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Construction of All-Substituted Pyrrolidine Derivative with Multiple Stereogenic Centers and Betti-Base-derived γ-Amino Alcohols by [1,2]-Wittig Rearrangement

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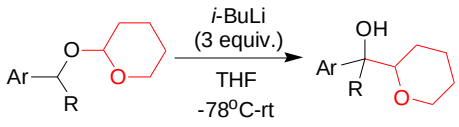
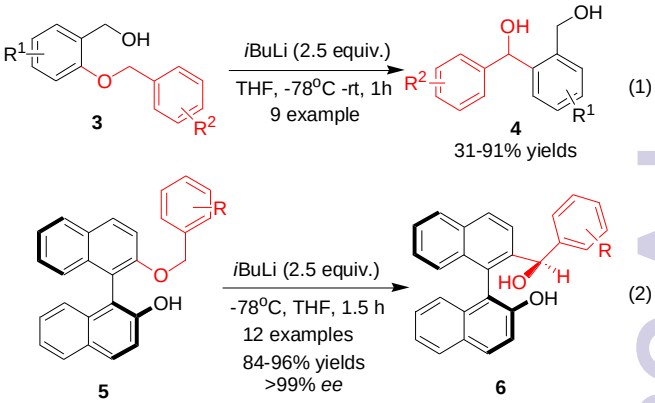
A new class of substituted γ-amino alcohols and downstream pyrrolidine derivatives has been synthesized successfully from simple 1-phenyl-ethylamine, in which a representative all-substituted pyrrolidine derivative with multiple stereogenic centers was obtained by highly diastereoselective [1,2]-Wittig rearrangement and intramolecular cyclization with perfect chirality transfer (up to >99.9% *de*) and good yields.

The Wittig rearrangement is a synthetically useful tool in organic chemistry, especially for the preparation of secondary alcohols and biological active molecules.[1] Among the Wittig rearrangements, the [2,3]-Wittig rearrangement is certainly synthetically mature and one of the most studied rearrangement reactions.[2] Similarly, the [1,2]-Wittig rearrangement is also very important and has been the subject of numerous mechanistic studies as well as synthetic application in organic synthesis.[3] The conventional initiation of such rearrangement is generally accomplished by using a stoichiometric amount of strong bases, such as *n*-BuLi, *s*-BuLi, *t*-BuLi, or NaH, followed by [1,2]-sigmatropic recombination of a pair of radicals to provide corresponding alcohols.[3] In the past decades, many reaction systems as well as mechanistic studies for the [1,2]-Wittig rearrangement have been studied thoroughly[1-3] However, in comparison to that of [2,3]-Wittig rearrangement, the synthetic utilizations of the [1,2]-Wittig rearrangement remains severely limited because of the restricted range of substrates and rather low yields in most cases. For example, we have ever found that only few *sec*-aromatic THP acetal compounds could be used as suitable substrates for the [1,2]-Wittig rearrangement, in which three out of ten examples led to the moderate-to-high yields of generation of new carbon-carbon bond for the synthesis of aromatic tertiary alcohols (Scheme 1).[4] The unsuccessful findings on the [1,2]-Wittig rearrangement of THP acetal compounds showed that the synthe applications of [1,2]-Wittig rearrangement in organic synthesis have remained limited. In addition, although [1,2]-Wittig rearrangeme have stimulated intensive interest in organic chemistry, there are few successful examples on stereoselective [1,2]-Wittig rearrangement with high diastereoselectivity and enantioselectivity.[1-3,5]



2a: Ar = Ph, R = Ph, 87% yield;
2b: Ar = 3-OMePh, R = Ph, 71% yield;
2c: Ar = 4-OMePh, R = Ph, 47% yield;
2d: Ar = 2-OMePh, R = Ph, <5% yield;
2e: Ar = 4-MePh, R = Ph, <5% yield;
2f: Ar = 4-FPh, R = Ph, <5% yield;
2g: Ar = Ph, R = *i*-Pr, No reaction;
2h: Ar = Ph, R = Me, No reaction;
2i: Ar = 4-MePh, R = *i*-Pr, No reaction;
2j: Ar = Ph, R = *n*-Pr, No reaction

Scheme 1. Previous findings on the unsuccessful [1,2]-Wittig rearrangement of THP acetal compounds: Rather low yields and narrow substrate scope.[4]



Scheme 2. Neighboring lithium-assisted [1,2]-Wittig rearrangement (NLAWR).

