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Enantioselective Squaramide-Catalysed Domino Mannich–Cyclization Reaction of Isatin Imines

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Keywords: Organocatalysis / Asymmetric catalysis / Domino reactions / Nucleophilic addition / Oxygen heterocycles / Cyclization

An enantioselective domino reaction of 4-bromo-3-oxobutanoates with isatin-derived ketimines was developed to construct 3-amino-2-oxindoles with a quaternary stereocentre. In the presence of 1 mol-% of a bifunctional squaramide organocatalyst, the desired products were achieved in high yields (90–97 %) and with excellent enantioselectivities (92–99 % *ee*).

Introduction

The enantioselective addition of carbon nucleophiles to the C=N double bond of imines is one of the most direct methods to prepare optically active nitrogen-containing compounds. Due to the strategic importance of chiral amines and their derivatives in organic synthesis, tremendous efforts have been put into the development of catalytic asymmetric addition reactions of imines over the past decades.[1] Although great progress has been made in the addition reactions of aldimines (imines derived from aldehydes), the use of ketimines (imines derived from ketones) as electrophiles, which would lead to the enantioselective construction of quaternary stereocentres, remains challenging.[2,3] The reaction of isatin-derived ketimines has recently been the subject of great interest in the field of asymmetric catalysis.[4,5]

The reaction of isatin-derived ketimines as electrophiles gives a very straightforward approach to 3-substituted 3-amino-2-oxindoles,[6] which are privileged structural motifs that are found in many biologically active compounds and drug candidates.[7] Several catalytic asymmetric addition reactions of isatin-derived ketimines, including Mannich reactions,[5a–5c] Strecker reactions,[5d–5f] and several other reactions,[5g–5k] have been reported. However, to the best of our knowledge, the asymmetric domino reaction of isatin-derived ketimines has only rarely been reported in the literature.[5i–5k] As part of our ongoing interest in the asymmetric synthesis of 3,3-disubstituted 2-oxindoles by the addition of carbon nucleophiles to isatin derivatives,[8] in this paper, we report the enantioselective domino reaction of isatin-derived ketimines with 4-bromo-3-oxobutanoates[9] catalysed by tertiary-amine-based chiral bifunctional organocatalysts.[10]

Results and Discussion

We initially evaluated cinchona alkaloids catalysts for the domino reaction between isatin-derived *N*-Boc ketamine **1a** (Boc = *tert*-butyloxycarbonyl) and ethyl 4-bromoacetoacetate (**2a**). The reactions were carried out in toluene with $NaHCO_3$ as a scavenger of HBr at 25 °C for 3 d, and the results are summarized in Table 1. Cinchonine and quinidine gave the desired product (i.e., **3a**) with enantioselectivities higher than those seen with cinchonidine and quinine (Table 1, entries 1–4). However, cinchonine and cinchonidine had better catalytic activities than quinine and quinidine. The use of *O*-benzyl cinchonine derivative **C1** resulted in a poor conversion rate and negligible enantioselectivity (Figure 1; Table 1, entry 5), indicating that the presence of hydrogen-bond donors might be essential for this domino reaction. To improve the enantioselectivity of the reaction, we used tertiary-amine–thiourea and squaramide catalysts with a cinchona alkaloid scaffold.[11,12] Quinine-derived thiourea **C2** gave similar results to quinine (Table 1, cf. entries 6 and 3). Although excellent enantioselectivity was achieved with bifunctional squaramides **C3** and **C4** as catalysts, the yields of the reactions were unsatisfactory. Takemoto catalyst **C5** hardly catalysed the domino reaction (Table 1, entry 9).

In most of the cases described above (Table 1, entries 3–8), the low yields might have resulted from the low conversion rate of the substrates and/or the Mannich adducts. Fortunately, when Na_2CO_3 was used as the base, the domino Mannich/cyclization reaction gave excellent yields with both catalysts **C3** and **C4** (Table 1, entries 10 and 11). The catalyst loading of **C4** could be reduced to 5 mol-%, and

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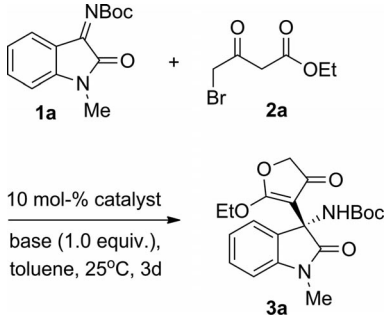
Table 1. Screening of the chiral organocatalysts.[a]



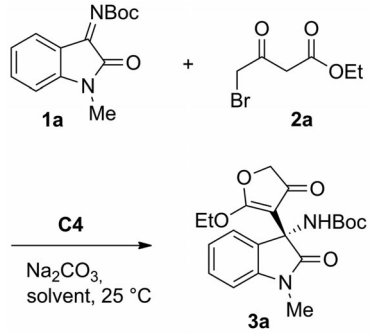
Entry	Catalyst	Base	Yield [%][b]	*ee* [%][c]
1	cinconine	$NaHCO_3$	72	76
2	cinchonidine	$NaHCO_3$	70	–55
3	quinine	$NaHCO_3$	42	–59
4	quinidine	$NaHCO_3$	37	75
5	**C1**	$NaHCO_3$	23	4
6	**C2**	$NaHCO_3$	37	78
7	**C3**	$NaHCO_3$	32	–95
8	**C4**	$NaHCO_3$	29	98
9	**C5**	$NaHCO_3$	trace	n.d.
10[d]	**C3**	Na_2CO_3	87	–91
11[d]	**C4**	Na_2CO_3	96	96
12[d,e]	**C4**	Na_2CO_3	82	97
13	**C4**	Et_3N	98	4

[a] Unless stated otherwise, the domino reactions were carried out with **1a** (0.15 mmol), **2a** (1.5 equiv.), base (1.0 equiv.), and catalyst (0.015 mmol) in toluene (1.0 mL) at 25 °C for 3 d. [b] Isolated yield. [c] The *ee* values were determined by chiral HPLC analysis. [d] Using 0.5 equiv. of base. [e] Using 5 mol-% of catalyst.

under these conditions, the desired product was formed in 82% yield with 97% *ee* (Table 1, entry 12). Although the addition of Et_3N as the base promoted the domino reaction to give the product in excellent yield, the enantioselectivity of this reaction was poor, probably due to a background reaction (Table 1, entry 13).

