Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2014

Supporting Information

Facile Construction of Three Contiguous Stereogenic Centers *via* Dynamic Kinetic Resolution in Asymmetric Transfer Hydrogenation of Quinolines

Mu-Wang Chen, Xian-Feng Cai, Zhang-Pei Chen, Lei Shi and Yong-Gui Zhou^{a,*} State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics Chinese Academy of Sciences, Dalian 116023, China Email: ygzhou@dicp.ac.cn

Table of Contents

| 1. | General and Materials | | |
|----|-----------------------------------------------------------------------------------|--|--|
| 2. | Synthesis of 4-Substituted-1,2,3,4-tetrahydroacridines | | |
| 3. | Synthesis of Dimethyl 2,6-Dipropyl-1,4-dihydropyridine-3,5-dicarboxylate (4g) | | |
| 4. | Typical Procedure for Asymmetric Transfer Hydrogenation of 4-Substituted- 1,2,3,4 | | |
| | tetrahydroacridines | | |
| 5. | The Determination of the Absolute Configuration of 2b | | |
| 6. | Copy of NMR Data | | |
| 7. | Copy of HPLC for Racemic and Chiral Products | | |

1. General and Materials:

General: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise noted. ¹H NMR and ¹³C NMR spectra were recorded at room temperature in CDCl₃ 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.

Materials: Commercially available reagents were used throughout without further purification other than those detailed below. The solvents for asymmetric transfer hydrogenation reaction were purchased without further purification.

2. Synthesis of 4-Substituted-1,2,3,4-tetrahydroacridines:

1,2,3,4-Tetrahydroacridine and 4-substituted-1,2,3,4-tetrahydroacridine derivatives **1a**, **1i**, **1f** are known compounds and can be conveniently synthesized from the easily accessible starting materials according to the known literature procedures. ^[1]

2.1. Synthesis of 4-substituted-1,2,3,4-tetrahydroacridines (1b-1h):^[2]



General procedure for synthesis of 4-substituted-1,2,3,4-tetrahydroacridine derivatives: To a stirred solution of 1,2,3,4-tetrahydroacridine (0.412 g, 2.3mmol) in anhydrous Et_2O (20 mL) at 0 °C under nitrogen was added a solution of 2.5 M *n*-butyllithium in hexanes (1.0 mL, 2.5mmol, 1.08 equiv). The resultant yellow solution was stirred at 0 °C for 10 min and stirred at room temperature for 2 h. After cooling down below 0 °C, R-X (2.8 mmol, 1.2 equiv) was added to the solution and stirred for overnight. A solution of saturated ammonium chloride (5 mL) was added to quench the reaction. This reaction mixture was then warmed to room temperature and was extracted with Et_2O (3×10 mL). The extracts were combined, dried over Na₂SO₄, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield the products **1b-1h**.

4-Ethyl-1,2,3,4-tetrahydroacridine (**1b**): 62% yield, yellow oil, $R_f = 0.50$ (petroleum ether/EtOAc= 15:1); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.5 Hz, 1H), 7.79 (s, 1H), 7.69 (d,

J = 8.2 Hz, 1H), 7.59 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 3.06 – 2.92 (m, 3H), 2.23 – 2.17 (m, 1H), 2.10 – 2.05 (m, 1H), 1.99 – (m, 1H), 1.87 – 1.77 (m, 2H), 1.71 – 1.65 (m, 1H), 1.05 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz,

CDCl₃) δ 162.7, 146.9, 134.8, 130.9, 128.6, 128.2, 127.1, 126.8, 125.5, 43.1, 29.7, 28.1, 27.0, 20.1, 11.8; HRMS (ESI) *m*/*z* Calculated for C₁₅H₁₈N [M+H]⁺212.1439, found 212.1437.

 ⁽a) C. S. Cho, B. T. Kim, T.-J. Kim, S. C. Shim, *Chem. Commun.* 2001, 2576; (b) H. Vander Mierde, P. Van Der Voort, D. De Vos, F. Verpoort, *Eur. J. Org. Chem.* 2008, 1625; (c) R. Martĺnez, D. J. Ramón, M. Yus, *J. Org. Chem.* 2008, 73, 9778; (d) V. A. Stonik, V. I. Vysotskii, M. N. Tilichenko, *Khim. Geterotsikl. Soedin.* 1972, 8, 611.

D.-W. Wang, X.-B. Wang, D.-S. Wang, S.-M. Lu, C.-B. Yu, Y.-G. Zhou, Y.-X. Li, J. Org. Chem. 2009, 74, 2780.

4-Propyl-1,2,3,4-tetrahydroacridine (1c): 42% yield, yellow oil, $R_f = 0.48$ (petroleum ether/EtOAc= 15:1); ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 8.5 Hz, 1H), 7.79 (s, 1H), 7.69 (d,



J = 8.1 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 10.0, 4.5 Hz, 1H), 2.96 (dd, J = 10.1, 6.0 Hz, 2H), 2.16 – 2.05 (m, 2H), 2.00 – 1.94 (m, 1H), 1.88 – 1.76 (m, 2H), 1.64 – 1.44 (m, 3H), 0.98 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.8, 146.8, 134.7, 130.8, 128.6, 128.2, 127.1,

126.8, 125.5, 41.6, 37.7, 29.6, 27.6, 20.6, 20.0, 14.3; HRMS (ESI) m/z Calculated for C₁₆H₂₀N [M+H]⁺226.1596, found 226.1600.

