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Supporting Information

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Noncovalent Catalysis for Enantioselective Direct Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones

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General information: Unless stated otherwise, all reactions were carried out with distilled and dried solvents under an atmosphere of N₂ or argon; oven (120 °C) dried glassware with standard vacuum line techniques was used. Organic solvents used for carrying out reactions were dried using standard methods.¹ All work up and purifications were carried out with reagent grade solvents in air. Thin-layer chromatography was performed using Merck silica gel 60 F₂₅₄ pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, ν_{max} in cm⁻¹ and the bands are characterized as broad (br), strong (s), medium (m), and weak (w). NMR spectra were recorded on Bruker Ultrashield spectrometer at 400MHz (¹H), 100 MHz (¹³C) and 76.28 MHz (⁷⁷Se). Chemical shifts are reported in ppm from tetramethylsilane (δ 0.00) with the solvent resonance as internal standard (CDCl₃: δ 7.26 for ¹H-NMR and CDCl₃: δ 77.0 for ¹³C NMR); Me₂Se was used as the external reference for ⁷⁷Se NMR. For ¹H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, dt = doublet of a triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectrometry was performed on Micromass Q-TOF Micro instrument. Optical rotations were measured on JASCO P-2000 polarimeter. Melting points were measured in open glass capillaries using ANALAB μ -Thermocal 10 melting point apparatus. All melting points were measured in open glass capillary and values are uncorrected. Enantiomeric ratios were determined by Shimadzu LC-20AD HPLC instrument and SPD-20A UV/Vis detector using stationary phase chiral columns (25 cm $\times$ 0.46 cm) in comparison with authentic racemic compounds.

(1) W. L. F. Armarego, D. D. Perrin, C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed., Butterworth Heinemann, Boston, **2003**.

A. Substrate preparation:

3-Acetylcoumarins were prepared according to the literature procedure.²

Pyrazole-4,5-diones were prepared according to the literature procedure.³

B. Preparation of racemic products (*rac*-3):

General procedure for the preparation of racemic products:

In a glass-vial, **1** (0.05 mmol, 1.0 equiv.), **2** (0.075 mmol, 1.5 equiv.) and catalyst **VII** (0.005 mmol, 0.1 equiv.) were taken along with 0.5 mL of toluene under positive argon pressure. The resulting reaction mixture was stirred at room temperature until TLC revealed complete consumption of **1**. The racemic product (*rac*-**3**) samples for HPLC analysis were obtained by purification using preparative TLC (Merck silica-gel 60 F254 pre-coated plates of 0.25 mm thickness).

C. Procedure for catalytic enantioselective aldol reaction of **2** to **1**:

General procedure for the enantioselective aldol reaction of 3-acetylcoumarin **2** to pyrazole-4,5-dione **1**

In an oven-dried reaction tube, pyrazole-4,5-dione **1** (0.1 mmol, 1.0 equiv.), 3-acetylcoumarin **2** (0.2 mmol, 2.0 equiv.) and catalyst **VI** (0.01 mmol, 0.1 equiv.) were taken along with 2.0 ml

(2) Y. Wang, Z.-H. Yu, H.-F. Zheng, D.-Q. Shi, *Org. Biomol. Chem.* **2012**, *10*, 7739.

(3) U. Kaya, P. Chauhan, S. Mahajan, K. Deckers, A. Valkonen, K. Rissanen, D. Enders, *Angew. Chem. Int. Ed.* **2017**, *56*, 15358.

mesitylene (0.05 M). The resulting mixture was allowed to stir at 25 °C until TLC showed complete consumption of **1**. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel (100-200 mesh) column chromatography to obtain the desired aldol product **3**.

D. Characterization data of the aldol products (**3**):

2-(*tert*-Butyl)-4-hydroxy-5-methyl-4-(2-oxo-2-(2-oxo-2*H*-chromen-3-yl)ethyl)-2,4-

dihydro-3*H*-pyrazol-3-one (3aa): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3aa** as a colorless oil (29.3 mg, 0.082 mmol; 82% yield). R_f = 0.35 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3582, 3351, 2925, 2341, 2336, 1585, 1042 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.52 (s; 1H), 7.65-7.67 (m; 2H), 7.35 (d, J = 7.0 Hz; 2H), 4.66 (s; 1H), 3.84 (d, J = 16.9 Hz; 1H), 3.45 (dd, J = 16.9, 3.1 Hz; 1H), 2.01 (s; 3H), 1.50 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 194.6, 173.9, 159.1, 157.4, 155.4, 148.4, 134.9, 130.5, 125.2, 126.5, 118.1, 116.7, 77.4, 57.5, 45.7, 28.0, 13.1; **HRMS (ESI+):** Calculated for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^+$): 379.1270, found: 379.1269; $[\alpha]_D^{22}$ +28.1 (c 2.00, CHCl_3) for an enantiomerically enriched sample with 97:3 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , τ_{major} = 12.03 min, τ_{minor} = 14.48 min).

