Recent Progress in Stereoselective Synthesis of Cyclic Organic Carbonates and Beyond

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Abstract: The recent developments in the stereoselective formation of cyclic organic carbonates are discussed, together with their use as intermediates in stereoselective synthesis of other valuable scaffolds.

Keywords: carbon dioxide; cyclic carbonates; homogeneous catalysis; post-synthetic conversions; stereoselectivity

1. Introduction

Atmospheric carbon dioxide is an abundant and alternative source of carbon representing about 750 billion tons of carbon in the atmosphere. Technologies towards both sequestration and utilization of this non-toxic, renewable and cheap C_1 waste product are highly desirable in order to reduce the dependence of our society on the limited amount of fossil fuels we have available. Therefore, valorization of CO_2 is currently receiving considerable attention from the scientific communities to convert it into organic molecules with commercial value [1-6].

Despite the disadvantage of a high kinetic stability of carbon dioxide, with the rapid development of organometallic chemistry and catalysis, efficient approaches to realize CO_2 utilization have been discovered in the past decades. Of particular interest is the development of chemical methodologies towards the incorporation of this carbon-based feedstock into useful synthetic organic molecules under sustainable mild conditions. The synthesis of cyclic organic carbonates (COCs; see Figure 1) and related linear and polycarbonates have been widely studied in this context of CO_2 valorization. Cyclic carbonates have been identified as key compounds in several applications ranging from their use as (non-protic) solvents to synthetic intermediates in organic synthesis [7-12].

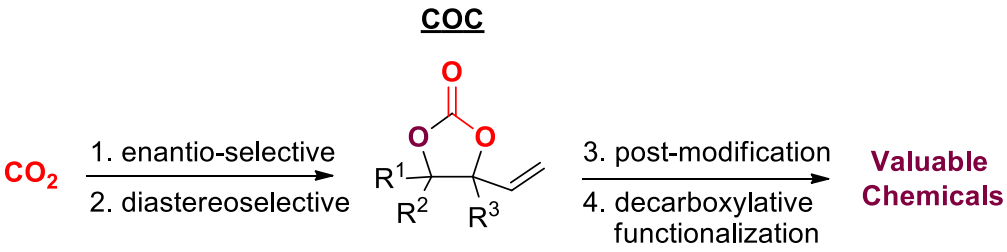

Figure 1. Recent progress in COC synthesis and their post-synthetic use.

Although the major portion of the reported catalytic approaches involving CO_2 as key reagent in the last years have focused on simple transformations for the synthesis of these heterocyclic derivatives, less focus has been directed towards stereocontrolled transformations (including diastereo- and enantioselective synthesis) for the preparation of value-added scaffolds [13,14]. In this review article, we highlight the latest achievements (2013–2016) in the area involving stereo-controlled COC synthesis, with a special focus on those contributions that have helped to understand the importance of COCs in synthetic chemistry by using these compounds as useful starting materials for more complex organic molecules (Figure 1).

2. Enantioselective Synthesis

Chiral cyclic carbonate scaffolds are important substructures of different biological compounds, and can also be regarded as useful synthetic intermediates in the pharmaceutical industry (*cf.*, masked 1,2-diols) and polymer industry [15]. The preparation of COCs *via* the coupling reaction of CO_2 and epoxides is one of the most promising routes for CO_2 conversion. However, despite the large diversity of catalyst systems developed for these transformations, the majority of reactions using CO_2 as feedstock concern the preparation of "simple" achiral chemicals, and only a handful of catalysts are able to mediate the synthesis of chiral COCs [14].

Since the seminal work reported by Yosihara [16] and Nguyen [17] in 1997 and 2001, respectively, several catalytic systems for the preparation of enantiomerically enriched COCs have been reported. The simplest way to prepare these enantiopure compounds is to use enantio-*specific* approaches by coupling enantiopure epoxides with CO_2, aiming for a high level of retention of the original chiral configuration. A recent example was provided by the Lu group who developed a bifunctional Al(III)salen complex with two pendant quaternary ammonium salts. This system showed high catalytic activity for the construction of COC with full retention of the initial configuration (>99% *ee*) in the coupling of different chiral epoxides and CO_2 through ring-opening at the non-substituted carbon center of the oxirane unit [18]. More recently, Capacchione and co-workers reported the use of a Fe(III) complex in combination with bromide as achiral binary catalyst that allows for enantio-specific conversion of CO_2 and chiral epoxides (*i.e.*, (*R*)-styrene oxide) giving moderates values of selectivity (*i.e.*, 72% *ee* for COC formation) [19].

