$NbCl_5$: A Novel Lewis Acid in Allylation Reactions

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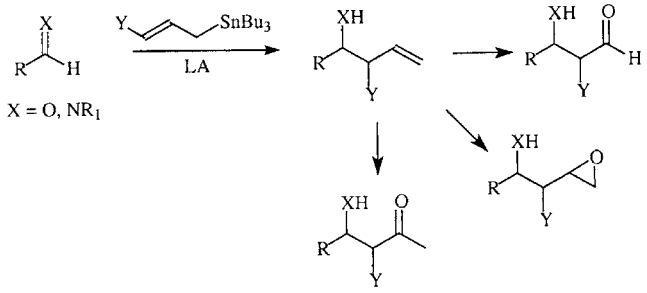
Abstract: Allylation reactions promoted by niobium pentachloride are described. Allylstannanes were added to aromatic and aliphatic aldehydes and aromatic imines in good yields. Excellent *syn* diastereoselectivities were obtained in the addition of (*E*)-cinnamylstannane to benzaldehyde (49:1) and in the addition of crotylstannane to *N*-benzylideneaniline (46:1).

Key words: allylation, homoallylic compounds, stereoselectivity, niobium pentachloride, Lewis acids

Introduction

Whereas the Lewis-acid-mediated addition of allylstannanes to carbonylic compounds has been extensively studied,[1] the allylation of aldimines still needs further development. The homoallylic alcohols and amines so obtained are important and versatile intermediates in the synthesis of more complex products since the double-bond moiety can be further functionalized (Scheme 1). This represents an advantage over the synthetically analogous aldol addition reaction.



Scheme 1

A variety of Lewis acids have been employed successfully in these reactions, including $TiCl_4$, $BF_3{\cdot}Et_2O$, $SnCl_4$, $InCl_3$, $AlCl_3$, and $MgBr_2$. The search for new reagents capable of mediating these reactions is still a matter of much concern. Suzuki et al.[2b] reported the double addition and exclusive formation of a cyclopropane derivative when allylsilanes (2 equiv) were reacted with aldehydes in the presence of $NbCl_5$ (Scheme 2). This constitutes a completely different outcome from the normal allylation products, which in turn could be obtained under shorter reaction periods (5 min, 60% yield).

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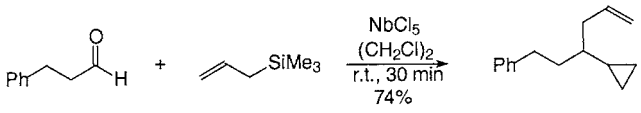


Scheme 2

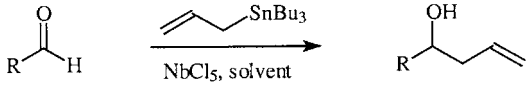
Motivated by this work and other recent works that demonstrated the Lewis acidity of niobium[2] and tantalum[2c,d,f] compounds in organic reactions, we decided to investigate the use of $NbCl_5$ on the allylation of aldehydes and imines with allylstannanes, which are far more nucleophilic than allylsilanes.[3]

$NbCl_5$ has a great oxophilicity and is readily available in our country since Brazil accounts for about 60% of total niobium production.[4] Furthermore, its use as a Lewis acid is restricted to a few reactions[2] and no work has been published regarding its use on allylation reactions.

This paper describes our results on the use of $NbCl_5$ as a Lewis acid with emphasis on the scope and stereoselectivity of these reactions as well as some mechanistic considerations.[5]

Allylation of Aldehydes

In order to investigate the feasibility of the allylation reaction, various aldehydes were reacted with allyltri-*n*-butylstannane, in the presence of $NbCl_5$ (Scheme 3).



1 R = Ph; **2** R= *p*-OMePh;
3 R = *p*-NO_2Ph; **4** R = *p*-ClPh;
5 R = 2-furyl

Scheme 3

In our search for the best experimental conditions, the following parameters were evaluated: solvent, temperature, stoichiometric relationship and the order in which the reagents were added. The results are summarized in Table 1.

The best results were obtained when 2 equivalents of the allylstannane were used, at –15 °C, in diethyl ether as the solvent (entries 6, 10 12, 14, and 16). $NbCl_5$ promoted the ring-opening of the THF, leading to polymeric products (entry 7). When the more coordinating solvents DME and

CH_3CN were used, the yields lowered (entries 9 and 13) or the reaction failed completely (entries 8, 11 and 15). When isobutyraldehyde was used yields were low (ca. 20–30%), probably due to the volatility of the product. In contrast, a much better yield was obtained when 2-phenylpropionaldehyde was employed (Table 2).

Table 1 Experimental Conditions and Results of the Reactions Between Aldehydes and Allyltri-*n*-buylstannane[a]

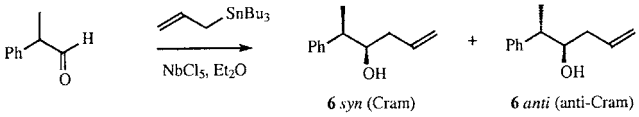
Entry	R	Solvent	Temp (°C)	Time (h)	Yield[c] (%)
1	Ph[b]	CH_2Cl_2	–78	2.5	41
2	Ph	CH_2Cl_2	–78	1.5	38
3	Ph	CH_2Cl_2	–15	1	45
4	Ph[b]	Et_2O	–78	2	48
5	Ph[b]	Et_2O	–15	2	47
6	Ph	Et_2O	–15	0.5	100
7	Ph[b]	THF	–78	2.5	–
8	Ph[b]	CH_3CN	–43	2	–
9	Ph	DME	–15	2	70
10	*p*-OMePh	Et_2O	–15	1.5	50
11	*p*-OMePh	DME	–15	2	–
12	*p*-NO_2Ph	Et_2O	–15	1.5	70
13	*p*-NO_2Ph	DME	–15	2	50
14	*p*-ClPh	Et_2O	–15	0.5	71
15	*p*-ClPh	DME	–15	2	–
16	2-furyl	Et_2O	–15	0.5	50

[a] Unless otherwise noted 2 equiv of allylstannane were employed.
[b] Reaction with 1 equiv of allylstannane in relation to the aldehyde.
[c] Isolated yields of the chromatographically pure products.

