**Electronic supplementary materials** *Mendeleev Commun.*, 2027, **37**, just accepted

# Carboxylation of epoxides using bifunctional ammonium-triorganoborane catalysts as borane-amine adducts

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## Experimental section

All manipulations with sensitive to air and moisture compounds were carried out under inert atmosphere of dry Ar by Schlenk technique or using MBRAUN glove box filled in Ar. NMR spectra were recorded on Bruker Avance III HD 400 instrument. Chemical shifts in $^1$H NMR were given relatively to residual signals of protonated solvents. THF was distilled over sodium/benzophenone ketyl-radical, piperidine, 1,2-ethylenediamine was distilled over KOH. Cyclopenetene oxide (**CPO**) and cyclohexene oxide (**CHO**) were distillated over NaH and $CHCl_3$ – over $P_4O_{10}$ followed by degassing procedures. Carbon dioxide has content of oxygen less than 1 ppm. Catalytic reactions were carried out in steel autoclaves crafted by "Parr Instruments Company" USA and IPS RAS. Synthesis of 9-BBN was performed according to the described procedure.[S1] Catalyst **1** was synthesized by a modified procedure due to poor solubility of **1a** in THF.[S2]

### 1,1-bis(3-((1s,5s)-9-Borabicyclo[3.3.1]nonan-9-yl)propyl)piperidin-1-ium bromide (**1**)

To a solution of **1a** (0.738 g, 3.0 mmol) in dry degassed $CHCl_3$ (6 ml) was added 9-BBN (0.976 g, 8.0 mmol) and the reaction mixture was heated with stirring at 57 – 60 °C for 2 h. The progress of the reaction was monitored by $^1$H NMR on the disappearance of signals of C=C bond. The solvent was removed under reduced pressure. To the residue was added freshly distilled $Et_2O$ and the precipitated was filtered under Ar, washed with $Et_2O$ and dried *in vacuo* to give **1** (1.45 g, 98.6%) as white powder. $^1$H NMR ($CDCl_3$, 400 MHz): 3.74-3.60 (m, 4H, $2CH_2N^+$); 3.46-3.42 (m, 4H, $2CH_2N^+$); 2.00-1.70 (m, 22H, BBN and Pip); 1.68-1.52 (m, 12H, BBN and Pip); 1.43 (t, $J$ = 7.7 Hz, 4H, $2CH_2$); 1.23-1.09 (m, 4H, $2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 60.5, 58.8, 33.2, 31.1, 23.7, 23.1, 20.60, 20.1, 17.1 ppm. $^{11}$B NMR ($CDCl_3$, 128 MHz): br.s. 87.8 ppm. *NMR spectra coincide with literature data.*[S2]

