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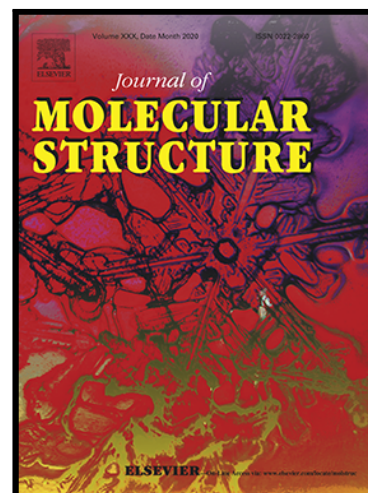
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# A one-pot synthesis and X-Ray structural characterization of new highly substituted-allyl carbamates

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## Research highlights

- One-pot synthesis of new variously substituted allylic carbamates starting from  $\beta$ -chloro- $\alpha,\beta$ -unsaturated aldehydes in high yields.
- Full characterization of the new compounds and the corresponding intermediates by NMR and IR spectroscopic techniques and HRMS.
- X-ray crystallography structural determination of two allyl carbamates.

## ABSTRACT

A one-pot synthesis of new variously substituted  $\gamma$ -chloro- $\gamma,\beta$ -allylic carbamates have been carried out starting from  $\beta$ -chloro- $\alpha,\beta$ -unsaturated aldehydes. The new carbamates and the corresponding intermediates, the  $\gamma$ -chloro- $\gamma,\beta$ -allylic alcohols, were fully characterized by (<sup>1</sup>H and <sup>13</sup>C) NMR, IR and HRMS spectroscopic techniques. The crystal structures of two allylic carbamates, were established by single-crystal X-ray diffraction.

**Keywords:**  $\beta$ -chlorovinylaldehydes; one-pot synthesis ; allylic carbamates; X-ray diffraction.

## 1. Introduction

Carbamates and allylic carbamates in particular, are of considerable interest due to their important role in various areas. Indeed, they belong to structural or functional part of many approved drugs [1-5] and prodrugs [6], which are used for the treatment of various diseases such as Alzheimer's disease [7], cancer [8], hepatitis C [1, 9], HIV infection [10], anxiety [11] and epilepsy [11]. They are found to be important raw materials in the synthesis of polyurethanes [12-14], paints [15], wood preservatives [15], pesticides, herbicides, insecticides and fungicides [16]. They are also used as intermediates in numerous organic synthesis [17, 18] as protecting amino groups in peptide synthesis [19, 20], polymers synthesis [21] and as linkers in combinatorial chemistry [22] as well as in the cyclic [23] and heterocyclic compounds synthesis [24-27]. Therefore continuous efforts have been

made to obtain this type of compounds, particularly the allylic carbamates, through simple and efficient methods. The conventional method for preparation is the reaction of an isocyanate with the corresponding allyl alcohol [28, 29] or through a *trans*-carbamoylation reaction of the hydroxyl group with the phenyl carbamate [30]. Coupling reaction of aryloxyallenes with CO<sub>2</sub> and amines using a silver-catalyzed is also reported [31] as well as the reaction of carbonyl compounds with N,N-dialkyl carbamoyl chloride [32]. However, the structural variation of allyl carbamates have shown serious limitations due to either the limited availability of various allyl alcohols bearing tri- or tetra-substituted double bond [28] or by the use of palladium complexes as catalysts strong bases [33] and strong oxidants [34] which are not suitable for allyl carbamates since they can promote unwanted cyclization reactions [35].

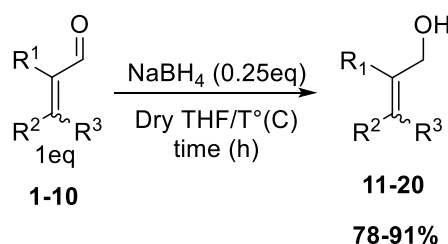
In our previous works, we have explored the reactivity of the  $\beta$ -chlorovinyl aldehydes as precursors of highly substituted  $\beta$ -fluoroalkoxyvinyl aldehydes and corresponding alcohols [36], benzenes [37], allylic alcohols [38], phosphoramidates [38], phosphonates and phosphates [39]. As an extension of our work, we report here the one-pot synthesis of a new series of variously substituted allylic carbamates. The new compounds were obtained in mild conditions with good to excellent yields and were fully confirmed by (<sup>1</sup>H and <sup>13</sup>C) NMR, IR spectroscopies and HRMS. The structures of two allyl carbamates were determined by X-Ray crystallography.

## 2. Results and discussion

### 2.1. Synthesis

The starting substrates **1**, **2** and **4-9** were synthesized from the corresponding  $\alpha$ -methylene ketones using the Vilsmeier-Haack reaction according to literature procedures [40]. The synthesis of the new  $\gamma$ -chloro- $\beta,\gamma$ -unsaturated alcohols (**11**, **12** and **14-18**) was performed via carbonyl reduction of the  $\beta$ -chloro- $\alpha,\beta$ -unsaturated aldehydes. The chlorovinylaldehydes and cinnamaldehyde (**1-10**) reacted with sodium borohydride as reducing agent in dry THF and gave the products (**11-20**) in good yields (Table1).

**Table1:** Optimized synthesis of  $\gamma$ -chloro- $\beta,\gamma$ -unsaturated alcohols (**11-20**).



Substrate (Z/E) <sup>a</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	time(h)	T(°C)	Product	Yield <sup>b</sup>	Ratio(Z/E) <sup>c</sup>
<b>1</b> (100/0)	-(CH <sub>2</sub> CH <sub>2</sub> )-	-(CH <sub>2</sub> CH <sub>2</sub> )-	Cl	3	Reflux	<b>11</b>	92	(100/0)
<b>2</b> (100/0)	-(CH <sub>2</sub> CH <sub>2</sub> )-	-(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )-	Cl	3	Reflux	<b>12</b>	96	(100/0)
<b>3</b> (0/100)	H	Ph	H	2	Reflux	<b>13</b>	89	(0/100)
<b>4</b> (95/5)	H	Ph	Cl	4	Reflux	<b>14</b>	92	(94/6)
<b>5</b> (5/95)	CH <sub>3</sub>	Ph	Cl	5	Reflux	<b>15</b>	87	(5/95)
<b>6</b> (100/0)	H	<sup>t</sup> Bu	Cl	4	Reflux	<b>16</b>	84	(100/0)
<b>7</b> (95/5)	H	CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Cl	2	Reflux	<b>17</b>	78	(95/5)

<b>8</b> (26/74)	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub>	Cl	5	Reflux	<b>18</b>	76	(24/76)
<b>9</b> (61/39)	Ph	CH <sub>3</sub>	Cl	5	Reflux	<b>19</b>	75	(64/36)
<b>10</b> (83/17)	CO <sub>2</sub> Et	CF <sub>3</sub>	Cl	12	(-10)	<b>20</b>	74	(83/17)

<sup>a</sup>: *Z/E* isomer ratios measured from <sup>1</sup>H NMR aldehydic signals <sup>b</sup> yields measured after purification. <sup>c</sup>: *Z/E* Isomer ratios measured in crude products from <sup>1</sup>H-NMR CH<sub>2</sub>OH signals.

Sodium borohydride reacted regioselectively with the vinylic aldehydes **1-10** in dry THF in good to excellent yields. The obtained pale yellow or colorless oils of allylic alcohols **11-20** are stable at room temperature with *Z/E* proportions identical to those of the starting aldehydes.

Different reaction conditions were attempted to optimize the synthesis of the target carbamates. When the reaction of *N*-phenyl isocyanate with the allylic alcohol **12** was carried out without any base in dry THF at 25°C, the desired product **27** was observed after 24 h in moderate conversion percentage (Table 2, entry 1). The use of Et<sub>3</sub>N with slight excess gave total conversion (>99%) with excellent yield (entry 3). In CH<sub>2</sub>Cl<sub>2</sub> or Et<sub>2</sub>O, the reaction led to lower conversion percentages (entries 4 and 5). The various explored conditions are displayed in Table 2.

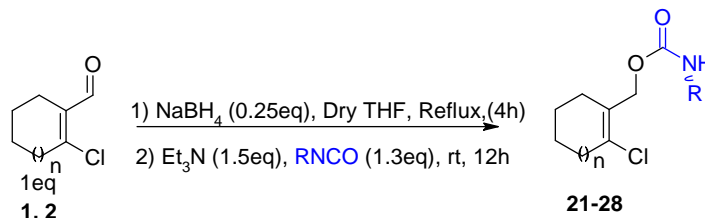
**Table 2:** Optimization of the reaction conditions of the allylic carbamate **27** at 25°C

Entry	Et <sub>3</sub> N (eq.)	Solvent	Time (h)	Conversion [%] <sup>a</sup>
1	0	THF	24	44
2	1	THF	12	96
3	1.5	THF	6	>99
4	1.5	DCM	12	74
5	1.5	Et <sub>2</sub> O	12	72

<sup>a</sup>: The conversion % was monitored by <sup>1</sup>H NMR spectroscopy in crude products.

With the optimal reaction conditions outlined above, the synthesized  $\gamma$ -chloro allylic alcohols **11-20** were subjected to carbamoylation reaction with commercial *N*-alkyl and *N*-aryl-isocyanates in dry THF in mild basic medium at room temperature affording successfully new series of enol carbamates **20-45** in moderate to excellent yields (52-95%). Moreover, both carbonyl reduction and carbamoylation were successfully realized in one-pot procedure, starting from the aldehydes. The resulting variously substituted carbamates from the cyclic aldehydes **21-28** (Table 3), of the cinnamaldehydes **29-37** (Table 4) or from the acyclic  $\alpha,\beta$ -unsaturated aldehydes (Table 5), were obtained as viscous oils or solids, soluble in both CHCl<sub>3</sub> and DMSO. All the reactions were monitored by TLC and <sup>1</sup>H-NMR. All final products were stable at 0°C and were characterized by IR, (<sup>1</sup>H and <sup>13</sup>C) NMR spectroscopies and HRMS.

**Table 3:** one-pot synthesis of carbamates from  $\sigma,\beta$ -unsaturated cyclic aldehydes (**21-28**)

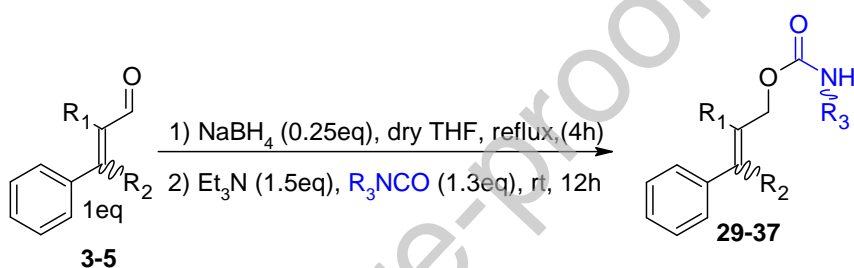


Entry	Substrate	R	Product (Yield%) <sup>a</sup>
1	<b>1</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>21</b> (69)
2	<b>1</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>22</b> (91)
3	<b>1</b>	Ph	<b>23</b> (93)

4	<b>1</b>	3-ClPh	<b>24</b> (68)
5	<b>2</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>25</b> (88)
6	<b>2</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>26</b> (87)
7	<b>2</b>	Ph	<b>27</b> (91)
8	<b>2</b>	3-ClPh	<b>28</b> (78)

<sup>a</sup>: yields after purification.

