Supporting Information

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1. General Considerations

All chemicals were purchased from commercial sources with purities ≥95% and used without further purification. Deuterated solvents were ordered from Deutero GmbH and stored over molecular sieves. NMR spectra were received using Bruker 300 Fourier, Bruker AV 300 and Bruker AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s= singlet, d= doublet, t= triplet and m= multiplet. NMR yields very determined by using mesitylene as internal standard. Gas chromatography was performed on Agilent 7890A GC System, mass spectra were measured on downstream 5975C inert XL MSD mass detector also from Agilent. The reported GC yields are based on a calibrated area of *n*-hexadecane as internal standard. Elementary analysis was performed on a TruSpec CHMS Micro from Leco. High resolution mass spectra (HRMS) were obtained either from a MAT 95 XP from Thermo (EI) or from an HPLC system 1200 and downstream ESI-TOF-MS 6210 from Agilent (ESI). IR spectra were recorded on a Nicolet iS10 MIR FT-IRspectrometer from Thermo Fisher Scientific. Thin layer chromatography was performed on Merck TLC-plates with fluorescence indication (silica type 60, F_{254}), spots were visualized using UV-light or vanilline. Flash chromatography was performed using silica with a grain size of 40–63 µm from Macherey-Nagel. It has to be considered that in some cases by addition of the epoxide to the catalyst a highly exothermic reaction was observed. This should be considered especially for upscaling experiments.

2. General Procedures (GP)

Coupling reaction of CO₂ and terminal epoxides under ambient conditions (GP1):

A 25 cm³ flask was charged with 5 mol% Cal₂, 5 mol% 18-crown-6 ether and 1 equiv epoxide **1**, **4** or **6** (2.00 g). The flask was constantly purged with CO₂ under atmospheric pressure. The reaction mixture was stirred for 24 h at 23 °C. The reaction mixture was filtered over silica gel (SiO₂) with cyclohexane:ethyl acetate= 1:1. After removal of all volatiles in vaccuo the product **2**, **5** or **7** was obtained. It has to be considered that in some cases by addition of the epoxide to the catalyst a

highly exothermic reaction was observed. This should be considered especially by upscaling experiments.

Coupling reaction of CO₂ and internal epoxides (GP2):

A 45 cm³ stainless-steel autoclave was charged with 5.0 mol% Cal₂, 5.0 mol% 18crown-6 ether, 1.0 equiv epoxide **8** or **10** (0.50–2.00 g), and in the case of a solid epoxide additionally 1.5 mL solvent were added. The autoclave was sealed, constantly purged with 10 bar CO₂, and the reaction mixture was stirred for 48 h at 45 °C. Subsequently the reactor was cooled to ≤ 20 °C with an ice bath and CO₂ was released slowly. The reaction mixture was filtered over silica gel (SiO₂) with cyclohexane:ethyl acetate= 2:1 or purified by flash chromatography. After removal of all volatiles in vaccuo the product **9** or **11** was obtained. It has to be considered that in some cases by addition of the epoxide to the catalyst a very exothermic reaction was observed. This should be considered especially for upscaling experiments.

Catalyst and parameter screening for the conversion of CO₂ with terminal epoxides using an autoclave (GP3):

A 45 cm³ stainless-steel autoclave was charged with 2.5 mol% of the catalyst, 2.5 mol% 18-crown-6 ether and 1.0 equiv *tert*-butyl glycidyl ether **1a** (2.00 g; 27.7 mmol). The autoclave was sealed, charged with 1–10 bar CO₂, and the reaction mixture was stirred for 4–24 h at 25 °C. Subsequently, the reactor was cooled to \leq 20 °C with an ice bath and CO₂ was released slowly. The conversion of the epoxide **1a** and yield of the desired carbonate **2a** were determined by ¹H NMR spectroscopy using mesitylene as internal standard.

