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Highly enantioselective hydrogenation of *N*-unprotected indoles using (*S*)-C_{10}—BridgePHOS as the chiral ligand

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ABSTRACT

(*S*)-C_{10}—BridgePHOS was successfully applied to a highly efficient Pd-catalyzed enantioselective hydrogenation of substituted indoles. The methodology was suitable for the hydrogenation of indoles substituted at the 2-, 3- and 2,3-positions. Products were obtained in quantitative conversion and up to 98% ee. The role the 2-position substituent plays in the hydrogenation process has been proposed. The methodology could be used as an alternative method to synthesize extremely important chiral indolines from *N*-unprotected indoles.

1. Introduction

Since the discovery of BINAP[1] many excellent chelating diphosphines possessing atropisomeric biaryl scaffolds, such as MeO-BIPHEP,[2] SEGPHO[3] etc, have been developed (Fig. 1).[4] Traditionally, the axial chirality of these atropisomeric ligands relied on the steric hindrance of the ortho substituents of the biaryl skeleton. These substituents limit the rotation of the two benzene rings around the axis, thus affecting the range of the dihedral angles the ligand can adopt, a significant factor, which influences asymmetric control.[2–5] Recently, our group developed a new class of atropisomeric diphosphine ligands (BridgePHOS ligands) based on our previous research of axial ligands[6] in which a bridge of variable length at the 5,5′-positions restricts the movement of the biaryl system.[7] The reduced steric hindrance resulting from the ortho hydrogen atoms, allows for a greater degree of control of the dihedral angles compared to traditional atropisomeric ligands. The largest bite angle of the ligand was obtained using a bridge of n=10 (C_{10}—BridgePHOS), which gave products in quantitative yields and up to 99% ee when subjected to Pd-catalyzed asymmetric hydrogenations of α-phthalimide ketones. In order to investigate the applicability of this ligand in asymmetric reactions, it was applied to Pd-catalyzed asymmetric hydrogenation reactions of *N*-unprotected indoles.

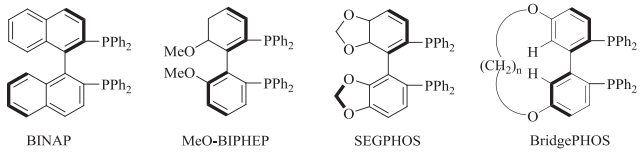

Fig. 1. Some atropisomeric ligands.

Chiral indolines especially fused ring indolines are important structural motifs, which are commonly used in the chemical and pharmaceutical industry.[8] A number of methods have been successfully developed to synthesize enantioenriched indoline intermediates. These methods include dynamic kinetic resolution[9] asymmetric catalysi[10] and chiral pool synthesi[11] amongst others.[12] Except for the aforementioned reactions, asymmetric hydrogenation is considered to be the most efficient and rapid approach to preparing chiral indoline molecules. These types of reactions provide a high degree of enantioselectivity with low catalyst loadings, and reduce the amount of unwanted byproducts in the transformation process.[13] Recent studies have predominantly focused on the reduction of *N*-protected indoles utilizing chiral Ru,

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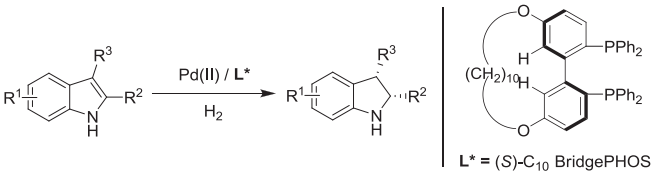
Rh, and Ir catalysts.[14] However, Zhang and Zhou reported the asymmetric hydrogenation of *N*-unprotected indoles using a Pd-catalyst.[15] We envisioned that our C_{10}–BridgePHOS ligand could be utilized in the above protocol, providing the desired products in high yields and enantioselectivities. Herein, we report our work concerning the highly enantioselective Pd-catalyzed hydrogenation of *N*-unprotected indoles using (*S*)-C_{10}–BridgePHOS as the chiral ligand (Scheme 1).

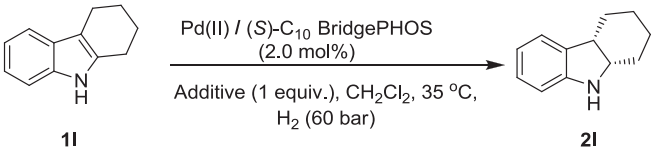


Scheme 1. Asymmetric hydrogenation of indole derivatives.

