Ammonium zincates as suitable catalyst for the room temperature cycloaddition of CO_2 to epoxides

1   **Nicola Panza[1], Matteo Alberti[1], Caterina Damiano[1], Alessandro Caselli[1*]**

2   [1] Department of Chemistry, Università degli Studi di Milano, and CNR-SCITEC, via Golgi 19,
3   20133 Milano, Italy.

4   *** Correspondence:**
5   Alessandro Caselli (Ocid ID: 0000-0002-5851-267X)
6   alessandro.caselli@unimi.it
7   https://sites.unimi.it/caselligroup/

8   **Keywords: Homogeneous catalysis, Zinc, Chemical utilization of CO_2, Cyclic carbonates,**
9   **Zincates. (Min.5-Max. 8)**

10 **Abstract**

11 We have recently shown that simple ammonium ferrates are competent catalyst for the cycloaddition
12 reaction of CO_2 to epoxides under moderate reaction conditions (T = 100 °C, P(CO_2) = 0.8 MPa). We
13 report here that ammonium zincates of general formulae $[TBA]_2[ZnX_4]$ (TBA =
14 tetrabutylammonium), simply obtained by treating an ethanolic solution of an appropriate zinc(II)
15 salt with two equivalents of tetrabutylammonium halides, outperform ammonium ferrates in the
16 synthesis of cyclic carbonates under milder reaction conditions (room temperature and atmospheric
17 CO_2 pressure). Using **$[TBA]_2[ZnBr_4]$** complex as homogeneous catalyst at 100 °C and P(CO_2) = 0.8
18 MPa a 52% conversion of styrene oxide with complete selectivity in styrene carbonate in just 15 min
19 was observed, corresponding to a Turnover frequency (TOF) of 416 h^{-1}. The same catalyst proved to
20 be very active even at room temperature and atmospheric or very moderate CO_2 pressures (0.2 MPa),
21 with a quite broad range of substrates, especially in the case of terminal epoxides, with high
22 selectivity towards cyclic carbonate products. The difference in reactivity of terminal and internal
23 epoxides could be exploited using 4-vinylcyclohexene dioxide, where the endocyclic epoxide
24 remained untouched when reacted at room temperature and the formation of the di-carbonate product
25 was observed only at harsher conditions. A multigram scale conversion of propylene oxide was
26 achieved (46 mmol) and the catalyst also proved to be recyclable (3 cycles) by distillation of the
27 product and subsequent addition of fresh reagent, maintaining high conversion values and complete
28 selectivity for propylene carbonate. This simple zinc-based catalytic system, which outperform the
29 recently reported iron-based one by working at much milder conditions, could represent a valuable
30 prospect in both laboratory and industrial scale, combining an inherent cheapness and synthetic
31 easiness that should be deeply considered when the goal is to give value to a *waste* product as CO_2.

32

33 **1   Introduction**

34 The growing interest in the use of greenhouse gas CO_2 as C1 building block in organic synthesis is
35 strongly correlated to the urgent need to find a solution towards the challenges that we are facing in
36 terms of global carbon emission and the new paradigm in managing the carbon cycle (Martens et al.,

37 2017; Das, 2020). Obviously, the replacement of fossil fuels-based chemistry cannot be the sole
38 solution, but the new technologies based on the substitution of non-sustainable feedstock into
39 renewable ones will help to the transition to a circular economy (Gabrielli et al., 2020; Modak et al.,
40 2020). In this regard, ring strained small heterocycles, such as aziridines and epoxides play a
41 prominent role in the field (Intrieri et al., 2019), since due to the high energy associated with these
42 molecules, reaction with thermodynamically stable CO_2 occurs smoothly (Dalpozzo et al., 2019). In
43 particular, the selective formation of cyclic carbonates (Sit et al., 2005; Aomchad et al., 2021a) or
44 polycarbonates (Inoue et al., 1969; Inoue, 1979) from the coupling reaction of epoxides with carbon
45 dioxide represents a highly coveted target and it is amongst the few processes that employ CO_2 as C1
46 feedstock that has been industrialized until now (Liu et al., 2015; Pescarmona, 2021). One the one
47 side, the use of high energy substrates such as epoxides provides the necessary driving force to
48 overcome the thermodynamical stability and kinetic inertness associated with the CO_2 molecule,
49 which is the most oxidized form of carbon (Bai et al., 2021). On the other side, in order to achieve a
50 close carbon cycle, catalysis and catalyst design are critical aspect in order to lower the energetic
51 requirements of the reaction and to limit the use of harsh reaction conditions (Keijer et al., 2019). For
52 that reason, a continuous effort, especially in the last decade, has been made to develop new catalysts
53 to promote this useful transformation under mild working conditions and with high efficiency
54 (Shaikh et al., 2018). Generally, both a Lewis acid (LA) and a Lewis base are necessary respectively
55 to activate the epoxide and for the nucleophilic attack that causes its ring opening (Pescarmona,
56 2021; Bhat and Darensbourg, 2022). Following that, the ring-opened epoxide can undergo either CO_2
57 insertion to form a carbonate or repetitive insertion to lead to polyether formation (Kamphuis et al.,
58 2019b). Especially in the case of less hindered terminal epoxides, once the carbonate is formed after
59 CO_2 insertion, a fast backbiting leads to the formation of industrially relevant cyclic carbonates
60 (Schäffner et al., 2010; Besse et al., 2013; Aresta et al., 2016; Sathish et al., 2016). Several very
61 efficient catalytic systems, either homogeneous (Castro-Osma et al., 2016; Rintjema and Kleij, 2017;
62 della Monica et al., 2018, 2019b, 2019a, 2020; Driscoll et al., 2019; Kamphuis et al., 2019a;
63 Damiano et al., 2020; Maquilón et al., 2020; Aomchad et al., 2021b) or heterogeneous (Liang et al.,
64 2019; Sodpiban et al., 2019, 2021; Wang et al., 2019; Singh Dhankhar et al., 2020; Liu et al., 2022b,
65 2022a), have recently been developed, where the former generally possess higher activities but lack
66 in recyclability. Very often the actual catalyst act as the Lewis acid and in most cases a co-catalyst,
67 typically organic halides, such as quaternary ammonium (Caló et al., 2002; Wang et al., 2012, 2021;
68 Montoya et al., 2015) or bis(triphenylphosphine)iminium salts (Sit et al., 2005), was added to
69 observe good reactivities. It is worth to note that in past literature, when a combination of a Lewis
70 acid (catalyst) and a Lewis base (co-catalyst) have been used to promote the coupling reaction
71 between CO_2 and epoxides, TOF values have been calculated only considering the amount of added
72 catalyst, neglecting the role played by the sole Lewis base (Campisciano et al., 2020). In the search of
73 more efficient catalysts, many recent efforts have been done in the design of materials embedding
74 both Lewis acidic and basic catalytic sites, for the CO_2 cycloaddition reaction under milder reaction
75 conditions, without the addition of any co-catalyst and both homogeneous (Tong et al., 2022) and
76 heterogeneous catalysts (Nguyen et al., 2022; Su et al., 2022) have been reported especially in the
77 last years. It should be noted that most of these catalysts work under solvent-free and ambient
78 pressure CO_2 reaction conditions, however the temperatures required to observe good conversion of
79 the starting epoxide are in the range 80-120 °C.

80 We have recently exploited the reactivity of tetrabutylammonium ferrates of the general formulae
81 [TBA][FeX$_3$Y] (TBA = ^{n}Bu$_4$N, X, Y = Cl, Br), that can be obtained from inexpensive chemicals such
82 as tetrabutylammonium halides and ferric salts (Wyrzykowski et al., 2006, 2007), as stand-alone
83 catalysts in the CO_2 cycloaddition to epoxides (Panza et al., 2022). The effect of the experimental
84 factors (reaction temperature, CO_2 pressure, type of nucleophile and recycling of the catalyst),

85   together with a full set of theoretical calculations, were studied in depth. Good yields of cyclic
86   carbonates were obtained, especially for terminal epoxides with a broad reaction scope. Reaction
87   conditions employed were quite mild, however, CO_2 pressures between 0.4 and 0.8 MPa and
88   temperatures between 100-150 °C were needed in order to observe full conversion with high
89   selectivity. We report here that analogous tetrabutylammonium zincates are competent catalysts for
90   the same selective transformation even at room temperature.

