

Supporting Information

N-Heterocyclic Carbene-Catalyzed [4 + 2] Cycloaddition of Ketenes and 3-Aroylcoumarins: Highly Enantioselective Synthesis of Dihydrocoumarin-Fused Dihydropyranones

Teng-Yue Jian, Xiang-Yu Chen, Li-Hui Sun and Song Ye*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of
Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of
Sciences, Beijing 100190 (China)

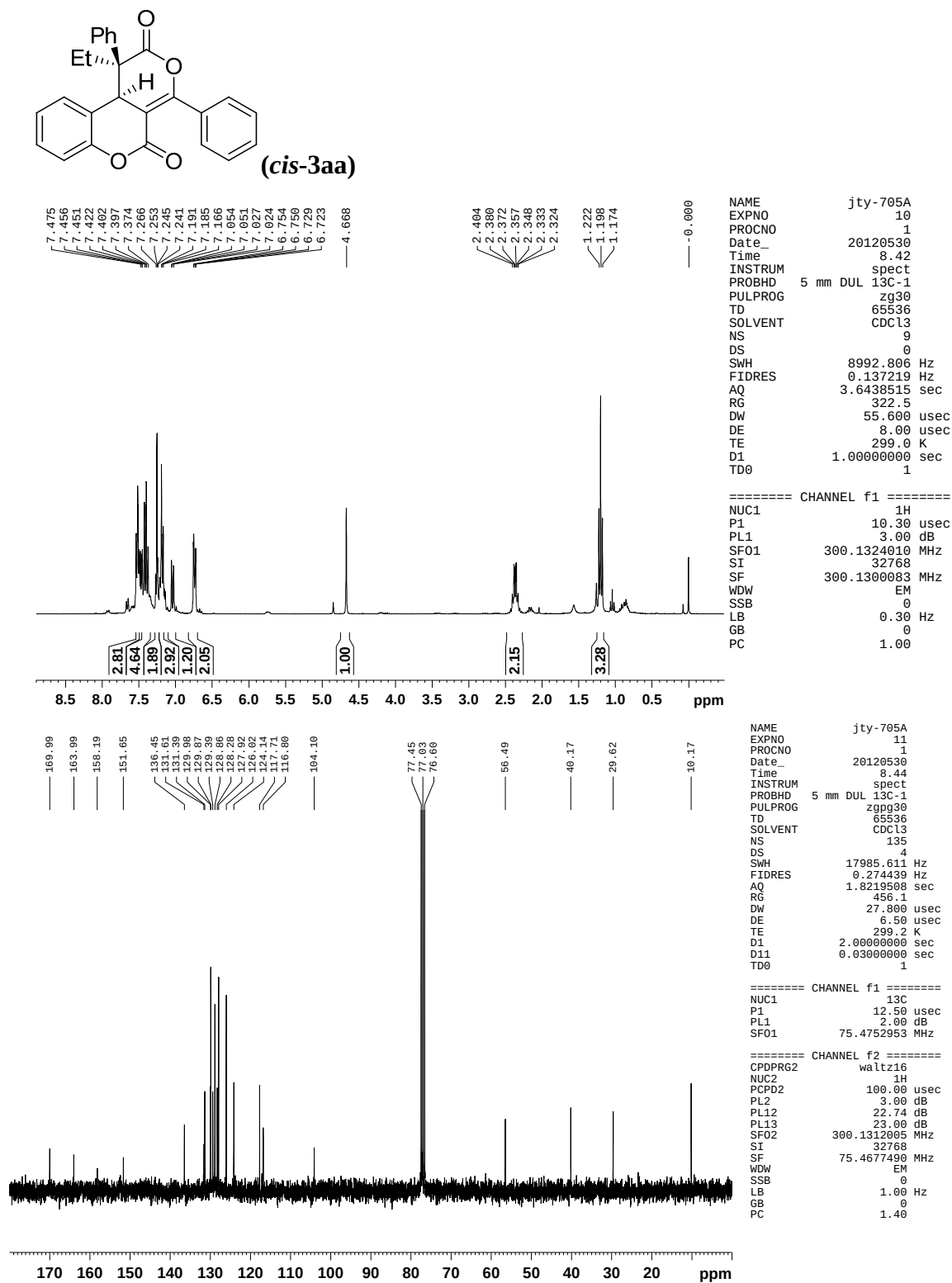
Fax: (+86) 10-6255-4449

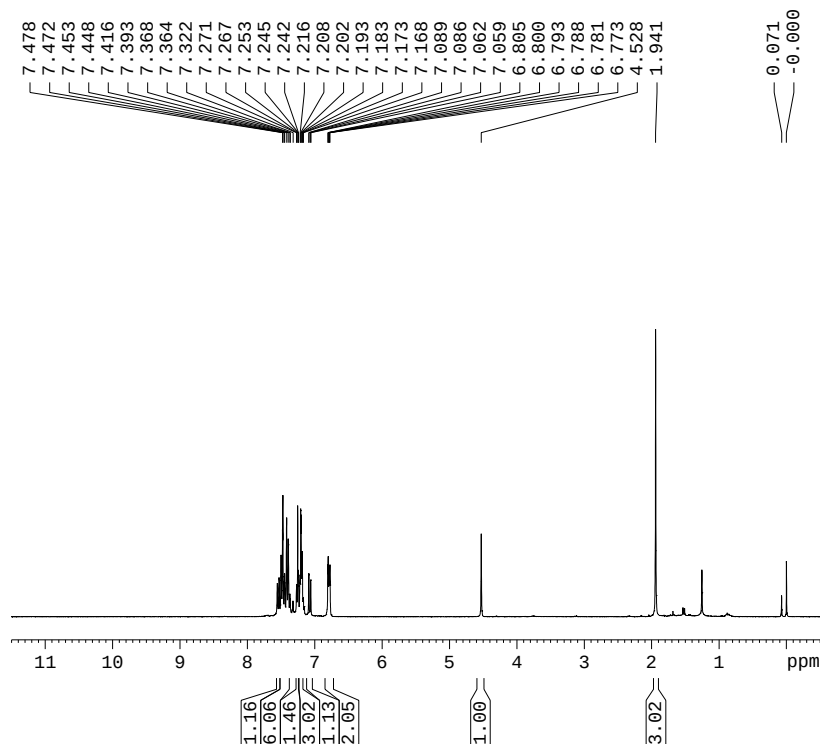
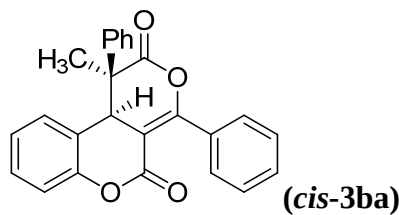
E-mail: songye@iccas.ac.cn

Table of Contents

PART I NMR SPECTRA	S2
PART II HPLC SPECTRA	S18

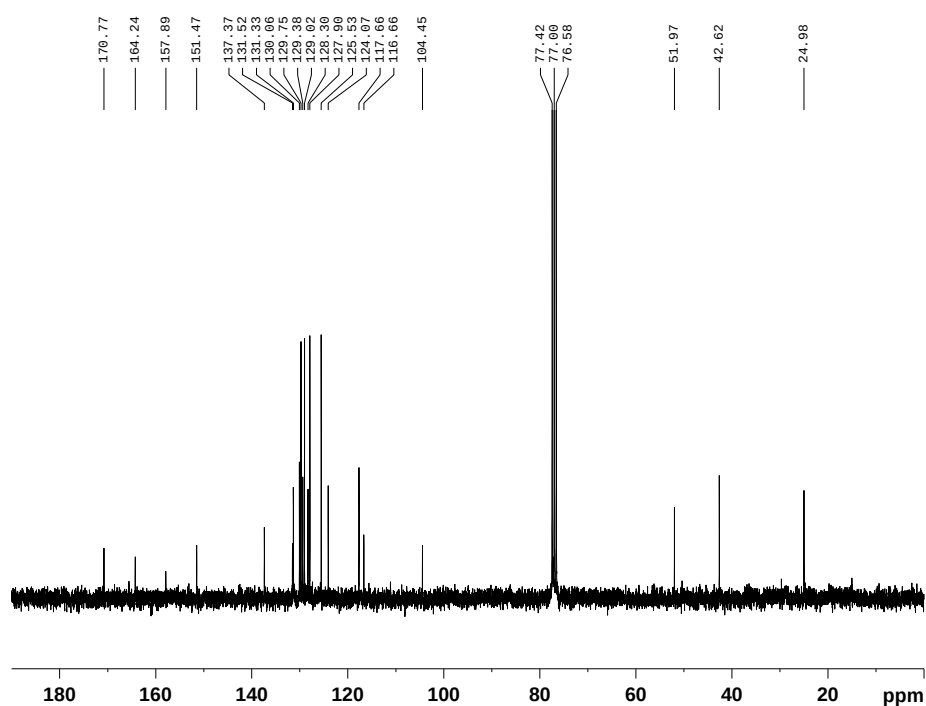
Part I NMR Spectra





NAME jty-799C
EXPNO 10
PROCNO 1
Date_ 20111230
Time 16.09
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 6
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 362
DW 55.600 usec
DE 8.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

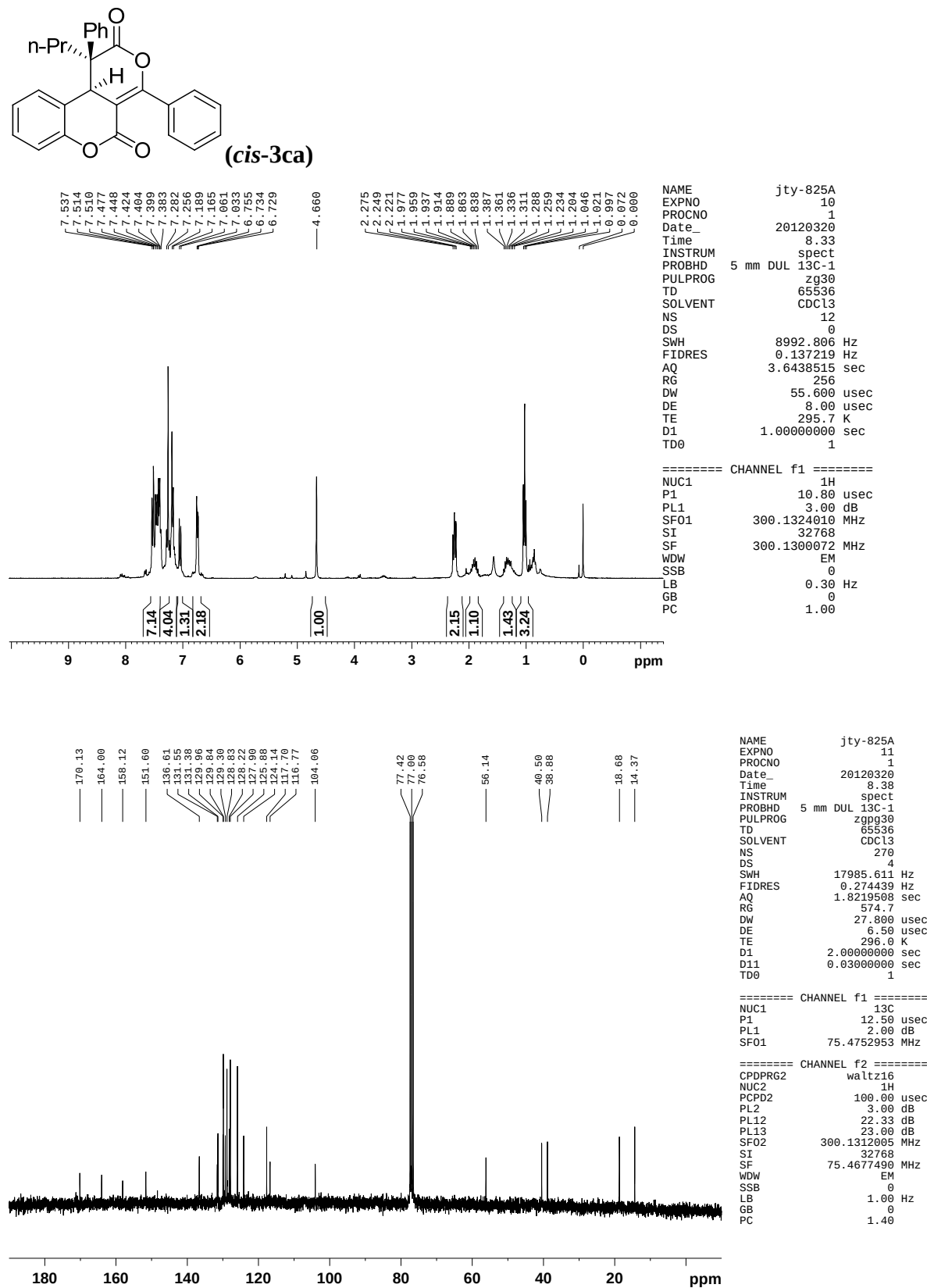
===== CHANNEL f1 =====
NUC1 1H
P1 10.80 usec
PL1 3.00 dB
SF01 300.1324010 MHz
SI 32768
SF 300.1300081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

