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Chiral Pentacarboxycyclopentadiene-Based Brønsted Acid-Catalyzed Enantioselective Desymmetrization of Meso-Epoxides by 2-Mercaptobenzothiazoles

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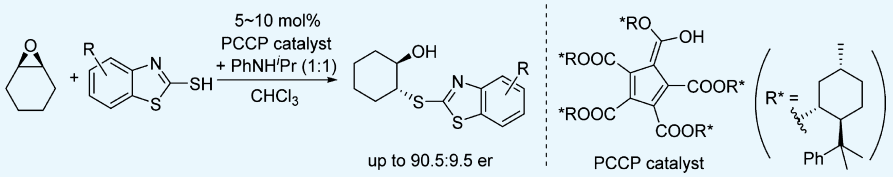
Supporting Information



ABSTRACT: Enantioselective desymmetrization of meso-epoxides by 2-mercaptobenzothiazoles was realized by using the pentacarboxycyclopentadiene-based chiral Brønsted acid in combination of *N*-isopropylaniline as amine additive to give up to 90.5:9.5 er of the ring opening products.

INTRODUCTION

Catalytic enantioselective desymmetrization of meso-epoxides is an attractive method to prepare chiral alcohols[1] because the meso-epoxide substrates are readily available and the 1,2-difunctionalized product structures with two adjacent chiral centers are very useful synthetic building blocks.[2] Various nucleophiles have been reported to participate in catalytic enantioselective desymmetrization of meso-epoxides, including amines,[3] azides,[4] alcohols,[5] carboxylic acids,[6] thiols,[7] and halides.[8] The majority of these reactions were catalyzed by Lewis acidic transition metal complexes.[1] In 2013, Sun et al. successfully realized the first Brønsted acid-catalyzed enantioselective desymmetrization of meso-epoxides by 2-mercaptobenzothiazoles.[7d] In that report, 1,1′-bi-2-naphthol (BINOL)-derived chiral phosphoric acid bearing 3,3′-(2,4,6-triisopropyl) substituents (commonly abbreviated as TRIP) was identified to be a good catalyst, and up to 92.5:7.5 er was obtained for the ring opening reaction of cyclohexene oxide.

While the research endeavor on strong Brønsted acid catalysis was dominated by BINOL-based chiral phosphoric acid derivatives[9] since the pioneering works from Akiyama et al. and Terada et al.,[10] syntheses of this class of catalysts were generally considered lengthy, laborious, and expensive, especially for some of the most successful chiral phosphoric acid-derived catalysts bearing bulky 3,3′-substituents, such as TRIP. Simplifying the preparation of strong Brønsted acid catalysts could be synthetically very useful.[11]

In 2016, Lambert et al. reported a novel, enantiopure, pentacarboxycyclopentadiene (PCCP)-based strong Brønsted acid catalyst, which could be easily prepared from readily available 1,2,3,4,5-pentacarbomethoxycyclopentadiene and chiral (−)-menthol in one transesterification step.[12] Catalytic asymmetric Mukaiyama−Mannich reactions and oxocarbenium aldol reactions were realized in good enantioselectivities (Scheme 1a).[12] Recently, Diels−Alder reactions between salicylaldehyde acetals and vinyl ethers catalyzed by a different PCCP catalyst were also reported.[13] Other groups have also reported transfer hydrogenations and preparations of chiral aminals using Lambert's catalyst.[14] We believe that the development of PCCP-based chiral strong Brønsted acid catalyst could potentially alleviate some of the problematic issues for using BINOL-based chiral phosphoric acid derivatives. Herein, we report the enantioselective desymmetrization of meso-epoxides by 2-mercaptobenzothiazoles using the PCCP-based chiral Brønsted acid with up to 90.5:9.5 er (Scheme 1b).

RESULTS AND DISCUSSION

We used the ring opening reaction of cyclohexene oxide (**1a**) with 2-mercaptobenzothiazole (**2a**) with chiral Brønsted acid **catalyst 1** as the model for optimization of reaction conditions. Initial trial in dichloromethane (DCM) solvent at room temperature (rt) overnight without the addition of chiral catalyst gave racemic product **3a** in 18% background yield (Table 1, entry 1). When 2.5 mol % PCCP-based catalyst derived from chiral (−)-menthol was used, 93% isolated yield and 57:43 er were obtained (entry 2).[15] We then screened a number of solvents for this reaction (entries 3−15). The best result (99% yield, 72:28 er) was obtained when chloroform was used as solvent (entry 8). We then tried to enhance the selectivity by lowering the reaction temperature. However, the enantioselectivity decreased to 60.5:39.5 er at 0 °C (entry 16) and 40.5:59.5 er at −44 °C (entry 17), which probably means that the favored transition state for the stereochemistry

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Scheme 1. Chiral PCCP-Based Brønsted Acid-Catalyzed Reactions

