Supporting Information

Tandem Vinylogous Aldol and Intramolecular [2+2] Cycloaddition toward Benzocyclobutenes by UV-Light Photocatalysis

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1. General information

**General.** $^1$H, $^{13}$C and 2D NMR (H-H COSY and C-H HSQC) spectra were recorded on a Bruker spectrometer (400 MHz). $^1$H and $^{13}$C NMR chemical shifts were determined relative to internal standard TMS at 0.0, DMSO-$d_6$ ($\delta$ ($^1$H), 2.50 ppm; $\delta$ ($^{13}$C), 39.52 ppm) and CDCl$_3$ ($\delta$ ($^1$H), 7.26 ppm; $\delta$ ($^{13}$C), 77.16 ppm). Chemical shifts ($\delta$) are reported in ppm, and coupling constants ($J$) are reported in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m =multiplet, dd = doublet of doublet, td = triplet of doublet. High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Q-Exactive (ESI-Orbitrap). X-ray single crystal diffraction data were collected on a Bruker SMART. The melting point was recorded on Hanon (MP-430) and uncorrected. The photocatalytic reactions were performed on a YunShuo UV-LED Light Reactor (YS-UV-18C, 365 nm, 240 W) and the distance from the light source to the irradiation vessel (quartz glass) is approximately 3-5 cm. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 200-300 mesh silica gel.

**Materials.** All the chemical reagents were purchased from commercial sources and used without further purification. Starting materials 1 and 2 are known compounds and were bought from Energy Chemical, Bidepharm, J&K Scientific, or Innochem (commercial sources).

**The Light Source.** Manufacturer: YunShuo light industry; Type: YS-UV-18C; Wavelength: 365 nm; Power: 240 W; Filter: No filters needed.
2. General procedure for preparing BCBs (3)

In a 20 mL tube, 2-methylbenzophenone 1 (1.0 mmol, 1 eq) and isatin 2 (1.0 mmol, 1 eq) were dissolved in methanol (15 mL). The reaction mixture was under irradiation of UV LEDs (365 nm) for 18 h. After completion (by TLC), the reaction mixture was evaporated to dryness in a vacuo. The residue was purified by medium-pressure chromatography (silica gel) using a mixed solvent of hexane and ethyl acetate (15-30% EA).

(R)-3-Hydroxy-3-((7R,8S)-8-hydroxy-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)indolin-2-one (3aa): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3aa was obtained as a colorless solid (298.4 mg, yield 87%) via flash chromatography on a silica gel (hexane/ethyl acetate = 3:1, v/v). m.p. 154-156 ºC; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 9.64 (s, 1H, N-H), 7.60 (d, 1H, J=7.2 Hz, Ar-H), 7.45 (t, 1H, J=7.2 Hz, Ar-H), 7.38 (t, 1H, J=7.2 Hz, Ar-H), 7.15 (d, 1H, J=7.2 Hz, Ar-H), 6.89-6.92 (m, 1H, Ar-H), 6.76-6.79 (m, 3H, Ar-H), 6.74 (s, 1H, O-H), 6.45 (t, 1H, J=7.2 Hz, Ar-H), 6.24 (d, 1H, J=7.2 Hz, Ar-H), 6.20 (s, 1H, O-H), 6.00 (d, 1H, J=6.8 Hz, Ar-H), 4.31 (s, 1H, CH); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 178.0, 149.7, 144.4, 142.0, 139.6, 129.8, 129.4, 128.6, 128.4, 127.4, 126.6, 125.5, 124.7, 122.5, 109.65, 82.7, 74.7, 65.2; HRMS (ESI), m/z calcd 344.1281 for C22H18NO3 [M+H]+, found 344.1285.

(R)-3-Hydroxy-3-((7R,8S)-8-hydroxy-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)-1-methylindolin-2-one (3ab): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3ab was obtained as a colorless solid (292.7 mg, yield 82%) via flash chromatography on a silica gel (hexane/ethyl acetate = 4:1, v/v). m.p. 154-156 ºC; 1H NMR (400 MHz, CDCl3); δ (ppm) 7.77 (d, 1H, J=7.2 Hz, Ar-H), 7.43 (t, 1H, J=7.2 Hz, Ar-H), 7.23 (d, 1H, J=7.2 Hz, Ar-H), 6.90-7.06 (m, 3H, Ar-H), 6.78 (brs, 2H, O-H), 6.64 (t, 1H, J=7.6 Hz, Ar-H),
6.53 (d, 1H, J=7.6 Hz, Ar-H), 6.04 (d, 1H, J=7.6 Hz, Ar-H), 4.62 (s, 1H, CH), 2.75 (s, 3H, CH₃);

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 176.3, 147.9, 143.0, 143.0, 137.8, 129.9, 129.2, 128.8, 127.0, 126.9, 126.7, 125.5, 124.9, 122.3, 122.3, 108.2, 83.4, 75.2, 65.3, 25.8; HRMS (ESI), m/z calcld 358.1438 for C₂₃H₂₀NO₃ [M+H]+, found 358.1441.

(R)-3-Hydroxy-3-((7R,8S)-8-hydroxy-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)-1-phenylindolin-2-one (3ac): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3ac was obtained as a colorless solid (368.7 mg, yield 88%) via flash chromatography on a silica gel (hexane/ethyl acetate = 3:1, v/v). m.p. 154-156 °C; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 9.64 (s, 1H, NH), 7.67 (d, 1H, J=6.8 Hz, Ar-H), 7.38-7.55 (m, 5H, Ar-H), 7.24 (d, 1H, J=7.2 Hz, Ar-H), 7.18 (d, 1H, J=7.2 Hz, Ar-H), 6.89-6.92 (m, 6H, Ar-H), 6.76-6.89 (m, 6H, Ar-H), 6.64 (t, 1H, J=7.2 Hz, Ar-H), 6.43 (d, 1H, J=6.8 Hz, Ar-H), 6.33 (s, 1H, OH), 6.28 (s, 1H, OH), 6.13 (d, 1H, J=7.6 Hz, Ar-H), 4.49 (s, 1H, CH); ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 175.8, 149.8, 144.2, 142.8, 140.1, 134.6, 130.6, 130.4, 129.6, 129.3, 128.9, 127.7, 127.3, 126.9, 126.5, 125.6, 125.2, 122.5, 122.1, 109.1, 82.7, 74.4, 65.2; HRMS (ESI), m/z calcld 420.1594 for C₂₈H₂₂NO₃ [M+H]+, found 420.1599.

