Organoboron-Mediated Ring-Opening Polymerization (ROP)

Speaker：Xiaowen Li

Advisor：Zhang-Jie Shi

Date：2024.04.26

Table of Contents

PART

I

Background

Background

FUDAN UNIVERSITY

- **Representative polymerization catalysts**

For alkene polymerization

(MAO: **M**ethyl**a**lumin**o**xane)

Ziegler–Natta Catalysts

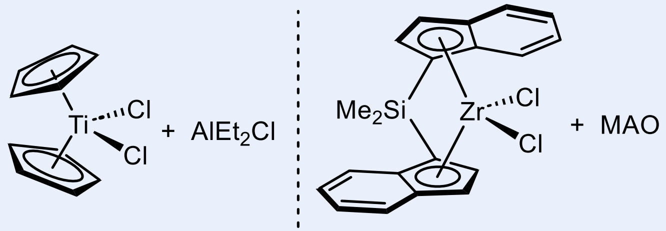
$TiCl_4$-$MgCl_2$-$AlEt_3$

$TiCl_4$-$AlCl_3$-$AlEt_2Cl$

$VOCl_3$-$Al_2Et_3Cl_3$

$VOCl_3$-$MgCl_2$-$AlEt_3$

Metallocene Catalysts



Advantages:

♠ Easy ligand-fine tuning

♠ Diverse ligand/metal combinations

♠ Narrow molecular weight distribution

Disadvantages:

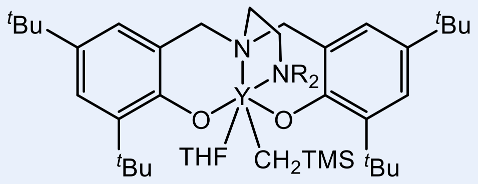
♣ Oxygen- and moisture-free conditions

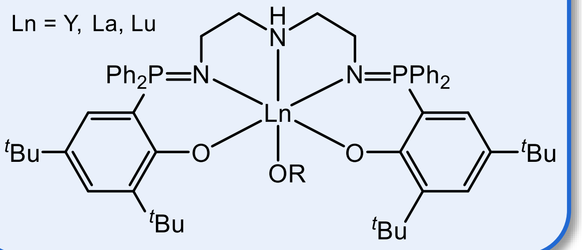
♣ Possible polymer degradation

♣ Potentially toxic metal residual

For lactide polymerization

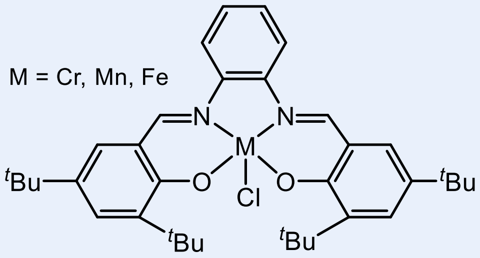
Rare-Earth Metal Catalysts

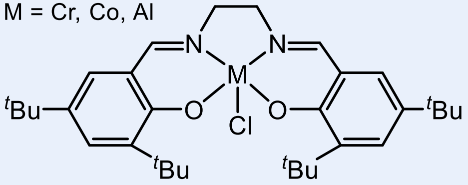




For polyesters synthesis

Salen/Salph-Supported Catalysts





Metal-free catalysts/initiators

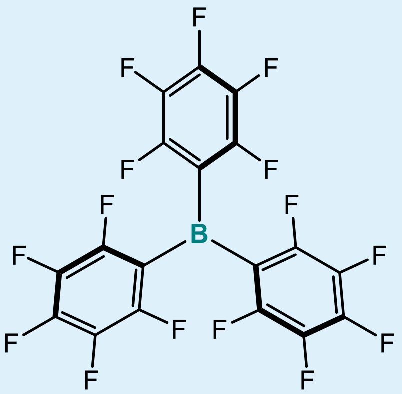
♠ *Environmentally friendly*

♠ *Readily available*

♠ *High atomic economy*

(a) The Beginner's Course: General Description of Transition Metal Catalysts and Catalytic Polymerization Reactions. In *Alkene Polymerization Reactions with Transition Metal Catalysts*; Kissin, Y. V., Eds; Elsevier B.V., 2007; pp 1-34; (b) Liu, X.; Cui, D. et al. *Organometallics* **2007**, *26*, 2747; (c) Bakewell, C.; Williams, C. K. et al. *Angew. Chem., Int. Ed.* **2014**, *53*, 9226; (d) Coates, G. W. et al. *Chem. Rev.* **2016**, *116*, 15167.

Background



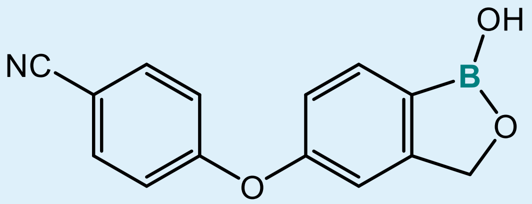
Tris(pentaflurophenyl)borane

[He]$2s^2 2p^1$ 10.811

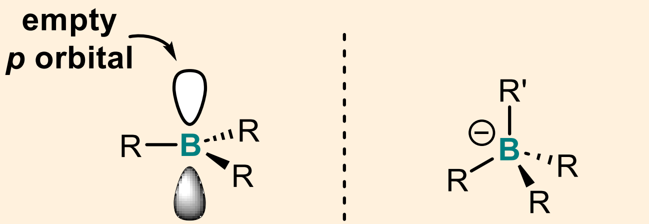
B

Boron

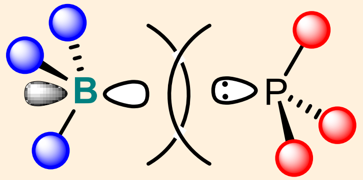
Electronegativity: 2.04
Atom Radius: 79.5 pm
Common Oxidation State: +3



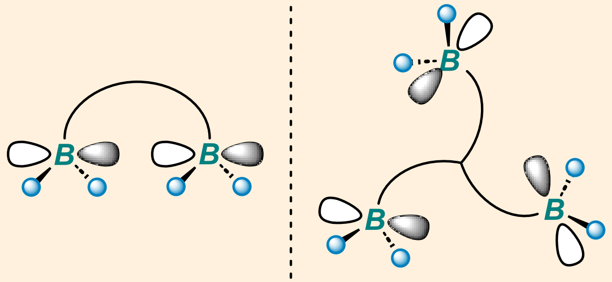
Crisaborole
(Anti-inflammatory drug)



Tricoordinated Tetracoordinated



Frustrated **L**ewis **P**airs
(**FLP**)

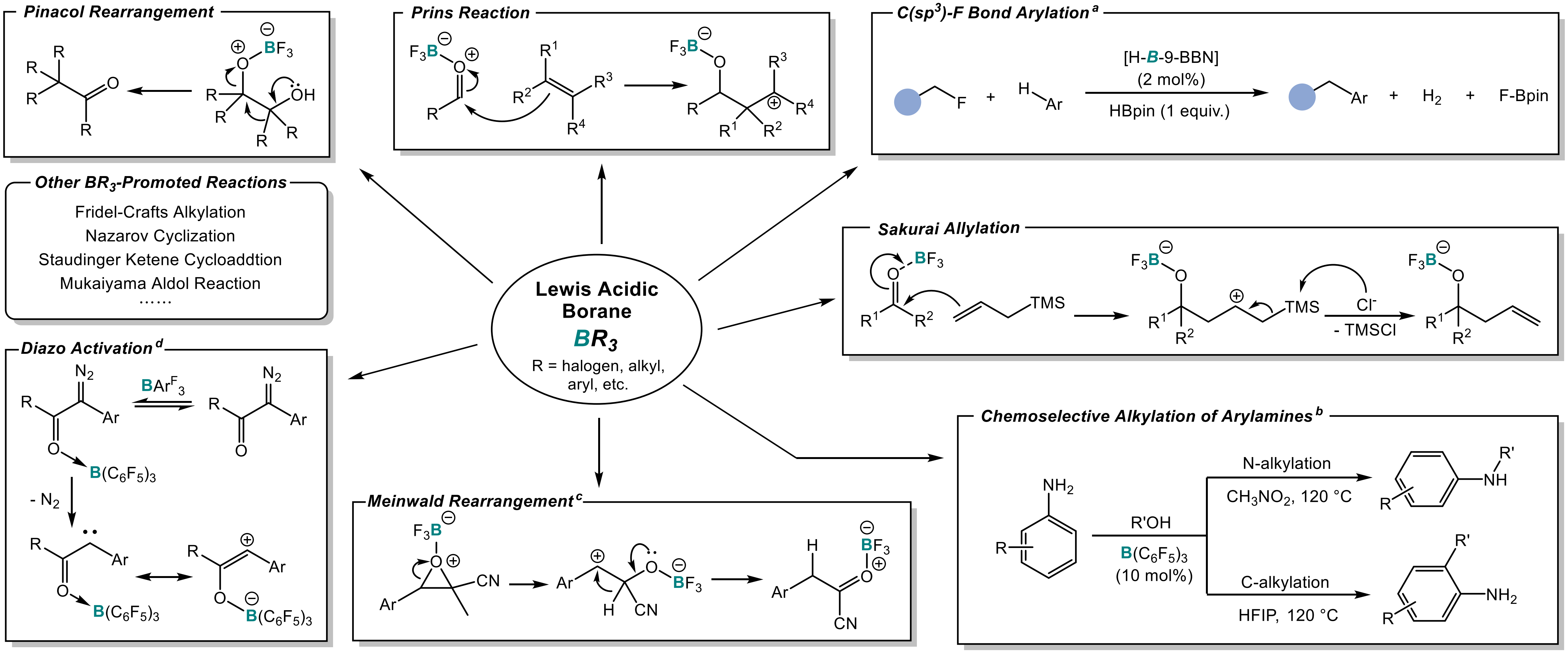


Multinuclear Boron Lewis Acids

a) Stephen, D. W. *Science* **2016**, *354*, 1248; b) Jarnagin, K. et al. *J. Drugs Dermatol.* **2016**, *15*, 390.

Background

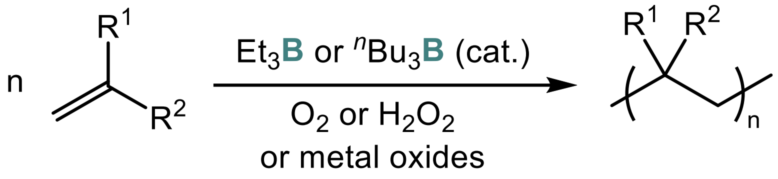
Borane-Catalyzed Organic Reactions



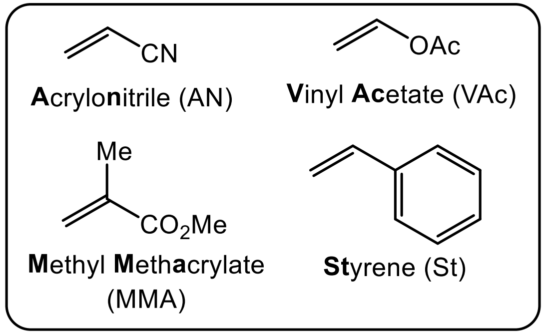
(a) Willcox, D. R.; Thomas, S. P. et al. *ACS Catal.* **2021**, *11*, 3190; (b) Meng, S.-S.; Zhao, J.-L.; Chan, A. S. C. et al. *ACS Catal.* **2019**, *9*, 8397; (c) Xu, C.; Xu, J. *Org. Biomol. Chem.* **2020**, *18*, 127; (d) Pramanlk, M.; Melen, R. L. *Synthesis* **2023**, *55*, 3906.

Background

- **Earliest reports of organoborane-mediated polymerization**

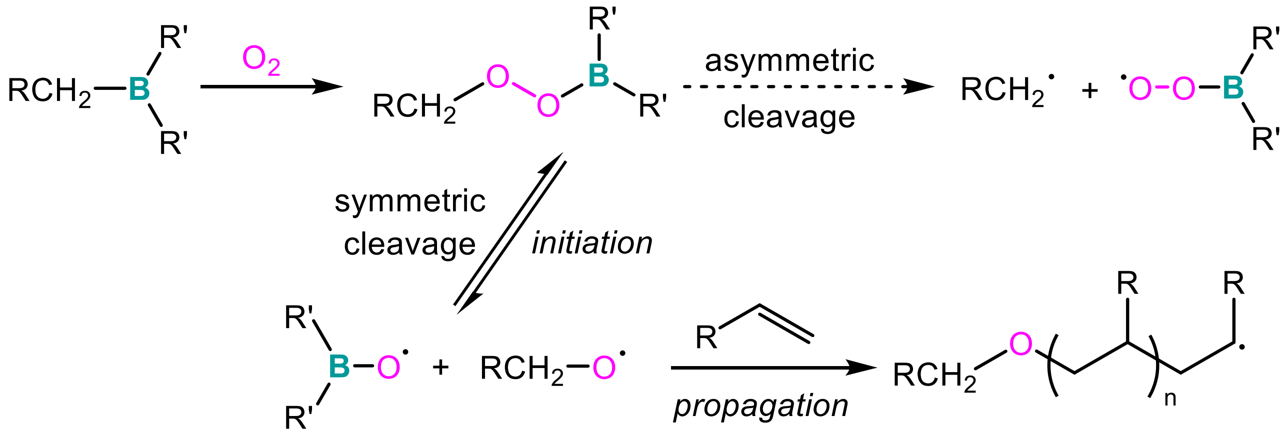


Monomer	Conv.	M_n ($g\cdot mol^{-1}$)
AN	67%	1.8×10^4
MMA	55%	5.2×10^4
VAc	42%	1.9×10^4
St	20%	—



(a) Furukawa, J. et al. *J. Polym. Sci.* **1957**, *26*, 234; (b) Furukawa, J.; Tsuruta, T. *J. Polym. Sci.* **1958**, *28*, 227;
(c) Kolesnikov, G. S.; Klimentova, N. V. *Bull. Acad. Sci. USSP, Div. Chem. Sci.* **1958**, *6*, 666;

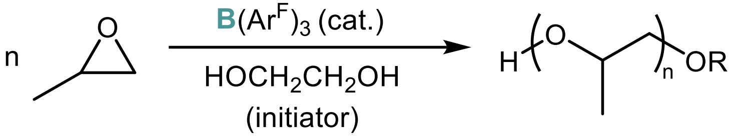
- **Mechanism of alkylborane-initiated radical polymerization**

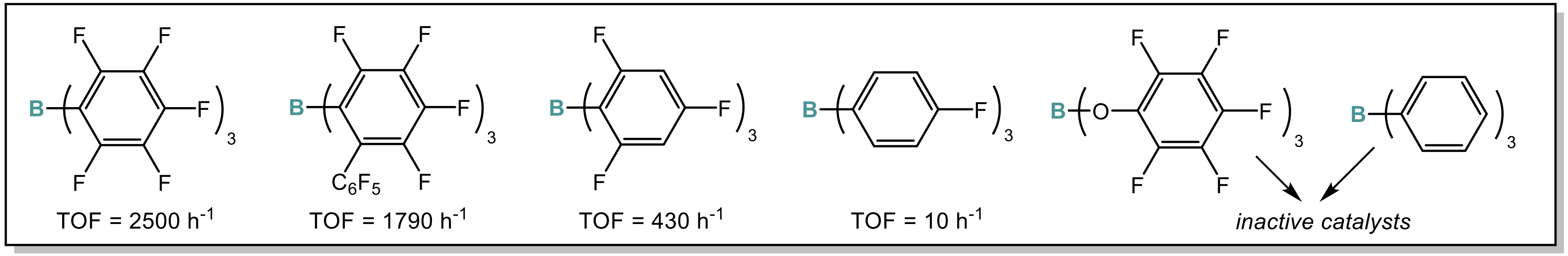


(d) Lu, H. L.; Chung, T. C. et al. *J. Am. Chem. Soc.* **1996**, *118*, 705.

