Supporting Information for

Highly Stereoselective Synthesis and Application of P-Chiral

Ferrocenyl Bisphosphorus Ligands for Asymmetric

Hydrogenation

Caiyou Chen, ^[a] Songwei Wen, ^[a] Xiu-Qin Dong^[a]*, and Xumu Zhang^[b, a]*

^[a] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei, 430072, P. R. China.

^[b] Department of Chemistry, South University of Science and Technology of China, Shenzhen, 518000, *P.R. China*.

Contents

General Remarks	2
Procedure for the synthesis of the ligands	2
General procedure for asymmetric hydrogenation	4
Characterization data of the ligands and intermediates	5
Methods for the determination of the ee for the asymmetric hydrogenation of	the
standard substrates	8
NMR Spectra	.10
HPLC and GC Spectra	.16
References	48

General Remarks

All reactions were performed in the argon-filled glovebox or under nitrogen using standard Schlenk techniques, unless otherwise noted. Solvents were dried with standard procedures and degassed with N₂. Column chromatography was performed using 200~400 mesh silica gel. Thin layer chromatography (TLC) was performed on EM reagents 0.25 mm silica 60-F plates. ¹H, ¹³C, ³¹P NMR spectrum were recorded on Bruker-400, with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in ppm, upfield to TMS (0.00 ppm) for and relative to CDCl₃ (7.26 ppm, 77.3 ppm) for ¹H NMR and ¹³C NMR. HPLC analysis was conducted on an Agilent 1260 Series instrument. GC analysis was carried out on SHIMADZU Lab Solution using chiral capillary columns. High resolution mass spectrum was obtained on Thermo LTQ XL Orbitrap. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. Substrates **3a-3p** were synthesized according to our previously developed method ^[1]. The characterization data of compounds **4a-4p** are as the same as those reported by our previous studies ^[1].

Procedure for the synthesis of the ligands

General procedure for method A

To an oven dried Schlenk flask was added (S)-Ugi's amine (10 mmol, 2.5715 g) and 20 mL of dry Et_2O under N_2 atmosphere. The resulting solution was cooled to -78 °C and t-BuLi (11 mmol, 1.5 M in pentane, 7.6 mL) was added carefully and dropwise. After the addition, the solution was allowed to warm to room temperature (rt) and stirred for 1.5 h. The Schlenk flask was cooed to -78 °C and PCl₃ (10 mmol, 1.0 mL) was added in one portion. The suspension was allowed to warm to rt and stirred for 1.5 h. The Schlenk flask was cooled to -78 $^{\circ}$ C and (2-(diphenylphosphanyl)phenyl)lithium or (dicyclohexylphosphanyl)phenyl)-lithium (11)mmol, prepared by treating (2-bromophenyl)diphenyl-phosphane or (2-bromophenyl)dicyclohexylphosphane with n-BuLi in an 1:1.1 molar ratio under -40 °C for 1.5 h in Et₂O) was added dropwise and the resulting suspension was allowed to warm to rt and stirred for 1 h. The Schlenk flask was cooled to -78 °C again and CH₃MgCl (3.0 M in Et₂O, 3.7 mL) or an aqueous solution of NaOH (15 wt%, 10 mL) was added dropwise. The resulting suspension was allowed to warm to rt and stirred for 3 h. Water (10 mL) was added into the Schlenk flask and the solution was stirred for 10 min. The organic phase was separated and the aqueous phase was extracted by ethyl acetate (50 mL X 3). The organic phases were combined, dried and concentrated under reduced pressure. The residue was purified by column chromatography to give the desired ligands as yellow solid.

General procedure for method B

Synthesis of the intermediate **2**: To an oven dried Schlenk flask was added (*S*)-Ugi's amine (10 mmol, 2.5715 g) and 20 mL of dry Et₂O under N₂ atmosphere. The resulting solution was cooled to -78 $\$ and *t*-BuLi (11 mmol, 1.5 M in pentane, 7.6 mL) was added carefully and dropwise. After the addition, the solution was allowed to warm to room temperature (rt) and stirred for 1.5 h. The Schlenk flask was cooled to -78 $\$ and PhPCl₂ (10 mmol, 1.79 g) was added in one portion. The suspension was allowed to warm to rt and stirred for 1.5 h. The Schlenk flask was cooled to -78 $\$ and (2-bromophenyl)magnesium chloride (11 mmol, prepared by treating 1-bromo-2-iodobenzene with *i*-PrMgCl in an 1:1.1 molar ratio under -40 $\$ for 1.0 h in Et₂O) was added dropwise and the resulting suspension was allowed to warm to rt and stirred for 3 h. Water (10 mL) was added into the Schlenk flask and the solution was stirred for 10 min. The organic phase was separated and the aqueous phase was extracted by ethyl acetate (50 mL X 3). The organic phases were combined, dried and concentrated under reduced pressure. The residue was purified by column chromatography to give the intermediate **2** as yellow solid.