2. Results and discussion

Initial experiments were performed on the substrate 2,3,4,9-tetrahydro-1*H*-carbazole (**1l**), due to its significance in the chemical and pharmaceutical industry. A catalytic system of $Pd(OCOCF_3)_2$ and (*S*)-C_{10}–BridgePHOS under an atmosphere of H_2 (60 bar) in CH_2Cl_2 at 35 °C was used.[8] As shown in Table 1, no reaction occurred in the absence of additives (entry 1), and only a trace amount of product was obtained with $PhCO_2H$ as an additive (entry 2). The application of a strongly acidic additive, TFA, proved to be successful in this transformation, with both reactivity and enantioselectivity increasing appreciably (entry 3). The acidity of the additive had a significant impact on the outcome of the reaction. Organic sulfonic acids, such as MsOH, TfOH, *para*-Cl-$PhSO_3H$, and $TsOH\cdot H_2O$, were examined, and almost all the reactions proceeded smoothly in good conversions with preferable enantioselectivities (entries 4–7). Finally, chiral D-camphorsulfonic acid (D-CSA) was used, resulting in a large increase in enantioselectivity (entry 8). However, the enantiomer of D-CSA, L-CSA, is inferior to its enantioisomer (entry 9), most likely because of the mismatch in chirality between the ligand and additive. Therefore D-CSA was selected as the additive in subsequent reactions.

Table 1
The effect of the additive on the reaction[a]

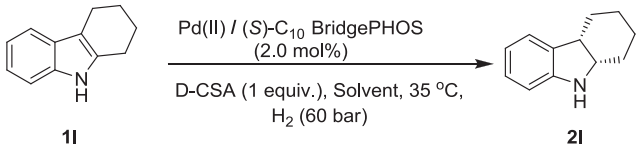


Entry	Additive	Conv. (%)[b]	ee (%)[c,d]
1	No	NR	NA
2	$PhCO_2H$	<5	NA
3	TFA	48	23 (*S*,*S*)
4	MsOH	>95	86 (*S*,*S*)
5	TfOH	65	85 (*S*,*S*)
6	*p*-Cl–$PhSO_3H$	>95	86 (*S*,*S*)
7	$TsOH\cdot H_2O$	>95	87 (*S*,*S*)
8	D-CSA	>95	90 (*S*,*S*)
9	L-CSA	85	75 (*S*,*S*)

[a] Conditions: **1l** (0.15 mmol), $Pd(OCOCF_3)_2$ (0.8 mg, 2.0 mol %), (*S*)-C_{10} BridgePHOS (2.0 mg, 2.4 mol %), additive (1 equiv), CH_2Cl_2 (1 mL), 24 h, 35 °C, 60 bar H_2 pressure.
[b] Determined by ^1H NMR analysis.
[c] Determined by chiral HPLC analysis.
[d] The absolute configuration of product was determined by comparison of the specific rotations with the literature data.[15a]

Further investigations focused on the effect of solvent (Table 2). TFE was first tested and gave full conversion and good enantioselectivity (entry 1). The use of THF and DMF resulted in poor catalytic behavior because of coordination of the solvent to the chiral catalyst (entries 2 and 3). CH_2Cl_2 gave the desired product in quantitative conversion with good enantiomeric excess (entry 4). Considering both CH_2Cl_2 and TFE were suitable for this reaction, a mixed solvent system consisting of CH_2Cl_2 and TFE (in a 1:1 ratio) was tested, providing the best results (entry 5). Therefore, this solvent system was used in subsequent reactions.

Table 2
The effect of the solvent, pressure and temperature on the reaction[a]



Entry	Solvent	Conv. (%)[b]	ee (%)[c,d]
1	TFE	>95	87 (*S*,*S*)
2	THF	<5	NA
3	DMF	<5	NA
4	CH_2Cl_2	>95	90 (*S*,*S*)
5	CH_2Cl_2/TFE (1/1)	>95	93 (*S*,*S*)
6[e]	CH_2Cl_2/TFE (1/1)	91	92 (*S*,*S*)
7[f]	CH_2Cl_2/TFE (1/1)	>95	91 (*S*,*S*)
8[g]	CH_2Cl_2/TFE (1/1)	>95	93 (*S*,*S*)
9[h]	CH_2Cl_2/TFE (1/1)	89	93 (*S*,*S*)

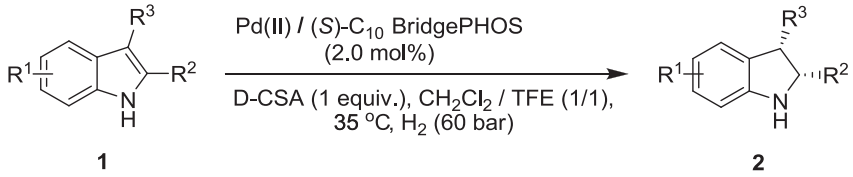
[a] Conditions: **1l** (0.15 mmol), $Pd(OCOCF_3)_2$ (0.8 mg, 2.0 mol %), (*S*)-C_{10} BridgePHOS (2.0 mg, 2.4 mol %), D-CSA (1 equiv), solvent (1 mL), 24 h, 35 °C, 60 bar H_2 pressure.
[b] Determined by ^1H NMR analysis.
[c] Determined by chiral HPLC analysis.
[d] The absolute configuration of product was determined by comparison of the specific rotations with the literature data.[15a]
[e] Reaction was carried out in 50 bar H_2 pressure.
[f] Reaction was carried out in 70 bar H_2 pressure.
[g] Reaction was carried out at 60 °C.
[h] Reaction was carried out under room temperature.

