

## Article

# Highly Active CO<sub>2</sub> Fixation into Cyclic Carbonates Catalyzed by Tetranuclear Aluminum Benzodiimidazole-Diylidene Adducts

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**Abstract:** A set of tetranuclear alkyl aluminum adducts **1** and **2** supported by benzodiimidazole-diylidene ligands **L**<sub>1</sub>, N,N'-(1,5-diisopropylbenzodiimidazole-2,6-diylidene)bis(propan-2-amine), and **L**<sub>2</sub>, N,N'-(1,5-dicyclohexyl-benzodiimidazole-2,6-diylidene)dicyclohexanamine were synthesized in exceptional yields and characterized by spectroscopic methods. These compounds were studied as catalysts for cyclic carbonate formation (**3a–o**) from their corresponding terminal epoxides (**2a–o**) and carbon dioxide utilizing tetrabutylammonium iodide as a nucleophile in the absence of a solvent. The experiments were carried out at 70 °C and 1 bar CO<sub>2</sub> pressure for 24 h and adduct **1** was the most efficient catalyst for the synthesis of a large variety of monosubstituted cyclic carbonates with excellent conversions and yields.

**Keywords:** alkyl aluminum adduct; cyclic carbonates; epoxides; carbon dioxide conversion; catalysis



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## 1. Introduction

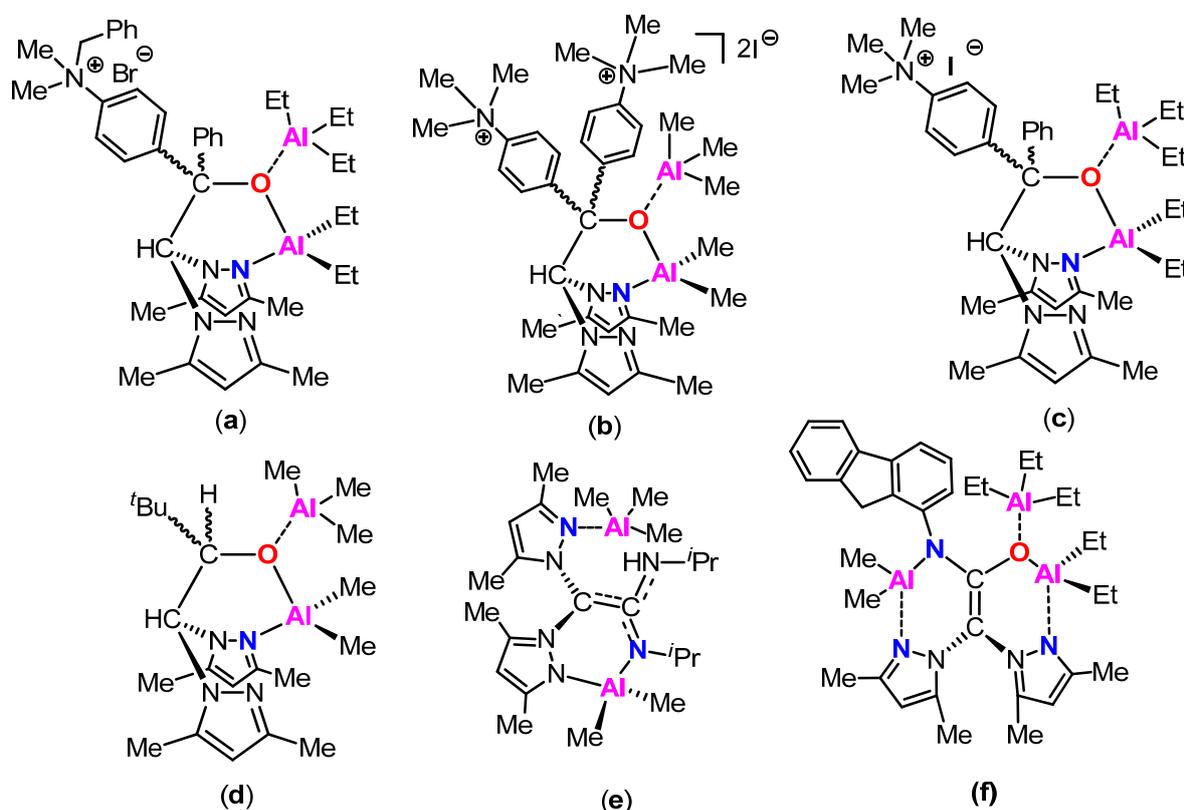
The accumulation of carbon dioxide (CO<sub>2</sub>) emissions in the atmosphere has a negative effect on the environment and has been recognized as the principal phenomenon responsible for global warming by the international community [1,2]. Consequently, reducing greenhouse gas emissions must be the main challenge in order to mitigate climate change, and the use of CO<sub>2</sub> as sustainable feedstock in the chemical industry could help to achieve this objective [1,3–5]. For this reason, the development of new technologies, such as CO<sub>2</sub> capture and storage (CCS) and CO<sub>2</sub> capture and usage (CCU) have acquired significant relevance over the past few years [6,7]. While CCS is the principal method to decrease CO<sub>2</sub> concentrations in the environment, CCU is the most promising for transforming CO<sub>2</sub> into highly value-added products, including organic molecules [8–12] and polymeric materials [13–17].

It is worth highlighting that one of the main uses of CO<sub>2</sub> is focused on the synthesis of cyclic carbonates. The preparation of these products is performed in different ways [18], and the reaction of CO<sub>2</sub> with epoxides is the most predominant [19–32], although ethylene glycol [33], halohydrins [34], and propargyl alcohols [35] can also be used as precursors to prepare cyclic carbonates. Specifically, epoxides, which are highly reactive substrates, have the ability to activate inert CO<sub>2</sub> molecules, overcoming their thermodynamic stability [1,36], which makes these substrates suitable for the preparation of cyclic carbonates, since their combination with CO<sub>2</sub> is a simple and effective reaction. Recently, the preparation of cyclic carbonates has grown enormously, attributed to their use as polar aprotic solvents [37,38], electrolytes for lithium-ion batteries [39,40], chemical intermediates [41], and monomers to produce polymers [14,42–44], making them products of elevated interest.

It is important to mention that the use of different catalytic systems is essential to perform high reaction conversions and produce yields for the synthesis of cyclic carbonates,

preferably under mild reaction conditions (low temperature and CO<sub>2</sub> pressure), therefore a wide array of catalysts have been designed to achieve this catalytic process. These catalysts are fundamentally based on highly efficient organometallic complexes [45–49] and organocatalysts [50–53]. Related to this matter, aluminum complexes have recently been studied [23,24,54–59], since aluminum is one of the most abundant elements in the Earth's crust, which makes it highly desirable for large-scale production.