Synthesis of ligands L5, L9-L10 from intermediate 2

To an oven dried Schlenk flask was added intermediate **2** (3.0 mmol, 1.56 g), TMEDA (N¹, N¹, N², N²-tetramethylethane-1, 2-diamine, 3.3 mmol, 383.5 mg) and 20 mL of dry Et₂O under N₂ atmosphere. The resulting solution was cooled to -78 $^{\circ}$ C and *n*-BuLi (3.3 mmol, 2.3 M, 1.4 mL) was added dropwise. The resulting solution was stirred at -78 $^{\circ}$ C for 1 h. The corresponding phosphine chloride was added dropwise at -78 $^{\circ}$ C and the resulting solution was allowed to warm to rt and stirred for 3 h. Water (20 mL) was added into the Schlenk flask and the solution was stirred for 10 min. The organic phase was separated and the water phase was extracted by ethyl acetate (30 mL X 3). The organic phases were combined, dried and concentrated under reduced pressure. The residue was purified by column chromatography to give the desired ligands as yellow solid.

Synthesis of ligand L11

To an oven dried Schlenk flask was added (S)-Ugi's amine (5 mmol, 1.2856 g) and 10 mL of dry Et₂O under N₂ atmosphere. The resulting solution was cooled to -78 $\,^{\circ}\mathrm{C}$ and t-BuLi (5.5 mmol, 1.5 M in pentane, 3.8 mL) was added carefully and dropwise. After the addition, the solution was allowed to warm to room temperature (rt) and stirred for 1.5 h. The Schlenk flask was cooed to -78 °C and t-BuPCl₂ (10 mmol, 1.79 g) was added in one portion. The suspension was allowed to warm to rt and stirred for 1.5 -78 C h. The Schlenk flask cooled was to and (2-(diphenylphosphanyl)phenyl)lithium (5.5)mmol, prepared by treating (2-bromophenyl)diphenylphosphane with n-BuLi in an 1:1.1 molar ratio under -40 $\,^{\circ}$ C for 1.5 h in Et₂O) was added dropwise and the resulting suspension was allowed to warm to rt and stirred for 3 h. Water (10 mL) was added into the Schlenk flask and the solution was stirred for 10 min. The organic phase was separated and the aqueous phase was extracted by ethyl acetate (50 mL X 3). The organic phases were combined, dried and concentrated under reduced pressure. The residue was purified by column chromatography to give ligand L11 as yellow solid.

General procedure for asymmetric hydrogenation

In an argon-filled glove box, $[Rh(NBD)_2]BF_4$ (0.01 mmol) and Wudaphos (0.011 mmol) were dissolved in EtOH (1 mL) and stirred for 30 min. 0.1 mL of the resulting solution was transferred by syringe into the vials charged with different substrates (0.1 mmol for each). Additional EtOH was added to bring the total reaction volume to

1 mL. The vials were subsequently transferred into an autoclave which was charged with hydrogen (10 bar). The reaction was then stirred at rt for 12 h. The hydrogen gas was released slowly and carefully in a well-ventilated hood. The solution was passed through a short column of silica gel (eluent: EtOAc) to remove the metal complex and concentrated to give the hydrogenation products. The ee values were then determined by HPLC analysis on a chiral stationary phase.

