



# 1,3-Dialkylimidazolium-2-carboxylates as versatile N-heterocyclic carbene–CO<sub>2</sub> adducts employed in the synthesis of carboxylates and $\alpha$ -alkylidene cyclic carbonates

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## ABSTRACT

1,3-Dialkylimidazolium-2-carboxylate compounds of formulas **1a**, **2**, and **4** have been synthesized and fully characterized by X-ray spectroscopy quite recently. Up today, these compounds have found some interesting applications as precursors of N-heterocyclic carbenes (NHCs) used as ligands for metal-complexes or in the synthesis of organic compounds and ionic liquids. We have recently reported the use of 1-butyl, 3-methylimidazolium-2-carboxylate and 1,3-dimethylimidazolium-2-carboxylate in a CO<sub>2</sub>-transfer reaction to CH<sub>3</sub>OH and acetophenone for the synthesis of methylcarbonate and benzoylacetate. The scope of this CO<sub>2</sub>-transfer reaction has been expanded to several organic compounds with active hydrogen (acetone, cyclohexanone, and benzylcyanide) for the synthesis of carboxylates of pharmaceutical interest, and to propargyl alcohols for the synthesis of  $\alpha$ -alkylidene cyclic carbonates.

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## 1. Introduction

1,3-Dialkylimidazolium-2-carboxylate compounds of formulas **1a**,<sup>1</sup> **2**,<sup>2</sup> and **4**<sup>3</sup> have been synthesized and fully characterized by X-ray spectroscopy quite recently (Scheme 1). Analogous compounds of formulas **1b**,<sup>4</sup> **3**,<sup>5</sup> and **5**,<sup>5</sup> as well as the 1,3-bis(2,4,6-trimethylphenyl)imidazolium-2-carboxylate (**6**) and 1,3-bis(2,6-

diisopropylphenyl)imidazolium-2-carboxylate (**7**)<sup>5</sup> have also been extensively characterized.

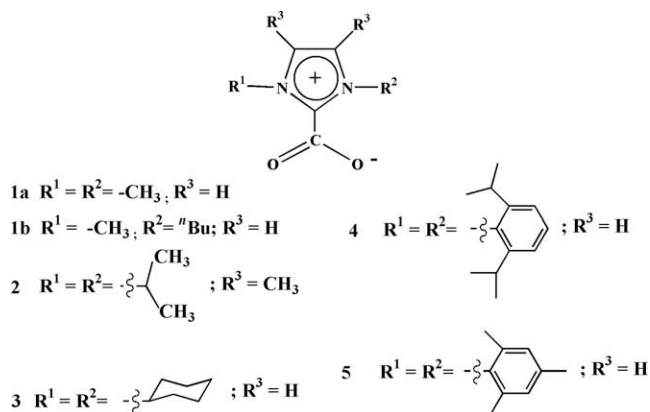
As N-alkyl and N-aryl substituted imidazol(in)ium-2-carboxylates are adducts of the corresponding carbene with CO<sub>2</sub>, they have been employed in synthetic chemistry both as organocatalysts in CO<sub>2</sub>-coupling reactions with epoxides<sup>6</sup> and as NHC-transfer agents. Studies about the thermal stability of several NHC–CO<sub>2</sub> adducts carried out by Louie,<sup>3</sup> and more recently by Lu and co-workers<sup>6</sup> have contributed significantly to the understanding of their reactivity. Notable examples of utilization of compound **1a** in chemical synthesis are the preparation of NHC-metal complexes,<sup>7,8</sup> amidates and thioamidates,<sup>9</sup> phosphonium adducts,<sup>10</sup> and ionic liquids.<sup>11</sup>

Several NHC-metal complexes prepared using compounds **3–7** have also been used as catalysts in olefin metathesis,<sup>5</sup> cyclopropanation reactions,<sup>5</sup> and Suzuki–Miyaura couplings.<sup>12</sup>

The employment of imidazol(in)ium-2-carboxylates in synthesis and catalysis seems interesting<sup>5–12</sup> as the generation of NHC from the corresponding carboxylate **1–7**, when applicable, shows the advantage to start from air- and moisture-stable species.<sup>5–8,12</sup>

