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Latent Pronucleophiles in Lewis Base Catalysis: Enantioselective Allylation of Silyl Enol Ethers with Allylic Fluorides

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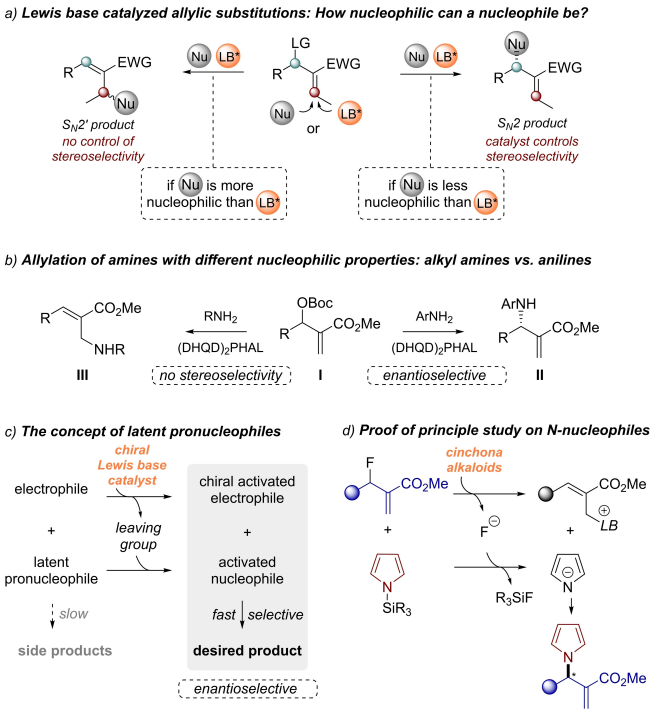
Dedicated to Prof. Dr. Wolfgang Weigand on the occasion of his 65th birthday.

Abstract: Lewis base catalyzed allylations of C-centered nucleophiles have been largely limited to the niche substrates with acidic C–H substituted for C–F bonds at the stabilized carbanionic carbon. Herein we report that the concept of latent pronucleophiles serves to overcome these limitations and allow for a variety of common stabilized C-nucleophiles, when they are introduced as the corresponding silylated compounds, to undergo enantioselective allylations using allylic fluorides. The reactions of silyl enol ethers afford the allylation products in good yields and with high degree of regio/stereoselectivity as well as diastereoselectivity when cyclic silyl enol ethers are used. Further examples of silylated stabilized carbon nucleophiles that undergo efficient allylation speak in favor of the general applicability of this concept to C-centered nucleophiles.

Introduction

In an enantioselective reaction involving a chiral Lewis base catalyst, an electrophile and a nucleophile, the latter must be less nucleophilic than the Lewis base catalyst.[1] If this is not the case, the reaction may proceed without involvement of the chiral Lewis base catalyst which deteriorates the enantioselectivity of the process or changes the regioselectivity of the reactions (as illustrated for allylic substitutions, Scheme 1a).[2] Most of the common chiral Lewis bases that achieve high enantioselectivities when used as catalysts are not highly nucleophilic in part owing to steric crowding around Lewis basic atom (Scheme 1b). For example, allylic substitutions catalyzed by cinchona alkaloid based catalysts are orders of magnitude slower than the corresponding reactions catalyzed by DABCO.[3] Therefore, the narrow reaction scope for the nucleophilic reaction partner remains the central problem in enantioselective Lewis base catalysis. This is illustrated by the



Scheme 1. a) Competition of the chiral Lewis base catalyst (LB) and the nucleophile (Nu) in reactions with model allylic electrophile. b) Reaction outcome dependent on the nucleophilicity (defined by the *N* parameter)[3] of the nucleophile and the Lewis base catalyst. c) Outline for the concept of latent pronucleophiles and d) The proof of principle study for the application of the concept of latent pronucleophiles to enantioselective *N* allylation of pyrroles.

