Supporting Information

Iridium-Catalyzed Asymmetric Hydrogenation of 4,6-Disubstituted 2-Hydroxypyrimidines

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1. General and Materials

General: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise noted. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded at room temperature in CDCl₃, CD₂Cl₂ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis or NMR analysis.

Materials: Commercially available reagents were used throughout without further purification. The solvents for asymmetric hydrogenation reaction were purchased without further purification.

2. Synthesis of Pyrimidin-2-ol Derivatives

4,6-Disubstituted pyrimidin-2-ols can be conveniently synthesized according to the known literature procedure.¹ The 1a,^{1a} 1b,^{1f} 1c,^{1b} 1d-1h,^{1f} 1i-1j,^{1c} 1k,^{1d} 1l,^{1c} 1m^{1e} and 1n-1p^{1f} are all known compounds. The 4,5,6-trisubstituted pyrimidin-2-ols can be synthesized according to the known literature procedure.² The 3a,² 3c-3d² are the known compounds.



General procedure: Copper(II) trifluoromethanesulfonate (0.271 g, 5.0 mol%) was added into a solution of arylaldehyde (15.0 mmol), urea (1.08 g, 18.0 mmol), ethyl 3-oxo-3-arylpropanoate (15.0 mmol) in 40 mL ethanol. After refluxing for 24 h, the reaction mixture was then cooled to 0 °C, the precipitation was collected by filtration and dried. The resulting white powder was triturated with cooled ethanol to afford **S-1** as a pale yellow powder.

A solution of the above **S-1** (3.0 mmol), copper(II) chloride dihydrate (5.1 mg, 1.0 mol%), potassium carbonate (41 mg, 10 mol%) in dichloromethane (6.0 mL) was heated at reflux for 30 min, and then 65 wt% tert-butyl hydroperoxide (0.832 g, 6.0 mmol) was added dropwise over a period of 10 minutes. The resulting mixture was stirred at 35 °C for 24 h. The saturated aqueous sodium thiosulfate (10 mL) was added to destroy *tert*-butyl hydroperoxide, then, the mixture was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, concentrated in *vacuo*. The crude product was purified by flash column chromategraphy to afford the products **3**.

Ethyl 2-hydroxy-4,6-di(*m*-tolyl)pyrimidine-5-carboxylate (3b): 1.104 g, 55% yield (2 steps), white solid, mp: 190-191 °C, $R_f = 0.51$ (dichloromethane/methanol = 20/1), new compound; ¹H



NMR (400 MHz, CDCl₃) δ 13.04 (s, 1H), 7.42–7.29 (m, 8H), 3.93 (q, J = 6.8 Hz, 2H), 2.38 (s, 6H), 0.88 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 157.2, 137.9, 133.7, 131.4, 128.2, 128.1, 124.6, 111.4, 61.2, 20.9, 12.9; HRMS (ESI) *m*/*z* Calculated for C₂₁H₂₁N₂O₃ [M+H]⁺ 349.1547, found 349.1553.

3. General Procedure for Asymmetric Hydrogenation



In a nitrogen-filled glove box, a mixture of $[Ir(COD)Cl]_2$ (2.0 mg, 0.003 mmol) and ligand (*S*,*S*)-f-Binaphane (5.3 mg, 0.0066 mmol) in isopropanol (1.0 mL) was stirred at room temperature for 10 min, then substrates **1** (0.3 mmol) and TCCA (7.0 mg, 0.03 mmol) together with ethanol (1.0 mL) and isopropanol (1.0 mL) were added to the above catalyst solution. The hydrogenation was performed at 40 °C under 800 psi of hydrogen for 24 h. After carefully releasing the hydrogen, excess solid sodium bicarbonate was added. The resulted mixture was stirred for 30 min, then filtrated off and concentrated in *vacuo*. Further purification was performed by a silica gel chromatography eluted with ethyl acetate/methanol to give the desired chiral product **2**. The enantiomeric excesses were determined by chiral HPLC for the corresponding benzamides.

(4R,6R)-(+)-4-Methyl-6-phenyltetrahydropyrimidin-2(1H)-one (2a): 35 mg (0.2 mmol scale), 92% yield, pale yellow solid, known compound, $R_f = 0.30$ (dichloromethane/methanol =



20:1), 95% ee, $[\alpha]^{20}{}_{D}$ = +44.1 (*c* 0.70, MeOH) [lit.²: for (*4R*,6*R*)-isomer $[\alpha]^{20}{}_{D}$ = +51.1 (*c* 0.28, MeOH) for 84% ee]; ¹H NMR (400 MHz, CD₂Cl₂) δ 7.35–7.26 (m, 5H), 5.96 (s, 1H), 5.63 (s, 1H), 4.47–4.44 (m, 1H), 3.61–3.57 (m, 1H), 1.98 (d, *J* = 12.8 Hz, 1H), 1.54–1.45 (m, 1H), 1.13 (d, *J* = 6.2 Hz,

3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 158.9, 143.9, 130.1, 129.2, 127.6, 56.8, 47.8, 41.7, 22.9; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 254 nm, flow rate: 0.80 mL/min, 30 °C), t₁ = 14.9 min (maj), t₂ = 16.8 min.

(+)-4-Methyl-6-*m*-tolyltetrahydropyrimidin-2(1*H*)-one (2b): 56 mg, 92% yield, white solid, new compound, mp: 143-144 °C, $R_f = 0.35$ (dichloromethane/methanol = 15:1), 95% ee, $[\alpha]^{20}_{D} =$

+62.1 (*c* 0.68, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.23 (m, 1H), Me +62.1 (*c* 0.68, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.23 (m, 1H), 7.16–7.11 (m, 3H), 5.15 (s, 1H), 4.83 (s, 1H), 4.50–4.47 (m, 1H), 3.71–3.63 (m, 1H), 2.35 (s, 3H), 2.04 (d, *J* = 13.2 Hz, 1H), 1.63–1.54 (m, 1H), 1.22 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.9, 141.9, 138.7, 128.9, 128.8, 126.8, 123.2, 55.6, 46.5, 40.2, 21.9, 21.4; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 254 nm, flow rate: 0.80 mL/min, 30 °C), t₁ = 12.2 min (maj), t₂ = 15.3 min; HRMS (ESI) *m/z* Calculated for C₁₂H₁₇N₂O [M+H]⁺ 205.1335, found 205.1335.

(+)-4-Methyl-6-*p*-tolyltetrahydropyrimidin-2(1*H*)-one (2c): 54 mg, 89% yield, white solid, new compound, mp: 88-89 °C, $R_f = 0.35$ (dichloromethane/methanol = 15:1); 94% ee, $[\alpha]^{20}_{D} =$



+63.1 (*c* 0.74, MeOH); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.28–7.20 (m, 4H), 5.06 (d, *J* = 29.0 Hz, 2H), 4.53–4.49 (m, 1H), 3.72–3.64 (m, 1H), 2.37 (s, 3H), 2.05–2.02 (m, 1H), 1.60–1.53 (m, 1H), 1.22 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 156.8, 139.3, 137.8, 129.4, 126.1, 55.3, 46.5,

40.2, 21.7, 20.8; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 254 nm, flow rate: 0.80 mL/min, 30 °C), $t_1 = 12.9 \text{ min (maj)}$, $t_2 = 15.1 \text{ min}$; HRMS (ESI) *m*/*z* Calculated for $C_{12}H_{17}N_2O [M+H]^+$ 205.1335, found 205.1335.

(+)-4-(3,5-Dimethylphenyl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2d): 58 mg, 89% yield, white solid, new compound, mp: 83-84 °C, $R_f = 0.36$ (dichloromethane/methanol = 15:1),



86% ee, $[α]^{20}_{D}$ = +41.8 (*c* 0.94, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 6.95–6.90 (m, 3H), 4.71 (d, *J* = 10.8 Hz, 2H), 4.46–4.42 (m, 1H), 3.69–3.63 (m, 1H), 2.31 (s, 6H), 2.04 (d, *J* = 13.2 Hz, 1H), 1.62–1.53 (m, 1H), 1.21 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 141.3, 138.1, 129.3, 123.4, 55.0, 46.0, 39.6, 21.4, 20.7; Enantiomeric excess was determined by

HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 254 nm, flow rate: 0.80 mL/min, 30 °C), $t_1 = 8.6$ min (maj), $t_2 = 14.2$ min; HRMS (ESI) m/z Calculated for $C_{13}H_{19}N_2O$ [M+H]+ 219.1492, found 219.1491.

