Green Chemistry

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Fatty acid based biocarbonates: Al-mediated stereoselective preparation of mono-, di- and tricarbonates under mild and solvent-less conditions

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A catalytic method for the preparation of a series of fatty acid derived biocarbonates has been developed using a binary Al-complex/PPNCl catalyst. This catalyst system allows to convert the fatty acid derived epoxides under comparatively mild reaction conditions (70–85ºC, 10 bar) while maintaining high levels of diastereospecificity with *cis*/*trans* ratios in the products of up to 97:3. Comparative catalysis data obtained for the reactions catalysed only by the nucleophilic halide based components shows that the presence of the Al-complex is crucial for retention of the original stereochemistry.

Introduction

The synthesis and use of cyclic organic carbonates (COCs) has witnessed a spectacular growth over the last years.[1] Nowadays, the single most used approach in COC synthesis is the coupling of epoxides and CO_2, representing a simple and efficient process when mediated by a suitable catalyst.[2] While their main application potential has primarily been recognized as green, non-protic solvents, electrolytes for Li-ion batteries and in some cases as monomers towards the formation of polycarbonates,[3] more recently various groups have used COCs as a prelude to more complex organic molecules including fine chemicals,[4] pharma-orientated structures[5] and (biobased) polymers.[6] In the latter context, the formation of organic molecules possessing more than one COC unit within the structural framework offers potential to use these molecules as a starting point for the preparation of isocyanate-free polyhydroxyurethanes.[7] Thus, such a new strategy improving the sustainability footprint of conventional polyurethane synthesis implemented in industrial processes[8] represents an attractive means to valorise COC structures into value-added materials.

In this respect, renewable olefin compounds based on fatty acids (also sometimes designated as oleochemicals) provide a widely available feed stock from the biodiesel industry. Medium to long-chain fatty acids such as oleic and linoleic acid comprise of *cis*-configured double bonds that can be converted in two steps into cyclic carbonates.[9] Recent work in this area has shown that such biocarbonates can be made easily through the use of suitable catalysts. For instance, Leitner and coworkers reported an effective binary system based on a polyoxometalate (POM) and an onium salt at 100ºC and around 13 MPa (130 bar) of CO_2 pressure for the conversion of various epoxidized fatty acids.[10] The use of the POM component was highly beneficial in terms of the overall kinetics; however, for a number of substrates containing multiple vicinal epoxide groups, the chemo-selectivity dropped significantly due to the occurrence of side-reactions such as epoxide hydrolysis. Site-isolation of multiple epoxide groups in other substrates restored the observed high chemo-selective conversion of the epoxide into cyclic carbonate groups noted for mono-epoxy fatty acids, and apparently the selective conversion of vicinal oxirane units is more challenging.

Beside the chemo-selectivity, controlling the stereoselective nature of these conversions (Fig. 1a) can also be quite challenging as reported recently in various contributions.[9-11] Werner *et al*. reported on binary catalysts comprising of MoO_3[11a] or $FeCl_3$[11b] in combination with phosphonium salts, or bifunctional phosphorus-based organocatalysts[11e] operated under similar reaction conditions (80–100ºC, p = 25–50 bar, 20–24 h) giving the fatty acid based products typically as a mixture of *cis*/*trans* diastereoisomers (*cf*., in the carbonate units). As far as we know, no catalyst has been reported thus far that is able to efficiently convert mono-, di- and even tri-epoxidized fatty acid structures with both high stereo- and chemo-selectivity. In order to control these features, a catalyst is required able to combine epoxide activation potential while minimizing parasitic pathways comprising the overall selectivity.Previous success while using binary catalysts based on the combination of trivalent or tetravalent metal-centred

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† Electronic Supplementary Information (ESI) available: experimental and catalytic procedures, substrate synthesis and full characterization data. See DOI: 10.1039/x0xx00000x

