

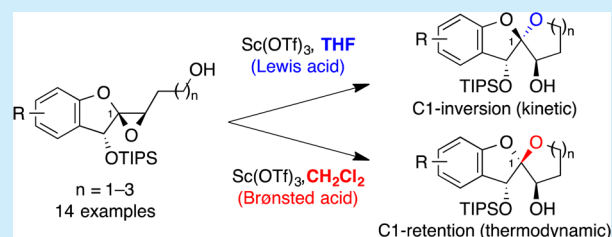
Solvent-Dependent Divergent Functions of $\text{Sc}(\text{OTf})_3$ in Stereoselective Epoxide-Opening Spiroketalizations

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S Supporting Information

ABSTRACT: A stereocontrolled synthesis of benzannulated spiroketals has been developed using solvent-dependent $\text{Sc}(\text{OTf})_3$ -mediated spirocyclizations of *exo*-glycal epoxides having alcohol side chains. In THF, the reaction proceeds via Lewis acid catalysis under kinetic control with inversion of configuration at the anomeric carbon. In contrast, in CH_2Cl_2 , Brønsted acid catalysis under thermodynamic control leads to retention of configuration. The reactions accommodate a variety of aryl substituents and ring sizes and provide stereochemically diverse spiroketals.



Benzannulated spiroketal natural products exhibit a broad array of biological activities.¹ Examples include the matrix metalloproteinase inhibitor berkeley acid,² the fungal cell wall glucan synthase inhibitory papulacandins,³ and the anti-inflammatory aquilarinoside A.⁴ Bisbenzannulated spiroketals include the rubromycin family of human telomerase and HIV reverse transcriptase inhibitors,⁵ the DNA helicase inhibitor heliquinomycin, and the antibiotic purpuromycin, which inhibits aminoacyl-tRNA synthesis by a novel mechanism involving direct binding to the tRNA substrate.⁶ Notably, the benzannulated spiroketal core is essential for telomerase inhibition in the rubromycin family.⁷ Numerous approaches to the synthesis of benzannulated spiroketals have been reported.^{8,9} Despite these notable advances, most strategies rely upon thermodynamically controlled reactions that often lead to stereoisomeric mixtures at the anomeric carbon.¹

We have previously developed stereocontrolled approaches to aliphatic spiroketals using stereocomplementary kinetic spirocyclization reactions of *endo*-glycal epoxides that proceed with either inversion or retention of configuration at the anomeric carbon, independent of thermodynamic preferences.¹⁰ We have also extended this approach to benzannulated spiroketals via incorporation of aromatic rings on the cyclizing side chain.¹¹ Unfortunately, this approach provides low diastereoselectivity in spirocyclization reactions with phenolic nucleophiles (45:55 to 58:42 dr).¹¹

To address this problem, we envisioned an alternative entry to phenolic spiroketals involving stereoselective spirocyclizations of benzannulated *exo*-glycal epoxides (dihydrobenzofuran spiroepoxides). Spirocyclizations of exocyclic enol ether epoxides have apparently not been explored previously, although classical acid-catalyzed spiroketalizations of the parent exocyclic enol ethers are well-known,¹² and the corresponding epoxides¹³ have been used in intermolecular alcohol additions.¹⁴

Thus, the requisite benzannulated *exo*-glycal epoxide substrates were synthesized from salicylaldehydes **1** via alkyne additions to form propargyl alcohols **2a–h** (Figure 1).¹⁵ Au(I)-mediated cycloisomerization, previously restricted to aromatic alkynes,^{15,16} then afforded *exo*-glycals **3a–h**. Diastereoselective *anti*-epoxidation with dimethyldioxirane (DMDO)¹⁷ provided *exo*-glycal epoxides **6a–h**. Interestingly, these epoxides were

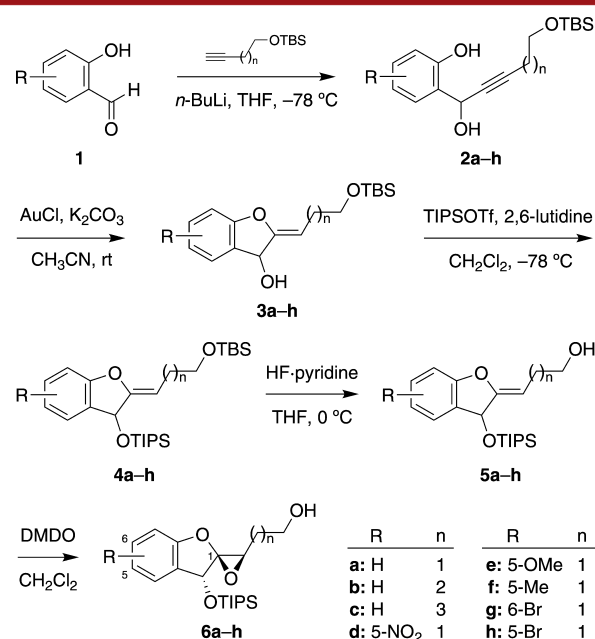


Figure 1. Synthesis of *exo*-glycal epoxide substrates **6a–h**.