Due to the high moisture and air sensitivity of imidazol-2-ylidenes, developing new methods for in situ generation of NHC is of crucial importance. In this context, the literature documents the development of wide applicable procedures that allow the facile use of NHCs in a variety of reactions.<sup>13–16</sup>

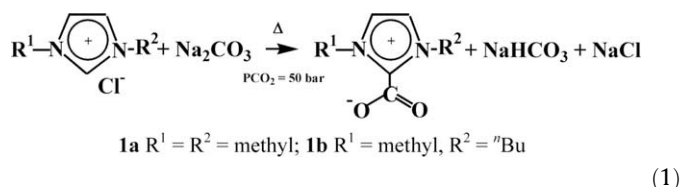
We have recently synthesized and fully characterized compounds **1a** and **1b** from 1-alkyl imidazoles and DMC.<sup>1</sup> We have also recently reported that compounds **1a** and **1b** can be prepared from



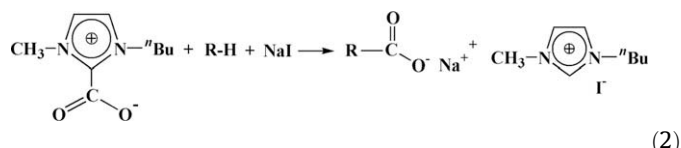
Scheme 1.

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1,3-dialkylimidazolium salts,  $\text{Na}_2\text{CO}_3$ , and  $\text{CO}_2$ , through a Kolbe–Smith type reaction,<sup>4</sup>



and that they behave as active  $\text{CO}_2$ -carriers, transferring  $\text{CO}_2$  to methanol and acetophenone for the synthesis of methylcarbonate and benzoylacetate salts in high yields (Eq. 2).<sup>17</sup>



Once having established that compounds **1a** and **1b** act as  $\text{CO}_2$ -transfer agent toward methanol and acetophenone (Eq. 2), we investigated several active hydrogen organic substrates of interest as their corresponding carboxylates are widely used as intermediates in chemical industry, and several propargyl alcohols which are known to react with  $\text{CO}_2$  undergoing a carboxylative cyclization reaction to afford  $\alpha$ -alkylidene cyclic carbonates.

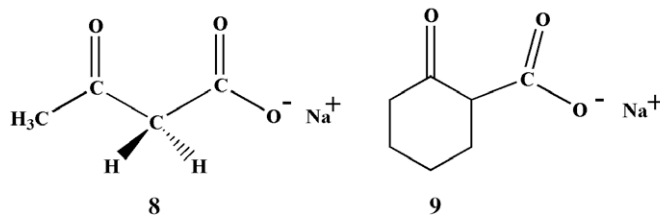
## 2. Carboxylation of ketones and benzylcyanide

Compounds like acetone, cyclohexanone, and benzylcyanide ( $\text{pK}_a \approx 20\text{--}22$ )<sup>18</sup> can be carboxylated according to the synthetic procedure shown in Eq. 2, under very mild conditions and in good yields affording the corresponding carboxylate salts (Scheme 2). The carboxylates shown in Scheme 2, both in the form of their salts ( $-\text{COOM}$ ), acids ( $-\text{COOH}$ ), or esters ( $-\text{COOR}$ ), are widely used as intermediates for pharmaceuticals and agrochemicals.<sup>19</sup> The classical synthesis of compounds shown in Scheme 2 is carried out by reaction of the organic substrate with strong and expensive bases like  $\text{NaNH}_2$ , hydrides, naphthalenes, and  $n$ -butyl lithium.<sup>20</sup>

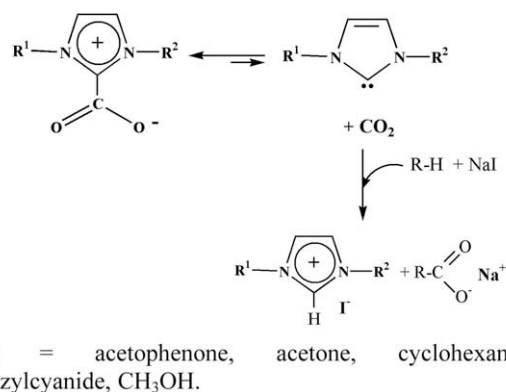
The strong base is required in order to generate the carbon anion that is able to react with carbon dioxide. Various alternative synthetic procedures were described in the scientific literature based on the use of various catalysts.<sup>21</sup> All these alternative synthetic procedures are affected by unsatisfactory yields, or require high catalyst loading.

