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Axially chiral BINIM and Ni(II)-catalyzed asymmetric chlorination of 3-substituted oxindoles

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ABSTRACT

Axially chiral BINIM–Ni(II) complexes are effective catalysts in the asymmetric chlorination of 3-substituted oxindoles and give the corresponding chlorinated adducts in good yields and up to 88% ee.

1. Introduction

Recently, the enantioselective electrophilic chlorination of the α-position of carbonyl compounds, such as aldehydes, ketones, acyl halides, β-ketoesters, or their derivatives, to stereoselectively construct a tertiary or quaternary stereocenter has attracted much attention from organic chemists.[1–4] In particularly, the enantioselective chlorination and other functionalization methods of 3-substituted oxindoles have been significantly developed over the last decade for the synthesis of optically active 3,3-disubstituted oxindole derivatives,[5] since they are important structural motifs found in a wide array of natural and biologically active molecules.[6] For example, the chlorination reaction of 3-aryloxindole has been developed by Shibata et al., who obtained the corresponding product in moderate enantioselectivity using a dbfox-Ph/Ni complex as the catalyst.[7] In 2011, Antilla et al. reported the chiral calcium VAPOL phosphate mediated asymmetric chlorination of 3-substituted oxindoles, obtaining the corresponding chlorinated products in high yields along with up to 99% ee.[8] Herein, we report that axially chiral BINIM–Ni(II) complexes are also effective catalysts in the asymmetric chlorination of 3-substituted oxindoles to give the corresponding chlorinated adducts in good yields and up to 88% ee.

2. Results and discussion

Axially chiral binaphthalenediimine (BINIM) ligands (chiral Schiff base ligands) **L1**–**L12** were synthesized from the reaction of commercially available (*R*)-1,1′-binaphthyl-2,2′-diamine (binaphthalenediamine, BINAM) or H_8-BINAM with a variety of aldehydes in the presence of 4 Å MS in toluene or alcohol, respectively according to the previous literature (Fig. 1). Amongst these ligands, chiral Schiff base ligands **L1**–**L8** were known products, which were prepared according to previously reported procedures.[9] Chiral ligands **L9**–**L12** were synthesized according to the procedures shown in Scheme 1. Their spectroscopic data are included in Section 4.

Initial examinations using *N*-Boc-protected 3-phenyloxindole **13a** and *N*-chlorosuccinimide (NCS) **14** as the substrates in the presence of axially chiral ligands **L1**–**L12** (10 mol %) and $Ni(ClO_4)_2{\cdot}6H_2O$ (10 mol %) in dichloromethane (DCM) were aimed at determining the best BINIM ligand in this reaction system; the results of these experiments are summarized in Table 1. We found that when using DCM as a solvent, the corresponding α-chlorination product **15a** was obtained in moderate to high yields but with low ee values in the presence of axially chiral ligands **L1**–**L6** at 0 °C; in some cases, no chiral induction was observed (Table 1, entries 1–6). Using **L7** as a chiral ligand afforded **15a** in 85% yield and 43% ee (Table 1, entry 7). We found that using **L8**, derived from BINAM and quinoline-2-carbaldehyde, as a chiral ligand produced **15a** in 92% yield and 81% ee (Table 1, entry 8). Since chiral ligand **L9** had an ethyl group at the 8-position of the quinoline-2-carbaldehyde, the corresponding product **15a** was obtained in 79% yield and 25% ee, presumably due to the steric effect (Table 1, entry 9). Chiral ligands **L10**–**L12**, which were derived from H_8-BINAM with quinoline-2-carbaldehyde combined with an Ni(II) salt, are not effective chiral catalysts in this reaction, affording **15a** in lower ee values (Table 1, entries 10–12).

Having identified the best chiral ligand for this reaction, we next examined the metal salt and temperature effect on this reaction. As can be seen from Table 2, $Ni(ClO_4)_2{\cdot}6H_2O$ or $Ni(BF_4)_2{\cdot}6H_2O$ combined with **L8** are effective catalysts in this reaction while the combination of $Zn(OTf)_2$, $Ni(OAc)_2$, AgOAc, $Cu(OAc)_2$ or CuOTf with **L8** did not give **15a** with a good ee value (Table 2, entries 1–7). Changing the reaction temperature to −10 °C, −20 °C, or 20 °C did not improve the ee of **15a** (Table 2, entries 8–10). We also examined other chlorinating reagents, such as trichloroquinolinone in this reaction. However, these did not work as well as

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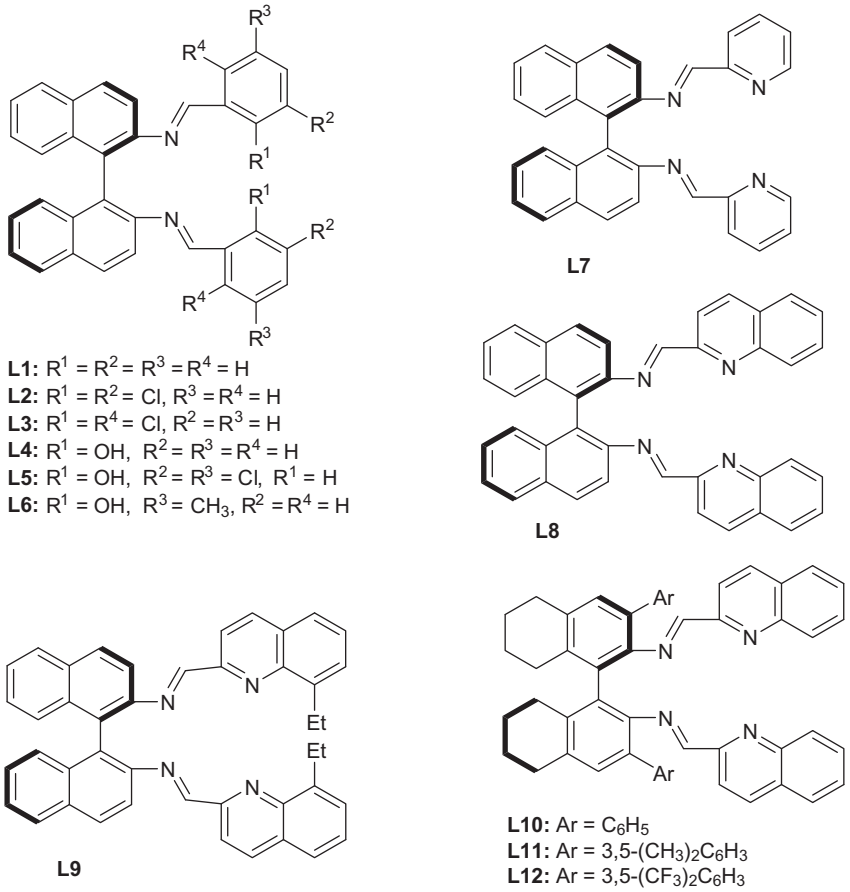


Figure 1. Axially chiral Schiff base ligands **L1**–**L12**.

