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Chiral Sulfonimide as a Brønsted Acid Organocatalyst for Asymmetric Friedel−Crafts Alkylation of Indoles with Imines

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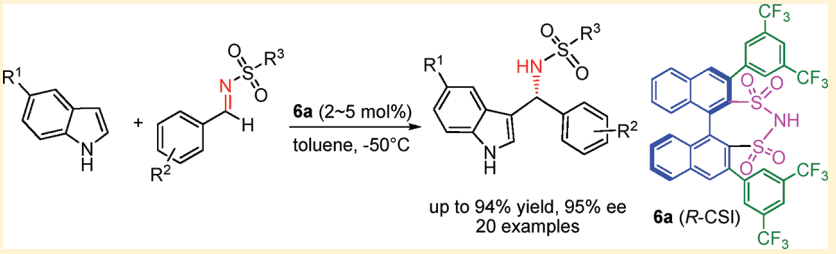
Supporting Information

ABSTRACT:



Binaphthyl-based chiral sulfonimide (CSI) is demonstrated for the first time to be an efficient, strong Brønsted acid in asymmetric organocatalysis. A series of CSIs were synthesized and screened in the asymmetric Friedel−Crafts alkylation of indoles with imines. Good to excellent yields and enantioselectivities have been achieved. It was proved that it was crucial to wash the CSI catalyst with HCl before use.

INTRODUCTION

Asymmetric organocatalysis, the use of small chiral organic molecules to catalyze enantioselective transformations, has captured the imagination of chemists around the world in recent years.[1] It has complemented the organometallic and enzymatic approaches to asymmetric catalysis in the construction of chiral molecules and molecular scaffolds.[2] Among various types of organocatalysts, many believe Brønsted acid catalysts have the potential to match up with the reactivities and selectivities provided by metal−chiral ligand type asymmetric catalysts.[3]

In comparison with other types of organocatalysts, the structural variations of strong Brønsted acid organocatalysts are relatively limited. For example, hundreds of Lewis base catalysts derived from primary or secondary amines are known.[1a,b] Hydrazine has also been recently explored by us and others as a new functionality for Lewis base organocatalysis.[4] In contrast, most widely used strong Brønsted acid catalysts are still the BINOL-derived chiral phosphoric acids (**1**) discovered independently by Akiyama[5] and Terada[6] in 2004 or the more acidic *N*-triflyl phosphoramides (**2**) developed by Yamamoto.[7] In addition, chiral binaphthyl disulfonic acids have also been used as Brønsted acid catalysts in organocatalysis by Ishihara.[8] In this paper, we report, for the first time, that chiral sulfonimide[9] (CSI) is an effective Brønsted acid scaffold for organocatalysis.

RESULTS AND DISCUSSION

Our idea on developing chiral sulfonimides as strong Brønsted acid organocatalysts was inspired by the reports of Barbero that *o*-benzenedisulfonimide (**3**) is a strong Brønsted acid for various acid-catalyzed transformations.[10] It has been reported that the pK_a value of **3** in water is −4.1,[10b] and those for the corresponding aliphatic cyclic sulfonimides **4** and **5** are −3.1 and −1.7, respectively.[11] We envision that a chiral version of **3** could be an effective Brønsted acid for asymmetric organocatalysis, and binaphthyl was selected as the chiral backbone in the design of the chiral sulfonimide (CSI **6**). It is also worth noting that binaphthyl sulfonimide has a C_2-symmetric topology, while the corresponding BINOL-derived chiral phosphoric acid is only pseudo-C_2-symmetric.

The synthesis of **6** was first reported by List[12] and Giernoth.[13] Giernoth only reported the preparation of the parent compound with no substituents at the 3,3′-positions. List and co-workers elegantly demonstrated the use of **6a** as an organocatalyst in Mukaiyama aldol reactions of ketene silyl acetals with aldehydes.[12] Nevertheless, the actual catalyst is not Brønsted acid **6a**. It is the in situ generated silyated sulfonimine **8**, which acts as a Lewis acidic catalyst. Recently, we also reported our synthetic approach of CSI **6**.[14]

Our synthesis of 3,3′-substituted chiral sulfonamides is slightly different from that of List and is more convergent. In the List's synthesis of **6**, the 3,3′-diaryl substitutents are already in place in the starting BINOL. In our approach (Scheme 1), we made use of the sulfonyl groups at 2,2′-positions as the directing groups for functionalization of the 3,3′-positions via ortho lithiation (**7a** to **7b**) followed by bromination or iodination.[14] The resulting

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Scheme 1. Phosphoric and Sulfonimidic Brønsted Acidic Organocatalysts

