Green Chemistry

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c6gc00671j

Cooperative catalyst system for the synthesis of oleochemical cyclic carbonates from CO_2 and renewables†

Nils Tenhumberg,[a] Hendrik Büttner,[a] Benjamin Schäffner,[b] Daniela Kruse,[b] Michael Blumenstein[c] and Thomas Werner*[a]

Received 7th March 2016,
Accepted 11th April 2016

DOI: 10.1039/c6gc00671j

www.rsc.org/greenchem

Phosphonium salts and various (transition-) metals were studied as catalysts in the synthesis of carbonated oleochemicals from the corresponding epoxides and carbon dioxide. In combination with tetra-*n*-butylphosphonium bromide molybdenum compounds were identified as highly active co-catalysts for the formation of cyclic carbonates. The co-catalyst accelerates the conversion of the epoxidized fatty acid ester considerably. The chemo- as well as the stereoselectivity of the carbonated oleochemicals can be controlled by the choice of the catalyst and the reaction conditions. Under optimized reaction conditions this new catalyst system allows the conversion of both mono- and polyepoxidized oleo compounds into the corresponding carbonates in good to excellent yields up to >99% under comparatively mild reaction conditions. This procedure has been applied to the synthesis of a potential renewable plasticizer and works well even at larger scale (200 g).

Introduction

The utilization of renewable resources as an alternative feedstock to petrochemicals has attracted much attention in recent years.[1–7] In this context, widespread and inexpensive vegetable oils are used in various applications in the chemical industry.[8,9] For example, epoxidized plant oils and fatty acid derivatives are employed as plasticizers and stabilizers in plastics such as polyvinyl chloride, as starting material for epoxy resins, as reactive diluents for paints and as intermediates for polyurethane-polyol production.[10,11] Moreover, epoxidized fatty acids and their methyl esters are discussed as sustainable and valuable intermediates for the synthesis of eco-friendly lubricants[12] as well as for carbonated oleochemicals produced by the coupling reaction of epoxides and carbon dioxide. The utilization of CO_2 has become a major field of research producing value-added organic chemicals from this C1 building block.[13] In this context the 100% atom efficient reaction between CO_2 and fossil-based epoxides is an attractive reaction. The conversion of epoxidized vegetable oils and fatty acid derivatives into cyclic carbonates benefits in two different ways; the synthesis of novel oleo compounds from renewable resources as well as the recycling and exploiting of carbon dioxide into the value chain. These oleochemical carbonates can be used for several applications and are already employed as novel precursors for the synthesis of non-isocyanate polyurethanes (NIPU). Moreover, the reaction of cyclic carbonates and amines permits not only the formation of polyurethanes but also the replacement of toxic isocyanates and additionally, interfering by-product formation can be prevented.[14–19] Oleochemical carbonates are also suggested as starting materials for polyesters and polycarbonates, potential industrial lubricants, fuel additives and polymer plasticizers.[20,21] The coupling reaction of epoxides with CO_2 is an intensively studied field of research and various homo- and heterogeneous catalysts have been reported.[22–30] Commonly nucleophilic organic salts are employed as (co-)catalyst. Additionally, Lewis acids are able to activate epoxides for the nucleophilic ring opening by coordination and as a result the formation of the cyclic carbonate can be accelerated. Hence, there are numerous reports on acidic co-catalysts and recent progress has been made by employing complexes based on aluminum,[31,32] iron(III),[33–35] or zinc[36–38] as well as niob compounds.[39–41] However, only a few reports deal with special emphasis on the formation of internal cyclic carbonates and the respective stereoselectivity.[23,42] This may be attributed to the fact that internal epoxides are less reactive than terminal epoxides because of steric hindrance.[43–46]

Carbonated oleo compounds are typically prepared from the corresponding epoxidized oleo-derivatives and CO_2 using tetra-*n*-butylammonium bromide ($[Bu_4N]Br$) as catalyst. For

---

[a] *Leibniz-Institut für Katalyse e. V. (LIKAT Rostock), Albert-Einstein-Str. 29 a, 18059 Rostock, Germany. E-mail: thomas.werner@catalysis.de*
[b] *Evonik Industries AG, Paul-Baumann-Str. 1, 45772 Marl, Germany*
[c] *Hobum Oleochemicals, Seehafenstraße 20, 21079 Hamburg, Germany*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6gc00671j

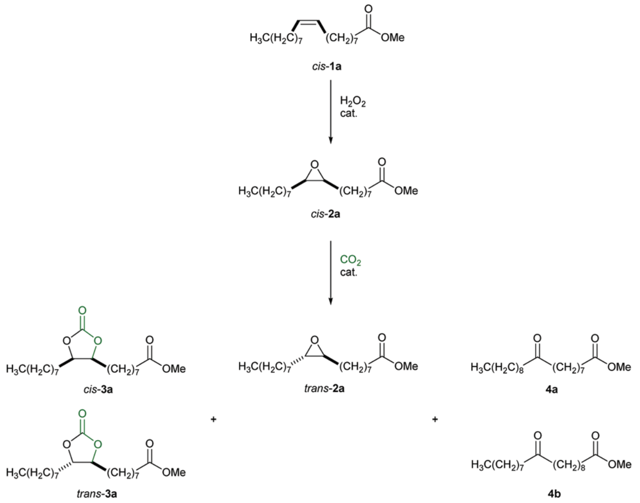
instance, Tamami *et al.* reported the catalytic synthesis of carbonated soybean oil (CSBO) from epoxidized soybean oil (ESBO) at atmospheric CO_2 pressure. However, a reaction time of 70 h at 110 °C was needed to obtain full conversion employing $[Bu_4N]Br$ as catalyst.[19] With the intention to produce polyurethanes from CSBO Yeganeh *et al.* employed 5.0 mol% $[Bu_4N]Br$ in combination with 2.5 mol% calcium chloride to convert ESBO with CO_2 for 72 h at 110 °C and ambient pressure.[47] An improved protocol for the synthesis of carbonated oleo compounds was described by Doll *et al.* using supercritical CO_2 as a reaction medium.[21,48] However, both reactions suffer from high catalyst loading of 5 mol% Bu_4NBr and either long reaction time of 70 h[19] or harsh reaction condition of $p(CO_2)$ = 100 bar.[21,48] A composite catalyst comprising $SnCl_4 \cdot 5H_2O$ and $[Bu_4N]Br$ showed an increased catalytic activity compared to separately employed catalysts $[Bu_4N]Br$ or $SnCl_4$, respectively.[18] A very active system composed of $[Bu_4N]Br$ and a Cr(III)-substituted silicotungstate was employed by Leitner *et al.* to obtain improved results at 100 °C in supercritical carbon dioxide.[49] However, in contrast to mono-epoxidized oleo compounds the polyoxometalate system seems to be less active for the conversion of poly-epoxidized oleo compounds as side reactions were encountered. Schäffner *et al.* tested simple alkali halides in combination with phase transfer catalysts in the reaction of epoxidized methyl linoleate with CO_2 to the respective bis-carbonate.[20] Sodium iodide and 15-crown-5 as well as the combination of potassium iodide and 18-crown-6 proved to be very active catalyst systems in the model reaction at 100 °C, 100 bar and 17 h with a conversion of 94% and 90%, respectively. Rokicki *et al.* already reported in 2006 that KI and 18-crown-6 can catalyze the carbonization of epoxidized soybean oil under somewhat harsh reaction conditions of 130 °C and 6 MPa.[50] However, Schäffner *et al.* tested several poly-ethylene-glycols of different molecular weights as alternative and inexpensive phase transfer catalysts. In the presence of 3.5 wt% KI and 3.5 wt% PEG400 84% of the epoxidized methyl linoleate was selectively converted to the corresponding bis-carbonate. Based on these results a life cycle analysis (LCA) was performed to evaluate environmental impacts for the replacement of diisononyl phthalate (DINP) by carbonated fatty methyl esters (CFAME) as potential plasticizers. Major savings of CFAME were accounted for greenhouse gas emissions and primary energy demand. Recently, Jerome and Tassaing *et al.* reported two-component catalyst system based on $[Bu_4N]Br$ and Brønsted acids as co-catalyst.[51] The conversion of epoxidized linseed oil and CO_2 by $[Bu_4N]Br$ was increased distinctly while phenolic or perfluoro Brønsted acids as co-catalysts were present. Detailed kinetic studies revealed optimized reaction conditions of 120 °C, 5.0 MPa, 10 h, 2.2 mol% $[Bu_4N]Br$ and 2.2 mol% perfluoro *tert*-butanol to couple CO_2 and epoxidized linseed oil in an organocatalytic approach.

In a preceded screening of Lewis acids as co-catalyst and suitable nucleophilic catalysts the reaction of methyl oleate and CO_2 was investigated to produce cyclic carbonates based on oleochemicals. Herein, we report the utilization of molybdenum compounds and tungstic acid as highly active co-catalyst for the synthesis of oleochemical cyclic carbonates in combination with tetra-*n*-butylphosphonium bromide ($[Bu_4P]Br$) as a source for a nucleophile. In 1980 Kisch *et al.* reported 0.5 mol% molybdenum(V) chloride in combination with 3 mol% triphenyl phosphane as catalysts for the synthesis of propylene carbonate at room temperature.[52,53] However, under these conditions an extraordinary long reaction time of 7 days was required to obtain 78% yield. Furthermore, in 2011 Chen *et al.* reported the direct synthesis of cyclic carbonates form the respective terminal olefin employing $MoO_2(acac)_2$ as an epoxidation catalyst.[54] However, in the cycloaddition reaction of the respective epoxide and CO_2 the molybdenum catalyst was inactive. This report will give a full account on the coupling reaction of CO_2 and epoxides based on renewable oleochemicals utilizing tetra-*n*-butylphosphonium salts in combination with metal-based co-catalysts.[55] Different organocatalysts were tested in order to study the influence of the halide on the reaction. Furthermore, the influence of the catalyst concentration and the reaction conditions were studied in detail with respect to the chemoselectivity of the reaction as well as for the stereoselectivity of the produced cyclic carbonates. Under optimized reaction conditions a variety of epoxidized fatty acid methyl esters were converted to the corresponding cyclic carbonates and the respective diastereoisomers were isolated. Additionally, epoxidized vegetables oils were employed to evaluate the catalyst system for the formation of carbonated oils which represent potential precursor molecules for non-isocyanate polyurethanes. Also a reaction scale up was realized to test the corresponding oleochemical cyclic carbonates as feedstock for the production of bio-based plasticizers.

Results and discussion

The conversion of epoxidized methyl oleate **2a** with CO_2 to carbonated methyl oleate (CMO) **3a** was studied as model reaction for the synthesis of carbonated oleo chemicals. Beforehand, the model substrate epoxidized methyl oleate *cis*-**2a** was prepared by oxidation of methyl oleate (*cis*-**1a**) with hydrogen peroxide.[56] An overall reaction sequence including the subsequent coupling with CO_2 and the expected products (by-) products of this reaction is shown in Scheme 1.[57]

Although the diastereomeric pure epoxide *cis*-**2a** was employed as starting material in the coupling reaction with CO_2 both diastereoisomers of CMO *cis*-**3a** and *trans*-**3a** were formed as products (Table 1). Depending on the catalyst system and the reaction conditions the formation of *trans*-epoxidized methyl oleate *trans*-**2a** as well as 9-ketostearic acid methyl ester **4a** and 10-ketostearic acid methyl ester **4b** were observed as by-products in very small amounts. Based on our recent results regarding the utilization of CO_2 as a C1 synthon and the development of sustainable catalyst recycling methods, the catalyst screening was performed at 100 °C, $p(CO_2$, 100 °C) = 50 bar, 16 h and solvent-free conditions (Table 1).[58–64] Carbonated oleo compounds are typical pre-



Scheme 1 General procedure of the synthesis of carbonated methyl oleate **3a**.

