Symmetry in Cascade Chirality-Transfer Processes: A Catalytic Atroposelective Direct Arylation Approach to BINOL

Derivatives

Jin-Zheng Wang[†], Jin Zhou[†], Chang Xu[†], Hongbin Sun[†]*, László Kürti[‡]* and Qing-Long Xu[†]*

[†]Jiangsu Key Laboratory of Drug Discovery for Metabolic Disease and State Key Laboratory of Natural Medicines, China Pharmaceutical University 24 Tongjia Xiang, Nanjing 210009 (P.R. China)

[‡]Department of Chemistry, Rice University, BioScience Research Collaborative, 6500 Main Street, Rm 380, Houston, TX 77030 (USA)

Table of contents

General Methods	S2
Figure 1 and Figure 4	S3
Optimization of the reaction conditions	S4
Explanation of substrate stereocontrol	S5
General procedure for synthesis of substrate 6	S6
General procedure for the enantioselective synthesis of biaryls	S9
General procedure for synthesis of chiral CPA 7i and used as a catalyst	S23
General procedure for synthesis of compound 9ea *	S24
References	S24
Copies of NMR and HPLC spectra	S25

General Methods.

All reactions were carried out in oven-dried glassware under air with magnetic stirring. All Naphthol compounds were purchased from Sigma-Aldrich Co. and used without further purification. Reactions were monitored by TLC on silica gel 60 F254 plates Column chromatography was carried out on silica gel (200-300 mesh). Proton (¹H) and carbon (¹³C) NMR spectra were recorded on an ACF* 3000 Bruker spectrometer operating at 300 MHz (or 500 MHz) for proton and 75 MHz (or 151 MHz) for carbon nuclei using $CDCl_3$ [or $(CD_3)_2SO$] as solvent, respectively. Chemical shifts are expressed as parts per million (δ , ppm) and are referenced to 7.26 (CDCl₃) or 2.50 (CD₃)₂SO for ¹H NMR and 77.23 (CDCl₃) or 39.51 (CD₃)₂SO for ¹³C NMR. Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br s = broad singlet, coupling constant (s) in Hz, integration). Data for ¹³C NMR are reported in terms of chemical shift (δ , ppm). High Resolution Mass Spectrometry was performed on a Agilent Technologies 6230 TOF LC/MS under the conditions of electrospray ionization (ESI) in both positive and negative mode. Optical rotations were measured using a 2-mL cell with a 10-cm path length on Rudolph Autopol[®] IV automatic polarimeter, and concentrations (c) were reported in $g \times (100 \text{ mL})^{-1}$. Analytical HPLC was recorded on a HPLC machine equipped with SHIMADZU LC-20AT HPLC Pump and SHIMADZU SPD-20A Photodiode Array Detector (SHIMADZU HPLC machine). The chiral stationary phase was Daicel Chiralpak AD-H or IA, IA-3 column $(\emptyset = 0.46 \text{ cm}, \text{ length} = 25.0 \text{ cm})$. Melting points were recorded on Tianjin Analysis Instrument Factory RY-1.



enriched axially and iminoquinones chiral BINOL aminal intermediate Figure 1. Organocatalytic atroposelective direct arylation of hydroxyarenes to afford

Centrally chiral

Phenols or naphthols

non-C2-symmetrical BINOLs.

Enantiomerically



Figure 4. The case is made for the aminal-formation/[3,3]-rearrangement sequence as opposed to a 1,4-direct addition.

→ 9aa.



entry	cat.	solvent	time (h)	ee (%) ^b
1	7a	CH_2Cl_2	48	25
2	7b	CH_2Cl_2	48	49
3	7c	CH_2Cl_2	48	77
4	7d	CH_2Cl_2	48	44
5	7e	CH_2Cl_2	8	25
6	7f	CH_2Cl_2	8	30
7	7g	CH_2Cl_2	8	46
8	7h	CH_2Cl_2	8	41
9	7c	CH ₃ CN	48	53
10	7c	toluene	48	72
11	7c	DCE	48	88
12	7c	THF	48	5
13	7c	CHCl ₃	48	81
14	7c	chlorobenzene	84	94
15	7c	1,3-di-CF ₃ -benzene	60	86
16 ^c	7c	DCE	24	88
17 ^c	7c	chlorobenzene	48	92
18^{d}	7c	DCE	8	82
19 ^{c,e}	7c	DCE	100	77

^{*a*} Reaction conditions: **2a** (0.075 mmol), **6a** (0.05 mmol), cat. (10 mol%), solvent (1 mL). ^{*b*} Determined by HPLC analysis. ^{*c*} Reacted at 50 °C. ^{*d*} Reacted at 80 °C. ^{*e*} Using 5 mol% **7c**.

Explanation of substrate stereocontrol.

The description about **9ea'** refers to the possibility that once the first axis of chirality was established in position #1 of the 2,3-dihydroxynaphthalene nucleus, the now existing axially chiral stereocenter would exert significant influence over the stereroselectivity of the second aryl-aryl bond-forming step in position #4. To demonstrate that this substrate control is truly operational and completely independent of the chirality of the acid catalyst, we conducted a control experiment (see scheme at



left) in which enantiomerically pure biaryl **9ea** was reacted with slight excess of iminoquinone **6a** (1.5

equivalents) at 50 °C in DCE using 10 mol% of the achiral diphenylphosphoric acid as catalyst. Indeed the product **9ea'** was obtained in excellent isolated yield and also as a single enantiomer (99% *ee*; the stereochemistry at the two chiral axes were determined to be R,R using X-ray crystallography). Not even traces of the *meso* diastereomer (R,S) were observed using LC/MS analysis.

Moreover, the coupling reaction between symmetrical quinone monoacetal **1a** and enantiomerically pure biaryl **9ea** was also successful (see scheme below) and gave rise to enantiomerically enriched terphenyl **9ea*** in 83% *ee*. Clearly substrate stereocontrol was operational in this case but to a lesser extent than during the formation of terphenyl **9ea**'. Since only a <u>symmetrical acetal intermediate</u> could be formed the system "*missed an opportunity*" to transfer chirality in the first step and the stereoselectivity of the second ary-aryl bond-forming step (i.e., via the [3,3]-sigmatropic rearrangement) could not be perfectly controlled by the substrate.



General procedure for synthesis of the substrates 6. ^[1]



The phenol (50.0 mmol) was dissolved in HCl (33 mL, 12 mol/L) and 95% ethanol (30 mL). NaNO₂ (5.0 g) was slowly added at 0 °C (5 min) maintaining the stirring for 1 h at 0 °C. Ethanol (10 mL) was then added and the stirring was matintained for a further hour at room temperature. The reaction mixture was diluted with water (300 mL) and extracted with ethyl ether. The organic phase was extracted with 10% aqueous Na₂CO₃ solution. The carbonate solution on acidification with HCl (3 mol/L) yielded a precipitate, wash the precipitate with hexane to eliminate soluble impurities. To an eggplant shaped bottle para-benzoquinone mono-oxime (10.0 mmol) was dissolved in CH₂Cl₂ (100 mL), then concentrated HCl (2 mL) was added. The solution was heated to reflux, then SnCl₂ (5.7 g, 30.0 mmol) was added. The mixture was heated to reflux for 24 h. Then remove the CH₂Cl₂ under reduced pressure, and the residue was dissolved in ethyl acetate and washed with concentrated aqueous Na₂SO₄ and the filtrate was concentrated under reduced pressure to afford the solid amino phenols.

Then the para-amino-phenol (5.0 mmol) was dissolved in dry pyridine (6 mL) and

cooled to 0 °C. Para-toluenesulfonyl chloride (1.14 g, 6.0 mmol) was added in small portions. The mixture was warmed to room temperature and stirred under nitrogen for 24 h. The reaction mixture was diluted with EtOAc and washed with HCl (10 mol/L), the organic layer was dried over anhydrous MgSO₄, filtered, and concentrated to yield the crude sulfonamide.

The N-tosyl-para-aminophenol (4.0 mmol) was dissolved in dry CH_2Cl_2 (15 mL) and Ag_2O (8.0 mmol) was added, and stirred. The reaction was monitored by TLC. When the reaction was completed, the solution was filtered through celatom. The organic layer was concentrated to yield the crude product. The product **6** was purified by silica gel column using petroleum ether/ acetone (20:1) as eluent. 35-45% yields (4 steps).



6a, yellow solid (920 mg, 45% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.83 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 2.46 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H).



6b, brown solid (620 mg, 40% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.64 (s, 1H), 6.75 (s, 1H), 3.40 (s, 3H), 2.10 (s, 3H), 2.03 (s, 3H).



6c, yellow solid (420 mg, 35% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 6.74 (s, 1H), 3.02-2.97 (m, 1H), 2.45 (s, 3H), 2.01 (s, 3H), 1.11 (d, *J* = 6.8 Hz, 6H).



6d, yellow solid (470 mg, 38% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.92-7.85 (m, 3H), 7.51 (d, *J* = 7.2 Hz, 2H), 6.60 (s, 1H), 3.00-2.92 (m, 1H), 2.45 (s, 3H), 2.07 (s, 3H), 1.05 (d, *J* = 7.2 Hz, 6H).



6e, brown solid (350 mg, 36% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.92-7.89 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.60-6.57 (m, 1H), 2.48 (s, 3H), 2.11 (s, 3H).



6f, orange solid (210 mg, 18% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.80 (s, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.42 (s, 2H), 2.39 (s, 3H), 2.25 (s, 6H).



6g, orange solid (235 mg, 22% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 2.47 (s, 3H), 2.37 (s, 3H), 2.23 (s, 3H), 2.05 (s, 3H).



6h, yellow solid (450 mg, 40% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 6.88 (s, 1H), 6.62 (s, 1H), 2.30 (s, 3H), 2.09 (s, 3H), 1.95 (s, 3H).



6i, yellow solid (380 mg, 38% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.38 (d , *J* = 8.4 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 1H), 6.75 (s, 1H), 2.25 (s, 3H), 1.91 (s, 3H).



