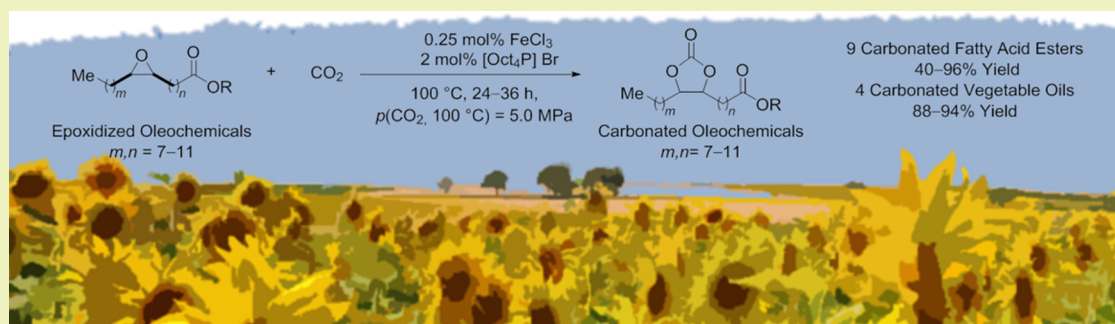# Iron-Based Binary Catalytic System for the Valorization of CO2 into Biobased Cyclic Carbonates

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S Supporting Information

ABSTRACT: The atom economic conversion of epoxidized vegetable oils and fatty acid derivatives with CO_2 into cyclic carbonates permits the synthesis of novel oleo compounds from renewable resources as well as the valorization of CO_2 as a C1-building block. Organic phosphorus salts proved to be selective catalysts for this reaction. In a widespread screening 11 inexpensive and nontoxic iron salts were evaluated as cocatalysts to enhance the reaction rate. In the presence of 0.25 mol % iron chloride the selectivity and conversion were significantly improved. The reaction parameters were optimized under solvent-free conditions, and the scope and limitation were evaluated for 9 epoxidized fatty acid esters and 4 epoxidized vegetable oils. The biobased carbonates were isolated in excellent yields up to 95% and can be considered to be based on 100% CO_2 in respect to carbon. This binary catalyst system features high efficiency and plain simplicity while valorizing CO_2 into cyclic carbonates based on renewable feedstocks.

KEYWORDS: Carbon dioxide, Fatty acid esters, Oleochemical carbonates, Cyclic carbonates, Phosphorus, Iron catalysis

INTRODUCTION

The development of sustainable processes in organic synthesis is a fundamental objective in current chemistry and is guided by the principles of green chemistry.[1] In this context, catalysis is undeniably one of the most influential aspects in order to transform substrate molecules into the desired target compounds. In particular, green catalytic processes aim at a higher degree of selectivity and elaborate procedures to increase the overall efficiency of employed resources and energy while reducing adverse environmental impacts. In order to achieve these goals, abundant, readily available, and nontoxic feedstocks derived from inexpensive and renewable resources are of vital significance. Iron is the second most abundant metal in the earth crust after aluminum.[2] As a matter of fact iron is inexpensive, abundant, and accessible in large scale. Moreover, this first-row transition metal is essential in several metabolisms of biologic systems; hence, it is characterized by low toxicity. Due to the fact that iron can adopt several oxidations states and provides strong Lewis acidic character several transformations can be facilitated by iron catalysts.[3] For instance, the insertion of heterocumulenes into strained ring systems can be catalyzed efficiently by Lewis acid containing catalyst systems. In this context, the formation of cyclic carbonates in the atom economical reaction from CO_2 and fossil-based epoxides gained great interests in recent years (Scheme 1).[4−8] The present Lewis acidic metal center activates the epoxide, while commonly a nucleophilic additive, e.g. ammonium salt, is required to enable the reaction.[6,9−15]

Kleij et al. developed catalysts for the insertion of CO_2 into fossil-based epoxides involving highly active iron complexes.[16,17] In the presence of tetra-*n*-butylammonium bromide or iodide the terminal epoxides were transformed into the corresponding carbonates at 25 °C, while for internal epoxides a reaction temperature of at least 70 °C was reasonable. Williams et al. presented a bimetallic iron(III) complex which produced either polycarbonate or cyclic carbonate, depending on reaction conditions and amount of cocatalyst.[18] Furthermore, Rieger et al. presented iron complex catalysts for the production of cyclic carbonates from CO_2 and fossil-based epoxides.[19,20] However, the production of internal cyclic carbonates utilizing iron based catalysts remains a challenging task. Due to steric hindrance for nucleophilic activation of the

Scheme 1. Formation of Cyclic Carbonates 2 from Epoxides 1 and CO_2 by Binary Catalyst Systems
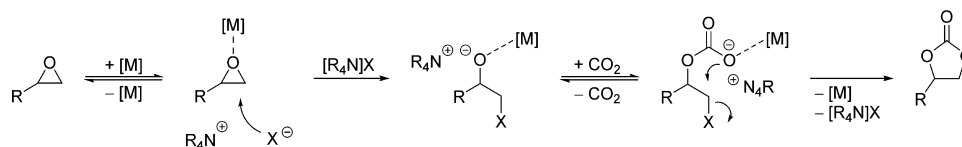
epoxide, reaction rates for internal carbonates are commonly lower compared to terminal ones.

The fixation of CO_2 into cyclic carbonates benefits from several perspectives. The utilization of CO_2 as a C_1 synthon in the production of chemicals indirectly saves limited fossil resources, while at the same time value-added products for various purposes are produced.[10,21−30] Moreover, carbonates produced from CO_2 and epoxidized fatty acid esters and the respective triglycerides have been reported as novel precursors for the synthesis of nonisocyanate polyurethanes (NIPU), as starting materials for polyesters and polycarbonates, as potential industrial lubricants, as fuel additives and polymer plasticizers.[31−38] A recent Life Cycle Assessment (LCA) revealed crucial advantages regarding environmental impacts of the reported biobased carbonates which are considered as potential plasticizers for polyvinyl chloride.[39] For instance, the global warming potential of carbonated fatty acid esters can be reduced by at least 40% (depending on the origin of utilized fatty acid esters) compared to the benchmark system diisononyl phthalate (DINP). Interestingly, the utilization of renewable carbon feedstocks exhibits a greater share of potential savings of CO_2 equivalents than chemical CO_2 fixation itself. This fact emphasizes the potential impact of utilizing renewable resources instead of fossil-based carbon feedstocks in respect to a sustainable process development. Despite this great potential, only very few catalytic systems have been reported for the conversion of epoxidized oleochemicals so far. Schäffner et al. reported KI (5 wt./%) in combination with polyethylene glycol 400 (PEG400) as cocatalyst to produce carbonated methyl linoleate in 84% at 100 °C in supercritical CO_2.[39] In contrast to the system of Rokicki based on alkali halides and crown ether as phase transfer catalyst,[40] PEG400 represents an inexpensive as well as efficient alternative. In both systems the alkali salts provide the nucleophilic species which is essential for catalytic ring-opening of the epoxide. Typically tetra-n-butylammonium salts [Bu$_4$N]X (5 mol %) were employed as catalyst under quite drastic conditions of ≥100 °C and ≥10 MPa.[41−43] The steric demand of the substituents of internal epoxides like in the respective epoxidized fatty acid ester hampers the ring-opening of epoxide by the nucleophile. As a consequence, in contrast to terminal substrates often high temperatures (≥100 °C) or pressures (≥10 MPa) are required to obtain reasonable rates of product formation. The catalytic efficiency of [Bu$_4$N]X was distinctly improved by the employment of a two-component catalyst system composed of an ammonium salt in combination with a Lewis or Brønsted acid cocatalyst. In this context Wang et al. reported that SnCl$_4$·5H$_2$O accelerated the carbonization of epoxidized soybean oil distinctly compared to single catalyst [Bu$_4$N]Br at 120 °C, 1.0 MPa, and 20 h.[44] Further progress has been made by Leitner et al. utilizing chromium polyoxometalate (POM) as suitable cocatalyst for the conversion of epoxidized fatty acid esters and CO_2 at 100 °C and a high pressure of 13 MPa.[45] Recently, Tassaing and Jerome et al. reported an interesting approach by applying perfluoro *tert*-

butanol as cocatalyst for the insertion of CO_2 into epoxidized linseed oil.[46,47] The reaction was carefully monitored by FTIR spectroscopy, whereas reaction conditions of 120 °C, 5.0 MPa, and 10 h proved to be the optimum. So far, the reported systems for the conversion of CO_2 and internal epoxides and particularly fatty acid ester derived epoxides to produce oleochemical carbonates require high catalyst loadings (≥2 mol %), high reaction temperatures (≥100 °C), and pressure (≥10 MPa) and/or exhibit only limited substrate scope. We recently reported the synthesis of cyclic carbonates from CO_2 and epoxides utilizing one- and two-component catalyst systems.[48−53] Due to this interest we turned our attention to the production of oleochemical cyclic carbonates.[54] We envisioned that phosphonium salts in combination with readily available Lewis acidic iron salts might lead to simple and highly active catalytic systems for the formation of cyclic carbonates from CO_2 and epoxidized oleochemicals.

