Synthesis X. Gao et al. Special Topic

Chiral Iminophosphorane Organocatalyzed Asymmetric Sulfenylation of 3-Substituted Oxindoles: Substrate-Interrelated Enantioselectivities

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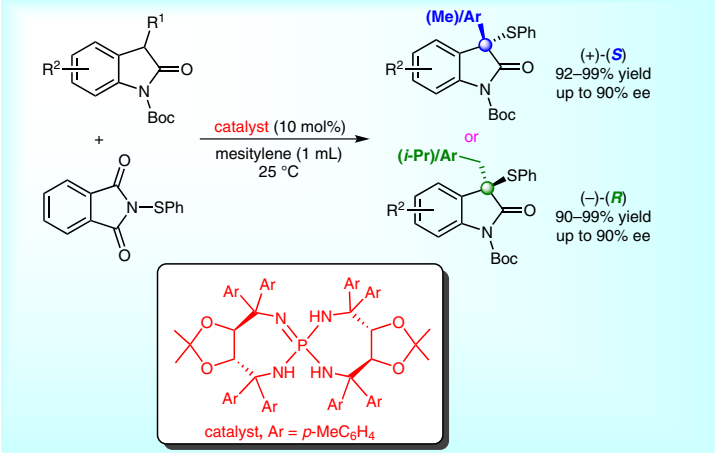
Dedicated to Prof. Dr. Dieter Enders on the occasion of his 70th birthday



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Abstract Catalytic asymmetric sulfenylation of 3-substituted oxindoles has been developed through efficient catalysis by tartaric acid derived chiral iminophosphoranes. With *N*-(phenylthio)phthalimide as the sulfur source, a wide range of optically active 3-phenylthiooxindoles were obtained in excellent yields (90–99%) and good enantiomeric excess (up to 90% ee). Interestingly, 3-aryl and 3-methyl substituted oxindoles afforded sulfenylated products in *S*-configuration, whereas substituted oxindoles with 3-arylidene or 3-isobutyl substituents gave the corresponding *R*-configured sulfenylated products.

Key words organocatalysis, phosphazene, iminophosphorane, sulfenylation, oxindole

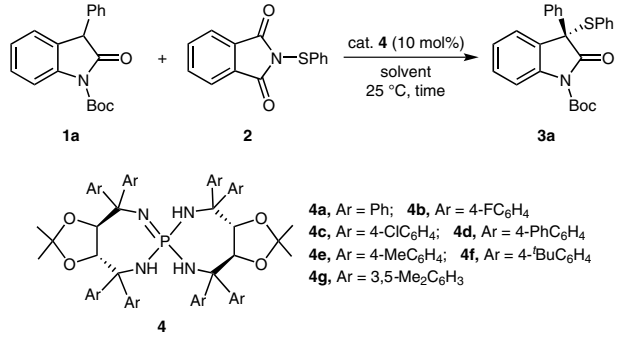
Oxindole derivatives have attracted much attention during the past decades because their core backbone is included in many biologically active natural and non-natural products.[1] Enantioselective synthesis of 3,3-disubstituted oxindoles has been explored intensively in the past, and various asymmetric synthetic methods have been established including organo- and transition-metal catalysis. As such, many excellent results were achieved with a variety of 3,3-disubstituted oxindoles. For example, 3-hydroxy-,[2] 3-amino-,[3] 3-fluoro-,[4] 3-chloro-,[5] and 3-thio-substituted[6] oxindoles were prepared in a catalytic manner. Importantly, it was reported that many oxindoles with a thio group at the carbon stereocenter at the 3-position have anticancer, antifungal, or antitubercular activities.[7]

Asymmetric sulfenylations employing either stoichiometric amounts of chiral agents or chiral auxiliaries have been reported since 1979,[8a] and there are a variety of strategies to achieve chiral thio-substituted compounds.[8] In recent years, several catalytic methods for the direct asymmetric sulfenylation of 3-substituted oxindoles have been developed and the desired products were obtained with both good yield and excellent enantioselectivities.[6] Feng reported catalytic asymmetric sulfenylation of unprotected 3-substituted oxindoles through cooperative catalysis of a chiral *N*,*N*′-dioxide-Sc(OTf)$_3$ complex in the presence of a Brønsted base and molecular sieves.[6a] Simultaneously, the groups of Enders, Cheng and Jiang reported organocatalytic sulfenylations of 3-substituted oxindoles independently with amino-squaramides, cinchona alkaloid or quinidines derivatives as catalysts.[6b,c,d] Soon after, Maruoka designed a family of chiral quaternary phosphonium bromides, which were applied in this reaction for evaluation of their catalytic ability as phase-transfer catalysts.[9] Very recently, the catalytic asymmetric sulfenylation of 3-pyrrolyl-oxindoles was achieved by Yuan et al. with cinchonidine as catalyst.[6e] Despite the significant advances that have been achieved in this field, further exploration of catalytic systems that can be used to deliver oxindoles bearing a 3-sulfenyl-substituted quaternary stereocenter with broad substrate scope remains necessary. We recently synthesized a class of chiral iminophosphoranes that was used as highly effective organocatalysts in the asymmetric chlorination of 3-substituted oxindoles.[5e] In this work, we exploited a similar strategy to catalyze asymmetric sulfenylation of oxindoles by using *N*-(phenylthio)phthalimide as the sulfenylating re-

agent. Interestingly, we found that stereocontrol based on changing the substituent in the substrates of 3-substituted oxindoles afforded the *S*- or *R*-configured sulfenylated products. Herein, we present details of these results.

Initially, we studied the sulfenylation of *N*-Boc-protected 3-phenyloxindole **1a** with *N*-(phenylthio)phthalimide (**2**) to optimize the reaction conditions and catalysts at room temperature (Table 1). Firstly, given the ready availability of iminophosphorane **4a**, we used this compound as catalyst to screen various solvents. Diethyl ether and ethyl acetate, which were found to be superior in our previous report of asymmetric chlorination,[5e] gave product **3a** in the sulfenylation in a comparable yield of 95% with the same enantiomeric excess of 46%. However, the reaction rate was much faster in ethyl acetate than in diethyl ether based on analysis by thin-layer chromatography (Table 1, entries 1 and 2). Further screening of the solvents showed that the use of chloroform and mesitylene led to a slight improvement in the ee to 53 and 57%, respectively (entries 7 and 11). Therefore, mesitylene was selected as solvent to investigate iminophosphorane catalysts **4b**–**g** in the model reaction, which was carried out at room temperature (entries 12–17). It was found that **4e** and **4f** were the most suitable catalysts in this reaction and that catalyst **4e** gave the best enantioselectivity (89% ee). Catalysts **4e** and **4f** feature alkyl substituents at the *para*-position of the aromatic motif within the iminophosphorane framework (entries 15 and 16). In contrast to **4e** and **4f**, the use of catalyst **4g**, bearing 3,5-dimethyl substituted phenyl rings, gave the desired product **3a** in 71% isolated yield with only 11% ee (entry 17). An attempt to decrease catalyst loading was then performed; the use of 1 mol% catalyst **4e** had a clear influence on both the productivity and the level of enantiodiscrimination (entry 18; 71% yield, 77% ee). It should be noted that the reaction was very sluggish when the HCl salt of **4a** was employed as catalyst. Moreover, only a racemic mixture of **3a** was obtained in this case (entry 19; 12% yield, 0% ee).

