Supplemental material for:

**Cu(II)-PHOX Catalyzed Enantioselective Malonate Addition onto 3-Hydroxy 2-Oxindoles: Application in the Synthesis of Dimeric Pyrroloindoline Alkaloids**

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Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under an inert atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled over sodium/benzophenone ketyl. Dichloromethane (CH₂Cl₂), toluene, and benzene were distilled over calcium hydride. All other solvents and reagents were used as received unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath temperature. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silica gel of particle size 100-200 mesh was used for flash chromatography. Melting points were recorded on a digital melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded 400, 500 MHz spectrometers with ¹³C operating frequencies of 100, 125 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent (CDCl₃) signal (δ = 7.26 for ¹H NMR and δ = 77.0 for ¹³C NMR). Data for ¹H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) and are reported in frequency of absorption (cm⁻¹). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) and Low-Resolution Mass Spectrometry (LRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent. Optical rotations were measured on an Autopol I automatic polarimeter. Enantiomeric excess was determined by chiral HPLC analysis performed on HPLC system with Daicel Chiralpak AD-H, Chiralpak OD-3, Chiralpak OZ-3 and Chiralpak IB, Chiralpak ID-3, columns.

Compounds 13b-c, 14 and 15a-b were synthesized as per literature known protocol.¹
**Synthetic preparation of compound 14:** To the solution of 5-bromoisatin (750 mg, 3.3 mmol, 1.0 equiv) in toluene (30 mL) under nitrogen atmosphere at 25 °C was added ethylene glycol (3.6 mL, 62.4 mmol, 19.0 equiv) and p-toluenesulphonic acid (28.5 mg, 0.2 mmol, 0.05 equiv). Then the reaction mixture was placed over a pre heated oil bath maintaining temperature 110 °C and stirring was continued for 4 h. Upon completion of starting material (judged by TLC analysis under UV light and I₂ stain), reaction mixture was cooled down to room temperature to dryness and residue was diluted with dichloromethane (10 mL) and washed with saturated sodium bicarbonate solution (5 mL). Then the organic compound was extracted with dichloromethane (10 mL X 3). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified through column chromatography using 30-40% (EtOAc/Hexane) as eluent to afford the desired product.

3-(5-Bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one:¹ Compound 14 was obtained as colorless solid. (3.3 mmol scale of reaction, 812 mg of product, 91% yield); R₇ = 0.60 (50% EtOAc in hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 7.47 (m, 1H), 7.43 - 7.41 (m, 1H), 6.72 (d, J = 8.3 Hz, 1H), 4.56 - 4.52 (m, 2H), 4.33 - 4.30 (m, 2H).
General procedure for the synthesis of compound 15a-b:\(^1\) To a solution of 14 (1.0 equiv) in ethylene glycol dimethyl ether (4 mL) under nitrogen atmosphere at 25 °C was added dichloro bis(triphenylphosphine)palladium(II) (0.03 equiv.). After 15 minutes stirring, phenylboronic acid (1.5 equiv), sodium bicarbonate (3.0 equiv), and water (4 mL) was added simultaneously. Then the reaction mixture was placed over a pre heated oil bath maintaining temperature 120 °C and stirring was continued for 2 h. Upon completion of starting material (judged by TLC analysis under UV light and I\(_2\) stain), the reaction mixture was cooled down to 25 °C and evaporated to dryness and residue was diluted with dichloromethane (20 mL) and washed with 10% sodium hydroxide solution (15 mL). The aqueous layer was extracted with dichloromethane (10 mL X 3). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified through column chromatography using 30-40% (EtOAc/Hexane) as eluent to afford the desired product.

5'-Phenylspiro[[1,3]dioxolane-2,3'-indolin]-2'-one:\(^1\) Compound 15a was obtained as colorless solid (3.4 mmol scale of reaction, 720 mg of product, 80% yield); R\(_f\) = 0.55 (50% EtOAc in hexane); \(^1\)H NMR (500 MHz, 0.5 mL CDCl\(_3\)) \(\delta\) 8.41 (brs, 1H), 7.59 - 7.58 (m, 1H), 7.53 - 7.50 (m, 3H), 7.42 - 7.39 (m, 2H), 7.33 - 7.30 (m, 1H), 6.88 (d, \(J = 8.1\) Hz, 1H), 4.60 - 4.58 (m, 2H), 4.36 - 4.34 (m, 2H).

5'-(3-Methoxyphenyl)spiro[[1,3]dioxolane-2,3'-indolin]-2'-one:\(^1\) Compound 15b was obtained as colorless solid (3.3 mmol scale of reaction, 590 mg of product, 60% yield); R\(_f\) = 0.56 (50% EtOAc in hexane); \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.67 (brs, 1H), 7.57 (d, \(J = 1.8\) Hz, 1H), 7.50 (dd, \(J = 8.1, 1.9\) Hz, 1H), 7.31 (t, \(J = 7.9\) Hz, 1H), 7.11 -
7.05 (m, 2H), 6.88 - 6.84 (m, 2H), 4.60 - 4.57 (m, 2H), 4.36 - 4.33 (m, 2H), 3.84 (s, 3H); 

$^{13}$C NMR (120 MHz, CDCl$_3$) δ 175.8, 159.9, 141.9, 141.3, 136.7, 136.5, 129.8, 124.9, 124.1, 119.4, 112.6, 112.5, 111.0, 102.5, 65.9, 55.3; MP 150 - 152 °C.

General procedure for the synthesis of compound 13b-c:$^1$ To the compound of 15 (1.0 equiv) in methanol (9 mL) at 25 °C was added conc. HCl (4 mL). Then the reaction mixture was placed over a pre heated oil bath maintaining temperature 70 °C for 5 h. Upon completion of starting material (judged by TLC analysis under UV light and cerium ammonium molybdate stain), the reaction mixture was evaporated to dryness. The residue was diluted with dichloromethane and washed with saturated sodium bicarbonate solution. Then the organic compound was extracted with dichloromethane (10 mL X 3). Then the combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified through column chromatography using 35-45% (EtOAc/Hexane) as eluent to afford the desired product.

5-Phenyindoline-2,3-dione: Compound 13b was obtained as colourless solid. (2.2 mmol scale of reaction; 400 mg of product; 80% yield; $R_f = 0.50$ (50% EtOAc in hexane); $^1$H NMR (400 MHz, DMSO) δ 10.38 (s, 1H), 7.77 - 7.75 (m, 1H), 7.7 (dd, $J = 8.1, 2.0$ Hz, 1H), 7.51 - 7.48 (m, 2H), 7.45 - 7.36 (m, 2H), 7.37 - 7.32 (m, 1H), 2.27(DMSO).
General procedure for the synthesis of 3-Hydroxy-3-indolyl-2-oxindole (±)-5a-e: In a round-bottom flask was charged with isatin (1.0 equiv) in MeOH (60 mL) under nitrogen atmosphere at 25 °C indole (1.2 equiv) and KOH (0.2 equiv) were added successively. Then the reaction mixture was then allowed to stir for 4 - 6 h. Upon completion of starting material (judged by TLC analysis under UV light and I₂ stain), the reaction mixture was quenched with water (60 mL) and organic compound was extracted with ethyl acetate (2 X 80 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified through column chromatography using hexane-EtOAc as eluent to afford the desired product.

3-Hydroxy-3-(1H-indol-3-yl)indolin-2-one: Compound (±)-5a was obtained as a colorless solid (13.6 mmol scale of reaction, 3.2 g of product, 88% yield); Rᵣ = 0.30 (50% EtOAc in hexane); ¹H NMR (400 MHz, DMSO) δ 10.94 (s, 1H), 10.32 (s, 1H), 7.31 - 7.28 (m, 2H), 7.24 - 7.19 (m, 2H), 7.06 (s, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.94 - 6.88 (m, 2H), 6.83 (t, J = 7.4 Hz, 1H), 6.37 (s, 1H), 3.68 (Water); IR (film) νₘₐₓ 3428, 2839, 2115, 1650, 1470, 1337, 1226, 1185, 1105, 940, 751 cm⁻¹, MP 350-352 °C.

3-(5-Bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one: Compound (±)-5b was obtained as a colorless solid (6.8 mmol scale of reaction, 1.95 g of product, 84% yield); Rᵣ = 0.30 (50% EtOAc in hexane); ¹H NMR (500 MHz, DMSO) δ 11.22 (s, 1H), 10.41 (s, 1H), 7.75 (s, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.32 - 7.28 (m, 2H), 7.21 (d, J = 8.2 Hz, 1H), 7.05 -
7.01 (m, 2H), 6.97 (d, \( J = 7.4 \text{ Hz}, 1H \)), 6.55 (s, 1H); \(^{13}\text{C NMR} \) (125 MHz, DMSO) \( \delta \) 178.8, 142.1, 136.0, 133.3, 129.8, 127.4, 125.6, 125.3, 124.2, 123.6, 122.4, 115.7, 114.1, 111.8, 110.3, 75.2; \(^{1}\text{H NMR} \) (400 MHz, 0.5 mL CDCl\(_3\), 0.1 mL DMSO-D\(_6\)) \( \delta \) 9.64 (s, 1H), 9.54 (s, 1H), 7.17 (d, \( J = 6.9 \text{ Hz}, 1H \)), 7.01 – 6.96 (m, 2H), 6.86 – 6.82 (m, 2H), 6.76 (t, \( J = 7.2 \text{ Hz}, 1H \)), 6.69 (d, \( J = 7.4 \text{ Hz}, 1H \)), 6.51 (d, \( J = 8.6 \text{ Hz}, 1H \)), 5.49 (s, 1H), 3.49 (s, 3H), 2.69 (s, 1H); \(^{13}\text{C NMR} \) (100 MHz, 0.5 mL CDCl\(_3\), 0.1 mL DMSO-D\(_6\)) \( \delta \) 179.3, 153.4, 141.4, 132.8, 132.2, 129.1, 125.4, 124.9, 124.3, 122.1, 114.8, 112.0, 111.6, 110.0, 102.5, 75.6, 55.5; \(^{1}\text{IR} \) (film) \( \nu_{\text{max}} \) 3416, 2861, 2832, 2106, 1792, 1704, 1622, 1499, 1094, 751 cm\(^{-1}\); \( \text{MP} \) 190 - 192 °C.

### 3-Hydroxy-3-(5-methoxy-1H-indol-3-yl)indolin-2-one

Compound (±)-5c was obtained as a colorless solid. (6.5 mmol scale of reaction, 1.7 g of product, 89% yield); \( R_f = 3.1 \) (50% EtOAc in hexane); \(^{1}\text{HNMR} \) (400 MHz, 0.5 mL CDCl\(_3\), 0.1 mL DMSO-D\(_6\)) \( \delta \) 9.64 (s, 1H), 9.54 (s, 1H), 7.17 (d, \( J = 6.9 \text{ Hz}, 1H \)), 7.01 – 6.96 (m, 2H), 6.86 – 6.82 (m, 2H), 6.76 (t, \( J = 7.2 \text{ Hz}, 1H \)), 6.69 (d, \( J = 7.4 \text{ Hz}, 1H \)), 6.51 (d, \( J = 8.6 \text{ Hz}, 1H \)), 5.49 (s, 1H), 3.49 (s, 3H), 2.69 (s, 1H); \(^{13}\text{C NMR} \) (100 MHz, 0.5 mL CDCl\(_3\), 0.1 mL DMSO-D\(_6\)) \( \delta \) 178.8, 142.1, 138.2, 133.5, 129.7, 125.2, 125.1, 124.6, 122.3, 122.2, 116.3, 114.6, 114.5, 110.3, 75.2, 75.2; \(^{1}\text{IR} \) (film) \( \nu_{\text{max}} \) 3416, 2861, 2832, 2106, 1792, 1704, 1622, 1469, 1071, 904, 751 cm\(^{-1}\); \( \text{MP} \) 194 - 196 °C.

### 3-(6-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one

Compound (±)-5d was obtained as a colorless solid. (6.8 mmol scale of reaction, 2.05 g of product, 88% yield); \( R_f = 2.5 \) (50% EtOAc in hexane); \(^{1}\text{HNMR} \) (400 MHz, DMSO-D\(_6\)) \( \delta \) 11.14 (s, 1H), 10.38 (s, 1H), 7.57 (s, 1H), 7.44 (d, \( J = 8.6 \text{ Hz}, 1H \)), 7.29 – 7.25 (m, 2H), 7.08 – 7.07 (m, 2H), 7.01 – 6.98 (m, 1H), 6.94 (d, \( J = 7.2 \text{ Hz}, 1H \)), 6.49 (s, 1H); \(^{13}\text{C NMR} \) (100 MHz, DMSO-D\(_6\)) \( \delta \) 178.8, 142.1, 138.2, 133.5, 129.7, 125.2, 125.1, 124.6, 122.3, 122.2, 116.3, 114.6, 114.5, 110.3, 75.2, 75.2; \(^{1}\text{IR} \) (film) \( \nu_{\text{max}} \) 3500, 2950, 2800, 2520, 1802, 1706, 1602, 1499, 1001, 984, 721 cm\(^{-1}\); \( \text{MP} \) >260 °C.
3-hydroxy-3-(7-iodo-1H-indol-3-yl)indolin-2-one: Compound \((\pm)-5e\) was obtained as a colorless solid. (6.5 mmol scale of reaction, 2.02 g of product, 80\% yield); \(R_f = 2.9\) (50\% EtOAc in hexane); \(^1H\) NMR (400 MHz, DMSO-D\(_6\)) \(\delta 10.9\) (s, 1H), 10.40 (s, 1H), 7.48 – 7.42 (m, 2H), 7.29 – 7.24 (m, 2H), 7.07 (s, 1H), 7.99 – 6.93 (m, 2H), 6.74 (s, 1H), 6.47 (s, 1H); \(^{13}C\) NMR (100 MHz, DMSO-D\(_6\)) \(\delta 178.6, 142.1, 138.9, 133.5, 130.6, 129.7, 125.9, 125.2, 124.8, 122.3, 121.0, 117.4, 110.2, 77.4, 75.5; \(\text{IR}\) (film) \(\nu_{\text{max}} 3560, 2960, 2852, 2116, 1709, 1662, 1409, 1001, 924, 701\) cm\(^{-1}\); \(\text{MP} > 260^\circ\text{C}\).

**General procedure for the synthesis of 3-Hydroxy-3-indolyl-2-oxindole \((\pm)-5f-g\):** In a round bottom flask was charged with isatin (1.0 equiv) in MeOH (60 mL) under nitrogen atmosphere at 25 \(^\circ\text{C}\) indole (1.2 equiv) and KOH (0.2 equiv) were added successively. Then the reaction mixture was then allowed to stir for 5-6 h. Upon completion of starting material (judged by TLC analysis under UV light and I\(_2\) stain), the reaction mixture was quenched with water (60 mL) and organic compound was extracted with ethyl acetate (2 X 80 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified through column chromatography using hexane-EtOAc as eluent to afford the desired product.
5-Bromo-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one: Compound (±)-5f was obtained as a colorless solid (3.3 mmol scale of reaction, 1.0 g of product, 84% yield); 

R_f = 3.2 (50% EtOAc in hexane); 

1H NMR (500 MHz, DMSO) δ 11.06 (s, 1H), 10.58 (s, 1H), 7.46 (d, J = 7.3 Hz, 1H), 7.38 (m, 3H), 7.19 (s, 1H), 7.08 (d, J = 12.6 Hz, 1H), 6.95 - 6.93 (m, 2H), 6.66 (s, 1H), (Water); 

13C NMR (125 MHz, DMSO) δ 178.5, 141.4, 137.3, 136.3, 132.3, 127.9, 125.1, 124.1, 121.8, 120.4, 119.3, 115.1, 114.0, 112.4, 112.2, 75.3; 

IR (film) υ_max 3416, 1792, 1644, 1492, 1335, 1247, 1177, 1121, 815, 715 cm⁻¹; 

MP 310 - 312 °C.

