# Organocatalytic Synthesis of Substituted Vinylene Carbonates

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**Abstract.** The organocatalytic synthesis of vinylene carbonates from benzoins and acyloins was studied using diphenyl carbonate as a carbonyl source. A range of *N*-Heterocyclic Carbene (NHC) precursors were screened and it was found that imidazolium salts were the most active for this transformation. The reaction occurs at 90°C under solvent-free conditions. A wide range of vinylene carbonates (symmetrical and unsymmetrical, aromatic or aliphatic), including some derived from natural products, were prepared with 20-99% isolated yields (24 examples). The reaction was also developed using thermomorphic polyethylene-supported organocatalysts as recoverable and recyclable species. The use of such species facilitates the workup and allows the synthesis of vinylene carbonates on the preparative scale (> 30 g after 5 runs).

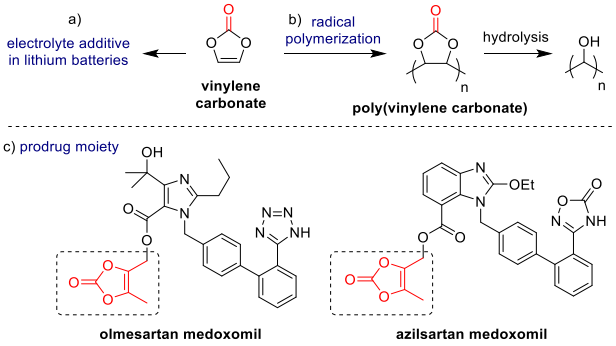
**Keywords:** Vinylene carbonates; Benzoin; Diphenyl carbonate; Organocatalysis; Thermomorphic polyethylene

## Introduction

Organic carbonates are currently the subject of intense research efforts, notably due to their general innocuity and biodegradability. Consequently, they have found numerous applications in electrolytes for lithium batteries,[1] renewable solvents[2] and monomers for the preparation of polycarbonates[3] and non-isocyanate polyurethanes (NIPUs).[4] In this vast field, organic cyclic carbonates largely dominate as they can be prepared from epoxides and $CO_2$, using a plethora of catalysts.[5]

In contrast, the chemistry of vinylene carbonates is considerably underdeveloped. Among these species, vinylene carbonate (1,3-dioxol-2-one) is the most representative. Similar to ethylene carbonate, vinylene carbonate can be used as an electrolyte additive in lithium batteries (Scheme 1, a).[6] Moreover, its unsaturated nature facilitates its use in other kind of applications. For example, it can be used for the preparation of poly(vinylenecarbonate)[7] through radical (co-)polymerization (Scheme 1, b). The resulting polymer can be further hydrolyzed to poly(hydroxymethylene), that has recently found applications in 3D printing.[8] Vinylene carbonates are also used in the medical field, notably in prodrugs such as olmesartan medoxomil[9] and azilsartan medoxomil,[10] where they serve as cleavable group to release the active species (Scheme 1, c).[11] In organic chemistry, vinylene carbonate is mainly used as a dienophile in Diels-Alder reactions[12] and other cycloadditions,[13] but also as a coupling partner in arylation reactions.[14]

Recently, vinylene carbonate has been mainly used as an acetylene[15] or ethynol[16] surrogate in annulation reactions.[17] Moreover, it was also demonstrated that it can act as an acetylation reagent in rhodium-catalyzed cyclisation.[18] Despite all of these various applications, the chemistry of vinylene carbonates remains undeveloped, mainly due to their limited availability linked to their problematic synthesis.

