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Palladium-Catalyzed Asymmetric Allylic Alkylation Reaction of 2-Monosubstituted Indolin-3-ones

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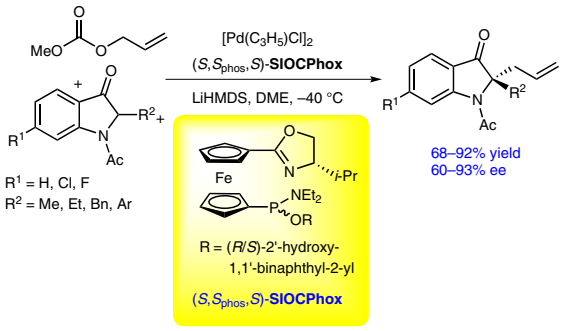

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Abstract An efficient and practical method was developed for the synthesis of 2,2-disubstituted indolin-3-ones by palladium-catalyzed asymmetric allylic alkylation. Enantioselective construction of quaternary carbon centers was also realized in this way.

Key words palladium, allylic substitution, asymmetric catalysis, indolines, quaternary carbon

The 2,2-disubstituted indolin-3-one moiety is an important structural motif in many natural products and compounds of pharmaceutical interest, such as austamide,[1] brevianamide A,[2] (+)-aristotetelone,[3] isatisine A,[4] hinckdentine A,[5] and others[6] (Figure 1). Therefore, their synthesis has attracted much attention from synthetic chemists. To date several methodologies have been developed,[7] however, the only successful protocol that proceeds through asymmetric catalysis involves addition reactions to the C–N double bond of 2-substituted 3*H*-indol-3-ones[7m–r] or their analogues.[7s] Only one report has appeared for the α-alkylation of 2-substituted indolin-3-ones catalyzed by a chiral catalyst, and the reaction proceeds with moderate enantioselectivity.[7t] Palladium-catalyzed asymmetric allylic alkylation (AAA) is one of the most important reactions for the enantioselective construction of C–C and C–hetero atom bonds in organic synthesis.[8] However, a few examples of α-amino ketones being used in the reaction as prenucleophiles via the enolates derived from ketones and carboxylic acid have been successfully demonstrated.[7t,9,10d–f,i] In the course of our research on palladium-catalyzed AAA during recent years,[10] we have successfully used different types of enolates as nucleophiles.[10d–f,i] In this paper, we would like to

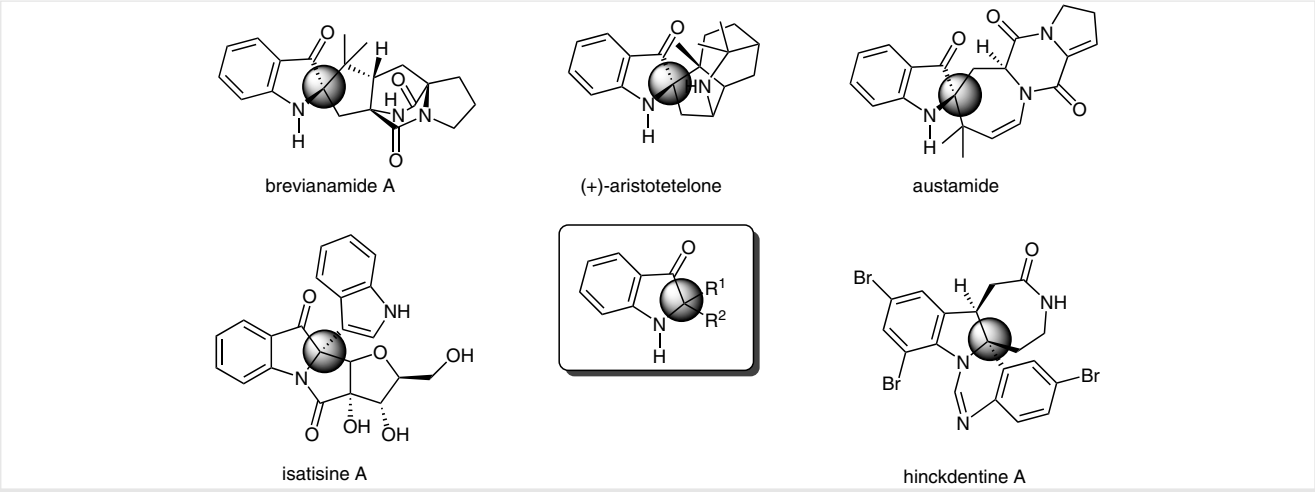


Figure 1 Some natural products containing the indolin-3-one substructure with an α-quaternary carbon center

report our further studies on the use of 2-substituted indolin-3-ones as prenucleophiles to construct chiral quaternary centers by palladium-catalyzed AAA.[10b,11]

Initially, the reaction of 1-acetyl-2-benzylindolin-3-one (**1a**) and allyl methyl carbonate (**2a**) was carried out in the presence of catalytic amounts of $[Pd(C_3H_5)Cl]_2$ and (*R*)-BINAP, using LiHMDS as base in tetrahydrofuran (THF) at –40 °C. The reaction afforded the product 2,2-disubstituted indolin-3-one **3a** in 83% yield and 38% ee (Table 1, entry 1). Encouraged by this result, the reaction parameters were investigated (Table 1).

