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# Synthesis of 5- to 8-membered cyclic carbonates from diols and CO<sub>2</sub>: a one-step, atmospheric pressure and ambient temperature procedure

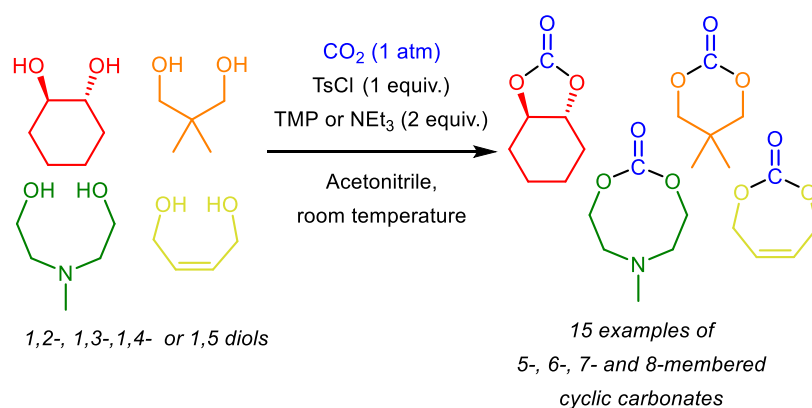
Thomas M. McGuire,<sup>a</sup> Eva M. López-Vidal,<sup>a</sup> Georgina L. Gregory<sup>a,b</sup> and Antoine Buchard<sup>a\*</sup>

<sup>a</sup> Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK. E-mail: a.buchard@bath.ac.uk.

Tel: +44 (0) 1225 386122; Fax: +44 (0) 1225 386231.

<sup>b</sup> Centre for Doctoral Training in Sustainable Chemical Technologies, University of Bath, Bath BA2 7AY, UK

## Abstract.



6-, 7- and 8-membered ring cyclic carbonates are of particular interest as monomers for ring-opening polymerisation towards more sustainable polymers. They are traditionally synthesised from diols and phosgene derivatives, and while alternative CO<sub>2</sub> methods exist to make 5- and 6-membered cyclic carbonates, there is no report of the synthesis of 7- and 8-membered cyclic carbonates made directly from CO<sub>2</sub>. Herein we report an efficient one-pot synthesis of cyclic carbonates which uses diols, CO<sub>2</sub>,

tosyl chloride and mild bases (NEt<sub>3</sub> or TMP), under ambient temperature and 1 atm of CO<sub>2</sub> pressure. Fifteen cyclic carbonates were synthesised, including twelve known monomers, and the first examples of 7- and 8-membered cyclic carbonates made using CO<sub>2</sub>.

**Highlights:**

- Cyclic carbonates are made in one step from CO<sub>2</sub> and diols.
- The method works at ambient temperature and 1 atm. of CO<sub>2</sub> pressure.
- No strong and moisture sensitive bases are needed, only common lab reagents.
- Fifteen 5- to 8-membered cyclic carbonates were synthesised, including twelve known monomers and three novel compounds.
- Six 7- and 8-membered cyclic carbonates were made for the first time using CO<sub>2</sub>.

**Keywords:** Carbon dioxide; Cyclization; Diols; Cyclic carbonates; Monomers.

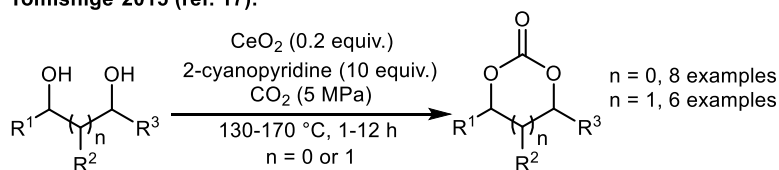
## 1. Introduction

The combination of depleting fossil fuel resources and the environmental persistence of traditional petroleum-derived polymers has been fuelling a wide research interest into sustainable polymers. Poly(carbonates) have been identified as promising such materials[1] as they can be obtained from natural feedstocks [2, 3], and show biodegradability [4, 5] and comparable thermal properties to crude-oil derived plastics [6-8]. Traditionally, the production of poly(carbonates) relies on the utilisation of phosgene and its derivatives, including dialkyl or diaryl carbonates, either by direct polycondensation with diols [9-12], or *via* the ring-opening polymerisation (ROP) of phosgene-derived, cyclic carbonate monomers (usually 6-, 7-, 8- or strained 5-membered rings) [13-15]. CO<sub>2</sub> has been investigated as a cheap, non-toxic, abundant, and renewable replacement for phosgene in these applications, primarily via its utilisation in the synthesis of dialkyl carbonates [16, 17]. The direct coupling of CO<sub>2</sub> with epoxides (or oxetanes) to form cyclic [18, 19] or polycarbonates [20, 21] is now also a well-established reaction, however it suffers from several limitations, such as restricted access to substrates and monomer units limited to 5 or 6 atoms. Broadening the scope of CO<sub>2</sub> utilisation to polymer with longer linkages is worth pursuing as poly(carbonates) made by ring-opening polymerisation (ROP) of functionalised 8-membered cyclic carbonates have for example recently shown great potential, including in the

