GDCh Communications Angewandte Chemie International Edition www.angewandte.org

How to cite: *Angew. Chem. Int. Ed.* **2022,** *61,* e202205053
International Edition: doi.org/10.1002/anie.202205053
German Edition: doi.org/10.1002/ange.202205053

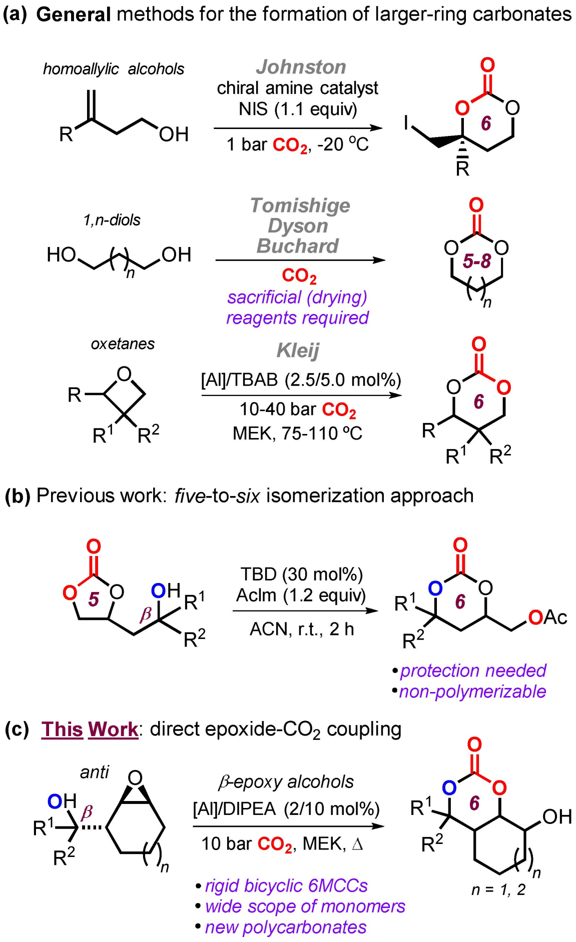
Homogeneous Catalysis

A Novel Catalytic Route to Polymerizable Bicyclic Cyclic Carbonate Monomers from Carbon Dioxide

*Chang Qiao, Wangyu Shi, Arianna Brandolese, Jordi Benet-Buchholz, Eduardo C. Escudero-Adán, and Arjan W. Kleij**

Abstract: A new catalytic route has been developed for the coupling of epoxides and CO_2 affording polymerizable six-membered bicyclic carbonates. Cyclic epoxides equipped with a β-positioned OH group can be transformed into structurally diverse bicyclic cyclic carbonates in good yields and with high selectivity. Key to the chemo-selectivity is the difference between the reactivity of *syn-* and *anti*-configured epoxy alcohols, with the latter leading to six-membered ring carbonate formation in the presence of a binary Al^{III} aminotriphenolate complex/DIPEA catalyst. X-ray analyses show that the conversion of the *syn*-configured substrate evolves via a standard double inversion pathway providing a five-membered carbonate product, whereas the *anti*-isomer allows for activation of the oxirane unit of the substrate opposite to the pendent alcohol. The potential use of these bicyclic products is shown in ring-opening polymerization offering access to rigid polycarbonates with improved thermal resistance.

The catalytic recycling of carbon dioxide into valuable chemicals useful as intermediates in synthetic chemistry[1] and polymer science[2] represents a seminal approach within the context of a circular economy.[3] The synthesis of cyclic carbonates through non-reductive coupling methods represents a valuable carbon dioxide reutilization approach and has advanced greatly in the last decade. In this regard, modern methods build on the [3+2] cycloaddition between readily available cyclic ethers and carbon dioxide (CO_2) under attractive process conditions.[4] Unlike for this well-established catalytic formation of 5-membered cyclic carbonates, traditional methods that allow for larger ring carbonate formation rely on the use of CO or $COCl_2$, which are extremely toxic.[5] (Semi)stoichiometric methods (Scheme 1a) include the use of homoallylic alcohols reported by Johnston[6] or diols as established by Buchard,[7a,b] Dyson[7c] and Tomishige.[7d] However, these entries to larger-ring cyclic carbonates typically require the presence of sacrificial reagents such as alkyl halides, tosyl chloride or cyano pyridines. Transesterification of polyols with activated forms



Scheme 1. a) General approaches for six-membered cyclic carbonate synthesis. b) Our previously reported synthesis of *O*-protected six-membered carbonates. c) A new and challenging direct coupling of an epoxide and CO_2 providing bicyclic carbonate heterocycles (This Work).