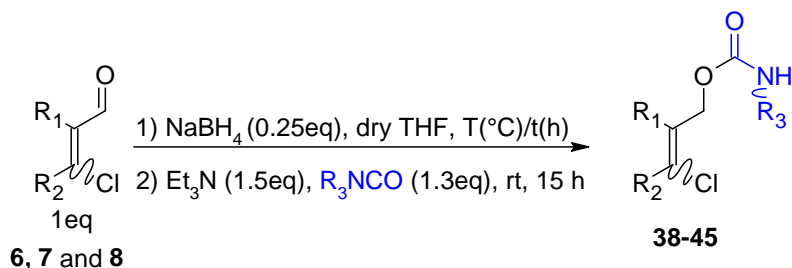
**Table 4:** One-pot synthesis of carbamates from cinnamaldehyde derivatives (**29-37**)



Entry	Substrate	R <sup>3</sup>	Products	Yield <sup>a</sup>	Ratio(Z/E) <sup>b</sup>
1	<b>3</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>29</b>	86	(0/100)
2	<b>3</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>30</b>	96	(0/100)
3	<b>3</b>	Ph	<b>31</b>	93	(0/100)
4	<b>3</b>	3-ClPh	<b>32</b>	52	(0/100)
5	<b>4</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>33</b>	63	(92/8)
6	<b>4</b>	3-ClPh	<b>34</b>	82	(93/7)
7	<b>5</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>35</b>	62	(3/97)
8	<b>5</b>	Ph	<b>36</b>	86	(4/96)
9	<b>5</b>	3-ClPh	<b>37</b>	62	(24/76)

<sup>a</sup>: yields after purification ; <sup>b</sup>: Z/E Isomer percentages measured in crude products from <sup>1</sup>H NMR spectra.

**Table 5:** One-pot synthesis of carbamates from alkylated  $\alpha$ ,  $\beta$ -unsaturated aldehydes (**38-45**)



Entry	Substrate	R <sup>3</sup>	T(°C)/t(h)	Product	Yield (%) <sup>a</sup>	Ratio(Z/E) <sup>b</sup>
1	<b>6</b>	Ph	Reflux./4	<b>38</b>	65	(100/0)
2	<b>8</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	Reflux./4	<b>39</b>	73	(30/70)
3	<b>8</b>	Ph	Reflux./4	<b>40</b>	50	(23/77)

4	<b>8</b>	3-ClPh	Reflux./4	<b>41</b>	59	(23/77)
5	<b>9</b>	Ph	Reflux./4	<b>42</b>	94	(66/34)
6	<b>9</b>	3-ClPh	Reflux./4	<b>43</b>	86	(66/34)
7	<b>10</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	<b>-10/12</b>	<b>44</b>	67	(83/17)
8	<b>10</b>	Ph	<b>-10/12</b>	<b>45</b>	73	(85/15)

<sup>a</sup>: yields after purification ; <sup>b</sup>: *Z/E* Isomer percentages measured in crude products from <sup>1</sup>H NMR spectra.

Analysis of the <sup>1</sup>H-NMR spectra showed the formation of the target carbamates by the presence of signals assigned to both N=CH and CONH protons. However, for the carbamate **42**, these signals appear to be duplicated due to *cis* and *trans* conformers. In particular, the compound **36**, after a long term storing or recording the corresponding spectrum in DMSO as solvent instead of CDCl<sub>3</sub>, the additional signals of the second conformer are observed. In all spectra, The NH-Ph signals had moved substantially from chemical shifts 6.6-7.58 ppm in CDCl<sub>3</sub> to 9.7-9.9 ppm in DMSO without significantly affecting the *cis* and *trans* ratios. This is obviously due to the favored formation of the H-bond between the carbamate and DMSO. This is in accordance with our previous work [41].

**Table 6:** (  $\delta_{\text{NH}}$  ppm) *cis/trans*-amide conformers and ratios in CDCl<sub>3</sub> and DMSO-d<sub>6</sub>

Entry	Product	( $\delta_{\text{NH}}$ ) CDCl <sub>3</sub> % ( <i>cis/trans</i> ) <sup>a</sup>	( $\delta_{\text{NH}}$ ) DMSO-d <sub>6</sub> % ( <i>cis/trans</i> ) <sup>a</sup>
1	<b>24</b>	7.54 (0/100)	9.97 (0/100)
2	<b>31</b>	7.17 (0/100)	9.74 (0/100)
3	<b>36</b>	6.94/7.58 (53/47)	9.98/9.74 (59/41)
4	<b>38</b>	6.82 (0/100)	9.74 (0/100)

<sup>a</sup>: *cis/trans*-amide ratio measured at room temperature from <sup>1</sup>H-NMR NH signals integration in CDCl<sub>3</sub> and DMSO-d<sub>6</sub>.

The same behavior was observed in <sup>13</sup>C-NMR spectra of compounds **36** and **42**, which revealed duplication not only around the CH-NH bonds, but also in more remote parts of the molecules, such as the carbonyl and the substituents in  $\gamma$  and  $\beta$  positions of the carbamates. The <sup>13</sup>C-NMR spectra of carbamates **23** and **27** in CDCl<sub>3</sub> show only one set of peaks corresponding to a single rotamer. The 2D-NOESY spectrum exhibited a cross correlation between NH and CH<sub>2</sub>O in compound **23** and **27** only indicating the *trans* conformation of OR group with respect of NH. However, no indication on the *trans* NH-CO conformation was collected from the spectrum.

On the other hand, it has been reported that, in IR spectroscopy of compounds bearing NH-CO group, the NH-stretching vibration  $\nu_{\text{NH}}$  at 3200 cm<sup>-1</sup> is assigned to the *cis*-amide whereas the  $\nu_{\text{NH}}$  above 3200 cm<sup>-1</sup> is attributed to the *trans*-amide with in addition, a characteristic band at 1540 cm<sup>-1</sup> [42]. In most cases, the infrared spectra of the compounds **20-45** in pure state (Table 6) showed two  $\nu_{\text{NH}}$  stretching bands; a large vibrational band ranging from 3330 to 3350 cm<sup>-1</sup> related to bound NH and a thin vibrational band ranging from 3420 to 3460 cm<sup>-1</sup> related to free NH. Furthermore, the presence of a thin and intense bending band at 1513-1590 cm<sup>-1</sup> indicate reliably the *trans* conformation of NH-CO. All the spectra show also intense bands related to the carbonyl C=O at about 1620–1700 cm<sup>-1</sup> and to the double bond C=C at 1625– 1685 cm<sup>-1</sup>. All the characteristic bands are summarized in Table 7.

**Table 7:** IR data of allylic carbamates **21-45** in cm<sup>-1</sup>

Entry	Product	$\nu_{\text{NH}}$	$\delta_{\text{NH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$	
1	<b>21</b>	-	3346	1526	1711	1695
2	<b>22</b>	3452	-	1515	1712	1619
3	<b>23</b>	3425	-	1524	1732	1600
4	<b>24</b>	3432	-	1523	1732	1598
5	<b>25</b>	3345	3337	1516	1710	1695
6	<b>26</b>	3452	3334	1516	1765	1704
7	<b>27</b>	3435	-	1524	1732	1602
8	<b>28</b>	3421	3325	1523	1735	1598
9	<b>29</b>	3448	-	1514	1720	1695
10	<b>30</b>	-	3340	1519	1695	-
11	<b>31</b>	3435	-	1524	1728	1601
12	<b>32</b>	3420	3338	1524	1731	1597
13	<b>33</b>	3446	3353	1514	1716	1638
14	<b>34</b>	3420	3336	1524	1732	1597
15	<b>35</b>	3445	3351	1515	1715	1698
16	<b>36</b>	3423	3338	1524	1732	1599
17	<b>37</b>	3406	3320	1524	1708	1594
18	<b>38</b>	3423	3336	1525	1731	1600
19	<b>39</b>	3469	3335	1532	1692	1660
20	<b>40</b>	3328	-	1524	1711	1600
21	<b>41</b>	3432	-	1523	1731	1598
22	<b>42</b>	3431	3301	1525	1727	1600
23	<b>43</b>	3432	-	1523	1733	1598
24	<b>44</b>	3450	-	1518	1735	1651
25	<b>45</b>	3432	-	1526	1740	1601

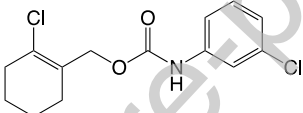
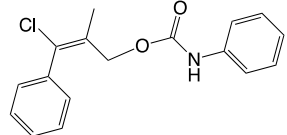
### Crystallographic data collection, structure determination and refinement

The proposed structures of allylic carbamates **24** and **36** were confirmed by single crystal X-ray diffraction (SCXRD) analysis. The suitable crystals for both compounds were prepared from their solution in cyclohexane/diethylether (1:4) by slow evaporation of the solvent. The corresponding intensities datasets were measured at room temperature using a RIGAKU *XtaLabPro* diffractometer equipped with a Mo microfocus sealed tube *MM003* generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD *PILATUS3R 200K* detector. *CrysAlisPro 1.171.39.46* [43] was employed for the data processing, with *SCALE3 ABSPACK* scaling algorithm implemented for the empirical absorption correction using spherical harmonics. The structures were readily solved by intrinsic phasing methods (SHELX-T program) [44]: one molecule of **24** was placed in the asymmetric unit (asu) of the orthorhombic unit cell, space group Pna2<sub>1</sub> and four independent conformers of **36** in that of the monoclinic unit cell, space group P2<sub>1</sub>. All the non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares methods on  $F^2$  using SHELX-L. [45] The crystal studied of **36** turned out to be an inversion twin whose component mass ratio refined to *ca* 0.52:0.48. H atoms could be identified in difference maps and therefore the methyl H atoms borne by C11 were allowed as rigid groups to rotate but not tip, so as to match the electron-density maxima. The other H atoms were positioned geometrically and refined with  $U_{\text{iso}}$  set to  $xU_{\text{eq}}(\text{C})$ ,  $x=1.2$  whereas  $x = 1.5$  for the methyl carbons. The positions of the hydrogen atoms in the amide groups were refined with N-H distance restrained to target 0.87(2) Å in **24** or to be similar in **36**, with  $U_{\text{iso}}$  set to  $1.2U_{\text{eq}}(\text{N})$  (only for **36**,  $U_{\text{iso}}$  being freely refined in **24**). Figure 1 shows the molecular structure of **24** whose correct orientation relative to the polar axis direction from the crystal picked up for data collection was established by means of the Flack  $x$  parameter; [46]  $x = -0.05$  (4), calculated [46] using