(R)-6-Fluoro-3-hydroxy-3-((7R,8S)-8-hydroxy-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)-1-phenylindolin-2-one (3ad): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3ad was obtained as a colorless solid (292.4 mg, yield 81%) via flash chromatography on a silica gel (hexane/ethyl acetate = 4:1, v/v). m.p. 154-156 °C; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 9.84 (s, 1H, NH), 7.60 (d, 1H, J=6.8 Hz, Ar-H), 7.46 (t, 1H, J=7.2 Hz, Ar-H), 7.39 (t, 1H, J=7.2 Hz, Ar-H), 7.18 (d, 2H, J=7.2 Hz, Ar-H), 6.99 (t, 1H, J=7.2 Hz, Ar-H), 6.85 (t, 2H, J=7.2 Hz, Ar-H), 6.76 (brs, 1H, OH), 6.17-6.29 (m, 3H, Ar-H), 6.11 (s, 1H, OH),
5.78 (dd, 1H, J=9.2 Hz, 2.0 Hz, Ar-H), 4.31 (s, 1H, CH); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 178.3, 164.1, 161.7, 149.5, 143.7, 143.6, 139.6, 129.5, 128.5, 127.4, 126.7, 126.6, 125.9, 125.8, 125.5, 122.6, 106.8, 98.0, 97.7, 82.7, 74.3, 65.1; HRMS (ESI), m/z calcd 362.1187 for C22H17FNO3 [M+H]+, found 362.1191.

(R)-3-Hydroxy-3-((7R,8S)-8-hydroxy-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)-7-(trifluoromethyl)indolin-2-one (3ae): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3ae was obtained as a colorless solid (345.2 mg, yield 84%) via flash chromatography on a silica gel (hexane/ethyl acetate = 3:1, v/v). m.p. 154-156 ºC; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.12 (s, 1H, NH), 7.62 (d, 1H, J=7.2 Hz, Ar-H), 7.48 (t, 1H, J=7.2 Hz, Ar-H), 7.41 (t, 1H, J=7.6 Hz, Ar-H), 7.19 (d, 1H, J=8.0 Hz, Ar-H), 7.04 (d, 1H, J=8.0 Hz, Ar-H), 6.78-6.86 (m, 4H, Ar-H), 6.76 (brs, 1H, OH), 6.66 (t, 1H, J=7.6 Hz, Ar-H), 6.48 (d, 1H, J=7.2 Hz, Ar-H), 6.28 (d, 2H, J=6.4 Hz, Ar-H), 4.38 (s, 1H, CH); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 178.5, 149.5, 143.7, 139.5, 131.9, 129.6, 128.6, 128.3, 127.3, 127.0, 126.6, 125.6, 122.7, 121.0, 82.7, 73.3, 65.1; HRMS (ESI), m/z calcd 412.1155 for C23H17F3NO3 [M+H]+, found 412.1120.

(R)-4-Bromo-3-hydroxy-3-((7R,8S)-8-hydroxy-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)-5-methylindolin-2-one (3af): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3af was obtained as a colorless solid (327.0 mg, yield 75%) via flash chromatography on a silica gel (hexane/ethyl acetate = 4:1, v/v). m.p. 154-156 ºC; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.86 (s, 1H, NH), 7.44-7.46 (m, 2H, Ar-H), 7.25-7.35 (m, 7H, Ar-H), 7.14 (td, 1H, J=7.2 Hz, 1.6 Hz, Ar-H), 6.81 (d, 1H, J=8.0 Hz, Ar-H), 6.45 (s, 1H, OH), 6.14 (d, 1H, J=7.2 Hz, Ar-H), 4.87 (s, 1H, CH), 2.33 (s, 3H, CH3); 13C NMR (100 MHz,
DMSO-$_d_6$): $\delta$ (ppm) 180.4, 150.9, 145.4, 140.9, 139.8, 132.4, 132.2, 129.8, 129.6, 129.5, 128.3, 127.4, 126.6, 122.7, 122.3, 121.5, 109.9, 84.7, 81.6, 65.5, 22.4; HRMS (ESI), m/z calcd 436.0543 for C$_{23}$H$_{19}$BrNO$_3$ [M+H]$^+$, found 436.0545.

Methyl (R)-3-hydroxy-3-((7R,8S)-8-hydroxy-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-yl)-2-oxoindoline-7-carboxylate (3ai): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3ai was obtained as a colorless solid (316.8 mg, yield 79%) via flash chromatography on a silica gel (hexane/ethyl acetate = 3:1, v/v). m.p. 149-151 ºC; $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ (ppm) 9.42 (s, 1H, NH), 7.64 (d, 1H, $J$=7.2 Hz, Ar-H), 7.48 (t, 1H, $J$=7.6 Hz, Ar-H), 7.40 (t, 1H, $J$=7.6 Hz, Ar-H), 7.33 (dd, 1H, $J$=8.0 Hz, 1.2 Hz, Ar-H), 7.18 (d, 1H, $J$=7.2 Hz, Ar-H), 6.77 (s, 1H, OH), 6.64-6.75 (m, 3H, Ar-H), 6.62 (t, 1H, $J$=8.0 Hz, Ar-H), 6.52 (d, 1H, $J$=7.2 Hz, Ar-H), 6.30 (d, 2H, $J$=7.2 Hz, Ar-H), 4.36 (s, 1H, CH$_3$), 3.79 (s, 3H, OCH$_3$); $^{13}$C NMR (100 MHz, DMSO-$_d_6$): $\delta$ (ppm) 178.1, 165.5, 149.4, 143.7, 142.9, 139.4, 129.7, 129.6, 128.9, 128.6, 127.2, 126.6, 126.3, 125.6, 122.7, 120.8, 111.5, 82.8, 73.6, 65.3, 52.2; HRMS (ESI), m/z calcd 402.1336 for C$_{24}$H$_{20}$NO$_5$ [M+H]$^+$, found 402.1339.