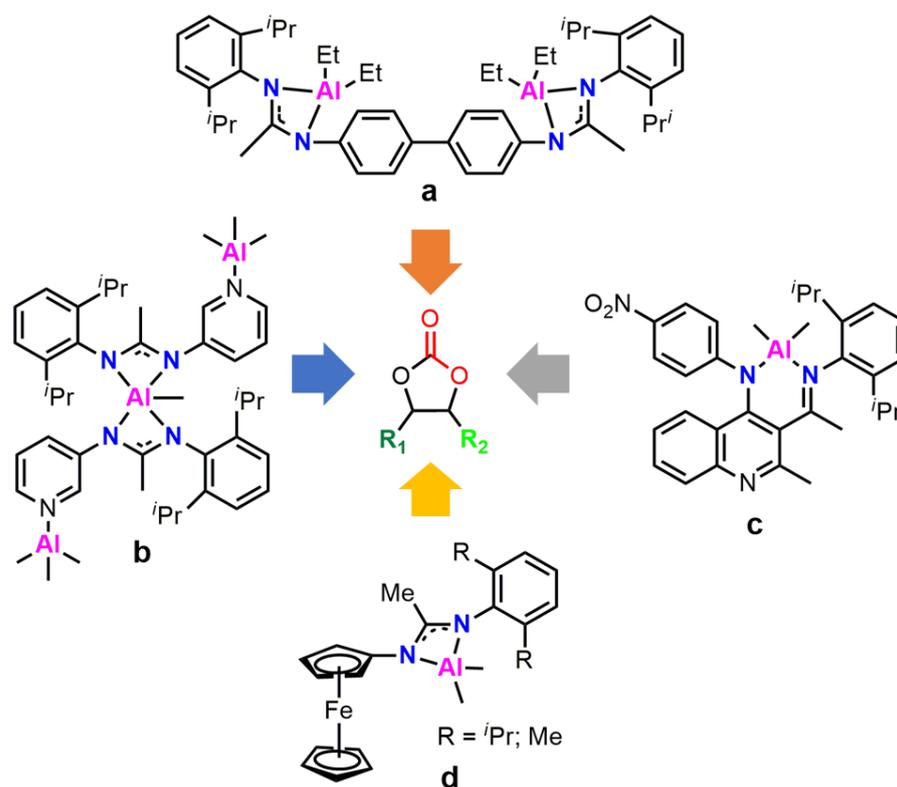
Among all aluminum catalysts recently developed for the preparation of cyclic carbonates, it is worth highlighting that only a few of them present adduct-type coordinations, which have shown exceptional catalytic results in this process. The most prominent aluminum compounds are those supported by scorpionate ligands in which a AlR<sub>3</sub> moiety (R = Me, Et) is attached to an oxygen or nitrogen atom through a dative bond, as can be seen in Figure 1 [23,60–64]. In that sense, the one-component aluminum adducts reported by Otero et al. have the ability to synthesize cyclic carbonates in the absence of a co-catalysts in high isolated yields (Figure 1a–c) [23,60,61]. Furthermore, the bimetallic (Figure 1d–e) [62,63] and trimetallic (Figure 1f) [64] aluminum complexes exhibited outstanding activity for the preparation of styrene carbonate using tetrabutylammonium bromide (TBAB) as a co-catalyst.



**Figure 1.** Aluminum adducts catalysts supported by scorpionate ligands: (a) [23]; (b) [60]; (c) [61]; (d) [62]; (e) [63]; (f) [64].

On the other hand, our research group has experience in the preparation of aluminum complexes that have proven to be efficient catalysts in the synthesis of cyclic carbonate formation (Figure 2) [65–68]. Firstly, the aluminum-based bis(amidinate) complex (Figure 2a) demonstrated excellent conversions (81–100%) and yields (57–87%) for the production of cyclic carbonates from disubstituted epoxides and CO<sub>2</sub> [65]. Additionally, trinuclear aluminum adduct (Figure 2b) showed exceptional catalytic activity for this transformation in relatively moderate reaction conditions (50 °C and 1 bar) under solvent-free conditions [66], as well the bulky aluminum complex supported by 4-amino-3-iminoquinoline ligand at 80 °C and 1 bar pressure of CO<sub>2</sub> (Figure 2c) [67]. Recently, there has been particular interest in the synthesis of heterobimetallic complexes (Figure 2d),

which are the first ferrocenyl amidinate aluminum complexes in CO<sub>2</sub> catalysis reported to date [68]. In this context, inspired by our previous work [66], in which it was found that bi- and trinuclear aluminum adducts were more active than their analogous monometallic aluminum complexes for the synthesis of a wide range of cyclic carbonates and by the high catalytic activity of the previously discussed aluminum adducts (Figure 1) [23,60–64], herein, we focused our attention in the preparation of new tetranuclear alkyl aluminum adducts supported by benzodiimidazole-diylidene ligands [69], which exhibited excellent performance for the chemical fixation of CO<sub>2</sub> into cyclic carbonates.



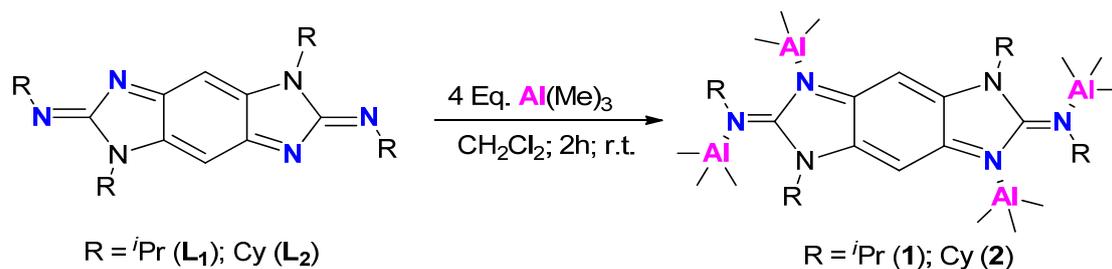
**Figure 2.** Aluminum complexes used for the synthesis of cyclic carbonates.

## 2. Results and Discussion

### 2.1. Tetranuclear Alkyl Aluminum Adduct Characterization

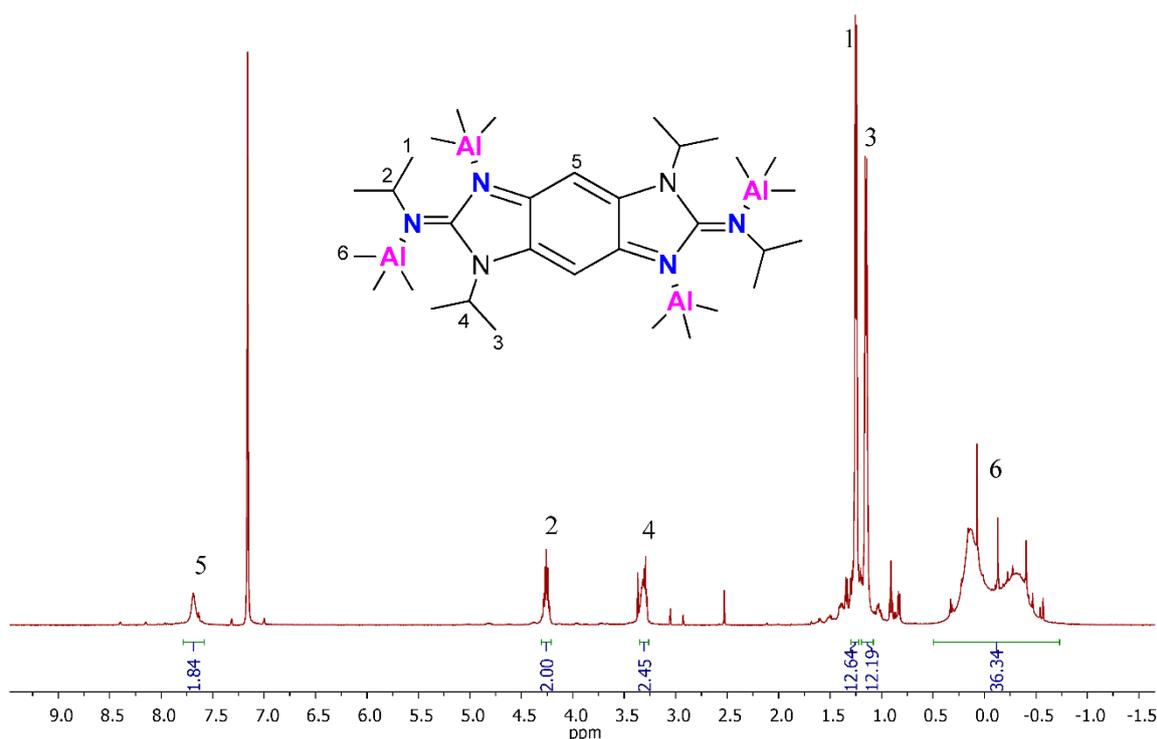
Benzodiimidazole-diylidene ligands **L**<sub>1</sub>, N,N'-(1,5-diisopropylbenzodiimidazole-2,6-diylidene)bis(propan-2-amine) and **L**<sub>2</sub>, N,N'-(1,5-dicyclohexyl-benzodiimidazole-2,6-diylidene)dicyclohexanamine were synthesized by the reaction of 1,4-bisguanidino aromatic precursors with Cu(OAc)<sub>2</sub> in acetonitrile with good yields, as previously reported [69].