6j, brown solid (280 mg, 34% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.19-8.15 (m, 1H), 7.89 (d, *J* = 7.9 Hz 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.63-6.55 (m, 2H), 2.48 (s, 3H), 2.06 (s, 3H).

General procedure for the enantioselective synthesis of biaryls.

To a stirred solution of **2a** (32.5 mg, 0.225 mmol) and **6a** (43.5 mg, 0.15 mmol) in DCE or chlorobenzene (3 mL), cat. CPA **7c** (11.2 mg, 10 mol%) was added in one portion at room temperature, and it was stirred at rt or 50 °C until the reaction was completed. Solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica-gel (petroleum ether/acetone = 8:1 to 1:1) to give pure product **9aa** (63.0 mg, 97% yield).



9aa, white solid, 97% yield (63.0 mg), 88% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 15.32$ (minor), 50.88 (major) min]. $[\alpha]_D^{20} = -82.7$ (c = 0.3, CH₃OH). ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.22 (br s, 1H), 9.14 (br s, 1H), 7.77 (d, *J*

= 7.9 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 6.4 Hz, 2H), 7.49 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.29-7.19 (m, 3H), 6.88 (s, 1H), 6.83 (d, J = 8.2 Hz, 1H), 2.31 (s, 3H), 2.12 (s, 3H), 1.21 (s, 3H). ¹³C NMR (75 MHz, DMSO- d_6) δ 152.45, 151.96, 142.45, 137.76, 133.50, 133.32, 131.54, 129.56, 129.41, 128.67, 128.08, 127.84, 126.67, 125.94, 125.86, 123.77, 122.26, 121.52, 118.51, 116.09, 21.00, 16.55, 14.36. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₃NO₄S [M+Na]⁺ 456.1240, Found: 456.1240. MP 139-141 °C.



9ba, brown solid, 87% yield (66.9 mg), 92% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 11.38$ (major), 16.62 (minor) min]. $[\alpha]_D^{20} = -56.0$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.19 (br s, 1H), 8.39 (br s, 1H), 8.17 (s, 1H), 7.78 (dd, *J* = 3.5, 6.2 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.38-7.25 (m, 4H), 6.95 (s, 1H), 6.80-6.73 (m, 1H), 2.30 (s, 3H), 2.14 (s, 3H), 1.18 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 152.66, 148.98, 142.85, 138.05, 133.68, 132.86, 131.56, 130.70, 129.80, 129.35, 127.42, 127.09, 126.80, 126.50, 124.39, 123.94, 122.83, 122.39, 119.60, 114.23, 21.39, 16.99, 14.74. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₂BrNO₄S [M+Na]⁺ 534.0345, Found: 534.0360. MP 113-115 °C.



9ca, Brown solid, 88% yield (67.6 mg), 78% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 11.53$ (major), 14.36 (minor) min]. $[\alpha]_D^{20} = -71.0$ (c = 0.3,

CH₃OH). ¹H NMR (300 MHz, DMSO- d_6) δ 9.41 (br s, 1H), 9.16 (br s, 1H), 8.03 (s, 1H), 7.74 (d, J = 8.9 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.41 (dd, J = 1.6, 8.8 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.9 Hz, 1H), 6.91 (s, 1H), 6.74 (d, J = 8.9 Hz, 1H), 2.32 (s, 3H), 2.12 (s, 3H), 1.16 (s, 3H). ¹³C NMR (75 MHz, DMSO- d_6) δ 153.39, 152.33, 142.82, 138.09, 133.62, 132.57, 130.18, 129.89, 129.83, 129.69, 129.20, 128.34, 127.08, 126.51, 126.29, 123.58, 122.09, 120.11, 116.91, 115.49, 21.37, 16.93, 14.67. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₂BrNO₄S [M+Na]⁺ 534.0345, Found: 534.0351. MP 113-115 °C.



9da, brown solid, 84% yield (64.6 mg), 81% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 11.60 (minor), 21.28 (major) min]. [α]_D²⁰ = -52.0 (c = 0.3, CH₃OH). ¹H NMR (300 MHz, CDCl₃) δ 7.83 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.44 (dd, *J* = 1.9, 11.2 Hz, 1H), 7.36 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.25 (s, 1H), 7.16 (d, *J* = 1.7 Hz, 1H), 6.14 (br s, 1H), 4.99 (br s, 1H), 4.60 (br s, 1H), 2.39 (s, 3H), 2.29 (s, 3H), 1.37 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 153.49, 151.86, 142.45, 137.84, 134.93, 133.23, 130.25, 129.86, 129.28, 128.79, 126.49, 126.00, 125.17, 125.08, 123.06, 121.74, 119.69, 119.09, 115.68, 20.92, 16.47, 14.27. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₂BrNO₄S [M+Na]⁺ 534.0345, Found: 534.0340. MP 129-131 °C.



9ea, white solid, 80% yield (54.0 mg), 96% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 25.50 (minor), 43.86 (major) min]. [α]_D²⁰ = -86.3 (c = 0.3 CH₃OH). ¹H NMR (300 MHz, CD₃OD) δ 7.60-7.55 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.23-7.18 (m, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.00 (s, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 2.35 (s, 3H), 2.18 (s, 3H), 1.33 (s, 3H). ¹³C NMR (75 MHz, CD₃OD) δ 153.47, 147.47, 145.79, 144.75, 138.97, 135.39, 131.59, 131.19, 130.66, 129.70, 128.45, 127.80, 127.37, 125.00, 124.65, 124.58, 124.02, 123.79, 117.09, 110.65, 21.63, 16.55, 15.00. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₃NO₅S [M+Na]⁺ 472.1189, Found: 472.1197. MP 138-140 °C.



9fa, white solid, 89% yield (61.9 mg), 85% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 31.69$ (major), 35.00 (minor) min]. $[\alpha]_D^{20} = -58.3$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.15 (br s, 1H), 8.58 (br s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.50 (br s, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.34 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.1 Hz, 1H), 6.88 (s, 1H), 6.75(d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 2.31 (s, 3H), 2.11 (s, 3H), 1.20 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 151.79, 148.41, 144.17, 142.35, 137.71, 133.14, 129.51, 129.32, 128.47, 128.37, 126.57, 126.51, 125.75, 123.49, 123.42, 122.83, 121.44, 116.79, 105.68, 55.51, 20.95, 16.46, 14.29. HRMS (ESI-TOF): Exact mass calcd. for C₂₆H₂₅NO₅S [M+Na]⁺ 486.1347. Found: 486.1352. MP 129-131 °C.



9ga, brown solid, 78% yield (52.6 mg), 85% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 16.30$ (minor), 25.72 (major) min]. $[\alpha]_D^{20} = +105.3$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.40 (s, 1H), 9.12 (s, 1H), 9.05 (s, 1H), 7.59 (t, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.41 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 8.86 (s, 1H), 6.80 (dd, *J* = 1.8, 8.8 Hz, 1H), 6.23 (d, *J* = 1.7 Hz, 1H), 2.27 (s, 3H), 2.12 (s, 3H), 1.15 (s, 3H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 155.52, 152.72, 151.83, 142.29, 137.94, 135.28, 133.39, 129.61, 129.32, 128.44, 126.58, 125.92, 124.12, 122.84, 121.32, 115.04, 114.74, 114.34, 105.49, 20.91, 16.47, 14.07. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₃NO₅S [M+Na]⁺ 472.1189, Found: 472.1186. MP 128-130 °C.



9ha, brown solid, 87% yield (60.5 mg), 89% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 11.92$ (minor), 22.11 (major) min]. $[\alpha]_D^{20} = -25.0$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.21 (br s, 1H), 9.16 (br s, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.52 (br s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.94 (dd, *J* = 2.1, 8.8 Hz, 1H), 6.70 (s, 1H), 6.28 (s, 1H), 3.64 (s, 3H), 2.32 (s, 3H), 2.07 (s, 3H), 1.39 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 159.34, 152.73, 151.90, 144.14, 136.91, 134.36, 133.15, 131.19, 130.97, 130.25, 129.75, 127.43, 127.33, 124.84, 123.75, 118.80, 115.66, 115.23,

111.33, 103.45, 55.46, 21.75, 16.16, 14.60. HRMS (ESI-TOF): Exact mass calcd. for C₂₆H₂₅NO₅S [M+Na]⁺ 486.1346, Found: 486.1339. MP 124-126 °C.



9ia, white solid, 90% yield (69.0 mg), 87% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 14.11$ (minor), 33.44 (major) min]. $[\alpha]_D^{20} = -110.33$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.40 (br s, 1H), 9.24 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.67 (br s, 1H), 7.60-7.45 (m, 5H), 7.43-7.35 (m, 3H). 7.23 (d, J = 8.9 Hz, 1H), 7.13 (s, 1H), 6.93 (d, J = 8.1 Hz, 2H), 6.78 (s, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 1.30 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 152.86, 152.02, 142.28, 140.93, 137.88, 137.64, 133.79, 133.58, 129.74, 129.02, 128.98, 128.66, 128.38, 127.40, 127.34, 126.77, 126.44, 125.89, 123.71, 121.57, 121.53, 121.35, 118.70, 116.54, 20.82, 16.49, 14.62. HRMS (ESI-TOF): Exact mass calcd. for C₃₁H₂₇NO₄S [M+Na]⁺ 532.1553, Found: 532.1543. MP 86-88 °C.



9ja, white solid, 62% yield (45.7 mg), 85% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 11.44$ (major), 16.66 (minor) min]. $[\alpha]_D^{20} = -92.3$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.79 (br s, 1H), 9.17 (s, 1H), 8.50 (s, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.77 (dd, *J* = 1.4, 8.9 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 1H), 6.92 (s, 1H), 6.86 (d, *J* = 8.9 Hz, 1H),

3.89 (s, 3H), 2.31 (s, 3H), 2.13 (s, 3H), 1.16 (s, 3H). ¹³C NMR (75 MHz, DMSO- d_6) δ 166.98, 155.41, 152.35, 142.85, 138.06, 136.44, 133.56, 131.19, 130.87, 130.18, 129.81, 127.37, 127.10, 126.29, 125.36, 124.55, 123.65, 123.56, 122.13, 119.89, 116.94, 52.36, 21.35, 16.94, 14.71. HRMS (ESI-TOF): Exact mass calcd. for C₂₇H₂₅NO₆S [M+Na]⁺ 514.1295, Found: 514.1291. MP 119-121 °C.