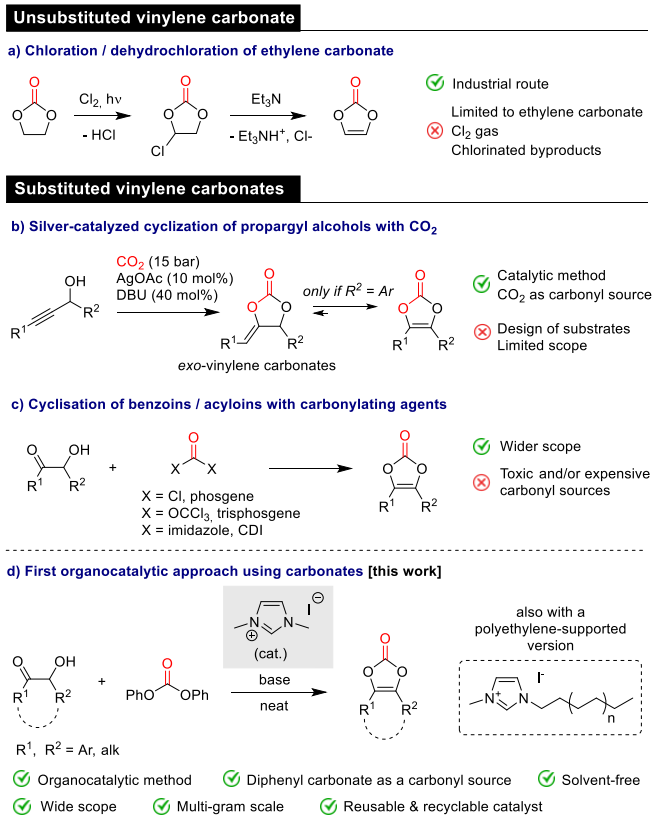



**Scheme 1.** Main applications of vinylene carbonates.

(Unsubstituted) vinylene carbonate is prepared from ethylene carbonate using a chlorination / dehydrochlorination sequence (Scheme 2, a).[19] This route has been developed industrially; however, it involves the use of chlorine gas and generates chlorinated byproducts, thus leading to tedious purification. Moreover, the formation of other vinylene carbonates through this route has not been demonstrated, showing that it is very specific.

On the contrary, several strategies has been reported for the formation of substituted vinylene carbonates. The silver-catalyzed reaction of propargylic alcohols with $CO_2$ affords *exo*-vinylene carbonates (also called α-vinylene carbonates),[20] that constitute another family of carbonates as they have different electronic

properties, reactivities and applications. In some occasions, *i.e.* when the substrate is carefully designed, *exo*-vinylene carbonates can be isomerized to *endo*-vinylene carbonates (Scheme 2, b). [21] However, this route is not general as only a limited range of products can be prepared through this method. The reaction of benzoins or acyloins with carbonylating agents affords vinylene carbonates in a straightforward way (Scheme 2, c). Moreover, this route is probably the most general as it allows the preparation of a wide range of products. The use of phosgene as a carbonylating agent usually leads to excellent yields but raises health and safety concerns. [13a,22] Trisphosgene can be used as an alternative.[23] However, the release of phosgene cannot be avoided.[24]




**Scheme 2.** Main strategies for the preparation of vinylene carbonates.

Alternatively, the preparation of vinylene carbonates can be achieved using carbonyl di-imidazole (CDI).[25] CDI is a mild carbonylating agent and hence it has to be used in excess, which is a drawback considering that it is expensive.[26] Moreover, its production involves phosgene, so the problem is displaced considering the overall process. In this context, it would be highly desirable to prepare vinylene carbonates using organic carbonates (*e.g.*, dimethyl or diphenyl carbonate) as carbonyl sources.[27] Indeed, such species are generally less toxic and safer to use. Moreover, they are produced from ethylene carbonate, so they also derive from $CO_2$. On the downside, they are less reactive, so the use of catalysis is mandatory to activate such species.

To the best of our knowledge, no catalytic method has been reported for the direct preparation of vinylene carbonates from benzoins or acyloins. In this context, we report here the first organocatalytic method for the preparation of vinylene carbonates using diphenyl carbonate as a carbonyl source (Scheme 2, d).[28] Moreover, the method was further developed with thermomorphic polyethylene-supported organocatalysts, additionally providing efficient, recoverable and recyclable catalysts that facilitates both the workup and the upscaling of the process.

