**Highly Enantioselective Synthesis of Dihydrocoumarin-fused Dihydropyrans via a Phosphine-catalyzed [4+2] Annulation of Allenones with 3-Aroylcoumarins**

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A. General Information

All the starting materials were obtained from commercial sources and were used without further purification unless otherwise stated. Toluene, THF and Et₂O were dried and distilled from sodium benzophenone prior to use. CHCl₃ and CH₂Cl₂ were distilled from CaH₂ prior to use. Dioxane was dried and distilled from Na prior to use. Optical rotations were measured using a Jasco DIP-1000 polarimeter. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thinlayer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Flash chromatographic separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. Enantiomeric excesses were determined by HPLC analysis on achiral stationary phase. The coumarine-based compound 1 and catalysts 4a–9 were synthesized according to literature reported methods. Allenone 2 was synthesized via Wittig reaction from the corresponding triphenyl phosphonium ylied with ethenone.

B. Representative Procedure For Phosphine-Mediated [4+2] Annulation of Allenones and 3-Aroylcoumarins

![Chemical Structure](Image)

To a solution of 3-aroylcoumarin 1 (0.1 mmol) in toluene (1 mL) was added allenone 2 (0.12 mmol), and the resulting mixture was stirred at room temperature for 24 h. At the end of the reaction, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 15:1 to 10:1) to afford the cyclization adducts 3 (83-94% yields, 76-94% ee’s).

C. Analytical Data and HPLC Chromatogram of [4+2]CyclizationAdducts

\((R,E)-2-(1\text{-Oxo-1-phenylpropan-2-ylidene})\text{-4-phenyl-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3a)}\)

\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{O} & \quad \text{Ph}
\end{align*}

89% yield, a white solid; \([\alpha]^{25}_D = -195.55 \text{ (c 1.00, CHCl}_3\text{)}; \:^1\text{H NMR (500 MHz, CDCl}_3\text{)} \delta 7.97 – 7.89 \text{ (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.57 – 7.50 (m, 3H), 7.49 – 7.44 (m, 2H), 7.31 (d, J = 7.8 Hz, 1H), 7.14 – 7.07 (m, 2H), 7.01 (d, J = 7.7 Hz, 1H), 3.94 (dd, J = 11.9Hz, 5.7 Hz, 1H), 3.47 (dd, J = 14.1Hz, 5.7 Hz, 1H), 2.44 (ddd, J = 14.1Hz, 12.0Hz, 2.1 Hz, 1H), 2.18 (d, J = 2.0 Hz, 3H);} \:^{13}\text{C NMR (126 MHz, CDCl}_3\text{)} \delta 197.63, 163.03, 162.33, 150.78, 150.16, 137.64, 133.58, 133.43, 130.72, 129.10, 128.96, 128.82, 128.86, 128.26, 125.19, 124.59, 123.07, 118.46, 117.08, 100.19, 31.45, 27.33, 14.04; \text{HRMS (APCI) m/z calcd for C}_{27}\text{H}_{21}\text{O}_4 [M+H]^+ = 409.1434, found = 409.1436; the ee value was 91%, } t_{R\text{ (major)}} = 29.5 \text{ min, } t_{R\text{ (minor)}} = 33.7 \text{ min (Chiralcel IE-H, } \lambda = 254 \text{ nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).}

\begin{align*}
\text{Racemic3a} \\
\text{Enantiomerically enriched 3a}
\end{align*}
(R,E)-7-Chloro-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3b)

91% yield, a white solid; [α]$_D^{25}$ = -98.26 (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.93 – 7.86 (m, 2H), 7.65 – 7.57 (m, 3H), 7.56 – 7.48 (m, 3H), 7.47 – 7.41 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 7.9 Hz, 1H), 6.89 (dd, J = 7.8Hz, 1.1 Hz, 1H), 3.93 (dd, J = 11.8Hz, 5.7 Hz, 1H), 3.44 (dd, J = 14.1Hz, 5.8 Hz, 1H), 2.43 (ddd, J = 14.0Hz, 8.0Hz, 2.1 Hz, 1H), 2.15 (d, J = 2.0 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.48, 163.65, 161.04, 149.70, 146.91, 137.51, 133.48, 133.25, 130.88, 129.65, 129.11, 129.02, 128.96, 128.28, 124.99, 124.65, 123.43, 122.14, 118.84, 99.26, 31.85, 29.70, 27.22, 14.07; HRMS (APCI) m/z calcd for C$_{27}$H$_{20}$ClO$_4$ [M+H]$^+$ =443.1045, found =443.1048; the ee value was 93%, $t_R$ (major) = 27.1 min, $t_R$ (minor) = 39.1 min (Chiralcel IE-H, λ = 254 nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).
(R,E)-7-Bromo-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3c)

