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Synthesis of Cyclic *N*-Tosyliminocarbonates by Lewis Acid Catalyzed Allylic Substitution of Trichloroacetimidates

Liene Grigorjeva[a] and Aigars Jirgensons*[a]

Keywords: Synthetic methods / Nitrogen heterocycles / Nucleophilic substitution / Cyclization / Lewis acids / Allylic compounds

Allylic trichloroacetimidates bearing a δ-*N*-tosylcarbamoyloxy group were prepared in two steps from the corresponding diols, and their Brønsted and Lewis acid catalyzed cyclization reactions were investigated. It was found that *N*-tosylcarbamates derived from secondary and tertiary alcohols bearing alkyl substituents undergo a chemoselective allylic alkylation to give *N*-tosyliminocarbonates in good isolated yields. In turn, aryl-substituted substrates tend to give oxazolines by abstraction of the carbamate functionality. The cyclization of *N*-tosylcarbamates derived from secondary alcohols preferentially give *trans*-iminocarbonates. However, the *trans* selectivity varied and depended on the substitution pattern, configuration of the substrate, and the catalyst. A high *trans* selectivity could be achieved from (*E*) substrates by using TMSOTf as the catalyst. The synthetic utility of iminocarbonates was demonstrated by transforming them into 1,2-diols and cyclic carbonates as well as into *N*-tosyloxazolidinones by a halide ion-induced rearrangement.

Introduction

Allylic substitutions to form C–heteroatom bonds have been achieved with a range of nucleophiles by using late transition-metal catalysts.[1] However, over the last decade, Lewis or Brønsted acid catalysts have emerged as a more eco-friendly and cheaper alternative. Allylic alcohols,[2] carboxylates,[2c,3] halides,[4] and trichloroacetimidates[5] have been used as substrates to achieve acid-catalyzed intramolecular substitution with N- and O-nucleophiles.

Our recent work was devoted to the cyclization of allylic bis(trichloroacetimidates) leading to 4-vinyloxazolines, highly versatile amino alcohol and amino acid precursors.[5f,5g] It was rationalized that the cyclization of bis(trichloroacetimidates) involves the substitution of a Lewis or Brønsted acid complexed imidate group with another imidate as the N-nucleophile. With these results, we began work to extend the scope of the acid-catalyzed allylic trichloroacetimidate substitution with other nucleophiles.

Iminocarbonates are valuable intermediates for the syntheses of 1,2-diols and 1,2-amino alcohols.[4,6] Nevertheless, there are a limited number of reports for the syntheses of iminocarbonates, and most of them involve the reaction of 1,2-diols with isocyanates.[6] An alternative method was reported by Giroux and Friesen.[4] They prepared *N*-tosyliminocarbonates through a silver(I)-promoted substitution of allyl diiodides which, in turn, were prepared by the iodination of allenyl *N*-tosylcarbamates. On the basis of their results, it was expected that the intramolecular acid-catalyzed allylic substitution of the imidate group in *N*-tosylcarbamates **1** (see Figure 1) should give *N*-tosyliminocarbonates **2** as the major products. This would complement an application of *N*-tosylcarbamates as O-nucleophiles in palladium(II)- and palladium(0)-catalyzed allylic substitutions that lead to oxazolidinones **3**.[7] In principle, the cyclization of substrate **1** could also result in the formation of oxazoline **4**, by elimination of the carbamate group.

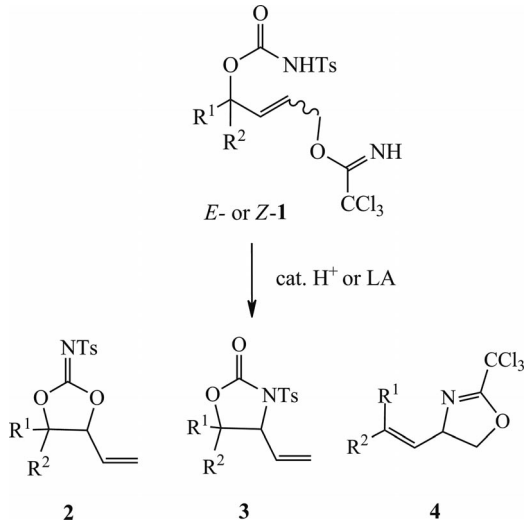

Figure 1. Potential products **2**–**4** in the cyclization of allylic trichloroacetimidates **1** bearing δ-*N*-tosylcarbamoyloxy group.

[a] Latvian Institute of Organic Synthesis,
Aizkraukles 21, 1006 Riga, Latvia
Fax: +371-675-414-08
E-mail: aigars@osi.lv
Homepage: http://osmg.osi.lv

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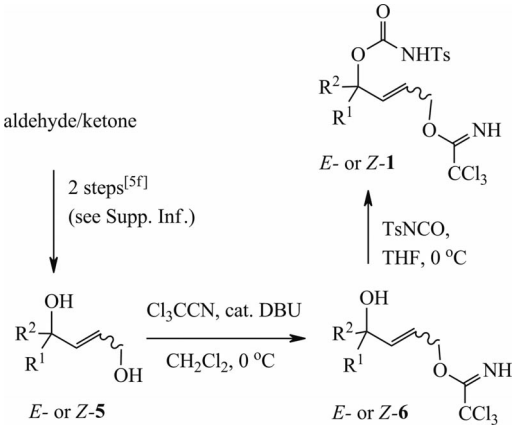
However, we hypothesized that the complexation of the acid catalyst to the more basic imidate group would provide iminocarbonate **2**, selectively.

Herein we report the syntheses of *N*-tosyliminocarbonates **2** through an acid-catalyzed intramolecular substitution of the allylic trichloroacetimidate moiety in *N*-tosylcarbamates **1**.

Results and Discussion

Substrates **1** were synthesized according to the general strategy shown in Scheme 1. Diols (*E*)-**5a**–(*E*)-**5k**, (*Z*)-**5a**, (*Z*)-**5b**, and (*Z*)-**5f** (see Scheme 1) were prepared in two steps by the addition of propargyl alcohol to the respective aldehyde or ketone followed by a stereoselective reduction of the triple bond (see Supporting Information).[5f] Next, the treatment of **5** with 1 equiv. of trichloroacetonitrile in the presence of 20 mol-% DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) afforded monoimidates **6** in good to excellent yields (see Table 1). Finally, the reaction of imidates **6** with tosylisocyanate provided the products (*E*)-**1a**–(*E*)-**1f**, (*E*)-**1h**–(*E*)-**1k**, (*Z*)-**1a**, (*Z*)-**1b**, and (*Z*)-**1f** in almost quantitative yields (see Scheme 1, Table 1). The only exception was imidate **6g** which did not afford the expected carbamate **1g**, but instead formed oxazoline **4g** when treated with tosyl isocyanate (Table 1, Entry 10).



Scheme 1. Preparation of δ-*N*-tosylcarbamates **1**.

Substrate (*E*)-**1a** was used as a model compound for the initial screening of the catalysts. The treatment of (*E*)-**1a** with 10 mol-% of CuCl, $NiCl_2$, $MgCl_2$, $Ti(OiPr)_4$, $AlCl_3$, $Zn(OTf)_2$, B-butyl-9-BBN (9-butyl-9-borabicyclo[3.3.1]-nonane), BEt_3, Et_2AlCl, CuI, $CuCl_2$, Me_3Al, PPTS (pyridinium *para*-toluenesulfonate), HCl in Et_2O, and BBr_3 in a CH_2Cl_2 solution did not lead to detectable conversion, by TLC, of the starting material. A slow conversion (ca. 50% in 3 d) was observed by using TFA (trifluoroacetic acid) as a catalyst. Finally, 10 mol-% of $BF_3{\cdot}OEt_2$, $B(C_6F_5)_3$, TMSOTf, $Cu(OTf)_2$, and $Cu_2(OTf)_2{\cdot}C_6H_6$, were found to be efficient catalysts for the cyclization reaction of (*E*)-**1a**. The efficiency of these catalysts could be attributed to the sufficient Lewis acidity and lack of nucleophilic counterions. To gain evidence for the effect of the counterion, substrate (*E*)-**1a** was subjected to 1 equiv. of $AlCl_3$. This resulted in complete conversion of the starting material in 2 h, but provided a product mixture that was difficult to separate. ^{1}H NMR and GC–MS analyses suggested that the major product formed was a derivative of (*E*)-**1** in which both the imidate and carbamate groups were substituted by chlorine. Likely, substitution reactions with the nucleophilic counterions competed with the cyclization leading to the deactivation of the Lewis acid catalysts.

Table 1. Substitution pattern and yields of monoimidates **6** and *N*-tosylcarbamates **1**.

Entry	R^1	R^2	% Yield[a] **6**	% Yield[a] **1**
1	*n*-pentyl	H	(*E*)-**6a**, 78	(*E*)-**1a**, 94
2	*n*-pentyl	H	(*Z*)-**6a**, 76	(*Z*)-**1a**, 97
3	*i*Pr	H	(*E*)-**6b**, 84	(*E*)-**1b**, 96
4	*i*Pr	H	(*Z*)-**6b**, 87	(*Z*)-**1b**, 96
5	Bn	H	(*E*)-**6c**, 80	(*E*)-**1c**, 90
6	$CH_2{=}CH(CH_2)_8{-}$	H	(*E*)-**6d**, 83	(*E*)-**1d**, 97
7	$Ph_2CH{-}$	H	(*E*)-**6e**, 82	(*E*)-**1e**, 96
8	Ph	H	(*E*)-**6f**, 68	(*E*)-**1f**, 85
9	Ph	H	(*Z*)-**6f**, 72	(*Z*)-**1f**, 95
10	*p*-MeOPh	H	(*E*)-**6g**, 80	–[b]
11	Me	Me	(*E*)-**6h**, 84	(*E*)-**1h**, 93
12	$-CH_2(CH_2)_3CH_2-$		(*E*)-**6i**, 91	(*E*)-**1i**, 96
13	$-(CH_2)_2NBoc(CH_2)_2-$		(*E*)-**6j**, 91	(*E*)-**1j**, 97
14	$-(CH_2)_2O(CH_2)_2-$		(*E*)-**6k**, 71	(*E*)-**1k**, 87

[a] Isolated yield. [b] Vinyloxazoline **4g** was isolated in 85% yield.

