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Synthesis of 1,1'-Spirobiindane-7,7'-Disulfonic Acid and Disulfonimide: Application for Catalytic Asymmetric Aminalization

Takumaru Kurihara,^[a] Shun Satake,^[a] Manabu Hatano,^[b] Kazuaki Ishihara,^[b] Tatsuhiko Yoshino,^{*[a]} and Shigeki Matsunaga^{*[a]}

Abstract: 1,1'-Spirobiindane-7,7'-disulfonic acid (SPISA) and 1,1'-spiropiindane-7,7'-disulfonimide were synthesized from 1,1'-spiropiindane-7,7'-diol (SPINOL) in 4 steps using Pd-catalyzed Newman-Kwart rearrangement as a key step. These new catalysts possessing a rigid spirocyclic backbone were evaluated in a catalytic asymmetric aminalization reaction, and SPISA/*i*-Pr₂NEt exhibited high enantioselectivity, demonstrating the utility of SPISA as a chiral Brønsted acid catalyst.

Chiral Brønsted acid catalysts are powerful tools for the stereoselective construction of C-C and C-hetero atom bonds in modern organic synthesis.^[1] Among a variety of catalysts reported to date, chiral 1,1'-binaphthyl-2,2'-disulfonic acids (BINSAs) and their disulfonimide derivatives (Figure 1, top)^[2,3] are attractive in terms of their stronger Brønsted acidity compared with chiral phosphoric acids and carboxylic acids.^[1] In addition to working as a Brønsted acid, these catalysts can be used as ligands for a metal center^[3b] and chiral anions to control enantioselectivity.^[3c,e,k,l,4] Their versatility and efficient catalytic activity have prompted chemists to pursue the steric and electronic tuning of these catalysts.^[3c,f,g,i] In general, catalytic asymmetric synthesis often requires fine-tuning of the catalyst to achieve high enantioselectivity with specific substrates, and increasing the diversity of available catalyst structures is crucial.

Here we report the synthesis of 1,1'-spiropiindane-7,7'-disulfonic acid (SPISA) **1** and 1,1'-spiropiindane-7,7'-disulfonimide **2** (Figure 1, bottom). The 1,1'-spiropiindane structure is an axially chiral backbone that is more rigid and less flexible than a 1,1'-binaphthyl backbone. The rigidity is sometimes beneficial in asymmetric catalysis because the conformational ambiguity in an enantio-determining step can be omitted. A variety of chiral ligands were synthesized from 1,1'-spiropiindane-7,7'-diol (SPINOL) **3** by Zhou^[5-8] and others,^[9,10] and exhibited excellent

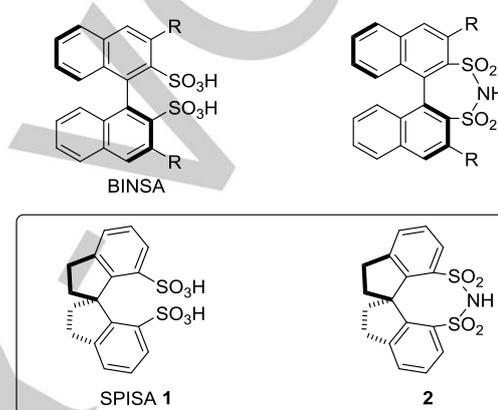


Figure 1. Structures of BINSAs (1,1'-binaphthyl-2,2'-disulfonic acid), SPISA (1,1'-spiropiindane-7,7'-disulfonic acid), and their disulfonimide derivatives

enantioselectivity in transition metal-catalyzed reactions. Although chiral phosphoric acids possessing the spirocyclic core were also reported,^[11] syntheses of SPISA **1** and sulfonimide **2** have not yet been reported.^[12]