3-Hydroxy-3-(1H-indol-3-yl)-5,7-dimethylindolin-2-one: Compound (±)-5g was obtained as a colorless solid (3.9 mmol scale of reaction, 1.0 g of product, 90% yield); 

R_f = 0.55 (50% EtOAc in hexane); 

1H NMR (500 MHz, 0.5 mL CDCl₃, 0.1 mL DMSO-D₆) δ 10.93 (s, 1H), 10.53 (s, 1H), 7.32 (dd, J = 47.6, 8.2 Hz, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.86 - 6.79 (m, 3H), 3.38 (s, 3H), 2.23 (d, J = 67.2 Hz, 3H); 

13C NMR (125 MHz, DMSO-D₆) δ 179.7, 137.9, 137.4, 134.7, 130.5, 129.9, 126.2, 124.8, 123.3, 121.4, 121.3, 118.9, 118.6, 115.1, 112.0, 55.4, 21.2, 1; 

IR (film) υ_max 3387, 3304, 2924, 2852, 1735, 1701, 1624, 1544, 1465, 1286, 1099, 740, 617 cm⁻¹; 

MP 210 - 212 °C.

General procedure for the synthesis of 3-Hydroxy-3-indolyl-2-oxindoles (±)-5h-j is like synthesis of (±)-5f-g.
3-Hydroxy-3-(1H-indol-3-yl)-5-phenylindolin-2-one: Compound (±)-5h was obtained as a colorless solid (3.5 mmol scale of reaction, 930 mg of product, 78% yield); \( R_f = 3.2 \) (50% EtOAc in hexane); \(^1\)H NMR (400 MHz, DMSO-D\(_6\)) \( \delta 10.96 \) (s, 1H), 10.42 (s, 1H), 7.55 - 7.47 (m, 3H), 7.41 - 7.22 (m, 5H), 7.01 (s, 1H), 7.01 - 6.82 (m, 3H), 6.41 (s, 1H), 3.32 (Water); \(^{13}\)C NMR (125 MHz, DMSO-D\(_6\)) \( \delta 178.9, 141.7, 140.6, 137.2, 134.6, 134.3, 129.4 (2C), 127.9, 127.2, 126.5 (2C), 125.3, 124.1, 123.4, 121.5, 120.7, 118.9, 115.7, 111.9, 110.5, 75.5; IR (film) \( \nu_{max} \) 3415, 3387, 2922, 2850, 2357, 1714, 1624, 1389, 1172, 744, 694 cm\(^{-1}\); MP > 300 °C.

3-Hydroxy-3-(1H-indol-3-yl)-5-(3-methoxyphenyl)indolin-2-one: Compound (±)-5i was obtained as an orange solid (2.0 mmol scale of reaction, 555 mg of product, 75% yield); \( R_f = 3.3 \) (50% EtOAc in hexane); \(^1\)H NMR (400 MHz, DMSO-D\(_6\)) \( \delta 10.96 \) (s, 1H), 10.42 (s, 1H), 7.55 (d, \( J = 8.1 \) MHz, 1H), 7.49 (s, 1H), 7.42 (d, \( J = 8.1 \) MHz, 1H), 7.32 - 7.25 (m, 2H), 7.09 - 7.06 (m, 2H), 7.02 - 6.95 (m, 3H), 6.87 - 6.81 (m, 2H), 6.41 (s, 1H), 3.75 (s, 3H), 3.33 (Water); \(^{13}\)C NMR (125 MHz, DMSO-D\(_6\)) \( \delta 183.7, 164.9, 146.9, 146.8, 146.6, 142.0, 139.3, 138.9, 135.1, 132.8, 130.1, 128.4, 128.2, 126.3, 125.5, 123.7, 123.6, 120.5, 117.6, 116.7, 116.6, 115.2, 80.2, 60.3; IR (film) \( \nu_{max} \) 3388, 2926, 2355, 1712, 1641, 1624, 1579, 1477, 1392, 1165, 1082, 821, 740 cm\(^{-1}\); MP > 300 °C.

Compound (±)-5j was prepared as per literature report.\(^3\)
Supporting Information

Compound (±)-9a and compounds (±)-9b-d were synthesized as per literature reports.

**Synthetic procedure for the compound (±)-5k:** In an oven-dried round bottom flask was charged with oxindole (±)-5a (1 g; 3.8 mmol; 1.0 equiv) in dichloromethane (15 mL) under nitrogen atmosphere at 25 ºC Lewis acid (0.38 mmol, 10 mol %) and MeOH (765 µl; 18.9 mmol, 5.0 equiv) was added. Then the reaction mixture was allowed to stir for 12 h. Upon completion of starting material (judged by TLC analysis under UV light and I2 stain), the reaction mixture was quenched with water (20 mL) and organic compound was extracted with ethyl acetate (2 X 30 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified through column chromatography using 25-40% (EtOAc/Hexane) as eluent to afford the desired product.

3-(1H-Indol-3-yl)-3-methoxyindolin-2-one: Compound (±)-5k was obtained as an orange solid (3.0 mmol scale of reaction, 760 mg of product, 92% yield); Rf = 3.3 (50% EtOAc in hexane); ¹H NMR (400 MHz, DMSO-d₆) δ 11.08 (s, 1H), 10.58 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 13.9, 7.6 Hz, 3H), 7.06 (q, J = 8.1 Hz, 2H), 6.97 - 6.92 (m, 3H), 3.43 (Water), 3.15 (s, 3H); ¹³C NMR (101 MHz, DMSO-d₆) δ 176.4, 142.8, 137.2, 130.3, 128.8, 125.7, 125.5, 124.8, 122.4, 121.8, 121.4, 119.2, 113.2, 112.0, 110.5,
Synthetic procedure for the compound (±)-5l: In an oven-dried round bottom flask was charged with isatin (1g; 6.8 mmol; 1.0 equiv) in methyl tert-butyl ether (15 mL) under nitrogen atmosphere at 25 ºC. To this solution, sesamol (8.2 mmol, 1.2 equiv) and Et₃N (1.3 mmol, 20 mol%) was added sequentially and the reaction mixture was allowed to stir for 15 h. Upon completion of starting material (judged by TLC analysis), the reaction mixture was quenched with water (20 mL) and organic compound was extracted with ethyl acetate (2 X 30 mL). Then the combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. This crude product was used for next step without purification.

To the crude product of 3-hydroxy 2-oxindoles (~6.3 mmol; 1.0 equiv) in dichloromethane (30 mL) under nitrogen atmosphere at 25 ºC Lewis acid (~0.63 mmol, 10 mol %) and MeOH (~31.5 mmol, 5.0 equiv) was added. Then the reaction mixture was allowed to stir for 12 h. Upon completion of starting material (judged by TLC analysis under UV light and I₂ stain), the reaction mixture was quenched with water (30 mL) and organic compound was extracted with ethyl acetate (2 X 40 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified through column chromatography using 30-40% (EtOAc/Hexane) as eluent to afford the desired product.
3-(6-Hydroxybenzo[d][1,3]dioxol-5-yl)-3-methoxyindolin-2-one: Compound (±)-5I was obtained as orange solid (6.8 mmol scale of reaction, 1.7 g of product, 86% yield over two steps); Rf = 3.3 (50% EtOAc in hexane); 1H NMR (500 MHz, DMSO-d6) δ 10.50 (s, 1H), 9.19 (s, 1H), 7.21 (ddd, J = 7.8, 5.9, 3.0 Hz, 1H), 7.16 (s, 1H), 6.91 - 6.89 (m, 2H), 6.84 (d, J = 7.7 Hz, 1H), 6.27 (s, 1H), 5.93 (d, J = 8.6 Hz, 2H), 3.46 (Water), 3.04 (s, 3H); 13C NMR (125 MHz, DMSO-d6) δ 176.3, 148.9, 147.2, 144.2, 140.0, 129.8, 128.7, 124.8, 122.1, 118.8, 109.7, 106.9, 101.2, 98.0, 81.0, 51.4; IR (film) νmax 3382, 2916, 2255, 1722, 1631, 1568, 1452, 1390, 1105, 1002, 911, 720 cm⁻¹.

General procedure for the synthesis of (±)-4a-t: 3-Hydroxy 2-oxindoles (0.38 mmol; 1.0 equiv) was taken in dry dichloromethane (2 mL) under nitrogen atmosphere and 10 mol % Cu(OTf)2 was added to this at room temperature under argon atmosphere. After 5 minutes stirring at room temperature, malonate (3 equiv) was added drop-wise over a period of 5 minutes. Then the reaction mixture was allowed to stir for 9 h. Upon completion of starting material (judged by TLC analysis under UV light and I₂ stain), the crude mixture was concentrated under reduced pressure and product was purified by column chromatography by using 25-40% (EtOAc/Hexane) as eluent to afford the desired products.

Table. Optimization of enantioselective malonate addition of (±)-5a with diethylmalonate.ᵃᵇ
<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>ligand</th>
<th>solvent</th>
<th>temp.</th>
<th>time</th>
<th>% yield</th>
<th>% ee</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Cu(OTf)$_2$</td>
<td>12 mol% L1</td>
<td>CH$_2$Cl$_2$</td>
<td>25 °C</td>
<td>12 h</td>
<td>79%</td>
<td>52%</td>
</tr>
<tr>
<td>2</td>
<td>Cu(OTf)$_2$</td>
<td>12 mol% L2</td>
<td>CH$_2$Cl$_2$</td>
<td>25 °C</td>
<td>13 h</td>
<td>80%</td>
<td>38%</td>
</tr>
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<td>12 h</td>
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<td>51%</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OTf)$_2$</td>
<td>12 mol% L4</td>
<td>CH$_2$Cl$_2$</td>
<td>25 °C</td>
<td>13 h</td>
<td>84%</td>
<td>72%</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OTf)$_2$</td>
<td>12 mol% L4</td>
<td>CH$_2$Cl$_2$</td>
<td>0 °C</td>
<td>16 h</td>
<td>83%</td>
<td>82%</td>
</tr>
<tr>
<td>6</td>
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</tr>
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<td>17 h</td>
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<td>80%</td>
</tr>
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</tr>
<tr>
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<td>0 °C</td>
<td>16 h</td>
<td>75%</td>
<td>88%</td>
</tr>
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<td>CH$_2$Cl$_2$</td>
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<td>12 h</td>
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<td>82%</td>
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<td>PhMe</td>
<td>0 °C</td>
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<td>71%</td>
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<td>THF</td>
<td>0 °C</td>
<td>6 h</td>
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<td>14%</td>
</tr>
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<td>CHCl$_3$</td>
<td>0 °C</td>
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<td>(CH$_2$Cl)$_2$</td>
<td>0 °C</td>
<td>20 h</td>
<td>55%</td>
<td>22%</td>
</tr>
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<td>20 mol% L4</td>
<td>DCB$_2$</td>
<td>0 °C</td>
<td>15 h</td>
<td>85%</td>
<td>59%</td>
</tr>
<tr>
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<td>20 mol% L5</td>
<td>CH$_2$Cl$_2$</td>
<td>0 °C</td>
<td>19 h</td>
<td>78%</td>
<td>24%</td>
</tr>
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</table>

S14
General procedure for the synthesis of enantioselective compounds: (R)-4a-s, (+)-4t:
An oven dried sample vial was charged with Lewis acid (0.1 equiv) and ligand (0.2 equiv) in dichloromethane (4 mL) at 25 °C under nitrogen atmosphere. The reaction mixture was stirred for 30 minutes to make the complex. After that the reaction vessel was cooled to 0 °C and malonate (3.0 equiv) was added to the mixture and stirring was continued for 15 minutes maintaining temperature 0 °C. Then, a solution of 3-hydroxy 2-oxindole in dichloromethane (0.5 mL) was added slowly to the reaction mixture. Then the reaction mixture was allowed to stir for respective times at 0 °C for condition A and -5 °C for condition B. After complete consumption of starting material (as judged by running TLC), the crude mixture was concentrated under reduced pressure and purified by column chromatography by using 30-40% EtOAc-hexane mixture as eluent to afford the desired compound.

**Diethyl (R)-2-(3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate**: Compound (R)-4a was obtained as yellow solid (0.08 mmol scale of reaction, 26 mg of product, 80% yield); R_f = 0.50 (50% EtOAc in hexane); ^1H NMR (400 MHz, 0.4 mL CDCl_3, 0.1 mL DMSO-D6) δ 9.63 (brs, 1H), 9.49 (brs, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.10 (t, J
= 8.3 Hz, 2H), 6.91 - 6.80 (m, 3H), 6.76 (d, J = 7.7 Hz, 1H), 6.51 - 6.50 (m, 1H), 4.99 (s, 1H), 3.77 - 3.66 (m, 4H), 0.76 (t, J = 14.2 Hz, 3H), 0.62 (t, J = 14.2 Hz, 3H); 13C NMR (100 MHz, 0.4 mL CDCl3, 0.1 mL DMSO-D6) δ 178.4, 167.3, 166.9, 142.5, 136.9, 129.8, 128.3, 126.9, 124.9, 124.2, 121.7, 121.4, 121.3, 118.8, 111.9, 111.2, 109.5, 61.1, 60.6, 56.4, 53.4, 13.2, 13.1; IR (film) υmax 3375, 2989, 2359, 1724, 1615, 1265, 1034, 747, 700 cm⁻¹; HRMS (ESI) m/z [M + H]+ Calcd for [C19H19N2O5]⁺ 407.1601; Found 407.1604;

MP 170 - 172 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak ID-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): tR minor = 4.88 min, tR major = 5.92 min. [α]D 23.0 = +128.6 (c = 0.18, CH2Cl2 for 94% ee).

**Dimethyl (R)-2-(3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate:** Compound (R)-4b was obtained as a colorless solid (0.08 mmol scale of reaction, 24 mg of product, 82% yield); Rf = 0.48 (50% EtOAc in hexane); 1H NMR (500 MHz, 0.4 mL CDCl3, 0.1 mL DMSO-D6) δ 9.25 (s, 1H), 9.18 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.20 (t, J = 7.1 Hz, 2H), 7.01 (q, J = 8.0 Hz, 2H), 6.95 (d, J = 7.9 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.65 (s, 1H), 5.15 (s, 1H), 3.40 (s, 3H), 3.38 (s, 3H); 13C NMR (125 MHz, 0.4 mL CDCl3, 0.1 mL DMSO-D6) δ 178.5, 168.0, 167.4, 142.4, 137.1, 129.8, 128.7, 127.1, 124.9, 124.4, 121.9, 121.7, 121.5, 119.4, 111.9, 111.5, 109.9, 56.5, 53.6, 52.4, 52.2; IR (film) υmax 3361, 3059, 2983, 2938, 2308, 1720, 1455, 1316, 1104, 1015, 913, 838, 743 cm⁻¹; HRMS (ESI) m/z [M + H]+ Calcd for [C21H19N2O5]⁺ 379.1288; Found 379.1309;

MP 240 - 242 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OZ-3 column; solvent: hexane/2-propanol = 70/30; flow rate: 1.0 mL/min; detection: at 254 nm): tR minor = 11.71 min, tR major = 14.29 min. [α]D 22.1 = +250.0 (c = 0.22, CHCl3 for 89% ee).
**Diisopropyl (R)-2-(3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate:** Compound (R)-4c was obtained as a yellow solid (0.08 mmol scale of reaction, 27 mg of product, 79% yield); $R_f = 0.52$ (50% EtOAc in hexane); $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.63 (brs, 1H), 8.15 (brs, 1H), 7.92 (d, $J = 6.3$ Hz, 1H), 7.24 - 7.18 (m, 2H), 7.06 - 7.05 (m, 3H), 6.84 (m, 1H), 6.53 (s, 1H), 5.16 (s, 1H), 4.71 - 4.70 (m, 2H), 1.01-0.91 (m, 6H), 0.68 - 0.59 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 179.1, 167.1, 166.6, 141.9, 137.0, 129.9, 128.7, 127.5, 125.1, 124.2, 122.4, 122.3, 122.1, 119.6, 112.8, 111.3, 109.9, 69.5, 68.6, 56.8, 53.7, 21.3, 21.2, 20.6, 20.6; IR (film) $\nu_{\text{max}}$ 3340, 2975, 2340, 2320, 1796, 1620, 1600, 1265, 1051, 700, 692 cm$^{-1}$; HRMS (ESI) m/z [M + H]$^+$ Calcd for [C$_{25}$H$_{27}$N$_2$O$_5$]$^+$ 435.1914; Found 435.1900; MP 110 - 112 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 40/30; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R$ minor = 5.45 min, $t_R$ major = 6.32 min. $[^{[a]}_D]^{23.0} = +179.7$ (c = 0.30, CHCl$_3$ for 89% ee).

