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One-Pot Synthesis of Pyrrolo[1,2-*a*]indoles by Chiral *N*-Triflyl Phosphoramide Catalyzed Friedel-Crafts Alkylation of 4,7-Dihydroindole with *β*,*γ*-Unsaturated *α*-Keto Esters

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Chiral *N*-triflyl phosphoramide was found an efficient catalyst for the enantioselective Friedel-Crafts alkylation reaction of 4,7-dihydroindole with *β*,*γ*-unsaturated *α*-keto esters. In the presence of 5 mol% of the optimized catalyst, various pyrrolo[1,2-*a*]indoles were obtained in excellent enantioselectivity, moderate yields and up to 3∶1 diastereoselectivity based on the one-pot synthesis including the Friedel-Crafts alkylation reaction and the subsequent *p*-benzoquinone oxidation.

Keywords *N*-triflyl phosphoramide, Friedel-Crafts, enantioselective, 4,7-dihydroindole, one-pot synthesis

Introduction

Pyrrolo[1,2-*a*]indole represents a common structural moiety widely existing in natural products or pharmaceuticals with interesting biological activities (Figure 1). For example, the mitomycin family has been studied as potent antitumor antibiotics.[1a,1b] Yuremamine has been isolated with psychoactive property.[1c] JTT-010 is a new structural class of protein kinase C-*β*-selective inhibitor.[1d] Flinderole C is a novel drug candidate which shows impressive antimalarial activity against the *Plasmodium falciparum*.[1e] Although several methodologies have been developed to synthesize the pyrrolo[1,2-*a*]indole derivatives,[2] the enantioselective variants of these reactions are still rare.[3] Thus, the exploration of efficient methodologies for the construction of these optically pure polycyclic ring structures in a single operation is highly desirable.

Chiral phosphoric acids[4] have been demonstrated to be efficient catalysts for the asymmetric Friedel-Crafts alkylation reactions[5] of aromatic rings with imines,[6] enamides,[7] *α*,*β*-unsaturated carbonyls,[8] nitroolefins,[9] and various other electrophilic partners.[10] Meanwhile, introduced by Yamamoto and co-workers, chiral *N*-triflyl phosphoramides have been widely applied to asymmetric catalytic reactions due to their even stronger acidity than phosphoric acids.[11,12] We recently reported a highly enantioselective Friedel-Crafts reaction of 4,7-dihydroindoles with *β*,*γ*-unsaturated *α*-keto esters catalyzed by the chiral *N*-triflyl phosphoramide.[13,14,6m,8d] As part of our ongoing efforts to develop highly efficient chiral phosphoramide catalyzed asymmetric Friedel-Crafts alkylation reactions,[15] we envisaged the one-pot enantioselective synthesis of pyrrolo[1,2-*a*]indoles including the Friedel-Crafts alkylation reaction of 4,7-dihydroindole with *β*,*γ*-unsaturated *α*-keto esters catalyzed by chiral *N*-triflyl phosphoramide and the subsequent *p*-benzoquinone oxidation (Scheme 1).

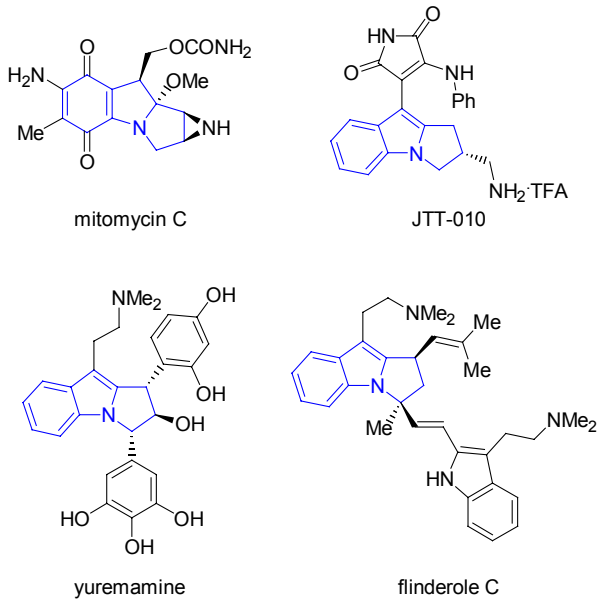

Figure 1 Representative compounds containing pyrrolo[1,2-*a*]-indole cores.

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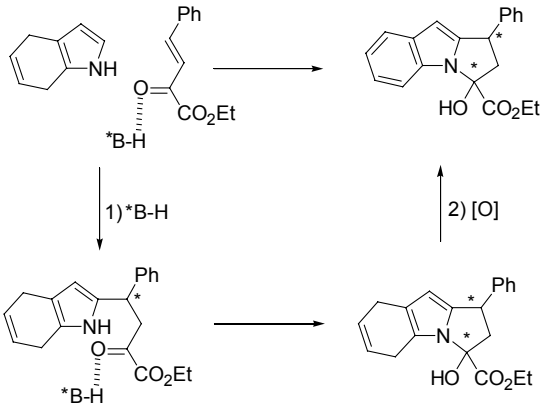
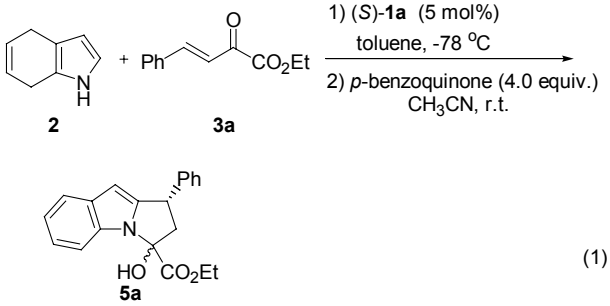
Herein, we report the results from this study.

Scheme 1



Results and Discussion

We began our study by examining the reaction of 4,7-dihydroindole (**2**) with β,γ-unsaturated α-keto ester **3a**. To our great delight, with 5 mol% of chiral phosphoramide (*S*)-**1a** as the catalyst, the reaction sequence proceeded smoothly, and the desired pyrrolo[1,2-*a*]indole compound **5a** was obtained in an overall 64% yield with 75% *ee* after an oxidation by *p*-benzoquinone (Eq. 1).