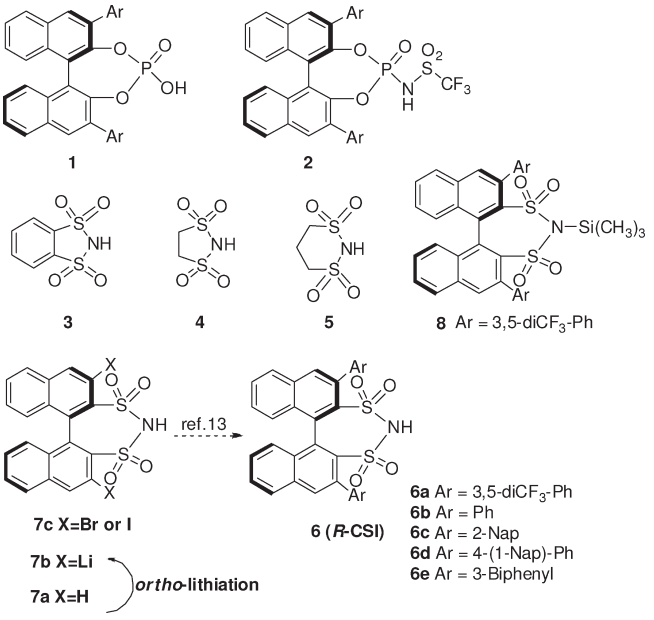
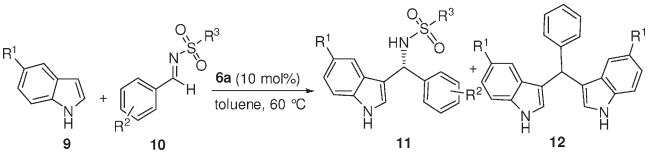


Table 1. Initial Studies on Unwashed-CSI-Catalyzed Asymmetric Friedel–Crafts Alkylation of Indoles with Imines



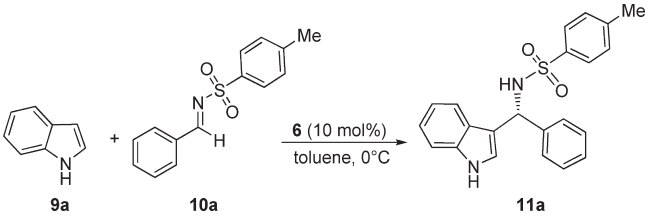
entry[a]	R^1	**10** R^2/R^3	t (h)	yield of **11** (%)[b]	ee (%)[c]
1	H	H/4-MePh (**10a**)	7	84	76
2	H	H/Ph	10	74	76
3	H	H/4-BrPh	8	74	76
4	H	H/2-Nap	3	90	76
5	Me	4-MeO/4-MePh	1	46	53
6	H	4-Br/4-MePh	3	66	77
7	Br	H/4-MePh	9	55	70
8	MeO	H/4-MePh	3	77	81
9	Me	H/4-MePh	6	87	83

[a] Reaction conditions: **10** (0.1 mmol), **9a** (3.0 equiv), **6a** (10 mol %), toluene (0.4 mL), 60 °C. [b] The yield was determined after flash chromatography. [c] Determined by HPLC analysis using a Chiralcel OD column.

dihalogenated **7c** could serve as the common precursor for a series of 3,3′-diaryl-substituted CSIs via coupling reactions.

C_2-symmetric BINOL-derived chiral sulfonimide is a new scaffold for organocatalysis. List has demonstrated that in situ generated silyated sulfonimine **8** is a Lewis acidic organocatalyst. More recently, a proline-attached CSI was used as a Lewis base in the Michael addition of ketone and aldehyde to nitroalkenes.[15] However, to the best of our knowledge, there has been no report of using chiral sulfonimide (CSI) as a Brønsted acid in organocatalysis. In this paper, we demonstrate that CSIs are effective

Table 2. HCl-Washed CSIs in Enantioselective Friedel–Crafts Alkylation of Indole with Imine



entry[a]	cat.[b]	t	yield (%)[c]	ee (%)[d]
1	**6a**	5 min	88	77
2	**6b**	2 h	77	46
3	**6c**	1 h	80	65
4	**6d**	30 min	84	75
5	**6e**	1 h	84	72

[a] Reaction conditions: **10a** (0.1 mmol), **9a** (3.0 equiv), **6** (10 mol %), toluene (1.0 mL), 0 °C. [b] Catalysts **6a–e** were washed with 1 M HCl before use. [c] Yield of product **11a** isolated after flash chromatography. [d] Determined by HPLC analysis using a Chiralcel OD column.

Brønsted acids in the asymmetric Friedel–Crafts alkylation of indoles with imines.