9ka, white solid, 99% yield (69.2 mg), 83% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 14.64$ (major), 17.57 (minor) min]. $[\alpha]_D^{20} = -63.7$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.21 (s, 1H), 9.06 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.56 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.21-7.16 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.73 (d, *J* = 9.1 Hz, 1H), 3.82 (s, 3H), 2.31 (s, 3H), 2.13 (s, 3H), 1.18 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 154.86, 151.85, 150.67, 142.38, 137.67, 133.19, 129.46, 129.37, 128.82, 128.65, 127.37, 126.62, 125.76, 125.29, 123.86, 121.45, 118.83, 118.18, 116.30, 106.47, 55.08, 21.00, 16.54, 14.31. HRMS (ESI-TOF): Exact mass calcd. for C₂₆H₂₅NO₅S [M+Na]⁺ 486.1346, Found: 486.1340. MP 200-202 °C.



91a, brown solid, 64% yield (42.6 mg), 76% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 50.36$ (minor), 55.42 (major) min]. $[\alpha]_D^{20} = -7.7$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.07 (s, 1H), 9.04 (s, 1H), 7.48 (d, *J* = 8.3)

Hz, 2H), 7.32-7.28 (m, 3H), 6.58 (s, 1H), 6.06 (dd, J = 2.2, 8.3 Hz, 2H), 3.69 (s, 3H), 3.52 (s, 3H), 2.34 (s, 3H), 1.99 (s, 3H), 1.37 (s, 3H). ¹³C NMR (75 MHz, DMSO- d_6) δ 160.10, 158.67, 156.25, 151.81, 142.27, 138.30, 133.84, 129.24, 128.67, 126.59, 125.40, 122.46, 120.63, 104.68, 93.72, 89.86, 55.20, 54.80, 20.94, 16.40, 14.59. HRMS (ESI-TOF): Exact mass calcd. for C₂₃H₂₅NO₆S [M+Na]⁺ 466.1295, Found: 466.129. MP 97-98 °C.



9ma, brown solid, 49% yield (30.0 mg), 75% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); n-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 9.42 (minor), 77.47 (major) min]. [α]_D²⁰ = +12.67 (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.09 (s, 1H), 9.72 (s, 1H), 7.45-7.41 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.71 (s, 1H), 6.49 (s, 2H), 2.35 (s, 3H), 2.18 (s, 3H), 2.06 (s, 3H), 1.66 (s, 3H), 1.30 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 154.63, 151.18, 142.51, 136.81, 129.39, 128.98, 125.80, 121.34, 120.75, 113.46, 21.00, 20.93, 19.27, 16.50, 14.34. HRMS (ESI-TOF): Exact mass calcd. for C₂₃H₂₅NO₄S [M+Na]⁺ 434.1367, Found: 434.1395. MP 119-121 °C.



9na, brown solid, 97% yield (69.4 mg), 21% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 10.10 (minor), 54.73 (major), min]. [α]_D²⁰ = +5.7 (c = 0.3,

CH₃OH). ¹H NMR (300 MHz, DMSO- d_6) δ 9.07 (s, 1H), 8.86 (br s, 1H), 7.49 (br s, 1H), 7.49 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.64 (s, 1H), 6.31 (s, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 3.35 (s, 3H), 2.34 (s, 3H), 2.04 (s, 3H), 1.48 (s, 3H). ¹³C NMR (75 MHz, DMSO- d_6) δ 152.59, 151.90, 151.83, 151.09, 142.41, 138.09, 134.53, 133.57, 129.31, 128.99, 126.66, 125.45, 122.51, 120.85, 109.82, 95.76, 60.43, 59.82, 55.39, 20.96, 16.50, 14.92. HRMS (ESI-TOF): Exact mass calcd. for C₂₄H₂₇NO₇S [M+Na]⁺ 496.1400, Found: 496.1403. MP 58-60 °C.



9ea', white solid, 90% yield (100.0 mg), 99% ee. [Daicel CHIRALPAK IC (0.46 cm x 25 cm); *n*-hexane/2-propanol = 60/40; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 29.12$ (major), 55.25 (minor) min]. $[\alpha]_D^{20} = +85.0$ (c = 0.3, CH₃OH). ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.18 (s, 2H), 8.41 (br s, 2H), 7.65-7.56 (m, 6H), 7.36-7.38 (m, 4H), 7.09-7.00 (m, 4H), 6.74 (s, 2H), 2.35 (s, 6H), 2.18 (s, 6H), 1.34 (s, 6H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 152.05, 143.80, 142.33, 137.88, 133.70, 129.60, 129.32, 128.10, 126.59, 125.88, 123.69, 123.21, 122.42, 121.41, 116.25, 20.99, 16.46, 14.56. HRMS (ESI-TOF): Exact mass calcd. for C₄₀H₃₈N₂O₈S₂ [M+Na]⁺ 761.1962, Found: 761.1975. MP 251-253 °C.



9eb, white solid, 98% yield (54.9 mg), 87% ee. [Daicel CHIRALPAK AD-H (0.46 cm

S17

x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 16.45$ (minor), 22.31 (major), min]. $[\alpha]_D^{20} = -2.3$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.75 (br s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.19-7.14 (m, 2H), 7.07-7.03 (m, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 2.92 (s, 3H), 2.18 (s, 3H), 1.73 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 152.40, 146.74, 144.89, 134.08, 129.61, 129.29, 128.35, 126.82, 126.32, 124.25, 123.86, 123.25, 123.09, 122.10, 117.40, 109.16, 40.24, 16.89, 15.64. HRMS (ESI-TOF): Exact mass calcd. for C₁₉H₁₉NO₅S [M+Na]⁺ 396.0876, Found: 396.0860. MP 127-129 °C.



9ec, brown solid, 68% yield (48.7 mg), 91% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 17.88$ (major), 20.24 (minor) min]. $[\alpha]_D^{20} = -32.3$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.07 (br s, 1H), 9.07 (s, 1H), 8.45 (br s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.51(d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 1H), 7.20-7.06 (m, 3H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.64 (s, 1H), 3.15-3.08 (m, 1H), 2.34 (s, 3H), 1.40 (s, 3H), 1.02 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 150.47, 146.13, 144.57, 142.38, 137.51, 133.39, 131.66, 129.23, 128.80, 127.90, 126.80, 126.06, 125.75, 124.51, 123.59, 123.32, 122.73, 122.55, 116.43, 108.72, 25.71, 22.51, 22.41, 20.87, 14.53. HRMS (ESI-TOF): Exact mass calcd. for C₂₇H₂₇NO₅S [M+Na]⁺ 500.1502, Found: 500.1482. MP 159-161 °C.



9ed, brown solid, 63% yield (45.1 mg), 73% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 11.98 (minor), 18.16 (major) min]. [α]_D²⁰ = -17.7 (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.07 (br s, 1H), 8.94 (s, 1H), 8.41 (br s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.30 (s, 1H), 7.18-7.14 (m, 2H), 7.05 (t, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.40 (s, 1H), 2.73-2.68 (m, 1H), 2.41 (s, 3H), 1.94 (s, 3H), 0.88 (d, *J* = 7.1 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 157.06, 151.14, 149.78, 148.86, 147.43, 144.48, 134.93, 134.41, 133.93, 133.62, 131.82, 130.96, 130.69, 129.06, 128.50, 127.60, 127.38, 126.08, 122.17, 113.67, 34.67, 26.93, 26.83, 25.98, 21.30. HRMS (ESI-TOF): Exact mass calcd. for C₂₇H₂₇NO₅S [M+Na]⁺ 500.1502, Found: 500.1483. MP 115-117 °C.



9ee, yellow solid, 56% yield (38.1 mg), 78% ee. [Daicel CHIRALPAK IA-3 (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 17.85$ (minor), 33.92 (major) min]. $[\alpha]_D^{20} = -42.33$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.02 (s, 1H), 9.37 (s, 1H), 8.95 (s, 1H), 8.48 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.18-7.04 (m, 3H), 6.88 (d, *J* = 11.8 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 2.30 (s, 3H), 1.21 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 150.39, 147.25, 146.10, 143.94, 142.71, 141.66, 137.25, 131.36, 129.49, 128.57, 127.41, 126.56, 125.79, 125.41, 123.19, 122.80 (d, *J* = 12.0 Hz), 114.25, 114.03 (d, *J* = 6.0 Hz), 108.62, 20.96, 13.99. HRMS (ESI-TOF): Exact mass calcd. for C₂₄H₂₀FNO₅S [M+Na]⁺ 476.0938, Found: 476.0918. MP 109-111 °C.



9ef, white solid, 31% yield (21.0 mg), 4% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 27.42$ (minor), 31.95 (major) min]. $[\alpha]_D^{20} = +1.0$ (c = 0.1, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.07 (br s, 1H), 8.98 (s, 1H), 8.82 (br s, 1H), 8.28 (br s, 1H), 7.57-7.52 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.09-7.18 (m, 3H), 6.87 (d, *J* = 1.9 Hz, 1H), 6.62 (s, 1H), 2.30 (s, 3H), 2.08 (s, 3H), 1.26 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 154.08, 146.14, 143.79, 142.26, 138.85, 138.30, 137.54, 129.44, 128.58, 127.82, 126.52, 125.67, 124.48, 123.71, 122.55, 121.28, 117.88, 114.63, 108.23, 20.92, 18.95, 15.42. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₃NO₅S [M+Na]⁺ 472.1189, Found: 472.0672. MP 167-169 °C.



