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# Selective catalytic synthesis of new terpenic chlorides using NaDCC as an eco-friendly and highly stable FAC agent†

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A simple, mild and efficient scope pathway for a selective catalytic chlorination of terpenic olefins is investigated in the presence of a highly efficient chlorination agent and a readily available Lewis acid catalyst. The sodium dichloroisocyanurate (NaDCC) used in the present work as an easy handling, sustainable and cost-effective chlorine donor due to its high free available chlorine (FAC), exhibits a high efficiency for selective catalytic chlorination. Herein, we report for the first-time the FeCl<sub>2</sub>/NaDCC combination system for the selective catalytic chlorination towards new functionalized terpenic olefins. In order to examine the general features of this catalytic reaction, the effects of pH, solvent, dilution, chlorination agent nature, stoichiometry and reaction kinetics are optimized using carvone as a model substrate. Among the studied parameters, catalyst stoichiometry was found to be determinant for highly controllable chlorination selectivity towards new allylic and vinylic chlorides. Indeed, the oxidation state, ligand and metal effects of the catalyst are examined using various Lewis acids, where the chlorinated ones (MCl<sub>x</sub>), such as FeCl<sub>2</sub>, FeCl<sub>3</sub> and SnCl<sub>2</sub>, exhibit a comprehensive approach for a controllable chlorination reaction. In addition, the homogeneous catalytic system shows good reusability with significant catalytic conversion depending on the FAC content in the reaction medium. The reaction proceeds under mild conditions with shorter reaction time and high selectivity towards new high added value allylic and vinylic chlorinated derivatives of naturally occurring terpenic olefins in good to excellent yields.

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## 1. Introduction

Terpenes are one of the most natural compounds bearing allyl, vinyl or isopropenyl groups as a part of their structures.<sup>1</sup> These groups are widely used as starting materials to obtain natural derived compounds or more complex atomic arrangements.<sup>2,3</sup> Among the natural products, terpenes provide a sustainable supply of intermediates to produce flavors, perfumes and fine chemicals used in various industries and synthetic organic chemistry.<sup>4–6</sup> For instance, the allylic chlorides are fundamental compounds in organic chemistry due to their strong electrophilic character.<sup>7</sup> They can be transformed by functionalization, substitution, alkylation, reduction or oxidation of the double bond leading to a wide range of products such as allylic

carbonates,<sup>8</sup> allylic amines,<sup>9</sup> allylic esters<sup>10</sup> or β,γ-unsaturated acids.<sup>11</sup> Thus, allylic chlorides can afford several functional groups for the synthesis of high added value natural compound derivatives.<sup>12–16</sup> On the other hand, the vinylic chlorides are versatile chemicals that serve as valuable intermediates for the synthesis of natural product derivatives, vinyl polymers, adhesives, pharmaceuticals and agrochemical compounds.<sup>17–21</sup> The presence of vinylic chloride in a backbone structure enhances the reactivity of the adjacent carbon–carbon double bond, enabling diverse chemical modifications such as oxidative or coupling reactions.<sup>19,22–25</sup>

Unlike their versatile importance in organic synthesis, few studies were devoted to vinylic halides preparation such as Barton synthesis from ketone-derived hydrazones,<sup>26</sup> from ketones *via* vinyl phosphate intermediates,<sup>27</sup> radical reaction of trichloromethylated substrates<sup>18</sup> or *via* stereospecific isomerization of allylic halides.<sup>28</sup> In contrast, the synthesis of allylic halides starting from allylic olefins is widely reported.<sup>29</sup> For instance, the allyl chloride derivatives could be prepared from the corresponding allylic alcohols in presence of different reagents, *e.g.*, titanium IV chloride,<sup>30</sup> thionyl chloride,<sup>31</sup> hydrochloric acid,<sup>32</sup> chlorosilanes,<sup>33</sup> sulfuryl chloride,<sup>34</sup> N-chlorosuccinimide (NCS)<sup>35</sup> or iridium catalyst.<sup>36,37</sup> However, the

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allylic chloride intermediates can be synthesized from aldehydes through sequences of olefination–reduction–halogenation.<sup>7</sup> In presence of NCS, Yb(OTf)<sub>3</sub>–TMSCl or aniline catalyst have been used to prepare allylic chlorides.<sup>38,39</sup> Recently, nicotine has been reported as catalyst for the chlorination promoted by hypochlorous acid.<sup>40</sup> Moreover, organoselenides have been used as catalysts for the allylic chlorination of simple and natural olefins.<sup>41–45</sup> On the other hand, electrochemical methods are reported for the allylic chlorination of a variety of isoprenoids using sodium chloride as halogen source.<sup>46,47</sup> While direct molecular chlorine bubbling through the reaction medium could be used for the chlorination, this method confronts various disadvantages including problems of handling chlorine gas.<sup>48</sup> Therefore, other methods are based on the use of calcium hypochlorite<sup>49,50</sup> or by a combination of Vilsmeier reagent and H<sub>2</sub>O<sub>2</sub> but this excludes the use of acid-sensitive substrates.<sup>51</sup> Besides, a combination of sodium hypochlorite and acetic acid was used for the chlorine generation with limitation to non-sensitive substrates.<sup>52</sup>

For a practical use, the replacement of Brønsted acid (*e.g.*, acetic acid) by Lewis acid catalysts is reported as milder environment in the presence of chlorine source under biphasic system.<sup>48</sup> Recently, we have reported the use of different Lewis acid catalysts in combination with NaClO for the chlorination of natural terpenic olefins.<sup>29</sup> Among the reported Lewis acid catalysts, metal chlorides (MCl<sub>x</sub>) such as CeCl<sub>3</sub>,<sup>48</sup> InCl<sub>3</sub>,<sup>53</sup> NbCl<sub>5</sub>,<sup>7</sup> MoCl<sub>5</sub>,<sup>54</sup> and AlCl<sub>3</sub> or FeCl<sub>3</sub><sup>29</sup> are the most reported for the catalytic chlorination of olefins. While the combination of MCl<sub>x</sub>/NaClO is considered as an efficient solution for the catalytic chlorination of olefins, the use of NaClO solution as chlorinating agent faces some limitations in terms of reaction reproducibility due to the free available chlorine (FAC) stability and handling in the reaction medium. Recently, Hondo *et al.* have reported that the FAC of NaClO decreases by 20% due to gradual degradation and evaporation during storage.<sup>55</sup> In this regard, the active chlorine content needs to be determined before each use for an efficient reaction reproducibility. Therefore, solid NaClO·5H<sub>2</sub>O has recently become commercially available to overcome the FAC limitations of using NaClO solution.<sup>56</sup> However, the low melting point of solid NaClO (*T*<sub>m</sub> ≈ 25 °C) makes handling the catalytic reaction difficult at room temperature.<sup>56–58</sup> In contrast, sodium dichloroisocyanurate (NaDCC), with a high melting point of 225 °C, was reported to be favored for laboratory experiments.<sup>56,59</sup> Hence, NaDCC is the most advantageous solid FAC donor over NaClO solution or solid NaClO·5H<sub>2</sub>O in terms of easy handling and high stability during both storage and use at room temperature. In this work, we propose the use of NaDCC as an advantageous, cost-effective and eco-friendly solid FAC donor alternative for the selective catalytic chlorination of terpenic olefins. Accordingly, the dissolution of NaDCC in water maintains an equilibrium with a slow release of hypochlorous acid (HClO) molecules (Scheme 1),<sup>55</sup> which might be advantageous in the catalytic chlorination.