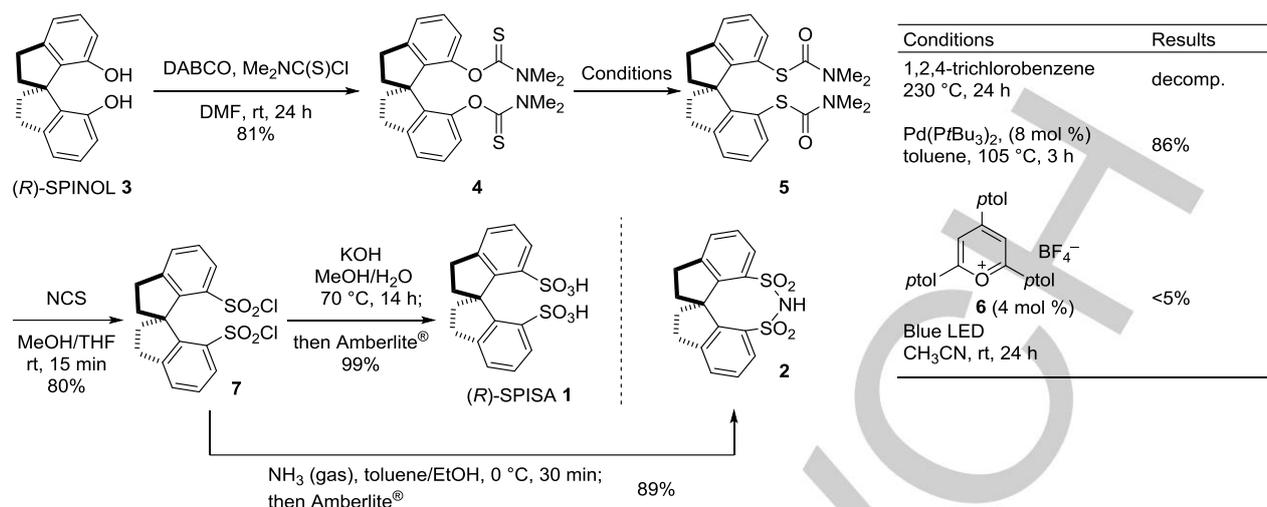
We synthesized **1** and **2** from (*R*)-SPINOL **3** using a route similar to that used for BINSAs (Scheme 1).^[3a,3d,13,14] Thiocarbonylation of the phenolic hydroxy groups of **3** under the reported conditions for BINOL (NaH, Me₂NC(S)Cl, DMF, 85 °C)^[3a,3d] resulted in poor conversion, but changing the base to DABCO^[15] significantly enhanced the reactivity, providing **4** in 81% at room temperature. With the precursor for key Newman-Kwart rearrangement (NKR) in hand, we investigated several conditions for NKR as shown in the table in Scheme 1.^[16] Although thermal conditions, which are usually used for the synthesis of BINSAs, afforded a complex mixture, Pd-catalyzed NKR reported by Lloyd-Jones *et al.*^[16b] furnished the desired product **5** in 86% yield. We also tried NKR under photo-redox catalysis using **6** reported by Nicewicz *et al.*^[16c] but the reaction barely occurred. Oxidation of **5** using *N*-chlorosuccinimide (NCS) in MeOH/THF smoothly proceeded to give disulfonyl chloride **7**, and subsequent hydrolysis and protonation afforded (*R*)-SPISA **1**. Disulfonimide **2** was also obtained in 89% yield by treating **7** with gaseous ammonia.

To evaluate the catalytic activity as a Brønsted acid as well as the stereoselection efficiency of **1** and **2**, we selected catalytic asymmetric aminalization of Cbz-protected imines with

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Scheme 1. Synthesis of (*R*)-SPISA **1** and disulfonimide **2** from (*R*)-SPINOL **3**.