The carboxylation of acetone has been carried out according to Eq. 2 by using the ketone as the co-solvent and reagent. After 70 h of reaction at room temperature, the sodium salt of 3-oxo-butanoic acid (**8**) was isolated in 77% yield.<sup>22</sup> The reaction is highly selective as the formation of the salt of 3-oxoglutaric acid as result of a double acetone carboxylation described by other Authors<sup>21</sup> was not observed.

The trans-carboxylation reaction of cyclohexanone affording selectively 2-oxo-cyclohexan-1-carboxylate product (**9**) (yield



Scheme 2.



Scheme 3.

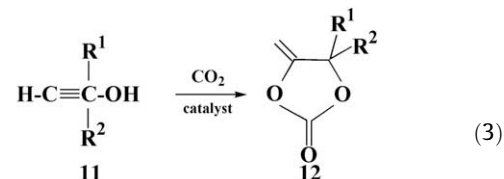
62%)<sup>23</sup> and the benzylcyanide carboxylation<sup>24</sup> affording product **10** (60% yield) were carried out by using a 1:1 ratio of reactants in  $\text{CH}_3\text{CN}$  as the solvent.

While the elucidation of the mechanism of the trans-carboxylation reaction deserves further investigations, some preliminary studies seem to indicate that preliminary generation of the free carbene may occur.<sup>17</sup> The carbene ( $\text{pK}_a$  of 22–24 has been reported)<sup>25</sup> could react with the organic substrate generating an anion able to react with  $\text{CO}_2$  (Scheme 3).

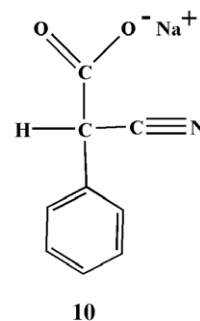
As far as the role of the metal cation is concerned ( $\text{Na}^+$  or  $\text{K}^+$ ), it could be involved both in the substrate activation and/or in the product stabilization.<sup>26</sup>

## 3. Synthesis of $\alpha$ -alkylidene cyclic carbonates

As reported in Eq. 2, compounds **1a** and **1b** have been used in the carbonation of  $\text{CH}_3\text{OH}$  for the synthesis of  $\text{CH}_3\text{OC(O)O}^- \text{M}^+$  ( $\text{M}^+ = \text{Na}^+, \text{K}^+$ ) and ionic liquids.<sup>17</sup> As an extension of the study on the reactivity toward alcohols, we investigated the reaction of 1,3-dimethylimidazolium-2-carboxylate and 1-butyl, 3-methylimidazolium-2-carboxylate with propargyl alcohols of formulas **11a–d** as it is known that these alcohols can react with  $\text{CO}_2$  undergoing a carboxylative cyclization reaction to give the corresponding cyclic carbonates **12a–d** (Eq. 3).<sup>27</sup>  $\alpha$ -Alkylidene cyclic carbonates **12a–d** are useful intermediates to oxazolidinones,  $\beta$ -oxopropyl carbonates, carbamates, and furanone derivatives.<sup>28</sup>



**11a** and **12a**,  $\text{R}^1 = \text{R}^2 = \text{CH}_3$ ; **11b** and **12b**,  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{C}_2\text{H}_5$ ; **11c** and **12c**,  $\text{R}^1\text{-R}^2 = -(\text{CH}_2)_5-$ ; **11d** and **12d**,  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{C}_6\text{H}_5$ .



**Table 1**  
Synthesis of  $\alpha$ -alkylidene cyclic carbonates **12a–d** from propargyl alcohols **11a–d** and CO<sub>2</sub><sup>a</sup>