**Ditert-butyl (R)-2-(3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate:** Compound (R)-4d was obtained as a colorless solid. (0.08 mmol scale of reaction, 29 mg of product, 79% yield); $R_f = 0.56$ (50% EtOAc in hexane); $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (brs, 1H), 8.11 - 8.02 (m, 3H), 7.28 - 7.25 (m, 2H), 7.12 - 7.04 (m, 3H), 6.88 (d, $J = 7.7$ Hz, 1H), 6.55 (s, 1H), 5.08 (s, 1H), 1.05 (s, 9H), 0.99 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 179.2, 166.8, 166.5, 141.7, 137.1, 130.4, 128.6, 127.7, 125.3, 124.2, 122.90, 122.4, 122.2, 119.6, 113.4, 111.2, 109.6, 82.6, 81.4, 58.1, 53.8, 27.3, 27.1; IR (film) $\nu_{\text{max}}$ 3340, 2975,
2340, 2320, 1720, 1620, 1600, 1265, 1051, 700, 692 cm\(^{-1}\); **HRMS** (ESI) m/z \([\text{M} + \text{Na}]^+\) Calcd for \([\text{C}_{27}\text{H}_{30}\text{N}_2\text{O}_5+\text{Na}]^+\) 485.2047; Found 485.2076; **MP** 138 - 140 \(^\circ\)C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): \(t_R\) minor = 4.78 min, \(t_R\) major = 6.86 min. \([\alpha]_D^{23.1} = +105.2\) (c = 0.18, CHCl\(_3\) for 77% ee).

\[\text{(+)1-Benzyl-3-ethyl-2-(-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate:}\] Compound (+)-4e was obtained as a yellow solid (0.08 mmol scale of reaction, 31 mg of product, 83% yield); \(R_f = 0.56\) (50% EtOAc in hexane); \(^1\text{H NMR}\) (400 MHz, DMSO-\(D_6\)) \(\delta\) 10.97 (b.r.s, 1H for major diastereomer + 1H for minor diastereome), 10.47 (b.r.s, 1H for minor diastereomer), 10.46 (s, 1H for major diastereomer), 7.76 (d, \(J = 7.3\) Hz, 1H for minor diastereomer), 7.71 (d, \(J = 7.3\) Hz, 1H for major diastereomer), 7.53 (d, \(J = 8.0\) Hz, 1H for major diastereomer), 7.49 (d, \(J = 8.1\) Hz, 1H for minor diastereomer), 7.36 - 7.22 (m, 3H for major diastereomer + 3H for minor diastereomer), 7.27 - 7.16 (m, 2H for major diastereomer + 2H for minor diastereomer), 7.04 - 6.95 (m, 3H for major diastereomer + 3H for minor diastereomer), 6.90 - 6.83 (m, 3H for major diastereomer + 3H for minor diastereomer), 6.66 (s, 1H for minor diastereomer), 6.63 (s, 1H for major diastereomer), 5.02 (s, 1H for major diastereomer), 5.01 (s, 1H for minor diastereomer), 4.93 - 4.81 (m, 2H for major diastereomer + 2H for minor diastereomer), 4.35 (Water), 3.81 - 3.80 (m, 2H for major diastereomer + 2H for minor diastereomer), 0.80 (t, \(J = 6.9\) Hz, 3H for major diastereomer), 0.65 (t, \(J = 6.8\) Hz, 3H for for minor diastereomer); \(^{13}\text{C NMR}\) (100 MHz, DMSO-\(D_6\)) \(\delta\) 178.1, 177.9, 167.4, 167.3, 166.90, 166.87, 143.5, 143.4, 137.4, 137.3, 135.7, 135.5, 130.2, 130.1, 129.13, 129.11, 128.8, 128.6, 128.5, 128.2, 127.9, 127.7, 127.2, 127.0, 125.3, 125.2, 124.92, 124.91, 121.8, 121.75, 121.72, 121.67, 121.63 (2 C), 119.2, 119.0, 112.5, 112.1, 111.9, 111.8, 110.2, 110.1, 66.9, 66.7, 61.7, 61.1, 56.65, 56.61, 53.5, 53.4, 13.7, 13.6; **IR** (film) \(\nu_{\text{max}}\) 3700, 3464, 2918, 2352, 1725, 1458,
1322, 1241, 1148, 738 cm\(^{-1}\); **HRMS** (ESI) m/z [M + Na]\(^+\) Calcd for [C\(_{28}\)H\(_{24}\)N\(_2\)O\(_5\)+Na]\(^+\) 491.1577; Found 491.1602; **MP** 190 - 192 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak AD-H column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): in case of minor diastereomer (\(t_R\) minor = 9.40 min, \(t_R\) major = 17.8.54 min. 84% ee), in case of major diastereomer (\(t_R\) minor = 11.88 min, \(t_R\) major = 22.05 min. 85% ee). \([\alpha]_D^{22.0} = +192.1 \) (c = 0.26, in CHCl\(_3\)).

**Dibenzyl (R)-2-(3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate**: Compound (R)-4f was obtained as a yellow solid (0.08 mmol scale of reaction 38 mg of product 90% yield); \(R_f = 0.60\) (50% EtOAc in hexane); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.99 (d, \(J = 7.6 \) Hz, 1H), 7.97 (s, 1H), 7.88 (d, \(J = 8.2 \) Hz, 1H), 7.68 (s, 1H), 7.28 – 7.23 (m, 6H), 7.19 – 7.15 (m, 3H), 7.09 – 7.04 (m, 4H), 6.86 (d, \(J = 7.1 \) Hz, 2H), 6.73 (d, \(J = 7.7 \) Hz, 1H), 6.62 (d, \(J = 2.7 \) Hz, 1H), 5.37 (s, 1H), 4.91 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 178.0, 167.2, 166.7, 141.4, 136.9, 135.0, 134.7, 129.4, 128.7, 128.4, 128.2, 128.2, 128.1, 127.9, 127.9, 127.3, 124.9, 124.3, 122.3, 122.3, 122.0, 120.0, 112.3, 111.4, 109.8, 67.3, 67.0, 56.5, 53.4; IR (film) \(\nu_{\text{max}}\) 3390, 2928, 2251, 1729, 1621, 1400, 1360, 1260, 1100, 1022, 756, 698 cm\(^{-1}\); **HRMS** (ESI) m/z [M + H]\(^+\) Calcd for [C\(_{33}\)H\(_{27}\)N\(_2\)O\(_5\)]\(^+\) 531.1914; Found 531.1939; **MP** 180 - 182 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): \(t_R\) minor = 4.69 min, \(t_R\) major = 9.21 min. \([\alpha]_D^{21.0} = +222.6 \) (c = 0.18, MeOH for >99% ee).
Diethyl \((R)-2\-(3\-(5\text{-methoxy-1H\text{-indol-3-yl})-2\text{-oxoindolin-3-yl})\text{-malonate}}\): Compound \((R)-4g\) was obtained as a colorless solid (0.08 mmol scale of reaction, 27 mg of product, 73% yield); \(R_f = 0.56\) (50% EtOAc in hexane); \(^1\text{H NMR}\) (400 MHz, DMSO-\(D_6\)) \(\delta\) 10.82 (s, 1H), 10.46 (s, 1H), 7.76 (d, \(J = 7.4\) Hz, 1H), 7.27 (td, \(J = 7.7, 0.9\) Hz, 1H), 7.16 (d, \(J = 8.8\) Hz, 1H), 7.01 (t, \(J = 7.3\) Hz, 1H), 6.90 (d, \(J = 7.7\) Hz, 1H), 6.76 (d, \(J = 1.8\) Hz, 1H), 6.66 - 6.63 (m, 2H), 4.86 (s, 1H), 3.90 - 3.76 (m, 4H), 3.58 (s, 3H), 3.48 (Water), 0.79 (t, \(J = 7.1\) Hz, 3H), 0.75 (t, \(J = 7.1\) Hz, 3H); \(^{13}\text{C NMR}\) (100 MHz, DMSO-\(D_6\)) \(\delta\) 178.2, 167.4, 167.0, 153.1, 143.6, 132.4, 130.2, 129.2, 127.3, 125.6, 125.3, 121.7, 112.6, 111.6, 111.4, 110.0, 103.6, 61.6, 61.0, 56.6, 55.6, 53.3, 13.7, 13.7; \(\text{IR}\) (film) \(\nu_{\max}\) 3381, 2982, 1715, 1471, 1371, 1299, 1246, 1189, 1031, 860, 816, 741 cm\(^{-1}\); \(\text{HRMS}\) (ESI) \(m/z\) [M + Na]\(^+\) Calcd for [C\(_{24}\)H\(_{24}\)N\(_2\)O\(_6\)+Na]\(^+\) 459.1527; Found 459.1551; \(\text{MP}\) 130 - 132 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IE-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm); \(t_R\) minor = 8.60 min, \(t_R\) major = 10.81 min. \([\alpha]_D^{24.0} = +110.0\) (\(c = 0.20\), CHCl\(_3\) for 76% ee).

Diethyl \((R)-2\-(3\-(5\text{-bromo-1H\text{-indol-3-yl})-2\text{-oxoindolin-3-yl})\text{-malonate}}\): Compound \((R)-4h\) was obtained as a brown solid (0.08 mmol scale of reaction, 30 mg of product, 77% yield); \(R_f = 0.56\) (50% EtOAc in hexane); \(^1\text{H NMR}\) (500 MHz, DMSO-\(D_6\)) \(\delta\) 11.23 (s, 1H), 10.57 (s, 1H), 7.82 - 7.76 (m, 2H), 7.35 - 7.30 (m, 2H), 7.18 (d, \(J = 8.7\) Hz, 1H), 7.08 (d, \(J = 7.8\) Hz, 1H), 6.94 (t, \(J = 6.1\) Hz, 1H), 6.73 (s, 1H), 4.91 (s, 1H), 3.93 – 3.81 (m, 4H), 0.84 (t, \(J = 7.1\) Hz, 3H), 0.73 (t, \(J = 3.1\) Hz, 3H); \(^{13}\text{C NMR}\) (125 MHz, DMSO-\(D_6\)) \(\delta\) 178.2, 167.4, 167.0, 153.1, 143.6, 132.4, 130.2, 129.2, 127.3, 125.6, 125.3, 121.7, 112.6, 111.6, 111.4, 110.0, 103.6, 61.6, 61.0, 56.6, 55.6, 53.3, 13.7, 13.7; \(\text{IR}\) (film) \(\nu_{\max}\) 3381, 2982, 1715, 1471, 1371, 1299, 1246, 1189, 1031, 860, 816, 741 cm\(^{-1}\); \(\text{HRMS}\) (ESI) \(m/z\) [M + Na]\(^+\) Calcd for [C\(_{24}\)H\(_{24}\)N\(_2\)O\(_6\)+Na]\(^+\) 459.1527; Found 459.1551; \(\text{MP}\) 130 - 132 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IE-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm); \(t_R\) minor = 8.60 min, \(t_R\) major = 10.81 min. \([\alpha]_D^{24.0} = +110.0\) (\(c = 0.20\), CHCl\(_3\) for 76% ee).
D₆) δ 178.0, 167.2, 166.7, 143.4, 136.1, 129.8, 129.2, 127.0, 126.9, 126.6, 124.1, 124.1, 121.8, 114.2, 111.8, 111.8, 110.1, 61.6, 61.0, 56.7, 53.2, 13.7, 13.6; IR (film) νₘₐₓ 3260, 3063, 2922, 2359, 1712, 1616, 1469, 1217, 1097, 1018, 746 cm⁻¹; HRMS (ESI) m/z [M + Na]^+ Calcd for [C₂₃H₂₁BrN₂O₅+Na]^+ 507.0526; Found 507.0534; MP 120 - 122 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 70/30; flow rate: 1.0 mL/min; detection: at 254 nm): tᵣ minor = 4.72 min, tᵣ major = 6.65 min. [α]D²⁴.¹ = +198.2 (c = 0.19, CHCl₃ for 88% ee).

Diethyl (R)-2-(5-bromo-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate: Compound (R)-4i was obtained as a brown solid (0.08 mmol scale of reaction, 27 mg of product, 70% yield); Rₐ = 0.60 (50% EtOAc in hexane); H NMR (100 MHz, DMSO-D₆) 11.02 (s, 1H), 10.65 (s, 1H), 7.96 - 7.95 (m, 1H), 7.50 (t, J = 6.7 Hz, 2H), 7.32 (d, J = 8.3 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.92 - 6.87 (m, 2H), 6.70 (d, J = 2.7 Hz, 1H), 4.95 (s, 1H), 3.92 - 3.79 (m, 4H), 3.34 (s, 3H), 0.87 (t, J = 7.1 Hz, 3H), 0.71 (t, J = 7.1 Hz, 3H); C NMR (100 MHz, DMSO-D₆) δ 177.5, 167.3, 166.7, 142.9, 137.3, 132.6, 131.8, 129.8, 125.0, 124.7, 121.7, 121.6, 119.1, 113.3, 112.2, 112.0, 111.1, 61.7, 61.1, 56.4, 53.6, 13.7, 13.6; IR (film) νₘₐₓ 3381, 2982, 1715, 1471, 1371, 1299, 1246, 1189, 1031, 860, 816, 741 cm⁻¹; HRMS (ESI) m/z [M + Na]^+ Calcd for [C₂₃H₂₁BrN₂O₅+Na]^+ 507.0526; Found 507.0530; MP 180 - 182 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 70/30; flow rate: 1.0 mL/min; detection: at 254 nm): tᵣ minor = 6.00 min, tᵣ major = 11.09 min. [α]D²₅.⁰ = +180.7 (c = 0.17, CHCl₃ for 88% ee).
Dibenzyl (R)-2-(3-(5-methoxy-1H-indol-3-yl)-2-oxoindolin-3-yl)malonate: Compound (R)-4j was obtained as a colorless solid (0.08 mmol scale of reaction, 36 mg of product, 80% yield); R_f = 0.57 (50% EtOAc in hexane; ^1H NMR (400 MHz, 0.5 mL CDCl_3, 0.1 mL DMSO-D_6) δ 9.05 (s, 1H), 8.95 (s, 1H), 7.91 (d, J = 7.5 Hz, 1H), 7.23 - 7.14 (m, 4H), 7.16 - 7.09 (m, 3H), 7.08 (d, J = 2.5 Hz, 1H), 7.03 - 6.92 (m, 3H), 6.87 - 6.78 (m, 2H), 6.76 (d, J = 7.7 Hz, 1H), 6.72 (dd, J = 8.8, 2.5 Hz, 1H), 6.63 (d, J = 2.8 Hz, 1H), 5.24 (s, 1H), 4.91 - 4.68 (m, 4H), 3.62 (s, 3H); 1H NMR (500 MHz, 0.5 mL CDCl_3, 0.1 mL DMSO-D_6) δ 9.66 - 9.64 (m, 2H), 7.99 - 7.96 (m, 1H), 7.79 - 7.74 (m, 1H), 7.29 - 7.16 (m, 5H), 7.13 - 7.01 (m, 4H), 6.99 - 6.88 (m, 3H), 6.71 - 6.67 (m, 2H), 6.62 - 6.58 (m, 1H), 6.54 - 6.51 (m, 1H), 5.23 - 5.20 (m, 1H), 4.84 - 4.82 (m, 2H), 4.74 - 4.72 (m, 1H), 4.67 - 4.61 (m, 1H), 3.69 - 3.60 (m, 3H), 2.36 (Water); 13C NMR (125 MHz, DMSO-D_6) δ 178.1, 167.1, 166.7, 153.5, 142.1, 134.8, 134.6, 132.0, 129.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.2, 124.9, 121.7, 112.3, 111.9, 111.4, 109.7, 103.0, 67.0, 66.7, 65.4, 53.3; IR (film) ν_max 3377, 2355, 1713, 1615, 1469, 1308, 1214, 1146, 735 cm^-1; HRMS (ESI) m/z [M + Na]^+ Calcd for [C_{34}H_{28}N_{2}O_{6}]+Na^+ 583.1840; Found 583.1855; MP 158 - 160 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 60/40; flow rate: 1.0 mL/min; detection: at 254 nm); t_R minor = 5.60 min, t_R major = 16.12 min. [α]_D^{22.5} = +70.0 (c = 0.10, MeOH for 96% ee).