(R)-3-Hydroxy-3-((7R,8S)-8-hydroxy-4-methyl-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)indolin-2-one (3ba): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3ba was obtained as a colorless solid (257.0 mg, yield 72%) via flash chromatography on a silica gel (hexane/ethyl acetate = 4:1, v/v). m.p. 157-159 ºC; $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ (ppm) 9.64 (s, 1H, NH), 7.44 (s, 1H, OH), 7.19 (d, 1H, $J$=7.6 Hz, Ar-H), 7.03 (d, 1H, $J$=7.2 Hz, Ar-H), 6.87-6.89 (m, 1H, Ar-H), 6.73-6.79 (m, 4H, Ar-H), 6.46 (t, 1H, $J$=7.2 Hz, Ar-H), 6.27 (d, 1H, $J$=7.2 Hz, Ar-H), 6.10 (s, 1H, OH), 5.98-6.01 (m, 2H, Ar-H), 4.27 (s, 1H, CH$_3$), 2.44 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, DMSO-$_d_6$): $\delta$ (ppm) 180.4, 150.9, 145.4,
(R)-3-Hydroxy-3-((7R,8S)-8-hydroxy-4-methyl-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)-7-(trifluoromethyl)indolin-2-one (3be): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3be was obtained as a colorless solid (327.3 mg, yield 77%) via flash chromatography on a silica gel (hexane/ethyl acetate = 3:1, v/v). m.p. 162-164 °C; 1H NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 10.16 (s, 1H, NH), 7.47 (s, 1H, OH), 7.23 (d, 1H, $J$=7.6 Hz, Ar-H), 7.08 (d, 1H, $J$=7.2 Hz, Ar-H), 7.04 (d, 1H, $J$=8.0 Hz, Ar-H), 6.78 (s, 1H, OH), 6.66-6.86 (m, 5H, Ar-H), 6.53 (d, 1H, $J$=11.2 Hz, Ar-H), 6.28 (s, 1H, Ar-H), 6.23 (s, 1H, Ar-H), 4.35 (s, 1H, CH), 2.46 (s, 3H, CH$_3$); 13C NMR (100 MHz, DMSO-d$_6$): $\delta$ (ppm) 178.6, 146.4, 143.6, 139.6, 139.3, 139.2, 138.9, 132.0, 129.4, 128.4, 127.3, 126.9, 126.6, 125.9, 125.4, 122.4, 121.0, 111.3, 110.9, 110.6, 110.3, 82.3, 73.3, 64.7, 22.4; HRMS (ESI), m/z calcd 426.1312 for C$_{24}$H$_{19}$F$_3$NO$_3$ [M+H]$^+$, found 426.1315.

*Methyl* (R)-3-hydroxy-3-((7R,8S)-8-hydroxy-4-methyl-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)-2-axoindoline-7-carboxylate (3bi): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3bi was obtained as a colorless solid (311.3 mg, yield 75%) via flash chromatography on a silica gel (hexane/ethyl acetate = 4:1, v/v). m.p. 151-153 °C; 1H NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 9.41 (s, 1H, NH), 7.45 (s, 1H, OH), 7.30 (dd, 1H, $J$=8.0 Hz, 1.2 Hz, Ar-H), 7.20 (d, 1H, $J$=7.6 Hz, Ar-H), 7.04 (d, 1H, $J$=7.6 Hz, Ar-H), 6.74 (s, 1H, OH), 6.69-6.78 (m, 3H, Ar-H), 6.52-6.64 (m, 2H, Ar-H), 6.24 (s, 1H, Ar-H), 6.19 (s, 1H, Ar-H), 4.29 (s, 1H, CH), 3.78 (s, 3H, OCH$_3$), 2.45 (s, 3H, CH$_3$); 13C NMR (100 MHz,
DMSO-\(d_6\): \(\delta\) (ppm) 178.1, 165.5, 146.3, 143.6, 142.8, 139.6, 138.9, 131.4, 129.6, 129.4, 129.0, 127.3, 126.6, 126.2, 125.9, 122.4, 120.8, 111.4, 82.3, 73.6, 64.9, 22.4; HRMS (ESI), m/z calcd 416.1492 for C\(_{25}\)H\(_{22}\)NO\(_5\) [M+H]\(^+\), found 416.1496.

(R)-5,6-Difluoro-3-hydroxy-3-((7R,8S)-8-hydroxy-4-methyl-8-phenylbicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)indolin-2-one (3bj): The title compound was prepared according to the general procedure on a 1 mmol scale, and 3bj was obtained as a colorless solid (279.0 mg, yield 71%) via flash chromatography on a silica gel (hexane/ethyl acetate = 3:1, v/v). m.p. 171-174 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 7.43 (s, 1H, Ar-H), 9.88 (s, 1H, NH), 7.23 (d, 1H, \(J=7.6\) Hz, Ar-H), 7.10 (d, 1H, \(J=7.6\) Hz, Ar-H), 6.98 (d, 1H, \(J=7.6\) Hz, Ar-H), 6.78-6.91 (m, 4H, Ar-H), 6.25 (s, 1H, OH), 6.22 (s, 1H, OH), 6.06 (dd, 1H, \(J=10.0\) Hz, 8.0 Hz, Ar-H), 5.97 (dd, 1H, \(J=10.8\) Hz, 6.8 Hz, Ar-H), 4.26 (s, 1H, CH), 2.45 (s, 3H, CH\(_3\)); \(^1\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 178.1, 146.3, 143.4, 139.9, 139.0, 129.4, 127.5, 126.9, 126.7, 125.8, 122.6, 113.8, 111.3, 99.5, 99.3, 82.3, 74.6, 64.6, 22.3; HRMS (ESI), m/z calcd 394.1429 for C\(_{23}\)H\(_{18}\)F\(_2\)NO\(_3\) [M+H]\(^+\), found 394.1433.

