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

Bidisha Ray, Soumya Jyoti Singha Roy, and Santanu Mukherjee*This manuscript is part of a . For the joint special collection with the European Journal of Organic Chemistry on the same topic, please click .
Non-Covalent Catalysis for Enantioselective Direct Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones

Bidisha Ray, Soumya Jyoti Singha Roy and Santanu Mukherjee*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, INDIA

sm@iisc.ac.in

SUPPORTING INFORMATION: PART A

General information S-2
A. Substrate preparation S-3
B. Preparation of racemic products (rac-3) S-3
C. Procedure for catalytic enantioselective aldol reaction of 2 to 1 S-3
D. Characterization data of the aldol products (3) S-4
**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 × 0.46 cm) in comparison with authentic racemic compounds.

---

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:

\[ \text{rac-3} \]

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

\[ \text{rac-3} \]

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

---


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-2H-chromen-3-yl)ethyl)-2,4-
dihydro-3H-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): \( \nu \) 3582, 3351, 2925, 2341, 2336, 1585, 1042 cm\(^{-1}\); \( ^1\text{H-NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 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\(_3\)): \( \delta \) 194.6, 173.9, 159.1, 157.4, 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 C\(_{19}\)H\(_{20}\)N\(_2\)O\(_5\)Na ([M + 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\(^{-1}\), \( \tau_{\text{major}} = 12.03 \) min, \( \tau_{\text{minor}} = 14.48 \) min).

2-(tert-Butyl)-4-hydroxy-5-methyl-4-(2-(6-methyl-2-oxo-2H-chromen-3-yl)-2-oxoethyl)-
2,4-dihydro-3H-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): \( \nu \) 3861, 2584, 3393, 2928, 2365, 2339, 1726, 1572, 1364, 1032 cm\(^{-1}\); \( ^1\text{H-NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 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\(_3\)): \( \delta \) 195.4, 173.7, 159.4, 157.1, 153.7, 148.6, 136.3, 135.1, 123.4, 117.9, 116.5, 77.6, 57.5, 45.0, 28.0, 20.7, 13.1; HRMS (ESI+): Calculated for C\(_{20}\)H\(_{22}\)N\(_2\)O\(_5\)Na ([M + 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\(^{-1}\), \( \tau_{\text{major}} = 12.97 \) min, \( \tau_{\text{minor}} = 15.00 \) 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 (3ae): Purification by silica gel (100-200 mesh) column chromatography (30% EtOAc in petroleum ether) afforded 3ae as a colorless oil (38 mg, 0.092 mmol; 92% yield). \( R_t = 0.45 \) (30% EtOAc in petroleum ether). \( R_f = 0.29 \) (30% EtOAc in petroleum ether). FT-IR (neat): ν 3384, 3340, 2966, 2360, 1728, 1614, 1565, 1487, 1364, 1183, 983, 831 cm\(^{-1}\); \(^1\)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; 9H); \(^13\)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 C\(_{23}\)H\(_{28}\)N\(_2\)O\(_3\)Na ([M + 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\(^{-1}\), \( \tau_{major} = 8.73 \) min, \( \tau_{minor} = 12.28 \) 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). \( R_t = 0.35 \) (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\(^{-1}\); \(^1\)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); \(^13\)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 C\(_{19}\)H\(_{19}\)FN\(_2\)O\(_3\)Na ([M + 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\(^{-1}\), \( \tau_{major} = 6.24 \) min, \( \tau_{minor} = 7.25 \) 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). \( R_t = 0.40 \) (30% EtOAc in petroleum ether). FT-IR (neat): ν 3601, 3451, 2965, 2381, 2346, 1595, 1032 cm\(^{-1}\); \(^1\)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); \(^13\)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 C_{19}H_{19}ClN_{2}O_{5}Na ([M + Na]^+): 413.0880, found: 413.0881; [α]_D^{22} +7.1 (c 2.00, CHCl_3) 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 = 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). Rr = 0.40 (30% EtOAc in petroleum ether). **FT-IR (neat):** ν 3328, 2978, 2925, 2363, 1737, 1690, 1363, 1182, 1021, 978, 826 cm⁻¹; **1H-NMR (400 MHz, CDCl_3):** δ 8.46 (s; 1H), 7.82 (d, J = 1.9 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, CDCl_3):** 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 C_{19}H_{19}BrN_{2}O_{5}Na ([M + Na]^+): 457.0375, found: 457.0372; [α]_D^{22} +5.7 (c 2.00, CHCl_3) 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). Rr = 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, CDCl_3):** 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, CDCl_3):** δ 194.3, 173.8, 158.4, 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 C_{19}H_{19}I_{2}O_{5}Na ([M + Na]^+): 505.0236, found: 505.0236; [α]_D^{22} +6.4 (c 1.00, CHCl_3) 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). Rf = 0.40 (30% EtOAc in petroleum ether). FT-IR (neat): v 3413, 2925, 1733, 1689, 1600, 1549, 1363, 1181, 1023, 980, 861 cm⁻¹.