H_2 pressure and reaction temperature had a marginal effect on the enantioselectivity but a significant effect on reaction conversion. Lower H_2 pressure and reaction temperature both led to a decrease in reaction activity (entries 6 and 9). Higher H_2 pressure and temperature showed little effect on both the reaction activity and the enantioselectivity (entries 7 and 8). Therefore, the following reaction was carried out using (*S*)-C_{10}–BridgePHOS as the chiral ligand in the presence of D-CSA, CH_2Cl_2/TFE (1/1, 1 mL) at 35 °C under 60 bar H_2 pressure.

With the optimal reaction condition in hand, applicability of this catalytic system was investigated on a series of *N*-unprotected indoles (Table 3). At first, the effect of R_2 for 2-substituted substrates on the reaction was investigated. The enantioselectivities of the products were improved by replacing the Me group with a Bn substituent (entries 1 and 2). A Bn group possessing a *para*-fluro or methyl group did not significantly affect the reaction outcome (entries 3 and 4). Replacing the Bn group with naphthylmethyl derivatives had little effect on catalytic behavior. Products with up to 96% ee were obtained (entries 5 and 6). The substituted group R_1 on the phenyl ring of the indoles was also examined. To our delight, addition of a Me group to the 7-position of the indoles gave excellent enantioselectivities (up to 98% ee) and quantitative conversions of products (entries 7–9).

Substrate scope was also expanded to 2,3-disubstituted indoles, because the corresponding products, 2,3-disubstituted indolines (especially those with fused ring), are commonly found in alkaloids and other natural products. A substrate with a Me group at the 2 and 3-position was subjected to our reaction conditions and the reaction proceeded smoothly to give the desired product in quantitative

Table 3
Asymmetric hydrogenation of a series of *N*-unprotected indoles[a]



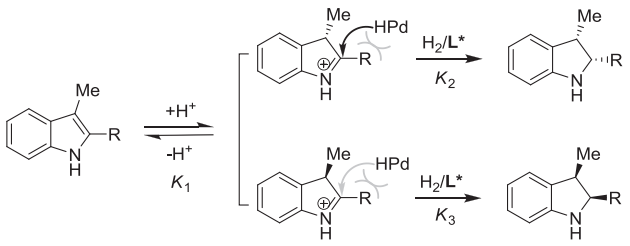
Entry	R^1	R^2	R^3	Product	Conv. (%)[b]	ee (%)[c,d]
1	H	Me	H	**2a**	>95	88(*S*)
2	H	Bn	H	**2b**	>95	95(*S*)
3	H	4-$FC_6H_4CH_2$–	H	**2c**	>95	94(*S*)
4	H	4-$MeC_6H_4CH_2$–	H	**2d**	>95	95(*S*)
5	H	1-Naphthylmethyl	H	**2e**	>95	96(*S*)
6	H	2-Naphthylmethyl	H	**2f**	>95	94(*S*)
7[e]	7-Me	Bn	H	**2g**	>95	97(*S*)
8[e]	7-Me	4-$FC_6H_4CH_2$–	H	**2h**	>95	97(*S*)
9[e]	7-Me	4-$MeC_6H_4CH_2$–	H	**2i**	>95	98(*S*)
10	H	Me	Me	**2j**	>95	90(*S*,*S*)
11	H	$-(CH_2)_3-$		**2k**	>95	59(*S*,*S*)
12	H	$-(CH_2)_4-$		**2l**	>95	93(*S*,*S*)
13	H	$-(CH_2)_5-$		**2m**	>95	90(*S*,*S*)
14	5-F	$-(CH_2)_4-$		**2n**	>95	89(*S*,*S*)
15	5-Me	$-(CH_2)_4-$		**2o**	>95	88(*S*,*S*)
16	5-MeO	$-(CH_2)_4-$		**2p**	>95	84(*S*,*S*)
17	7-Me	$-(CH_2)_4-$		**2q**	>95	95(*S*,*S*)
18[e]	H	H	Me	**2r**	>95	66(*S*)
19[e]	H	H	Bn	**2s**	>95	51(*S*)

