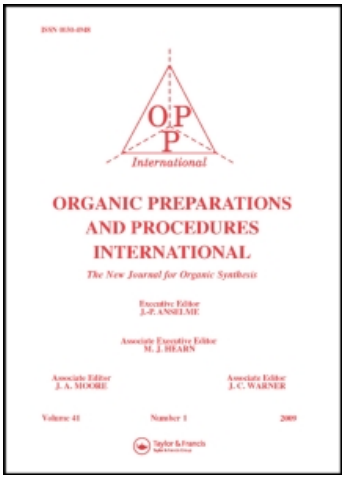


Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF ANTIMYCINS. A REVIEW

Yong-Qing Yang[a]; Yikang Wu[a]
[a] State Key Laboratory of Bioorganic and Natural Products Chemistry Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, P. R. CHINA

To cite this Article Yang, Yong-Qing and Wu, Yikang(2007) 'SYNTHESIS OF ANTIMYCINS. A REVIEW', Organic Preparations and Procedures International, 39: 2, 135 — 152
To link to this Article: DOI: 10.1080/00304940709356008
URL: http://dx.doi.org/10.1080/00304940709356008

ORGANIC PREPARATIONS AND PROCEDURES INT., 39 (2), 135-152 (2007)

SYNTHESIS OF ANTIMYCINS. A REVIEW

Yong-Qing Yang and Yikang Wu*

State Key Laboratory of Bioorganic and Natural Products Chemistry
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
354 Fenglin Road, Shanghai 200032, P. R. CHINA
e-mail: yikangwu@mail.sioc.ac.cn

SYNTHESIS OF ANTIMYCINS. A REVIEW

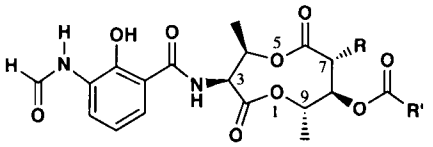
Yong-Qing Yang and Yikang Wu*

State Key Laboratory of Bioorganic and Natural Products Chemistry
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
354 Fenglin Road, Shanghai 200032, P. R. CHINA
e-mail: yikangwu@mail.sioc.ac.cn

THE HISTORY OF THE ANTIMYCINS

In 1948 Leben[1] and Keith reported an anti-fungi antibiotic preparation obtained from an unidentified *Streptomyces* species. They did not manage to isolate any pure substance from the mixture. However, they noticed the unique properties of the preparations and hence proposed a new name antimycin for the unidentified substance. One year later, Dunshee[2] *et al.* disclosed the isolation of an apparently homogeneous bioactive crystalline substance from the crude preparation. Because there existed other active yet unidentified antibiotic components in the crude mixture, the isolated crystalline substance was named antimycin A. Interestingly, the seemingly pure crystalline substance was later shown[3] to be a mixture of at least four bioactive components, which were consequently named as antimycin A_1, A_2, A_3, and A_4, respectively, in the order of increasing R_f values. In the late 1950's, several other groups[4] also reported isolation of antimycins, though under different names such as blastmycin[4b] and 720-A.[4c] However, those names were practically abandoned after those isolates were found[5] to be identical to antimycin A_3.

The structures of antimycins were established[6] for the first time in 1961, through the demonstration of the gross structure of antimycin A_3 and A_1, the two major components of the antimycin complex. The stereochemistry of the threonine part was unequivocally established by degradation. The absolute configurations of the remaining chiral centers in the 9-membered ring, however, remained unknown until Kinoshita *et al.*[7] finished a chiron-based synthesis of (+)-blastmycinolactol (which was the antipode of the corresponding lactol derived from degradation of antimycin A_3) in 1971. It should perhaps be noted here that in the whole antimycin family, only A_3 was experimentally proven through enantioselective synthesis to possess the depicted absolute configurations.



General structure of antimicyin A

Table 1. Current Members of the Antimycin Family (cf. the General Structure above)

Name	R	R'	Name	R	R'
A_{1a}	$(CH_2)_5Me$	$CHMeCH_2Me$	A_{7b}	$(CH_2)_2CHMe_2$	CH_2CH_2Me
A_{1b}	$(CH_2)_5Me$	CH_2CHMe_2	A_{8a}	$(CH_2)_2CHMe_2$	$CHMeCH_2Me$
A_{2a}	$(CH_2)_5Me$	$CHMe_2$	A_{8b}	$(CH_2)_2CHMe_2$	CH_2CHMe_2
A_{2b}	$(CH_2)_5Me$	CH_2CH_2Me	A_{9a}	$(CH_2)_3Me$	CH_2Ph
A_{3a}	$(CH_2)_3Me$	$CHMeCH_2Me$	A_{10a}	$(CH_2)_3CHMeCH_2Me$	$CHMeCH_2Me$
A_{3b}	$(CH_2)_3Me$	CH_2CHMe_2	A_{10b}	$(CH_2)_3CHMeCH_2Me$	CH_2CHMe_2
A_{4a}	$(CH_2)_3Me$	$CHMe_2$	A_{11a}	$(CH_2)_3Me$	$(CH_2)_2CHMe_2$
A_{4b}	$(CH_2)_3Me$	CH_2CH_2Me	A_{12a}	$(CH_2)_2CHMe_2$	$(CH_2)_2CHMe_2$
A_{5a}	CH_2Me	$CHMeCH_2Me$	A_{13a}	$(CH_2)_3Me$	$(CH_2)_2CHMeCH_2Me$
A_{5b}	CH_2Me	CH_2CHMe_2	A_{14a}	$(CH_2)_2CHMe_2$	$(CH_2)_2CHMeCH_2Me$
A_{6a}	CH_2Me	$CHMeCH_2Me$	A_{15a}	$(CH_2)_5Me$	$(CH_2)_2CHMe_2$
A_{6b}	CH_2Me	CH_2CH_2Me	A_{16a}	$(CH_2)_5Me$	$(CH_2)_2CHMeCH_2Me$
A_{7a}	$(CH_2)_2CHMe_2$	$CHMe_2$	A_{17a}	$(CH_2)_4Me$	$CHMeCH_2Me$

The presence of A_5 to A_6 as minor components in the antimycin complex was demonstrated by Berti[8] *et al.* through pyrolysis-gas liquid chromatography in 1970. The A_7 and A_8 were identified much later by Barrow[9] and co-workers in 1997. By then it was already clear that almost all known antimycins from A_1 to A_8 were in fact mixtures of two isomers, differing at the acyl group on the C-8 hydroxyl oxygen. To differentiate these isomers, a second subscript, either a or b, was attached to the corresponding names (*e. g.*, A_{1a}, A_{1b}) in some papers. Very recently, A_9, A_{10} to A_{16}, and A_{17} were reported by Shiomi[10] *et al.*, Hosotani[11] *et al.*, and Lin[12] *et al.*, respectively. Like all previously known antimycins, most of the newly-reported members also consisted of two isomers differing only at the acyl group on the C-8 (*Table 1*). Some of the isomers (*e. g.*, A_{3a} and A_{4a}) carry a C-8 acyl that contains a stereogenic center. However up to now, only the stereogenic center of A_{3a} was shown to have the *S* configuration on the basis of Tsunoda's[13] total synthesis.

Various bioactivities have been reported for the antimycins, including killing of insects,[14a] mites,[14a] and fungi,[14b-e] inhibition of electron transport system[15a] as well as certain enzymes,[15b-d] and destruction[16] of cancer cells. All these, along with the interesting structure, inspired many chemists to carry out synthesis of antimycins.