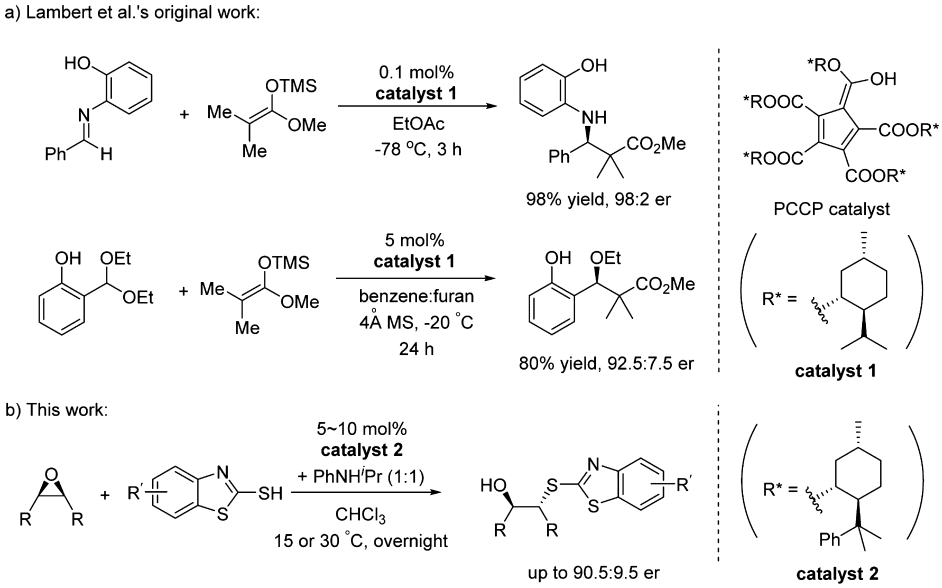
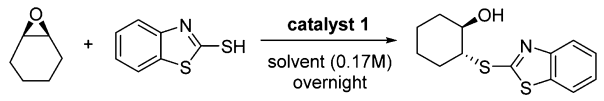


Table 1. Optimization of Reaction Conditions



1a **2a** (1.2 eq) **3a**

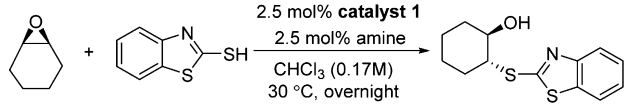
entry	catalyst loading (mol %)	solvent	temp (°C)	yield (%)[a]	er
1	0[b]	CH_2Cl_2	10	18	
2	2.5	CH_2Cl_2	11	93	57:43
3	5	toluene	12	97	49.4:50.5
4	2.5	$ClCH_2CH_2Cl$	10	74	56.5:43.5
5	2.5	PhCl	15	99	52:48
6	2.5	hexane	16	45	42:58
7	2.5	CCl_4	25	83	60:40
8	2.5	$CHCl_3$	22	99	72:28
9	2.5	THF	15	6	50:50
10	2.5	dioxane	16	10	52:48
11	2.5	EtOAc	12	30	46.5:53.5
12	2.5	acetone	16	42	50.5:49.5
13	2.5	MeCN	10	21	52:48
14	2.5	DMF	12	trace	
15	2.5	EtOH	16	31	50.5:49.5
16	2.5	$CHCl_3$	0	92	60.5:39.5
17	2.5	$CHCl_3$	−44 to 5[c]	89	40.5:59.5
18	2.5	$CHCl_3$	30	99	70.5:29.5

[a]Isolated yield. [b]Without catalyst. [c]−44 °C for 13 h then −44 to 5 °C for 9 h.

determining step might be reversed at lower temperatures. Further increasing the reaction temperature to 30 °C led to 99% yield and 70.5:29.5 er (entry 18).

We then tried a number of other sulfur and nitrogen nucleophiles for the ring opening reaction of cyclohexene oxide (**1a**), but none of the results seemed promising (see Supporting Information for details). However, the addition of catalytic quantity of amine bases to react with the PCCP-based chiral Brønsted acid catalyst and form corresponding hydrogen-bonding adducts or ammonium salts did have some favorable effects on the enantioselectivity (Table 2). Specifically, triethylamine and diisopropylamine gave poor

Table 2. Optimization of Amine Additives[a]



1a **2a** (1.2 eq) **3a**

entry	amine	er
1	Et_3N	50.5:49.5[b]
2	$^iPr_2NH$	50:50[c]
3	$PhNH_2$	70.5:29.5
4	$PhNH^iPr$ (**4a**)	74:26
5	Ph_2NH	72:28
6	Ph_3N	70.5:29.5
7	pyridine (C_5H_5N)	72:28
8	2,6-Me_2-C_5H_3N	69:31
9	2,6-$^tBu_2$-C_5H_3N	73:27
10	2,6-Ph_2-C_5H_3N	71.5:28.5
11[d]	**4a**	72:28
12[e]	**4a**	73:27
13[f]	no amine additive	70.5:29.5