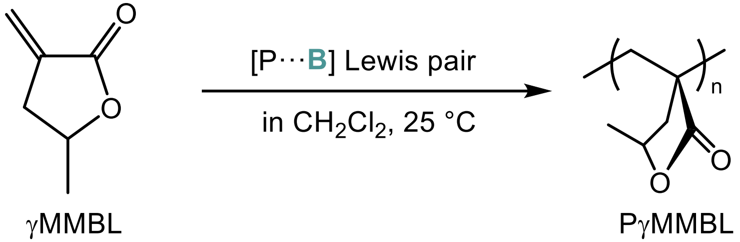
Background

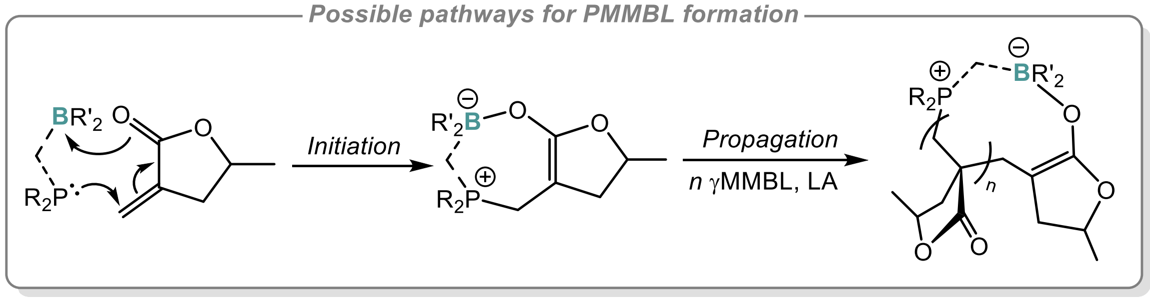
- **Pioneer work of organoborane-catalyzed ROP of epoxide**

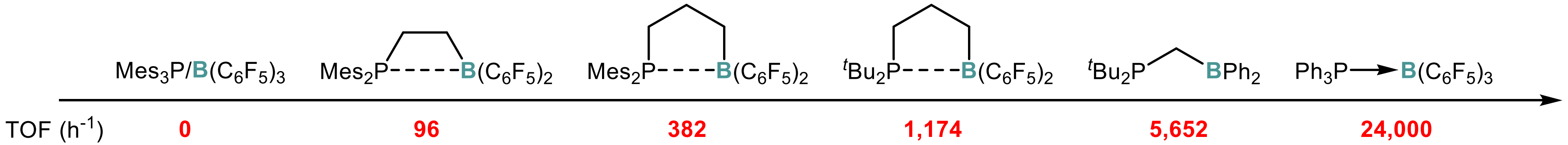




- **First LPP by *P*/*B* Lewis pairs**



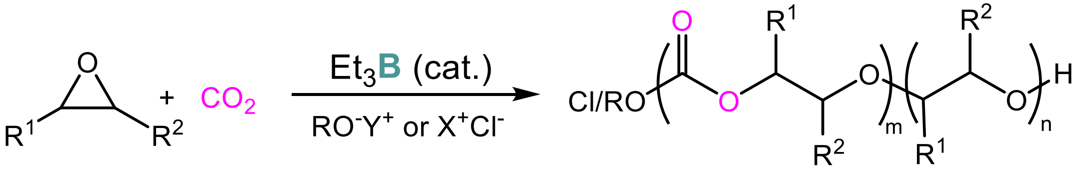




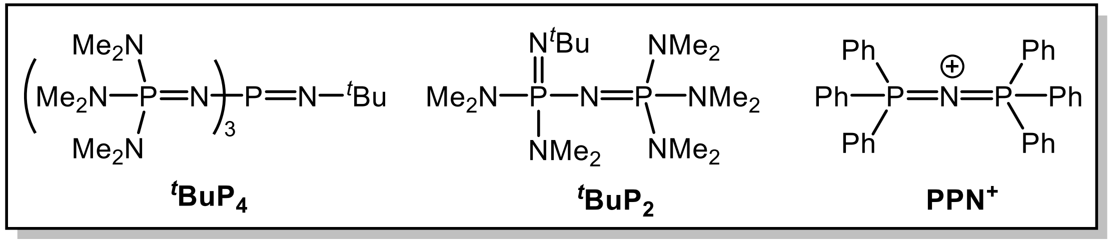
(a) Chakraborty, D.; Chen, E. Y.-X. et al. *Macromolecules* **2003**, *36*, 5470; (b) Xu, T.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2014**, *136*, 1774.

Background

- **First metal-free copolymerization of CO_2 with epoxides**



RO^- : BnO^-, $^tBuO^-$ Y^+: $^tBuP_4^+$, $^tBuP_2^+$, K^+ X^+: NBu_4^+, PPN^+, PPh_4^+, PBu_4^+



Mild conditions	***High TONs***	***High M_n***	***High PC content and narrow PDI***
2 eq. TEB to initiator, 10 bars of CO_2, 60 ~ 80 °C	up to 490 (for PO) up to 4000 (for CHO)	up to 50.0 kDa (for PO) up to 76.4 kDa (for CHO)	up to 99% PDI < 1.20 (for PPO)

Polymerization
- Condensation polymerization
- **Ring-opening polymerization (ROP)**
- Addition polymerization

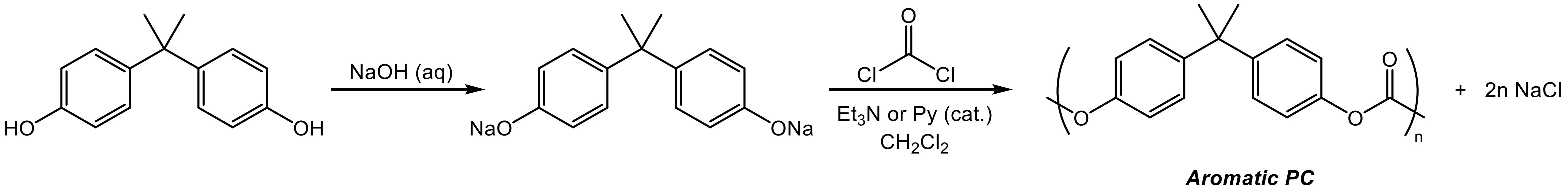
♠ *Complementary process for polycondensation*
♠ *Stereoregularity* ♠ *Post-modification*
♠ *Block polymers* ♠ *Biodegradable polymers*

(a) Gnanou, Y.; Feng, X. et al. *J. Am. Chem. Soc.* **2016**, *138*, 11117; (b) Pask, S. D.; Nuyken, O. *Polymers* **2013**, *5*, 361.

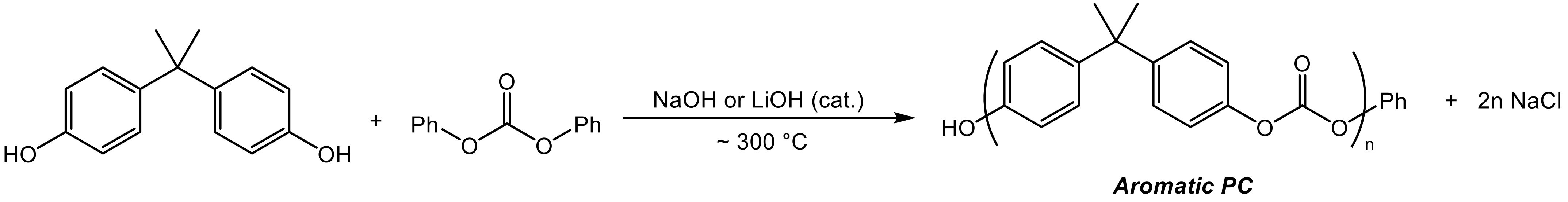
Background

- **Industrial production of polycarbonate**

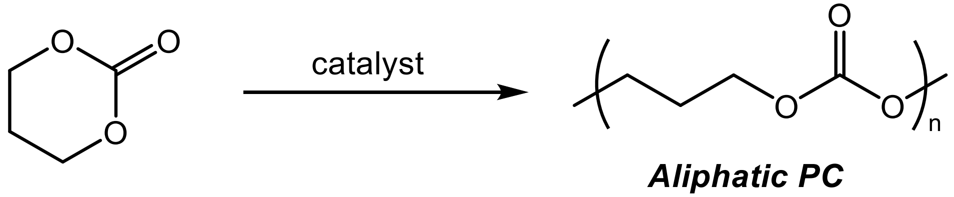
(a) Interfacial polymerization (room temperature)



(b) Melt condensation polymerization



(c) Ring-opening polymerization (less use)



Catalysts:
organic base (e.g. DBU, Thiourea)
metallic comounds (e.g. metal clcoholates)
allkyl hallides, etc

(a) Polycarbonate Synthesis. In *Encyclopedia of Polymeric Nanomaterials*; : Kobayashi, S., Müllen, K., Eds; Springer, Berlin, 2015; pp 1793-1796; https://doi.org/10.1007/978-3-642-29648-2_419 ; (b) Arno, M. C.; Dove, A. P. et al. *Chem. Rev.* **2021**, *121*, 10865.

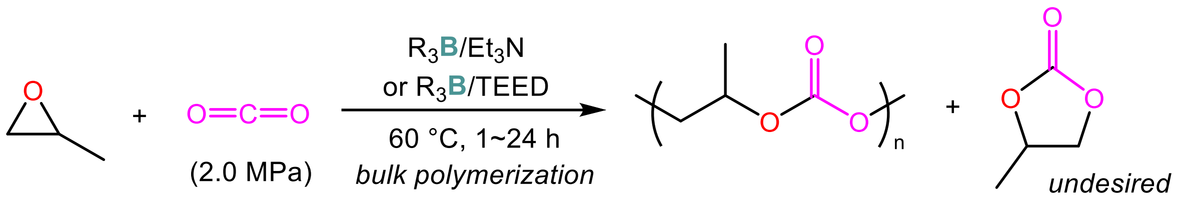
PART

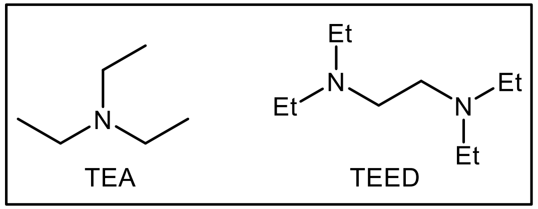
II

Mononuclear-Organoboron-Mediated Ring-Opening Polymerizations

R_3B/R'_3N-Catalyzed ROCOP of PO/CO_2

Zhang, 2021
(anionic)





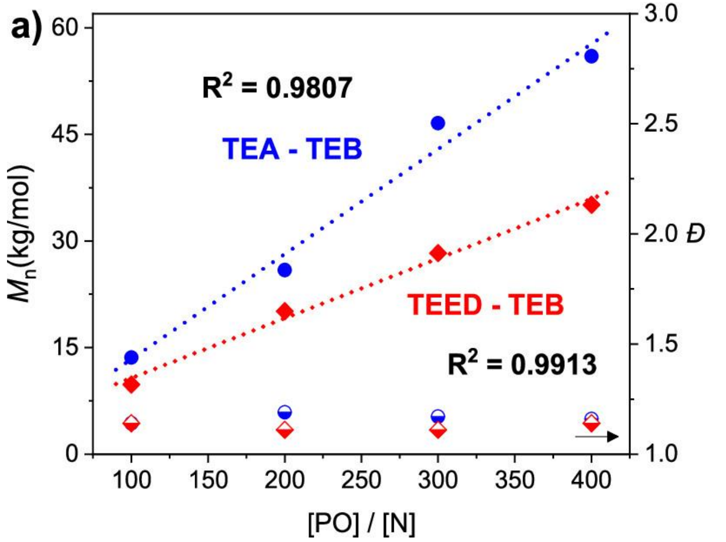
Entry	LA	LA/TEA/PO	Time	Conv.	PPC selec. (%)	productivity (g/g)	F_{CO_2}	M_n (kDa)	$Đ$
1	TEB	1:1:100	4 h	90%	88	40	>99%	13.6	1.14
2	TEB	1:1:200	12 h	95%	91	89	>99%	25.9	1.19
3	TEB	1:1:300	18 h	87%	96	128	>99%	46.6	1.17
4	TEB	1:1:400	24 h	87%	96	171	>99%	56.0	1.16
5	TEB	1:1:500	30 h	—	—	—	—	—	—

Performance: TEED > TEA

Double base site of TEED benefited the initiating efficiency

Entry	LA	LA/TEED/PO	Time	Conv.	PPC selec. (%)	productivity (g/g)	F_{CO_2}	M_n (kDa)	$Đ$
6	TEB	1:0.5:100	4 h	84	87	40	>99%	9.8	1.14
7	TEB	1:0.5:200	6 h	87	98	94	>99%	20.1	1.11
8	TEB	1:0.5:300	9 h	84	96	134	>99%	28.3	1.11
9	TEB	1:0.5:400	12 h	85	93	175	>99%	35.1	1.14
10	TEB	1:0.5:500	15 h	83	94	216	>99%	33	1.13

- **M_n-[PO]/[N] relation**

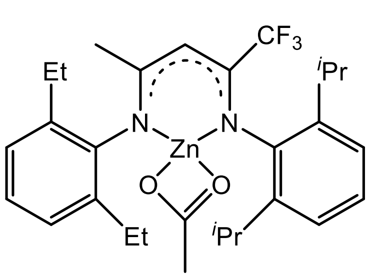


PO/CO_2 copolymerization can be regulated

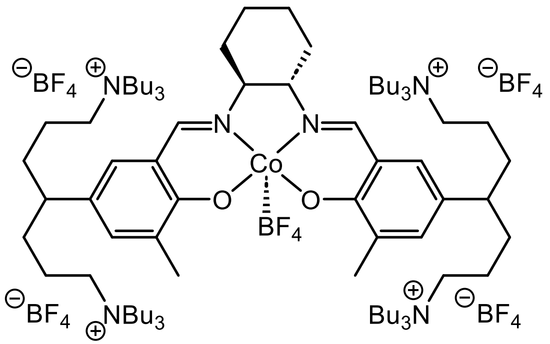
Wang, Y.; Zhang, J.-Y.; Zhang, X.-H. et al. *Macromolecules* **2021**, *54*, 2178.

