Iron(III)-BPsalan complexes catalyzed asymmetric chlorination of cyclic β-keto esters and *N*-Boc oxindoles

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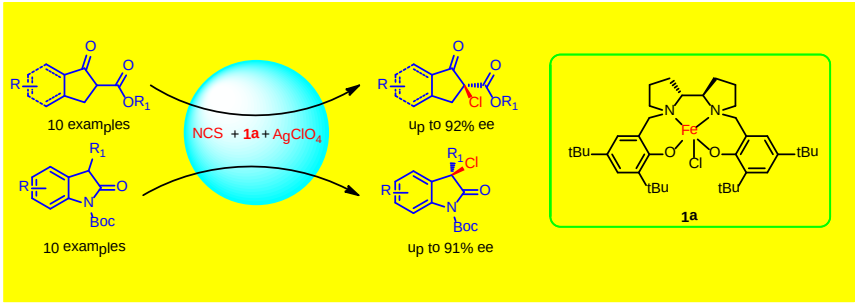

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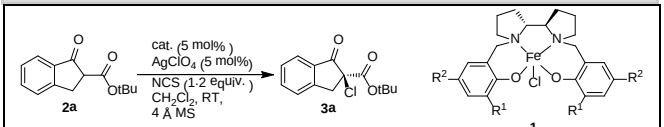
Abstract An efficient iron(III)-BPsalan complexes catalyzed asymmetric chlorination reaction of cyclic β-keto esters and *N*-Boc oxindoles was developed to afford the corresponding chlorinated products in high yield and up to 92% ee with NCS as chlorination reagent under mild reaction conditions.

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

α-Chlorinated carbonyl compounds are important structure motif found in various biological active natural products and can be used as valuable synthetic intermediates with numerous application.[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 an environmentally benign and one of the most earth abundant transition metal and their application in C-H functionalization has been receiving growing interest.[6] In our endeavor to develop practical iron-catalysed 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 at mild reaction conditions.

Table 1 Screen of catalysts[a]

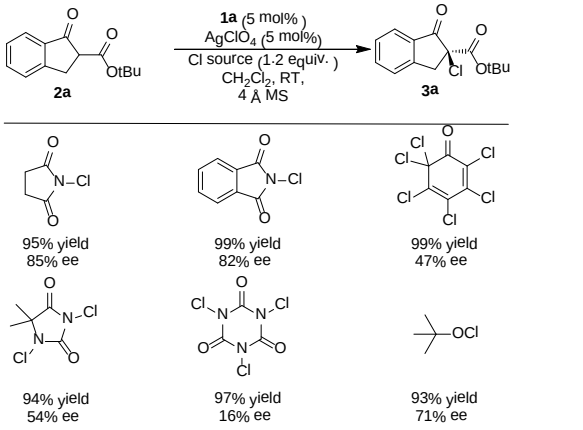


entry	Cat.	R^1	R^2	yield[b] (%)	ee[c] (%)
1	**1a**	^{t}Bu	^{t}Bu	95	85
2	**1b**	^{t}Bu	Br	86	74
3	**1c**	Br	Br	93	45
4	**1d**	^{t}Bu	F	98	11
5	**1e**	^{t}Bu	Cl	93	7
6	**1f**	Ph	Br	99	70
7	**1g**	Ad	Br	95	0

[a] Reaction conditions: substrates (0.15 mmol), cat. (5 mol%) and NCS (1.2 eq.) were stirred in DCM with 4Å MS at room temperature under Ar atmosphere. [b] isolated yield. [c] determined by chiral HPLC.

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 eq.) 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**-**1g** showed high activity in the chlorination reactions, the in-situ generated cationic complexes efficiently prompted the reactions to afford α-chlorinated product **3a** in high yields, while the ee values of **3a** were significantly affected by the R1 and R2 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 of **3a** dropped (Table 1, entry 2). When complex **1c** with two Br substituents was used, a much lower ee of 45% was obtained (Table 1, entry 3). When R2 was changed to steric less

hindered F and Cl, even lower ee were obtained (Table 1, entries 4-5). Changing R1 to phenyl led to a moderate 70% ee (Table 1, entry 6) while when the sterically more hindered adamantanyl group was incorporated only racemic product was obtained (Table 1, entry 7).