---

[*] C. Qiao, W. Shi, Dr. A. Brandolese, Dr. J. Benet-Buchholz, Dr. E. C. Escudero-Adán, Prof. A. W. Kleij
Institute of Chemical Research of Catalonia (ICIQ), the Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona (Spain)
E-mail: akleij@iciq.es

C. Qiao, W. Shi
Universitat Rovira i Virgili, C/Marcel · lí Domingo s/n, 43007 Tarragona (Spain)

Prof. A. W. Kleij
Catalan Institute of Research and Advanced Studies (ICREA)
Pg. Lluís Companys 23, 08010 Barcelona (Spain)

of CO_2[8] and the direct coupling of oxetanes and CO_2 (Scheme 1a)[9] also have shown potential to access larger carbonate heterocycles.

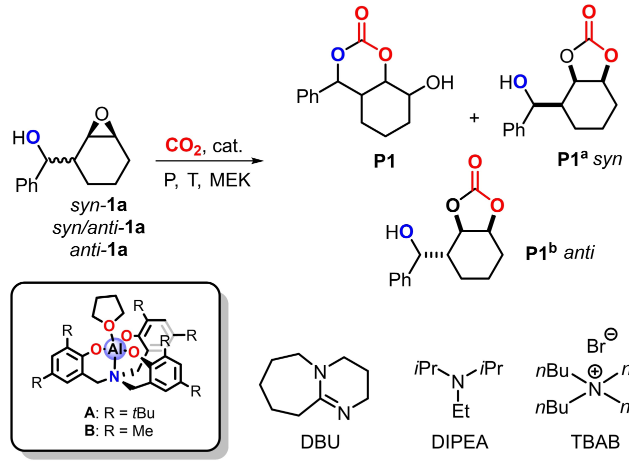
Larger ring-carbonates have important incentives in the area of polymer chemistry for the design of new types of functional macromolecules with tuneable mechanical and thermal properties.[10] Therefore, conceptually new catalytic methods that enable a wider scope of such monomers while being created from a renewable carbon source can create important incentives for future low-carbon emission polymers.

Recently we disclosed an unusual isomerization of five- to six-membered cyclic carbonates (Scheme 1b).[11a] A tertiary, β-positioned alcohol group in the smaller-sized heterocycles plays a crucial role as it acts as a pro-nucleophile able to attack the carbonate C-center thereby forming a larger-ring cyclic carbonate. Key to the success of this ring-expanding approach is the higher kinetic feasibility to intercept the primary alcohol present in the six-membered compound. The protected six-membered carbonates were examined under standard ring-opening polymerization (ROP) conditions but failed to deliver a polycarbonate product as *O*-deprotection and back-isomerization to the thermodynamically more stable five-membered carbonate occurs. This lack of polymerization potential motivated us to design a different strategy that could build on our previously established substrate-directed CO_2 activation manifold.[11b–d]

By rigidifying the substrate scaffold though preserving the presence of a β-positioned alcohol, we discovered a salient difference between *syn*- and *anti*-configured β-epoxy alcohols in their coupling with CO_2 leading to cyclic carbonates (Scheme 1c). The *anti* substrates deliver in one step six-membered bicyclic carbonates in good yield and selectivity under binary catalysis. The mechanistic pathway towards the observed chemo-selectivity is discussed and supported through X-ray structural studies, and diversification studies show that these heterocycles have both utility and stability upon modification. ROP of representative bicyclic six-membered carbonates is successfully demonstrated, illustrating the importance of backbone rigidity to substantially increase the thermal resistance of the resultant polycarbonate.

At the onset of our screening studies, we examined various conditions for the conversion of both *syn*- and *anti*-**1a** (Table 1).[12] Based on our previous experience,[11] various combinations of Al-complexes **A** and **B** and additives

Table 1: Trials conducted with epoxy alcohol substrate **1a** using various catalysts under different conditions.[a]



Entry	1a	Cat. [mol%]	P/T [bar/°C]	Conv [%]	P1 [%]	P1[a] [%]	P1[b] [%]
1	*syn*	**A**/DIPEA, 10	30/50	<1	–	–	–
2	*syn*	**A**/DIPEA, 10	10/100	18	0	0	0
3	*syn*	**A**/TBAB, 5	10/100	84	0	35	0
4	*syn*	TBAB, 5	10/100	74	0	**37**	0
5	*syn*	DBU, 10	10/100	94	0	0	26
6[b]	*syn*	TBAB/DBU	10/100	95	0	12	29
7[d]	[c]	**A**/DIPEA, 10	10/100	61	20	0	0
8[d]	[c]	**A**/TBAB, 5	10/100	>99	20	18	0
9[d]	*anti*	**A**/TBAB, 5	10/100	>99	83	0	0
10[d]	*anti*	**A**/DIPEA, 10	10/100	95	**85**	0	0
11	*anti*	**A**	10/100	36	11	0	0
12	*anti*	DIPEA, 10	10/100	14	0	0	0
13[d]	*anti*	**B**/DIPEA, 10	10/100	>99	77	0	0

[a] Reaction performed under the indicated pressure and temperature, MEK as solvent (0.4 mL), *syn*-**1a** or **1a** (0.5 mmol) or *anti*-**1a** (0.2 mmol), Al-complex **A** or **B** (2 mol%), additive (indicated), 22 h. The amount of **P1**, **P1**^{a} and **P1**^{b} and the overall conversion of **1a** was determined by ^1H NMR ($CDCl_3$). [b] TBAB (5 mol%) and DBU (10 mol%). [c] A 3:1 mixture of *syn*/*anti*-**1a** was used. [d] Yields of the isolated product are reported for these entries.