Table 1 Optimization of the Reaction Conditions[a]

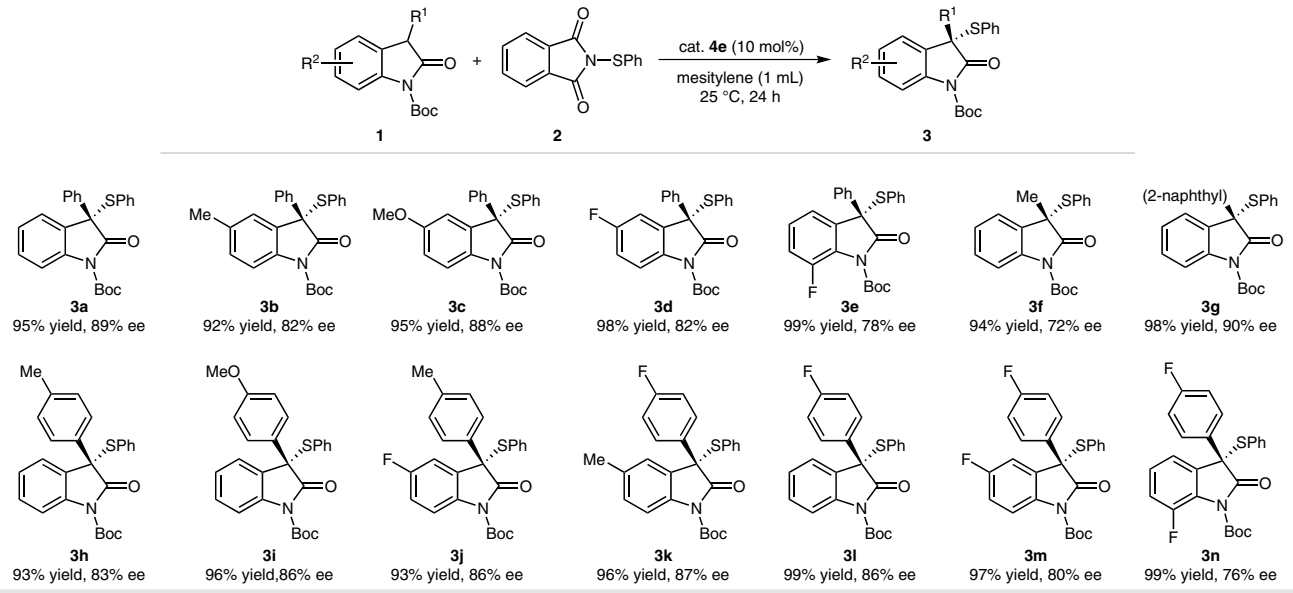


Entry	Cat. **4**	Solvent	Time (h)	Yield (%)[b]	*ee* (%)[c]
1	**4a**	Et_2O	28	95	46
2	**4a**	EtOAc	6	95	46
3	**4a**	THF	9	98	10
4	**4a**	MeOH	6	99	6
5	**4a**	MeCN	6	99	0
6	**4a**	CH_2Cl_2	9	99	30
7	**4a**	$CHCl_3$	6	94	53
8	**4a**	DCE	6	98	23
9	**4a**	hexane	24	89	41
10	**4a**	toluene	6	93	31
11	**4a**	mesitylene	24	97	57
12	**4b**	mesitylene	24	53	11
13	**4c**	mesitylene	24	44	4
14	**4d**	mesitylene	24	86	51
15	**4e**	mesitylene	24	98	89
16	**4f**	mesitylene	24	99	86
17	**4g**	mesitylene	24	71	11
18[d]	**4e**	mesitylene	24	71	77
19[e]	**4a**·HCl	mesitylene	24	12	0

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv) and catalyst **4** (10 mol%) were dissolved in solvent (1 mL), then **2** (1.5 equiv) was added into this stirring solution, after completion of the reaction at 25 °C, the solution mixture was purified directly by silica gel column chromatography to afford product **3a**.
[b] Isolated yield.
[c] The enantiopurity of the product was determined by HPLC analysis using a chiral column (CHIRALCEL OD-H) with hexane–isopropanol as solvent.
[d] Compound **4e** (1 mol%) was used.
[e] A premade HCl salt of **4a** was used.

With the optimized reaction conditions described above, we then explored the generality of the reaction with respect to substrate scope by varying the structure of *N*-Boc-protected oxindoles **1**, as summarized in Scheme 1 and Scheme 2. Scheme 1 shows the results obtained with 3-aryl and 3-methyl substituted N-Boc-oxindoles **1** with *N*-(phenylthio)phthalimide (**2**) under the catalysis of imino-phosphorane **4e** at 25 °C. Generally, products **3** were obtained in excellent yields and with good enantiomeric excess after 24 hours (Scheme 1, 3a–n, 92–99% yields, 72–90% ee). In the case of 7-fluoro substituted oxindoles **3e** and **3n**, the desired products were obtained in excellent yields but the enantiomeric excess was slightly decreased (78 and 76% ee, respectively). Notably, 3-(2-naphthyl) substituted oxindole **1g** gave product **3g** in both excellent yield (98%) and with high enantioselectivity (90% ee). In contrast, the use of 3-methyl substituted oxindole **1f** in this reaction gave product **3f** in only 72% ee, although with excellent yield (94%). Notably, the absolute *S*-configuration of the sulfenylated oxindole product **3a**–**n** was determined by correlation of the measured specific rotation values with the corresponding reported data.[6b,c]

