

# Supplementary Material

Cellulose modified with BINAP support Rh as an efficient heterogeneous catalyst for asymmetric hydrogenation

Cuiping Yu<sup>1</sup>, Weilong Wu<sup>2</sup>, Min Gao,<sup>1\*</sup> Yu Liu<sup>1\*</sup>

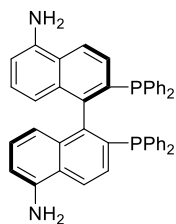
1 State key Laboratory of Bio-based Material and Green Papermaking, Qilu University of Technology, Jinan, Shandong, 250353, PR China

2 College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, 471934, P. R. of China

Corresponding Author:

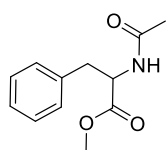
\*E-mail: leoliuyu@163.com (Yu Liu); shdgaomin@whu.edu.cn (Min Gao)

## NMR spectra



### *R*-5,5'-diamino Binap:

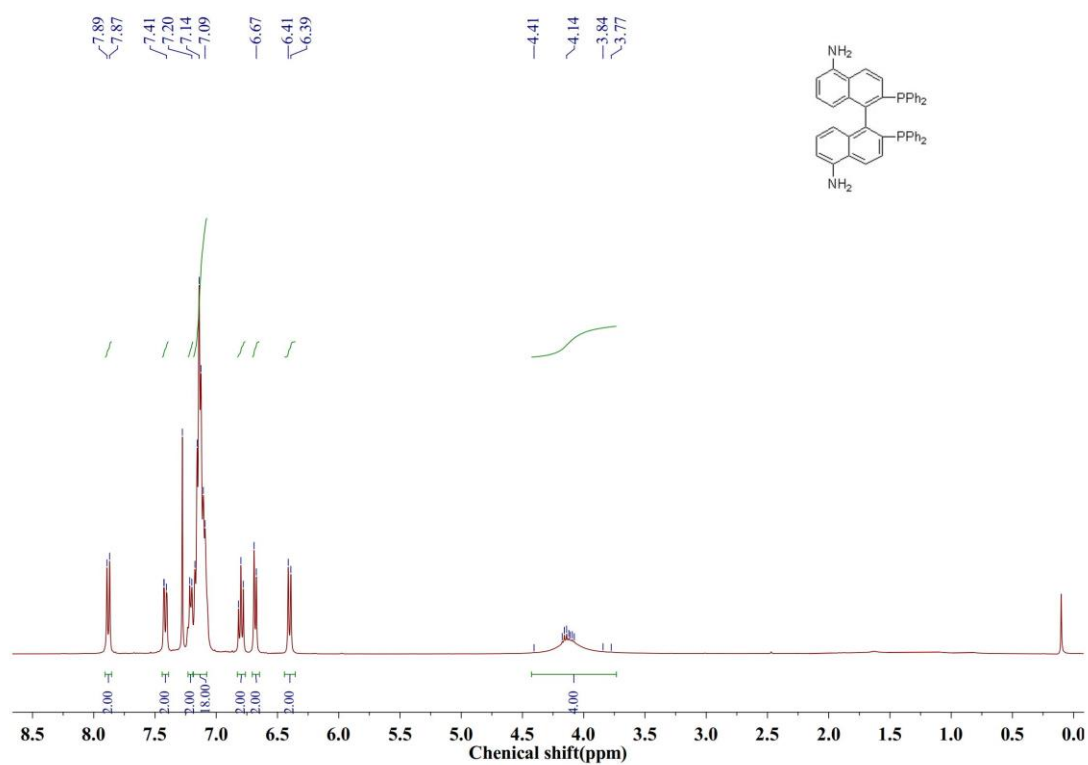
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.7$  Hz, 2H), 7.44 – 7.39 (m, 2H), 7.21 (d,  $J = 6.7$  Hz, 2H), 7.13 (td,  $J = 13.6, 6.6$  Hz, 18H), 6.80 (t,  $J = 7.9$  Hz, 2H), 6.68 (d,  $J = 7.3$  Hz, 2H), 6.40 (d,  $J = 8.4$  Hz, 2H), 4.43 – 3.73 (m, 4H).



### methyl acetylphenylalaninate:

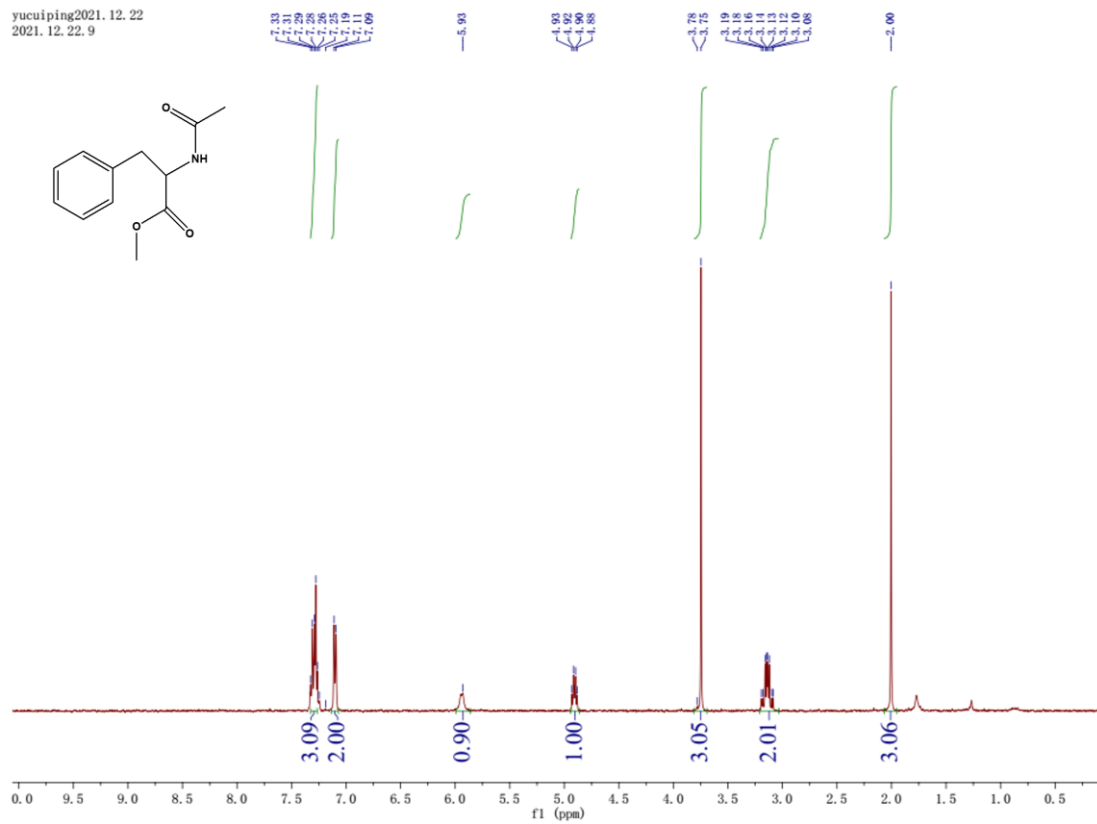
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.26 (m, 3H), 7.10 (d,  $J = 6.7$  Hz, 2H), 5.93 (s, 1H), 4.91 (dd,  $J = 13.5, 5.8$  Hz, 1H), 3.75 (s, 3H), 3.14 (qd,  $J = 13.9, 5.7$  Hz, 2H), 2.00 (s, 3H).