pared from the corresponding epoxidized oleo compounds and CO_2 using $[Bu_4N]Br$ which represents the benchmark catalyst. Under this reaction conditions a conversion of 39% of *cis*-**2a** and a yield of 32% of the cyclic carbonate **3a** was observed if tetra-*n*-butylammonium bromide was employed as catalyst (entry 1). As an alternative to $[Bu_4N]Br$ the respective phosphonium salt was tested in order to compare the impact of the cations (entry 2). In the presence of tetra-*n*-butylphosphonium bromide 49% of the epoxide *cis*-**2a** was converted while an excellent selectivity of 94% was determined (entry 2). Since selectivity and conversion of $[Bu_4P]Br$ were increased distinctively compared to $[Bu_4N]Br$ further investigations regarding the effects of the halide compound were conducted with the phosphorus-based catalysts. The employment of $[Bu_4P]Cl$ led to the formation of carbonate **3a** solely and a high selectivity of 99% was determined (entry 3). With regard to the stereoselectivity of carbonated methyl oleate **3a** $[Bu_4P]Cl$ provided almost exclusively the *cis*-isomer (*cis*-**3a**) and *cis* : *trans* ratio of 90 : 10 was observed. With increasing atomic number of the halide, both chemo- and stereoselectivity decreased noticeably. Accordingly, for $[Bu_4P]Br$ still an excellent chemoselectivity of 94% was observed but $[Bu_4P]I$ led only to 71% (entries 2 and 4). Among the $[Bu_4P]^+$-based catalysts the bromide showed the highest catalytic activity and the following order of reactivity for $[Bu_4P]X$ was observed X = Br > Cl > I. This order of reactivity reflects a combination of nucleophilicity (Cl > Br > I) and leaving group character (I > Br > Cl).[49] Hence, the co-catalyst screening was conducted using 2 mol% $[Bu_4P]Br$ and an equimolar amount of the respective Lewis acid. With aluminum-based co-catalysts (entries 5 and 6) and calcium chloride (entry 7) the yields of the cyclic carbonate **3a** were considerably increased up to 62%. A significant improvement was observed while molybdenum compounds as well as tungstic acid (H_2WO_4) as co-catalyst were present (entries 8–14). Molybdenum compounds and especially MoO_3 and $MoO_2(acac)_2$ as well as H_2WO_4 are reported as catalysts for the hydroxylation of fatty acid methyl esters by H_2O_2.[65–67] In these reactions the corresponding epoxide is formed as intermediate and both transition metals are probably able to activate the epoxide for the nucleophilic ring-opening by water. Therefore, we assumed that both compounds are suitable co-catalysts for the activation of the epoxides **2** in the coupling reaction with CO_2 to form cyclic carbonates **3**. In fact, the highest yield of 84% of CMO **3a** was obtained using MoO_3 as co-catalyst in combination with $[Bu_4P]Br$ (entry 8). Compared to single organocatalyst $[Bu_4P]Br$, the yield of **3a** was almost doubled from 46% to 84%. However, the selectivity towards CMO **3a** decreased to 85% and the formation of ketone **4** increased slightly to 6%. In general, we observed that an employment of a co-catalyst led to *cis* : *trans*-ratios of **3a** between 69 : 31 and 40 : 60, which was less selective than single organocatalyst $[Bu_4P]Br$ alone (entries 2 and 5–14).

Investigations concerning the concentration of the co-catalyst showed that even small amounts of MoO_3 resulted in a sig-

Table 1 Screening of different catalysts and co-catalysts for the synthesis of cyclic carbonate **3**[a]

			Conversion (%)	Selectivity (%)		Yield (%)		
Entry	Catalyst	Co-catalyst	*cis*-**2a**	**3a**	*cis* : *trans*	**3a**	*trans*-**2a**	**4**
1	$[Bu_4N]Br$	—	39	82	46 : 56	32	1	1
2	$[Bu_4P]Br$	—	49	94	71 : 29	46	0	0
3	$[Bu_4P]Cl$	—	39	99	90 : 10	38	0	0
4	$[Bu_4P]I$	—	35	71	57 : 43	25	0	1
5	$[Bu_4P]Br$	$Al(OiPr)_3$	66	76	56 : 44	50	1	5
6	$[Bu_4P]Br$	$AlCl_3$	87	71	54 : 46	62	1	5
7	$[Bu_4P]Br$	$CaCl_2$	71	86	51 : 49	61	1	2
8	$[Bu_4P]Br$	MoO_3	99	85	66 : 34	84	0	6
9	$[Bu_4P]Br$	MoO_2	80	90	66 : 34	72	0	1
10	$[Bu_4P]Br$	$Na_2MoO_4 \cdot 2H_2O$	83	89	69 : 31	74	0	1
11	$[Bu_4P]Br$	H_2MoO_4	96	85	49 : 51	82	2	3
12	$[Bu_4P]Br$	$Mo(CO)_6$	93	83	40 : 60	77	2	3
13	$[Bu_4P]Br$	$MoO_2(acac)_2$	94	77	52 : 48	72	4	5
14	$[Bu_4P]Br$	H_2WO_4	80	93	66 : 34	74	0	1

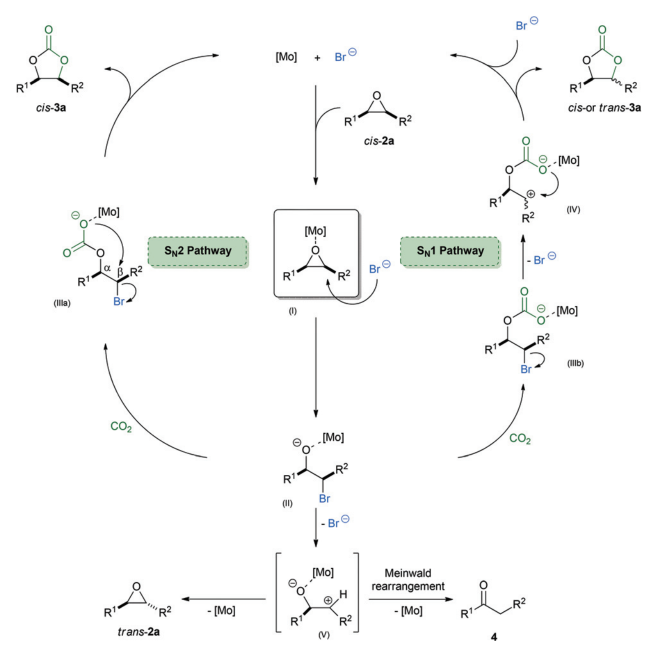
[a] Reaction conditions: 5.0 mmol *cis*-**2a**, 2.0 mol% catalyst, 2.0 mol% co-catalyst, $p(CO_2$, 100 °C) = 50 bar, 100 °C, 16 h, solvent-free.

Table 2 Catalyst variation of binary catalytic system[a]

		Conversion (%)	Selectivity (%)		Yield (%)		
Entry	MoO_3 (mol%)	*cis*-**2a**	**3a**	*cis* : *trans*	**3a**	*trans*-**2a**	**4a**
1	—	49	94	71 : 29	46	0	0
2	0.10	90	91	68 : 32	82	1	2
3	0.25	95	91	64 : 36	86	1	2
4	0.50	98	89	60 : 40	87	1	3
5	1.00	99	88	57 : 43	87	1	3
6	2.00	99	85	66 : 34	84	0	6

[a] Reaction conditions: 5.0 mmol *cis*-**2a**, 2.0 mol% $[Bu_4P]Br$, 0.1–2.0 mol% MoO_3, $p(CO_2, 100\ °C) = 50$ bar, 100 °C, 16 h, solvent-free.

nificant improvement in the conversion of *cis*-**2a** (Table 2). High yields ≥82% and selectivities up to 91% of **3a** were already observed employing 0.1 mol% or 0.25 mol% of MoO_3 (entries 2 and 3). Indeed, higher amounts of MoO_3 of 0.50–2.00 mol% resulted in excellent conversion of *cis*-**2a**, but both chemo- and stereoselectivity decreased and the formation of ketone **4** was increased slightly (entries 4–6). In the presence of 0.25 mol% MoO_3 high chemoselectivity towards **3a** with 91% was obtained, while high conversion of *cis*-**2a** and good yield on **3a** was observed, too.



Scheme 2 Proposed reaction mechanism for the synthesis of carbonated methyl oleate **3a**.

Therefore, a catalyst concentration of 2 mol% $[Bu_4P]Br$ and 0.25 mol% of MoO_3 as a co-catalyst was the optimum ratio. Moreover, the results at high co-catalyst concentration imply that MoO_3 can promote the formation of by-products **4** (entry 6). According to the reaction results and recent reports,[28,31,68] a plausible reaction mechanism for the formation of carbonated methyl oleate **3a**, and the by-products *trans*-**2a** as well as ketone **4** is depicted Scheme 2. The first step in the reaction mechanism involves the activation of the epoxide *cis*-**2a** by the co-catalyst MoO_3 ([Mo]; (**I**)). In general, in the presence of MoO_3 an enhancement of the coupling efficiency compared to $[Bu_4P]Br$ alone was observed. This cooperative effect is attributed to the C–O bond polarization by coordination of MoO_3 to *cis*-**2a** which accelerates the ring-opening of the internal epoxide *cis*-**2a** by the halide.[68] Subsequently, the nucleophilic reaction of the bromide forms an alcoholate (**II**) which results in an inversion of the configuration at the respective carbon atom. Notably, no conversion is observed in the absence of the phosphonium salt. This indicates the involvement of the bromide in the epoxide opening resulting in the formation of alcoholate (**II**) which seems to be the initial step in both reaction pathways. Alcoholate (**II**) is able to attack CO_2 and forms a linear carbonate species (**III**). Due to the fact, that both diastereoisomers *cis*- and *trans*-**3a** were produced, it is reasonable to consider both types of nucleophilic substitutions, S_N1 and S_N2 in the ring-closure of the linear carbonate species.

In aprotic solvents nucleophilic substitutions involving chlorides react predominantly *via* S_N2 mechanism due to the weak leaving group character of the chloride while iodides rather tends to react in a S_N1 mechanism. Hence, further coupling experiments were conducted employing $[Bu_4P]$-based organocatalysts with different halides and MoO_3 to confirm the duality of ring-closure (Table 3).

Tetra-*n*-butylphosphonium chloride ($[Bu_4P]Cl$) in combination with MoO_3 led to the formation of carbonate **3a** with high chemo- and stereoselectivity (entry 1). Nearly complete retention of the stereochemistry of the starting material *cis*-**2a** was observed and **3a** was obtained with a *cis* : *trans* ratio of 94 : 6. In the S_N2 pathway of the proposed mechanism the

Table 3 Chemo- and stereocontrol of the coupling reaction of *cis*-**2a** and CO_2 producing **3a** depending on the halide[a]

		Conversion (%)	Selectivity (%)		Yield (%)		
Entry	Catalyst	*cis*-**2a**	**3a**	*cis* : *trans*	**3a**	*trans*-**2a**	**4a**
1	$[Bu_4P]Cl$	64(39)	92(99)	94 : 6(90 : 10)	59(38)	0(0)	0(0)
2	$[Bu_4P]Br$	95(49)	91(94)	64 : 36(71 : 29)	86(46)	1(9)	2(0)
3	$[Bu_4P]I$	89(35)	79(71)	39 : 61(57 : 43)	70(25)	7(0)	11(1)

[a] Reaction conditions: 5.0 mmol *cis*-**2a**, 2.0 mol% $[Bu_4P]X$, 0.25 mol% MoO_3, $p(CO_2, 100\ °C) = 50$ bar, 100 °C, 16 h, solvent-free. Results in parenthesis were obtained in absence of MoO_3.

aliphatic carbonate anion attacks the C_β atom and an inversion of the configuration occurs (**IIIa**) (Scheme 2). Hence, the relative configuration of substrate *cis*-**2a** will be retained and *cis*-**3a** will be produced. The employment of $[Bu_4P]Br$ and especially of $[Bu_4P]I$ resulted in the formation of higher amounts of *trans*-**3a** with *cis* : *trans* ratios of 64 : 36 and 39 : 61, respectively (entries 2 and 3). A loss of the stereochemical information of *cis*-**2a** occurred. In contrast to the S_N2 pathway, the formation of a carbenium ion (**IV**) after bromide dissociation of the linear carbonate anion (**IIIb**) in the S_N1 pathway enables the formation of both *cis*-and *trans*-**3a**. Therefore, it can be assumed that the formation of thermodynamically favored carbonate *trans*-**3a** proceeds *via* S_N1 ring-closure. In addition, when $[Bu_4P]I$ and MoO_3 were employed the formation of the by-products *trans*-**2a** and **4** were increased too and yields up to 7 and 11% were obtained, respectively (entry 3). These by-products are most reasonably formed *via* [Mo] dissociation and/or Meinwald rearrangement of intermediate (**V**). Considering these results, the chemo- and especially the stereoselectivity exceedingly depend on the halide species of $[Bu_4P]X$ catalysts. As a consequence, the stereoselectivity can be controlled by the choice of the catalyst. A similar stereochemical control in the formation of fossil-based cyclic carbonates was observed by Kleij *et al.* employing tetra-*n*-butylammonium salts and a special dinuclear iron complex.[42] In summary, among the tested organocatalysts $[Bu_4P]Br$ combines high activity and high chemoselectivity which result from both, good nucleophilicity and good leaving group ability. Thus, further investigations regarding the catalyst concentration were conducted using $[Bu_4P]Br$ (Table 4).