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stable upon warming to rt, in stark contrast to the corresponding *endo*-glycol epoxides, which cyclize spontaneously at $-35\text{ }^{\circ}\text{C}$.¹⁸

We next explored spirocyclization reactions of benzannulated *exo*-glycol epoxide **6a** (Table 1). Notably, **6a** proved unreactive

Table 1. Spirocyclization Reactions of *exo*-Glycol Epoxide **6a^a**

entry	reagent (equiv)	solvent, temp ($^{\circ}\text{C}$)	7a:8a
1	MeOH (excess)	MeOH, rt	NR
2	Ti(O ^{<i>i</i>} Pr) ₄ (2.0)	CH ₂ Cl ₂ , rt	NR
3		toluene, 120	NR
4	Sc(OTf) ₃ (2.0)	CH ₂ Cl ₂ , $-78 \rightarrow 0$	75:25
5	Sc(OTf) ₃ (2.0)	THF, $-78 \rightarrow 0$	>98:2
6	Sc(OTf) ₃ (1.0)	THF, $-78 \rightarrow 0$	>98:2
7	Sc(OTf) ₃ (0.1)	THF, $-78 \rightarrow 0$	93:7
8	Sc(OTf) ₃ (1.0)	THF, -20	>98:2
9	Sc(OTf) ₃ (1.0)	THF, rt	90:10
10	Sc(OTf) ₃ (1.0)	CH ₂ Cl ₂ , $0 \rightarrow \text{rt}$	<2:98
11	Sc(OTf) ₃ (0.5)	CH ₂ Cl ₂ , $0 \rightarrow \text{rt}$	<2:98
12	Sc(OTf) ₃ + DTBMP (1.0 + 1.0)	THF, -20	>98:2
13	ScCl ₃ (1.0)	THF, rt	>98:2
14	TfOH (1.0)	THF, -20	30:70
15	Sc(OTf) ₃ + DTBMP (0.5 + 0.5)	CH ₂ Cl ₂ , $0 \rightarrow \text{rt}$	75:25
16	TfOH (0.5)	CH ₂ Cl ₂ , $0 \rightarrow \text{rt}$	<2:98
17	TfOH + DTBMP (0.5 + 0.5)	CH ₂ Cl ₂ , $0 \rightarrow \text{rt}$	51:49

^aProduct ratios determined by ¹H NMR analysis of crude reaction products. NR = no reaction; DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine. See the Supporting Information for the complete table.

under our previously reported MeOH and Ti(O-*i*-Pr)₄ spirocyclization conditions, as well as upon heating to $120\text{ }^{\circ}\text{C}$ in toluene (entries 1–3). After investigating a wide range of Lewis acids,¹⁶ we were encouraged to find that Sc(OTf)₃ favored the inversion product **7a** (entry 4), which could be formed exclusively by changing the reaction solvent from CH₂Cl₂ to THF (entry 5). The diastereoselectivity decreased slightly with substoichiometric Sc(OTf)₃ (entries 6 and 7). Other Lewis acids gave lower or even reversed diastereoselectivity.¹⁶

In low-temperature ¹H NMR experiments, we found that the Sc(OTf)₃-mediated spirocyclization begins to occur at $-35\text{ }^{\circ}\text{C}$.¹⁶ Complete selectivity for spirocyclization with inversion of configuration was maintained when the reaction was run at $-20\text{ }^{\circ}\text{C}$ (entry 8), but selectivity decreased at higher temperatures (entry 9), suggesting that the reaction proceeds under kinetic control between -35 and $-20\text{ }^{\circ}\text{C}$.

Strikingly, when the room-temperature reaction was carried out in CH₂Cl₂ instead of THF, thermodynamic equilibration of an initially formed diastereomeric mixture afforded the retention product **8a** with complete stereoselectivity (entries 10, 11).¹⁹ A structural rationale for the observed thermodynamic preference is nonobvious, due to the conformational flexibility of 5-membered rings,²⁰ and remains a subject for further investigation. However, on the basis of these results, it is apparent that Sc(OTf)₃ plays divergent roles in the

spirocyclization reactions depending upon solvent selection (THF vs CH₂Cl₂, entry 9 vs 10).