As part of our ongoing research interest on the functionalization of natural terpenic olefins, herein we report an efficient, reliable and practical method for the selective catalytic chlorination of terpenes using a novel combination of FeCl<sub>2</sub>/NaDCC

catalytic system. This catalytic chlorination system shows high selectivity and efficiency towards new allylic and vinylic terpenic derivatives. Moreover, various parameters such as effect of pH, solvent, dilution, chlorination agent nature, stoichiometry, reaction kinetics, and catalytic system reusability are studied using carvone as a model substrate. The present reported catalytic system represents an excellent high FAC tool towards new high added value functionalized natural compound derivatives under mild conditions, with reproducible quantitative yields.

## 2. Results and discussion

The use of NaDCC as high and stable FAC agent combined with Lewis acid catalyst (FeCl<sub>2</sub>) is selective for the catalytic chlorination of carvone **a** as model substrate (Scheme 2).

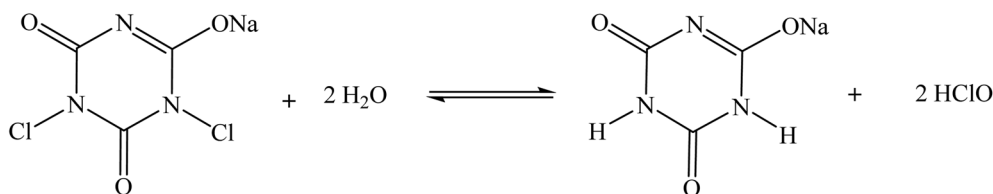
### 2.1. Optimization of FeCl<sub>2</sub> and NaDCC amounts

First, we examined the effect of the Lewis acid and the chlorinating agent (FeCl<sub>2</sub>/NaDCC) amounts in the catalytic chlorination (Fig. 1). In absence of FeCl<sub>2</sub>, poor conversion was observed in presence of NaDCC even after 30 min of reaction. In presence of 4 eq. of NaDCC, an increase of FeCl<sub>2</sub> amount enhances the conversion of carvone **a** with a variation in the selectivity of major reaction products (allylic monochloride **b** and vinyl allyl dichloride **d**) accompanied with byproducts formation (dichloride **c** and trichloride **e**). Hence, while (i) FeCl<sub>2</sub> amount <1.75 eq. reveals a highly selective reaction towards **b** as major product; (ii) FeCl<sub>2</sub> amount >1.75 eq. switches the selectivity towards the formation of **d** as major product with a good selectivity. Thereafter, 2.5 eq. of FeCl<sub>2</sub> was chosen as an optimum for the formation of **d** and the effect of NaDCC amount on the allylic chlorination reaction was studied. While in absence of NaDCC no reaction took place, the use of 4 eq. reveals a high conversion (99%) with a maximum of selectivity (78%) towards **d**.

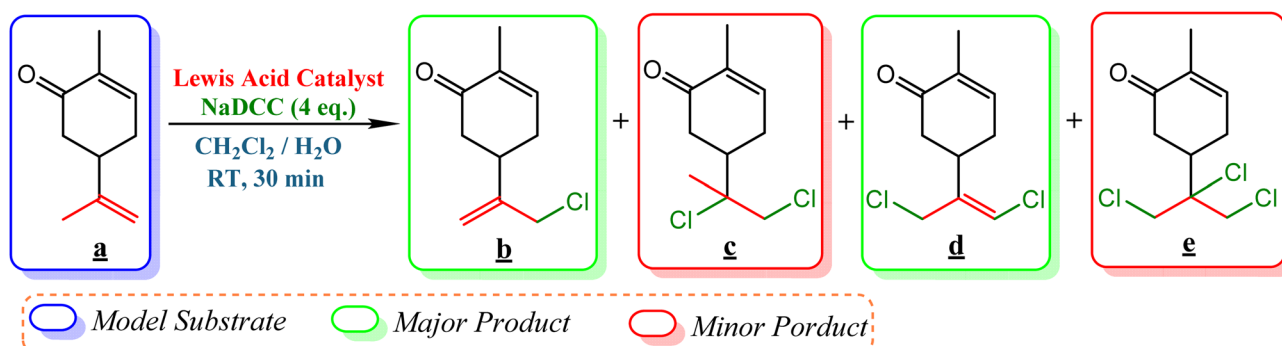
### 2.2. Influencing parameters on the selective chlorination reaction

**2.2.1. Effect of pH.** The pH effect on the selective catalytic chlorination reaction was investigated to understand the optimized equivalence, conversion and selectivity (Fig. 2). Hence, the amount of FeCl<sub>2</sub> has no effect and shows a constant pH = 5 within the course of reaction (Fig. 2a). However, NaDCC has a significant effect on the pH (Fig. 2b), which affects the active chlorine content in the reaction medium as well as the catalytic chlorination. While (i) an amount of NaDCC <1.5 eq. shows a fluctuation in pH from 5 to 2 within the course of reaction; (ii) the use of an amount ≥1.5 eq. maintains a stable pH = 5. Thus, the pH diagram could explain the total conversion obtained while using an amount of NaDCC ≥1.5 eq., which is reported as pH range for higher FAC.<sup>60</sup> Accordingly, different distributions of aqueous chlorine species Cl<sub>2</sub>, HClO and ClO<sup>−</sup> are observed depending on pH.<sup>61</sup> The diagram for chlorine/hypochlorous acid in aqueous solution shows a total predominance of dissolved Cl<sub>2</sub> at pH < 1, HClO at 2 < pH < 6 and ClO<sup>−</sup> at pH > 9. It is





Scheme 1 Dissolution of NaDCC in aqueous medium.