(+)-4-(2-Methoxyphenyl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2e): 59 mg, 89% yield, pale oil, new compound, $R_f = 0.30$ (dichloromethane/methanol = 15:1), 90% ee, $[\alpha]_D^{20} = +87.6$ (*c*)

0.78, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.40 (m, 1H), 7.29–7.25 (m, 1H), 6.99 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 5.31 (s, 1H), 4.97–4.93 (m, 1H), 4.88 (s, 1H), 3.83 (s, 3H), 3.73–3.65 (m, 1H), 2.20–2.12 (m, 1H), 1.53–1.44 (m, 1H), 1.21 (d, J = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 158.3, 131.8, 130.6, 127.7, 122.9, 112.4, 57.3, 50.5, 48.4, 39.4, 23.7; Enantiomeric excess was determined by HPLC for the corresponding benzamide (IC column,

n-Hexane/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.70 mL/min, 30 °C), $t_1 = 21.9$ min (maj), $t_2 = 29.2$ min; HRMS (ESI) *m/z* Calculated for $C_{12}H_{17}N_2O_2$ [M+H]⁺ 221.1285, found 221.1286.

(-)-4-(3-Methoxyphenyl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2f): 58 mg, 88% yield, white solid, new compound, mp: 184-185 °C, $R_f = 0.26$ (dichloromethane/methanol = 15:1), 92%



ee, $[\alpha]^{20}{}_{\rm D}^{\rm D} = -25.8$ (*c* 0.72, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.28–7.25 (m, 1H), 6.92–6.80 (m, 3H), 5.27 (s, 1H), 4.91 (s, 1H), 4.51–4.48 (m, 1H), 3.80 (s, 3H), 3.71–3.63 (m, 1H), 2.05 (d, *J* = 13.0 Hz, 1H), 1.58 (q, *J* = 12.0 Hz, 1H), 1.21 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ

160.1, 157.1, 143.6, 129.9, 118.4, 113.7, 111.4, 55.6, 55.3, 46.5, 40.1, 21.8; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 254 nm, flow rate: 0.70 mL/min, 30 °C), $t_1 = 23.6$ min, $t_2 = 25.6$ min (maj); HRMS (ESI) *m/z* Calculated for C₁₂H₁₇N₂O₂ [M+H]⁺ 221.1285, found 221.1286.

(+)-4-(4-Methoxyphenyl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2g): 62 mg, 94% yield, white solid, new compound, mp: 148-149 °C, $R_f = 0.26$ (dichloromethane/methanol = 15:1), 93%



ee, $[\alpha]^{20}_{D}$ = +49.3 (*c* 0.86, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.18 (s, 1H), 4.83 (s, 1H), 4.48–4.44 (m, 1H), 3.80 (s, 3H), 3.68–3.63 (m, 1H), 2.04–1.96 (m, 1H), 1.58–1.55 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, 1.58–1.55 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, 1.58–1.55 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, 1.58–1.55 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, 1.58–1.55 (m, 1H), 1.20 (m, 1H), 1.58–1.55 (m, 1H), 1.20 (m, 1H), 1.20 (m, 1H), 1.58–1.55 (m, 1H), 1.58–1.55 (m, 1H), 1.20 (m, 1H), 1.58–1.55 (m, 1H), 1.58–1.58 (m, 1H), 1.58–1.55 (m, 1H), 1.58–1.58 (m, 1H), 1.58–1.

CDCl₃) δ 158.9, 156.5, 133.4, 126.8, 113.7, 54.8, 54.5, 46.0, 39.7, 21.3; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.70 mL/min, 30 °C), t₁ = 16.0 min (maj), t₂ = 20.0 min; HRMS (ESI) *m/z* Calculated for C₁₂H₁₇N₂O₂ [M+H]⁺ 221.1285, found 221.1287.

(+)-4-(3,4-Dimethoxyphenyl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2h): 67 mg, 89% yield, pale oil, new compound, $R_f = 0.18$ (dichloromethane/methanol = 15:1), 90% ee, $[\alpha]^{20}_{D} =$ +46.8 (*c* 1.16, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 6.88–6.80 (m, 3H), 5.21 (s, 1H), 4.88 (s, 1H), 4.49–4.46 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.70–3.65 (m, 1H), 2.08–1.99 (m, 1H),



(+)-4-(4-Chlorophenyl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2i): 63 mg, 94% yield, yellowish solid, new compound, mp: 257-258 °C, $R_f = 0.35$ (dichloromethane/methanol = 15:1),



93% ee, $[\alpha]^{20}_{D}$ = +49.3 (*c* 0.96, MeOH); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.39–7.33 (m, 4H), 5.32 (s, 2H), 4.54–4.52 (m, 1H), 3.74–3.61 (m, 1H), 2.06–2.03 (m, 1H), 1.59–1.50 (m, 1H), 1.21 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 156.9, 141.0, 133.4, 128.8, 127.7, 54.9, 46.4, 40.0,

21.6; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 230 nm, flow rate: 0.8 mL/min, 30 °C), $t_1 = 14.0$ min (maj), $t_2 = 18.2$ min; HRMS (ESI) *m*/*z* Calculated for C₁₁H₁₄N₂OCl [M+H]⁺ 225.0789, found 225.0785.

(+)-4-(3,4-Dichlorophenyl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2j): 70 mg, 90% yield, pale oil, new compound, $R_f = 0.38$ (dichloromethane/methanol = 15:1), 91% ee, $[\alpha]_D^{20} = +46.1$ (*c*



0.70, MeOH); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.49–7.46 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 5.83 (s, 1H), 5.75 (s, 1H), 4.55–4.41 (m, 1H), 3.70–3.55 (m, 1H), 2.12–1.96 (m, 1H), 1.54–1.46 (m, 1H), 1.18 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 157.3, 142.9, 132.6, 131.4, 130.7, 128.3, 125.8,

54.4, 46.2, 39.9, 21.4; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 230 nm, flow rate: 0.8 mL/min, 30 °C), $t_1 = 14.5 \text{ min (maj)}$, $t_2 = 20.4 \text{ min; HRMS (ESI)}$ *m/z* Calculated for C₁₁H₁₃N₂OCl₂ [M+H]⁺ 259.0399, found 259.0400.

(+)-4-(4-Fluorophenyl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2k): 56 mg, 91% yield, white solid, new compound, mp: 145-146 °C, $R_f = 0.30$ (dichloromethane/methanol = 15:1), 96%



ee, $[\alpha]^{20}_{D} = +69.0$ (*c* 0.80, MeOH); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.39–7.36 (m, 2H), 7.11–7.07 (m, 2H), 5.39 (s, 1H), 5.29 (s, 1H), 4.56–4.52 (m, 1H), 3.71–3.63 (m, 1H), 2.10–1.99 (m, 1H), 1.60–1.55 (m, 1H), 1.21 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 162.3 (d, J = 245.4 Hz),

156.9, 138.2 (d, J = 3.0 Hz), 127.9 (d, J = 8.2 Hz), 115.5 (d, J = 21.6 Hz), 54.9, 46.4, 40.2, 21.6; ¹⁹F NMR (376 MHz, CD₂Cl₂) δ -115.2; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 230 nm, flow rate: 0.8 mL/min, 30 °C), t₁ = 12.4 min (maj), t₂ = 17.5 min; HRMS (ESI) *m/z* Calculated for C₁₁H₁₄N₂OF [M+H]⁺ 209.1085, found 209.1085.

(-)-4-Methyl-6-(4-(trifluoromethyl)phenyl)tetrahydropyrimidin-2(1*H*)-one (2l): 66 mg, 86% yield, yellowish solid, new compound, mp: 191-192 °C, $R_f = 0.33$ (dichloromethane/



methanol = 20:1), 83% ee, $[\alpha]^{20}{}_{D}$ = -35.4 (*c* 0.76, MeOH); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.65 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 6.02 (s, 1H), 5.98 (s, 1H), 4.64–4.49 (m, 1H), 3.70–3.52 (m, 1H), 2.12–1.96 (m, 1H), 1.55–1.46 (m, 1H), 1.17 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 157.5, 146.7, 129.7 (q, *J* = 32.4 Hz), 126.6, 125.6 (q, *J* = 3.8

Hz), 124.2 (q, J = 272 Hz) 55.0, 46.3, 40.1, 21.4; ¹⁹F NMR (376 MHz, CD₂Cl₂) δ -62.8; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 254 nm, flow rate: 0.8 mL/min, 30 °C), t₁ =13.3 min (maj), t₂ = 15.8 min; HRMS (ESI) *m/z* Calculated for C₁₂H₁₄N₂OF₃ [M+H]⁺ 259.1053, found 259.1052.

