

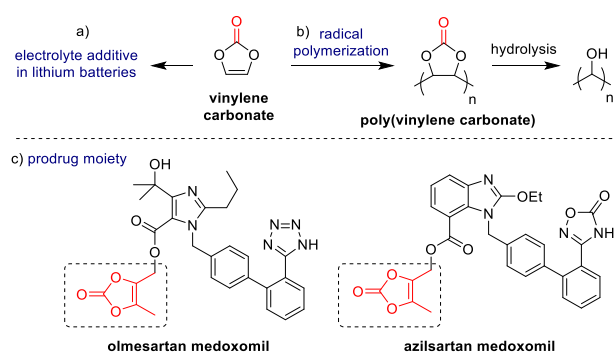
# Organocatalytic synthesis of vinylene carbonates

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**Abstract:** The organocatalytic synthesis of vinylene carbonates from benzoin and acyloin 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).

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,<sup>1</sup> renewable solvents<sup>2</sup> and monomers for the preparation of polycarbonates<sup>3</sup> and non-isocyanate polyurethanes (NIPUs).<sup>4</sup> In this vast field, organic cyclic carbonates largely dominate as they can be prepared from epoxides and CO<sub>2</sub>, using a plethora of catalysts.<sup>5</sup> 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).<sup>6</sup> Moreover, its unsaturated nature facilitates its use in other kind of applications. For example, it can be used for the preparation of poly(vinylencarbonate)<sup>7</sup> 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.<sup>8</sup> Vinylene carbonates are also used in the medical field, notably in prodrugs such as olmesartan medoxomil<sup>9</sup> and azilsartan medoxomil,<sup>10</sup> where they serve as cleavable group to release the active species (Scheme 1, c).<sup>11</sup> In organic chemistry, vinylene carbonate is mainly used as a dienophile in Diels-Alder reactions<sup>12</sup> and other cycloadditions,<sup>13</sup> but also as a coupling partner in arylation reactions.<sup>14</sup>

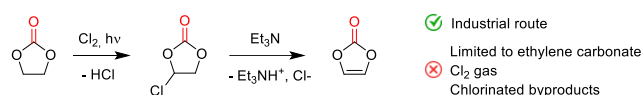


**Scheme 1.** Main applications of vinylene carbonates.

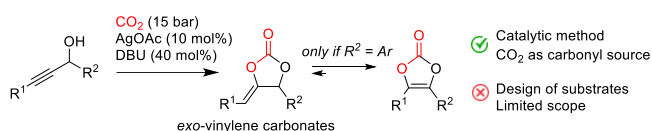
Recently, vinylene carbonate has been mainly used as an acetylene<sup>15</sup> or ethynol<sup>16</sup> surrogate in annulation reactions.<sup>17</sup> Moreover, it was also demonstrated that it can act as an acetylation reagent in rhodium-catalyzed cyclization.<sup>18</sup> Despite all of these various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

The synthesis of vinylene carbonate was first reported from ethylene carbonate using a chlorination / dehydrochlorination sequence (Scheme 2, a).<sup>19</sup> This route has been developed industrially; however, it involves the use of chlorine gas and generates chlorinated byproducts, thus leading to tedious purification. The silver-catalyzed reaction of propargylic alcohols with CO<sub>2</sub> affords *exo*-vinylene carbonates (also called  $\alpha$ -vinylene carbonates),<sup>20</sup> 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).<sup>21</sup> However, this route is not general as only a limited range of products can be prepared through this method. The reaction of benzoin or acyloin 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.

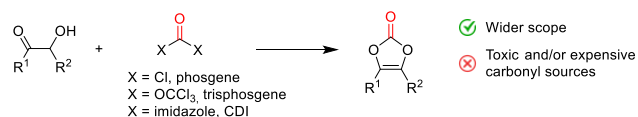
a) Chlorination / dehydrochlorination of ethylene carbonate



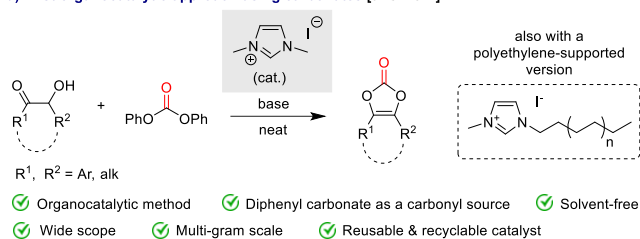
b) Silver-catalyzed cyclization of propargyl alcohols with CO<sub>2</sub>



c) Cyclization of benzoin / acyloins with carbonylating agents



d) First organocatalytic approach using carbonates [this work]



