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Synthesis of Optically Pure 3,3′-Diaryl Binaphthyl Disulfonic Acids *via* Stepwise N−S Bond Cleavage

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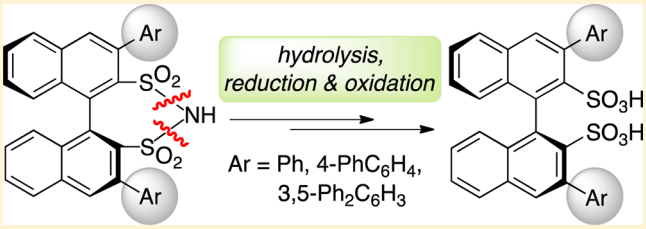
Supporting Information

ABSTRACT: We developed a practical synthesis of optically pure 3,3′-diaryl-1,1′-binaphthyl-2,2′-disulfonic acids (i.e., (*R*)- or (*S*)-3,3′-Ar$_2$-BINSAs) from the parent chiral sulfonimides *via* stepwise N−S bond cleavage of the sulfonimides and the resultant sulfonamides. This unusual synthesis, which provides arylsulfonic acids from arylsulfonamides, is valuable since common methods particularly give amines with the decomposition of sulfone groups during deprotection.



INTRODUCTION

Among a variety of recent powerful and environmentally benign organocatalysts, many researchers have become interested in chiral Brønsted acid catalysts. In particular, strong Brønsted acid catalysts such as phosphoric acids,[1] *N*-triflyl phosphoramide,[2] disulfonic acids,[3] and sulfonimides[4] with a chiral 3,3′-disubstituted binaphthyl backbone[5] are highly attractive since their simple C_2-symmetric structures are useful for the design of a variety of reactions. However, the introduction of 3,3′-disubstituents has not been well established for chiral 1,1′-binaphthyl-2,2′-disulfonic acid (BINSA),[3] due to synthetic difficulties, unlike for chiral binaphthyl phosphoric acid.[1] In particular, the key to synthesizing chiral 3,3′-Ar$_2$-BINSAs (**1**) from chiral BINOL (1,1′-bi-2-naphthol) should be Suzuki−Miyaura coupling, Newman−Kwart rearrangement, and oxidation (Scheme 1). Only one successful example has been reported by List,[4a] who synthesized (*R*)-3,3′-[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$-BINSA, since the Newman−Kwart rearrangement (95% yield) and subsequent oxidation (81% yield) are facilitated by taking advantage of electron-withdrawing substituents at the 3,3′-positions (Scheme 1, route a).[6] In this regard, we have reported the synthesis of (*R*)-3,3′-Ph$_2$-BINSA ((*R*)-**1a**) in the same way, but the yield was low in the rearrangement (25%) and oxidation (30%).[3f] Moreover, we also reported the second synthetic route, which employed Suzuki−Miyaura coupling in the last step, but the yield was low (<10%) (Scheme 1, route b).[3f] As the third synthetic route to chiral 3,3′-Ar$_2$-BINSAs, the deprotection of 3,3′-diaryl-1,1′-binaphthyl-2,2′-sulfonimides ((*R*)-**2**) may be possible (Scheme 1, route c). Remarkably, Lee recently developed a practical synthesis of (*R*)-**2** from the parent (*R*)-3,3′-dibromo compound by Suzuki−Miyaura coupling with ArB(OH)$_2$.[4c] Therefore, in this paper, we envisioned that chiral 3,3′-Ar$_2$-BINSAs (**1**) could be obtained efficiently if we cleaved the two stable N−S bonds in **2**.

In general, arylsulfonic acids have been used to protect amino functions due to the high stability of the corresponding arylsulfonamides.[7] Inevitably, for cleavage of the protecting sulfone group from the amino group, drastic reaction conditions are usually needed, including the use of strong acids,[8] strong bases,[9] SmI_2,[10] $TiCl_3$,[11] Bu_3SnH/2,2′-azodiisobutyronitrile (AIBN),[12] Li and Mg powder,[13] Na/naphthalene,[14] photolysis,[15] and electrolysis.[16] Most importantly, these methods have been developed *for amines, but not for sulfonic acids,* and we can obtain deprotected amines selectively, while sulfonic acids would usually decompose and be discarded. As a good example, Fukuyama and Kan's nitrobenzenesulfonamide (Ns) can provide the desired amines even under mild basic conditions with thiolates (Scheme 2).[17] However, an arylsulfone moiety would decompose with the release of SO_2 *via* the Meisenheimer complex.

RESULTS AND DISCUSSION

Cleavage of the N−S Bond of Sulfonimide (*R*)-2a. We initially examined the N−S cleavage of (*R*)-3,3′-Ph$_2$-1,1′-binaphthyl-2,2′-sulfonimide ((*R*)-**2a**)[4c] as a probe compound (Scheme 3). However, (*R*)-**2a** was perfectly intact under strong acidic (8 M HCl aq.) or strong basic (2 M NaOH/MeOH) conditions, since NH_3 is a poor leaving group. In particular, the deprotonation of sulfonimide under basic conditions might strengthen the N−S bond due to the conjugated structure. Therefore, we decided to replace the active proton with a methyl group using the Meerwein reagent ($Me_3O{\cdot}BF_4$). Compound (*R*)-**2a** was transformed to a *N*-Me compound ((*R*)-**3a**), and we could cleave the first N−S bond of sulfonimide (*R*)-**3a** with the use of 2 M NaOH in MeOH at reflux temperature, to give (*R*)-**4a** in quantitative yield. Compound (*R*)-**4a** still has an active proton, and we protected

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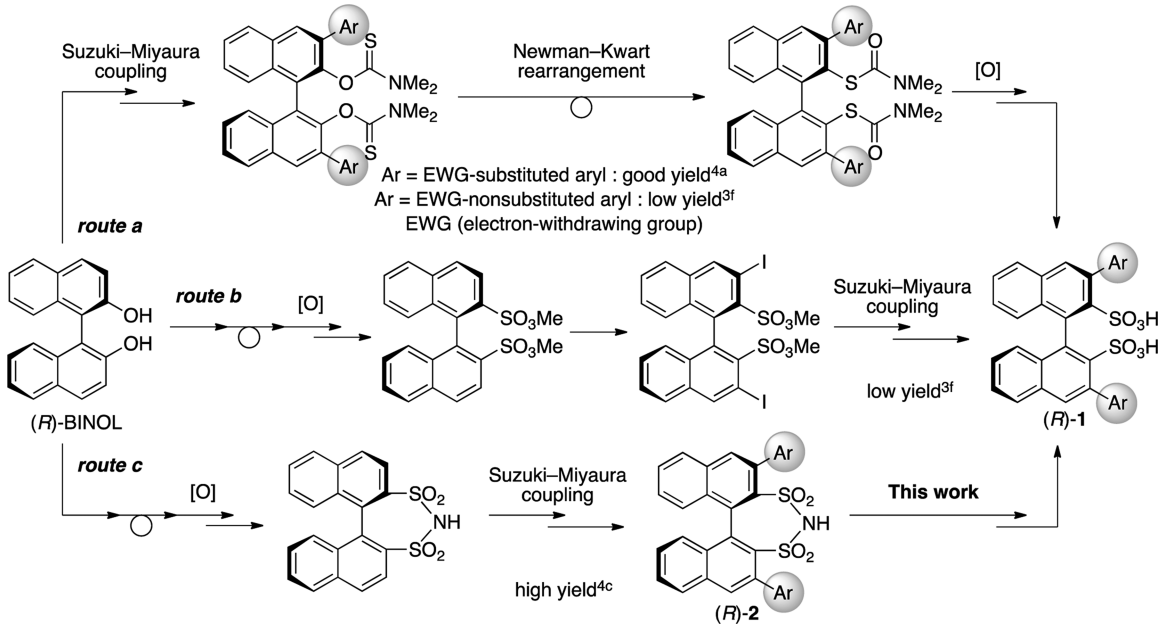
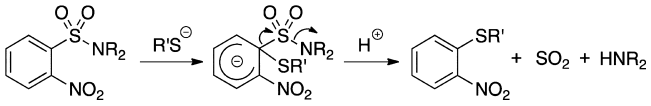
Scheme 1. Synthesis of (*R*)-3,3′-Ar$_2$-BINSAs



Scheme 2. Deprotection of Nitrobenzenesulfonamide (Ns Amide) with the Release of SO$_2$



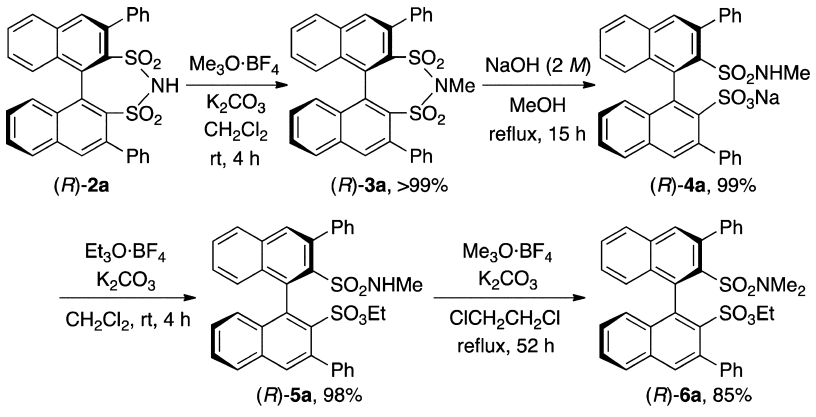
the SO_3Na moiety with $Et_3O{\cdot}BF_4$ ((*R*)-**5a**, 98% yield) and the SO_2NHMe moiety with $Me_3O{\cdot}BF_4$ ((*R*)-**6a**, 85% yield). Noteworthy is that SO_3Et is much more stable than SO_3Me, which would be easily hydrolyzed to SO_3H and recyclized even by silica gel chromatography.