4-Butyl-1,2,3,4-tetrahydroacridine (1d): 41% yield, pale solid, mp = 41-42 °C, $R_f = 0.60$ (petroleum ether/EtOAc = 15:1); ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.78 (s,



1H), 7.69 (d, J = 7.6 Hz, 1H), 7.59 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.46 – 7.38 (m, 1H), 3.06 (dd, J = 10.0, 4.3 Hz, 1H), 2.96 (dd, J = 10.3, 6.1 Hz, 2H), 2.20 – 2.03 (m, 2H), 2.03 – 1.91 (m, 1H), 1.89 – 1.72 (m, 2H), 1.65 (dd, J = 7.8, 2.4 Hz, 1H), 1.51 – 1.29 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz,

CDCl₃) δ 163.0, 146.9, 135.0, 131.0, 128.7, 128.4, 127.2, 126.9, 125.7, 41.9, 35.4, 29.9, 29.8, 27.6, 23.2, 20.1, 14.4; HRMS (ESI) *m/z* Calculated for C₁₇H₂₂N [M+H]⁺ 240.1752, found 240.1750.

4-Allyl-1,2,3,4-tetrahydroacridine (1e): 81% yield, yellow oil, $R_f = 0.68$ (petroleum ether/EtOAc = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.6 Hz, 1H), 7.78 (s, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.59 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 6.02 - 5.78 (m, 1H), 5.07 (ddd, J = 13.6, 10.9, 0.6 Hz, 2H), 3.21 - 3.08 (m, 1H),

4-Ethyl-7-methoxy-1,2,3,4-tetrahydroacridine (1g): 61% yield, pale solid, mp = 92-93 °C, $R_f = 0.67$ (petroleum ether/EtOAc = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 9.2 Hz, 1H), 7.68 (s, 1H), 7.27 – 7.24 (m, 1H), 6.96 (d, J = 2.8 Hz, 1H), 3.90 (s, 3H), 2.93 (t, J = 6.7 Hz, 3H), 2.20 – 2.14 (m, 1H), 2.09 – 2.03 (m, 1H), 1.97 – 1.92 (m, 1H), 1.87 – 1.73 (m, 2H), 1.69 – 1.64 (m, 1H), 1.03 (t, J = 7.4 Hz,

3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 157.1, 143.0, 133.7, 131.1, 130.0, 127.8, 120.9, 104.3, 55.4, 42.8, 29.7, 28.1, 27.1, 20.1, 11.8; HRMS (ESI) *m*/*z* Calculated for C₁₆H₂₀NO [M+H]⁺ 242.1545, found 242.1543.

4-Ethyl-7-fluoro-1,2,3,4-tetrahydroacridine (1h): 53% yield, a yellow oil, $R_f = 0.67$ (petroleum ether/EtOAc = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.08 – 7.91 (m, 1H), 7.35 (t, *J* =

8.7 Hz, 1H), 7.30 – 7.19 (m, 1H), 2.93 (s, 3H), 2.30 – 2.12 (m, 1H), 2.11 – 2.02 (m, 1H), 2.03 – 1.88 (m, 1H), 1.89 – 1.74 (m, 2H), 1.72 – 1.58 (m, 1H), 1.04 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.1, 160.1 (d, J =

244.0 Hz), 144.1, 134.2 (d, J = 5.3 Hz), 132.0, 131.2 (d, J = 9.1 Hz), 127.6 (d, J = 9.0 Hz), 118.5 (d, J = 15.0 Hz), 109.7 (d, J = 21.0 Hz), 43.2, 29.8, 28.2, 27.2, 20.2, 12.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.3; HRMS (ESI) *m*/*z* Calculated for C₁₅H₁₇NF [M+H]⁺230.1345, found 242.1340.

2.2. Synthesis of 4-phenyl-1,2,3,4-tetrahydroacridine (1i):



Typical procedure: a mixture of 2-aminobenzyl alcohol (0.616 mg, 5.0 mmol), 2-phenylcyclohexanone (1.307 mg, 7.5 mmol), $RuCl_2(PPh_3)_3$ (0.024 mg, 0.025 mmol) and KO'Bu (0.561 mg, 5.0 mmol) in 1,4-dioxane (10 ml) was placed in a dry 50 mL Schlenk tube. The system was flushed with argon and allowed to react at 80 °C for 16 h. The reaction mixture was filtered through a short silica gel column (ethyl acetate), washed with brine and dried over Na_2SO_4 . Removal of the solvent left a crude mixture, which was separated by flash chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield the product **1**i.

4-Phenyl-1,2,3,4-tetrahydroacridine (1i): Pale solid, 72% yield, mp = 133-134 °C, $R_f = 0.43$ (petroleum ether/EtOAc = 15:1); ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.83 (m, 2H), 7.70 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.3 Hz, 1H), 7.17 (dt, J = 13.2, 7.1 Hz, 3H), 6.96 (d, J = 7.1 Hz, 2H), 4.54 (d, J = 4.7 Hz, 1H), 3.16 – 2.85 (m, 2H), 2.38 – 2.07 (m, 2H), 1.98 – 1.63 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 147.1, 146.3, 135.2, 131.5, 129.1, 128.8, 128.4, 128.1, 127.4, 126.8, 125.9, 125.8, 48.3, 32.6, 29.3, 19.2; HRMS (ESI) *m/z* Calculated for C₁₉H₁₈N [M+H]⁺ 260.1439, found 260.1440.