Entry	Alcohol	Substituents	Catalyst	Carbonate	Yield <sup>b</sup> (%)
1	<b>11a</b>	R <sup>1</sup> = R <sup>2</sup> = CH <sub>3</sub>	1,3-Dimethylimidazolium-2-carboxylate	<b>12a</b>	77
2	<b>11b</b>	R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> = C <sub>2</sub> H <sub>5</sub>	1,3-Dimethylimidazolium-2-carboxylate	<b>12b</b>	75
3	<b>11c</b>	R <sup>1</sup> -R <sup>2</sup> = -(CH <sub>2</sub> ) <sub>5</sub> -	1-Butyl, 3-methylimidazolium-2-carboxylate	<b>12c</b>	51
4	<b>11d</b>	R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> = C <sub>6</sub> H <sub>5</sub>	1-Butyl, 3-methylimidazolium-2-carboxylate	<b>12d</b>	73 (67) <sup>c</sup>

<sup>a</sup> Reaction conditions: 10.3 mmol of alcohol; 0.79 mmol of catalyst (catalyst loading 7.7%); 60 bar CO<sub>2</sub>; 100 °C; 15 h.

<sup>b</sup> Gas-chromatographic yield.

<sup>c</sup> Isolated yield.

The reaction depicted in Eq. 3 requires a catalyst. Several transition metals have been successfully employed including Pd,<sup>29</sup> Ru,<sup>30</sup> Co,<sup>31</sup> Cu,<sup>32,33</sup> and Ag,<sup>34</sup> but the reaction is also promoted by tertiary phosphines.<sup>35,36</sup>

An overview of data reported in the literature about this reaction allows to conclude that (i) tertiary propargyl alcohols are more reactive substrates;<sup>37</sup> (ii) higher yields are usually obtained when R<sup>1</sup>-R<sup>2</sup> (Eq. 3) are represented by linear alkyl groups (alcohols **11a–b**, 65–99% yield), while substrates with R<sup>1</sup>-R<sup>2</sup> represented by bulky (alcohol **11c**, 58–75% yield) or phenyl groups (alcohol **11d**, 32–50% yield) gave lower yields.<sup>29–36</sup>

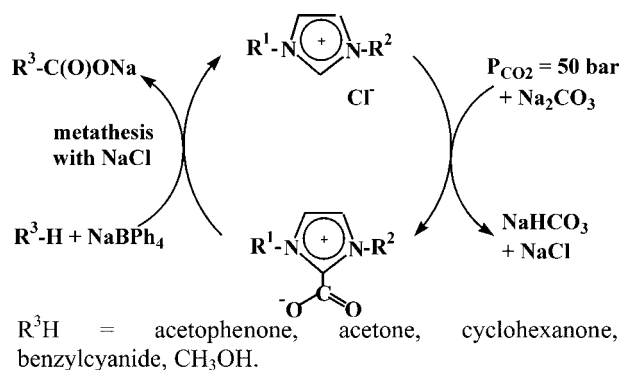
Very recently a Japanese Patent<sup>38</sup> reported the use of imidazol- and imidazolin-2-ylidenes with bulky *N*-alkyl and *N*-aryl substituents and their CO<sub>2</sub>-adducts as catalysts in the synthesis of carbonate **12a** (obtained in 88% yield). These data confirm that NHCs compete with phosphines for donating properties<sup>39</sup> and catalytic activity, and open the question about the role of the NHC in the carboxylative cyclization reaction.

As the steric bulk of NHC *N*-substituents has been often reported to influence significantly their reactivity,<sup>13,15</sup> we decided to investigate the activity of compounds **1a** and **1b** as catalysts of the carboxylative cyclization of terminal propargyl alcohols. Results of our study are summarized in Table 1. Interestingly, with respect to yields obtained by using different catalysts,<sup>40</sup> a higher yield was obtained by using the less reactive 2-phenyl, 3-butyn-2-ol (entry 4, 67% isolated yield). In all experiments, catalyst loading was 7.7%, and selectivity in carbonates **12a–d** was >99%.

## 4. Conclusion

### 4.1. Synthesis of carboxylates

Coupling the synthesis of compound **1b** with CO<sub>2</sub> (Eq. 1) and the trans-carboxylation reaction of CO<sub>2</sub> from compound **1b** to organic substrates (Eq. 2) allow to describe a new advanced synthetic methodology for the preparation of organic carboxylates using CO<sub>2</sub>.



Considering the carboxylation reaction reported in Eq. 1, it is worth to note that Na<sub>2</sub>CO<sub>3</sub><sup>41</sup> is stoichiometrically consumed while we have shown that the imidazolium moiety can be recycled several times without significant decomposition (Scheme 4).<sup>4</sup>

We consider, thus, the imidazolium cation acting as a recyclable specie for the synthesis of carboxylates using CO<sub>2</sub>.