[a]Full conversion for all entries, except for entries 1 and 2. [b]36% yield. [c]52% yield. [d]1.25 mol % amine **4a** was added. [e]5 mol % amine **4a** was added. [f]Same as Table 1, entry 18.

yields and enantioselectivities (entries 1 and 2), but a number of aniline derivatives and pyridine derivatives (entries 3−12) all gave full conversion to the desired product **3a** and in certain cases increased enantioselectivities comparing with the result we obtained using the chiral Brønsted acid **catalyst 1** alone (entry 13). When *N*-isopropylaniline **4a** was used (entry 4), we achieved the highest 74:26 er, whereas using half or double amount of **4a** did not help to increase the enantioselectivity (entries 11 and 12). Presumably, the aniline- and pyridine-type bases (entries 3−12) could form more tightly associated hydrogen-bonding adducts or ammonium salts with the PCCP-based chiral Brønsted acid catalyst through $\pi-\pi$

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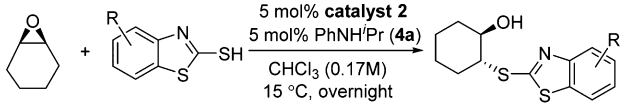
stacking interactions and thus achieve higher enantioselectivity than triethylamine and diisopropylamine (entries 1 and 2).

Further enhancement of enantioselectivity was achieved by using chiral Brønsted acid **catalyst 2**, which was similarly synthesized using Lambert's protocol with readily available (−)-8-phenylmenthol as the chiral source. Under the optimized reaction conditions (see Table S2 in the Supporting Information for details on the temperature optimization for **catalyst 2**), 99% yield and 89.5:10.5 er were obtained for product **3a** (Table 3, entry 1). The increased steric bulkiness of **catalyst 2** might contribute to its better performance. We then surveyed a number of substituted 2-mercaptobenzothiazoles, and modest-to-good enantioselectivities were obtained (entries 2−10). Up to 99% yield and 90.5:9.5 er of product **3c** were achieved using the 5-trifluoromethoxy-2-mercaptobenzothiazole (**2c**) as nucleophile for this ring opening reaction with cyclohexene oxide (**1a**). 2-Mercaptobenzothiazole nucleophiles with electron-donating or electron-neutral substituents generally gave better results (entries 1−8). The low yield for product **3g** was probably due to the poor solubility of substrate **2g** under the reaction conditions (entry 7). For substrates containing electron-withdrawing substituents, lower yields and er's were obtained (entries 9−10). When the reaction between substrates **1a** and **2a** was conducted on 5 mmol scale, the product **3a** was also obtained in 99% yield and 89:11 er, and 89% of **catalyst 2** was recovered, which showed the same catalytic activity for further reactions.

We then explored the substrate scope for meso-epoxides using 10 mol % catalyst loading for the sake of slightly better enantioselectivity (Table 4). We should also note that the best enantioselectivity for different epoxides were obtained at either 15 or 30 °C but generally decreased at temperatures higher than 30 °C (see Table S3 in the Supporting Information for details). Epoxide ring opening products **3a**, **3l**, **3m**, and **3p** were obtained with better enantioselectivities (entries 1, 3, 4, and 7), while the results for **3k**, **3n**, and **3o** were moderate (entries 2, 5, 6). The double epoxide ring opening reaction of substrate **1h** with 2.2 equiv **2a** gave the desired product **3q** with 89:11 er with moderate isolated yield.

Table 3. Substrate Scope for 2-Mercaptobenzothiazoles

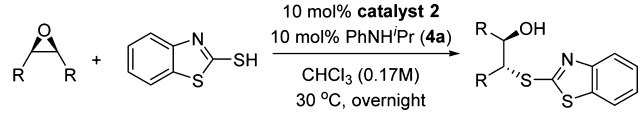


1a **2a-2j** (1.2 eq) **3a-3j**

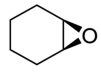
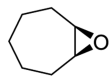
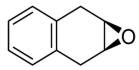
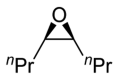
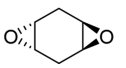
entry	2 (R)	3	yield (%)[a]	er
1	**2a** (H)	**3a**	99	89.5:10.5
2	**2b** (5-OMe)	**3b**	86	86:14
3	**2c** (5-OCF_3)	**3c**	99	90.5:9.5
4	**2d** (5-Me)	**3d**	96	88.5:11.5
5	**2e** (6-Me)	**3e**	99	89.5:10.5
6	**2f** (5-Cl)	**3f**	61	90.5:9.5
7	**2g** (6-Cl)	**3g**	19	82.5:17.5
8	**2h** (5-F)	**3h**	92	89.5:10.5
9	**2i** (5-CN)	**3i**	51	87:13
10	**2j** (5-NO_2)	**3j**	32	81:19

[a]Isolated yield for 0.3 mmol scale reactions.