Dibenzyl (R)-2-(5-bromo-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate: Compound (R)-4k was obtained as a yellow solid (0.08 mmol scale of reaction, 36 mg of product, 74% yield); R_f = 0.60 (40% EtOAc in hexane); ^1H NMR (500 MHz, 0.5 mL CDCl_3, 0.1 mL DMSO-D_6) δ 9.66 - 9.64 (m, 2H), 7.99 - 7.96 (m, 1H), 7.79 - 7.74 (m, 1H), 7.29 - 7.16 (m, 5H), 7.13 - 7.01 (m, 4H), 6.99 - 6.88 (m, 3H), 6.71 - 6.67 (m, 2H), 6.62 - 6.58 (m, 1H), 6.54 - 6.51 (m, 1H), 5.23 - 5.20 (m, 1H), 4.84 - 4.82 (m, 2H), 4.74 - 4.72 (m,
2H), 13C NMR (125 MHz, DMSO) δ 177.6, 167.1, 166.6, 141.8, 137.2, 134.8, 134.7, 131.7, 131.4, 129.9, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 124.8, 124.5, 121.8, 121.7, 119.4, 114.0, 111.6, 111.4, 67.2, 66.9, 56.4, 53.7; IR (film) υ max 3388, 3066, 2924, 2854, 2840, 1728, 1620, 1471, 1465, 1442, 1311, 1273, 1250, 1217, 1145, 750, 686 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ Calcd for [C₃₃H₂₅BrN₂O₅+Na]⁺ 631.0839; Found 631.0839; MP 220 - 222 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 60/40; flow rate: 1.0 mL/min; detection: at 254 nm): tR minor = 6.18 min, tR major = 13.88 min. [α]D²⁵.⁰ = +120.0 (c = 0.16, CHCl₃ for 94% ee).

**Dibenzyl (R)-2-(3-(5-bromo-1H-indol-3-yl)-2-oxoindolin-3-yl)malonate:** Compound (R)-4l was obtained as a colorless solid (0.08 mmol scale of reaction, 38 mg of product, 80% yield); Rf = 0.55 (50% EtOAc in hexane); 1H NMR (400 MHz, 0.5 mL CDCl₃, 0.1 mL DMSO-D₆) δ 9.85 (br, 1H), 9.41 (br, 1H), 7.98 (s, 1H), 7.83 - 7.81 (m, 1H), 7.1 - 7.08 (m, 9H), 6.95 - 6.91 (m, 3H), 6.7 - 6.73 (m, 3H), 6.5 - 6.53 (m, 1H), 5.16 (s, 1H), 4.81 - 4.72 (m, 4H); 13C NMR (125 MHz, DMSO-D₆) δ 178.1, 167.2, 166.7, 142.4, 142.4, 135.9, 134.8, 134.7, 129.2, 128, 4128.4, 128.3, 128.1, 127.9, 127.7, 126.9, 126.6, 126.1, 124.5, 124.3, 121.8, 113.2, 112.7, 111.5, 110.1, 67.2, 66.9, 56.5, 53.4; IR (film) υ max 3391, 2925, 2257, 1728, 1621, 1471, 1379, 1312, 1266, 1147, 1025, 1005, 755, 698 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ Calcd for [C₃₃H₂₅BrN₂O₅+Na]⁺ 631.0839; Found 631.0867; MP 110 - 112 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 60/40; flow rate: 1.0 mL/min; detection: at 254 nm): tR minor = 4.65 min, tR major = 9.13 min. [α]D²⁵.² = +200.0 (c = 0.18, MeOH for 92% ee).
**Diethyl (R)-2-(3-(1H-indol-3-yl)-2-oxo-5-phenylindolin-3-yl)malonate:** Compound (R)-4m was obtained as a brown solid (0.08 mmol scale of reaction, 28 mg of product, 74% yield); R_f = 0.55 (40% EtOAc in hexane); ^1H NMR (500 MHz, 0.5 mL CDCl_3, 0.1 mL DMSO-D_6) δ 9.72 - 9.68 (m, 2H), 8.29 - 8.28 (m, 1H), 7.86 - 7.85 (m, 1H), 7.61 - 7.48 (m, 3H), 7.42 - 7.35 (m, 2H), 7.31 - 7.24 (m, 2H), 7.06 - 6.97 (m, 3H), 6.73 - 6.71 (m, 1H) 5.21 (s, 1H), 3.94 - 3.83 (m, 4H), 2.73 (Water), 0.92 - 0.87 (m, 3H), 0.78 - 0.75 (m, 3H); ^13C NMR (125 MHz, 0.5 mL CDCl_3, 0.1 mL DMSO-D_6) δ 178.6, 167.4, 167.0, 142.1, 141.1, 137.2, 134.7, 130.6, 128.6, 127.2, 126.6, 126.5, 125.1, 124.4, 121.9, 121.5, 119.1, 111.5, 110.0, 61.4, 60.8, 56.6, 53.7, 13.4, 13.2; IR (film) ν max 3394, 3062, 2926, 2357, 1720, 1624, 1473, 1307, 1236, 827, 746 cm^{-1}; HRMS (ESI) m/z [M + H]^+ Calcd for [C_{29}H_{27}N_2O_5]^+ 483.1914; Found 483.1906; MP 180 - 182 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 6.56 min, t_R major = 8.17 min. [α]_D^{24.2} = +109.0 (c = 0.21, MeOH for 91% ee).

**Diethyl (R)-2-(3-(1H-indol-3-yl)-5-(3-methoxyphenyl)-2-oxoindolin-3-yl)malonate:** Compound (R)-4n was obtained as a colorless solid (0.08 mmol scale of reaction, 31 mg of product, 77% yield); R_f = 0.56 (40% EtOAc in hexane); ^1H NMR (400 MHz, 0.5 mL CDCl_3, 0.1 mL DMSO-D_6) δ 9.72 (brs, 1H), 9.68 (brs, 1H), 9.08 (brs, 1H), 8.08 (s, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.16 - 7.08 (m, 2H), 6.71 - 6.99 (m, 1H), 6.94 (s, 1H), 6.82 - 6.86 (m, 1H) 6.82 - 6.80 (m, 2H), 6.67 - 6.65 (m, 1H), 6.55 (s, 1H), 5.00 (s, 1H), 3.75 - 3.67 (m, 7H), 2.65 (Water), 0.75 - 0.72 (m, 3H), 0.61 - 0.57(m, 3H); ^13C NMR
Diethyl (R)-2-(3-(1H-indol-3-yl)-5,7-dimethyl-2-oxoindolin-3-yl)malonate: Compound (R)-4o was obtained as a colorless solid (0.08 mmol scale of reaction, 27 mg of product, 79% yield); Rf = 0.56 (40% EtOAc in hexane); H NMR (500 MHz, 0.5 mL CDCl3, 0.1 mL DMSO-D6) δ 9.47 - 9.45 (m, 2H), 7.74 - 7.72 (m, 1H), 7.48 (s, 1H), 7.12 - 7.08 (m, 1H), 6.93-6.84 (m, 2H), 6.75 - 6.74 (m, 1H), 6.51 - 6.50 (m, 1H), 5.01 (s, 1H), 3.77 - 3.67 (m, 4H), 2.56 (Water), 2.17 (s, 3H), 2.02 (s, 3H); C NMR (125 MHz, 0.5 mL CDCl3, 0.1 mL DMSO-D6) δ 179.1, 167.4, 167.1, 138.5, 137.1, 130.8, 130.3, 129.5, 125.1, 125.0, 124.5, 122.2, 121.4, 118.6, 112.3, 111.3, 61.2, 60.7, 56.5, 54.0, 21.2, 16.5, 13.2 (2c); IR (film) νmax 3444, 3386, 2920, 2848, 1707, 1624, 1456, 1456, 1261, 1103, 744 cm⁻¹; HRMS (ESI) m/z [M + H]+ Calcd for [C30H29N2O6]+ 513.2020; Found 513.2022; 513.2020; MP 190 - 192 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak ID-3 column; solvent: hexane/2-propanol = 70/30; flow rate: 1.0 mL/min; detection: at 254 nm): tR minor = 7.09 min, tR major = 10.79 min. [α]D = +45.2 (c = 0.30, MeOH for 90% ee).
Diethyl (R)-2-(5-chloro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)malonate: Compound (R)-4p was obtained as a brown solid (0.08 mmol scale of reaction, 25 mg of product, 70% yield); R_f = 0.55 (40% EtOAc in hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 8.09 (d, J = 2.6 Hz, 1H), 8.05 (d, J = 2.2 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 3.6 Hz, 1H), 7.24 – 7.23 (m, 1H), 7.15 – 7.05 (m, 2H), 6.76 (d, J = 8.3 Hz, 1H), 6.62 (d, J = 2.7 Hz, 1H), 5.19 (s, 1H), 4.00 – 3.84 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H), 0.77 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.3, 167.3, 166.8, 140.4, 137.0, 131.5, 128.8, 127.6, 127.7, 124.8, 124.1, 122.4, 122.1, 119.9, 111.9, 111.4, 110.8, 61.9, 61.2, 56.4, 53.9, 13.5, 13.3; IR (film) ν_max 3389, 2990, 1721, 1620, 1461, 1381, 1289, 1256, 1159, 1011, 870, 800, 761, 720 cm⁻¹; HRMS (ESI) m/z [M + Na]^+ Calcd for [C₂₃H₂₂ClN₂O₅]^+ 441.12; Found 441.1236; MP 192 - 194 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 70/30; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 5.10 min, t_R major = 7.48 min. [α]_D²⁴.⁵ = +201.8 (c = 0.10, MeOH for 86% ee).

Dibenzyl (R)-2-(3-(1H-indol-3-yl)-5,7-dimethyl-2-oxoindolin-3-yl)malonate: Compound (R)-4q was obtained as a colourless solid (0.08 mmol scale of reaction, 34 mg of product, 78% yield); R_f = 0.61 (40% EtOAc in hexane); ¹H NMR (400 MHz, DMSO-D₆) δ 10.11 (s, 1H), 9.51 (s, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.51 - 6.30 (m, 8H), 6.23 - 6.18 (m, 3H), 6.08 - 5.97 (m, 4H), 5.77 (s, 1H), 4.29 (s, 1H) 4.12 - 4.01 (m, 4H), 1.31 (s, 3H), 1.28 (s, 3 H); ¹³C NMR (100 MHz, DMSO-D₆) δ 182.9, 172.1, 171.7, 144.1, 143.8, 142.2, 140.3, 140.2, 135.5, 134.9, 134.5, 133.5, 133.4, 133.2, 132.9, 132.7, 132.6, 130.0, 129.9, 126.7, 126.3, 123.8, 123.6, 116.9, 116.7, 116.7, 116.7, 116.1, 71.8, 71.5, 61.5, 58.4, 26.1, 21.7; IR
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(film) $\nu_{\text{max}}$ 3385, 3064, 2924, 2854, 1718, 1612, 1471, 1465, 1311, 1273, 1217, 1155, 742, 696 cm$^{-1}$; HRMS (ESI) m/z [M + Na]$^+$ Calcd for [C$_{33}$H$_{30}$N$_2$O$_5$+Na]$^+$ 581.2047; Found 581.2064; MP 201 - 203 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak AD-H column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R$ minor = 29.05 min, $t_R$ major = 35.36 min. $[\alpha]_D^{25.0} = +45.9$ (c = 0.40, MeOH for 93% ee).

Dibenzyl (R)-2-(3-(6-bromo-1H-indol-3-yl)-2-oxoindolin-3-yl)malonate: Compound (R)-4r was obtained as a yellow solid (0.08 mmol scale of reaction, 23 mg of product, 92% yield; $R_f = 0.60$ (40% EtOAc in hexane); $^1$H NMR (400 MHz, DMSO-D$_6$) $\delta$ 11.14 (s, 1H), 10.53 (s, 1H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.64 (d, $J = 8.7$ Hz, 1H), 7.55 (s, 1H), 7.37 - 7.30 (m, 2H), 7.29 – 7.28 (m, 2H), 7.22 (d, $J = 7.1$ Hz, 1H), 7.16 (t, $J = 7.4$ Hz, 2H), 7.06 – 6.98 (m, 4H), 6.88 (d, $J = 7.8$ Hz, 1H), 6.77 (d, $J = 7.4$ Hz, 2H), 6.67 (s, 1H), 5.12 (s, 1H), 5.00 – 4.80 (m, 4H); $^{13}$C NMR (100 MHz, DMSO-D$_6$) $\delta$ 177.7, 167.3, 166.7, 143.3, 138.4, 135.5, 135.5, 129.7, 129.2, 128.8, 128.6, 128.5, 128.3, 127.9, 127.8, 126.9, 126.2, 124.2, 123.7, 122.1, 121.8, 114.9, 114.6, 112.1, 110.3, 67.1, 66.8, 56.5, 53.2; IR (film) $\nu_{\text{max}}$ 3455, 3364, 2994, 2830, 1717, 1622, 1491, 1409, 1301, 1221, 1210, 1100, 772, 636 cm$^{-1}$; HRMS (ESI) m/z [M + Na]$^+$ Calcd for [C$_{33}$H$_{32}$BrN$_2$O$_5$+Na]$^+$ 631.0835; Found 631.0839; MP 195 - 197 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak ID-3 column; solvent: hexane/2-propanol = 60/40; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R$ minor = 7.18 min, $t_R$ major = 10.29 min. $[\alpha]_D^{22.2} = +95.9$ (c = 0.18, CH$_2$Cl$_2$ for 98% ee).
Dibenzyl (R)-2-(3-(7-ido-1H-indol-3-yl)-2-oxoindolin-3-yl)malonate: Compound (R)-4s was obtained as a yellow solid (0.08 mmol scale of reaction, 44 mg of product, 85% yield); \( R_f = 0.63 \) (40% EtOAc in hexane); \(^1\)H NMR (400 MHz, DMSO-D\(_6\)) \( \delta \) 8.0 (s, 1H), 7.9 (d, \( J = 7.6 \) Hz, 1H), 7.9 (s, 1H), 7.8 (d, \( J = 8.2 \) Hz, 1H), 7.5 (d, \( J = 7.5 \) Hz, 1H), 7.25 – 7.14 (m, 7H), 7.06 – 7.00 (m, 3H), 6.84 – 6.78 (m, 3H), 6.69 (d, \( J = 7.7 \) Hz, 1H), 6.64 (d, \( J = 2.7 \) Hz, 1H), 5.27 (s, 1H), 4.95 – 4.86 (m, 4H); \(^{13}\)C NMR (100 MHz, DMSO-D\(_6\)) \( \delta \) 177.9, 167.1, 166.6, 141.5, 138.4, 134.9, 134.6, 131.0, 129.0, 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.3, 125.1, 124.6, 122.5, 122.3, 121.7, 114.1, 110.0, 76.9, 67.4, 67.1, 56.5, 53.6; IR (film) \( \nu_{max} \) 3443, 3364, 2994, 2804, 1719, 1622, 1441, 1400, 1301, 1290, 1200, 1105, 792, 606 cm\(^{-1}\); HRMS (ESI) m/z [M + H]\(^+\) Calcd for [C\(_{33}\)H\(_{26}\)IN\(_2\)O\(_5\)]\(^+\) 657.0881; Found 657.0853; MP 150 - 152 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IC-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): \( t_R \) minor = 4.93 min, \( t_R \) major = 6.44 min. [\( \alpha \)]\(_D\)\(^{20.6} \) = +243.2 (c = 0.15, CH\(_2\)Cl\(_2\) for 90% ee).