3. General procedure for preparing aldol products (4)

In a 20 mL tube, 2-methylbenzophenone 1 (1.0 mmol, 1 eq) and isatin 2 (1.0 mmol, 1 eq) were dissolved in methanol (15 mL). The reaction mixture was under irradiation of UV LEDs (365 nm) for 9 h. After completion (by TLC), the reaction mixture was evaporated to dryness in a vacuo. The residue was purified by medium-pressure chromatography (silica gel) using a mixed solvent of hexane and ethyl acetate (10-20% EA).

3-(2-Benzoylbenzyl)-3-hydroxyindolin-2-one (4aa): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4aa was obtained as a white solid.
(274.4 mg, yield 80%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v).

m.p. 174-176 °C; 1H NMR (400 MHz, CDCl3): δ (ppm) 8.45 (s, 1H, NH), 7.76 (d, 1H, J=7.6 Hz, Ar-H), 7.59 (t, 1H, J=7.6 Hz, Ar-H), 7.33-7.49 (m, 5H, Ar-H), 7.16-7.22 (m, 2H, Ar-H), 6.84-6.96 (m, 3H, Ar-H), 6.12 (s, 1H, O-H), 3.62 (d, 1H, J=14.0 Hz, C-H2), 3.02 (d, 1H, J=14.0 Hz, C-H2);

13C NMR (100 MHz, CDCl3): δ (ppm) 199.3, 181.0, 140.3, 138.6, 137.6, 134.8, 133.8, 133.5, 131.7, 131.0, 130.7, 129.4, 128.3, 126.3, 125.7, 110.3, 40.7; HRMS (ESI), m/z calcd 344.1281 for C22H18NO3 [M+H]+, found 344.1286.

3-(2-Benzoylbenzyl)-3-hydroxy-1-methylindolin-2-one (4ab): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4ab was obtained as a white solid (267.8 mg, yield 75%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v).

m.p. 104-106 °C; 1H NMR (400 MHz, CDCl3): δ (ppm) 7.72-7.74 (m, 2H, Ar-H), 7.57-7.62 (m, 1H, Ar-H), 7.39-7.47 (m, 4H, Ar-H), 7.34 (dd, 1H, J=7.2 Hz, 1.2 Hz, Ar-H), 7.22-7.26 (m, 2H, Ar-H), 6.90-6.94 (m, 2H, Ar-H), 6.79 (d, 1H, J=7.6 Hz, Ar-H), 5.78 (s, 1H, O-H), 3.63 (d, 1H, J=14.0 Hz, C-H2), 3.15 (s, 3H, CH3), 2.97 (d, 1H, J=14.0 Hz, C-H2); 13C NMR (100 MHz, CDCl3): δ (ppm) 199.0, 178.4, 143.2, 138.7, 137.7, 134.9, 133.6, 133.4, 131.0, 130.8, 130.6, 130.3, 129.4, 128.3, 126.3, 125.3, 122.4, 108.2, 40.7, 26.2; HRMS (ESI), m/z calcd 358.1438 for C23H20NO3 [M+H]+, found 358.1441.

3-(2-Benzoylbenzyl)-3-hydroxy-1-phenylindolin-2-one (4ac): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4ac was obtained as a white solid (326.8 mg, yield 78%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v).

m.p. 66-68 °C; 1H NMR (400 MHz, CDCl3): δ (ppm) 7.68 (d, 2H, J=7.2 Hz, Ar-H), 7.57 (t, 1H, J=7.2 Hz, Ar-H), 7.31-7.49 (m, 12H, Ar-H), 7.07-7.15 (m, 2H, Ar-H), 6.89 (t, 1H, J=7.6 Hz,
Ar-H), 6.73 (d, 1H, J=7.6 Hz, Ar-H), 5.51 (s, 1H, OH), 3.80 (d, 1H, J=13.6 Hz, CH₂), 3.19 (d, 1H, J=13.6 Hz, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 198.7, 177.5, 143.1, 138.7, 137.7, 134.7, 134.2, 133.6, 133.3, 130.9, 130.6, 129.8, 129.5, 129.3, 128.2, 128.0, 126.4, 126.3, 125.5, 109.4, 41.2; HRMS (ESI), m/z calcd 420.1594 for C₂₈H₂₂NO₃ [M+H]⁺, found 420.1599.

3-(2-Benzoylbenzyl)-6-fluoro-3-hydroxyindolin-2-one (4ad): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4ad was obtained as a white solid (267.1 mg, yield 74%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 155-157 ºC; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 10.24 (s, 1H, N-H), 7.60-7.64 (m, 1H, Ar-H), 7.39-7.50 (m, 5H, Ar-H), 7.27-7.31 (m, 2H, Ar-H), 7.16 (d, 1H, J=7.6 Hz, Ar-H), 6.63 (dd, 1H, J=8.0 Hz, 6.4 Hz, Ar-H), 6.42 (dd, 1H, J=7.2 Hz, 2.4 Hz, Ar-H), 6.29-6.33 (m, 1H, Ar-H), 6.08 (s, 1H, OH), 3.60 (d, 1H, J=13.2 Hz, CH₂), 3.06 (d, 1H, J=13.2 Hz, CH₂); ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 199.0, 178.4, 143.2, 138.7, 137.7, 134.9, 133.6, 133.4, 131.0, 130.8, 130.6, 130.3, 129.4, 126.3, 125.3, 122.4, 108.2, 40.7, 26.2; HRMS (ESI), m/z calcd 362.1187 for C₂₂H₁₇FNO₃ [M+H]⁺, found 362.1191.