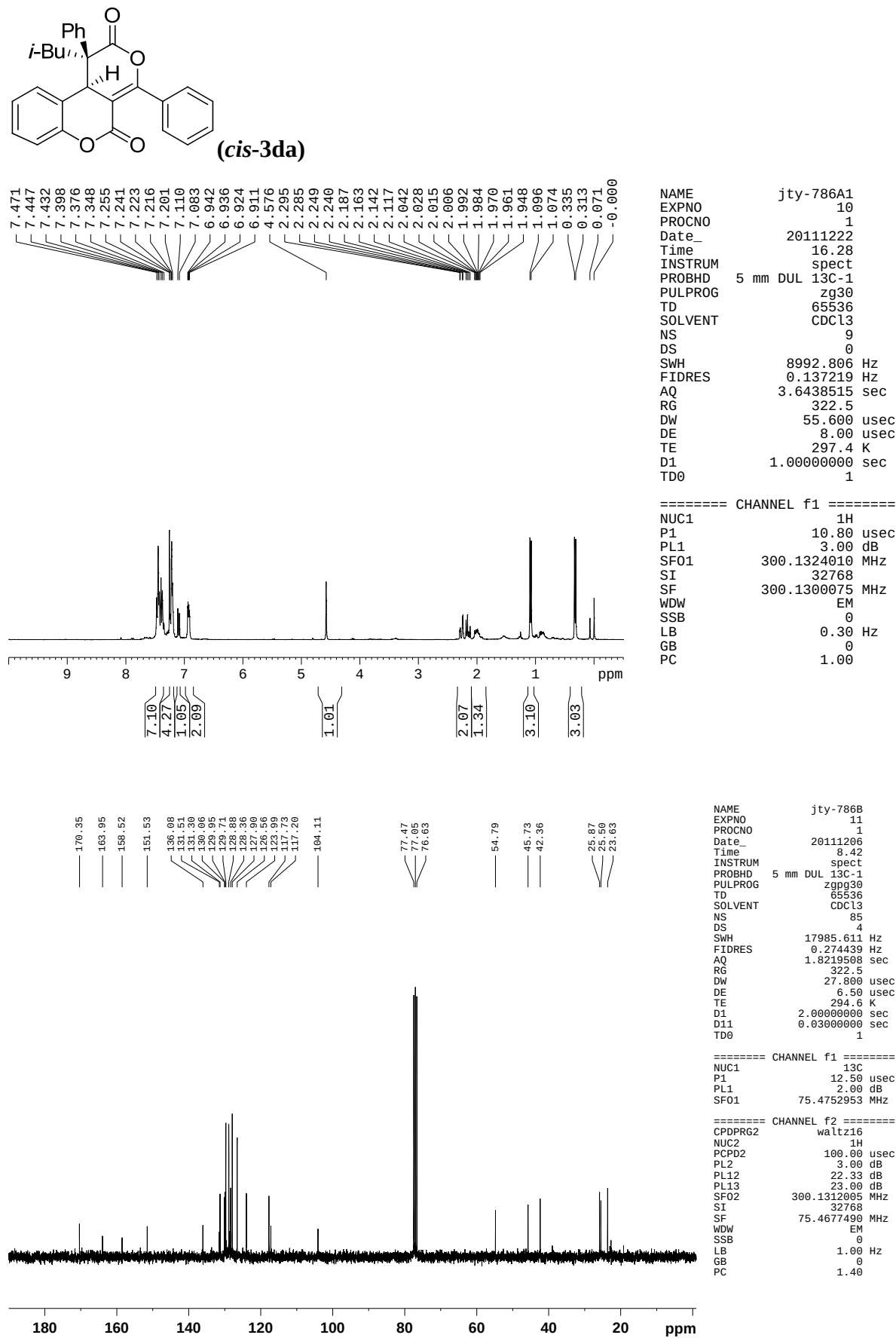


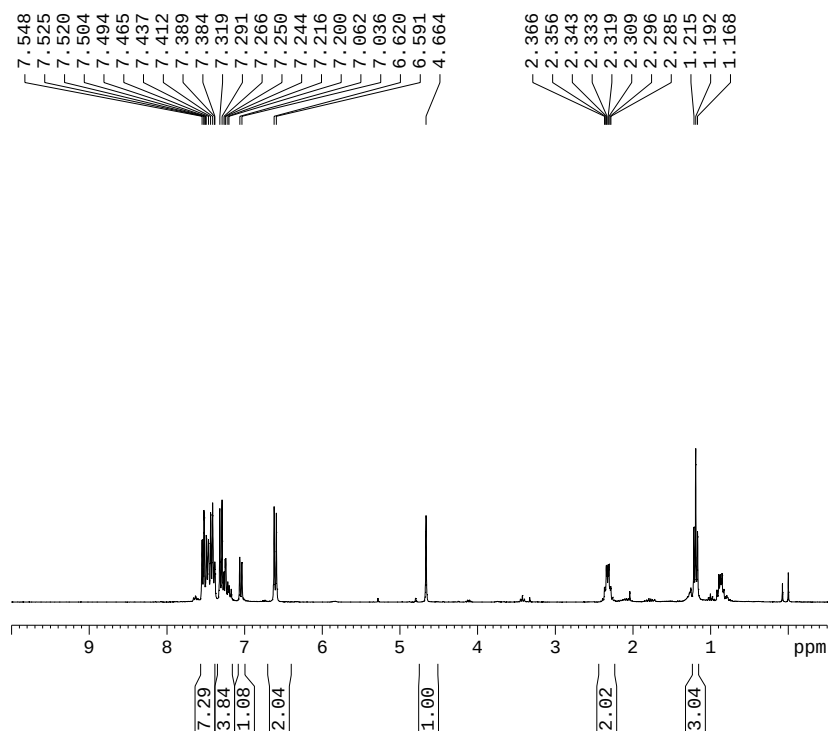
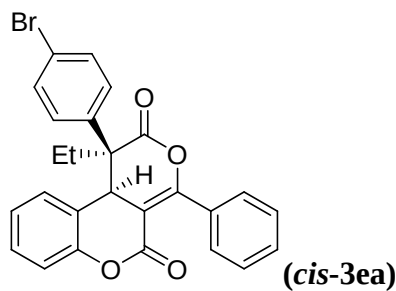
NAME jty-799C
EXPNO 11
PROCNO 1
Date_ 20111230
Time 16.13
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 171
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 812.7
DW 27.800 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SF01 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.33 dB
PL13 23.00 dB
SF02 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40







```

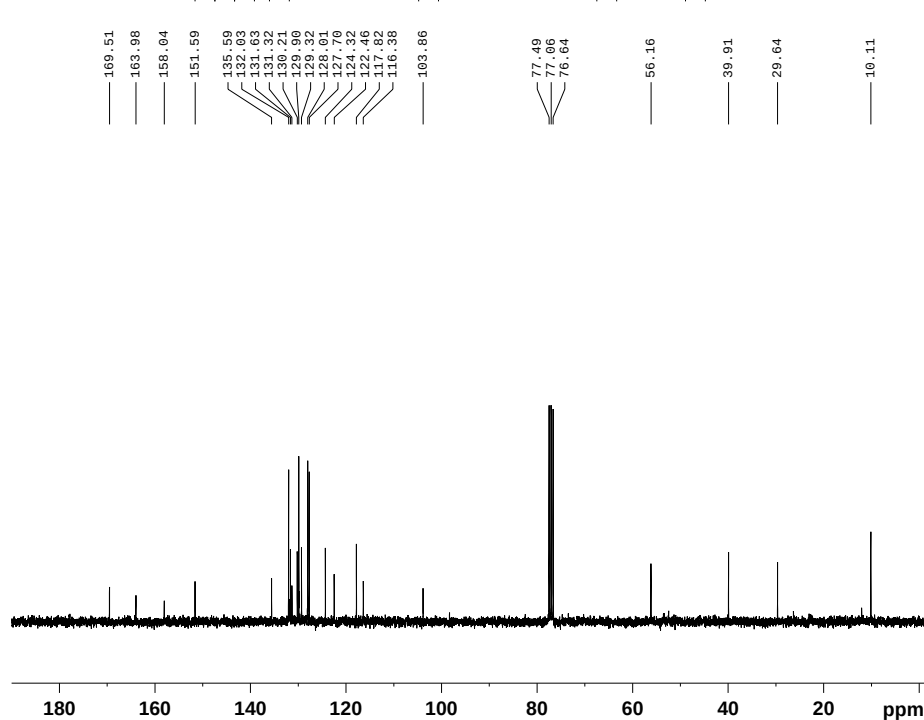
NAME                jty-790B
EXPNO                10
PROCNO              1
Date_                20111213
Time                8.26
INSTRUM              spect
PROBHD              5 mm DUL 13C-1
PULPROG              zg30
TD                  65536
SOLVENT              CDCl3
NS                   6
DS                   0
SWH                  8992.806 Hz
FIDRES              0.137219 Hz
AQ                  3.6438515 sec
RG                   128
DW                   55.600 usec
DE                   8.00 usec
TE                   295.5 K
D1                   1.00000000 sec
TD0                  1

```

```

===== CHANNEL f1 =====
NUC1                1H
P1                  10.80 usec
PL1                 3.00 dB
SF01                300.1324010 MHz
SI                  32768
SF                  300.1300087 MHz
WDW                  EM
SSB                  0
LB                   0.30 Hz
GB                   0
PC                   1.00

```



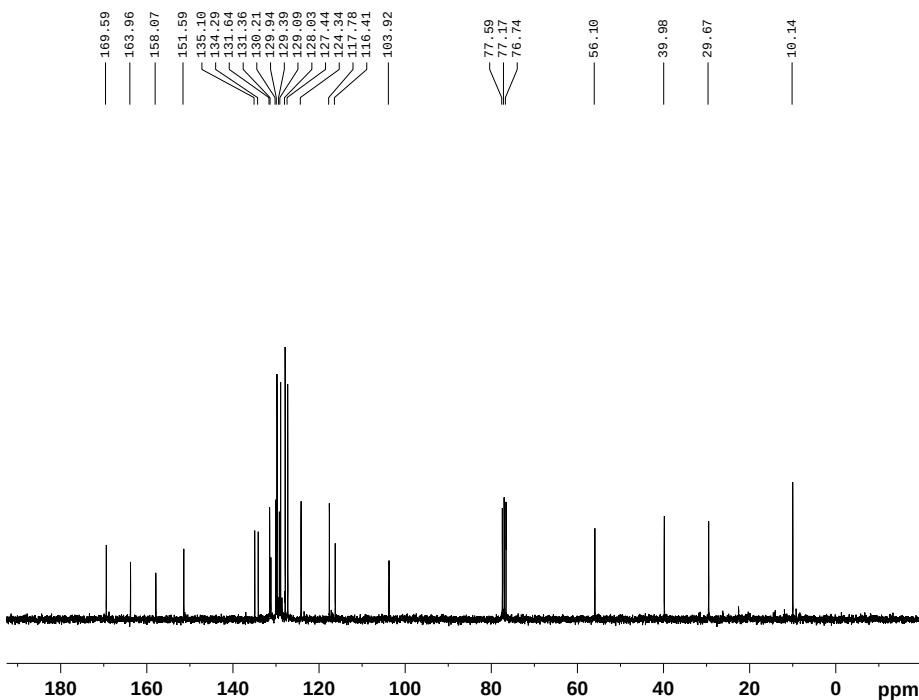
NAME	jty-790B		
EXPNO			11
PROCNO			1
Date_	20111213		
Time			8.29
INSTRUM			spect
PULPROG	5 mm	DUL	13C-1
TD			zgpg30
SOLVENT			65536
NS			CDCL3
DS			64
SWH			4
FIDRES		17985.611	Hz
AQ		0.274439	Hz
RG		1.8219508	sec
DW		362	
DE		27.800	usec
TE		6.50	usec
D1		295.9	K
D11		2.00000000	
D11		0.03000000	sec
TD0			

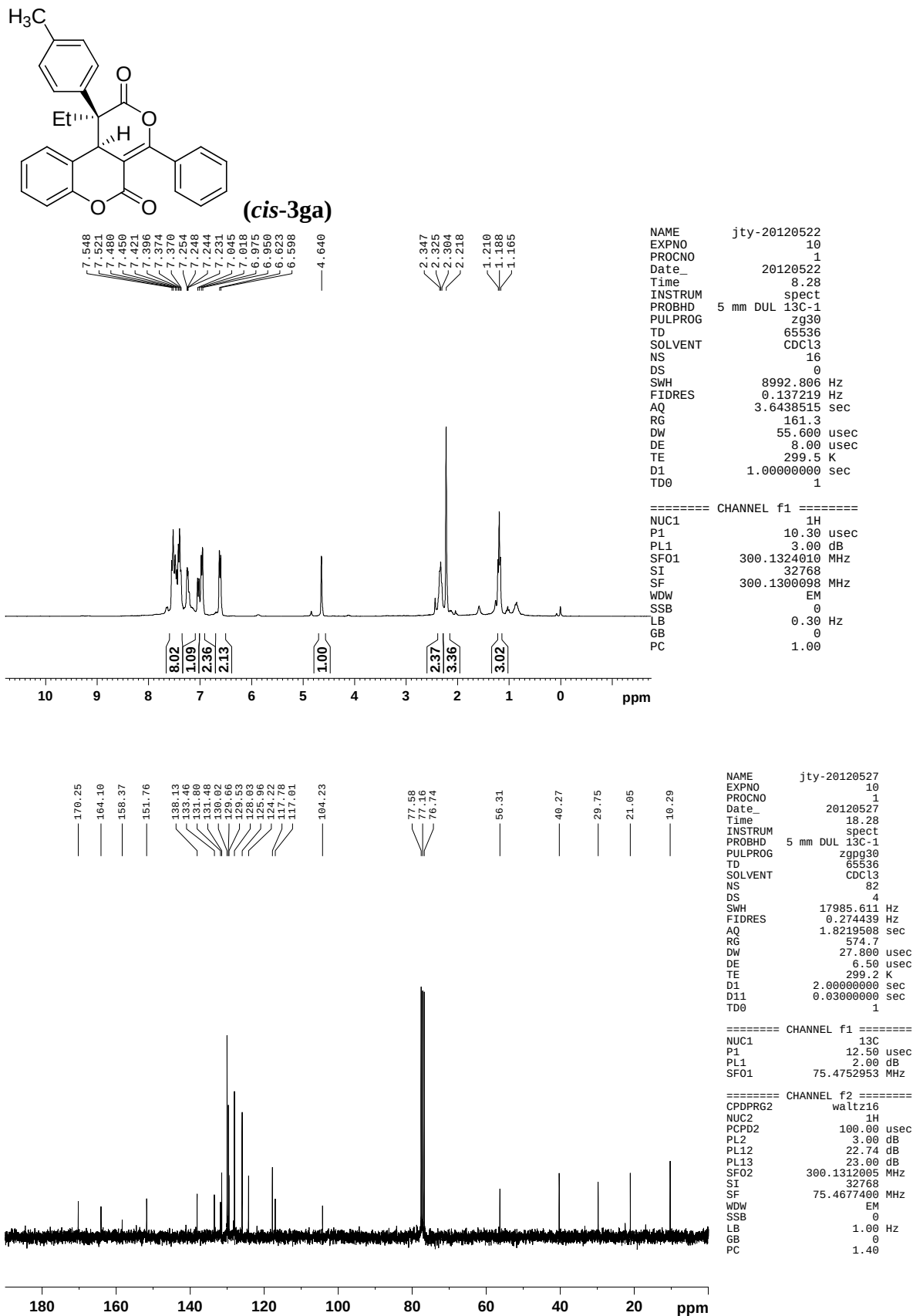
```
===== CHANNEL f1 =====  
NUC1                13C  
P1                  12.50 usec  
PL1                 2.00 dB  
SF01               75.4752953 MHz
```

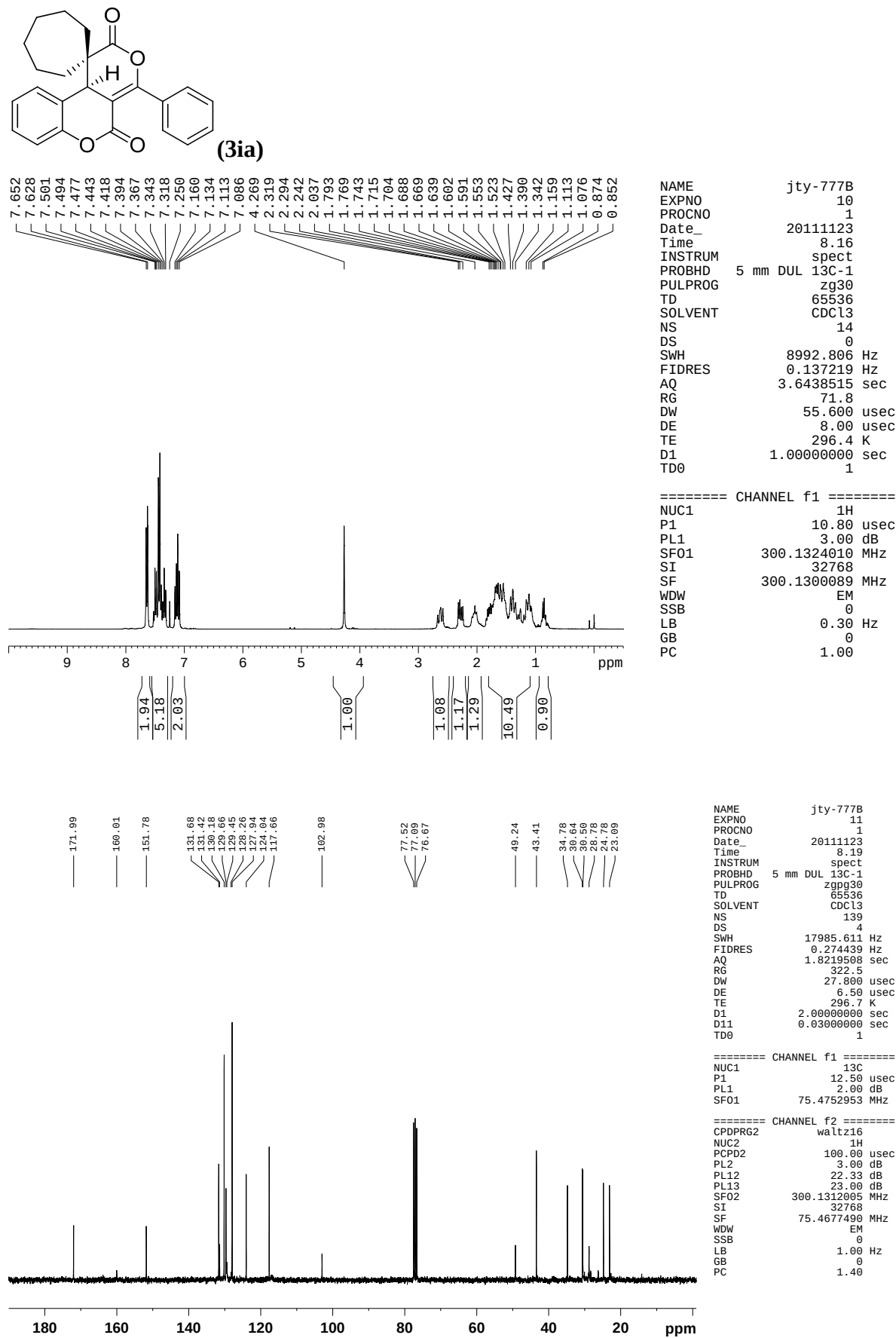
```

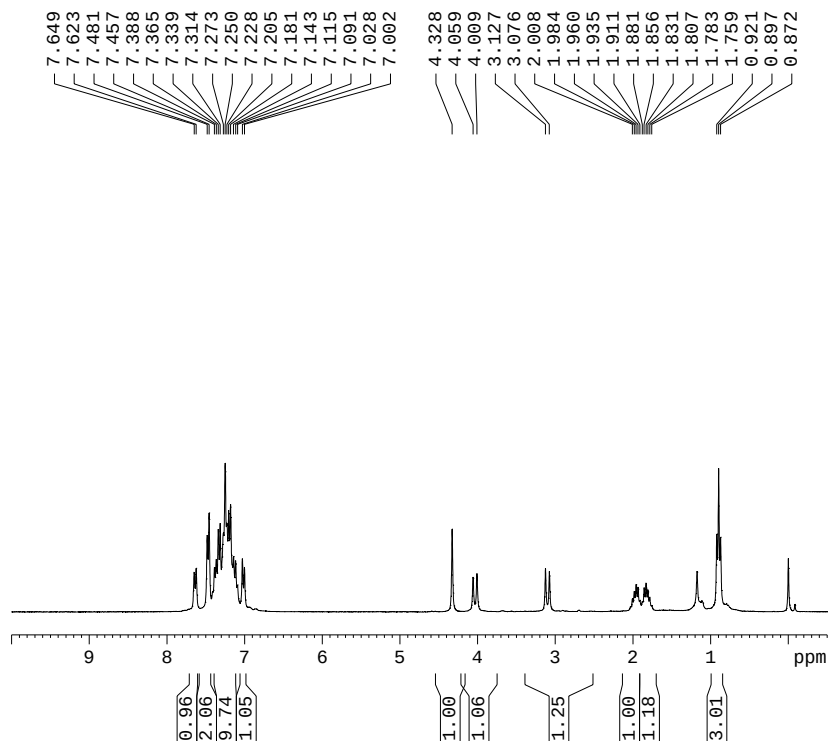
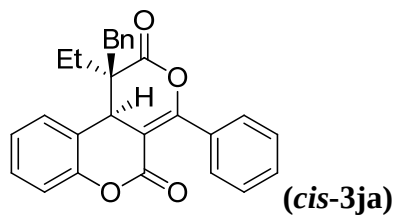
===== CHANNEL f2 =====
CPDPRG2      wait1z16
NUC2          1H
PCPD2         100.00 usec
PL2           3.00 dB
PL12          22.33 dB
PL13          23.00 dB
SF02          300.1312005 MHz
SI            32768
SF            75.4677490 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40