The asymmetric Friedel–Crafts alkylation reaction of indoles with imines is an important method for the preparation of optically active 3-substituted indole derivatives.[3d,16] The resulting chiral 3-indolyl methanamine motif is embedded in numerous biologically active indole alkaloids and synthetic indole derivatives.[17] The first BINOL-derived chiral phosphoric acid catalyzed enantioselective Friedel–Crafts alkylation reaction of indoles with imines was reported by You.[18] Recently, the use of SPINOL-derived chiral phosphoric acids in the same reaction system has also been reported.[19]

Our investigations started with the examination of the reaction between indole **9a** and imine **10a** in the presence of 10 mol % of CSI **6a** in toluene. We were disappointed that the reaction proceeded very slowly at room temperature. Only when the temperature was raised to 60 °C could the reaction proceed smoothly in reasonable conversion with moderate ee, along with a significant amount of the bis-indole product **12**[20] (14% yield, Table 1, entry 1). These discouraging initial results are summarized in Table 1. The best ee was up to 83%, achieved by 5-methylindole with imine **10a** (Table 1, entry 9).

It has been pointed out by Ishihara that BINOL-derived phosphoric acids are readily neutralized to adventitious metal salts such as alkali- and alkaline-earth-metal salts during purification on silica gel and warned that such impurities might have a substantial influence on the catalyst's performance.[21] Ding also reported that phosphoric acid washed with HCl improved the catalytic activity in the Baeyer–Villiger reaction.[22] Recently, List reported a detailed analysis of the phosphate salt impurities of a chiral BINOL phosphoric acid and confirmed that it is easily contaminated during synthesis and silica gel column chromatography.[23] We speculated that similar contamination could happen with our CSI catalysts and decided to wash the sulfonimide catalysts with dilute HCl (followed by water and brine) before use.

To our delight, the acid-washed CSI was much more reactive. Using 10 mol % of HCl-washed CSI **6a**, the reaction was completed at 0 °C *within 5 min* with a high yield of the desired

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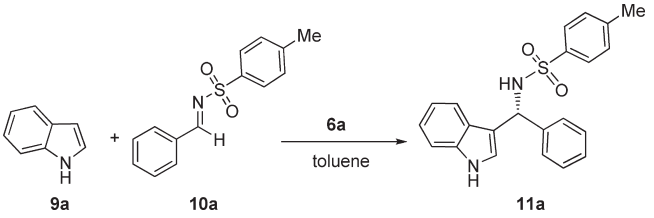
Table 3. Optimization of Reaction Conditions



entry[a]	amt of **6a** (mol %)	T (°C)	t	yield (%)[b]	ee (%)[c]
1	10	0	5 min	88	77
2	10	−40	10 min	90	89
3	10	−50	50 min	82	92
4	10	−60	3 h	86	93
5	10	−78	5 h	70	93
6	5	−50	1.5 h	90	93
7	2	−50	5 h	64	93

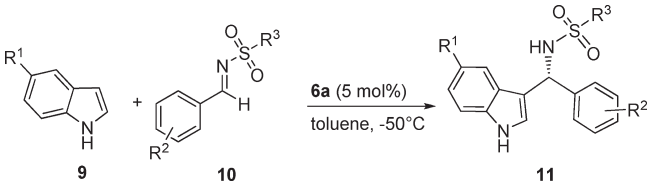
[a] Reaction conditions: **10a** (0.1 mmol), **9a** (3.0 equiv), toluene (1.0 mL). [b] Yield of product isolated after flash chromatography. [c] Determined by HPLC analysis using a Chiralcel OD column.

product and no contamination of the byproduct **12** (Table 2, entry 1). Under the same conditions, we screened several HCl-washed CSI catalysts with different Ar groups at the 3- and 3′-positions of the binaphthyl scaffold. From the results given in Table 2, the best-performing catalyst with regard to reactivity, yield, and stereoselectivity was **6a**. Notably, CSI **6d** had similar performance but the reactivity was slightly lower (30 min vs 5 min, Table 2, entries 4 and 1).

We then investigated the effect of the reaction temperature and catalyst loading using CSI **6a**. The results are summarized in Table 3. In general, lower reaction temperatures decreased the reaction rate with enhanced enantioselectivity. At −40 °C, the reaction was still relatively fast (10 min, Table 3, entry 2) and the ee increased to 89%. At −50 °C, the reaction could be completed in 50 min with an increase in ee to 92% (Table 3, entry 3). Lowering the reaction temperature to −78 °C only marginally increased the enantioselectivity, but the reaction time was greatly lengthened (Table 3, entries 4 and 5). By lowering the catalyst loading to 5% or 2%, the same level of enantioselectivity could be maintained but the reaction rate was decreased (Table 3, entries 6 and 7). Therefore, we concluded that −50 °C and 5 mol % of **6a** were the optimized conditions. In addition to toluene, we also tested other solvents such as THF, TBME, DCM, and MeCN. However, they all resulted in a significant drop of both the reaction rate and enantioselectivity.

A wide range of substituted indoles and imines have been tested under the optimized conditions. The scope of the substrates is summarized in Table 4. Several substituted indoles, containing either electron-donating groups or electron-withdrawing groups, have been examined. The enantioselectivities were found to be sensitive to the electronic property of the indole rings. 5-Methylindole has the best performance, with an ee value up to 95% (Table 4, entry 2). When 5-methoxyindole was used, the reaction proceeded very quickly and gave 93% ee with 94% yield in 1 h (Table 4, entry 3). Even with 2 mol % of catalyst, good enantioselectivity and yield could be maintained, though a slightly longer reaction time was needed (Table 4, entry 4). However, the introduction of an electron-withdrawing group onto the indole ring led to a decrease in enantioselectivity (5-Br, Table 4, entry 5).

