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Chiral Hypervalent Organoiodine-Catalyzed Enantioselective Oxidative Spirolactonization of Naphthol Derivatives

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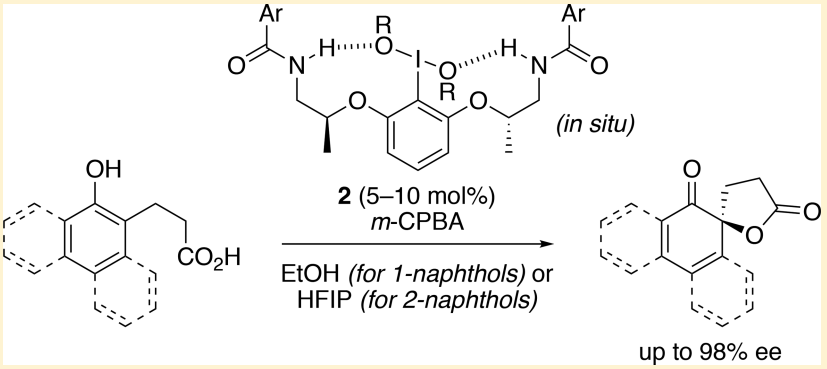
Supporting Information

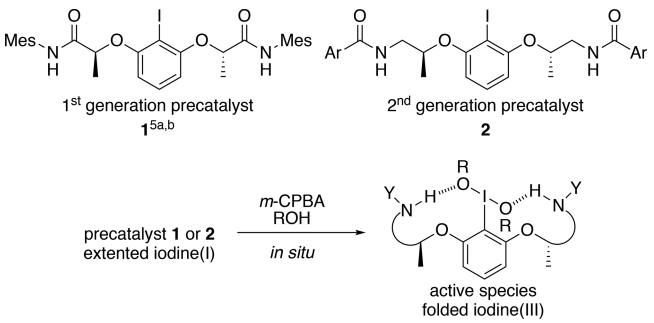


ABSTRACT: Highly enantioselective oxidative dearomatization of 2-naphthol derivatives was achieved for the first time by using conformationally flexible organoiodine catalysts derived from 2-aminoalcohol as a chiral source. Moreover, with the use of these catalysts, excellent enantioselectivities were also achieved for 1-naphthol derivatives, which had previously been obtained with only lower enantioselectivities. Furthermore, the product obtained from the present reaction could be transformed to a highly functionalized spirolactone in high yield and with excellent stereoselectivity.

The enantioselective oxidative dearomatization of arenols and their analogues is a useful method for the synthesis of several important medicinally and biologically active compounds.[1] On the other hand, the development of asymmetric redox catalysis based on hypervalent iodine chemistry is currently one of the most progressive research areas in asymmetric organocatalysis.[2,3] Kita and colleagues succeeded in the first enantioselective oxidative dearomatization of 1-naphthol derivatives with chiral a μ-oxo-bridged-hypervalent iodine(III), which has a conformationally rigid 1,1-spiroindanone backbone.[4] In contrast to Kita's conformationally rigid catalysts, we demonstrated the rational design of conformationally flexible hypervalent organoiodines(III) as chiral catalysts based on secondary nonbonding interactions (i.e., intramolecular hydrogen-bonding interactions between the acidic amido protons and the iodine(III) ligands) for the same reaction (Scheme 1).[5,6]

In 2010, we designed C_2-symmetric organoiodine **1** (1st-generation precatalyst) derived from lactate as a chiral source for the catalytic enantioselective oxidative spirolactonization of 1-naphthol derivatives **3** to the corresponding spirolactones **4** (Scheme 2, eq 1).[5a,b] However, **1** was found to be insufficient for the oxidation of phenols **5**, which were less reactive than 1-naphthols, with respect to not only reactivity but also enantioselectivity.[6a] To overcome these limitations, we designed new chiral organoiodines **2** derived from 2-aminoalcohol instead of lactate as a chiral source (Scheme 1), and the desired cyclohexadienone spirolactones **6** could be obtained

Scheme 1. Conformationally Flexible Chiral Organoiodine(III) Catalysts



with excellent enantioselectivities (up to 99% ee, Scheme 2, eq 2).[6a] Moreover, we succeeded in rationally controlling the desired associated pathway[1h,7] using alcohol additives such as methanol or ethanol (for electron-rich phenols) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) (for electron-deficient phenols).[6] X-ray diffraction and NOE (Nuclear Overhauser Effect)−NMR analyses of in situ-generated organoiodines(III) showed that a suitable chiral environment around the

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Scheme 2. Enantioselective Oxidative Dearomatization of Arenols

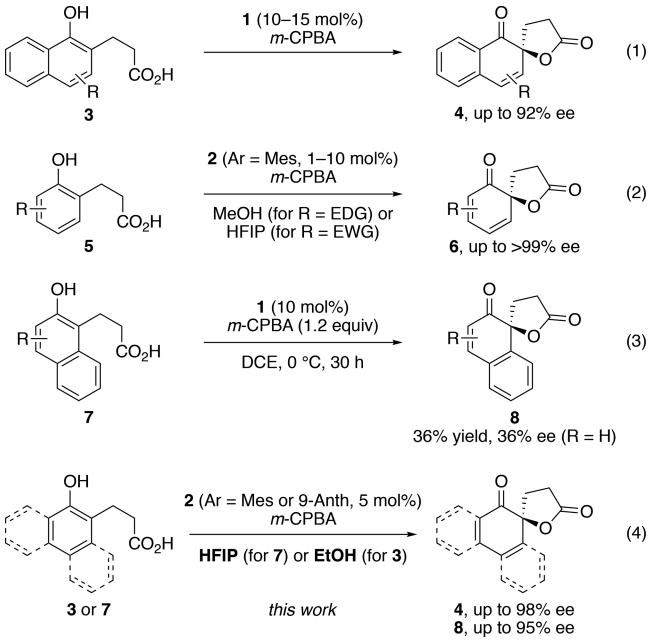
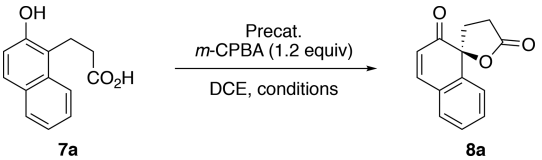


Table 1. Enantioselective Oxidative Dearomatization of 2-Naphthol 7a[a]



entry	precat (mol %)	additive (equiv)	T (°C), t (h)	**8a**, yield (%)	**8a**, ee (%)[b]
1	**1** (10)	–	0, 30	36	36
2	**2a** (10)	–	0, 4	84	77
3	**2b** (10)	–	0, 6	71	86
4	**2b** (10)	–	−20, 18	72	89
5	**2b** (5)	–	−20, 24	63	89
6	**2b** (10)	EtOH (6)[c]	−20, 24	72	76
7	**2b** (5)	HFIP (50)[d]	−20, 15	87	95
8	**2a** (5)	HFIP (50)[d]	−20, 15	89	94
9	**1** (10)	HFIP (50)[d]	−20, 15	50	79

[a]Reactions were performed using purified *m*-CPBA (>99% purity). [b]Determined by HPLC analysis. [c]**8a** was obtained in 20% yield with 73% ee in the presence of **2a** as a precatalyst and MeOH (25 equiv)[6a] as an additive under identical conditions. [d]Dichloromethane was used as a solvent instead of DCE.

iodine(III) center was constructed via intramolecular hydrogen-bonding interactions (Scheme 1).[6a]

Further studies revealed that our first-generation precatalyst **1** was less effective for the oxidation of not only phenols **5** but also 2-naphthol derivatives **7**, which were both less reactive than **3** (Scheme 2, eq 3). On the other hand, arylative[8] or oxidative[9] methods for the enantioselective dearomatization of 2-naphthol derivatives have recently been reported with the use of transition metal or organocatalysts. Here, we report the first transition metal-free enantioselective oxidative dearomatization of 2-naphthols.[10] We achieved a highly enantioselective oxidative dearomatization of 2-naphthol derivatives **7** by using our second-generation precatalysts **2** in the presence of HFIP as an additive (Scheme 2, eq 4). Moreover, we also achieved excellent enantioselectivities (up to 98% ee) for the oxidative dearomatization of 1-naphthol derivatives **3** by using **2** in the presence of ethanol as an additive (Scheme 2, eq 4).

