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Cyclic carbonates through the photo-induced carboxylative cyclization of allylic alcohol with CO₂: a comprehensive kinetic study of the reaction mechanism by in-situ ATR-IR spectroscopy.

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Abstract: A one-pot multicomponent green process is investigated for the synthesis of perfluoroalkylated cyclic carbonate which merges the photo-promoted Atom Transfer Radical Addition (ATRA) of a perfluoroalkyl iodide (Rf-I) onto allyl alcohols with the Lewis base promoted carboxylative cyclization. The evolution of the complex mixture during the reaction was monitored by in-situ ATR-IR and Raman spectroscopies that provided insights into the reaction mechanism. The effect on the kinetics and the carbonate yields of key parameters such as the stoichiometry of reagents, the nature of the Lewis base and the solvent, the temperature and the pressure of the solvent were evaluated. It was found that high yields were obtained using strong Lewis bases that played both the role of activating the allyl alcohol for the generation of the allyl carbonate in the presence of CO₂ and promoting the ATRA reaction through the activation of C₄F₉I by halogen bonding. This protocol was also extended to various unsaturated alcohols.

Keywords: CO₂ organocatalysis; photo-promoted ATRA; cyclic carbonates;

1. Introduction

During the last decade, many academic and industrial researches have been devoted to the development of sustainable synthetic pathways to produce five membered cyclic carbonates by the catalytic coupling of CO₂ with epoxides [1-5] using appropriate organic or transition metal catalysts. This 100% atom economic reaction is very attractive as it represents a greener and safer alternative to the conventional synthesis of cyclic carbonates from diols and toxic phosgene. Today, these precursors find applications as electrolytes in Li-ion batteries, intermediates for fine chemical synthesis and polar aprotic solvents replacing DMF, DMSO, NMP and acetonitrile. [6] They also serve as raw materials for the synthesis of polycarbonates [7, 8] and isocyanate-free polyurethanes [9-12] (NIPUs) that become more and more attractive for industry as an alternative to classical polyurethanes (PUs). In view of the broad scope of applications of cyclic carbonates and their strong economic potential, there is still a need to improve their synthesis and decrease their production costs. In particular, whereas the synthesis of terminal cyclic carbonates from the coupling of CO₂ with epoxides is well established, the conversion of internal tri- and tetra-substituted epoxides into their corresponding five membered carbonates is still very challenging even though of great interest. [13] On the other hand, the synthesis of six membered cyclic carbonates by oxetane/CO₂ coupling [13-15] remains challenging because of i) the lower reactivity of four membered ether rings compared to epoxides even

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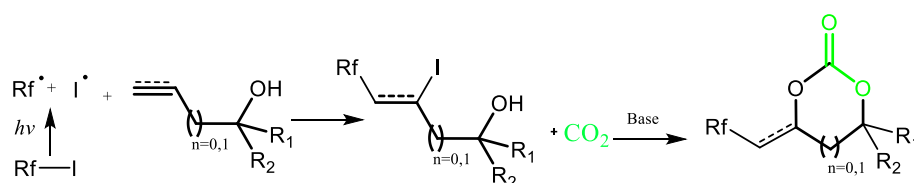


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under harsh experimental conditions, and ii) a poor reaction selectivity. Interestingly, α -alkylidene cyclic carbonates that are synthesized by coupling CO₂ with propargylic alcohols using organocatalysts or metal based catalysts are intermediates of great interest in organic and polymer synthesis. [16-24] However, at present, the substrate scope is mainly restricted to tertiary alcohols as only few examples are reported using primary and secondary alcohols.[25-27] Finally, 1,2 and 1,3-diols [28-32] were subjected to carbonation in order to afford five- and six-membered cyclic carbonates, respectively, but their reaction with CO₂ is limited due to the formation of water as a by-product. To circumvent this drawback, both homogeneous and heterogeneous catalysts (Bu₂SnO, K₂CO₃, CeO₂...) used in combination with dehydrating systems were developed.[33, 34] Although one efficient system involving CeO₂ as the catalyst and 2-Cyanopyridine as dehydrating agent has been developed [34], this process requires harsh reaction conditions (150 °C, 5 MPa) and a large excess of an expensive dehydrating agent. Alternative protocols have been recently suggested to overcome the limitation induced by the formation of water by combining the use of an organic base and an alkylating agent under mild conditions. For example, Zhang et al. [35] and Buchard et al. [36, 37] have combined strong Lewis bases and Tosyl chloride (TsCl) as the alkylating agent to promote the synthesis of 6-membered cyclic carbonates. A similar strategy has been proposed by Kitamura et al.[38] and Dyson et al. [31] using alkyl halides as the alkylating agents for the synthesis of cyclic carbonates. The effect of the addition of ionic liquids to these systems to obtain cyclic carbonates from diols was also investigated.[39] A critical assessment of the reaction mechanism at work in such metal-free dual activating systems for the coupling of CO₂ with 1,x-diols to afford (a)cyclic carbonates has been recently proposed by Brege et al. [40]. In particular, it was shown that choosing either DBU/EtBr or TEA/TsCl as the organic dual activating system, it was possible to control the product selectivity to substituted cyclic and/or acyclic carbonates depending on the nature of the substrate. Therefore, there is still a need to develop innovative routes to broaden the structural diversity of cyclic carbonates that could be exploited for the design of novel functionalized chemicals and polymers.

In this context, light-driven CO₂ fixation through C-C bond formation to give added value chemicals and monomers remains a relatively unexplored area although it represents a very promising field and a green attractive route.[41-45]

A recent review reports several typical examples on the photochemical fixation of CO₂ into heterocyclic scaffolds with detailed mechanistic descriptions of the various proposed synthetic routes.[46] For example, an original radical synthetic route was proposed for the synthesis of oxazolidinones through the photopromoted base-catalyzed coupling of CO₂ with allylamines [43] or propargyl amines [47] in the presence of perfluoroalkyl iodides and iodine, respectively. In the work by Wang et al. [43] allyl alcohols were investigated to a limited extent although the reaction could be very useful for the preparation of cyclic carbonates. Also, the proposed mechanism was supported by a few mechanistic experiments conducted mostly using ¹H NMR. Very recently, Jain et al. reported the first photochemical synthesis of linear carbonates from the reaction of CO₂ with alcohols using a silver-doped ceria nanocomposite at room temperature under visible light irradiation. [48] In this context, we decided to investigate the synthesis of cyclic carbonates through a one-pot multicomponent metal-free process which merges the photo-promoted Atom Transfer Radical Addition (ATRA) of a perfluoroalkyl iodide (Rf-I) onto unsaturated alcohols with the Lewis base promoted carboxylative cyclization (Scheme 1). A detailed *in situ* ATR-IR and Raman spectroscopic study led to the optimization of reaction conditions and provided insights into the reaction mechanism. In addition, the stoichiometry of reagents, the nature of the Lewis base, the effects of the temperature, the pressure and the solvent on the kinetics and the carbonate yields were evaluated. Finally, using optimized conditions, the carbonation scope was extended to a variety of unsaturated alcohol substrates.



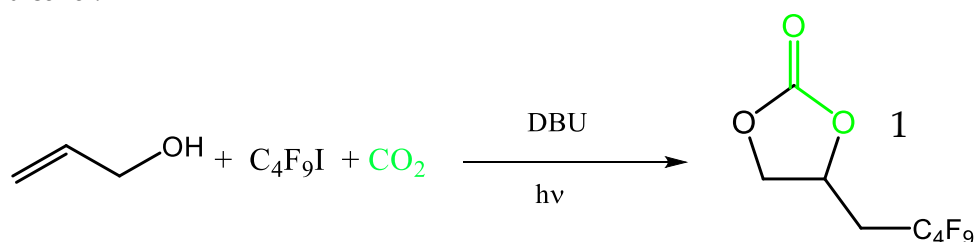
Scheme 1. Proposed synthesis of 5–6 membered cyclic carbonates through a photo-promoted ATRA reaction followed by a Lewis base-promoted carboxylative cyclization.

2. Results and discussion

2.1. Synthesis of perfluorobutyl cyclic carbonate **1** from the coupling of CO₂ with allylic alcohol and perfluorobutyl iodide: Mechanistic study

2.1.1. Model reaction using allyl alcohol, DBU and C₄F₉I

An *in-situ* ATR-IR/Raman kinetic study for the preparation of carbonate **1** was first performed under UVA irradiation at 365 nm (LED) in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), perfluorobutyl iodide (C₄F₉I) and allyl alcohol. The reaction was conducted in acetonitrile (CH₃CN) at T = 25 °C under a low carbon dioxide pressure of 0.3 MPa (Scheme 2) using a slight excess of DBU (1.05 eq) and C₄F₉I (1.25 eq) relative to allyl alcohol.



Scheme 2. Benchmark reaction for the synthesis of the perfluorobutyl carbonate **1**. DBUH⁺-I⁻ is obtained as a by-product.

Typical ATR-IR spectra of the mixture obtained at different reaction times are depicted in Fig. 1 where specific spectral signatures of reactants, intermediates and products could be identified. From the spectrum of the reaction mixture before the addition of CO₂, we have identified specific peaks of interest.