It is known that metal triflates can serve as a mild source of triflic acid.²¹ Thus, we carried out mechanistic studies to differentiate between the Lewis and Brønsted acid activities of Sc(OTf)₃. Inclusion of the noncoordinating Brønsted base, 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP),^{21a} in the reaction in THF did not affect diastereoselectivity (entry 8 vs 12). Treatment with ScCl₃ at rt also led to complete stereoselectivity for the contrathermodynamic spiroketal **7a** (entry 13). In contrast, spirocyclization with TfOH afforded a diastereomeric mixture favoring the retention product **8a** (entry 14). Taken together, these results suggest that Sc(OTf)₃ acts as a Lewis acid in THF at reduced temperatures, catalyzing formation of the contrathermodynamic spiroketal **7a** under kinetic control.

We next carried out the analogous experiments in CH₂Cl₂ where, upon warming to rt, Sc(OTf)₃ favors the retention product **8a** (entry 11). In contrast, inclusion of DTBMP resulted in a diastereomeric mixture favoring the inversion product **7a** (entry 15). However, spirocyclization with TfOH provided the retention product **8a** exclusively (entry 16). Treatment with both TfOH and DTBMP afforded a diastereomeric mixture of spiroketals, similar to the result observed with Sc(OTf)₃ and DTBMP (entry 17 vs 15). Collectively, these results suggest that Sc(OTf)₃ acts as a mild source of Brønsted acid in CH₂Cl₂ at rt, catalyzing formation of the thermodynamically favored spiroketal **8a** under equilibrium control.

We then investigated the scope of these stereocomplementary Sc(OTf)₃-catalyzed spirocyclization reactions. Substrates with longer side chains (**6b**, **6c**) and various aryl substituents (**6d–h**) were synthesized from the corresponding alkyne and salicylaldehyde precursors (Figure 1). The bromide intermediate **4h** was also used to introduce other substituents (aryl, alkyne, azide, aldehyde, ester, imide) in **4i–n** to examine the functional group tolerance of the spirocyclization reactions (Figure S2, Supporting Information).¹⁶ The *exo*-glycols **4i–n** were then converted to the corresponding epoxide substrates **6i–n** (Figure S2, Supporting Information).¹⁶

In the spirocyclization reactions, both diastereomers of the larger 6- and 7-membered ring spiroketals (**7b,c** and **8b,c**) could be obtained with complete diastereoselectivity based on solvent selection (Figure 2). For **8b**, equilibration with Sc(OTf)₃ in CH₂Cl₂ required elevated temperature ($60\text{ }^{\circ}\text{C}$). The 7-membered ring spiroketal **7c** was obtained in somewhat lower yield due to an unexpected anti-Markovnikov 6-*exo* epoxide opening side reaction leading to a benzofuran product.¹⁶

Next, we investigated the electronic effects of various aryl substituents. A wide range of electron-withdrawing and -donating groups were tolerated (**7d–n**, **8d–n**), and high diastereoselectivities were maintained. Notably, the nitro-substituted substrate **6d** was less reactive and required more forcing conditions (**7d**: rt; **8d**: 6 h). Conversely, the methoxy-substituted substrate **6e** was highly reactive, providing slightly decreased diastereoselectivity in the THF reaction (**7e**: 93:7 dr) and rapid equilibration in the CH₂Cl₂ reaction (**8e**: 1 h). These results are consistent with the expected electronic influence of these *para* substituents upon the reactive anomeric spiroepoxide center.¹⁸

The reactions also tolerated other reactive functionalities including alkyne (**7j**, **8j**), azide (**7k**, **8k**), aldehyde (**7l**, **8l**), ester (**7m**, **8m**), and phthalimide (**7n**, **8n**) groups. In the case of