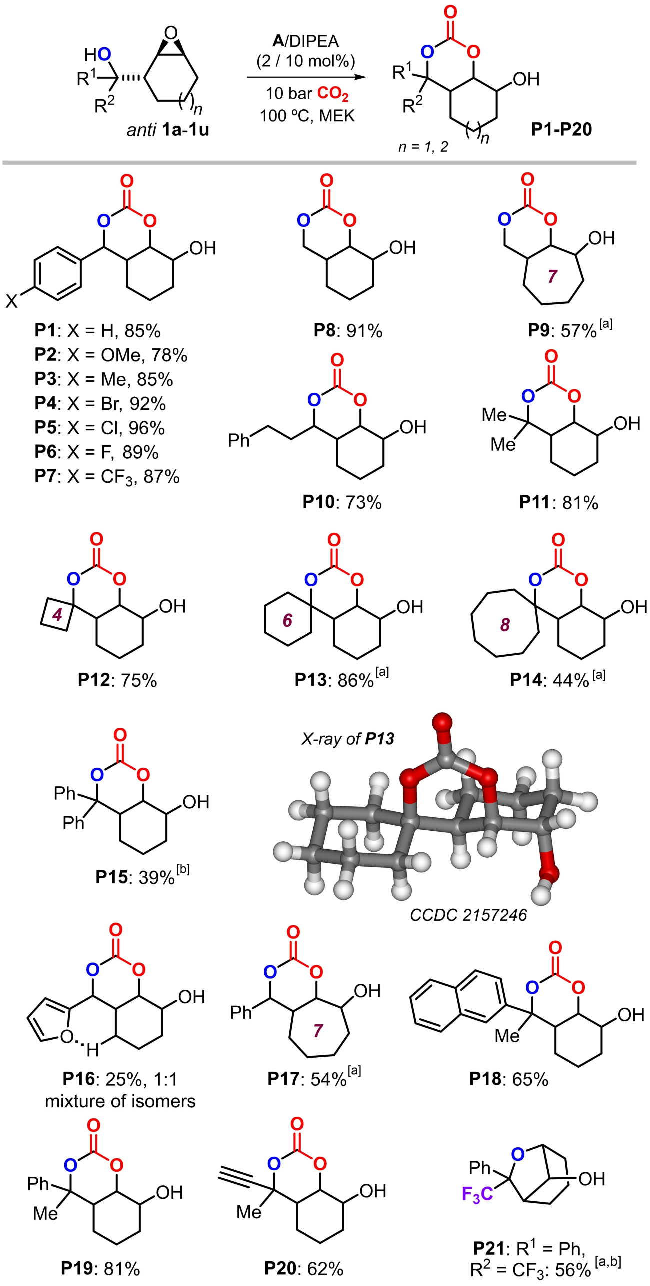
(DBU, DIPEA and TBAB) were scrutinized to examine their effect on the chemo-selectivity of this benchmark conversion.[13] First, a low-temperature approach was chosen (entry 1) with **A** and DIPEA as binary catalyst at relatively high CO_2 pressure but this proved to be unproductive By increasing the reaction temperature and lowering the pressure to 10 bar, low conversion of **1a** was noted but no carbonate products were detected (entry 2). We found that a reaction temperature of 100 °C was key towards carbonate formation (see Table S1 and below). In the presence of TBAB (entries 3 and 4), the five-membered ring carbonate *syn*-**P1**^{a} was formed suggesting the occurrence of a standard double inversion pathway.[14] Interestingly, in the presence of base catalyst (entry 5), a configurationally different five-membered cyclic carbonate (*anti*-**P1**^{b}) was produced as the major reaction component as supported by X-ray crystallography (see the Supporting Information).[15,16] The presence of both TBAB and DBU (entry 6) leads to a mixture of five-membered cyclic carbonates *syn*-**P1**^{a} and *anti*-**P1**^{b}.