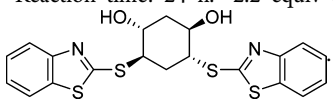
Table 4. Substrate Scope for Meso-Epoxides



1a-1h **2a** (1.2 eq) **3a, 3k-3q**

entry	1	3	yield (%)[a]	er
1[b]		**1a** **3a**	99	90:10
2		**1b** **3k**	73	81.5:18.5
3[b, c]		**1c** **3l**	74	87:13
4		**1d** **3m**	80	86.5:13.5
5		**1e** **3n**	93	81.5:18.5
6[d]		**1f** **3o**	62	68:32
7		**1g** **3p**	90	85:15
8[e]		**1h** **3q**[f]	49	89:11

[a]Isolated yield for 0.3 mmol scale reactions. [b]Run at 15 °C. [c]15 mol % catalyst loading. [d]Reaction time: 24 h. [e]2.2 equiv of **2a** was used. [f]Structure of **3q**:



CONCLUSIONS

In conclusion, we identified the (−)-8-phenylmenthol-derived chiral PCCP-based Brønsted acid combined with equal molar amount of amine additive *N*-isopropylaniline as an efficient catalyst system for the enantioselective desymmetrization of meso-epoxides by 2-mercaptobenzothiazoles. Up to 99% yield and 90.5:9.5 er of the ring opening product were obtained for this reaction, showcasing the potential for further development and application of Lambert's PCCP-based Brønsted acid catalysts. Other research along this line will be reported in due course.

EXPERIMENTAL SECTION

General Information. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Thin-layer chromatography was performed on silica gel 60-F254-coated 0.2 mm plates. Flash column chromatography was performed using silica gel (200−300 mesh). All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. All solvents were purchased from commercial suppliers and purified by standard techniques. The enantiomeric excesses were determined by HPLC analysis, which employed a chiral stationary phase column specified in the individual experiment, by comparing

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the samples with the appropriate racemic mixtures. The meso-epoxides **1c**,[16] **1d**,[17] **1e**,[17] **1f**,[6b] **1g**,[18] and **1h**[19] were prepared according to the reported literature procedures.

The **PCCP catalysts 1** and **2** were prepared according to the reported literature procedures.[20] Pentacarbomethoxycyclopentadiene (307 mg, 0.86 mmol), (1*R*,2*S*,5*R*)-(−)-8-phenylmenthol (2.00 g, 8.61 mmol, 97%), and *N*-methylimidazole (0.412 mL, 5.16 mmol) were dissolved in 8.6 mL of toluene (0.1 M) in a two-neck flask. A steady flow of dry N_2 was allowed for the removal of methanol. The reaction solution was stirred at 125 °C in an oil bath for 48 h. Upon completion, the reaction was cooled down to rt and concentrated in vacuo. The crude material was purified by silica gel chromatography (0 → 5% MeOH/CH_2Cl_2), washed with 1 M HCl/CH_2Cl_2 (3×), and dried with anhydrous $MgSO_4$ to afford **catalyst 2**.

*1,2,3,4,5-Pentacarbo-(−)-menthoxycyclopentadiene (PCCP **Catalyst 1**).*[20] Brown solid. 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 20.30 (s, 1H), 5.05−4.60 (m, 5H), 2.58−0.68 (m, 90H).

*1,2,3,4,5-Pentacarbo-(−)-8-phenylmenthoxycyclopentadiene (**PCCP Catalyst 2**).* Brown solid. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 20.06 (s, 1H), 7.45−6.80 (m, 25H), 5.40−4.75 (m, 5H), 2.95−0.60 (m, 85H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.8, 165.4, 164.6, 163.8, 162.1, 161.9, 161.3, 159.7, 152.2, 151.6, 151.3, 151.1, 150.4, 150.4, 150.2, 149.5, 144.5, 140.3, 138.6, 137.0, 129.3, 128.8, 128.3, 128.0, 128.0, 127.8, 127.7, 127.0, 125.8−124.7, 123.4, 107.6, 79.8, 77.9, 77.7, 77.1, 75.6, 75.3, 60.2, 51.7, 51.1, 50.7, 50.4, 50.2, 50.1, 49.4, 42.4, 41.6, 41.5, 41.3, 41.1, 41.0, 40.7, 40.6, 40.6, 40.5, 40.3, 39.7, 39.4, 35.4, 34.9, 34.7, 34.3, 32.2, 31.8−30.9, 29.3, 28.9, 27.8, 27.4, 27.1, 26.5, 26.4, 22.9, 22.6, 22.3, 22.1, 22.0, 21.9, 21.7, 21.6, 21.4, 14.1. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{90}H_{117}O_{10}$, 1357.8641; found, 1357.8649.

