Supplementary Information

Highly regio- and stereoselective (3+2) annulation reaction of allenoates with 3-methyleneindolin-2-ones catalyzed by planar chiral [2.2]paracyclophane-based bifunctional phosphine-phenol catalyst

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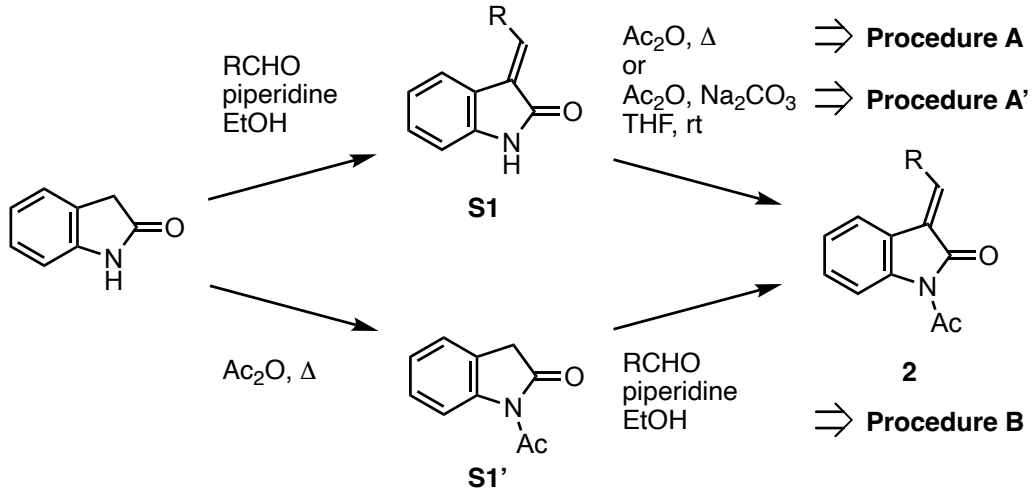
General Method. Melting point (mp) was measured by Yanaco melting point apparatus MP-500D and uncorrected. Infrared spectra (IR) were measured in $CHCl_3$ using a JASCO FT/IR-4100 spectrometer; absorptions are reported in reciprocal centimeters (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded by a Bruker Avance III 600 spectrometer operating at 600 MHz (150 MHz for ^{13}C NMR) at 25 °C with tetramethylsilane (δ = 0.0 ppm) as an internal standard. The data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant (Hz). ^{31}P NMR spectra were recorded with 85% H_3PO_4 (δ = 0.0 ppm) as an external standard. High resolution mass spectra were measured with a Thermo Scientific Exactive Plus Orbitrap. Analytical thin-layer chromatography (TLC) was performed on MERCK silica gel, grade 60 F_{254}. The spots and bands were detected by UV light of irradiation (254 nm) and/or by staining with 5% phosphomolybdic acid followed by heating. Column chromatography for isolation of the products was carried out on KANTO Sillica Gel 60 (230-400 mesh). HPLC analyses were performed using Interigent UV/VIS Detector JASCO UV-2075 Plus and UV-4075. The chiral columns included Chiralpak IA-3, IB-3 and IC-3 (Daicel Chemical Industries, Ltd., 0.46 Φ x 25 cm). Optical rotations were measured on a JASCO P-2200. Commercially available reagents were used throughout without purification unless otherwise stated. All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Organic extracts were dried over anhydrous Na_2SO_4. Catalysts (S_p)-**1a**–**1c** were prepared using our previously reported method.[1]

Typical Procedure for Preparation of Alkylideneindolinones



Scheme S1

Procedure A

To a solution of oxindole in EtOH were added aldehyde (1.1 equiv.) and piperidine (0.2 equiv.). After being stirred at 80 °C for 1 h, the precipitate was collected by filtration and dried under reduced pressure to give crude **S1**, which was used in the next step without further purification. The solution of **S1** in acetic anhydride (0.2 M) was stirred for 24 h at 100 °C, diluted with water and extracted with EtOAc. The combined extracts were washed with 2 M aqueous NaOH, water and brine. The organic layer was dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Hexane) to provide **2**.

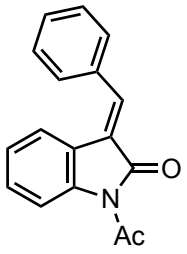
Procedure A'

To a solution of oxindole in EtOH were added aldehyde (1.1 equiv.) and piperidine (0.2 equiv.). After being stirred at 80 °C for 1 h, the precipitate was collected by filtration and dried under reduced pressure to give crude **S1**, which was used in the next step without further purification. To a stirred mixture of **S1** and Na_2CO_3 (6 equiv.) in THF was added acetic anhydride (6 equiv.). The mixture was stirred for 24 h at room temperature, diluted with water and extracted with EtOAc. The combined extracts were washed with water and brine. The organic layer was dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Hexane) to provide **2**.