It was found that good yield was achieved, although enantioselectivity was not high, with ligands **L2**–**L5** (Figure 2 and Table 1, entry 2–5). The ee value decreased significantly when allyl *tert*-butyl carbonate (**2b**) was used (Table 1, entry 6 vs 2). A screen of SIOCPhox ligands developed by our group[10] revealed that the ligand (S,S_{phos},S)-SIOCPhox **L6** afforded better results with respect to both yield and enantioselectivity (entry 7) whereas the other SIOCPhox ligands **L7**–**L14** provided inferior results (entries 8–15).

On the basis of the above results, the effects of solvents and bases using $[Pd(C_3H_5)Cl]_2$ and (S,S_{phos},S)-**L6** as catalyst was investigated. It can be seen that dimethoxyethane (DME) gave better results (Table 1, entry 17) among various solvents screened, including toluene, DME, Et_2O and CH_2Cl_2 (entries 16–19), whereas LiHMDS was found to be the most suitable base (entry 17). Both yield and ee value decreased significantly when NaHMDS, KHMDS, or LDA was used as base (entries 20–22), and NaH and *t*-BuONa gave only trace amounts of product (not shown). The use of some common additives, such as LiCl, $ZnCl_2$, and $Bn(Et)_3NCl$, did not improve the yield and/or ee (entries 23–25).

Under the optimized conditions, the substrate scope was then explored; the results are summarized in Table 2. Generally the reactions proceeded smoothly for all substrates, with yields of 62–99% and ee values of 68–92% being obtained for substrates with benzyl (entry 1), methyl (entry 2), ethyl (entry 9), phenyl (entry 7), *o*-Br substituted phenyl (entry 8) and benzyl with electron-withdrawing or electron-donating substituent on phenyl group (entries 10–13) at the α-position to the carbonyl. The reaction was also suitable for indolinones with Cl or F at the 6-position (entries 3–6). It should be noted that the reactions of **1g**, **1h**, **1l**, and **1m** afforded the corresponding products in lower yields (not shown), however, the yields were improved when the reaction was carried out at 0 or 15 °C. Substrate **1g** afforded the product **3g** in 86% yield with 92% ee and substrate **1h** gave **3h** in 92% yield and 87% ee at 15 °C (entries 7 and 8), whereas **1l** gave **3l** in 93% yield and 84% ee, and **1m** provided **3m** in 83% yield and 68% ee at 0 °C (entries 12 and 13). Substrate **1n**, with a furan-2-ylmethyl substituent, provided **3n** in 80% yield and 76% ee (entry 14). It should be pointed out that the product **3h** could be used as a key intermediate in the total synthesis of hinckdentine A.[5b,c]

The absolute configuration of **3a** was determined as *R* by comparing the sign of the optical rotation of the product with that previously reported.[7t]

In summary, we have realized the palladium-catalyzed asymmetric allylic alkylation of 2-substituted indolin-3-ones with allyl methyl carbonate in good yields and with good enantioselectivities. A chiral quaternary carbon center was also constructed during the reaction. These synthetically useful products could find applications in organic synthesis.[5b,c] Investigations to extend the scope of the reaction and develop further its application in organic synthesis are in progress.

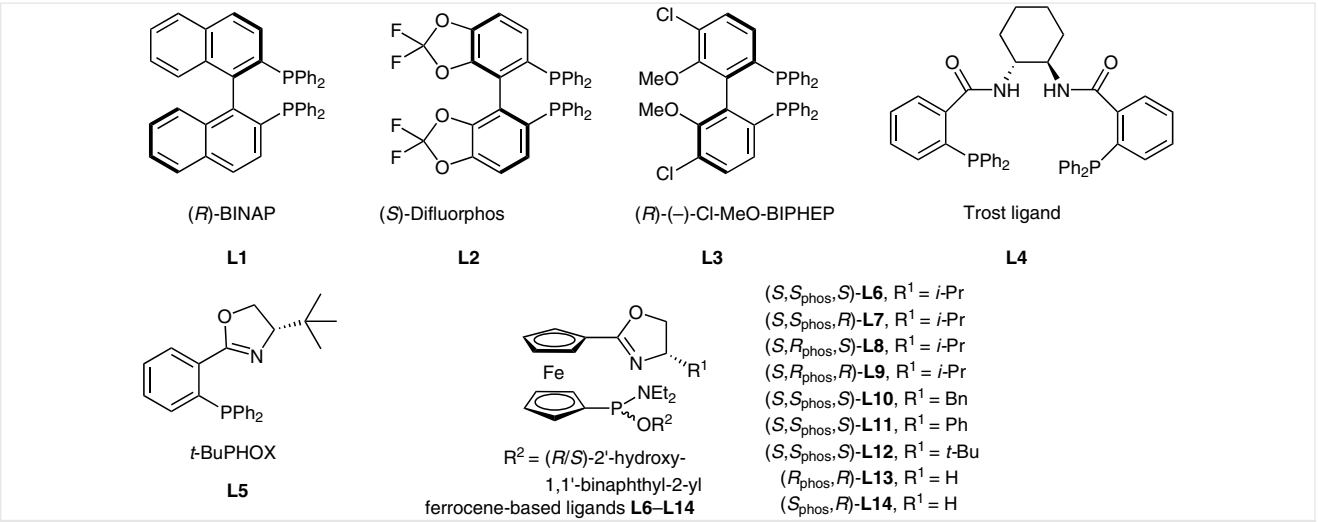
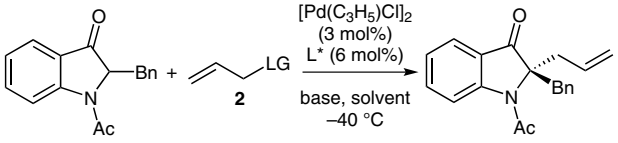