```



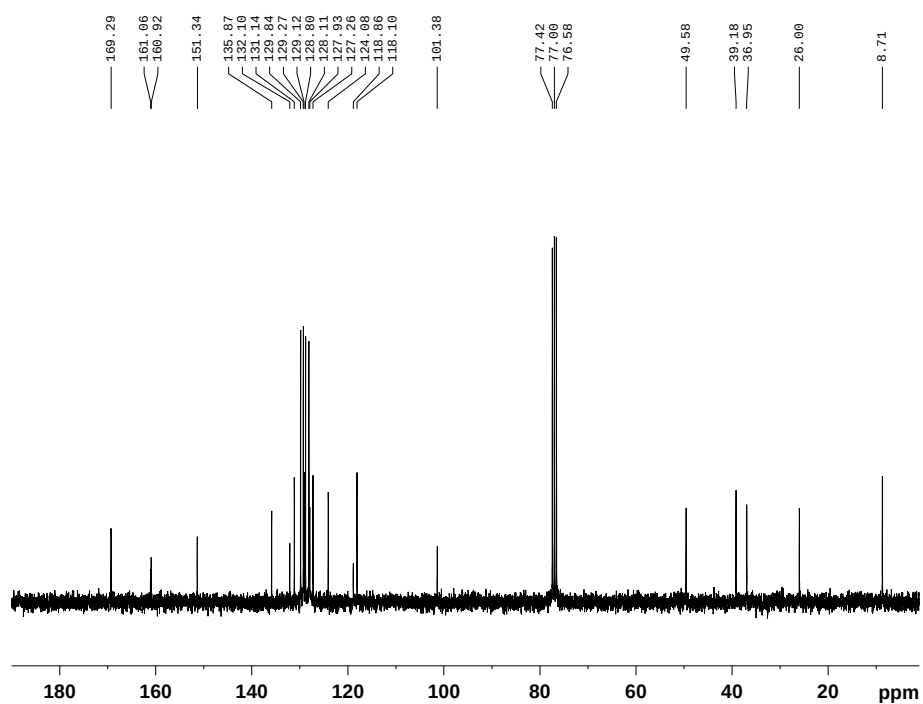






NAME jty-748A
EXPNO 20
PROCNO 1
Date_ 20120321
Time 22.51
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 7
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 71.8
DW 55.600 usec
DE 8.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

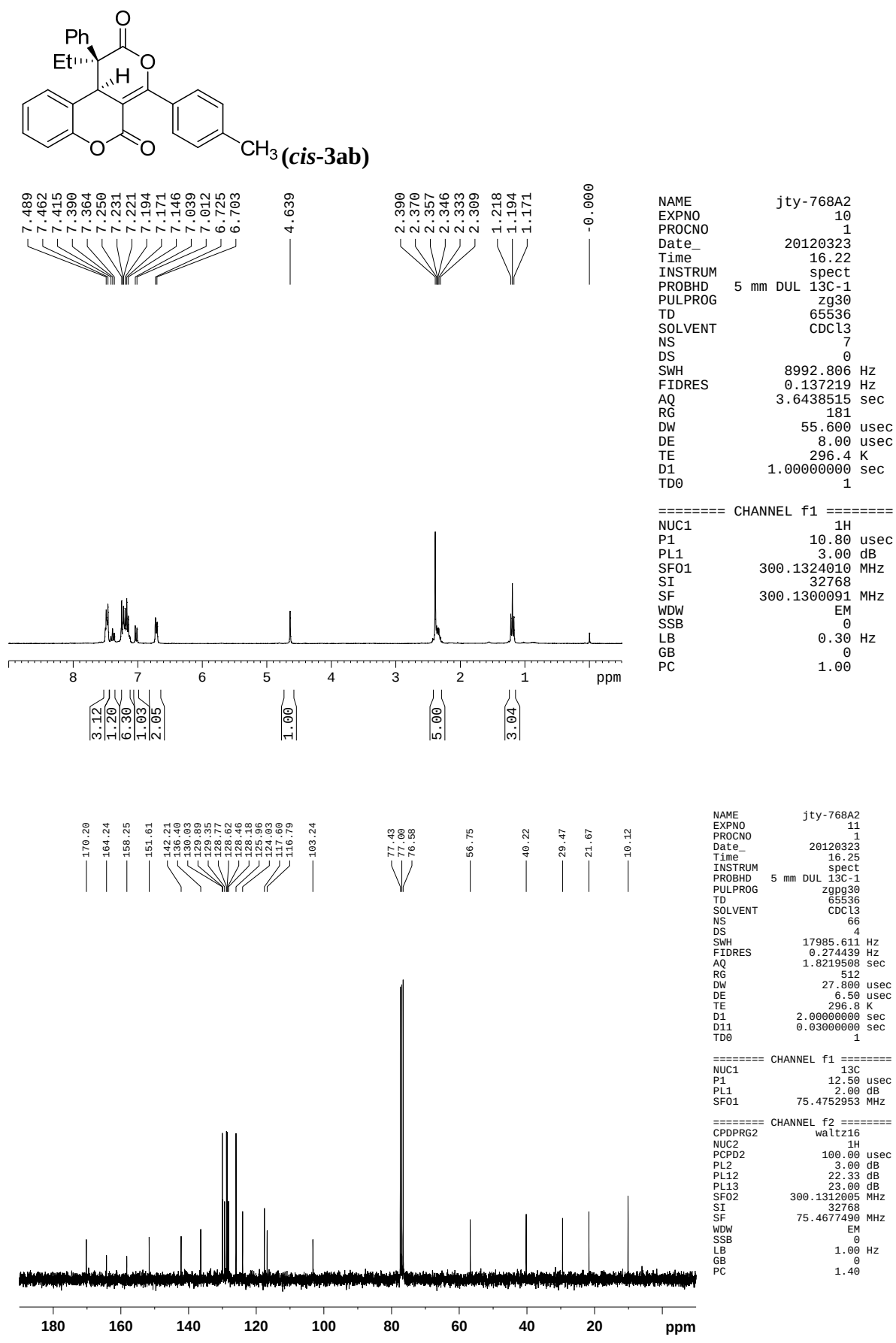
===== CHANNEL f1 =====
NUC1 1H
P1 10.80 usec
PL1 3.00 dB
SF01 300.1324010 MHz
SI 32768
SF 300.1300399 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

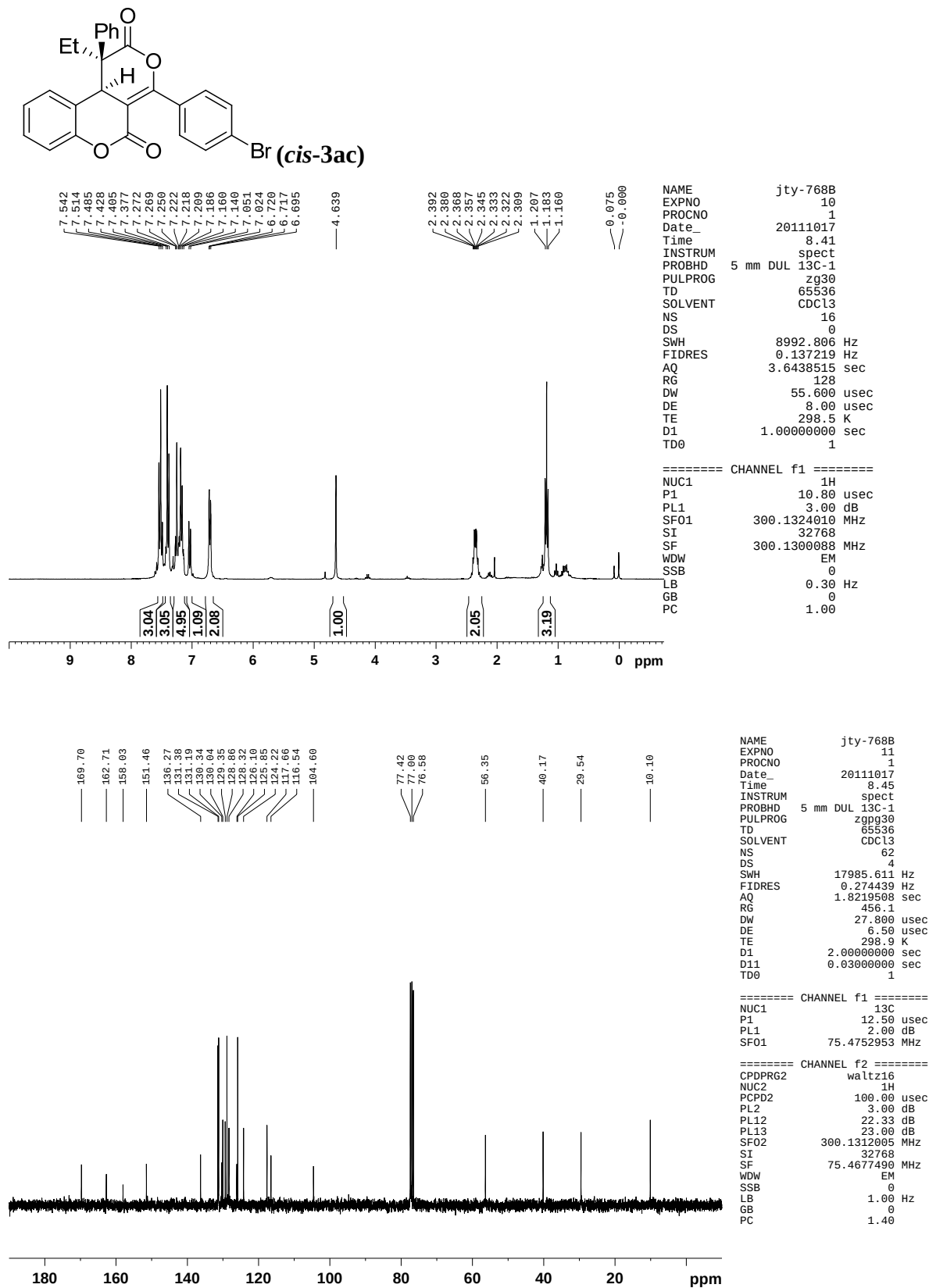


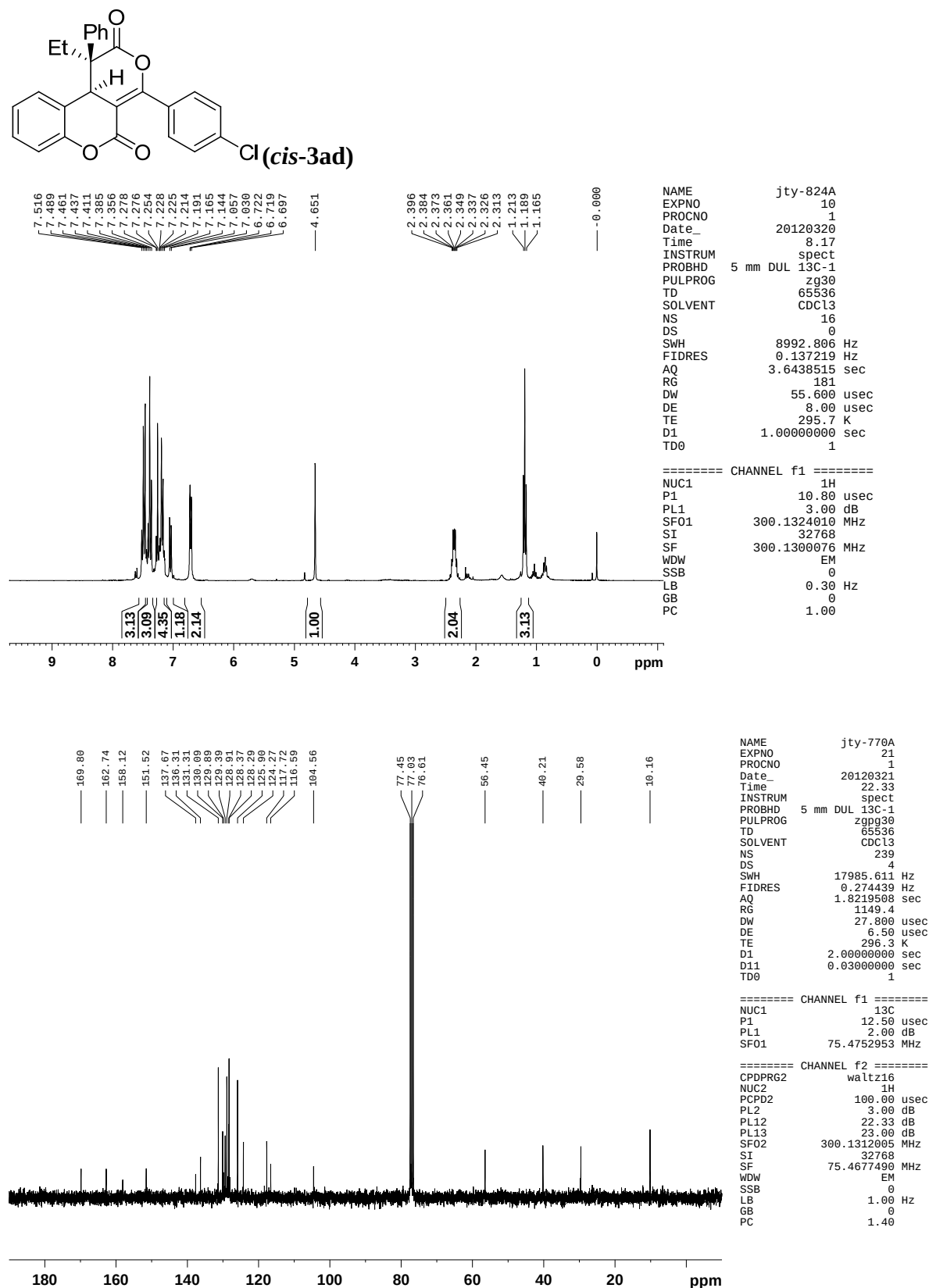
NAME jty-748A
EXPNO 21
PROCNO 1
Date_ 20120321
Time 22.53
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 29
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 512
DW 27.800 usec
DE 8.50 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

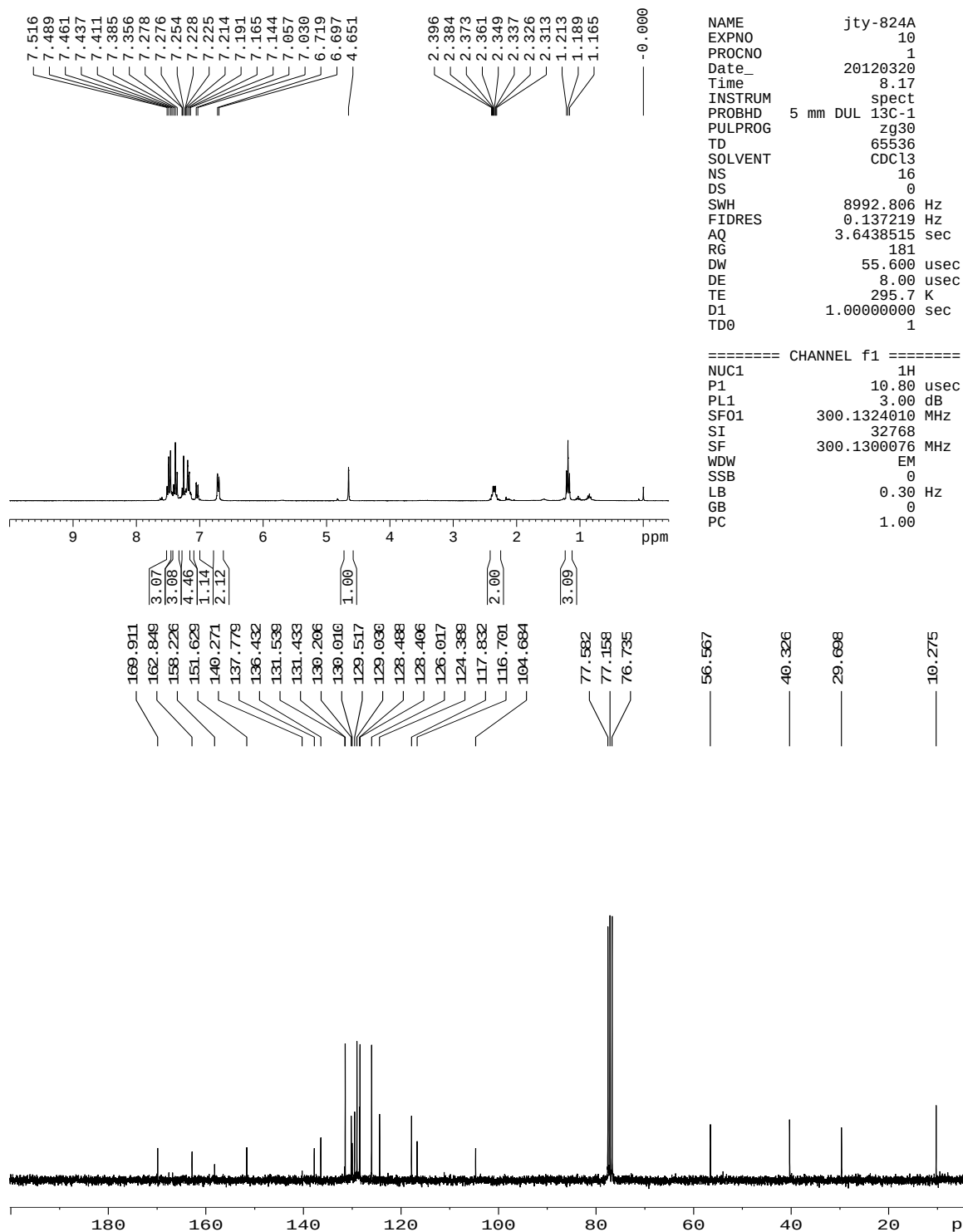
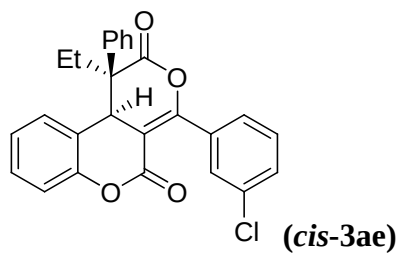
===== CHANNEL f1 =====
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SF01 75.4752953 MHz

