

Preparation of (2,3-Dihydrobenzofuran-3-yl)acetic Acid via Rh-Catalyzed Asymmetric Hydrogenation

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A preparation via Rh-catalyzed asymmetric hydrogenation has been developed for (2,3-dihydrobenzofuran-3-yl)-acetic acid derivatives, a key intermediate in the synthesis of the active pharmaceutical ingredient for GPR40 agonist, fasiglifam. Use of a cationic rhodium–Et-FerroTANE complex yielded the desired product in high enantiomeric excess (91%) and quantitative yield, and was thus recommended for further process development.

Optically active 2,3-dihydrobenzofuran derivatives are key scaffolds for a variety of active pharmaceutical ingredients such as selective kappa opioid receptor agonists,[1a] subtype selective PPARα agonists,[1b] selective cannabinoid receptor 2 agonists,[1c] as well as natural products such as (+)-myrtopsine,[1d] and endophytic fungus *Xylaria* sp.[1e] GPR40 agonist fasiglifam, [(3*S*)-6-({2′,6′-dimethyl-4′-[3-(methylsulfonyl)propoxy]biphenyl-3-yl}methoxy)-2,3-dihydrobenzofuran-3-yl]acetic acid hemihydrate (Figure 1), a candidate as a novel antidiabetic agent,[2] was also built around this scaffold.

Various synthetic methods, such as asymmetric epoxidation, asymmetric dihydroxylation, chiral pool synthesis, and optical resolution, have been developed to obtain optically active 2,3-dihydrobenzofuran derivatives.[1,2] Although asymmetric hydrogenation is a straightforward approach to obtain optically active hydrogenated heterocycles, including 2,3-dihydrobenzofuran derivatives, the harsh reaction conditions required make successful reactions rare.[3] We envisioned that recent advancements in ligand designs might enable us to overcome the issues of reactivity and enantioselectivity.

We describe herein an efficient asymmetric hydrogenation of (6-hydroxybenzofuran-3-yl)acetic acid, according to a strategy comprising substrate, chiral ligand, and additive selection. The strategy is expected to be utilized for the synthesis of other substituted 2,3-dihydrobenzofuran derivatives.

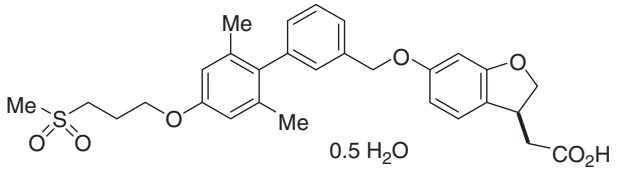

Figure 1. Structure of fasiglifam.

A great deal of effort has been devoted to developing efficient and potent chiral ligands for use in asymmetric hydrogenation.[4] We previously reported asymmetric hydrogenation of allylamines with complexes prepared from rhodium and ferrocene-based diphosphines, demonstrating that selection of a suitable catalyst can pave the way for achieving high reactivity and enantioselectivity.[5] The lesson has encouraged us to investigate the asymmetric hydrogenation of benzofuran derivatives **1a** and **1b**, considered to be challenging.[3] In general, olefins carrying an ester moiety are considered advantageous in asymmetric hydrogenation due to the anchoring ability, solubility, and stability provided by the ester functionality; this led us to choose compound **1a** as a promising candidate substrate.[4i]

We evaluated various chiral rhodium precatalysts, which were prepared in situ from 1 mol % each of $[Rh(cod)_2]OTf$ and ferrocene-based phosphine ligands in MeOH at room temperature. In preliminary trials using ligands **3a**–**3c** and **3k**–**3q**,[6,7] hydrogenation of compound **1a** gave poor to moderate enantioselectivities and/or chemical yields (Table 1).

These findings showed that compound **1a** is not a promising substrate for asymmetric hydrogenation under these conditions. Thus, we concentrated our efforts on developing an asymmetric hydrogenation of the corresponding carboxylic acid **1b**. In the asymmetric hydrogenation of compound **1b**, the same reaction conditions were employed, but with the addition of a base such as sodium methoxide (Table 2), referring to the literature.[8]

As shown in Table 2, most ligands gave good to excellent chemical yields. Josiphos ligands carrying electron-rich and bulky substituents ($R^2 = t$-Bu) yielded good overall outcomes for compound **1b** (Table 2, Entries 4 and 10). The effect of the electronic properties of the R^1 groups on the resulting enantioselectivities seems to be limited (Table 2, Entries 4 vs.