In the presence of 2.0 mol% of $[Bu_4P]Br$ nearly quantitative conversion of epoxide *cis*-**2a** and a high yield of 86% of carbonate **3a** was obtained (entry 5). A decrease of catalyst amount followed the trends observed in the reaction screening regarding the co-catalyst concentration (Table 2) and led to rather low conversions of *cis*-**2a** and cyclic carbonate **3a** yield. However, if no $[Bu_4P]Br$ was present no formation of the cyclic carbonate **3a** was observed indicating that MoO_3 acted only as co-catalyst and was not able to catalyze the coupling reaction between the epoxide *cis*-**2a** and CO_2 on its own (entry 1). In addition to catalyst concentration investigations, screening experiments regarding temperature, CO_2 pressure and reaction time were conducted employing 2.0 mol% $[Bu_4P]Br$ and 0.25 mol% MoO_3.

Table 4 Variation of the catalyst concentration of $[Bu_4P]Br^a$

		Conversion (%)	Selectivity (%)		Yield (%)		
Entry	$[Bu_4P]Br$ (mol%)	*cis*-**2a**	**3a**	*cis* : *trans*	**3a**	*trans*-**2a**	**4a**
1	—	1	0	—	0	0	0
2	0.25	11	83	61 : 39	9	0	1
3	0.50	31	90	79 : 21	28	2	2
4	1.00	74	88	71 : 29	65	1	4
5	2.00	95	91	64 : 36	86	1	2

[a] Reaction conditions: 5 mmol *cis*-**2a**, 0–2.0 mol% $[Bu_4P]Br$, 0.25 mol% MoO_3, $p(CO_2, 100\ °C) = 50$ bar, 100 °C, 16 h, solvent-free.

Table 5 Variation of the reaction temperature and effects on the coupling reaction of *cis*-**2a** and CO_2^a

		Conversion (%)	Selectivity (%)		Yield (%)		
Entry	*T* (°C)	*cis*-**2a**	**3a**	*cis* : *trans*	**3a**	*trans*-**2a**	**4a**
1	80	37	>99	82 : 18	37	0	0
2	90	57	>99	79 : 21	57	0	1
3	100	95	91	64 : 36	86	1	2
4	120	>99	88	58 : 42	87	1	6

[a] Reaction conditions: 5.0 mmol *cis*-**2a**, 2.0 mol% $[Bu_4P]Br$, 0.25 mol% MoO_3, $p(CO_2, T) = 50$ bar, 16 h, solvent-free.

The reaction temperature was investigated in the range of 80–120 °C (Table 5). Within 80–100 °C both the conversion of *cis*-**2a** and the yield of **3a** increased considerably with ascending temperature (entries 1–3). At 120 °C full conversion of *cis*-**2a** was obtained, but the selectivity towards **3** decreased noticeably (entry 4). The formation of ketone **4** as a by-product was still low, however a certain yield of 6% was detected. Accordingly, the selectivity of the carbonate **3a** decreased to 88%. Also the formation of the thermodynamically favored carbonate *trans*-**3a** increased at elevated temperature of 120 °C. However, at 100 °C both an excellent reactivity of the catalyst system and a high chemoselectivity towards the formation cyclic carbonate **3a** were observed (entry 3). Hence, further investigations of the coupling reactions of epoxide *cis*-**2a** and CO_2 were carried out at 100 °C.

The dependence of the CO_2 pressure for the synthesis of cyclic carbonate **3a** is depicted in Fig. 1. Within the range from 10 to 50 bar CO_2 high conversions ≥95% of the epoxide *cis*-**2a** were obtained. The synthesis of carbonated oleochemicals often is performed at high pressure ≥100 bar under supercriti-

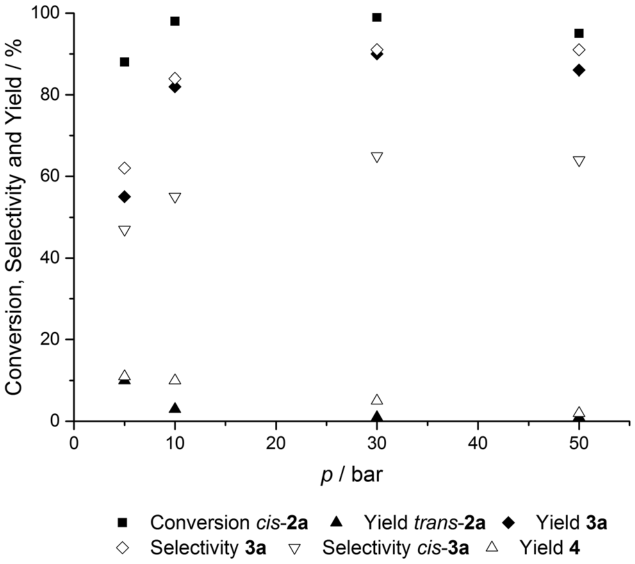
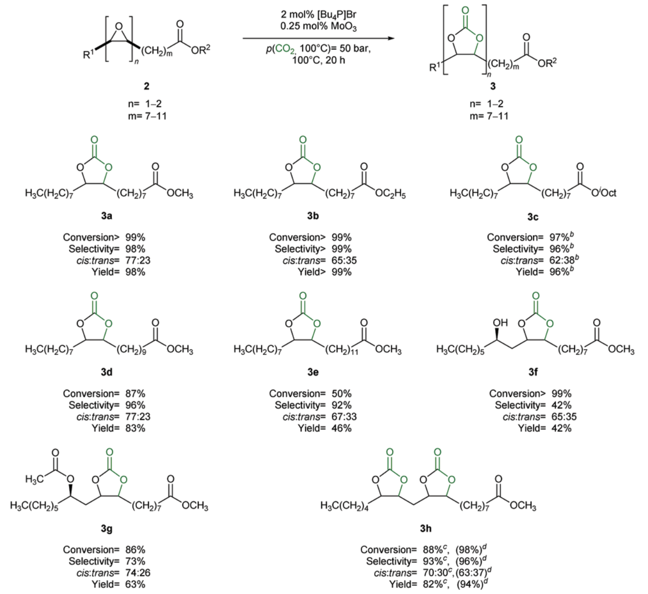


Fig. 1 Effect of the CO_2 pressure in the coupling reaction of *cis*-**2a** and CO_2. Reaction conditions: 5.0 mmol *cis*-**2a**, 2.0 mol% $[Bu_4P]Br$, 0.25 mol% MoO_3, $p(CO_2, 100\ °C) = 5–50$ bar, 100 °C, 16 h, solvent-free.

cal reaction conditions to realize high conversion and selectivity.[20,21,48,49] In contrast, the catalytic system based on [Bu_4P]Br and MoO_3 was even able to convert 98% of *cis*-**2a** at 10 bar with an excellent selectivity of 84%. In general, a distinct trend regarding the chemo- and stereoselectivity was also observed in dependence of the applied CO_2 pressure. At high pressure ≥30 bar CO_2 high selectivities ≥90% towards carbonate **3a** were obtained. In contrast to this at a rather low pressure of 5 bar carbonate **3a** was formed only with a moderate selectivity of 62%. Moreover, both by-products *trans*-**2a** and **4** were formed in amounts yielding 10% and 11%, respectively. Thus, a pressure of at least 10 bar is appropriate whereas the best result regarding reactivity and selectivity was obtained at 50 bar. Accordingly, investigations to evaluate the optimized reaction time were carried out and the respective results are plotted in Fig. 2. In a series of batch experiments with a reaction time of 4–24 h at 100 °C and $p(CO_2, 100\ °C) = 50$ bar conversions, yields and selectivities were determined. Conversions of ≥95% were obtained after 16 h. The highest yield of carbonate **3a** amounting to 94% was achieved after 20 h. Further prolonging of reaction time did not lead to any improvement of reaction outcome. In all experiments epoxide *trans*-**2a** was only formed in small amounts ≤2%.



Scheme 3 Isolated yields of oleochemical carbonates **3** employing the binary catalyst system [Bu_4P]Br and MoO_3. Conversion and selectivities in brackets were determined by ^1H NMR spectroscopy. Reaction conditions: 2.0 mol% [Bu_4P]Br, 0.25 mol% MoO_3, $p(CO_2, 100\ °C) = 50$ bar, 100 °C, 20 h. [b] 3.2 mol% [Bu_4P]Br, 0.4 mol% MoO_3. [c] 40 h. [d] 2.0 mol% [Bu_4P]Br/epoxide moiety and 0.25 mol% MoO_3/epoxide moiety; conversion, selectivity and yield were determined by ^1H NMR spectroscopy.

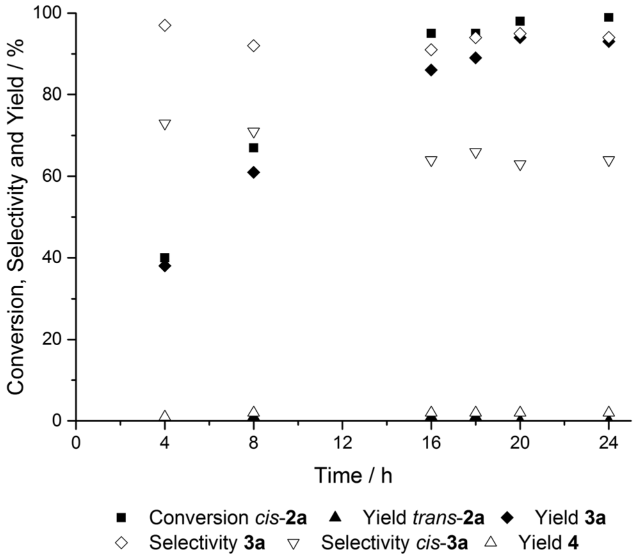
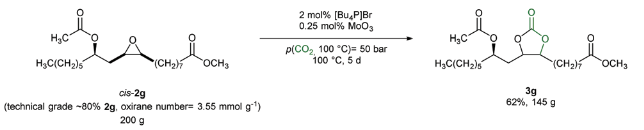


Fig. 2 Effect of the reaction time in the coupling reaction of *cis*-**2a** and CO_2. Reaction conditions: 5.0 mmol *cis*-**2a**, 2.0 mol% [Bu_4P]Br, 0.25 mol% MoO_3, $p(CO_2, 100\ °C) = 50$ bar, 100 °C.

In order to evaluate the substrate scope of the catalyst system various mono- as well as bis-epoxidized oleo compounds were converted to the corresponding cyclic carbonates **3** employing [Bu_4P]Br and MoO_3 as catalytic system under optimized reaction conditions (Scheme 3). The respective epoxides **2** were prepared according to the epoxidation protocol mentioned above from the respective olefins utilizing hydrogen peroxide and a ruthenium-based catalyst system at room temperature.[57] In addition to the model substrate epoxidized methyl oleate *cis*-**2a** the corresponding ethyl (*cis*-**2b**) and isooctyl oleate (*cis*-**2c**) were converted into the cyclic carbonates **3a**–**3c** in high yields of 98%, >99% and 96%, respectively. The *cis* : *trans* selectivities of the corresponding carbonated diastereoisomers were quite similar and did not exceed a ratio of 77 : 23 for the isomer *cis*-**3a**. A distinct trend with regard to the *cis*-isomers was observed for all the isolated carbonates **3**. Epoxidized methyl eicosenoate (*cis*-**2d**) was isolated in a very good yield of 83%, however for epoxidized methyl erucate (*cis*-**2e**) a conversion of only 50% was observed under these reaction conditions and 46% of **3e** was isolated. Epoxidized methyl ricinoleate (*cis*-**2f**) proved to be a challenging substrate. Although full conversion of *cis*-**2f** was achieved at 100 °C, 50 bar and 20 h, only 42% of *cis*-**2f** was selectively converted to the corresponding carbonate **3f**. NMR and GC-MS studies revealed the formation of a 5-membered ether derivative in 39% yield as a by-product.[57] This isomerization product is most reasonably formed due to an intramolecular substitution reaction of the alcohol moiety and the epoxide. However, if the alcohol moiety was protected by an acetyl group, the yield and selectivity were increased considerably. Under the given reaction conditions a conversion of 86% was obtained while 63% of the desired carbonate **3g** was isolated. Epoxidized methyl linoleate (*cis*-**2h**) was also employed as a substrate. Considering the fact that bis-epoxide *cis*-**2h** was only converted to 75% with a selectivity of 89% towards **3h** the time was prolonged to 40 h to obtain a higher conversion of 88% while the selectivity was increased to 93%. Moreover, if the amount of catalyst was adjusted to 2 mol% [Bu_4P]Br and 0.25 mol% MoO_3 per



Scheme 4 Upscaling of the coupling reaction of **2g** and CO_2 to produce **3g** employing two component catalyst system composed of $[Bu_4P]Br$ and MoO_3.

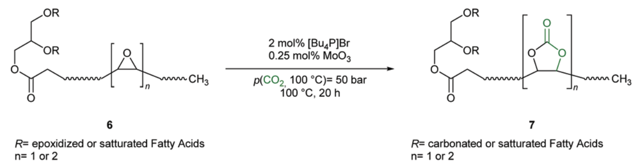
epoxide unit almost full conversion was obtained and an excellent selectivity of 96% was determined after 20 h. Additionally, *cis*- and *trans*-carbonate diastereoisomers of the mono-carbonated products **3a–3g** could be separated by column chromatography and were analyzed by NMR. We were also interested in an upscaling of the reaction producing carbonated fatty acid esters **3** in a multigram scale as they are considered to be a potential feedstock for renewable plasticizers for PVC. Carbonated *O*-acetyl methyl ricinoleate (**3g**) provides a useful additional ester moiety, thus enabling additional follow-up chemistry. Hence **2g** was employed in multigram scale reaction (Scheme 4).

