Enantioselective Synthesis of 3*H*-Pyrrolo[1,2-*a*]indole-2-carbaldehydes via an Organocatalytic Domino Aza-Michael/Aldol Condensation Reaction

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Dedicated to Professor Martin Jansen on the occasion of his 65th birthday

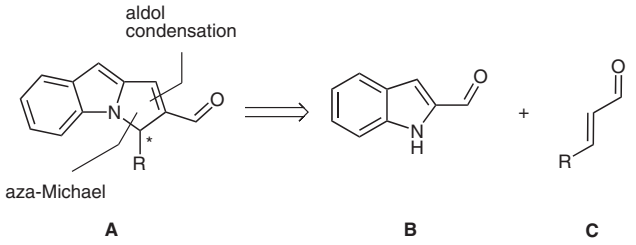
Abstract: A simple organocatalytic aza-Michael/aldol condensation domino reaction protocol opens an efficient and enantioselective entry to the tricyclic pyrrolo indole core, a characteristic structural unit of many bioactive natural products.

Key words: pyrrolo[1,2-*a*]indole, organocatalysis, domino reaction, aza-Michael reaction, asymmetric synthesis

The indole subunit is a crucial structural feature in a large number of naturally occurring and synthetic alkaloids with various biological and pharmacological activities.[1] The family of 3*H*-pyrrolo[1,2-*a*]indoles is of continuously growing interest and a highly pursued synthetic target due to its structural analogy to mitomycins, which are endowed with an extraordinary ability of cross-linking DNA and used as antitumor and chemotherapeutic agents.[2,3] Despite many efforts to construct this structural motif in the past decades, the efficient asymmetric synthesis of 3*H*-pyrrolo[1,2-*a*]indole derivatives has not been achieved and still remains a great synthetic challenge.

After intense explorations in recent years, organocatalytic domino reactions have been proven as a powerful tool for the efficient and stereoselective synthesis of complex molecules in a single process, which were difficult to access by traditional methods.[4–7] Domino reactions using the aza-Michael addition provide a simple and direct way for the synthesis of nitrogen containing heterocycles.[8,9] We now wish to report a simple and efficient organocatalytic domino strategy for the asymmetric synthesis of 3*H*-pyrrolo[1,2-*a*]indoles **A** starting from the commercially available 1*H*-indole-2-carbaldehyde (**B**) and α,β-unsaturated aldehydes **C** (Scheme 1). This novel domino reaction consists of an aza-Michael addition/intramolecular aldol condensation cascade following the iminium ion/enamine activation sequence.

Initially we performed the reaction with 1*H*-indole-2-carbaldehyde (**1**) and (*E*)-3-(2-methoxyphenyl)acrylaldehyde (**2a**) in toluene at room temperature utilizing diphenylprolinol silyl ether **4**[10,11] as a catalyst. Encouragingly, the domino reaction to form the pyrroloindole aldehyde **3a** occurred in moderate yield (40%) and good enantioselectivity (81% ee), (Table 1, entry 1). The brief solvent



Scheme 1 Secondary amine-catalyzed domino aza-Michael/aldol condensation reaction – retrosynthetic analysis

screening indicated that the polar solvents such as DMF and ethanol showed a detrimental effect to the level of the asymmetric induction (Table 1, entries 2 and 3). Performing the reaction in dichloromethane provided a better yield (60%) without improving the enantiomeric excess (81% ee, Table 1, entry 4). In the case of MTBE, the domino product was obtained after a longer reaction time (4 d) in a higher enantioselectivity (85% ee) and moderate yield (53%).

Next, three additional secondary amine catalysts were evaluated with dichloromethane as solvent. Under the catalysis of (*S*)-diphenylprolinol (**5**) or diarylprolinol silyl ether **6** [Ar = 3,5-$(CF_3)_2C_6H_3$], no conversion of the starting materials was observed after two days (Table 1, entries 6 and 7), while (*S*)-proline (**7**) showed also a very low catalytic activity in the domino reaction (Table 1, entry 8).