■ EXPERIMENTAL SECTION

General Procedures for the Catalyst Screening and Parameter Optimization (GP1). A 45 cm^3 stainless steel autoclave was charged with metal based cocatalyst (0−0.0025 equiv), and epoxidized methyl oleate (1.0 equiv, *cis*-**1a**) was added immediately. Afterward the onium salt (0−0.03 equiv) was added to the suspension, and the reactor was sealed and purged with CO_2. Subsequently, an initial CO_2 pressure of 0.5−3.5 MPa was set, and the reactor was heated to 90−100 °C for 16−24 h; while $p(CO_2$, 90−100 °C) was kept constant at 1.0−5.0 MPa. Afterward 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 (FID) and *n*-hexadecane as an internal standard directly from the crude reaction mixture.

General Procedures for the Synthesis of Carbonated Fatty Acid Esters and Oils (GP2). A 45 cm^3 stainless steel autoclave was charged with FeCl$_3$ (0.0025 equiv) and [Oct$_4$P]Br (0.02 equiv). The epoxide fatty acid esters **1** (1.0 equiv) or epoxidized vegetable oil **5** (1.0 equiv) was added dropwise. The reactor was immediately sealed and purged with CO_2. An initial CO_2 pressure of 3.5 MPa was set, and the reactor was heated to 100 °C for 24 h; while $p(CO_2$, 100 °C) was kept constant at 5.0 MPa. Afterward the reactor was cooled with an ice bath below 20 °C, and CO_2 was released slowly. Conversion and selectivity were determined by ^{1}H NMR and/or GC-FID from the reaction mixture. The crude product was directly purified by filtration on silica gel (SiO$_2$) or if necessary 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 **2** or **6**, respectively.

Tetra-n-octylphosphonium Bromide:[55] A Schlenk flask was charged with tri-*n*-octylphosphine (5.56 mmol, 2.06 g) and 1-bromooctane (5.59 mmol, 1.08 g) under argon. The resulting mixture was allowed to stir for 24 h at 100 °C. Subsequently, all volatiles were removed in vacuum to yield tetra-*n*-octylphosphonium bromide (5.28 mmol, 3.98 g, 95%) as a colorless solid. ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.86 (t, $^3J_{H,H}$ = 6.7 Hz, 12H), 1.25−1.64 (m, 48H), 2.39−2.49 (m, 8H) ppm; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.1 (4 × CH$_3$), 19.4 (d, $^1J_{C,P}$ = 46.9 Hz, 4 × CH$_2$), 22.0 (d, $^3J_{C,P}$ = 4.7 Hz, 4 × CH$_2$), 22.6 (4 × CH$_2$), 29.0 (8 × CH$_2$), 30.8 (d, $^2J_{C,P}$ = 14.6 Hz, 4 × CH$_2$), 31.7 (4 × CH$_2$) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$, 22

°C): δ = 33.1 ppm; HRMS (ESI-TOF/MS): *m/z* calcd. for $C_{32}H_{68}P^+$ [M^+]: 483.5053 found: 483.5058.

cis-Methyl 8-(3-Octyloxiran-2-yl)octanoate (*cis*-1a):[56] Methyl oleate (*cis*-6a, 40.00 mmol, 11.86 g) was added to a suspension of Ru(acac)₃ (0.20 mmol, 80 mg) and dipicolinic acid (4.00 mmol, 669 mg) in acetonitrile (160 mL, 0.25 M in respect to the olefin). The resulting suspension was sonicated to obtain a homogeneous mixture. Subsequently, aqueous hydrogen peroxide (35%, 132 mmol, 12.8 mL) was added in portions, and the reaction mixture was allowed to stir for 4 h at 25 °C. The resulting mixture was extracted with cyclohexane (4 × 200 mL), and the combined organic layers were concentrated to 200 mL and subsequently washed with H₂O (200 mL). The organic phase was dried over MgSO₄, and all volatiles were removed in vacuum to yield *cis*-1a (37.89 mmol, 11.84 g, 95%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃, 22 °C): δ = 0.89 (t, $^3J_{H,H}$ = 6.7 Hz, 3H), 1.27−1.66 (m, 26H), 2.31 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 2.86−2.95 (m, 2H), 3.67 (s, 3H) ppm; ¹³C{¹H} NMR (75 MHz, CDCl₃, 22 °C): δ = 14.2 (CH₃), 22.7 (CH₂), 25.0 (CH₂), 26.6 (CH₂), 26.7 (CH₂), 27.9 (CH₂), 27.9 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 34.1 (CH₂), 51.5 (OCH₃), 57.3 (CH), 57.3 (CH), 174.3 (C=O) ppm.

Methyl 8-(5-Octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (2a):[45] According to **GP2**, FeCl₃ (13 μmol, 2.1 mg), [Oct₄P]Br (0.10 mmol, 58 mg), and epoxidized methyl oleate (*cis*-1a, 5.02 mmol, 1.57 g) were allowed to react with CO₂. The crude product was purified by flash chromatography (SiO₂, *c*Hex:EtOAc = 20:1 to 5:1) to yield 2a (4.52 mmol, 1.61 g, 90%, *cis*:*trans* = 63:37) as a colorless oil. R_f (*c*Hex:EtOAc = 10:1) = 0.21; ¹H NMR (300 MHz, CDCl₃, 22 °C): δ = 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 1.27−1.72 (m, 26H), 2.31 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.67 (s, 3H), 4.21−4.24 (m, 2H, *trans*-2a), 4.60−4.64 (m, 2H, *cis*-2a) ppm; ¹³C{¹H} NMR (75 MHz, CDCl₃, 22 °C): δ = 14.1 (2 × CH₃), 22.6 (2 × CH₂), 24.6 (2 × CH₂), 24.8 (2 × CH₂), 25.5 (CH₂), 25.6 (CH₂), 28.8 (CH₂), 28.9 (2 × CH₂), 28.9 (CH₂), 28.9 (2 × CH₂), 29.0 (CH₂), 29.0 (CH₂), 29.1 (2 × CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.3 (2 × CH₂), 31.8 (2 × CH₂), 33.8 (CH₂), 33.8 (CH₂), 34.0 (2 × CH₂), 51.4 (2 × OCH₃), 79.9 (CH), 79.9 (CH), 81.9 (CH), 82.0 (CH), 154.7 (C=O), 154.7 (C=O), 174.2 (C=O), 174.2 (C=O) ppm; elemental analysis calcd. (%) for $C_{20}H_{36}O_5$: C, 67.38; H, 10.18, found: C, 67.41; H, 10.30.

Ethyl 8-(5-Octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (2b):[45] According to **GP2**, FeCl₃ (10 μmol, 1.7 mg), [Oct₄P]Br (0.083 mmol, 47 mg), and epoxidized ethyl oleate (*cis*-1b, 4.13 mmol, 1.35 g) were allowed to react with CO₂. The crude product was purified by flash chromatography (SiO₂, *c*Hex:EtOAc = 20:1 to 5:1) to yield 2b (3.16 mmol, 1.17 g, 76%, *cis*:*trans* = 69:31) as a colorless oil. R_f (*c*Hex:EtOAc= 5:1) = 0.41; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ = 0.90 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 1.24−1.43 (m, 21H), 1.43−1.74 (m, 8H), 2.29 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 4.13 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 4.22−4.23 (m, 2H, *trans*-2b), 4.61−4.63 (m, 2H, *cis*-2b) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ = 14.1 (2 × CH₃), 14.2 (2 × CH₃), 22.6 (2 × CH₂), 24.6 (2 × CH₂), 24.8 (2 × CH₂), 25.5 (CH₂), 25.5 (CH₂), 26.9 (CH₂), 28.8 (CH₂), 28.9 (2 × CH₂), 28.9 (CH₂), 29.0 (2 × CH₂), 29.1 (CH₂), 29.1 (CH₂), 29.1 (CH₂), 29.2 (2 × CH₂), 29.3 (CH₂), 29.3 (CH₂), 31.8 (2 × CH₂), 33.8 (2 × CH₂), 34.2 (2 × CH₂), 60.1 (2 × OCH₂), 79.9 (CH), 79.9 (CH), 82.0 (CH), 82.0 (CH), 154.7 (C=O), 154.7 (C=O), 173. (2 × C=O) ppm; elemental analysis calcd. (%) for $C_{21}H_{38}O_5$: C, 68.07; H, 10.34, found: C, 68.00; H, 10.28.