[a] Conditions: **1a**–**s** (0.15 mmol), $Pd(OCOCF_3)_2$ (0.8 mg, 2.0 mol %), (*S*)-C_{10} BridgePHOS (2.0 mg, 2.4 mol %), D-CSA (1 equiv), CH_2Cl_2/TFE (1/1, 1 mL), 24 h, 35 °C, 60 bar H_2 pressure.
[b] Determined by ^1H NMR analysis.
[c] Determined by chiral HPLC analysis.
[d] The absolute configuration of the products were determined by comparison of the specific rotations with the literature data.[15a]
[e] Reaction is carried out for 36 h.

conversion and 90% ee (entry 10). Our attention then turned to the 2,3-disubstituted fused ring indolines, of which a synthesis has not been widely reported. The reduction of five to seven fused ring indoles were investigated first, with products being obtained with up to 93% ee (entries 11–13). Interestingly, both electron donating and withdrawing R_1 substituents at the 5-position on the phenyl ring of the indole substrates, decreased the enantioselectivities of the reactions (entries 14–16). However, a methyl group at the 7-position of the indoles provided better enantioselectivity (95% ee, entry 17). Finally, reactions of 3-substituted indoles were investigated and only moderate enantioselectivities were obtained, albeit with full conversion of the substrates to the products. (entries 18 and 19).

The results mentioned above show that substrates possessing substituents at the 2-position or 2,3-position, reacted very well in our catalytic system. Substrates with groups at the 3-position gave medium enantioselectivities. It appears that groups at the 2-position play a significant role in the asymmetric hydrogenation. Considering the reaction pathway and mechanism, a dynamic kinetic resolution hydrogenation process is proposed, which has been studied by Zhou and Zhang. Herein, we propose a more detailed description (Scheme 2).

The indole first reacts with the acidic additive to give iminium species via protonation of the C=C double bond. The iminium species can then be reduced via a hydride anion to give two possible enantiomers. If 2-substituted or 2,3-substituted indoles were used, reaction of the intermediate iminium ion with the hydride anion becomes more difficult because of the steric hindrance imposed by the group at the 2-positon. This results in the equilibrium rate of the formation of the iminium intermediate from the indole being much faster than the hydrogenation process ($k_1 \gg k_2$). Good to excellent enantioselectivity was then observed for the hydrogenation of the intermediate iminium during the enantioselectivity-determining step. If the R group is replaced by an H atom, the rate of hydride addition to the C=N double bond of the intermediate iminium species increases because of a reduction in steric hindrance. Additionally, the difference between K_2 and K_3 also decreases for the increased reaction rate. The two combined aspects result in only moderate enantioselectivities for the whole reaction process.



Scheme 2. Proposed reaction pathway.

3. Conclusion

To summarize, we have applied the axially chiral diphosphine (*S*)-C_{10}–BridgePHOS ligand to a highly efficient Pd-catalyzed enantioselective hydrogenation of substituted indoles. The methodology is suitable for the hydrogenation of indoles substituted at the 2-, 3- and 2,3-positions. Products were obtained in quantitative conversion and up to 98% ee. The role the 2-position substituent plays in the hydrogenation process has been proposed. Further work to improve the reaction for indoles substituted at the 3-position is ongoing.

4. Experimental section

4.1. General

All the moisture and air sensitive reactions were carried out under nitrogen or argon. All organic solvents were dried and freshly distilled before use with standard methods. Purification of the

products was accomplished by flash chromatography on silica gel (100–200 mesh). Identification of compounds were recorded on Varian Mercury Plus 400 with ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz). Specific rotation was measured on the Rudolph Autopol VI Automatic Polarimeter. HRMS was measured on UMS Q-Tof (ESI) Premier.

4.2. General procedure for Pd-catalyzed asymmetric hydrogenation

(*S*)-C_{10}–BridgePHOS (2.0 mg, 2.4 mol %) and $Pd(OCOCF_3)_2$ (0.8 mg, 2 mol %) were placed into an oven dried flask under a nitrogen atmosphere, and degassed fresh dry acetone (2 mL) was added. The mixture was stirred at room temperature for 1 h. Then acetone was removed under vacuum and a solvent system of CH_2Cl_2/TFE (1/1, 1 mL) was added to the mixture to afford the catalyst solution. The substrate **1** (0.15 mmol) and additive (1 equiv) were placed in a reaction tube under nitrogen and the above catalyst solution was added to the tube. The mixture was then degassed and transferred to a stainless steel autoclave in a glove box. After exchanging the gas three times, the hydrogenation was carried out at 35 °C under 60 bar H_2. After several hours, the reaction mixture was concentrated under reduced pressure. After alkalization with saturated $NaHCO_3$, the percentage conversion of product was determined by ^{1}H NMR analysis of the crude product. The organic residue was purified by flash chromatography with ethyl acetate/petrol ether (1:50) to give pure product **2**. Enantiomeric excess was determined using a Daicel Chiralcel column with hexane/*i*-propyl alcohol as the eluant.