One of the few reports not dealing with *metal*-catalyzed synthesis of enantiopure COCs was presented by Jamison in 2013 [20]. In this contribution the authors described a continuous flow process for the enantio-specific formation of COCs from oxiranes with excellent retention of configuration. The enantiopure epoxides [(*R*)-styrene oxide and (*S*)-phenyl glycidyl ether] were combined with CO_2 in the presence of *in situ* produced bromide radicals, and the corresponding COCs were obtained with full retention of the stereochemical information.

In other recent contributions, optically active cyclic carbonates were prepared by catalytic kinetic resolution of *racemic* epoxides in the presence of CO_2 [21], with preferred

activation of one of the two enantiomers of the (*rac*) epoxide. After initial attempts reported by Dibenedetto and Aresta [22] giving rather low *ee* (22%), important advances have been published over the last years. Most of these focused on the use of metallosalen complexes, and Co-based systems have shown exceptional potential for the kinetic resolution of (*rac*) epoxides to afford chiral COCs [13, 21].

Jiang an co-workers have developed bifunctional Co(salen) complexes equipped with imidazolium halide groups for catalytic asymmetric coupling of epoxides with CO_2 [23]. These newly developed catalysts operate under mild reaction conditions (25ºC, 1.2 MPa) providing the COCs in moderate *ee´*s of up to 57%, and showing high stability. Essential in this design is the length of the linker between the imidazolium unit and the metal center, with improved activities when using longer linkers but, unfortunately, at the expense of the chiral induction efficiency.

Although a number of different metal-based salen complexes have been developed, only a few catalytic systems gave comparable results to the Co-based ones. In 2015 North and co-workers reported the use of Al(III) and Cr(III) salen complexes for the kinetic resolution of terminal epoxides upon coupling with CO_2 [24]. The results of this work indicated that the combination of a Al(III) or Cr(III) salen catalyst and a *n*-Bu_4NBr co-catalyst (chloride based nucleophile in the case of the Cr(III) complex) is one of the most selective catalytic systems for the synthesis of chiral cyclic carbonates from (*rac*) epoxides with enantiomeric ratios of up to 93:7 (86% *ee*; diphenyl-substituted epoxyamine as substrate), although the kinetic resolution efficiency for less functional epoxides was poorer.

Chiral mixed metal-organic frameworks (MOF) based on enantiopure nickel(II) salen metalloligands combined with tetranuclear cadmium clusters have been reported as recyclable catalysts for the enantioselective synthesis of COCs with modest levels of chiral induction (45–52% *ee*) when using (*rac*) propylene oxide [25]. The results demonstrate that MOFs can act as self-supported, and comparatively very active heterogeneous catalysts for the synthesis of chiral COCs with potential for further optimization. In the context of heterogeneous systems for kinetic resolution of (*rac*) epoxides, Qi and co-workers reported an elegant asymmetric auto-tandem epoxidation/epoxide-CO_2 coupling sequence catalyzed by chiral polyoxometalate-based metal-organic frameworks (POMOFs). These systems incorporate a chiral organocatalyst, POM units that consist of Lewis acid sites and POM linking units (amino-bipyridines). The latter can interact with CO_2 molecules leading to a synergistic activation of a series of styrenes and α,β-unsaturated aldehydes towards the one-pot formation of chiral COCs in good yields and high *ee´*s of up to 80% [26].