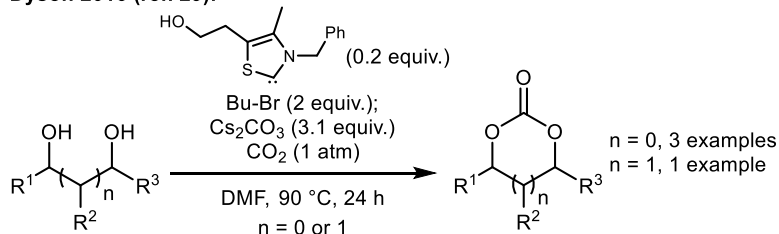
biomedical field [14, 22-24]. It would also allow to incorporate a wider range of bio-based molecules into sustainable polycarbonates. However, there is currently no reported synthetic procedure to make such large rings from CO<sub>2</sub>.

The direct coupling of CO<sub>2</sub> with diols to form cyclic and poly(carbonates) has the potential to realise this goal as diols with potentially any structure and linkages length could be in theory be used. However, this ideal reaction is limited by kinetics and thermodynamics [25], and consequently, while several homogeneous and heterogeneous catalytic protocols have been developed [26-31], they require a large excess of chemical dehydrating agents to obtain high yields (e.g. propylene oxide [32], 2-cyanopyridine [26, 27] or bromobutane [29]). Furthermore, very few of these procedures work under low CO<sub>2</sub> pressure, or have been applied to substrates other than 1,2-diols. It is indeed worth mentioning that 5-membered cyclic carbonates are usually not prone to ring-opening polymerisation (except when their ring-strain is large, as for products 8b and 9b, *vide infra*). Scheme 1 presents some of the methodologies reported for the direct coupling of CO<sub>2</sub> with 1,3-diols into 6-membered cyclic carbonates monomers. Recently, we developed a 2-step procedure that used strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and a tosyl chloride/triethylamine (NEt<sub>3</sub>) leaving/dehydrating group strategy, to form 6-membered cyclic carbonates at ambient temperature and low CO<sub>2</sub> pressure in chloroform (Scheme 1) [33]. This procedure has since been applied in the synthesis of chiral sugar-based cyclic carbonate monomers, the resulting polymer of which displayed interesting thermal properties, semi-crystallinity and functionalisation potential [34-36]. However, this methodology has been hampered by the need for two sequential steps, as well as the use of a strong and moisture sensitive base (DBU).

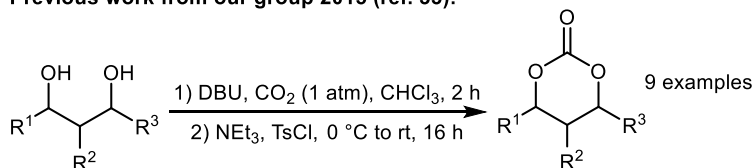
Tomishige 2015 (ref. 17):



Dyson 2016 (ref. 29):



Previous work from our group 2015 (ref. 33):

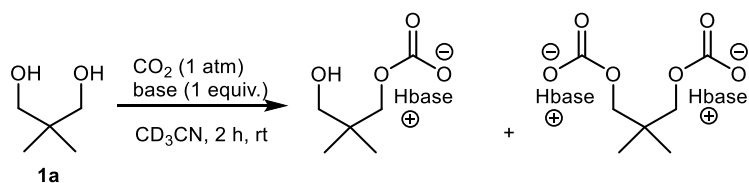


**Scheme 1.** Key papers on the direct coupling of CO<sub>2</sub> with diols into cyclic carbonates monomers (6-membered rings). (1 column figure)

Herein, we report a simplified one pot/one step procedure for the synthesis of cyclic carbonate from diols using only stoichiometric amounts of tosyl chloride and mild bases (all common reagents, and more benign than traditional phosgene derivatives such as triphosgene), under 1 atm. of CO<sub>2</sub> pressure and at ambient temperature. The protocol has been successfully applied to the synthesis of a wide scope of cyclic carbonates, including the first reported examples of 7- and 8-membered cyclic carbonates synthesised directly from CO<sub>2</sub> and three novel compounds.