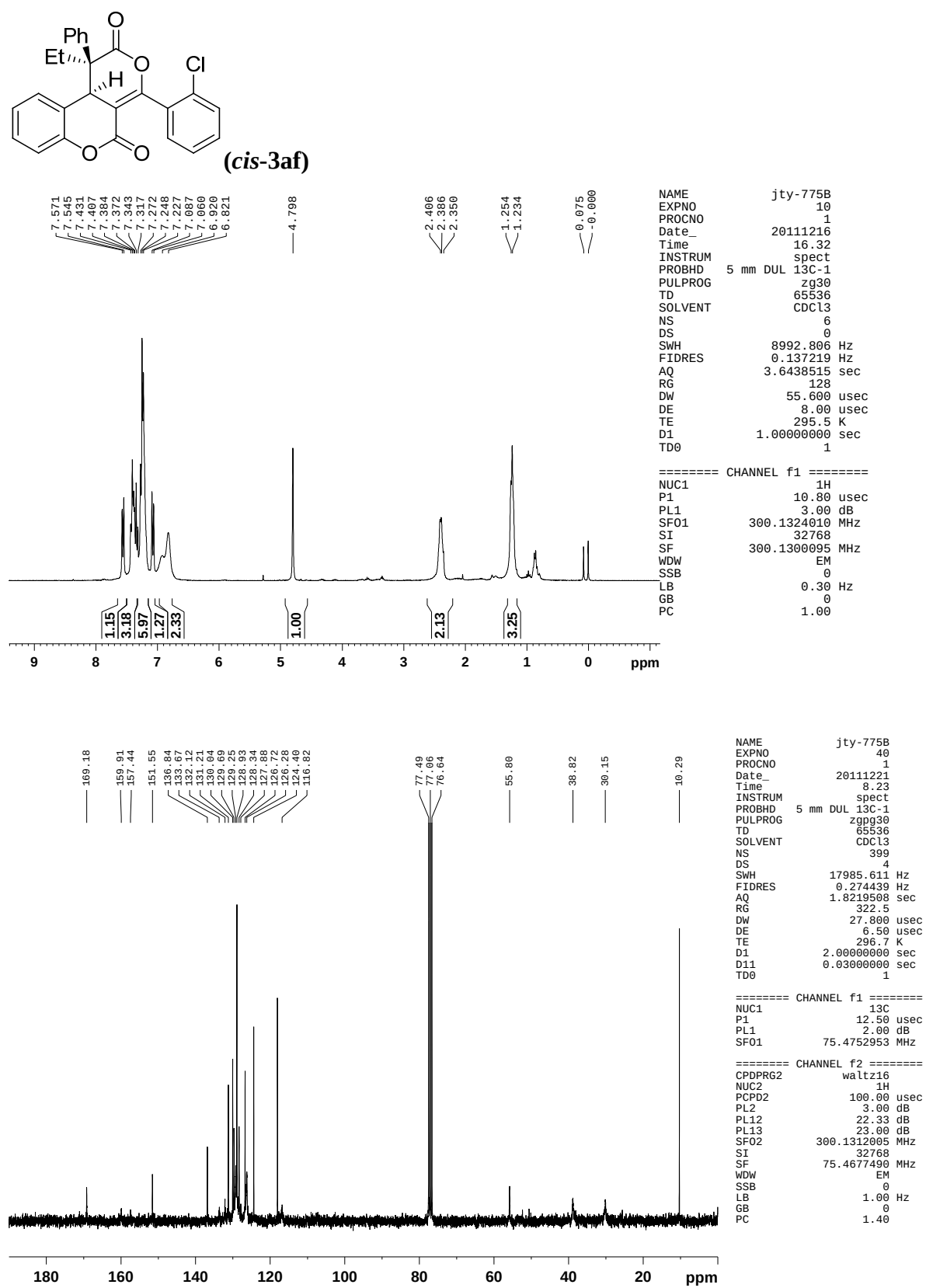
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.33 dB
PL13 23.00 dB
SF02 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

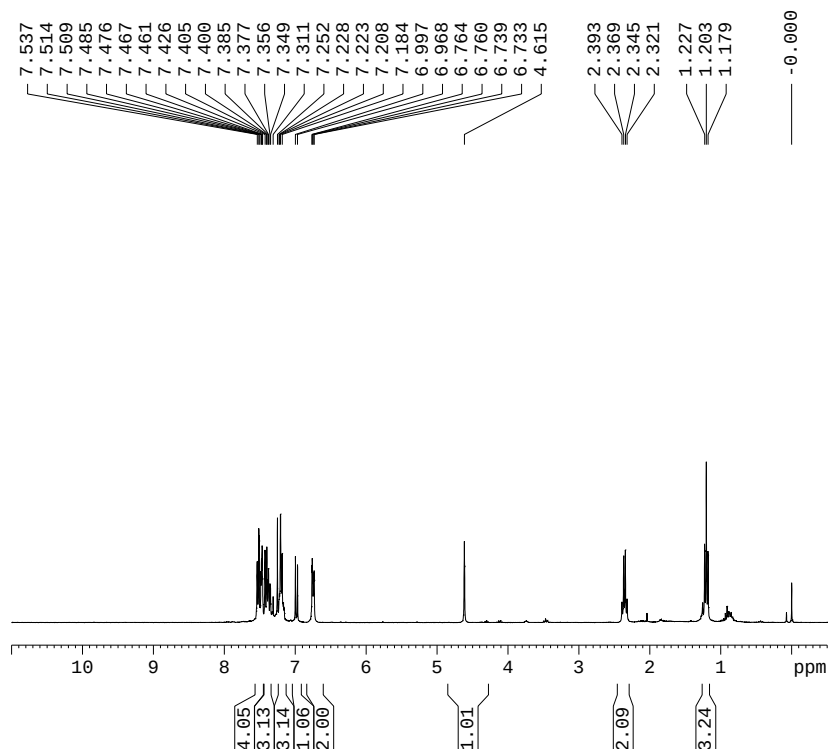
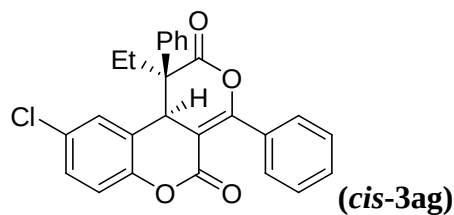






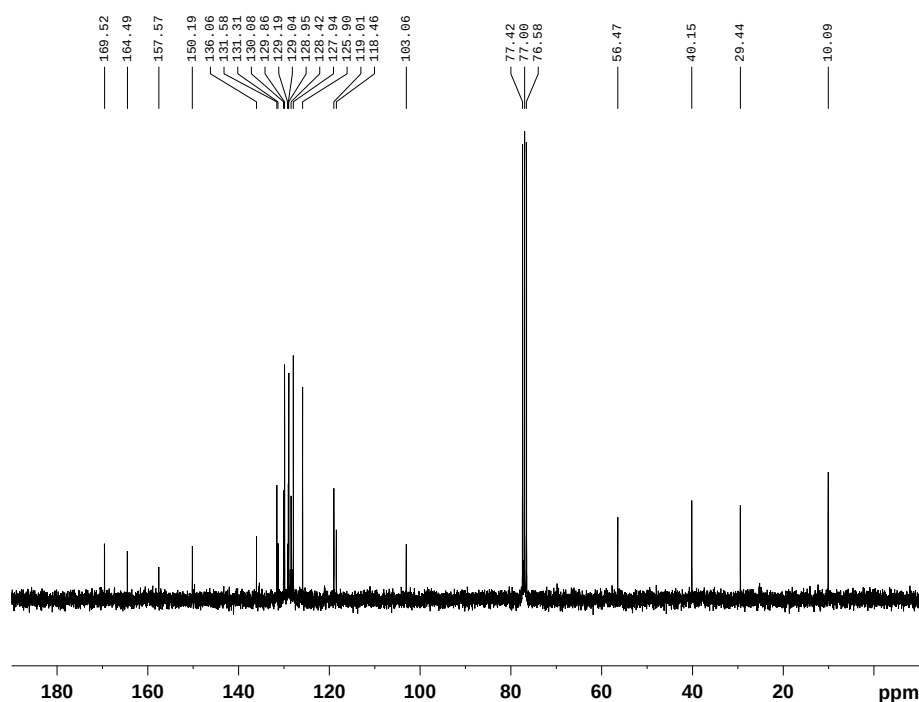






NAME jty-769A
EXPNO 10
PROCNO 1
Date_ 20111017
Time 8.51
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 228.1
DW 55.600 usec
DE 8.00 usec
TE 298.6 K
D1 1.00000000 sec
TD0 1

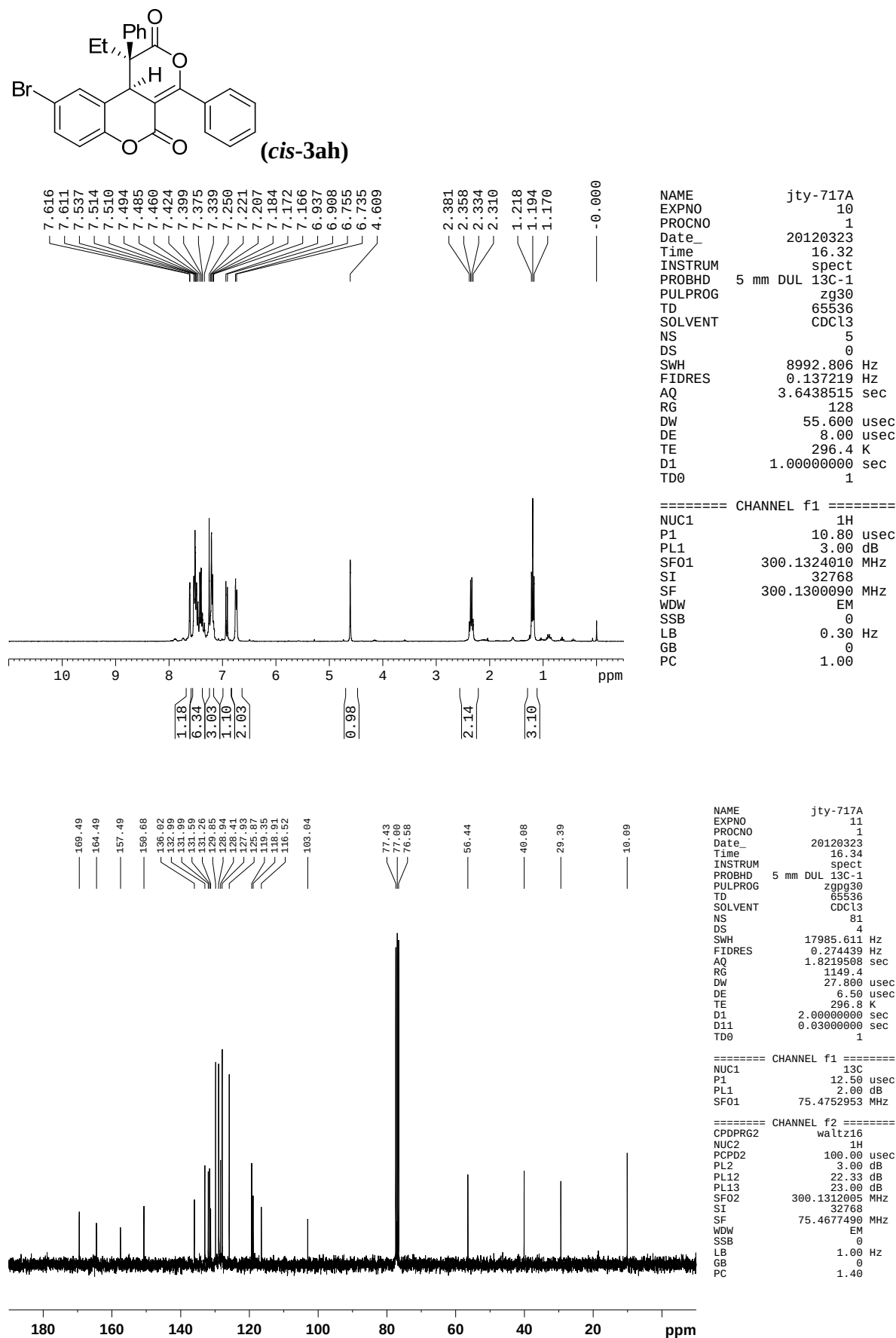
===== CHANNEL f1 =====
NUC1 ¹H
P1 10.80 usec
PL1 3.00 dB
SF01 300.1324010 MHz
SI 32768
SF 300.1300085 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



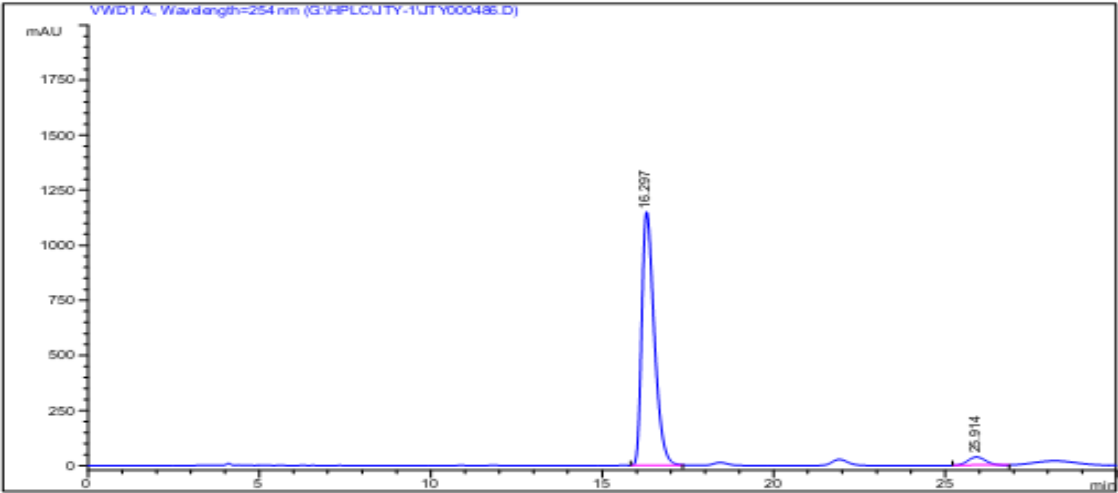
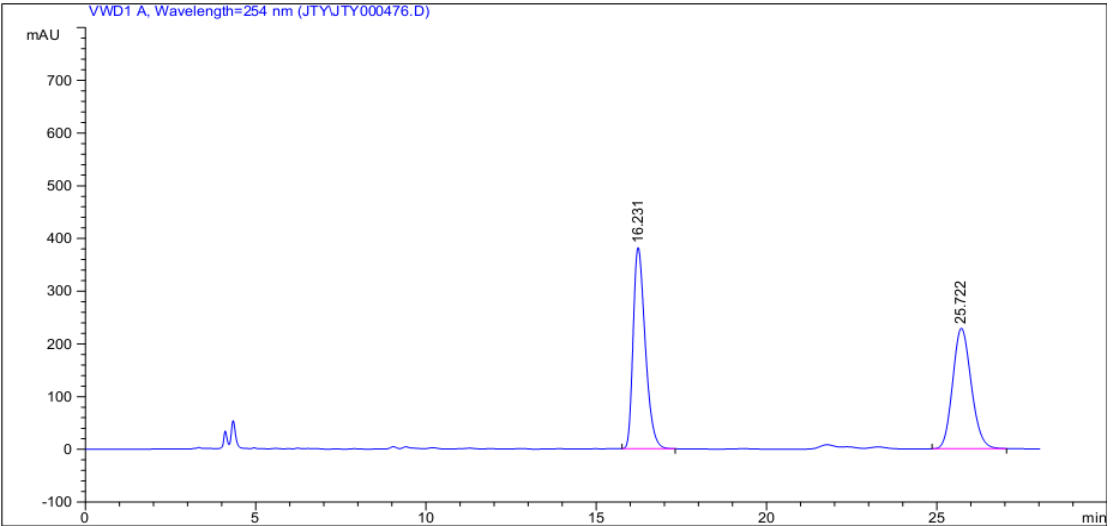
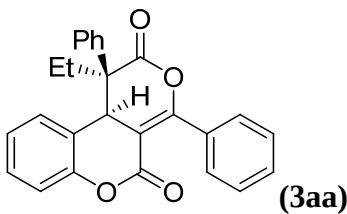
NAME jty-769A
EXPNO 11
PROCNO 1
Date_ 20111017
Time 8.54
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 85
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1149.4
DW 27.800 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 ¹³C
P1 12.50 usec
PL1 2.00 dB
SF01 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.33 dB
PL13 23.00 dB
SF02 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Part II HPLC Spectra