Typical Procedure for the Synthesis of 2-Mercaptobenzothiazoles (2b−2j). The synthesis by a modified literature method[21] is given as follows: To a solution of potassium ethylxanthate (1.76 g, 11.0 mmol) in dimethylformamide (7.5 mL) was added 2-bromo-5-methoxyaniline (1.00 g, 5.0 mmol). The reaction mixture was stirred for 12 h at 120 °C in an oil bath. After cooling down to rt, the reaction mixture was poured into ice water (200 mL), followed by adding 1 M HCl until pH = 2. Then, the mixture was filtered and the cake was washed by deionized water, dried under infrared, and then recrystallized from chloroform. Then, the solid was dissolved in EtOAc, stirred with 200 mg activated charcoal (powder) for 30 min at rt, and filtered through celite to yield 5-methoxybenzo[*d*]thiazole-2-thiol (**2b**) as a white solid (221 mg, 22%).

*5-Methoxybenzo[d]thiazole-2-thiol (**2b**).*[22] White solid. 22% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.63 (s, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 3H).

*5-(Trifluoromethoxy)benzo[d]thiazole-2-thiol (**2c**).* **2c** was prepared from 2-bromo-5-trifluoromethoxyaniline. Reaction condition: 120 °C, 4 h. Colorless crystal, 57% yield. mp 193−195 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.90 (s, 1H), 7.85−7.80 (m, 1H), 7.34−7.28 (m, 1H), 7.21 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 191.9, 147.8, 142.5, 128.9, 123.8, 120.5 (q, *J* = 263 Hz), 117.5, 105.5. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_8H_5F_3NOS_2$, 251.9759; found, 251.9760.

*5-Methylbenzo[d]thiazole-2-thiol (**2d**).*[23] **2d** was prepared from 2-chloro-5-methylaniline. Reaction condition: 150 °C, 14 h. White solid. 31% yield.

*6-Methylbenzo[d]thiazole-2-thiol (**2e**).*[24] **2e** was prepared from 2-chloro-4-methylaniline. Reaction condition: 150 °C, 12 h. White solid. 40% yield.

*5-Chlorobenzo[d]thiazole-2-thiol (**2f**).*[22] **2f** was prepared from 2,5-dichloroaniline. Reaction condition: 120 °C, 12 h. White solid. 56% yield.

*6-Chlorobenzo[d]thiazole-2-thiol (**2g**).*[22] **2g** was prepared from 2,4-dichloroaniline. Reaction condition: 120 °C, 4 h. White solid. 74% yield.

*5-Fluorobenzo[d]thiazole-2-thiol (**2h**).*[25] **2h** was prepared from 2,5-difluoroaniline. Reaction condition: 120 °C, 11 h. White solid. 55% yield.

*2-Mercaptobenzo[d]thiazole-5-carbonitrile (**2i**).*[26] **2i** was prepared from 3-amino-4-chlorobenzonitrile. Reaction condition: 120 °C, 4 h. Yellow solid. 42% yield.

*5-Nitrobenzo[d]thiazole-2-thiol (**2j**).*[27] **2j** was prepared from 2-chloro-5-nitroaniline. Reaction condition: 100 °C, 4 h. Yellow solid. 41% yield.

General Procedure for the Synthesis of Racemic Ring Opening Products (rac-3). To a suspension of 2-mercaptobenzothiazole (0.15 mmol) and meso-epoxide (0.15 mmol) in DCM (2 mL) was added a catalytic amount of TsOH. The reaction mixture was stirred at a 40 °C water bath for 10 min and then concentrated under reduced pressure. The residue was purified by flash column chromatography to give the desired product.

General Procedure for the Asymmetric Synthesis of Ring Opening Products (3). A flame-dried 10 mL Schlenk tube was charged with 2-mercaptobenzothiazole (0.36 mmol), cyclopentadiene (0.015 mmol), *N*-isopropylaniline (0.015 mmol), and dry chloroform (1.8 mL). The reaction mixture was brought to 15 °C and then meso-epoxide (0.3 mmol) was added. The reaction mixture was stirred overnight, and then $NaHCO_3$ powder (200 mg) was added to the reaction solution. Then, the reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to give the desired product.

*(1R,2R)-2-(Benzo[d]thiazol-2-ylthio)cyclohexan-1-ol (**3a**)*[7d] *(90:10 er).* $[\alpha]_D^{20}$ +21.5 (*c* 1.0, $CHCl_3$). Colorless liquid, 79 mg, 99% yield. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 14.8 min (9.9%): t_R = 17.7 min (90.1%).

Absolute configuration was determined by the comparison of the HPLC retention time in ref 7d.

*(1R,2R)-2-((5-Methoxybenzo[d]thiazol-2-yl)thio)-cyclohexan-1-ol (**3b**)*[7d] *(86:14 er).* $[\alpha]_D^{20}$ +10.7 (*c* 1.0, $CHCl_3$). Colorless liquid, 76 mg, 86% yield. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 17.0 min (13.8%): t_R = 21.0 min (86.2%).