Subsequently, an additive screening was undertaken. Employing bases as additives led to a decrease both in yield and enantioselectivity (Table 1, entries 9–11). Notably, no desired product was formed when the reaction was carried out under acidic conditions (Table 1, entries 12 and 13), probably due to the indole protonation. Performing the reaction at a lower temperature resulted in a slightly improved enantioselectivity (84% ee), but a drastically diminished yield (21%), (Table 1, entry 14)

The scope of the reaction was evaluated by varying the structure of the enals **2** under the optimal conditions. In the cases of cinnamaldehyde (**2b**) and the substituted aromatic enals **2a**, **2c**–**g**, the domino products **3a**–**g** were obtained in high enantiomeric excesses (85 to >99% ee) and with moderate to good yields (40–71%, Table 2, entries 1–7). Notably, when **2b** and **2c** were used as the substrates, the products **3b** and **3c** precipitated and could simply be isolated by suction. The aliphatic enals afforded only traces of the product. Interestingly, utilizing the het-

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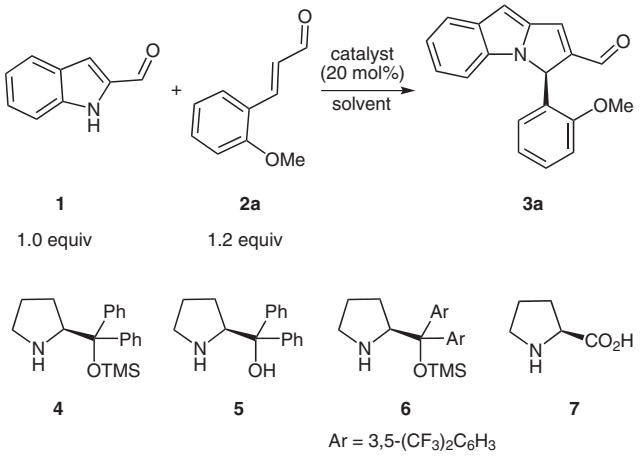
Table 1 Solvent, Additive and Catalyst Screening for the Enantioselective Organocatalytic Domino Reaction[a]



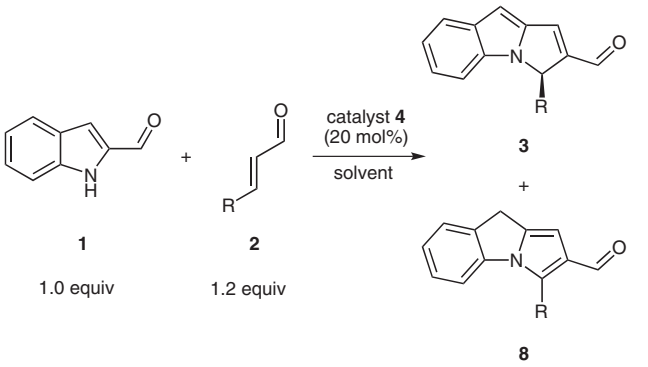
Entry	Cat.	Solvent	Additive	Time (d)	Yield (%)[b]	ee (%)[c]
1	**4**	toluene	–	2	40	81
2	**4**	DMF	–	2	47	53
3	**4**	EtOH	–	2	52	68
4	**4**	CH_2Cl_2	–	2	60	81
5	**4**	MTBE	–	4	53	85
6	**5**	CH_2Cl_2	–	2	0	–
7	**6**	CH_2Cl_2	–	2	0	–
8	**7**	CH_2Cl_2	–	2	trace[d]	n.d.[e]
9	**4**	MTBE	Et_3N	2	20	85
10	**4**	CH_2Cl_2	NaOAc	2	40	81
11	**4**	CH_2Cl_2	K_2CO_3	2	38	78
12	**4**	CH_2Cl_2	AcOH	2	0	–
13	**4**	MTBE	$4\text{-}O_2NC_6H_4CO_2H$	2	0	–
14[f]	**4**	CH_2Cl_2	–	4	21	84

[a] Unless otherwise specified, reactions were performed on a 1 mmol scale of **1** using 1.2 equiv of (*E*)-3-(2-methoxyphenyl)acrylaldehyde (**2a**), 20 mol% catalyst **4**, **5**, **6**, or **7**, and 20 mol% the corresponding additive at r.t. in 2.0 mL of solvent.
[b] Yield of the isolated product after flash chromatography.
[c] Determined by HPLC analysis on a chiral stationary phase.
[d] Determined by GC analysis.
[e] Not determined.
[f] Reaction performed at 3 °C.

eroaromtic furylacrolein **2h** led to the formation of the isomer 9*H*-pyrrolo[1,2-*a*]indole **8** instead of the expected product (Table 2, entry 8).