NCS under identical conditions, giving the corresponding product in 47% yield and 32% ee.

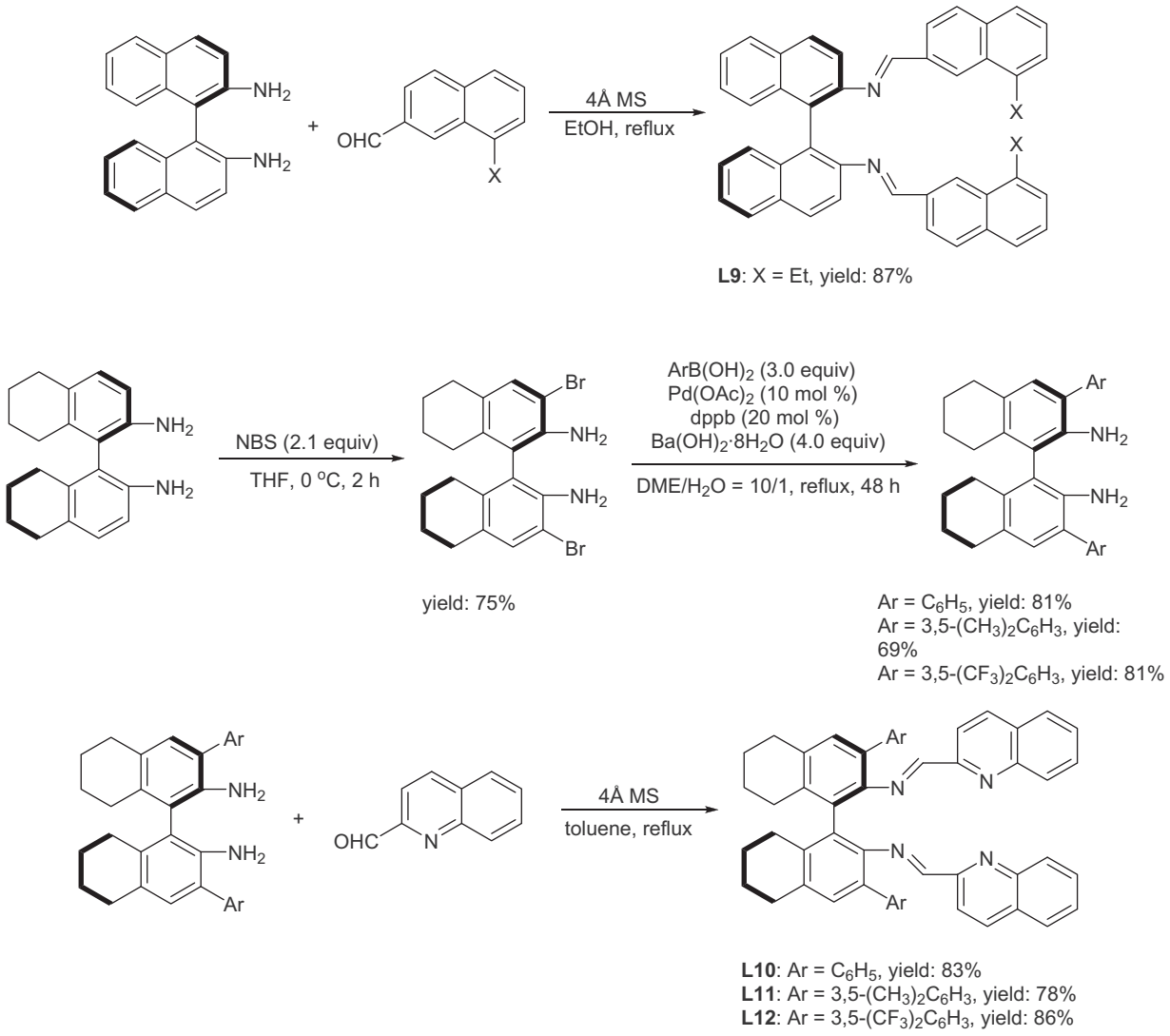
Examination of the solvent effect revealed that in acetonitrile, the desired product **15a** could be obtained in >99% yield along with 85% ee and using other solvents such as DCE, THF, toluene or $CHCl_3$ gave **15a** in lower ee values under otherwise identical conditions (Table 3, entries 1–6). We considered that the protic solvents may enhance the stability of the transition state of this asymmetric chlorination and can provide a hydrogen bond from a protic solvent with the substrate, which may cause some unexpected result for the reaction. Thus, we added 0.1 equiv of *tert*-butanol, CF_3CH_2OH (TFE) or $(CF_3)_2CHOH$ (HFIP) as an additive into the reaction system using acetonitrile as the solvent. However, we found that these additives did not improve the reaction outcomes (Table 3, entries 7–9). When the addition of NCS was divided into three portions, the desired product **15a** was formed in 90% yield and 55% ee (Table 3, entry 10).

With the determination of the optimal reaction conditions, the generality of this **L8**/Ni(II)-catalyzed asymmetric chlorination is examined using a variety of *N*-Boc-protected 3-aryloxindoles **13**. The results are summarized in Table 4. All reactions proceeded smoothly to give the corresponding products **3** in good yields and moderate to good ee values under the optimal conditions (Table 3). Whether R^1 is an electron-donating or -withdrawing group on electron-rich or -deficient aromatic rings, the reactions proceeded smoothly to give the corresponding adducts **15b**–**15k** in good yields and 55–88% ee values, respectively (Table 3, entries 1–10). Only in the cases of *N*-Boc-protected 3-aryloxindoles **13m**, **13n** and **13o** in which R^1 is CH_3O, H and CH_3, respectively, and R^2 is a *para*-methylphenyl group, the corresponding adducts **15m**, **15n** and **15o** were obtained in good yields along with low ee values (7–15% ee), perhaps due to the electronic property of R^1 and R^2 (Table 3, entries 12–14). It is plausible that the elimination and rebounding of the Cl anion can cause racemization, but we think that the electronic effect plays a more important role in this reaction because when R^1 and R^2 are both electron-rich groups, the ee values decreased significantly. When R^2 is an aliphatic group (R^2 = Me), the reaction also proceeded efficiently to afford the corresponding product **15l** in 86% yield and 20% ee (Table 3, entry 11). Changing the *N*-Boc-protecting group to an *N*-phenyl or *N*-benzyl group provided the corresponding products **15p** and **15q** in 47% yield and 52% yield, respectively, with no ee value, thus suggesting that the carbonyl group in the *N*-Boc-protecting group plays a significant role in this reaction (Table 4, entries 15 and 16). The spectroscopic data are summarized in Section 4 and their absolute configurations have been assigned as (*R*) by comparison of the sign of the specific rotation with the literature values.[7,8]

The possible transition state for this asymmetric chlorination of 3-substituted oxindole can be explained as the approach of NCS towards the hexacoordinated Ni(II) complex and 3-substituted oxindole as illustrated in Figure 2. The enolized 3-substituted oxindoles could react with NCS from the *Re* face to form the (*R*)-products in accordance with the experimental results.