3-(2-Benzoylbenzyl)-3-hydroxy-7-(trifluoromethyl)indolin-2-one (4ae): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4ae was obtained as a white solid (324.7 mg, yield 79%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 172-174 ºC; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.69 (d, 2H, J=7.2 Hz, Ar-H), 7.65 (brs, 1H, N-H), 7.55 (t, 1H, J=7.6 Hz, Ar-H), 7.31-7.41 (m, 6H, Ar-H), 7.05-7.11 (m, 2H, Ar-H), 6.95 (d, 1H, J=8.0 Hz, Ar-H), 6.40 (s, 1H, OH), 3.55 (d, 1H, J=14.0 Hz, CH₂), 2.93 (d, 1H, J=14.0 Hz, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 198.3, 178.4, 143.2, 138.7, 137.5,
3-(2-Benzoylbenzyl)-3-hydroxy-6-methyldindolin-2-one (4ag): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4ag was obtained as a white solid (299.9 mg, yield 84%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 187-189 °C; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.01 (brs, 1H, N-H), 7.60-7.64 (m, 1H, Ar-H), 7.24 (td, 1H, J=7.2 Hz, 1.6 Hz, Ar-H), 7.08 (d, 1H, J=8.0 Hz, Ar-H), 6.73 (d, 1H, J=8.0 Hz, Ar-H), 6.47-6.49 (m, 2H, Ar-H), 6.02 (s, 1H, OH), 3.76 (d, 1H, J=13.2 Hz, CH2), 3.38 (s, 3H, CH3), 3.09 (d, 1H, J=13.2 Hz, CH2); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 197.4, 179.3, 140.7, 139.4, 139.2, 137.7, 135.4, 133.3, 133.0, 130.8, 130.4, 130.3, 129.7, 129.5, 128.5, 126.3, 125.8, 109.4, 77.3, 39.0, 20.7; HRMS (ESI), m/z calcd 358.1438 for C23H20NO3 [M+H]+, found 358.1443.

3-(2-Benzoylbenzyl)-3-hydroxy-5,7-dimethyldindolin-2-one (4ah): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4ah was obtained as a white solid (296.8 mg, yield 80%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 193-195 °C; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.03 (brs, 1H, N-H), 7.59-7.63 (m, 1H, Ar-H), 7.32-7.45 (m, 6H, Ar-H), 7.08 (td, 1H, J=8.8 Hz, 2.0 Hz, Ar-H), 7.08 (dd, 1H, J=7.6 Hz, Ar-H), 6.54 (s, 1H, Ar-H), 6.28 (s, 1H, Ar-H), 5.91 (s, 1H, OH), 3.69 (d, 1H, J=13.2 Hz, CH2), 3.05 (d, 1H, J=13.2 Hz, CH2), 1.99 (s, 3H, CH3), 1.75 (s, 3H, CH3); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 197.4, 179.7, 140.7, 139.4, 137.9, 137.8, 135.4, 133.2, 133.1, 131.0, 130.7, 130.6, 130.3, 129.6, 128.5, 126.2, 123.2, 118.5, 77.3, 20.7, 20.5; HRMS (ESI), m/z calcd 372.1594 for C24H22NO3 [M+H]+, found 372.1599.
3-(2-Benzoylbenzyl)-5-chloro-3-hydroxyindolin-2-one (4ak): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4ak was obtained as a white solid (278.9 mg, yield 74%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 185-187 °C; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.26 (brs, 1H, N-H), 7.60-7.64 (m, 1H, Ar-H), 7.28-7.35 (m, 2H, Ar-H), 7.15-7.17 (m, 1H, Ar-H), 7.02 (d, 1H, J=8.0 Hz, Ar-H), 6.63 (d, 1H, J=8.0 Hz, Ar-H), 6.21 (s, 1H, O-H), 3.65 (d, 1H, J=13.2 Hz, CH2), 2.08 (d, 1H, J=13.2 Hz, CH2); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 197.4, 179.0, 140.7, 139.5, 137.7, 134.9, 133.4, 133.1, 133.0, 130.4, 130.3, 129.7, 129.2, 128.7, 126.6, 126.1, 125.3, 111.2, 77.0, 39.0; HRMS (ESI), m/z calcd 378.0891 for C22H17ClNO3 [M+H]+, found 378.0895.

3-(2-benzoyl-5-methylbenzyl)-3-hydroxyindolin-2-one (4ba): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4ba was obtained as a white solid (278.5 mg, yield 78%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 165-167 °C; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.16 (brs, 1H, N-H), 7.62 (d, 1H, J=6.8 Hz, Ar-H), 7.45-7.51 (m, 4H, Ar-H), 6.61-6.74 (m, 3H, Ar-H), 6.05 (s, 1H, O-H), 3.62 (d, 1H, J=13.2 Hz, CH2), 3.13 (d, 1H, J=13.2 Hz, CH2), 2.29 (s, 3H, CH3); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 197.4, 179.4, 141.9, 139.9, 138.2, 136.9, 135.4, 133.7, 131.1, 130.4, 129.9, 128.5, 126.8, 125.1, 121.6, 109.7, 76.9, 39.2, 21.5; HRMS (ESI), m/z calcd 358.1438 for C23H20NO3 [M+H]+, found 358.1442.

