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Asymmetric Chlorination of Cyclic β-Keto Esters and *N*-Boc Oxindoles Catalyzed by an Iron(III)-BPsalan Complex

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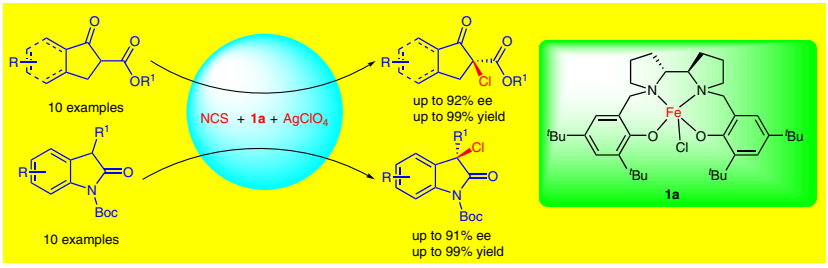

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Abstract An iron(III)-BPsalan complex was found to efficiently catalyze the asymmetric chlorination reaction of cyclic β-keto esters and *N*-Boc oxindoles, affording the corresponding chlorinated products in high yield and up to 92% ee with NCS as chlorination reagent under mild reaction conditions.

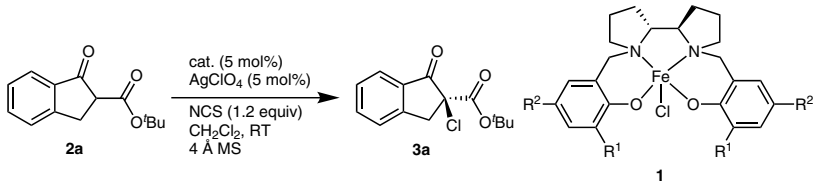
Key words iron catalysis, BPsalan ligand, asymmetric chlorination, cyclic β-keto ester, *N*-Boc oxindole, asymmetric bromination

α-Chlorinated carbonyl compounds are important structure motifs found in various biologically active natural products and can be used as valuable synthetic intermediates with numerous applications.[1,2] The direct chlorination of carbonyl compounds with either metal complexes or organocatalysts as catalyst is the most straightforward method for the construction of α-chlorinated carbonyl compounds.[3] In the past decades, a panel of metal and organo catalysts have been developed and applied in the asymmetric electrophilic chlorination of 1,3-dicarbonyl derivatives such as β-keto esters[4] and *N*-Boc oxindoles,[5] which led to enantiomer-enriched chlorinated products bearing one tertiary or quaternary stereocenter. Despite the recent progress in this area, it is still of great interest to develop new catalytic system with readily available, cheap, and nontoxic catalyst to meet the need of sustainable and green catalysis. Iron is environmentally benign and one of the most earth-abundant transition metals and its application in C–H functionalization has been receiving growing interest.[6] In our endeavor to develop practical iron-catalyzed organic reactions,[7] recently we have reported the synthesis of a series of novel Fe(III)-Bpsalan complexes and their application in highly efficient asymmetric fluorination and hydroxylation reaction of β-keto esters and *N*-Boc oxindoles.[8,9] Herein we report the application of these iron complexes as efficient catalysts in the asymmetric chlorination of β-keto esters and *N*-Boc oxindoles to give the corresponding chlorinated products in excellent yield and up to 92% ee under mild reaction conditions.

Initially the catalytic chlorination reactions were explored with cyclic β-keto ester **2a** (0.15 mmol) as the model substrate and *N*-chlorosuccinimide (NCS, 1.2 equiv) as a chlorination reagent, in the presence of 5 mol% of the iron complexes and 5 mol% $AgClO_4$ in CH_2Cl_2 (1 mL) with 4Å MS (100 mg) at room temperature. All the iron complexes **1a–g** showed high activity in the chlorination reactions, the in situ generated cationic complexes efficiently prompted the reactions to afford the α-chlorinated product **3a** in high yields, while the ee values of **3a** were significantly affected by the R^1 and R^2 substituents in the iron complexes (Table 1). When complex **1a** with two *tert*-butyl substituents was used as catalyst, **3a** was obtained in 95% yield and 85% ee (Table 1, entry 1). To our surprise, when the previously best catalyst complex **1b** in asymmetric fluorination and hydroxylation reaction[9] was used as catalyst, both the yield and ee value of **3a** dropped (entry 2). When complex **1c** with two Br substituents was used, a much lower ee value of 45% was obtained (entry 3). When R^2 was changed to sterically less hindered F and Cl, even lower ee values were obtained (entries 4, 5). Changing R^1 to phenyl led to a moderate 70% ee (entry 6), while when the sterically more hindered adamantanyl group was incorporated only racemic product was obtained (entry 7).