=====
Area Percent Report
=====

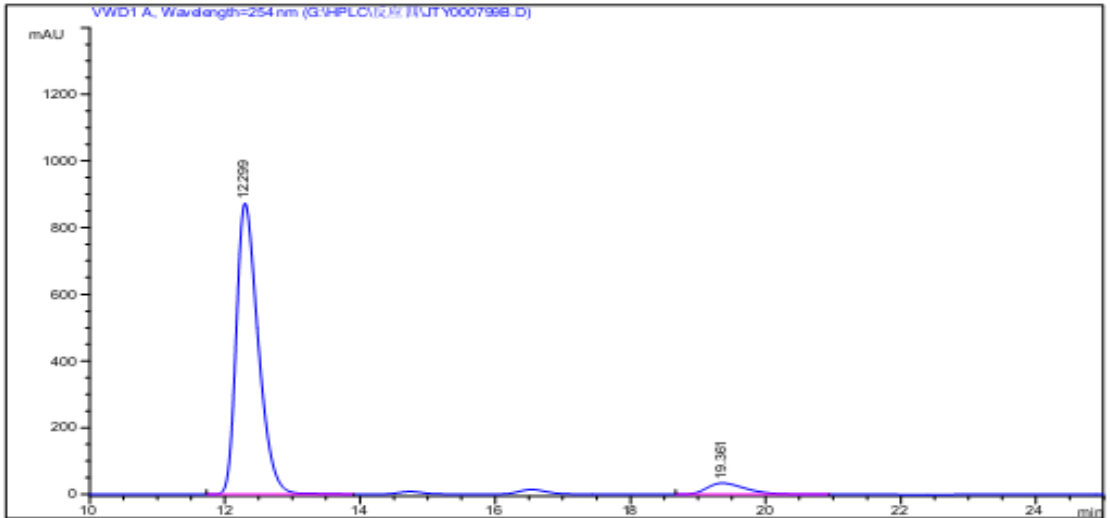
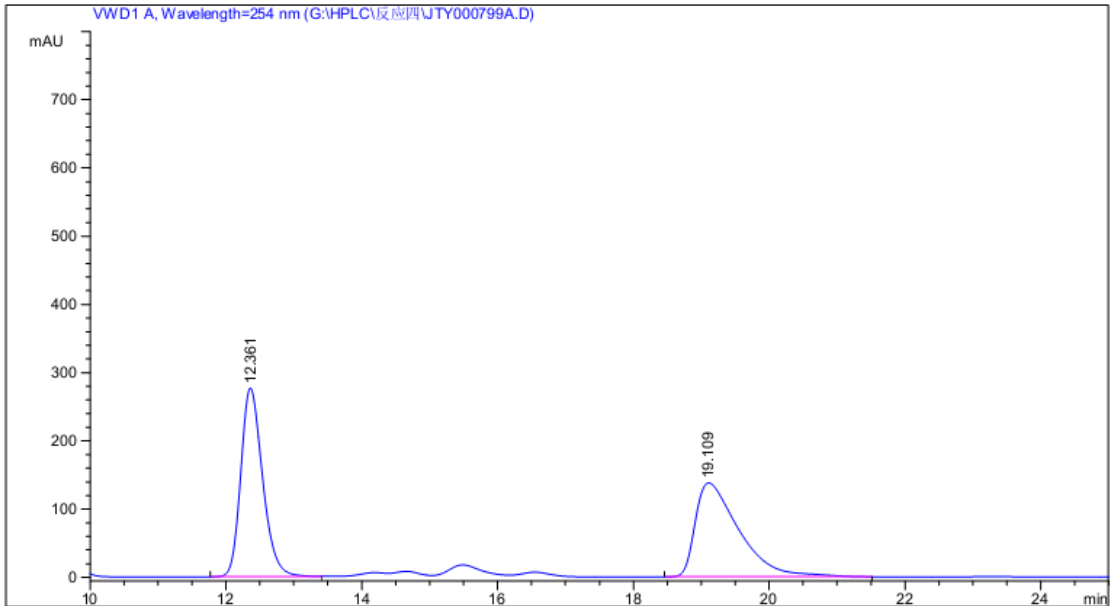
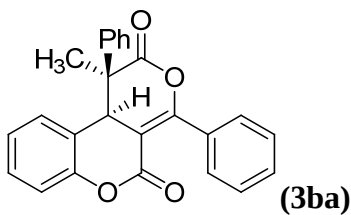
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	16.297	BB	0.3887	2.91422e4	95.5043	1150.43677
2	25.914	BB	0.5685	1371.83289	4.4957	37.71310

Totals : 3.05141e4 1188.14987

=====
*** End of Report ***
=====



=====
Area Percent Report
=====

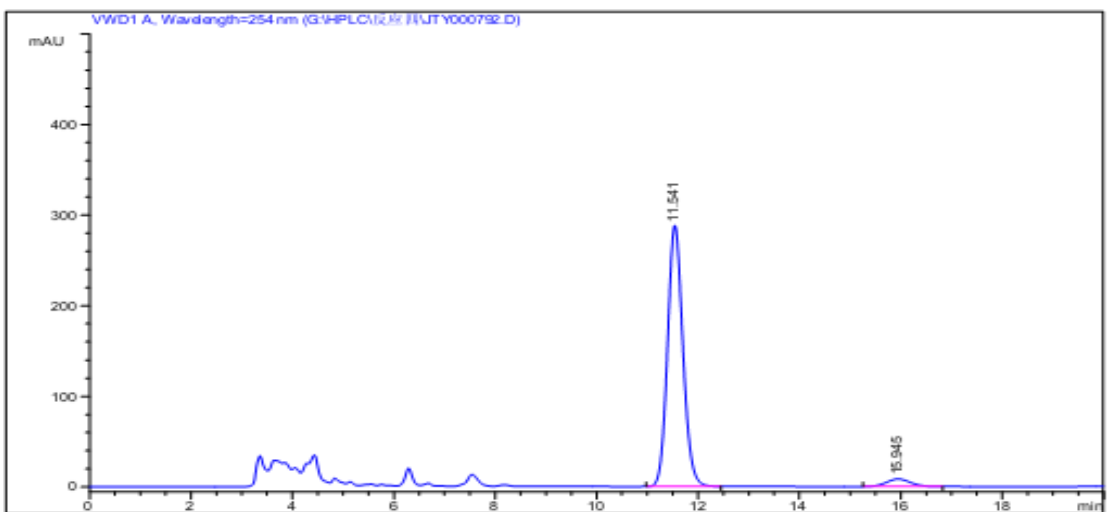
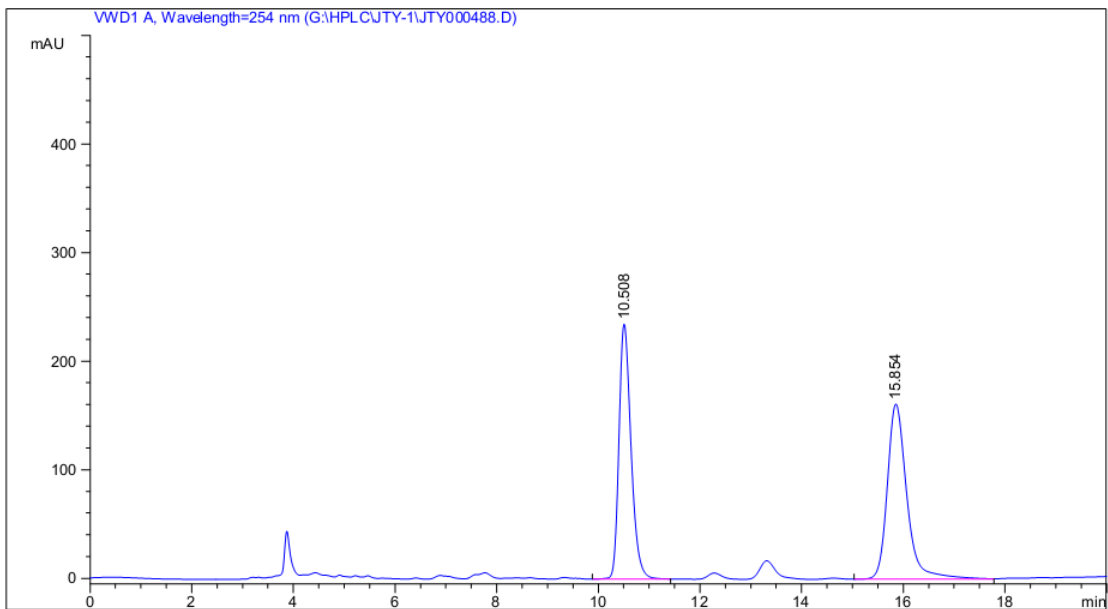
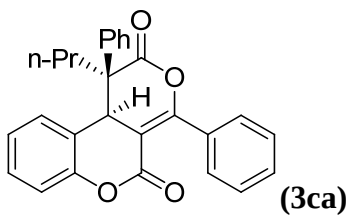
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	12.299	BB	0.3445	1.96763e4	873.11322	93.4891
2	19.361	BB	0.6178	1370.32056	34.06836	6.5109

Totals : 2.10466e4 907.18158

=====
*** End of Report ***



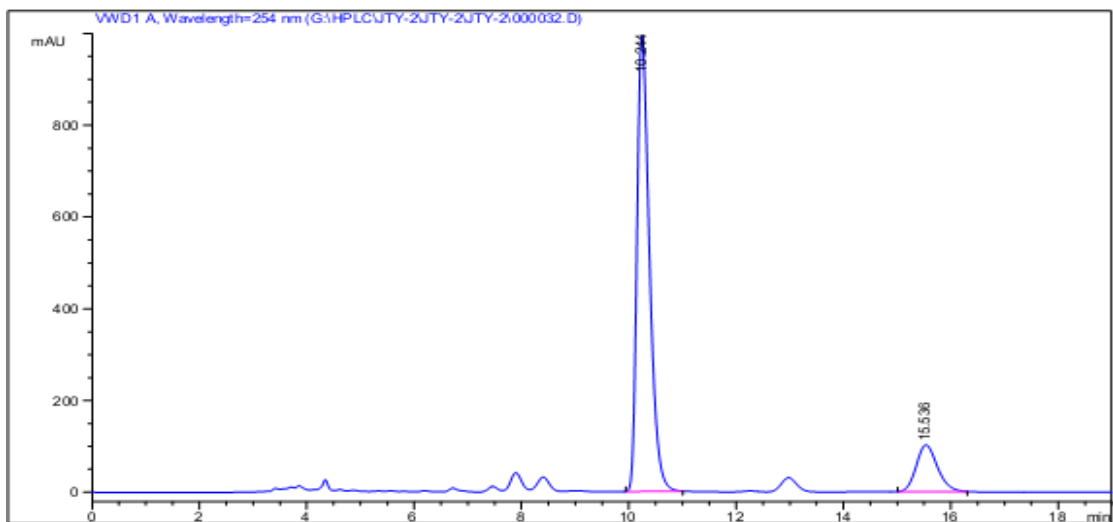
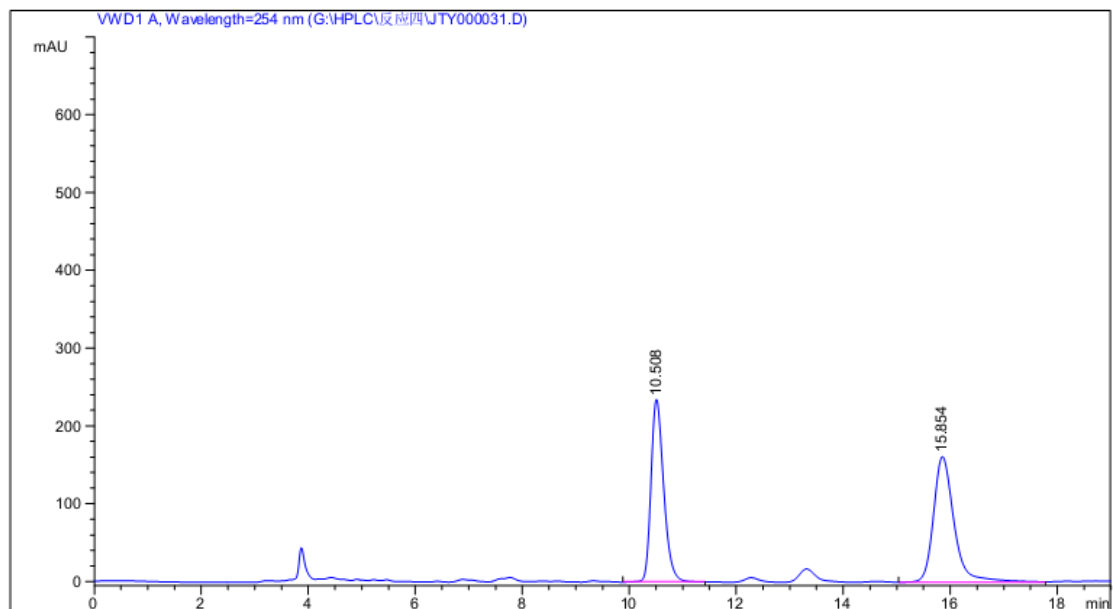
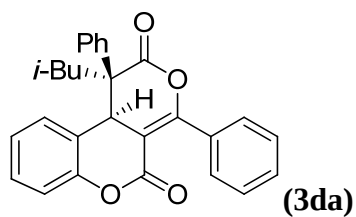
=====
Area Percent Report
=====

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

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	11.541	BB	0.3242	6066.02539	288.17859	95.5563
2	15.945	BB	0.5178	282.09125	8.35111	4.4437
Totals :				6348.11664	296.52970	

=====
*** End of Report ***
=====



Area Percent Report

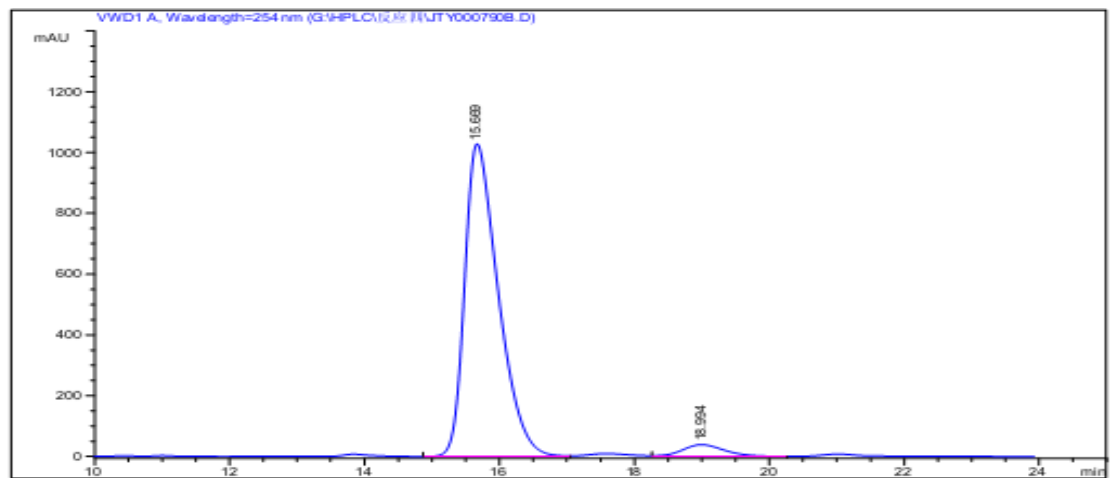
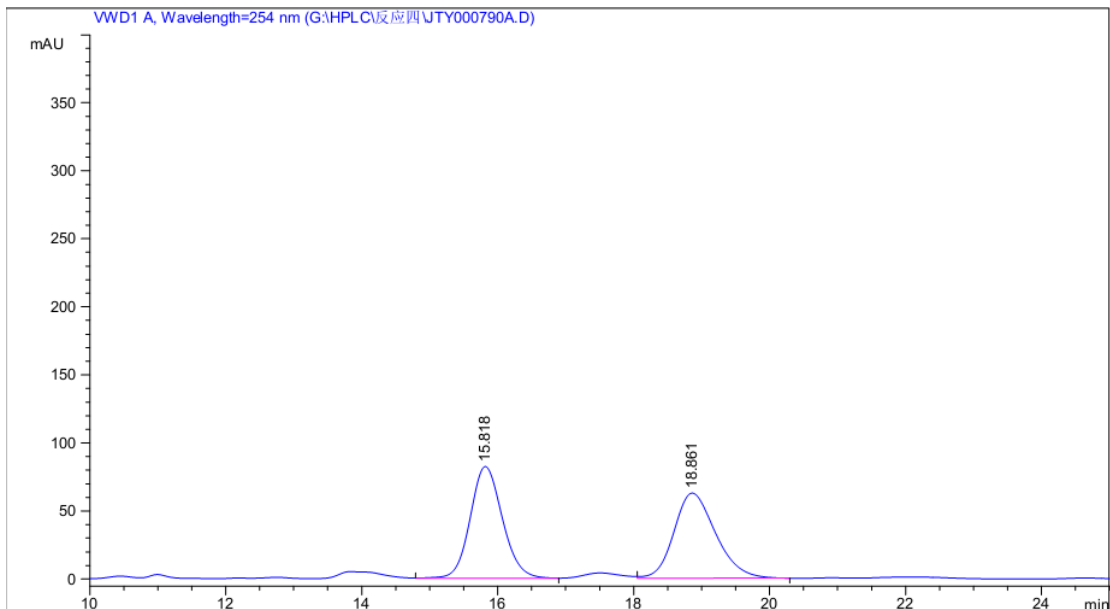
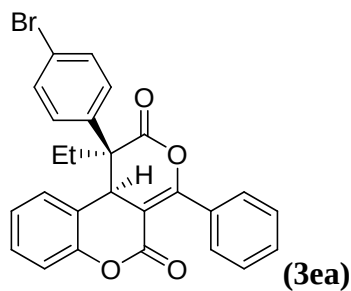
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	10.244	BB	0.2463	1.60289e4	84.9837	994.59863
2	15.536	BB	0.4239	2832.23560	15.0163	102.17484