*4.2.1. (−)-(S)-2-Methylindoline (**2a**).*[15a] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J=7.2 Hz, 1H), 7.04 (t, J=7.6 Hz, 1H), 6.72 (t, J=7.2 Hz, 1H), 6.63 (d, J=7.6 Hz, 1H), 4.09–3.93 (m, 1H), 3.76 (br s, 1H), 3.17 (dd, J=15.4, 8.6 Hz, 1H), 2.66 (dd, J=15.4, 7.8 Hz, 1H), 1.31 (d, J=6.0 Hz, 3H); $[\alpha]_D^{20}$ −10.78 (*c* 0.18, benzene); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/*i*-PrOH 98:2, UV 254 nm, 25 °C, 0.5 mL/min, t_1=14.5 min (minor), t_2=20.3 min (major), 88% ee.

*4.2.2. (−)-(S)-2-Benzylindoline (**2b**).*[15a] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, J=7.2 Hz, 2H), 7.28–7.21 (m, 3H), 7.10 (d, J=7.6 Hz, 1H), 7.02 (t, J=7.6 Hz, 1H), 6.73 (td, J=7.2, 0.8 Hz, 1H), 6.64 (d, J=7.6 Hz, 1H), 4.17–4.06 (m, 1H), 3.15 (dd, J=15.8, 8.4 Hz, 1H), 2.97–2.76 (m, 3H); $[\alpha]_D^{20}$ −78.9 (*c* 1.00, $CHCl_3$); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralcel AD-H), hexane/*i*-PrOH 99:1, UV 254 nm, 25 °C, 1.0 mL/min, t_1=12.2 min (minor), t_2=15.3 min (major), 95% ee.

*4.2.3. (−)-(S)-2-(4′-Flurobenzyl)indoline (**2c**).* As a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.16 (m, 2H), 7.10 (d, J=6.4 Hz, 1H), 7.06–7.01 (m, 3H), 6.72 (td, J=7.6, 0.8 Hz, 1H), 6.60 (d, J=7.6 Hz, 1H), 4.11–4.02 (m, 1H), 3.71 (br s, 1H), 3.14 (dd, J=15.2, 8.4 Hz, 1H), 2.94–2.74 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 160.6, 149.8, 134.8, 134.7, 130.8, 130.7, 128.8, 127.7, 125.1, 119.5, 115.7, 115.5, 110.0, 61.3, 41.8, 35.9; HRMS (ESI+Tof) calculated for $C_{15}H_{15}NF$ $[M+H]^+$ 228.1189, found 228.1163; $[\alpha]_D^{20}$ −17.4 (*c* 0.14, benzene); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralcel OD-H), hexane/*i*-PrOH 99:1, UV 254 nm, 25 °C, 1.0 mL/min, t_1=17.9 min (minor), t_2=21.1 min (major), 94% ee.

*4.2.4. (−)-(S)-2-(4′-Methylbenzyl)indoline (**2d**).*[15a] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.13 (m, 3H), 7.12 (d, J=7.6 Hz, 1H), 7.05 (td, J=7.4, 0.8 Hz, 1H), 6.74 (td, J=7.4, 0.8 Hz, 1H), 6.61 (d, J=8.0 Hz, 1H), 4.15–4.04 (m, 1H), 3.78 (br s, 1H), 3.17 (dd, J=15.4, 8.6 Hz, 1H), 2.95–2.79 (m, 3H), 2.39 (s, 3H); $[\alpha]_D^{20}$ −82.3 (*c* 1.00, $CHCl_3$); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralcel OD-H), hexane/*i*-PrOH 99:1, UV 254 nm, 25 °C, 1.0 mL/min, t_1=12.1 min (minor), t_2=13.3 min (major), 95% ee.

*4.2.5. (−)-(S)-2-(1-Naphtylmethyl)indoline (**2e**).*[15a] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J=7.2 Hz, 1H), 7.93–7.88 (m, 1H), 7.80 (d, J=8.2 Hz, 1H), 7.58–7.49 (m, 2H), 7.46 (t, J=7.6 Hz, 1H), 7.38 (d, J=6.8 Hz, 1H), 7.13 (d, J=7.2 Hz, 1H), 7.04 (t, J=7.6 Hz, 1H), 6.73 (t, J=7.4 Hz, 1H), 6.57 (d, J=7.6 Hz, 1H), 4.32–4.21 (m, 1H), 3.89 (br s, 1H), 3.41–3.26 (m, 2H), 3.21 (dd, J=16.0, 8.8 Hz, 1H), 2.93 (dd, J=15.6, 6.8 Hz, 1H); $[\alpha]_D^{20}$ −40.9 (*c* 1.50, $CHCl_3$); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OD-H), hexane/*i*-PrOH 90:10, UV 254 nm, 25 °C, 0.8 mL/min, t_1=14.9 min (minor), t_2=19.5 min (major), 96% ee.