Trials for Cleavage of the N−S Bond of Sulfonamide (*R*)-6a. We next examined cleavage of the N−S bond in sulfonamide (*R*)-**6a**. However, treatment of (*R*)-**6a** with either an acid or base was again ineffective (Scheme 4, eq 1). The desired (*R*)-3,3′-Ph$_2$-BINSA salts were not obtained, and the sulfonamide moieties in recovered (*R*)-**7a** and (*R*)-**8a** were intact. Very recently, Tomooka reported a nucleophilic substitution reaction at the nitrogen of arylsulfonamides with a phosphide anion such as $KPPh_2$ to provide phosphamides, in addition to unstable arylsulfinic acid[18] ($ArSO_2H$).[19] According to this report, we examined the reaction of (*R*)-**6a** with $KPPh_2$, but the desired arylsulfinic acid (*R*)-**9a** was not obtained (Scheme 4, eq 2).

As another promising method, the nucleophilic substitution of trialkylaminosulfonates with N−S cleavage has been reported.[20] We investigated the reaction of model compound **10** with MeOTf and subsequent workup with water (Scheme 5, eq 3). As a result, the desired **11** was obtained in 55% yield. Encouraged by this preliminary result, we next examined the reaction of (*R*)-**6a** under the same conditions. However, since (*R*)-**6a** was much less reactive than **10**, arylsulfone (*R*)-**12**, instead of the desired product, was obtained by an intramolecular Friedel−Crafts reaction (Scheme 5, eq 4).[21]

Sulfonamide to Sulfonic Acid *via* Stepwise Reduction and Oxidation. Finally, we examined reductive cleavage of the N−S bond of sulfonamides with aluminum hydride reagents, which has scarcely been developed[22] since the products would be a mixture of unstable sulfinic acids, sulfenic acids, thiols, and disulfides. However, we expected that the desired sulfonic acids could be convergently obtained if we treated the mixture without purification with suitable strong oxidants.[3c] Under this assumption, we conducted the stepwise reduction and

Scheme 3. Cleavage of the N−S Bond of Sulfonimide (*R*)-2a



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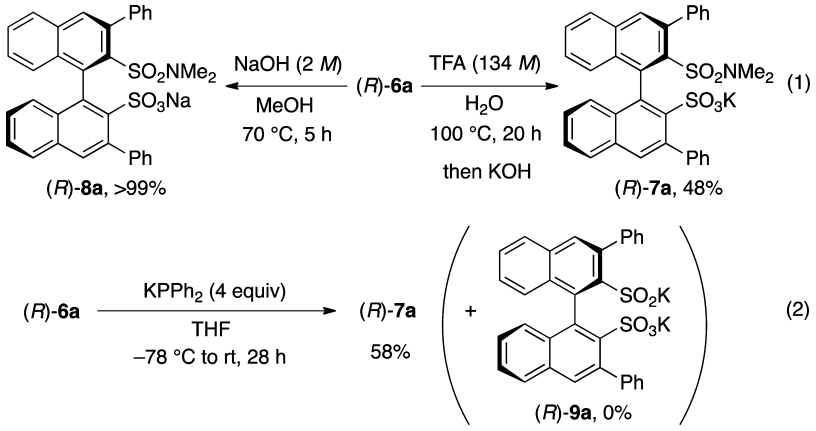
Scheme 4. Trials for Cleavage of the N−S Bond of (*R*)-6a



Scheme 5. Nucleophilic Substitution of Trialkylaminosulfonates

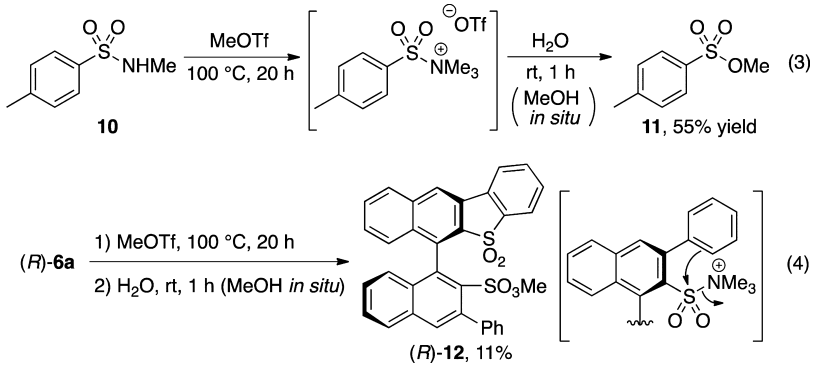
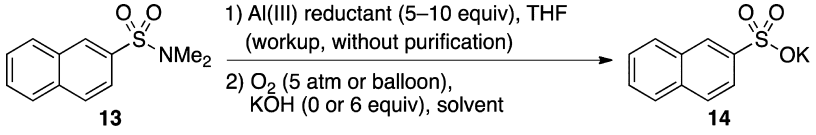


Table 1. Transformation of Sulfonamide to Sulfonic Acid via Stepwise Reduction and Oxidation



entry	reduction conditions[a]	oxidation conditions[b]	yield (%) of **14**
1[a]	DIBAL (10 equiv), THF, 40 °C, 22 h	O_2 (5 atm), KOH, HMPA, 80 °C, 10 h	0
2	$LiAlH_4$ (10 equiv), THF, 40 °C, 22 h	O_2 (5 atm), KOH, HMPA, 80 °C, 10 h	46 (ca. 30)[c]
3	Red-Al (10 equiv), THF, 40 °C, 22 h	O_2 (5 atm), KOH, HMPA, 80 °C, 10 h	71 (ca. 5)[c]
4	Red-Al (5 equiv), THF, rt, 5 h	O_2 (balloon), DMF, 60 °C, 16 h	97

[a]DIBAL = *i*-Bu_2AlH, Red-Al = $NaAlH_2(OC_2H_4OCH_3)_2$. [b]HMPA = hexamethylphosphoramide, DMF = *N*,*N*-dimethylformamide. [c]Yield (%) of naphthalene.

oxidation for **13** as a preliminary investigation (Table 1). $LiAlH_4$ (10 equiv) gave the desired product **14** in 46% yield in two steps, while *i*-Bu_2AlH (DIBAL) showed low reactivity (entries 1 and 2). Moreover, a significant amount of naphthalene was obtained due to overreaction with reactive $LiAlH_4$.[23] In place of $LiAlH_4$, when we used less reactive $NaAlH_2(OC_2H_4OCH_3)_2$ (Red-Al, 10 equiv),[24] **14** was obtained in 71% yield (entry 3). In entry 3, more than three spots were observed in TLC analysis after the reduction step.

To investigate the major compounds which were obtained in entry 3 in Table 1, we conducted the reduction step by using Red-Al (10 equiv) in THF at 40 °C (Scheme 6, eq 5). After the workup and purification, a major product was identified as 2-naphthyl disulfide (**16**) (70% yield). In sharp contrast, we could isolate 2-naphthalenesulfinic acid (**15**) in 95% yield when we used Red-Al (5 equiv) in THF at room temperature (Scheme 6, eq 5). Moreover, we found that the oxidation of **15** can readily proceed (up to 97% yield) with or without KOH in HMPA or DMF under O_2 (balloon) conditions (Scheme 6, eq 6), while the oxidation of **16** was sluggish (64% yield) even if KOH was used under O_2 (balloon) (Scheme 6, eq 7). This result means that the selective reduction of sulfonamide to sulfinic acid is important for stepwise reduction and oxidation to synthesize sulfonic acid from sulfonamide. Ultimately, the yield of **14** was improved up to 97% (Table 1, entry 4), when we used Red-Al (5 equiv) and then O_2 (balloon) without KOH in DMF in place of HMPA without purification after the reduction.