### 1,1-bis(3-((1s,5s)-9-Borabicyclo[3.3.1]nonan-9-yl)propyl)piperidin-1-ium trifluoromethanesulfonate (2)

#### a) Preparation of *N,N*-diallylpiperidinium trifluoromethanesulfonate (1b)

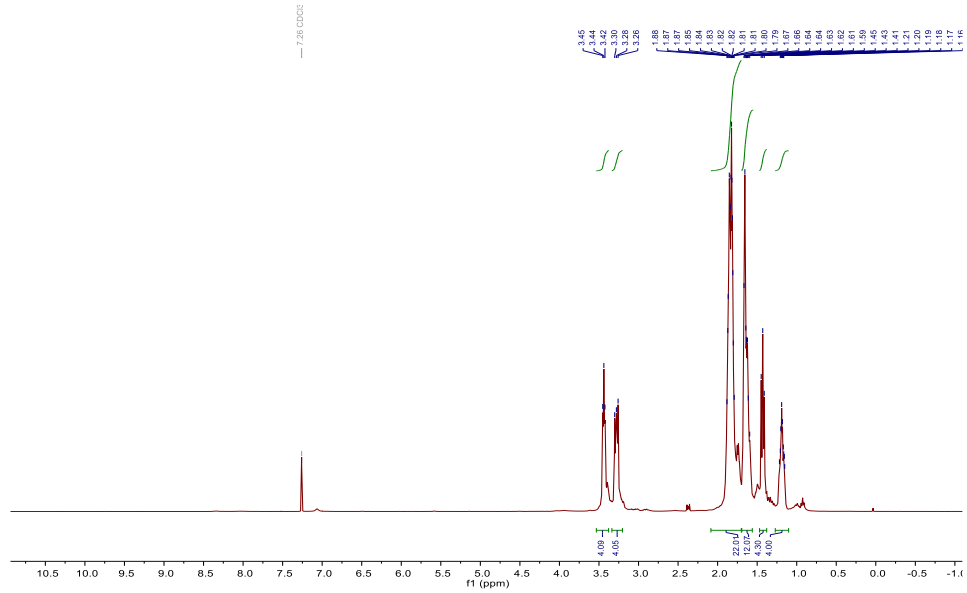
To a solution of **1a** (1.23 g, 5.0 mmol) in $CHCl_3$ (10 ml) was added fine powder of AgOTf (1.29 g, 5.0 mmol) and the mixture was stirred for 24h at ambient temperature in a flask wrapped in Al-foil. A precipitate of AgBr was filtered through a pad of Super Cel, washed with $CHCl_3$. The filtrate was evaporated to dryness under reduced pressure and additionally dried in vacuum at 80 °C to give **1b** (1.55 g, 98%) as white powder. $^1$H NMR ($CDCl_3$, 400 MHz): 5.94 (ddt, $J$ = 17.1, 10.0, 7.3 Hz, 2H, 2CH=), 5.80–5.62 (m, 4H, $2CH_2$=), 3.93 (d, $J$ = 7.3 Hz, 4H, $2CH_2N^+$), 3.39 (t, $J$ = 5.8 Hz, 4H,

$2CH_2N^+$), 1.88 (m, 4H, Pip), 1.72 (m, 2H, Pip) ppm.$^{19}$F NMR (376 MHz, $CDCl_3$) δ -78.41 ppm. Anal. Calcd. for $C_{12}H_{20}F_3NO_3S$ (315.35): C, 45.70; H, 6.39; N, 4.44. Found: C, 45.58; H, 6.42; N, 4.37.

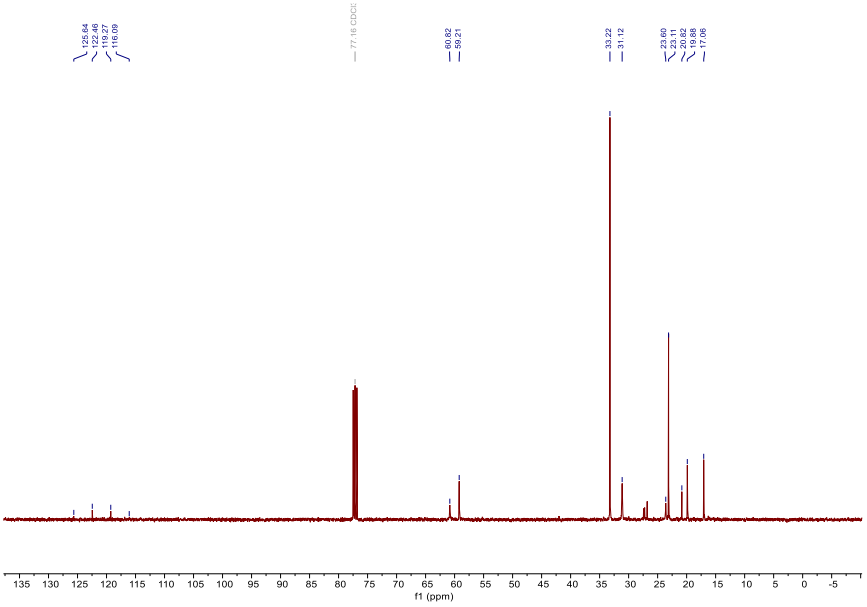
**b) Preparation of 2 by hydroboration of 1b with 9-BBN**