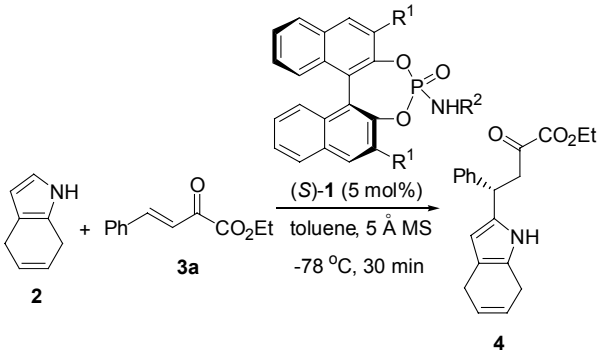
(1)

64% yield, *dr* = 3:1, 75% *ee*

To further optimize the reaction conditions, various chiral phosphoramides were screened for the enantioselective Friedel-Crafts alkylation reaction between 4,7-dihydroindole (**2**) and β,γ-unsaturated α-keto ester **3a**. The reaction was performed in toluene at −78 ℃ with 100 mg 5 Å MS for 30 min. In the presence of 5 mol% of the chiral phosphoramides, all the reactions of **3a** with 2 equivalents of **2** worked well to give the desired product **4**. The best result (73% yield, 87% *ee*) was obtained using *N*-triflyl phosphoramide **1a** bearing the bulky 2,4,6-(i-Pr)$_3$-C$_6$H$_2$ groups (Entry 1, Table 1). Chiral phosphoramide **1l** also catalyzed the Friedel-Crafts alkylation well giving similar results (84% *ee* vs. 87% *ee*; Entry 12, Table 1). It was found that the molecular sieves were critical for obtaining reasonable yield (Entry 13, Table 1).

With the optimal catalyst (*S*)-**1a** in hand, reaction temperatures and solvents were then examined. As

Table 1 Screening of chiral phosphoramides



Entry[a]	**1** R^1, R^2	**4** Yield[b]/%	**4** *ee*[c]/%
1	**1a** 2,4,6-(i-Pr)$_3$-C$_6$H$_2$, Tf	73	87
2	**1b** 4-NO$_2$-C$_6$H$_4$, Tf	29	−29
3	**1c** 9-anthryl, Tf	44	24
4	**1d** 9-phenanthryl, Tf	46	27
5	**1e** 1-naphthyl, Tf	73	8
6	**1f** SiPh$_3$, Tf	57	9
7	**1g** 4-biphenyl, Tf	58	8
8	**1h** 4-3',5'-(CF$_3$)$_2$-biphenyl, Tf	58	16
9	**1i** pyrenyl, Tf	74	8
10	**1j** 3,5-(CH$_3$)$_2$-C$_6$H$_3$, Tf	52	0
11	**1k** 3,5-(CF$_3$)$_2$-C$_6$H$_3$, SO$_2$C$_4$F$_9$	54	4
12	**1l** 2,4,6-(i-Pr)$_3$-C$_6$H$_2$, SO$_2$C$_8$F$_{17}$	59	84
13[d]	**1a** 2,4,6-(i-Pr)$_3$-C$_6$H$_2$, Tf	31	81

[a] Reaction conditions: 2.0 equiv. of **2**, 5 mol% of (*S*)-**1**, 0.20 mol/L of **3a**, 100 mg 5 Å MS, −78 ℃ in toluene. [b] Isolated yields. [c] Determined by HPLC analysis (Chiralcel OD-H). [d] Without 5 Å MS.

summarized in Table 2, the reaction proceeded smoothly in various common solvents and toluene remained to be the optimal one. Unfortunately, when the reaction was conducted at higher temperature, the enantioselectivity was decreased (Entries 5—7, Table 2).

The ratio of 4,7-dihydroindole (**2**) and β,γ-unsaturated α-keto ester **3a** has also been examined. The results are summarized in Table 3. Interestingly, increasing the amount of dihydroindole **2** caused the decrease of yield (Entries 1—5, Table 3), and utilization of 1.5 equivalents of dihydroindole **2** provided the best result (82% yield, 86% *ee*; Entry 2, Table 3). Notably, when β,γ-unsaturated α-keto ester **3a** was added to the reaction by syringe pump over 15 min, the desired product **4** was obtained in 95% yield with 91% *ee* (Entry 6, Table 3).

Under the optimized reaction conditions [1.5 equiv. of **2**, 0.20 mol/L **3** in toluene, 5 mol% of (*S*)-**1a**, −78 ℃, 100 mg 5 Å MS, and **3** was added to the reaction by syringe pump over 15 min], the one-pot synthesis of pyrrolo[1,2-*a*]indoles including the Friedel-Crafts alkylation reaction and the subsequent *p*-benzoquinone oxidation was explored. Simple work-up was performed to

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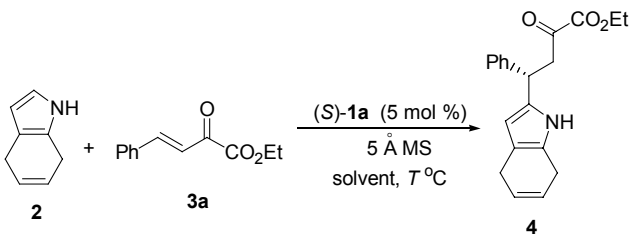
Table 2 Screening of reaction conditions

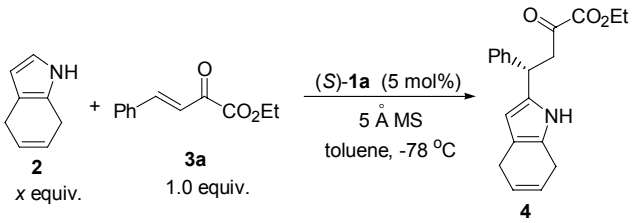


2 **3a** **4**

Entry[a]	Solvent	T/℃	Yield[b]/%	*ee*/%
1	THF	−78	51	40
2	Et_2O	−78	54	43
3	CH_2Cl_2	−78	61	58
4	toluene	−78	73	87
5	toluene	−60	67	74
6	toluene	−40	90	60
7	toluene	−20	59	47
8	*o*-xylene	−20	66	51

[a] Reaction conditions: 2.0 equiv. of **2**, 5 mol% of (*S*)-**1a**, 0.20 mol/L of **3a**, 100 mg 5 Å MS in solvent. [b] Isolated yields. [c] Determined by HPLC analysis (Chiralcel OD-H).

Table 3 Screening of ratio of the substrates



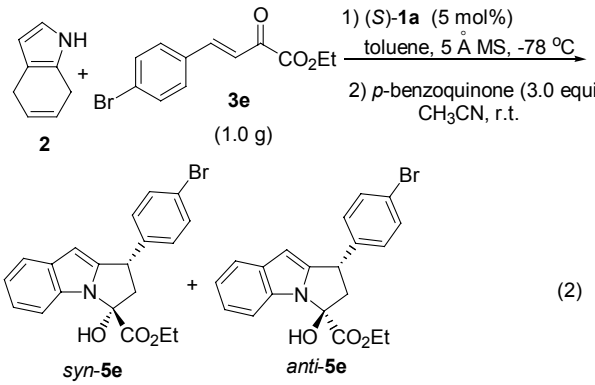
2 *x* equiv. **3a** 1.0 equiv. **4**

Entry[a]	*x*	Yield[b]/%	*ee*[c]/%
1	1.1	81	74
2	1.5	82	86
3	2	73	87
4	3	42	89
5	4	55	89
6[d]	1.5	95	91

