CHEMISTRY & SUSTAINABILITY

CHEMSUSCHEM

ENERGY & MATERIALS

Accepted Article

Title: Efficient Aluminum Catalysts for the Chemical Conversion of CO2 into Cyclic Carbonates at Room Temperature and Atmospheric CO2 Pressure

Authors: Yoseph Kim, Kyunglim Hyun, Duseong Ahn, Ran Kim, Myung Hwan Park, and Youngjo Kim

To be cited as: *ChemSusChem* 10.1002/cssc.201901661

Link to VoR: http://dx.doi.org/10.1002/cssc.201901661

A Journal of

ChemPubSoc Europe

WILEY-VCH

www.chemsuschem.org

Efficient Aluminum Catalysts for the Chemical Conversion of CO_2 into Cyclic Carbonates at Room Temperature and Atmospheric CO_2 Pressure

Yoseph Kim, Kyunglim Hyun, Duseong Ahn, Ran Kim, Myung Hwan Park,* and Youngjo Kim*

Y. Kim, K. Hyun, D. Ahn, R. Kim, Prof. Dr. Y. Kim
Department of Chemistry and BK21+ Program Research Team, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea
E–mail: ykim@chungbuk.ac.kr

Prof. Dr. M. H. Park
Department of Chemistry Education, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea
E–mail: mhpark98@chungbuk.ac.kr

K. Hyun and D. Ahn contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/cssc.201901661.

Abstract: We have synthesized dimeric aluminum compounds $[Al(OCMe_2CH_2N(R)CH_2X)]_2$ (X = pyridin–2–yl, R = H (**Pyr^{H}**); X = pyridin–2–yl, R = Me (**Pyr^{Me}**); X = furan–2–yl, R = H (**Fur^{H}**); X = furan–2–yl, R = Me (**Fur^{Me}**); X = thiophen–2–yl, R = H (**Thio^{H}**); and X = thiophen–2–yl, R = Me (**Thio^{Me}**)) containing heterocyclic pendant group attached to the nitrogen. These complexes were used to catalyze the coupling of CO_2 with epoxides under ambient conditions. A comparison of their catalytic activities with those of aluminum complexes without *N*–functionalized pendants (X = H, R = H (**H^{H}**); X = H, R = Me (**H^{Me}**)) or with non–heterocyclic pendants (X = $–CH_2CH_2OMe$, R = H (**OMe^{H}**); X = $–CH_2CH_2NMe_2$, R = H (**NMe2^{H}**); and X = $–CH_2CH_2NMe_2$, R = Me (**NMe2^{Me}**)) revealed that aluminum complexes containing heterocycles, in conjunction with $(n–Bu)_4NBr$ as a cocatalyst, showed higher catalytic activities than other complexes for the synthesis of cyclic carbonates under the same ambient conditions. The best catalytic system for this reaction was the **Pyr^{H}**/$(n–Bu)_4NBr$ system, which showed a TON of 99 and a TOF of 4.1 h^{-1}, making it 14–fold and 20–fold more effective than **H^{H}**/$(n–Bu)_4NBr$ and **H^{Me}**/$(n–Bu)_4NBr$, respectively. Although no direct interactions between the aluminum and the heteroatoms in the heterocyclic pendants, its electronic effects combined with the increased local concentration of CO_2 around the active centers influences the catalytic activity in the coupling of CO_2 with epoxides. In addition, **Pyr^{H}**/$(n–Bu)_4NBr$ showed the broad epoxide substrate scope, and seven terminal epoxides and two internal epoxides underwent the designed reaction.

Introduction

The increase in the atmospheric concentration of carbon dioxide (CO_2) has caused many environmental problems, such as global warming due to its greenhouse effects, and reducing this concentration has become a global issue that must be addressed to achieve a sustainable society. Since CO_2 is safe, inexpensive, abundant, and renewable, it is a good candidate as a C1 synthon for various chemical reactions; the chemical transformation of CO_2 into industrially valuable compounds, such as urea, methanol, cyclic carbonates, poly(alkylene carbonate), and sodium 2–hydroxybenzoate, is a active field of research in CO_2 fixation and green chemistry.[1] Within this field, the most active area of research into CO_2 transformations is the coupling of CO_2 with epoxides to produce the corresponding cyclic carbonates, which can be used as aprotic solvents, electrolytes for lithium–ion batteries, monomers for polymerizations, and pharmaceutical intermediates.[2] To date, many catalytic systems, including metal–based catalysts and organocatalysts, for the synthesis of cyclic carbonates from CO_2 and epoxides have been developed.[3] Even though the synthesis of a cyclic carbonate from CO_2 and an epoxide is a thermodynamically favorable process, the industrial-scale syntheses of cyclic carbonates require high reaction temperatures and high CO_2 pressures to complete this reaction, and thus overall, this process consumes more energy that it releases and it is associated with additional, indirect CO_2 emissions.[4] Therefore, it is necessary to develop efficient catalytic systems for the synthesis of cyclic carbonates from CO_2 and epoxides that are effective under ambient temperature and pressure.

Several catalytic systems, including metal–based catalysts and organocatalysts for converting CO_2 into cyclic carbonates at room temperature and 1 bar CO_2, have been reported.[3,5] In particular, aluminum, the most abundant metal in the earth's crust (the metals are in the order Al, Fe, Ca, Na, K, Mg, and Ti), is a very attractive metal for this study due to its low cost, low toxicity and high Lewis acidity. However, only a few examples of efficient non–toxic catalysts with aluminum metal centers capable of operating at ambient temperature and 1 bar CO_2 are known (see Figure 1).[6] As

63 shown in Figure 1, styrene oxide is usually used as the model substrate for coupling reactions with
64 CO_2 because it has moderate reactivity relative to other epoxides along with lower toxicity and a
65 higher boiling point.[1a] However, non–toxic Al–based catalysts require catalyst loading (> 2.5
66 mol%) and a long reaction time (24 h) to reach a high conversion to styrene carbonate under ambient
67 conditions. Their catalytic activities are in the range of TON = 8.4–39.2 and TOF = 0.63–3.73 h^{-1},[6]
68 which are slightly higher than organocatalysts, but organocatalysts are among the least active
69 catalysts for the synthesis of cyclic carbonates under ambient conditions.[5] Thus, the development
70 of new, more active Al–based catalytic systems that allow lower catalyst loading (< 1.0 mol%) and
71 a high TON (> 100) under ambient conditions is needed.

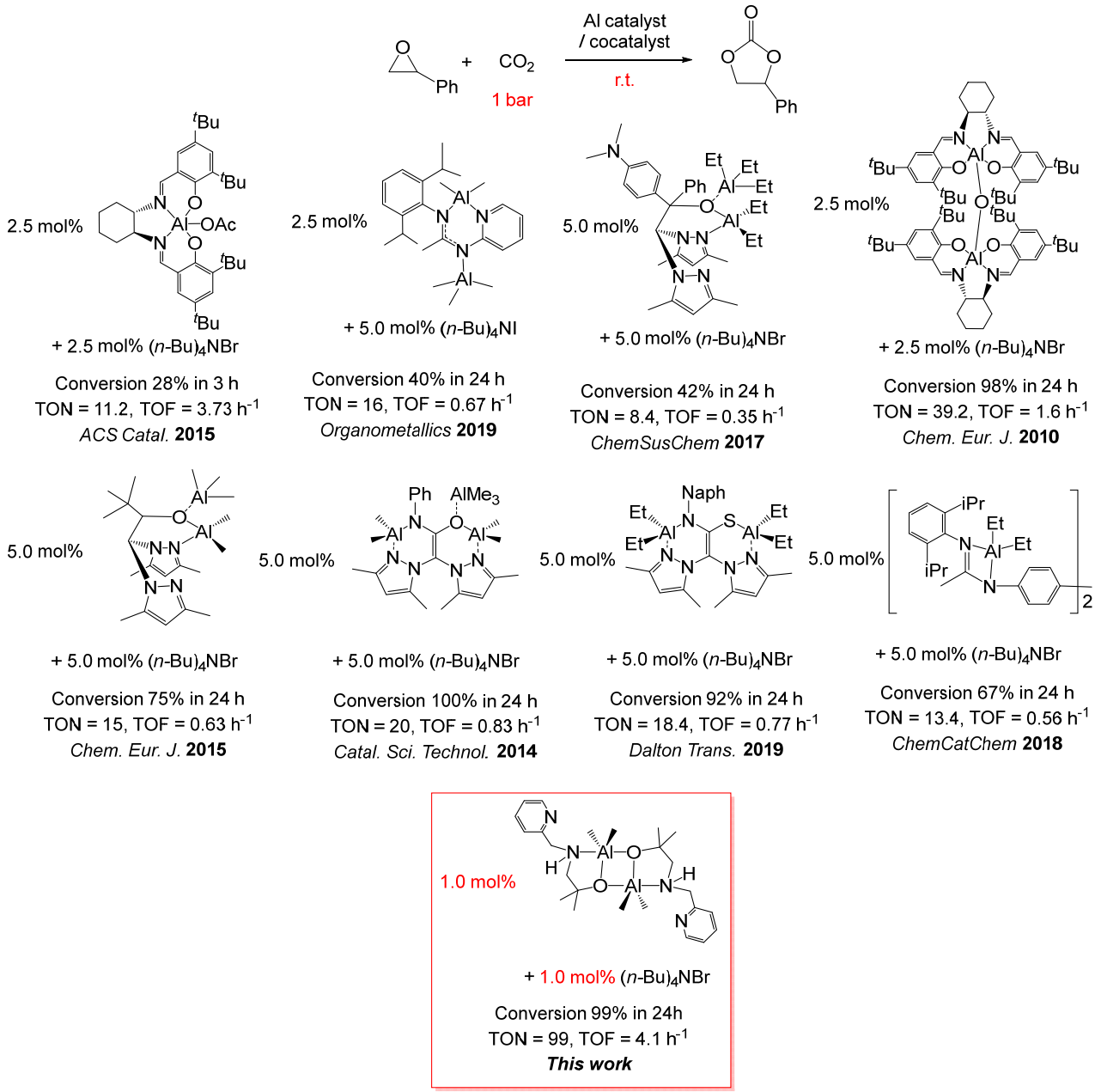
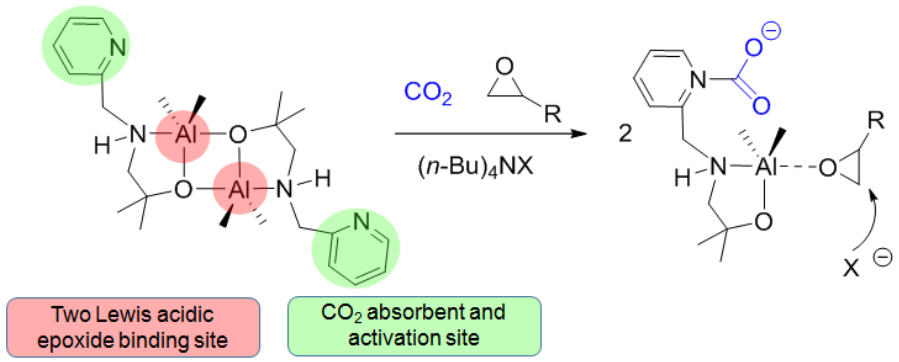