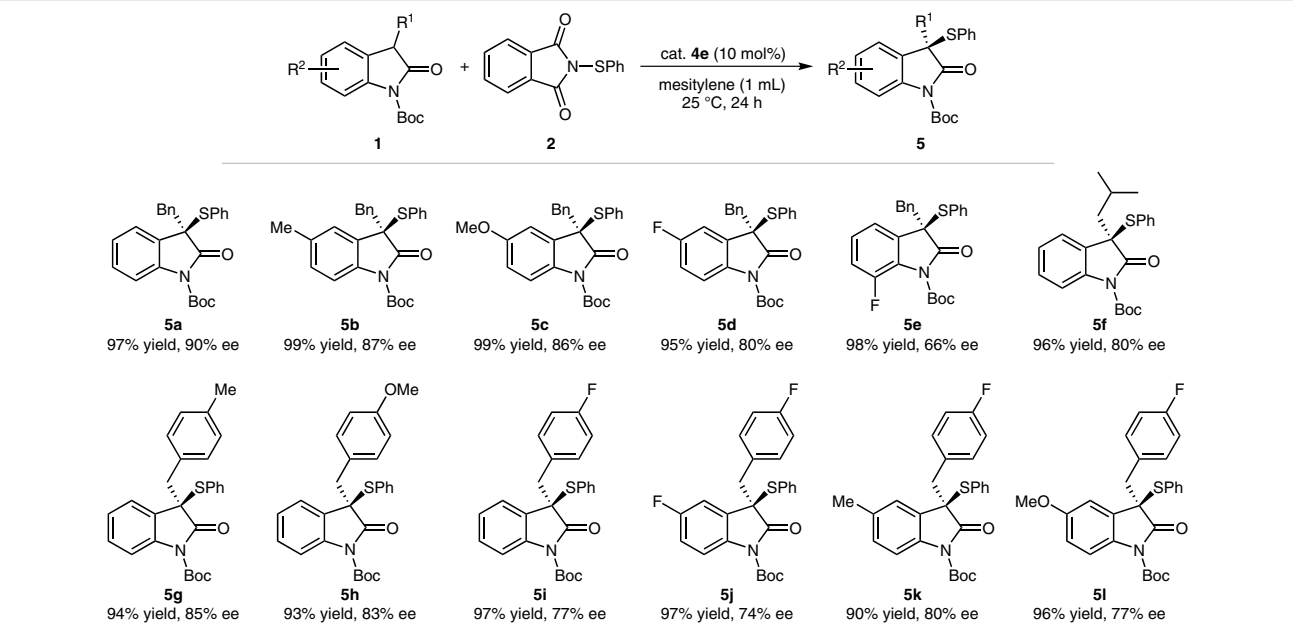
Subsequently, a selection of 3-benzyl-substituted *N*-Boc-oxindoles **1** were treated with *N*-(phenylthio)phthalimide **2** under the same reaction conditions; the results are summarized in Scheme 2. We achieved the



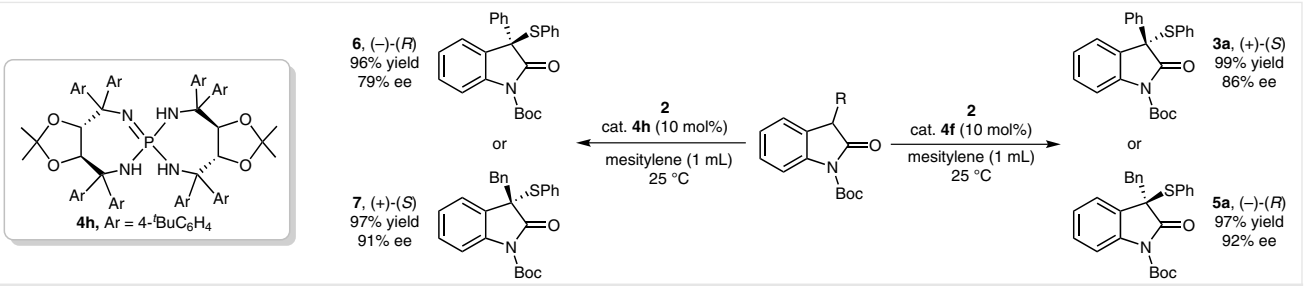
Scheme 1 Substrate scope of the reaction with 3-aryl- or 3-methyl-substituted oxindoles

products **5a**–**l** in excellent yields (90–99%) and with good enantiomeric excess (66–90% ee); the enantiomeric excess of **5i**–**l** were lower than those of **5g**–**h** when a fluoro-substituted benzyl group was present in the *para*-position of the phenyl ring (**5i**–**l**, 74–80% ee). Product **5e** was obtained in only 66% ee, which, together with the results obtained for 3-aryl products **3e** and **3n** (Scheme 1), suggested that 7-fluoro-substituted oxindoles gave unsatisfactory enantioselectivities with this catalytic system. Of note, 3-isobutyloxindole as a substrate afforded **5f** in 96% yield together with 80% ee (Scheme 2, 5f). Interestingly, the absolute *R*-configuration of products **5a**–**l** was determined by both specific rotation values and high-performance liquid chromatography (HPLC) data in comparison to the previously reported data (see Scheme 1 and Scheme 2).[6b,c] Especially, opposite absolute configurations of 3-methyl- and 3-isobutyloxindoles **3f** and **5f**, respectively, were observed.

Additionally, with a selection of iminophosphorane catalysts **4f** and **4h** (a pair of enantiomers) in hand,[5e] asymmetric synthesis of both enantiomeric products of sulfe-



Scheme 2 Substrate scope of the reaction with 3-benzyl- or 3-isobutyl-substituted oxindoles



Scheme 3 Representative examples of stereodivergence

nylated oxindoles with 3-phenyl or 3-benzyl group was attempted. As shown in Scheme 3, the reactions catalyzed by **4f** gave the products (*S*)-3-phenyloxindole **3a** and (*R*)-3-benzyloxindole **5a** in excellent yields and with good enantiomeric excess (99% yield, 86% ee and 97% yield, 92% ee, respectively). Similarly, catalyst **4h** delivered the products (*R*)-3-phenyloxindole **6** in 96% yield, 79% ee and (*S*)-3-benzyloxindole **7** in 97% yield, 91% ee under the same conditions.

In summary, we have developed an organocatalytic, asymmetric sulfenylation of *N*-Boc-protected oxindoles by using *N*-(phenylthio)phthalimide as the sulfenylating agent. In the presence of chiral iminophosphoranes as the catalyst, the reaction proceeded smoothly at room temperature, and afforded a series of sulfenylated products in excellent yields (90–99%) and with good enantioselectivities (up to 92% ee). The sulfenylations extend the substrate scope of asymmetric sulfenylation of 3-substituted oxindoles. In particular, the reactions provided the corresponding sulfenylation products with reverse absolute configuration according to the 3-substituted group of oxindoles. Further investigations into the mechanism of this catalytic system are in progress in our laboratory.

N-(Phenylthio)phthalimide was used as obtained from commercial sources (CAS 14204-27-4, TCI, >98.0%). 1,3,5-Trimethylbenzene was obtained from Shanghai Tianlian Chemical Technology Co., Ltd. (CAS 108-67-8). Flash column chromatography was performed with SiliaFlash® P60 (230–400 mesh, UltraPure SILICA GELS, SiliCycle). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded with a Mercury 300 NMR spectrometer, and TMS was used as a reference. ^{1}H NMR spectroscopic data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants in hertz (Hz), integration, assignment. ^{13}C and ^{19}F NMR spectroscopic data are reported in ppm. IR spectra were recorded with a Nicolet iN10 MX spectrometer and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra were measured with an Agilent Technologies 6224 TOF LC/MS spectrometer. Enantiomeric excess was measured by HPLC with CHIRALCEL OD-H on an DIONEX UltiMate 3000, NO.8074238, ThermoScientific. Optical rotation was measured with an Autopol I, serial number 30575. All melting points were determined with a digital melting point apparatus and are uncorrected. The starting oxindole derivatives were prepared according to reported procedures.[10]

Chiral Iminophosphorane Organocatalyzed Asymmetric Sulfenylation of 3-Substituted Oxindoles; General Procedure

To a reaction tube was added oxindole **1** (0.1 mmol, 1.0 equiv), **4e** (10.7 mg, 0.01 mmol, 10 mol%) and mesitylene (1 mL, 0.1 M) at 25 °C with magnetic stirring. *N*-(Phenylthio)phthalimide (**2**; 38.3 mg, 0.15 mmol, 1.5 equiv) was then added to the mixture of oxindole and catalyst. After stirring for 24 h at 25 °C, the reaction mixture was purified directly by silica gel column chromatography to give product **3** or **5**. The ee of the product was determined by chiral HPLC analysis.