(+)-4-Ethyl-6-phenyltetrahydropyrimidin-2(1*H*)-one (2m): 55 mg, 90% yield, pale oil, new compound, $R_f = 0.38$ (dichloromethane/methanol = 15:1), 96% ee, $[\alpha]_D^{20} = +50.6$ (*c* 0.72, MeOH);



¹H NMR (400 MHz, CDCl₃) δ 7.41–7.29 (m, 5H), 5.39 (s, 1H), 5.00 (s, 1H), 4.53–4.49 (m, 1H), 3.52–3.42 (m, 1H), 2.14–2.04 (m, 1H), 1.57–1.51 (m, 3H), 0.95 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.4, 142.1, 128.9, 128.1, 126.1, 55.5, 52.2, 37.8, 28.9, 9.5; Enantiomeric excess was determined

by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 75/25, detector: 230 nm, flow rate: 0.8 mL/min, 30 °C), $t_1 = 12.3$ min (maj), $t_2 = 15.0$ min; HRMS (ESI) *m/z* Calculated for $C_{12}H_{17}N_2O$ [M+H]⁺ 205.1335, found 205.1336.

(+)-4-Isopropyl-6-phenyltetrahydropyrimidin-2(1*H*)-one (2n): 58 mg, 89% yield, white solid, new compound, mp: 183-184 °C, $R_f = 0.35$ (dichloromethane/methanol = 15:1), 83% ee,



 $[\alpha]^{20}{}_{D}$ = +13.3 (*c* 0.52, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.30 (m, 5H), 5.21 (s, 1H), 5.06 (s, 1H), 4.54–4.46 (m, 1H), 3.42–3.33 (m, 1H), 2.02–1.71 (m, 1H), 1.70–1.68 (m, 1H), 1.65–1.55 (m, 1H), 0.98–0.93 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 142.9, 129.7, 129.0, 127.0, 57.2, 56.3,

35.7, 33.1, 19.0, 18.5; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.7 mL/min, 30 °C), $t_1 = 17.6 \text{ min}$, $t_2 = 19.2 \text{ min}$ (maj); HRMS (ESI) *m/z* Calculated for $C_{13}H_{19}N_2O$ [M+H]⁺ 219.1492, found 219.1496.

(-)-4-Cyclohexyl-6-methyltetrahydropyrimidin-2(1*H*)-one (20): 48 mg, 81% yield, white solid, new compound, mp: 157-158 °C, $R_f = 0.30$ (ethyl acetate/methanol = 20:1), 86% ee, $[\alpha]^{20}_{D} =$



-0.6 (*c* 0.86, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 4.82 (s, 1H), 4.66 (s, 1H), 3.53–3.45 (m, 1H), 3.23–3.18 (m, 1H), 1.87–1.65 (m, 6H), 1.33–1.21 (m, 4H), 1.18 (d, J = 6.4 Hz, 3H), 1.15–0.94 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.3, 55.6, 46.2, 42.4, 33.5, 28.6, 28.3, 26.4, 26.1, 26.0, 22.0; Enantiometric

excess was determined by HPLC for the corresponding benzamide (OD-H column, Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min, 30 °C), $t_1 = 7.0$ min (maj), $t_2 = 9.9$ min; HRMS (ESI) *m/z* Calculated for $C_{11}H_{21}N_2O[M+H]^+$ 197.1648, found 197.1652.

(+)-4-(Furan-2-yl)-6-methyltetrahydropyrimidin-2(1*H*)-one (2p): 49 mg, 91% yield, pale yellow solid, new compound, mp: 159-160 °C, $R_f = 0.20$ (ethyl acetate/methanol = 20:1), 83% ee,



 $[\alpha]^{20}{}_{D}$ = +6.4 (*c* 0.52, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.33 (m, 1H), 6.37–6.31 (m, 1H), 6.29–6.23 (m, 1H), 5.71–5.58 (m, 1H), 5.52–5.40 (m, 1H), 4.67–4.58 (m, 1H), 3.68–3.61 (m, 1H), 2.18 (d, *J* = 12.8 Hz, 1H), 1.78–1.69 (m, 1H), 1.24 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ

157.0, 153.8, 142.2, 110.4, 105.6, 48.8, 46.0, 36.0, 21.7; Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-H column, *n*-Hexane/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min, 30 °C), $t_1 = 12.0$ min (maj), $t_2 = 13.8$ min; HRMS (ESI) *m/z* Calculated for C₉H₁₃N₂O₂ [M+H]⁺ 181.0972, found 181.0971.

General procedure for asymmetric hydrogenation of 4,5,6-trisubstituted pyrimidin-2-ols:



In a nitrogen-filled glove box, a mixture of $[Ir(COD)Cl]_2$ (2.0 mg, 0.003 mmol) and (*S*,*S*)f-Binaphane (5.3 mg, 0.0066 mmol) in isppropanol (1.0 mL) was stirred at room temperature for 10 min, then substrates **3** (0.3 mmol) and TCCA (7.0 mg, 0.03 mmol) together with isppropanol (1.0 mL) and ethanol (1.0 mL) were added to the mixture. The hydrogenation was performed at 40 °C under 800 psi of hydrogen for 48 h. After carefully releasing the hydrogen, excess solid sodium bicarbonate was added. The resulted mixture was stirred for 30 min, then filtrated off and concentrated in *vacuo*. Further purification was performed by a silica gel column eluted with ethyl acetate/methanol to give the desired chiral product **4**.

(+)-Ethyl 2-oxo-4,6-diphenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4a): 86 mg, 89% yield, white solid, known compound, $R_f = 0.80$ (ethyl acetate), 68% ee, $\left[\alpha\right]_{D}^{20} = +10.5$ (c 0.98,



MeOH), [Lit.² $[\alpha]^{20}_{D} = -31.1$ (*c* 0.44, MeOH) for 97% ee]; ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.27 (m, 10H), 6.99 (d, *J* = 5.2 Hz, 1H), 5.86 (s, 1H), 5.50 (d, *J* = 2.8 Hz, 1H), 3.89–3.78 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 152.5, 146.8, 143.4, 135.1, 129.6, 128.9, 128.3, 128.1, 128.0, 126.6, 102.5, 60.1, 56.1, 13.5; Enantiomeric excess

was determined by HPLC (AD-H column, *n*-Hexane/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 0.70 mL/min, 30 °C) $t_1 = 14.4 \text{ min (maj)}, t_2 = 17.7 \text{ min}.$

(+)-Ethyl 2-oxo-4,6-dim-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4b): 95 mg, 90% yield, white solid, new compound, mp: 196-197 °C, $R_f = 0.70$ (ethyl acetate), 83% ee, $[\alpha]^{20}_{D} =$



+17.4 (*c* 1.34, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 7.6 Hz, 1H), 7.26–7.21 (m, 4H), 7.16–7.11 (m, 3H), 6.68 (s, 1H), 5.62 (s, 1H), 5.47 (d, *J* = 2.8 Hz, 1H), 3.89–3.81 (m, 2H), 2.36 (s, 6H), 0.84 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 152.3, 146.7, 143.3, 138.5, 138.1, 135.1, 130.3, 128.9, 128.8, 128.5, 128.2, 127.4,

125.0, 123.7, 102.5, 60.0, 56.2, 21.6, 21.3, 13.5; Enantiomeric excess was determined by HPLC (AD-H column, *n*-Hexane/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 0.70 mL/min, 30 °C) t_1 =12.1 min (maj), t_2 = 15.2 min; HRMS (ESI) *m*/*z* Calculated for C₂₁H₂₃N₂O₃ [M+H]⁺ 351.1703, found 351.1705.

(+)-Ethyl 2-oxo-4,6-dip-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4c): 94 mg, 90% yield, white solid, known compound, $R_f = 0.70$ (ethyl acetate), 81% ee, $[\alpha]^{20}_{D} = +32.3$ (*c* 0.90,



MeOH), [Lit.² [α]²⁰_D = -31.9 (*c* 0.26, MeOH) for 93% ee]; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (s, 1H), 7.30–7.27 (m, 2H), 7.22–7.19 (m, 2H), 7.17–7.12 (m, 4H), 6.32 (s, 1H), 5.37 (d, *J* = 3.0 Hz, 1H), 3.85 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 153.1, 147.2, 140.7, 139.6, 137.6,

132.1, 129.5, 128.9, 128.0, 126.5, 102.1, 60.0, 55.5, 21.4, 21.2, 13.7; Enantiomeric excess was determined by HPLC (AD-H column, *n*-Hexane/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 0.70 mL/min, 30 °C) t_1 = 16.9 min (maj), t_2 = 18.4 min.

(+)-Ethyl 2-oxo-4,6-bis(3-methoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4d):

105 mg, 92% yield, known compound, white solid, $R_f = 0.70$ (ethyl acetate), 75% ee, $[\alpha]_{D}^{20} =$



+14.1 (*c* 0.74, MeOH), [Lit.² $[\alpha]^{20}{}_{D}$ = -22.4 (*c* 0.58, MeOH), for 99% ee]; ¹H NMR (400 MHz, CDCl₃) δ 7.28 (dd, *J* = 7.8, 5.0 Hz, 2H), 7.02–6.97 (m, 2H), 6.94–6.90 (m, 2H), 6.87–6.82 (m, 2H), 6.11 (s, 1H), 5.44 (d, *J* = 2.8 Hz, 1H), 3.88–3.81 (m, 2H), 3.79 (s, 3H), 3.79 (s, 3H), 0.85 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100

MHz, CDCl₃) δ 165.2, 159.9, 159.4, 152.7, 146.7, 144.9, 136.2, 129.9, 129.4, 120.4, 118.8, 115.3, 113.4, 113.3, 112.5, 102.3, 60.1, 55.8, 55.4, 55.2, 13.6; Enantiomeric excess was determined by HPLC (AD-H column, *n*-Hexane/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 0.70 mL/min, 30 °C) t₁ = 26.9 min (maj), t₂ = 30.2 min.