Figure 1. Representative Al–based catalysts for the synthesis of styrene carbonate at ambient temperature and 1 bar CO_2

Recently, we reported dimeric aluminum compounds containing ethanolateamine ligands with simple heteroatom sidechains, such as OMe and NMe_2, as catalysts for the coupling of CO_2 with propylene oxide in the presence of $(n\text{–Bu})_4NI$ with 0.1 mol% catalyst loading and 10 bar CO_2 at 70 °C.[7] We have demonstrated that the activities of the complexes are highly dependent on the nature of the substituent on the nitrogen atom; thus, their activities increased as the nucleophilicity of the sidechain increased (NMe_2 > OMe). These aluminum complexes also have a C_2 axis at the centroid of the plane of the Al_2O_2 ring, and we thought that these complexes would be good

candidates for efficient catalysts in the coupling of CO_2 with epoxides under ambient conditions if a basic residue could be introduced to increase the local concentration of CO_2 around the active center. Thus, we chose dimeric aluminum compounds with ethanolateamine ligands with pyridine or furyl groups instead of NMe_2 or OMe as model catalysts in this study. Some studies have shown that catalysts with pyridine or furyl heterocyclic side chains have improved catalytic activities and lifetimes and that the pyridine moieties could increase the local concentration of CO_2 around active centers. For example, a titanium bis(amidinate) catalyst with a pyridine sidechain showed a higher activity in the synthesis of isotactic polypropylene than the corresponding catalyst with NMe_2 arms.[8] In addition, chromium complexes containing bis(phosphanyl)amine with a donor group on the nitrogen of the ligand are more effective for ethylene trimerization and tetramerization and have longer catalytic lifetimes than those without a donor group on the nitrogen of the ligand.[9] Furthermore, pyridinemethanol, which can bind CO_2 to the N atom of pyridine, can be used as an organocatalyst for the coupling of epichlorohydrin with CO_2; however, benzyl alcohol did not show any catalytic activity under the same conditions.[10]

Herein, we report the synthesis of C_2–symmetric aluminum complexes chelated by substituted ethanolateamine bearing heterocyclic pendant moieties such as pyridin–2–yl (**Pyr**), furan–2–yl (**Fur**), and thiophen–2–yl (**Thio**) attached to the nitrogen atom (as shown in Figure 2) and their use as catalysts for coupling CO_2 and epoxides at ambient temperature and 1 bar CO_2. Their catalytic activities were then compared with those of the analogous species containing simple dimethylamino (**NMe2**) and methoxy (**OMe**) pendants attached to the nitrogen and with no sidechains (**H**) under the same reaction conditions.



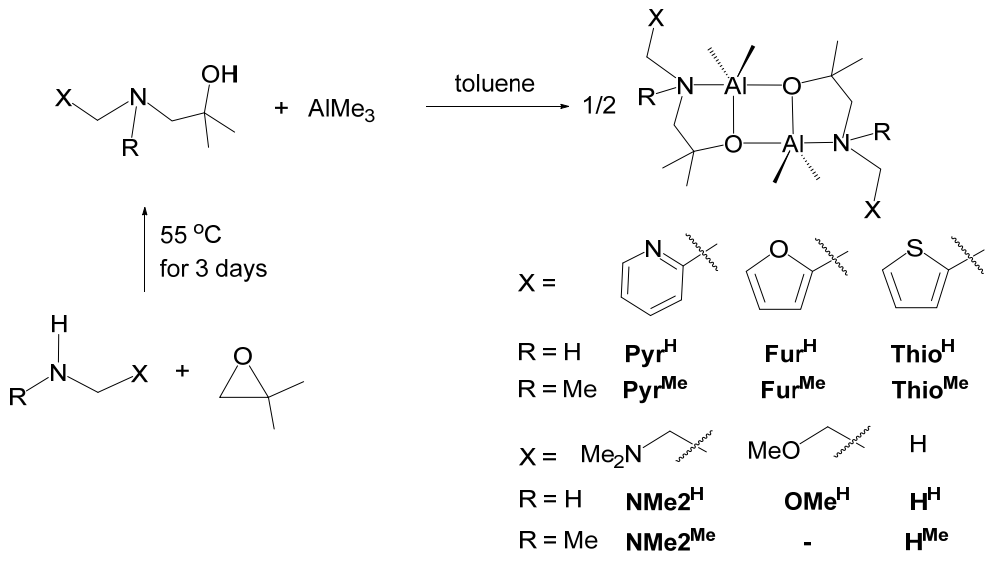
C_2-symmetric aluminum complexes as catalyst for cyclic carbonates

- ✓ pyridine substituent increasing local CO_2 concentration around Al center
- ✓ atmospheric CO_2 pressure
- ✓ room temperature
- ✓ broad substrate scope

Figure 2. Dimeric aluminum complexes were used as catalysts for the synthesis of cyclic carbonates in this study.

Results and Discussion

Synthesis and Characterization



Scheme 1. Synthetic routes for aluminum complexes. Each aluminum complex ($\mathbf{X^R}$) is abbreviated by using substituents X and R.

The free ligands, $HOCMe_2CH_2N(R)CH_2X$, were synthesized according to previously reported procedures[7] by the reaction of $RNHCH_2X$ with isobutylene oxide in almost quantitative yields. The alcoholysis of $AlMe_3$ is a useful synthetic route for accessing dimeric aluminum compounds $[Al(OCMe_2CH_2N(R)CH_2X)]_2$. In all cases, the aluminum complexes were prepared under an inert atmosphere. As depicted in Scheme 1, the direct complexation of *N*–substituted amino–2–

methylpropan–2–ol with $AlMe_3$ in toluene proceeds rapidly with the evolution of methane gas to give the eleven aluminum compounds in high yields (75–90%). The reaction temperature (0 °C) and time (12 h) were optimized to obtain the maximum yield of the aluminum compounds. The crude compounds were purified by washing with *n*–hexane, and analytically pure aluminum compounds were obtained as colorless crystals after recrystallization from toluene. They were not stable in air but were thermally stable even at 130 °C. Especially, aluminum complexes $\mathbf{Pyr^H}$ and $\mathbf{Pyr^{Me}}$ with a heterocyclic pendant attached to the nitrogen are much more thermally stable than $\mathbf{H^H}$ and $\mathbf{H^{Me}}$, which are the analogous aluminum complexes with no heterocyclic ring (See Supporting Information). As given in the Supporting Information, all the compounds were characterized by ^1H and ^{13}C NMR spectroscopy and by elemental analysis, and the structure of $\mathbf{Thio^H}$ was confirmed by single–crystal X–ray crystallography.

The ^1H and ^{13}C NMR spectra were consistent with the expected structures, and all the chemical shifts of the protons and carbon atoms were in the expected ranges. The ^1H NMR spectra of aluminum compounds $[Al(OCMe_2CH_2N(R)CH_2X)]_2$ did not differ significantly from those of free ligands $HOCMe_2CH_2N(R)CH_2X$. However, a strongly shielded resonance for Al–*Me* at approximately –1.0 ppm in the ^1H NMR spectrum and at approximately –6.0 ppm in the ^{13}C NMR spectrum confirmed the successful complexation of the ligand with the aluminum center. Interestingly, all the Al–*Me* resonances in $\mathbf{X^{Me}}$ complexes showed greater downfield shifts than those of the Al–*Me* resonances of the corresponding $\mathbf{X^H}$ complexes. Unlike complexes $\mathbf{X^{Me}}$, the –$OCMe_2C\mathit{H}_2NHC\mathit{H}_2$– methylene protons in $\mathbf{X^H}$ complexes were appeared as doublets due to the presence of a proton on the nitrogen atom.

10.1002/cssc.201901661

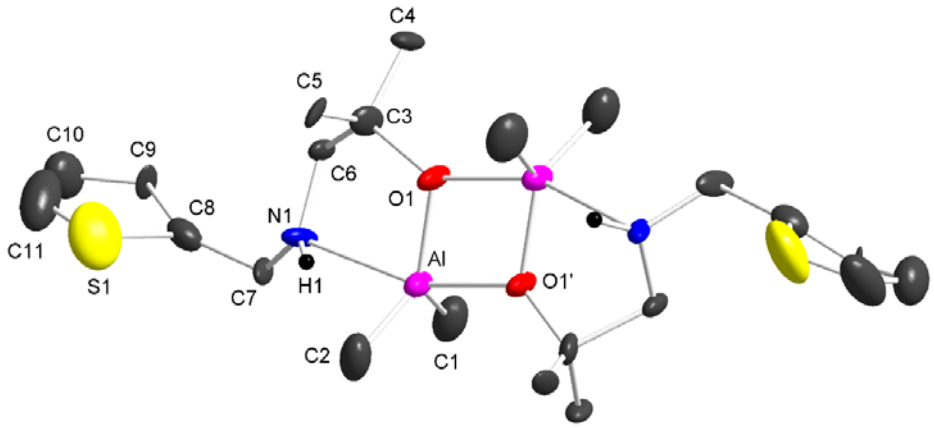
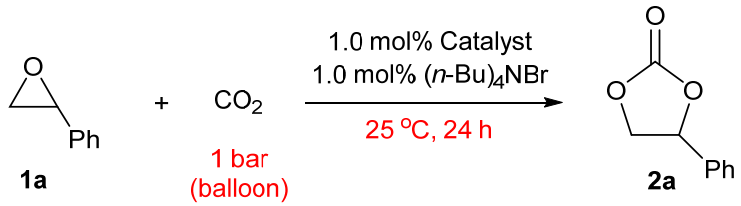


Figure 3. X–ray structure of **Thio^{H}** (50% thermal ellipsoids). For clarity, all H atoms are omitted except for H atom attached to the nitrogen.