Initially, iodoarenes **2** were examined as precatalysts for the enantioselective oxidative cyclization of 2-naphthol derivative **7a** in the presence of *m*-CPBA as an oxidant in 1,2-dichloroethane (DCE) (Table 1).[11] As in our previous studies on the oxidation of phenols,[6a] bis(mesityl carboxamide) **2a** was superior to first-generation precatalyst **1** with respect to both reactivity and enantioselectivity (entry 2 versus entry 1). The oxidation of **7a** in the presence of 10 mol % of **2a** gave **8a** in 84 yield with 77% ee (entry 2). Furthermore, bis(9-anthracenyl carboxamide) **2b**, a new precatalyst, was superior to **2a** (entry 3), and the enantioselectivity was increased to 89% ee at −20 °C (entry 4). Notably, the catalyst loading of **2b** could be reduced to 5 mol % without affecting the enantioselectivity, although the chemical yield was slightly decreased (entry 5). Next, additional effects of alcohols[6a] on the reactivity and enantioselectivity were examined for the present oxidation. The enantioselectivity of **9a** significantly decreased in the presence of ethanol or methanol as an additive (entry 6). On the other hand, in sharp contrast to the results with 1-naphthols,[5a,11] the additional use of HFIP in dichloromethane improved both the reactivity and enantioselectivity for the oxidation of 2-naphthols, and **8a** was obtained in 87% yield with 95% ee after a shorter reaction time (entry 7).[12] Interestingly, the use of precatalyst **2a** gave the same high reactivity and enantioselectivity (89% yield, 94% ee) in the presence of HFIP (entry 8). The beneficial effect of HFIP for the present oxidation was also confirmed with the use of lactate-based precatalyst **1** (entry 9 versus entry 1). Although the additional effects of alcohols are not yet clear, the beneficial effect of HFIP for the oxidation of 2-naphthols, which are less reactive than 1-naphthols, is similar to our previous results regarding the oxidation of phenols, where HFIP was used for the oxidation of less-reactive phenols.[6a]

To explore the generality and substrate scope of the present oxidative spirolactonization, several 2-naphthol derivatives **7** were examined as substrates in the presence of 5 mol % of **2a** as a precatalyst and HFIP as an additive under optimized conditions in dichloromethane (Table 2).[11] The corresponding spirolactones **8b–i** were obtained in moderate to high yields and with high enantioselectivities (87–95% ee). As an exception, the use of **2b** instead of **2a** as a precatalyst for the oxidation of **7e** gave slightly higher enantioselectivity (entry 4). The oxidation of alkoxy group-substituted **7f** and **7h** gave relatively lower chemical yields as well as enantioselectivities, due to formation of several unidentified side-products (entries 5 and 7). Importantly, enantiomerically almost pure (99% ee) **8b** was obtained after a single recrystallization (entry 1). The absolute configurations of **8** were determined to be (*S*) on the basis of the X-ray diffraction analysis of **8b**.[11,14]

Next, the enantioselective oxidative spirolactonization of 1-naphthol derivatives **3** was examined using 5 mol % of **2a** as a precatalyst in DCE (Table 3).[11] In contrast to the results with 2-naphthols (Table 1), the use of ethanol as an additive for the oxidation of 1-naphthols **3** provided higher enantioselectivity.[13] As a result, the oxidative dearomatization of known 1-naphthol derivatives **3b–g**[5] and a new substrate **3h** gave the corresponding spirolactones (*S*)-**4b–h** in high yields and with high to excellent enantioselectivities (91–98%). Notably, these

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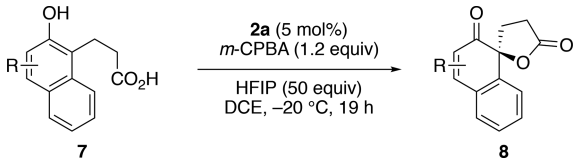
Table 2. Enantioselective Oxidative Dearomatization of 2-Naphthols 7[a]

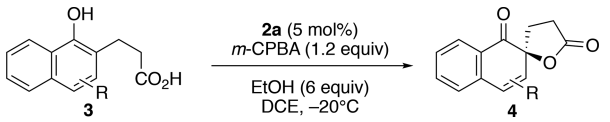


7 8

entry	R	7	8, yield (%)	8, ee (%)[b]
1	3-Br	**7b**	85	89 (99)[c]
2	6-Br	**7c**	95	95
3	8-F	**7d**	92	95
4[d]	4-Me	**7e**	83	95
5	7-OMe	**7f**	51	89
6	7-OMOM	**7g**	85	91
7	7-OBn	**7h**	57	87
8	6-CN	**7i**	99	95

[a]Reactions were performed using purified *m*-CPBA (>99% purity). [b]Determined by HPLC analysis. [c]After a single recrystallization. [d]Precatalyst **2b** was used instead of **2a**. **8e** was obtained in 65% yield with 89% ee using **2a** under identical conditions.

Table 3. Enantioselective Oxidative Dearomatization of 1-Naphthols 3[a]



3 4

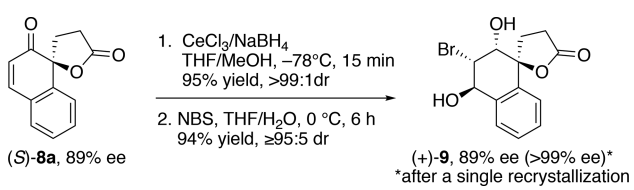
entry	R	3	time (h)	4, yield (%)	4, ee (%)[b]
1	H	**3a**	36	86	98
2[c]	4-Cl	**2b**	23	93	98
3	4-Br	**3c**	24	99	95
4	4-Ph	**3d**	43	90	96
5	4-CO(*p*-BrC$_6$H$_4$)	**3e**	23[d]	99	96
6	3-CH$_2$OBn	**3f**	60	74	97
7[c]	6-OMe	**3g**	23	73	97
8	5-NHTs	**3h**	36	56	91

[a]Reactions were performed using purified *m*-CPBA (>99% purity). [b]Determined by HPLC analysis. [c]**2a** (10 mol %). [d]At 0 °C.

spirolactones **4b–g** were obtained in lower chemical yield (40–94% yield) with lower enantioselectivities (83–92% ee) with the use of our first-generation precatalyst **1**.[5]

With a versatile and enantioselective synthesis of spirolactones in hand, we sought to demonstrate the further synthetic utility of these compounds (Scheme 3). The stereoselective reduction of **8a** under Luche conditions[15] gave a single diastereomer of allylic alcohol in 96% yield, which was diastereoselectively transformed to bromohydrin (+)-**9** in 94% yield (≥95:5 dr) using NBS. Fortunately, enantiomerically pure (+)-**9** (>99% ee) was obtained after a single recrystallization. The relative stereochemistry of **9** was determined by X-ray diffraction analysis.[11,14]

Scheme 3. Transformation of 8a to 9



(*S*)-**8a**, 89% ee (+)-**9**, 89% ee (>99% ee)*
*after a single recrystallization

In summary, we achieved an enantioselective oxidative dearomatization of 2-naphthol derivatives for the first time by using our conformationally flexible organoiodine catalysts. Moreover, excellent enantioselectivities were achieved for 1-naphthol derivatives, which had previously been obtained with lower enantioselectivities. Interestingly, the use of HFIP and methanol as additives[6] was crucial to induce high enantioselectivity for 2-naphthol and 1-napthols, respectively. Furthermore, a highly functionalized spirolactone can be synthesized from the oxidation of 2-naphthol derivative in high yield and with excellent stereoselectivity.