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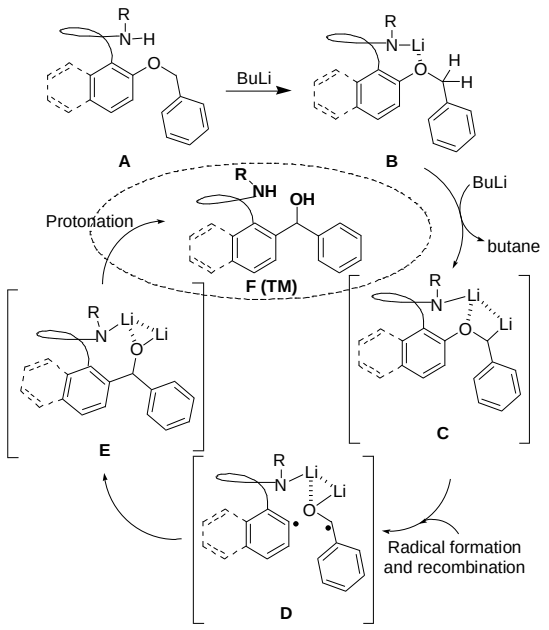
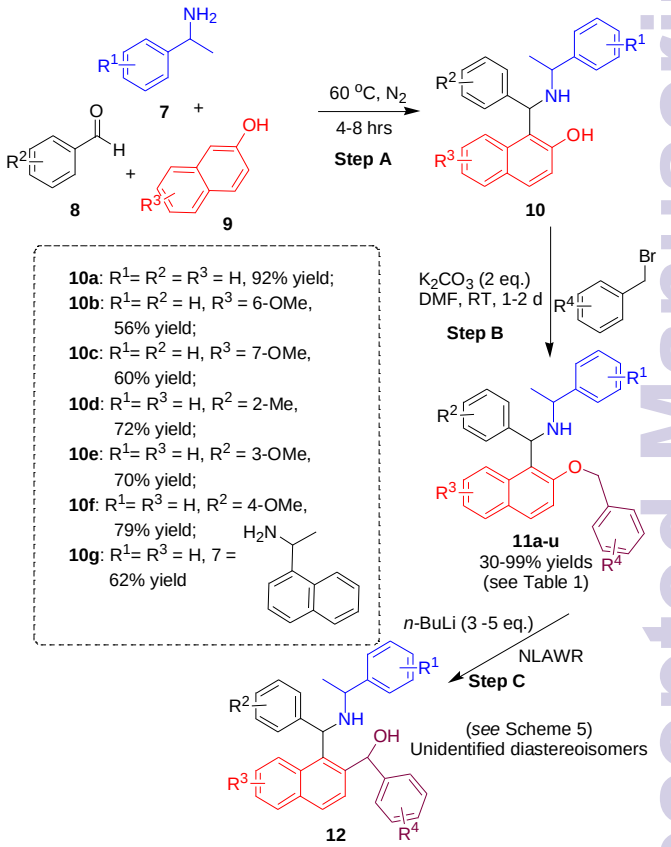
In order to widen the substrate scope of [1,2]-Wittig rearrangement, we have sought to employ benzyl ethers substrates bearing alcohol groups based on the hypothesis that the neighboring lithium was able to accelerate the deprotonation/lithiation of α-carbon center of benzyl moiety to the subsequent [1,2]-Wittig rearrangement (Scheme 2).[5] Fortunately in this work, related benzyl ether substrates were found to undergo [1,2]-Wittig rearrangement with good results when treated with a strong base. More importantly, the axial chiral monobenzylated BINOLs could transformed into a synthetically useful 1,1'-binaphthalene-2-α-arylmethanol-2'-ol (Ar-BINMOL) with axial and sp^3 central chirality through the strategy of neighboring lithium-assisted [1,2]-Wittig rearrangement (Equation 2 of Scheme 2).[5] Especially, the stereoselective [1,2]-Wittig rearrangement showed very broad substrate scope with excellent diasteroselectivities/enantioselectivities and yields.[6] Thus, the strategy of neighboring lithium-assisted [1,2]-Wittig rearrangement gave us an opportunity to overcome the inherent limitation of certain [1,2]-Wittig rearrangement in narrow substrate scope as well as poor yields. Especially in the past years, we have reported the powerful potentials of Ar-BINMOLs and its derivatives as chiral ligands in asymmetric catalysis, in which the strategy of NLAWR plays key role in the development of novel and useful ligands.[7]



Scheme 3. Proposed reaction system for the synthesis of amino alcohol through neighboring lithium-assisted [1,2]-Wittig rearrangement (NLAWR)