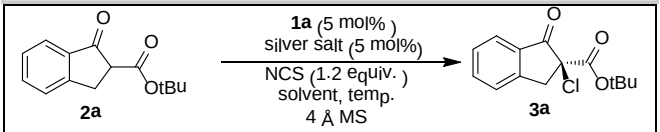
Scheme 1 Screen of various chlorination reagents

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*-chlorophthalimide 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.

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 DCM gave the best ee of 85% and the other solvents such as toluene, chloroform, acetonitrile, 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 high ee of **3a**, when the reaction was done without 4Å MS the ee value of **3a** dropped significantly to 18% (Table 2, 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 (Table 2, 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 (Table 2, 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% (Table 2, entry 14).

With the established optimized reactions conditions at hand, the asymmetric chlorination of various cyclic β-keto esters **2a-2j** was investigated; the corresponding products **3a-3j** 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-3d** with electron withdrawing Cl group led to relative lower ee (Table 3, entries 3-4). It is interesting that substrates **3e-3f** with strong electron donating methoxy group also led to only moderate ee (Table 3, 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 (Table 3, entry 1 *vs* entries 7-8). The six-member ring cyclic β-keto ester **2i** also underwent the reaction well to afford **3i** in 84% yield and 76% ee (Table 3, 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 (Table 3, entry 10). Non-cyclic β-keto ester **2k** was inactive to the reaction and only trace amount of product was formed after 24 h (Table 3, entry 11).

Table 2 Optimization of reaction conditions[a]



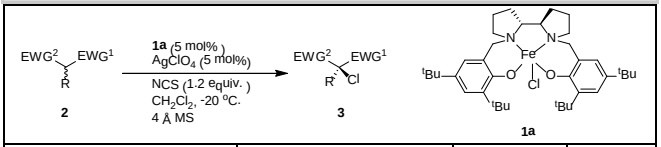
entry	solvent	Silver salt	Temp. (°C)	yield[b] (%)	ee[c] (%)
1	DCM	$AgClO_4$	25	95	85
2	toluene	$AgClO_4$	25	89	40
3	$CHCl_3$	$AgClO_4$	25	99	34
4	MeCN	$AgClO_4$	25	99	70
5	Et_2O	$AgClO_4$	25	99	72
6	THF	$AgClO_4$	25	99	7
7[d]	DCM	$AgClO_4$	25	99	18
8	DCM	-	25	91	5
9	DCM	AgOTf	25	94	83
10	DCM	NaBArF	25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

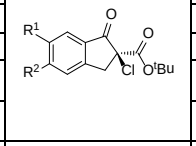
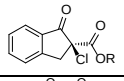
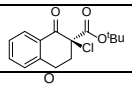
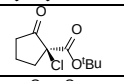
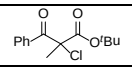
[a] Reaction conditions: substrates (0.15 mmol), cat. (5 mol%) and NCS (1.2 eq.) were stirred in DCM with 4Å MS at room temperature under Ar atmosphere.
[b] isolated yield.
[c] determined by chiral HPLC.
[d] without 4Å MS

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 motif found in natural products and pharmaceuticals. To our delight, various *N*-Boc oxindole derivatives **4a-4j** were suitable substrates

