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Chiral *N*-Fluorodibenzenesulfonimide Analogues for Enantioselective Electrophilic Fluorination and Oxidative Fluorination

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This work describes the design, synthesis, and application of de novo chiral fluorinating agents as analogues of popular *N*-fluorodibenzenesulfonimide (NFSI). The fluorination step by means of elemental fluorine is presented. Enantioselective fluorination is demonstrated in cyclic β-keto esters and in the synthesis of BMS-204352 (up to 86 % *ee*). Oxidative amino-fluorination is also examined.

Introduction

The importance of chirality in pharmaceutical molecules associated with the astonishing properties of fluorine-containing compounds led to huge efforts in the development of effective methodologies for the preparation of chiral non-racemic fluorinated molecules.[1] There are two strategies for the construction of fluorinated stereogenic centers.[2] The first strategy involves the use of fluorinated building blocks that are subjected to asymmetric transformations early in a multistep process. The second strategy involves the introduction of the fluorine atom in a late stage of a synthetic plan with concomitant control of the stereogenic centers. Basically, in the second strategy, the construction can be realized by nucleophilic substitution with a fluoride anion, by addition of an electropositive fluorine, or by radical fluorination. Asymmetric electrophilic fluorination, in either a diastereoselective or an enantioselective manner, is so far the most successful approach.[1a,1c] The success of this approach relies to a great extent upon the design of efficient neutral N–F or charged $[N–F]^+$ electrophilic fluorinating agents that include chiral, nonracemic agents.[1,3] In this way, a (pro)chiral substrate is transformed into a chiral fluorinated product with concomitant creation of a fluorinated stereogenic center. The most successful electrophilic fluorinating agents are *N*-fluorobenzenesulfonimide (NFSI)[4] and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor®),[5] both of which have been exploited in enantiocontrolled fluorination in organocatalysis and in transition-metal catalysis. In particular, NFSI is now quite successful not only as an electrophilic fluorinating agent in enantioselective catalysis[6] but also as an oxidant for organometallic intermediates to promote reductive elimination through high-oxidation-state transition metals, as an amination reagent, and even as a phenylsulfonyl group transfer reagent.[7] Alongside these facts, we were interested in chiral analogues of NFSI. The chiral analogues of Selectfluor® were independently reported by Shibata[8] and Cahard[9] in 2000 as *N*-fluoroammonium salts of cinchona alkaloids. The *N*-fluoroammonium salts of cinchona alkaloids that feature a quinuclidine moiety are closely structurally related to Selectfluor® and, as such, could be presented as chiral analogues. Selectfluor® analogues having a chiral C_8-BINOL-derived phosphate as a counteranion was also recently described by Toste and co-workers through in situ generation (BINOL = 1,1′-bi-2-naphthol).[10] It is surprising that an NFSI analogue bearing an element of chirality, that is, chiral *N*-fluorodiarylsulfonimide, has not yet been reported, although chiral *N*-fluorosulfonamides[11,12] and a sterically very demanding achiral NFSI analogue[13] have been described. In this context, we herein disclose the design and synthesis of de novo fluorinating agents, chiral NFSIs **1**, that combine the sulfonimide moiety of popular NFSI and the axial chirality of the well-established 1,1′-binaphthyl unit (Figure 1). Enantioselective fluorination of β-keto es-

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ters and oxindole was demonstrated for the evaluation of reagents **1** to provide the fluorinated products with up to 86%*ee*. Aminofluorination of indene was also attempted to explore the potential of **1** for oxidative reactions.