The molecular structure of **Thio^{H}** was determined by single–crystal X–ray diffraction analysis. X–ray-quality crystals were obtained from an NMR tube containing **Thio^{H}** in $CDCl_3$ at room temperature. The crystallographic data and structure refinement details are summarized in Table S1 (Supporting Information), and the molecular structure is shown in Figure 3. As shown in Figure 3, *pseudo*–C_2 symmetric **Thio^{H}** contains a four–membered Al_2O_2 ring with a C_2 axis at the center of the ring. The two bridging O atoms link the two $AlMe_2$ moieties, and consequently, **Thio^{H}** is dimeric with two five–coordinate Al centers joined through two bridged oxygen atoms, O1 and O1′. Each of the aluminum centers in **Thio^{H}** is bound to one N, two O, and two C atoms of methyl groups. In particular, Figure 3 shows that the thiophene moiety is oriented away from the aluminum center and does not coordinate to the metal. Furthermore, there is no direct interaction between the two aluminum atoms. All Al–O, Al–N, and Al–C bond lengths are similar to those found in related pentacoordinate aluminum complexes.[11] The distortion of the coordination around the 5–coordinate Al metal center can be determined by the trigonality parameter, τ.[12] Since the largest bond angle (α) and the second largest angle (β) around the Al center are ∠N1–Al–O1′ [155.67(29)°] and ∠O1–Al–C2 [120.51(13)°], respectively, the trigonality parameter (τ = [α – β]/60) for **Thio^{H}** was calculated to be 0.59. Thus, the two aluminum centers in **Thio^{H}** have intermediate geometries between trigonal bipyramidal and square pyramidal.

Synthesis of cyclic carbonates



Scheme 2. Synthesis of styrene carbonate (**2a**) from styrene oxide (**1a**) by using aluminum catalysts.

As shown in Scheme 2, the synthesis of styrene carbonate (**2a**) from styrene oxide (**1a**) and CO_2 at 25 °C and 1 bar CO_2 without solvent for 24 h using 1 mol% (n–Bu)$_4$NBr and 1 mol% catalyst was chosen as the model reaction to screen the aluminum complexes given in Scheme 1. Each reaction was analyzed by ^{1}H NMR spectroscopy to determine the conversion of **1a** into **2a**. **1a** was easily converted into **2a** with high selectivity (> 99%) without any polymerized byproducts. The results are summarized in Table 1.

Table 1. Catalyst screening for the model reaction between CO_2 and styrene oxide (**1a**).[a]

Entry	Catalyst	Conversion[b] (%)	TON[c]	TOF[d] (h^{-1})
1	**Pyr^{H}**	99	99	4.1
2	**Pyr^{Me}**	90	90	3.8
3	**Fur^{H}**	76	76	3.2
4	**Fur^{Me}**	32	32	1.3
5	**Thio^{H}**	32	32	1.3
6	**Thio^{Me}**	27	27	1.1
7	**NMe2^{H}**	31	31	1.3
8	**NMe2^{Me}**	20	20	0.83
9	**OMe^{H}**	23	23	0.96
10	**H^{H}**	7	7	0.29
11	**H^{Me}**	5	5	0.21

[a] Reaction conditions: **1a** (10 mmol), catalyst (0.1 mmol, 1.0 mol%), (n–Bu)$_4$NBr (0.1 mmol, 1.0 mol%), r.t., 1 bar CO_2 (balloon), 24 h. [b] Conversion was determined by ^{1}H NMR spectroscopy of an aliquot of the reaction mixture after 24 h (see the Supporting Information). [c] Turnover number = (mol of **1a** consumed)/(mol of catalyst used). [d] Turnover frequency = TON/h.

The eleven synthesized aluminum complexes showed various catalytic activities for the synthesis of **2a** under ambient conditions. Among them, **Pyr^{H}** gave almost complete conversion of **1a** into **2a** at 1 atm of CO_2 and 25 °C after 24 h. Complex **Pyr^{H}** in the presence of (n–Bu)$_4$NBr showed the highest activity with a TON of 99 and TOF of 4.1 h^{-1} (Table 1, entry 1). Under the same conditions, **Pyr^{Me}**, which contained a sterically hindered methyl group instead of a hydrogen atom on the

nitrogen, showed a TON of 90 and a TOF of 3.8 h^{-1}, which are lower than those of **Pyr^{H}** (Table 1, entry 2). Similar trends were observed between **Fur^{H}** and **Fur^{Me}** (Table 1, entries 3 and 4) and between **Thio^{H}** and **Thio^{Me}** (Table 1, entries 5 and 6). Interestingly, the difference in activities between **Fur^{H}** and **Fur^{Me}** is much larger than that between **Pyr^{H}** and **Pyr^{Me}** and that between **Thio^{H}** and **Thio^{Me}**. Based on the heterocyclic pendant group attached to a nitrogen atom, we found that the activity decreases in the order pyridine > furan > thiophene (Table 1, entries 1, 3, and 5 and entries 2, 4, and 6). The best catalyst, **Pyr^{H}**, showed an activity 3.2 times higher than that of **NMe2^{H}** with dimethylamino pendant groups (Table 1, entry 7), 4.3 times higher than that of **OMe^{H}** with methoxy pendant groups (entry 9) and 14.1 times higher than that of **H^{H}** without *N*–substituents (entry 10). Similarly, **Pyr^{H}** was 4.9 times more active than **NMe2^{Me}** (Table 1, entry 8) and 19.8 times more active than **H^{Me}** (entry 11).

Table 2. Cocatalyst screening for the coupling of CO_2 with styrene oxide (**1a**) using **Pyr^{H}**.[a]

Entry	Cocatalyst	Conversion[b] (%)	TON[c]	TOF[d] (h^{-1})
1	(*n*–Bu)$_4$NCl	18	18	0.75
2	(*n*–Bu)$_4$NBr	99	99	4.1
3	(*n*–Bu)$_4$NI	77	77	3.2
4	(*n*–Bu)$_4$PBr	34	34	1.4
5	PPNCl	23	23	0.96
6	PPNBr	25	25	1.0
7	DMAP	3	3	0.13
8	MTBD	1	1	0.042

[a] Reaction conditions: **1a** (10 mmol), **Pyr^{H}** (0.1 mmol, 1.0 mol%), cocatalyst (0.1 mmol, 1.0 mol%), r.t., 1 bar CO_2 (balloon), 24 h. [b] Conversion was determined by ^{1}H NMR spectroscopy of an aliquot of the reaction mixture after 24 h (see the Supporting Information). [c] Turnover number = (mol of **1a** consumed)/(mol of **Pyr^{H}** used). [d] Turnover frequency = TON/h.

The reaction was further optimized and the effect of the cocatalyst on the coupling of CO_2 with styrene oxide (**1a**) was investigated by using the most active catalyst (**Pyr^{H}**) in conjunction with six different cocatalysts, namely, (*n*–Bu)$_4$NCl, (*n*–Bu)$_4$NBr, (*n*–Bu)$_4$NI, (*n*–Bu)$_4$PBr, PPNCl, and PPNBr (Table 2). As shown in entry 2 of Table 2, (*n*–Bu)$_4$NBr as a cocatalyst resulted in better activity than the other five compounds. The catalytic activity decreased in the order of Br > I > Cl for the tetrabutylammonium salts at 25 °C and 1 bar CO_2 (Table 2, entries 1–3). These results are in

good agreement with previous works,[6a,c–f] and our catalytic system also needed a balance between nucleophilicity and leaving-group ability. Phosphonium–based bromides such as (*n*–Bu)$_4$PBr was not as effective in this reaction as the corresponding ammonium–based cocatalyst such as (*n*–Bu)$_4$NBr (Table 2, entries 2 and 4). Sterically hindered phosphonium salts gave activities similar to that of (*n*–Bu)$_4$PBr (Table 2, entries 4–6). Non–halide cocatalysts such as dimethylaminopyridine (DMAP) (Table 2, entry 7) and 1,3,4,6,7,8-Hexahydro-1-methyl-2*H*-pyrimido[1,2-a]pyrimidine (MTBD) (entry 8) gave the trace amount of **1b** under the same condition. Since (*n*–Bu)$_4$NBr in conjunction with **Pyr^{H}** showed the highest activity, this pair was selected as the optimal cocatalyst system.

Table 3. Synthesis of styrene carbonate (**2a**) using **Pyr^{H}** and (*n*–Bu)$_4$NBr.[a]

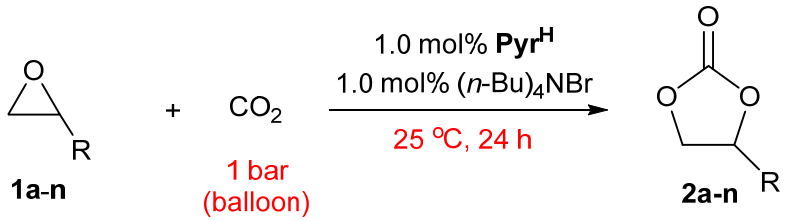
Entry	**Pyr^{H}** [mol%]	(*n*–Bu)$_4$NBr [mol%]	Conversion[b] [%]	TON[c]	TOF[d] [h^{-1}]
1	1.0	0	15	15	0.63
2	0	1.0	7	7	0.29
3	1.0	1.0	99	99	4.1
4	1.0	0.5	42	42	1.8
5	0.5	0.5	31	62	2.6
6	0.5	1.0	48	96	4.0
7	0.1	0.1	8	80	3.3
8	0.05	0.05	4	80	3.3

[a] Reaction conditions: **1a** (10 mmol), 25 °C, 1 bar CO_2 (balloon), and 24 h. [b] Conversion was determined by ^{1}H NMR spectroscopy of an aliquot of the reaction mixture after 24 h (see the Supporting Information). [c] Turnover number = (mol of **1a** consumed)/(mol of **Pyr^{H}** used). [d] Turnover frequency = TON/h.