3-(2-benzoyl-5-methylbenzyl)-6-fluoro-3-hydroxyindolin-2-one (4bd): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4bd was obtained as a white solid (281.3 mg, yield 75%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1,
(v/v). m.p. 173-175 °C; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.26 (brs, 1H, N-H), 7.60-7.62 (m, 1H, Ar-H), 7.42-7.45 (m, 4H, Ar-H), 7.03-7.10 (m, 3H, Ar-H), 6.63-6.66 (m, 1H, Ar-H), 6.27-6.43 (m, 2H, Ar-H), 6.07 (s, 1H, OH), 3.62 (d, 1H, J=13.2 Hz, CH2), 3.06 (d, 1H, J=13.2 Hz, CH2), 2.28 (s, 3H, CH3); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 197.3, 179.6, 143.6, 143.5, 140.0, 137.9, 136.7, 133.8, 133.1, 130.3, 129.9, 128.5, 126.9, 126.6, 107.8, 107.6, 98.0, 97.8, 76.6, 39.3, 21.4; HRMS (ESI), m/z calcd 376.1343 for C23H18FNO3 [M+H]+, found 376.1348.

3-(2-benzoyl-5-methylbenzyl)-5,6-difluoro-3-hydroxyindolin-2-one (4bj): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4bj was obtained as a white solid (302.6 mg, yield 77%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 177-179 °C; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.26 (brs, 1H, N-H), 7.61-7.63 (m, 1H, Ar-H), 7.40-7.46 (m, 4H, Ar-H), 7.04-7.14 (m, 3H, Ar-H), 6.59-6.63 (m, 2H, Ar-H), 6.24 (s, 1H, OH), 3.70 (d, 1H, J=12.8 Hz, CH2), 3.07 (d, 1H, J=12.8 Hz, CH2), 2.29 (s, 3H, CH3); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 197.1, 179.2, 143.6, 143.5, 140.3, 137.6, 136.3, 134.7, 133.9, 133.3, 130.1, 128.6, 127.1, 114.9, 114.7, 99.8, 99.6, 77.1, 60.2, 39.0, 21.4; HRMS (ESI), m/z calcd 394.1429 for C23H18F2NO3 [M+H]+, found 394.1433.

3-(2-benzoyl-5-methylbenzyl)-5-chloro-3-hydroxyindolin-2-one (4bk): The title compound was prepared according to the general procedure on a 1 mmol scale, and 4bk was obtained as a white solid (270.5 mg, yield 69%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 181-183 °C; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 2.28 (s, 3H, CH3), 10.30 (brs, 1H, N-H), 7.60-7.62 (m, 1H, Ar-H), 7.42-7.45 (m, 4H, Ar-H), 7.00-7.13 (m, 4H, Ar-H), 6.58-6.65 (m, 2H, Ar-H), 6.21 (s, 1H, OH), 3.70 (d, 1H, J=13.2 Hz, CH2), 3.07 (d, 1H, J=13.2 Hz, CH2).
13C NMR (100 MHz, DMSO-<sub>d6</sub>): δ (ppm) 197.4, 179.1, 140.7, 140.2, 138.0, 136.7, 135.1, 133.9, 133.2, 133.1, 130.2, 129.1, 128.6, 127.0, 126.1, 125.4, 111.2, 77.1, 38.9, 21.4;

HRMS (ESI), m/z calcd 392.1048 for C<sub>23</sub>H<sub>16</sub>ClNO<sub>3</sub> [M+H]<sup>+</sup>, found 392.1052.

**Methyl 3-(2-benzoylphenyl)-2-hydroxy-2-methylpropanoate (4aL):** The title compound was prepared according to the general procedure on a 1 mmol scale, and 4aL was obtained as a white solid (256.3 mg, yield 86%) via flash chromatography on a silica gel (hexane/ethyl acetate = 6:1, v/v). m.p. 135-137 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.78-7.81 (m, 2H, Ar-H), 7.56-7.58 (m, 1H, Ar-H), 7.42-7.47 (m, 3H, Ar-H), 4.28 (brs, 1H, OH), 3.67 (s, 3H, OC<sub>2</sub>H<sub>3</sub>), 3.19 (d, 1H, J=13.2 Hz, CH<sub>2</sub>), 1.44 (s, 3H, C<sub>2</sub>H<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 198.8, 176.7, 139.1, 137.8, 135.9, 133.2, 132.2, 130.7, 130.6, 130.1, 128.4, 126.1, 75.4, 52.6, 42.0, 26.3; HRMS (ESI), m/z calcd 299.1278 for C<sub>18</sub>H<sub>19</sub>O<sub>4</sub> [M+H]<sup>+</sup>, found 299.1280.

**2-(2-Benzoylbenzyl)-2-hydroxyacenaphthylene-1(2H)-one (4am):** The title compound was prepared according to the general procedure on a 1 mmol scale, and 4am was obtained as a white solid (336.4 mg, yield 89%) via flash chromatography on a silica gel (hexane/ethyl acetate = 5:1, v/v). m.p. 143-135 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.04-8.08 (m, 1H, Ar-H), 7.91 (d, 1H, J=7.2 Hz, Ar-H), 7.80 (d, 1H, J=8.0 Hz, Ar-H), 7.67-7.73 (m, 3H, Ar-H), 7.57-7.61 (m, 1H, Ar-H), 7.31-7.53 (m, 6H, Ar-H), 7.23 (d, 1H, J=7.6 Hz, Ar-H), 7.16 (d, 1H, J=7.6 Hz, Ar-H), 6.18 (brs, 1H, OH), 3.65 (d, 1H, J=14.0 Hz, CH<sub>2</sub>), 3.02 (d, 1H, J=14.0 Hz, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 205.5, 199.3, 141.0, 139.7, 138.6, 137.7, 135.7, 133.8, 133.5, 131.9, 131.0, 130.7, 130.6, 128.5, 128.4, 128.3, 128.2, 126.3, 125.1, 122.1, 122.0, 80.1, 40.6; HRMS (ESI), m/z calcd 379.1329 for C<sub>26</sub>H<sub>19</sub>O<sub>3</sub> [M+H]<sup>+</sup>, found 379.1332.
4. X-ray crystallographic analysis of 3aa (CCDC-2308324)

Single crystals of product 3aa were obtained via slow volatilization in a mixed solution of hexane/ethyl acetate. A suitable crystal was selected and measured on a Bruker SMART diffractometer (MoKα λ = 0.71073 Å). The crystal was kept at 296(2) during data collection.