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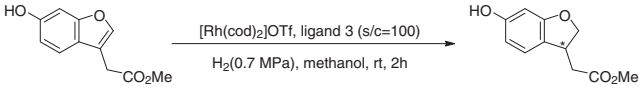
Table 1. Asymmetric Hydrogenation of Compound **1a** with Josiphos, Et-FerroTANE, BoPhoz, DUPHOS, and BPE[a)]

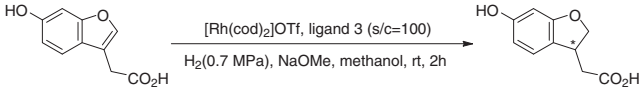


1a **2a**

Entry	Ligand	ee/%[b)]	Yield/%[b)]
1	**3a**	0	68
2	**3b**	27	90
3	**3c**	6	50
4	**3k**	4	68
5	**3l**	19	66
6	**3m**	0	75
7	**3n**	30	31
8	**3o**	0	46
9	**3p**	48	42
10	**3q**	43	52

a) Structure of ligands are shown in Table 2. Reaction conducted on 0.25 mmol scale at room temperature under 0.7 MPa of H_2. b) Determined by HPLC analysis using CHIRALPAK AS-H column.

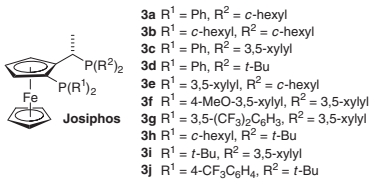
Table 2. Asymmetric Hydrogenation of Compound **1b** with Josiphos, Et-FerroTANE, BoPhoz, DUPHOS, and BPE[a)]

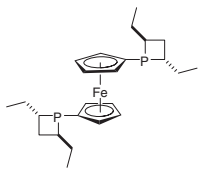


1b **2b**

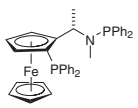
Entry	Ligand	ee/%[b)]	Yield/%[b)]
1	**3a**	6	95
2	**3b**	8	92
3	**3c**	2	81
4	**3d**	79	90
5	**3e**	36	27
6	**3f**	27	93
7	**3g**	58	23
8	**3h**	41	66
9	**3i**	35	95
10	**3j**	81	91
11	**3k**	91	88
12	**3l**	15	65
13	**3m**	75	95
14	**3n**	67	95
15	**3o**	62	99
16	**3p**	59	98
17	**3q**	46	98

a) Reaction conducted on 0.25 mmol scale at room temperature under 0.7 MPa of H_2, using NaOMe (0.5 equiv to **1b**). b) Determined by HPLC analysis using CHIRALPAK AD-H column.

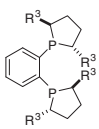




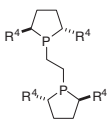
3k Et-FerroTANE



3l BoPhoz



3m Me-DuPHOS R^3=Me
3n Et-DuPHOS R^3=Et
3o *i*Pr-DuPHOS R^3=*i*Pr



3p Me-BPE R^4=Me
3q Et-BPE R^4=Et

10); however, their steric properties may have a considerable influence (Table 2, Entries 4 vs. 8).

Et-FerroTANE, ligand **3k**, gave the best combination of good enantioselectivity and chemical yield (Table 2, Entry 11). To the best of our knowledge, this is the first asymmetric hydrogenation of substituted (benzofuran-3-yl)acetic acid **1b** using Rh–Et-FerroTANE catalyst under low hydrogen pressure (less than 1 MPa).[9] The proximity of a chirogenic center to phosphorus in Et-FerroTANE could be beneficial to the achievement of high enantioselectivitiy. DUPHOS and BPE gave moderate enantioselectivities, as shown in Table 2 (Entries 13–17). This finding clearly indicates a particular utility for Et-FerroTANE yielding a favorable outcome for this reaction.