(*S*)-*tert*-Butyl 2-Oxo-3-phenyl-3-(phenylthio)indoline-1-carboxylate (3a)

Yield: 39.7 mg (95%); white solid; mp 104–105 °C; $[\alpha]_D^{27}$ +133.4 (*c* = 1.27, $CHCl_3$); 89% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 4.54 (major), 5.85 (minor) min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.0 Hz, 2 H), 7.61–7.53 (m, 1 H), 7.48–7.30 (m, 4 H), 7.29–7.20 (m, 3 H), 7.19–7.04 (m, 4 H), 1.55 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.68, 148.85, 139.52, 136.80, 135.89, 130.06, 129.53, 129.32, 129.16, 128.89, 128.76, 128.68, 128.64, 126.51, 124.75, 114.97, 84.38, 63.02, 28.25.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{23}NO_3SNa^+$: 440.1291; found: 440.1292.

(*S*)-*tert*-Butyl 5-Methyl-2-oxo-3-phenyl-3-(phenylthio)indoline-1-carboxylate (3b)[6b]

Yield: 39.7 mg (92%); white solid; mp 109–110 °C; $[\alpha]_D^{28}$ +85.5 (*c* = 1.12, $CHCl_3$); 82% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 4.51 (major), 5.76 (minor) min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 8.0, 1.2 Hz, 2 H), 7.47 (d, *J* = 8.3 Hz, 1 H), 7.43–7.30 (m, 3 H), 7.29–7.23 (m, 1 H), 7.21 (s, 1 H), 7.19–7.03 (m, 5 H), 2.38 (s, 3 H), 1.55 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.72, 148.91, 137.17, 136.82, 136.08, 134.39, 130.02, 129.92, 129.65, 128.87, 128.73, 128.69, 128.63, 126.79, 114.80, 84.19, 63.16, 28.27, 21.44.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{25}NO_3SNa^+$: 454.1447; found: 454.1449.

(*S*)-*tert*-Butyl 5-Methoxyl-2-oxo-3-phenyl-3-(phenylthio)indoline-1-carboxylate (3c)[6c]

Yield: 42.5 mg (95%); white solid; mp 132–133 °C; $[\alpha]_D^{27}$ +75.5 (*c* = 1.48, $CHCl_3$); 88% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 7.12 (major), 9.48 (minor) min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.4 Hz, 2 H), 7.51 (d, *J* = 8.9 Hz, 1 H), 7.43–7.30 (m, 3 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 7.11 (t, *J* = 7.7 Hz, 2 H), 6.95 (d, *J* = 2.5 Hz, 1 H), 6.80 (dd, *J* = 8.9, 2.7 Hz, 1 H), 3.79 (s, 3 H), 1.53 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.67, 157.05, 148.90, 136.76, 135.94, 132.98, 130.08, 129.55, 128.91, 128.77, 128.70, 116.07, 115.03, 111.61, 84.18, 63.40, 55.98, 28.26.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{25}NO_4SNa^+$: 470.1397; found: 470.1397.

(*S*)-*tert*-Butyl 5-Fluoro-2-oxo-3-phenyl-3-(phenylthio)indoline-1-carboxylate (3d)[6c]

Yield: 42.7 mg (98%); white solid; mp 81–82 °C; $[\alpha]_D^{27}$ +129.5 (*c* = 1.31, $CHCl_3$); 82% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 5.43 (major), 7.24 (minor) min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 8.1, 1.5 Hz, 2 H), 7.58 (dd, *J* = 9.0, 4.6 Hz, 1 H), 7.44–7.32 (m, 3 H), 7.31–7.23 (m, 1 H), 7.23–7.08 (m, 5 H), 6.96 (td, *J* = 8.9, 2.8 Hz, 1 H), 1.54 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.32, 160.05 (d, *J* = 243.9 Hz), 148.78, 136.79, 135.45 (d, *J* = 2.3 Hz), 135.35, 130.86 (d, *J* = 8.2 Hz), 130.30, 129.18, 129.04, 128.99, 128.81, 128.51, 116.45 (d, *J* = 7.8 Hz), 116.08 (d, *J* = 23.0 Hz), 113.48 (d, *J* = 24.7 Hz), 84.58, 63.05, 28.23.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –117.44 (td, *J* = 8.3, 4.6 Hz).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{22}FNO_3SNa^+$: 458.1197; found: 458.1198.

(*S*)-*tert*-Butyl 7-Fluoro-2-oxo-3-phenyl-3-(phenylthio)indoline-1-carboxylate (3e)

Yield: 43.1 mg (99%); white solid; mp 107–108 °C; $[\alpha]_D^{28}$ +81.0 (*c* = 1.19, $CHCl_3$); 78% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 6.06 (major), 8.69 (minor) min.

IR (KBr): 3067, 3015, 2996, 2981, 2930, 1783, 1722, 1620, 1595, 1581, 1486, 1461, 1454, 1442, 1394, 1369, 1338, 1283, 1263, 1242, 1204, 1143, 1067, 1026, 1005, 990, 924, 864, 842, 801, 785, 769, 747, 732, 701, 694, 668, 617, 582 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 8.0, 1.5 Hz, 2 H), 7.43–7.09 (m, 10 H), 7.05–6.95 (m, 1 H), 1.49 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.23, 148.51 (d, *J* = 251.8 Hz), 146.97, 136.68, 135.42, 132.38 (d, *J* = 1.6 Hz), 130.37, 129.17, 129.02, 128.97, 128.40, 126.61 (d, *J* = 9.9 Hz), 125.63 (d, *J* = 7.0 Hz), 122.38 (d, *J* = 3.6 Hz), 117.25 (d, *J* = 20.5 Hz), 84.94, 63.43, 27.80.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –120.26 (dd, *J* = 11.1, 4.2 Hz).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{22}FNO_3SNa^+$: 458.1197; found: 458.1198.

(*S*)-*tert*-Butyl 3-Methyl-2-oxo-3-(phenylthio)indoline-1-carboxylate (3f)

Yield: 33.4 mg (94%); colorless syrup; $[\alpha]_D^{27}$ +73.7 (*c* = 0.89, $CHCl_3$); 72% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 4.55 (major), 8.98 (minor) min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.46 (m, 1 H), 7.43–7.34 (m, 1 H), 7.29–7.04 (m, 7 H), 1.72 (s, 3 H), 1.55 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.54, 148.85, 138.82, 136.75, 130.28, 129.98, 129.48, 129.20, 128.63, 124.81, 124.00, 114.85, 84.26, 54.85, 28.27, 21.42.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{21}NO_3SNa^+$: 378.1134; found: 378.1135.