Figure 2 The structure of ligands**L1**–**L14**

Table 1 Optimization of Parameters for the Reaction of **1a** with **2**[a]



Entry	L*	Base	Solvent	LG (**2**)	Yield (%)[b]	ee (%)[c]
1	**L1**	LiHMDS	THF	OCO_2Me (**2a**)	83	38
2	**L2**	LiHMDS	THF	OCO_2Me (**2a**)	89	55
3	**L3**	LiHMDS	THF	OCO_2Me (**2a**)	95	40
4	**L4**	LiHMDS	THF	OCO_2Me (**2a**)	68	–48[d]
5	**L5**	LiHMDS	THF	OCO_2Me (**2a**)	75	6
6	**L2**	LiHMDS	THF	OCO_2tBu (**2b**)	90	21
7	**L6**	LiHMDS	THF	OCO_2Me (**2a**)	99	61
8	**L7**	LiHMDS	THF	OCO_2Me (**2a**)	98	42
9	**L8**	LiHMDS	THF	OCO_2Me (**2a**)	97	–44[d]
10	**L9**	LiHMDS	THF	OCO_2Me (**2a**)	90	–21[d]
11	**L10**	LiHMDS	THF	OCO_2Me (**2a**)	73	61
12	**L11**	LiHMDS	THF	OCO_2Me (**2a**)	87	–16[d]
13	**L12**	LiHMDS	THF	OCO_2Me(**2a**)	95	9
14	**L13**	LiHMDS	THF	OCO_2Me (**2a**)	96	–31[d]
15	**L14**	LiHMDS	THF	OCO_2Me (**2a**)	91	48
16	**L6**	LiHMDS	toluene	OCO_2Me (**2a**)	51	42
17	**L6**	LiHMDS	DME	OCO_2Me (**2a**)	99	76
18	**L6**	LiHMDS	Et_2O	OCO_2Me (**2a**)	99	63
19	**L6**	LiHMDS	CH_2Cl_2	OCO_2Me (**2a**)	97	51
20	**L6**	NaHMDS	DME	OCO_2Me (**2a**)	7	–16[d]
21	**L6**	KHMDS	DME	OCO_2Me (**2a**)	10	9
22	**L6**	LDA	DME	OCO_2Me(**2a**)	6	37
23[e]	**L6**	LiHMDS	DME	OCO_2Me (**2a**)	69	72
24[f]	**L6**	LiHMDS	DME	OCO_2Me (**2a**)	71	66
25[g]	**L6**	LiHMDS	DME	OCO_2Me (**2a**)	76	54

[a] Reaction was carried out at –40 °C, molar ratio of **1a**/**2**/$[Pd(C_3H_5)Cl]_2$/**L**/base = 100:150:3:6:120.
[b] Yields of **3a** based on **1a**.
[c] Determined by chiral HPLC analysis.
[d] Reverse sequence of peaks by HPLC.
[e] LiCl as additive.
[f] $BnN(Et)_3Cl$ as additive.
[g] $ZnCl_2$ as additive.

All the experiments were carried out in flame-dried glassware under a dry argon atmosphere. The solvents were purified and dried over appropriate drying agents and distilled under argon prior to use. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ using TMS as internal standard with Bruker Avance 300 MHz, 400 MHz, or 600 MHz, spectrometers at r.t. HRMS measurements were carried out with a Finnigan MAT 8430 spectrometer.