Carbonated iso-Octyl Oleate (2c):[54] According to **GP2**, FeCl₃ (7.4 μmol, 1.2 mg), [Oct₄P]Br (0.090 mmol, 51 mg), and epoxidized *iso*-octyl oleate (*cis*-1c, technical grade, oxirane numer = 2.46 mmol/g, 2.88 mmol, 1.17 g) were allowed to react with CO₂ for 36 h. The crude product was purified by filtration (SiO₂, *c*Hex:EtOAc = 1:1) to yield 2c (1.25 g, 96%, *cis*:*trans* = 61:39) as a colorless oil. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.88−0.91 (m, 9H), 1.21−1.69 (m, 35H), 2.29 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 3.96−3.98 (m, 2H), 4.20−4.23 (m, 2H, *trans*-2c), 4.60−4.63 (m, 2H, *cis*-2c) ppm; ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = 11.0 (2 × CH₃), 14.0 (2 × CH₃), 14.0 (2 × CH₃), 22.6 (2 × CH₂), 22.9 (2 × CH₂), 23.7 (2 × CH₂), 24.6 (CH₂), 24.9 (2 × CH₂), 25.5 (CH₂), 25.6 (CH₂), 28.8 (2 × CH₂), 28.9 (4 ×

CH₂), 28.9 (CH₂), 28.9 (2 × CH₂), 29.0 (CH₂), 29.0 (CH₂), 29.0 (2 × CH₂), 29.1 (CH₂), 29.1 (2 × CH₂), 29.1 (CH₂), 29.2 (2 × CH₂), 29.3 (CH₂), 29.2 (2 × CH₂), 31.8 (CH₂), 33.8 (CH₂), 34.3 (CH₂), 38.7 (2 × CH), 66.6 (2 × CH₂), 79.9 (CH), 79.9 (CH), 81.9 (CH), 82.0 (CH), 154.7 (2 × C=O), 173.9 (2 × C=O); elemental analysis calcd. (%) for $C_{27}H_{50}O_5$: C, 71.32; H, 11.08, found: C, 71.29; H, 11.15.

Methyl 10-(5-Octyl-2-oxo-1,3-dioxolan-4-yl)decanoate (2d):[54] According to **GP2**, FeCl₃ (8.6 μmol, 1.4 mg), [Oct₄P]Br (0.071 mmol, 40 mg), and epoxidized methyl eicosenoate (*cis*-1d, 3.44 mmol, 1.17 g) were allowed to react with CO₂. The crude product was purified by flash chromatography (SiO₂, *c*Hex:EtOAc = 10:1) to yield 2d (3.04 mmol, 1.17 g, 89%, *cis*:*trans* = 70:30) as a colorless oil. R_f (*c*Hex:EtOAc = 10:1) = 0.18; ¹H NMR (300 MHz, CDCl₃, 23 °C): δ = 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 1.25−1.41 (m, 22H), 1.48−1.73 (m, 8H), 2.31 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.67 (s, 3H), 4.19−4.26 (m, 2H, *trans*-2d), 4.59−4.66 (m, 2H, *cis*-2d) ppm; ¹³C{¹H} NMR (75 MHz, CDCl₃, 23 °C): δ = 14.0 (2 × CH₃), 22.6 (2 × CH₂), 24.6 (2 × CH₂), 24.9 (2 × CH₂), 25.5 (2 × CH₂), 28.9 (2 × CH₂), 29.0 (CH₂), 29.1 (3 × CH₂), 29.1 (3 × CH₂), 29.2 (CH₂), 29.2 (6 × CH₂), 29.3 (2 × CH₂), 31.7 (2 × CH₂), 33.8 (2 × CH₂), 34.1, (2 × CH₂), 51.4 (2 × OCH₃), 79.9 (2 × CH), 82.0 (2 × CH), 154.7 (C=O), 154.7 (C=O), 174.2 (2 × C=O) ppm; elemental analysis calcd. (%) for $C_{22}H_{40}O_5$: C, 68.71; H, 10.48, found: C, 68.79; H, 10.45.

Methyl 12-(5-Octyl-2-oxo-1,3-dioxolan-4-yl)dodecanoate (2e):[54] According to **GP2**, FeCl₃ (7.4 μmol, 1.2 mg), [Oct₄P]Br (0.071 mmol, 40 mg), and epoxidized methyl erucate (*cis*-1e, 3.20 mmol, 1.18 g) were allowed to react with CO₂. The crude product was purified by filtration (SiO₂, CH₂Cl₂) to yield 2e (2.62 mmol, 1.08 g, 82%, *cis*:*trans* = 63:37) as a colorless oil. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.89 (t, $^3J_{H,H}$ = 6.7 Hz, 3H), 1.24−1.40 (m, 24H), 1.49−1.78 (m, 8H), 2.31 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.67 (s, 3H), 4.19−4.26 (m, 2H, *trans*-2e), 4.59−4.66 (m, 2H, *cis*-2e) ppm; ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = 14.0 (2 × CH₃), 22.6 (2 × CH₂), 24.6 (2 × CH₂), 24.9 (2 × CH₂), 25.6 (2 × CH₂), 28.8 (2 × CH₂), 29.1 (2 × CH₂), 29.1 (2 × CH₂), 29.1 (2 × CH₂), 29.2 (6 × CH₂), 29.3 (2 × CH₂), 29.3 (2 × CH₂), 29.4 (2 × CH₂), 29.4 (2 × CH₂), 31.7 (2 × CH₂), 33.8 (2 × CH₂), 34.0 (2 × CH₂), 51.4 (2 × OCH₃), 79.9 (2 × CH), 82.0 (2 × CH₂), 154.7 (C=O), 154.8 (C=O), 174.3 (2 × C=O) ppm; elemental analysis calcd. (%) for $C_{24}H_{44}O_5$: C, 69.86; H, 10.75, found: C, 69.90; H, 10.62.

Methyl 8-(5-((2R)-Hydroxyoctyl)-2-oxo-1,3-dioxolan-4-yl)-octanoate (2f):[54] According to **GP2**, FeCl₃ (8.0 μmol, 1.3 mg), [Oct₄P]Br (0.074 mmol, 42 mg), and epoxidized methyl ricinoleate (*cis*-1f, 3.32 mmol, 1.09 g) were allowed to react with CO₂. The crude product was purified by flash chromatography (SiO₂, *c*Hex:EtOAc = 10:1 to 2:1) to yield 2f (1.35 mmol, 503 mg, 40%) as a colorless oil as a mixture of two diastereroisomers (*dr* = 66:34). R_f (*c*Hex:EtOAc = 2:1) = 0.33; ¹H NMR (300 MHz, CDCl₃, 22 °C): δ = 0.88 (t, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.27−1.43 (m, 15H), 1.47−1.95 (m, 10H), 2.30 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.66 (s, 3H), 3.82 (m, 1H), 4.62−4.70 (m, 1H), 4.84−4.91 (m, 1H), 4.97−5.04 (m, 1H) ppm; ¹³C{¹H} NMR (75 MHz, CDCl₃, 22 °C): δ = 14.1 (2 × CH₃), 22.6 (2 × CH₂), 24.8 (2 × CH₂), 25.4 (CH₂), 25.4 (CH₂), 25.5 (2 × CH₂), 28.9 (2 × CH₂), 29.0 (3 × CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.2 (2 × CH₂), 31.8 (2 × CH₂), 34.0 (2 × CH₂), 35.9 (CH₂), 36.1 (CH₂), 37.0 (CH₂), 38.3 (CH₂), 51.5 (2 × OCH₃), 67.7 (CH₂), 69.2 (CH), 77.0 (CH), 77.9 (CH), 80.0 (2 × CH), 154.5 (2 × C=O), 174.3 (2 × C=O) ppm; HRMS (ESI−TOF/MS): *m/z* calcd. for $C_{20}H_{37}O_6$ [M^++H]: 373.2585, found: 373.2584 [M^++H].