Other substrates were subsequently subjected to the $BF_3{\cdot}OEt_2$, $B(C_6F_5)_3$, TMSOTf, $Cu(OTf)_2$, and $Cu_2(OTf)_2{\cdot}C_6H_6$ catalysts. *N*-Tosylcarbamates (*E*)-**1a**–(*E*)-**1e**, (*E*)-**1h**–(*E*)-**1k**, (*Z*)-**1a**, and (*Z*)-**1b** gave the corresponding iminocarbonates **2a**–**2e** and **2h**–**2k** as the intramolecular substitution products in good to excellent yields, when exposed to previously established Lewis acid catalysts (see Tables 2 and 3). A mixture of products (with oxazoline **4f** as the major component) was obtained from substrates (*E*)-**1f** and (*Z*)-**1f** bearing a phenyl group (see Table 2, Entries 22 and 23). This implies that the method is not applicable if a very stable carbenium ion is generated by the abstraction of the tosylcarbamate. Nevertheless, tosylcarbamates (*E*)-**1h**–(*E*)-**1k**, derived from tertiary alcohols, were still suitable substrates for the syntheses of iminocarbonates **2h**–**2k** (see Table 3).

The proposed structure of compound **2i** was corroborated by 2D ^{1}H/^{13}C HSQC (heteronuclear single quantum correlation) and HMBC (heteronuclear multiple bond correlation) NMR experiments (see Supporting Information). The characteristic ^{13}C NMR shift for the allylic carbon in iminocarbonates **2** ($\delta_C \approx 80$ ppm) easily allowed us to distinguish them from the regioisomeric oxazolidinones **3** ($\delta_C \approx 60$ ppm). The *trans* configuration for iminocarbonates *trans*-**2a**–*trans*-**2e** was revealed by NOESY NMR experiments (see Supporting Information). In addition to these spectroscopic studies, the structures of *trans*-**2a**–*trans*-**2c** and **2i**–**2k** were confirmed by transforming them into known compounds (vide infra). Finally, the structure of iminocarbonate **2i** was unambiguously proved by single-crystal X-ray diffraction (see Supporting Information).

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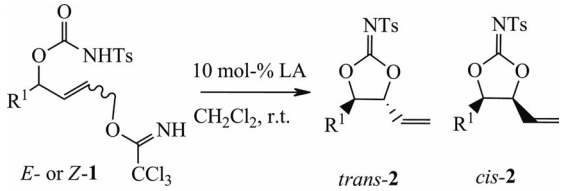
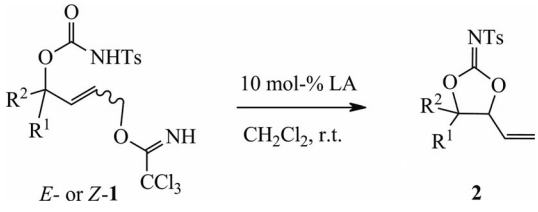
Table 2. Cyclization of *N*-tosylcarbamates **1a**–**1f** derived from secondary alcohols.



Entry	R^1	Substrate	Lewis acid	Time [h]	% Yield[c]	*trans*/*cis* ratio[d]
1	*n*-pentyl	(*E*)-**1a**	$BF_3{\cdot}OEt_2$	24	**2a**, 72	15:1
2	*n*-pentyl	(*Z*)-**1a**	$BF_3{\cdot}OEt_2$	72[b]	**2a**, 87	5:1
3	*n*-pentyl	(*E*)-**1a**	TMSOTf	4	**2a**, 82	34:1
4	*n*-pentyl	(*Z*)-**1a**	TMSOTf	72[b]	**2a**, 51	4:1
5	*n*-pentyl	(*E*)-**1a**	$Cu(OTf)_2$	60[b]	**2a**, 76	6:1
6	*n*-pentyl	(*E*)-**1a**	CuOTf[a]	80[b]	**2a**, 75	2:1
7	*n*-pentyl	(*E*)-**1a**	$B(C_6F_5)_3$	80[b]	**2a**, 73	3:1
8	*i*Pr	(*E*)-**1b**	$BF_3{\cdot}OEt_2$	18	**2b**, 90	15:1
9	*i*Pr	(*Z*)-**1b**	$BF_3{\cdot}OEt_2$	48[b]	**2b**, 85	80:1
10	*i*Pr	(*E*)-**1b**	TMSOTf	3	**2b**, 80	14:1
11	*i*Pr	(*Z*)-**1b**	TMSOTf	72[b]	**2b**, 70	50:1
12	*i*Pr	(*E*)-**1b**	$Cu(OTf)_2$	20	**2b**, 80	25:1
13	*i*Pr	(*E*)-**1b**	$B(C_6F_5)_3$	26	**2b**, 75	35:1
14	Bn	(*E*)-**1c**	$BF_3{\cdot}OEt_2$	48[b]	**2c**, 73	3:1
15	Bn	(*E*)-**1c**	TMSOTf	22	**2c**, 70	25:1
16	Bn	(*E*)-**1c**	$Cu(OTf)_2$	48[b]	**2c**, 74	6:1
17	Bn	(*E*)-**1c**	$B(C_6F_5)_3$	48[b]	**2c**, 63	5:1
18	$CH_2{=}CH(CH_2)_8$	(*E*)-**1d**	$BF_3{\cdot}OEt_2$	26[b]	**2d**, 69	6:1
19	$CH_2{=}CH(CH_2)_8$	(*E*)-**1d**	TMSOTf	26[b]	**2d**, 75	11:1
20	Ph_2CH	(*E*)-**1e**	$BF_3{\cdot}OEt_2$	3	**2e**, 85	14:1
21	Ph_2CH	(*E*)-**1e**	TMSOTf	2.5	**2e**, 82	45:1
22	Ph	(*E*)-**1f**	$BF_3{\cdot}OEt_2$	24	**4f**, 44	–
23	Ph	(*Z*)-**1f**	$BF_3{\cdot}OEt_2$	24	n.d.[e]	–

[a] $Cu_2(OTf)_2{\cdot}C_6H_6$. [b] Additional portions of Lewis acid (10 mol-%) were added after each 24 h. [c] Isolated yield. [d] Determined by using ^1H NMR, LC–MS and HPLC (210 nm). Ratio is given as determined by HPLC. [e] n.d. = not determined.

Table 3. Cyclization of tosylcarbamates (*E*)-**1h**–(*E*)-**1k** derived from tertiary alcohols.



Entry	R^1, R^2	Substrate	Catalyst	Time	% Yield **2**[a]
1	Me	(*E*)-**1h**	$BF_3{\cdot}OEt_2$	18 h	**2h**, 93
2	Me	(*E*)-**1h**	TMSOTf	0.5 h	**2h**, 77
3	$-CH_2(CH_2)_3CH_2-$	(*E*)-**1i**	$BF_3{\cdot}OEt_2$	1 h	**2i**, 90
4	$-CH_2(CH_2)_3CH_2-$	(*E*)-**1i**	TMSOTf	10 min	**2i**, 74
5	$-(CH_2)_2NBoc(CH_2)_2-$	(*E*)-**1j**	$BF_3{\cdot}OEt_2$	1 h	**2j**, 88
6	$-(CH_2)_2NBoc(CH_2)_2-$	(*E*)-**1j**	TMSOTf	10 min	**2j**, 80
7	$-(CH_2)_2O(CH_2)_2-$	(*E*)-**1k**	$BF_3{\cdot}OEt_2$	1 h	**2k**, 83

[a] Isolated yield.

Substrates with the (*E*)-configured double bond reacted in shorter times (see Table 2, Entries 1 vs. 2, Entries 3 vs. 4, Entries 8 vs. 9, and Entries 10 vs. 11), particularly if TMSOTf was used as a catalyst (see Table 2, Entries 3, 10, and 15). In addition, using TMSOTf induced a faster conversion in the cases of the *N*-tosylcarbamates derived from tertiary alcohols (*E*)-**1h**–(*E*)-**1k**. However, when using $BF_3{\cdot}Et_2O$ as the catalyst, the yields were slightly better (see Table 3).

As can be seen from Table 2, the *N*-tosylcarbamates derived from secondary alcohols **1a**–**1e** provided the *trans*-iminocarbonates *trans*-**2a**–*trans*-**2e**, preferentially (see Table 2). The *trans* selectivity varied depending on the configuration of the double bond and the substitution pattern in substrates (*E*)- and (*Z*)-**1a**–(*E*)- and (*Z*)-**1b** as well as on the Lewis acid catalyst. Isomer (*E*)-**1a**, bearing the *n*-pentyl substituent, resulted in considerably better *trans* selectivity in comparison to isomer (*Z*)-**1a**, when $BF_3{\cdot}OEt_2$, TMSOTf, and $Cu(OTf)_2$ were used as catalysts (see Table 2, Entries 1–4), from which TMSOTf was superior. The exposure of substrates (*E*)- and (*Z*)-**1b**, bearing the sterically more demanding isopropyl substituent, to $BF_3{\cdot}OEt_2$, TMSOTf, $Cu(OTf)_2$, and $B(C_6F_5)$ catalysts gave iminocarbonate **2b** with a high *trans* selectivity from both isomers (see Table 2, Entries 8–13). Although in this case, isomer (*Z*)-**1b** appeared to give a higher *trans* selectivity.