91   **2   Results and discussion**

92   **2.1   Synthesis of the ammonium zincates [TBA]$_2$[ZnX$_4$] (X = Cl, Br, I)**

93   A series of ammonium zincates, **[TBA]$_2$[ZnX$_4$]**, (X = Cl, Br, I) was synthesized by simply treating
94   an ethanolic solution of 2 equivalents of the appropriate tetrabutylammonium halide with 1
95   equivalent of the zinc salt. As detailed in the Materials and methods section and in the
96   Supplementary Material, ammonium zincates were obtained in good yields and purity by simple
97   recrystallization from cold methanol (-20 °C). The purity was confirmed by elemental analyses,
98   whilst accurate high resolution mass spectra were carried out in CH_3CN with the double aim to assess
99   the proposed structure and to study the equilibria between the undissociated dianion $[ZnX_4]^{2-}$ and the
100   solvated forms ($[ZnX_3]^- + X^-$) and ($ZnX_2 + 2X^-$). This kind of equilibria between "ate" and neutral
101   salts and its relevance to the nucleophilic ring opening of epoxides has been already disclosed by us
102   in the case of the tetrabutylammonium ferrates (Panza et al., 2022), and it was already predicted by
103   Capacchione and co-workers in the case of $[FeBr_4]^-$ anion (Della Monica et al., 2019b). Recently it
104   has been also disclosed the existence of such an equilibrium by Baalbaki *et al.* in the case of indium
105   bromide (Baalbaki et al., 2021). In the case of the tetrabutylammonium zincates, by ESI(-)-HRMS
106   the expected dianion $[ZnX_4]^{2-}$ was not found, but instead a more persistent monoanion $[ZnX_3]^-$ was
107   detected in the case of X = Cl, Br, while in the case of $[ZnI_4]^{2-}$ only I^- and I^{3-} were detected most
108   likely due to the higher lability of the compound. Table 1 collects the yields of the
109   tetrabutylammonium zincates synthesized and used as catalyst in the CO_2 cycloaddition to epoxides,
110   whilst for their synthesis and characterization (elemental analyses and HRMS), the reader is referred
111   to the Supplementary Material.

112   **2.2   Zincates catalyzed cyclic carbonate synthesis**

113   We used styrene epoxide (SO), **1a**, as the benchmark substrate to optimize the reaction conditions by
114   employing the different tetrahalogenozincates salts in solvent-free conditions. Since the optimized
115   conditions with the recently reported "ferrate" catalysts were found to be 0.5 mol% catalyst loading
116   at 100 °C and under 0.8 MPa of CO_2, initially we set there the starting point for the optimization
117   using tetrachloro-, tetrabromo- and tetraiodo-zincates. Under the previously described conditions,
118   when using **[TBA][FeCl$_3$Br]** as the catalyst, 83% of SO was converted into styrene carbonate (SC),
119   **2a**, in 4 h with 95% selectivity (Panza et al., 2022). To our delight, all the zincate catalysts tested
120   gave instead quantitative conversions of the starting epoxide in 4 h reaction time, with excellent
121   selectivity in the case of the bromide and iodide salts (94 and 95% respectively, entries 2 and 3,
122   Table 2). We should emphasize, however, that in this case 0.5 mol% of the catalyst contains the
123   double of equivalents of the ammonium cation with respect to the monoanionic ferrates analogues,
124   but we already showed that its role is limited essentially to a rigid shift of all energies towards lower
125   values (Panza et al., 2022). When we reduced the reaction time at 2h, we still observed a quantitative
126   conversion, except for **[TBA]$_2$[ZnCl$_4$]** as catalyst, with selectivity in the range 91-98% (entries 4-6,
127   Table 2). The most promising catalyst resulted to be the **[TBA]$_2$[ZnBr$_4$]** complex, that in just 1 h of
128   reaction converted 98% of starting **1a** with 96% selectivity in **2a** (entry 8, Table 2). As we already
129   noticed in the case of [Zn(II)pyclen] complexes reported recently as efficient catalysts for the

130 chemical fixation of CO_2 with epoxides (Cavalleri et al., 2021), the chloro-zincate salt was the less
131 active one. Among the three zincates, the activity increased in the order X = Cl$^-$ < I$^-$ < Br$^-$ (compare
132 entries 7, 8 and 9, Table 2) and this trend can be rationalized considering the following
133 considerations regarding the overall catalytic activity: i) lability of the halide from the zincate anion
134 (*vide supra*, ESI(-)-HRMS analyses); ii) the nucleophilicity of the halide in the ring opening of the
135 epoxide; and iii) the halide leaving group ability, in order to promote the cyclic carbonate formation
136 in the ring closing step (Kamphuis et al., 2019a). Given the aprotic media in which the reactions are
137 run, we must assume that the nucleophilicity increases in the order I$^-$ < Br$^-$ < Cl$^-$, whereas the leaving
138 ability decreases in the same order. Bromide seemed to provide the best balance between these three
139 properties, as already observed by us also for related ferrate complexes (Panza et al., 2021), thus
140 leading to the best observed catalytic activities. For instance, using **[TBA]$_2$[ZnBr$_4$]** salt as catalyst, a
141 52% conversion in just 15 min was observed, corresponding to the remarkable Turnover frequency
142 (TOF) of 416 h^{-1} (Entry 14, Table 2).

143 It is worth to note that, as known from the literature, the activity of simple quaternary ammonium
144 halides, *i.e.* TBAX, in this reaction is not negligible (Caló et al., 2002; Wang et al., 2012; Montoya et
145 al., 2015). However, we have already shown that under the same reaction conditions, both TBACl
146 and TBABr are underperforming, albeit maintaining very high selectivity (Panza et al., 2022). We
147 repeated the reaction under the same catalytic conditions by using TBAI that performed comparably
148 to the others ammonium halides and gave only a 42% conversion with 95% selectivity in **2a** (See
149 Supplementary Material). Finally, it should be pointed out that it has been reported that mixtures of
150 metal halides and alkylammonium iodides can act as suitable catalyst in the cyclic carbonate
151 synthesis (Kisch et al., 1986). However, ammonium zincates are less hygroscopic and easier to
152 handle than the respective starting materials (zinc and tetrabutyl ammonium halides) and we have
153 recently shown that in the case of tetrabutyl ammonium ferrates (Panza et al., 2022), a mixture of an
154 iron(III) salt with tetrabutyl ammonium halides indeed act as a catalyst, but with lower conversion
155 and TOF with respect to the pre-formed ammonium ferrate, so that there is no advantage in their *in*
156 *situ* synthesis.

2.3 Effect of the temperature and the CO_2 pressure

158 With the aim to find milder reaction conditions, we next studied the effect of lower temperatures and
159 CO_2 pressures on the reaction outcome. Initially we reduced the CO_2 pressure to 0.1 MPa and
160 reactions were performed in sealed vials with a CO_2 balloon at 100 °C. In all cases lower conversion
161 but especially lower selectivity, due to competing rearrangement side reactions of the starting SO,
162 were observed (entries 1-3, Table 3). When the same reactions were repeated at T = 50 °C, given to
163 the better solubility of CO_2 under these conditions, selectivity was again improved, albeit at the cost
164 of lower conversion (entries 4-6, Table 3). Finally, we tested the reactivity of the catalytic system at
165 room temperature (we set an equilibrating bath at 30 °C in order to have reproducible results) and
166 under CO_2 pressure (0.8 MPa) in autoclave. In this case we used a 1 mol% catalyst loading and we
167 extended the reaction time to 16 h. Again, the less active catalyst resulted to be the chloro-zincate
168 salt, that gave only a 11% conversion of the starting epoxide (entry 7, Table 3), whilst both
169 **[TBA]$_2$[ZnBr$_4$]** and **[TBA]$_2$[ZnI$_4$]** gave almost quantitative conversions with full selectivity towards
170 **2a** (entries 8 and 9, Table 3).