3. Synthesis of Dimethyl 2,6-dipropyl-1,4-dihydropyridine-3,5-dicarboxylate (4g)



In a dry Schlenk tube, 7.209 g (50.0 mmol, 2.0 eq.) of methyl 3-oxohexanoate, 2.538 g (25.0 mmol, 1.0 eq.) of formaldehyde solution (37-40%) and 2.891 g (37.5 mmol, 1.5 eq.) of ammonium acetatein at 80 °C under a nitrogen atmosphere. The solution was stirred until complete consumption of methyl 3-oxohexanoate (monitored by TLC). Allowed to stand at room temperature and to facilitate crystallization of the compounds, the reaction mixture was scratched with a glass rod. Yellow crystals of dimethyl 2,6-dipropyl-1,4-dihydropyridine-3,5-dicarboxylate was formed. The product was recrystallized from ethanol. ^[3]

Dimethyl 2,6-dipropyl-1,4-dihydropyridine-3,5-dicarboxylate (4g): Yellow solid, 32% yield, mp = 107-108 °C, $R_f = 0.46$ (petroleum ether/EtOAc = 10:1); ¹H NMR (400 MHz, CDCl₃)



δ 5.31 (s, 1H), 3.69 (s, 6H), 3.27 (s, 2H), 2.61 – 2.49 (m, 4H), 1.56 (dd, J = 15.3, 7.5 Hz, 4H), 0.97 (t, J = 7.3 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 149.9, 98.8, 51.1, 34.3, 25.1, 21.8, 14.1; HRMS (ESI) m/z Calculated for C₁₅H₂₄NO₄ [M+H]⁺ 283.1778, found 283.1741.

^[3] M. Anniyappan, D. Muralidharan, P. T. Perumal, Synth. Commun. 2002, 32, 659.

4. Typical Procedure for Asymmetric Transfer Hydrogenation of 4-Substituted -1,2,3,4-tetrahydroacridines 2:



Typical procedure: In a dry Schlenk tube, 4-substituted-1,2,3,4-tetrahydroacridines 1 (0.20mmol), and phosphoric acid (R)-3f (5.8 mg, 0.01 mmol) and Hanztsch ester 4g (134.9 mg, 0.48 mmol) were dissolved in 1,4-dioxane (3 mL) at 25 °C under a nitrogen atmosphere. The solution was stirred until complete consumption of 1 (monitored by TLC). After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 30:1) to afford the desired products.

Typical procedure for preparation of racemates of 2: In a dry Schlenk tube, 4-substituted -1,2,3,4-tetrahydroacridines 1 (0.20 mmol), and 1,1'-Binaphthyl-2,2'-diylhydrogenphosphate (3.5 mg, 0.01 mmol), and Hanztsch ester 4a (134.9 mg, 0.48 mmol) were dissolved in 1,4-dioxane (3 mL) at 25 °C under a nitrogen atmosphere. The solution was stirred until complete consumption of 1 (monitored by TLC). After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 30:1) to afford the desired products.

(45,4a5,9aR)-4-Methyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2a): Pale solid, mp = 51-53 °C, 99% yield, $R_f = 0.82$ (petroleum ether/EtOAc =30:1), 82% ee, $[\alpha]_D^{21} = -45.8$ (c 0.90, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 6.96 (m, 2H), 6.56 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J*

Āе

= 7.9 Hz, 1H), 3.50 (brs, 1H), 3.03 (dd, J = 10.4, 4.5 Hz, 1H), 2.65 (dd, J = 16.0, 4.8 Hz, 1H), 2.43 (dd, J = 15.9, 11.8 Hz, 1H), 2.09 - 1.91 (m, 1H), 1.90 - 1.80 (m, 1H), 1.79 - 1.70 (m, 1H), 1.67 - 1.58 (m, 2H), 1.57 - 1.45 (m, 2H), 0.98 (d, J = 7.1 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 129.0, 126.7, 120.9, 116.4, 113.3, 58.6, 34.9, 32.6, 32.4, 31.4, 30.1, 19.9, 11.9; HPLC (OJ-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 0.8 mL/min), 30 °C, $t_1 = 11.7$ min (maj), $t_2 = 18.0$ min; HRMS (ESI) m/z Calculated for C₁₄H₂₀N [M+H]⁺ 202.1596, found 202.1591.

(4R,4aS,9aR)-4-methyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2a'): $R_f = 0.83$ (petroleum ether/EtOAc = 30:1); ¹H NMR (400 MHz, CDCl₃) δ 6.94 (dd, J = 14.8, 7.5 Hz, 2H), 6.56 (dd, J = 10.6, 4.0 Hz, 1H), 6.46 (d, J = 7.9 Hz, 1H), 3.58 (s, 1H), 3.37 (t, J = 2.6 Hz, 1H), 3.04 (dd, J = 16.2, 5.7 Hz, 1H), 2.41 (d, J = 15.3 Hz, 1H), 1.86 (s, 1H), 1.77 -1.62 (m, 2H), 1.33 (dt, J = 8.0, 6.3 Hz, 5H), 1.01 (d, J = 7.1 Hz, 3H); ¹³C NMR Ме (100 MHz, CDCl₃) δ 144.0, 129.8, 126.5, 119.7, 116.6, 113.6, 54.3, 36.0, 34.9, 34.0, 27.4, 26.0, 25.9, 18.5; HRMS (ESI) m/z Calculated for C₁₄H₂₀N [M+H]⁺ 202.1596, found 202.1599.

