

# 4-Hydroxybenzyl-substituted Amino Acid Derivatives from

## *Gastrodia elata*

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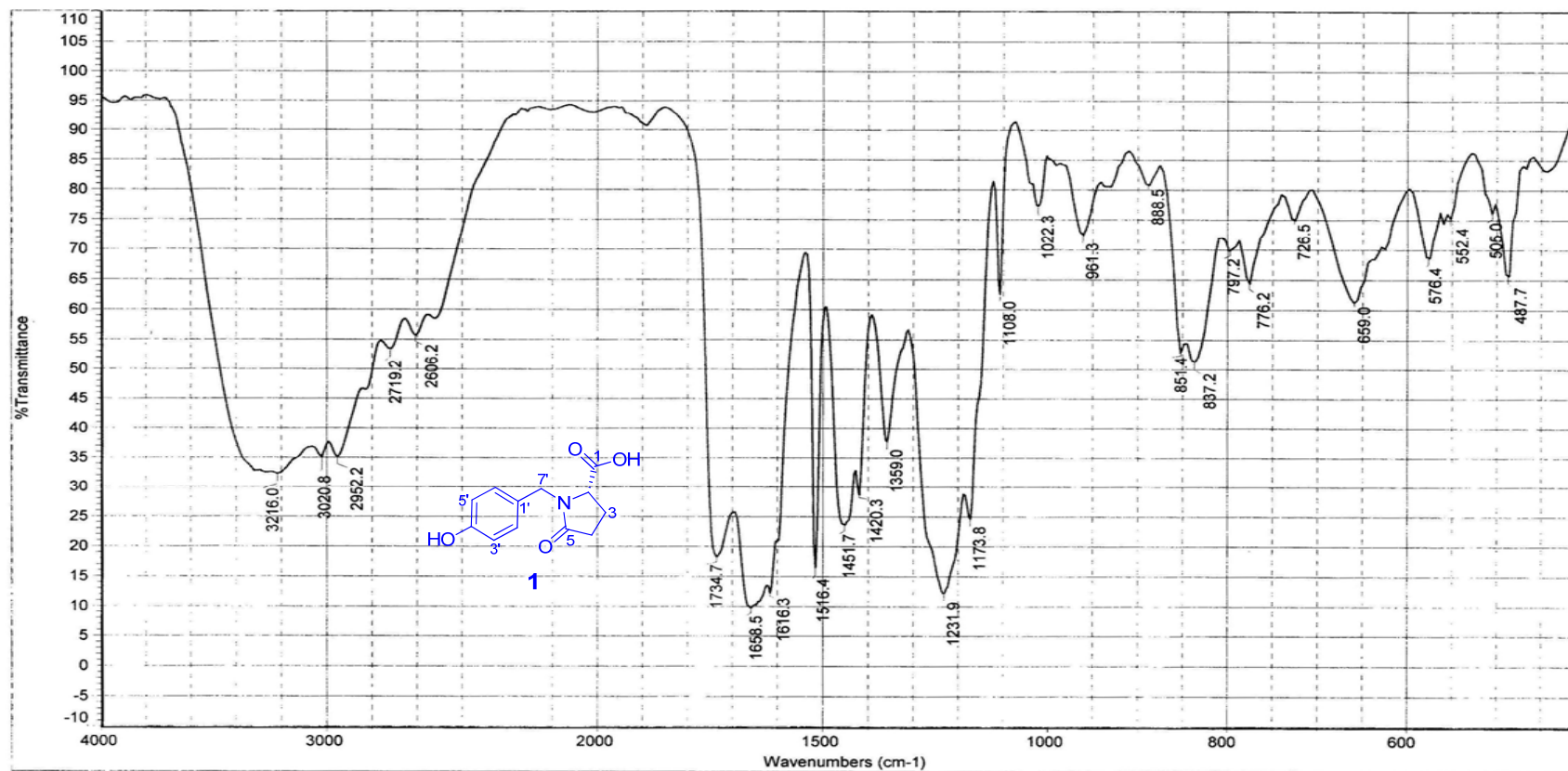
**Isolation of the Known Compounds.** Fraction C2-1 (52.5 g) was chromatographed over silica gel and eluted with a gradient of MeOH (0–100%) in CHCl<sub>3</sub> yielded C2-1-1–C2-1-6. Subfraction C2-1-1 (9.5 g) were further separated by Sephadex LH-20 (CH<sub>3</sub>OH-H<sub>2</sub>O, 1:1) to yield subfractions C2-1-1-1–C2-1-1-8, and C2-1-1-2 (45 mg) was subjected to RP-HPLC (C<sub>18</sub> column, 2.0 mL/min), using CH<sub>3</sub>OH-H<sub>2</sub>O (14:86) containing 0.1% TFA as the mobile phase, to yield bis-[(4-hydroxybenzyl)sulfide] (10 mg, *t<sub>R</sub>* = 43.2 min). Subfraction C2-1-2 (7.2 g) was chromatographed over silica gel and eluted with a gradient of MeOH (0–100%) in CHCl<sub>3</sub> to afford subfractions C2-1-2-1– C2-1-2-5. Of these, C2-1-2-1 (230 mg) was separated by silica gel CC (CHCl<sub>3</sub>-MeOH, 10:1), and purified by RP HPLC (45% MeOH in H<sub>2</sub>O, C<sub>18</sub> column, 2.0 mL/min) to give ethyl (+)-(2*S*)-2-hydroxy-3-(4-hydroxyphenyl)propanoate (10 mg, *t<sub>R</sub>* = 20.2 min) and 1-(4-hydroxyphenyl)propane-1,2-dione (4.3 mg, *t<sub>R</sub>* = 24.5 min). Subfraction C2-1-2-3 (1.8 g) was separated by flash chromatography over RP silica gel and eluted with a gradient of MeOH (0–50%) in H<sub>2</sub>O to give C2-1-2-3-1– C2-1-2-3-7. C2-1-2-3-1 (200 mg) was crystallized in MeOH to afford 1-ethyl citrate (130 mg), and the parent solution was separated by CC over HW-40C (MeOH) to afford 4-(hydroxymethyl)-5-nitrobenzene-1,2-diol (4.5 mg). C2-1-2-3-3 (0.5 g) was chromatographed over MCI (50% MeOH in H<sub>2</sub>O), and purified by RP HPLC (40% MeOH in H<sub>2</sub>O, containing 0.1% TFA, C<sub>18</sub> column, 2.0 ml/min) to yield (–)-(6*R*)-6,7-dihydroxy-3,7-dimethyloct-2(*Z*)-enoic acid (2.5 mg, *t<sub>R</sub>* = 24.1 min) and 6-ethyl citrate (5.3 mg, *t<sub>R</sub>* = 26.2 min).

Subfraction C3-1-4-4-2 (26 mg) was separated by CC over HW-40F (MeOH) to give C3-1-4-4-2-1–C3-1-4-4-2-2, which were separately purified by RP HPLC using 25% MeOH in H<sub>2</sub>O (containing 0.1% TFA) to afford cyclo[glycine-*L-S*-(4''-hydroxybenzyl)cysteine] (2 mg, *t<sub>R</sub>* = 32.3 min, C<sub>18</sub> column, 2.0 mL/min) from C3-1-4-4-2-1, and using 8% MeOH in H<sub>2</sub>O (containing 0.1% TFA) to afford (–)-4-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyloxybenzyl alcohol (3.1 mg, *t<sub>R</sub>* = 36.2 min, C<sub>18</sub> column, 2.0 mL/min) from C3-1-4-4-2-2. Subfraction of C3-5-2 was separated by CC over Sephadex LH-20 (CH<sub>3</sub>OH-H<sub>2</sub>O, 1:1) to afford C3-5-2-1–C3-5-2-4. Of these, C-3-5-2-4 was subjected to RP-HPLC purification using CH<sub>3</sub>OH-H<sub>2</sub>O (15:85, containing 0.1% TFA, Ph column, 2.0 mL/min) to afford parishin E (6 mg, *t<sub>R</sub>* = 28.1 min) and 2-[4-*O*-(β-D-glucopyranosyl)benzyl]

citrate (16.2 mg,  $t_R = 33.4$  min).

**HPLC–ESIMS Analysis of the Aqueous and a CH<sub>3</sub>CN-eluted Fraction.** The aqueous extract of *Gastrodia elata* rhizomes and a CH<sub>3</sub>CN-eluted fraction, which was prepared by chromatography of the aqueous extract (50 mg) over a reversed-phase C<sub>18</sub> silica gel (2 g) by successive elution with H<sub>2</sub>O (300 mL) and CH<sub>3</sub>CN (100 mL), were analyzed by HPLC–ESIMS using the ion extraction method. Sample analyses were performed on an Agilent 1100 series LC/MSD trap (Agilent Technologies, Waldbronn, Germany) equipped with an ESI source. A Zorbax SB-Aq C<sub>18</sub> column (4.6× 150 mm, 5 μm; Agilent, USA) with an inline filter was used for separation: flow rate was 1.0 mL min<sup>-1</sup>; approximately 50% of the elution inlet into the mass spectrometer by splitting through a T-piece; column temperature at 25 °C. The crude aqueous extract was analyzed under an isocratic elution with 15% CH<sub>3</sub>CN in H<sub>2</sub>O containing 0.1% TFA. The CH<sub>3</sub>CN-eluted fraction was analyzed using a programmed elution of solvents A (H<sub>2</sub>O containing 0.1% TFA) and B (CH<sub>3</sub>CN): 15% B in A for 30 min, increasing B from 30% to 45% in 30–45 min, and then system re-equilibration with A for 10 min.

Compounds **1** and **2** were observed in the crude aqueous extract (Figures S125–S126), and compound **3** in the MeCN-eluted fraction (Figures S127).



日期: 星期五 12月 14 10:37:18 2012 (GMT+08: Sample Name : TMG - 52B

( 显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100

傅里叶变换显微镜红外(FT-IR Microscope): Centaurus

分辨率: 8.000

美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S1. The IR Spectrum of Compound 1

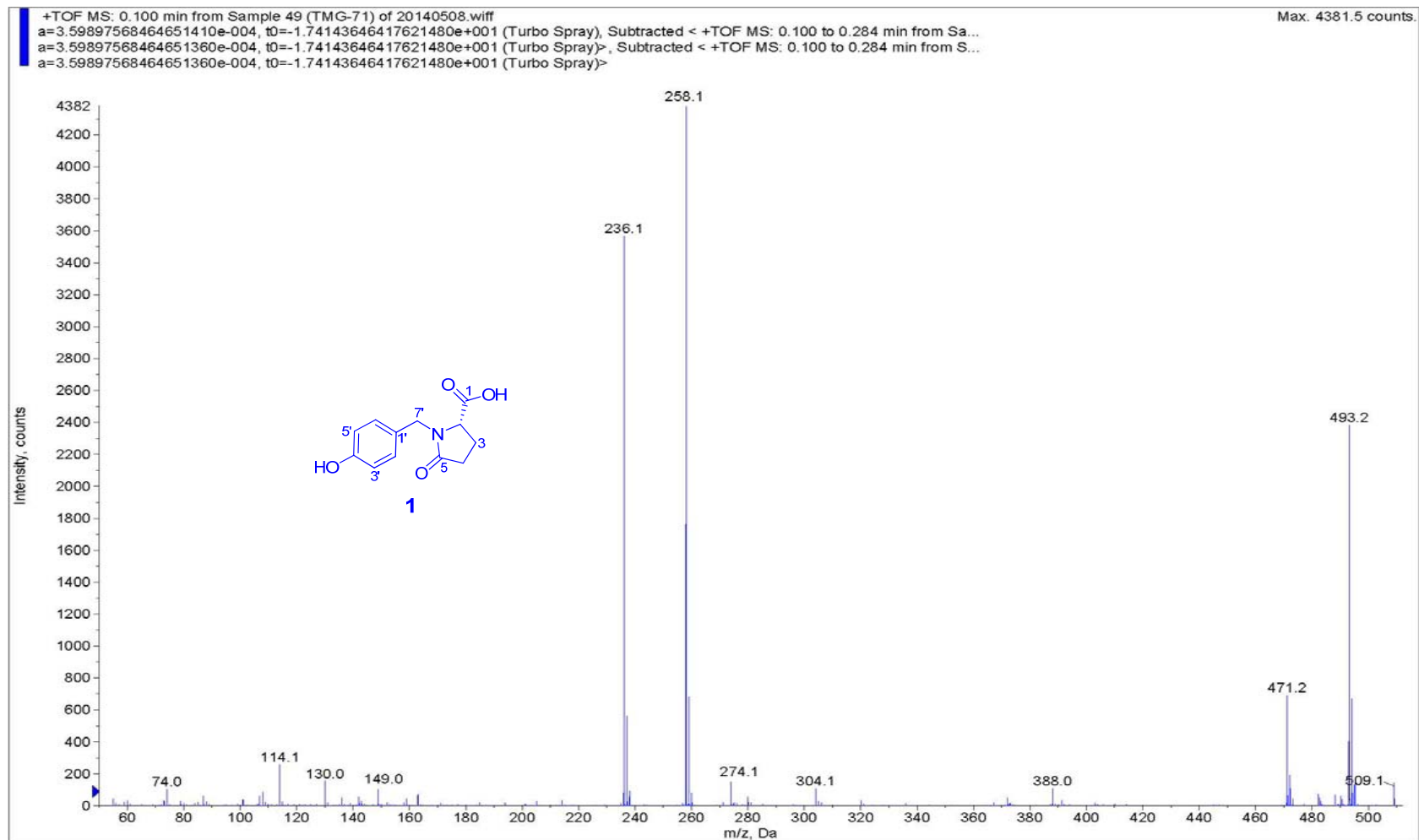
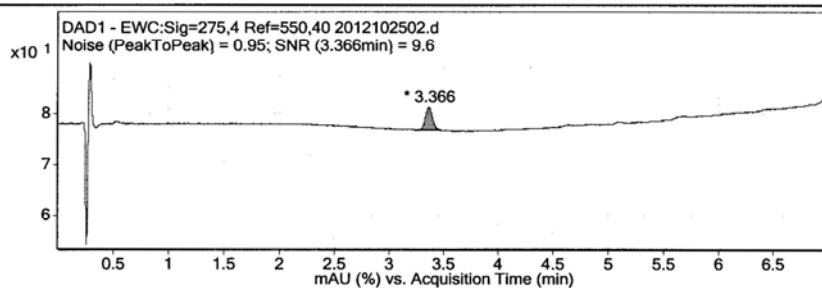


Figure S2. The (+)-ESIMS Spectrum of Compound 1

## Qualitative Analysis Report

<b>Data Filename</b>	2012102502.d	<b>Sample Name</b>	TMG-66
<b>Sample Type</b>	Sample	<b>Position</b>	P1-D6
<b>Instrument Name</b>	Instrument 1	<b>User Name</b>	
<b>Acq Method</b>		<b>IRM Calibration Status</b>	Some Ions Missed
<b>DA Method</b>	TEST LCMS.m	<b>Comment</b>	

### User Chromatograms



### Integration Peak List

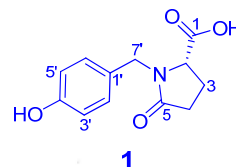
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	3.275	3.366	3.481	2.04	9.124	100	9.6

### Noise Measurements

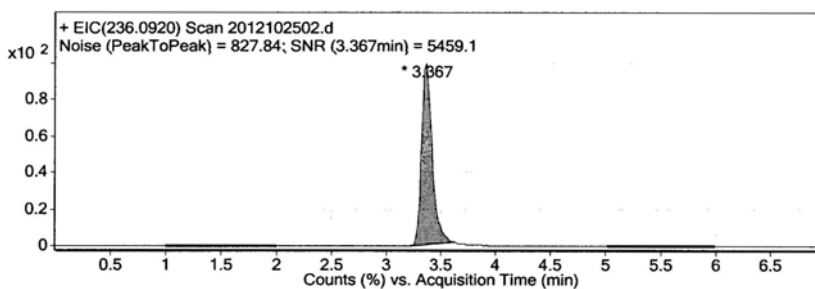
Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0.951028824

### Noise Regions

Start	End
1	2
5	6
8.6	9.4
9.8	11



Fragmentor Voltage 135 Collision Energy 0 Ionization Mode ESI



### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	3.222	3.367	3.625	671400	4519238	100	5459.1

### Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	827.8362427

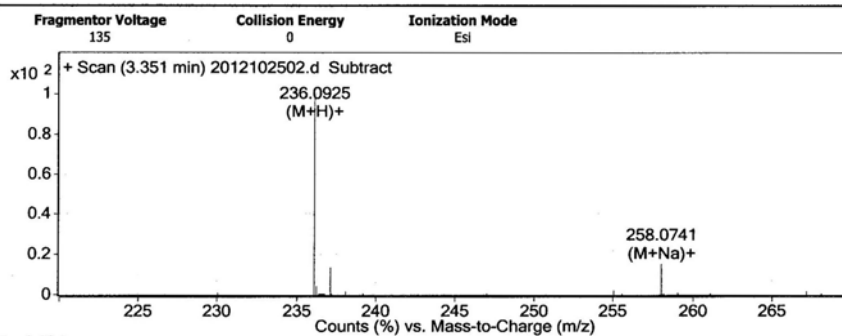
### Noise Regions

Start	End
1	2
5	6
8.6	9.4
9.8	11

**Figure S3.** The (+)-HRESIMS Report of Compound 1, Page 1

# Qualitative Analysis Report

## User Spectra



### Peak List

m/z	z	Abund	Formula	Ion
107.0499		57617		
236.0925	1	653650	C12 H14 N O4	(M+H)+
237.0975	1	87698	C12 H14 N O4	(M+H)+
258.0741		97314	C12 H13 N Na O4	(M+Na)+
471.1773		75679		
493.159		103444		

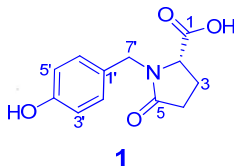
### Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	4
S	0	2
Cl	0	0
Br	0	1

### Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C12 H13 N O4	TRUE	235.0849	235.0845	-1.79	C12 H13 N Na O4	96.45
C12 H14 N O4	TRUE	235.0853	235.0845	-3.4	C12 H14 N O4	99.52

--- End Of Report ---



**Figure S4.** The (+)-HRESIMS Report of Compound **1**, Page 2

MS Formula Results: + Scan (3.351 min) Sub (2012102502.d)

m/z	Ion	Formula	Abundance											
236.0925	(M+H) <sup>+</sup>	C <sub>12</sub> H <sub>14</sub> N <sub>1</sub> O <sub>4</sub>	653650.1											
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
✓	C <sub>12</sub> H <sub>13</sub> N <sub>1</sub> O <sub>4</sub>	C <sub>12</sub> H <sub>14</sub> N <sub>1</sub> O <sub>4</sub>	236.0917	99.52		235.0853	235.0845	-3.4	3.4	99.99	98.67	99.67	236.0925	7
m/z	Ion	Formula	Abundance											
258.0741	(M+Na) <sup>+</sup>	C <sub>12</sub> H <sub>13</sub> N <sub>1</sub> Na <sub>1</sub> O <sub>4</sub>	97313.6											
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
✓	C <sub>12</sub> H <sub>13</sub> N <sub>1</sub> O <sub>4</sub>	C <sub>12</sub> H <sub>13</sub> N <sub>1</sub> Na <sub>1</sub> O <sub>4</sub>	258.0737	96.45		235.0849	235.0845	-1.79	1.79	96.68	89.22	99.92	258.0741	7

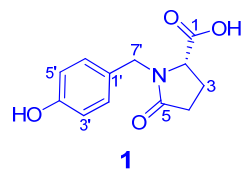


Figure S5. The (+)-HRESIMS Report of Compound 1, Page 3

VNS-600 PROTON TMG-71 IN acetone May 30 2014

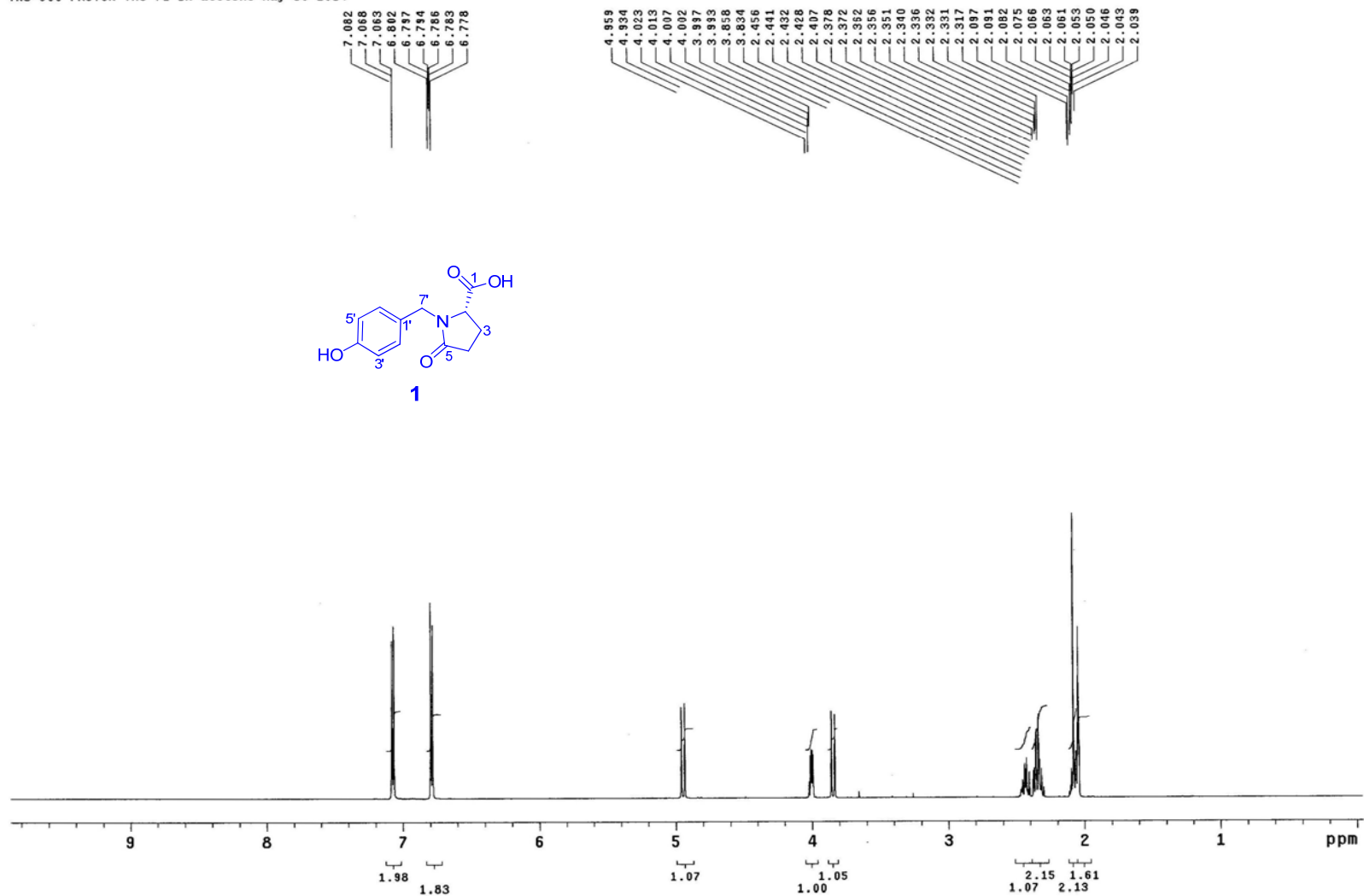
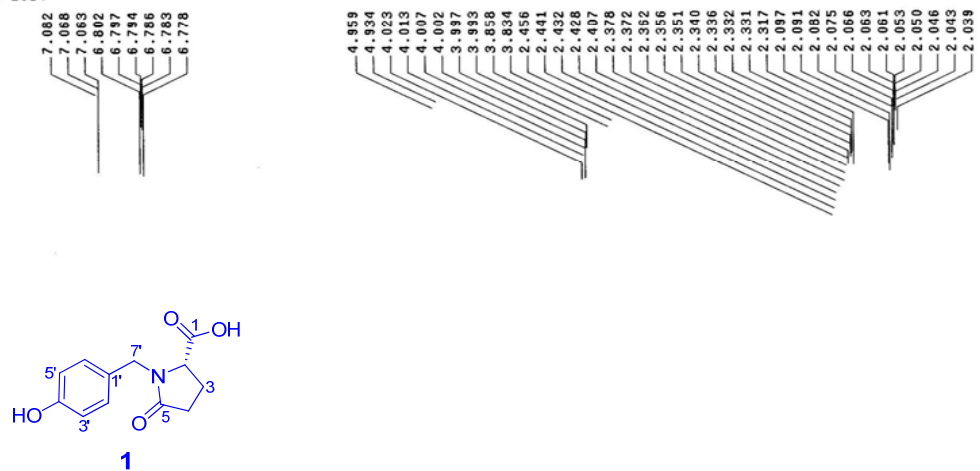


Figure S6. The  $^1\text{H}$  NMR Spectrum of Compound **1** in  $\text{Me}_2\text{CO}-d_6$  (600 MHz)



VNS-600 CARBON TMG-71 IN acetone May 29 2014

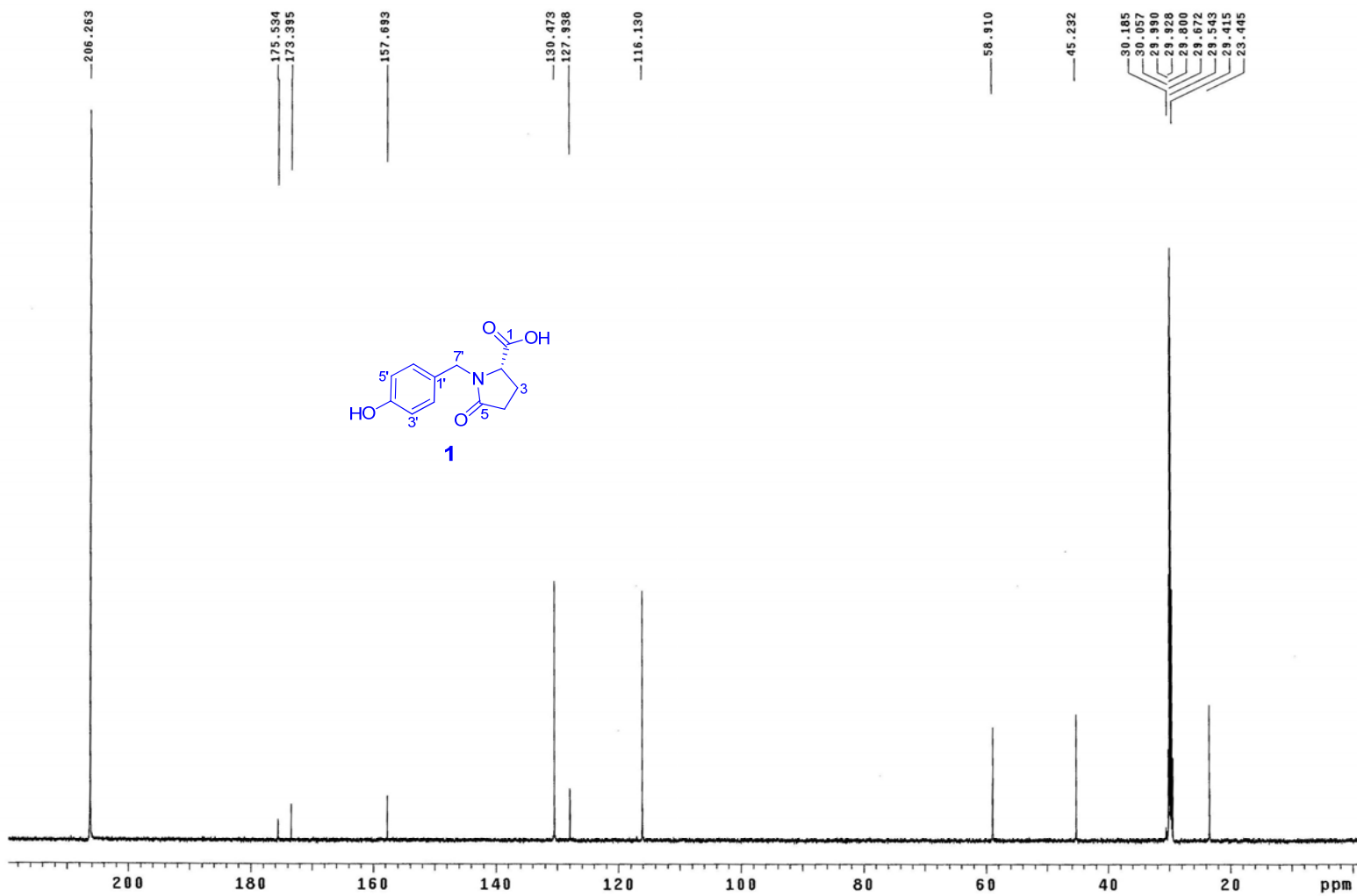
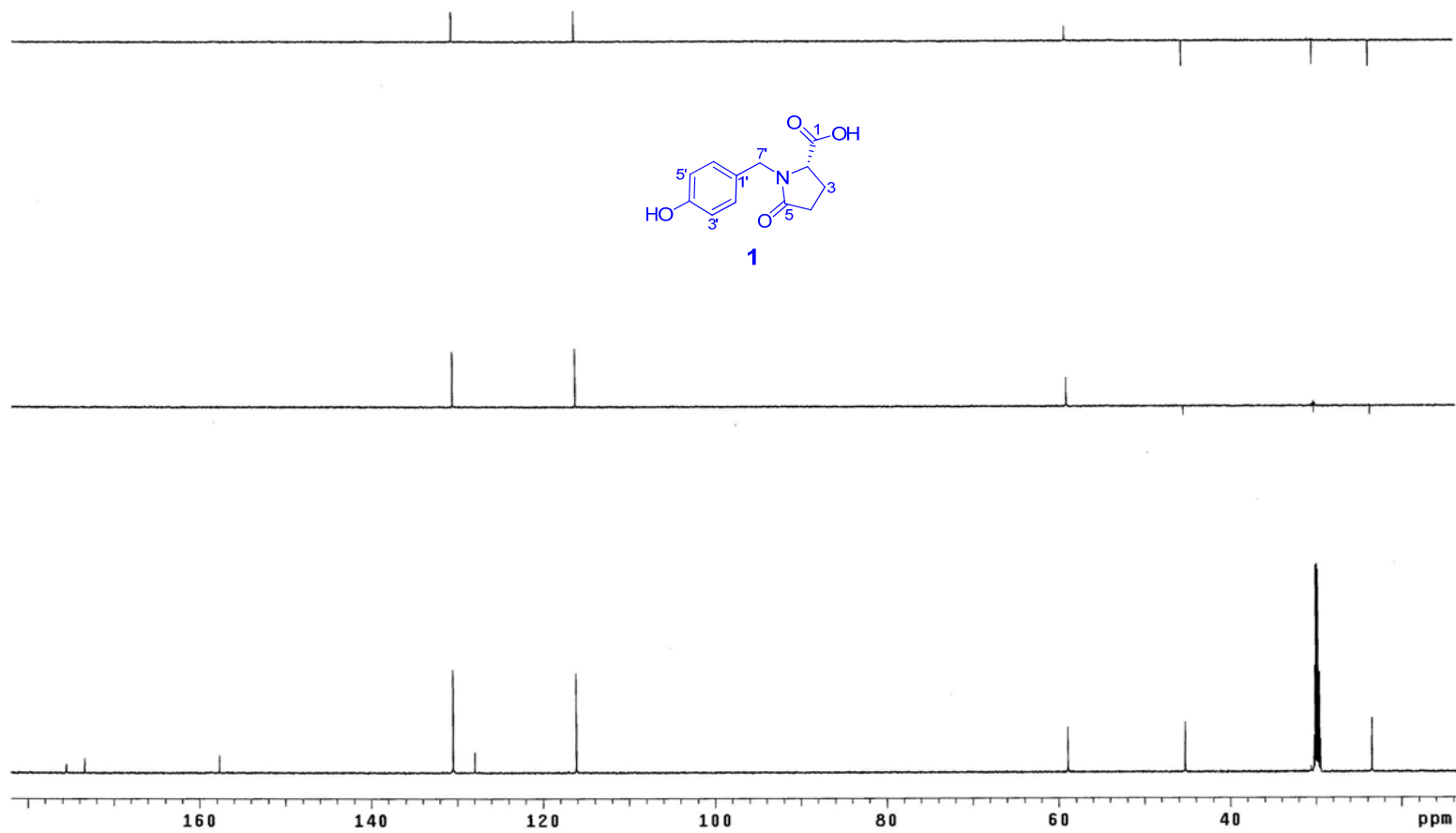


Figure S7. The <sup>13</sup>C NMR Spectrum of Compound 1 in Me<sub>2</sub>CO-*d*<sub>6</sub> (150 MHz)

VNS-600 DEPT TMG-71 IN acetone May 30 2014

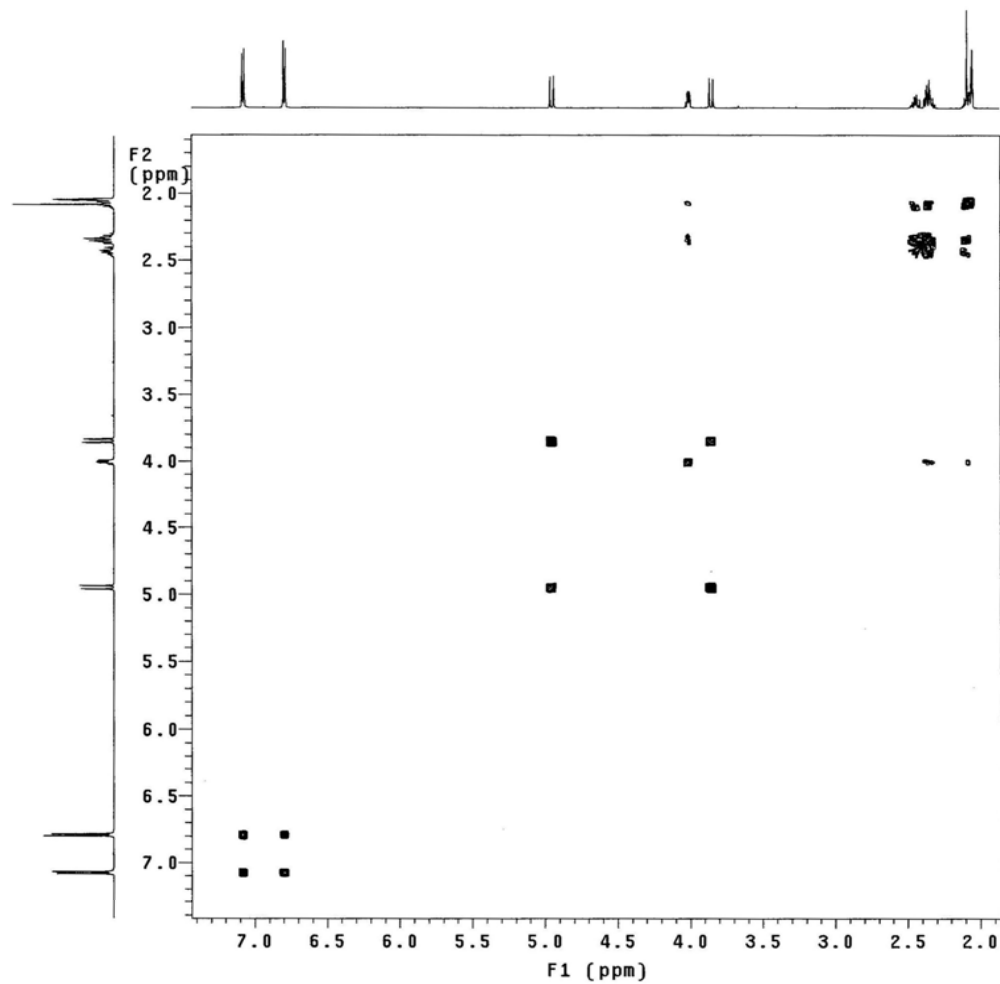
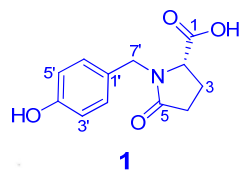