The cyclopropane compound obtained by Suzuki (Scheme 2) was never observed in the reaction with allylstannane. These interesting results show the versatility of $NbCl_5$ as a Lewis acid.

After establishing the best experimental conditions, we turned our attention to the stereoselectivity of these reactions. The Cram/anti-Cram selectivity was addressed in the reaction between (±)-2-phenylpropionaldehyde and allylstannane in the presence of $NbCl_5$ (Scheme 4).

The diastereofacial selectivity was low (3:1), even at –78 °C. These results are similar to those obtained with other Lewis acids such as $BF_3{\cdot}Et_2O$ and $TiCl_4$.[6] The diastereomers were identified by the ^1H NMR chemical shifts of the methyl groups (*syn* δ 1.35, d, J = 6.9 Hz; *anti* δ 1.30, d, J = 7.1 Hz) by comparison with those in the literature[7] and quantified by GC.



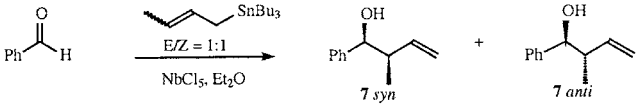
Scheme 4

Table 2 Results of the Reaction Between Allylstannane and (±)-2-Phenylpropionaldehyde in Diethyl Ether

Entry	Temp (°C)	*Syn*:*anti*	Yield (%)[a]
1	–78	3:1	63
2	–15	1.6:1	75

[a] Isolated yields of the chromatographically pure products (*syn*:*anti* mixture).

Next we examined the stereo- and regioselectivity of these $NbCl_5$ promoted allylation reactions. In this way, crotylstannane (3-methylallylstannane, 1:1 mixture of isomers) and benzaldehyde were reacted in the presence of $NbCl_5$, in a variety of conditions (Table 3). The reaction proved to be regiospecific in that no linear product was formed under any conditions (Scheme 5).



Scheme 5

Table 3 Results of the Reaction Between Crotylstannane[a] and Benzaldehyde in Diethyl Ether

Entry	Temp (°C)	Mode of addition	*Syn*:*anti*[c]	Time (h)	Yield[d] (%)
1	–15	normal	1.9:1	1.5	63
2	–15	normal	2.6:1	0.3	91
3[b]	–15	normal	2.5:1	0.3	83
4	–15	inverse	2.2:1	0.3	91

[a] In all cases 2 equiv of crotylstannane were used.
[b] 2 equiv of $NbCl_5$ were used.
[c] Ratio determined by GC and ^1H NMR integration.
[d] Isolated yields of the chromatographically pure products (*syn*:*anti* mixture).

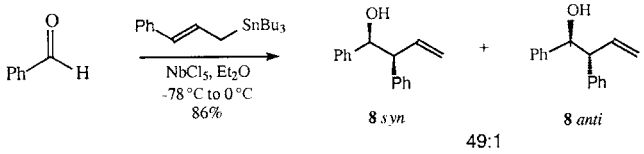
It is reported that the mode of addition of the reagents in $SnCl_4$- and $TiCl_4$-mediated allylation reactions alters the diastereomer ratio of the homoallylic alcohol as well as the regiochemistry of the reaction, due to transmetallation.[8] The reactions performed with normal addition (addition of crotylstannane to a suspension of benzaldehyde and $NbCl_5$ in Et_2O) afforded a mixture of diastereomers in good yields (Table 3, entries 1 to 3). The diastereomeric ratio was determined by GC analysis of the mixture of

products and by ^{1}H NMR integration of the carbinolic protons (*syn*: δ 4.60, d, J = 5.3 Hz and *anti*: δ 4.35, d, J = 7.2 Hz). These data are in accordance with those reported.[9]

The best results were obtained at –15°C with shorter reaction periods. When the reactions were performed at lower temperatures (–78 °C) or when 2 equiv of $NbCl_5$ were used (entry 3), no significant improvements were achieved either in yield or in selectivity.

In the reactions with inverse addition (addition of benzaldehyde to a suspension of crotylstannane and $NbCl_5$ in Et_2O), the yields and diastereoselectivities were similar to those obtained with normal addition (entry 4). Furthermore, linear products were not detected under any conditions, as already mentioned. Although no spectroscopic studies were performed,[10] these results suggest that the transmetallation process is not occurring.

In order to get a better insight into the diastereoselectivity and to confirm the influence of the stannane geometry on the diastereomeric ratios obtained in the $NbCl_5$-mediated additions to aldehydes, the reaction between *E*-cinnamylstannane[11] (3-phenylallylstannane) and benzaldehyde was studied (Scheme 6).



Scheme 6

The reaction proceeded smoothly, but in this case the *syn* diastereomer was obtained almost exclusively, in good yield. The diastereomeric ratio (49:1) was determined by GC.

This result is in sharp contrast to those obtained with $ZnCl_2$ in DMF[12] and $SnCl_2$ in CH_3CN,[13] which gave predominantly the *anti* isomer.[14] In both cases, a cyclic transition state was proposed to explain the *anti* stereoselectivity. Although it is reported that $BF_3{\cdot}Et_2O$ is also *syn* selective,[12] the reaction is run at –78 °C. The advantage here is that the reaction can be warmed to 0 °C without lowering the selectivity.