R_3B/R'_3N-Catalyzed ROCOP of PO/CO_2

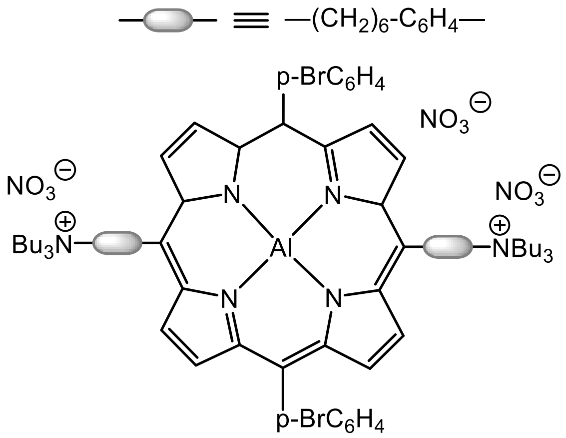
• Comparison of typical catalysts for PO/CO_2 ROCOP



conditions: 5 °C, 0.7 MPa
productivity: 84 g/g
F_{CO2} > 99%

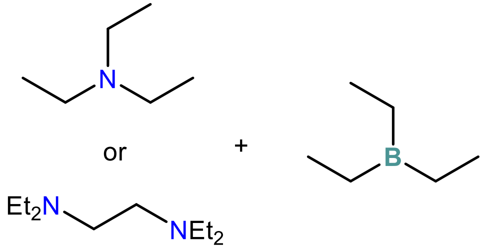


conditions: 80 °C, 1.7-2.0 MPa
productivity: 761 g/g
F_{CO2} > 99%



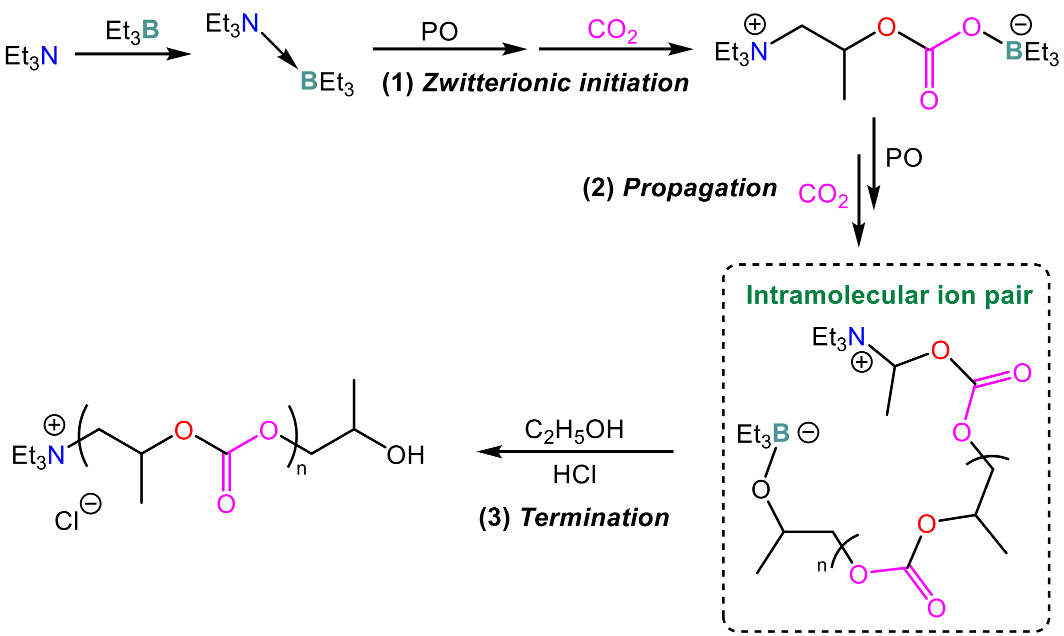
conditions: 80 °C, 3.0 MPa
productivity: 376 g/g
F_{CO2} = 94%

Good activity
Commercially available

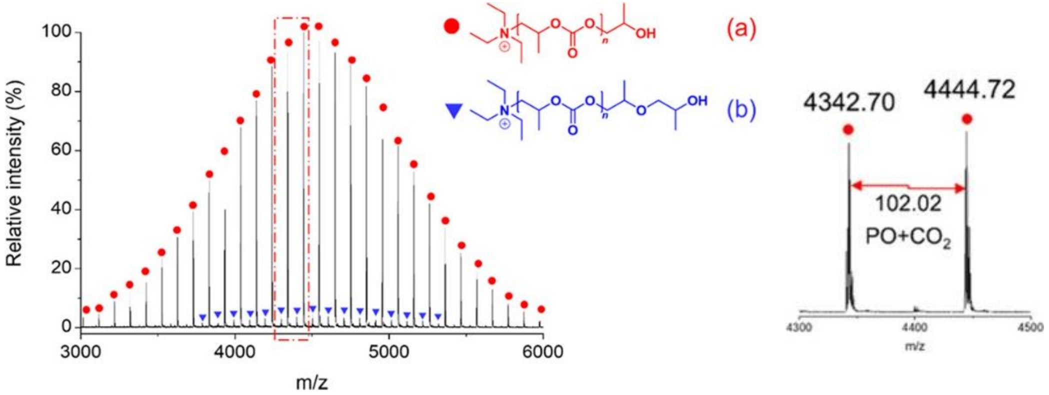


conditions: 60 °C, 2.0 MPa
productivity: 171 g/g (TEA+TEB),
216 g/g (TEED+TEB)
F_{CO2} > 99%

• Proposed zwitterionic copolymerization mechanism



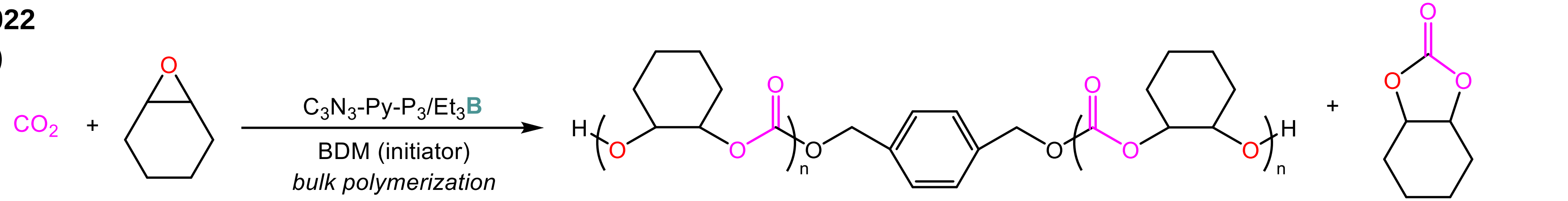
• MALDI-TOF MS spectra of resulting PPC



TEB/Phosphazene-Catalyzed Polycarbonate Synthesis

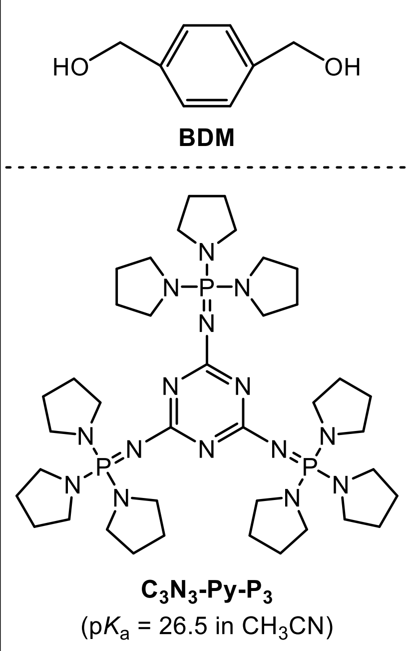
FUDAN UNIVERSITY

Li & Liu, 2022
(anionic)



PCHC
Poly(**c**yclo**h**exene **c**arbonate)

CHC
Cyclo**h**exene **c**arbonate)



Entry	CHO/base /BDM/TEB	T (°C)	t (h)	CO_2 (MPa)	Conv. (%)	TON	TOF (h^{-1})	M_n (kDa)	$Đ$	PCHC/CHC (%)	Ether (%)
1	500:1:1:2	80	2	1	60	300	150	15.4	1.26		
2	2000:1:1:2	80	3	1	52	1040	347	22.5	1.26		
3	4000:1:1:2	80	3	1	39	1560	520	21.9	1.23		
4	8000:1:1:2	80	12	1	76	6080	507	117.8	1.23	> 99	0
5	16000:1:1:2	80	12	1	42	6720	560	121.0	1.25		
6	24000:1:1:2	80	30	1	51	12240	408	275.5	1.59		
7	500:1:2:2	25	5	0.1	36	180	36	5.5	1.09		
8	500:1:2:6	25	2	0.1	38	190	95	5.4	1.10		

1.**High catalytic efficiency**: TON up to 12240;
2.**Perfect polycarbonate selectivity**: no ether linkage, no cyclic carbonate;
3.**High molecular weight**: M_n (up to 275.5 kg/mol);
4.**Ambient conditions polymerization**: 25 °C, 1 atm, TOF up to 95 h^{-1}.

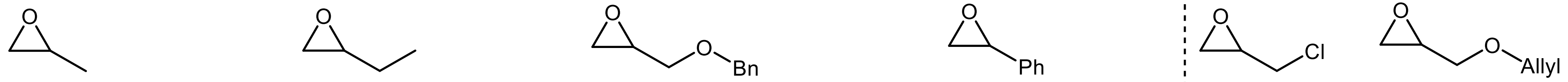
Zhang, J.; Liu, S.; Li, Z. et al. *Angew. Chem., Int. Ed.* **2022**, *61*, e202111197.

TEB/Phosphazene-Catalyzed Polycarbonate Synthesis

FUDAN UNIVERSITY

- **Copolymerization of CO_2 with diverse epoxides (12.5 μmol C_3N_3-Py-P_3, 60 °C, 1 MPa CO_2)**

PC: **p**oly**c**arbonate CC: **c**yclic **c**arbonate

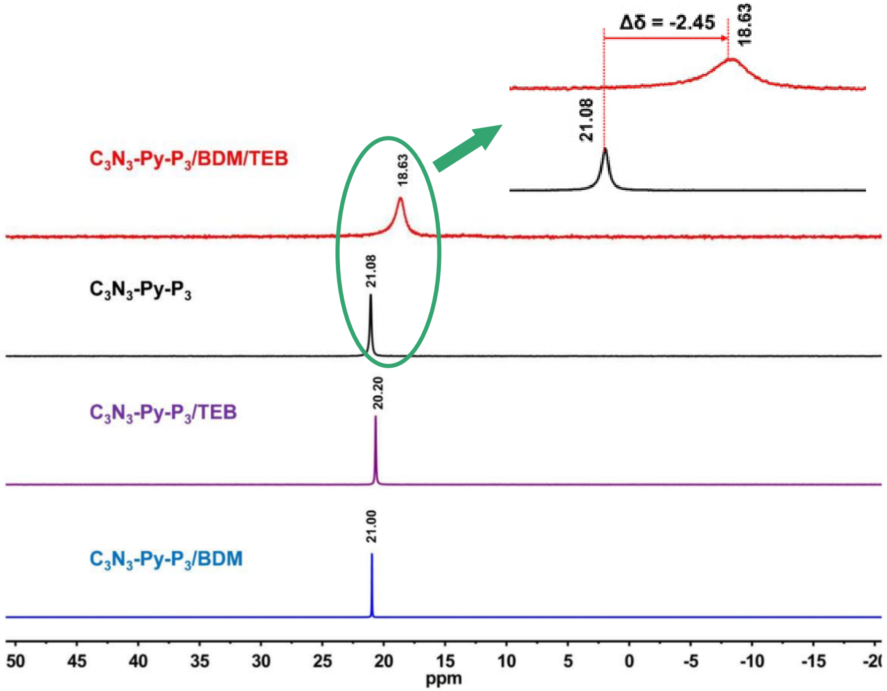


PO	**BO**	**PGE**	**StO**
Conv. = 72%, PC/CC = 98/2	Conv. = 69%, PC/CC = 97/3	Conv. = 35%, PC/CC = 99/1	Conv. = 37%, PC/CC = 99/1
M_n = 16.8 kDa, $Đ$ = 1.09	M_n = 27.1 kDa, $Đ$ = 1.11	M_n = 11.2 kDa, $Đ$ = 1.28	M_n = 10.1 kDa, $Đ$ = 1.14

ECH **AGE**

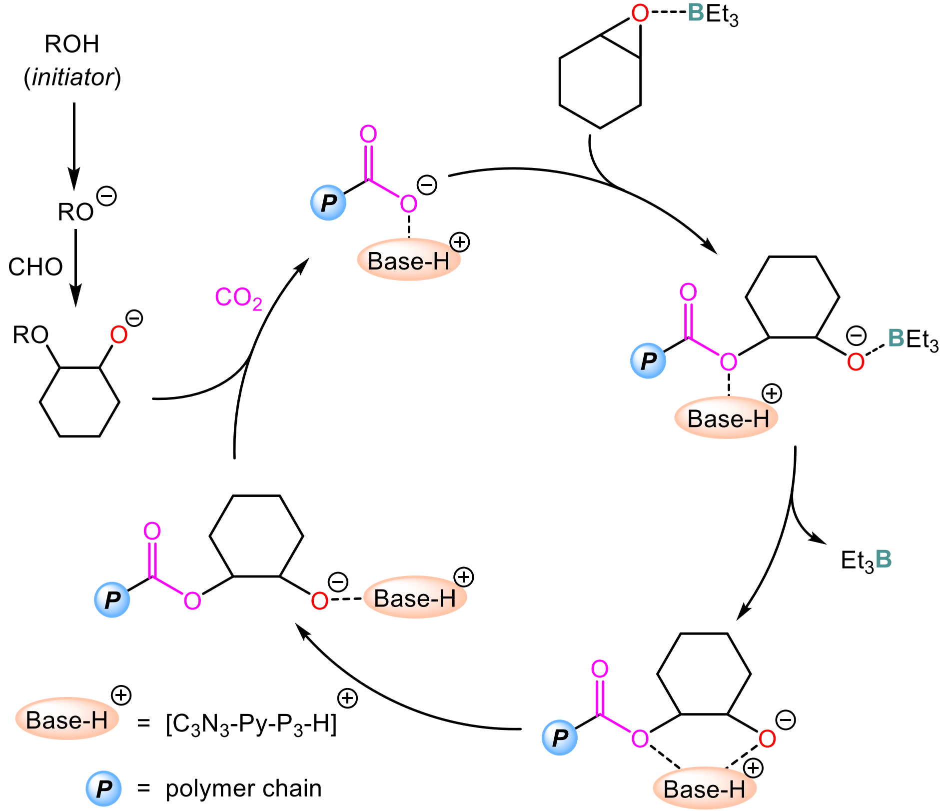
Only cyclic carbonate

- **31P NMR experiments**



Weak interaction between TEB and phosphazene

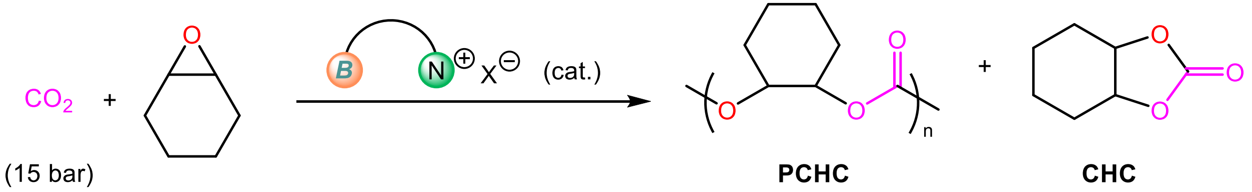
- **Putative mechanism**

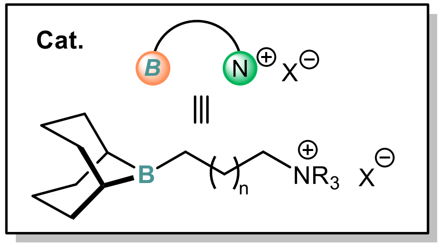


B-N$^+$ Bifunctional Catalyst for ROCOP of CHO/CO_2

Wu, 2020

(anionic)