With **1a** as catalyst, various chlorination reagents were tested in the asymmetric chlorination reaction (Scheme 1). The results revealed that NCS and its analogue *N*-chloro-

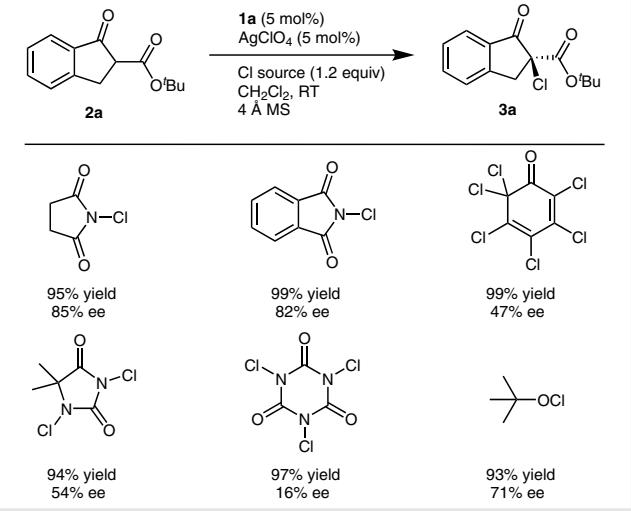
Table 1 Screening of Catalysts[a]



Entry	Cat.	R^1	R^2	Yield (%)[b]	ee (%)[c]
1	**1a**	^{t}Bu	^{t}Bu	95	85
2	**1b**	^{t}Bu	Br	86	74
3	**1c**	Br	Br	93	45
4	**1d**	^{t}Bu	F	98	11
5	**1e**	^{t}Bu	Cl	93	7
6	**1f**	Ph	Br	99	70
7	**1g**	Ad	Br	95	0

[a] Reaction conditions: substrate (0.15 mmol), catalyst (5 mol%), $AgClO_4$ (5 mol%), and NCS (1.2 equiv) were stirred in CH_2Cl_2 with 4Å MS at room temperature under an argon atmosphere.
[b] Isolated yield.
[c] Determined by chiral HPLC.

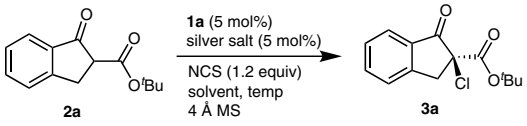
phthalimide were the best to afford **3a** in excellent yield and high ee (85% and 82% ee, respectively), while the other chlorination reagents were less selective to afford **3a** with only low to moderate ee. As NCS is cheap and readily available, we chose NCS as the chlorination reagent in the subsequent investigation.



Scheme 1 Screening of various chlorination reagents

The effect of solvent and additive in the chlorination reaction were also explored. As can be seen from Table 2, the chlorination reaction underwent well in all the common organic solvents screened to afford **3a** in high yield, but only dichloromethane gave the best ee of 85% and the other sol-

Table 2 Optimization of Reaction Conditions[a]



Entry	Solvent	Silver salt	Temp (°C)	Yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	$AgClO_4$	25	95	85
2	toluene	$AgClO_4$	25	89	40
3	$CHCl_3$	$AgClO_4$	25	99	34
4	MeCN	$AgClO_4$	25	99	70
5	Et_2O	$AgClO_4$	25	99	72
6	THF	$AgClO_4$	25	99	7
7[d]	CH_2Cl_2	$AgClO_4$	25	99	18
8	CH_2Cl_2	–	25	91	5
9	CH_2Cl_2	AgOTf	25	94	83
10	CH_2Cl_2	NaBArF	25	99	70
11	CH_2Cl_2	AgOAc	25	98	4
12	CH_2Cl_2	NaOPiv	25	97	16
13	CH_2Cl_2	$AgClO_4$	0	98	90
14	CH_2Cl_2	$AgClO_4$	–20	99	92
15	CH_2Cl_2	$AgClO_4$	–40	90	78

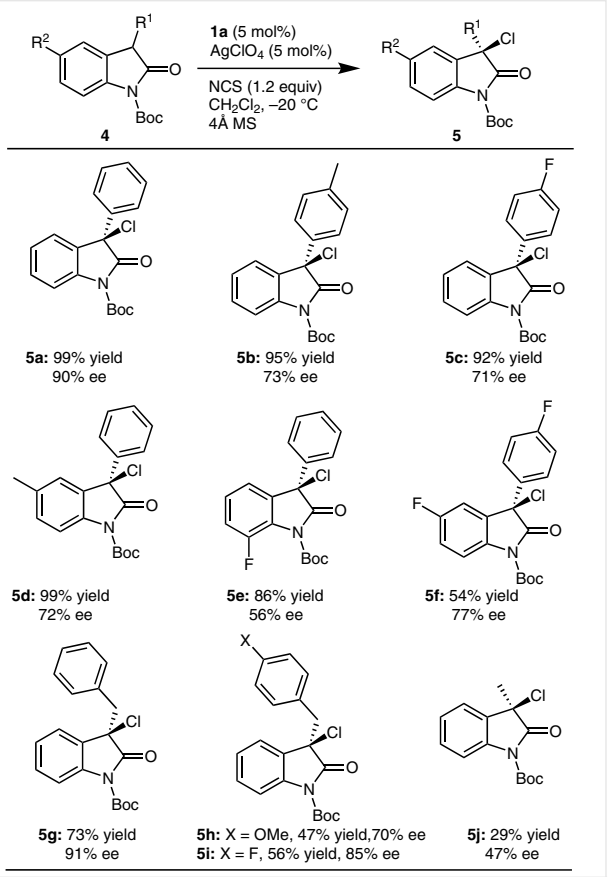
[a] Reaction conditions: substrate (0.15 mmol), cat. (5 mol%), silver salt (5 mol%), and NCS (1.2 equiv) were stirred in CH_2Cl_2 with 4Å MS at the indicated temperature under an argon atmosphere.
[b] Isolated yield.
[c] Determined by chiral HPLC.
[d] Without 4Å MS.