### 4.2. Synthesis of $\alpha$ -alkylidene cyclic carbonates

By comparison with data reported in the Japanese Patent, 1, 3-dimethylimidazolium-2-carboxylate and 1-butyl, 3-methylimidazolium-2-carboxylate show a good activity. Moreover, catalyst **1b** shows a better specificity for the less reactive 2-phenyl-1,3-butyn-2-ol (**11d**) substrate.

### Acknowledgments

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22. *Carboxylation of acetone*. In a Schlenk flask, 1-butyl, 3-methylimidazolium-2-carboxylate (3.38 g, 18.5 mmol), dry NaI (2.78 g (18.5 mmol) dry acetone (25 mL), and  $CH_3CN$  (10 mL) were reacted, under nitrogen atmosphere at room temperature for 70 h. The initially clear solution after a few hours became cloudy with copious white precipitate and a light yellow supernatant. The reaction mixture was then dried in vacuo, and the residual solid washed with  $CH_3CN$  ( $2 \times 20$  mL) and dry acetone ( $2 \times 20$  mL). The white solid obtained (1.78 g, 77.3%) was characterized as sodium salt of the 3-oxo-butanonic acid. Anal. Calcd for  $C_4H_5NaO_3$ : Na, 18.53. Found: Na, 18.32. IR (Nujol, KBr): 1712, 1604  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $D_2O$ ):  $\delta$ , protons due to  $-CH_2-$  group were not observed because of fast exchange with  $D_2O$ , 2.14 (s,  $CH_3-$ );  $^{13}C\{^1H\}$  NMR (101 MHz,  $D_2O$ ):  $\delta$ , 29.8 ( $CH_3-$ ), 52.9 (broad multiplet because of fast exchange with  $D_2O$ ), 175.3 ( $CH_2-C(O)-$ ), 201.1 ( $CH_3-C(O)-CH_2$ ).
23. *Carboxylation of cyclohexanone*. In a Schlenk flask, 1-butyl, 3-methylimidazolium-2-carboxylate (3.19 g, 17.5 mmol), NaI (2.65 g, 17.7 mmol), and cyclohexanone (3 mL) were reacted in dry  $CH_3CN$  (25 mL). The reaction mixture was stirred under nitrogen atmosphere at room temperature for 70 h, after which the solution was concentrated to dryness in vacuo. The residual solid was washed with THF ( $3 \times 15$  mL) to remove excess of cyclohexanone, then with acetone ( $3 \times 15$  mL). A light yellow solid was obtained (1.79 g, 62.2% yield) characterized as sodium 2-oxo-cyclohexane-1-carboxylate. Anal. Calcd for  $C_7H_9NaO_3$ : Na, 14.01. Found: Na, 13.91. IR (Nujol, KBr): 1573 and 1697  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $D_2O$ ):  $\delta$ , 1.54 (1H) and 1.61 (m, 1H) ( $C(4)-H_2$ ), 1.68 (m, 2H,  $C(5)H_2$ ), 2.12 (m, 1H) and 2.19 (m, 1H) ( $C(6)-H_2$ ), 2.38 (m, 1H) and 2.43 (m, 1H,  $C(3)H_2$ ), 3.26 (t, approximately 0.7 ( $C(1)H$ )).  $^{13}C\{^1H\}$  NMR (101 MHz,  $D_2O$ ):  $\delta$ , 22.64, 26.63, 31.10, 40.98, 61.06 (C1), 177.79 ( $-C(O)-$ ), 215.65 ( $-C(O)-$ ).
24. *Carboxylation of benzylicanide*. In a Schlenk flask were reacted, under nitrogen atmosphere, 1-butyl, 3-methylimidazolium-2-carboxylate (2.73 g, 14.98 mmol), NaI (2.32 g, 15.01 mmol), and benzylicanide (1.85 mL, 15.79 mmol) in dry  $CH_3CN$  (15 mL) at room temperature for 4 days. The reaction mixture was dried in vacuo, and washed three times with  $CH_3CN$  ( $3 \times 7$  mL). A light yellow solid was obtained (1.74 g, yield 60%) characterized as sodium 2-cyano, 2-phenylacetate salt. Anal. Calcd for  $C_9H_9NNaO_2$ : Na, 12.55. Found: Na, 12.40. IR (Nujol, KBr): 1712, 1604  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $D_2O$ ):  $\delta$ , 7.27 (broad signal due to overlapping aromatic protons).  $^{13}C\{^1H\}$  NMR (101 MHz,  $H_2O$ ):  $\delta$ , 46.25 (C–H tertiary carbon), 119.94 (–CN), 127.82 (*ortho-Ph*), 128.32 (*para-Ph*), 129.15 (*meta-Ph*), 132.79, (*ipso-Ph*), 170.8 (–C(O)O–).