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

The use of phosgene as a carbonylating agent usually leads to excellent yields but raises health and safety concerns.<sup>13a, 22</sup> Trisphosgene can be used as an alternative.<sup>23</sup> However, the release of phosgene cannot be avoided.<sup>24</sup> Alternatively, the preparation of vinylene carbonates can be achieved using carbonyl di-imidazole (CDI).<sup>25</sup> CDI is a mild carbonylating agent and hence it has to be used in excess, which is a drawback considering that it is expensive. 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.<sup>26</sup> Indeed, such species are generally less toxic and safer to use. Moreover, they are produced from ethylene carbonate, so they also derive from CO<sub>2</sub>. 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 benzoin 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). 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.

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.<sup>27</sup> 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<sub>2</sub>CO<sub>3</sub> (5 mol%) at 90°C for 2 hours under solvent-free conditions (Table 1).

**Table 1.** Screening of NHC precursors and bases.<sup>[a]</sup>

Entry	precatalyst	Base	Yield <sup>[b]</sup> <b>3</b> (%)
1	<b>PC1</b>	K <sub>2</sub> CO <sub>3</sub>	< 5
2	<b>PC2</b>	K <sub>2</sub> CO <sub>3</sub>	< 5
3	<b>PC3</b>	K <sub>2</sub> CO <sub>3</sub>	< 5
4	<b>PC4</b>	K <sub>2</sub> CO <sub>3</sub>	11
5	<b>PC5</b>	K <sub>2</sub> CO <sub>3</sub>	27
6	<b>PC6</b>	K <sub>2</sub> CO <sub>3</sub>	7
7	<b>PC7</b>	K <sub>2</sub> CO <sub>3</sub>	< 5
8	<b>PC8</b>	K <sub>2</sub> CO <sub>3</sub>	< 5
9	<b>PC9</b>	K <sub>2</sub> CO <sub>3</sub>	74
10	<b>PC10</b>	K <sub>2</sub> CO <sub>3</sub>	97
11	<b>PC10</b>	Na <sub>2</sub> CO <sub>3</sub>	83
12	<b>PC10</b>	Cs <sub>2</sub> CO <sub>3</sub>	98
13	<b>PC10</b>	NaOH	99
14	<b>PC10</b>	Et <sub>3</sub> N	60
15	<b>PC10</b>	TBD	85
16 <sup>[c]</sup>	<b>PC11</b>	-	72
17 <sup>[c]</sup>	<b>PC12</b>	-	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.

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 analogue **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). 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<sub>2</sub>CO<sub>3</sub> led to a lower yield while Cs<sub>2</sub>CO<sub>3</sub> gave a similar result than K<sub>2</sub>CO<sub>3</sub> (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<sub>3</sub>N and triazabicyclodecene (TBD) also gave the desired product but with lower yields (entries 14-15). Finally, NHC-CO<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub> but only traces of the desired carbonate **3** were obtained, thus indicating the combined crucial role of both species in the catalytic system. Several reaction parameters were next investigated (Table 2).

**Table 2.** Optimization of precatalyst and base loadings.<sup>[a]</sup>

Entry	DPC, <b>2</b> (equiv)	Precatalyst <b>PC10</b> loading (mol%) <sup>1</sup>	K <sub>2</sub> CO <sub>3</sub> loading (mol%)	Yield <sup>[b]</sup> <b>3</b> (%)
1	1.1	5	5	96
2	2	5	5	82
3	3	5	5	38
4	1.1	1	1	< 5
5	1.1	0.1	0.1	< 5
6	1.1	10	10	90
7	1.1	20	20	89
8	1.1	5	10	85
9	1.1	5	20	71
10	1.1	5	50	99

[a] Reaction conditions: benzoin **1** (1 mmol), diphenylcarbonate (DPC) **2** (1.1-3 mmol), 1,3-dimethylimidazolium iodide **PC10**, K<sub>2</sub>CO<sub>3</sub>, 90°C, 2 h. [b] Yields were determined by GC/FID with *n*-hexadecane as an internal standard.