(45,4a5,9aR)-4-Ethyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2b): Pale solid, mp = 66-68 °C, 91% yield, $R_f = 0.83$ (petroleum ether/EtOAc = 30:1), 88% ee, $[\alpha]^{20}_{D} = -49.2$ (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.99 – 6.86 (m, 2H), 6.54 (td, J = 7.4, 0.9 Hz, 1H), 6.45 (d, J = 7.9 Hz, 1H), 3.48 (brs, 1H), 3.06 (dd, J = 10.5, 4.2 Hz, 1H), 2.62 (dd, J = 16.0, 4.8 Hz, 1H), 2.40 (dd, J = 16.0, 11.7 Hz, 1H), 1.89 - 1.80 (m, 2H), 1.75 - 1.59 (m, 3H), 1.54 - 1.38 (m, 3H), 1.36 - 1.22



(m, 1H), 1.05 – 0.95 (m, 1H), 0.92 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 129.0, 126.7, 120.8, 116.3, 113.3, 59.3, 40.6, 35.0, 32.6, 30.8, 27.2, 19.9, 17.3, 12.9; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 0.8 mL/min), 30 °C, t₁ = 9.2 min (maj), t₂ = 16.1 min; HRMS

(ESI) m/z Calculated for C₁₅H₂₂N [M+H]⁺ 216.1752, found 216.1758.

(4*S*,4*aS*,9*aR*)-4-Propyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2c): Pale solid, mp = 39-40 °C, 84% yield, $R_f = 0.80$ (petroleum ether/EtOAc = 30:1), 84% ee, $[\alpha]^{22}_{D} = -39.9$ (*c* 0.80, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.00 – 6.85 (m, 2H), 6.55 (t, J = 7.1 Hz, 1H), 6.46 (d, J = 7.9 Hz, 1H), 3.48 (brs, 1H), 3.05 (dd, J = 10.5, 4.4 Hz, 1H), 2.63 (dd, J = 16.0, 4.8 Hz, 1H), 2.41 (dd, J = 15.9, 11.7 Hz, 1H), 1.91 – 1.63 (m, 4H), 1.62 – 1.39 (m, 6H), 1.37 – 1.15 (m, 2H), 1.05 – 0.95 (m, 1H), 0.92 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 129.0, 126.7, 120.8, 116.3, 113.2, 59.2, 38.4, 35.0, 32.6, 30.8, 27.9, 27.0, 21.6, 20.0, 14.5; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 0.8 mL/min), 30 °C, t₁ = 7.2 min (maj), t₂ = 8.3 min; HRMS (ESI) *m/z* Calculated for C₁₆H₂₄N [M+H]⁺ 230.1909, found 230.1918.

(4*S*,4*aS*,9*aR*)-4-Butyl-1,2,3,4,4*a*,9,9*a*,10-octahydroacridine (2d): Pale solid, mp = 44-45 °C, 71% yield, $R_f = 0.81$ (petroleum ether/EtOAc = 30:1), 85% ee, $[\alpha]^{21}_{D} = -37.9$ (*c* 0.87, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.00 – 6.84 (m, 2H), 6.55 (td, J = 7.4, 0.9 Hz, ¹H), 6.46 (d, J = 7.9 Hz, 1H), 3.48 (brs, 1H), 3.06 (dd, J = 10.5, 4.4 Hz, 1H), ²Co3 (dd, J = 16.0, 4.8 Hz, 1H), 2.41 (dd, J = 16.0, 11.7 Hz, 1H), 1.89 – 1.77 (m, 2H), 1.76 – 1.63 (m, 2H), 1.63 – 1.46 (m, 4H), 1.45 – 1.28 (m, 4H), 1.23 – 1.12 (m, 1H), 1.06 – 0.94 (m, 1H), 0.91 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 129.0, 126.7, 120.8, 116.3, 113.2, 59.2, 38.6, 35.0, 32.6, 30.8, 30.7, 27.8, 24.3, 23.1, 20.0, 14.2; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 254 nm, flow rate: 0.7 mL/min), 30 °C, t₁ = 9.7 min (maj), t₂ = 11.1 min; HRMS (ESI) m/z Calculated for C₁₇H₂₆N [M+H]⁺ 244.2065, found 244.2068.

(4R,4aS,9aR)-4-Allyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2e): Pale oil, 82% yield, R_f = 0.65 (petroleum ether/EtOAc = 30:1), 89% ee, $[\alpha]^{22}_{D}$ = -52.6 (*c* 0.67, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.96 - 6.74 (m, 2H), 6.49 (td, *J* = 7.4, 0.9 Hz, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 5.81 - 5.61 (m, 1H), 5.06 - 4.81 (m, 2H), 3.46 (s, 1H), 3.04 (dd, *J* = 10.5, 1H), 5.81 - 5.61 (m, 1H), 5.81 - 5.61 (m, 2H), 5.81 - 5.61 (m, 2H), 5.81 - 5.81 (m, 2H), 5.81 (m, 2H), 5.81 (m, 2H), 5.81 (m, 2H), 5.81

4.4 Hz, 1H), 2.57 (dd, J = 16.0, 4.8 Hz, 1H), 2.35 (dd, J = 15.9, 11.8 Hz, 2H), 2.08 - 1.88 (m, 1H), 1.86 - 1.70 (m, 3H), 1.70 - 1.54 (m, 1H), 1.50 - 1.30 (m,

3H), 1.01 - 0.87 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 138.5, 129.0, 126.7, 120.8, 116.5, 115.5, 113.4, 58.8, 38.2, 34.9, 32.5, 30.8, 29.7, 27.5, 19.8; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 0.8 mL/min), 30 °C, t₁ = 11.2 min (maj), t₂ = 13.0 min; HRMS (ESI) *m*/*z* Calculated for C₁₆H₂₂N [M+H]⁺ 228.1752, found 228.1741.