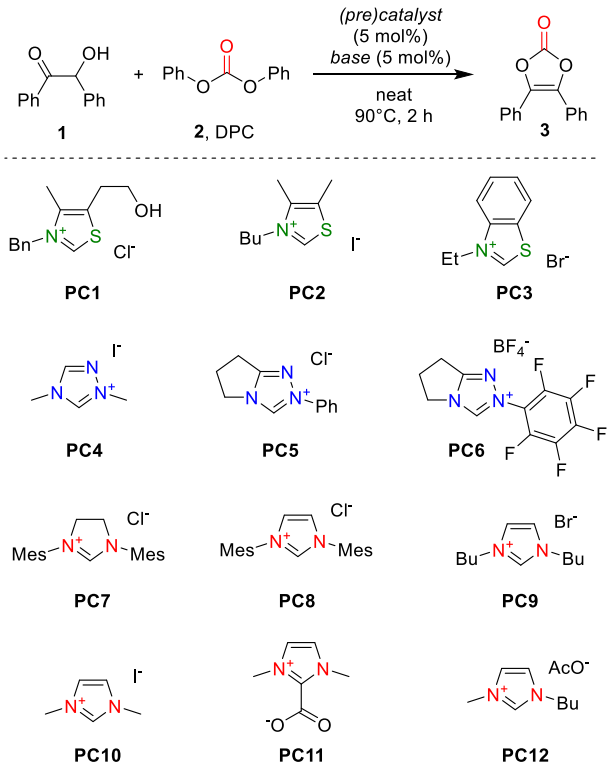
## Results and Discussion

The reaction was developed using diphenyl carbonate (DPC) as a carbonyl source considering that it is a reactive carbonate, which is obtained on an industrial scale for the production of polycarbonates.[29] Diphenyl carbonate can be prepared from phosgene but this process is progressively replaced by other routes, notably the transcarbonation of dimethyl carbonate with phenol.[30] This process has been implemented industrially by the Asahi-Kasei company for the production of Bisphenol A-polycarbonate.[31]

*N*-Heterocyclic carbenes are excellent nucleophilic organocatalysts that are able to promote the formation of acyl azolium species.[32] Moreover, they have been found active enough to react with weak electrophiles such as organic carbonates.[33] From a mechanism point of view, the NHC-catalysed synthesis of vinylene carbonates from benzoins/acyloins with diphenyl carbonate would involve a first transcarbonation to form a mixed carbonate intermediate, that would undergo a second transcarbonation to give the desired compounds (see ESI for mechanism hypotheses). Considering that both steps could be catalysed by NHCs, such species were selected as nucleophilic organocatalysts to promote the formation of vinylene carbonate using diphenyl carbonate as a carbonyl source.

The reaction of benzoin **1** with diphenyl carbonate **2** was first investigated with a range of NHC precursors (5 mol%) in the presence of $K_2CO_3$ (5 mol%) at 90°C for 2 hours under solvent-free conditions (Table 1). Under these conditions, only traces of vinylene carbonate **3** were obtained using thiazolium salts **PC1-PC3** (entries 1-3). Triazolium salts **PC4** and **PC5** led to the formation of the product with very moderate yields, however higher than the one obtained when pentafluorophenyl anologue **PC6** was used (entries 4-6). Popular NHC ligands SIMes (**PC7**) and IMes (**PC8**) were tested here as organocatalysts but only traces of product were detected, probably due to steric reasons (entries 7-8). On the contrary, dibutylimidazolium bromide **PC9** led to the formation of **3** with 74% yield (entry 9).

**Table 1.** Screening of NHC precursors and bases.[a]



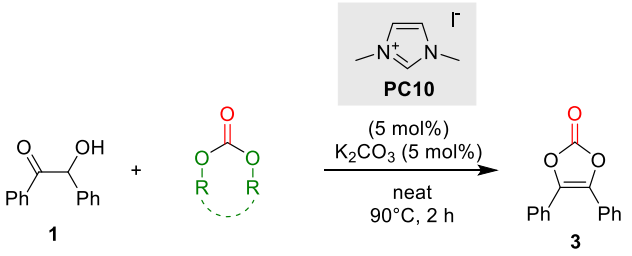

| Entry | precatalyst | base | Yield[b] **3** (%) |
|---|---|---|---|
| 1 | **PC1** | $K_2CO_3$ | < 5 |
| 2 | **PC2** | $K_2CO_3$ | < 5 |
| 3 | **PC3** | $K_2CO_3$ | < 5 |
| 4 | **PC4** | $K_2CO_3$ | 11 |
| 5 | **PC5** | $K_2CO_3$ | 27 |
| 6 | **PC6** | $K_2CO_3$ | 7 |
| 7 | **PC7** | $K_2CO_3$ | < 5 |
| 8 | **PC8** | $K_2CO_3$ | < 5 |
| 9 | **PC9** | $K_2CO_3$ | 74 |
| 10 | **PC10** | $K_2CO_3$ | 97 |
| 11 | **PC10** | $Na_2CO_3$ | 83 |
| 12 | **PC10** | $Cs_2CO_3$ | 98 |
| 13 | **PC10** | NaOH | 99 |
| 14 | **PC10** | $Et_3N$ | 60 |
| 15 | **PC10** | TBD | 85 |
| 16[c] | **PC11** | - | 72 |
| 17[c] | **PC12** | - | 63 |