Given the potential synthetic utility of and biological relevance of substituted amino alcohols, we sought to further examine the strategy of neighboring lithium-assisted [1,2]-Wittig rearrangement in the synthesis of amino alcohols. In our proposed system, the neighboring lithium-assisted [1,2]-Wittig rearrangement could be controlled by chiral secondary amine group on the functional Betti base molecule bearing benzyl ether. The proposed [1,2]-Wittig rearrangement reaction is shown in Scheme 3.[1-3] At first, deprotonation of N-H of secondary amine by strong base followed by double deprotonation of C-H benzyl ether with the aid of neighboring lithium provides organic lithium intermediate **C**. Conventional radical formation and subsequent recombination is terminated at the [1,2]-Wittig rearrangement to the desired product **E**. Finally, protonation of compound **E** resulted in the amino alcohol bearing secondary α-arylmethanol.



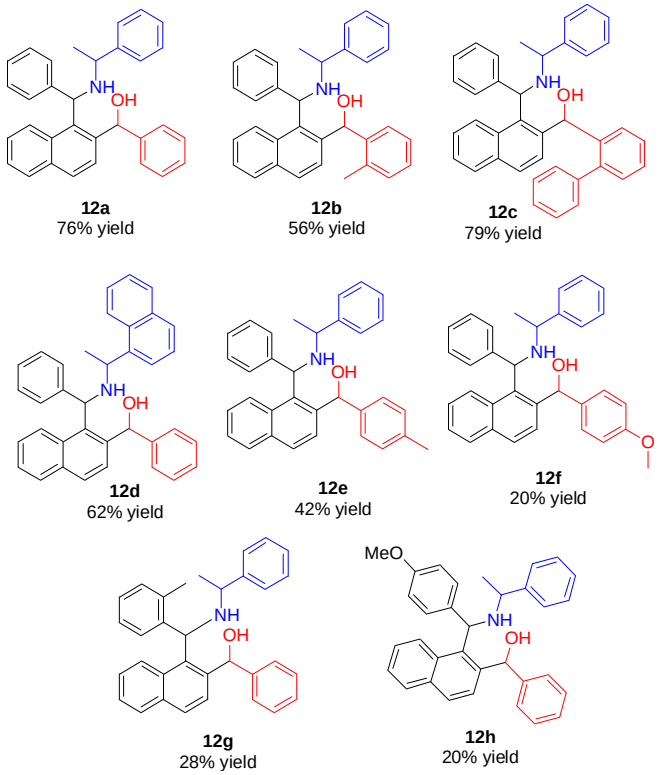
Scheme 4. The synthetic procedure to Betti base-derived amino alcohols **12**.

To ascertain the viability of the proposed neighboring lithium-assisted [1,2]-Wittig rearrangement, we attempted the synthesis of Betti base as the starting material because the Betti base is arguably the synthetically useful molecules in organic synthesis and asymmetric catalysis.[8] The synthesis of Betti base-derived compound bearing benzyl ether showed in Scheme 4 was performed under the reported reaction conditions. In addition, various derivatives were also achieved with the similar method (Scheme 4). At the first step, we selectively synthesized representative Betti bases from the commercial available 1-phenyl-ethylamine (Step A). Similarly to previous reports,[9] these Betti bases were obtained easily by condensation of 2-naphthol, aromatic aldehydes, and 1-phenyl-ethylamine, in good to excellent yields within a short time. Alkylation of Betti base with various benzylic bromides resulted in selective synthesis of products **11a-u** bearing benzyl ether (Step B of Scheme 4). In this step, most of reactions gave the desired products in good yields (Table 1). And we then initially studied the neighboring lithium-assisted [1,2]-Wittig rearrangement of benzylated Betti base **11a**. Subjection of compound **11a** to our previously developed conditions (*n*-BuLi, THF, -78 °C) afforded 76% yield of product **12a** resulting from [1,2]-Wittig rearrangement, consistent with the fact that the existence of secondary amine group on this molecule is crucial to the [1,2]-Wittig rearrangement.