carboxamides, which were previously reported using BINSAs,^[3i,17] as a model reaction. Optimization of the reaction conditions using **8a** and **9a** is summarized in Table 1. The use of **1** or **2** as a sole catalyst promoted the reaction in the presence of MgSO₄ as desiccant in CH₂Cl₂ at 0 °C, but low enantioselectivities were observed (entries 1 and 2). We next investigated the effect of amine additives using disulfonic acid **1** as the catalyst. Formation of the mono ammonium salt of **1** was expected to improve the enantioselectivity because the ammonium moiety can increase steric bulkiness around the catalytic site without introducing *ortho*-substituents.^[3i,18] Screening of various amines (entries 3–8) revealed that *i*Pr₂NEt was the best additive, affording **10aa** in 84% ee. In the previous report using BINSAs,^[3i] 2,6-diarylpyridines were effective additives in terms of enantioselectivity. In contrast, bulky trialkylamines were clearly better than 2,6-Ph₂-pyridine (entry 3, 14% ee) in this case, indicating that the chiral environment of SPISA **1** differs somewhat from that of BINSAs. Although neither changing the solvent nor changing the desiccant further improved the result (entries 9–13),^[19] higher enantioselectivity was obtained by performing the reaction at –40 °C for 12 h (entry 14). Under the optimized conditions, **10aa** was obtained in 75% yield and 93% ee.^[20]

The substrate scope of the (*R*)-SPISA **1**-catalyzed enantioselective amination under the optimized conditions is shown in Scheme 2. The substituent of the aromatic carboxamides had almost no effect on the enantioselectivity, and the products were obtained in moderate to good yield and with high enantioselectivity (**10aa–10ac**).^[21] Acrylamide **9d** was also compatible under the same conditions, although the enantioselectivity was slightly diminished (**10ad**). In addition to imine **8a**, both electron-rich and electron-deficient imines gave high enantioselectivity (**10ba–10bc**, **10ca**).

In summary, we synthesized (*R*)-SPISA **1** and disulfonimide **2** in 4 steps from (*R*)-SPINOL **3** using Pd-catalyzed Newman-Kwart rearrangement as a key step. These new chiral Brønsted acid catalysts were evaluated in the catalytic asymmetric amination of imines **8** and carboxamides **9**, and the combination of **1** and *i*Pr₂NEt exhibited high enantioselectivity. These catalysts can be a useful and good option for the development of asymmetric

Brønsted acid catalysis as well as asymmetric counteranion-directed catalysis.^[4] Further application of (*R*)-SPISA **1** and disulfonimide **2** as well as their structural tuning at the 6,6'-positions are ongoing.

Table 1. Optimization for enantioselective amination.^[a]

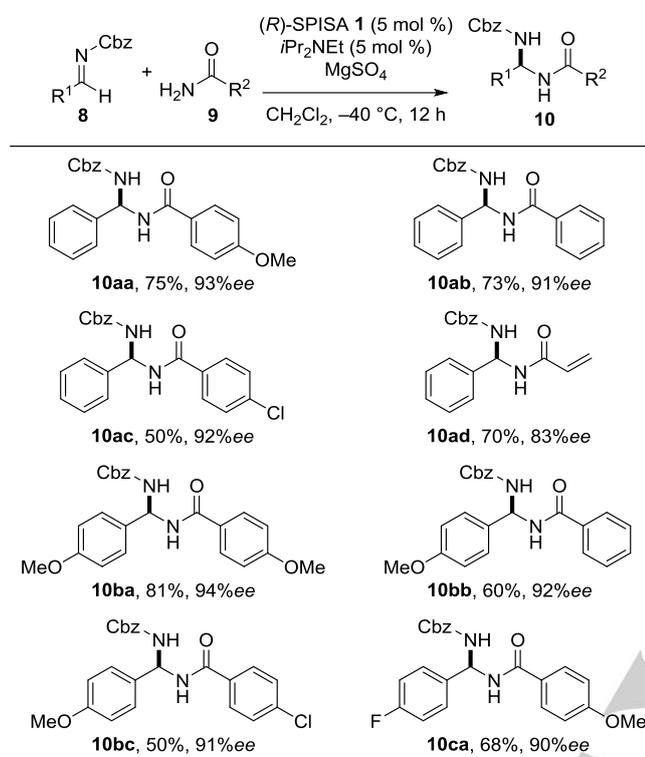
Entry	Catalyst	Amine	Desiccant	Solvent	% Yield ^[b]	% ee ^[c]
1	1	none	MgSO ₄	CH ₂ Cl ₂	82	7 ^[d]
2	2	none	MgSO ₄	CH ₂ Cl ₂	88	31
3	1	2,6-Ph ₂ -pyridine	MgSO ₄	CH ₂ Cl ₂	84	14
4	1	Me ₂ NBu	MgSO ₄	CH ₂ Cl ₂	>95	66
5	1	Me ₂ NCy	MgSO ₄	CH ₂ Cl ₂	49	73
6	1	Bu ₃ N	MgSO ₄	CH ₂ Cl ₂	42	75
7	1	Cy ₂ NMe	MgSO ₄	CH ₂ Cl ₂	64	83
8	1	<i>i</i> Pr ₂ NEt	MgSO ₄	CH ₂ Cl ₂	75	84
9	1	<i>i</i> Pr ₂ NEt	MgSO ₄	toluene	54	67
10	1	<i>i</i> Pr ₂ NEt	MgSO ₄	THF	58	43
11	1	<i>i</i> Pr ₂ NEt	MgSO ₄	DCE	68	75
12	1	<i>i</i> Pr ₂ NEt	MS4A	CH ₂ Cl ₂	70	79
13	1	<i>i</i> Pr ₂ NEt	Drierite [®]	CH ₂ Cl ₂	81	83
14 ^[e]	1	<i>i</i> Pr ₂ NEt	MgSO ₄	CH ₂ Cl ₂	75	93