## NMR spectra of *R*-5,5'-diamino Binap

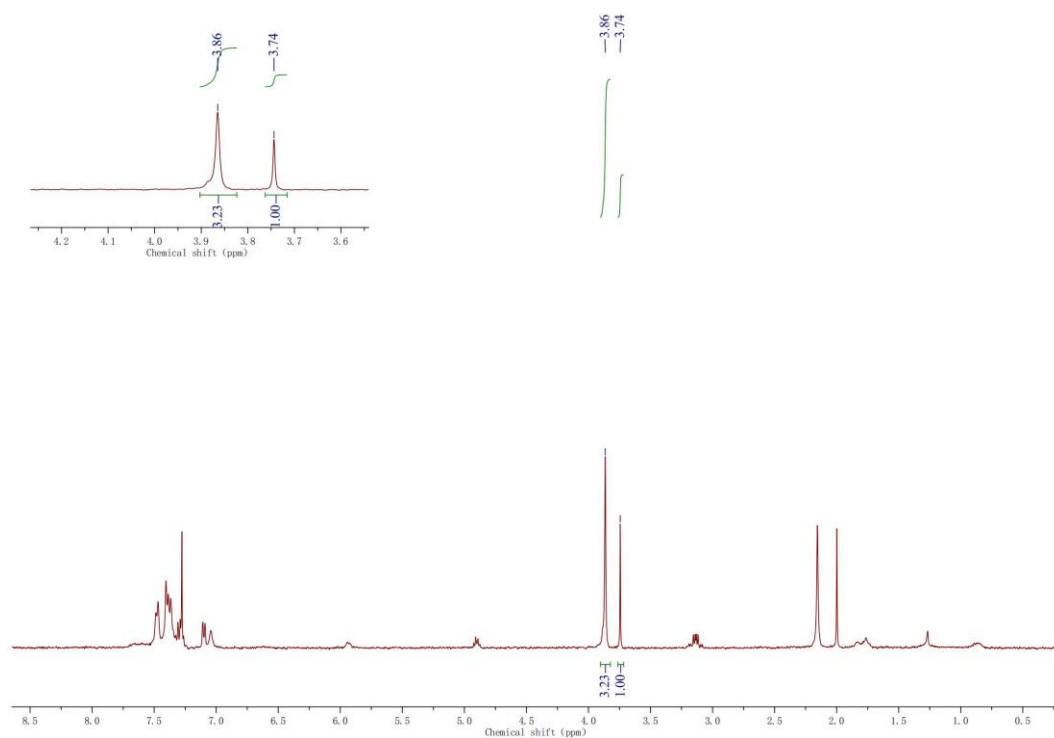


## NMR spectra of methyl acetylphenylalaninate

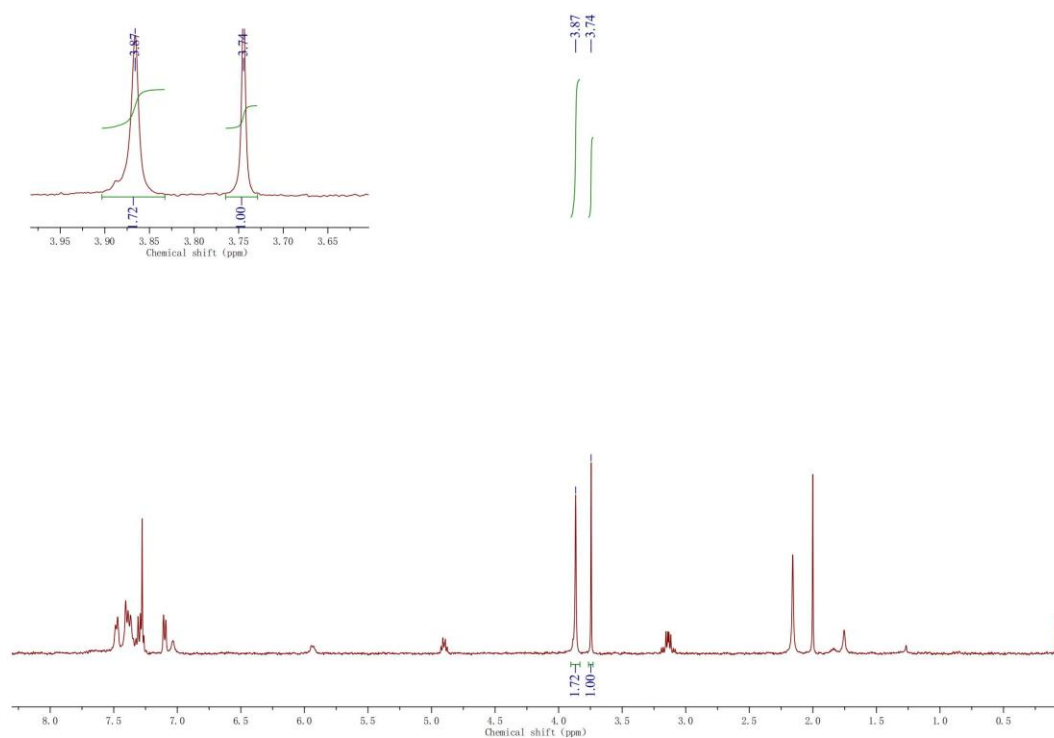
yucuiping2021.12.22  
2021.12.22.9



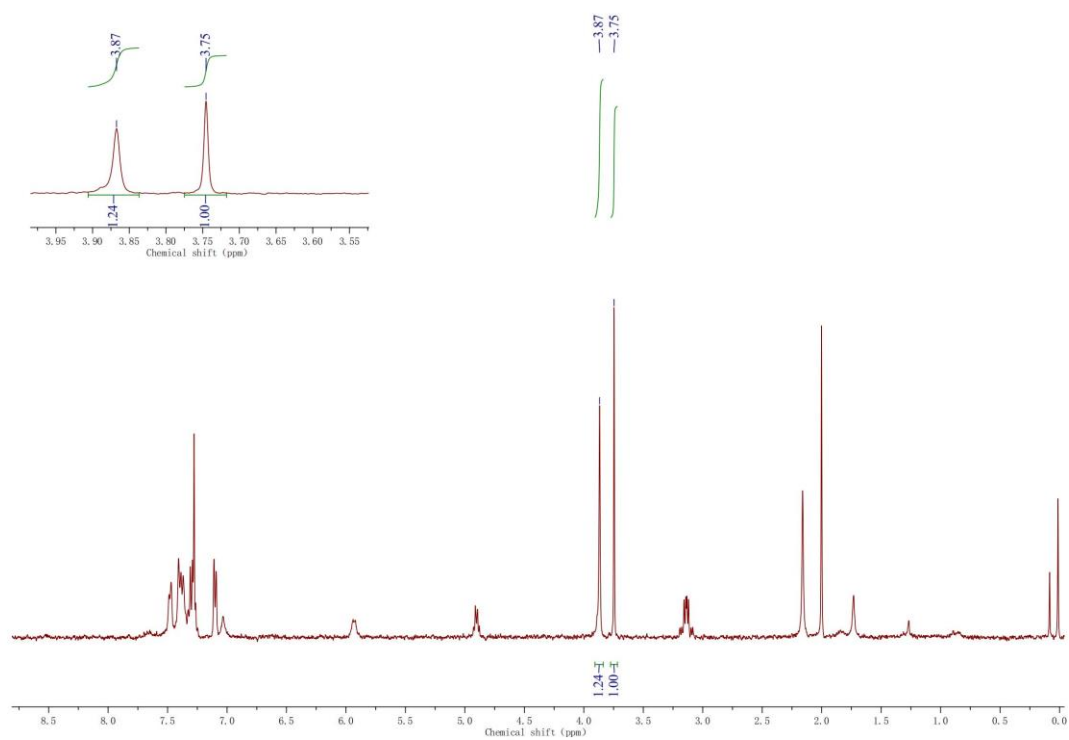
## NMR spectra of 23% conversion



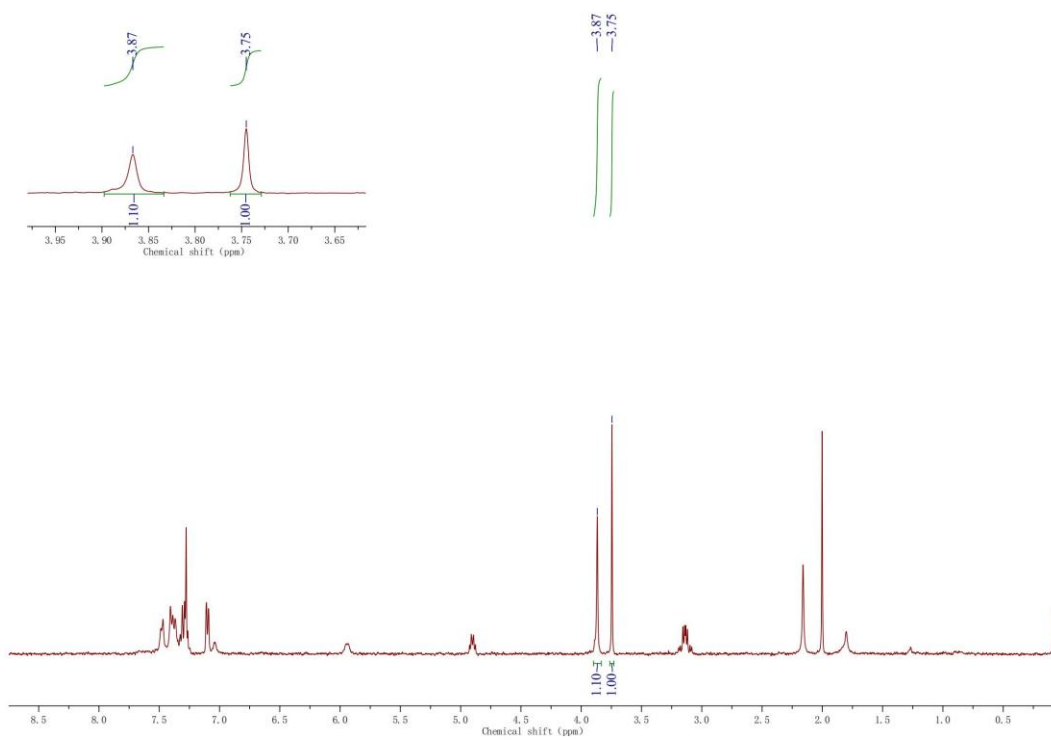
## NMR spectra of 37% conversion



## NMR spectra of 45% conversion

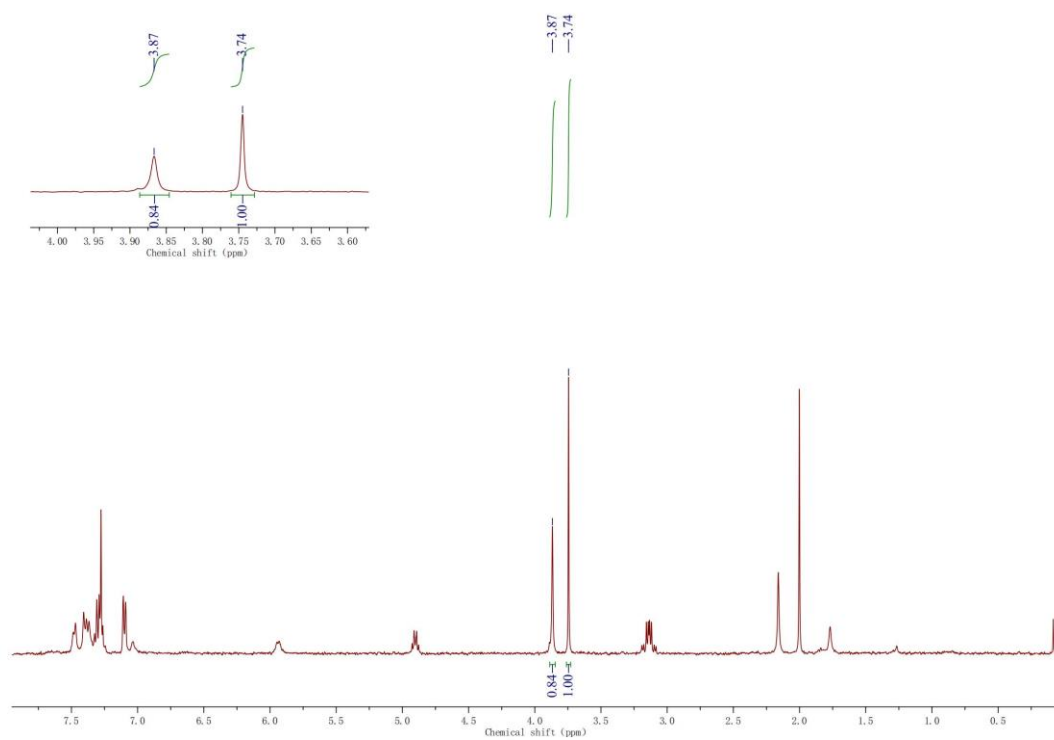


## NMR spectra of 48% conversion

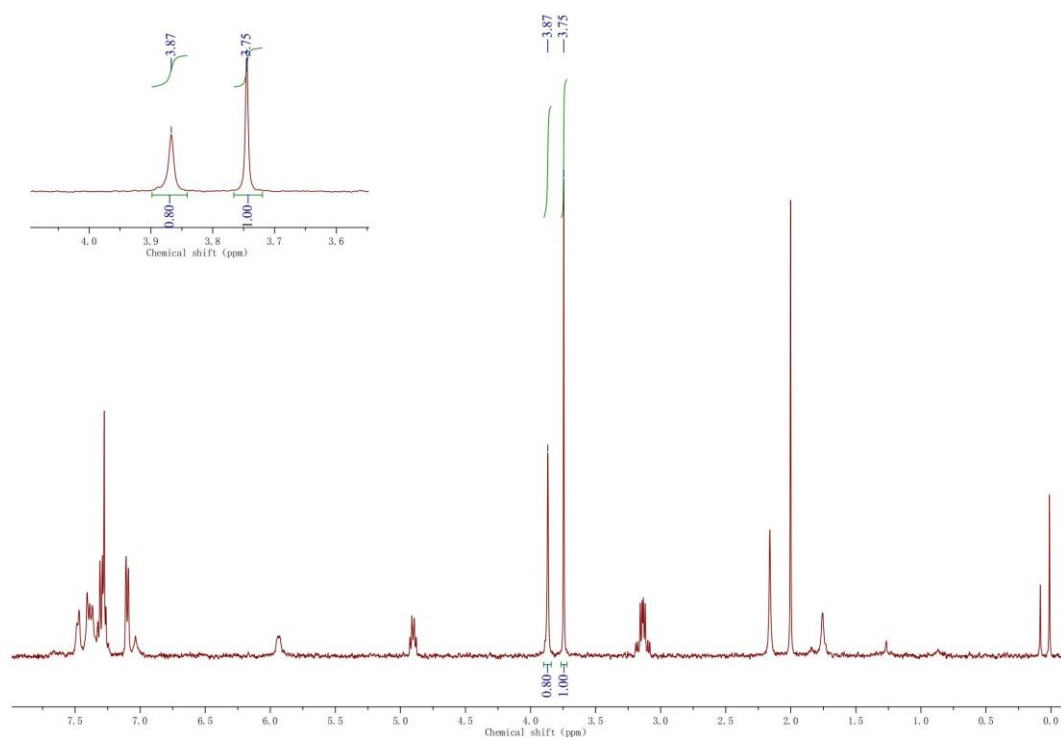




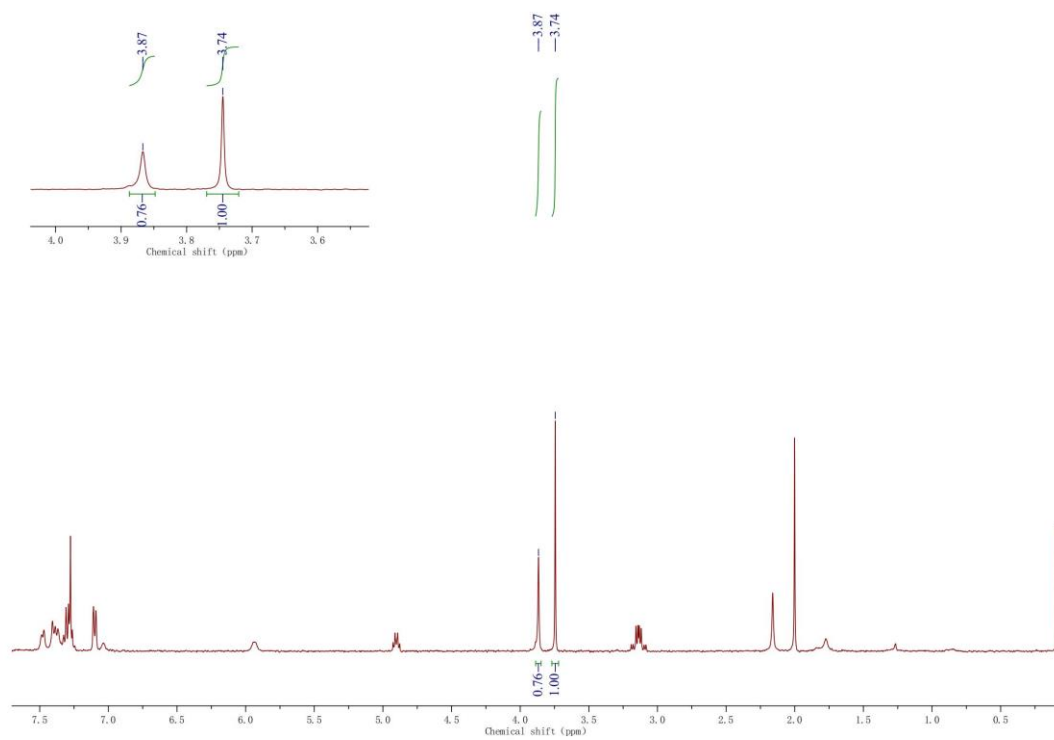
## NMR spectra of 54% conversion



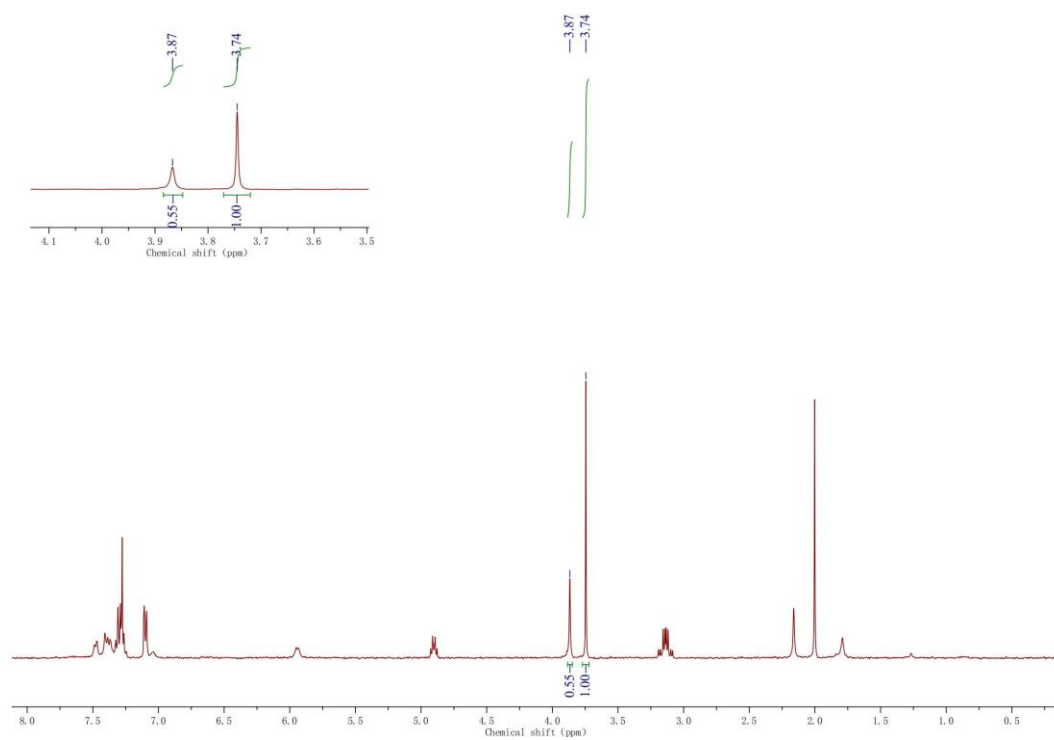
## NMR spectra of 56% conversion



## NMR spectra of 57% conversion



## NMR spectra of 65% conversion



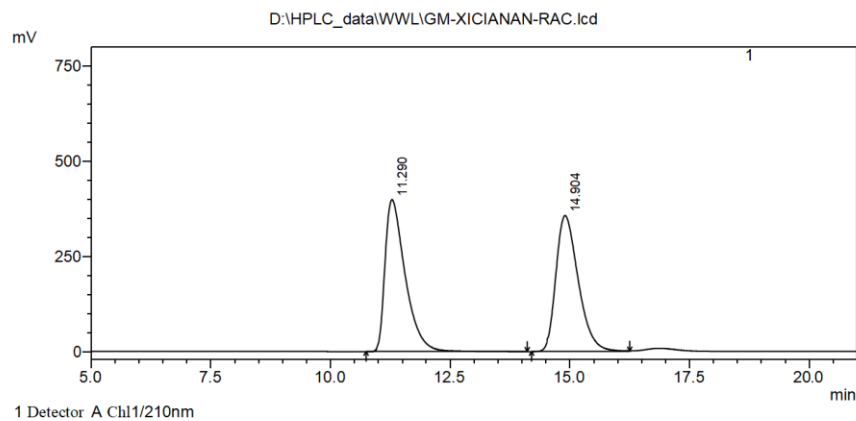
## HPLC spectra of Table 1

### Racemate

2021-9-9 17:30:51 1 / 1

#### ==== Shimadzu LCsolution analysis report ====

Acq.Operator : Admin  
Acq.Instrument : GM-XICIANAN-RAC  
Acq.ID :  
Acq. : 1  
Seq.Line# : 3  
Inj Volume. : 5 uL  
Sample name : GM-XICIANAN-RAC.lcd  
Acq.Method. : wwl-90-10-210-1-30min-OD.lcm  