As previously commented, it was found that alkyl aluminum adducts were more active than their analogous complexes for the synthesis of cyclic carbonates [66]; therefore, inspired by these catalytic results, the preparation of tetranuclear alkyl aluminum adducts **1** and **2** supported by benzodiimidazole-diylidene ligands was carried out with the main purpose of obtaining excellent catalytic performance in this catalytic process. Adducts **1** and **2** were synthesized by a Lewis acid–base reaction of the corresponding ligands, **L**<sub>1</sub> and **L**<sub>2</sub>, with four equivalents of Al(CH<sub>3</sub>)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> for 2 h at room temperature under nitrogen atmosphere (Scheme 1). Adducts **1** and **2** were isolated in exceptional yields (>95%) as white solids.



**Scheme 1.** Synthesis of alkyl aluminum adducts **1** and **2**.

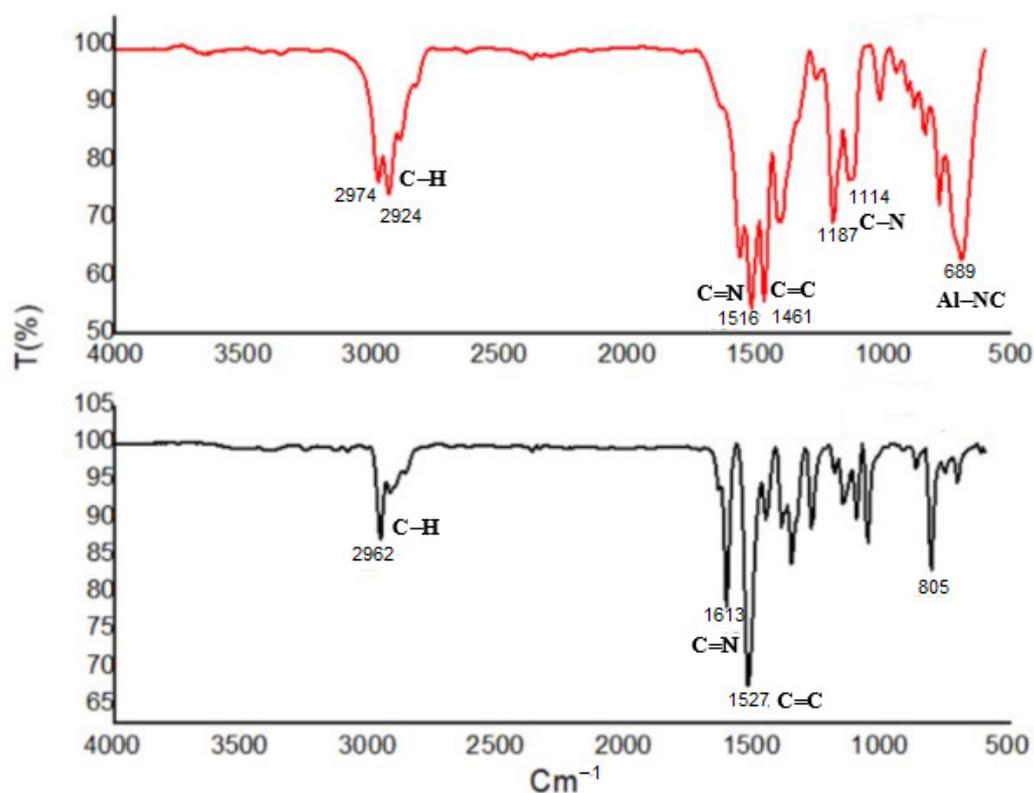
Alkyl aluminum adducts **1** and **2** were characterized by spectroscopic methods (<sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, <sup>1</sup>H–<sup>13</sup>C g-HSQC, <sup>1</sup>H NOESY-1D and FT-IR). The <sup>1</sup>H NMR spectra of these compounds show a broad signal around (−0.58)–0.30 ppm for **1** (Figure 3) and (−0.61)–0.46 ppm for **2** (see Supplementary Materials), which belong to the methyl groups coordinated to the aluminum centers. The corresponding signals of the isopropyl groups are observed at 1.27 and 1.18 ppm (CH), 4.27 and 3.31 ppm (CH<sub>3</sub>) in adduct **1** (Figure 3), while the resonances belonging to the CH<sub>2</sub> and CH groups from the cyclohexyl substituent appear around 0.94–4.07 ppm in adduct **2** (see Supplementary Materials). Finally, aromatic signals are shifted to 7.73 ppm in **1** and 7.96 ppm in **2**. Two-dimensional experiments were carried out to assign the majority of <sup>1</sup>H NMR signals and <sup>1</sup>H–<sup>13</sup>C g-HSQC experiments were carried out to locate resonances from carbon atoms (see Supplementary Materials).



**Figure 3.** <sup>1</sup>H NMR spectrum of alkyl aluminum adduct **1** in C<sub>6</sub>D<sub>6</sub>.

FT-IR spectroscopy is also an efficient tool to confirm the formation of new compounds. In that regard, a slight variation and broadening was observed in most IR bands between adducts and ligand precursors (**1** versus **L**<sub>1</sub> and **2** versus **L**<sub>2</sub>), which is characteristic of the interaction between a metal and an organic structure. As an example, the IR spectrum of **1** shows two signals at 1516 and 1461 cm<sup>−1</sup> corresponding to the C=N and C=C groups, respectively, whereas those same two signals appear at 1613 (C=N) and 1527 (C=C) cm<sup>−1</sup> in the IR spectrum of **L**<sub>1</sub>, in which a clear displacement is detected, as can be seen in Figure 4 [69]. Other evidence of the phenomenon mentioned above can be found in the

bands belonging to the C–N stretching frequencies ( $1187$  and  $1114\text{ cm}^{-1}$  for adduct **1** and  $1356$  and  $1063\text{ cm}^{-1}$  for **L<sub>1</sub>**) [69]. In addition, as  $\text{Al}(\text{CH}_3)_3$  is a metallic precursor with low atomic mass, a characteristic broad band of adduct **1** appears at  $689\text{ cm}^{-1}$  corresponding to the Al–NC interaction. A similar FT-IR discussion can apply to adduct **2** and **L<sub>2</sub>** (see Supplementary Materials for further details).



**Figure 4.** FT-IR spectrum for alkyl aluminum adduct **1** (red) versus benzodiimidazole-diylidene ligand **L<sub>1</sub>** (black).

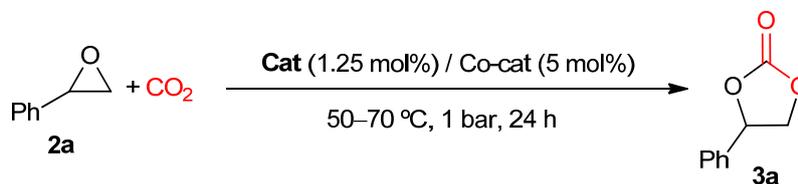
Characterization of adducts **1** and **2** performed by NMR and FT-IR spectroscopy allowed us to propose a structure for these compounds in which the benzodiimidazole-diylidene ligand is coordinated to four aluminum centers via dative bonds.

## 2.2. Catalytic Studies

Once the new tetranuclear aluminum adducts **1** and **2** were prepared, their potential utility as catalysts for the formation of cyclic carbonates from the reaction between  $\text{CO}_2$  and epoxides was explored. Firstly, reaction conditions were optimized using styrene oxide **2a** as substrate. As shown in Table 1, moderate conversions were observed with catalysts **1** and **2** when tetrabutylammonium iodide (TBAI), TBAB, or tetrabutylammonium chloride (TBAC) was used as a co-catalyst (Table 1, entries 1–3 and 6–8), however, no conversion was obtained in the presence of tetrabutylammonium fluoride (TBAF) (Table 1, entries 4 and 9) at  $50\text{ }^\circ\text{C}$  and 1 bar of  $\text{CO}_2$  pressure for 24 h. It was found that TBAI was a more efficient co-catalyst than TBAB, TBAC, or TBAF under the same reaction conditions, which could be due to the superior leaving group ability and nucleophilicity of the iodide ion versus bromide, chloride, and fluoride ions. In addition, the lower electrostatic interaction between the ammonium cation and the iodide anion compared to bromide, chloride, and fluoride anions is caused by the ion pairing effect. Accordingly, the iodide is farther away from the ammonium cation and, consequently, the nucleophilic attack of the iodide atom to the epoxide is favored [70,71]. According to these results, the reaction temperature was increased to  $70\text{ }^\circ\text{C}$  and higher conversions were obtained (Table 1, entries 5 and 10). At this reaction temperature, adduct **1** was more active than **2**, probably due to the higher steric

hindrance generated by cyclohexyl groups compared to isopropyl groups, which makes the approximation of epoxide to the metal centers more difficult.