An important lead result was accomplished in the conversion of a 3:1 *syn*/*anti* substrate mixture (entries 7 and 8) leading to substantial formation (20 %, close to the amount of the *anti*-isomer in *syn*/*anti*-**1a**) of the target six-membered cyclic carbonate **P1** (see the Supporting Information). The selectivity towards **P1** could be further increased by using *anti*-**1a** (entries 9–13). Compared to the presence of TBAB, the use of DIPEA shows slightly higher selectivity for **P1** (entries 9 and 10, see Tables S1 and S2 for further details) but, more importantly does not necessitate the use of halide-containing additives.[17] In the presence of Al-complex **A** only the reaction had low efficiency (entry 11; 11 % yield of **P1**) while DIPEA individually did not show any selectivity towards the formation of **P1** (entry 12). It therefore appears that a cooperative action of both catalyst components is required for efficient and selective substrate conversion. Though Al-complex **B** also showed good potential towards the formation of the desired product (entry 13), a somewhat lower yield of **P1** was noted. In the screening studies (Table 1 and S1), we found that other products may also be formed, the details of which can be found in the Supporting Information.

The scope of this new CO_2 transformative process (Scheme 2) was then examined using the conditions reported in entry 10 of Table 1. Aryl-substituted bicyclic carbonates **P2**–**P7** could be prepared in good yields from their β-epoxy alcohols precursors (**1b**–**1g**; having secondary alcohol groups) providing, in some cases, useful functional groups for post-synthetic modifications. Then we also examined precursors comprising primary alcohol groups and this allowed us to prepare **P8** (91 %) and **P9** (57 %) in excellent and moderately high yield, respectively. The lower yield for **P9** is ascribed to the more flexible nature of the cycloheptyl ring and a higher energy requirement to produce a reactive conformation.

In order to widen the scope, epoxy alcohol substrates with groups other than aryls were also tested, providing access to bicyclic carbonates **P10**–**P14** in good yields (except for **P14**: 44 %). In some of these cases, a longer reaction time was needed to reach higher substrate conversion such as for spiranes **P13** and **P14**. In the latter case the twisted nature of the cyclooctyl ring likely increases the steric impediment around the alcohol group, leading to slower intramolecular attack on the oxirane unit. A similar "steric" effect probably holds for the synthesis of **P15** (39 %), whereas the low yield of the furan-derivative **P16** (25 %) is ascribed to (thermal) decomposition over time which likely involves the reactive furan group.[18]

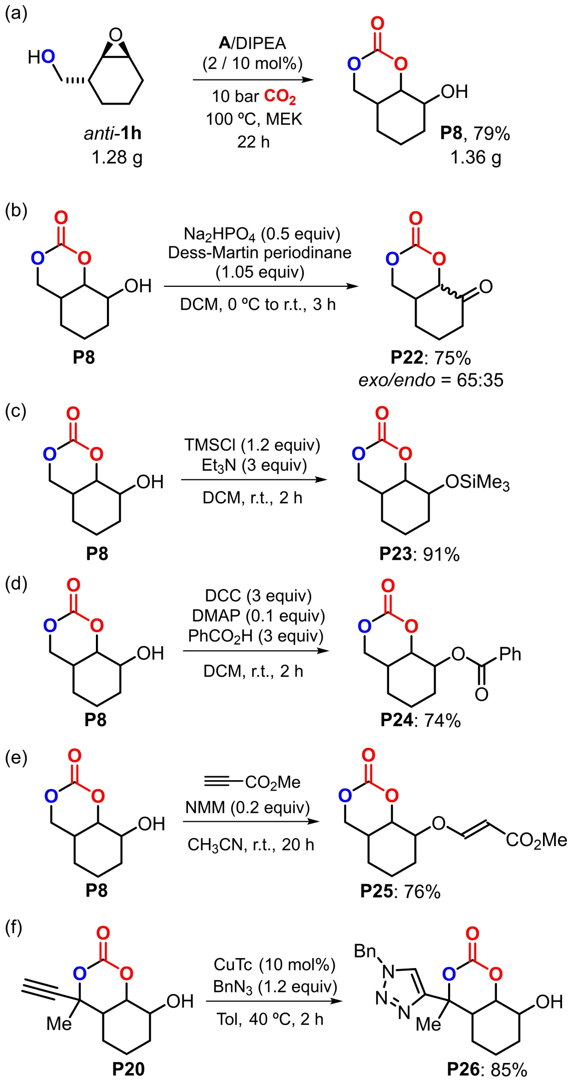
P16 was isolated as a mixture of rotamers as suggested by molecular modelling studies. The isomers relate to the



Scheme 2. Scope of six-membered bicyclic carbonates (**P1**–**P20**) by coupling of epoxy alcohols **1a**–**1u** and CO_2 in the presence of Al-complex **A** and DIPEA. [a] Reaction time was 72 h. [b] Using TBAB (5 mol %) instead of DIPEA.