Procedure B

A solution of oxindole in acetic anhydride (5 M) was stirred for 20 h at 130 °C. After cooling, the precipitate was filtered, rinsed with Et_2O and dried under reduced pressure to give crude **S1'**. The solution of **S1'** in EtOH were added aldehyde (1.1 equiv.) and piperidine (0.1 equiv.). After being stirred at room temperature for 24 h, the precipitate was collected by filtration and dried under reduced pressure to provide **2**.

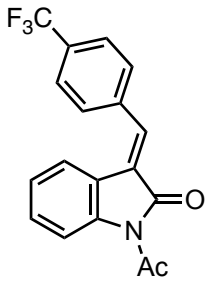
(*E*)-1-Acetyl-3-benzylideneindolin-2-one (2a)[2,3,4]



The title compound was prepared according to Procedure A. Yellow crystals: *E*:*Z* = >20:1; IR 3030, 3009, 1735, 1710, 1634, 1601 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.74 (s, 3H), 7.01 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.30 (dt, 1H, *J* = 1.2, 8.4 Hz), 7.44-7.48 (m, 3H), 7.62 (d, 2H, *J* = 7.8 Hz), 7.68 (d, 1H, *J* = 7.8 Hz), 7.86 (s, 1H), 8.30 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz,

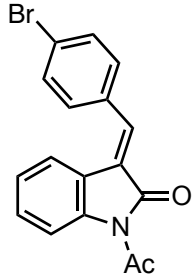
$CDCl_3$): δ 26.9, 116.7, 121.8, 122.1, 124.4, 126.0, 128.7 (2C), 129.1 (2C), 130.0, 130.2, 134.4, 138.6, 140.2, 168.5, 170.8; HRMS (DART) calcd for $C_{17}H_{14}NO_2$ [*M*+H]$^+$: 264.1019, found 264.1014.

(*E*)-1-Acetyl-3-(4-(trifluoromethyl)benzylidene)indolin-2-one (2b)[2]



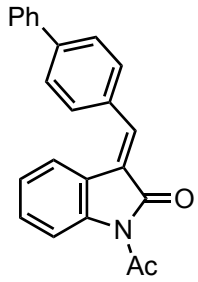
The title compound was prepared according to Procedure B. Yellow solids: *E*:*Z* = >20:1; IR 3029, 1740, 1713, 1637, 1602 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.78 (s, 3H), 7.06 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.37 (dt, 1H, *J* =1.2, 7.8 Hz), 7.56 (d, 1H, *J* = 7.8 Hz), 7.76 (m, 4H), 7.86 (s, 1H), 8.35 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.7, 116.7, 121.0, 122.0, 123.5 (*J* = 272 Hz), 124.4, 125.6 (2C, *J* = 3 Hz), 127.6, 129.1 (2C), 130.7, 131.3 (*J* = 32 Hz), 135.8, 137.9, 140.4, 167.9, 170.5; HRMS (DART) calcd for $C_{18}H_{13}F_3NO_2$ [*M*+H]$^+$: 332.0893, found 332.0884.

(*E*)-1-Acetyl-3-(4-bromobenzylidene)indolin-2-one (2c)[2]



The title compound was prepared according to Procedure A' and then recrystallization from MeOH. Yellow solids: *E*:*Z* = >20:1; IR 2996, 2951, 1738, 1711, 1634, 1602 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.76 (s, 3H), 7.05 (t, 1H, *J* =7.8 Hz), 7.34 (t, 1H, *J* =7.8 Hz), 7.51 (d, 2H, *J* =8.4 Hz), 7.61-7.64 (m, 3H), 7.77 (s, 1H) , 8.32 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.7, 116.6, 121.3, 121.9, 124.0, 124.3, 126.3, 130.3, 130.5 (2C), 131.9 (2C), 133.0, 136.7, 140.2, 168.1, 170.6; HRMS (DART) calcd for $C_{17}H_{13}BrNO_2$ [*M*+H]$^+$: 342.0124 found 342.0117.

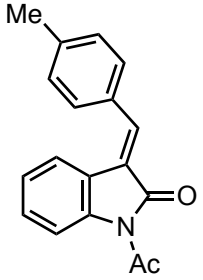
(*E*)-1-Acetyl-3-(biphenyl-4-ylmethylene)indolin-2-one (2d)[2]



The title compound was prepared according to Procedure B. Yellow solids: *E*:*Z* = 8:1; IR 2993, 2954, 1734, 1716, 1699, 1684, 1653, 1635 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.78 (s, 3H), 7.07 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.35 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.41 (tt, 1H, *J* = 1.2, 7.2 Hz), 7.49 (t, 2H, *J* = 7.8 Hz), 7.68 (d, 2H, *J* = 7.2 Hz), 7.73 (d, 2H, *J* = 8.4 Hz), 7.76 (d, 2H, *J* = 8.4 Hz), 7.83 (d, 1H, *J* = 7.2 Hz), 7.92 (s, 1H), 8.34 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 27.0, 116.8, 122.0, 122.2, 124.5, 125.9, 127.1, 127.4, 128.1, 129.0, 130.0, 130.3, 133.3, 138.4, 140.0, 140.3, 143.0, 168.7, 170.9; HRMS (DART) calcd

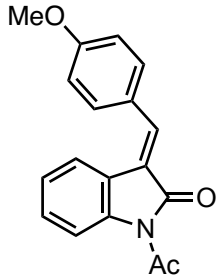
for $C_{23}H_{18}NO_2$ [*M*+H]$^+$: 340.1332, found 340.1327.