3. Conclusion

In conclusion, axially chiral C_2-symmetric BINIM **L8** prepared from BINAM with quinoline-2-carbaldehyde was found to be a reasonably effective chiral ligand for the Ni(II)-promoted asymmetric chlorination of 3-substituted oxindoles to give the corresponding



Scheme 1. Synthesis of ligands **L9–L12**.

adducts in good yields and moderate to good enantioselectivities. Efforts are currently underway to elucidate the mechanistic details of this asymmetric chlorination of 3-substituted oxindoles and to disclose the exact structure of the active species in this catalytic system.

4. Experimental section

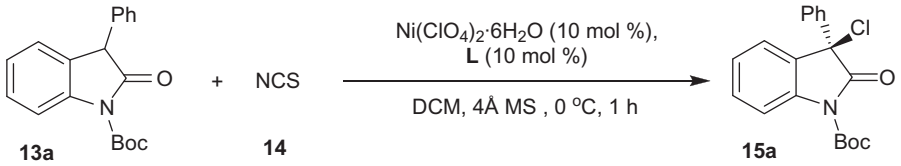
4.1. General methods

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined in a solution of $CHCl_3$ at 20 °C by using a Perkin–Elmer-341 MC polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. ^{1}H NMR spectra were recorded on a Bruker AM-300 or Bruker AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are given in Hertz. ^{19}F spectra were recorded on a Bruker AM-300 and AM-400 spectrophotometers with complete proton decoupling spectrophotometers. Mass spectra were recorded by EI, ESI, MALDI and HRMS was measured on an HP-5989 instrument. Infrared spectra were recorded on a Perkin–Elmer PE-983 spectrometer with absorption in cm^{-1}. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai $60F_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. All chlorinations were performed under argon using standard Schlenk techniques. The enantiomeric purities of compounds **15a–q** were determined by HPLC analysis using a chiral stationary phase column [column, Daicel Co. Chiralcel AD, AS, IC, OD and Regis (*S*,*S*)-Whelk-O1] and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation. 3-Substituted oxindoles **13a–q** were synthesized according to the previous literature.[10]

4.2. Typical procedure for the preparation of ligands L9–L12

Ligand **L9** was prepared by stirring (*R*)-BINAM (286 mg, 1.0 mmol), 8-ethylquinoline-2-carbaldehyde (389 mg, 2.1 mmol) and 4 Å MS (200 mg) in ethanol (30 mL) for 24 h at reflux. The hot solvent was then removed by filtration, after which an extra 10 mL ethanol were added to wash the filtration cake. The gray solid was redissolved in DCM (20 mL). After stirring for another 0.5 h, the 4 Å MS were filtered and the solvent was removed from the flask under reduced pressure to give the crude product. After a sin-

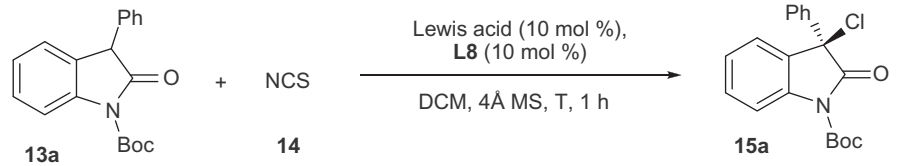
Table 1
Screening of chiral ligands for the asymmetric chlorination of 3-phenyloxindole **13a**



Entry[a]	Ligand	Yield[b] (%) **15a**	ee[c] (%) **15a**
1	**L1**	57	0
2	**L2**	63	26
3	**L3**	99	20
4	**L4**	76	22
5	**L5**	65	0
6	**L6**	79	16
7	**L7**	85	43
8	**L8**	92	81
9	**L9**	79	25
10	**L10**	92	10
11	**L11**	90	7
12	**L12**	90	7

[a] Reaction conditions: **13a** (0.1 mmol), **14** (0.12 mmol), $Ni(ClO_4)_2·6H_2O$ (10 mol %), ligand (10 mol %), DCM (1.0 mL), 4 Å MS (10 mg), and the reaction was carried out at 0 °C for 1 h.
[b] Isolated yield after column chromatography.
[c] Determined by chiral HPLC analysis.

Table 2
Examination of the metal salt and temperature effect for the asymmetric chlorination of 3-phenyloxindole **13a**



Entry[a]	Lewis acid	*T* (°C)	Yield[b] (%) **15a**	ee[c] (%) **15a**
1	$Ni(ClO_4)_2·6H_2O$	0	92	81
2	$Zn(OTf)_2$	0	4	15
3	$Ni(OAc)_2$	0	64	17
4	AgOAc	0	85	24
5	$Cu(OAc)_2$	0	Trace	0
6	CuOTf	0	74	0
7	$Ni(BF_4)_2·6H_2O$	0	94	82
8	$Ni(BF_4)_2·6H_2O$	20	88	81
9	$Ni(BF_4)_2·6H_2O$	−10	80	73
10	$Ni(BF_4)_2·6H_2O$	−20	68	55

[a] Reaction conditions: **13a** (0.1 mmol), **14** (0.12 mmol), metal (10 mol %), **L8** (10 mol %), DCM (1.0 mL), 4 Å MS (10 mg), and the reaction was carried out for 1 h.
[b] Isolated yield after column chromatography.
[c] Determined by chiral HPLC analysis.

gle recrystallization by DCM/petroleum ether to give **L9** as a yellow solid (540 mg, 87% yield).

The precursors of ligands **L10**–**L12** were prepared form (*R*)-H_8-BINAM according to the literature.[11] In the last step, toluene was used instead of ethanol compared with the preparation of **L9**. Ligands **L10**–**L12** were used directly without recrystallization.

4.2.1. Ligand L1

This is a known compound.[9] Yield: (90 mg, 39%). $[\alpha]_D^{20} = +161.8$ (*c* 0.50, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 7.25–7.31 (8H, m), 7.34–7.42 (10H, m), 7.90 (2H, d, *J* = 8.1 Hz), 7.95 (2H, d, *J* = 8.1 Hz), 8.18 (2H, s).

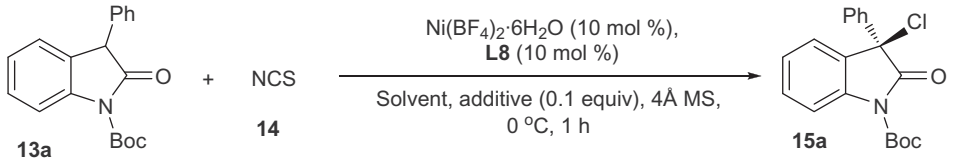
4.2.2. Ligand L2

This is a known compound.[9] Yield: (235 mg, 79%). $[\alpha]_D^{20} = +217.5$ (*c* 0.50, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 7.02 (2H, t, *J* = 7.8 Hz), 7.26–7.48 (12H, m), 7.92 (2H, d, *J* = 7.8 Hz), 7.98 (2H, d, *J* = 7.8 Hz), 8.63 (2H, s).