EXPERIMENTAL SECTION

General Information. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet, brs = broad singlet), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) spectrometers. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.00 ppm). ^{19}F NMR spectra were measured on a JEOL ECS-400 (376 MHz) spectrometer. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), cerium ammonium molybdate and phosphomolybdic acid. The products were purified by column chromatography on silica gel (E. Merck Art. 9385, Kanto Chemical Co., Inc. 37560 or Fuji Silysia Chemical, Cromatorex NH-DM1020). High-resolution mass spectral analyses (HRMS) were performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700). The mass analyzer type used for HRMS measurements is magnetic sector. High-performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP and chiral column of Daicel CHIRALCEL OD-H (4.6 mm × 25 cm), OD-3 (4.6 mm × 25 cm), IA-3 (4.6 mm × 25 cm), IC-3 (4.6 mm × 25 cm), AS-3 (4.6 mm × 25 cm).

In experiments that required dry solvents, toluene, tetrahydrofuran (THF), dichloromethane and dichloroethane, were purchased from Wako Pure Chemical Industries Ltd. or Kanto Chemical Co., Inc. as the "anhydrous" and stored over 4 Å molecular sieves. Chloroform was purchased from Nacalai Tesque, Inc. (Lot No.; V2H8527, Code; 08402–55). Other solvents were purchased from Aldrich, Wako or Kanto and used without further purification. Precatalyst **1**[5] and **2a**,[6a] substrates **3a–g**[5] and products **4a–g**[5] are known compounds. Precatalyst **1** can be purchased from Wako Pure Chemical Industries, Ltd. or Tokyo Chemical Industry Co., Ltd. Other simple chemicals were analytical-grade and obtained commercially and used without further purification.

Commercially available *m*-CPBA (Aldrich, ca. 77% purity) was purified by standard methods[16] to give pure *m*-CPBA (≥99% purity). Although the commercial *m*-CPBA could be also used, purified *m*-CPBA gave more reproducible results. Phosphate buffer (pH 7.8 at 23.7 °C) was prepared from $NaH_2PO_4{\cdot}2H_2O$ (2.40 g) and Na_2HPO_4 (23.4 g) in distilled H_2O (900 mL), and used for purification of *m*-CPBA.

*N,N′-(2S,2′S)-2,2′-(2-Iodo-1,3-phenylene)bis(oxy)bis(propane-2,1-diyl)dianthracene-9-carboxamide (**2b**).* This compound was prepared as **2a** from (2*S*,2′*S*)-2,2′-(2-iodo-1,3-phenylene)bis(oxy)-dipropan-1-amine[6a] with 9-anthracenecarbonyl chloride in 73% yield (0.544 g, 0.730 mmol).[6a] Pale yellow solid; TLC, R_f = 0.50 (hexane–EtOAc = 1:1); IR (KBr) 3395, 3300–3200, 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48 (d, J = 6.0 Hz, 6H), 3.65–3.72 (m, 2H), 4.19 (ddd, J = 3.2, 6.8, 13.6 Hz, 2H), 4.84–4.88 (m, 2H), 6.61–6.66

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(m, 4H), 7.32 (t, J = 8.4 Hz, 1H), 7.10−8.20 (m, 16H), 8.44 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 17.7, 45.0, 75.0, 82.4, 107.2, 124.9, 125.3, 126.5, 127.9, 128.3, 128.4, 130.0, 130.9, 131.4, 157.7, 169.7; HRMS (FAB) m/z calcd for $[C_{42}H_{35}IN_2O_4 + H]^+$ 759.1714, found 759.1720; $[\alpha]^{25.8}_D$ = +140.9 (c 1.0, $CHCl_3$).

*3-(1-Hydroxy-5-(4-methylphenylsulfonamido)naphthalen-2-yl)-propanoic acid (**3h**).* This compound was prepared as **3a**−**g** from *N*-(5-hydroxynaphthalen-1-yl)-4-methylbenzenesulfonamide[17] in 55% yield for 3 steps (1.06 g, 2.75 mmol).[5a,b] Brown solid; TLC, R_f = 0.37 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3433, 3244, 1697 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.31 (s, 3H), 2.54 (t, J = 7.8 Hz, 2H), 2.96 (t, J = 7.8 Hz, 2H), 7.08 (d, J = 8.2 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 7.28−7.32 (m, 3H), 7.54 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 8.2 Hz, 2H), 8.05 (d, J = 8.2 Hz, 1H), 9.19 (brs, 1H), 10.06 (s, 1H), 12.19 (brs, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 21.0, 25.3, 34.2, 114.7, 120.6, 122.0, 122.1, 124.2, 126.4, 126.8, 128.5, 129.4, 129.6, 132.4, 137.5, 143.0, 149.5, 174.3; HRMS (FAB) m/z calcd for $[C_{20}H_{19}NO_5S + H]^+$ 386.1062, found 386.1053.

Representative Experimental Procedures for the Preparation of 7a−f (7a as an Example).[18] To a stirred solution of 2-naphthol (1.44 g, 10.0 mmol) and amberlyst (1.00 g) in toluene (30.0 mL) was added acrylic acid (1.36 mL, 20.0 mmol) and the resulting mixture was refluxed overnight. The resulting suspension was filtered through Celite and the solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: hexane−EtOAc = 20:1) to give 1,2-dihydro-3*H*-benzo[*f*]chromen-3-one (1.78 g, 9.00 mmol, 90% yield). To a solution of this lactone (1.78 g, 9.00 mmol) in THF (40.0 mL) was added 1 M LiOH (30.0 mL), and the resulting mixture was stirred for 6 h at 25 °C. The resulting mixture was poured into 1 M HCl (100 mL), and aqueous layer was separated and extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, and solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: hexane−EtOAc = 4:1 to 1:1) to give **3a** (1.95 g, 9.00 mmol) quantitatively.

*3-(2-Hydroxynaphthalen-1-yl)propanoic Acid (**7a**).*[10b,18] White solid; TLC, R_f = 0.52 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.95 (t, J = 6.4 Hz, 2H), 3.33 (t, J = 6.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 8.4 Hz, 1H), 7.50 (t, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 19.4, 33.5, 117.9, 119.4, 122.0, 123.2, 126.7, 128.7, 128.9, 129.5, 132.7, 151.6, 180.4.

*3-(3-Bromo-2-hydroxynaphthalen-1-yl)propanoic Acid (**7b**).* This compound was prepared as **7a** from 3-bromo-2-naphthol in 78% yield for 2 steps (1.15 g, 3.90 mmol). White solid; TLC, R_f = 0.44 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3600−3300, 1696 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.49 (t, J = 8.0 Hz, 2H), 3.30 (t, J = 8.0 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H), 9.38 (brs, 1H), 12.31 (brs, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 21.3, 33.8, 114.4, 122.1, 122.8, 123.9, 126.9, 127.7, 129.4, 130.2, 131.8, 148.3, 174.4; HRMS (FAB) m/z calcd for $[C_{13}H_{11}BrO_3 + H]^+$ 294.9970, found 294.9967.