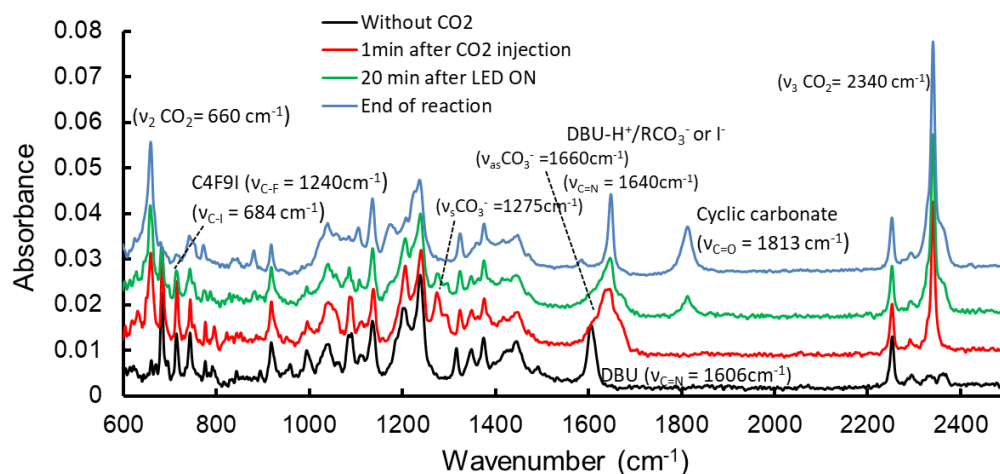


Figure 1. ATR-IR spectra of the reaction medium at several times during the reaction. Conditions: allyl alcohol (48 μL, 0.5 mmol), DBU (1.05 equiv.), C₄F₉I (1.25 equiv.), CH₃CN (1 mL), 25 °C, CO₂ (0.3 MPa), irradiation at 365 nm (LED) under stirring.

Before addition of CO₂ to the ternary mixture of allyl alcohol, DBU and C₄F₉I, a narrow band is observed at 1606 cm⁻¹ that is characteristic of the C=N stretching mode of DBU indicating that there is no specific interaction and/or reaction between DBU and another reactant of the mixture (black curve). In particular, there is no deprotonation of the alcohol moiety by DBU, as well as no alkylation of DBU by C₄F₉I. We have also identified a peak at 684 cm⁻¹ that is assigned to a C-I stretching mode coupled with the C-F bending modes of C₄F₉I. Unfortunately, we do not detect any contribution of the allyl alcohol. After the addition of CO₂ at a pressure of 0.3 MPa (red curve), the DBU absorption band shifts at 1642 cm⁻¹, which has been assigned to the C=NH⁺ stretching mode of protonated DBU. [40, 49] Concomitantly, a shoulder of this broad peak appears around 1660 cm⁻¹, as well as a new peak at 1275 cm⁻¹, both being attributed to C-O stretching modes of the allyl carbonate anion CH₂=CHCH₂CO₃⁻. [50] Thus in the dark, a trimolecular reaction between CO₂, allyl alcohol and DBU occurs which leads to the formation of the organic salt CH₂=CHCH₂CO₃⁻/DBUH⁺. We emphasize that the peak of DBU is barely detected as a shoulder at about 1606 cm⁻¹ whose intensity gives an estimated concentration between 0.05 and 0.1eq of DBU still present in the mixture under these experimental conditions that is consistent with the thermodynamic data of Heldebrant et al. [51]. Therefore, the allylic alcohol is quantitatively transformed into its carbonated form during this first step of the reaction that occurs within 5 minutes as it is mainly controlled by CO₂ solubilisation kinetic in the organic phase. Then, when the LED is switched ON and during the course of the kinetic (green and blue curves), the main absorption of DBUH⁺ is slightly shifted toward higher wavenumbers from 1642 cm⁻¹ to 1648 cm⁻¹ and gets thinner as the shoulder due to the carbonate anion tends to disappear. The slight shift is ascribed to anion metathesis of DBUH⁺/RCO₃⁻ to DBUH⁺/I⁻ that should occur upon carbonate cyclization (scheme 1). Accordingly, the characteristic peak of RCO₃⁻ at 1275 cm⁻¹ gets weaker as a function of time. Concomitantly, the new absorption band at 1813 cm⁻¹, assigned to the C=O stretching mode of the perfluoroalkylated cyclic carbonate, smoothly increases with time. In the same time the band at 684 cm⁻¹ associated with C₄F₉I has vanished at the end of the reaction. We emphasize that the intermediate ATRA product with the formation of a C-I bond was not detectable in our experimental conditions as the C-I stretching mode is observable by ATR-IR at wavenumbers lower than 600 cm⁻¹. Thus, the rate of the concentration evolution of C₄F₉I, RCO₃⁻, and the cyclic carbonate could be monitored by ATR-IR from the height of the peak at 684 cm⁻¹, 1275 cm⁻¹ and 1813 cm⁻¹, respectively. To have complementary information from the allyl function of the alcohol that is not detectable by ATR-IR, the kinetic of the same model reaction was monitored by in-situ Raman spectroscopy in order to follow the evolution of the height of the peak at 1645 cm⁻¹ characteristic of the C=C bond of the allyl alcohol (or allyl carbonate anion at the same wavenumber) and that of cyclic carbonate observed at 1813 cm⁻¹ (see ESI Figure S1).

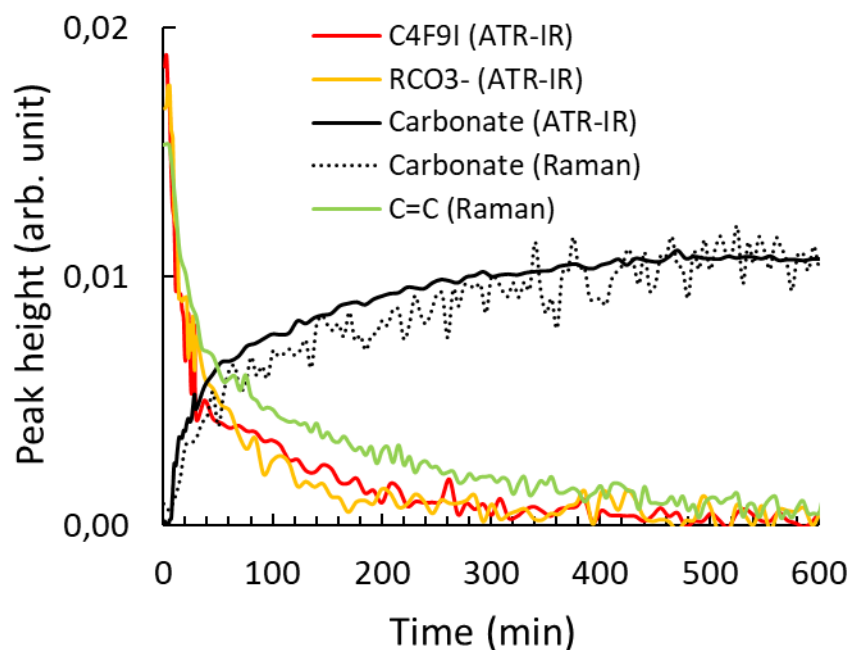


Figure 2. Kinetic profiles followed on the same model reaction by ATR-IR and Raman spectroscopies. The kinetics were recorded once the LED (365 nm) was switched on, i.e. 5 min after the solution containing the allyl alcohol (0.5 mmol), DBU (1.05 equiv.), C₄F₉I (1.25 equiv.), CO₂ (0.3 MPa) in CH₃CN (1 mL) has been prepared.

Figure 2 displays the kinetic profiles of the disappearance of the C₄F₉I substrate and allyl carbonate intermediate generated quantitatively before irradiation, as well as of the appearance of the cyclic carbonate product **1**. For comparison, the kinetic profiles of the cyclic carbonate bands measured in Raman and ATR-IR have been scaled to their maximum intensity at 600 minutes. By the same token, the maximum of the kinetic profile at $t=0$ of the C=C and RCO₃⁻ band have been scaled at about the maximum peak height of the C₄F₉I band. Good agreement is observed between the IR and Raman follow-ups of the cyclic carbonates thus validating the repeatability of our experimental procedure. The profiles show that the reaction is completed in about 8 h, time after which the reagents have been fully consumed, while the cyclic carbonate **1** was formed with a yield > 95% as determined by ATR-IR using equation (1) in paragraph 3.3. The reaction thus occurs with an excellent selectivity. The ATRA process is supported by the smooth decrease of the intensity of the Raman band assigned to the C=C stretching mode of the allyl carbonate. Interestingly, the kinetic profiles reveal that the rates of formation of **1** and consumption of the allyl carbonate and C₄F₉I occurs with the same rates, thus showing that the rate of the intramolecular cyclization is much higher than that of the ATRA process.

2.1.2. Effect of reagent stoichiometry

In order to investigate the influence of the stoichiometry of DBU and C₄F₉I on the reaction outcome, *in situ* ATR-IR kinetic studies of the photoinduced carboxylative coupling of CO₂ with allyl alcohol were performed.