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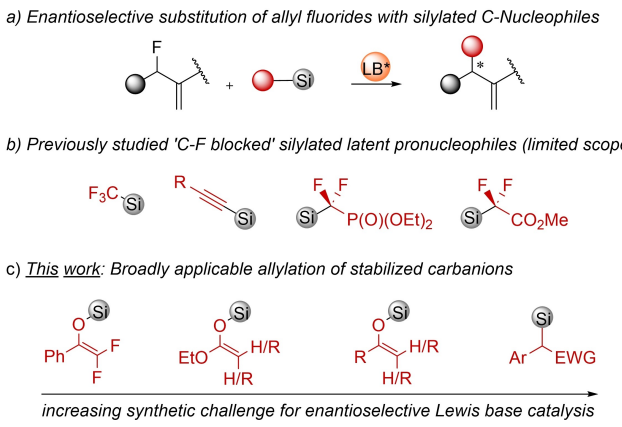
fact that chiral Lewis base catalysts have not yet been successfully used in allylation of fairly nucleophilic primary or secondary alkyl amines with allylic electrophiles although related enantioselective Lewis base catalyzed allylations of less nucleophilic anilines are known.[2a–b]

We introduced the concept of latent nucleophiles in Lewis base catalysis which addresses this problem through the use of latent nucleophiles and latent pronucleophiles that feature a modification which lowers their nucleophilicity and enables their activation at an opportune moment during the reaction when the activated electrophile is already present in the reaction mixture (Scheme 1c).[4] In a proof-of-concept study, silylated pyrroles, indoles and carbazoles were used as latent N-centered nucleophiles in chiral Lewis base catalyzed allylic substitutions of Morita-Baylis–Hillman (MBH) fluorides (Scheme 1d).

In the area of C-centered nucleophiles, Shibata's pioneering studies have demonstrated that alkynyl, trifluoromethyl and some benzylic silanes can be used as C-centered pronucleophiles in allylic substitutions of allylic fluorides catalyzed by chiral Lewis bases (Scheme 2).[5] We took advantage of the same approach to achieve enantioselective allylation of difluoromethylphosphonate and, for the first time, produced bioisosters of allyl phosphates in an enantioselective manner.[6] Unlike amines and other nitrogen centered nucleophiles, the C–H acidic precursors of carbanions are not strongly nucleophilic and they thus avoid the problems outlined above. The carbanions are, however, strong Brønsted bases, and we initially considered this an unsurmountable limitation associated with their general use as pronucleophiles in allylic substitutions. The activated nucleophile, a stabilized carbanion, could act as a base and deprotonate any acidic C–H bonds within the pronucleophile or the reaction product which would lead to their quenching during the reaction (illustrated in Scheme 6b). For this reason, the severe limitation in the scope of the current methods is that any acidic C–H bonds in the pronucleophile were substituted by C–F bonds (e.g., difluoromethyl esters and difluoromethyl phosphonates instead of regular esters and phosphonates, Scheme 2b).



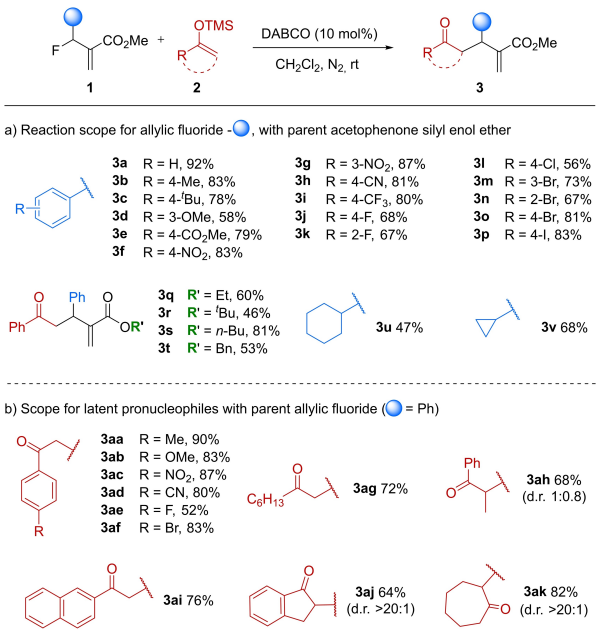
Scheme 2. a) General illustration for the enantioselective allylic substitution using allyl fluorides b) Previous examples of niche carbanionic latent pronucleophiles in allylic substitutions.[5a,c,d,6] c) Expanding the scope of Lewis base catalyzed allylic substitutions to common stabilized C-centered pronucleophiles.