2-(*tert*-Butyl)-4-hydroxy-5-methyl-4-(2-(6-methyl-2-oxo-2*H*-chromen-3-yl)-2-oxoethyl)-2,4-

2,4-dihydro-3*H*-pyrazol-3-one (3ab): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ab** as a colorless oil (32 mg, 0.086 mmol; 86% yield). R_f = 0.35 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3861, 2584, 3393, 2928, 2365, 2339, 1726, 1572, 1364, 1032 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.50 (s; 1H), 7.47-7.49 (m; 1H), 7.43 (s; 1H), 7.25-7.27 (s; 1H), 3.83 (d, J = 17.2 Hz; 1H), 3.32 (dd, J = 17.2, 2.8 Hz; 1H), 2.42 (s; 3H), 2.03 (s; 3H), 1.50 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 195.4, 173.7, 159.4, 157.1, 153.7, 148.6, 136.3, 135.1, 130.1, 123.4, 117.9, 116.5, 77.6, 57.5, 45.0, 28.0, 20.7, 13.1; **HRMS (ESI+):** Calculated for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^+$): 393.1426, found: 393.1429; $[\alpha]_D^{22}$ +4.2 (c 1.00, CHCl_3) for an enantiomerically enriched sample with 94:6 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , τ_{major} = 12.97 min, τ_{minor} = 15.00 min).

2-(tert-Butyl)-4-(2-(6-(tert-butyl)-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-

methyl-2,4-dihydro-3H-pyrazol-3-one (3ac): Purification by silica gel (100-200 mesh) column chromatography (30% EtOAc in petroleum ether) afforded **3ac** as a colorless oil (38 mg, 0.092 mmol; 92% yield). R_f = 0.45 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3584, 3340, 2966, 2360, 1728, 1614, 1565, 1487, 1364, 1183, 983, 831 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.53 (s; 1H), 7.70-7.73 (m; 1H), 7.60 (d, J = 2.1 Hz; 1H), 7.29 (d, J = 8.8 Hz; 1H), 4.52 (s; 1H), 3.84 (d, J = 17.5 Hz; 1H), 3.40-3.45 (m; 1H), 2.01 (s; 3H), 1.49 (s; 3H), 1.35 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 194.9, 173.8, 159.5, 157.4, 153.5, 149.0, 148.4, 132.9, 126.6, 123.2, 117.6, 116.3, 77.5, 57.4, 45.5, 34.6, 31.2, 28.0, 13.1; **HRMS (ESI+):** Calculated for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^+$): 435.1896, found: 435.1893; $[\alpha]_D^{22}$ +13.9 (c 2.00, CHCl_3) for an enantiomerically enriched sample with 96:4 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , τ_{major} = 8.73 min, τ_{minor} = 12.28 min).

2-(tert-Butyl)-4-(2-(6-fluoro-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-methyl-

2,4-dihydro-3H-pyrazol-3-one (3ad): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ad** as a colorless oil (30 mg, 0.080 mmol; 80% yield). R_f = 0.35 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3368, 3927, 3854, 2362, 1734, 1614, 1566, 1490, 1363, 1265, 1189, 1091, 1021, 985, 824 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.46 (s; 1H), 7.33-7.41 (m; 3H), 3.82 (d, J = 17.5 Hz; 1H), 3.42 (d, J = 17.5 Hz; 1H), 2.01 (s; 3H), 1.49 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 194.4, 173.8, 160.1, 158.7, 157.4, 151.5, 147.3, 124.4, 122.6, 122.4, 118.8, 118.5, 115.4, 115.1, 77.5, 57.5, 45.7, 28.0, 13.0; **HRMS (ESI+):** Calculated for $\text{C}_{19}\text{H}_{19}\text{FN}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^+$): 397.1176, found: 397.1174; $[\alpha]_D^{22}$ +3.7 (c 2.00, CHCl_3) for an enantiomerically enriched sample with 92:8 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 60:40, 1.0 mL min^{-1} , τ_{major} = 6.24 min, τ_{minor} = 7.25 min).

