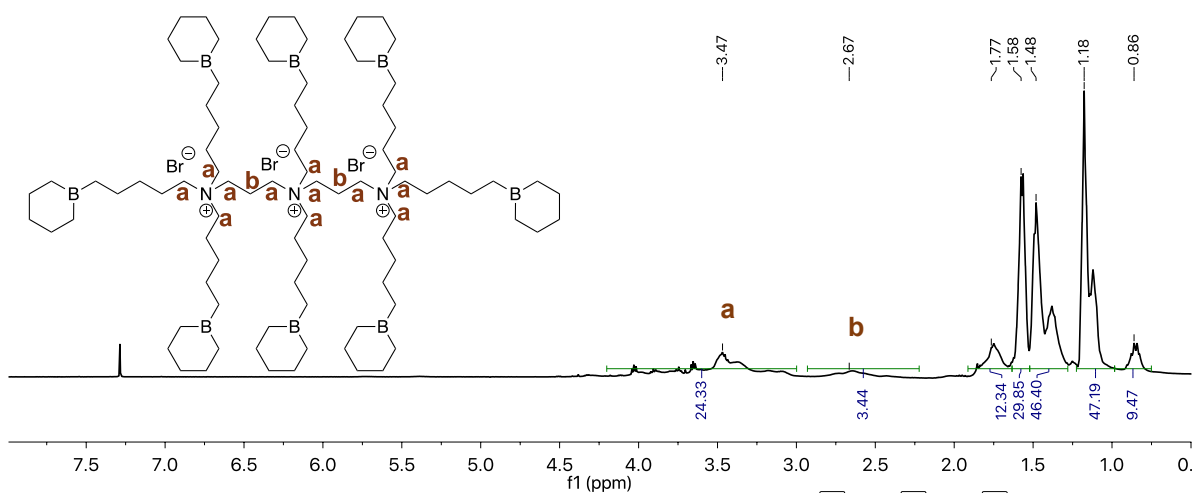
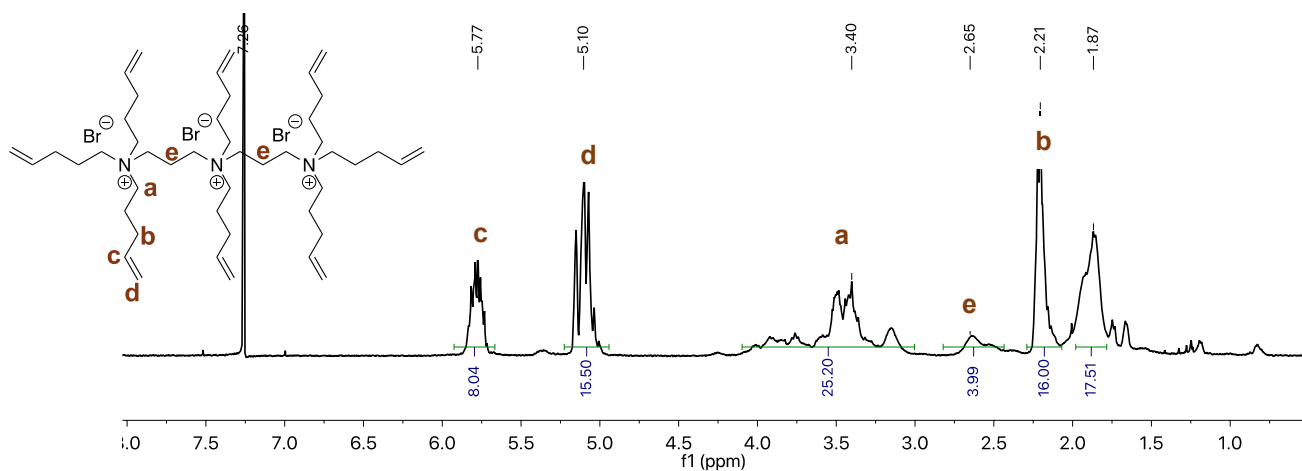


Figure S2: ^1H NMR of quaternary ammonium salt from step-2 of Catalyst-B in CDCl_3 (top); ^1H NMR of quaternary ammonium salt-Borane from step-3 of Catalyst-B in CDCl_3 (middle); ^{11}B NMR of quaternary ammonium salt-Borane from step-3 of Catalyst-B (bottom) in CDCl_3 .



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figure S3: ¹H NMR of quaternary ammonium salt from step-2 of Catalyst-C in CDCl₃ (top); ¹H

NMR of quaternary ammonium salt-Borane from step-3 of Catalyst-C in CDCl_3 (middle); ^{11}B

NMR of quaternary ammonium salt-Borane from step-3 of Catalyst-C (bottom) in CDCl_3 .