Next, the solvent effect was investigated using **C4** (5 mol-%) as catalyst and Na_2CO_3 (0.5 equiv.) as base (Table 2). The domino reaction did not take place in *n*-hexane due to

Table 2. Optimization of the reaction conditions.[a]



Entry	Solvent	**C4** [mol-%]	Na_2CO_3 [equiv.]	Time [d]	Yield [%][b]	*ee* [%][c]
1	*n*-hexane	5	0.5	3	trace	–
2	CH_2Cl_2	5	0.5	3	80	98
3	CH_3Cl	5	0.5	3	68	98
4	CCl_4	5	0.5	3	75	96
5	$ClCH_2CH_2Cl$	5	0.5	3	65	98
6	THF	5	0.5	3	79	47
7	CH_3CN	5	0.5	3	93	63
8	CH_2Cl_2	5	1.0	2	98	98
9	CH_2Cl_2	3	1.0	2	96	98
10	CH_2Cl_2	2	1.0	2	95	98
11	CH_2Cl_2	1	1.0	2	92	98
12	CH_2Cl_2	0.5	1.0	2	81	95
13[d]	CH_2Cl_2	1	1.0	2	70	98
14[e]	CH_2Cl_2	1	1.0	1	97	97
15[f]	CH_2Cl_2	1	1.0	2	82	98
16[g]	CH_2Cl_2	1	1.0	2	93	97

[a] Unless stated otherwise, the domino reactions were carried out with **1a** (0.15 mmol), **2a** (1.5 equiv.) and catalyst **C4** (0.015 mmol), in solvent (1.0 mL) at 25 °C. [b] Isolated yield. [c] The *ee* values were determined by chiral HPLC analysis. [d] The reactions were carried out at 0 °C. [e] The reactions were carried out at 40 °C. [f] The amount of solvent was 1.5 mL. [g] The amount of solvent was 0.75 mL.

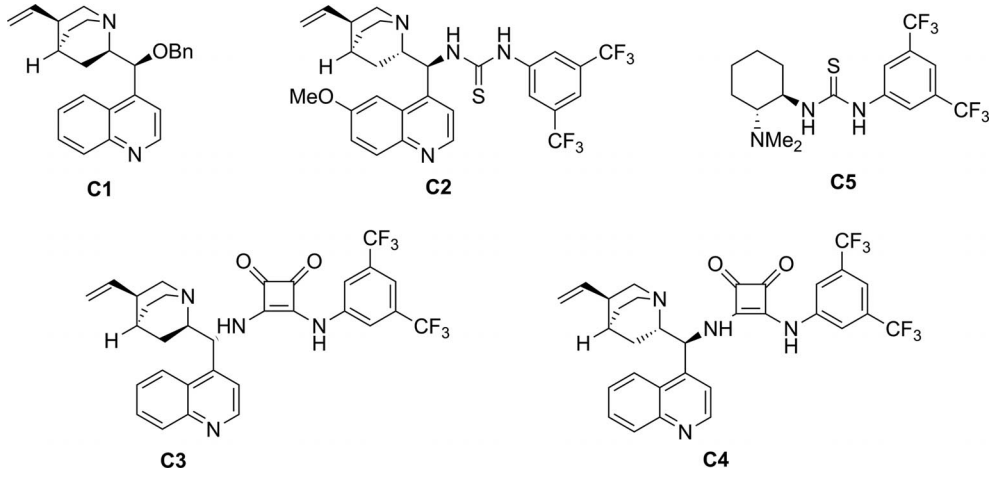


Figure 1. Structures of the organocatalysts screened.

the poor solubility of **1a** (Table 2, entry 1). Alkyl halides such as CH_2Cl_2, CH_3Cl, CCl_4, and $ClCH_2CH_2Cl$ led to excellent enantioselectivities but moderate yields (96–98% *ee*, 65–80% yield; Table 2, entries 2–5). The reaction in THF gave a moderate yield and a low enantioselectivity (Table 2, entry 6). In the cases described above, the Mannich adduct could be detected by TLC analysis. Although the use of CH_3CN as solvent resulted in an excellent yield, the enantioselectivity was low (Table 2, entry 7).

To accelerate the intramolecular cyclization step, the amount of Na_2CO_3 was tentatively increased to 1.0 equiv., and this did indeed result in a shorter reaction time with a comparably excellent yield and selectivity (Table 2, cf. entries 8 and 2). When the catalyst loading was decreased to 1 mol-% (Table 2, entries 8–12), the domino reaction still proceeded with excellent results (92% yield and 98% *ee*; Table 2, entry 11). The reaction temperature (Table 2, entries 13 and 14) and the substrate concentration (Table 2, entries 15 and 16) both influenced the yield but not the enantioselectivity of the model reaction.

Under the optimal reaction conditions [**C4** (1 mol-%) and Na_2CO_3 (1.0 equiv.) in CH_2Cl_2 at 25 °C], we examined the substrate scope of the reaction with various 4-bromoacetoacetates and isatin-derived ketimines (Table 3). The results indicated that methyl, ethyl, and *n*-butyl 4-bromoacetoacetates gave similarly good yields and enantioselectivities (Table 3, entries 1–3). The 1-phenyl ketimine derived from isatin also gave excellent yields and enantioselectivities (Table 3, entry 4). Irrespective of the electronic and steric properties, the substituents on the phenyl group of the isatin-derived ketimines had a minimal effect on the reaction (Table 3, entries 5–15). Ketimines containing either electron-withdrawing or electron-donating groups at the 5-, 6-, or 7-position gave high yields (93–97%) and excellent enantioselectivities (92–98% *ee*). The absolute configuration of product **3j** was determined to be *R* by X-ray analysis (Figure 2, Table S1), and the configurations of the other products were tentatively assigned by comparing with **3j**.