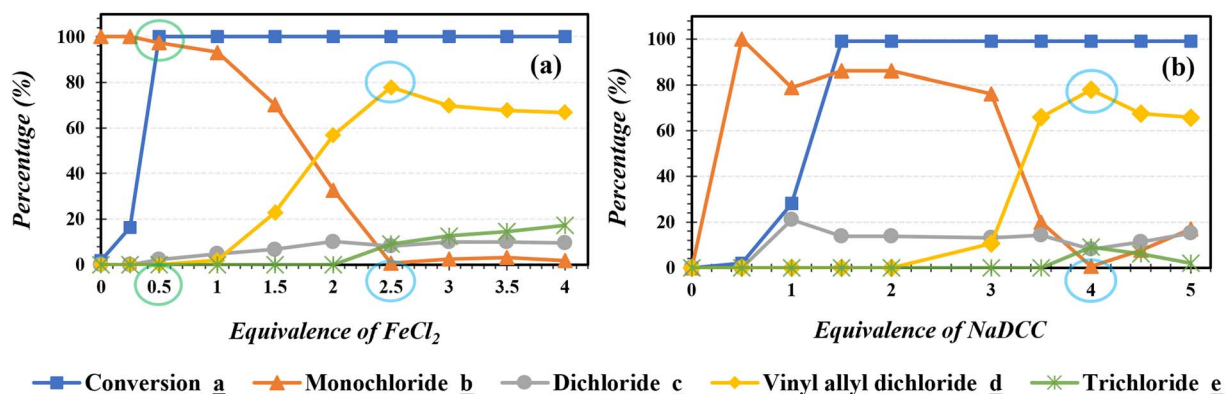
Scheme 2 Catalytic chlorination of carvone **a** using NaDCC.

well known that HClO is much faster than  $\text{ClO}^-$  in terms of kinetics and reactivity.<sup>62</sup> Therefore, the NaDCC solid reagent is acidic in solution and tends to reduce the pH of water favoring the formation of undissociated HClO. However, the chlorine loses its effectiveness through the dissociation of HClO at higher pH.<sup>63</sup> In addition, hypochlorite ( $\text{ClO}^-$ ), being alkaline, tends to disadvantageously increase the pH, resulting to the HClO dissociation.<sup>64</sup> In contrast, the capacity of NaDCC to continue significant releasing amounts of HClO allows it to operate over a wider pH range.<sup>65</sup>

**2.2.2. Solvent effect.** The solvent effect on the conversion and the selectivity of the catalytic chlorination reaction was studied. Under the optimized conditions leading to the major formation of **d**, a variety of polar, apolar, protic and aprotic

solvents were examined (Table 1). The use of non-chlorinated protic and aprotic solvents leads to a complex mixture of reaction products. However, among the studied chlorinated solvents,  $\text{CH}_2\text{Cl}_2$  gave the best result. While  $\text{CHCl}_3$  favored the formation of **b** in moderated selectivity,  $\text{CCl}_4$  shows a good conversion (79%) with a poor reaction selectivity. The obtained results can be explained by the polar character of  $\text{CH}_2\text{Cl}_2$  compared to  $\text{CHCl}_3$  and  $\text{CCl}_4$ , respectively. In contrast, the catalytic chlorination carried out in neat water reveals the formation of a complex mixture of reaction products with **e** as the major one.

The obtained results confirm that the chlorinated solvents have the best solvation effect and reveal the complexity of replacing  $\text{CH}_2\text{Cl}_2$  with other alternatives in the catalytic

Fig. 1 Effect of (a)  $\text{FeCl}_2$  and (b) NaDCC amounts on the selective catalytic chlorination reaction.

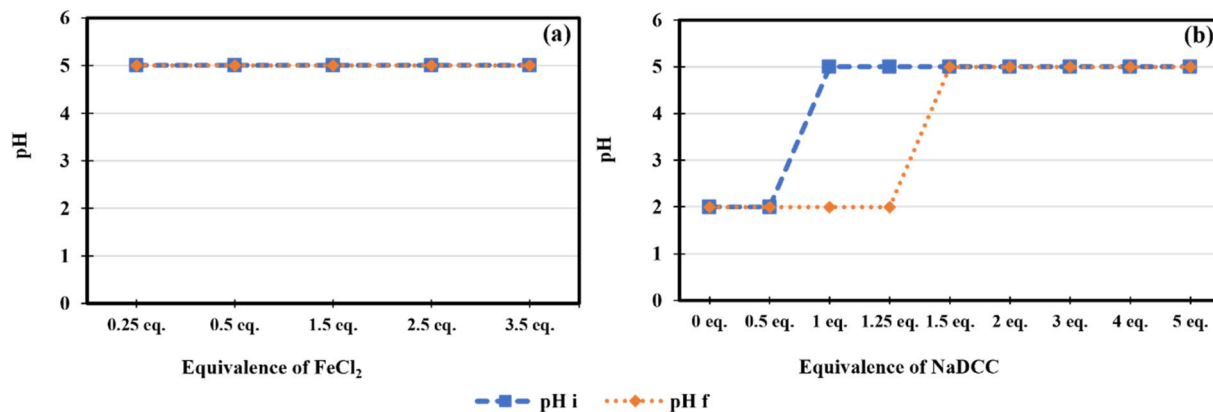


Fig. 2 Effect of pH on the selective catalytic chlorination reaction while varying (a)  $\text{FeCl}_2$  and (b) NaDCC amounts.

chlorination reaction.<sup>29,48,53,54</sup> In addition to the reported solvents in Table 1, other solvents such as carbonate ester were investigated with no significant results. Despite of the critical use of  $\text{CH}_2\text{Cl}_2$ , the reaction is handled at RT and the solvent is recycled under vacuum, which could decrease its environmental impact. Moreover, its unique abilities have helped to advance scientific research and improve the quality of numerous processes.<sup>66,67</sup> Hence, it is crucial to ensure a balance between maximizing its benefits in industrial progress and minimizing its environmental and health impacts by exploring safer recovery methods and technologies.<sup>67,68</sup>

**2.2.3. Effect of dilution.** Next, we have studied the effect of dilution of both  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  on the catalytic chlorination (Fig. 3). The increase of  $\text{H}_2\text{O}$  volume decreased the selectivity of **d** due to the dilution of the FAC content in the reaction medium. 5 mL of  $\text{H}_2\text{O}$  was found to be the optimum dissolution volume for the optimized equivalence of NaDCC. In contrast,  $\text{CH}_2\text{Cl}_2$  volume has no effect on the selective catalytic chlorination.