4. Asymmetric Hydrogenation at Gram Scale



In a nitrogen-filled glove box, a mixture of $[Ir(COD)Cl]_2$ (18.1 mg, 0.027 mmol) and (*S*,*S*)f-Binaphane (48 mg, 0.059 mmol) in isppropanol (3.0 mL) was stirred at room temperature for 15 min, then substrates **1a** (1.005g, 5.4 mmol) and TCCA (63 mg, 0.27 mmol) together with isppropanol (13.0 mL) and ethanol (8.0 mL) were added to the mixture. The hydrogenation was performed at 40 °C under 800 psi of hydrogen for 48 h. After carefully releasing the hydrogen, excess solid sodium bicarbonate was added. The resulted mixture was stirred for 30 min, then filtrated off and concentrated in *vacuo*. Further purification was performed by a silica gel column eluted with ethyl acetate/methanol to give the chiral product **2a** 0.945 g in 92% yield and 95% ee.

5. Mechanistic Investigation

5.1 Control Experiments



In order to further verify our hypothesis that the hydrogenation carried out *via* the oxo form of the 2-hydroxypyrimidine, we synthesized the hydroxyl protected 2-methoxy-4-methyl-6-phenyl pyrimidine **5** according to the literature method.³ Asymmetric hydrogenation of **5** was proceeded under the standard hydrogenation condition $[Ir(COD)Cl]_2/(S,S)$ -f-Binaphane/TCCA/EtOH:^{*i*}PrOH (1:2), no reaction occurred.

5.2 Isotopic Labeling Experiments

Asymmetric Hydrogenation with D_2 : 4-Methyl-6-phenylpyrimidin-2-ol 1a was hydrogenated in D_2 (400 psi) with the [Ir(COD)Cl]₂/(*S*,*S*)-f-Binaphane/TCCA/MeOH condition.



¹H NMR analysis of the crude hydrogenation product showed that deuterium atoms were incorporated to the 4,5,6-position (C4: 61%; C5: 11% and 17%; C6: 63%) of the hydrogenation product 4-methyl-6-phenyltetrahydropyrimidin-2(1H)-one [D]-**2a** (Figure S1). These experimental results confirmed that the **1a** might be hydrogenated *via* imine form by the chiral iridium catalyst.



Figure S1. ¹H NMR of [D]-2a

Asymmetric Hydrogenation in CD₃OD:



¹H NMR analysis of the crude hydrogenation product showed that deuterium atoms were incorporated to the 4,5,6-position (C4: 11%; C5: 59% and 62%; C6: 16%) of 4-methyl-6-phenyltetrahydropyrimidin-2(1H)-one [D]-**2a'**, which suggested that a rapid reversible process of enmine-imime existed during reaction process (Figure S2).



6. Product Elaboration



According to the known report²: A mixture of chiral cyclic urea (+)-2a (98% ee, 76 mg, 0.4 mmol), 60 wt% sodium hydride (40 mg, 1.0 mmol) in 1,4-dioxane (4.0 mL) was refluxed for 15 min. The suspension was cooled to 25 °C, and benzyl bromide (151 mg, 0.88 mmol) was added. The mixture was refluxed for 16 h, cooled and filtered. The solvent was evaporated from the filtrate, to afford the crude product, followed by purification by a silica gel column using hexanes/ ethyl acetate as eluent to give the pure product (+)-11.

(+)-1,3-Dibenzyl-4-methyl-6-phenyltetrahydropyrimidin-2(1*H*)-one (11): 122 mg, pale oil, 82% yield, new compound, $[\alpha]^{20}_{D} = +45.3$ (*c* 1.06, CHCl₃), $R_f = 0.85$ (hexanes/ethyl acetate = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.21 (m, 13H), 7.21 (d, *J* = 7.4 Hz, 2H), 5.60 (d, *J* = 15.2 Hz, 1H), 5.38 (d, *J* = 15.6 Hz, 1H), 4.45 (t, *J* = 6.2 Hz, 1H), 4.24 (d, *J* = 15.8 Hz, 1H), 3.67 (d, *J* = 15.2 Hz, 1H), 3.53–3.46 (m, 1H), 2.24–2.18 (m, 1H), 2.07–2.00 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.9, 141.0, 138.5, 138.1, 128.3, 128.0, 127.9, 127.6, 127.1, 127.0, 126.6, 126.4, 126.3, 56.6, 48.6, 48.2, 47.5, 38.1, 19.8; HRMS (ESI) m/z Calculated for C₂₅H₂₇N₂O [M+H]⁺ 371.2118, found 371.2117.

A mixture of lithium aluminum hydride (63 mg, 1.65 mmol) and **11** (122 mg, 0.33 mmol) in anhydrous ether (5.0 mL) was refluxed for 4 h. The reaction was quenched with water (3.0 mL), and 10% aqueous sodium hydroxide (3.0 mL) was added. After being stirred for 15 minutes, the mixture was diluted with ethyl acetate, filtered through Celite. The filtrate was extracted with ethyl acetate there times. The combined organic layer was dried over anhydrous sodium sulfate and concentrated in *vacuo* to give the crude product, which was subjected to hydrolysis without further purification.

To the crude product obtained above was added 5 % HCl in methanol (3.0 mL). The mixture was stirred at 25 °C until TLC revealed complete conversion. The reaction mixture was adjusted to pH 8~9 with 10 % ammonia solution. After being stirred for 15 minutes, the mixture was extracted with chloroform. The combined organic layer were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated in *vacuo*. The crude product was purified by silica gel chromatography using dichloromethane/methanol as eluent to give 1,3-diamine (+)-12.

(+)-*N*,*N*-Dibenzyl-1-phenylbutane-1,3-diamine (12): 86 mg, pale yellow oil, 75% yield (two steps), 98% ee, new compound, $[\alpha]^{20}_{D} = +26.8$ (*c* 0.60, CHCl₃), $R_f = 0.2$ (dichloromethane/ methanol = 15/1); ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.24 (m, 13H), 7.11 (d, *J* = 7.2 Hz, 2H), 4.99 (s, 2H), 4.06 (d, *J* = 13.2 Hz, 1H), 3.71–3.68 (m, 2H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 2.94–2.91 (m, 1H), 2.23–2.14 (m, 1H), 1.70–1.68 (m, 1H), 1.22 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 139.2, 128.8, 128.8, 128.6, 128.5, 128.3, 127.8, 127.5, 127.2, 126.9, 126.0, 62.2, 53.5, 50.9, 50.1, 43.5, 19.5; Enantiomeric excess was determined by HPLC (OD-H, elute: *n*-Hexane/*i*-PrOH = 85/15, 0.05% Et₃N, detector: 254 nm, flow rate: 0.6 mL/min, 30 °C), t₁ = 7.3 min (maj), t₂ = 8.5 min; HRMS (ESI) m/z Calculated for C₂₄H₂₉N₂ [M+H]⁺ 345.2325, found 345.2324.

7. References

- [1] (a) Murray, T. P.; Hay, J. V.; Portlock, D. E.; Wolfe, J. F. J. Org. Chem. 1974, 39, 595; (b) Nigam, S. C.; Saharia, G. S.; Sharma, H. R. J. Indian Chem. Soc. 1982, 59, 709; (c) Mcarthur, S. G.; Erwin, G.; Juergen, W.; Woltering, T. WO 2007110337 A1, 2007; (d) Shoichi, C.; Yojiro, U.; Tomiyosi, A.; Kyoichi, I. WO 9607641 A1, 1996; (e) Sakamoto, T.; Sakasai, T.; Yoshizawa, H.; Tanji, K.; Nishimura, S.; Yamanaka, H. Chem. Pharm. Bull.1983, 31, 4554; (f) 1b [CAS: 1697101-66-8]; 1d [CAS: 1698634-89-7]; 1e [CAS: 1159816-34-8]; 1f [CAS: 1702115-48-7]; 1g [CAS: 1695255-01-6]; 1h [CAS: 1972241-84-1]; 1n [CAS: 1412958-83-8]; 1o [CAS: 1412958-07-6], 1p [CAS: 1412960-34-9], these compounds are commercially available.
- [2] Feng, G.-S.; Chen, M.-W.; Shi, L.; Zhou, Y.-G. Angew. Chem. Int. Ed. 2018, 57, 5853.
- [3] Gompper, R. Chem. Ber. 1960, 93, 198.