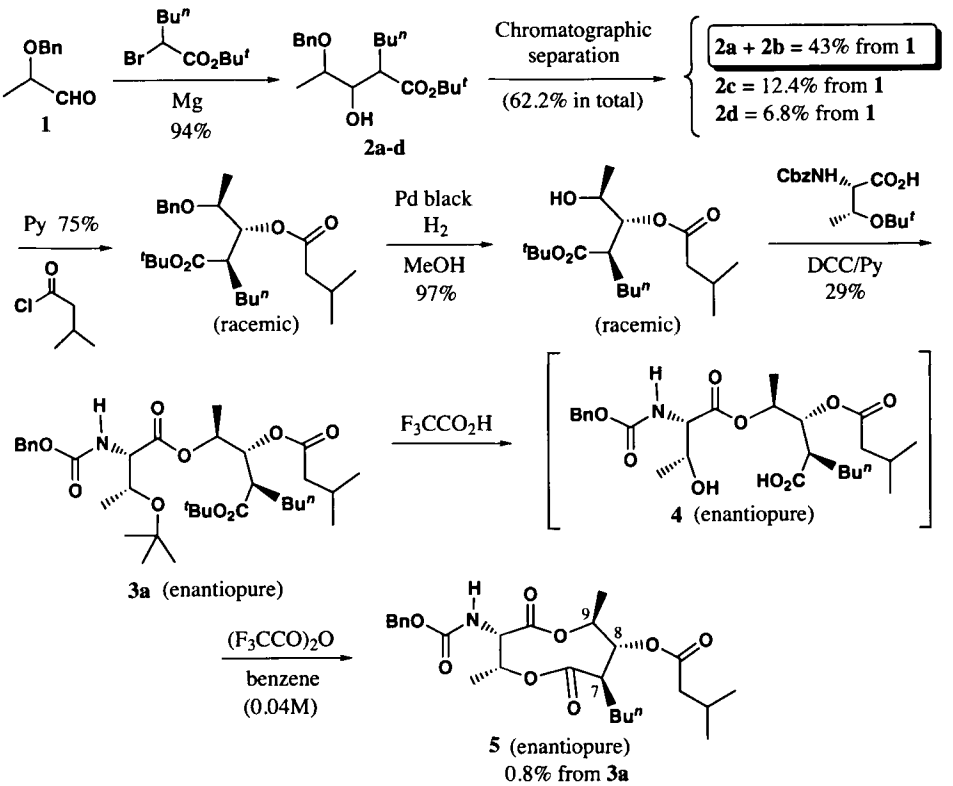
I. PUBLISHED SYNTHESES

Up to now synthetic studies on antimycins were performed only on A_3 (mostly A_{3b}), presumably because the first synthesis of this class of compounds was prompted by structural elucidation of A_{3b}, the first fully-characterized member in the antimycin family. To date there have been one racemic[17] and three enantioselective[13,18] total syntheses published, along with at least four formal[19] syntheses. Because the C-3 and C-4 of the antimycins are of the same configurations as those of L-threonine, all the syntheses published in the literature simply made use of the natural amino acid as the chiral building block for the needed moiety. Thus, the main issue to be considered in the synthesis is how to construct the remaining stereogenic centers, *i. e.* the C-7, C-8, and C-9.

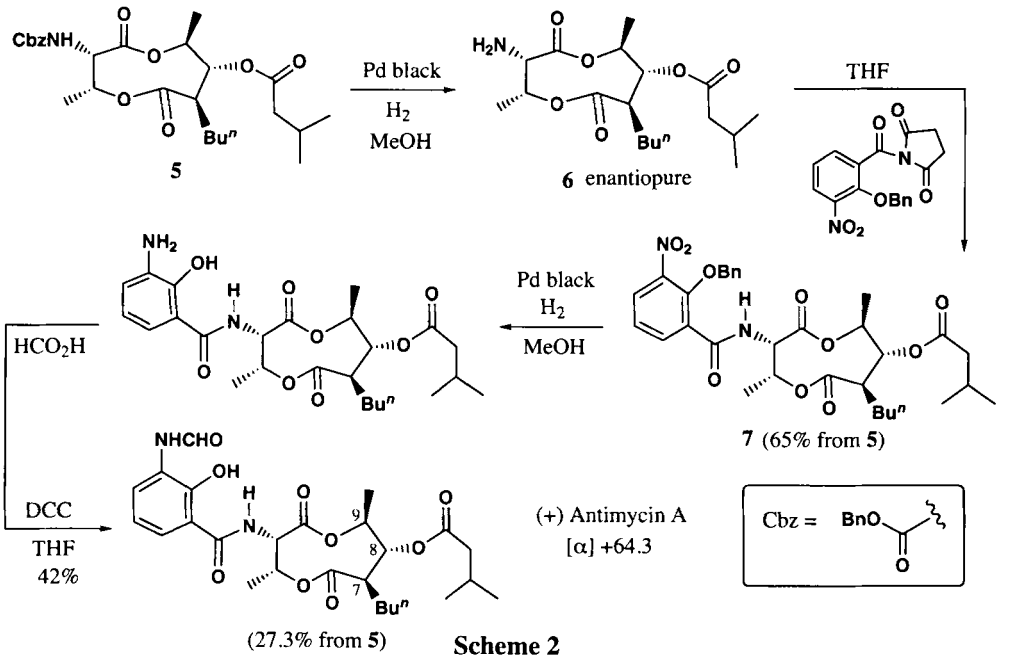
1. Kinoshita's Synthesis

The first synthesis of enantiopure antimycin (A_{3b}) was completed by Kinoshita's group. Their route is shown in *Schemes 1* and *2*. The whole synthesis consisted of 11 steps, with an overall yield of 0.019%.

The strategy of the Kinoshita's synthesis is quite straightforward, with the C-8 ester functionality being introduced immediately after creation of the C-8 hydroxyl group. However,