**2.2.4. Effects of chlorinating agent and FAC.** To shed more light on the effects of chlorinating agent and FAC, we have carried out the catalytic chlorination reaction using NaDCC, NCS or NaClO in catalyst-free, 0.5 eq. and 2.5 eq. of  $\text{FeCl}_2$ , respectively (Table 2). In presence of NCS, a slow reaction kinetics was observed with a slight catalytic effect on the reaction. However, with NaClO no reaction took place in catalyst-free condition even after a prolonged reaction time. While the

use of 0.5 eq. of  $\text{FeCl}_2$  in presence of NaClO provides a very poor conversion (7%) with the only formation of **b**, the use of 2.5 eq. of catalyst almost leads to a total conversion with a mainly distributed selectivity between **b** and **d** (56 and 32%, respectively). The previously highlighted necessity of using a highly stable FAC chlorinating agent explains the significant results of NaDCC compared to NaClO in both reaction conditions. It has been reported that the amount of the added chlorine agents affects the reaction rate.<sup>55</sup> Accordingly, the use of NaDCC improves the reaction time compared to the other chlorinating agents due to the formation of 2 mol of HClO while using only 1 mol of NaDCC (Scheme 1).

In a comparative purpose, both NaClO and NaDCC rely on HClO as active chlorine species with important differences in their performance. While NaClO releases all its chlorine as FAC, NaDCC releases only  $\approx 50\%$  of its chlorine as FAC.<sup>69</sup> However, the balance remaining while using NaDCC is considered as “reservoir chlorine” in the form of chlorinated isocyanurate (Scheme 1). Thereafter, when the FAC is depleted, the equilibrium is disturbed *via* an immediate FAC releasing from the “reservoir” until the total consumption of chlorine.<sup>60</sup> Therefore, the use of NaDCC presents the advantage of manipulating at variable pH by taking into consideration that HClO is a weak acid tending to dissociate in water at increased pH, which explains the obtained results compared to the other chlorinating agents.

Table 1 Solvent effect on the selective catalytic chlorination of carvone **a**<sup>a</sup>

Solvent	Conversion <b>a</b> (%)	Monochloride <b>b</b> (%)	Dichloride <b>c</b> (%)	Vinyl allyl dichloride <b>d</b> (%)	Trichloride <b>e</b> (%)
$\text{CH}_2\text{Cl}_2$	100	Trace	8	78	9
$\text{CHCl}_3$	99	53	8	19	16
$\text{CCl}_4$	79	4	13	17	20
Neat water	100	5	4	Trace	47
EtOH	100	2	6	—	25
Acetonitrile	100	5	—	5	30
Hexane	58	2	5	4	34

<sup>a</sup> Reaction conditions:  $\text{FeCl}_2$  (2.5 eq.), NaDCC (4 eq. in 5 mL  $\text{H}_2\text{O}$ ), solvent/ $\text{H}_2\text{O}$  (10 mL (5 : 5)), RT, 30 min. Conversion was determined by GC using an internal standard.



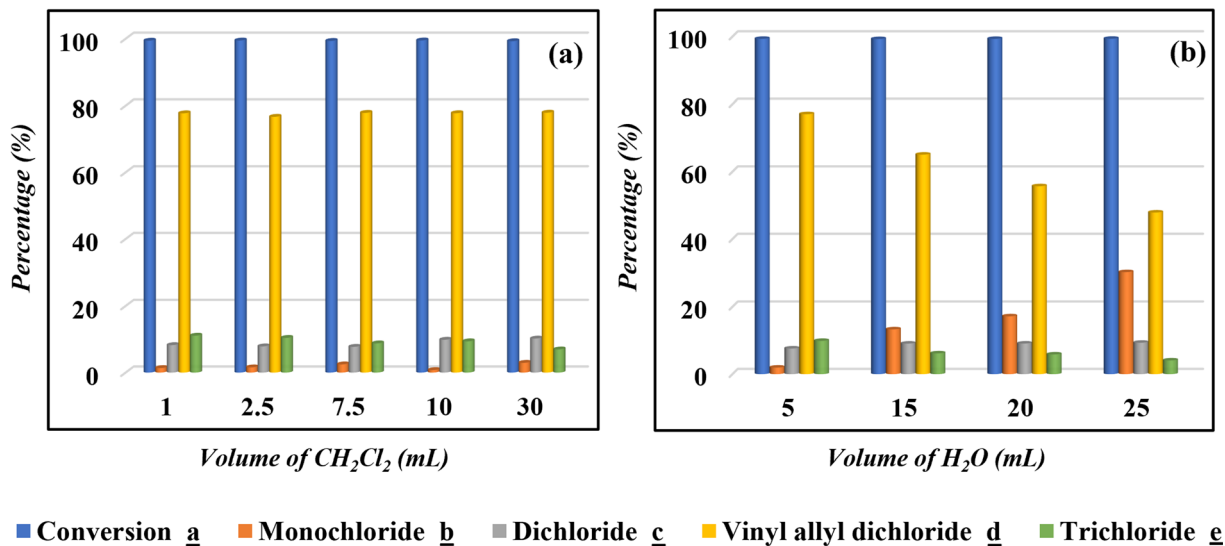


Fig. 3 Effect of dilution of (a)  $\text{CH}_2\text{Cl}_2$  and (b)  $\text{H}_2\text{O}$  on the selective catalytic chlorination of carvone a.

Table 2 Chlorinating agent and FAC effects on the selective catalytic chlorination of carvone a <sup>a,c</sup>

Chlorinating agent	Catalyst amount (eq.)	Time (h)	Conversion a (%)	Monochloride b (%)	Dichloride c (%)	Vinyl allyl dichloride d (%)	Trichloride e (%)	
NCS	Catalyst-free	0.5	NR	NR	NR	NR	NR	
		24	34	74	26	—	—	
	0.5	0.5	NR	NR	NR	NR	NR	
		24	52	46	54	—	—	
		2.5	0.5	Trace	Trace	—	—	
NaDCC	Catalyst-free	0.5	Trace	Trace	—	—	—	
		24	58	30	61	9	—	
	0.5	0.5	100	97	2	—	—	
		2.5	0.5	100	Trace	8	78	9
		2.5	0.5	100	56	12	32	6
NaClO <sup>b</sup>	Catalyst-free	0.5	NR	NR	NR	NR	NR	
		0.5	7	100	—	—	—	
		2.5	100	56	12	32	6	

<sup>a</sup> Reaction conditions:  $\text{FeCl}_2$  (in 5 mL  $\text{H}_2\text{O}$ ), chlorinating agent (4 eq. in 5 mL  $\text{H}_2\text{O}$ ),  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  (10 mL (5 : 5)), RT. Conversion was determined by GC using an internal standard. <sup>b</sup> 5–10% FAC. <sup>c</sup> NR: no reaction.

**2.2.5. Catalyst effects.** To further enlighten the catalytic effect on the selective catalytic chlorination, a study of different types of Lewis acid catalysts, *via* the investigation of the oxidation state, ligand and metal effects, was carried out.