1: n = 1, R = Et, X = Br
2: n = 2, R = Et, X = Br
3a: n = 3, R = Et, X = Cl
3b: n = 3, R = Et, X = Br
3c: n = 3, R = Et, X = I
4: n = 4, R = Et, X = Br
5: n = 5, R = Et, X = Br
6: n = 3, R = Pr, X = Br
7: n = 3, R = Bu, X = Br

PCHC/CHC > 99%   Ether linkage = 0%   (in all cases)

Entry	cat.	mon./cat.	t (h)	T (°C)	Conv. (%)	TON	TOF (h^{-1})	Efficiency (g/g)	M_n (kDa)	*Đ*
1	**1**	5000	3	80	7	350	117	150	15.6	1.11
2	**2**	5000	3	80	26	1300	433	520	19.2	1.14
3	**3a**	5000	3	80	22	1100	367	480	27.2	1.16
4	**3b**	5000	3	80	31	1550	517	590	29.8	1.14
5	**3c**	5000	3	80	19	950	317	320	22.7	1.23
6	**4**	5000	3	80	25	1250	417	460	26.6	1.13
7	**5**	5000	3	80	26	1300	433	460	23.4	1.13
8	**6**	5000	3	80	30	1500	500	510	22.3	1.11
9	**7**	5000	3	80	29	1450	483	450	21.2	1.12
10	**3b**	5000	12	25	2	100	8	40	7.8	1.13
11	**3b**	5000	3	100	58	2900	967	1110	30.3	1.20
12	**3b**	5000	0.5	150	49	2450	4900	940	18.7	1.25
13	**3b**	10000	26	80	74	7400	285	230	27.1	1.15
14	**3b**	20000	48	80	65	13000	271	4960	24	1.18

Bromide anion is the best

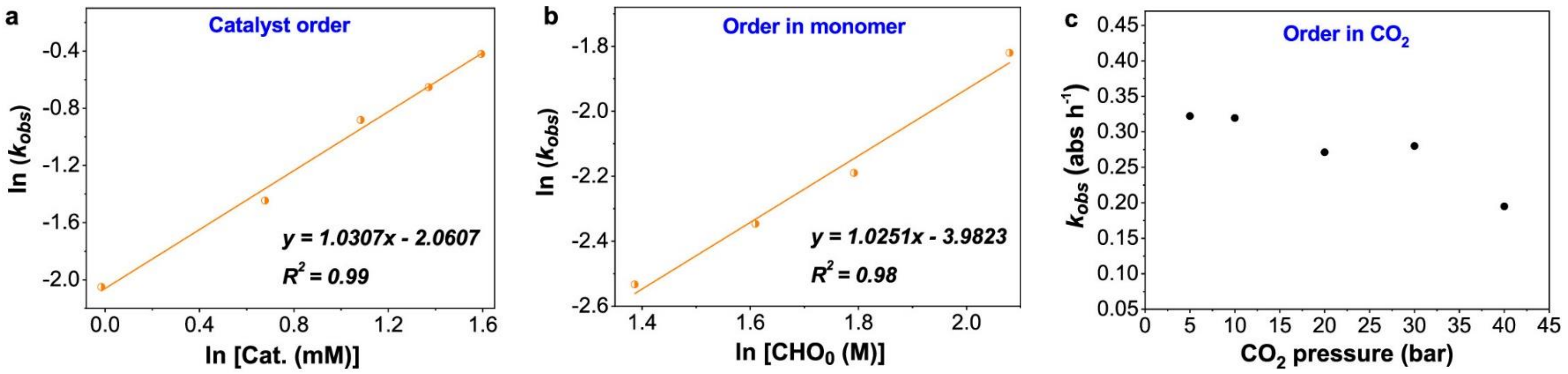
Temperature from 25 to 150 °C
(up to 4900 h^{-1} TOF)

Extremely high efficiency
(up to 4.96 kg/g)

Yang, G.-W.; Wu, G.-P. et al. *J. Am. Chem. Soc.* **2020**, *142*, 12245.

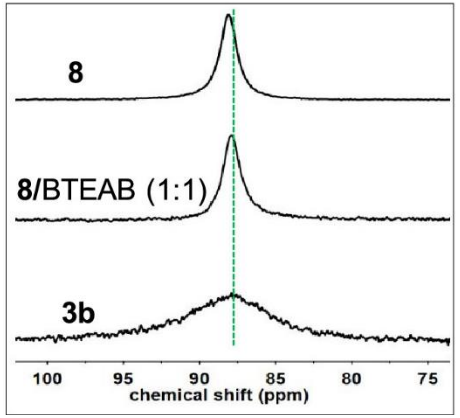
B-N+ Bifunctional Catalyst for ROCOP of CHO/CO_2

- Kinetic experiments



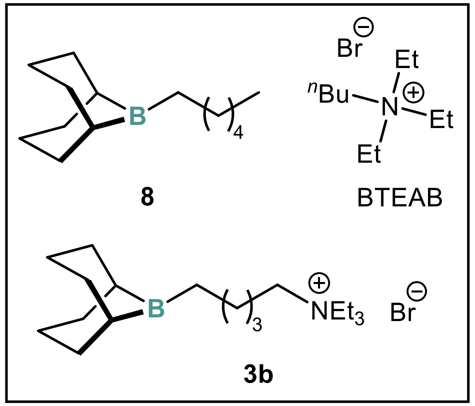
Only one catalyst molecule is involved in RDS → ***Intramolecular catalysis***

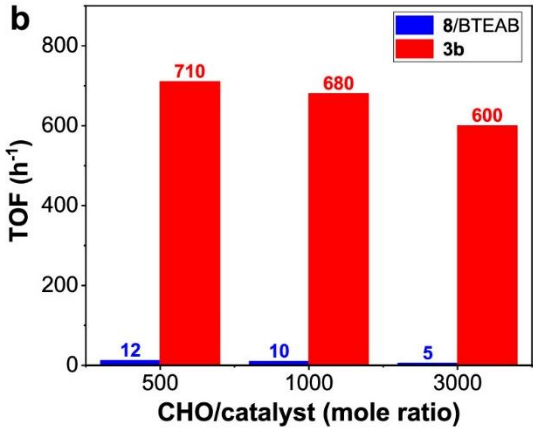
- ^{11}B NMR spectra



Dynamic equilibrium among *B---Br⁻---N⁺*

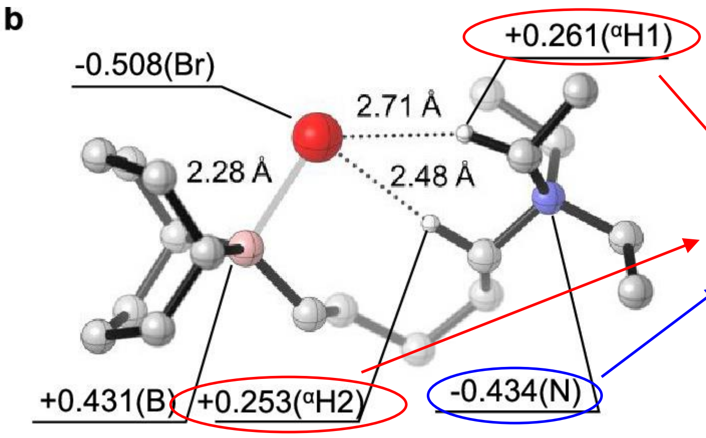
- Control experiments





Intramolecular synergistic effect between *B* and *N⁺*

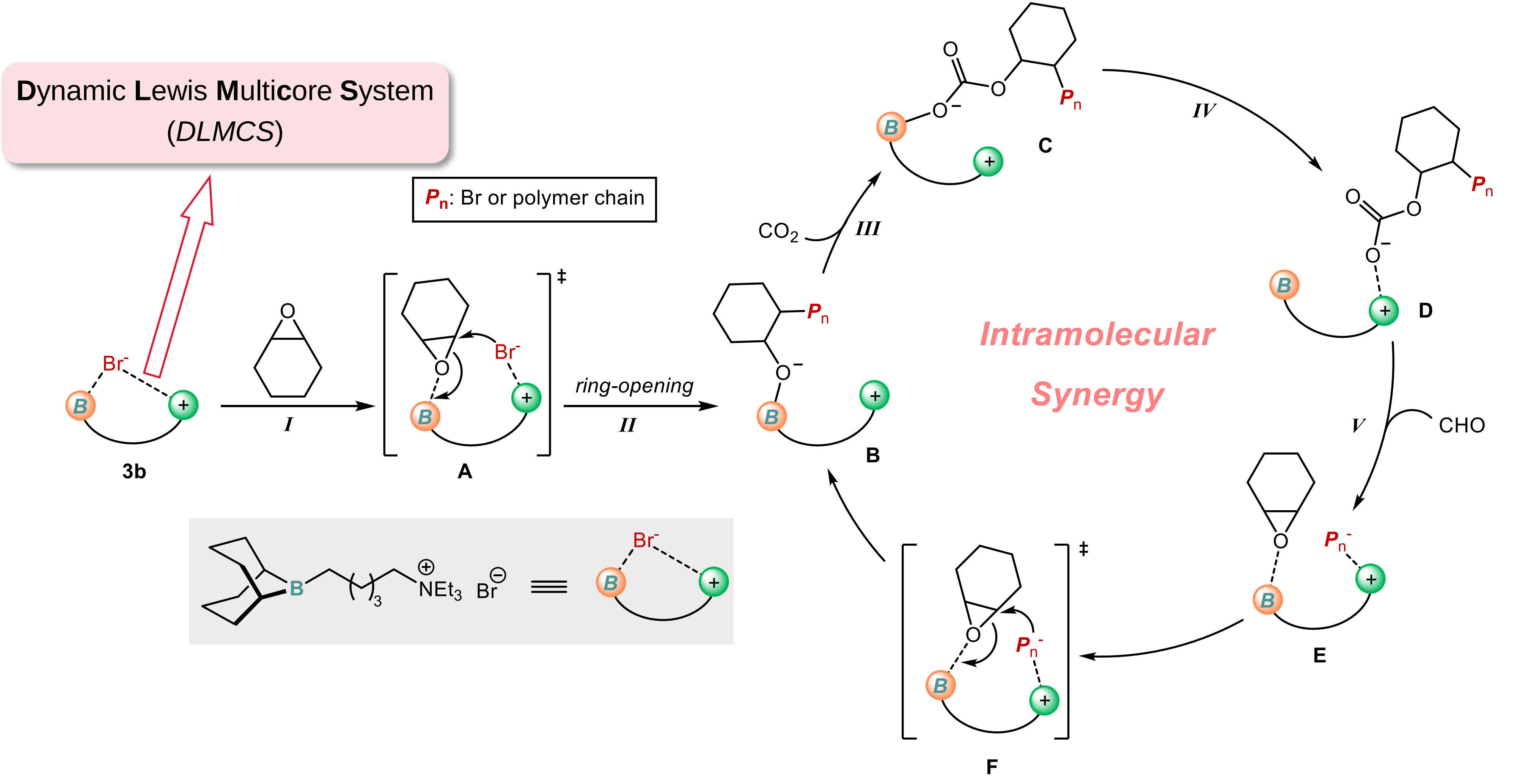
- The optimized structure of 3b by DFT



N⁺ distribute positive charge on adjacent *H*

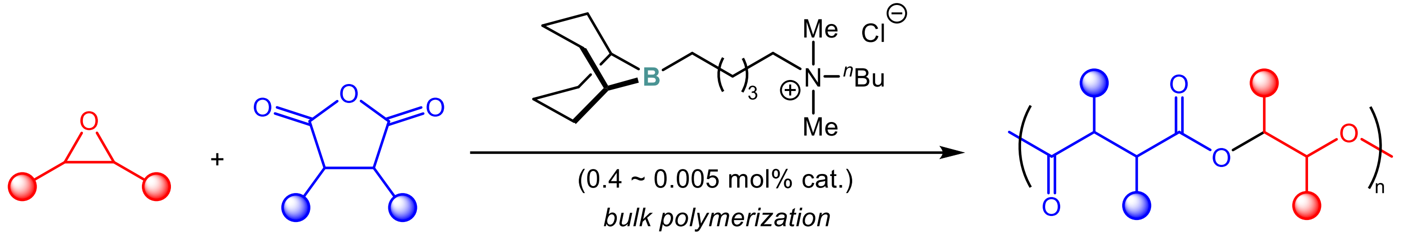
B-N$^+$ Bifunctional Catalyst for ROCOP of CHO/CO_2

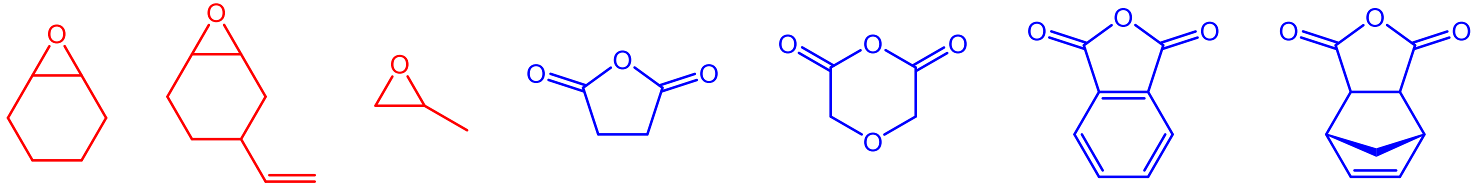
- **Proposed mechanism**



Other DLMCS-Catalyzed ROCOPs

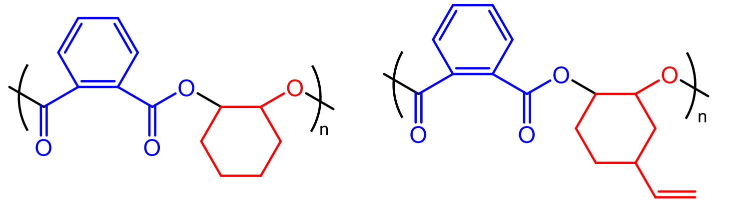
- **Copolymerization of epoxides and cyclic anhydrides**