**Table 1.** Optimization of reaction conditions for the preparation of styrene carbonate (**3a**).<sup>1</sup>



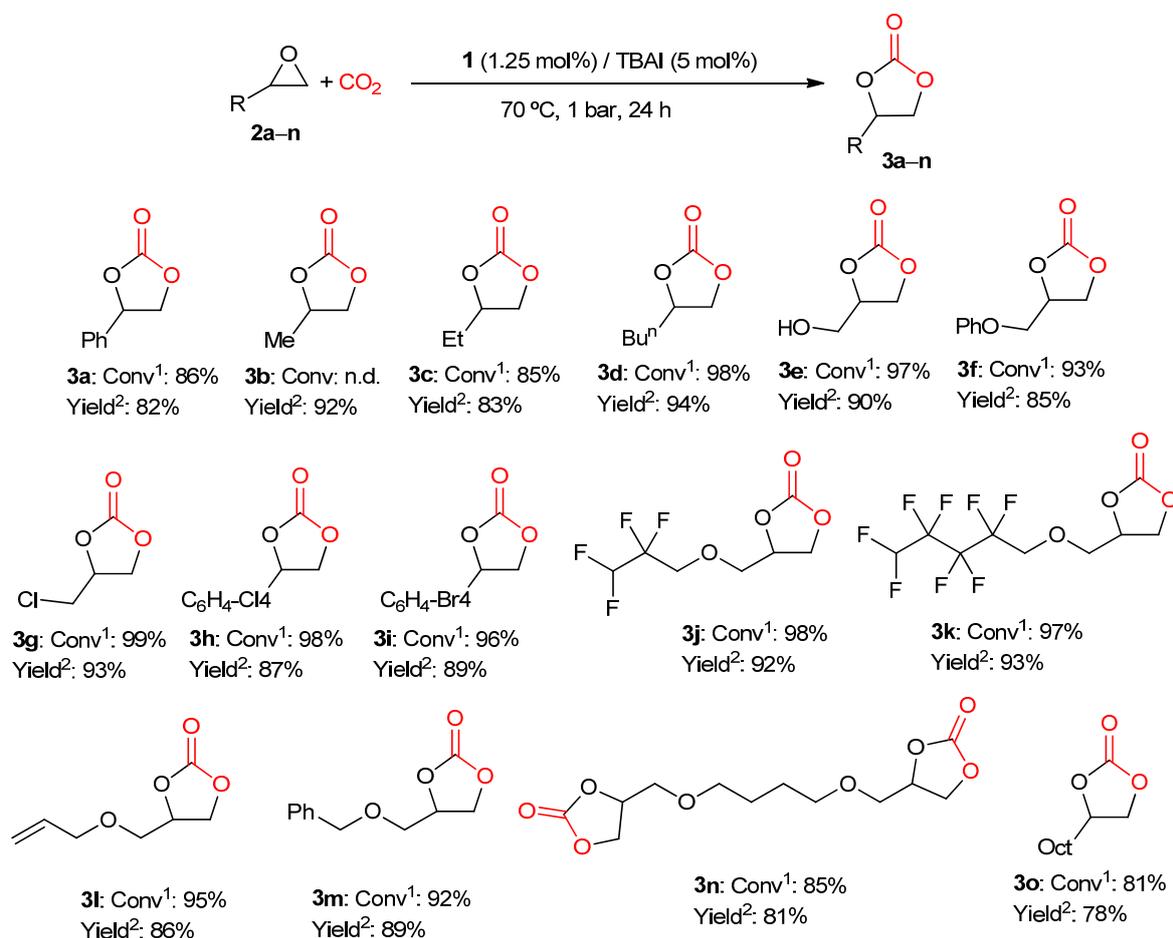
Entry	Catalyst	Co-Catalyst	Temperature (°C)	Conversion <sup>2,3</sup> (%)
1	<b>1</b>	TBAI	50	70
2	<b>1</b>	TBAB	50	62
3	<b>1</b>	TBAC	50	46
4	<b>1</b>	TBAF	50	1
5	<b>1</b>	TBAI	70	86
6	<b>2</b>	TBAI	50	42
7	<b>2</b>	TBAB	50	35
8	<b>2</b>	TBAC	50	31
9	<b>2</b>	TBAF	50	2
10	<b>2</b>	TBAI	70	53
11 <sup>4</sup>	Al(CH <sub>3</sub> ) <sub>3</sub>	TBAI	50	20
12 <sup>4</sup>	Al(CH <sub>3</sub> ) <sub>3</sub>	TBAI	70	31
13 <sup>5</sup>	Al(CH <sub>3</sub> ) <sub>3</sub>	TBAI	70	18
14 <sup>6</sup>	<b>1</b>	-	70	0
15 <sup>7</sup>	-	TBAI	70	5

<sup>1</sup> Reactions were carried out at 70 °C and 1.0 bar CO<sub>2</sub> pressure using 1.25 mol% of catalyst and 5 mol% of co-catalyst under solvent-free conditions; <sup>2</sup> established by <sup>1</sup>H NMR of crude reaction mixture; <sup>3</sup> selectivity toward the cyclic carbonate >99%; <sup>4</sup> 5 mol% of both Al(CH<sub>3</sub>)<sub>3</sub> and pyridine was added; <sup>5</sup> 5 mol% of Al(CH<sub>3</sub>)<sub>3</sub> was added; no pyridine was added; <sup>6</sup> no tetrabutylammonium iodide (TBAI) was added; <sup>7</sup> no catalyst **1** was added. TBAB, tetrabutylammonium bromide. TBAC, tetrabutylammonium chloride. TBAF, tetrabutylammonium fluoride.

The compound pyridine–Al(CH<sub>3</sub>)<sub>3</sub> was also tested at 50 and 70 °C (Table 1, entries 11 and 12), showing minor catalytic activity compared to adducts **1** and **2** at those temperatures (Table 1, entries 1 and 6 versus entry 11; entries 5 and 10 versus entry 12), confirming the great effectiveness of benzodiimidazole-diylidene ligands in this catalytic process. Additionally, with the main challenge of demonstrating that the coordination of adducts to metal centers greatly favors the synthesis of cyclic carbonates, an experiment using Al(CH<sub>3</sub>)<sub>3</sub> and TBAI in the absence of adducts was performed under the same reaction conditions, 70 °C and 1 bar CO<sub>2</sub> pressure for 24 h (Table 1, entry 13) and, as expected, a lower conversion occurred (Table 1, entry 13 versus entries 5, 10, and 12). Finally, control experiments were carried out to prove that both catalyst **1** and TBAI are essential for the catalytic production of **3a** (Table 1, entries 14 and 15).

Once the reaction conditions for the preparation of styrene carbonate **3a** from styrene oxide **2a** and CO<sub>2</sub> were optimized as 1.25 mol% of adduct **1** and 5 mol% of TBAI at 70 °C and 1 bar of CO<sub>2</sub> pressure for 24 h, a wide variety of monosubstituted cyclic carbonates **3a–o** were prepared from their corresponding terminal epoxides **2a–o** (Figure 5). It is worth highlighting that in most cases, elevated conversions and isolated yields were afforded using **1**/TBAI as the catalyst system with selectivity toward cyclic carbonate product under the conditions mentioned above. Cyclic carbonates **3b–d** and **3o**, which contain an alkyl group in their structure, were isolated in exceptional yields of 78–94%. Moreover, it was found that **1**/TBAI prepared glycerol carbonate **3e** with excellent yield (90%), despite glycidol being highly likely to form polymers [72–74]. In addition, the preparation of highly fluorinated cyclic carbonates **3j** and **3k** was performed with excellent yields. These cyclic carbonates have hardly been investigated and could be used in lithium-ion batteries as electrolytes [75–77]. Finally, cyclic carbonates **3l–n** were also obtained in high yields

(81–89%). Particularly, product **3n** is an interesting substrate since it can be employed as building blocks for the preparation of non-isocyanate polyurethanes (NIPUs) by its reaction with diamines [78,79]. It is notable that the catalyst system (**1**/TBAB) was able to prepare a great variety of cyclic carbonates with different functional groups such as aryl, alkyl, alcohol, ether, and halide. These catalytic results show that this catalyst system has great potential for cyclic carbonate production.