(*E*)-1-Acetyl-3-(4-methylbenzylidene)indolin-2-one (2e)[2]



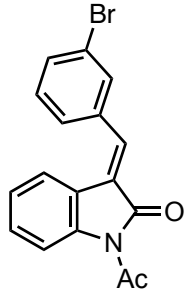
The title compound was prepared according to Procedure A'. Yellow solids: *E*:*Z* = 19:1; IR 3031, 2925, 1736, 1708, 1629, 1601 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.42 (s, 3H), 2.74 (s, 3H), 7.02 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.27 (d, 2H, *J* = 7.8 Hz), 7.29 (t, 1H, *J* = 7.8 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 7.75 (d, 1H, *J* = 7.8 Hz), 7.83 (s, 1H), 8.30 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.5, 26.8, 116.6, 121.9, 122.0, 124.3, 125.1, 129.3 (2C), 129.4 (2C), 129.9, 131.4, 139.0, 140.0, 140.6, 168.7, 170.8; HRMS (DART) calcd for $C_{18}H_{16}NO_2$ [*M*+H]$^+$: 278.1176, found 278.1171.

(*E*)-1-Acetyl-3-(4-methoxybenzylidene)indolin-2-one (2f)



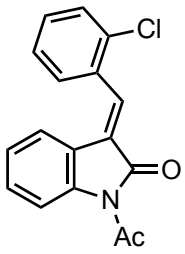
The title compound was prepared according to Procedure A' and then recrystallization from MeOH. Yellow solids: *E*:*Z* = 8:1; IR 3030, 2937, 1735, 1708, 1627, 1599 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.76 (s, 3H), 3.89 (s, 3H), 7.00 (d, 2H, *J* = 7.2 Hz), 7.06 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.31 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.65 (d, 2H, *J* = 7.8 Hz), 7.83 (s, 1H), 7.84 (d, 1H, *J* = 7.8 Hz), 8.32 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.9, 55.5, 114.2 (2C), 116.7, 121.7, 122.2, 124.0, 124.4, 126.7, 129.8, 131.5 (2C), 139.0, 139.9, 161.3, 168.9, 171.0; HRMS (DART) calcd for $C_{18}H_{16}NO_3$ [*M*+H]$^+$: 294.1125, found 294.1119.

(*E*) -1-Acetyl-3-(3-bromobenzylidene)indolin-2-one (2g)[2]



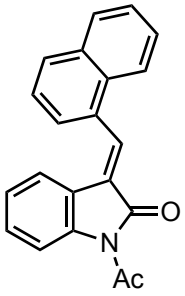
The title compound was prepared according to Procedure B. Yellow solids: *E*:*Z* = 13:1; IR 2993, 2927, 1734, 1716, 1683, 1652, 1636 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.77 (s, 3H), 7.06 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.34-7.38 (m, 2H), 7.56-7.61 (m, 3H), 7.77 (s, 1H), 7.78 (s, 1H), 8.33 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.9, 116.9, 121.4, 122.3, 122.9, 124.7, 127.2, 127.5, 130.4, 130.7, 131.8, 132.8, 136.4, 136.5, 140.5, 168.3, 170.8; HRMS (DART) calcd for $C_{17}H_{13}BrNO_2$ [*M*+H]$^+$: 342.0124, found 342.0118.

(*E*)-1-Acetyl-3-(2-chlorobenzylidene)indolin-2-one (2h)[5]



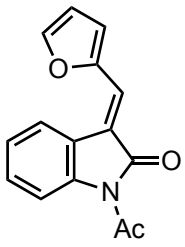
The title compound was prepared according to Procedure A'. Yellow solids: *E*:*Z* = >20:1; IR 3034, 2994, 1739, 1710, 1637, 1603 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 2.78 (s, 3H), 7.01 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.32-7.43 (m, 4H), 7.53 (dd, 1H, *J* = 1.2, 8.4 Hz), 7.68 (dd, 1H, *J* = 1.2, 7.8 Hz), 7.92 (s, 1H), 8.32 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.8, 116.8, 121.4, 122.4, 124.5, 126.7, 127.5, 129.8, 130.1, 130.6, 131.0, 133.1, 134.4, 134.9, 140.5, 168.0, 170.8; HRMS (DART) calcd for $C_{17}H_{13}ClNO_2$ $[M+H]^+$: 298.0629, found 298.0624.