92% yield, a white solid; [α]_{D}^{25} = -172.19 (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, J = 7.2 Hz, 2H), 7.63 (dt, J = 15.5 Hz, 4.4 Hz, 3H), 7.58 – 7.50 (m, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.01 – 6.94 (m, 2H), 3.96 (dd, J = 11.8 Hz, 5.7 Hz, 1H), 3.46 (dd, J = 14.1 Hz, 5.8 Hz, 1H), 2.45 (ddd, J = 14.0 Hz, 12.0 Hz, 2.1 Hz, 1H), 2.18 (d, J = 1.9 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 197.51, 163.62, 161.13, 149.70, 147.93, 137.48, 133.50, 133.22, 132.73, 130.89, 129.12, 129.04, 128.97, 128.29, 125.17, 124.99, 124.21, 118.85, 111.00, 99.34, 31.91, 27.18, 14.10; HRMS (APCI) m/z calcd for C₂₇H₂₀BrO₄ [M+H⁺] = 487.0539, found = 487.0535; the ee value was 90%, tₐ (major) = 14.7 min, tₐ (minor) = 20.2 min (Chiralcel IE-H, λ = 254 nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).
(R,E)-8-Bromo-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3d)

93% yield, white solid; [α]_{D}^{25} = -105.44 (c 1.00, CHCl₃); $^1$H NMR (500 MHz, CDCl₃) δ 7.95 – 7.88 (m, 2H), 7.65 (ddd, J = 8.7 Hz, 2.4 Hz, 1.2 Hz, 1H), 7.62 – 7.50 (m, 5H), 7.49 – 7.43 (m, 2H), 7.27 – 7.20 (m, 2H), 6.88 (dd, J = 8.1 Hz, 0.8 Hz, 1H), 3.87 (dd, J = 11.5 Hz, 5.9 Hz, 1H), 3.45 (dd, J = 14.1 Hz, 5.7 Hz, 1H), 2.41 (ddd, J = 14.1 Hz, 12.0 Hz, 2.2 Hz, 1H), 2.17 (d, J = 2.0 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl₃) δ 197.46, 163.62, 160.54, 151.31, 149.73, 137.51, 133.48, 133.37, 130.84, 129.10, 128.96, 128.93, 128.29, 127.58, 126.52, 122.19, 121.74, 120.30, 118.78, 99.39, 31.29, 27.19, 14.05; HRMS (APCI) m/z calcd for C₂₇H₂₀BrO₄ [M+H]+ = 487.0539, found = 487.0542; the ee value was 90%, tᵣ (major) = 29.1 min, tᵣ (minor) = 32.3 min (Chiralcel IE-H, λ = 254 nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).
(R,E)-9-Methyl-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3e)

83% yield, a white solid; $[\alpha]_{D}^25 = -50.12$ (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.96 – 7.89 (m, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.49 (m, 5H), 7.49 – 7.43 (m, 2H), 7.09 (d, $J = 7.9$ Hz, 1H), 6.98 (d, $J = 8.2$ Hz, 1H), 6.82 (s, 1H), 3.91 (dd, $J = 11.9$ Hz, 5.7 Hz, 1H), 3.50 (dd, $J = 14.2$ Hz, 5.7 Hz, 1H), 2.44 (dd, $J = 14.2$ Hz, 12.1 Hz, 2.2 Hz, 1H), 2.30 (s, 3H), 2.17 (d, $J = 2.0$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 197.73, 162.83, 162.53, 150.48, 148.64, 137.63, 134.24, 133.64, 133.36, 130.66, 129.31, 129.12, 128.96, 128.93, 128.24, 125.61, 122.63, 118.30, 116.77, 100.51, 31.44, 27.28, 20.82, 14.05; HRMS (APCI) m/z calcld for C$_{28}$H$_{23}$O$_4$ [M+H]$^+$ = 423.1591, found = 423.1596; the ee value was 90%, $t_R$ (minor) = 13.5 min, $t_R$ (major) = 12.0 min (Chiralcel IF-H, $\lambda = 254$ nm, 30% iPrOH/hexanes, flow rate = 1.0 mL/min).