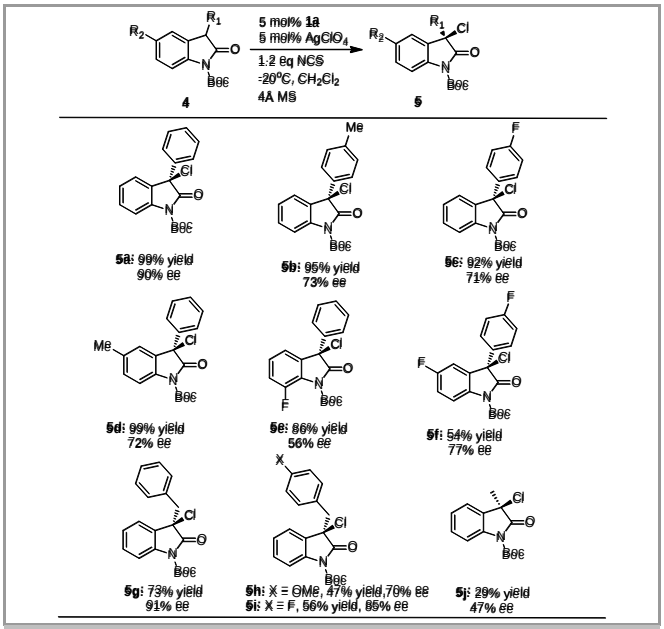
under the same reaction conditions to afford the corresponding chlorinated product in high yield and moderate to high ee (Scheme 2). 3-Phenyl substituted oxindole **4a** underwent the reaction smoothly to afford the chlorinated product in quantitative yield and 90% ee. 3-Aryl substituted oxindole derivatives **4b**-**4f** were also efficiently chlorinated to afford **5b**-**5f** in good yield and moderate to good ee. It is noteworthy that 3-benzyl substituted oxindoles **4g**-**4i** were also suitable substrates in the asymmetric chlorination reaction to afford the products **5g**-**5i** in 47%-73% yield and 70% to 91% ee. 3-Methyl substituted substrate **4j** was less efficient in the asymmetric chlorination reaction to afford **5j** in much lower yield and ee.

Table 3 iron complex **1a** catalyzed asymmetric chlorination of β-keto esters

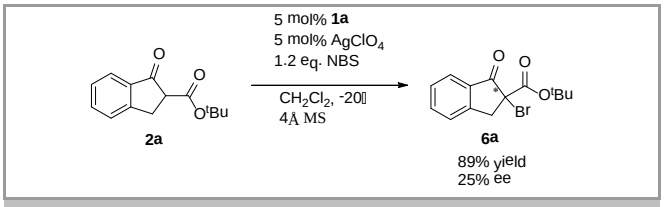


Entry		Product	Yield [b] (%)	ee[c] (%)
1		**3a**: R^1 = H, R^2 = H	99	92
2		**3b**: R^1 = Me, R^2 = H	97	86
3		**3c**: R^1 = Cl, R^2 = H	99	64
4		**3d**: R^1 = H, R^2 = Cl	93	79
5		**3e**: R^1 = OMe, R^2 = H	97	66
6		**3f**: R^1 = OMe, R^2 = OMe	99	77
7		**3g**: R = Me	81	53
8		**3h**: R = Et	91	48
9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

[a]Reaction conditions: substrates (0.15 mmol), cat. (5 mol%), AgClO4 (5 mol%) and NCS (1.2 eq.) were stirred in DCM with 4Å MS at -20 °C under Ar atmosphere;
[b] Isolated yield;
[c] Determined by chiral HPLC or GC.

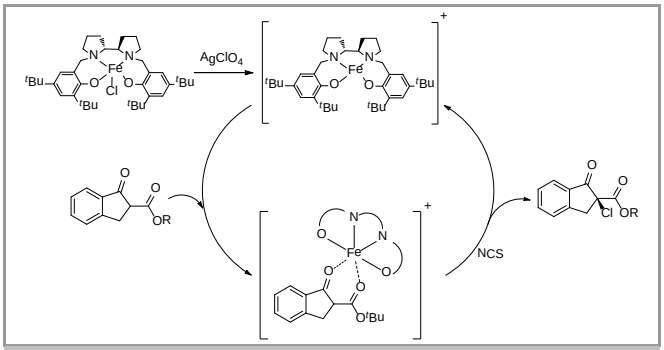


Scheme 2 iron complex **1a** catalyzed asymmetric chlorination of *N*-Boc oxindoles



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

A plausible mechanism for the iron(III)-BPsalan complex **1a** 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 to 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.