Characterization data of the ligands and intermediates



L1: Yellow solid, m.p. = 125-127 °C, 58% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.21 (m, 10H), 7.17 – 7.02 (m, 3H), 6.98 – 6.89 (m, 1H), 4.393 – 4.343 (m, 3H), 4.12 (s, 5H), 4.07 (dd, J = 6.7, 2.8 Hz, 1H), 1.66 (s, 6H), 1.30 (d, J = 4.5 Hz, 3H), 1.26 (d, J = 6.3 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 134.14 (d, J = 19.5 Hz), 133.65 (d, J = 19.2 Hz), 133.33 (d, J = 6.6 Hz), 131.42 (d, J = 9.7 Hz), 128.38 (d, J =3.0 Hz), 128.35 (d, J = 16.3 Hz), 128.22, 127.46, 77.52 (d, J = 52.7 Hz), 69.71, 69.59 (d, J = 4.9 Hz), 68.06 (d, J = 2.6 Hz), 56.85, 39.68, 12.70 (dd, J = 10.2, 1.8 Hz) ppm; ³¹P NMR (162 MHz, CDCl₃): δ -16.79 (d, J = 164.5 Hz), -50.76 (d, J = 164.1 Hz) ppm.



L3: Yellow solid, m.p. = 160-163 °C, 55% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.43 – 7.35 (m, 1H), 7.13 (td, J = 7.4, 1.2 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.91 (dt, J= 6.5, 2.7 Hz, 1H), 4.43 (s, 1H), 4.40 (t, J = 2.3 Hz, 1H), 4.30 (s, 1H), 4.15 (s, 5H), 3.98 (dd, J = 6.7, 3.2 Hz, 1H), 2.09-1.82 (m, 2 H), 1.77 (s, 6H), 1.72-1.49 (m, 10H), 1.45-1.07 (m, 16H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 153.23 (dd, J = 31.9, 14.4 Hz), 137.77 (dd, J = 26.9, 14.9 Hz), 131.73, 131.14 (d, J = 8.9 Hz), 127.85, 126.43, 97.48 (d, J = 25.3 Hz), 78.08 (dd, J = 14.3, 12.0 Hz), 70.22 (dd, J = 4.6, 2.6 Hz), 69.68, 68.34, 60.44, 56.77 (d, J = 8.4 Hz), 40.31, 36.26 (dd, J = 13.8, 3.0 Hz), 33.97 (dd, J = 12.5, 5.1 Hz), 30.82 – 30.48 (m), 30.28 (d, J = 11.7 Hz), 28.72 (d, J = 5.6 Hz), 27.40 (dd, J = 7.5, 2.8 Hz), 27.34 (d, J = 41.4 Hz), 27.25, 26.49 (d, J = 7.2 Hz), 21.11, 14.24, 13.49 (dd, J = 10.1, 5.9 Hz), 11.81 ppm; ³¹P NMR (162 MHz, CDCl₃): δ -13.73 (d, J = 147.0 Hz), -48.37 (d, J = 147.1 Hz) ppm.



L8: Yellow solid, m.p. = 207-210 °C, 38% yield. $[\alpha]_D^{20} = +151.6$ (c 0.5, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 8.58 (d, J = 517.9 Hz, 1H), 7.62 – 7.48 (m, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 4.50 (s, 1H), 4.43 (s, 1H), 4.38 (d, J = 1.7Hz, 1H), 4.34 (s, 5H), 4.05 (dd, J = 13.2, 6.6 Hz, 1H), 2.15 – 2.06 (m, 1H), 2.03 – 1.88 (m, 2H), 1.85 – 1.43 (m, 15H), 1.38 – 1.03 (m, 13H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 139.14 (dd, J = 23.4, 11.3 Hz), 132.51-132.15 (m), 130.05, 127.87 (d, J =11.9 Hz), 74.16 (dd, J = 10.5, 4.6 Hz), 72.01, 70.89, 70.41, 70.35 (d, J = 11.7 Hz), 69.03 (d, J = 11.0 Hz), 57.40, 39.37, 35.59 (d, J = 14.3 Hz), 33.59 (d, J = 11.9 Hz), 30.43 (d, J = 14.1 Hz), 30.22, 30.06 (d, J = 7.6 Hz), 29.12 (d, J = 6.1 Hz), 27.53, 27.44 (d, J = 6.1 Hz), 27.00 (dd, J = 10.5, 6.4 Hz), 26.35 (d, J = 11.8 Hz), 8.77 ppm; ³¹P NMR (162 MHz, CDCl₃): δ 14.87 (d, J = 66.8 Hz), -14.29 (d, J = 66.6 Hz) ppm.