In the literature, the origin of this diastereoselectivity has been studied for several acid-catalyzed intramolecular allylic substitutions with both O- and N-nucleophiles.[2c,2e] These studies reveal that the given reactions are reversible leading to a thermodynamically controlled diastereomeric

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ratio. We subjected the diastereomeric mixtures of **2a** and **2b**, enriched with the minor isomer (**2a**, *trans*/*cis*, 3:1; **2b**, *trans*/*cis*, 6:1), to 10 mol-% TMSOTf. No changes in the isomeric ratios were observed for **2a** over 4 h or for **2b** over 3 h, suggesting that the cyclization reactions of *N*-tosylcarbamates **1** to *N*-tosyliminocarbonates **2** are kinetically controlled.

The chemoselective cyclization of substrates **1** leading to iminocarbonates **2** could be explained by the complexation of the Lewis acid to the most basic imidate functionality,[8] leading to an allylcarbenium ion which prefers to react with the harder oxygen versus nitrogen center of the *N*-tosylcarbamate, analogous to the mechanism proposed by Friesen and Giroux (see Figure 2).[4] It is evident, however, that for formation of iminocarbonates **2**, the S_N1-type mechanism involving a solvent-separated ion pair is not the (only) operational pathway. Such a mechanism would lead to a constant *trans*/*cis* product ratio independent of the catalyst and configuration of substrate **1**. The varying *trans*/*cis* ratio (see Table 2) could be explained by an S_N2' reaction mechanism (see Figure 2). The differences in the reaction rates for (*E*)-**1** and (*Z*)-**1**, which was remarkable in the case of TMSOTf as a catalyst, also supports an S_N2' mechanism. One could expect that the transition state for the cyclization through an S_N2' mechanism is facilitated for (*E*)-**1** in comparison to (*Z*)-**1**. In addition, the Thorpe–Ingold substrates (*E*)-**1h**–(*E*)-**1k** underwent reaction faster than the less branched analogues (*E*)-**1a**–(*E*)-**1e**. This again is in accordance with an S_N2' mechanism, which involves a cyclization reaction along with simultaneous imidate substitution. The Thorpe–Ingold effect should not significantly influence the reaction rate of the S_N1 mechanism where carbenium ion formation is the rate-limiting step. It is actually possible that both S_N1 and S_N2' mechanisms are operational. The switch between these mechanistic pathways could explain the different *trans*/*cis* ratios for compounds **2**, depending on the catalyst and configuration of substrates **1**. On the basis of these considerations, it can be hypothesized that using TMSOTf as a catalyst and starting with the (*E*) configuration of the substrate are prerequisites to induce the faster and *trans* selective pathway through the S_N2' mechanism. Alternatively, the S_N1 mechanism through the intimate ion pair can be invoked, assuming that no change takes place in the double-bond configuration of the intermediate carbenium ion, when starting from (*E*)-**1** or (*Z*)-**1**. However, in the case of substrate (*Z*)-**1a** compared to (*E*)-**1a**, this could not explain the less *trans* selective reaction.

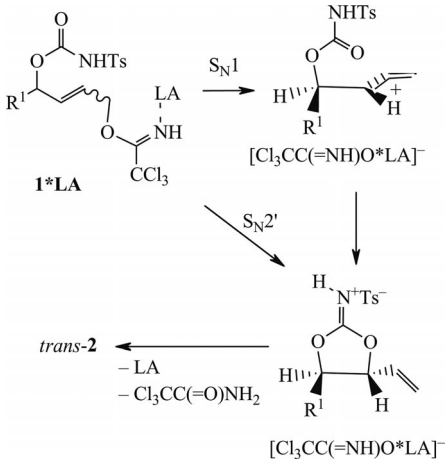
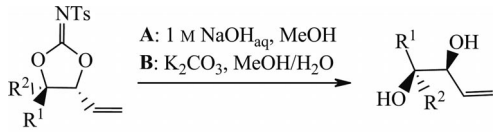


Figure 2. Hypothetical mechanisms for the formation of iminocarbonates **2**.

To demonstrate the utility of the iminocarbonates, the cyclization products **2a**, **2c**, and **2i**–**2k** were hydrolyzed under basic reaction conditions to the corresponding diols **7a**, **7c**, and **7i**–**7k** (see Table 4). Thus, the cyclization of *N*-tosylcarbamates **1**, derived from secondary alcohols, followed by hydrolysis represents a new method for syntheses of *syn*-1,2-diols, as exemplified by the transformation of *trans*-iminocarbonates, that is, *trans*-**2a** and *trans*-**2c** into the diols *syn*-**7a** and *syn*-**7c**.

Table 4. Hydrolysis of iminocarbonates **2** to diols **7**.



Entry	R^1	R^2	Method	% Yield[a] **7**[b]
1	*n*-pentyl	H	A	**7a**, 71
2	Bn	H	A	**7c**, 87
3	$-CH_2(CH_2)_3CH_2-$		A	**7i**, 88
4	$-(CH_2)_2NBoc(CH_2)_2-$		B	**7j**, 89
5	$-(CH_2)_2O(CH_2)_2-$		B	**7k**, 86

[a] Isolated yield. [b] Compounds **7a**,[9] **7c**,[10] and **7i**[11] are known, and their spectroscopic characterizations match with literature data.

By using TMSOTf as an acid source, acidic hydrolysis conditions were applied to transform iminocarbonate **2b** into cyclic carbonate **8b** (see Table 5, Entry 2). *N*-tosylcarbamates **1a** and **1i** were transformed into carbonates **8a** and **8i**, respectively, in a one-pot procedure. First, the cyclization reactions of **1a** and **1i** were performed with TMSOTf as a catalyst, and then water was added to achieve the hydrolysis without isolation of the iminocarbonate intermediate. Also, a one-pot procedure was tried with 10 mol-% $BF_3{\cdot}Et_2O$ and substrate **1i**. After the cyclization was complete, water was added. However, no carbonate **8i** formation was observed after 16 h. Additional 10 mol-% of $BF_3{\cdot}Et_2O$ was added, which resulted in approximately 7% formation of **8i** after 8 h, according to ^1H NMR analysis of the crude mixture.

Iminocarbonates are valuable substrates for halide ion-promoted rearrangement to oxazolidinones.[6] To demonstrate this, iminocarbonates *trans*-**2a**–*trans*-**2c** and **2i** were regioselectively rearranged into vinyl *N*-tosyloxazolidinones *trans*-**3a**–*trans*-**3c** and **3i** (see Table 6). More forcing conditions were required for the transformation of branched iminocarbonate **2i** into oxazolidinone **3i** (see Table 6, En-

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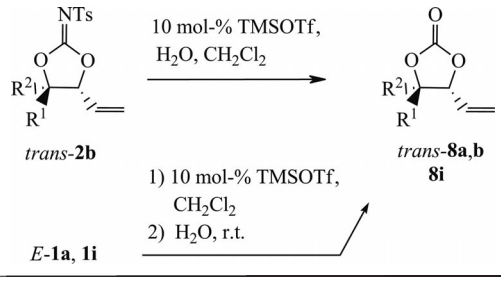
Table 5. Hydrolysis of iminocarbonates **2** to carbonates **8**.

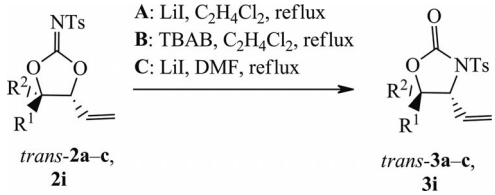


Entry	R^1	R^2	Substrate	% Yield[a] **8**[b]
1	*n*-pentyl	H	**1a**	*trans*-**8a**, 67
2	*i*Pr	H	*trans*-**2b**	*trans*-**8b**, 70
3	$-CH_2(CH_2)_3CH_2-$		**1i**	**8i**, 73

[a] Isolated yield. [b] Compounds **8a**, **8b**,[13] and **8i**[14] are known, and their spectroscopic characterizations match with literature data.

try 4). Oxazolidinones can easily be transformed into amino alcohols. Thus, the cyclization of tosylcarbamates **1** followed by rearrangement provides straightforward access to valuable vinyl amino alcohol derivatives.[6,7,12]

Table 6. Rearrangement of iminocarbonates **2** to oxazolidinones **3**.



Entry	R^1	R^2	Method	% Yield[a] **3**[b]
1	*n*-pentyl	H	B	*trans*-**3a**, 73
2	*i*Pr	H	A	*trans*-**3b**, 63
3	Bn	H	B	*trans*-**3c**, 74
4	$-CH_2(CH_2)_3CH_2-$		C	**3i**, 85

[a] Isolated yield. [b] Compounds **3a**, **3b**,[6b] and **3i**[15] are known, and their spectroscopic characterizations match with literature data.

Conclusions

In summary, we have demonstrated that allylic trichloroacetimidates **1** bearing a δ-*N*-tosylcarbamoyloxy group undergo intramolecular Lewis acid catalyzed allylic substitution to give cyclic *N*-tosyliminocarbonates **2**. If substrates with the (*E*) configuration are used in combination with TMSOTf as a catalyst, the carbamates derived from secondary alcohols provided the highly selective formation of *trans*-iminocarbonates. We also demonstrated the conversion of iminocarbonates **2** into unsaturated 1,2-diols **7**, carbonates **8**, and oxazolidinones **3**. Thus, this methodology based on Lewis acid catalyzed allylic substitution allows efficient access to these valuable products and avoids the use of expensive and toxic late transition-metal catalysts.

Experimental Section

General Remarks: The reagents and starting materials were obtained from commercial sources and used as received. The solvents were purified and dried by standard procedures prior to use, and petroleum ether of a boiling range of 60–80 °C was used. All of the reactions were performed under an argon atmosphere. Flash chromatography was carried out using Merck Kieselgel (230–400 mesh). Thin layer chromatography was performed on silica gel and visualized by staining with $KMnO_4$. The NMR spectroscopic data were recorded with a Varian Mercury spectrometer (400 MHz). The chemical shifts values (δ) are given in ppm relative to TMS with the residual chloroform signal as the internal standard. HRMS data were obtained with a Q-TOF micro high-resolution mass spectrometer with ESI (ESI^+/ESI^-). LC–MS analyses was performed with a LC system Aliance separation module 2695 with the mass selective detector Waters SQ3100. Olefins (*E*)- and (*Z*)-**5** were synthesized in two steps from the corresponding aldehydes or ketones as reported previously[5f] (see also Supporting Information).