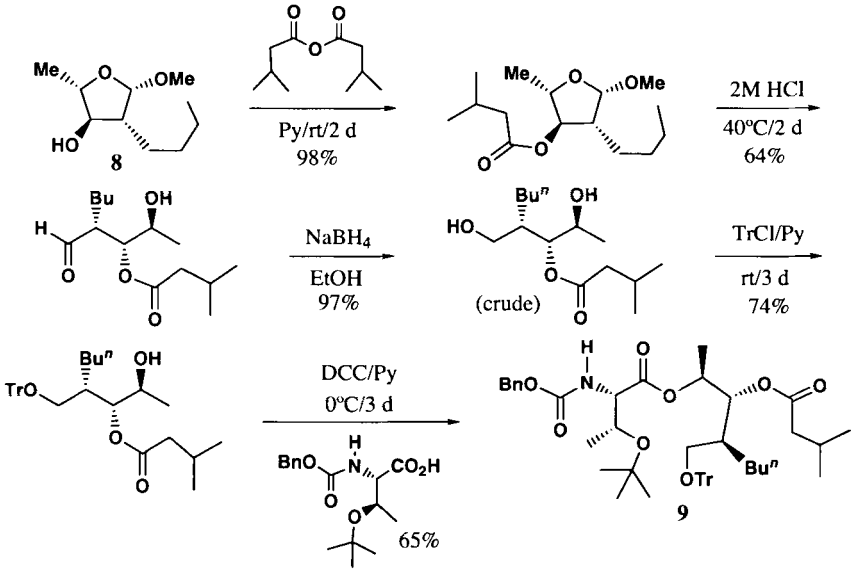
Scheme 1



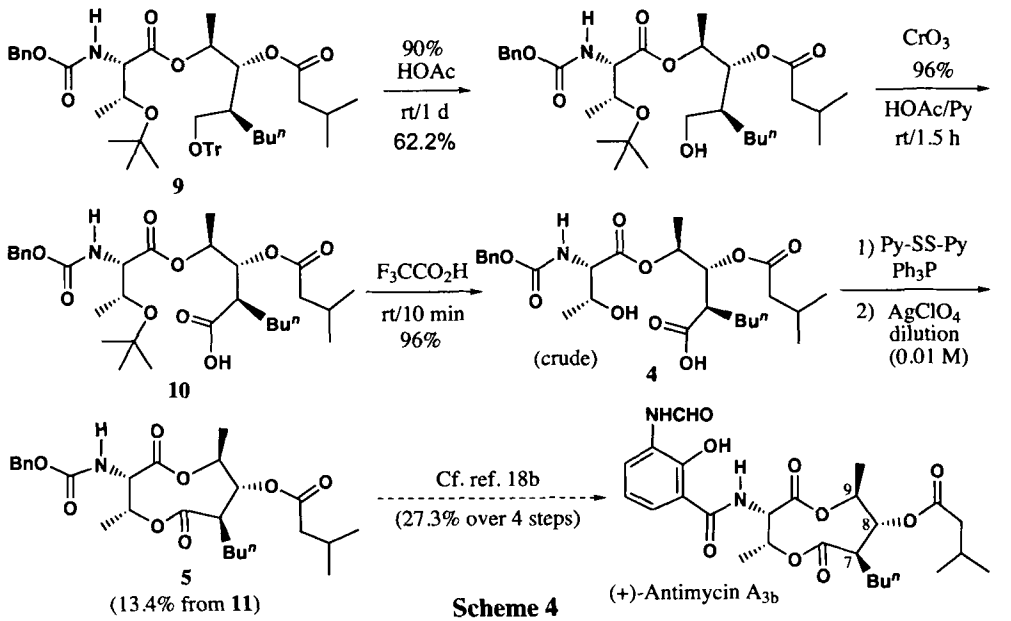
Scheme 2

the closure of the nine-membered dilactone ring suffered from very low yields (0.8%), giving the first sign for the severe adverse effect of the C-8 ester on the lactonization. Besides, the lack of enantioselectivity during the generation of the C-7, C-8, and C-9 stereogenic centers was also a major shortcoming.

The problems encountered in the first total synthesis were partially solved in their second generation (formal) synthesis (*Schemes 3* and *4*) published[19a] a few years later.



Scheme 3



Scheme 4

In the later routes, the C-7, C-8 and C-9 stereogenic centers were derived from an advanced carbohydrate precursor (**8**) with the desired configuration. The ring-closure yield was also raised to 13.4% using PySSPy/Ph_3P and $AgClO_4$ instead of the original $(F_3CCO)_2O$.

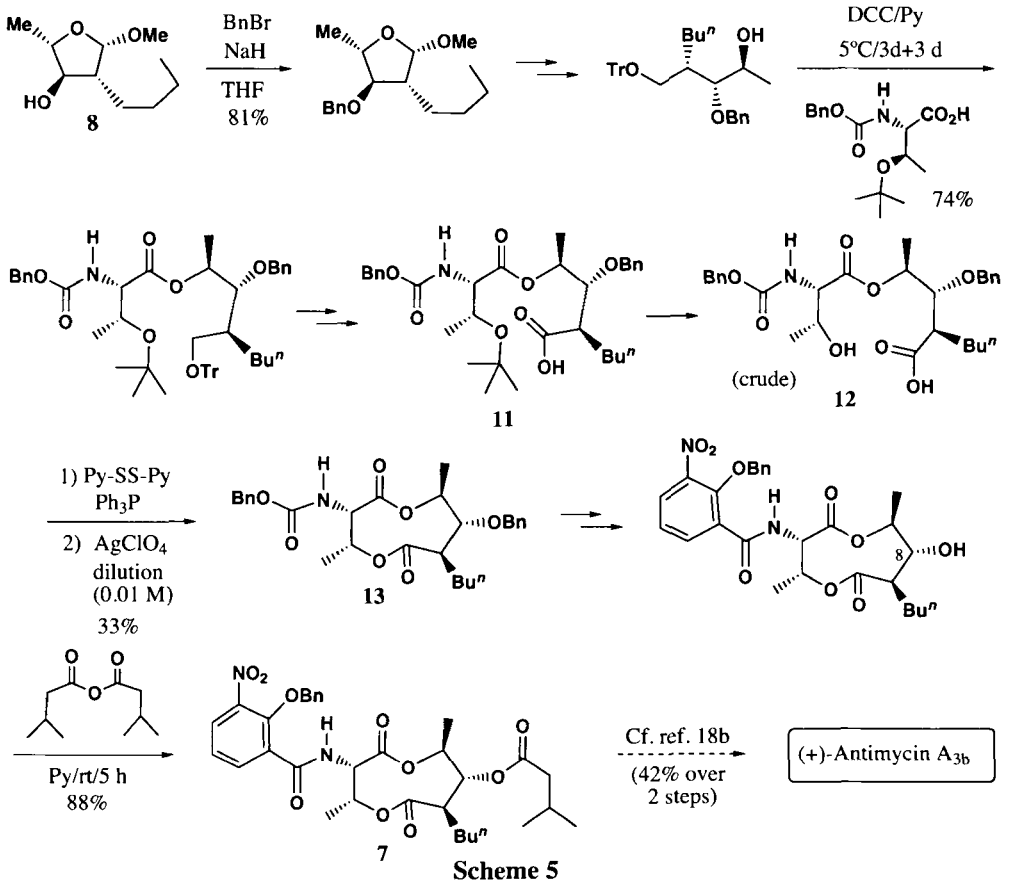
Apparently unsatisfied with the still too low yield at the lactonization step, Kinoshita and co-workers also examined an alternative strategy, *i. e.*, to use a stable protecting group such as benzyl group (Bn) to mask the C-8 hydroxyl group before completing the ring-closure of the dilactone ring (*Scheme 5*) and introducing the C-8 ester functionality at a later stage.

Such a change indeed led to favorable changes in the ring-closure step and the yield for the key lactonization was raised to 33%. After completion of the lactonization step, the benzyl protecting group was removed by hydrogenolysis and the C-8 acyl group was introduced after acylation of the threonine amino group to give the **7**, an intermediate in the Kinoshita's first total synthesis. The overall yields for this formal route was 3.6%, which was a remarkable progress compared with the previous 0.019%.

2. Oishi's Formal Synthesis

Another formal synthesis of antimycin A_{3b} was reported by Oishi[19b] and co-workers in 1983 (*Scheme 6*). They started from racemic bromide **14** through nine steps of reactions to reach a key compound **7**, an intermediate in the 1979 route of Kinoshita (*Scheme 5*).

The C-8 and C-9 stereogenic centers were generated by substrate-induced asymmetric reduction of the corresponding ketone carbonyl group with $Zn(BH_4)_2$. As in the first synthesis of Kinoshita, the racemic mixture was not separated until the optically-active threonine residue was incorporated.