2.4 Effect of the catalyst loading

172 Since the best compromise between activity and selectivity was always found with **[TBA]$_2$[ZnBr$_4$]**
173 as the catalyst, we decided to further optimize the reaction conditions and to study the scope of the
174 reaction using this complex. Our aim was to find the mildest conditions to run the reaction, with the

175 best compromise between catalyst loading, temperature and CO_2 pressure. To do so, we initially set
176 room temperature (25 °C) and atmospheric CO_2 pressure as the target and we changed the catalyst
177 loading in order to maximize the yield of SC **2a**. Reactions were performed by assuring CO_2
178 atmosphere with a balloon. We noticed that in 24 h of reactions, the conversion observed of starting
179 SO **1a** was not linearly correlated with the catalyst loading. If 0.5 mol % of catalyst at 25 °C
180 converted 34% of the starting epoxide with good selectivity, with a reasonable TOF of 2.8 h^{-1}, a
181 double amount of the catalyst gave only the 47% of conversion, with a TOF of 2.0 h^{-1} (entries 1 and
182 2, Table 4). Surprisingly, a 5 mol% amount of catalyst gave the same conversion (entry 3, Table 4),
183 corresponding to a TOF of only 0.4 h^{-1}. This negative result was not justified by solubility limits of
184 the zincate salt in neat epoxide **1a**. We reasoned that this effect might be due to inhibition of the
185 catalyst by the product formation or to the fact that despite the presence of the balloon, CO_2
186 concentration after prolonged reaction times started to diminish. It is known that rubber balloons are
187 not gas-tight and that carbon dioxide may leak through (Edwards and Pickering). To test this
188 hypothesis, we repeated the same reaction, but working under CO_2 flow at atmospheric pressure and
189 we observed an increased conversion (69%) of starting **1a**, with complete selectivity in favor of the
190 SC, **2a**, and with an increased TOF of 4.3 h^{-1} (entry 5, Table 4).

191 Since the CO_2 wasted working under constant bubbling is however a limiting factor, we next
192 monitored the effect of the catalyst loading working at room temperature but increasing CO_2 pressure
193 up to 0.8 MPa in autoclave (entries 6-8, Table 4). A loading of just 0.1 mol% of the catalyst was too
194 low and only a 5% of conversion was observed, whilst even at room temperature a gratifying TOF of
195 7.3 h^{-1} was observed with a 0.5 mol% of **[TBA]$_2$[ZnBr$_4$]**. The best compromise between conversion
196 and selectivity was obtained by using a 1 mol% loading of the catalyst. When we repeated the same
197 reaction with just 0.2 MPa of CO_2 pressure, we obtained almost identical results (entry 9, Table 4),
198 proving that pressure is not a limiting factor while providing a sufficient quantity of CO_2 and thus we
199 set those as the optimal conditions to further study the reaction scope.

200 ## 2.5 Reaction scope

201 Having in hand the best catalyst, **[TBA]$_2$[ZnBr$_4$]**, and the optimized reaction conditions, room
202 temperature (T = 30 °C), solvent free and 0.2 MPa of CO_2 pressure, we next studied the reaction
203 scope by changing the steric and electronic factors of the starting epoxide. Results are summarized in
204 Table 5. All terminal epoxides tested were well tolerated and cyclic carbonates were formed in good
205 to excellent yields. Surprisingly, the activated epichlorohydrin **1b**, in the optimized reaction
206 conditions gave only a modest 64% conversion, albeit with full selectivity for the cyclic carbonate **2b**
207 (entry 1, Table 5). Linear alkyl substituted epoxides, **1c-e**, were all transformed with high
208 selectivities (>99%) into cyclic carbonates, **2c-e**. The best results in terms of conversion, with a
209 remarkable TOF of 6.2 h^{-1}, were observed in the case of 1,2-epoxyhexane **2e** (entry 5, Table 5). The
210 observed reactivity trend is the opposite to that we have found for the related cycloaddition reaction
211 of CO_2 to epoxide catalyzed by **[TBA][FeCl$_3$Br]**, where we observed a decreased reactivity of the
212 catalytic system in less polar media (Panza et al., 2022). We thus repeated the reaction of propylene
213 epoxide, **1c**, at the same temperature but with an increased CO_2 pressure (1 MPa) and we observed a
214 slightly improved conversion rate (entry 3, Table 5). Several glycidyl ethers, **1f-j**, were also tested
215 and very high conversion with excellent selectivity in favor of the cyclic carbonate was observed
216 (entries 6-10, Table 5). The only exceptions were phenyl glycidyl ether, **1g**, and 2-methylphenyl
217 glycidyl ether, **1h**, were an off-white tar, most probably due to polymeric material, was also formed
218 in 24% selectivity. The presence of a coordinating heterocyclic group such as in the case of furfuryl
219 glycidyl ether, **1j**, was well tolerated and a TOF of 5.4 h^{-1} was observed (entry 10, Table 5). Internal
220 or more sterically hindered epoxides, as expected (Kamphuis et al., 2019a), gave less satisfactory

221 results and *trans*-Stilbene epoxide, **1k**, almost failed to react (entry 12, Table 5). It should be noted,
222 however, that in this case, since this product is solid at room temperature, CH_3CN (0.5 mL) was
223 added to the reaction mixture as the solvent. 1,2-Epoxy-methylpropane, **1l**, and cyclohexene oxide,
224 **1m**, on the other hand could be converted to the corresponding cyclic carbonates only under harsher
225 reaction conditions (T = 100 °C, $P(CO_2)$ = 0.8 MPa, entries 13 and 15, Table 5). However, it should
226 be emphasized that, especially in the case of cyclohexene oxide, generally considered a less reactive
227 epoxide (della Monica et al., 2019a), when increasing the pressure to 1.6 MPa and running the
228 reaction for 16 h we observed a remarkable yield (80%; 89% selectivity) of cyclic carbonate **2i**, and
229 no formation of any polymeric material (entry 16, Table 5). A trisubstited epoxide such as
230 limonene oxide, **1n**, failed to react also under those harsher reaction conditions (entry 17, Table 5).

231 This difference in reactivity between terminal and more sterically hindered epoxides could be
232 switched from a disadvantage to a selective useful tool. For example, when we reacted 4-
233 vinylcyclohexene dioxide, **1o**, containing both a terminal and an internal epoxide, at room
234 temperature and low CO_2 pressure, (0.2 MPa), we observed a 78% conversion of the starting material
235 with the selective formation of the cyclic carbonate at the less substituted epoxide, **2o** (Scheme 1,
236 right). When the reaction was repeated with a double amount of catalyst (1 mol% of **[TBA]₂[ZnBr₄]**
237 for each epoxide present in the substrate) and under harsher reaction conditions, T = 100 °C and 0.8
238 MPa of CO_2, we observed a quantitative conversion of the starting epoxide, with a 72% selectivity in
239 favor of the mono-cyclic carbonate, **2o**, and a 28% selectivity for the di-carbonate product **2o'**
240 (Scheme 1, left), proving that modulating the reaction conditions can affect strongly the chemo-
241 selectivity of such reaction.

242 Finally, other two terminal di-epoxides were tested as substrates for their possible application as non-
243 isocyanate polyurethane monomers (Rix et al., 2016). In both cases, CH_3CN was successfully
244 employed as solvent and 2 mol% of catalyst loading was employed (1 mol% per mol of epoxide
245 moiety). The *bis*-carbonate of (bisphenol-A)diglycidyl ether (BADGE), **2p**, was obtained in 64%
246 yield (85% selectivity, 75% conversion of starting **1p**) in 16 h at 30 °C. To the best of our
247 knowledge, this is the highest yield obtained under such mild reaction conditions for this very
248 interesting product (Scheme 2). Under the same reaction conditions, 1,4-*bis*(benzyloxy)diglycidyl
249 ether was converted in the *bis*-carbonate product **2q** with a 52% yield (91% selectivity, 57%
250 conversion of starting **1o**, Scheme 3), outperforming our previously reported synthesis employing
251 ferrates as catalysts (Panza et al., 2022).