General Procedure for Synthesis of Monotrichloroacetimidate 6: To a solution of diol **5** (2.5 mmol) in CH_2Cl_2 (25 mL) were added molecular sieves (4 Å). The solution was cooled to 0 °C, and then DBU (0.5 mmol, 20 mol-%) was added. The reaction mixture was stirred at 0 °C for 30 min, and to this was added trichloroacetonitrile (2.5 mmol, 1 equiv.). The reaction mixture was stirred until TLC indicated a complete conversion of the starting material (ca. 0.5–4 h). The solvent was removed, and the residue was purified by flash column chromatography on silica gel eluting with a mixture of light petroleum ether and EtOAc (4:1) to give monotrichloroacetimidate **6** as a colorless oil.

(*E*)-4-Hydroxynon-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-6a]: ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, N*H*), 5.90–5.88 (m, 2 H, C*H*=C*H*), 4.80 (d, *J* = 4.3 Hz, 2 H, OCH_2), 4.19–4.14 (m, 1 H, C*H*), 1.59–1.55 [m, 8 H, $(CH_2)_4CH_3$], 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.48, 138.88, 123.48, 91.36, 72.10, 68.91, 37.02, 31.68, 24.96, 22.57, 13.99 ppm. Unstable under conditions for HRMS.

(*Z*)-4-Hydroxynon-2-enyl 2,2,2-Trichloroacetimidate [(*Z*)-6a]: ^1H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 1 H, N*H*), 5.74 (dd, *J* = 11.0 and 7.8 Hz, 1 H, C*H*=$CHCH_2$), 5.67–5.61 (m, 1 H, CH=C*H*CH_2), 5.11 (dd, *J* = 12.5 and 8.2 Hz, 1 H, OCH_2), 4.85 (dd, *J* = 12.5 and 6.7 Hz, 1 H, OCH_2), 4.54–4.48 (m, 1 H, C*H*), 3.25 (d, *J* = 2.7 Hz, 1 H, O*H*), 1.66–1.26 [m, 8 H, $(CH_2)_4CH_3$], 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.89, 138.81, 123.57, 91.27, 67.58, 65.32, 36.85, 31.76, 24.93, 22.59, 14.01 ppm. Unstable under conditions for HRMS.

(*E*)-4-Hydroxy-5-methylhex-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-6b]: ^1H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1 H, N*H*), 5.94–5.85 (m, 2 H, C*H*=C*H*), 4.82 (d, *J* = 4.3 Hz, 1 H, OCH_2), 3.93 (m, 1 H, C*H*), 1.72 [octet, *J* = 7.0 Hz, 1 H, C*H*$(CH_3)_2$], 0.93 [d, *J* = 6.7 Hz, 3 H, CH(CH_3)$_2$], 0.90 [d, *J* = 7.0 Hz, 3 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.44, 136.11, 124.46, 91.37, 68.87, 33.71, 18.11, 17.74 ppm. Unstable under conditions for HRMS.

(*Z*)-4-Hydroxy-5-methylhex-2-enyl 2,2,2-Trichloroacetimidate [(*Z*)-6b]: ^1H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 1 H, N*H*), 5.77 (dd, *J* = 11.3 and 7.8 Hz, 1 H, C*H*=$CHCH_2$), 5.73–5.67 (m, 1 H, CH=C*H*CH_2), 5.11 (dd, *J* = 12.5 and 8.2 Hz, 1 H, OCH_2), 4.87 (dd, *J* = 12.5 and 5.5 Hz, 1 H, OCH_2), 4.22 (t, *J* = 7.1 Hz, 1 H, C*H*), 3.25 (d, *J* = 2.7 Hz, 1 H, O*H*), 1.74 [octet, *J* = 6.7 Hz, 1 H, C*H*$(CH_3)_2$], 0.97 [d, *J* = 6.7 Hz, 3 H, CH(CH_3)$_2$], 0.90 [d, *J* =

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6.7 Hz, 3 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.90, 137.03, 124.40, 91.27, 72.58, 65.44, 33.60, 18.05 ppm. Unstable under conditions for HRMS.

(*E*)-4-Hydroxy-5-phenylpent-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-6c]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, N*H*), 7.33–7.21 (m, 5 H, C_6H_5), 5.97 (dd, *J* = 15.7 and 5.1 Hz, 1 H, C*H*=CHCH$_2$), 5.90 (dt, *J* = 15.7 and 5.1 Hz, 1 H, CH=C*H*CH$_2$), 4.80 (d, *J* = 5.1 Hz, 2 H, OCH_2), 4.45–4.39 (m, 1 H, C*H*), 2.90 (dd, *J* = 13.7 and 5.1 Hz, 1 H, CH_2Ph), 2.80 (dd, *J* = 13.7 and 8.2 Hz, 1 H, CH_2Ph), 1.72 (d, *J* = 3.9 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.45, 137.33, 136.37, 129.55, 128.54, 126.67, 123.87, 91.37, 72.50, 68.77, 43.82 ppm. HRMS (EI): calcd. for $C_{13}H_{14}Cl_3NO_2Na$ [M + Na]$^+$ 343.9988; found 344.0009.

(*E*)-4-Hydroxytetradeca-2,13-dienyl 2,2,2-Trichloroacetimidate [(*E*)-6d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, N*H*), 5.93–5.87 (m, 2 H, C*H*=C*H*), 5.80 (ddt, *J* = 17.2, 10.2, and 6.7 Hz, 1 H, C*H*=CH$_2$), 4.98 (d, *J* = 17.2 Hz, 1 H, CH_2=CH), 4.92 (d, *J* = 10.2 Hz, 1 H, CH_2=CH), 4.80 (d, *J* = 3.9 Hz, 2 H, CH_2O), 4.16 (br. s, 1 H, O*H*), 2.04 (q, *J* = 6.7 Hz, 2 H, CH$_2$=CHCH_2), 1.64–1.24 [m, 14 H, (CH_2)$_7$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.48, 139.18, 137.88, 123.46, 114.11, 91.37, 72.08, 68.91, 37.05, 33.78, 29.48, 29.47, 29.37, 29.08, 28.89, 25.28 ppm. Unstable under conditions for LC–MS and HRMS.

(*E*)-4-Hydroxy-5,5-diphenylpent-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-6e]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1 H, N*H*), 7.38–7.15 (m, 10 H, C_6H_5), 5.94–5.83 (m, 2 H, C*H*=C*H*), 4.92 (dt, *J* = 8.2 and 3.9 Hz, 1 H, C*H*O), 4.71 (d, *J* = 4.3 Hz, 2 H, OCH_2) 4.98 (d, *J* = 8.6 Hz, 1 H, C*H*Ph$_2$), 1.80 (d, *J* = 3.9 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.27, 141.26, 140.60, 135.00, 128.78, 128.77, 128.57, 128.55, 126.99, 126.70, 124.73, 91.31, 73.73, 68.60, 58.63 ppm. Unstable under conditions for LC–MS. HRMS (EI): calcd. for $C_{19}H_{18}Cl_3NO_2Na$ [M + Na]$^+$ 420.0301; found 420.0335.

(*E*)-4-Hydroxy-4-phenylbut-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-6f]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1 H, N*H*), 7.39–7.27 (m, 5 H, C_6H_5), 6.09 (dd, *J* = 15.7 and 5.5 Hz, 1 H, C*H*=CHCH$_2$), 6.01 (dt, *J* = 15.7 and 5.5 Hz, 1 H, CH=C*H*CH$_2$), 5.27 (t, *J* = 3.9 Hz, 1 H, C*H*), 4.83 (d, *J* = 5.5 Hz, 2 H, OCH_2), 2.12 (d, *J* = 3.9 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.46, 142.23, 136.42, 128.62, 127.91, 126.35, 124.09, 91.30, 74.21, 68.72 ppm. Unstable under conditions for HRMS.

(*Z*)-4-Hydroxy-4-phenylbut-2-enyl 2,2,2-Trichloroacetimidate [(*Z*)-6f]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H, N*H*), 7.42–7.27 (m, 5 H, C_6H_5), 5.96 (dd, *J* = 11.0 and 7.8 Hz, 1 H, C*H*=CHCH$_2$), 5.77–5.70 (m, 1 H, CH=C*H*CH$_2$), 5.64 (dd, *J* = 7.4 and 2.3 Hz, 1 H, C*H*), 5.23 (dd, *J* = 12.5 and 8.2 Hz, 1 H, OCH_2), 5.00 (dd, *J* = 12.5 and 5.9 Hz, 1 H, OCH_2), 3.74 (d, *J* = 2.7 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.94, 142.53, 137.89, 128.57, 127.61, 126.0, 123.64, 91.23, 69.92, 65.25 ppm. Unstable under conditions for HRMS.

(*E*)-4-Hydroxy-4-(4-methoxyphenyl)but-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-6g]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, N*H*), 7.28 (d, *J* = 8.6 Hz, 2 H, C_6H_4), 6.88 (d, *J* = 8.6 Hz, 2 H, C_6H_4), 6.07 (dd, *J* = 15.3 and 5.1 Hz, 1 H, *H*C=CHCH$_2$), 5.98 (dt, *J* = 15.3 and 5.5 Hz, 1 H, HC=C*H*CH$_2$), 5.22 (t, *J* = 3.9 Hz, 1 H, C*H*), 4.82 (d, *J* = 5.1 Hz, 2 H, OCH_2), 3.80 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.47, 159.30, 136.63, 134.47, 127.72, 123.72, 113.99, 91.32, 73.74, 68.79, 55.28 ppm. Unstable under conditions for HRMS.