[a] Reaction conditions: *x* equiv. of **2**, 5 mol% of (*S*)-**1a**, 0.20 mol/L of **3a**, 100 mg 5 Å MS, −78 ℃ in toluene. [b] Isolated yields. [c] Determined by HPLC analysis (Chiralcel OD-H). [d] **3a** was added to the reaction mixture over 15 min.

the reaction mixture after the completion of the first step, and 3 equiv. of *p*-benzoquinone were then introduced to the next step. As summarized in Scheme 2, in general, all the tested *β*,*γ*-unsaturated *α*-keto ester **3** were transformed to the corresponding pyrrolo[1,2-*a*]indoles **5** in moderate to good yields (48%—87%) for two steps. Either electron-withdrawing or electron-donating substituents on the phenyl moiety of *β*,*γ*-unsaturated *α*-keto ester **3** were well tolerated to give the desired products **5** with satisfactory enantioselectivity (**5a**—**5f**, **5k**, Scheme 2). *β*,*γ*-Unsaturated *α*-keto esters **3** bearing bulky substituents such as 1-naphthyl or 2-naphthyl were also good substrates, and **5g**—**5h** were achieved with satisfactory enantioselectivity (Scheme 2). Meanwhile, *β*,*γ*-unsaturated *α*-keto esters **3** bearing heteroaromatic rings such as 1-furyl or 1-thienyl were also tested. As shown in Scheme 3, **5j** was obtained with excellent enantioselectivity (96% *ee*) and **5i** was obtained with a moderate enantioselectivity (77% *ee*). However, the diastereoselectivity of this reaction sequence was only poor to moderate, and *anti*-selective products were obtained as major ones for most substrates[16].

To show the synthetic value of this enantioselective reaction sequence, the reaction of 4,7-dihydroindole (**2**) and *β*,*γ*-unsaturated *α*-keto ester **3e** was performed on a gram scale with 5 mol% of catalyst (Eq. 2). To our great delight, the desired product **5e** could be obtained without notable loss of yield as well as enantioselectivity following the same reaction conditions and work-up procedure (48% yield, 75∶25 *anti*∶*syn*, 96% *ee*). Furthermore, absolute configuration of *anti*-**5e** was determined to be (1*S*,3*S*) by an X-ray crystallographic analysis (Figure 2).[16] Thus, the absolute configuration of **4**, the product for the first Friedel-Crafts alkylation reaction, should be (*S*).



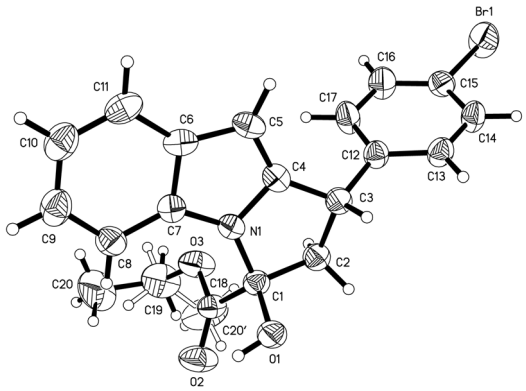
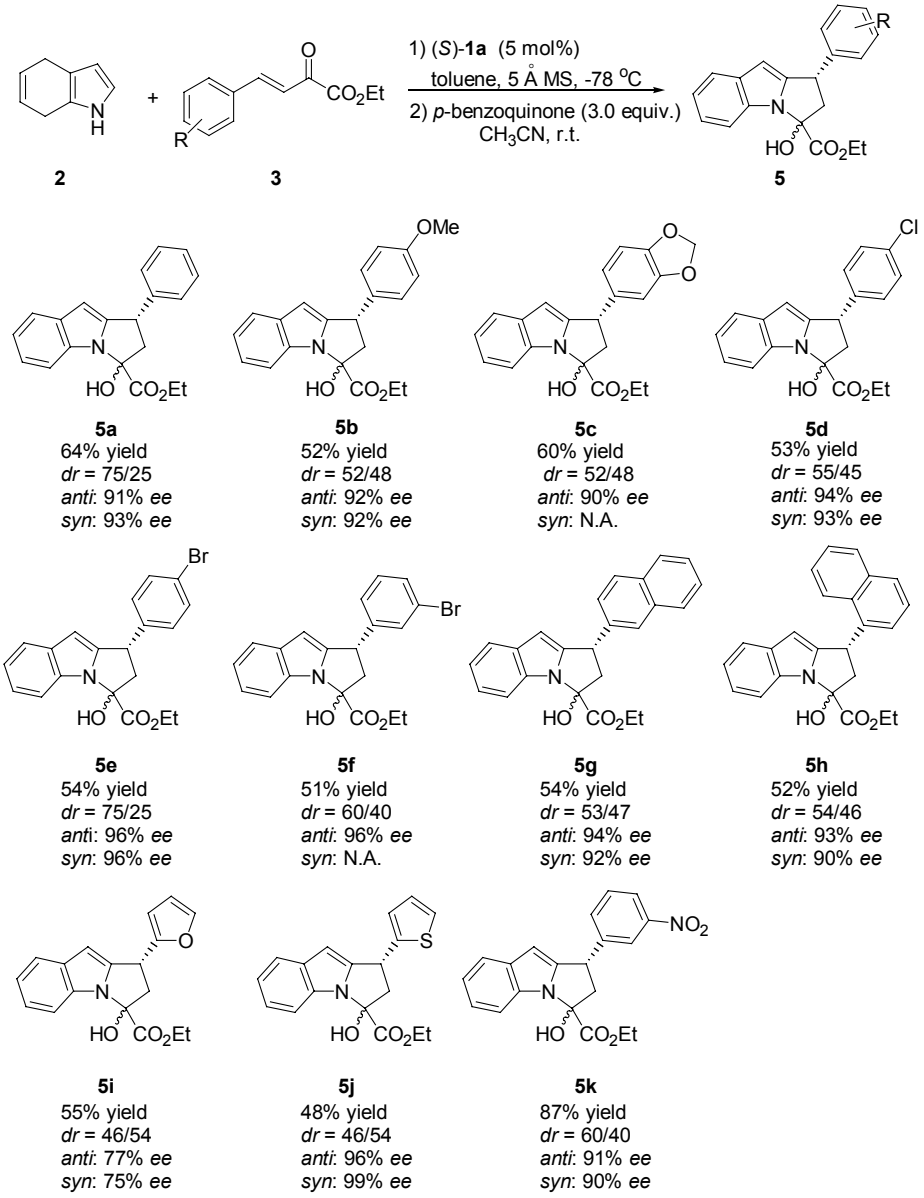