vents such as toluene, chloroform, acetonitrile, diethyl ether, or THF gave only low to moderate ee (Table 2, entries 1–6). It is noteworthy that the addition of 4Å MS was essential for achieving a high ee value for **3a**: when the reaction was carried out without 4Å MS, the ee value of **3a** dropped significantly to 18% (entry 7). And the addition of silver salts was also critical for better chirality induction. When the reaction was done without addition of silver salts, almost racemic **3a** was obtained (entry 8). This may be attributed to the higher activity of the cationic in situ formed active catalyst upon addition of silver salts with non-coordination counter anion, which suppressed the non-selective background reaction. This is supported by the fact that silver salt with non-coordinative counter anion gave better results than that of silvers salts with coordinative counter anion (entries 1, 9, 10 vs entries 11, 12) and $AgClO_4$ gave the best result. Lowering the reaction temperature to –20 °C further improved the ee value of **3a** to 92% (entry 14).

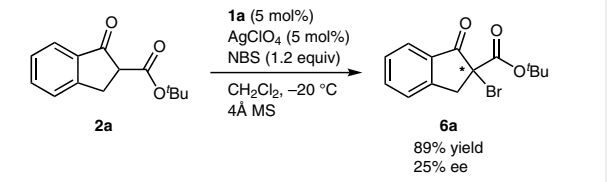
With the established optimized reactions conditions at hand, the asymmetric chlorination of various cyclic β-keto esters **2a–j** was investigated; the corresponding products **3a–j** are depicted in Table 3. In contrast to the Fe(III)-BPsalan complexes catalyzed asymmetric fluorination reaction of cyclic β-keto esters, the substituents on the phenyl ring can affect the ee value of the chlorinated product significantly. Cyclic β-keto ester **2b** with the electron-donating methyl group underwent the reaction smoothly to afford **3b** in 97% yield and 86% ee (Table 3, entry 2), while **3c**,**d** with electron-withdrawing Cl group led to relative lower ee (entries 3, 4). It is interesting that substrates **3e**,**f** with strong electron-donating methoxy group also led to only moderate ee (entries 5, 6). This might be attributed to the possible coordination of the methoxy group to the catalyst, thus led to lower ee of the chlorination product. The size of the ester group also played important role in the reaction and the sterically more hindered ester group led to higher ee than the smaller ones (entry 1 vs entries 7, 8). The six-membered ring cyclic β-keto ester **2i** also underwent the reaction well to afford **3i** in 84% yield and 76% ee (entry 9). Cyclic β-keto ester **2j** was also suitable substrate for the chlorination reaction to afford the product **3j** in high yield and 83% ee (entry 10). Noncyclic β-keto ester **2k** was inactive to the reaction and only trace amount of product was formed after 24 hours (entry 11).

With the successful application of iron complex **1a** in asymmetric chlorination of cyclic β-keto esters, we turned our attention to the asymmetric chlorination of *N*-Boc oxindoles, as the corresponding chiral chlorinated products could be useful intermediates for the synthesis of 3,3′-disubstituted chiral oxindole derivatives, which are important structure motifs found in natural products and pharmaceuticals. To our delight, various *N*-Boc oxindole derivatives **4a–j** were suitable substrates under the same reaction conditions to afford the corresponding chlorinated products in high yields and moderate to high ee (Scheme 2). 3-Phenyl-substituted oxindole **4a** underwent the reaction smoothly to afford the chlorinated product in quantitative yield and 90% ee. 3-Aryl-substituted oxindole derivatives **4b–f** were also efficiently chlorinated to afford **5b–f** in good yields and moderate to good ee. It is noteworthy that 3-benzyl-substituted oxindoles **4g–i** were also suitable substrates in the asymmetric chlorination reaction to afford the products **5g–i** in 47–73% yields and 70–91% ee. 3-Methyl-substituted substrate **4j** was less efficient in the asymmetric chlorination reaction to afford **5j** in much lower yield and ee.

In addition to the chlorination reaction, we also tried one example of bromination reaction of cyclic β-keto ester **2a** catalyzed by iron complex **1a** with $AgClO_4$ as additive and NBS as a bromination reagent (Scheme 3). The bromi-

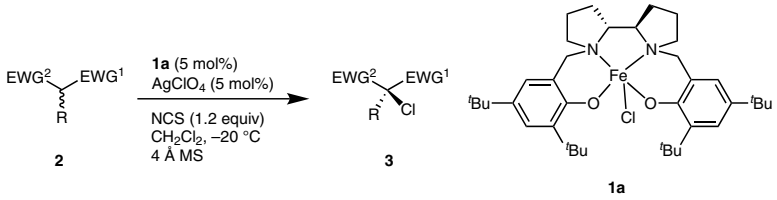


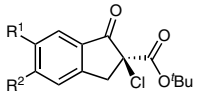
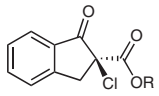
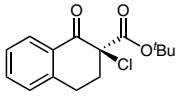
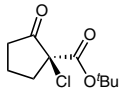
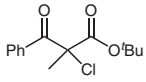
Scheme 2 Iron complex **1a**-catalyzed asymmetric chlorination of *N*-Boc oxindoles