## 2. Results and discussion

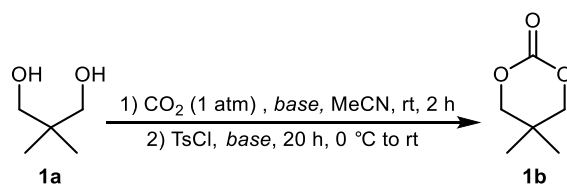
In a effort to increase the applicability of our previous approach, various commercially available mild bases were tested for CO<sub>2</sub> insertion with 2,2-dimethyl-1,3-propanediol, **1a** as the model substrate, and compared with DBU. In these tests, less toxic, non-chlorinated acetonitrile could advantageously replace the chloroform previously used. Compared with DBU, 2,2,6,6-tetramethylpiperidine (TMP) and NEt<sub>3</sub> were found to only promote a small amount of CO<sub>2</sub> mono-insertion into the diol (Table 1 and Fig. S32), in agreement with pKa considerations (18.6 and 18.8 respectively vs 24.3 for DBU in acetonitrile).[37, 38].

**Table 1.** CO<sub>2</sub> insertion into **1a** facilitated by pyridine, TMP, NEt<sub>3</sub> and DBU in CD<sub>3</sub>CN.<sup>[a]</sup>

Entry	Base	% Insertion	Monocarbonate	Biscarbonate
1	DBU	85%	59%	41%
2	TMP	2% <sup>[b]</sup>	100%	0%
3	NEt <sub>3</sub>	4%	100%	0%
4	Pyridine	0%	-	-

<sup>[a]</sup> **1a** (1.7 mol L<sup>-1</sup> in MeCN-D<sub>3</sub>), base (1 equiv.), CO<sub>2</sub> (1 atm), 2 h, room temperature (rt). <sup>[b]</sup> NMR taken in CDCl<sub>3</sub> due to insolubility of 2,2,6,6-tetramethylpiperidinium salts in CD<sub>3</sub>CN.

Nevertheless, the desired cyclic carbonate **1b** could be obtained more efficiently using NEt<sub>3</sub> and TMP than with the combination of DBU and NEt<sub>3</sub> (Table 2), including as previously reported in chloroform [33].

**Table 2.** One pot, two steps cyclocarbonation of **1a** with CO<sub>2</sub>.<sup>[a]</sup>

Entry	Base (1 <sup>st</sup> equiv.)	Base (2 <sup>nd</sup> equiv.)	Conversion to cyclic carbonate <b>1b</b> <sup>[b]</sup>
1	DBU	NEt <sub>3</sub>	78%
2	NEt <sub>3</sub>	NEt <sub>3</sub>	81%
3	TMP	TMP	89%

<sup>[a]</sup> One pot, two steps procedure: diol (1.7 mol L<sup>-1</sup> in MeCN), DBU (1 equiv.), CO<sub>2</sub> (1 atm), 2 h, then NEt<sub>3</sub> (1 equiv.), TsCl (1 equiv., 0.5 mol L<sup>-1</sup>), 0 °C to rt. Final diol concentration is then 0.4 mol L<sup>-1</sup>. <sup>[b]</sup> Determined by relative integration in the <sup>1</sup>H spectrum (CDCl<sub>3</sub>) of product methylene signal (4.01 ppm, 4H) vs aromatic signal in internal standard 1,3,5-trimethoxybenzene (6.01 ppm, 3H).

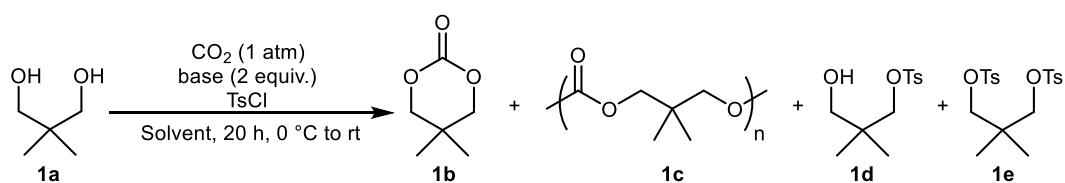
Furthermore, we pleasingly found that the reaction could be carried out in a single step, without the need for sequential addition of reagents, and that the cyclic carbonate product, **1b**, then formed in higher conversion than with our previous DBU-based, two step procedure (Table 3, entries 2 and 7 vs. entry 1). Conversion and selectivity of the reaction with both NEt<sub>3</sub> and TMP was however found to be

highly dependent on the solvent, with maximum product formation and best selectivity observed in acetonitrile (Table 3, entries 2-4 and 7, 12-13).