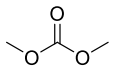
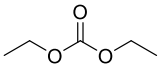
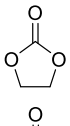
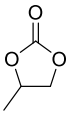
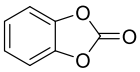
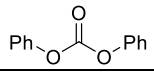
[a] Reaction conditions: benzoin **1** (1 mmol), diphenylcarbonate **2** (1.1 mmol), precatalyst (5 mol%), base (5 mol%), 90°C, 2 h. [b] Yields were determined by GC/FID with *n*-hexadecane as an internal standard. [c] Reactions were performed without external base. TBD = 1,5,7-triazabicyclo [4.4.0]dec-5-ene.

Satisfyingly, the use of less-hindered dimethylimidazolium iodide **PC10** led to an excellent 97% yield (entry 10). Other bases were also tested. The use of $Na_2CO_3$ led to a lower yield while $Cs_2CO_3$ gave a similar result than $K_2CO_3$ (entries 11-12). The results could be explained by a better solubility of these inorganic carbonates in the (neat) reaction mixture. Interestingly, NaOH also gave a full conversion of benzoin **1** to vinylene carbonate **3** (entry 13). However, the use of such base should be avoided due to its ability to hydrolyze vinylene carbonates upon heating and/or prolonged reaction time. Organic bases such as $Et_3N$ and triazabicyclodecene (TBD) also gave the desired product but with lower yields (entries 14-15). Finally, NHC-$CO_2$ adduct **PC11** and imidazolium acetate **PC12** were tested without external base thanks to their ability to generate *in-situ* the free carbene, which is supposed to be the active species in this process. Considering that they gave lower yields (entries 16-17) than the precatalyst/base couple, **PC10** was selected as organocatalyst for further optimization. Control experiments were performed using either **PC10** or $K_2CO_3$ but only traces of the desired carbonate **3** were obtained, thus indicating the combined crucial role of both species in the catalytic system.

Other organic carbonates were tested as a carbonyl source (Table 2).