8. Copy of NMR and HPLC



























-23.73

~159.49 ~158.33

13C NMR GF-6-69B in CDCI3











-46.46 --40.11

<55.55 55.30 -21.79

13C NMR GF-6-57C IN CDCI3

-160.07



¹³C NMR (100 MHz, CDCl₃)



























19F NMR GF-6-70C IN CD2CI2





S35






---62.7972

19F NMR GF-6-99B IN CD2Cl2











f1 (ppm)







13C NMR GF-6-69A CDCI3

































-13.59

13C NMR GF-9-78B IN CDCL3







13C NMR GF-6-36A in CDCl3



-56.64 48.57 47.51 ---38.10







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		(modified after loading)						
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25,	0.8 mL/min,	1	30 oC,	254	nm	



Area Percent Report
Sorted By : Signal
Multiplier: : 1.0000

Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm



*** End of Report ***

Data File C:\CHEM32\1\DATA\ZH0U-17\YZN003769.D Sample Name: GF-6-17G

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*** End of Report ***

Instrument 1 8/17/2017 8:25:58 AM

Page 1 of 1

(+/-)-2a'

Instrument 1 8/17/2017 8:28:07 AM

Data File C:\CHEM32\1\DATA\ZH0U-17\YZN003404.D Sample Name: GF-6-52E

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Injection Date	:	2/24/2017 10:58:19 PM						
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		(modified after loading)						
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25,	0.8 mL/min,	31	JoC, ∶	254 nm		



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Dilution:		:	1.0000
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Signal 1: VWD1 A, Wavelength=254 nm







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Signal 1: VWD1 A, Wavelength=254 nm

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1 12.158 BB	0.4092 1098.16577	41.29942	97.4913	Me
2 15.303 BB	0.6219 28.25838	6.67647e-1	2.5087	
Totals :	1126.42415	41.96707		(+)-2b'



Instrument 1 2/24/2017 11:19:40 PM 0

Page 1 of 1

Instrument 1 3/29/2018 8:29:56 PM

Data File C:\CHEM32\1\DATA\ZH0U-17\YZN003405.D Sample Name: GF-6-53F

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Signal 1: VWD1 A, Wavelength=254 nm



*** End of Report ***





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Signal 1: VWD1 A, Wavelength=254 nm





Instrument 1 2/24/2017 11:55:21 PM 0

Page 1 of 1

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Sample Info	:	OD-H, Hexane/i-PrOH = 75/25,	0.8 mL/min,	31	DoC,	254 n	ш	



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Use Multiplier (Dilution	Factor	with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm





*** End of Report ***

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Page 1 of 1

Instrument 1 2/27/2017 10:15:09 PM 0

Data File C:\CHEM32\1\DATA\ZHOU-17\YZNO04171.D Sample Name: GF-6-69B(+-)

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		(modified after loading)						
Sample Info	:	IC, Hexane/i-PrOH = 70/30, 0.7	mL/min,	30	oC, 3	254 nm		



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Use Multiplier	& Dilution	Factor wit	th ISTDs	

Signal 1: VWD1 A, Wavelength=254 nm





*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN004173.D Sample Name: GF-6-69B

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Acq. Operator	:	0				
Acq. Instrument	:	Instrument 1	Location	:	Vial	1
Injection Date	:	5/9/2017 9:21:57 PM				
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M				
Last changed	:	5/9/2017 9:12:32 PM by 0				
		(modified after loading)				
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M				
Last changed	:	8/17/2017 8:53:30 AM by				
		(modified after loading)				
Sample Info	:	IC, Hexane/i-PrOH = 70/30, 0.7	mL/min, 🗄	30	oC,	254 nm



-----Area Percent Report -----Sorted By Signal .

Multiplier: : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs







*** End of Report ***

Instrument 1 8/17/2017 8:52:13 AM

Page 1 of 1

Instrument 1 8/17/2017 8:53:35 AM

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003475.D Sample Name: GF-6-57C (rac)

Acq. Operator	:	0					
Acq. Instrument	:	Instrument 1	Location	:	Vial	1	
Injection Date	:	3/2/2017 8:12:33 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	3/2/2017 7:58:00 PM by 0					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	3/2/2017 8:46:52 PM by 0					
		(modified after loading)					
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25,	0.7 mL/min,	31	DoC,	254 nm	



Area Percent Report Sorted By : Signal Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm





(+/-)-2f'

Bz .

*** End of Report ***

Data File C:\CHEM32\1\DATA\ZH0U-17\YZN003477.D Sample Name: GF-6-57C

	-		
Acq. Operator	:	0	
Acq. Instrument	:	Instrument l Location : Vial 1	
Injection Date	:	3/2/2017 10:08:21 PM	
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M	
Last changed	:	3/2/2017 9:35:56 PM by 0	
		(modified after loading)	
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M	
Last changed	:	3/2/2017 10:42:22 PM by 0	
		(modified after loading)	
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25, 0.7 mL/min, 30oC, 254 nm	



Area Percent Report

Sorted By : Signal Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs



*** End of Report ***

Instrument 1 3/2/2017 8:47:07 PM 0

Page 1 of 1

.Bz

.OMe

Instrument 1 3/2/2017 10:42:29 PM 0

Page 1 of 1

.OMe

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003391.D Sample Name: GF-6-51A(rac)

Acq. Operator	:	0					
Acq. Instrument	:	Instrument l Location : Vial 1					
Injection Date	:	2/24/2017 2:27:46 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	2/24/2017 2:26:10 PM by 0					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	2/24/2017 3:04:24 PM by 0					
		(modified after loading)					
Sample Info	:	OD-H, Hexane/i-PrOH = 70/30, 0.7 mL/min, 30oC, 254nm					



	Ar	ea Percen	t Report		
Sorted By	:	Signal			
Multiplier:		:	1.0000		
Dilution:		:	1.0000		
Use Multiplier a	Dilution F	actor wit	h ISTDs		
Signal 1: VWD1 A	, Wavelengt	:h=254 nm			0
Signal 1: VWD1 A Peak RetTime Tvp	, Wavelengt e Width	h=254 nm Area	Height	Area	0
Signal 1: VWD1 A Peak RetTime Typ # [min]	, Wavelengt e Width [min] m	h=254 nm Area	Height [mAU]]	Area	O Bz、, L., Bz
Signal 1: VWD1 A Peak RetTime Typ # [min] 	, Wavelengt e Width [min] m - -	h=254 nm Area AU *s	Height [mAU]	Àrea *	Bz∖Ŋ́Bz
Signal 1: VWD1 & Peak RetTime Typ # [min] 	, Wavelengt e Width [min] m - - 0.5738 1	h=254 nm Area AU *s 	Height [mAU] 	Area % 49.7715	Bz N Bz

*** End of Report ***

2.04149e4 481.37975

(+/-)-2g' OMe

Data File C:\CHEM32\1\DATA\ZH0U-17\YZN003403.D Sample Name: GF-6-51A

Acq. Operator	:	0					
Acq. Instrument	:	Instrument 1	Location	:	Vial	1	
Injection Date	:	2/24/2017 10:08:15 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	2/24/2017 10:07:21 PM by 0					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	2/24/2017 10:34:21 PM by 0					
		(modified after loading)					
Sample Info	:	OD-H, Hexane/i-PrOH = 70/30,	0.7 mL/min,	30	JoC,	254	nm



-----Area Percent Report •

Multiplier: : 1.000 Dilution: : 1.000 Use Multiplier & Dilution Factor with ISTI	Sort	ted By		:	Sign	nal		
Dilution: : 1.000 Use Multiplier & Dilution Factor with IST	Mult	tiplier:			:		1.0000	Э
Use Multiplier & Dilution Factor with IST	Dilu	ution:			:		1.0000	0
-	Use	Multiplier	6	Dilution	Factor	with	ISTD:	3

Signal 1: VWD1 A, Wavelength=254 nm





Instrument 1 2/24/2017 3:04:34 PM 0

Totals :

Page 1 of 1

Instrument 1 2/24/2017 10:34:30 PM 0

Page 1 of 1

`OMe

Data File C:\CHEM32\1\DATA\ZH0U-17\YZN003754.D Sample Name: GF-6-71G(+-)

				-		.===	
Acq. Operator	:	0					
Acq. Instrument	:	Instrument 1	Location	:	Vial	1	
Injection Date	:	3/30/2017 1:56:39 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	3/30/2017 1:55:56 PM by 0					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF_LC.M					
Last changed	:	3/29/2018 8:39:28 PM					
		(modified after loading)					
Sample Info	:	OD-H, Hexane/i-PrOH = 70/30,	0.7 mL/min,	1	30 oC,	230	nm