252 **2.6 Scale-up and recycling**

253 The ability of a catalytic system to undergo a scale-up reaction is an important feature that gives a
254 preliminary idea about a possible industrial application. For this reason, we tested **[TBA]₂[ZnBr₄]** in
255 the cycloaddition of propylene oxide **1c** and CO_2 in a multigram scale reaction, using 1 mol%
256 catalyst loading and 3.24 mL (46 mmol) of PO at 1.0 MPa CO_2 pressure, T = 30 °C for 16 hours. The
257 product mixture was weighted and analyzed by ^{1}H NMR analysis. At the end of the reaction only
258 propylene carbonate **2c** was recovered with a remarkable isolated yield of 94%, corresponding to
259 4.250 g of PC. Moreover, the possibility to recycle the catalyst for further reactions is indeed crucial,
260 even if not always simple in the case of homogeneous systems. In our case, the product of the scale
261 up reaction was distilled in vacuum to obtain pure propylene carbonate and pure **[TBA]₂[ZnBr₄]**. To
262 the latter, 46 mmol of fresh propylene oxide were added and the mixture was subjected to the same
263 procedure described before. The product was obtained and analyzed as previously detailed, obtaining
264 again propylene carbonate as the sole product (selectivity for **2c** >99%). The robustness of the
265 catalyst was assured for a total of 3 cycles, after which a total of amount of 12.65 g of pure **2c** was

266   obtained (results are summarized in the Supplementary Material). **[TBA]₂[ZnBr₄]** as a catalyst
267   proved to be recyclable without losing activity nor selectivity, making it an attractive tool for a
268   possible further large-scale study.

269   **3**   **Conclusions**

270   In summary, we have shown that very simple inexpensive tetrabutylammonium zincates are efficient
271   catalyst, without the need of any co-catalyst and in the absence of any solvent, for the cycloaddition
272   of CO_2 to epoxides under mild reaction conditions. The bifunctional nature of the catalyst, both as
273   Lewis acid and nucleophilic Lewis base, is assured by the "ate" equilibrium between the dianoinic
274   zincate salt and the monoanionic $[ZnX_3]^-$ moiety and the halide anion. We have recently reported a a
275   theoretical calculation of the reaction mechanism and the role played by the combination of the
276   Lewis acid (iron salt) and nucleophile (halide ion) in the case of the ammonium ferrate catalyzed
277   cycloaddition of CO_2 to epoxides (Panza et al., 2022). The formation of the cyclic carbonate can be
278   schematized as occurring in three consecutive steps, in agreement with literature results (Pescarmona,
279   2021): (a) the halide anion act as the nucleophile attacking a carbon atom of the epoxide ring, which
280   opens by breaking a C-O bond in a concerted mechanism; (b) the oxygen atom of the former epoxide
281   attacks the C atom of carbon dioxide thus forming an open carbonate species; (c) the carbonate closes
282   the ring and the formation of a C-O bond induces simultaneous breaking of the carbon - halide bond,
283   releasing the halide ion. Although DFT calculations were not performed in the present case, we must
284   assume that the also in this case zinc act as a Lewis acid lowering the barrier for the ring opening of
285   the epoxide and stabilizing the first reaction intermediate (the open epoxide species). When no Lewis
286   acid is present, the rate determining step of the whole process is the epoxide ring-opening. On the
287   other hand, when the zinc atom interacts with the oxygen of the epoxide, this transition state is
288   lowered in energy and the rate determining step becomes the ring closure to give the cyclic
289   carbonate.
290   The best catalytic performances have been obtained by using the bromide-zincate **[TBA]₂[ZnBr₄]**,
291   which can be conveniently prepared in high yield and purity by mixing an ethanolic solution of
292     $ZnBr_2$ with TBABr, and a TOF of 416 h^{-1} in the styrene carbonate synthesis at T = 100 °C has been
293   observed. It should be emphasized, from a practical point of view, that the handling of the zincates
294   salts, that are less hygroscopic than their staring materials, is easy and does not require any special
295   caution. Moreover, all the zincate tested proved to be quite robust and at the end of the reaction they
296   can be recovered by simply distilling off the organic products formed (cyclic carbonates).
297   Remarkably, quantitative conversion of terminal epoxides with full selectivity towards the cyclic
298   carbonate have been obtained at low temperature (T = 30 °C) and under just 0.2 MPa of CO_2
299   pressure. Reactions occur smoothly also at room temperature and under atmospheric CO_2, at a big
300   difference from most recently reported homogeneous (Tong et al., 2022) and heterogeneous (Nguyen
301   et al., 2022; Su et al., 2022) systems operating without any co-catalyst added and in solvent free
302   conditions, that normally are reported to be most performing at T 80 – 120 °C.
303   Finally, the recyclability of the **[TBA]₂[ZnBr₄]** salt has been assessed by distilling off the pure
304   propylene carbonate formed in the reaction with propylene oxide and restoring the catalytic cycle
305   three times without any loss of catalytic activity observed. Reaction could also be scaled up and a
306   total amount of 12.65 g of pure PC could be isolated with a global TON of 279. Based on these
307   results, we think that amongst the several homogeneous catalysts reported in the last years for the
308   synthesis of cyclic carbonates by cycloaddition of CO_2 to epoxides, terabutylammonium zincates
309   represents a considerable case of study for highly efficient greenhouse gas re-utilization.

310   **4**   **Materials and Methods**

311   **4.1**   **General considerations**

312 All chemicals and solvents were commercially available and used as received except where specified.
313 ^{1}H NMR analyses were performed with 400 MHz spectrometers at room temperature. The coupling
314 constants (J) are expressed in hertz (Hz), and the chemical shifts (δ) in ppm. Catalytic tests were
315 analysed by ^{1}H NMR spectroscopy. Low resolution MS spectra were acquired with instruments
316 equipped with ESI/ion trap sources. High resolution MS spectra were acquired on a Q-ToF SYNAPT
317 G2-Si HDMS 8K instrument (Waters) equipped with a ZsprayTM ESI source (Waters). The values
318 are expressed as mass−charge ratio and the relative intensities of the most significant peaks are
319 shown in brackets. Elemental analyses were recorded in the analytical laboratories of Università degli
320 Studi di Milano. The collected data for all the cyclic carbonate reported are in accordance with those
321 reported in literature. (Yu et al., 2021; Panza et al., 2022)

4.2   Synthesis of the zincate salts

323 All the tetrahalogenozincate salts were prepared following a slightly modified procedure reported for
324 the synthesis of the ferrate analogues (Panza et al., 2022), by mixing in an appropriate stoichiometric
325 ratio an ethanolic solution of **TBAX** and **ZnX$_2$** with good yield, after recrystallization (Table 1). All
326 the so-prepared materials were analysed by Elemental Analysis and HRMS. All the details about the
327 synthesis and analyses can be found in the Supplementary Materials.

4.3   General catalytic procedure in autoclave

329 A 250 mL stainless steel autoclave reactor was equipped with three 2.5 mL glass vials, containing the
330 catalyst/epoxide mixture (250 µL of substrate). The vials were equipped with magnetic stirring bars
331 and sealed with specific caps. The autoclave was then charged with a specific amount of CO_2 and
332 placed in a thermostated heating bath for a specific amount of time. The reactor was then cooled to
333 room temperature (when needed) and the CO_2 released. To each vial the appropriate amount of the
334 internal standard (mesitylene) and 0.5 mL of CDCl$_3$ were added to perform quantitative ^{1}H NMR
335 analysis.

4.4   General catalytic procedure in sealed vials

337 Reactions performed at ambient pressure of CO_2 were placed in glass vials containing the epoxide,
338 the catalyst and a magnetic stirring bar, sealed with a silicon septum and aluminium cap. A CO_2
339 balloon, sealed to a plastic syringe, was inserted in the vial using a needle to ensure the pressure of
340 CO_2. At the end of the reaction, the appropriate amount of the internal standard (mesitylene) and 0.5
341 mL of CDCl$_3$ were added to perform quantitative ^{1}H NMR analysis.

5   Conflict of Interest

343 The authors declare that the research was conducted in the absence of any commercial or financial
344 relationships that could be construed as a potential conflict of interest.

6   Author Contributions

346 **Nicola Panza**: Data curation and experimental procedures, Writing - original draft, Visualization.
347 **Matteo Alberti**: Data curation and experimental procedures. **Caterina Damiano**: Data analysis and
348 Writing – review & editing. **Alessandro Caselli**: Conceptualization, Methodology, Writing – original
349 draft, review & editing, Supervision, Project administration, Funding acquisition. All the authors
350 critically revised and approved the final version of the manuscript.

7   Funding

352 This work was supported by the University of Milan (PSR 2020 – financed project ''Catalytic
353 strategies for the synthesis of high added-value molecules from bio-based starting materials'').