2-(tert-Butyl)-4-(2-(6-chloro-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-methyl-

2,4-dihydro-3H-pyrazol-3-one (3ae): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ae** as a colorless oil (32 mg, 0.082 mmol; 82% yield). R_f = 0.40 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3601, 3451, 2965, 2381, 2346, 1595, 1032 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.42 (d, J = 9.0 Hz; 1H), 7.59-7.63 (m; 1H), 7.30-7.33 (m; 2H), 3.81 (d, J = 17.4 Hz; 1H), 3.41 (dd, J = 17.3, 2.3 Hz; 1H), 2.01 (s; 3H), 1.49 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 195.1, 173.7, 158.5, 157.3, 153.6, 147.0, 146.1, 134.2, 129.1, 124.5, 118.1,

77.5, 57.5, 45.6, 30.5, 28.0, 13.0; **HRMS (ESI⁺)**: Calculated for C₁₉H₁₉ClN₂O₅Na ([M + Na]⁺): 413.0880, found: 413.0881; [α]_D²² +7.1 (*c* 2.00, CHCl₃) for an enantiomerically enriched sample with 96:4 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, *n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, τ_{major} = 17.67 min, τ_{minor} = 22.92 min).

4-(2-(6-Bromo-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-2-(tert-butyl)-4-hydroxy-5-methyl-

2,4-dihydro-3H-pyrazol-3-one (3af): Purification by silica gel (100-200 mesh) column chromatography (30% EtOAc in petroleum ether) afforded **3af** as a colorless oil (35 mg, 0.080 mmol; 80% yield). **R_f** = 0.40 (30% EtOAc in petroleum ether). **FT-IR (neat)**: ν 3328, 2978, 2925, 2362, 1737, 1690, 1363, 1182, 1021, 978, 826 cm⁻¹; **¹H-NMR (400 MHz, CDCl₃)**: δ 8.46 (s; 1H), 7.82 (d, *J* = 2.1 Hz; 1H), 7.75-7.78

(m; 1H), 7.29 (d, *J* = 5.1 Hz; 1H), 3.84 (d, *J* = 18.0 Hz; 1H), 3.48 (d, *J* = 17.4 Hz; 1H), 2.04 (s; 3H), 1.52 (s; 9H); **¹³C-NMR (100 MHz, CDCl₃)**: δ 194.2, 173.8, 158.5, 157.4, 154.1, 146.8, 137.4, 132.4, 124.4, 119.6, 118.4, 117.7, 77.5, 57.5, 45.8, 28.0, 13.0; **HRMS (ESI⁺)**: Calculated for C₁₉H₁₉BrN₂O₅Na ([M + Na]⁺): 457.0375, found: 457.0372; [α]_D²² +5.7 (*c* 2.00, CHCl₃) for an enantiomerically enriched sample with 93:7 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, *n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, τ_{major} = 18.73 min, τ_{minor} = 25.19 min).

2-(tert-Butyl)-4-hydroxy-4-(2-(6-iodo-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-5-methyl-2,4-

dihydro-3H-pyrazol-3-one (3ag): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ag** as a colorless oil (34 mg, 0.070 mmol; 70% yield). **R_f** = 0.35 (30% EtOAc in petroleum ether). **FT-IR (neat)**: ν 3365, 2927, 2363, 1734, 1692, 1601, 1551, 1474, 1363, 1181, 977, 823 cm⁻¹; **¹H-NMR (400 MHz, CDCl₃)**: δ 8.42 (s; 1H), 7.97 (d, *J* = 1.9 Hz; 1H), 7.90 (dd, *J* = 8.7, 1.9

Hz; 1H), 7.11 (d, *J* = 17.4 Hz; 1H), 3.81 (d, *J* = 8.7 Hz; 1H), 3.81 (d, *J* = 17.0, 2.3 Hz; 1H), 3.42 (d, *J* = 17.0 Hz; 1H), 2.01 (s; 3H), 1.49 (s; 9H); **¹³C-NMR (100 MHz, CDCl₃)**: δ 194.3, 173.8, 158.4, 157.4, 154.8, 146.8, 143.1, 138.6, 124.3, 120.1, 118.6, 87.8, 77.5, 57.5, 45.7, 28.0, 13.0; **HRMS (ESI⁺)**: Calculated for C₁₉H₁₉IN₂O₅Na ([M + Na]⁺): 505.0236, found: 505.0236; [α]_D²² +6.4 (*c* 1.00, CHCl₃) for an enantiomerically enriched sample with 91:9 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, *n*-Hexane/EtOH = 60:40, 1.0 mL min⁻¹, τ_{major} = 8.48 min, τ_{minor} = 12.13 min).