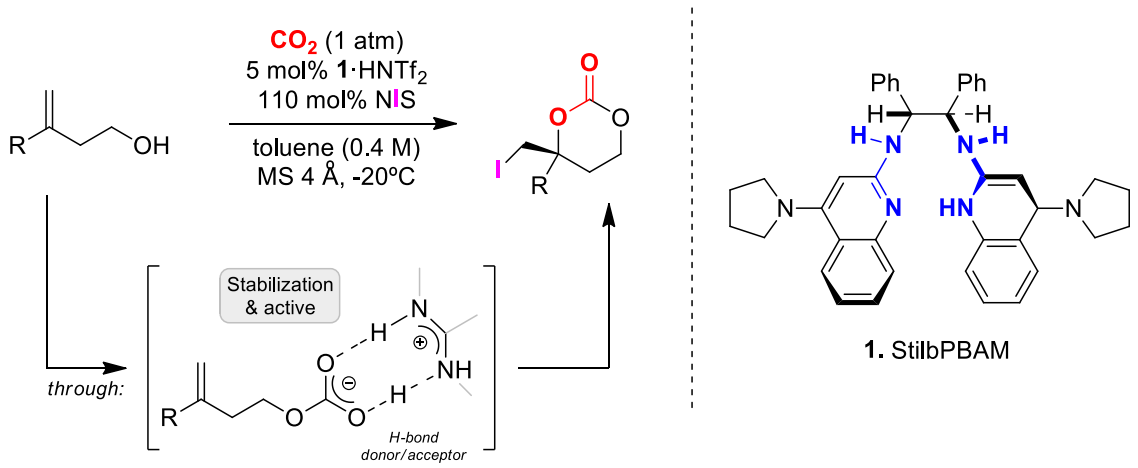

Figure 2. Enantioselective organocatalytic preparation of six-membered COCs reported by Johnston.

However, one of the most recent and important achievements in the enantioselective conversion of CO_2 was reported in 2015 by Johnston and co-workers (Figure 2) [27]. In this contribution the authors described the use of pyrrolidine-substituted bis(amidine)s as organocatalysts (Figure 2: **1**, StilbPBAM) in the presence of a Brønsted acid ($HNTf_2$) than can mediate the three component reaction between homoallylic alcohols, CO_2 and an electrophilic source of iodine. This conceptual approach provides an effective route towards the preparation of chiral six-membered COCs (16 examples, typical yields 70-95%, *ee´*s typically 74-95%). The catalyst developed uses the combination of a dual Brønsted acid/base activation to achieve high levels of enantioselectivity.

3. Diastereoselective Conversions

Diastereoselective control in COC synthesis has become a topic of increasing interest and the relative orientation of the substituents in these heterocycles may influence properties of the resultant materials upon ring-opening polymerization (ROP). Thus, it is important to control the relative configuration of pending substituents and the degree of this selectivity. In the most recent years various diastereoselective strategies for the synthesis of such COCs have been developed, ranging from the use of unsaturated allylic or homoallylic alcohols and propargylic (linear) carbonates to the use of internal epoxides as substrates [13].

Amongst the most recent accomplishments in this area, it has been shown that for the conversion of 2,3-disubstituted epoxides into their respective COCs (*cis* or *trans*) there exist two stereo-divergent pathways [7]. Initial co-polymerization of the epoxide and CO_2 followed by a depolymerization step, proceeds with the formal inversion of the initial configuration. Direct cyclic carbonate formation, however, preserves the original stereochemical configuration through two consecutive S_N2 processes. The group of Darensbourg has achieved extensive progress addressing the first conceptual approach [28-33]. They developed effective catalytic systems based on combinations of Co(III) and

Cr(III) salen complexes with different co-catalysts (quaternary ammonium and phosponium salts) which allow for the diastereoselective synthesis of COCs through a metal-bound or metal-free backbiting mechanism depending on the substrate and the reaction conditions. Both types of processes may occur through so-called "carbonate" or "alkoxide" backbiting and the experimental conditions can be fine-tuned towards one preferred pathway.

In the direct stereospecific synthesis of COCs from internal epoxides, various contributions have been communicated. In 2013 North and co-workers presented a bimetallic Al(salen) catalyst which is able to convert internal oxiranes into their corresponding carbonates with overall retention of the configuration and in moderate to high yields **[34]**. The same group has been also interested in exploring the use of other metals than aluminum. In a subsequent contribution they showed that Cr(III) salophen complexes are also effective for the stereospecific synthesis of internal cyclic carbonates under relative mild conditions **[35]**. This work build on previous success with other Lewis acid catalysts based on Fe(III) and Al(III) aminotriphenolate complexes **[13, 36]**.

Other significant advances were made by the Kleij group **[37]**. They illustrated that a single Fe(III) aminotriphenolate/TBAX (X = halide) binary catalyst system can achieve high levels of stereospecificity in COC synthesis using pure *cis*- or *trans*-isomers of 2,3-dimethylepoxybutane depending on the reaction conditions. Interestingly, both the *trans* and *cis* epoxide could be converted into the *cis*- and *trans*-COC, respectively, with high stereospecificity of up to >99%. Other relevant Fe(III) complexes were disclosed by Capacchione and co-workers: a series of dinuclear iron (III) complexes bearing thioether-triphenolate ligands were prepared by this group and their use as catalysts for the coupling of CO_2 and diastereopure internal epoxides was reported with comparable results for the known Fe(II) complexes **[38]**.