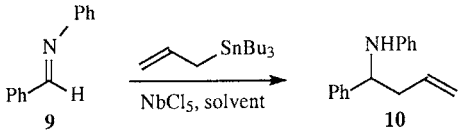
To confirm these results, an enriched (5:1) mixture of the *anti* isomer was prepared following a procedure of Wilson et al.[15] The spectroscopic data for the major isomer matched those reported for the *anti* isomer[16] whereas the data for the minor isomer are the same we obtained in the $NbCl_5$-mediated reaction.[17]

Allylation of Imines

As already mentioned, there is much less work in the literature dealing with allylation of imines as compared to aldehydes. Recent improvements in this reaction deal with imine activation by chlorotrimethylsilane,[18] catalytic lanthanide triflates[19] and catalytic Pd(II) or Pt(II) complexes.[20]

We initiated our study by searching for the best solvent system. Ethyl ether, acetonitrile and dichloromethane were investigated in the allylation of *N*-benzylideneaniline (**9**) at different temperatures (Scheme 7). The results are shown in Table 4.

Either CH_3CN or CH_2Cl_2 gave satisfactory results at –15 °C. The yields were the same at lower temperatures using CH_2Cl_2 (entry 1) and decreased in all cases when the reaction was allowed to reach room temperature. In contrast to the allylation of aldehydes, Et_2O was not a good solvent (entry 2). A control experiment indicated that no reaction takes place in the absence of $NbCl_5$.



Scheme 7

Table 4 Experimental Conditions and Yields of the Reactions between *N*-Benzylideneaniline (**9**) and Allyltri-*n*-butylstannane[a]

		Yields (%)[b]		
Entry	Solvent	0 °C → r.t.	–15 °C	–78 °C
1	CH_2Cl_2	27	82	83
2	Et_2O	18	41	–
3	CH_3CN	62	80	–

[a] 1 equiv of $NbCl_5$ and 2 equiv of allylstannane were employed.
[b] Isolated yields of the chromatographically pure products.

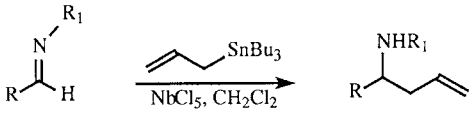
Next, the stoichiometry of the reaction was assessed (Table 5). We found that an excess of stannane improves the yields but is not critical to the success of the reaction, except when Et_2O was used (entry 2). The lower yields obtained with 1 equiv of allylstannane may be due to its slight decomposition in the presence of $NbCl_5$.

Table 5 Influence of an Excess of Allylstannane on the Allylation of *N*-Benzylideneaniline (**9**), at –15 °C

		Yields (%)[a]	
Entry	Solvent	–15 °C[b]	–15 °C[c]
1	CH_2Cl_2	72	82
2	Et_2O	17	41
3	CH_3CN	60	80

[a] Isolated yields of the chromatographically pure products.
[b] Imine:$NbCl_5$:stannane = 1:1:1
[c] Imine:$NbCl_5$:stannane = 1:1:2

In this way, we defined the ideal conditions for the $NbCl_5$-mediated allylation of imines as being CH_2Cl_2 as the solvent,[21] at –15 °C and using an excess of allylstannane. Under these conditions a variety of aromatics aldimines were allylated in reasonable to good yields (Scheme 8, Table 6).



Scheme 8

Table 6 Results of the Reactions Between Aldimines and Allyltri-*n*-butylstannane

Entry	Amine	R	R_1	Yield[a] (%)
1	**10**	Ph	Ph	82
2	**11**	*p*-NO_2Ph	Ph	80
3	**12**	2-Furyl	Ph	59
4	**13**	*p*-ClPh	Ph	51
5	**14**	*p*-ClPh	*n*-Bu	35
6	**15**	*p*-OMePh	Ph	85

[a] Isolated yields of the chromatographically pure products.

In some cases, bis-allylated[22] by-products were also obtained (ca 10–15%) when 2 equiv of allylstannane were used (Figure 1). This can be circumvented using only a slight excess of this reagent.

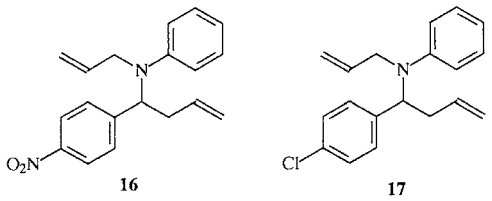
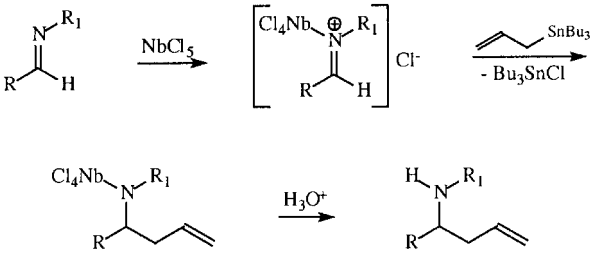


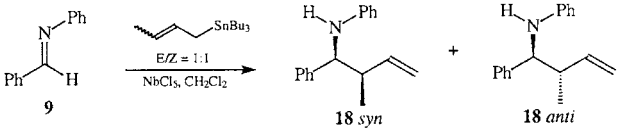
Figure 1 Bis-allylated by-products

The activation of the imines probably occurs via the formation of an iminium salt with $NbCl_5$ (Scheme 9). As an example, a dark-orange precipitate forms when imine **9** is added to a suspension of $NbCl_5$ in CH_2Cl_2. Similarly, a white precipitate attributed to the iminium salt formed when TMSCl was used as additive has been observed.[23]

The stereo- and regioselectivity of these $NbCl_5$-promoted allylation reactions were assessed in the reaction between crotylstannane (3-methylallylstannane, 1:1 mixture of isomers) and imine **9** in the presence of $NbCl_5$ (Scheme 10, Table 7).