relative positioning of the furan group to the bicyclic scaffold with CH⋅⋅⋅O interactions being competitive to HO⋅⋅⋅OC(O)O hydrogen bonding. Finally, we examined the use of an aryl-substituted cycloheptane oxide and "mixed" substituted epoxy alcohols which allowed to prepare the carbonate products **P17**–**P20** in appreciable yields. Notably, **P20** (62 % yield) featuring a terminal alkyne offers a synthetic handle while building up molecular complexity. Substrate **1u** having a strongly electron-withdrawing CF_3 group changed the chemo-selectivity drastically. Only a trace amount of the desired product could be detected in the crude by ^1H NMR. From the reaction mixture we were able to isolate and characterize bicycle **P21** (see the Supporting Information for details).[19]

The synthetic potential and stability of bicyclic carbonates **P8** and **P20** was then examined (Scheme 3). Scaling up the synthesis of **P8** (79 %) was straightforward providing gram-quantity of this bicyclic carbonate (Scheme 3a). Dess–Martin oxidation of **P8** (Scheme 3b) gave access to the ketone product **P22** in 75 % yield as a mixture of isomers as the carbonyl fragment can have two relative orientations (*exo* and *endo*) with respect to the cyclic carbonate ring. *O*-protection in **P8** was simple and straightforward (Scheme 3c, d) with both silylated **P23** (91 %) and phenylester **P24** (75 %) isolated in good yields. Acrylic ester derivative **P25** (76 %, Scheme 3e) was produced by coupling of **P8** with a propargylic ester, and a Cu-catalyzed azide-alkyne "click" coupling of **P20** resulted cleanly into the formation of 1,2,3-triazole derivative **P26** (Scheme 3f, 85 %).



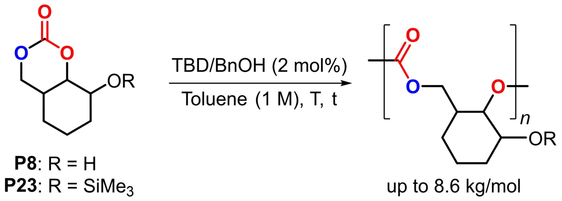
Scheme 3. Scale up of **P8** and product diversification studies using both **P8** and **P20**.

Finally, we used monomers **P8** and **P23** to examine their ROP potential under standard conditions (Table 2).[10a,e,20] Monomer **P8** could be oligomerized (entry 1, M_n = 1.7 kg mol^{-1}, $Đ$ = 1.47) at incomplete conversion, and extension of the reaction time to 48 h (entry 2) led to (partial) degradation of this oligocarbonate. These data indicated that the free alcohol present in **P8** might interfere with the ROP process. We therefore then examined silyl-protected **P23** (entry 3) and found that nearly full monomer conversion was achieved at r.t. after 20 h, with the polycarbonate having improved features (M_n = 5.9 kg mol^{-1}, $Đ$ = 1.34). Scale up of this process (entry 4) further improved the efficiency (M_n = 7.8 kg mol^{-1}, $Đ$ = 1.32) and the new polycarbonate could be isolated as a white solid in 80 %. Performing the ROP of **P23** at higher temperature (entry 5 versus 3) did not provoke any significant change in the polymer properties, which is in line with the non-innocent nature of the free alcohol in **P8** during the polymerization process. A slightly higher molecular weight polymer was produced in DCM (entry 6 versus 3), while lowering the catalyst loading (entry 7) gave the polycarbonate with slightly improved molecular weight. The isolated polycarbonate from entry 4 was subjected to thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The T_g of this new polycarbonate is substantially higher (at 52 °C) than the unsubstituted polycarbonate that is generated from the ROP of trimethylenecarbonate (T_g = −26 °C for a sample having a molecular weight of around 7 kg mol^{-1}).[21] This more rigid polycarbonate also exhibits a high T_d^5 of 234 °C favourable to process the polymer beyond its glass transition.

The marked difference in reactivity between the *syn* and *anti* isomer of **1a** can be rationalized by a stereochemical model where the Al-complex activates the oxirane at one side of the *anti*-configured cyclic epoxide. The alcohol (in the presence of a suitable base) enables the activation of CO_2 from the other face (Scheme 4, lower part; note, molecular structure of *anti*-**1o** as a structural model)[22] allowing for ring-opening and straightforward formation of bicyclic product **P1**. Such reactivity would not be possible with the *syn* isomer of **1a** (cf., X-ray of *syn*-**1a** and Table 1, entry 2) though a double inversion process is feasible in the presence of TBAB leading to the five-membered cyclic carbonate **P1^a^**.