The substrate **2g** was delivered by Hobum Oleochemicals in technical grade (purity ~80%) and an oxirane number of 3.55 mmol g^{-1} was determined prior to its application. Initially, the exothermic coupling reaction of **2g** and CO_2 was performed in a 20 g substrate scale in respect to **2g** to adapt to the reactor infrastructure. After 48 h at 100 °C, $p(CO_2, 100\ °C) = 50$ bar, 2.0 mol% $[Bu_4P]Br$ and 0.25 mol% MoO_3 a yield of 83% of cyclic carbonate **3g** was isolated. Hence, to obtain reasonable yields of the desired product the reaction time needed to be adjusted. Subsequently, the reaction was performed in a 200 g scale in respect to **2g**. After a reaction time of 5 days a yield of 62% was isolated which corresponds to 145 g of carbonated *O*-acetyl methyl ricinoleate (**3g**) as a product. Further investigations regarding the scope and limitation of the reaction protocol were conducted employing epoxidized vegetable oils **6** as substrates (Table 6). The respective oils **6** were employed in technical grade and the catalyst amount was adjusted in respect to the oxirane number, determined by ^1H NMR with mesitylene as an internal standard.

Epoxidized high-oleic sunflower oil **6a** is enriched in epoxidized methyl oleate triglyceride, hence it is akin to the model substrate *cis*-**2a**. Under the optimized reaction conditions full conversion of **6a** was obtained yielding 95% of the corresponding carbonated species **7a** (entry 1). The comparison of the FTIR spectra of substrate **6a** and the carbonated oil **7a** revealed very vividly the specific product band at 1797 cm^{-1} which corresponds to the ν(C–O) stretching vibration of the cyclic carbonate (Fig. 3). Likewise to the FTIR investigations also ^1H NMR studies of both, the product **7a** and substrate **6a**, reflect that the reaction proceeds smoothly under these conditions. The typical resonances in the range of 3.20 to 2.85 ppm correspond to the epoxide **6a** and disappeared in the spectra of the product **7a**. Accordingly, in the range of 4.65 to 4.10 ppm the specific product resonances appeared, which are in the expected range for cyclic carbonate protons.[50] This is also the typical range for CH_2-protons of the triglyceride backbone, thus these additional resonances superimpose with cyclic carbonate **7a** resonances.

The oxirane number of 4.02 mmol g^{-1} of epoxidized high-oleic sunflower oil (**6a**) was relatively low, due to the fact that **6a** is enriched on epoxidized oleate which exhibits only one epoxide unit per fatty acid ester. In contrast, for epoxidized sunflower oil (**6b**) an oxirane number of 7.02 mmol g^{-1} was determined, representing a higher concentration of epoxidized unsaturated double bonds. As a consequence the potential amount of fixed CO_2 is almost doubled when using **6b** compared to **6a**. Under the optimized reaction conditions the corresponding carbonate **7b** was obtained in a yield of 96% (entry 2). EPOXOL D65 (**6c**), an epoxidized triglyceride based on soybean oil, was also fully converted and 89% isolated yield on **7c** was achieved (entry 3). Carbonated soybean oil is a well investigated compound, since it is a starting material for non-isocyanate polyurethanes based on renewables. Very recently,

Table 6 Insertion of CO_2 into epoxidized vegetable oils **6** producing the corresponding carbonated oils **7**[a]



Entry	Substrate **6**[b]	Carbonate **7**	Conversion **6** (%)	Selectivity **7** (%)	Yield **7**[c] (%)
1	Epoxidized high-oleic sunflower oil (**6a**)	**7a**	>99	95	95
2	Epoxidized sunflower oil (**6b**)	**7b**	98	98	96
3	Epoxidized soybean oil EPOXOL D65 (**6c**)	**7c**	99	90	89
4	Epoxidized linseed oil (**6d**)	**7d**	97	79	77
5	Epoxidized methyl soyate (**6e**)	**7e**	84	>99	84

[a] Reaction conditions: 2.0 mol% $[Bu_4P]Br$, 0.25 mol% MoO_3, $p(CO_2, 100\ °C) = 50$ bar, 100 °C, 20 h; conversion und selectivity were determined by ^1H NMR. The employed epoxidized oils are of technical grade. [b] Oxirane numbers: **6a** 4.87 mmol g^{-1}; **6b** 7.02 mmol g^{-1}, **6c** 4.81 mmol g^{-1}, **6d** 8.62 mmol g^{-1}, **6e** 4.36 mmol g^{-1}. [c] Isolated yield after filtration of the reaction mixture.

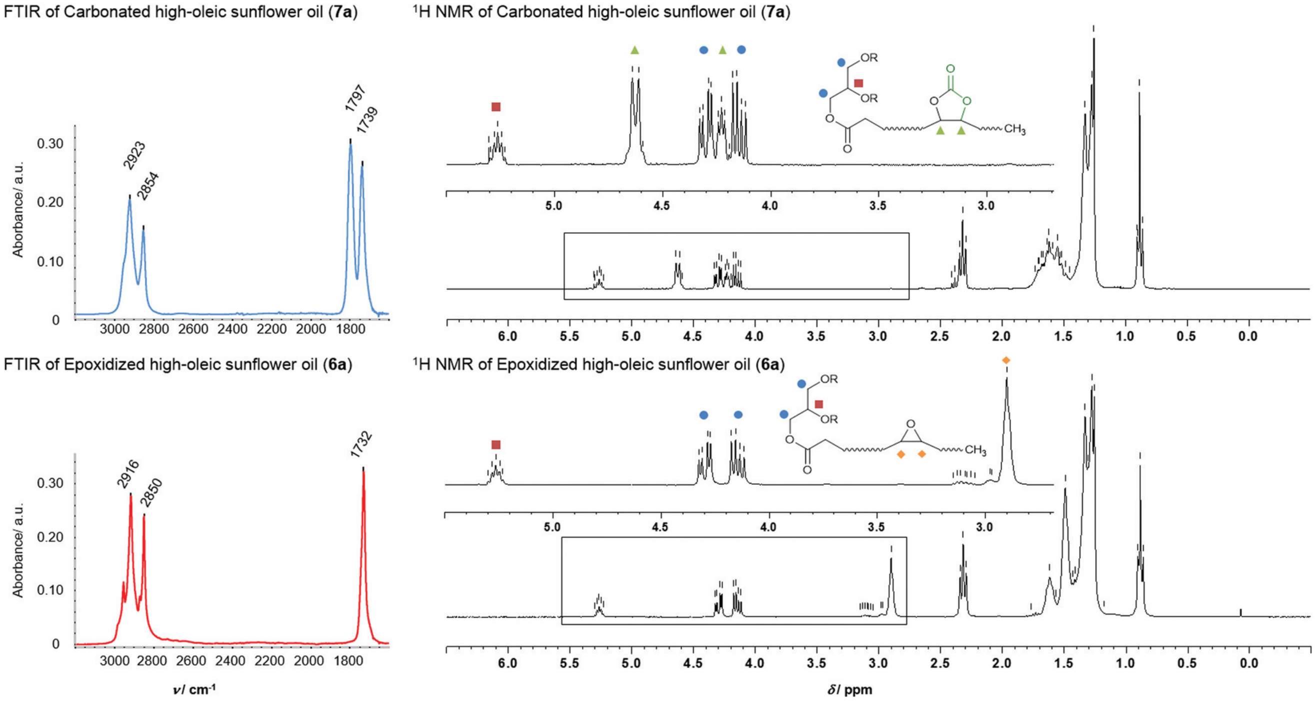


Fig. 3 FTIR and ^{1}H NMR spectra of carbonated high-oleic sunflower oil (**7a**) and the corresponding spectra of the substrate **6a**. Characteristic FTIR bands in the range of 1600–3000 cm^{-1} for **7a**: 2923 cm^{-1} (ν(C–H), asymmetric CH$_2$ stretching vibration), 2854 cm^{-1} (ν(C–H), symmetric CH$_2$ stretching vibration), 1797 cm^{-1} (ν(C–O), stretching vibration of the carbonate groups) and 1739 cm^{-1} (ν(C–O), stretching vibration of the ester groups); for **6a**: 2916 cm^{-1} (ν(C–H), asymmetric CH$_2$ stretching vibration), 2850 cm^{-1} (ν(C–H), symmetric CH$_2$ stretching vibration) and 1732 cm^{-1} (ν(C–O), stretching vibration of the ester groups). Characteristic ^{1}H NMR resonances for **7a**: cyclic carbonate –C*H*– protons δ 4.19–4.24 and 4.59–4.64 ppm (triangle), triglyceride –C*H*$_2$– protons δ 4.15 and 4.30 (dot), –C*H*– 5.23–5.30 (square) ppm; characteristic ^{1}H NMR resonances for **6a**: epoxide –C*H*– protons δ 2.85–3.20 ppm (diamond), triglyceride –C*H*$_2$– protons δ 4.15 and 4.30 (dot), –C*H*– 5.23–5.30 (square) ppm.[17,50,51]

Rokicki *et al.* reported in a very detailed review suitable catalytic systems for the carbonization of epoxidized vegetable oils.[14] However, to obtain reasonable rates of product formation either high catalyst loadings of up to 5 mol% per epoxy group and/or drastic reaction conditions up to 180 °C or 185 bar CO$_2$ pressure were required. In contrast to that, the employed catalyst system [Bu$_4$P]Br and MoO$_3$ showed excellent results under comparatively mild reaction conditions. Among the employed epoxidized vegetable oils, linseed oil **6d** exhibits the highest epoxide content with an oxirane number of 8.62 mmol g^{-1} (entry 4). Almost full conversion was obtained, while a good yield of 77% on **7d** was isolated. The organocatalytic approach for the synthesis of carbonated linseed oil was reported recently and involves also an two-component catalyst system.[51] Detailed kinetic studies revealed optimized reaction conditions of 120 °C, 5.0 MPa, 10 h, 2.2 mol% [Bu$_4$N]Br and 2.2 mol% perfluoro *tert*-butanol. However, the reaction time for the [Bu$_4$P]Br and MoO$_3$ system was longer, the carbonated vegetable oil **7d** was isolated under less drastic reaction conditions in a good yield of 77%. Finally we tested NEXO E1, representing methyl ester of soybean oil in technical grade (entry 5). Under the present reaction conditions a good conversion of 84% was detected. An identical yield of 84% represents excellent carbonate selectivity for NEXO E1 as a substrate. In general, the adaption of the catalytic system [Bu$_4$P]Br and MoO$_3$ to epoxidized vegetable oils **6** of technical grade was smoothly carried out and excellent conversions with selectivities up to >99% were obtained.

Conclusions

In summary, tetra-*n*-butylphosphonium bromide and molybdenum trioxide were found as a highly active catalyst system for the synthesis of oleochemical cyclic carbonates from CO$_2$ and the corresponding epoxides. MoO$_3$ considerably accelerated the reaction rate of the organocatalyst [Bu$_4$P]Br. The produced cyclic carbonates were obtained as *cis*- and *trans*-diastereoisomers and two different ring-closure pathways elucidate the formation of both products in the proposed mechanism. Moreover, the stereochemistry can be controlled by the catalyst, in particular by the halide of the [Bu$_4$P]-based catalyst. Among all tested organocatalysts, [Bu$_4$P]Br showed both, high chemoselectivity as well as a high reaction rate. Investigations regarding effects of catalyst ratio and concentration, temperature, CO$_2$ pressure and time on the coupling efficiency revealed optimized reaction conditions. Hence, 8 mono- and polyepoxidized fatty acid esters were employed to evaluate the scope and limitation of the reaction protocol. High yields of up to >99% and selectivities up to >99% were obtained and proved that this system is very efficient in the coupling reaction. However, during the reaction optimization by-products were obtained only in small amounts; only epoxidized methyl ricinoleate led to an intramolecular formed by-product. The protection of alcohol moiety by an acetyl-group enabled good conversion and selectivity, too. In addition to epoxidized fatty acid methyl esters, 5 epoxidized vegetable oils and derivatives were employed as substrates. These carbonated oils are considered to be a suitable feedstock for the production of non-isocyanate polyurethanes. Usually harsh reaction conditions and high catalyst loadings are required to facilitate reasonable reaction rates. Under comparatively mild reaction conditions of 100 °C, $p(CO_2, 100\ °C) = 50$ bar, 20 h and 2.0 mol% $[Bu_4P]Br$ and 0.25 mol% MoO_3 per epoxide conversions between 84–99% were obtained while selectivities up to >99% were determined. Finally, the coupling reaction of epoxidized *O*-acetyl methyl ricinoleate and CO_2 was scaled up to obtain 145 g of the desired product in a single batch.