L9: Yellow solid, m.p. = 60-65 °C, 80% yield. $[\alpha]_D^{20} = +214.0$ (c 0.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.59 (m, 2H), 7.38 – 7.37 (m, 3H), 7.21-7.20 (m, 4H), 4.39 (s, 1H), 4.20-4.13 (m, 5H), 3.87 (s, 1H), 3.59 (s, 1H), 1.93-1.55 (m, 18H), 1.30-1.06 (m, 12H), 0.89-0.82 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 140.92 (d, *J* = 7.2 Hz), 139.01 (d, *J* = 9.4 Hz), 135.28 (d, *J* = 21.1 Hz), 132.50 (d, *J* = 18.9 Hz), 128.89, 128.07 (d, *J* = 7.5 Hz), 127.51 (d, *J* = 6.8 Hz), 127.32, 77.21, 77.15, 77.12, 74.47 (d, *J* = 18.4 Hz), 73.59 (d, *J* = 4.1 Hz), 73.46 (d, *J* = 5.5 Hz), 72.38, 71.66, 71.34, 71.12 (dd, *J* = 13.4, 3.5 Hz), 57.40 (d, *J* = 6.3 Hz), 39.03, 34.06 (d, *J* = 12.5 Hz), 33.27 (d, *J* = 10.5 Hz), 31.23 (d, *J* = 14.6 Hz), 30.85 (d, *J* = 15.0 Hz), 29.98 (d, *J* = 11.0 Hz), 29.68 (d, *J* = 7.3 Hz), 27.72-27.44 (m), 26.61 ppm; ³¹P NMR (162 MHz, CDCl₃): δ -7.99 (s), -23.44 (s) ppm. HRMS (ESI) calculated for C₃₈H₅₀NFeP₂⁺ [M + H⁺]: 638.2762; found: 638.2745.



L10: Yellow solid, m.p. = 113-118 °C, 43% yield. $[\alpha]_D^{20} = +179.0$ (c 0.2, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.61-7.57 (m, 2H), 7.35 – 7.34 (m, 3H), 7.19 – 7.18 (m, 5H), 4.38 (s, 1H), 4.22 – 4.15 (m, 5H), 3.85 (s, 1H), 3.67 (s, 1H), 1.75 (s, 6 H), 1.26 – 1.25 (m, 3H), 1.13 (d, *J* = 11.4 Hz, 9H), 1.01 (d, *J* = 11.1 Hz, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 140.95 (d, *J* = 6.2 Hz), 139.07 (d, *J* = 9.6 Hz), 135.43 (d, *J* = 21.3 Hz), 132.55 (d, *J* = 19.0 Hz), 128.98, 128.17 (d, *J* = 7.5 Hz), 127.57 (d, *J* = 6.9 Hz), 127.38, 77.50, 77.17, 75.78 (d, *J* = 21.6 Hz), 74.35 (d, *J* = 5.7 Hz), 72.90, 72.83, 72.52, 72.07, 71.45, 57.44, 39.03, 32.84 (dd, *J* = 51.2, 20.0 Hz), 30.96 (dd, *J* = 63.7, 13.2 Hz) ppm; ³¹P NMR (162 MHz, CDCl₃): δ 27.13 (s), -23.36 (s) ppm. HRMS (ESI) calculated for C₃₄H₄₆NFeP₂⁺ [M + H⁺]: 586.2449; found: 586.2435.



L11: Yellow solid, m.p. = 148-150 °C, 33% yield. $[\alpha]_D^{20}$ = -349.8 (c 0.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.47 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 7.31 – 7.22 (m, 6H), 7.19 – 7.13 (m, 1H), 7.10 – 7.04 (m, 2H), 4.54 (dd, J = 2.3, 1.2 Hz, 1H), 4.41 (s, 1H), 4.34 (t, J = 2.3 Hz, 1H), 4.19 (s, 5H), 2.62 (q, J = 6.6 Hz, 1H), 1.53 (s, 6H), 1.31 (d, J = 11.8 Hz, 9H), 1.22 (d, J = 6.7 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 146.45 (dd, J = 34.7, 21.0 Hz), 143.52 (dd, J = 32.0, 11.3 Hz), 139.53 (dd, J = 14.7, 7.3 Hz), 138.72 (dd, J = 14.9, 3.0 Hz), 136.20 (dd, J = 7.3, 2.4 Hz), 134.82 (dd, J = 6.6, 1.9 Hz), 134.65 (d, J = 20.4 Hz), 133.44 (d, J = 18.3 Hz), 99.32 (d, J = 16.6 Hz), 76.59 (dd, J = 23.6, 9.2 Hz), 70.32, 69.85, 69.62 (d, J = 3.0 Hz), 67.18, 56.97 (d, J = 4.9 Hz), 42.20, 32.60 (d, J = 16.0 Hz), 30.05 (dd, J = 12.9, 3.1 Hz), 18.13 ppm; ³¹P NMR (162 MHz, CDCl₃): δ -9.77 (d, J = 157.6 Hz), -15.72 (d, J = 157.5 Hz) ppm. HRMS (ESI) calculated for C₃₆H₄₂NFeP₂⁺ [M + H⁺]: 606.2136; found: 606.2122.