(+)-Diethyl 2-(3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-2-oxoindolin-3-yl)malonate: Compound (+)-4t was obtained as a colourless solid (0.08 mmol scale of reaction, 31 mg of product, 90% yield); \( R_f = 0.52 \) (40% EtOAc in hexane); \(^1\)H NMR (400 MHz, Chloroform-d\(_2\)) \( \delta \) 9.90 (s, 1H), 8.74 (s, 1H), 8.01 (d, \( J = 7.2 \) Hz, 1H), 7.30 (td, \( J = 7.7, 1.3 \) Hz, 1H), 7.16 (td, \( J = 7.7, 1.2 \) Hz, 1H), 6.93 (d, \( J = 7.7 \) Hz, 1H), 6.51 (s, 1H), 6.32 (s, 1H), 5.80 (dd, \( J = 20.8, 1.5 \) Hz, 2H), 5.33 (s, 1H), 4.06 (q, \( J = 7.1 \) Hz, 2H), 3.82 (qd, \( J = 7.1, 4.7 \) Hz, 2H), 1.09 (t, \( J = 7.1 \) Hz, 3H), 0.85 (t, \( J = 7.1 \) Hz, 3H); \(^{13}\)C NMR (101 MHz,
Chloroform-$d$) $\delta$ 182.0, 167.2, 166.6, 152.4, 148.5, 141.6, 140.7, 129.5, 128.3, 123.5, 113.6, 110.7, 108.7, 101.9, 101.3, 61.8, 61.5, 57.8, 54.4, 13.3, 13.4; IR (film) $\nu_{\text{max}}$ 3355, 3264, 2884, 1719, 1451, 1465, 1311, 1273, 1217, 1155, 742, 696 cm$^{-1}$; HRMS (ESI) m/z [M + H]$^+$ Calcld for $[\text{C}_{22}\text{H}_{22}\text{NO}_8]^+$ 428.1340; Found 428.1331; MP 135 - 137 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak AD-H column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R$ minor = 7.17 min, $t_R$ major = 24.25 min. $[\alpha]_D^{23.1}$ = +34.2 ($c = 0.16$, MeOH for 50% ee).

**Synthetic procedure for the synthesis of compound (R)-8:** To a stirred solution of (R)-4f (300 mg, 0.6 mmol; 1.0 equiv) in DMSO (5 mL) at 25 ºC was added lithium chloride (96 mg, 2.3 mmol, 4.0 equiv) and H$_2$O (104 µL, 5.6 mmol, 10.0 equiv). After 5 minutes stalling, the reaction mixture was transferred to a pre-heated oil bath (140 ºC) and stirring was continued for 24 h. After complete consumption of starting material (as judged by running TLC), reaction mixture was cooled down to 25 ºC and quenched with water (4 mL). The organic compound was extracted with ethyl acetate (2 X 10 mL). Then the combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude material was purified by column chromatography by using 20 - 30 % (EtOAc/Hexane) to afford compound (R)-8 as a colorless solid.

**Benzyl (R)-2-(3-(1H-indol-3-yl)-2-oxoindolin-3-yl)acetate:** Compound (R)-8 was obtained as a yellow solid (0.6 mmol scale of reaction, 195 mg of product, 80% yield); $R_f$ = 0.45 (40% EtOAc in hexane); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.08 (s, 1H), 10.56
(s, 1H), 7.35 - 7.21 (m, 10H), 7.18 - 7.11 (m, 3H), 7.03 - 6.99 (m, 2H), 6.95 - 6.90 (m, 2H), 6.80 (t, J = 7.5 Hz, 1H), 4.92 (s, 3H), 3.63 (d, J = 16.0 Hz, 1H), 3.51 (d, J = 16.1 Hz, 2H), 3.44 (Water); 13C NMR (100 MHz, DMSO-d6) δ 179.4, 169.9, 143.3, 137.2, 136.3, 133.1, 128.8, 128.6, 128.3, 128.1, 125.1, 124.4, 124.0, 121.8, 121.6, 119.8, 119.1, 114.2, 112.1, 109.9, 65.9, 49.8; IR (film) υ_{max} 3415, 3310, 2929, 2802, 1728, 1642, 1619, 1480, 1327, 1154, 1059, 878, 760 cm\(^{-1}\); HRMS (ESI) m/z [M + Na\(^{+}\)] Calcd for [C\(_{25}\)H\(_{20}\)N\(_2\)O\(_3\)+Na\(^{+}\)] 419.1366; Found 419.1380; MP 165 - 167 °C; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): \(t_R\) minor = 5.71 min, \(t_R\) major = 13.53 min. [\(\alpha\)]\(_D\)\(^{21.0}\) = +122.0 (c = 0.24, MeOH for 99% ee).

**Synthetic procedure for compound** (R)-9: Compound (R)-8 (200 mg, 0.5 mmol; 1.0 equiv) was taken in dimethyl sulfoxide (3 mL) under nitrogen atmosphere. The reaction mixture was cooled to 0 °C and potassium tert-butoxide (119 mg, 1.1 mmol, 2.2 equiv) was added to it. After 5 min of stirring, methyl iodide (66 µL, 1.1 mmol, 2.2 equiv) was added at same temperature and stirring was continued for 3 h. Upon completion of starting material (as judged by running TLC), the reaction mixture was quenched with careful addition of water (2 mL) and organic compound was extracted with ethyl acetate (2 X 10 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude material was purified by column chromatography by using 20-30 % (EtOAc/Hexane) to afford compound (R)-9 as a white solid.
Benzyl (R)-2-(1-methyl-3-(1-methyl-1H-indol-3-yl)-2-oxindolin-3-yl)acetate:

Compound (R)-9 was obtained as a brown solid (0.5 mmol scale of reaction, 191 mg of product, 94% yield); R_f = 0.53 (40% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) 7.30 - 7.28 (m, 3H), 7.09 - 7.04 (m, 6H), 6.85 - 6.81 (m, 2H), 6.52 (d, J = 7.8 Hz, 1H), 6.47 (d, J = 7.8 Hz, 1H), 4.89 - 4.81 (m, 2H), 4.37 (d, J = 16.7 Hz, 1H), 3.80 (s, 1H), 3.42 (d, J = 16.8 Hz, 1H), 3.13 (s, 3H), 3.05 (s, 3H); ^13C NMR (125 MHz) δ177.8, 169.6, 144.4, 137.7, 135.3, 131.4, 128.6, 128.5, 128.4, 127.1, 125.5, 123.9, 122.4, 121.9, 120.8, 119.5, 112.9, 109.5, 108.3, 66.5, 49.7, 40.9, 32.7, 26.3; IR (film) υ max 3415, 2924, 2852, 1726, 1622, 1481, 1307, 1174, 1029, 848, 748 cm⁻¹; HRMS (ESI) m/z [M + H]^+ Calcd for [C_{27}H_{25}N_{2}O_{3}]^+ 425.1860; Found 425.1883; MP 68 - 70 ºC; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 50/50; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 7.82 min, t_R major = 13.17 min. [α]D^{24.1} = +12.5 (c = 0.19, CHCl_3 for 99.5% ee).

Synthetic procedure for compound 10: Compound (R)-9 (150 mg, 0.33 mmol; 1.0 equiv) was taken in acetic acid (3 mL) at 25 ºC. To this solution was added HCl (61 µL, 1.7 mmol, 5.0 equiv), followed by dimethyl sulfoxide (236 µL, 3.3 mmol, 10.0 equiv). Then the reaction mixture was placed over a pre-heated oil bath maintaining 50 ºC for 3 h. Upon completion of starting material (as judged by running TLC), the reaction mixture was quenched with sat. Na_2CO_3 (2 mL) and organic compound was extracted with ethyl acetate (2 X 10 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude material was purified by
column chromatography by using 20-30% (EtOAc/Hexane) to afford compound 10 as an orange solid.

**Benzyl 2-((3'R)-1,1'-dimethyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)acetate** (10):
Compound 10 (major diastereomer) was obtained as an orange colour gel (0.3 mmol scale of reaction, 85 mg of product, 50% yield); $R_f = 0.44$ (40% EtOAc in hexane); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 - 7.29 (m, 3H), 7.10 - 7.05 (m, 6H), 6.84 (td, $J = 7.6$, 1.4 Hz, 1H), 6.52 (d, $J = 7.8$ Hz, 1H), 6.47 (d, $J = 7.8$ Hz, 1H), 4.89 - 4.81 (m 2H), 4.37 (dd, $J = 16.8$, 1.3 Hz, 1H), 3.80 (s, 1H), 3.44 - 3.39 (m, 1H), 3.13 (d, $J = 1.4$ Hz, 1H), 3.13 (s, 3H), 3.05 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.3, 174.7, 169.7, 144.0, 143.9, 135.3, 128.7, 128.6, 128.4, 128.1, 128.1, 126.8, 124.3, 123.6, 122.4, 122.1, 121.9, 107.9, 107.6, 66.3, 51.3, 49.6, 37.5, 25.9, 25.8; IR (film) $\nu_{\text{max}}$ 3425, 2914, 2862, 1721, 1612, 1482, 1317, 1124, 1009, 808, 758 cm$^{-1}$; HRMS (ESI) m/z [M + H]$^+$ Calcd for [C$_{27}$H$_{25}$N$_2$O$_4$]$^+$ 441.1809; Found 441.1810

**Synthetic procedure for compound 11:** Compound 10 (100 mg, 0.2 mmol; 1.0 equiv) was taken in toluene (2 mL) under nitrogen atmosphere at 0 °C. To this solution was added tetrabutyl ammonium hydrogen sulphate (16 mg, 0.05 mmol, 20 mol%), followed by 50% aq. sodium hydroxide (742 µL, 9.28 mmol, 40 equiv). After 5 minutes of stirring at 0 °C, bromoethyl acetate (53 µL, 0.5 mmol, 2.0 equiv) was added to the reaction mixture. Then the reaction mixture allowed stirring for 20 h at the same temperature. Upon completion of starting material (monitored by running TLC), the reaction mixture
was diluted with water (2 mL) and organic compound was extracted with ethyl acetate (2 X 10 mL). Then the organic layer was dried with anhydrous sodium sulphate and concentrated in vacuo. The crude material was purified by column chromatography by using 20-30% (EtOAc/Hexane) to afford compound 11 as an orange solid.

**Benzyl 2-(3'- (2-ethoxy-2-oxoethyl)-1,1'-dimethyl-2,2'-dioxo-[3,3’-biindolin]-3-yl)acetate:** Compound 11 was obtained as a colourless solid (0.22 mmol scale of reaction, 98 mg of product, 85% yield); 

**Rf** = 0.53 (40% EtOAc in hexane); **1H NMR** (700 MHz) δ 7.19 - 7.17 (m, 3H), 6.96 - 6.91 (m, 2H), 6.31 - 6.29 (m, 1H), 6.20 - 6.19 (m, 1H), 4.68 - 4.62 (m, 2H), 4.02 (d, J = 16.0 Hz, 1H), 3.95 (d, J = 16.0 Hz, 1H), 3.73 - 3.64 (m, 2H) 3.18 (d, J = 16.0 Hz, 1H), 3.11 (d, J = 16.0 Hz, 1H), 3.00 (s, 3H), 0.83 (d, J = 7.11 Hz, 3H); **13C NMR** (175 MHz) δ 176.6, 176.4, 169.7, 169.6, 143.8, 143.7, 135.2, 128.8, 128.7, 128.4, 128.3, 128.2, 126.8, 126.7, 122.8, 121.5, 121.4, 107.5, 107.3, 77.2, 77.1, 76.8, 66.4, 60.4, 52.5, 52.4, 33.9 (2C), 25.8, 25.5, 13.7; **IR** (film) υ_{max} 3446, 3435, 2956, 2922, 2850, 2350, 2090, 1735, 1712, 1612, 1494, 1456, 1338, 1188, 1118, 1095, 906, 754 cm^{-1}; **HRMS** (ESI) m/z [M + H]^+ Calcd for [C_{23}H_{21}N_{2}O_{6}]^+ 549.1996; Found 549.2013; **MP** 135 - 137 °C.

**Synthetic procedure for the synthesis of compound (3S,3S)-12:** Compound 11 (50 mg, 0.1 mmol; 1.0 equiv) was taken in diethyl ether (2 mL) under nitrogen atmosphere at 0 °C. To this solution was added LiBH₄ (225 µL, 0.45 mmol, 5.0 equiv) followed by
methanol (44 µL, 0.9 mmol, 10.0 equiv). Then the reaction mixture allowed stirring for 1 h at the same temperature. Upon completion of starting material (monitored by running TLC), the reaction mixture was quenched with water (2 mL) and organic compound was extracted with ethyl acetate (2 X 5 mL). Then the organic layer was dried with anhydrous sodium sulphate and concentrated in vacuo. The crude material was purified by column chromatography by using 80 - 90% (EtOAc/Hexane) to afford compound (S,S)-12 as a white crystalline solid.

(3S,3S)-Bis(2-hydroxyethyl)-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione: Compound (3S, 3'S)-12 was obtained as a colourless solid (0.1 mmol scale of reaction, 33 mg of product, 88% yield); Rf = 0.20 (in EtOAc); 1H-NMR (400 MHz, CDCl3) δ 7.03-6.99 (m, 4H), 6.81 (t, J = 7.5 Hz, 2H), 6.39 (d, J = 7.7 Hz, 2H), 3.42-3.36 (m, 2H), 3.22-3.17 (m, 2H), 3.13-3.06 (m, 2H), 3.03 (s, 6H), 2.63-2.55 (m, 2H); 13C NMR (175 MHz) δ 178.1, 143.4, 128.4, 127.2, 123.5, 121.5, 107.5, 59.7, 54.9, 31.4, 25.7; Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak AD-3 column; solvent: 2-propanol /hexane= 30/80; flow rate: 1.0 mL/min; detection: at 254 nm): tR major = 16.66 min. tR minor = 20.41 min. [α]D 23.0 = −145.2 (c = 0.4, CHCl3 for 99.5% ee).

Synthesis of compound (±)-17 from enantioselective method: An oven dried sample vial was charged with Cu(OTf)2 (0.1 equiv) and 'Bu-PHOX (0.2 equiv) in dichloromethane (4 mL) at 25 ºC under nitrogen atmosphere. The reaction mixture was stirred for 30 minutes to make the complex. After that the reaction vessel was cooled to -
5 °C and tert-Butyl acetoacetate (3.0 equiv) was added to the mixture and stirring was continued for 15 minutes maintaining temperature -5 °C. Then, a solution of 3-hydroxy 2-oxindole in dichloromethane (0.5 mL) was added slowly to the reaction mixture. Then the reaction mixture was allowed to stir for 4 h at -5 °C. After complete consumption of starting material (as judged by running TLC), the crude mixture was concentrated under reduced pressure and purified by column chromatography by using 20-30% EtOAc-hexane mixture as eluent to afford the desired compound.

**tert-Butyl-2-(3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-3-oxobutanoate**: Compound (±)-17 was obtained as a colourless solid (0.08 mmol scale of reaction, 31 mg of product, 95% yield); dr = 1.1:1 (determined from un purified reaction mixture) of (±)-17; Rf = 0.51 (40% EtOAc in hexane); \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\), spectrum contains ~1:1 diastereomers) \(\delta\) 8.57 (d, \(J = 9.4\), 1H for minor diastereomer), 8.44 (d, \(J = 8.7\), 1H for major diastereomer), 8.20 - 8.17 (m, 2H for major + minor diastereomers), 8.06 - 8.02 (m, 2H for major + minor diastereomers), 7.93 (d, \(J = 7.5\), 1H for major diastereomer), 7.85 (d, \(J = 7.5\), 1H for minor diastereomer), 7.25 - 7.16 (m, 4H), 7.16 - 6.99 (m, 6H for major + minor diastereomers), 6.81 - 6.76 (m, 2H for major + minor diastereomers), 6.52 (s, 1H for minor diastereomer), 6.41 (s, 1H for major diastereomer), 5.43 (s, 1H for major diastereomer), 5.07 (s, 1H for minor diastereomer), 2.08 - 2.04 (m, 7H for major + minor diastereomers), 1.04 - 1.02 (m, 9H for major diastereomer), 0.99 (s, 9H for minor diastereomer) \(^1\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\), spectrum contains ~1:1 diastereomers) \(\delta\) 202.5, 201.5, 179.4, 178.9, 178.1, 166.7, 141.8, 141.5, 137.2, 137.1, 130.4, 130.1, 128.5, 128.4, 128.0, 126.5, 125.4 (two carbons), 124.9, 124.4, 122.6 (two carbons), 122.4, 122.1 (two carbons), 122.1, 121.7 (two carbons), 119.7, 119.6, 111.8, 111.3, 110.1, 109.8, 83.1, 81.9, 65.0, 61.4, 54.2, 53.5, 32.4, 29.3, 27.2, 27.2, 27.1; \(\text{IR} \) (film) \(\nu_{\text{max}}\) 3455, 3364, 3220, 2884, 2019, 1722, 1711, 1665, 1461, 1223, 1207, 1185, 702, 606 cm\(^{-1}\); \(\text{HRMS} \) (ESI) m/z.
[M + Na]⁺ Calcd for [C₂₄H₂₄N₂O₄ + Na]⁺ 427.1628; Found 427.1606; MP 120 - 122 °C; Enantiomeric peaks was determined via HPLC analysis using a Chiralpak OZ-3 column; solvent: hexane/2-propanol = 70/30; flow rate: 1.0 mL/min; detection: at 254 nm); in case of major diastereomer \( t_{R1} = 4.93 \) min, \( t_{R2} = 17.01 \) min. for 0% ee; in case of minor diastereomer \( t_{R1} = 8.58 \) min, \( t_{R2} = 10.53 \) min. for 0% ee.