Methyl 8-(5-((2R)-Acetoxyoctyl)-2-oxo-1,3-dioxolan-4-yl)-octanoate (2g):[54] According to **GP2**, FeCl₃ (9.2 μmol, 1.5 mg), [Oct₄P]Br (0.076 mmol, 43 mg), and epoxidized methyl *O*-acetyl ricinoleate (*cis*-1g, 3.81 mmol, 1.41 g) were allowed to react with CO₂. The crude product was purified by flash chromatography (SiO₂, *c*Hex:EtOAc = 20:1 to 1:1) to yield 2g (3.06 mmol, 1.27 g, 81%) as a colorless oil as a mixture of four diastereroisomers (*dr* = 9:10:44:37). R_f (*c*Hex:EtOAc = 2:1) = 0.61; ¹H NMR (300 MHz, CDCl₃, 22 °C): δ = 0.87 (t, $^3J_{H,H}$ = 6.4 Hz, 3H), 1.24−1.42 (m, 15H), 1.46−2.01 (m, 9H), 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), 4.20−4.35 (m, 2H, *trans*-isomers), 4.59−4.66 (m, 2H, *cis*-isomer), 4.69−4.76 (m, 2H, *cis*-isomer), 4.96−5.05 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.0 (CH$_3$), 21.1 (CH$_3$), 21.1 (CH$_3$), 22.5 (CH$_2$), 24.7 (CH$_2$), 24.9 (CH$_2$), 25.1 (CH$_2$), 25.3 (CH$_2$), 25.4 (CH$_2$), 26.8 (CH$_2$), 28.9 (CH$_2$), 28.9 (CH$_2$), 29.0 (CH$_2$), 31.6 (CH$_2$), 33.2 (CH$_2$), 33.4 (CH$_2$), 33.9 (CH$_2$), 34.1 (CH$_2$), 34.4 (CH$_2$), 34.6 (CH$_2$), 51.4 (OCH$_3$), 70.3 (CH), 70.7 (CH), 70.9 (CH), 76.4 (CH), 76.8 (CH), 79.5 (CH), 79.6 (CH), 81.9 (CH), 82.0 (CH), 154.2 (C=O), 154.3 (C=O), 170.3 (C=O), 170.9 (C=O), 174.1 (C=O) ppm; elemental analysis calcd. (%) for C$_{22}$H$_{38}$O$_7$: C, 63.74; H, 9.24, found: C, 63.78; H, 9.30.

Methyl 8-(2-Oxo-5-((2-oxo-5-pentyl-1,3-dioxolan-4-yl)methyl)-1,3-dioxolan-4-yl)octanoate (2h):[45] According to **GP2**, FeCl$_3$ (14 μmol, 2.2 mg), [Oct$_4$P]Br (0.11 mmol, 64 mg), and epoxidized methyl linoleate (**1h**, 5.30 mmol, 1.73 g) were allowed to react with CO$_2$ for 48 h at 100 °C. The crude product was purified by flash chromatography (SiO$_2$, *c*Hex:EtOAc = 20:1 to 1:1) to yield **2h** (4.49 mmol, 1.86 g, 85%) as a colorless oil as a mixture of four diastereoisomers (*dr* = 24:57:12:7). R_f (*c*Hex:EtOAc = 2:1) = 0.16; ^1H NMR (400 MHz, CDCl$_3$, 24 °C): δ = 0.91 (t, $^3J_{H,H}$ = 6.5 Hz, 3H), 1.23−2.26 (m, 22H), 2.31 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 3.67 (s, 3H), 4.27−4.37 (m, 2H), 4.45−4.53 (m, 2H), 4.67−4.85 (m, 2H), 4.86−4.96 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$, 24 °C): δ = 13.8 (CH$_3$), 22.3 (CH$_2$), 22.3 (CH$_2$), 22.3 (CH$_2$), 22.3 (CH$_2$), 24.1 (CH$_2$), 24.1 (CH$_2$), 24.7 (CH$_2$), 24.7 (CH$_2$), 25.2 (CH$_2$), 25.2 (CH$_2$), 25.4 (CH$_2$), 25.4 (CH$_2$), 25.5 (CH$_2$), 28.5 (CH$_2$), 28.8 (CH$_2$), 28.8 (CH$_2$), 28.9 (CH$_2$), 28.9 (CH$_2$), 29.0 (CH$_2$), 31.2 (CH$_2$), 31.2 (CH$_2$), 31.2 (CH$_2$), 32.0 (CH$_2$), 33.3 (CH$_2$), 33.7 (CH$_2$), 51.4 (OCH$_3$), 74.3 (CH), 75.2 (CH), 75.4 (CH), 75.7 (CH), 77.2 (CH), 77.7 (CH), 78.1 (CH), 79.2 (CH), 79.3 (CH), 79.4 (CH), 79.4 (CH), 80.8 (CH), 80.9 (CH), 82.0 (CH), 82.1 (CH), 153.6 (C=O), 153.6 (C=O), 153.7 (C=O), 153.8 (C=O), 174.1 (C=O) ppm; elemental analysis calcd. (%) for C$_{21}$H$_{34}$O$_8$: C, 60.85; H, 8.27, found: C, 60.76; H, 8.41.

Methyl 9-(2-Oxo-1,3-dioxolan-4-yl)nonanoate (2i):[48] According to **GP2**, FeCl$_3$ (13 μmol, 2.1 mg), [Oct$_4$P]Br (0.10 mmol, 59 mg), and epoxidized methyl 9-(oxiran-2-yl)nonanoate (**1i**, 5.04 mmol, 1.08 g) were allowed to react with CO$_2$ for 6 h at 100 °C. The crude product was purified by filtration (SiO$_2$, CH$_2$Cl$_2$) to yield **2i** (4.22 mmol, 1.09 g, 84%) as a colorless oil. ^1H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 1.21−1.90 (m, 14H), 2.30 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.66 (s, 3H), 4.06 (dd, $^2J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 7.2 Hz, 1H), 4.53 (dd, $^2J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.9 Hz, 1H), 4.63−4.77 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (300 MHz, CDCl$_3$, 25 °C): δ = 24.3 (CH$_2$), 24.8 (CH$_2$), 29.0 (CH$_2$), 29.0 (2 × CH$_2$), 29.1 (CH$_2$), 33.8 (CH$_2$), 34.0 (CH$_2$), 51.4 (OCH$_3$), 69.3 (CH), 77.0 (CH), 155.0 (C=O). 174.2 (C=O) ppm; elemental analysis calcd. (%) for C$_{13}$H$_{22}$O$_5$: C, 60.45; H, 8.58, found: C, 60.46; H, 8.43.

Methyl 9-Oxooctadecanoate (3aa) and Methyl 10-Oxooctade-canoate (3ab). The formation of ketone **3aa** and **3ab**, respectively, was observed in varying amounts during the conversion of *cis*-**1a** and CO$_2$ while screening of catalyst and cocatalyst as well evaluation of the reaction conditions. As a mixture of isomers (*dr* = 50:50) R_f (*c*Hex:EtOAc = 1:1) = 0.74; ^1H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 3H), 1.27−1.31 (m, 18H), 1.51−1.64 (m, 6H), 2.31 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 2.39 (t, $^3J_{H,H}$ = 7.5 Hz, 4H), 3.67 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.05 (CH$_3$), 22.62 (CH$_2$), 23.69 (CH$_2$), 23.76 (CH$_2$), 23.83 (CH$_2$), 24.81 (CH$_2$), 24.85 (CH$_2$), 28.89 (CH$_2$), 28.99 (CH$_2$), 29.02 (CH$_2$), 29.10 (CH$_2$), 29.12 (CH$_2$), 29.16 (CH$_2$), 29.22 (CH$_2$), 29.33 (CH$_2$), 29.38 (CH$_2$), 31.77 (CH$_2$), 31.81 (CH$_2$), 33.99 (CH$_2$), 34.01 (CH$_2$), 42.66 (CH$_2$), 42.70 (CH$_2$), 42.79 (CH$_2$), 51.40 (OCH$_3$), 174.19 (C=O), 174.23 (C=O), 211.55 (C=O, isomer **3ab**), 211.62 (C=O, isomer **3aa**); MS (EI): *m/z* (%): 312 (1), 281 (16), 214 (13), 207 (18), 200 (22), 185 (19), 170 (23), 168 (16), 164 (9), 158 (16), 157 (28) 156 (33), 155 (21), 153 (11), 144 (11), 143 (33) 142 (21), 141 (20), 140 (18), 139 (15), 153 (11), 130 (11), 125 (51), 111 (35), 97 (45), 95 (20), 83 (43), 71 (79), 69 (41), 55 (100), 43 (78), 41 (54).