Methods for the determination of the ee for the asymmetric

hydrogenation of the standard substrates

Products	Methods
	Determined by chiral GC analysis on Chiral β -dex 225 column.
	Conditions: Gasify room temerature = 220 °C, column temperature =
	70-210 °C (hold at 70 °C for 5 min, increase the temperature at the
	rate of 6 °C/min, and hold at 210 °C for 5 min), detector temperature
	= 230 °C, N ₂ flow rate = 1.0 mL/min, t_R = 19.6 min (minor), 20.0 min
	(major).
COOMe	Determined by chiral GC analysis on Chiral β -dex 225 column.
MeOOC [*]	Conditions: Gasify room temerature = 250 °C, column temperature =

	80-120 °C (increase the temperature at the rate of 2 °C/min), detector
	temperature = 260 °C, N ₂ flow rate = 1.0 mL/min, t_R = 13.8 min
	(major), 14.1 min (minor).
COOMe	Determined by chiral GC analysis on Chiral β -dex 225 column after
HOOC ~	esterification with CH_2N_2 . Conditions: Gasify room temerature = 250
	°C, column temperature = 80-120 °C (increase the temperature at the
	rate of 2 °C/min), detector temperature = 260 °C, N ₂ flow rate = 1.0
	mL/min, $t_R = 13.8 \text{ min}$ (major), 14.1 min (minor).
NHAc	Determined by chiral HPLC analysis on Chiralpak OJ-H column.
COOMe	Conditions: hexane/isopropanol = 80:20, flow rate = 1.0 mL/min,
	uv-vis detection at $\lambda = 210$ nm, $t_{\rm R} = 7.1$ min (minor), 9.6 min (major).
г~~*_соон	Determined by chiral HPLC analysis on Chiralpak OJ-H column after
	esterification with CH_2N_2 . Conditions: hexane/isopropanol = 99:1,
	flow rate = 1.0 mL/min, uv-vis detection at λ = 220 nm, $t_{\rm R}$ = 6.8 min
	(minor), 7.6 min (major).
*	Determined by chiral HPLC analysis on Chiralpak OJ-H column after
Соон	esterification with CH_2N_2 . Conditions: hexane/isopropanol = 99 :1,
	flow rate = 1.0 mL/min, uv-vis detection at λ = 205 nm, t _R = 15.0 min
	(major), 18.9 min (minor).