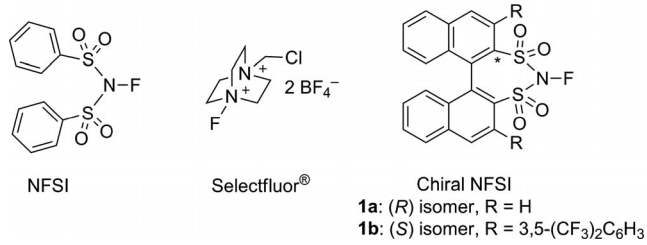
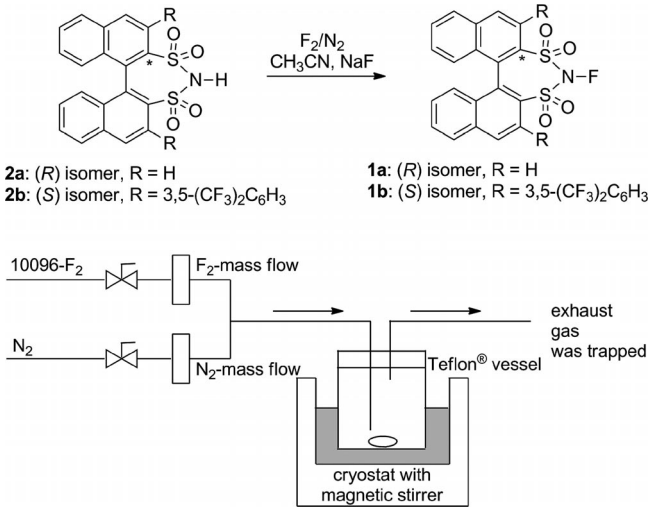


Figure 1. Structures of the fluorinating reagents NFSI, Selectfluor®, and chiral NFSIs **1**.

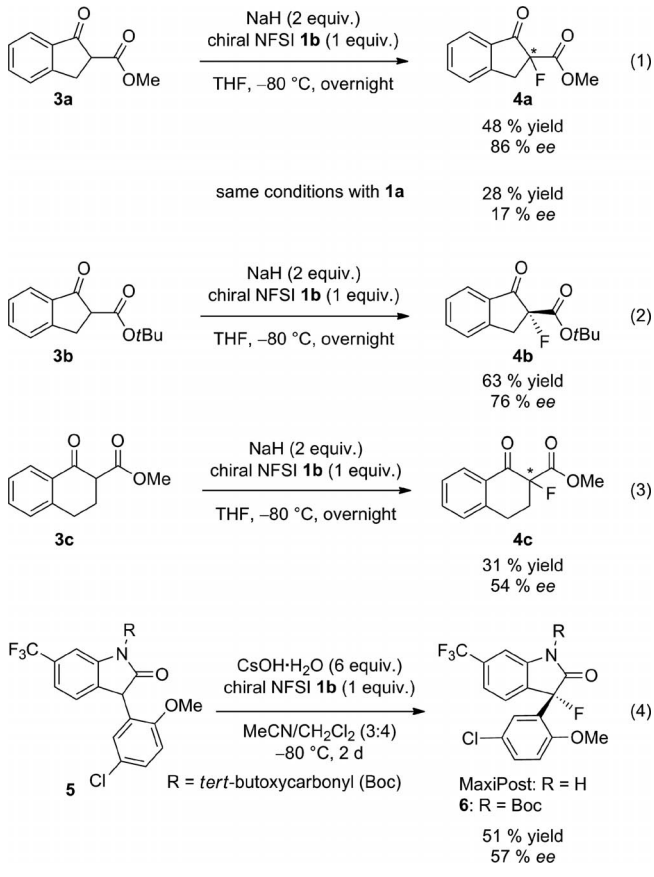
Results and Discussion

The NH precursors of **1**, 1,1′-binaphthyl-2,2′-bis(sulfonamide) scaffolds **2**, were designed by List[14] and Giernoth[15] and demonstrated a wide scope in organocatalysis for this type of chiral Brønsted acid.[14b] The fluorination step of NH precursors **2** to afford **1** was conducted by means of elemental fluorine in the presence of sodium fluoride in acetonitrile. The fluorination and its reaction vessel, having a supply channel for F_2 and N_2 to mix, are shown in Scheme 1. The best yield for the fluorination of the unsubstituted NH precursor to afford **1a** was 67%, whereas that for a substituted NH precursor featuring two sterically demanding 3,5-bis(trifluoromethyl)phenyl groups at the 3,3′-positions was 27%. In both cases, side products were obtained, although they were not characterized.