*4.2.6. (−)-(S)-2-(2-Naphtylmethyl)indoline (**2f**).* As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.78 (m, 3H), 7.68 (s, 1H), 7.53–7.43 (m, 2H), 7.39 (d, J=8.4 Hz, 1H), 7.11 (d, J=7.2 Hz, 1H), 7.02 (t, J=7.6 Hz, 1H), 6.71 (t, J=7.2 Hz, 1H), 6.57 (d, J=7.6 Hz, 1H), 4.26–4.09 (m, 1H), 3.88 (br s, 1H), 3.18 (dd, J=15.6, 8.4 Hz, 1H), 3.04 (ddd, J=22.0, 13.2, 7.2 Hz, 2H), 2.86 (dd, J=15.6, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 136.8, 133.8, 132.4, 128.6, 128.5, 127.9, 127.7, 127.6, 126.4, 125.8, 125.1, 61.1, 43.1, 36.2; HRMS (ESI+Tof) calculated for $C_{19}H_{18}N$ $[M+H]^+$ 260.1441, found 260.1439; $[\alpha]_D^{20}$ −50.4 (*c* 0.16, benzene); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralcel OD-H), hexane/*i*-PrOH 90:10, UV 254 nm, 25 °C, 1.0 mL/min, t_1=11.1 min (minor), t_2=13.9 min (major), 94% ee.

*4.2.7. (−)-(S)-7-Methyl-2-benzylindoline (**2g**).* As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.34 (m, 2H), 7.32–7.23 (m, 3H), 6.99 (d, J=7.2 Hz, 1H), 6.89 (d, J=7.2 Hz, 1H), 6.68 (t, J=7.4 Hz, 1H), 4.20–4.04 (m, 1H), 3.66 (br s, 1H), 3.19 (dd, J=15.4, 8.6 Hz, 1H), 2.96–2.81 (m, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 139.3, 129.3, 128.9, 128.5, 127.9, 126.7, 122.5, 119.0, 118.8, 61.0, 43.0, 36.4, 17.1; HRMS (ESI+Tof) calculated for $C_{16}H_{18}N$ $[M+H]^+$ 224.1439, found 224.1421; $[\alpha]_D^{20}$ −24.6 (*c* 0.18, benzene); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralpak IA), hexane/*i*-PrOH 99:1, UV 254 nm, 25 °C, 1.0 mL/min, t_1=6.8 min (minor), t_2=7.8 min (major), 97% ee.

*4.2.8. (−)-(S)-7-Methyl-2-(4′-flurobenzyl)indoline (**2h**).* As a pale red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.16 (m, 2H), 7.07–7.00 (m, 2H), 6.97 (d, J=7.2 Hz, 1H), 6.88 (d, J=7.6 Hz, 1H), 6.67 (t, J=7.2 Hz, 1H), 4.13–4.00 (m, 2H), 3.64 (br s, 1H), 3.16 (dd, J=15.6, 8.4 Hz, 1H), 2.93–2.75 (m, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 160.6, 149.1, 135.0, 134.9, 130.8, 130.7, 128.5, 127.7, 122.5, 119.0, 118.8, 115.7, 115.5, 61.0, 42.1, 36.3, 17.0; HRMS (ESI+Tof) calculated for $C_{16}H_{17}NF$ $[M+H]^+$ 242.1345, found 242.1334; $[\alpha]_D^{20}$ −22.2 (*c* 0.21, benzene); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralcel OD-H), hexane/*i*-PrOH 99:1, UV 254 nm, 25 °C, 1.0 mL/min, t_1=17.5 min (minor), t_2=19.7 min (major), 97% ee.

*4.2.9. (−)-(S)-7-Methyl-2-(4′-methylbenzyl)indoline (**2i**).* As a p ale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.10 (m, 4H), 6.99 (d, J=7.2 Hz, 1H), 6.93–6.85 (m, 1H), 6.68 (t, J=7.4 Hz, 1H), 4.14–4.02 (m, 1H), 3.73 (br s, 1H), 3.19 (dd, J=15.6, 8.4 Hz, 1H), 2.93–2.77 (m, 3H), 2.38 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 136.2, 136.1, 129.5, 129.2, 128.5, 127.9, 122.5, 118.9, 118.7, 61.0, 42.5, 36.4, 21.3, 17.1; HRMS (ESI+Tof) calculated for $C_{17}H_{20}N$ $[M+H]^+$ 238.1596, found 238.1565; $[\alpha]_D^{20}$ −64.5 (*c* 0.50, benzene); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IE), hexane/*i*-PrOH 99:1, UV 254 nm, 25 °C, 0.5 mL/min, t_1=11.6 min (major), t_2=12.3 min (minor), 98% ee.