*(1R,2R)-2-((5-(Trifluoromethoxy)benzo[d]thiazol-2-yl)-thio)cyclohexan-1-ol (**3c**) (90.5:9.5 er).* $[\alpha]_D^{20}$ +7.1 (*c* 1.0, $CHCl_3$). Colorless solid, 104 mg, 99% yield. mp 37−39 °C. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 10.3 min (9.6%): t_R = 11.1 min (90.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74−7.69 (m, 2H), 7.20−7.16 (m, 1H), 4.21 (d, *J* = 3.2 Hz, 1H), 3.77−3.69 (m, 1H), 3.68−3.60 (m, 1H), 2.30−2.18 (m, 2H), 1.84−1.74 (m, 2H), 1.63−1.51 (m, 1H), 1.51−1.42 (m, 1H), 1.41−1.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 153.2, 147.9, 133.8, 121.6, 120.5 (q, *J* = 258.6 Hz), 118.0, 113.9, 74.6,

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55.6, 35.6, 32.2, 26.0, 24.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}F_3NO_2S_2$, 350.0491; found, 350.0499.

(1R,2R)-2-((5-Methylbenzo[d]thiazol-2-yl)thio)-cyclohexan-1-ol ***(3d)*** *(88.5:11.5 er).* $[\alpha]_D^{20}$ +13.2 (c 1.0, $CHCl_3$). Colorless liquid, 81 mg, 96% yield. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 14.0 min (11.5%): t_R = 16.7 min (88.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 4.77 (s, 1H), 3.66−3.58 (m, 2H), 2.44 (s, 3H), 2.26−2.17 (m, 2H), 1.81−1.72 (m, 2H), 1.59−1.39 (m, 2H), 1.38−1.28 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.2, 152.9, 136.3, 132.6, 126.2, 121.7, 120.5, 74.9, 55.6, 35.7, 32.2, 26.1, 24.1, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{18}NOS_2$, 280.0824; found, 280.0828.

(1R,2R)-2-((6-Methylbenzo[d]thiazol-2-yl)thio)-cyclohexan-1-ol ***(3e)*** *(89.5:10.5 er).* $[\alpha]_D^{20}$ +24.4 (c 1.0, $CHCl_3$). Colorless solid, 83 mg, 99% yield. mp 84−86 °C. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 20.5 min (10.4%): t_R = 43.0 min (89.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 1H), 7.49 (s, 1H), 7.19 (d, J = 8.0 Hz, 1H), 4.81 (br s, 1H), 3.66−3.56 (m, 2H), 2.42 (s, 3H), 2.26−2.16 (m, 2H), 1.80−1.71 (m, 2H), 1.58−1.38 (m, 2H), 1.37−1.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 150.7, 135.8, 134.8, 127.7, 121.1, 120.8, 74.8, 55.6, 35.6, 32.2, 26.1, 24.1, 21.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{18}NOS_2$, 280.0824; found, 280.0828.

(1R,2R)-2-((5-Chlorobenzo[d]thiazol-2-yl)thio)-cyclohexan-1-ol ***(3f)***[7d] *(90.5:9.5 er).* $[\alpha]_D^{20}$ +12.2 (c 1.0, $CHCl_3$). White solid, 55 mg, 61% yield. mp 74−76 °C. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 15.5 min (9.6%): t_R = 17.4 min (90.4%).

(1R,2R)-2-((6-Chlorobenzo[d]thiazol-2-yl)thio)-cyclohexan-1-ol ***(3g)*** *(82.5:17.5 er).* $[\alpha]_D^{20}$ +14.2 (c 1.0, $CHCl_3$). White solid, 17 mg, 19% yield. mp 87−89 °C. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 19.9 min (17.6%): t_R = 29.5 min (82.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76−7.71 (m, 1H), 7.70−7.67 (m, 1H), 7.38−7.32 (m, 1H), 4.35 (br s, 1H), 3.71−3.56 (m, 2H), 2.30−2.15 (m, 2H), 1.82−1.73 (m, 2H), 1.61−1.40 (m, 2H), 1.40−1.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 151.1, 136.7, 130.5, 126.9, 122.1, 120.6, 74.6, 55.7, 35.5, 32.2, 26.0, 24.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}ClNOS_2$, 300.0278; found, 300.0282.

(1R,2R)-2-((5-Fluorobenzo[d]thiazol-2-yl)thio)cyclohexan-1-ol ***(3h)*** *(89.5:10.5 er).* $[\alpha]_D^{20}$ +14.5 (c 1.0, $CHCl_3$). White solid, 78 mg, 92% yield. mp 72−73 °C. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 16.2 min (10.4%): t_R = 17.4 min (89.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, J = 8.8, 5.2 Hz, 1H), 7.48 (dd, J = 9.6, 2.4 Hz, 1H), 7.87 (dt, J = 8.8, 2.4 Hz, 1H), 4.33−4.29 (m, 1H), 3.67−3.53 (m, 2H), 2.22−2.11 (m, 2H), 1.77−1.68 (m, 2H), 1.55−1.43 (m, 1H), 1.43−1.32 (m, 1H), 1.32−1.17 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2, 161.9 (d, J = 244.4 Hz), 153.4 (d, J = 12.1 Hz), 130.8, 121.6 (d, J = 10.1 Hz), 113.1 (d, J = 25.3 Hz), 108.0 (d, J = 24.2 Hz), 74.8, 55.7, 35.6, 32.2, 26.1, 24.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}FNOS_2$, 284.0574; found, 284.0580.