Increasing the amount of **2** from 1.1 to 3 equivalents led to a drastic drop in yield (entries 1-3). This result has been attributed to the dilution of the reaction medium under solvent-free conditions. Decreasing both the precatalyst and base loadings to 1 and 0.1 mol% led to very poor yields (entries 4-5), while increasing them to 10 and 20 mol% only slightly affected the yield of **3**, which reaches 90 and 89%, respectively (entries 6-7). Subsequently, the concentration of K<sub>2</sub>CO<sub>3</sub> was studied with a precatalyst loading set at 5 mol%. Adding 2 to 4 times more base slightly decreased the yield to 71% (entries 8-9). Interestingly, increasing the base to 50 mol% gave full conversion of benzoin **1** and an excellent 99% yield for the desired vinylene carbonate **3** (entry 10).

Other organic carbonates were tested as a carbonyl source (Table 3). Dimethyl and diethyl carbonates **4** and **5** were first used but only traces of **3** were obtained, despite the use of 4 Å 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.<sup>28</sup> 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<sub>2</sub>. However, no reaction occurred with such carbonates and the starting material was recovered unaltered (entries 3-4).

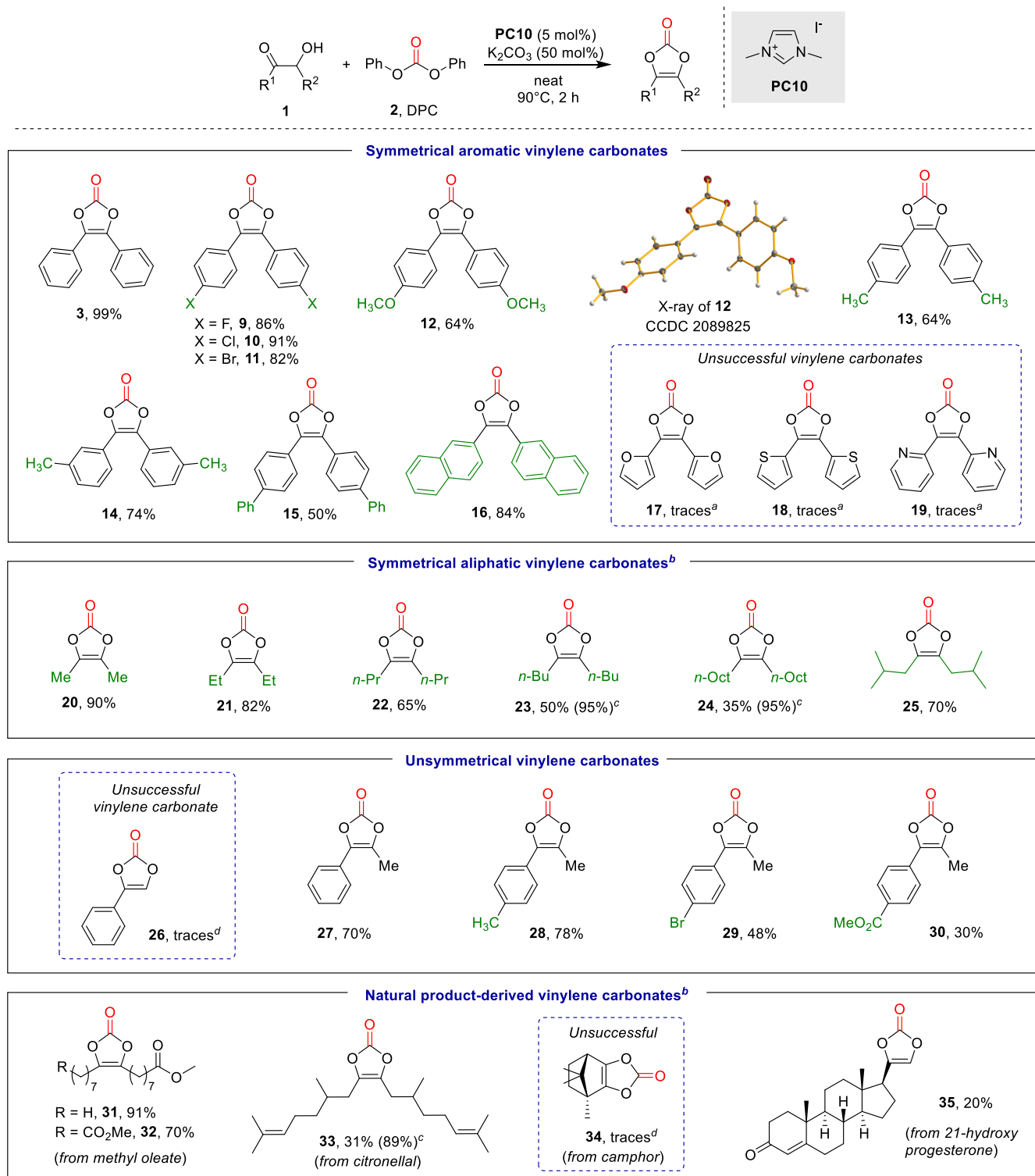
**Table 3.** Screening of carbonates as carbonyl sources.<sup>[a]</sup>