Catalyst and parameter screening for the conversion of CO₂ with terminal epoxides using a schlenk flask (GP4):

A 25 mL schlenk flask was charged with 2.5–5.0 mol% of the catalyst, 2.5–5.0 mol% 18-crown-6 ether and 1.0 equiv *tert*-butyl glycidyl ether **1a** (2.00 g; 27.7 mmol). The flask was constantly purged with CO₂ under atmospheric pressure and the reaction mixture was stirred for 24 h at 23 °C. Subsequently the conversion of the epoxide **1a** and yield of the desired carbonate **2a** were determined by ¹H NMR spectroscopy using mesitylene as internal standard.

Parameter optimization for the conversion of CO₂ with internal epoxides (GP5):

A 45 cm³ stainless-steel autoclave was charged with 5.0–10 mol% Cal₂, 5.0–10 mol% 18-crown-6 ether and 1.0 equiv cyclohexene oxide **5e** (2.00 g; 20.4 mmol). The autoclave was sealed, charged with 10 bar CO₂, and the reaction mixture was stirred for 24–48 h at 23–45 °C. Subsequently the reactor was cooled to \leq 20 °C with an ice bath and CO₂ was released slowly. The conversion of the epoxide **5e** and the yield of cyclohexene carbonate **6e** were determined by ¹H NMR spectroscopy using mesitylene as internal standard.

Solvent screening for the conversion of CO₂ with internal epoxides (GP6):

A 45 cm³ stainless-steel autoclave was charged with 5.0 mol% Cal₂, 5.0 mol% 18crown-6 ether, 1.0 equiv trans-stilben oxide **5I** (0.50 g; 2.55 mmol), and 3 mL solvent. The autoclave was sealed, charged with 10 bar CO₂, and the reaction mixture was stirred for 24 h at 23–45 °C. Subsequently the reactor was cooled to \leq 20 °C with an ice bath and CO₂ was released slowly. The conversion of the epoxide **5I** and the yield of the desired carbonate **6I** were determined by ¹H NMR spectroscopy using mesitylene as internal standard.

3. Screening Reactions

Catalyst screening

[#] BuO) + CO ₂	2.5 mol% CaX ₂ 2.5 mol% 18-crown-6 25 °C, 4 h, $p(CO_2) = 10$ bar	⁰ ™BuO 2a
Entry	Catalyst	Ligand	Yield 2a ^a / %
1	CaCl ₂	18-crown-6	0
2	CaBr ₂	18-crown-6	16
3	Cal ₂	18-crown-6	64
4	Cal_2	-	7
5	Ca(OAc) ₂	18-crown-6	0
6	Ca(CO ₃)	18-crown-6	0
7	Ca(D-Glu) ₂	18-crown-6	0
8	Ca(OTf) ₂	18-crown-6	0
9	Ca(acac) ₂	18-crown-6	0
10	Ca(ox)	18-crown-6	0
11	CaSiO ₃	18-crown-6	0
12	CaTiO₃	18-crown-6	0
13	Ca(OMe) ₂	18-crown-6	0

^aReaction conditions: 45 cm³ stainless-steel autoclave, 1.0 equiv **1a** (15.4 mmol), 0.025 equiv catalyst and ligand (1:1), solvent-free. Yield determined by ¹H NMR with mesitylene as internal standard (**GP1**).

Parameter optimization for the conversion of CO₂ with internal epoxides



Entry	Cal ₂ / 18-crown-6	T/ ℃	p/bar	<i>t /</i> h	Yield 4e ^a / %
1 ^b	5	23	1 atm.	24	5
2	5	23	10	24	22
3	10	23	10	24	24
4	5	23	10	48	33
5	10	23	10	48	46
6	5	45	10	48	90
7	10	45	10	48	91

^aReaction conditions: 45 cm³ stainless-steel autoclave, 1.0 equiv **5e** (20.4 mmol), 0.05–0.10 equiv catalyst and ligand (1:1), solvent-free. Yield determined by ¹H NMR with mesitylene as internal standard (**GP4**). ^bReaction conditions: 25 mL schlenk flask, 1.0 equiv **5e** (20.4 mmol), 0.05 equiv catalyst and ligand (1:1), solvent-free under atmospheric pressure of CO₂.