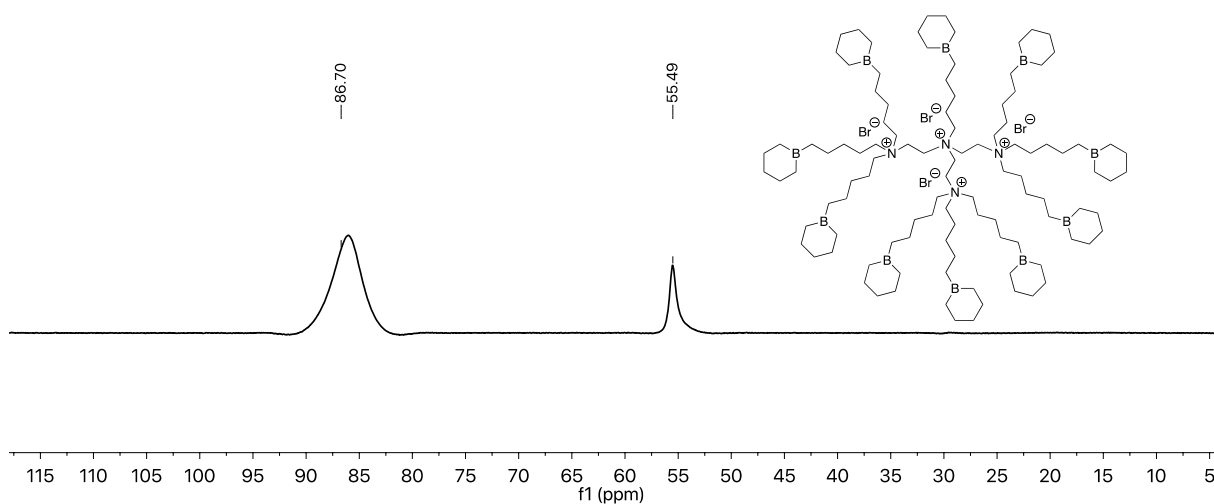
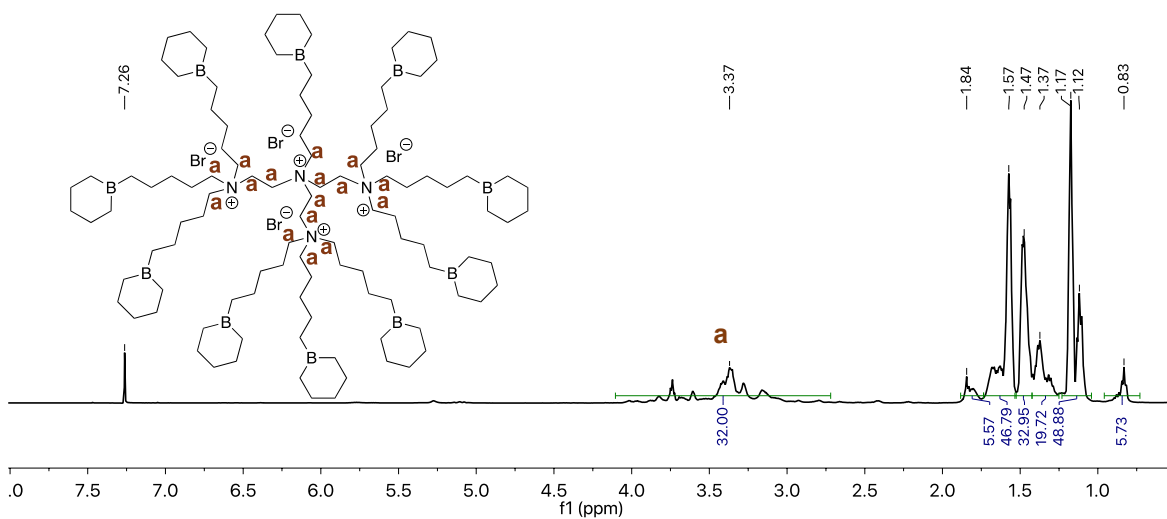
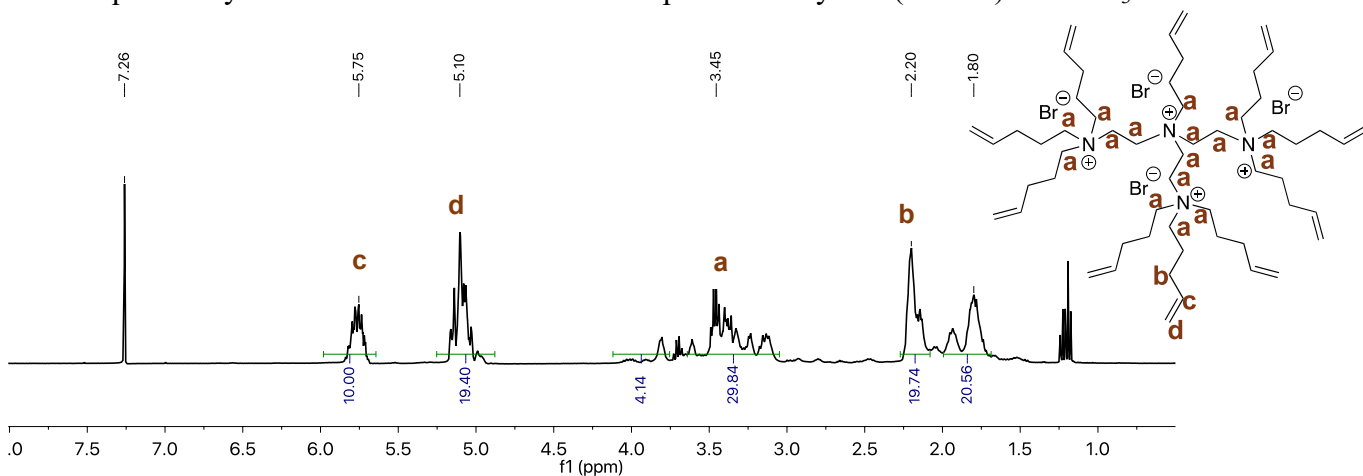


Figure S4: ^1H NMR of quaternary ammonium salt from step-2 of Catalyst-D in CDCl_3 (top); ^1H NMR of quaternary ammonium salt-Borane from step-3 of Catalyst-D in CDCl_3 (middle); ^{11}B NMR of quaternary ammonium salt-Borane from step-3 of Catalyst-D (bottom) in CDCl_3 .

3.3. General Procedure for the ROP of epoxides by Catalysts A, B, C or D

Inside a glovebox, the synthesized catalysts A, B, C and D were dissolved in THF to obtain a 0.1M solution of the respective catalyst in THF. In a typical polymerization procedure, required quantity of dried and distilled epoxide (PO or ECH or GA) was added to a flame dried 25 mL volume Schlenk flask followed by required amount of 1M catalyst solution. The reaction was maintained at specific temperature and time. The reaction progress was monitored by taking an aliquot from reaction mixture under inert atmosphere and by ^1H NMR spectroscopy. The obtained crude product was analyzed for ^1H NMR and GPC characterizations.

3.3.1. Representative Procedure for the ROP of PO by catalyst B and corresponding to entry-2, Table-1

Inside a glovebox, 3000 eq. PO (3 mL, 42.9 mmol) and 1 eq. catalyst B in THF containing 3 eq. ammonium bromides (0.1M, 143.1 μL , 0.0143 mmol) were added, in the same order, to a flame dried 25 mL volume Schlenk flask. A highly exothermic reaction was observed immediately upon addition of catalyst B and reaction mixture turned viscous almost instantaneously. The reaction mixture was further stirred at 25 $^\circ\text{C}$ for additional 10 minutes. The resultant crude product was dissolved in 1-2 mL THF and characterized by ^1H NMR and GPC analysis.