The absolute configuration of **3b** was unambiguously determined to be *R* by X-ray crystal structure analysis (Figure 1), which is in agreement with the results of other diphenylprolinol silyl ether catalyzed Michael additions to enals.[7,9]

Table 2 Organocatalytic Domino Reaction of Enals **2a–h** and 1*H*-Indole-2-carbaldehyde (**1**)[a]



Entry	R	Solvent	Time (d)	Yield (%)[b]	ee (%)[c]
1	$2\text{-}MeOC_6H_4$ (**3a**)	MTBE	4	53	85
2[d]	Ph (**3b**)	MTBE	3	55	>99
3[d]	$4\text{-}MeOC_6H_4$ (**3c**)	MTBE	3	51	90
4[e]	$4\text{-}ClC_6H_4$ (**3d**)	MTBE	3	71	89
5	*p*-tolyl (**3e**)	MTBE	1	60	87
6	piperonyl (**3f**)	–[f]	3	58	>99
7	$4\text{-}FC_6H_4$ (**3g**)	MTBE	4	40	>99
8[e]	furan-2-yl (**8**)	CH_2Cl_2	4	30	–

[a] Reactions were performed on a 1 mmol scale of **1** using 1.2 equiv of enals **2**, 20 mol% catalyst **4** at r.t. in 2.0 mL of solvent.
[b] Yield of the isolated product after flash chromatography.
[c] Determined by HPLC analysis on a chiral stationary phase.
[d] Workup procedure B (see experimental part).
[e] Pyrrolidine (40 mol%) was utilized as catalyst. With the catalyst **4** the same product **8** was formed, but not analytically pure.
[f] Reactions were performed in a mixture of MTBE (2 mL) and CH_2Cl_2 (0.4 mL).

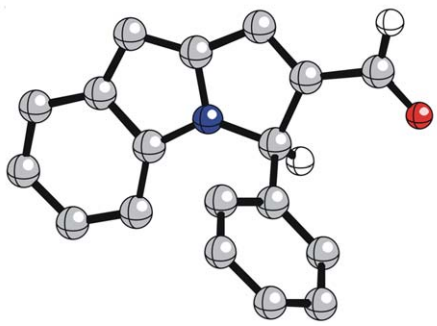
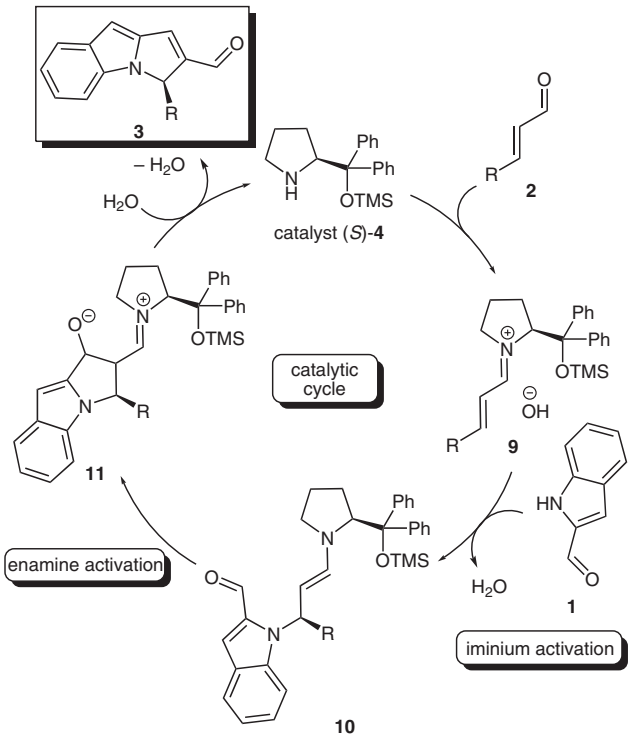


Figure 1 X-ray crystal structure of **3b**[12]

A plausible catalytic cycle for the domino reaction is described in Scheme 2. In the first step, the enal **2** is activated by the chiral amine through the formation of the iminium ion **9**, to which the 1*H*-indole-2-carbaldehyde (**1**) performs an intermolecular aza-Michael addition. The resulting enamine **10** subsequently undergoes an intramolecular aldol reaction affording intermediate **11**. Finally,



Scheme 2 Proposed catalytic cycle of the domino reaction

the catalyst is regenerated for the next catalytic cycle through hydrolysis of the intermediate **11** and dehydration to form the 3*H*-pyrrolo[1,2-*a*]indole products **3**.

