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Practical, highly stereoselective allyl- and crotylsilylation of aldehydes catalyzed by readily available *Cinchona* alkaloid amide†

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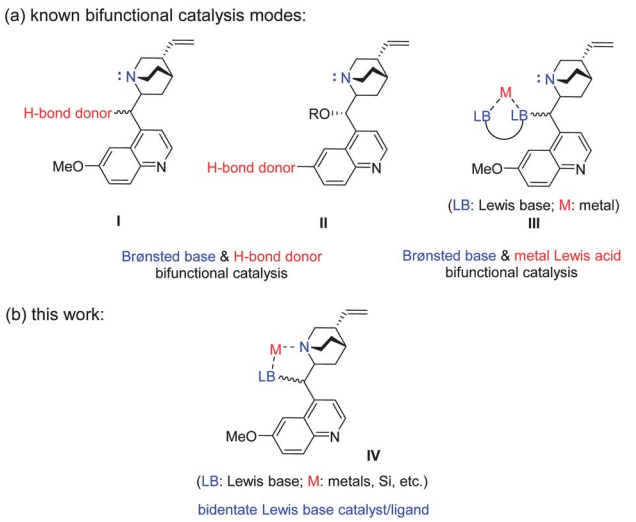
We have demonstrated that bidentate Lewis base catalysts can be constructed based on the *Cinchona* alkaloid structure that promote highly stereoselective reactions of allyl- and crotyltrichlorosilane with aromatic as well as aliphatic aldehydes (90–99% ee, >98% diastereoselectivity). The catalysts are available in a one-pot procedure in >70% yield from cheap starting materials and promote the allylation reactions at ambient temperature. Gram scale reactions with catalyst recovery and reuse showcased the practicality of the catalytic system.

Introduction

Cinchona alkaloids and their derivatives have played a significant role as a privileged scaffold in asymmetric catalysis.[1] The strongly basic quinuclidine nitrogen can effectively serve as a ligand for metal catalysis[2] or as a Brønsted/Lewis base in organocatalytic reactions.[3] By incorporating into the catalyst structure another H-bond donor[4] or a metal-based Lewis acid,[5] structures such as **I, II** and **III** (Scheme 1a) have proven powerful bifunctional catalysts for various organic transformations. Surprisingly, the construction of a simple bidentate ligand or catalyst, employing the quinuclidine nitrogen and another Lewis basic donor moiety (as shown in Scheme 1b), has remained elusive in asymmetric catalysis.



Scheme 1 Catalyst design and application. (a) Known catalyst design based on *Cinchona* alkaloids. (b) Proposed new bidentate Lewis base catalyst.

Towards the development of such a catalyst scaffold that will certainly benefit from the readily available, inexpensive *Cinchona* alkaloids, we chose the addition of allyl- and crotyltrichlorosilane to aldehydes as our model reaction, not only because it is a mechanically well-established reaction that can be catalyzed by a bidentate Lewis base,[6] but more importantly, it represented the first catalytic approach to realize predictable, diastereospecific crotylation (Type I allylation,[6a] where the use of *E*- or *Z*-crotylsilane provides *anti*- or *syn*-products with >98% fidelity through the closed chair transition state), which is a key requirement in the formation of propionate units that are ubiquitous in polyketide natural products.[7] Many catalytic systems have been developed for this reaction, which are dominantly chiral phosphoramides and *N*-oxides reported from the groups of Denmark and Fu,[6d] Nakajima *et al.*,[6e,f] Malkov and Kočovský *et al.*,[6g,h] Hayashi *et al.*,[6i] and Snapper and Hoveyda.[6j] While the great potential of these methods in chemical synthesis has been demonstrated,[8] one common limitation is the lack of reactivity for aliphatic aldehydes, with the only exception being the highly stereoselective allyl- and crotylation of aliphatic aldehydes from the Iseki group that required an impractically long reaction time (2–4 weeks).[6k] In a related area of research, recent work from the Krische group has revolutionized the field of aldehyde allylation that bypasses the use of allylmetal reagents and can be conducted from either the aldehyde or alcohol oxidation level for both aromatic and aliphatic aldehydes;[9] by the clever choice of substituted allyl acetates or butadiene, crotylation products with high