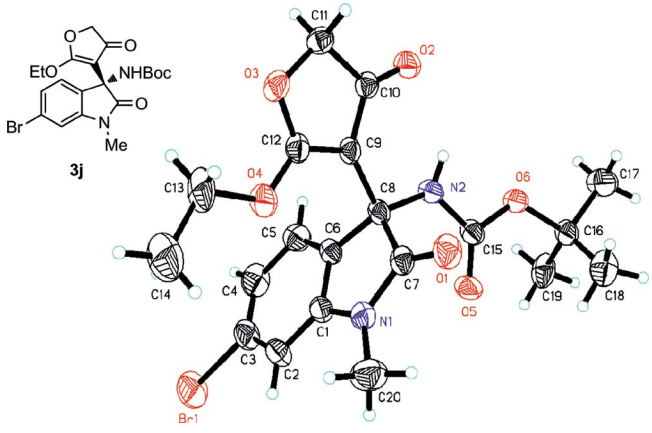
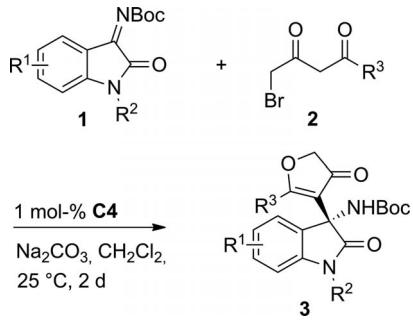


Figure 2. X-ray crystal structure of product **3j**.

Table 3. Substrate scope of the domino reaction.[a]



Entry	R^1	R^2	R^3	Product	Yield [%][b]	*ee* [%][c]
1	H	Me	Et	**3a**	92	98
2	H	Me	Me	**3b**	91	99
3	H	Me	Bn	**3c**	90	98
4	H	Ph	Et	**3d**	93	98
5	5-Me	Me	Et	**3e**	93	97
6	5-MeO	Me	Et	**3f**	97	95
7	5-Cl	Me	Et	**3g**	96	92
8	5-Br	Me	Et	**3h**	97	95
9	6-Cl	Me	Et	**3i**	96	94
10	6-Br	Me	Et	**3j**	96	95
11	7-Me	Me	Et	**3k**	95	98
12	7-F	Me	Et	**3l**	97	95
13	7-Cl	Me	Et	**3m**	97	95
14	7-Br	Me	Et	**3n**	97	98
15	7-CF_3	Me	Et	**3o**	97	95

[a] The reactions were carried out with **1** (0.15 mmol), **2** (1.5 equiv.), Na_2CO_3 (1.0 equiv.), and catalyst **C4** (0.0015 mmol) in CH_2Cl_2 (1 mL) at 25 °C. [b] Isolated yield. [c] The *ee* values were determined by chiral HPLC analysis.

Conclusions

In conclusion, we have developed a highly efficient domino reaction of 4-bromo-3-oxobutanoates with isatin-derived *N*-Boc ketimines. With only 1 mol-% of a bifunctional squaramide catalyst, 3-substituted-3-amino-2-oxindoles were formed in excellent yields and with excellent enantioselectivities. A wide range of substituted ketimines and 4-bromo-3-oxobutanoates were tolerated.

Experimental Section

General Methods: Optical rotations were measured with a WZZ-2A digital polarimeter at the wavelength of the sodium D line (589 nm). ^1H and ^{13}C NMR spectra were recorded with a Bruker 400 spectrometer using $CDCl_3$ as solvent. Chemical shifts were referenced to tetramethylsilane (δ = 0.00 ppm). IR spectra were recorded with a Nicolet Magna-I 550 spectrometer. High Resolution Mass spectra (HRMS) were recorded with a Micromass GCT instrument using the Electrospray Ionization (ESI) technique. HPLC analysis was carried out with a Waters instrument using a Chiralpak AD-H or Chiralcel OD-H column.

THF was freshly distilled from sodium–benzophenone. CH_2Cl_2, CH_3Cl, CCl_4, $ClCH_2CH_2Cl$, and CH_3CN were freshly distilled from CaH_2. Thin-layer chromatography (TLC) was carried out on 10–40 μm silica gel plates. Column chromatography was carried out using silica gel (300–400 mesh), eluting with ethyl acetate and CH_2Cl_2. The isatin-derived *N*-Boc ketimines were synthesized ac-

cording to literature procedures.[5b] 4-Bromoacetoacetates were synthesized from the corresponding acetoacetates.[13] Catalysts **C1**–**C5** were prepared according to literature procedures.[14]

Typical Procedure for the Enantioselective Domino Reaction:

The 4-bromoacetoacetate (0.225 mmol) was added to a solution of catalyst **C4** (0.0015 mmol, 0.9 mg), isatin-derived *N*-Boc ketimine (0.15 mmol), and Na_2CO_3 (0.15 mmol, 16.0 mg) in CH_2Cl_2 (1.0 mL) at 25 °C. The resulting mixture was stirred at this temperature (monitored by TLC), and then it was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the desired product (i.e., **3**). The *ee* value was determined by HPLC analysis with a chiralpak AD-H or chiralcel OD-H column.