Generally of the procedure is similar to synthesis of cat. **1**. Triflate **1b** (1.42 g, 4.5 mmol) was dissolved in dry degassed $CHCl_3$ (6 ml) followed by the addition of 9-BBN (1.54 g, 12.6 mmol) with stirring. The reaction mixture was heated at 56-60 °C for 16 h. Subsequent treatment and isolation furnished **2** (2.44 g, 97%) as white solid. $^1$H NMR ($CDCl_3$, 400 MHz): 3.53-3.35 (m, 4H, $2CH_2N^+$); 3.23-3.08 (m, 4H, $2CH_2N^+$); 1.98-1.72 (m, 19H, 9BBN and Pip); 1.70-1.55 (m, 11H, 9BBN and Pip); 1.54-1.29 (m, 7H, $2CH_2N^+$, 9BBN and $C\underline{H}_AH_B$); 1.25-1.12 (m, 4H, $2CH_2$); 1.07-0.87 (m, 1H, $CH_A\underline{H}_B$) ppm. $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 120.8 (q., $CF_3$); 60.8, 59.2, 33.2, 31.1(C-B), 23.6 (C-B), 23.1, 20.8, 19.9, 17.1 ppm. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -78.29 ppm. $^{11}$B NMR ($CDCl_3$, 128 MHz): br.s. 88.2 ppm.

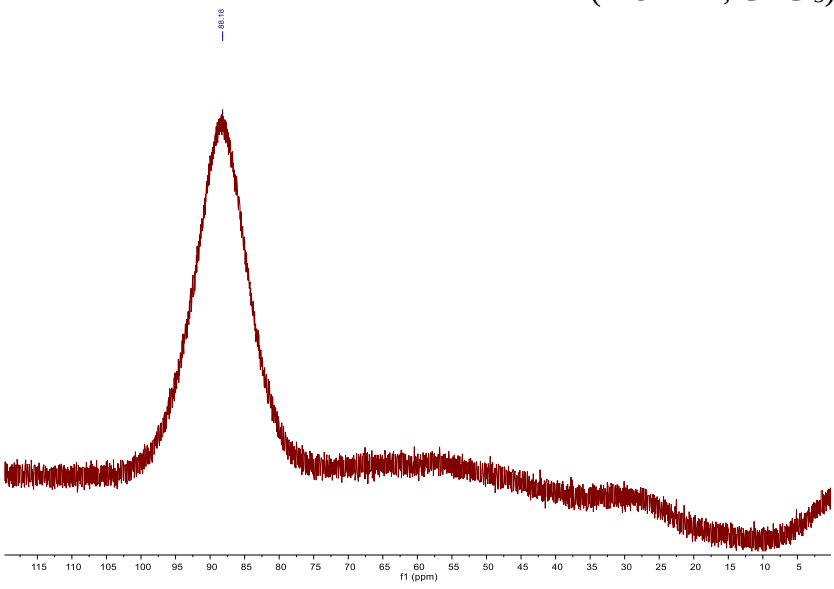
**Figure S1.** NMR spectra of **2**: $^1$H NMR (400 MHz, $CDCl_3$)



$^{13}$C NMR (101 MHz, $CDCl_3$)



$^{11}$B NMR (128 MHz, $CDCl_3$)