Synthesis of (*R*)-3,3′-Ph_2-BINSA from (*R*)-6a. With this optimized method in hand, we transformed sulfonamide (*R*)-**6a** to the disulfonates (*R*)-**17a**, where both the SO_2NMe_2 and SO_3Et moieties might be reduced and oxidized (Scheme 7, eq 8). As a result, (*R*)-**17a** was obtained in 39% yield in two steps

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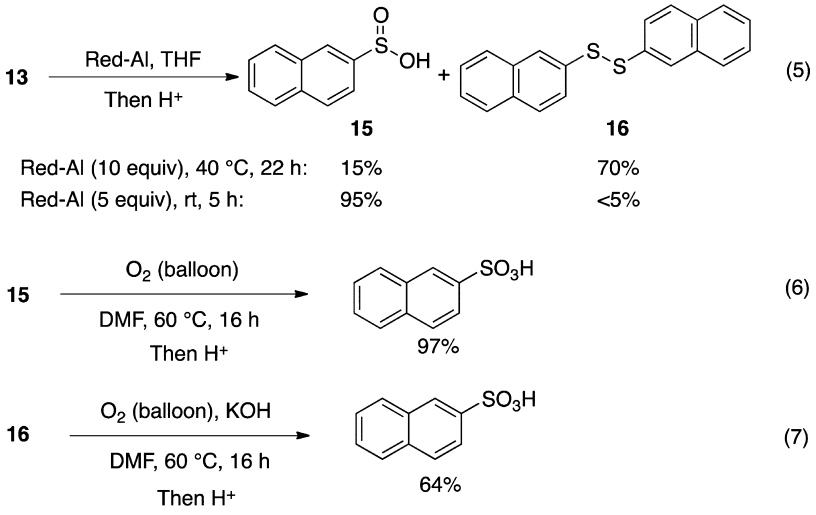
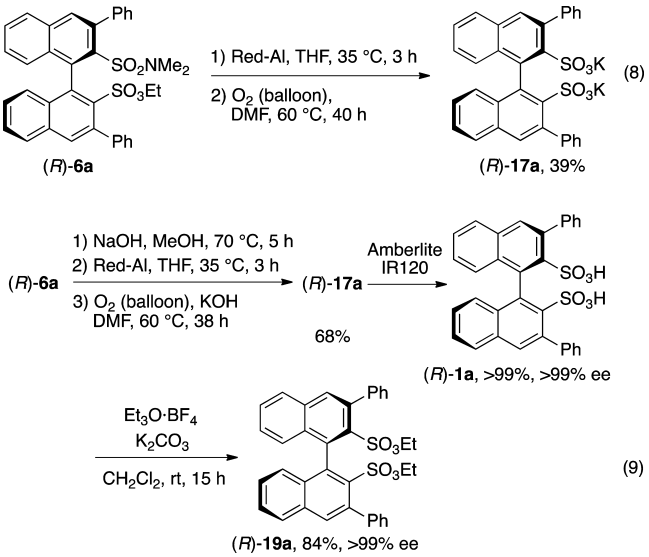
Scheme 6. Reduction of Sulfonamide and Oxidation of Sulfinic Acid and Disulfide



Scheme 7. Synthesis of (*R*)-3,3′-Ph$_2$-BINSA ((*R*)-1a)



with 3,3′-diphenyl-1,1′-binaphthalene (**18**) (<5% yield). This moderate yield was due to the over-reduction of the more reactive SO_3Et moiety compared to the SO_2NMe_2 moiety, and it was difficult to oxidize these over-reduction intermediates under the mild reaction conditions without KOH. Therefore, to avoid the over-reduction, (*R*)-**6a** was hydrolyzed in advance to sulfonate (*R*)-**8a**, and then we tried the reduction/oxidation procedure. As a result, the yield of (*R*)-**17a** was improved to 68% (Scheme 7, eq 9). Subsequent protonation by ion exchange ultimately provided the desired (*R*)-3,3′-Ph$_2$-BINSA (**1a**) without a loss of optical purity (>99% ee), which was determined by HPLC analysis of diethyl ester (*R*)-**19a** and (*S*)-**19a** from (*R*)-**1a** and (*S*)-**1a**, respectively. Not surprisingly, the reduction/oxidation procedure was not effective for (*R*)-**2a**, (*R*)-**3a**, (*R*)-**4a**, or (*R*)-**5a**, and a complex mixture was obtained with the generation of **18**.

Synthesis of (*S*)-3,3′-Ar$_2$-BINSAs from (*S*)-20. This methodology was effective for the synthesis of bulky (*R*)- and (*S*)-3,3′-Ar$_2$-BINSAs (**1**). We could use *N*-Me sulfonimide (*S*)-**21** as a common intermediate after the *N*-methylation of (*S*)-**20**[4c] in the initial step (Scheme 8). Overall, we demonstrated that (*S*)-compounds with phenyl, 4-biphenyl, and 3,5-terphenyl substituents could be synthesized smoothly without serious problems, as shown in Scheme 8. The total yield of (*S*)-**1a**–**c** in nine steps from (*S*)-**20** was 33%, 46%, and 46%, respectively. Later, we could develop the improved method by double *N*,*O*-methylation of (*S*)-**4b** with the use of $Me_3O{\cdot}BF_4$ and hydrolysis to give (*S*)-**8b**, which would be transformed to (*S*)-**17b** *via* reduction and oxidation (Scheme 9). Therefore, we can synthesize chiral 3,3′-Ar$_2$-BINSAs from the known compound **20** in eight steps.

CONCLUSIONS

In summary, we have developed a practical synthesis of optically pure 3,3′-Ar$_2$-BINSAs from the parent sulfonimides *via* stepwise N–S bond cleavage of the sulfonimides and the resultant sulfonamides. (*R*)- or (*S*)-3,3′-Ar$_2$-BINSAs would be highly attractive as chiral organocatalysts and chiral bidentate ligands. Moreover, basically, this synthesis should be valuable as a general method for obtaining arylsulfonic acids from arylsulfonamides.

EXPERIMENTAL SECTION

General Information. Reactions were performed under nitrogen unless otherwise noted. Reagents were purchased from commercial suppliers and used without purification unless otherwise noted. Solvents such as dichloromethane, 1,2-dichloroethane, methanol, and THF were distilled prior to use. NMR spectra were measured on a 400 MHz spectrometer for ^{1}H NMR and a 100 MHz spectrometer for ^{13}C NMR. High resolution mass spectral analyses (HRMS) were performed by FAB, EI, and ESI techniques. High performance liquid chromatography (HPLC) analysis was conducted with a chiral column (250 mm). Column chromatography was performed using silica gel (100–210 mesh).

(*R*)-*N*-Methyl-3,3′-diphenyl-1,1′-binaphthyl-2,2′-sulfonimide ((*R*)-3a). A well dried Schlenk flask was charged with (*R*)-**2a**[4c] (328.6 mg, 0.60 mmol) and K_2CO_3 (249 mg, 1.80 mmol) under a nitrogen atmosphere. Dichloromethane (10 mL) was added, and the suspension was cooled to 0 °C. Trimethyloxonium tetrafluoroborate (266.2 mg, 1.80 mmol) was added, and the mixture was warmed to room temperature for 4 h by monitoring with TLC. Then a saturated NH_4Cl aqueous solution (5 mL) was poured into the reaction mixture, and the product was extracted with ethyl acetate (15 mL × 2). The combined extracts were washed with brine (10 mL) and dried over $MgSO_4$. The organic phase was concentrated under a reduced pressure, and the crude product was purified by silica gel column

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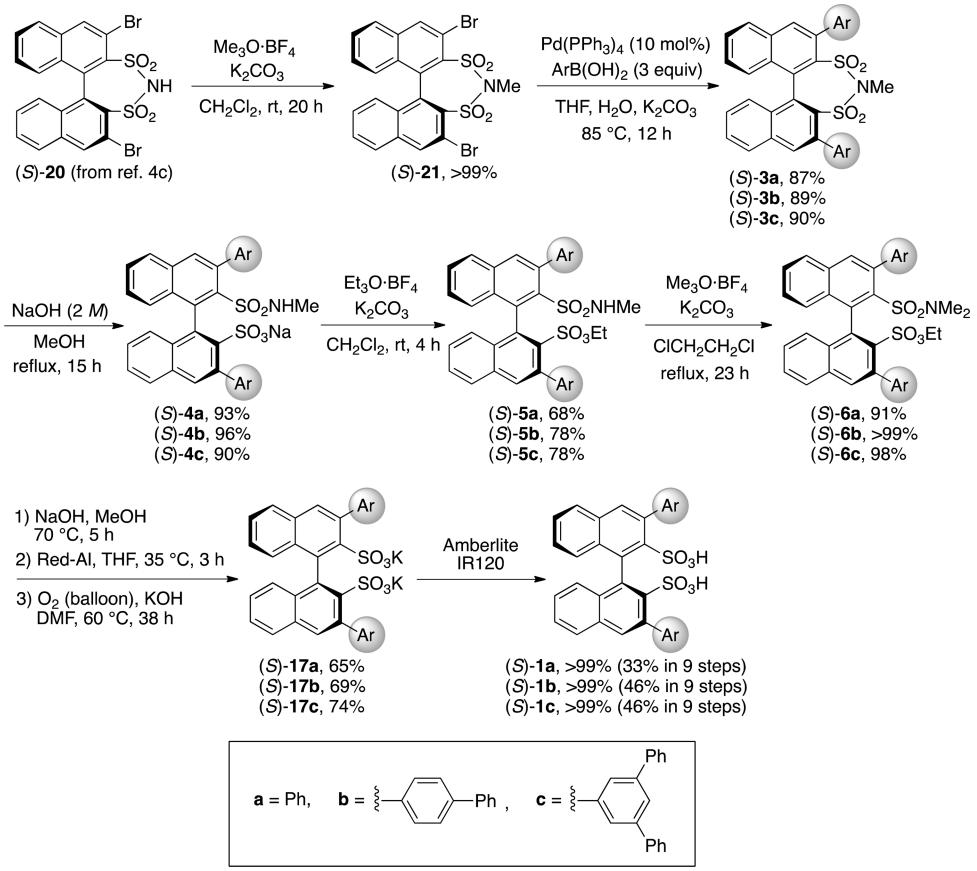
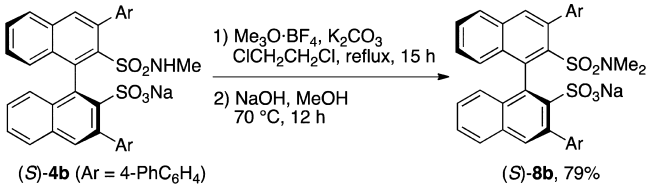
Scheme 8. Synthesis of (*S*)-3,3′-Ar$_2$-BINSAs ((*S*)-1a−c) (a: Ar = Ph, b: Ar = 4-biphenyl, c: Ar = 3,5-terphenyl)