Table 1. The reaction results of various Betti base-derived benzyl ethers **11** in the etherification of Betti bases **10**.[a]

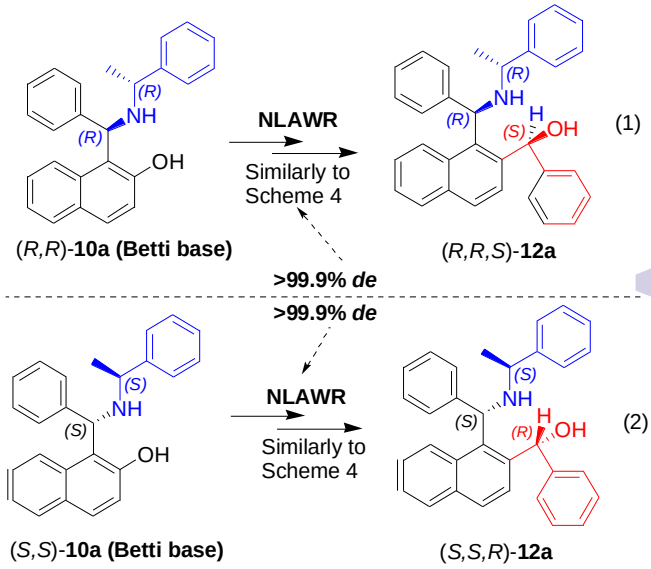
Entry	R^1	R^2	R^3	R^4	Yield (%)[b]
1	H	H	H	H	**11a**: 85
2	H	H	H	2-Me	**11b**: 65
3	H	H	H	4-Me	**11c**: 85
4	H	H	H	4-*t*Bu	**11d**: 99
5	H	H	H	4-OMe	**11e**: 80
6	H	H	H	2-Ph	**11f**: 90
7	H	H	H	allyl ether	**11g**: 80
8	H	H	H	2,3,4,5,6-F_5	**11h**: 62
9	H	H	H	4-F	**11i**: 82
10	H	H	H	2-F	**11j**: 80
11	H	H	H	3-Br	**11k**: 60
12	H	H	H	4-Br	**11l**: 68
13	H	H	H	2-Br,5-F	**11m**: 77
14	H	H	H	2,4-F_2	**11n**: 73
15	H	H	H	4-NO_2	**11o**: 36
16	H	H	H	3-NO_2	**11p**: 30
17		10g		H	**11q**: 83
18	H	H	H	3-Me	**11r**: 86
19	H	H	7-OMe	H	**11s**: 60
20	H	4-OMe	H	H	**11t**: 68
21	H	2-Me	H	H	**11u**: 40

[a] The step B of Scheme 4 was carried out with at least 5 mmol of starting materials and the detailed experimental procedure was provided in Supporting Information. [b] Total isolated yield (%) of diastereoisomer mixtures, and the Betti base-derived benzyl ethers **11** could not be purified by flash column chromatography according to previous reports on the synthesis of Betti bases[8].



Scheme 5. The reaction results of neighboring lithium-assisted [1,2]-Wittig rearrangement (NLAWR) of Betti base-derived benzyl ethers **11** to Betti base-derived amino alcohols **12**.

Based on these promising observations, we continued to evaluated the scope of neighboring lithium-assisted [1,2]-Wittig rearrangement of **11** (Table 1). Unexpectedly, the substituent on the phenyl ring of the compound **11** appears to have a remarkable effect on the [1,2]-Wittig rearrangement. As shown in Scheme 5, we found that the desired amino alcohols **12** were obtained in different yields from 20-79% because of differentiated reactivity in this radical process. When an electron-donating group, such as methyl, methoxyl, or phenyl group, was introduced at the phenyl ring, the [1,2]-Wittig rearrangement reaction occurred with varied conversions in comparison to that of other substituents on phenyl ring of Betti base-derived benzyl ethers. As expected, halide- and nitro-substituted substrates were not suitable reactants in this reaction. These results showed that the [1,2]-Wittig rearrangement was limited to the substituents on the Betti base-derived benzyl ethers, and perhaps there was some underlying factor for the radical formation and subsequent recombination. Notably, when the secondary amine group was transferred into tertiary amine group, the desired product through [1,2]-Wittig rearrangement was not observed. Although the substrate scope of [1,2]-Wittig rearrangement of Betti base-derived benzyl ethers is not perfect or narrow, our reaction system provides an approach to the synthesis of structurally diverse γ-amino alcohols (Scheme 5).