In summary, we have developed a novel organocatalytic domino reaction between 1*H*-indole-2-carbaldehyde and α,β-unsaturated aldehydes under diphenylprolinol silyl ether catalysis following an iminium/enamine activation mode. The new asymmetric synthesis provides an efficient entry to synthetically useful and potentially bioactive 3-substituted 3*H*-pyrrolo[1,2-*a*]indoles in moderate to good yields (40–71%) and high to excellent enantiomeric excesses (85 to >99% ee).

Unless otherwise noted, all commercially available compounds were used without further purification. Cinnamaldehyde was freshly distilled. Racemic samples of 3*H*-pyrrolo[1,2-*a*]indoles **3a–g** were prepared using pyrrolidine (40 mol%) as a catalyst in MTBE at r.t. Preparative column chromatography: Merck silica gel 60, particle size 0.040–0.063 mm (230–240 mesh, flash). Analytical TLC: silica gel 60 F_{254} plates from Merck, Darmstadt. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with anisaldehyde. Optical rotation values were measured on a PerkinElmer 241 polarimeter. Microanalyses were performed with a Vario EL element analyzer. Mass spectra were acquired on a Finnigan SSQ7000 (EI 70 eV) spectrometer and high-resolution mass spectra on a Finnigan MAT 95. IR spectra were taken on a PerkinElmer FT-IR 1760 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at r.t. on Gemini 300, Varian Mercury 300, or Inova 400 instruments with TMS as an internal standard. Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (Chiralcel OD).

Domino Aza-Michael/Aldol Condensation; General Procedure

Catalyst **4** (0.2 mmol, 20 mol%) was added to a solution of 1*H*-indole-2-carbaldehyde (**1**; 1 mmol) and α,β-unsaturated aldehyde **2** (1.2 mol, 1.2 equiv) in MTBE or CH_2Cl_2 (2 mL) at r.t. The reaction mixture was stirred for the time displayed in Table 2. Workup A: Direct flash chromatography (silica gel, pentane–Et2O, 10:1 to 4:1) of the reaction mixture afforded the pure 3*H*-pyrrolo[1,2-*a*]indoles **3**. Workup B: The precipitated product was isolated by suction through a funnel. The filtrate was concentrated in vacuum and the resulting additional precipitate was suspended in MTBE (0.5 mL) and suctioned again. The combined solids were dissolved in CH_2Cl_2 and passed through a short column (silica gel, CH_2Cl_2) affording the pure 3*H*-pyrrolo[1,2-*a*]indoles **3**.

(*R*)-3-(2-Methoxyphenyl)-3*H*-pyrrolo[1,2-*a*]indole-2-carbaldehyde (3a)

Yield: 153 mg (53%); bright yellow solid; mp 128 °C; $[\alpha]_D^{20}$ –506 (*c* = 0.65, $CHCl_3$).

HPLC: t_R = 7.76 and 11.08 min [Chiralcel OD, *n*-heptane–*i*-PrOH (8:2), 1.0 mL/min]; t_R = 7.76 min; ee = 85%.

IR (KBr): 3306, 3120, 3056, 3013, 2975, 2940, 2840, 2817, 2716, 2472, 2325, 2185, 2107, 1999, 1926, 1811, 1778, 1722, 1659, 1600, 1562, 1493, 1463, 1335, 1330, 1308, 1292, 1246, 1212, 1189, 1166, 1150, 1112, 1094, 1051, 1023, 984, 933, 881, 819, 787, 749, 695, 668 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.78 (s, 1 H), 7.63–7.66 (m, 2 H), 7.22–7.28 (m, 1 H), 6.98–7.11 (m, 4 H), 6.69–6.78 (m, 3 H), 6.56 (s, 1 H), 3.97 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.5, 157.5, 149.0, 142.5, 136.2, 134.2, 132.8, 129.8, 127.6, 124.1, 123.7, 122.4, 121.2, 120.0, 111.6, 110.2, 98.8, 57.3, 56.0.