*3-(6-Bromo-2-hydroxynaphthalen-1-yl)propanoic Acid (**7c**).* This compound was prepared as **7a** from 6-bromo-2-naphthol in 21% yield for 2 steps (0.310 g, 1.05 mmol). White solid; TLC, R_f = 0.44 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3500−3200, 1703 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.40 (t, J = 8.0 Hz, 2H), 3.18 (t, J = 8.0 Hz, 2H), 7.20 (d, J = 9.2 Hz, 1H), 7.52 (d, J = 9.2 Hz, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 8.03 (s, 1H), 9.85 (brs, 1H), 12.19 (brs, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 20.3, 33.7, 115.2, 118.4, 119.2, 124.9, 126.9, 129.0, 129.5, 130.1, 131.5, 152.9, 174.2; HRMS (FAB) m/z calcd for $[C_{13}H_{11}BrO_3 + H]^+$ 294.9970, found 294.9966.

*3-(8-Fluoro-2-hydroxynaphthalen-1-yl)propanoic Acid (**7d**).* This compound was prepared as **7a** from 8-fluoro-2-naphthol[19] in 69% yield for 2 steps (0.808 g, 3.45 mmol). White solid; TLC, R_f = 0.48 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3500−3200, 1685 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.43 (t, J = 8.2 Hz, 2H), 3.28−3.32 (m, 2H), 7.17−7.24 (m, 3H), 7.60 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 9.87 (brs, 1H), 12.12 (brs, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 22.4 (d, J_{C-F} = 11 Hz), 34.8, 111.6 (d, J_{C-F} = 24 Hz), 116.1 (d, J_{C-F} = 5 Hz), 119.0, 122.2 (d, J_{C-F} = 9 Hz), 123.1 (d, J_{C-F} = 11 Hz), 125.0 (d, J_{C-F} = 3 Hz), 127.8, 130.8 (d, J_{C-F} = 5 Hz), 153.6, 158.1 (d, J_{C-F} = 248 Hz), 174.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ − 117.8; HRMS (FAB) m/z calcd for $[C_{13}H_{11}FO_3 + H]^+$ 235.0770, found 235.0775.

*3-(2-Hydroxy-4-methylnaphthalen-1-yl)propanoic Acid (**7e**).* This compound was prepared as **7a** from 4-methyl-2-naphthol[20] in 66% yield for 2 steps (0.760 g, 3.30 mmol). White solid; TLC, R_f = 0.44 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3500−3300, 1690 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.39 (t, J = 8.2 Hz, 2H), 2.55 (s, 3H), 3.17 (t, J = 8.2 Hz, 2H), 7.02 (s, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.87−7.90 (m, 2H), 9.47 (brs, 1H), 12.10 (brs, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 19.1, 20.2, 34.0, 115.9, 118.9, 122.2, 122.7, 124.7, 126.1, 127.4, 133.1, 133.5, 151.7, 174.3; HRMS (FAB) m/z calcd for $[C_{14}H_{14}O_3 + H]^+$ 231.1021, found 231.1021.

*3-(2-Hydroxy-7-methoxynaphthalen-1-yl)propanoic Acid (**7f**).* This compound was prepared as **7a** from 7-methoxy-2-naphthol in 84% yield for 2 steps (1.03 g, 4.20 mmol). White solid; TLC, R_f = 0.48 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3500−3200, 1692 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.45 (t, J = 7.6 Hz, 2H), 3.18 (t, J = 7.6 Hz, 2H), 3.87 (s, 3H), 6.92 (dd, J = 2.8, 8.8 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 2.8 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 9.60 (brs, 1H), 12.17 (brs, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 20.5, 33.6, 55.0, 101.5, 114.4, 115.4, 117.2, 123.5, 127.3, 130.1, 134.2, 153.0, 157.8, 174.6; HRMS (FAB) m/z calcd for $[C_{14}H_{14}O_4 + H]^+$ 247.0970, found 247.0979.

*3-(2-Hydroxy-7-(methoxymethoxy)naphthalen-1-yl)propanoic Acid (**7g**).* To a stirred solution of 9-hydroxy-1,2-dihydro-3H-benzo[*f*]chromen-3-one[18] (0.670 g, 3.12 mmol) and (*i*-Pr)$_2$NEt (1.10 mL, 6.24 mmol) in CH_2Cl_2 (30.0 mL) was added methoxymethyl chloride (0.280 mL, 3.74 mmol) at 0 °C. After stirring overnight at 25 °C, the resulting mixture was poured into H_2O (10.0 mL). The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: hexane−EtOAc = 10:1 to 4:1) to give methoxymethyl ether (0.770 g, 2.96 mmol, 95% yield) as a yellow solid. To a solution of this methoxymethyl ether (0.770 g, 2.96 mmol) in THF (10.0 mL) and MeOH (10.0 mL) was added 2 M NaOH (10.0 mL), and the resulting mixture was stirred overnight at 25 °C. The resulting mixture was poured into 1 M HCl (30.0 mL), and the aqueous layer was separated and extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: hexane−EtOAc = 4:1 to 1:2) to give **7g** (0.540 g, 1.95 mmol) in 66% yield. Pale yellow solid; TLC, R_f = 0.41 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3500−3000, 1682 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.95 (t, J = 6.4 Hz, 2H), 3.27 (t, J = 6.4 Hz, 2H), 3.54 (s, 3H), 5.31 (s, 2H), 7.04 (d, J = 8.7 Hz, 1H), 7.11 (dd, J = 2.4, 8.7 Hz, 1H), 7.31 (d, J = 2.4 Hz, 1H), 7.52 (brs, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 9.10 (brs, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 19.5, 33.2, 56.1, 94.5, 105.7, 115.3, 117.2, 117.5, 125.4, 128.4, 130.4, 134.0, 152.3, 155.8, 180.2; HRMS (FAB) m/z calcd for $[C_{15}H_{16}O_5 + H]^+$ 277.1076, found 277.1080.

*3-(7-(Benzyloxy)-2-hydroxynaphthalen-1-yl)propanoic Acid (**7h**).* To a stirred solution of 9-hydroxy-1,2-dihydro-3H-benzo[*f*]chromen-3-one[18] (1.50 g, 7.00 mmol), K_2CO_3 (1.45 g, 10.5 mmol) and tetrabutylammonium iodide (0.260 g, 0.700 mmol) in acetone (70.0 mL) was added benzyl bromide (1.00 mL, 8.40 mmol) at 25 °C, and the resulting mixture was refluxed for 4 h. The solvents were removed in vacuo. To the residue was added H_2O (40.0 mL), and the aqueous layer was separated and extracted with EtOAc. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and solvents were removed in vacuo. The residue was purified by flash

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column chromatography on silica gel (eluent: hexane−EtOAc = 10:1 to 5:1) to give benzyl ether (2.13 g, 7.00 mmol, > 99% yield). To a solution of this benzyl ether (2.13 g, 7.00 mmol) in THF (30.0 mL) and MeOH (30.0 mL) was added 2 M NaOH (30.0 mL) and the resulting mixture was stirred overnight at 25 °C. The resulting mixture was poured into 1 M HCl (100 mL), and the aqueous layer was separated and extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: hexane−EtOAc = 4:1 to 1:2) to give **8h** (1.69 g, 5.25 mmol) in 75% yield. Pale yellow solid; TLC, R_f = 0.48 (hexane−EtOAc−$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3400−3000, 1685 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.36 (t, J = 7.8 Hz, 2H), 3.17 (t, J = 7.8 Hz, 2H), 5.24 (s, 2H), 6.98−7.00 (m, 2H), 7.28 (d, J = 2.3 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.3 Hz, 2H), 7.51−7.55 (m, 3H), 7.68 (d, J = 9.2 Hz, 1H), 9.58 (brs, 1H), 12.17 (brs, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 20.4, 33.5, 69.2, 103.0, 114.7, 115.5, 117.1, 123.6, 127.2, 127.9, 128.5, 130.0, 134.1, 137.2, 152.9, 156.7, 174.4; HRMS (FAB) m/z calcd for $[C_{20}H_{18}O_4 + H]^+$ 323.1283, found 323.1286.