Synthesis of 2,2-Substituted Indolin-3-ones 3; General Procedure

2-Substituted indolin-3-one **1** (0.1 mmol) and DME (1.0 mL) were added into a dry Schlenk tube. LiHMDS (1.0 M in THF, 0.12 mL, 0.12 mmol) was added dropwise and the mixture was stirred for 30 min at –40 °C. In a separate flask, $[Pd(C_3H_5)Cl]_2$ (1.1 mg, 0.003 mmol) and ligand (S,S_{phos},S)-SIOCPhox (**L6**; 4.1 mg, 0.006 mmol) were dissolved in DME (1.0 mL) and the mixture was stirred at r.t. for 30 min, before being added to the above enolate solution at the temperature indicated in Table 2. Allyl methyl carbonate **2a** (0.15 mmol) was then added and the resulting mixture was stirred at the stated temperature. Upon completion (reaction monitored by TLC), the reaction mixture was quenched by sat. aq NH_4Cl (5.0 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; petroleum ether–EtOAc, 10:1) to afford the desired product.

1-Acetyl-2-allyl-2-benzylindolin-3-one (3a)

Yield: 30.2 mg (99%); pale-yellow solid; mp 72–75 °C; $[\alpha]_D^{24}$ +10.0 (*c* 1.0, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (5:95); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 18.8 (minor), 15.4 (major) min; ee = 75%.

IR (KBr): 3028, 2962, 2921, 2851, 1711, 1667, 1604, 1469, 1433, 1371, 1308, 1031, 751, 703 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.2 Hz, 1 H), 7.39 (t, *J* = 7.2 Hz, 1 H), 7.12 (d, *J* = 5.6 Hz, 1 H), 6.99–6.93 (m, 6 H), 5.36–5.25 (m, 1 H), 5.04 (d, *J* = 16.8 Hz, 1 H), 4.83 (d, *J* = 9.6 Hz, 1 H), 3.74 (d, *J* = 12.4 Hz, 1 H), 3.36 (br, 1 H), 3.22 (d, *J* = 13.2 Hz, 1 H), 2.82 (br, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0, 168.6, 152.5, 136.7, 135.1, 131.2, 129.4, 127.8, 126.7, 125.3, 124.1, 123.2, 119.4, 114.7, 77.0, 41.6, 40.4, 27.1.

MS (EI): *m*/*z* (%) = 305 (39) $[M]^+$, 264 (21), 222 (61), 214 (17), 172 (100), 144 (10), 130 (10), 115 (12), 91 (50), 77 (13), 43 (30).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{20}NO_2$: 306.1489; found: 306.1495.

1-Acetyl-2-allyl-2-methylindolin-3-one (3b)

Yield: 14.2 mg (62%); pale-yellow solid; mp 90–91 °C; $[\alpha]_D^{27}$ +52.9 (*c* 1.00, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (2:98); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 18.7 (minor), 21.1 (major) min; ee = 88%.

IR (KBr): 3072, 1703, 1667, 1641, 1608, 1471, 1432, 1371, 1343, 1310, 1191, 1100, 930, 750 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.32 (br, 1 H), 7.78 (d, *J* = 7.6 Hz, 1 H), 7.65 (dt, *J* = 7.8, 1.2 Hz, 1 H), 7.20 (t, *J* = 7.6 Hz, 1 H), 5.33–5.23 (m, 1 H), 5.02 (d, *J* = 16.8 Hz, 1 H), 4.86 (d, *J* = 9.6 Hz, 1 H), 3.10 (br, 1 H), 2.76 (br, 1 H), 2.51 (s, 3 H), 1.60 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.8, 168.7, 152.8, 137.4, 131.1, 124.7, 123.9, 119.5, 117.1, 116.1, 72.0, 40.9, 26.7, 22.8.

MS (EI): *m*/*z* (%) = 229 (14) $[M]^+$, 188 (37), 147 (15), 146 (100), 144 (9), 117 (10), 91 (10), 77 (15).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{16}NO_2$: 230.1176; found: 230.1182.

Table 2 Substrate Scope for Palladium-Catalyzed AAA[a]

1a: R^1 = H, R^2 = Bn **1f:** R^1 = F, R^2 = Me **1k:** R^1 = H, R^2 = *p*-(*i*-Pr)$C_6H_4CH_2$
1b: R^1 = H, R^2 = Me **1g:** R^1 = H, R^2 = Ph **1l:** R^1 = H, R^2 = *o*-NC$C_6H_4CH_2$
1c: R^1 = Cl, R^2 = Bn **1h:** R^1 = H, R^2 = *o*-BrC_6H_4 **1m:** R^1 = H, R^2 = *m*-Me$C_6H_4CH_2$
1d: R^1 = Cl, R^2 = Me **1i:** R^1 = H, R^2 = Et **1n:** R^1 = H, R^2 = furan-2-ylmethyl
1e: R^1 = F, R^2 = Bn **1j:** R^1 = H, R^2 = *o*-Br$C_6H_4CH_2$