8 11 12 13 7

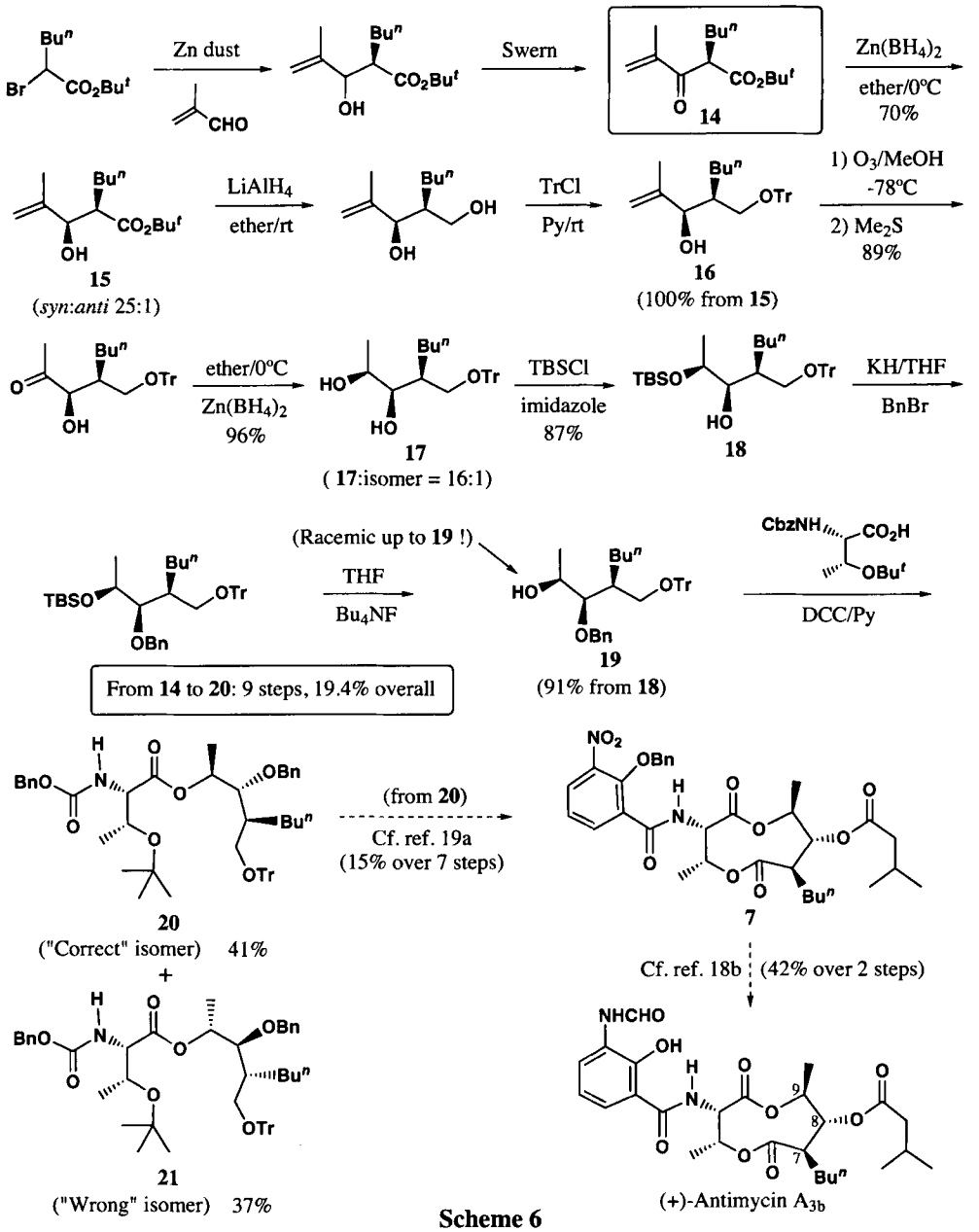
Scheme 5

To complete the remaining steps from the **20** using the Kinoshita's sequence, the formal synthesis would require 18 steps, with an overall yield of 1.22%. Although establishment of the three stereogenic centers in this approach was not very economical (because about half of the material was of wrong configuration), the diastereomeric selectivity in the ketone reduction was rather impressive (25:1 and 16:1, respectively).

3. Wasserman's Formal Synthesis

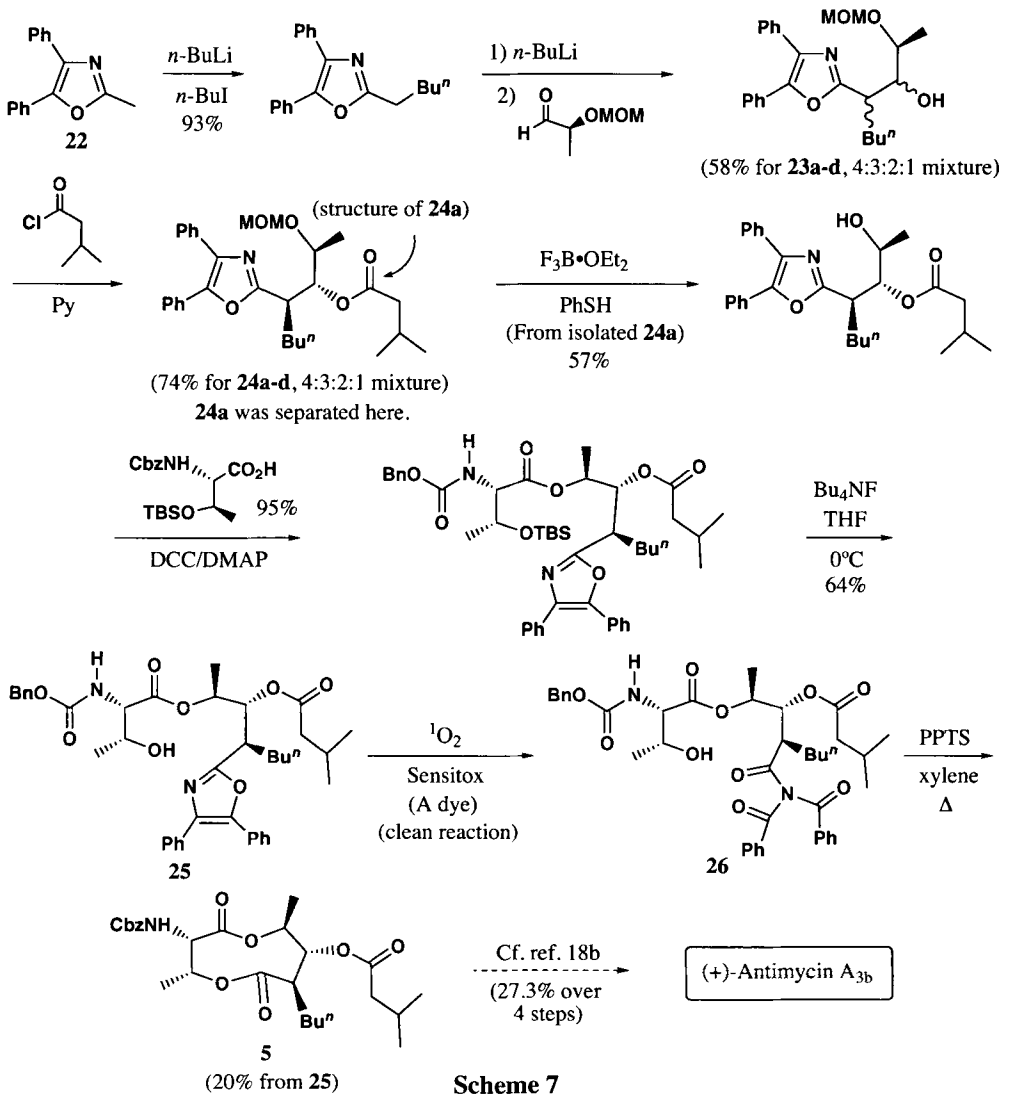
In 1985, Wasserman and Gambale[19c,d] completed a rather short formal synthesis of antimycin A_{3b} (*Scheme 7*). In their route, the C-9 stereogenic center was derived from L-lactate and the C-7/C-8 aldol moiety was constructed by a substrate-induced asymmetric aldolization.