Scheme 9



Scheme 10

Table 7 Results of the Reaction Between Crotylstannane[a] and *N*-Benzylideneaniline (**9**) in CH_2Cl_2

Entry	Temp (°C)	Mode of addition	*Syn*:*anti*	Yield[b] (%)
1	–15	normal	9:1	60
2	–78	normal	46:1	62

[a] 2 equiv of crotylstannane were used.
[b] Isolated yields of chromatographically pure products (*syn*:*anti* mixture).

Similar to the allylation of aldehydes, the allylation of imines proved to be regiospecific and no linear products were formed under any conditions. The allylated products were obtained in good yields and excellent diastereoselectivities (entries 1 and 2). The diastereomeric ratio was determined by GC analysis of the mixture of products and by ^{1}H NMR integration of the proton on the carbon attached to the nitrogen (*syn*: δ 4.33, d, J = 4.5 Hz and *anti*: δ 4.07, d, J = 7.2 Hz) and methyl groups (*syn*: δ 1.01, d, J = 6.9 Hz and *anti*: δ 0.99, d, J = 6.9 Hz). These data are in accordance with those reported.[24]

At –78 °C, the *syn* isomer is obtained almost exclusively, regardless of the stereochemistry of the stannane double bond. These results are even superior to those obtained with other Lewis acids such as $BF_3{\cdot}Et_2O$ and $TiCl_4$.[24,25] Also, this is in sharp contrast to the results obtained on the allylation of aldehydes (Scheme 5, Table 3). This led us to propose different transition states for these reactions as discussed below.

Mechanistic considerations

The mechanism of these reactions is still a matter of much controversy. Yamamoto et al.[6] proposed an acyclic *anti-periplanar* transition state for the $BF_3{\cdot}Et_2O$-mediated reaction between crotylstannane and benzaldehyde, in

which the *syn* isomer is obtained almost exclusively, regardless of the double-bond geometry in the crotylstannane.[26]

Based on the results obtained here on the allylation of aldehydes, it seems that the geometry of the crotylstannane double bond plays an important role in the reaction selectivity.

In this way, the *syn-synclinal* transition state proposed by Keck et al.[27] seems to furnish a more reasonable explanation to account for the low selectivity obtained. In this conformation, the stannane methylene group resides in a *syn* orientation in relation to the carbonyl oxygen, allowing an interaction between the HOMO of the olefin and the LUMO of the carbonyl group (Figure 2).

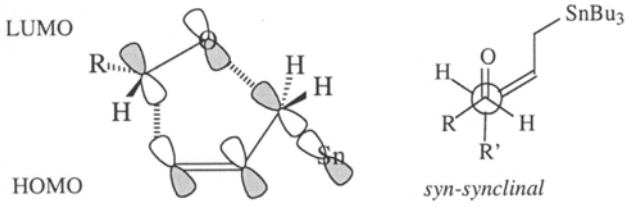


Figure 2 Frontier orbital interaction between the allylstannane and the aldehyde

Figure 3 represents the *syn-synclinal* transition states for the *E*- and *Z*-crotylstannane (**ET1** to **ET4**) proposed by Keck and adapted for the $NbCl_5$-mediated reactions. Transition state **ET1**, according to Keck, is the lowest in energy since there is only one steric interaction between the aldehyde phenyl group and the stannane methyl group. **ET2** and **ET4** show interactions between the stannane methylene group and the Lewis acid and between the phenyl group and the methyl group. **ET3** shows an interaction between the methyl group and the bulky Lewis acid.

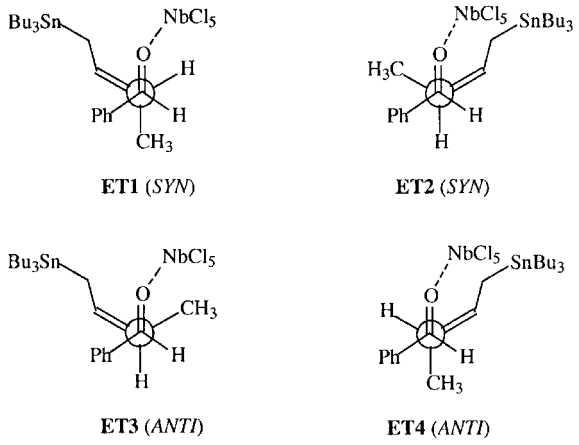


Figure 3 *Syn-synclinal* transition states for *E*- and *Z*-crotylstannanes

Based on this model, we can postulate that the slight overall preference for the *syn* homoallylic alcohol in these $NbCl_5$ mediated reactions (1:1 mixture of stannanes) is due to a relatively large preference for transition state **ET1** over **ET4** (for the *E* substrate) while there is no clear preference between **ET2** and **ET3** (for the *Z* substrate) which have steric interactions similar in energy.

In the *E*-cinnamylstannane allylation of aldehydes, a *syn-synclinal* transition state (**ET5**) can also be invoked to explain the selective formation of the *syn* isomer although the *antiperiplanar* transition state (**ET6**) should not be ruled out[28] (Figure 4).

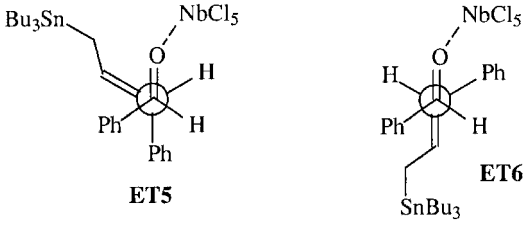


Figure 4 *Syn-synclinal* and *antiperiplanar* transition states for *E*-cinnamylstannane

Our results on the allylation of imines indicated that the selectivity is not affected by the double-bond geometry and the *syn* isomer is obtained almost exclusively. This could be better explained through an acyclic *antiperiplanar* transition state (Figure 5). Among the possible geometries, including the *synclinals*, the *antiperiplanar* (**ET7**) seems to be preferred since it has less steric crowding as compared to the others.