*4.2.10. (−)-(S,S)-cis-2,3-Dimethylindoline (**2j**).*[15a] As a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, J=7.2 Hz, 1H), 7.02 (t, J=7.6 Hz,

1H), 6.74 (t, J=7.6 Hz, 1H), 6.64 (d, J=7.6 Hz, 1H), 4.01–3.88 (m, 1H), 3.35–3.19 (m, 1H), 1.18 (d, J=7.2 Hz, 2H), 1.15 (d, J=6.4 Hz, 2H); $[\alpha]_D^{20}$ −15.6 (c 0.40, $CHCl_3$); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OJ-H), hexane/i-PrOH 99:1, UV 254 nm, 25 °C, 1.0 mL/min, t_1=21.8 min (major), t_2=28.9 min (major), 90% ee.

*4.2.11. (−)-(3aS,8bS)-1,2,3,3a,4,8b-Hexahydrocyclopenta[b]indole (**2k**).*[16] As a pale red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, J=7.2 Hz, 1H), 7.00 (t, J=7.6 Hz, 1H), 6.70 (td, J=7.2, 0.8 Hz, 1H), 6.58 (d, J=7.6 Hz, 1H), 4.42–4.34 (m, 1H), 3.74–3.82 (m, 1H), 1.89–2.01 (m, 1H), 1.82–1.59 (m, 4H), 1.58–1.51 (m, 1H); $[\alpha]_D^{20}$ −25.4 (c 0.20, $CHCl_3$); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/i-PrOH 95:5, UV 254 nm, 25 °C, 0.5 mL/min, t_1=10.6 min (minor), t_2=13.6 min (major), 59% ee.

*4.2.12. (−)-(2S,3S)-5,6,7,8,8a,9-Hexahydro-4bH-carbazole (**2l**).*[15a] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.07 (m, 1H), 7.03 (tdd, J=7.6, 1.2, 0.8 Hz, 1H), 6.75 (td, J=7.2, 0.8 Hz, 1H), 6.68 (d, J=8.0 Hz, 1H), 3.77–3.70 (m, 1H), 3.11 (q, J=6.6 Hz, 1H), 1.74–1.81 (m, 2H), 1.48–1.70 (m, 3H), 1.30–1.45 (m, 3H); $[\alpha]_D^{20}$ −28.2 (c 1.10, $CHCl_3$); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/i-PrOH 98:2, UV 254 nm, 25 °C, 1.0 mL/min, t_1=6.5 min (minor), t_2=11.9 min (major), 93% ee.

*4.2.13. (−)-(2S,3S)-5,5a,6,7,8,9,10,10a-Octahydrocyclohepta[b]indole (**2m**).*[15a] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06–6.97 (m, 2H), 6.72 (td, J=7.4, 1.0 Hz, 1H), 6.61 (d, J=7.6 Hz, 1H), 4.10–4.01 (m, 1H), 3.47 (td, J=10.4, 3.6 Hz, 1H), 2.01–1.92 (m, 1H), 1.91–1.66 (m, 6H), 1.46–1.28 (m, 3H); $[\alpha]_D^{20}$ −31.7 (c 0.50, $CHCl_3$); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/i-PrOH 99:1, UV 254 nm, 25 °C, 0.5 mL/min, t_1=16.4 min (minor), t_2=24.7 min (major), 90% ee.

*4.2.14. (−)-(4aS,9aS)-5-Fluoro-2,3,4,4a,9,9a-hexahydro-1H-carbazole (**2n**).*[17] As a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (ddd, J=8.4, 2.6, 1.0 Hz, 1H), 6.72–6.66 (m, 1H), 6.55 (dd, J=8.4, 4.4 Hz, 1H), 3.76–3.70 (m, 1H), 3.47 (br s, 1H), 3.08 (q, J=6.6 Hz, 1H), 1.74–1.69 (m, 2H), 1.68–1.48 (m, 3H), 1.44–1.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 156.2, 146.9, 146.8, 135.6, 135.5, 113.1, 112.9, 111.0, 110.7, 110.5, 110.4, 60.4, 41.4, 29.3, 27.0, 22.6, 21.8; $[\alpha]_D^{20}$ −8.6 (c 0.41, benzene); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/i-PrOH 99:1, UV 254 nm, 25 °C, 0.5 mL/min, t_1=12.2 min (minor), t_2=18.7 min (major), 89% ee.