***tert*-Butyl (*R*)-[3-(2-Ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxoindolin-3-yl]carbamate (3a):** White solid, 92% yield, 98% *ee*, m.p. 169.8–170.0 °C. $[a]_D^{20}$ = –136.2 (*c* = 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (br. s, 1 H), 7.28–7.24 (m, 2 H), 7.01 (t, *J* = 7.2 Hz, 1 H), 6.79 (d, *J* = 8.0 Hz, 1 H), 4.60 (d, *J* = 16.0 Hz, 1 H), 4.54 (d, *J* = 16.0 Hz, 1 H), 4.30–4.18 (m, 2 H), 3.26 (s, 3 H), 1.33 (s, 9 H), 1.18 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.38, 179.52, 174.90, 153.76, 143.19, 128.73, 122.72, 122.54, 107.18, 91.22, 79.55, 77.20, 74.78, 66.92, 59.33, 28.15, 26.18, 14.14 ppm. IR (KBr): $\tilde{\nu}$ = 3350, 3165, 1723, 1614, 1587, 1471, 1367, 1252, 1101, 706, 599 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{25}N_2O_6$ [M + H]$^+$ 389.1713; found 389.1705. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 24.26 min (minor), 32.68 min (major).

***tert*-Butyl (*R*)-[3-(2-Methoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxoindolin-3-yl]carbamate (3b):** White solid, 91% yield, 99% *ee*, m.p. 159.7–160.6 °C. $[a]_D^{20}$ = –133.0 (*c* = 0.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (br. s, 1 H), 7.30–7.24 (m, 2 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 4.61 (d, *J* = 16.0 Hz, 1 H), 4.55 (d, *J* = 16.0 Hz, 1 H), 3.89 (s, 3 H), 3.27 (s, 3 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.59, 179.52, 174.40, 154.17, 143.73, 128.80, 122.79, 122.58, 107.92, 91.42, 79.57, 74.80, 57.36, 29.91, 27.97, 26.37 ppm. IR (KBr): $\tilde{\nu}$ = 3417, 2981, 1738, 1718, 1585, 1491, 1353, 1252, 1169, 1009, 937, 760 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{23}N_2O_6$ [M + H]$^+$ 375.1556; found 375.1529. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 57.38 min (minor), 62.67 min (major).

***tert*-Butyl (*R*)-{3-[2-(benzyloxy)-4-oxo-4,5-dihydrofuran-3-yl]-1-methyl-2-oxoindolin-3-yl}carbamate (3c):** White solid, 90% yield, 98% *ee*, m.p. 145.4–146.9 °C. $[a]_D^{20}$ = –137.7 (*c* = 0.29, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (br. s, 1 H), 7.38–7.32 (m, 3 H), 7.27–7.21 (m, 2 H), 7.06 (d, *J* = 6.4 Hz, 2 H), 7.03–6.98 (t, *J* = 7.6 Hz, 1 H), 6.61 (d, *J* = 7.6 Hz, 1 H), 5.16 (d, *J* = 11.6 Hz, 1 H), 5.12 (d, *J* = 11.6 Hz, 1 H), 4.64 (d, *J* = 16.0 Hz, 1 H), 4.58 (d, *J* = 16.0 Hz, 1 H), 2.86 (s, 3 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.47, 179.14, 174.10, 153.91, 143.06, 132.79, 129.25, 128.64, 128.38, 122.68, 122.49, 107.72, 91.22, 79.63, 77.20, 75.04, 72.29, 28.17, 25.99, 18.34 ppm. IR (KBr): $\tilde{\nu}$ = 3421, 3292, 1719, 1670, 1597, 1456, 1365, 1252, 1008, 914, 756, 536 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{26}N_2NaO_6$ [M + Na]$^+$ 473.1689; found 473.1701. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 31.67 min (minor), 42.82 min (major).

***tert*-Butyl (*R*)-[3-(2-Ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-2-oxo-1-phenylindolin-3-yl]carbamate (3d):** White solid, 93% yield, 98% *ee*, m.p. 137.8–139.3 °C. $[a]_D^{20}$ = –111.6 (*c* = 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (br. s, 1 H), 7.53–7.52 (m, 4 H), 7.40–7.34 (m, 2 H), 7.18 (t, *J* = 7.2 Hz, 1 H), 7.04 (t, *J* = 7.2 Hz, 1 H), 6.80 (s, 1 H), 4.63 (d, *J* = 16.0 Hz, 1 H), 4.58 (d, *J* = 16.0 Hz, 1 H), 4.34–4.26 (m, 2 H), 1.35 (s, 9 H), 1.16 (t, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.54, 179.45, 173.76, 153.96, 135.02, 129.37, 128.59, 127.73, 126.53, 123.16, 123.08, 108.96, 91.17, 79.72, 77.20, 74.86, 67.32, 59.54, 28.22, 14.41 ppm. IR (KBr): $\tilde{\nu}$ = 3414, 2979, 1740, 1716, 1596, 1499, 1172, 1017, 914, 756, 625 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{26}N_2NaO_6$ [M + Na]$^+$ 473.1689; found 473.1709. HPLC analysis (OD-H column; λ = 254 nm; *n*-hexane/*i*-PrOH, 90:10; flow rate = 0.9 mL/min): t_R = 36.37 min (minor), 39.45 min (major).

***tert*-Butyl (*R*)-[3-(2-Ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1,5-dimethyl-2-oxoindolin-3-yl]carbamate (3e):** White solid, 93% yield, 97% *ee*, m.p. 183.1–183.9 °C. $[a]_D^{20}$ = –120.3 (*c* = 0.16, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (br. s, 1 H), 7.10 (s, 1 H), 7.05 (d, *J* = 7.6 Hz, 1 H), 6.67 (d, *J* = 7.6 Hz, 1 H), 4.59 (d, *J* = 16.0 Hz, 1 H), 4.54 (d, *J* = 16.0 Hz, 1 H), 4.32–4.16 (m, 2 H), 3.23 (s, 3 H), 2.29 (s, 3 H), 1.34 (s, 9 H), 1.20 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.53, 179.49, 174.10, 153.79, 140.85, 128.62, 123.26, 107.15, 91.48, 79.66, 77.20, 74.78, 66.90, 30.93, 28.19, 26.43, 21.00, 13.54 ppm. IR (KBr): $\tilde{\nu}$ = 3417, 3240, 2974, 1721, 1606, 1502, 1391, 1360, 1169, 1014, 790, 550 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{26}N_2NaO_6$ [M + Na]$^+$ 425.1689; found 425.1677. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 20.57 min (minor), 28.38 min (major).