Totals : 1.88611e4 1096.77347

*** End of Report ***



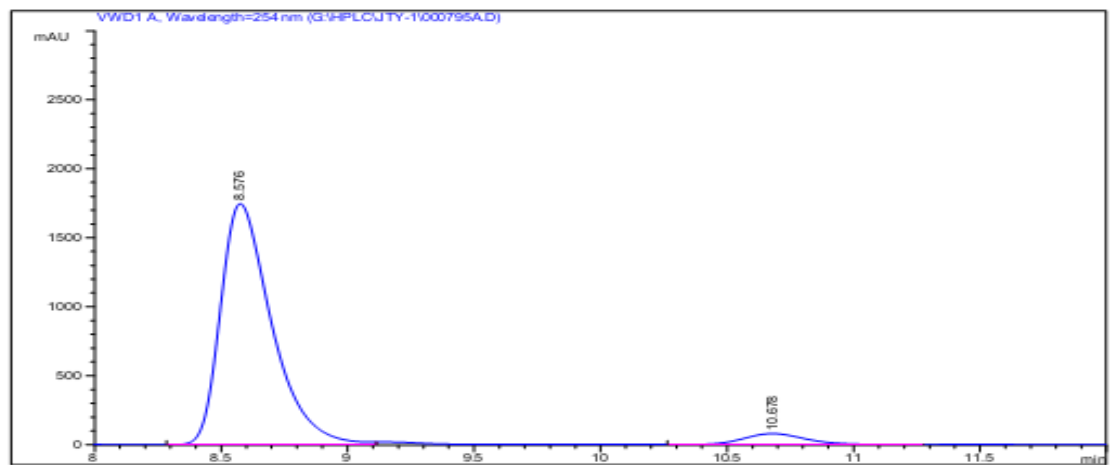
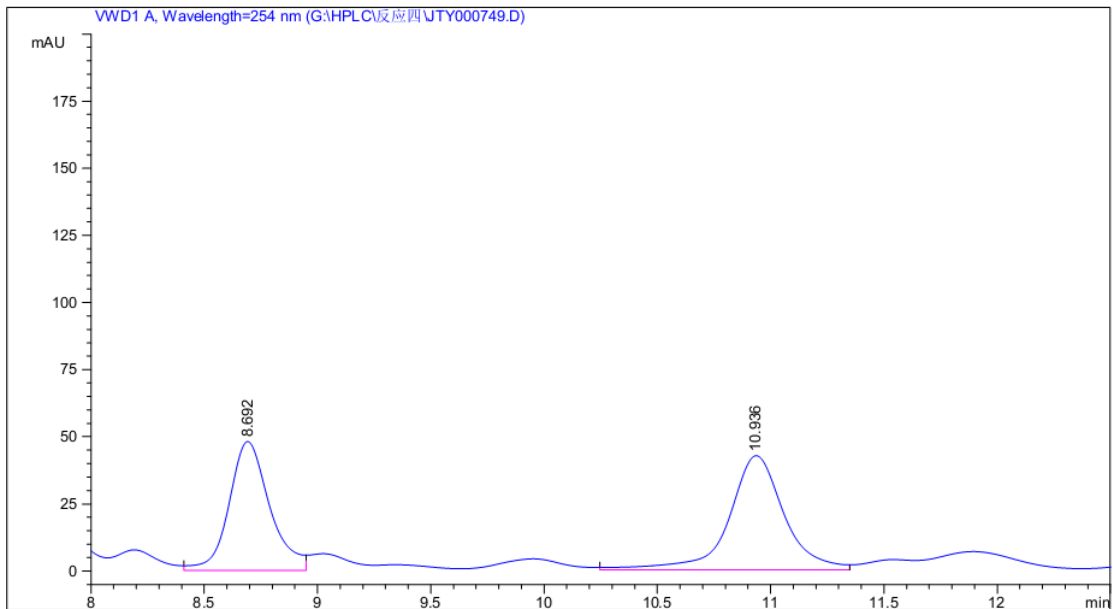
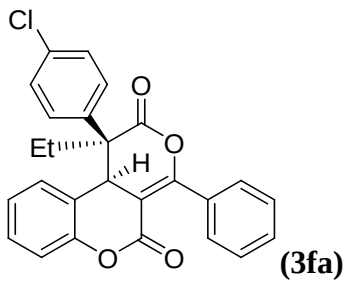
=====
Area Percent Report
=====

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

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	15.669	BV	0.5242	3.55431e4		1028.07043	95.3694
2	18.994	VB	0.6763	1725.76172		38.89533	4.6306
Totals :				3.72688e4		1066.96577	

=====
*** End of Report ***



=====
Area Percent Report
=====

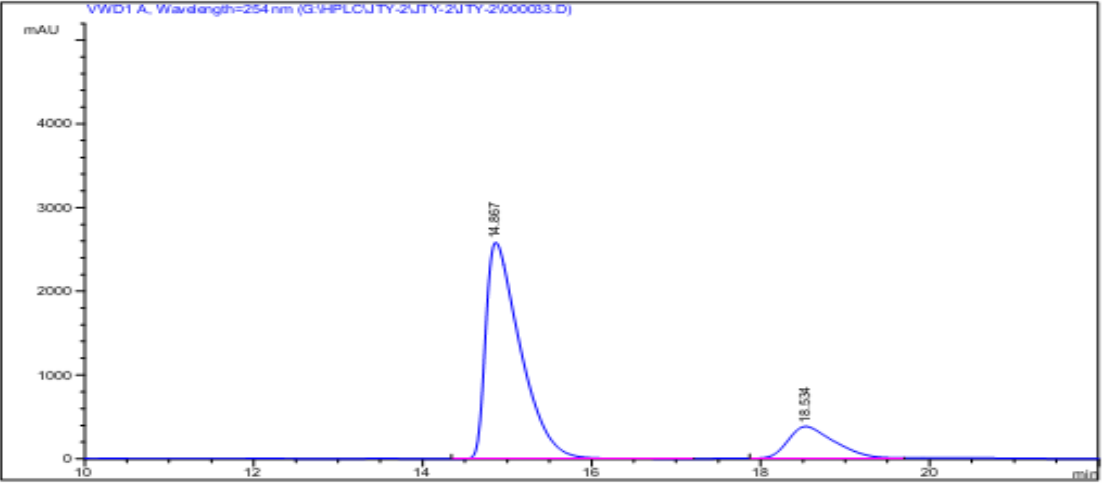
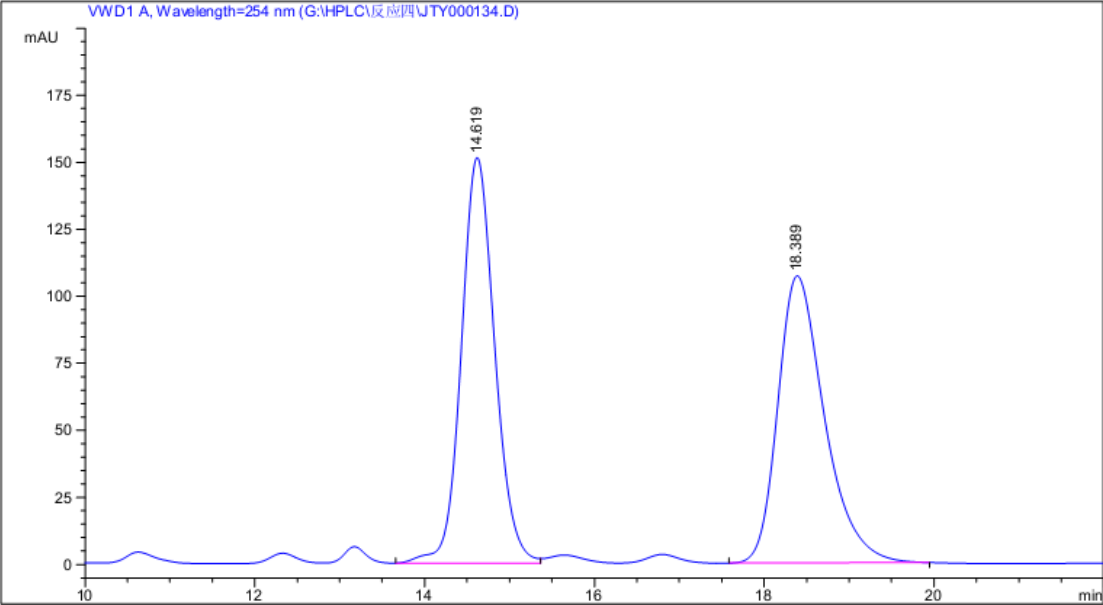
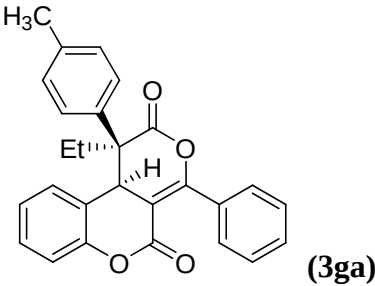
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.576	BV	0.2131	2.44853e4	1746.01221	94.7159
2	10.678	WV	0.2639	1366.00330	79.75955	5.2841

Totals : 2.58513e4 1825.77176

=====
*** End of Report ***
=====



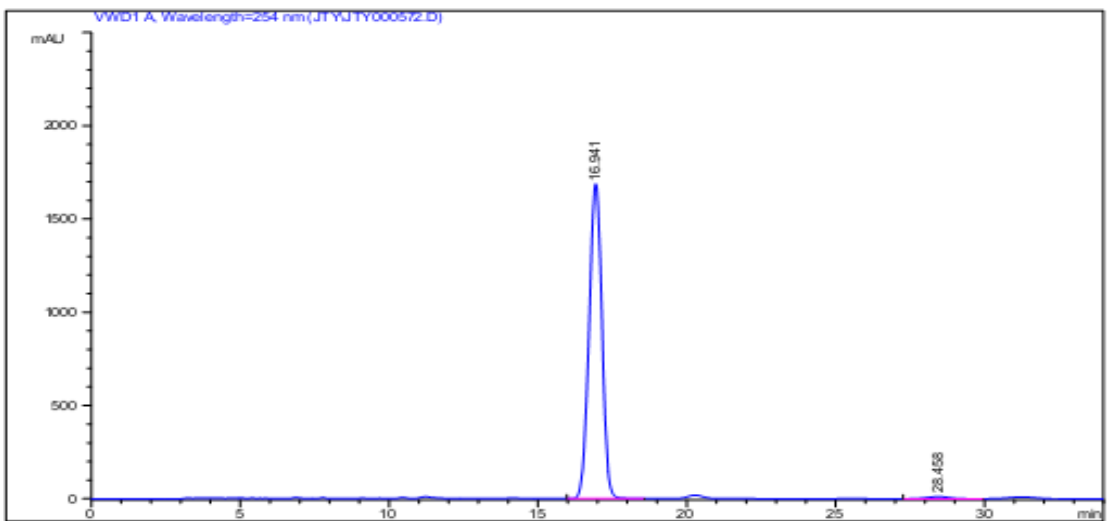
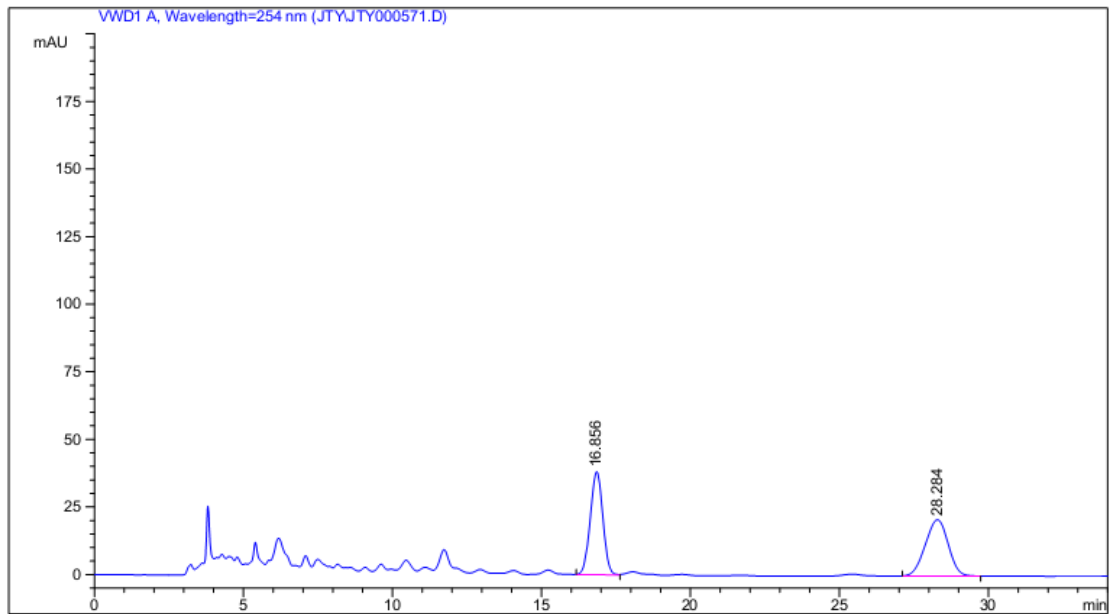
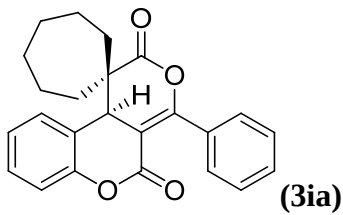
=====
Area Percent Report
=====

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

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	14.867	VB	0.4243	7.32993e4		2582.42432	83.0566
2	18.534	VV	0.5714	1.49529e4		384.71555	16.9434
Totals :				8.82522e4		2967.13986	