(*E*)-4-Hydroxy-4-methylpent-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-6h]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, N*H*), 6.01 (d, *J* = 15.7 Hz, 1 H, *H*C=CHCH$_2$), 5.87 (dt, *J* = 15.7 and 5.5 Hz, 1 H, HC=C*H*CH$_2$), 4.80 (dd, *J* = 5.9 and 1.2 Hz, 2 H, OCH_2), 1.35 [s, 6 H, C(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.53, 142.64, 120.09, 91.38, 70.58, 69.15, 29.58 ppm. Unstable under conditions for HRMS.

(*E*)-3-(1-Hydroxycyclohexyl)allyl 2,2,2-Trichloroacetimidate [(*E*)-6i]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1 H, N*H*), 5.98 (d, *J* = 16.0 Hz, 1 H, *H*C=CHCH$_2$), 5.90 (dt, *J* = 15.7 and 5.5 Hz, 1 H, HC=C*H*CH$_2$), 4.80 (d, *J* = 5.5 Hz, 2 H, OCH_2), 1.67–1.20 [m, 10 H, CH_2(CH_2)$_3$CH_2] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.49, 142.59, 120.62, 91.41, 71.26, 69.31, 37.66, 25.39, 21.90 ppm. Unstable under conditions for HRMS.

(*E*)-3-[1-(*tert*-Butoxycarbonyl)-4-hydroxypiperidin-4-yl]allyl 2,2,2-Trichloroacetimidate [(*E*)-6j]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, N*H*), 5.94–5.92 (m, 2 H, C*H*=C*H*), 4.81 (d, *J* = 4.3 Hz, 2 H, OCH_2), 3.89–3.81 [m, 2 H, CH_2N(Boc)], 3.24–3.18 [m, 2 H, CH_2N(Boc)], 1.71–1.49 [m, 4 H, CH_2CH_2N(Boc)CH$_2$CH_2], 1.45 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.42, 154.73, 141.24, 121.63, 91.30, 79.49, 69.68, 68.85, 36.80, 28.43 ppm. HRMS (EI): calcd. for $C_{15}H_{23}Cl_3N_2O_4Na$ [M + Na]$^+$ 423.0582; found 423.0621.

(*E*)-3-(4-Hydroxytetrahydro-2*H*-pyran-4-yl)allyl 2,2,2-Trichloroacetimidate [(*E*)-6k]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H, N*H*), 5.98 (d, *J* = 16.0 Hz, 1 H, C*H*=CHCH$_2$), 5.92 (dt, *J* = 15.6 and 5.1 Hz, 1 H, CH=C*H*CH$_2$), 4.82 (d, *J* = 4.7 Hz, 2 H, CH_2O), 3.85–3.72 (m, 4 H, CH_2OCH_2), 1.87–1.80 (m, 2 H, CH_2CH$_2$OCH$_2$CH_2), 1.57–1.52 (m, 2 H, CH_2CH$_2$OCH$_2$CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.43, 141.35, 121.58, 91.31, 68.89, 68.87, 63.55, 37.60 ppm. Unstable under conditions for HRMS.

General Procedure for Synthesis of *N*-Tosylcarbamate 1: To a solution of monotrichloroacetimidate **6** (2 mmol) in THF (20 mL) were added molecular sieves (4 Å). The reaction mixture was cooled to 0 °C, and then TsNCO (2 mmol, 1 equiv.) was added dropwise. The solution was stirred at room temperature until TLC indicated the complete conversion of the starting material (ca. 2 h). The solvent was removed, and the residue was purified by flash column chromatography on silica gel eluting with a mixture of light petroleum ether and EtOAc (2:1) to give tosylcarbamate **1** as a colorless oil.

(*E*)-4-(Tosylcarbamoyloxy)non-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-1a]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H, C=N*H*), 7.90 (d, *J* = 8.6 Hz, 2 H, C_6H_4Me), 7.40 (br. s, 1 H, N*H*Ts), 7.33 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 5.81 (dt, *J* = 15.7 and 5.1 Hz, 1 H, CH=C*H*CH$_2$), 5.70 (dd, *J* = 15.7 and 6.7 Hz, 1 H, C*H*=CHCH$_2$), 5.14 (q, *J* = 6.7 Hz, 1 H, C*H*), 4.74 (d, *J* = 5.5 Hz, 2 H, OCH_2), 2.45 (s, 3 H, $C_6H_4CH_3$), 1.63–1.50 [m, 2 H, CH_2(CH_2)$_3$CH_3], 1.28–1.11 [m, 6 H, CH$_2$(CH_2)$_3$CH$_3$], 0.84 [t, *J* = 6.7 Hz, 3 H, CH$_2$(CH_2)$_3$-CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.28, 149.76, 144.99, 135.63, 131.16, 129.56, 128.33, 126.58, 91.22, 77.11, 68.14, 34.04, 31.32, 24.36, 22.39, 21.67, 13.89 ppm. HRMS (EI): calcd. for $C_{19}H_{25}Cl_3N_2O_5SNa$ [M + Na]$^+$ 521.0447; found 521.0396.

(*Z*)-4-(Tosylcarbamoyloxy)non-2-enyl 2,2,2-Trichloroacetimidate [(*Z*)-1a]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1 H, C=N*H*), 7.90 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.53 (br. s, 1 H, N*H*Ts), 7.33 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 5.77 (dt, *J* = 11.0 and 6.7 Hz, 1 H, CH=C*H*CH$_2$), 5.51–5.37 (m, 2 H, C*H*C*H*=CHCH$_2$), 4.91 (dd, *J* = 12.9 and 6.7 Hz, 1 H, OCH_2), 4.83 (dd, *J* = 12.9 and 6.7 Hz, 1 H, OCH_2), 2.45 (s, 3 H, $C_6H_4CH_3$), 1.69–1.45 [m, 2 H, CH_2(CH_2)$_3$-CH_3], 1.30–1.15 [m, 6 H, CH$_2$(CH_2)$_3$CH$_3$], 0.85 [t, *J* = 6.7 Hz, 3 H, CH$_2$(CH_2)$_3$CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.32,

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149.67, 145.00, 135.61, 131.73, 129.57, 128.32, 127.17, 91.17, 73.66, 64.90, 34.27, 31.43, 24.36, 22.41, 21.67, 13.92 ppm. HRMS (EI): calcd. for $C_{19}H_{25}Cl_3N_2O_5SNa$ [M + Na]$^+$ 521.0447; found 521.0396.

(*E*)-5-Methyl-4-(tosylcarbamoyloxy)hex-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-1b]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H, C=N*H*), 7.90 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.69 (br. s, 1 H, N*H*Ts), 7.33 (d, *J* = 8.6 Hz, 2 H, C_6H_4Me), 5.75 (dt, *J* = 15.7 and 5.1 Hz, 1 H, CH=C*H*CH$_2$), 5.67 (dd, *J* = 15.7 and 6.3 Hz, 1 H, C*H*=CHCH$_2$), 4.97 (t, *J* = 6.3 Hz, 1 H, C*H*), 4.73 (d, *J* = 4.7 Hz, 2 H, OCH_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 1.83 [octet, *J* = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 0.82 [d, *J* = 7.0 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.22, 149.81, 144.98, 135.65, 129.58, 129.29, 128.26, 127.41, 91.23, 81.57, 68.05, 31.92, 21.66, 17.75, 17.64 ppm. HRMS (EI): calcd. for $C_{17}H_{21}Cl_3N_2O_5SNa$ [M + Na]$^+$ 493.0134; found 493.0158.

(*Z*)-5-Methyl-4-(tosylcarbamoyloxy)hex-2-enyl 2,2,2-Trichloroacetimidate [(*Z*)-1b]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1 H, C=N*H*), 7.90 (d, *J* = 8.6 Hz, 2 H, C_6H_4Me), 7.33 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 5.83 (dt, *J* = 11.3 and 6.6 Hz, 1 H, CH=C*H*CH$_2$), 5.46 (dd, *J* = 11.3 and 9.8 Hz, 1 H, C*H*=CHCH$_2$), 5.18 (dd, *J* = 9.4 and 6.6 Hz, 1 H, C*H*), 4.93–4.82 (m, 2 H, OCH_2), 2.45 (s, 3 H, $C_6H_4CH_3$), 1.84 [octet, *J* = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 0.85 [d, *J* = 6.6 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.35, 149.80, 144.95, 135.67, 129.69, 129.56, 128.23, 91.16, 77.79, 65.06, 32.06, 21.66, 17.81, 17.66 ppm. HRMS (EI): calcd. for $C_{17}H_{21}Cl_3N_2O_5SNa$ [M + Na]$^+$ 493.0134; found 493.0089.

(*E*)-5-Phenyl-4-(tosylcarbamoyloxy)pent-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-1c]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, C=N*H*), 7.86 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.71 (br. s, 1 H, N*H*Ts), 7.31 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.23–7.17 (m, 3 H, CH$_2C_6H_5$), 7.07–7.05 (m, 2 H, CH$_2C_6H_5$), 5.78–5.69 (m, 2 H, C*H*=C*H*), 5.39–5.34 (m, 1 H, C*H*), 4.69 (d, *J* = 2.7 Hz, 2 H, OCH_2), 2.92 (dd, *J* = 14.0 and 7.0 Hz, 1 H, CH_2Ph), 2.84 (dd, *J* = 14.0 and 6.3 Hz, 1 H, CH_2Ph), 2.45 (s, 3 H, $C_6H_4CH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.21, 149.48, 145.00, 135.53, 135.49, 130.01, 129.58, 129.52, 128.35, 128.29, 126.93, 126.76, 91.17, 77.05, 67.94, 40.63, 21.67 ppm. HRMS (EI): calcd. for $C_{21}H_{21}Cl_3N_2O_5SNa$ [M + Na]$^+$ 541.0134; found 541.0145.