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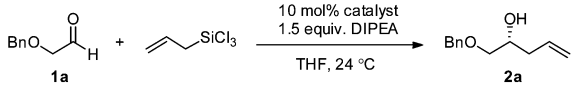
diastereo- and enantioselectivities can also be accessed.[10] However, considering the diastereospecific nature of Type I allylation, where pure *anti*- or *syn*-isomers can be accessed simply based on the choice of crotylating reagent, chiral Type I reagents (mainly allylborations such as Brown allylation,[11] Roush allylation[12] and the recent addition of allylsilylation from the Leighton group[13]) are still commonly used in asymmetric synthesis; a catalytic Type I allylation that can address the limitations of previous systems is therefore still desired.[14] Here we present a *Cinchona* alkaloid amide as a highly efficient and stereoselective catalyst for the allylation and crotylation of a wide range of aldehydes, and in particular, aliphatic aldehydes (95–99% ee). This system also provides significant practical advantages that enable large scale production: the catalyst can be prepared in a one-pot procedure from inexpensive starting materials, can be easily recovered and reused, and promotes the allylation reactions at ambient temperature (instead of low temperatures of −40 to −78 °C for most previous systems).

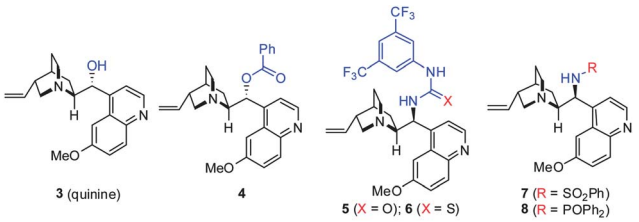
Results and discussion

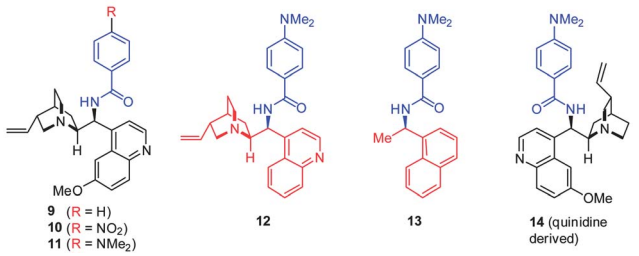
We initiated our studies by examining the catalytic activity of a variety of quinine-derived compounds for the addition of allyltrichlorosilane to **1a**, the product of which is highly synthetically useful but was not previously available using Lewis base catalysis (Table 1). Quinine **3** and quinine ester **4** that were previously widely used as nucleophilic catalysts[3] proved inefficient for our purpose, presumably due to limited Lewis base activation from the monodentate quinuclidine nitrogen (entries 1–2). The well-established bifunctional catalysts[4] (Brønsted base coupled with H-bond donor) urea **5** and thiourea **6** were also poor catalysts (entries 3 and 4). Sulfonamide **7** (ref. 15) and phosphoric amide **8** may serve as bidentate Lewis bases, and interestingly we did obtain product enriched in the opposite enantiomer (40% ee with **7** or **8** *vs.* −41% ee by using **5**), however the level of efficiency and selectivity were far from satisfactory (entries 5 and 6). To our delight, a simple quinine amide such as **9**, that has rarely proved successful in asymmetric catalysis,[16,17] provided the desired product with high efficiency and excellent enantioselectivity (entry 7). Evaluation of the electronics of the aryl group (entries 7–9) clearly showed that the amide moiety serves as a Lewis base (instead of a H-bond donor in which case the catalyst would be more effective with an electron-withdrawing substituent installed such as **10**), with catalyst **11** possessing a strongly electron-donating dimethylamino group being the optimal catalyst (88% conv., 96% ee). Cinchonidine-derived **12** (only lacking the methoxy substituent on quinoline) provided essentially the same result