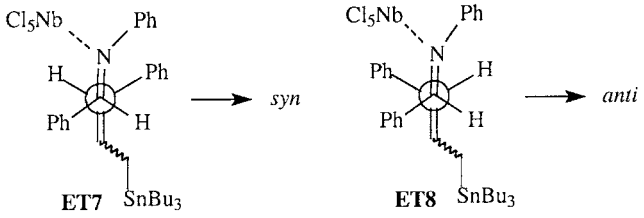
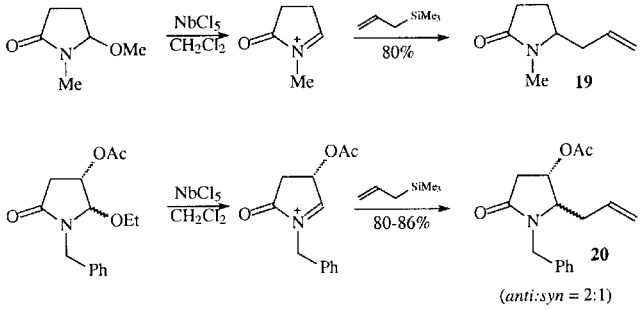


Figure 5 *Antiperiplanar* transition states proposed for the allylation of imines

Current work

Our current work on allylation reactions deals with the generation of *N*-acyliminium ions by $NbCl_5$ and subsequent addition of allylsilane (Scheme 11). Some applications of this methodology in the synthesis of alkaloids are in progress. So far, our preliminary results are promising, as can be seen by the yields of the allylated products **19** and **20**, and will be published in more details soon.



Scheme 11

Conclusion

In summary, the scope and limitations of the $NbCl_5$-mediated allylation of aldehydes and imines have been studied. The methodology allows the obtention of homoallylic alcohols and amines in good yields with excellent regio- and stereoselectivities. $NbCl_5$ proved to be an effective Lewis acid and a promising tool in the control of diastereoselectivity in these reactions. The exceptional selectivity obtained with cinnamylstannane (aldehydes) and with crotylstannane (imines) makes $NbCl_5$ an attractive choice when the *syn* isomer is required.

All reactions involving $NbCl_5$ were performed under argon in a flame-dried flask. Ethereal solvents were distilled from sodium benzophenone ketyl. CH_2Cl_2 and CH_3CN were distilled from CaH_2 prior to use. $NbCl_5$ was supplied by Companhia Brasileira de Mineração e Metalurgia (CBMM) and sublimed before use. Aldehydes were distilled immediately before use except *p*-nitrobenzaldehyde, which is solid. Imines were prepared from the corresponding aldehydes and amines in CH_2Cl_2, in the presence of Na_2SO_4. Crotyl and cinnamylstannane were prepared according to a literature procedure.[11]

IR spectra were recorded on a BOMEM Hartman & Braun-Michelson MB series 100 LASER FT-IR. ^1H NMR spectra were recorded on Varian EM390, Bruker ARX 200 and DRX 400 spectrometers. Chemical shifts are reported in ppm from tetramethylsilane as internal reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, etc), integration, coupling constant and assignment. ^{13}C NMR spectra were recorded on Bruker ARX 200 (50 MHz) and DRX 400 (100 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with solvent as internal standard ($CDCl_3$: δ = 77.0). Data are reported as follows: chemical shift and assignment. Mass spectra were obtained on a Perkin-Elmer Q-Mass 910 mass spectrometer.

GC analyses were performed on Shimadzu GC-14B and Varian Star 3400 spectrometers using DB-WAX column. Column chromatography was performed on silica gel (70-230 mesh).

Allylation of Aldehydes; General Procedure

To a fresh sublimed $NbCl_5$ (1 mmol) suspension in Et_2O (8 mL) at –15 °C, under an Ar atmosphere was added the aldehyde (1 mmol), followed by the addition of allylstannane (2 mmol). After the time specified in Table 1, the reaction was quenched with sat. NH_4Cl (10 mL), extracted with Et_2O (3 × 15 mL) and stirred for 1 h with 10% KF in H_2O (10 mL). The reaction mixture was then washed several times with brine, dried with Na_2SO_4 and concentrated at reduced pressure to furnish the crude product which was purified by silica gel chromatography (hexanes–EtOAc).

1-Phenyl-3-buten-1-ol (1)

IR (film): 3390, 3076, 1641, 1453, 757, 700 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.26–7.40 (m, 5 H, Ph), 5.71–5.94 (m, 1 H, CH), 5.10–5.24 (m, 2 H, CH_2), 4.75 (dd, 1 H, *J* = 7.3, 3.0 Hz, CH), 2.48–2.58 (m, 2 H, CH_2), 2.12 (br, 1 H, OH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.7 (CH_2), 73.2 (CH), 118.3 (CH_2), 125.8 (CH), 127.7 (CH), 128.4 (CH), 134.5 (CH), 143.8 (C_0).

MS: *m*/*z* (%) = 51 (20), 63 (3), 79 (88), 91 (3), 107 (100), 115 (4), 130 (4).

1-(4-Methoxyphenyl)-3-buten-1-ol (2)

IR (film): 3403, 3075, 1640, 1513, 1463 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.28 (d, 2 H, *J* = 8.3 Hz, Ph), 6.88 (d, 2 H, *J* = 8.3, Ph), 5.69–5.90 (m, 1 H, CH), 5.07–5.20 (m, 2H, CH_2), 4.67 (t, 1 H, *J* = 6.5 Hz, CH), 3.80 (s, 3 H, CH_3), 2.4 (tt, 2 H, *J* = 6.8, 1.2 Hz, CH_2), 2.28 (br, 1 H, OH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.8 (CH_2), 55.2 (CH_3), 73.1 (CH), 113.7 (CH), 118.2 (CH_2), 127.0 (CH), 134.7 (CH), 136.1 (C_0), 159.0 (C_0).