**Figure 5.** Cyclic carbonates **3a–o** were synthesized by **1**/TBAB in a 1:4 molar ratio. Reactions were carried out at 70 °C and 1.0 bar CO<sub>2</sub> pressure under solvent-free conditions. <sup>1</sup> Conversions were established by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. <sup>2</sup> Isolated yields were achieved from purified cyclic carbonate.

### 2.3. Catalysis Comparison

In recent years, a significant number of catalytic systems based on aluminum complexes have been reported in the literature for the synthesis of cyclic carbonates. Many of them require CO<sub>2</sub> pressure greater than 1 bar to perform the catalytic process, although there are some examples of aluminum compounds that show outstanding catalytic activity at atmospheric pressure (1 bar). For this reason, the catalytic results displayed by aluminum adduct **1** can be compared with other aluminum complexes found in the literature to determine whether adduct formation shows significant improvements in cyclic carbonate synthesis. The catalytic performance of these catalysts is presented in Table 2. For styrene carbonate (**3a**) formation (Table 2, entries 1–6), it is relevant to mention that the Al(Salen) catalyst prepared by North et al. [80] displayed the best TOF value (7.65) under ambient conditions (Table 1, entry 2). The bimetallic aluminum complex [66] required 2.5 mol% of catalyst loading to obtain an isolated yield of 85% (Table 2, entry 3), whereas adduct **1** afforded a similar result using only 1.25 mol%. Moreover, the aluminum

complex supported by aminoquinoline ligand [67] showed an almost identical TOF value as adduct **1** (Table 2, entry 5), although this catalyst required a higher temperature (80 °C). In addition, another aluminum complex reported by Otero and co-workers [60] exhibited excellent conversion for the synthesis of styrene carbonate at 35 °C (Table 2, entry 6). It is also worth noting the elevated TOF value presented by another Al(Salen) complex [56] for the preparation of cyclic carbonate **3g** (Table 2, entry 8), which is clearly more active than adduct **1**, although this complex required 100 °C to accomplish the catalytic activity. On the other hand, various aluminum catalysts have recently been used for the preparation of 3-phenoxypropylene carbonate, **3f** [57,63,68,81,82]. The Al(Salen) molecular cage [57] (Table 2, entry 10) and the aluminum catalyst reported by Xu et al. [81] (Table 2, entry 11) have proven to be exceptional catalysts for the synthesis of **3f**, although these catalysts also had important disadvantages, including that the Al-cage required 10 mol% of TBAB to reach a medium yield (Table 2, entry 10) and the Al-Schiff needed an elevated reaction temperature, 100 °C (Table 2, entry 11). Finally, the potassium organoaluminate compound [82] and the aluminum ferrocenyl amidine complex [68] achieved lower catalytic activity than adduct **1** (Table 2, entries 12 and 14) for the preparation of **3f**. In conclusion, the catalytic system (**1**/TBAI) developed in this work afforded the formation of a significant variety of cyclic carbonates **3a–o** under moderate reaction conditions (70 °C and 1 bar) and has proven to be one of the most active aluminum catalysts for the preparation of cyclic carbonates at 1 bar CO<sub>2</sub> pressure.

**Table 2.** Comparison of catalytic activity of different aluminum complexes <sup>1</sup>.

Entry	Epoxide	Catalyst System (mol%)	Reaction Conditions: T (°C), time (h)	Yield (%) <sup>2</sup>	TOF (h <sup>-1</sup> ) <sup>3</sup>	Reference
1	<b>2a</b>	1/TBAI (1.25/5.0)	70, 24	82	2.73	This work
2	<b>2a</b>	Al(Salen)/TBAB (2.5/2.5)	25, 3	57	7.65	[80]
3	<b>2a</b>	Al cat/TBAI (2.5/5.0)	50, 24	85	1.41	[66]
4	<b>2a</b>	Al cat/TBAI (5.0/5.0)	25, 24	80	0.66	[65]
5	<b>2a</b>	Al cat/TBAI (1.5/1.5)	80, 24	90	2.5	[67]
6	<b>2a</b>	Al cat/TBAI (5.0/5.0)	35, 24	100 <sup>4</sup>	-	[60]
7	<b>2g</b>	1/TBAI (1.25/5.0)	70, 24	93	3.10	This work
8	<b>2g</b>	Al(Salen) (0.25)	100, 24	63	10.50	[56]
9	<b>2f</b>	1/TBAI (1.25/5.0)	70, 24	85	2.83	This work
10	<b>2f</b>	Al-cage/TBAB (0.33/10.0)	rt, 24	54	3.40	[57]
11	<b>2f</b>	Al-Schiff/TBAB (0.3/0.9)	100, 18	94	17.41	[81]
12 <sup>5</sup>	<b>2f</b>	Al-K/TBAI (5.0/2.5)	50, 24	73	0.61	[82]
13	<b>2f</b>	Al cat/TBAB (5.0/5.0)	35, 18	80 <sup>4</sup>	-	[63]
14	<b>2f</b>	Al-Fe/TBAI (1.7/1.7)	80, 24	71	1.74	[68]

<sup>1</sup> Reactions were carried out at 1.0 bar CO<sub>2</sub> pressure under solvent-free conditions. <sup>2</sup> Isolated yield from purified cyclic carbonate. <sup>3</sup> mol of product/(mol of catalyst · time). <sup>4</sup> No isolated yield was reported under these reaction conditions. <sup>5</sup> 1 mL of THF was added. TOF, turnover frequency.

### 3. Materials and Methods

#### 3.1. Materials and Equipment

All experiments were carried out in the absence of oxygen employing Schlenk-line and standard glovebox techniques. Reagent-grade solvent was acquired from E. Merck.  $\text{CH}_2\text{Cl}_2$  was dried using an Innovative Technology Pure Solv model PS-MD-5. The compounds trimethylaluminum ( $\text{Al}(\text{CH}_3)_3$ ), epoxides, TBAF, TBAC, TBAB, and TBAI were obtained from Merck and used as received.  $\text{L}_1$ ,  $N,N'$ -(1,5-diisopropylbenzodiimidazole-2,6-diylidene)bis(propan-2-amine) and  $\text{L}_2$ ,  $N,N'$ -(1,5-dicyclohexyl-benzodiimidazole-2,6-diylidene)dicyclohexanamine were prepared according to published procedures [69].

The following equipment was employed for the characterization of tetranuclear alkyl aluminum adducts:  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained on a Bruker Avance-400 spectrometer. The coupling constants and chemical shifts are registered in Hertz and parts per million ( $\text{SiMe}_4$  as standard), respectively. NMR signals were supported by supplementary 2D NMR experiments, and the numbers of scans used for  $^{13}\text{C}\{^1\text{H}\}$  NMR ranged from 0.5 to 2 K depending on the experimental concentration. FT-IR spectra were obtained on a Bruker Vector-22 spectrophotometer using KBr pellets, and the infrared frequencies are reported in  $\text{cm}^{-1}$ .