**Figure S8.** The DEPT Spectrum of Compound **1** in Me<sub>2</sub>CO-*d*<sub>6</sub> (150 MHz)

VNS-600 gCOSY TMG-71 IN acetone May 30 2014

Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.150 sec  
Width 8169.9 Hz  
2D Width 8169.9 Hz  
2 repetitions  
200 increments  
OBSERVE H1, 599.6907961 MHz  
DATA PROCESSING  
Sq. sine bell 0.075 sec  
F1 DATA PROCESSING  
Sq. sine bell 0.021 sec  
FT size 4096 x 4096  
Total time 8 min 33 sec



**Figure S9.** The <sup>1</sup>H-<sup>1</sup>H gCOSY Spectrum of Compound 1 in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)

VNS-600 gHSQCAD IMG-71 IN acetone May 30 2014

Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.150 sec  
Width 8169.9 Hz  
2D Width 30154.5 Hz  
8 repetitions  
140 increments  
OBSERVE H1, 599.6907961 MHz  
DECOUPLE C13, 150.8059420 MHz  
Power 36 dB  
on during acquisition  
off during delay  
W40\_NEW-SW modulated  
DATA PROCESSING  
Sine bell 0.027 sec  
F1 DATA PROCESSING  
Sine bell 0.005 sec  
FT size 4096 x 2048  
Total time 22 min

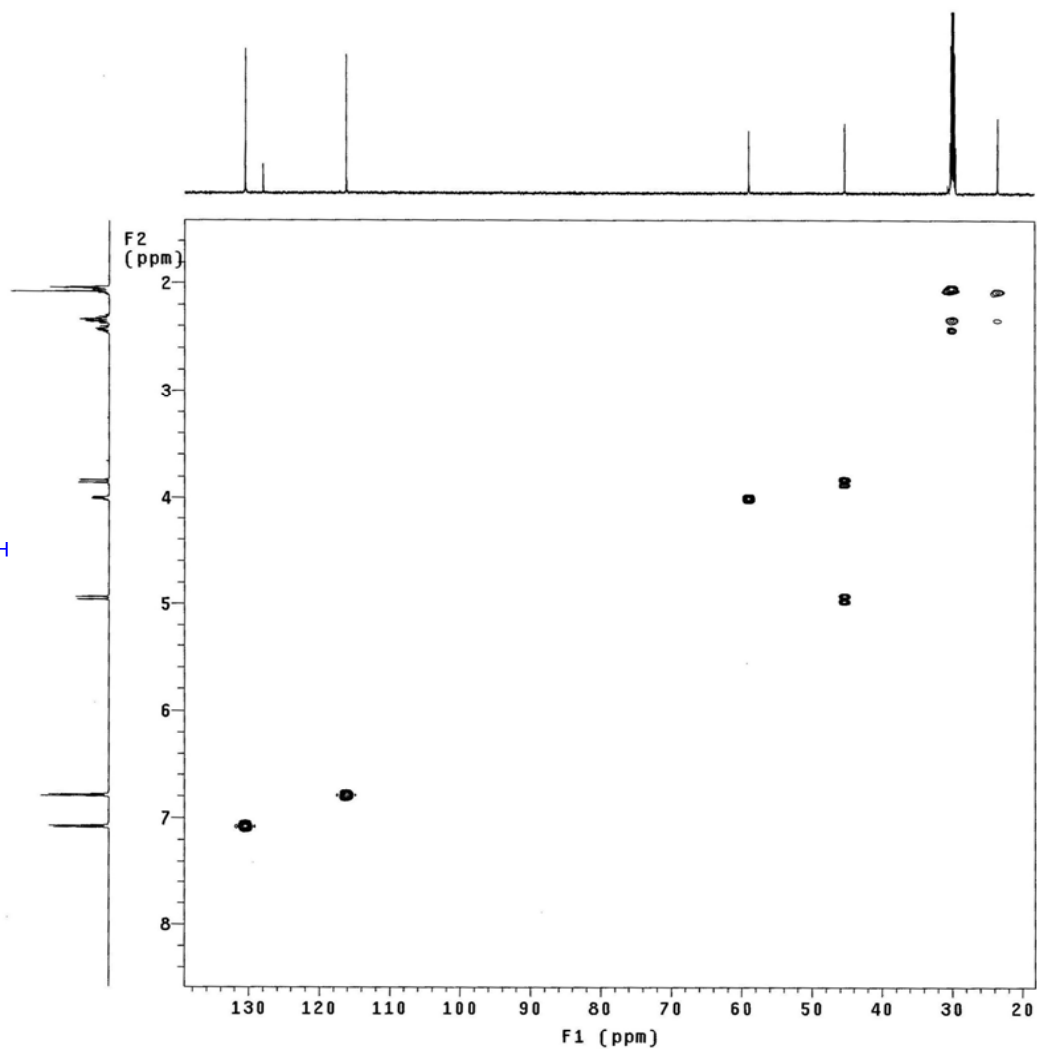
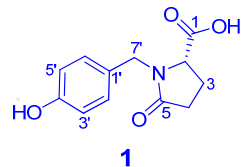
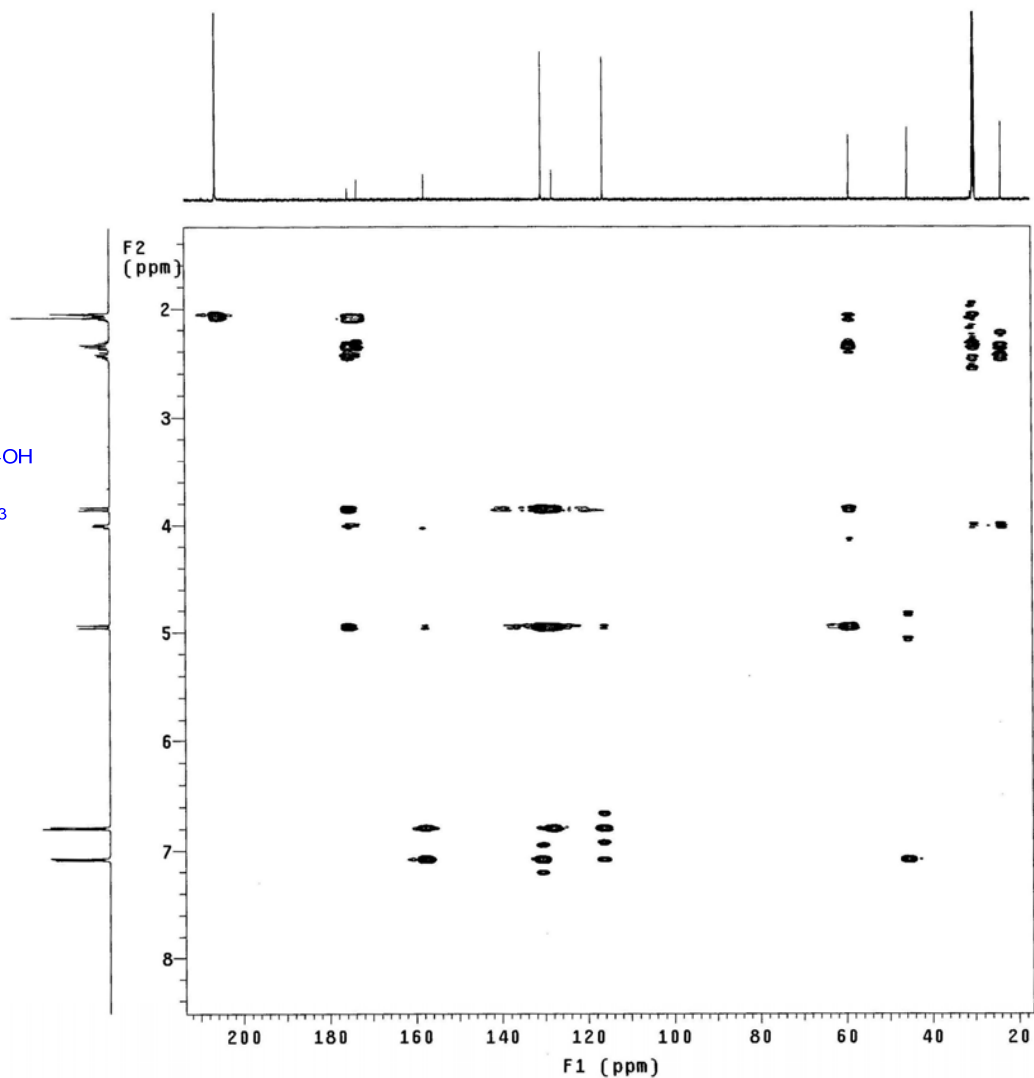
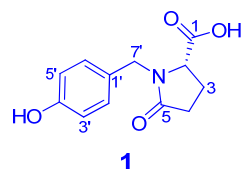


Figure S10. The gHSQC Spectrum of Compound 1 in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)

VNS-600 gHMBCAD TMG-71 IN acetone May 30 2014

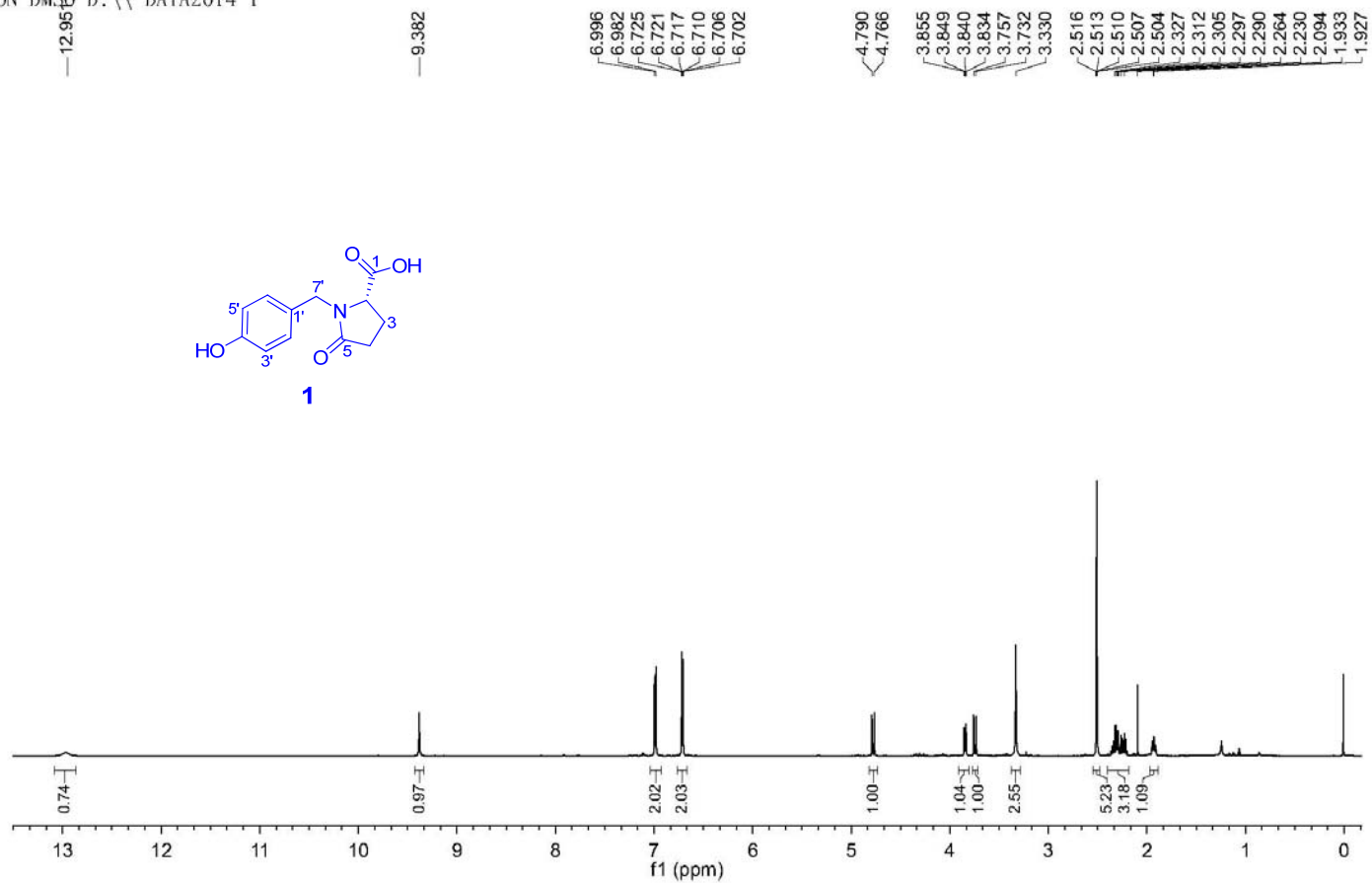
Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.150 sec  
Width 8169.9 Hz  
2D Width 36182.7 Hz  
16 repetitions  
2 x 80 increments  
OBSERVE H1, 599.6907961 MHz  
DATA PROCESSING  
Sq. sine bell 0.075 sec  
F1 DATA PROCESSING  
Gauss apodization 0.002 sec  
FT size 4096 x 2048  
Total time 53 min

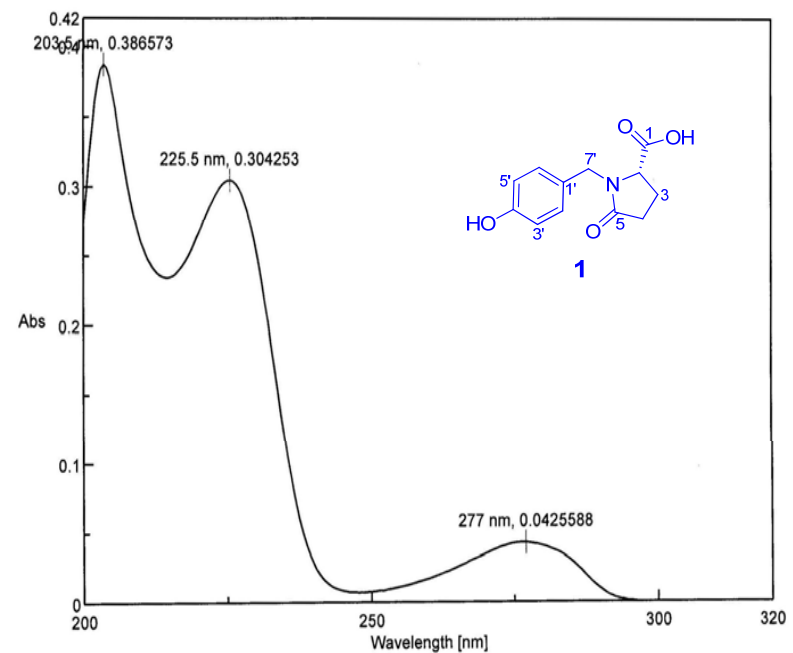


**Figure S11.** The gHMBC Spectrum of Compound **1** in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)

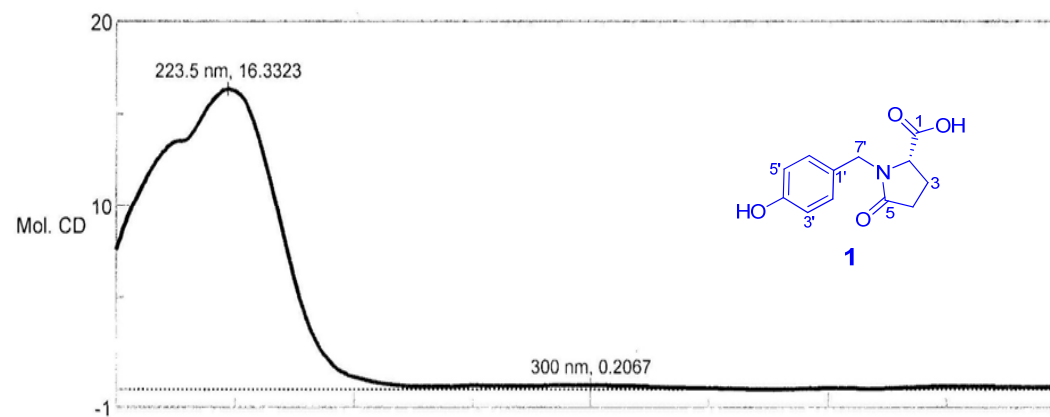
20140625 TMG-71  
Bruker AVIIIHD 600 20140624  
PROTON DMSO D:\DATA2014 1



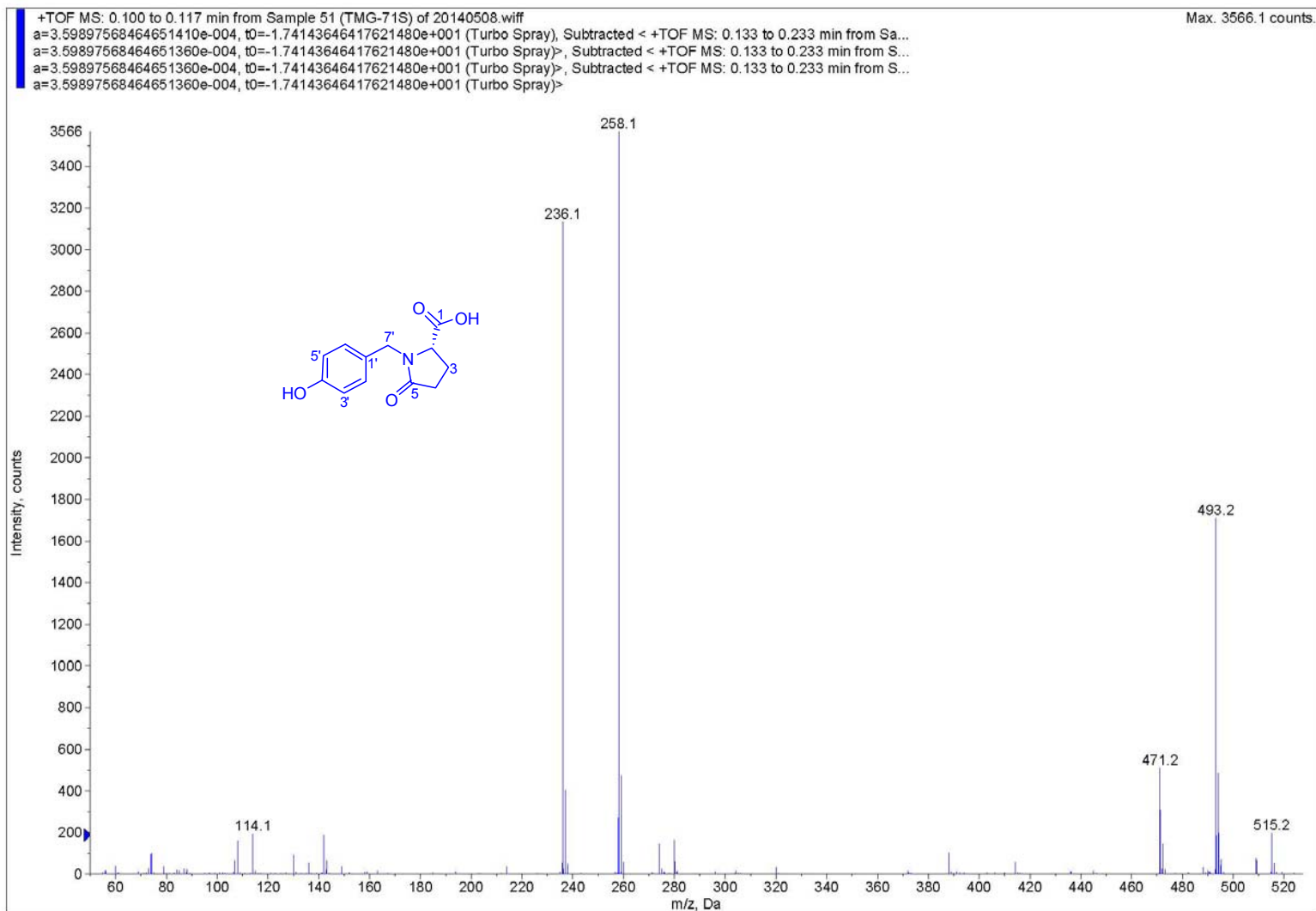
**Figure S12.** The <sup>1</sup>H NMR Spectrum of Compound **1** in DMSO-*d*<sub>6</sub> (600 MHz)



**Figure S13.** The UV Spectrum of Compound **1** in MeOH



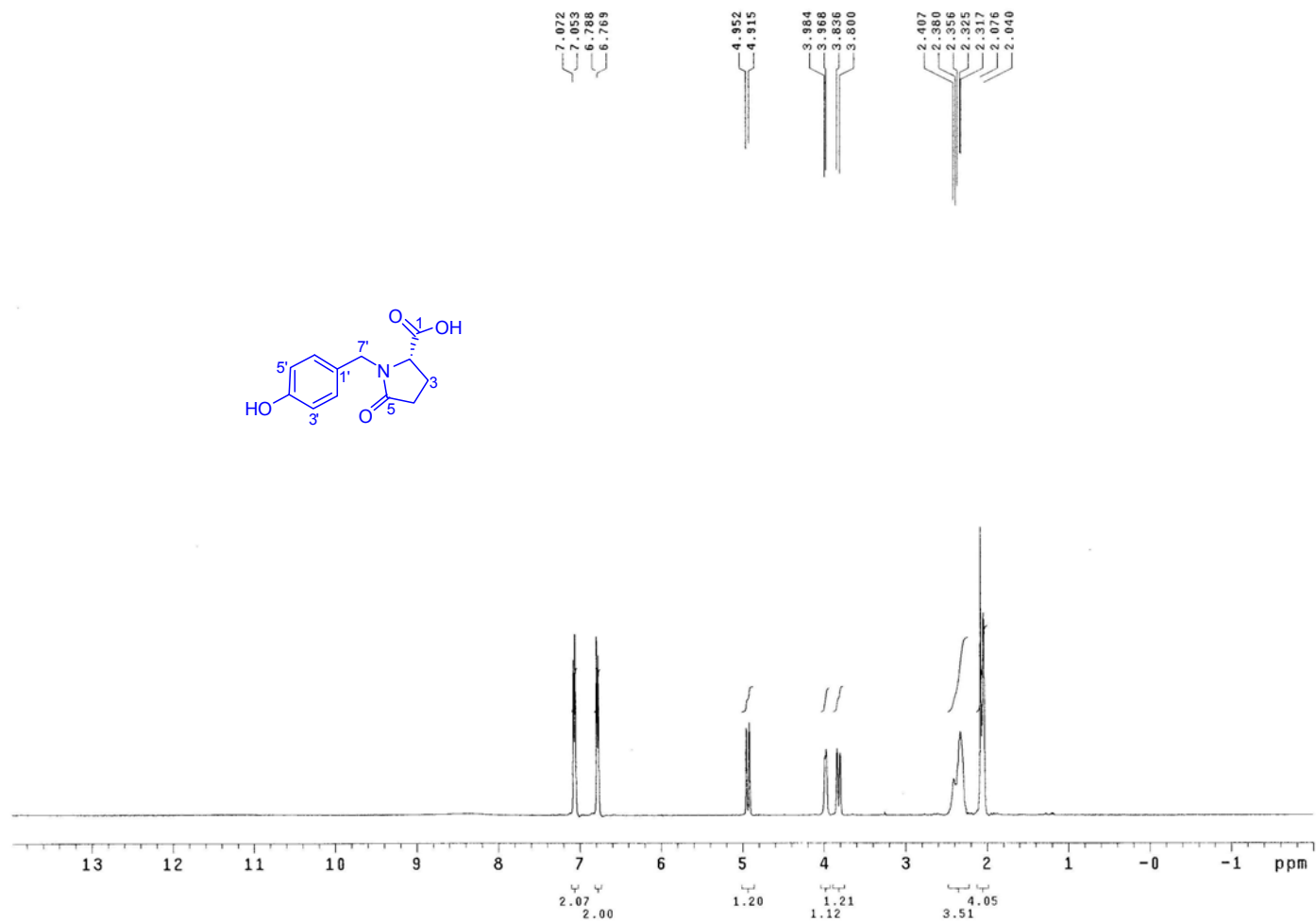
**Figure S14.** The CD Spectrum of Compound **1** in MeOH



**Figure S15.** The (+)-ESIMS Spectrum of the Synthesized (+)-(S)-[N-(4'-Hydroxybenzyl)]pyroglutamate (**1**)

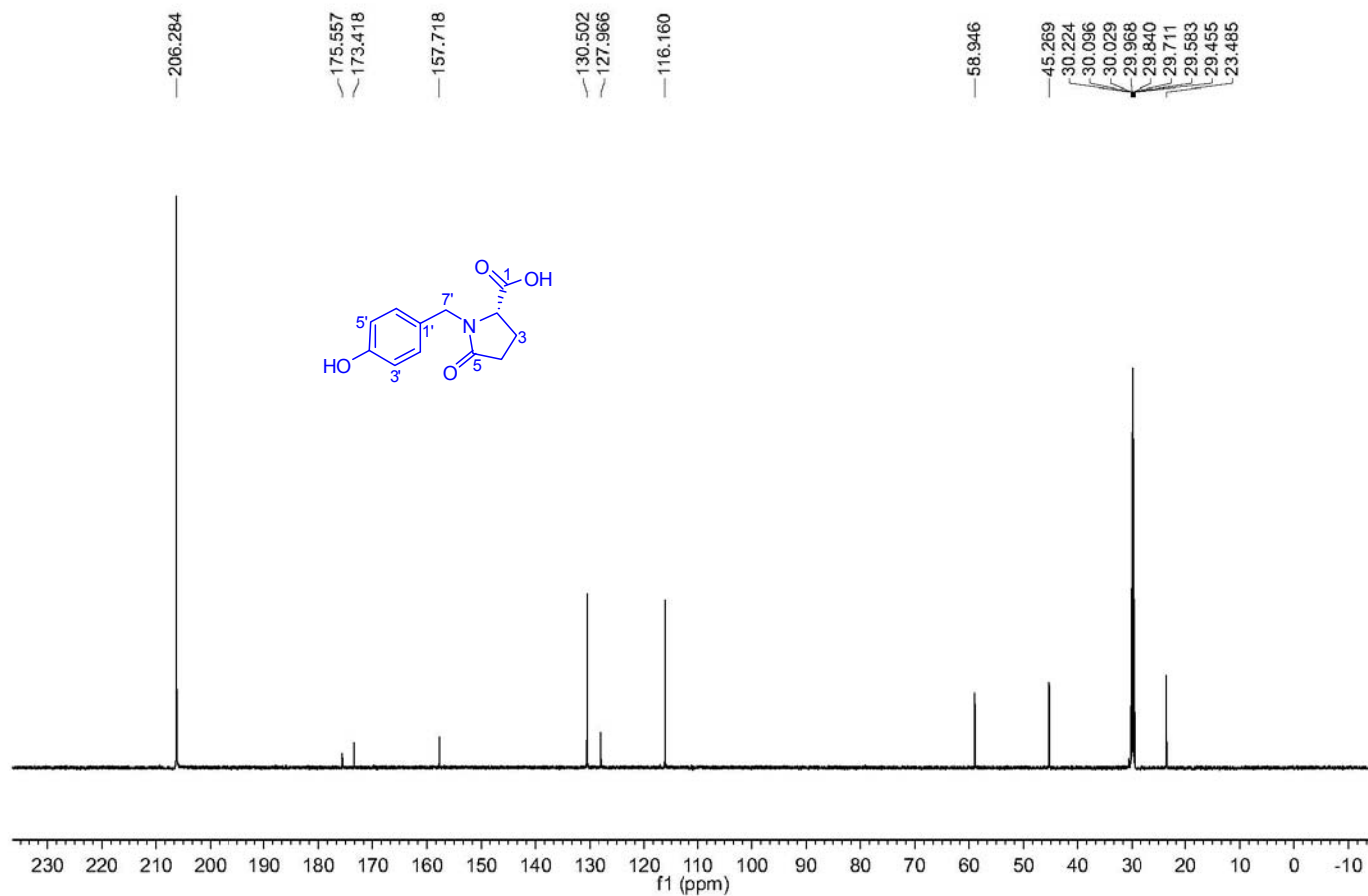


Mercury400, 1H-NMR TMO-71s in acetone

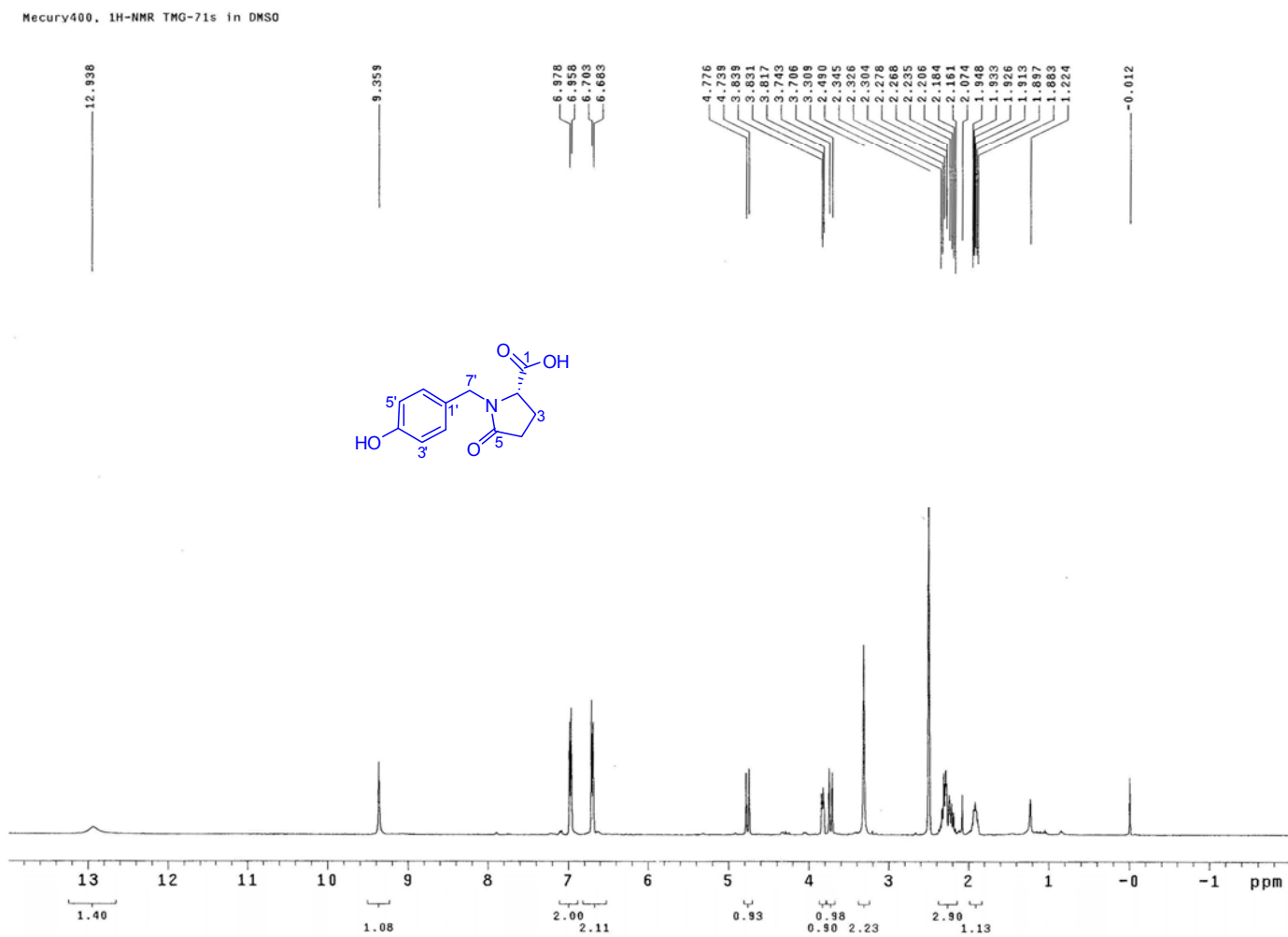


**Figure S16.** The <sup>1</sup>H NMR Spectrum of the Synthesized (+)-(S)-[N-(4'-Hydroxybenzyl)]pyroglutamate (1) in Me<sub>2</sub>CO-*d*<sub>6</sub> (400 MHz)

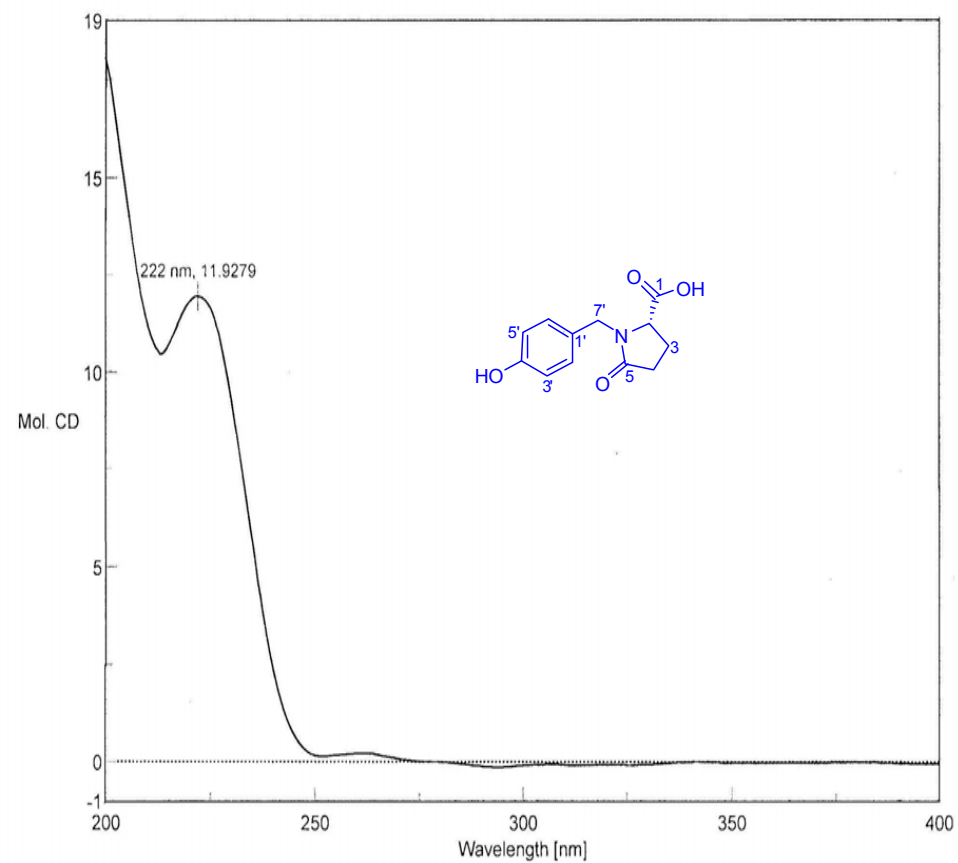
20140513 TMG-71S  
Bruker AVANCEIII 400 20140513  
C13 Acetone D:\ DATA-2014 5