**1,1-bis(3-((1s,5s)-9-Borabicyclo[3.3.1]nonan-9-yl)propyl)piperidin-1-ium bromide bis-methylamine adduct (3)**

To a solution of **1** (140 mg, 0.285 mmol) in dry degassed $CHCl_3$ (4.0 ml) was added a solution of $MeNH_2$ 4.9M in MeOH (0.143 ml, 0.7 mmol) with stirring. The reaction mixture was evaporated to dryness under reduced pressure and the residue was dried in vacuum to give **3** (151 mg, 96%) as beige solid. $^1$H NMR ($CDCl_3$, 400 MHz): δ 4.23 (q, *J* = 6.4 Hz, 4H, $2NH_2$ ), 3.38 (t, *J* = 5.6 Hz, 4H, $2CH_2N^+$), 3.17 (t, *J* = 8.3 Hz, 4H, $2CH_2N^+$), 2.27 (t, *J* = 6.3 Hz, 6H, $2CH_3$), 1.92–1.77 (m, 7.5H, 9BBN and Pip), 1.76–1.58 (m, 18H, 9BBN and Pip), 1.58–1.34 (m, 16.5H, 9BBN and Pip), 0.48 (s, 4H, $2CH_2$), 0.31-0.20 (m, 4H, $2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 64.06, 59.38, 32.21, 30.77, 25.33, 25.15, 24.45, 22.66, 21.47, 20.13, 18.26, 14.97 ppm. $^{11}$B NMR ($CDCl_3$, 128 MHz): δ br.s. -5.5 ppm. Anal. Calcd. for $C_{29}H_{60}B_2N_3Br$ (552.34): C, 63.06; H, 10.95; N, 7.61. Found: C, 63.12; H, 10.97; N, 7.72.

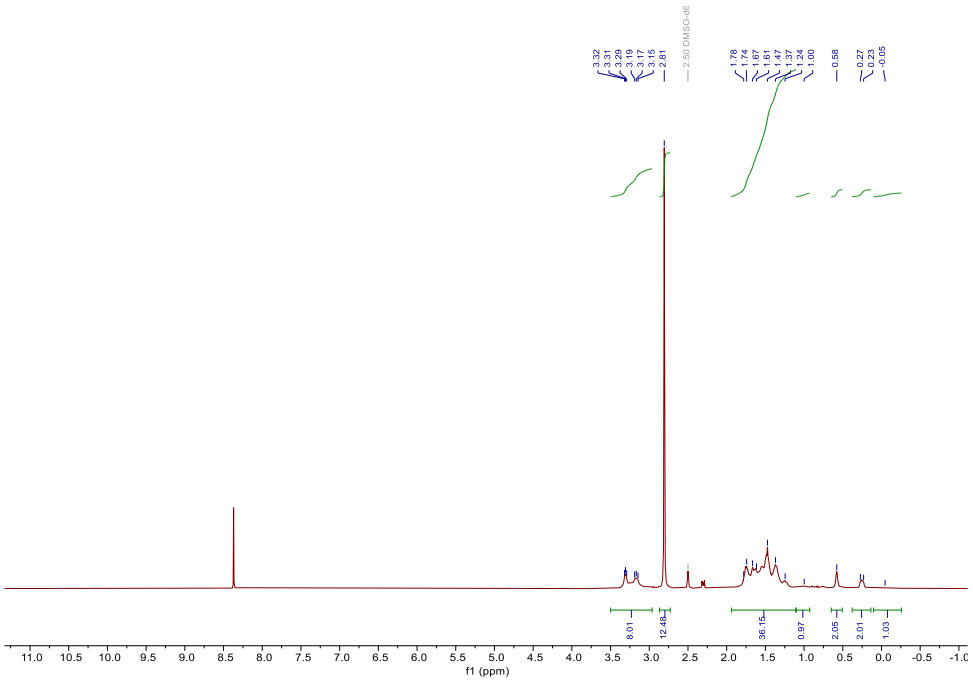
**1,1-bis(3-((1s,5s)-9-Borabicyclo[3.3.1]nonan-9-yl)propyl)piperidin-1-ium bromide 1,2-ethylenediamine adduct (4)**