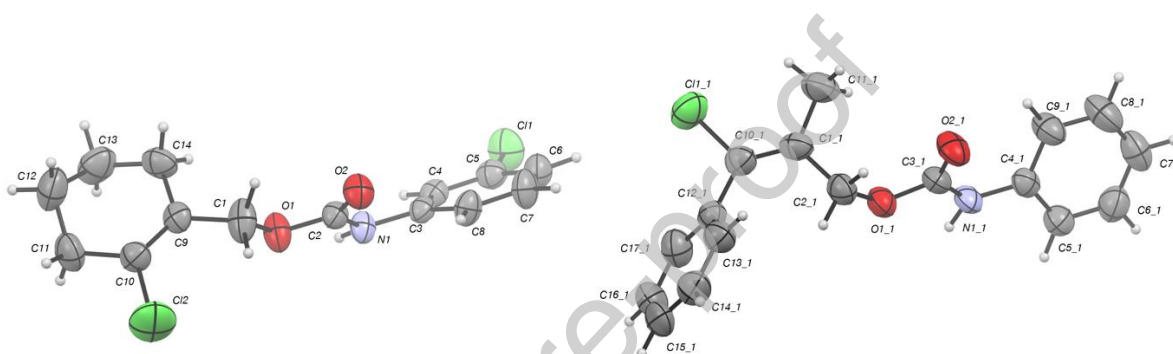


1334 quotients of the type  $[(I^+) - (I^-)] / [(I^+) + (I^-)]$  and one copy of the highly flexible E-isomer molecular structure of **36**. The conformational differences between the four copies are highlighted in an overlay diagram shown in Figure 2. In its asu, these molecules are elongated along the [010] direction and those relatively oriented in parallel way are linked by N–H ... O hydrogen bonds [graph set  $C^1_1(4)$  commonly found in structures made of simple amides, as well in the **24** one] developing along the [0 0 1] direction molecular chains (Figure 3), stacking on top of each other in antiparallel way in the *a* direction and segregated at the  $x, \frac{1}{4}, z$  and  $x, \frac{3}{4}, z$  interfaces of  $2_1$  symmetry-related (chloromethyl)benzene moieties through edge-to-face and Cl...Cl contacts ( $d_{Cl-Cl} = 3.79 \text{ \AA} \geq$  van der Waals radii sum). In **24**, the N–H ... O chains propagate infinitely along the [1 0 0] direction developing paddlewheel structure motifs centered around  $x, 0.25, 0$  and  $x, 0.75, 0.5$  positions, involving molecules related by the glide plane perpendicular to [0 1 0] with glide component 0.5, 0, 0 (Figure 4). No halogen contacts are noticed in the **24** crystal packing. Crystal data, data collection and structure refinement details are summarized in Table 8. CCDC 2084634 (**24**) - 2084224 (**36**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

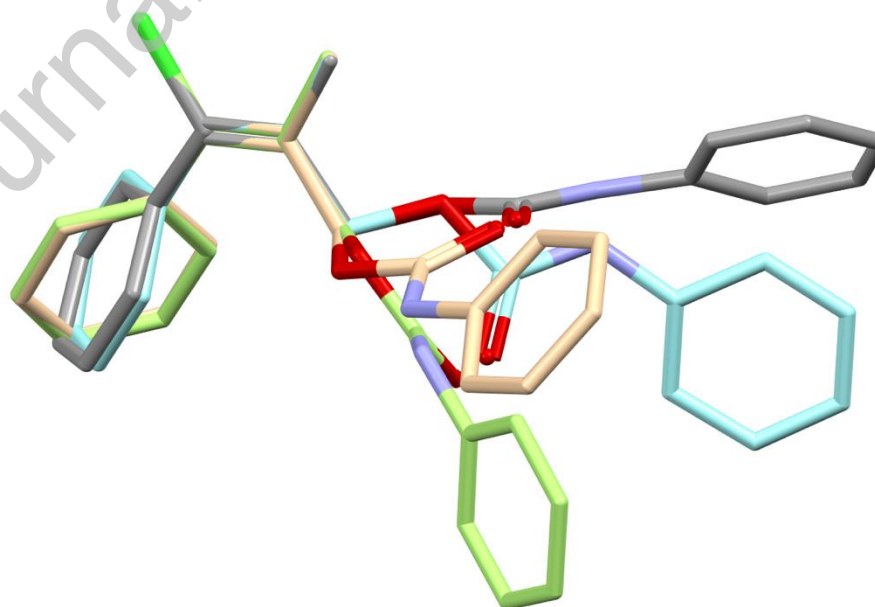
**Table 8:** Crystal data and structure refinement for compounds **24** and **36**

Compound	<b>24</b>	<b>36</b>
		
	(2-chlorocyclohex-1-en-1-yl)methyl(3-chlorophenyl)carbamate	( <i>E</i> )-3-chloro-2-methyl-3-phenylallyl phenylcarbamate
Empirical formula	C <sub>14</sub> H <sub>15</sub> Cl <sub>2</sub> N O <sub>2</sub>	C <sub>17</sub> H <sub>16</sub> Cl N O <sub>2</sub>
Formula weight	300.17	301.76
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Orthorhombic, P na <sub>2</sub> <sub>1</sub>	Monoclinic, P 2 <sub>1</sub>
Unit cell dimensions (Å)	9.9172(7) 10.2917(8) 14.0882(10)	9.2313(5) 34.2963(12) 10.0818(5)
(°)	90 90 90	90 105.979(6) 90
Volume (Å <sup>3</sup> )	1437.91(18)	3068.5(3)
Z,	4,	8,
Calculated density (Mg/m <sup>3</sup> )	1.387	1.306
Absorption coefficient (mm <sup>-1</sup> )	0.448	0.252
F(000)	1264	1264
Crystal size (mm)	0.44 x 0.20 x 0.17	0.45 x 0.23 x 0.05
θ range for data collection (°)	4.063 to 27.102	3.639 to 25.350
Limiting indices	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -18 ≤ l ≤ 18	-10 ≤ h ≤ 11, -41 ≤ k ≤ 40, -11 ≤ l ≤ 12
Reflections collected / unique	14153 / 3127 0.0749	22490 / 10718 0.0434

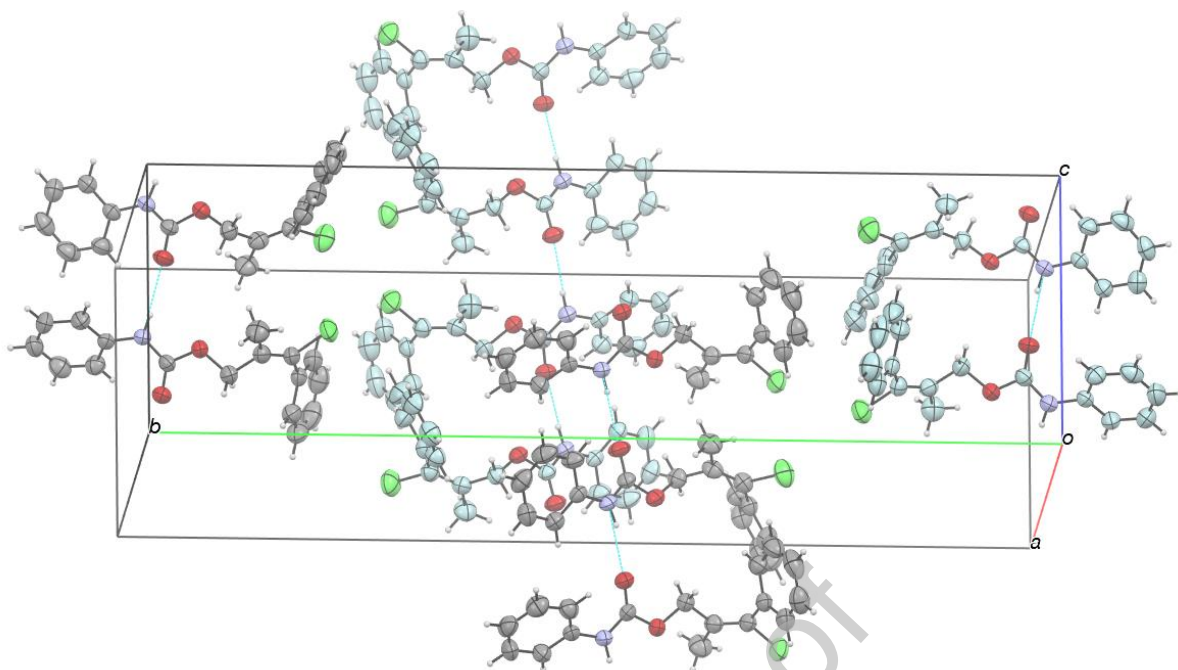
R(int)		
Completeness to $\theta_{\text{full}}$ (%)	99.6	99.6
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.860	1.000 and 0.468
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	3127 / 2 / 176	10716 / 7 / 774
Goodness-of-fit on $F^2$	1.053	0.996
Final R indices [ $I > 2\sigma(I)$ ]	R1, wR2	0.0445, 0.1224
R indices (all data)	R1, wR2	0.0459, 0.1241
Largest $\Delta$ peak and hole ( $e\cdot\text{\AA}^{-3}$ )	0.285 and -0.200	0.292 and -0.211
CCDC deposit number	2084634	2084224



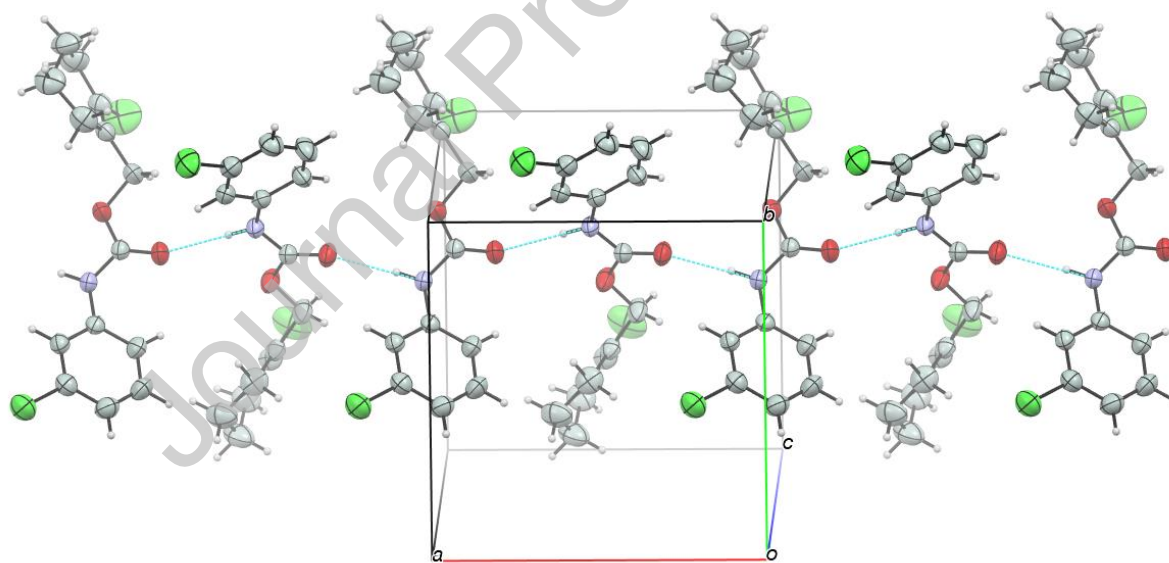
**Figure 1** Ortep view of **24** (left), and one **36** conformer (right) in their asu with their respective atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The H atoms are shown as small spheres of arbitrary radii.