They utilized a diphenyl substituted oxazole as carbanion stabilizer to facilitate introduction of the butyl group and the nucleophilic addition to the aldehyde carbonyl group. The oxazole also served as a latent activated carboxylic group, which was required in the later lactonization step. The selectivity for the desired isomer **24a**, however, was not very good, with the ratio between the four isomers being 4:3:2:1.



Scheme 6

The Wasserman and Gambale route also adopted a strategy of the introduction of the C-8 ester functionality at an early stage, which made the synthesis rather expeditious. After installation of the threonine moiety, the oxazole ring was cleanly cleaved with singlet oxygen to yield an activated carboxylic group. The lactonization was then achieved in 20% yield by treatment with PPTS in refluxing toluene. The yield from **22** to **5** over the eight steps was 1.1%, which means that the formal overall yield (using Kinoshita's sequence to convert **5** to antimycin A_{3b}) would be 0.3%.

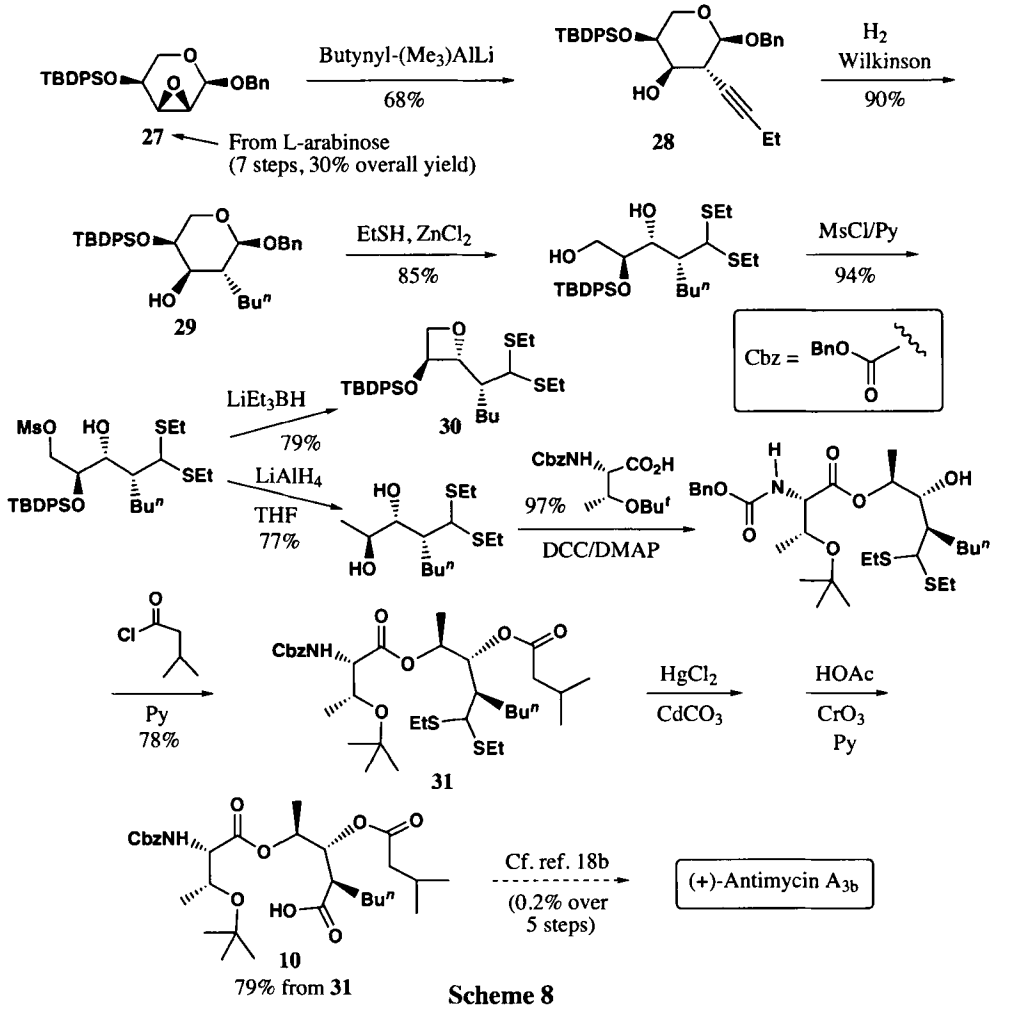


Scheme 7

4. Frejd's Formal Synthesis

Using an advanced chiron (which was derived from L-arabinose in 30% yield over seven steps) as the starting material Inghart and Frejd[19e] synthesized **10** through nine steps (*Scheme 8*), completing another formal synthesis of antimycin A_{3b}.

The stereogenic centers at C-7, C-8 and C-9 in this case were ideally set from the beginning. A regioselective opening of the epoxy ring followed by homogeneous hydrogenation of the triple bond without touching the benzyl protecting group highlights the elegance of this route. Besides, the deoxygenation to yield the C-9 methyl group was also informative. Interestingly, if utilizing $LiBHEt_3$ instead of $LiAlH_4$, a four-membered cyclic ether **30** was formed as the major product.