To a solution of **1** (145 mg, 0.296 mmol) in dry degassed $CHCl_3$ (4.0 ml) was added 1,2-ethylenediamine (17.8 mg, 19.7 μL, 0.296 mmol) with stirring. Immediately after diamine addition a suspension was formed, which was heated at reflux, cooled and precipitate was filtered under argon. The precipitated was washed with $CHCl_3$ and dried *in vacuo* to give **4** (145 mg, 89%) as white solid. $^1$H NMR (DMSO-$d_6$, 400 MHz): 5.75 (s, 1H, $NH_2B$); 3.30 (br.s, 2.6H); 3.20 (br.s, 5.4H); 2.93-2.57 (m, 4H); 2.42-2.20 (m, 1H); 1.78-1.68 (m, 15H); 1.54-1.39 (m, 18H); 1.24-1.11 (m, 3H); 0.43-0.38 (m, 3H); 0.27-0.15 (m, 3H) ppm. $^{13}$C NMR (DMSO-$d_6$, 101 MHz): δ 61.21, 58.74, 57.82, 54.88, 54.21, 54.00, 38.30, 32.11, 30.22, 24.86, 24.63, 22.62, 22.29, 21.05, 19.04, 16.09, 15.33 ppm. $^{11}$B NMR (DMSO-$d_6$, 128 MHz) δ br.s. -5.5 ppm. Anal. Calcd. for $C_{29}H_{58}B_2N_3Br$ (550.33): C, 63.29; H, 10.62; N, 7.64. Found: C, 63.08; H, 10.75; N, 7.80.

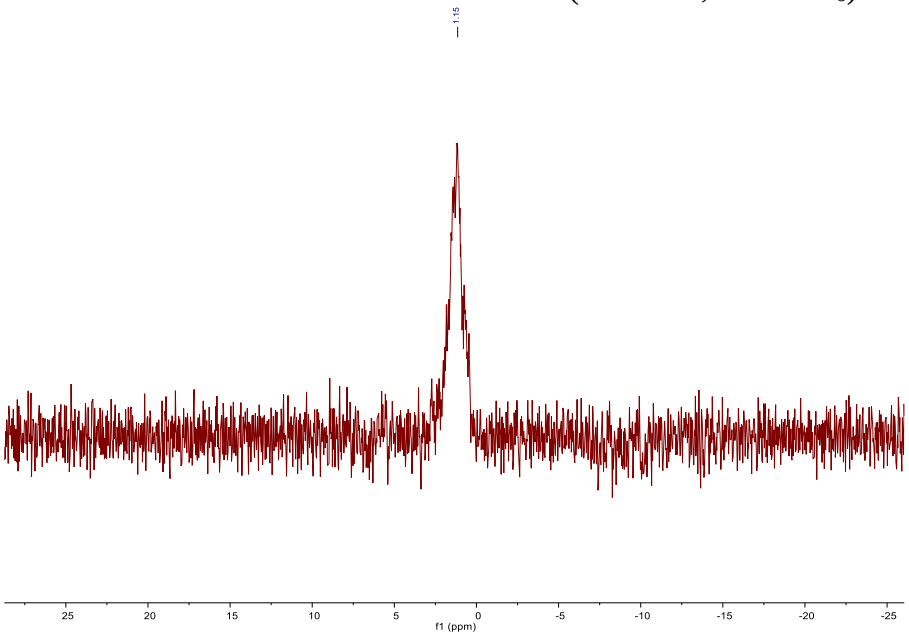
**1,1-bis(3-((1s,5s)-9-Borabicyclo[3.3.1]nonan-9-yl)propyl)piperidin-1-ium bromide 1,4-diazabicyclo[2.2.2]octane adduct (5)**

Solid **1** (245 mg, 0.50 mmol) and DABCO (56 mg, 0.50 mmol) were dissolved in dry degassed $CHCl_3$ (3.0 ml) with stirring. The reaction mixture was evaporated to dryness and dried in vacuum to give **5** (301 mg, 100%) as white solid. $^1$H NMR (DMSO-$d_6$, 400 MHz): 3.32-3.15 (br. m, 8H); 2.81 (s, 12H, DABCO); 1.78-1.24 (m, 36H); 1.00 (br. s, 1H); 0.58 (s, 2H); 0.27-0.23 (m, 2H); -0.05 (br. s, 1H) ppm. $^{11}$B NMR (DMSO-$d_6$, 128 MHz) δ br. s 1.15 ppm. $^{13}$C NMR spectrum is low informative due to broadening of signals.