1H-NMR (400 MHz, CDCl₃): 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); 13C-NMR (100 MHz, CDCl₃): 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 C₂₀H₂₂N₂O₅Na ([M + Na]+): 393.1426, found: 393.1427; [α]D²² +10.3 (c 1.00, CHCl₃) 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, t_major = 12.58 min, t_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). Rf = 0.35 (30% EtOAc in petroleum ether). FT-IR (neat): v 3413, 2925, 1735, 1690, 1603, 1551, 1363, 1218, 1182, 1077, 980, 861 cm⁻¹; 1H-NMR (400 MHz, CDCl₃): 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); 13C-NMR (100 MHz, CDCl₃): 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 C₁₉H₁₈ClN₂O₅Na ([M + Na]+): 413.0880, found: 413.0878; [α]D²² +9.2 (c 2.00, CHCl₃) 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, t_major = 13.77 min, t_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, 0.087 mmol; 85% yield). Rf = 0.40 (30% EtOAc in petroleum ether). FT-IR (neat): v 3413, 2925, 1735, 1689, 1600, 1549, 1363, 1181, 1023, 980, 861 cm⁻¹; 1H-NMR (400 MHz, CDCl₃): 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); 13C-NMR (100 MHz, CDCl₃): 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.
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-A, Page S-8

45.6, 28.0, 13.0; HRMS (ESI+): Calculated for C_{19}H_{19}BrN_{2}O_{5}Na ([M + Na]⁺): 457.0375, found: 457.0374; [α]D^{22} +5.4 (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} = 14.90 min, τ_{minor} = 21.66 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; ¹H-NMR (400 MHz, CDCl₃): δ 8.52 (s; 1H), 7.50 (t, J = 7.6 Hz; 2H), 7.22-7.26 (m; 1H), 4.29 (s; 1H), 3.83 (d, J = 17.6 Hz; 1H), 3.45-3.40 (m; 1H), 2.45 (s; 3H), 2.02 (s; 3H), 1.49 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): 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_{2}O_{5}Na ([M + Na]⁺): 393.1426, found: 393.1426; [α]D^{22} +3.5 (c 2.00, CHCl₃) 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} = 10.07 min, τ_{minor} = 13.65 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; ¹H-NMR (400 MHz, CDCl₃): δ 8.48 (s; 1H), 7.89 (d, J = 7.9 Hz; 1H), 7.61 (d, J = 7.9 Hz; 1H), 7.22-7.24 (m; 1H), 3.82 (d, J = 17.3 Hz; 1H), 3.37 (d, J = 17.3 Hz; 1H), 2.03 (s; 3H), 1.50 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): δ 194.6, 173.7, 158.1, 157.2, 153.8, 149.4, 148.0, 138.2, 129.7, 125.8, 119.3, 110.3, 77.5, 57.5, 45.3, 28.0, 13.1; HRMS (ESI+): Calculated for C_{19}H_{19}BrN_{2}O_{5}Na ([M + Na]⁺): 457.0375, found: 457.0375; [α]D^{22} +2.6 (c 2.00, CHCl₃) 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, τ_{major} = 15.17 min, τ_{minor} = 19.67 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). \(R_t = 0.30\) (30% EtOAc in petroleum ether). FT-IR (neat): \(\nu\) 3754, 3585, 3273, 2966, 1735, 1671, 1595, 1462, 1186, 1073, 931 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 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 C\(_{21}\)H\(_{24}\)N\(_2\)O\(_5\)Na ([M + 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). \(R_t = 0.40\) (30% EtOAc in petroleum ether). FT-IR (neat): \(\nu\) 3694, 3593, 3183, 2966, 1735, 1690, 1595, 1462, 1174, 1023 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 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 C\(_{19}\)H\(_{18}\)Cl\(_2\)N\(_2\)O\(_3\)Na ([M + 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). \(R_t = 0.40\) (30% EtOAc in petroleum ether). FT-IR (neat): \(\nu\) 3758, 3585, 3273, 2929, 1745, 1680, 1585, 1362, 1184, 1023, 831 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 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\textsubscript{20}H\textsubscript{20}ClN\textsubscript{2}O\textsubscript{3}Na ([M + Na]+): 427.1037, found: 427.1039; \([\alpha]\)D\textsuperscript{22} +5.0 (c 2.00, CHCl\textsubscript{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\textsuperscript{-1}, \(\tau\)\textsubscript{major} = 14.63 min, \(\tau\)\textsubscript{minor} = 22.36 min).