MS (EI, 70 eV): *m*/*z* (%) = 289 (11, [M$^+$]), 260 (6.5), 244 (11), 228 (20), 216 (50), 202 (11), 189 (32), 178 (26), 163 (17), 153 (72), 140 (21), 126 (62), 115 (26), 102 (26), 89 (55), 77 (98), 63 (93), 51 (100).

Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.87; H, 5.14; N, 4.83.

(*R*)-3-Phenyl-3*H*-pyrrolo[1,2-*a*]indole-2-carbaldehyde (3b)

Yield: 143 mg (55%); bright yellow solid; mp 183 °C; $[\alpha]_D^{20}$ –959 (*c* = 1.0, $CHCl_3$).

HPLC: t_R = 8.85 and 13.84 min [Chiralcel OD, *n*-heptane–*i*-PrOH (8:2), 1.0 mL/min]; t_R = 8.85 min; ee = >99%.

IR (KBr): 3285, 3120, 3057, 3032, 2909, 2834, 2657, 2464, 2323, 2090, 1981, 1931, 1895, 1811, 1710, 1646, 1549, 1491, 1450, 1381, 1356, 1311, 1234, 1206, 1158, 1101, 1029, 1005, 982, 933, 879, 856, 820, 800, 740, 691, 672 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.76 (s, 1 H), 7.67–7.70 (m, 1 H), 7.59 (m, 1 H), 7.25–7.29 (m, 3 H), 7.05–7.14 (m, 4 H), 6.89–6.92 (m, 1 H), 6.79 (s, 1 H), 6.03 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.0, 148.8, 142.2, 136.0, 135.9, 134.1, 132.6, 128.6, 128.3, 127.1, 123.8, 122.4, 120.1, 110.1, 99.1, 63.7.

MS (EI, 70 eV): *m*/*z* (%) = 259 (22, [M$^+$]), 230 (100), 202 (5.9), 176 (1.1), 154 (4.2), 127 (2.6), 114 (4.8), 101 (2.6), 89 (1.4), 77 (3.2), 63 (1.1), 51 (2.9).

Anal. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.00; H, 5.01; N, 5.35.

(*R*)-3-(4-Methoxyphenyl)-3*H*-pyrrolo[1,2-*a*]indole-2-carbaldehyde (3c)

Yield: 147 mg (51%); bright yellow solid; mp 180 °C; $[\alpha]_D^{20}$ –1130 (*c* = 0.7, $CHCl_3$).

HPLC: t_R = 9.99 and 17.05 min [Chiralcel OD, *n*-heptane–*i*-PrOH (8:2), 1.0 mL/min]; t_R = 9.99 min; ee = 90%.

IR (KBr): 3307, 3051, 2962, 2909, 2837, 2728, 2285, 2077, 1931, 1900, 1783, 1660, 1612, 1557, 1514, 1459, 1447, 1424, 1354, 1328, 1308, 1254, 1210, 1175, 1149, 1027, 1105, 984, 932, 882, 838, 780, 742, 692, 667 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.75 (s, 1 H), 7.66–7.69 (m, 1 H), 7.56 (s, 1 H), 7.03–7.08 (m, 4 H), 6.91–6.93 (m, 1H), 6.76–6.81 (m, 3 H), 5.98 (s, 1 H), 3.50 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.5, 159.6, 149.2, 142.3, 136.1, 134.3, 132.8, 128.5, 128.0, 123.9, 122.6, 120.3, 114.2, 110.3, 99.2, 63.3, 55.2.

MS (EI, 70 eV): *m*/*z* (%) = 289 (20, [M^+]), 260 (85), 245 (10), 228 (9.3), 216 (100), 204 (7.5), 189 (26), 182 (15), 163 (14), 153 (62), 140 (12), 126 (50), 115 (16), 102 (28), 92 (35), 89 (44), 77 (47), 63 (78), 51 (51).

Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.91; H, 5.28; N, 4.80.

(*R*)-3-(4-Chlorophenyl)-3*H*-pyrrolo[1,2-*a*]indole-2-carbaldehyde (3d)

Yield: 208 mg (71%); bright yellow solid; mp 154 °C; $[\alpha]_D^{20}$ –937 (*c* = 0.45, $CHCl_3$).

HPLC: t_R = 14.21 and 25.18 min [Chiralcel OD, *n*-heptane–*i*-PrOH (9:1), 1.0 mL/min]; t_R = 14.21 min; ee = 89%.