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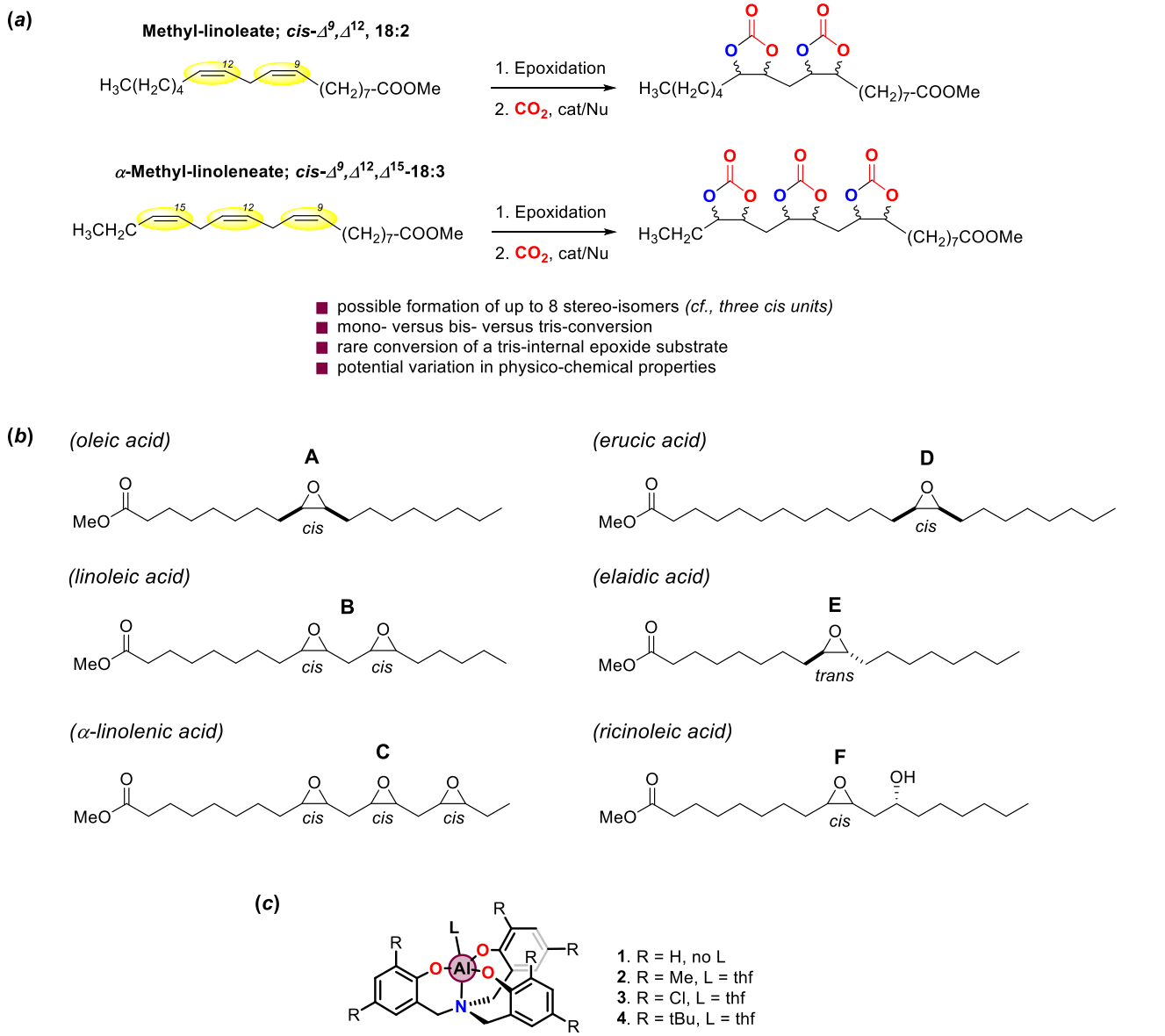

Fig. 1 (*a*) Schematic representation of the conversion of epoxidised fatty acids and the stereo-chemical implications. (b) Methyl esters of the epoxidized fatty acids **A–F** used as substrates in this work and the origin of these substrates. (*c*) Structures of the Al(III) aminotriphenolate complexes **1–4**.

aminotriphenolate complexes (M = Al, Fe, V) and ammonium halides in the coupling of terminal and internal di/tri-substituted epoxides and CO_2[2a,4a,12] motivated us to use these binary systems (Fig. 1c) as catalysts for epoxy fatty acid conversion into their corresponding bio-carbonates. Further to this, the stereoselective preparation of disubstituted COCs using Fe(III) complexes[12b] provided us with a useful starting point to control the selectivity features of these reactions. Here we report on the conversion of mono-, di- and triepoxy fatty acid compounds under excellent stereo- and chemo-selectivity control using relatively mild reaction conditions (70–85°C, $p(CO_2)^o$ = 10 bar). Further to this, we also present a new manifold for the conversion of hydroxy-

substituted fatty acid precursors that also allows for high levels of stereo- and chemo-selectivity.

Results and Discussion

For the catalytic studies we selected six substrates **A–F** (Fig. 1b) and Al(III) complexes **1–4** (Fig. 1c) to investigate the CO_2/epoxide coupling reactions at different temperatures, different loadings of catalysts and different nucleophilic additives. All ester-protected fatty acid precursors were first epoxidised under standard conditions (see ESI for details).[†] Substrate **A** was then first examined under various catalytic conditions (see Table 1).