Experimentals

General procedures (GP)

Catalyst screening and parameter optimization (GP1). A 45 cm^3 stainless steel autoclave was charged with metal based co-catalyst (0–0.02 equiv.) and a respective organocatalyst (0–0.02 equiv.). After epoxidized methyl oleate (*cis*-**2a**, 1.0 equiv.) was added dropwise the reactor was sealed and immediately purged with CO_2. Subsequently, the initial reaction pressure was set to 0.2–3.5 MPa and the reactor was heated to 80–120 °C for 4–24 h while $p(CO_2, 100\ °C)$ was kept constant at 0.5–5.0 MPa. Afterwards the reactor was cooled with an ice bath below 20 °C and CO_2 was released slowly. Conversion, selectivity and yield were determined by GC with a flame ionization detector and *n*-hexadecane as an internal standard directly from the reaction mixture.

Epoxidation of fatty acid esters 2 (GP2). The fatty acid ester **1** (1.0 equiv.) was added to a solution of $Ru(acac)_3$ (0.005–0.010 equiv.) and dipicolinic acid (0.1–0.2 equiv.) in acetonitrile (0.25 M in respect to **1**). The resulting suspension was sonicated to obtain a homogeneous mixture. Subsequently, aqueous hydrogen peroxide (35%, 3.3 equiv.) was added in portions and the reaction mixture was allowed to stir for 4–24 h at 25 °C. The resulting mixture was extracted with cyclohexane (*c*Hex) and the combined organic layers were concentrated to approximately 1/4 of the initial volume and subsequently washed with water. The organic phase was dried over $MgSO_4$ and all volatiles were removed in vacuum to yield product **2**. If necessary the crude product was purified by flash chromatography on silica (SiO_2) employing cyclohexane (*c*Hex)/ethyl acetate (EtOAc) as eluent.

Synthesis of carbonated fatty acid esters 3 (GP3). A 45 cm^3 stainless steel autoclave was charged with MoO_3 (0.0025 equiv.) and tetra-*n*-butylphosphonium bromide (0.02 equiv.). After the epoxide **2** (1.0 equiv.) was added dropwise the reactor was immediately sealed and purged with CO_2. Subsequently, an initial CO_2 pressure of 3.5 MPa was set and the reactor was heated to 100 °C for 20 h while $p(CO_2, 100\ °C)$ was kept constant at 5.0 MPa. Afterwards the reactor was cooled with an ice bath below 20 °C and CO_2 was released slowly. Conversion and selectivity were determined by ^1H NMR and/or GC from the reaction mixture. The crude product was directly purified by flash chromatography on silica gel (SiO_2) employing cyclohexane (*c*Hex)/ethyl acetate (EtOAc) as eluent. All volatiles were removed in vacuum to obtain the cyclic carbonate **3**.

Synthesis of carbonated oils (GP4). A 45 cm^3 stainless steel autoclave was charged with MoO_3 (0.0025 equiv.) and tetra-*n*-butylphosphonium bromide (0.02 equiv.). After the epoxidized oil **6** (1.0 equiv.) was added dropwise the reactor was immediately sealed and purged with CO_2. Subsequently, an initial CO_2 pressure of 3.5 MPa was set and the reactor was heated to 100 °C for 20 h while $p(CO_2, 100\ °C)$ was kept constant at 5.0 MPa. Afterwards the reactor was cooled with an ice bath below 20 °C and CO_2 was released slowly. Conversion and selectivity were determined by ^1H NMR from the reaction mixture. After the reaction mixture was filtrated over SiO_2 employing cyclohexane (*c*Hex)/ethyl acetate (EtOAc) or dichloromethane (DCM) as eluent all volatiles were removed in vacuum to obtain the carbonated oils **7**.

***cis*-Methyl 8-(3-octyloxiran-2-yl)octanoate (*cis*-2a).**[56] According to **GP2**, methyl oleate (*cis*-**1a**, 11.84 g, 39.93 mmol), $Ru(acac)_3$ (80 mg, 0.20 mmol), dipicolinic acid (668 mg, 4.00 mmol) and hydrogen peroxide (35%, 12.8 g, 132 mmol) in acetonitrile (160 mL) were stirred for 4 h at 25 °C. Subsequently, the reaction mixture was extracted with cyclohexane (4 × 200 mL), the combined organic layers were concentrated to 100 mL and washed with H_2O (100 mL). After removal of all volatiles in vacuum *cis*-**2a** (12.08 g, 38.66 mmol, 97%) was obtained as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): $\delta = 0.88$ (t, $^3J_{H,H} = 6.7$ Hz, 3H), 1.23–1.54 (m, 24H), 1.57–1.67 (m, 2H), 2.30 (t, $^3J_{H,H} = 7.5$ Hz, 2H), 2.86–2.92 (m, 2H), 3.66 (s, 3H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 22 °C): $\delta = 14.07$ (CH_3), 22.63 (CH_2), 24.86 (CH_2), 26.52 (CH_2), 26.57 (CH_2), 27.76 (CH_2), 27.80 (CH_2), 29.00 (CH_2), 29.15 (CH_2), 29.19 (CH_2), 29.30 (CH_2), 29.50 (CH_2), 29.52 (CH_2), 31.82 (CH_2), 34.02 (CH_2), 51.42 (OCH_3), 57.15 (CH), 57.20 (CH), 174.23 (C═O) ppm; MS (EI): *m*/*z* (%): 281 (1) $[M^+ - OCH_3]$, 264 (1), 199 (14), 171 (17), 155 (100), 153 (20), 139 (19), 127 (23), 121 (10), 109 (26), 97 (34), 87 (32), 83 (32), 74 (54), 69 (46), 55 (63), 43 (29), 41 (35); elemental analysis calcd (%) for $C_{19}H_{36}O_3$ (312.49): C 73.03, H 11.61, found: C 73.01, H 11.73.

Cyclic carbonates

Methyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (3a).[49] According to **GP3**, MoO_3 (1.8 mg, 0.013 mmol), tetra-*n*-butylphosphonium bromide (34 mg, 0.10 mmol) and epoxidized methyl oleate (*cis*-**2a**, 1.56 g, 5.00 mmol) were allowed to react with CO_2. The crude product was purified by flash chromatography (SiO_2, *c*Hex : EtOAc = 20 : 1 to 10 : 1) to yield **3a** (1.74 g, 4.88 mmol, 98%, *cis* : *trans* = 77 : 23) as a colorless oil. *cis*-**3a**: $R_f = 0.21$ (*c*Hex : EtOAc = 10 : 1); ^1H NMR (300 MHz, $CDCl_3$, 22 °C): $\delta = 0.88$ (t, $^3J_{H,H} = 6.8$ Hz, 3H), 1.20–1.44 (m, 18H), 1.46–1.75 (m, 8H), 2.30 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 3.67 (s, 3H), 4.58–4.66 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 22 °C) δ = 14.05 (CH_3), 22.60 (CH_2), 24.78 (CH_2), 25.51 (CH_2), 25.56 (CH_2), 28.83 (CH_2), 28.86 (CH_2), 28.89 (CH_2), 28.95 (CH_2), 28.99 (CH_2), 29.11 (CH_2), 29.20 (CH_2), 29.28 (CH_2), 31.75 (CH_2), 33.96 (CH_2), 51.45 (OCH_3), 79.88 (CH), 79.93 (CH), 154.75 (C═O), 174.18 (C═O) ppm; MS (EI): *m*/*z* (%): 357 (1) [M^+ + H], 325 (34), 294 (9), 262 (20), 239 (64), 221 (10), 181 (13), 164 (16), 155 (38), 135 (26), 121 (34), 109 (47), 95 (77), 81 (78), 69 (59), 55 (100), 43 (56), 41 (56); HRMS (EI): *m*/*z* calcd for $C_{20}H_{36}O_5$ [M^+ + H]: 357.2636; found: 357.2634; *trans*-**3a**: R_f = 0.12 (*c*Hex : EtOAc = 10 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.85 (t, $^{3}J_{H,H}$ = 6.8 Hz, 3H), 1.19–1.50 (m, 20H), 1.54–1.75 (m, 6H), 2.28 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 3.64 (s, 3H), 4.17–4.24 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 13.97 (CH_3), 22.50 (CH_2), 24.48 (CH_2), 24.52 (CH_2), 24.69 (CH_2), 28.79 (CH_2), 28.84 (2 × CH_2), 29.00 (CH_2), 29.05 (CH_2), 29.19 (CH_2), 31.66 (CH_2), 33.67 (CH_2), 33.68 (CH_2), 33.85 (CH_2), 51.34 (OCH_3), 81.87 (CH), 81.91 (CH), 154.60 (C═O), 174.05 (C═O) ppm; MS (EI): *m*/*z* (%): 357 (1) [M^+ + H], 325 (35), 294 (7), 262 (17), 241 (25), 239 (32), 221 (18), 181 (11), 164 (14), 155 (24), 135 (25), 121 (34), 109 (55), 95 (86), 81 (83), 69 (60), 55 (100), 43 (55), 41 (56); HRMS (ESI-TOF): *m*/*z* calcd for $C_{20}H_{36}O_5$ [M^+ + H]: 357.2636; found: 357.2634.

Ethyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (3b). According to **GP3**, MoO_3 (0.6 mg, 0.0042 mmol), tetra-*n*-butylphosphonium bromide (13 mg, 0.038 mmol) epoxidized ethyl oleate (*cis*-**2b**, 600 mg, 1.84 mmol) were allowed to react with CO_2. The crude product was purified by flash chromatography (SiO_2, *c*Hex : EtOAc = 20 : 1 to 10 : 1) to yield **3b** (680 mg, 1.84 mmol, >99%, *cis* : *trans* = 65 : 35) as a colorless oil. *cis*-**3b**: R_f = 0.50 (*c*Hex : EtOAc = 10 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.88 (t, $^{3}J_{H,H}$ = 6.8 Hz, 3H), 1.23–1.43 (m, 21H), 1.47–1.74 (m, 8H), 2.29 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 4.12 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2H), 4.58–4.66 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 14.05 (CH_3), 14.22 (CH_3), 22.60 (CH_2), 24.81 (CH_2), 25.52 (CH_2), 25.57 (CH_2), 28.84 (CH_2), 28.86 (CH_2), 28.90 (CH_2), 28.96 (CH_2), 29.00 (CH_2), 29.11 (CH_2), 29.21 (CH_2), 29.29 (CH_2), 31.76 (CH_2), 34.24 (CH_2), 60.17 (OCH_2), 79.88 (CH), 79.93 (CH), 154.75 (C═O), 173.76 (C═O) ppm; MS (EI): *m*/*z* (%): 325 (50) [M^+ − OEt], 262 (17), 241 (14), 239 (47), 221 (8), 171 (16), 164 (12), 155 (35), 149 (16), 135 (23), 123 (28), 121 (31), 109 (51), 95 (79), 81 (80), 69 (63), 67 (58), 55 (100), 43 (50), 41 (49); HRMS (ESI-TOF): *m*/*z* calcd for $C_{21}H_{38}O_5$ [M^+ + Na]: 393.2612; found: 393.2612; *trans*-**3b**: R_f = 0.42 (*c*Hex : EtOAc = 10 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.88 (t, $^{3}J_{H,H}$ = 6.8 Hz, 3H), 1.23–1.53 (m, 23H), 1.57–1.78 (m, 6H), 2.29 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 4.12 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2H), 4.19–4.26 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 14.05 (CH_3), 14.22 (CH_3), 22.59 (CH_2), 24.57 (CH_2), 24.60 (CH_2), 24.80 (CH_2), 28.87 (CH_2), 28.94 (2 × CH_2), 29.08 (CH_2), 29.14 (CH_2), 29.27 (CH_2), 31.74 (CH_2), 33.78 (2 × CH_2), 34.23 (CH_2), 60.17 (OCH_2), 81.95 (CH), 81.99 (CH), 154.69 (C═O), 173.74 (C═O) ppm; MS (EI): *m*/*z* (%): 341 (1) [M^+ − OEt], 325 (29), 241 (12), 239 (15), 221 (9), 207 (20), 155 (15), 149 (10), 135 (16), 123 (25), 121 (24), 109 (47), 95 (72), 81 (73), 69 (59), 67 (54), 55 (100), 43 (53), 41 (52); HRMS (ESI-TOF): *m*/*z* calcd for $C_{21}H_{38}O_5$ [M^+ + Na]: 393.2612; found: 393.2612.