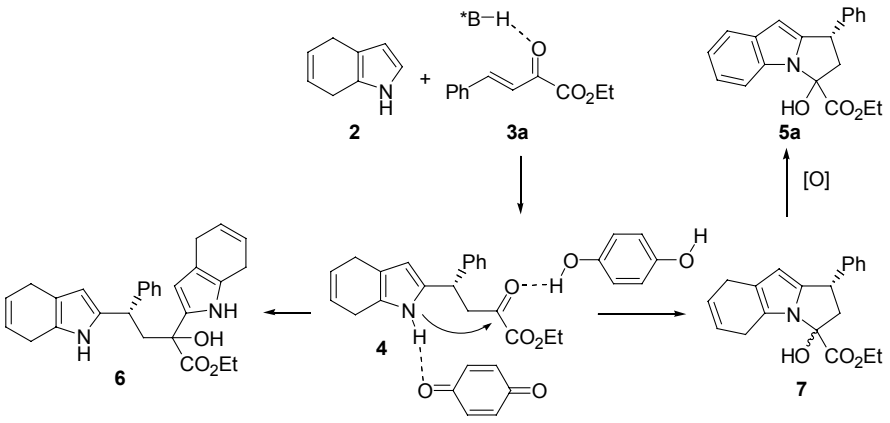
Figure 2 The X-ray structure of (*1S*,*3S*)-**5e**.

A plausible reaction pathway was proposed, as depicted in Scheme 3. Chiral *N*-triflyl phosphoramide activates **3a** through the hydrogen bonding with the car-

Scheme 2 Substrate scope for the one-pot synthesis of pyrrolo[1,2-*a*]indoles



Scheme 3 Plausible reaction pathway



bonyl group, enabling the first Friedel-Crafts alkylation between **2** and **3a** in highly enantioselective control. The obtained product (*S*)-**4**, which is highly reactive, can either further react with **2** in an intermolecular

manner to provide **6** or react in an intramolecular manner to provide **7**. Further oxidation of **7** delivers the final product **5a**. It should be pointed out that compound **7** can be isolated to support our hypothesis.

Conclusions

In conclusion, chiral *N*-triflyl phosphoramide was found an efficient catalyst for the enantioselective Friedel-Crafts alkylation reaction of 4,7-dihydroindole with *β*,*γ*-unsaturated *α*-keto esters. In the presence of 5 mol% of the optimized catalyst, various pyrrolo[1,2-*a*]-indoles were obtained in excellent enantioselectivity, moderate yields and up to 3∶1 diastereoselectivity based on the one-pot synthesis including the Friedel-Crafts alkylation reaction and the subsequent *p*-benzoquinone oxidation. A plausible mechanism was also provided.

Experimental

General methods

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300/400 MHz and 75/100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (*δ*), multiplicity (s＝singlet, d＝doublet, t＝triplet, m＝multiplet or unresolved, br＝broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (*δ*).

General procedure for the one-pot synthesis (asymmetric Friedel-Crafts reaction/oxidation)

In a dry Schlenk tube, 4,7-dihydroindole 2 (0.15 mmol), *N*-triflyl phosphoramide **1** (0.005 mmol) and 100 mg 5 Å MS were dissolved in toluene (0.5 mL) under argon. The solution was stirred for 5 min at room temperature and then for another 5 min at −78 ℃. Subsequently, *β*,*γ*-unsaturated *α*-keto ester **3** was added to the reaction by syringe pump over 15 min at −78 ℃. After the reaction was complete (monitored by TLC), saturated aqueous $NaHCO_3$ (3 mL) was added to quench the reaction. The mixture was resumed to room temperature, extracted with CH_2Cl_2. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the residue was dissolved in 2 mL CH_3CN, then *p*-benzoquinone (32.4 mg, 0.30 mmol) was added to the vial. After the reaction was complete (monitored by ^{1}H NMR), The reaction was diluted with 20 mL of CH_2Cl_2 and the organic layer was washed with 2 mol/L NaOH (20 mL×2), brine (20 mL), and dried over anhydrous Na_2SO_4. The organic layer was concentrated *in vacuo*. The residue was purified by silica gel column chromatography [*V*(ethyl acetate)/*V*(petroleum ether)＝1/10—1/5] to afford compound **5**.

(1*S*)-Ethyl 3-hydroxy-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5a) Yellow solid, 64% yield, *dr*＝75/25 (*anti*/*syn*). *anti*-**5a**: 91% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 1.16 (t, *J*＝7.2 Hz, 3H), 3.09—3.13 (m, 2H), 4.26—4.31 (m, 2H), 4.78 (s, H), 4.80 (t, *J*＝8.4 Hz, 1H), 6.10 (s, 1H), 7.10—7.20 (m, 3H), 7.26—7.37 (m, 5H), 7.52—7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 13.9, 41.5, 51.8, 63.7, 86.3, 95.2, 109.4, 120.4, 121.0, 121.4, 127.1, 127.8, 128.7, 130.7, 134.0, 141.8, 147.0, 171.8; DEPT *δ*: CH/CH_3 13.9, 41.5, 95.2, 109.4, 120.4, 121.0, 121.4, 127.1, 127.8, 128.7; CH_2: 51.8, 63.7; C: 86.3, 130.7, 134.0, 141.8, 147.0, 171.8; IR (thin film) ν_{max}: 3390, 3058, 2959, 2925, 2853, 1732, 1604, 1557, 1494, 1453, 1365, 1333, 1304, 1260, 1212, 1158, 1097, 1023, 971, 752, 699, 667, 508 cm^{-1}; MS (EI, *m*/*z*, rel. intensity) 321 (M^+, 71), 248 (100); HRMS (EI) calcd for $C_{20}H_{19}NO_3$ (M^+): 321.1365, found 321.1363; the enantiomeric ratio was determined by Daicel Chiralcel OD-H (25 cm), Hexanes/IPA＝60/40, 0.5 mL/min, *λ*＝254 nm, *t*(major)＝15.09 min, *t*(minor)＝19.14 min; $[\alpha]_D^{20}$ +14.0 (*c*＝0.255, CH_2Cl_2). *syn*-**5a**: 93% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 1.19 (t, *J*＝7.2 Hz, 3H), 2.75 (dd, *J*＝7.8, 13.8, 1H), 3.47 (dd, *J*＝9.0, 13.8 Hz, 1H), 4.18—4.35 (m, 2H), 4.64 (t, *J*＝8.4 Hz, 1H), 4.80 (s, 1H), 6.08 (s, 1H), 7.10—7.14 (m, 2H), 7.24—7.41 (m, 6H), 7.52—7.54 (m, 1H); the enantiomeric ratio was determined by Daicel Chiralcel OD-H (25 cm), Hexanes/IPA＝60/40, 0.5 mL/min, *λ*＝254 nm, *t*(minor)＝10.68 min, *t*(major)＝12.68 min; $[\alpha]_D^{20}$ −47.9 (*c*＝0.195, CH_2Cl_2).