***tert*-Butyl (*R*)-[3-(2-Ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-5-methoxy-1-methyl-2-oxoindolin-3-yl] carbamate (3f):** White solid, 97% yield, 95% *ee*, m.p. 158.7–159.4 °C. $[a]_D^{20}$ = –76.4 (*c* = 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (br. s, 1 H), 6.90 (s, 1 H), 6.81 (d, *J* = 8.4 Hz, 1 H), 6.70 (d, *J* = 8.4 Hz, 1 H), 4.61 (d, *J* = 16.0 Hz, 1 H), 4.55 (d, *J* = 16.0 Hz, 1 H), 4.32–4.18 (m, 2 H), 3.77 (s, 3 H), 3.23 (s, 3 H), 1.34 (s, 9 H), 1.19 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.34, 179.28, 173.91, 156.25, 153.96, 136.77, 113.37, 109.61, 108.23, 90.84, 79.51, 77.20, 74.75, 66.91, 59.83, 55.72, 28.16, 26.17, 14.12 ppm. IR (KBr): $\tilde{\nu}$ = 3397, 3284, 2997, 2949, 1706, 1654, 1596, 1510, 1391, 1289, 1166, 1025, 914, 756, 558 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{26}N_2NaO_7$ [M + Na]$^+$ 441.1638; found 441.1637. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 18.01 min (minor), 43.96 min (major).

***tert*-Butyl (*R*)-[5-chloro-3-(2-ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxoindolin-3-yl]carbamate (3g):** White solid, 96% yield, 92% *ee*, m.p. 163.3–164.2 °C. $[a]_D^{20}$ = –65.7 (*c* = 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (br. s, 1 H), 7.25–7.22 (m, 2 H), 6.73 (d, *J* = 8.0 Hz, 1 H), 4.62 (d, *J* = 16.4 Hz, 1 H), 4.58 (d, *J* = 16.4 Hz, 1 H), 4.32–4.19 (m, 2 H), 3.24 (s, 3 H), 1.35 (s, 9 H), 1.19 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.38, 178.77, 173.86, 153.77, 142.27, 128.60, 127.73, 123.10, 108.42, 90.34, 79.69, 77.20, 74.88, 67.09, 59.67, 28.15, 26.40, 14.15 ppm. IR (KBr): $\tilde{\nu}$ = 3407, 3217, 2982, 1717, 1600, 1490, 1389, 1346, 1169, 1013, 923, 828, 545 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{23}ClN_2NaO_6$ [M + Na]$^+$ 445.1142; found 455.1144. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 24.28 min (minor), 33.47 min (major).

***tert*-Butyl (*R*)-[5-Bromo-3-(2-ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxoindolin-3-yl]carbamate (3h):** White solid, 97% yield, 95% *ee*, m.p. 169.3–170.4 °C. $[a]_D^{20}$ = –83.6 (*c* = 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (br. s, 1 H), 7.38 (d, *J* = 5.2 Hz, 2 H), 6.68 (d, *J* = 8.8 Hz, 1 H), 4.61 (d, *J* = 16.0 Hz, 1 H), 4.57 (d, *J* = 16.0 Hz, 1 H), 4.32–4.21 (m, 2 H), 3.23 (s, 3 H), 1.34 (s, 9 H), 1.19 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

194.06, 179.18, 173.75, 153.69, 142.80, 131.51, 125.84, 115.23, 115.23, 109.11, 89.98, 79.89, 77.20, 67.10, 59.14, 28.14, 26.36, 14.16 ppm. IR (KBr): $\tilde{\nu}$ = 3397, 3208, 2990, 1737, 1715, 1596, 1490, 1389, 1167, 1010, 923, 828, 532 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{24}BrN_2O_6$ $[M + H]^+$ 467.0818; found 467.0795. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 21.56 min (minor), 32.57 min (major).

***tert*-Butyl (*R*)-[6-Chloro-3-(2-ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxoindolin-3-yl]carbamate (3i):** White solid, 96% yield, 94% *ee*, m.p. 167.4–168.3 °C. $[\alpha]_D^{20}$ = –67.2 (*c* = 0.20, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (br. s, 1 H), 7.19 (d, *J* = 8.0 Hz, 1 H), 6.98 (d, *J* = 7.2 Hz, 1 H), 6.79 (s, 1 H), 4.61 (d, *J* = 16.0 Hz, 1 H), 4.56 (d, *J* = 16.0 Hz, 1 H), 4.30–4.20 (m, 2 H), 3.24 (s, 3 H), 1.33 (s, 9 H), 1.21 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.07, 179.01, 174.27, 154.01, 144.95, 134.38, 123.54, 122.53, 108.44, 90.02, 80.27, 77.20, 74.88, 67.12, 59.52, 28.16, 26.19, 14.20 ppm. IR (KBr): $\tilde{\nu}$ = 3417, 3291, 2980, 1735, 1607, 1577, 1495, 1392, 1164, 1073, 714, 558 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{23}ClN_2NaO_6$ $[M + Na]^+$ 445.1142; found 445.1136. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 21.30 min (minor), 28.81 min (major).