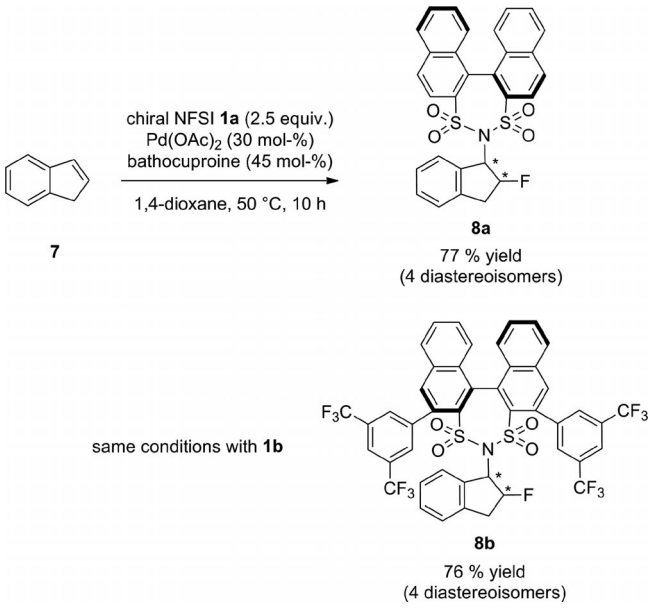
Scheme 1. Preparation of enantiopure electrophilic fluorinating agents, chiral NFSIs **1**.

With chiral reagents **1** in hand, we first evaluated the enantioselective electrophilic fluorination of β-keto ester derivatives **3a**–**c** [Scheme 2, Eqs. (1–3)]. β-Keto esters **3a**–**c** were deprotonated by sodium hydride in THF to form the corresponding sodium enolates, which reacted with chiral NFSI analogues **1**. The ability of fluorinating agents **1** to promote enantioselective fluorination was directly compared with organocatalytic approaches. From Equation (1), the fluorination only provided moderate yields of expected α-fluoro-β-keto ester **4a** with rather high enantioselectivity of 86% if more sterically hindered chiral N–F reagent **1b** was used. This level of enantioselection is comparable to that observed with other enantioselective approaches. Notably, **4a** was previously obtained by using chiral phase-transfer catalysts derived from cinchona alkaloids with 69%*ee*,[16] bifunctional phase-transfer ammonium salts having hydromethyl appendages with 68%*ee*,[17] and a bifunctional chiral thiourea with 99%*ee*.[18] Substituted NF reagent **1b** is clearly more enantioselective than unsubstituted reagent **1a** [86 vs. 17%*ee*; Scheme 2, Eq. (1)]. The fluorination of indanone carboxylate **3b** and tetralone carboxylate **3c** by **1b** gave fluorination products **4b** and **4c** with moderate enantioselectivities of 76 and 54%*ee*, respectively. The enantioselective synthesis of the potent Maxi-K potassium channel opener MaxiPost[19] was realized under different conditions starting from **5** by using cesium hydroxide as the base in a mixture of acetonitrile and dichloromethane to give target product **6** in 51% yield with 57%*ee* [Scheme 2, Eq. (4)]. We next examined an oxidative aminofluorination,[7c] which is one of the recent alternative uses of NFSI for nonelectrophilic fluorination reactions. The



Scheme 2. Enantioselective fluorination by means of chiral NFSIs **1**.

aminofluorination of indene (**7**) was attempted, for which **1a** and **1b** acted as a fluorination agent and as an amination reagent consecutively to provide 1-sulfonimido-2-fluoroindane derivatives **8a** and **8b** in 76–77% yield as a mixture of four diastereoisomers, although no asymmetric induction was observed (Scheme 3).



Scheme 3. Oxidative aminofluorination by means of chiral NFSIs **1a** and **1b**.