S11







S14



S15

HPLC and GC Spectra

	========					=	
Acq. Operator :	SYSTEM			Seq. Line	: 8		
Acq. Instrument :	1260HPL	C-DAD		Location	: Vial 80		
Injection Date :	11/7/20	15 2:31:30 E	M	Inj	: 1		
				Inj Volume	: 5.000 µl	-	
Acq. Method :	E:\DATA	\WB\WEIB-201	51107\DAD-C	J1-2-90-10 45MIN.M	-WB-2015110	07-2 2015-11-07 11-12-35	ō
Last changed :	11/7/20	15 12:28:53	PM by SYSTE	M			
Analysis Method :	E.\DATA	\WB\WEIB-201	51107\DAD-0	T1-2-90-10	-WB-2015110	17-2 2015-11-07 11-12-35	5
indiyoto neenoa .		(1-6) - 95 - 5 - 1	OML-ALLNM-	45MIN M (S	equence Met	(hod)	, ,
Last changed :	8/16/20	16 3:17:53 E	PM by SYSTEM	 	equence net		
Additional Info .	(modifiered)	ed after loa	ding)				
DAD1 G. Sig=20)5.4 Ref=off (E	:\DATA\WB107\D	AD-0J1-2-90-10-W	/B-20151107-2 2	015-11-07 11-12-35	5\080-0801.D)	
mAU					2	····· ····,	
					1 <u>7.</u> 8		
	0 I					800	
200	人人					21.	
	ſ	СООН				Λ	
	, 4a						
450							
150 -	rac						
-							
100 -							
-	k						
- -							
50-							
-							
0							
0	5		10	15	20	25	min
						=	
		Area Percent ======	Report			-	
Sorted By		Signal					
Multiplier		1.0000					
Dilution		1 0000					
Do not use Multin	lier & D	ilution Fact	or with TOT	De			
Do not use Multip	TTEL & D	IIUCION FACE	OI WICH ISI	05			
Signal 1: DAD1 G.	Sig=205	.4 Ref=off					
	229 200	, - 1.01 011					
Peak RetTime Ture	Width	Area	Height	Area			
# [min]	[min]	[m]]Ita]	[mail]	Alea			
# [min]	[min]	[IIIAU^S]		ۍ ۱			
	0 4450	7206 02441	236 26070	50 0460			
I I/.891 BB	0.4458	7206.02441	230.269/6	50.0469			
7 71.800 BB	0.5434	1192.52832	194.51363	49.9531			
Totals :		1.43986e4	430.78339				
						=	

*** End of Report ***

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\021-0201.D Sample Name: ccy-7-14-1

Data File E:\DATA\CCY\CCY-6-133\CCY-6-133 2015-11-28 10-55-00\023-0401.D Sample Name: ccy-6-133-3

*** End of Report ***

S20

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\022-1101.D Sample Name: ccy-7-14-2

Totals: 6344.23053 54.44329

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\026-0601.D Sample Name: ccy-7-14-6

Totals: 1357.31158 44.18303

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\027-0701.D Sample Name: ccy-7-14-7

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\028-0801.D Sample Name: ccy-7-14-8

Totals: 2781.59279 76.69164

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\029-0901.D Sample Name: ccy-7-14-9

S30

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\030-1001.D Sample Name: ccy-7-14-10

Totals: 1508.56238 26.36496

S32

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\032-1201.D Sample Name: ccy-7-14-12

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\023-0301.D Sample Name: ccy-7-14-3

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\024-0401.D Sample Name: ccy-7-14-4

Data File E:\DATA\CCY\CCY-7-11-14\CCY-6-13-14 2016-04-15 07-56-48\025-0501.D Sample Name: ccy-7-14-5

Data File E:\DATA\CCY\CCY-7-99\CCY-7-99 2016-06-25 13-00-00\081-0201.D Sample Name: ccy-7-99-1

1260HPLC-DAD 9/5/2016 8:53:00 PM SYSTEM

Data File E:\DATA\WSW\WSW-2-90A\WSW-2-90A 2017-06-29 15-04-22\043-0401.D Sample Name: wsw-2-90-1-3

Acq. Operator : S	SYSTEM Seq. Line : 4
Acq. Instrument : 1	1260HPLC-DAD Location : Vial 43
Injection Date : 6	6/29/2017 4:20:08 PM Inj : 1
	Inj Volume : 10.000 µl
Acq. Method : E	E:\DATA\WSW\WSW-2-90A\WSW-2-90A 2017-06-29 15-04-22\DAD-0J(1-6)-99-1-10UL-
1	IML-30MIN.M
Last changed : 6	5/29/2017 3:04:23 FM by SISTEM
Analysis Mechou : E	S: (DAIA(WSW/WSW-2-30A(WSW-2-30A 2017-08-23 13-04-22(DAD-08(1-8)-33-1-100D- IML-30MIN M (Sequence Method)
Last changed : 6	5/29/2017 6:24:28 PM by SYSTEM
((modified after loading)
Additional Info : P	Peak(s) manually integrated
DAD1 C, Sig=210,4	4 Ref=360,100 (E:\DATA\WSW\WSW-2-90A\WSW-2-90A 2017-06-29 15-04-22\043-0401.D)
mAU	
	E
2000 1 1 54	m
949	
	4
1500 -	0 0
-	Ň
-	
1000 -	
-	
500	
-	ß
	8
0	
15 16	17 18 19 20 21 22 23 24 min
	Juca Depart Depart
	Area reicent report
Sorted By	: Signal
Multiplier	: 1.0000
Do not use Multipli	: 1.0000
Do not use Marcipii	
Signal 1: DAD1 C, S	3ig=210,4 Ref=360,100
Peak RetTime Type	Width Area Height Area
# [min]	[min] [mAU*s] [mAU] %
-	
1 18.205 BV	0.3359 2096.53223 94.82519 3.2091
2 20.024 BV	0.5613 6.32348e4 1409.76868 96.7909