(*E*)-1-Acetyl-3-(naphthalen-1-ylmethylene)indolin-2-one (2i)[2]



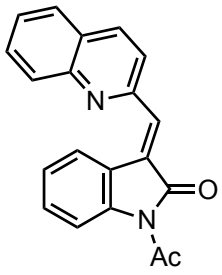
The title compound was prepared according to Procedure A'. Yellow solids: *E*:*Z* = 10:1; IR 3030, 3010, 2928, 1736, 1709, 1634, 1602 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 2.81 (s, 3H), 6.89 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.23 (d, 1H, *J* = 7.8 Hz), 7.27 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.52-7.58 (m, 3H), 7.80 (d, 1H, *J* = 7.2 Hz), 7.93-7.98 (m, 3H), 8.31 (d, 1H, *J* = 7.8 Hz) , 8.38 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.7, 116.4, 121.6, 122.3, 124.2, 124.4, 124.9, 126.3, 126.5, 126.8, 127.5, 128.5, 130.0, 130.2, 130.9, 131.5, 133.4, 136.5, 140.1, 168.1, 170.7; HRMS (DART) calcd for $C_{21}H_{16}NO_2$ $[M+H]^+$: 314.1176, found 314.1171.

(*E*)-1-Acetyl-3-(furan-2-ylmethylene)indolin-2-one (2j)[2,3]



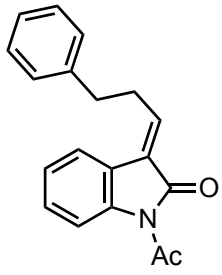
The title compound was prepared according to Procedure A. Yellow crystals: *E*:*Z* = >20:1; IR 2993, 2952, 1732, 1625, 1600 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 2.76 (s, 3H), 6.67 (dd, 1H, *J* = 1.8, 3.6 Hz), 7.00 (d, 1H, *J* = 3.6 Hz), 7.26 (m, 1H), 7.38 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.50 (s, 1H), 7.82 (d, 1H, *J* = 1.2 Hz), 8.35 (d, 1H, *J* = 7.8 Hz), 8.60 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 27.0, 113.5, 116.3, 120.9, 121.3, 121.4, 122.3, 124.3, 124.8, 129.8, 139.8, 146.5, 151.1, 169.5, 171.0; HRMS (DART) calcd for $C_{15}H_{12}NO_3$ $[M+H]^+$: 254.0812, found 254.0809.

(*E*)-1-Acetyl-3-(quinolin-2-ylmethylene)indolin-2-one (2k)[2]



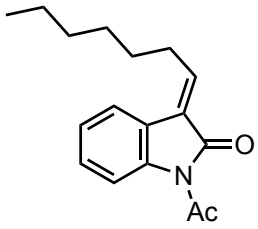
The title compound was prepared according to Procedure A'. Yellow solids: *E*:*Z* = >20:1; IR 2928, 1736, 1715, 1653, 1635, 1601 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 2.76 (s, 3H), 7.24 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.41 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.61 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.65 (d, 1H, *J* = 8.4 Hz), 7.79 (dt, 1H, *J* = 1.2, 8.4 Hz), 7.84 (dd, 1H, *J* = 1.2, 8.4 Hz), 7.85 (s, 1H), 8.21 (dd, 2H, *J* = 1.2, 7.8 Hz), 8.33 (d, 1H, *J* = 8.4 Hz), 9.38 (dd, 1H, *J* = 0.6, 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 27.0, 116.2, 122.3, 124.7, 124.8, 127.4, 127.6, 127.7, 127.9, 128.9, 129.6, 130.3, 131.3, 135.8, 136.6, 141.1, 148.1, 153.2, 169.3, 170.8; HRMS (DART) calcd for $C_{20}H_{15}N_2O_2$ $[M+H]^+$: 315.1128, found 315.1124.

(*E*)-1-Acetyl-3-(3-phenylpropylidene)indolin-2-one (2l)



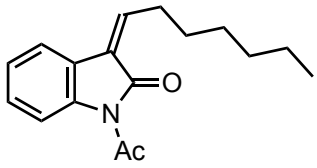
The title compound was prepared according to Procedure B. Yellow crystals: *E*:*Z* = >20:1; IR 2992, 2931, 1742, 1715, 1652, 1604 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 2.72 (s, 3H), 2.97-3.05 (m, 4H), 7.14 (t, 1H, *J* = 7.2 Hz), 7.20 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.23-7.27 (m, 3H), 7.32-7.36 (m, 3H), 7.60 (d, 1H, *J* = 7.2 Hz), 8.32 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.8, 31.2, 34.5, 116.7, 122.8, 123.0, 124.8, 126.5, 127.0, 128.3 (2C), 128.7 (2C), 129.4, 139.7, 140.3, 142.5, 167.8, 171.0; HRMS (DART) calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332, found 292.1328.