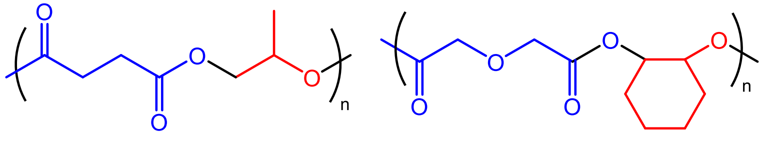
CHO	VCHO	PO	SA	DGA	PA	CPMA

(a) Xie, R.; Wu, G.-P. et al. *Angew. Chem., Int. Ed.* **2021**, *60*, 19253.



poly(PA-*alt*-CHO)
Esterlinkage > 99%
M_n = 96.8 kDa, $Đ$ = 1.34

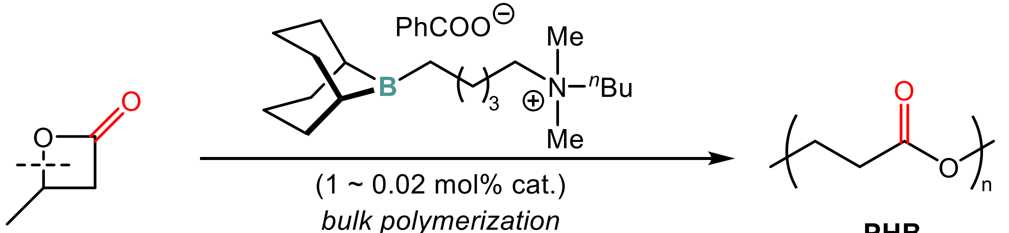
poly(PA-*alt*-VCHO)
Esterlinkage > 99%
M_n = 26.1 kDa, $Đ$ = 1.22



poly(SA-*alt*-PO)
Esterlinkage > 99%
M_n = 3.1 kDa, $Đ$ = 1.26

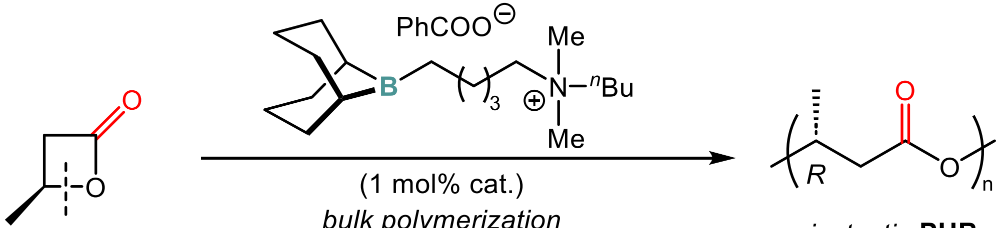
poly(DGA-*alt*-CHO)
Esterlinkage = 89%
M_n = 4.2 kDa, $Đ$ = 1.83

- **Ring-opening polymerization of *β*-Butyrolactone**



rac-BBL

PHB
***P**oly(β-**h**ydroxy**b**utyrate)*



(*S*)-BBL

isotactic-**PHB**
T_m = 148 °C, [α] = +7.9°

♠ TOF up to 129 h^{-1} ♠ Controlled polymerization
♠ M_n up to 17.3 kDa ♠ Narrow polydispersity ($Đ$ < *1.21*)

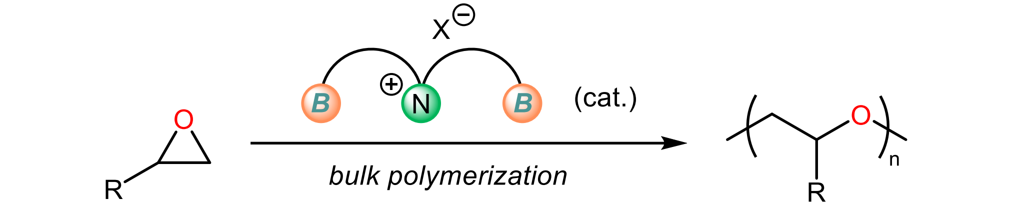
(b) Yang, L.; Wu, G.-P. et al. *Macromolecules* **2021**, *54*, 5509.

PART III

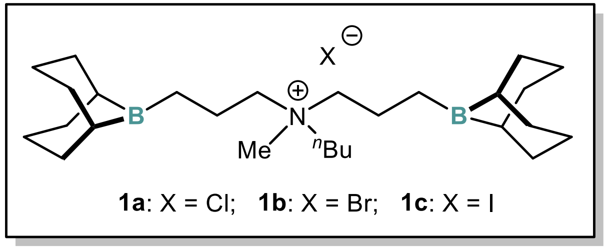
Multinuclear-Organoboron-Mediated Ring-Opening Polymerizations

B-N$^+$-B Bifunctional Catalyst for ROP of Epoxides

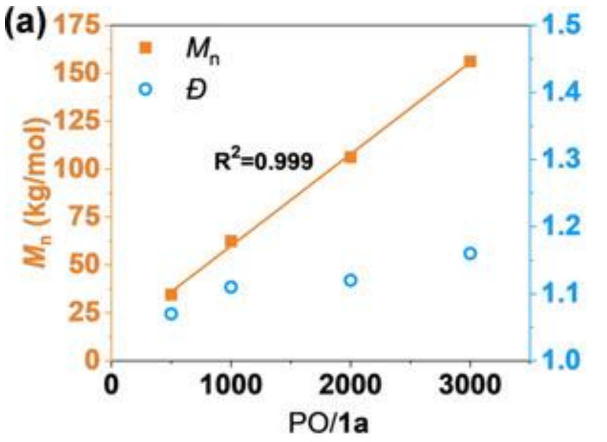
Wu, 2020
(anionic)



PO (R = Me) or **EO** (R = H) **PPO** (R = Me) or **PEO** (R = H)



Entry	Mon.	Cat.	Mon./Cat.	T (°C)	t (h)	Conv. (%)	TON	M_n (kDa)	*Đ*
1	PO	**1a**	500/1	-20	0.5	99.9	500	34.6	1.07
2	PO	**1a**	1000/1	-20	2	99.9	1000	62.5	1.11
3	PO	**1a**	2000/1	-20	4	99.9	2000	106.3	1.12
4	PO	**1a**	3000/1	-20	6	99.9	3000	156.2	1.17
5	PO	**1a**	10000/1	-20	6	35.0	3500	177.3	1.17
6	PO	**1b**	10000/1	-20	6	35.1	3510	181.2	1.16
7	PO	**1c**	10000/1	-20	6	34.6	3460	172.7	1.19
8	PO	**1b**	30000/1	-20	60	99.9	30000	1050.1	1.23
9	PO	**1b**	100000/1	-20	144	56.5	56500	219.5	1.10
10	EO	**1b**	10000/1	0	0.33	99.9	10000	120.1	1.25
11	EO	**1b**	200000/1	0	12	99.9	200000	343.6	1.33



Controlled polymerization process

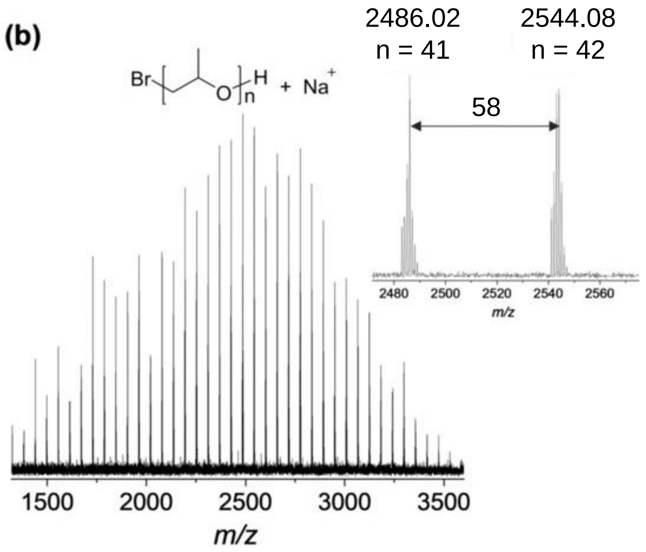
High M_n: up to 1×10^3 kDa
Low cat. loading, high TON

Yang, G.-W.; Wu, G.-P. et al. *Angew. Chem., Int. Ed.* **2020**, *59*, 16910.

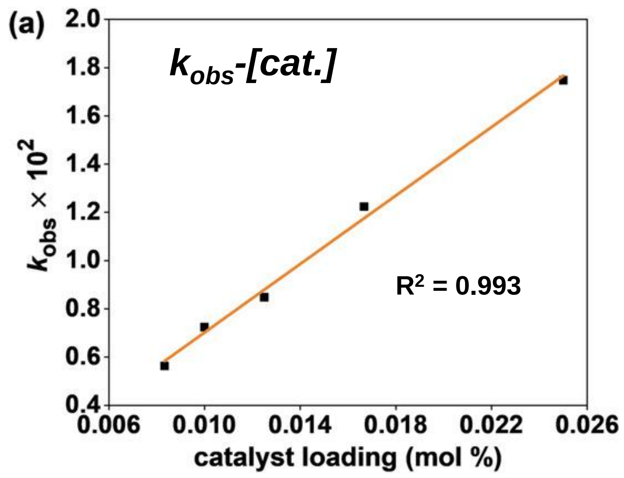
B-N$^+$-B Bifunctional Catalyst for ROP of Epoxides

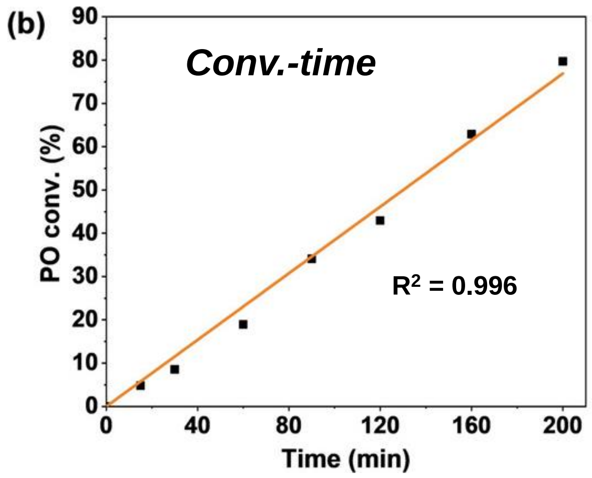
FUDAN UNIVERSITY

● **MALDI-TOF mass spectrum**



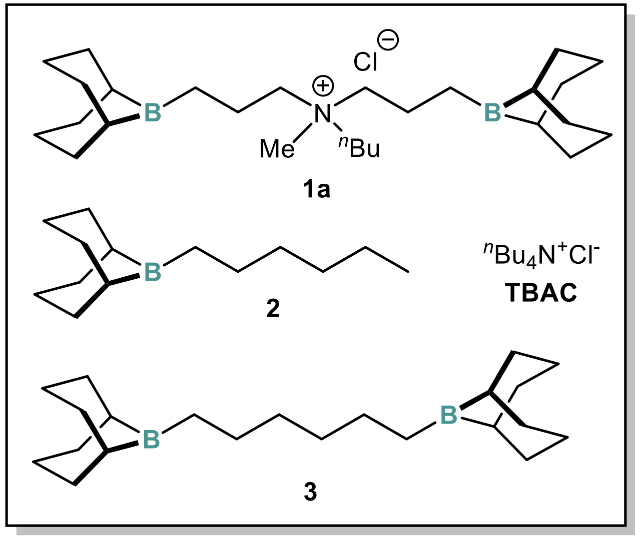
● **Kinetic experiments**





First-order for [cat.], quasi-zero-order for [mon.]