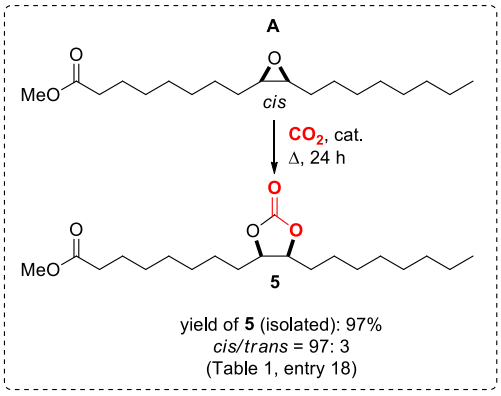

Table 1 Screening and optimisation of the coupling between epoxidised methyl oleate **A** and CO_2 under various reaction conditions using Al-complexes **1–3** and different nucleophiles (**Nu**).[a]

Entry	[Al] (mol%)	Nu (mol%)	Solv.	Conv.[b] (%)	Sel.[b] (%)	*cis/trans*[c]
1	**1**, 1.0	TBAB, 5.0	neat	>99	>99	72:28
2	**2**, 1.0	TBAB, 5.0	neat	>99	>99	72:28
3	**3**, 1.0	TBAB, 5.0	neat	94	>99	76:24
4	–	TBAB, 5.0	neat	>99	>99	51:49
5	**2**, 1.0	PPNCl, 5.0	neat	92	>99	98:2
6	**2**, 1.0	PPNCl, 3.0	neat	65	>99	98:2
7	–	PPNCl, 5.0	neat	53	>99	96:4
8	–	PPNCl, 3.0	neat	40	>99	98:2
9	–	PPNCl, 5.0	Tol	61	>99	96:4
10	–	PPNCl, 3.0	Tol	31	>99	99:1
11	**2**, 1.0	PPNCl, 5.0	Tol	90	>99	95:5
12	**2**, 1.0	PPNCl, 3.0	Tol	37	>99	97:3
13	**2**, 0.5	PPNCl, 3.0	neat	81	>99	95:5
14	**2**, 0.5	PPNCl, 2.0	neat	56	>99	>99:1
15	**2**, 0.5	PPNCl, 3.0	Tol	46	>99	98:2
16	**3**, 1.0	PPNCl, 5.0	neat	>99	>99	95:5
17	**3**, 0.5	PPNCl, 5.0	neat	>99	>99	96:4
18	**3**, 0.5	PPNCl, 3.0	neat	>99	>99	97:3
19	**3**, 1.0	TBAC, 5.0	neat	>99	>99	96:4
20	–	TBAC, 5.0	neat	6	>99	>99:1

[a]General conditions: 0.32 mmol **A**, 70ºC, 24 h, $p(CO_2)$º = 10 bar, medium indicated: neat or toluene (0.1 mL). [b]Conversion/selectivity was determined by ^{1}H NMR ($CDCl_3$). [c]*Cis/trans* ratios were determined by ^{1}H NMR, see for details the ESI.[†]

Complexes **1–3** (1.0 mol%) were combined with a bromide based nucleophile (tetrabutylammonium bromide: TBAB; 5.0 mol%)[13] at 70ºC and an initial CO_2 pressure of 10 bar (entries 1–3). Under these conditions (nearly) quantitative and chemo-selective conversion of substrate **A** into COC product **5** was achieved with a *cis*/*trans* ratio of up to 76:24.

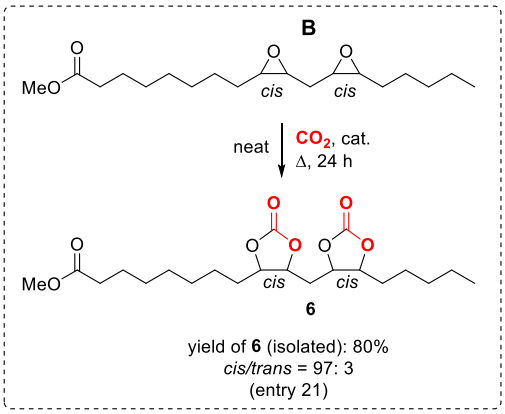

Table 2 Screening and optimisation of the coupling between epoxidised methyl linoleate **B** and CO_2 under various reaction conditions using Al-complexes **2** and **3** and different chloride based nucleophiles (**Nu**).[a]