=====
*** End of Report ***



```

=====
Area Percent Report
=====

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

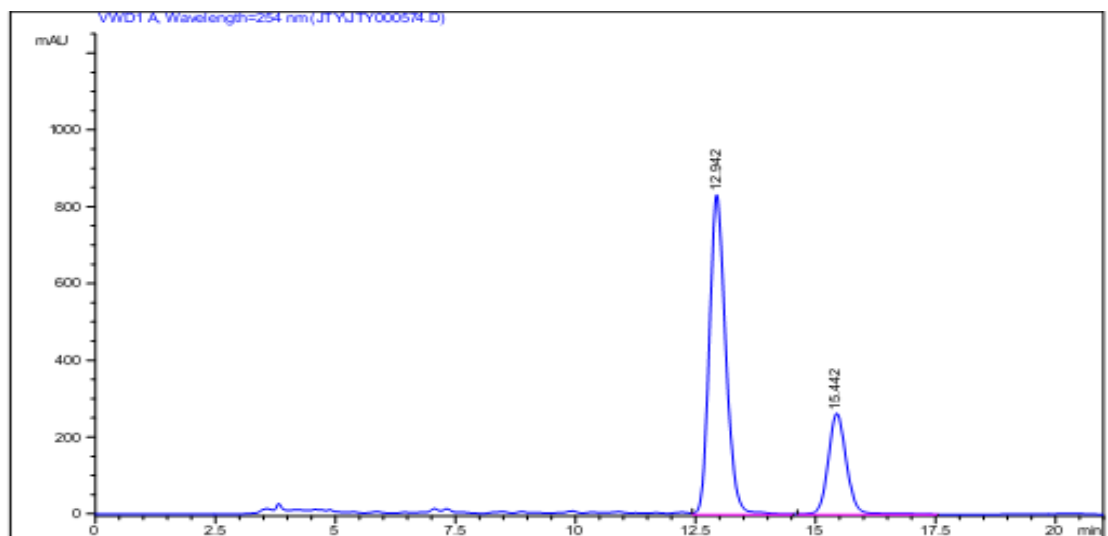
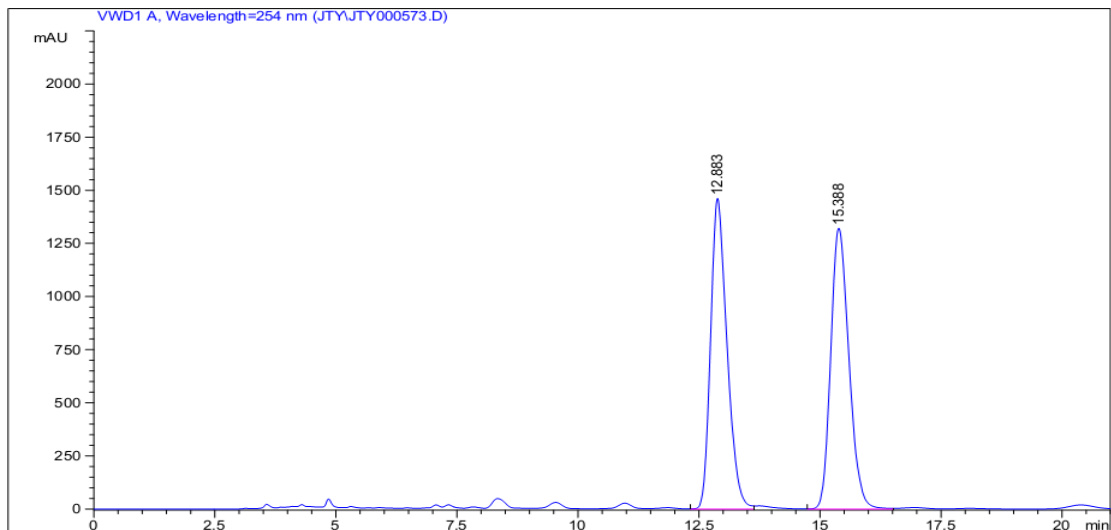
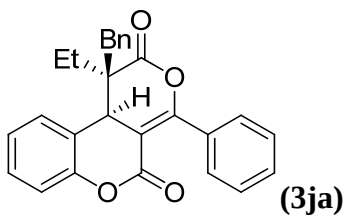
Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU] %
-----|-----|-----|-----|-----|-----|
1 16.941 VB 0.4709 5.04466e4 1688.53162 98.7641
2 28.458 BB 0.8586 631.26917 11.66238 1.2359

Totals : 5.10779e4 1700.19400

=====
*** End of Report ***
=====

```



=====
Area Percent Report
=====

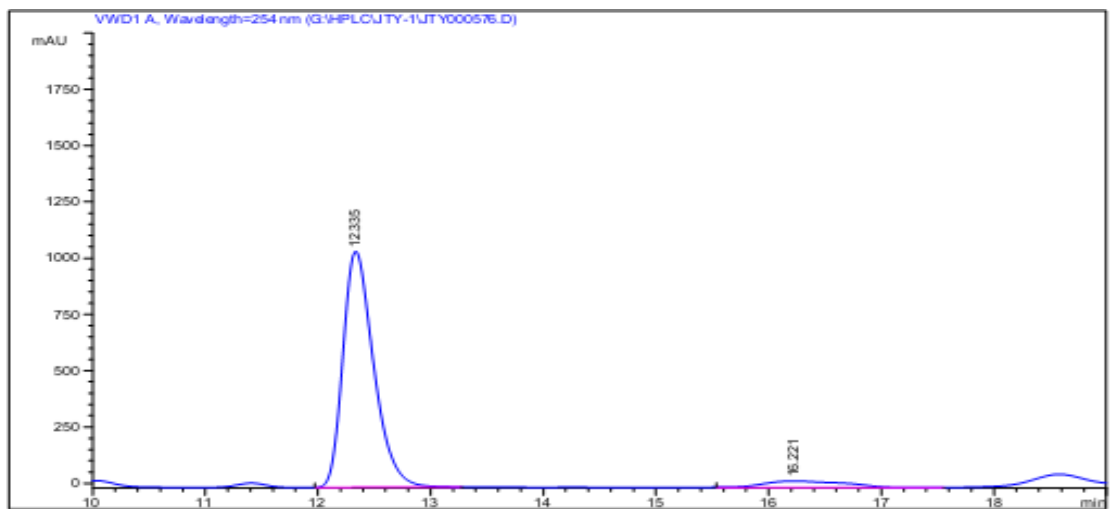
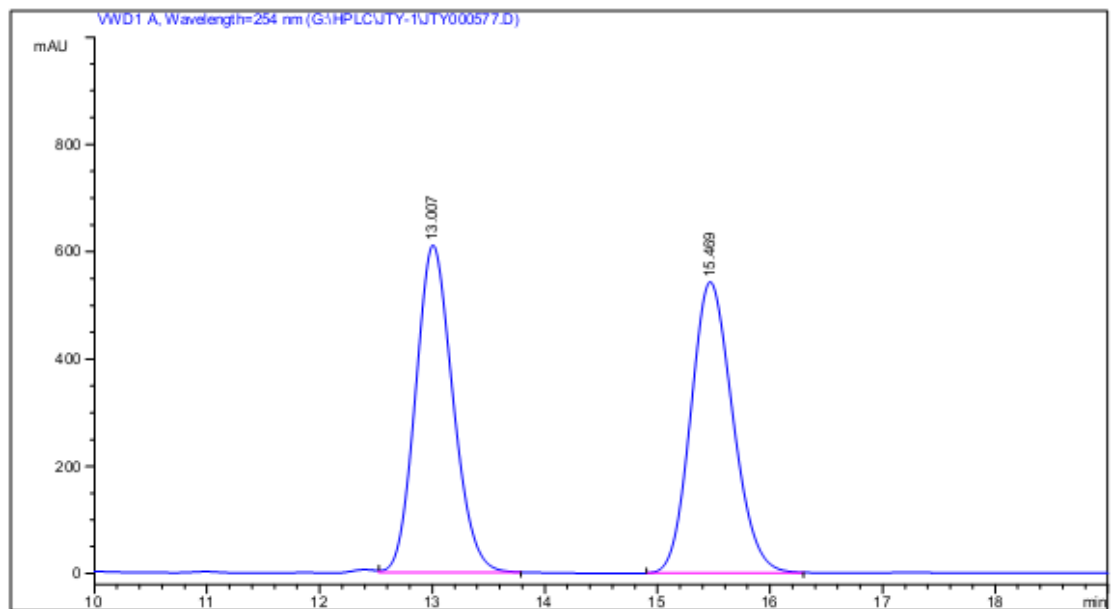
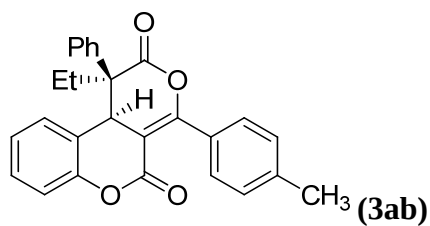
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	12.942	VB	0.3595	1.96102e4	831.94019	73.7918
2	15.442	BB	0.4068	6964.84473	262.78244	26.2082

Totals : 2.65750e4 1094.72263

=====
*** End of Report ***
=====



=====
Area Percent Report
=====

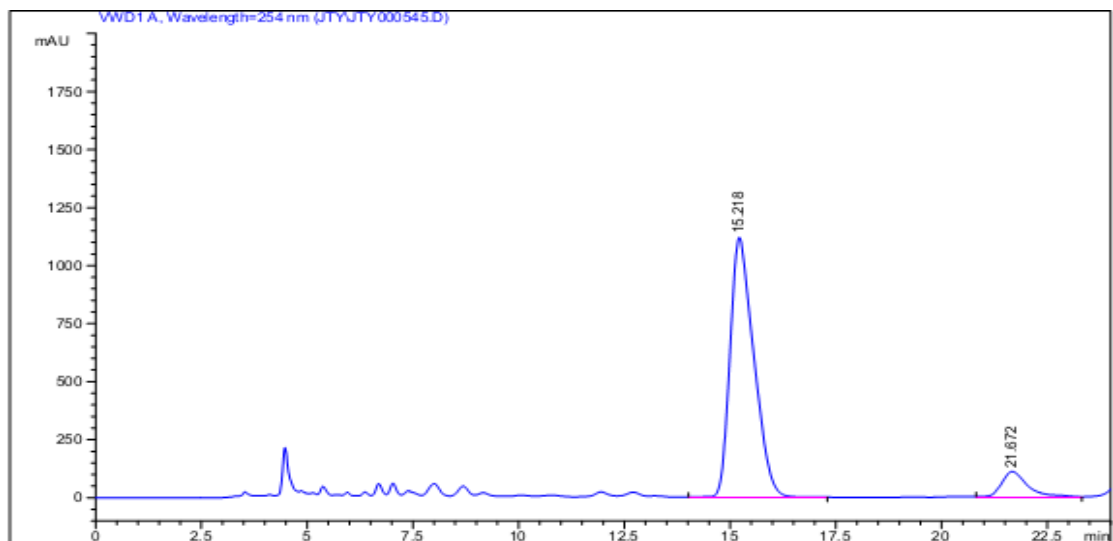
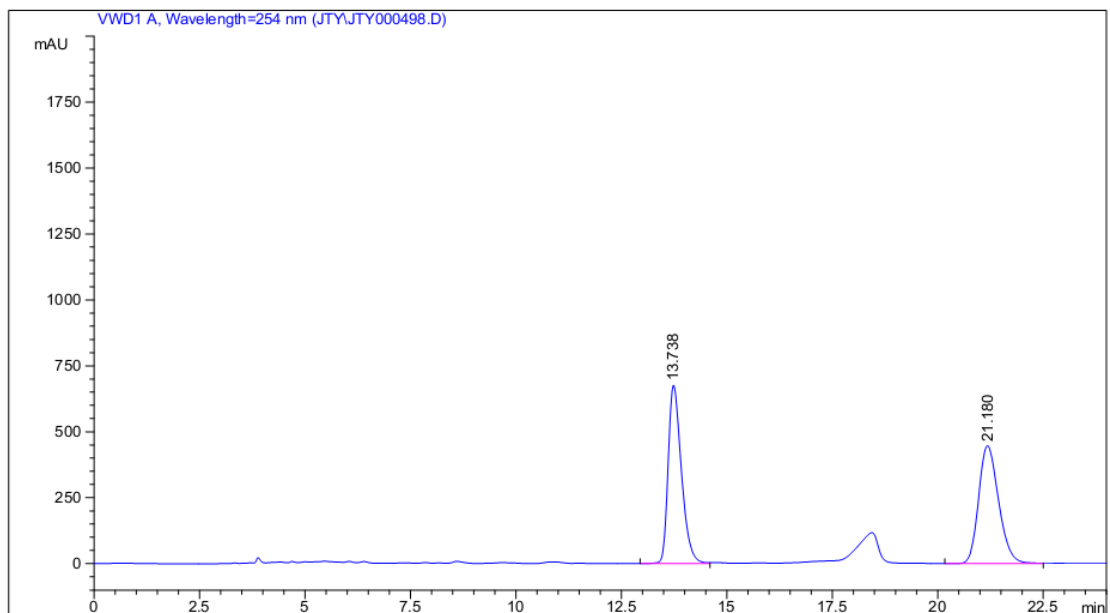
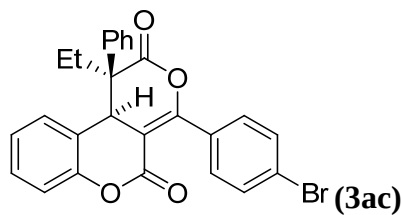
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	12.335	BB	0.2914	1.99177e4	93.3647	1049.10437
2	16.221	BB	0.7206	1415.51538	6.6353	28.43234

Totals : 2.13332e4 1077.53671

=====
*** End of Report ***
=====



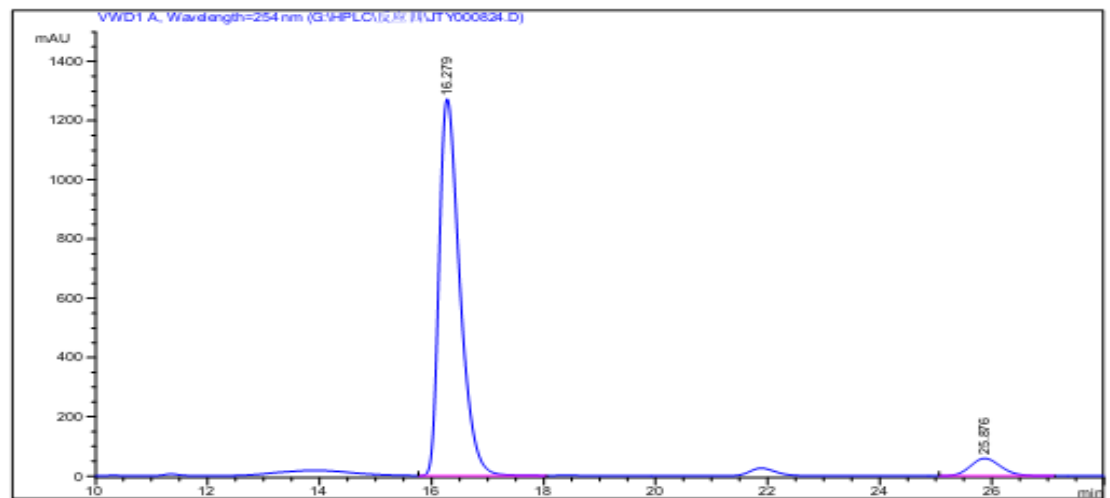
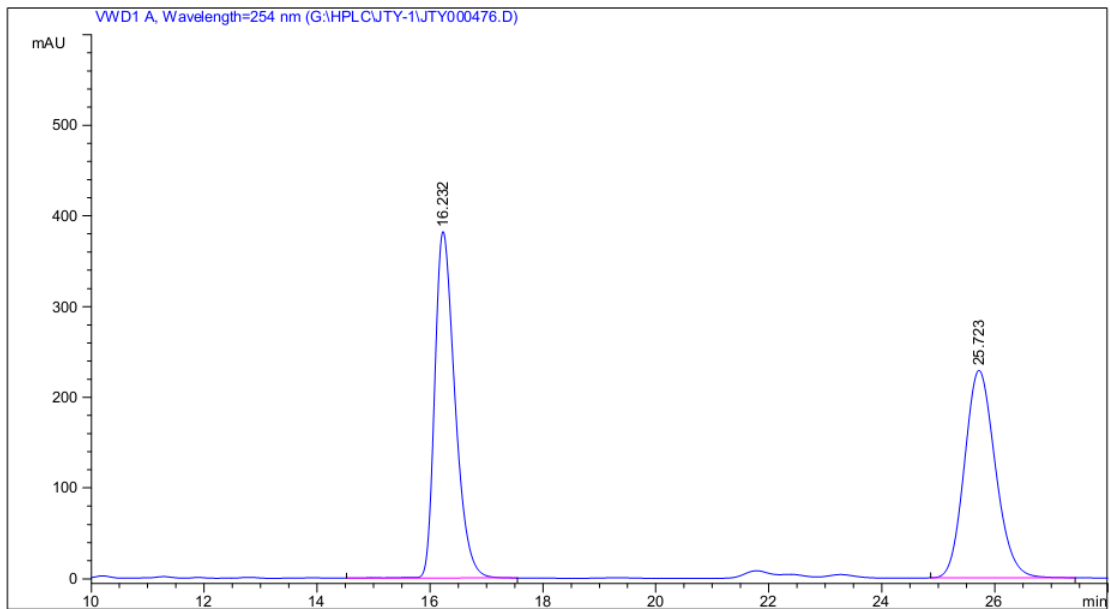
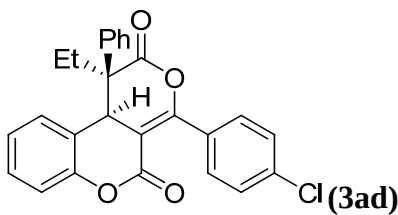
Area Percent Report

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

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	15.218	BB	0.5713	4.36596e4	1119.87463	89.9881	
2	21.672	VV	0.6487	4857.49951	110.71214	10.0119	