(*E*)-1-Acetyl-3-heptylideneindolin-2-one (2m)



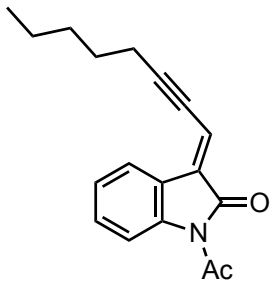
The title compound was prepared according to Procedure A. Yellow crystals: *E*:*Z* = >20:1; IR 2930, 1740, 1705, 1652 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 0.91 (m, 3H), 1.32-1.35 (m, 4H), 1.42-1.47 (m, 2H), 1.66 (quin, 2H, *J* = 7.8 Hz), 2.71 (q, 2H, *J* = 7.8 Hz), 2.72 (s, 3H), 7.12 (t, 1H, *J* = 7.8 Hz), 7.22 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.34 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.62 (d, 1H, *J* = 7.8 Hz), 8.33 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.1, 22.6, 26.9, 28.5, 29.2, 29.5, 31.6, 116.7, 123.0 (2C), 124.8, 126.5, 129.2, 139.6, 144.5, 167.9, 171.0; HRMS (DART) calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1645, found 272.1642.

(*Z*)-1-Acetyl-3-heptylideneindolin-2-one ((*Z*)-2m)



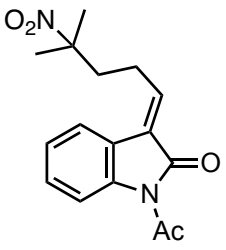
The title compound was prepared according to Procedure A. Yellow crystals: *Z*:*E* = >20:1; IR 3030, 2929, 1734, 1704, 1647, 1606 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 0.90 (m, 3H), 1.31-1.34 (m, 4H), 1.39-1.43 (m, 2H), 1.58 (quin, 2H, *J* = 7.8 Hz), 2.71 (s, 3H), 2.98 (q, 2H, *J* = 7.8 Hz), 6.96 (t, 1H, *J* = 7.8 Hz), 7.17 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.29 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.44 (dd, 1H, *J* = 0.6, 7.8 Hz), 8.23 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.1, 22.6, 26.8, 28.2, 29.0, 29.1, 31.6, 116.6, 118.4, 123.6, 124.6, 125.8, 129.0, 138.2, 145.2, 167.4, 171.1; HRMS (DART) calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1645, found 272.1643.

(*E*)-1-Acetyl-3-(oct-2-yn-1-ylidene)indolin-2-one (2n)[2]



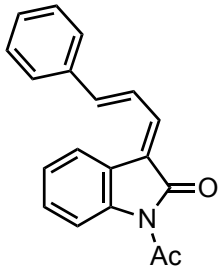
The title compound was prepared according to Procedure A. Orange crystals: *E*:*Z* = >20:1; IR 3032, 2933, 2203, 1740, 1714, 1619, 1603 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 0.92 (t, 3H, *J* = 7.2 Hz), 1.39 (sext, 2H, *J* = 7.8 Hz), 1.43-1.48 (m, 2H), 1.68 (quin, 2H, *J* = 7.2 Hz), 2.59 (dt, 2H, *J* = 2.4, 7.2 Hz), 2.69 (s, 3H), 6.81 (t, 1H, *J* = 2.4 Hz), 7.19 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.35 (dt, 1H, *J* = 1.2, 7.8 Hz), 8.16 (dd, 1H, *J* = 1.2, 7.8 Hz), 8.25 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.9, 20.5, 22.2, 26.7, 28.0, 31.2, 79.2, 111.2, 116.45, 116.47, 122.6, 122.7, 124.8, 130.5, 132.5, 139.7, 167.8, 170.7; HRMS (DART) calcd for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1489, found 282.1487.

(*E*)-1-Acetyl-3-(4-methyl-4-nitropentylidene)indolin-2-one (2o)



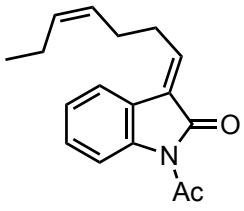
The title compound was prepared according to Procedure B. Brown crystals: *E*:*Z* = >20:1; IR 3028, 2992, 1743, 1715, 1654, 1603, 1541 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.69 (s, 6H), 2.23-2.26 (m, 2H), 2.66-2.71 (m, 2H), 2.71 (s, 3H), 6.97 (t, 1H, *J* = 7.8 Hz), 7.23 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.36 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.53 (d, 1H, *J* = 7.8 Hz), 8.32 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 24.2, 26.0 (2C), 26.8, 39.1, 87.5, 116.8, 122.3, 123.0, 125.1, 127.5, 129.8, 139.9, 140.1, 167.6, 170.9; HRMS (DART) calcd for $C_{16}H_{19}N_2O_4$ $[M+H]^+$: 303.1339, found 303.1334.