Entry	[Al] (mol%)	Nu (mol%)	t (ºC)	Conv.[b] (%)	Sel.[b] (%)	*cis/trans*[c]
1	**2**, 0.5	TBAC, 5.0	70	59	>99	99:1
2	–	TBAC, 5.0	70	80	>99	98:2
3	**2**, 1.0	PPNCl, 5.0	70	>99	>99	98:2
4	**2**, 1.0	PPNCl, 5.0	85	>99	>99	80:20
5	**2**, 0.5	PPNCl, 5.0	70	>99	>99	86:14
6	**2**, 0.5	PPNCl, 5.0	85	>99	>99	93:7
7	**2**, 0.5	PPNCl, 3.0	70	90	>99	76:24
8	**2**, 0.5	PPNCl, 3.0	85	>99	>99	79:21
9	**2**, 0.3	PPNCl, 5.0	70	85	>99	95:5
10	–	PPNCl, 3.0	70	47	>99	>99:1
11	–	PPNCl, 3.0	85	92	>99	96:4
12	–	PPNCl, 5.0	70	66	>99	>99:1
13	–	PPNCl, 5.0	85	95	>99	95:5
14	**3**, 1.0	TBAC, 5.0	70	97	>99	85:15
15	**3**, 1.0	PPNCl, 5.0	70	95	>99	82:18
16	**3**, 1.0	PPNCl, 5.0	85	>99	>99	83:17
17	**3**, 0.5	PPNCl, 5.0	70	>99	>99	83:17
18	**3**, 0.5	PPNCl, 5.0	85	>99	>99	92:8
19	**3**, 0.5	PPNCl, 3.0	70	87	>99	73:27
20	**3**, 0.5	PPNCl, 3.0	85	>99	>99	87:13
21	**3**, 0.3	PPNCl, 5.0	70	>99	>99	97:3
22	**3**, 0.2	PPNCl, 5.0	70	97	>99	94:6
23	**3**, 0.1	PPNCl, 5.0	70	87	>99	95:5
24	**3**, 0.3	PPNCl, 3.0	70	94	>99	92:8

[a]General conditions: 0.32 mmol **B**, 70-85ºC, 24 h, $p(CO_2)$º = 10 bar, neat. Note that the amount of [Al] or PPNCl is per epoxide unit. [b]Conversion/selectivity of epoxy groups was determined by ^{1}H NMR ($CDCl_3$). [c]*Cis/trans* ratios were determined by ^{1}H NMR and refer to the total % of *cis* and/or *trans* units in the COC product **6**. See for details the ESI.[†]

The use of 5.0 mol% of TBAB alone (entry 4) also gave quantitative conversion but with a significantly reduced stereoselectivity (51:49). Further experiments conducted with Al-complex **2** and **3** in the presence of chloride based nucleophiles (PPNCl = bis(triphenylphosphine)iminium chloride, TBAC = tetrabutylammonium chloride; entries 5–20) allowed to optimize the synthesis of **5** combining high conversion, chemo-selectivity and stereocontrol. Interestingly, the use of chloride based nucleophiles proved to be beneficial to produce almost exclusively the *cis*-configured COC **5**. The use of a solvent was less productive (entries 9–12 and 15), and the best compromise between high conversion and selectivity with a minimal Al-complex and nucleophile loading proved to be the conditions reported in entry 18 (0.5 mol% **3**, 3.0 mol% PPNCl; conversion/selectivity >99%, *cis*/*trans* = 97:3).[14] Using these optimized conditions, we isolated COC **5** in 97%.[15]

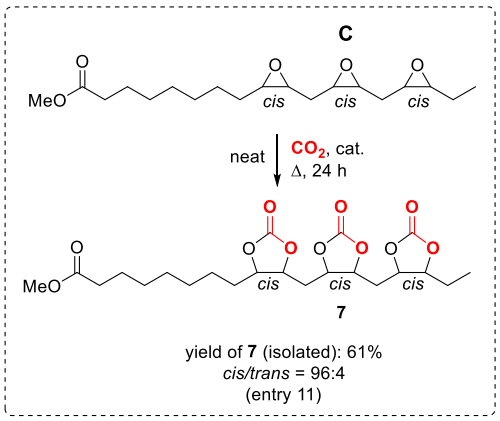

Table 3 Screening and optimisation of the coupling between epoxidised methyl linolenate **C** and CO_2 under various reaction conditions using Al-complexes **2–4** and PPNCl as nucleophile (**Nu**).[a]

Entry	[Al] (mol%)	Nu (mol%)	t (ºC)	Conv.[b] (%)	Sel.[b] (%)	*cis*/*trans*[c]
1	**3**, 0.5	PPNCl, 5.0	70	>99	>99	53:47
2[d]	**3**, 0.5	PPNCl, 5.0	70	96	>99	61:39
3	**3**, 0.3	PPNCl, 5.0	70	90	>99	66:34
4[d]	**3**, 0.3	PPNCl, 5.0	70	81	>99	71:29
5	**3**, 0.3	PPNCl, 3.0	70	81	>99	67:33
6[d]	**3**, 0.3	PPNCl, 5.0	70	81	>99	73:27
7	**3**, 0.2	PPNCl, 5.0	70	>99	>99	68:32
8[d]	**3**, 0.2	PPNCl, 5.0	70	92	>99	69:31
9	**2**, 0.5	PPNCl, 5.0	70	>99	>99	62:38
10	**4**, 0.5	PPNCl, 5.0	70	75	>99	87:13
11	**4**, 1.0	PPNCl, 5.0	70	92	>99	96:4
12	**4**, 1.5	PPNCl, 5.0	70	91	>99	96:4
13	–	PPNCl, 5.0	70	75	>99	90:10