9eg, yellow solid, 68% yield (47.3 mg), 21% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 19.42$ (major), 21.77 (minor) min]. $[\alpha]_D^{20} = +14.7$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.94 (br s, 1H), 9.03 (s, 1H), 8.35 (br s, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.12 (s, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 2.29 (s, 3H), 2.09 (s, 3H), 1.18 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 151.55, 146.17, 142.13, 136.59, 134.66, 134.38, 129.40, 128.78, 127.99, 126.55, 125.75, 124.93, 123.62, 122.72, 122.58, 121.09, 120.70, 116.82, 108.62, 20.92, 16.33, 15.37, 12.97. HRMS

(ESI-TOF): Exact mass calcd. for $C_{26}H_{25}NO_5S [M+Na]^+$ 486.1346, Found: 486.1334. MP 134-136 °C.



9Ic, brown solid, 48% yield (34.0 mg), 83% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 13.93$ (minor), 47.81 (major), min]. $[\alpha]_D^{20} = -6.0$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.08 (br s, 1H), 8.97 (s, 1H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.02 (br s, 1H), 6.36 (s, 1H), 6.11 (d, *J* = 7.2 Hz, 2H), 3.73 (s, 3H), 3.57 (s, 3H), 3.08-3.04 (m, 1H), 2.38 (s, 3H), 1.63 (s, 3H), 0.93 (m, 6H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 160.75, 159.34, 156.90, 151.10, 142.87, 138.60, 134.68, 131.37, 129.72, 127.39, 126.25, 124.27, 122.95, 104.91, 94.33, 90.56, 55.78, 55.31, 26.17, 23.00, 22.91, 21.41, 15.39. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₉NO₆S [M+Na]⁺ 494.1608, Found: 494.1593. MP 206-208 °C.



9eh, white solid, 98% yield (49.6 mg), 76% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 80/20; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 8.64$ (minor), 12.96 (major), min]. $[\alpha]_D^{20} = -3.7$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.09 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.20-7.15 (m, 2H), 7.08-7.04 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 2.17 (s, 3H), 2.00 (s, 3H), 1.62 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 167.98, 150.56, 146.24, 144.44, 130.41, 128.78, 128.04, 127.88, 127.44, 125.81, 123.64, 123.25, 122.61, 120.97,

117.19, 108.55, 23.03, 16.49, 14.73. HRMS (ESI-TOF): Exact mass calcd. for $C_{20}H_{19}NO_4 [M+H]^+$ 338.1387, Found: 338.1382. MP 129-131 °C.



9ei, yellow solid, 69% yield (45.7 mg), 58% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 6.57$ (minor), 11.19 (major) min]. $[\alpha]_D^{20} = +1.0$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.07 (s, 1H), 8.35 (d, *J* = 8.6 Hz, 2H), 8.21 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.21-7.07 (m, 4H), 6.99 (d, *J* = 8.2 Hz, 1H), 2.24 (s, 3H), 1.68 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 163.71, 151.47, 149.00, 146.23, 144.55, 140.56, 131.87, 128.95, 128.80, 128.23, 128.04, 127.08, 125.85, 123.61, 123.56, 123.49, 122.71, 122.64, 121.36, 116.98, 108.64, 16.45, 14.85. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₀N₂O₆ [M+Na]⁺ 467.1214, Found: 467.1204. MP 103-105 °C.



9aj and **9aj**', white solid, 99% yield (63 mg), 82% ee for **9aj**. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230 nm; $t_R = 19.59$ (minor), 30.77 (major) min]. $[\alpha]_D^{20} = -42.7$ (c = 0.3, CH₃OH). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.16 (br s, 1H), 8.92 (br s, 1H), 7.75-7.68 (m, 2H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.32-7.15 (m, 6H), 6.70 (s, 1H), 6.42 (s, 1H), 2.21 (s, 3H), 2.08 (s, 3H). HRMS (ESI-TOF): Exact mass calcd. for C₂₄H₂₁NO₄S [M+Na]⁺ 442.1084, Found: 442.1089. MP 89-91 °C.

General procedure for synthesis of chiral CPA 7i and used as a catalyst.

The **9aa** (0.15 mmol, 87% ee) was dissolved in dry pyridine in a three-necked flask. Under the argon condition, POCl₃ (0.3 mmol) was added dropwise. The mixture was allowed to stir at room temperature for 3 h and the reaction. Then the mixture was cooled to 0 °C, add water (0.5 mL) slowly and stirred at room temperature for 30 min. Add CH₂Cl₂ to dissolve the mixture completely, wash the organic phase using 1N HCl. Then the organic phase was dried over anhydrous Na₂SO₄ and the filtrate was concentrated under reduced pressure. The product was purified column chromatography on silica-gel (AcOEt : MeOH = 25:1 to 7:1) to give the white solid. Dissolved the solid to CH₂Cl₂ and washed with 1N HCl, The organic phase was dried over anhydrous Na₂SO₄ and the filtrate was dried over anhydrous Na₂SO₄ and the filtrate solid. Dissolved the solid to CH₂Cl₂ and washed with 1N HCl, The organic phase was dried over anhydrous Na₂SO₄ and the filtrate was concentrated under reduced pressure. 7i, white solid, 50% yield (74 mg). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.46 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.43-7.30 (m, 5H), 6.70-6.96 (m, 2H), 2.41 (s, 3H), 2.24 (s, 3H), 1.42 (s, 3H). ³¹P NMR (75 MHz, DMSO-*d*₆) δ 2.74. HRMS (ESI-TOF): Exact mass calcd. for C₂₅H₂₂NO₆PS [M+Na]⁺ 518.0798, Found: 518.0794.



The novel non- C_2 -symmetrical CPA 7i proved to be a viable catalyst for the coupling of 2a and 6a and afforded functionalized biaryl 9aa in 88% isolated yield. The level of enantio-induction was poor (-20%, giving rise to the (*S*)-enantiomer) which was

not surprising as no steric modifier is present in **7i** in the 2'-position of the naphthalene nucleus that plays a huge role in determining the stereoselectivity of the reactions in our manuscript.

General procedure for synthesis of compound 9ea*.

To a stirred solution of **9ea** (45 mg, 0.1 mmol) and **6k** (27 mg, 0.15 mmol) in toluene or DCE (3 mL), TFA (1.2 mg, 0.8 uL, 0.01 mmol) or (PhO)₂PO₂H was added in one portion at room temperature, and it was stirred at 100 °C for 3-8 hours. Solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica-gel (hexane/ethyl acetate = 5:1 to 1:1) to give pure product 9ea* (48 mg, 80% yield), 83% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 1.0 mL/min; detection wavelength = 230nm; $t_{\rm R} = 9.73$ (minor), 46.05 (major) min]. ¹H NMR (300 MHz, DMSO- d_6) δ 9.18 (s, 1H), 8.38 (br s, 3H), 7.65 (br s, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.07-7.03 (m, 2H), 7.02-6.97 (m, 2H), 6.76-6.73 (m, 2H), 6.64 (s, 1H), 3.65 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H), 2.16 (s, 3H), 1.82 (s, 3H), 1.31 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 152.97, 152.25, 150.16, 144.75, 144.27, 143.31, 138.75, 134.36, 132.24, 130.26, 130.37, 130.25, 129.04, 128.85, 127.49, 126.79, 124.94, 124.59, 124.47, 123.33, 123.26, 122.38, 121.68, 118.15, 116.88, 115.54, 60.34, 21.90, 17.38, 16.89, 15.50, 14.11. MP 165-167 °C. HRMS (ESI-TOF): Exact mass calcd. for C₃₄H₃₃NO₇S [M+Na]⁺ 622.1870, Found: 622.1862.

Reference:

[1] Uliana, M. P.; Servilha, B. M.; Alexopoulos, O.; de Oliveira, K. T.; Tormena, C. F.;
Ferreira, M. A. B.; Brocksom, T. J. *Tetrahedron* 2014, 70, 6963.












































S46


















































































LabSolutions Analysis Report	
(Samla information)	
Sample : wjz-f3-standard xiaoxuan	
ID : wjz-f3-standard ziaozuan Data Name : wjz-f3-standard ziaozuan led Method Name : fang lem Vial ::::::::::::::::::::::::::::::::::::	
Inj.Volume : 10 uL Acquisition Date : 2015-11-14 17:45:22 Operator : System Administrator	
Modified Date : 2015-11-14 18:32:34	
<pre>KChromatogram></pre>	
2010000	
150000-	
0 1000000-	
50000- ĝ	
	TsHN、 🔨 .Me
<pre>Peak table></pre>	Me ² OH
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
1 12.296 40600816 1691632 50.244	
2 42.930 40205099 456565 49.150 M	Jad
LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjr=f2=rongji3 ID : wjr=f2=rongji3 Data Name : wjr=f2=rongji3.lcd Method Name : 10d.lcm Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-7-20 12:52:38 Operator : System Administrator Modifiad Data : 2015-7-20 16:12:37	
<pre>Chromatogram></pre>	
1500000	
1250000-	
1000000	
750000-	
50000-	
0 10 20 30 40 50 60 min	
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name [min] [mAU*s] [mAU] %	
1 14.671 4815894 183645 6.066 2 46.903 74576787 858588 93.934	_