(*E*)-1-Acetyl-3-((*E*)-3-phenylallylidene)indolin-2-one (2p)[5]



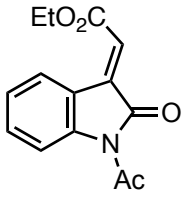
To a suspension of oxindole (1.00 g, 7.50 mmol) in dry THF (7.51 mL) were added *trans*-cinnamaldehyde (1.13 mL, 9.00 mmol), pyridine (0.24 mL, 3.0 mmol) and Ti(O*i*Pr)$_4$ (1.79 mL, 6.00 mmol) in dry THF (4.5 mL) . After being stirred for 18 h at room temperature, the mixture was quenched with water and filtered. The residue was recrystallized from acetone and dichloromethane to provide 1.00 g (54%) of **S1p** (R = cinnamyl, Scheme S1) as orange crystals. To a suspension of **S1p** (541 mg, 2.19 mmol) in dry THF (1.9 mL) were added Na_2CO_3 (1.13 g, 10.7 mmol) and acetic anhydride (1.00 mL, 10.6 mmol). The mixture was stirred for 46 h at room temperature, diluted with water and extracted with EtOAc. The combined extracts were washed with water and brine. The organic layer was dried and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc, 6:1) and then recrystallized from methanol to provide 42.7 mg (7%) of **3e** as yellow crystals: *E*:*Z* = >20:1; IR 3020, 1732, 1708, 1614, 1589 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.74 (s, 3H), 7.20 (d, 1H, *J* = 15.6 Hz), 7.25 (dt,1H, *J* = 1.2, 7.8 Hz), 7.34 (dt,1H, *J* = 1.2, 7.8 Hz), 7.39 (t, 1H, *J* = 7.8 Hz), 7.42 (t, 2H, *J* = 7.2 Hz), 7.51 (d, 1H, *J* = 12.0 Hz), 7.59 (d, 2H, *J* = 7.2 Hz), 7.65 (dd, 1H, *J* = 12.0, 15.6 Hz), 7.78 (d, 1H, *J* = 7.2 Hz), 8.33 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.8, 116.8, 122.8, 123.0, 123.2, 123.7, 124.8, 127.8, 129.0, 129.3, 130.1, 135.8, 137.1, 139.6, 145.9, 168.6, 170.9; HRMS (DART) calcd for $C_{19}H_{16}NO_2$ [*M*+H]$^+$: 290.1176, found 290.1172.

(*E*)-1-Acetyl-3-((*Z*)-hept-4-en-1-ylidene)indolin-2-one (2q)



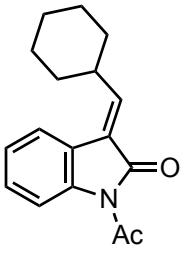
The title compound was prepared according to Procedure A. Orange crystals: *E*:*Z* = >20:1; IR 2932, 1743, 1716, 1653, 1605 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.00 (t, 3H, *J* = 7.8 Hz), 2.08 (quin, 2H, *J* = 7.8 Hz), 2.40 (q, 2H, *J* = 7.2 Hz), 2.71 (s, 3H), 2.75 (q, 2H, *J* = 7.8 Hz), 5.37-5.41 (m, 1H), 5.47-5.51 (m, 1H), 7.08 (t, 1H, *J* = 7.8 Hz), 7.20 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.33 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.60 (d, 1H, *J* = 7.8 Hz), 8.31 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.3, 20.7, 26.0, 26.8, 29.6, 116.7, 122.9, 123.0, 124.8, 126.8, 129.3, 133.7, 139.7, 143.4, 167.8, 171.0; HRMS (DART) calcd for $C_{17}H_{20}NO_2$ [*M*+H]$^+$: 270.1489, found 270.1485.

Ethyl (*E*)-2-(1-acetyl-2-oxoindolin-3-ylidene)acetate (2r)[6]



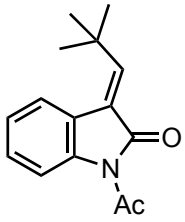
A solution of isatin (500 mg, 3.40 mmol) in acetic anhydride (34 mL) were stirred for 1.5 h at 130 °C. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine, dried and concentrated under reduce pressure. The residue was recrystallized from pentane to give *N*-acetylisatin (612 mg 95 %) as yellow solids. To a stirred solution of *N*-acetylisatin (76.0 mg, 0.402 mmol) in $CHCl_3$ (1.0 mL) were added (carbethoxymethylene)triphenylphosphorane (70.0 mg, 0.201 mmol). After being stirred for 19 h at 60 °C, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Hexane = 1:20) to provide 33.2 mg (64%) of **2r** as pale yellow solids: *E*:*Z* = >20:1; IR 3025, 2988, 1748, 1716, 1645, 1601 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.39 (t, 3H, *J* = 7.2 Hz), 2.72 (s, 3H), 4.35 (q, 2H, *J* = 7.2 Hz), 6.92 (s, 1H), 7.24 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.45 (dt, 1H, *J* = 1.2, 7.8 Hz), 8.29 (d, 1H, *J* = 8.4 Hz), 8.69 (dd, 1H, *J* = 1.2, 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.2, 26.9, 61.5, 116.4, 120.4, 123.5, 125.4, 128.2, 132.9, 136.3, 142.1, 165.2, 168.0, 170.3; HRMS (DART) calcd for $C_{14}H_{14}NO_4$ $[M+H]^+$: 260.0917, found 260.0914.