[a]General conditions: 0.32 mmol **C**, 70ºC, 24 h, $p(CO_2)$º = 10 bar, neat unless stated otherwise. Note that the amount of [Al] or PPNCl is per epoxide unit. [b]Conversion/selectivity of epoxy groups was determined by ^{1}H NMR ($CDCl_3$). [c]*Cis*/*trans* ratios were determined by ^{1}H NMR and refer to the total % of *cis* and/or *trans* units in the COC product **7**. See for details the ESI.† [d]Toluene (0.1 mL) was added as solvent.

The reaction conditions and preferred Al-complex/nucleophile combination **3**/PPNCl were then used as starting point for the catalytic coupling of the bis-epoxy derivative of methyl linoleate **B** and CO_2 (Table 2).[16] COC product **6** could also be attained in good yield, high chemoselectivity (>99%) and with excellent stereoselectivity (*cis*/*trans* = 97:3; entry 21).

From the catalytic data presented in Table 2 it can be inferred that higher reaction temperatures typically lead to a decrease in stereocontrol as previously also observed by other authors.[10,11a-b,e] Fortunate, the use of binary catalysts comprising of **2** or **3** and chloride based nucleophiles allows for very high to quantitative conversions of substrate **B** with excellent chemo- and stereo-selectivity (*cf*., entries 9 and 21). Comparatively, the use of the chloride-substituted Al-complex **3** gave the best results and COC **6** was isolated in high yield (80%) using the optimized conditions of entry 21.

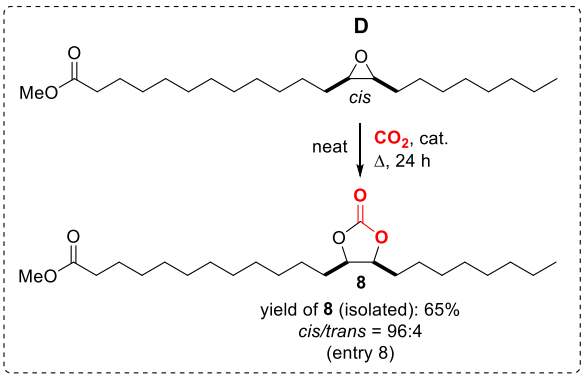

Table 4 Screening and optimisation of the coupling between epoxidised methyl erucate **D** and CO_2 under various reaction conditions using Al-complex **3** and PPNCl as nucleophile (**Nu**).[a]

Entry /Sub.	[Al] (mol%)	Nu (mol%)	t (ºC)	Conv.[b] (%)	Sel.[b] (%)	*cis*/*trans*[c]
1	**3**, 0.5	PPNCl, 5.0	70	5	>99	99:1
2[d]	**3**, 0.5	PPNCl, 5.0	85	>99	>99	96:4
3[d]	**3**, 0.5	PPNCl, 3.0	85	>99	>99	96:4
4[d]	–	PPNCl, 3.0	85	1[f]	>99	99:1
5[d]	–	PPNCl, 5.0	85	1[f]	>99	99:1
6[d,e]	–	PPNCl, 3.0	85	1[f]	>99	99:1
7[d,e]	–	PPNCl, 5.0	85	1[f]	>99	99:1
8[d,e]	**3**, 0.5	PPNCl, 3.0	85	>99	>99	96:4

[a]General conditions: 0.32 mmol **D**, 70ºC, 24 h, $p(CO_2)$º = 10 bar, neat unless stated otherwise. [b]Conversion/selectivity was determined by ^{1}H NMR ($CDCl_3$). [c]*Cis*/*trans* ratios were determined by ^{1}H NMR and refer to the total % of *cis* and/or *trans* units in the COC product **8**. See for details the ESI.† [d]Reaction time was 48 h. [e]Toluene (0.1 mL) was added as solvent. [f]The nucleophilic additive was not (fully) soluble.

Inspired by the successful preparation of COCs **5** and **6** from oleic and linoleic acid precursors, we then shifted our attention to the use of epoxidised methyl linolenate **C** (Fig. 1b)[17] to further challenge the binary catalyst system based on Al-complex **3** and PPNCl (Table 3). In general, the synthesis of tricarbonate product **7** proved to be more challenging, in particular the overall stereoselectivity control was markedly lower and the use of both Al-complexes **2** and **3** with PPNCl gave high to excellent

conversions but with *cis*/*trans* ratios not exceeding 71:29 (entry 4). Fortunate, the use of tBu-substituted Al-complex **4** (Fig. 1c) showed a significant improvement in the observed *cis*/*trans* ratio of 87:13 compared to the use of either **2** (entry 9) or **3** (entry 1).