Data Collection : 2021 3-30 16:13:41  
Data Processing : 2021 3-30 16:43:44



#### Area Percent Report

Peak#	RetTime	Area	Area %
1	11.290	11681852	50.402
2	14.904	11495525	49.598
Totals		23177377	100.000

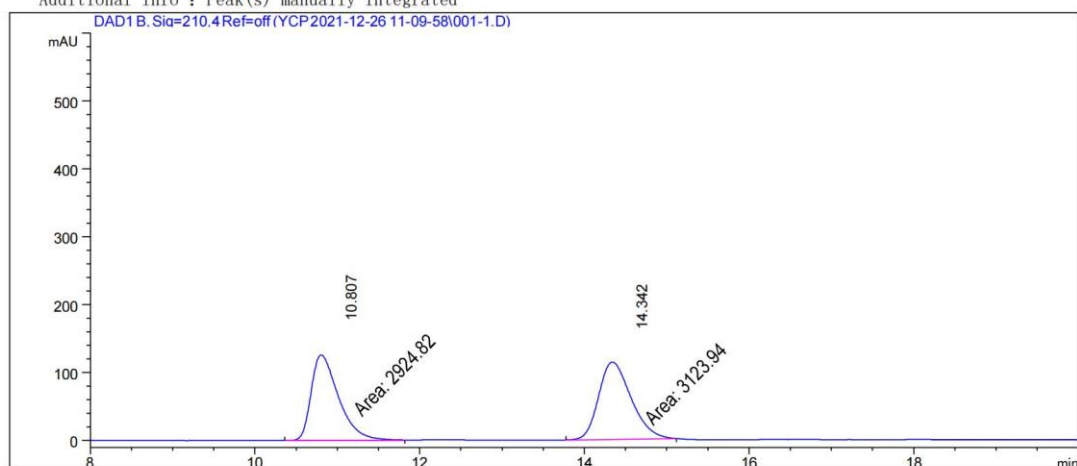
D:\HPLC\_data\WWL\GM-XICIANAN-RAC.lcd

## Table 1-entry1

Date File: d:\Chem32\1\Data\YCP 2021-12-26 11-09-58\001-1.D

Sample Name: 20211226YCP-1

```
=====
Acq. Operator   : Admin
Acq.           : 1
Instrument      : 1260
Entry date     : 2021/12/26 11:11:26
Inj            : 1
Inj Volume.    : 5.000 µl
Acq. Method.   : d:\Chem32\1\Data\YCP 2021-12-26 11-09-58\YCP.M
Analysis Method : d:\Chem32\1\Data\YCP 2021-12-26 11-09-58\YCP.M
                (Sequence Method)
Last Changed   : 2021/12/26 11:12:15 : AM by SYSTEM(modified
                after loading)
Additional Info : Peak(s) manually integrated
```



### Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
DO not use Multiplier & Dilution Factor with ISTDs
signal 1: DAD1 B, Sig=210,4 Ref=off
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.807	MM	0.3871	2924.82104	125.93480	48.3541