Formation of **1b** also significantly decreased with increasing temperature (Table 3, entries 5-6 vs entry 2), alongside a higher proportion of tosylated side products (higher temperatures favouring deinsertion of CO<sub>2</sub>) and of oligomers (likely due to oligomerisation of **1b** promoted by higher temperatures). The concentration of diol in solution had limited impact on the conversion of the diol **1a** as well as on the selectivity of the reaction (Table 3, entries 8-10 vs entry 7). Reactions in bulk diol (when possible) only led to oligomeric products.

The use of two equivalents of strong bases (DBU or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)) resulted in poor conversion and in a significant proportion of oligomeric products (Table 3, entries 14-15). This is likely due to an increased formation of the bis-carbonate intermediate [33] (DFT suggesting that cyclisation is then hindered by a high activation barrier (Fig. S36)), as well as *in-situ* polymerisation of the cyclic carbonate catalysed by DBU or TBD, respectively. Less bulky base 4-dimethylaminopyridine (DMAP, pKa 17.9 in acetonitrile) as well as weaker bases such as 1-Me-imidazole and pyridine showed good diol conversion but poor selectivity for the desired cyclic carbonate, with a significant proportion of tosylated products (Table 3, entries 16-18), likely due to a lack of CO<sub>2</sub> insertion in the diol (Fig. S34). No cyclic carbonate was formed in the absence of base (Table 3, entry 19), and when using only one equivalent of NEt<sub>3</sub>, conversion was halved (Table 3, entry 2). We therefore propose that the first equivalent of base promotes mono-carbonation of the diol whilst the second equivalent activates the remaining alcohol moiety then traps the leaving tosylate group.

Finally, whilst our reactions were carried out using a CO<sub>2</sub> gas cylinder, the procedure could also be performed using sublimed dry ice (Fig. S1), with minimal effect on overall conversion, no effect on selectivity (Table 1, entry 11 vs entry 7), and significant increased applicability.

**Table 3.** One-pot, one step cyclocarbonation of 2,2-dimethyl-1,3-propanediol (**1a**), with CO<sub>2</sub>.<sup>[a]</sup>

Entry	Base	Solvent	T	% Diol conversion <sup>[b]</sup>	Cyclic carbonate <b>1b</b> :oligomers <b>1c</b> : <b>1d</b> : <b>1e</b> <sup>[c]</sup>
1 <sup>[d]</sup>	DBU/NEt <sub>3</sub>	MeCN	rt	95%	82:18:0:0
2	NEt <sub>3</sub>	MeCN	rt	91% [44%] <sup>[e]</sup>	100:0:0:0 [100:0:0:0] <sup>[e]</sup>
3	NEt <sub>3</sub>	DCM	rt	75%	87:13:0:0
4	NEt <sub>3</sub>	THF	rt	7%	100:0:0:0
5	NEt <sub>3</sub>	MeCN	40 °C	60%	91:0:8:2
6	NEt <sub>3</sub>	MeCN	60 °C	49%	67:11:18:4
7	TMP	MeCN	rt	95%	100:0:0:0
8 <sup>[f]</sup>	TMP	MeCN	rt	93%	100:0:0:0
9 <sup>[g]</sup>	TMP	MeCN	rt	95%	100:0:0:0
10 <sup>[h]</sup>	TMP	MeCN	rt	93%	100:0:0:0
11 <sup>[i]</sup>	TMP	MeCN	rt	88%	100:0:0:0
12	TMP	DCM	rt	30%	100:0:0:0
13	TMP	THF	rt	16%	100:0:0:0
14	TBD	MeCN	rt	56%	53:47:0:0
15	DBU	MeCN	rt	64%	60:40:0:0
16	DMAP	MeCN	rt	80%	34:18:26:22
17	1-Me-Imd	MeCN	rt	74%	7:10:51:32
18	Pyridine	MeCN	rt	80%	1:2:80:17
19	No base	MeCN	rt	0%	N/A