2-(((1R,2R)-2-Hydroxycyclohexyl)thio)benzo[d]thiazole-5-carbonitrile ***(3i)*** *(87:13 er).* $[\alpha]_D^{20}$ +4.2 (c 1.5, $CHCl_3$). White solid, 44 mg, 51% yield. mp 114−116 °C. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 20/80, flow rate = 1.0 mL/min): t_R = 22.2 min (13.0%): t_R = 24.3 min (87.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 3.84−3.75 (m, 1H), 3.73−3.70 (m, 1H), 3.69−3.61 (m, 1H), 2.33−2.18 (m, 2H), 1.86−1.76 (m, 2H), 1.66−1.54 (m, 1H), 1.54−1.44 (m, 1H), 1.44−1.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0, 152.3, 140.4, 127.0, 125.1, 122.0, 118.6, 109.9, 74.3, 55.7, 35.5, 32.2, 26.0, 24.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}N_2OS_2$, 291.0620; found, 291.0624.

(1R,2R)-2-((5-Nitrobenzo[d]thiazol-2-yl)thio)cyclohexan-1-ol ***(3j)*** *(81:19 er).* $[\alpha]_D^{20}$ +1.7 (c 1.0, $CHCl_3$). White solid, 30 mg, 32% yield. mp 116−118 °C. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 30/70, flow rate = 1.0 mL/min): t_R = 12.4 min (19.2%): t_R = 17.4 min (80.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 2.4 Hz, 1H), 8.17 (dd, J = 8.8, 2.4 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 3.86−3.79 (m, 1H), 3.70−3.62 (m, 2H), 2.34−2.27 (m, 1H), 2.26−2.19 (m, 1H), 1.86−1.77 (m, 2H), 1.67−1.56 (m, 1H), 1.55−1.45 (m, 1H), 1.44−1.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 152.5, 146.8, 142.0, 121.3, 119.1, 116.6, 74.4, 55.8, 35.6, 32.2, 26.0, 24.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}N_2O_3S_2$, 311.0519; found, 311.0518.

(1R,2R)-2-(Benzo[d]thiazol-2-ylthio)cyclopentan-1-ol ***(3k)*** *(81.5:18.5 er).* $[\alpha]_D^{20}$ +66.5 (c 1.0, $CHCl_3$). Colorless liquid, 55 mg, 73% yield. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 10.7 min (18.4%): t_R = 14.2 min (81.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.44−7.38 (m, 1H), 7.33−7.27 (m, 1H), 5.34 (br s, 1H), 4.38 (dd, J = 12.0, 8.0 Hz, 1H), 3.90 (dd, J = 16.0, 8.0 Hz, 1H), 2.37−2.26 (m, 1H), 2.20−2.09 (m, 1H), 1.94−1.75 (m, 3H), 1.67−1.56 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.7, 152.3, 135.0, 126.3, 124.6, 121.0, 121.0, 81.5, 54.2, 34.3, 30.9, 23.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}NOS_2$, 252.0511; found, 252.0516.

(1R,2R)-2-(Benzo[d]thiazol-2-ylthio)cycloheptan-1-ol ***(3l)*** *(87:13 er).* $[\alpha]_D^{20}$ +27.3 (c 1.0, $CHCl_3$). Colorless liquid, 62 mg, 74% yield. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 13.1 min (13.1%): t_R = 16.4 min (86.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.4 Hz, 1H), 7.74 (dd, J = 8.0, 0.4 Hz, 1H), 7.44−7.38 (m, 1H), 7.33−7.27 (m, 1H), 5.03 (d, J = 2.0 Hz, 1H), 4.10 (ddd, J = 6.4, 3.6, 2.4 Hz, 1H), 3.96 (ddd, J = 8.8, 6.8, 3.2 Hz, 1H), 2.18−2.10 (m, 1H), 1.96−1.49 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 152.5, 135.3, 126.2, 124.5, 121.2, 121.0, 77.9, 58.3, 34.8, 31.8, 29.0, 27.1, 23.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{18}NOS_2$, 280.0824; found, 280.0827.