2	14.342	MM	0.4572	3123.93994	113.88740	51.6459

Totals : 6048.76099 239.82220

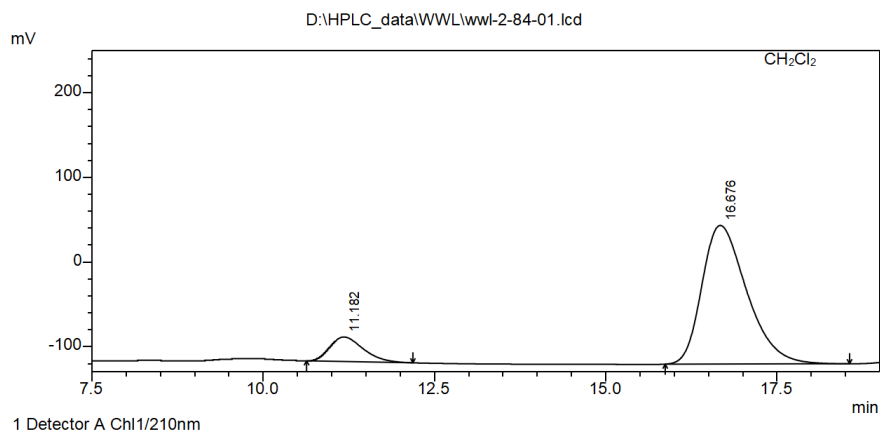
\*\*\* End of Report \*\*\*

## Table 1-entry2

2021-9-9 16:16:03 1 / 1

### ==== Shimadzu LCsolution analysis report ====

Acq.Operator : Admin  
 Acq.Instrument : wwl-2-84-01  
 Acq.ID :  
 Acq. : 1  
 Seq.Line# : 2  
 Inj Volume : 2 uL  
 Sample name : wwl-2-84-01.lcd  
 Acq.Method : wwl-90-10-210-1-25min-OD.lcm  
 Data Collection : 2021 9-5 14:39:46  
 Data Processing : 2021 9-5 15:04:48



Area Percent Report

Peak#	RetTime	Area	Area %
1	11.182	987850	11.677
2	16.676	7471666	88.323
Totals		8459517	100.000

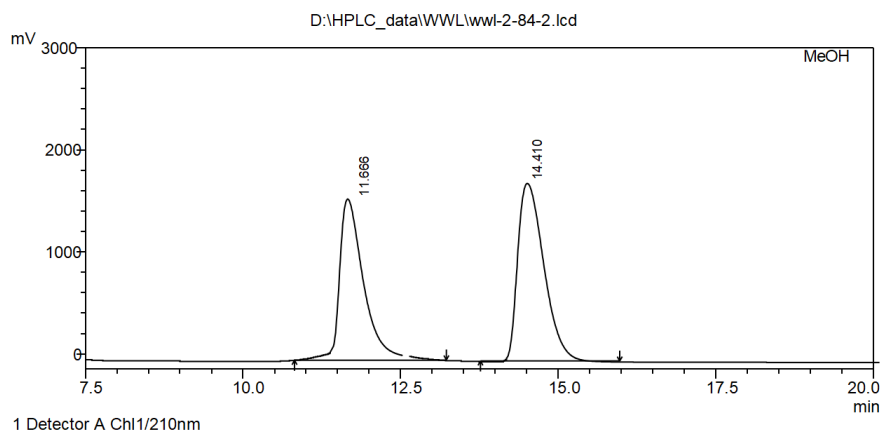
D:\HPLC\_data\WWL\wwl-2-84-01.lcd

## Table 1-entry3

2021-9-9 16:30:45 1 / 1

### ==== Shimadzu LCsolution analysis report ====

Acq.Operator : Admin  
Acq.Instrument : wwl-2-84-2  
Acq.ID :  
Acq. : 1  
Seq.Line# : 3  
Inj Volume. : 5 uL  
Sample name : wwl-2-84-01.lcd  
Acq.Method : wwl-90-10-210-1-25min-OD.lcm  
Data Collection : 2021 9-4 16:15:34  
Data Processing : 2021 9-9 16:19:42