<sup>[a]</sup> One pot, one step procedure: diol (0.4 mol L<sup>-1</sup> in MeCN), base (2 equiv.), TsCl (1 equiv.), CO<sub>2</sub> (1 atm), 0 °C to rt (room temperature, unless stated otherwise). <sup>[b]</sup> Determined by relative integration in the <sup>1</sup>H spectrum (CDCl<sub>3</sub>) of starting product CH<sub>2</sub> signal (4.01 ppm, 4H) vs aromatic signal in internal standard 1,3,5-trimethoxybenzene (6.01 ppm, 3H) (Fig. S2). <sup>[c]</sup> Determined by relative integration in the <sup>1</sup>H spectrum (CDCl<sub>3</sub>) of product methylene signal (4.01 ppm, 4H) vs oligomer signals (3.2-3.4/3.6-3.8 ppm, 4H) vs monotosylated product signals (3.12 and 3.62 ppm, 2 × 2H) vs ditosylated product signal (3.53 ppm, 4H) vs aromatic signal in internal standard 1,3,5-trimethoxybenzene (6.01 ppm, 3H). <sup>[d]</sup> One pot, two steps procedure: diol (1.7 mol L<sup>-1</sup> in MeCN), DBU (1 equiv.), CO<sub>2</sub> (1 atm), 2 h, then NEt<sub>3</sub> (1 equiv.), TsCl (1 equiv., 0.5 mol L<sup>-1</sup>), 0 °C to rt (unless stated otherwise). Final diol

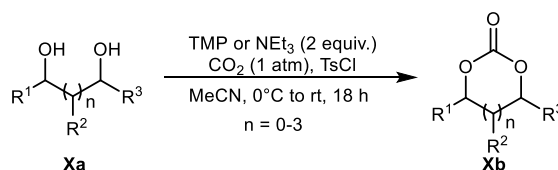


concentration is then 0.4 mol L<sup>-1</sup>. <sup>[e]</sup> Using only 1 equiv. of NEt<sub>3</sub>. <sup>[f]</sup> Diol concentration: 0.1 mol L<sup>-1</sup>. <sup>[g]</sup> Diol concentration: 0.8 mol L<sup>-1</sup>. <sup>[h]</sup> Diol concentration: 1.7 mol L<sup>-1</sup>. <sup>[i]</sup> Using sublimed solid CO<sub>2</sub> (dry ice). (1 column table and figure)

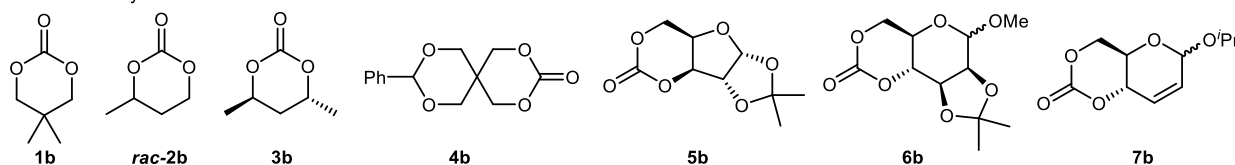
Next, the scope of these new reaction protocols was investigated (Table 4). Whilst in the case of 1,3-diol 2,2-dimethyl-1,3-propanediol, **1a**, using either TMP or NEt<sub>3</sub> had little impact on the diol conversion (95 vs 91% conversion, respectively, Table 3 entries 2 and 7), and no consequence on the selectivity of the reaction (100% selectivity towards the desired cyclic carbonate), for other substrates some differences were seen. In general, using TMP as a base was found to lead to higher overall conversion of the diol and greater selectivity towards the desired cyclic carbonates than when using NEt<sub>3</sub>, except for pentaerythritol-derived 1,3-diol, **4a**, and for 1,4-diol substrates **10a** and **11a** (Table 4, entries 4, 10-11). Using <sup>1</sup>H NMR spectroscopy side products were identified as oligomers formed and tosylated products (see Figs. S34-35).

Conversion and selectivity towards the cyclic carbonates was excellent for aliphatic and alicyclic 1,2- and 1,3-diols **1-4a** and **8a**, with isolated yields of the related 5- and 6-membered rings comparing well with (and in the case of **4b** exceeding) those observed with traditional phosgene methods (Table 4, entries 1-4 and 8). Sugar diols **5-7a**, despite being notoriously difficult to cyclise using phosgene derivatives could also be successfully transformed, albeit with lesser yields. In particular, the glucal-derived cyclic carbonate, **7b**, for which other direct CO<sub>2</sub>-diol coupling methods failed to give appreciable conversion [39], was found to form using TMP. When using 1,4- and 1,5-diols, lower selectivity towards the cyclic carbonates were observed, likely due to increased competing intermolecular condensation (increased backbone flexibility of the diols) and oligomerisation (increased ability to polymerise of the resulting cyclic carbonates) (Table 4, entries 10-15). Yet, the isolated yield of **10b** exceeds that obtained with phosgene (Table 4, entry 10) [47]. Furthermore, 7-membered cyclic carbonates **12b** and **13b**, as well as 8-membered cyclic carbonates **14b** are novel compounds. Notably, to the best of our knowledge, this represents the largest scope of any method yet reported for the coupling of CO<sub>2</sub> with diols, including the first report for the synthesis of 1,2-trans 5- and 7 and 8-membered cyclic carbonates using CO<sub>2</sub>.