4.2.3. Ligand L3

This is a known compound.[9] Yield: (212 mg, 71%). $[\alpha]_D^{20} = -109.5$ (*c* 0.50, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 6.99–7.04 (2H, m), 7.09–7.12 (4H, m), 7.24–7.42 (8H, m), 7.90 (2H, d, *J* = 7.8 Hz), 7.99 (2H, d, *J* = 7.8 Hz), 8.63 (2H, s).

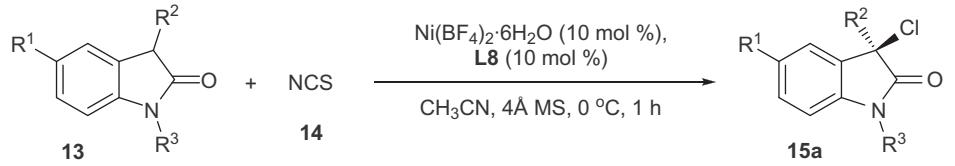
Table 3
Optimization of reaction conditions for the asymmetric chlorination of 3-phenyloxindole **13a**



Entry[a]	Solvent	Additive	Yield[b] (%) **15a**	ee[c] (%) **15a**
1	DCE	—	59	51
2	THF	—	85	70
3	CH_3CN	—	>99	85
4	Toluene	—	91	30
5	$CHCl_3$	—	76	37
6	Et_2O	—	98	38
7	CH_3CN	^tBuOH	92	75
8	CH_3CN	TFE	92	32
9	CH_3CN	HFIP	92	80
10[d]	CH_3CN	—	90	55

TFE = CH_3CH_2OH, HFIP = $(CF_3)_2CHOH$.
[a] Reaction conditions: **13a** (0.1 mmol), **14** (0.12 mmol), $Ni(BF_4)_2{\cdot}6H_2O$ (10 mol %), **L8** (10 mol %), solvent (1.0 mL), additive (0.1 equiv), 4 Å MS (10 mg) and the reaction was carried out for 1 h.
[b] Isolated yield after column chromatography.
[c] Determined by chiral HPLC analysis.
[d] NCS was added for three times.

Table 4
Scope and limitations of asymmetric chlorination of 3-substituted oxindoles **13**



Entry[a]	Oxindole **13** ($R^1/R^2/R^3$)	Yield[b] (%) **15**	ee[c] (%) **15**[d]
1	**13b** (CH_3/Ph/Boc)	**15b**, 88	67
2	**13c** (F/Ph/Boc)	**15c**, 99	88
3	**13d** (OCH_3/Ph/Boc)	**15d**, 82	82
4	**13e** (H/*p*-FC_6H_4/Boc)	**15e**, 92	74
5	**13f** (CH_3/*p*-FC_6H_4/Boc)	**15f**, 90	60
6	**13g** (F/*p*-$CH_3C_6H_4$/Boc)	**15g**, 90	75
7	**13h** (OCH_3/*p*-FC_6H_4/Boc)	**15h**, 84	72
8	**13i** (F/*p*-$CH_3C_6H_4$/Boc)	**15i**, 93	85
9	**13j** (H/*m*-$CH_3C_6H_4$/Boc)	**15j**, 92	72
10	**13k** (H/β-naphthyl/Boc)	**15k**, 78	52
11	**13l** (H/CH_3/Boc)	**15l**, 86	20
12	**13m** (OCH_3/*p*-$CH_3C_6H_4$/Boc)	**15m**, 83	15
13	**13n** (H/*p*-$CH_3C_6H_4$/Boc)	**15n**, 86	7
14	**13o** (CH_3/*p*-$CH_3C_6H_4$/Boc)	**15o**, 83	7
15	**13p** (H/Ph/Ph)	**15p**, 47	0
16	**13q** (H/Ph/Bn)	**15q**, 52	0

[a] Reaction conditions: **13** (0.1 mmol), **14** (0.12 mmol), $Ni(BF_4)_2{\cdot}6H_2O$ (10 mol %), **L8** (10 mol %), CH_3CN (1.0 mL), 4 Å MS (10 mg), and the reaction was carried out at 0 °C for 1 h.
[b] Isolated yield after column chromatography.
[c] Determined by chiral HPLC analysis.
[d] The absolute configuration of **15** has been assigned as (*R*)-configuration by comparison of the sign of optical rotation with the previous literature.

4.2.4. Ligand L4

This is a known compound.[9] Yield: (212 mg, 80%). $[\alpha]_D^{20} = +509.2$ (*c* 0.50, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 12.12 (s, 2H), 8.69 (s, 2H), 8.13 (d, *J* = 9.2 Hz, 2H), 8.00 (d, *J* = 8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.50–7.46 (m, 2H), 7.33–7.27 (m, 4H), 7.23–7.19 (M, 4H), 6.82–6.78 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 2H).

4.2.5. Ligand L5

This is a known compound.[9] Yield: (160 mg, 51%). $[\alpha]_D^{20} = -549.6$ (*c* 0.50, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 7.10 (2H, d, *J* = 2.4 Hz), 7.17 (2H, d, *J* = 8.4 Hz), 7.19–7.28 (4H, m), 7.49 (2H, t, *J* = 5.4 Hz), 7.61 (2H, d, *J* = 8.1 Hz), 7.98 (2H, d, *J* = 8.1 Hz), 8.11 (2H, d, *J* = 8.1 Hz), 8.56 (2H, s), 12.76 (2H, s).

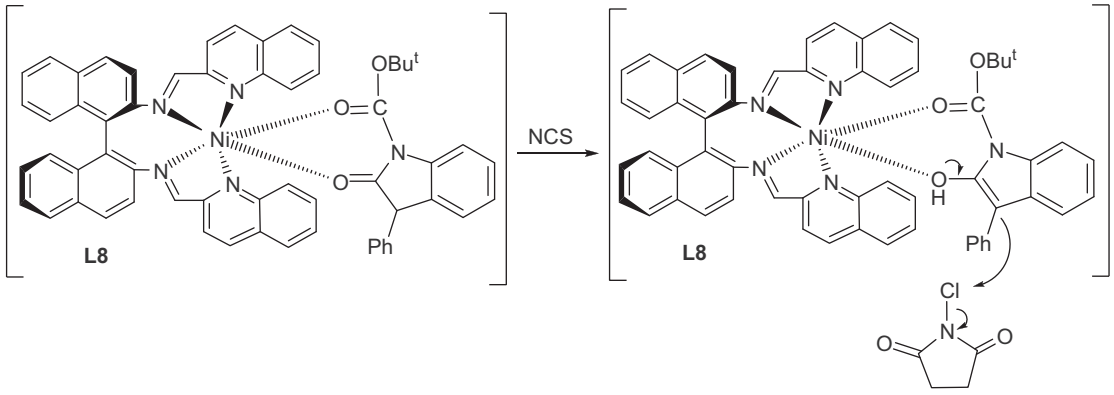


Figure 2. Proposed transition state for the enantioselectivity.