Scheme 9. Improved Method by Double *N,O*-Methylation of (*S*)-4b and Hydrolysis



chromatography (eluent: hexane/EtOAc = 3:1), to give the desired product ((*R*)-**3a**) (337.0 mg, >99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (s, 3H), 7.25 (d, J = 8.2 Hz, 2H), 7.39−7.48 (m, 12H), 7.68 (t, J = 7.3 Hz, 2H), 7.98 (d, J = 8.2 Hz, 2H), 8.06 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 127.3 (2C), 127.8 (2C), 127.9 (2C), 128.3 (2C), 128.4 (2C), 128.5 (2C), 128.7 (2C), 130.0 (2C), 130.4 (2C), 131.8 (2C), 132.2 (2C), 133.8 (2C), 134.5 (2C), 138.0 (2C), 139.0 (2C), 139.8 (2C). Mp 278 °C (decomposed). IR (KBr) 3056, 2932, 1366, 1349, 1176, 1029 cm^{-1}. $[\alpha]_D^{24}$ = 38.8 (c 1.0, $CHCl_3$, (*R*)). HRMS (FAB+, Magnetic sector) calcd for $C_{33}H_{24}NO_4S_2$ $[M + H]^+$ 562.1147, found 562.1150.

Sodium (*R*)-2′-(*N*-Methylsulfamoyl)-3,3′-diphenyl-(1,1′-binaphthyl)-2-sulfonate ((*R*)-4a). To a solution of NaOH (8.0 g, 200 mmol) in methanol (100 mL), (*R*)-**3a** (561.1 mg, 1.0 mmol) was added. The solution was warmed to 70 °C for 15 h by monitoring with TLC. Then the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The colorless precipitate was acidified with a 1 M HCl aqueous solution at 0 °C and extracted with ethyl acetate (15 mL × 2). The combined extracts were washed with brine (10 mL) and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: $CHCl_3$/MeOH = 5:1), to give the desired product ((*R*)-**4a**) (597.0 mg, 99% yield). ^{1}H NMR (400 MHz, CD_3OD) δ 2.30 (s, 3H), 6.96 (d, J = 8.7 Hz, 1H), 7.16−7.38 (m, 6H), 7.39−7.48 (m, 4H), 7.51 (t, J = 7.3 Hz, 1H), 7.57−7.69 (m, 4H), 7.76 (s, 1H), 7.80 (s, 1H), 7.85 (d, J = 9.1 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) Many peaks overlapped. δ 28.9, 127.3, 127.4, 127.7, 127.9, 128.2, 128.4, 128.5, 128.6, 129.4, 130.9, 131.2, 131.3, 132.8, 134.0, 134.5, 134.7, 135.4, 136.1, 138.7, 140.3, 140.4, 142.4, 142.7, 144.6. Mp 273 °C (decomposed). IR (KBr) 3376, 1494, 1326, 1170, 1041 cm^{-1}. $[\alpha]_D^{23}$ = 155 (c 1.0, CH_3OH, (*R*)). HRMS (FAB+, Magnetic sector) calcd for $C_{33}H_{24}NNa_2O_5S_2$ $[M + Na]^+$ 624.0891, found 624.0899.

(*R*)-Ethyl 2′-(*N*-Methylsulfamoyl)-3,3′-diphenyl-(1,1′-binaphthyl)-2-sulfonate ((*R*)-5a). A well dried Schlenk flask was charged with (*R*)-**4a** (120.3 mg, 0.20 mmol) and K_2CO_3 (69.1 mg, 0.50 mmol) under a nitrogen atmosphere. Dichloromethane (7.5 mL) was added, and the suspension was cooled to 0 °C. Then a 1.0 M CH_2Cl_2 solution of triethyloxonium tetrafluoroborate (0.50 mL, 0.50 mmol) was added, and the mixture was warmed to room temperature for 20 h by monitoring with TLC. Then 5 mL of saturated NH_4Cl aqueous solution were poured into the reaction mixture, and the product was extracted with ethyl acetate (15 mL × 2). The combined extracts were washed with brine (10 mL) and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc = 4:1), to give the desired product ((*R*)-**5a**) (119.3 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 2.33 (d, J = 5.0 Hz, 3H), 3.29 (q, J = 5.0 Hz, 1H), 3.70 (dq, J = 9.6, 6.9 Hz, 1H), 3.86 (dq, J = 9.6, 6.9 Hz, 1H), 7.25 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 8.7 Hz, 1H), 7.37−7.55 (m, 8H), 7.57−7.74 (m, 5H), 7.79 (m, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.93 (s, 1H), 7.94 (s 1H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 14.4, 28.8, 66.2, 127.2, 127.54, 127.56, 127.61, 127.91, 127.94, 128.0, 128.3, 128.5, 128.8, 129.1, 129.1, 130.0, 132.1, 132.3, 132.5, 132.6, 132.7, 133.5, 133.9, 134.8, 136.1, 137.4, 138.5, 139.6, 140.0, 140.6. Mp 214−217 °C (decomposed). IR (KBr) 3372, 3055, 1332, 1183, 1000 cm^{-1}. $[\alpha]_D^{25}$ =

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186.4 (*c* 1.0, $CHCl_3$, (*R*)). HRMS (FAB+, Magnetic sector) calcd for $C_{35}H_{30}NO_5S_2$ $[M + H]^+$ 608.1565, found 608.1555.

(*R*)-Ethyl 2′-(*N*,*N*-Dimethylsulfamoyl)-3,3′-diphenyl-(1,1′-binaphthyl)-2-sulfonate ((*R*)-6a). A well dried Schlenk flask with a condenser was charged with (*R*)-**5a** (30.4 mg, 0.050 mmol) and K_2CO_3 (13.8 mg, 1.0 mmol) under a nitrogen atmosphere. 1,2-Dichloroethane (2 mL) was added, and the suspension was cooled to 0 °C. Then a dichloromethane solution of trimethyloxonium tetrafluoroborate (14.8 mg, 0.10 mmol) was added portionwise (30 min), and the mixture was warmed to 90 °C for 52 h by monitoring with TLC. Then 2 mL of saturated NH_4Cl aqueous solution were poured into the reaction mixture, and the product was extracted with ethyl acetate (10 mL × 2). The combined extracts were washed with brine (5 mL) and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc = 4:1), to give the desired product ((*R*)-**6a**) (26.6 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3H), 2.10 (s, 6H), 3.73 (m, 1H), 3.90 (m, 1H), 7.27−7.32 (m, 2H), 7.33−7.50 (m, 8H), 7.53−7.78 (m, 6H), 7.86 (s, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.94 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 14.5, 34.5, 66.3, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.4, 128.9, 129.2, 129.8, 132.1, 132.2, 132.5, 132.6, 133.1, 133.7, 134.1, 135.1, 137.5, 137.7, 139.6, 139.9, 140.7, 141.4. Mp 235−237 °C (decomposed). IR (KBr) 3057, 2927, 1355, 1325, 1183, 1137 cm^{-1}. $[\alpha]_D^{24}$ = 337.5 (*c* 1.0, $CHCl_3$, (*R*)). HRMS (FAB+, Magnetic sector) calcd for $C_{36}H_{32}NO_5S_2$ $[M + H]^+$ 622.1722, found 622.1711.