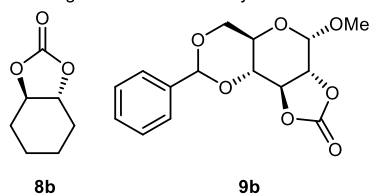
**Table 4.** Synthesis of various cyclic carbonates using CO<sub>2</sub>, and comparison with literature methods using phosgene derivatives.<sup>[a]</sup>



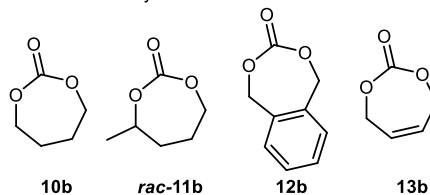
6-membered cyclic carbonates:



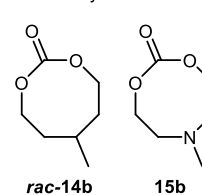
*trans*-configured 5-membered cyclic carbonates:



7-membered cyclic carbonates:



8-membered cyclic carbonates:

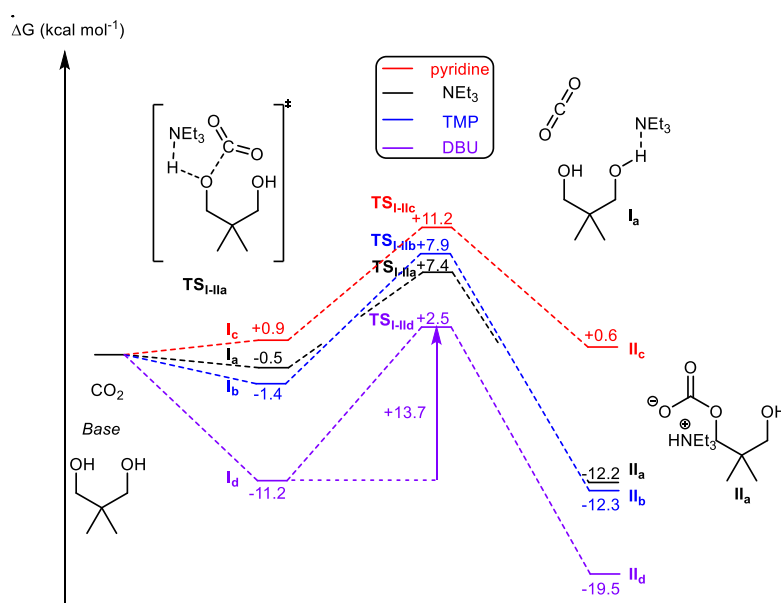


Entry	Cyclic Carbonate (CC)	Base: TMP % diol conversion [CC: oligomers: Ts products] <sup>[b]</sup>	Base: NEt <sub>3</sub> % diol conversion [CC: oligomers: Ts products] <sup>[b]</sup>	CC isolated yield <sup>[c]</sup>	Phosgene-derived protocol Yield (reagent) <sup>[d]</sup>
	1	<b>1b</b>	95% [95:0:0]	91% [91:0:0]	71%
2	<b>2b</b>	99% [99:0:0]	84% [75:3:6]	69%	86% (dimethyl carbonate)[41]
3	<b>3b</b>	97% [97:0:0]	89% [79:10:0]	63%	87% (triphosgene)[42]
4	<b>4b</b>	78% [78:0:0]	97% [97:0:0]	80% <sup>[c]</sup>	52% (ethylchloro-formate)[43]
5	<b>5b</b>	92% [64:0:28]	66% [46:0:20]	36%	53% (triphosgene)[44]
6	<b>6b</b>	87% [65:0:22]	74% [40:0:34]	55%	-
7	<b>7b</b>	44% [25:12:7]	29% [9:11:9]	21%	40% (triphosgene)[39]
8	<b>8b</b>	90% [90:0:0]	83% [76:0:7]	70%	84% (triphosgene)[45]
9	<b>9b</b>	81% [53:0:28]	70% [28:0:42]	51%	100% (triphosgene)[46]
10	<b>10b</b>	83% [45:38:0]	88% [76:12:0]	46% <sup>[c]</sup>	32% (phosgene)[47]
11	<b>11b</b>	77% [10:67:0]	53% [43:10:0]	31% <sup>[c]</sup>	51% (triphosgene)[48]
12	<b>12b</b>	96% [61:35:0]	72% [12:60:0]	34%	-
13	<b>13b</b>	92% [70:22:0]	83% [58:25:0]	61%	-
14	<b>14b</b>	87% [73:14:0]	94% [20:74:0]	43%	-
15	<b>15b</b>	84% [57:27:0]	83% [46:37:0]	32%	85% (triphosgene)[49]