The effect of reducing the catalyst loading in the coupling reaction of styrene oxide (**1a**) with 1 bar pressure of CO_2 at 25 °C with the best catalyst system (**Pyr^{H}**/(*n*–Bu)$_4$NBr) was investigated, and the results are shown in Table 3. Control experiments (Table 3, entries 1 and 2) showed that neither (*n*–Bu)$_4$NBr nor **Pyr^{H}** alone displayed significant catalytic activity with 15% and 7% conversion in the absence of the other catalyst component under the same reaction conditions, and this is a further demonstration of the synergistic effect of using **Pyr^{H}** with (*n*–Bu)$_4$NBr. When 1.0 mol% **Pyr^{H}** and 1.0 mol% (*n*–Bu)$_4$NBr loading was used at 25 °C, the reaction was complete (99%) within 24 h (Table 3, entry 3). In addition, when the **Pyr^{H}** loading was reduced from 1.0 mol% to 0.5 mol% to

0.1 mol% to 0.05 mol% while keeping a **Pyr^{H}** to (n–Bu)$_4$NBr ratio of 1:1, the yield of styrene carbonate gradually decreased from 99% to 31% to 8% to 4%, respectively (Table 3, entries 3, 5, 7, and 8). A 2:1 ratio of **Pyr^{H}** to (n–Bu)$_4$NBr showed a half reduction in the yield of **2a** (Table 3, entry 4). Increasing the ratio of catalyst to cocatalyst from 1:1 to 1:2 increased the yield of styrene carbonate (Table 3, entries 5 and 6). At least 1 mol% **Pyr^{H}** and 1 mol% (n–Bu)$_4$NBr should be used when screening epoxides at 25 °C and 1 bar CO_2 for 24 h.

Table 4. Synthesis of **2a**–**n** from epoxides **1a**–**n** using **Pyr^{H}** and (n–Bu)$_4$NBr.[a]



1, **2**: **a**, R = Ph; **b**, R = Me; **c**, R = Et; **d**, R = Bu; **e**, R = C_8H_{17}; **f**, R = $C_{10}H_{21}$; **g**, R = CH_2OMe; **h**, R = CH_2OPh; **i**, R = CH_2O^tBu; **j**, R = CH_2Cl; **k**, R = CH_2Br; **l**, R = 4-F-C_6H_4; **m**, R = 4-Cl-C_6H_4; **n**, R = 4-Br-C_6H_4

Entry	substrate	Conversion[c] [%]	Yield[d] [%]	TON[e]	TOF[f] [h^{-1}]
1	**1a**	99	97	99	4.1
2	**1b**	99	93	99	4.1
3	**1c**	99	99	99	4.1
4	**1d**	99	98	99	4.1
5	**1e**	67	65	67	2.8
6	**1f**	56	53	56	2.3
7	**1g**	98	95	98	4.1
8	**1h**	94	92	94	3.9
9	**1i**	94	90	94	3.9
10[b]	**1j**	99	98	99	8.3
11[b]	**1k**	99	97	99	8.3
12	**1l**	99	96	99	4.1
13	**1m**	99	97	99	4.1
14	**1n**	95	91	95	4.0

[a] Reaction conditions: epoxides (10 mmol), **Pyr^{H}** (0.1 mmol, 1.0 mol%), (n–Bu)$_4$NBr (0.1 mmol, 1.0 mol%), 25 °C, 1 bar CO_2 (balloon), and 24 h. [b] 12h. [c] Conversion was determined by ^{1}H NMR spectroscopy of an aliquot of the reaction mixture after 24 h (see the Supporting Information). [d] isolated yield. [e] Turnover number = (mol of **1a** consumed)/(mol of **Pyr^{H}** used). [f] Turnover frequency = TON/h.

We next investigated the substrate scope using 1.0 mol% **Pyr^{H}** and 1.0 mol% (n–Bu)$_4$NBr at 25 °C and 1 bar CO_2 for 24 h, and the results are shown in Table 4. The tested substrates were fourteen

terminal epoxides, namely, styrene oxide (**1a**), propylene oxide (**1b**), 1,2–epoxybutane (**1c**), 1,2–epoxyhexane (**1d**), 1,2–epoxydecane (**1e**), 1,2–epoxydodecane (**1f**), 1,2–epoxy–3–methoxypropane (**1g**), 1,2–epoxy–3–phenoxypropane (**1h**), *tert*–butyl glycidyl ether (**1i**), epichlorohydrin (**1j**), epibromohydrin (**1k**), 2-(4-fluorophenyl)oxirane (**1l**), 2-(4-chlorophenyl)oxirane (**1m**), and 2-(4-bromophenyl)oxirane (**1n**). In all cases except for **1e** and **1f**, excellent isolated yields (> 90%) and conversions (> 94%) of these substrates into the corresponding cyclic carbonates were obtained. The fact that epoxides **1a**–**1d** showed complete conversion within 24 h means that the chain length and steric hindrance from the substituents on the epoxides did not affect the catalytic activity (Table 4, entries 1–4). However, long and straight octyl and decyl substituents on the epoxides reduced the conversion (Table 4, entries 5 and 6). Although **Pyr^{H}**/(*n*–Bu)$_4$NBr still showed high activity for **1e**–**1g**, the presence of a heteroatom in the substituent on the epoxide and steric hindrance from the substituents resulted in a slight decrease in activity because heteroatoms in the epoxide substrate may bind to the aluminum center (Table 4, entries 7–9). As expected, very reactive epichlorohydrin (**1j**) and epibromohydrin (**1k**) showed the complete conversion within 12 h (Table 4, entries 10 and 11). In addition, other epoxides containing halogens and aromatic halogens showed the excellent catalytic activities (Table 4, entries 10–14).

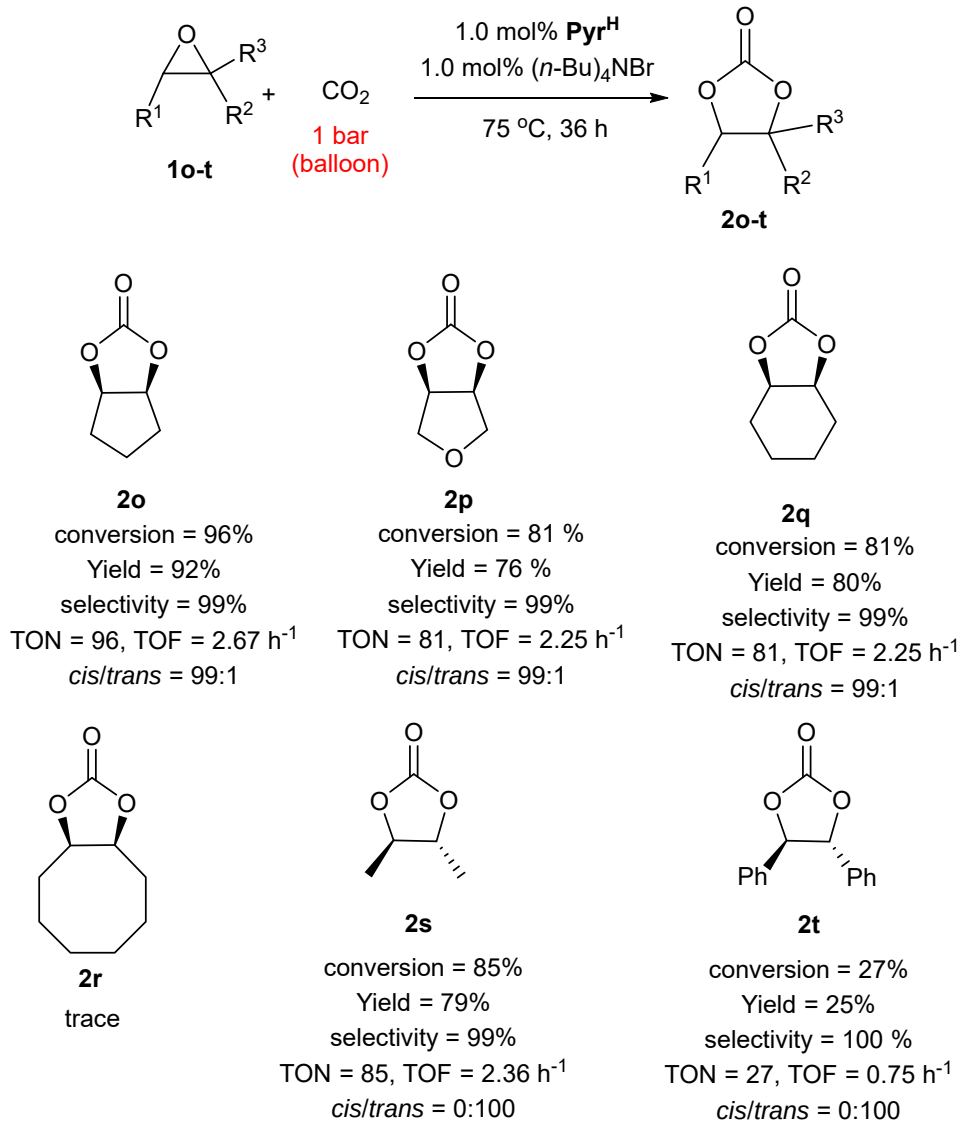
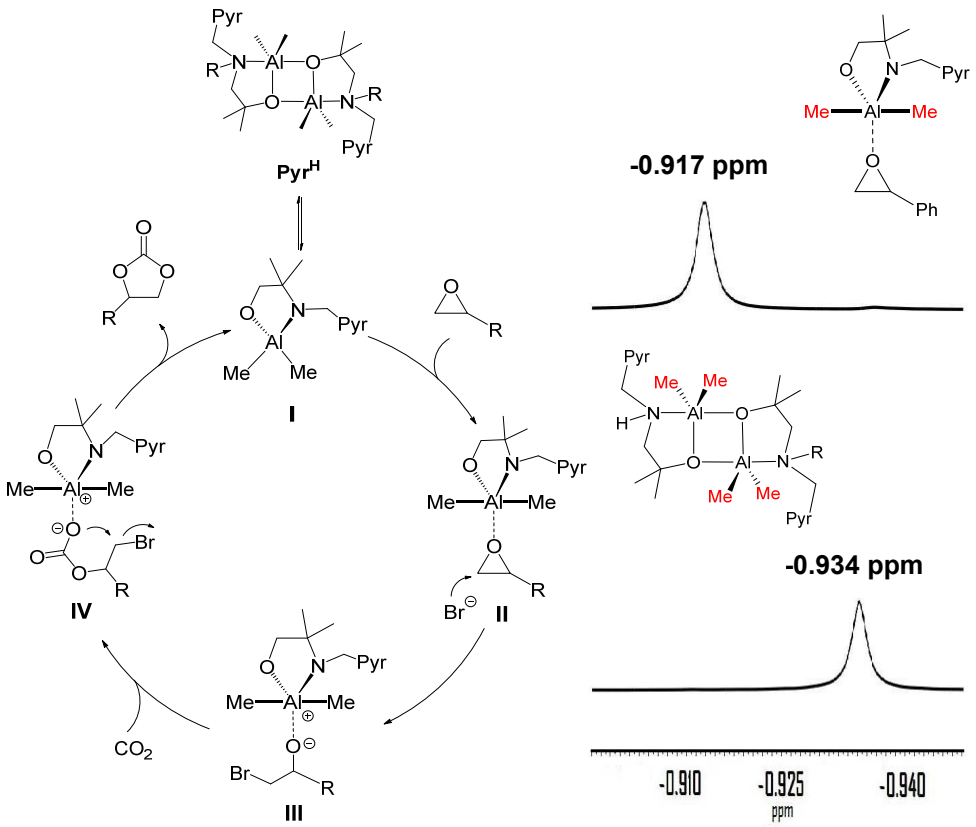


Figure 4. Synthesis of cyclic carbonates **2o**–**t** from epoxides **1o**–**t** and CO_2 catalyzed by **Pyr^H** and (n–Bu)$_4$NBr.