3.3.2. Representative Procedure for the ROP of ECH by catalyst B and corresponding to entry-2, Table-2

Inside a glovebox, 750 eq. ECH (3 mL, 38.3 mmol) and 1 eq. catalyst B in THF containing 3 eq. ammonium bromides (0.1M, 0.51 mL, 0.051 mmol) were added, in the same order, to a flame

dried 25 mL volume Schlenk flask. The flask was immediately immersed in cold bath regulated at -20 °C and stirred for 3 hours. The resultant crude product was dissolved in 1-2 mL THF and characterized by ¹H NMR and GPC analysis.

3.3.3. Representative Procedure for the ROP of ECH by catalyst B and corresponding to entries 1a, 1b, 1c in Table-3

Inside a glovebox, 750 eq. ECH (3 mL, 38.3 mmol) and 1 eq. catalyst B in THF containing 3 eq. ammonium bromides (0.1M, 0.51 mL, 0.051 mmol) were added, in the same order, to a flame dried 25 mL volume Schlenk flask. The flask was immediately immersed in cold bath regulated at -20 °C and stirred for 3 hours. An aliquot was collected under inert atmosphere and characterized by ¹H NMR and GPC analysis. The flask was transferred to pre heated oil bath at 80 °C and stirred up to 48 hours. An aliquot was collected after 3 hours and 48 hours and characterized by ¹H NMR and GPC analysis. The resultant crude product was dissolved in 1-2 mL THF and characterized by ¹H NMR and GPC analysis.

3.3.4. Representative Procedure for the ROP of GA by catalyst B and corresponding to entry-3, Table-4

Inside a glovebox, 750 eq. GA (3 mL, 37.54 mmol) and 1 eq. catalyst B in THF containing 3 eq. ammonium bromides (0.1M, 0.50 mL, 0.050 mmol) were added, in the same order, to a flame dried 25 mL volume Schlenk flask. The flask was immediately immersed in cold bath regulated at -20 °C and stirred for 72 hours. The resultant crude product was dissolved in 1-2 mL THF and characterized by ¹H NMR and GPC analysis.

3.4. General Procedure for the ROCOP of epoxides and CO₂ by Catalysts A, B, C or D

Inside a glovebox, the synthesized catalysts A, B, C and D were dissolved in THF to obtain a 0.1M solution of the respective catalyst in THF. In a typical polymerization procedure, a thoroughly

dried high-pressure Parr reactor vessel was charged with required amount of 1M catalyst solution in THF. Required volume of epoxide (PO or ECH) was carefully added to a separate glass vial and the vial was carefully immersed into the catalyst solution such that both solutions were isolated without mixing with each other. The reactor was sealed and purged with 10 bar CO₂ gas. Now the Parr reactor was vigorously shaken such that catalyst solution and epoxide mix with each other. The reaction was carried out at specified temperature and time. After completion, the reaction mixture was quenched with 5% HCl in THF and then precipitated in Hexane/MeOH/water. The resulting polymer product was dried under vacuum at 45 °C until it was completely dry. The resultant product was characterized by ¹H NMR and GPC analysis.

3.4.1. Representative polymerization procedure for the ROCOP of PO and CO₂ by Catalyst-B and corresponding to entry-2, Table-5

Inside a glovebox, 3000 eq. PO (3 mL, 42.9 mmol) was added to the glass vial and 1 eq. catalyst B in THF containing 3 eq. ammonium bromides (0.1M, 143.1 μL, 0.0143 mmol) was added to the reactor vessel. The reactor was sealed under inert atmosphere and purged with 10 bar CO₂ gas. The Parr reactor was vigorously shaken such that catalyst solution and PO mix with each other. The reaction mixture was stirred at 40 °C and 200 rpm for 12 h. The reaction mixture was quenched with 5% HCl in THF and characterized by ¹H NMR and GPC analysis. The resulting polymer product was further precipitated in Hexane/MeOH/water and dried under vacuum at 45 °C until it was completely dry.

3.4.2. Representative polymerization procedure for the ROCOP of ECH and CO₂ by Catalyst-B and corresponding to entry-8, Table-5

Inside a glovebox, 750 eq. ECH (3 mL, 38.3 mmol) was added to the glass vial and 1 eq. catalyst B in THF containing 3 eq. ammonium bromides (0.1M, 0.51 mL, 0.051 mmol) was added to the

reactor vessel. The reactor was sealed under inert atmosphere and purged with 10 bar CO₂ gas. The Parr reactor was vigorously shaken such that catalyst solution and PO mix with each other. The reaction mixture was stirred at 40 °C and 200 rpm for 12 h. The reaction mixture was quenched with 5% HCl in THF and characterized by ¹H NMR and GPC analysis. The resulting polymer product was further precipitated in Hexane/MeOH/water and dried under vacuum at 45 °C until it was completely dry.

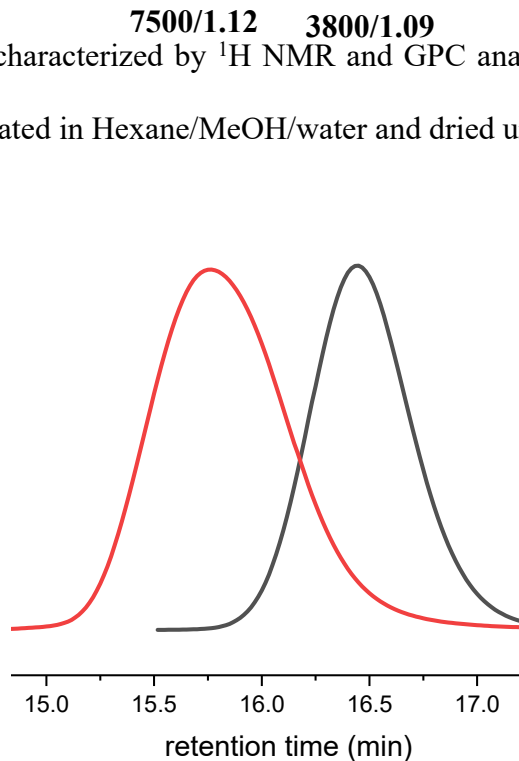


Figure S5. GPC traces for PPO samples formed by catalyst-B. Black trace represents PPO formed from first batch of PO and Red trace represents PPO formed after addition of second batch of PO.