(*E*)-4-(Tosylcarbamoyloxy)tetradeca-2,13-dienyl 2,2,2-Trichloroacetimidate [(*E*)-1d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H, C=N*H*), 7.90 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.56 (br. s, 1 H, N*H*Ts), 7.33 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 5.86–5.67 (m, 3 H, C*H*=C*H*, CH$_2$=C*H*), 5.14 (q, *J* = 7.6 Hz, 1 H, C*H*O), 5.98 (d, *J* = 17.2 Hz, 1 H, CH_2=CH), 4.92 (d, *J* = 10.2 Hz, 1 H, CH_2=CH), 4.74 (d, *J* = 5.5 Hz, 2 H, CH_2O), 2.44 (s, 3 H, CH_3), 2.03 (q, *J* = 6.1 Hz, 2 H, CH_2CH=CH$_2$), 1.63–1.10 [m, 14 H, (CH_2)$_7$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.27, 149.69, 145.01, 139.12, 135.61, 131.12, 129.57, 128.35, 126.65, 114.16, 91.23, 77.15, 68.11, 34.09, 33.76, 29.34, 29.31, 29.18, 29.04, 28.86, 24.72, 21.68 ppm. Unstable under conditions for LC–MS.

(*E*)-5,5-Diphenyl-4-(tosylcarbamoyloxy)pent-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-1e]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1 H, C=N*H*), 7.75 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.26 (d, *J* = 7.8 Hz, 2 H, C_6H_4Me), 7.23–7.08 (m, 10 H, C_6H_5), 5.94 (dd, *J* = 9.4, 6.3 Hz, 1 H, C*H*CHPh), 5.77 (dt, *J* = 15.7 and 4.7 Hz, 1 H, CH=C*H*CH$_2$), 5.68 (dd, *J* = 15.7 and 6.3 Hz, 1 H, C*H*=CHCH$_2$), 4.61 (d, *J* = 4.7 Hz, 2 H, OCH_2), 4.10 (d, *J* = 9.8 Hz, 1 H, C*H*Ph), 2.45 (s, 3 H, $C_6H_4CH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.98, 149.65, 144.73, 139.93, 139.70, 135.42, 129.49, 129.44, 128.58, 128.54, 128.37, 128.06, 128.05, 127.57, 126.95, 126.65, 91.10, 77.56, 67.71, 55.88, 21.64 ppm. Unstable under conditions for LC–MS.

(*E*)-4-Phenyl-4-(tosylcarbamoyloxy)but-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-1f]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 1 H, C=N*H*), 7.88 (d, *J* = 8.6 Hz, 2 H, C_6H_4Me), 7.34–7.27 (m, 5 H, C_6H_4Me and C_6H_5), 7.22–7.20 (m, 2 H, C_6H_5), 6.15 (d, *J* = 5.7 Hz, 1 H, C*H*), 5.96 (dd, *J* = 15.7 and 5.5 Hz, 1 H, C*H*=CHCH$_2$), 5.87 (dt, *J* = 15.7 and 5.5 Hz, 1 H, CH=C*H*CH$_2$), 4.78 (d, *J* = 5.1 Hz, 2 H, OCH_2), 2.44 (s, 3 H, $C_6H_4CH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.26, 149.62, 144.90, 137.21, 135.48, 130.66, 129.61, 129.52, 128.56, 128.22, 127.02, 126.34, 91.09, 77.91, 68.05, 21.60 ppm. HRMS (EI): calcd. for $C_{20}H_{19}Cl_3N_2O_5SNa$ [M + Na]$^+$ 526.9978; found 527.0172.

(*Z*)-4-Phenyl-4-(tosylcarbamoyloxy)but-2-enyl 2,2,2-Trichloroacetimidate [(*Z*)-1f]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1 H, C=N*H*), 7.88 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.35–7.27 (m, 7 H, C_6H_4Me and C_6H_5), 6.45 (d, *J* = 8.6 Hz, 1 H, C*H*), 5.88–5.76 (m, 2 H, C*H*=C*H*), 4.99 (dd, *J* = 13.3 and 6.3 Hz, 1 H, OCH_2), 4.92 (dd, *J* = 13.3 and 5.9 Hz, 1 H, OCH_2), 2.44 (s, 3 H, $C_6H_4CH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.30, 149.46, 145.05, 137.55, 135.47, 131.05, 129.59, 128.71, 128.57, 128.32, 127.17, 126.66, 91.09, 74.45, 64.82, 21.67 ppm. HRMS (EI): calcd. for $C_{20}H_{19}Cl_3N_2O_5SNa$ [M + Na]$^+$ 526.9978; found 526.9928.

(*E*)-4-Methyl-4-(tosylcarbamoyloxy)pent-2-enyl 2,2,2-Trichloroacetimidate [(*E*)-1h]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, C=N*H*), 7.88 (d, *J* = 8.6 Hz, 2 H, C_6H_4Me), 7.33 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 6.00 (d, *J* = 16.0 Hz, 1 H, C*H*=CHCH$_2$), 5.76 (dt, *J* = 16.0 and 5.5 Hz, 1 H, CH=C*H*CH$_2$), 4.75 (d, *J* = 5.5 Hz, 2 H, OCH_2), 2.45 (s, 3 H, $C_6H_4CH_3$), 1.49 [s, 6 H, C(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.33, 148.62, 144.85, 139.40, 137.27, 129.53, 128.23, 122.93, 91.24, 83.25, 68.55, 26.38, 21.67 ppm. HRMS (EI): calcd. for $C_{16}H_{19}Cl_3N_2O_5SNa$ [M + Na]$^+$ 478.9978; found 479.0020.

(*E*)-3-[1-(Tosylcarbamoyloxy)cyclohexyl]allyl 2,2,2-Trichloroacetimidate [(*E*)-1i]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1 H, C=N*H*), 7.88 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.48 (br. s, 1 H, N*H*Ts), 7.33 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 5.94 (d, *J* = 16.0 Hz, 1 H, C*H*=CHCH$_2$), 5.64 (dt, *J* = 16.0 and 5.9 Hz, 1 H, CH=C*H*CH$_2$), 4.70 (d, *J* = 5.5 Hz, 2 H, OCH_2), 2.45 (s, 3 H, $C_6H_4CH_3$), 2.15–2.08 [m, 2 H, CH_2(CH$_2$)$_3$CH_2], 1.58–1.44 [m, 8 H, CH_2(CH_2)$_3$CH_2] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.25, 148.42, 144.80, 136.67, 135.90, 129.55, 128.12, 126.45, 123.90, 91.27, 84.57, 68.63, 34.89, 24.99, 21.67, 21.60 ppm. HRMS (EI): calcd. for $C_{19}H_{24}Cl_3N_2O_5S$ [M + H]$^+$ 497.0472; found 497.0449.

(*E*)-3-[1-(*tert*-Butoxycarbonyl)-4-(tosylcarbamoyloxy)piperidin-4-yl]-allyl 2,2,2-Trichloroacetimidate [(*E*)-1j]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1 H, C=N*H*), 7.86 (d, *J* = 8.6 Hz, 2 H, C_6H_4Me), 7.68 (br. s, 1 H, N*H*Ts), 7.34 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 5.96 (d, *J* = 16.0 Hz, 1 H, C*H*=CHCH$_2$), 5.67 (dt, *J* = 16.0 and 5.5 Hz, 1 H, CH=C*H*CH$_2$), 4.71 (d, *J* = 5.5 Hz, 2 H, OCH_2), 3.82–3.68 [m, 2 H, CH_2N(Boc)CH_2], 3.10–2.95 [m, 2 H, CH_2N(Boc)CH_2], 2.45 (s, 3 H, $C_6H_4CH_3$), 2.15–2.09 [m, 2 H, CH_2CH$_2$N(Boc)CH$_2$CH_2], 1.71–1.63 [m, 2 H, CH_2CH$_2$N(Boc)-CH$_2$CH_2], 1.41 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.16, 154.54, 148.39, 145.04, 135.79, 134.94, 129.65, 128.00, 125.02, 91.15, 82.15, 79.83, 68.22, 34.28, 28.38, 21.68 ppm. HRMS (EI): calcd. for $C_{23}H_{30}Cl_3N_3O_7SNa$ [M + Na]$^+$ 620.0768; found 620.0828.

(*E*)-3-[4-(Tosylcarbamoyloxy)tetrahydro-2*H*-pyran-4-yl]allyl 2,2,2-Trichloroacetimidate [(*E*)-1k]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1 H, C=N*H*), 7.86 (d, *J* = 8.2 Hz, 2 H, C_6H_4Me), 7.81 (br.

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s, 1 H, NHTs), 7.34 (d, J = 8.2 Hz, 2 H, C_6H_4Me), 5.98 (d, J = 16.0 Hz, 1 H, C*H*=CHCH$_2$), 5.70 (dt, J = 16.0 and 5.5 Hz, 1 H, CH=C*H*CH$_2$), 4.74 (d, J = 5.5 Hz, 2 H, OCH_2), 3.68 (dt, J = 11.7 and 3.9 Hz, 2 H, CH_2OCH_2), 3.63–3.57 (m, 2 H, CH_2OCH_2), 2.45 (s, 3 H, C_6H_4CH_3), 2.11–2.08 (m, 2 H, CH_2CH$_2$OCH$_2$CH_2), 1.89–1.82 (m, 2 H, CH_2CH$_2$OCH$_2$CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.17, 148.47, 145.00, 135.83, 134.98, 129.63, 128.01, 125.15, 91.16, 81.39, 68.23, 63.26, 35.13, 21.67 ppm. HRMS (EI): calcd. for $C_{18}H_{21}Cl_3N_2O_6SNa$ [M + Na]$^+$ 521.0084; found 521.0143.