<sup>[a]</sup> Diol (0.4 mol L<sup>-1</sup> in MeCN), TMP or NEt<sub>3</sub> (2 equiv.), TsCl (1 equiv.), CO<sub>2</sub> (1 atm), 0 °C to rt, 20 h (see ESI and footnote for detailed typical procedure). Diols **2a**, **11a** and **14a** were used as racemic mixtures, and **3a** is *trans*-1,2-cyclohexanediol. <sup>[b]</sup> Conversion were determined by relative integration in the <sup>1</sup>H spectrum (CDCl<sub>3</sub>) of products vs aromatic signal in internal standard 1,3,5-trimethoxybenzene (6.01 ppm, 3H). <sup>[c]</sup> Isolated yields were obtained from

reactions using TMP (the most selective towards the desired cyclic carbonates), except for entries 4, 10 and 11. <sup>[d]</sup> Yields from phosgene-derived methods were taken from the literature (best results according to Reaxys database accessed on 8/08/18). (2 column table and figure)

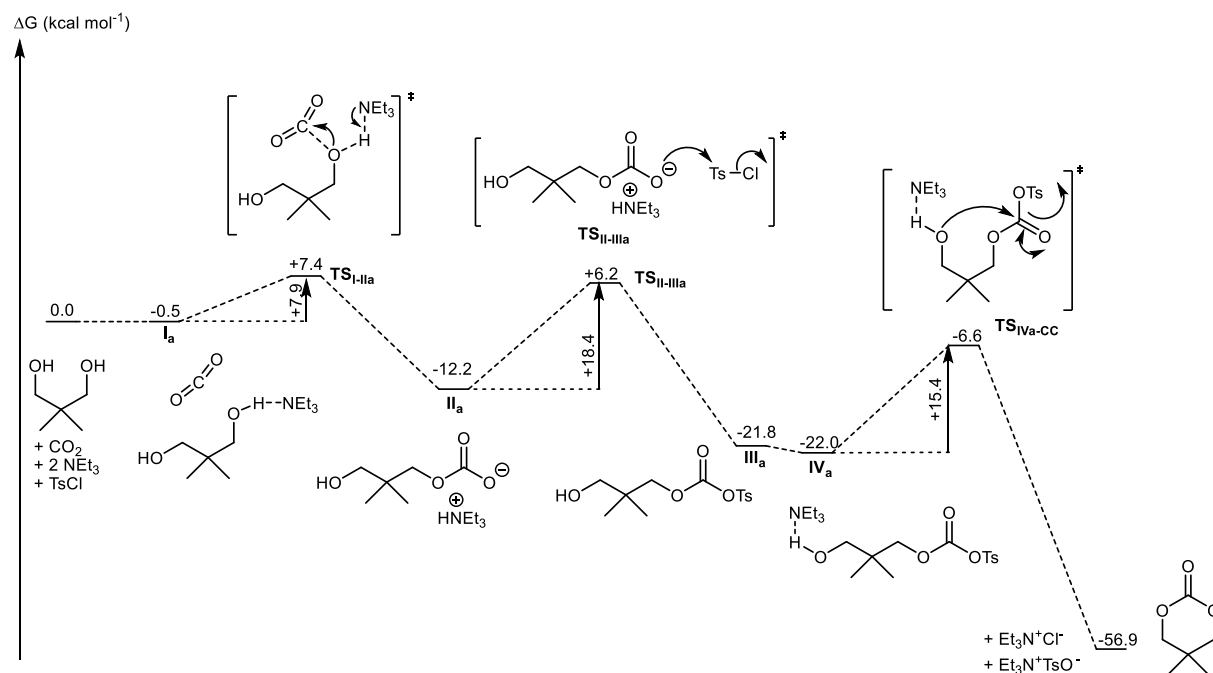
DFT calculations were carried out to shed some light on the reaction mechanism, using **1a** as the model substrate (details in ESI). In agreement with experiments using TMP and NEt<sub>3</sub> (Table 1) that could identified intermediate **IIa** by NMR spectroscopy, but only in small quantities, mono-insertion of CO<sub>2</sub> into the diol was found to be significantly less favoured for pyridine (no CO<sub>2</sub> insertion observed), NEt<sub>3</sub> and TMP than for DBU (+0.6, -12.2 and -12.8 kcal mol<sup>-1</sup> vs -19.5 kcal mol<sup>-1</sup>, respectively) (Fig. 1).