A much more general application for these reactions would be found if more common stabilized carbanions derived from compounds that feature acidic C–H bonds like ketones could be accommodated. This led us to examine the reactions of silyl enol ethers as surrogates of arguably the most useful stabilized carbanions, enolates. Herein we report an efficient enantioselective Lewis base catalyzed allylation of silyl enol ethers with MBH allylic fluorides that demonstrates the generality of the concept of latent pronucleophiles in Lewis base catalysis and broadens its applications to latent pronucleophiles derived from common stabilized carbanions (Scheme 2c).

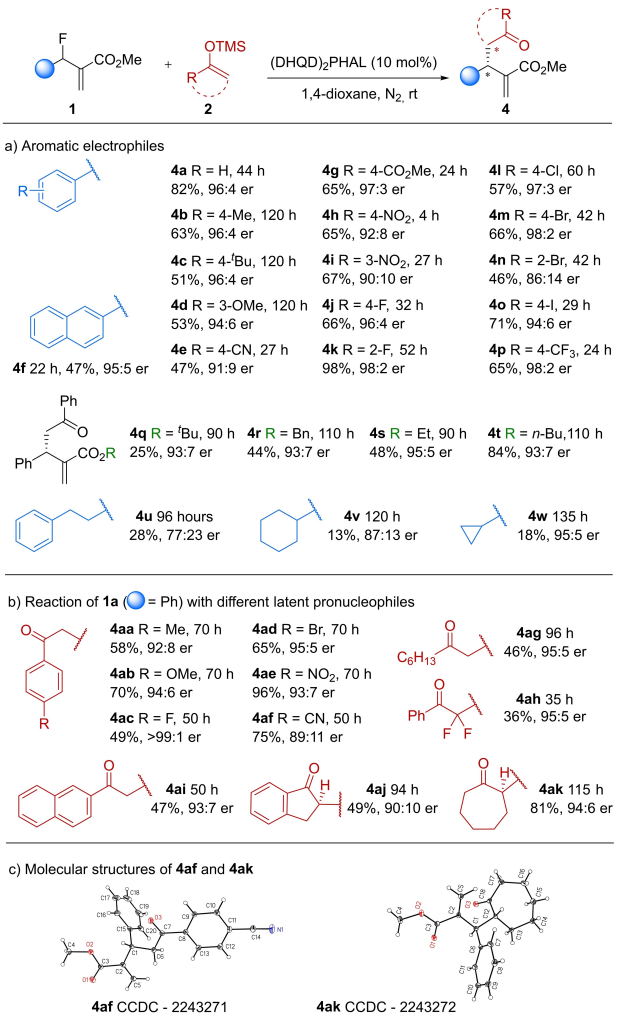
Results and Discussion

Previous work on Lewis base catalyzed allylations of ketones and esters showed severe limitations with respect to regioselectivity, diastereoselectivity, enantioselectivity of the reaction, and with respect to the substrate scope as only highly acidic carbonyl compounds, such as 1,3-dicarbonyls, could be used in combination with allylic carbonates.[7] This called for a ground-up investigation of a simple model system consisting of an achiral Lewis base catalyst, the model MBH fluoride **1a** and silyl enol ethers derived from acetophenone. Our initial optimization focused on the identity of the silyl group, identity of the catalyst, the catalyst loading, solvent, and temperature (for details see the Supporting Information). The optimal reaction conditions involved slight excess of the TMS enol ether as latent pronucleophile with 10 mol% of DABCO in dichloromethane at room temperature. Lower catalyst loading was effective but impractical on the reaction scale used in the optimization process.