Entry	Substrate	Product	Yield (%)[b]	ee (%)[c]
1	**1a**	**3a**	99	75
2	**1b**	**3b**	62	88
3	**1c**	**3c**	80	74
4	**1d**	**3d**	70	86
5	**1e**	**3e**	76	86
6	**1f**	**3f**	66	86
7[d]	**1g**	**3g**	86	92
8[d]	**1h**	**3h**	92	87
9	**1i**	**3i**	60	78
10	**1j**	**3j**	83	84
11	**1k**	**3k**	81	75
12[e]	**1l**	**3l**	93	84
13[e]	**1m**	**3m**	83	68
14	**1n**	**3n**	80	76

[a] Reaction was carried out at –40 °C, molar ratio of **1**/**2a**/[Pd(C_3H_5)Cl]$_2$/**L6**/base = 100:150:3:6:120.
[b] Yield of **3** based on **1**.
[c] Determined by chiral HPLC analysis.
[d] Reaction was carried out at 15 °C.
[e] Reaction was carried out at 0 °C.

1-Acetyl-2-allyl-2-benzyl-6-chloroindolin-3-one (3c)

Yield: 27.1 mg (80%); pale-yellow solid; mp 50–52 °C; $[\alpha]_D^{24}$ +43.2 (*c* 1.04, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (5:95); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 11.7 (minor), 11.0 (major) min; ee = 74%.

IR (KBr): 3083, 2956, 2925, 2854, 1716, 1673, 1603, 1574, 1428, 1370, 1312, 1272, 1083, 992, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.2 Hz, 1 H), 7.13 (s, 1 H), 7.00–6.92 (m, 6 H), 5.34–5.24 (m, 1 H), 5.05 (d, *J* = 17.2 Hz, 1 H), 4.87 (d, *J* = 9.2 Hz, 1 H), 3.72 (br, 1 H), 3.34–3.22 (m, 2 H), 2.81 (br, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.6, 168.5, 153.0, 143.3, 134.9, 130.9, 129.4, 128.1, 127.0, 125.0, 123.9, 119.8, 115.1, 77.8, 41.6, 40.5, 27.1.

MS (EI): *m*/*z* (%) = 341 (39) $[M]^+$, 339 (95) $[M]^+$, 298 (45), 258 (67), 256 (100), 208 (97), 207 (97), 206 (100), 164 (26), 143 (33), 115 (29), 91 (96).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{19}ClNO_2$: 340.1099; found: 340.1098.

1-Acetyl-2-allyl-6-chloro-2-methylindolin-3-one (3d)

Yield: 18.4 mg (70%); slightly yellow oil; $[\alpha]_D^{20}$ +51.3 (*c* 1.05, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (3:97); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 12.8 (minor), 13.5 (major) min; ee = 86%.

IR (KBr): 3080, 2979, 2928, 2855, 1717, 1672, 1602, 1574, 1425, 1368, 1341, 1269, 1183, 979, 925, 826 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (br, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.15 (dd,*J* = 8.0, 1.2 Hz, 1 H), 5.29–5.18 (m, 1 H), 5.00 (d, *J* = 16.8 Hz, 1 H), 4.86 (d, *J* = 10.4 Hz, 1 H), 3.00 (br, 1 H), 2.73 (br, 1 H), 2.47 (s, 3 H), 1.56 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 168.7, 153.1, 143.8, 130.6, 125.2, 124.6, 121.8, 119.8, 117.8, 71.8, 41.1, 26.1, 22.9.

MS (EI): *m*/*z* (%) = 265 (6) $[M]^+$, 263 (20) $[M]^+$, 224 (11), 222 (38), 182 (34), 180 (100), 117 (11), 110 (14), 75 (20), 43 (55).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}ClNO_2$: 264.0786; found: 264.0780.

1-Acetyl-2-allyl-2-benzyl-6-fluoroindolin-3-one (3e)

Yield: 24.5 mg (76%); pale-solid; mp 81–83 °C; $[\alpha]_D^{20}$ +17.2 (*c* 1.12, $CHCl_3$); HPLC [Chiralpak AD; *i*-PrOH–hexane (5:95); flow rate: 0.6 mL/min; λ = 214 nm]: t_R = 15.0 (minor), 13.9 (major) min; ee = 86%.

IR (KBr): 3084, 3032, 2931, 1716, 1677, 1619, 1589, 1488, 1436, 1372, 1275, 1184, 924, 703 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (t, *J* = 4.8 Hz, 1 H), 7.03–7.00 (m, 3 H), 6.94–6.92 (m, 2 H), 6.81 (br, 1 H), 6.72 (dt, *J* = 8.1, 2.0 Hz, 1 H), 5.37–5.26 (m, 1 H), 5.07 (d, *J* = 17.2 Hz, 1 H), 4.89 (d, *J* = 8.8 Hz, 1 H), 3.73 (br, 1 H), 3.36–3.23 (m, 2 H), 2.83 (br, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 168.5, 168.2 (d, J_{C-F} = 255.0 Hz), 153.9, 134.9, 131.0, 129.4, 128.0, 126.9, 126.3, 121.9, 119.7, 111.4 (d, J_{C-F} = 22.6 Hz), 102.6 (d, J_{C-F} = 27.1 Hz), 77.9, 41.6, 40.4, 27.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –97.44.