Table 1 Optimization of allylation of aliphatic aldehydes[a]



Entry	Catalyst	Conv.[b] (%)	ee[c] (%)	Entry	Catalyst	Conv.[b] (%)	ee[c] (%)
1[d]	**3**	15	−8	7	**9**	83	95
2[d]	**4**	10	−5	8	**10**	35	81
3	**5**	30	−41	9	**11**	**88**	**96**
4	**6**	40	−20	10	**12**	83	96
5	**7**	36	40	11	**13**	35	9
6	**8**	45	40	12	**14**	**88**	**−96**





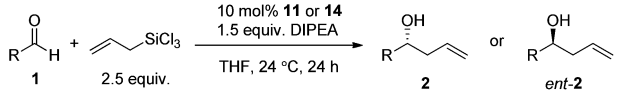
[a] Unless otherwise stated, reactions were run for 24 h. See ESI for details. [b] Conv. determined by ^{1}H NMR of the crude reaction mixture. [c] ee determined by HPLC analysis. [d] Reactions were run for 48 h.

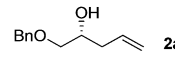
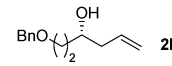
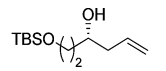
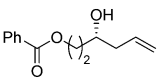
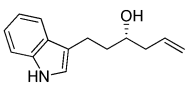
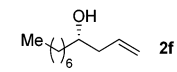
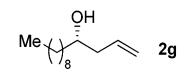
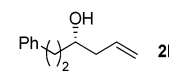
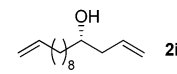
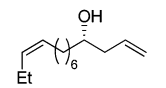
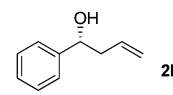
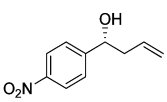
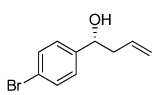
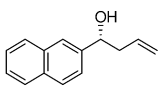
as **11**, suggesting that the quinoline moiety in the catalyst structure is not directly involved in activation of the silylating reagent (entry 10). Compound **13**, possessing the analogous chiral amide moiety but lacking quinuclidine, was much less efficient and selective, which further supported our hypothesis of bidentate Lewis base activation of allyltrichlorosilane (entry 11). Finally, as *Cinchona* alkaloids exist as pseudo-enantiomers, quinidine-derived **14** was also tested, and provided the enantiomeric product *ent*-**2a** with the same excellent enantioselectivity (entry 12).

The evaluation of reaction parameters showed that DIPEA was necessary for the reaction to take place. THF was the optimal solvent in terms of reactivity as well as enantioselectivity. The optimal reaction conditions can be employed to produce a wide range of homoallylic alcohols in excellent enantioselectivity (Table 2). The reactions were carried out with **11** or **14** that yielded both antipodes of the products in comparable excellent enantioselectivity. The enantioselectivities for allylations of aliphatic aldehydes are uniformly high (95–99%). It is noteworthy that various functional groups such as ethers and silyl ethers (entries 1–3), esters (entry 4) as well as *N*-heterocycles (entry 5) are all well-tolerated, in addition to simple alkyl and alkenyl aldehydes (entries 6–10). This unprecedented scope bodes well for application in complex natural product synthesis. The allylation of β-chiral aldehyde **1o** was also examined (Scheme 2). While allylation of **1o** (96% ee) catalyzed by **11** provided **2o** with 98 : 2 diastereomeric ratio, suggesting >98% selectivity for the installation of the new stereogenic center, the other diastereomer *epi*-**2o** could be obtained with a high diastereomeric ratio of 97.5 : 2.5 from the reaction catalyzed by **14**. Aromatic aldehydes also work under the same conditions to yield products with enantioselectivities ranging between 90 and 94% ee (entries 11–14, Table 2).