![Racemic 3e](image1.png)

![Enantiomerically enriched 3e](image2.png)
(R,E)-9-Bromo-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3f)

88% yield, a white solid; \([\alpha]^{25}_D = -141.83\) (c 1.00, CHCl\(_3\)); \(^1\)H NMR (500 MHz, Acetone-\(d_6\)) \(\delta\) 8.02 – 7.94 (m, 2H), 7.72 – 7.67 (m, 1H), 7.67 – 7.57 (m, 4H), 7.53 – 7.42 (m, 4H), 7.28 – 7.23 (m, 1H), 7.00 (d, \(J = 8.6\) Hz, 1H), 4.11 (dd, \(J = 11.8\) Hz, 5.7 Hz, 1H), 3.49 (dd, \(J = 14.1\) Hz, 5.7 Hz, 1H), 2.51 (ddd, \(J = 14.1\) Hz, 11.9Hz, 2.1 Hz, 1H), 2.14 (d, \(J = 2.0\) Hz, 3H); \(^1^3\)C NMR (126 MHz, acetone-\(d_6\)) \(\delta\) 13C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 196.66, 162.99, 150.22, 150.06, 148.07, 134.29, 133.10, 131.52, 130.23, 129.10, 128.99, 128.90, 128.51, 128.15, 127.98, 126.14, 118.55, 118.20, 116.33, 99.78, 31.24, 27.01, 13.15; HRMS (APCI) m/z calcd for C\(_{27}\)H\(_{20}\)BrO\(_4\) [M+H]\(^+\) = 487.0539, found = 487.0545; the ee value was 91%, \(t_8\) (major) = 19.7 min, \(t_8\) (minor) = 21.2 min (Chiralcel IF-H, \(\lambda = 254\) nm, 10% iPrOH/hexanes, flow rate = 1.2 mL/min).
(R,E)-7-Bromo-9-chloro-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3g)

89% yield, a white solid; \([\alpha]^{25}_D = -81.74\) (c 1.00, CHCl₃); \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.94 – 7.87 (m, 2H), 7.66 (ddd, \(J = 6.9\)Hz, 2.3Hz, 1.1 Hz, 1H), 7.62 – 7.51 (m, 6H), 7.49 – 7.44 (m, 2H), 6.97 (dd, \(J = 2.3\)Hz, 1.3 Hz, 1H), 3.95 (dd, \(J = 11.7\)Hz, 5.7 Hz, 1H), 3.44 (dd, \(J = 14.1\)Hz, 5.7 Hz, 1H), 2.46 (dd, \(J = 14.0\)Hz, 11.8Hz, 2.1 Hz, 1H), 2.17 (d, \(J = 2.0\) Hz, 3H); \(^13\)C NMR (126 MHz, CDCl₃) \(\delta\) 197.35, 164.21, 160.57, 149.22, 146.81, 137.29, 133.58, 133.06, 132.20, 131.01, 129.88, 129.13, 129.01, 129.00, 128.31, 126.03, 124.46, 119.27, 111.56, 98.48, 31.99, 26.92, 14.12; HRMS (APCI) \(m/z\) calcld for C₂₇H₁₉BrClO₄ [M+H]⁺ = 521.0150, found = 521.0145; the ee value was 94%, \(t_R\) (major) = 18.6 min, \(t_R\) (minor) = 23.5 min (Chiralcel IE-H, \(\lambda = 254\) nm, 8% iPrOH/hexanes, flow rate = 1.0 mL/min).
(R,E)-7,9-Dichloro-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyran[3,4-c]chromen-5-one (3h)