(1*S*)-Ethyl 3-hydroxy-1-(4-methoxyphenyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5b) Brown solid, 52% yield, *dr*＝52/48 (*anti*/*syn*). *anti*-**5b**: 92% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 1.20 (t, *J*＝6.9 Hz, 3H), 3.02—3.16 (m, 2H), 3.81 (s, 3H), 4.26—4.38 (m, 2H), 4.70 (s, 1H), 4.78 (t, *J*＝8.7 Hz, 1H), 6.09 (s, 1H), 6.88 (d, *J*＝8.4 Hz, 2H), 7.08—7.20 (m, 3H), 7.29 (d, *J*＝8.4 Hz, 2H), 7.52—7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 14.0, 40.8, 52.0, 55.3, 63.7, 86.3, 95.0, 109.4, 114.1, 120.4, 121.0, 121.4, 128.8, 130.8, 133.8, 134.1, 147.5, 158.7, 171.8; IR (thin film) ν_{max}: 3459, 3053, 2958, 2926, 2853, 1736, 1611, 1584, 1557, 1513, 1453, 1422, 1363, 1327, 1304, 1249, 1208, 1178, 1157, 1102, 1033, 859, 833, 779, 751, 582, 528 cm^{-1}; MS (EI, *m*/*z*, rel. intensity) 351 (M^+, 3), 84 (100); HRMS (EI) calcd for $C_{21}H_{21}NO_4$ (M^+): 351.1471, found 351.1466; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA＝90/10, 1.0 mL/min, *λ*＝254 nm, *t*(minor)＝16.09 min, *t*(major)＝21.44 min; $[\alpha]_D^{20}$ +38.2 (*c*＝0.085, CH_2Cl_2). *syn*-**5b**: 92% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 1.19 (t, *J*＝6.9 Hz, 3H), 2.71 (dd, *J*＝7.5, 13.5 Hz, 1H), 3.44 (dd, *J*＝9.0, 13.5 Hz, 1H), 3.81 (s, 3H),4.16—4.38 (m, 2H), 4.60 (t, *J*＝8.4 Hz, 1H), 4.78 (s, 1H), 6.07 (s, 1H), 6.88 (d, *J*＝8.7 Hz, 2H), 7.08—7.16 (m, 2H), 7.29—7.34 (m, 3H), 7.53 (d, *J*＝8.4 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ: 14.0, 41.4, 50.8, 55.3, 63.5, 87.1, 94.8, 109.8, 114.1, 120.4, 120.9, 121.1, 128.8, 130.8, 134.1, 146.8, 158.6, 171.7; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, t(major)=26.36 min, t(minor)=37.42 min; $[\alpha]_D^{20}$ −12.5 (c=0.210, CH_2Cl_2).

1-(Benzo[*d*][1,3]dioxol-5-yl)-3-hydroxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5c) Brown solid, 60% yield, *dr*=52/48 (*anti*/*syn*). *anti*-**5c**: 90% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.21 (t, J=7.2 Hz, 3H), 3.01—3.16 (m, 2H), 4.28—4.39 (m, 2H), 4.70 (s, 1H), 4.76 (t, J=8.4 Hz, 1H), 5.95 (s, 2H), 6.10 (s, 1H), 6.76—6.87 (m, 3H), 7.11—7.18 (m, 2H), 7.52—7.56 (m, 2H); IR (thin film) ν_{max}: 3467, 2924, 2854, 1736, 1610, 1504, 1488, 1452, 1377, 1305, 1250, 1207, 1157, 1102, 1039, 935, 894, 861, 811, 747, 601 cm^{-1}; MS (EI, *m/z*, rel. intensity) 365 (M^+, 10), 57 (100); HRMS (EI) calcd for $C_{21}H_{19}NO_5$ (M^+): 365.1263, found 365.1267; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, t(minor)=22.38 min, t(major)=27.96 min; $[\alpha]_D^{20}$ +4.6 (c=0.130, CH_2Cl_2). *syn*-**5c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19 (t, J=6.9 Hz, 3H), 2.69 (dd, J=7.5, 13.5 Hz, 1H), 3.44 (dd, J=9.0, 13.5 Hz, 1H), 4.19—4.35 (m, 2H), 4.57 (t, J=9.0 Hz, 1H), 4.78 (s, 1H), 5.94 (s, 2H), 6.09 (s, 1H), 6.75—6.79 (m, 1H), 6.85—6.86 (m, 1H), 6.87 (s, 1H), 7.11—7.16 (m, 2H), 7.29—7.34 (m, 1H), 7.52—7.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 41.9, 50.7, 63.5, 87.1, 94.9, 101.0, 108.1, 108.2, 109.9, 120.5, 120.8, 120.9, 121.2, 130.8, 134.0, 136.0, 146.5, 146.7, 148.0, 171.6; $[\alpha]_D^{20}$ −22.4 (c=0.235, CH_2Cl_2).

(1*S*)-Ethyl 1-(4-chlorophenyl)-3-hydroxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5d) Brown solid, 53% yield, *dr*=55/45 (*anti*/*syn*). *anti*-**5d**: 94% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19 (t, J=7.2 Hz, 3H), 3.02—3.19 (m, 2H), 4.23—4.40 (m, 2H), 4.72 (s, 1H), 4.80 (t, J=8.4 Hz, 1H), 6.10 (s, 1H), 7.11—7.17 (m, 3H), 7.28—7.33 (m, 4H), 7.54—7.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 41.0, 51.8, 63.8, 86.3, 95.3, 109.4, 120.6, 121.1, 121.6, 128.8, 129.2, 130.8, 132.9, 134.0, 140.4, 146.5, 171.7; IR (thin film) ν_{max}: 3478, 3053, 2959, 2924, 2853, 1736, 1612, 1557, 1492, 1452, 1410, 1391, 1362, 1334, 1302, 1257, 1208, 1157, 1143, 1091, 1015, 859, 830, 783, 747, 707, 514 cm^{-1}; MS (EI, *m/z*, rel. intensity) 355 (M^+, 3), 57 (100); HRMS (EI) calcd for $C_{20}H_{18}ClNO_3$ (M^+): 355.0975, found 355.0979; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, t(minor)=15.22 min, t(major)=32.82 min; $[\alpha]_D^{20}$ =+7.3 (c=0.335, CH_2Cl_2). *syn*-**5d**: 93% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19 (t, J=7.2 Hz, 3H), 2.70 (dd, J=7.2, 13.8 Hz, 1H), 3.48 (dd, J=9.0, 13.8 Hz, 1H), 4.19—4.35 (m, 2H), 4.62 (t, J=8.1 Hz, 1H), 4.80 (s, 1H), 6.07 (s, 1H), 7.09—7.19 (m, 3H), 7.32—7.38 (m, 4H), 7.49—7.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 38.6, 49.7, 63.6, 87.2, 95.6, 109.9, 120.6, 120.9, 121.3, 123.1, 124.8, 125.7, 125.8, 126.3, 127.8, 129.1, 131.1, 131.3, 134.1, 137.7, 145.6, 171.6; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, t(major)=17.77 min, t(minor)=26.47 min; $[\alpha]_D^{20}$ −34.1 (c=0.170, CH_2Cl_2).