IR (KBr): 3316, 3122, 3062, 2902, 2828, 2724, 2681, 2459, 2325, 2216, 2112, 1982, 1942, 1908, 1789, 1722, 1662, 1596, 1557, 1490, 1445, 1410, 1354, 1323, 1309, 1255, 1235, 1207, 1186, 1165, 1152, 1100, 1014, 982, 935, 878, 857, 840, 796, 779, 736, 692, 668 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.76 (s, 1 H), 7.68–7.70 (m, 1 H), 7.59–7.60 (m, 1 H), 7.24–7.27 (m, 2 H), 7.04–7.14 (m, 4 H), 6.87–6.90 (m, 1 H), 6.80 (s, 1 H), 6.00 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.2, 148.6, 142.2, 136.3, 134.8, 134.2 (2 C), 132.8, 129.0, 128.7, 124.2, 122.7, 120.5, 110.2, 99.7, 63.1.

MS (EI, 70 eV): *m*/*z* (%) = 293 (48, [M^+]), 264 (100), 228 (55), 202 (9.8), 189 (0.9), 176 (3.3), 149 (3.7), 128 (23), 114 (22), 101 (8.0), 89 (11), 75 (8.5), 63 (9.9), 51 (8.4).

Anal. Calcd for $C_{18}H_{12}ClNO$: C, 73.60; H, 4.12; N, 4.77. Found: C, 73.36; H, 4.30; N, 4.83.

(*R*)-3-*p*-Tolyl-3*H*-pyrrolo[1,2-*a*]indole-2-carbaldehyde (3e)

Yield: 164 mg (60%); bright yellow solid; mp 168 °C; $[\alpha]_D^{20}$ –1604 (*c* = 0.25, $CHCl_3$).

HPLC: t_R = 7.90 and 11.79 min [Chiralcel OD, *n*-heptane–*i*-PrOH (8:2), 1.0 mL/min]; t_R = 7.90 min; ee = 87%.

IR (KBr): 3313, 3120, 3047, 2922, 2827, 2803, 2728, 2461, 2323, 2112, 1989, 1928, 1899, 1810, 1721, 1661, 1555, 1512, 1478, 1448, 1354, 1321, 1235, 1206, 1147, 1103, 1007, 982, 879, 834, 778, 739, 692, 671 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1 H), 7.67 (m, 1 H), 7.58 (s, 1 H), 6.92–7.07 (m, 7 H), 6.77 (s, 1 H), 6.00 (s, 1 H), 2.29 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.2, 149.0, 142.2, 138.0, 135.9, 134.1, 132.9, 132.6, 129.4, 127.0, 123.7, 122.4, 120.1, 110.1, 99.0, 63.5, 21.2.

MS (EI, 70 eV): *m*/*z* (%) = 273 (21, [M^+]), 244 (100), 228 (9.5), 215 (2.0), 202 (2.7), 189 (1.4), 182 (1.2), 167 (1.0), 153 (4.3), 127 (4.9), 121 (10), 114 (5.6), 91 (3.2), 89 (3.8), 77 (2.8), 63 (4.6), 51 (4.3).

HRMS (ESI-TOF): *m*/*z* calcd for $C_{19}H_{15}NO$: 273.1154; found: 273.1148.

(*R*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-3*H*-pyrrolo[1,2-*a*]indole-2-carbaldehyde (3f)

Yield: 176 mg (58%); bright yellow solid; mp 178 °C; $[\alpha]_D^{20}$ –790 (*c* = 0.25, $CHCl_3$).

HPLC: t_R = 10.16 and 14.04 min [Chiralcel OD, *n*-heptane–*i*-PrOH (7:3), 1.0 mL/min]; t_R = 10.16 min; ee = >99%.

IR (KBr): 3303, 3045, 3005, 2915, 2832, 2726, 2681, 2456, 2323, 2074, 2019, 1997, 1933, 1901, 1832, 1782, 1753, 1715, 1657, 1555, 1482, 1443, 1375, 1352, 1324, 1308, 1241, 1152, 1102, 1033, 983, 933, 909, 877, 827, 779, 742, 693, 666 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.76 (s, 1 H), 7.66–7.68 (m, 1 H), 7.57 (s, 1 H), 7.05–7.12 (m, 2 H), 6.96–6.98 (m, 1 H), 6.75 (m, 3 H), 6.45 (s, 1 H), 5.88–6.02 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.4, 150.0, 148.1, 147.8, 142.2, 132.8, 136.2, 132.9, 129.9, 124.0, 122.6, 121.4, 120.4, 110.3, 108.5, 107.2, 101.2, 99.4, 63.5.