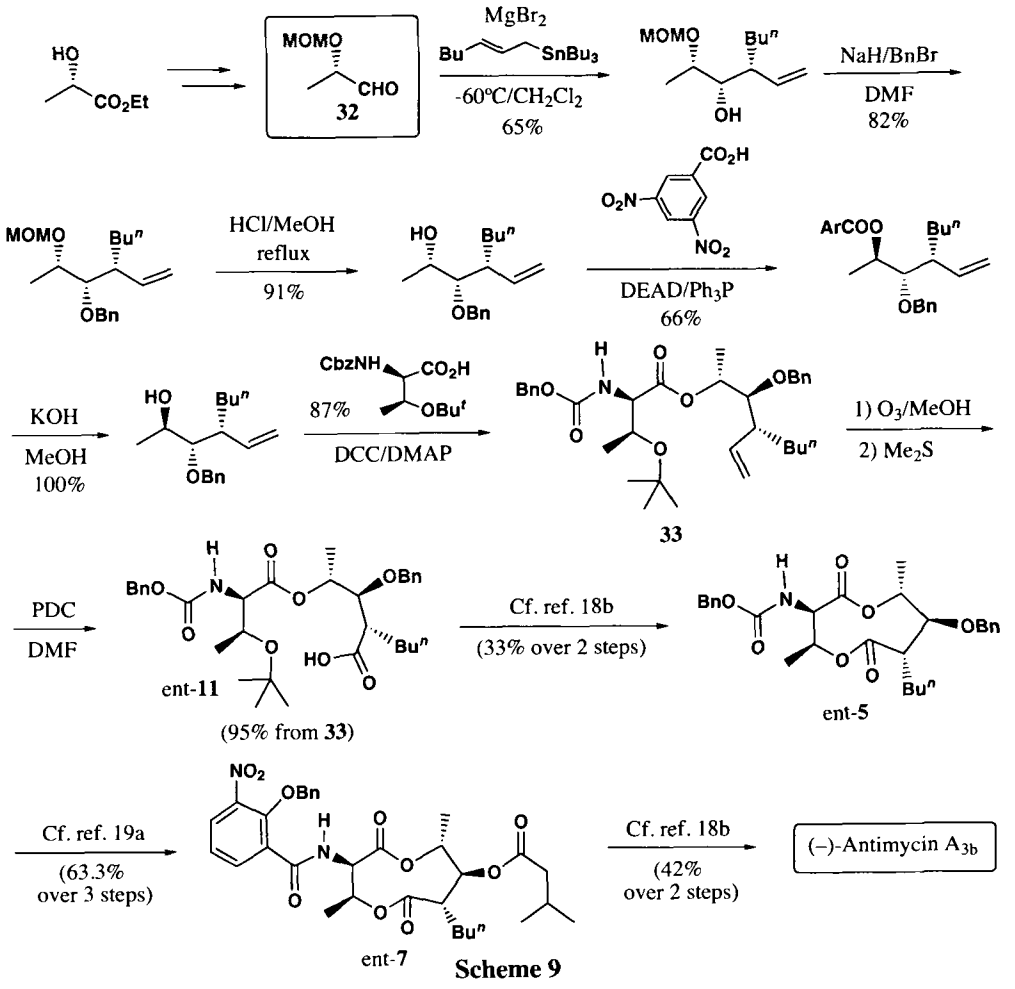
Scheme 8

As the end product of this work was an intermediate in Kinoshita's first total synthesis, the formal overall yield from **27** to antimycin A_{3b} would be 0.05% over the 14 steps.

5. Kiyota's Formal Synthesis

In 2000 Kiyota[19f] and co-workers developed a new route (*Scheme 9*). They utilized a substrate induced asymmetric allylation to construct the C-7 and C-8 stereogenic centers. Starting from L-lactate through eight steps, they obtained ent-**11** in 26.5% yield. Then following Kinoshita's route, they completed the whole synthesis of the antipode of antimycin A_{3b} in 14-15 steps with an overall yield of 2.32%.

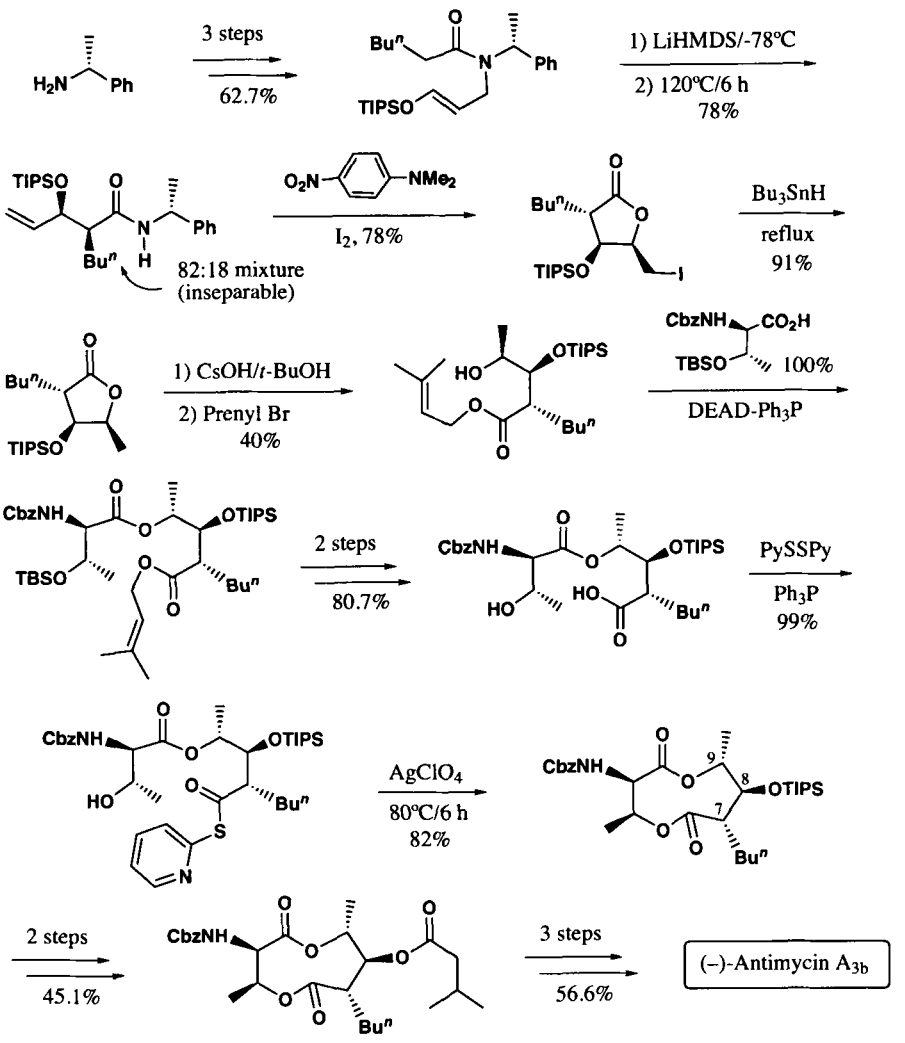
Similarly, starting from D-lactate using the same route, they also synthesized **5**, constituting a formal total synthesis of natural antimycin A_{3b}. It should be noted that in order to obtain the correct configurations at the C-7 and C-8, the stereogenic center at the C-9 must be of the "wrong" configuration. An otherwise unnecessary Mitsunobu reaction was therefore inevitable.



Scheme 9

6. Tsunoda's Synthesis

A new strategy for construction of the C-7, C-8 and C-9 stereogenic centers was recently demonstrated by Tsunoda[13a] and co-workers (*Scheme 10*) through their synthesis of the antipode of antimycin A_{3b}. They utilized (*R*)-phenylmethylamine as the source of chirality to induce the two stereogenic centers at the C-7 and C-8 through an aza-Claisen rearrangement. The C-9 chirality was then created through a substrate-induced asymmetric iodolactonization. The configuration at the C-9 in this case was also opposite to that in the end product. Hence they inverted the stereochemistry at the coupling of the aldol moiety with the threonine residue under the Mitsunobu conditions. Unlike the early investigators, Tsunoda and co-workers abandoned the strategy of introducing the C-8 acyl group at an early stage. Instead, a very stable triisopropylsilyl (TIPS) protecting group was installed on the C-8 hydroxyl group from the very beginning. With this modification, the yield for the formation of the nine-membered dilactone ring reached 82%.

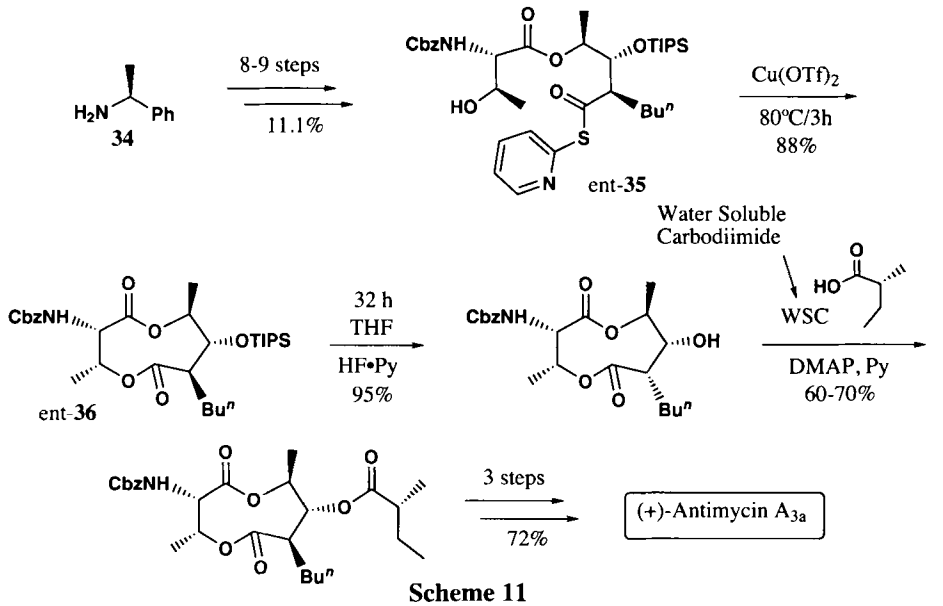


Scheme 10

In combination of the structural determination of antimycin A_{3a}, Tsunoda[13b] and co-workers later improved their synthesis at the macrolactonization step by employing $(CuOTf)_2$•PhH to replace the $AgClO_4$ and thus further raised the yield to an unprecedented 88% (*Scheme 11*). Besides, cleavage of the TIPS protecting group with HFΣPy also improved the yield by 10% (from the previous 85% with tetrabutylammonium fluoride (TBAF) to 95%). With these improvements, the overall yield of the whole synthesis was raised to ca. 4.6%.