Synthesis of compound (±)-19 from enantioselective method: An oven dried sample vial was charged with Cu(OTf)₂ (0.1 equiv) and \(^7\)Bu-PHOX (0.2 equiv) in dichloromethane (4 mL) at 25 °C under nitrogen atmosphere. The reaction mixture was stirred for 30 minutes to make the complex. After that the reaction vessel was cooled to -5 °C and compound 18 (3.0 equiv) was added to the mixture and stirring was continued for 15 minutes maintaining temperature -5 °C. Then, a solution of 3-hydroxy 2-oxindole in dichloromethane (0.5 mL) was added slowly to the reaction mixture. Then the reaction mixture was allowed to stir for 6 h at -5 °C. After complete consumption of starting material (as judged by running TLC), the crude mixture was concentrated under reduced pressure and purified by column chromatography by using 30-40% EtOAc-hexane mixture as eluent to afford the desired compound.

Ethyl-1-(3-(1H-indol-3-yl)-2-oxindolin-3-yl)-2-oxocyclopentane-1-carboxylate:
Compound (±)-19 was obtained as a colourless solid (0.08 mmol scale of reaction, 25 mg of product, 80% yield); \( \text{dr} = 4.7:1 \) (determined from un purified reaction mixture) of (±)-19; \( R_f = 0.31 \) (40% EtOAc in hexane); \(^1\)H NMR (400 MHz, CDCl₃, spectrum contains ~4.7:1 diastereomers) \( \delta 8.92 \) (s, 2H for major + minor diastereomers), 8.65 (s,
2H for major + minor diastereomers), 8.26 (s, 2H for major + minor diastereomers), 7.87 (s, 1H for minor diastereomer), 7.67 (s, 1H for major diastereomer), 7.31 - 6.96 (m, 12H for major + minor diastereomers), 6.73 (s, 2H for major + minor diastereomers), 4.06 - 3.74 (m, 4H for major + minor diastereomers), 3.15 - 2.94 (m, 4H for major + minor diastereomers), 2.63 - 2.28 (m, 4H for major + minor diastereomers), 2.00 - 1.76 (m, 4H for major + minor diastereomers), 1.06 - 0.64 (m, 6H for major + minor diastereomers);

$^{13}$C NMR (100 MHz, CDCl$_3$, spectrum contains ~4.7:1 diastereomers) δ 213.5, 212.8, 179.8, 179.0, 170.9, 170.2, 141.1, 141.1, 136.6, 136.5, 131.9, 131.6, 128.7, 128.6, 128.4, 128.3, 127.4, 127.3, 125.9, 125.8, 122.2, 121.8, 121.8, 121.7, 121.6, 121.3, 119.7, 119.6, 111.6, 110.6, 110.1, 109.7, 109.6, 109.1, 66.5, 66.3, 61.8, 61.7, 55.7, 55.7, 39.1, 38.7, 33.4, 33.1, 19.6, 19.4, 13.7, 13.5; IR (film) $\nu_{\text{max}}$ 3545, 3334, 3210, 2980, 2119, 1742, 1721, 1645, 1601, 1423, 1287, 1285, 1002, 806 cm$^{-1}$; HRMS (ESI) m/z [M + Na]$^+$ Calcd for [C$_{24}$H$_{22}$N$_2$O$_4$ + Na]$^+$ 425.1472; Found 425.1460; MP 100 - 102 °C; Enantiomeric peaks was determined via HPLC analysis using a Chiralpak AS-3 column; solvent: hexane/2-propanol = 60/40; flow rate: 1.0 mL/min; detection: at 254 nm); in case of minor diastereomer $t_{R1}$ = 5.24 min, $t_{R2}$ = 12.72 min; for 0% ee; in case of major diastereomer $t_{R1}$ = 7.11 min, $t_{R2}$ = 21.71 min; for 0% ee.

References and notes:

Spectral Graphics

NMR spectra of compound 14

$^1$H NMR (400 MHz, CDCl$_3$) of compound 14
$^1$H NMR (500 MHz, CDCl$_3$) of compound 15a
$^1$H NMR (400 MHz, CDCl$_3$) of compound 15b
$^1$H NMR (100 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound 13b
$^{13}$C NMR (100 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound 13b
$^1$H NMR (400 MHz, DMSO-D$_6$) of compound (±)-5a
$^1$H NMR (500 MHz, DMSO-D$_6$) of compound (±)-5b
$^{13}$C NMR (125 MHz, DMSO-$d_6$) of compound (±)-5b
^1^H NMR (400 MHz, CDCl\textsubscript{3}) of compound (±)-5c
$^{13}$C NMR (100 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (±)-5c
$^{1}$H NMR (400 MHz, DMSO-D$_6$) of compound (±)-5d
$^{13}$C NMR (100 MHz, DMSO-D$_6$) of compound (±)-5d
$^{1}$H NMR (400 MHz, DMSO-D$_6$) of compound (±)-5e
$^{13}$C NMR (100 MHz, DMSO-D$_6$) of compound $(\pm)$-5e
$^1$H NMR (500 MHz, DMSO-D$_6$) of compound (±)-5f
$^{13}$C NMR (125 MHz, DMSO-$D_6$) of compound (±)-5f
\(^1\)H NMR (500 MHz, DMSO-D<sub>6</sub>) of compound (±)-5g
$^{13}$C NMR (125 MHz, DMSO-D$_6$) of compound (±)-5g
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$^1$H NMR (500 MHz, DMSO-$D_6$) of compound (±)-5h

![NMR spectrum](image)

H$_2$O
$^{13}$C NMR (125 MHz, DMSO-D$_6$) of compound (±)-5h
$^1$H NMR (500 MHz, DMSO-D$_6$) of compound (±)-5i
$^{13}$C NMR (125 MHz, DMSO-$D_6$) of compound ($\pm$)-5i
$^1$H NMR (500 MHz, DMSO-D$_6$) of compound (±)-5k
$^{13}$C NMR (125 MHz, DMSO-D$_6$) of compound (±)-5k
$^1$H NMR (500 MHz, DMSO-D$_6$) of compound (±)-5l
$^{13}$C NMR (125 MHz, DMSO-D$_6$) of compound (±)-S1
$^1$H NMR (400 MHz, 0.5 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4a
$^{13}$C NMR (100 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4a
Scanned copy of mass spectrum of (R)-4a
$^1$H NMR (500 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4b
$^{13}$C NMR (100 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4b
Scanned copy of mass spectrum of (R)-4b
$^{1}$H NMR (400 MHz, CDCl$_3$) of compound (R)-4c
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (R)-4c
Scanned copy of mass spectrum of (R)-4c
$^1$H NMR (400 MHz, CDCl$_3$) of compound (R)-4d
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (R)-4d
Scanned copy of mass spectrum of (R)-4d
$^1$H NMR (400 MHz, DMSO-D$_6$) of compound (+)-4e
$^{13}$C NMR (100 MHz, DMSO-D$_6$) of compound (+)-4e
Scanned copy of mass spectrum of (\(+\))-4e
$^1$H NMR (500 MHz, CDCl$_3$) of compound (R)-4f
$^1$H NMR (500 MHz, CDCl$_3$) of compound (R)-4f
Scanned copy of mass spectrum of (R)-4f
$^1$H NMR (400 MHz, DMSO-$D_6$) of compound (R)-4g
$^{13}$C NMR (100 MHz, DMSO-$d_6$) of compound (R)-4g
Scanned copy of mass spectrum of (R)-4g
\(^{1}\text{H NMR (500 MHz, DMSO-D}_6\text{)}\) of compound \((R)-4h\)
$^{13}$C NMR (125 MHz, DMSO-$d_6$) of compound $(R)$-4h
Scanned copy of mass spectrum of (R)-4h
$^1$H NMR (400 MHz, DMSO-$d_6$) of compound (R)-4i
$^{13}$C NMR (100 MHz, DMSO-D$_6$) of compound (R)-4i
Scanned copy of mass spectrum of (R)-4i
$^1$H NMR (0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4j
$^{13}$C NMR (0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R-4j)
Display Report

Analysis Info
Analysis Name: Supporting Information
Method: HRLCMS-20 Sept tune wide.m
Sample Name: Dr.A.Bisai-AB-KNB-02-280
Comment:

Acquisition Parameter
Source Type: ESI
Focus: Not active
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Scan End: 3000 m/z
Ion Polarity: Positive
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Set End Plate Offset: -500 V
Set Collision Cell RF: 600.0 Vpp
Set Nebulizer: 1.2 Bar
Set Dry Heater: 260 °C
Set Dry Gas: 7.0 k/min
Set Divert Valve: Waste

Scan #1: Dr.A.Bisai-AB-KNB-02-280_1-A.6_01_3610.d: UV Chromatogram, 200-400 nm
Scan #2: +MS, 0.9-1.0min #52-61
Scan #3: +MS, 0.9-1.0min #52-61
C34H28N2O6, M+Na, 583.16

Scanned copy of mass spectrum of (R)-4j
$^1$H NMR (500 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4k
$^{13}$C NMR (120 MHz, 0.4 mL CDCl$_3$, 0.1 (R)-4k)

Supporting Information 95
Supporting Information

Display Report

Analysis Info
Analysis Name: D:\Data\user data\2017\MAY 2017\25 may\Dr A Bisi-KNB-02-324_1-E_4_01_1707.d
Method: hrlcms_pos_mid_tunemix.m
Sample Name: Dr A Bisi-KNB-02-324
Comment:

Acquisition Parameter
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Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z
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Set End Plate Offset: -500 V
Set Collision Cell RF: 450.0 Vpp
Set Nebulizer: 0.3 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Waste

Scanned copy of mass spectrum of (R)-4k
$^1$H NMR (400 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4I
$^{13}$C NMR (100 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4l
Scanned copy of mass spectrum of *(R)-41*
$^1$H NMR (500 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4m
$^{13}$C NMR (125 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4m
Scanned copy of mass spectrum of \((R)-4m\)
$^1$H NMR (500 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4n
$^{13}$C NMR (100 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4n
Scanned copy of mass spectrum of (R)-4n
$^1$H NMR (500 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4o
$^{13}$C NMR (125 MHz, 0.4 mL CDCl$_3$, 0.1 mL DMSO-D$_6$) of compound (R)-4o
Scanned copy of mass spectrum of (R)-40
$^1$H NMR (500 MHz, 0.4 mL CDCl$_3$) of compound (R)-4p
$^{13}$C NMR (125 MHz, 0.4 mL CDCl$_3$) of compound (R)-4p
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Scanned copy of mass spectrum of \((R)-4p\)
$^1$H NMR (400 MHz, DMSO-D$_6$) of compound (R)-4q
$^{13}$C NMR (100 MHz, DMSO-D$_6$) of compound (R)-4q
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Scanned copy of mass spectrum of $(R)$-4q
Supporting Information

$^1$H NMR (400 MHz, DMSO-D$_6$) of compound (R)-4r
$^{13}$C NMR (100 MHz, DMSO-$D_6$) of compound (R)-4r
Mass spectrum of (R)-4r
$^1$H NMR (400 MHz, CDCl$_3$) of compound (R)-4s
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (R)-4s
Mass spectrum of (R)-4s
$^1$H NMR (400 MHz, CDCl$_3$) of compound (+)-4t
$^{13}$C NMR (100 MHz, DMSO-D$_6$) of compound (+)-4t
Scanned copy of mass spectrum of (+)-4t
1H NMR (400 MHz, DMSO-D₆) of compound (R)-8
$^{13}$C NMR (400 MHz, DMSO-$D_6$) of compound ($R$)-8
Scanned copy of mass spectrum of \((R)-8\)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (R)-9
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (R)-9
Display Report

Supporting Information 129

Acquisition Date: 7/29/2016 1:31:50 PM

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Method: hrlcsm-pos_mid_tune wide.m
Sample Name: Dr.A_Bisai-AB-KNB-03-170
Comment:

Acquisition Parameter
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Scan End: 3000 m/z
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Set Collision Cell RF: 450.0 Vpp
Set Nebulizer: 0.3 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Waste

Scanned copy of mass spectrum of (R)-9
$^1$H NMR (400 MHz, CDCl$_3$) of compound 10
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 10
Scanned copy of mass spectrum of 10
$^1$H NMR (400 MHz, CDCl$_3$) of compound 11
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 11
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Scanned copy of mass spectrum of **11**
$^1$H NMR (400 MHz, CDCl$_3$) of compound (3S, 3'S)-12
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (3S, 3’S)-12
$^1$H NMR (400 MHz, CDCl$_3$) of compound (±)-17
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (±)-17
Mass spectrum of (±)-17
$^1$H NMR (400 MHz, CDCl$_3$) of compound (±)-19
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (±)-19
Mass spectrum of (±)-19
Determination of diastereomeric ratio of compound 10 from $^1\text{H}$ NMR of crude reaction

$^1\text{H}$ NMR (400 MHz, CDCl$_3$) of crude compound 10
Determination of diastereomeric ratio of compound (±)-17 from $^1$H NMR of crude reaction

$^1$H NMR (400 MHz, CDCl$_3$) of crude compound (±)-17
Determination of diastereomeric ratio of compound 19 from $^1$H NMR of crude reaction

$^1$H NMR (400 MHz, CDCl$_3$) of crude compound ($\pm$)-19
HPLC Traces

HPLC data of compound-(±)-4a

Data File C:\CHEM32\1\DATA\NARESH\2018-02-1317-34-13AB-KNB-05-048-ID3-50-1-254-50MRAC.D
Sample Name: AB-KNB-05-048-ID3-50-1-254-50MRAC

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 9.79021e4 4256.37061

*** End of Report ***
HPLC data of compound (R)-4a

Sample Name: AB-KNB-05-048-ID3-50-1-254-50M-CHIRAL2

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 5.50595e4 3015.90790

*** End of Report ***
HPLC data of compound (R)-4a from 5k

![Diagram of (R)-4a](image)

Sample Name: AB-KNB-05-048-ID3-50-1-254-50M-CHIRAL6

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 5.51864e4 3093.90964

*** End of Report ***
HPLC data of compound (±)-4b

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Sample Name: AB-KNB-03-006-OZ3-30-1-254-50M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 2.45066e4 319.72617

*** End of Report ***
HPLC data of compound \((R)-4b\)

Data File C:\CHEM321\DATA\NARESH\2018-03-0718-32-53AB-KNB-05-055-OZ3-30-1-254-50M.D
Sample Name: AB-KNB-05-055-OZ3-30-1-254-50M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 4.35806e4  450.31857

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HPLC data of compound (±)-4c

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Sample Name: AB-KNB-02-E-001-IB-30-1-254-50 M RACE

Signal 1: DAD1 A, Sig=254,4 Ref=360,100 (NARESH2018-01-2614-07-11AB-KNB-02-E-001-IB-30-1-254-50 M RACE.D)

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Totals : 1.50979e4 570.82730

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HPLC data of compound \((R)-4c\)

Data File C:\CHEM32\1\DATA\NARESH\2018-01-2614-47-16AB-KNB-02-E-001-IB-30-1-254-50 M CHI.D
Sample Name: AB-KNB-02-E-001-IB-30-1-254-50 M CHI.