354 **8   Acknowledgments**

361 **9   Supplementary Material**

362 Experimental details of the synthetic procedures and the catalytic reactions, HRMS analyses and ^{1}H
363 NMR data, are given in the Supplementary Material.

364 **10   References**

365 Aomchad, V., Cristòfol, À., Della Monica, F., Limburg, B., D'Elia, V., and Kleij, A. W. (2021a).
366   Recent progress in the catalytic transformation of carbon dioxide into biosourced organic
367   carbonates. *Green Chem.* 23, 1077–1113. doi: 10.1039/d0gc03824e.

368 Aomchad, V., del Gobbo, S., Yingcharoen, P., Poater, A., and D'Elia, V. (2021b). Exploring the
369   potential of group III salen complexes for the conversion of CO_2 under ambient conditions.
370   *Catal. Today* 375, 324–334. doi: 10.1016/J.CATTOD.2020.01.021.

371 Aresta, M., Dibenedetto, A., and Quaranta, E. (2016). State of the art and perspectives in catalytic
372   processes for CO_2 conversion into chemicals and fuels: The distinctive contribution of chemical
373   catalysis and biotechnology. *J. Catal.* 343, 2–45. doi: https://doi.org/10.1016/j.jcat.2016.04.003.

374 Baalbaki, H. A., Roshandel, H., Hein, J. E., and Mehrkhodavandi, P. (2021). Conversion of dilute
375   CO_2 to cyclic carbonates at sub-atmospheric pressures by a simple indium catalyst. *Catal. Sci.*
376   *Technol.* 11, 2119–2129. doi: 10.1039/d0cy02028a.

377 Bai, S. T., de Smet, G., Liao, Y., Sun, R., Zhou, C., Beller, M., et al. (2021). Homogeneous and
378   heterogeneous catalysts for hydrogenation of CO_2 to methanol under mild conditions. *Chem.*
379   *Soc. Rev.* 50, 4259–4298. doi: 10.1039/d0cs01331e.

380 Besse, V., Camara, F., Voirin, C., Auvergne, R., Caillol, S., and Boutevin, B. (2013). Synthesis and
381   applications of unsaturated cyclocarbonates. *Polym. Chem.* 4, 4545–4561. doi:
382   10.1039/C3PY00343D.

383 Bhat, G. A., and Darensbourg, D. J. (2022). Progress in the catalytic reactions of CO2 and epoxides
384   to selectively provide cyclic or polymeric carbonates. *Green Chem.*, 5007–5034. doi:
385   10.1039/d2gc01422j.

386 Caló, V., Nacci, A., Monopoli, A., and Fanizzi, A. (2002). Cyclic carbonate formation from carbon
387   dioxide and oxiranes in tetrabutylammonium halides as solvents and catalysts. *Org. Lett.* 4,
388   2561–2563. doi: 10.1021/ol026189w.

389 Campisciano, V., Calabrese, C., Giacalone, F., Aprile, C., lo Meo, P., and Gruttadauria, M. (2020).
390   Reconsidering TOF calculation in the transformation of epoxides and CO_2 into cyclic
391   carbonates. *J. CO2 Util.* 38, 132–140. doi: https://doi.org/10.1016/j.jcou.2020.01.015.

392 Castro-Osma, J. A., Lamb, K. J., and North, M. (2016). Cr(salophen) Complex Catalyzed Cyclic
393   Carbonate Synthesis at Ambient Temperature and Pressure. *ACS Catal.* 6, 5012–5025. doi:
394   10.1021/acscatal.6b01386.

395 Cavalleri, M., Panza, N., Biase, A., Tseberlidis, G., Rizzato, S., Abbiati, G., et al. (2021).
396   [Zinc(II)(Pyridine-Containing Ligand)] Complexes as Single-Component Efficient Catalyst for
397   Chemical Fixation of CO_2 with Epoxides . *Eur. J. Org. Chem.* 2021, 2764–2771. doi:
398   10.1002/ejoc.202100409.

399 Dalpozzo, R., Ca, N. della, Gabriele, B., and Mancuso, R. (2019). Recent advances in the chemical
400   fixation of carbon dioxide: A green route to carbonylated heterocycle synthesis. *Catalysts* 9. doi:
401   10.3390/catal9060511.

402 Damiano, C., Sonzini, P., Intrieri, D., and Gallo, E. (2020). Synthesis of cyclic carbonates by
403   ruthenium(VI) bis -imido porphyrin/TBACl-catalyzed reaction of epoxide with CO_2. *J.Porphyr.*
404   *Phthalocyanines* 24, 809–816. doi: 10.1142/S1088424619501888.

405 Das, S., (2020) CO_2 as a Building Block in Organic Synthesis, John Wiley & Sons. doi:
406   10.1002/9783527821952.

407 Della Monica, F., Buonerba, A., Capacchione, C., (2019a). Homogeneous Iron Catalysts in the
408   Reaction of Epoxides with Carbon Dioxide. *Adv. Synth. Catal.* 361, 265–282. doi:
409   10.1002/adsc.201801281.

410 Della Monica, F., Buonerba, A., Paradiso, V., Milione, S., Grassi, A., Capacchione, C., et al.
411   (2019b). [OSSO]-Type Fe(III) Metallate as Single-Component Catalyst for the CO_2
412   Cycloaddition to Epoxides. *Adv. Synth. Catal.* 361, 283–288. doi: 10.1002/adsc.201801240.

413 Della Monica, F., Maity, B., Pehl, T., Buonerba, A., de Nisi, A., Monari, M., et al. (2018). [OSSO]-
414   Type Iron(III) Complexes for the Low-Pressure Reaction of Carbon Dioxide with Epoxides:
415   Catalytic Activity, Reaction Kinetics, and Computational Study. *ACS Catal.* 8, 6882–6893. doi:
416   10.1021/acscatal.8b01695.

417 Della Monica, F., Paradiso, V., Grassi, A., Milione, S., Cavallo, L., and Capacchione, C. (2020). A
418   Novel [OSSO]-Type Chromium(III) Complex as a Versatile Catalyst for Copolymerization of
419   Carbon Dioxide with Epoxides. *Chem. Eur. J.* 26, 5347–5353. doi: 10.1002/chem.201905455.

420 Driscoll, O. J., Hafford-Tear, C. H., McKeown, P., Stewart, J. A., Kociok-Köhn, G., Mahon, M. F., et
421   al. (2019). The synthesis, characterisation and application of iron(iii)-acetate complexes for
422   cyclic carbonate formation and the polymerisation of lactide. *Dalton Trans.* 48, 15049–15058.
423   doi: 10.1039/c9dt03327k.

424 Edwards, J. D., and Pickering, S. F. (1920). Permeability of rubber to gases. *Scientific Papers of the*
425   *Bureau of Standards* 16, 327–361. doi: https://dx.doi.org/10.6028/nbsscipaper.062.

426 Gabrielli, P., Gazzani, M., and Mazzotti, M. (2020). The Role of Carbon Capture and Utilization,
427   Carbon Capture and Storage, and Biomass to Enable a Net-Zero-CO2 Emissions Chemical
428   Industry. *Ind. Eng. Chem. Res.* 59, 7033–7045. doi: 10.1021/acs.iecr.9b06579.

429 Inoue, S. (1979). Copolymerization of Carbon Dioxide and Epoxide. *Am. Chem. Soc. Div. Polym.*
430   *Chem. Prepr.* 20, 142–145. doi: 10.1007/978-94-009-3923-3_18.

431 Inoue, S., Koinuma, H., and Tsuruta, T. (1969). Copolymerization of carbon dioxide and epoxide. *J.*
432   *Polym. Sci. B Poly. Lett.* 7, 287–292. doi: https://doi.org/10.1002/pol.1969.110070408.

433 Intrieri, D., Damiano, C., Sonzini, P., and Gallo, E. (2019). Porphyrin-based homogeneous catalysts
434   for the CO 2 cycloaddition to epoxides and aziridines. *J. Porphyr. Phthalocyanines* 23, 305–
435   328. doi: 10.1142/S1088424619300015.