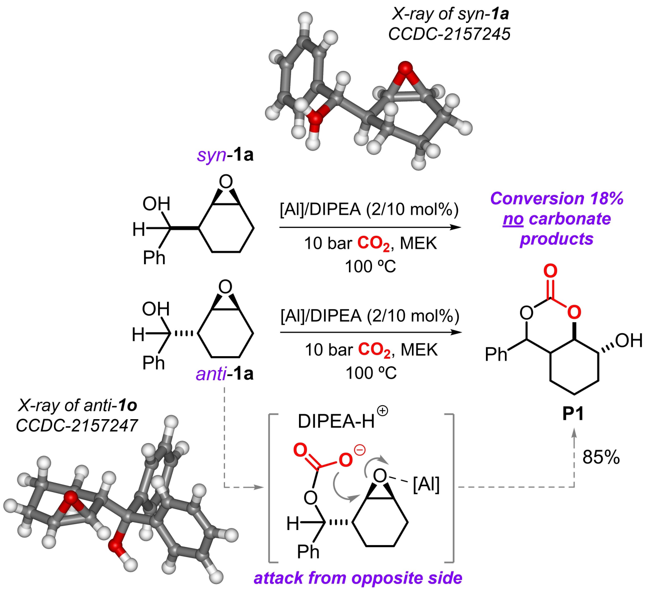
In summary, we here describe a novel catalytic approach that allows the coupling between β-epoxy alcohols and CO_2 leading to the direct formation of an unusual scope of larger-ring bicyclic carbonates in good yields. Crucial in this manifold is the stereo-configuration of the substrate with the *anti*-isomer leading exclusively to a six-membered bicyclic

Table 2: ROP studies using **P8** and **P23** as monomers, and TBD/BnOH as catalyst/initiator.[a]



Entry	Mon.	Solvent	t/T [h]/[° C]	Conv. [%][b]	Mn[c] [kg mol^{-1}]	$Đ$[c]
1[d]	**P8**	toluene	20, r.t.	–	1.7	1.47
2[d]	**P8**	toluene	48, r.t.	–	0.5	3.83
3	**P23**	toluene	20, r.t.	96	5.9	1.34
4[e]	**P23**	toluene	20, r.t.	> 99[f]	7.8	1.32
5	**P23**	toluene	20, 100	94	5.5	1.20
6	**P23**	DCM	20, r.t.	88	6.4	1.27
7[e,g]	**P23**	toluene	20, r.t.	> 99	8.6	1.27

[a] For monomer **P8**: 20 mg ($1.17\cdot10^{-4}$ mol), TBD/BnOH = 1:1, 2 mol%, 117 μL of solvent. For monomer **P23**: 20 mg (8.2×10^{-5} mol), TBD/BnOH = 1:1, 2 mol%, 82 μL of solvent. For both monomers: time and temperature indicated. Note that only one of the two possible regio-isomers is shown. [b] Conversion determined by ^{1}H NMR ($CDCl_3$). [c] M_n and $Đ$ values obtained through GPC analysis in THF using PS standards. [d] Incomplete conversion, accurate determination of monomer conversion not possible due to too much signal overlap. [e] **P23** (200 mg, 8.2×10^{-4} mol), TBD/BnOH = 1:1, 2 mol%, 820 μL of solvent. [f] Yield of the isolated polycarbonate: 80%. [g] TBD/BnOH = 1:1, 1 mol%.



Scheme 4. Reactivity comparison between both stereoisomers of **1 a** under similar conditions, and stereochemical model for the conversion of β-epoxy alcohol *anti*-**1 a** in the presence of binary catalyst **A**/DIPEA.

carbonate while the corresponding *syn*-isomer only provides access to five-membered ring carbonates. The potential of these bicyclic carbonates has been further illustrated in ROP experiments, and the substitution degree and functionality thus hold promise for the design and preparation of a whole new range of (functional) and above all rigidified polycarbonates obtained from CO_2-based monomers.

Acknowledgements

We thank the Cerca program/Generalitat de Catalunya, ICREA, MINECO (PID2020-112684GB-100) and the Ministerio de Ciencia e Innovación (Severo Ochoa Excellence Accreditation 2020–2023 CEX2019-000925-S) for support. C.Q. and W.S. acknowledge the Chinese Research Council for predoctoral fellowships (2018-06200078 and 2021-06350046).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Carbon Dioxide · Cyclic Carbonates · Homogeneous Catalysis · Monomers · Ring-Opening Polymerization

---

[1] a) Z. Zhang, J.-H. Ye, T. Ju, L.-L. Liao, H. Huang, Y.-Y. Gui, W.-J. Zhou, D.-G. Yu, *ACS Catal.* **2020**, *10*, 10871–10885; b) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933; c) Y. Zhang, T. Zhang, S. Das, *Green Chem.* **2020**, *22*, 1800–1820; d) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709–1742; e) B. Limburg, À. Cristòfol, F. Della Monica, A. W. Kleij, *ChemSusChem* **2020**, *13*, 6056–6065.