More importantly, we demonstrated that our catalytic system can be applied to the crotylation of aliphatic aldehydes with high enantioselectivity as well as reliable diastereospecificity, characteristic of Type I allylation. As shown in Table 3, with the use of either *E*- or *Z*-crotyltrichlorosilane **15** (each prepared in one step from commercially available starting materials),[18] the alcohol products **16** of the two ether-containing substrates were obtained with excellent ee as well as high dr (>99% transfer of the geometry of crotylsilane to the product diastereomeric ratio). In contrast, the classical chiral Lewis acid-catalyzed addition of allylic organometallic reagents (Si, Sn, B) to aldehydes (Type II allylation; open transition state) provides a mixture of diastereomers, predominantly *syn*-isomer, independent of starting allylic geometry, while the addition of allylic organometallic reagents (Cr, Zn, In) generated *in situ* from the corresponding allylic halides catalyzed by chelating ligands (Type III allylation) yields predominantly the *anti*-isomer regardless of starting allylic geometry.[6a]

Table 2 Substrate scope for allylation of aldehydes[a]

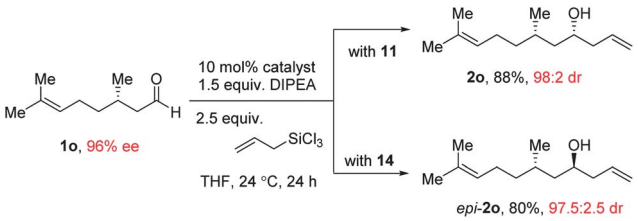


Entry	Product 2	With **11** Yield (%); ee (%)	With **14** Yield (%); ee (%)
1	 **2a**	83; 96	86; −97
2	 **2b**	89; 99	82; −98
3	 **2c**	70; 95	73; −96
4	 **2d**	90; 98	88; −98
5	 **2e**	75; 95	80; −96
6	 **2f**	80; 96	74; −96
7	 **2g**	76; 96	71; −95
8[b]	 **2h**	76; 97	70; −98
9	 **2i**	78; 97	85; −96
10	 **2j**	83; 96	80; −96
11[c]	 **2k**	77; 90	75; −91
12[c]	 **2l**	83; 92	90; −92
13[c]	 **2m**	77; 94	80; −93
14[c]	 **2n**	86; 93	89; −92

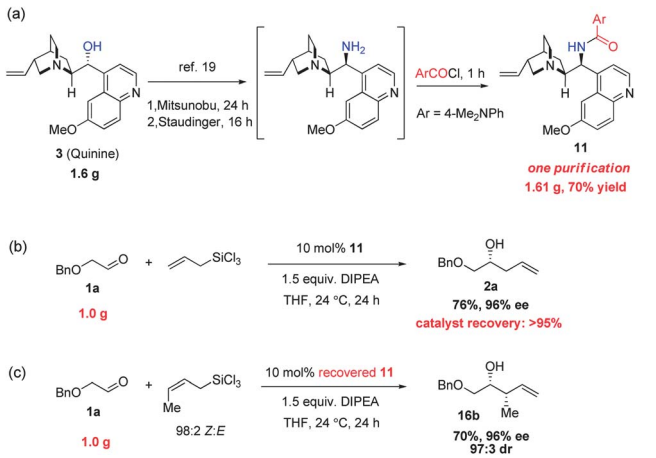
[a] All reactions were carried out at ambient temperature for 24 h. The yields are isolated yields based on the average of two runs. See ESI for details. [b] 20 mol% catalyst was used. [c] Toluene was used as the solvent that provided higher conversion for aromatic aldehydes.

Practical, scalable allylation and crotylation

It is noteworthy that the current catalytic system is simple to apply at ambient temperature using a readily available catalyst, and commercial reagents (allyltrichlorosilane, DIPEA, *etc.*) as received from popular vendors without further purification. As stated earlier, the catalyst can be easily prepared from inexpensive starting materials *via* a one-pot procedure that includes the previously reported Mitsunobu reaction of quinine with



Scheme 2 Allylation of chiral aldehyde.



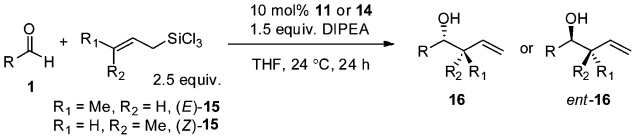
Scheme 3 One-pot catalyst synthesis and gram-scale reactions with catalyst recovery and reuse.