**Figure 2** Overlay of the four independent molecules of **36**.



**Figure 3.** Two independent hydrogen-bonded (N-H...O) chains (underscored by different colors applied to carbon atoms) of molecules in the central part of the unit cell of **36** running along the *c* axis and framed by  $2_1$  symmetry-related molecules. Cyan dashed lines indicate N-H...O intermolecular hydrogen bonds (see table 9).



**Figure 4.** One hydrogen-bonded (N-H...O) chain of the molecules in the unit cell of **24** running along the *a* axis. Cyan dashed lines indicate N-H...O intermolecular hydrogen bonds (see table 9).

**Table 9:** Hydrogen bonds for **24** and **36** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1...O2 <sup>#1</sup>	0.85(2)	2.11(3)	2.942(3)	169(4)
N1(1)-H1N(1)...O2(2)	0.88(3)	2.21(4)	3.013(5)	152(4)
N1(2)-H1N(2)...O2(1) <sup>#2</sup>	0.87(3)	2.18(3)	3.030(5)	168(5)
N1(3)-H1N(3)...O2(4)	0.87(3)	2.18(3)	3.032(5)	163(5)
N1(4)-H1N(4)...O2(3) <sup>#3</sup>	0.85(3)	2.19(4)	2.998(5)	160(5)

Symmetry transformations used to generate equivalent atoms:

(**24**) #1  $x+1/2, -y+3/2, z$ ; (**36**) #2  $x, y, z-1$  #3  $x, y, z+1$

### 3. Conclusion

In summary, new series of  $\gamma$ -chloro- $\gamma,\beta$ -unsaturated alcohols and corresponding enol carbamates have been synthesized from  $\beta$ -chloro- $\alpha,\beta$ -unsaturated aldehydes using a facile and efficient method in most cases. The major advantage of this transformation is the non-use of metal catalysts or toxic reagents. The desired compounds were obtained in high yields and characterized by different spectroscopic techniques and X-Ray crystallography.

### Experimental Section

#### Instruments and chemicals

All solvents were dried, distilled and stored over molecular sieves (4 Å) using standard techniques. [47] The starting aldehydes were prepared using Vilsmeier–Haack reaction. [40] TLC was performed on silica gel, 60F-250 (0.26 mm thickness) plates. The plates were visualized using a UV lamp light (254 nm) or by use of potassium permanganate and 5 g  $K_2CO_3$ /100 mL water. NMR spectra were performed on Bruker AVANCE 300 MHz spectrometer at the Faculty of Pharmacy at University Paris-Saclay in France or an Ultrafield AVANCE 300 MHz spectrometer at High Institute of Environmental Sciences and Technology at University of Carthage in Tunisia. All NMR spectra were recorded at ambient temperature (290K) unless otherwise noted.  $^1H$  NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Chemical shifts ( $\delta$ ) were given in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard in  $CDCl_3$  solution. High resolution mass spectra were obtained using a Bruker Esquire electrospray ionization apparatus at the Faculty of Pharmacy at University Paris-Saclay in France.

FTIR spectra were recorded on Nicolet IR200 spectrometer within the wave number range of 4000-400 $cm^{-1}$  at 25°C at High Institute of Environmental Sciences and Technology at University of Carthage in Tunisia.

Unless otherwise noted, commercially available  $NaBH_4$ , isocyanates and triethylamine were purchased from various commercial sources (Acros, Aldrich) and used without further purification.

#### General Procedure for preparation of $\gamma$ -chloro- $\gamma,\beta$ -allylic alcohols (11-19).

To a stirred solution of  $\beta$ -chloro- $\alpha,\beta$ -vinyl aldehyde (1 mmol) in dry THF (10 mL) was added  $\text{NaBH}_4$  (0.25 mmol) at  $0^\circ\text{C}$ . The reaction mixture was stirred at adequate temperature. The progress of the reaction was monitored by TLC until the conversion of  $\beta$ -chloro- $\alpha,\beta$ -unsaturated aldehydes was complete. Then, cold distilled water (100 mL) was added to the mixture. The product was extracted with diethyl ether (3\*30mL) and washed by 10 mL of a saturated solution of NaCl. The solvent (diethyl ether) was evaporated, and the crude product was purified by short-column chromatography using (cyclohexane:diethylether) (8:2) as eluent. The same procedure will be used for the reduction of cinnamaldehyde.

**(2-chlorocyclohex-1-en-1-yl) methanol (11)**

Light Yellow oil, **FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3317 (OH), 1663 (C=C);  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 4.16 (s, 2H,  $\text{CH}_2\text{OH}$ ), 3.37 (s, 1H, OH), 2.27 (m, 2H,  $\text{CH}_2\text{cyc}$ ), 2.18-2.16 (m, 2H,  $\text{CH}_2\text{cyc}$ ), 1.66-1.56 (m, 4H,  $\text{CH}_2\text{CH}_2\text{cyc}$ );  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 132.52 (C-Cl), 128.35 (C=C- $\text{CH}_2\text{OH}$ ), 62.68 ( $\text{CH}_2\text{OH}$ ), 33.81 ( $\text{CH}_2\text{cyc}$ ), 27.78 ( $\text{CH}_2\text{cyc}$ ), 23.79 ( $\text{CH}_2\text{cyc}$ ), 22.13 ( $\text{CH}_2\text{cyc}$ ).

**(2-chlorocyclohept-1-en-1-yl) methanol (12)**

Light Yellow oil, **FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3307 (OH), 1651 (C=C);  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 4.21 (s, 2H,  $\text{CH}_2\text{OH}$ ), 2.58-2.55 (m, 2H,  $\text{CH}_2\text{cyc}$ ), 2.50 (s, 1H, OH), 2.34-2.30 (m, 2H,  $\text{CH}_2\text{cyc}$ ), 1.73-1.48 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{cyc}$ );  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 137.51 (C-Cl), 132.56 (C=C-Cl), 64.75 ( $\text{CH}_2\text{OH}$ ), 38.87 ( $\text{CH}_2\text{cyc}$ ), 31.24 ( $\text{CH}_2\text{cyc}$ ), 30.37 ( $\text{CH}_2\text{cyc}$ ), 26.10 ( $\text{CH}_2\text{cyc}$ ), 25.23 ( $\text{CH}_2\text{cyc}$ ).

**3-Phenylprop-2-en-1-ol (13)**

Colorless oil, **FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3308 (OH), 1657 (C=C);  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 7.42-7.25 (m, 5H,  $\text{H}_{\text{arm}}$ ), 6.64 (d,  $^3J_{\text{H-H}} = 15.9\text{Hz}$ , 1H,  $\text{CHPh}=\text{CH}$ ), 6.39 (dt,  $^3J_{\text{H-H}} = 15.9\text{Hz}$ ,  $^3J_{\text{H-H}} = 5.66\text{Hz}$ , 1H,  $\text{CHPh}=\text{CH}$ ), 4.33 (m, 2H,  $\text{CH}_2\text{O}$ ), 2.28 (t,  $^3J_{\text{H-H}} = 5.59\text{Hz}$ , 1H, OH);  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 136.76 (C=C-Ph) 131.04-127.66 ( $\text{C}_{\text{arm}}$ ), 126.48 ( $\text{HC}=\text{CPh}$ ), 63.56 ( $\text{CH}_2\text{OH}$ ).

**3-chloro-3-phenylprop-2-en-1-ol (14)**

Light Yellow oil, **FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3307 (OH), 1636 (C=C);  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 7.63-7.35 (m, 5H,  $\text{H}_{\text{arm}}$ ), 6.37 (Z, t,  $^3J_{\text{H-H}} = 5.90\text{Hz}$ , 1H, CH), 6.22 (E, t,  $^3J_{\text{H-H}} = 7.25\text{Hz}$ , 1H, CH), 4.54 (Z, d,  $^3J_{\text{H-H}} = 5.90\text{Hz}$ , 2H,  $\text{CH}_2\text{OH}$ ), 4.16 (E, d,  $^3J_{\text{H-H}} = 7.23\text{Hz}$ , 2H,  $\text{CH}_2\text{OH}$ ), 3.45 (Z+E, s, 1H,  $\text{CH}_2\text{OH}$ );  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 137.26 (Z, C-Cl), 136.33 (E, C-Cl), 133.70-126.44 ( $\text{C}_{\text{arm}}$ ), 128.92 (Z,  $\text{HC}=\text{CCl}$ ), 128.68 (E,  $\text{HC}=\text{CCl}$ ), 60.50 (Z,  $\text{CH}_2\text{OH}$ ), 59.76 (E,  $\text{CH}_2\text{OH}$ ).

**3-chloro-2-methyl-3-phenylprop-2-en-1-ol (15)**

Light Yellow oil, **FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3317 (OH), 1644 (C=C);  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 7.30 (m, 5H,  $\text{H}_{\text{arm}}$ ), 4.40 (Z, s, 2H,  $\text{CH}_2\text{OH}$ ), 3.99 (E, s, 2H,  $\text{CH}_2\text{OH}$ ), 2.04 (E, s, 3H,  $\text{CH}_3$ ), 1.79 (Z, s, 3H,  $\text{CH}_3$ );  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 138.24 (E, C-Cl), 133.47-128.30 ( $\text{C}_{\text{arm}}$ ), 128.54 (E, C=C- $\text{CH}_3$ ), 63.73 (E,  $\text{CH}_2\text{OH}$ ), 22.72 (Z,  $\text{CH}_3$ ), 17.93 (E,  $\text{CH}_3$ ).

**3-chloro-4,4-dimethylpent-2-en-1-ol (16)**

Light Yellow oil, **FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3307 (OH), 2969-2872 (CH<sub>3</sub> and CH<sub>2</sub>), 1649 (C=C); **<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$ :** 5.65 (t, <sup>3</sup>J<sub>H-H</sub>= 5.80Hz, 1H, CH), 4.21 (d, <sup>3</sup>J<sub>H-H</sub>= 5.80Hz, 2H, CH<sub>2</sub>OH), 3.89 (s, 1H, OH), 1.11 (s, 3H, 'Bu); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 145.62 (C-Cl), 121.99 (C=CCl), 60.03 (CH<sub>2</sub>OH), 38.40 (C(CH<sub>3</sub>)<sub>2</sub>), 28.59 (C(CH<sub>3</sub>)<sub>2</sub>).

**Ethyl 2-chloro-4-hydroxybut-2-enoate (17)**

Light Yellow oil; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.19 (t, 1H, CH, <sup>3</sup>J<sub>H-H</sub>= 5.45Hz), 4.50 (d, 2H, CH<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub>= 5.45Hz), 4.30 (q, 2H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H-H</sub>= 7Hz), 2.11 (s, 1H, OH), 1.34 (t, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>H-H</sub>= 7Hz); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 161.94 (C=O), 140.84 (C-Cl), 124.10 (C=CH), 62.55 (CH<sub>3</sub>CH<sub>2</sub>O), 60.30 (CH<sub>2</sub>OH), 14.09 (CH<sub>3</sub>CH<sub>2</sub>O).