MS: *m*/*z* (%) = 31 (5), 44 (5), 51 (20), 61 (28), 76 (28), 113 (78), 128 (41), 142 (63), 157 (100), 160 (59), 174 (14).

1-(4-Nitrophenyl)-3-buten-1-ol (3)

IR (film): 3412, 3078, 1641, 753, 700 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 8.16 (d, 2 H, *J* = 9.2 Hz, Ph), 7.50 (d, 2 H, *J* = 9.2 Hz, Ph), 5.66–5.87 (m, 1 H, CH), 5.08–5.20 (m, 2 H, CH_2), 4.86 (dd, 1 H, *J* = 7.3, 5.1 Hz, CH), 2.64 (br, 1 H, OH), 2.6–2.61 (m, 2 H, CH_2)

^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.7 (CH_2), 72.0 (CH), 119.4 (CH_2), 123.5 (CH), 126.7 (CH), 133.3 (CH), 147.1 (C_0), 151.2 (C_0).

MS: *m*/*z* (%) = 46 (4), 50 (24), 63 (1), 77 (41), 93 (1), 104 (28), 127 (72), 151 (100), 174 (9).

1-(4-Chlorophenyl)-3-buten-1-ol (4)

IR (film): 3372, 3078, 1641, 1492, 745, 720 cm^{-1}.

^1H NMR (90 MHz, CCl_4): δ = 7.4 (s, 4 H, Ph), 5.7–6.2 (m, 1 H, CH), 5.1–5.4 (m, 2 H, CH_2), 4.8 (t, 1 H, *J* = 7.2 Hz, CH), 2.5 (t, 2 H, *J* = 7.2 Hz, CH_2), 2.0 (s, 1 H, OH).

MS: *m*/*z* (%) = 51 (2), 63 (4), 77 (89), 113 (27), 129 (7), 141 (100), 164 (2).

1-(2-Furyl)-3-buten-1-ol (5)

IR (film): 3393, 3078, 1642, 1433, 737 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.27 (s, 1 H, Ar), 6.20-6.40 (m, 2 H, Ar), 5.70-6.10 (m, 1 H, CH), 5.00-5.40 (m, 2 H, CH_2), 4.77 (t, 1 H, *J* = 7.2 Hz, CH), 2.64 (t, 2 H, *J* = 7.2 Hz, CH_2), 2.0 (br, 1 H, OH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.0 (CH_2), 66.9 (CH), 106.1 (CH), 109.8 (CH), 118.5 (CH_2), 133.5 (CH), 141.6 (CH), 146.5 (C_0).

MS: *m*/*z* (%) = 28 (4), 39 (23), 49 (17), 63 (23), 77 (9), 89 (38), 91 (100), 96 (34), 119 (55).

2-Phenyl-5-hexen-3-ol (6)

IR (film): 3422, 3084, 1641, 1453, 762, 700 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): *anti* isomer: δ = 7.10–7.40 (m, 5 H, Ph), 5.70–6.00 (m, 1 H, CH), 5.00–5.30 (m, 2 H, CH_2), 3.60–3.90 (m, 1 H, CH), 2.70–2.90 (m, 1 H, CH), 1.90–2.20 (m, 2 H, CH_2), 1.56 (s, 1H, OH), 1.30 (d, 3 H, *J* = 7.1 Hz, CH_3). *syn* isomer: δ = 7.10–7.40 (m, 5 H, Ph), 5.70–6.00 (m, 1 H, CH), 5.00–5.30 (m, 2 H,

CH_2), 3.60–3.90 (m, 1 H, CH), 2.70–2.90 (m, 1 H, CH), 1.90–2.20 (m, 2 H, CH_2), 1.56 (s, 1 H, OH), 1.35 (d, 3 H, *J* = 6.9 Hz, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ 16.4 (CH_3, *syn*), 17.7 (CH_3, *anti*), 38.9 (CH, *anti*), 39.5 (CH, *syn*), 45.3 (CH_2), 74.9 (CH), 117.7 (CH, *anti*), 118.1 (CH, *syn*), 126.4, 126.6, 127.7, 128.1, 128.4, 135.0, 143.2, 144.3.

MS: *m*/*z* (%) = 51 (12), 57 (11), 77 (34), 91 (73), 105 (100), 128 (41), 143 (26), 157 (15).

2-Methyl-1-phenyl-3-buten-1-ol (7)
IR (film): 3411, 1638, 1453, 761, 701 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): *anti* isomer: δ = 7.20–7.40 (m, 5 H, Ph), 5.64–5.90 (m, 1 H, CH), 4.90–5.30 (m, 2 H, CH_2), 4.35 (d, 1 H, *J* = 7.8 Hz, CH), 2.50 (m, 1 H, CH), 1.60 (s, 1 H, OH), 0.86 (d, 3 H, *J* = 6.8 Hz, CH_3). *syn* isomer: δ = 7.20–7.40 (m, 5 H, Ph), 5.64-5.90 (m, 1 H, CH), 4.90–5.30 (m, 2 H, CH_2), 4.60 (d, 1 H, *J* = 5.4 Hz, CH), 2.50 (m, 1 H, CH), 2.00 (s, 1 H, OH), 1.00 (d, 3 H, *J* = 6.8 Hz, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (CH_3, *syn*), 16.5 (CH_3, *anti*), 44.6 (CH, *syn*), 46.1 (CH, *anti*), 77.2 (CH), 115.4 (CH_2, *syn*), 116.7 (CH_2, *anti*), 126.0, 126.8, 127.3, 127.6, 128.0, 128.2, 140.3 (CH, *syn*), 142.6 (CH, *anti*).