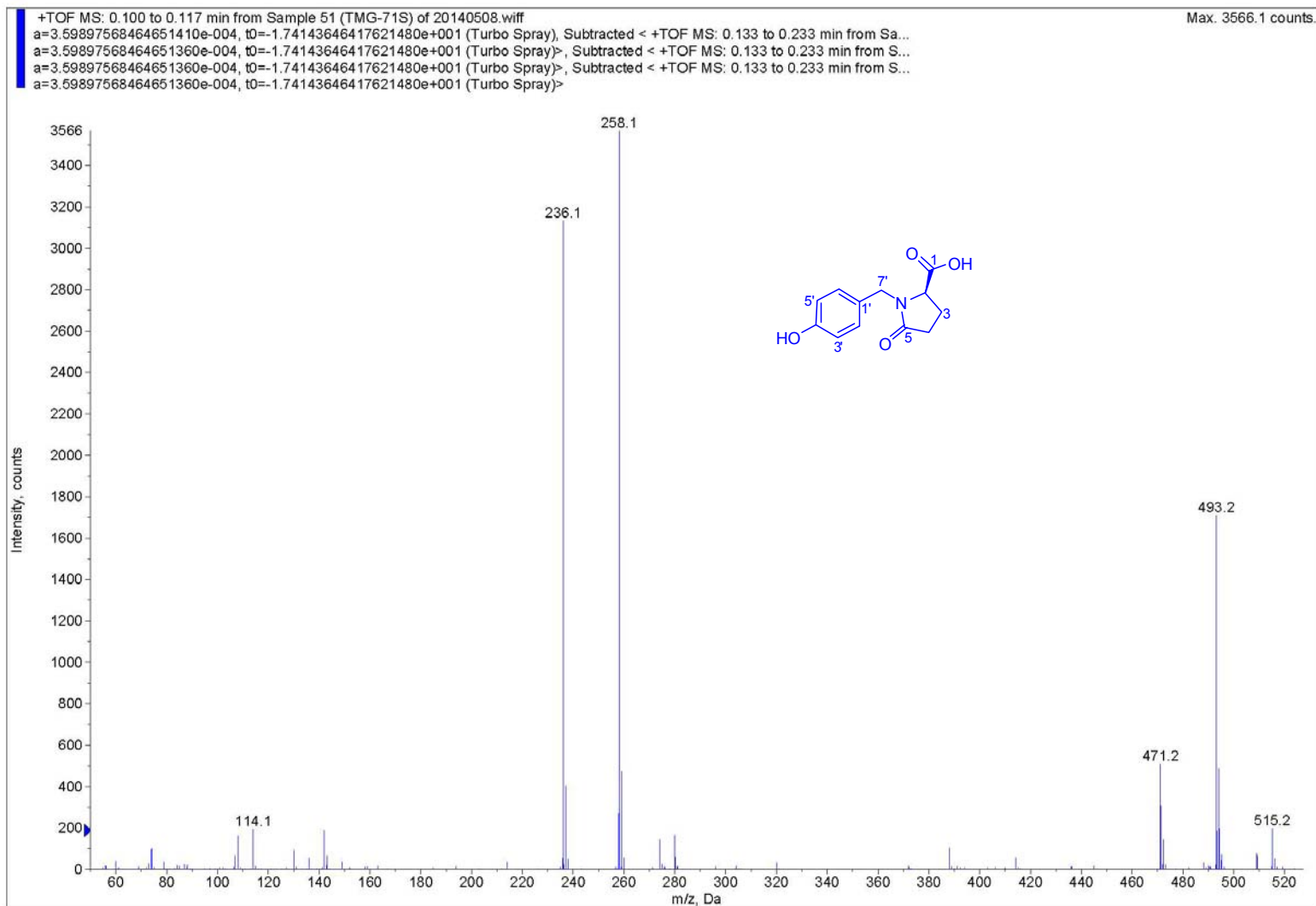
**Figure S17.** The <sup>13</sup>C NMR Spectrum of the Synthesized (+)-(S)-[N-(4'-Hydroxybenzyl)]pyroglutamate (1) in Me<sub>2</sub>CO-*d*<sub>6</sub> (100 MHz)



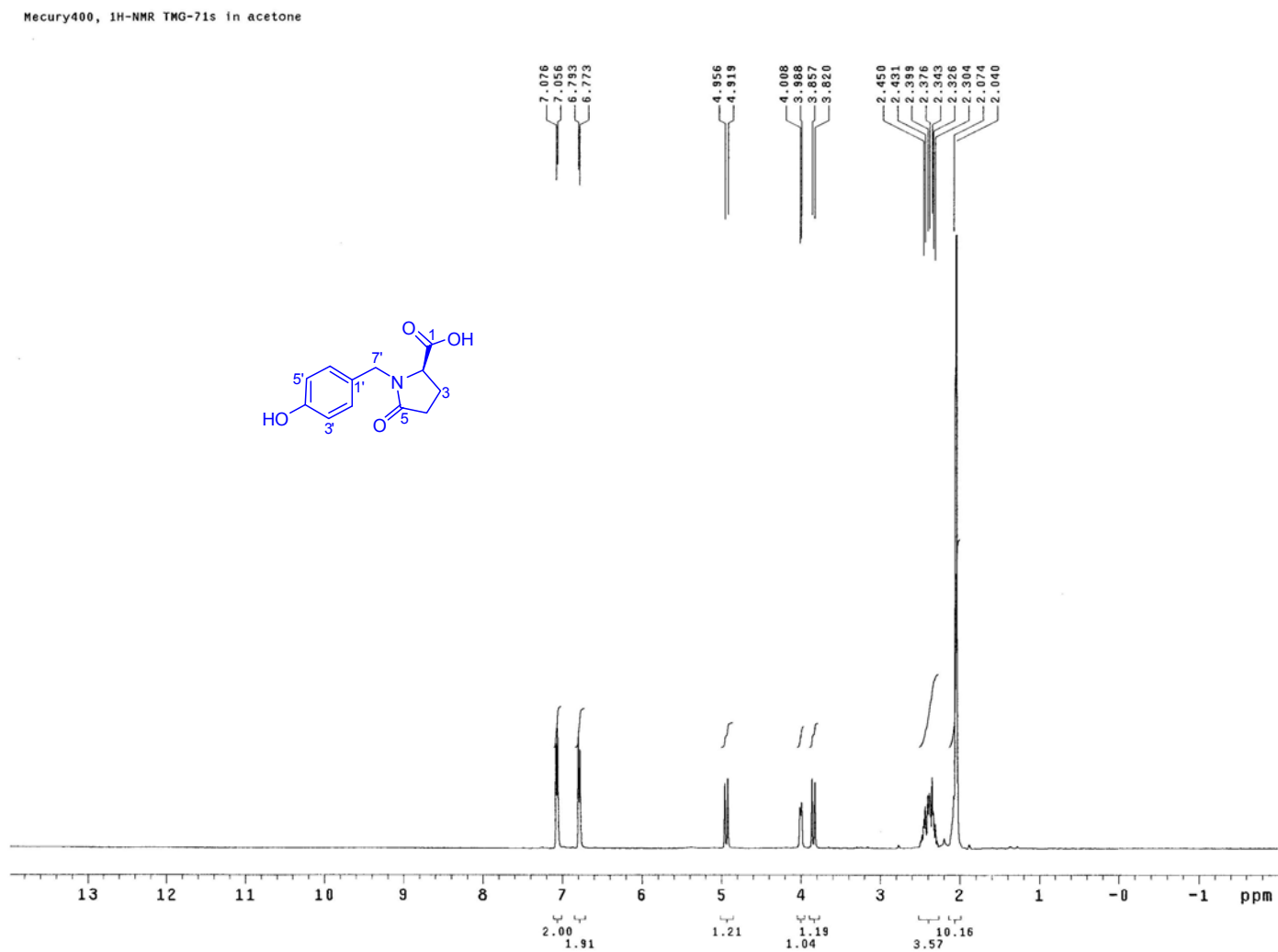
**Figure S18.** The  $^1\text{H}$  NMR Spectrum of the Synthesized (+)-(-)-[N-(4'-Hydroxybenzyl)]pyroglutamate (**1**) in  $\text{DMSO-}d_6$  (400 MHz)



**Figure S19.** The CD Spectrum of the Synthesized (+)-(*S*)-[*N*-(4'-Hydroxybenzyl)]pyroglutamate (**1**) in MeOH

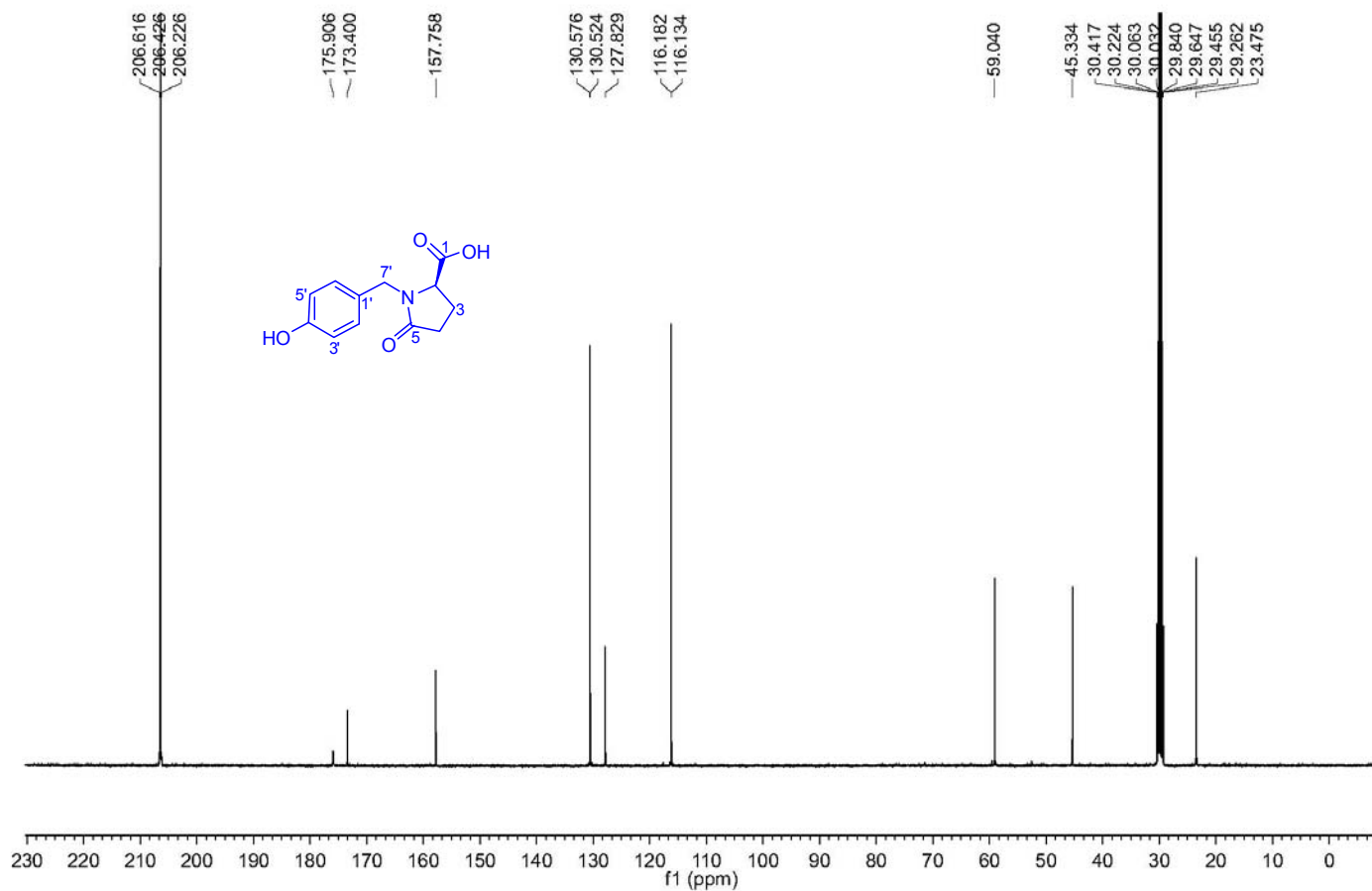


**Figure S20.** The (+)-ESIMS Spectrum of the Synthesized (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate

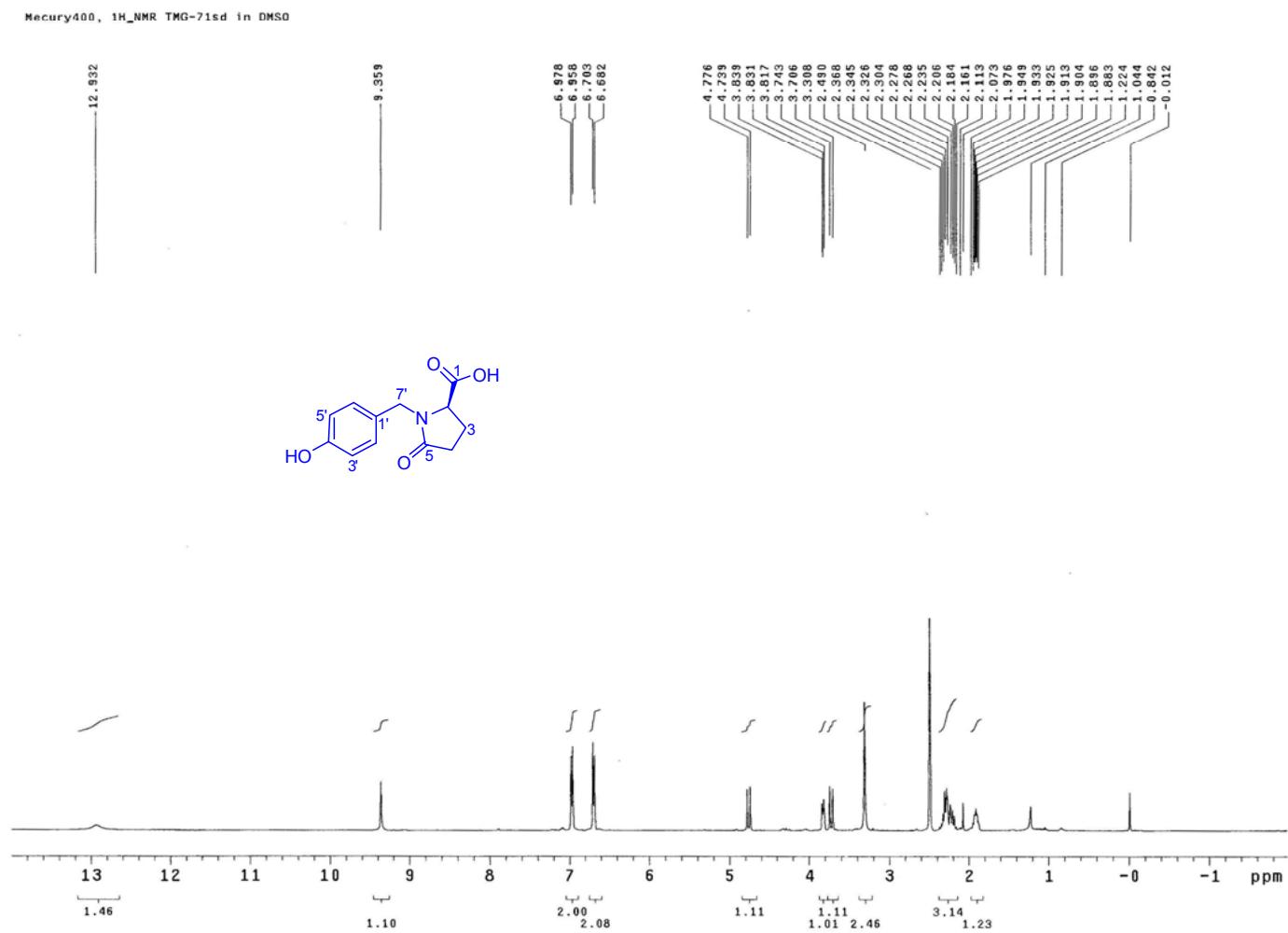


**Figure S21.** The  $^1\text{H}$  NMR Spectrum of the Synthesized (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate in  $\text{Me}_2\text{CO}-d_6$  (400 MHz)

20140513 TMG-71SD  
Bruker AVANCEIII 400 20140513  
C13 Acetone D:\ DATA-2014 5

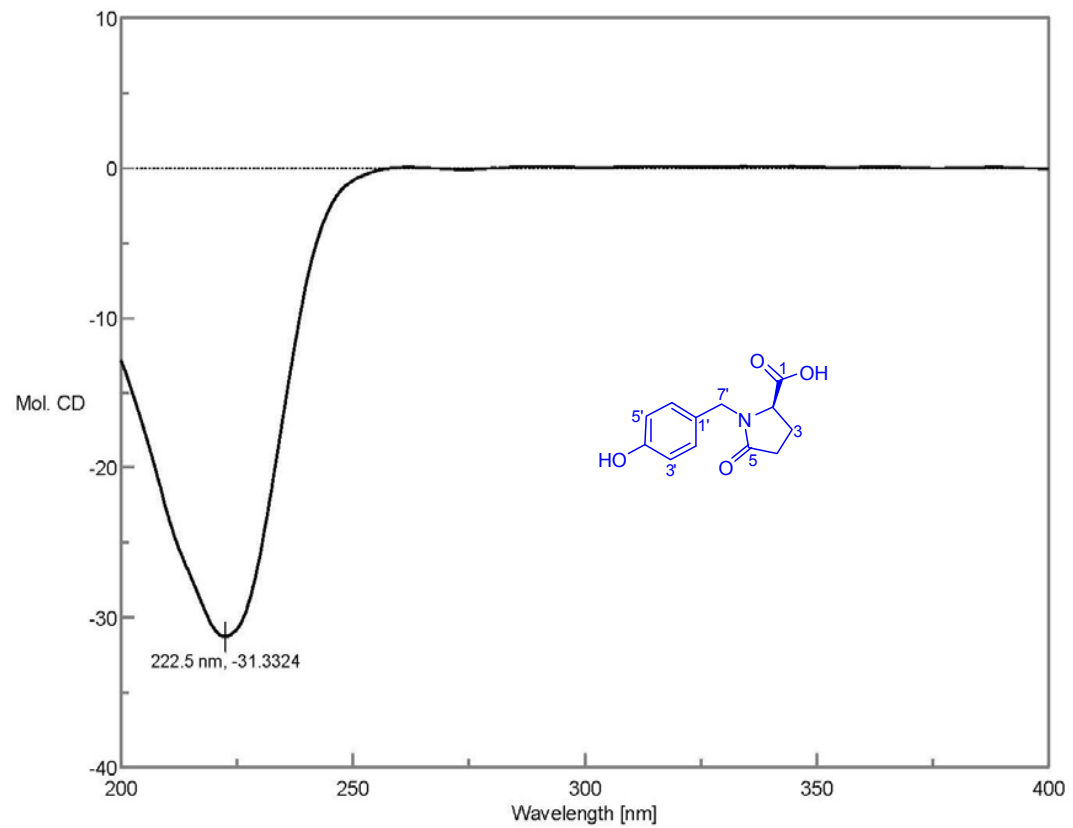


**Figure S22.** The <sup>13</sup>C NMR Spectrum of the Synthesized (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate in Me<sub>2</sub>CO-*d*<sub>6</sub> (100 MHz)

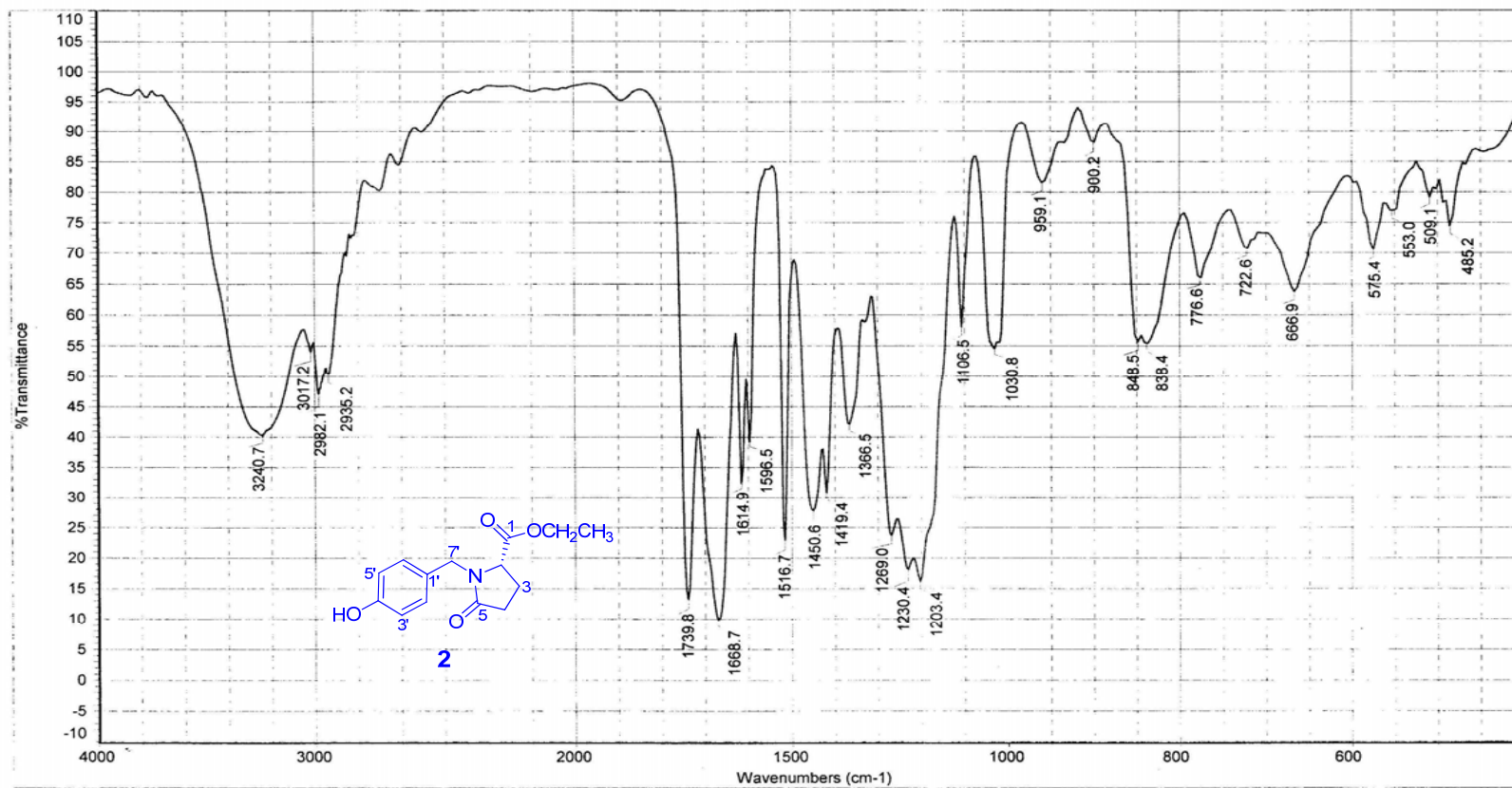


**Figure S23.** The  $^1\text{H}$  NMR Spectrum of the Synthesized (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate in DMSO- $d_6$  (400 MHz)





**Figure S24.** The CD Spectrum of the Synthesized (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate in MeOH



日期: 星期五 12月 14 11:52:36 2012 (GMT+08: Sample Name : TMG - 22b

(显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100

傅里叶变换显微镜红外 (FT-IR Microscope): Centaurus

分辨率: 8.000

美国热电公司 (Thermo) 傅里叶变换红外光谱仪: Nicolet 5700

Figure S25. The IR Spectrum of Compound 2

TMG-22b #373-376 RT: 0.83-0.84 AV: 4 SB: 55 0.71-0.76 , 0.93-0.99 NL: 5.13E6  
T: ITMS + c ESI Full ms [50.00-800.00]

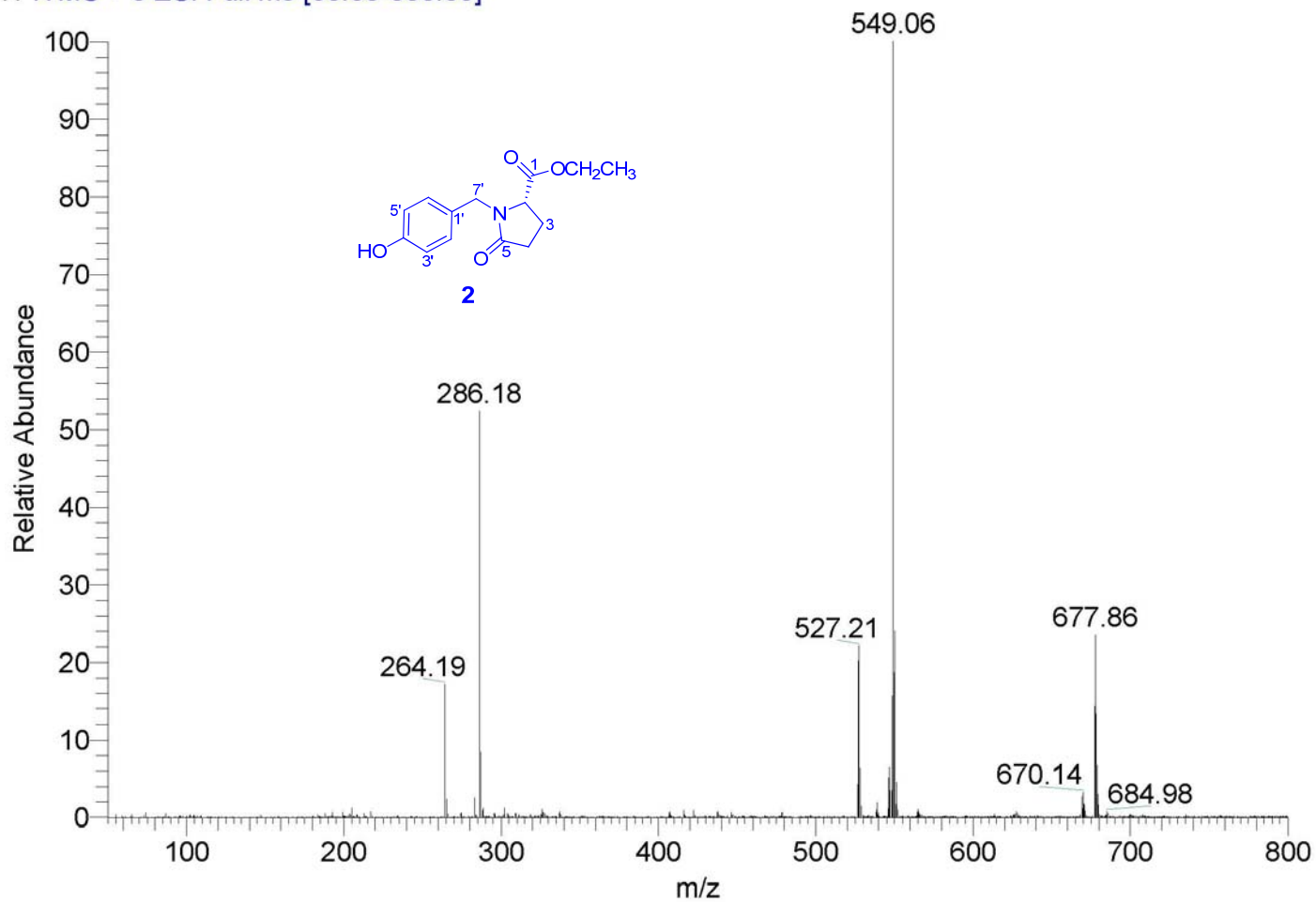
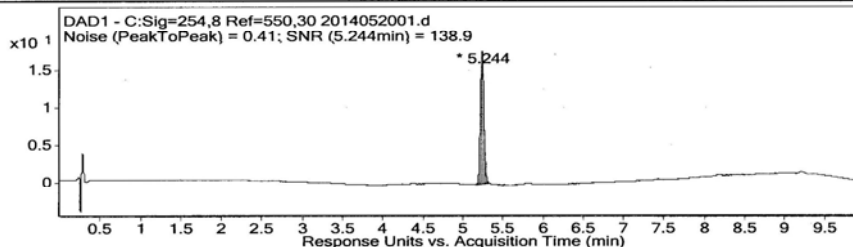


Figure S26. The (+)-ESIMS Spectrum of Compound 2

## Qualitative Analysis Report

Data Filename	2014052001.d	Sample Name	TMG-22b
Sample Type	Sample	Position	P1-C2
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	XXXXXXXXXX
DA Method	TEST LCMS.m	Comment	

### User Chromatograms



### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.158	5.244	5.331	17.68	56.38	100	138.9

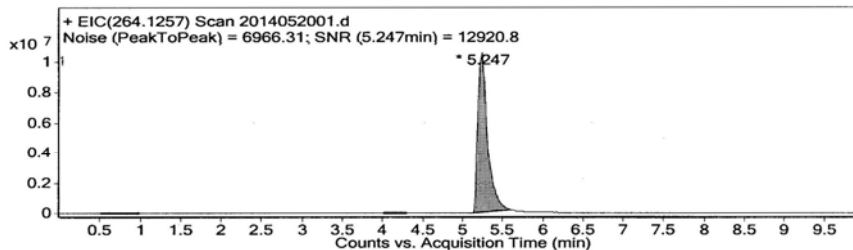
### Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0.405788422

### Noise Regions

Start	End
0.5	1
4	4.3
9.99	11

Fragmentor Voltage    135    Collision Energy    0    Ionization Mode    ESI



### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.134	5.247	5.601	10530697	90010129	100	12920.8

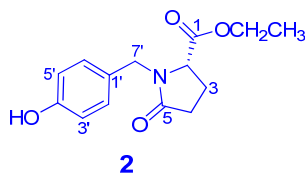
### Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	6966.310547

### Noise Regions

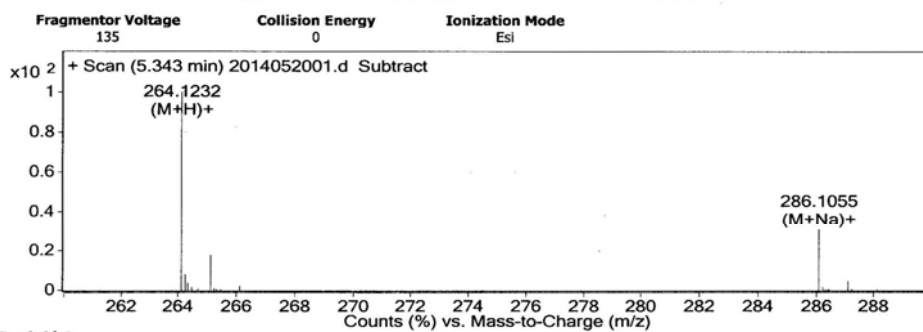
Start	End
0.5	1
4	4.3
9.99	11

### User Spectra



**Figure S27.** The (+)-HRESIMS Report of Compound 2, Page 1

## Qualitative Analysis Report



**Peak List**

m/z	z	Abund	Formula	Ion
264.1232	1	3051864	C14 H18 N O4	(M+H)+
264.2593		247535		
265.1269	1	537857	C14 H18 N O4	(M+H)+
286.1055	1	944559	C14 H17 N Na O4	(M+Na)+
287.1087	1	154073	C14 H17 N Na O4	(M+Na)+
527.2398	1	623166		
528.2426	1	205437		
549.2218	1	1819492		
550.2257	1	627933		

**Formula Calculator Element Limits**

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	5
S	0	2
Cl	0	0
Br	0	0
Si	0	0
F	0	0
P	0	0

**Formula Calculator Results**

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C14 H17 N O4	TRUE	263.1159	263.1158	-0.6	C14 H18 N O4	99.87
C15 H13 N5		263.1159	263.1171	4.47	C15 H14 N5	99.6
C14 H17 N O4	TRUE	263.1163	263.1158	-1.99	C14 H17 N Na O4	99.94
C15 H13 N5		263.1163	263.1171	3.08	C15 H13 N5 Na	99.71

--- End Of Report ---



**Figure S28.** The (+)-HRESIMS Report of Compound 2, Page 2

MS Formula Results: + Scan (5.343 min) Sub (2014052001.d)

m/z	Ion	Formula	Abundance
264.1232	(M+H) <sup>+</sup>	C <sub>14</sub> H <sub>18</sub> N O <sub>4</sub>	3051863.8

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>14</sub> H <sub>17</sub> N O <sub>4</sub>	C <sub>14</sub> H <sub>18</sub> N O <sub>4</sub>	264.123	99.87		263.1159	263.1158	-0.6	0.6	99.61	99.94	99.99	264.1232	7
<input type="checkbox"/>	C <sub>15</sub> H <sub>13</sub> N <sub>5</sub>	C <sub>15</sub> H <sub>14</sub> N <sub>5</sub>	264.1244	99.6		263.1159	263.1171	4.47	4.47	99.85	99.69	99.4	264.1232	12

m/z	Ion	Formula	Abundance
286.1055	(M+Na) <sup>+</sup>	C <sub>14</sub> H <sub>17</sub> N Na O <sub>4</sub>	944559.3

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>14</sub> H <sub>17</sub> N O <sub>4</sub>	C <sub>14</sub> H <sub>17</sub> N Na O <sub>4</sub>	286.105	99.94		263.1163	263.1158	-1.99	1.99	99.97	100	99.9	286.1055	7
<input type="checkbox"/>	C <sub>15</sub> H <sub>13</sub> N <sub>5</sub>	C <sub>15</sub> H <sub>13</sub> N <sub>5</sub> Na	286.1063	99.71		263.1163	263.1171	3.08	3.08	99.45	99.95	99.75	286.1055	12