Totals : 4.85171e4 1230.58677



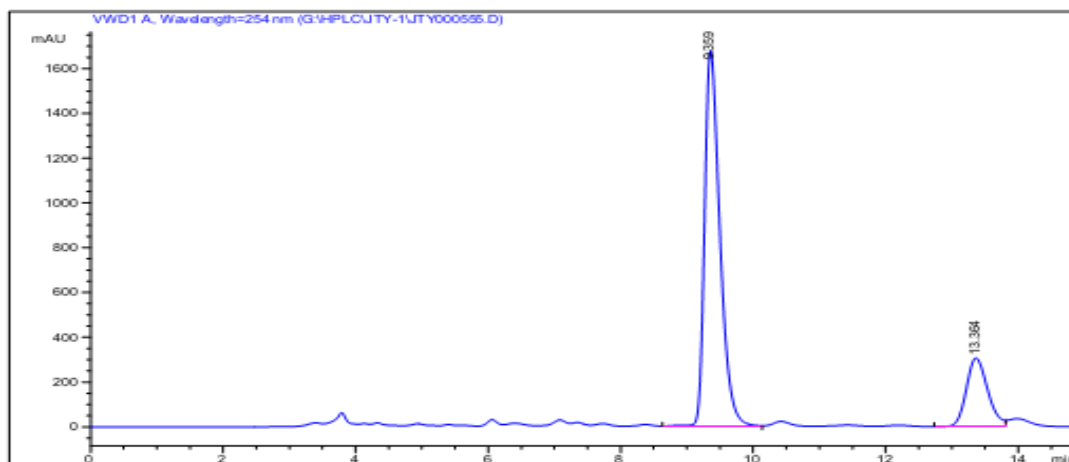
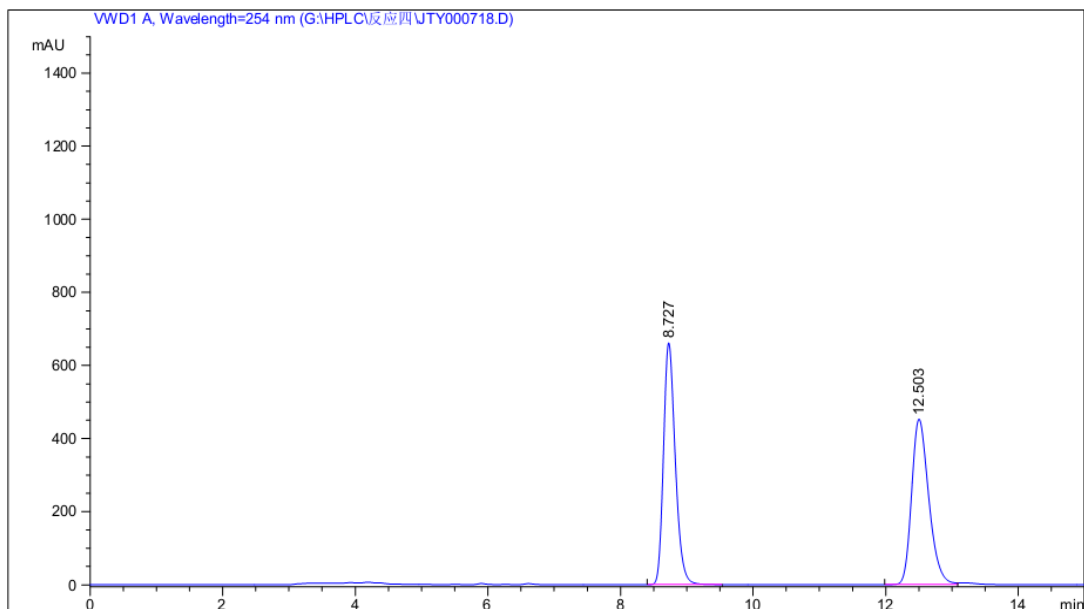
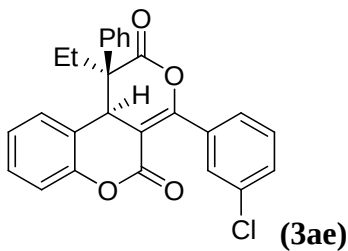
=====
Area Percent Report
=====

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

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	16.279	VB	0.3919	3.25953e4	93.5119	1272.95337
2	25.876	BB	0.5899	2261.53711	6.4881	59.38419
Totals :				3.48569e4		1332.33756

=====
*** End of Report ***



=====
Area Percent Report
=====

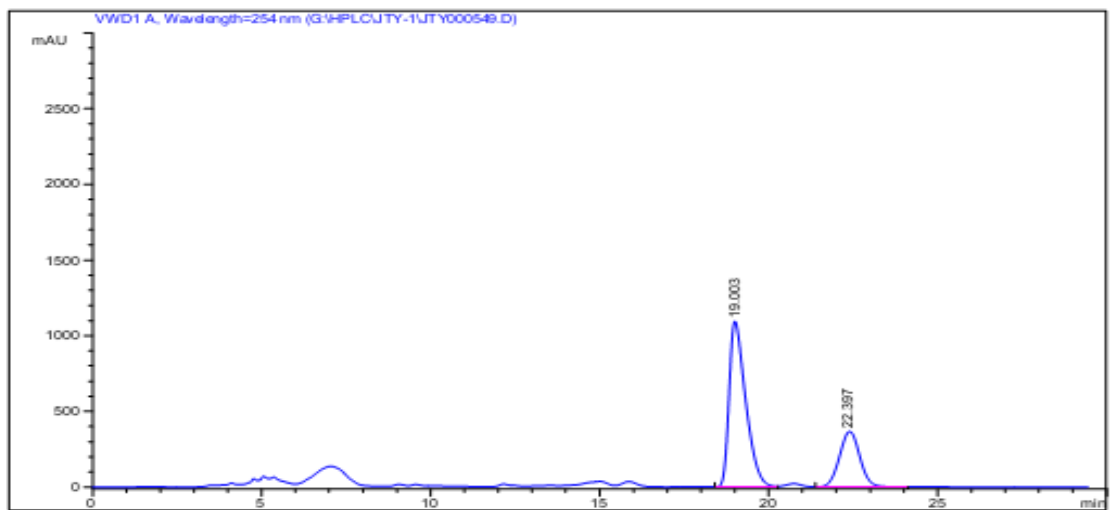
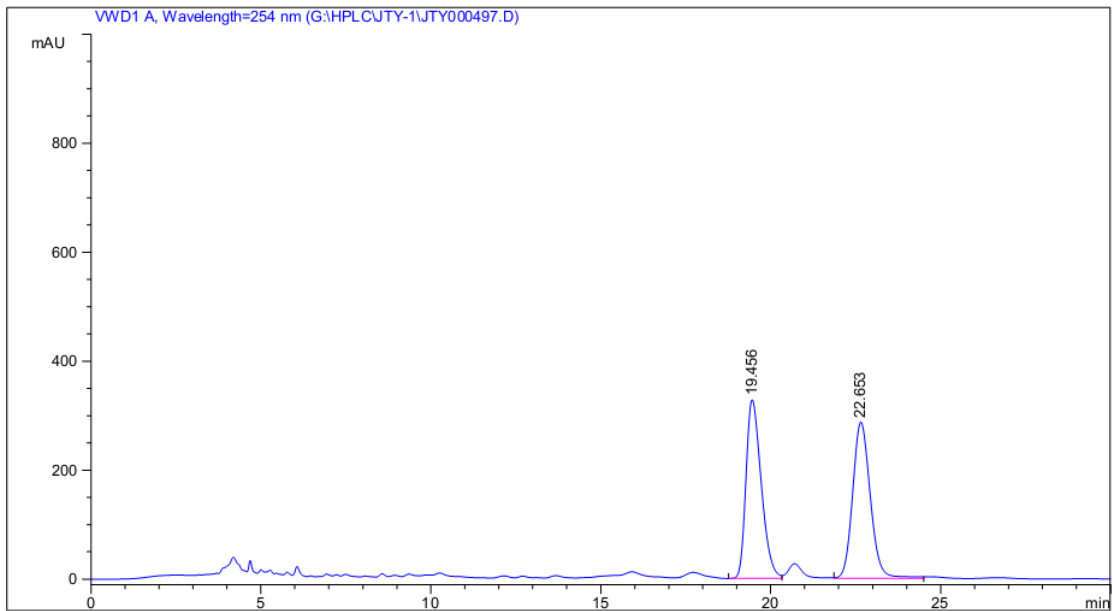
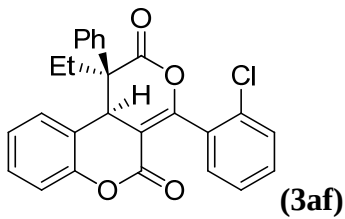
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.359	VV	0.2464	2.71057e4	1680.30640	79.8088
2	13.364	VV	0.3473	6857.60400	306.08212	20.1912

Totals : 3.39633e4 1986.38852

=====
*** End of Report ***



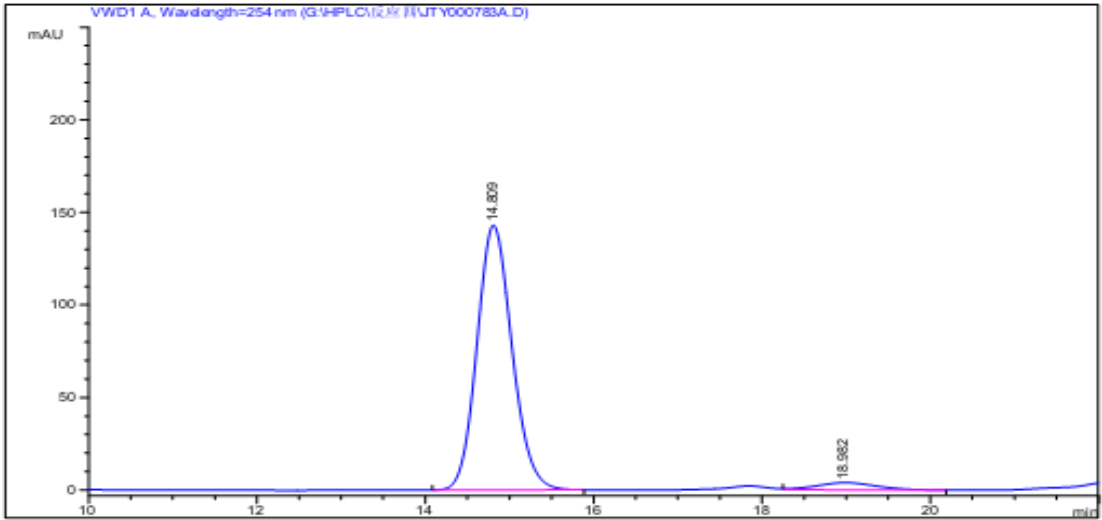
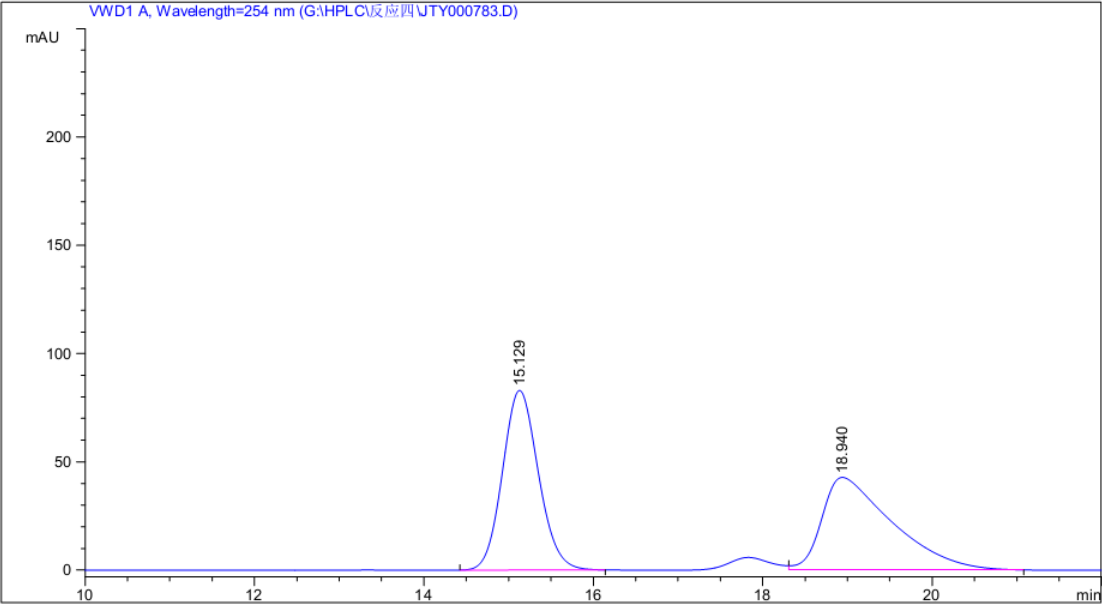
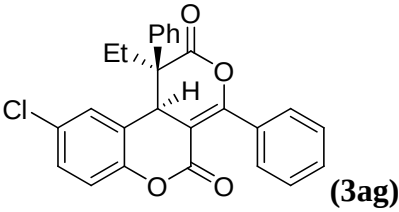
=====
Area Percent Report
=====

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

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.003	VV	0.5111	3.72987e4	1094.71167	70.8708
2	22.397	VB	0.6491	1.53304e4	366.88153	29.1292
Totals :				5.26292e4	1461.59320	

=====
*** End of Report ***
=====



=====
Area Percent Report
=====

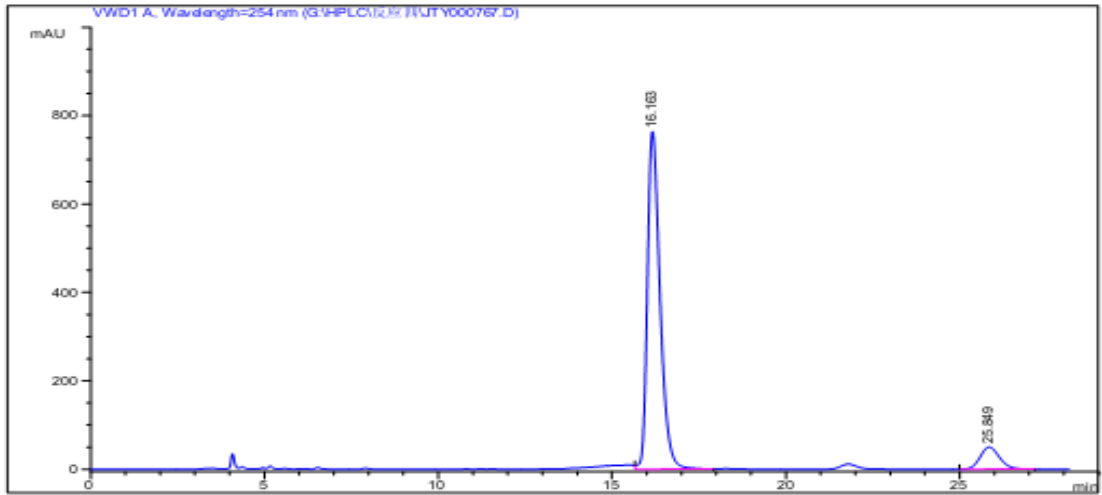
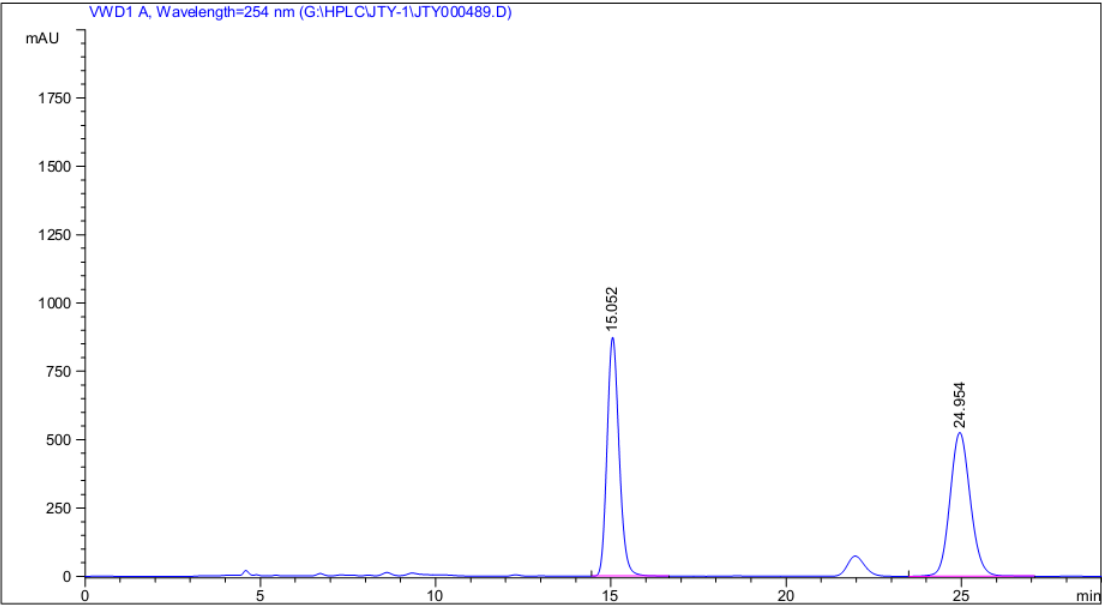
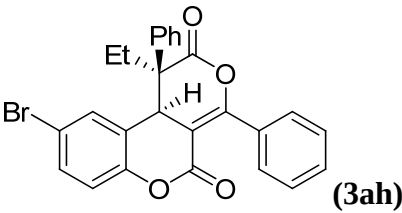
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	14.809	BB	0.4492	4150.95654	143.03116	95.3122
2	18.982	VB	0.7357	204.15945	3.99719	4.6878

Totals : 4355.11600 147.02835

=====
*** End of Report ***
=====



=====
Area Percent Report
=====

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

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.163	VB	0.3864	1.92965e4	763.88861	90.7751
2	25.849	BB	0.6082	1960.96912	50.09086	9.2249
Totals :				2.12574e4	813.97947	

=====
*** End of Report ***