MS: *m*/*z* (%) = 51 (9), 65 (4), 77 (32), 79 (55), 107 (100), 129 (40), 144 (15).

1,2-Diphenyl-3-buten-1-ol (8)
Syn Isomer

IR (film): 3382, 3080, 1637, 1453, 750, 690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01–7.38 (m, 10 H, Ph), 5.89 (ddd, 1 H, *J* = 18.1, 10.3, 7.9 Hz, CH), 4.78–5.04 (m, 3 H, CH and CH_2), 3.63 (t, 1 H, *J* = 8.1 Hz, CH), 1.94 (s, 1 H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 58.5 (CH), 77.5 (CH), 117.2 (CH), 127.0, 127.8, 128.1, 128.7, 128.8, 137.0, 140.2, 141.9.

MS: *m*/*z* (%) = 51 (52), 65 (20), 79 (88), 91 (51), 107 (95), 128 (100), 165 (4), 206 (7).

Anti Isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00–7.38 (m, 10 H, Ph), 6.25 (ddd, 1 H, *J* = 19.1, 10.2, 8.9 Hz, CH), 5.10–5.30 (m, 3 H, CH and CH_2), 3.54 (t, 1 H, *J* = 8.3 Hz, CH), 2.34 (d, 1 H, J = 2.1 Hz, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.2 (CH), 77.2 (CH), 118.4 (CH), 126.5, 126.6, 127.4, 127.9, 128.3, 128.7, 137.8, 140.5, 141.7.

Allylation of Imines; General Procedure
To a fresh sublimed $NbCl_5$ (1 mmol) suspension in CH_2Cl_2 (1.5 mL) at –15 °C, under an argon atmosphere, was added a solution of the imine (1 mmol) in CH_2Cl_2 (1.5 mL), followed by the addition of allylstannane (2 mmol), after 10 min. The reaction was monitored by TLC and after the consumption of the imine (1–2 h) it was quenched with sat. NH_4Cl (10 mL), extracted with Et_2O (3 × 15 mL) and stirred for 2 h with 10% KF in H_2O (10 mL). The reaction mixture was then washed several times with brine, dried with Na_2SO_4 and concentrated at reduced pressure to furnish the crude product, which was purified by silica gel chromatography (hexanes–EtOAc).

***N*-(1-Phenyl-3-butenyl)phenylamine (10)**
IR (film): 3411, 3078, 2853, 1640, 1601, 1452, 993, 917, 748, 692 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.17–7.39 (m, 5 H, Ar), 7.03–7.10 (m, 2 H, Ar), 6.59–6.67 (m, 1 H, Ar), 6.46–6.50 (m, 2 H, Ar), 5.65–5.86 (m, 1 H, CH), 5.10–5.23 (m, 2 H, CH_2), 4.37 (dd, 1 H, *J* = 7.9 and 5.2 Hz, CH), 4.15 (br, 1 H, NH), 2.39–2.68 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.3 (CH_2), 57.1 (CH), 117.3 (CH), 118.3 (CH_2), 125.5 (CH), 126.3 (CH), 127.0 (CH), 129.0 (CH), 134.6 (CH), 143.6 (C_0), 147.4 (C_0).

***N*-[1-(4-Nitrophenyl)-3-butenyl)]phenylamine (11)**
IR (film): 3410, 3072, 2922, 2853, 1640, 1603, 1519, 1345, 993, 922, 854, 751, 693 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.18 (d, 2 H, *J* = 8.8 Hz, Ar), 7.54 (d, 2 H, *J* = 8.5 Hz, Ar), 7.03–7.13 (m, 2 H, Ar), 6.64–6.72 (m, 1 H, Ar), 6.42 (dd, 2 H, *J* = 6.5, 2.0 Hz, Ar), 5.63–5.84 (m, 1 H, CH), 5.15–5.26 (m, 2 H, CH_2), 4.50 (dd, 1 H, *J* = 8.0, 5.2 Hz, CH), 4.23 (br, 1 H, NH), 2.41–2.70 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.8 (CH_2), 56.9 (CH), 113.5 (CH), 118.1 (CH_2), 119.3 (CH_2), 123.0 (CH), 127.3 (CH), 129.3 (CH), 133.4 (CH), 146.5 (C_0), 147.1 (C_0), 151.5 (C_0).

MS: *m*/*z* (%) = 77 (1), 181 (39), 227 (100), 268 (0.2).

***N*-[1-(2-Furyl)-3-butenyl]phenylamine (12)**
IR (film): 3411, 3077, 3052, 2918, 1640, 1603, 994, 921, 748, 691 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.33 (dd, 1 H, *J* = 1.8, 0.9 Hz, Ar), 7.08–7.22 (m, 2 H, Ar), 6.56–6.73 (m, 3 H, Ar), 6.27 (dd, 1 H, *J* = 3.2, 1.8 Hz, Ar), 6.15 (dt, 1 H, *J* = 3.2, 0.8 Hz, Ar), 5.64–5.85 (m, 1 H, CH), 5.08–5.21 (m, 2 H, CH_2), 4.54 (t, 1 H, *J* = 6.2 Hz, CH), 3.97 (br, 1 H, NH), 2.61–2.68 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.2 (CH_2), 51.3 (CH), 106.0 (CH), 110.1 (CH), 113.5 (CH), 117.8 (CH), 118.4 (CH_2), 129.1 (CH), 133.9 (CH), 141.5 (CH), 146.5 (C_0), 155.3 (C_0).