We also investigated the synthesis of more challenging cyclic carbonates using internal epoxides such as *cis*–cyclopentene oxide (**1o**), *cis*–3,4–epoxytetrahydrofuran (**1p**), *cis*–cyclohexene oxide (**1q**), *cis*–cyclooctene oxide (**1r**), *trans*–2,3–butylene oxide (**1s**), and *trans*–stilbene oxide(**1t**) to elucidate the mechanism of this reaction, and the results are shown in Figure 4. The coupling reactions were performed at 75 °C and 1 bar CO_2 over 36 h using 1.0 mol% **Pyr^H**/(n–Bu)$_4$NBr. Internal epoxides **1o**–**t** were all converted to the corresponding cyclic carbonates without any polymeric side products (selectivity > 99%). Epoxide **1o**, with a five–membered ring, was more reactive than epoxides with heteroatom (**1p**) and six–membered ring (**2q**). Eight–membered ring

system (**1r**) did not show any catalytic activity. The steric hindrance of the substituents from methyl (**1s**) to phenyl (**1t**) resulted in a dramatic decrease in activity. We found the retention of the stereochemistry of all starting epoxides were observed. As expected, the cyclic carbonates obtained from 1,2–disubstituted epoxides showed configurational retention from two consecutive S_N2 reactions. This means that two stereochemical inversions occur at the carbon atom of the epoxide during the reaction. Thus, a plausible mechanism for the synthesis of the cyclic carbonates from epoxides and CO_2 by using **Pyr^H** in the presence of (n–Bu)$_4$NBr as a cocatalyst is shown in Figure 5. This mechanism is similar to the mechanism previously proposed for the synthesis of cyclic carbonates using other catalyst systems.



(a) (b)

Figure 5. (a) A plausible mechanism for the synthesis of cyclic carbonates from epoxides and CO_2 by using **Pyr^H** in the presence of (n–Bu)$_4$NBr. (b) The chemical shift of Al–Me in **Pyr^H** in the ^{1}H NMR spectrum before (down) and after (up) adding 2 equivalents of styrene oxide in $CDCl_3$.

The dimeric five–coordinate complex **Pyr^{H}** becomes monomeric four–coordinate intermediate **I,** and then the epoxide attaches to the Al atom of intermediate **I**, and resulting five–coordinate complex **II** is activated by the bromide anion of the cocatalyst. The nucleophilic ring opening of the epoxide gives carbonato species **III**, which is converted into coordinated Al complex **IV** by the insertion of CO_2. Finally, cyclic carbonate as the final product and regenerated intermediate **I** are produced. The ^{1}H NMR spectra of **Pyr^{H}** with and without styrene oxide clearly confirm the existence of intermediate **I**. A clear downfield shift in the signal of Al–Me of **Pyr^{H}** from –0.934 ppm to –0.917 ppm was observed, indicating that the epoxide binds to the Al metal center to generate intermediate **I**.

CONCLUSION

In conclusion, we developed one of the most effective aluminum catalysts to date for the generation of cyclic carbonates via the coupling of epoxides and CO_2 under ambient temperature and CO_2 pressure. Aluminum complexes **X^{R}** (X = **Pyr**, **Fur, Thio**; R = H, Me) chelated by substituted ethanolateamine ligands bearing heterocyclic pendant moieties such as pyridin–2–yl (**Pyr**), furan–2–yl (**Fur**), and thiophen–2–yl (**Thio**) on the nitrogen atom were rationally designed. Among these complexes, the solid-state structure of **Thio^{H}** was determined by single–crystal X–ray diffraction analysis, and *pseudo–C*$_2$ symmetric dimeric **Thio^{H}** contains a four–membered Al_2O_2 ring with a C_2 axis at the center of the ring. All the aluminum complexes were used as catalysts for the coupling of CO_2 with epoxides, and among the eleven catalysts, complex **Pyr^{H}** showed the highest activity for the synthesis of styrene carbonate with a TON of 99 and TOF of 4.1 h^{-1} at room temperature and 1 bar CO_2. The best catalyst, **Pyr^{H}**, showed 3.2 times higher activity than **NMe2^{H}** with dimethylamino pendant groups, 4.3 times higher activity than **OMe^{H}** with methoxy pendant groups and 14.1 times higher activity than **H^{H}** without nitrogen substituents with fixed catalyst and (*n*–Bu)$_4$NBr loading (both at 1.0 mol%), a reaction temperature of 25 °C, 1 bar CO_2, and a reaction time of 24 h. In addition, the **Pyr^{H}**/(*n*–Bu)$_4$NBr catalytic system was highly effective for forming

cyclic carbonates with a wide range of terminal and internal epoxides. In particular, the cyclic carbonates obtained from 1,2–disubstituted epoxides showed configurational retention indicative of two consecutive S_N2 reactions.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a dry, inert atmosphere in a glovebox or with a dual–manifold Schlenk line using the appropriate techniques for conducting air-sensitive reactions under a nitrogen atmosphere.[13] Nitrogen was deoxygenated with an activated Cu catalyst and dried with Drierite.[14] All chemicals were purchased from commercial sources (purity > 95%) and used as received unless otherwise indicated. Toluene and *n*–hexane were purified by a Grubbs solvent purification system under a nitrogen atmosphere and stored over activated molecular sieves (4 Å).[15] Carbon dioxide (99.999%) was used as received without further purification. All epoxides were purified by treatment with calcium hydride to remove residual water. $CDCl_3$ was dried with activated molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature with a Bruker DPX–500 MHz NMR spectrometer with standard parameters. All chemical shifts are reported in δ units referenced to the residual $CDCl_3$ (δ 7.24 for ^{1}H NMR; δ 77.00 for ^{13}C NMR). Elemental analyses were performed with an EA 1110–FISONS analyzer. High–resolution mass spectrometry (HRMS) data were acquired on a high–resolution Q–TOF mass spectrometer (ionization mode: ESI).

Synthesis. Ligands *N*–methyl–1–(pyridin–2–yl)methanamine,[16] 1–(furan–2–yl)–*N*–methylmethanamine,[17] *N*–methyl–1–(thiophen–2–yl)methanamine,[17] 1–((2–(dimethylamino)ethyl)(methyl)amino)–2–methylpropan–2–ol,[18] and 2–methyl–1–(methylamino)propan–2–ol[19] and aluminum complexes **NMe2^{H}**,[7] **OMe^{H}**,[7] and **H^{Me}**[20] were prepared by literature procedures.

Synthesis of 2–methyl–1–((pyridin–2–ylmethyl)amino)propan–2–ol. Isobutylene oxide (0.72 g, 10 mmol) and pyridin–2–ylmethaneamine (1.08 g, 10 mmol) were added to a 25-mL screw cap vial containing a stirring bar. The vial was tightly sealed with Teflon tape and paraffin film. The mixture was maintained at room temperature overnight and was then heated for 3 days at 55 °C. The removal of the volatile compounds at reduced pressure gave the desired product as a colorless oil (80%, 1.44 g). ^{1}H NMR ($CDCl_3$): δ 8.47 (m, 1H, pyridine–*H*), 7.57 (m, 1H, pyridine–*H*), 7.20 (m, 1H, pyridine–*H*), 7.08 (m, 1H, pyridine–*H*), 3.88 (s, 2H, –$CMe_2CH_2NHCH_2$–), 2.51 (s, 2H, –$CMe_2CH_2NHCH_2$–), 1.11 (s, 6H, –$CMe_2CH_2NHCH_2$–). ^{13}C NMR ($CDCl_3$): δ 159.6, 149.1, 136.4, 122.1, 121.9 (pyridine), 69.28 (–$CMe_2CH_2NHCH_2$–), 59.92 (–$CMe_2CH_2NHCH_2$–), 55.52 (–$CMe_2CH_2NHCH_2$–), 27.27 (–$CMe_2CH_2NHCH_2$–). HRMS *m/z* calcd for [$C_{10}H_{16}N_2O$ + H] 181.1341. Found: 181.1335.

Synthesis of 1–((furan–2–ylmethyl)amino)–2–methylpropan–2–ol. In a manner analogous to that used in the synthesis of 2–methyl–1–((pyridin–2–ylmethyl)amino)propan–2–ol, 1–((furan–2–ylmethyl)amino)–2–methylpropan–2–ol was prepared from furan–2–ylmethanamine (0.97 g, 10 mmol) and isobutylene oxide (0.72 g, 10 mmol) in a yield of 83% (1.40 g). ^{1}H NMR ($CDCl_3$): δ 7.26 (q, 1H, J = 1.0 Hz, furan–*H*), 6.21 (q, 1H, J = 2.0 Hz, furan–*H*), 6.07 (dd, 1H, J_1 = 4.0 Hz, J_2 = 0.5 Hz, furan–*H*), 3.72 (s, 2H, –$CMe_2CH_2NHCH_2$–), 2.44 (s, 2H, –$CMe_2CH_2NHCH_2$–), 1.08 (s, 6H, –$CMe_2CH_2NHCH_2$–). ^{13}C NMR ($CDCl_3$): δ 153.9, 141.5, 109.9, 106.5 (furan), 69.18 (–$CMe_2CH_2NHCH_2$–), 59.33 (–$CMe_2CH_2NHCH_2$–), 46.58 (–$CMe_2CH_2NHCH_2$–), 27.13 (–$CMe_2CH_2NHCH_2$–). HRMS *m/z* calcd for [$C_9H_{15}NO_2$ + H] 170.1181. Found: 170.1176.