436 Kamphuis, A. J., Milocco, F., Koiter, L., Pescarmona, P. P., and Otten, E. (2019a). Highly Selective
437   Single-Component Formazanate Ferrate(II) Catalysts for the Conversion of CO2 into Cyclic
438   Carbonates. *ChemSusChem* 12, 3635–3641. doi: 10.1002/cssc.201900740.

439 Kamphuis, A. J., Picchioni, F., and Pescarmona, P. P. (2019b). CO2-fixation into cyclic and
440   polymeric carbonates: Principles and applications. *Green Chem.* 21, 406–448. doi:
441   10.1039/c8gc03086c.

442 Keijer, T., Bakker, V., and Slootweg, J. C. (2019). Circular chemistry to enable a circular economy.
443   *Nat. Chem.* 11, 190–195. doi: 10.1038/s41557-019-0226-9.

444 Kisch, H., Millini, R., and Wang, I.-J. (1986). Bifunktionelle Katalysatoren zur Synthese cyclischer
445   Carbonate aus Oxiranen und Kohlendioxid. *Chem Ber* 119, 1090–1094. doi:
446   https://doi.org/10.1002/cber.19861190329.

447 Liang, J., Huang, Y. B., and Cao, R. (2019). Metal–organic frameworks and porous organic polymers
448   for sustainable fixation of carbon dioxide into cyclic carbonates. *Coord. Chem. Rev.* 378, 32–65.
449   doi: 10.1016/J.CCR.2017.11.013.

450 Liu, F., Duan, X., Dai, X., Du, S., Ma, J., Liu, F., et al. (2022a). Metal-decorated porous organic
451   frameworks with cross-linked pyridyl and triazinyl as efficient platforms for CO2 activation and
452   conversion under mild conditions. *Chem. Eng. J.* 445, 136687. doi: 10.1016/J.CEJ.2022.136687.

453 Liu, M., Zhao, P., Zhang, W., Cheng, X., Fei, H., Ma, J., et al. (2022b). Rational self-assembly of
454   triazine- and urea-functionalized periodic mesoporous organosilicas for efficient CO2 adsorption
455   and conversion into cyclic carbonates. *Fuel* 315, 123230. doi: 10.1016/J.FUEL.2022.123230.

456 Liu, Q., Wu, L., Jackstell, R., and Beller, M. (2015). Using carbon dioxide as a building block in
457   organic synthesis. *Nat. Commun.* 6. doi: 10.1038/ncomms6933.

458 Maquilón, C., Limburg, B., Laserna, V., Garay-Ruiz, D., González-Fabra, J., Bo, C., et al. (2020).
459   Effect of an Al(III) Complex on the Regio-and Stereoisomeric Formation of Bicyclic Organic
460   Carbonates. *Organometallics* 39, 1642–1651. doi: 10.1021/acs.organomet.9b00773.

461 Martens, J. A., Bogaerts, A., de Kimpe, N., Jacobs, P. A., Marin, G. B., Rabaey, K., et al. (2017). The
462   Chemical Route to a Carbon Dioxide Neutral World. *ChemSusChem* 10, 1039–1055. doi:
463   10.1002/cssc.201601051.

464 Modak, A., Bhanja, P., Dutta, S., Chowdhury, B., and Bhaumik, A. (2020). Catalytic reduction of
465   CO_2 into fuels and fine chemicals. *Green Chem*. doi: 10.1039/D0GC01092H.

466 Montoya, C. A., Paninho, A. B., Felix, P. M., Zakrzewska, M. E., Vital, J., Najdanovic-Visak, V., et
467   al. (2015). Styrene carbonate synthesis from CO_2 using tetrabutylammonium bromide as a non-
468   supported heterogeneous catalyst phase. *J. Supercrit. Fluids* 100, 155–159. doi:
469   10.1016/j.supflu.2015.01.027.

470 Nguyen, Q. T., Do, X. H., Cho, K. Y., Lee, Y. R., and Baek, K. Y. (2022). Amine-functionalized
471   bimetallic Co/Zn-zeolitic imidazolate frameworks as an efficient catalyst for the CO2
472   cycloaddition to epoxides under mild conditions. *J. CO2 Util.* 61, 102061. doi:
473   10.1016/J.JCOU.2022.102061.

474 Panza, N., Biase, A., Gallo, E., and Caselli, A. (2021). Unexpected " ferrate " species as single-
475   component catalyst for the cycloaddition of CO_2 to epoxides. *J. CO2 Util.* 51, 101635. doi:
476   10.1016/j.jcou.2021.101635.

477 Panza, N., Soave, R., Cargnoni, F., Trioni, M. I., and Caselli, A. (2022). Experimental and theoretical
478   insight into the mechanism of CO_2 cycloaddition to epoxides catalyzed by ammonium ferrates.
479   *J. CO2 Util.* 62, 102062. doi: 10.1016/J.JCOU.2022.102062.

480 Pescarmona, P. P. (2021). Cyclic carbonates synthesised from CO2: Applications, challenges and
481   recent research trends. *Curr. Opin. Green Sustain. Chem.* 29. doi: 10.1016/j.cogsc.2021.100457.

482 Rintjema, J., and Kleij, A. W. (2017). Aluminum-Mediated Formation of Cyclic Carbonates:
483   Benchmarking Catalytic Performance Metrics. *ChemSusChem* 10, 1274–1282. doi:
484   10.1002/cssc.201601712.

485 Rix, E., Grau, E., Chollet, G., and Cramail, H. (2016). Synthesis of fatty acid-based non-isocyanate
486   polyurethanes, NIPUs, in bulk and mini-emulsion. *Eur. Polym. J.* 84, 863–872. doi:
487   10.1016/j.eurpolymj.2016.07.006.

488 Sathish, M., Sreeram, K. J., Raghava Rao, J., and Unni Nair, B. (2016). Cyclic Carbonate: A
489   Recyclable Medium for Zero Discharge Tanning. *ACS Sustain. Chem. Eng.* 4, 1032–1040. doi:
490   10.1021/acssuschemeng.5b01121.

491 Schäffner, B., Schäffner, F., Verevkin, S. P., and Börner, A. (2010). Organic carbonates as solvents
492   in synthesis and catalysis. *Chem. Rev.* 110, 4554–4581. doi: 10.1021/cr900393d.

493 Shaikh, R. R., Pornpraprom, S., and D'Elia, V. (2018). Catalytic Strategies for the Cycloaddition of
494   Pure, Diluted, and Waste CO2 to Epoxides under Ambient Conditions. *ACS Catal.* 8, 419–450.
495   doi: 10.1021/acscatal.7b03580.

496 Singh Dhankhar, S., Ugale, B., Nagaraja, C. M., and Minireview,] (2020). Co-Catalyst-Free
497   Chemical Fixation of CO 2 into Cyclic Carbonates by using Metal-Organic Frameworks as

498   Efficient Heterogeneous Catalysts. *Chem. Asian J.* 2020, 2403–2427. doi:
499   10.1002/asia.202000424.

500   Sit, W. N., Ng, S. M., Kwong, K. Y., and Lau, C. P. (2005). Coupling reactions of CO2 with neat
501   epoxides catalyzed by PPN salts to yield cyclic carbonates. *J. Org. Chem.* 70, 8583–8586. doi:
502   10.1021/jo051077e.

503   Sodpiban, O., del Gobbo, S., Barman, S., Aomchad, V., Kidkhunthod, P., Ould-Chikh, S., et al.
504   (2019). Synthesis of well-defined yttrium-based Lewis acids by capturing a reaction
505   intermediate and catalytic application for cycloaddition of CO_2 to epoxides under atmospheric
506   pressure. *Catal. Sci. Technol.* 9, 6152. doi: 10.1039/c9cy01642b.

507   Sodpiban, O., Phungpanya, C., del Gobbo, S., Arayachukiat, S., Piromchart, T., and D'Elia, V.
508   (2021). Rational engineering of single-component heterogeneous catalysts based on abundant
509   metal centers for the mild conversion of pure and impure CO_2 to cyclic carbonates. *Chem. Eng,
510   J.* 422, 129930. doi: 10.1016/J.CEJ.2021.129930.

511   Su, Z., Ma, J., Wei, J., M., Bai, X., Wang, N., and Li, J. (2022). A zinc porphyrin polymer as
512   efficient bifunctional catalyst for conversion of CO_2 to cyclic carbonates. *Appl. Organomet.
513   Chem.* 36, e6632. doi: 10.1002/aoc.6632.