*4.2.15. (−)-(4aS,9aS)-5-Methyl-2,3,4,4a,9,9a-hexahydro-1H-carbazole (**2o**).*[18] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94–6.90 (m, 1H), 6.88–6.82 (m, 1H), 6.60 (d, J=7.6 Hz, 1H), 3.77–3.64 (m, 1H), 3.08 (q, J=6.6 Hz, 1H), 2.28 (s, 3H), 1.82–1.74 (m, 2H), 1.69–1.50 (m, 3H), 1.45–1.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 134.0, 128.3, 127.5, 124.1, 110.3, 60.0, 41.2, 29.4, 27.1, 22.7, 22.0, 21.2; $[\alpha]_D^{20}$ −17.5 (c 0.40, benzene); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/i-PrOH 90:10, UV 254 nm, 25 °C, 1.0 mL/min, t_1=4.6 min (minor), t_2=8.3 min (major), 88% ee.

*4.2.16. (−)-(4aS,9aS)-5-Methoxy-2,3,4,4a,9,9a-hexahydro-1H-carbazole (**2p**).* As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73–6.71 (m, 1H), 6.63–6.56 (m, 2H), 3.76 (s, 3H), 3.74–3.67 (m, 1H), 3.09 (q, J=6.4 Hz, 1H), 1.80–1.70 (m, 2H), 1.69–1.49 (m, 3H), 1.45–1.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 144.6, 135.5, 111.6, 110.8, 110.5, 60.2, 56.1, 41.6, 29.4, 27.1, 22.7, 22.0; HRMS (ESI+Tof) calculated for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1388, found 204.1351; $[\alpha]_D^{20}$ −22.9 (c 0.38, benzene); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/i-PrOH 90:10, UV 254 nm, 25 °C, 1.0 mL/min, t_1=9.3 min (minor), t_2=12.9 min (major), 84% ee.

*4.2.17. (−)-(4aS,9aS)-7-Methyl-2,3,4,4a,9,9a-hexahydro-1H-carbazole (**2q**).*[15a] As a pale blue oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, J=7.6 Hz, 1H), 6.88 (d, J=7.6 Hz, 1H), 6.70 (t, J=7.4 Hz, 1H), 3.79–3.68 (m, 1H), 3.12 (q, J=6.4 Hz, 1H), 2.15 (s, 3H), 1.81–1.71 (m, 2H), 1.69–1.51 (m, 3H), 1.44–1.30 (m, 3H); $[\alpha]_D^{20}$ −18.0 (c 0.70, $CHCl_3$); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/i-PrOH 99:1, UV 254 nm, 25 °C, 1.0 mL/min, t_1=5.4 min (minor), t_2=6.3 min (major), 95% ee.

*4.2.18. (−)-(S)-3-Methylindoline (**2r**).*[15e] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.08 (m, 1H), 7.07–7.01 (m, 1H), 6.75 (td, J=7.4, 0.8 Hz, 1H), 6.68–6.63 (m, 1H), 3.71 (t, J=8.6 Hz, 1H), 3.48 (br s, 1H), 3.42–3.32 (m, 1H), 3.12 (t, J=8.6 Hz, 1H), 1.34 (d, J=6.8 Hz, 3H); $[\alpha]_D^{20}$ −13.4 (c 0.25, $CHCl_3$); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralpak IC-3), hexane/i-PrOH 95:5, UV 254 nm, 25 °C, 0.5 mL/min, t_1=12.3 min (minor), t_2=14.4 min (major), 66% ee.

*4.2.19. (−)-(S)-3-Benzylindoline (**2s**).*[16] As a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.29 (m, 2H), 7.24 (dd, J=8.8, 7.2 Hz, 3H), 7.05 (t, J=7.6 Hz, 1H), 6.98 (d, J=7.6 Hz, 1H), 6.76–6.62 (m, 2H), 3.67–3.57 (m, 1H), 3.55 (t, J=8.6 Hz, 1H), 3.29 (dd, J=8.6, 6.4 Hz, 1H), 3.12 (dd, J=13.8, 6.0 Hz, 1H), 2.83 (dd, J=13.8, 8.8 Hz, 1H); $[\alpha]_D^{20}$ −24.0 (c 0.70, $CHCl_3$); HPLC conditions: the enantiomeric excess was determined by HPLC (Chiralcel AD-H), hexane/i-PrOH 90:10, UV 254 nm, 25 °C, 0.5 mL/min, t_1=14.4 min (minor), t_2=16.8 min (major), 51% ee.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.06.016.

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