Methyl 8-(5-Hexyl-3-hydroxytetrahydrofuran-2-yl)octanoate (4). As a mixture of diastereoisomers (*dr* = 50:50); R_f (*c*Hex:EtOAc = 5:1) = 0.35; ^1H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.87 (t, $^3J_{H,H}$ = 6.8

Hz, 3H), 1.27−1.73 (m, 24H), 2.06 (s, br., 1H), 2.26−2.37 (m, 3H), 3.65 (s, 3H), 3.69−3.75 (m, 1H), 3.89−3.98 (m, 1H), 3.99−4.05 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.02 (CH$_3$), 22.54 (CH$_2$), 24.83 (CH$_2$), 25.77 (CH$_2$), 25.98 (CH$_2$), 28.97 (CH$_2$), 29.06 (CH$_2$), 29.25 (CH$_2$), 29.37 (CH$_2$), 31.76 (CH$_2$), 32.93 (CH$_2$), 34.01 (CH$_2$), 36.55 (CH$_2$), 40.75 (CH$_2$), 51.41 (OCH$_3$), 76.57 (CH), 77.02 (CH), 84.55 (CH), 174.32 (C=O); MS (EI): *m/z* (%): 310 (2), 294 (1), 279 (3), 225 (24), 193 (11), 187 (43), 156 (10), 155 (100), 109 (16), 95 (10), 81 (12), 69 (11), 67 (13), 57 (18), 55 (21), 43 (12), 41 (11).

Carbonated Linseed Oil (6a):[54] According to **GP2**, FeCl$_3$ (30 μmol, 4.8 mg), [Oct$_4$P]Br (0.243 mmol, 137 mg), and epoxidized linseed oil (**5a**, oxirane number = 8.62 mmol·g^{-1}, 11.5 mmol, 1.33 g) were allowed to react with CO$_2$. The crude product was purified by filtration (SiO$_2$, *c*Hex:EtOAc = 1:1) to yield **6a** (1.65 g, 90%) as a pale yellow oil. ^1H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.76−0.83 (m, 5H), 0.92−1.01 (m, 4H), 1.16−2.07 (m, 68H), 2.22 (t, $^3J_{H,H}$ = 6.8 Hz, 2H) 4.02−4.08 (m, 2H), 4.18−4.23 (m, 2H), 4.36−5.00 (m, 11H), 5.13−5.19 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 22 °C): δ = 8.4 (CH$_3$), 9.8−10.0 (multiple signals, CH$_3$), 13.6 (CH$_3$), 13.8 (CH$_3$), 13.8 (CH$_3$), 21.9−33.7 (multiple signals, CH$_2$), 61.7 (CH$_2$), 68.6 (CH), 75.4 (CH), 76.8 (CH), 79.4 (CH), 79.7 (CH), 80.9 (CH), 81.8 (CH), 153.2−154.5 (multiple signals, C=O), 172.5 (C=O), 172.8 (C=O), 173.0 (C=O) ppm; FTIR (ATR) ν_{max} = 2926 (w), 2855 (w), 2256 (vw), 1790 (vs), 1736 (m), 1552 (vw), 1462 (w), 1368 (w), 1172 (s), 1045 (s), 909 (m), 774 (m), 729 (vs), 690 (w) cm^{-1}.

Carbonated High-Oleic Sunflower Oil (6b):[54] According to **GP2**, FeCl$_3$ (20 μmol, 3.3 mg), [Oct$_4$P]Br (0.17 mmol, 95 mg), and epoxidized high-oleic sunflower oil (**5b**, oxirane number = 4.71 mmol·g^{-1}, 7.77 mmol, 1.65 g) were converted with CO$_2$. The crude product was purified by filtration (SiO$_2$, CH$_2$Cl$_2$) to yield **6b** (1.75 g, 88%) as a pale yellow oil. ^1H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.85 (t, $^3J_{H,H}$ = 6.7 Hz, 9H), 1.15−1.66 (m, 80H), 2.28 (t, $^3J_{H,H}$ = 7.4 Hz, 6H), 4.11 (dd, $^2J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H), 4.15−4.22 (m, 2H), 4.27 (dd, $^2J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 4.3 Hz, 2H), 4.55−4.65 (m, 3H), 5.17−5.27 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 22 °C): δ = 14.1 (CH$_3$), 22.7−34.1 (multiple signals, CH$_2$), 62.1 (CH$_2$), 68.9 (CH), 80.0 (CH), 80.0 (CH), 82.0 (CH), 82.1 (CH), 154.8 (C=O), 173.2 (C=O) ppm; FTIR (ATR) ν_{max} = 2923 (m), 2854 (m), 1797 (vs), 1739 (s), 1466 (w), 1370 (w), 1240 (w), 1165 (s), 1090 (m), 1038 (s), 775 (m), 724 (w), 688 (w) cm^{-1}.

Carbonated Soybean Oil (6c):[54] According to **GP2**, FeCl$_3$ (7.4 μmol, 1.2 mg), [Oct$_4$P]Br (0.062 mmol, 35 mg), and epoxidized soybean oil (**5c**, EPOXOL D65, oxirane number = 4.81 mmol·g^{-1}, 2.91 mmol, 604 mg) were converted with CO$_2$. The crude product was purified by filtration (SiO$_2$, *c*Hex:EtOAc = 1:1) to yield **6c** (0.689 g, 94%) as a pale yellow oil. ^1H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.86−0.93 (m, 9H), 1.06−1.13 (m, 1H), 1.23−2.05 (m, 77H), 2.32 (t, $^3J_{H,H}$ = 7.2 Hz, 6H), 4.14 (dd, $^2J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H), 4.22−4.36 (m, 3H), 4.46−4.93 (m, 7H), 5.23−5.29 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 22 °C): δ = 13.9 (CH$_3$), 14.0 (CH$_3$), 14.1 (CH$_3$), 22.3−34.0 (multiple signals, CH$_2$), 62.0 (CH$_2$), 68.9 (CH$_3$), 75.4 (CH), 75.5 (CH), 76.0 (CH), 79.4 (CH), 79.4 (CH), 79.9 (CH), 80.0 (CH), 82.0 (CH), 153.8 (C=O), 154.8 (C=O), 172.7 (C=O), 173.1 (C=O), 173.3 (C=O) ppm; FTIR (ATR) ν_{max} = 2925 (m), 2855 (w), 1793 (vs), 1737 (s), 1462 (vw), 1369 (w), 1169 (s), 1045 (s), 773 (m), 725 (w), 688 (vw) cm^{-1}.

Carbonated Methyl Soyate NEXO E1 (6d):[39] According to **GP2**, FeCl$_3$ (27 μmol, 4.4 mg), [Oct$_4$P]Br (0.229 mmol, 129 mg), and epoxidized methyl soyate NEXO E1 (**5d**, oxirane number = 4.36 mmol·g^{-1}, 6.54 mmol, 1.50 g) were converted with CO$_2$. The crude product was purified by filtration (SiO$_2$, *c*Hex:EtOAc = 1:1) to yield **6d** (1.61 g, 89%) as a pale yellow oil. ^1H NMR (300 MHz, CDCl$_3$, 22 °C): δ = 0.85−0.92 (m, 3H), 1.25−1.99 (m, 25H), 2.30 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 3.66 (s, 3H), 4.22−4.92 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$, 22 °C): δ = 13.9 (CH$_3$), 14.1 (CH$_3$), 14.1 (CH$_3$), 22.3−34.1 (multiple signals, CH$_2$), 51.4 (CH$_3$), 51.5 (CH$_3$), 75.3 (CH), 75.4 (CH), 75.8 (CH), 77.7 (CH), 77.8 (CH), 79.3 (CH), 79.4 (CH), 79.4 (CH), 79.5 (CH), 79.9 (CH), 80.0 (CH), 80.9 (CH), 81.0 (CH),
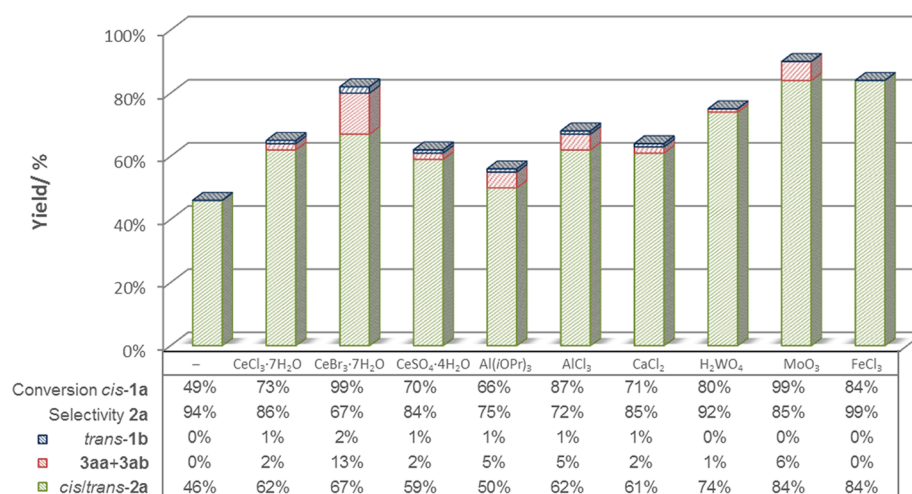
Figure 1. Screening of Lewis acidic cocatalyst and comparison with $FeCl_3$. Reaction conditions: 5.00 mmol of cis-**1a**, 2 mol % $[Bu_4P]Br$, 2.0 mol % cocatalyst, 100 °C, $p(CO_2, 100 °C) = 5.0$ MPa, 16 h. Conversion, yields, and selectivities were determined by GC-FID using n-hexadecane as an internal standard.