Table 4. CSI-Catalyzed Enantioselective Friedel−Crafts Alkylation of Indoles with *N*-Sulfonyl Imines[a]



Entry	R^1	**10** R^2 / R^3	t (h)	Product **11**	Yield(%)[b]	ee (%)[c]
1	H	H/4-MePh	1.5	**11a**	90	93
2	Me	H/4-MePh	2.5	**11b**	88	95
3	MeO	H/4-MePh	1	**11c**	94	93
4[d]	MeO	H/4-MePh	3.5	**11c**	95	93
5	Br	H/4-MePh	2	**11d**	87	88
6	H	H/4-BrPh	3	**11e**	60	90
7	H	H/Ph	2.5	**11f**	93	90
8	H	H/2-Nap	2.5	**11g**	83	90
9	H	4-Br/4-MePh	1.5	**11h**	60	88 (*R*)[e]
10	H	4-Me/4-MePh	2.5	**11i**	87	92
11	H	3-Cl/4-MePh	2	**11j**	83	92
12	H	2-Br/4-MePh	4	**11k**	65	87
13	H	4-Cl/4-MePh	4	**11l**	65	93
14	H	3-OMe/4-MePh	2.5	**11m**	91	87
15	H	4-OMe/4-MePh	2.5	**11n**	88	84
16[f]	H		1	**11o**	90	40
17	H		1	**11p**	44	10
18	Me	4-Cl/4-MePh	4	**11q**	71	90
19	Me	4-Me/4-MePh	2	**11r**	81	94
20	MeO	4-Me/4-MePh	1	**11s**	83	93

[a] Unless otherwise noted, all reactions were carried out using **6a** (5 mol %), **10** (0.1 mmol), and **9** (3.0 equiv) in toluene (1.0 mL) at −50 °C. [b] Yield of product isolated after flash chromatography. [c] Determined by HPLC analysis using a Chiralcel OD column. [d] Using 2 mol % **6a**. [e] The absolute configuration was determined by comparison of the optical rotation with the known compounds in the literature.[18,20] [f] Reaction at −78 °C.

When the sulfonyl group in **10** was changed from 4-methylphenyl to other sulfonyl groups such as phenyl, 4-bromophenyl, and 2-naphthyl, the enantioselectivities were slightly decreased (Table 4, entries 1 and 6−8).

N-4-Methylphenyl sulfonyl arylimines with various R^2 groups reacted smoothly to afford the corresponding products in good to excellent yields and enantioselectivities. The enantioselectivities were not very sensitive to the electronic properties of the arylimines. An electron-withdrawing group such as Cl at the 3- or 4-position gave a slightly higher ee value than an electron-donating group such as MeO (Table 4, entries 11, 13 and 14, 15). The bromo-substituted arylimine reacted much more slowly with decreased enantioselectivity because of poor solubility (Table 4, entry 12). In addition, the enantioselectivities for furylimine and alkylimine were poor (Table 4, entries 16 and 17).

On the basis of the transition state models of BINOL-phosphoric acids[24] and the L-proline-based binaphthyl sulfonimides,[15]

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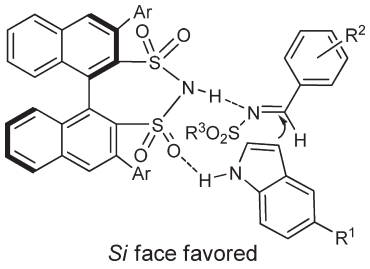

Figure 1. Plausible transition state.

we propose a plausible transition state model as depicted in Figure 1. As a strong Brønsted acid, CSI is assumed to link the two substrates together by hydrogen bonds, leading to an efficient attack from the *Si* face of the imine transition state and thus giving *R* configuration products.

CONCLUSIONS

In conclusion, we have demonstrated for the first time that chiral sulfonimides (CSIs) are effective Brønsted acids for organocatalysis: in particular, the enantioselective Friedel–Crafts alkylation of indoles with imines. Considering the reaction time, catalyst loadings, and enantioselectives, CSIs exhibited excellent activities comparable to those of phosphoric acids. Together with the results of the List group, our results have shown that CSIs are effective Lewis and Brønsted acids in organocatalysis. Further explorations of this new chiral sulfonimide scaffold in other asymmetric transformations are in progress.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, solvents and starting materials were obtained from commercial suppliers. All chemicals used were of reagent grade, without further purification before use. ^{1}H NMR and ^{13}C NMR spectra were recorded (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ or acetone-d_6. Chemical shifts were recorded in ppm (δ) relative to $CHCl_3$ at 7.26 or to TMS at 0.00 for ^{1}H NMR and 77.0 for ^{13}C NMR or to acetone at 2.05 for ^{1}H NMR and 29.8 for ^{13}C NMR. Melting points were determined with a melting point apparatus and are reported in degrees Celsius (uncorrected). Optical rotations were taken on a digital polarimeter. Enantiomeric excesses of compounds were determined by HPLC using a Daicel Chiralpak OD (0.46 cm × 25 cm) column with OD guard (UV detection monitored at 254 nm). High-resolution mass spectra (HRMS) were recorded on a MALDI-TOF MS instrument. Organocatalysts **6a**–**e** were prepared according to the procedure[13] we reported recently.