General Procedure for Synthesis of Iminocarbonate 2: Molecular sieves (4 Å) and the Lewis acid catalyst (0.05 mmol, 10 mol-%) were added to a stirred solution of tosylcarbamate **1** (0.50 mmol) in DCM (dichloromethane, 10 mL) at room temperature. After the reaction was complete (as indicated by TLC), the solvent was removed under reduced pressure. The residue was purified by chromatography on a short silica gel column eluting with a mixture of light petroleum ether and EtOAc (2:1) to afford product **2** as an oil.

***trans*-4-Pentyl-2-tosylimino-5-vinyl-1,3-dioxolane (2a):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.2 Hz, 2 H, $C_6H_4CH_3$), 7.26 (d, J = 8.2 Hz, 2 H, $C_6H_4CH_3$), 5.83 (ddd, J = 17.2, 10.6, and 7.0 Hz, 1 H, C*H*=CH$_2$), 5.50 (d, J = 16.0 Hz, 1 H, CH=CH_2), 5.46 (d, J = 10.2 Hz, 1 H, CH=CH_2), 4.81 (t, J = 7.4 Hz, 1 H, CH$_2$=CHC*H*), 4.46 (q, J = 5.1 Hz, 1 H, C*H*CH$_2$CH$_2$), 2.40 (s, 3 H, $C_6H_4CH_3$), 1.79–1.67 [m, 2 H, CH_2(CH$_2$)$_3$CH$_3$], 1.48–1.20 [m, 6 H, CH$_2$(CH_2)$_3$CH$_3$], 0.87 [t, J = 6.7 Hz, 3 H, CH$_2$(CH$_2$)$_3$-CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.23, 143.21, 138.54, 130.39, 129.15, 127.14, 122.87, 85.64, 85.19, 32.12, 31.07, 24.16, 22.23, 21.46, 13.80 ppm. HRMS (EI): calcd. for $C_{17}H_{24}NO_4S$ [M + H]$^+$ 338.1426; found 338.1447.

***trans*-4-Isopropyl-2-tosylimino-5-vinyl-1,3-dioxolane (2b):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.4 Hz, 2 H, $C_6H_4CH_3$), 7.27 (d, J = 8.4 Hz, 2 H, $C_6H_4CH_3$), 5.83 (ddd, J = 17.2, 10.1, and 7.0 Hz, 1 H, C*H*=CH$_2$), 5.50 (d, J = 16.8 Hz, 1 H, CH=CH_2), 5.46 (d, J = 10.6 Hz, 1 H, CH=CH_2), 4.92 (t, J = 7.0 Hz, 1 H, CH$_2$=CHC*H*), 4.27 [t, J = 7.0 Hz, 1 H, C*H*CH(CH$_3$)$_2$], 2.41 (s, 3 H, $C_6H_4CH_3$), 1.99 [octet, J = 6.6 Hz, 1 H, C*H*(CH$_3$)$_2$], 0.98 [d, J = 6.6 Hz, 3 H, CH(CH_3)$_2$], 0.94 [d, J = 6.6 Hz, 3 H, CH-(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.14, 143.18, 138.47, 131.38, 129.16, 127.20, 122.33, 89.38, 83.49, 31.16, 21.50, 17.19, 17.16 ppm. HRMS (EI): calcd. for $C_{15}H_{19}NO_4SNa$ [M + Na]$^+$ 332.0932; found 332.0948.

***trans*-4-Benzyl-2-tosylimino-5-vinyl-1,3-dioxolane (2c):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.4 Hz, 2 H, $C_6H_4CH_3$), 7.28–7.12 (m, 5 H, $C_6H_4CH_3$ and C_6H_5), 7.12 (d, J = 7.9 Hz, 2 H, C_6H_5), 5.66 (ddd, J = 17.6, 10.6, and 7.1 Hz, 1 H, C*H*=CH$_2$), 5.32 (d, J = 10.6 Hz, 1 H, CH=CH_2), 5.30 (d, J = 16.8 Hz, 1 H, CH=CH_2), 4.88 (t, J = 7.5 Hz, 1 H, CH$_2$=CHC*H*), 4.70 (q, J = 7.5 Hz, 1 H, C*H*Bn), 3.12 (dd, J = 14.5 and 7.9 Hz, 1 H, CH_2C$_6$H$_5$), 3.02 (dd, J = 14.5 and 5.7 Hz, 1 H, CH_2C$_6$H$_5$), 2.38 (s, 3 H, $C_6H_4CH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.11, 143.33, 138.30, 133.15, 130.22, 129.48, 129.24, 129.00, 127.76, 127.21, 122.57, 85.03, 84.60, 37.81, 21.50 ppm. HRMS (EI): calcd. for $C_{19}H_{20}NO_4S$ [M + H]$^+$ 358.1113; found 358.1125.

***trans*-4-(Dec-9-en-1-yl)-2-tosylimino-5-vinyl-1,3-dioxolane (2d):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.2 Hz, 2 H, C_6H_4Me), 7.24 (d, J = 7.8 Hz, 2 H, C_6H_4Me), 5.85–5.71 (m, 2 H, CH$_2$=C*H*CH and CH$_2$=C*H*CH$_2$), 5.46 (d, J = 18.0 Hz, 1 H, CH_2=CHCH), 5.43 (d, J = 10.6 Hz, 1 H, CH_2=CHCH), 4.95 (d, J = 16.8 Hz, 1 H, CH_2=CHCH$_2$), 4.89 (d, J = 10.2 Hz, 1 H, CH_2=CHCH$_2$), 4.80 (t, J = 7.4 Hz, 1 H, C*H*CH=CH$_2$), 4.47 (q, J = 7.8 Hz, 1 H, CHC*H*CH$_2$), 2.37 (s, 3 H, CH_3), 2.00 (q, J = 7.0 Hz, 2 H, CH$_2$=CHCH_2), 1.76–1.64 (m, 2 H, CH_2CH), 1.42–1.21 [m, 12 H, (CH_2)$_6$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.23, 143.14, 138.90, 138.25, 130.31, 129.07, 127.06, 122.76, 114.07, 85.64, 85.15, 33.59, 33.04, 29.10, 29.05, 28.85, 28.68, 24.38, 21.39 ppm. LC–MS (ESI): m/z = 406.28 [M + H]$^+$. HRMS (EI): calcd. for $C_{22}H_{32}NO_4S$ [M + H]$^+$ 406.2052; found 406.2057.

***trans*-4-Diphenylmethyl-2-tosylimino-5-vinyl-1,3-dioxolane (2e):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.4 Hz, 2 H, C_6H_4Me), 7.33–7.23 (m, 10 H, C_6H_5), 7.17 (d, J = 7.9 Hz, 2 H, C_6H_4Me), 5.57 (ddd, J = 16.8, 10.1, and 6.6 Hz, 1 H, CH$_2$=C*H*), 5.21 (d, J = 10.1 Hz, 1 H, CH_2=CH), 5.19 (t, J = 7.5 Hz, 1 H, C*H*CHPh), 5.12 (d, J = 16.8 Hz, 1 H, CH_2=CH), 4.93 (t, J = 7.1 Hz, 1 H, C*H*CH=CH$_2$), 4.18 (d, J = 7.9 Hz, 1 H, C*H*Ph), 2.38 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.86, 143.17, 138.09, 137.94, 137.88, 130.41, 129.12, 129.10, 128.88, 128.48, 128.40, 127.95, 127.61, 127.29, 121.86, 85.95, 84.15, 53.70, 21.49 ppm. LC–MS (ESI): m/z = 434.20 [M + H]$^+$.

Compound 2g: This product was crystallized from EtOAc; m.p. 124–125 °C.

4,4-Dimethyl-2-tosylimino-5-vinyl-1,3-dioxolane (2h): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.6 Hz, 2 H, $C_6H_4CH_3$), 7.27 (d, J = 8.4 Hz, 2 H, $C_6H_4CH_3$), 5.78 (ddd, J = 17.2, 10.2, and 6.7 Hz, 1 H, C*H*=CH$_2$), 5.52 (d, J = 16.8 Hz, 1 H, CH=CH_2), 5.49 (d, J = 10.6 Hz, 1 H, CH=CH_2), 4.82 (d, J = 7.0 Hz, 1 H, C*H*), 2.41 (s, 3 H, $C_6H_4CH_3$), 1.56 [s, 3 H, C(CH_3)$_2$], 1.33 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.65, 143.13, 138.65, 129.15, 127.95, 127.17, 122.88, 88.32, 80.43, 25.29, 21.81, 21.53 ppm. HRMS (EI): calcd. for $C_{14}H_{17}NO_4SNa$ [M + Na]$^+$ 318.0776; found 318.0754.

2-Tosylimino-4-vinyl-1,3-dioxaspiro[4.5]decane (2i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.1 Hz, 2 H, $C_6H_4CH_3$), 7.26 (d, J = 8.5 Hz, 2 H, $C_6H_4CH_3$), 5.76 (ddd, J = 17.1, 10.0, and 6.6 Hz, 1 H, C*H*=CH$_2$), 5.47 (d, J = 17.3 Hz, 1 H, CH=CH_2), 5.46 (d, J = 10.3 Hz, 1 H, CH=CH_2), 4.75 (d, J = 6.8 Hz, 1 H, C*H*), 2.40 (s, 3 H, CH_3), 1.92–1.20 [m, 10 H, CH_2(CH_2)$_3$CH_2] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.75, 143.09, 138.66, 129.15, 128.16, 127.18, 122.50, 90.37, 88.50, 34.73, 31.01, 24.46, 21.95, 21.49, 21.35 ppm. HRMS (EI): calcd. for $C_{17}H_{22}NO_4S$ [M + H]$^+$ 336.1270; found 336.1241.