Further increase in the loading of Al-complex **4** (entries 11 and 12; 1.0 mol%/epoxide unit) resulted in excellent stereocontrol (*dr* = 96:4; entry 11) and an improved conversion rate. As far as we know, the selective formation of tricarbonate **7** (61% yield)[15] is a rare example of the challenging conversion of a substrate with three vicinal epoxide groups under excellent stereocontrol. Next, we examined a longer alkyl tail fatty acid derivative (*i.e.*, the methyl ester of epoxidised erucic acid, **D** in Fig. 1; see also Table 4). The presence of a longer alkyl chain significantly decreased the solubility of the nucleophilic additive PPNCl, and even in the presence of toluene as solvent no full dissolution was observed after the reaction mixture had been vented and cooled down to ambient temperature. Therefore, in these cases the total conversion remained very low (entries 4–7). This was also the case when Al-complex **3** was combined with PPNCl at 70ºC, and only a low conversion (5%) of **D** was achieved (entry 1).

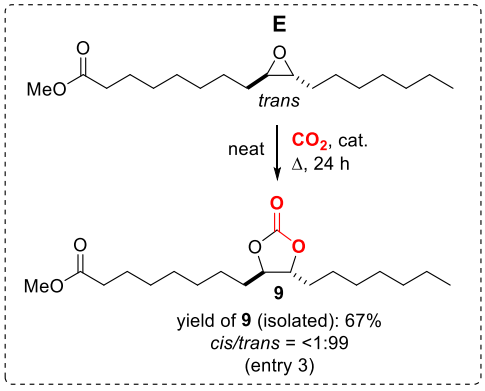

Table 5 Screening and optimisation of the coupling between epoxidised methyl elaidate **E** and CO_2 under various reaction conditions using Al-complexes **2** and **3** and PPNCl as nucleophile (**Nu**).[a]

Entry /Sub.	[**Al**] (mol%)	**Nu** (mol%)	t (ºC)	Conv.[b] (%)	Sel.[b] (%)	*cis*/*trans*[c]
1	**2**, 0.5	PPNCl, 5.0	70	28	>99	<1:99
2	**3**, 0.5	PPNCl, 5.0	70	65	>99	<1:99
3[d,e]	**3**, 0.5	PPNCl, 5.0	85	75	>99	<1:99
4	–	PPNCl, 5.0	70	0[f]	–	–
5[d,e]	–	PPNCl, 5.0	70	0[f]	–	–
6[d,e]	–	PPNCl, 5.0	85	0[f]	–	–

[a]General conditions: 0.32 mmol **E**, 70ºC, 24 h, $p(CO_2)$º = 10 bar, neat unless stated otherwise. [b]Conversion/selectivity was determined by ^{1}H NMR ($CDCl_3$). [c]*Cis*/*trans* ratios were determined by ^{1}H NMR and refer to the total % of *cis* and/or *trans* units in the COC product **9**. See for details the ESI.† [d]Reaction time was 48 h. [e]Toluene (0.1 mL) was added as solvent. [f]The nucleophilic additive was not (fully) soluble.

Fortunately, in the presence of Al-complex **3** homogeneous mixtures were attained at 85ºC (Table 4, entries 2 and 3; the crude products were clear liquids) giving high conversion of substrate **D** into the COC product **8** and importantly, also with high diastereoselectivity (*dr* = 96:4) towards the *cis*-configured product. The results with substrate **D** help to confirm that binary catalysts derived from Al(III)aminotriphenolate complexes and chloride-based nucleophiles are efficient catalysts for a wider range of stereoselective fatty acid conversions, and apparently, the mechanistic manifold involves two sequential S_N2 reactions (*cf.*, a double inversion pathway).[10,12b]

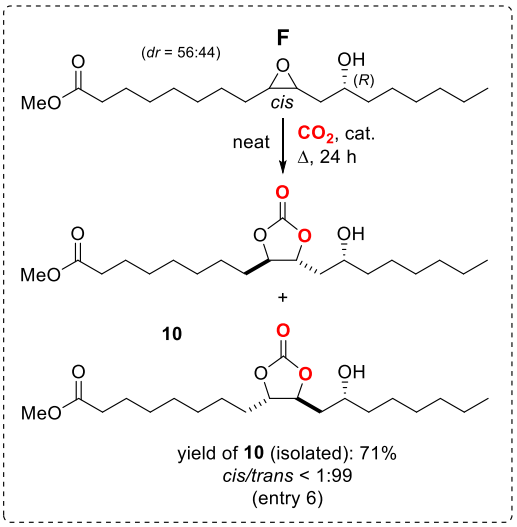

Table 6 Screening and optimisation of the coupling between epoxidised methyl ricinoleate **F** and CO_2 under various reaction conditions using Al-complexes **2** and **3** and PPNCl as nucleophile (**Nu**).[a]