2-(\textit{tert}-Butyl)-4-(2-(7,8-dimethyl-2-oxo-2\textit{H}-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-methyl-2,4-dihydro-3\textit{H}-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). \(R\)\textsubscript{r} = 0.35 (30% EtOAc in petroleum ether). FT-IR (neat): \(\nu\) 3582, 3340, 2924, 2363, 1726, 1598, 1554, 1362, 1185, 1100, 1021, 974, 814 cm\textsuperscript{-1}, \(^1\)H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.44 (s; 1H), 7.32 (d, \(J = 8.0\) Hz; 1H), 7.09 (d, \(J = 8.0\) Hz; 1H), 4.46 (s; 1H), 3.77 (d, \(J = 17.4\) Hz; 1H), 3.36 (d, \(J = 17.4\) Hz; 1H), 2.36 (s; 3H), 2.29 (s; 3H), 1.96 (s; 3H), 1.43 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 195.1, 173.8, 159.6, 157.4, 153.7, 149.2, 145.8, 145.5, 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\textsubscript{21}H\textsubscript{20}N\textsubscript{2}O\textsubscript{3}Na ([M + Na]+): 407.1583, found: 407.1583; \([\alpha]\)D\textsuperscript{22} +5.2 (c 2.00, CHCl\textsubscript{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\textsuperscript{-1}, \(\tau\)\textsubscript{major} = 10.38 min, \(\tau\)\textsubscript{minor} = 14.35 min).

2-(\textit{tert}-Butyl)-4-(2-(5,8-dimethyl-2-oxo-2\textit{H}-chromen-3-yl)-2-oxoethyl)-4-hydroxy-5-methyl-2,4-dihydro-3\textit{H}-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, 0.09 mmol; 94% yield). \(R\)\textsubscript{r} = 0.35 (30% EtOAc in petroleum ether). FT-IR (neat): \(\nu\) 3754, 3583, 3283, 2926, 1726, 1585, 1362, 1184, 1023, 831 cm\textsuperscript{-1}; \(^1\)H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.688-8.692 (m; 1H), 7.32 (d, \(J = 7.5\) Hz; 1H), 6.99 (d, \(J = 7.5\) Hz; 1H), 4.35 (s; 1H), 3.80 (d, \(J = 17.4\) Hz; 1H), 3.34-3.38 (m; 1H), 2.49 (s; 3H), 2.33 (s; 3H), 2.95 (s; 3H), 1.44 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 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\textsubscript{21}H\textsubscript{20}N\textsubscript{2}O\textsubscript{3}Na ([M + Na]+): 407.1586, found: 407.1586; \([\alpha]\)D\textsuperscript{22} +6.6 (c 2.00, CHCl\textsubscript{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\textsuperscript{-1}, \(\tau\)\textsubscript{major} = 9.96 min, \(\tau\)\textsubscript{minor} = 14.47 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): \( \nu \) 3748, 3336, 2974, 2925, 2363, 1730, 1594, 1549, 1540, 1539, 1532, 1389, 1259, 1191, 1188, 1168, 777, 757 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.74 (s; 1H), 6.98 (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); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \( \delta \) 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\(^{-1}\), \( \tau \) major = 12.03 min, \( \tau \) 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): \( \nu \) 3374, 2970, 2901, 2977, 1717, 1690, 1627, 1545, 1409, 1347, 1163, 1071, 965 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 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); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \( \delta \) 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 C\(_{24}\)H\(_{22}\)N\(_2\)O\(_5\)Na ([M + 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\(^{-1}\), \( \tau \) major = 11.41 min, \( \tau \) 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): \( \nu \) 3344, 2978, 2928, 1715, 1691, 1607, 1560, 1454, 1367, 1183, 1091, 975, 838 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 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); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \( \delta \) 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,
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-A, Page S-12