(4R,4aS,9aR)-4-Benzyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2f): Pale solid, mp = 72-74 °C, 82% yield, $R_f = 0.82$ (petroleum ether/EtOAc = 30:1), 67% ee, $[\alpha]^{22}_D = -103.9$ (c 1.03, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 6.95 (dd, J = 15.1, 7.4 Hz, 2H), 6.59 (dd, J = 10.5, 4.1 Hz, 1H), 6.45 (d, J = 7.9 Hz,

^H \dot{B}_{n} 1H), 3.57 (s, 1H), 3.19 (dd, J = 10.5, 4.5 Hz, 1H), 3.03 (dd, J = 14.0, 3.6 Hz, 1H), 2.69 (dd, J = 16.0, 4.7 Hz, 1H), 2.51 (ddd, J = 27.6, 14.9, 11.2 Hz, 2H), 2.18 – 2.04 (m, 1H), 2.00 – 1.78 (m, 2H), 1.74 – 1.59 (m, 2H), 1.61 – 1.47 (m, 1H), 1.46 – 1.32 (m, 1H), 1.99-0.99 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 142.4, 129.1, 129.0, 128.3, 126.8, 125.7, 120.8, 116.6, 113.5, 59.0, 40.8, 34.9, 32.6, 31.7, 30.9, 27.5, 20.0; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2,

detector: 254 nm, flow rate: 0.8 mL/min), 30 °C, $t_1 = 10.1$ min (maj), $t_2 = 13.0$ min; HRMS (ESI) m/z Calculated for C₂₀H₂₄N [M+H]⁺ 278.1909, found 278.1906.

(4*S*,4*aS*,9*aR*)-4-Ethyl-7-methoxy-1,2,3,4,4a,9,9a,10-octahydroacridine (2g): Pale solid, mp = 71-72 °C, 60% yield, $R_f = 0.67$ (petroleum ether/EtOAc = 30:1), 87% ee, $[\alpha]^{29}_{D} = -45.5$ (*c* 0 N_{H} , C_{Et} ,

(4*S*,4*aS*,9*aR*)-4-Ethyl-7-fluoro-1,2,3,4,4a,9,9a,10-octahydroacridine (2h): Pale oil, 97% yield, $R_f = 0.69$ (petroleum ether/EtOAc = 30:1), 88% ee, $[\alpha]^{29}{}_D = -53.5$ (*c* 0.80, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.64 (ddd, J = 9.1, 7.5, 4.3 Hz, 2H), 6.37 (dd, J = 8.5, 4.8 Hz, 1H), 3.41 (brs, 1H), 3.02 (dd, J = 10.6, 4.2 Hz, 1H), 2.60 (dd, J = 16.3, 5.0 Hz, 1H), 2.38 (dd, J = 16.0, 11.8 Hz, 1H), 1.84 (dd, J = 12.9, 2.6 Hz, 2H), 1.71 – 1.59 (m, 3H), 1.54 – 1.38 (m, 2H), 1.37 – 1.23 (m, 2H), 1.03 – 0.87 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 155.1 (d, J = 233 Hz), 141.2, 122.0 (d, J = 6.6 Hz), 115.1 (d, J = 21 Hz), 113.79 (d, J = 7.6 Hz), 113.1 (d, J = 22 Hz), 59.3, 40.5, 35.0, 32.5, 30.6, 27.1, 19.8, 17.3, 12.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -129.2; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 0.8 mL/min), 30 °C, t₁ = 6.9 min (maj), t₂ = 7.7 min; HRMS (ESI) *m*/z Calculated for C₁₅H₂₁NF [M+H]⁺ 234.1658, found 234.1668.

 $(4R,4aR,9aR)-4-Phenyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2i): Pale oil, 40% yield, R_f = 0.60 (petroleum ether/EtOAc = 30:1), 46% ee, [a]^{29}_{D} = +32.4 (c 0.16, CHCl_3); ¹H NMR (400 MHz, CDCl_3) & 7.44 (d, J = 7.4 Hz, 2H), 7.31 - 7.23 (m, 2H), 7.20 (dt, J = 9.4, 4.3 Hz, 1H), 6.92 (dd, J = 16.9, 8.0 Hz, 2H), 6.57 (td, J = 7.4, 1.0 Hz, 1H), 6.34 (d, J = 8.0 Hz, 1H), 3.48 (brs, 1H), 3.43 - 3.15 (m, 2H), 2.75 (dd, J = 15.9, 4.6 Hz, 1H), 2.48 (dd, J = 15.9, 11.5 Hz, 1H), 2.34 - 2.20 (m, 1H), 2.08 - 1.98 (m, 2H), 1.98 - 1.85 (m, 1H), 1.63 - 1.49 (m, 3H), 1.17 - 1.04 (m, 1H); ¹³C NMR (100 MHz, CDCl_3) & 144.5, 142.3, 130.1, 129.1, 128.2, 126.7, 126.1, 121.1, 116.6, 113.9, 58.6, 43.5, 35.8, 32.8, 32.2, 31.4, 20.7;HPLC (OJ-H, elute: Hexanes/$ *i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min), 30 °C, t₁ = 9.4 min (maj), t₂ = 13.2 min; HRMS (ESI)*m*/z Calculated for C₁₉H₂₂N [M+H]⁺ 264.1752, found 264.1745.