● **Synergistic effect investigation**



Conditions: PO/cat. = 10000/1, -20 °C, 6 h

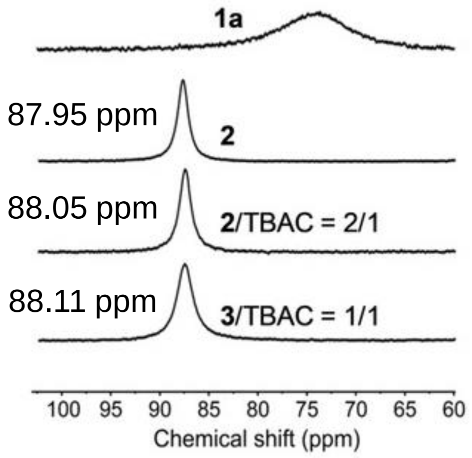
For **1a**: TOF = 583 h^{-1}

For **2**/TBAC (2/1): TOF = 9 h^{-1}

For **3**/TBAC (1/1): TOF = 80 h^{-1}

Synergistic effect among B---N$^+$---B

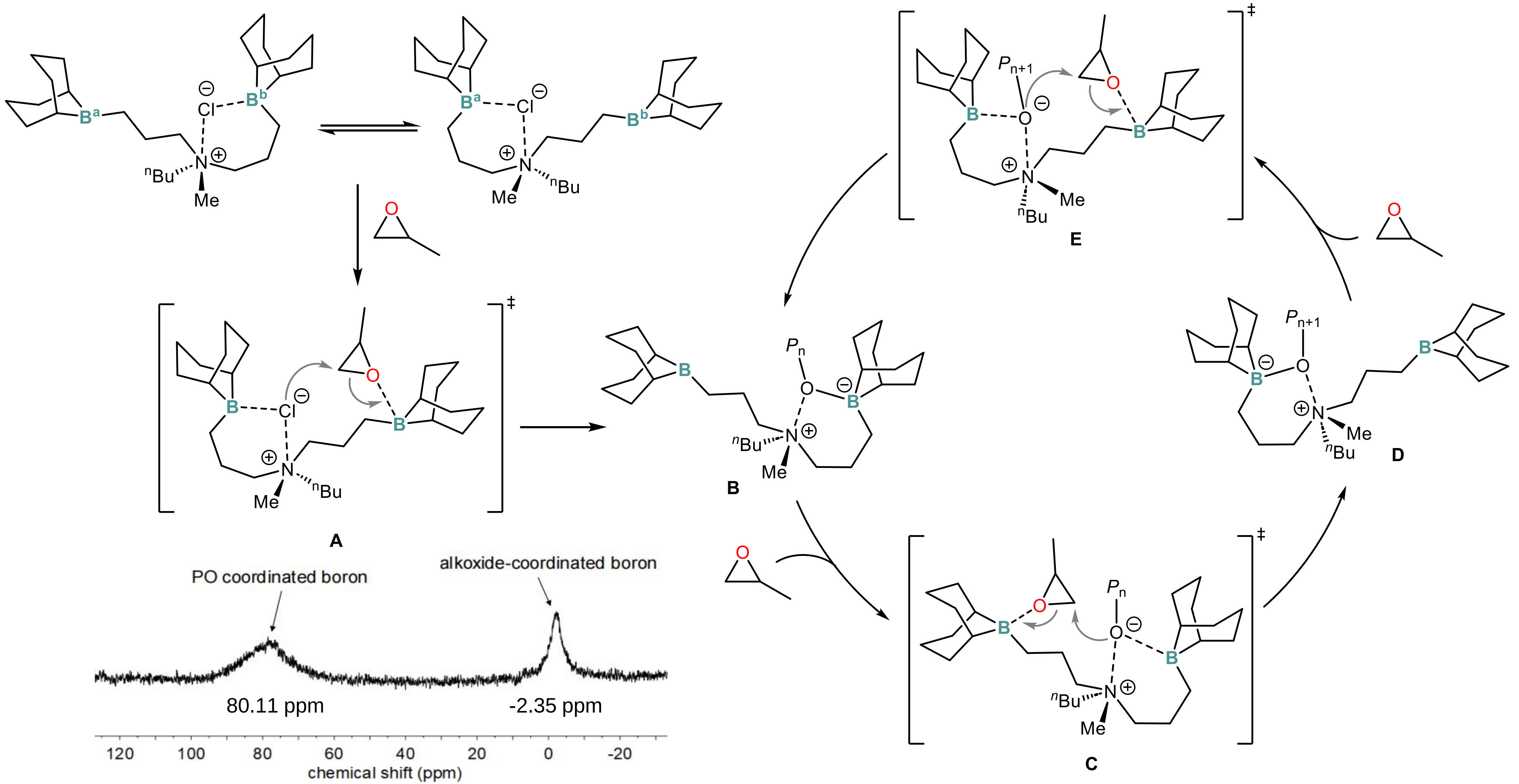
● **^{11}B NMR**



Dynamic exchange of Cl^- among B---N$^+$---B

B-N$^+$-B Bifunctional Catalyst for ROP of Epoxides

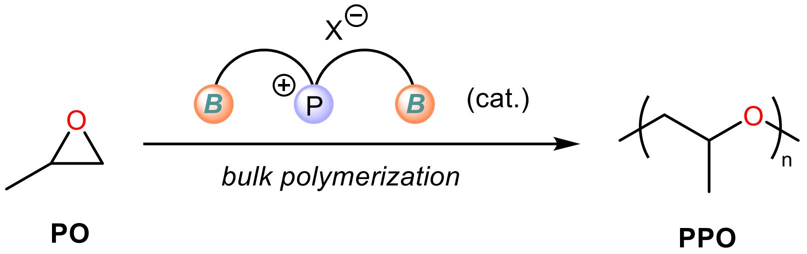
- **Proposed intramolecular *N*$^+$ assisted SN$_2$ mechanism**

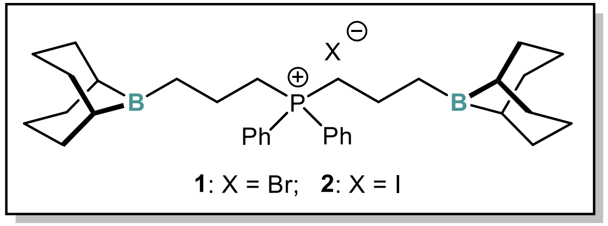


^{11}B NMR (**1a** + 10 equiv. PO) in $CDCl_3$

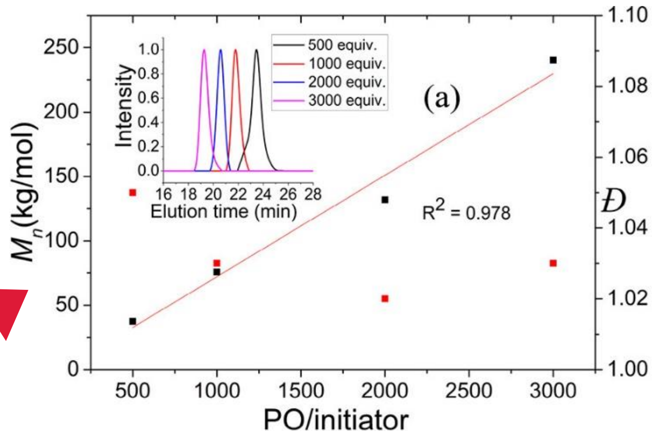
B-P$^+$-B Bifunctional Catalyst for ROP of Epoxides

Li & Zhong, 2022
(anionic)





Entry	Cat.	Mon./Cat.	T (°C)	t (min)	Conv. (%)	TOF (h^{-1})	M_n (kDa)	$Đ$
1	**1**	500/1	-30	10	> 99	3000	28.0	1.03
2	**2**	500/1	-30	10	>99	3000	28.4	1.04
3	**1**	500/1	0	30	>99	1000	34.0	1.15
4	**1**	500/1	-20	10	>99	3000	32.4	1.05
5	**1**	1000/1	-20	30	97	1940	70.7	1.03
6	**1**	2000/1	-20	60	>99	1980	127.0	1.02
7	**1**	3000/1	-20	60	>99	3000	235.4	1.03
8	**1**	10000/1	-10	360	97	1616	449.4	1.24
9	**1**	10000/1	-20	360	97	1616	489.5	1.20
10	**1**	10000/1	0	360	69	1150	341.7	1.24
11	**1**	10000/1	25	360	30	500	132.6	1.25
12	**1**	30000/1	-10	720	36	900	368.0	1.34



Controlled polymerization process

***N*$^+$-centered catalyst:**

Conv. = 35.1%, TOF = 585 h^{-1},

M_n = 181.2 kDa

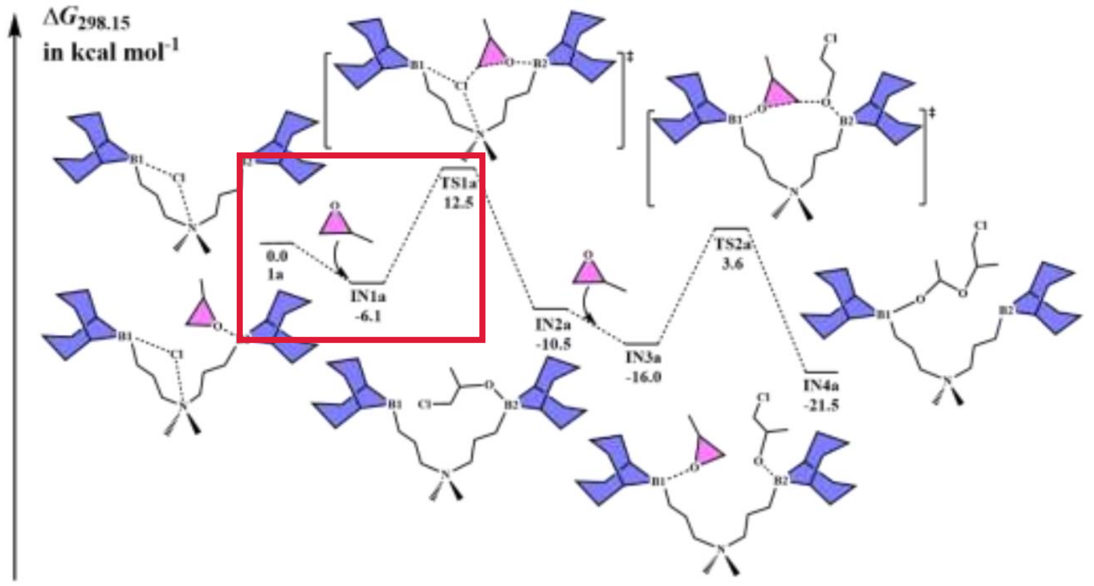
P$^+$-counterpart has
higher conversion and M_n!

Wang, X.; Li, Z. et al. *ACS Catal.* **2022**, *12*, 8434.

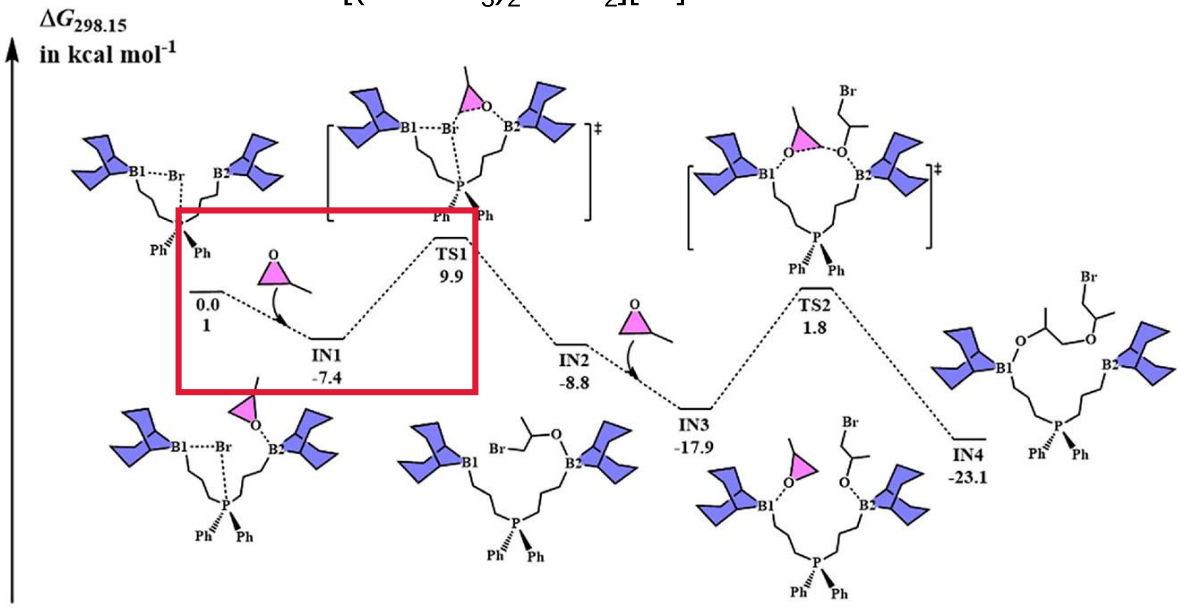
B-P^{+}-B Bifunctional Catalyst for ROP of Epoxides

- **Comparison of *N*$^{+}$-centered and *P*$^{+}$-centered catalysts**

[(BBN-C$_3$)$_2$-NMe$_2$][Cl]



[(BBN-C$_3$)$_2$-PPh$_2$][Br]



Activation energy: 18.6 (*N*) vs 17.3 (*P*) kcal/mol

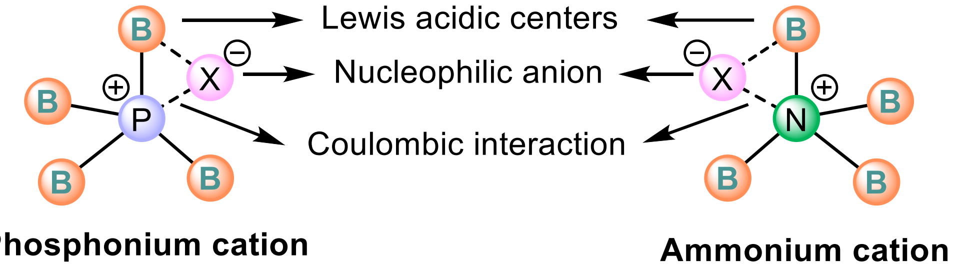
Initiation energy: 12.5 (*N*) vs 9.9 (*P*) kcal/mol

Radius of *P* was lager than that of *N* → Lager space for coordination and ROP

N^+-centered VS P^+-centered DLMCS catalysts

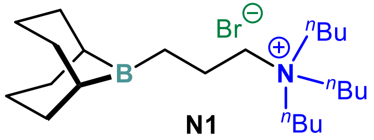
FUDAN UNIVERSITY

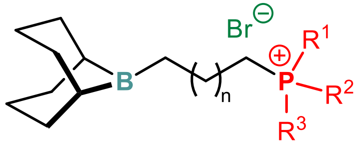
Wu, 2022
(anionic)



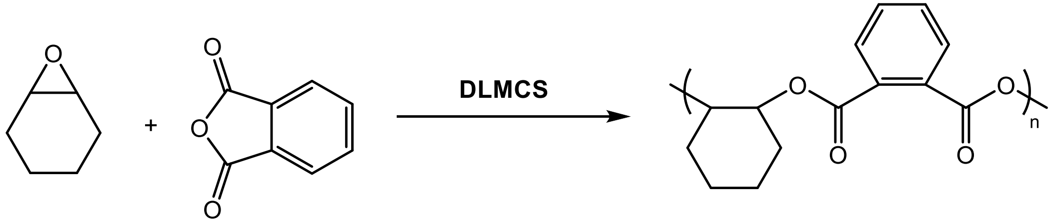
***N^+ vs P^+*:**

1. P has lager atomic radius than N;
2. Phosphonium salts show superior thermal stability;
3. P atom has greater steric tolerance.





P1: n = 1, $R^1 = R^2 = R^3 = {}^n$Bu
P2: n = 1, $R^1 = R^2$ = Ph, $R^3 = {}^n$Bu
P3: n = 1, $R^1 = R^2 = R^3$ = Ph
P4: n = 2, $R^1 = R^2 = R^3 = {}^n$Bu
P5: n = 3, $R^1 = R^2 = R^3 = {}^n$Bu
P6: n = 4, $R^1 = R^2 = R^3 = {}^n$Bu



Entry	Cat.	[CHO]/[PA]/[cat.]	T (°C)	t (min)	Conv. (%)	TOF (h^{-1})	M_n (kDa)	*Đ*
1	**P1**	400/200/1	120	30	76.1	304	29.2	1.16
2	**P2**	400/200/1	120	40	75.3	226	28.9	1.17
3	**P3**	400/200/1	120	40	54.5	164	17.5	1.17
4	**P4**	400/200/1	120	10	80.7	1004	31.4	1.18
5	**P5**	400/200/1	120	10	87.9	1055	33.6	1.15
6	**P6**	400/200/1	120	10	85.3	1024	32.9	1.60
7	**P5**	2000/1000/1	200	20	95.2	2856	87.6	1.20
8	**P1**	3000/1	120	40	75.3	190	23.5	1.17
9	**N1**	10000/1	120	40	4.8	36	4.2	1.18

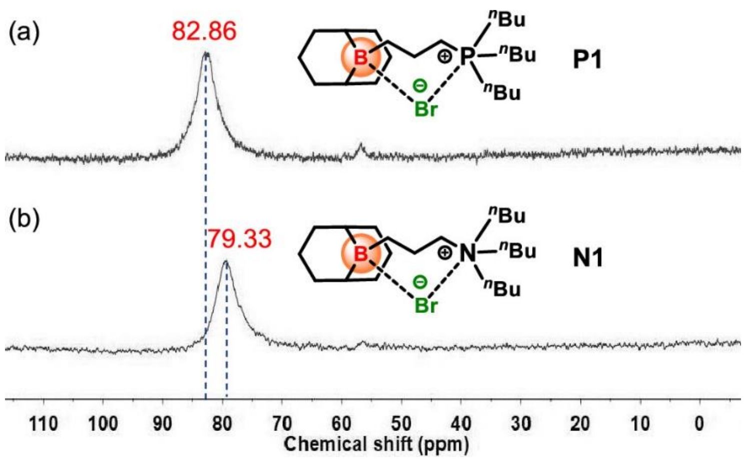
Steric hindrance weaken P^+---Br^- interactions

P1 shows superior activity than **N1**

Zhang, Y.-Y.; Wu, G.-P. et al. *Macromolecules* **2022**, *55*, 6443.