Scheme 3 Asymmetric bromination reaction of cyclic β-keto ester **2a**

Table 3 Iron Complex **1a**-Catalyzed Asymmetric Chlorination of β-Keto Esters[a]



Entry		Product	Yield (%)[b]	ee (%)[c]
1		**3a**: R^1 = H, R^2 = H	99	92
2		**3b**: R^1 = Me, R^2 = H	97	86
3		**3c**: R^1 = Cl, R^2 = H	99	64
4		**3d**: R^1 = H, R^2 = Cl	93	79
5		**3e**: R^1 = OMe, R^2 = H	97	66
6		**3f**: R^1 = OMe, R^2 = OMe	99	77
7		**3g**: R = Me	81	53
8		**3h**: R = Et	91	48
9		**3i**	84	76
10		**3j**	83	83
11		**3k**	<5%	–

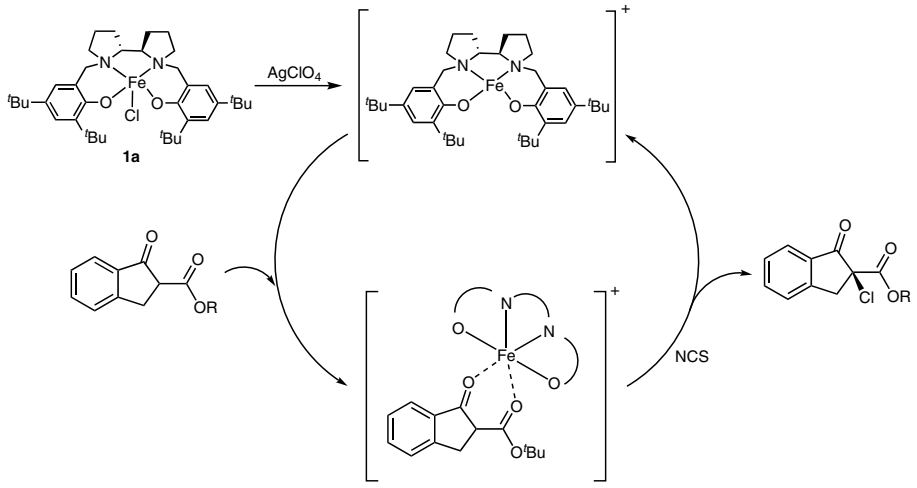
[a] Reaction conditions: substrate (0.15 mmol), catalyst (5 mol%), $AgClO_4$ (5 mol%), and NCS (1.2 equiv) were stirred in CH_2Cl_2 with 4Å MS at –20 °C under an argon atmosphere.
[b] Isolated yield.
[c] Determined by chiral HPLC or GC.

nated product **6a** was obtained in 89% yield albeit with a lower ee of 25%, maybe due to the strong background reaction.

A plausible mechanism for the iron(III)-BPsalan complex catalyzed asymmetric chlorination reaction is proposed and depicted in Scheme 4. Similar to that of the previously reported fluorination reaction, iron complex **1a** was converted in situ into an active cationic intermediate upon addition of $AgClO_4$, which subsequently coordinate to the substrate to form the 'chiral-at-iron' intermediate and further reaction with NCS to give the desired enantiomer enriched chlorination product.

In conclusion, we have developed an efficient and practical iron(III)-BPsalan complex catalyzed asymmetric chlorination of both cyclic β-keto ester and *N*-Boc oxindole derivatives. The corresponding chlorinated products were obtained in high yields and moderate to good ee under mild reaction conditions with cheap NCS as chlorination reagent. Moreover, preliminary result revealed that the iron(III)-BPsalan could also catalyze the asymmetric bromination reaction of cyclic β-keto ester and the optimization of the this reaction is currently underway in our laboratory.

All manipulations were carried out using standard Schlenk line or dry-box techniques under an argon atmosphere. All reactions were carried out with anhydrous solvents unless otherwise noted. Solvents were dried and freshly distilled under an argon atmosphere. Flash chromatography (FC) was performed with Merck silica gel 60 (230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (300 MHz) or Agilent 400 (400 MHz) spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to TMS. Chemical shifts (δ values) were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference. Standard abbreviations are used to indicate multiplicity. Coupling constants were reported in hertz (Hz). Low-resolution mass spectra were obtained with Agilent GC-MS 5975C and Agilent 1100 LC-MSD SL. High-resolution mass spectra (HRMS) were measured on an Agilent



Scheme 4 Plausible mechanism of the asymmetric chlorination catalyzed by **1a**

Technologies 6224 TOF LC/MS spectrometer. HRMS/LRMS were obtained in ESI/EI mode. Chiral HPLC analysis was performed on a DIONEX UltiMate 3000, No. 8074238, ThermoScientific. Chiral GC analysis was performed on an Agilent GC 7820 equipment. Optical rotations were measured on an Autopol I polarimeter. (*R*,*R*)-2,2′-Bipyrrolidine was synthesized according to the literature procedures.[10,11] All iron complexes and β-keto esters were synthesized according to the literature procedures.[9] All *N*-Boc oxindoles were synthesized according to the literature procedures.[5d,9] NCS and NBS were purchased from commercial sources and used as received without further purification. All other reagents were commercially available and used as received. The absolute configurations of products were assigned by comparing HPLC data and optical rotations with those of the known compound reported in the literature, or by analogy.