In 2014 Ema *et al.* contributed to this sub-area by devising highly active bifunctional metalloporphyrin catalysts (Figure 3) **[39]**. In their work they presented a Mg(II) and Zn(II) porphyrin-based bifunctional system which was able to convert a *trans*-1,2-disubstituted epoxide into its corresponding *trans*-COC with excellent retention of the configuration (99:1 *trans*/*cis*). Alternatively, the Leitner group studied in detail the combination of halide based nucleophiles and polyoxometalates (POMs) as binary catalyst systems for the insertion of CO_2 into *cis*-monoepoxides originating from plant oils as biogenic feedstock towards the stereoselective synthesis of biobased COCs **[40]**. This latter study revealed that the combination of the classical ammonium halide catalysts such as tetrabutylammonium bromide (TBAB) together with a tetraheptylammonium silicotungstates (THA-Cr-Si-POM) as the polyoxometalate component particularly give the best results in terms of selectivity (highest *dr* 96:4) and yield working under supercritical CO_2 conditions with equimolar amounts of both catalyst components (2.0 mol%) leading to high overall catalyst performance.

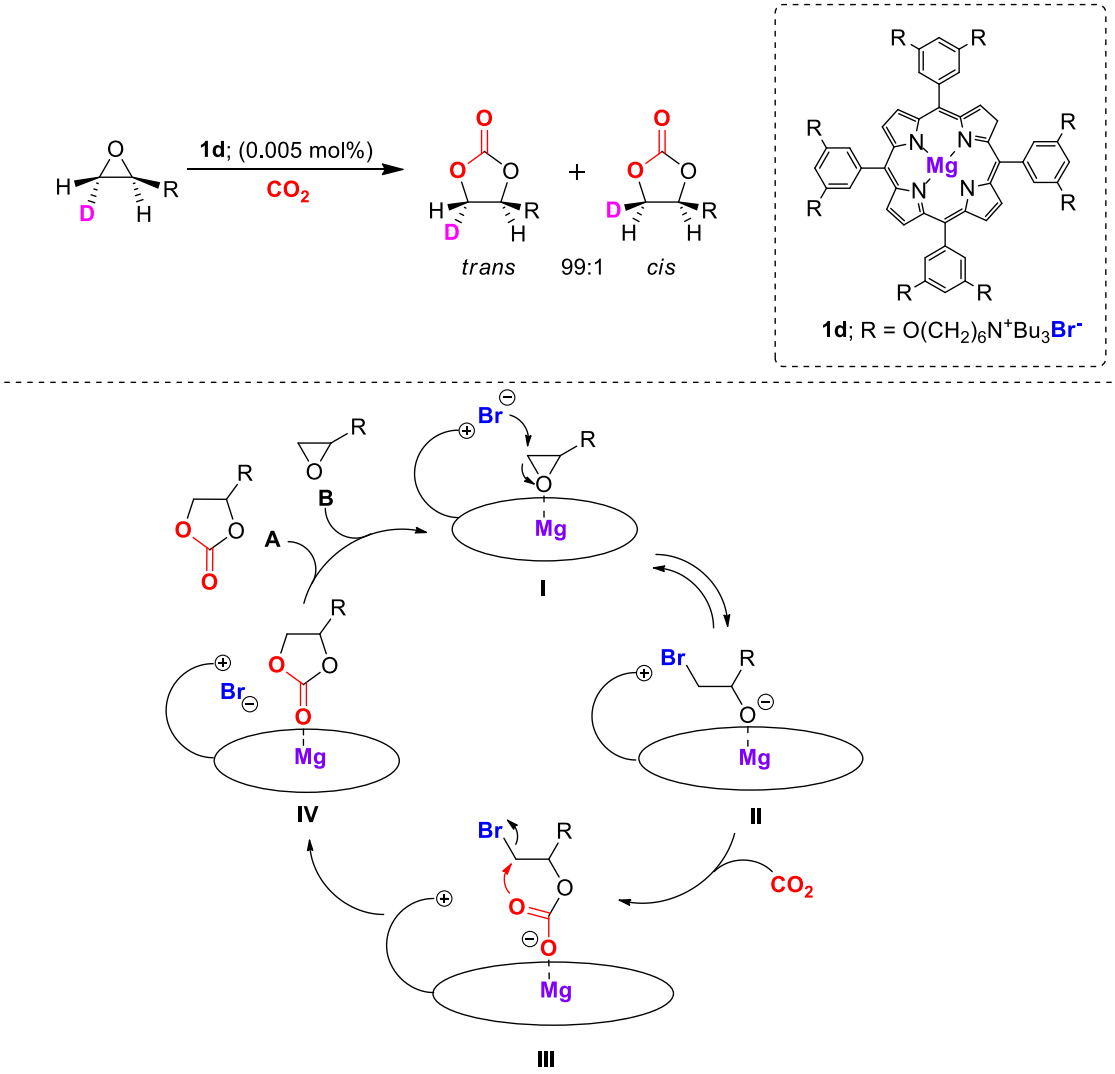

Figure 3. Bifunctional metalloporphyrin catalyst for the diastereoselective formation of COCs.