**3-chloro-2-methylpent-2-en-1-ol (18)**

Yellow oil, **FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3408 (OH), 1741(C=C) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 4.22 (Z, s, 2H, CH<sub>2</sub>OH), 4.09 (E, s, 2H, CH<sub>2</sub>OH), 2.92 (Z+E, s, 1H, OH), 2.43 (E, q, <sup>3</sup>J<sub>H-H</sub>= 7.38Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 2.37 (Z, q, <sup>3</sup>J<sub>H-H</sub>= 7.44Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.87 (E, s, 3H, CH<sub>3</sub>), 1.79 (Z, s, 3H, CH<sub>3</sub>), 1.11-1.05 (Z+E, t, 3H, CH<sub>2</sub>CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 135.47 (E, CCl), 132.15 (Z, CCl), 129.82 (E, CH<sub>3</sub>C=CCl), 129.38 (E, CH<sub>3</sub>C=CCl), 64.06 (Z, CH<sub>2</sub>OH), 62.44 (E, CH<sub>2</sub>OH), 28.94 (Z, CH<sub>2</sub>CH<sub>3</sub>), 28.58 (E, CH<sub>2</sub>CH<sub>3</sub>), 17.85 (E, CH<sub>3</sub>), 15.85 (Z, CH<sub>3</sub>), 13.13 (E, CH<sub>2</sub>CH<sub>3</sub>), 12.01 (Z, CH<sub>2</sub>CH<sub>3</sub>).

**3-chloro-2-phenylbut-2-en-1-ol (19)**

Yellow oil, **FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3326 (OH), 1651(C=C) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.40-7.23 (m, 5H, H<sub>arm</sub>), 4.57 (Z, s, 2H, CH<sub>2</sub>OH), 4.42 (E, s, 2H, CH<sub>2</sub>OH), 2.37 (E, s, 3H, CH<sub>3</sub>), 2.08 (Z, s, 3H, CH<sub>3</sub>), 2.08 (s, 1H, OH); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 139.28 (E, C-Cl), 138.47 (Z, C-Cl), 136.65-128.32 (C<sub>arm</sub>), 127.58 (Z, CCH<sub>3</sub>), 127.45 (E, CCH<sub>3</sub>), 64.39 (Z, CH<sub>2</sub>OH), 63.30 (E, CH<sub>2</sub>OH), 23.99 (E, CH<sub>3</sub>), 22.88 (Z, CH<sub>3</sub>).

**General Procedure for preparation of  $\gamma$ -chloro- $\gamma,\beta$ -allylic alcohols (20).**

0.25 mmol of NaBH<sub>4</sub> was added to the ethyl 3-chloro-4,4,4-trifluoro-2-formylbut-2-enoate aldehyde (1mmol) stirred at -10°C in absolute ethanol. The progress of the reaction was monitored by TLC (by dissolving the sample in ether) using cyclohexane : diethylether (8:2) until the conversion of the aldehyde was complete. Then, water (100 mL) was added to the mixture. The product was extracted with diethyl ether (3x30mL) and washed 2 times with 10 mL of a saturated solution of NaCl. The solvent (diethylether) was evaporated, and the crude product was purified by column chromatography using (cyclohexane:diethylether) as eluent (8:2).

**Ethyl 3-chloro-4,4,4-trifluoro-2-(hydroxymethyl)but-2-enoate (20)**

colorless oil, **FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3442 (OH), 11727(C=O) cm<sup>-1</sup>; 1652(C=C) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 4.59 (Z+E, s, 2H, CH<sub>2</sub>O), 4.42-4.29 (Z+E, m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 2.68 (Z, s, 1H, OH), 2.25 (E, s, 1H, OH), 1.40-1.32 (Z+E, m, 3H, CH<sub>2</sub>CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 165.01 (E, CO<sub>2</sub>Et), 164.44 (Z, CO<sub>2</sub>Et), 139.73 (Z, CCl), 132.69 (E, C=CCl), 119.46 (Z+E, q, CF<sub>3</sub>, <sup>3</sup>J<sub>C-F</sub>=271.68Hz), 62.71 (Z, CH<sub>2</sub>CH<sub>3</sub>), 62.51(E,

$\underline{\text{C}}\text{H}_2\text{CH}_3$ ), 61.27 (*Z*,  $\underline{\text{C}}\text{H}_2\text{O}$ ), 59.05 (*E*,  $\underline{\text{C}}\text{H}_2\text{O}$ ), 13.92 (*E*,  $\text{CH}_2\underline{\text{C}}\text{H}_3$ ), 13.72 (*Z*,  $\text{CH}_2\underline{\text{C}}\text{H}_3$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  : -61.55 (*E*, s,  $\text{CF}_3$ ), -65.03 (*Z*, s,  $\text{CF}_3$ ).

**General Procedure for preparation of allylic carbamates (21-45).**

To a stirred solution of 3-chloro allyl alcohols (1 mmol) in dry THF (10 mL) with triethylamine (1.5mmol) was added commercial isocyanates (1.3 mmol) at 0°C. The reaction mixture was stirred at room temperature for 2–12 h. the progress of the reaction was monitored by TLC. After, the reaction mixture was evaporated and the crude product was purified by column chromatography on silica gel using cyclohexane: diethyl ether (8:2) as the eluent to give the allylic carbamates products.

**(2-chlorocyclohex-1-en-1-yl) methylpropylcarbamate (21)**

**FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3346 (NH), 1711 (C=O), 1695 (C=C), 1043 (C-O), 734 (C-Cl)  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$**  5.05 (s, 1H, NH), 4.65 (s, 2H,  $\underline{\text{C}}\text{H}_2\text{O}$ ), 3.08-3.02 (m, 2H,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 2.27 (m, 2H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 2.07 (m, 2H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 1.67-1.50 (m, 4H,  $\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 1.48-1.41 (m, 2H,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 0.88-0.81 (*Cis+Trans*, m, 3H,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ );  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 156.59 ( $\underline{\text{C}}=\text{O}$ ), 130.17 (C= $\underline{\text{C}}\text{Cl}$ ), 128.99 ( $\underline{\text{C}}=\underline{\text{C}}\text{Cl}$ ), 64.46 ( $\underline{\text{C}}\text{H}_2\text{O}$ ), 44.29/42.71 (*cis/trans*,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 33.79 ( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 27.68 ( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 23.56 ( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 23.08/21.00 (*trans/cis*,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 21.90 ( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 11.06/10.93 (*trans/cis*,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ); **HRMS (ESI), m/z:** calcd for  $[\text{C}_{11}\text{H}_{18}\text{ClNO}_2\text{Na}]^+$  254.0924  $[\text{M} + \text{Na}]^+$ ; found 254.0926.

**(2-chlorocyclohex-1-en-1-yl)methylbutylcarbamate (22)**

**FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3452 (NH), 1712 (C=O), 1515 (C=C), 1137 (C-O), 667 (C-Cl)  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$**  : 5.11 (s, 1H, NH), 4.63 (s, 2H,  $\underline{\text{C}}\text{H}_2\text{O}$ ), 3.06 (*Cis+Trans*, q,  $^3\text{J}_{\text{H-H}} = 6.41\text{Hz}$ , 2H,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 2.24 (m, 2H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 2.04 (m, 2H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 1.62-1.53 (m, 4H,  $\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 1.43-1.12 (*Cis+Trans*, q,  $^3\text{J}_{\text{H-H}} = 6.33\text{Hz}$ , 4H,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 0.81 (*Cis+trans*, t,  $^3\text{J}_{\text{H-H}} = 7.30\text{Hz}$ , 3H,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ );  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$**  : 156.57 ( $\underline{\text{C}}=\text{O}$ ), 130.04 (C= $\underline{\text{C}}\text{Cl}$ ), 129.00 ( $\underline{\text{C}}=\underline{\text{C}}\text{Cl}$ ), 64.40 ( $\underline{\text{C}}\text{H}_2\text{O}$ ), 40.67 ( $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 33.76 ( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 31.93/29.52 (*trans/cis*,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 27.63 ( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 23.55 ( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 21.88 ( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 20.75/19.76 (*cis/trans*,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 14.01/13.55 (*cis/Trans*,  $\text{NHCH}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ); **HRMS (ESI), m/z:** calcd for  $[\text{C}_{12}\text{H}_{21}\text{ClNO}_2\text{Na}]^+$  268.1080  $[\text{M}+\text{Na}]^+$ ; found 268.1077.

**(2-chlorocyclohex-1-en-1-yl)methyl phenylcarbamate (23)**

**FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3425 (NH), 1732 (C=O), 1601 (C=C), 1050 (C-O)  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$**  : 7.40-7.03(m, 5H, Harm), 7.01(s,1H,NH), 4.84 (s, 2H,  $\underline{\text{C}}\text{H}_2\text{O}$ ), 2.34-2.32 (m, 2H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 2.18- 2.14 (m, 2H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 1.70-1.59 (m, 4H,  $\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ );  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 153.67( $\underline{\text{C}}=\text{O}$ ), 137.90( $\underline{\text{C}}-\text{Cl}$ ), 128.97 ( $\underline{\text{C}}\text{Cl}=\underline{\text{C}}$ ), 131.15-118.72( $\text{C}_{\text{arm}}$ ), 65.12( $\underline{\text{C}}\text{H}_2\text{O}$ ), 33.89( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 27.93( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 23.58( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 21.94( $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ); **HRMS (ESI), m/z:** calcd for  $[\text{C}_{14}\text{H}_{16}\text{ClNO}_2\text{Na}]^+$  288.0767  $[\text{M}+\text{Na}]^+$ ; found 288.0769.

**(2-chlorocyclohex-1-en-1-yl)methyl (3-chlorophenyl)carbamate (24)**

**FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3432 (NH), 1732 (C=O), 1598(C=C), 1049 (C-O), 667 (C-Cl)  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 7.54 (s, 1H, NH), 7.26-7.02 (m, 4H,  $\text{H}_{\text{arm}}$ ), 4.86 (s, 2H,  $\underline{\text{C}}\text{H}_2\text{O}$ ), 2.37 (m, 2H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 2.18 (m, 2H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ ), 1.73-1.62 (m, 4H,  $\underline{\text{C}}\text{H}_2\underline{\text{cyc}}$ );  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 153.43 ( $\underline{\text{C}}=\text{O}$ ), 139.16 (C= $\underline{\text{C}}\text{Cl}$ ), 134.69-

118.78 (C<sub>arm</sub>), 116.72 (C=C<sub>Cl</sub>), 65.39 (C<sub>H</sub>2O), 33.90 (C<sub>H</sub>2cyc), 27.99 (C<sub>H</sub>2cyc), 23.58 (C<sub>H</sub>2cyc), 21.95 (C<sub>H</sub>2cyc); **HRMS** (ESI), m/z: calcd for [C<sub>14</sub>H<sub>15</sub>Cl<sub>2</sub>NO<sub>2</sub>Na]<sup>+</sup> 322.0378 [M + Na]<sup>+</sup>; found 322.0374.