2-(tert-Butyl)-4-hydroxy-5-methyl-4-(2-(7-methyl-2-oxo-2H-chromen-3-yl)-2-oxoethyl)- **2,4-dihydro-3H-pyrazol-3-one (3ah):**

Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ah** as a colorless oil (36 mg, 0.097 mmol; 97% yield). R_f = 0.40 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3861, 2584, 3383, 2920, 2365, 2339, 1730, 1570, 1354, 1030

cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.52 (s; 1H), 7.53 (d, J = 7.8 Hz; 1H), 7.16 (s; 2H), 4.50 (s; 1H), 3.83 (d, J = 17.4 Hz; 1H), 3.37 (d, J = 16.2 Hz; 1H), 2.49 (s; 3H), 2.02 (s; 3H), 1.50 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 195.0, 173.8, 159.5, 157.3, 155.6, 148.6, 147.2, 130.3, 126.6, 122.2, 116.9, 115.9, 77.5, 57.4, 45.3, 28.0, 22.2, 13.1; **HRMS (ESI+):** Calculated for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^+$): 393.1426, found: 393.1427; $[\alpha]_D^{22}$ +10.3 (c 1.00, CHCl_3) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , τ_{major} = 12.58 min, τ_{minor} = 16.46 min).

2-(tert-Butyl)-4-(2-(7-chloro-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-methyl- **2,4-dihydro-3H-pyrazol-3-one (3ai):**

Purification by silica gel (100-200 mesh) column chromatography (30% EtOAc in petroleum ether) afforded **3ai** as a colorless oil (30 mg, 0.077 mmol; 77% yield). R_f = 0.35 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3583, 3346, 2925, 2853, 1735, 1690, 1603, 1551, 1363, 1218, 1182, 1077,

980, 861 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.48 (s; 1H), 7.60 (d, J = 8.2 Hz; 1H), 7.31-7.35 (m; 2H), 3.81 (d, J = 17.1 Hz; 1H), 3.46 (d, J = 17.1 Hz; 1H), 2.01 (s; 3H), 1.49 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 194.2, 173.9, 158.5, 157.5, 155.5, 147.5, 141.2, 131.2, 125.9, 123.2, 117.1, 116.7, 77.4, 57.5, 45.8, 28.0, 13.0; **HRMS (ESI+):** Calculated for $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^+$): 413.0880, found: 413.0878; $[\alpha]_D^{22}$ +9.2 (c 2.00, CHCl_3) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , τ_{major} = 13.77 min, τ_{minor} = 19.46 min).

4-(2-(7-Bromo-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-2-(tert-butyl)-4-hydroxy-5-methyl- **2,4-dihydro-3H-pyrazol-3-one (3aj):**

Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3aj** as a colorless oil (37 mg, 0.085 mmol; 85% yield). R_f = 0.40 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3583, 3343, 2925, 1733, 1689, 1600, 1549, 1363, 1181, 1023, 980, 861 cm^{-1} ;

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.48 (s; 1H), 7.47-7.53 (m; 3H), 4.47 (s; 1H), 3.81 (d, J = 17.4 Hz; 1H), 3.42 (d, J = 17.4 Hz; 1H), 2.01 (s; 3H), 1.49 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 194.4, 173.8, 158.4, 157.3, 155.4, 147.6, 131.2, 129.6, 128.8, 123.5, 120.1, 117.0, 77.6, 57.5,

45.6, 28.0, 13.0; **HRMS (ESI+)**: Calculated for $C_{19}H_{19}BrN_2O_5Na$ ($[M + Na]^+$): 457.0375, found: 457.0374; $[\alpha]_D^{22} +5.4$ (c 2.00, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 14.90\text{ min}$, $\tau_{\text{minor}} = 21.66\text{ min}$).

2-(tert-Butyl)-4-hydroxy-5-methyl-4-(2-(8-methyl-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-2,4-dihydro-3H-pyrazol-3-one (3ak): Purification by silica gel (100-200 mesh) column

chromatography (35% EtOAc in petroleum ether) afforded **3ak** as a colorless oil (35 mg, 0.094 mmol; 95% yield). $R_f = 0.45$ (30% EtOAc in petroleum ether). **FT-IR (neat)**: ν 3572, 3345, 2924, 2351, 2346, 1585, 1034 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, $CDCl_3$)**: δ 8.52 (s; 1H), 7.50 (t, $J = 7.6\text{ Hz}$; 2H), 7.22-7.26 (m; 1H), 4.29 (s; 1H), 3.83 (d, $J = 17.6$

Hz; 1H), 3.34-3.40 (m; 1H), 2.45 (s; 3H), 2.02 (s; 3H), 1.49 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, $CDCl_3$)**: δ 195.2, 173.7, 159.3, 157.2, 153.8, 149.0, 136.3, 128.3, 126.4, 124.8, 123.1, 117.9, 77.6, 57.4, 45.3, 28.0, 15.4, 13.1; **HRMS (ESI+)**: Calculated for $C_{20}H_{22}N_2O_5Na$ ($[M + Na]^+$): 393.1426, found: 393.1426; $[\alpha]_D^{22} +3.5$ (c 2.00, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 10.07\text{ min}$, $\tau_{\text{minor}} = 13.65\text{ min}$).