***tert*-Butyl (*R*)-[6-Bromo-3-(2-ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxoindolin-3-yl]carbamate (3j):** White solid, 96% yield, 95% *ee*, m.p. 164.2–165.4 °C. $[\alpha]_D^{20}$ = –73.3 (*c* = 0.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.14 (br. s, 1 H), 7.14 (s, 2 H), 6.94 (s, 1 H), 4.61 (d, *J* = 16.0 Hz, 1 H), 4.55 (d, *J* = 16.0 Hz, 1 H), 4.30–4.20 (m, 2 H), 3.23 (s, 3 H), 1.33 (s, 9 H), 1.21 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.43, 179.01, 174.13, 153.80, 144.60, 125.47, 123.90, 122.09, 111.09, 90.55, 80.09, 77.20, 74.87, 67.13, 59.33, 28.15, 26.20, 14.20 ppm. IR (KBr): $\tilde{\nu}$ = 3421, 3294, 2981, 1720, 1597, 1516, 1458, 1365, 1165, 1007, 914, 756, 536 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{24}BrN_2O_6$ $[M + H]^+$ 467.0818; found 467.0810. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 20.72 min (minor), 29.04 min (major).

***tert*-Butyl (*R*)-[3-(2-Ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1,7-dimethyl-2-oxoindolin-3-yl]carbamate (3k):** White solid, 95% yield, 98% *ee*, m.p. 175.3–175.4 °C. $[\alpha]_D^{20}$ = –125.6 (*c* = 0.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (br. s, 1 H), 7.13 (d, *J* = 7.2 Hz, 1 H), 6.98 (d, *J* = 7.6 Hz, 1 H), 6.89 (t, *J* = 7.6 Hz, 1 H), 4.58 (d, *J* = 16.0 Hz, 1 H), 4.52 (d, *J* = 16.0 Hz, 1 H), 4.33–4.18 (m, 2 H), 3.53 (s, 3 H), 2.56 (s, 3 H), 1.34 (s, 9 H), 1.23 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.75, 178.97, 174.72, 153.27, 141.38, 132.41, 122.65, 120.59, 118.92, 91.76, 79.70, 77.20, 74.70, 66.84, 58.96, 29.54, 28.15, 18.55, 14.16 ppm. IR (KBr): $\tilde{\nu}$ = 3437, 3306, 2982, 1719, 1599, 1513, 1457, 1355, 1164, 1095, 1011, 775, 560 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{26}N_2NaO_6$ $[M + Na]^+$ 425.1689; found 425.1697. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 24.96 min (minor), 31.12 min (major).

***tert*-Butyl (*R*)-[3-(2-Ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-7-fluoro-1-methyl-2-oxoindolin-3-yl]carbamate (3l):** White solid, 97% yield, 95% *ee*, m.p. 134.1–135.3 °C. $[\alpha]_D^{20}$ = –80.3 (*c* = 0.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (br. s, 1 H), 7.07–6.93 (m, 3 H), 4.61 (d, *J* = 16.0 Hz, 1 H), 4.56 (d, *J* = 16.0 Hz, 1 H), 4.31–4.24 (m, 2 H), 3.47 (s, 3 H), 1.34 (s, 9 H), 1.24 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.05, 179.34, 174.20, 154.17, 148.85, 146.18, 123.34, 118.41, 116.58, 90.90, 80.25, 77.20, 74.86, 67.13, 59.86, 29.21, 28.18, 14.17 ppm. IR (KBr): $\tilde{\nu}$ = 3311, 2981, 1721, 1603, 1487, 1454, 1357, 1167, 1041, 930, 857, 741, 562 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{23}FN_2NaO_6$ $[M + Na]^+$ 429.1438; found 429.1421. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 20.72 min (minor), 24.10 min (major).

***tert*-Butyl (*R*)-[7-Chloro-3-(2-ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxoindolin-3-yl]carbamate (3m):** White solid, 97% yield, 95% *ee*, m.p. 159.9–161.3 °C. $[\alpha]_D^{20}$ = –89.2 (*c* = 0.21, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.24 (br. s, 1 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 6.92 (t, *J* = 7.6 Hz, 1 H), 4.61 (d, *J* = 16.0 Hz, 1 H), 4.55 (d, *J* = 16.0 Hz, 1 H), 4.33–4.21 (m, 2 H), 3.62 (s, 3 H), 1.34 (s, 9 H), 1.24 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.09, 179.13, 174.66, 153.78, 139.42, 130.86, 123.49, 121.10, 114.96, 90.34, 79.84, 77.20, 74.83, 67.12, 59.13, 29.70, 28.12, 14.10 ppm. IR (KBr): $\tilde{\nu}$ = 3416, 2984, 1721, 1608, 1506, 1462, 1391, 1172, 1109, 1014, 742, 562 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{23}ClN_2NaO_6$ $[M + Na]^+$ 445.1142; found 445.1136. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 23.13 min (minor), 26.94 min (major).

***tert*-Butyl (*R*)-[7-Bromo-3-(2-ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxoindolin-3-yl]carbamate (3n):** White solid, 97% yield, 98% *ee*, m.p. 162.1–162.8 °C. $[\alpha]_D^{20}$ = –130.1 (*c* = 0.20, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (br. s, 1 H), 7.35 (d, *J* = 8.0 Hz, 1 H), 7.21 (t, *J* = 6.8 Hz, 1 H), 6.87–6.84 (m, 1 H), 4.61 (d, *J* = 16.0 Hz, 1 H), 4.55 (d, *J* = 16.0 Hz, 1 H), 4.32–4.19 (m, 2 H), 3.63 (s, 3 H), 1.34 (s, 9 H), 1.24 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.20, 179.13, 174.84, 153.79, 140.74, 134.19, 123.91, 121.64, 102.04, 90.48, 79.87, 77.20, 74.84, 67.13, 59.13, 29.90, 28.15, 14.13 ppm. IR (KBr): $\tilde{\nu}$ = 3437, 2983, 1719, 1598, 1513, 1457, 1327, 1164, 1109, 1014, 742, 562 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{24}BrN_2O_6$ $[M + H]^+$ 467.0818; found 467.0813; HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 24.37 min (minor), 27.57 min (major).