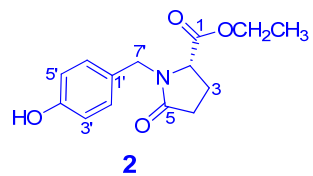


Figure S29. The (+)-HRESIMS Report of Compound 2, Page 3

VNS-600 PROTON TMG-22b IN acetone Jun 18 2014

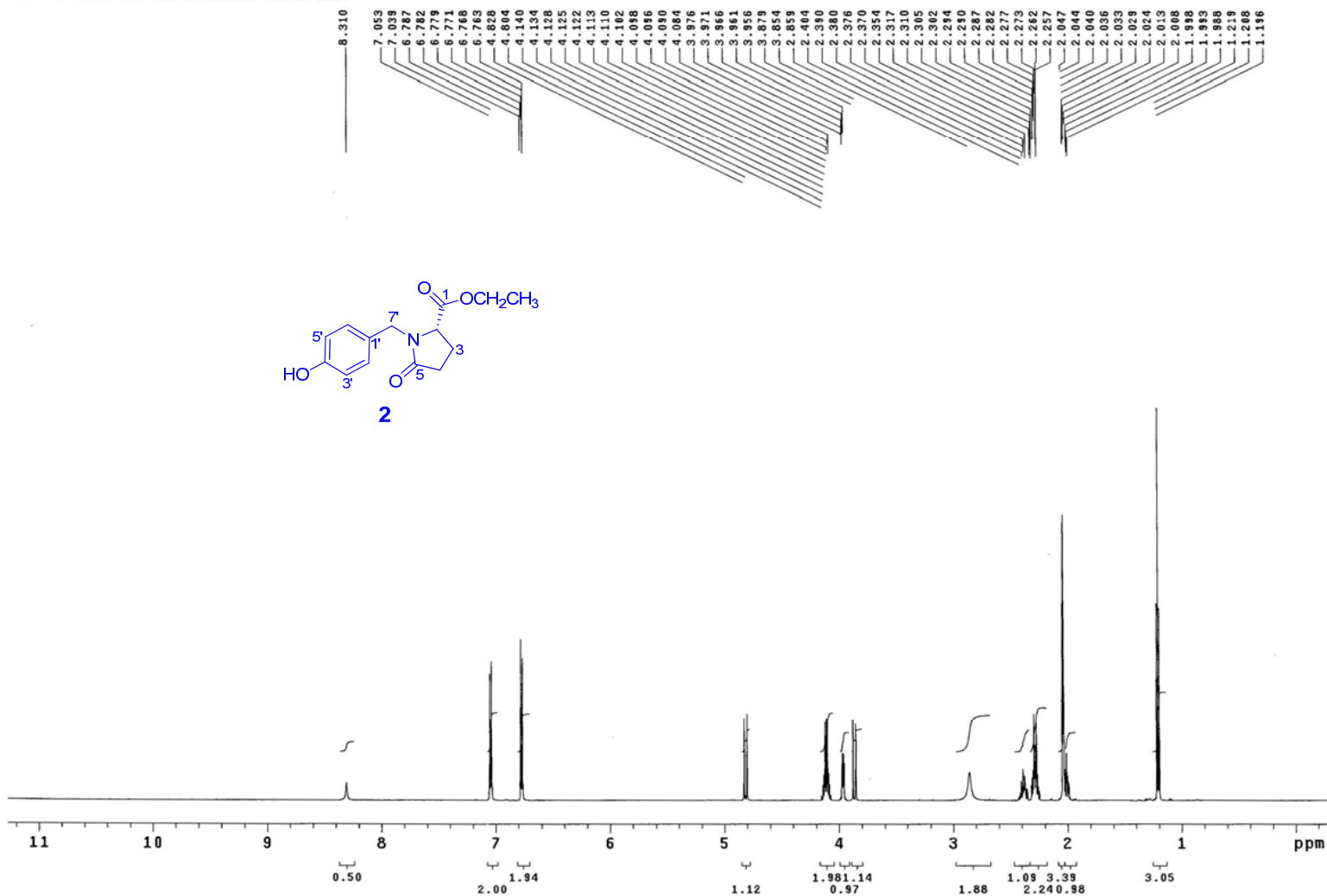


Figure S30. The  $^1\text{H}$  NMR Spectrum of Compound **2** in  $\text{Me}_2\text{CO}-d_6$  (600 MHz)

VNS-600 CARBON TMG-22b IN acetone May 21 2014

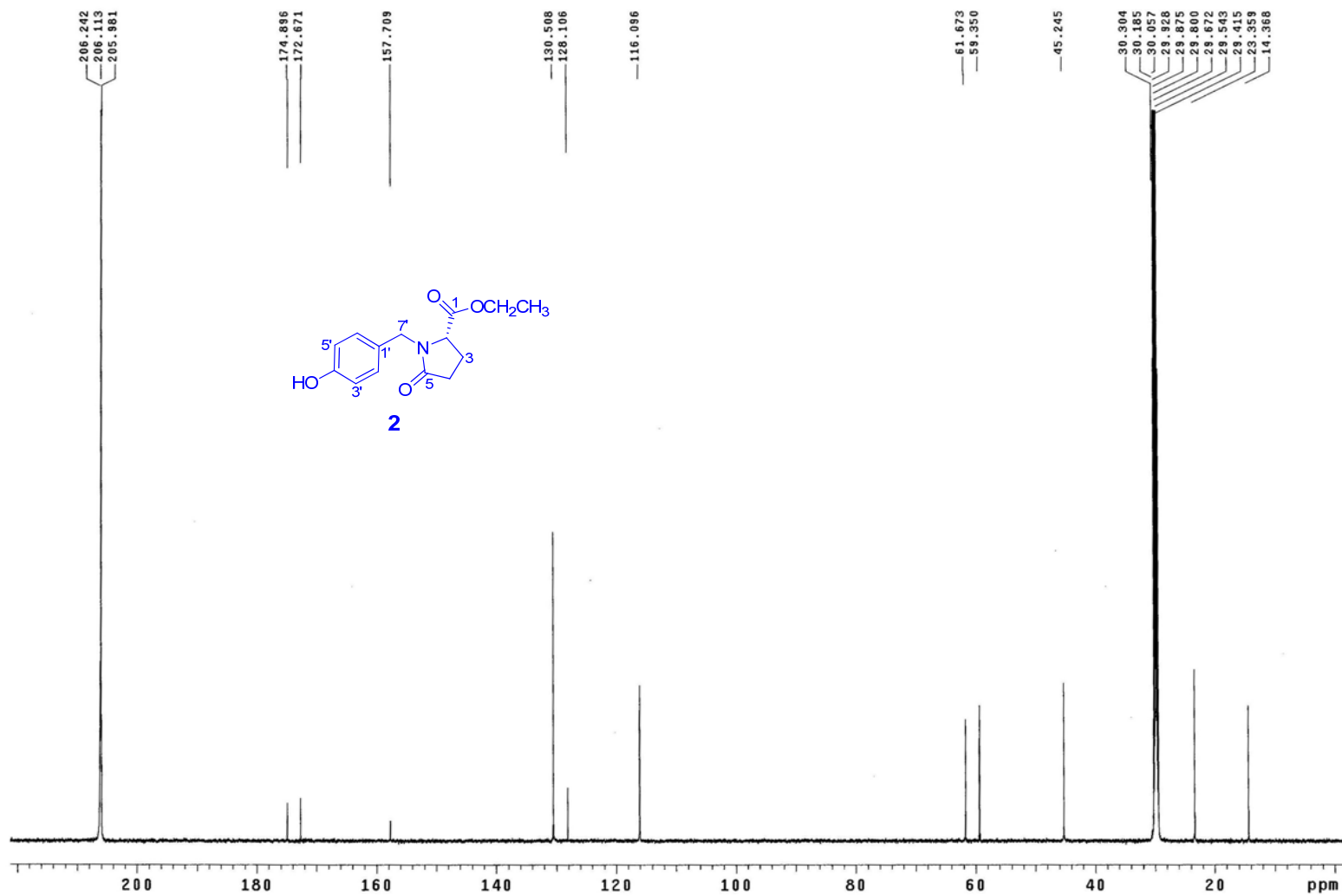


Figure S31. The  $^{13}\text{C}$  NMR Spectrum of Compound 2 in  $\text{Me}_2\text{CO}-d_6$  (150 MHz)



VNS-600 DEPT TMG-22b IN acetone May 21 2014

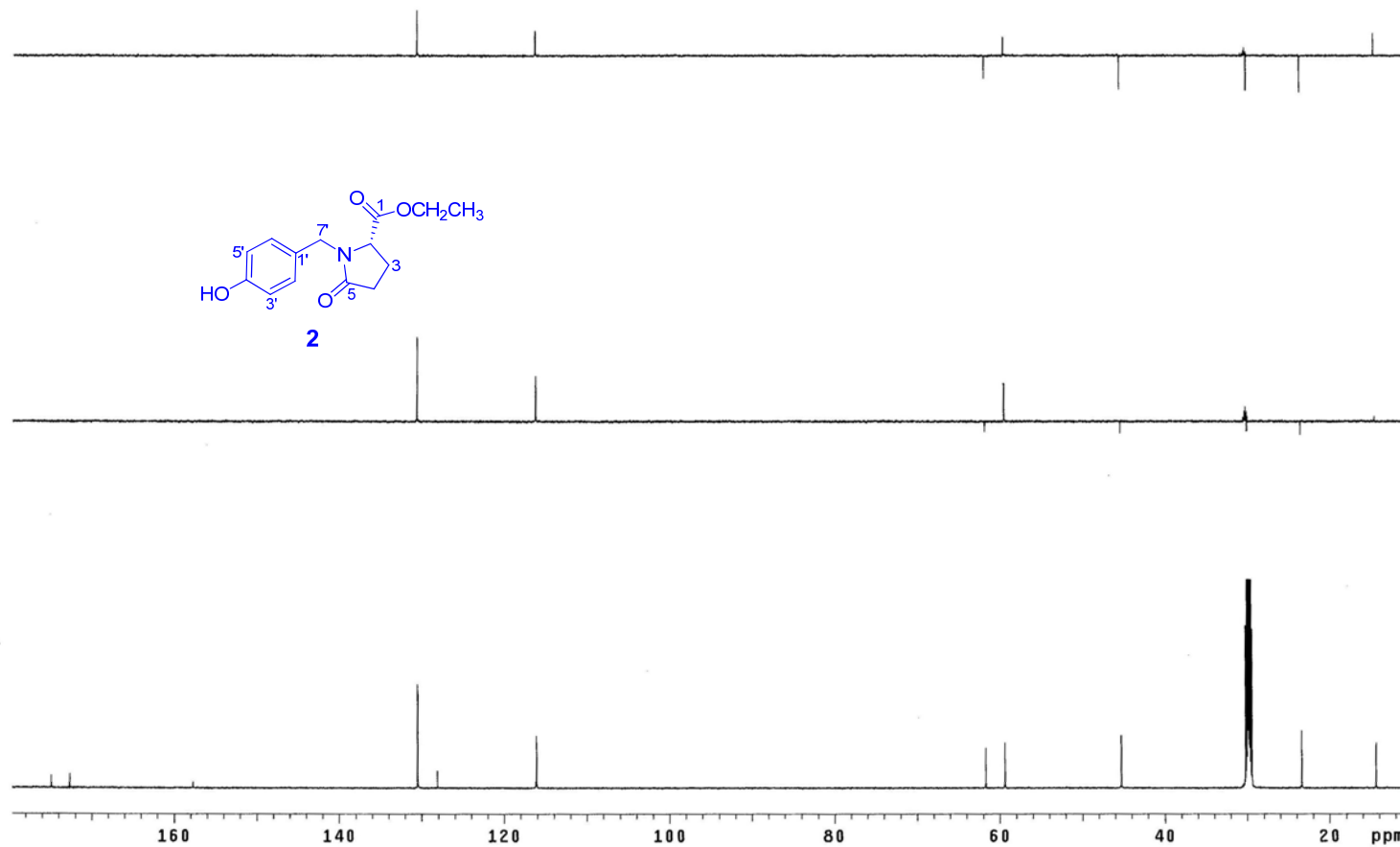
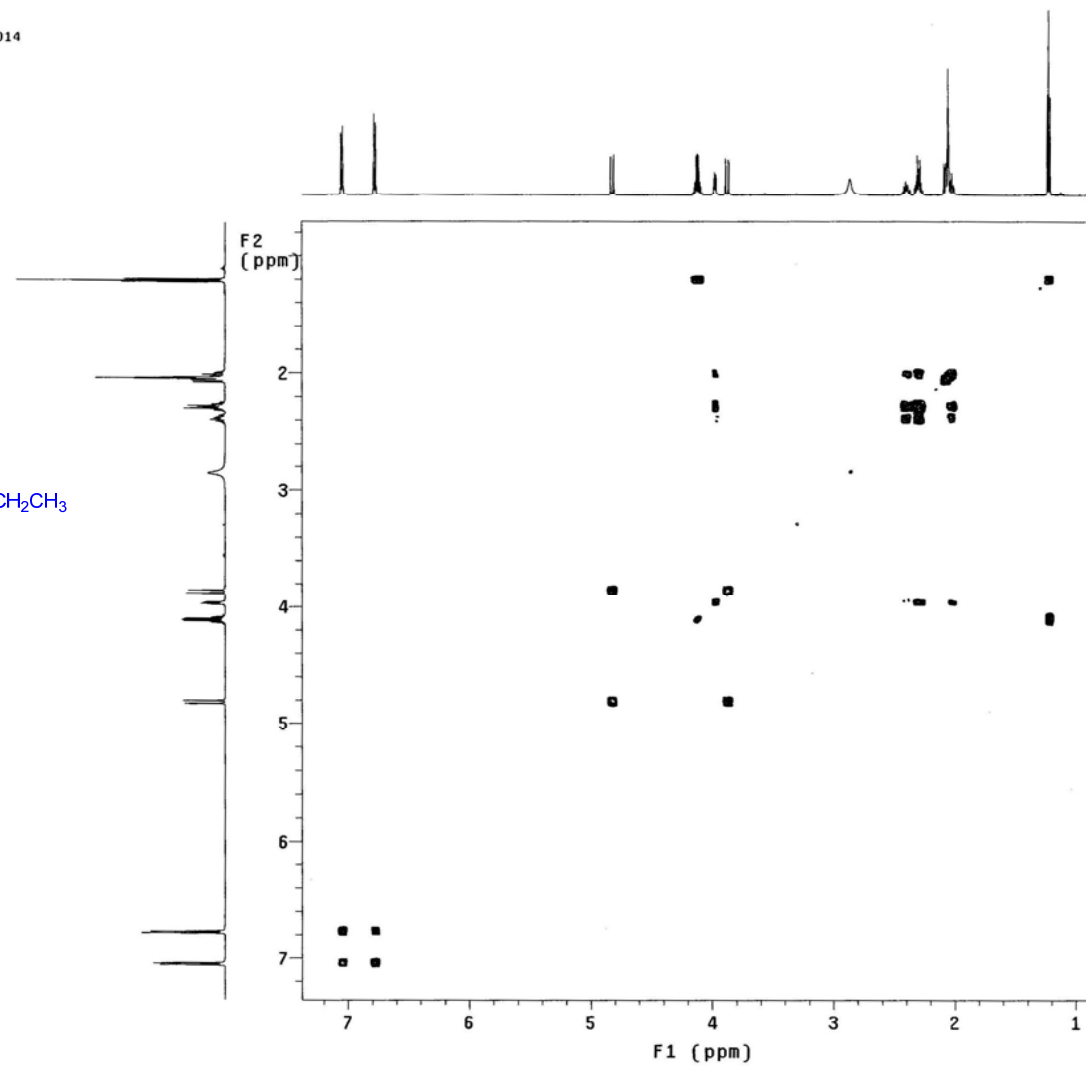
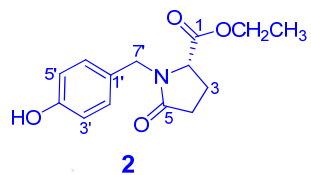


Figure S32. The DEPT Spectrum of Compound 2 in  $\text{Me}_2\text{CO}-d_6$  (150 MHz)

VNS-600 gCOSY TMG-22b IN acetone May 22 2014

Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.150 sec  
Width 5733.9 Hz  
2D Width 5733.9 Hz  
2 repetitions  
256 increments  
OBSERVE H1, 599.690863 MHz  
DATA PROCESSING  
Sq. sine bell 0.075 sec  
F1 DATA PROCESSING  
Sq. sine bell 0.027 sec  
FT size 2048 x 2048  
Total time 10 min



**Figure S33.** The <sup>1</sup>H-<sup>1</sup>H gCOSY Spectrum of Compound 2 in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)

VNS-600 gHSQCAD TMG-22b IN acetone May 22 2014

Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.150 sec  
Width 5733.9 Hz  
2D Width 30154.5 Hz  
48 repetitions  
140 increments  
OBSERVE H1, 599.6908006 MHz  
DECOUPLE C13, 150.8059420 MHz  
Power 36 dB  
on during acquisition  
off during delay  
W40\_NEW-SW modulated  
DATA PROCESSING  
Sine bell 0.016 sec  
F1 DATA PROCESSING  
Sine bell 0.005 sec  
FT size 4096 x 2048  
Total time 2 hr, 14 min

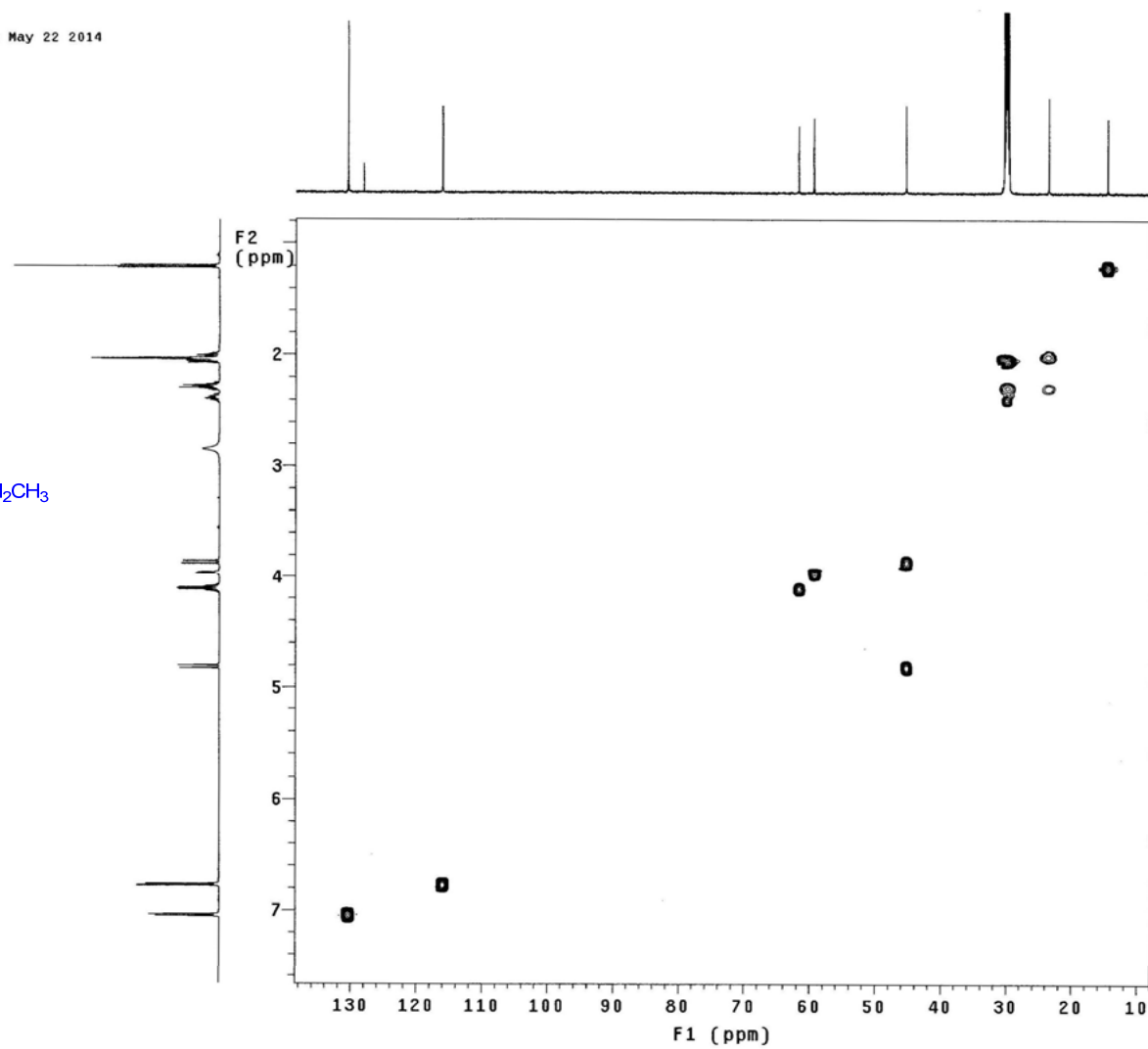
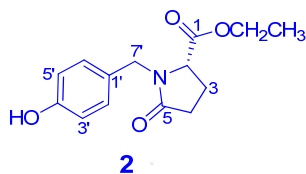


Figure S34. The gHSQC Spectrum of Compound 2 in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)

VNS-600 gHMBCAD TNG-22b IN acetone May 22 2014

Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.150 sec  
Width 5733.9 Hz  
2D Width 36182.7 Hz  
36 repetitions  
2 x 80 increments  
OBSERVE F1 599.6908009 MHz  
DATA PROCESSING  
Sq. sine bell 0.075 sec  
F1 DATA PROCESSING  
Gauss apodization 0.002 sec  
F1 size 4096 x 2048  
Total time 5 hr, 16 min

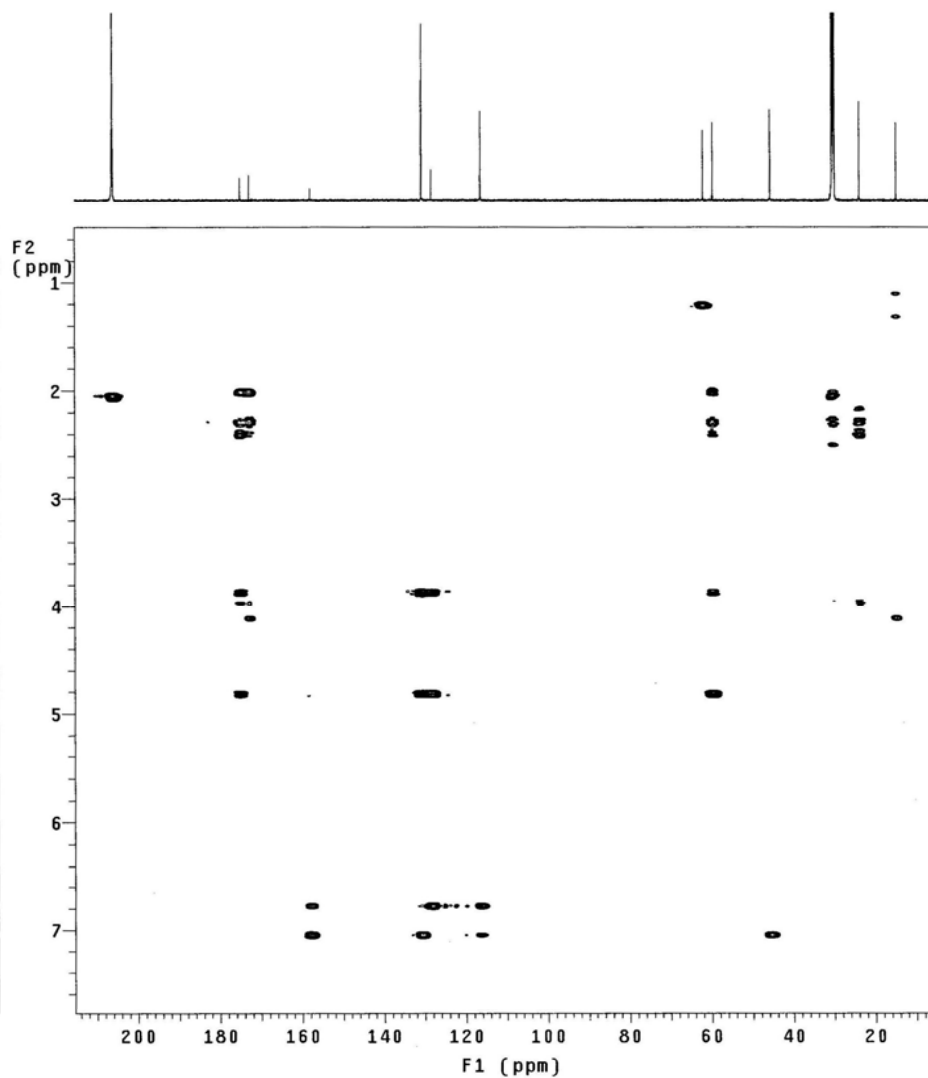
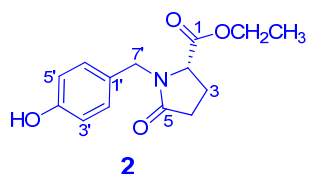
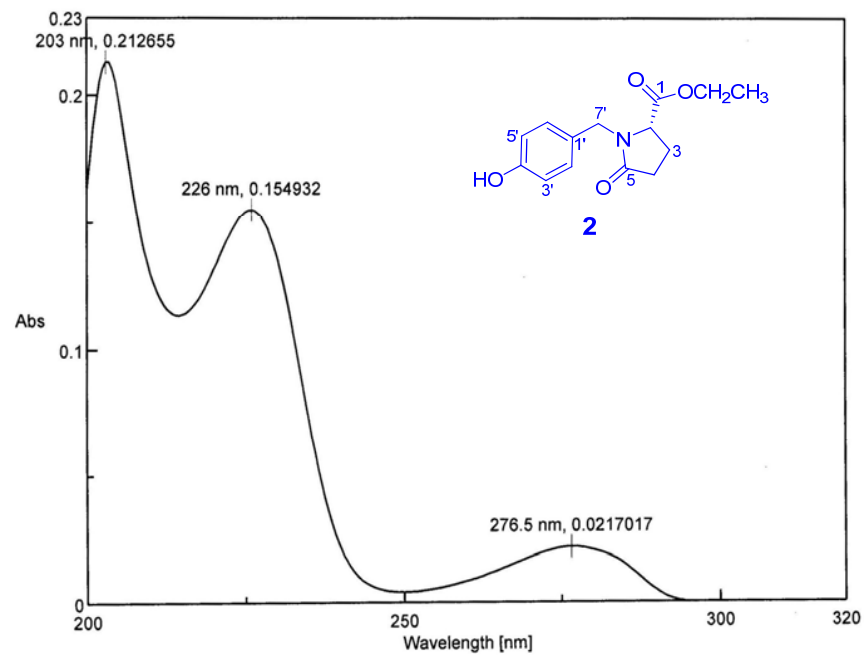
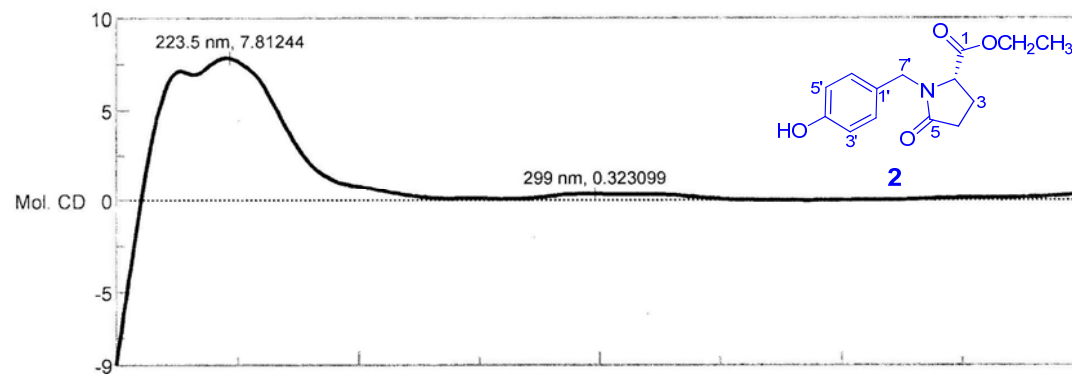


Figure S35. The gHMBC Spectrum of Compound 2 in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)

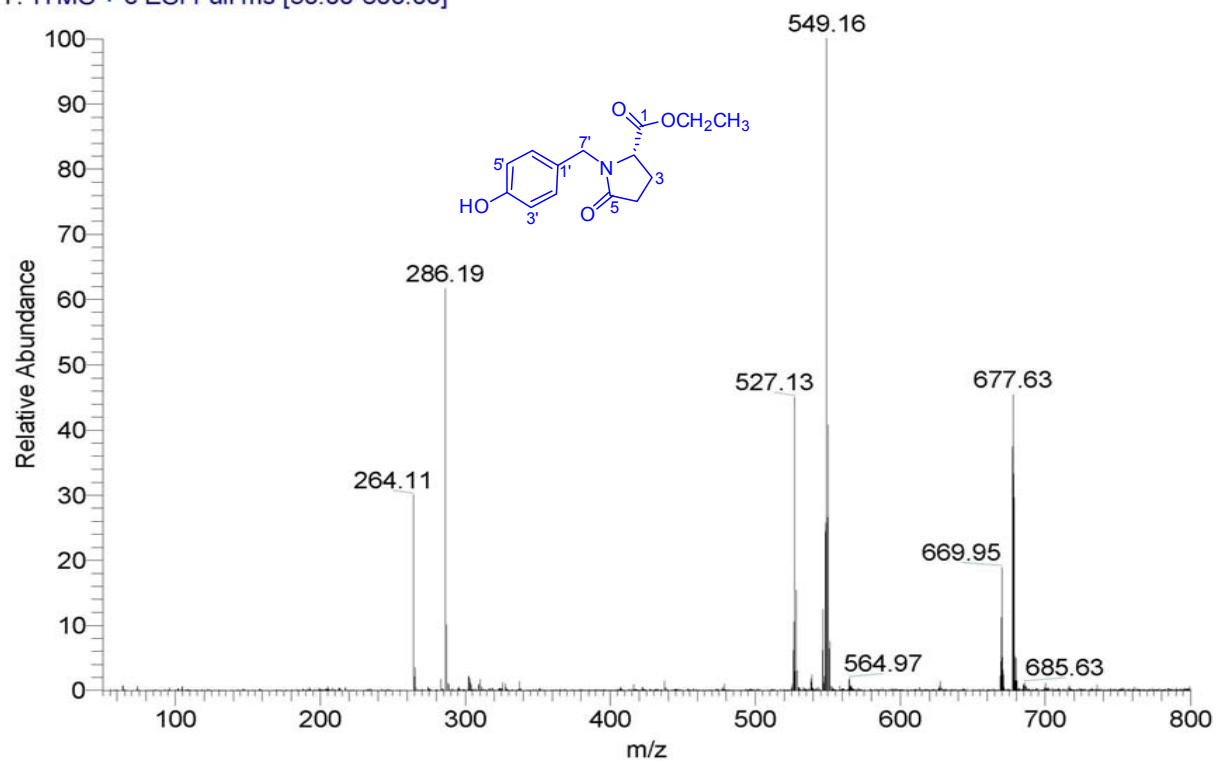


**Figure S36.** The UV Spectrum of Compound **2** in MeOH



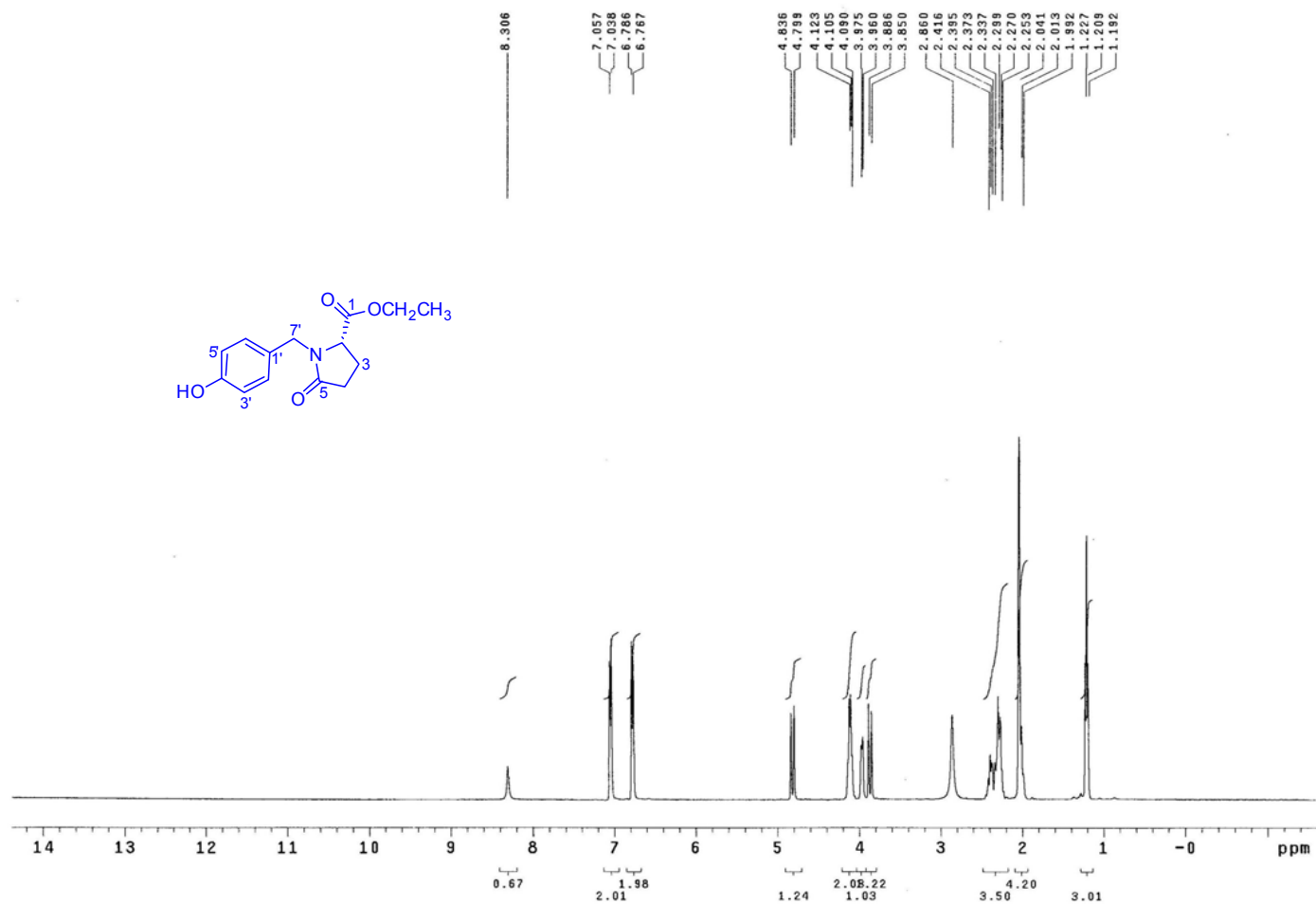
**Figure S37.** The CD Spectrum of Compound **2** in MeOH

TMG-22bs\_- #871-878 RT: 1.92-1.93 AV: 8 SB: 69 1.79-1.86 , 2.06-2.14 NL: 1.82E6  
T: ITMS + c ESI Full ms [50.00-800.00]