4-(2-(8-Bromo-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-2-(tert-butyl)-4-hydroxy-5-methyl-

2,4-dihydro-3H-pyrazol-3-one (3al): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3al** as a colorless oil (32 mg, 0.074 mmol; 74% yield).

$R_f = 0.40$ (30% EtOAc in petroleum ether). **FT-IR (neat)**: ν 3583, 3351, 2925, 2361, 2336, 1595, 1022 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, $CDCl_3$)**: δ 8.48 (s; 1H), 7.89 (d, $J = 7.9\text{ Hz}$; 1H), 7.61 (d, $J = 7.9\text{ Hz}$; 1H), 7.22-7.24 (m; 1H), 3.82 (d, $J = 17.3\text{ Hz}$; 1H), 3.37 (d, $J = 17.3\text{ Hz}$; 1H), 2.03 (s; 3H), 1.50 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, $CDCl_3$)**: δ 194.6, 173.7, 158.1, 157.1, 152.1, 149.4, 148.0, 138.2, 129.7, 125.8, 124.2, 119.3, 110.3, 77.5, 57.5, 45.3, 28.0, 13.1; **HRMS (ESI+)**: Calculated for $C_{19}H_{19}BrN_2O_5Na$ ($[M + Na]^+$): 457.0375, found: 457.0375; $[\alpha]_D^{22} +2.6$ (c 2.00, $CHCl_3$) for an enantiomerically enriched sample with 81:19 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 15.17\text{ min}$, $\tau_{\text{minor}} = 19.67\text{ min}$).

2-(tert-Butyl)-4-(2-(6,8-dimethyl-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-

methyl-2,4-dihydro-3H-pyrazol-3-one (3am): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3am** as a colorless oil (35 mg, 0.091 mmol; 91% yield). $R_f = 0.30$ (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3754, 3585, 3273, 2966, 1735, 1671, 1595, 1462, 1186, 1073, 931 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.39 (s; 1H), 7.18 (s; 2H), 4.31

(s; 1H), 3.75 (d, $J = 17.4$ Hz; 1H), 3.30 (d, $J = 17.4$ Hz; 1H), 2.35 (s; 6H), 1.95 (s; 3H), 2.30 (s; 3H), 1.95 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 195.4, 173.8, 159.6, 157.2, 152.1, 149.0, 137.7, 134.6, 127.8, 126.0, 123.0, 117.7, 77.6, 57.4, 45.2, 28.0, 20.6, 15.3, 13.1; **HRMS (ESI $^{+}$):** Calculated for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^{+}$): 407.1583, found: 407.1581; $[\alpha]_D^{22} +6.2$ (c 2.00, CHCl_3) for an enantiomerically enriched sample with 96:4 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 10.69$ min, $\tau_{\text{minor}} = 13.68$ min).

2-(tert-Butyl)-4-(2-(6,8-dichloro-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-

methyl-2,4-dihydro-3H-pyrazol-3-one (3an): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3an** as a colorless oil (36 mg, 0.085 mmol; 85% yield). $R_f = 0.40$ (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3694, 3593, 3183, 2926, 1735, 1690, 1595, 1462, 1174, 1023 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.41 (s; 1H), 7.68-7.69 (m; 1H), 7.56

(d, $J = 2.3$ Hz; 1H), 3.80 (d, $J = 17.3$ Hz; 1H), 3.42-3.49 (m; 1H), 2.01 (s; 3H), 1.49 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 193.9, 173.8, 157.5, 157.4, 149.5, 146.5, 134.4, 130.3, 127.9, 125.1, 122.7, 119.9, 77.5, 57.6, 45.8, 28.0, 13.0; **HRMS (ESI $^{+}$):** Calculated for $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^{+}$): 447.0490, found: 447.0492; $[\alpha]_D^{22} +5.39$ (c 2.00, CHCl_3) for an enantiomerically enriched sample with 95:5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 19.25$ min, $\tau_{\text{minor}} = 27.46$ min).