------Area Percent Report _ Sorted By Signal . Multiplier: : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Туре	Width [min]	Ar mAU	ea *s	Heiç [mAU	nt 1	Area %
1	23.975	VV VB	1.1771	7432.	53564 78857	94.7	16222	50.1611 49.8389
Total	ls :		1	1.481	.73e4	175.8	3734	



*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003748.D Sample Name: GF-6-71G

..... Acq. Operator : O Acq. Instrument : Instrument 1 Location : Vial 1 Injection Date : 3/29/2017 1:54:47 PM Acq. Method : C:\CHEM32\1\METHODS\DEF LC.M Last changed : 3/29/2017 1:53:58 PM by 0 (modified after loading) Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M Last changed : 3/29/2017 3:19:25 PM by 0 (modified after loading) : OD-H, Hexane/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 230 nm Sample Info



-----Area Percent Report _

Signal Sorted By . Multiplier: 1.0000 : Dilution: 1.0000 Use Multiplier & Dilution Factor with ISTDs



*** End of Report ***

Instrument 1 3/29/2018 8:39:32 PM

Page 1 of 1

Instrument 1 3/29/2017 3:19:29 PM 0

Data File C:\CHEM32\1\DATA\ZH0U-17\YZN003674.D Sample Name: GF-6-71F(+-)

Acq. Operator	:	0				
Acq. Instrument	:	Instrument 1 Location : Vial 1				
Injection Date	:	3/22/2017 4:46:51 PM				
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M				
Last changed	:	3/22/2017 4:17:58 PM by 0				
		(modified after loading)				
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M				
Last changed	:	3/22/2017 5:11:18 PM by 0				
		(modified after loading)				
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25, 0.8 mL/min, 30 oC, 230 nm				



-----Area Percent Report _____ Sorted By Signal . Multiplier:

: 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm



*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003676.D Sample Name: GF-6-71F

Acq. Operator :	0	
Acq. Instrument :	Instrument 1	Location : Vial 1
Injection Date :	3/22/2017 9:08:55 PM	
Acq. Method :	C:\CHEM32\1\METHODS\DEF LC.M	
Last changed :	3/22/2017 8:33:13 PM by 0	
	(modified after loading)	
Analysis Method :	C:\CHEM32\1\METHODS\DEF LC.M	
Last changed :	3/22/2017 9:33:33 PM by 0	
	(modified after loading)	
Sample Info :	OD-H, Hexane/i-PrOH = 75/25,	0.8 mL/min, 30 oC, 230 nm



-----Area Percent Report -----Sorted By Signal . Multiplier: : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs Signal 1: VWD1 A, Wavelength=230 nm Peak RetTime Type Width Area Height Area
 # [min]
 main]
 max
 max
 max

 1
 13.990
 VB
 0.4737
 7600.73486
 247.21846
 96.2682

 2
 18.188
 BB
 0.7460
 294.63754
 5.98611
 3.7318
 Totals : 7895.37241 253.20457 (+)-2i'

*** End of Report ***

Instrument 1 3/22/2017 5:11:48 PM 0

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Instrument 1 3/22/2017 9:33:42 PM 0

Data File C:\CHEM32\1\DATA\ZH0U-17\YZN003468.D Sample Name: GF-6-56B(rac)

Acq. Operator	:	0						
Acq. Instrument	:	Instrument 1	Location	:	Vial	. 1		
Injection Date	:	3/2/2017 10:14:19 AM						
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M						
Last changed	:	3/2/2017 10:12:42 AM by 0						
		(modified after loading)						
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M						
Last changed	:	3/2/2017 10:39:10 AM by 0						
		(modified after loading)						
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25,	0.7 mL/min,	31	JoC,	230	nm	



Area Percent Report

Sorted By : Signal Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm



*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003459.D Sample Name: GF-6-56B

Acq. Operator	:	0						
Acq. Instrument	:	Instrument 1	Location	:	Vial	1		
Injection Date	:	3/1/2017 6:16:55 PM						
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M						
Last changed	:	3/1/2017 6:00:47 PM by 0						
		(modified after loading)						
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M						
Last changed	:	3/1/2017 6:42:28 PM by 0						
		(modified after loading)						
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25,	0.8 mL/min,	30	DoC,	230 i	лm	



-----Area Percent Report -----Sorted By Signal . Multiplier: : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs Signal 1: VWD1 A, Wavelength=230 nm Peak RetTime Type Width Area Height Area 1 14.566 BB 0.5054 9088.79688 276.80811 95.6367 2 20.433 BB 0.7747 414.66150 8.18273 4.3633 Totals : 9503.45837 284.99084 (+)-2j'

*** End of Report ***

Instrument 1 3/2/2017 10:42:19 AM 0

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Instrument 1 3/1/2017 6:42:38 PM 0

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003643.D Sample Name: GF-6-70C(+-)

Acq. Operator	÷	0						
Acq. Instrument	:	Instrument 1	Location	:	Vial 1			
Injection Date	:	3/20/2017 9:50:00 PM						
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M						
Last changed	:	3/20/2017 9:49:18 PM by 0						
		(modified after loading)						
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M						
Last changed	:	3/20/2017 10:25:02 PM by 0						
		(modified after loading)						
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25,	0.8 mL/min,		30 oC, 230 nm			



Area Percent Report _ Sorted By Signal . Multiplier:

: 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm



*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003631.D Sample Name: GF-6-70C

..... Acq. Operator : O Acq. Instrument : Instrument 1 Location : Vial 1 Injection Date : 3/19/2017 9:35:51 PM Acg. Method : C:\CHEM32\1\METHODS\DEF LC.M Last changed : 3/19/2017 9:29:24 PM by 0 (modified after loading) Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M Madayab medical : 0.1052017 10:03:04 PM by 0 (modified after loading) Sample Info : 0D-H, Hexame/i-PrOH = 75/25, 0.8 mL/min, 30 oC, 230 nm



_____ Area Percent Report _ Signal Sorted By . Multiplier: 1.0000 : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs Signal 1: VWD1 A, Wavelength=230 nm Peak RetTime Type Width Area Height Area # [min] [min] mAU *s [mAU] ÷ Bz 1 12.419 VB 2 17.501 BB 0.4096 3192.06250 119.88960 97.8643 0.6501 69.66007 1.62030 2.1357 Totals : 3261.72257 121.50990 (+)-2k'



Instrument 1 3/20/2017 10:25:15 PM 0

Page 1 of 1

Instrument 1 3/19/2017 10:03:16 PM 0

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN004109.D Sample Name: GF-6-99B(+-)

Acq. Operator	:	0					
Acq. Instrument	:	Instrument 1	Location	:	Vial .	1	
Injection Date	:	4/27/2017 9:16:30 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	4/27/2017 8:48:16 PM by 0					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	4/27/2017 9:44:40 PM by 0					
		(modified after loading)					
Sample Info	:	OD-H, Hexane/i-PrOH = 75/25,	0.8 mL/min,	3	30 oC,	254	nm



Area Percent Report

Sorted By : Signal Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm



*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-17\YZN004108.D Sample Name: GF-6-99B

Acq. Operator :	0							
Acq. Instrument :	Instrument 1	Location :	Vial l					
Injection Date :	4/27/2017 4:51:42 PM							
Acq. Method :	C:\CHEM32\1\METHODS\DEF LC.M							
Last changed :	4/27/2017 4:50:21 PM by 0							
	(modified after loading)							
Analysis Method :	C:\CHEM32\1\METHODS\DEF LC.M							
Last changed :	4/27/2017 5:12:38 PM by 0							
	(modified after loading)							
Sample Info :	OD-H, Hexane/i-PrOH = 75/25,	0.8 mL/min,	30 oC, 254 nm					



Area Percent Report

 Sorted By
 Signal

 Multiplier:
 :
 1.0000

 Dilution:
 :
 1.0000

 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type # [min] 	Width Area [min] mAU *s	Height [mAU]	Area %	BZ N BZ
1 13.253 VB 2 15.772 BB	0.5481 2251.06079 0.6412 212.98126	62.97016 4.88458	91.3564 8.6436	
Totals :	2464.04205	67.85474		IVIE
	*** Frad of			(+)-2l' CF ₃

Instrument 1 4/27/2017 9:44:49 PM 0

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Instrument 1 4/27/2017 5:12:59 PM 0

Data File C:\CHEM32\1\DATA\FGS\YZ000121.D Sample Name: GF-6-51B-rac

Acq. Operator :							
Acq. Instrument :	Instrument 1	Location	: Vial l				
Injection Date :	2/21/2017 2:42:42 AM						
Acq. Method :	C:\HPCHEM\1\METHODS\DEF LC1.M						
Last changed :	2/21/2017 2:39:40 AM by						
	(modified after loading)						
Analysis Method :	C:\CHEM32\1\METHODS\DEF LC.M						
Last changed :	8/17/2017 11:00:12 PM by						
-	(modified after loading)						
Sample Info :	OD-H, Hexane/iPrOH = 75/25, 0.8	mL/min, 3	0 oC, 230				
	nm						



Area Percent Report

Sorted By : Signal : 1.0000 : 1.0000 Multiplier: Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm







Injection Date : 2/21/2017 2:21:28 AM Acq. Method : C:\HPCHEN\\\METHOD\$\DEF LCL.M Last changed : 2/21/2017 2:19:51 AM by (modified after loading) Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M Last changed : 8/17/2017 11:02:01 PM by (modified after loading) : OD-H, Hexane/iPrOH = 75/25, 0.8 mL/min, 30 oC, 230 Sample Info

> Norm. 140 -

> > 120 -

10.0

80 -

60 -

40 ·

20 -

Acq. Operator :

Data File C:\CHEM32\1\DATA\FGS\YZ000120.D Sample Name: GF-6-51B

Acq. Instrument : Instrument 1

nm

VWD1 A, Wavelength=230 nm (FG S\YZD00120.D)

.....