Ph + Ph + 10c	$CO_{2} \xrightarrow{5 \text{ mol}\% \text{ Cal}_{2}}{5 \text{ mol}\% 18 \text{-crown-6}}$ $23-45 ^{\circ}\text{C}, 24 \text{ h},$ $P(CO_{2})= 10 \text{ bar},$ solvent	Ph Ph Ph 11c	
Entry	Solvent	T/ °C	Yield 4j ^a / %
1	DCM	45	96
2	Chloroform	45	91
3	EE	45	3
4	THF	45	5
5	MTBE	45	2
6	1,4-dioxane	45	<1
	Di-PG-di-methylether	45	0
	CH₃CN	45	97
	Toluol	45	<1
	CF ₃ (CF ₂) ₃ OMe	45	93
	MEK	45	62
7	DCM	23	86
8	CH₃CN	23	94
9	CF ₃ (CF ₂) ₃ OMe	23	<1

Solvent screening for the conversion of CO_2 with internal epoxides

^aReaction conditions: 45 cm³ stainless-steel autoclave, 1.0 equiv **3j** (2.55 mmol), 0.05 equiv catalyst and ligand (1:1), 3 mL solvent. Yield determined by ¹H NMR with mesitylene as internal standard (**GP4**).

4. ¹H NMR and ¹³C NMR spectra

4-(*tert*-Butoxymethyl)-1,3-dioxolan-2-one (2a)^[1]



4-(Hydroxymethyl)-1,3-dioxolan-2-one (2b)^[1] ¹H-NMR



4-(Methoxymethyl)-1,3-dioxolan-2-one (2c)^[2]



4-((Prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one (2d)^[3]



4-((Allyloxy)methyl)-1,3-dioxolan-2-one (2e)^[1]

¹H NMR



(2-Oxo-1,3-dioxolan-4-yl)methyl methacrylate (2f)^[1]



4-((Furan-2-ylmethoxy)methyl)-1,3-dioxolan-2-one (2g)







4-(((tert-Butyldimethylsilyl)oxy)methyl)-1,3-dioxolan-2-one (2h)







²⁹Si NMR



4-((2,2,3,3-tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one (2i)^[4]



4-((2,2,3,3,3-pentafluoropropoxy)methyl)-1,3-dioxolan-2-one (2j)^[5]



4-(((2,2,3,3,4,4,5,5-Octafluoropentyl)oxy)methyl)-1,3-dioxolan-2-one (2k)





¹³C NMR





4-Methyl-1,3-dioxolan-2-one (5a)^[1]



4-Ethyl-1,3-dioxolan-2-one (5b)^[1]

¹H NMR



4-Butyl-1,3-dioxolan-2-one (5c)^[1]

¹H-NMR



4-Hexyl-1,3-dioxolan-2-one (5d)^[1]



4-(Chloromethyl)-1,3-dioxolan-2-one (5e)^[1]







4-(Morpholinomethyl)-1,3-dioxolan-2-one (5g)^[3]



4-Phenyl-1,3-dioxolan-2-one (5h)^[1]



4,4-Dimethyl-1,3-dioxolan-2-one (7a)^[3]



4-(Chloromethyl)-4-methyl-1,3-dioxolan-2-one (7b)^[7]

¹H NMR



4-(Chloromethyl)-4-ethyl-1,3-dioxolan-2-one (7c)







Methyl 4-methyl-2-oxo-1,3-dioxolane-4-carboxylate (7d)





4-Methyl-4-phenyl-1,3-dioxolan-2-one (7e)^[8]







cis Tetrahydrofuro[3,4-*d*][1,3]dioxol-2-one (4d)^[1]



cis Cyclohexene carbonate (9c)^[1]