Sodium (*R*)-2′-(*N*,*N*-Dimethylsulfamoyl)-3,3′-diphenyl-(1,1′-binaphthalene)-2-sulfonate ((*R*)-8a). A well dried flask was charged with (*R*)-**6a** (124.4 mg, 0.20 mmol) and NaOH (1.60 g, 40 mmol). Methanol (20 mL) was added, and the mixture was stirred at 70 °C for 5 h by monitoring with TLC. Then the volatiles were removed under reduced pressure. A 2 M HCl aqueous solution was poured into the reaction mixture, and the product was extracted with ethyl acetate (20 mL × 3). The combined extracts were dried over Na_2SO_4. The organic phase was concentrated, and the crude product (almost quantitative yield) was used without purification. ^1H NMR (400 MHz, CD_3OD) δ 2.12 (s, 6H), 6.98 (d, J = 8.7 Hz, 1H), 7.20−7.39 (m, 7H), 7.40−7,50 (m, 3H), 7.51−7.60 (m, 3H), 7.63 (d, J = 6.9 Hz, 2H), 7.75 (s, 1H), 7.76 (s, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) Many peaks overlapped. δ 35.5, 127.3, 127.4, 127.7, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7, 129.5, 129.6, 130.5, 130.9, 131.4, 132.8, 133.3, 133.7, 134.3, 134.5, 135.0, 135.6, 136.1, 139.2, 140.5, 143.4, 143.8, 144.6. Mp 283 °C (decomposed). IR (KBr) 3444, 3054, 2923, 1491, 1322, 1188, 1135, 1042 cm^{-1}. $[\alpha]_D^{22}$ = 88.8 (*c* 1.0, CH_3OH, (*R*)). HRMS (FAB−, Magnetic sector) calcd for $C_{34}H_{26}NO_5S_2$ $[M - Na]^-$ 592.1252, found 592.1252.

Procedure for Preparation of Arylsulfone (*R*)-12. A well dried Schlenk flask was charged with (*R*)-**6a** (91.1 mg, 0.145 mmol) under a nitrogen atmosphere. Methyl trifluoromethanesulfonate (2.0 mL, 23.6 mmol) was added at 0 °C, and the mixture was warmed to 100 °C for 20 h by monitoring with TLC. After the mixture cooled to room temperature, water and then a saturated NH_4Cl aqueous solution (5 mL) were poured into the reaction mixture, and the product was extracted with ethyl acetate (15 mL × 2). The combined extracts were washed with brine (10 mL) and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc = 4:1 to 2:1), to give the desired product ((*R*)-**12**) (9.7 mg, 11% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 3.45 (s, 3H), 7.28 (d, J = 8.7 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.42−7.52 (m, 6H), 7.55−7.74 (m, 6H), 7.95 (d, J = 8.2 Hz, 1H), 8.01−8.05 (m, 2H), 8.06 (s, 1H), 8.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 121.3, 121.8, 122.0, 127.0, 127.7, 127.8, 127.9, 128.0, 128.4, 128.6, 129.2, 129.3, 129.7, 130.3, 131.9, 132.2, 132.6, 133.0, 133.8, 134.0, 134.1, 134.4, 134.8, 135.4, 137.4, 138.4, 140.3. Mp 168−171 °C. IR (KBr) 3060, 1361, 1303, 1185, 1168 cm^{-1}. $[\alpha]_D^{23}$ = 130 (*c* 1.0, $CHCl_3$, (*R*)). HRMS (FAB+, Magnetic sector) calcd for $C_{33}H_{23}O_5S_2$ $[M + H]^+$ 563.0987, found 563.0997.

***N*,*N*-Dimethylnaphthalene-2-sulfonamide (13).**[25] To a solution of naphthalene-2-sulfonyl chloride (1.13 g, 5.0 mmol) in THF, a 50% aqueous solution of dimethylamine (2.7 mL, 25 mmol) was added at room temperature. The resultant reaction mixture was stirred at room temperature for 1.5 h, poured into ice water, and extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous $MgSO_4$, and the excess solvent was removed in vacuo. The resultant residue was purified by silica gel column chromatography with hexane/chloroform (1:1) as the eluent affording **13** (1.18 g, >99% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 6H), 7.60−7.70 (m, 2H), 7.78 (dd, J = 8.7, 1.8 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.99 (m, 2H), 8.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.8, 122.8, 127.4, 127.7, 128.6, 128.8, 190.3, 129.1, 132.0, 132.3, 134.6. Mp 95−96 °C. IR (KBr) 3632, 3053, 3055, 2877, 2840, 1335, 1160, 1131 cm^{-1}. HRMS (FAB+, Magnetic sector) calcd for $C_{12}H_{14}NO_2S$ $[M + H]^+$ 236.0745, found 236.0755.

Potassium Naphthalene-2-sulfonate (14).[26] A solution of **13** (23.5 mg, 0.10 mmol) in THF (4 mL) under a nitrogen atmosphere was cooled to 0 °C, and a 65 wt % solution of bis(2-methoxyethoxy)-aluminumhydride in toluene (0.15 mL, 0.50 mmol) was added. The reaction mixture was stirred at room temperature for 5 h and then cooled to 0 °C. With the suspension vigorously stirring, a saturated Na_2SO_4 aqueous solution was added, and the reaction mixture was extracted with ethyl acetate (10 mL × 2). The combined extracts were washed with brine (5 mL) and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure. The crude products were used in the next step without further purification. To a solution of crude products, 1 mL of *N*,*N*-dimethylformamide (DMF) was added. Then O_2 (balloon) was charged. The reaction mixture was heated to 60 °C for 16 h. The reaction mixture was cooled to room temperature and was purified by silica gel column chromatography using $CHCl_3$/MeOH (1:1) as the eluent to give **14** (23.9 mg, 97% yield). ^1H NMR (400 MHz, CD_3OD) δ 7.55 (m, 2H), 7.85−8.00 (m, 4H), 8.34 (s, 1H). ^{13}C NMR (100 MHz, d_6-DMSO/D_2O = 3:1) δ 124.0, 126.0, 128.5, 129.0, 129.1, 129.8, 129.9, 133.1, 134.7, 143.1. IR (KBr) 3422, 1624, 1230, 1186, 1101, 1045 cm^{-1}. HRMS (FAB−, Magnetic sector) calcd for $C_{10}H_7O_3S$ $[M - K]^-$ 207.0116, found 207.0118.

2-Naphthalenesulfinic Acid (15).[27] ^1H NMR (400 MHz, CD_3OD) δ 7.54−7.57 (m, 2H), 7.84 (d, J = 8.3 Hz, 1H), 7.91−8.00 (m, 3H), 8.15 (s, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 122.7, 125.0, 127.8, 128.1, 129.2, 129.8, 129.9, 134.7, 135.9, 154.3. Mp 92−96 °C. IR (KBr) 3421, 3050, 2925, 1587, 1500, 1340, 1269, 1204, 1047 cm^{-1}. HRMS (ESI−, Q-TOF) calcd for $C_{10}H_7O_2S$ $[M - H]^-$ 191.0172, found 191.0174.

1,2-Di(naphthalen-2-yl)disulfane (16).[28] ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.49 (m, 4H), 7.61−7.63 (m, 2H), 7.72−7.80 (m, 6H), 7.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.7, 126.3, 126.6, 126.8, 127.5, 127.8, 129.1, 132.6, 133.5, 134.3. Mp 136−139 °C. IR (KBr) 3449, 3051, 2921, 1579, 1498, 1336, 1267, 1131 cm^{-1}. HRMS (EI, TOF) calcd for $C_{20}H_{14}S_2$ $[M]^+$ 318.0537, found 318.0539.

Potassium (*R*)-3,3′-Diphenyl-(1,1′-binaphthyl)-2,2′-disulfonate ((*R*)-17a).[3f] A solution of (*R*)-**8a**, which was obtained from (*R*)-**6a** (0.20 mmol) without purification, in THF (8 mL) under a nitrogen atmosphere was cooled to 0 °C, and a 65 wt % solution of bis(2-methoxyethoxy)aluminumhydride (Red-Al) in toluene (0.90 mL, 3.0 mmol) was added. The reaction mixture was heated to 35 °C for 3 h and then cooled to 0 °C. With the suspension vigorously stirring, a saturated Na_2SO_4 aqueous solution was added, and the reaction mixture was extracted with ethyl acetate (20 mL × 3). The combined extracts were washed with brine (20 mL) and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure. Crude products were used in the next step without further purification. To a solution of crude products in DMF (2 mL), powdered KOH (66 mg, 1.20 mmol) was added. Then the O_2 (balloon) was charged. The reaction mixture was heated to 60 °C for 38 h. The reaction mixture was cooled to room temperature and was purified by silica gel column chromatography using $CHCl_3$/MeOH (1:1) as the eluent to give (*R*)-**17a** (88.5 mg, 68% yield (3 steps), based on (*R*)-**6a**). ^1H NMR (400

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MHz, CD_3OD) δ 7.06 (d, J = 8.6 Hz, 2H), 7.18 (t, J = 8.0 Hz, 2H), 7.26−7.35 (m, 6H), 7.41 (t, J = 7.6 Hz, 2H), 7.66 (d, J = 7.6 Hz, 4H), 7.69 (s, 2H), 7.81 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 127.0 (2C), 127.1 (2C), 127.6 (4C), 127.8 (2C), 128.3 (2C), 129.2 (2C), 131.4 (4C), 132.2 (2C), 134.2 (2C), 134.3 (2C), 138.1 (2C), 140.3 (2C), 140.4 (2C), 145.2 (2C). IR (KBr) 3056, 1231, 1186, 1038 cm^{-1}. $[\alpha]_D^{24}$ = 91.3 (c 0.80, CH_3OH, (R)). HRMS (FAB+, Magnetic sector) calcd for $C_{32}H_{21}Na_2O_6S_2$ $[M - 2K + 2Na + H]^+$ 611.0575, found 611.0584; (FAB−, Magnetic sector) calcd for $C_{32}H_{20}NaO_6S_2$ $[M - 2K + Na]^-$ 587.0599, found 587.0608.