(1*S*)-Ethyl 1-(4-bromophenyl)-3-hydroxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5e) Yellow solid, 54% yield, *dr*=75/25 (*anti*/*syn*). *anti*-**5e**: 96% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.17 (t, J=7.2 Hz, 3H), 2.99—3.16 (m, 2H), 4.23—4.35 (m, 2H), 4.75 (t, J=8.1 Hz, 1H), 4.78 (s, 1H), 6.08 (s, 1H), 7.11—7.23 (m, 5H), 7.45 (d, J=8.1 Hz, 2H), 7.53—7.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 40.9, 51.7, 63.7, 86.3, 95.2, 109.4, 120.5, 120.9, 121.0, 121.5, 129.5, 130.7, 131.7, 133.9, 140.9, 146.3, 171.6; IR (thin film) ν_{max}: 3401, 3054, 2982, 2925, 2850, 1732, 1614, 1557, 1488, 1452, 1366, 1302, 1260, 1215, 1159, 1099, 1074, 1011, 928, 859, 826, 751, 667, 511 cm^{-1}; MS (EI, *m/z*, rel. intensity) 399 (M^+, 56), 326 (100); HRMS (EI) calcd for $C_{20}H_{18}BrNO_3$ (M^+): 399.0470, found 399.0471; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, t(minor)=13.64 min, t(major)=15.85 min; $[\alpha]_D^{20}$ −11.4 (c=1.0, CH_2Cl_2). *syn*-**5e**: 96% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.10 (t, J=7.2 Hz, 3H), 2.63 (dd, J=7.5, 13.8 Hz, 1H), 3.41 (dd, J=9.3, 13.8 Hz, 1H), 4.14—4.22 (m, 2H), 4.55 (t, J=7.8 Hz, 1H), 5.01 (s, 1H), 6.04 (s, 1H), 7.07—7.12 (m, 2H), 7.19 (d, J=8.1 Hz, 2H), 7.33—7.49 (m, 1H), 7.38 (d, J=8.1 Hz, 2H), 7.50 (d, J=6.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 41.4, 50.3, 63.4, 87.0, 94.9, 109.8, 120.4, 120.7, 120.8, 121.2, 129.4, 130.7, 131.6, 133.8, 141.0, 145.7, 171.2; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, t(major)=18.52 min, t(minor)=25.78 min; $[\alpha]_D^{20}$ −21.1 (c=1.0, CH_2Cl_2).

(1*S*)-Ethyl 1-(3-bromophenyl)-3-hydroxy-2,3-dihydro-1*H*-pyrrolo[1,2-a]indole-3-carboxylate (5f) Yellow solid, 51% yield, *dr*=60/40 (*anti*/*syn*). *anti*-**5f**: 96% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.20 (t, J=7.2 Hz, 3H), 3.09—3.22 (m, 2H), 4.22—4.40 (m, 2H), 4.75 (s, 1H), 4.79 (t, J=8.4 Hz, 1H), 6.13 (s, 1H), 7.13—7.24 (m, 4H), 7.29—7.32 (m, 1H), 7.42 (d, J=7.8 Hz, 1H), 7.51 (s, 1H), 7.55—7.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 41.1, 51.6, 63.9, 86.3, 95.5, 109.5, 120.6, 121.1, 121.6, 122.8, 126.6, 130.2, 130.3, 130.8, 130.9, 134.0, 144.4, 146.1, 171.7; IR (thin film) ν_{max}: 3370, 2924, 2853, 1732, 1596, 1568, 1474, 1453, 1426, 1367, 1259, 1216, 1160, 1099, 1073, 1024, 997, 927, 860, 758, 692, 668 cm^{-1}; MS (EI, *m/z*, rel. intensity) 399 (M^+, 37), 57 (100); HRMS (EI) calcd for $C_{20}H_{18}BrNO_3$ (M^+): 399.0470, found 399.0475; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, t(minor)=12.56 min, t(major)=13.91 min; $[\alpha]_D^{20}$ −17.5 (c=0.765, CH_2Cl_2). *syn*-**5f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (t, J=7.2 Hz, 3H), 2.72 (dd, J=

7.2, 13.8 Hz, 1H), 3.48 (dd, *J*=8.7, 13.8, 1H), 4.19—4.35 (m, 2H), 4.60 (t, *J*=8.7 Hz, 1H), 4.80 (s, 1H), 6.10 (s, 1H), 7.12—7.17 (m, 2H), 7.21 (t, *J*=6.0 Hz, 1H), 7.40—7.42 (m, 1H), 7.53—7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 41.7, 50.4, 63.6, 87.0, 95.2, 109.9, 120.6, 121.0, 121.4, 122.7, 126.4, 130.2, 130.3, 130.8, 130.9, 134.0, 144.4, 145.5, 171.5.

(1*S*)-Ethyl 3-hydroxy-1-(naphthalen-2-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5g) Brown solid, 54% solid, *dr*=53/47 (*anti*/*syn*). *anti*-**5g**: 94% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19 (t, *J*=7.2 Hz, 3H), 3.22 (d, *J*=8.7 Hz, 1H), 4.26—4.39 (m, 2H), 4.76 (s, 1H), 5.00 (t, *J*=8.7 Hz, 1H), 6.14 (s, 1H), 7.13—7.23 (m, 3H), 7.43—7.58 (m, 4H), 7.79—7.86 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 41.7, 51.8, 63.8, 86.4, 95.4, 109.4, 120.5, 121.1, 121.5, 125.8, 125.9, 126.3, 126.4, 127.6, 127.7, 128.6, 132.1, 132.6, 133.4, 134.1, 139.1, 147.0, 171.9; IR (thin film) ν_{max}: 3479, 3053, 2925, 2854, 1756, 1634, 1601, 1558, 1508, 1453, 1369, 1350, 1334, 1303, 1257, 1206, 1157, 1143, 1127, 1104, 1021, 894, 858, 820, 749, 667, 606, 478 cm^{-1}; MS (EI, *m/z*, rel. intensity) 371 (M^+, 86), 298 (100); HRMS (EI) calcd for $C_{24}H_{21}NO_3$ (M^+): 371.1521, found 371.1519; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, *t*(minor)=13.53 min, *t*(major)=17.01 min; $[\alpha]_D^{20}$ +34.8 (*c*=0.290, CH_2Cl_2). *syn*-**5g**: 92% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.22 (t, *J*=7.2 Hz, 3H), 2.85 (dd, *J*=7.5, 13.8 Hz, 1H), 3.54 (dd, *J*=8.7, 13.8 Hz, 1H), 4.21—4.38 (m, 2H), 4.82 (t, *J*=8.1 Hz, 1H), 4.84 (s, 1H), 6.11 (s, 1H), 7.10—7.18 (m, 2H), 7.37 (d, *J*=7.2 Hz, 1H), 7.46—7.56 (m, 4H), 7.79 — 7.86 (m, 4H); the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, *t*(major) =27.26 min, *t*(minor)=29.68 min; $[\alpha]_D^{20}$ +7.6 (*c*= 0.155, CH_2Cl_2).