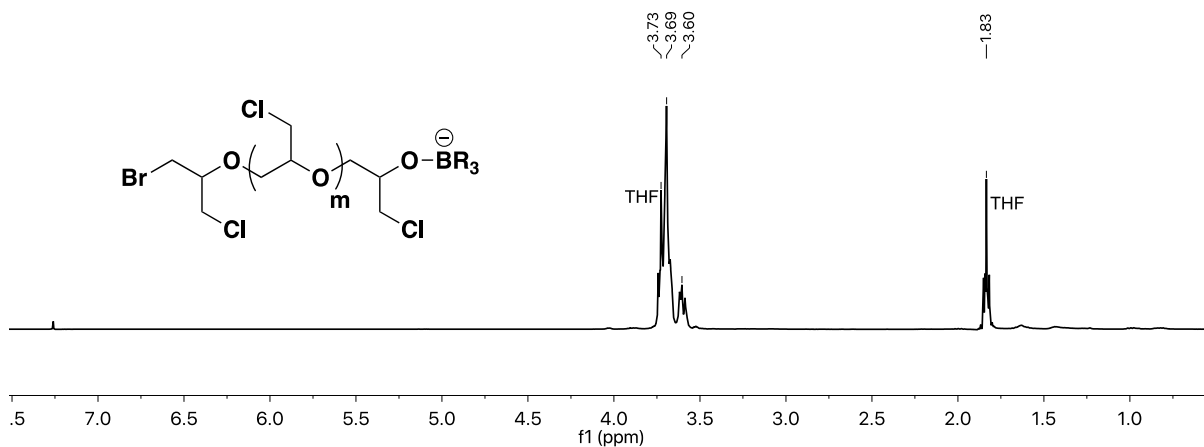


Figure S6: Representative ^1H NMR of poly(epichlorohydrin) crude product synthesized at $-20\text{ }^\circ\text{C}$ from entry-2, Table-2.

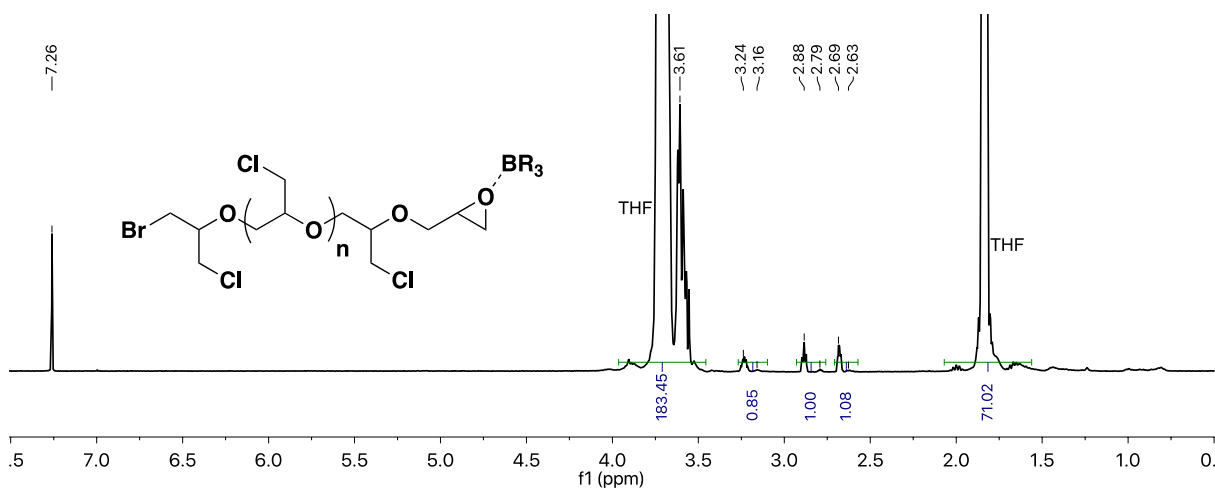


Figure S7: Representative ^1H NMR of poly(epichlorohydrin) crude product synthesized at $25\text{ }^\circ\text{C}$ from entry-5, Table-2.

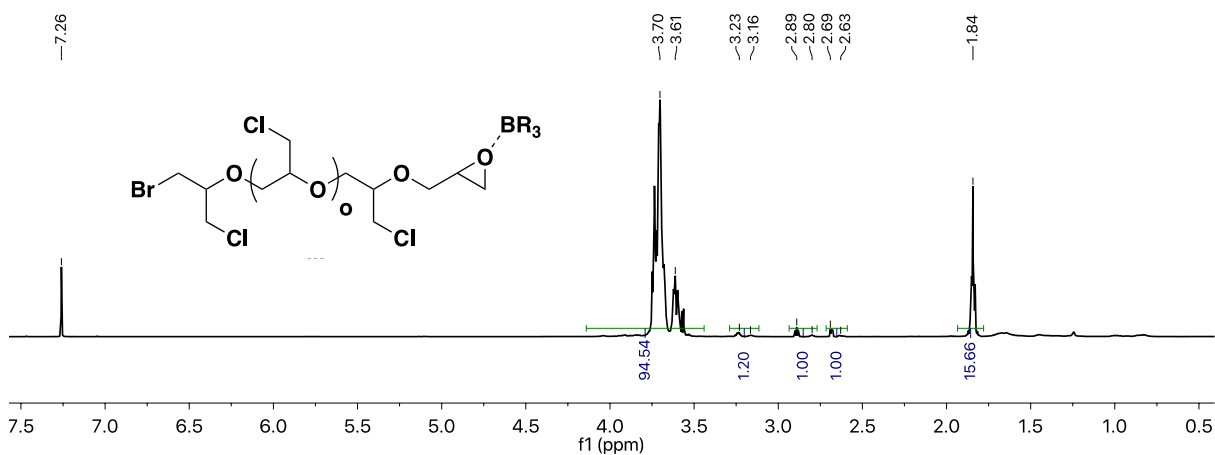


Figure S8: Representative ^1H NMR of poly(epichlorohydrin) crude product synthesized at $80\text{ }^\circ\text{C}$ for 3h from entry-6, Table-2.