#### 3.2. Catalyst Preparation and Characterization

**Synthesis of 1.** A solution of trimethylaluminum ( $\text{Al}(\text{CH}_3)_3$ ) (81.35 mg, 1.13 mmol) in  $\text{CH}_2\text{Cl}_2$  was immediately added to a solution of  $\text{L}_1$  (100.0 mg, 0.28 mmol) in  $\text{CH}_2\text{Cl}_2$ . Then, the reaction mixture was agitated for 2 h at room temperature. All volatiles were eliminated under reduced pressure, and the resulting solid was washed with cold pentane to remove impurities. Adduct **1** was isolated as a white solid (178.2 mg, 99%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  = 7.73 (s, 2H, CH-Ar), 4.27 (m, 2H, CH- $i$ Pr), 3.31 (m, 2H, CH- $i$ Pr), 1.27 (d,  $^3J_{\text{HH}} = 6.6$  Hz, 12H,  $\text{CH}_3$ - $i$ Pr), 1.18 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 12H,  $\text{CH}_3$ - $i$ Pr), (-0.58)–0.39 ppm (br, d, 36H,  $\text{CH}_3$ -Al).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  = 162.2 (C-Ar), 155.2 ( $\text{CN}_3$ ), 132.2 (C-Ar), 98.8 (CH-Ar), 54.5 (CH- $i$ Pr), 49.4 (CH- $i$ Pr), 25.6 ( $\text{CH}_3$ - $i$ Pr), 20.8 ( $\text{CH}_3$ - $i$ Pr), -4.5 ppm (br,  $\text{CH}_3$ -Al). FT-IR (KBr)  $\tilde{\nu}/\text{cm}^{-1}$  = 2974 (C–H), 2925 (C–H), 1516 (C=N), 1461 (C=C), 1187 (C–N), 1114 (C–N), 689 (Al–NC).

**Synthesis of 2.** A solution of trimethylaluminum ( $\text{Al}(\text{CH}_3)_3$ ) (56.02 mg, 0.77 mmol) in  $\text{CH}_2\text{Cl}_2$  was immediately added to a solution of  $\text{L}_2$  (100.0 mg, 0.19 mmol) in  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was agitated for 2 h at room temperature. All volatiles were eliminated under reduced pressure, and the resulting solid was washed with cold pentane to remove impurities. Adduct **2** was isolated as a white solid (151.06 mg, 99%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  = 7.96 (s, 2H, CH–Ar), 4.07 (m, 2H, CH–Cy), 2.97 (m, 2H, CH–Cy), 2.19–2.06 (m, 2H,  $\text{CH}_2$ -Cy), 1.87–0.94 (m, 12H,  $\text{CH}_2$ -Cy), (-0.61)–0.46 ppm (br, d, 36H,  $\text{CH}_3$ -Al).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  = 162.4 ( $\text{CN}_3$ ), 132.3 (C-Ar), 129.2 (C-Ar), 99.0 (CH-Ar), 63.5 (CH-Cy), 57.9 (CH-Cy), 36.7 ( $\text{CH}_2$ -Cy), 31.0 ( $\text{CH}_2$ -Cy), 27.0 ( $\text{CH}_2$ -Cy), 26.6 ( $\text{CH}_2$ -Cy), 25.9 ( $\text{CH}_2$ -Cy), 25.8 ( $\text{CH}_2$ -Cy), -4.3, -6.9 ppm (br,  $\text{CH}_3$ -Al). FT-IR (KBr)  $\tilde{\nu}/\text{cm}^{-1}$  = 2931 (C–H), 2859 (C–H), 1516 (C=N), 1461 (C=C), 1194 (C–N), 1078 (C–N), 689 (Al–NC).

#### 3.3. General Procedure for Catalyst Screening at 1 bar Pressure

Styrene oxide **2a** (1.66 mmol), alkyl aluminum catalysts **1** and **2**, pyridine– $\text{Al}(\text{CH}_3)_3$  or  $\text{Al}(\text{CH}_3)_3$  (0.021–0.083 mmol), and co-catalysts (0.083 mmol) were placed in individual glass reaction tubes with a magnetic stirrer bar in a Carousel 12 Place Reaction Station multipoint reactor under constant pressure of 1 bar of  $\text{CO}_2$ . The reaction was agitated at 50–70 °C for 24 h, and then the styrene carbonate **3a** conversion was determined by  $^1\text{H}$  NMR spectroscopy.

### 3.4. General Method for Preparation of Cyclic Carbonates 3a–o

Epoxide **2a–o** (1.66 mmol), alkyl aluminum adduct **1** (20.7  $\mu$ mol), and TBAI (83.0  $\mu$ mol) were placed in individual glass reaction tubes with a magnetic stirrer bar in a Carousel 12 Place Reaction Station multipoint reactor under constant pressure of 1 bar of CO<sub>2</sub>. The reaction mixture was agitated at 70 °C for 24 h. Cyclic carbonate conversion was then determined by analyzing an aliquot by <sup>1</sup>H NMR spectroscopy. The rest of the sample was filtered across a plug of silica, eluting with CH<sub>2</sub>Cl<sub>2</sub> to eliminate the catalyst. The eluent was vaporized under reduced pressure to obtain either the purified cyclic carbonate or a mixture of unreacted epoxide and cyclic carbonate. However, in the last case, the mixture was purified by flash chromatography using the following solvent system: first hexane, then hexane:EtOAc (6:1), then hexane:EtOAc (3:1), then EtOAc to give the purified cyclic carbonate. Cyclic carbonates **3a–o** are all known compounds and the spectroscopic data for samples prepared using alkyl aluminum adduct **1** were consistent with those reported in the literature.

### 3.5. NMR Data for Cyclic Carbonates 3a–o

**Styrene carbonate (3a)**. Obtained as a white solid (196.2 mg, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.36–7.43 (m, 3H, ArH), 7.32–7.36 (m, 2H, ArH), 5.65 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, OCH), 4.77 (t, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, 1H, OCH<sub>2</sub>), 4.29 ppm (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H, OCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 155.0, 135.9, 129.7, 129.2, 126.0, 78.1, 71.2 ppm.

**Propylene carbonate (3b)**. Obtained as a colorless liquid (155.9 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 4.80–4.86 (m, 1H, OCH), 4.53 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, OCH<sub>2</sub>), 4.00 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, OCH<sub>2</sub>), 1.44 ppm (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 155.1, 73.6, 70.7, 19.4 ppm.

**1,2-Butylene carbonate (3c)**. Obtained as a colorless liquid (160.0 mg, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 4.59–4.65 (m, 1H, OCH), 4.49 (t, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, 1H, OCH<sub>2</sub>), 4.05 (t, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, 1H, OCH<sub>2</sub>), 1.66–1.84 (m, 2H, CH<sub>2</sub>), 0.99 ppm (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 155.1, 78.0, 69.0, 27.0, 8.5 ppm.

**1,2-Hexylene carbonate (3d)**. Obtained as a colorless liquid (225.0 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 4.67–4.74 (m, 1H, OCH), 4.53 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, OCH<sub>2</sub>), 4.07 (dd, <sup>3</sup>J<sub>HH</sub> = 8.5, 7.0 Hz, 1H, OCH<sub>2</sub>), 1.76–1.86 (m, 1H, CH<sub>2</sub>), 1.63–1.73 (m, 1H, CH<sub>2</sub>), 1.31–1.49 (m, 4H, 2OCH<sub>2</sub>), 0.93 ppm (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 155.1, 77.1, 69.4, 33.6, 26.5, 22.3, 13.8 ppm.

**Glycerol carbonate (3e)**. Obtained as a colorless liquid (176.4 mg, 90%); <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO, 298 K):  $\delta$  = 4.70–4.77 (m, 1H, OCH), 4.46 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, OCH<sub>2</sub>), 4.38 (dd, <sup>3</sup>J<sub>HH</sub> = 8.0, 5.5 Hz, 1H, OCH<sub>2</sub>), 3.89–3.96 (m, 1H, CH<sub>2</sub>OH), 3.61–3.69 ppm (m, 1H, CH<sub>2</sub>OH); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, [D<sub>6</sub>]DMSO, 298 K):  $\delta$  = 155.1, 77.4, 65.7, 61.7 ppm.

**3-Phenoxypropylene carbonate (3f)**. Obtained as a white solid (274.8 mg, 85%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.27–7.33 (m, 2H, 2OArH), 7.03 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H, ArH), 6.90–6.96 (m, 2H, 2OArH), 4.99–5.08 (m, 1H, OCH), 4.62 (t, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, 1H, OCH<sub>2</sub>), 4.55 (dd, <sup>3</sup>J<sub>HH</sub> = 9.0, 6.0 Hz, 1H, OCH<sub>2</sub>), 4.24 (dd, <sup>3</sup>J<sub>HH</sub> = 10.5, 4.5 Hz, 1H, CH<sub>2</sub>OPh), 4.16 ppm (dd, <sup>3</sup>J<sub>HH</sub> = 10.5, 3.5 Hz, 1H, CH<sub>2</sub>OPh); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 157.8, 154.6, 129.7, 122.0, 114.6, 74.1, 66.9, 66.2 ppm.