(1*S*)-Ethyl 3-hydroxy-1-(naphthalen-1-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5h) Brown solid, 52% yield, *dr*=54/46 (*anti*/*syn*). *anti*-**5h**: 93% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.12 (t, *J*=6.9 Hz, 3H), 3.19 (dd, *J*=7.8, 13.5 Hz, 1H), 3.38 (dd, *J*= 9.0, 13.8 Hz, 1H), 4.22—4.30 (m, 2H), 4.81 (s, 1H), 5.56 (t, *J*=8.4 Hz, 1H), 6.21 (s, 1H), 7.13—7.20 (m, 3H), 7.42 (t, *J*=8.1 Hz, 1H), 7.52—7.62 (m, 4H), 7.82 (d, *J*=8.1 Hz, 1H), 7.91—7.94 (m, 1H), 8.08—8.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 38.5, 50.7, 63.7, 86.5, 95.8, 109.5, 120.5, 121.0, 121.4, 123.4, 125.0, 125.6, 125.7, 126.2, 127.8, 129.0, 130.9, 131.4, 134.0, 134.1, 137.3, 146.1, 172.0; IR (thin film) ν_{max}: 3478, 3050, 2924, 2853, 1733, 1598, 1510, 1453, 1397, 1363, 1334, 1305, 1259, 1208, 1157, 1144, 1126, 1104, 1080, 1012, 860, 801, 779, 748 cm^{-1}; MS (EI, *m/z*, rel. intensity) 371 (M^+, 86), 298 (100); HRMS (EI) calcd for $C_{24}H_{21}NO_3$ (M^+): 371.1521, found 371.1526; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ= 254 nm, *t*(major)=16.48 min, *t*(minor)=19.00 min; $[\alpha]_D^{20}$ −79.9 (*c*=0.195, CH_2Cl_2). *syn*-**5h**: 90% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.24 (t, *J*=7.2 Hz, 3H), 2.84 (dd, *J*=7.5, 13.8 Hz, 1H), 3.70 (dd, *J*=9.3, 13.8 Hz, 1H), 4.23—4.44 (m, 2H), 4.75 (s, 1H), 5.42 (t, *J*= 8.4 Hz, 1H), 6.20 (s, 1H), 7.15—7.17 (m, 2H), 7.35—7.38 (m, 1H), 7.40—7.44 (m, 1H), 7.52—7.62 (m, 4H), 7.81 (d, *J*=8.4 Hz, 1H), 7.93 (d, *J*=8.4 Hz, 1H), 8.10 (d, *J*=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 41.5, 50.5, 63.6, 87.1, 95.1, 109.9, 120.6, 121.0, 121.4, 125.8, 128.9, 129.1, 130.8, 132.9, 134.0, 140.7, 145.9, 171.5; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, *t*(minor)=19.47 min, *t*(major) =21.53 min; $[\alpha]_D^{20}$ −19.8 (*c*=0.165, CH_2Cl_2).

(1*R*)-Ethyl 1-(furan-2-yl)-3-hydroxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5i) Brown solid, 55% yield, *dr*=46/54 (*anti*/*syn*). *anti*-**5i**: 75% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19 (t, *J*=7.2 Hz, 3H), 3.09 (dd, *J*=8.4, 13.8 Hz, 1H), 3.28 (dd, *J*=7.8, 13.2 Hz, 1H), 4.24—4.37 (m, 2H), 4.73 (s, 1H), 4.91 (t, *J*= 8.4 Hz, 1H), 6.23—6.24 (m, 1H), 6.28 (s, 1H), 6.34—6.35 (m, 1H), 7.10—7.20 (m, 2H), 7.31—7.33 (m, 1H), 7.39 (m, 1H), 7.55—7.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 35.1, 47.8, 63.7, 86.3, 95.3, 105.9, 109.5, 110.3, 120.5, 121.1, 121.6, 130.8, 133.9, 142.0, 143.8, 154.0, 171.7; IR (thin film) ν_{max}: 3478, 3119, 3053, 2925, 2854, 1736, 1613, 1560, 1506, 1453, 1355, 1335, 1304, 1256, 1208, 1156, 1105, 1012, 927, 896, 884, 860, 783, 742, 599 cm^{-1}; LRMS-ESI *m/z*: 312.0 [M + H], 334.0 [M + Na]; HRMS (MALDI/DHB): Calcd for $C_{18}H_{18}NO_4$ [M + H]: 312.1230, found 312.1239; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ=254 nm, *t*(minor)=14.31 min, *t*(major) =24.78 min; $[\alpha]_D^{20}$ −5.2 (*c*=0.345, CH_2Cl_2). *syn*-**5i**: 75% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.15 (t, *J*=7.2 Hz, 3H), 2.90 (dd, *J*=7.5, 13.5 Hz, 1H), 3.42 (dd, *J*= 8.7, 13.5 Hz, 1H), 4.15—4.26 (m, 2H), 4.73 (s, 1H), 4.74 (t, *J*=8.7 Hz, 1H), 6.24 (s, 1H), 6.25—6.28 (m, 1H), 6.33—6.35 (m, 1H), 7.08—7.15 (m, 2H), 7.31—7.33 (m, 1H), 7.38—7.39 (m, 1H), 7.54—7.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 35.4, 47.1, 63.5, 87.0, 95.2, 105.8, 110.0, 110.4, 120.5, 121.0, 121.4, 130.9, 133.8, 142.0, 143.1, 154.1, 171.3; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA=90/10, 1.0 mL/min, λ= 254 nm, *t*(major)=14.25 min, *t*(minor)=21.20 min; $[\alpha]_D^{20}$ −80.1 (*c*=0.250, CH_2Cl_2).