It has been reported that a phenolic hydroxy group of a substrate was essential to obtain a good enantioselectivity in some asymmetric hydrogenations.[10] To clarify the role of the hydroxy group in this case, the 6-hydroxy group in compound **1a** and **1b** was replaced with a 6-methoxy group (Table 3 and Table 4).

Hydrogenation of compound **1c**, the analogue of compound **1a**, gave the same enantioselectivity compared with **1a** (Table 1, Entries 5, 8, 9 vs. Table 3). Furthermore, the same tendency was obtained by the asymmetric hydrogenation of compound **1d**, the analogue of compound **1b** (Table 2 vs. Table 4). The replacement of the 6-hydroxy group by the 6-methoxy group did not affect the nature of the reaction. This finding suggests that the 6-hydroxy group may be situated outside the coordination sphere of the Rh–Et-FerroTANE **1b** complex and not affect the asymmetric hydrogenation.

It has been reported that sodium carboxylate is superior to carboxylic acid as a substrate for Rh-catalyzed asymmetric hydrogenations.[8] In our study, the corresponding sodium carboxylate enhances reactivity as expected.

The tolerance toward base may indicate that both the counter cation and the nucleophilicity of the carboxylate group have little effect on reactivity and selectivity (Table 5). The reaction proceeded smoothly, even in the presence of substoichiometric sodium methoxide (0.1 to 0.5 equiv) (Table 5, Entries 1, 2, and 3). Additional investigation may be needed to clarify the role of base in this reaction.

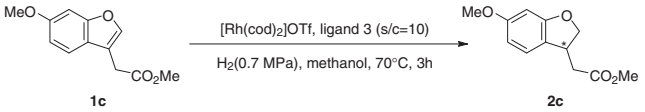
The robustness of this reaction was successfully confirmed by the preparation of **2b** on an approximately 25 g-scale reaction (Table 5, Entry 3, see Experimental).

Further investigation has revealed that the asymmetric hydrogenation of (benzofuran-3-yl)acetic acid **1b** using Rh–Et-FerroTANE is a suitable method to synthesize fasiglifam in a large scale (Scheme 1).[2]

In conclusion, we have accomplished the asymmetric hydrogenation of (6-hydroxybenzofuran-3-yl)acetic acid **1b** using Rh–Et-FerroTANE in quantitative yield and good enantio-

selectivity. The reaction is capable of considerably further scale-up. Our success in realizing the highly enantioselective hydrogenation of compound **1b** indicates that recent advancement in asymmetric catalysis, coupled with an optimization strategy for additives and alternative substrates, has enabled us to expand the applicability of asymmetric hydrogenation.

Table 3. Asymmetric Hydrogenation of Compound **1c** with BoPhoz, DUPHOS, and BPE[a)]

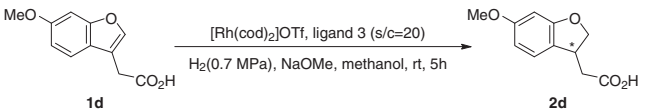


1c 2c

Entry	Ligand	ee/%[b)]	Yield/%[b)]
1	**3l**	14	90
2	**3o**	4	74
3	**3p**	53	24

a) Reaction conducted on 0.25 mmol scale at room temperature under 0.7 MPa of H_2. b) Determined by HPLC analysis using CHIRALPAK AD-RH column.

Table 4. Asymmetric Hydrogenation of Compound **1d** with Josiphos, Et-FerroTANE, BoPhoz, DUPHOS, and BPE[a)]



1d 2d

Entry	Ligand	ee/%[b)]	Yield/%[b)]
1	**3a**	7	85
2	**3b**	7	93
3	**3c**	8	91
4	**3d**	82	96
5	**3g**	63	38
6	**3h**	40	75
7	**3i**	27	96
8	**3j**	80	88
9	**3k**	86	88
10	**3l**	7	79
11	**3m**	71	88
12	**3n**	39	86
13	**3o**	56	95
14	**3p**	47	90
15	**3q**	66	88

a) Reaction conducted on 0.25 mmol scale at room temperature under 0.7 MPa of H_2, using NaOMe (0.5 equiv to **1d**). b) Determined by HPLC analysis using CHIRALPAK AS-H column.