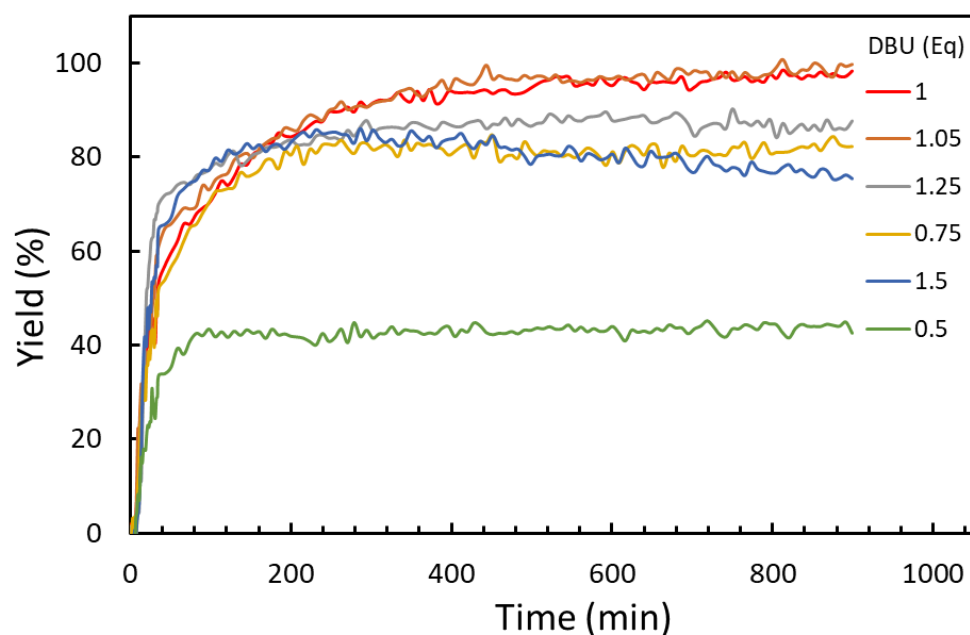


Figure 3. Influence of the amount of DBU on the rate of formation and yield of carbonate **1** followed in situ by ATR-IR spectroscopy. Conditions: allyl alcohol (48 μ L, 0.5 mmol), DBU (0.5-1.5 equiv.), C_4F_9I (1.25 equiv.), CH_3CN (1 mL), 25 $^{\circ}C$, CO_2 (0.3 MPa), $h\nu = 365$ nm (LED).

Fixing the amount of C_4F_9I (1.25 equiv.), the quantity of DBU was varied from 0.5 to 1.5 equiv. (see figure 3). While increasing the amount of DBU from 0.5 to 1.5 equiv. did not affect the initial reaction rates, lower yields of **1** were obtained when deviating from the optimal amount of about 1-1.05 equiv. Using 0.5 and 0.75 equiv. of DBU led to decreased yields of **1** by about ~ 55% and 20%, respectively. This is what is expected when considering the mechanism of scheme 1 in which the DBU combined with CO_2 , first reacts quickly and quantitatively in the dark with allyl alcohol to generate the allyl carbonate/DBUH⁺ ion pair which then, under light irradiation undergoes the ATRA reaction followed by intramolecular cyclization to deliver **1** and DBUH⁺/I⁻. More surprising is the detrimental effect on the yield when using an excess of DBU, the yield of **1** decreasing of ~ 10% and 20% with 1.25 and 1.5 equiv. of DBU, respectively. In agreement with our previous study,^[52] this could be ascribed to the side-reactivity of DBU with RfI, most probably to generate DBUC₄F₉H⁺-I⁻. This would ultimately lead to the consumption of a significant amount of RfI.

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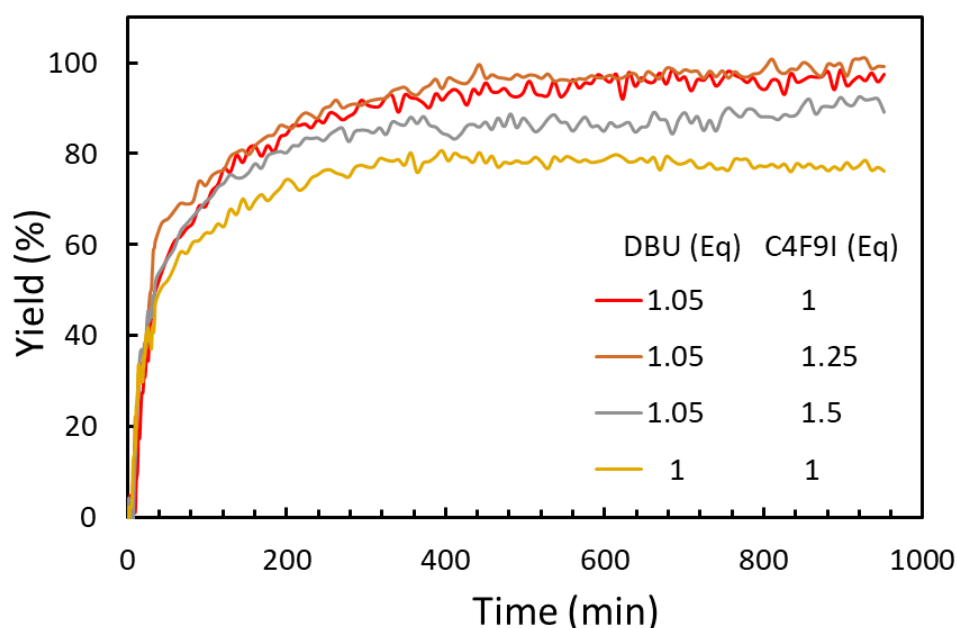


Figure 4. Influence of the amount of C₄F₉I on the kinetic of formation of perfluorobutyl carbonate followed by in situ ATR-IR spectroscopy. Conditions: allyl alcohol (48 μL, 0.5 mmol), DBU (1.05-1 equiv.), C₄F₉I (1-1.5 equiv.), CH₃CN (1 mL), 25 °C, CO₂ (0.3 MPa), *hν* = 365 nm (LED).

Then, using a slight excess amount of DBU (1.05 equiv.), we have varied the quantity of C₄F₉I from 1 to 1.5 equiv. (see figure 4). Although a barely detected improvement of the yield is observed upon an increase of the amount of C₄F₉I from 1 to 1.25, a further increase of the amount of C₄F₉I up to 1.5 equiv. has a detrimental effect on the yield. Finally, using 1 equiv. of DBU and 1 equiv. of C₄F₉I led to a significantly reduced yield.

Therefore, to further investigate our model reaction, we have used an excess amount of DBU (1.05 equiv.) and C₄F₉I (1.25 equiv.) for which we obtained the maximum yield.

2.1.3. Halogen bonding effect

The presence of DBU is mandatory in order to deprotonate the allyl alcohol in the presence of CO₂ to form the allyl carbonate anion. We have also shown recently that DBU could form a halogen bond with RfI [52] thus potentially weakening the Rf-I bond, but also that the UV-absorption of the [RfI-DBU] halogen bond complex was enhanced and red-shifted compared to that of RfI, thus facilitating the direct photolysis of the Rf-I bond to generate Rf radicals which initiate a radical chain process.[53] In order to verify that halogen bonding is playing a key role for the ATRA reaction, we performed first a reaction without DBU. The follow-up of the reaction displayed in figure 5 revealed that the peak height of C₄F₉I at 684 cm⁻¹ was constant over time hence showing that C₄F₉I was not consumed during the reaction, confirming that DBU was playing a crucial role in the ATRA process. A reaction was then performed using allyl benzene as a substrate in the presence of catalytic amount of DBU, i.e. 10 mol%. Allyl benzene was chosen in order to avoid the presence of the hydroxyl group on the substrate in order to avoid the carbonation step promoted by DBU and leading to its protonation. As seen in figure 5, using a catalytic amount of DBU, a fast consumption of C₄F₉I is observed, i.e. ~ 50% in 40 min while full consumption is achieved in about 5h. Therefore, as reported before, [52] DBU catalyzes the light-promoted iodoperfluoroalkylation reaction, most likely thanks to an halogen bond interaction with C₄F₉I. Thus, in the photo-induced carboxylative cyclization reaction, the Bronsted and Lewis basicities of DBU are both playing a key role.

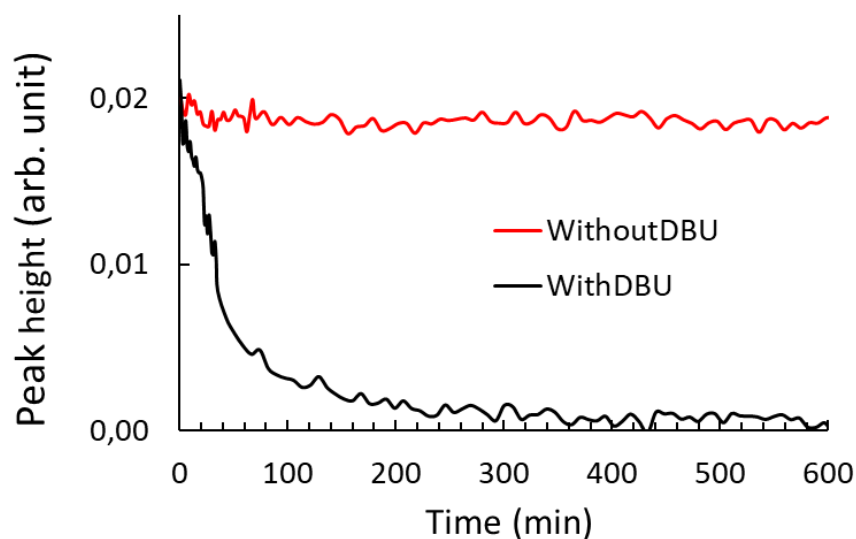


Figure 5. Evolution of the height of the peak at 684 cm^{-1} of $\text{C}_4\text{F}_9\text{I}$ in the presence of DBU (with allyl benzene) or without DBU (with allyl alcohol) followed by in situ ATR-IR spectroscopy. Conditions: allyl alcohol or allyl benzene (0.5 mmol) without DBU or DBU (0.1 equiv.) respectively, $\text{C}_4\text{F}_9\text{I}$ (1.25 equiv.), CH_3CN (1 mL), $25\text{ }^\circ\text{C}$, CO_2 (0.3 MPa), $h\nu = 365\text{ nm}$ (LED).