58.2, 47.7, 28.0; HRMS (ESI+): Calculated for C_{24}H_{21}ClN_{2}O_{5}Na ([M + Na]): 475.1037, found: 475.1037; [α]_{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, τ_{major} = 11.11 min, τ_{minor} = 15.67 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; ¹H-NMR (400 MHz, CDCl₃): δ 8.42 (s; 1H), 7.82 (d, J = 8.0 Hz; 2H), 7.58-7.64 (m; 2H), 7.29-7.32 (m; 2H), 7.15 (d, J = 8.0 Hz; 2H), 4.58 (s; 1H), 4.06 (d, J = 17.4 Hz; 1H), 3.67 (d, J = 17.4 Hz; 1H), 2.31 (s; 3H), 1.59 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): 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_{2}O_{5}Na ([M + Na]): 455.1583, found: 455.1580; [α]_{D}^{22} +2.9 (c 2.00, CHCl₃) 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, τ_{major} = 9.94 min, τ_{minor} = 16.16 min).
Non-Covalent Catalysis for Enantioselective Direct Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones

Bidisha Ray, Soumya Jyoti Singha Roy and Santanu Mukherjee*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, INDIA

sm@iisc.ac.in

SUPPORTING INFORMATION: PART B
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-2
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-3

Daicel Chiralpak IB column \( (n\text{-Hexane/EtOH} = 85:15, \text{1.0 mL min}^{-1}, 20 \, ^\circ \text{C}, 254 \text{ nm}) \)
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-5

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

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.070</td>
<td>80272</td>
<td>51.820</td>
</tr>
<tr>
<td>2</td>
<td>15.025</td>
<td>74635</td>
<td>48.180</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>154908</td>
<td>100.000</td>
</tr>
</tbody>
</table>

PDA Ch1 254nm 4mm

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.973</td>
<td>1036719</td>
<td>95.903</td>
</tr>
<tr>
<td>2</td>
<td>15.003</td>
<td>67210</td>
<td>6.097</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1104028</td>
<td>100.000</td>
</tr>
</tbody>
</table>
Aldol Reaction of 3-Acetlycoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-6
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min$^{-1}$, 20 °C, 254 nm)
Daicel Chiralpak IB column (n-Hexane/EtOH = 60:40, 1.0 mL min⁻¹, 20 °C, 254 nm)
Aldol Reaction of 3-Acetyl coumarins to Pyrazole-4,5-diones: Ray et al., SL-Part-B, Page S-10
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-12
Daicel Chiralpak IB column \((n\text{-Hexane/EtOH} = 85:15, \text{1.0 mL min}^{-1}, 20 \, ^{\circ}\text{C}, 254 \, \text{nm})\)
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-14
Daicel Chiralpak IB column (n-Hexane/EtOH = 60:40, 1.0 mL min\(^{-1}\), 20 °C, 254 nm)
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min$^{-1}$, 20 °C, 254 nm)
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min$^{-1}$, 20 °C, 254 nm) 273-01
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-24
Daicel Chiralpak IB column ($n$-Hexane/EtOH = 85:15, 1.0 mL min$^{-1}$, 20 °C, 254 nm)
Aldol Reaction of 3-Acetyl coumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-26
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-27

Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-28
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-29

Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min\(^{-1}\), 20 °C, 254 nm) 272-01
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-31

Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-32
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-33

Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min\(^{-1}\), 20 °C, 254 nm) 258-01
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-34
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm) 275-01
Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm)
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-40
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-41

Daicel Chiralpak IB column (n-Hexane/EtOH = 85:15, 1.0 mL min⁻¹, 20 °C, 254 nm) 341-01
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-42
Aldol Reaction of 3-Acetylcoumarins to Pyrazole-4,5-diones: Ray et al., SI-Part-B, Page S-43

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