94% yield, a white solid; [α]$_D^{25}$ = -174.28 (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.95 – 7.89 (m, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.62 – 7.50 (m, 5H), 7.47 (t, J = 7.5 Hz, 2H), 7.38 (d, J = 2.3 Hz, 1H), 6.95 – 6.88 (m, 1H), 3.94 (dd, J = 11.8 Hz, 5.7 Hz, 1H), 3.44 (dd, J = 14.1 Hz, 5.8 Hz, 1H), 2.46 (ddd, J = 14.0 Hz, 11.9 Hz, 2.1 Hz, 1H), 2.17 (d, J = 2.0 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.35, 164.25, 160.51, 149.21, 145.73, 137.28, 133.58, 133.06, 131.03, 129.53, 129.34, 129.13, 129.00 (2 carbon overlap), 128.32, 126.12, 123.75, 122.99, 119.28, 98.39, 31.93, 26.93, 14.11; HRMS (APCI) m/z calcd for C$_{27}$H$_{19}$Cl$_2$O$_4$ [M+H]$^+$ = 477.0655, found = 477.0658; the ee value was 92%, $t_{R_k}$ (major) = 17.9 min, $t_{R_l}$ (minor) = 22.5 min (Chiralcel IE-H, λ = 254 nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).
(R,E)-9-Nitro-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyran[3,4-c]chromen-5-one (3i)

90% yield, a yellow solid; [α]D²⁵ = -174.28 (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.21 (ddd, J = 8.9 Hz, 2.6 Hz, 0.7 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.71 – 7.65 (m, 1H), 7.63 – 7.52 (m, 4H), 7.49 (t, J = 7.4 Hz, 2H), 7.28 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.9 Hz, 2H), 4.01 (dd, J = 11.9 Hz, 5.7 Hz, 1H), 3.55 (dd, J = 14.0 Hz, 5.7 Hz, 1H), 2.50 (ddd, J = 14.0 Hz, 11.9 Hz, 2.2 Hz, 1H), 2.19 (d, J = 2.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 197.25, 164.87, 155.32, 148.95, 144.30, 137.27, 133.71, 133.06, 131.13, 129.14, 129.06, 128.93, 128.38, 128.23, 124.86, 124.39, 121.56, 119.67, 117.97, 97.89, 31.56, 26.95, 14.11; HRMS (APCI) m/z calc'd for C₂₇H₂₀NO₆ [M+H]+ = 454.1285, found = 454.1294; the ee value was 83%, tR (major) = 35.8 min, tR (minor) = 25.0 min (Chiralcel ID-H, λ = 254 nm, 30% iPrOH/hexanes, flow rate = 1.2 mL/min).

Racemic3i

Enantiomerically enriched 3i
(R,E)-9-Chloro-2-(1-oxo-1-phenylpropan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyran[3,4-c]chromen-5-one (3j)

87% yield, a white solid; [α]_{D}^{25} = -169.36 (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.95 – 7.90 (m, 2H), 7.69 – 7.64 (m, 1H), 7.61 – 7.56 (m, 2H), 7.56 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 7.31 – 7.24 (m, 1H), 7.20 (dd, J = 6.6 Hz, 6.0 Hz, 1H), 7.05 – 6.98 (m, 2H), 3.93 (dd, J = 11.9 Hz, 5.7 Hz, 1H), 3.46 (dd, J = 14.1 Hz, 5.7 Hz, 1H), 2.45 (dd, J = 14.1 Hz, 12.0 Hz, 2.2 Hz, 1H), 2.18 (d, J = 2.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 197.48, 163.68, 149.62, 149.34, 137.41, 133.54, 130.87, 129.78, 129.14, 129.05, 129.00, 128.95, 128.90, 128.30, 128.24, 125.38, 124.75, 118.90, 118.41, 99.24, 31.51, 27.05, 14.09; HRMS (APCI) m/z calcd for C₂₇H₂₀ClO₄ [M+H]^⁺ = 443.1045, found = 443.1047; the ee value was 90%, tₘ (minor) = 9.0 min, tₘ (major) = 11.1 min (Chiralcel IF-H, λ = 254 nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).
(R,E)-4-(4-Fluorophenyl)-2-(1-oxo-1-phenylpropan-2-ylidene)-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3k)