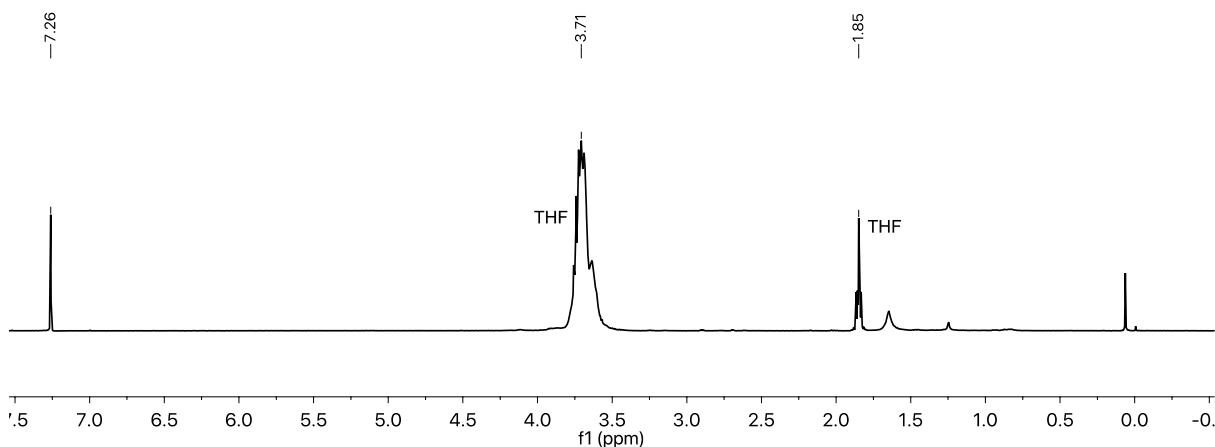


Figure S9: Representative ^1H NMR of poly(epichlorohydrin) crude product synthesized at $80\text{ }^\circ\text{C}$ for 48h (prolonged reaction of entry-6, Table-2).

Rate of propagation: $R_p = k_p [I] * [M]$

Rate of transfer: $R_{tr} = k_{tr} [I] * \frac{[M]}{[I]} = k_{tr} [M]$

$$\frac{R_{tr}}{R_p} = \frac{k_{tr} [M]}{k_p [I][M]}$$

Assuming $k_p > k_{tr}$

$$\frac{R_{tr}}{R_p} = \frac{k_{tr}}{k_p [I]}$$

For low degree of polymerization, $[I]$ is high and therefore $k_p [I]$ is high enough. Therefore,

$$\frac{R_{tr}}{R_p} \approx 0$$

For high degree of polymerization, $[I]$ is low and therefore $k_p [I]$ is comparable to k_{tr}

Figure S10: Rate equations for comparison of rate of propagation vs. rate of transfer reactions at different initiator concentrations in ECH polymerization

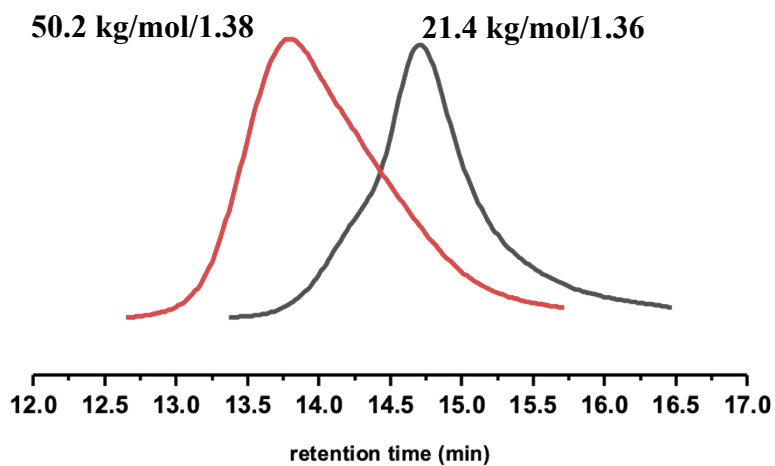
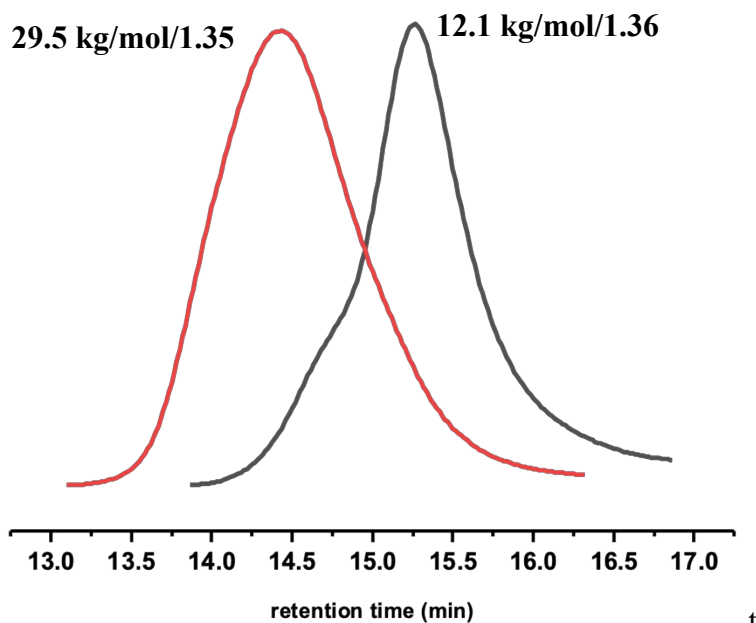


Figure S11. Representative GPC traces for poly(epichlorohydrin) synthesized as per entries 1a and 1b in Table-3. Traces from left to right: black trace (entry-1a, Table-3), red trace (entry-1b, Table-3).