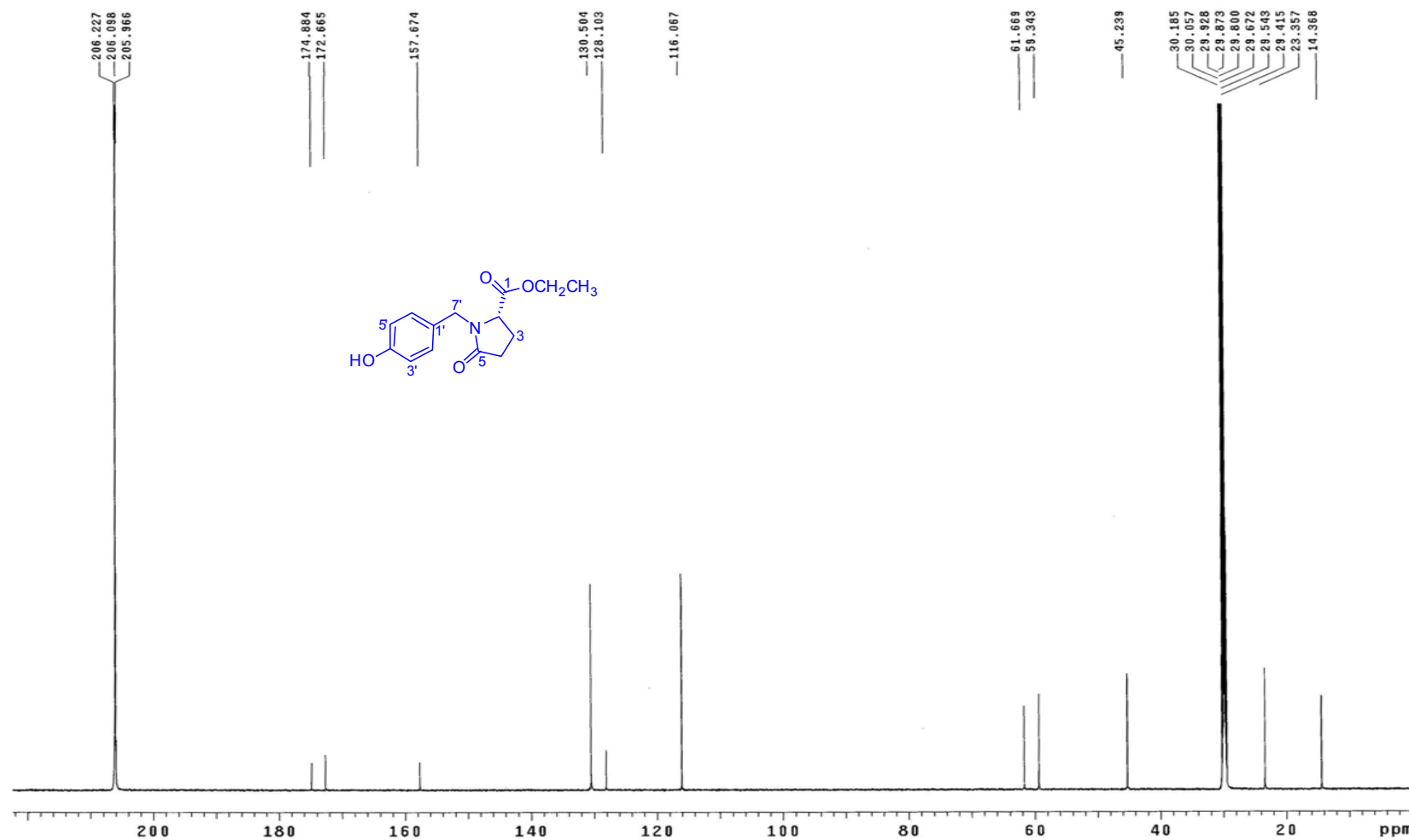
**Figure S38.** The (+)-ESIMS Spectrum of the Synthesized Ethyl (+)-(S)-[N-(4'-Hydroxybenzyl)]pyroglutamate (**2**)

MERCURY-400 1H-NMR TMG-22bs in ACETONE



**Figure S39.** The <sup>1</sup>H NMR Spectrum of the Synthesized Ethyl (+)-(S)-[N-(4'-Hydroxybenzyl)]pyroglutamate (2) in Me<sub>2</sub>CO-*d*<sub>6</sub> (400 MHz)

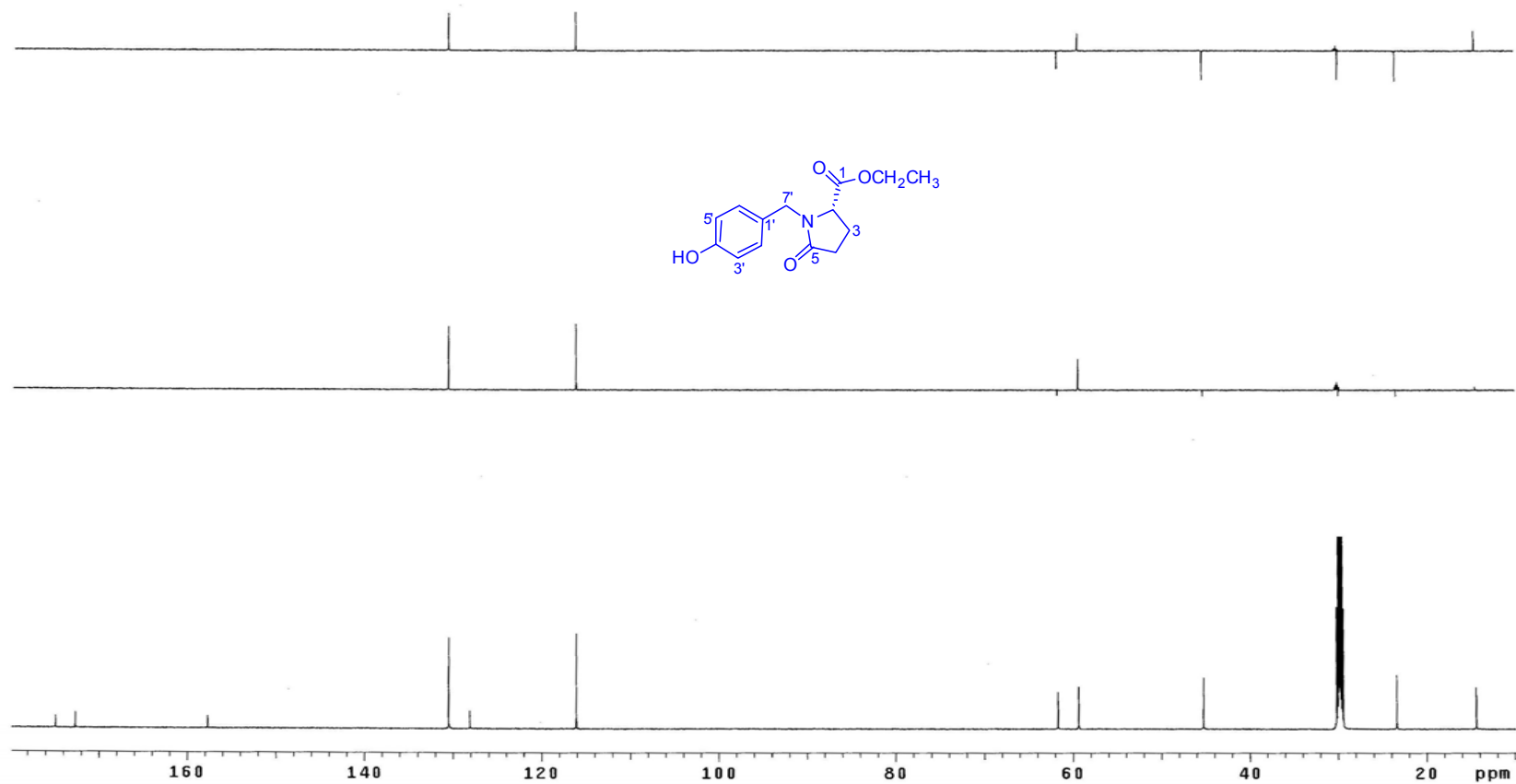
VNS-600 CARBON TMG-22b IN acetone Feb 13 2014



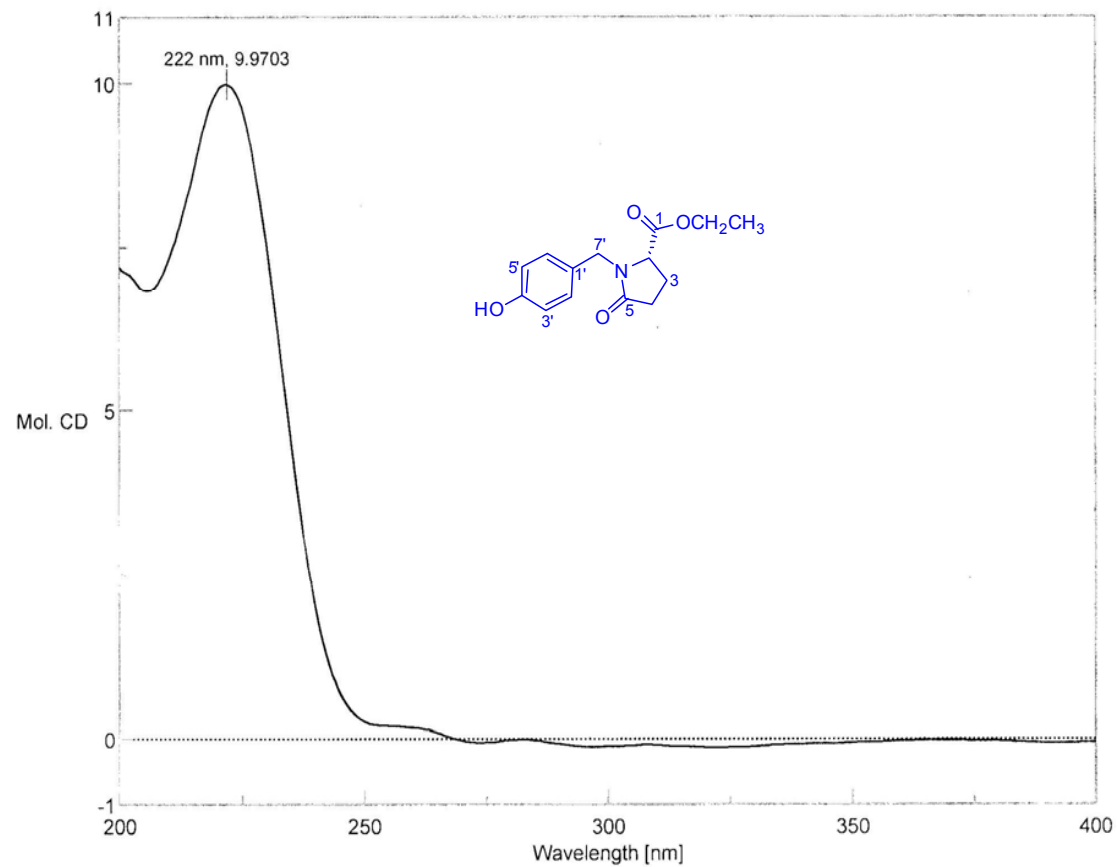
**Figure S40.** The <sup>13</sup>C NMR Spectrum of the Synthesized Ethyl (+)-(*S*)-[*N*-(4'-Hydroxybenzyl)]pyroglutamate (**2**) in Me<sub>2</sub>CO-*d*<sub>6</sub> (150 MHz)



VNS-600 DEPT TMG-22b IN acetone Feb 13 2014

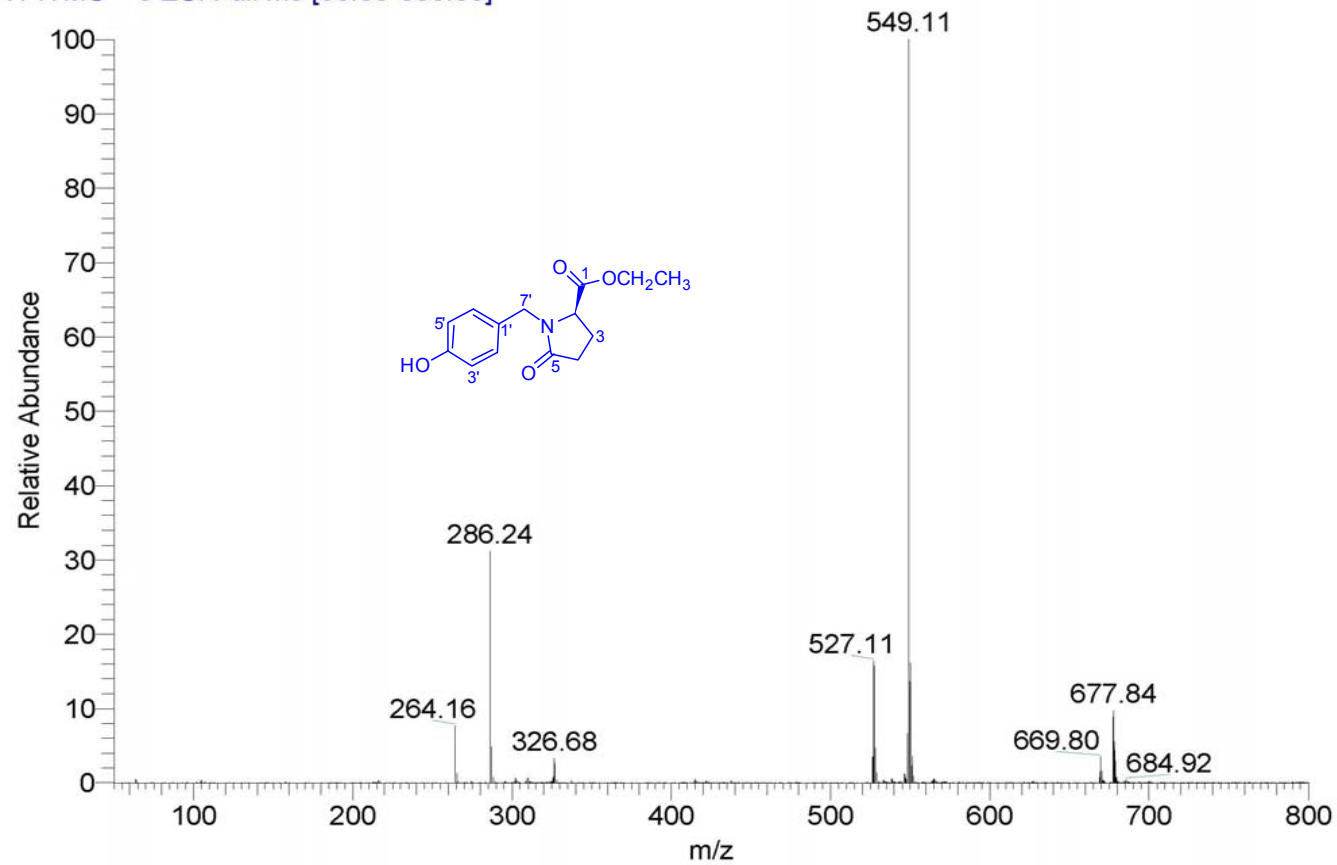


**Figure S41.** The DEPT Spectrum of the Synthesized Ethyl (+)-(S)-[N-(4'-Hydroxybenzyl)]pyroglutamate (**2**) in Me<sub>2</sub>CO-*d*<sub>6</sub> (150 MHz)

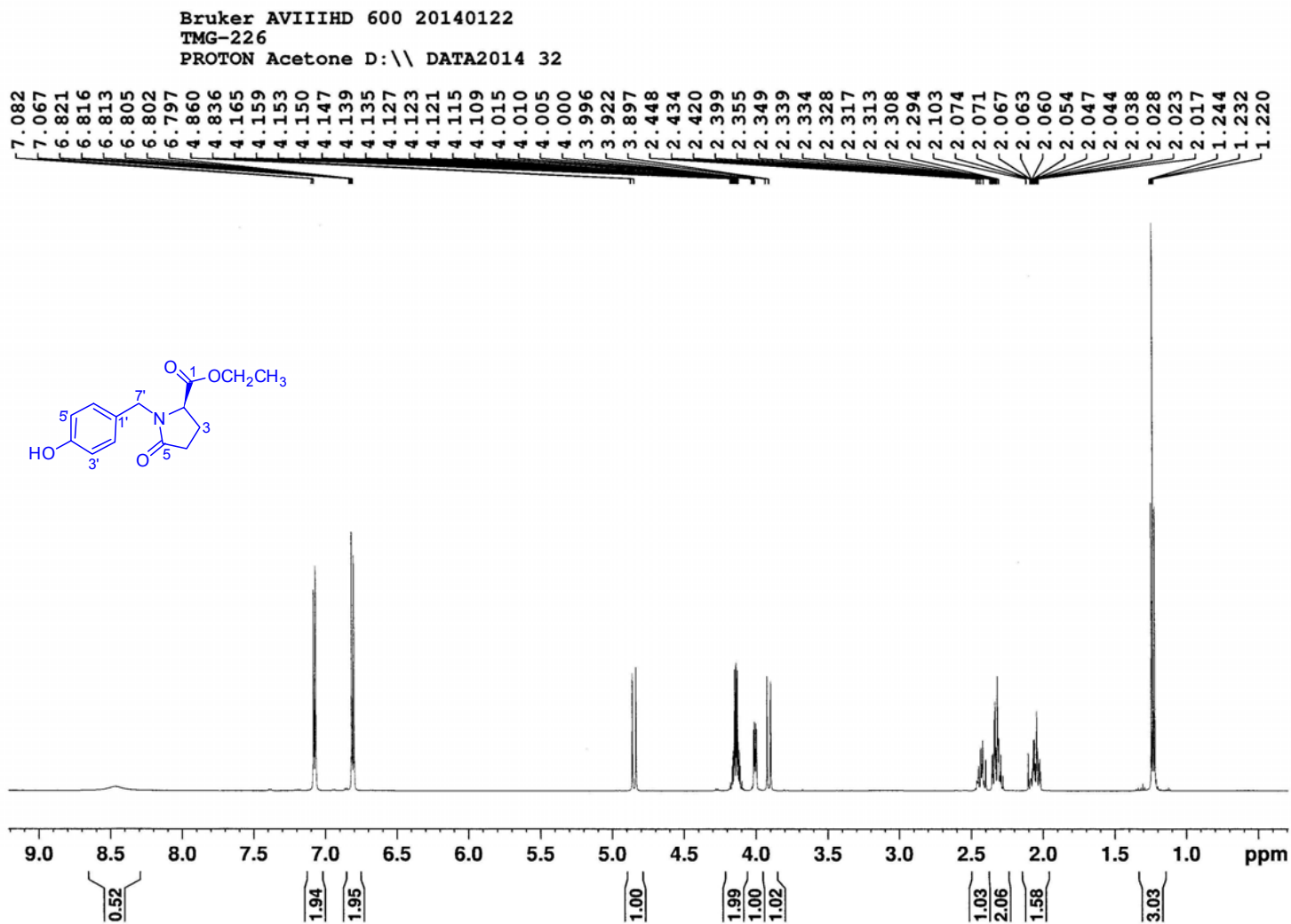


**Figure S42.** The CD Spectrum of the Synthesized Ethyl (+)-(*S*)-[*N*-(4'-Hydroxybenzyl)]pyroglutamate (**2**) in MeOH

TMG-22bsD #206-211 RT: 0.46-0.47 AV: 6 SB: 43 0.38-0.44 , 0.51-0.54 NL: 5.45E6  
T: ITMS + c ESI Full ms [50.00-800.00]



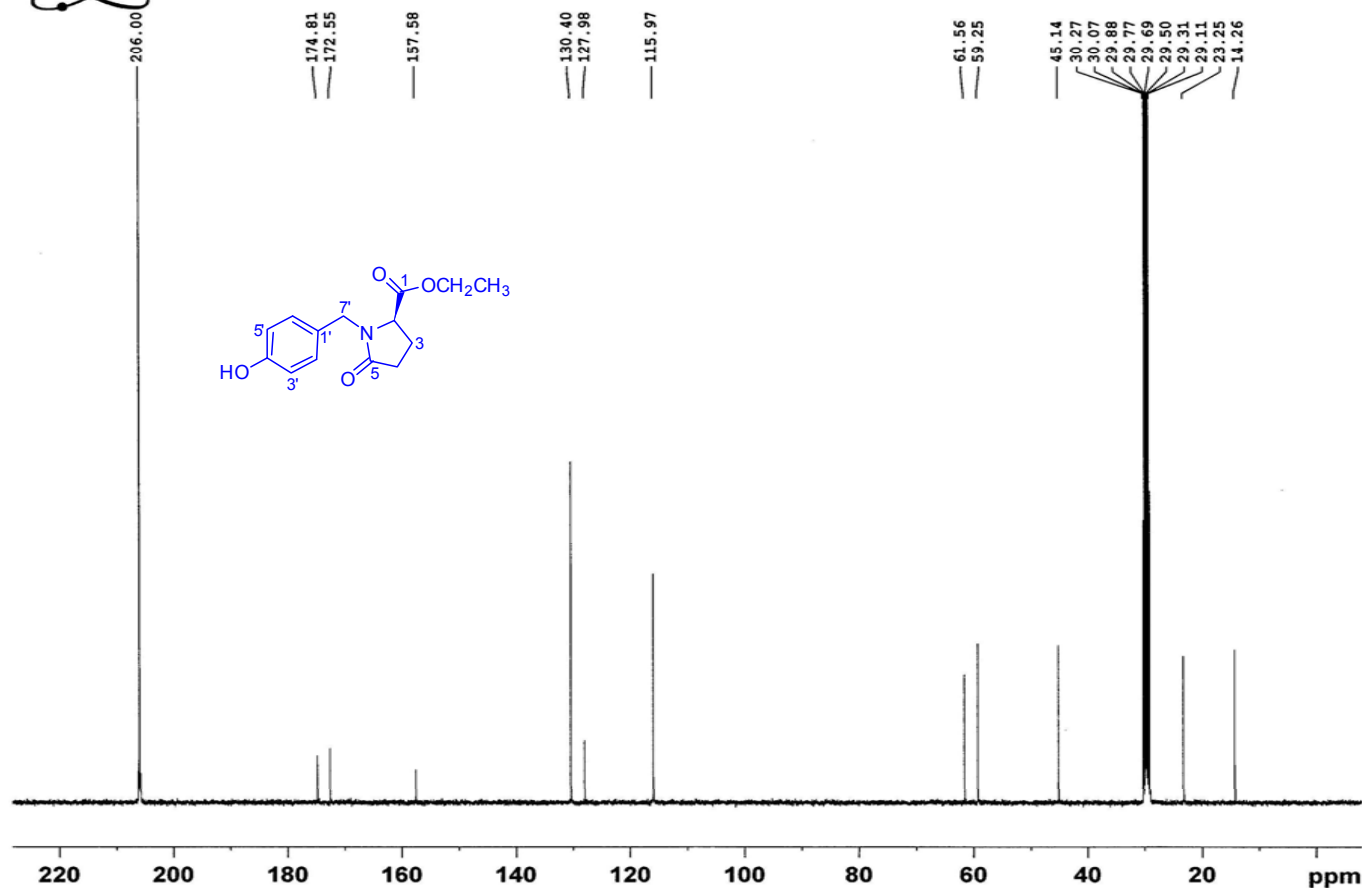
**Figure S43.** The (+)-ESIMS Spectrum of the Synthesized Ethyl (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate



**Figure S44.** The  $^1\text{H}$  NMR Spectrum of the Synthesized Ethyl (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate in  $\text{Me}_2\text{CO}-d_6$  (600 MHz)



Bruker AVANCEIII 400 20140213  
C13 Acetone D: \\ DATA-2014 35



Current Data Parameters  
NAME 20140213 TMG-22bSD  
EXPNO 2  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140213  
Time 15.26  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpg30  
TD 65536  
SOLVENT Acetone  
NS 1497  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 194.76  
DW 20.800 usec  
DE 6.50 usec  
TE 298.1 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TD0 300

CHANNEL f1  
SFO1 100.6238345 MHz  
NUC1 13C  
P1 10.00 usec  
PLW1 70.00000000 W

CHANNEL f2  
SFO2 400.1316005 MHz  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 80.00 usec  
PLW2 14.45400047 W  
PLW12 0.23497000 W  
PLW13 0.15038000 W

F2 - Processing parameters  
SI 32768  
SF 100.6126933 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

Figure S45. The  $^{13}\text{C}$  NMR Spectrum of the Synthesized Ethyl (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate in  $\text{Me}_2\text{CO}-d_6$  (100 MHz)



Bruker AVANCEIII 400 20140213 TMG-22bSD  
DEPT Acetone D:\\ DATA-2014 35

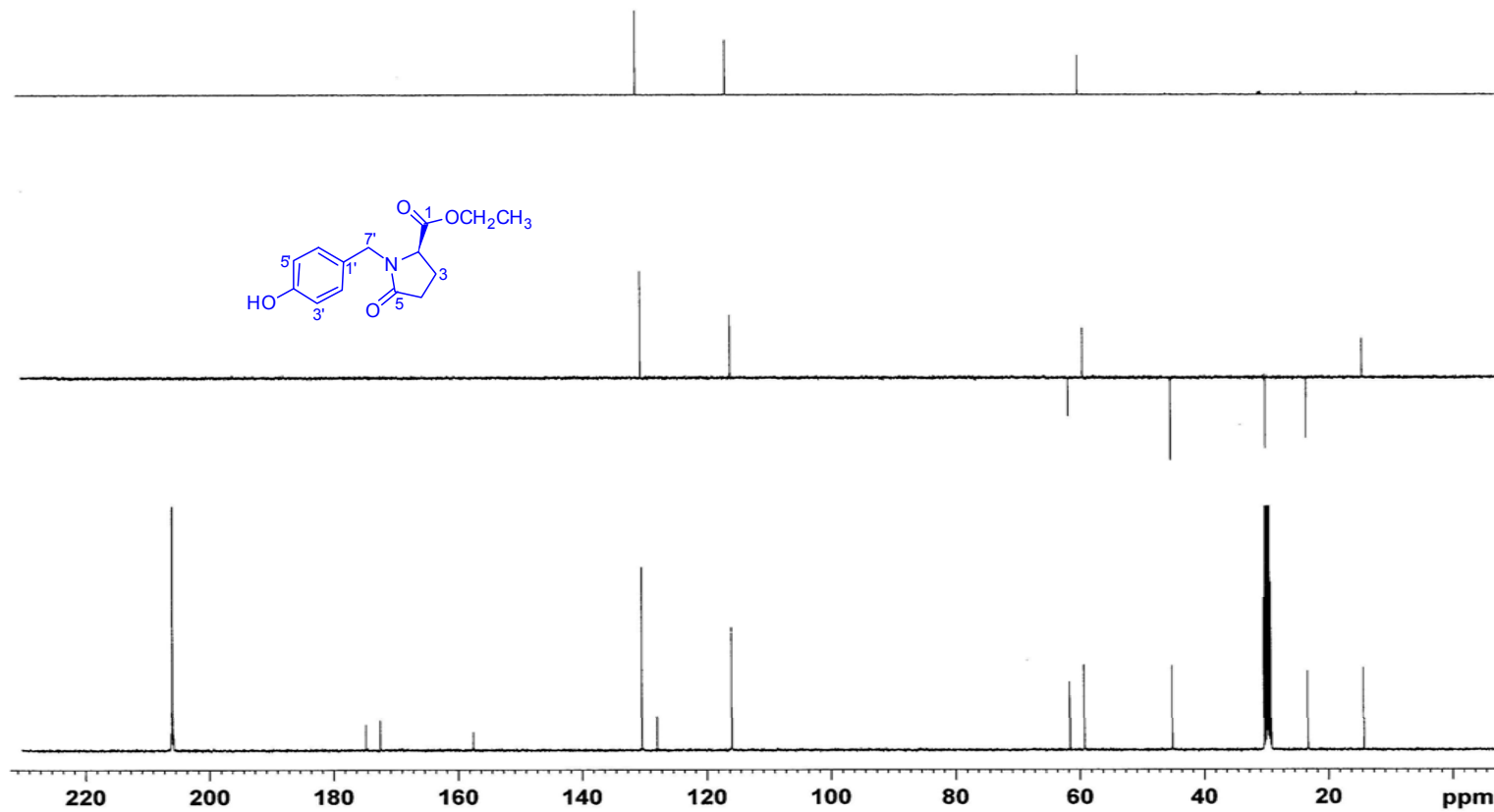
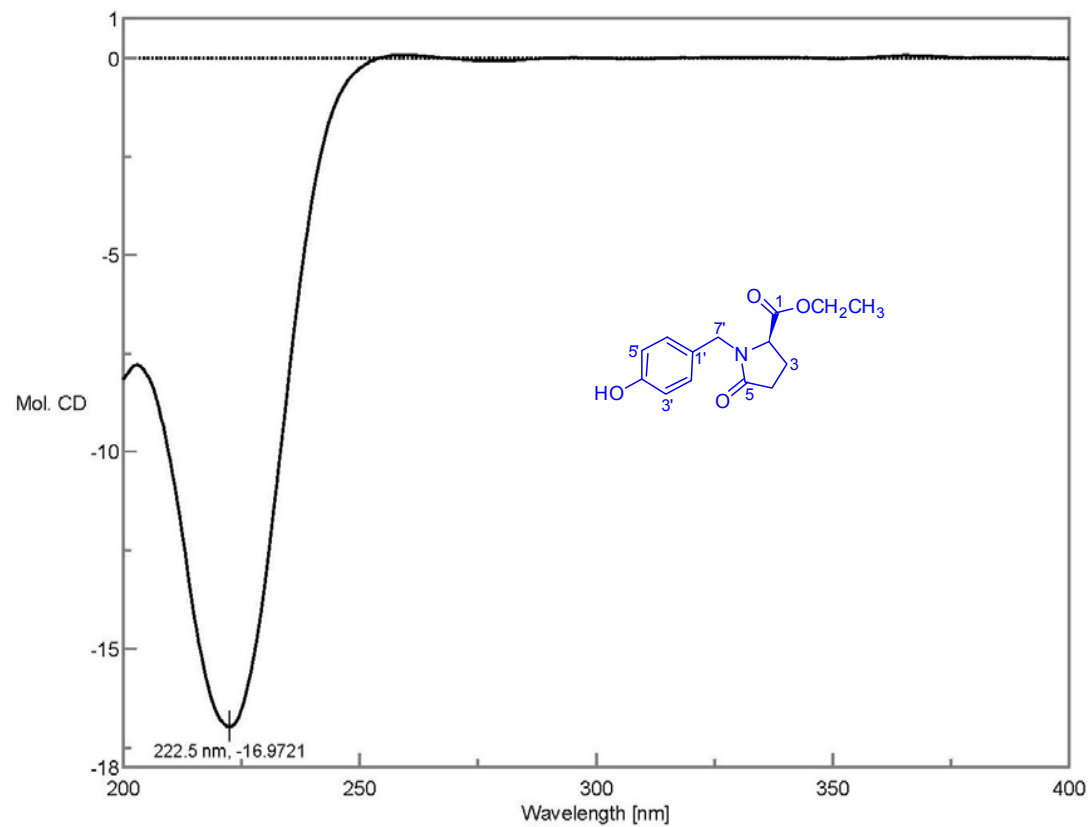


Figure S46. The DEPT Spectrum of the Synthesized Ethyl (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate in Me<sub>2</sub>CO-*d*<sub>6</sub> (100 MHz)



**Figure S47.** The CD Spectrum of the Synthesized Ethyl (-)-(R)-[N-(4'-Hydroxybenzyl)]pyroglutamate in MeOH

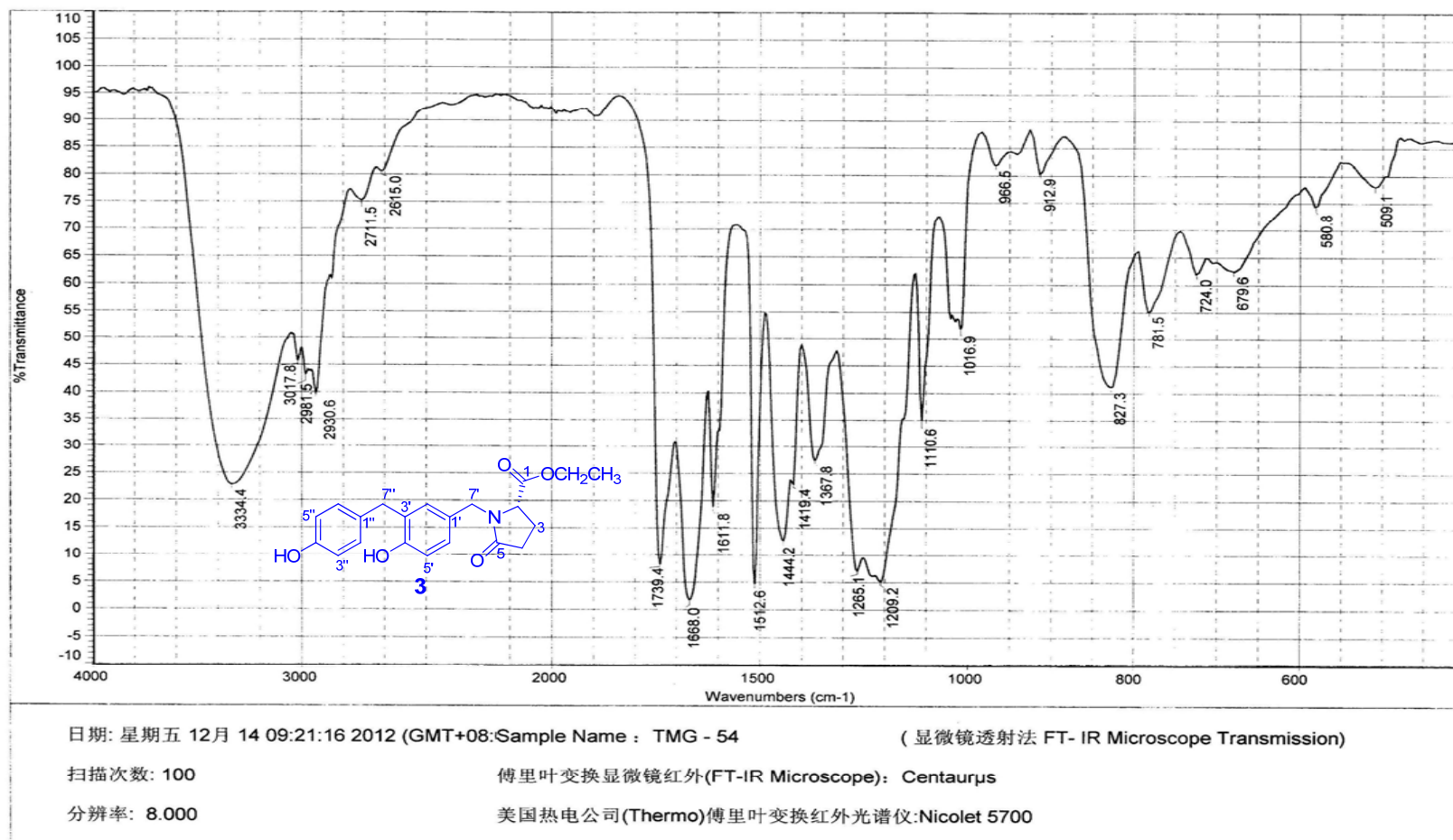
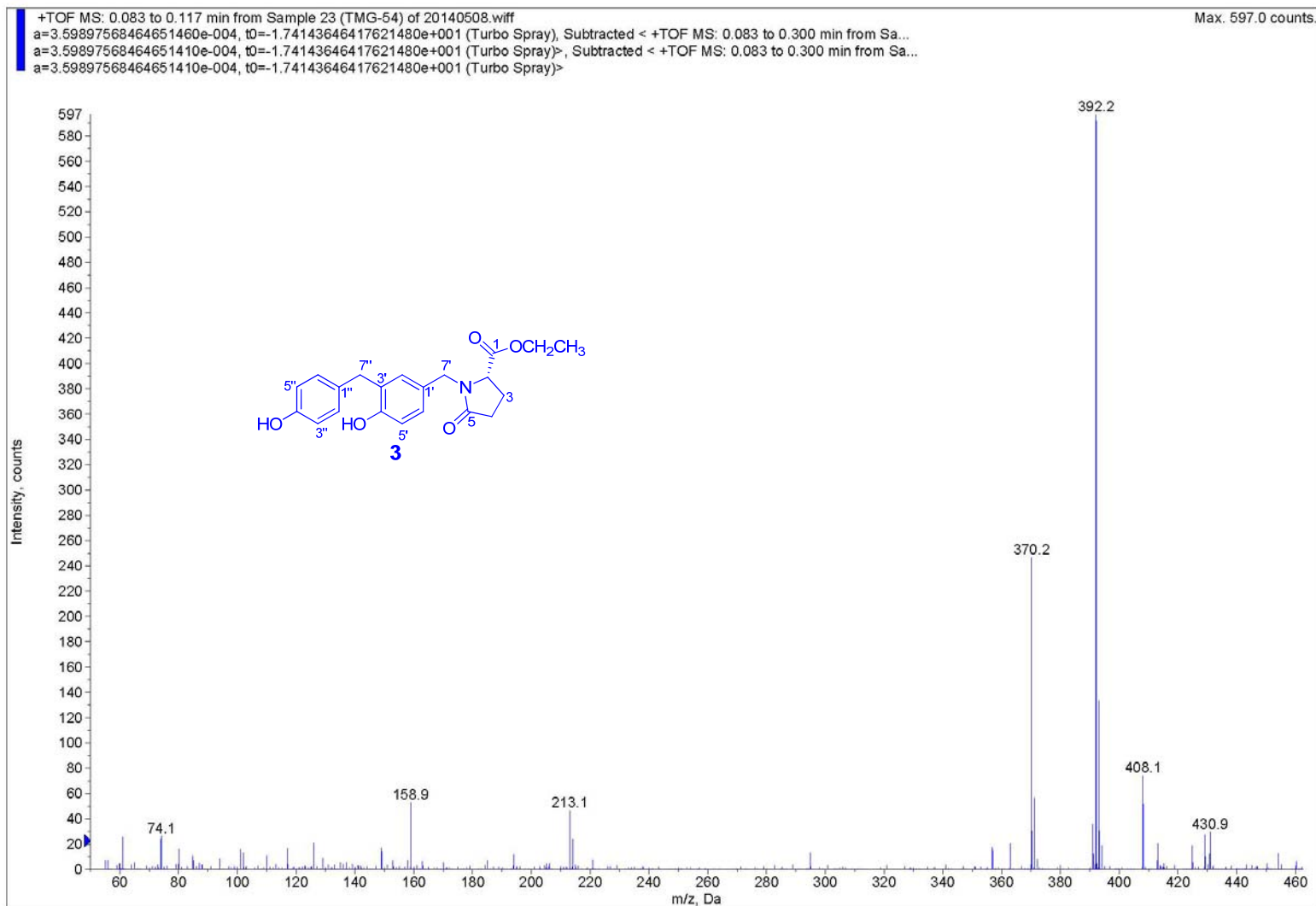