(*4R,4aS,9aS*)-4-phenyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2i'): Pale oil, 9% yield, $R_f = 0.59$ (petroleum ether/EtOAc = 30:1); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, J = 7.3 Hz, 2H), 7.23 (d, J = 7.3 Hz, 1H), 7.16 (d, J = 7.2 Hz, 2H), 6.98 (d, J = 7.3 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.60 (t, J = 7.3 Hz, 1H), 6.25 (d, J = 7.9 Hz, 1H), 3.72 (s, 1H), 3.32 (dd, J = 10.7, 4.1 Hz, 1H), 3.09 (dd, J = 15.1, 12.1 Hz, 1H), 2.77 (dd, J = 15.3, 7.2 Hz, 1H), 2.63 – 2.46 (m, 2H), 1.90 – 1.84 (m, 2H), 1.65 (qd, J = 12.1, 6.3 Hz, 3H), 1.27 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 144.1, 143.1, 129.6, 128.7, 128.1, 126.9, 126.7, 120.4, 116.8, 114.1, 57.5, 46.6, 33.3, 31.8, 30.6, 27.7, 20.8; HRMS (ESI) *m/z* Calculated for C₁₉H₂₂N [M+H]⁺ 264.1752, found 264.1776. (4-Bromophenyl)((4S,4aS,9aR)-4-ethyl-2,3,4,4a,9,9a-hexahydroacridin-10(1H)-yl)metha none (5b) Pale solid, mp = 154-156 °C, 94% yield, $R_f = 0.21$ (petroleum ether/EtOAc = 30:1),

98% ee, $[α]^{29}_{D}$ = +355.4 (*c* 1.77, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 6.8 Hz, 1H), 6.96 (dd, *J* = 34.5, 7.3 Hz, 3H), 6.83 (d, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 4.05 (d, *J* = 11.4 Hz, 1H), 2.82 (s, 1H), 2.57 – 2.33 (m, 2H), 1.91 (s, 1H), 1.80 (d, *J* = 13.4 Hz, 1H), 1.59 (s, 2H), 1.49 – 1.33 (m, 2H), 1.17 (s, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz,

CDCl₃) δ 169.9, 139.2, 136.3, 136.2, 131.1, 130.1, 126.9, 126.3, 125.3, 123.7, 67.6, 40.1, 39.1, 35.2, 33.5, 27.2, 21.2, 18.9, 12.9; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 1.0 mL/min), 30 °C, t₁ = 12.0 min (maj), t₂ = 20.1 min; HRMS (ESI) *m/z* Calculated for C₂₂H₂₄NOBrNa [M+Na]⁺ 420.0939, found 420.0940.

5. The Determination of the Absolute Configuration of 2b



A mixture of 4-bromobenzoyl chloride (88 mg, 0.40 mmol), Et₃N (56 μ L, 0.40 mmol) and 4-Ethyl-1,2,3,4,4a,9,9a,10-octahydroacridine **2b** (82 mg, 0.38 mmol) dissolved in 5 mL CH₂Cl₂ was stirred for 2 h. After concentrating in *vacuo*, the resulting precipitate was directly purified by column chromatography on silica gel using hexane/EtOAc (30:1) to give the corresponding *N*-4-bromobenzoyl derivative **5b**. The product was recrystallized from DCM/hexane, and ee up to >98%.

CCDC 994490 contains the structure and supplementary crystallographic data for the crystal structure of (4-bromophenyl) ((4*S*,4*aS*,9*aR*)-4-ethyl-2,3,4,4a,9,9a-hexahydroacridin-10(1H)-yl) methanone **5b**. These data can be obtained free of charge via www.ccdc.com.ac.uk/data_request/cif from the Cambridge Crystallographic Data Centre.

6.1 Copy of NMR for 4-Substituted-1,2,3,4-tetrahydroacridines







9008 9165 53966 5784 4263 4072

S11



13C NMR MC-5-97B in CDCl3







1H NMR MC-5-100B in CDCI3





-41.91 -41.91 -35.37 -29.86 -29.86 -23.22 -20.12 -14.41



1H N MR MC-6-20B in CDCI3









| 9264 | 11396 002477 002477 002477 002477 00247 00252 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 00265 0000 0000 |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 10 | ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ |



1H NMR MC-7-26A1 in CDCl3

1h _ر ا ¹H NMR (400 MHz, CDCl₃)











1H NMR MC-5-11 in CDCI3









6.3 Copy of NMR for 1,2,3,4-tetrahydroquinolines

6.9643 6.9453 6.9453 6.9229 6.5769 6.5769 6.5769 6.5769 6.4726 6.4726



1H NMR MC-6-10A in CDCl3









1H NMR MC-10-15A2 in CDCI3









1H NMR MC-6-11A in CDCI3







1H NMR MC-6-12A in CDCI3







1H NMR MC-6-12B in CDCI3













1H NMR MC-6-11B in CDCI3









13C NMR MC-7-26C in CDCl3







1H NMR MC-7-29A in CDCI3





S43











1H NMR MC-11-8B CDCL3

111155 H Ē 2i'

¹H NMR (400 MHz, CDCl₃)







13C NMR MC-11-8B CDCL3







Data File C:\CHEM32\1\DATA\ZHOU-13\YZN003361.D Sample Name: MC-5-27+-

| Acq. Operator | : YZ | | |
|-----------------|----------------------------------|-------------|----------|
| Acq. Instrument | : Instrument 1 | Location | : Vial l |
| Injection Date | : 8/21/2013 2:14:53 PM | | |
| Acq. Method | : C:\CHEM32\1\METHODS\DEF LC.M | | |
| Last changed | : 8/21/2013 1:53:40 PM by YZ | | |
| | (modified after loading) | | |
| Analysis Method | : C:\CHEM32\1\METHODS\DEF LC.M | | |
| Last changed | : 11/13/2013 4:45:07 PM by B | | |
| | (modified after loading) | | |
| Sample Info | : 0J-H, H/i-PrOH = 95/5, 0.8 mL/ | 'min, 30oC, | 254nm |



