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Diastereoselective Addition of Allyl Reagents to *N*-Monoprotected and *N,N*-Diprotected L-Alaninals

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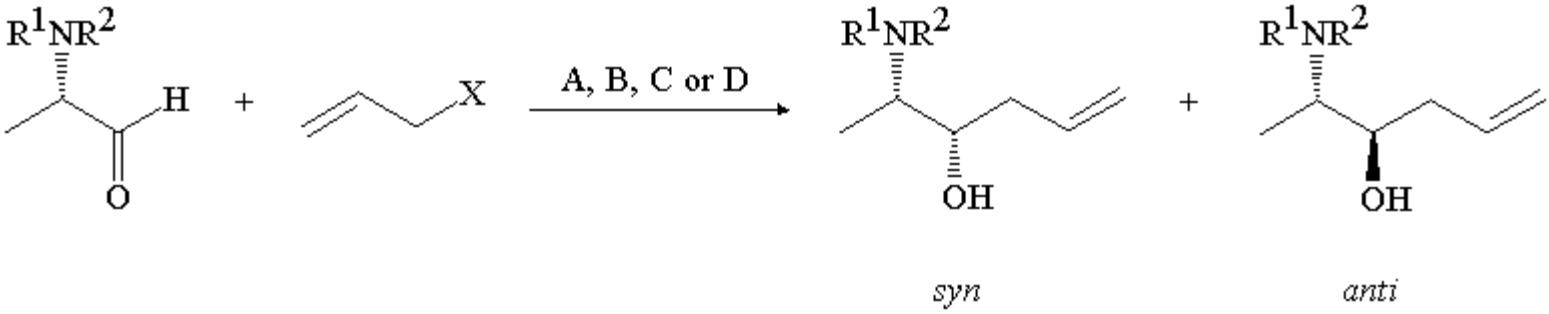
Abstract: In this communication, we report diastereoselective addition of allyl reagents to *N*-monoprotected and *N,N*-diprotected L-alaninals, and the characterization of the products.

Keywords: Diastereoselective addition, allyl reagents, L-alaninals.

Introduction

Amino aldehydes are the versatile chirons, frequently used in the stereocontrolled synthesis of natural products, including amino sugars.[1-3] Stereoselective elongation of the carbon skeleton is the crucial point of the synthesis of amino sugars from amino acids and their derivatives.[4-6] We recently described several C_4-elongation of -amino aldehydes via high- preassure 4+2 cycloaddition,[7,8] Lewis acid-mediated cyclocondensation,[9] and furyllithium addition.[10] We considered it very interesting to study other types of reactions of protected -amino aldehydes. Therefore we decided to investigate the addition reaction of various allyl reagents to *N*-monoprotected and *N,N*-diprotected L-alaninals under various conditions.

All aldehydes were obtained from L-alanine via oxidation of appropriate alcohols. The TEMPO oxidation[11-13] was the method of choice because only under these conditions L-alaninal derivatives do not racemizate.



Scheme 1

A

X = MgCl, THF, 0C or -78C

Entry	R^1	R^2	Time	Yield (%)	*syn:anti*
1	H	Boc	41	31	57 : 43
2	H	Cbz	41	50	56 : 44
3	H	Ts	41	46	59 : 41
4	Bn	Boc	20	88	12 : 88
5	Bn	Cbz	18	89	18 : 82
6	Bn	Ts	18	81	12 : 88

B

X=Br, Zn, NH_4Cl_{aq}/ THF, RT

Entry	R^1	R^2	Time	Yield (%)	*syn: anti*
1	H	Boc	2	88	50: 50
2	H	Cbz	3	93	50: 50
3	H	Ts	3	66	50: 50
4	Bn	Boc	3.5	99	20: 80
5	Bn	Cbz	3	99	10: 90
6	Bn	Ts	5	71	14: 86

C

X= Br, $SnCl_2 \cdot H_2O$, NaI, DMF, RT

Entry	R^1	R^2	Time	Yield (%)	*syn: anti*
1	H	Boc	18	99	50: 50
2	H	Cbz	18	99	50: 50
3	H	Ts	1.5	65	50: 50
4	Bn	Boc	2.5	82	16: 84
5	Bn	Cbz	1	90	5: 95
6	Bn	Ts	3	99	7: 93