MS (EI): *m*/*z* (%) = 323 (55) [M]$^+$, 282 (20), 240 (95), 232 (30), 191 (28), 190 (100), 162 (19), 148 (17), 91 (62).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{19}FNO_2$: 324.1394; found: 324.1381.

1-Acetyl-2-allyl-6-fluoro-2-methylindolin-3-one (3f)

Yield: 16.3 mg (66%); slightly yellow oil; $[\alpha]_D^{20.7}$ +63.0 (*c* 1.00, $CHCl_3$); HPLC [Chiralpak AD-H;*i*-PrOH–hexane (3:97); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 13.6 (minor), 14.7 (major) min; ee = 86%.

IR (KBr): 3082, 2980, 2931, 2856, 1717, 1673, 1618, 1589, 1437, 1370, 1345, 1267, 1192, 987, 924, 843 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (br, 1 H), 7.73 (dd, *J* = 8.0, 6.4 Hz, 1 H), 6.87 (t, *J* = 8.4 Hz, 1 H), 5.29–5.18 (m, 1 H), 4.99 (d, *J* = 16.8 Hz, 1 H), 4.85 (d, *J* = 10.0 Hz, 1 H), 2.99 (br, 1 H), 2.74 (br, 1 H), 2.45 (s, 3 H), 1.56 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.6, 170.3, 168.6, 166.9, 154.0, 130.5, 126.3, 119.6, 112.0 (d, J_{C-F} = 23.9 Hz), 105.1, 72.1, 41.0, 25.9, 22.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –97.04.

MS (EI): *m*/*z* (%) = 247 (41) [M]$^+$, 206 (89), 165 (44), 164 (100), 162 (21), 135 (24), 109 (22), 95 (25), 94 (36).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}FNO_2$: 248.1081; found: 248.1072.

1-Acetyl-2-allyl-2-phenylindolin-3-one (3g)

Yield: 25.0 mg (86%); pale solid; mp 121–123 °C; $[\alpha]_D^{25.5}$ +338.9 (*c* 0.70, $CHCl_3$); HPLC [Chiralpak AD; *i*-PrOH–hexane (5:95); flow rate: 0.6 mL/min; λ = 214 nm]: t_R = 23.2 (minor), 22.0 (major) min; ee = 92%.

IR (KBr): 3067, 2919, 2852, 1721, 1670, 1606, 1460, 1370, 1337, 1292, 1149, 914, 756, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 8.0 Hz, 1 H), 7.76–7.72 (m, 2 H), 7.38–7.32 (m, 3 H), 7.28–7.24 (m, 3 H), 5.46–5.36 (m, 1 H), 5.19 (d, *J* = 16.8 Hz, 1 H), 5.02 (d, *J* = 10.0 Hz, 1 H), 3.66 (dd, *J* = 13.2, 4.8 Hz, 1 H), 3.15 (dd, *J* = 13.2, 8.0 Hz, 1 H), 2.00 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 170.1, 154.6, 137.8, 137.6, 129.6, 129.5, 128.5, 125.1, 124.8, 124.7, 122.3, 120.6, 118.9, 74.7, 40.2, 25.1.

MS (EI): *m*/*z* (%) = 291 (64) [M]$^+$, 250 (96), 220 (21), 209 (91), 208 (100), 180 (31), 152 (27), 77 (42).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}NO_2$: 292.1332; found: 292.1334.

1-Acetyl-2-allyl-2-(2-bromophenyl)indolin-3-one (3h)

Yield: 33.9 mg (92%); pale-yellow solid; mp 120–122 °C; $[\alpha]_D^{25.5}$ +157.4 (*c* 1.09, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (20:80); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 14.9 (minor), 19.8 (major) min; ee = 87%.

IR (KBr): 3077, 2923, 2850, 1718, 1668, 1607, 1588, 1460, 1369, 1339, 1291, 1197, 1004, 911, 750 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (br, 1 H), 7.76 (m, 3 H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 1 H), 7.23–7.15 (m, 2 H), 5.41–5.25 (m, 1 H), 5.08 (d, *J* = 15.9 Hz, 1 H), 4.88 (d, *J* = 10.2 Hz, 1 H), 3.37 (br, 1 H), 3.23 (br, 1 H), 1.95 (br, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 168.5, 154.3, 137.2, 135.2, 130.5, 130.0, 129.6, 127.8, 125.7, 124.2, 123.3, 121.6, 120.8, 119.0, 74.4, 41.8, 25.1.

MS (EI): *m*/*z* (%) = 371 (5) [M]$^+$, 369 (6) [M]$^+$, 330 (17), 328 (23), 290 (53), 288 (93), 286 (95), 207 (100), 178 (18), 151 (18), 102 (18), 76 (36).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}BrNO_2$: 370.0437; found: 370.0437.