**Table 2.** Screening of carbonates as carbonyl sources.[a]



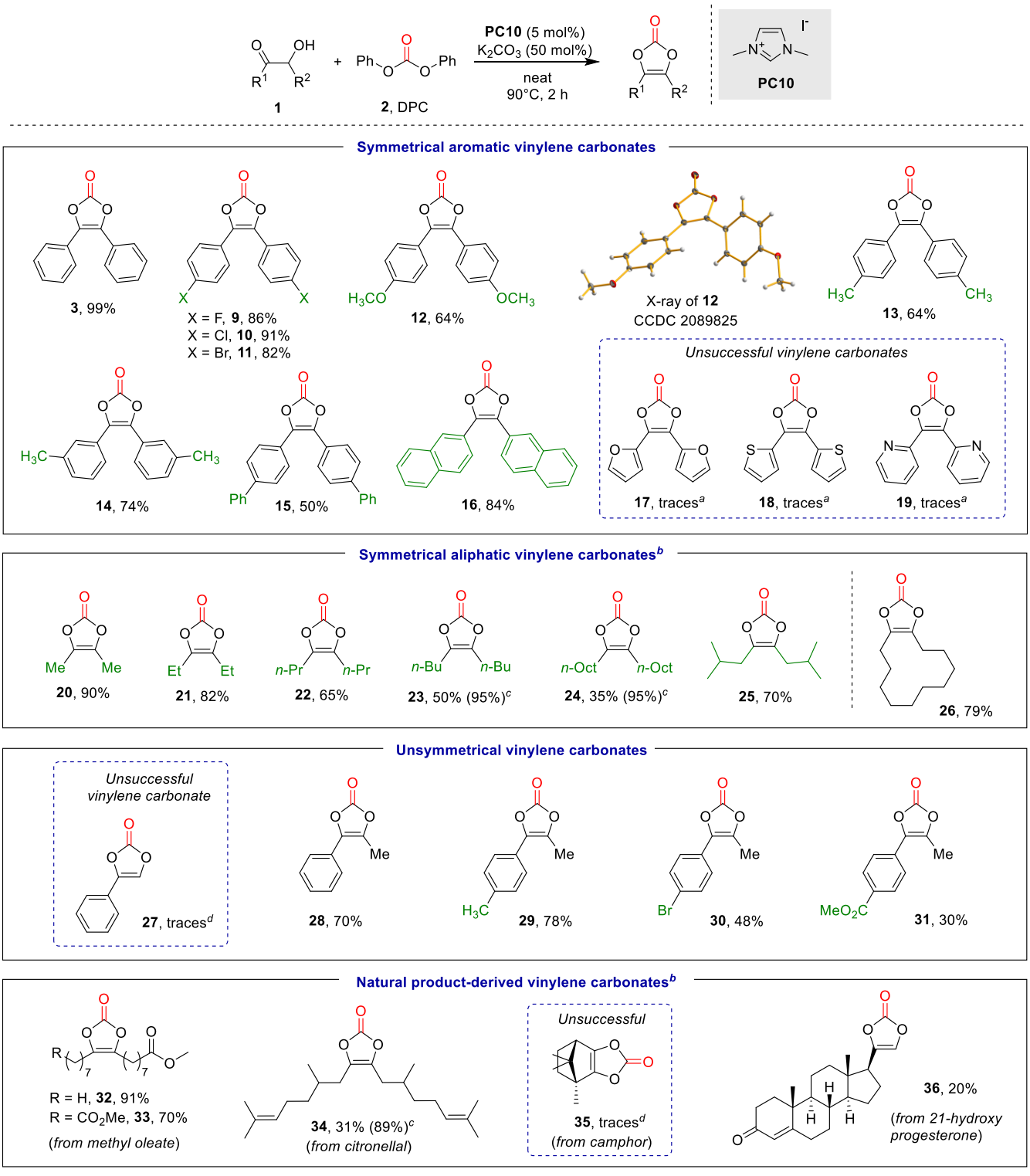

| Entry | Carbonyl source | | Yield[b] **3** (%) |
|---|---|---|---|
| 1[c] |  | **4** | 2 |
| 2[c] |  | **5** | < 1 |
| 3 |  | **6** | < 1 |
| 4 |  | **7** | < 1 |
| 5 |  | **8** | 71 |
| 6 |  | **2** | 96 |

[a] Reaction conditions: benzoin **1** (1 mmol), carbonate **2, 4-8** (1.1 mmol), 1,3-dimethylimidazolium iodide **PC10** (5 mol%), $K_2CO_3$ (5 mol%), 90°C, 2 h. [b] Yields were determined by GC/FID with *n*-hexadecane as an internal standard. [c] 3 equivalents of carbonate and 4Å MS (100 mg / 20 mg of alcohol) were used.

Dimethyl and diethyl carbonates **4** and **5** were first used but only traces of **3** were obtained, despite the use of 4Å molecular sieves (entries 1-2). In these two cases, benzil was observed as the only product. The formation of benzil from benzoin has been already

reported by Okumura under similar conditions.[34] Ethylene and propylene carbonates **6** and **7** were also considered as carbonyl sources as they directly arise from the cycloaddition of ethylene and propylene oxides with $CO_2$. However, no reaction occurred with such carbonates and the starting material was recovered unaltered (entries 3-4).Finally, catechol carbonate **8**, prepared following a reported method,[35] proved to be a good candidate as it gave vinylene carbonate **3** with 71% yield (entry 5), but it is not competing with diphenyl carbonate (entry 6). The success of the reaction when diphenyl carbonate **2**, or catechol carbonate **8** to a lesser extent, was used probably lies in the leaving group ability of the phenolate ion by comparison with other alcoholates.

The substrate scope was then investigated using the optimized conditions (see ESI) (Scheme 3).




**Scheme 3.** Scope of vinylene carbonates. Yields of isolated products are given. [a] The corresponding diketones were obtained as major products. [b] 3 equivalents of diphenyl carbonate were used. [c] GC yields in brackets. [d] The intermediate mixed carbonate was obtained as major product.