2-(tert-Butyl)-4-(2-(6-chloro-8-methyl-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-

methyl-2,4-dihydro-3H-pyrazol-3-one (3ao): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ao** as a colorless oil (34 mg, 0.084 mmol; 84% yield). $R_f = 0.40$ (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3758, 3585, 3273, 2929, 1745, 1680, 1585, 1362, 1184, 1023, 831 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.41 (s; 1H), 7.46

(s; 2H), 4.44 (s; 1H), 3.82 (d, $J = 17.2$ Hz; 1H), 3.43 (d, $J = 17.2$ Hz; 1H), 2.44 (s; 3H), 2.02 (s; 3H), 1.49 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 194.6, 173.8, 158.7, 157.3, 151.2, 147.6,

135.7, 129.9, 128.4, 126.9, 124.1, 118.7, 77.5, 57.5, 45.6, 28.0, 15.3, 13.1 ; **HRMS (ESI+)**: Calculated for $C_{20}H_{21}ClN_2O_5Na$ ($[M + Na]^+$): 427.1037, found: 427.1039; $[\alpha]_D^{22} +5.0$ (c 2.00, $CHCl_3$) for an enantiomerically enriched sample with 94:6 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/ EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 14.63\text{ min}$, $\tau_{\text{minor}} = 22.36\text{ min}$).

2-(tert-Butyl)-4-(2-(7,8-dimethyl-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-

methyl-2,4-dihydro-3H-pyrazol-3-one (3ap): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ap** as a colorless oil (34 mg, 0.088 mmol; 88% yield). $R_f = 0.35$ (30% EtOAc in petroleum ether). **FT-IR (neat)**: ν 3582, 3340, 2924, 2363, 1726, 1598, 1554, 1362, 1185, 1100, 1021, 974, 814 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, $CDCl_3$)**: δ 8.44 (s;

1H), 7.32 (d, $J = 8.0\text{ Hz}$; 1H), 7.09 (d, $J = 8.0\text{ Hz}$; 1H), 4.46 (s; 1H), 3.77 (d, $J = 17.4\text{ Hz}$; 1H), 3.36 (d, $J = 17.4\text{ Hz}$; 1H), 2.36 (s; 3H), 2.29 (s; 3H), 1.96 (s; 3H), 1.43 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, $CDCl_3$)**: δ 195.1, 173.8, 159.6, 157.4, 153.7, 149.2, 145.8, 127.5, 126.8, 124.7, 121.7, 116.0, 77.5, 57.4, 45.4, 28.0, 20.8, 13.1, 11.4; **HRMS (ESI+)**: Calculated for $C_{21}H_{24}N_2O_5Na$ ($[M + Na]^+$): 407.1583, found: 407.1583; $[\alpha]_D^{22} +5.2$ (c 2.00, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 10.38\text{ min}$, $\tau_{\text{minor}} = 14.35\text{ min}$).

2-(tert-Butyl)-4-(2-(5,8-dimethyl-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-

methyl-2,4-dihydro-3H-pyrazol-3-one (3aq): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3aq** as a colorless oil (36 mg, 0.094 mmol; 94% yield). $R_f = 0.35$ (30% EtOAc in petroleum ether). **FT-IR (neat)**: ν 3754, 3583, 3283, 2926, 1735, 1680, 1585, 1362, 1184,

1023, 831 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, $CDCl_3$)**: δ 8.688-8.692 (m; 1H), 7.32 (d, $J = 7.5\text{ Hz}$; 1H), 6.99 (d, $J = 7.5\text{ Hz}$; 1H), 4.35 (s; 1H), 3.80 (d, $J = 17.4\text{ Hz}$; 1H), 3.34-3.38 (m; 1H), 2.49 (s; 3H), 2.33 (s; 3H), 2.95 (s; 3H), 1.44 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, $CDCl_3$)**: δ 195.3, 173.8, 159.3, 157.3, 154.4, 146.2, 136.9, 136.2, 125.9, 123.9, 121.9, 117.0, 77.5, 57.4, 45.4, 28.0, 18.2, 15.2, 13.1; **HRMS (ESI+)**: Calculated for $C_{21}H_{24}N_2O_5Na$ ($[M + Na]^+$): 407.1583, found: 407.1586; $[\alpha]_D^{22} +6.6$ (c 2.00, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 9.96\text{ min}$, $\tau_{\text{minor}} = 14.47\text{ min}$).