In a similar approach, Werner and co-workers reported on binary catalysts to address the stereoselective conversion of mono-, di- and tri-epoxides derived from fatty acid precursors [41]. Albeit not with very high diasteroselectivities, oleo-chemical based COC synthesis was realized through the use of MoO_3 as highly active co-catalyst in combination with tetra-*n*-butylphosphonium bromide ([Bu_4P]Br) as nucleophile. The chemo- as well as the stereoselectivity of the carbonated oleochemicals could be controlled to a certain extent (typical *dr´*s ~70:30) by a proper choice of the catalyst components and reaction conditions. The same authors presented in a recent similar contribution the use of other binary catalyst systems composed of [Oct_4P]Br and $FeCl_3$ for the COC formation from oleochemical epoxides [42]. Although this Fe-based binary catalyst did not increase the diastereoisomeric control in these reactions ratios, enhanced reaction rates could be attained. Judging from these recent results, there still remains a

need for the development of new active catalysts that can combine very high chemo- and stereoselectivity.

4. Stereoselective Synthesis using Cyclic Carbonates as Synthons

The stereoselective synthesis of cyclic carbonates has attracted significant attention in the last years as mentioned in the previous sections. However, little attention has been focusing on the use of functional COCs as potential precursors or intermediates in organic synthesis involving stereoselective transformations [43-45]. For example, COCs can be regarded as masked *syn*-diols with CO_2 acting as an easily removable protecting group: this has allowed the chemo-selective preparation of a wide range of di- and tricyclic organic carbonates in excellent diastereoselectivities providing, after base hydrolysis, synthetically useful *cis*-1,2-diol scaffolds [46]. A *cis*-configured bi/tricyclic epoxide is first converted into a *cis*-COC with retention of configuration under Al-catalysis followed by treatment of the cyclic carbonate with a suitable base (NaOH or K_2CO_3) affording the corresponding vicinal diols in high yields and stereoselectivities.

More recently, Kleij *et al*. reported another example of controlling stereoselectivity utilizing organic carbonates as intermediates in synthetic organic chemistry [47]. In this case, they reported a stereodivergent carbamate synthesis by *in situ* trapping of an organic carbonate. Delicate optimization of the ratio and amount of catalyst components allows for formation of either cyclic or polymeric carbonates which are conveniently intercepted by amine reagents resulting in a controlled and selective aminolysis process forming carbamate products with either *cis* (through a cyclic carbonate intermediate) or *trans* (through a oligomeric/polymeric carbonate intermediate) stereo-chemistry. Thus, this unprecedented approach allows for stereodivergence from a single oxirane substrate with easy access to both *cis* and *trans* carbamate isomers in high stereoselectivity (*dr´*s >19:1). This mode of stereocontrol represents a new tool in the synthesis of CO_2-derived fine chemicals.

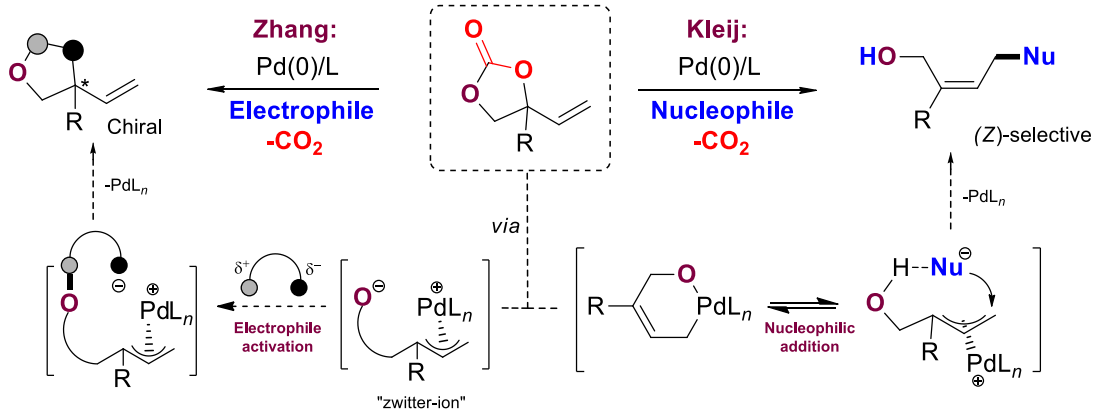

Figure 4. Two different approaches using vinyl carbonate as substrates in stereo-selective synthesis of various organic compounds.