Table 1. Screening of Various Iron Salts as Cocatalyst in the Model Reaction[a]

entry	cocatalyst	conversion 1a [%]	yield 2a [%]	selectivity 2a [%]	cis:trans ratio of 2a	ketone 3 [%]
1	FeF_3	77	68	89	75:25	1
2	$FeCl_3$	84	84	>99	87:13	0
3	$FeCl_3 \cdot 6H_2O$	47	39	83	86:14	<1
4	$FeBr_3$	100	81	81	38:62	6
5	$FeBr_2$	100	83	83	39:61	9
6	$Fe(acac)_3$	78	67	86	94:6	<1
7	$Fe(OTf)_3$	100	3	3	100:0	54
8	$Fe(OAc)_2$	58	50	86	80:20	1
9	$Fe(stearate)_3$	57	46	80	79:21	1
10	$FeSO_4 \cdot 7H_2O$	27	26	98	86:14	0
11	$Fe(citrate)_3 \cdot (aq.)$	37	37	99	80:20	0

[a]Reaction conditions: 5.00 mmol of cis-**1a**, 2.0 mol % catalyst, 2.0 mol % cocatalyst, 100 °C, $p(CO_2, 100 °C) = 5.0$ MPa, 16 h. Conversion, yields, and selectivites were determined by GC-FID using n-hexadecane as an internal standard. Selectivity corresponds toward **2a** based on the yield **2a** and conversion of **1a**.

82.0 (CH), 82.0 (CH), 82.1 (CH), 153.7 (C=O), 153.8 (C=O), 153.8 (C=O), 154.8 (C=O), 174.2 (C=O), 174.3 (C=O) ppm; FTIR (ATR) ν_{max} = 2925 (m), 2855 (m), 1794 (vs), 1733 (s), 1460 (w), 1437 (w), 1366 (m), 1249 (w), 1171 (s), 1046 (s), 881 (vw), 773 (m), 725 (w), 689 (w) cm^{-1}.

RESULTS AND DISCUSSION

The conversion of epoxidized methyl oleate (cis-**1a**) and CO_2 was chosen as a suitable model reaction for the evaluation of catalytic systems for the formation of oleochemical cyclic carbonates (Figure 1). Depending on the catalyst and reaction conditions the desired cyclic carbonate **2a** might be formed as a mixture of two diastereoisomers cis-**2a** and trans-**2a**. In addition certain catalyst systems can mediate isomerization reactions of substrate cis-**1a**. This can lead to the respective trans-epoxide (trans-**1a**) but also to the ketones **3aa** and **3ab**, the latter are most reasonably formed by Meinwald rearrangement.[57,58] Prior to the (co)catalyst screening experiments, the respective unsaturated methyl oleate was oxidized on a multiple gram scale using hydrogen peroxide as oxidant following a protocol reported by Behr and co-workers.[56] Hence, **1a** was obtained in 95% yield as expected exclusively as the cis-isomer. Initially, various Lewis acid cocatalysts were screened, and the obtained results were compared to readily available $FeCl_3$. The

conversion of the test substrate cis-**1a** was performed in the presence of 2 mol % $[Bu_4P]Br$ and 2 mol % cocatalyst at 100 °C, 16 h, and 5.0 MPa CO_2 pressure. Notably, in comparison with all tested cocatalysts $FeCl_3$ showed the highest efficiency yielding the desired cyclic carbonate **2** in 84% yield and >99% chemoselectivity.

Hence, we turned our attention to the evaluation of readily available iron salts as cocatalyst and their impact on chemo- and stereoselectivity. In total, 11 iron salts alongside with $[Bu_4P]Br$ were tested in the carbonization reaction of cis-**1a** and CO_2 to produce the corresponding cyclic carbonate **2a** (Table 1). At first iron halides were tested as potential cocatalysts due to the good results obtained with $FeCl_3$ (Entries 1−5). FeF_3 gave **2a** in slightly lower chemo- and stereoselectivity compared to $FeCl_3$ (Entries 1 and 2). $FeCl_3 \cdot 6H_2O$ resulted in only moderate conversion of 47%, yielding 39% of **2a** (Entry 3). This indicates an interfering impact of water within the catalytic system. Additional water lowers the Lewis acidity of the Fe^{3+} center due to Lewis acid/Lewis base interaction compared to anhydrous $FeCl_3$.[59] Even though quantitative conversion was obtained for $FeBr_3$, only a moderate selectivity of 81% of **2a** was observed (Entry 4). Moreover, ketones **3** were formed in 6% yield. A significant difference in reaction outcome depending on the oxidation state of the iron species was not observed, and similar

Table 2. Parameter Optimization and Influence of Different Phosphonium Salts[a]

entry	catalyst	cocat.	[Fe] [mol %]	T [°C]	t [h]	$p(CO_2)$ [MPa]	conversion cis-**1a** [%]	yield **2a** [%]	selectivity **2a** [%]	cis:trans ratio **2a**	**3** [%]
1	[Bu$_4$P]Cl			100	16	5.0	38	38	99	90:10	
2	[Bu$_4$P]Br			100	16	5.0	49	46	94	71:29	
3	[Bu$_4$P]I			100	16	5.0	66	44	68	53:47	2
4	[Bu$_4$P]Cl	FeCl$_3$	2.0	100	16	5.0	72	58	80	88:12	1
5	[Bu$_4$P]Br	FeCl$_3$	2.0	100	16	5.0	84	84	>99	87:13	
6	[Bu$_4$P]I	FeCl$_3$	2.0	100	16	5.0	96	62	65	50:50	10
7	[Bu$_4$P]Br	FeCl$_3$	2.0	100	24	5.0	>99	85	85	58:42	3
8	[Bu$_4$P]Br	FeCl$_3$	0.25	100	24	5.0	84	84	99	67:33	1
9	[Bu$_4$P]Br[b]	FeCl$_3$	0.25	100	24	5.0	>99	94	94	61:39	1
10	[Bu$_4$P]Br[b]	FeCl$_3$	0.25	90	24	5.0	55	55	>99	78:22	
11	[Bu$_4$P]Br[b]	FeCl$_3$	0.25	100	24	2.5	91	80	89	71:29	0
12	[Bu$_4$P]Br[b]	FeCl$_3$	0.25	100	24	1.0	87	83	95	69:31	1
13	[Oct$_4$P]Br	FeCl$_3$	0.25	100	24	5.0	>99	96	96	68:32	
14		FeCl$_3$	0.25	100	24	5.0	4				

[a]Reaction conditions: 5.00 mmol of cis-**1a**, 2−3 mol % catalyst, 0.25−2.0 mol % cocatalyst, 90−100 °C, $p(CO_2$, 100 °C) = 1−5 MPa, 16−24 h. Conversion, yields, and selectivities were determined by GC-FID using n-hexadecane as an internal standard. [b]3.0 mol % catalyst. Selectivity corresponds toward **2a** based on the yield **2a** and conversion of **1a**.

results were obtained in the presence of FeBr$_2$. These experiments not only emphasized the high activity of bromide species within the catalyst system but also revealed the limitation regarding product selectivity. Interestingly, the amount of trans-**2a** prevail in the diastereomeric product mixture of **2a** for FeBr$_3$ and FeBr$_2$ cocatalyst reaching cis:trans ratios of 38:62. Fe(acac)$_3$ gave **2a** in moderate chemoselectivity (Entry 6). The corresponding triflate salt Fe(OTf)$_3$ proved to be an inappropriate cocatalyst since the selectivity of 3% toward the formation of cyclic carbonate **2a** was not exceeded, and the formation of ketones **3** was detected in a yield of 54% (Entries 7). In the presence of Fe(OAc)$_2$ and Fe(stearate)$_3$ selectivities of 86% and 80% toward **2a** were obtained, respectively (Entries 8 and 9). FeSO$_4$·7H$_2$O and Fe(citrate)$_3$·(aq.) showed chemoselectivities comparable to FeCl$_3$ of ≥98% (Entries 10 and 11). However, the reactions were significantly slower, and low conversions <40% were achieved under the given reaction conditions.