Conclusions

Two chiral analogues of NFSI, **1a** and **1b**, were designed and synthesized for the first time based on the C_2-symmetric chiral binaphthyl bis(sulfonimide) topology as a privileged motif for asymmetric synthesis. The use of chiral NFSI analogue **1b**, which features two bulky 3,5-bis(trifluoromethyl)phenyl groups at the 3,3′-positions of the binaphthol backbone, was found to be advantageous from an enantioselectivity point of view. This level of enantioselection is comparable to that observed with other enantioselective approaches for the selected example. Oxidative aminofluorination was also possible by using **1** to deliver products in high chemical yields. Although the present results are just preliminary examples of the use of chiral NFSIs **1**, a wide variety of applications should be possible on the basis of recent successful applications of NFSI.[7]

Experimental Section

General Information: All reactions were performed in oven-dried glassware under a positive pressure of nitrogen or argon. Solvents were transferred by syringe and were introduced into the reaction vessels though a rubber septum. The reactions were monitored by thin-layer chromatography (TLC) performed with 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light and $KMnO_4$ in water or *p*-anisaldehyde in ethanol/heat. Column chromatography was performed on a column packed with silica-gel 60N spherical neutral size 63-210 μm or Wako-gel C-300™. ^1H NMR (300 and 400 MHz) and ^{19}F NMR (282 MHz) spectra for solutions in $CDCl_3$ and CD_3CN were recorded with a Bruker Avance 400 and a Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane, $CDCl_3$, or CD_3CN. Optical rotations were measured with a Horiba SEPA-300 operating at 589 nm. HPLC analyses were performed with a JASCO U-2080 Plus by using a 4.6 × 250 mm Chiralcel OD-H or Chiralpak AD-3 column. Mass spectra were recorded with a Shimadzu LCMS-2010EV. Infrared spectra were recorded with a Jasco FTIR-200 spectrometer.

Synthesis of Chiral NFSI: A mixture of **2b** (600.8 mg, 0.733 mmol) and NaF (7.44 g, 177 mmol) in acetonitrile (300 mL) in a Teflon™ vessel was cooled to –40 °C with stirring. F_2 gas (0.068 mL min^{-1}) diluted with N_2 gas (29.8 mL min^{-1}) was then bubbled through the mixture for 4 h. Upon completion of the reaction, as monitored by TLC analysis, N_2 (29.8 mL min^{-1}) was bubbled through the mixture for 1 h at –40 °C, and then the mixture was warmed to room temperature. The solid was removed from the reaction mixture by filtration, and the filtrate was concentrated under reduced pressure to provide crude **1b** (0.78 g) as a brown-yellow solid. Crude **1b** was purified by SiO_2 column chromatography (Wako-gel C-300™), and then a yellow solid (357 mg), which contained **1b** (248 mg, 0.296 mmol), was obtained (40%).

(*S*)-*N*-Fluoro-{3,3′-bis[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl}-2,2′-disulfonimide (1b): $[\alpha]_D^{25}$ = –4.32 (*c* = 0.74, THF). ^1H NMR (400 MHz, CD_3CN): δ = 7.25 (d, *J* = 0.8 Hz, 1 H), 7.27 (d, *J* = 0.8 Hz, 1 H), 7.52 (t, *J* = 1.6 Hz, 1 H), 7.54 (t, *J* = 1.2 Hz, 1 H), 7.81–7.85 (m, 2 H), 8.00 (s, 2 H), 8.03 (s, 2 H), 8.06 (s, 2 H), 8.12 (s, 1 H), 8.14 (s, 1 H), 8.23 (s, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –61.94 (s), –61.90 (s), –44.97 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2963, 1621, 1378, 1280, 1178, 1136, 901, 803, 683, 541 cm^{-1}. HRMS: calcd. for $C_{36}H_{15}NO_4F_{13}S_2$ $[M - H]^-$ 836.0235; found 836.0247.