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Figure S12. Representative GPC traces for poly(epichlorohydrin) synthesized as per entries 2a and 2b in Table-3. Traces from left to right: black trace (entry-2a, Table-3), red trace (entry-2b, Table-3).

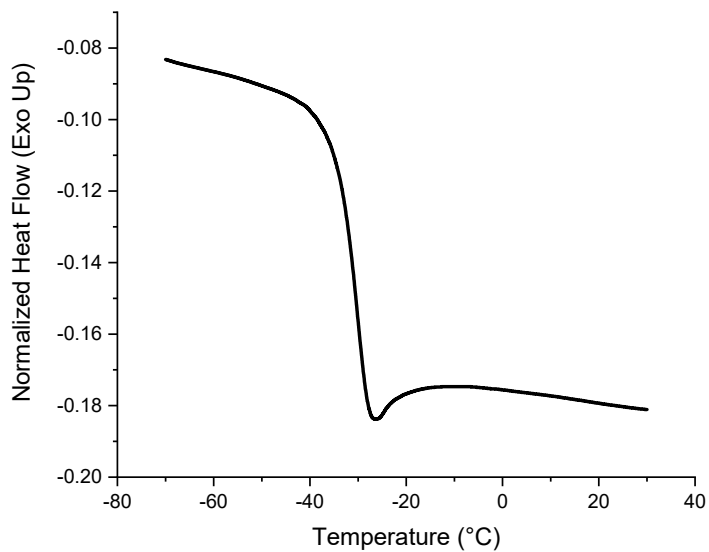


Figure S13. PECH from entry 3a, Table-3 (before coupling). T_g observed is -32 °C.

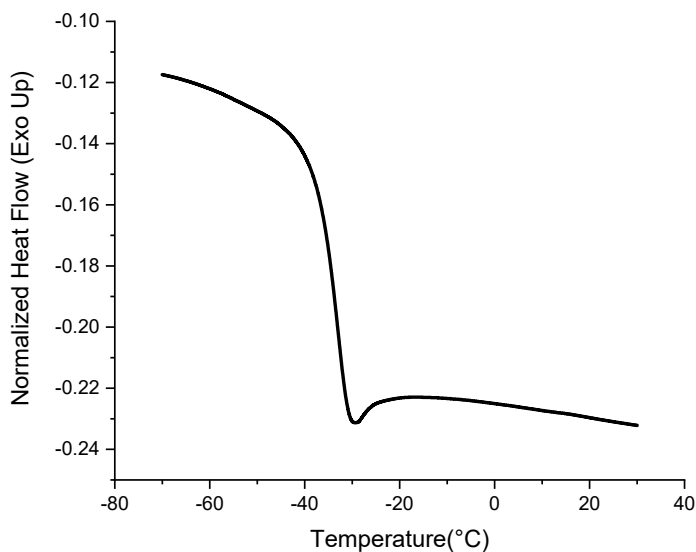


Figure S14. PECH from entry 3b, Table-3 (after coupling). T_g observed is -32.4 °C.

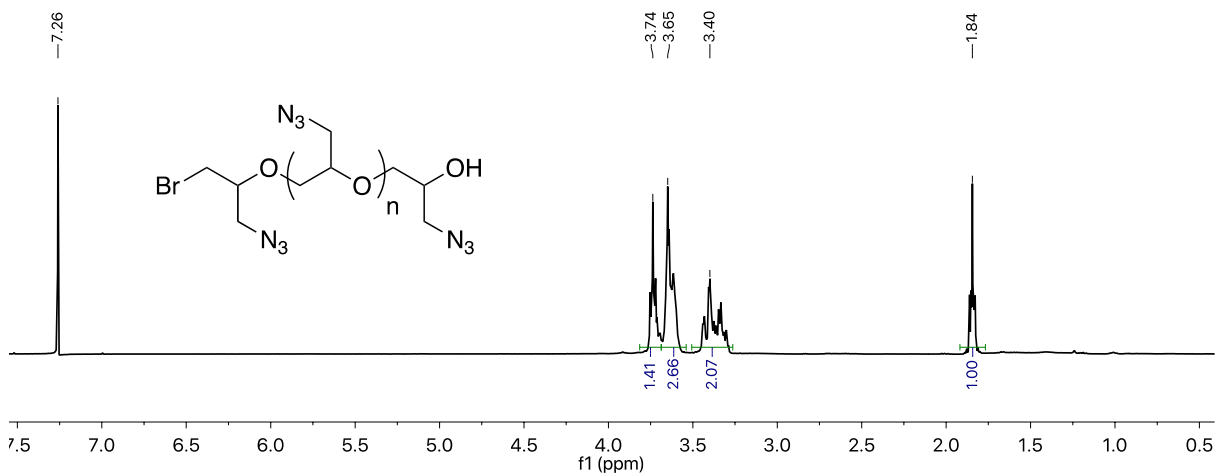


Figure S15: Representative ^1H NMR of poly(glycidyl azide) crude product synthesized from entry-2, Table-4.