**Figure S2.** NMR spectra of **5**: $^1$H NMR (400 MHz, DMSO-$d_6$)



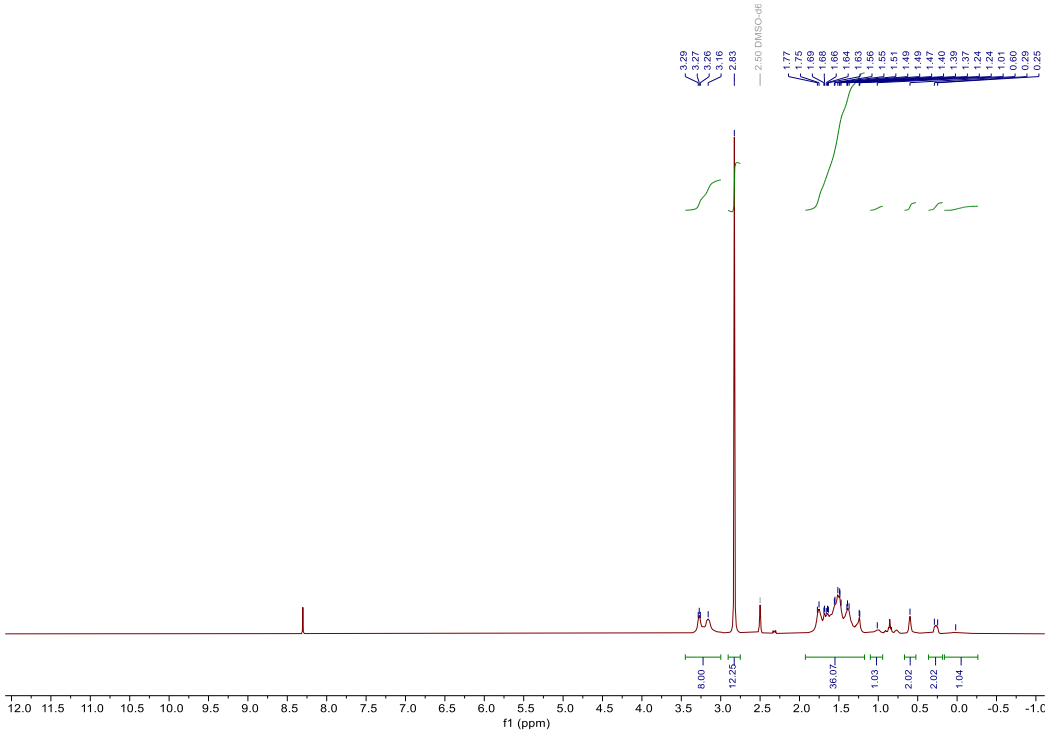

$^{11}$B NMR (128 MHz, DMSO-$d_6$)



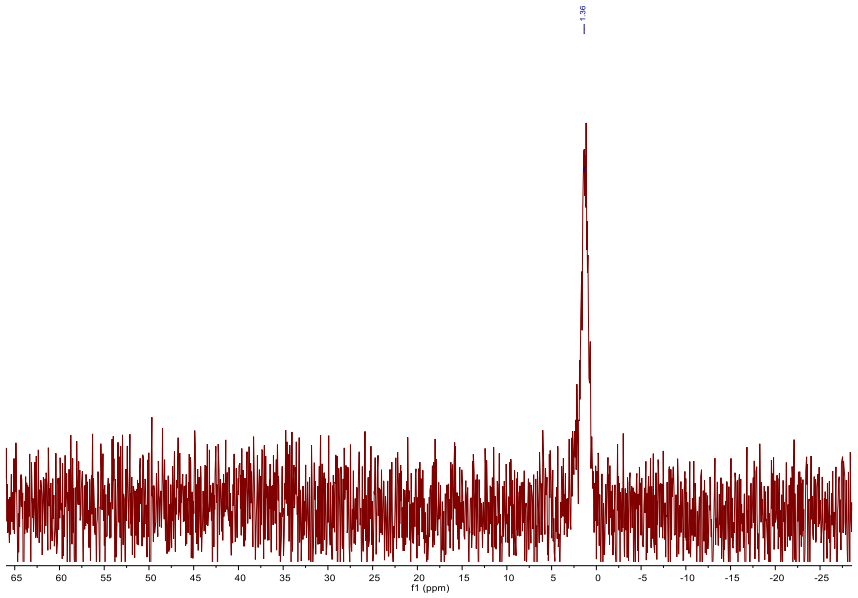
**1,1-bis(3-((1s,5s)-9-Borabicyclo[3.3.1]nonan-9-yl)propyl)piperidin-1-ium trifluoromethanesulfonate 1,4-diazabicyclo[2.2.2]octane adduct (6)**