Iso-octyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (3c). According to **GP3**, MoO_3 (2.2 mg, 0.015 mmol), tetra-*n*-butylphosphonium bromide (41 mg, 0.12 mmol) and epoxidized iso-octyl oleate (*cis*-**3c**, 1.50 g, 3.69 mmol) were allowed to react with CO_2. The crude product was purified by flash chromatography (SiO_2, *c*Hex : EtOAc = 1 : 1) to yield **3c** (1.61 g, 3.54 mmol, 96%, *cis* : *trans* = 62 : 38) as a colorless oil. *cis*-**3c**: R_f = 0.42 (*c*Hex : EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.87–0.92 (m, 9H), 1.22–1.46 (m, 26H), 1.46–1.78 (m, 9H), 2.31 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 3.94–4.04 (m, 2H), 4.59–4.65 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 10.96 (CH_3), 14.02 (CH_3), 14.05 (CH_3), 22.60 (CH_2), 22.94 (CH_2), 23.75 (CH_2), 24.88 (CH_2), 25.54 (CH_2), 25.57 (CH_2), 28.84 (CH_2), 28.87 (2 × CH_2), 28.94 (CH_2), 28.99 (CH_2), 29.03 (CH_2), 29.11 (CH_2), 29.21 (CH_2), 29.29 (CH_2), 30.37 (CH_2), 31.76 (CH_2), 34.30 (CH_2), 38.69 (CH), 66.64 (CH_2), 79.88 (CH), 79.92 (CH), 154.74 (C═O), 173.96 (C═O) ppm; MS (EI): *m*/*z* (%): 343 (1), 325 (100), 239 (9), 155 (11), 112 (22), 109 (14), 97 (15), 95 (21), 83 (26), 81 (22), 71 (27), 67 (16), 57 (42), 55 (38), 43 (25), 41 (20); HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{50}O_5$ [M^+ + H]: 455.3731; found: 455.3731; *trans*-**3c**: R_f = 0.50 (*c*Hex : EtOAc = 10 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.86–0.91 (m, 9H), 1.22–1.48 (m, 28H), 1.51–1.79 (m, 7H), 2.30 (t, $^{3}J_{H,H}$ = 7.4 Hz, 2H), 3.93–4.03 (m, 2H), 4.19–4.26 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 10.96 (CH_3), 14.02 (CH_3), 14.05 (CH_3), 22.59 (CH_2), 22.94 (CH_2), 23.75 (CH_2), 24.60 (CH_2), 24.87 (CH_2), 28.88 (CH_2), 28.92 (CH_2), 28.97 (2 × CH_2), 29.09 (CH_2), 29.14 (CH_2), 29.27 (CH_2), 30.37 (CH_2), 31.50 (CH_2), 31.75 (CH_2), 33.79 (2 × CH_2), 34.29 (CH_2), 38.70 (CH), 66.64 (CH_2), 81.95 (CH), 81.99 (CH), 154.69 (C═O), 173.94 (C═O) ppm; MS (EI): *m*/*z* (%): 343 (1), 325 (100), 239 (4), 155 (5), 123 (9), 112 (21), 109 (15), 97 (14), 95 (22), 83 (25), 81 (21), 71 (25), 67 (17), 57 (40), 55 (38), 43 (26), 41 (21); HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{50}O_5$ [M^+ + H]: 455.3731; found: 455.3731.

Methyl 10-(5-octyl-2-oxo-1,3-dioxolan-4-yl)decanoate (3d). According to **GP3**, MoO_3 (1.1 mg, 0.0076 mmol), tetra-*n*-butylphosphonium bromide (20 mg, 0.059 mmol) and epoxidized methyl eicosenoate (*cis*-**2d**, 1.00 g, 2.94 mmol) were allowed to react with CO_2. The crude product was purified by flash chromatography (SiO_2, *c*Hex : EtOAc = 20 : 1 to 10 : 1) to yield **3d** (940 mg, 2.44 mmol, 83%, *cis* : *trans* = 77 : 23) as a colorless oil. *cis*-**3d**: R_f = 0.66 (*c*Hex : EtOAc = 2 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.89 (t, $^{3}J_{H,H}$ = 6.7 Hz, 3H), 1.20–1.44 (m, 22H), 1.46–1.78 (m, 8H), 2.31 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 3.67 (s, 3H), 4.58–4.69 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 14.06 (CH_3), 22.61 (CH_2), 24.88 (CH_2), 25.57 (2 × CH_2), 28.86 (2 × CH_2), 29.05 (CH_2), 29.12 (2 × CH_2), 29.18 (CH_2), 29.22 (2 × CH_2), 29.25 (CH_2), 29.30 (CH_2), 31.76 (CH_2), 34.04 (CH_2), 51.43 (OCH_3), 79.93 (2 × CH), 154.77 (C═O), 174.27 (C═O) ppm; MS (EI): *m*/*z* (%): 353 (40) [M^+ − OMe], 267 (53), 249 (14), 225 (23), 155 (30), 149 (18), 135 (25), 123 (28), 109 (40), 98 (100), 95 (70), 87 (19), 81 (69), 74 (34), 69 (63), 55 (90), 43 (55), 41 (53); HRMS (ESI-TOF): *m*/*z* calcd for $C_{22}H_{40}O_5$

[M^+ + H]: 385.2949; found: 385.2945; *trans*-**3d**: R_f = 0.76 (*c*Hex : EtOAc = 2 : 1); ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 1.20–1.54 (m, 24H), 1.56–1.80 (m, 6H), 2.31 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.67 (s, 3H), 4.19–4.26 (m, 2H) ppm; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.05 (CH$_3$), 22.59 (CH$_2$), 24.61 (2 × CH$_2$), 24.87 (CH$_2$), 29.04 (CH$_2$), 29.10 (2 × CH$_2$), 29.13 (2 × CH$_2$), 29.20 (CH$_2$), 29.23 (CH$_2$), 29.27 (CH$_2$), 31.75 (CH$_2$), 33.80 (2 × CH$_2$), 34.03 (CH$_2$), 51.43 (OCH$_3$), 81.99 (2 × CH), 154.72 (C=O), 174.26 (C=O) ppm; MS (EI): *m*/*z* (%): 353 (42) [M^+ – OMe], 267 (20), 249 (23), 225 (32), 155 (17), 149 (17), 135 (13), 123 (34), 109 (45), 98 (100), 95 (74), 87 (18), 81 (72), 74 (32), 69 (60), 55 (85), 43 (51), 41 (51); HRMS (ESI-TOF): *m*/*z* calcd for $C_{22}H_{40}O_5$ [M^+ + H]: 385.2949; found: 385.2946.

Methyl 12-(5-octyl-2-oxo-1,3-dioxolan-4-yl)dodecanoate (3e). According to **GP3**, MoO$_3$ (0.5 mg, 0.0035 mmol), tetra-*n*-butylphosphonium bromide (9 mg, 0.03 mmol) and epoxidized methyl erucate (**2e**, 460 mg, 1.25 mmol) were allowed to react with CO$_2$. The crude product was purified by flash chromatography (SiO$_2$, *c*Hex : EtOAc = 20 : 1) to yield **3e** (238 mg, 0.577 mmol, 46%, *cis* : *trans* = 67 : 33) as a colorless oil; *cis*–**3e**: R_f = 0.63 (*c*Hex : EtOAc = 2 : 1); ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 1.20–1.43 (m, 26H), 1.47–1.75 (m, 8H), 2.30 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.66 (s, 3H), 4.58–4.66 (m, 2H) ppm; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.05 (CH$_3$), 22.60 (CH$_2$), 24.90 (CH$_2$), 25.56 (2 × CH$_2$), 28.86 (2 × CH$_2$), 29.09 (CH$_2$), 29.11 (CH$_2$), 29.20 (3 × CH$_2$), 29.29 (CH$_2$), 29.31 (CH$_2$), 29.35 (CH$_2$), 29.40 (CH$_2$), 29.44 (CH$_2$), 31.76 (CH$_2$), 34.06 (CH$_2$), 51.40 (OCH$_3$), 79.94 (2 × CH), 154.77 (C=O), 174.29 (C=O) ppm; MS (EI): *m*/*z* (%): 381 (26) [M^+ – OMe], 295 (27), 277 (10), 253 (12), 239 (15), 155 (21), 137 (13), 123 (21), 112 (36), 109 (34), 98 (100), 95 (58), 87 (17), 83 (46), 81 (54), 74 (31), 69 (52), 55 (37), 43 (43), 41 (38); HRMS (ESI-TOF): *m*/*z* calc. for $C_{24}H_{44}O_5$ [M^+ + H]: 413.3262; found: 413.3258*;* *trans*-**3e**: R_f = 0.74 (*c*Hex : EtOAc = 2 : 1); ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 1.20–1.60 (m, 28H), 1.61–1.80 (m, 6H), 2.31 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.67 (s, 3H), 4.19–4.26 (m, 2H) ppm; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.06 (CH$_3$), 22.60 (CH$_2$), 24.62 (2 × CH$_2$), 24.91 (CH$_2$), 29.10 (2 × CH$_2$), 29.14 (2 × CH$_2$), 29.20 (CH$_2$), 29.30 (2 × CH$_2$), 29.35 (CH$_2$), 29.39 (CH$_2$), 29.45 (CH$_2$), 31.76 (CH$_2$), 33.81 (2 × CH$_2$), 34.07 (CH$_2$), 51.42 (OCH$_3$), 82.00 (2 × CH), 154.73 (C=O), 174.31 (C=O) ppm; MS (EI): *m*/*z* (%): 381 (28) [M^+ – OMe], 295 (12), 277 (15), 253 (6), 239 (7), 155 (11), 137 (15), 123 (24), 112 (35), 109 (37), 98 (100), 95 (60), 87 (16), 83 (45), 81 (55), 74 (30), 69 (50), 55 (69), 43 (40), 41 (36); HRMS (ESI-TOF): *m*/*z* calcd for $C_{24}H_{44}O_5$ [M^+ + H]: 413.3262; found: 413.3256.

Methyl 8-(5-((2*R*)-hydroxyoctyl)-2-oxo-1,3-dioxolan-4-yl)octanoate (3f). According to **GP3**, MoO$_3$ (1.1 mg, 0.0076 mmol), tetra-*n*-butylphosphonium bromide (21 mg, 0.062 mmol) and epoxidized methyl ricinoleate (**2f**, 1.01 g, 3.07 mmol) were allowed to react with CO$_2$. The crude product was purified by flash chromatography (SiO$_2$, *c*Hex : EtOAc = 20 : 1 to 5 : 1) to yield **3f** (472 mg, 1.27 mmol, 42%, dr = 26 : 39 : 35) as a colorless oil as a mixture of three diastereoisomers. *cis*-**3f**: as a mixture of two diastereomers (dr = 60 : 40); R_f = 0.08 (*c*Hex : EtOAc = 2 : 1); ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.88 (t, $^3J_{H,H}$ = 6.5 Hz, 3H), 1.20–1.67 (m, 22H), 1.68–1.94 (m, 2H), 2.00–2.12 (m, 1H), 2.30 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.66 (s, 3H) 3.77–3.89 (m, 1H), 4.63–4.69 (m, 1H), 4.83–4.90 (m, 1H, isomer 1), 4.96–5.03 (m, 1H, isomer 2) ppm; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 22 °C): as a mixture of two diastereomers (dr = 60 : 40) δ = 13.99 (2 × CH$_3$), 22.51 (2 × CH$_2$), 24.73 (2 × CH$_2$), 25.28 (CH$_2$), 25.34 (CH$_2$), 25.38 (2 × CH$_2$), 28.83 (2 × CH$_2$), 28.89 (4 × CH$_2$), 28.99 (CH$_2$), 29.06 (CH$_2$), 29.10 (2 × CH$_2$), 31.69 (2 × CH$_2$), 33.93 (2 × CH$_2$), 35.78 (CH$_2$), 36.05 (CH$_2$), 36.96 (CH$_2$), 38.22 (CH$_2$), 51.42 (2 × OCH$_3$), 67.60 (CH), 69.07 (CH), 76.94 (CH), 77.82 (CH), 79.90 (2 × CH), 154.38 (C=O), 154.71 (C=O), 174.21 (2 × C=O) ppm; MS (EI): *m*/*z* (%): 341 (1) [M^+ – OMe], 323 (10), 287 (8), 255 (100), 237 (19), 226 (21), 211 (13), 193 (11), 164 (49), 155 (17), 135 (17), 121 (19), 113 (17), 109 (15), 98 (27), 97 (27), 83 (23), 81 (38), 74 (17), 69 (29), 67 (26), 57 (22), 55 (70), 43 (34), 41 (30); HRMS (EI): *m*/*z* calc. for $C_{20}H_{36}O_6$ [M^+ + H]: 373.2585; found: 373.2579; *trans*-**3f**: R_f = 0.25 (*c*Hex : EtOAc = 2 : 1); ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.89 (t, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.23–1.96 (m, 25H), 2.31 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 3.67 (s, 3H), 3.74–3.85 (m, 1H), 4.23–4.58 (m, 2H) ppm; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.01 (CH$_3$), 22.53 (CH$_2$), 24.49 (CH$_2$), 24.76 (CH$_2$), 25.37 (CH$_2$), 28.80 (CH$_2$), 28.84 (2 × CH$_2$), 29.12 (CH$_2$), 31.70 (CH$_2$), 33.55 (CH$_2$), 33.95 (CH$_2$), 37.58 (CH$_2$), 40.20 (CH$_2$), 51.46 (OCH$_3$), 68.21 (CH), 79.79 (CH), 82.00 (CH), 154.57 (C=O), 174.23 (C=O) ppm; MS (EI): *m*/*z* (%): 323 (6), 287 (10), 255 (100), 226 (10), 164 (26), 121 (12), 113 (14), 109 (11), 98 (18), 83 (17), 81 (30), 74 (13), 69 (22), 67 (20), 55 (51), 43 (25), 41 (21); HRMS (EI): *m*/*z* calcd for $C_{20}H_{36}O_6$ [M^+ + H]: 373.2585; found: 373.2587.