The early success in optimization study prompted a detailed investigation of the functional group tolerance and the reactions scope with respect to both the allylic fluoride and the silyl enol ether (Scheme 3). Reaction scope for allylic fluoride reflected the scope of the previously reported allylic substitutions with similar substrates.[4–6,8] Both electron rich (**3b**–**3d**) and electron poor (**3e**–**3h**) allylic fluorides gave moderate to excellent yields. When halogenated allylic fluorides (**3i**–**3p**) were used, the corresponding products were also obtained in good yields. Alkyl fluorides (**3u**–**3v**) were competent under the standard conditions even though the yields dropped to around 50% due to a competing fluoride elimination.[8] The methyl, ethyl, n-butyl, benzyl, and t-butyl esters within the MBH fluoride (**3q**–**3t**) were suitable substrates albeit yields declined with the increase of steric bulk at the ester. More importantly, the scope for the silyl enol ethers proved to be universal. Various silyl enol ethers derived from substituted acetophenones featuring electron donating groups (**3aa**–**3ab**) and electron withdrawing groups (**3ac**–**3ad**) produced the desired product with high yields. Aryl halides were well tolerated (**3ae**–**3af**). Silyl enol ethers derived from acyclic aliphatic ketones (**3ag**) were found to be lower in reactivity but still delivered the products in good yields. For those derived from cyclic ketones, however, higher



Scheme 3. a) Scope of the allylic fluoride **1** in Lewis base catalyzed allylation of trimethyl((1-phenylvinyl)oxy)silane **2a**. b) Scope of C-centered latent pronucleophiles with allylic fluoride **1a**. The reaction of **1** with **2** (1.5 equiv.) and DABCO (10 mol%) was carried out in anhydrous dichloromethane under nitrogen atmosphere at room temperature.



Scheme 4. a) Substrate scope of allylic fluoride **1** in chiral Lewis base catalyzed allylation of trimethyl((1-phenylvinyl)oxy)silane **2a**. b) Substrate scope of C-centered latent pronucleophiles with allylic fluoride **1a**. The reaction of **1** (2 equiv.), with **2** and $(DHQD)_2PHAL$ (10 mol%) was carried out in 1,4-dioxane at room temperature under N_2 atmosphere. c) Molecular structures of **4af** and **4ak**.

yields could be obtained due to enhanced nucleophilicity of the corresponding anion[9] (**3aj** and **3ak**) and the reactions proceeded with diastereoselectivity greater than 20:1 favoring the *anti*-diastereomer. When *Z*-silylenolether derived from propiophenone was used, product (**3ah**) was isolated in high yields but as a statistical mixture of diastereomers.

The process catalyzed by DABCO proved to be general with high chemo- and regioselectivity observed across the board and with good yields achieved after a short reaction time. Encouraged by these results we investigated analogous enantioselective reactions using chiral Lewis base catalysts with focus on cinchona alkaloid-based catalysts proven to deliver good stereocontrol in similar processes.[10] For the optimization we elaborated the identity of the catalyst, the catalyst loading, temperature, reaction time and the ratio of reaction partners (for details see the Supporting Information). We found that the desired product was obtained in high yield and high enantioselectivity with 10 mol% of $(DHQD)_2PHAL$ at room temperature in 1,4-dioxane as a solvent. Like many related processes, these reactions proceeded as kinetic resolutions of the allylic fluoride which is why excess of allylic fluoride was used.

Upon the optimization of reaction conditions, substrate scope was evaluated with a variety of allylic fluorides (Scheme 4a). Qualitatively, higher reaction rates were observed with fluorides bearing electron withdrawing groups compared to those with electron donating groups. Both electron rich (**4b**–**4d**) and electron poor fluorides (**4e**–**4i**) produced the desired products in moderate to good yields and with enantiomeric ratios between 90:10 and 97:3. Enantiomeric ratios as high as 98:2 were observed with allylic fluorides featuring aryl halides in their structures (**4j**–**4p**). Alkyl substituted fluorides (**4u**–**4w**) were also found to give the corresponding products with ratios of enantiomers up to 95:5, though the yields dropped significantly. A variety of different esters were tested (**4q**–**4t**) and similar trends in yields were observed like in the reactions catalyzed by DABCO but enantioselectivity remained nearly constant (95:5 to 97:3 er).