Entry	Carbonyl source	Yield <sup>[b]</sup> <b>3</b> (%)
1 <sup>[c]</sup>		2
2 <sup>[c]</sup>		< 1
3		< 1
4		< 1
5		71
6		96

[a] Reaction conditions: benzoin **1** (1 mmol), carbonate **2, 4-8** (1.1 mmol), 1,3-dimethylimidazolium iodide **PC10** (5 mol%), K<sub>2</sub>CO<sub>3</sub> (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 4 Å MS (100 mg / 20 mg of alcohol) were used.

Finally, catechol carbonate **8**, prepared following a reported method,<sup>29</sup> 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 (Scheme 3).



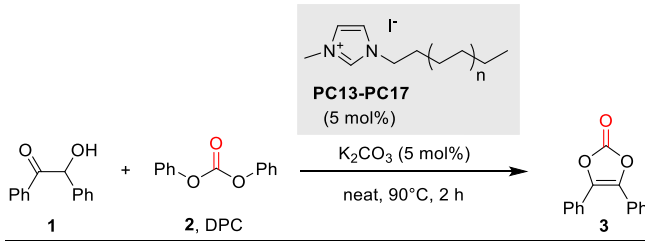
**Scheme 3.** Scope of vinylene carbonates. Yields of isolated products are given. <sup>a</sup> The corresponding diketones were obtained as major products. <sup>b</sup> 3 equivalents of diphenyl carbonate were used. <sup>c</sup> GC yields in brackets. <sup>d</sup> The mixed carbonate intermediate was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

*Symmetrical benzoin*s were first considered and benzoin gave the corresponding vinylene carbonate **3** with an excellent 99% yield. Good yields were also obtained using *para*-substituted benzoin 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. 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 benzoin 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.<sup>30</sup> *Symmetrical acyloin*s 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 formation of such product is probably favored 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%). *Unsymmetrical aryl alkyl acyloins* were next considered. Unfortunately, carbonate **26** 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 **27-30** were prepared with decent yields (30-78%). Finally, *natural-product derived acyloins* were also considered. Vinylene carbonates **31** and **32**, derived from methyl oleate and its self-metathesis derivative, were obtained with high yields. The use of citronellal led to **33** with a moderate isolated yield, while the camphor derivative only gave traces of **34** due to the formation of a mixed carbonate intermediate. Finally, vinylene carbonate **35** 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. 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 CO<sub>2</sub> insertion into epoxides,<sup>31</sup> including vegetable oil derivatives.<sup>32</sup> 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<sub>n</sub>*) ranging from 740 to 1800 g mol<sup>-1</sup> (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 4). A quantitative yield of vinylene carbonate **3** was obtained using short chain catalysts **PC13** and **PC14**, with a *M<sub>n</sub>* of 740 and 850 g.mol<sup>-1</sup>, 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<sub>n</sub>* of 1000, 1500 and 1800 g mol<sup>-1</sup>, 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 4) 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.

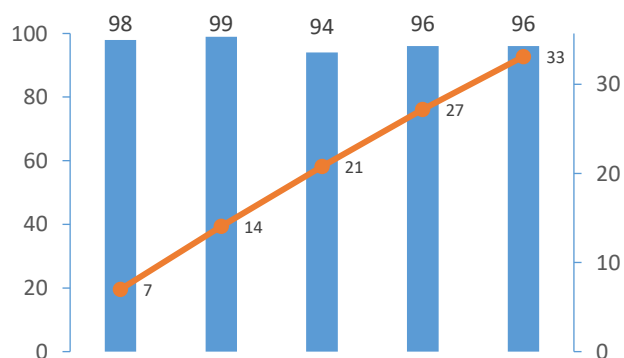
**Table 4.** Synthesis of vinylene carbonate using polyethylene-supported organocatalysts.<sup>[a]</sup>