Area Percent Report Sorted By Signal : : 1.0000 : 1.0000 Multiplier: Dilution: Use Multiplier & Dilution Factor with ISTDs Signal 1: WWD1 A, Wavelength=254 nm н Me Peak RetTime Type Width Area Height Area # [min] [min] mAU *s [mAU] ÷ (+/-)-2a # |####; |####; ###0 0 ,###0 , . . 1 11.658 BB 0.2168 713.17542 50.61831 50.1338 2 17.986 BB 0.3918 709.36865 27.85067 49.8662 Totals : 1422.54407 78.46898

*** End of Report ***

Data File C:\CHEM32\1\DATA\ZH0U-13\YZN003365.D Sample Name: MC-6-10A Acq. Operator : YZ Acq. Instrument : Instrument 1 Location : Vial 1 Injection Date : 8/21/2013 4:10:53 PM Acq. Method : C:\CHEM32\1\METHOBXDEF LC.M Last changed : 8/21/2013 4:07:54 PM by YZ (modified after 1 oading) Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M Last changed : 11/13/2013 4:45:07 PM by B (modified after 1 oading)

Sample Info : 0J-H, H/i-PrOH = 95/5, 0.8 mL/min, 30oC, 254nm







Instrument 1 11/13/2013 4:45:11 PM B

Page 1 of 1

Instrument 1 11/13/2013 4:46:30 PM B

Data File G:\YZ004873.D Sample Name: MC-6-10C+-

| Acq. Operator : | ZHOU | | | |
|-------------------|----------------------------------|------------|----------|--|
| Acq. Instrument : | Instrument 1 | Location | : Vial 1 | |
| Injection Date : | 8/27/2013 10:41:52 AM | | | |
| Acq. Method : | C:\HPCHEM\1\METHODS\DEF LC.M | | | |
| Last changed : | 8/27/2013 9:51:22 AM by ZHOU | | | |
| | (modified after loading) | | | |
| Analysis Method : | C:\CHEM32\1\METHODS\DEF LC.M | | | |
| Last changed : | 11/19/2013 2:42:02 PM by B | | | |
| | (modified after loading) | | | |
| Sample Info : | OJ-H, H/i-PrOH = 95/5, 0.8 mL/m: | in, 30 oC, | 254 nm | |
| | | | | |





Data File G:\Y2004874.D
Sample Name: MC-5-11A

Acg. Operator : 2HOU
Acg. Instrument : Instrument 1 Location : Vial 1
Injection Date : 8/27/2013 11:02:30 AM
Acg. Method : C:\HPCHEW\LMETHODS\DFF LC.M
Last changed : 8/27/2013 9:51:22 AM by ZHOU
(modified after loading)
Analysis Method : C:\CHEM32\LMETHODS\DFF LC.M
Last changed : 11/19/2013 2:42:02 PM by B
(modified after loading)
Sample Info : 0-7H, H/-PrCH = 95/5, 0.8 mL/min, 30 oC, 254 mm







Area Percent Report

Instrument 1 11/19/2013 2:43:08 PM B

Page 1 of 1

Instrument 1 11/19/2013 2:42:08 PM B



Page 1 of 1

Instrument 1 9/20/2012 4:59:41 PM ZC

Data File C:\CHEM32\1\DATA\ZHOU-11\YZN001324.D Sample Name: MC-6-12D+-

| Acq. Operator | : | | |
|-----------------|---|--------------------------------------------------|--|
| Acq. Instrument | : | Instrument 1 Location : Vial 1 | |
| Injection Date | : | 12/27/2011 10:55:34 AM | |
| Acq. Method | : | C:\CHEM32\1\METHODS\SW.M | |
| Last changed | : | 12/27/2011 10:49:42 AM | |
| | | (modified after loading) | |
| Analysis Method | : | C:\CHEM32\1\METHODS\SW.M | |
| Last changed | : | 12/1/2011 7:50:33 PM | |
| Sample Info | : | OJ-H, H/i-PrOH = 98/2, 0.7 mL/min, 30 oC, 254 nm | |





*** End of Report ***

| Data File C:\CHEN32\1\DATA\ZHOU-11\YZN001331.D Sample Name: NC-6-12B | | | | | |
|-------------------------------------------------------------------------------|---|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|--|
| | | | | | |
| Acq. Operator | : | | | | |
| Acq. Instrument | : | Instrument 1 Location : Vial 1 | | | |
| Injection Date | : | 12/27/2011 4:35:50 PM | | | |
| Acq. Method | : | C:\CHEN32\1\METHODS\SW.N | | | |
| Last changed | : | 12/27/2011 4:32:33 PM | | | |
| | | (modified after loading) | | | |
| Analysis Method | : | C:\CHEM32\1\METHODS\ABC LC.M | | | |
| Last changed | : | 9/20/2012 5:00:51 PM by ZC | | | |
| - | | (modified after loading) | | | |
| Sample Info | : | 0J-H, H/i-PrOH = 98/2, 0.7 mL/min, 30 oC, 254 nm | | | |
| Acq. Method Last changed Analysis Method Last changed Sample Info | | C:\CHEM32.1\METHOD\$\SWLM 12/27/2014 4:32:33 PM (modified after loading) C:\CHEM32.1\METHOD\$XABC LC.M 9/20/2012 5:00:51 PM by ZC (modified after loading) 0J-H, H/1-PrOH = 96/2, 0.7 mL/min, 30 oC, 254 nm | | | |