General Procedure for CSI-Catalyzed Friedel–Crafts Alkylation of Indoles with Imines. To a solution of *N*-sulfonyl imine (0.1 mmol) in 1.0 mL of dry toluene in a Schlenk tube under N_2 was added CSI ((*R*)-**6a**, 0.005 mmol). The solution was stirred at −50 °C for 15 min, and indole (0.3 mmol) was added in one portion. The reaction mixture was kept stirring at −50 °C until consumption of the *N*-sulfonyl imine. After the reaction was complete, the mixture was purified by flash column chromatography with petroleum ether/ethyl acetate (3/1, v/v) as eluent to afford the product.

11a: white solid, 90% yield, 93% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 10.138 min (major), $T_R(2)$ = 15.717 min (minor)); mp 162.5–163.5 °C; $[\alpha]_D^{22}$ = +12.5° (*c* 1.35, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (br, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.24–7.15 (m, 7H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.02–6.98 (m, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 5.85 (d, *J* = 6.8 Hz, 1H), 5.05 (d, *J* = 6.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.2, 137.4, 136.5, 129.2, 128.3, 127.3, 127.2, 127.1, 125.3, 123.8, 122.5, 119.9, 119.2, 116.3, 111.2, 55.0, 21.4; HRMS (MALDI-TOF) $C_{22}H_{20}N_2NaO_2S$ $(M + Na)^+$ *m*/*z* calcd 399.1138, found 399.1125.

11b: white solid, 88% yield, 95% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 8.944 min (major), $T_R(2)$ = 19.030 min (minor)); mp 159–160 °C; $[\alpha]_D^{21}$ = +21.0° (*c* 0.91, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (br, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.28–7.20 (m, 5H), 7.15 (t, *J* = 8.6 Hz, 3H), 6.97 (dd, J_1 = 1.2 Hz, J_2 = 8.3 Hz, 1H), 6.85 (d, *J* = 0.6 Hz, 1H), 6.53 (d, *J* = 2.3 Hz, 1H), 5.78 (d, *J* = 6.4 Hz, 1H), 5.07 (d, *J* = 6.4 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.4, 137.3, 134.7, 129.3, 129.2, 128.2, 127.3, 127.2, 127.1, 125.5, 124.2, 124.1, 118.5, 115.8, 110.9, 54.8, 21.5, 21.3; HRMS (MALDI-TOF) $C_{23}H_{21}N_2O_2S$ $(M - H)^-$ *m*/*z* calcd 389.1329, found 389.1347.

11c: white solid, 94% yield, 93% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 8.842 min (major), $T_R(2)$ = 25.673 min (minor)); mp 142–143 °C; $[\alpha]_D^{22}$ = +38.4° (*c* 0.62, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (br, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.24–7.16 (m, 6H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.82 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 5.82 (d, *J* = 7.0 Hz, 1H), 5.17 (d, *J* = 7 Hz, 1H), 3.72 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 139.2, 135.1, 131.8, 128.6, 128.5, 127.9, 127.4, 127.1, 127.0, 125.6, 125.1, 121.7, 115.5, 113.5, 112.8, 55.0; HRMS (MALDI-TOF) $C_{23}H_{21}N_2O_3S$ $(M - H)^-$ calcd *m*/*z* 405.1278, found 405.1290.

11d: white solid, 87% yield, 88% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 8.142 min (major), $T_R(2)$ = 15.051 min (minor)); mp 184–185 °C; $[\alpha]_D^{22}$ = +21.4° (*c* 0.74, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (br, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.26–7.20 (m, 5H), 7.17–7.11 (m, 5H), 6.71 (d, *J* = 2.3 Hz, 1H), 5.72 (d, *J* = 6.4 Hz, 1H), 5.08 (d, *J* = 6.4 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.1, 137.0, 135.1, 129.5, 128.5, 127.6, 127.1, 127.0, 125.4, 125.2, 121.5, 116.1, 113.3, 112.7, 54.6, 21.6; HRMS (MALDI-TOF) $C_{22}H_{19}BrN_2NaO_2S$ $(M + Na)^+$ *m*/*z* calcd 479.0224, found 479.0241.