Synthesis of 2–methyl–1–((thiophen–2–ylmethyl)amino)propan–2–ol. In a manner analogous to that used in the synthesis of 2–methyl–1–((pyridin–2–ylmethyl)amino)propan–2–ol, 2–methyl–1–((thiophen–2–ylmethyl)amino)propan–2–ol was prepared from thiophen–2–ylmethanamine (1.13 g, 10 mmol) and isobutylene oxide (0.72 g, 10 mmol) in a yield of 83% (1.54 g). ^{1}H NMR ($CDCl_3$): δ 7.19 (dd, 1H, J_1 = 6.0 Hz, J_2 = 1.5 Hz, thiophene–*H*), 6.93 (m, 1H, thiophene–*H*), 6.90 (m, 1H, thiophene–*H*), 4.02 (d, 2H, J = 1.0 Hz,–$CMe_2CH_2NHCH_2$–), 2.57 (s, 2H, –$CMe_2CH_2NHCH_2$–),

1.16 (s, 6H, –C*Me*$_2$CH$_2$NHCH$_2$–). ^{13}C NMR ($CDCl_3$): δ 144.2, 126.5, 124.6, 124.3 (thiophene), 69.30 (–CMe$_2$CH$_2$NH*C*H$_2$–), 59.34 (–CMe$_2$*C*H$_2$NHCH$_2$–), 48.87 (–*C*Me$_2$CH$_2$NHCH$_2$–), 27.25 (–C*Me*$_2$CH$_2$NHCH$_2$–). HRMS *m/z* calcd for [$C_9H_{15}NOS$ + H] 186.0953. Found: 186.0948.

Synthesis of 2–methyl–1–(methyl(pyridin–2–ylmethyl)amino)propan–2–ol. In a manner analogous to that used in the synthesis of 2–methyl–1–((pyridin–2–ylmethyl)amino)propan–2–ol, 2–methyl–1–(methyl(pyridin–2–ylmethyl)amino)propan–2–ol was prepared from *N*–methyl–1–(pyridin–2–yl)methanamine (1.22 g, 10 mmol) and isobutylene oxide (0.72 g, 10 mmol) in a yield of 90% (1.75 g). ^{1}H NMR ($CDCl_3$): δ 8.51 (m, 1H, pyridine–*H*), 7.62 (m, 1H, pyridine–*H*), 7.28 (m, 1H, pyridine–*H*), 7.12 (m, 1H, pyridine–*H*), 3.80 (s, 2H, –CMe$_2$CH$_2$NMeC*H*$_2$–), 2.50 (s, 2H, –CMe$_2$C*H*$_2$NMeCH$_2$–), 2.39 (s, 3H, –CMe$_2$CH$_2$N*Me*CH$_2$–), 1.14 (s, 6H, –C*Me*$_2$CH$_2$NMeCH$_2$–). ^{13}C NMR ($CDCl_3$): δ 159.5, 149.1, 136.5, 122.6, 122.1 (pyridine), 70.28 (–CMe$_2$CH$_2$N*Me*CH$_2$–), 68.47 (–CMe$_2$CH$_2$NMe*C*H$_2$–), 65.51 (–CMe$_2$*C*H$_2$NMeCH$_2$–), 45.61 (–*C*Me$_2$CH$_2$NMeCH$_2$–), 27.84 (–C*Me*$_2$CH$_2$NMeCH$_2$–). HRMS *m/z* calcd for [$C_{11}H_{18}N_2O$ + H] 195.1497. Found: 195.1492.

Synthesis of 1–((furan–2–ylmethyl)(methyl)amino)–2–methylpropan–2–ol. In a manner analogous to that used in the synthesis of 2–methyl–1–((pyridin–2–ylmethyl)amino)propan–2–ol, 1–((furan–2–ylmethyl)(methyl)amino)–2–methylpropan–2–ol was prepared from 1–(furan–2–yl)–*N*–methylmethanamine (1.11 g, 10 mmol) and isobutylene oxide (0.72 g, 10 mmol) in a yield of 94% (1.72 g). ^{1}H NMR ($CDCl_3$): δ 7.35 (q, 1H, J = 1.0 Hz, furan–*H*), 6.29 (m, 1H, furan–*H*), 6.17 (m, 1H, furan–*H*), 3.65 (s, 2H, –CMe$_2$CH$_2$NMeC*H*$_2$–), 3.20 (s, 1H, *H*OCMe$_2$CH$_2$NMeCH$_2$–), 2.42 (s, 2H, –CMe$_2$C*H*$_2$NMeCH$_2$–), 2.38 (s, 3H, –CMe$_2$CH$_2$N*Me*CH$_2$–), 1.15 (s, 6H, –C*Me*$_2$CH$_2$NMeCH$_2$–). ^{13}C NMR ($CDCl_3$): δ 152.9, 142.2, 110.1, 108.5 (furan), 70.12 (–CMe$_2$CH$_2$N*Me*CH$_2$–), 67.18 (–CMe$_2$CH$_2$NMe*C*H$_2$–), 56.18 (–CMe$_2$*C*H$_2$NMeCH$_2$–), 45.26 (–*C*Me$_2$CH$_2$NHCH$_2$–), 27.97 (–C*Me*$_2$CH$_2$NHCH$_2$–). HRMS *m/z* calcd for [$C_{10}H_{17}NO_2$ + H] 184.1338. Found: 184.1332.

Synthesis of 2–methyl–1–(methyl(thiophen–2–ylmethyl)amino)propan–2–ol. In a manner

analogous to that used in the synthesis of 2–methyl–1–((pyridin–2–ylmethyl)amino)propan–2–ol, 2–methyl–1–(methyl(thiophen–2–ylmethyl)amino)propan–2–ol was prepared from *N*–methyl–1–(thiophen–2–yl)methanamine (1.27 g, 10 mmol) and isobutylene oxide (0.72 g, 10 mmol) in a yield of 95% (1.89 g). ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 1H, thiophene–*H*), 6.93 (m, 1H, thiophene–*H*), 6.87 (m, 1H, thiophene–*H*), 3.83 (s, 2H, –$CMe_2CH_2NMeCH_2$–), 2.44 (s, 2H, $CMe_2CH_2NMeCH_2$), 2.36 (s, 3H, –$CMe_2CH_2NMeCH_2$–), 1.17 (s, 6H, –$CMe_2CH_2NMeCH_2$–). ^{13}C NMR ($CDCl_3$): δ 142.6, 126.4, 125.7, 124.7 (thiophene), 70.03 (–$CMe_2CH_2NMeCH_2$–), 67.43 (–$CMe_2CH_2NMeCH_2$–), 58.60 (–$CMe_2CH_2NMeCH_2$–), 44.68 (–$CMe_2CH_2NHCH_2$–), 27.79 (–$CMe_2CH_2NHCH_2$–). HRMS *m/z* calcd for [$C_{10}H_{17}NOS$ + H] 200.1109. Found: 200.1104.

Synthesis of [$Me_2Al(OCMe_2CH_2NHCH_2(C_5H_4N))]_2$ (Pyr^H). $AlMe_3$ (1.0 mL of 2.0 M solution in toluene, 2.0 mmol) was added to a stirred solution of 2–methyl–1–((pyridin–2–ylmethyl)amino)propan–2–ol (0.36 g, 2.0 mmol) in toluene at 0 °C. The mixture was warmed to room temperature and stirred overnight. The residue, which was obtained by removing the solvent under vacuum, was washed with *n*–hexane and recrystallized from toluene. The desired product, $\mathbf{Pyr^H}$, was isolated as colorless crystals after the solution had been stored at –20 °C in a freezer for a few days (80%, 0.47 g). ^{1}H NMR ($CDCl_3$): δ 8.56 (m, 2H, pyridine–*H*), 7.62 (m, 2H, pyridine–*H*), 7.17 (m, 4H, pyridine–*H*), 3.80 (d, J = 6.5 Hz, 4H, pyridine–CH_2N–), 2.37 (d, 4H, J = 8.6 Hz, –CH_2CMe_2–), 1.24 (s, 12H, –CMe_2–), –0.93 (s, 12H, Al–*Me*). ^{13}C NMR ($CDCl_3$): δ 157.3, 149.7, 136.5, 122.8, 122.3 (pyridine), 70.36 (–CMe_2O–), 59.83 (pyridine–CH_2N–), 52.38 (–CH_2CMe_2–), 27.64 (–CMe_2O–), –5.98 (Al–*Me*). Anal. Calcd for $C_{24}H_{42}N_4O_2Al_2$: C, 61.00; H, 8.96; N, 11.86. Found: C, 60.97; H, 8.94; N, 12.05.

Synthesis of [$Me_2Al(OCMe_2CH_2N(Me)CH_2(C_5H_4N))]_2$ (Pyr^{Me}). In a manner analogous to that used in the synthesis of $\mathbf{Pyr^H}$, desired product $\mathbf{Pyr^{Me}}$ was prepared as colorless crystals from a solution of $AlMe_3$ (1.0 mL of 2.0 M solution in toluene, 2.0 mmol) and 2–methyl–1–(methyl(pyridin–2–ylmethyl)amino)propan–2–ol (0.39 g, 2.0 mmol) in toluene in a yield of 75%

(0.38 g). ^{1}H NMR ($CDCl_3$): δ 8.49 (d, 2H, J = 4.3 Hz, pyridine–*H*), 7.56 (m, 2H, pyridine–*H*), 7.23 (d, 2H, J = 7.7 Hz, pyridine–*H*), 7.10 (m, 2H, pyridine–*H*), 3.77 (s, 4H, pyridine–C*H*$_2$N–), 2.59 (s, 4H, –C*H*$_2$CMe$_2$–), 2.19 (s, 6H, N–*Me*), 1.23 (s, 12H, –C*Me*$_2$–), –0.87 (s, 12H, Al–*Me*). ^{13}C NMR ($CDCl_3$): δ 156.9, 149.2, 136.2, 124.5, 122.3 (pyridine), 72.98 (–*C*Me$_2$O–), 67.20 (pyridine–*C*H$_2$N–), 64.41 (–*C*H$_2$CMe$_2$–), 43.89 (N–*Me*), 30.68 (–C*Me*$_2$O–), –5.95 (Al–*Me*). Anal. Calcd for $C_{26}H_{46}N_4O_2Al_2$: C, 62.38; H, 9.26; N, 11.19. Found: C, Found: C, 62.37; H, 9.32; N, 11.07.