(*S*)-*tert*-Butyl 3-(Naphthalen-2-yl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (3g)

Yield: 45.8 mg (98%); white solid; mp 119–120 °C; $[\alpha]_D^{28}$ +111.8 (*c* = 1.47, $CHCl_3$); 90% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 4.82 (major), 7.00 (minor) min.

IR (KBr): 3054, 3003, 2978, 2927, 1792, 1762, 1728, 1603, 1572, 1505, 1475, 1463, 1438, 1393, 1370, 1337, 1306, 1285, 1247, 1144, 1089, 1019, 996, 839, 816, 769, 757, 704, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 7.97–7.79 (m, 4 H), 7.66 (d, *J* = 7.3 Hz, 1 H), 7.55–7.44 (m, 3 H), 7.35–7.19 (m, 5 H), 7.13 (t, *J* = 7.5 Hz, 2 H), 1.58 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.66, 148.92, 139.57, 136.88, 133.30, 133.26, 130.14, 129.54, 129.46, 129.00, 128.78, 128.74, 128.68, 128.17, 127.81, 126.99, 126.64, 126.57, 126.14, 124.87, 115.09, 84.47, 63.27, 28.29.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{29}H_{25}NO_3SNa^+$: 490.1447; found: 490.1447.

(*S*)-*tert*-Butyl 3-(4-Methylphenyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (3h)[6c]

Yield: 40.1 mg (93%); white solid; mp 95–96 °C; $[\alpha]_D^{27}$ +117.9 (*c* = 1.34, $CHCl_3$); 83% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 4.76 (major), 7.14 (minor) min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.54 (m, 3 H), 7.48–7.42 (m, 1 H), 7.29–7.05 (m, 9 H), 2.35 (s, 3 H), 1.55 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.33, 148.41, 139.04, 138.21, 136.31, 132.40, 129.54, 129.14, 128.79, 128.58, 128.16, 128.08, 126.03, 124.25, 114.47, 83.82, 62.39, 27.79, 20.92.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{25}NO_3SNa^+$: 454.1447; found: 454.1448.

(*S*)-*tert*-Butyl 3-(4-Methoxyphenyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate(3i)[6b,c]

Yield: 43.0 mg (96%); white solid; mp 91–92 °C; $[\alpha]_D^{27}$ +125.4 (*c* = 1.44, $CHCl_3$); 86% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 8.56 (major), 12.65 (minor) min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.9 Hz, 2 H), 7.60–7.53 (m, 1 H), 7.48–7.41 (m, 1 H), 7.29–7.19 (m, 3 H), 7.18–7.04 (m, 4 H), 6.91 (d, *J* = 8.9 Hz, 2 H), 3.79 (s, 3 H), 1.54 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.42, 159.47, 148.42, 139.02, 136.28, 129.54, 129.25, 128.82, 128.52, 128.18, 127.21, 126.05, 124.26, 114.51, 113.76, 83.85, 62.04, 55.11, 27.79.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{25}NO_4SNa^+$: 470.1397; found: 470.1397.

(*S*)-*tert*-Butyl 5-Fluoro-3-(4-methylphenyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (3j)

Yield: 41.8 mg (93%); white solid; mp 141–142 °C; $[\alpha]_D^{28}$ +118.2 (*c* = 1.31, $CHCl_3$); 86% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 4.24 (major), 6.00 (minor) min.

IR (KBr): 3057, 2976, 2918, 1764, 1734, 1608, 1573, 1511, 1482, 1437, 1393, 1368, 1342, 1295, 1264, 1158, 1145, 1094, 1045, 1025, 978, 857, 819, 800, 789, 755, 735, 704, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.51 (m, 3 H), 7.31–7.08 (m, 8 H), 6.95 (td, *J* = 8.9, 2.6 Hz, 1 H), 2.36 (s, 3 H), 1.54 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.46, 160.05 (d, *J* = 243.8 Hz), 148.83, 138.96, 136.76, 135.43 (d, *J* = 2.3 Hz), 132.33, 131.03 (d, *J* = 8.3 Hz), 130.24, 129.74, 129.31, 128.79, 128.36, 116.39 (d, *J* = 7.9 Hz), 116.00 (d, *J* = 23.0 Hz), 113.45 (d, *J* = 24.7 Hz), 84.52, 62.88, 28.23, 21.37.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –117.56 (td, *J* = 8.4, 4.7 Hz).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{24}FNO_3SNa^+$: 472.1353; found: 472.1356.

(*S*)-*tert*-Butyl 3-(4-Fluorophenyl)-5-methyl-2-oxo-3-(phenylthio)indoline-1-carboxylate (3k)

Yield: 43.2 mg (96%); white solid; mp 150–152 °C; $[\alpha]_D^{27}$ +107.7 (*c* = 1.24, $CHCl_3$); 87% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 4.16 (major), 4.93 (minor) min.

IR (KBr): 3077, 3060, 2986, 2974, 2924, 1760, 1730, 1598, 1572, 1504, 1490, 1472, 1437, 1392, 1368, 1336, 1299, 1281, 1250, 1224, 1152, 1111, 1097, 1045, 1025, 1008, 967, 865, 837, 818, 760, 748, 735, 704, 690, 534, 525, 501 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.70 (s, 2 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.32–6.92 (m, 9 H), 2.38 (s, 3 H), 1.53 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.62, 162.93 (d, *J* = 248.5 Hz), 148.81, 137.14, 136.79, 134.49, 131.77 (d, *J* = 2.5 Hz), 130.73 (d, *J* = 8.2 Hz), 130.14, 130.08, 129.47, 128.68, 128.48, 126.70, 115.72 (d, *J* = 21.6 Hz), 114.91, 84.33, 62.43, 28.23, 21.42.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –113.78 (s).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{24}FNO_3SNa^+$: 472.1353; found: 472.1356.

(*S*)-*tert*-Butyl 3-(4-Fluorophenyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (3l)[6b,c]

Yield: 43.1 mg (99%); white solid; mp 66–67 °C; $[\alpha]_D^{27}$ +145.1 (*c* = 1.23, $CHCl_3$); 86% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 4.69 (major), 5.69 (minor) min.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.66 (m, 2 H), 7.61–7.54 (m, 1 H), 7.45–7.39 (m, 1 H), 7.30–7.20 (m, 3 H), 7.17–7.01 (m, 6 H), 1.54 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.13, 162.53 (d, *J* = 249.7 Hz), 148.30, 139.05, 136.33, 131.17, 130.24 (d, *J* = 8.1 Hz), 129.74, 129.06, 128.91, 128.26, 128.10, 125.98, 124.39, 115.32 (d, *J* = 21.5 Hz), 114.65, 84.06, 61.86, 27.78.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –113.55 to –113.69 (m).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{22}FNO_3SNa^+$: 458.1197; found: 458.1198.