Among the tested cocatalyst, FeCl$_3$ showed the highest chemoselectivity (>99%) at high conversion of 84%. Hence, optimization of the reaction parameters was conducted with iron(III) chloride employing several organocatalysts in order to elucidate activity and selectivity relationships from the employed organocatalyst (Table 2). Initially; the nucleophile providing organocatalysts [Bu$_4$P]X with different counterions was tested in the absence of FeCl$_3$ to evaluate the impact of the halide (Entries 1−3). While [Bu$_4$P]Cl and [Bu$_4$P]I resulted in similar conversion rates of 38% and 35%, respectively, the corresponding bromide salt [Bu$_4$P]Br showed the highest conversion (49%) of cis-**1a**. However, the chemoselectivity toward the product formation of **2a** as well as the stereoselectivity regarding the cis:trans ratio of **2a** distinguish considerably from the employed halide. While for chloride and bromide [Bu$_4$P]-based organocatalysts excellent selectivities of 99% and 94% were obtained, respectively, only a moderate selectivity of 72% toward cyclic carbonate **2** was observed for [Bu$_4$P]I.

In combination with 2 mol % FeCl$_3$ the 2 mol % tetra-n-butylphosphonium or−ammonium salts[60] were employed as catalysts in the model reaction at 100 °C, 5.0 MPa, and 16 h. For the respective phosphonium salts [Bu$_4$P]Cl, [Bu$_4$P]Br, and

[Bu$_4$P]I an increasing conversion was detected for the following counterion order Cl < Br < I (Entries 4−6). Among these, for [Bu$_4$P]Br the highest product selectivity of >99% was observed (Entry 5). Remarkably, for [Bu$_4$P]I 2% of the byproducts **3** were detected, indicating a higher degree of substrate activation by iodide counterions which leads on the one hand to high conversion and on the other hand to low selectivity considering a higher amount of the Meinwald rearrangement product **3** from cis-**1a**. Likewise to phosphorus-based organocatalysts the corresponding ammonium salts [Bu$_4$N]X were employed.[60] Trends regarding conversion and product selectivity in dependence on the halide were similar compared to [Bu$_4$P]-based catalysts, except the best selectivity among these was obtained in the presence of chloride salt [Bu$_4$N]Cl as catalyst. Considering the high selectivity toward cyclic carbonate formation and a high conversion of 84% of cis-**1a** for the [Bu$_4$P]Br/FeCl$_3$ system further investigations regarding the (co)catalyst amount and parameter optimization were conducted with this binary catalyst system. In order to increase the conversion of substrate cis-**1a** the reaction time was prolonged to 24 h (Entry 7). Even though full conversion was achieved under these conditions, the product selectivity toward **2a** decreased to 85%. In addition, the influence of the catalyst/cocatalyst ratio ([Bu$_4$P]Br/FeCl$_3$) was investigated.[60] In general, a reduction of the cocatalyst amount resulted in a decrease of the conversion rate; however, the product selectivity increased while reducing the FeCl$_3$ concentration from 2 mol % to 0.25 mol % (Entry 8). Moreover, the amount of cis-**2a** within the diastereomeric product mixture increased from 58:42 to 67:33 with descending FeCl$_3$ concentration. Increasing the catalyst amount to 3 mol % [Bu$_4$P]Br resulted in full conversion, and only a slight decrease of product selectivity from 99% to 94% was determined compared to 2 mol % organocatalyst (Entry 9). In addition to experiments regarding the catalyst amount, the influence of temperature and CO$_2$ pressure in the model reaction was examined (Entries 10−12). The carbonization reaction was performed at 90 °C, 24 h, and a carbon dioxide pressure of 5.0 MPa employing 3.0 mol % [Bu$_4$P]Br and 0.25 mol % FeCl$_3$ (Entry 10). An excellent selectivity toward **2a** of >99% was obtained; however, only a moderate conversion of 55% was observed. A decrease in CO$_2$

pressure from 5.0 MPa to 2.5 and 1.0 MPa led to significant lower yields and selectivities (Entry 9 vs Entries 11 and 12). As a result reaction conditions of 100 °C, 24 h, and 5.0 MPa were found to be optimal to facilitate the formation of cyclic carbonate **2a** from epoxidized methyl oleate (*cis-***1a**) and CO_2. Finally, tetra-*n*-octylphosphonium bromide [Oct$_4$P]Br was employed as catalyst since previous investigations regarding the bulkiness of the cationic center have also shown a significant impact on the catalytic performance (Entry 13).[48] Hence, both catalysts [Bu$_4$P]Br and [Oct$_4$P]Br were tested in the presence of 0.25 mol % FeCl$_3$ at 100 °C, 24 h, and 5.0 MPa.[60] Accordingly, [Oct$_4$P]Br resulted in higher rates of conversion, yield, and selectivity compared to [Bu$_4$P]Br. The optimal catalyst amount was found to be 2.0 mol % of [Oct$_4$P]Br (Entry 13). In combination with 0.25 mol % cocatalyst a conversion of >99% was obtained, while an excellent selectivity of 96% regarding **2a** was observed. With respect to the organocatalyst [Oct$_4$P]Br a turnover number (TON) of 48 was determined. Finally, experiments in the absence of the organocatalyst revealed that FeCl$_3$ seems to be the cocatalyst in this reaction, since no product formation was observed in the absence of [Oct$_4$P]Br or [Bu$_4$P]Br (Entry 14).

In order to evaluate the substrate scope of this binary catalyst system several epoxidized fatty acid esters **1** were employed in the reaction with CO_2 to produce the corresponding cyclic carbonates **2** (Scheme 2). Under the optimized reaction conditions of 2.0 mol % [Oct$_4$P]Br, 0.25 mol % FeCl$_3$ at 100 °C, 24 h, and 5.0 MPa the carbonated methyl oleate **2a** was isolated in a yield of 90% in a *cis:trans* ratio of 63:37. The
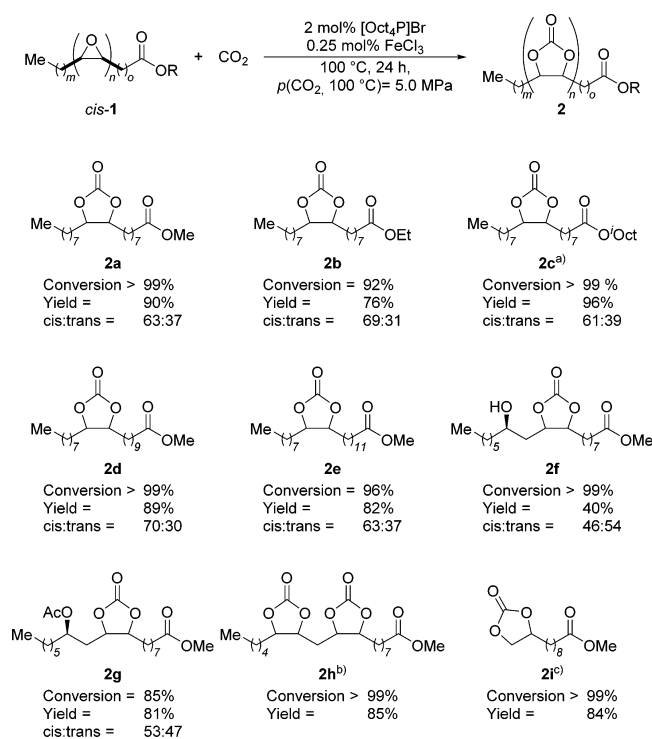
respective epoxidized ethyl oleate *cis-***1b** was isolated in a good yield of 76% under these conditions. Carbonated *iso*-octyl oleate **2c** was produced in 57% yield only; hence, to obtain full conversion for the substrate *cis-***1c**, the reaction conditions had to be adjusted. The cyclic carbonate **2c** was isolated in a yield of 96% in the presence of 3 mol % [Oct$_4$P]Br after 36 h at 100 °C. Interestingly, the alkyl chain length of the ester moiety had an impact on the conversion rate of the epoxide **1**. Both cyclic carbonates formed in the reaction of CO_2 with either epoxidized methyl eicosenoate (*cis-***1d**) or epoxidized methyl erucate (*cis-***1e**) and were isolated in very good yields of 89% and 82%, respectively. In contrast, epoxidized methyl ricinoleate (*cis-***1f**) was indeed fully converted. Nonetheless, only a yield of 40% was isolated. GC-MS studies revealed an isomerization side reaction of *cis-***1f** producing a tetrahydrofuran-derivative **4**.[60] This byproduct was most reasonably formed by an intramolecular cyclization reaction of the alcohol moiety and the epoxide group. However, if the alcohol moiety is protected by an acetyl group the reaction proceeds smoothly, and a conversion of 85% was observed for *cis-***1g** yielding 81% of the corresponding cyclic carbonate **2g**. To convert epoxidized methyl linoleate (**1h**) into the double carbonated product **2h** the reaction conditions were adjusted to 48 h. A yield of 85% on **2h** was isolated as a complex mixture of diastereoisomers. Due to the fact, that internal epoxides exhibit a steric hindrance for the nucleophilic attack of the halide of the catalytic system the conversion rates are usually lower than observed for less hindered terminal epoxides. As a consequence methyl 9-(2-oxo-1,3-dioxolan-4-yl)nonanoate (**2i**) was isolated in a yield of 84% after a short reaction time of 6 h.