Scheme 6. The synthesis of chiral Betti base-derived amino alcohols: Perfect diastereoselectivity (>99.9% *de*) in the [1,2]-Wittig rearrangement

As the neighboring lithium-assisted [1,2]-Wittig rearrangement of BINOL-derived benzyl ethers proceed with a satisfactory level of diastereoselectivity,[5] the stage was set to evaluate the diastereoselective induction by the remote stereogenic centers on the enantiomerically pure Betti base. As described in the previous reports,[8] the construction of optically pure Betti base and its derivatives is not an easy task. Most of Betti bases achieved from the condensation of 2-naphthol, aromatic aldehydes, and chiral 1-phenyl-ethylamine were not enantiomerically pure. Thus inspired by the work on the synthesis of chiral Betti base-derived amino phosphine ligands reported by Ding and coworkers,[10] we chose **11a** as a model molecule to investigate the diastereoselective [1,2]

Wittig rearrangement. The diastereomerically pure Betti base **10a** and its benzylated ether **11a** was prepared according to the literature method.[9,10] And then the compound **11a** was converted to amino alcohol **12a** under the NLAWR conditions (Scheme 6). The resulting amino alcohol **12a** was turned out to be diastereomerically pure that determined by chiral HPLC analysis (See Supporting Information). And the absolute configuration of amino alcohols showed in Scheme 6, that could be derived from (*R*)-1-phenyl-ethylamine or (*S*)-1-phenyl-ethylamine in good yield respectively, was established by experimental electronic circular dichroism (ECD) spectra in combination with theory calculation.[11] On the basis of the good agreement observed between experimental and calculated CD spectra (*See* Supporting Information), the absolute configuration of novel amino alcohol in equation 1 is (*R,R,S*)-configuration and that of the other is (*S,S,R*)-configuration (Figure 1). This result means that perfect stereocontrol does occur during the [1,2]-Wittig rearrangement, and hence no further crystallization or separation of the reaction product is required to obtain the single stereoisomer of the rearrangement product. In fact, we can conclude that this protocol is an efficient approach to multifunctional amino alcohols because every step of chirality transfer occurs in a stereospecific manner. For example, the three-component condensation of 2-naphthol, benzaldehyde, with (*R*)-1-phenyl-ethylamine, led to the stereoselective construction of new carbon-stereogenic center as (*R*)-configuration, and in the last step, (*S*)-carbon-stereogenic center was formed in the secondary amine-controlled Wittig rearrangement (>99.9% *de*). Similarly to our previous work on the NLAWR of BINOL-derived benzyl ether,[5] the stereoselective outcome is in accordance with the proposed mechanism of neighboring lithium-assisted [1,2]-Wittig rearrangement (Scheme 2). The observed and complete diastereoselectivity in this [1,2]-Wittig rearrangement may be a result from a stereospecific deprotonation of the carbon anion of benzyl ether, following the initial radical formation and subsequent recombination mediated by neighboring lithium secondary amine group.

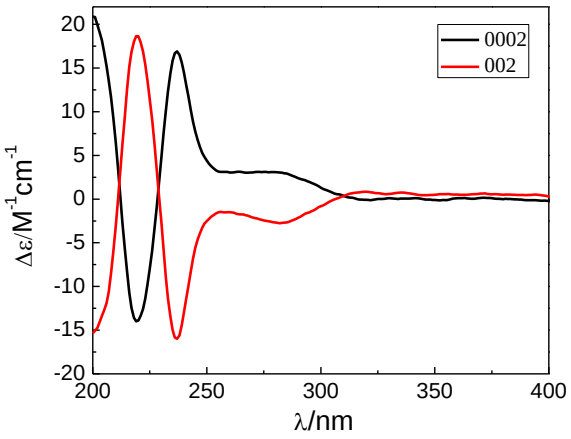
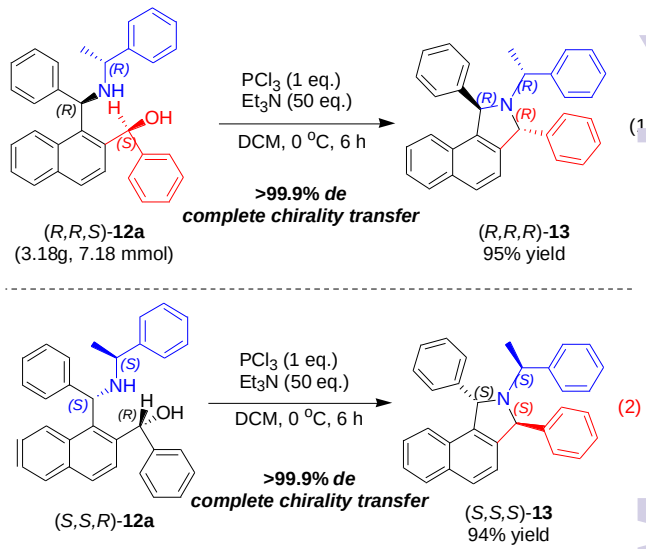


Figure 1. The circular dichroism (CD) spectra of (*R,R,S*)-**12a** (as line 0002) and (*S,S,R*)-**12a** (as line 002).