Experimental

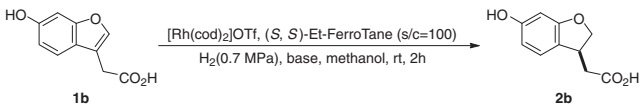
General. All experiments were carried out under argon atmosphere by standard Schlenk techniques. Reagents and solvents were obtained from commercial sources and used without further purification.

Compounds **1a** and **1b** were synthesized by the reported method.[2] Compound **1c** was synthesized from compound **1a** using MeI and K_2CO_3 in DMF at 70 °C. Compound **1d** was synthesized from compound **1c** using 1 M NaOH aqueous solution in MeOH at 60 °C.

The purity of compounds was assessed by elemental analysis or analytical HPLC (>95%).

(*S*)-Methyl (6-Hydroxy-2,3-dihydrobenzofuran-3-yl)acetate (2a). To methyl (6-hydroxybenzofuran-3-yl)acetate (**1a**) (51 mg, 0.25 mmol) in a glass autoclave was added a solution of (*R*,*R*)-BPE (**3p**, 6.5 mg, 0.025 mmol) and $[Rh(cod)_2]OTf$ (12 mg, 0.025 mmol, s/c = 10) in methanol (2.5 mL) by cannula. Hydrogen (0.7 MPa) was introduced, and the reaction mixture was stirred at room temperature. After 2 h, enantiomeric excess (48%) and chemical yield (42%) were determined by HPLC analysis using racemic compound of **2a** as the external standard. (CHIRALPAK AS-H, eluted with *n*-hexane/2-propanol = 85/15 (v/v); flow rate, 0.75 mL min^{-1}; detection, 220 nm; room temperature).

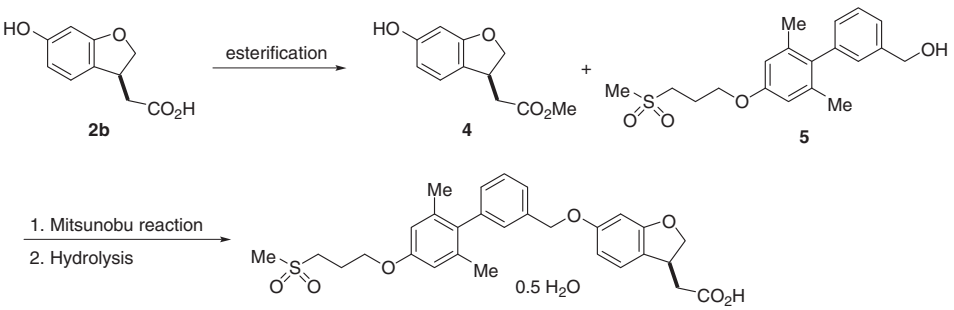
Table 5. Asymmetric Hydrogenation of Compound **1b** with Various Bases[a)]



1b 2b

Entry	Base (equiv to **1b**)	ee/%[b)]	Yield/%[b)]
1	NaOMe (0.1 equiv)	90	95
2	NaOMe (0.5 equiv)	91	98
3[c)]	NaOMe (0.5 equiv)	90	100
4	NaOMe (1.0 equiv)	91	65
5	*t*-BuOK (0.5 equiv)	90	100
6	K_2CO_3 (0.5 equiv)	90	100
7	Cs_2CO_3 (0.5 equiv)	91	100
8	Li_2CO_3 (0.5 equiv)	91	100

a) Reaction conducted on 0.25 mmol scale at room temperature under 0.7 MPa of H_2. b) Determined by HPLC analysis (CHIRALPAK AD-H column). (*S*,*S*)-Et-FerroTANE affords (*S*)-configuration of compound **2b**. c) Reaction conducted on 25 g scale.



2b 4 5

Scheme 1. Preparation of fasiglifam.

^{1}H NMR spectrum and Elemental analysis data were obtained after purification.