(*E*)-1-Acetyl-3-(cyclohexylmethylene)indolin-2-one (2s)



The title compound was prepared according to Procedure A. Orange crystals: *E*:*Z* = >20:1; IR 3028, 2932, 1738, 1707, 1650, 1603 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.31-1.45 (m, 5H), 1.76 (m, 1H), 1.83-1.89 (m, 4H), 2.71 (s, 3H), 2.96 (m, 1H), 6.97 (d, 1H, *J* = 10.2 Hz), 7.21 (dt, 1H, *J* = 0.6, 7.8 Hz), 7.33 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.58 (d, 1H, *J* = 7.8 Hz), 8.32 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 25.5 (2C), 25.7, 26.9, 31.5 (2C), 38.2, 116.7, 122.6, 122.9, 124.8, 124.9, 129.2, 139.6, 148.9, 168.3, 171.0; HRMS (DART) calcd for $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1489, found 270.1487.

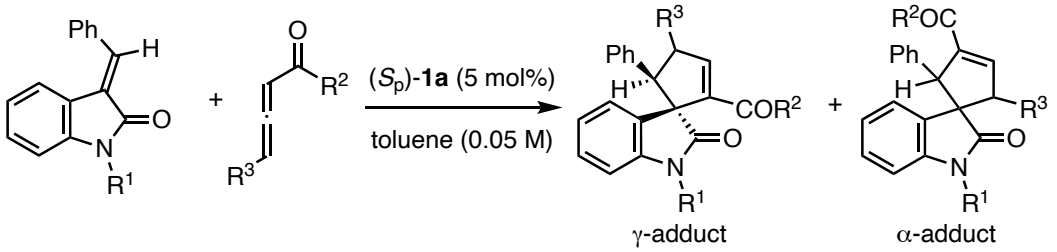
(*E*)-1-Acetyl-3-(2,2-dimethylpropylidene)indolin-2-one (2t)[7]



The title compound was prepared according to Procedure A. Orange crystals: *E*:*Z* = >20:1; IR 3031, 2965, 1737, 1707, 1630, 1602 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.41 (s, 9H), 2.72 (s, 3H), 7.23 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.26 (s, 1H), 7.34 (dt, 1H, *J* = 1.2, 7.8 Hz), 7.78 (d, 1H, *J* = 7.8 Hz), 8.36 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 27.0, 29.1 (3C), 32.9, 116.6, 121.3, 124.5, 125.6, 126.0, 129.2, 140.3, 154.8, 169.1, 171.0; HRMS (DART)

calcd for $C_{15}H_{18}NO_2$ $[M+H]^+$: 244.1332, found 244.1329.

Table S1. Protecting Group Manipulations of the Benzylideneindolinone and Allenoate.



Entry	R^1	R^2	R^3	Temp.	Time	Yield (%)[a]	γ : α[b]	ee of γ (%)[c]
1	Ac	OEt	H	rt	45 min	97	10:1	65
2	Boc	OEt	H	rt	50 min	99	3.3:1	31
3	Ts	OEt	H	rt	30 min	99	2:1	69
4	Bn	OEt	H	rt	50 min	99	5.7:1	15
5	Me	OEt	H	rt	30 min	95	3.5:1	35
6	H	OEt	H	rt	1 h	trace	–	–
7	Ac	O-*t*-Bu	H	rt to 60 °C	7 h	98	1.8:1	45
8	Ac	OPh	H	rt	24 h	72	4.9:1	3
9[d]	Ac	OEt	Ph	rt	40 min	33	1:>20	7[e]