Entry	Supported precatalyst	<i>M<sub>n</sub></i> <sup>[b]</sup> (g.mol <sup>-1</sup> )	<i>T<sub>m</sub></i> (°C)	Yield <sup>[c]</sup> <b>3</b> (%)
1	<b>PC13</b>	740	109	99 (99) <sup>[d]</sup>
2	<b>PC14</b>	850	113	99 (99) <sup>[d]</sup>
3	<b>PC15</b>	1,000	115	54 (99) <sup>[d]</sup>
4	<b>PC16</b>	1,500	119	43 (99) <sup>[d]</sup>
5	<b>PC17</b>	1,800	124	23 (99) <sup>[d]</sup>

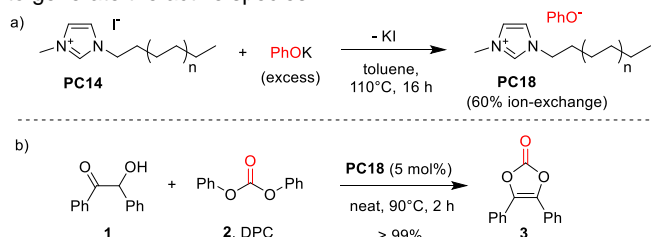
[a] Reaction conditions: benzoin **1** (1 mmol), diphenylcarbonate **2** (1.1 mmol), thermomorphic polyethylene-supported organocatalysts **PC13-PC17** (5 mol%), K<sub>2</sub>CO<sub>3</sub> (5 mol%), 90°C, 2 h. [b] *M<sub>n</sub>* were determined by <sup>1</sup>H NMR. [c] Yields were determined by GC/FID with *n*-hexadecane as an internal standard. [d] Reactions were performed at 120°C.

To further highlight the interest of such supported organocatalysts, recycling studies were performed on the model reaction using precatalyst **PC14** (5 mol%) and K<sub>2</sub>CO<sub>3</sub> (5 mol%) at 90°C (Figure 2). 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 2, 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 2, orange curve).



**Figure 2.** Recycling studies of thermomorphic polyethylene-supported organocatalysts. Blue bars represent yield (%) of vinylene carbonate **3** and orange curve represents the cumulative mass 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** ( $M = 860 \text{ g mol}^{-1}$ , 5 mol%),  $\text{K}_2\text{CO}_3$  (5 mol%) and were stirred at  $90^\circ\text{C}$  for 2 hours. The yields were determined by GC/FID with *n*-hexadecane as an internal standard.

$^1\text{H}$  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  $^1\text{H}$  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.<sup>33</sup> To confirm this hypothesis, catalyst **PC18** was prepared from **PC14** by ion metathesis using potassium phenolate (Scheme 4, a). The  $^1\text{H}$  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  $\text{K}_2\text{CO}_3$  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).

In conclusion, we have developed the first organocatalytic method to prepare vinylene carbonates from benzoin 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.

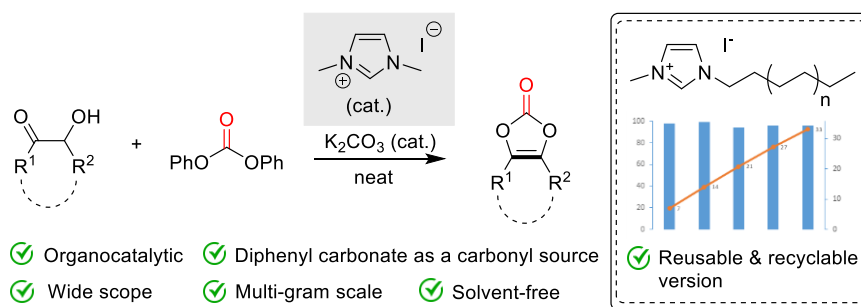
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**Keywords:** Vinylene carbonates • Benzoin • Diphenyl carbonate • Organocatalysis • Thermomorphic polyethylene

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Vinylene carbonates were prepared from benzoin / acyloins using diphenyl carbonate as a carbonyl source. The reaction is catalyzed by imidazolium salts under solvent-free conditions. The reaction was also developed using thermomorphic polyethylene-supported organocatalysts as recoverable and recyclable species, allowing the synthesis of vinylene carbonates on the multigram scale.