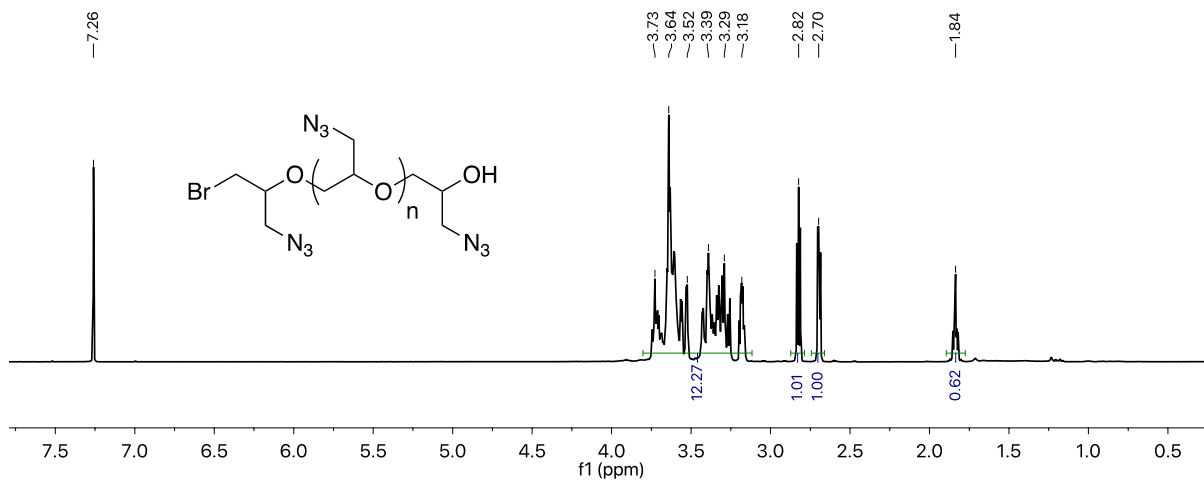


Figure S16: Representative ^1H NMR of poly(glycidyl azide) crude product with 63% conversion synthesized from entry-4, Table-4.

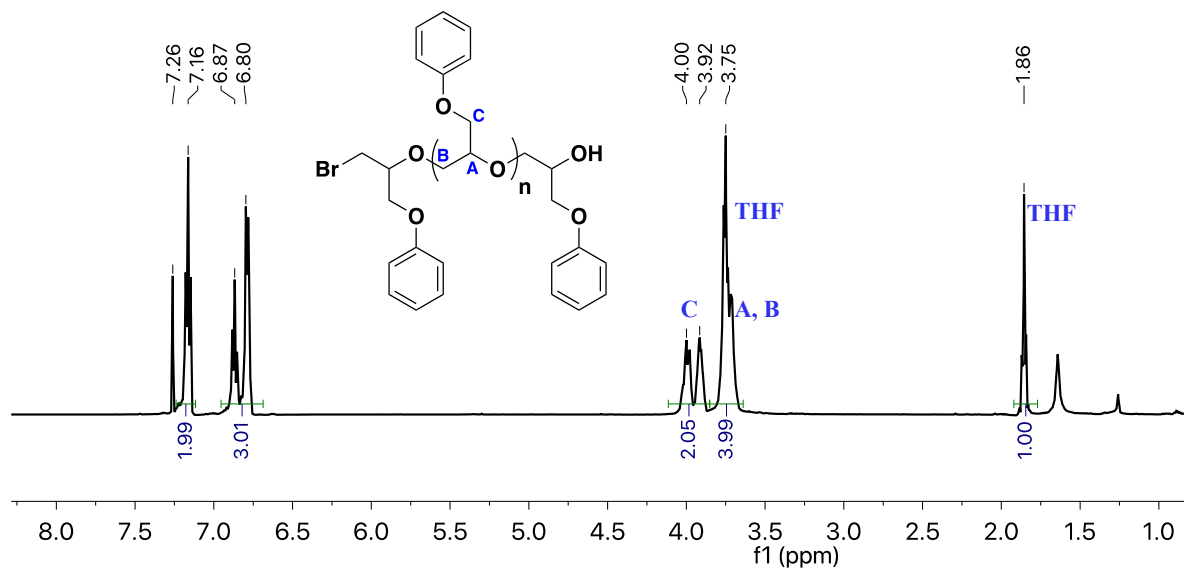


Figure S17. ¹H NMR spectrum of poly(phenyl glycidyl ether) synthesized by catalyst B at 25 °C from entry-7, Table-4.

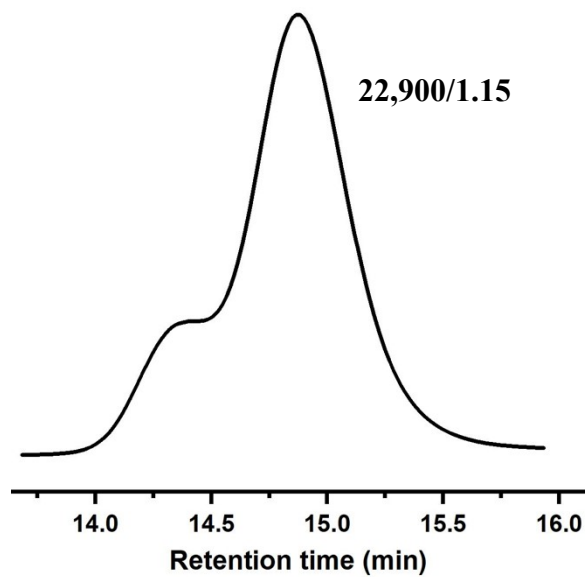


Figure S18. GPC trace for poly(phenyl glycidyl ether) synthesized by catalyst B at 25 °C from entry-7, Table-4.

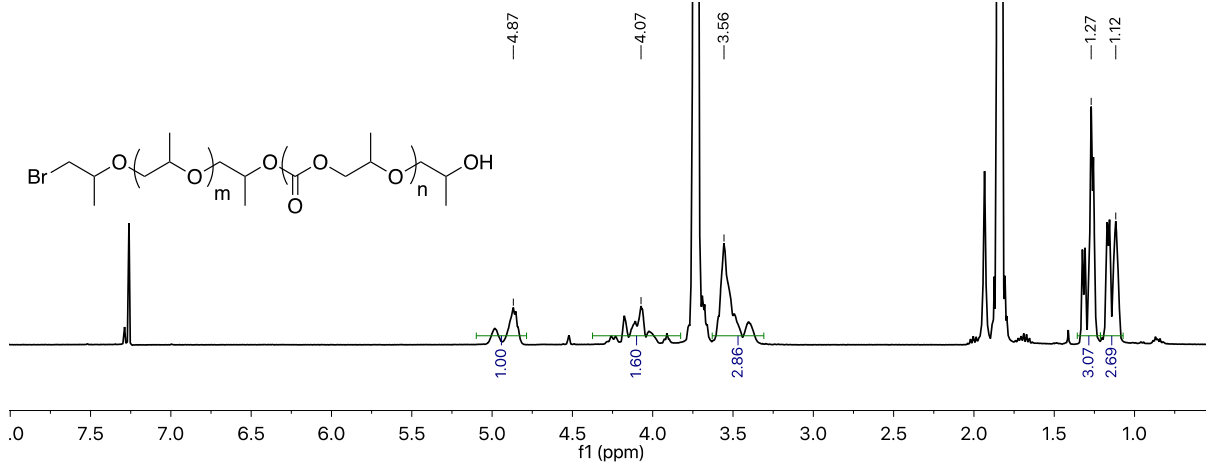


Figure S19: Representative ^1H NMR of poly(propylene ether carbonate) crude product from entry-1, Table-5.