Methyl 8-(5-((2*R*)-acetoxyoctyl)-2-oxo-1,3-dioxolan-4-yl)octanoate (3g). According to **GP3**, MoO$_3$ (1.0 mg, 0.006.9 mmol), tetra-*n*-butylphosphonium bromide (18 mg, 0.053 mmol) and epoxidized *O*-acetylricinoleic acid methyl ester (**2g**, 1.01 g, 2.73 mmol) were allowed to react with CO$_2$. The crude product was purified by flash chromatography (SiO$_2$, *c*Hex : EtOAc = 5 : 1) to yield **3g** (472 mg, 1.73 mmol, 63%, *cis* : *trans* = 74 : 26) as a colorless oil as a mixture of four diastereoisomers (dr = 44 : 30 : 14 : 12). *cis*-**3g**: as a mixture of two diastereoisomers (dr = 60 : 40); R_f = 0.16 (*c*Hex : EtOAc = 5 : 1); ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3H), 1.20–1.38 (m, 15H), 1.42–1.70 (m, 5H), 1.73–2.01 (m, 2H), 2.05 (s, 3H, isomer 1), 2.07 (s, 3H, isomer 2), 2.30 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.66 (s, 3H), 4.59–4.77 (m, 2H,) 4.96–5.04 (m, 1H) ppm; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 22 °C): δ = 13.99 (2 × CH$_3$), 21.07 (CH$_3$,), 21.13 (CH$_3$), 22.49 (2 × CH$_2$), 24.76 (2 × CH$_2$), 24.94 (CH$_2$), 25.16 (CH$_2$), 25.33 (CH$_2$,), 25.46 (CH$_2$), 28.88 (2 × CH$_2$), 28.94 (4 × CH$_2$), 28.99 (2 × CH$_2$), 29.03 (2 × CH$_2$), 31.60 (2 × CH$_2$), 33.25 (CH$_2$), 33.59 (CH$_2$), 33.94 (2 × CH$_2$), 34.09 (CH$_2$), 34.59 (CH$_2$), 51.43 (2 × OCH$_3$), 70.71 (CH), 70.91 (CH), 76.41 (CH), 76.84 (CH), 79.51 (CH), 79.65 (CH), 154.19 (C=O), 154.26 (C=O), 170.35 (C=O), 170.88 (C=O), 174.15 (2 × C=O) ppm; MS (EI): *m*/*z* (%): 383 (1) [M^+ – OMe], 341 (9), 323 (9), 292 (11), 287 (31), 258 (12), 255 (45), 225 (13), 167 (24), 164 (17), 150 (10), 135 (16), 121 (21), 113 (37), 109 (18), 98 (29), 95 (37), 83 (30), 81 (50), 74 (19), 69 (36), 67 (38), 57 (19), 55 (69), 43 (100), 41 (27); HRMS (ESI-TOF): *m*/*z* calcd for $C_{22}H_{38}O_7$ [M^+ + H]: 415.2690; found: 415.2692; *trans*-**3g**: as a mixture of two diastereoisomers (dr = 52 : 48); R_f = 0.21 (*c*Hex : EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.87 (t, $^3J_{H,H}$ = 6.7 Hz, 3H), 1.20–1.50 (m, 16H), 1.53–1.75 (m, 6H), 1.79–2.03 (m, 2H), 2.06 (s, 3H, isomer 1), 2.06 (s, 3H, isomer 2), 2.30 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.66 (s, 3H), 4.20–4.35 (m, 2H), 4.95–5.04 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 14.01 (2 × CH_3), 21.09 (2 × CH_3), 22.47 (2 × CH_2), 24.57 (CH_2), 24.61 (CH_2), 24.75 (2 × CH_2), 24.89 (CH_2), 25.12 (CH_2), 28.85 (2 × CH_2), 28.90 (4 × CH_2), 28.95 (2 × CH_2), 31.58 (2 × CH_2), 33.42 (2 × CH_2), 33.93 (2 × CH_2), 34.14 (CH_2), 34.40 (CH_2), 38.10 (CH_2), 38.39 (CH_2), 51.43 (2 × OCH_3), 70.30 (CH), 70.75 (CH), 78.90 (CH), 79.05 (CH), 81.92 (CH), 81.92 (CH), 154.18 (C═O), 154.28 (C═O), 170.39 (C═O), 170.69 (C═O), 174.14 (2 × C═O) ppm; MS (EI): *m*/*z* (%): 383 (1) [M^+ − OMe], 341 (5), 323 (8), 287 (25), 255 (52), 167 (13), 164 (11), 135 (14), 121 (18), 113 (40), 109 (18), 98 (24), 95 (35), 83 (27), 81 (50), 74 (18), 69 (35), 67 (37), 57 (19), 55 (66), 43 (100), 41 (28); HRMS (EI): *m*/*z* calcd for $C_{22}H_{38}O_7$ [M^+ + H]: 415.2690; found: 415.2691.

Methyl 8-(2-oxo-5-((2-oxo-5-pentyl-1,3-dioxolan-4-yl)methyl)-1,3-dioxolan-4-yl)octanoate (3h).[48] According to **GP3**, (0.7 mg, 0.0049 mmol), tetra-*n*-butylphosphonium bromide (14 mg, 0.041 mmol) and epoxidized methyl linoleate (**2h**, 653 mg, 2.00 mmol) were allowed to react with CO_2. The crude product was purified by flash chromatography (SiO_2, *c*Hex : EtOAc = 10 : 1) to yield **3h** (681 mg, 1.64 mmol, 82%) as a colorless oil as a mixture of four diastereroisomers (dr = 14 : 16 : 35 : 35). R_f = 0.08 (*c*Hex : EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.89–0.93 (m, 3H), 1.26–1.45 (m, 12H), 1.52–1.79 (m, 8H), 1.83–2.08 (m, 2H), 2.31 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.67 (s, 3H), 4.27–4.43 (m, 2H, isomer 1), 4.41–4.52 (m, 2H, isomer 2), 4.71–4.78 (m, 2H, isomer 3), 4.86–4.96 (m, 2H, isomer 4) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 13.85 (CH_3), 22.31 (CH_2), 22.33 (CH_2), 24.10 (CH_2), 24.35 (2 × CH_2), 25.27 (CH_2), 25.43 (CH_2), 25.54 (2 × CH_2), 24.73 (CH_2), 28.84 (2 × CH_2), 28.89 (CH_2), 28.95 (2 × CH_2), 31.19 (CH_2), 31.22 (CH_2), 33.32 (CH_2), 33.40 (CH_2), 33.93 (CH_2), 34.02 (CH_2), 51.45 (OCH_3), 75.22 (CH), 75.35 (CH), 77.59 (CH), 77.64 (CH), 79.24 (CH), 79.35 (CH), 79.40 (CH), 81.90 (CH), 81.96 (CH), 82.07 (CH), 153.64 (C═O), 153.66 (C═O), 153.70 (C═O), 153.72 (C═O), 174.16 (C═O) ppm;[69] MS (EI): *m*/*z* (%): 383 (13) [M^+ − OMe], 320 (9), 151 (26), 121 (18), 109 (21), 107 (21), 95 (45), 84 (49), 81 (57), 74 (26), 69 (42), 67 (46), 55 (100), 44 (74), 41 (61); HRMS (EI): *m*/*z* calcd for $C_{21}H_{34}O_8$ [M^+ + H]: 415.2326; found: 415.2329.

Carbonated oils

Carbonated high-oleic sunflower oil (7a). According to **GP4**, MoO_3 (2.5 mg, 0.017 mmol), tetra-*n*-butylphosphonium bromide (48 mg, 0.14 mmol) and epoxidized high-oleic sunflower oil (**6a**, oxirane number = 4.71 mmol g^{-1}, 1.51 g, 7.07 mmol) were converted with CO_2. After filtration (SiO_2, CH_2Cl_2) the carbonated product **7a** (1.73 g, 95%) was isolated as a pale yellow oil. **7a**: ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.86–0.91 (m, 9H), 1.25–1.73 (m, 78H), 2.32 (t, $^3J_{H,H}$ = 7.5 Hz, 6H), 4.15 (dd, $^2J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H), 4.19–4.24 (m, 2H), 4.30 (dd, $^2J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 4.3 Hz, 2H), 4.59–4.64 (m, 3H), 5.23–5.30 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 14.05 (CH_3), 22.59–34.06 (multiple signals, CH_2), 62.05 (OCH_2), 68.87 (CH), 79.87 (CH), 79.93 (CH), 81.95 (CH), 82.00 (CH), 154.67 (C═O), 154.73 (C═O), 172.72 (C═O), 173.12 (C═O) ppm; ATR IR: ν_{max} = 2923 (m), 2854 (m), 1797 (vs, C═O), 1739 (s, C═O), 1165 (m), 1038 (m) cm^{-1}.

Carbonated sunflower oil (7b). According to **GP4**, MoO_3 (4.0 mg, 0.028 mmol), tetra-*n*-butylphosphonium bromide (72 mg, 0.21 mmol) and epoxidized sunflower oil (**6b**, oxirane number = 7.02 mmol g^{-1}, 1.50 g, 10.5 mmol) were converted with CO_2. After filtration (SiO_2, *c*Hex : EtOAc = 1 : 1) the carbonated product (1.93 g) was isolated as a mixture of carbonate **7b** (96%) and **6b** (2%) as a brown solid. **7b**: ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.84–0.93 (m, 9H), 1.21–2.09 (m, 76H), 2.28–2.33 (m, 6H), 4.14 (dd, $^2J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H), 4.24–4.31 (m, 3H), 4.41–4.95 (m, 7H), 5.21–5.29 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ = 13.82–14.04 (multiple signals, CH_3), 19.09–34.01 (multiple signals, CH_2), 62.01 (CH_2), 68.85 (CH), 75.28–81.99 (multiple signals, CH), 153.74 (C═O) 154.71 (C═O), 172.66 C═O), 173.06 C═O); ATR IR: ν_{max} = 2923 (m), 2836 (m), 1795 (vs, C═O), 1739 (s, C═O), 1167 (m), 1046 (m), 773 (m) cm^{-1}.

Carbonated EPOXOL D65 (7c).[70] According to **GP4**, MoO_3 (2.0 mg, 0.014 mmol), tetra-*n*-butylphosphonium bromide (41 mg, 0.12 mmol) and EPOXOL D65 (**6c**, oxirane number = 4.81 mmol g^{-1}, 1.04 g, 5.00 mmol) were converted with CO_2. After filtration (SiO_2, *c*Hex/EtOAc = 1 : 1) the carbonated product (1.13 g) was isolated as a mixture of carbonate **7c** (89%) and **6c** (<1%) as a yellow oil. **7c**: ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.82–0.89 (m, 9H), 1.20–1.74 (m, 73H), 2.29–2.35 (m, 6H), 4.08–4.14 (m, 2H), 4.24–4.28 (m, 2H), 4.29–4.93 (m, 8H), 5.19–5.26 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C) δ = 13.78 (CH_3), 13.97 (CH_3), 13.99 (CH_3) 22.25–33.91 (multiple signals, CH_2), 61.97 (CH_2), 68.81 (CH), 75.42 (CH), 79.36 (CH), 79.89 (CH), 81.96 (CH), 153.74 (C═O), 154.68 (C═O), 172.63 (C═O), 173.03 (C═O), 173.18 (C═O); ATR IR: ν_{max} = 2924 (m), 2854 (m), 1794 (vs, C═O), 1738 (s), 1170 (m), 1046 (m), 773 (m) cm^{-1}.