3,3′-Diphenyl-1,1′-binaphthalene (18). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 6.9 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.44−7.54 (m, 8H), 7.79 (d, J = 6.9 Hz, 4H), 7.85 (d, J = 1.8 Hz, 2H), 8.01 (d, J = 8.2 Hz, 2H), 8.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.8 (2C), 126.2 (2C), 126.4 (2C), 126.5 (2C), 127.5 (4C), 127.6 (2C), 127.7 (2C), 128.6 (2C), 129.0 (4C), 132.1 (2C), 134.0 (2C), 138.1 (2C), 139.0 (2C), 140.8 (2C). IR (neat) 3056, 1595, 1495, 1448 cm^{-1}. HRMS (EI, TOF) calcd for $C_{32}H_{22}$ $[M]^+$ 406.1722, found 406.1729.

(*R*)-3,3′-Diphenyl-(1,1′-binaphthyl)-2,2′-disulfonic Acid ((*R*)-1a).[3f] A solution of (R)-**17a** (37.9 mg, 0.059 mmol) in methanol (1 mL) was passed through a cation exchange column (100 cm^3, Amberlite IR120 ion-exchange resin. The cation exchange resin is converted to the H^+ form by washing with 3 M HCl and then water, in advance.). The eluate was concentrated in vacuo. The remaining water was removed by azeotropic distillation with toluene. The resultant white-brown powder of (R)-**1a** was dried in vacuo for 12 h (33.4 mg, >99% yield). ^{1}H NMR (400 MHz, CD_3OD) δ 7.07 (d, J = 8.6 Hz, 2H), 7.25 (t, J = 7.3 Hz, 2H), 7.29−7.43 (m, 6H), 7.50 (t, J = 6.9 Hz, 2H), 7.61 (d, J = 7.0 Hz, 4H), 7.80 (s, 2H), 7.89 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 127.5 (2C), 127.6 (2C), 127.9 (4C), 128.6 (2C), 128.7 (2C), 129.0 (2C), 131.0 (4C), 132.8 (2C), 134.0 (2C), 134.5 (2C), 138.4 (2C), 138.6 (2C), 140.0 (2C), 144.2 (2C). Mp 216−219 °C (decomposed). IR (KBr) 3420, 3053, 1229, 1182, 1035 cm^{-1}. $[\alpha]_D^{24}$ = 121 (c 1.0, MeOH, (R)). HRMS (FAB+, Magnetic sector) calcd for $C_{32}H_{22}O_6S_2$ $[M]^+$ 566.0858, found 566.0862.

(*R*)-Diethyl 3,3′-Diphenyl-(1,1′-binaphthyl)-2,2′-disulfonate ((*R*)-19a). A well dried Schlenk flask was charged with (R)-**1a** (31.0 mg, 0.055 mmol) and K_2CO_3 (69.1 mg, 0.50 mmol) under a nitrogen atmosphere. Dichloromethane (2 mL) was added, and the suspension was cooled to 0 °C. Then a 1.0 M CH_2Cl_2 solution of triethyloxonium tetrafluoroborate (0.50 mL, 0.50 mmol) was added, and the mixture was warmed to room temperature for 15 h by monitoring with TLC. Then 5 mL of saturated NH_4Cl aqueous solution were poured into the reaction mixture, and the product was extracted with ethyl acetate (15 mL × 2). The combined extracts were washed with brine (10 mL) and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc = 3:1), to give the desired product ((R)-**19a**) (28.8 mg, 84% yield). Optical purity was determined by HPLC analysis, and >99% ee was confirmed. [IA, hexane/i-PrOH = 9:1, 1.0 mL/min, t_R = 9.0 min (S), 16.9 min (R). (S)-**19a** was prepared from (S)-**1a** by the same procedure.] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 6.9 Hz, 6H), 3.66−3.75 (m, 2H), 3.79−3.88 (m, 2H), 7.25 (d, J = 8.7 Hz, 2H), 7.39−7.75 (m, 14H), 7.92 (d, J = 8.2 Hz, 2H), 7.96 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 14.5, 66.3, 127.5, 127.8, 127.9, 128.1, 129.3, 129.7, 130.3, 132.2, 132.7, 133.0, 134.1, 137.7, 138.9, 140.6. IR (KBr) 3056, 2984, 2256, 1580, 1493, 1444, 1354, 1185, 1001 cm^{-1}. $[\alpha]_D^{24}$ = 112.0 (c 0.20, $CHCl_3$, (R)). HRMS (FAB+, Magnetic sector) calcd for $C_{36}H_{31}O_6S_2$ $[M + H]^+$ 623.1562, found 623.1563.

(*S*)-*N*-Methyl-3,3′-dibromo-(1,1′-binaphthyl)-2,2′-sulfonimide ((*S*)-21). A well dried Schlenk was charged with (S)-3,3′-dibromo-1,1′-binaphthyl-2,2′-sulfonimide ((S)-**20**)[4c] (27.7 mg, 0.050 mmol) and K_2CO_3 (20.7 mg, 0.15 mmol) under a nitrogen atmosphere. Dichloromethane (2 mL) was added, and the suspension was cooled to 0 °C. Trimethyloxonium tetrafluoroborate (22.2 mg, 0.15 mmol) was added, and the mixture was warmed to room temperature for 20 h by monitoring with the TLC. Then a saturated NH_4Cl aqueous solution (5 mL) was poured into the reaction mixture, and the product was extracted with chloroform (15 mL × 2). The combined extracts were washed brine (10 mL) and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc = 6:1 to 3:1), to give the desired product ((S)-**21**) (28.3 mg, >99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (s, 3H), 7.00 (d, J = 8.7 Hz, 2H), 7.36 (t, J = 7.3 Hz, 2H), 7.66 (t, J = 7.6 Hz, 2H), 7.91 (d, J = 8.1 Hz, 2H), 8.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, 114.1 (2C), 127.6 (2C), 128.4 (2C), 128.7 (2C), 130.7 (2C), 131.2 (2C), 135.5 (2C), 137.3 (4C), 140.8 (2C). Mp 283 °C (decomposed). IR (KBr) 3419, 1551, 1372, 1348, 1183, 1156, 1132, 1044 cm^{-1}. $[\alpha]_D^{25}$ = 131.2 (c 0.20, $CHCl_3$, (S)). HRMS (EI, TOF) calcd for $C_{21}H_{13}Br_2NO_4S_2$ $[M]^+$ 564.8653, found 564.8657.

Representative Procedure for Preparation of 3. To a two-necked flask equipped with a condenser were placed (S)-**21** (567 mg, 1.0 mmol), phenyl boronic acid (366 mg, 3.0 mmol), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol), K_2CO_3 (1.38 g, 10 mmol), THF (20 mL), and water (5 mL). The mixture was heated at 85 °C for 12 h. After the mixture cooled to room temperature, a saturated NH_4Cl aqueous solution (5 mL) was poured into the reaction mixture, and the product was extracted with chloroform (30 mL × 2). The combined extracts were washed brine (30 mL) and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc = 6:1 to 3:1), to give the desired product ((S)-**3a**) (490 mg, 87% yield). (S)-**3b** and (S)-**3c** were obtained in the respective yield of 89% and 90%.

(S)-N-Methyl-3,3′-di(biphenyl)-(1,1′-binaphthyl)-2,2′-sulfonimide ((S)-3b). 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (s, 3H), 7.27 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.39−7.49 (m, 6H), 7.51−7.60 (m, 4H), 7.62−7.74 (m, 10H), 8.00 (d, J = 8.2 Hz, 2H), 8.07 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 30.7, 125.8, 126.5, 127.1, 127.4, 128.2, 128.4, 128.7, 129.1, 129.9, 130.8, 131.6, 131.9, 133.8, 134.4, 137.5, 138.7, 138.9, 140.3, 140.5. Mp 194−196 °C. IR (KBr) 3028, 1576, 1487, 1369, 1349, 1177 cm^{-1}. $[\alpha]_D^{23}$ = 12.8 (c 0.50, $CHCl_3$, (S)). HRMS (FAB+, Magnetic sector) calcd for $C_{45}H_{31}NO_4S_2$ $[M]^+$ 713.1694, found 713.1702.