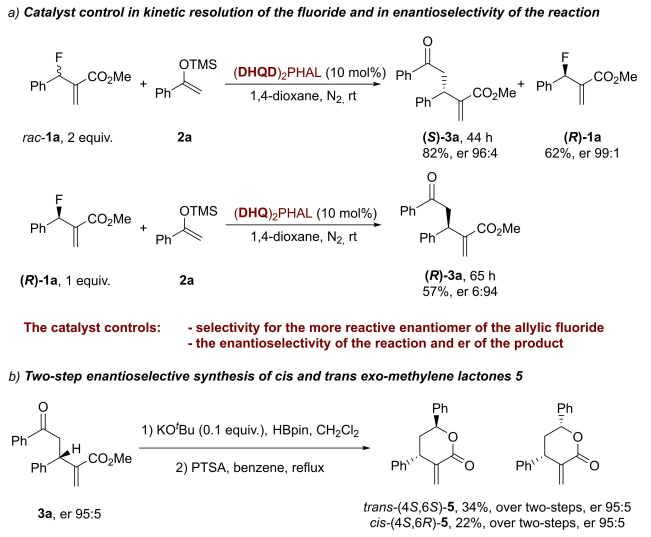
The nucleophilic reaction partner also allowed for different substitution patterns and a variety of substituents (Scheme 4b). Electron rich (**4aa**–**4ab**) and electron poor (**4ae**–**4af**) silyl enol ethers produced products in good yields (up to 96%) with high enantioselectivity (up to 93:7 er). Halide substituted silyl enol ethers (**4ac**–**4ad**) furnished the products in moderate to high yields virtually reaching enantiopurity (>99:1) for **4ac**. Cyclic alkyl silyl enol ether **4aj** and **4ak** provided products with 49% and 81% yield with enantiomeric ratios up to 94:6. Acyclic silyl enol ethers (**4ag**) showed good reactivity with allylic fluoride

with high enantiomeric ratio (up to 95:5) but slightly lower in yield. The reaction of silylated α,α-difluoro acetophenone furnished **4ah** in 35% yield with good enantiocontrol (er of 95:5).

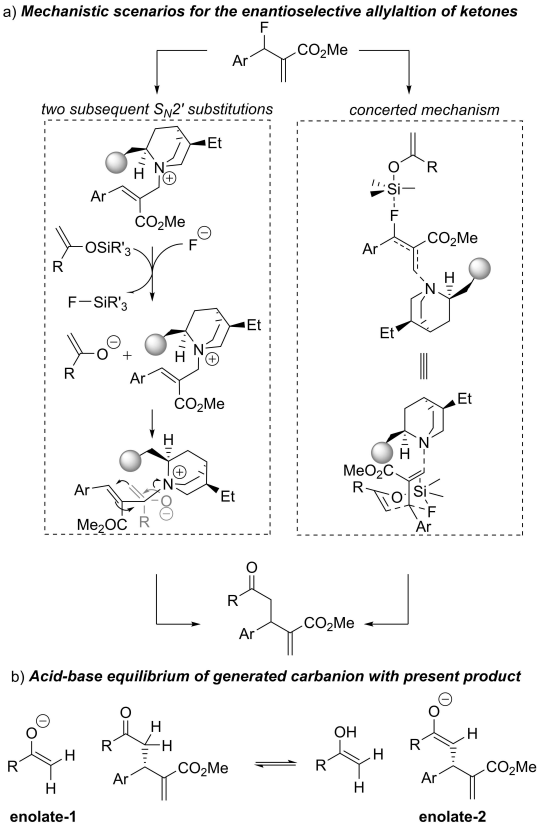
The configuration of the enantiomer predominantly formed when $(DHQD)_2PHAL$ was used as the catalysts was assigned as *S* based on the analogy with previous reports.[4–5] Similar to the previously reported allylations using allylic fluorides, these reactions also proceed as kinetic resolutions of the starting allylic fluoride. The residual fluorides that could be isolated at the end of the reactions were typically highly enantioenriched. When reisolated, enantiomerically enriched fluoride (***R***)-**1a** was reacted under the same conditions using the pseudoenantiomeric catalyst $(DHQ)_2PHAL$, the antipode of the allylation product was formed (Scheme 5a).[6] The reaction proceeded with comparable efficiency and stereocontrol as the parent reaction which emphasizes that both enantiomers of the product can easily be accessed by the use of commercially available cinchona alkaloid based catalysts.