8-(*tert*-Butoxycarbonyl)-2-tosylimino-4-vinyl-1,3-dioxa-8-azaspiro-[4.5]decane (2j): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.6 Hz, 2 H, C_6H_4Me), 7.28 (d, J = 8.2 Hz, 2 H, C_6H_4Me), 5.76 (ddd, J = 17.2, 10.2, and 7.0 Hz, 1 H, C*H*=CH$_2$), 5.53 (d, J = 16.8 Hz, 1 H, CH=CH_2), 5.51 (d, J = 10.2 Hz, 1 H, CH=CH_2), 4.80 (d, J = 7.0 Hz, 1 H, C*H*), 4.09–3.94 [m, 2 H, CH_2N(Boc)CH_2], 3.12–2.89 [m, 2 H, CH_2N(Boc)CH_2], 2.41 (s, 3 H, $C_6H_4CH_3$), 1.91–1.58 [m, 4 H, CH_2CH$_2$N(Boc)CH$_2$CH_2], 1.44 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.12, 154.25, 143.37, 138.44, 129.27, 127.47, 127.16, 123.29, 88.03, 84.90, 80.30, 33.98, 30.78, 28.33, 21.52 ppm. HRMS (EI): calcd. for $C_{21}H_{29}N_2O_6S$ [M + H]$^+$ 437.1746; found 437.1751.

2-Tosylimino-4-vinyl-1,3,8-trioxaspiro[4.5]decane (2k): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.2 Hz, 2 H, C_6H_4Me), 7.29 (d, J = 8.2 Hz, 2 H, C_6H_4Me), 5.77 (ddd, J = 17.2, 10.6, and 7.0 Hz, 1 H, C*H*=CH$_2$), 5.55 (d, J = 17.0 Hz, 1 H, CH=CH_2), 5.52 (d, J = 10.6 Hz, 1 H, CH=CH_2), 4.81 (d, J = 6.7 Hz, 1 H, C*H*), 3.90–3.58 (m, 4 H, CH_2OCH_2), 2.41 (s, 3 H, $C_6H_4CH_3$), 1.94–1.67 (m, 4 H, CH_2CH$_2$OCH$_2$CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.16, 143.33, 138.47, 129.25, 127.50, 127.16, 123.25, 88.15, 88.03, 63.49, 63.21, 34.45, 31.38, 21.51 ppm. HRMS (EI): calcd. for $C_{16}H_{19}NO_5SNa$ [M + Na]$^+$ 360.0882; found 360.0914.

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General Procedure for Synthesis of Diol 7

Method A: To a solution of iminocarbonate **2** (0.3 mmol) in MeOH (5 mL) was added NaOH (1 M aqueous solution, 5 mL), and the resulting mixture was stirred overnight at room temperature. After the reaction was complete (as monitored by TLC), the MeOH was removed under reduced pressure. The residue was neutralized with HCl (1 M aqueous solution) to pH ≈ 7, and the resulting solution was extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were combined and washed with brine. The organic phase was dried with Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography on a silica gel column eluting with a mixture of light petroleum ether and ethyl acetate (from 4:1 to 2:1) to afford product **7**.

Method B: To iminocarbonate **2** (0.3 mmol) was added K_2CO_3 (0.5 M solution) in MeOH/H_2O (1:1, 5 mL), and the resulting mixture was stirred at room temperature. After the reaction was complete (as monitored by TLC), the solvent was removed under reduced pressure. The residue was purified by chromatography on a silica gel column eluting with a mixture of light petroleum ether and ethyl acetate (from 4:1 to 2:1) to afford the product **7**. Compounds **7a**,[9] **7c**,[10] and **7i**[11] have been described previously in literature.

1-(*tert*-Butoxycarbonyl)-4-hydroxy-4-(1-hydroxyallyl)piperidine (7j): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.91 (ddd, J = 17.2, 10.2, and 6.7 Hz, 1 H, C*H*=CH), 5.31 (d, J = 17.2 Hz, 1 H, CH=CH_2), 5.28 (d, J = 10.2 Hz, 1 H, CH=CH_2), 3.99–3.87 [m, 2 H, CH_2N(Boc)-CH_2], 3.86 (d, J = 7.0 Hz, 1 H, C*H*), 3.17–3.08 [m, 2 H, CH_2N-(Boc)CH_2], 2.12 (br. s, 1 H and 1 H, 2 O*H*), 1.67–1.47 [m, 4 H, CH_2CH$_2$N(Boc)CH$_2$CH_2], 1.45 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.81, 135.94, 118.60, 79.49, 79.42, 71.44, 33.66, 31.87, 28.44 ppm. HRMS (EI): calcd. for $C_{13}H_{23}NO_4Na$ [M + Na]$^+$ 280.1525; found 280.1473.

4-(1-Hydroxyallyl)tetrahydro-2*H*-pyran-4-ol (7k): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.91 (ddd, J = 17.2, 10.2, and 7.0 Hz, 1 H, C*H*=CH$_2$), 5.31 (d, J = 17.2 Hz, 1 H, CH=CH_2), 5.27 (d, J = 10.1 Hz, 1 H, CH=CH_2), 3.84 (d, J = 7.0 Hz, 1 H, C*H*), 3.80–3.70 (m, 4 H, CH_2OCH_2), 2.44 (br. s, 1 H, O*H*), 1.93 (br. s, 1 H, O*H*), 1.76–1.56 (m, 3 H, CH_2CH$_2$OCH$_2$CH_2), 1.45–1.39 (m, 1 H, CH_2CH$_2$OCH$_2$CH$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.87, 118.54, 79.58, 70.56, 63.50, 63.30, 34.45, 32.74 ppm. Unstable under conditions for HRMS.

General Procedure for Synthesis of Carbonate 8

Method A: Trimethylsilyl trifluoromethanesulfonate (0.05 mmol, 10 mol-%) and H_2O (10 μL) were added to a stirred solution of iminocarbonate **2** (0.5 mmol) in CH_2Cl_2 (10 mL) at room temperature. After the reaction was complete (as monitored by TLC), the solvent was removed under reduced pressure. The residue was purified by chromatography on a silica gel column eluting with a mixture of light petroleum ether and ethyl acetate (from 4:1 to 2:1) to afford product **8**.

Method B: Trimethylsilyl trifluoromethanesulfonate (0.08 mmol, 10 mol-%) was added to a stirred solution of tosylcarbamate **1** (0.8 mmol) in CH_2Cl_2 (15 mL) at room temperature. After reaction was complete (as indicated by TLC), H_2O (10 μL) was added, and then the reaction mixture was stirred at room temperature until the full conversion of intermediate **2** was observed (indicated by TLC). The solvent was removed under reduced pressure, and the residue was purified by chromatography on a silica gel column eluting with a mixture of light petroleum ether and ethyl acetate (from 4:1 to 2:1) to afford product **8**. Compounds **8a**, **8b**,[13] and **8i**[14] have been described previously in literature.

General Procedure for the Rearrangement leading to Vinyloxazolidinone 3:

LiI (0.6 mmol, 1.2 equiv., Methods A or C) or TBAB (tetrabutylammonium bromide, 0.6 mmol, 1.2 equiv., Method B) was added to a stirred solution of iminocarbonate **2** (0.5 mmol) in $C_2H_4Cl_2$ (10 mL, Methods A or B) or DMF (dimethylformamide, Method C). The reaction mixture was refluxed for approximately 2 h, until the complete conversion of starting material was achieved (as monitored by TLC). The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by chromatography on a silica gel column eluting with a mixture of light petroleum ether and ethyl acetate (3:1) to afford product **3**. Compounds **3a**, **3b**,[7b] and **3i**[15] have been described previously in literature.

(4,5-*trans*)-5-Benzyl-3-tosyl-4-vinyloxazolidin-2-one (3c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.4 Hz, 2 H, C$_6H_4$CH$_3$), 7.34–7.16 (m, 7 H, C$_6H_4$CH$_3$ and C$_6H_5$), 5.75 (ddd, J = 17.0, 8.8, and 6.6 Hz, 1 H, C*H*=CH$_2$), 5.30 (d, J = 10.1 Hz, 1 H, CH=CH_2), 5.28 (d, J = 17.0 Hz, 1 H, CH=CH_2), 4.55 (dd, J = 7.9 and 4.2 Hz, 1 H, C*H*CH=CH$_2$), 4.39 (ddd, J = 10.4, 6.2, and 4.1 Hz, 1 H, C*H*Bn), 3.02 (dd, J = 14.3 and 6.2 Hz, 1 H, CH_2Ph), 2.93 (dd, J = 14.3 and 6.2 Hz, 1 H, CH_2Ph), 2.44 (s, 3 H, C$_6$H$_4$CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.21, 145.38, 134.89, 133.84, 133.78, 129.64, 129.47, 128.87, 128.44, 127.45, 120.30, 80.11, 63.22, 39.24, 21.68 ppm. HRMS (EI): calcd. for $C_{19}H_{20}N_2O_4S$ [M + Na]$^+$ 358.1113; found 358.1098.

Supporting Information (see footnote on the first page of this article): Synthesis and characterization of (*E*)- and (*Z*)-**5**, NMR spectra of intermediates and final products, X-ray ORTEP drawing of **2i**.

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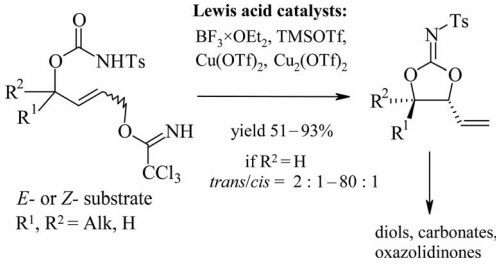

N-Tosyliminocarbonates were prepared by a Lewis acid catalyzed cyclization of allylic trichloroacetimidates bearing a δ-*N*-tosylcarbamoyloxy group. The synthetic utility of iminocarbonates was demonstrated by transforming them into 1,2-diols, cyclic carbonates, and *N*-tosyloxazolidinones.

Keywords: Synthetic methods / Nitrogen heterocycles / Nucleophilic substitution / Cyclization / Lewis acids / Allylic compounds

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