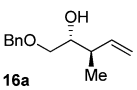
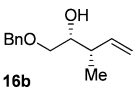
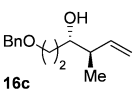
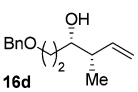
diphenylphosphoryl azide followed by Staudinger reaction to yield 9-amino-9-deoxy-quinine,[19] and finally acylation using commercially available 4-(dimethylamino)benzoyl chloride to yield the amide catalyst (Scheme 3a). The yield for the one-pot procedure, after a single purification by silica gel chromatography, was over 70%. To further showcase the utility of the system, gram-scale allylation of **1a** was carried out that yielded **2a** with comparable chemical yield and enantioselectivity to the small scale reactions (Scheme 3b *vs.* Table 2). The selectivity of this system is not sensitive towards concentration or heat transfer (as it is carried out at ambient temperature) so scaling up was straightforward. Although a relatively high catalyst loading of 10 mol% is required for the reaction, the catalyst could be easily recovered nearly quantitatively. When the recovered catalyst was used for another gram-scale crotylation of **1a**, alcohol **16b** was obtained in high diastereo- and enantioselectivity (Scheme 3c).

Mechanistic considerations

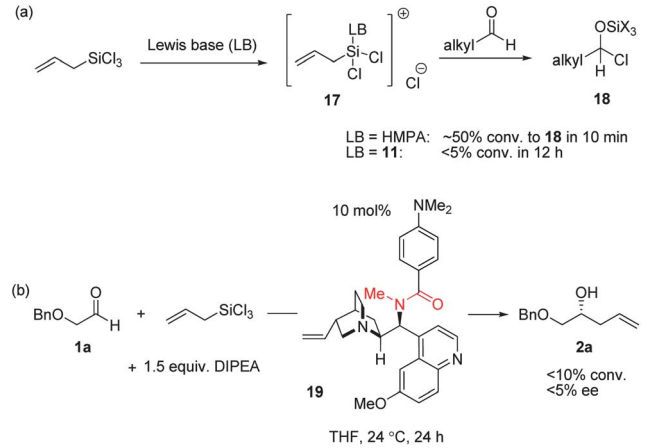
It has been showcased by the Denmark group that a Lewis base can liberate a chloride ion from $SiCl_4$ or allyltrichlorosilane to form a silicate intermediate (**17** in Scheme 4a).[20] In the case of aliphatic aldehydes, however, this chloride adds to the aldehyde to form the corresponding α-chloro silyl ether **18** that is presumably responsible for the lack of allylation reactivity for such substrates. In our case, it was also observed that catalyst **11** binds to $SiCl_4$ to liberate a chloride that quickly adds to aliphatic aldehydes to generate the α-chloro silyl ethers (>60% conv. in 10 min). On the other hand, the related product was not clearly observed when we mixed **11** with allyltrichlorosilane and aliphatic aldehyde (Scheme 4). This is in large contrast to the control experiment using HMPA, which promotes this undesired reaction with both $SiCl_4$ and allyltrichlorosilane. This may be due to the relatively lower Lewis basicity of our catalyst compared to HMPA, which is a fortunate character for the success of aliphatic aldehyde allylation.

Table 3 Diastereospecific crotylation of aliphatic aldehydes[a]