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 3170.18256 91.02535

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HPLC data of compound (±)-4d

Data File C:\CHEM32\1\DATA\NARESH\2018-02-1422-35-25AB-KNB-02-268-R-OD3-50-1-254-50M RAC.D
Sample Name: AB-KNB-02-268-R-OD3-50-1-254-50M RAC

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 5.88935e4 3622.58081

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HPLC data of compound \((R)-4d\)

![Image of compound (R)-4d]

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Sample Name: AB-KNB-02-268-R-OD3-50-1-254-50M CHI

![Graph of HPLC data]

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 5.11352e4 2610.92227

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*** End of Report ***
HPLC data of compound (±)-4e

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<td>1.03880e4</td>
<td>112.91732</td>
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<tr>
<td>4</td>
<td>23.003</td>
<td>BB</td>
<td>1.8207</td>
<td>1.53972e4</td>
<td>126.08580</td>
<td>29.5507</td>
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Totals : 5.21044e4 683.39642

==================================================================================================

*** End of Report ***
**HPLC data of compound \((R)-4e\)**

![HPLC spectrum diagram](image_url)

**Data File:** C:\CHEM32\1\DATA\NARESH\2017-10-1121-53-38AB-KNB-02-265-R2-AD-H-50-1-254-50M.D  
**Sample Name:** AB-KNB-02-265-R2-AD-H-50-1-254-50M

**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

<table>
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<tr>
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<td>VBA</td>
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**Totals:**

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<tbody>
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*** End of Report ***
HPLC data of compound (±)-4f

Data File C:\CHEM32\1\DATA\NARESH\2015-07-20AB-KNB-2-250-R-OD-3-50-254-1-50M.D
Sample Name: AB-KNB-2-250-R-OD-3-50-254-1-50M

<table>
<thead>
<tr>
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<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.3314e+04</td>
<td>767.55292</td>
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<td>9.554</td>
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Totals : 2.64572e+04 1060.80881

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*** End of Report ***
HPLC data of compound \((R)-4f\)

![HPLC Graph]

**Data File C:\CHEM321\DATA\NARESH\AB-KNB-03-012-N11-OD-3-50-254-1-50M.D**

**Sample Name: AB-KNB-03-012-N11-OD-3-50-254-1-50M**

**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

<table>
<thead>
<tr>
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<th>Height</th>
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<tr>
<td>1</td>
<td>4.697</td>
<td>MM</td>
<td>0.6926</td>
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<td>9.218</td>
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<td>0.6744</td>
<td>1.36330e5</td>
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**Totals:**

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<td>1.36952e5</td>
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*** End of Report ***
HPLC data of compound (R)-4f from (R)-4a

Data File C:\Chem32\1\Data\Naresh\2015-09-03AB-KNB-03-010-R-OD-3-50-254-1-50M.D
Sample Name: AB-KNB-03-010-R-OD-3-50-254-1-50M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
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<td>0.7370</td>
<td>3.20811e4</td>
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Totals: 3.45682e4 823.76000

*** End of Report ***
HPLC data of compound (±)-4g

![Chemical Structure Image]

Sample Name: AB-KNB-04-346-2-IE-3-40-1-254-40 M RACE

### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
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<th>Area %</th>
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<tbody>
<tr>
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<td>[min]</td>
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<td></td>
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<tr>
<td>1</td>
<td>8.529</td>
<td>BV</td>
<td>0.3407</td>
<td>4.44467e4</td>
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<td>0.5020</td>
<td>4.52498e4</td>
<td>1332.96252</td>
<td>50.4477</td>
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Totals : 8.96965e4 3262.55115

*** End of Report ***
HPLC data of compound (R)-4g

Sample Name: AB-KNB-04-347-2-IE-3-40-1-254-40 M CHI

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
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<tr>
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<tbody>
<tr>
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<td>8.602</td>
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<tr>
<td>2</td>
<td>10.810</td>
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<td>0.4874</td>
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Totals: 3.94932e4 1275.98793

*** End of Report ***
HPLC data of compound $(\pm)-4h$

Data File C:\CHEM32\..\TA\NARESH\2018-03-1011-18-24AB-KNB-05-061-IB-30-1-254-50M-RACEMIC.D
Sample Name: AB-KNB-05-061-IB-30-1-254-50M-RACEMIC

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
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<tr>
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<td>3.65746e4</td>
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<td>0.3596</td>
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Totals: 7.37409e4 3969.30786

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*** End of Report ***
HPLC data of compound (R)-4h

Data File C:\CHEM32\1\DATA\NARESH\2018-03-1011-32-49AB-KNB-05-061-IB-30-1-254-50M-CHIRAL.D
Sample Name: AB-KNB-05-061-IB-30-1-254-50M-CHIRAL

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
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<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>4.727</td>
<td>MM</td>
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<td>3741.52417</td>
<td>256.66464</td>
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<td>2</td>
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<td>0.3800</td>
<td>5.83646e4</td>
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Totals : 6.21061e4 2511.50156
HPLC data of compound (±)-4i

Data File C:\CHEM32\1\DATA\NARESH\2018-02-0619-14-30AB-KNB-E-02-205-IB-30-1-254-50M RAC.D
Sample Name: AB-KNB-E-02-205-IB-30-1-254-50M RAC

Signal 1: DAD1 A, Sig=254,4 Ref=360,100 (NARESH2018-02-0619-14-30AB-KNB-E-02-205-IB-30-1-254-50M RAC.D)

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<th>Height [mAU]</th>
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</thead>
<tbody>
<tr>
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<td>6.008</td>
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<td>0.3547</td>
<td>5.54719e4</td>
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<td>0.8487</td>
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Totals: 1.11585e5 3402.82446

*** End of Report ***
HPLC data of compound \((R)-4i\)

Data File C:\CHEM2\1\DATA\NARESH\2018-02-0620-57-23AB-KNB-E-02-271-IB-30-1-254-50M CHI.D
Sample Name: AB-KNB-E-02-271-IB-30-1-254-50M CHI

Signal 1: DAD1 A, Sig=254,4 Ref=360,100 (NARESH\2018-02-0620-57-23AB-KNB-E-02-271-IB-30-1-254-50M CHI.D)

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<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>BB</td>
<td>0.3577</td>
<td>8029.52490</td>
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<td>10.915</td>
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Totals: 1.31846e5 2502.41562

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*** End of Report ***
HPLC data of compound (±)-4j

Data File C:\CHEM32\1\DATA\NARESH\2018-03-1210-25-34AB-KNB-02-280-ID3-50-1-254-50M-RACE.D
Sample Name: AB-KNB-02-280-ID3-50-1-254-50M-RACE.D

Signal 1: DAD1 A, Sig=254.4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
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<tbody>
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<td>BV</td>
<td>0.3940</td>
<td>1.75442e4</td>
<td>631.78333</td>
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<td>9.494</td>
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<td>0.7071</td>
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Totals: 3.54984e4 994.76938

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*** End of Report ***
HPLC data of compound (R)-4j

Data File C:\CHEM32\1\DATA\NARESH\2018-03-1210-41-58AB-KNB-02-280-ID3-50-1-254-50M-CHI.D
Sample Name: AB-KNB-02-280-ID3-50-1-254-50M-CHI

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
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<td>2061.82764</td>
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Totals: 1.19949e5 2670.52600

*** End of Report ***
HPLC data of compound $(\pm)$-4k

Data File C:\CHEM32\1\DATA\NARESH\2015-08-03AB-KNB-2-281-RACEMIC-3-OD-3-40-254-1-60.D
Sample Name: AB-KNB-2-281-RACEMIC-3-OD-3-40-254-1-60

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>#</td>
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<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
</tr>
<tr>
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<tr>
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Totals : 3.55593e+4 980.24739

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*** End of Report ***
HPLC data of compound (R)-4k

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-03-266-F-OD-3-40-254-1-60M.D
Sample Name: AB-KNB-03-266-F-OD-3-40-254-1-60M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>6.189</td>
<td>MM</td>
<td>1.5425</td>
<td>1613.61279</td>
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<tr>
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<td>BBA</td>
<td>1.9180</td>
<td>5.35778e4</td>
<td>396.61786</td>
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Totals: 5.51914e4 414.05252

*** End of Report ***
HPLC data of compound (±)-4l

Data File C:\CHEM32\1\DATA\NARESH\2015-08-03AB-KNB-2-279-RACEMIC-OD-3-40-254-1-60.D
Sample Name: AB-KNB-2-279-RACEMIC-OD-3-40-254-1-60

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.711</td>
<td>MM</td>
<td>0.3406</td>
<td>9148.41016</td>
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<td>2</td>
<td>9.011</td>
<td>BB</td>
<td>0.8137</td>
<td>9432.57910</td>
<td>173.66725</td>
<td>50.7647</td>
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Totals: 1.85810e4 621.34181

*** End of Report ***
HPLC data of compound \((R)-4l\)

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-03-265-F1-OD-3-40-254-1-60M.D
Sample Name: AB-KNB-03-265-F1-OD-3-40-254-1-60M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
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<th>Area</th>
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<th>Area %</th>
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<tbody>
<tr>
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</tr>
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<tr>
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<td>4.13716e4</td>
<td>554.30914</td>
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Totals: 4.31358e4  626.06078

*** End of Report ***
HPLC data of compound (±)-4m

Sample Name: AB-KNB-A-03-E-303-IB-46-1-254-50 M RACE

![HPLC graph]

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
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<td>MM</td>
<td>0.2646</td>
<td>2.98346e4</td>
<td>1879.07813</td>
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<td>MM</td>
<td>0.5584</td>
<td>2.90844e4</td>
<td>868.13904</td>
<td>49.3634</td>
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Totals: 5.89189e4 2747.21716

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*** End of Report ***
HPLC data of compound (R)-4m

Sample Name: AB-KNB-A-03-001-ADH-40-1-254-50M CHIRAL

Signal 1: DAD1 A, Sig=254,4 Ref=360,100 (NARESH\2018-01-2622-22-52AB-KNB-A-03-001-ADH-40-1-254-50M CHIRAL.D)

<table>
<thead>
<tr>
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<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<tbody>
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<td>1</td>
<td>6.565</td>
<td>BB</td>
<td>0.2145</td>
<td>454.80374</td>
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</tr>
<tr>
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<td>8.176</td>
<td>BV</td>
<td>0.4949</td>
<td>9690.63867</td>
<td>281.99026</td>
<td>95.5172</td>
</tr>
</tbody>
</table>

Totals: 1.01454e4 313.10776

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*** End of Report ***
HPLC data of compound (±)-4n

Data File C:\CHEM32\1\DATA\NARESH\2018-02-1317-34-13AB-KNB-05-048-ID3-50-1-254-50MRAC.D
Sample Name: AB-KNB-05-048-ID3-50-1-254-50MRAC

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time [min]</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.043</td>
<td>0.2780</td>
<td>4.92836e4</td>
<td>2457.59082</td>
<td>50.3397</td>
</tr>
<tr>
<td>2</td>
<td>6.270</td>
<td>0.4505</td>
<td>4.86185e4</td>
<td>1798.77979</td>
<td>49.6603</td>
</tr>
</tbody>
</table>

Totals: 9.79021e4 4256.37061

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*** End of Report ***
HPLC data of compound (R)-4n

Data File C:\CHEM32\1\DATA\NARESH\2018-02-1317-56-33AB-KNB-03-303-IB3-40-1-254-50MCHI.D
Sample Name: AB-KNB-03-303-IB3-40-1-254-50MCHI

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>5.052</td>
<td>0.273</td>
<td>670.75250</td>
<td>33.53104</td>
<td>6.0841</td>
</tr>
<tr>
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<td>0.421</td>
<td>1.03540e4</td>
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Totals : 1.10247e4  367.90479

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*** End of Report ***
HPLC data of compound ($\pm$)-40

**Supporting Information**

Data File C:\CHEM31\1\DATA\NARESH\2018-02-1414-37-51AB-KNB-05-037R-ID3-30-1-254-50M RAC.D
Sample Name: AB-KNB-05-037R-ID3-30-1-254-50M RAC

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**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

<table>
<thead>
<tr>
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<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.959</td>
<td>VB</td>
<td>0.5579</td>
<td>3.32450e4</td>
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<td>BB</td>
<td>0.8681</td>
<td>3.32924e4</td>
<td>559.60413</td>
<td>50.0357</td>
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</tbody>
</table>

Totals: 6.65374e4 1433.39246

*** End of Report ***
HPLC data of compound \((R)-4o\)

Data File: C:\\CHEM32\1\DATA\NARESH\2016-02-1415-04-43AB-KNB-05-037R-ID3-30-1-254-50M CHI.D
Sample Name: AB-KNB-05-037R-ID3-30-1-254-50M CHI

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
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<th>Type</th>
<th>Width</th>
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<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>7.099</td>
<td>MM</td>
<td>0.5332</td>
<td>4325.61035</td>
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<td>5.1425</td>
</tr>
<tr>
<td>#2</td>
<td>10.796</td>
<td>MM</td>
<td>1.0725</td>
<td>7.97891e4</td>
<td>1239.91064</td>
<td>94.8575</td>
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</tbody>
</table>

Totals: 8.41147e4 1375.11752

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*** End of Report ***
HPLC data of compound (±)-4p

Data File: C:\CHEM32\DATA\NARESH\2018-02-1421-28-55AB-KNB-02-207-OD3-30-1-254-50M RAC.D
Sample Name: AB-KNB-02-207-OD3-30-1-254-50M RAC

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.104</td>
<td>BV</td>
<td>0.170</td>
<td>2.83956e4</td>
<td>2509.90649</td>
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<tr>
<td>2</td>
<td>7.493</td>
<td>VB</td>
<td>0.2763</td>
<td>2.86807e4</td>
<td>1576.14160</td>
<td>50.2498</td>
</tr>
</tbody>
</table>

Totals: 5.70763e4 4086.04810

*** End of Report ***
**HPLC data of compound (R)-4p**

![Chemical Structure](image)

Data File C:\CHEM32\1\DATA\NARESH\2018-02-1421-16-00AB-KNB-02-207-OD3-30-1-254-50M CHI.D
Sample Name: AB-KNB-02-207-OD3-30-1-254-50M CHI

### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
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<th>Type</th>
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<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.109</td>
<td>VB</td>
<td>0.1667</td>
<td>3396.52783</td>
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<td>6.8866</td>
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<tr>
<td>2</td>
<td>7.482</td>
<td>BBA</td>
<td>0.2746</td>
<td>4.59240e4</td>
<td>2543.94702</td>
<td>93.1134</td>
</tr>
</tbody>
</table>

**Totals:**

- Area: 4.93205e4
- Area %: 2851.90109

**End of Report**
HPLC data of compound (±)-4q

Data File C:\CHEM32\1\DATA\NARESH\2016-06-15AB-KNB-03-292-AD-H-50-1-60M.D
Sample Name: AB-KNB-03-292-AD-H-50-1-60M

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.630</td>
<td>BB</td>
<td>2.1526</td>
<td>2533.41504</td>
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<td>50.0737</td>
</tr>
<tr>
<td>2</td>
<td>34.958</td>
<td>MM</td>
<td>2.9643</td>
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<td>14.20229</td>
<td>49.9263</td>
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<tr>
<td>Totals:</td>
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<td></td>
<td>5059.37427</td>
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</table>

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HPLC data of compound $(R)-4q$

Data File C:\CHEM32\1\DATA\NARESH\2016-06-16AB-KNB-03-310-F1-AD-H-50-1-60M.D
Sample Name: AB-KNB-03-310-F1-AD-H-50-1-60M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100 (NARESH\2016-06-16AB-KNB-03-310-F-AD-H-50-1-60M.D)

<table>
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<tr>
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<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.052</td>
<td>MM</td>
<td>3.3103</td>
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<td>1.27165</td>
</tr>
<tr>
<td>2</td>
<td>35.361</td>
<td>MM</td>
<td>3.3765</td>
<td>7035.78955</td>
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</table>

Totals: 7288.36337 36.00053
HPLC data of compound (±)-4r

![Chemical Structure Image]

Data File C:\CHEM32\1\DATA\NARESH\2018-05-10AB-KNB-04-112-RAC-ID-3-40-254-50M.D
Sample Name: AB-KNB-04-112-RAC-ID-3-40-254-50M