(*R*)-*N*-Fluoro-(1,1′-binaphthyl)-2,2′-disulfonimide (1a): $[\alpha]_D^{25}$ = –124 (*c* = 0.33, THF). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.34–8.25 (m, 4 H), 8.11 (d, *J* = 8.1 Hz, 2 H), 7.76 (t, *J* = 6.9 Hz, 2 H), 7.47 (t, *J* = 8.1 Hz, 2 H), 7.31–7.26 (m, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –39.00 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3079, 2923, 1581, 1389, 1376, 1189, 1106, 822, 750, 703, 664, 536 cm^{-1}. HRMS: calcd. for $C_{20}H_{11}NO_4FS_2$ $[M - H]^-$ 412.0114; found 412.0112.

Methyl 2-Fluoro-1-oxoindan-2-carboxylate (4a): A solution of **3a** (7.5 mg, 0.0394 mmol) in THF (0.4 mL) was added dropwise to a suspension of NaH (3.2 mg, 0.0788 mmol) in THF (0.4 mL) at –80 °C, and the mixture was stirred for 1 h. A solution of **1b** (33 mg, 0.0394 mmol) in THF (0.1 mL) was then added dropwise to the mixture. The resulting mixture was stirred overnight at –80 °C. The reaction was quenched by the addition of water, and the reaction mixture was extracted with ethyl acetate. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) to give (–)-**4a** (3.9 mg, 0.0189 mmol, 48%, 86%*ee*).

Compound (–)-**4a** was obtained from **1b** under the same conditions, yield 3.9 mg, 0.0189 mmol, 48%, 86%*ee*. $[\alpha]_D^{25}$ = –16.4 (*c* = 0.13, $CHCl_3$) [(–)-**4a**, 86%*ee*]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.8 Hz, 1 H), 7.72 (t, *J* = 7.5 Hz, 1 H), 7.52–7.45 (m, 2 H), 3.81 (dd, *J* = 11.7, 18.0 Hz, 1 H), 3.80 (s, 3 H), 3.45 (dd, *J* = 18.0, 23.1 Hz, 1 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –165.04 (dd, *J* = 11.7, 23.1 Hz) ppm. MS (APCI): *m*/*z* = 226 $[M + H]^+$. HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH = 99:1, flow = 0.5 mL min^{-1}, λ = 254 nm): t_R = 30.3 (minor), 33.2 (major) min.

Compound (+)-**4a** was obtained from **1a** under the same conditions, yield 2.3 mg, 0.011 mmol, 28%, 17%*ee*. $[\alpha]_D^{25}$ = +3.44 (*c* = 0.077, $CHCl_3$) [(+)-**4a**, 17%*ee*]. HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH = 99:1, flow = 0.5 mL min^{-1}, λ = 254 nm): t_R = 36.8 (major), 38.8 (minor) min.

(*R*)-*tert*-Butyl 2-Fluoro-1-oxoindan-2-carboxylate (4b): A solution of **3b** (9.2 mg, 0.0394 mmol) in THF (0.4 mL) was added dropwise to a suspension of NaH (3.2 mg, 0.0788 mmol) in THF (0.4 mL) at –80 °C, and the mixture was stirred for 1 h. A solution of **1b** (33 mg, 0.0394 mmol) in THF (0.1 mL) was then added dropwise to the mixture. The resulting mixture was stirred overnight at –80 °C. The reaction was quenched by the addition of water, and the reaction mixture was extracted with ethyl acetate. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) to give **4b** (6.2 mg, 0.0248 mmol, 63%, 76%*ee*). $[\alpha]_D^{25}$ = +1.17 (*c* = 0.21, $CHCl_3$) [(*R*)-**4b**, 76%*ee*]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.1 Hz, 1 H), 7.69 (t, *J* = 7.5 Hz, 1 H), 7.51–7.43 (m, 2 H), 3.73 (dd, *J* = 10.9, 17.7 Hz, 1 H), 3.40 (dd, *J* = 17.7, 22.8 Hz, 1 H), 1.44 (s, 9 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –164.51 (dd, *J* = 10.9, 22.8 Hz) ppm. MS (APCI): *m*/*z* = 268 $[M + NH_4]^+$. HPLC (Chiralpak AD-3, *n*-hexane/*i*PrOH = 99:1, flow = 0.5 mL min^{-1}, λ = 254 nm): t_R = 27.4 (minor), 31.8 (major) min. The absolute configuration of **4b** corresponded to that given in ref.[6b] {ref.[6b] $[\alpha]_D^{24}$ = –3.93 (*c* = 0.41, $CHCl_3$) [(*S*)-**2a**, 99%*ee*]}.