***tert*-Butyl (*R*)-[3-(2-Ethoxy-4-oxo-4,5-dihydrofuran-3-yl)-1-methyl-2-oxo-7-(trifluoromethyl)indolin-3-yl]carbamate (3o):** White solid, 97% yield, 95% *ee*, m.p. 163.2–163.6 °C. $[\alpha]_D^{20}$ = –96.3 (*c* = 0.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.34 (br. s, 1 H), 7.56–7.47 (m, 2 H), 7.09 (s, 1 H), 4.63 (d, *J* = 16.0 Hz, 1 H), 4.57 (d, *J* = 16.0 Hz, 1 H), 4.28–4.21 (m, 2 H), 3.45 (s, 3 H), 1.39 (s, 9 H), 1.17 (t, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.74, 179.30, 175.28, 153.97, 141.46, 133.52, 126.50, 126.03, 124.95, 122.05, 90.35, 80.22, 77.20, 74.89, 67.22, 58.43, 29.03, 28.15, 13.89 ppm. IR (KBr): $\tilde{\nu}$ = 3416, 2984, 1740, 1599, 1461, 1461, 1346, 1169, 1042, 929, 742, 562 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{23}F_3N_2NaO_6$ $[M + Na]^+$ 479.1406; found 479.1426. HPLC analysis (AD-H column; λ = 254 nm; *n*-hexane/EtOH, 90:10; flow rate = 0.9 mL/min): t_R = 14.25 min (minor), 16.10 min (major).

CCDC-943424 (for **3j**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra and HPLC chromatograms of the products; X-ray analysis for compound **3i**.

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[1] For recent reviews of catalytic asymmetric additions to imines, see: a) S. Kobayashi, Y. Mori, J. S. Fossey, M. M. Salter, *Chem.*

Rev. **2011**, *111*, 2626–2704; b) Y. Wei, M. Shi, *Acc. Chem. Res.* **2010**, *43*, 1005–1018; c) E. Marqués-López, P. Merino, T. Tejero, R. P. Herrera, *Eur. J. Org. Chem.* **2009**, 2401–2420; d) G. K. Friestad, A. K. Mathies, *Tetrahedron* **2007**, *63*, 2541–2569.

[2] For selected references of metal-catalysed enantioselective additions to ketimines, see: a) H.-N. Yuan, S. Wang, J. Nie, W. Meng, Q.-W. Yao, J.-A. Ma, *Angew. Chem.* **2013**, *125*, 3961–3965; *Angew. Chem. Int. Ed.* **2013**, *52*, 3869–3873; b) H. Wang, T. Jiang, M. H. Xu, *J. Am. Chem. Soc.* **2013**, *135*, 971–974; c) Y. Du, L.-W. Xu, Y. Shimizu, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2008**, *130*, 16146–16147; d) Y.-J. Chen, C. Chen, *Tetrahedron: Asymmetry* **2008**, *19*, 2201–2209; e) P. Fu, M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc.* **2008**, *130*, 5530–5541; f) S. J. Connon, *Angew. Chem.* **2008**, *120*, 1194–1197; *Angew. Chem. Int. Ed.* **2008**, *47*, 1176–1178; g) R. Wada, T. Shibuguchi, S. Makino, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2006**, *128*, 7687–7691.

[3] For selected references of metal-free enantioselective additions to ketimines, see: a) D. Enders, A. Rembiak, M. Seppelt, *Tetrahedron Lett.* **2013**, *54*, 470–473; b) F. R. Bou-Hamdan, J. L. Leighton, *Angew. Chem.* **2009**, *121*, 2439–2442; *Angew. Chem. Int. Ed.* **2009**, *48*, 2403–2406; c) G. T. Notte, J. L. Leighton, *J. Am. Chem. Soc.* **2008**, *130*, 6676–6677; d) P. M. A. Rabbat, V. S. C. Aldez, J. L. Leighton, *Org. Lett.* **2006**, *8*, 6119–6121; e) W. Zhuang, S. Saaby, K. A. Jørgensen, *Angew. Chem.* **2004**, *116*, 4576–4578; *Angew. Chem. Int. Ed.* **2004**, *43*, 4476–4478; f) P. Alejandro, A. Ricardo, M. Leyre, M. C. Alberto, L. G. R. José, A. José, *Chem. Commun.* **2012**, *48*, 9759–9761.

[4] For recent reviews of the reaction of isatin-derived ketimines, see: a) P. Chauhan, S. S. Chimni, *Tetrahedron: Asymmetry* **2013**, *24*, 343–356; b) R. Dalpozzo, G. Bartoli, G. Bencivenni, *Chem. Soc. Rev.* **2012**, *41*, 7247–7290.