(1R,6R)-6-(Benzo[d]thiazol-2-ylthio)cyclohex-3-en-1-ol ***(3m)*** *(86.5:13.5 er).* $[\alpha]_D^{20}$ +40.5 (c 1.0, $CHCl_3$). Colorless solid, 63 mg, 80% yield. mp 59−61 °C. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 11.3 min (13.7%): t_R = 19.0 min (86.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.44−7.38 (m, 1H), 7.33−7.28 (m, 1H), 5.70−5.64 (m, 1H), 5.63−5.57 (m, 1H), 4.32 (br s, 1H), 4.03−3.93 (m, 2H), 2.79−2.61 (m, 2H), 2.40−2.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.0, 152.5, 135.5, 126.3, 125.3, 124.7, 124.7, 121.6, 121.0, 70.8, 51.3, 34.8, 31.8.

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HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}NOS_2$, 264.0511; found, 264.0518.

*(2R,3R)-3-(Benzo[d]thiazol-2-ylthio)-1,2,3,4-tetrahydronaphthalen-2-ol (**3n**) (81.5:18.5 er).* $[\alpha]_D^{20}$ −3.2 (*c* 1.0, $CHCl_3$). Colorless liquid, 87 mg, 93% yield. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 15.0 min (18.3%): t_R = 18.2 min (81.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.46−7.40 (m, 1H), 7.36−7.30 (m, 1H), 7.21−7.13 (m, 3H), 7.12−7.08 (m, 1H), 4.57 (br s, 1H), 4.25−4.11 (m, 2H), 3.45 (dd, J = 16.4, 5.6 Hz, 1H), 3.34 (dd, J = 16.0, 5.6 Hz, 1H), 3.08 (dd, J = 16.4, 10.4 Hz, 1H), 3.00 (dd, J = 16.0, 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 152.5, 135.5, 134.3, 133.9, 129.0, 128.0, 126.7, 126.4, 126.3, 124.8, 121.6, 121.1, 71.7, 51.9, 38.2, 34.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}NOS_2$, 314.0668; found, 314.0669.

*(4R,5R)-5-(Benzo[d]thiazol-2-ylthio)octan-4-ol (**3o**) (68:32 er).* $[\alpha]_D^{20}$ +11.4 (*c* 1.0, $CHCl_3$). Colorless liquid, 55 mg, 62% yield. HPLC (Daicel CHIRALPAK AD-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 5.8 min (31.9%): t_R = 7.8 min (68.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.43−7.38 (m, 1H), 7.33−7.27 (m, 1H), 4.13 (s, 1H), 3.89 (s, 1H), 3.73−3.66 (m, 1H), 1.97−1.79 (m, 2H), 1.69−1.39 (m, 6H), 0.94 (dt, J = 7.2, 2.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 152.7, 135.6, 126.2, 124.5, 121.4, 121.0, 73.4, 56.4, 38.3, 34.0, 20.7, 19.2, 14.1, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{22}NOS_2$, 296.1137; found, 296.1143.

*(1R,2R)-2-(Benzo[d]thiazol-2-ylthio)-1,2-diphenylethan-1-ol (**3p**) (85:15 er).* $[\alpha]_D^{20}$ −338.7 (*c* 1.5, $CHCl_3$). Colorless liquid, 98 mg, 90% yield. HPLC (Daicel CHIRALPAK AS-H column, ^{i}PrOH/hexane = 10/90, flow rate = 1.0 mL/min): t_R = 9.0 min (15.2%): t_R = 10.6 min (84.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.48−7.42 (m, 1H), 7.35−7.30 (m, 1H), 7.25−7.17 (m, 10H), 5.29−5.26 (m, 1H), 5.22−5.16 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 152.4, 141.7, 137.9, 135.6, 128.6, 128.4, 128.1, 128.0, 127.8, 126.8, 126.3, 124.7, 121.6, 121.1, 78.8, 61.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}NOS_2$, 364.0824; found, 364.0829.

*(1R,3R,4R,6R)-4,6-Bis(benzo[d]thiazol-2-ylthio)-cyclohexane-1,3-diol (**3q**) (89:11 er).* $[\alpha]_D^{20}$ −191.3 (*c* 1.0, $CHCl_3$). Colorless solid, 65 mg, 49% yield. mp 41−42 °C. HPLC (Daicel CHIRALPAK AS-H column, ^{i}PrOH/hexane = 20/80, flow rate = 1.0 mL/min): t_R = 8.5 min (88.9%): t_R = 13.9 min (11.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.40−7.34 (m, 2H), 7.30−7.24 (m, 2H), 4.32 (dd, J = 12.0, 6.0 Hz, 2H), 4.24 (br s, 2H), 4.16 (dd, J = 12.0, 6.0 Hz, 2H), 2.59 (t, J = 6.0 Hz, 2H), 2.19 (t, J = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.7, 152.6, 135.3, 126.3, 124.7, 121.6, 121.0, 69.6, 50.4, 38.0, 31.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}N_2O_2S_4$, 447.0324; found, 447.0320.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01207.

Experimental details of the condition optimization; ^{1}H NMR and ^{13}C NMR spectra; and HPLC trace for products (PDF)

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Notes

The authors declare no competing financial interest.

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