**2.2.5.1. Effects of iron oxidation state and ligand.** The catalytic activity of iron-based catalysts with different oxidation states on the selective catalytic chlorination has been studied with 0.5 and 2.5 eq. of catalyst (Fig. 4). While both Fe(II) and Fe(III) oxidation states reveal a good control of selectivity when varying the catalyst amount, Fe(0) shows a slow reaction kinetics with a loss in conversion and a lack of selectivity towards **d** due to its heterogeneous nature.

We have also studied the ligand effect in the presence of various iron-based Lewis acid catalysts (Fig. 4). The result indicates that chloride ligand is the most suitable for Lewis acid catalyst for a better controllable selectivity towards allylic and/or vinylic chlorides as major products. Moreover, sulfate ligand could also be suitable for a selective chlorination reaction. The

slow reaction kinetics, conversion and lack in selectivity of **d** observed with  $\text{Fe}_2\text{O}_3$  can be also due to the heterogeneous nature of the catalyst.

**2.2.5.2. Metal effect.** Furthermore, the selective catalytic chlorination was carried out in presence of different metal(II) chloride ( $\text{MCl}_2$ , with M = Fe; Cu; Zn or Sn) under optimized conditions (Fig. 5). Accordingly, the comparative study indicates that iron is the most suitable metal for  $\text{MCl}_2$  Lewis acid catalyst for a better controllable selectivity. Additionally,  $\text{SnCl}_2$  is also revealed as suitable Lewis acid catalyst for a selective formation of **d**.

### 2.3. Reaction kinetics

It has been reported that 30 min represents the optimum reaction time for the catalytic chlorination.<sup>29,48,53,54</sup> In order to gain a better insight on the reaction kinetics, the follow-up of the course of the catalytic performance under optimized conditions was investigated (Fig. 6). The reaction exhibits a significant reaction progress



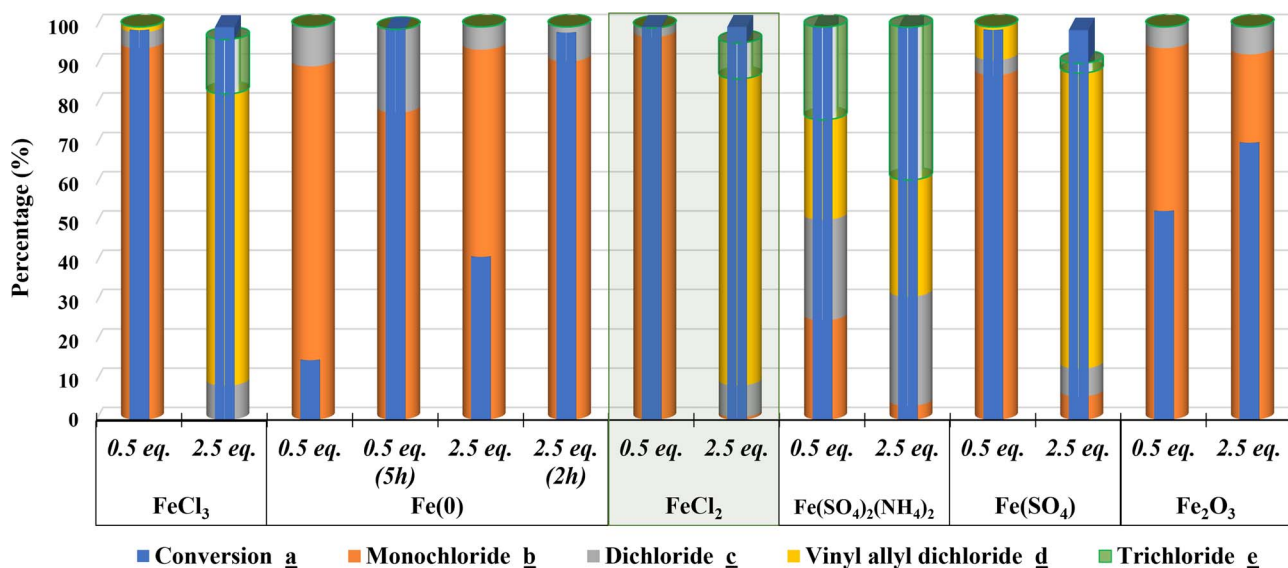


Fig. 4 Effects of iron oxidation state and ligand on the selective catalytic chlorination of carvone a.

at  $t = 0$  min (after the last drop of the chlorinating agent) with a high to good reaction selectivity. While the use of 0.5 eq. of FeCl<sub>2</sub> leads to a complete reaction at about 5–10 min, the amount of 2.5 eq. exhibits a noticeable total conversion at  $t = 0$  min. The reaction progress with a switching in selectivity started after 1 min of reaction between the two major products (**b** and **d**). In addition, the high selectivity obtained while using 2.5 eq. of FeCl<sub>2</sub> after 5 min of reaction indicates the mechanistic pathway for the vinylic chloride formation **d**. Thus, the formation of **d** can be explained from the second allylic chlorination of **b**. However, the formation

of byproducts (**c** and **e**) may be explained by the addition reaction of two chloride atoms. In addition to the better control of selectivity, the use of NaDCC enhances the catalytic performance in terms of reaction kinetics compared to the previous works.<sup>29,48,53,54</sup>

#### 2.4. Reusability of the catalytic system

In catalysis, it is well known that the ability of a catalyst recycling is uncommon in homogenous catalysis compared to the heterogenous one, due to the complexity of the homogeneous