Asymmetric Chlorination of Cyclic β-Keto Esters and *N*-Boc Oxindoles Catalyzed by Iron Complex 1a; General Procedure

A mixture of iron complex **1a** (5 mol%, 0.0075 mmol), $AgClO_4$ (5 mol%, 0.0075 mmol), and 4Å molecular sieves (100 mg) in CH_2Cl_2 (1 mL) under an argon atmosphere was stirred at r.t. for 1 h. After cooling the reaction to –20 °C, the β-keto ester or *N*-Boc oxindole (0.15 mmol) was added and stirred for 20 min, then NCS or NBS (1.2 equiv, 0.18 mmol) was added in one portion at once. The reaction mixture was stirred until completion (monitored by TLC, hexane/EtOAc 5:1). The mixture was filtered and the filtrate was concentrated under vacuum and the product was isolated by flash column chromatography (hexane/EtOAc 5:1).

tert-Butyl (*S*)-2-Chloro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (3a)[4h]

Yield: 40 mg (99%); colorless solid; mp 76–78 °C; $[\alpha]_D^{33}$ +29.4 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak OJ-H, hexane/*i*-PrOH (95:5), 0.7 mL/min, 254 nm, t_R (major) = 13.7 min, t_R (minor) = 17.0 min; 92% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.85 (d, *J* = 7.6 Hz, 1 H, ArH), 7.68 (t, *J* = 7.3 Hz, 1 H, ArH), 7.46 (m, *J* = 8.9 Hz, 2 H, ArH), 4.02 (d, *J* = 17.7 Hz, 1 H, CH_2), 3.54 (d, *J* = 17.7 Hz, 1 H, CH_2), 1.43 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 284.1 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{19}ClNO_3^+$ ($[M + NH_4]^+$): 284.1048; found: 284.1051.

tert-Butyl (*S*)-2-Chloro-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3b)[4l]

Yield: 41 mg (97%); pale yellow oil; $[\alpha]_D^{25}$ +21.9 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (9:1), 0.7 mL/min, 214 nm, t_R (major) = 6.9 min, t_R (minor) = 7.2 min; 86% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64 (s, 1 H, ArH), 7.50 (d, *J* = 7.7 Hz, 1 H, ArH), 7.36 (d, *J* = 7.8 Hz, 1 H, ArH), 3.96 (d, *J* = 17.6 Hz, 1 H, CH_2), 3.48 (d, *J* = 17.6 Hz, 1 H, CH_2), 2.43 (s, 3 H, CH_3), 1.43 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 298.1 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{21}ClNO_3^+$ ($[M + NH_4]^+$): 298.1204; found: 298.1202.

tert-Butyl (+)-2,6-Dichloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3c)

Yield: 45 mg (99%); pale yellow oil; $[\alpha]_D^{25}$ +13.2 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (9:1), 0.7 mL/min, 214 nm, t_R (major) = 7.1 min, t_R (minor) = 6.7 min; 64% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (s, 1 H, ArH), 7.69–7.60 (d, *J* = 8.1 Hz, 1 H, ArH), 7.43 (d, *J* = 8.1 Hz, 1 H, ArH), 3.98 (d, *J* = 17.8 Hz, 1 H, CH_2), 3.49 (d, *J* = 17.8 Hz, 1 H, CH_2), 1.44 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.4, 165.5, 148.8, 136.3, 134.9, 134.4, 127.5, 125.5, 84.8, 69.0, 43.2, 27.8.

MS (ESI): *m*/*z* = 318.0 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}Cl_2NO_3^+$ ($[M + NH_4]^+$): 318.0658; found: 318.0657.

tert-Butyl (*S*)-2,5-Dichloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3d)[4l]

Yield: 42 mg (93%); pale yellow oil; $[\alpha]_D^{25}$ +20.7 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak ID-3, hexane/*i*-PrOH (95:5), 0.7 mL/min, 214 nm, t_R (major) = 5.3 min, t_R (minor) = 5.8 min; 79% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (d, *J* = 8.2 Hz, 1 H, ArH), 7.48 (s, 1 H, ArH), 7.44 (d, *J* = 8.2 Hz, 1 H, ArH), 4.00 (d, *J* = 17.9 Hz, 1 H, CH_2), 3.51 (d, *J* = 17.9 Hz, 1 H, CH_2), 1.44 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 318.0 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}Cl_2NO_3^+$ ($[M + NH_4]^+$): 318.0658; found: 318.0659.

tert-Butyl (*S*)-2-Chloro-6-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3e)[4l]

Yield: 43 mg (97%); pale yellow oil; $[\alpha]_D^{33}$ +10.5 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (9:1), 0.7 mL/min, 214 nm, t_R (major) = 8.1 min, t_R (minor) = 7.7 min; 66% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36 (d, *J* = 8.0 Hz, 1 H, ArH), 7.27 (m, 2 H, ArH), 3.93 (d, *J* = 17.4 Hz, 1 H, CH_2), 3.86 (s, 3 H, OCH_3), 3.46 (d, *J* = 17.4 Hz, 1 H, CH_2), 1.43 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 314.1 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{21}ClNO_4^+$ ($[M + NH_4]^+$): 314.1154; found: 314.1154.

tert-Butyl (*S*)-2-Chloro-5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3f)[4f]

Yield: 48 mg (99%); pale yellow oil; $[\alpha]_D^{33}$ +20.1 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (9:1), 0.7 mL/min, 214 nm, t_R (major) = 14.7 min, t_R (minor) = 13.5 min; 77% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.23 (s, 1 H, ArH), 6.89 (s, 1 H, ArH), 4.00 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 3.93 (d, *J* = 20 Hz, 1 H, CH_2), 3.45 (d, *J* = 17.5 Hz, 1 H, CH_2), 1.44 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 344.1 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{23}ClNO_5^+$ ($[M + NH_4]^+$): 344.1259; found: 344.126.