(S)-N-Methyl-3,3′-di(terphenyl)-(1,1′-binaphthyl)-2,2′-sulfonimide ((S)-3c). 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (s, 3H), 7.30−7.40 (m, 6H), 7.40−7.50 (m, 10H), 7.66−7.76 (m, 14H), 7.87 (m, 2H), 8.01 (d, J = 8.2 Hz, 2H), 8.16 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 30.7, 125.3, 126.4, 127.2, 127.4, 127.5, 127.6, 128.2, 128.3, 128.8, 128.9, 130.0, 131.7, 132.0, 133.9, 134.4, 137.6, 139.1, 140.6, 140.7, 141.2. Mp 194−196 °C. IR (KBr) 2940, 1593, 1574, 1496, 1370, 1349, 1177, 1028 cm^{-1}. $[\alpha]_D^{24}$ = −30.0 (c 0.50, $CHCl_3$, (S)). HRMS (EI, TOF) calcd for $C_{57}H_{39}NO_4S_2$ $[M]^+$ 865.2321, found 865.2336.

Sodium (*S*)-2′-(*N*-Methylsulfamoyl)-3,3′-di(biphenyl)-(1,1′-binaphthyl)-2-sulfonate ((*S*)-4b). 96% yield. ^{1}H NMR (400 MHz, d_8-THF) δ 2.10 (s, 3H), 4.30 (br, 1H), 6.90 (d, J = 8.6 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 7.16−7.22 (m, 2H), 7.23−7.32 (m, 2H), 7.32−7.46 (m, 6H), 7.55−7.84 (m, 16H). ^{13}C NMR (100 MHz, d_8-THF) Many peaks overlapped. δ 28.8, 126.1, 126.3, 126.9, 127.3, 127.6, 128.1, 128.2, 128.4, 129.0, 129.4, 129.6, 131.0, 131.4, 131.7, 132.5, 132.6, 133.8, 134.2, 134.4, 135.5, 135.9, 137.6, 139.3, 139.8, 140.8, 141.1, 141.2, 141.3, 141.9, 142.7, 144.0. Mp 284−286 °C. IR (KBr) 3373, 3065, 1486, 1393, 1329, 1229, 1203, 1042 cm^{-1}. $[\alpha]_D^{22}$ = −81.9 (c 0.20, $CHCl_3$, (S)). HRMS (ESI−, Q-TOF) calcd for $C_{45}H_{32}NO_5S_2$ $[M - Na]^-$ 730.1727, found 730.1723.

Sodium (*S*)-2′-(*N*-Methylsulfamoyl)-3,3′-di(terphenyl)-(1,1′-binaphthyl)-2-sulfonate ((*S*)-4c). 90% yield. ^{1}H NMR (400 MHz, d_8-THF) δ 2.18 (s, 3H), 4.10 (br, 1H), 7.03 (d, J = 8.7 Hz, 1H), 7.14 (m, 2H), 7.20 (t, J = 7.8 Hz, 1H), 7.24−7.50 (m, 14H), 7.68−8.05 (m, 18H). ^{13}C NMR (100 MHz, d_8-THF) Many peaks overlapped. δ 28.9, 124.4, 125.6, 127.3, 127.6, 127.9, 128.0, 128.1, 128.3, 128.4, 129.0, 129.4, 129.6, 129.7, 132.6, 133.1, 134.0, 134.2, 134.3, 136.3, 136.5, 138.3, 139.5, 139.9, 140.8, 141.4, 141.7, 141.9, 142.2, 143.7, 145.2. Mp 282−284 °C. IR (KBr) 3374, 3058, 1593, 1496, 1330, 1232, 1169, 1040 cm^{-1}. $[\alpha]_D^{23}$ = −125.2 (c 0.20, $CHCl_3$, (S)). HRMS (ESI−, Q-TOF) calcd for $C_{57}H_{40}NO_5S_2$ $[M - Na]^-$ 882.2353, found 882.2367.

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(*S*)-Ethyl 2′-(*N*-Methylsulfamoyl)-3,3′-di(biphenyl)-(1,1′-binaphthyl)-2-sulfonate ((*S*)-5b). 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.8 Hz, 3H), 2.38 (d, J = 4.9 Hz, 3H), 3.48 (q, J = 5.0 Hz, 1H), 3.77 (dq, J = 10.1, 7.1 Hz, 1H), 3.92 (dq, J = 10.1, 7.1 Hz, 1H), 7.25−7.53 (m, 10H), 7.60−7.83 (m, 13H), 7.88 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.99 (s, 1H), 8.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 14.9, 28.8, 66.3, 126.0, 126.6, 126.9, 127.1, 127.2, 127.3, 127.4, 127.6, 127.7, 127.8, 128.0, 128.1, 128.8, 128.9, 129.0, 129.2, 129.6, 130.6, 132.2, 132.4, 132.7, 132.8, 133.6, 134.1, 134.8, 135.9, 137.2, 138.7, 139.1, 139.8, 140.0, 140.3, 140.7, 141.2. Mp 163−165 °C. IR (KBr) 3373, 3030, 1487, 1353, 1331, 1183 cm^{-1}. $[\alpha]_D^{23}$ = −76.0 (c 0.20, $CHCl_3$, (*S*)). HRMS (FAB+, Magnetic sector) calcd for $C_{47}H_{38}NO_5S_2$ $[M + H]^+$ 760.2191, found 760.2203.

(*S*)-Ethyl 2′-(*N*-Methylsulfamoyl)-3,3′-di(terphenyl)-(1,1′-binaphthyl)-2-sulfonate ((*S*)-5c). 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 7.0 Hz, 3H), 2.40 (d, J = 5.0 Hz, 3H), 3.56 (q, J = 5.5 Hz, 1H), 3.75 (m, 1H), 3.86 (m, 1H), 7.29−7.54 (m, 16H), 7.59−7.67 (m, 2H), 7.70−7.80 (m, 8H), 7.82−8.00 (m, 7H), 8.03 (m, 1H), 8.08 (s, 1H), 8.10 (s 1H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 14.6, 29.2, 66.4, 125.3, 126.2, 126.9, 127.5, 127.7, 127.9, 128.5, 128.6, 129.2, 129.3, 129.4, 129.6, 132.6, 132.8, 132.9, 133.0, 133.9, 134.3, 135.2, 136.3 137.6, 139.0, 140.1, 140.3, 140.4, 140.8, 141.0, 141.1, 141.2, 141.4, 141.7, 141.8, 142.0. Mp 193−194 °C. IR (KBr) 3376, 3034, 1593, 1496, 1330, 1182 cm^{-1}. $[\alpha]_D^{22}$ = −112.0 (c 0.20, $CHCl_3$, (*S*)). HRMS (FAB+, Magnetic sector) calcd for $C_{59}H_{46}NO_5S_2$ $[M + H]^+$ 912.2817, found 912.2814.

(*S*)-Ethyl 2′-(*N*,*N*-Dimethylsulfamoyl)-3,3′-di(biphenyl)-(1,1′-binaphthyl)-2-sulfonate ((*S*)-6b). >99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 6.9 Hz, 3H), 2.16 (s, 6H), 3.79 (dq, J = 10.1, 7.3 Hz, 1H), 3.79 (dq, J = 10.1, 7.3 Hz, 1H), 7.30−7.52 (m, 10H), 7.58−7.80 (m, 14H), 7.79−7.96 (m, 3H), 7.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 14.5, 34.5, 66.3, 126.0, 126.4, 126.9, 127.1, 127.4, 127.5, 127.6, 127.7, 127.9, 128.0, 128.8, 128.9, 129.2, 130.3, 132.2, 132.3, 132.5, 132.8, 133.1, 133.7, 134.1, 135.2, 137.1, 137.4, 139.8, 139.9, 140.1, 140.3, 140.4, 140.5, 140.7. Mp 171−173 °C. IR (KBr) 3029, 1487, 1355, 1324, 1136, 1067 cm^{-1}. $[\alpha]_D^{24}$ = −91.9 (c 0.20, $CHCl_3$, (*S*)). HRMS (FAB+, Magnetic sector) calcd for $C_{48}H_{40}NO_5S_2$ $[M + H]^+$ 774.2348, found 774.2359.

(*S*)-Ethyl 2′-(*N*,*N*-Dimethylsulfamoyl)-3,3′-di(terphenyl)-(1,1′-binaphthyl)-2-sulfonate ((*S*)-6c). 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 6.9 Hz, 3H), 2.20 (s, 6H), 3.77 (m, 1H), 3.90 (m, 1H), 7.30−7.52 (m, 16H), 7.59−7.68 (m, 2H), 7.70−8.03 (m, 17H), 8.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) Many peaks overlapped. δ 14.4, 34.8, 66.2, 124.7, 125.1, 126.0, 127.2, 127.3, 127.4, 127.5, 127.7, 127.9, 128.0, 128.9, 129.0, 129.1, 129.3, 132.3, 132.7, 133.1, 133.7, 134.1, 135.2, 137.3, 137.4, 139.9, 140.1, 140.6, 140.8, 140.9, 141.2, 141.6, 142.3. Mp 189−191 °C. IR (KBr) 3035, 1593, 1576, 1497, 1355, 1322, 1183, 1137 cm^{-1}. $[\alpha]_D^{23}$ = −93.9 (c 0.20, $CHCl_3$, (*S*)). HRMS (FAB+, Magnetic sector) calcd for $C_{60}H_{48}NO_5S_2$ $[M+H]^+$ 926.2974, found 926.2969.