Entry /Sub.	[**Al**] (mol%)	**Nu** (mol%)	t (ºC)	Conv.[b] (%)	Sel.[b] (%)	*cis*/*trans*[c]
1	**3**, 0.5	PPNCl, 3.0	70	>99	91	8:92
2	**3**, 0.5	PPNCl, 5.0	70	>99	92	10:90
3[d]	**3**, 0.5	PPNCl, 3.0	70	>99	87	4:96
4	–	PPNCl, 5.0	70	>99	94	26:74
5	–	PPNCl, 3.0	70	>99	95	22:78
6	**3**, 1.0	–	70	>99	99	<1:99

[a]General conditions: 0.32 mmol **F**, 70ºC, 24 h, $p(CO_2)$º = 10 bar, neat unless stated otherwise. [b]Conversion/selectivity was determined by ^{1}H NMR ($CDCl_3$). [c]*Cis*/*trans* ratios were determined by ^{1}H NMR and refer to the total % of *cis* and/or *trans* units in the COC product **10**. See for details the ESI.† [d]Toluene (0.1 mL) was added as solvent.

In order to examine further the existence of such a double inversion pathway, we used substrate **E** derived from the *trans* configured elaidic acid (Fig. 1). The utilization of the binary catalysts **2** or **3** combined with PPNCl (Table 5, entries 1–3)[18] showed full retention of stereochemistry and the product COC **9** was formed exclusively as the *trans* isomer. Although the expected, thermodynamically most stable isomer of **9** is formed, the retention of configuration in the carbonate unit is in line with a double inversion pathway efficiently mediated by the combination of the Al-complex **3** and a chloride nucleophile.[19]

As a more functional example, the conversion of epoxidised methyl ricinoleate **F** was also studied in the presence of the binary catalyst **3**/PPNCl (Table 6). The stereochemical course of this conversion proved to be interesting as the binary catalyst

system provided the COC product **10** with high inversion of configuration (*dr* = 90:10, *trans* isomer major product, entry 2). The use of the nucleophile also gave high conversion towards the COC target but with significantly lower diastereoselectivity (entries 4 and 5). Interestingly, in the absence of any nucleophile (entry 6; using only Al-complex **3**) the reaction proceeds also well with exclusive formation of the *trans* product **10**.

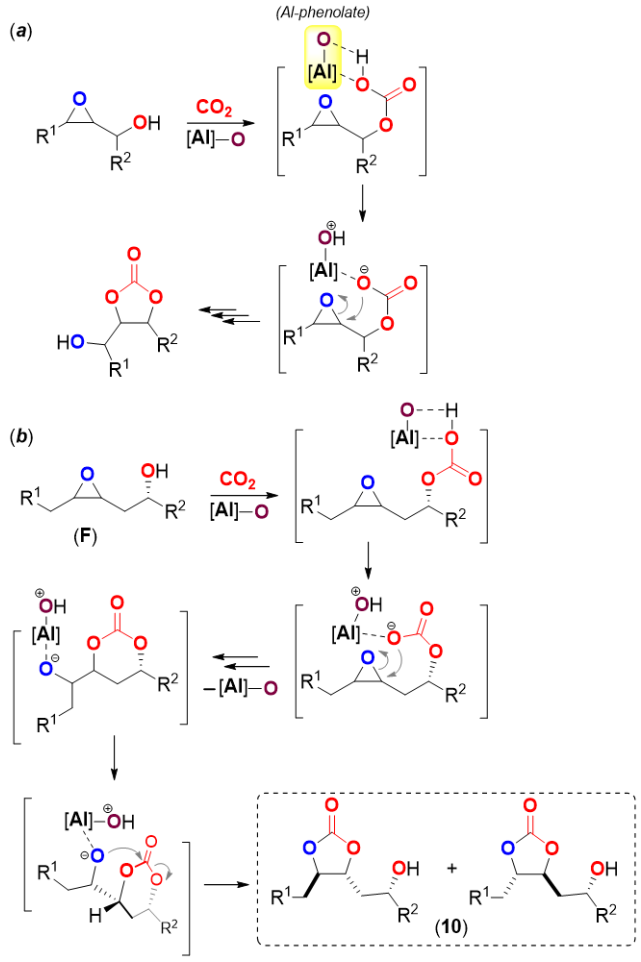

Fig. 2 (*a*) Previously reported mechanistic manifold in the conversion of epoxy-alcohol derivatives. (*b*) Proposed sequence of steps in the conversion of hydroxy-substituted substrate **F** into its five-membered COC product **10**.