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>7.212</td>
<td>0.3040</td>
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</tr>
<tr>
<td>2</td>
<td>10.420</td>
<td>0.4554</td>
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<td>119.09343</td>
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Totals: 7195.89795 314.71904

*** End of Report ***
HPLC data of compound (R)-4r

Data File C:\CHEM32\1\DATA\NARESH\2018-05-10AB-KNB-05-123-4-CHI-ID-3-40-254-50M.D
Sample Name: AB-KNB-05-123-4-CHI-ID-3-40-254-50M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
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<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>7.189</td>
<td>MM</td>
<td>0.359</td>
<td>94.03797</td>
<td>4.35985</td>
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</tr>
<tr>
<td>2</td>
<td>10.297</td>
<td>BB</td>
<td>0.463</td>
<td>1.07675e4</td>
<td>345.30496</td>
<td>99.1342</td>
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</table>

Totals: 1.08615e4 349.66482

*** End of Report ***
HPLC data of compound (±)-4s

Data File C:\CHEM32\DATA\NARESH\2018-05-20AB-KNB-05-122-2-IC3-50-1-254-50M-RAC.D
Sample Name: AB-KNB-05-122-2-IC3-50-1-254-50M-RAC

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
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</tr>
<tr>
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<td>4.862</td>
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<td>0.3542</td>
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<td>6.469</td>
<td>VB</td>
<td>0.4538</td>
<td>4108.74316</td>
<td>138.63490</td>
<td>49.2514</td>
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Totals: 8342.39063 317.45662

*** End of Report ***
HPLC data of compound \((R)-4s\)
HPLC data of compound (±)-4t

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-060-50-254-1-70M.D
Sample Name: AB-KNB-060-50-254-1-70M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.177</td>
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<td>0.2905</td>
<td>2.03153e4</td>
<td>1055.81726</td>
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<tr>
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<td>23.323</td>
<td>BB</td>
<td>1.0790</td>
<td>2.01400e4</td>
<td>285.49423</td>
<td>49.7833</td>
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</table>

Totals: 4.04553e4 1341.31149

*** End of Report ***
HPLC data of compound (R)-4t

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-061-50-254-1-70M.D
Sample Name: AB-KNB-061-50-254-1-70M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
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<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>#</td>
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<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
</tr>
<tr>
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<td>7.173</td>
<td>0.2970</td>
<td>7107.71436</td>
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<tr>
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<td>305.07852</td>
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<tr>
<td>Totals</td>
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<td></td>
<td>2.87360e4</td>
<td>661.02115</td>
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*** End of Report ***
HPLC data of compound (±)-8

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-03-168-OD-3-50-254-1-40M.D
Sample Name: AB-KNB-03-168-OD-3-50-254-1-40M

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>MM</td>
<td>0.4080</td>
<td>4.33269e4</td>
<td>1769.70911</td>
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<td>12.898</td>
<td>BBA</td>
<td>1.0583</td>
<td>4.34388e4</td>
<td>601.63898</td>
<td>50.0645</td>
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</table>

Totals: 8.67657e4 2371.34808

*** End of Report ***
HPLC data of compound (R)-8

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-03-231-OD-3-3-50-254-1-50M.D
Sample Name: AB-KNB-03-231-OD-3-3-50-254-1-50M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
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<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.6229</td>
<td>582.06079</td>
<td>15.57285</td>
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</tr>
<tr>
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<td>13.534</td>
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<td>1.21085e5</td>
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</table>

Totals: 1.21667e5 1396.61033

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*** End of Report ***
HPLC data of compound (±)-9

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-03-321-2-ADH-50-254-1;5-50M.D
Sample Name: AB-KNB-03-321-2-ADH-50-254-1;5-50M

Signal 1: DAD1 A, Sig=254.4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
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<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
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<td>0.3110</td>
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<td>2</td>
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<td>BB</td>
<td>0.8913</td>
<td>2.32392e4</td>
<td>389.91284</td>
<td>49.0789</td>
</tr>
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</table>

Totals: 4.73506e4 1681.98291

==================================================================
*** End of Report ***
HPLC data of compound (R)-9

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-03-320-ADH-50-254-1;5-50M.D
Sample Name: AB-KNB-03-320-ADH-50-254-1;5-50M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.428</td>
<td>MM</td>
<td>0.2912</td>
<td>352.27847</td>
<td>20.16364</td>
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</tr>
<tr>
<td>2</td>
<td>16.796</td>
<td>BB</td>
<td>0.9376</td>
<td>7.15597e4</td>
<td>1138.11145</td>
<td>99.5101</td>
</tr>
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</table>

Totals: 7.19119e4 1158.27509

*** End of Report ***
HPLC data of compound (±)-12

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-03-323-RACEMIC-AD-3-30-254-1-40M.D
Sample Name: AB-KNB-03-323-Racemic-AD-3-30-254-1-40M

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>[min]</td>
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<td>[mAU]</td>
<td></td>
<td></td>
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<tr>
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<td>16.781</td>
<td>BB</td>
<td>0.7787</td>
<td>9.02859e4</td>
<td>1771.29431</td>
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<tr>
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<td>20.578</td>
<td>BB</td>
<td>0.9058</td>
<td>9.20173e4</td>
<td>1538.41589</td>
<td>50.4749</td>
</tr>
</tbody>
</table>

Totals : 1.82303e5 3309.71021

*** End of Report ***
HPLC data of compound (3S,3'S)-12

![Chemical Structure](image)

Data File C:\CHEM32\1\DATA\NARESH\AB-KNB-03-324-CHIRAL-R-AD-3-30-254-1-40M.D
Sample Name: AB-KNB-03-324-Chiral-R-AD-3-30-254-1-40M

**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
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<th>Height</th>
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Totals: 1.01372e5 1920.76179

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*** End of Report ***
HPLC data of compound (±)-17

Data File C:\CHEM32\1\DATA\NARESH\2015-07-07 23-36-20AB-KNB-02-218-OZ-3-30-1-254-60.D
Sample Name: AB-KNB-02-218-OZ-3-30-1-254-60

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals : 4453.17059 129.96683

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*** End of Report ***
HPLC data of compound (±)-17 under optimized condition

Data File C:\CHEM32\1\DATA\NARESH\2015-07-09 15-59-20AB-KNB-2-221-OZ-3-30-1-254-60.D
Sample Name: AB-KNB-2-221-OZ-3-30-1-254-60

DAD1 A, Sig=254.4 Ref=360,100 (NARESH\2015-07-09 15-59-20AB-KNB-2-221-OZ-3-30-1-254-60.D)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 9.11682e4 2280.30092

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*** End of Report ***
HPLC data of compound (±)-17

Data File C:\CHEM32\1\DATA\NARESH\2015-07-04 13-03-21AB-KNB-2-217-AS3-40-1--254-60.D
Sample Name: AB-KNB-2-217-AS3-40-1--254-60

Signal 1: DAD1 A, Sig=254.4 Ref=360,100

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Totals: 6.29038e4  687.78567

*** End of Report ***
HPLC data of compound (±)-19 under optimized condition

Data File C:\CHEM32\1\DATA\NARESH\2015-07-04 13-03-21AB-KNB-2-217-AS3-40-1--254-60.D
Sample Name: AB-KNB-2-217-AS3-40-1--254-60

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 6.23524e4 686.56884

*** End of Report ***
**Cu-Bu-PHOX preparation for EPR studies:**

EPR experiment was performed with Bu-PHOX under nitrogen atmosphere. The EPR tube was evacuated and backfilled with argon and then CH$_2$Cl$_2$ was added to the mixture. The reaction mixture was irradiated under light for 1-2 min, and then an EPR spectrum was recorded and did not show any EPR signal.

![Chemical reaction diagram](image)

The reaction was performed using 0.007 mmol of Bu-PHOX (L4) and 0.007 mmol of Cu(I)OTf.PhMe in an EPR tube under nitrogen atmosphere. The EPR tube was evacuated and backfilled with argon and then CH$_2$Cl$_2$ was added to the mixture. The reaction mixture was irradiated under light for 1-2 min and then an EPR spectrum was recorded and observed the EPR signal with a coupling constant ($g = 2.1120$) which indicates Cu(I) is converting to Cu(II) in the reaction course.

![Chemical reaction diagram](image)

The reaction was performed using 0.034 mmol of Bu-PHOX (L4) and 0.034 mmol of Cu(OTf)$_2$ in an EPR tube under nitrogen atmosphere. The EPR tube was evacuated and backfilled with argon and then CH$_2$Cl$_2$ was added to the mixture. The reaction mixture was irradiated under light for 1-2 min and then an EPR spectrum was recorded and observed the EPR signal with a coupling constant ($g = 2.1062$) which indicates the Cu(II) complex is the intermediate in the reaction course.
EPR studies of Cu-complex with 1^Bu-PHOX (L4)

X-band EPR spectra of 1^Bu-PHOX (L4) at 110K under nitrogen atmosphere (solid sample).

X-band EPR spectra of a complex of 1 equiv. of Cu(I)OTf.PhMe with 1 equiv. of 1^Bu-PHOX (L4) in dichloromethane at 110K under nitrogen atmosphere.
X-band EPR spectra of a complex of 1 equiv. of Cu(II)OTf with 1 equiv. of t-Bu-PHOX (L4) in dichloromethane at 110K under nitrogen atmosphere.

**Cu-t-Bu-PHOX preparation for $^1$H-NMR and $^{31}$P-NMR studies:**

$^1$H-NMR of only t-Bu-PHOX in CDCl$_3$ shows good spitting pattern of upfield protons.

The reaction was performed using 0.034 mmol of t-Bu-PHOX (L4) and 0.034 mmol of Cu(OTf)$_2$ in an NMR tube under nitrogen atmosphere in CDCl$_3$. The NMR spectrum was recorded and observed no NMR signal of the free t-Bu-PHOX protons in the spectrum. This indicates that Cu(II) complex (paramagnetic species) is forming.
The reaction was performed using 0.034 mmol of \( t^\text{Bu}-\text{PHOX} \) (L4) and 0.034 mmol of Cu(I)OTf.PhMe in an NMR tube under nitrogen atmosphere in CDCl3. The NMR spectrum was recorded and observed the no NMR signal of the free \( t^\text{Bu}-\text{PHOX} \) protons in the spectrum. This indicates that Cu(I) is converting to Cu(II) (paramagnetic species) complex.

\[ ^{31}\text{P}-\text{NMR of only } t^\text{Bu}-\text{PHOX in CDCl}_3 \text{ shows } ^{31}\text{P signal at } -5.96 \text{ ppm}. \]

The reaction was performed using 0.034 mmol of \( t^\text{Bu}-\text{PHOX} \) (L4) and 0.034 mmol of Cu(OTf)\textsubscript{2} in an NMR tube under nitrogen atmosphere in CDCl\textsubscript{3}. The \( ^{31}\text{P} \) NMR spectrum was recorded and observed no \( ^{31}\text{P} \) signal of the \( t^\text{Bu}-\text{PHOX} \) in the spectrum. This indicates that phosphorus atom is bound with Cu(II) complex.

\[ \text{The reaction was performed using 0.034 mmol of } t^\text{Bu}-\text{PHOX (L4) and 0.034 mmol of Cu(I)} \text{OTf.PhMe in an NMR tube under nitrogen atmosphere in CDCl}_3. \text{ The } ^{31}\text{P NMR spectrum was recorded and observed no } ^{31}\text{P signal of the } t^\text{Bu}-\text{PHOX in the spectrum. This indicates that phosphorus atom is bound with Cu(II) complex.} \]

\[ \text{This indicates that phosphorus atom is bound with Cu(II) complex, which is converted from Cu(I)} \text{OTf.PhMe.} \]
$^1$H-NMR and $^{31}$P-NMR studies of Cu-complex with $^t$Bu-PHOX (L4)

$^1$H-NMR of $^t$Bu-PHOX (L4) (400 MHz, 0.4 mL CDCl$_3$)

$^1$H-NMR of $^t$Bu-PHOX (L4) (400 MHz, 0.4 mL CDCl$_3$)
$^1$H-NMR of Cu(OTf)$_2$ + t-Bu-PHOX (L4) (500 MHz, 0.4 mL CDCl$_3$), sample prepared under nitrogen atmosphere.
$^{31}$P-NMR of $^t$Bu-PHOX (L4) (400 MHz, 0.4 mL CDCl$_3$)

$^{31}$P-NMR of Cu(OTf)$_2$ + $^t$Bu-PHOX (L4) (500 MHz, 0.4 mL CDCl$_3$), sample prepared under nitrogen atmosphere.
\(^{31}\)P-NMR of (CuOTf)\(_2\) + \(^t\)Bu-PHOX (L4) (500 MHz, 0.4 mL CDCl\(_3\)), sample prepared under nitrogen atmosphere.

**Cu-\(^t\)Bu-PHOX (L2) preparation for Cyclic Voltagram studies:**

Cyclic voltammetry (CV) were carried out by three electrode configuration with a glassy carbon (GC) working electrode, a platinum counter electrode, and standard calomel electrode (SCE) as reference electrode.

**Reaction condition:** Cu-\(^t\)Bu-PHOX complex crystals (5 mg) in 5 mL CH\(_2\)Cl\(_2\) containing 1.0 M tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)).
Cyclic Voltogram of Cu(OTf)$_2$ + $i$-Bu-PHOX (L2)

X-ray structure of Cu(OTf)$_2$ + $i$-Bu-PHOX complex:
Figure: X-ray structure of Cu(OTf)$_2$ + $^t$Bu-PHOX with 50% thermal ellipsoids.
checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: M2_a

Bond precision: C-C = 0.0083 Å  Wavelength=0.71073

Cell:  
a=9.3999(9)  b=22.436(2)  c=11.7542(11)  
alpha=90  beta=107.400(2)  gamma=90

Temperature:  130 K

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Correction method= Not given

Data completeness= 1.94/1.00  Theta(max)= 28.000

R(reflections)= 0.0491( 9001)  wR2(reflections)= 0.1312( 11406)

S = 0.830  Npar= 590

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
Alert level B

PLAT98_ALERT_1_B The Flack x is ▶ 0 - Do a BASF/TWIN Refinement

Please Check

Alert level C

PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ

Please Check
PLAT043_ALERT_1_C Calculated and Reported Mol. Weight Differ by .

6.97 Check
PLAT069_ALERT_1_C Reported P000 Differs from Calculated (or Missing)... Please Check
PLAT220_ALERT_2_C Non-Solvent Resid 1 / C Ueq(max)/Ueq(min) Range

3.2 Ratio
PLAT244_ALERT_4_C Low ‘Solvent’ Ueq as Compared to Neighbors of

S004 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds

............ 0.00831 Ang.

Alert level G

FORMO1_ALERT_2_G There is a discrepancy between the atom counts in the

chemical_formula_sum and the formula from the atom_site* data.

Atom count from chemical_formula_sum: C50 H51 C1 F5 N3 O3 P2 S1

Atom count from the atom_site_data: C51 H52 C3 F3 N2 O5 P2 S1

CELL201_ALERT_1_G Difference between formula and atom_site contents detected.

CELL201_ALERT_1_G ALERT: Large difference may be due to a

symmetry error - see SYMM tests

From the CIF: _cell_formula_units_2 2

From the CIF: _chemical_formula_sum C50 H51 C1 F5 N3 O3 P2 S1

TEST: Compare cell contents of formula and atom_site data

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PLAT033_ALERT_4_G Flack x Valus Deviates > 3.0 * sigma from Zero .

0.032 Note
PLAT244_ALERT_4_G ‘Solvent’ Ueq as Compared to Neighbors of

C01Q Check
PLAT398_ALERT_2_C Deviating C-O-C Angle from 120 Deg for 0005

107.2 Degree
PLAT398_ALERT_2_C Deviating C-O-C Angle from 120 Deg for 0006

105.6 Degree
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .............

110 Note
PLAT791_ALERT_4_G The Model has Chirality at C00B (Chiral SPGR)

S Verify
PLAT791_ALERT_4_G The Model has Chirality at C00C (Chiral SPGR)

S Verify

0 ALERT level A = Most likely a serious problem - resolve or explain
1 ALERT level B = A potentially serious problem, consider carefully
6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
10 ALERT level G = General information/check it is not something unexpected

6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
6 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check