Synthesis of [Me$_2$Al(OCMe$_2$CH$_2$NHCH$_2$(C$_4$H$_3$O))]$_2$ (Fur^{H}). In a manner analogous to that used in the synthesis of **Pyr^{H}**, desired product **Fur^{H}** was prepared as colorless crystals from a solution of $AlMe_3$ (1.0 mL of 2.0 M solution in toluene, 2.0 mmol) and 1–((furan–2–ylmethyl)amino)–2–methylpropan–2–ol (0.34 g, 2.0 mmol) in toluene in a yield of 87% (0.39 g). ^{1}H NMR ($CDCl_3$): δ 7.37 (m, 2H, furan–*H*), 6.32 (m, 2H, furan–*H*), 6.19 (d, 2H, J = 3.2 Hz, furan–*H*), 3.72 (d, 4H, J = 7 Hz, furan–C*H*$_2$N–), 2.40 (d, 4H, J = 8.8 Hz, –C*H*$_2$CMe$_2$–), 2.09 (t, 2H, J = 7.5 Hz, –NH–), 1.21 (s, 12H, –C*Me*$_2$–), –0.96 (s, 12H, –Al–*Me*). ^{13}C NMR ($CDCl_3$): δ 151.8, 142.5, 110.3, 108.3 (furan), 70.39 (–*C*Me$_2$O–), 59.42 (furan–*C*H$_2$NH–), 44.16 (–*C*H$_2$CMe$_2$–), 27.63 (–C*Me*$_2$O–), –6.16 (Al–*Me*). Anal. Calcd for $C_{22}H_{40}N_2O_4Al_2$: C, 58.65; H, 8.95; N 6.22. Found: C, 58.42; H, 9.08; N, 6.17.

Synthesis of [Me$_2$Al(OCMe$_2$CH$_2$N(Me)CH$_2$(C$_4$H$_3$O))]$_2$ (Fur^{Me}). In a manner analogous to that used in the synthesis of **Pyr^{H}**, desired product **Fur^{Me}** was prepared as colorless crystals from a solution of $AlMe_3$ (1.0 mL of 2.0 M solution in toluene, 2.0 mmol) and 1–((furan–2–ylmethyl)(methyl)amino)–2–methylpropan–2–ol (0.37 g, 2.0 mmol) in toluene in a yield of 90% (0.43 g). ^{1}H NMR ($CDCl_3$): δ 7.39 (m, 2H, furan–*H*), 6.34 (m, 2H, furan–*H*), 6.23 (d, 2H, J = 3.1 Hz, furan–*H*), 3.73 (s, 4H, furan–C*H*$_2$N–), 2.51 (s, 4H, –C*H*$_2$CMe$_2$–), 2.24 (s, 6H, N–*Me*), 1.32 (s, 12H, –C*Me*$_2$–), –0.83 (s, 12H, Al–*Me*). ^{13}C NMR ($CDCl_3$): δ 150.0, 142.5, 110.6, 110.2 (furan), 70.83 (–*C*Me$_2$O–), 65.90 (furan–*C*H$_2$N–), 53.48 (–*C*H$_2$CMe$_2$–), 43.27 (N–*Me*), 31.58 (–C*Me*$_2$O–), –6.22 (Al–*Me*). Anal. Calcd for $C_{24}H_{44}N_2O_4Al_2$: C, 60.23; H, 9.27; N, 5.85. Found: C, 60.34; H, 9.13; N, 5.81.

Synthesis of [$Me_2Al(OCMe_2CH_2NHCH_2(C_4H_3S))]_2$ ($Thio^H$). In a manner analogous to that used in the synthesis of Pyr^H, desired product $Thio^H$ was prepared as colorless crystals from a solution of $AlMe_3$ (1.0 mL of 2.0 M solution in toluene, 2.0 mmol) and 2–methyl–1–((thiophen–2–ylmethyl)amino)propan–2–ol (0.37 g, 2.0 mmol) in toluene in a yield of 89% (0.43 g). ^{1}H NMR ($CDCl_3$): δ 7.24 (m, thiophene–*H*), 6.98 (m, 2H, thiophene–*H*), 6.92 (d, 2H, J = 2.8 Hz, thiophene–*H*), 3.92 (d, 4H, J = 6.9 Hz, thiophene–CH_2N–), 2.47 (d, 4H, J = 8.8 Hz, –CH_2CMe_2–), 1.82 (d, 2H, J = 7.3 Hz, –N*H*–), 1.22 (s, 12H, –CMe_2–), –0.91 (s, 12H, Al–*Me*). ^{13}C NMR ($CDCl_3$): δ 140.9, 127.2, 126.7, 125.4 (thiophene), 70.46 (–*C*Me_2O–), 59.19 (thiophene–*C*H_2N–), 46.01 (–*C*H_2CMe_2–), 27.65 (–C*Me*$_2$O–), –5.91 (Al–*Me*). Anal. Calcd for $C_{22}H_{40}N_2O_2S_2Al_2$: C, 54.75; H, 8.35; N, 5.80. Found: C, 54.61; H, 8.51; N, 5.84.

Synthesis of [$Me_2Al(OCMe_2CH_2N(Me)CH_2(C_4H_3S))]_2$ ($Thio^{Me}$). In a manner analogous to that used in the synthesis of Pyr^H, desired product $Thio^{Me}$ was prepared as colorless crystals from a solution of $AlMe_3$ (1.0 mL of 2.0 M solution in toluene, 2.0 mmol) and 2–methyl–1–(methyl(thiophen–2–ylmethyl)amino)propan–2–ol (0.40 g, 2.0 mmol) in toluene in a yield of 88% (0.45 g). ^{1}H NMR ($CDCl_3$, ppm): δ 7.26 (m, thiophene–*H*), 6.98 (m, 2H, thiophene–*H*), 6.91 (d, 2H, J = 3.0 Hz, thiophene–*H*), 3.94 (s, 4H, thiophene–CH_2N–), 2.54 (s, 4H, –CH_2CMe_2–), 2.27 (s, 6H, –N*Me*–), 1.34 (s, 12H, –CMe_2–), –0.79 (s, 12H, Al–*Me*). ^{13}C NMR ($CDCl_3$): δ 136.9, 128.6, 126.7, 125.7 (thiophene), 71.92 (–*C*Me_2O–), 66.11 (thiophene–N*Me*–), 56.23 (thiophene–*C*H_2N–), 43.14 (–*C*H_2CMe_2–), 31.20 (–C*Me*$_2$O–), –6.02 (Al–*Me*). Anal. Calcd for $C_{24}H_{44}N_2O_2S_2Al_2$: C, 56.44; H, 8.68; N, 5.49. Found: C, 56.17; H, 8.68; N, 5.37.

Synthesis of [$Me_2Al(OCMe_2CH_2N(Me)CH_2CH_2NMe_2)]_2$ ($NMe2^{Me}$). In a manner analogous to that used in the synthesis of Pyr^H, desired product $NMe2^{Me}$ was prepared as colorless crystals from a solution of $AlMe_3$ (1.0 mL of 2.0 M solution in toluene, 2.0 mmol) and 1–((2–(dimethylamino)ethyl)(methyl)amino)–2–methylpropan–2–ol (0.35 g, 2.0 mmol) in toluene in a yield of 85% (0.39 g). ^{1}H NMR ($CDCl_3$): δ 2.68 (t, 4H, J = 7.9 Hz, Me_2NCH_2–) 2.49 (s, 4H, –

454 C*H*$_2$CMe$_2$–), 2.43 (t, 4H, *J* = 5.5 Hz, Me$_2$NCH$_2$C*H*$_2$–), 2.31 (s, 6H, –N*Me*–), 1.29 (s, 12H, –C*Me*$_2$–),
455 –0.87 (s, 12H, Al–*Me*). ^{13}C NMR (CDCl$_3$): δ 71.39 (–NCH$_2$*C*Me$_2$–), 68.07 (–N*C*H$_2$CH$_2$NMe$_2$),
456 56.67 (–NCH$_2$*C*H$_2$NMe$_2$), 54.28 (–N*C*H$_2$CMe$_2$–), 45.92 (–N*Me*$_2$), 43.77 (–N*Me*–), 31.27 (–
457 NCH$_2$C*Me*$_2$–), −5.91 (Al–*Me*). Anal. Calcd for $C_{22}H_{54}N_4O_2Al_2$: C, 57.36; H, 11.82; N, 12.16. Found:
458 C, 57.30; H, 11.97; N, 12.01.

459 **Synthesis of [Me$_2$Al(OCMe$_2$CH$_2$NHMe)]$_2$ (H^H).** In a manner analogous to that used in the
460 synthesis of **Pyr^H**, desired product **H^H** was prepared as colorless crystals from a solution of AlMe$_3$
461 (1.0 mL of 2.0 M solution in toluene, 2.0 mmol) and 1–((2–methoxyethyl)(methyl)amino)–2–
462 methylpropan–2–ol in toluene (0.21 g, 2.0 mmol) in toluene in a yield of 78% (0.25 g). ^{1}H NMR
463 (CDCl$_3$): δ 2.42 (d, 4H, *J* = 8.9 Hz,–C*H*$_2$N–), 2.35 (d, 6H, *J* = 6.2 Hz, N–*Me*), 1.75 (t, 2H, *J* = 6.4
464 Hz, N–*H*), 1.23 (s, 12H, –C*Me*$_2$–), –1.01 (s, 12H, Al–*Me*). ^{13}C NMR (CDCl$_3$): δ 70.06 (–*C*Me$_2$O–),
465 62.45 (–*C*H$_2$N–), 34.37 (N–*Me*), 27.68 (–C*Me*$_2$O–), –4.97 (Al–*Me*). Anal. Calcd for $C_{14}H_{36}N_2O_2Al_2$:
466 C, 52.81; H, 11.40; N, 8.80. Found: C, 52.66; H, 11.51; N, 8.62.

467 **General procedure for catalyst screening under ambient conditions.** Styrene oxide (**1a**, 10
468 mmol), catalyst (0.1 mmol), and (*n*–Bu)$_4$NBr (32 mg, 0.1 mmol) were charged in a 20-mL round
469 bottomed flask with a magnetic stirring bar in a glovebox. A rubber balloon containing
470 approximately 2 L of CO$_2$ was connected to the flask, and then the reaction vessel was well sealed
471 with Parafilm®. The reaction vessel was stirred at 25 °C for 24 h. After the desired time was reached,
472 an aliquot of the reaction mixture was transferred to an NMR cell, and the conversion of styrene
473 oxide (**1a**) into styrene carbonate (**2a**) was determined by 1H NMR spectroscopy.