*3-(6-Cyano-2-hydroxynaphthalen-1-yl)propanoic Acid (**7i**).* This compound was prepared as **3a**−**g** from 6-cyano-2-naphthol in 73% yield for 3 steps (0.881 g, 3.65 mmol).[5a,b] White solid; TLC, R_f = 0.29 (Hexane−EtOAc−AcOH = 10:10:1); IR (KBr) 3350−3150, 1633 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.42 (t, J = 7.8 Hz, 2H), 3.18 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 8.7 Hz, 1H), 7.69 (dd, J = 1.4, 8.7 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H), 8.41 (d, J = 1.4 Hz, 1H), 10.33 (brs, 1H), 12.19 (brs, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ 20.2, 33.6, 104.3, 118.7, 119.6, 119.7, 124.0, 126.6, 127.0, 128.7, 134.6, 134.8, 155.5, 174.1; HRMS (FAB) m/z calcd for $[C_{14}H_{11}NO_3 + H]^+$ 242.0812, found 242.0806.

Representative Procedure for the Enantioselective Synthesis of 4 (4a as an Example). A solution of **3a** (0.0216 g, 0.100 mmol), **2a** (3.20 mg, 0.005 mmol, 5 mol %), *purified m*-CPBA (>99% purity; 0.0207 g, 0.120 mmol, 1.2 equiv) and EtOH (0.0350 mL, 0.600 mmol, 6 equiv) in DCE (5.00 mL) was stirred at −20 °C. After 36 h, the resulting mixture was poured into aqueous $Na_2S_2O_3$ (5 mL) and aqueous $NaHCO_3$. The aqueous layer was separated and extracted with $CHCl_3$ (2 times). The combined organic layers were dried over anhydrous $MgSO_4$ and solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: hexane−EtOAc = 10:1 to 4:1) to give **4a**[5] (0.0184 g, 0.0860 mmol) in 86% yield. Enantiomeric excess of **4a** was determined to be 98% ee by HPLC analysis.

*(S)-1′H,3H-Spiro[furan-2,2′-naphthalene]-1′,5(4H)-dione (**4a**).*[5a,b] White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.18 (ddd, J = 9.6, 11.0, 13.5 Hz, 1H), 2.49 (ddd, J = 1.8, 9.6, 13.5 Hz, 1H), 2.60 (ddd, J = 1.8, 9.6, 17.6 Hz, 1H), 2.92 (ddd, J = 9.6, 11.0, 17.6 Hz, 1H), 6.21 (d, J = 10.4 Hz, 1H), 6.66 (d, J = 10.4 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.62 (t, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 26.5, 31.2, 83.4, 127.3, 127.8, 127.9, 127.9, 129.0, 132.3, 135.7, 136.8, 176.5, 196.5; HPLC (OD-H column), Hexane−EtOH = 10:1 as eluent, 1.0 mL/min, t_R = 23.4 min, t_S = 27.6 min.

*(S)-4′-Chlorospiro[tetrahydrofuran-2,2′-(1′H-naphthaline)]-1′,5-dione (**4b**).*[5] 93% yield (0.0231 g, 0.0929 mmol), 98% ee. White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.23 (ddd, J = 9.6, 11.0, 13.4 Hz, 1H), 2.45 (ddd, J = 2.3, 9.6, 13.4 Hz, 1H), 2.62 (ddd, J = 2.3, 9.6, 17.9 Hz, 1H), 2.91 (ddd, J = 9.6, 11.0, 17.9 Hz, 1H), 6.40 (s, 1H), 7.52 (dt, J = 1.8, 7.4 Hz, 1H), 7.70−7.79 (m, 2H), 8.06 (d, J = 7.4 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 26.5, 31.5, 83.4, 126.1, 127.3, 128.1, 129.1, 130.1, 131.8, 134.5, 135.8, 175.7, 194.7; HPLC (OD-H column), Hexane−EtOH = 10:1 as eluent, 1.0 mL/min, t_R = 23.4 min, t_S = 25.7 min.

*(S)-4′-Bromospiro[tetrahydrofuran-2,2′-(1′H-naphthaline)]-1′,5-dione (**4c**).*[5] 99% yield (0.0290 g, 0.0989 mmol), 95% ee. White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.24 (ddd, J = 9.6, 11.0, 13.5 Hz, 1H), 2.46 (ddd, J = 2.3, 9.6, 13.5 Hz, 1H), 2.62 (ddd, J = 2.3, 9.6, 17.9 Hz, 1H), 2.90 (ddd, J = 9.6, 11.0, 17.9 Hz, 1H), 6.67 (s, 1H), 7.49−7.53 (m, 1H), 7.73−7.78 (m, 2H), 8.05 (d, J = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 26.5, 31.2, 84.2, 122.5, 127.0, 128.0, 128.8, 130.1, 133.4, 135.1, 135.9, 175.7, 194.7; HPLC (OD-H column), Hexane−EtOH = 10:1 as eluent, 1.0 mL/min, t_R = 24.7 min, t_S = 28.4 min.

*(S)-4′-Phenyl-1′H,3H-spiro[furan-2,2′-naphthalene]-1′,5(4H)-dione (**4d**).*[5] 90% yield (0.0261 g, 0.0899 mmol), 96% ee. Colorless crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.27 (ddd, J = 9.6, 11.0, 13.3 Hz, 1H), 2.54 (ddd, J = 2.3, 9.6, 13.3 Hz, 1H), 2.63 (ddd, J = 2.3, 9.6, 17.6 Hz, 1H), 2.93 (ddd, J = 9.6, 11.0, 17.6 Hz, 1H), 6.12 (s, 1H), 7.15 (d, J = 7.3 Hz, 1H), 7.34−7.50 (m, 6H), 7.56 (dt, J = 1.4, 7.3 Hz, 1H), 8.10 (dd, J = 1.4, 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 26.7, 31.5, 83.7, 127.4, 127.6, 128.2, 128.4, 128.6, 128.7, 128.9, 130.6, 135.3, 137.4, 137.6, 139.8, 176.3, 196.4; HPLC (OD-H column), Hexane−EtOH = 10:1 as eluent, 1.0 mL/min, t_S = 21.7 min, t_R = 27.1 min.