^{1}H NMR ($CDCl_3$): δ 2.50–2.61 (m, 1H), 2.69–2.79 (m, 1H), 3.72 (s, 3H), 3.73–3.85 (m, 1H), 4.26 (dd, $J = 9.0$ and 6.0 Hz, 1H), 4.75 (t, $J = 9.0$ Hz, 1H), 4.86 (s, 1H), 6.30–6.35 (m, 2H), 6.95–7.00 (m, 1H). MS m/z 209 $(M + H)^+$. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%. Found: C, 63.49; H, 5.81%.

(*S*)-(6-Hydroxy-2,3-dihydrobenzofuran-3-yl)acetic Acid (2b). To a solution of (6-hydroxy-1-benzofuran-3-yl)acetic acid (**1b**) (1.92 g, 10 mmol), NaOMe (0.27 g, 5 mmol) in methanol (35 mL) in a glass autoclave was added a solution of 1,1′-bis((2*S*,4*S*)-2,4-diethylphosphotano)ferrocene (**3k**, 44 mg, 0.1 mmol) and $[Rh(cod)_2]OTf$ (47 mg, 0.1 mmol, s/c = 100) in methanol (15 mL) by cannula. Hydrogen (0.7 MPa) was introduced, and the reaction mixture was stirred at room temperature. After 2 h, enantiomeric excess (90%) and chemical yield (quantitative) were determined by HPLC analysis using racemic compound of **2b** as the external standard. (CHIRALPAK AD-H, eluted with *n*-hexane/ethanol/trifluoroacetic acid = 900/100/1 (v/v/v); flow rate, 1.0 mL min^{-1}; detection, 220 nm; room temperature). The reaction mixture was concentrated. The residue was diluted with water and 1 M aqueous HCl solution and extracted with AcOEt. The extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (AcOEt: hexane = 35:65 and then 100:0) to afford **2b** (1.76 g, 91%) as a slightly yellow solid.

^{1}H NMR (DMSO-d_6): δ 2.39–2.49 (m, 1H), 2.61–2.71 (m, 1H), 3.56–3.68 (m, 1H), 4.14 (dd, $J = 9.0$, 6.8 Hz, 1H), 4.64 (t, $J = 9.0$ Hz, 1H), 6.15 (d, $J = 2.2$ Hz, 1H), 6.23 (dd, $J = 8.0$, 2.2 Hz, 1H), 6.98 (dd, $J = 8.0$, 0.7 Hz, 1H), 9.27 (br s, 1H), 12.33 (br s, 1H).

Anal. Calcd for $C_{10}H_{10}O_4 \cdot 0.2H_2O$: C, 60.73; H, 5.30%. Found: C, 60.84; H, 5.35%.

Gram-Scale Synthesis of (*S*)-(6-Hydroxy-2,3-dihydrobenzofuran-3-yl)acetic Acid (2b). To a solution of (6-hydroxy-1-benzofuran-3-yl) acetic acid (**1b**) (26.9 g, 140 mmol), NaOMe (3.8 g, 70 mmol) in methanol (500 mL) in a glass autoclave was added a solution of 1,1′-bis((2*S*,4*S*)-2,4-diethylphosphotano)-ferrocene (**3k**, 620 mg, 1.4 mmol) and $[Rh(cod)_2]OTf$ (656 mg, 1.4 mmol, s/c = 100) in methanol (200 mL) by cannula. Hydrogen (0.7 MPa) was introduced, and the reaction mixture was stirred at room temperature. After 2 h, enantiomeric excess (90%) and chemical yield (quantitative) were determined by HPLC analysis using racemic **2b** as the external standard. (CHIRALPAK AD-H, eluted with *n*-hexane/ethanol/trifluoroacetic acid = 900/100/1 (v/v/v); flow rate, 1.0 mL min^{-1}; detection, 220 nm; room temperature).

The reaction mixture was concentrated. The residue was diluted with water and 1 M HCl aqueous solution and extracted with AcOEt. The extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated to afford **2b** as a brown solid (28.0 g, purity 99%, quantitative). The residue was used for the next step without further purification.

Supporting Information

^{1}H NMR spectra of compound **2a**, **2b**, and HPLC charts of racemic compound of **2a**, **2b**. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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