7. Wu's Synthesis

Recently, we developed an expeditious route[18c] to antimycin A_{3b} (*Scheme 12*). In our synthesis, the C-7 and C-8 stereogenic centers were established directly from chiral auxilary-induced asymmetric aldolization under the Crimmins[20] conditions. Immediately after creation of



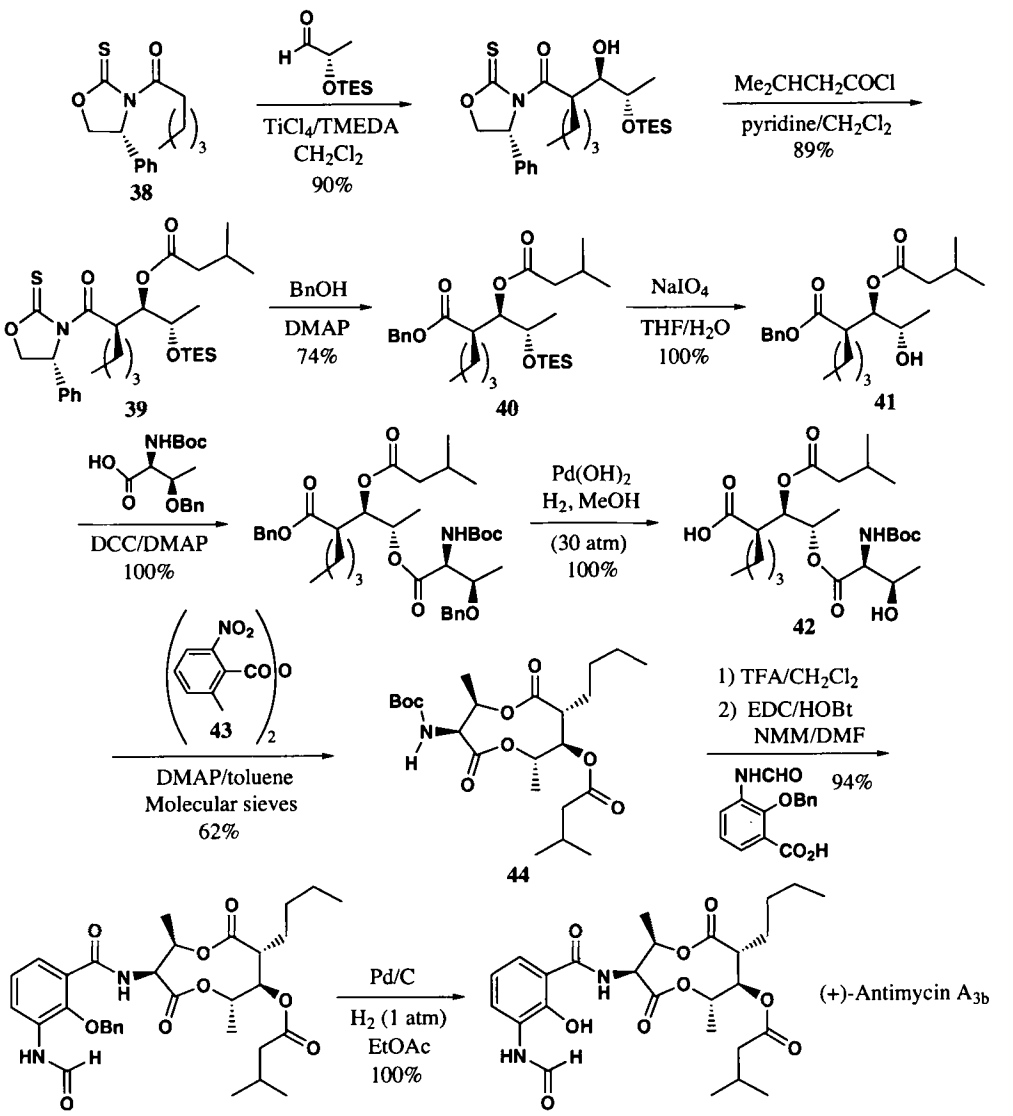
Scheme 11

the C-8 hydroxyl group, the desired acyl group was introduced to the C-8. The oxazolidinethione chiral auxiliary was then removed with benzyl alcohol (BnOH) in the presence of DMAP and the carboxylic group was concurrently protected as a benzyl ester,[21] which provided the advantage of allowing for facile deprotection at a late stage in the synthesis.

The choice of the chiral auxiliary was of critical importance. Although oxazolidinones, oxazolidinethiones, and thiazolidinethiones auxiliaries were all of more or less the same efficiency (in terms of yield and diastereoselectivity) in the aldolization step under the Crimins conditions, only the sulfur-containing ones could be readily removed under the BnOH/DMAP[21] conditions. Compared with the corresponding thiaxolidinethiones, the oxazolidinethiones are much easier to prepare as a result of appearance of our recent procedure.[22]

Removal of the triethylsilyl (TES) protecting group in **40** is worth mentioning. Because of the great tendency to form[23] a five-membered lactone (blastmycinone) through the attack of the newly-generated hydroxyl group at the benzyl ester, many commonly employed desilylating agents such as TBAF,[24a] IBX,[24b] Pd-C,[24c] and $FeCl_3$[24d] failed to give satisfactory results here. Finally the transformation was achieved in quantitative yield by using the $NaIO_4$ protocol of Yin[24e].

The long-standing problem of lactonization in the presence of the C-8 ester functionality was also solved in this work. After exhaustive attempts of many existing methods for lactonization, including TCBC (trichlorobenzoyl chloride),[25] DCC/DMAP,[26] PySSPy/PPh_3,[13b] DPKO,[27] MNBA (2-methyl-6-nitrobenzoic anhydride, **43**) of Shiina[28] was found to be the best reagent for the reaction. Using MNBA, the desired lactone **44** could be obtained in 62% yield in the presence of activated/powdered 4Å molecular sieves. The whole synthesis took 10 steps



Scheme 12

from the acyl oxazolidinethione **38** and the overall yield from **38** to the end product ((+)-antimycin A_{3b}) was 34.5%.

II. CONCLUSION

Because of their interesting structures and significant biological activities, the antimycins have been attractive targets for asymmetric synthesis since the 1970's. As seen from the published work, the problems that contributed significantly to the low efficiency of the previous syntheses were mainly enantioselective construction of the stereogenic centers at C-

7/C-8 and closing of the nine-membered dilactone ring in the presence of the C-8 ester functionality. By using a chiral auxiliary induced asymmetric aldolization under the Crimmins conditions and the Shiina reagent at the lactonization step, respectively, these problems now have been overcome with a good degree of satisfaction.