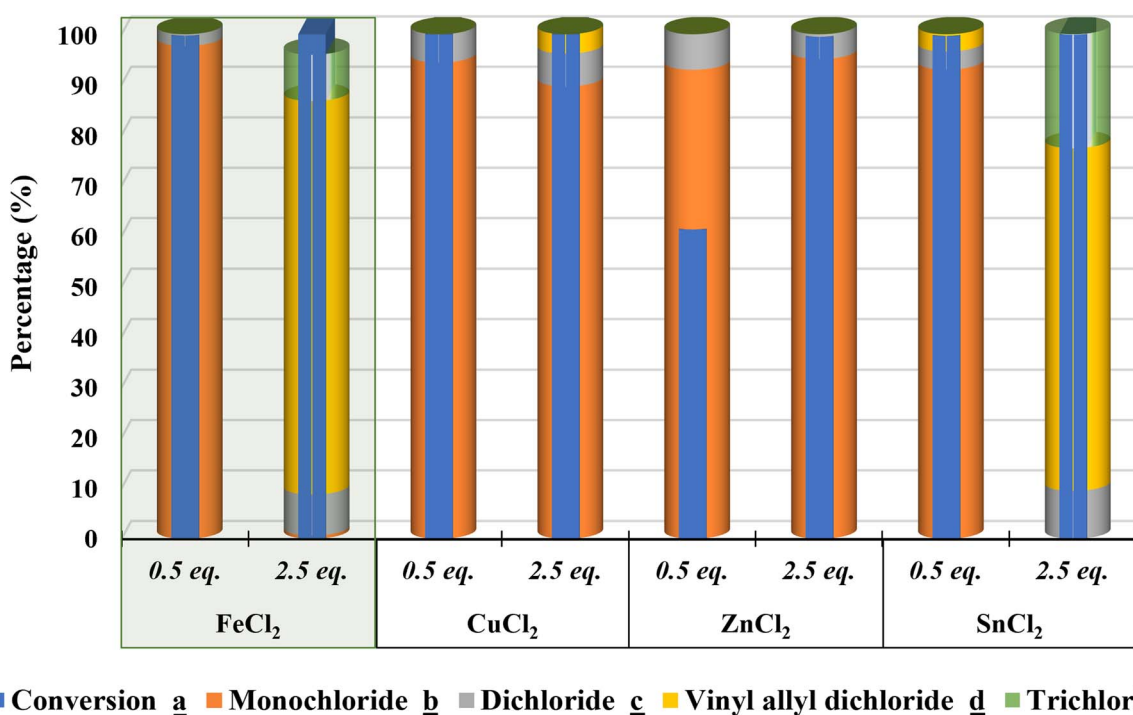


Fig. 5 Metal effect on the selective catalytic chlorination of carvone a.



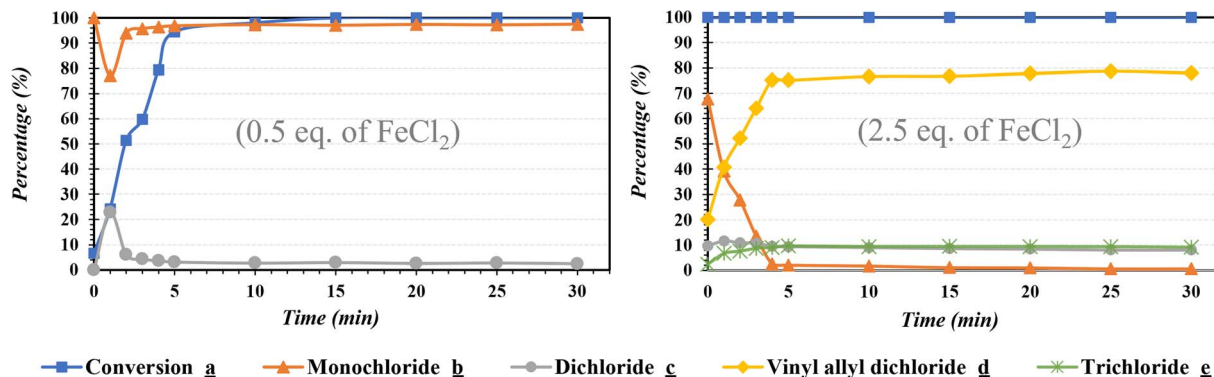


Fig. 6 Reaction kinetics of the selective catalytic chlorination of carvone a using 0.5 and 2.5 eq. of  $\text{FeCl}_2$ .

reaction medium. However, we have studied the catalyst recycling ability of the optimized catalytic system  $\text{FeCl}_2/\text{NaDCC}$  under the optimized reaction conditions (Fig. 6). Hence, the use of 0.5 eq. of  $\text{FeCl}_2$  shows a possible reusability of the catalytic system for three consecutive cycles (Fig. 7a). After each cycle, the catalytic system was recycled by removing the organic phase and reusing the aqueous one (catalytic system) for another cycle. At the third run, a poor conversion (16%) was observed, which indicates a depletion of the active chlorine ( $\text{HClO}$ ) in the reaction medium that was confirmed by the addition of 1.5 eq. of NaDCC (optimized amount for a total chlorination (Fig. 1)), giving rise to a re-increased conversion. On the other hand, the use of 2.5 eq. of  $\text{FeCl}_2$  allows three consecutive cycles of reusing (Fig. 7b). At the fourth run, no reaction took place and the addition of 1.5 eq. of NaDCC confirms the depletion of the active chlorine *via* a re-increased conversion. Hence, the used recycling method for the studied homogeneous system allows us to evaluate both the reuse of the Lewis acid catalyst and the lifetime of the FAC during cycles. We can assume that the studied recyclability process confirms the great catalytic activity

of the iron-based catalyst with a stable and continuous reusability depending on a significant presence of FAC in the reaction medium.

### 2.5. Selective catalytic chlorination of various terpenic olefins

To enlighten the scope and limitations of the studied catalytic system  $\text{FeCl}_2/\text{NaDCC}$ , the selective catalytic chlorination was extended to a much more demanding functionalized terpenic olefins such as limonene oxide (f), nootkatone (i), pulegone (m), perillyl aldehyde (p), perillyl alcohol (s) and limona ketone (t) (Table 3). The results depicted in Table 3 show that all substrates were converted to the corresponding allylic monochlorides as major products in presence of 0.5 eq. of  $\text{FeCl}_2$ .<sup>29</sup> In contrast, limona ketone (t)<sup>70</sup> affords only the addition reaction even with 0.5 or 2.5 eq. of  $\text{FeCl}_2$ , towards dichloride (u) as major product in good agreement with our previous study.<sup>29</sup>

Due to the high interest of vinyl chlorides in organic synthesis and biological activities,<sup>19–21</sup> the selective catalytic