#### Area Percent Report

Peak#	RetTime	Area	Area%
1	11.666	42076576	45.347
2	14.410	50711834	54.653
Totals		92788411	100.000

D:\HPLC\_data\WWL\wwl-2-84-2.lcd

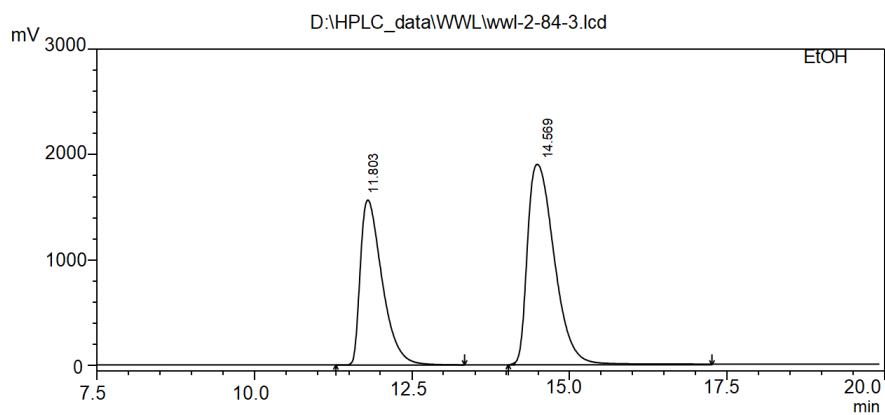


# Table 1-entry4

2021-9-9 16:32:52 1 / 1

## ==== Shimadzu LCsolution analysis report ====

Acq.Operator : Admin  
 Acq.Instrument : wwl-2-84-3  
 Acq.ID :  
 Acq. : 1  
 Seq.Line# : 4  
 Inj Volume : 5 uL  
 Sample name : wwl-2-84-3.lcd  
 Acq.Method : wwl-90-10-210-1-25min-OD.lcm  
 Data Collection : 2021 9-4 16:40:59  
 Data Processing : 2021 9-4 17:06:02



1 Detector A Ch11/210nm

### Area Percent Repc

Peak#	RetTime	Area	Area%
1	11.803	37669700	40.336
2	14.569	55720684	59.664
Totals		93390384	100.000

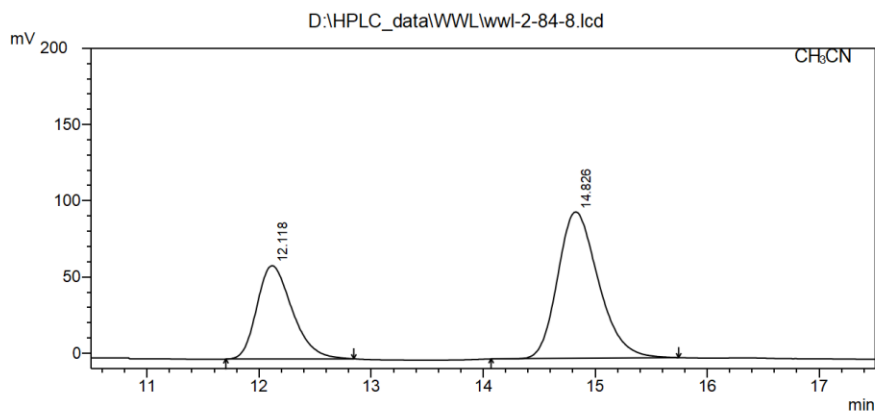
D:\HPLC\_data\WWL\wwl-2-84-3.lcd

# Table 1-entry5

2021-9-9 16:54:25 1 / 1

## ==== Shimadzu LCsolution analysis report ====

采集人 : Admin  
 样品名称 : ww1-2-84-8  
 样品 ID :  
 样品架 : 1  
 样品瓶# : 9  
 进样体积 : 2 uL  
 数据文件名 : ww1-2-84-8.lcd  
 方法文件名 : ww1-90-10-210-1-25min-OD-td.lcm  
 批处理文件名 : ww1-gm01-2-84.lcb  
 报告文件名 : Default.lcr  
 数据采集 : 2021 9-5 15:56:08  
 数据处理 : 2021 9-5 16:21:11  
 Acq.Operator : Admin  
 Acq.Instrument : ww1-2-84-8  
 Acq.ID :  
 Acq. : 1  
 Seq.Line# : 9  
 Inj.Volume : 5 uL  
 Sample name : ww1-2-84-8.lcd  
 Acq.Method : ww1-90-10-210-1-25min-OD.lcm  
 Data Collection : 2021 9-5 15:56:08  
 Data Processing : 2021 9-5 16:21:11



### Area Percent Report

Peak#	RetTime	Area	Area%
1	12.118	1341924	35.560
2	14.826	2431734	64.440
Totals		3773658	100.000

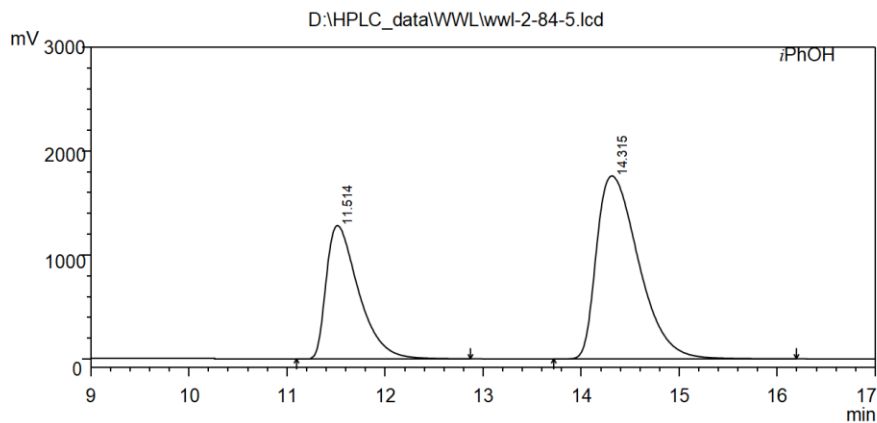
D:\HPLC\_data\WWL\ww1-2-84-8.lcd

# Table 1-entry6

2021-9-9 16:45:55 1 / 1

## ==== Shimadzu LCsolution analysis report ====

Acq.Operator : Admin  
 Acq.Instrument : wwl-2-84-3  
 Acq.ID :  
 Acq. : 1  
 Seq.Line# : 6  
 Inj Volume. : 5 uL  
 Sample name : wwl-2-84-5.lcd  
 Acq.Method. : wwl-90-10-210-1-25min-OD.lcm  
 Data Collection : 2021 9-4 17:31:55  
 Data Processing : 2021 9-4 17:56:58



### Area Percent Report

Peak#	RetTime	Area	Area%
1	11.514	29423776	35.859
2	14.315	52629883	64.141
Totals		82053659	100.000

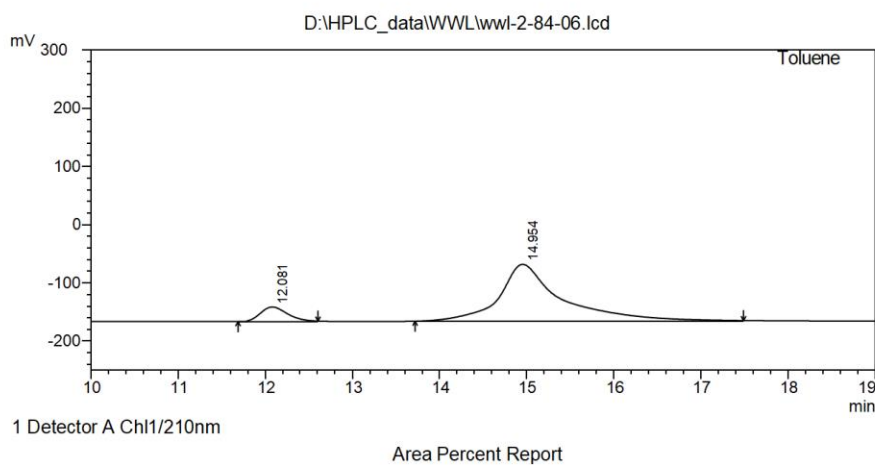
D:\HPLC\_data\WWL\wwl-2-84-5.lcd

# Table 1-entry7

2021-9-9 16:49:18 1 / 1

## ==== Shimadzu LCsolution analysis report ====

Acq.Operator : Admin  
 Acq.Instrument : wwl-2-84-3  
 Acq.ID :  
 Acq. : 1  
 Seq.Line# : 7  
 Inj Volume : 5 uL  
 Sample name : wwl-2-84-06.lcd  
 Acq.Method : wwl-90-10-210-1-25min-OD.lcm  
 Data Collection : 2021 9-5 15:05:12  
 Data Processing : 2021 9-5 15:30:17