**Fig. 1.** Computed energy diagram for pyridine (red), NEt<sub>3</sub> (black), TMP (blue) and DBU (purple) facilitated CO<sub>2</sub> insertion of CO<sub>2</sub> into 2,2-dimethyl-1,3-propanediol (**1a**). Computed at the rwb97xD/6-31+g(d)/cpcm=acetonitrile/298K level of theory. Free enthalpies given in kcal mol<sup>-1</sup>. Geometries, energies and vibrational data are available for all structures, from output files in digital repository DOI: [10.6084/m9.figshare.5831538](https://doi.org/10.6084/m9.figshare.5831538).

The complete DFT-reaction profile was further calculated for NEt<sub>3</sub> due to the tendency of 2,2,6,6-tetramethylpiperidinium salts to precipitate from acetonitrile solution. Calculations suggest that CO<sub>2</sub> insertion happens first, and that the formation of the product proceeds *via* tosylation of the carbonate then addition/elimination (Fig. 2), rather than *via* tosylation of the alcohol then S<sub>N</sub>2-type cyclisation mechanism (activation barriers for tosylation step: +18.4 vs +20.0; for cyclisation: +15.4 vs +24.9 kcal mol<sup>-1</sup>, respectively) (see ESI Fig. S37). The stereochemistry of the diol is therefore expected to be

retained in the cyclic carbonate product. This was confirmed experimentally by  $^1\text{H}$  NMR spectroscopy (furthermore for all bases tested), when using diastereotopic 2,4-R,R- pentanediol, **3a** and 1,2-transcyclohexanediol, **8a**, (Table 2, entries 3 and 8).



**Fig. 2.** DFT computed free enthalpy diagram for the cyclocarbonation of **1a** with  $\text{CO}_2$  using 2 equiv. of  $\text{NEt}_3$  and 1 equiv. of  $\text{TsCl}$  (pathway of less energy, for alternative routes see ESI section 4.3). Protocol: rwb97xD/6-31+g(d)/cpcm=acetonitrile/298K. Geometries, energies and vibrational data are available for all structures, including for alternative pathways, from output files in digital repository [DOI: 10.6084/m9.figshare.5831538](https://doi.org/10.6084/m9.figshare.5831538). (2 column figure)

### 3. Conclusion

In summary, a one-step methodology for the coupling of  $\text{CO}_2$  with diols to form cyclic carbonates has been developed, which avoids the use of strong moisture sensitive bases, can use sublimed dry ice as a source  $\text{CO}_2$ , and has a wide substrate scope, in particular towards cyclic carbonate monomers. We also report the first synthesis of 7- and 8-membered cyclic carbonates from  $\text{CO}_2$ , including three novel compounds. Furthermore, yields obtained are comparable, and in some instances, exceed, those observed with phosgene methods.

## 4. Experimental

Typical procedure for the synthesis of cyclic carbonate: A 0.40 mol L<sup>-1</sup> solution of diol (1.70 mmol) and tosylchloride (325 mg, 1.7 mmol, 1 equiv.) in anhydrous acetonitrile (4.3 mL) is prepared in a flask. The atmosphere of the flask is exchanged for CO<sub>2</sub> and the solution saturated with CO<sub>2</sub>. Under a continuous feed of gas, TMP (575 μL, 3.40 mmol, 2 equiv.) is added dropwise at 0 °C, then the reaction is left to reach room temperature and stirring. After approximately 20 minutes, a bright white precipitate forms and CO<sub>2</sub> stopped being fed to the vessel. After 20 hours, the reaction mixture is diluted with non-anhydrous acetonitrile (10 mL) and the liquid phase separated by centrifugation (3 x 5 minutes at 3000 rpm). The solvent is then removed *in vacuo*. Purification by column chromatography (diameter of column = 1.5 cm, mass of silica = 19.0 g, 1-20% acetone/CHCl<sub>3</sub> or 1:1 EtOAc:Hex (for (4aR,8aS)-6-isopropoxy-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-2-one, **7b**)) affords the cyclic carbonate product. \*The procedure is identical when using NEt<sub>3</sub> instead of TMP, but without the need for the centrifugation step.

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## Appendix A. Supplementary Data

Appendix A contains full experimental and spectroscopy data, DFT calculations data and associated digital repositories.

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