Due to the fact that the binary catalytic system produces both diastereoisomers *cis-***2a** and *trans-***2a** in significant amounts, S$_N$1 and S$_N$2 reaction pathways were considered in the proposed reaction mechanism, which is in accordance with previous proposed mechanisms and reports (Scheme 3).[14,61,62] The first step involves the activation of the epoxide *cis-***2a** by the Lewis acidic cocatalyst facilitating the nucleophilic ring-opening of the epoxide by the bromide. The formed alcoholate is able to attack CO_2 as a nucleophile which in turn leads to a linear carbonate.

Scheme 2. Substrate Scope for the Binary Catalyst System [Oct$_4$P]Br and FeCl$_3$ for the Formation of Carbonated Fatty Acid Esters 2[a]

**2a**
Conversion > 99%
Yield = 90%
cis:trans = 63:37

2b
Conversion = 92%
Yield = 76%
cis:trans = 69:31

2c[a)]
Conversion > 99 %
Yield = 96%
cis:trans = 61:39

2d
Conversion > 99%
Yield = 89%
cis:trans = 70:30

2e
Conversion = 96%
Yield = 82%
cis:trans = 63:37

2f
Conversion > 99%
Yield = 40%
cis:trans = 46:54

2g
Conversion = 85%
Yield = 81%
cis:trans = 53:47

2h[b)]
Conversion > 99%
Yield = 85%

2i[c)]
Conversion > 99%
Yield = 84%

[a]Reaction conditions: 2 mol % [Oct4P]Br, 0.25 mol % FeCl$_3$, 100 °C, 24 h, p(CO$_2$, 100 °C) = 5.0 MPa. a) 3 mol % [Oct$_4$P]Br, 36 h. b) 48 h. c) 6 h.

Scheme 3. Proposed Reaction Mechanism for the Production of Oleochemical Cyclic Carbonates 2 from CO_2 and Renewable Epoxides 1
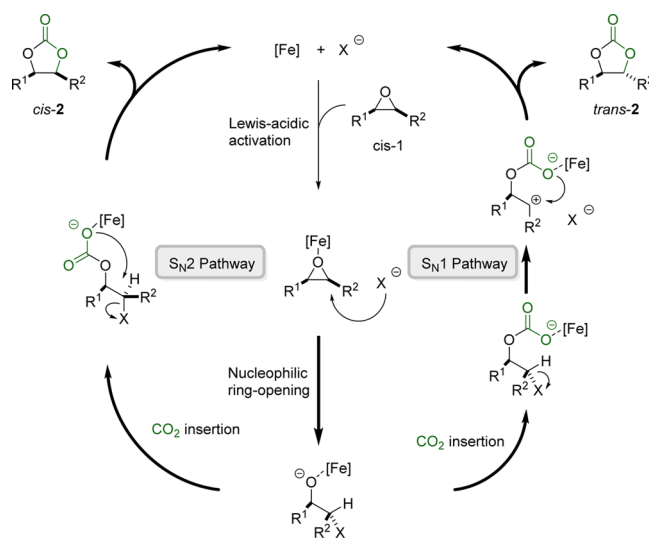
Considering the S_N2 pathway, the linear carbonate might produce *cis*-**2** by intramolecular nucleophilic substitution. The double inversion will lead to overall retention of the relative stereochemistry compared to the substrate *cis*-**1**. In contrast the S_N1 pathway gives rise to a carbenium ion by heterolytic C−Br bond cleavage. Intramolecular ring closure gives rise to *trans*-**2** under thermodynamic control. The halogen leaving group tendency and thus in turn the trend to form a carbenium ion is I > Cl > Br. This explains the observed dependency of the stereoselectivity on the nature of the phosphonium salt anion (X = Cl, Br, I) (Table 2, e.g. Entries 1−3). If [Bu₄P]Cl is employed the reaction proceeds predominantly via the S_N2 pathway in favor to *cis*-**2a** since chloride is a poor leaving group. In contrast the use of [Bu₄P]I leads to an iodide species which is prone to form a carbenium ion and thus leads to increased formation of *trans*-**2a** via the S_N2 pathway.

A comprehensive review article by Rokicki et al. emphasized the benefit of cyclic carbonates obtained from CO_2 and epoxidized vegetable oils as potential precursor for the synthesis of nonisocyanate polyurethanes (NIPU).[31,37,38,63] This procedure relinquishes the employment of toxic isocyanates to obtain highly valuable polyurethanes. Thus, the preparation of carbonates **6** from epoxidized oils **5** was studied using the developed [Oct₄P]Br/FeCl₃ catalyst system (Table 3). The epoxidized vegetable oils were employed in technical

Table 3. Insertion of CO_2 in Epoxidized Vegetable Oils[a]
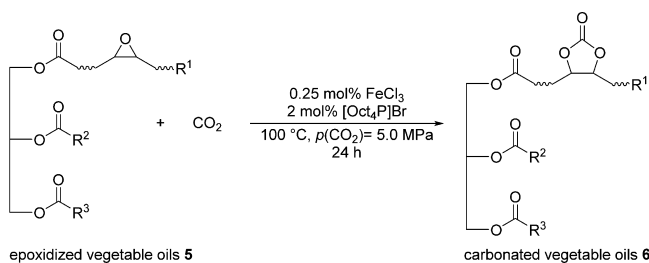
entry	substrate **5**	conversion **5** [%][b]	carbonate **6**	yield **6** [%]
1	epox. linseed oil (**5a**)	>99	**6a**	90
2	epox. high-oleic sunflower oil (**5b**)	>99	**6b**	88
3	epox. soybean oil EPOXOL D65 (**5c**)	>99	**6c**	94
4	epox. methyl soyate NEXO E1 (**5d**)	>99	**6d**	89

[a]Reaction conditions: 2 mol % [Oct₄P]Br, 0.25 mol % FeCl₃, 100 °C, $p(CO_2, 100 °C)$ = 5.0 MPa, 24 h. [b]Determined by ^1H NMR from a crude reaction mixture.

grade. To maintain the catalyst ratio in respect to the epoxy moiety the oxirane-number was determined by ^1H NMR prior to the conversion. For all tested epoxides **5** full conversions were observed under the given reaction conditions, and the desired products were obtained in excellent yields up to 94% after simple filtration over silica gel (Entries 1−4). Considering the fact that the biosynthesis of oils and fats is based on CO_2 as carbon source products **6** are 100% CO_2 based in respect to carbon.

CONCLUSION

The catalytic performance of simple [Bu₄P]Br in combination with Lewis acidic cocatalysts was evaluated for the conversion of epoxidized methyl oleate as model reaction. FeCl₃ proved to be a highly efficient cocatalyst yielding the desired product in >99% selectivity. A wide screening of readily available iron salts in combination with phosphonium salts was performed. This screening revealed a distinct dependency of the chemo- and diastereoselectivity on the nature of the anions of the (co)catalyst. Under the optimized, solvent-free reaction conditions the best binary catalyst system composed of [Oct₄P]Br and FeCl₃ was employed to convert 9 epoxidized fatty acid esters **1** with CO_2 to the corresponding cyclic carbonates **2**. Except for **2f** the desired products **2** were obtained in good to excellent yields up to 96%. Moreover, this catalyst system proved to be very active to produce cyclic carbonates **6** based on vegetable oils in yields up to 94%. A mechanistic proposal has been given which explains the connection between the nature of anion and the observed stereochemistry in the products. In total, 13 epoxides based on renewable feedstocks were converted to the corresponding carbonates, while inexpensive, abundant, and sustainable 0.25 mol % FeCl₃ as cocatalyst was totally sufficient to significantly improve the catalytic activity of the phosphonium salts. Considering the utilization of CO_2 in combination with renewables, the obtained oleochemical cyclic carbonates are up to 100% based on CO_2.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b01092.

Experimental details, ^1H NMR, ^{13}C NMR, and FTIR spectra of the prepared cyclic carbonates (PDF)

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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Prof. Dr. Angelika Brückner on the occasion of her 60th birthday.

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