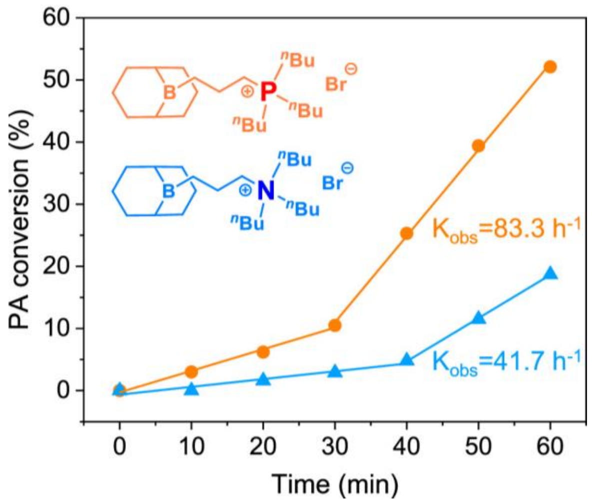
N^+-centered VS P^+-centered DLMCS catalysts

● ^{11}B NMR experiments



Stronger Coulombic interaction in P^+ than in N^+

● PA conversion versus time plots

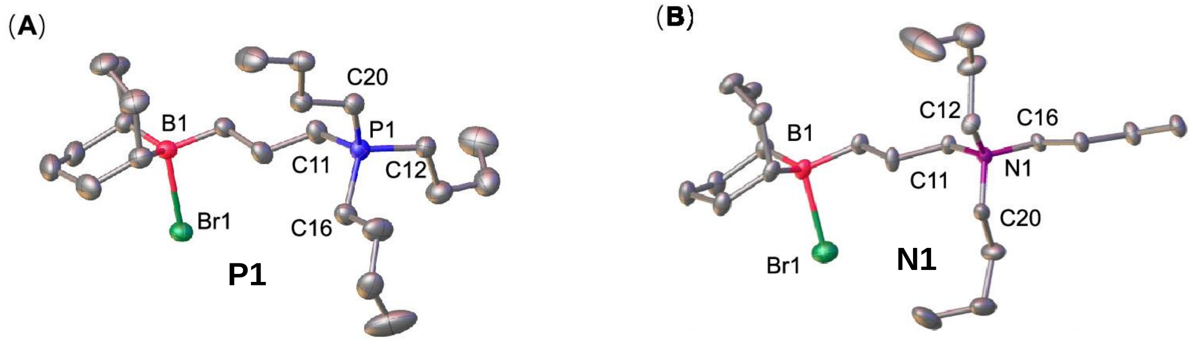


For P1:

shorter initiation time

higher propagation rate

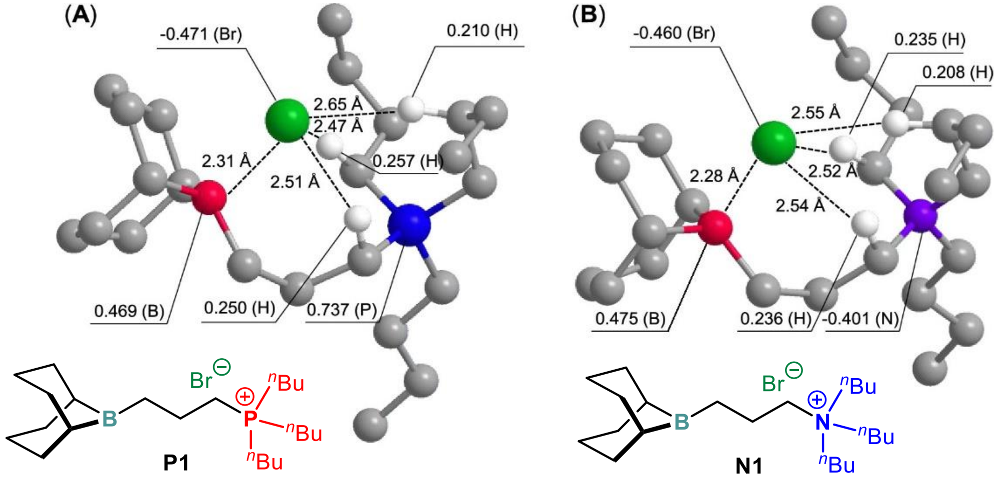
● Single crystal structures of catalysts P1 and N1



B---Br$^-$: 2.312 Å (in **P1**) vs 2.271 Å (in **N1**)

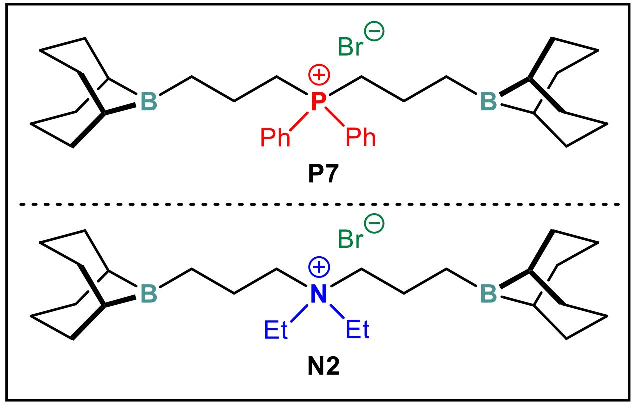
B---P: 5.439 Å vs B---N: 5.212 Å

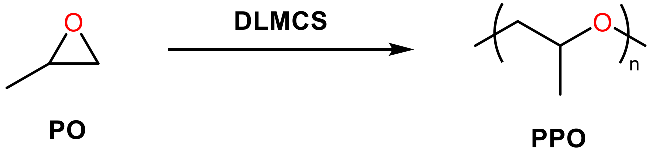
● Optimized structures of N1 and P1



B---Br$^-$: 2.31 Å (in **P1**) vs 2.28 Å (in **N1**)

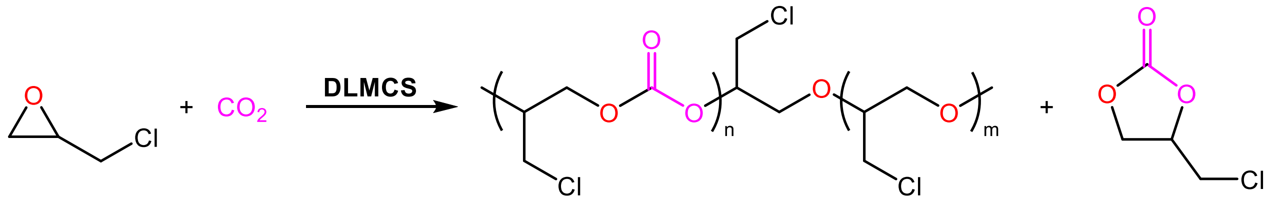
N^+-centered VS P^+-centered DLMCS catalysts

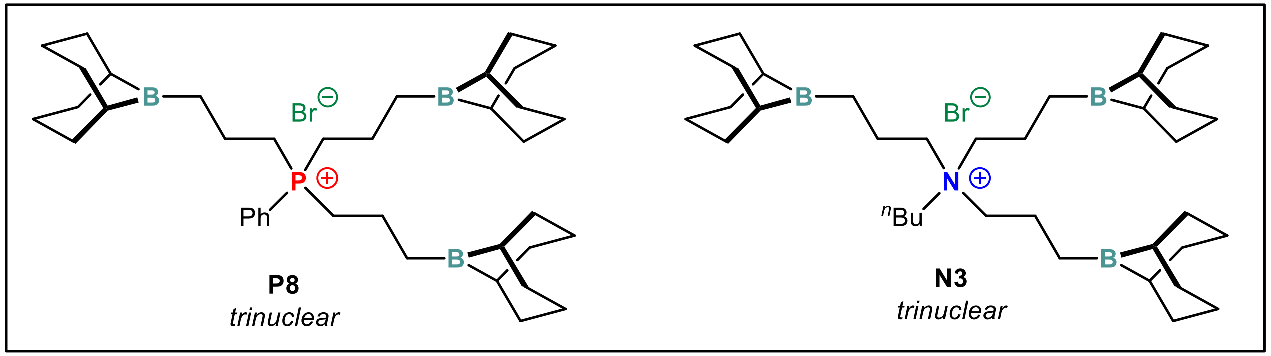


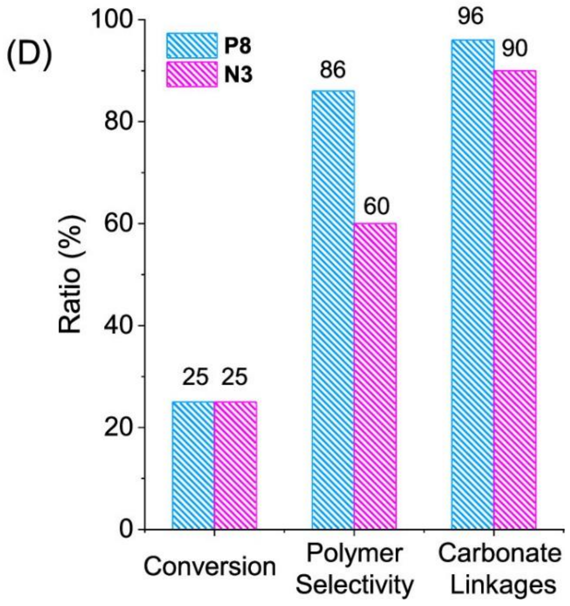


Entry	Cat.	[PO]/[cat.]	t	Conv. (%)	TOF (h^{-1})	M_n (kDa)	$Đ$
1	**P7**	2000/1	8 min	22.3	3345	24.3	1.19
2	**N2**	2000/1	20 min	26.7	1602	12.6	1.18
3	**P7**	10000/1	6 h	66.7	1112	220.0	1.20
4	**N2**	10000/1	6 h	36.4	606	187.0	1.21

P7 owns superior activity to **N2**







P8 exhibits better selectivity (86% vs 60%)