Peak#	RetTime	Area	Area%
1	12.081	528552	9.966
2	14.954	4775090	90.034
Totals		5303642	100.000

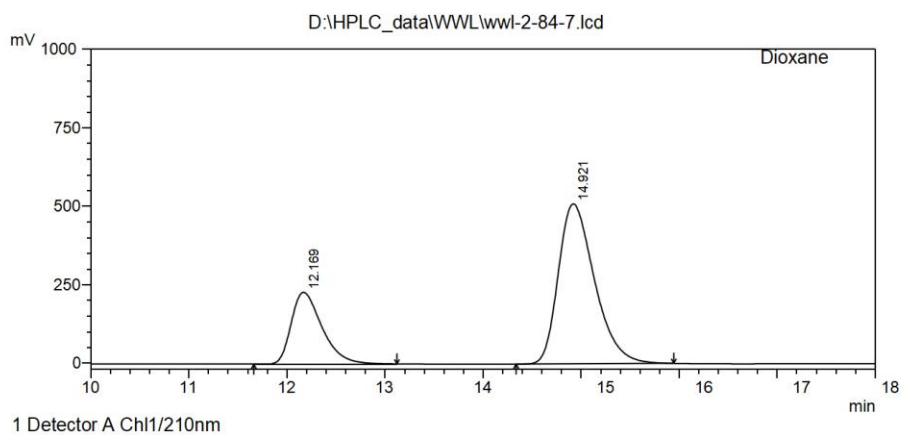
D:\HPLC\_data\WWL\wwl-2-84-06.lcd

# Table 1-entry8

2021-9-9 16:51:46 1 / 1

## ==== Shimadzu LCsolution analysis report ====

Acq.Operator : Admin  
 Acq.Instrument : wwl-2-84-7  
 Acq.ID :  
 Acq. : 1  
 Seq.Line# : 8  
 Inj Volume. : 5 uL  
 Sample name : wwl-2-84-7.lcd  
 Acq.Method : wwl-90-10-210-1-25min-OD.lcm  
 Data Collection : 2021 9-5 15:30:42  
 Data Processing : 2021 9-5 15:55:44



### Area Percent Report

Peak#	RetTime	Area	Area%
1	12.169	5022026	27.704
2	14.921	13105326	72.296
Totals		18127352	100.000

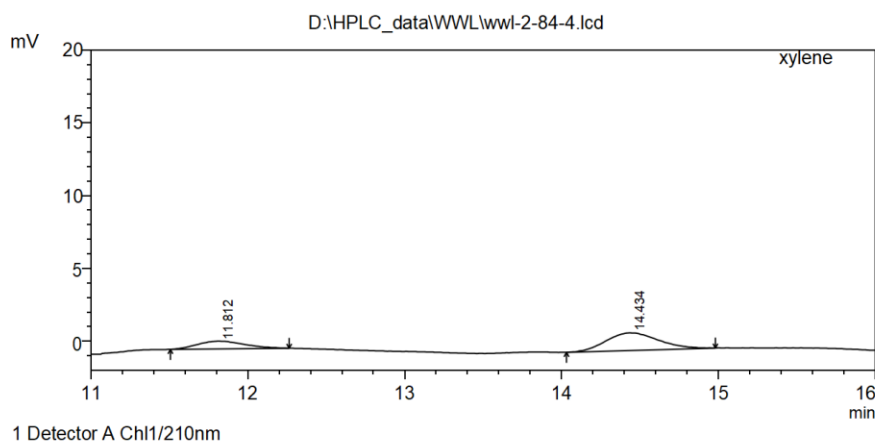
D:\HPLC\_data\WWL\wwl-2-84-7.lcd

# Table 1-entry9

2021-9-9 16:36:11 1 / 1

## ==== Shimadzu LCsolution analysis report ====

Acq.Operator : Admin  
 Acq.Instrument : wwl-2-84-3  
 Acq.ID :  
 Acq. : 1  
 Seq.Line# : 5  
 Inj.Volume : 5 uL  
 Sample name : wwl-2-84-4.lcd  
 Acq.Method : wwl-90-10-210-1-25min-OD.lcm  
 Data Collection : 2021 9-4 17:06:27  
 Data Processing : 2021 9-4 17:31:30



### Area Percent Report

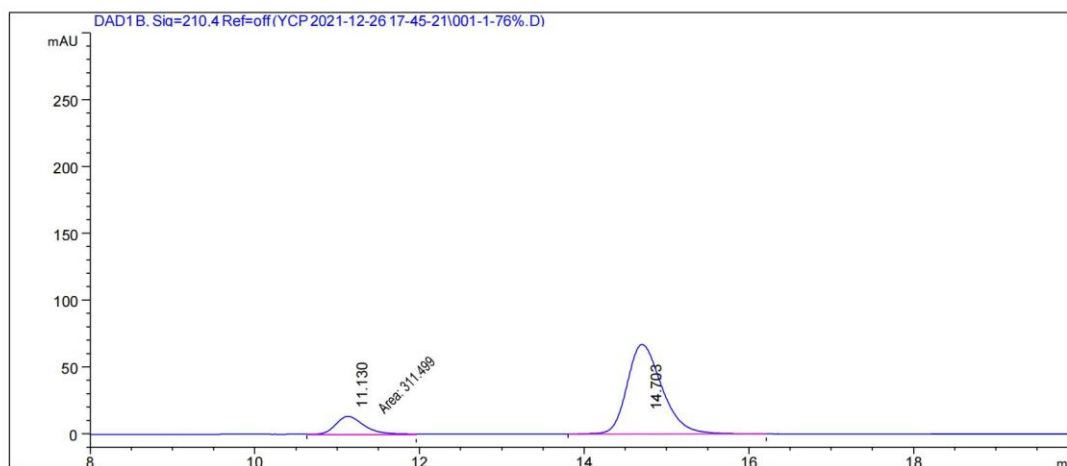
Peak#	RetTime	Area	Area%
1	11.812	11123	28.257
2	14.434	28241	71.743
Totals		39364	100.000

D:\HPLC\_data\WWL\wwl-2-84-4.lcd

## Table 1-entry10

Date File: d:\Chem32\1\Data\YCP 2021-12-26 17-45-21\001-1-76%.D  
Sample Name: 20211225-GM-1

```
=====
Acq. Operator   : Admin                      Acq.       : 1
Instrument      : 1260                      Location  : 1
Entry date     : 2021/12/26 17:46:48        Inj       : 1
Inj Volume     : 5.000 µl
Acq. Method    : d:\Chem32\1\Data\YCP 2021-12-26 17-45-21\YCP.M
Analysis Method : 2021/12/26 17:45:45
Analysis Method.: d:\Chem32\1\Data\YCP 2021-12-26 17-45-21\YCP.M (Sequence
Method)
Last Changed   : 2021/12/26 19:06:53 : AM by SYSTEM(modified
after loading)
Additional Info : Peak(s) manually integrated
=====
```



### Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
DO not use Multiplier & Dilution Factor with ISTDs
signal 1: DAD1 B, Sig=210,4 Ref=off
=====
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.130	MM	0.3910	311.49854	13.27631	13.5764
2	14.703	BB	0.4531	1982.90503	67.03899	86.4236