2.1.4. Lewis base effect

The influence of the nature of the base, i.e. tertiary amines (TEA, TMEDA, DABCO) and guanidines (TMG, MTBD), was then studied on the model reaction.

In comparison with the reference amidine (DBU), the acyclic guanidine (TMG) showed similar reactivity, although the rate of formation of the cyclic carbonate with TMG is significantly faster. A fast initial rate is also observed with the cyclic guanidine MTBD but the reaction stops at $\sim 65\%$. This could be ascribed to secondary reactions such as the nucleophilic attack of the allyl alcohol to **1** that that was shown to occur in the MTBD-catalysed coupling of 2-methyl-3-butyn-2-ol with CO_2 .^[20] Alternatively, the strong absorption of the MTBD-RfI halogen bonded complex in the UVA spectral range as reported in reference ^[52] could be responsible for secondary photochemical reactions that would ultimately lead to the consumption of a significant amount of RfI.

Using tertiary amines, the reaction proceeds at a very slow rate, the yields of cyclic carbonate after 15 h reaching only $\sim 25\%$ with TEA and $\sim 15\%$ with TMEDA and DABCO. Therefore, it appears that although strong (Brønsted/Lewis) bases are needed in order to reach high yields for such reaction, TMG and DBU displays the higher selectivity towards the synthesis of **1**.

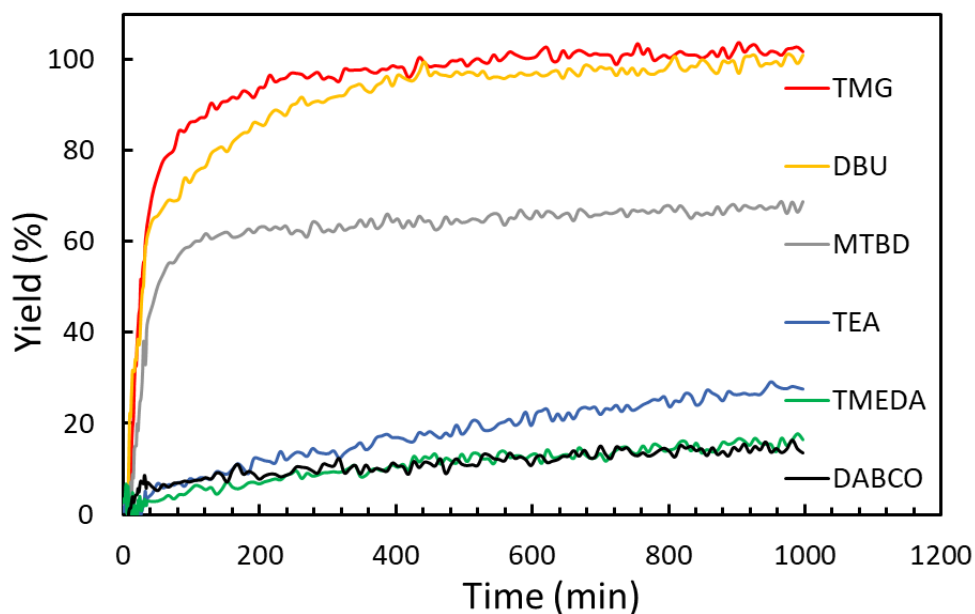
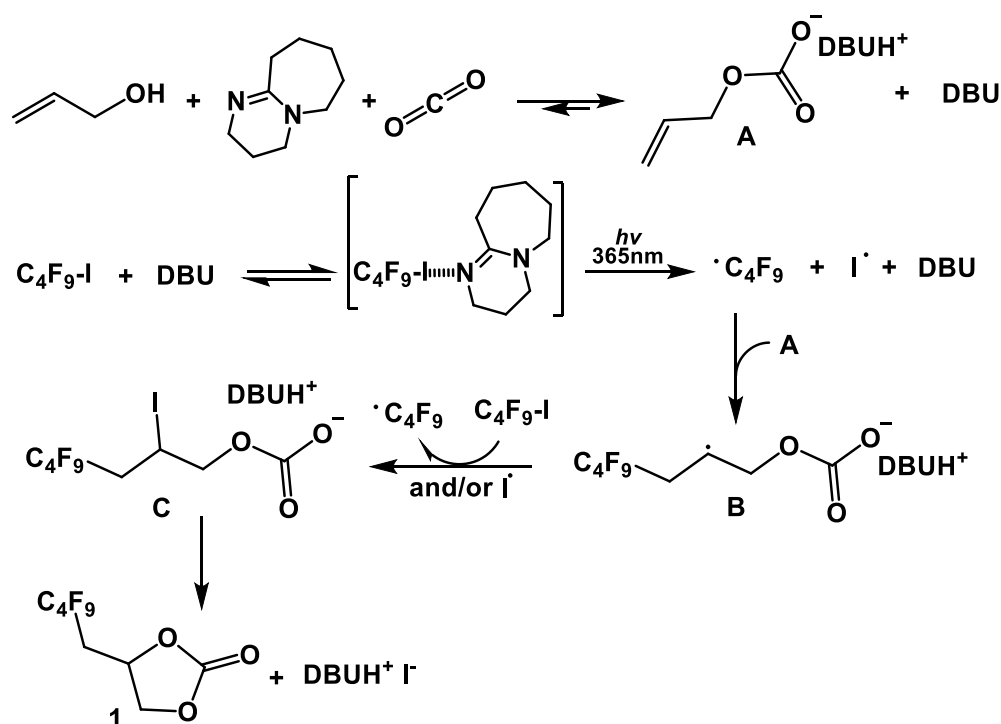


Figure 6. Influence of the nature of the base on the kinetic of formation of perfluorobutyl carbonate followed by in situ ATR-IR spectroscopy. Conditions: allyl alcohol (48 μ L, 0.5 mmol), Base (1.05 equiv.), C_4F_9I (1.25 equiv.), CH_3CN (1 mL), 25 $^{\circ}C$, CO_2 (0.3 MPa), $h\nu = 365$ nm (LED).

2.1.5. Mechanism

Thus, from the experimental results obtained above, a plausible mechanism for the photoinduced carboxylative coupling of CO_2 with allyl alcohol is depicted in Scheme (3).

The first step, which occurs in the dark during the preparation of the reaction mixture, is the carbonation of the alcohol group that leads to the carbonate **A** along with unreacted DBU (~ 10%). When the LED is switched on, the CF_2-I bond activated by DBU through a halogen bond undergoes a homolytic cleavage to generate $I\bullet$ and $C_4F_9\bullet$ radicals, the latter adding onto carbonate **A** to give the radical intermediate **B**. **B** could then react with $I\bullet$ or, more likely, abstracts the iodine atom of C_4F_9I to afford the iodocarbonate **C** and $C_4F_9\bullet$ which propagates a radical chain process. Finally, the fast intramolecular cyclization affords the cyclic carbonate **1** along with $DBUH^+I^-$.



Scheme 3. Mechanism proposal for the formation of the perfluorobutyl carbonate 1.

2.2. Influence of experimental parameters

Considering the model reaction using allyl alcohol, 1.05eq DBU and 1.25eq $\text{C}_4\text{F}_9\text{I}$, the influence of different reaction conditions on kinetics and yields for the formation of perfluorobutyl cyclic carbonate were investigated including the temperature, the pressure, the irradiation wavelength and the nature of the solvent.