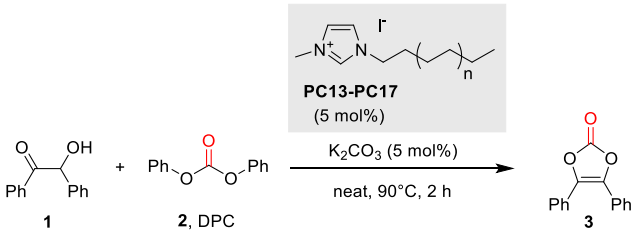
*Symmetrical benzoins* were first considered and benzoin gave the corresponding vinylene carbonate **3** with an excellent 99% yield. Good yields were also obtained using *para*-substituted benzoins bearing halogen such as fluorine (86 %, **9**), chlorine (91 %, **10**) or bromine (82 %, **11**). The use of anisoin gave **12**, with 64% yield, whose structure was confirmed by X-ray.[36] The reaction was also successful with *para*- and *meta*-methyl groups, giving **13** and **14** with 64 and 74% yield, respectively. However, the corresponding vinylene carbonate bearing *ortho*-methyl groups could not be produced due to the difficult preparation method of the starting material. Phenyl- and 2-naphthyl substituted benzoins gave carbonates **15-16** with 50 and 84% yield. In contrast, vinylene carbonates **17-19** bearing heteroaromatic groups (2-furanyl, 2-thiophenyl, 2-pyridinyl) could not be prepared under the optimized conditions. In these cases, the corresponding 1,2-diketones were formed, probably through NHC-catalyzed decarbonylation of instable vinylene carbonate intermediates.[37] *Symmetrical acyloins* were then tested under the standard conditions. However, despite a full conversion, only traces of the desired carbonates were detected due to the formation of a mixed carbonate intermediate (see ESI). The isolation of such species corroborates our initial mechanistic hypotheses. Its formation is probably favoured by the high concentration of the (neat) reaction medium and the low steric hindrance around the hydroxyl function of the acyloin. The problem was solved by increasing the amount of diphenyl carbonate to three equivalents. These new conditions were successfully applied to several symmetrical linear acyloins leading to the corresponding vinylene carbonates **20-24** with 35-90% isolated yields. It is worth noting that compound **20** is the key starting material for the preparation of the medoxomil group in prodrugs. Vinylene carbonate **25** bearing isobutyl groups was also produced in good yield (70%). The cyclic acyloin 2-hydroxycyclododecan-1-one was reacted successfully to give carbonate **26** with 79% yield. *Unsymmetrical aryl alkyl acyloins* were next considered. Unfortunately, carbonate **27** could not be obtained from 2-hydroxy-1-phenylethan-1-one, due to the formation of a mixed carbonate, that was found to prohibit cyclization. On the contrary, with an extra methyl group, the cyclization occurs smoothly and vinylene carbonates **28-31** were prepared with decent yields (30-78%). Finally, *natural-product derived acyloins* were also considered. Vinylene carbonates **32** and **33**, derived from methyl oleate and its self-metathesis derivative,[38] were obtained with high yields. The use of citronellal led to **34** with a moderate isolated yield, while the camphor derivative only gave traces of **35** due to the formation of a mixed carbonate intermediate. Finally, vinylene carbonate **36** derived from 21-hydroxyprogesterone was obtained with 20% yield.

Overall, we have developed an organocatalytic method for the synthesis of vinylene carbonates with good yields on a wide scope. Nevertheless, to date, this method was found unsuccessful for the preparation of unsubstituted vinylene carbonate. Indeed, the reaction of glycol aldehyde dimer with diphenyl carbonate did not allow its synthesis, probably due to the difficulty to generate the monomeric form under our reaction conditions.

Recovery and reuse of the catalyst might be the next step for an even improved method. Indeed, in this context, we have recently developed thermomorphic polyethylene-supported organocatalysts for the preparation of saturated cyclic carbonates by CO2 insertion into epoxides,[39] including vegetable oil derivatives.[40] The thermomorphic behavior of the polyethylene support allows the catalyst to exhibit similar reactivity to a homogeneous systems while being fully recyclable. Therefore, we envisioned that such innovative supported catalysts would be perfectly suitable for the synthesis of vinylene carbonates.

Hence, several supported imidazolium salts were prepared with various polyethylene molar masses, thus giving organocatalysts **PC13-PC17** with number-average molar masses ($M_n$) ranging from 740 to 1800 g mol$^{-1}$ (see ESI for details). These supported organocatalysts were tested at 90°C for the model reaction using benzoin **1** and diphenylcarbonate **2** as substrates (Table 3).