88% yield, a white solid; [α]$_D^{25}$ = -96.93 (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.99 – 7.88 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.59 – 7.44 (m, 4H), 7.28 (t, J = 11.9 Hz, 2H), 7.20 – 7.14 (m, 1H), 7.09 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 7.7 Hz, 1H), 3.97 (dd, J = 12.0Hz, 5.6 Hz, 1H), 3.48 (dd, J = 14.2Hz, 5.6 Hz, 1H), 2.45 (ddd, J = 14.2Hz, 12.1Hz, 2.2 Hz, 1H), 2.14 (d, J = 2.1 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.61, 161.37, 150.60, 150.02, 137.61, 133.45, 132.13, 130.23, 129.11, 128.97, 128.91, 125.35, 124.59, 124.14, 122.44, 118.67, 117.17, 116.08, 115.19, 103.07, 31.25, 27.47, 13.93.; HRMS (APCI) m/z calcd for C$_{27}$H$_{20}$FO$_4$ [M+H]$^+$ = 427.1340, found = 427.1345; the ee value was 93%, $t_R$ (major) = 23.3 min, $t_R$ (minor) = 28.1 min (Chiralcel IE-H, λ = 254 nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).

**Racemic 3k**

**Enantiomerically enriched 3k**
(R,E)-4-(2-Fluorophenyl)-2-(1-oxo-1-phenylpropan-2-ylidene)-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3l)

92% yield, a white solid; [α]_{D}^{25} = -90.97 (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.92 (dd, J = 8.2 Hz, 1.1 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.62 – 7.51 (m, 4H), 7.31 (t, J = 8.0 Hz, 1H), 7.19 – 7.06 (m, 4H), 7.01 (d, J = 7.7 Hz, 1H), 3.93 (dd, J = 11.9Hz, 5.7 Hz, 1H), 3.47 (dd, J = 14.2Hz, 5.7 Hz, 1H), 2.43 (dd, J = 14.1Hz, 12.0Hz, 2.2 Hz, 1H), 2.17 (d, J = 2.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 197.53, 162.35, 161.92, 150.69, 149.99, 137.54, 133.49, 131.20, 131.13, 129.11, 128.97, 128.92, 125.17, 124.67, 122.94, 118.53, 117.08, 115.55, 115.37, 100.30, 31.44, 27.25, 14.05; HRMS (APCI) m/z calcd for C₂₇H₂₀FO₄ [M+H]+ = 427.1344, found = 427.1340; the ee value was 91%, tₑ (major) = 24.2 min, tᵣ (minor) = 27.7 min (Chiralcel IE-H, λ = 254 nm, 20% iPrOH/hexanes, flow rate = 1.0mL/min).
(R,E)-4-Methyl-2-(1-oxo-1-phenylpropan-2-ylidene)-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3m)

94% yield, acolorless oil; [α]_D^{25} = -118.26 (c 1.00, CHCl₃); ^1H NMR (500 MHz, CDCl₃) δ 7.89 (dd, J = 8.2 Hz, 1.1 Hz, 2H), 7.69 – 7.59 (m, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.24 (t, J = 7.7 Hz, 1H), 7.04 (dd, J = 12.6 Hz, 4.8 Hz, 2H), 6.89 (d, J = 7.7 Hz, 1H), 3.84 – 3.74 (m, 1H), 3.38 (dd, J = 14.3 Hz, 5.2 Hz, 1H), 2.55 (d, J = 2.2 Hz, 3H), 2.28 (ddd, J = 14.4Hz, 12.2Hz, 2.2 Hz, 1H), 2.09 (d, J = 2.2 Hz, 3H); ^13C NMR (126 MHz, CDCl₃) δ 197.78, 165.24, 162.43, 150.56, 150.28, 137.78, 133.31, 129.02, 128.91, 128.58, 125.33, 124.40, 122.36, 117.62, 116.92, 99.29, 30.39, 27.97, 20.10, 13.77; HRMS (APCI) m/z calcd for C₂₂H₁₉O₄ [M+H]^+ = 347.1278, found = 347.1282; the ee value was 76%, t_R (major) = 17.5 min, t_R (minor) = 20.2 min (Chiralcel IE-H, λ = 254 nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).
(R,E)-4-Isopropyl-2-(1-oxo-1-phenylpropan-2-ylidene)-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3n)