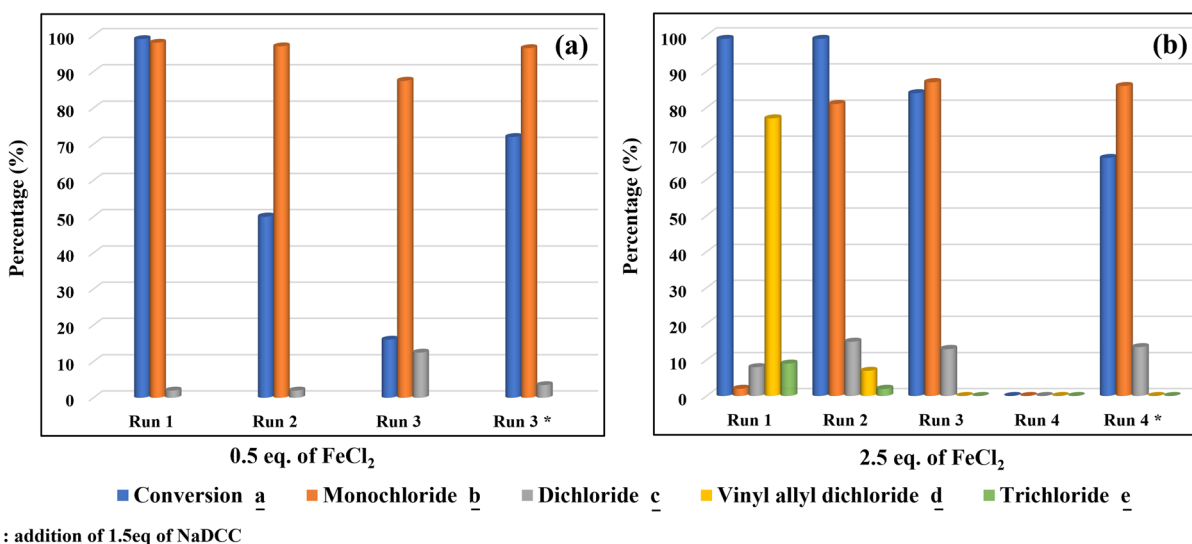


Fig. 7 Reusability of the catalytic system in the selective chlorination of carvone a using (a) 0.5 and (b) 2.5 eq. of  $\text{FeCl}_2$ .



Table 3 Selective catalytic chlorination of various terpenic olefins<sup>a</sup>

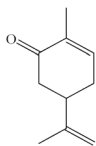
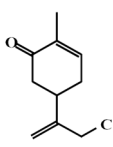
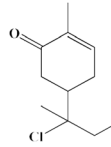
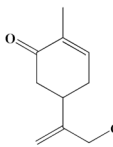
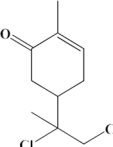
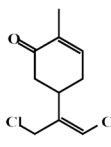
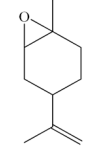
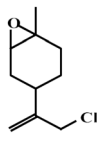
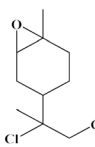
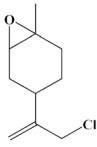
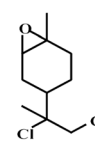
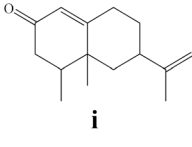
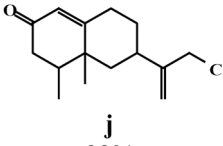
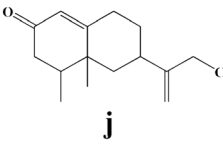
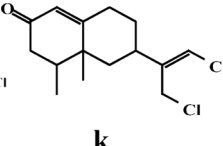
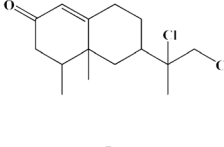
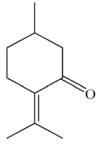
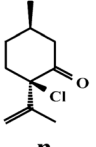
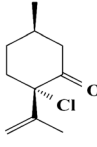
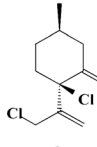
Substrate	Conversion (%)	FeCl <sub>2</sub> amount (eq.)	TOF (s <sup>-1</sup> )	Product/isolated yield (%)		
 <b>a</b>	99%	0.5	$3.81 \times 10^{-3}$	 <b>b</b> 97%	 <b>c</b> trace	
		2.5	$7.80 \times 10^{-4}$	 <b>b</b> trace	 <b>c</b> 8%	 <b>d</b> 78%
 <b>f</b>	99%	0.5	$3.80 \times 10^{-3}$	 <b>g</b> 85%	 <b>h</b> 12%	
		2.5	$7.70 \times 10^{-4}$	 <b>g</b> 8%	 <b>h</b> 49%	
 <b>i</b>	98%	0.5	$2.60 \times 10^{-3}$	 <b>j</b> 92%		
		2.5	$5.32 \times 10^{-4}$	 <b>j</b> trace	 <b>k</b> 66%	 <b>l</b> 15%
 <b>m</b>	98%	0.5	$3.72 \times 10^{-3}$	 <b>n</b> 54%	 <b>n'</b> 28%	 <b>o</b> 16%





Table 3 (Contd.)

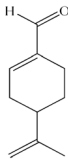
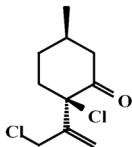
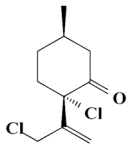
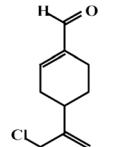
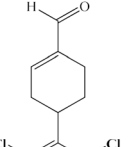
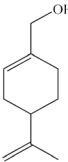
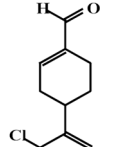
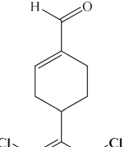
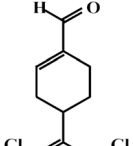
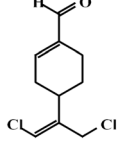
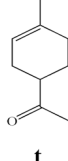
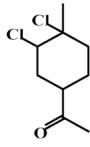
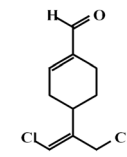

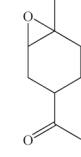
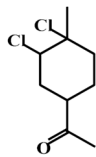
Substrate	Conversion (%)	FeCl <sub>2</sub> amount (eq.)	TOF (s <sup>-1</sup> )	Product/isolated yield (%)	
 <b>p</b>	99%	2.5	$7.62 \times 10^{-4}$	 <b>o</b> 61%	 <b>o'</b> 34%
				 <b>q</b> 90%	 <b>r</b> 8%
 <b>s</b>	99%	0.5	$3.81 \times 10^{-3}$	 <b>q</b> 80%	 <b>r</b> 14%
				 <b>r</b> 78%	 <b>r</b> 73%
 <b>t</b>	98%	2.5	$7.80 \times 10^{-4}$	 <b>q</b> 5%	 <b>r</b> 73%
				 <b>u</b> 53%	 <b>v</b> 30%



Table 3 (Contd.)