514   Tong, H., Qu, Y., Li, Z., He, J., Zou, X., Zhou, Y., et al. (2022). Halide-free pyridinium saccharinate
515   binary organocatalyst for the cycloaddition of CO_2 into epoxides. *Chem. Eng. J.* 444, 135478.
516   doi: 10.1016/J.CEJ.2022.135478.

517   Wang, J. Q., Dong, K., Cheng, W. G., Sun, J., and Zhang, S. J. (2012). Insights into quaternary
518   ammonium salts-catalyzed fixation carbon dioxide with epoxides. *Catal. Sci. Technol.* 2, 1480–
519   1484. doi: 10.1039/c2cy20103h.

520   Wang, S., Peng, J., Yang, H.-J., Ban, B., Wang, L., Lei, B., et al. (2019). β-
521   Cyclodextrin/Quaternary Ammonium Salt as an Efficient Catalyst System for Chemical Fixation
522   of CO_2. *J. Nanosci. Nanotechnol.* 19, 3263–3268. doi: 10.1166/jnn.2019.16610.

523   Wang, Z., Wang, Y., Xie, Q., Fan, Z., and Shen, Y. (2021). Aliphatic carboxylic acid as a hydrogen-
524   bond donor for converting CO_2 and epoxide into cyclic carbonate under mild conditions. *New J.
525   Chem.* 45, 9403–9408. doi: 10.1039/d1nj01285a.

526   Wyrzykowski, D., Kruszyñski, R., Klak, J., Mrozinski, J., and Warnke, Z. (2007). Magnetic
527   characteristics of tetrabutylammonium tetrahalogenoferrates(III): X-ray crystal structure of
528   tetrabutylammonium tetrabromoferrate(III). *Z. Anorg. Allg. Chem.* 633, 2071–2076. doi:
529   10.1002/zaac.200700261.

530   Wyrzykowski, D., Kruszyński, R., Kucharska, U., and Warnke, Z. (2006). Structural and
531   physicochemical characteristics of tetrabutylammonium tetrahalogenoferrates(III),$[(C_4H_9)_4N]$
532        $[FeBr_{4-n}Cl_n]$. *Z. Anorg. Allg. Chem.* 632, 624–628. doi: 10.1002/zaac.200500472.

533   Yu, W. D., Zhang, Y., Han, Y. Y., Li, B., Shao, S., Zhang, L. P., et al. (2021). Microwave-Assisted
534   Synthesis of Tris-Anderson Polyoxometalates for Facile CO_2 Cycloaddition. *Inorg. Chem.* 60,
535   3980–3987. doi: 10.1021/acs.inorgchem.1c00019.

536

537 **TABLES**

538 **Table 1.** Synthesis and characterization of the ammonium zincates.[a]

539

$$ZnX_2 + 2\,[TBA]X \xrightarrow{\text{EtOH}} [TBA]_2[ZnX_4]$$

ZnX$_2$	[TBA]X	[TBA]$_2$[ZnX$_4$]	Yield %
ZnCl$_2$	[TBA]Cl	[TBA]$_2$[ZnCl$_4$]	63
ZnBr$_2$	[TBA]Br	[TBA]$_2$[ZnBr$_4$]	71
ZnI$_2$	[TBA]I	[TBA]$_2$[ZnI$_4$]	88

540 [a] Reaction conditions and details reported in the Supplementary Materials.

541

542

543 **Table 2.** Cycloaddition of CO$_2$ to styrene oxide catalysed by the tetrahalogenozincate-salts.[a]

544

$$\text{Ph}\overset{O}{\triangle}\ \text{1a}\ +\ CO_2 \xrightarrow[\substack{\text{neat}\\100\,°C;\,0.8\,\text{MPa}}]{\substack{[TBA]_2[ZnX_4]\\0.5\,\text{mol\%}}} \text{Ph}\underset{\text{2a}}{\overset{O}{\bigcirc}}\!\!O$$

Entry	Cat. 0.5 mol%	t (h)	Con. 1a %	Sel. 2a %	TON[b]	TOF[b] (h^{-1})
1	[TBA]$_2$[ZnCl$_4$]	4	97	86	194	49
2	[TBA]$_2$[ZnBr$_4$]	4	>99	94	200	50
3	[TBA]$_2$[ZnI$_4$]	4	>99	95	200	50
4	[TBA]$_2$[ZnCl$_4$]	2	82	98	164	82
5	[TBA]$_2$[ZnBr$_4$]	2	>99	95	200	99
6	[TBA]$_2$[ZnI$_4$]	2	>99	91	200	99
7	[TBA]$_2$[ZnCl$_4$]	1	56	95	112	112
8	[TBA]$_2$[ZnBr$_4$]	1	98	96	196	196
9	[TBA]$_2$[ZnI$_4$]	1	78	85	156	156
10	[TBA]$_2$[ZnCl$_4$]	0.5	30	93	60	120
11	[TBA]$_2$[ZnBr$_4$]	0.5	87	99	174	348
12	[TBA]$_2$[ZnI$_4$]	0.5	42	99	84	168
13	[TBA]$_2$[ZnCl$_4$]	0.25	11	>99	22	88
14	[TBA]$_2$[ZnBr$_4$]	0.25	52	92	104	416
15	[TBA]$_2$[ZnI$_4$]	0.25	21	86	42	168
16	TBACl	4	41	99	82	21
17	TBABr	4	33	99	66	17
18	TBAI	4	42	99	84	21
19	none	-	3	n.d.	6	2

545 [a] Reactions performed in an autoclave. Reaction conditions: styrene oxide (SO) 250 μl (2.19 mmol); cat. 0.5 mol%;
546 P(CO$_2$) = 0.8 MPa; T = 100 °C. Conversion and selectivity determined by ^{1}H NMR using mesitylene as the internal
547 standard. [b] Turnover number (mol$_{1a(converted)}$·mol$_{cat}^{-1}$) and Turnover frequency (mol$_{1a(converted)}$·mol$_{cat}^{-1}$·reaction time^{-1}).
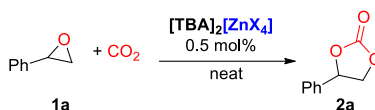
548

549

550

551

552

553 **Table 3.** Cycloaddition of CO_2 to styrene oxide: effect of the pressure and the temperature.[a]

554

Entry	Cat.	T (°C)	P(CO_2) (MPa)	Con. 1a %	Sel. 2a %	TON[b]	TOF[b] (h^{-1})
1	[TBA]$_2$[ZnCl$_4$]	100	0.1	63	89	126	31.5
2	[TBA]$_2$[ZnBr$_4$]	100	0.1	87	63	174	43.5
3	[TBA]$_2$[ZnI$_4$]	100	0.1	80	83	160	40
4	[TBA]$_2$[ZnCl$_4$]	50	0.1	11	91	22	5.5
5	[TBA]$_2$[ZnBr$_4$]	50	0.1	47	96	94	23.5
6	[TBA]$_2$[ZnI$_4$]	50	0.1	22	82	44	11
7[c]	[TBA]$_2$[ZnCl$_4$]	30	0.8	11	73	11	0.7
8[c]	[TBA]$_2$[ZnBr$_4$]	30	0.8	95	>99	95	5.9
9[c]	[TBA]$_2$[ZnI$_4$]	30	0.8	>99	>99	100	6.2

555 [a] Reaction performed in sealed vials with a CO_2 balloon. Reaction conditions: styrene oxide (SO) 2.19 mmol; cat. 0.5
556 mol%; t = 4h. Conversion and selectivity determined by ^{1}H NMR using mesitylene as the internal standard. [b] Turnover
557 number (mol$_{1a(converted)}$·mol$_{cat}$$^{-1}$) and Turnover frequency (mol$_{1a(converted)}$·mol$_{cat}$$^{-1}$·reaction time^{-1}). [c] Cat loading 1 mol%; t
558 = 16 h. Reaction performed in an autoclave.