Totals : 2294.40356 80.31530

\*\*\* End of Report \*\*\*

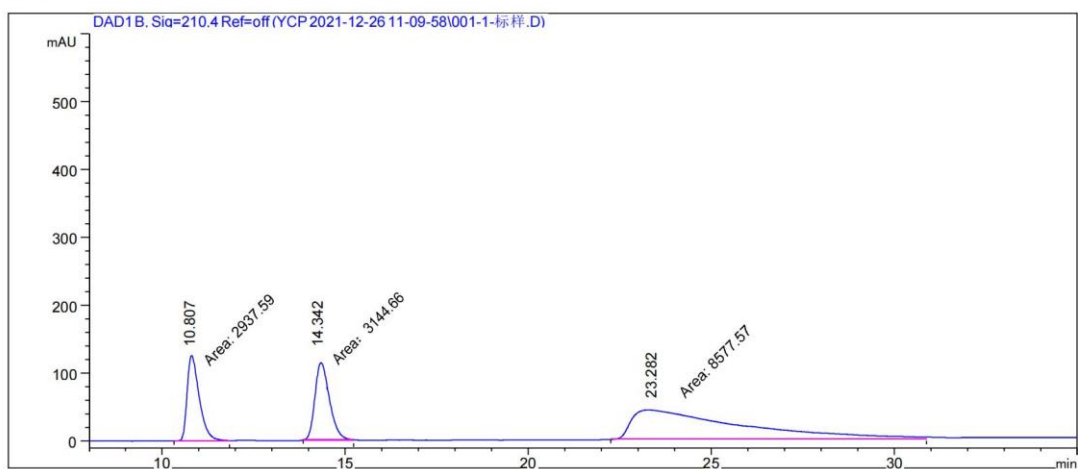
## HPLC spectra of Table 2

### standard solution

Date File: d:\Chem32\1\Data\YCP 2021-12-26 11-09-58\001-1-standard.D

Sample Name: standard

```
=====
Acq. Operator   : Admin                      Acq.       : 1
Instrument      : 1260                      Location  : 1
Entry date     : 2021/12/26 11:11:26        Inj       : 1
Inj Volume     : 5.000 µl
Acq. Method    : d:\Chem32\1\Data\YCP 2021-12-26 11-09-58\YCP.M
Analysis Method: d:\Chem32\1\Data\YCP 2021-12-26 11-09-58\YCP.M (Sequence
Method)
Last Changed   : 2021/12/26 15:37:18 : AM by SYSTEM(modified after
loading)
Additional Info : Peak(s) manually integrated
=====
```



#### Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
DO not use Multiplier & Dilution Factor with ISTDs
signal 1: DAD1 B, Sig=210,4 Ref=off
=====
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.807	MM	0.3882	2937.59424	126.13116	20.0384
2	14.342	MM	0.4600	3144.65796	113.94315	21.4509
3	23.282	MM	2.2841	8577.57129	43.92063	58.5107
Totals :				1.46598e4	283.99495	

\*\*\* 报告结束 \*\*\*



## Table 2- Cycle 1

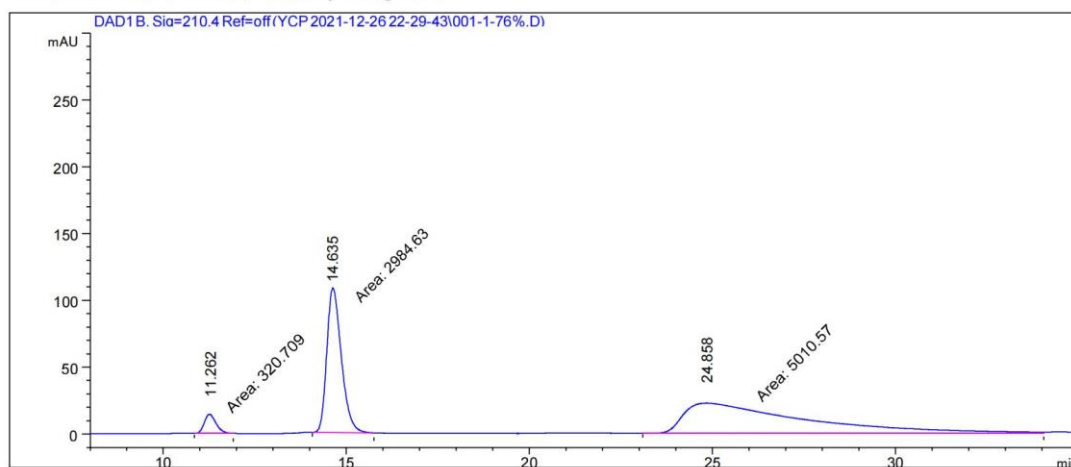
Date File: d:\Chem32\1\Data\YCP 2021-12-26 22-29-43\001-1-76%.D  
Sample Name: GM-1

=====

Acq. Operator	: Admin	Acq.	: 1
Instrument	: 1260	Location	: 1
Entry date	: 2021/12/26 22:31:10	Inj:	1
Inj Volume.	: 5.000 µl		
Acq. Method.	: d:\Chem32\1\Data\YCP 2021-12-26 22-29-43\YCP.M		
Analysis Method	: d:\Chem32\1\Data\YCP 2021-12-26 22-29-43\YCP.M (Sequence Method)		

Last Changed : 2021/12/26 23:14:57 : AM by SYSTEM(modified after loading)

Additional Info : Peak(s) manually integrated



### Area Percent Report

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
DO not use Multiplier & Dilution Factor with ISTDs  
signal 1: DAD1 B, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.262	MM	0.3724	320.70917	14.35367	3.8566
2	14.635	MM	0.4605	2984.62866	108.02036	35.8906
3	24.858	MM	3.6967	5010.56885	22.59050	60.2528
Totals	:			8315.90668	144.96454	

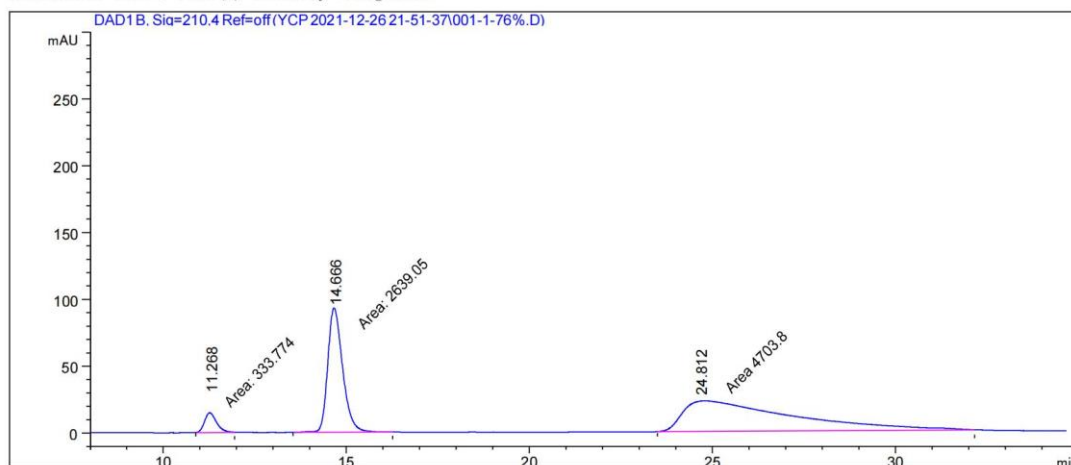
\*\*\* End of Report \*\*\*

## Table 2- Cycle 2

Date File: d:\Chem32\1\Data\YCP 2021-12-26 21-51-37\001-1-76%.D  
Sample Name: GM-2

=====

Acq. Operator : Admin Acq. : 1  
Instrument : 1260 Location : 1  
Entry date : 2021/12/26 21:53:03 Inj : 1  
Inj Volume. : 5.000 µl  
Acq. Method. : d:\Chem32\1\Data\YCP 2021-12-26 21-51-37\YCP.M  
Analysis Method : d:\Chem32\1\Data\YCP 2021-12-26 21-51-37\YCP.M (Sequence Method)  
Last Changed : 2021/12/26 22:35:28 : AM by SYSTEM(modified after loading)  
Additional Info : Peak(s) manually integrated



### Area Percent Report

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
DO not use Multiplier & Dilution Factor with ISTDs  
signal 1: DAD1 B, Sig=210,4 Ref=off

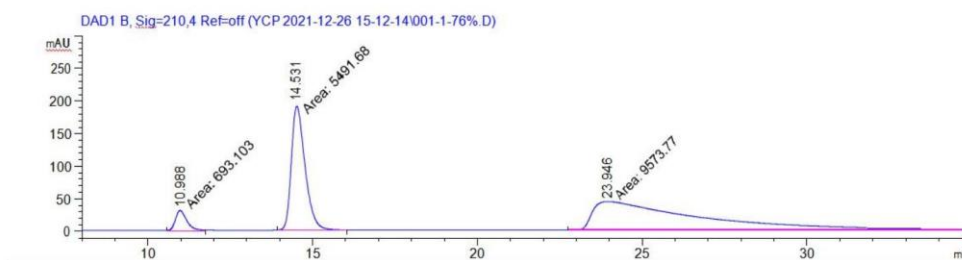
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.268	MM	0.3773	333.77365	14.74219	4.3479
2	14.666	MM	0.4730	2639.05347	92.99316	34.3778
3	24.812	MM	3.4355	4703.79883	22.81958	61.2743
Totals :				7676.62595	130.55493	

\*\*\* End of Report \*\*\*

## Table 2- Cycle 3

Date File: d:\Chem32\1\Data\YCP 2021-12-26 15-12-14\001-1-76%.D  
Sample Name: GM-3

```
=====
Acq. Operator   : Admin                      Acq.       : 1
Instrument      : 1260                      Location    : 1
Entry date     : 2021/12/26 15:13:40        Inj         : 1
Inj Volume.    : 5.000 µl
Acq. Method.   : d:\Chem32\1\Data\YCP 2021-12-26 15-12-14\YCP.M
Analysis Method : d:\Chem32\1\Data\YCP 2021-12-26 15-12-14\YCP.M
                (Sequence Method)
Last Changed   : 2021/12/26 22:10:10 : AM by SYSTEM(modified after
                loading)
Additional Info : Peak(s) manually integrated
=====
```



### Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
DO not use Multiplier & Dilution Factor with ISTDs
signal 1: DAD1 B, Sig=210,4 Ref=off
=====
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.988	MM	0.3803	693.10272	30.37226	4.3983
2	14.531	MM	0.4814	5491.68164	190.11597	34.8489
3	23.946	MM	3.6648	9573.77246	43.53986	60.7529

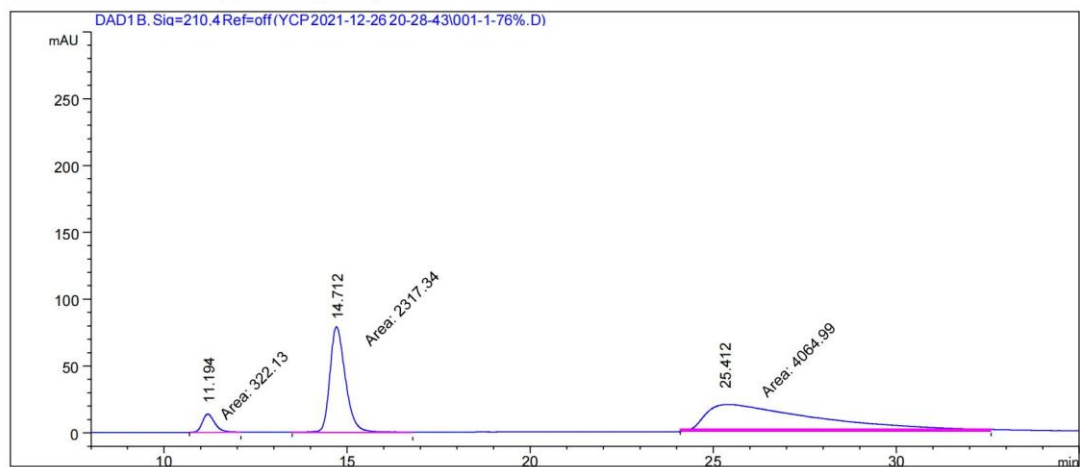
Totals : 1.57586e4 264.02808

\*\*\* End of Report \*\*\*

## Table 2- Cycle 4

Date File: d:\Chem32\1\Data\YCP 2021-12-26 20-28-43\001-1-76%.D  
Sample Name: gm-4

```
=====
Acq. Operator   : Admin                      Acq.       : 1
Instrument      : 1260                      Location    : 1
Entry date     : 2021/12/26 20:30:12        Inj        : 1
Inj Volume     : 5.000 µl
Acq. Method    : d:\Chem32\1\Data\YCP 2021-12-26 20-28-43\YCP.M
Analysis Method : d:\Chem32\1\Data\YCP 2021-12-26 20-28-43\YCP.M
                  (Sequence Method)
Last Changed   : 2021/12/26 21:14:39 : AM by SYSTEM(modified
                  after loading)
Additional Info : Peak(s) manually integrated
=====
```



### Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
DO not use Multiplier & Dilution Factor with ISTDs
signal 1: DAD1 B, Sig=210.4 Ref=off
=====
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.194	MM	0.3931	322.13019	13.65763	4.8047
2	14.712	MM	0.4894	2317.34229	78.92244	34.5642
3	25.412	MM	3.3846	4064.98535	20.01729	60.6311

Totals : 6704.45782 112.59735

\*\*\* End of Report \*\*\*

## Table 2- Cycle 5

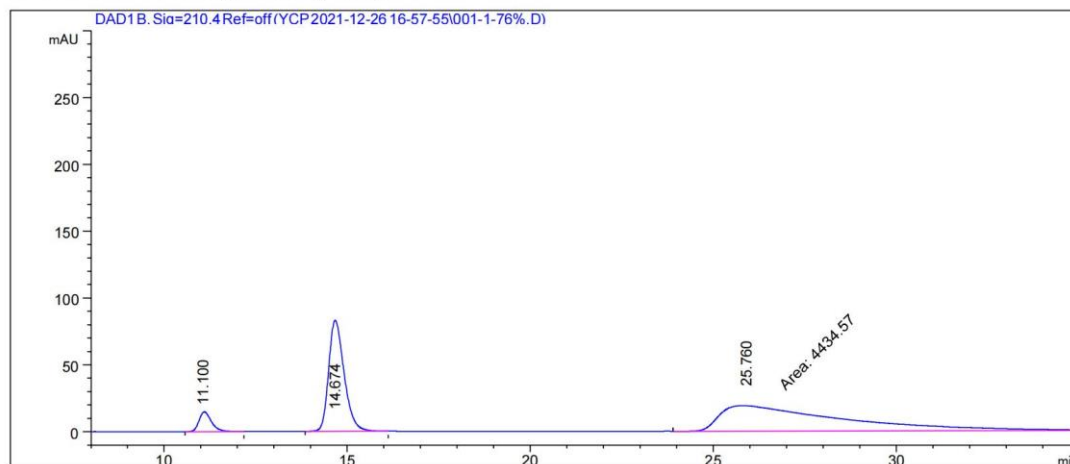
Date File: d:\Chem32\1\Data\YCP 2021-12-26 16-57-55\001-1-76%.D  
Sample Name:GM-5

=====

Acq. Operator : Admin Acq. : 1  
Instrument : 1260 Location : 1  
Entry date : 2021/12/26 16:59:24 Inj : 1  
Inj Volume. : 5.000 µl  
Acq. Method. : d:\Chem32\1\Data\YCP 2021-12-26 16-57-55\YCP.M  
Analysis Method : d:\Chem32\1\Data\YCP 2021-12-26 16-57-55\YCP.M (Sequence Method)

Last Changed : 2021/12/26 17:44:22 : AM by SYSTEM(modified after loading)

Additional Info : Peak(s) manually integrated



### Area Percent Report

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
DO not use Multiplier & Dilution Factor with ISTDs  
signal 1: DAD1 B, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.100	BB	0.3580	348.62469	14.73816	4.8201
2	14.674	BB	0.4521	2449.56372	83.06202	33.8676
3	25.760	MM	3.8830	4434.56787	19.03411	61.3123

Totals: 7232.75629 116.83429

\*\*\* End of Report \*\*\*

## Table 2- Cycle 6

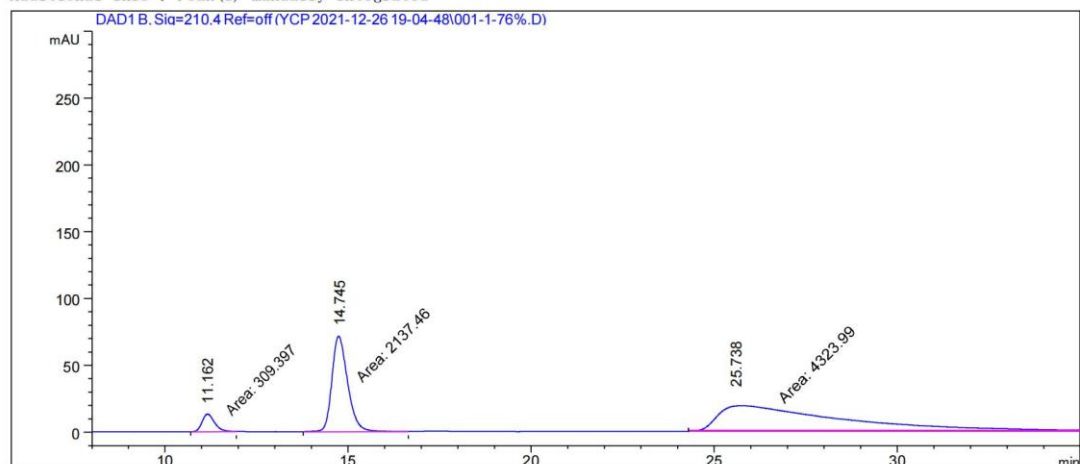
Date File: d:\Chem32\1\Data\YCP 2021-12-26 19-04-48\001-1-76%.D  
Sample Name: GM-6

=====

Acq. Operator	: Admin	Acq.	: 1
Instrument	: 1260	Location	: 1
Entry date	: 2021/12/26 19:06:14	Inj	: 1
Inj Volume.	: 5.000 µl		
Acq. Method.	: d:\Chem32\1\Data\YCP 2021-12-26 19-04-48\YCP.M		
Analysis Method	: d:\Chem32\1\Data\YCP 2021-12-26 19-04-48\YCP.M (Sequence Method)		

Last Changed : 2021/12/26 19:51:41 : AM by SYSTEM(modified after loading)

Additional Info : Peak(s) manually integrated



### Area Percent Report

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
DO not use Multiplier & Dilution Factor with ISTDs  
signal 1: DAD1 B, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.162	MM	0.3927	309.39694	13.13089	4.5695
2	14.745	MM	0.4989	2137.45996	71.41241	31.5686
3	25.738	MM	3.7952	4323.98926	18.98874	63.8619

Totals: 6770.84616 103.53205

\*\*\* End of Report \*\*\*