The structure was solved with the Bruker SHELXTL structure solution program using Direct Methods and refined with the SHELXL (Sheldrick, 2014) refinement package using Least Squares minimization. The ellipsoid contour percent probability level of 3aa is 15%.

Table 1. Crystal data of compound 3aa.

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5. Structure characterization spectra of BCBs (3)

**SI-Fig. 1.** $^1$H NMR spectrum of compound 3aa. (400 MHz, DMSO-$d_6$)

**SI-Fig. 2.** $^{13}$C NMR spectrum of compound 3aa. (100 MHz, DMSO-$d_6$)
SI-Fig. 3. DEPT135 spectrum of compound 3aa. (100 MHz, DMSO-\textit{d}_6)

SI-Fig. 4. \textit{^1}H NMR spectrum of compound 3ab. (400 MHz, CDCl\textsubscript{3})
SI-Fig. 5. $^{13}$C NMR spectrum of compound 3ab. (100 MHz, CDCl$_3$)

SI-Fig. 6. DEPT135 spectrum of compound 3ab. (100 MHz, CDCl$_3$)
SI-Fig. 7. $^1$H NMR spectrum of compound 3ac. (400 MHz, DMSO-$d_6$)

SI-Fig. 8. $^{13}$C NMR spectrum of compound 3ac. (100 MHz, DMSO-$d_6$)
SI-Fig. 9. DEPT135 spectrum of compound 3ac. (100 MHz, DMSO-\textit{d}_6)

SI-Fig. 10. $^1$H NMR spectrum of compound 3ad. (400 MHz, DMSO-\textit{d}_6)
SI-Fig. 11. $^{13}$C NMR spectrum of compound 3ad. (100 MHz, DMSO-$d_6$)

SI-Fig. 12. DEPT135 spectrum of compound 3ad. (100 MHz, DMSO-$d_6$)
SI-Fig. 13. $^1$H NMR spectrum of compound 3ae. (400 MHz, DMSO-$d_6$)

SI-Fig. 14. $^{13}$C NMR spectrum of compound 3ae. (100 MHz, DMSO-$d_6$)
SI-Fig. 15. DEPT135 spectrum of compound 3ae. (100 MHz, DMSO-\textit{d}_6)

SI-Fig. 16. \textsuperscript{1}H NMR spectrum of compound 3af. (400 MHz, DMSO-\textit{d}_6)
SI-Fig. 17. $^{13}$C NMR spectrum of compound 3af. (100 MHz, DMSO-$d_6$)

SI-Fig. 18. DEPT135 spectrum of compound 3af. (100 MHz, DMSO-$d_6$)
SI-Fig. 19. $^1$H NMR spectrum of compound 3ai. (400 MHz, DMSO-$d_6$)

SI-Fig. 20. $^{13}$C NMR spectrum of compound 3ai. (100 MHz, DMSO-$d_6$)
SI-Fig. 21. DEPT135 spectrum of compound 3ai. (100 MHz, DMSO-$d_6$)

SI-Fig. 22. $^1$H NMR spectrum of compound 3ba. (400 MHz, DMSO-$d_6$)
SI-Fig. 23. $^{13}$C NMR spectrum of compound 3ba. (100 MHz, DMSO-$d_6$)

SI-Fig. 24. DEPT135 spectrum of compound 3ba. (100 MHz, DMSO-$d_6$)
SI-Fig. 25. $^1$H NMR spectrum of compound 3be. (400 MHz, DMSO-$d_6$)

SI-Fig. 26. $^{13}$C NMR spectrum of compound 3be. (100 MHz, DMSO-$d_6$)
SI-Fig. 27. DEPT135 spectrum of compound 3be. (100 MHz, DMSO-\textit{d}_6)

SI-Fig. 28. $^1$H NMR spectrum of compound 3bi. (400 MHz, DMSO-\textit{d}_6)
SI-Fig. 29. $^{13}$C NMR spectrum of compound 3bi. (100 MHz, DMSO-$d_6$)

SI-Fig. 30. DEPT135 spectrum of compound 3bi. (100 MHz, DMSO-$d_6$)
SI-Fig. 31. $^1$H NMR spectrum of compound 3bj. (400 MHz, DMSO-$d_6$)

SI-Fig. 32. $^{13}$C NMR spectrum of compound 3bj. (100 MHz, DMSO-$d_6$)
SI-Fig. 33. DEPT135 spectrum of compound 3bj. (100 MHz, DMSO-$d_6$)
6. Structure characterization spectra of aldol products (4)

SI-Fig. 34. $^1$H NMR spectrum of compound 4aa. (400 MHz, CDCl$_3$)

SI-Fig. 35. $^{13}$C NMR spectrum of compound 4aa. (100 MHz, CDCl$_3$)
SI-Fig. 36. DEPT135 spectrum of compound 4aa. (100 MHz, CDCl$_3$)

SI-Fig. 37. $^1$H NMR spectrum of compound 4ab. (400 MHz, CDCl$_3$)
SI-Fig. 38. $^{13}$C NMR spectrum of compound 4ab. (100 MHz, CDCl$_3$)

SI-Fig. 39. DEPT135 spectrum of compound 4ab. (100 MHz, CDCl$_3$)
SI-Fig. 40. $^1$H NMR spectrum of compound 4ac. (400 MHz, CDCl$_3$)