(*S*)-*tert*-Butyl 5-Fluoro-3-(4-fluorophenyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (3m)

Yield: 44.0 mg (97%); white solid; mp 119–120 °C; $[\alpha]_D^{28}$ +137.2 (*c* = 1.28, $CHCl_3$); 80% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 4.15 (major), 4.96 (minor) min.

IR (KBr): 3063, 2984, 2932, 1764, 1732, 1598, 1506, 1478, 1437, 1405, 1392, 1369, 1344, 1298, 1264, 1222, 1145, 1094, 1045, 1026, 1009, 980, 920, 877, 864, 850, 818, 811, 796, 773, 757, 739, 705, 691, 669, 600, 591, 541, 522, 506 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.63 (m, 2 H), 7.57 (dd, *J* = 9.0, 4.6 Hz, 1 H), 7.32–7.24 (m, 1 H), 7.20–7.03 (m, 7 H), 6.97 (td, *J* = 8.9, 2.7 Hz, 1 H), 1.54 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.17, 163.07 (d, *J* = 249.2 Hz), 160.06 (d, *J* = 244.4 Hz), 148.70, 136.75, 135.44, 131.09 (d, *J* = 2.9 Hz), 130.53 (d, *J* = 8.4 Hz), 130.45 (d, *J* = 4.0 Hz), 129.03, 128.86, 116.58 (d, *J* = 7.7 Hz), 116.25 (d, *J* = 25.1 Hz), 115.94 (d, *J* = 21.8 Hz), 113.40 (d, *J* = 24.7 Hz), 84.70, 62.34, 28.21.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –113.07 to –113.26 (m), –117.25 (td, *J* = 8.3, 4.8 Hz).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{21}F_2NO_3SNa^+$: 476.1102; found: 476.1102.

(*S*)-*tert*-Butyl 7-Fluoro-3-(4-fluorophenyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (3n)

Yield: 44.9 mg (99%); white solid; mp 96–97 °C; $[\alpha]_D^{27}$ +102.3 (*c* = 1.17, $CHCl_3$); 76% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 5.83 (major), 6.65 (minor) min.

IR (KBr): 3060, 2982, 2933, 1793, 1755, 1731, 1623, 1601, 1506, 1488, 1463, 1439, 1408, 1395, 1370, 1344, 1290, 1247, 1210, 1145, 1069, 1013, 873, 843, 812, 779, 767, 750, 734, 692, 581, 519 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.61 (m, 2 H), 7.34–6.96 (m, 10 H), 1.48 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.12, 163.04 (d, *J* = 249.0 Hz), 148.53 (d, *J* = 251.6 Hz), 146.86, 136.65, 132.01 (d, *J* = 1.7 Hz), 131.11 (d, *J* = 3.2 Hz), 130.49, 130.38, 129.02, 128.98, 126.60 (d, *J* = 9.9 Hz), 125.72 (d, *J* = 7.0 Hz), 122.31 (d, *J* = 3.6 Hz), 117.43 (d, *J* = 20.6 Hz), 115.92 (d, *J* = 21.6 Hz), 85.09, 62.69, 27.77.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –113.08 to –113.28 (m), –120.06 (dd, *J* = 11.1, 4.1 Hz).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{21}F_2NO_3SNa^+$: 476.1102; found: 476.1103.

(*R*)-*tert*-Butyl 3-Benzyl-2-oxo-3-(phenylthio)indoline-1-carboxylate (5a)[6b,c]

Yield: 41.9 mg (97%); colorless syrup; $[\alpha]_D^{27}$ –42.5 (*c* = 1.07, $CHCl_3$); 90% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 30:1; 1.0 mL/min): t_R = 6.58 (major), 5.16 (minor) min.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.41 (m, 1 H), 7.38–7.31 (m, 1 H), 7.28–7.18 (m, 3 H), 7.17–7.03 (m, 7 H), 7.02–6.94 (m, 2 H), 3.56 (d, *J* = 13.4 Hz, 1 H), 3.41 (d, *J* = 13.4 Hz, 1 H), 1.51 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.46, 148.62, 139.55, 136.93, 134.88, 130.55, 129.96, 129.15, 128.71, 128.29, 127.74, 127.19, 125.09, 124.38, 114.84, 84.18, 60.40, 41.29, 28.24.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{25}NO_3SNa^+$: 454.1447; found: 454.1450.

(*R*)-*tert*-Butyl 3-Benzyl-5-methyl-2-oxo-3-(phenylthio)indoline-1-carboxylate (5b)

Yield: 44.1 mg (99%); white solid; mp 135–136 °C; $[\alpha]_D^{28}$ –22.6 (*c* = 0.90, $CHCl_3$); 87% ee determined by chiral HPLC analysis (CHIRAL-

CEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 7.47 (major), 5.39 (minor) min.

IR (KBr): 3061, 3026, 2969, 2918, 1782, 1713, 1592, 1485, 1454, 1438, 1393, 1370, 1308, 1277, 1254, 1221, 1150, 1117, 1088, 1074, 941, 921, 841, 816, 771, 748, 717, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.20 (m, 5 H), 7.19–7.05 (m, 5 H), 7.02–6.91 (m, 3 H), 3.54 (d, *J* = 13.4 Hz, 1 H), 3.40 (d, *J* = 13.4 Hz, 1 H), 2.38 (s, 3 H), 1.51 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.53, 148.67, 137.21, 136.96, 134.96, 133.97, 130.55, 129.94, 129.75, 129.22, 128.71, 128.27, 127.57, 127.14, 125.46, 114.66, 84.04, 60.32, 41.24, 28.24, 21.46.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{27}H_{27}NO_3SNa^+$: 468.1604; found: 468.1606.

(*R*)-*tert*-Butyl 3-Benzyl-5-methoxyl-2-oxo-3-(phenylthio)indoline-1-carboxylate (5c)

Yield: 45.7 mg (99%); pale-yellow solid; mp 110–111 °C; $[\alpha]_D^{29}$ –18.6 (*c* = 1.37, $CHCl_3$); 86% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 10.73 (major), 7.99 (minor) min.

IR (KBr): 3060, 2979, 2930, 2836, 1765, 1728, 1616, 1488, 1471, 1447, 1434, 1393, 1369, 1334, 1310, 1270, 1249, 1228, 1147, 1106, 1068, 1034, 1008, 922, 844, 823, 769, 750, 701, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.26 (t, *J* = 8.0 Hz, 4 H), 7.18–7.06 (m, 5 H), 7.05–6.98 (m, 2 H), 6.96 (d, *J* = 2.5 Hz, 1 H), 6.67 (dd, *J* = 8.9, 2.5 Hz, 1 H), 3.81 (s, 3 H), 3.54 (d, *J* = 13.4 Hz, 1 H), 3.40 (d, *J* = 13.4 Hz, 1 H), 1.51 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.56, 156.71, 148.63, 136.87, 134.84, 132.97, 130.57, 129.99, 129.09, 128.97, 128.76, 128.33, 127.24, 115.88, 114.58, 110.51, 84.02, 60.63, 55.95, 41.33, 28.24.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{27}H_{27}NO_4SNa^+$: 484.1553; found: 484.1555.