Scheme 7. The practical synthesis of optically pure and all-substituted pyrrolidine derivative **13** via intramolecular cyclization.

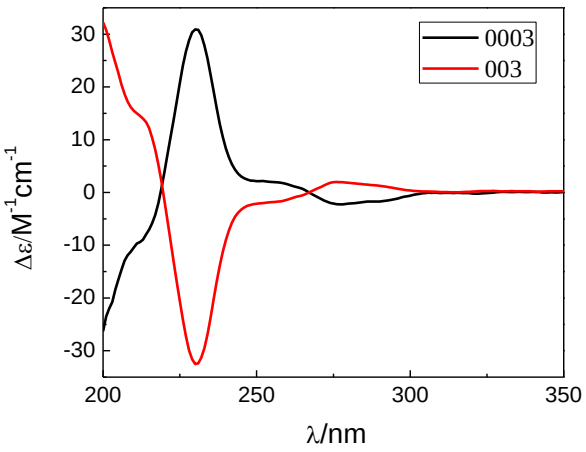


Figure 2. The circular dichroism (CD) spectra of (*R,R,R*)-**13** (as line 0003) and (*S,S,S*)-**13** (as line 003).

With these observations in hand, we turned our attention to the further application of such optically pure amino alcohol **12a** in the synthesis of new compounds, especially for the construction of chiral amino ligands. Thus we selected the (*R,R,S*)-**12a** and (*S,S,R*)-**12a** as the chiral course with a viewpoint that both optically pure molecules could be achieved with more than ten gram by the [1,2]-Wittig rearrangement. Fortunately, we found that t cyclization/amination of the (*R,R,S*)-**12a** or (*S,S,R*)-**12a** afforded the substituted pyrrolidine derivative with excellent yields (≥94% isolated yield) in the presence of PCl_3 and Et_3N (Scheme 7). And t chiral HPLC and CD analysis revealed that the cyclization/amination proceed with complete inversion of the benzylic carbon-stereogenic center to give all-substituted pyrrolidine derivative (*R,R,R*)-**13a** or (*S,S,R*)-**13a** exclusively. A key feature of the present approach is the complete inversion of secondary alcohol-linked carbon on the chi amino alcohol to the highly stereoselective synthesis of a substituted pyrrolidine derivative (**13**). Thus the perfe

diastereoselectivity was observed for the examples examined in this study. Notably, the use of $SOCl_2$ in the presence tertiary amine, or the combined reagent (TMSCl/NaI) resulted in the mixture of diastereoisomers with moderated diastereoselectivity (<90:10 d.r.). Similarly to the above strategy of investigation on the determination of absolute configuration of amino alcohol **12a** by CD analysis, the absolute configuration of novel pyrrolidine derivative in equation 1 is (*R,R,R*)-configuration and that of the other is (*S,S,S*)-configuration on the basis of the good agreement observed between experimental and calculated CD spectra (Figure 2 and *see* Supporting Information).

Conclusions

In summary, we have developed the first example of neighboring lithium-assisted [1,2]-Wittig rearrangement (NLAWR) of Betti base-derived benzyl ethers to construct γ-amino alcohols. The corresponding products were obtained in promising isolated yields (up to 79%). It is interesting to find that the highly diastereoselective [1,2]-Wittig rearrangement of Betti base-derived benzyl ethers gave the corresponding chiral amino alcohols in highly diastereoselective manner (>99.9% *de*). The complete chirality transfer provides an unprecedented strategy for the stereoselective construction of substituted amino alcohols from simple primary amine. More importantly, we have demonstrated that the optically pure amino alcohols could be converted into all substituted pyrrolidine derivatives bearing multiple stereogenic centers through intramolecular cyclization. In the [1,2]-Wittig rearrangement and subsequent cyclization, the corresponding reaction were performed in a highly stereospecific manner to afford the γ-amine alcohols and pyrrolidine derivatives respectively. In addition, on the basis of present example showed in this work, we have shown the powerful potential of the strategy of neighboring lithium-assisted [1,2]-Wittig rearrangement in the construction of new chiral backbone and optically pure secondary alcohols through chirality transfer. The scope and limitation of the present approach as well as the application of optically pure γ-amino alcohols and substituted pyrrolidine derivatives to natural product synthesis and asymmetric catalysis are in progress.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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