Substrate	Conversion (%)	FeCl <sub>2</sub> amount (eq.)	TOF (s <sup>-1</sup> )	Product/isolated yield (%)
		2.5	8.40 × 10 <sup>-4</sup>	 <b>u</b> 73%

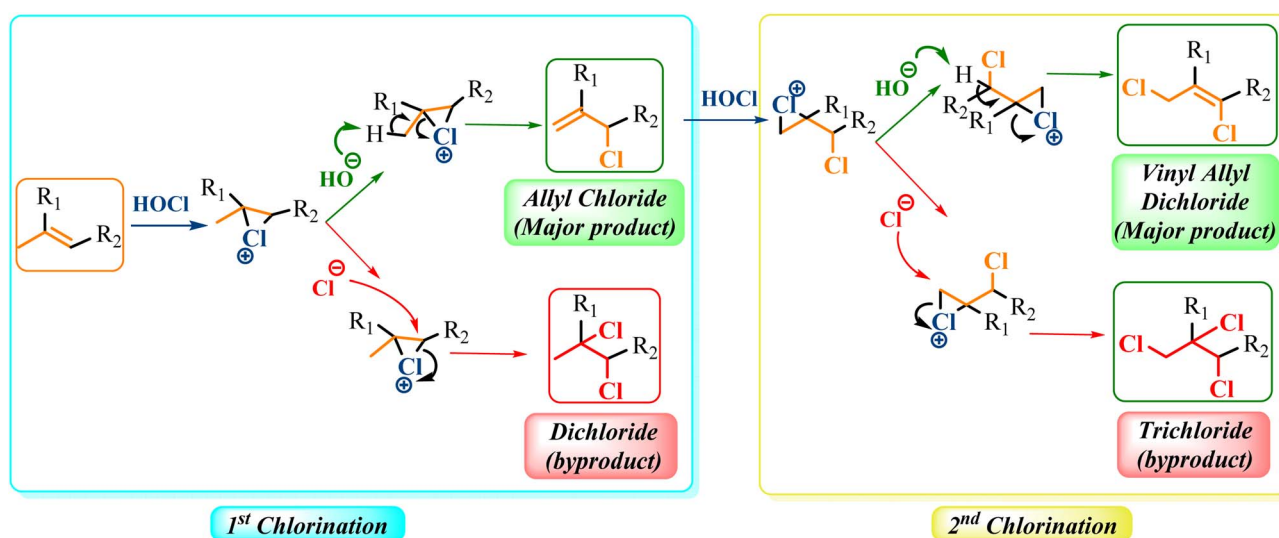
<sup>a</sup> Reaction conditions: FeCl<sub>2</sub> (0.5 eq. and 2.5 eq.), NaDCC (4 eq. in 10 mL H<sub>2</sub>O), CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (30 mL (15:15)), RT, 30 min. Conversion was determined by GC using an internal standard.

formation of vinylic chloride represents a good pathway for their direct one-step synthesis. The use of 2.5 eq. of FeCl<sub>2</sub> leads to new vinyl allyl dichlorides **d**, **k** and **r** in good to excellent yields starting from **a**, **i** and **p** or **s** (Table 3, entries 1, 3, 5 and 6), respectively. However, **f**, **m** and **t** are not reactive towards vinylic chlorination. Moreover, **f** and **t** favor the addition reaction with the formation of **h** and **u** as major products, respectively. In contrast, **m** reveals a possible second allylic reactive site. To the best of our knowledge, **m** leads for the first time to easily separable diastereomers (**n**: (*R,R*), **n'**: (*R,S*)) and (**o**: (*R,R*), **o'**: (*R,S*)). It is noteworthy to mention that no addition products are revealed in the catalytic chlorination of **m**, **p** and **s**.

## 2.6. Proposed mechanism for the selective catalytic chlorination reaction

To give further insight on the selective catalytic chlorination, a mechanistic pathway is proposed based on the obtained results

(Scheme 3). Accordingly, the catalytic chlorination towards allylic or vinylic chlorides may be explained by a 1<sup>st</sup> and a simultaneous 2<sup>nd</sup> allylic chlorination, respectively. The chlorination reaction is probably based on the mild generation of electrophilic chloronium cation (Cl<sup>+</sup>) from the active chlorine species HOCl, which further chlorinates the corresponding alkene *via* cationic intermediates (Scheme 3).<sup>29</sup> While the loss of proton from the cationic intermediate in the 1<sup>st</sup> chlorination leads to the formation of the allylic chlorinated derivative, the 2<sup>nd</sup> chlorination leads to the formation of vinyl allyl dichlorinated derivative. However, a side reaction through competitive additions that form dichloride and trichloride derivatives is revealed. Based on the experimental results, we can assume that the addition products are not formed neither from the allyl nor the vinyl allyl derivatives, respectively. Furthermore, in the presence of metal ions, HOCl can also generate anionic chlorine (Cl<sup>-</sup>).<sup>64,71</sup> Hence, the addition reaction could probably be explained by the ring-opening of the cationic intermediates *via* the attack of the generated anionic chlorine (Scheme 3).



Scheme 3 Proposed mechanism for the catalytic chlorination reaction.



### 3. Conclusion

In a summary, we have described a simple and efficient methodology for selective catalytic chlorination of naturally occurring terpenic olefins under mild conditions. A combination of cost-effective and highly stable FAC donor (NaDCC) with a readily available Lewis acid catalyst ( $\text{FeCl}_2$ ) in a biphasic system ( $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ ) was developed. The present reported catalytic system  $\text{FeCl}_2/\text{NaDCC}$  reveals high conversion with a highly controllable selectivity towards allylic and/or novel vinylic chlorination reaction in a shorter reaction time. Various influencing parameters on the catalytic reaction (solvent, dilution, chlorination agent nature, FAC, stoichiometry, and reaction kinetics) were optimized using carvone as a model substrate. The optimization process reveals NaDCC as a mild, sustainable and cost-effective chlorine donor due to its high FAC efficiency for the selective catalytic chlorination reaction. Furthermore, the chlorinated Lewis acid catalyst ( $\text{MCl}_x$ ), such as  $\text{FeCl}_2$ ,  $\text{FeCl}_3$  and  $\text{SnCl}_2$ , and its stoichiometry were found to be determinant for highly controllable chlorination selectivity towards allylic or vinylic derivatives. Moreover, the chlorination of various terpenic olefins under the optimized conditions indicates that the substrates reactivity is also determinant for a better controllable selectivity. The studied homogeneous catalytic chlorination system ( $\text{FeCl}_2/\text{NaDCC}$ ) shows good reusability and represents an efficient tool to produce selectively and reproductively new high added value allylic and vinylic terpenic derivatives in good to excellent yields under mild conditions.

### 4. General procedure

In a typical procedure, terpenic olefin (0.16 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$  is added to a stirred solution of  $\text{FeCl}_2$  (0.5 or 2.5 eq.) in 5 mL of  $\text{H}_2\text{O}$  at room temperature. Next, NaDCC (4 eq.) is dissolved in a minimum volume of  $\text{H}_2\text{O}$  (5 mL) and added dropwise during 30 second to the mixture under vigorous stirring. After 30 min, the reaction is quenched with a saturated aqueous  $\text{Na}_2\text{SO}_3$  solution and the organic layer is extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent is removed and the crude is separated by silica gel column chromatography using hexane and ethyl acetate as eluents to obtain the pure chlorinated products. The isolated products were characterized by NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and mass spectrometry (GC-MS) (ESI $^+$ ).

### Conflicts of interest

The authors declare that they have no conflicts of interest.

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