Solid **2** (150 mg, 0.268 mmol) and DABCO (36 mg, 0.268 mmol) were dissolved in dry degassed $CHCl_3$ (2.0 ml) with stirring. The reaction mixture was evaporated to dryness and dried in vacuum to give **6** (186 mg, 100%) as highly hygroscopic white solid. $^{1}$H NMR (DMSO-$d_6$, 400 MHz): 3.29-3.16 (br. m, 8H); 2.83 (s, 12H, DABCO); 1.77-1.24 (m, 36H); 1.01 (br. s, 1H); 0.8 (s, 2H); 0.29-0.25 (m, 2H); 0.02 (br. s, 1H) ppm. $^{11}$B NMR (DMSO-$d_6$, 128 MHz) δ br. s 1.36 ppm. $^{13}$C NMR spectrum is low informative due to broadening of signals.

**Figure S3.** NMR spectra of **6**: $^{1}$H NMR (400 MHz, DMSO-$d_6$)




$^{11}$B NMR (128 MHz, DMSO-$d_6$)



**General procedure for CPO cyclocarboxylation / copolymerization with $CO_2$**

Steel autoclave was charged with boron catalyst under Ar atmosphere and then **CPO** (5.2 ml, 5.0 g, 59.6 mmol) was injected via syringe. The autoclave was pressurized with oxygen free $CO_2$ (20 bar) and the mixture was stirred for indicated time at 75 °C. After the autoclave had cooled, the pressure was released and the reaction mixture was analyzed by NMR.

S1. J.A. Soderquist and A. Negron, 9-Borabicyclo[3.3.1]nonane dimer. *Org. Synth.*, **1992**, 70, 169. DOI: 10.15227/orgsyn.070.0169

S2. R. Xie, Y. Y. Zhang, G. W. Yang, X. F. Zhu, B. Li and G.-P. Wu, Record Productivity and Unprecedented Molecular-Weight for Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides Enabled by Organoboron Catalysts. *Angew. Chem. Int. Ed*., **2021**, 60, 19253. DOI: 10.1002/anie.202104981