2.2.1. Temperature and pressure effect.

The influence of the temperature on the kinetics and yields is illustrated in Fig. 7. At a fixed pressure of 0.3 MPa, the temperature increase from 25 °C to 50 °C did not affect the reaction significantly. In contrast, heating up to 70 °C led to a maximum yield of about 30%. This agrees with previous works who showed that the carbonation of alcohols promoted by a super base such as DBU is exothermic and highly effective at room temperature, and that heating at 90 °C shifted the equilibrium towards the starting reactants.[51, 54]

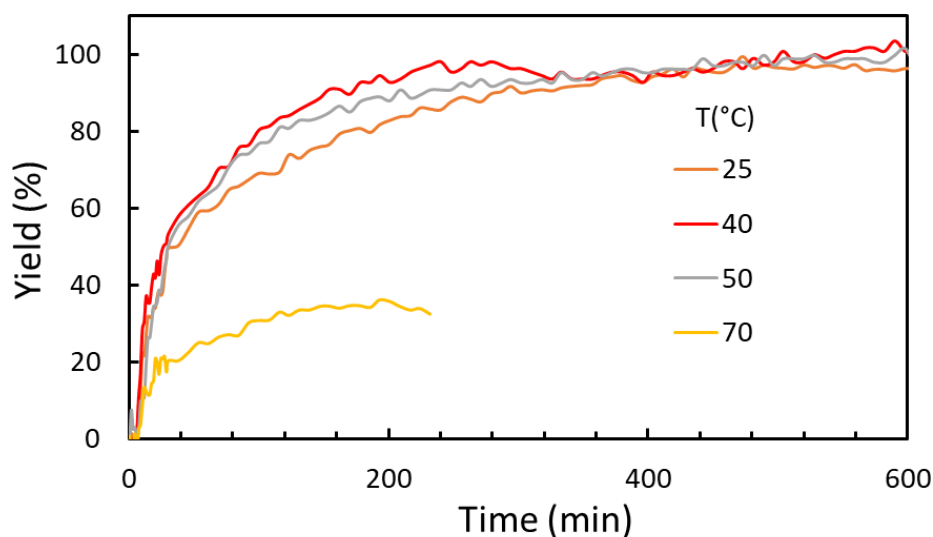


Figure 7. Influence of temperature on the kinetic of formation of **1** followed by in situ ATR-IR spectroscopy. Conditions: allyl alcohol (48 μ L, 0.5 mmol), DBU (1.05 equiv.), C_4F_9I (1.25 equiv.), CH_3CN (1 mL), T (25, 40, 50, 70 $^{\circ}C$), CO_2 (0.3 MPa), $h\nu = 365$ nm (LED).

Similar rates and yields were obtained when conducting the reaction at 0.15, 0.35 and 2 MPa. Thus, using DBU, the reaction proceeds very effectively in the presence of slight excess of the base with respect to allyl alcohol and at low CO_2 pressure. In agreement with Heldebrant's work and the results of this study, the alcohol group predominantly exists in the form of a carbonate in the reaction conditions which ensures a highly effective carboxylative cyclization compared to the possible competitive epoxidation from the iodo-perfluoroalkyl alcohol.

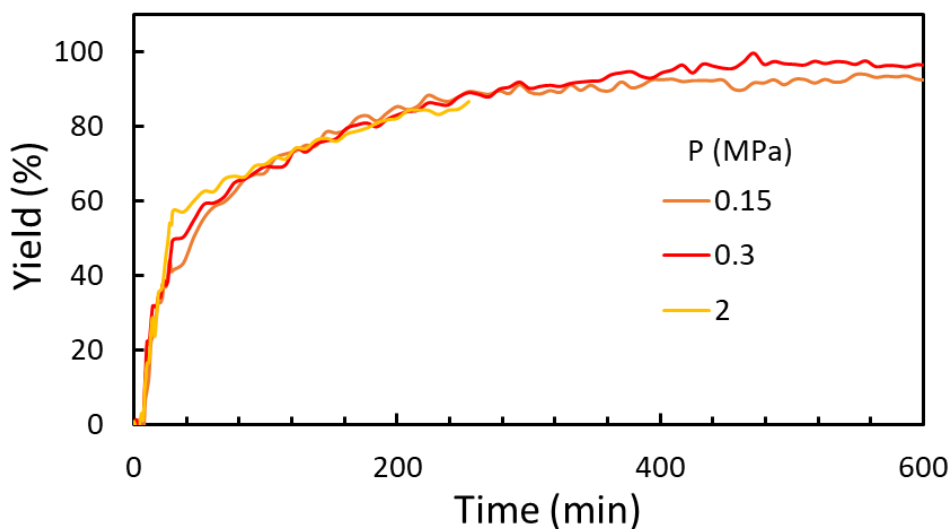


Figure 8. Influence of pressure of CO_2 on the kinetic of formation of **1** followed by in situ ATR-IR spectroscopy. Conditions: allyl alcohol (48 μ L, 0.5 mmol), DBU (1.05 equiv.), C_4F_9I (1.25 equiv.), CH_3CN (1 mL), T = 25 $^{\circ}C$, CO_2 (0.15, 0.3, 2 MPa), $h\nu = 365$ nm (LED).

2.2.2. Irradiation wavelength effect

The effect of the irradiation wavelength on the kinetic and yield of the reaction have been studied using a UVA LED (365 nm), a blue LED (405 nm) and a white light LED (425-700 nm). As shown in the figure 9, the UVA and blue light irradiation led to similar reaction rates and yields while white light irradiation (> 425 nm) led to a slower rate and moderate yield (~ 60%) in 10 h. Thus, due to the formation of the halogen bond complex [C_4F_9I -

DBU] whose absorption tails up to the blue region of the optical spectrum,[52] rather low energy blue photons promote the homolytic cleavage of the C₄F₉-I bond to generate Rf• which initiates a radical chain process.

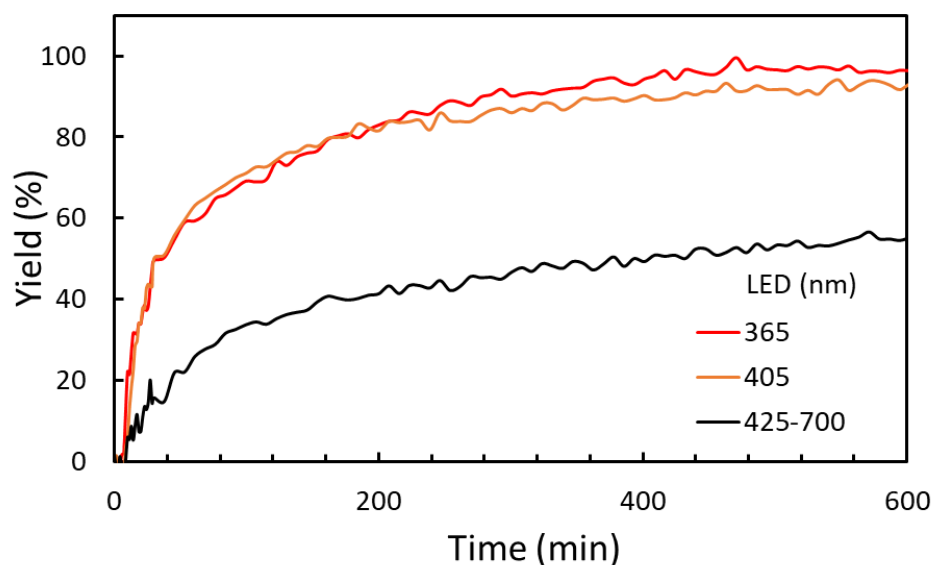


Figure 9. Influence of the irradiation wavelength on the kinetic of formation of **1** followed by in situ ATR-IR spectroscopy. Conditions: allyl alcohol (48 μ L, 0.5 mmol), DBU (1.05 equiv.), C₄F₉I (1.25 equiv.), CH₃CN (1 mL), T = 25 $^{\circ}$ C, CO₂ (0.3 MPa), $h\nu$ = 365 nm, 405 nm and 425-700 nm (LED-).

2.2.3. Solvent effect

The influence of the nature of the solvent on the kinetics and the yields of the reaction was then evaluated with various organic solvents such as THF, DMSO and anisole, the latter being the less toxic.[55] Although CH₃CN appears to be the best solvent for this reaction in terms of kinetic and yield, the perfluorobutyl carbonate **1** could be formed in a good yield (~85%) using DMSO (see figure 10). Lower yields of about 60 and 30% were obtained with THF and anisole, respectively.

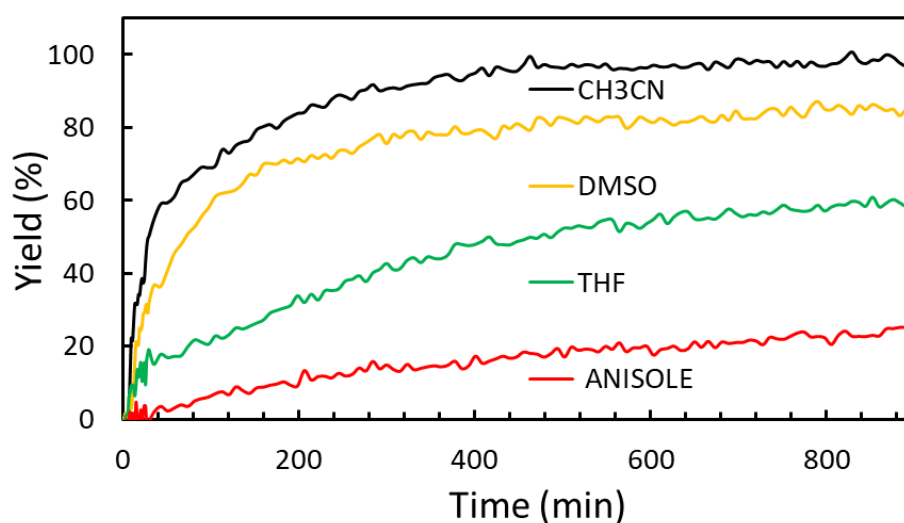
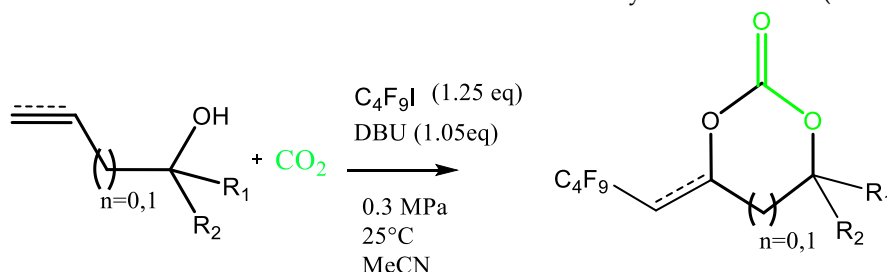


Figure 10. Influence of the solvent on the kinetic of formation of **1** followed by in situ ATR-IR spectroscopy. Conditions: allyl alcohol (48 μ L, 0.5 mmol), DBU (1.05 equiv.), C₄F₉I (1.25 equiv.), solvent (1 mL), T = 25 $^{\circ}$ C, CO₂ (0.3 MPa), $h\nu$ = 365 nm (LED).