Instrument 1 12/27/2011 11:08:49 AM

Page 1 of 1

Instrument 1 9/20/2012 5:00:54 PM ZC



Instrument 1 9/20/2012 3:58:15 PM ZX

Page 1 of 1

Instrument 1 9/20/2012 3:59:15 PM ZX

Data File C:\CHEM32\1\DATA\ZHOU-11\YZN001309.D Sample Name: MC-6-10D(+-)

| Acq. Operator | : | |
|-----------------|---|--------------------------------------------------|
| Acq. Instrument | : | Instrument 1 Location : Vial 1 |
| Injection Date | : | 12/23/2011 4:09:43 PM |
| Acq. Method | : | C:\CHEM32\1\METHODS\SW.M |
| Last changed | : | 12/23/2011 4:06:48 PM |
| | | (modified after loading) |
| Analysis Method | : | C:\CHEN32\1\METHODS\SW.M |
| Last changed | : | 12/1/2011 7:50:33 PM |
| Sample Info | : | AD-H, H/i-PrOH = 98/2, 0.8 mL/min, 30 oC, 254 nm |





| Noroca pr | | to an other other | | | |
|-------------------|-------------|-------------------|----------------|------------|-------------|
| Multiplier: | | : | 1.0000 | | |
| Dilution: | | : | 1.0000 | | |
| Use Multiplier | & Dilution | Factor with | h ISTDs | | |
| - | | | | \sim | $\sim \sim$ |
| | | | | ſ ` | ΥΎ |
| Signal L. VID L | Norrelens | th-254 pm | | | |
| Signai I. VWDI | A, waverenç | 1011-234 1111 | | <u>ر</u> ب | イト |
| Deals Deamine The | | A | TT - d - de te | , V | ´`N´ 🗸 |
| Peak Retlime Iv | pe width | Area | neight | Area | 11 1 |
| # [min] | [min] | mau *s | [mAU] | * | н . |
| | | | | | Bn |
| 1 10.194 VB | 0.1833 | 1199.73535 | 100.25727 | 49.9954 | 1.1.) 26 |
| 2 13.139 VB | 0.2339 | 1199.95398 | 79.03433 | 50.0046 | (+/-)-21 |
| | | | | | |
| Totals : | | 2399 68933 | 179 29160 | | |
| loodib . | | 2000.000000 | 110110100 | | |
| | | | | | |

*** End of Report ***



*** End of Report ***

Page 1 of 1

Instrument 1 12/24/2011 11:09:28 AM



Instrument 1 9/20/2012 4:02:40 PM ZX



Instrument 1 9/20/2012 4:05:53 PM ZX



| Acq. Operator | : | ZX | | |
|-----------------|---|---------------------------------------------------|--|--|
| Acq. Instrument | : | Instrument 1 Location : Vial 1 | | |
| Injection Date | : | 12/18/2012 6:33:10 AM | | |
| Acq. Method | : | C:\HPCHEM\1\METHODS\SW.M | | |
| Last changed | : | 12/18/2012 6:30:42 AM by ZX | | |
| | | (modified after loading) | | |
| Analysis Method | : | C:\CHEM32\1\METHODS\DEF LC.M | | |
| Last changed | : | 4/17/2014 2:51:12 PM by Z | | |
| | | (modified after loading) | | |
| Sample Info | : | OJ-H, H/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm | | |





*** End of Report ***

Data File D:\l\Y2003633.D Sample Name: MC-7-99 Acc. Operator : ZX Acq. Instrument : Instrument 1 Location : Vial 1 Injection Date : 12/25/2012 1:01:48 AM Acq. Method : C:\HFCHEMI\METHODS\SU.M Last changed : 12/25/2012 12:51:22 AM by ZX (modified after loading) Analysis Method : C:\CTEMS2.l\METHODS\DFF LC.M Last changed : 4/17/2014 2:51:12 FM by Z (modified after loading) Sample Info : 0J-H, H/1-FCH = 90/10, 1.0 mL/min, 30 oC, 254 nm





*** End of Report ***

Instrument 1 4/17/2014 2:52:11 PM Z

Page 1 of 1

Instrument 1 4/17/2014 2:52:42 PM Z



| Acq. Operator : | ZHOU | | | |
|-------------------|-------------------------------|---------------------|--|--|
| Acq. Instrument : | Instrument 1 | Location : Vial 1 | | |
| Injection Date : | 11/23/2013 7:01:17 AM | | | |
| Acq. Method : | C:\HPCHEM\1\METHODS\DEMOCAL2. | M | | |
| Last changed : | 11/23/2013 6:55:42 AM by ZHOU | | | |
| | (modified after loading) | | | |
| Analysis Method : | C:\CHEM32\1\METHODS\DEF LC.M | | | |
| Last changed : | 4/17/2014 2:53:03 PM by Z | | | |
| | (modified after loading) | | | |
| Sample Info | AD-H, H/i-PrOH = 95/5, 1.0 mL | /min, 30 oC, 254 nm | | |





*** End of Report ***

Data File D:\1\Y2005319.D Sample Name: NC-6-20A Acg. Operator : 2HOU Acg. Instrument : Instrument 1 Location : Vial 1 Injection Date : 11/23/2013 7:29:52 AM Acg. Method : C:\1HP/EHWI.\NWETHODSNDEMOCAL2.M Last changed : 11/23/2013 6:55:42 AM by ZHOU (modified after loading) Analysis Hethod : C:\CHEMBALJ.\NETHODSNDEF C.M Last changed : 4/17/2014 2:54:34 PM by Z (modified after loading) Sample Info : AD-H, H/1-PrOH = 95/5, 1.0 mL/min, 30 oC, 254 nm







Instrument 1 4/17/2014 2:53:11 PM Z

Page 1 of 1

Instrument 1 4/17/2014 2:56:00 PM Z