2-(tert-Butyl)-4-(2-(5,7-dimethyl-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-

methyl-2,4-dihydro-3H-pyrazol-3-one (3ar): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ar** as a colorless oil (34 mg, 0.088 mmol; 88% yield). $R_f = 0.30$ (30% EtOAc in petroleum ether). **FT-IR** (neat): ν 3748, 3336, 2974, 2925, 2363, 1730, 1594, 1549, 1360,

1189, 1022, 850 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.74 (s; 1H), 6.99 (s; 2H), 4.47 (s; 1H), 3.86 (d, $J = 17.7$ Hz; 1H), 3.38 (d, $J = 17.4$ Hz; 1H), 2.55 (s; 3H), 2.43 (s; 3H), 2.02 (s; 3H), 1.50 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 195.3, 173.8, 159.5, 157.3, 156.4, 147.2, 145.9, 139.2, 127.8, 121.1, 115.0, 114.8, 77.6, 57.4, 45.2, 28.0, 22.2, 18.3, 13.1; $[\alpha]_D^{22} +5.4$ (c 2.00, CHCl_3) for an enantiomerically enriched sample with 96:4 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/ EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 12.03$ min, $\tau_{\text{minor}} = 17.23$ min).

2-(tert-Butyl)-4-hydroxy-4-(2-oxo-2-(2-oxo-2H-chromen-3-yl)ethyl)-5-phenyl-2,4-

dihydro-3H-pyrazol-3-one (3ba): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ba** as a colorless oil (39 mg, 0.093 mmol; 93% yield).

$R_f = 0.45$ (30% EtOAc in petroleum ether). **FT-IR** (neat): ν 3374, 2970, 2901, 1717, 1690, 1627, 1545, 1409, 1347, 1163, 1071, 965 cm^{-1} ;

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.46 (s; 1H), 7.93-7.95 (m; 2H), 7.60-7.64 (m; 2H), 7.31-7.35 (m; 5H), 4.45 (s; 1H), 4.08 (d, $J = 17.5$ Hz; 1H), 3.65 (d, $J = 17.5$ Hz; 1H), 1.59 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 194.4, 174.3, 159.1, 155.3, 154.4, 148.4, 134.8, 130.5, 130.2, 130.0, 128.6, 126.5, 125.1, 123.4, 118.1, 116.7, 77.9, 58.1, 47.4, 28.1; **HRMS (ESI+):** Calculated for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M} + \text{Na}]^+$): 441.1426, found: 441.1429; $[\alpha]_D^{22} +3.8$ (c 2.00, CHCl_3) for an enantiomerically enriched sample with 86:14 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 11.41$ min, $\tau_{\text{minor}} = 15.56$ min).

2-(tert-Butyl)-5-(4-chlorophenyl)-4-hydroxy-4-(2-oxo-2-(2-oxo-2H-chromen-3-yl)ethyl)-

2,4-dihydro-3H-pyrazol-3-one (3ca): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3ca** as a colorless oil (38 mg, 0.084 mmol; 84% yield).

$R_f = 0.40$ (30% EtOAc in petroleum ether). **FT-IR** (neat): ν 3344, 2978, 2928, 1715, 1691, 1607, 1560, 1454, 1367, 1183, 1091, 975, 838 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, CDCl_3):** δ 8.45 (s; 1H), 7.87 (d,

$J = 8.4$ Hz; 2H), 7.61-7.65 (m; 2H), 7.31-7.33 (m; 5H), 4.66 (s; 1H); 4.06 (d, $J = 17.7$ Hz; 1H), 3.69 (d, $J = 17.7$ Hz; 1H), 1.59 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, CDCl_3):** δ 194.0, 174.3, 159.1, 155.3, 153.6, 148.5, 135.9, 134.9, 130.5, 128.9, 128.7, 127.8, 125.1, 123.2, 118.1, 116.7, 77.7,

58.2, 47.7, 28.0; **HRMS (ESI+)**: Calculated for $C_{24}H_{21}ClN_2O_5Na$ ($[M + Na]^+$): 475.1037, found: 475.1037; $[\alpha]_D^{22} +3.2$ (c 2.00, $CHCl_3$) for an enantiomerically enriched sample with 93.5:6.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 11.11\text{ min}$, $\tau_{\text{minor}} = 15.67\text{ min}$).

2-(tert-Butyl)-4-hydroxy-4-(2-oxo-2-(2-oxo-2H-chromen-3-yl)ethyl)-5-(p-tolyl)-2,4-

dihydro-3H-pyrazol-3-one (3da): Purification by silica gel (100-200 mesh) column chromatography (35% EtOAc in petroleum ether) afforded **3da** as a colorless oil (37 mg, 0.086 mmol; 86% yield). $R_f = 0.40$ (30% EtOAc in petroleum ether). **FT-IR (neat)**: ν 3583, 3344, 2925, 1731, 1688, 1607, 1560, 1452, 1368, 1182, 1021, 975, 826 cm^{-1} ; **$^1\text{H-NMR}$ (400 MHz, $CDCl_3$)**: δ 8.42 (s; 1H), 7.82 (d,