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

In conclusion, we have developed an efficient and practical iron(III)-BPsalan complex catalyzed asymmetric chlorination of both cyclic β-keto esters and *N*-Boc oxindoles 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 lab.

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All manipulations were carried out using standard Schlenk line or drybox techniques under dry 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 tetramethylsilane (TMS). Chemical shifts (δ values) were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained with Agilent GC-MS 5975C, Agilent 1100 LC-MSD SL. High resolution mass spectra (HRMS) were measured on a Agilent 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 a 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[9,5d]. N-chlorosuccinimide (NCS) and N-bromosuccinimide (NBS) were purchased from commercial sources and used as received without further purifications. All other reagents were commercially available and used as received. The absolute configurations of products was assigned by comparing HPLC data and Optical rotations with those of the known compound reported in the literature, or by analogy.

Procedures

General procedure for the asymmetric chlorination of cyclic β-keto esters and *N*-Boc oxindoles catalyzed by iron complex **1a:**

A solution of iron complex (5 mol%, 0.0075 mmol), $AgClO_4$ (5 mol%, 0.0075 mmol) and 4Å molecular sieves (100 mg) in DCM (1 mL) under an argon atmosphere was stirred at room temperature for 1 h. After the reaction was cooled 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 eq., 0.18 mmol) was added in one portion at once. The reaction was stirred until completion (monitored by TLC, hexane/EtOAc = 5/1). The reaction mixture was filtered and the filtrate was concentrated under vacuum and the product was isolated by flash column chromatography (hexane/EtOAc = 5/1).

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

Yield: 40 mg (99%); colorless solid; mp 76-78°C; $[\alpha]^{33}_D$ = +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.

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

Yield: 41 mg (97%); pale yellow oil; $[\alpha]^{25}_D$ = +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-1H-indene-2-carboxylate (**3c**):

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

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

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

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

Yield: 43 mg (97%); pale yellow oil; $[\alpha]^{33}_D$ = +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, 2H, 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.

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

Yield: 48 mg (99%); pale yellow oil; $[\alpha]^{33}_D$ = +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, 9H, $C(CH_3)_3$).

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.

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

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

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

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

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

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

(*S*)-*t*-Butyl 1-chloro-2-oxocyclopentanecarboxylate(**3j**)[4f]

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

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

Yield: 51 mg (99%); pale yellow oil; $[\alpha]^{27}_D$ = -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.

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

Yield: 51 mg (95%), pale yellow oil; $[\alpha]^{27}_D$ = -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.

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

Yield: 50 mg (92%); colorless oil; $[\alpha]^{26}_D$ = -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 analysis: 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.

(*R*)-*tert*-butyl 3-chloro-5-methyl-2-oxo-3-phenlindoline-1-carboxylate(**5d**)[5d]

Yield: 53 mg (99%); pale yellow oil; $[\alpha]^{27}_D$ = -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.

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

Yield: 47 mg (86%); pale yellow oil; $[\alpha]^{27}_D$ = -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.

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

Yield: 31 mg (54%); yellow oil; $[\alpha]^{27}_D$ = -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.

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

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

HPLC analysis: 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; $[\alpha]^{26}_D$ = -10.1 (*c* = 1.00, CH_2Cl_2).

HPLC analysis: 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, OMe), 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; $[\alpha]^{27}_D$ = -9.8 (*c* = 1.00, CH_2Cl_2).

HPLC analysis: 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 – -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; $[\alpha]^{27}_D$ = -32.6 (*c* = 0.15, $CHCl_3$).

HPLC analysis: 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; $[\alpha]^{26}_D$ = +6.2 (*c* = 1.00, CH_2Cl_2).

HPLC analysis: 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

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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