**3-Chloropropylene carbonate (3g)**. Obtained as a colorless liquid (210.8 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 4.93–5.00 (m, 1H, OCH), 4.58 (t, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, 1H, OCH<sub>2</sub>), 4.39 (dd, <sup>3</sup>J<sub>HH</sub> = 8.5, 5.5 Hz, 1H, OCH<sub>2</sub>), 3.79 (dd, <sup>3</sup>J<sub>HH</sub> = 12.0, 5.5 Hz, 1H, CH<sub>2</sub>Cl), 3.71 ppm (dd, <sup>3</sup>J<sub>HH</sub> = 12.5, 3.5 Hz, CH<sub>2</sub>Cl); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 154.2, 74.4, 67.0, 44.0 ppm

**4-Chlorostyrene carbonate (3h)**. Obtained as a white solid (286.8 mg, 87%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.39–7.41 (m, 2H, ArH), 7.29–7.32 (m, 2H, ArH), 5.66 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, OCH), 4.80 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, OCH<sub>2</sub>), 4.30 ppm (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, OCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 154.6, 135.7, 134.4, 129.5, 127.3, 77.3, 71.0 ppm.

**4-Bromostyrene carbonate (3i).** Obtained as a white solid (360.5 mg, 89%)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 7.51\text{--}7.57$  (m, 2H, ArH), 7.19–7.24 (m, 2H, ArH), 5.62 (t,  $^3J_{\text{HH}} = 8.0$  Hz, 1H, OCH), 4.77 (t,  $^3J_{\text{HH}} = 8.0$  Hz, 1H, OCH), 4.27 ppm (dd,  $^3J_{\text{HH}} = 8.8, 7.6$  Hz, 1H,  $\text{OCH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 154.2, 135.4, 134.0, 129.2, 127.0, 77.0, 70.7$  ppm.

**4-((2,2,3,3-Tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one (3j).** Obtained as a colorless liquid (354.4 mg, 92%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 5.83$  (tt,  $^3J_{\text{HH}} = 52.8, 4.8$  Hz, 1H,  $\text{CHCF}_2$ ), 4.76–4.81 (m, 1H, OCH), 4.45 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 1H,  $\text{OCH}_2$ ), 4.29 (dd,  $^3J_{\text{HH}} = 7.6, 6.0$  Hz, 1H,  $\text{OCH}_2$ ), 3.87 (dt,  $^3J_{\text{HH}} = 12.8, 2.0$  Hz, 2H  $\text{OCH}_2\text{CF}_2$ ), 3.80 (dd,  $^3J_{\text{HH}} = 11.2, 3.2$  Hz, 1H,  $\text{OCH}_2\text{CH}$ ), 3.70 ppm (dd,  $^3J_{\text{HH}} = 11.2, 4.0$  Hz, 1H,  $\text{OCH}_2\text{CH}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 159.9$  (C=O), 113.9 (tt,  $^3J_{\text{CF}} = 994.0, 107.6$  Hz,  $\text{CHCF}_2$ ), 108.2 (tt,  $^3J_{\text{CF}} = 991.6, 138.8$  Hz,  $\text{CF}_2$ ), 77.4 (CH), 70.4 ( $\text{CH}_2$ ), 67.4 (t,  $^3J_{\text{CF}} = 112.4$  Hz,  $\text{CF}_2\text{CH}_2$ ), 64.9 ppm ( $\text{CH}_2$ ).  $^{19}\text{F NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = (-139.3)\text{--}(-139.4)$  (m, 2F),  $(-125.1)\text{--}(-125.0)$  ppm (m, 2F).

**4-(((2,2,3,3,4,4,5,5-Octafluoropentyl)oxy)methyl)-1,3-dioxolan-2-one (3k).** Obtained as a colorless liquid (512.8 mg, 93%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 6.01$  (tt,  $^3J_{\text{HH}} = 52.0, 5.6$  Hz, 1H,  $\text{CHF}_2$ ), 4.75–4.83 (m, 1H, OCH), 4.46 (t,  $^3J_{\text{HH}} = 8.8$  Hz, 1H,  $\text{OCH}_2$ ), 4.31 (dd,  $^3J_{\text{HH}} = 8.4, 6.0$  Hz, 1H,  $\text{OCH}_2$ ), 3.90–4.10 (m, 2H,  $\text{OCH}_2\text{CF}_2$ ), 3.83 (dd,  $^3J_{\text{HH}} = 11.2, 3.2$  Hz, 1H,  $\text{OCH}_2\text{CH}$ ), 3.75 ppm (dd,  $^3J_{\text{HH}} = 11.2, 3.6$  Hz, 1H,  $\text{OCH}_2\text{CH}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 153.8$  (C=O), 103.9–117.2 (m, 3  $\times$   $\text{CF}_2$ ), 106.7 (tt,  $^3J_{\text{CF}} = 1009.2, 123.2$  Hz,  $\text{CHCF}_2$ ), 73.8 (CH), 70.6 ( $\text{CH}_2$ ), 67.3 (t,  $^3J_{\text{CF}} = 102.8$  Hz,  $\text{CH}_2$ ), 64.8 ppm ( $\text{CH}_2$ ).  $^{19}\text{F NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = (-137.6)\text{--}(-136.7)$  (m, 2F),  $(-130.4)\text{--}(-129.5)$  (m, 2F),  $(-125.6)\text{--}(-125.7)$  (m, 2F),  $(-120.0)\text{--}(-120.1)$  ppm (m, 2F).

**4-((allyloxy)methyl)-1,3-dioxolan-2-one (3l).** Obtained as a colorless liquid (225.77 mg, 86%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 5.77\text{--}5.91$  (m, 1H,  $\text{CH}_2=\text{CH}$ ), 5.13–5.31 (m, 1H,  $\text{CH}_2=\text{CH}$ ), 4.73–4.84 (m, 1H, OCH), 4.44–4.49 (m, 1H,  $\text{OCH}_2$ ), 4.34–4.38 (m, 1H,  $\text{OCH}_2$ ), 3.96–4.07 (m, 1H,  $\text{CH}_2\text{OCH}=\text{CH}_2$ ), 3.58–3.68 ppm (m, 2H,  $\text{CH}_2\text{OCH}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 154.9, 133.7, 118.0, 75.0, 72.7, 68.9, 66.3$  ppm.

**4-((benzyloxy)methyl)-1,3-dioxolan-2-one (3m).** Obtained as a colorless liquid (307.61 mg, 89%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 7.27\text{--}7.40$  (m, 5H, Ph), 4.76–4.86 (m, 1H, OCH), 4.53–4.66 (m, 1H,  $\text{OCH}_2\text{Ph}$ ), 4.43–4.51 (m, 1H,  $\text{OCH}_2$ ), 4.36–4.41 (m, 1H,  $\text{OCH}_2$ ), 3.67–3.74 (m, 1H,  $\text{CH}_2\text{OCH}$ ) 3.59–3.64 ppm (m, 1H,  $\text{CH}_2\text{OCH}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 155.0, 137.1, 128.6, 128.1, 127.8, 75.1, 73.7, 68.9, 66.3$  ppm.

**4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (3n).** Obtained as a colorless liquid (390.30 mg, 81%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 4.62\text{--}4.72$  (m, 1H, OCH), 4.35 (t,  $^3J_{\text{HH}} = 8.5$  Hz, 1H,  $\text{CH}_2\text{O}$ ), 4.21–4.29 (m, 1H,  $\text{OCH}_2$ ), 3.50–3.57 (m, 1H,  $\text{CH}_2\text{OCH}$ ) 3.43–3.48 (m, 1H,  $\text{CH}_2\text{OCH}$ ) 3.30–3.39 (m, 1H,  $\text{OCH}_2\text{CH}_2$ ) 1.44–1.55 ppm (m, 1H,  $\text{OCH}_2\text{CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 154.5, 74.7, 71.2, 69.2, 65.7, 25.6$  ppm.