4.2.6. Ligand L6

This is a known compound.[9] Yield: (171 mg, 66%). $[\alpha]_D^{20} = -375.3$ (*c* 0.50, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.20 (6H, s), 6.62 (2H, d, *J* = 8.1 Hz), 6.98 (4H, d, *J* = 10.8 Hz), 7.22–7.30 (4H, m), 7.44 (2H, t, *J* = 7.5 Hz), 7.61 (2H, d, *J* = 8.1 Hz), 7.96 (2H, d, *J* = 8.4 Hz), 8.10 (2H, d, *J* = 8.4 Hz), 8.59 (2H, s), 11.85 (2H, s).

4.2.7. Ligand L7

This is a known compound.[9] Yield: (134 mg, 58%). $[\alpha]_D^{20} = +102$ (*c* 0.25, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 7.15–7.20 (3H, m), 7.24–7.33 (3H, m), 7.38–7.43 (4H, m), 7.45–7.52 (4H, m), 7.92 (2H, d, *J* = 8.1 Hz), 7.99 (2H, d, *J* = 8.1 Hz), 8.45 (2H, s), 8.48–7.51 (2H, m).

4.2.8. Ligand L8

This is a known compound.[9] Yield: (230 mg, 82%). $[\alpha]_D^{20} = +16.1$ (*c* 0.35, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 7.29–7.43 (6H, m), 7.51–7.64 (8H, m), 7.75 (2H, d, *J* = 8.1 Hz), 7.89 (2H, d, *J* = 8.7 Hz), 7.95 (4H, d, *J* = 8.7 Hz), 8.05 (2H, d, *J* = 9.0 Hz), 8.63 (s, 2H).

4.2.9. Ligand L9

Yield: (540 mg, 87%). A yellow solid, mp: 144–146 °C. $[\alpha]_D^{20} = +225$ (*c* 0.25, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 8.56 (s, 2H), 8.03–8.00, (m, 2H), 7.95–7.91 (m, 4H), 7.63–7.61 (m, 2H), 7.57–7.50 (m, 4H), 7.46–7.39 (m, 8H), 7.31–7.27 (m, 2H), 3.07–2.90 (m, 4H), 1.14–1.11 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 153.7, 147.8, 146.1, 143.5, 136.4, 133.5, 132.1, 129.2, 128.7, 127.9, 127.8, 127.7, 127.3, 127.1, 126.5, 125.4, 125.1, 118.5, 117.9, 24.1, 14.7; IR (neat) *v* 2962, 1936, 1593, 1569, 1501, 1207, 966, 844, 746 cm^{-1}; MS (ESI) *m/z* 641.3 ($M+Na^+$, 100); HRMS (ESI) calcd for $C_{44}H_{34}N_4$ requires ($M+Na^+$): 641.2681, found: 641.2696.

4.2.10. Ligand L10

Yield: (180 mg, 83%). A yellow solid, mp: 132–133 °C. $[\alpha]_D^{20} = -812$ (*c* 0.2, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 8.47 (s, 1H), 8.29–8.23 (m, 1H), 8.03–7.94 (m, 5H), 7.88–7.60 (m, 6H), 7.49–7.38 (m, 6H), 7.30–7.06 (m, 6H), 7.01 (s, 1H), 2.90–2.63 (m, 4H), 2.47–2.27 (m, 4H), 1.81–1.58 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 154.9, 147.6, 145.6, 139.9, 137.3, 136.2, 134.7, 133.7, 130.3, 129.9, 129.6, 129.4, 129.1, 128.7, 128.5, 127.8, 127.5, 127.2, 126.1, 118.2, 117.3, 29.6, 27.6, 23.3, 23.0; IR (neat) *v* 2930, 1710, 1592, 1500, 1462, 1204, 1051, 843, 745 cm^{-1}; MS (ESI) *m/z* 745.3 ($M+Na^+$, 100); HRMS (ESI) calcd for $C_{52}H_{42}N_4$ requires ($M+Na^+$): 745.3307, found: 745.3301.

4.2.11. Ligand L11

Yield: (140 mg, 78%). A yellow solid, mp: 107–109 °C. $[\alpha]_D^{20} = -769$ (*c* 0.25, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 8.43 (s, 2H), 8.08–8.03 (m, 4H), 7.92–7.90 (m, 1H), 7.85–7.81 (m, 1H), 7.78–7.76 (m, 2H), 7.70–7.64 (m, 2H), 7.53–7.49 (m, 2H), 6.99 (s, 2H), 6.94 (s, 4H), 6.70 (s, 2H), 2.79–2.64 (m, 4H), 2.44–2.30 (m, 4H), 2.13 (s, 12H), 1.72–1.62 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 155.1, 147.7, 139.7, 137.0, 136.2, 134.5, 133.5, 130.4, 130.3, 129.62, 129.55, 129.5, 129.4, 129.2, 128.8, 127.8, 127.7, 127.6, 127.2, 118.4, 117.4, 29.6, 27.6, 23.4, 23.1, 21.2; IR (neat) *v* 2970, 1937, 1594, 1501, 1203, 829, 749 cm^{-1}; MS (ESI) *m/z* 801.4 ($M+Na^+$, 100); HRMS (ESI) calcd for $C_{56}H_{50}N_4$ requires ($M+Na^+$): 801.3933, found: 801.3936.

4.2.12. Ligand L12

Yield: (130 mg, 86%). A yellow solid, mp: 119–121 °C. $[\alpha]_D^{20} = -462$ (*c* 0.3, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 8.39 (s, 1H), 8.19–8.13 (m, 2H), 8.03–8.01 (m, 2H), 7.95–7.90 (m, 4H), 7.83 (s, 3H), 7.79–7.65 (m, 4H), 7.59–7.51 (m, 4H), 7.44–7.38 (m, 1H), 6.95 (s, 1H), 2.84–2.58 (m, 4H), 2.40–2.20 (m, 4H), 1.68–1.57 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 154.1, 147.8, 145.6, 141.9, 137.3, 136.7, 136.5, 134.7, 131.4 (q, *J* = 33.2 Hz), 130.8, 130.44, 130.37, 130.2, 130.04, 130.01, 129.7 (q, *J* = 3.8 Hz), 129.1, 128.9, 128.7, 127.8, 127.6 (q, *J* = 3.8 Hz), 126.7, 123.3 (q, *J* = 271.3 Hz), 119.9, 119.8, 117.7, 117.3, 29.5, 27.9, 23.1, 22.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.7; IR (neat) *v* 2962, 1936, 1593, 1569, 1501, 1207, 966, 844, 746 cm^{-1}; MS (ESI) *m/z* 1017.3 ($M+Na^+$, 100); HRMS calcd for $C_{56}H_{38}F_{12}N_3$ ($M+Na^+$): 1017.2803, found: 1017.2809.