***N*-[1-(4-Chlorophenyl)-3-butenyl]phenylamine (13)**
IR (film): 3413, 3077, 2925, 2852, 1639, 1601, 993, 918, 823, 749, 692 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.28 (s, 4 H, Ar), 7.02–7.12 (m, 2 H, Ar), 6.61–6.69 (m, 1 H, Ar), 6.41–6.48 (m, 2 H, Ar), 5.63–5.83 (m, 1 H, CH), 5.11–5.23 (m, 2 H, CH_2), 4.35 (dd, 1 H, *J* = 7.9, 5.2 Hz, CH), 4.10 (br, 1 H, NH), 2.36–2.65 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.2 (CH_2), 56.6 (CH), 113.5 (CH), 117.7 (CH_2), 118.7 (CH_2), 127.7 (CH), 128.8 (CH), 129.1 (CH), 132.6 (C_0), 134.2 (CH), 142.2 (C_0), 147.1 (C_0).

***N*-Butyl-1-(4-chlorophenyl)-3-butenyl-1-amine (14)**
IR (film): 3331, 3077, 2928, 1640, 1639, 1595, 1090, 993, 917, 828, 741, 681 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.26 (d, 4 H, *J* = 1.7 Hz, Ar), 5.58–5.80 (m, 1 H, CH), 5.02–5.12 (m, 2 H, CH_2), 3.61 (t, 1 H, *J* = 6.8 Hz, CH), 2.30–2.45 (m, 4 H, 2 CH_2), 1.53 (br, 1 H, NH), 1.18–1.49 (m, 4 H, 2 CH_2), 0.86 (t, 3 H, *J* = 6.9 Hz, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (CH_3), 20.4 (CH_2), 32.4 (CH_2), 43.2 (CH_2), 47.4 (CH_2), 61.9 (CH), 118.0 (CH), 128.4 (CH), 128.5 (CH), 132.4 (C_0), 135.2 (CH), 142.8 (C_0).

***N*-[1-(4-Methoxyphenyl)-3-butenyl]phenylamine (15)**
IR (film): 3410, 3004, 2922, 2834, 1638, 1603, 1246, 993, 918, 829, 749, 692 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.28–7.35 (m, 2 H, Ar), 7.02–7.17 (m, 2 H, Ar), 6.86–6.93 (m, 2 H, Ar), 6.64–6.72 (m, 1 H, Ar), 6.51–6.57 (m, 2 H, Ar), 5.70–5.90 (m, 1 H, CH), 5.14–5.27 (m, 2 H, CH_2), 4.38 (dd, 1 H, *J* = 7.7, 5.4 Hz, CH), 4.18 (br, 1 H, NH), 3.82 (s, 3 H, OCH_3), 2.43–2.70 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.2 (CH_2), 55.2 (CH), 56.5 (CH_3), 113.4 (CH), 113.9 (CH), 117.9 (CH), 118.2 (CH_2), 127.3 (CH), 129.1 (CH), 134.8 (CH), 135.5 (C_0), 147.4 (C_0), 158.5 (C_0).

***N*-Allyl-*N*-[1-(4-nitrophenyl)-3-butenyl]phenylamine (16)**
^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.16 (d, 2 H, *J* = 8.8 Hz, Ar), 7.45 (d, 2 H, *J* = 9.0 Hz, Ar), 7.16–7.27 (m, 3 H, Ar), 6.60–6.85 (m, 2 H, Ar), 5.63–6.05 (m, 2 H, 2 CH), 5.02–5.19 (m, 5 H, 1 CH, 2 CH_2), 3.75–3.80 (m, 2 H, CH_2), 2.77–2.87 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 36.3 (CH_2), 49.4 (CH_2), 61.9 (CH), 115.2 (CH), 116.6 (CH_2), 117.8 (CH_2), 118.3 (CH), 123.6 (CH), 128.5 (CH), 129.2 (CH), 134.8 (CH), 135.3 (CH).

MS: *m*/*z* (%) = 77 (17), 178 (18), 268 (100), 308 (17).

***N*-Allyl-*N*-[1-(4-chlorophenyl)-3-butenyl]phenylamine (17)**
^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.15–7.30 (m, 6 H, Ar), 6.70–6.80 (m, 3 H, Ar), 5.61–5.93 (m, 2 H, 2 CH), 4.96–5.16 (m, 5 H, 1 CH, 2 CH_2), 3.73 (d, 2 H, *J* = 4.9 Hz, CH_2), 2.75 (t, 2 H, *J* = 7.0 Hz, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 36.0 (CH_2), 48.7 (CH_2), 61.5 (CH), 128.5 (CH), 129.0 (CH), 129.1 (CH), 132.8 (C_0), 135.4 (CH), 136.0 (CH), 139.4 (C_0), 148.7 (C_0).

MS: *m*/*z* (%) = 77 (17), 178 (18), 268 (100), 308 (17).

***N*-(2-Methyl-1-phenyl-3-butenyl)phenylamine (18)**
IR (film): 3414, 1638, 1602, 1090, 994, 918, 748, 692 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.18–7.37 (m, 5 H, Ar), 6.99–7.10 (m, 2 H, Ar), 6.56–6.64 (m, 1 H, Ar), 6.47 (d, 2 H, *J* = 7.6 Hz, Ar), 5.65–5.84 (m, 1 H, CH), 5.09–5.24 (m, 2 H, CH_2), 4.33 (d, 1 H, *J* = 4.5 Hz, CH), 4.20 (br, 1 H, NH), 2.43–2.76 (m, 1 H, CH), 1.01 (d, 3 H, J = 6.9 Hz, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.3 (CH_3), 43.6 (CH), 61.3 (CH), 113.3 (CH), 115.8 (CH_2), 117.1 (CH), 126.9 (CH), 127.4 (CH), 128.1 (CH), 129.0 (CH), 140.2 (CH), 142.6 (C_0), 147.1 (C_0).

MS: *m*/*z* (%) = 77 (22), 104 (15), 182 (100), 237 (1).

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