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26. The role played by the metal cations ( $Na^+$ ,  $K^+$ ) could be quite complex. It is known that Group I cations can interact with organic substrates in organic solvents behaving essentially as weak Lewis acids (Stanley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920–5921; Wieting, R. D.; Stanley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 924–926). At the same time the metal cation could shift the equilibrium toward the products by stabilizing the carboxylate or carbonate anions. The precipitation of the salts may also drive the reaction to the products.
27. *Synthesis of  $\alpha$ -alkylidene cyclic carbonates*: In a case experiment: 0.79 mmol of 1,3-dialkylimidazolium-2-carboxylate and 10.3 mmol of the propargyl alcohol were placed, under nitrogen atmosphere, into a glass reactor of a magnetically stirred stainless steel autoclave and added with 4 mL of dry  $CH_3CN$ . After closing the autoclave, it was pressurized by  $CO_2$ , and the mixture was heated to 100 °C for 15 h under continuous stirring ( $P_{CO_2} = 60$  bar). The reaction was then stopped by cooling and depressurizing the autoclave, and the reaction mixture was analyzed via GC. The products were isolated by silica gel column chromatography. Carbonates **12a–d** are known compounds. Spectroscopic data for products were in agreement with those reported in the literature: Joumier, J. M.; Fournier, J.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3271–3274.
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37. *Note*: most of data reported in the literature indicate that primary and secondary propargylic alcohols do not undergo carboxylative cyclization reaction. Recently Jiang et al.: Jiang, H.-F.; Wang, A.-Z.; Liu, H.-L.; Qi, C.-R. *Eur. J. Org. Chem.* **2008**, 2309–2312. reported the carboxylative cyclization of several secondary alcohols in  $SC-CO_2$ .
38. *Note*: Kayaki, H.; Ikariya, T. JP 2006137733, 2006; *Chem. Abstr.* **145**, 27996; These authors have used imidazol-2-ylidenes and imidazolin-2-ylidenes with 'Bu, 'Pr, 2,4,6-trimethylphenyl N-substituents as well as some thiazol-2-ylidenes. The internal alcohol 2-methyl-4-phenyl-3-butyn-2-ol gave the corresponding cyclic carbonate in 75% yield under 100 bar  $CO_2$  pressure. Our study was focused on the more reactive terminal propargylic alcohols.
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40. *Note*: yields in 4-methyl-5-methylen-4-phenyl-1,3-dioxolan-2-one (carbonate **12d**) reported from other Authors with different catalysts were (Refs. 29–35 of this Letter): 32% (Dixneuf et al., by using  $P^tBu_3$ : 100 °C,  $P_{CO_2} = 50$  bar, 20 h, catalyst loading 8%), 51% (Inoue et al., by using  $K_2CO_3/CE$ , 80 °C,  $P_{CO_2} = 5$  bar, 50 h, catalyst loading 25%), 45% (Deng et al., by using Cu/ionic liquid, 120 °C,  $P_{CO_2} = 10$  bar, 8 h, catalyst loading 2%). The product was not obtained working with Cu/polymer supported catalyst in  $SC-CO_2$  (Jiang et al.).
41. *Note*: it is worthy to note that  $Na_2CO_3$  itself cannot be used in the direct carboxylation of compounds with active hydrogen. To the best of our knowledge in the scientific literature can be found only one example of direct utilization of  $K_2CO_3$  in the carboxylation of acetophenone with  $CO_2$  by implementation of the mechanochemistry technique (Haruki, H. JP 55151532, 1980; *Chem. Abstr.* **1981**, *94*, 174894).