Sodium (*S*)-2′-(*N*,*N*-Dimethylsulfamoyl)-3,3′-di(biphenyl)-(1,1′-binaphthyl)-2-sulfonate ((*S*)-8b). ^{1}H NMR (400 MHz, d_8-THF) δ 1.91 (s, 6H), 6.77 (br, 1H), 6.90 (d, J = 8.7 Hz, 1H), 7.08−7.40 (m, 12H), 7.42−7.50 (m, 4H), 7.50−7.56 (m, 4H), 7.60 (d, J = 7.8 Hz, 1H), 7.64 (s, 1H), 7.75 (br, 2H), 7.80−7.86 (m, 2H). ^{13}C NMR (100 MHz, d_8-THF) Many peaks overlapped. δ 33.9, 124.9, 125.8, 126.5, 126.6, 126.7, 126.8, 127.1, 127.5, 127.7, 128.3, 128.4, 128.7, 130.8, 131.4, 131.7, 131.9, 132.8, 132.9, 133.1, 133.9, 134.3, 134.8, 137.8, 138.7, 138.9, 140.3, 140.5, 140.8, 141.4, 142.8, 143.0. Mp 289−292 °C (decomposed). IR (KBr) 3422, 3029, 1619, 1487, 1322, 1190, 1135, 1041 cm^{-1}. $[\alpha]_D^{23}$ = 107.2 (c 0.20, $CHCl_3$, (*S*)). HRMS (FAB−, Magnetic sector) calcd for $C_{46}H_{34}NO_5S_2$ $[M-Na]^-$ 744.1878, found 744.1860.

Sodium (*S*)-2′-(*N*,*N*-Dimethylsulfamoyl)-3,3′-di(terphenyl)-(1,1′-binaphthyl)-2-sulfonate ((*S*)-8c). ^{1}H NMR (400 MHz, d_8-THF) δ 2.00 (s, 6H), 6.98 (d, J = 8.7 Hz, 1H), 7.12−7.35 (m, 13H), 7.35−7.46 (m, 4H), 7.62−7.88 (m, 18H). ^{13}C NMR (100 MHz, d_8-THF) Many peaks overlapped. δ 34.5, 123.2, 124.0, 126.0, 126.6, 126.9, 127.0, 127.1, 127.3, 127.5, 128.2, 128.5, 128.7, 129.0, 131.9, 132.7, 133.1, 133.3, 133.7, 135.0, 137.6, 138.7, 139.8, 140.0, 140.5, 140.7, 140.9, 141.1, 141.5, 142.8, 143.2, 144.7. Mp 293−296 °C (decomposed). IR (KBr) 3407, 3033, 1594, 1497, 1319, 1188, 1041 cm^{-1}. $[\alpha]_D^{23}$ = −155.2 (c 0.20, $CHCl_3$, (*S*)). HRMS (FAB−, Magnetic sector) calcd for $C_{58}H_{42}NO_5S_2$ $[M-Na]^-$ 896.2504, found 896.2528.

Potassium (*S*)-3,3′-Di(biphenyl)-(1,1′-binaphthyl)-2,2′-disulfonate ((*S*)-17b). 69% yield. ^{1}H NMR (400 MHz, CD_3OD) δ 7.04 (m, 2H), 7.18 (t, J = 8.2 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 7.42 (t, J = 7.6 Hz, 6H), 7.59 (d, J = 8.2 Hz, 4H), 7.66 (d, J = 7.8 Hz, 4H), 7.72−7.81 (m, 6H), 7.83 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) Many peaks overlapped. δ 126.4, 127.2, 127.9, 128.0, 128.1, 128.4, 129.2, 129.7, 131.7, 132.3, 134.2, 134.4, 138.3, 139.8, 140.2, 142.7, 144.2. IR (KBr) 3371, 1620, 1485, 1220, 1175, 1036 cm^{-1}. $[\alpha]_D^{23}$ = −10.0 (c 0.20, CH_3OH, (*S*)). HRMS (FAB−, Magnetic sector) calcd for $C_{44}H_{28}NaO_6S_2$ $[M - 2K + Na]^-$ 739.1225, found 739.1205.

Potassium (*S*)-3,3′-Di(terphenyl)-(1,1′-binaphthyl)-2,2′-disulfonate ((*S*)-17c). 74% yield. ^{1}H NMR (400 MHz, CD_3OD) δ 7.10 (m, 2H), 7.24 (t, J = 7.3 Hz, 2H), 7.32 (t, J = 7.3 Hz, 4H), 7.40−7.53 (m, 10H), 7.73−7.85 (m, 10H), 7.86−8.00 (m, 8H). ^{13}C NMR (100 MHz, CD_3OD) Many peaks overlapped. δ 124.8, 127.4, 128.1, 128.4, 128.5, 129.2, 129.3, 129.7, 132.5, 134.3, 134.4, 138.3, 139.8, 141.4, 143.0, 146.0. IR (KBr) 3406, 1594, 1215, 1182, 1038 cm^{-1}. $[\alpha]_D^{23}$ = −72.0 (c 0.20, CH_3OH, (*S*)). HRMS (FAB−, Magnetic sector) calcd for $C_{56}H_{36}NaO_6S_2$ $[M - 2K + Na]^-$ 891.1851, found 891.1841.

(*S*)-3,3′-Di(biphenyl)-(1,1′-binaphthyl)-2,2′-disulfonic Acid ((*S*)-1b). >99% yield. ^{1}H NMR (400 MHz, CD_3OD) δ 7.10 (d, J = 8.6 Hz, 2H), 7.27 (t, J = 7.0 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.44 (t, J = 7.8 Hz, 4H), 7.51 (t, J = 7.8 Hz, 2H), 7.62−7.67 (m, 4H), 7.68−7.74 (m, 8H), 7.86 (s, 2H), 7.91 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) Many peaks overlapped. δ 126.5, 127.7, 127.9, 128.1, 128.7, 128.8, 129.1, 129.8, 131.6, 132.9, 134.1, 134.6, 138.5, 138.7, 139.7, 140.6, 142.4, 143.3. Mp 220−224 °C (decomposed). IR (KBr) 3382, 1697, 1486, 1220, 1164, 1033 cm^{-1}. $[\alpha]_D^{22}$ = −20.8 (c 1.0, MeOH, (*S*)). HRMS (FAB−, Magnetic sector) calcd for $C_{44}H_{29}O_6S_2$ $[M - H]^-$ 717.1406, found 717.1391.

(*S*)-3,3′-Di(terphenyl)-(1,1′-binaphthyl)-2,2′-disulfonic Acid ((*S*)-1c). >99% yield. ^{1}H NMR (400 MHz, CD_3OD) δ 7.16 (br, 2H), 7.27 (t, J = 7.3 Hz, 2H), 7.32 (t, J = 7.3 Hz, 4H), 7.40−7.53 (m, 10H), 7.73−7.85 (m, 10H), 7.86−8.00 (m, 8H). ^{13}C NMR (100 MHz, CD_3OD) Many peaks overlapped. δ 124.9, 127.6, 128.2, 128.4, 128.5, 128.6, 129.2, 129.3, 129.7, 132.7, 134.2, 134.5, 139.9, 141.5, 142.8, 145.4. Mp 232−235 °C (decomposed). IR (KBr) 3389, 1497, 1218, 1186, 1035 cm^{-1}. $[\alpha]_D^{23}$ = −69.2 (c 0.20, CH_3OH, (*S*)). HRMS (FAB−, Magnetic sector) calcd for $C_{56}H_{37}O_6S_2$ $[M-H]^-$ 869.2032, found 869.2014.

Procedure for Improved Method by Double *N*,*O*-Methylation of (*S*)-4b and Hydrolysis to (*S*)-8b. A well dried Schlenk flask with a condenser was charged with (*S*)-**4b** (550 mg, 0.73 mmol) and K_2CO_3 (1.01 g, 7.3 mmol) under a nitrogen atmosphere. 1,2-Dichloroethane (20 mL) was added, and the suspension was cooled to 0 °C. Then a dichloromethane solution (5 mL) of trimethyloxonium tetrafluoroborate (650 mg, 4.4 mmol) was added portionwise (30 min), and the mixture was warmed to 90 °C for 15 h by monitoring with TLC. Then 20 mL of saturated NH_4Cl aqueous solution was poured into the reaction mixture at room temperature, and the product was extracted with dichloromethane (20 mL × 2). The combined extracts were dried over Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude products (i.e., the mixture of R*SO_3Me and R*SO_3H) were used without further purification. To the residue obtained, a solution of NaOH (5.84 g, 200 mmol) in methanol (70 mL) was added. The solution was warmed to 70 °C for 12 h by monitoring with the TLC. Then the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The colorless precipitate was acidified with 1 M HCl aqueous solution at 0 °C and extracted with ethyl acetate (20 mL × 3). The combined extracts were washed with brine (10 mL) and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column

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chromatography (eluent: $CHCl_3$/MeOH = 5:1), to give the desired product ((*S*)-**8b**) (444 mg, 79% yield).

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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