2.3. Substrate scope

In an effort to extend the applicability of the protocol used for the synthesis of perfluorobutyl carbonate, several commercially available allylic and propargylic alcohols were tested for the formation of both 5 and 6 membered cyclic carbonates (Scheme 4).



Scheme 4. Substrate scope using optimal conditions of the model reaction.

Figure 11 shows the time dependence of the formation of 5 and 6 membered cyclic carbonates from various alcohols. Allylic alcohols such as 1-pentene-3-ol, crotyl alcohol and geraniol were converted into 5 membered cyclic carbonates but in lower yield than that obtained for allyl alcohol. No cyclic carbonate was formed from the tertiary allylic alcohol 2-methyl 3 butene-2-ol. Contrasting with other alcohols, the alkyl carbonate anion RCO_3^- did not form upon addition of CO_2 at a pressure of 0.3 MPa. Interestingly, it was possible to convert 3-butene-1-ol into a 6 membered cyclic carbonate albeit in a lower IR yield compared to allyl alcohol. Finally, propargyl alcohol could not be converted into any 5 membered cyclic carbonate. This is probably due to the fact that the intramolecular nucleophilic substitution on an sp^2 carbon is more difficult to achieve.

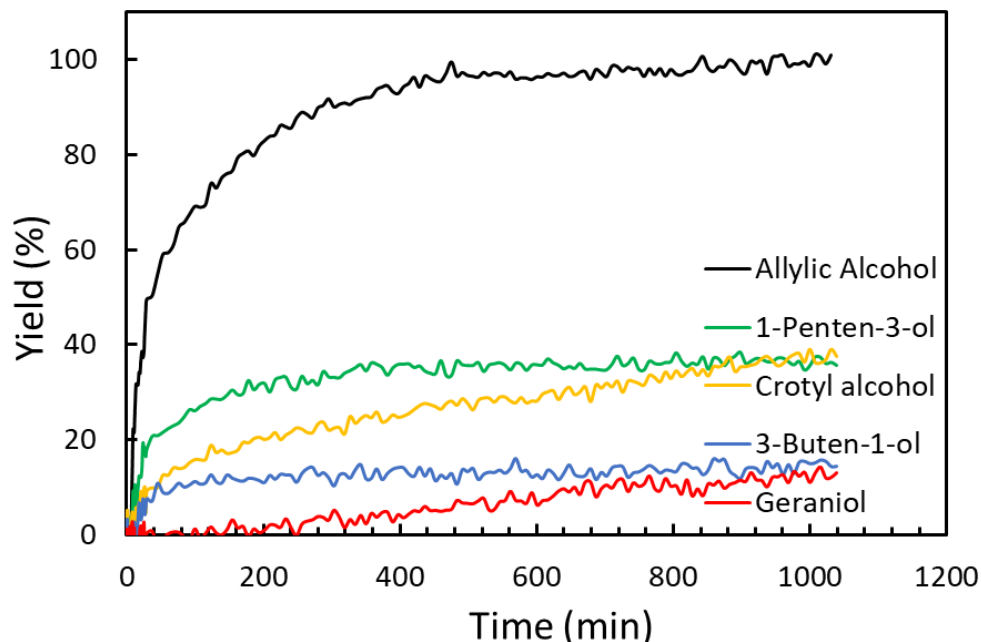


Figure 11. Kinetic investigation of the substrate scope to afford 5 and 6 membered perfluorobutyl cyclic carbonate. Conditions: substrate (0.5 mmol), Base (1.05 Eq), $\text{C}_4\text{F}_9\text{I}$ (1.25 Eq), CH_3CN (1 mL), 25°C , CO_2 (0.3 MPa), $h\nu = 365 \text{ nm}$ (LED).

3. Materials and Methods

3.1. Material

Allyl alcohol (Sigma Aldrich), 1-pentene-3-ol (Sigma Aldrich), Crotyl alcohol (Sigma Aldrich), Geraniol (Sigma Aldrich), 3-butene-1-ol (Sigma Aldrich), 2-methyl 3 butene-2-ol (Sigma Aldrich), propargyl alcohol (Sigma Aldrich), acetonitrile (CH_3CN , Sigma Aldrich),

dimethyl sulfoxide (DMSO, Sigma Aldrich), tetrahydrofuran (THF, Sigma Aldrich), Anisole (Alfa Aesar), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Alfa Aesar), triethylamine (Et₃N, Sigma Aldrich), 7-Methyl-1,5,7-Triazabicyclo[4.4.0]dec-5-ene (MTBD, Sigma Aldrich), TetramethylGuanidine (TMG, Alfa Aesar), Tetramethylethylenediamine, (TMEDA, Sigma Aldrich), 1,4-Diazabicyclo[2.2.2]octane (DABCO, Sigma Aldrich) and Perfluorobutyl iodide (C₄F₉I, Sigma Aldrich) were used without further purification.

3.3. In situ kinetics methods

The reactions were monitored *in situ* by ATR-IR spectroscopy using a home-made Ge ATR accessory suitable for high-pressure measurements (up to 5 MPa) and high temperature (up to 100 °C) (See ESI, Fig. S2) coupled with a ThermoOptek interferometer (type 6700) equipped with a globar source, a KBr/Ge beamsplitter and a DTGS (Deuterated Triglycine Sulphate) detector. Single beam spectra recorded in the spectral range (600-4000 cm⁻¹) with a 4 cm⁻¹ resolution were obtained after the Fourier transformation of 20 accumulated interferograms for the first 20 spectra (one spectrum every 80 sec), and then Fourier transformation of 120 accumulated interferograms until the end of reaction time (one spectrum every 8 min).

The in-situ Raman scattering investigations were performed using a Jobin-Yvon Horiba XploRA confocal Raman microscope equipped with a 10X objective and a laser diode at a wavelength $\lambda = 785$ nm and 100 % laser power of 45 mW. The spectral range from 140 to 2600 cm⁻¹ was recorded with a grating of 600 l/mm and a resolution of about 5 cm⁻¹. The spectra result from two acquisitions of 20 seconds each to improve the signal-to-noise ratio. A home-made high pressure cell (up to 10 MPa with a volume of 3 mL) equipped with two sapphire windows was used in order to simultaneously measure the Raman spectra and irradiate the mixture with the same LED than that used on the ATR-IR set-up.

The LEDs used in this study were purchased from Thorlabs. The LED at 365nm (M365FP1) used for most of the experiments delivers an irradiance of about 5mW/cm² on the sample. Two other LEDs (M405FP1) 405nm and MWWHF2 (425-700nm) were used for comparison at the same irradiance (5mW/cm²).

The alcohol (0.5 mmol) was solubilized in a 2 mL vial with 1 mL of solvent. C₄F₉I (1.25 eq) was added to the vial and then the Lewis base (1.05 eq) was added to the vial. The whole mixture was then transferred to the reaction chamber (volume: 5 mL) which was directly fixed on the Ge crystal of the ATR-IR device and on which a sapphire window allows the irradiation of the mixture with a LED. The mixture was constantly homogenized during the experiment using a magnetically driven stirrer disposed in the reaction chamber. An optical lens was connected to the sapphire window's support and the LED was connected to the optical lens via an optical fibre in order to ensure a good reproducibility for the irradiation of all the mixtures investigated. The setup was sealed with the CO₂ feed pipe. A first spectrum was recorded and then, once CO₂ was introduced in the sample chamber at the desired pressure, the kinetic was started. Few minutes later, the LED was then switched on in order to start the photoinduced carboxylative coupling of CO₂ with various alcohols. At the end of the reaction, in order to determine the yield, the ATR-IR spectrum of the reaction mixture was compared with the corresponding spectrum of the neat carbonate recorded under the same conditions. The absorbance (A (1810)) of the peak associated to the $\nu(\text{C}=\text{O})$ stretching mode at 1810 cm⁻¹ of the cyclic carbonate was used to determine the yield for the entire kinetic deduced by proportionality according to Equation 1. A number of experiments were conducted at least twice in order to check for reproducibility. We emphasize that ATR-IR spectroscopy can be considered as a quantitative method like ¹H NMR as demonstrated in our previous work [40] with an accuracy of about ± 3 % and can highlight the potential formation of by-products.

$$\text{Yield (\%)} = \frac{[A(t)(1810)](\text{reaction mixture})}{[A(1810)](\text{neat carbonate})} \quad (1)$$