1-Acetyl-2-allyl-2-ethylindolin-3-one (3i)

Yield: 14.6 mg (60%); slightly yellow oil; $[\alpha]_D^{24.5}$ +6.3 (*c* 1.00, $CHCl_3$); HPLC [Chiralpak AD; *i*-PrOH–hexane (5:95); flow rate: 0.6 mL/min; λ = 214 nm]: t_R = 13.6 (minor), 14.1 (major) min; ee = 78%.

IR (KBr): 3079, 2971, 2934, 2878, 1714, 1667, 1609, 1460, 1370, 1295, 920, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (br, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.65 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 5.33–5.23 (m, 1 H), 5.01 (d, *J* = 16.8 Hz, 1 H), 4.85 (d, *J* = 10.0 Hz, 1 H), 3.14 (br, 1 H), 2.72–2.52 (m, 5 H), 2.04 (br, 1 H), 0.56 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 202.2, 168.3, 152.9, 137.2, 131.2, 125.1, 124.1, 123.6, 119.3, 115.2, 74.4, 40.6, 29.6, 26.9, 7.8.

MS (EI): *m*/*z* (%) = 243 (20) [M]$^+$, 202 (50), 161 (18), 160 (100), 132 (26), 130 (19), 117 (15), 77 (18).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{18}NO_2$: 244.1332; found: 244.1333.

1-Acetyl-2-allyl-2-(2-bromobenzyl)indolin-3-one (3j)

Yield: 31.8 mg (83%); pale-yellow solid; mp 55–57 °C; $[\alpha]_D^{24.5}$ –20.2 (*c* 1.00, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (5:95); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 22.0 (minor), 17.3 (major) min; ee = 84%.

IR (KBr): 3077, 2929, 1715, 1668, 1608, 1470, 1435, 1369, 1298, 1024, 926, 751 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (br, 1 H), 7.61 (d, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.8 Hz, 1 H), 7.30 (d, *J* = 8.1 Hz, 1 H), 7.06–6.96 (m, 3 H), 6.86 (t, *J* = 8.1 Hz, 1 H), 5.37–5.24 (m, 1 H), 5.08 (d, *J* = 16.2 Hz, 1 H), 4.89 (d, *J* = 9.9 Hz, 1 H), 3.85 (br, 1 H), 3.52 (br, 1 H), 3.43 (d, *J* = 14.1 Hz, 1 H), 2.91 (br, 1 H), 2.50 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 200.6, 168.5, 152.2, 136.6, 135.0, 132.8, 132.1, 131.2, 128.3, 126.7, 125.2, 125.0, 124.3, 123.3, 119.6, 115.0, 76.3, 40.7, 39.9, 27.0.

MS (EI): *m*/*z* (%) = 385 (36) [M]$^+$, 383 (37) [M]$^+$, 344 (24), 342 (27), 302 (69), 300 (72), 220 (52), 214 (98), 173 (84), 172 (100), 144 (33), 130 (28), 115 (25), 90 (25).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{19}BrNO_2$: 384.0594; found: 384.0593.

1-Acetyl-2-allyl-2-(4-isopropylbenzyl)indolin-3-one (3k)

Yield: 28.1 mg (81%); slightly yellow oil; $[\alpha]_D^{24.6}$ +6.4 (*c* 0.92, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (5:95); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 15.4 (minor), 12.5 (major) min; ee = 75%.

IR (KBr): 3080, 2960, 2927, 2871, 1716, 1670, 1609, 1470, 1372, 1311, 1290, 924, 795 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.6 Hz, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.13 (d, *J* = 6.4 Hz, 1 H), 7.00 (t, *J* = 7.6 Hz, 1 H), 6.86–6.81 (m, 4 H), 5.38–5.27 (m, 1 H), 5.06 (d, *J* = 17.2 Hz, 1 H), 4.86 (d, *J* = 10.0 Hz, 1 H), 3.72 (d, *J* = 12.4 Hz, 1 H), 3.40–3.33 (m, 1 H), 3.20 (d, *J* = 13.2 Hz, 1 H), 2.85–2.80 (m, 1 H), 2.69–2.61 (m, 1 H), 2.46 (s, 3 H), 1.05 (d, *J* = 2.4 Hz, 3 H), 1.03 (d, *J* = 2.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.2, 168.7, 152.6, 147.3, 136.6, 132.4, 131.4, 129.4, 125.8, 125.5, 124.3, 123.1, 119.4, 114.9, 74.3, 41.3, 40.3, 33.6, 27.2, 23.9.

MS (EI): *m*/*z* (%) = 347 (15) [M]$^+$, 264 (21), 214 (12), 172 (100), 133 (38), 117 (18), 105 (11), 91 (11).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{26}NO_2$: 348.1958; found: 348.1959.