(1*R*)-Ethyl 3-hydroxy-1-(thiophen-2-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5j) Brown solid, 48% yield, *dr*=46/54 (*anti*/*syn*). *anti*-**5j**: 96% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.16 (t, *J*=7.2 Hz, 3H), 3.20 (d, *J*=8.4 Hz, 2H), 4.26—4.36 (m, 2H), 4.73 (s, 1H), 5.13 (t, *J*=7.8 Hz, 1H), 6.28 (s, 1H), 6.98—7.00 (m, 1H), 7.06—7.07 (m, 1H), 7.12—7.20 (m, 3H), 7.24 (d, *J*=8.4 Hz, 1H), 7.56—7.59 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1, 36.7, 51.9, 63.8, 86.2, 95.6, 109.4, 120.5, 121.2, 121.7, 124.3, 124.9, 126.8,

130.8, 133.8, 144.8, 146.0, 171.7; IR (thin film) ν_{max}: 3362, 2923, 2853, 1735, 1655, 1616, 1522, 1456, 1376, 1304, 1258, 1215, 1158, 1097, 1021, 761, 699, 668 cm^{-1}; MS (EI, *m/z*, rel. intensity) 327 (M^+, 12), 84 (100); HRMS (EI) calcd for $C_{18}H_{17}NO_3S$ (M^+): 327.0929, found 327.0926; $[\alpha]_D^{20}$ −11.9 (*c* = 0.375, CH_2Cl_2). *syn*-**5j**: 99% *ee*; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.20 (t, *J* = 7.2 Hz, 3H), 2.86 (dd, *J* = 8.1, 13.5 Hz, 1H), 3.49 (dd, *J* = 8.4, 13.5 Hz, 1H), 4.18—4.35 (m, 2H), 4.76 (s, 1H), 4.95 (t, *J* = 8.4 Hz, 1H), 6.25 (s, 1H), 6.97—7.00 (m, 1H), 7.07—7.15 (m, 3H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.55—7.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0, 37.1, 50.7, 63.6, 86.9, 95.4, 109.9, 120.5, 121.1, 121.4, 124.3, 124.8, 126.9, 130.8, 133.8, 144.8, 145.2, 171.4; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, *t*(major) = 20.33 min, *t*(minor) = 30.64 min; $[\alpha]_D^{20}$ −26.7 (*c* = 0.32, CH_2Cl_2).

(1*S*)-Ethyl 3-hydroxy-1-(3-nitrophenyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (5k) Brown solid, 87% yield, *dr* = 60/40 (*anti*/*syn*). *anti*-**5k**: 91% *ee*; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.18 (t, *J* = 7.5 Hz, 3H), 3.12 (dd, *J* = 7.8, 13.8 Hz, 1H), 3.26 (dd, *J* = 9.0, 13.8 Hz, 1H), 4.25—4.41 (m, 2H), 4.82 (s, 1H), 4.94 (t, *J* = 8.1 Hz, 1H), 6.12 (s, 1H), 7.09—7.24 (m, 3H), 7.50—7.58 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 8.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 41.0, 51.5, 63.9, 86.3, 95.6, 109.5, 120.7, 121.2, 121.8, 122.2, 122.7, 129.6, 130.8, 133.9, 134.1, 144.3, 145.4, 148.5, 171.4; IR (thin film) ν_{max}: 3478, 3055, 2926, 2854, 1736, 1614, 1582, 1530, 1477, 1452, 1350, 1305, 1250, 1210, 1159, 1100, 1024, 927, 808, 750, 684 cm^{-1}; LRMS-ESI *m/z*: 367.0 [M+H], 389.0 [M + Na]; HRMS (MALDI/DHB): calcd for $C_{20}H_{19}N_2O_5$ [M+H]: 367.1288, found 367.1299; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, *t*(minor) = 20.88 min, *t*(major) = 32.16 min; $[\alpha]_D^{20}$ −16.1 (*c* = 1.0, $CHCl_3$). *syn*-**5k**: 90% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.21 (t, *J* = 7.2 Hz, 3H), 2.74 (dd, *J* = 7.2, 14.0 Hz, 1H), 3.56 (dd, *J* = 8.8, 13.6 Hz, 1H), 4.23—4.37 (m, 2H), 4.76 (t, *J* = 7.8 Hz, 1H), 4.87 (s, 1H), 6.12 (s, 1H), 7.14—7.19 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.50—7.56 (m, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 8.13—8.16 (m, 1H), 8.29 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 41.6, 50.2, 63.8, 87.0, 95.5, 109.9, 120.8, 121.1, 121.7, 122.3, 122.9, 129.8, 130.9, 133.9, 144.3, 144.8, 148.4, 171.3; the enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, *t*(major) = 25.03 min, *t*(minor) = 31.22 min; $[\alpha]_D^{20}$ −10.7 (*c* = 0.37, $CHCl_3$).

Ethyl 4-(4,7-dihydro-1*H*-indol-2-yl)-2-oxo-4-phenylbutanoate (4) ^1H NMR (300 MHz, $CDCl_3$) δ: 1.33 (t, *J* = 7.2 Hz, 3H), 3.15 (s, 4H), 3.44 (dd, *J* = 6.6, 18.3 Hz, 1H), 3.66 (dd, *J* = 7.8, 18.3 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.58 (t, *J* = 7.2 Hz, 1H), 5.71 (d, *J* = 2.1 Hz, 1H), 5.81 (dt, *J* = 2.1, 15.9 Hz, 2H), 7.23—7.34 (m, 5H), 7.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.9, 23.8, 24.8, 39.0, 45.5, 62.6, 104.2, 113.6, 122.7, 123.7, 125.7, 127.0, 127.6, 127.9, 128.5, 128.7, 132.2, 142.2, 160.6, 193.1; IR (thin film) ν_{max}: 3412, 3060, 3027, 2982, 2890, 2856, 2826, 1728, 1656, 1604, 1492, 1454, 1369, 1342, 1260, 1150, 1083, 1069, 1038, 967, 952, 857, 750, 702, 667 cm^{-1}; LRMS-ESI (*m/z*): 324.2 [M+H]; HRMS (MALDI/DHB) calcd for $C_{20}H_{22}NO_3$ [M+H]: 324.1594, found 324.1603.

Ethyl 3-hydroxy-1-phenyl-2,3,5,8-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (7) ^1H NMR (300 MHz, $CDCl_3$) δ: 1.27 (t, *J* = 7.5 Hz, 3H), 2.88—3.05 (m, 3H), 3.15—3.23 (m, 3H), 4.24—4.40 (m, 2H), 4.46 (s, 1H), 4.64 (t, *J* = 8.1 Hz, 1H), 5.61 (s, 1H), 5.76—5.88 (m, 2H), 7.25—7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0, 22.7, 25.4, 41.3, 52.1, 63.6, 86.5, 99.4, 118.7, 120.6, 122.1, 125.6, 126.8, 127.5, 127.6, 128.5, 138.9, 142.8, 172.2; IR (thin film) ν_{max}: 3479, 3061, 3027, 2960, 2919, 2850, 1732, 1652, 1603, 1558, 1520, 1496, 1454, 1430, 1368, 1304, 1261, 1188, 1161, 1142, 1095, 1057, 1022, 951, 861, 799, 749, 699, 667, 632 cm^{-1}; MS (EI, *m/z*, rel. intensity) 324 (M^+, 22), 208 (100); LRMS-ESI *m/z*: 312.0 [M+H], 334.0 [M+Na]; HRMS (MALDI/DHB) calcd for $C_{20}H_{22}NO_3$ [M+H]: 324.1594, found 324.1608.

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[16] See the Supporting Information for detailed information.

(Zhao, X.)