D

X=$SiCl_3$, DMF, 0C

Entry	R^1	R^2	Time	Yield (%)	*syn: anti*
1	H	Boc	5	90	75: 25
2	H	Cbz	3	87	75: 25
3	H	Ts	2	20	75: 25
4	Bn	Boc	2	29	5: 95
5	Bn	Cbz	5	72	5: 95
6	Bn	Ts	8	64	23: 77

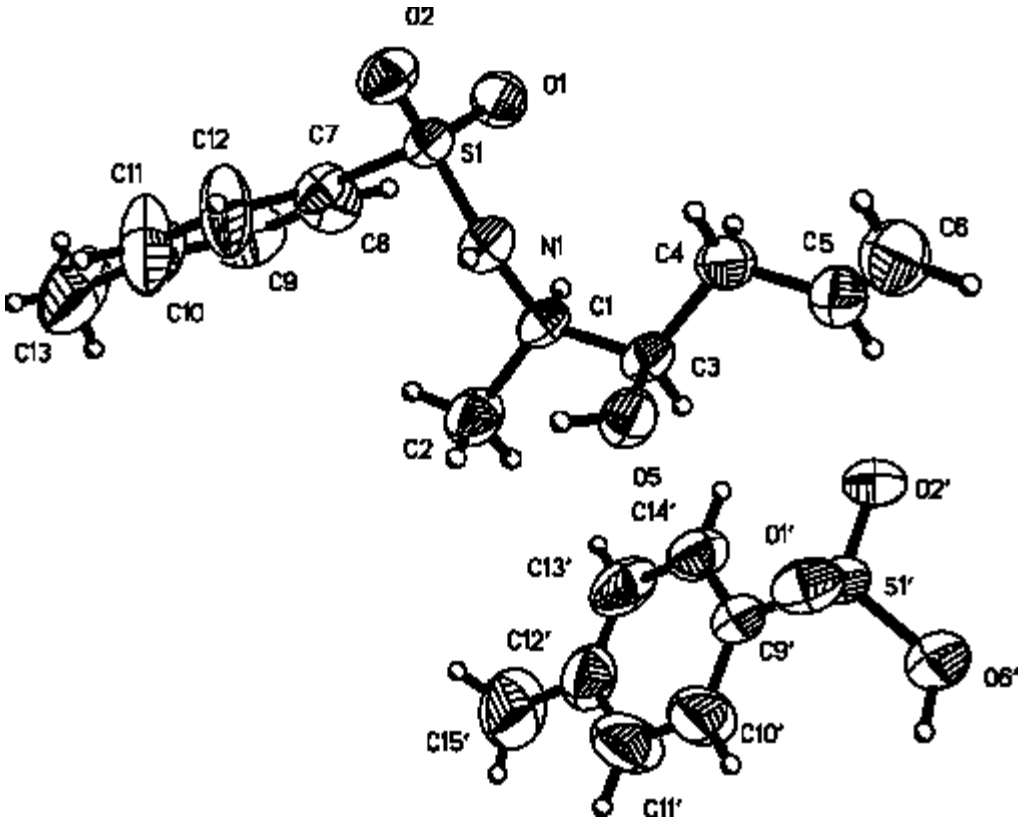


Fig.1 ORTEP diagram of *syn*-**6** showing asymmetric unit.