Methyl 2-Fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-carboxylate (4c): A solution of **3c** (8.0 mg, 0.0394 mmol) in THF (0.4 mL) was added dropwise to a suspension of NaH (3.2 mg, 0.0788 mmol) in THF (0.4 mL) at –80 °C, and the mixture was stirred for 1 h. A solution of **1b** (33 mg, 0.0394 mmol) in THF (0.1 mL) was added dropwise to the mixture. The resulting mixture was stirred overnight at –80 °C. The reaction was quenched by the addition of water, and the reaction mixture was extracted with ethyl acetate. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) to give (–)-**4c** (2.7 mg, 0.0122 mmol, 31%, 54%*ee*). $[\alpha]_D^{25}$ = –2.56 (*c* = 0.090, $CHCl_3$) [(–)-**4c**, 54%*ee*]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.8 Hz, 1 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.40–7.28 (m, 2 H), 3.84 (s, 3 H), 3.23–3.05 (m, 2 H), 2.78–2.66 (m, 1 H), 2.62–2.54 (m, 1 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –164.68 (dd, *J* = 11.8, 22.3 Hz) ppm. MS (APCI): *m*/*z* = 223 $[M + H]^+$. HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH = 90:10, flow = 1.0 mL min^{-1}, λ = 254 nm): t_R = 14.2 (major), 15.2 (minor) min.

(*S*)-*N*-*tert*-Butoxycarbonyl-3-(5-chloro-2-methoxyphenyl)-3-fluoro-6-trifluoromethyl-2-oxindole (6): A mixture of **1b** (16.8 mg, 0.02 mmol) and CsOH monohydrate (18.0 mg, 0.12 mmol) in CH_3CN/CH_2Cl_2 (3:4, 0.3 mL) was stirred under a nitrogen atmosphere at –80 °C for 30 min. A solution of **5** (8.8 mg, 0.02 mmol) in CH_3CN/CH_2Cl_2 (3:4, 0.1 mL) was added to the mixture. The reaction mixture was stirred for 2 d with monitoring by TLC, and the reaction was stopped by the addition of water. The reaction mixture was then diluted with ethyl acetate; washed with 2 N HCl, saturated aqueous sodium hydrogen carbonate solution, and brine; and dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 8:2) to give **6** (4.7 mg, 0.0102 mmol, 51%, 57%*ee*). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (s, 1 H), 7.79 (s, 1 H), 7.43–7.28 (m, 3 H), 6.76 (d, *J* = 9.0 Hz, 1 H), 3.54 (s, 3 H), 1.67 (s, 9 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –63.33 (s), –154.08 (s) ppm. MS (APCI): *m*/*z* = 479 $[M + NH_4]^+$. HPLC (Chiralcel OD-Hx2, *n*-hexane/*i*PrOH = 98:2, 0.5 mL/min, 254 nm) t_R (major-isomer) = 23.6 min, t_R (minor-isomer) = 30.0 min. The absolute configuration of **6** was corresponded the reference 6b. Lit.[6b] HPLC: (Chiralcel OD-Hx2, *n*-hexane/*i*PrOH = 98:2, flow = 0.5 mL min^{-1}, λ = 254 nm): t_R = 21.8 [(*S*)-(+)-isomer], 28.3 [(*R*)-(–)-isomer] min.