To demonstrate the synthetic utility of these allylation reactions in synthesis of enantioenriched motifs relevant in synthesis or natural products or bioactive molecules, ketone **3a** was reduced with pinacolborane in the presence of potassium *tert*-butoxide to give rise to two diastereomeric alcohols in equal quantities. These alcohols were directly converted to the lactones *trans*-**5** and *cis*-**5** by transesterification in the presence of *p*-toluenesulfonic acid with both diastereomers isolated in pure form without deterioration of enantiomeric ratio showing that two stereogenic centers can be set in a short sequence.[11] Furthermore, the reactions of silyl enol ethers derived from cyclic ketones appeared to be highly diastereoselective and furnished products **4aj** and **4ak** featuring two stereogenic centers with high degree of stereocontrol.[12]

The mechanism of related reactions has been debated in the past. The reactions may proceed via (i) two consecutive S_N2' additions involving an ammonium ion, produced by the attack of the Lewis base catalysts on MBH fluoride and the consequent elimination of fluoride, and a short-lived activated anionic nucleophile (Scheme 6a, left),[4] or (ii) via concerted mechanism involving a highly ordered ternary transition state consisting of the fluoride, silyl enol ether and the catalyst proposed by Shibata for the related processes (Scheme 6a, right).[5] Besides these two border scenarios, a silicon-assisted cleavage of the C–F bond has been proposed.[12] The central point appears to be whether a free anionic activated nucleophile is produced during the reactions or not. The concerns over the presence of acidic C–H bonds in the starting materials and products stem from this unknown. If the enolate is produced from silyl enol ether during the reaction, it would be sufficiently basic to deprotonate any already formed product which may result in double allylation of the product and/or quenching of the enolate (Scheme 6b). Since the allylations of silyl enol ethers proceed without overallylation and in high yields, it may appear that they better fit with the proposed concerted mechanism. While the concerted mechanism requires a highly ordered ternary transition state which may be kinetically and entropically disfavored,[13] existence of anionic activated nucleophiles has been indicated in the related allylations of indoles.[4] In analogy to these reactions, we favor the stepwise mechanism in allylations of silyl enol ethers too. The nucleophilicity of the enolates from the starting silyl enol ether (**2a**) and the product



Scheme 5. a) Comparative test with $(DHQ)_2PHAL$ instead of $(DHQD)_2PHAL$ and reaction with enantioenriched allylic fluoride. b) Synthesis of exo-methylene lactones from **3a**.



Scheme 6. a) Two mechanistic proposals based on a stepwise mechanism (left) and a concerted mechanism (right) b) Virtual equilibrium of activated nucleophile and the product.

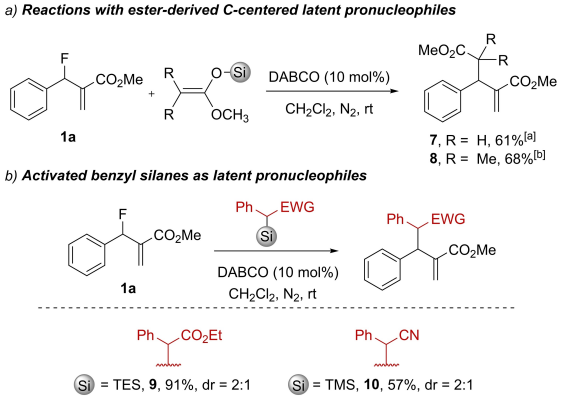
(**3 a**) should be, due to steric reasons, sufficiently different to favor reactions of **enolate-1** over **enolate-2** and avoid over-allylation.

The fact that reactions of cyclic silyl enol ethers give products with good diastereoselectivity may suggest that more ordered transition states are involved in these reactions. However, the fact that diastereoselectivity in allylation of acyclic Z-silyl enol ethers is not preserved in the product (**3 ah**, Scheme 3) is an indication that conformational preferences of the ring may be the reason behind the high diastereoselectivity observed in the former case. Base promoted isomerization of the ketone product may also prove important in achieving high diastereoselectivity with cyclic silyl enol ethers.