4.3. Typical reaction procedure for the chlorination of 3-substituted oxindoles

The catalyst was prepared by stirring $Ni(BF_4)_2{\cdot}6H_2O$ (3.4 mg, 0.01 mmol, 10 mol %), ligand **L8** (5.6 mg, 0.01 mmol, 10 mol %) and 4 Å MS (10 mg) in CH_3CN (1.0 mL) for 0.5 h under argon at room temperature. Next, the reaction mixture was cooled to 0 °C, after which 3-substituted oxindole **13** (0.1 mmol) and NCS **14** (0.12 mmol, 1.2 equiv) were added and the resulting mixture was stirred at 0 °C for 1 h. When the reaction was complete as monitored by TLC plate, the corresponding pure adduct was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1).

4.3.1. (*R*)-*tert*-Butyl 3-chloro-2-oxo-3-phenylindoline-1-carboxylate 15a

A pale yellow oil.[8] ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.52–7.50 (m, 2H), 7.48–7.42 (m, 2H), 7.38–7.35

(m, 3H), 7.30–7.26 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 149.0, 139.1, 136.3, 130.7, 129.1, 128.9, 128.6, 127.9, 126.1, 125.4, 115.6, 85.2, 66.5, 28.0; IR (neat) ν 2986, 1771, 1733, 1689, 1391, 1365, 1339, 1284, 1140, 722 cm^{-1}; $[\alpha]_D^{20} = -124$ (*c* 0.05, $CHCl_3$) for 85% ee; Chiralcel OJ-H, hexane/*i*PrOH = 90/10, 0.5 mL/min, 254 nm, t_{minor} = 11.50 min, t_{major} = 13.31 min.

4.3.2. (*R*)-*tert*-Butyl 3-chloro-5-methyl-2-oxo-3-phenylindoline-1-carboxylate 15b

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.45–7.42 (m, 2H), 7.30–7.28 (m, 3H), 7.18–7.14 (m, 2H), 2.30 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 149.0, 136.7, 136.5, 135.2, 131.3, 129.1, 128.9, 128.5, 127.8, 126.4, 115.4, 85.0, 66.8, 28.0, 21.0; IR (neat) ν 3333, 2948, 2837, 1747, 1713, 1489, 1381, 1206, 1010 cm^{-1}; MS (EI) *m/z* 357 (M^+, 1%), 257 (20), 222 (100), 207 (13), 194 (18), 165 (7), 57 (18); HRMS calcd for $C_{20}H_{20}ClNO_3$ (M^+): 357.1132, found: 357.1136; $[\alpha]_D^{20} = -77.7$ (*c* 1.0, $CHCl_3$) for 67% ee; Chiralcel AS-H, hexane/*i*PrOH = 99/1, 0.5 mL/min, 230 nm, t_{minor} = 8.88 min, t_{major} = 9.38 min.

4.3.3. (*R*)-*tert*-Butyl 3-chloro-5-fluoro-2-oxo-3-phenylindoline-1-carboxylate 15c

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.50–7.48 (m, 2H), 7.39–7.37 (m, 3H), 7.18–7.12 (m, 2H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 160.2 (d, *J* = 244.5 Hz), 148.9, 135.8, 135.0 (d, *J* = 1.8 Hz), 130.6 (d, *J* = 8.1 Hz), 129.4, 128.7, 127.6, 117.6 (d, *J* = 22.8 Hz), 117.2 (d, *J* = 7.7 Hz), 113.3 (d, *J* = 24.8 Hz), 85.3, 66.1 (d, *J* = 1.6 Hz), 28.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.8; IR (neat) ν 3091, 1778, 1734, 1483, 1339, 1293, 1262, 1144, 1098 cm^{-1}; MS (EI) *m/z* 361 (M^+, 1%), 261 (26), 226 (100), 198 (16), 170 (7), 57 (69), 41 (10); HRMS calcd for $C_{19}H_{17}ClFNO_3$ (M^+): 361.0881, found: 361.0886. $[\alpha]_D^{20} = -96.7$ (*c* 1.7, $CHCl_3$) for 88% ee; Chiralcel AS-H, hexane/*i*PrOH = 95/5, 0.5 mL/min, 214 nm, t_{minor} = 8.48 min, t_{major} = 8.93 min.

4.3.4. (*R*)-*tert*-Butyl 3-chloro-5-methoxy-2-oxo-3-phenylindoline-1-carboxylate 15d

A pale yellow oil.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.2 Hz, 1H), 7.53–7.50 (m, 2H), 7.38–7.36 (m, 3H), 7.00–6.95 (m, 2H), 3.81 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 157.4, 149.0, 136.3, 132.3, 129.9, 129.1, 128.6, 127.8, 116.7, 116.3, 111.2, 84.9, 66.8, 55.8, 28.0; IR (neat) ν 2982 1774, 1732, 1488, 1334, 1294, 1277, 1248, 1148, 1101, 1036, 1002 cm^{-1}; $[\alpha]_D^{20} = -101.3$ (*c* 1.35, $CHCl_3$) for 82% ee; Chiralcel OJ-H, hexane/*i*PrOH = 90/10, 0.5 mL/min, 230 nm, t_{major} = 14.42 -min, t_{minor} = 18.53 min.

4.3.5. (*R*)-*tert*-Butyl 3-chloro-3-(4-fluorophenyl)-2-oxoindoline-1-carboxylate 15e

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.52–7.42 (m, 4H), 7.31–7.28 (m, 1H), 7.07–7.02 (m, 2H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 163.1 (d, *J* = 247.5 Hz), 148.9, 139.1, 132.2 (d, *J* = 2.7 Hz), 130.9, 130.0 (d, *J* = 9.1 Hz), 128.5, 125.7 (d, *J* = 57.6 Hz), 115.7, 115.6, 115.4, 85.3, 65.8, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.2; IR (neat) ν 2984, 1777, 1733, 1507, 1467, 1340, 1287, 1249, 1144, 1093 cm^{-1}; MS (EI) *m/z* 361 (M^+, 1%), 261 (18), 226 (100), 198 (9), 170 (4), 57 (11); HRMS calcd for $C_{19}H_{17}ClFNO_3$ (M^+): 361.0881, found: 361.0889; $[\alpha]_D^{20} = -107.9$ (*c* 1.5, $CHCl_3$) for 74% ee; Chiralcel AS-H, hexane/*i*PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 13.04 min, t_{major} = 13.88 min.