**(2-chlorocyclohept-1-en-1-yl)methylpropylcarbamate (25)**

**FTIR: neat (cm<sup>-1</sup>):** ν 3345/3337 (NH), 1710 (C=O), 1695 (C=C), 1135 (C-O) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ:** 4.80 (s, 1H, NH), 4.65(s, 2H, C<sub>H</sub>2O), 3.08-3.04 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.55-2.52(m, 2H, C<sub>H</sub>2cyc), 2.20-2.17(m, 2H, C<sub>H</sub>2cyc), 1.68-1.65 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.56-1.41 (m, 6H, C<sub>H</sub>2cycCH<sub>2</sub>cycCH<sub>2</sub>cyc), 0.87- 0.82 (Cis+Trans, m, 3H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ:** 156.60(C=O), 134.74(C=C<sub>Cl</sub>), 133.78(C=C<sub>Cl</sub>), 66.37(C<sub>H</sub>2O), 44.38/42.77 (cis/trans, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 38.90 (C<sub>H</sub>2cyc), 31.24 (C<sub>H</sub>2cyc), 30.28 (C<sub>H</sub>2cyc), 25.75 (C<sub>H</sub>2cyc), 25.07 (C<sub>H</sub>2cyc), 23.16/21.07 (Trans/cis, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 11.12/11.01 (Trans/cis, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); **HRMS** (ESI), m/z: calcd for [C<sub>12</sub>H<sub>20</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 268.1080[M + Na]<sup>+</sup>; found 268.1080.

**(2-chlorocyclohept-1-en-1-yl)methyl butylcarbamate (26)**

**FTIR: neat (cm<sup>-1</sup>):** ν 3452/3334 (NH), 1704 (C=O), 1516 (C=C), 1135(C-O), 666 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ :** 5.20 (s, 1H, NH), 4.63 (s, 2H, C<sub>H</sub>2O), 3.10-3.05 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.54-2.50 (m, 2H, C<sub>H</sub>2cyc), 2.19-2.16 (m, 2H, C<sub>H</sub>2cyc), 1.66-1.62 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.55-1.50 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.47-1.20 (m, 6H, C<sub>H</sub>2CH<sub>2</sub>CH<sub>2</sub>cyc), 0.84 (t, <sup>3</sup>J<sub>H-H</sub>= 7.27Hz, 3H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ:** 156.58 (C=O), 134.33 (C-Cl), 133.80 (ClC=C), 66.06 (C<sub>H</sub>2O), 40.64 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 38.79 (C<sub>H</sub>2cyc), 31.92 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.16 (C<sub>H</sub>2cyc), 30.05 (C<sub>H</sub>2cyc), 25.65 (C<sub>H</sub>2cyc), 24.98 (C<sub>H</sub>2cyc), 19.75 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.55 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); **HRMS** (ESI), m/z: calcd for [C<sub>13</sub>H<sub>22</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 282.1237 [M + Na]<sup>+</sup>; found 282.1239.

**(2-chlorocyclohept-1-en-1-yl)methyl phenylcarbamate (27)**

**FTIR: neat (cm<sup>-1</sup>):** ν 3435 (NH), 1732 (C=O), 1602 (C=C), 1051 (C-O), 667 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ :** 7.44-7.07 (m, 5H, H<sub>arm</sub>), 6.82 (s, 1H, NH), 4.87 (s, 2H, C<sub>H</sub>2O), 2.67-2.63 (m, 2H, C<sub>H</sub>2cyc), 2.35-2.31 (m, 2H, C<sub>H</sub>2cyc), 1.81-1.53 (m, 6H, C<sub>H</sub>2CH<sub>2</sub>CH<sub>2</sub>cyc); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ:** 153.26 (C=O), 139.08 (C-Cl), 116.64 (ClC=C), 135.94-118.76(C<sub>arm</sub>), 67.30 (C<sub>H</sub>2O), 38.97 (C<sub>H</sub>2cyc), 31.20 (C<sub>H</sub>2cyc), 30.60 (C<sub>H</sub>2cyc), 25.81 (C<sub>H</sub>2cyc), 25.04 (C<sub>H</sub>2cyc); **HRMS** (ESI), m/z: calcd for [C<sub>15</sub>H<sub>18</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 302.0924 [M+Na]<sup>+</sup>; found 302.0923.

**(2-chlorocyclohept-1-en-1-yl)methyl (3-chlorophenyl)carbamate (28)**

**FTIR: neat (cm<sup>-1</sup>):** ν 3428/3322 (NH), 1711 (C=O), 1596(C=C), 1051 (C-O), 680 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ:** 7.43 (s, 1H, NH), 7.13-6.78 (m, 4H, H<sub>arm</sub>), 4.75 (s, 2H, C<sub>H</sub>2O), 2.56-2.52 (m, 2H, C<sub>H</sub>2cyc), 2.23-2.19 (m, 2H, C<sub>H</sub>2cyc), 1.68-1.44 (m, 6H, C<sub>H</sub>2CH<sub>2</sub>CH<sub>2</sub>cyc); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ:** 153.32 (C=O), 134.75 (C-Cl), 123.45 (ClC=C), 139.09-116.68 (C<sub>arm</sub>), 67.29 (C<sub>H</sub>2O), 38.96 (C<sub>H</sub>2cyc), 31.19 (C<sub>H</sub>2cyc), 30.57 (C<sub>H</sub>2cyc), 25.80 (C<sub>H</sub>2cyc), 25.04 (C<sub>H</sub>2cyc); **HRMS** (ESI), m/z: calcd for [C<sub>15</sub>H<sub>17</sub>Cl<sub>2</sub>NO<sub>2</sub>Na]<sup>+</sup> 336.0534 [M+Na]<sup>+</sup>; found 336.0532.

**Cinnamylpropylcarbamate (29)**

**FTIR: neat (cm<sup>-1</sup>):** ν 3448 (NH), 1720 (C=O), 1695 (C=C), 1037 (C-O) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ** 7.40-7.20 (m, 5H, H<sub>arm</sub>), 6.61 (d, <sup>3</sup>J<sub>H-H</sub>= 15.90Hz, 1H, PhCH=CH), 6.30 (td, <sup>3</sup>J<sub>H-H</sub>= 6Hz, <sup>3</sup>J<sub>H-H</sub>= 15.90Hz, 1H,



$\text{CH}=\text{CHPh}$ ), 5.06 (s, 1H,  $\text{NH}$ ), 4.74 (d,  $^3J_{\text{H-H}}=6\text{Hz}$ , 2H,  $\text{CH}_2\text{OH}$ ), 3.20-3.13 (m, 2H,  $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ), 1.60-1.48 (m, 2H,  $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ), 0.93 (t,  $^3J_{\text{H-H}}=7.37\text{Hz}$ , 3H,  $\text{NHCH}_2\text{CH}_2\text{CH}_3$ );  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 156.4853 ( $\text{C}=\text{O}$ ), 136.43 ( $\text{C}=\text{CPh}$ ), 133.41-126.57 ( $\text{C}_{\text{arm}}$ ), 124.19 ( $\text{CH}=\text{CPh}$ ), 65.22 ( $\text{CH}_2\text{O}$ ), 42.81 ( $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ), 23.19 ( $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ), 11.18 ( $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ); **HRMS** (ESI),  $m/z$ : calcd for  $[\text{C}_{13}\text{H}_{17}\text{NO}_2\text{Na}]^+$  242.1157 [ $\text{M} + \text{Na}$ ] $^+$ ; found 242.1157.

### *Cinnamyl butylcarbamate (30)*

**FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3340 (NH), 1695 ( $\text{C}=\text{O}$ ), 1519 ( $\text{C}=\text{C}$ ), 1137 ( $\text{C}-\text{O}$ )  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 7.26-7.11 (m, 5H,  $\text{H}_{\text{arm}}$ ), 6.50 (d,  $^3J_{\text{H-H}}=15.91\text{Hz}$ , 1H,  $\text{PhCH}=\text{CH}$ ), 6.16 (dt,  $^3J_{\text{H-H}}=15.88\text{Hz}$ ,  $^3J_{\text{H-H}}=6.28\text{Hz}$ , 1H,  $\text{PhCH}=\text{CH}$ ), 4.98 (s, 1H,  $\text{NH}$ ), 4.60 (d,  $^3J_{\text{H-H}}=6.03\text{ Hz}$ , 2H,  $\text{CH}_2\text{O}$ ), 3.16-3.03 (*cis+trans*, m, 2H,  $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.39-1.18 (m, 4H,  $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.80 (*trans*, t,  $^3J_{\text{H-H}}=7.25$ , 3H,  $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ );  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 156.48/156.41 (*Trans/cis*,  $\text{C}=\text{O}$ ), 133.36-126.54 ( $\text{C}_{\text{arm}}$ ), 136.42 ( $\text{CH}=\text{CHPh}$ ), 124.18 ( $\text{PhHC}=\text{CH}$ ), 65.20 ( $\text{CH}_2\text{O}$ ), 40.79/40.39 (*Trans/Cis*,  $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 32.05/31.76 (*Trans/Cis*,  $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 20.14/19.88 (*Cis/Trans*,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 13.70 (*Trans*,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); **HRMS** (ESI),  $m/z$ : calcd for  $[\text{C}_{14}\text{H}_{19}\text{ClNO}_2\text{Na}]^+$  256.1313 [ $\text{M}+\text{Na}$ ] $^+$ ; found 256.1310.

### *Cinnamylphenylcarbamate (31)*

**FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3435 (NH), 1728 ( $\text{C}=\text{O}$ ), 1601( $\text{C}=\text{C}$ ), 1050 ( $\text{C}-\text{O}$ )  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$  (300MHz,  $\text{CDCl}_3$ )  $\delta$ :** 7.50-7.11 (m, 11H,  $\text{H}_{\text{arm}}+\text{NH}$ ), 6.74 (d,  $^3J_{\text{H-H}}=15.89\text{Hz}$ , 1H,  $\text{CH}$ ), 6.39 (dt, ( $^3J_{\text{H-H}}$ )doublet= 15.87Hz, ( $^3J_{\text{H-H}}$ )triplet= 6.38 Hz, 1H,  $\text{CH}=\text{CHPh}$ ), 4.90 (d,  $^3J_{\text{H-H}}=6.35\text{Hz}$ , 2H,  $\text{CH}_2\text{O}$ );  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.70 ( $\text{C}=\text{O}$ ), 138.05-123.52 ( $\text{C}_{\text{arm}}$ ), 134.23 ( $\text{PhHC}=\text{CH}$ ), 119.05 ( $\text{PhHC}=\text{CH}$ ), 65.85 ( $\text{CH}_2\text{O}$ ); **HRMS** (ESI),  $m/z$ : calcd for  $[\text{C}_{16}\text{H}_{15}\text{NO}_2\text{Na}]^+$  276.1000 [ $\text{M}+\text{Na}$ ] $^+$ ; found 276.1003.

### *Cinnamyl (3-chlorophenyl) carbamate (32)*

**FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3322 (NH), 1713 ( $\text{C}=\text{O}$ ), 1596( $\text{C}=\text{C}$ ), 1048 ( $\text{C}-\text{O}$ ), 692 ( $\text{C}-\text{Cl}$ )  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 7.58 (s, 1H,  $\text{NH}$ ), 7.43-7.06 (m, 9H,  $\text{H}_{\text{arm}}$ ), 6.71 (d,  $^3J_{\text{H-H}}=15.90\text{Hz}$ , 1H,  $\text{PhCH}=\text{CH}$ ), 6.34 (td,  $^3J_{\text{H-H}}=6.40\text{Hz}$ ,  $^3J_{\text{H-H}}=15.90\text{Hz}$ , 1H,  $\text{PhCH}=\text{CH}$ ), 4.87 (d,  $^3J_{\text{H-H}}=6.39\text{Hz}$ , 2H,  $\text{CH}_2\text{OH}$ );  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.65 ( $\text{C}=\text{O}$ ), 139.37-117.08 ( $\text{C}_{\text{arm}}$ ), 134.46 ( $\text{PhC}=\text{CH}$ ), 126.67 ( $\text{PhC}=\text{CH}$ ), 66.16 ( $\text{CH}_2\text{O}$ ); **HRMS** (ESI),  $m/z$ : calcd for  $[\text{C}_{16}\text{H}_{14}\text{ClNO}_2\text{Na}]^+$  310.0611 [ $\text{M}+\text{Na}$ ] $^+$ ; found 310.0603.