(*R*)-*tert*-Butyl 3-Benzyl-5-fluoro-2-oxo-3-(phenylthio)indoline-1-carboxylate (5d)

Yield: 42.7 mg (95%); white solid; mp 71–72 °C; $[\alpha]_D^{28}$ –39.5 (*c* = 1.08, $CHCl_3$); 80% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 7.80 (major), 5.93 (minor) min.

IR (KBr): 3033, 2981, 2929, 1767, 1730, 1608, 1483, 1455, 1439, 1394, 1369, 1343, 1298, 1269, 1250, 1225, 1145, 1111, 1068, 1001, 923, 865, 843, 820, 750, 700, 689 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.19 (m, 4 H), 7.18–7.05 (m, 6 H), 7.03–6.95 (m, 2 H), 6.81 (td, *J* = 8.9, 2.4 Hz, 1 H), 3.56 (d, *J* = 13.4 Hz, 1 H), 3.35 (d, *J* = 13.4 Hz, 1 H), 1.50 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.18, 159.81 (d, *J* = 243.5 Hz), 148.49, 136.86, 135.46 (d, *J* = 2.3 Hz), 134.50, 130.47, 130.17, 129.82 (d, *J* = 8.2 Hz), 128.86, 128.74, 128.45, 127.38, 116.25 (d, *J* = 7.9 Hz), 115.80 (d, *J* = 22.9 Hz), 112.20 (d, *J* = 24.6 Hz), 84.43, 60.54, 41.25, 28.22.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –117.91 (td, *J* = 8.3, 4.5 Hz).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{26}H_{24}FNO_3SNa^+$: 472.1353; found: 472.1357.

(*R*)-*tert*-Butyl 3-Benzyl-7-fluoro-2-oxo-3-(phenylthio)indoline-1-carboxylate (5e)

Yield: 44.1 mg (98%); colorless syrup; $[\alpha]_D^{29}$ –7.9 (*c* = 1.31, $CHCl_3$); 66% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 200:1; 0.5 mL/min): t_R = 43.91 (major), 42.14 (minor) min.

IR (KBr): 3061, 3032, 2981, 2931, 1789, 1753, 1727, 1624, 1600, 1489, 1465, 1455, 1439, 1394, 1369, 1347, 1292, 1264, 1246, 1188, 1144, 1067, 1024, 1001, 937, 919, 869, 843, 820, 799, 764, 749, 728, 700, 584 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.19 (m, 4 H), 7.19–7.01 (m, 6 H), 6.97–6.80 (m, 3 H), 3.54 (d, *J* = 13.3 Hz, 1 H), 3.35 (d, *J* = 13.2 Hz, 1 H), 1.39 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.15, 148.43 (d, *J* = 251.8 Hz), 146.67, 136.71, 134.30, 131.42 (d, *J* = 1.8 Hz), 130.31, 130.17, 129.00, 128.76, 128.39, 127.41, 126.65 (d, *J* = 9.6 Hz), 125.40 (d, *J* = 7.0 Hz), 120.91 (d, *J* = 3.5 Hz), 117.19 (d, *J* = 20.8 Hz), 84.48, 61.21, 42.02, 27.69.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –119.96 (dd, *J* = 11.1, 4.1 Hz).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{26}H_{24}FNO_3SNa^+$: 472.1353; found: 472.1358.

(*R*)-*tert*-Butyl 3-Isobutyl-2-oxo-3-(phenylthio)indoline-1-carboxylate (5f)

Yield: 38.2 mg (96%); colorless oil; $[\alpha]_D^{28}$ –57.5 (*c* = 1.07, $CHCl_3$); 80% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 0.2 mL/min): t_R = 19.21 (major), 20.03 (minor) min.

IR (KBr): 3054, 2959, 2931, 2871, 1793, 1766, 1731, 1606, 1477, 1466, 1438, 1393, 1369, 1348, 1292, 1252, 1150, 1105, 1073, 1025, 1005, 912, 844, 750, 704, 691, 661, 589 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.43 (m, 1 H), 7.38–7.31 (m, 1 H), 7.27–7.13 (m, 3 H), 7.11–7.01 (m, 4 H), 2.24 (dd, *J* = 13.9, 8.0 Hz, 1 H), 2.11 (dd, *J* = 13.8, 5.7 Hz, 1 H), 1.59–1.45 (m, 1 H), 1.53 (s, 9 H), 0.67 (dd, *J* = 12.7, 6.6 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.01, 148.82, 139.37, 136.90, 129.95, 128.96, 128.54, 128.51, 124.69, 124.54, 114.86, 84.11, 58.92, 42.81, 28.26, 26.35, 23.98, 22.93.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{27}NO_3SNa^+$: 420.1604; found: 420.1604.

(*R*)-*tert*-Butyl 3-(4-Methylbenzyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (5g)[6b]

Yield: 41.9 mg (94%); colorless syrup; $[\alpha]_D^{28}$ –36.0 (*c* = 1.21, $CHCl_3$); 85% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 6.33 (major), 5.90 (minor) min.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 6.4 Hz, 1 H), 7.36 (d, *J* = 7.3 Hz, 1 H), 7.29–7.19 (m, 3 H), 7.19–7.08 (m, 4 H), 6.88 (s, 4 H), 3.53 (d, *J* = 13.4 Hz, 1 H), 3.39 (d, *J* = 13.4 Hz, 1 H), 2.18 (s, 3 H), 1.52 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.55, 148.66, 139.55, 136.92, 136.68, 131.75, 130.44, 129.95, 129.15, 129.10, 129.03, 128.70, 127.86, 125.11, 124.39, 114.83, 84.17, 60.46, 40.78, 28.25, 21.29.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{27}H_{27}NO_3SNa^+$: 468.1604; found: 468.1605.

(*R*)-*tert*-Butyl 3-(4-Methoxybenzyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (5h)

Yield: 42.9 mg (93%); pale-yellow syrup; $[\alpha]_D^{29}$ –37.7 (*c* = 1.22, $CHCl_3$); 83% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 9.74 (major), 8.69 (minor) min.

IR (KBr): 3053, 2979, 2930, 2835, 1792, 1763, 1731, 1610, 1583, 1512, 1477, 1465, 1438, 1393, 1369, 1347, 1290, 1249, 1147, 1106, 1077, 1035, 1003, 937, 892, 827, 754, 703, 692, 582, 550, 527 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.0 Hz, 1 H), 7.35 (d, *J* = 7.8 Hz, 1 H), 7.29–7.06 (m, 7 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 6.60 (d, *J* = 8.5 Hz, 2 H), 3.66 (s, 3 H), 3.50 (d, *J* = 13.5 Hz, 1 H), 3.36 (d, *J* = 13.5 Hz, 1 H), 1.52 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.59, 158.60, 148.61, 139.56, 136.89, 131.62, 129.92, 129.14, 129.11, 128.69, 127.85, 126.84, 125.05, 124.39, 114.85, 113.63, 84.18, 60.50, 55.26, 40.38, 28.23.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{27}NO_4SNa^+$: 484.1553; found: 484.1550.