**1,2-Decylene carbonate (3o).** Obtained as a colorless liquid (259.4 mg, 78%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 4.66\text{--}4.79$  (1H, m, OCH), 4.51 (1H, t  $^3J_{\text{HH}} = 8.5$  Hz,  $\text{OCH}_2$ ), 4.04 (1H,  $^3J_{\text{HH}} = 6.0, 2.0$  Hz,  $\text{OCH}_2$ ), 1.61–1.83 (2H, m,  $\text{CH}_2$ ), 1.40–1.52 (2H, m,  $\text{CH}_2$ ), 1.20–1.37 (10H, m,  $\text{CH}_2$ ), 0.87 ppm (3H,  $^3J_{\text{HH}} = 7.0$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 154.8, 69.1, 33.6, 31.6, 29.2, 29.1, 29.0, 28.8, 24.1, 22.4, 13.8$  ppm.

#### 4. Conclusions

New tetranuclear alkyl aluminum adducts, **1** and **2**, were synthesized from the reaction between benzodiiimidazole-diylidene ligands, **L**<sub>1</sub> and **L**<sub>2</sub>, and  $\text{Al}(\text{CH}_3)_3$  in a molar ratio of 1:4. The characterization of **1** and **2** was carried out by NMR and FT-IR spectroscopy, allowing the proposal of a structure in which the aluminum centers are coordinated through a dative bond to the nitrogen atoms of the benzodiiimidazole-diylidene moiety.

These adducts were shown to be effective catalysts for the preparation of cyclic carbonates from terminal epoxides and  $\text{CO}_2$  using tetrabutylammonium iodide as a co-catalyst under solvent-free conditions. Initially, the election of the co-catalyst was optimized and

TBAI was selected as the best co-catalyst over TBAB, TBAC, and TBAF, probably due to the ion pairing effect. It is important to mention that the incorporation of benzodiimidazole-diylidene ligands with the  $\text{Al}(\text{CH}_3)_3$  precursor significantly improved the catalytic activity of the synthesized adducts compared to the adduct pyridine– $\text{Al}(\text{CH}_3)_3$ . It is also remarkable that the adducts prepared in this work (**1**, **2**, and pyridine– $\text{Al}(\text{CH}_3)_3$ ) achieved higher activity than the  $\text{Al}(\text{CH}_3)_3$  precursor, which confirms that adduct preparation is beneficial for the synthesis of cyclic carbonates. Adduct **1** displayed higher catalytic activity than **2** for the synthesis of styrene carbonate (**3a**), since the steric hindrance of isopropyl groups is lower than that of cyclohexyl, which facilitates the approach of the epoxide to the catalyst. Adduct **1** was able to prepare a wide variety of monosubstituted cyclic carbonates **3a–o** under relatively moderate reaction conditions (70 °C and 1 bar  $\text{CO}_2$  pressure for 24 h).

After analyzing the catalytic results for the preparation of cyclic carbonates between **1**/TBAI and other previously reported aluminum catalysts, it can be concluded that the catalytic system developed in this work was among the most active at 1 bar of  $\text{CO}_2$  pressure, which confirms that the preparation of new adducts could be stimulating for this catalytic process.

It is important to note that these compounds are the first alkyl aluminum adducts supported by benzodiimidazole-diylidene ligands which have been used in the formation of cyclic carbonates from epoxides and  $\text{CO}_2$ . Further research will be directed toward the development of novel ligands that allow the design of new multinuclear aluminum adducts that could be utilized for the transformation of  $\text{CO}_2$  into cyclic carbonates.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/2073-4344/11/1/2/s1>, Figure S1:  $^1\text{H}$  NMR spectrum for alkyl aluminum adduct **1** in  $\text{C}_6\text{D}_6$ ; Figure S2:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum for alkyl aluminum adduct **1** in  $\text{C}_6\text{D}_6$ ; Figure S3:  $^1\text{H}-^1\text{H}$  COSY NMR spectrum for alkyl aluminum adduct **1** in  $\text{C}_6\text{D}_6$ ; Figure S4:  $^{13}\text{C}\{^1\text{H}\}$ -HMQC NMR spectrum for alkyl aluminum adduct **1** in  $\text{C}_6\text{D}_6$ ; Figure S5:  $^{13}\text{C}\{^1\text{H}\}$ -HMQC NMR spectrum for alkyl aluminum adduct **1** in  $\text{C}_6\text{D}_6$  (range (−1.1)–1.7 ppm in  $^1\text{H}$ -NMR and (−7.5)–42.0 ppm in  $^{13}\text{C}$ -NMR); Figure S6:  $^{13}\text{C}\{^1\text{H}\}$ -HMQC NMR spectrum for alkyl aluminum adduct **1** in  $\text{C}_6\text{D}_6$  (range 3.0–8.2 ppm in  $^1\text{H}$ -NMR and 42.0–105.0 ppm in  $^{13}\text{C}$ -NMR); Figure S7: FT-IR spectrum for alkyl aluminum adduct **1** (red) versus benzodiimidazole-diylidene ligand **L**<sub>1</sub> (black); Figure S8:  $^1\text{H}$  NMR spectrum for alkyl aluminum adduct **2** in  $\text{C}_6\text{D}_6$ ; Figure S9:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum for alkyl aluminum adduct **2** in  $\text{C}_6\text{D}_6$ ; Figure S10:  $^1\text{H}-^1\text{H}$  COSY NMR spectrum for alkyl aluminum adduct **2** in  $\text{C}_6\text{D}_6$ ; Figure S11:  $^{13}\text{C}\{^1\text{H}\}$ -HMQC NMR spectrum for alkyl aluminum adduct **2** in  $\text{C}_6\text{D}_6$ ; Figure S12:  $^{13}\text{C}\{^1\text{H}\}$ -HMQC NMR spectrum for alkyl aluminum adduct **2** in  $\text{C}_6\text{D}_6$  (range (−0.8)–2.4 ppm in  $^1\text{H}$ -NMR and (−12.0)–45.0 ppm in  $^{13}\text{C}$ -NMR); Figure S13:  $^{13}\text{C}\{^1\text{H}\}$ -HMQC NMR spectrum for alkyl aluminum adduct **2** in  $\text{C}_6\text{D}_6$  (range 2.5–8.2 ppm in  $^1\text{H}$ -NMR and 53.0–103.0 ppm in  $^{13}\text{C}$ -NMR); Figure S14: FT-IR spectrum for alkyl aluminum adduct **2** versus benzodiimidazole-diylidene ligand **L**<sub>2</sub>; Figure S15: NMR spectra for styrene carbonate **3a** in  $\text{CDCl}_3$ ; Figure S16: NMR spectra for propylene carbonate **3b** in  $\text{CDCl}_3$ ; Figure S17: NMR spectra for 1,2-butylene carbonate **3c** in  $\text{CDCl}_3$ ; Figure S18: NMR spectra for 1,2-hexylene carbonate **3d** in  $\text{CDCl}_3$ ; Figure S19: NMR spectra for glycerol carbonate **3e** in  $[\text{D}_6]\text{DMSO}$ ; Figure S20: NMR spectra for 3-phenoxypropylene carbonate **3f** in  $\text{CDCl}_3$ ; Figure S21: NMR spectra for 3-chloropropylene carbonate **3g** in  $\text{CDCl}_3$ ; Figure S22: NMR spectra for 4-chlorostyrene carbonate **3h** in  $\text{CDCl}_3$ ; Figure S23: NMR spectra for 4-bromostyrene carbonate **3i** in  $\text{CDCl}_3$ ; Figure S24: NMR spectra for 4-((2,2,3,3-tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one **3j** in  $\text{CDCl}_3$ ; Figure S25: NMR spectra for 4-(((2,2,3,3,4,4,5,5-Octafluoropentyl)oxy)methyl)-1,3-dioxolan-2-one **3h** in  $\text{CDCl}_3$ ; Figure S26: NMR spectra for 4-((allyloxy)methyl)-1,3-dioxolan-2-one **3l** in  $\text{CDCl}_3$ ; Figure S27: NMR spectra for 4-((benzyloxy)methyl)-1,3-dioxolan-2-one **3m** in  $\text{CDCl}_3$ ; Figure S28: NMR spectra for 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) **3n** in  $\text{CDCl}_3$ ; Figure S29: NMR spectra 1,2-decylene carbonate **3o** in  $\text{CDCl}_3$ .

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