91% yield, a white solid; $[\alpha]_{D}^{25} = -28.49$ (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.89 (dd, $J = 8.2$ Hz, 1.2 Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.54 (dd, $J = 10.8$ Hz, 4.4 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.09 – 7.02 (m, 2H), 6.91 (d, $J = 7.7$ Hz, 1H), 4.04 (dt, $J = 13.6$ Hz, 6.8 Hz, 1H), 3.78 (dd, $J = 12.1$ Hz, 5.3 Hz, 1H), 3.39 (dd, $J = 14.3$ Hz, 5.3 Hz, 1H), 2.26 (ddd, $J = 14.3$ Hz, 12.2 Hz, 2.2 Hz, 1H), 2.11 (d, $J = 2.1$ Hz, 3H), 1.38 (d, $J = 6.8$ Hz, 3H), 1.19 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.77, 172.24, 162.11, 150.72, 150.60, 137.86, 133.26, 129.03, 128.89, 128.70, 125.26, 124.40, 122.66, 117.52, 116.85, 97.73, 30.63, 30.57, 27.83, 20.26, 19.62, 13.61; HRMS (APCI) m/z calcd for C$_{24}$H$_{23}$O$_4$ [M+H]$^+$ = 375.1591, found = 375.1594; the ee value was 94%, $t_\text{R}$ (major) = 7.2 min, $t_\text{R}$ (minor) = 6.2 min (Chiralcel IB-H, $\lambda = 254$ nm, 10% iPrOH/hexanes, flow rate = 1.0 mL/min).
(R,E)-2-(1-Oxo-1-phenylbutan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyran[3,4-c]chromen-5-one (3o)

91% yield, a white solid; $[\alpha]_{D}^{25} = -81.74$ (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 7.1$ Hz, 2H), 7.69 – 7.63 (m, 1H), 7.62 – 7.50 (m, 5H), 7.47 (dd, $J = 8.0$ Hz, 6.5 Hz, 2H), 7.34 – 7.25 (m, 1H), 7.14 – 7.06 (m, 2H), 6.93 (d, $J = 8.0$ Hz, 1H), 3.92 (dd, $J = 11.9$ Hz, 5.7 Hz, 1H), 3.26 (dd, $J = 14.1$ Hz, 5.7 Hz, 1H), 2.72 (q, $J = 7.5$ Hz, 2H), 2.41 (dd, $J = 13.8$ Hz, 12.1 Hz, 1H), 1.14 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 197.62, 163.20, 162.39, 150.78, 148.36, 138.08, 133.63, 133.55, 130.69, 129.04, 129.02, 128.92, 128.83, 128.26, 125.08, 124.86, 124.54, 123.11, 117.07, 100.04, 31.51, 27.64, 21.55, 12.89; HRMS (APCI) m/z calcd for C$_{28}$H$_{23}$O$_4$ [M+H]$^+$ = 423.1591, found = 423.1598; the ee value was 93%, $t_8$ (major) = 20.9 min, $t_8$ (minor) = 27.0 min (Chiralcel IE-H, $\lambda = 254$ nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).

Racemic 3o

Enantiomerically enriched 3o
(R,E)-2-(3-Oxo-1-phenylbutan-2-ylidene)-4-phenyl-1,10b-dihydro-2H,5H-pyrano[3,4-c]chromen-5-one (3p)

81% yield, a colorless oil; [$\alpha$]_{D}^{25} = -48.67 (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.49 – 7.31 (m, 9H), 7.27 – 7.21 (m, 4H), 7.13 (dd, $J = 8.1$ Hz, 1.1 Hz, 1H), 4.59 (dd, $J = 14.7$ Hz, 5.7 Hz, 1H), 4.12 – 4.00 (m, 3H), 2.69 – 2.57 (m, 1H), 2.28 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 201.09, 162.42, 161.77, 155.47, 150.77, 138.46, 133.17, 130.62, 128.96, 128.88, 128.81, 128.17, 127.91, 126.61, 124.76, 122.93, 121.29, 117.11, 101.42, 32.52, 31.07, 30.14, 26.73; HRMS (APCI) m/z calcd for C$_{28}$H$_{23}$O$_4$ [M+H]$^+$ = 423.1591, found = 423.1593; the ee value was 87%, t$_R$ (minor) = 23.3 min, t$_R$ (major) = 20.0 min (Chiralcel IIE-H, $\lambda = 254$ nm, 20% iPrOH/hexanes, flow rate = 1.0 mL/min).
D. Determination of Absolute Configurations of [4+2] Cyclization Adducts

X-Ray crystal structure of 3a
E. NMR Spectra of the [4+2] Cyclization Adducts

3a

Ph

O

O

Ph

O

O

Ph

3a

Ph

O

O

Ph

O

O

Ph

3a

Ph

O

O

Ph

O

O

Ph