2-[(1-Acetyl-2-allyl-3-oxoindolin-2-yl)methyl]benzonitrile (3l)

Yield: 30.7 mg (93%); pale-solid; mp 83–85 °C; $[\alpha]_D^{24.7}$ –14.3 (*c* 1.35, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (8:92); flow rate: 1.0 mL/min; λ = 214 nm]: t_R = 22.9 (minor), 20.6 (major) min; ee = 84%.

IR (KBr): 3080, 3025, 2937, 2854, 2225, 1707, 1674, 1608, 1470, 1368, 1272, 933, 910, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.0 Hz, 1 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 7.41 (d, *J* = 7.2 Hz, 1 H), 7.35 (br, 1 H), 7.28 (t, *J* = 7.6 Hz, 1 H), 7.14 (t, *J* = 7.2 Hz, 2 H), 7.05 (t, *J* = 7.2 Hz, 1 H), 5.36–5.26 (m, 1 H), 5.10 (d, *J* = 17.2 Hz, 1 H), 4.91 (d, *J* = 9.6 Hz, 1 H), 3.98 (d, *J* = 10.8 Hz, 1 H), 3.52–3.43 (m, 2 H), 2.90 (br, 1 H), 2.56 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.4, 168.8, 152.5, 138.9, 137.1, 133.1, 132.1, 131.4, 130.9, 127.5, 124.8, 124.5, 123.5, 120.1, 118.1, 115.2, 113.5, 76.1, 40.0, 39.7, 27.1.

MS (EI): *m*/*z* (%) = 330 (13) [M]$^+$, 288 (6), 248 (18), 247 (100), 214 (20), 172 (67), 144 (7), 130 (7), 116 (19), 89 (16).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{19}N_2O_2$: 331.1441; found: 331.1445.

1-Acetyl-2-allyl-2-(3-methylbenzyl)indolin-3-one (3m)

Yield: 26.5 mg (83%); pale-solid; mp 62–64 °C; $[\alpha]_D^{24.6}$ +8.2 (*c* 1.10, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (5:95); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 15.5 (minor), 12.9 (major) min; ee = 68%.

IR (KBr): 3079, 3024, 2961, 2924, 1715, 1670, 1609, 1471, 1436, 1372, 1300, 804, 781, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 8.0 Hz, 1 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 7.02 (t, *J* = 7.2 Hz, 1 H), 6.87 (t, *J* = 7.2 Hz, 1 H), 6.78–6.73 (m, 3 H), 5.37–5.27 (m, 1 H), 5.06 (d, *J* = 17.2 Hz, 1 H), 4.85 (d, *J* = 9.6 Hz, 1 H), 3.71 (d, *J* = 12.8 Hz, 1 H), 3.38 (dd, *J* = 12.0, 8.0 Hz, 1 H), 3.20 (d, *J* = 13.2 Hz, 1 H), 3.82 (dd, *J* = 11.6, 8.0 Hz, 1 H), 2.45 (s, 3 H), 2.09 (s, 3 H).

^{13}C NMR (150 MHz, acetone-d_6): δ = 201.9, 169.5, 153.6, 138.0, 137.7, 136.1, 132.4, 130.9, 128.5, 128.1, 127.3, 126.1, 124.2, 123.9, 119.4, 116.2, 77.2, 42.0, 41.2, 27.3, 21.2.

MS (EI): *m*/*z* (%) = 319 (35) [M]$^+$, 278 (13), 236 (68), 214 (15), 172 (100), 115 (12), 105 (34), 77 (22).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{22}NO_2$: 320.1645; found: 320.1637.

1-Acetyl-2-allyl-2-(furan-2-ylmethyl)indolin-3-one (3n)

Yield: 23.6 mg (80%); slightly yellow oil; $[\alpha]_D^{24.6}$ +10.1 (*c* 1.00, $CHCl_3$); HPLC [Chiralpak AD-H; *i*-PrOH–hexane (5:95); flow rate: 0.7 mL/min; λ = 214 nm]: t_R = 25.0 (minor), 20.5 (major) min; ee = 76%.

IR (KBr): 3080, 2982, 2853, 1716, 1668, 1607, 1504, 1435, 1371, 1292, 973, 922, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 7.27 (br, 1 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 6.95 (s, 1 H), 5.98 (s, 1 H), 5.85 (s, 1 H), 5.36–5.26 (m, 1 H), 5.05 (d, *J* = 17.2 Hz, 1 H), 4.86 (d, *J* = 10.0 Hz, 1 H), 3.85 (d, *J* = 9.2 Hz, 1 H), 3.28 (br, 2 H), 2.77 (br, 1 H), 2.48 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 168.6, 150.2, 141.6, 136.8, 131.0, 124.9, 124.5, 123.3, 119.6, 114.9, 110.0, 107.9, 75.4, 40.1, 34.3, 27.0.

MS (EI): *m*/*z* (%) = 295 (20) [M]$^+$, 253 (21), 214 (71), 173 (32), 172 (100), 154 (17), 144 (30), 130 (29), 81 (52).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{18}NO_3$: 296.1281; found: 296.1275.

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Supporting Information

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