**Table 3.** Synthesis of vinylene carbonate using polyethylene-supported organocatalysts.[a]




| Entry | Supported precatalyst | $M_n$[b] (g.mol$^{-1}$) | $T_m$ (°C) | Yield[c] **3** (%) |
|---|---|---|---|---|
| 1 | **PC13** | 740 | 109 | 99 (99)[d] |
| 2 | **PC14** | 850 | 113 | 99 (99)[d] |
| 3 | **PC15** | 1,000 | 115 | 54 (99)[d] |
| 4 | **PC16** | 1,500 | 119 | 43 (99)[d] |
| 5 | **PC17** | 1,800 | 124 | 23 (99)[d] |

[a] Reaction conditions: benzoin **1** (1 mmol), diphenylcarbonate **2** (1.1 mmol), thermomorphic polyethylene-supported organocatalysts **PC13-PC17** (5 mol%), $K_2CO_3$ (5 mol%), 90°C, 2 h. [b] $M_n$ were determined by $^1$H NMR. [c] Yields were determined by GC/FID with *n*-hexadecane as an internal standard. [d] Reactions were performed at 120°C.

A quantitative yield of vinylene carbonate **3** was obtained using short chain catalysts **PC13** and **PC14**, with a $M_n$ of 740 and 850 g.mol$^{-1}$, respectively (entries 1-2). However, the yield of **3** progressively decreased from 54 to 23% with catalysts **PC15-PC17** which have higher molar masses ($M_n$ of 1000, 1500 and 1800 g mol$^{-1}$, entries 3-5). This phenomenon could be explained by the fact that catalysts with high molar

masses are not completely melted in the reaction mixture at 90°C. These results also suggest a direct correlation between molar masses / melting temperatures (determined by DSC in Table 3) of the catalysts and their catalytic activity. To confirm our hypothesis, the reaction was performed at 120°C. As expected, a quantitative yield of **3** was obtained for all supported catalysts at such temperature (entries 1-5, results in brackets). These results clearly highlight the tunability of the thermomorphic polyethylene-supported organocatalysts to address reactions at various temperature.

To further highlight the interest of such supported organocatalysts, recycling studies were performed on the model reaction using precatalyst **PC14** (5 mol%) and $K_2CO_3$ (5 mol%) at 90°C (Figure 1). The reaction was initially carried out using 30 mmol of benzoin. After reaction, the catalyst precipitates upon cooling and was filtered over sintered glass (EtOAc was added to facilitate the filtration). The desired vinylene carbonate **3** was obtained from the filtrate with 98% yield (7.0 g). The catalyst was recovered with 99% yield and reused as such for further reactions. The catalyst proves to be recyclable over five consecutive runs without significant loss of activity (94-99% yield, Figure 1, blue bars). About 33 g of vinylene carbonate **3** were obtained by combining all products recovered from each run, thus highlighting the synthetic utility of our method on the preparative scale (Figure 1, orange curve).

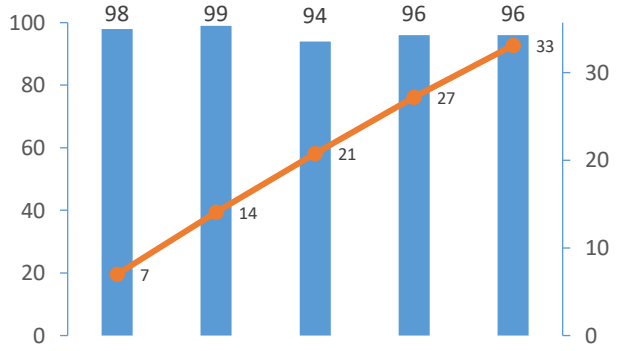
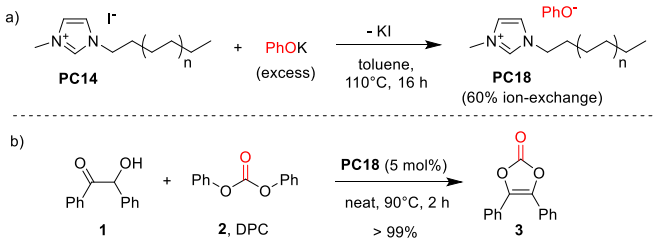



**Figure 1.** Recycling studies of thermomorphic polyethylene-supported organocatalysts. Blue bars represent yield (%) of vinylene carbonate **3** and orange curve represents the cumulative mass (g) of **3** produced over the runs. The reactions were performed with benzoin (30 mmol for runs 1-3, 28 mmol for run 4 and 26 mmol for run 5, 1 equiv), diphenylcarbonate (1.1 equiv), precatalyst **PC14** (M = 860 g $mol^{-1}$, 5 mol%), $K_2CO_3$ (5 mol%) and were stirred at 90°C for 2 hours. The yields were determined by GC/FID with *n*-hexadecane as an internal standard.