(*R*)-*tert*-Butyl 3-(4-Fluorobenzyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (5i)

Yield: 43.6 mg (97%); white solid; mp 99–100 °C; $[\alpha]_D^{28}$ –38.2 (*c* = 1.04, $CHCl_3$); 77% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 5.86 (major), 6.32 (minor) min.

IR (KBr): 3062, 3012, 2981, 2931, 1758, 1736, 1604, 1508, 1480, 1465, 1440, 1393, 1369, 1348, 1306, 1289, 1250, 1215, 1163, 1149, 1076, 1003, 841, 824, 773, 762, 744, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.42 (m, 1 H), 7.35 (d, *J* = 8.2 Hz, 1 H), 7.29–7.07 (m, 7 H), 6.94 (dd, *J* = 8.3, 5.6 Hz, 2 H), 6.75 (t, *J* = 8.7 Hz, 2 H), 3.53 (d, *J* = 13.5 Hz, 1 H), 3.37 (d, *J* = 13.5 Hz, 1 H), 1.52 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.42, 162.02 (d, *J* = 245.5 Hz), 148.51, 139.53, 136.94, 132.09 (d, *J* = 8.0 Hz), 130.58 (d, *J* = 3.3 Hz), 130.03, 129.30, 128.94, 128.74, 127.48, 124.94, 124.48, 115.18 (d, *J* = 21.2 Hz), 114.93, 84.35, 60.31, 40.35, 28.21.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.82 to –115.96 (m).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{24}FNO_3SNa^+$: 472.1353; found: 472.1359.

(*R*)-*tert*-Butyl 5-Fluoro-3-(4-fluorobenzyl)-2-oxo-3-(phenylthio)indoline-1-carboxylate (5j)

Yield: 45.4 mg (97%); colorless syrup; $[\alpha]_D^{29}$ –36.8 (*c* = 1.36, $CHCl_3$); 74% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 5.84 (major), 6.56 (minor) min.

IR (KBr): 3057, 2981, 2930, 1792, 1766, 1732, 1606, 1509, 1482, 1456, 1439, 1418, 1394, 1370, 1344, 1297, 1269, 1223, 1146, 1111, 1070, 1016, 1003, 942, 910, 892, 866, 830, 796, 748, 735, 703, 692, 611, 590, 561 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.18 (m, 4 H), 7.18–7.08 (m, 3 H), 6.98–6.88 (m, 2 H), 6.86–6.71 (m, 3 H), 3.52 (d, *J* = 13.5 Hz, 1 H), 3.30 (d, *J* = 13.5 Hz, 1 H), 1.49 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.09, 162.10 (d, *J* = 246.0 Hz), 159.83 (d, *J* = 243.8 Hz), 148.39, 136.86, 135.46 (d, *J* = 2.2 Hz), 132.02 (d, *J* = 8.0 Hz), 130.24 (d, *J* = 2.2 Hz), 130.22, 129.60 (d, *J* = 8.1 Hz), 128.88, 128.58, 116.36 (d, *J* = 7.9 Hz), 115.95 (d, *J* = 22.9 Hz), 115.34 (d, *J* = 21.3 Hz), 112.05 (d, *J* = 24.6 Hz), 84.56, 60.47, 40.36, 28.19.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.41 to –115.60 (m), –117.70 (td, *J* = 8.3, 4.6 Hz).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{23}F_2NO_3SNa^+$: 490.1259; found: 490.1260.

(*R*)-*tert*-Butyl 3-(4-Fluorobenzyl)-5-methyl-2-oxo-3-(phenylthio)indoline-1-carboxylate (5k)

Yield: 41.7 mg (90%); white solid; mp 88–89 °C; $[\alpha]_D^{29}$ –24.8 (*c* = 0.73, $CHCl_3$); 80% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 0.5 mL/min): t_R = 11.01 (major), 11.59 (minor) min.

IR (KBr): 3004, 2977, 2930, 1785, 1714, 1603, 1508, 1484, 1438, 1393, 1370, 1331, 1306, 1275, 1250, 1222, 1149, 1121, 1080, 944, 923, 876, 830, 815, 769, 750, 725, 705, 693 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.18 (m, 5 H), 7.13 (t, *J* = 7.5 Hz, 2 H), 6.97–6.86 (m, 3 H), 6.74 (t, *J* = 8.6 Hz, 2 H), 3.48 (d, *J* = 13.5 Hz, 1 H), 3.34 (d, *J* = 13.5 Hz, 1 H), 2.37 (s, 3 H), 1.49 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.43, 162.00 (d, *J* = 245.4 Hz), 148.58, 137.23, 136.97, 134.08, 132.07 (d, *J* = 8.0 Hz), 130.68 (d, *J* = 3.2 Hz), 129.99, 129.89, 129.08, 128.73, 127.34, 125.29, 115.14 (d, *J* = 21.2 Hz), 114.74, 84.16, 60.20, 40.38, 28.22, 21.44.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.92 to –116.08 (m).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{26}FNO_3SNa^+$: 486.1510; found: 486.1511.

(*R*)-*tert*-Butyl 3-(4-Fluorobenzyl)-5-methoxyl-2-oxo-3-(phenylthio)indoline-1-carboxylate (5l)

Yield: 46.0 mg (96%); pale-yellow solid; mp 114–115 °C; $[\alpha]_D^{29}$ –20.2 (*c* = 1.37, $CHCl_3$); 77% ee determined by chiral HPLC analysis (CHIRALCEL OD-H; 254 nm; *n*-hexane/*i*-PrOH, 50:1; 1.0 mL/min): t_R = 7.57 (major), 8.45 (minor) min.

IR (KBr): 3056, 3003, 2973, 2935, 1785, 1712, 1615, 1601, 1572, 1509, 1487, 1440, 1393, 1369, 1320, 1286, 1269, 1248, 1233, 1221, 1176, 1150, 1078, 1041, 944, 888, 831, 814, 767, 752, 725, 704, 695, 658, 623, 564 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.21 (m, 4 H), 7.14 (t, *J* = 7.6 Hz, 2 H), 6.99–6.91 (m, 3 H), 6.77 (t, *J* = 8.6 Hz, 2 H), 6.68 (dd, *J* = 8.9, 2.4 Hz, 1 H), 3.82 (s, 3 H), 3.50 (d, *J* = 13.5 Hz, 1 H), 3.34 (d, *J* = 13.5 Hz, 1 H), 1.50 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.44, 162.04 (d, *J* = 245.5 Hz), 156.78, 148.54, 136.87, 132.97, 132.08 (d, *J* = 8.0 Hz), 130.56 (d, *J* = 3.2 Hz), 130.03, 128.95, 128.78, 115.96, 115.19 (d, *J* = 21.2 Hz), 114.50, 110.49, 84.14, 60.54, 55.94, 40.46, 28.21.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.76 to –115.90 (m).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{26}FNO_4SNa^+$: 502.1459; found: 502.1460.

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Supporting Information

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