559

560

561 **Table 4.** Cycloaddition of CO_2 to styrene oxide: effect of the catalyst loading.[a]
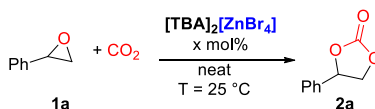
562

Entry	Cat. loading (mol%)	P(CO_2) (MPa)	t (h)	Con. 1a %	Sel. 2a %	TON[b]	TOF[b] (h^{-1})
1	0.5	0.1	24	34	97	68	2.8
2	1	0.1	24	47	>99	47	2.0
3	5	0.1	24	47	>99	9.4	0.4
4	1	0.1	16	42	98	42	2.6
5[c]	1	0.1	16	69	>99	69	4.3
6[d]	0.1	0.8	16	5	>99	50	3.1
7[d]	0.5	0.8	16	58	97	116	7.3
8[d]	1	0.8	16	87	98	87	5.4
9[d]	1	0.2	16	88	>99	88	5.5

563 [a] Reaction performed in sealed vials with a CO_2 balloon. Reaction conditions: styrene oxide (SO) 2.19 mmol; T = 25
564 °C. Conversion and selectivity determined by ^{1}H NMR using mesitylene as the internal standard. [b] Turnover number
565 (mol$_{1a(converted)}$·mol$_{cat}$$^{-1}$) and Turnover frequency (mol$_{1a(converted)}$·mol$_{cat}$$^{-1}$·reaction time^{-1}). [c] Reaction performed under CO_2
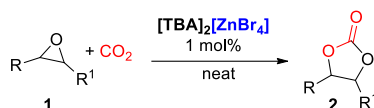566 flow. [d] Reactions performed in an autoclave.

567

568

569

570

571 **Table 5.** Reaction scope.[a]

572

| Entry	Substrate	Product	T (°C)	P(CO$_2$) (MPa)	t (h)	Con. 1a %	Sel. 2a %	TOF[b] (h^{-1})
1	1b	2b	30	0.2	16	64	>99	4.0
2	1c	2c	30	0.2	16	88	99	5.5
3[c]			30	1.0	16	94	99	5.9
4	1d	2d	30	0.2	16	86	>99	5.4
5	1e	2e	30	0.2	16	>99	>99	6.2
6	1f	2f	30	0.2	16	85	>99	5.3
7[d]	1g	2g	30	0.2	16	75	76	4.7
8[d]	1h	2h	30	0.2	16	75	76	4.7
9	1i	2i	30	0.2	16	99	97	6.2
10	1j	2j	30	0.2	16	87	96	5.4
11[e]	1k	2k	30	0.2	16	-	-	-
12[e]			100	1.6	16	6	80	0.4
13[f]	1l	2l	100	0.8	2	56	77	28.0
14	1m	2m	30	0.2	16	12	-	0.8
15			100	0.8	2	18	99	9.0
16			100	1.6	16	90	89	5.6
17	1n	2n	100	0.8	2	12	-	6.0

573 [a] Reaction performed in autoclave. Reaction conditions: epoxide 250 µl; cat. 1 mol%. Conversion and selectivity
574 determined by ^{1}H NMR using mesitylene as the internal standard. [b] Turnover frequency (mol$_{1(converted)}$·mol$_{cat}^{-1}$·reaction
575 time^{-1}). [c] Isolated yield. [d] Unidentified by-products, possibly of polymeric nature, accounted for the rest of the mass
576 balance. [e] CH$_3$CN (0.5 mL) was added to solubilize 1k. [f] *Iso*-butyraldehyde was also formed, accounting for the rest
577 of mass balance.

578   **FIGURES and SCHEMES**

579   **Scheme 1.** Selective synthesis of mono (right) and di-cyclic carbonates (left) of 4-vinylcyclohexene
580   dioxide, **1o**. Reaction conditions: epoxide 250 μl (1.94 mmol); cat. 1 or 2 mol%. Conversion and
581   selectivity determined by ^{1}H NMR using mesitylene as the internal standard. Turnover frequency
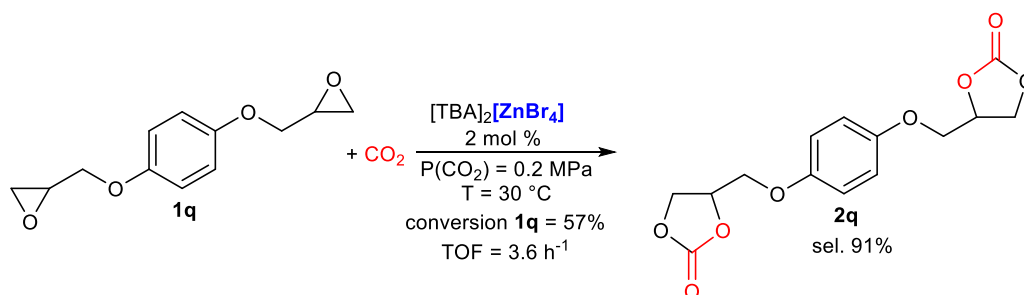582   (mol$_{1o(converted)}$·mol$_{cat}^{-1}$·reaction time^{-1}).
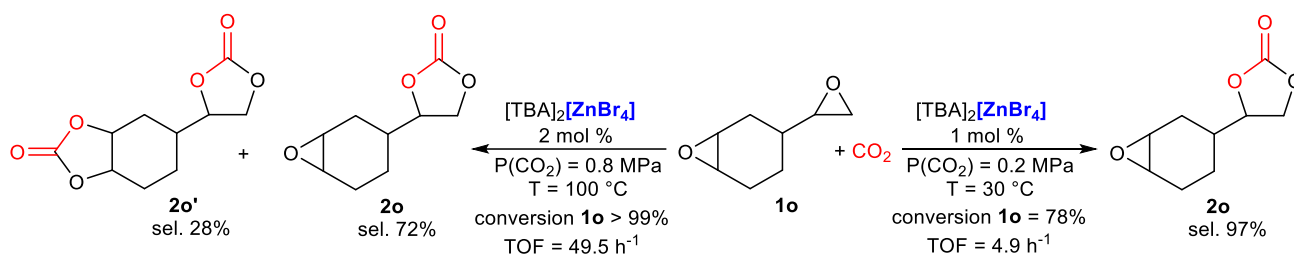
583
584

585   **Scheme 2.** Selective synthesis of *bis*-carbonate of (bisphenol-A)diglycidyl ether (BADGE), **2p**.
586   Reaction conditions: epoxide, **1p**, (340 mg, 1 mmol) dissolved in CH$_3$CN (0.5 ml); cat. 2 mol%.
587   Conversion and selectivity determined by ^{1}H NMR using mesitylene as the internal standard.
588   Turnover frequency (mol$_{1p(converted)}$·mol$_{cat}^{-1}$·reaction time^{-1}).
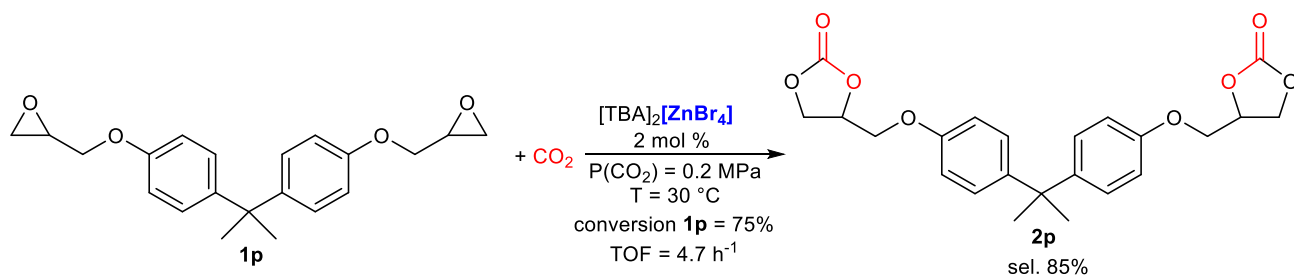
589

590   **Scheme 3.** Selective synthesis of *bis*-carbonate of 1,4-*bis*(benzyloxy)diglycidyl ether, **2q**. Reaction
591   conditions: epoxide, **1q**, (222 mg, 1 mmol) dissolved in CH$_3$CN (0.5 ml); cat. 2 mol%. Conversion
592   and selectivity determined by ^{1}H NMR using mesitylene as the internal standard. Turnover frequency
593   (mol$_{1q(converted)}$·mol$_{cat}^{-1}$·reaction time^{-1}).

594

595