$^1$H NMR analysis of the recovered catalyst after five runs did not show any sign of degradation, indicating that the catalyst is quite robust under the tested conditions (see ESI). However, the presence of aromatic signals in the $^1$H NMR spectrum suggested that the original iodine ion has been partially exchanged with a phenolate ion. This has probably occurred through protonation of the free carbene with phenol.[41] To confirm this hypothesis, catalyst **PC18** was prepared from **PC14** by ion metathesis using potassium phenolate (Scheme 4, a). The $^1$H NMR spectrum of both **PC18** and recovered **PC14** were found to be identical, thus confirming our hypothesis. Catalyst **PC18** was then tested in the model reaction in absence of $K_2CO_3$ external base (Scheme 4, b). Vinylene carbonates **3** was obtained in quantitative yield, indicating the ability of the phenolate ion to act as an internal base to generate the active species.




**Scheme 4.** Preparation of catalyst **PC18** by anion metathesis (top) and its use in the synthesis of vinylene carbonate without external base (bottom).

## Conclusion

In conclusion, we have developed the first organocatalytic method to prepare vinylene carbonates from benzoins and acyloins using diphenyl carbonate as a carbonyl source. A wide range of symmetrical and unsymmetrical vinylene carbonates was produced (24 examples, including renewable substrates) with 20-99% isolated yield, thus considerably increasing the scope of synthesized products over the existing methods. Moreover, we have also developed this method using thermomorphic polyethylene-supported organocatalysts, which proved to be as active as their unsupported analogues. Their recoverability, reusability and recyclability were demonstrated over five runs. Finally, the method was also implemented on the multi-gram scale, thus demonstrating its synthetic utility.

## Experimental Section

**General procedure for the preparation of vinylene carbonates.** Diphenylcarbonate (1.1 equiv. or 3 equiv.), *N*,*N*-dimethylimidazolium iodide (5 mol%), potassium carbonate (0.5 equiv.) and the corresponding acyloin (1 equiv.) were introduced in a dry glass reactor equipped with a stirring bar. The reactor was inerted with argon and the reaction mixture was heated at 90°C with oil bath or aluminium block for 2 hours. After TLC or GC confirmed the completion of the reaction, the reaction mixture was cooled down to room temperature. Ethyl acetate (2.5 mL/mmol) was added to the reaction mixture and it was transferred to a separatory funnel. The organic layer was washed with an aqueous solution of sodium hydroxide (1N, 2 mL/mmol), and then washed twice with a saturated aqueous solution of sodium chloride (2 mL/mmol). The organic layer was then dried over magnesium sulfate, filtrated and the filtrate was evaporated to give the crude

compound. The crude vinylene carbonate was purified by flash chromatography column (25 g of silica/mmol) with a mixture of ethyl acetate and cyclohexane as eluent to give the desired pure product.

**General procedure for the preparation of vinylene carbonates with polyethylene-supported organocatalyst.** Diphenylcarbonate (1.1 equiv. or 3 equiv.), polyethylene-supported methyl imidazolium iodide (5 mol%), potassium carbonate (5 mol%) and the corresponding acyloin (1 equiv.) were introduced in a dry glass reactor equipped with a stirring bar or a motor and a stirring blade. The reactor was inerted with argon and the reaction mixture was heated at 90°C with oil bath or aluminium block for 2 hours. After TLC or GC confirmed the completion of the reaction, the reaction mixture was cooled down to 60°C. Ethyl acetate (2.5 mL/mmol) was added and the reaction mixture was further cooled to room temperature, the precipitation of the catalyst was observed. The mixture was vacuum filtered on paper membrane (0.1 µm) and the solid catalyst was washed twice with 25 mL of ethyl acetate. The filtrate was transferred into a separatory funnel. The organic layer was washed with an aqueous solution of sodium hydroxide (1N, 2 mL/mmol), and then washed twice with a saturated aqueous solution of sodium chloride (2 mL/mmol). The organic layer was then dried over magnesium sulfate, filtered and the filtrate was evaporated to give the crude compound. The crude vinylene carbonate was purified by flash chromatography column (25 g of silica/mmol) with a mixture of ethyl acetate and cyclohexane as eluent to give the desired pure product.

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