*(S)-4′-(4-Bromobenzoyl)-1′H,3H-spiro[furan-2,2′-naphthalene]-1′,5(4H)-dione (**4e**).*[5] 99% yield (0.0393 g, 0.0989 mmol), 96% ee. White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.27 (ddd, J = 9.6, 11.0, 13.3 Hz, 1H), 2.52 (ddd, J = 1.8, 9.6, 13.3 Hz, 1H), 2.63 (ddd, J = 1.8, 9.6, 17.6 Hz, 1H), 2.92 (ddd, J = 9.6, 11.0, 17.6 Hz, 1H), 6.38 (s, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.50 (dt, J = 0.9, 7.8 Hz, 1H), 7.60−7.66 (m, 3H), 7.83 (d, J = 8.7 Hz, 1H), 8.12 (dd, J = 1.4, 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 26.2, 31.2, 82.5, 126.8, 127.3, 128.6, 129.8, 129.9, 131.4, 132.3, 133.7, 134.2, 134.7, 135.8, 137.2, 175.7, 193.5, 195.0; HPLC (IA-3 column), Hexane−EtOH = 4:1 as eluent, 1.0 mL/min, t_R = 30.9 min, t_S = 33.0 min.

*(S)-3′-(Benzyloxymethyl)-1′H,3H-spiro[furan-2,2′-naphthalene]-1′,5(4H)-dione (**4f**).*[5a,b] 74% yield (0.0247 g, 0.0739 mmol), 97% ee. Colorless amorphous; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.30−2.37 (m, 1H), 2.43−2.55 (m, 2H), 2.69−2.79 (m, 1H), 4.25 (d, J = 12.8 Hz, 1H), 4.36 (d, J = 12.8 Hz, 1H), 4.60 (s, 2H), 6.70 (s, 1H), 7.25 (d, J = 7.8 Hz, 1H) 7.30−7.40 (m, 6H), 7.62 (t, J = 7.8 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 26.1, 30.4, 68.9, 73.3, 85.8, 124.6, 126.7, 127.7, 127.8(2C), 128.0, 128.5, 128.6 135.6, 136.8, 137.5, 140.0, 176.6, 196.9; HPLC (OD-H column), Hexane−*i*-PrOH = 85:15 as eluent, 1.0 mL/min, t_S = 20.8 min, t_R = 38.3 min.

*(S)-6′-Methoxy-1′H,3H-spiro[furan-2,2′-naphthalene]-1′,5(4H)-dione (**4g**).*[5a,b] 73% yield (0.0178 g, 0.0729 mmol), 97% ee. White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.17 (ddd, J = 9.6, 11.0, 13.3 Hz, 1H), 2.40 (ddd, J = 2.2, 9.6, 13.3 Hz, 1H), 2.61 (ddd, J = 2.2, 9.6, 17.6 Hz, 1H), 2.95 (ddd, J = 9.6, 11.0, 17.6 Hz, 1H), 3.94 (s, 3H), 6.21 (d, J = 9.6 Hz, 1H), 6.60 (d, J = 9.6 Hz, 1H), 6.72 (d, J = 2.8 Hz, 1H), 6.91 (dd, J = 2.8, 8.7 Hz, 1H), 8.01 (d, J = 8.7 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 26.8, 31.6, 55.7, 82.8, 112.9, 114.2, 120.6, 127.9, 130.5, 133.3, 139.1, 165.6, 176.3, 194.8; HPLC (AD-H column), Hexane−*i*-PrOH = 85:15 as eluent, 1.0 mL/min, t_S = 30.7 min, t_R = 35.6 min.

*(S)-N-(1′,5-Dioxo-4,5-dihydro-1′H,3H-spiro[furan-2,2′-naphthalen]-5′-yl)-4-methylbenzenesulfonamide (**4h**).* 56% yield (0.0215 g, 0.0561 mmol), 91% ee. Yellow solid; TLC, R_f = 0.57 (hexane−EtOAc = 1:2); IR (KBr) 3254, 1786, 1693 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.08−2.17 (m, 1H), 2.32−2.38 (m, 1H), 2.42 (s, 3H), 2.58 (ddd, J = 1.8, 9.6. 17.8 Hz, 1H), 2.80−2.90 (m, 1H), 6.12 (d, J = 10.6 Hz, 1H), 6.74 (d, J = 10.6 Hz, 1H), 6.76 (s, 1H), 7.25−7.36 (m, 4H), 7.55 (d, J = 8.3 Hz, 2H), 7.90 (d, J = 6.9 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.6, 26.4, 31.2, 82.9, 122.1, 127.0, 127.3, 128.3, 129.2, 129.9, 132.3, 132.8, 133.3, 134.5, 135.6, 144.5, 176.3, 196.0; HPLC (IA-3 column), Hexane−EtOH = 2:1 as eluent, 0.7 mL/min, t_R = 47.0 min, t_S = 75.1 min; HRMS (FAB) m/z calcd for $[C_{20}H_{17}NO_5S + H]^+$ 384.0906, found 384.0902; $[\alpha]^{27.9}_D$ = −48.5 (c 0.80, $CHCl_3$) for 91% ee.

Representative Procedure for the Enantioselective Synthesis of 8 (8a as an Example). A solution of **7a** (0.0216 g, 0.100 mmol), **2a** (3.20 mg, 0.005 mmol, 5 mol %), *purified m*-CPBA (>99% purity; 0.0207 g, 0.120 mmol, 1.2 equiv) and HFIP (0.526 mL, 5.000 mmol, 5 equiv) in dichloromethane (5.00 mL) was stirred at −20 °C. After 15 h, the resulting mixture was poured into aqueous $Na_2S_2O_3$ (5 mL) and aqueous $NaHCO_3$. The aqueous layer was separated and extracted with $CHCl_3$ (2 times). The combined organic layers were dried over anhydrous $MgSO_4$ and solvents were removed in vacuo.

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The residue was purified by flash column chromatography on silica gel (eluent: hexane−EtOAc = 10:1 to 4:1) to give **8a** (0.0191 g, 0.0891 mmol) in 89% yield. Enantiomeric excess of **8a** was determined to be 94% ee by HPLC analysis.

*(S)-2′H,3H-Spiro[furan-2,1′-naphthalene]-2′,5(4H)-dione (**8a**).*[10] White solid; TLC, R_f = 0.70 (hexane−EtOAc = 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.11−2.20 (m, 1H), 2.62−2.70 (m, 2H), 2.81−2.91 (m, 1H), 6.18 (d, J = 9.6 Hz, 1H), 7.36 (dd, J = 1.6, 7.6 Hz, 1H), 7.41 (dt, J = 1.6, 7.6 Hz, 1H), 7.46−7.50 (m, 2H), 7.56 (d, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 26.5, 35.7, 85.8, 122.4, 125.6, 129.0, 129.1, 129.7, 131.0, 140.4, 146.0, 176.4, 197.5; HPLC (OD-H column), Hexane−EtOH = 10:1 as eluent, 1.0 mL/min, t_S = 26.2 min, t_R = 40.2 min; $[\alpha]^{23.0}_D$ = −340.0 (c 1.4, $CHCl_3$) for 95% ee.

*(S)-3′-Bromo-2′H,3H-spiro[furan-2,1′-naphthalene]-2′,5(4H)-dione (**8b**).*[10a] 85% yield (0.0249 g, 0.0849 mmol), 89% ee. Optically pure (*S*)-**8b** (99% ee) was obtained after a single recrystallization from hexane/ethanol at 0 °C. Colorless crystal; Mp: 117−119 °C; TLC, R_f = 0.57 (hexane−EtOAc = 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15−2.23 (m, 1H), 2.64−2.72 (m, 2H), 2.82−2.92 (m, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.42 (dt, J = 1.6, 7.2 Hz, 1H), 7.51 (dt, J = 1.6, 7.2 Hz, 1H), 7.55 (dd, J = 1.6, 7.2 Hz, 1H), 7.92 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 26.4, 36.1, 86.4, 118.2, 126.0, 128.8, 129.4, 129.6, 131.4, 139.9, 147.3, 175.9, 191.2; HPLC (OD-H column), Hexane−EtOH = 10:1 as eluent, 1.0 mL/min, t_S = 29.5 min, t_R = 42.2 min; $[\alpha]^{22.9}_D$ = −197.8 (c 1.0, $CHCl_3$) for 99% ee.