Figure S48. The IR Spectrum of Compound 3





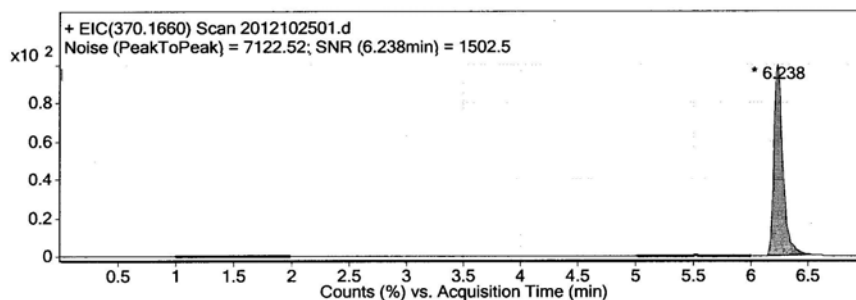
**Figure S49.** The (+)-ESIMS Spectrum of Compound **3**

## Qualitative Analysis Report

<b>Data Filename</b>	2012102501.d	<b>Sample Name</b>	TMG-54
<b>Sample Type</b>	Sample	<b>Position</b>	P1-D5
<b>Instrument Name</b>	Instrument 1	<b>User Name</b>	
<b>Acq Method</b>		<b>IRM Calibration Status</b>	Some Ions Missed
<b>DA Method</b>	TEST LCMS.m	<b>Comment</b>	

### User Chromatograms

Fragmentor Voltage 135    Collision Energy 0    Ionization Mode ESI



#### Integration Peak List

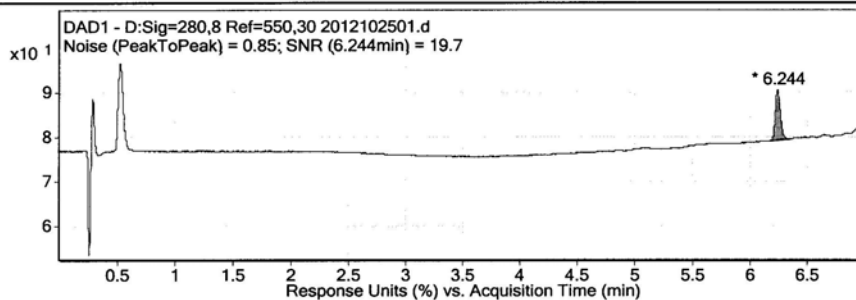
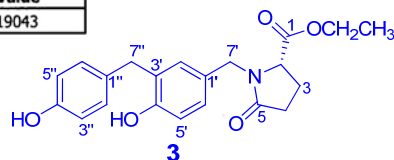
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	6.142	6.238	6.528	1911669	10701722	100	1502.5

#### Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	7122.519043

#### Noise Regions

Start	End
1	2
5	6
8.6	9.4
9.8	11



#### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	6.17	6.244	6.364	5.33	16.66	100	19.7

#### Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	0.845432281

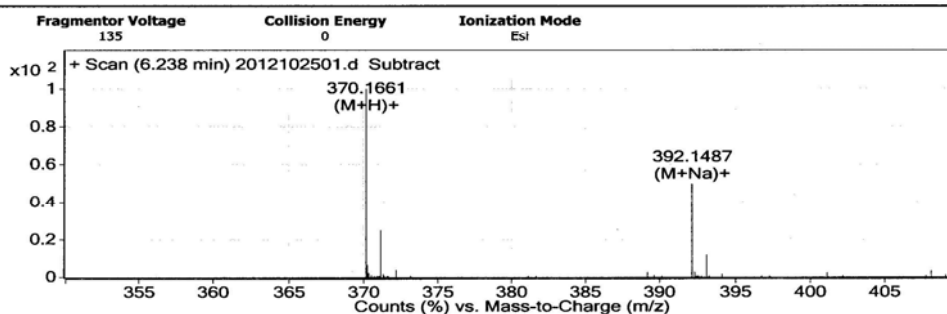
#### Noise Regions

Start	End
1	2
8.6	9.4
9.8	11

### User Spectra

**Figure S50.** The (+)-HRESIMS Report of Compound 3, Page 1

## Qualitative Analysis Report



**Peak List**

m/z	z	Abund	Formula	Ion
370.1661	1	1916112	C21 H24 N O5	(M+H)+
370.328		127040		
371.17	1	480516	C21 H24 N O5	(M+H)+
392.1487	1	952095	C21 H23 N Na O5	(M+Na)+
393.1516	1	233075	C21 H23 N Na O5	(M+Na)+
429.2397		164907		
739.325	1	233104		
740.3281	1	109783		
761.308	1	638908		
762.3107	1	302903		

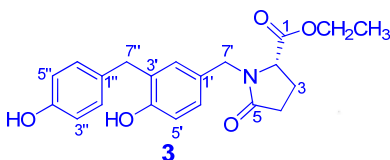
**Formula Calculator Element Limits**

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	4
S	0	2
Cl	0	0
Br	0	1

**Formula Calculator Results**

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C21 H23 N O5	TRUE	369.1588	369.1576	-3.31	C21 H24 N O5	99.75
C18 H27 N O5 S		369.1588	369.161	5.82	C18 H28 N O5 S	98.08
C21 H23 N O5	TRUE	369.1595	369.1576	-5.08	C21 H23 N Na O5	99.61
C18 H27 N O5 S		369.1595	369.161	4.04	C18 H27 N Na O5 S	98.51

--- End Of Report ---



**Figure S51.** The (+)-HRESIMS Report of Compound **3**, Page 2

MS Formula Results: + Scan (6.238 min) Sub (2012102501.d)

m/z	Ion	Formula	Abundance
370.1661	(M+H) <sup>+</sup>	C <sub>21</sub> H <sub>24</sub> N O <sub>5</sub>	1916112.4

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>21</sub> H <sub>23</sub> N O <sub>5</sub>	C <sub>21</sub> H <sub>24</sub> N O <sub>5</sub>	370.1649	99.75		369.1588	369.1576	-3.31	3.31	99.78	99.94	99.65	370.1661	11
<input type="checkbox"/>	C <sub>18</sub> H <sub>27</sub> N O <sub>5</sub> S	C <sub>18</sub> H <sub>28</sub> N O <sub>5</sub> S	370.1683	98.08		369.1588	369.161	5.82	5.82	95.61	99.38	98.91	370.1661	6

m/z	Ion	Formula	Abundance
392.1487	(M+Na) <sup>+</sup>	C <sub>21</sub> H <sub>23</sub> N Na O <sub>5</sub>	952094.6

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>21</sub> H <sub>23</sub> N O <sub>5</sub>	C <sub>21</sub> H <sub>23</sub> N Na O <sub>5</sub>	392.1468	99.61		369.1595	369.1576	-5.08	5.08	99.91	99.97	99.25	392.1487	11
<input type="checkbox"/>	C <sub>18</sub> H <sub>27</sub> N O <sub>5</sub> S	C <sub>18</sub> H <sub>27</sub> N Na O <sub>5</sub> S	392.1502	98.51		369.1595	369.161	4.04	4.04	95.87	99.64	99.52	392.1487	6

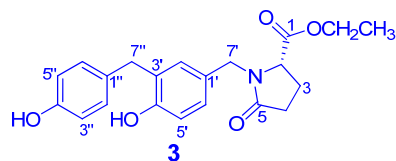


Figure S52. The (+)-HRESIMS Report of Compound 3, Page 3

VNS-600 PROTON TMG-66 IN CD3COCD3 Nov 18 2012

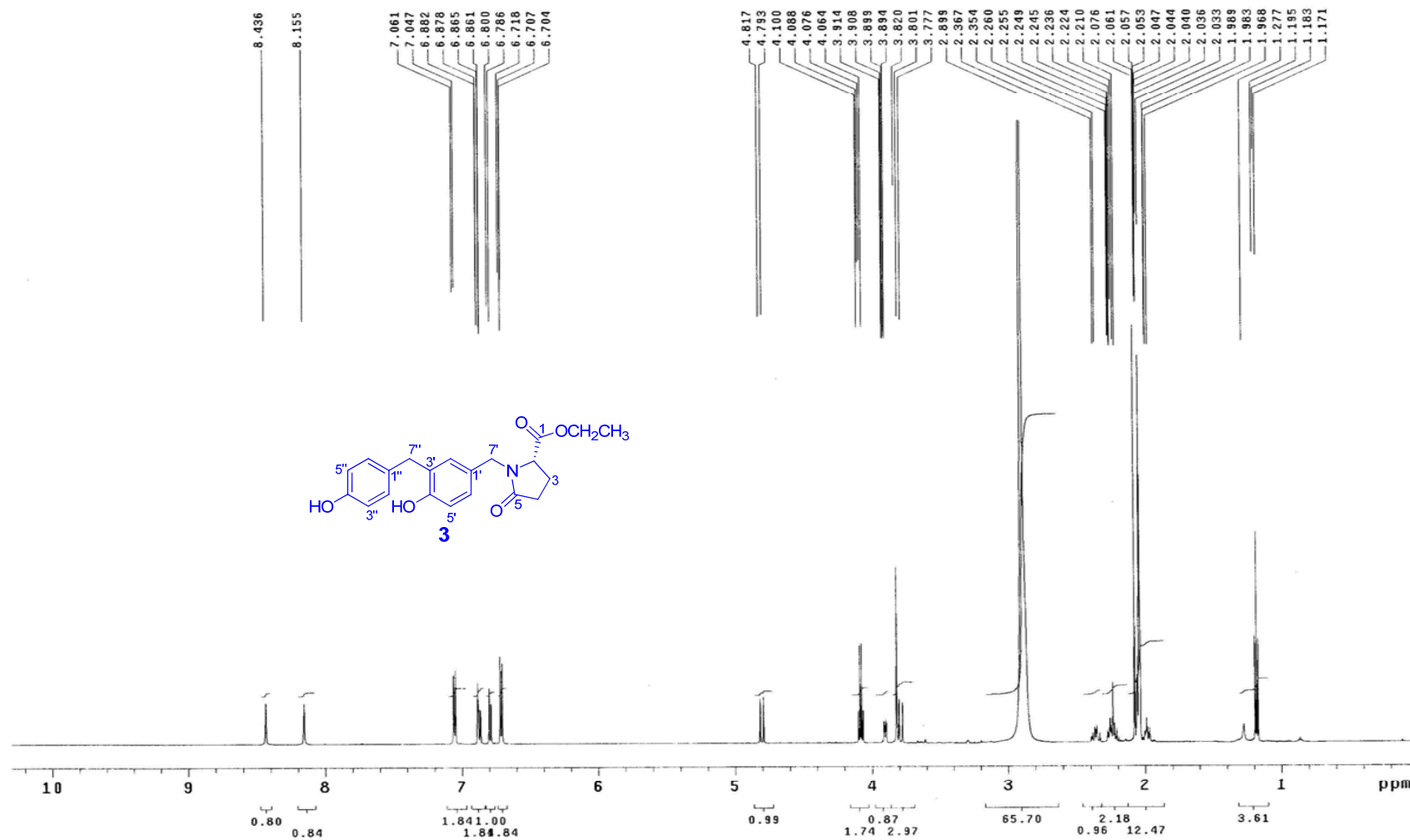


Figure S53. The <sup>1</sup>H NMR Spectrum of Compound 3 in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)

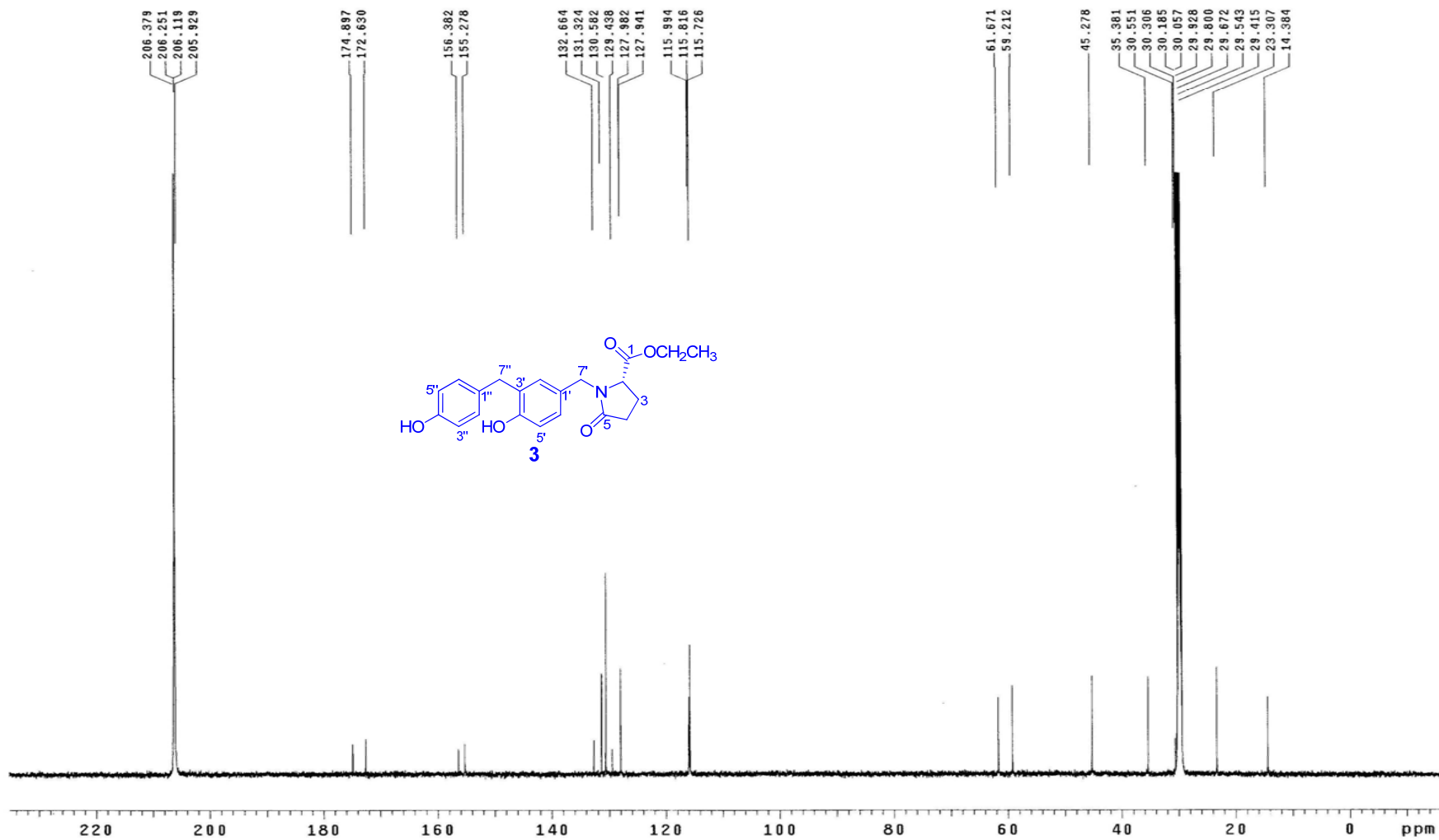


Figure S54. The <sup>13</sup>C NMR Spectrum of Compound 3 in Me<sub>2</sub>CO-*d*<sub>6</sub> (150 MHz)

VNS-600 gCOSY TMG-66 IN CD3COCD3 Nov 18 2012

Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.150 sec  
Width 6313.1 Hz  
2D Width 6313.1 Hz  
2 repetitions  
256 increments  
OBSERVE H1, 599.6929249 MHz  
DATA PROCESSING  
Sq. sine bell 0.075 sec  
F1 DATA PROCESSING  
Sq. sine bell 0.027 sec  
FT size 2048 x 2048  
Total time 10 min

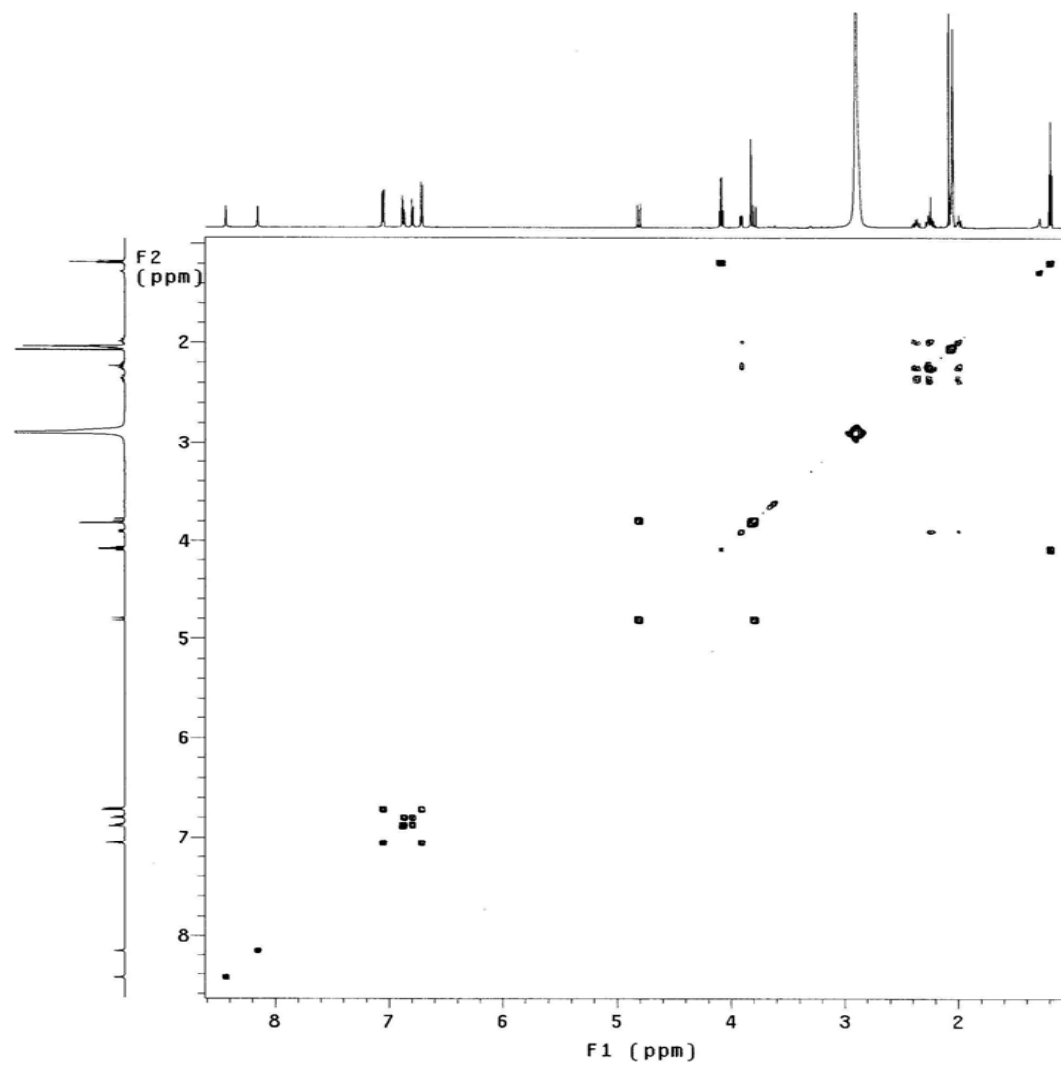
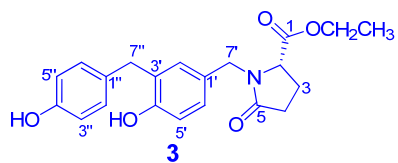


Figure S55. The  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum of **3** in  $\text{Me}_2\text{CO}-d_6$  (600 MHz)

VNS-600 gHSQCAD TMG-66 IN CD3COCD3 Nov 18 2012

Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.228 sec  
Width 6313.1 Hz  
2D Width 30154.5 Hz  
64 repetitions  
140 increments  
OBSERVE H1, 599.6929302 MHz  
DECOUPLE C13, 150.8062867 MHz  
Power 35 dB  
on during acquisition  
off during delay  
W40\_NEW-SW modulated  
DATA PROCESSING  
Sine bell 0.028 sec  
F1 DATA PROCESSING  
Sine bell 0.003 sec  
FT size 4096 x 2048  
Total time 2 hr, 13 min

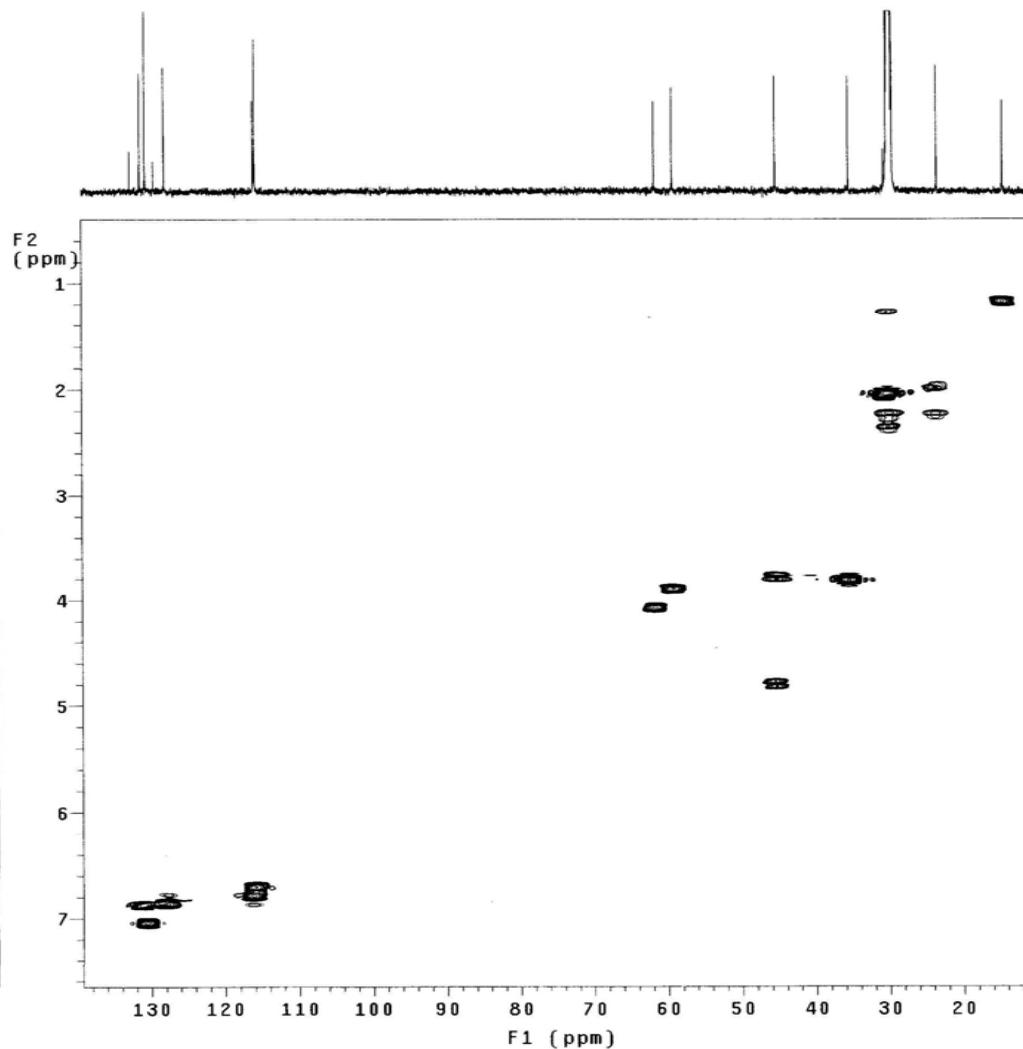
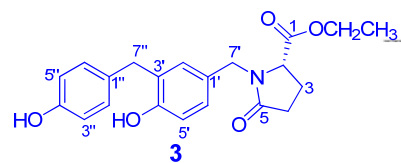


Figure S56. The gHSQC Spectrum of Compound **3** in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)



VNS-600 gHMCAD TMG-66 IN CD3COCD3 Nov 18 2012

Temp. 25.0 C / 298.1 K  
Sample #12, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.228 sec  
Width 6313.1 Hz  
2D Width 36182.7 Hz  
96 repetitions  
160 increments  
OBSERVE H1, 599.6929240 MHz  
DATA PROCESSING  
Sine bell 0.089 sec  
F1 DATA PROCESSING  
Sine bell 0.004 sec  
FT size 4096 x 2048  
Total time 4 hr, 15 min

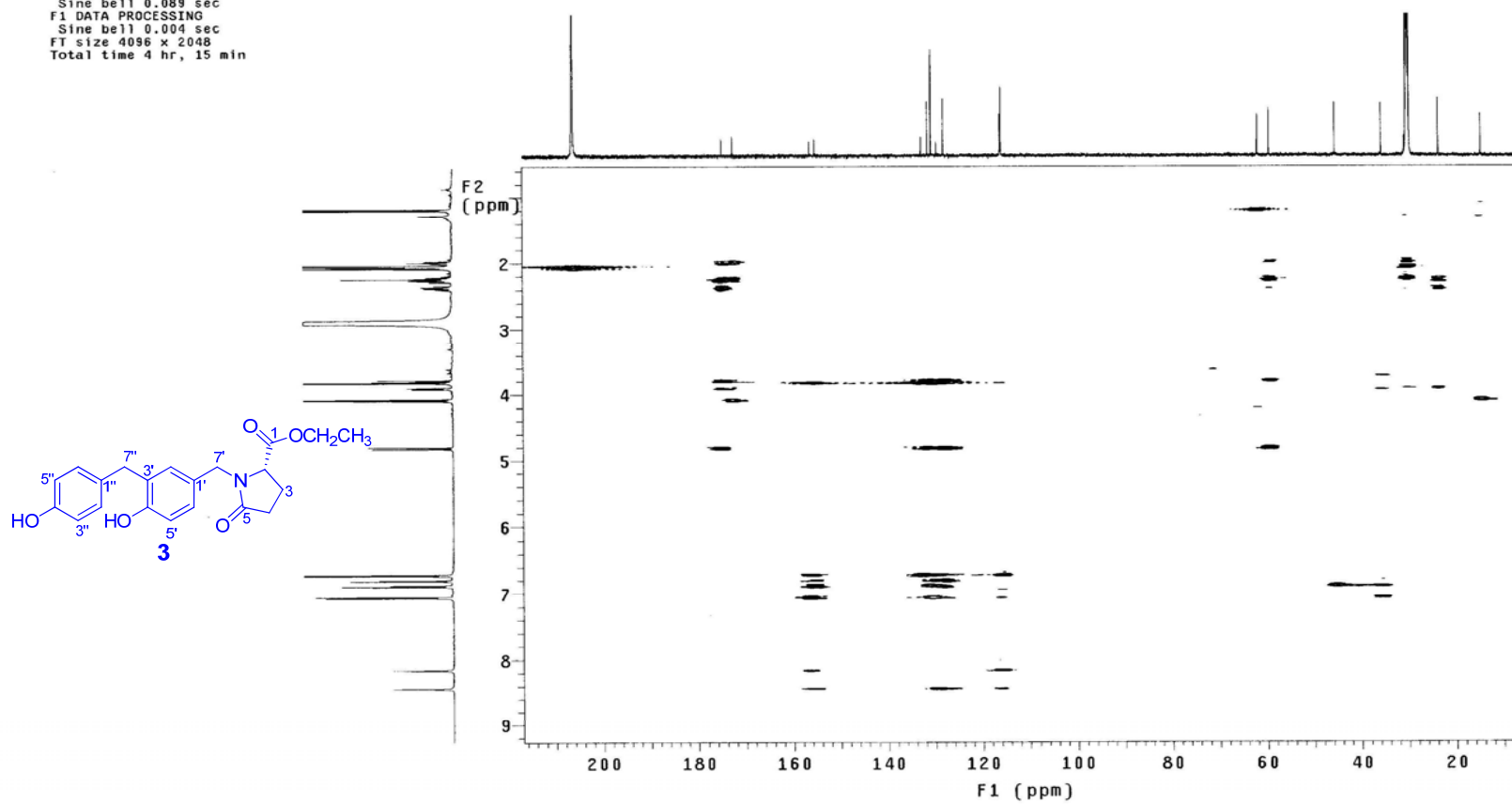
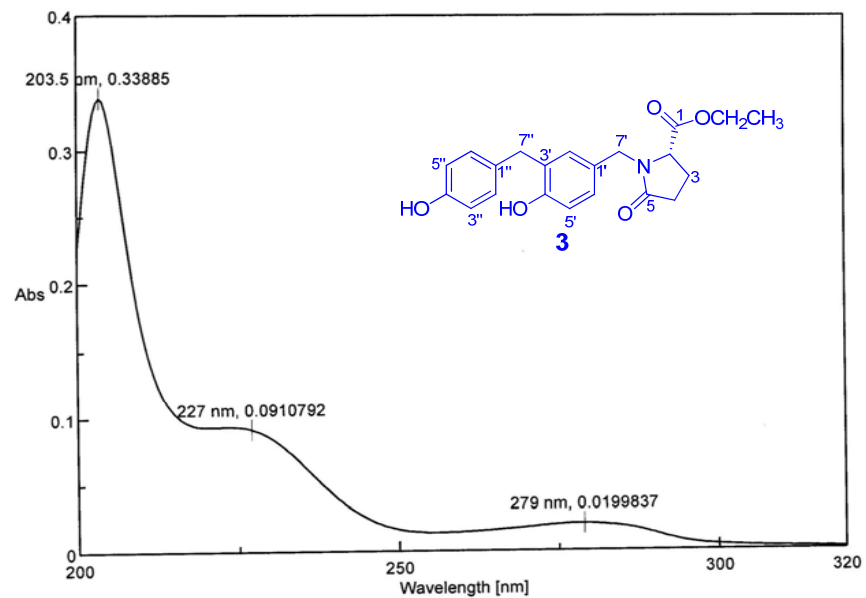
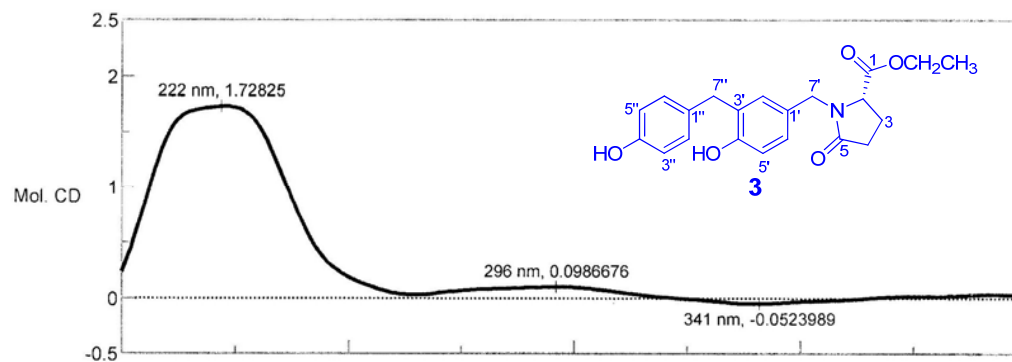