[2] a) B. Grignard, S. Gennen, C. Jérôme, A. W. Kleij, C. Detrembleur, *Chem. Soc. Rev.* **2019**, *48*, 4466–4514; b) W. Yu, E. Maynard, V. Chiaradia, M. C. Arno, A. P. Dove, *Chem. Rev.* **2021**, *121*, 10865–10907; c) B. Song, A. Qin, B. Z. Tang,

Cell Rep. Phys. Sci. **2022**, *3*, 100719; d) M. Scharfenberg, J. Hilf, H. Frey, *Adv. Funct. Mater.* **2018**, *28*, 1704302.

[3] T. Keijer, V. Bakker, J. C. Slootweg, *Nat. Chem.* **2019**, *11*, 190–195.

[4] a) J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, *Green Chem.* **2015**, *17*, 1966–1987; b) M. Alves, B. Grignard, R. Mereau, C. Jérôme, T. Tassaing, C. Detrembleur, *Catal. Sci. Technol.* **2017**, *7*, 2651–2684; c) R. Rajjak Shaikh, S. Pornpraprom, V. D'Elia, *ACS Catal.* **2018**, *8*, 419–450; d) A. J. Kamphuis, F. Picchioni, P. P. Pescarmona, *Green Chem.* **2019**, *21*, 406–448; e) P. P. Pescarmona, *Curr. Opin. Green Sustainable Chem.* **2021**, *29*, 100457; f) P. Rollin, L. K. Soares, A. M. Barcellos, D. R. Araujo, E. J. Lenardão, R. G. Jacob, G. Perin, *Appl. Sci.* **2021**, *11*, 5024; g) L. Guo, K. J. Lamb, M. North, *Green Chem.* **2021**, *23*, 77–118; h) F. Della Monica, A. W. Kleij, *Catal. Sci. Technol.* **2020**, *10*, 3483–3501; i) Y.-Y. Zhang, G.-W. Yang, R. Xie, L. Yang, B. Li, G.-P. Wu, *Angew. Chem. Int. Ed.* **2020**, *59*, 23921–23298; *Angew. Chem.* **2020**, *132*, 23491-23498.

[5] a) G. Rokicki, *Prog. Polym. Sci.* **2000**, *25*, 259–342; b) A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951–976; c) B. Gabriele, R. Mancuso, G. Salerno, L. Veltri, M. Costa, A. Dibenedetto, *ChemSusChem* **2011**, *4*, 1778–1786; d) D. M. Pearson, N. R. Conley R M Waymouth, *Adv. Synth. Catal.* **2011**, *353*, 3007–3013.

[6] B. A. Vara, T. J. Struble, W. Wang, M. C. Dobish, J. N. Johnston, *J. Am. Chem. Soc.* **2015**, *137*, 7302–7305.

[7] For methods utilizing diols as principal reagents see a) G. L. Gregory, M. Ulmann, A. Buchard, *RSC Adv.* **2015**, *5*, 39404–39408; b) T. M. McGuire, E. M. López-Vidal, G. L. Gregory, A. Buchard, *J. CO_2 Util.* **2018**, *27*, 283–288; c) F. D. Bobbink, W. Gruszka, M. Hulla, S. Das, P. J. Dyson, *Chem. Commun.* **2016**, *52*, 10787–10790; d) M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, *ACS Catal.* **2014**, *4*, 1893–1896. For an example that does not require sacrificial reagents, see: e) Z.-F. Diao, Z.-H. Zhou, C.-X. Guo, B. Yu, L.-N. He, *RSC Adv.* **2016**, *6*, 32400–32404.

[8] a) P. Furtwengler, L. Avérous, *Sci. Rep.* **2018**, *8*, 9134; b) E. R. Baral, J. H. Lee, J. G. Kim, *J. Org. Chem.* **2018**, *83*, 11768–11776; c) M. Selva, A. Perosa, S. Guidi, L. Cattelan, *Beilstein J. Org. Chem.* **2016**, *12*, 1911–1924.

[9] a) J. Rintjema, W. Guo, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *Chem. Eur. J.* **2015**, *21*, 10754–10762; b) D. J. Darensbourg, A. Horn, Jr., A. I. Moncada, *Green Chem.* **2010**, *12*, 1376–1379.

[10] a) T. M. McGuire, C. Pérale, R. Castaing, G. Kociok-Köhn, A. Buchard, *J. Am. Chem. Soc.* **2019**, *141*, 13301–13305; b) J. Huang, P. Olsén, E. Svensson Grape, A. K. Inge, K. Odelius, *Macromolecules* **2022**, *55*, 608–614; c) S. Tempelaar, L. Mespouille, O. Coulembier, P. Dubois, A. P. Dove, *Chem. Soc. Rev.* **2013**, *42*, 1312–1336; d) W. Guerin, A. K. Diallo, E. Kirilov, M. Helou, M. Slawinski, J.-M. Brusson, J.-F. Carpentier, S. M. Guillaume, *Macromolecules* **2014**, *47*, 4230–4235; e) Y. Song, X. Yang, Y. Shen, M. Dong, Y.-N. Lin, M. B. Hall, K. L. Wooley, *J. Am. Chem. Soc.* **2020**, *142*, 16974–16981; f) W. Zhang, J. Dai, Y.-C. Wu, J.-X. Chen, S.-Y. Shan, Z. Cai, J.-B. Zhu, *ACS Macro Lett.* **2022**, *11*, 173–178.