[5] a) Q.-X. Guo, Y.-W. Liu, X.-C. Li, L.-Z. Zhong, Y.-G. Peng, *J. Org. Chem.* **2012**, *77*, 3589–3594; b) W. Yan, D. Wang, J. Feng, P. Li, D. Zhao, R. Wang, *Org. Lett.* **2012**, *14*, 2512–2515; c) N. Hara, S. Nakamura, M. Sano, R. Tamura, Y. Funahashi, N. Shibata, *Chem. Eur. J.* **2012**, *18*, 9278–9280; d) D. Wang, J. Liang, J. Feng, K. Wang, Q. Sun, L. Zhao, D. Li, W. Yan, R. Wang, *Adv. Synth. Catal.* **2013**, *355*, 548–558; e) Y.-L. Liu, J. Zhou, *Chem. Commun.* **2013**, *49*, 4421–4423; f) Y.-L. Liu, F. Zhou, J.-J. Cao, C.-B. Ji, M. Ding, J. Zhou, *Org. Biomol. Chem.* **2010**, *8*, 3847–3850; g) J. Feng, W. Yan, D. Wang, P. Li, Q. Sun, R. Wang, *Chem. Commun.* **2012**, *48*, 8003–8005; h) F.-L. Hu, Y. Wei, M. Shi, S. Pindi, G. Li, *Org. Biomol. Chem.* **2013**, *11*, 1921–1924; i) B. Zhang, P. Feng, L.-H. Sun, Y. Cui, S. Ye, N. Jiao, *Chem. Eur. J.* **2012**, *18*, 9198–9203; j) H. Lv, B. Tiwari, J. Mo, C. Xing, Y. R. Chi, *Org. Lett.* **2012**, *14*, 5412–5414; k) X. Chen, H. Chen, X. Ji, H. Jiang, Z.-J. Yao, H. Liu, *Org. Lett.* **2013**, *15*, 1846–1849.

[6] For selected references of enantioselective amination reactions to prepare 3-substituted 3-amino-2-oxindoles, see: a) X. Companyo, G. Valero, O. Pineda, T. Calvet, M. Font-Bardia, A. Moyano, R. Rios, *Org. Biomol. Chem.* **2012**, *10*, 431–439; b) L.-N. Jia, J. Huang, L. Peng, L.-L. Wang, J.-F. Bai, F. Tian, G.-Y. He, X.-Y. Xu, L.-X. Wang, *Org. Biomol. Chem.* **2012**, *10*, 236–239; c) T. Bui, G. Hernandez-Torres, C. Milite, C. F. Barbas III, *Org. Lett.* **2010**, *12*, 5696–5699; d) Z. Yang, Z. Wang, S. Bai, K. Shen, D. Chen, X. Liu, L. Lin, X. Feng, *Chem. Eur. J.* **2010**, *16*, 6632–6637; e) S. Mouri, Z. Chen, H. Mitsunuma, M. Furutachi, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2010**, *132*, 1255–1257; f) Z. Q. Qian, F. Zhou, T. P. Du, B. L. Wang, M. Ding, X. L. Zhao, J. Zhou, *Chem. Commun.* **2009**, 6753–6755; g) L. Cheng, L. Liu, D. Wang, Y. J. Chen, *Org. Lett.* **2009**, *11*, 3874–3877.

[7] a) M. Ochi, K. Kawasaki, H. Kataoka, Y. Uchio, H. Nishi, *Biochem. Biophys. Res. Commun.* **2001**, *283*, 1118–1123; b) K. Bernard, S. Bogliolo, J. Ehrenfeld, *Br. J. Pharmacol.* **2005**, *144*, 1037–1015; c) A. K. Ghosh, G. Schiltz, R. S. Perali, S. Leshchenko, S. Kay, D. E. Walters, Y. Koh, K. Maeda, H. Mitsuya, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1869–1873.

[8] a) J.-Y. Qian, C.-C. Wang, F. Sha, X.-Y. Wu, *RSC Adv.* **2012**, *2*, 6042–6048; b) C.-C. Wang, X.-Y. Wu, *Tetrahedron* **2011**, *67*, 2974–2978; c) T.-Z. Li, X.-B. Wang, F. Sha, X.-Y. Wu, *Tetrahedron* **2013**, *69*, 7314–7319.

[9] a) N.-H. Luo, X. Sun, Y.-Y. Yan, S.-Z. Nie, M. Yan, *Tetrahedron: Asymmetry* **2011**, *22*, 1536–1541; b) X. Dou, X. Han, Y. Lu, *Chem. Eur. J.* **2012**, *18*, 85–89.

[10] For selected reviews on bifunctional organocatalysis, see: a) S. J. Connon, *Chem. Commun.* **2008**, 2499–2510; b) Y. Takemoto, *Chem. Pharm. Bull.* **2010**, *58*, 593–601; c) L. Q. Lu, X. L. An, J. R. Chen, W. J. Xiao, *Synlett* **2012**, 490–508.

[11] For reviews on squaramide catalysis, see: a) R. I. Storer, C. Aciro, L. H. Jones, *Chem. Soc. Rev.* **2011**, *40*, 2330–2346; b) J. Alemán, A. Parra, H. Jiang, K. A. Jørgensen, *Chem. Eur. J.* **2011**, *17*, 6890–6899.

[12] a) H. X. He, W. Yang, D. M. Du, *Adv. Synth. Catal.* **2013**, *355*, 1137–1148; b) H. X. He, D. M. Du, *RSC Adv.* **2013**, *3*, 16349–16358.

[13] a) Y. Yasohara, N. Kizaki, J. Hasegawa, M. Wada, M. Kataoka, S. Shimizu, *Tetrahedron: Asymmetry* **2001**, *12*, 1713–1718; b) P. Cheruku, A. Paptchikhine, M. Ali, J.-M. Neudörfl, P. G. Andersson, *Org. Biomol. Chem.* **2008**, *6*, 366–369; c) S. Wolfe, C. Akuche, S. Ro, M.-C. Wilson, C.-K. Kim, Z. Shi, *Can. J. Chem.* **2003**, *81*, 915–920.

[14] a) B. Vakulya, S. Varga, A. Csámpai, T. Soós, *Org. Lett.* **2005**, *7*, 1967–1969; b) M.-M. Lian, Z. Li, J. Du, Q.-W. Meng, Z.-X. Gao, *Eur. J. Org. Chem.* **2010**, 6525–6530; c) W. Yang, D.-M. Du, *Org. Lett.* **2010**, *12*, 5450–5453; d) T. He, J.-Y. Qian, H.-L. Song, X.-Y. Wu, *Synlett* **2009**, 3195–3197; e) A. Berkessel, B. Seelig, *Synthesis* **2009**, 2113–2115.

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