In order to explain this inversion of configuration, a mechanistic rationale based on a double inversion pathway can be discarded. Also, the occurrence of an overall "S_N1" type manifold is unlikely as the reactivity is controlled by the Al-complex **3** only. Therefore, a different mechanistic explanation is required. We recently reported that hydroxy-oxetanes[20] and epoxy alcohols[4d] react with CO_2 in the absence of external nucleophiles but in the presence of Al(III) aminotriphenolate complexes to give either five- or six-membered COCs. In these cases, the Al(III) complex is able to stabilize a proposed hemi-ester of a linear carbonate derived from initial reaction of the alcohol unit in the substrate and CO_2. Intramolecular proton-transfer from the hemi-carbonic ester to one of the phenolate O–donors of the ligand allows for the *in situ* formation of a carbonate species that acts as an intramolecular nucleophile towards epoxide ring-opening (Fig. 2a). Such a manifold is also feasible with substrate **F** that contains a homo-allylic alcohol unit (Fig. 2b).

In this manifold, the alcohol unit reacts with CO_2 to form a carbonic acid like intermediate, and following a similar proton-shuttling to one of the phenolate donors of the Al-complex, a nucleophilic species is produced that attacks the oxirane unit with inversion of configuration. At this stage a six-membered COC is formed which is thermodynamically less stable than its five-membered analogue. Therefore, the alcoholate unit in the intermediate cyclic carbonate product stabilized by the Al complex, is involved in a nucleophilic attack onto the carbon centre of the six-membered COC giving finally the five-membered COC product **10**. The overall process, according to this manifold, produces the product carbonate **10** with inversion of the initial *cis* configuration and fits the experimental observations. This alternative mechanism gives additional potential to control the stereoselective conversion of more functional fatty acid precursors.

Conclusions

In summary, we here report the use of a binary catalyst comprising of an Al(III) aminotriphenolate complex that combined with PPNCl allows for the stereoselective conversion of methyl esters of various epoxy fatty acid derivatives under comparatively mild reaction conditions. Specifically, the selective conversion of mono- (oleate), di- (linoleate) and tris-epoxy (linolenate) substrates with sterically challenging combinations of vicinal epoxide groups has been achieved with the highest levels of stereocontrol (*dr*´s up to >99:1) reported to date. Furthermore, the conversion of hydroxy-functionalized substrates follows a different mechanistic manifold and opposed to the stereo-retention observed for substrates **A–E**, formal and quantitative inversion of configuration is noted when **F** is coupled to CO_2 in the presence of Al-complex **3** but essentially in the absence of an external nucleophile. The developed protocol therefore represents an unprecedented, potentially scalable[21] example of chemo- and stereo-selective conversion of renewable oleochemical compounds into their COC derivatives that have shown potential in the sustainable formation of isocyanate-free polyhydroxyurethanes.

Acknowledgements

We thank the ICREA, the CERCA Program/Generalitat de Catalunya, the Gobierno de Aragón (E11 Group co-financed by the European Regional Development Funds) and the Spanish Ministerio de Economía y Competitividad (MINECO: CTQ-2014-60419-R, CTQ-2014-52367-R and Severo Ochoa Excellence Accreditation 2014–2018, SEV-2013-0319) for financial support. LP and VD thank MINECO for their FPI predoctoral fellowships. We also thank Dr. Noemí Cabello for the MS studies.

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15 The isolated yields of all fatty acid carbonates were obtained by using the optimal reaction conditions and scaling up five times the reactions (1.6 mmol of epoxide) utilizing an autoclave with a Teflon insert having an internal volume of 40 mL.

16 Note that this bis-epoxide may exist as a mixture of 4 stereoisomers (two pairs of enantiomers) having both epoxides with a *cis* configuration though with a different relative orientation of these units.

17 The epoxidised methyl linolenate is a mixture of eight stereosiomers, *i.e*. four pairs of enantiomers.

18 Under the conditions used, as noted for substrate **D**, the PPNCl was not (fully) soluble giving no observable conversion. Note that the presence of the Al complex facilitated the dissolution of the PPNCl as after the reaction mixture had cooled down and was vented, a clear homogeneous mixture was obtained. Apparently, the solubility of the nucleophile is highly dependent on the nature of the fatty acid precursor.

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experiments carried out with 0.32 mmol of **A** and the same amount of Al-complex **3** and PPNCl. After 48 h, the conversion of **A** under neat conditions was 94% (isolated yield: 72%, *cis*/*trans* ratio 96:4) whereas the conversion was rather similar when using a solvent (toluene; 89%). Apparently the CO_2 dissolution kinetics were affected upon increasing the solvent volume to contact surface ratio. Nonetheless, the scaling experiment reported here shows the potential of these fatty acid conversions to be carried out with larger quantities of material while maintaining similar levels of stereoselectivity.