Methyl (*S*)-2-Chloro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (3g)[4n]

Yield: 27 mg (81%); pale yellow oil; $[\alpha]_D^{25}$ +33.5 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (9:1), 0.7 mL/min, 214 nm, t_R (major) = 10.9 min, t_R (minor) = 11.5 min; 53% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (d, *J* = 7.6 Hz, 1 H, ArH), 7.71 (t, *J* = 7.4 Hz, 1 H, ArH), 7.48 (t, *J* = 8.4 Hz, 2 H, ArH), 4.11 (d, *J* = 17.8 Hz, 1 H, CH_2), 3.82 (s, 3 H, OCH_3), 3.57 (d, *J* = 17.8 Hz, 1 H, CH_2).

MS (ESI): *m*/*z* = 242.0 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{13}ClNO_3^+$ ($[M + NH_4]^+$): 242.0578; found: 242.0578.

Ethyl (*S*)-2-Chloro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (3h)[4o]

Yield: 32 mg (91%); colorless oil; $[\alpha]_D^{33}$ +30.5 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (9:1), 0.7 mL/min, 214 nm, t_R (major) = 12.0 min, t_R (minor) = 12.7 min; 48% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (d, *J* = 7.6 Hz, 1 H, ArH), 7.71 (t, *J* = 7.3 Hz, 1 H, ArH), 7.48 (t, *J* = 8.9 Hz, 2 H, ArH), 4.27 (q, *J* = 7.0 Hz, 2 H, CH_2Me), 4.10 (d, *J* = 17.8 Hz, 1 H, $ArCH_2$), 3.57 (d, *J* = 17.8 Hz, 1 H, $ArCH_2$), 1.27 (t, *J* = 7.1 Hz, 3 H, CH_3).

MS (ESI): *m*/*z* = 256.0 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{15}ClNO_3^+$ ($[M + NH_4]^+$): 256.0735; found: 256.0737.

tert-Butyl (*S*)-2-Chloro-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (3i)[4o]

Yield: 35 mg (84%); pale yellow oil; $[\alpha]_D^{26}$ +9.8 (*c* = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak ID-3, hexane/*i*-PrOH (95:5), 0.7 mL/min, 214 nm, t_R (major) = 5.9 min, t_R (minor) = 6.7 min; 76% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (d, *J* = 7.6 Hz, 1 H, ArH), 7.53 (t, *J* = 7.2 Hz, 1 H, ArH), 7.35 (t, *J* = 7.2 Hz, 1 H, ArH), 7.27 (d, *J* = 7.1 Hz, 1 H, ArH), 3.25 (m, 1 H, CH_2), 3.10–2.86 (m, 2 H, CH_2), 2.50 (m, 1 H, CH_2), 1.46 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 298.1 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{21}ClNO_3^+$ ($[M + NH_4]^+$): 298.1204; found: 298.1204.

tert-Butyl (*S*)-1-Chloro-2-oxocyclopentanecarboxylate (3j)[4f]

Yield: 27 mg (83%); colorless oil; $[\alpha]_D^{26}$ +4.1 (*c* = 1.00, CH_2Cl_2).

GC: cp-chiralsil-DEX CB, T_1 = 90 °C, t_1 = 70 min, v_1 = 5 °C/min, T_2 = 120 °C, t_2 = 10 min, v_2 = 20 °C /min, T_3 = 200 °C, t_3 = 5 min, t_R (major) = 60.2 min, t_R (minor) = 61.9 min; 83% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.71 (m, 1 H, CH_2), 2.59–2.46 (m, 1 H, CH_2), 2.38 (m, 2 H, CH_2), 2.11 (m, 2 H, CH_2), 1.49 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 236.1 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{10}H_{19}ClNO_3^+$ ($[M + NH_4]^+$): 236.1048; found: 236.105.

tert-Butyl (*R*)-3-Chloro-2-oxo-3-phenylindoline-1-carboxylate (5a)[5d]

Yield: 51 mg (99%); pale yellow oil; $[\alpha]_D^{27}$ –77.8 (*c* = 0.96, CH_2Cl_2).

HPLC: Daicel Chiralpak OJ-H, hexane/*i*-PrOH (9:1), 1.0 mL/min, 254 nm, t_R (major) = 8.7 min, t_R (minor) = 7.0 min; 90% ee.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.00 (d, *J* = 8.1 Hz, 1 H, ArH), 7.57–7.23 (m, 8 H, ArH), 1.63 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 361.1 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{22}ClN_2O_3^+$ ($[M + NH_4]^+$): 361.1313; found: 361.1312.

tert-Butyl (*R*)-3-Chloro-2-oxo-3-*p*-tolylindoline-1-carboxylate (5b)[5d]

Yield: 51 mg (95%); pale yellow oil; $[\alpha]_D^{27}$ –53.2 (*c* = 0.85, CH_2Cl_2).