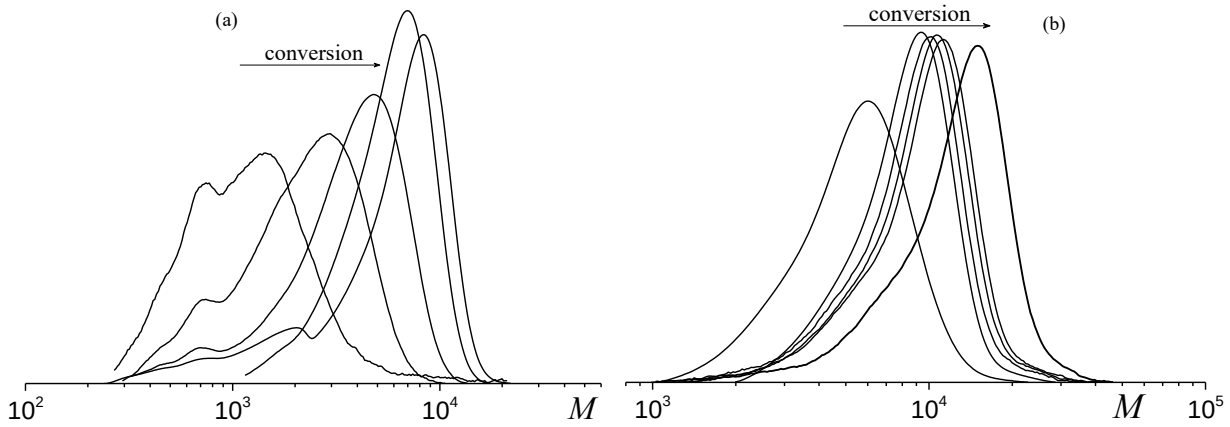
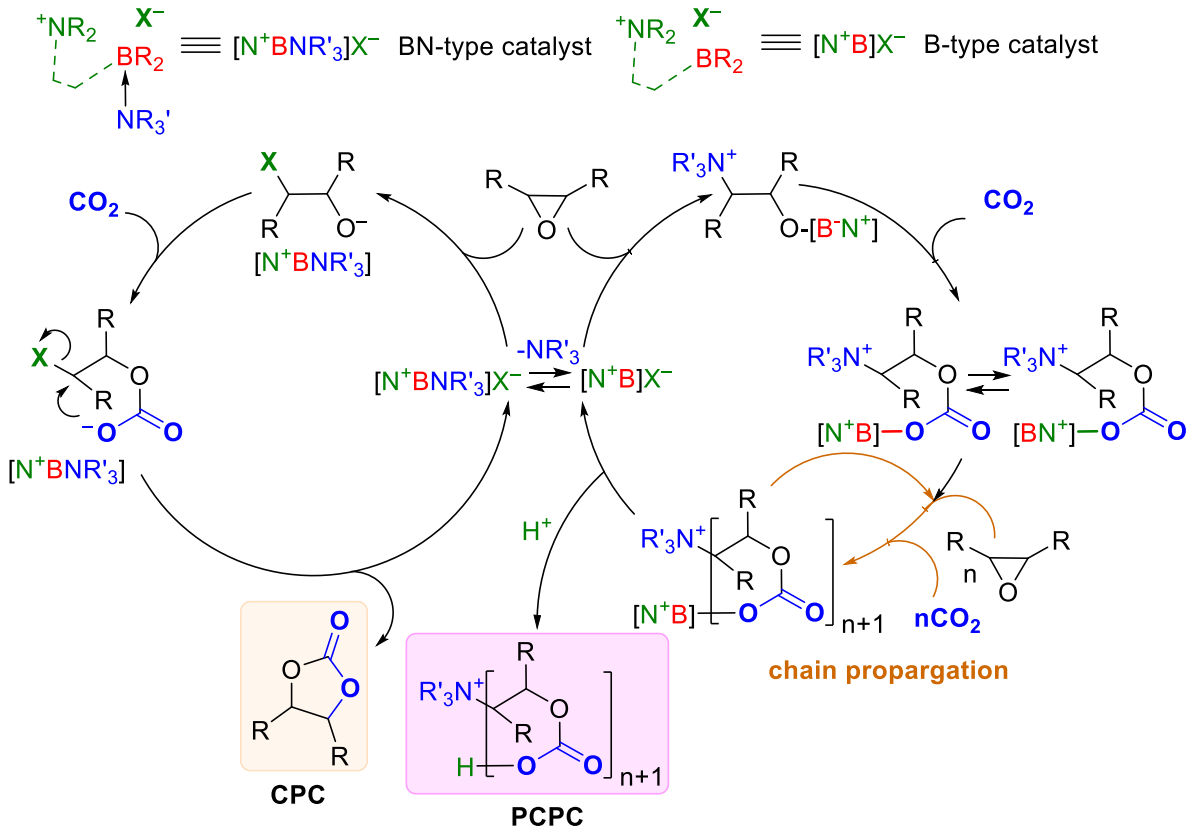



**Figure S4.** MWD curves of **PCPC** (a) and **PCHC** (b) formed in the presence of **6** catalyst under $CO_2$ pressure of 2.0 MPa. T = 65 (a) and 70°C (b).




**Scheme S1**. Proposed mechanism of BN-catalyzed formation of **CPC** and **PCPC**.