S88

LabSolutions Analysis Report	-)
(Sample information)	
Sample : wjz=f3-e xiaoxuan	
ID : wjz-f3-e xiaoxuan Data Name : wiz-f3-e xiaoxuanO1.lcd	
Method Name : 7a.lcm Vial : 1-1	
Inj. Volume : 15 uL	
Modified Date : 2015-013 10:55:05 Operator : System Rdministrator	
(Ohvanataavan)	
uV	
1000000	
750000-	
2 I I I I I I I I I I I I I I I I I I I	
8	
500000-	
250000	
	TsHN 🛧 Me
0 5 10 15 20 25 30	
	Me 🗡 OH
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	Var Br
1 11.510 13001469 582111 49.991 M	0 ha
2 16.799 13006157 405987 50.009	5 0a
LabSolutions Analysis Report	1
(Sample information)	
	-
Sample : wiz-f3-e shouring	
Sample : wjz-f3-e shouxing ID : wjz-f3-e shouxing	
Sample : wjz-63-e shouxing ID : wjz-63-e shouxing Data Name : wjz-63-e shouxing01.lcd Method Name : Ta.lcm	
Sample : wjr-f3-e shouxing ID : wjr-f3-e shouxing Data Name : wjr-f3-e shouxing01.lcd Method Name : 7a.lcm Vial : 1-1 Tai Volume : 15 ul	
Sample : wjr-f3-e shouxing ID : wjr-f3-e shouxing Data Name : wjr-f3-e shouxing Data Name : 7a.lcm Wial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat	
Sample : wjz=23-e shouxing ID : wjz=23-e shouxing Data Name : wjz=23-e shouxing01.1cd Method Name : 7a.1cm Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37	2
Sample : wjr=73-e shouxing ID : wjr=73-e shouxing Data Name : wjr=73-e shouxing01.1cd Method Name : 7a.1cm Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37	
Sample : wjr=53-e shouxing ID : wjr=53-e shouxing Data Name : wjr=53-e shouxing01.1cd Method Name : 7a.1cm Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37 (Chromatogram)	
Sample : wjr=53-e shouxing ID : wjr=53-e shouxing Data Name : wjr=53-e shouxing01.1cd Method Name : 7a.1cm Wial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37 (Chromatogram) uV	
Sample : wjr=53-e shouxing ID : wjr=53-e shouxing Data Name : wjr=53-e shouxing01.1cd Method Name : 7a.1cm Wial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37 (Chromatogram> uV S000000	
Sample : wjr=73-e shouxing ID : wjr=73-e shouxing Data Name : wjr=73-e shouxing01.1cd Method Name : 7a.1cm Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37 CChromatogram> uV S000000	
Sample : wjr=73-e shouxing ID : wjr=73-e shouxing Data Name : wjr=73-e shouxing Method Name : 7a.lcm Wial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator Modified Date : 2015-11-13 14:05:37 CChromatogram> uV S000000	
Sample : wjr-f3-e shouxing ID : wjr-f3-e shouxing Data Name : wjr-f3-e shouxing Method Name : 7a.1cm Myial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37 CChromatogram> uV S000000 4000000- 	
Sample : wjr=73-e shouxing ID : wjr=73-e shouxing Data Name : wjr=73-e shouxing Method Name : 7a_1cm Mill : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator Modified Date : 2015-11-13 14:05:37 CChromatogram> uV S000000- 3000000-	
Sample : wjr=73-e shouxing ID : wjr=73-e shouxing Data Name : wjr=73-e shouxing01.1cd Method Name : Ta_1cm Mithod Name : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator Modified Date : 2015-11-13 14:05:37 V	
Sample : wjr=73-e shouxing ID : wjr=73-e shouxing Data Name : wjr=73-e shouxing01.1cd Method Name : Ta_1cm Mithod Name : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator Modified Date : 2015-11-13 14:05:37 V	
Sample : wjr=73-e shouxing ID : wjr=73-e shouxing Data Name : wjr=73-e shouxing Method Name : 7a_1cm Mill : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator Modified Date : 2015-11-13 14:05:37 V S000000-	
Sample : wjr=73-e shouxing ID : wjr=73-e shouxing Data Name : wjr=73-e shouxing Method Name : 7a_1cm Mill : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator Modified Date : 2015-11-13 14:05:37 V	
Sample : wjr=3>e shouxing ID : wjr=3>e shouxing Data Name : wjr=3>e shouxing Method Name : Ta_1cm Method Name : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator Modified Date : 2015-11-13 14:05:37 CChromatogram> uV S000000-	
Sample : wjr-13-e shouxing ID : wjr-13-e shouxing Data Name : wjr-13-e shouxing Method Name : 7a.1cm Wial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37 CChromatogram> uV S000000 4000000- 2000000- 100000- 1000000- 1000000- 1000000- 1000000- 1000000- 1000000- 1000000- 1000000- 1000000- 1000000- 10000000- 10000000- 10000000- 100000000- 1000000000- 10000000000	
Sample : wjr:53-e shouxing ID : wjr:53-e shouxing Data Name : wjr:53-e shouxing Nial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37 CChromatogram> uV S000000 4000000 0 0 0 0 0 0 5 10 10 15 20 20 20 20 20 20 20 20 20 20	
Sample : wjr-37= shouxing ID : wjr-13= shouxing Data Name : wjr-13= shouxing Nethod Name : 7a.1cm Wial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37 CChromatogram> uV S000000 4000000 0 0 0 0 0 5 10 15 20 25 30 min 20 15 10 15 20 25 30 0 10 15 20 25 30 0 10 15 20 25 30 0 10 15 20 25 30 0 10 15 20 25 30 0 10 15 20 25 30 0 10 15 20 25 30 0 15 10 15 20 25 30 0 15 10 15 20 25 30 0 15 10 15 20 25 30 0 15 10 15 20 25 30 0 15 10 15 20 25 30 0 15 10 15 20 25 30 0 15 10 15 20 25 30 0 15 10 10 15 10 10 10 10 10 10 10 10 10 10	
Sample : wjr-f3-e shouxing ID : wjr-f3-e shouxing Data Name : wjr-f3-e shouxing Name : wjr-f3-e shouxing Method Name : 7a.1cm Wial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Modified Date : 2015-11-13 14:05:37	
Sample : wjr-13-e shouxing ID : wjr-13-e shouxing Data Name : wjr-13-e shouxing Name : wjr-13-e shouxing Method Name : 7a.1cm Wial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-13 20:57:07 Operator : System Administrat Medified Date : 2015-11-13 14:05:37	
Sample : wjr=f3-e shouring ID : wjr=f3-e shouring Data Name : wjr=f3-e shouring01.1cd Method Name : Ta Lon Vial : 1-1 Inj. Volume :: 15 uL Acquisition Date :: 2015-8-13 20:57:07 Operator : System Administrat Modified Date :: 2015-11-13 14:05:37	
Sample : wjr=f3-e shouring ID : wjr=f3-e shouring Data Name : wjr=f3-e shouring01.1cd Method Name : Ta Lon Vial : 1-1 Inj. Volume :: 15 uL Acquisition Date :: 2015-8-13 20:57:07 Operator : System Administrat Modified Date :: 2015-11-13 14:05:37	
Sample : wjr=53 = shouring ID : wjr=53 = shouring Date Name : wjr=53 = shouring01.lcd Method Name : wjr=53 = shouring01.lcd Method Name : 10 Acquistion Date : 2015-8-13 20:57:07 Operator Modified Date : 2015-11-13 14:05:37 CChronatogram> uV S000000 4000000 0 5 0 15	

LabSolutions Analysis Report	Ţ
(Sample information)	
Sample : wjz-f3-b	
LU wjz=f3=b Data Name wjz=f3=b.lcd	
Method Hame : Im-1.1cm Vial : 1-1	
Acquisition Date : 2015-8-3 20:32:13 Operator : System Administrator	
modified bate . 2015-0-5 21.20.11	
(Chromatogram)	
	÷
3000000	
250000-	
2000000	
150000-	
50000-	TallN - Mo
0 5 10 15 20 25 30 	
<peak table=""></peak>	Me OH
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	Br 🔨 🏏
2 14.126 44916049 1616695 49.958 V	9ca
LabSolutions Analysis Report	
(Sample information)	
Sample : wjz=f3-b shouxing	
Data Name : wjr-13-b shouring lcd	
Vial 1-15 vi	
Acquisition Date : 2015-8-3 21:35:07 Operator : System Administrator Modified Date : 2015-8-3 22:11:21	
(Chronatogram)	
UV 300000	
2	
250000-	
2000000-	
150000	
1000000	
50000	
<pesk table=""></pesk>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
finited finited finited by	
[mm] [mA0'3] [mA0] %	

LabSolutions Analysis Report	
(Sample information)	
Sample <th:wjr=f3-a< th=""> ID <td:wjr=f3-a< td=""> Data Nane <td:wjr=f3-a< td=""> Method Nane <td:wjr=f3-a< td=""> ID <td:wjr=f3-a< td=""> Mathod Nane <td:wjr=f3-a< td=""> ID <td:wjr=f3-a< td=""> ID <td:wjr=f3-a< td=""> Intit Vial <td:wjr=f3-a< td=""> Inj.Volume <td:state< td=""> Inj.Volume <td:state< td=""> Acquisition Date <td:2015-8-3 17:00:46<="" td=""> Operator Modified Date : 2015-8-3 23:28:29</td:2015-8-3></td:state<></td:state<></td:wjr=f3-a<></td:wjr=f3-a<></td:wjr=f3-a<></td:wjr=f3-a<></td:wjr=f3-a<></td:wjr=f3-a<></td:wjr=f3-a<></td:wjr=f3-a<></th:wjr=f3-a<>	
(Chromatogram)	
750000	
500000- 8 8 8	
	TsHN
<peak table=""></peak>	NIE OH
Detector A Ch1 230nm	Br
Peak [min] Ret Time [mAU*s] Area [mAU] Height % Area % Unit Mark Compound Name 1 11.131 13491431 609991 50.024 2 20.518 13478388 329321 49.976	9da
LabSolutions Analysis Report	1
<pre> Sample information> Sample : wjr=f3~Ashouxing ID : wjr=f3~Ashouxing Data Name : wjr=f3~Ashouxing.lcd Method Name : I⁺I.lcm Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-8-3 19:34:07 Operator : System Administrato Modified Date : 2015-11-13 23:59:03 </pre>	
(Chronatogram)	4
uV	1
1500000-	
1000000- 1000000-	
500000- 	
0 5 10 15 20 25 30 35 40	
e e e e e e e e e e e e e e e e e e e	4 7
<peak table=""></peak>	4
Detector A Ch1 230nm	4
Peak Area Height Area Unit Mark Compound Name [min] [mAU*5] [mAU] % % </td <td></td>	
1 11.596 4329529 197377 9.672 M 2 21.275 40435627 973850 90.328 S	1

LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjz-f3-c ID : wjz-f3-c Data Name : wjz-f3-c.lcd Maddad Mane : wjz-f3-c.lcd	
Mictao Rume : 11-1. Inj.Volume : 15 uL	
Acquisition Date : 2015-8-3 22:13:17 Operator : System Administratom Modified Date : 2015-11-13 13:56:48	
<pre>Chromatogram></pre>	
uV	
50000-	
250000-	
8 8 8	
	TsHN Me
	Ме ОН
<peak table=""></peak>	ОН
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	ОН
1 22.397 6007055 117383 49.960 M 2 38.277 6016602 70898 50.040 S	9ea
LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjr-f3-c shouxing rt ID : wjr-f3-c shouxing rt	
Method Name : 7a.1cm Wial : 1-1	
Inj.Volume : 15 uL Acquisition Date : 2015-8-13 16:17:45 Operator : System Administratos Madifia Data : 2015-8-13 22:37:23	
<pre></pre>	
ů ř	
50000-	
250000-	
0 10 20 30 40 50 60 min	
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name [min] [mAU*s] [mAU] %	
1 25.499 909393 16103 1.696	

LabSolutions Analysis Report	-
(Sounda information)	
Sample information/	
ID : wjr-E3-d xiaoxuan Data Name : wjr-E3-d xiaoxuan01.1cd	
Method Name : fa.lcm Vial : 1-1	
Inj.Volume : 15 uL Acquisition Date : 2015-8-14 17:20:38 Operator : System Administrator	
Modified Date : 2015-11-13 14:02:13	
<pre></pre> chromatogram> uV	
500000- 250000-	
	TsHN
	МеОН
<peak table=""></peak>	DH
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
1 29.981 29995006 492212 49.619 2 32.220 30455909 454072 50.381 SV	9fa
LabSolutions Analysis Report	
Sample information>	
ID wir-f3-d shouxing Data Name : wjr-f3-d shouxing 01.1cd Method Name : Ta.1cm Vial : 1-1	
Inj.Volume : 20 uL Acquisition Date : 2015-9-17 10:41:57 Operator : System Administrator Modified Date : 2015-9-17 11:25:06	
("hvomatoovam)	
uV	
750000-	
50000-	
1	
250000	
- 10 20 30 40 50 80	
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name [min] [mAU*s] [mAU] %	
1 31 690 49210218 763828 92 473 V	

LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjr-f3-J xiaoxuan ID : wjr-f3-J xiaoxuan Data Name : wjr-f3-JU xiaoxuan01.1cd Method Name : 7a.1cm Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-9-11 18:35:09 Operator : System Administrator Modified Date : 2015-11-13 14:20:38	
(Chromatogram)	
nA ouround color man	
750000-	
50000- 9 9 9 9	
250000-	
	TsHN Me Me OH
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time [min] Area [mAU*s] Height [mAU] Area % Unit Mark Compound Name 1 16.305 13889619 367158 50.011 M 2 24.412 13883289 260167 49.989 M	9ga
LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjr=75-j shouxing ID : wjr=75-j shouxing Dats Name : wjr=75-j shouxing01.1cd Method Name : 7a.1cm Vial : 1-1	
Inj. Volume : 3 uL Acquisition Date : 2015-9-12 16:26:13 Operator : System Administrator Modified Date : 2015-9-12 16:59:23	
(Chronatogram)	
uV 1000000	
750000-	
50000-	
250000-	
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time [min] Area [mAU*s] Height [mAU] Area % Unit Mark Compound Name 1 16.297 2851285 70857 7.698 S	
2 25.724 31788824 535414 92.302 S	

LabSolutions Analysis Report	
<sample information=""> Sample : wjr=10-fixiaoxuan TTD</sample>	
Data Name : wjr-15-1 xlaoxuan Data Name : yjr-15-1 xlaoxuan Method Name : 7a.lcm Vial : 1-1 Tai Volume : 12 ul	
Acquisition Date : 2015-9-5 17:15:13 Operator : System Administrator Modified Date : 2015-11-13 14:07:18	
<pre>Chromatogram></pre>	
w ^V 5000000	
4000000-	
3000000-	
2000000-	
1000000-	TsHN、 🔨 Me
0 0 5 10 15 20 25 30 35 40 min	Ма
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time [min] Area [mAU*s] Height [mAU] Area % Unit Mark Compound Name 1 11.157 45785530 2118290 49.909 M 49.909 M 2 20.727 45982860 1172845 50.091 M 40.001	9ha
LabSolutions Analysis Report	
<pre>Sample information> Sample : wjr-f3-f shouring ID : wjr-f3-f shouring Data Name : wjr-f3-f shouring01.lcd Method Name : 7a.lcm</pre>	
Vial : 1-1 Inj.Volume : 12 uL Acquisition Date : 2015-9-5 19:13:54 Operator : System Administrator Modified Date : 2015-10-11 17:17:17	
(Chromatogram)	
2000000	
150000-	
1000000-	
500000-	
0 10 20 30 40 50 min	
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
Limit Limitor 70 1 11.923 2886610 135419 5.363 III 2 22.107 50935775 1241832 94,637 S II	

$\frac{\frac{Simple information}{E}}{\frac{E}{2}} \frac{\frac{1}{2}}{\frac{1}{2}} \frac{\frac{1}{2}} \frac{\frac{1}{2}}{\frac{1}{2}} \frac{\frac{1}{2}}{\frac{1}{2}} \frac{\frac{1}{2}}{\frac{1}{2}} \frac{\frac{1}{2}} \frac{\frac{1}{2}}{\frac{1}{2}} \frac{\frac{1}{2}}{\frac{1}{2}} \frac{\frac{1}{2}} \frac{$	LabSolutions Analysis Report	
$\frac{\left[\frac{1}{2}\frac{1}{1}1$	(Sample information)	
$ \frac{\left[\frac{1}{2} \frac{1}{2$	Sample : wjr-f3-6ph ziaozuan ID : wjr-f3-6ph ziaozuan Data Name : wjr-f3-7ph ziaozuan Mathod Name : 7a.lom Vial : 1-1 Inj. Volume : 15 uL Acquisition Data : 2015-9-26 17:03:10 Operator : System Administrator	
$ \frac{\left[\frac{1}{10000} - \frac{1}{100000} - \frac{1}{100000} - \frac{1}{1000000} - \frac{1}{10000000} - \frac{1}{100000000000000} + \frac{1}{10000000000000000000000000000000000$	Modified Date : 2015-9-26 19:28:27	
$\frac{1}{10000} \frac{1}{10000} \frac{1}{10000} \frac{1}{100000} \frac{1}{1000000} \frac{1}{10000000000000000000000000000000000$	<pre>(Chromatogram)</pre>	
$\frac{1}{2} \frac{1}{2} \frac{1}$	1000000	
$\frac{250000}{10} \frac{1}{10} \frac{1}{$	750000- SC0000-	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	250000-	
CPeaktable> Interpretation Interpr		TsHN Me
Detector A Chi 230mm Information information Information information Set Time information <th< td=""><td><peak table=""></peak></td><td></td></th<>	<peak table=""></peak>	
Pask Time Area (mAU) (mAU) Height Area (mAU) Mark Compound Name Sum 1 14 100 18201390 586517 50 033 S	Detector A Ch1 230nm	
SHIMACCU LabSolutions Analysis Report (Sample information)	Peak [min] Ret Time [mAU*s] Area [mAU] Height % Area % Unit Mark % Compound Name 1 14.100 18281380 568517 50.033 S 2 32.756 18257218 255521 49.967 S	9ia
SHIMADZU LabSolutions Analysis Report (Sample information) Seeple : vjr:37-6ph showing Data Base : vjr:37-6ph showing Mail :: 1-1 Ray Value :: 15 ul. Acquisition Date :: 2015-9-26 19:47:51 Medified Date :: 2015-9-27 00:03:04 Chromatogram vv 1000000 500000 250000 250000 40 500000 40 50 500000 40 50 50 50 50 50 50 50 50 50 5	· · · · · · · · · · · · · · · · · · ·	
CSample information> Emergine : wjr-f3-6ph showing if the Wate is wjr-f3-6ph showing if the Wate is wjr-f3-6ph showing if the Wate is wjr-f3-f9h showing led with Wate is wjr-f3-6ph showing led with Wate is is used to with the Wate is wjr-f3-6ph showing led with iteration is wjr-f3-6ph showing led with the Wate is 2015-9-26 19:47.51 Operator : System Administrator Yolu : 1-1 :: 2015-9-26 19:47.51 Operator : System Administrator Chronatogram> :: 2015-9-27 00:03:04 CChronatogram> :: 2015-9-27 00:03:04 S00000- :: 2015-9-27 00:03:04	LabSolutions Analysis Report	-
Inj. Volume 15 uL 2015-9-28 19:47:51 Operator : System Administrator Modified Date : 2015-9-27 00:03:04 Operator : System Administrator CChronatogram>	<pre>Sample information> Sample : wjz=f3-6ph shouxing ID : wjz=f3-6ph shouxing Data Name : wjz=f3-7ph shouxing.lcd Method Name : Ta.lcm Vial : 1-1</pre>	
Chronatogram> 1000000 1000000 750000 250000 0 0 250000 0	Inj. Volume : 15 uL Acquisition Date : 2015-9-26 19:47:51 Operator : System Administratom Modified Date : 2015-9-27 00:03:04	
swy 1000000 750000 500000 250000 500000 0 50 250000 50 0 10 20 30 40 50 min 50 2 30 40 50 min 50 0 10 20 30 40 50 min 50 0 10 2 30 40 50 min 50 min 50 1 14.114 2 13.439 38 50 50 50	(Chronatogram>	
750000- 500000- 250000- 50 0 -	1000000	
250000 50 0 10 20 30 40 50 min Peak table> Detector A Ch1 230nm Peak [min] (mAU') % 1 14.114 2475467 75413 6.315 SV	750000- 頁 月	
Area Unit Mark Compound Name 1 14.114 2475467 75413 6.315 SV 2 3.439 36523094 495563 93.685 SV	250000-	
Peak table> Area [mAU] Height Area [mAU] Mark Compound Name 1 14.114 2475467 75413 6.315 SV 2 33.439 36723094 4955663 93.685 SV		
Detector A Ch1 230nm Peak Ret Time [min] Area [mAU] Unit % Mark Compound Name 1 14.114 2475467 75413 6.315 SV 2 33.439 38723094 495563 93.685 SV		
Peak Ret Time [min] Area [mAU*s] Height [mAU] Area % Unit Mark Compound Name 1 14.114 2475467 75413 6.315 SV	Detector A Ch1 230mm	
Linky Linky 70 1 14.114 2475467 75413 6.315 SV 2 33.459 36723094 4955663 93.685 SV	Peak Ret Time Area Height Area Unit Mark Compound Name	
	1 14.114 2475467 75413 6.315 SV 2 33.439 36723094 495563 93.685 SV	_