*(S)-6′-Bromo-2′H,3H-spiro[furan-2,1′-naphthalene]-2′,5(4H)-dione (**8c**).* 95% yield (0.0279 g, 0.0952 mmol), 95% ee. White solid; TLC, R_f = 0.57 (hexane−EtOAc = 1:2); IR (KBr) 1788, 1683 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.08−2.17 (m, 1H), 2.62−2.69 (m, 2H), 2.79−2.89 (m, 1H), 6.22 (d, J = 9.6 Hz, 1H), 7.41 (d, J = 9.6 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 1.8 Hz, 1H), 7.60 (dd, J = 1.8, 8.4 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 26.4, 35.6, 85.4, 123.1, 123.8, 127.4, 130.9, 132.3, 133.7, 139.2, 144.4, 176.0, 196.7; HRMS (FAB) m/z calcd for $[C_{13}H_9BrO_3 + H]^+$ 292.9813, found 292.9814; HPLC (OD-H column), Hexane−EtOH = 10:1 as eluent, 1.0 mL/min, t_S = 29.6 min, t_R = 36.7 min; $[\alpha]^{23.9}_D$ = −142.8 (c 1.4, $CHCl_3$) for 95% ee.

*(S)-8′-Fluoro-2′H,3H-spiro[furan-2,1′-naphthalene]-2′,5(4H)-dione (**8d**).* 92% yield (0.0213 g, 0.0918 mmol), 95% ee. White solid; TLC, R_f = 0.57 (hexane−EtOAc = 1:2); IR (KBr) 1787, 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41−2.56 (m, 2H), 2.78 (ddd, J = 3.2, 10.1, 17.4 Hz, 1H), 2.99 (dt, J = 10.6, 17.4 Hz, 1H), 6.23 (d, J = 10.1 Hz, 1H), 7.16−7.21 (m, 2H), 7.41−7.46 (m, 1H), 7.48 (dd, J = 1.8, 10.1 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 27.1, 32.6, 81.0, 118.8 (d, J_{C-F} = 22 Hz), 123.8, 125.8 (d, J_{C-F} = 3 Hz), 126.2 (d, J_{C-F} = 10 Hz), 131.3, 131.4, 145.5 (d, J_{C-F} = 4 Hz), 161.5, (d, J_{C-F} = 251 Hz), 176.4, 196.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ − 111.5; HRMS (FAB) m/z calcd for $[C_{13}H_9FO_3 + H]^+$ 233.0614, found 233.0620; HPLC (IA-3 column), Hexane−EtOH = 4:1 as eluent, 1.0 mL/min, t_R = 19.9 min, t_S = 22.5 min; $[\alpha]^{23.1}_D$ = −145.3 (c 1.8, $CHCl_3$) for 95% ee.

*(S)-4′-Methyl-2′H,3H-spiro[furan-2,1′-naphthalene]-2′,5(4H)-dione (**8e**).* 83% yield (0.0190 g, 0.0832 mmol), 95% ee. White solid; TLC, R_f = 0.57 (hexane−EtOAc = 1:2); IR (KBr) 1786, 1673 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.10−2.19 (m, 1H), 2.40 (s, 3H), 2.56−2.68 (m, 2H), 2.81−2.91 (m, 1H), 6.11 (s, 1H), 7.43 (dt, J = 1.4, 7.3 Hz, 1H), 7.49 (dt, J = 1.4, 7.3 Hz, 1H), 7.56−7.58 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 20.5, 26.8, 36.1, 85.7, 122.0, 125.6, 126.0, 128.9, 130.4, 130.8, 140.3, 154.0, 176.5, 196.7; HRMS (FAB) m/z calcd for $[C_{14}H_{12}O_3 + H]^+$ 229.0865, found 229.0871; HPLC (IA-3 column), Hexane−EtOH = 4:1 as eluent, 1.0 mL/min, t_R = 17.4 min, t_S = 18.8 min; $[\alpha]^{28.7}_D$ = −333.3 (c 1.6, $CHCl_3$) for 95% ee.

*(S)-7′-Methoxy-2′H,3H-spiro[furan-2,1′-naphthalene]-2′,5(4H)-dione (**8f**).* 51% yield (0.0125 g, 0.0512 mmol), 89% ee. White solid; TLC, R_f = 0.60 (hexane−EtOAc = 1:2); IR (KBr) 1786, 1682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.09−2.18 (m, 1H), 2.61−2.70 (m, 2H), 2.79−2.89 (m, 1H), 3.87 (s, 3H), 6.04 (d, J = 9.6 Hz, 1H), 6.88 (dd, J = 1.8, 8.7 Hz, 1H), 7.08 (d, J = 1.8 Hz, 1H), 7.28 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 9.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 26.5, 36.1, 55.7, 86.0, 111.5, 114.4, 119.7, 122.1, 131.5, 143.0, 146.0, 162.1, 176.5, 197.5; HRMS (FAB) m/z calcd for $[C_{14}H_{12}O_4 + H]^+$ 245.0814, found 245.0808; HPLC (OD-H column), Hexane−EtOH = 10:1 as eluent, 1.0 mL/min, t_S = 32.5 min, t_R = 41.0 min; $[\alpha]^{25.3}_D$ = −327.6 (c 1.2, $CHCl_3$) for 89% ee.

*(S)-7′-(Methoxymethoxy)-2′H,3H-spiro[furan-2,1′-naphthalene]-2′,5(4H)-dione (**8g**).* 85% yield (0.0233 g, 0.0849 mmol), 91% ee. Yellow solid; TLC, R_f = 0.50 (hexane−EtOAc = 1:2); IR (KBr) 1786, 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.05−2.19 (m, 1H), 2.61−2.69 (m, 2H), 2.79−2.89 (m, 1H), 3.48 (s, 3H), 5.19 (d, J = 6.9 Hz, 1H), 5.25 (d, J = 6.9 Hz, 1H), 6.06 (d, J = 9.6 Hz, 1H), 7.04 (dd, J = 2.8, 8.7 Hz, 1H), 7.20 (d, J = 2.8 Hz, 1H), 7.26 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 9.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 26.5, 36.0, 56.3, 85.8, 94.1, 114.0, 116.0, 120.2, 123.1, 131.4, 142.8, 145.8, 159.6, 176.4, 197.4; HRMS (FAB) m/z calcd for $[C_{15}H_{14}O_5 + H]^+$ 275.0919, found 275.0921; HPLC (IA-3 column), Hexane−EtOH = 4:1 as eluent, 1.0 mL/min, t_S = 33.1 min, t_R = 45.1 min; $[\alpha]^{27.9}_D$ = −239.8 (c 1.7, $CHCl_3$) for 91% ee.