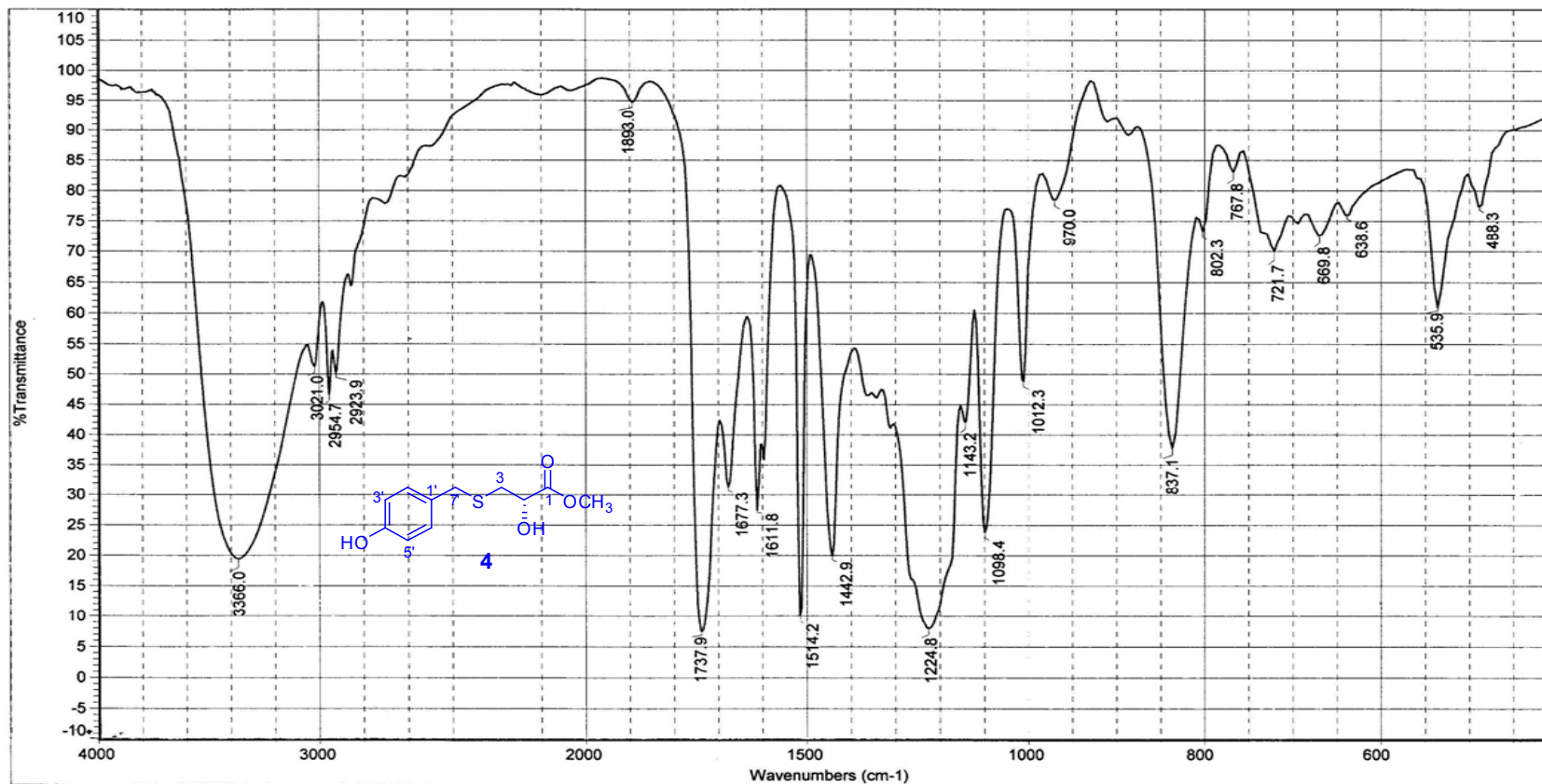
Figure S57. The gHMBC Spectrum of Compound 3 in Me<sub>2</sub>CO-*d*<sub>6</sub> (600 MHz)



**Figure S58.** The UV Spectrum of Compound **3** in MeOH



**Figure S59.** The CD Spectrum of Compound **3** in MeOH



日期: 星期一 5月 07 10:16:41 2012 (GMT+08:00) Sample Name : WYN - 82B

(显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100

傅里叶变换红外显微镜(FT-IR Microscope): Centaurus

分辨率: 8.000

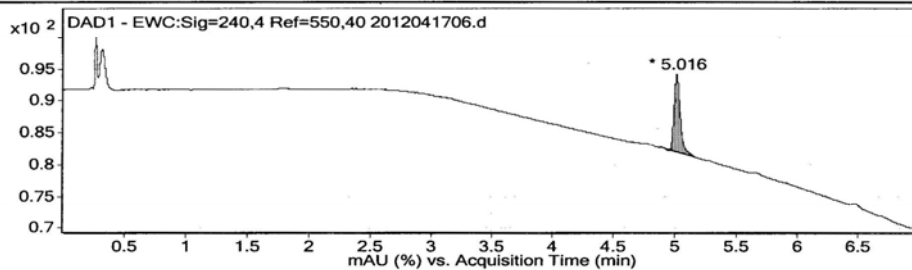
美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S60. The IR Spectrum of Compound 4

## Qualitative Analysis Report

Data Filename	2012041706.d	Sample Name	WYN-82B
Sample Type	Sample	Position	P1-D7
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	XXXXXXXXXX
DA Method	TEST LCMS.m	Comment	

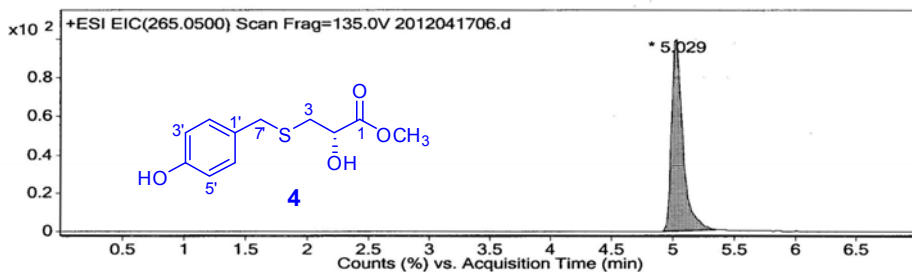
### User Chromatograms



#### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	4.921	5.016	5.164	12.31	42.84	100

Fragmentor Voltage 135    Collision Energy 0    Ionization Mode ESI



#### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	4.916	5.029	5.351	1054939	6927092	100

#### User Spectra

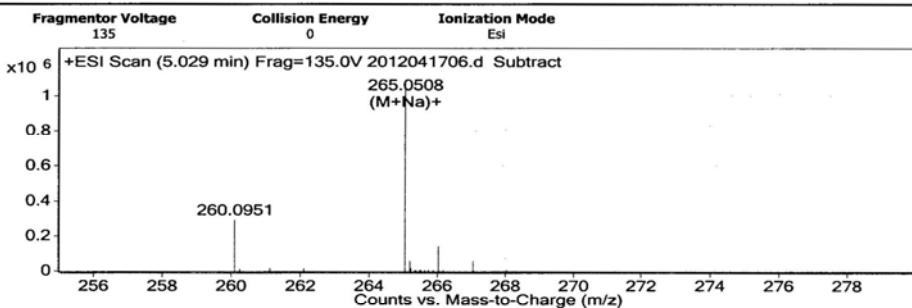


Figure S61. The (+)-HRESIMS Report of Compound 4, Page 1

## Qualitative Analysis Report

### Peak List

m/z	z	Abund	Formula	Ion
107.0434		156050		
260.0951		294656		
265.0508	1	1058089	C11 H14 Na O4 S	(M+Na)+
265.1919		56419		
266.0534	1	145574	C11 H14 Na O4 S	(M+Na)+
267.0487	1	59855	C11 H14 Na O4 S	(M+Na)+
507.1122		199488		

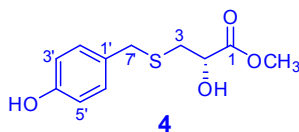
### Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	120
O	0	30
N	0	4
S	0	3
Cl	0	0

### Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C11 H14 O4 S	TRUE	242.0615	242.0613	-1.11	C11 H14 Na O4 S	99.92
C12 H10 N4 S		242.0615	242.0626	4.41	C12 H10 N4 Na S	99.67
C7 H14 O9		242.0615	242.0638	9.24	C7 H14 Na O9	96.67
C15 H6 N4		242.0615	242.0592	-9.51	C15 H6 N4 Na	96.57

--- End Of Report ---



**Figure S62.** The (+)-HRESIMS Report of Compound 4, Page 2

MS Formula Results: + Scan (5.029 min) Sub (2012041706.d)

m/z	Ion	Formula	Abundance
265.0508	(M+Na) <sup>+</sup>	C <sub>11</sub> H <sub>14</sub> NaO <sub>4</sub> S	1058088.6

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> S	C <sub>11</sub> H <sub>14</sub> NaO <sub>4</sub> S	265.0505	99.92		242.0615	242.0613	-1.11	1.11	99.87	99.88	99.97	265.0508	5
<input type="checkbox"/>	C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> S	C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> NaS	265.0518	99.67		242.0615	242.0626	4.41	4.41	99.66	100	99.51	265.0508	10
<input type="checkbox"/>	C <sub>7</sub> H <sub>14</sub> O <sub>9</sub>	C <sub>7</sub> H <sub>14</sub> NaO <sub>9</sub>	265.053	96.67		242.0615	242.0638	9.24	9.24	93.93	97.55	97.87	265.0508	1
<input type="checkbox"/>	C <sub>15</sub> H <sub>6</sub> N <sub>4</sub>	C <sub>15</sub> H <sub>6</sub> N <sub>4</sub> Na	265.0485	96.57		242.0615	242.0592	-9.51	9.51	94.18	97.08	97.75	265.0508	15

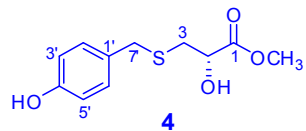


Figure S63. The (+)-HRESIMS Report of Compound 4, Page 3

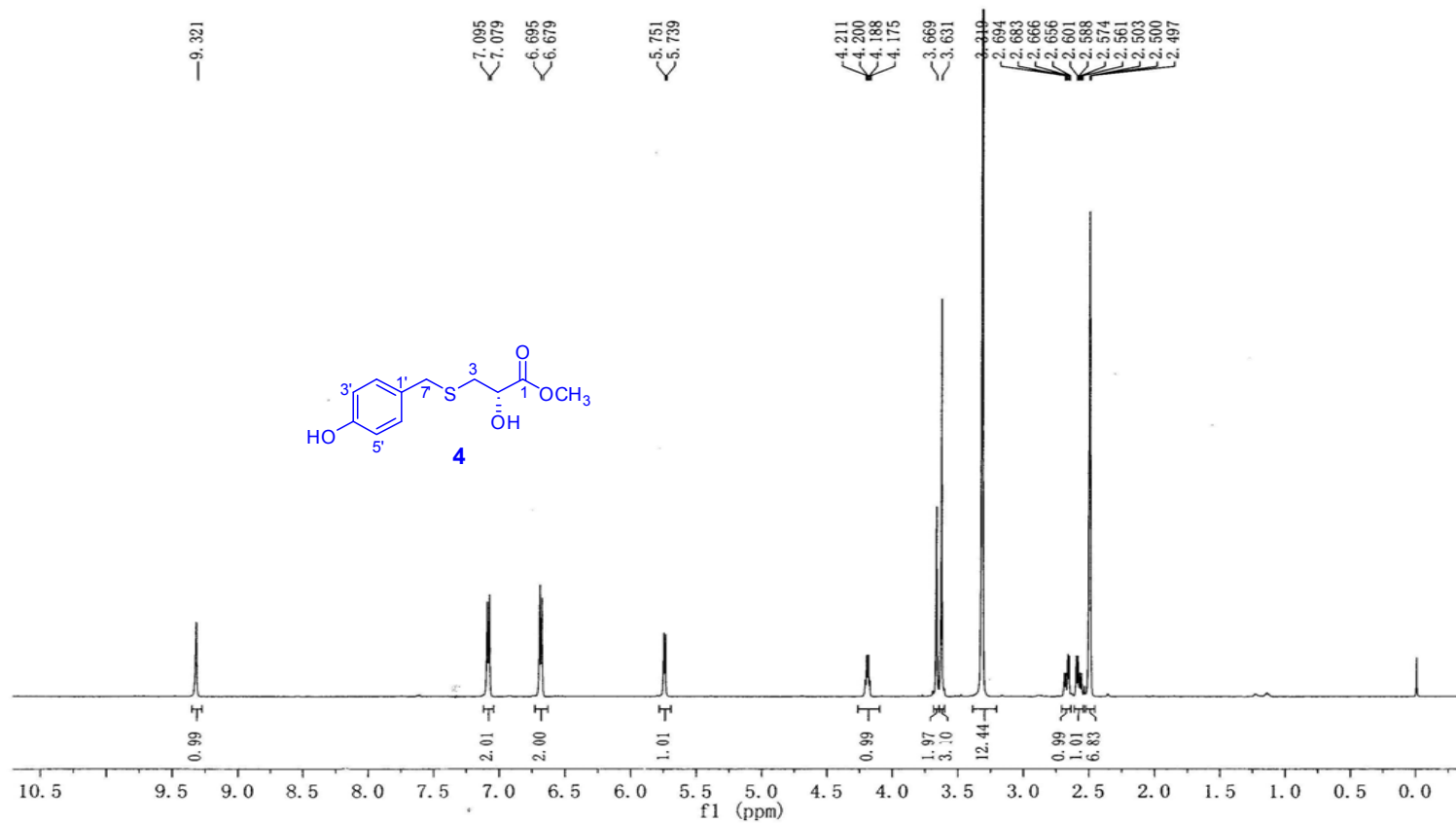
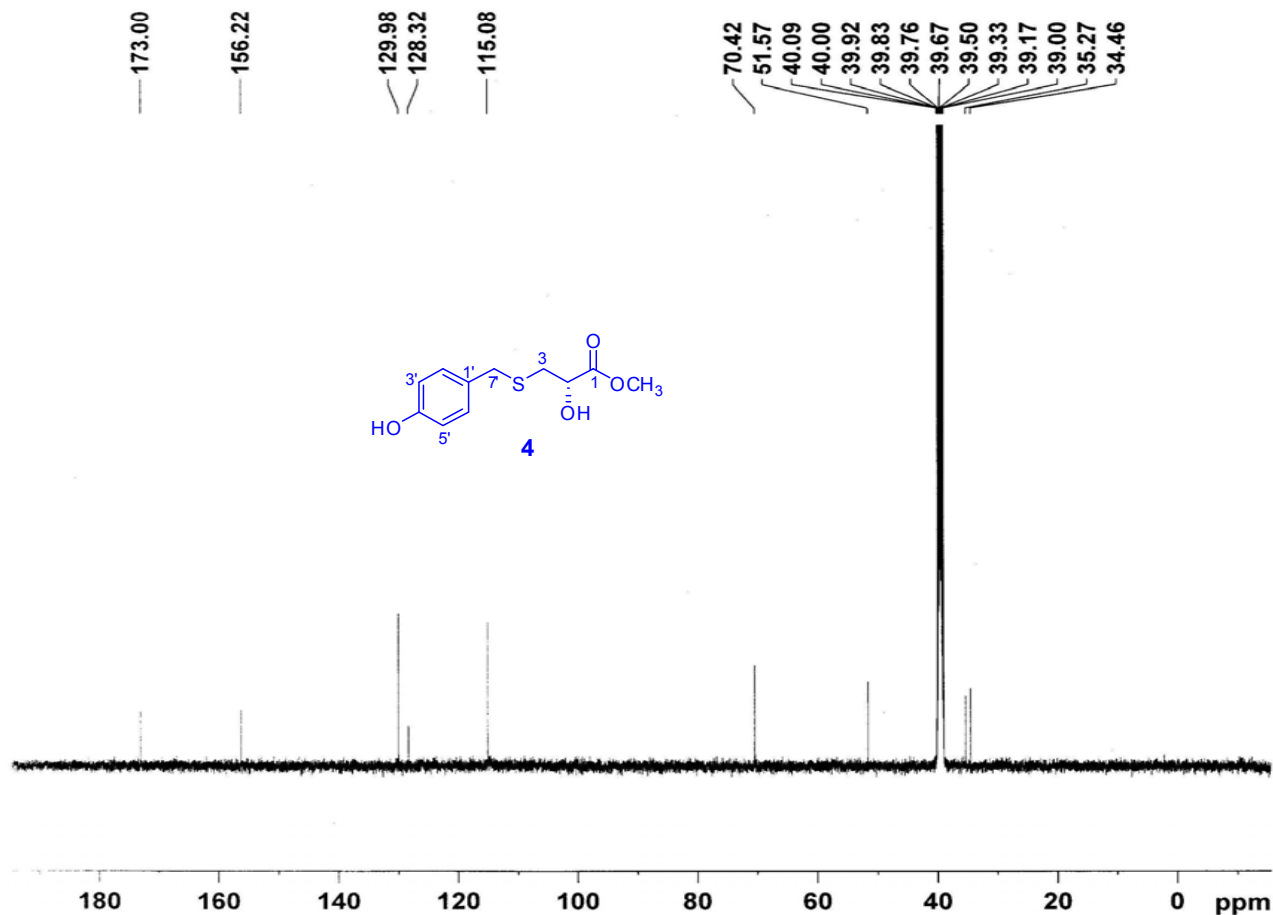


Figure S64. The <sup>1</sup>H NMR Spectrum of Compound 4 in DMSO-d<sub>6</sub> (500 MHz)