4. Conclusion

In this paper, we have investigated an original protocol for the synthesis of perfluoro-alkylated cyclic carbonate by the photoinduced carboxylative cyclization of allyl alcohols with CO₂ promoted by visible/UVA light irradiation using perfluoroalkyl iodides. Under optimised conditions, quantitative yields up to 99 % in perfluorobutyl carbonate were reached in less than 8 h at 298 K and 0.15 MPa under blue irradiation at 405nm. In situ kinetic studies by ATR-IR and Raman spectroscopy revealed the evolution of all the components of the complex mixture during the reaction while varying key parameters such as the stoichiometry of the reactants, the nature of the Lewis base, the temperature, the pressure, the irradiation wavelength, the solvent and the substrate scope. Such fundamental kinetic studies enabled the determination of the reaction mechanism and provided insight into the underlying reason for the observed kinetics and selectivity. In particular, it was found that strong Lewis bases are needed that played both the role of activating the allyl alcohol for the generation of the allyl carbonate in the presence of CO₂ and promoting the ATRA reaction through the activation of C₄F₉I by halogen bonding. Various allylic alcohols such as 1-pentene-3-ol, crotyl alcohol and geraniol (a biobased substrate) were converted into 5 membered cyclic carbonates. Interestingly, it was possible to convert 3-butene-1-ol into a 6 membered cyclic carbonate although to a lower yield. Thus, this route offers a sustainable and promising approach for the valorisation of CO₂ as a chemical feedstock through efficient usage of light energy.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: title; Table S1: title; Video S1: title.

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Data Availability Statement: The raw/processed data required to reproduce these findings can be shared upon request sent to the corresponding author by e-mail.

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References

1. North, M.; Pasquale, R.; Young, C., Synthesis of cyclic carbonates from epoxides and CO₂. *Green Chem.*, **2010**, *12*, 1514-1539.
2. Cokoja, M.; Wilhelm, M.E.; Anthofer, M.H.; Herrmann, W.A.; Kühn, F.E., Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Organocatalysts. *ChemSuschem*, **2015**, *8*, 2436-2454.
3. Gennen, S.; Alves, M.; Méreau, R.; Tassaing, T.; Gilbert, B.; Detrembleur, C.; Jerome, C.; Grignard, B., Fluorinated Alcohols as Activators for the Solvent-Free Chemical Fixation of Carbon Dioxide into Epoxides. *ChemSuschem*, **2015**, *8*, 1845-1849.
4. Alves, M.; Grignard, B.; Gennen, S.; Mereau, R.; Detrembleur, C.; Jerome, C.; Tassaing, T., Organocatalytic promoted coupling of carbon dioxide with epoxides: a rational investigation of the cocatalytic activity of various hydrogen bond donors. *Catal. Sci. Tech.*, **2015**, *5*, 4636-4643.
5. Alves, M.; Grignard, B.; Mereau, R.; Jerome, C.; Tassaing, T.; Detrembleur, C., Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: catalyst design and mechanistic studies. *Catal. Sci. Tech.*, **2017**, *7*, 2651-2684.
6. Shaikh, A.-a.G.; Sivaram, S., Organic carbonates. *Chem. Rev.*, **1996**, *96*, 951-976.
7. Tempelaar, S.; Mespouille, L.; Coulembier, O.; Dubois, P.; Dove, A.P., Synthesis and post-polymerisation modifications of aliphatic poly(carbonate)s prepared by ring-opening polymerisation. *Chemical Society Reviews*, **2013**, *42*, 1312-1336.
8. Grignard, B.; Gennen, S.; Jérôme, C.; Kleij, A.W.; Detrembleur, C., Advances in the use of CO₂ as a renewable feedstock for the synthesis of polymers. *Chemical Society Reviews*, **2019**, DOI: 10.1039/c9cs00047j.
9. Maisonneuve, L.; Lamarzelle, O.; Rix, E.; Grau, E.; Cramail, H., Isocyanate-Free Routes to Polyurethanes and Poly(hydroxy Urethane)s. *Chem. Rev.*, **2015**, *115*, 12407-12439.
10. Grignard, B.; Thomassin, J.M.; Gennen, S.; Poussard, L.; Bonnaud, L.; Raquez, J.M.; Dubois, P.; Tran, M.P.; Park, C.B.; Jerome, C.; Detrembleur, C., CO₂-blown microcellular non-isocyanate polyurethane (NIPU) foams: from bio- and CO₂-sourced monomers to potentially thermal insulating materials. *Green Chem.*, **2016**, *18*, 2206-2215.

11. Gennen, S.; Grignard, B.; Tassaing, T.; Jérôme, C.; Detrembleur, C., CO₂-Sourced α -Alkylidene Cyclic Carbonates: A Step Forward in the Quest for Functional Regioregular Poly(urethane)s and Poly(carbonate)s. *Angew. Chem. Int. Ed.*, **2017**, *56*, 10394-10398. 493-495
12. Monie, F.; Grignard, B.; Thomassin, J.-M.; Mereau, R.; Tassaing, T.; Jerome, C.; Detrembleur, C., Chemo- and Regioselective Additions of Nucleophiles to Cyclic Carbonates for the Preparation of Self-Blowing Non-Isocyanate Polyurethane Foams. *Angew. Chem. Int. Ed.*, **2020**, *59*, 17033-17041. 496-498
13. Martín, C.; Fiorani, G.; Kleij, A.W., Recent Advances in the Catalytic Preparation of Cyclic Organic Carbonates. *ACS Catal.*, **2015**, *5*, 1353-1370. 499-500
14. Rintjema, J.; Guo, W.; Martin, E.; Escudero-Adan, E.C.; Kleij, A.W., Highly Chemoselective Catalytic Coupling of Substituted Oxetanes and Carbon Dioxide. *Chemistry*, **2015**, *21*, 10754-10762. 501-502
15. Alves, M.; Grignard, B.; Boyaval, A.; Méreau, R.; De Winter, J.; Gerbaux, P.; Detrembleur, C.; Tassaing, T.; Jérôme, C., Organocatalytic Coupling of CO₂ with Oxetane. *ChemSuschem*, **2017**, *10*, 1128-1138. 503-504
16. Besse, V.; Camara, F.; Voirin, C.; Auvergne, R.; Caillol, S.; Boutevin, B., Synthesis and applications of unsaturated cyclocarbonates. *Polym. Chem.*, **2013**, *4*, 4545-4561. 505-506
17. Zhao, Y.; Yang, Z.; Yu, B.; Zhang, H.; Xu, H.; Hao, L.; Han, B.; Liu, Z., Task-specific ionic liquid and CO₂-cocatalysed efficient hydration of propargylic alcohols to [small alpha]-hydroxy ketones. *Chemical Science*, **2015**, *6*, 2297-2301. 507-508
18. Song, Q.-W.; He, L.-N., in *Advances in CO₂ Capture, Sequestration, and Conversion*, American Chemical Society, 2015, vol. 1194, ch. 2, pp. 47-70. 509-510
19. Rintjema, J.; Kleij, A.W., Substrate-Assisted Carbon Dioxide Activation as a Versatile Approach for Heterocyclic Synthesis. *Synthesis*, **2016**, DOI: 10.1055/s-0035-1562520, DOI: 10.1055/s-0035-1562520. 511-512
20. Boyaval, A.; Méreau, R.; Grignard, B.; Detrembleur, C.; Jerome, C.; Tassaing, T., Organocatalytic Coupling of CO₂ with a Propargylic Alcohol: A Comprehensive Mechanistic Study. *ChemSuschem*, **2017**, *10*, 1241-1248. 513-514
21. Li, M.; Abdolmohammadi, S.; Hoseininezhad-Namin, M.S.; Behmagham, F.; Vessally, E., Carboxylative cyclization of propargylic alcohols with carbon dioxide: A facile and Green route to α -methylene cyclic carbonates. *J. CO₂ Util.*, **2020**, *38*, 220-231. 515-517
22. Huang, J.; Jehanno, C.; Worch, J.C.; Ruipérez, F.; Sardon, H.; Dove, A.P.; Coulembier, O., Selective Organocatalytic Preparation of Trimethylene Carbonate from Oxetane and Carbon Dioxide. *ACS Catal.*, **2020**, *10*, 5399-5404. 518-519
23. Méreau, R.; Grignard, B.; Boyaval, A.; Detrembleur, C.; Jerome, C.; Tassaing, T., Tetrabutylammonium Salts: Cheap Catalysts for the Facile and Selective Synthesis of α -Alkylidene Cyclic Carbonates from Carbon Dioxide and Alkynols. *ChemCatChem*, **2018**, *10*, 956-960. 520-522
24. Grignard, B.; Ngassamtounzoua, C.; Gennen, S.; Gilbert, B.; Méreau, R.; Jerome, C.; Tassaing, T.; Detrembleur, C., Boosting the Catalytic Performance of Organic Salts for the Fast and Selective Synthesis of α -Alkylidene Cyclic Carbonates from Carbon Dioxide and Propargylic Alcohols. *ChemCatChem*, **2018**, *10*, 2584-2592. 523-525
25. Dabral, S.; Bayarmagnai, B.; Hermsen, M.; Schießl, J.; Mormul, V.; Hashmi, A.S.K.; Schaub, T., Silver-Catalyzed Carboxylative Cyclization of Primary Propargyl Alcohols with CO₂. *Org. Lett.*, **2019**, *21*, 1422-1425. 526-527
26. Cervantes-Reyes, A.; Saxl, T.; Stein, P.M.; Rudolph, M.; Rominger, F.; Asiri, A.M.; Hashmi, A.S.K., Expanded Ring NHC Silver Carboxylate Complexes as Efficient and Reusable Catalysts for the Carboxylative Cyclization of Unsubstituted Propargylic Derivatives. *ChemSuschem*, **2021**, *14*, 2367-2374. 528-530
27. Cervantes-Reyes, A.; Farshadfar, K.; Rudolph, M.; Rominger, F.; Schaub, T.; Ariafard, A.; Hashmi, A.S.K., Copper-catalysed synthesis of α -alkylidene cyclic carbonates from propargylic alcohols and CO₂. *Green Chem.*, **2021**, *23*, 889-897. 531-532
28. Kindermann, N.; Jose, T.; Kleij, A.W., Synthesis of Carbonates from Alcohols and CO₂. *Top Curr Chem (Cham)*, **2017**, *375*, 15. 533-534
29. Tamura, M.; Honda, M.; Nakagawa, Y.; Tomishige, K., Direct conversion of CO₂ with diols, aminoalcohols and diamines to cyclic carbonates, cyclic carbamates and cyclic ureas using heterogeneous catalysts. *J. Chem. Technol. Biotechnol.*, **2014**, *89*, 19-33. 535-537
30. Hosseinian, A.; Farshbaf, S.; Mohammadi, R.; Monfared, A.; Vessally, E., Advancements in six-membered cyclic carbonate (1,3-dioxan-2-one) synthesis utilizing carbon dioxide as a C1 source. *RSC Adv.*, **2018**, *8*, 17976-17988. 538-539
31. Bobbink, F.D.; Gruszka, W.; Hulla, M.; Das, S.; Dyson, P.J., Synthesis of cyclic carbonates from diols and CO₂ catalyzed by carbenes. *Chem. Comm.*, **2016**, *52*, 10787-10790. 540-541
32. Brege, A.; Grignard, B.; Méreau, R.; Detrembleur, C.; Jerome, C.; Tassaing, T., En Route to CO₂-Based (a)Cyclic Carbonates and Polycarbonates from Alcohols Substrates by Direct and Indirect Approaches. *Catalysts*, **2022**, *12*, 124. 542-543
33. Honda, M.; Tamura, M.; Nakagawa, Y.; Tomishige, K., Catalytic CO₂ conversion to organic carbonates with alcohols in combination with dehydration system. *Catal. Sci. Technol.*, **2014**, *4*, 2830-2845. 544-545
34. Honda, M.; Tamura, M.; Nakao, K.; Suzuki, K.; Nakagawa, Y.; Tomishige, K., Direct Cyclic Carbonate Synthesis from CO₂ and Diol over Carboxylation/Hydration Cascade Catalyst of CeO₂ with 2-Cyanopyridine. *ACS Catal.*, **2014**, *4*, 1893-1896. 546-547
35. Reithofer, M.R.; Sum, Y.N.; Zhang, Y., Synthesis of cyclic carbonates with carbon dioxide and cesium carbonate. *Green Chem.*, **2013**, *15*, 2086-2090. 548-549
36. Mcguire, T.M.; López-Vidal, E.M.; Gregory, G.L.; Buchard, A., Synthesis of 5- to 8-membered cyclic carbonates from diols and CO₂: A one-step, atmospheric pressure and ambient temperature procedure. *J. CO₂ Util.*, **2018**, *27*, 283-288. 550-551