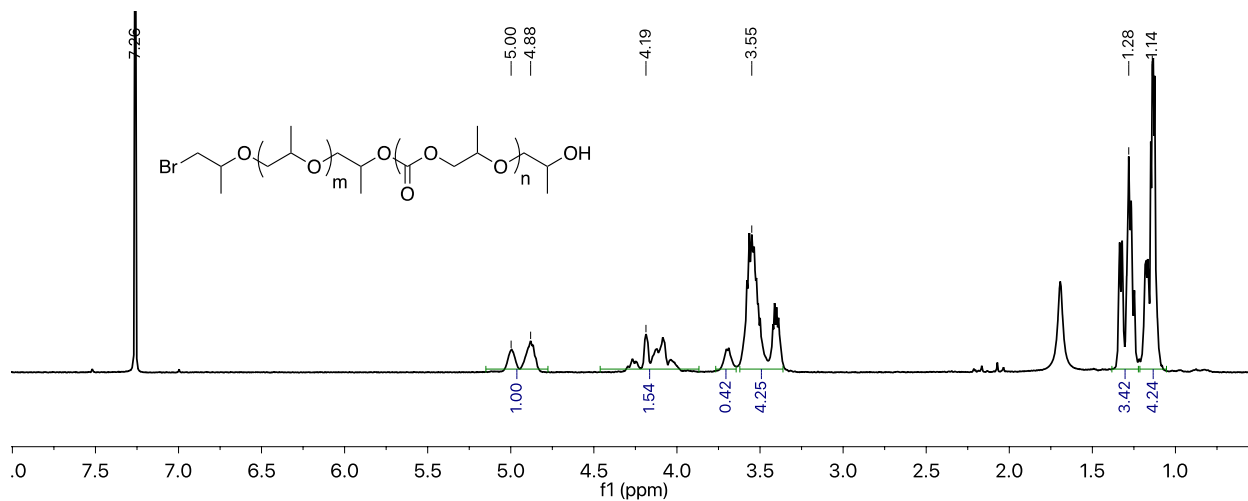


Figure S20: Representative ^1H NMR of poly(propylene ether carbonate) pure product from entry-3, Table-5.

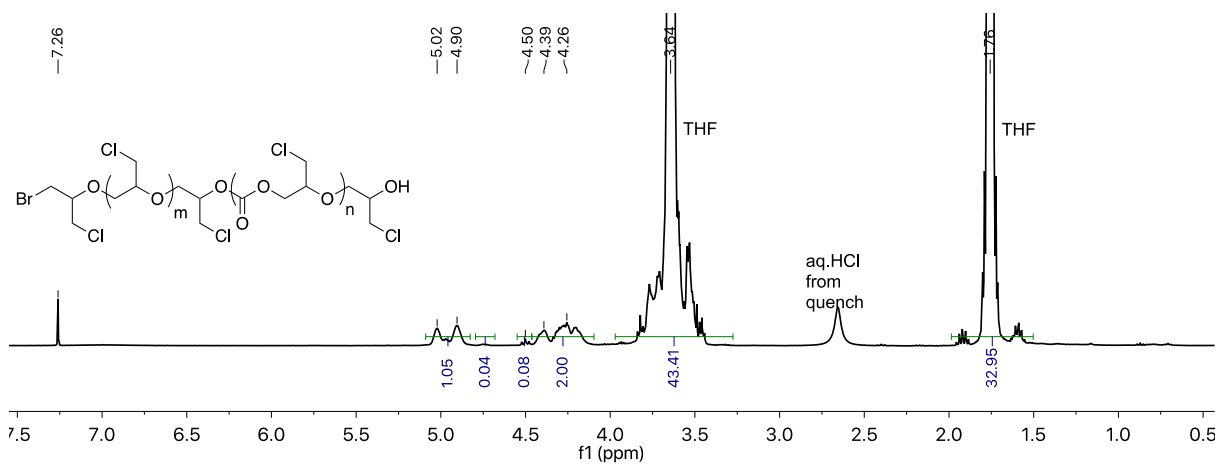


Figure S21: Representative ¹H NMR of poly(epichlorohydrin ether carbonate) crude product synthesized from entry-6, Table-5.

5. References

1. Gharakhanian, E. G.; Deming, T. J., Versatile Synthesis of Stable, Functional Polypeptides via Reaction with Epoxides. *Biomacromolecules* **2015**, *16* (6), 1802-1806.
2. Jia, M.; Hadjichristidis, N.; Gnanou, Y.; Feng, X., Monomodal Ultrahigh-Molar-Mass Polycarbonate Homopolymers and Diblock Copolymers by Anionic Copolymerization of Epoxides with CO₂. *ACS Macro Letters* **2019**, *8* (12), 1594-1598.
3. Brown, H. C.; Pai, G. G., Organoboranes: XXVIII. Convenient procedures for the synthesis of borinane. *Journal of Organometallic Chemistry* **1983**, *250* (1), 13-22.
4. Chen, C.; Gnanou, Y.; Feng, X., Borinane-based organoboron catalysts for alternating copolymerization of CO₂ with cyclic ethers: improved productivity and facile recovery. *Polymer Chemistry* **2022**, *13* (45), 6312-6321.