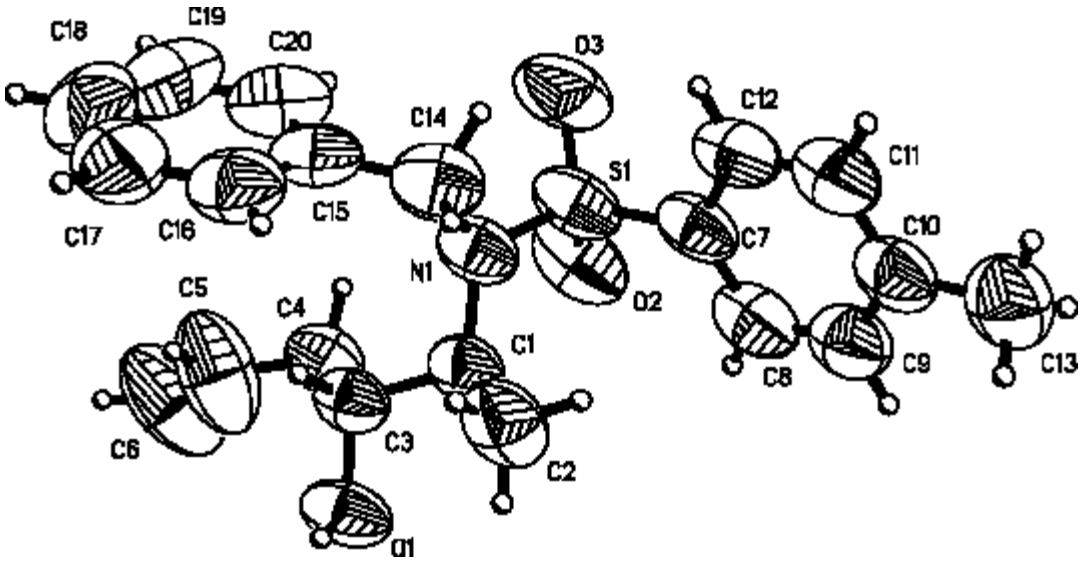
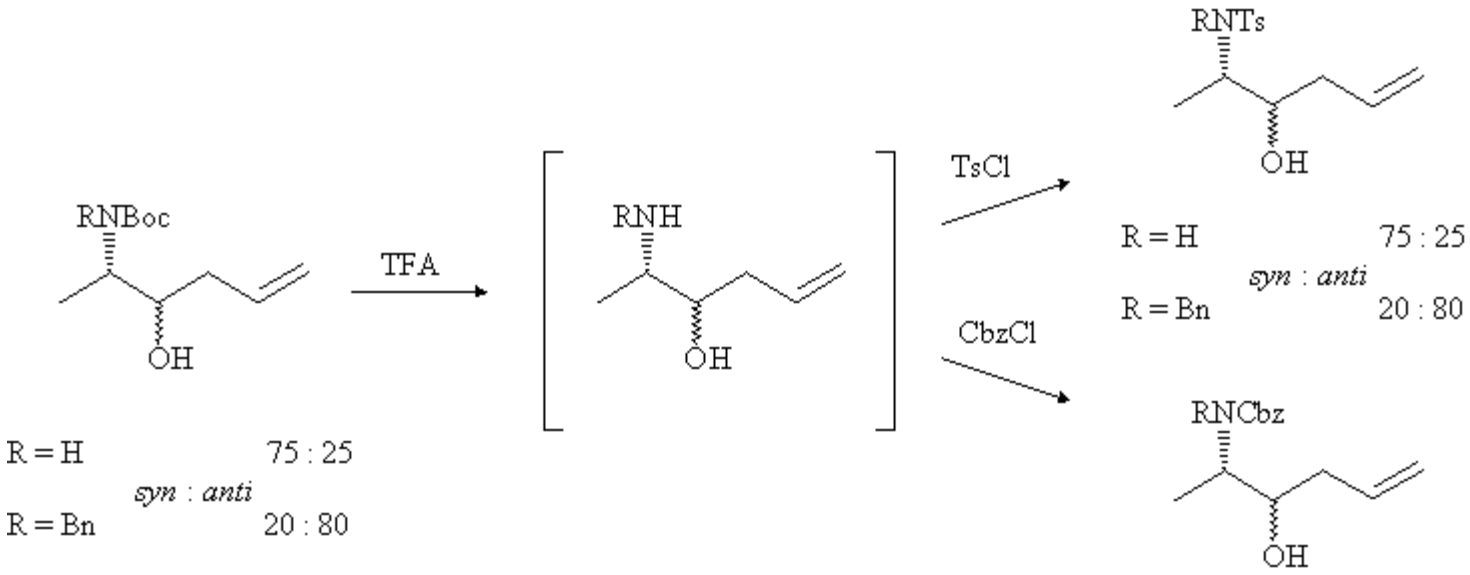


Fig. 2. ORTEP diagram of the molecule of compound *anti*-**9**.



Scheme 2

Conclusion

In all cases of additions to *N,N*-diprotected -amino aldehydes studied, *anti*-diastereoselectivity was observed as evidence a of nonchelation control. Contrary, addition to *N*-monoprotected -amino aldehydes afforded rather poor *syn*-diastereoselectivities, the best diastereoselectivity in this case was obtained for addition of allyltrichlorosilane (*syn:anti,* 75:25).

References and Notes

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Comments

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