4.3.6. (*R*)-*tert*-Butyl 3-chloro-3-(4-fluorophenyl)-5-methyl-2-oxoindoline-1-carboxylate 15f

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.52–7.48 (m, 2H), 7.27–7.22 (m, 2H), 7.07–7.03 (m, 2H), 2.39 (s, 3H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 163.1 (d, *J* = 248.4 Hz), 148.9, 136.7, 135.4, 132.3 (d, *J* = 3.4 Hz), 131.5, 130.0 (d, *J* = 8.6 Hz), 128.4, 126.3, 115.6 (d, *J* = 6.8 Hz), 115.4, 85.1, 66.1, 28.0, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.4; IR (neat) ν 2987, 1774, 1735, 1506, 1491, 1332, 1300, 1277, 1248, 1149, 1113 cm^{-1}; MS (EI) *m/z* 375 (M^+, 1%), 275 (13), 240 (100), 225 (11), 212 (28), 183 (7), 57 (7); HRMS calcd for $C_{20}H_{19}ClFNO_3$ (M^+): 375.1037, found: 375.1039; $[\alpha]_D^{20} = -87.0$ (*c* 1.6, $CHCl_3$) for 60% ee; Chiralcel AS-H, hexane/*i*PrOH = 95/5, 0.5 mL/min, 214 nm, t_{minor} = 8.13 min, t_{major} = 8.98 min.

4.3.7. (*R*)-*tert*-Butyl 3-chloro-5-fluoro-3-(4-fluorophenyl)-2-oxoindoline-1-carboxylate 15g

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.51–7.47 (m, 2H), 7.20–7.13 (m, 2H), 7.09–7.05 (m, 2H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 163.2 (d, *J* = 248.8 Hz), 160.2 (d, *J* = 244.0 Hz), 148.8, 135.0 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 3.4 Hz), 130.1 (d, *J* = 8.5 Hz), 129.8 (d, *J* = 8.5 Hz), 117.8 (d, *J* = 22.9 Hz), 117.4 (d, *J* = 7.5 Hz), 115.7 (d, *J* = 22.0 Hz), 113.2 (d, *J* = 24.8 Hz), 85.5, 65.5, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.7 (d, *J* = 2.26 Hz), −115.6 (d, *J* = 1.13 Hz); IR (neat) ν 2989, 1788, 1742, 1507, 1484, 1339, 1295, 1262, 1144, 802 cm^{-1}; MS (EI) *m/z* 379 (M^+, 1%), 279 (17), 244 (100), 216 (51), 188 (7), 169 (5), 57 (10); HRMS calcd for $C_{19}H_{16}ClF_2NO_3$ (M^+): 379.0787, found: 379.0790; $[\alpha]_D^{20} = -63.3$ (*c* 1.6, $CHCl_3$) for 75% ee; Chiralcel AD-H, hexane/*i*PrOH = 98/2, 0.5 mL/min, 230 nm, t_{minor} = 11.29 min, t_{major} = 13.40 min.

4.3.8. (*R*)-*tert*-Butyl 3-chloro-3-(4-fluorophenyl)-5-methoxy-2-oxoindoline-1-carboxylate 15h

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.2 Hz, 1H), 7.52–7.49 (m, 2H), 7.07–6.95 (m, 4H), 3.82 (s, 3H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 163.1 (d, *J* = 248.5 Hz), 157.4, 148.9, 132.3, 132.2 (d, *J* = 3.0 Hz), 130.0 (d, *J* = 7.7 Hz), 129.5, 116.6 (d, *J* = 40.9 Hz), 115.6, 115.4, 111.2, 85.1, 66.1, 55.7, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.3; IR (neat) ν 3111, 1770, 1726, 1687, 1485, 1333, 1295, 1278, 1249, 1148 cm^{-1}; MS (EI) *m/z* 391 (M^+, 2%), 291 (38), 256 (100), 242 (5), 228 (20), 213 (10), 185 (13), 57 (10); HRMS calcd for $C_{20}H_{19}ClFNO_4$ (M^+): 391.0987, found: 391.0995; $[\alpha]_D^{20} = -106.9$ (*c* 1.65, $CHCl_3$) for 72% ee; Chiralcel OD-H, hexane/*i*PrOH = 98/2, 0.7 mL/min, 230 nm, t_{major} = 7.68 min, t_{minor} = 8.43 min.

4.3.9. (*R*)-*tert*-Butyl 3-chloro-5-fluoro-2-oxo-3-(*p*-tolyl)indoline-1-carboxylate 15i

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.37 (d, *J* = 8.8, 2H), 7.19–7.13 (m, 4H), 2.35 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 160.1 (d, *J* = 243.9 Hz), 149.0, 139.5, 135.0, 132.8, 132.8, 130.7 (d, *J* = 9.2 Hz), 129.4, 127.6, 117.5 (d, *J* = 22.4 Hz), 117.2 (d, *J* = 7.8 Hz), 113.3 (d, *J* = 24.7 Hz), 85.3, 66.1, 28.0, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.9; IR (neat) ν 2988, 1780, 1734, 1483, 1340, 1294, 1262, 1144, 1096 cm^{-1}; MS (EI) *m/z* 375 (M^+, 1%), 275 (17), 240 (100), 212 (13), 57 (15); HRMS calcd for $C_{20}H_{19}ClFNO_3$ (M^+): 375.1037, found: 375.1039; $[\alpha]_D^{20} = -87.0$ (*c* 1.45, $CHCl_3$) for 85% ee; Chiralcel AD-H, hexane/*i*PrOH = 98/2, 0.5 mL/min, 214 nm, t_{minor} = 10.23 min, t_{major} = 11.73 min.

4.3.10. (*R*)-*tert*-Butyl 3-chloro-2-oxo-3-(*m*-tolyl)indoline-1-carboxylate 15j

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.47–7.40 (m, 2H), 7.35 (s, 1H), 7.30–7.23 (m, 3H), 7.17–7.15 (m, 1H), 2.35 (s, 3H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 149.0, 139.1, 138.4, 136.2, 130.6, 129.9, 129.1, 128.5, 128.4, 126.1, 125.4, 124.8, 115.6, 85.1, 66.6, 28.0, 21.5; IR (neat) ν 2984, 1771, 1734, 1490, 1332, 1278, 1152 cm^{-1}; MS (ESI) *m/z*: 380.1 [M+Na$^+$] HRMS calcd for $C_{20}H_{20}ClNO_3$ (M+Na$^+$): 380.1029,

found: 380.1029; $[\alpha]_D^{20} = -2.2$ (*c* 1.5, $CHCl_3$) for 72% ee; Chiralcel IC-H, hexane/*i*PrOH = 98/2, 0.7 mL/min, 230 nm, t_{minor} = 10.43 min, t_{major} = 11.53 min.