474 **General procedure for the synthesis of terminal cyclic carbonates 2a–2g under ambient**
475 **conditions.** Epoxides **1a**–**1g** (10 mmol), **Pyr^H** (47 mg, 0.1 mmol), and (*n*–Bu)$_4$NBr (32 mg, 0.1
476 mmol) were charged in a 20 mL round bottomed flask with a magnetic stirring bar in glovebox. A
477 rubber balloon containing approximately 2 L CO$_2$ was connected to the flask, and then the reaction

vessel was well sealed with Parafilm®. The reaction vessel was stirred at 25 °C for 24 h. After the desired time was reached, an aliquot of the reaction mixture was transferred to an NMR cell, and the conversion of epoxides (**1a**–**1g**) into cyclic carbonate (**2a**–**2g**) was determined by ^{1}H NMR spectroscopy. Cyclic carbonates **2a**–**2g** were purified by column chromatography.

General procedure for the synthesis of 2h and 2i at 1 bar pressure. Epoxides **1h**–**1i** (10 mmol), **Pyr^{H}** (47 mg, 0.1 mmol), and (*n*–Bu)$_4$NBr (32 mg, 0.1 mmol) were charged in a 20 mL round bottomed flask with a magnetic stirring bar in glovebox. A rubber balloon containing approximately 2 L CO_2 was connected to the flask, and then the reaction vessel was well sealed with Parafilm®. The reaction vessel was stirred at 75 °C for 36 h. After the desired reaction time, an aliquot of the reaction mixture was transferred to an NMR tube, and the conversion of the epoxide (**1h**–**1i**) into the cyclic carbonate (**2h**–**2i**) was determined by ^{1}H NMR spectroscopy.

X–ray crystallographic structure determination. The crystallographic measurements were performed at 100(2) K for **Thio^{H}** using a Bruker Apex II diffractometer with Mo K$_\alpha$ (λ = 0.71073 Å) radiation. Specimens of suitable quality and size were selected, mounted, and centered on the X–ray beam using a video camera. The structures were solved by direct methods and refined by full–matrix least–squares methods using the SHELXTL program package with anisotropic thermal parameters for all non–hydrogen atoms, resulting in the X–ray crystallographic data of **Thio^{H}** in CIF format. Final refinement based on the reflections (I > 2σ(I)) converged at $R1$ = 0.0423, $wR2$ = 0.1103, and GOF = 1.079. Further details and selected bond lengths and angles are given in Tables S1and S2 (see the Supporting Information). CCDC 1893339 (**Thio^{H}**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Acknowledgments

This work was financially supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (No. 2018R1A2B6004037) and the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry and Energy (MOTIE) of the Republic of Korea (No. 20172010202000).

Conflict of interest

The authors declare no competing financial interests.

Keywords: aluminum catalysts · cyclic carbonates · room temperature · atmospheric CO_2 pressure · epoxides

[1] a) F. D. Bobbink, A. P. van Muyden, P. J. Dyson, *Chem. Commun.* **2019**, *55*, 1360–1373; b) Q.–W. Song, Z.–H. Zhou, L.–N. He, *Green. Chem.* **2017**, *19*, 3707–3728.

[2] Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nature Comm.* **2015**, *6*, 5933.

[3] Selected recent reviews: a) H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, *Top. Curr. Chem.* **2017**, *375*, 50; b) M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing, C. Detrembleur, *Catal. Sci. Technol.* **2017**, *7*, 2651–2684; c) M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann, F. E. Kühn, *ChemSusChem* **2015**, *8*, 2436–2454; d) G. Fiorani, W. Guo, A. W. Kleij, *Green Chem.* **2015**, *17*, 1375–1389; e) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353–1370; f) J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, *Green Chem*. **2015**, *17*, 1966–1987.

[4] M. Mikkelsen, M. Jørgensen, F. C. Krebs, *Energy Environ. Sci.* **2010**, *3*, 43–81.

[5] selected reviews a) R. R. Shaikh, S. Pornpraprom, V. D'Elia, *ACS Catal.* **2018**, *8*, 419–450; b) F. D. Monica, A. Buonerba, C. Capacchione, *Adv. Synth. Catal.* **2019**, *361*, 265–282.

[6] a) M. North, S. C. Z. Quek, N. E. Pridmore, A. C. Whitwood, X. Wu, *ACS Catal.* **2015**, *5*, 3398–3402; b) Y. R. Yepes, C. Quintero, D. O. Meléndez, C. G. Daniliuc, J. Martínez, R. S. Rojas, *Organometallics* **2019**, *38*, 469–478; c) J. Martínez, J. A. Castro–Osma, C. Alonso–Moreno, A.

Rodríguez–Diéguez, M. North, A. Otero, A. Lara–Sánchez, *ChemSusChem* **2017**, *10*, 1175–1185; d) J. Martínez, J. A. Castro–Osma, A. Earlam, C. Alonso–Moreno, A. Otero, A. Lara–Sánchez, M. North, A. Rodríguez–Diéguez, *Chem. Eur. J.* **2015**, *21*, 9850–9862; e) W. Clegg, R. W. Harrington, M. North, R. Pasquale, *Chem. Eur. J.* **2010**, *16*, 6828–6843; f) J. A. Castro–Osma, C. Alonso–Moreno, A. Lara–Sánchez, J. Martínez, M. North, A. Otero, *Catal. Sci. Technol.* **2014**, *4*, 1674–1684; g) M. A. Gaoan, F. de la Cruz–Martínez, J. Fernández–Baeza, L. F. Sánchez–Barba, C. Alonso–Moreno, A. M. Rodríguez, A. Rodríguez–Diéguez, J. A. Castro–Osma, A. Otero, A. Lara–Sánchez, *Dalton Trans*. **2019**, *48*, 4218–4227; h) D. O. Meléndez, A. Lara–Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro–Osma, M. North, R. S. Rojas, *ChemCatChem.* **2018**, *10*, 2271–2277.

[7] S. H. Kim, D. Ahn, M. J. Go, M. H. Park, M. Kim, J. Lee, Y. Kim, *Organometallics* **2014**, *33*, 2770–2775.

[8] T. Elkin, M. Botoshansky, R. M. Waymouth, M. S. Eisen, *Organometallics* **2014**, *33*, 840–843.

[9] P. R. Elowe, C. McCann, P. G. Pringle, S. K. Spitzmesser, J. E. Bercaw, *Organometallics* **2006**, *25*, 5255–5260.

[10] L. Wang, G. Zhang, K. Kodama, T. Hirose, *Green Chem.* **2016**, *18*, 1229–1233.

[11] W. H. Woo, K. Hyun, Y. Kim, J. Y. Ryu, J. Lee, M. Kim, M. H. Park, Y. Kim, *Eur. J. Inorg. Chem.* **2017**, 5372–5378.

[12] A. W. Addison, T. N. Rao, J. Reedjik, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans*. **1984**, 1349–1356.

[13] a) D. F. Shriver, M. A. Drezdzon, *The Manipulation of Air–Sensitive Compounds*, Wiley, New York, 2nd edn, **1986**; b) G. S. Girolami, T. B. Rauchfuss, R. J. Angelici, *Synthesis and Technique in Inorganic Chemistry*, University Science Books, Sausalito, 3rd edn, **1999**.

[14] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, Elsevier, New York, 6th edn, **2009**.

[15] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518–1520.

[16] M. C. Joshi, J. Okombo, S. Nsumiwa, J. Ndove, D. Taylor, L. Wiesner, R. Hunter, K. Chibale, T. J. Egan, *J. Med. Chem.* **2017**, *60*, 10245–10256.

[17] Y. Ren, Y. Su, L. Sun, S. He, L. Meng, D. Liao, X. Liu, Y. Ma, C. Liu, S. Li, H. Ruan, X. Lei, X. Wang, Z. Zhang, *J. Med. Chem.* **2017**, *60*, 972–986.

[18] S. M. George, B. K. Park, C. G. Kim, T.–M. Chung, *Eur. J. Inorg. Chem.* **2014**, 2002–2010.

[19] B. Glowacki, R. Pallach, M. Lutter, F. Roesler, H. Alnasr, C. Thomas, D. Schollmeyer, K. Jurkschat, *Chem. Eur. J.* **2018**, *24*, 19266–19279.

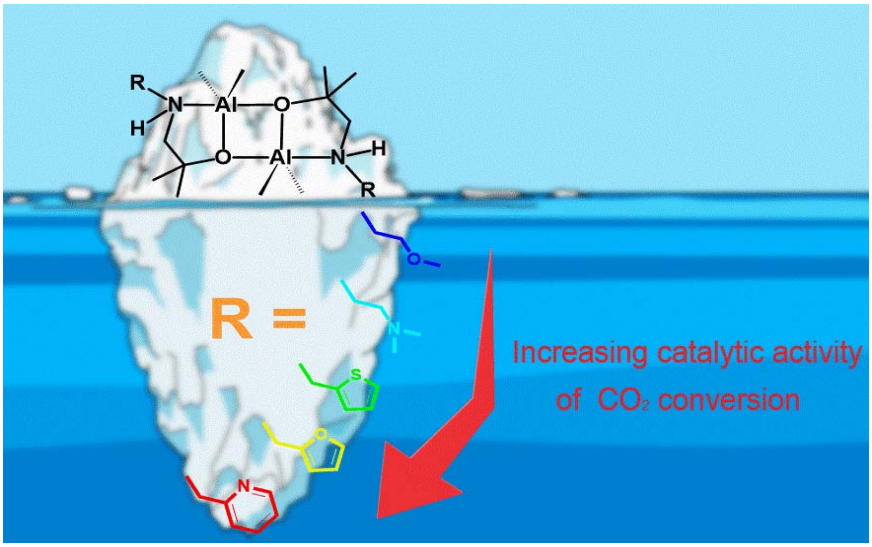
[20] S. H. Kim, S. Y. Han, J. H. Kim, Y. Y. Kang, J. Lee, Y. Kim, *Eur. J. Inorg. Chem.* **2015**, 2323–2329.

10.1002/cssc.201901661

560

561

562 Table of Contents (TOC)



563