$J = 8.0\text{ Hz}$; 2H), 7.58-7.64 (m; 2H), 7.29-7.32 (m; 2H), 7.15 (d, $J = 8.0\text{ Hz}$; 2H), 4.58 (s; 1H), 4.06 (d, $J = 17.4\text{ Hz}$; 1H), 3.67 (d, $J = 17.4\text{ Hz}$; 1H), 2.31 (s; 3H), 1.59 (s; 9H); **$^{13}\text{C-NMR}$ (100 MHz, $CDCl_3$)**: δ 194.2, 174.3, 159.0, 155.3, 148.2, 140.1, 134.7, 130.4, 129.3, 127.5, 126.4, 125.0, 123.4, 118.1, 116.6, 77.9, 58.0, 47.7, 28.1, 21.4; **HRMS (ESI+)**: Calculated for $C_{25}H_{24}N_2O_5Na$ ($[M + Na]^+$): 455.1583, found: 455.1580; $[\alpha]_D^{22} +2.9$ (c 2.00, $CHCl_3$) for an enantiomerically enriched sample with 78:22 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, n -Hexane/EtOH = 85:15, 1.0 mL min^{-1} , $\tau_{\text{major}} = 9.94\text{ min}$, $\tau_{\text{minor}} = 16.16\text{ min}$).

Non-Covalent Catalysis for Enantioselective Direct Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones

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SUPPORTING INFORMATION: PART B

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.398	491602	50.962
2	14.765	473038	49.038
Total		964640	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.028	2570981	96.885
2	14.475	82674	3.115
Total		2653655	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.070	80272	51.820
2	15.025	74635	48.180
Total		154908	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.973	1036719	93.903
2	15.003	67310	6.097
Total		1104028	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.010	1312840	50.019
2	12.602	1311855	49.981
Total		2624695	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.725	5921831	95.775
2	12.280	261205	4.225
Total		6183036	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.313	627691	49.538
2	7.311	639410	50.462
Total		1267100	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 60:40, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.241	2389974	92.300
2	7.254	199386	7.700
Total		2589361	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.290	133054	50.476
2	25.618	130546	49.524
Total		263600	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.728	2784816	92.921
2	25.190	212160	7.079
Total		2996976	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.497	662941	50.574
2	12.119	647904	49.426
Total		1310845	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 60:40, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.475	2783704	90.726
2	12.128	284551	9.274
Total		3068254	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.793	335299	50.179
2	16.394	332910	49.821
Total		668209	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.580	6090000	98.110
2	16.459	117287	1.890
Total		6207287	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.044	173331	49.527
2	19.756	176643	50.473
Total		349973	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.774	3490668	98.351
2	19.463	58522	1.649
Total		3549190	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.985	266367	50.183
2	21.573	264420	49.817
Total		530786	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.901	2844553	95.983
2	21.659	119034	4.017
Total		2963587	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.226	109387	50.531
2	13.693	107088	49.469
Total		216475	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm) 273-01

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.069	9492133	97.655
2	13.652	227930	2.345
Total		9720063	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.246	470612	49.440
2	19.710	481281	50.560
Total		951893	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.168	683155	81.032
2	19.669	159915	18.968
Total		843070	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.734	702496	50.090
2	13.626	699962	49.910
Total		1402458	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.689	4295432	95.777
2	13.677	189390	4.223
Total		4484822	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.805	547740	50.072
2	26.632	546165	49.928
Total		1093906	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm) 272-01

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.252	3282702	94.591
2	27.456	187698	5.409
Total		3470400	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.648	1012695	49.651
2	22.257	1026934	50.349
Total		2039629	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.630	1641005	93.984
2	22.363	105037	6.016
Total		1746042	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.337	1488702	50.152
2	14.056	1479696	49.848
Total		2968398	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm) 258-01

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.379	8782917	97.165
2	14.349	256248	2.835
Total		9039165	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.065	80298	50.691
2	14.468	78108	49.309
Total		158406	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.964	2280740	99.327
2	14.468	15461	0.673
Total		2296201	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.370	168654	50.087
2	17.350	168069	49.913
Total		336723	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm) 275-01

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.030	6196873	95.873
2	17.227	266775	4.127
Total		6463649	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.455	1470590	50.134
2	15.508	1462719	49.866
Total		2933310	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.411	2038213	86.029
2	15.563	330995	13.971
Total		2369208	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.320	519250	50.429
2	15.827	510418	49.571
Total		1029668	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm) 341-01

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.105	3357045	93.498
2	15.668	233438	6.502
Total		3590483	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.000	297714	50.612
2	16.211	290513	49.388
Total		588227	100.000

Daicel Chiralpak IB column (*n*-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.941	503007	77.955
2	16.157	142245	22.045
Total		645252	100.000