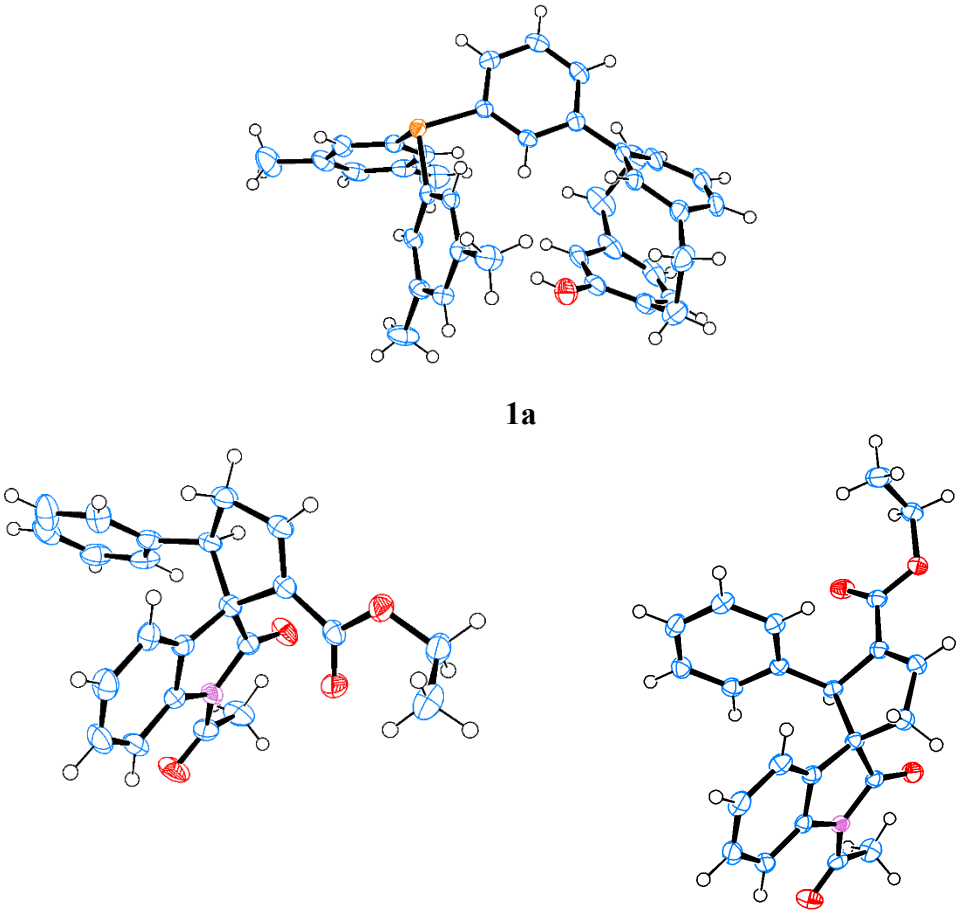
[a] Yield of a γ/α mixture. [b] Determined by ^{1}H NMR of the crude product. [c] Determined by HPLC. [d] Reaction was performed in CH_2Cl_2 (1 M). [e] Ee of α-adduct.

Computational Methods

Geometry optimizations for the energy minima and TSs were performed without any constrains via DFT methods using B3LYP exchange-correlation functional with 6-31G(d) basis sets. Vibrational frequency calculations were conducted to confirm them as energy minima (without imaginary frequencies) and TSs (with a single imaginary frequency) and to obtain Gibbs energies at 1.00 atm and 298.15 K. Intrinsic reaction coordinate (IRC) calculations and following full geometry optimizations for all TSs were performed to identify two energy minima directly connected to each TS. To obtain the reliable energies, single-point energy calculations were performed using M06-2X exchange-correlation functional with 6-311+G(d) basis sets. For the single-point energy calculations, the SMD solvent model were employed to account for the toluene environment. Relative energies of all optimized geometries of energy minima and TSs were thermodynamically corrected using Gibbs energies at 1.0 atm and 298.15 K (including zero-point energies). All calculations were performed using Gaussian16 software.[8]

X-ray data of 1a, γ-*trans*-4a and α-*trans*-4a

X-ray diffraction data of the crystals reported in this paper were collected on a Rigaku R-AXIS RAPID diffractometer employing graphite-monochromated CuKα radiation. The structures were solved by direct method with SIR-92 program[9] and refined with SHELXL program.[10] The structural models were drawn with ORTEP-3 program.[11] Further information on the crystal structure determinations have been deposited with the Cambridge Crystallographic Data Center (**1a**: CCDC 2343914, γ-*trans*-**4a**: CCDC 2343919 and **α**-*trans*-**4a** : CCDC 2343921). Figure S1 shows the ORTEP drawing of compounds **1a**, γ-*trans*-**4a** and α-*trans*-**4a**. The details of their refinements are given Tables S2.



1a

γ-*trans*-**4a** (major product)

α-*trans*-**4a** (minor product)

Figure S1 X-ray structure of compounds **1a**, γ-*trans*-**4a** and α-*trans*-**4a** (thermal ellipsoid plot at the 50% probability level)

Table S2 Crystallographic data and structural refinements for compounds **1a**, γ-*trans*-**4a** and α-*trans*-**4a**

Compound	**1a**	γ-*trans*-**4a**	α-*trans*-**4a**
CCDC	2343914	2343919	2343921
Empirical formula	$C_{38}H_{37}OP$	$C_{23}H_{21}NO_4$	$C_{23}H_{21}NO_{4v}$
Formula weight	540.65	375.41	375.41
Temperature (K)	296	123	123
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1$	*P*-1	*P*-1
a (Å)	9.79364 (19)	13.0103(8)	9.2471 (2)
b (Å)	10.5919 (2)	17.3840(11)	10.8522 (3)
c (Å)	14.5081 (3)	17.8554(11)	11.3167 (3)
α(°)	90	88.347 (6)	64.284 (5)
β(°)	95.211 (7)	69.418 (5)	80.943 (6)
γ(°)	90	88.399 (6)	65.621 (5)
Volume (Å^3)	1498.75 (5)	3778.4 (4)	931.61 (7)
Z	2	8	2
$D_{calcd.}$ (g/cm^3)	1.198	1.320	1.338
R_1	0.0460	0.1191	0.0514
wR_2	0.1160	0.3774	0.1382
Goodness-of-fit	1.104	1.075	1.041

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