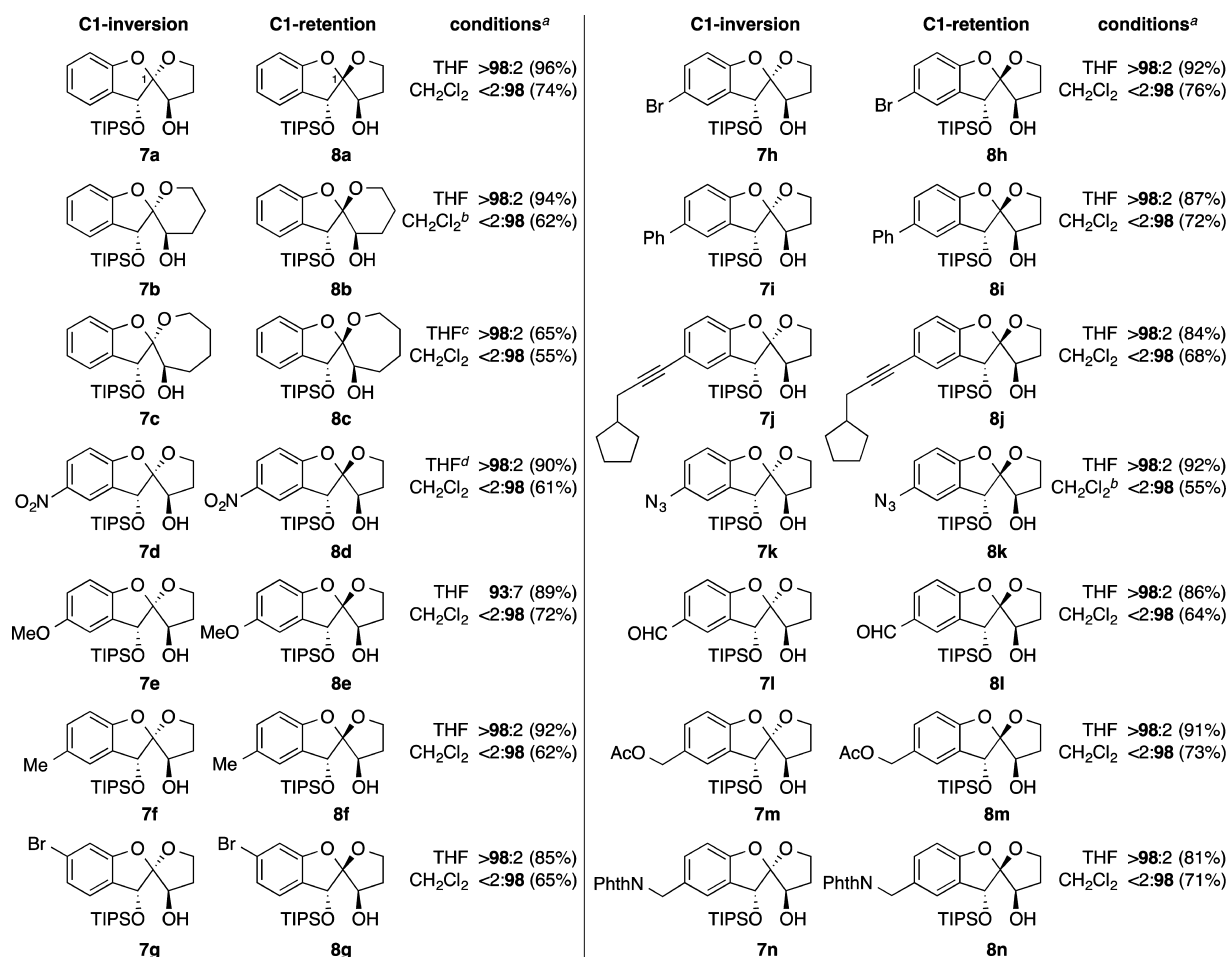


Figure 2. Scope of Sc(OTf)₃-mediated spirocyclization reactions. (a) THF: 1.0 equiv Sc(OTf)₃, THF, -20 °C, 2–3 h; CH₂Cl₂: 0.5 equiv Sc(OTf)₃, CH₂Cl₂, 0 °C to rt, 1–12 h; diastereomeric ratios determined by ¹H NMR analysis of crude reaction mixtures; stereochemistry assigned based on NOESY analysis except 8b, which was determined by X-ray crystallography;¹⁶ isolated yields after column chromatography shown in parentheses. (b) 60 °C. (c) 30% anti-Markovnikov 6-*exo*-cyclization side product also recovered.¹⁶ (d) rt.

azide **8k**, Sc(OTf)₃ equilibration in CH₂Cl₂ required elevated temperature (60 °C).

In conclusion, we have developed novel, solvent-dependent Sc(OTf)₃-mediated spirocyclizations of *exo*-glycal epoxides for the stereocontrolled synthesis of benzannulated spiroketals. This *exo*-glycal-based approach overcomes a key limitation of our previous *endo*-glycal-based approach and tolerates a wide range of functionalities. Applications to the diversity-oriented synthesis of stereochemically diverse spiroketal libraries are ongoing and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and analytical data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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