4.3.11. (*R*)-*tert*-Butyl 3-chloro-3-(naphthalen-2-yl)-2-oxoindoline-1-carboxylate 15k

A pale yellow solid. Mp: 146.1–147.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.88–7.74 (m, 5H), 7.53–7.48 (m, 4H), 7.34–7.30 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 148.9, 139.2, 133.6, 133.2, 132.5, 130.8, 128.8, 128.7, 128.5, 127.6, 127.3, 127.2, 126.6, 126.2, 125.5, 125.1, 115.7, 85.2, 66.8, 28.0; IR (neat) ν 3128, 1770, 1731, 1689, 1337, 1287, 1251, 1141, 1090, 757 cm^{-1}; MS (EI) *m/z* 393 (M^+, 1%), 316 (4), 293 (8), 259 (100), 230 (63), 215 (7), 202 (7), 57 (6); HRMS calcd for $C_{23}H_{20}ClNO_3$ (M^+): 393.1132, found: 393.1139; $[\alpha]_D^{20} = -45.9$ (*c* 1.5, $CHCl_3$) for 52% ee; Chiralcel IC-H, hexane/*i*PrOH = 98/2, 0.7 mL/min, 230 nm, t_{minor} = 10.43 min, t_{major} = 11.53 min.

4.3.12. (*R*)-*tert*-Butyl 3-chloro-3-methyl-2-oxoindoline-1-carboxylate 15l

A colourless oil.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.40–7.38 (m, 1H), 7.33–7.29 (m, 1H), 7.19–7.14 (m, 1H), 1.88, (s, 3H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 148.9, 138.2, 130.5, 129.8, 125.2, 123.8, 115.5, 85.0, 61.9, 28.0, 26.4; IR (neat) ν 2983, 1779, 1734, 1609, 1370, 1343, 1289, 1249, 1149, 842 cm^{-1}; $[\alpha]_D^{25} = -15.6$ (*c* 1.26, $CHCl_3$) (20% ee); Chiralcel AS-H, hexane/*i*PrOH = 200/1, 0.5 mL/min, 214 nm, t_{minor} = 10.15 min, t_{major} = 10.62 min.

4.3.13. (*R*)-*tert*-Butyl 3-chloro-5-methoxy-2-oxo-3-(*p*-tolyl) indoline-1-carboxylate 15m

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 4.4 Hz, 1H), 7.39 (d, *J* = 4.4 Hz, 2H), 7.18–7.16 (m, 2H), 6.99–6.95 (m, 2H), 3.81 (s, 3H), 2.34 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 157.3, 149.1, 139.3, 133.3, 132.3, 130.0, 129.3, 127.8, 116.7, 116.3, 111.2, 84.8, 66.8, 55.7, 28.0, 21.1; IR (neat) ν 2930, 1774, 1723, 1489, 1333, 1294, 1277, 1248, 1148, 1100 cm^{-1}; MS (EI) *m/z* 387 (M^+, 1%), 316 (4), 287 (26), 252 (100), 237 (5), 224 (11), 210 (11), 181 (6), 57 (7); HRMS calcd for $C_{21}H_{22}ClNO_4$ (M^+): 387.1237, found: 387.1243; $[\alpha]_D^{20} = -14.9$ (*c* 1.50, $CHCl_3$), for 72% ee; Regis (*S,S*)-Whelk-O1, hexane/*i*PrOH = 98/2, 0.6 mL/min, 214 nm, t_{major} = 22.78 min, t_{minor} = 37.48 min.

4.3.14. (*R*)-*tert*-Butyl 3-chloro-2-oxo-3-(*p*-tolyl)indoline-1-carboxylate 15n

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.47–7.38 (m, 4H), 7.30–7.28 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 149.0, 139.2, 139.1, 133.4, 130.6 129.2, 129.0, 127.8, 126.1, 125.3, 115.6, 85.0, 66.5, 28.0, 21.1; IR (neat) ν 2975, 1778, 1729, 1478, 1467, 1341, 1288, 1249, 1145, 1093 cm^{-1}; MS (EI) *m/z* 357 (M^+, 1%), 257 (17), 222 (100), 194 (9), 57 (12); HRMS calcd for $C_{20}H_{20}ClNO_3$ (M^+): 357.1132, found: 357.1139; $[\alpha]_D^{20} = -4.2$ (*c* 1.50, $CHCl_3$), for 7% ee; Chiralcel AS-H, hexane/*i*PrOH = 95/5, 0.5 mL/min, 214 nm, t_{minor} = 8.48 min, t_{major} = 8.93 min.

4.3.15. (*R*)-*tert*-Butyl 3-chloro-5-methyl-2-oxo-3-(*p*-tolyl) indoline-1-carboxylate 15o

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.22–7.17(m, 4H), 2.37 (s, 3H), 2.34 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 149.1, 139.2, 136.7, 135.2, 133.5, 131.3, 129.2, 128.9, 127.8, 126.4, 115.4, 84.9, 66.8, 28.0, 21.1, 21.0; IR (neat) ν 2982, 1776, 1733, 1490, 1333, 1298, 1276, 1248, 1150, 1108 cm^{-1}; MS (EI) *m/z* 371 (M^+, 1%), 271 (17), 236 (100), 208 (16), 194 (11), 57 (11); HRMS calcd for $C_{21}H_{22}ClNO_3$ (M^+): 371.1288, found: 371.1292; $[\alpha]_D^{20} = -4.6$ (*c* 0.70, $CHCl_3$), for 7% ee; Chiralcel AS-H, hexane/*i*PrOH = 95/5, 0.5 mL/min, 214 nm, t_{minor} = 8.08 min, t_{major} = 8.53 min.

4.3.16. (*R*)-3-Chloro-1,3-diphenylindolin-2-one 15p

A pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2H), 7.55–7.47 (m, 3H), 7.45–7.31 (m, 7H), 7.22–7.18 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 142.8, 136.7, 133.8, 130.3, 130.1, 129.7, 129.0, 128.6, 128.5, 127.6, 126.5, 126.3, 124.0, 110.2, 66.4; IR (neat) ν 2991, 1742, 1611, 1499, 1466, 1367, 1255, 1167, 1023, 796 cm^{-1}; MS (ESI) *m/z* 319.9 ($M+H^+$, 100); HRMS calcd for $C_{21}H_{14}ClNO$ ($M+H^+$): 320.0837, found: 320.0845; Chiralcel AD-H, hexane/*i*PrOH = 90/10, 0.7 mL/min, 230 nm, t_{minor} = 12.72 min, t_{major} = 18.92 min.

4.3.17. (*R*)-1-Benzyl-3-chloro-3-phenylindolin-2-one 15q

A pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.56 (m, 2H), 7.42 (m, 5H), 7.32–7.24 (m, 5H), 7.14–7.10 (m, 1H); 6.79–6.77 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 141.9, 136.6, 135.1, 130.3, 128.9, 128.6, 127.8, 127.5, 127.3, 127.13, 127.08, 126.0, 123.7, 110.0, 66.3, 44.2; IR (neat) ν 3032, 1733, 1612, 1488, 1358, 1189, 1030, 798, 694 cm^{-1}; MS (ESI) *m/z* 334.0 ($M+H^+$, 100); HRMS calcd for $C_{21}H_{16}ClNO$ ($M+H^+$): 334.0993, found: 334.0993; Chiralcel AS-H, hexane/*i*PrOH = 80/20, 0.7 mL/min, 214 nm, t_{minor} = 11.29 min, t_{major} = 12.45 min.

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