Carbonated linseed oil (7d).[51] According to **GP4**, MoO_3 (4.7 mg, 0.033 mmol), tetra-*n*-butylphosphonium bromide (88 mg, 0.26 mmol) and epoxidized linseed oil (**6d**, oxirane number = 8.62 mmol g^{-1}, 1.51 g, 13.0 mmol) were converted with CO_2. After filtration (SiO_2, *c*Hex/EtOAc = 1 : 1) the carbonated product (1.65 g) was isolated as a mixture of carbonate **7d** (77%) and **6d** (3%) as a yellow oil. **7d**: ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.83–0.90 (m, 5H), 1.02–1.08 (m, 4H), 1.22–2.14 (m, 68H), 2.27–2.31 (m, 6H), 4.10 (dd, *J* = 11.8 Hz, 5.9 Hz, 2H), 4.20–4.35 (m, 3H), 4.39–5.06 (m, 10H); 5.21–5.24 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C) δ = 9.98 (CH_3), 10.39 (CH_3), 10.51 (CH_3), 13.79 (CH_3), 13.97 (CH_3), 14.00 (CH_3), 22.10–33.96 (multiple signals, CH_2), 61.95 (CH_2), 68.78

(CH), 75.47 (CH), 79.47–81.97 (multiple signals, CH), 153.83 (C═O), 153.93 (C═O), 154.73 (CO_3), 172.67 (C═O), 173.06 (C═O), 173.13 (C═O); ATR IR: ν_{max} = 2924 (m), 2854 (m), 1790 (vs, C═O), 1737 (s), 1171 (m), 1034 (m), 773 (m) cm^{-1}.

Carbonated methyl soyate NEXO E1 (7e).[20] According to **GP4**, MoO_3 (2.4 mg, 0.017 mmol), tetra-*n*-butylphosphonium bromide (44 mg, 0.13 mmol) and methyl soyate NEXO E1 (**6e**, oxirane number = 4.36 mmol g^{-1}, 1.50 g, 6.54 mmol) were converted with CO_2. After filtration (SiO_2, *c*Hex/EtOAc = 1 : 1) the carbonated product (1.75 g) was isolated as a mixture of carbonate **7e** (84%) and **6e** (16%) as a yellow oil. **7e**: ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 0.83–0.90 (m, 3H), 1.24–1.66 (m, 25H), 2.27–2.32 (m, 2H), 3.65 (s, 3H); 4.20–4.94 (m, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C) δ = 13.82 (CH_3), 14.02 (CH_3), 14.06 (CH_3), 22.31–34.05 (multiple signals, CH_2), 51.37 (CH), 51.42 (CH), 57.14 (CH), 57.19 (CH), 75.22–81.98 (multiple signals, CH), 153.67 (C═O), 154.73 (C═O), 174.15 (C═O), 174.30 (C═O); ATR IR: ν_{max} = 2924 (m), 2854 (m), 1798 (vs, C═O), 1736 (s), 1170 (m), 1047 (m), 773 (m) cm^{-1}.

Acknowledgements

We wish to thank the Federal Ministry of Research and Education (BMBF) for financial support (Chemische Prozesse und stoffliche Nutzung von CO_2: Technologien für Nachhaltigkeit und Klimaschutz, grant 01 RC 1004A) as well as Prof. M. Beller for the support and advice. The support of M. Jurrat and J. Janke is gratefully acknowledged. Epoxidized vegetable oils were provided by HOBUM Oleochemicals and are gratefully acknowledged.

Notes and references

1 J. H. Clark and F. Deswarte, *Introduction to Chemicals from Biomass*, John Wiley & Sons, Ltd, Chichester, 2015.

2 W. Schwab, C. Fuchs and F.-C. Huang, *Eur. J. Lipid Sci. Technol.*, 2013, **115**, 3–8.

3 U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schäfer, *Angew. Chem., Int. Ed.*, 2011, **50**, 3854–3871.

4 A. Behr and J. P. Gomes, *Eur. J. Lipid Sci. Technol.*, 2010, **112**, 31–50.

5 G. Centi and R. A. v. Santen, *Catalysis for Renewables: From Feedstock to Energy Production*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007.

6 A. Behr and A. Westfechtel, *Chem. Ing. Tech.*, 2007, **79**, 621–636.

7 S. Nordhoff, H. Höcker and H. Gebhardt, *Chem. Ing. Tech.*, 2007, **79**, 551–560.

8 D. J. Anneken, S. Both, R. Christoph, G. Fieg, U. Steinberner and A. Westfechtel, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000, DOI: 10.1002/14356007.a10_245.pub2.

9 K. Noweck and W. Grafahrend, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000, DOI: 10.1002/14356007.a10_277.pub2.

10 M. A. R. Meier, J. O. Metzger and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1788–1802.

11 M. R. g. Klaas and S. Warwel, in *Recent Developments in the Synthesis of Fatty Acid Derivates*, ed. G. Knothe and J. T. P. Derksen, AOCS Press, Champaign, Illinois, 1999, pp. 157–181.

12 M. J. S. Küppers, D. H. Müller, F. Pontzen, D. Herzog, M. A. Liauw and L. Greiner, in *Friction, Wear and Wear Protection*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009, DOI: 10.1002/9783527628513.ch64.

13 M. Poliakoff, W. Leitner and E. S. Streng, *Faraday Discuss.*, 2015, **183**, 9–17.

14 G. Rokicki, P. G. Parzuchowski and M. Mazurek, *Polym. Adv. Technol.*, 2015, **26**, 707–761.

15 H. Blattmann, M. Fleischer, M. Bähr and R. Mülhaupt, *Macromol. Rapid Commun.*, 2014, **35**, 1238–1254.

16 M. Bähr and R. Mülhaupt, *Green Chem.*, 2012, **14**, 483–489.

17 A. Boyer, E. Cloutet, T. Tassaing, B. Gadenne, C. Alfos and H. Cramail, *Green Chem.*, 2010, **12**, 2205–2213.

18 Z. Li, Y. Zhao, S. Yan, X. Wang, M. Kang, J. Wang and H. Xiang, *Catal. Lett.*, 2008, **123**, 246–251.

19 B. Tamami, S. Sohn and G. L. Wilkes, *J. Appl. Polym. Sci.*, 2004, **92**, 883–891.

20 B. Schäffner, M. Blug, D. Kruse, M. Polyakov, A. Köckritz, A. Martin, P. Rajagopalan, U. Bentrup, A. Brückner, S. Jung, D. Agar, B. Rüngeler, A. Pfennig, K. Müller, W. Arlt, B. Woldt, M. Graß and S. Buchholz, *ChemSusChem*, 2014, **7**, 1133–1139.

21 K. M. Doll and S. Z. Erhan, *Green Chem.*, 2005, **7**, 849–854.

22 J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, *Green Chem.*, 2015, **17**, 1966–1987.

23 C. Martín, G. Fiorani and A. W. Kleij, *ACS Catal.*, 2015, **5**, 1353–1370.

24 M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann and F. E. Kühn, *ChemSusChem*, 2015, **8**, 2436–2454.

25 A. Decortes, A. M. Castilla and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2010, **49**, 9822–9837.

26 T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312–1330.

27 W.-L. Dai, S.-L. Luo, S.-F. Yin and C.-T. Au, *Appl. Catal., A*, 2009, **366**, 2–12.

28 M. North and R. Pasquale, *Angew. Chem., Int. Ed.*, 2009, **48**, 2946–2948.

29 J. Sun, S.-i. Fujita and M. Arai, *J. Organomet. Chem.*, 2005, **690**, 3490–3497.

30 A.-A. G. Shaikh and S. Sivaram, *Chem. Rev.*, 1996, **96**, 951–976.

31 C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo and A. W. Kleij, *Chem. – Eur. J.*, 2014, **20**, 2264–2275.

32 J. A. Castro-Osma, C. Alonso-Moreno, A. Lara-Sanchez, J. Martinez, M. North and A. Otero, *Catal. Sci. Technol.*, 2014, **4**, 1674–1684.

33 M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak and P. P. Pescarmona, *ChemSusChem*, 2015, **8**, 1034–1042.

34 A. Buonerba, A. De Nisi, A. Grassi, S. Milione, C. Capacchione, S. Vagin and B. Rieger, *Catal. Sci. Technol.*, 2015, **5**, 118–123.

35 A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212–214.

36 M. Adolph, T. A. Zevaco, C. Altesleben, S. Staudt and E. Dinjus, *J. Mol. Catal. A: Chem.*, 2015, **400**, 104–110.

37 M. A. Fuchs, S. Staudt, C. Altesleben, O. Walter, T. A. Zevaco and E. Dinjus, *Dalton Trans.*, 2014, **43**, 2344–2347.

38 R. Luo, X. Zhou, W. Zhang, Z. Liang, J. Jiang and H. Ji, *Green Chem.*, 2014, **16**, 4179–4189.

39 A. Chen, C. Chen, Y. Xiu, X. Liu, J. Chen, L. Guo, R. Zhang and Z. Hou, *Green Chem.*, 2015, **17**, 1842–1852.

40 M. E. Wilhelm, M. H. Anthofer, R. M. Reich, V. D'Elia, J.-M. Basset, W. A. Herrmann, M. Cokoja and F. E. Kuhn, *Catal. Sci. Technol.*, 2014, **4**, 1638–1643.

41 A. Monassier, V. D'Elia, M. Cokoja, H. Dong, J. D. A. Pelletier, J.-M. Basset and F. E. Kühn, *ChemCatChem*, 2013, **5**, 1321–1324.

42 C. J. Whiteoak, E. Martin, E. Escudero-Adán and A. W. Kleij, *Adv. Synth. Catal.*, 2013, **355**, 2233–2239.

43 J. Sun, S. Zhang, W. Cheng and J. Ren, *Tetrahedron Lett.*, 2008, **49**, 3588–3591.

44 Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu and K. Ding, *Angew. Chem., Int. Ed.*, 2007, **46**, 7255–7258.

45 F. Li, C. Xia, L. Xu, W. Sun and G. Chen, *Chem. Commun.*, 2003, 2042–2043.

46 A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori and R. Sartorio, *Tetrahedron Lett.*, 2003, **44**, 2931–2934.

47 M. Jalilian, H. Yeganeh and M. N. Haghighi, *Polym. Int.*, 2008, **57**, 1385–1394.

48 K. M. Doll and S. Z. Erhan, *J. Agric. Food Chem.*, 2005, **53**, 9608–9614.

49 J. Langanke, L. Greiner and W. Leitner, *Green Chem.*, 2013, **15**, 1173–1182.

50 P. G. Parzuchowski, M. Jurczyk-Kowalska, J. Ryszkowska and G. Rokicki, *J. Appl. Polym. Sci.*, 2006, **102**, 2904–2914.

51 M. Alves, B. Grignard, S. Gennen, C. Detrembleur, C. Jerome and T. Tassaing, *RSC Adv.*, 2015, **5**, 53629–53636.

52 M. Ratzenhofer and H. Kisch, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 317–318.

53 M. Ratzenhofer and H. Kisch, *Angew. Chem., Int. Ed. Engl.*, 1980, **92**, 303–303.

54 F. Chen, T. Dong, T. Xu, X. Li and C. Hu, *Green Chem.*, 2011, **13**, 2518–2524.

55 B. Schäffner, M. Blug, T. Werner, H. Büttner and N. Tenhumberg, *DE*, 102013206167.6, 2013.

56 A. Behr, N. Tenhumberg and A. Wintzer, *Eur. J. Lipid Sci. Technol.*, 2012, **114**, 905–910.

57 For detailed experimental procedures and synthesis see ESI.†

58 H. Büttner, J. Steinbauer and T. Werner, *ChemSusChem*, 2015, **8**, 2655–2669.

59 H. Büttner, K. Lau, A. Spannenberg and T. Werner, *ChemCatChem*, 2015, **7**, 459–467.

60 C. Kohrt and T. Werner, *ChemSusChem*, 2015, **8**, 2031–2034.

61 J. Großeheilmann, H. Büttner, C. Kohrt, U. Kragl and T. Werner, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2817–2822.

62 W. Desens, C. Kohrt, M. Frank and T. Werner, *ChemSusChem*, 2015, **8**, 3815–3822.

63 T. Werner and H. Büttner, *ChemSusChem*, 2014, **7**, 3268–3271.

64 T. Werner, N. Tenhumberg and H. Büttner, *ChemCatChem*, 2014, **6**, 3493–3500.

65 U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J. O. Metzger, M. Rüsch gen. Klaas, H. J. Schäfer and M. P. Schneider, *Angew. Chem., Int. Ed.*, 2000, **112**, 2292–2310.

66 U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J. O. Metzger, M. Rüsch gen. Klaas, H. J. Schäfer and M. P. Schneider, *Angew. Chem., Int. Ed.*, 2000, **39**, 2206–2224.

67 M. Rüsch, G. Klaas, P. Bavaj and S. Warwel, *Lipid/Fett*, 1995, **97**, 359–367.

68 B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang and S.-J. Zhang, *Green Chem.*, 2015, **17**, 108–122.

69 Due to the complex mixture of diastereoisomers a conclusive assignment of resonances was omitted.

70 I. Javni, D. P. Hong and Z. S. Petrović, *J. Appl. Polym. Sci.*, 2013, **128**, 566–571.