### *3-Chloro-3-phenylallyl propylcarbamate (33)*

**FTIR: neat ( $\text{cm}^{-1}$ ):**  $\nu$  3346/3353 (NH), 1716 ( $\text{C}=\text{O}$ ), - ( $\text{C}=\text{C}$ ), 1037 ( $\text{C}-\text{O}$ )  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ :** (*Z*) 7.62-7.34 (m, 5H,  $\text{H}_{\text{arm}}$ ), 6.30 (t,  $^3J_{\text{H-H}}=6.04\text{Hz}$ , 1H,  $\text{ClC}=\text{CH}$ ), 4.94 (s, 1H,  $\text{NH}$ ), 4.95 (d,  $^3J_{\text{H-H}}=6.04\text{Hz}$ , 2H,  $\text{CH}_2\text{OH}$ ), 3.18-3.16 (m, 2H,  $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ), 1.61-1.49 (m, 2H,  $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ), 1.74-1.63 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.93 (t,  $^3J_{\text{H-H}}=6.64\text{Hz}$ , 3H,  $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ). (*E*): 6.17 (t,  $^3J_{\text{H-H}}=5.83\text{Hz}$ , 1H,  $\text{CH}$ ), 4.56 (d,  $^3J_{\text{H-H}}=5.80\text{Hz}$ , 2H,  $\text{CH}_2\text{OH}$ );  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 156.33 (*Z*,  $\text{C}=\text{O}$ ), 137.13 (*Z*,  $\text{C}-\text{Cl}$ ), 135.46-126.48 ( $\text{C}_{\text{arm}}$ ), 124.36 (*E*,  $\text{ClC}=\text{CH}$ ), 122.47 (*Z*,  $\text{ClC}=\text{CH}$ ), 62.31 (*Z*,  $\text{CH}_2\text{O}$ ), 42.85 ( $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ), 23.18 ( $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ), 11.16 ( $\text{NHCH}_2\text{CH}_2\text{CH}_3$ ); **HRMS** (ESI),  $m/z$ : calcd for  $[\text{C}_{13}\text{H}_{16}\text{ClNO}_2\text{Na}]^+$  276.076 [ $\text{M}+\text{Na}$ ] $^+$ ; found 276.0767.

### *3-chloro-3-phenylallyl (3-chlorophenyl) carbamate (34)*

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3420/3336 (NH), 1732 (C=O), 1597 (C=C), 1062 (C-O) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.64-7.05 (m, 10H, H<sub>arm</sub>), 6.95 (s, 1H, NH), 6.35 (Z, t, <sup>3</sup>J<sub>H-H</sub>= 6.23Hz, 1H, CH), 6.20 (E, t, <sup>3</sup>J<sub>H-H</sub>= 7.5Hz, 1H, CH), 5.06 (Z, d, <sup>3</sup>J<sub>H-H</sub>= 6.23Hz, 2H, CH<sub>2</sub>O), 4.69 (E, d, <sup>3</sup>J<sub>H-H</sub>= 7.5Hz, 2H, CH<sub>2</sub>O); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 153.14 (C=O), 138.96-116.76 (C<sub>arm</sub>), 136.91 (Z, C=C<sub>Cl</sub>), 121.34 (Z, C=C<sub>Cl</sub>), 120.84 (E, C=C<sub>Cl</sub>), 62.88 (Z, CH<sub>2</sub>O), 62.29 (E, CH<sub>2</sub>O); **HRMS (ESI), m/z:** calcd for [C<sub>16</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub>Na]<sup>+</sup> 344.0221 [M+Na]<sup>+</sup>; found 344.0247.

**3-chloro-2-methyl-3-phenylallyl propylcarbamate (35)**

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3445/3351 (NH), 1715 (C=O), 1699 (C=C), 1135 (C-O), 667 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.34 (m, 5H, H<sub>arm</sub>), 4.92 (s, 1H, NH), 4.54 (E, s, 2H, CH<sub>2</sub>O), 3.11 (m, <sup>3</sup>J<sub>H-H</sub>= 6.69Hz, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.05 (E, s, 3H, CH<sub>3</sub>), 1.78 (Z, s, 3H, CH<sub>3</sub>), 1.57-1.45 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.91 (t, <sup>3</sup>J<sub>H-H</sub>= 7.37Hz, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 156.30 (C=O), 138.46 (Z, C<sub>Cl</sub>), 137.96 (E, C<sub>Cl</sub>), 132.27-128.27 (C<sub>arm</sub>), 128.62 (C=C<sub>Cl</sub>), 66.96 (Z, CH<sub>2</sub>O), 65.36 (E, CH<sub>2</sub>O), 44.42 (Z, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 43.42/42.79 (cis/Trans E, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 23.14/21.12 (trans/Cis, E, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 17.95 (E, CH<sub>3</sub>), 17.52 (Z, CH<sub>3</sub>), 11.15 (Cis+Trans, E, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); **HRMS (ESI), m/z:** calcd for [C<sub>14</sub>H<sub>18</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 290.0924 [M+Na]<sup>+</sup>; found 290.0930.

**3-chloro-2-methyl-3-phenylallyl phenylcarbamate (36)**

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3423/3338 (NH), 1732 (C=O), 1599 (C=C), 1047 (C-O), 895 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.41-7.08 (m, 10H, H<sub>arm</sub>), 6.73 (s, 1H, NH), 5.10 (Z, s, 2H, CH<sub>2</sub>O), 4.66 (E, s, 2H, CH<sub>2</sub>O), 2.12 (E, s, 3H, CH<sub>3</sub>), 1.85 (Z, s, 3H, CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 153.17 (C=O), 137.86 (E, C=C<sub>Cl</sub>), 137.68 (Z, C=C<sub>Cl</sub>), 133.03-123.61 (C<sub>arm</sub>), 119.79 (Z, C=C<sub>Cl</sub>), 118.75 (E, C=C<sub>Cl</sub>), 65.93 (E, CH<sub>2</sub>O), 22.29 (Z, CH<sub>3</sub>), 18.11 (E, CH<sub>3</sub>); **HRMS (ESI), m/z:** calcd for [C<sub>17</sub>H<sub>16</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 324.0767 [M+Na]<sup>+</sup>; found 324.0765.

**3-chloro-2-methyl-3-phenylallyl (3-chlorophenyl) carbamate (37)**

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3406/3320 (NH), 1708 (C=O), 1594 (C=C), 1043 (C-O), 696 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.52 (s, 1H, NH), 7.38-6.96 (m, 9H, H<sub>arm</sub>), 5.10 (Z, s, 2H, CH<sub>2</sub>O), 4.67 (E, s, 2H, CH<sub>2</sub>O), 2.11 (E, s, 3H, CH<sub>3</sub>), 1.90 (Z, s, 3H, CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 153.07 (C=O), 138.99-116.79 (C<sub>arm</sub>), 137.80 (E, CH<sub>3</sub>C=C<sub>Cl</sub>), 123.63 (E, CH<sub>3</sub>C=C<sub>Cl</sub>), 68.34 (Z, CH<sub>2</sub>O), 66.17 (E, CH<sub>2</sub>O), 18.10 (E, CH<sub>3</sub>), 17.82 (Z, CH<sub>3</sub>); **HRMS (ESI), m/z:** calcd for [C<sub>17</sub>H<sub>15</sub>Cl<sub>2</sub>NO<sub>2</sub>Na]<sup>+</sup> 258.0378 [M+Na]<sup>+</sup>; found 258.0381.

**(Z)-3-chloro-4,4-dimethylpent-2-en-1-yl phenylcarbamate (38)**

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3423/3336 (NH), 1731 (C=O), 1600 (C=C), 1061 (C-O) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.43-7.06 (m, 5H, H<sub>arm</sub>), 6.62 (s, 1H, NH), 5.76 (t, <sup>3</sup>J<sub>H-H</sub>= 5.92Hz, 1H, ClC=CH), 4.87 (d, <sup>2</sup>J<sub>H-H</sub>= 5.92Hz, 1H, CH<sub>2</sub>O), 1.22 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 153.60/153.54 (cis/trans, C=O), 148.65 (CH=CCl), 137.83-118.74 (cis+trans, C<sub>arm</sub>), 117.40 (CH=CCl), 62.77 (CH<sub>2</sub>O), 38.81 (C(CH<sub>3</sub>)<sub>3</sub>), 28.65 (C(CH<sub>3</sub>)<sub>3</sub>); **HRMS (ESI), m/z:** calcd for [C<sub>14</sub>H<sub>18</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 290.0924 [M+Na]<sup>+</sup>; found 290.0921.

**3-chloro-2-ethylbut-2-en-1-yl propylcarbamate (39)**

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3335 (NH), 1692 (C=O), 1660 (C=C), 1042 (C-O) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 4.86 (s, 1H, NH), 4.68 (Z, s, 2H, CH<sub>2</sub>O), 4.52 (E, s, 2H, CH<sub>2</sub>O), 3.07-3.05 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.43 (E, q,

$^3J_{H-H}$  = 7.38Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 2.34 (*E*, q,  $^3J_{H-H}$  = 7.47Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.79 (*E*, s, CH<sub>3</sub>), 1.69 (*Z*, s, CH<sub>3</sub>), 1.51-1.39 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.04 (*E*, t,  $^3J_{H-H}$  = 7.4Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.03(*Z*, t,  $^3J_{H-H}$  = 7.38Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.84 (t,  $^3J_{H-H}$  = 7.39Hz, 3H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>);  $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 156.58/156.40 (*cis/trans*, C=O), 137.39 (*Z+E*, C=C(Cl)), 126.20 (*E*, C=C(Cl)), 120.82 (*Z*, C=C(Cl)), 65.72 (*Z*, CH<sub>2</sub>O), 64.18 (*E*, CH<sub>2</sub>O), 44.37 (*Z*, CH<sub>2</sub>CH<sub>3</sub>), 42.76 (*E*, CH<sub>2</sub>CH<sub>3</sub>), 28.95 (*Z*, CH<sub>3</sub>), 28.82 (*E*, CH<sub>3</sub>), 23.11/21.05 (*Trans/ Cis*, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 18.10/15.70 (*Trans Cis*, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.01 (*E*, CH<sub>2</sub>CH<sub>3</sub>), 11.98 (*Z*, CH<sub>2</sub>CH<sub>3</sub>), 11.08/10.98 (*Trans/Cis*, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); HRMS (ESI), m/z: calcd for [C<sub>10</sub>H<sub>18</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 242.0924 [M+ Na]<sup>+</sup>; found 242.0917.