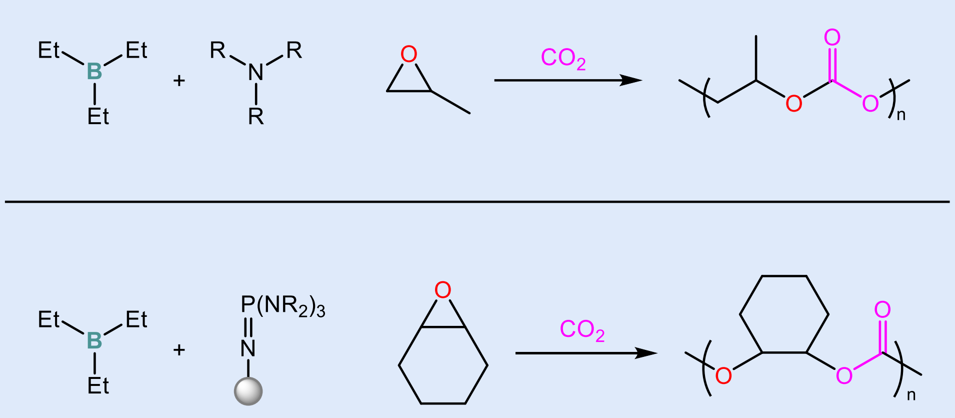
PART

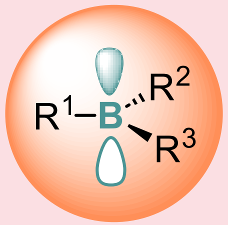
Ⅳ

Summary and Outlook

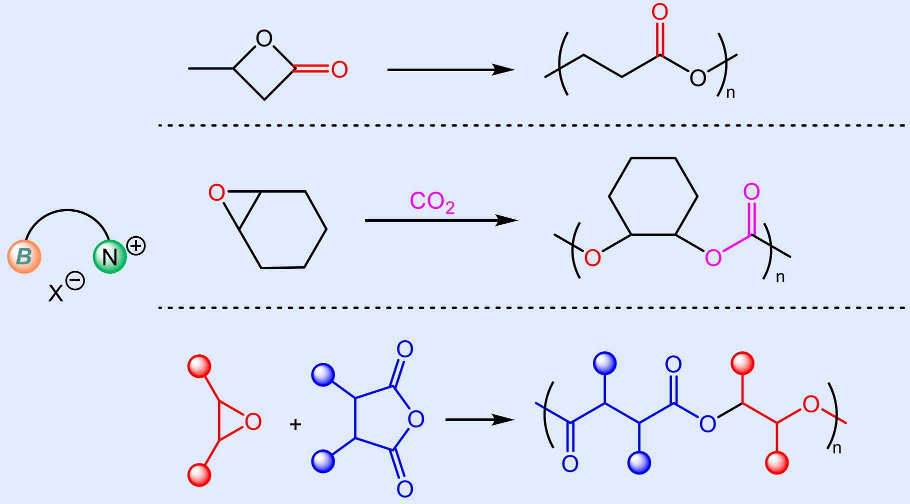
Summary

Triethylborane catalyst



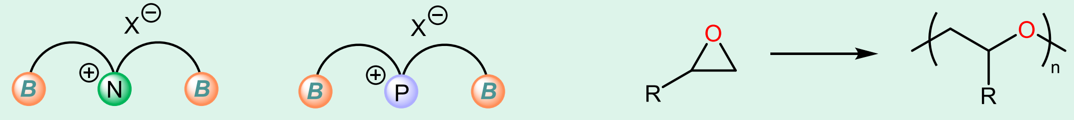


Mononuclear DLMCS

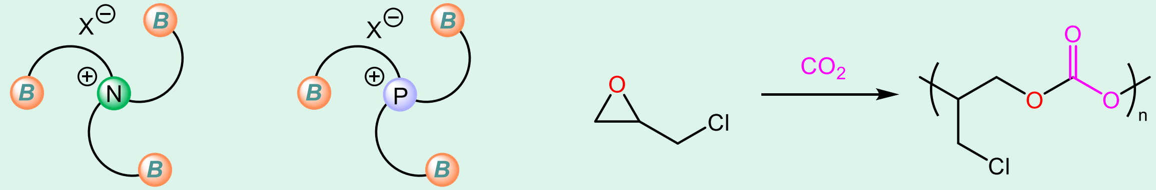


Multinuclear DLMCS

Dinuclear

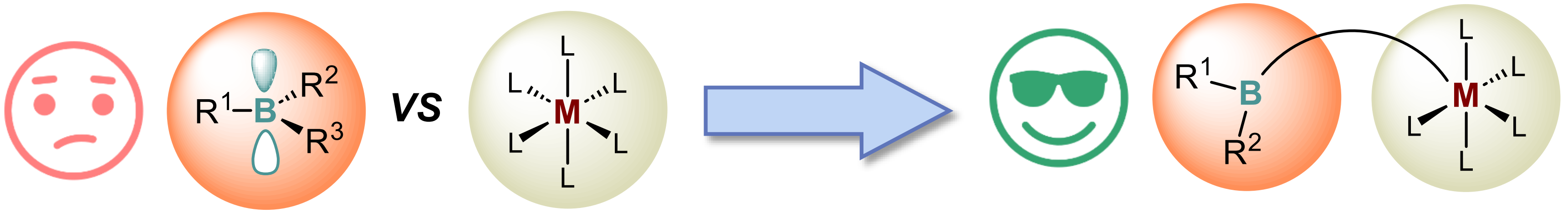


Trinuclear



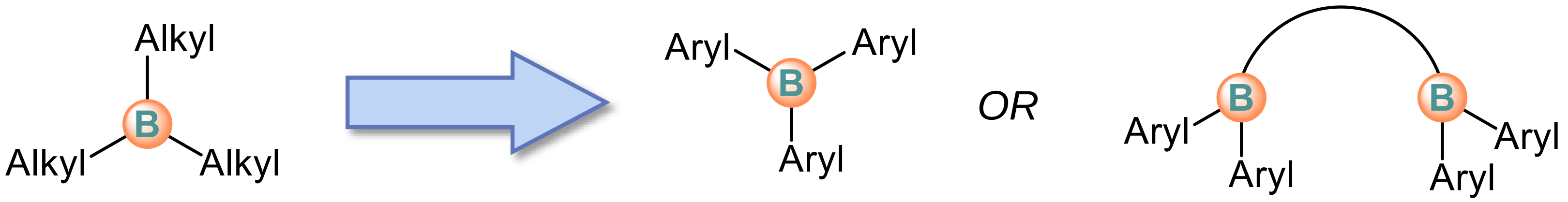
Outlook

- Organoboron catalysts are still less competent than metallic catalysts.



Boron-metal multifunctional catalysts

- Alkylboranes are less Lewis acidic, they can only catalyze ROP of small rings.



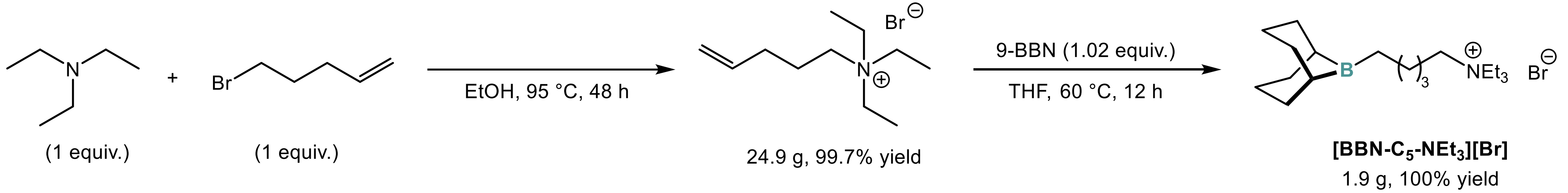
- Develop chiral organoboranes for asymmetric synthesis of stereoregular polymer.

Thank you for listening

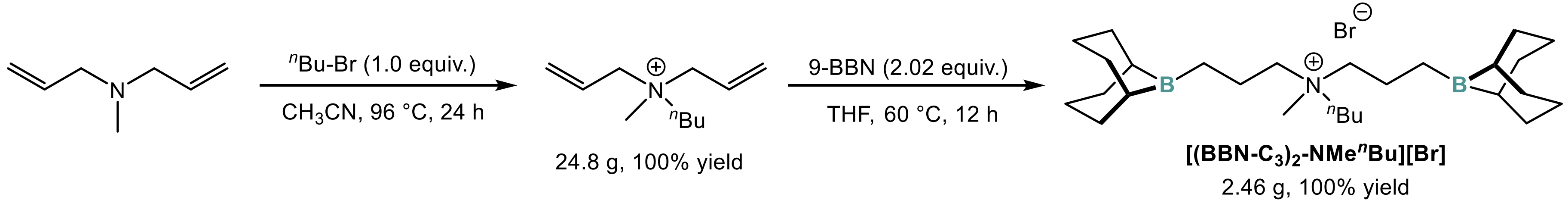
Supporting Information

DLMCS-Catalyzed ROP Reactions

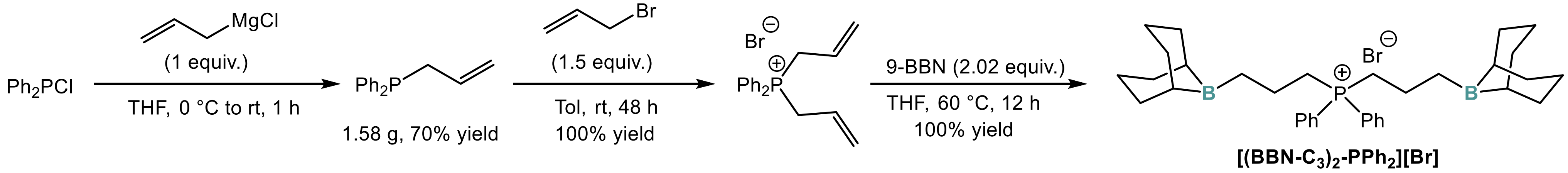
- **Preparation of DLMCS catalysts**



(a) Yang, G.-W.; Wu, G.-P. et al. *J. Am. Chem. Soc.* **2020**, *142*, 12245.



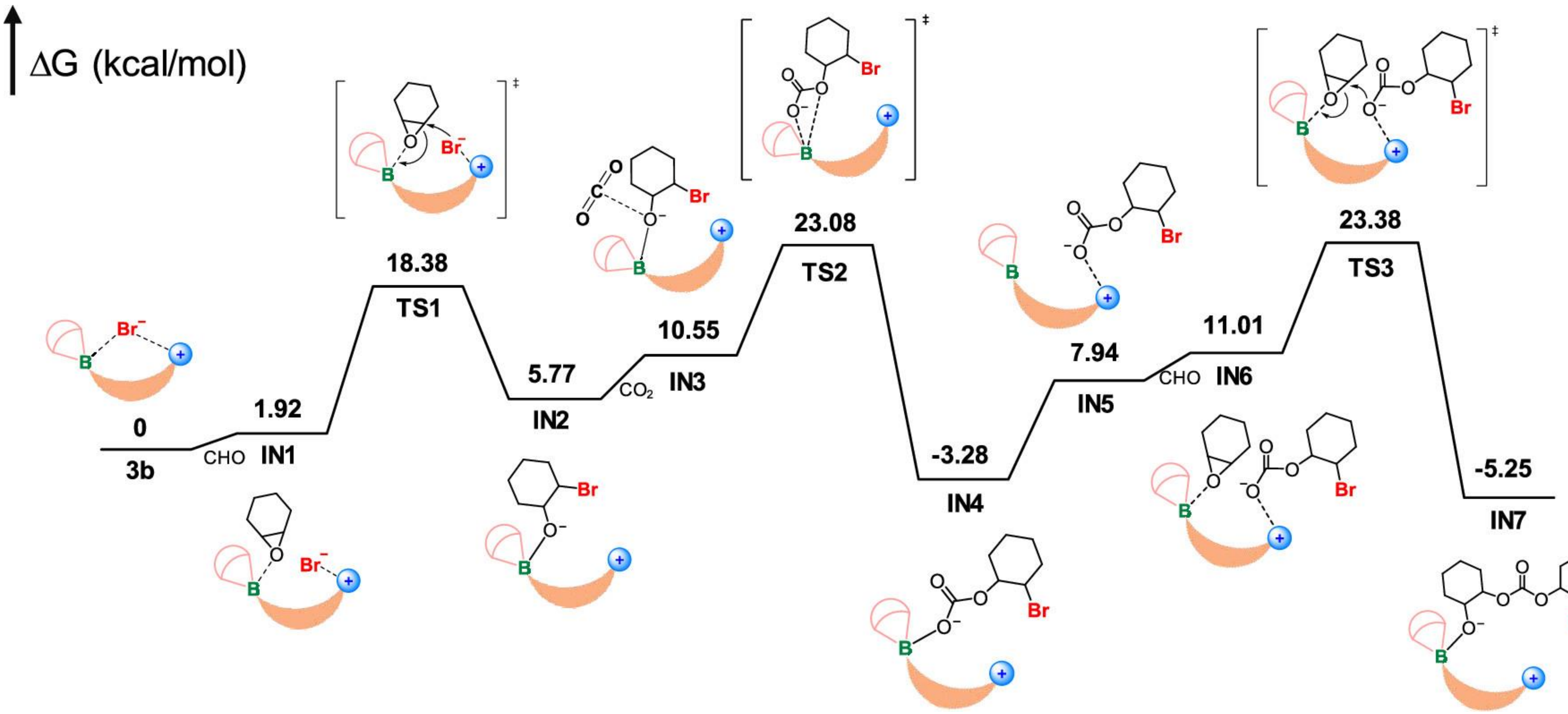
(b) Yang, G.-W.; Wu, G.-P. et al. *Angew. Chem., Int. Ed.* **2020**, *59*, 16910.



(c) Wang, X.; Li, Z. et al. *ACS Catal.* **2022**, *12*, 8434; (d) Zhang, Y.-Y.; Wu, G.-P. et al. *Macromolecules* **2022**, *55*, 6443.

B-N+ Bifunctional Catalyst for ROCOP of CHO/CO_2

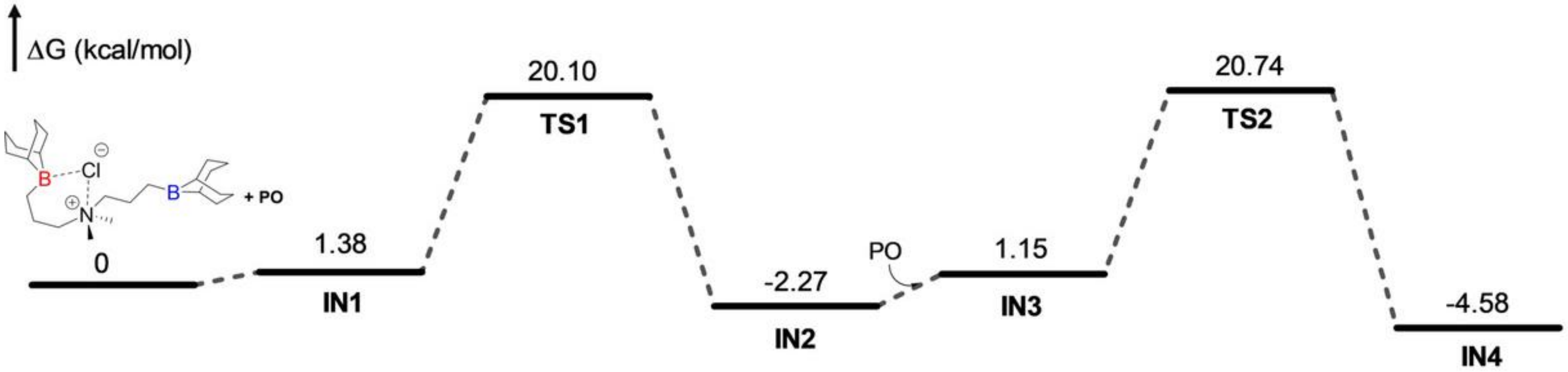
- **Free energy profiles of [BBN-C_5-NEt_3][Br]-catalyzed CHO/CO_2 copolymerization**

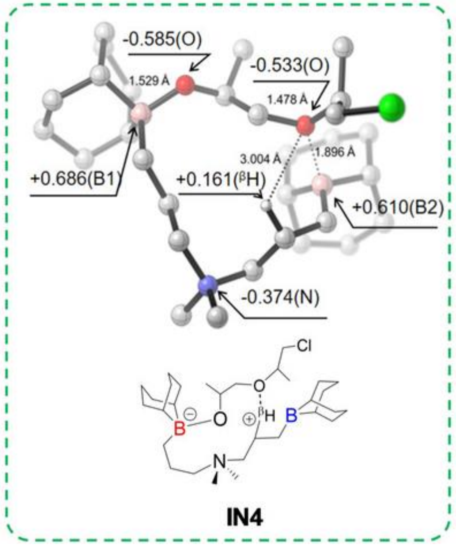


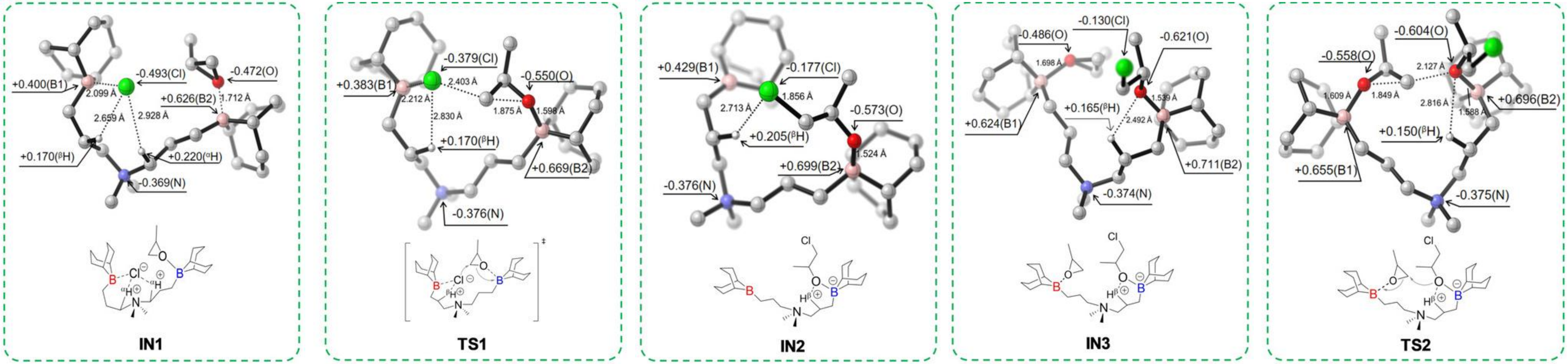
Yang, G.-W.; Wu, G.-P. et al. *J. Am. Chem. Soc.* **2020**, *142*, 12245.

B-N+-B Bifunctional Catalyst for ROP of Epoxides

- **Free energy profiles of [(BBN-C$_3$)$_2$-NMe^{n}Bu][Br]-catalyzed PO polymerization**







Yang, G.-W.; Wu, G.-P. et al. *Angew. Chem., Int. Ed.* **2020**, *59*, 16910.