LabSolutions Analysis Report
<sample information=""></sample>
Sample : wjr=f3-r xiaoxuan ID : wjr=f3-r xiaoxuan Data Name : wjr=f3-r xiaoxuan lcd Method Name : lc.lcd Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-10-24 22:42:11 Operator : System Administrator Medified Data : 2015-10-24 23:33:45
modified bate . 2013-10-24 23.33.43
(Chromatogram)
uV 1500000
1250000-
1000000-
750000-
50000-
0 5 10 15 20 25 30 min
<peak table=""></peak>
Detector A Ch1 230nm
Peak Ret Time [min] Area [mAU*s] Height [mAU] Area % Unit Mark Compound Name 1 14.399 17712234 619873 50.189 MeO MeO 2 17.155 51.169 40.911 SV MeO MeO
2 11.150 11515150 511055 45.011 57 58
LabSolutions Analysis Report
<sample information=""></sample>
Sample : wjz-f3-z shouxing HD : wjz-f3-z shouxing Data Name : wjz-f3-z shouxing.lcd Method Name : lc.lcm
Niau 1-1 Inj.Volume 15 uL Acquisition Date : 2015-10-25 11:25:10 Operator : System Administrator Modified Date : 2015-10-25 12:14:56
1250000-
1000000-
750000-
500000-
250000-
0 5 10 15 20 25 30 min
<peak table=""></peak>
Detector A Ch1 230nm
Peak Ret Time Area Height Area Unit Mark Compound Name [min] [mAU*s] [mAU] %
1 14 641 30571939 1050288 91 233

LabSolutions Analysis Report	•
(Cample information)	
Sample : wjz-f3~k xiaoxuan IC	
ID : w]r-f3-k xiaoxuan IC Data Name : wjr-f3-k xiaoxuan ICO4.lcd Method Name : 7a.lcm Vial : 1-1	
Inj.Volume : 15 uL Acquisition Date : 2015-9-16 14:11:10 Operator : System Administrator Modified Date : 2015-9-17 00:20:01	
KChromatogram>	
uV 200000	
20000	
150000-	
0.0012	
A A	
50000-	TsHN
	Ме ОН
(Parktable)	MeO
Creak table>	
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	ÓMe
1 50.072 8237848 66976 49.121 V 2 55.714 8532814 63768 50.879 V	9la
LabSolutions Analysis Report	
Sample information>	
ID : wjr-f3-k shouxing IC Data Name : wjr-f3-k shouxing ICO1.lcd Method Name : 7a.lcm Vial : 1-1	
Inj.Volume : 15 uL Acquisition Date : 2015-9-18 15:14:52 Operator : System Administrator	
Modified Date : 2015-9-17 00:19:57	
KChromatogram>	
uv	
2000	
150000-	
n and the second s	
50000-	
0 25 50 75 100	
Real tables	
Datator A Ch1 230nm	
Peak RetTime Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	
2 55.419 15294360 119247 87.988 V	

SHIMADZU LabSolutions	Analysis	Report		+
Sample information>				
Sample : wjr=f3-r xiaox ID : wjr=f3-r xiaox Data Name : wjr=f3-r xiaox Method Name : fan Lon Vial : 1-1	uan uan uan. lcd			
Inj. Volume : 15 uL Acquisition Date : Modified Date :	2015-11-15 13:56:05 2015-11-15 15:16:49	Operator	: System Administrator	
< <u>Chromatogram</u> >				
50000- 250000-				
	25		200 °EL	TsHN Me
			min	
<peak table=""></peak>				
Detector A Ch1 230nm	Height Area	Unit Mark Compo	and Name	
Image: Text and	[mAU] % 512845 49.772 56320 50.228	SV SV		Me 9ma
SHIMADZU LabSolutions	Analysis	Report		
<pre><sample information=""> Sample : wjr=f3=r 1114 ID : wjr=f3=r 1114 Data Name : wjr=f3=r 1114 Method Name : fang.lom</sample></pre>	ad7-3. led			
Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : Modified Date :	2015-11-14 20:05:10 2015-11-14 22:11:47	Operator :	System Administratoz	
<pre>Chromatogram></pre>				
ν.v				
500000-				
250000- - 			47.4	
	25	50	,F	
			min	
<peak table=""></peak>				
Peak Ret Time Area 1	Height Area I	Unit Mark Compo	und Name	
[min] [mAU*s] [1 9.415 2349337	[mAU] % 128185 12 590			
2 77.474 16311645	100176 87.410	SV		

LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjr-f3-y xiaoxuan ID : wjr-f3-y xiaoxuan Data Name : wjr-f3-y xiaoxuan.lcd	
Method Name : 1c.1cm Vial : 1-1 Tai Valuma : 15 uT	
Acquisition Date : 2015-10-25 14:34:19 Operator : System Administrator Modified Date : 2015-10-26 10:10:58	
<pre>KChronatogram></pre>	
300000	
250000-	
20000-	
150000-	
100000-	
8	TsHN 🛧 Me
50000-	
$0 \frac{1}{10}$, $\lambda d \lambda h A / \lambda_{-}$, λh	Ме
min	MeO OH
<peak table=""></peak>	
Peak Ret Time Area Height Area Unit Mark Compound Name	MeO
[min] [mAU*s] [mAU] %	OMe
2 50.150 3484296 33737 49.701 SV	9na
LabSolutions Analysis Report	
<sample information=""></sample>	
ID : wjz=13-w 25 Data Name : wjz=13-w 25.lcd	
Method Name : 11.1cm Vial : 1-1	
[Ln]; Volume : 15 uL Acquisition Date : 2016-1-26 10:56:37 Operator : System Administrator Modified Date : 2016-1-26 13:21:02	
u٧ 600000	
500000-	
400000-	
300000-	
200000	
100000-	
0 10 20 30 40 50 60 min	
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name [min] [mAU*s] [mAU] %	
1 10.078 11087055 449342 30.228 2 54 175 25590441 216102 69.772 5	
	L



LabSolutions Analysis Report	
Sample information>	
Sample : wjz-f3-q xiaoxuan ID : wjz-f3-q xiaoxuan Data Name : wjz-f3-q xiaoxuan01.lcd	
Method Name : 7a.lom Vial : 1-1 Tai Moluna : 15.J	
Acquisition Date : 2015-9-17 21:08:00 Operator : System Administrator Modified Date : 2015-9-17 22:20:45	
Chromatogram>	
uY 1000000	
750000-	
500000-	
250000-	
	MsHN Me
	Ме ОН
Detector A Ch1 230nm	ОН
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] % 1 16.526 33526723 872956 49.589 2 22.642 34062075 668436 50.411 SV	9eb
LabSolutions Analysis Report	
<sample information=""> Sample : wir=f3-c shousing</sample>	
ID wjz-f3-q shouring Data Name wjz-f3-q shouring01.lcd	
Method Name : 7a.1cm Vial : 1-1 Ini Volume : 15 uL	
Acquisition Date : 2015-9-17 22:20:40 Operator : System Administrator Modified Date : 2015-9-17 22:54:53	
<pre> Chromatogram></pre>	
uV 4000000	
3000000-	
2000000-	
1000000-	
0 10 20 30 40 50 min	
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name [min] [mAU*s] [mAU] % %	
1 16.451 10595043 259571 6.506 2 22.307 152258287 2881612 93.494	

LabSolutions Analysis Report	-
<sample information=""> Sample : wirf3~n xiaoxuan</sample>	
ID': wjr=f3=n xiaoxuan Data Name : wjr=f3=n xiaoxuanO1.lcd Method Name : 7.a.lcm	
Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-9-17 11:21:49 Operator : System Administrator	
Modified Date : 2015-11-13 14:12:46	
<pre>K Chromatogram></pre>	
uv	
750000-	
500000- 2	
0 <u>````````````````````````````````````</u>	1
	T LINE IN
	IsHN /Pr
	Ме ОН
Detector A Ch1 230nm	OH COH
Peak RetTime Area Height Area Unit Mark Compound Name	
1 17.453 13718035 356532 50.074	••••••••••••••••••••••••••••••••••••••
2 20.001 2001403 000000 40.000 Fill	560
LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjz-f3-n shouxing ID : wjz-f3-n shouxing	
Mathod Name : wjrt57m Shouxing01.1cd Mathod Name : 7a.1cm Vial : 1-1	
Inj. Volume : 15 uL Acquisition Date : 2015-9-17 12:34:45 Operator : System Administrator Modified Date : 2015-9-17 13:59:25	
VChronatogram>	
1250000-	
100000-	
750000-	
50000-	
250000-	
<peak table=""></peak>	
Detector A Ch1 230nm Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	
2 20.238 2194007 42535 4.494 V	

LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjz-f3-o ziaozuan	
Data Name : wjz-15-o ziaozuan01.1cd	
Vial : 1-1	
Inj.Volume : 15 uL Acquisition Date : 2015-9-17 14:02:02 Operator : System Administrator	
Modified Date : 2015-9-17 14:38:55	
<pre>KChromatogram></pre>	
uV	
50000-	
400000-	
a 300000-	
200000-	
100000-	
	ⁱ Pr OH
<pesk table=""></pesk>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
[mm] [mAU*s] [mAU] %	У У `ОН
2 17.948 6195769 147302 50.454 S	9ed
LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjz=f3-o shouxing ID : wjz=f3-o shouxing	
Data Name : wjz-f3-o shouxing02.lcd Method Name : 7a.lcm	
Vial : 1-1 Ini Volume : 15 uL	
Acquisition Date : 2015-9-17 15:29:25 Operator : System Administrator	
addired bace	
<chromatogram></chromatogram>	
1000000	
150000-	
5	
50000-	
20000-1 8 1	
01.4	
0 5 10 15 00 05 00 05	
0 5 10 15 20 25 30 35 	
0 5 10 15 20 25 30 35 min	
0 5 10 15 20 25 30 35 min <pre></pre>	
0 5 10 15 20 25 30 35 min	
0 5 10 15 20 25 30 35 nin <pesk table=""> Detector A Ch1 230nm</pesk>	

LabSolutions Analysis Report	
(Sample information)	
Eample : wjz=f3=p ia xiaoxuan ID : wjz=f3=p ia xiaoxuan	
Data Name : wjz-f3-p ia xiaoxuanUZ.lcd Method Name : Ta.lcm Wial : 1-1	
Inj.Volume : 20 uL Acquisition Date : 2015-9-18 16:20:30 Operator : System Administrator	
Modified Date : 2015-9-18 17:09:03	
(Chromatogram)	
ч ^ү	
50000	
3. 6.65	
250000-	
	TsHNF
0 10 20 30 40 50 60	
min	Me OH
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] % 1 16.944 31249922 300070 50.350 SV	CH CH
2 33.646 30815848 270879 49.650 V	9ee
LabSolutions Analysis Report	
(Sample information)	
Sample : wjr=f3-p ia shouxing ID : wjr=f3-p ia shouxing	
Dats Name : wjz-f3-p is shouxing01.lcd Method Name : 7a.lcm Vial : 1-1	
Inj.Volume : 20 uL Acquisition Date : 2015-9-18 17:09:03 Operator : System Administrator	
Modified Date : 2015-9-18 18:16:36	
(Chronatogram)	
50000	
400000-	
300000-	
۹	
20000	
100000	
0 10 20 30 40 50 60 min	
<peak table=""></peak>	
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name [min] [mAU] % % <	
1 17.845 3361594 16804 11.030 S 2 33.921 27114589 218577 88.970 S	
	L

LabSolutions Analysis Report	
<pre> {Sample information> Sample : wjr=f3-1 ad xiaoxuan ID : wjr=f3-1 ad xiaoxuan Data Name : yjr=f3-1 ad xiaoxuan1113.lcd Method Name : G7.lcm Vial : 1-1 Inj, Volume : 15 uL Acquisition Date : 2015-11-13 19:14:33 Operator : System Administrator Modified Date : 2015-11-13 19:52:46 </pre>	
<chromatogram> uV 300000</chromatogram>	
250000- 200000- 150000-	
$\begin{bmatrix} 100000 \\ 50000 \\ 0 \\ 0 \\ 0 \\ 10 \\ 20 \\ 30 \\ 40 \\ 50 \\ min \\ mi$	TsHN
<peak table=""></peak>	Me OH
Detector A Ch1 230nm Peak Ret Time [min] Area [mAU*s] Height [mAU] Area % Unit Mark Compound Name 1 25.670 7396168 122616 49.603 2 29.032 7514511 110133 50.397 V	9ef
LabSolutions Analysis Report	
<pre> {Sample information> Sample : wjr=f3-1 shouring 1108 ID : wjr=f3-1 shouring 1108 Data Name : wjr=f3-1 shouring 1108.lcd Method Name : f7 lcm Vial : 1-1 Inj,Volume : 15 uL Acquisition Date : 2015-11-8 20:38:59 Operator : System Administrator Modified Date : 2015-11-8 22:01:53 </pre>	
<pre></pre>	
50000- 50000-	
400000-	
<pre></pre>	
Detector A Ch1 230nm	
Peak Ret Time [min] Area [mAU*5] Height [mAU] Area % Unit Mark Compound Name 1 27.424 8615226 114929 47.983 2 31.952 9339574 103819 52.017 SV	

LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjr-f3-m xiaoxuan ID : wjr-f3-m xiaoxuan Data Name : wjr-f3-m xiaoxuan01.1cd Method Name : 7.a.1cm	
Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-9-17 16:27:08 Operator : System Administrator Modified Date : 2015-11-13 14:10:55	
<pre></pre>	
250000	
2000000-	
150000- 8 8	
1000000-	
500000-	TsHN Me
0 10 20 30 40 50 min	
<peak table=""></peak>	Me ⁻ OH
Detector A Ch1 230nm	
Peak Ret Time [min] Area [mAU*s] Height [mAU] Area % Unit Mark Compound Name 1 20.515 50540490 1102185 49.407 <td< td=""><td>С</td></td<>	С
2 22.961 51763322 992420 50.593 SV	9eg
CLIMAD 711	
LabSolutions Analysis Report	
<sample information=""></sample>	
Sample : wjr-f3~m shouxing ID : wjr-f3~m shouxing Data Mame : wjr-f3~m shouxing01.lcd Method Name : 7lcm	
Vial : 1-1 Inj. Volume : 15 uL Acquisition Date : 2015-9-17 17:00:21 Operator : System Administrator Modified Date : 2015-9-17 17:28:31	
(Chromatogram)	
1500000	
125000-	
75000-	
500000	
25000-	
Sreak table>	
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	
2 21.770 22183232 431063 39.491 V	
LabSolutions Analysis Report	
--	----------------------
<sample information=""></sample>	
Sample : wjz-f3-t xiaoxuan ID : wjz-f3-t xiaoxuan Data Name : wjz-f3-t xiaoxuan lcd Method Name : G7.1cm Vial : 1-1 Inj. Volume : 15 uL Acquisition Date : 2015-10-27 16:16:34 Operator : System Administrator	
Modified Date : 2015-11-13 14:22:05	
«Chronatogram»	
750000-	
500000-	
- 86 - 11	
250000-	TsHN ⁱ Pr
	МеОН
min min	MeO
<peak table=""></peak>	
Peak Ret Time Area Heirht Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	ÓMe
1 13.958 8608450 310491 49.931 M 2 49.062 8632345 84628 50.069 SV	9lc
LabSolutions Analysis Report	
<pre><sample information=""> Sample : wjr=f3-t shouring ID : wjr=f3-t shouring Data Name : wjr=f3-t shouring lcd Method Name : GY.lcm</sample></pre>	
Vial : 1-1 Inj.Volume : 15 uL Acquisition Date : 2015-10-27 17:43:40 Operator : System Administratom Modified Date : 2015-10-27 19:42:55	
KChromatogram>	
uv .	
750000-	
500000- 	1
250000	
(Pask+shla>	1
Detector A Ch1 230nm	
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	
2 47.809 41708258 403066 91.541 SV	1

S109

SHIMADZII IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII	
LabSolutions Analysis Report	
(Sample information)	
Sample : wjz-f4-yixianji lvben xiaoxuan ID : wjz-f4-yixianji lvben xiaoxuan	
Data Name : wjz-f4-yizianji lvben ziaozuan001.1cd Method Name : 7a.1cm	
Tal 1-1 Inj. Volume : 15 uL	
Modified Date : 2015-10-7 21:51:14 Operator : System Administrator Modified Date : 2015-11-13 14:58:27	
<pre> Chromatogram></pre>	
uV	
200000-	
1500000-	
3 8 62	
1000000-	
50000-	
0 + · · · · · · · · · · · · · · · · · ·	
0 5 10 15 20 25	
<pesk table=""></pesk>	Me ^r Y OH
Detector A Ch1 230nm	OH
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	ОН
1 8.625 23617862 1126696 50.006 M 2 12.973 23672325 865618 49.994 M	9eh
	_
SHIMADZU Analysis Report	
Labsolutions milarysis Report	
(Samle information)	
Sample : wjr-f4-yixianji lvben shouxing	
Data Name : wjz-f4-yixianji lvben shouxing Data Name : wjz-f4-yixianji lvben shouxing.lcd	
Nethod Name : 1a.1cm Vial : 1-1	
Lnj. Volume : 15 uL Acquisition Date : 2015-10-7 22:09:24 Operator : System Administrator M.J.Sfild Bate : 2015-11-13 14:57:05	
(Chumatagram)	
200000-	
150000-	
1000000-	
1	
5/0000-	
24	
0 5 10 15 20 25	
min	
Detector A Chi 120mm	
Peak Ref Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] %	
1 8.642 3570662 145182 12.000 2 12.962 26184696 897833 88.000	

LabSolutions Analysis Report	
<sample information=""> Sample : wjr=f3=v</sample>	
ID Data Name : wjz-f4-v1.lcd Method Name : lc.lcd	
Vial : 1-1 Inj. Volume : 15 uL	
Acquisition Date : 2015-10-24 17:22:39 Operator : System Administrator Modified Date : 2015-11-13 14:54:21	
<pre></pre>	
150000	
1250000-	
1000000-	
750000-	
50000-	O-N A
25000-	
0.0 2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0	
	Ma
Creak table>	
Peak Ret Time Area Height Area Unit Mark Compound Name	
[min] [mAU*s] [mAU] % 1 6.567 11652234 833467 49.882	
2 11.018 11707166 477065 50.118 1	9ei
LabSolutions Analysis Report	
<pre>Sample information></pre>	
Sample : wjr-f3-v shouring ID : wjr-f3-v shouring Date Mana : wir-f3-v shouring	
Method Name : 1c.lcd Vial : 1-1	
Inj.Volume : 15 uL Acquisition Date : 2015-10-24 20:20:05 Operator : System Administrat	oz
Modified Date : 2015-10-24 20:42:41	
<pre> Chromatogram></pre>	_
uV 150000	1
1250000-	
100000-	
750000-	
50000- 50000-	
250000-	
0,0 2,5 5,0 7,5 10,0 12,5 15,0 17,5 20,0	
mii	
<peak table=""></peak>	-
Detector A Cn1 230nm Peak Ret Time Area Unit Mark Compound Name	-
[min] [mAU*s] [mAU] %	4
1 0.013 0041321 404021 21.005	-1