Finally, a short survey of related types of nucleophiles showed that various silylated stabilized carbon nucleophiles are competent substrates in Lewis base catalyzed allylations with allylic fluorides (Scheme 7). These include silylated nucleophiles derived from esters with different degree of substitution (including those that form quaternary carbon centers) and nitriles. Detailed investigations of these and related nucleophiles will be reported in due course.

Conclusions

The concept of latent pronucleophiles enables the scope of enantioselective Lewis base catalyzed allylation reactions of *C*-centered nucleophiles to be greatly expanded from the niche nucleophiles derived from compounds with the blocked acidic C–H to the broad range of common silylated stabilized carbanions. Based on this concept, we have developed the enantioselective allylation of model substrates, silyl enol ethers, using allylic fluorides. The reactions are simple, efficient, regio-, enantio- and diastereoselective (when cyclic silyl enol ethers are used) and they produce synthetically useful building blocks with up to two stereogenic centers in enantioenriched form. Commercially available cinchona-based catalysts allow access to both product enantiomers. Related latent pronucleophiles derived from other stabilized carbanions are also competent substrates for such reaction and demonstrate the generality of the process.



Scheme 7. Extension of the concept to a) silyl enol ethers derived from esters and b) activated benzyl silanes. [a] TBS was used as silyl protecting group. [b] TMS was used as silyl protecting group.

Experimental Section

General procedure for allylation of silyl enol ethers: The silyl enol ether or latent pronucleophile (1.5 equiv.) and DABCO (10 mol%) were added to a round bottom flask and the flask was evacuated and refilled with nitrogen (2–3 times). A solution of allylic fluoride (0.1 mmol, 1 equiv.) in dichloromethane (0.4 mL) was added slowly to the reaction mixture. After the completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by column chromatography using ethyl acetate in petroleum ether solvent mixtures to afford the corresponding product.

Methyl 2-methylene-5-oxo-3,5-diphenylpentanoate (3 a): Prepared following the general procedure described above. Yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$) 7.94–7.91 (m, 2H), 7.57–7.51 (m, 1H), 7.45–7.40 (m, 2H), 7.27–7.24 (m, 4H), 7.21–7.16 (m, 1H), 6.30 (s, 1H), 5.60 (s, 1H), 4.68 (t, J = 7.1 Hz, 1H), 3.68 (s, 3H), 3.64–3.59 (m, 1H), 3.47 (dd, J = 17.1,7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.73, 167.08, 142.85, 141.90, 136.97, 133.26, 128.73, 128.63, 128.16, 128.03, 126.83, 124.84, 52.05, 43.48, 42.14. HRMS [ESI]: m/z calculated for $C_{19}H_{18}O_3$ $[M+H]^+$295.1334, found 295.1332. IR (ATR): ν = 2947, 1739, 1423, 1365, 1265, 1215, 1091, 894, 702 cm^{-1}.

General procedure for enantioselective allylation of silyl enol ethers: A round bottom flask was charged with silyl enol ether (0.1 mmol, 1 equiv.) and $(DHQD)_2PHAL$ (10 mol%). After evacuating and refilling the flask with nitrogen (2–3 times). A solution of MBH fluoride (0.2 mmol, 2 equiv.) in anhydrous 1,4-dioxane (0.8 mL) was slowly added to the reaction mixture. The reaction was stirred at room temperature until judged to be completed (monitored by NMR yield of the remaining MBH fluoride determine by ^{1}H NMR). The mixture was concentrated under reduced pressure and purified by column chromatography using ethyl acetate in petroleum ether to afford the corresponding product.

Methyl (S)-2-methylene-5-oxo-3,5-diphenylpentanoate (4 a): Prepared following the general procedure described above. Yield: 82%. Spectral data matched those of **3 a**, 96:4 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 19.90 min, t (minor) = 26.01 min].

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: enantioselective · latent pronucleophiles · Lewis base catalysis · silyl enol ethers · stereoselective

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[12] During preparation of this manuscript, the group of Companyó published a draft manuscript on similar reactions focusing on the diastereoselective allylation of cyclic silyl enol ethers where larger excess of silyl enol ethers are required as well as higher catalyst loading compared to the work described here. For details, see J. Duran, J. Mateos, A. Moyano, X. Companyó, 10.26434/chemrxiv-2023-wxmzv.

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