*(S)-7′-(Benzyloxy)-2′H,3H-spiro[furan-2,1′-naphthalene]-2′,5(4H)-dione (**8h**).* 57% yield (0.0183 g, 0.0571 mmol), 87% ee. Yellow solid; TLC, R_f = 0.63 (hexane−EtOAc = 1:2); IR (KBr) 1786, 1673 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.06−2.15 (m, 1H), 2.58−2.68 (m, 2H), 2.78−2.88 (m, 1H), 5.12 (s, 2H), 6.04 (d, J = 10.1 Hz, 1H), 6.95 (dd, J = 2.3, 8.2 Hz, 1H), 7.17 (d, J = 2.3 Hz, 1H), 7.27 (d, J = 8.2 Hz, 1H), 7.32−7.44 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 26.5, 36.1, 70.4, 85.9, 112.6, 115.1, 119.9, 122.4, 127.5, 128.3, 128.7, 131.5, 135.9, 143.0, 145.9, 161.2, 176.4, 197.4; HRMS (FAB) m/z calcd for $[C_{20}H_{16}O_4 + H]^+$ 321.1127, found 321.1124; HPLC (OD-H column), Hexane−EtOH = 4:1 as eluent, 1.0 mL/min, t_S = 16.3 min, t_R = 20.0 min; $[\alpha]^{25.2}_D$ = −197.7 (c 1.8, $CHCl_3$) for 87% ee.

*(S)-2′,5-Dioxo-4,5-dihydro-2′H,3H-spiro[furan-2,1′-naphthalene]-6′-carbonitrile (**8i**).* 99% yield (0.0237 g, 0.0991 mmol), 95% ee. White solid; TLC, R_f = 0.30 (Hexane−EtOAc = 1:1); IR ($CHCl_3$) 2237, 1800, 1693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.04−2.20 (m, 1H), 2.65−2.73 (m, 2H), 2.78−2.89 (m, 1H), 6.32 (d, J = 9.6 Hz, 1H), 7.49 (d, J = 9.6 Hz, 1H), 7.68 (s, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 26.2, 35.5, 85.2, 113.5, 117.4, 124.5, 126.6, 130.3, 132.6, 134.0, 143.4, 145.0, 175.5, 195.8; HRMS (FAB) m/z calcd for $[C_{14}H_9NO_3 + H]^+$ 240.0655, found 240.0657; HPLC (OD-H column), Hexane−EtOH = 2:1 as eluent, 0.8 mL/min, t_S = 19.5 min, t_R = 25.6 min; $[\alpha]^{22.3}_D$ = −157.8 (c 2.1, $CHCl_3$) for 95% ee.

*(1′S,2′R,3′S,4′R)-3′-Bromo-2′,4′-dihydroxy-3′,4′-dihydro-2′H,3H-spiro[furan-2,1′-naphthalen]-5(4H)-one ((+)-**9**).* To a solution of (*S*)-**8a** (0.214 g, 1.00 mmol, 89% ee) and $CeCl_3{\cdot}7H_2O$ (0.373 g, 1.00 mmol) in MeOH (25.0 mL) and THF (25.0 mL) was added $NaBH_4$ (0.0380 g, 1.00 mmol) at −78 °C. After stirring for 15 min at same temperature, the reaction mixture was diluted with EtOAc and washed with 1 M HCl and brine. The combined organic layers were dried over anhydrous $MgSO_4$ and the solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: hexane−EtOAc = 10:1 to 4:1) to give (1′*S*,2′*S*)-2′-hydroxy-2′*H*,3*H*-spiro[furan-2,1′-naphthalen]-5(4*H*)-one (0.205 g, 0.950 mmol, 95% yield) as a white solid. TLC, R_f = 0.72 (hexane−EtOAc = 1:2); IR (KBr) 3600−3250, 1772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.87 (ddd, J = 6.4, 10.5, 13.1 Hz, 1H), 2.50−2.65 (m, 2H), 2.70−2.78 (m, 1H), 3.09 (ddd, J = 7.3, 10.5, 13.1 Hz, 1H), 5.04−5.06 (m, 1H), 5.90 (dd, J = 1.8, 9.6 Hz, 1H), 6.41 (dd, J = 2.8, 9.6 Hz, 1H), 7.09−7.12 (m, 1H), 7.23−7.34 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 27.0, 29.0, 73.1, 91.2, 122.8, 126.8, 127.6, 128.3, 128.5, 130.7, 131.7, 137.8, 178.4; HRMS (FAB) m/z calcd for $[C_{13}H_{12}O_3 + H]^+$ 217.0865, found 217.0868; $[\alpha]^{24.3}_D$ = −22.9 (c 0.7, $CHCl_3$) for 89% ee.

To a solution of this allylic alcohol (0.0360 g, 0.170 mmol) in THF (1.70 mL) and H_2O (1.70 mL) was added NBS (recrystallized, 0.0590 g, 0.340 mmol) at 0 °C. After stirring for 6 h at 0 °C, the resulting mixture was poured into aqueous $Na_2S_2O_3$ (5 mL) and the aqueous layer was separated and extracted with EtOAc (twice). The combined organic layers were dried over anhydrous $MgSO_4$ and solvents were removed in vacuo. The residue was purified by flash column

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chromatography on silica gel (eluent: hexane−EtOAc = 10:1 to 3:2) to give **9** (0.0500 g, 0.160 mmol, 94% yield) as a white solid. Enantiomeric excess of **9** was determined to be 89% ee by HPLC analysis. Optically pure (+)-**9** (>99% ee) was obtained after a single recrystallization from hexane/ethanol at 0 °C. Colorless crystal; Mp: 165−167 °C; TLC, R_f = 0.57 (hexane−EtOAc = 1:2); IR (KBr) 3600−3250, 1739 cm^{-1}; ^1H NMR (CD_3CN, 400 MHz) δ 2.51−2.58 (m, 1H), 2.72−2.90 (m, 3H), 4.01 (d, J = 7.3 Hz, 1H), 4.20 (d, J = 5.5 Hz, 1H), 4.37 (dd, J = 2.3, 5.5 Hz, 1H), 4.52 (dd, J = 2.3, 7.3 Hz, 1H), 4.95 (t, J = 7.3 Hz, 1H), 7.38−7.56 (m, 4H); $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz) δ 29.9, 31.0, 58.7, 72.0, 74.6, 87.6, 128.2, 129.2, 129.7, 130.2, 136.2, 138.6, 177.0; HRMS (FAB) m/z calcd for $[C_{13}H_{13}BrO_4 + H]^+$ 313.0075, found 313.0070; HPLC (IA-3 column), Hexane−EtOH = 1:1 as eluent, 0.7 mL/min, t_1 = 9.2 min, t_2 = 11.7 min; $[\alpha]^{26.2}_D$ = 134.3 (c 1.3, CH_3CN) for >99% ee.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01941.

Additional experiments, HPLC analysis of products **4**, **8** and **9**, spectral data for new compounds, and crystal data and structure refinement for **8b** and **9** (PDF)

Crystal data for **8b** (CIF)

Crystal data for **9** (CIF)

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Notes

The authors declare no competing financial interest.

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(12) On the basis of our previous study[6a] for the oxidation of electron deficient phenols, 50 equiv of HFIP was used as an additive for the oxidation of 2-naphthols.

(13) The beneficial effect of ethanol and methanol for the oxidation of high-reactive phenols was discussed before.[6a] In the present study, initially, commercially available chloroform that contains ethanol (1 wt %, 6 equiv per substrate) as a stabilizer was used as a solvent. The use of 6 equiv of ethanol was found to be optimal for the oxidation of 1-naphthols with respect to both chemical yield and enantioselectivity. For details, see the Supporting Information.

(14) X-ray crystallographic data for compounds (*S*)-**8b** and (+)-**9** have been deposited with the Cambridge Crystallographic Data Centre database (http://www.ccdc.cam.ac.uk/) under codes **CCDC830343** and **CCDC833531**, respectively.

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