MS (EI, 70 eV): *m*/*z* (%) = 303 (30, [M^+]), 274 (100), 244 (2.6), 215 (22), 202 (9.8), 189 (3.0), 178 (1.5), 163 (231.2), 154 (3.4), 136 (11), 126 (3.2), 123 (7.1), 109 (13), 95 (7.8), 82 (3.4), 75 (5.3), 63 (11), 51 (7.6).

HRMS (ESI-TOF): *m*/*z* calcd for $C_{19}H_{13}NO_3$: 303.0895; found: 153.0890.

(*R*)-3-(4-Fluorophenyl)-3*H*-pyrrolo[1,2-*a*]indole-2-carbaldehyde (3g)

Yield: 111 mg (40%); bright yellow solid; mp 132 °C; $[\alpha]_D^{20}$ –1073 (*c* = 0.3, $CHCl_3$).

HPLC: t_R = 10.16 and 14.04 min [Chiralcel OD, *n*-heptane–*i*-PrOH (7:3), 0.7 mL/min]; t_R = 10.16 min; ee = >99%.

IR (KBr): 3293, 3121, 3059, 2925, 2848, 2328, 2083, 1935, 1897, 1777, 1652, 1605, 1554, 1505, 1449, 1417, 1357, 1318, 1260, 1226, 1156, 1103, 1109, 983, 936, 883, 835, 787, 739, 692, 671 cm^{-1}.

^1H NMR (400 MHz, C_6D_6): δ = 9.17 (s, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 6.92–7.02 (m, 2 H), 6.64–6.71 (m, 3 H), 6.53 (t, *J* = 8.8 Hz, 2 H), 6.46 (s, 1 H), 6.37 (m, 1 H), 5.28 (s, 1 H).

^{13}C NMR (101 MHz, C_6D_6): δ = 183.9, 162.4 (d, $J_{C,F}$ = 247 Hz, 1 C), 148.9, 142.3, 134.6, 134.2, 133.0, 132.1, 123.8, 122.5, 120.4, 115.5, 115.3, 110.3, 98.7, 62.7.

MS (EI, 70 eV): *m*/*z* (%) = 277 (98, [M^+]), 248 (100), 227 (2.3), 220 (10), 194 (2.7), 182 (3.7), 158 (2.1), 154 (18), 133 (5.0), 127 (8.0), 114 (9.2), 102 (11), 95 (9.4), 89 (5.7), 77 (12), 75 (15), 63 (13), 51 (12).

HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{12}FNO$: 277.0903; found: 277.0891.

3-(Furan-2-yl)-9*H*-pyrrolo[1,2-*a*]indole-2-carbaldehyde (8)

Yield: 75 mg (30%); bright yellow solid; mp 147 °C.

IR (KBr): 3147, 3119, 3066, 2912, 2821, 2747, 2323, 2190, 2083, 2024, 1958, 1900, 1831, 1759, 1658, 1605, 1563, 1515, 1477, 1409, 1390, 1369, 1329, 1309, 1280, 1249, 1219, 1182, 1163, 1134, 1094, 1068, 1028, 995, 950, 912, 882, 846, 790, 744, 710, 691, 663 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.79 (s, 1 H), 7.72 (m, 1 H), 7.44 (d, *J* = 7.4 Hz, 1 H), 7.19–7.28 (m, 2 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 6.65–6.74 m, (m, 3 H), 3.94 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.0, 143.5, 141.9, 139.6, 138.0, 135.2, 129.3, 127.6, 125.8, 125.0, 123.8, 113.8, 112.7, 111.7, 100.8, 28.8.

MS (EI, 70 eV): *m*/*z* (%) = 249 (28, [M^+]), 220 (65), 204 (4.5), 191 (100), 178 (4.9), 165 (22), 152 (39.6), 140 (17.4), 126 (10), 117 (8.6), 102 (5.8), 89 (45), 75 (18), 63 (934), 51 (31).

HRMS (ESI-TOF): *m*/*z* calcd for $C_{16}H_{11}NO_2$: 249.0790; found: 249.0782.

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