Acknowledgement.- This work was supported by the National Natural Science Foundation of China (20025207, 20272071, 20372075, 20321202, 20672129, 20621062), and the Chinese Academy of Sciences ("Knowledge Innovation" project, KGCX2-SW-209, and KJCX2.YW.H08).

REFERENCES

1. C. Leben and G. W. Keitt, *Phytopathology*, **38**, 899 (1948).

2. B. R. Dunshee, C. Leben, G. W. Keitt and F. M. Strong, *J. Am. Chem. Soc.*, **71**, 2436 (1949).

3. (a) H. G. Schneider, G. M. Tener and F. M. Strong, *Arch. Biochem. Biophys.*, **37**, 147 (1952). (b) J. L. Lockwood, C. Leben and G. W. Keitt, *Phytopathology*, **44**, 438 (1954).

4. (a) Y. Sakagami, S. Takeuchi, H. Yonehara, H. Sakai and M. Takashima, *J. Antibiot.*, **9**, 1 (1956). (b) K. Watanabe,T. Tanaka, K. Fukuhara, N. Miyairi, H. Yonehara and H. Umezawa, *J. Antibiot. Ser. A*, **10**, 39 (1957). (c) H. Yonehara and S. Takeuchi, *J. Antibit. Ser. A*, **11**, 254 (1958).

5. W.-C. Liu and F. M. Strong, *J. Am. Chem. Soc.*, **81**, 4387 (1959).

6. G. Schilling, D. Berti, and D. Kluepfel, *J. Antibiot.*, **23**, 81 (1970).

7. C. Barrow, J. Oleynek, V. Marinelli, H. H. Sun, P. Kaplita, D. M. Sedlock, A. M. Gillum, C. C. Chadwick and R. Cooper, *J. Antibiot.*, **50**, 729 (1997).

8. K. Shiomi, K. Hatae, H. Hatanho, A. Matsumoto, Y. Takahashi, C.-L. Jiang, H. Tomoda, S. Kobayashi, H. Tanaka and S. Omura, *J. Antibiot.*, **58**, 74 (2005).

9. N. Hosotani, K. Kumagai, H. Nakagawa, T. Shimatani and I. Saji, *J. Antibiot.*, **58**, 460 (2005).

10. G. Chen, B. Lin, Y. Lin, F. Xie, W. Lu and W.-F. Fong, *J. Antibiot.*, **58**, 519 (2005).

11. (a) E. E. Van Tamelen, J. P. Dickie, M. E. Loomans, R. S. Dewey and F. M. Strong, *J. Am. Chem. Soc.*, **83**, 1639 (1961). (b) A. J. Birch, D. W. Cameron, Y. Harada and R. W. Rickards, *J. Chem. Soc.*, 889 (**1961**).

12. M. Kinoshita, S. Asuraki and S. Umezawa, *J. Antibiot.*, **25**, 373 (1972).

13. (a) T. Tsunoda, T. Nishii, M. Yoshizuka, C. Yamasaki, T. Suzuki and S. Ito, *Tetrahedron Lett.*, **41**, 7667 (2000). (b) T. Nishii, S. Suzuki, K. Yoshida, K. Araki and T. Tsunoda, *Tetrahedron Lett.*, **44**, 7829 (2003).

14. (a) G. S. Kido and E. Spyhalski, *Science,* **112**, 172 (1950). (b) C. Leben and G. W. Keitt, *Phytopathology*, **39**, 529 (1949). (c) ref. 10 above. (d) K. Nakayama, F. Okamoto and Y. Harada, *J. Antibiot.*, **9**, 63 (1956).

15. (a) V. R. Potter and A. E. Reif, *J. Biol Chem.* **194**, 287 (1952). (b) ref. 7 above. (c) M. B. Thorn, *Biochem J.* **63**, 420 (1956). (d) A. E. Reif and V. R. Potter, *Cancer Res.*, **13**, 49 (1953).

16. (a) M. A. King, *Cytometry, Part A*, **63A**, 69 (2005). (b) S. -P. Tzung, K. M. Kim, G. Basañez, C. D. Giedt, J. Simon, J. Zimmerberg, K. Y. J. Zhang and D. M. Hockenbery, *Nat. Cell Biol.*, **3**, 183 (2001).

17. M. Kinoshita, M. Wada and S. Umezawa, *J. Antibiot.*, **22**, 580 (1969).

18. (a) M. Kinoshita, M. Wada, S. Aburagi and S. Umezawa, *J. Antibiot.*, **24**, 724 (1971). (b) M. Kinoshita, S. Aburaki, M. Wada, and S. Umezawa, *Bull. Chem. Soc. Jpn*, **46**, 1279 (1973). (c) Y.-K. Wu and Y.-Q. Yang, *J. Org. Chem.*, **71**, 4296 (2006). (d) For a condensed version of the present review written in Chinese, see: Y.-K. Wu and Y.-Q. Yang, *Chin. J. Org. Chem.*, **26**, 1370 (2006).

19. (a) S. Aburaki and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, 52, 198 (1979). (b) T. Nakata, M. Fukui and T. Oishi, *Tetrahedron Lett.*, **24**, 2657 (1983). (c) H. H. Wasserman and R. J. Gambale, *J. Am. Chem. Soc.*, **107**, 1423 (1985). (d) H. H. Wasserman and R. J. Gambale, *Tetrahedron,* **48**, 7059 (1992). (e) T. Inghart and T. Frejd, *Tetrahedron,* **47**, 6483 (1991). (f) H. Kondo, T. Oritani and H. Kiyota, *Heterocycl. Commun.*, **6,** 211 (2000).

20. M. T. Crimmins, B. W. King and E. Tabet, E. *J. Am. Chem. Soc.*, **119**, 7883 (1997).

21. Y.-K. Wu, Y.-P. Sun, Y.-Q. Yang, Q. Hu and Q. Zhang, *J. Org. Chem.*, **69**, 6141 (2004).

22. Y.-K. Wu, Y.-Q. Yang and Q. Hu, *J. Org. Chem.*, **69**, 3990 (2004).

23. Y.-Q. Yang and Y.-K. Wu, *Chin. J. Chem.*, **23**, 1519 (2005).

24. (a) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972). (b) Y.-K. Wu, J.-H. Huang, X. Shen, Q. Hu, C.-J. Tang and L. Li, *Org. Lett.*, **4**, 2141 (2002). (c) D. Rotulo-Sims and J. Pruent, *Org. Lett.*, **4**, 4701 (2002). (d) Y.-Q. Yang, J.-R. Cui, L.-G. Zhu, Y.-P. Sun, and Y.-K. Wu, *Synlett,* 1260 (**2006**). (e) M. Wang, C. Li, D. Yin, and X.-T. Liang, *Tetrahedron Lett.*, **43**, 8727 (2002).

25. M. Yamaguchi, J. Innaga, K. Hirata, H. Saeki and T. Katsuki, *Bull. Chem. Soc. Jpn,* **52**, 1989 (1979).

26. E. P. Boden and G. E. Keck, *J. Org. Chem.*, **50**, 2394 (1985).

27. C. Palomo, M. Oiarbide, J. M. Garcia, A. Gonzalez, R. Pazos, J. M. Odriozola, P. Banuelos, M. Tello and A. Linden, *J. Org. Chem.*, **69**, 4126 (2004).

28. I. Shiina, M. Kubota, H. Oshiumi and M. Hashizume, *J. Org. Chem.*, **69**, 1822 (2004).

(Received November 2, 2006; in final form January 11, 2007)