11e: white solid, 60% yield, 90% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 11.084 min (major), $T_R(2)$ = 21.859 min (minor)); mp 133–135 °C; $[\alpha]_D^{20}$ = +75.6° (*c* 1.0, acetone); ^{1}H NMR (400 MHz, acetone-d_6) δ 10.13 (br, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.47–7.42 (m, 3H), 7.38–7.34 (m, 4H), 7.20 (d, *J* = 5.6 Hz, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 5.95 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 142.1, 142.0, 137.9, 132.3, 129.5, 128.9, 128.2, 127.8, 126.7, 126.6, 124.9, 122.5, 120.1, 119.8, 116.5, 112.2, 56.0; HRMS (MALDI-TOF) $C_{21}H_{17}BrN_2NaO_2S$ $(M + Na)^+$ *m*/*z* calcd 465.0067, found 465.0070.

11f: white solid, 93% yield, 90% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 10.564 min (major), $T_R(2)$ = 15.734 min (minor)); mp 130–132 °C; $[\alpha]_D^{22}$ = +16.5° (*c* 1.50, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.29–7.23 (m, 4H), 7.19–7.12 (m, 6H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 2.1 Hz, 1H), 5.86 (d, *J* = 7.2 Hz, 1H), 5.34 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 140.0, 136.5, 132.2, 128.6, 128.3, 127.4, 127.1, 127.0, 125.3, 123.8, 122.4, 119.9, 119.2, 116.1, 111.3, 55.0; HRMS (MALDI-TOF) $C_{21}H_{18}N_2O_2S$ (M^+) *m*/*z* calcd 362.1084, found 362.1072.

11g: white solid, 83% yield, 90% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 12.716 min (major), $T_R(2)$ = 21.536 min (minor)); mp 179−180 °C; $[\alpha]_D^{21}$ = −8.5° (*c* 0.70, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (br, 1H), 7.94−7.89 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78−7.72 (m, 2H), 7.63−7.53 (m, 3H), 7.27−7.21 (m, 3H), 7.14−7.06 (m, 4H), 6.95−6.92 (m, 1H), 6.86 (s, 1H), 6.63 (d, *J* = 2.1 Hz, 1H), 5.93 (d, *J* = 7.0 Hz, 1H), 5.24 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 137.2, 136.5, 134.6, 131.9, 129.2, 128.9, 128.6, 128.5, 128.3, 127.7, 127.5, 127.2, 127.1, 125.3, 123.8, 122.6, 122.4, 120.0, 119.3, 116.1, 111.2, 55.2; HRMS (MALDI-TOF) $C_{25}H_{20}KN_2O_2S$ $(M + K)^+$ *m*/*z* calcd 451.0877, found 451.0860.

11h: white solid, 60% yield, 88% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 11.729 min (major), $T_R(2)$ = 18.329 min (minor)); mp 185−187 °C; $[\alpha]_D^{25}$ = +19.8° (*c* 1.03, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br, 1H), 7.55 (d, *J* = 15.6 Hz, 2H), 7.32−7.29 (m, 3H), 7.22−7.17 (m, 2H), 7.16−7.10 (m, 4H), 7.03−6.99 (m, 1H), 6.62 (d, *J* = 1.9 Hz, 1H), 5.78 (d, *J* = 6.8 Hz, 1H), 5.18 (d, *J* = 6.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 139.3, 137.2, 136.5, 131.3, 129.3, 128.9, 127.1, 125.1, 123.7, 122.7, 121.3, 120.1, 119.1, 115.7, 111.3, 54.4, 21.5; HRMS (MALDI-TOF) $C_{22}H_{19}BrNaN_2O_2S$ $(M + Na)^+$ *m*/*z* calcd 479.0224, found 479.0200.

11i: white solid, 87% yield, 92% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 9.760 min (major), $T_R(2)$ = 15.349 min (minor)); mp 164−165 °C; $[\alpha]_D^{22}$ = +12.3° (*c* 0.56, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (br, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, J_1 = 0.7 Hz, J_2 = 8.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.17 (dd, J_1 = 1.0 Hz, J_2 = 7.1 Hz, 1H), 7.11−7.14 (m, 4H), 7.02−6.97 (m, 3H), 6.74 (d, *J* = 2.5 Hz, 1H), 5.81 (d, *J* = 6.7 Hz, 1H), 4.96 (d, *J* = 6.7 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.6, 137.4, 137.1, 136.6, 129.2, 129.0, 127.2, 127.1, 125.4, 123.7, 122.5, 119.9, 119.4, 116.6, 111.2, 54.9, 21.4, 21.0; HRMS (MALDI-TOF) $C_{23}H_{22}NaN_2O_2S$ $(M + Na)^+$ *m*/*z* calcd 413.1294, found 413.1311.