HPLC: Daicel Chiralpak OJ-H, hexane/*i*-PrOH (9:1), 1.0 mL/min, 254 nm, t_R (major) = 12.3 min, t_R (minor) = 6.8 min; 73% ee.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.00 (d, *J* = 8.1 Hz, 1 H, ArH), 7.51–7.35 (m, 4 H, ArH), 7.29 (t, *J* = 7.6 Hz, 1 H, ArH), 7.18 (d, *J* = 7.8 Hz, 2 H, ArH), 2.35 (s, 3 H, CH_2), 1.63 [s, 9 H, $C(CH_3)_3$].

MS (ESI): *m*/*z* = 375.1 $[M + NH_4]^+$.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{24}ClN_2O_3^+$ ($[M + NH_4]^+$): 375.147; found: 375.147.

tert-Butyl (*R*)-3-Chloro-3-(4-fluorophenyl)-2-oxoindoline-1-carboxylate (5c)[5d]

Yield: 50 mg (92%); colorless oil; $[\alpha]_D^{26}$ –75.6 (*c* = 1.00, CH_2Cl_2).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.99 (d, *J* = 8.2 Hz, 1 H, ArH), 7.58–7.37 (m, 4 H, ArH), 7.35–7.23 (m, 1 H, ArH), 7.04 (t, *J* = 8.6 Hz, 2 H, ArH), 1.62 [s, 9 H, $C(CH_3)_3$].

HPLC: Daicel Chiralpak OJ-H, hexane/*i*-PrOH (9:1), 0.3 mL/min, 254 nm, t_R (major) = 28.1 min, t_R (minor) = 25.2 min; 71% ee.

MS (ESI): m/z = 279.1 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{19}H_{21}ClFN_2O_3^+$ ([M + NH_4]$^+$): 379.1219; found: 379.1218.

***tert*-Butyl (*R*)-3-Chloro-5-methyl-2-oxo-3-phenylindoline-1-carboxylate(5d)**[5d]

Yield: 53 mg (99%); pale yellow oil; $[\alpha]_D^{27}$ –0.2 (c = 0.725, CH_2Cl_2).

HPLC: Daicel Chiralpak IC-3, hexane/*i*-PrOH (99:1), 0.7 mL/min, 214 nm, t_R (major) = 19.3 min, t_R (minor) = 17.8 min; 72% ee.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.87 (d, J = 8.2 Hz, 1 H, ArH), 7.59–7.46 (m, 2 H, ArH), 7.42–7.30 (m, 3 H, ArH), 7.29–7.19 (m, 2 H, ArH), 2.38 (s, 3 H, CH_3), 1.63 [s, 9 H, $C(CH_3)_3$].

MS (ESI): m/z = 375.1 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{20}H_{24}ClN_2O_3^+$ ([M + NH_4]$^+$): 375.147; found: 375.1468.

***tert*-Butyl (*R*)-3-Chloro-7-fluoro-2-oxo-3-phenylindoline-1-carboxylate (5e)**[5d]

Yield: 47 mg (86%); pale yellow oil; $[\alpha]_D^{27}$ –52.3 (c = 0.84, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (96:4), 0.7 mL/min, 214 nm, t_R (major) = 8.7 min, t_R (minor) = 9.4 min; 56% ee.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.57–7.45 (m, 2 H, ArH), 7.43–7.31 (m, 3 H, ArH), 7.30–7.14 (m, 3 H, ArH), 1.60 [s, 9 H, $C(CH_3)_3$].

MS (ESI): m/z = 379.1 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{19}H_{21}ClFN_2O_3^+$ ([M + NH_4]$^+$): 379.1219; found: 379.1217.

***tert*-Butyl (*R*)-3-Chloro-5-fluoro-3-(4-fluorophenyl)-2-oxoindoline-1-carboxylate (5f)**[5d]

Yield: 31 mg (54%); yellow oil; $[\alpha]_D^{27}$ –75.0 (c = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (96:4), 0.7 mL/min, 214 nm, t_R (major) = 7.2 min, t_R (minor) = 6.1 min; 77% ee.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.00 (dd, J = 8.8, 4.4 Hz, 1 H, ArH), 7.54–7.41 (m, 2 H, ArH), 7.22–7.10 (m, 2 H, ArH), 7.06 (t, J = 8.6 Hz, 2 H, ArH), 1.61 [s, 9 H, $C(CH_3)_3$].

MS (ESI): m/z = 397.1 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{19}H_{20}ClF_2N_2O_3^+$ ([M + NH_4]$^+$): 397.1125; found: 397.1122.

***tert*-Butyl (*R*)-3-Chloro-3-benzyl-2-oxoindoline-1-carboxylate (5g)**[5d]

Yield: 39 mg (73%); yellow oil; $[\alpha]_D^{27}$ –6.6 (c = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak AD-H, hexane/*i*-PrOH (96:4), 0.7 mL/min, 214 nm, t_R (major) = 7.0 min, t_R (minor) = 6.6 min; 91% ee.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (d, J = 8.1 Hz, 1 H, ArH), 7.31 (dd, J = 17.8, 7.9 Hz, 2 H, ArH), 7.24–7.04 (m, 4 H, ArH), 6.94 (d, J = 6.6 Hz, 2 H, ArH), 3.58 (q, J = 13.3 Hz, 2 H, CH_2), 1.58 [s, 9 H, $C(CH_3)_3$].