Location : Vial 1



Sigmal : 1.0000 : 1.0000 Sorted By : Multiplier: Dilution: Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Туре	Width [min]	A1 mAU	tea *s	Heid [mAU	nt]	Area %
1	12.306	VB	0.3815	1544.	88354	62.5	0751	97.7377
2	15.045	BB	0.6873	35.	75892	7.7858	le-1	2.2623
Total	ls :			1580.	64246	63.2	8609	



14

16

*** End of Report ***

Instrument 1 8/17/2017 11:00:17 PM

Page 1 of 1

(+/-)-2m'

Instrument 1 8/17/2017 11:02:11 PM
Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003611.D Sample Name: GF-6-69A(Rac)

Acq. Operator	: 0								
Acq. Instrument	: Instrument l	Location : Vial 1							
Injection Date	: 3/18/2017 11:33:40 AM								
Acq. Method	: C:\CHEM32\1\METHODS\DEF LC.M								
Last changed	: 3/18/2017 11:32:08 AM by 0								
	(modified after loading)								
Analysis Method	: C:\CHEM32\1\METHODS\DEF LC.M								
Last changed	: 3/18/2017 11:58:35 AM by 0								
	(modified after loading)								
Sample Info	: OD-H, Hexane/i-PrOH = 90/10, 0.	.7 mL/min, 30 oC, 254 nm							



-----Area Percent Report _ Sorted By Signal ÷ . Multiplier: : 1.0000 : 1.0000 Dilution:

Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm



*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-17\YZN003610.D Sample Name: GF-6-69A

..... Acq. Operator : O Acq. Instrument : Instrument 1 Location : Vial 1 Injection Date : 3/18/2017 11:08:07 AM Acq. Method : C:\CHEM32\1\METHOD\$\DEF LC.M Last changed : 3/18/2017 10:58:06 AM by 0 (modified after loading) Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M Last changed : 3/18/2017 11:36:41 AM by 0 (modified after loading) : OD-H, Hexane/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 254 nm Sample Info



-----Area Percent Report _ Sorted By Signal . Multiplier: : 1.0000 : 1.0000

Dilution: Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak	RetTime	Туре	Width	. A	rea	Heig	ht	Area	B7 B	,
#	min		min	100 I	*8	mau		ء اا	N N	•
1	17.578	BV	0.5284	196	.40308	5.6	4203	8.3080		
2	19.225	VB	0.5860	2167	.62524	56.8	5307	91.6920	\checkmark	1
Total	.s :			2364	.02832	62.4	9509			
									(+)-2n'	
									 () =	
				***	End of	Report	***			

Instrument 1 3/18/2017 11:58:39 AM 0

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Instrument 1 3/18/2017 11:37:20 AM 0

Page 1 of 1

0

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN004250.D Sample Name: GF-7-17A(+-)

Acq. Operator	:	0					
Acq. Instrument	:	Instrument 1	Location	:	Vial	1	
Injection Date	:	5/17/2017 9:06:48 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	5/17/2017 8:52:09 PM by 0					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	5/17/2017 9:25:14 PM by 0					
		(modified after loading)					
Sample Info	:	OD-H, Hexane/i-PrOH = 70/30, 0.	.7 mL/min,	1	30 oC,	, 254 nm	



-----Area Percent Report • Sorted By : Signal

SOLCER DY		SIGU	ar
Multiplier:		:	1.0000
Dilution:		:	1.0000
Use Multiplier	& Dilution	Factor	with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm







Data File C:\CHEM32\1\DATA\ZH0U-17\YZN004251.D Sample Name: GF-7-17A

Acq. Ope	rator :	0					
Acq. Ins	trument :	Instrument 1	Location	:	Vial	1	
Injectio	n Date :	5/17/2017 10:41:23 PM					
Acq. Met	hod :	C:\CHEM32\1\METHODS\DEF LC.M					
Last cha	nged :	5/17/2017 10:15:38 PM by 0					
		(modified after loading)					
Analysis	Method :	C:\CHEM32\1\METHODS\DEF LC.M					
Last cha	nged :	5/17/2017 10:55:36 PM by 0					
		(modified after loading)					
Sample I	nfo :	OD-H, Hexane/i-PrOH = 70/30,	0.7 mL/min,	- 3	30 oC,	254	nm



-----Area Percent Report -----Signal Sorted By . Multiplier: : 1.0000 : 1.0000

Dilution: Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

	· · · · · · · · · · · · · · ·			0
Peak RetTime Type # [min]	Width Area [min] mAU *s	Height [mAU]	Area %	BZ_N K_N-BZ
 1 7.066 WW	0.1665 2653 20679	243.27797	93,1690	
2 9.880 BB	0.3018 194.52969	9.78569	6.8310	Me
Totals :	2847.73648	253.06366		
				(+)-20'
	ttt End of	Deport ttt		



Instrument 1 5/17/2017 9:25:38 PM 0

Page 1 of 1

Instrument 1 5/17/2017 10:56:21 PM 0

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN004249.D Sample Name: GF-7-11A(+-)

Acq. Operator	:	0					
Acq. Instrument	:	Instrument 1	Location	: V:	ial 1	L	
Injection Date	:	5/17/2017 8:34:41 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	5/17/2017 8:26:26 PM by 0					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	5/17/2017 8:52:44 PM by 0					
		(modified after loading)					
Sample Info	:	OD-H, Hexane/i-PrOH = 70/30,	0.7 mL/min,	30	oC,	254	nm



Area Percent Report

Sorted By	:	Sign	nal
Multiplier:		:	1.0000
Dilution:		:	1.0000
Use Multiplier (Dilution	Factor	with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm









Data File C:\CHEM32\1\DATA\ZH0U-17\YZN004248.D Sample Name: GF-7-11A

Acq. Operator	:	0					
Acq. Instrument	:	Instrument 1	Location	:	Vial J	1	
Injection Date	:	5/17/2017 8:06:08 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	5/17/2017 7:45:29 PM by 0					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	5/17/2017 8:29:41 PM by 0					
		(modified after loading)					
Sample Info	:	OD-H, Hexane/i-PrOH = 70/30,	0.7 mL/min,	- 3	30 oC,	254 n	TO



Area Percent Report

orted By			Sign	ai	
ultiplier:			:	1	.0000
ilution:			:	1	.0000
se Multiplier	6	Dilution	Factor	with	ISTDs

Signal 1: VWD1 A, Wavelength=254 nm





Page 1 of 1

Instrument 1 5/17/2017 8:29:54 PM 0

Data File C:\CHEM32\1\DATA\ZH0U-18\YZN009474.D Sample Name: GF-9-77A(+-)

Acq. Operator	:				
Acq. Instrument	: Instrument 1	Location	:	-	
Injection Date	: 7/25/2018 7:47:05 PM				
Acq. Method	: C:\CHEM32\1\METHODS\DEF_LC.M				
Last changed	: 7/25/2018 7:27:15 PM				
	(modified after loading)				
Analysis Method	: C:\CHEM32\1\METHODS\DEF_LC.M				
Last changed	: 8/1/2018 2:56:39 PM				
	(modified after loading)				
Sample Info	: AD-H, Hexane/iPrOH = 80/20, 0.	7 mL/min, 3	30 oC	C, 254 nm	



------Area Percent Report _ Sorted By Signal . Multiplier: : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime # [min] 	Type Width [min]	Area mAU *s	Height [mAU] 	Area %
1 14.290 2 17.627	BB 0.2941 BB 0.3786	1276.25305 1277.11487	66.83783 51.93041	49.9831 50.0169
Totals :		2553 36792	118 76824	

HN OFt (+/-)-4a

*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009478.D Sample Name: GF-9-77A