11j: white solid, 83% yield, 92% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ = 254 nm, $T_R(1)$ = 11.971 min (major), $T_R(2)$ = 13.349 min (minor)); mp 155−157 °C; $[\alpha]_D^{22}$ = +14.9° (*c* 0.70, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (br, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.32−7.23 (m, 2H), 7.18−7.10 (m, 7H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 5.81 (d, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 142.3, 137.2, 136.5, 134.2, 129.6, 129.3, 127.5, 127.4, 127.1, 125.5, 125.2, 123.7, 122.7, 120.1, 119.1, 115.8, 111.4, 54.5, 21.4; HRMS (MALDI-TOF) $C_{22}H_{19}ClKN_2O_2S$ $(M + K)^+$ *m*/*z* calcd 449.0487, found 449.0474.

11k: white solid, 65% yield, 87% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.70 mL/min, λ 254 nm, $T_R(1)$ = 9.554 min (major), $T_R(2)$ = 17.904 min (minor)); mp 190−192 °C; $[\alpha]_D^{22}$ = +60° (*c* 0.74, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (br, 1H), 7.71 (d, *J* = 1.6 Hz, 2H), 7.55 (dd, J_1 = 1.6 Hz, J_2 = 7.7 Hz, 1H), 7.45 (dd, J_1 = 1.2 Hz, J_2 = 6.8 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.25−7.21 (m, 3H), 7.19−7.15 (m, 2H), 7.09 (td, J_1 = 1.7 Hz, J_2 = 7.8 Hz, 1H), 7.0 (td, J_1 = 0.9 Hz, J_2 = 7.2 Hz, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 6.18 (d, *J* = 5.7 Hz, 1H), 5.09 (d, *J* = 5.7 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.4, 136.8, 132.9, 129.5, 129.0, 128.8, 127.4, 127.3, 125.4, 124.1, 122.7, 118.9, 115.1, 111.3, 54.2, 21.5; HRMS (MALDI-TOF) $C_{22}H_{19}ClKN_2O_2S$ $(M + K)^+$ *m*/*z* calcd 494.9963, found 494.9948.

11l: white solid, 65% yield, 93% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 11.268 min (major), $T_R(2)$ = 17.290 min (minor)); mp 183−184 °C; $[\alpha]_D^{22}$ = +16.5° (*c* 1.0, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (br, 1H), 7.57 (d, *J* = 12.2 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.21−7.14 (m, 8H), 7.02 (t, *J* = 7.1 Hz, 1H), 6.64 (d, *J* = 2.4 Hz, 1H), 5.82 (d, *J* = 6.6 Hz, 1H), 5.04 (d, *J* = 6.6 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.8, 137.2, 136.5, 133.2, 129.4, 128.6, 128.4, 127.2, 125.1, 123.7, 122.8, 120.2, 119.1, 115.9, 111.3, 54.4, 21.5; HRMS (MALDI-TOF) $C_{22}H_{19}ClNaN_2O_2S$ $(M + Na)^+$ *m*/*z* calcd 433.0748, found 433.0722.

11m: white solid, 91% yield, 87% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 11.622 min (major), $T_R(2)$ = 15.989 min (minor)); mp 164−165 °C; $[\alpha]_D^{20}$ = +9.1° (*c* 0.77, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.30−7.26 (m, 2H), 7.18−7.10 (m, 4H), 7.02−6.98 (m, 1H), 6.74−6.69 (m, 3H), 5.82 (d, *J* = 6.8 Hz, 1H), 5.10 (d, *J* = 6.8 Hz, 1H), 3.68 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 143.0, 141.8, 137.4, 136.5, 129.3, 127.2, 125.3, 123.8, 122.5, 119.9, 119.6, 119.2, 116.2, 113.0, 112.6, 111.2, 55.1, 55.0, 20.5; HRMS (MALDI-TOF) $C_{23}H_{22}NaN_2O_3S$ $(M + Na)^+$ *m*/*z* calcd 429.1243, found 429.1267.

11n: white solid, 88% yield, 84% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 12.089 min (major), $T_R(2)$ = 20.999 min (minor)); mp 135−136 °C; $[\alpha]_D^{21}$ = −32.7° (*c* 0.50, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.16−7.21 (m, 1H), 7.14−7.12 (m, 5H), 6.99 (td, J_1 = 0.9 Hz, J_2 = 8.0 Hz, 1H), 6.75−6.71 (m, 3H), 5.79 (d, *J* = 6.7 Hz, 1H), 5.01 (d, *J* = 6.7 Hz, 1H), 3.77 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 142.9, 137.4, 136.6, 132.4, 129.2, 128.4, 127.2, 125.3, 123.7, 122.5, 119.9, 119.3, 116.6, 113.6, 111.2, 55.2, 54.6, 21.5; HRMS (MALDI-TOF) $C_{23}H_{22}KN_2O_3S$ $(M + K)^+$ *m*/*z* calcd 445.0983, found 445.0953.

