Electronic Supplementary Material (ESI) for Natural Product Reports.

Supplementary Information

Current biochemical understanding regarding the metabolism of acinetobactin, the major siderophore of the human pathogen *Acinetobacter baumannii*, and outlook for discovery of novel anti-infectious agents based thereon

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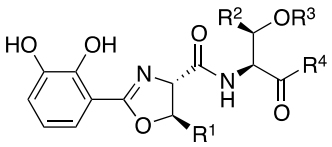
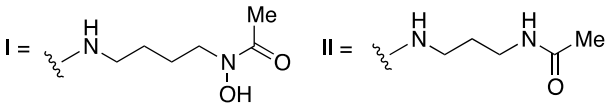
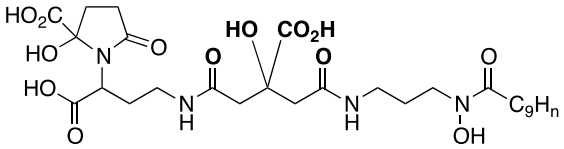


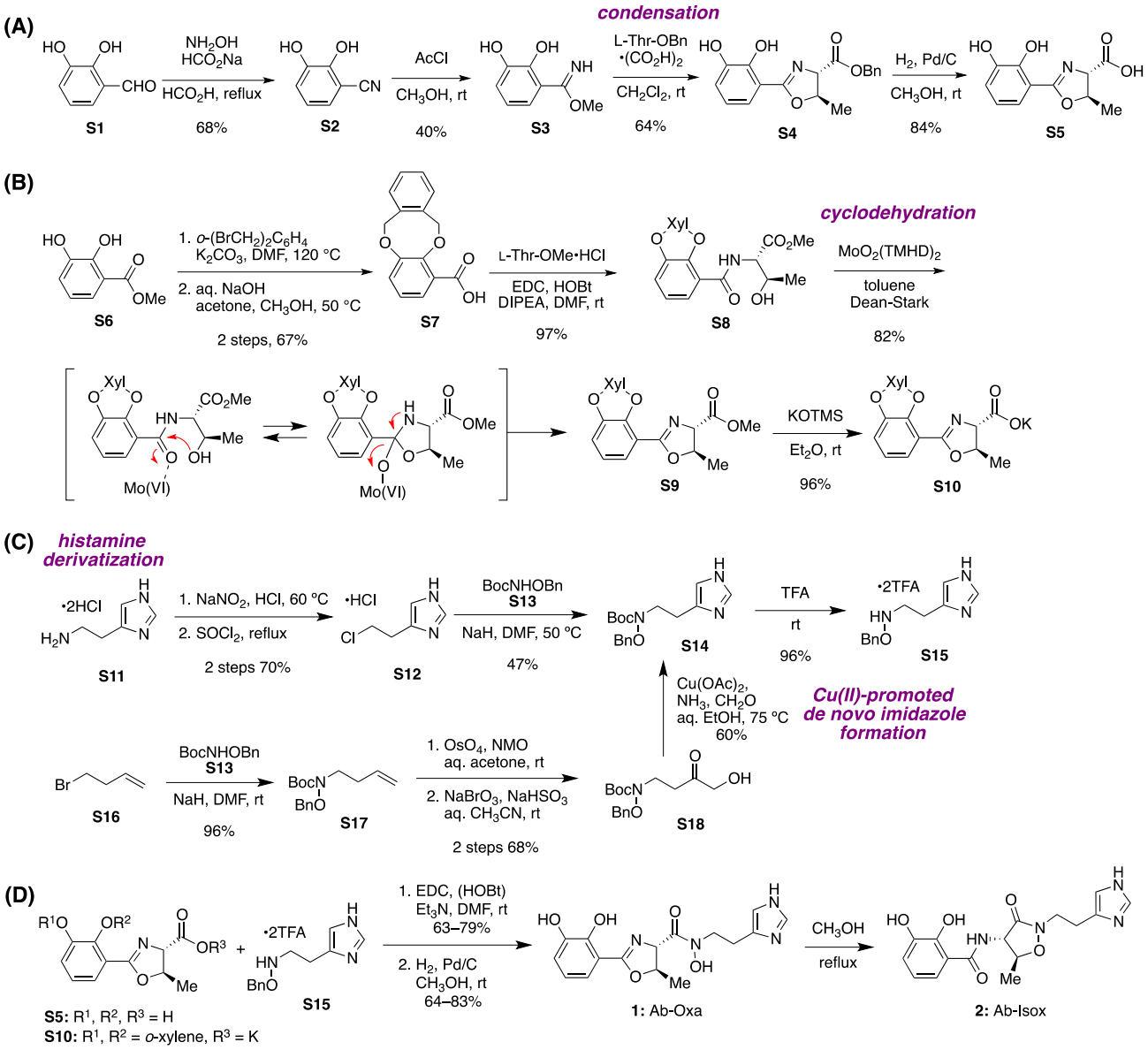
	R^1	R^2	R^3	R^4
fimsbactin A	H	H		I
fimsbactin B	Me	H		I
fimsbactin C	Me	Me		I
fimsbactin D	H	H		II
fimsbactin E	H	H		OH
fimsbactin F	H	H	H	I





n = 17: baumannoferrin A
n = 19: baumannoferrin B

Supplementary Figure 1. Structures of fimsbactins and baumannoferrins, other siderophores for *Acinetobacter baumanii*.



Supplementary Scheme 1. Total synthesis of acinetobactin. Currently, two synthetic routes have been devised by Takeuchi and Kim laboratories,[S1, S2] and they share a common theme in that two fragments, oxazoline acid and *N*-hydroxy histamine derivatives, are prepared first and a subsequent combination between them followed by global deprotection completes the total synthesis. (A) Preparation of oxazoline acid fragment **S5** by Takeuchi laboratory involving a condensation between imidate **S3** and L-Thr-OBn to construct the oxazoline ring of **S4**. (B) Preparation of oxazoline acid fragment **S10** by Kim laboratory, in which the oxazoline ring of **S9** was constructed by dehydrative cyclization from **S8** using a molybdenum oxide catalyst. (C) Preparation of *N*-hydroxy histamine fragment **S15**. Takeuchi laboratory accessed this fragment directly from histamine **S11** involving replacement of a primary amine group with chloride followed by a nucleophilic substitution with protected hydroxyl amine precursor **S13**. Kim and co-workers undertook a different approach involving a Cu(II)-promoted de novo imidazole formation (**S18** → **S14**) from simple alkenyl halide precursor **S16**. (D) Completion of total syntheses of Ab-Oxa (**1**) and Ab-Isox (**2**). Both research laboratories used the same methods to finish the syntheses initiated by amide formation between oxazoline acid fragment **S5** or **S10** and *N*-hydroxy histamine fragment **S15**. Global deprotection based on hydrogenolysis successfully yielded Ab-Oxa (**1**). Then, this compound could be readily converted to Ab-Isox (**2**) by simple reflux in methanol, corroborating the biosynthetic proposal by Walsh and co-worker described in the main text.

References

S1. Y. Takeuchi, S. Ozaki, M. Satoh, K.-i. Mimura, S.-i. Hara, H. Abe, H. Nishioka and T. Harayama, *Chem. Pharm. Bull.*, 2010, **58**, 1552-1553.

S2. J. Kim, J. E. Lee, H. Ree and H. J. Kim, *Bull. Kor. Chem. Soc.*, 2015, **36**, 439-441.