[a] Reactions were run using **8a** (0.30 mmol), **9a** (0.20 mmol), catalyst (0.01 mmol, 5 mol %), amine (0.01 mmol, 5 mol %), and MgSO₄ (0.34 mmol), MS4A (40 mg), or Drierite[®] (40 mg) in solvent (1.0 mL) at 0 °C for 1 h unless otherwise noted. [b]

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Isolated yield. [c] Determined by chiral HPLC analysis. See Supporting Information for more details. [d] The opposite enantiomer was obtained as a major product. [e] –40 °C, 12 h.



Scheme 2. Substrate scope of *(R)*-SPISA **1**-catalyzed asymmetric amidination.

Acknowledgements

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Keywords: chiral Brønsted acid • 1,1'-spirobiindane • disulfonic acid • disulfonimide • amidination

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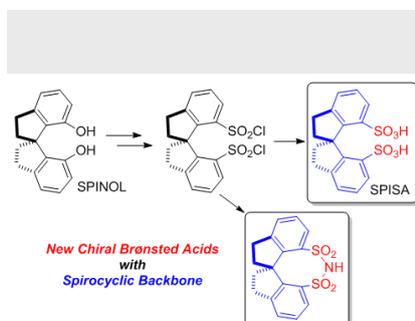
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- [18] Although **2** showed better enantioselectivity than **1**, we considered **1** would be suitable for this acid-base combined catalysis because **1** has two acidic functional groups. Therefore, **1** was chosen as a catalyst for further investigation.
- [19] The effect of Mg²⁺ as a Lewis acid cannot be ruled out, but would be limited, because almost comparable results were obtained with other desiccants.
- [20] When we performed a reaction for 20 min under the optimized conditions (Table 1, entry 14), **10aa** was obtained in 28% yield and 93% ee, indicating that no racemization of **10aa** occurred under these conditions.
- [21] The optical rotation of **10ab** was opposite to that of the (S)-isomer reported in reference [3i]. Thus, the absolute configuration of **10ab** was determined to be (R).

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New chiral Brønsted acid catalysts with a spirocyclic backbone were developed. SPISA and its disulfonimide were synthesized from SPINOL using Pd-catalyzed Newman-Kwart rearrangement as a key step, and evaluated in a catalytic asymmetric aminolization reaction. These new catalysts can provide a new good option for the development of asymmetric catalysis.



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Synthesis of 1,1'-Spirobiindane-7,7'-Disulfonic Acid and Disulfonimide: Application for Catalytic Asymmetric Aminolization