37. Gregory, G.L.; Ulmann, M.; Buchard, A., Synthesis of 6-membered cyclic carbonates from 1,3-diols and low CO₂ pressure: a novel mild strategy to replace phosgene reagents. *RSC Adv.*, **2015**, *5*, 39404-39408. 552-553
38. Kitamura, T.; Inoue, Y.; Maeda, T.; Oyamada, J., Convenient synthesis of ethylene carbonates from carbon dioxide and 1,2-diols at atmospheric pressure of carbon dioxide. *Synth. Commun.*, **2015**, *46*, 39-45. 554-555
39. Lim, Y.N.; Lee, C.; Jang, H.-Y., Metal-Free Synthesis of Cyclic and Acyclic Carbonates from CO₂ and Alcohols. *Eur. J. Org. Chem.*, **2014**, *2014*, 1823-1826. 556-557
40. Brege, A.; Méreau, R.; McGehee, K.; Grignard, B.; Detrembleur, C.; Jerome, C.; Tassaing, T., The coupling of CO₂ with diols promoted by organic dual systems: Towards products divergence via benchmarking of the performance metrics. *J. CO₂ Util.*, **2020**, *38*, 88-98. 558-560
41. Baran, T.; Dibenedetto, A.; Aresta, M.; Kruczała, K.; Macyk, W., Photocatalytic Carboxylation of Organic Substrates with Carbon Dioxide at Zinc Sulfide with Deposited Ruthenium Nanoparticles. *ChemPlusChem*, **2014**, *79*, 708-715. 561-562
42. Masuda, Y.; Ishida, N.; Murakami, M., Light-Driven Carboxylation of o-Alkylphenyl Ketones with CO₂. *J. Am. Chem. Soc.*, **2015**, *137*, 14063-14066. 563-564
43. Wang, M.-Y.; Cao, Y.; Liu, X.; Wang, N.; He, L.-N.; Li, S.-H., Photoinduced radical-initiated carboxylative cyclization of allyl amines with carbon dioxide. *Green Chem.*, **2017**, *19*, 1240-1244. 565-566
44. Gui, Y.-Y.; Zhou, W.-J.; Ye, J.-H.; Yu, D.-G., Photochemical Carboxylation of Activated C(sp³)-H Bonds with CO₂. *ChemSuschem*, **2017**, *10*, 1337-1340. 567-568
45. Murata, K.; Numasawa, N.; Shimomaki, K.; Takaya, J.; Iwasawa, N., Construction of a visible light-driven hydrocarboxylation cycle of alkenes by the combined use of Rh(i) and photoredox catalysts. *Chem. Commun.*, **2017**, *53*, 3098-3101. 569-570
46. Long Ngo, H.; Kumar Mishra, D.; Mishra, V.; Chien Truong, C., Recent advances in the synthesis of heterocycles and pharmaceuticals from the photo/electrochemical fixation of carbon dioxide. *Chem. Eng. Sci.*, **2021**, *229*, 116142. 571-572
47. He, X.; Yao, X.Y.; Chen, K.H.; He, L.N., Metal-Free Photocatalytic Synthesis of exo-Iodomethylene 2-Oxazolidinones: An Alternative Strategy for CO₂ Valorization with Solar Energy. *ChemSuschem*, **2019**, *12*, 5081-5085. 573-574
48. Malik, A.; Bhatt, S.; Soni, A.; Khatri, P.K.; Guha, A.K.; Saikia, L.; Jain, S.L., Visible-light driven reaction of CO₂ with alcohols using a Ag/CeO₂ nanocomposite: first photochemical synthesis of linear carbonates under mild conditions. *Chem. Commun.*, **2023**, *59*, 1313-1316. 575-577
49. Heldebrant, D.J.; Jessop, P.G.; Thomas, C.A.; Eckert, C.A.; Liotta, C.L., The Reaction of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) with Carbon Dioxide. *J. Org. Chem.*, **2005**, *70*, 5335-5338. 578-579
50. Onwukamike, K.N.; Tassaing, T.; Grelier, S.; Grau, E.; Cramail, H.; Meier, M.a.R., Detailed Understanding of the DBU/CO₂ Switchable Solvent System for Cellulose Solubilization and Derivatization. *ACS Sustainable Chemistry & Engineering*, **2018**, *6*, 1496-1503. 580-582
51. Heldebrant, D.J.; Yonker, C.R.; Jessop, P.G.; Phan, L., Organic liquid CO₂ capture agents with high gravimetric CO₂ capacity. *Energy Environ. Sci.*, **2008**, DOI: 10.1039/b809533g, 487-493. 583-584
52. Grondin, J.; Aupetit, C.; Vincent, J.-M.; Méreau, R.; Tassaing, T., Visible-light induced photochemistry of Electron Donor-Acceptor Complexes in Perfluoroalkylation Reactions: Investigation of halogen bonding interactions through UV-Visible absorption and Raman spectroscopies combined with DFT calculations. *J. Mol. Liq.*, **2021**, *333*, 115993. 585-587
53. Postigo, A., Electron Donor-Acceptor Complexes in Perfluoroalkylation Reactions. *Eur. J. Org. Chem.*, **2018**, *2018*, 6391-6404. 588-589
54. Smith, C.A.; Cramail, H.; Tassaing, T., Insights into the Organocatalyzed Synthesis of Urethanes in Supercritical Carbon Dioxide: An In Situ FTIR Spectroscopic Kinetic Study. *ChemCatChem*, **2014**, *6*, 1380-1391. 590-591
55. Prat, D.; Wells, A.; Hayler, J.; Sneddon, H.; Mcelroy, C.R.; Abou-Shehada, S.; Dunn, P.J., CHEM21 selection guide of classical- and less classical-solvents. *Green Chem.*, **2016**, *18*, 288-296. 592-593

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