SI-Fig. 41. $^{13}$C NMR spectrum of compound 4ac. (100 MHz, CDCl$_3$)
SI-Fig. 42. DEPT135 spectrum of compound 4ac. (100 MHz, CDCl₃)

SI-Fig. 43. ¹H NMR spectrum of compound 4ad. (400 MHz, DMSO-ｄ₆)
SI-Fig. 44. $^{13}$C NMR spectrum of compound 4ad. (100 MHz, DMSO-$d_6$)

SI-Fig. 45. DEPT135 spectrum of compound 4ad. (100 MHz, DMSO-$d_6$)
SI-Fig. 46. $^1$H NMR spectrum of compound 4ae. (400 MHz, CDCl$_3$)

SI-Fig. 47. $^{13}$C NMR spectrum of compound 4ae. (100 MHz, CDCl$_3$)
SI-Fig. 48. DEPT135 spectrum of compound 4ae. (100 MHz, CDCl₃)

SI-Fig. 49. ¹H NMR spectrum of compound 4ag. (400 MHz, DMSO-d₆)
SI-Fig. 50. $^{13}$C NMR spectrum of compound 4ag. (100 MHz, DMSO-$d_6$)

SI-Fig. 51. DEPT135 spectrum of compound 4ag. (100 MHz, DMSO-$d_6$)
SI-Fig. 52. $^1$H NMR spectrum of compound 4ah. (400 MHz, DMSO-$d_6$)

SI-Fig. 53. $^{13}$C NMR spectrum of compound 4ah. (100 MHz, DMSO-$d_6$)
SI-Fig. 54. DEPT135 spectrum of compound 4ah. (100 MHz, DMSO-$d_6$)

SI-Fig. 55. $^1$H NMR spectrum of compound 4ak. (400 MHz, DMSO-$d_6$)
SI-Fig. 56. $^{13}$C NMR spectrum of compound 4ak. (100 MHz, DMSO-\textit{d}_6)

SI-Fig. 57. DEPT135 spectrum of compound 4ak. (100 MHz, DMSO-\textit{d}_6)
SI-Fig. 58. $^1$H NMR spectrum of compound 4ba. (400 MHz, DMSO-$d_6$)

SI-Fig. 59. $^{13}$C NMR spectrum of compound 4ba. (100 MHz, DMSO-$d_6$)
SI-Fig. 60. DEPT135 spectrum of compound 4ba. (100 MHz, DMSO-d$_6$)

SI-Fig. 61. $^1$H NMR spectrum of compound 4bd. (400 MHz, DMSO-d$_6$)
SI-Fig. 62. $^{13}$C NMR spectrum of compound 4bd. (100 MHz, DMSO-$d_6$)

SI-Fig. 63. DEPT135 spectrum of compound 4bd. (100 MHz, DMSO-$d_6$)
SI-Fig. 64. $^1$H NMR spectrum of compound 4bj. (400 MHz, DMSO-$d_6$)

SI-Fig. 65. $^{13}$C NMR spectrum of compound 4bj. (100 MHz, DMSO-$d_6$)
SI-Fig. 66. DEPT135 spectrum of compound 4bj. (100 MHz, DMSO-$d_6$)

SI-Fig. 67. $^1$H NMR spectrum of compound 4bk. (400 MHz, DMSO-$d_6$)
SI-Fig. 68. \textsuperscript{13}C NMR spectrum of compound 4bk. (100 MHz, DMSO-\textit{d}_6)

SI-Fig. 69. DEPT135 spectrum of compound 4bk. (100 MHz, DMSO-\textit{d}_6)
SI-Fig. 70. $^1$H NMR spectrum of compound 4al. (400 MHz, CDCl$_3$)

SI-Fig. 71. $^{13}$C NMR spectrum of compound 4al. (100 MHz, CDCl$_3$)
SI-Fig. 72. DEPT135 spectrum of compound 4al. (100 MHz, CDCl₃)

SI-Fig. 73. ¹H NMR spectrum of compound 4am. (400 MHz, CDCl₃)
SI-Fig. 74. $^{13}$C NMR spectrum of compound 4am. (100 MHz, CDCl$_3$)

SI-Fig. 75. DEPT135 spectrum of compound 4am. (100 MHz, CDCl$_3$)
7. 2D-NMR spectra of compounds 3aa and 4aa.

SI-Fig. 76. H-H COSY spectrum of compound 3aa. (100 MHz, DMSO-\textit{d}_6)

SI-Fig. 77. H-H COSY spectrum of compound 3aa. (100 MHz, DMSO-\textit{d}_6)
SI-Fig. 78. H-H COSY spectrum of compound 4aa. (100 MHz, DMSO-$d_6$)

SI-Fig. 79. H-H COSY spectrum of compound 4aa. (100 MHz, DMSO-$d_6$)
8. ORTEP diagram of crystal structure of 3aa (CCDC-2308324)

SI-Fig. 80. ORTEP diagram of crystal structure of 3aa. (15% probability).
9. Computational section

Geometrical optimization was carried out at the m062x 6-31g(d,p) theoretical level using the SCRF model (MeCN as solvent) \(^1\)\(^-\)\(^3\). Frequency analysis and the thermodynamic correctional data were obtained at the same level. In addition, the IRC pathways \(^4\) calculations were also performed for transition state (TS1 and TS2) to identify whether the transition state can connect the reactants and the key intermediate (IM3). All of the computational experiments were conducted by using the Gaussian 16 program package \(^5\).

SI-Fig. 81. Optimized structures of TS1 at m062x, 6-31g(d,p) theoretical level.
SI-Fig. 82. Optimized structures of TS2 at m062x, 6-31g(d,p) theoretical level.

SI-Fig. 83. Optimized structures of IM3 at m062x, 6-31g(d,p) theoretical level.
SI-Fig. 84. Intrinsic reaction coordinate (IRC) of transition state TS1.

SI-Fig. 85. Intrinsic reaction coordinate (IRC) of transition state TS2.
10. References