Recently Zhang and co-workers reported a series of Pd-catalyzed decarboxylative strategies using vinyl substituted COC as key reagents (Figure 4) [48]. Upon decarboxylation, a postulated zwitterionic "allyl–Pd" complex is formed *in situ* that was combined with different electrophiles to accomplish the synthesis of various chiral compounds. In general this strategy utilizes the vinyl functionality to induce highly reactive pi-allylpalladium intermediates which display ambivalent reactivity. For instance, in the presence of Michael acceptors (substituted methylenemalononitriles) as coupling partners [49], simple access to chiral and highly substituted furans containing two quaternary stereo-centres was achieved with high levels of diastereo- and enantioselectivity (yields >90% and *ee´*s 85–95% typically). These products can be transformed straightforwardly into the corresponding chiral amino acids, which are useful intermediates for the synthesis of natural products.

The same authors also used other electrophilic coupling partners such as formaldehyde furnishing (*R*)-1,3-dioxolanes with high enantioselectivities (>90% *ee*) and yields (≥ 84%) [50]. These products can be hydrolysed easily into the corresponding chiral vicinal diols without loss of stereochemical information, and thus provide a practical entry for the preparation of pharmaceuticals. Two other contributions reported by the same group demonstrates the generality of the approach, and following similar experimental conditions employing isocyanates [51] and imines [52], the preparation of chiral 4-vinyloxazolidin-2-ones and 4-vinyloxazolidines, respectively, was attained in high yields and high enantio- and diastereoselective control.

Although electrophiles were shown to be useful in these coupling reactions with vinyl substituted COCs, the ambivalent character of the postulated Pd-allyl species formed *in situ* can also serve to activate nucleophiles. This conceptually different strategy was recently probed by Kleij and co-workers (Figure 4), who reported a general stereoselective methodology for the formation of highly substituted (*Z*)-configured olefinic compounds based on a Pd-catalyzed decarboxylative functionalization using suitable nucleophiles. This protocol features vinyl carbonates and nucleophiles as starting materials, where the formation of a (*Z*)-configured six-membered palladacyclic intermediate was computationally determined to be key to the high level of stereocontrol. Nucleophilic attack on the *in situ* formed (*Z*)-palladacycle by aromatic/aliphatic amines gave access to an extensive series of challenging (*Z*) allylic amines with *Z*/*E* ratios >99:1 in most cases [53], whereas the use of H_2O as nucleophile allowed the preparation of elusive (*Z*)-1,4-but-2-ene-diols in good yields and high stereo-control as observed for the allylic amines [54].

The examples of stereoselective synthesis based on the post-modification or use of functional COCs showcase the increasing importance and versatility of these (mostly) CO_2 derived building blocks in synthetic chemistry. Since many different functional groups can be envisaged, this area of research should have a bright future and more interesting developments are expected.

5. Summary and Conclusions

This concise review presents the latest progress in the CO_2-mediated stereoselective formation of COC and developments aiming for their post-synthetic use in organic synthesis. From the examples discussed herein it is clear that synthetic chemists are continuously improving on the use of CO_2 to create more complex structures through innovative catalysis procedures. Relevant progress has been reported in enantio- and diasteroselective approaches towards COCs and derived products. A rather new and exciting development is to use the potential of functionalized COCs as valuable precursors in stereoselective transformations to produce useful intermediates for fine chemical and pharmaceutical synthesis. However despite the impressive progress in the the stereoselective conversion of CO_2, there remain some challenges open. Among these is the use of CO_2 to target molecules and materials with a higher degree of relevance for industrial applications and significant evolution of asymmetric methodology is still necessary in COC synthesis and beyond. Important in this respect is a further optimization of the catalysis of cyclic ether/CO_2 coupling reactions to supply the synthetic communities with COC scaffolds that incorporate additional and new functionality that will amplify the accessibility of new synthons with added value in academic and commercial laboratories.

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