..... Acq. Operator : Acq. Instrument : Instrument 1 Injection Date : 7/25/2018 10:06:24 PM Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M Location : -Last changed : 7/25/2018 10:04:51 PM (modified after loading) Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M Andrysis method : (Vommos i um house ter_et.m) Last changed : 8/1/2018 2:57:47 PM [modified after loading] Sample Info : AD-H, Hexame/iFrOH = 80/20, 0.7 mL/min, 30 oC, 254 nm



Area Percent Report _ Sorted By Signal . Multiplier: 1.0000 : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs Signal 1: VWD1 A, Wavelength=254 nm C Peak RetTime Type Width Area Height Area 'NН 1 14.367 BB 0.2940 2619.87500 137.25410 84.2062 2 17.719 BB 0.3776 491.38809 20.05382 15.7938 Totals : 3111.26309 157.30793 C `OEt (+)-4a

*** End of Report ***

Instrument 1 8/1/2018 2:56:42 PM

Page 1 of 1

Instrument 1 8/1/2018 2:57:50 PM

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009475.D Sample Name: GF-9-77B(+-)

Acq. Operator	:						
Acq. Instrument	:	Instrument 1	Location	:	-		
Injection Date	:	7/25/2018 8:17:33 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF_LC.M					
Last changed	:	7/25/2018 8:13:23 PM					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF_LC.M					
Last changed	:	8/1/2018 2:55:20 PM					
		(modified after loading)					
Sample Info	:	AD-H, Hexane/iPrOH = 80/20, 0.	.7 mL/min,	30	oC,	254 r	лm



Area Percent Report _ Sorted By Signal . Multiplier: : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs



*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009479.D Sample Name: GF-9-77B

..... Acq. Operator : Acq. Instrument : Instrument 1 Location : -Injection Date : 7/25/2018 10:28:33 PM Acg. Method : C:\CHEM32\1\METHODS\DEF LC.M Last changed : 7/25/2018 10:27:29 PM (modified after loading) Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M Last changed : 8/1/2018 2:54:14 PM (modified after loading) Sample Info : AD-H, Hexame/IFtOH = 80/20, 0.7 mL/min, 30 oC, 254 nm



_____ Area Percent Report _ Signal Sorted By . Multiplier: 1.0000 : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs Signal 1: VWD1 A, Wavelength=254 nm Peak RetTime Type Width Area Height Area # [min] [min] mAU *s [mAU] ÷ HN

*** End of Report ***

1 12.128 BB 0.2498 4925.64209 302.29993 91.4323 2 15.228 BB 0.3234 461.55756 22.00071 8.5677 Totals : 5387.19965 324.30064



Instrument 1 8/1/2018 2:55:23 PM

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Instrument 1 8/1/2018 2:54:19 PM

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009476.D Sample Name: GF-9-78A(+-)

				==:			
Acq. Operator	:						
Acq. Instrument	:	Instrument 1	Location	:	-		
Injection Date	:	7/25/2018 8:49:54 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF_LC.M					
Last changed	:	7/25/2018 8:48:24 PM					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF_LC.M					
Last changed	:	8/1/2018 2:52:41 PM					
		(modified after loading)					
Sample Info	:	AD-H, Hexane/iPrOH = 80/20, 0.7	mL/min,	30	oC,	254 1	лm



-----Area Percent Report _ Sorted By Signal . Multiplier: : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs Signal 1: VWD1 A, Wavelength=254 nm 0 Peak RetTime Type Width Area Height Area # [min] [min] mAU *s [mAU] \$ 1 16.842 BB 0.3621 1355.86792 57.88870 50.0842 2 18.366 BB 0.4074 1351.31018 51.11972 49.9158

OE (+/-)-4c

*** End of Report ***

2707.17810 109.00842

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009480.D Sample Name: GF-9-78A

```
.....
Acq. Operator :
Acq. Instrument : Instrument 1
                                               Location : -
Injection Date : 7/25/2018 10:50:45 PM
Acc. Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed : 7/25/2018 10:48:46 PM
                 (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 8/1/2018 2:51:36 PM
              (modified after loading)
: AD-H, Hexame/iPrOH = 80/20, 0.7 mL/min, 30 oC, 254 nm
Sample Info
```



_____ Area Percent Report _ Signal Sorted By . Multiplier: 1.0000 : Dilution: 1.0000 Use Multiplier & Dilution Factor with ISTDs \cap Signal 1: VWD1 A, Wavelength=254 nm Peak RetTime Type Width Area Height Area HN NF # [min] [min] mAU *s [mAU] ÷ 1 16.882 BB 0.3630 6386.17969 271.74756 90.4997 2 18.385 BB 0.4124 670.39899 25.07199 9.5003 Ó OF Totals : 7056.57867 296.81955 (+)-4c *** End of Report ***

Instrument 1 8/1/2018 2:52:43 PM

Totals :

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Instrument 1 8/1/2018 2:51:39 PM

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009477.D Sample Name: GF-9-78B(+-)

	==	
Acq. Operator	:	
Acq. Instrument	:	Instrument 1 Location : -
Injection Date	:	7/25/2018 9:28:48 PM
Acq. Method	:	C:\CHEM32\1\METHODS\DEF_LC.M
Last changed	:	7/25/2018 9:27:27 PM
		(modified after loading)
Analysis Method	:	C:\CHEM32\1\METHODS\DEF_LC.M
Last changed	:	8/1/2018 2:47:49 PM
		(modified after loading)
Sample Info	:	AD-H, Hexane/iPrOH = 80/20, 0.7 mL/min, 30 oC, 254 nm



Area Percent Report Sorted By : Signal Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs



*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009481.D Sample Name: GF-9-78B

Acq. Operator	:						
Acq. Instrument	:	Instrument 1	Location	:	-		
Injection Date	:	7/25/2018 11:17:09 PM					
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	7/25/2018 11:15:33 PM					
		(modified after loading)					
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC.M					
Last changed	:	8/1/2018 2:49:51 PM					
-		(modified after loading)					
Sample Info	:	AD-H, Hexane/iPrOH = 80/20, 0.	/ mL/min,	30	oC,	254	n



-----Area Percent Report _ Signal Sorted By . Multiplier: : 1.0000 : 1.0000 Dilution: Use Multiplier & Dilution Factor with ISTDs Signal 1: VWD1 A, Wavelength=254 nm Peak RetTime Type Width Area Height Area HN `NH # [min] [min] mAU *s [mAU] \$ OMe MeO 1 26.926 BB 0.5987 4994.88574 129.45207 87.2827 2 30.216 BB 0.6834 727.76941 16.64476 12.7173 0 `OEt Totals : 5722.65515 146.09683 (+)-4d

*** End of Report ***

Instrument 1 8/1/2018 2:47:57 PM

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Instrument 1 8/1/2018 2:49:58 PM

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN007217.D Sample Name: GF-7-36B-S3(+-)

Acq. Operator	:	
Acq. Instrument	:	Instrument 1 Location : Vial 1
Injection Date	:	1/13/2018 8:40:32 AM
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M
Last changed	:	1/13/2018 8:45:41 AM
		(modified after loading)
Analysis Method	:	C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed	:	8/8/2018 2:56:12 PM
		(modified after loading)
Sample Info	:	OD-H, Hexane/i-PrOH = 85/15 (0.05% Et3N), 0.6 mL/min, 3
		0 oC, 254 nm



------Area Percent Report -----

 Sorted By
 :
 Signal

 Multiplier:
 :
 1.0000

 Dilution:
 :
 1.0000

 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm



*** End of Report ***

Instrument 1 8/8/2018 2:56:19 PM

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Data File C:\CHEM32\1\DATA\ZHOU-18\YZN007220.D Sample Name: GF-7-36B-S3

Acq. Operator	:					
Acq. Instrument	:	Instrument 1	Location	:	Vial	1
Injection Date	:	1/13/2018 10:00:47 AM				
Acq. Method	:	C:\CHEM32\1\METHODS\DEF LC.M				
Last changed	:	1/13/2018 10:06:01 AM				
		(modified after loading)				
Analysis Method	:	C:\CHEM32\1\METHODS\DEF LC11.M				
Last changed	:	8/8/2018 2:54:03 PM				
		(modified after loading)				
Sample Info	:	OD-H, Hexane/i-PrOH = 85/15 (0.0)5% Et3N),	, 1	0.6 ml	J/min, 3
		0 oC, 254 nm				



-----Area Percent Report •----

Sorted By	:	Signa	al
Multiplier:		:	1.0000
Dilution:		:	1.0000
Use Multiplier	& Dilution	Factor 1	with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Aı mAU	rea *s	Hei [mAU	.qht]	Area %	
1	7.292	VV	0.1675	5020.	94678	441.	91907	98.8832	
2	8.511	VB	0.2314	56.	70562	з.	63624	1.1168	
Total	з:			5077.	.65239	445.	55530		

*** End of Report ***

Instrument 1 8/8/2018 2:54:11 PM

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Bn NH HN Bn

(+)-12