### 3-chloro-2-ethylbut-2-en-1-yl phenylcarbamate (40)

**FTIR:** neat (cm<sup>-1</sup>):  $\nu$  3328 (NH), 1711 (C=O), 1600(C=C), 1048 (C-O) cm<sup>-1</sup>;  **$^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.48-7.07 (m, 6H, H<sub>arm</sub>+NH), 4.94 (*Z*, s, 2H, CH<sub>2</sub>O), 4.75 (*E*, s, 2H, CH<sub>2</sub>O), 2.56 (*E*, q,  $^3J_{H-H}$  = 7.38Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 2.46 (*Z*, s,  $^3J_{H-H}$  = 7.43Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.95 (*E*, s, 3H, CH<sub>3</sub>), 1.84 (*Z*, s, 3H, CH<sub>3</sub>), 1.18 (*E*, t,  $^3J_{H-H}$  = 7.38Hz, H, CH<sub>2</sub>CH<sub>3</sub>), 1.17 (*Z*, t,  $^3J_{H-H}$  = 7.43Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>);  **$^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 153.87/153.71 (*cis/trans*, C=O), 138.05 (*E*, C=C(Cl)), 137.93 (*Z*, C=C(Cl)), 134.50-119.02 (C<sub>arm</sub>), 123.57 (*E*, C=C(Cl)), 123.50 (*Z*, C=C(Cl)), 66.31 (*Z*, CH<sub>2</sub>O), 64.68 (*E*, CH<sub>2</sub>O), 29.08 (*Z*, CH<sub>2</sub>CH<sub>3</sub>), 28.95 (*E*, CH<sub>2</sub>CH<sub>3</sub>), 18.28 (*E*, CH<sub>3</sub>), 15.91 (*Z*, CH<sub>3</sub>), 13.15 (*E*, CH<sub>2</sub>CH<sub>3</sub>), 12.09 (*Z*, CH<sub>2</sub>CH<sub>3</sub>); **HRMS** (ESI), m/z: calcd for [C<sub>13</sub>H<sub>16</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 276.0767 [M+ Na]<sup>+</sup>; found 276.0769.

### 3-chloro-2-ethylbut-2-en-1-yl (3-chlorophenyl) carbamate (41)

**FTIR:** neat (cm<sup>-1</sup>):  $\nu$  3432 (NH), 1731 (C=O), 1598(C=C), 1050 (C-O), 668 (C-Cl) cm<sup>-1</sup>;  **$^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.55/7.52 (*cis/trans*, s, 1H, NH), 7.23-6.95 (m, 4H, H<sub>arm</sub>), 4.89 (*Z*, s, 2H, CH<sub>2</sub>O), 4.73 (*E*, s, 2H, CH<sub>2</sub>O), 2.54 (*E*, q,  $^3J_{H-H}$  = 7.39Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 2.44 (*Z*, q,  $^3J_{H-H}$  = 7.41Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.92 (*E*, s, 3H, CH<sub>3</sub>), 1.83 (*Z*, s, 3H, CH<sub>3</sub>), 1.15 (*E*, t,  $^3J_{H-H}$  = 7.39Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.14 (*Z*, t,  $^3J_{H-H}$  = 7.41Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>);  **$^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 153.17/152.86 (*trans/cis*, C=O), 138.37 (*E*, C(Cl)), 138.05 (*Z*, C(Cl)), 138.99-116.74 (C<sub>arm</sub>), 123.56 (*E*, C=C(Cl)), 123.48 (*Z*, C=C(Cl)), 66.57 (*Z*, CH<sub>2</sub>O), 64.93 (*E*, CH<sub>2</sub>O), 29.06 (*Z*, CH<sub>2</sub>CH<sub>3</sub>), 28.93(*E*, CH<sub>2</sub>CH<sub>3</sub>), 18.28 (*E*, CH<sub>3</sub>), 16.00 (*Z*, CH<sub>3</sub>), 13.11 (*E*, CH<sub>2</sub>CH<sub>3</sub>), 12.04 (*Z*, CH<sub>2</sub>CH<sub>3</sub>); **HRMS** (ESI), m/z: calcd for [C<sub>13</sub>H<sub>15</sub>Cl<sub>2</sub>NO<sub>2</sub>Na]<sup>+</sup> 310.0378 [M+ Na]<sup>+</sup>; found 310.0386.

### 3-chloro-2-phenylbut-2-en-1-yl phenylcarbamate (42)

**FTIR:** neat (cm<sup>-1</sup>):  $\nu$  3431/3301(NH), 1727 (C=O), 1600 (C=C), 1053 (C-O), 692 (C-Cl) cm<sup>-1</sup>;  **$^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.58-6.85 (m, H<sub>arm</sub>), 6.68/6.61 (*Trans/cis*, s, 1H, NH), 5.20/5.16 (*cis/Trans*, *Z*, s, 2H, CH<sub>2</sub>O), 5.02/4.97 (*trans/Cis E*, s, 2H, CH<sub>2</sub>O), 2.46/2.34 (*trans/Cis E*, s, 3H, CH<sub>3</sub>), 2.12/2.02 (*trans/Cis Z*, s, 3H, CH<sub>3</sub>);  **$^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 155.56/153.16 (*trans/Cis*, C=O), 132.54/132.07 (*Trans /cis Z* C=C(Cl)), 131.53/131.16 (*trans/Cis E*, C=C(Cl)), 124.11/124.04 (*Cis/trans E*, C=C(Cl)), 123.59/123.42 (*Cis/trans Z*, C=C(Cl)), 138.00-118.08 (*Cis+Trans Z+E*, C<sub>arm</sub>), 67.69/66.76 (*Trans/cis E*, CH<sub>2</sub>O), 66.06/65.09 (*Trans/cis Z*, CH<sub>2</sub>O), 24.13/23.94 (*Trans/cis Z*, CH<sub>3</sub>), 23.31/23.10 (*trans/Cis E*, CH<sub>3</sub>); **HRMS** (ESI), m/z: calcd for [C<sub>17</sub>H<sub>16</sub>ClNO<sub>2</sub>Na]<sup>+</sup> 324.0767 [M+Na]<sup>+</sup>; found 324.0763.

### 3-chloro-2-phenylbut-2-en-1-yl (3-chlorophenyl)carbamate (43)

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3432 (NH), 1733 (C=O), 1598 (C=C), 1214 (C-O), 667 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.35- 6.91 (m, 5H, H<sub>arm</sub>), 6.54 (*E*, s, 1H, NH), 6.47 (*Z*, s, 1H, NH), 5.07 (*Z*, s, 2H, CH<sub>2</sub>O), 4.90 (*E*, s, 2H, CH<sub>2</sub>O), 2.34 (*E*, s, 3H, CH<sub>3</sub>), 1.99 (*Z*, s, 3H, CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 152.83 (C=O), 139.10-116.68 (C<sub>arm</sub>), 129.99 (*E*, PhC=C<sub>Cl</sub>), 129.92 (*Z*, PhC=C<sub>Cl</sub>), 123.64 (*E*, PhC=C<sub>Cl</sub>), 123.49 (*Z*, PhC=C<sub>Cl</sub>), 66.28 (*Z*, CH<sub>2</sub>O), 65.30 (*E*, CH<sub>2</sub>O), 24.11 (*Z*, CH<sub>3</sub>), 23.28 (*E*, CH<sub>3</sub>); **HRMS (ESI), m/z:** calcd for [C<sub>17</sub>H<sub>15</sub>Cl<sub>2</sub>NO<sub>2</sub>Na]<sup>+</sup> 358.0378 [M+Na]<sup>+</sup>; found 358.0383.

***Ethyl 3-chloro-4,4,4-trifluoro-2-(((propylcarbamoyl)oxy)methyl)but-2-enoate (44)***

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3450 (NH), 1735 (C=O), 1651(C=C), 1215 (C-O), 667 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$ :** 4.97 (*Z+E*, s, 2H, CH<sub>2</sub>O), 4.23 (*Z+E*, m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 3.11 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.42 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.27 (*Z+E*, m, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.87 (m, 2H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 163.92 (*E*, CO<sub>2</sub>Et), 163.35 (*Z*, CO<sub>2</sub>Et), 155.08 (C=O), 137.49 (*E*, CCl), 136.29 (*Z*, CCl), 121.21 (*Z*, C=CCF<sub>3</sub>), 119.40 (*Z+E*, q, <sup>3</sup>J<sub>C-F</sub>= 271.87Mhz, CF<sub>3</sub>), 62.50 (*E*, CH<sub>2</sub>O), 62.34 (*Z*, CH<sub>2</sub>O), 61.71 (*Z*, CH<sub>2</sub>CH<sub>3</sub>), 59.56 (*E*, CH<sub>2</sub>CH<sub>3</sub>), 43.39/42.86 (*Cis/trans*, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 22.93/22.29 (*trans/Cis*, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.81 (*E*, CH<sub>2</sub>CH<sub>3</sub>), 13.64 (*Z*, CH<sub>2</sub>CH<sub>3</sub>), 10.92/10.14 (*trans/Cis*, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); **<sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>)  $\delta$ :** - 61.83 (*E*, s, CF<sub>3</sub>), -65.15 (*Z*, s, CF<sub>3</sub>); **HRMS (ESI), m/z:** calcd for [C<sub>11</sub>H<sub>15</sub>ClNO<sub>4</sub>F<sub>3</sub>Na]<sup>+</sup> 340.0539 [M+Na]<sup>+</sup>; found 340.0534.

***Ethyl 3-chloro-4,4,4-trifluoro-2-(((phenylcarbamoyl)oxy)methyl)but-2-enoate (45)***

**FTIR: neat (cm<sup>-1</sup>):**  $\nu$  3432 (NH), 1740 (C=O), 1601(C=C), 1214 (C-O), 666 (C-Cl) cm<sup>-1</sup>; **<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$ :** 7.35-7.06 (m, 5H, H<sub>arm</sub>), 6.95 (s, 1H, NH), 5.12 (*Z+E*, s, 2H, CH<sub>2</sub>O), 4.31 (*Z+E*, m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.29 (*Z+E*, m, 3H, CH<sub>2</sub>CH<sub>3</sub>); **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ :** 164.00 (*E*, CO<sub>2</sub>Et), 163.44 (*Z*, CO<sub>2</sub>Et), 152.22 (C=O), 137.22 (*Z*, CCl), 135.75-117.62 (C<sub>arm</sub>), 119.43 (*Z*, q, <sup>3</sup>J<sub>C-F</sub>= 272.43Hz, CF<sub>3</sub>), 62.82 (*Z*, CH<sub>2</sub>O), 62.65 (*E*, CH<sub>2</sub>O), 62.07 (*Z*, CH<sub>2</sub>CH<sub>3</sub>), 59.61(*E*, CH<sub>2</sub>CH<sub>3</sub>), 13.88 (*E*, CH<sub>2</sub>CH<sub>3</sub>), 13.71 (*Z*, CH<sub>2</sub>CH<sub>3</sub>); **<sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>)  $\delta$ :** -61.62 (*E*, s, CF<sub>3</sub>), -64.98 (*Z*, s, CF<sub>3</sub>); **HRMS (ESI), m/z:** calcd for [C<sub>14</sub>H<sub>13</sub>ClNO<sub>4</sub>F<sub>3</sub>Na]<sup>+</sup> 374.0383 [M+Na]<sup>+</sup>; found 374.0394.

## CRedit author statement

**S. G.** performed and validated the experiments,

**P. R.** XRay and structural investigation

**B. C.** provided expertise and feedback.

**T. B. S.** conceived, supervised, wrote the original manuscript and revised it.

**conflict of interest**

**None**

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