11o: white solid, 90% yield, 40% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 9.426 min (major), $T_R(2)$ = 15.636 min (minor)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (br, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 6.6 Hz, 1H), 7.22 (q, *J* = 0.8 Hz, 1H), 7.17 (td, J_1 = 1.0 Hz, J_2 =7.2 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.04 (td, J_1 = 0.9 Hz, J_2 = 7.1 Hz, 1H), 6.92 (d, *J* = 2.2 Hz, 1H), 6.19 (q, *J* = 2.2 Hz, 1H), 6.09 (d, *J* = 3.2 Hz, 1H), 5.92 (d, *J* = 7.4 Hz, 1H), 5.19 (d, *J* = 7.4 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 142.9, 142.1, 137.3, 136.3, 129.2, 127.0, 125.2, 123.3, 122.5, 120.0, 119.3, 113.7, 111.2, 110.2, 107.7, 49.1, 21.4; HRMS (MALDI-TOF) $C_{20}H_{18}NaN_2O_3S$ $(M + Na)^+$ *m*/*z* calcd 389.0899, found 389.0899.

11p: white solid, 44% yield, 10% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ = 254 nm, $T_R(1)$ = 6.798 min (major), $T_R(2)$ = 9.043 min (minor)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (br, 1H), 7.40 (d, *J* = 8.2 Hz, 3H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.13 (td, J_1 = 0.9 Hz, J_2 = 7.1 Hz, 1H), 7.01 (td, J_1 = 1.0 Hz, J_2 = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 2.4 Hz, 1H), 4.86 (d, *J* = 7.9 Hz, 1H), 4.33 (d, *J* = 7.9 Hz, 1H), 2.24 (s, 3H), 2.05−1.73 (m, 3H), 1.46−1.15 (m, 4H), 1.12−0.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.4, 136.2, 129.7, 128.7, 126.8, 122.4, 122.1, 119.6, 119.2, 111.1, 57.3, 42.8, 30.0, 29.9, 26.2, 26.0, 21.5, 21.3.

11q: white solid, 94% yield, 90% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 9.289 min (major), $T_R(2)$ = 19.855 min (minor)); mp 184−185 °C; $[\alpha]_D^{22}$ = +11.5° (*c* 0.50, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.26−7.17 (m, 7H), 7.00−6.98 (m, 1H), 6.80 (s, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 5.74 (d, *J* = 6.1 Hz, 1H), 5.04 (d, *J* = 6.1 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.1, 137.2,

134.7, 133.1, 129.4, 128.6, 128.4, 127.2, 125.3, 124.3, 124.0, 118.3, 115.4, 110.0, 54.1, 21.5, 21.3; HRMS (MALDI-TOF) $C_{23}H_{21}ClNaN_2O_2S$ $(M + Na)^+$ m/z calcd 447.0904, found 447.0903.

11r: white solid, 81% yield, 94% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 8.503 min (major), $T_R(2)$ = 17.847 min (minor)); mp 155−156 °C; $[\alpha]_D^{21}$ = +28.9° (*c* 0.45, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.16−7.13 (m, 5H), 7.03 (d, J = 7.1 Hz, 2H), 6.97 (dd, J_1 = 1.3 Hz, J_2 = 8.3 Hz, 1H), 6.86 (d, J = 0.7 Hz, 1H), 6.56 (d, J = 1.9 Hz, 1H), 5.74 (d, J = 6.5 Hz, 1H), 5.10 (d, J = 6.5 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.5, 137.3, 136.9, 134.7, 129.2, 129.0, 128.9, 127.2, 127.0, 125.5, 124.1, 124.0, 118.5, 115.8, 110.9, 54.6, 21.4, 21.3, 21.0; HRMS (MALDI-TOF) $C_{24}H_{23}N_2O_2S$ $(M - H)^-$ m/z calcd 403.1486, found 403.1491.

11s: white solid, 95% yield, 93% ee (Daicel Chiralcel OD column guarded with Chiracel OD Guard column, *n*-hexane/*i*-PrOH 60/40, flow rate 0.75 mL/min, λ 254 nm, $T_R(1)$ = 8.889 min (major), $T_R(2)$ = 27.446 min (minor)); mp 170−171 °C; $[\alpha]_D^{22}$ = +20.7° (*c* 0.44, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (br, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.8 Hz, 1H), 7.12−7.09 (m, 4H), 7.01 (d, J = 8.0 Hz, 2H), 6.99 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 6.75 (d, J = 2.3 Hz, 1H), 6.64 (d, J = 2.4 Hz, 1H), 5.78 (d, J = 6.8 Hz, 1H), 5.06 (d, J = 6.8 Hz, 1H), 3.73 (s, 3H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 142.9, 137.5, 137.2, 137.0, 131.5, 129.2, 128.9, 127.1, 127.07, 125.8, 124.4, 116.2, 112.8, 111.9, 100.9, 55.7, 54.8, 21.4, 21.0; HRMS (MALDI-TOF) $C_{24}H_{24}NaN_2O_3S$ $(M + Na)^+$ m/z calcd 443.1400, found 443.1419.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Figures giving NMR spectra and HPLC chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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