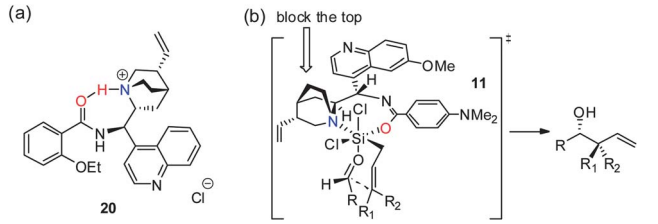


Entry	**15** $E:Z$	Product **16**	With **11** Yield (%); ee (%)	With **14** Yield (%); ee (%)
1	(*E*)-**15**; 94 : 6	 **16a**	78; 97; 94 : 6 dr	75; −98; 94 : 6 dr
2	(*Z*)-**15**; 2 : 98	 **16b**	78; 96; 98 : 2 dr	75; −95; 98 : 2 dr
3	(*E*)-**15**; 94 : 6	 **16c**	74; 96; 94 : 6 dr	70; −98; 94 : 6 dr
4	(*Z*)-**15**; 2 : 98	 **16d**	72; 96; 98 : 2 dr	73; −97; 98 : 2 dr

[a] See Table 2 and ESI.



Scheme 4 Exploration of chloride ion liberation and catalyst modification.



Scheme 5 Proposed reaction transition state model.

It is noteworthy that the secondary amide moiety in our catalyst may react with allyltrichlorosilane in the presence of DIPEA to generate the corresponding *O*-silyl imidate, in which process the chloride ion that is liberated from the silane will be sequestered as part of the DIPEA·HCl salt (and thus avoid the undesired α-chloro silyl ether formation). As stated earlier, DIPEA was found to be essential for the allylation reaction to proceed to high conversion. Preliminary NMR studies by mixing the catalyst, silane, and DIPEA in a 1 : 1 : 1 ratio were inconclusive as a complex mixture was formed; however, the resulting mixture was shown to be catalytically active. We have further tested the activity of catalyst **19** with a methylated amide moiety, which, under otherwise identical conditions, led to only <10% conv. to the allylation product with <5% ee (Scheme 4b). While the steric hindrance of this catalyst may certainly contribute to this low activity and selectivity, it provides support for the *O*-silyl imidate formation from catalyst **11** and **14**. More extensive mechanistic studies as well as calculations will be carried out to further elucidate the nature of the active catalytic species as well as the turnover of the "anionic" catalyst.

The conformational analysis of related *Cinchona* alkaloid amides both in solution and in the solid state has been performed by the Brunner group using NMR, X-ray as well as molecular orbital calculations during their studies of enantioselective decarboxylation reactions using these catalysts as chiral Brønsted bases.[16] These studies showed that these molecules prefer the open conformation,[21] where the quinuclidine nitrogen points away from the quinoline unit, and in turn, towards the 9-amide moiety. In particular, the calculated minimum energy conformation of the protonated cinchonine amide **20** (Scheme 5a) possesses a H-bond interaction between the amide oxygen and the ammonium hydrogen.[16b] These data pointed to the possibility of 9-amide and quinuclidine serving as a bidentate catalyst. We have also carried out kinetic studies of our catalytic system, which suggested that the allylation reaction is first-order dependent on the catalyst (see ESI† for details), lending further evidence for the bidentate nature of our catalyst. Based on the above rationale, we propose the transition state model (with catalyst **11**) in Scheme 5b.

On the basis of the principles and mechanistic studies presented by the Denmark group[22a] and others,[22b,c] the aldehyde was placed *trans* to chloride to increase its electrophilicity; the allyl group, on the other hand, would coordinate *trans* to the strongly Lewis basic quinuclidine nitrogen, rendering it more nucleophilic. While the quinoline moiety points away to the back, the quinuclidine moiety effectively blocks the top of the complex so that the aldehyde is placed underneath. Allylation/crotylation through the chair like Zimmerman–Traxler transition state[23] then provides the desired product in excellent enantioselectivity and predictable, perfect diastereoselectivity.

Conclusions

In conclusion, we have demonstrated, for the first time, the utility of bidentate Lewis base catalysts constructed from *Cinchona* alkaloids in the highly stereoselective allyl- and crotylsilylation of aldehydes. The catalytic procedure provides a practical, scalable preparation of various homoallylic alcohols that are useful building blocks in organic synthesis. Current efforts in these laboratories are focused on detailed mechanistic studies to further elucidate the origin of the asymmetric induction, further extending the synthetic utility of the system to allyl/crotylation of chiral aldehydes and application of this family of catalysts to other important organic transformations.

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