¹H NMR







5-Methylhexahydrobenzo[d][1,3]dioxol-2-one (9e)^[6]



cis 5-vinylhexahydrobenzo[*d*][1,3]dioxol-2-one (9f)^[6]





¹H NMR



cis hexahydro-4*H*-cyclohepta[*d*][1,3]dioxol-2-one (9h)^[6]



trans 4,5-Dimethyl-1,3-dioxolan-2-one (11a)^[1]



cis 4,5-Dimethyl-1,3-dioxolan-2-one (11b)^[1]



trans 4,5-Diphenyl-1,3-dioxolan-2-one (11c)^[1]



trans 4-Methyl-5-phenyl-1,3-dioxolan-2-one (11e)^[10]

¹H NMR





trans Ethyl 2-oxo-5-phenyl-1,3-dioxolane-4-carboxylate (11g)^[11]

¹H NMR





5. Formation of product 13 and proposed mechanism



6. NMR-Investigations



All solutions were prepared in CH_3CN and CD_3CN was used as NMR-solvent.

To investigate the in situ complexation of the Cal₂ by 18C6 we conducted some 1 H-NMR experiments. In the spectrum on the bottom the signal of the 18C6 protons at 3.50 ppm is shown in a pure 18C6 solution. In the spectrum above the signal of the two epoxide protons at 3.96 ppm of a pure trans stilbenoxide solution is shown. The third spectrum from below shows a spectrum from a 1:1 mixture of 18C6 and trans stilbenoxide which indicates that the crown ether and the substrate don't interact. The spectrum above this shows the signals of a solution with a 1:1 mixture of Cal₂ and 18C6. In this spectrum the signal of the 18C6 compound at 3.50 ppm disappears entirely and a new signal at 3.82 ppm appears. This indicates that all the crown ether coordinates to the Cal₂ salt and the new signal at 3.82 ppm can be attributed to a Cab/18C6 complex. Furthermore we prepared a solution containing the trans stilbenoxide substrate and 5 mol% of Cal₂ and 18C6 to simulate the concentration ratios under reaction conditions. The spectrum of this solution is the second spectrum from the top. In this spectrum also the signal of the 18C6 is entirely disappeared, which indicates a highly selective complexation of the Cal₂ salt by the crown ether under reaction conditions. Furthermore, even at much higher catalyst concentrations the complexation is highly selective (spectrum at the top).

7. Crystallographic Data

Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.) and refined by full-matrix least-squares procedures on *F*² (SHELXL-2014: Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3.). Mercury (Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M., van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453.) was used for graphical representations.

Crystal data for Cal₂/18C6-complex **3**-2 DMF: C₁₈H₃₈Cal₂N₂O₈, *M* = 704.38, triclinic, space group $P\bar{1}$, *a* = 7.4395(2), *b* = 10.2984(3), *c* = 10.4052(3) Å, *α* = 118.1251(6), *β* = 94.6199(7), γ = 92.7499(7)°, *V* = 697.42(3) Å³, *T* = 150(2) K, *Z* = 1, 19016 reflections measured, 3203 independent reflections (R_{int} = 0.0198), final *R* values (*I* > 2 σ (*I*)): R_1 = 0.0158, wR_2 = 0.0361, final *R* values (all data): R_1 = 0.0173, wR_2 = 0.0369, 148 parameters.

Crystal data for **11i**: $C_{10}H_{10}O_4$, M = 194.18, orthorhombic, space group $P2_12_12_1$, a = 8.6487(2), b = 9.6280(2), c = 10.6343(2) Å, V = 885.51(3) Å³, T = 150(2) K, Z = 4, 6385 reflections measured, 1657 independent reflections ($R_{int} = 0.0181$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0282$, $wR_2 = 0.0707$, final R values (all data): $R_1 = 0.0283$, $wR_2 = 0.0708$, 131 parameters, Flack parameter x = 0.02(4).

CCDC 1532107 and 1542896 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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