[11] a) C. Qiao, A. Villar-Yanez, J. Sprachmann, B. Limburg, C. Bo, A. W. Kleij, *Angew. Chem. Int. Ed.* **2020**, *59*, 18446–18451; *Angew. Chem.* **2020**, *132*, 18604–18609; b) J. Rintjema, R. Epping, G. Fiorani, E. Martín, E. C. Escudero-Adán, A. W. Kleij, *Angew. Chem. Int. Ed.* **2016**, *55*, 3972–3976; *Angew. Chem.* **2016**, *128*, 4040–4044; c) S. Sopeña, M. Cozzolino, C. Maquilón, E. C. Escudero-Adán, M. Martínez Belmonte, A. W. Kleij, *Angew. Chem. Int. Ed.* **2018**, *57*, 11203–11207; *Angew. Chem.* **2018**, *130*, 11373–11377; d) R. Huang, J. Rintjema, J. González-Fabra, E. Martin, E. C. Escudero-Adán, C. Bo, A. Urakawa, A. W. Kleij, *Nat. Catal.* **2019**, *2*, 62–70.

[12] a) T. Itoh, K. Jitsukawa, K. Kaneda, S. Teranishi, *J. Am. Chem. Soc.* **1979**, *101*, 159–169; b) K. B. Sharpless, R. C. Michaelson, *J. Am. Chem. Soc.* **1973**, *95*, 6136–6137.

[13] For a full description of the chemo-selectivity of these screening reactions, please refer to the Supporting Information Table S1.

[14] For a review on catalytic mechanisms leading to cyclic carbonates, see: ref [4h]. Note that a combination of the Al-complex and TBAB also leads to the target six-membered cyclic carbonate **P1**, a result which can be rationalized by a sequence that involves first bromide-induced epoxide ring-opening (internal carbon), following attack of a carbonate species formed through activation of CO_2 by the pendent alcohol.

[15] The formation of configurationally distinct, though constitutional rather similar five-membered bicyclic carbonates has been previously been studied, see: C. Maquilón, B. Limburg, V. Laserna, D. Garay-Ruiz, J. González-Fabra, C. Bo, M. Martínez Belmonte, E. C. Escudero-Adán, A. W. Kleij, *Organometallics* **2020**, *39*, 1642–1651.

[16] Deposition Numbers 2157244, 2157245, 2157246, and 2157247 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

[17] Halide-free synthesis of cyclic carbonates is considered to be more sustainable, see: a) A. W. Kleij, *Curr. Opin. Green Sustainable Chem.* **2020**, *24*, 72–81; b) "Halide-Free Synthesis of Cyclic and Polycarbonates": I. D. V. Ingram, M. North, X. Wu in *Chemistry Beyond Chlorine* (Eds.: P. Tundo, L.-N. He, E. Lokteva, C. Mota), Springer, Cham, **2016**.

[18] Ring-opening and isomerization reactions may occur at elevated temperatures and in the presence of a Lewis acid, see: M. Clerc, F. Stricker, S. Ulrich, M. Sroda, N. Bruns, L. F. Boesel, J. Read de Alaniz, *Angew. Chem. Int. Ed.* **2021**, *60*, 10219–10227; *Angew. Chem.* **2021**, *133*, 10307–10315.

[19] Under the optimized reaction condition, substrates **1o**, **1p** and **1q** display relatively low conversion under the catalytic conditions though high chemo-selectivities toward the products.

[20] a) M. Helou, O. Miserque, J.-M. Brusson, J.-F. Carpentier, S. M. Guillaume, *Chem. Eur. J.* **2010**, *16*, 13805–13813; b) C. Maquilón, F. Della Monica, B. Limburg, A. W. Kleij, *Adv. Synth. Catal.* **2021**, *363*, 4033–4040.

[21] K. J. Zhu, R. W. Hendren, K. Jensen, C. G. Pitt, *Macromolecules* **1991**, *24*, 1736–1740.

[22] Note that *anti*-**1a** is a viscous liquid and therefore *anti*-**1o** was selected as a closely related structural model for *anti*-**1a** demonstrating the favorable relative positioning of the alcohol and the oxirane towards the formation of the six-membered bicyclic carbonate **P1**.

Manuscript received: April 6, 2022
Accepted manuscript online: April 20, 2022