***N*-(2-Fluoro-2,3-dihydro-1*H*-inden-1-yl)-*N*-(*S*)-3,3′-bis[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl-2,2′-disulfonimide (8b):** In a dried Schlenk tube, palladium acetate (1.2 mg, 0.00515 mmol), bathocuproine (2.8 mg, 0.00772 mmol), and **1b** (35.9 mg, 0.0429 mmol) were dissolved in 1,4-dioxane (0.1 mL, degassed with argon) under an argon atmosphere, and then indene (2.0 μL, 0.0172 mmol) was added. The reaction mixture was stirred at 50 °C for 10 h. The reaction mixture was concentrated under reduced pressure and purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 9:1–1:1) to give **8b** (12.4 mg, 0.0131 mmol, *trans*-**8b** and *cis*-**8b** could not be separated, and the spectrum of the mixture of isomers is listed below). $[\alpha]_D^{25}$ = +2.55 (*c* = 0.41, THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–6.72 (m, 20 H), 5.90–5.73 (m, 0.8 H), 5.68–5.51 (m, 0.35 H), 5.31–5.14 (m, 0.6 H), 5.02–4.82 (m, 0.15 H), 4.60–4.46 (m, 0.15 H), 4.21 (dq, *J* = 1.6, 7.2 Hz, 0.6 H), 3.76 (s, 0.1 H), 3.68–3.54 (m, 0.3 H), 3.47 (t, *J* = 7.6 Hz, 0.2 H), (dt, *J* = 7.6, 19.0 Hz, 0.45 H), 3.19–3.14 (m, 0.2 H), 3.01–2.77 (m, 1 H), 2.56 (d, *J* = 6.0 Hz, 0.1 H), 2.47 (t, *J* = 7.6 Hz, 0.15 H), 2.38–2.28 (m, 0.3 H), 2.19–2.08 (m, 0.15 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.77, 140.47, 136.56, 134.27, 132.19, 130.85, 129.45, 129.40, 129.18, 128.81, 128.63, 127.39, 127.10, 125.22, 125.18, 124.31, 123.68, 122.49, 122.44, 121.99, 121.94, 98.21, 97.62, 69.75, 68.33, 49.63 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –63.14 (m), –170.47 (m), –175.88 (m), –185.63 (m) ppm. IR (KBr): $\tilde{\nu}$ = 1372, 1280, 1177, 1137, 846, 755, 707, 683, 656, 574 cm^{-1}. HRMS: calcd. for $C_{45}H_{24}NO_4F_{13}NaS_2$ $[M + Na]^+$ 976.0837 found 976.0834.

***N*-(2-Fluoro-2,3-dihydro-1*H*-inden-1-yl)-*N*-(*R*)-(1,1′-binaphthyl)-2,2′-disulfonimide (8a):** Same conditions with **1a** (15.2 mg, 0.0368 mmol) to give **8a** (6.0 mg, 0.0113 mmol, 77%, *trans*-**8a** and *cis*-**8a** could not be separated, and the spectrum of the mixture of isomers is listed below). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.27 (s, 1.40 H), 8.17–8.16 (m, 0.80 H), 8.08–8.06 (m, 1.75 H), 7.71–7.68 (m, 1.50 H), 7.48–7.41 (m, 2.55 H), 7.39–7.28 (m, 2.20 H), 7.27–7.19 (m, 1.35 H), 7.13–7.10 (m, 0.4 H), 7.00–6.99 (m, 0.50 H), 6.30–6.14 (m, 0.85 H), 5.88–5.75 (m, 0.70 H), 5.60–5.41 (m, 0.17 H), 5.37–5.27 (m, 0.18 H), 3.81–3.68 (m, 0.85 H), 3.56–3.48 (m, 0.20 H), 3.43–3.30 (m, 0.25 H), 3.24–3.06 (m, 1.00 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –171.02 (m), –171.94 (m), –183.05 (m), –184.12 (m) ppm. HRMS: calcd. for $C_{29}H_{20}NO_4FNaS_2$ $[M + Na]^+$ 552.0715 found 552.0714.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H, ^{19}F, ^{13}C NMR spectra and HPLC analysis.

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