1260HPLC-DAD 6/29/2017 6:24:35 PM SYSTEM

Data File E:\DATA\CCY\CCY-7-130-131\CCY-7-130-131 2016-07-16 15-36-28\030-0301.D Sample Name: CCY-7-131-2

Acq. Operator	: SYSTEM Seq. Line : 3
Acq. Instrument	: 1260HPLC-DAD Location : Vial 30
Injection Date	: 7/16/2016 4:34:29 PM Inj : 1
	Inj Volume : 5.000 µl
Acq. Method	: E:\DATA\CCY\CCY-7-130-131\CCY-7-130-131 2016-07-16 15-36-28\DAD-0J(1-6)-99-
	1-1.0ML-5UL-45MIN-ALL.M
Last changed	: 7/16/2016 4:56:46 PM by SYSTEM
	(modified after loading)
Analysis Method	: E:\DATA\CCY\CCY-7-130-131\CCY-7-130-131 2016-07-16 15-36-28\DAD-0J(1-6)-99-
	1-1.0ML-5UL-45MIN-ALL.M (Sequence Method)
Last changed	: 9/3/2016 4:25:47 PM by SYSTEM
	(modified after loading)
Additional Info	: Peak(s) manually integrated
DAD1 B, Sig	=210,4 Ref=off (E:\DATA\CCY\CCY-7-130-131\CCY-7-130-131 2016-07-16 15-36-28\030-0301.D)
mAU C	
l i i i	
700	COOBn
	6
600	
	Λ β
1	
500	$\langle \rangle$
400 -	
1	
-	
300 -	
200	
200	
100 -	
-	
9	10 11 12 13 14 mi
	Area Percent Report
Sorted By	: Signal
Multiplier	: 1.0000
Dilution	: 1.0000
Use Multiplier	& Dilution Factor with ISTDs
Signal 1: DAD1	B, Sig=210,4 Ref=off
1983	a an of
Peak RetTime Ty	pe Width Area Height Area
# [min]	[min] [mAU*s] [mAU] %
1 10.307 BB	0.2177 8224.67969 579.01904 49.9209
2 12.250 BB	0.2535 8250.75488 497.45221 50.0791
D	
Totals .	1.64754e4 1076.47125
TOCATO .	1.51.0101 FUELD

1260HPLC-DAD 9/3/2016 4:26:05 PM SYSTEM

Data File E:\DATA\WSW\WSW-2-90\WSW-2-90 2017-06-29 00-59-19\047-0801.D Sample Name: WSW-2-90-4A

1260HPLC-DAD 6/29/2017 8:54:06 AM SYSTEM

Data File E:\DATA\WWL\WWL-3-175-1\WWL-3-175-1 2016-06-27 22-45-34\031-0601.D Sample Name: ccy-7-99-2

1260HPLC-DAD 9/3/2016 9:00:57 PM SYSTEM

Data File E:\DATA\WSW\WSW-2-90\WSW-2-90 2017-06-29 00-59-19\045-0601.D Sample Name: WSW-2-90-3A

1260HPLC-DAD 6/29/2017 9:00:56 AM SYSTEM

Totals :

Page 1 of 2

4.65585e4 704.65790

Data File E:\DATA\WWL\WWL-3-175-1\WWL-3-175-1 2016-06-27 22-45-34\032-0701.D Sample Name: ccy-7-99-3

1260HPLC-DAD 9/3/2016 5:27:43 PM SYSTEM

Data File E:\DATA\WSW\WSW-2-90\WSW-2-90 2017-06-29 00-59-19\043-0401.D Sample Name: WSW-2-90-2A

1260HPLC-DAD 6/29/2017 9:06:14 AM SYSTEM

References

 C. Chen, Z. Zhang, S. Jin, X. Fan, M. Geng, Y. Zhou, S. Wen, X. Wang, L. W. Chung, X.-Q. Dong, X. Zhang, *Angew. Chem. Int. Ed*, **2017**, *56*, 6808-6812.