MS (ESI): m/z = 375.1 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{20}H_{24}ClN_2O_3^+$ ([M + NH_4]$^+$): 375.147; found: 375.1468.

***tert*-Butyl (–)-3-Chloro-3-(4-methoxybenzyl)-2-oxoindoline-1-carboxylate (5h)**

Yield: 27 mg (47%); pale yellow oil; $[\alpha]_D^{26}$ –10.1 (c = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak OD-H, hexane/*i*-PrOH (96:4), 0.7 mL/min, 214 nm, t_R (major) = 7.8 min, t_R (minor) = 8.8 min; 70% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66 (d, J = 8.1 Hz, 1 H, ArH), 7.30 (dt, J = 15.5, 7.6 Hz, 2 H, ArH), 7.19 (t, J = 7.5 Hz, 1 H, ArH), 6.85 (d, J = 8.3 Hz, 2 H, ArH), 6.64 (d, J = 8.4 Hz, 2 H, ArH), 3.71 (s, 3 H, OCH_3), 3.52 (q, J = 13.5 Hz, 2 H, CH_2), 1.59 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.0, 159.0, 148.6, 139.0, 131.7, 130.5, 127.7, 125.1, 125.0, 124.8, 115.3, 113.6, 84.9, 65.5, 55.2, 45.3, 28.1.

MS (ESI): m/z = 405.1 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{21}H_{26}ClN_2O_4^+$ ([M + NH_4]$^+$): 405.1573; found: 405.1576.

***tert*-Butyl (–)-3-Chloro-3-(4-fluorobenzyl)-2-oxoindoline-1-carboxylate (5i)**

Yield: 32 mg (56%); pale yellow oil; $[\alpha]_D^{27}$ –9.8 (c = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak OD-H, hexane/*i*-PrOH (96:4), 0.7 mL/min, 214 nm, t_R (major) = 6.5 min, t_R (minor) = 7.0 min; 85% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.67 (d, J = 8.1 Hz, 1 H, ArH), 7.31 (dd, J = 22.0, 10.2 Hz, 2 H, ArH), 7.20 (t, J = 7.5 Hz, 1 H, ArH), 6.96–6.86 (m, 2 H, ArH), 6.80 (t, J = 8.2 Hz, 2 H, ArH), 3.55 (q, J = 13.4 Hz, 2 H, CH_2), 1.59 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.8, 163.5, 148.5, 139.0, 132.2 (d, J = 8.1 Hz), 130.6, 128.9, 127.3, 124.9 (d, J = 8.1 Hz), 115.4, 115.2, 115.0, 85.1, 65.3, 45.3, 28.1.

^{19}F NMR ($CDCl_3$, 282 MHz): δ = –114.91 to –115.20 (m).

MS (ESI): m/z = 393.1 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{20}H_{23}ClFN_2O_3^+$ ([M + NH_4]$^+$): 393.1376; found: 393.1374.

***tert*-Butyl (–)-3-Chloro-3-methyl-2-oxoindoline-1-carboxylate (5j)**[5d]

Yield: 12 mg (29%); pale yellow oil; $[\alpha]_D^{27}$ –32.6 (c = 0.15, $CHCl_3$).

HPLC: Daicel Chiralpak OJ-H, hexane/*i*-PrOH (95:5), 0.5 mL/min, 220 nm, t_R (major) = 11.31 min, t_R (minor) = 10.15 min; 47% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (d, J = 8.3 Hz, 1 H, ArH), 7.46 (dd, J = 7.5, 0.9 Hz, 1 H, ArH), 7.38 (td, J = 8.0, 1.4 Hz, 1 H, ArH), 7.22 (dd, J = 7.6, 0.9 Hz, 1 H, ArH), 1.95 (s, 3 H, CH_3), 1.65 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.4, 149.0, 138.3, 130.6, 129.9, 125.3, 123.9, 115.6, 85.2, 62.0, 28.1, 26.6.

MS (ESI): m/z = 299.1 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{14}H_{20}ClN_2O_3^+$ (M + NH_4^+): 299.1157; found: 299.1151.

***tert*-Butyl 2-Bromo-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (6a)**[12]

Yield: 42 mg (89%); colorless oil; $[\alpha]_D^{26}$ +6.2 (c = 1.00, CH_2Cl_2).

HPLC: Daicel Chiralpak OJ-H, hexane/*i*-PrOH (95:5), 0.7 mL/min, 254 nm, t_R (major) = 17.0 min, t_R (minor) = 21.1 min; 25% ee.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.86 (d, J = 7.8 Hz, 1 H, ArH), 7.69 (t, J = 7.4 Hz, 1 H, ArH), 7.46 (m, 2 H, ArH), 4.13 (d, J = 18.1 Hz, 1 H, CH_2), 3.66 (d, J = 18.1 Hz, 1 H, CH_2), 1.46 [s, 9 H, $C(CH_3)_3$].

MS (ESI): m/z = 328.0 [M + NH_4]$^+$.

HRMS (ESI): m/z calcd for $C_{14}H_{19}BrNO_3^+$ ([M + NH_4]$^+$): 328.0543; found: 328.054.

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Supporting Information

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