BRUKER AV500-III 13C-NMR WYN-82B IN DMSO 2011.06.29  
 C13CPD DMSO D:\\ shijiangong 2



```

Current Data Parameters
NAME      20110629-WYN-82B
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20110704
Time      16.50
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   DMSO
NS         2860
DS         4
SWH       29761.904 Hz
FIDRES    0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         298.9 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0        600

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1        0.90 dB
PL1W       73.29839325 W
SFO1       125.7527610 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        2.00 dB
PL12       16.77 dB
PL13       16.77 dB
PL2W       12.39386463 W
PL12W      0.41324416 W
PL13W      0.41324416 W
SFO2       500.0620002 MHz

F2 - Processing parameters
SI         32768
SF         125.7402476 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

Figure S65. The <sup>13</sup>C NMR Spectrum of Compound 4 in DMSO-*d*<sub>6</sub> (125 MHz)



BRUKER AV500-III DEPT-NMR WYN-82B IN DMSO 2011.06.29  
C13CPD DMSO D:\ shijiangong 2

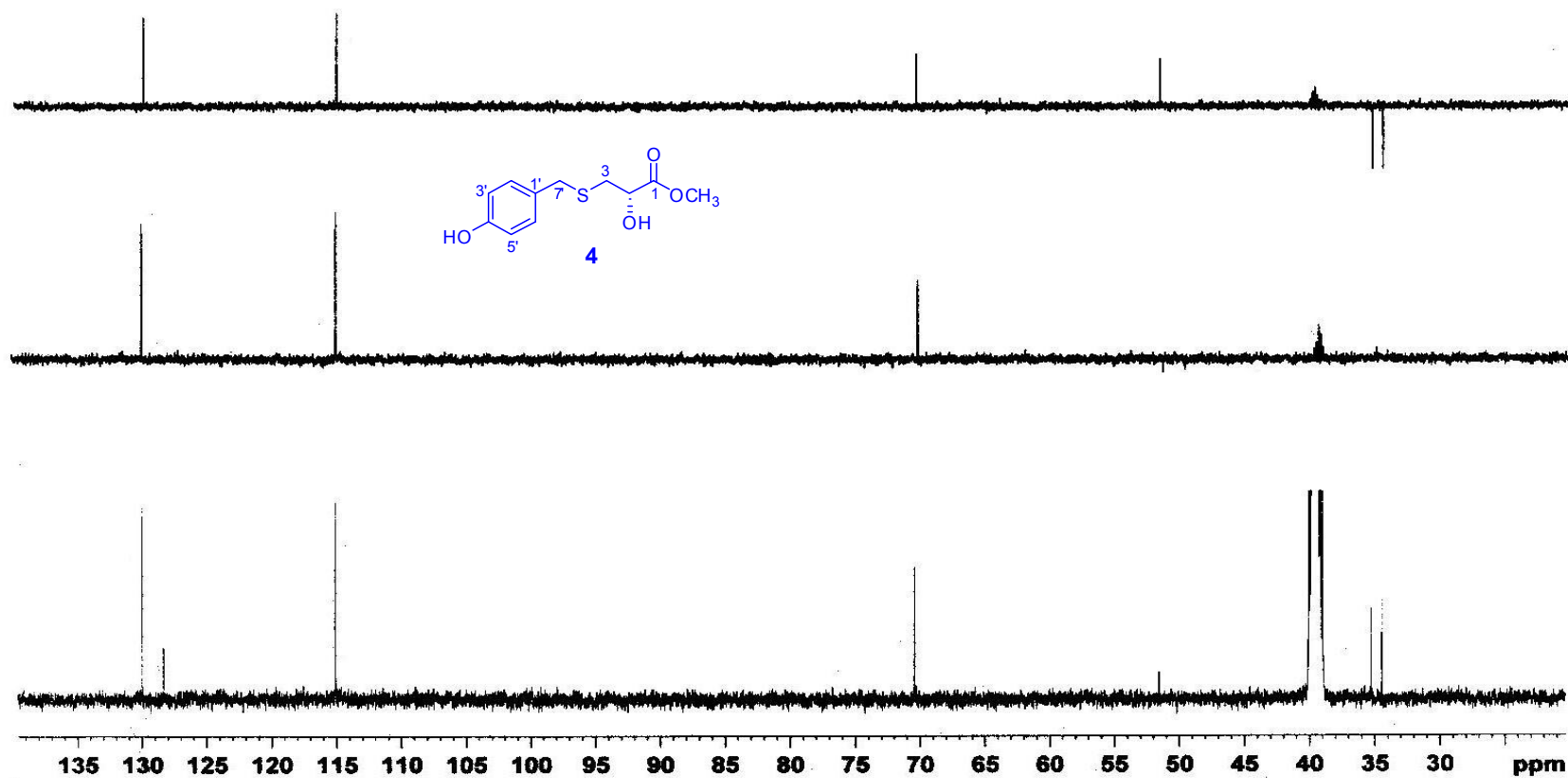


Figure S66. The DEPT Spectrum of Compound 4 in DMSO-*d*<sub>6</sub> (125 MHz)

BRUKER AV500-III COSY-NMR WYN-82B IN DMSO 2011.08.26  
 COSYGMFSW DMSO D:\ shjiangong

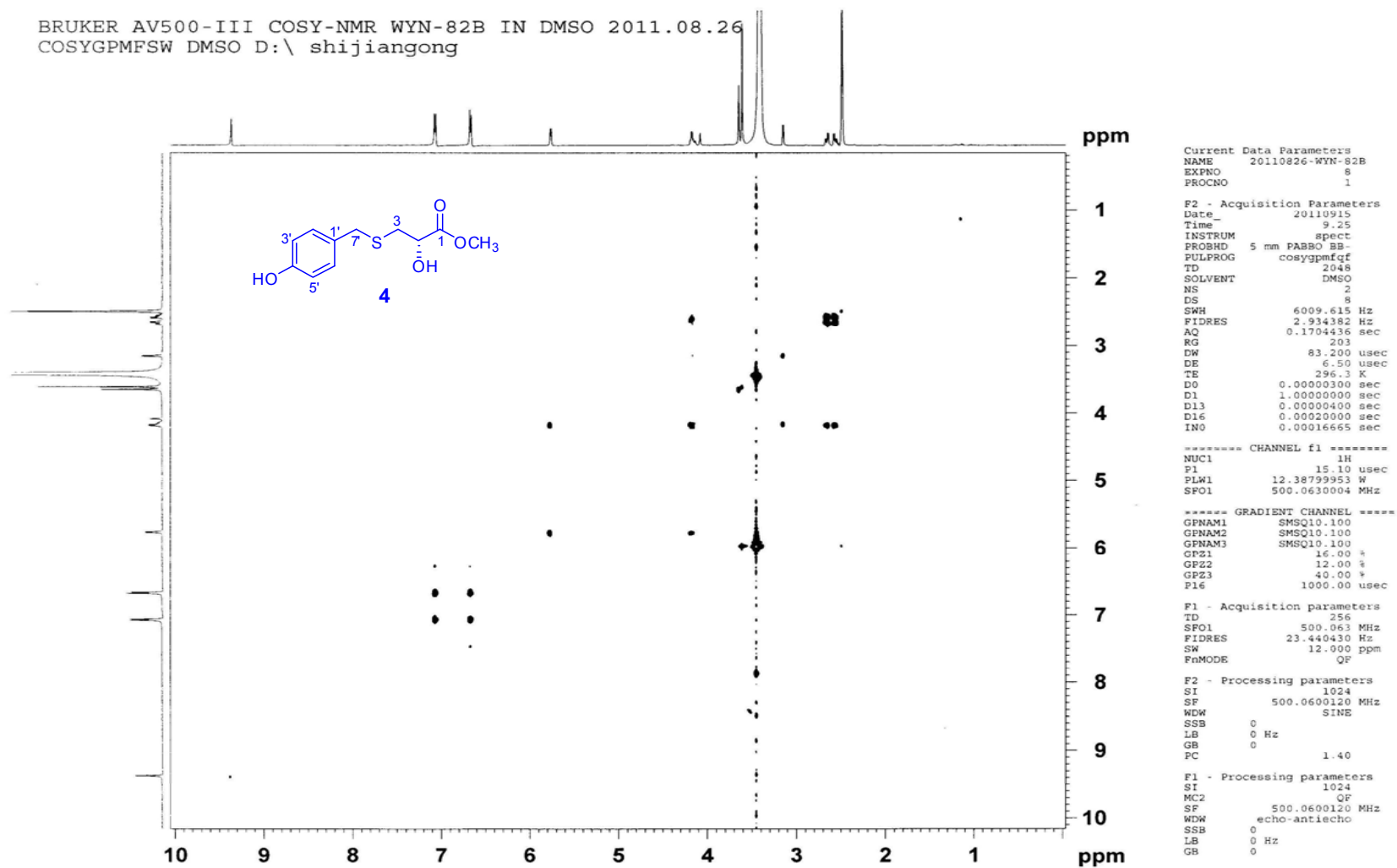


Figure S67. The  $^1\text{H}$ - $^1\text{H}$  COSY Spectrum of Compound **4** in DMSO- $d_6$  (500 MHz)

BRUKER AV500-III HSQC-NMR WYN-82B IN DMSO 2011.08.26  
 HSQCETGPSI DMSO D:\ shijiangong

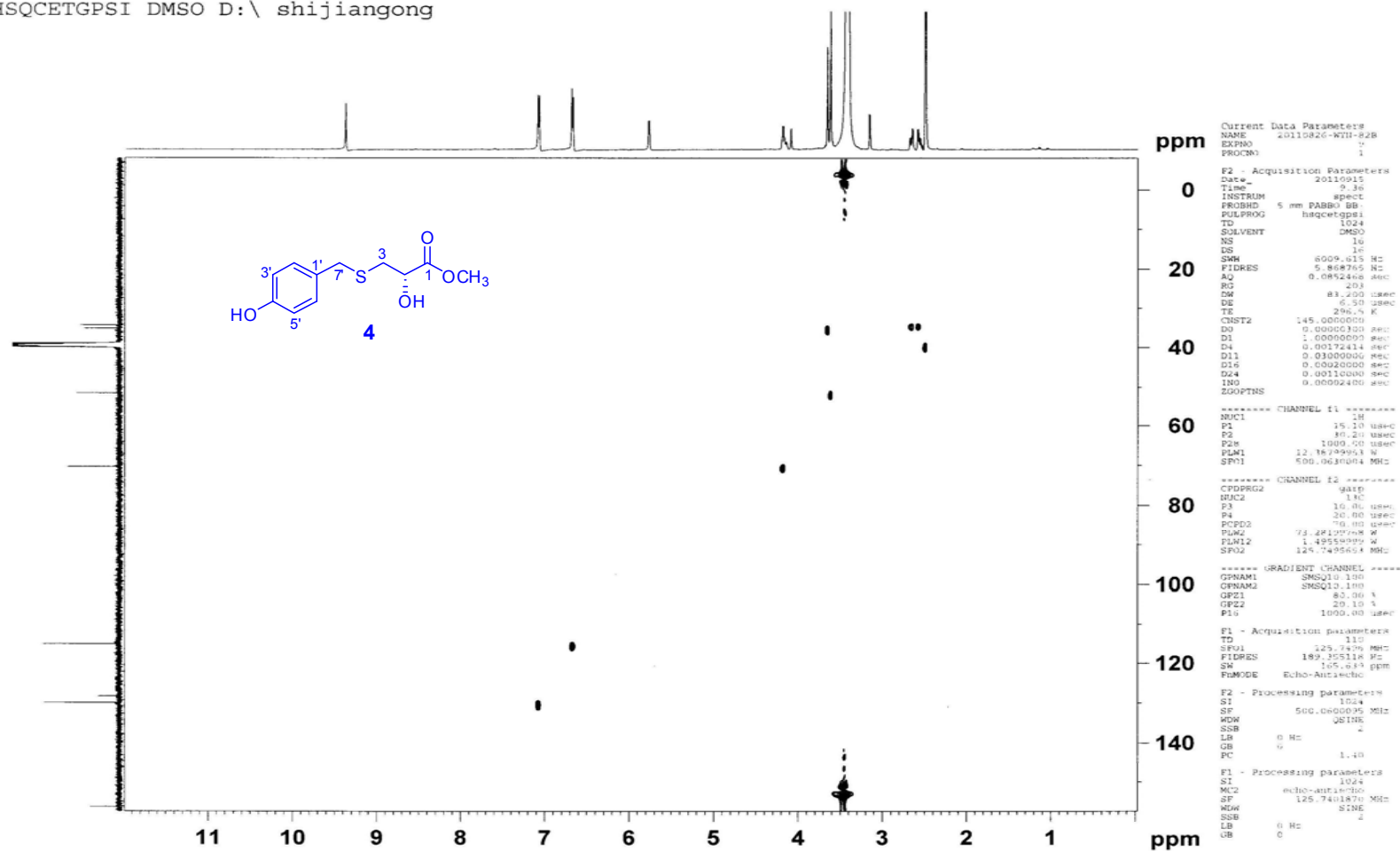


Figure S68. The HSQC Spectrum of Compound 4 in DMSO-*d*<sub>6</sub> (500 MHz)

BRUKER AV500-III HMBC-NMR WYN-82B IN DMSO 2011.08.26  
 HMBCGPNDDMSO D:\ shijiangong

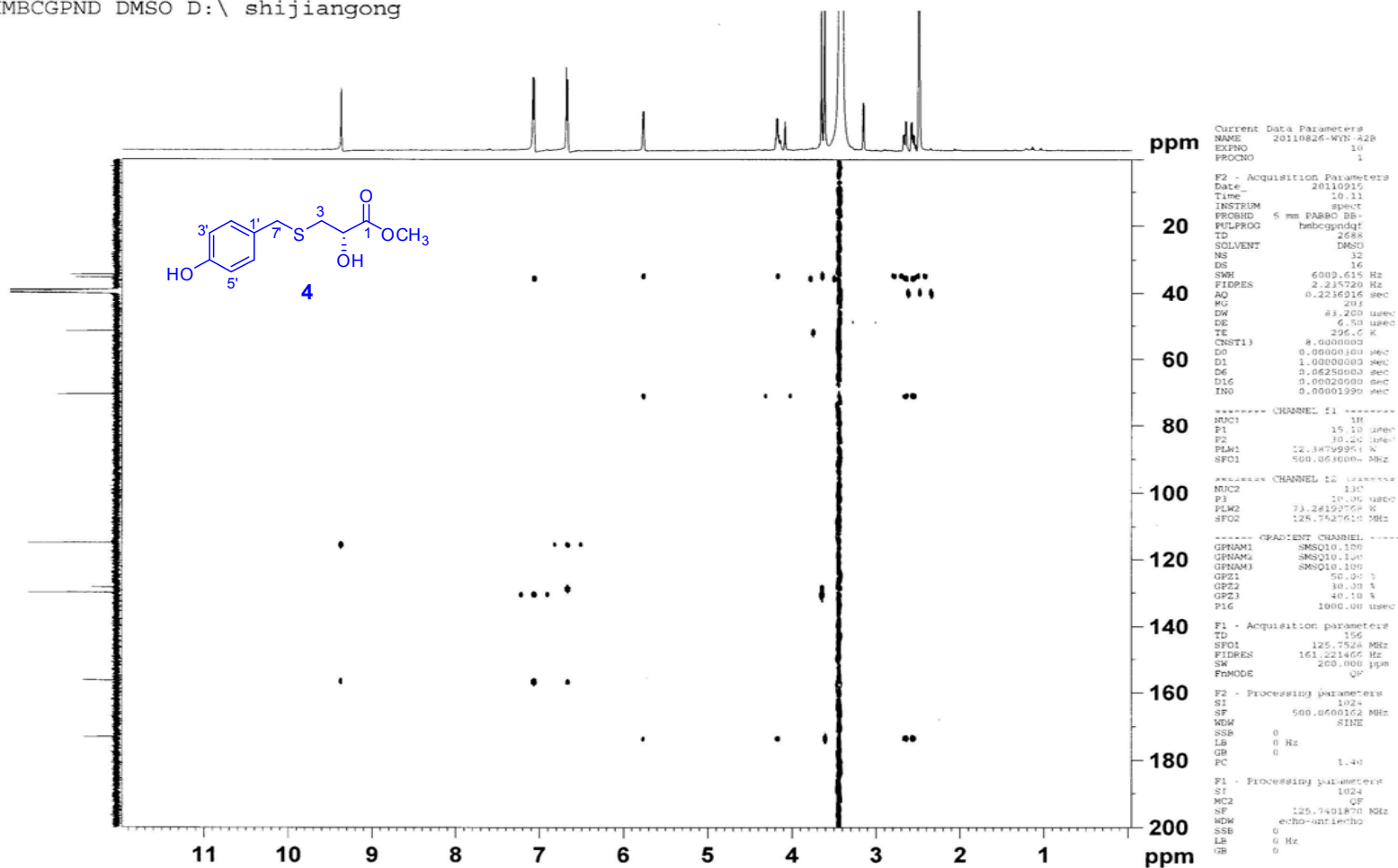
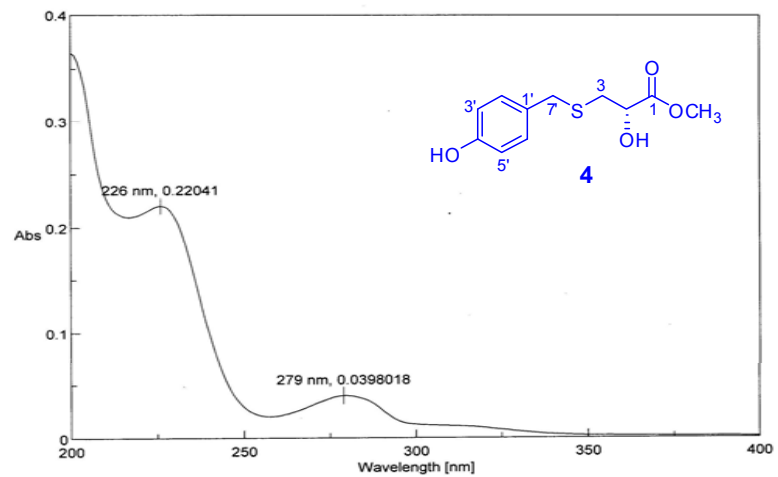
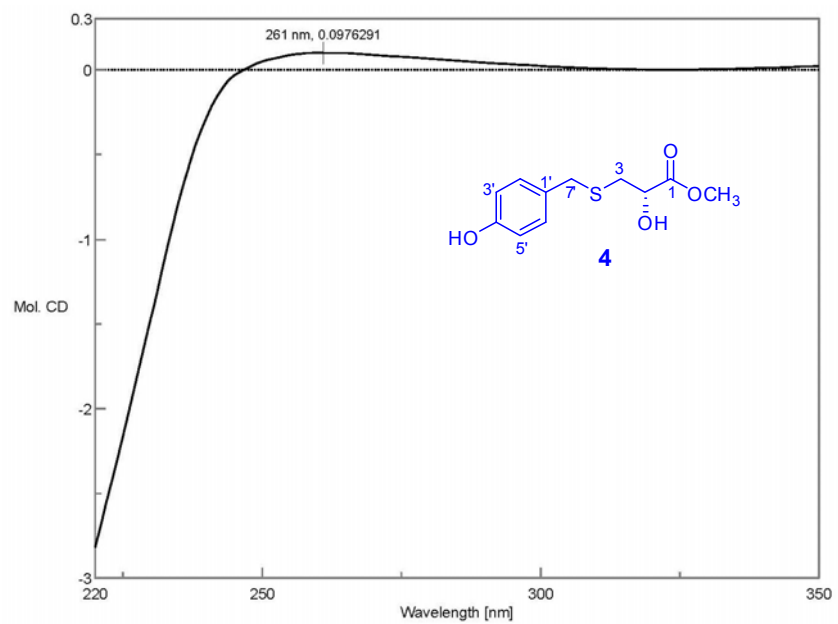


Figure S69. The HMBC Spectrum of Compound 4 in DMSO-*d*<sub>6</sub> (500 MHz)



**Figure S70.** The UV Spectrum of Compound **4** in MeOH



**Figure S71.** The CD Spectrum of Compound **4** in CH<sub>2</sub>Cl<sub>2</sub>

BRUKER Bruker AVANCEIII400 1H-NMR, in CDCl<sub>3</sub>, WYN-82B 2013/01/14

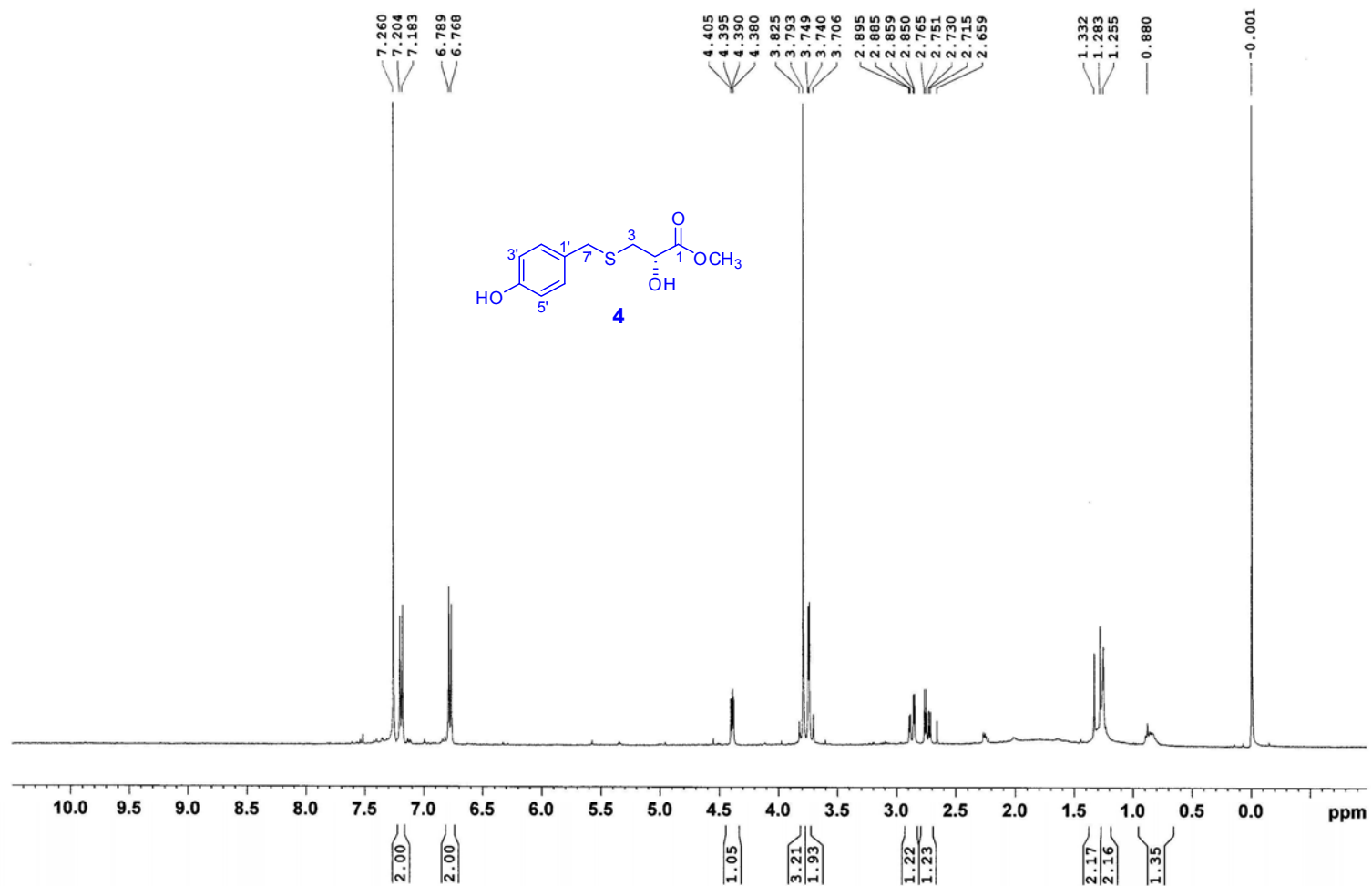


Figure S72. The <sup>1</sup>H NMR Spectrum of Compound 4 in CD<sub>3</sub>Cl (400 MHz)

BRUKER Bruker AVANCEIII400 1H-NMR, in CDCl<sub>3</sub>, WYN-82B (R)-MPA 2013/01/31

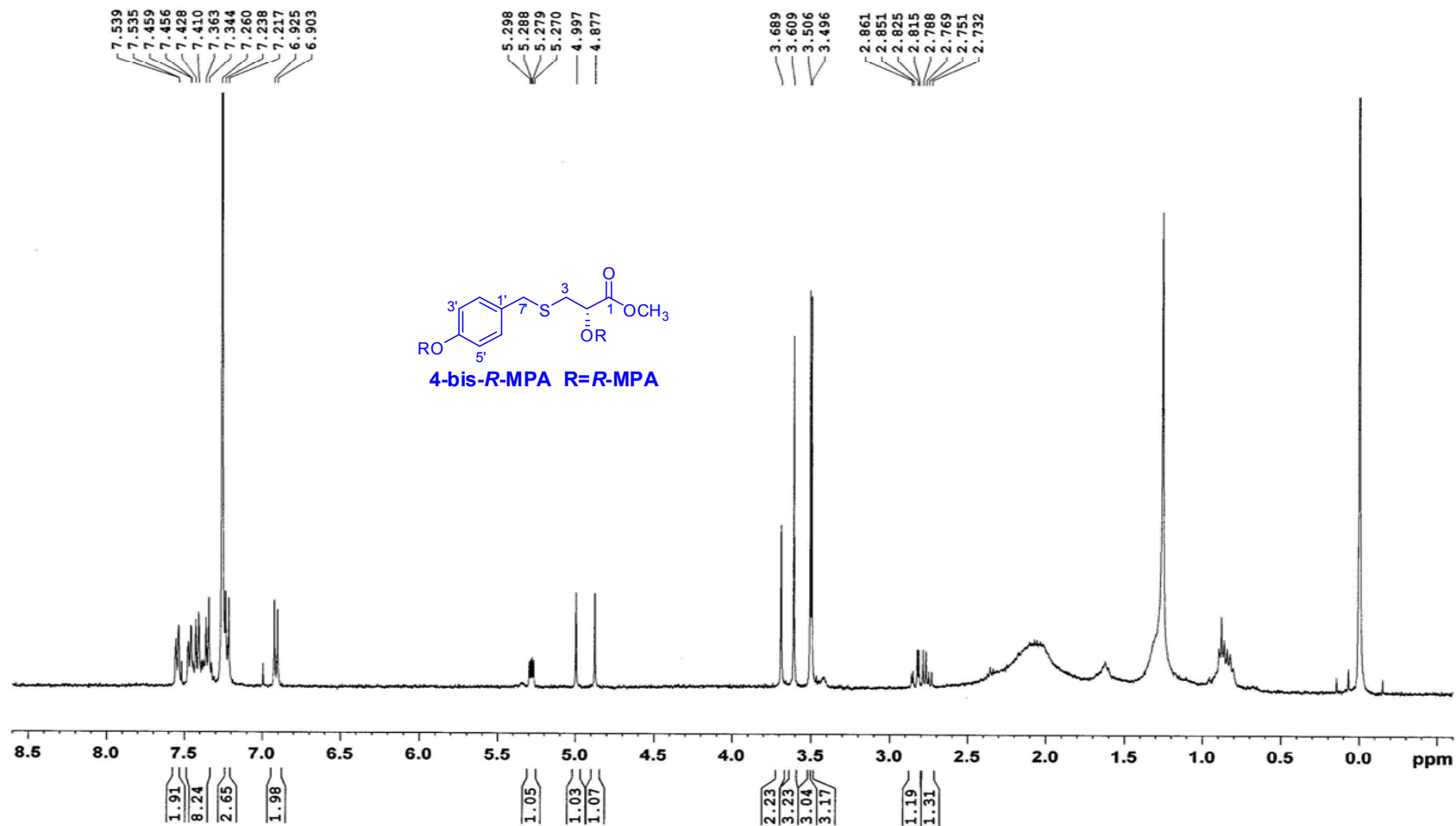


Figure S73. The <sup>1</sup>H NMR Spectrum of Compound 4-bis-(R)-MPA in CD<sub>3</sub>Cl (400 MHz)

BRUKER AVANCEIII400 1H-NMR, in CDCl3, WYN-82B (S)-MPA 2013/01/31

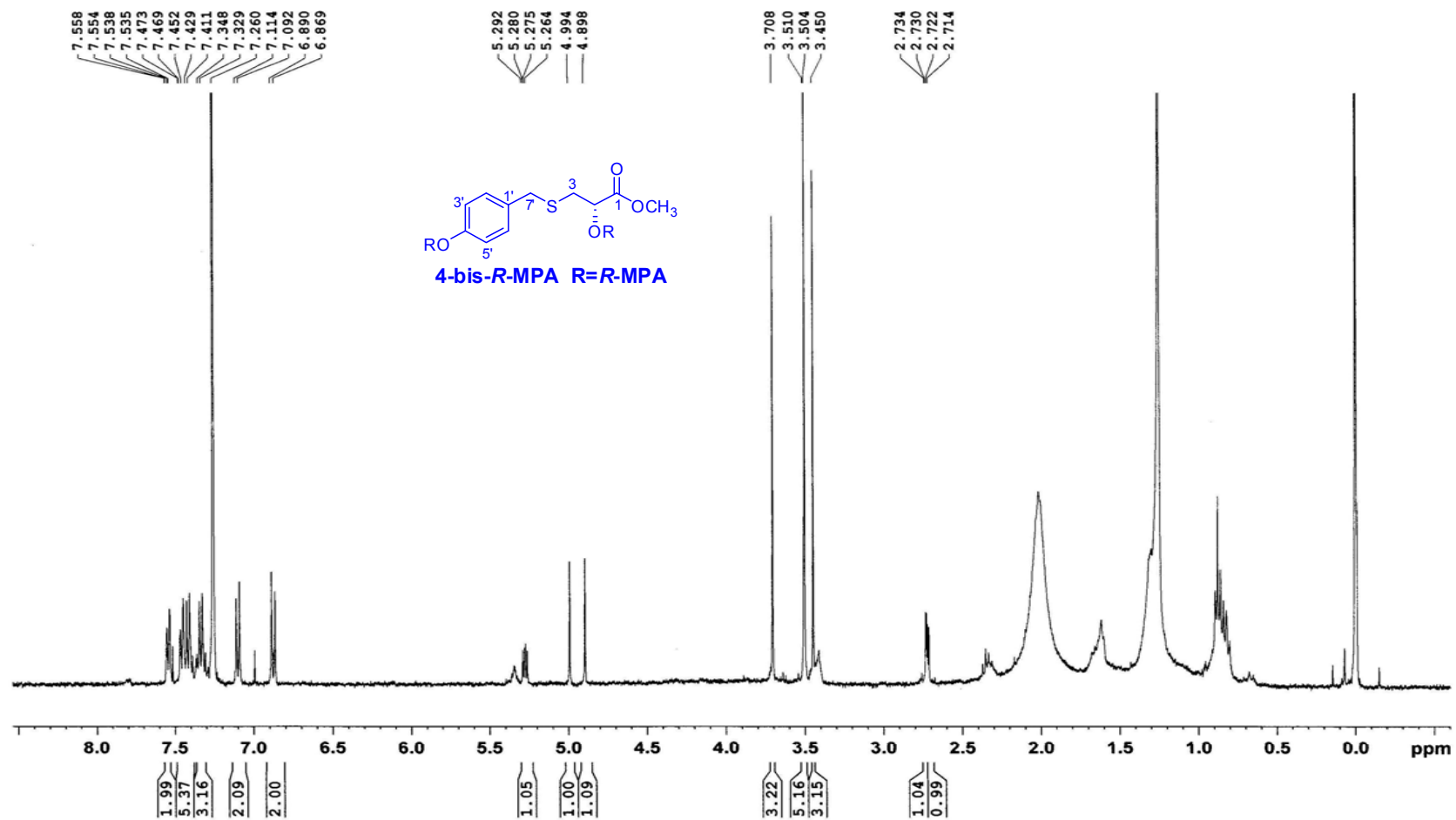


Figure S74. The  $^1\text{H}$  NMR Spectrum of Compound 4-bis-(S)-MPA in  $\text{CD}_3\text{Cl}$  (400 MHz)



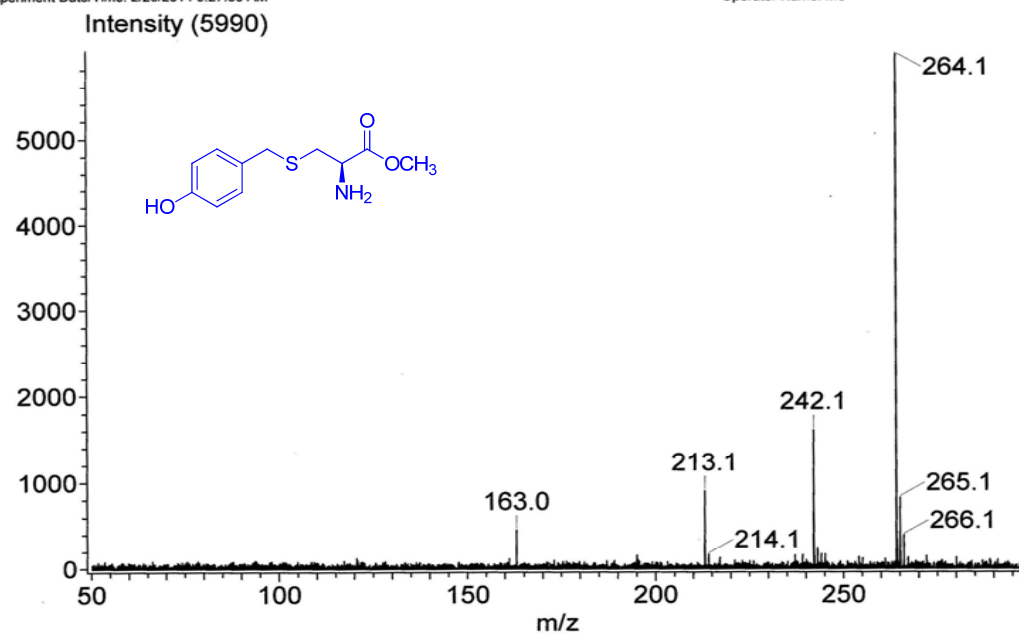
JEOL AccuTOF CS (JMS T100CS)

National Research Center for Analysis of Drugs and Metabolites

Acq. Data Name: 10N  
Internal Sample Id:  
Ionization Mode: ESI+  
MS Calibration Name: TFA<sub>Na</sub>\_ESI+\_100-1000  
Reduction History: Subtract(Average(MS[1] 0.24..0.28)-1.0\*Average(MS[1] 0.13..0.17);Correct Base[5.0%];D:\TESTDATA\TEST2013\20140220\BK1,2,0);Average(MS[1] 0.27..0....  
Experiment Date/Time: 2/20/2014 9:27:30 AM

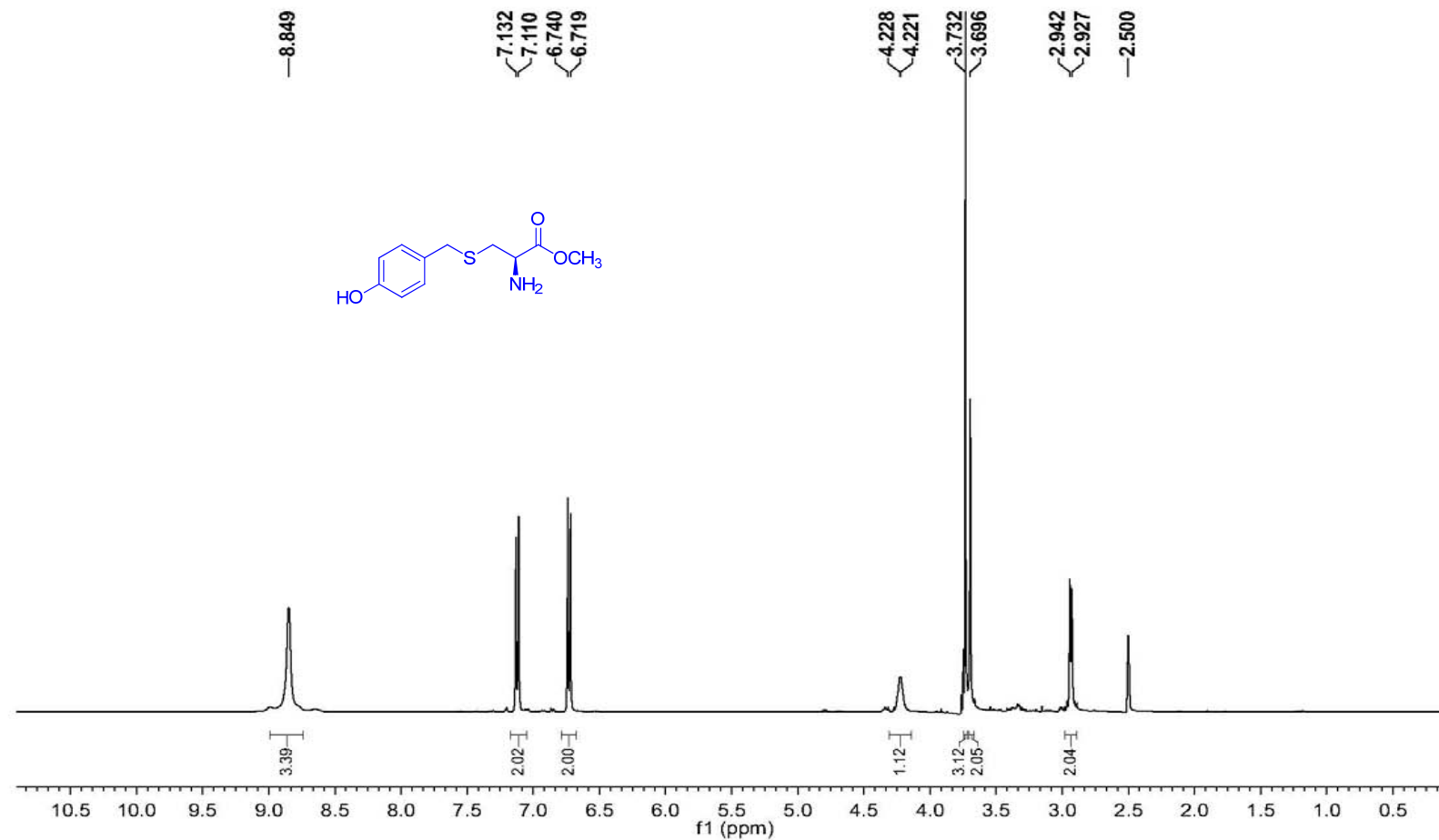
Orifice1 Volt Sweep: 60V  
Acquired m/z Range: 50.0..1000.0

Spec. Record Interval: 1.0[s]  
Ring Lens Volt: 20[V]  
Time of Maximum: 0.000[min]  
Operator Name: MS



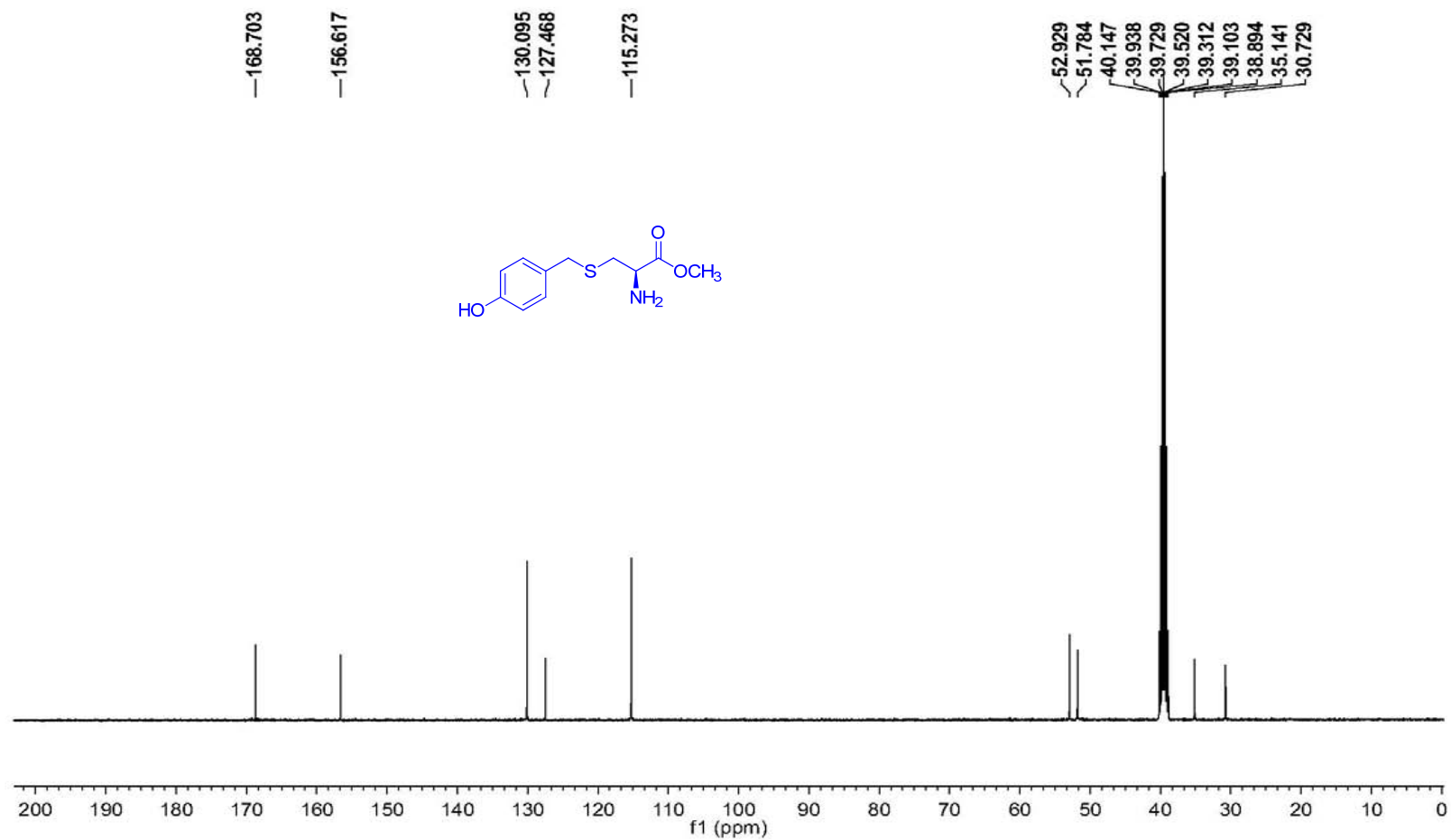
**Figure S75.** The (+)-ESIMS Spectrum of the Synthesized Methyl *S*-(4'-Hydroxybenzyl)-L-cysteinate

20140121 10N  
Bruker AVANCEIII 400 20140117  
PROTON2 DMSO D:\ DATA-2014 21

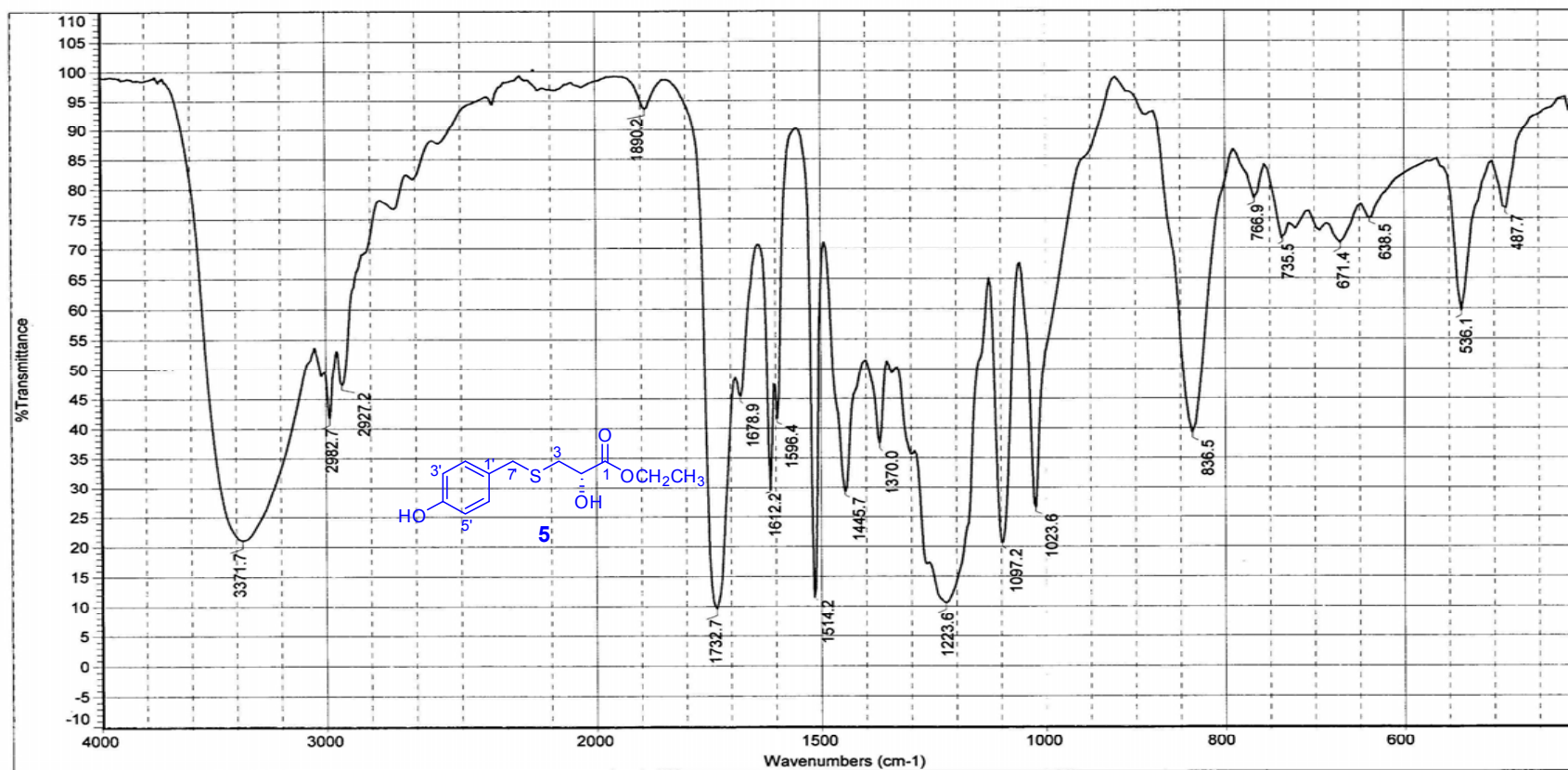


**Figure S76.** The <sup>1</sup>H NMR Spectrum of the Synthesized Methyl *S*-(4'-Hydroxybenzyl)-L-cysteinate in DMSO-*d*<sub>6</sub> (400 MHz)

20140121 10N  
Bruker AVANCEIII 400 20140117  
C13 DMSO D:\ DATA-2014 21



**Figure S77.** The <sup>13</sup>C NMR Spectrum of the Synthesized Methyl S-(4'-Hydroxybenzyl)-L-cysteinate in DMSO-d<sub>6</sub> (100 MHz)



日期: 星期一 5月 07 10:28:34 2012 (GMT+08:00) Sample Name : WYN - 88B

(显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100

傅里叶变换红外显微镜 (FT-IR Microscope): Centaurus

分辨率: 8.000

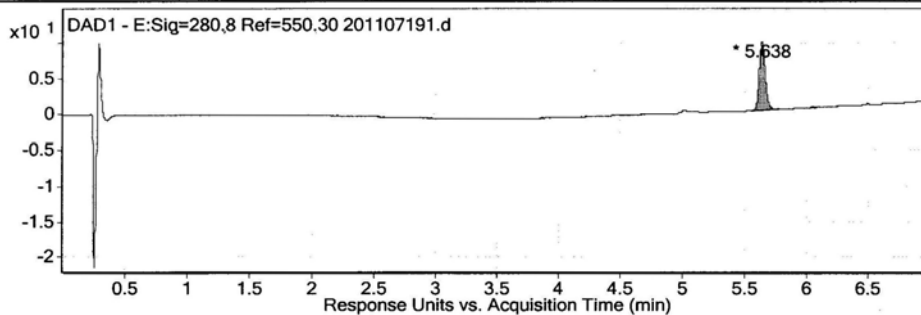
美国热电公司 (Thermo) 傅里叶变换红外光谱仪: Nicolet 5700

**Figure S78.** The IR Spectrum of Compound 5

## Qualitative Analysis Report

Data Filename	201107191.d	Sample Name	WYN-88B
Sample Type	Sample	Position	P1-C8
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	XXXXXXXXXX
DA Method	TEST LCMS.m	Comment	

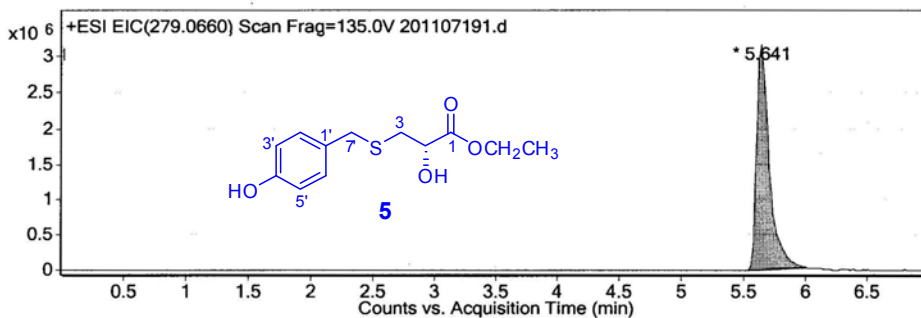
### User Chromatograms



#### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	5.545	5.638	5.781	9.54	31.29	100

Fragmentor Voltage 135    Collision Energy 0    Ionization Mode ESI

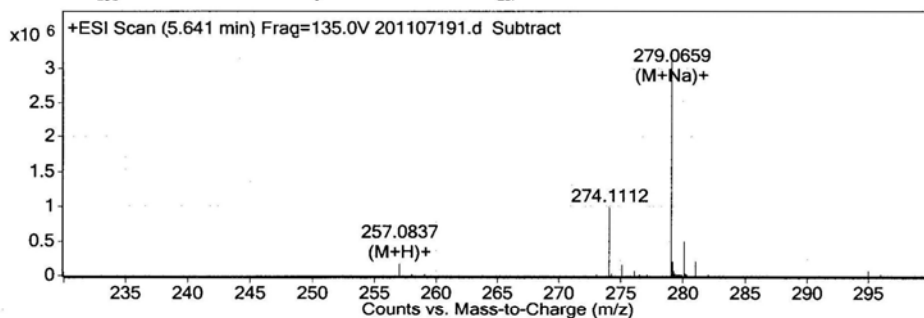


#### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	5.529	5.641	6.011	3161508	22728855	100

### User Spectra

Fragmentor Voltage 135    Collision Energy 0    Ionization Mode ESI



**Figure S79.** The (+)-HRESIMS Report of Compound 5, Page 1

## Qualitative Analysis Report

### Peak List

m/z	z	Abund	Formula	Ion
107.0431		440910		
257.0837		175008	C12 H17 O4 S	(M+H)+
274.1112		970918		
279.0659	1	3167434	C12 H16 Na O4 S	(M+Na)+
279.2106		205954		
280.0695	1	495496	C12 H16 Na O4 S	(M+Na)+
281.0647	1	210903	C12 H16 Na O4 S	(M+Na)+
535.1441	1	854594		
536.1466	1	251982		

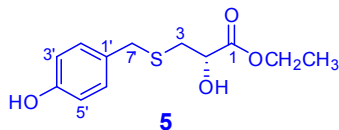
### Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	120
O	0	30
N	0	5
S	0	5
Cl	0	0

### Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C12 H16 O4 S	TRUE	256.0767	256.0769	0.79	C12 H16 Na O4 S	99.9
C13 H12 N4 S		256.0767	256.0783	6	C13 H12 N4 Na S	99.41
C16 H8 N4		256.0767	256.0749	-7.15	C16 H8 N4 Na	96.91
C12 H16 O4 S	TRUE	256.0764	256.0769	2.07	C12 H17 O4 S	99.47
C13 H12 N4 S		256.0764	256.0783	7.29	C13 H13 N4 S	98.5
C16 H8 N4		256.0764	256.0749	-5.85	C16 H9 N4	93.87

--- End Of Report ---



**Figure S80.** The (+)-HRESIMS Report of Compound **5**, Page 2

MS Formula Results: + Scan (5.641 min) Sub (201107191.d)

m/z	Ion	Formula	Abundance
257.0837	(M+H) <sup>+</sup>	C <sub>12</sub> H <sub>17</sub> O <sub>4</sub> S	175008.1

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> S	C <sub>12</sub> H <sub>17</sub> O <sub>4</sub> S	257.0842	99.47		256.0764	256.0769	2.07	2.07	99.02	99.21	99.87	257.0837	5
<input type="checkbox"/>	C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> S	C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> S	257.0855	98.5		256.0764	256.0783	7.29	7.29	97.76	99.51	98.43	257.0837	10
<input type="checkbox"/>	C <sub>16</sub> H <sub>8</sub> N <sub>4</sub>	C <sub>16</sub> H <sub>9</sub> N <sub>4</sub>	257.0822	93.87		256.0764	256.0749	-5.85	5.85	88.7	89.85	98.99	257.0837	15

m/z	Ion	Formula	Abundance
279.0659	(M+Na) <sup>+</sup>	C <sub>12</sub> H <sub>16</sub> NaO <sub>4</sub> S	3167433.8

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> S	C <sub>12</sub> H <sub>16</sub> NaO <sub>4</sub> S	279.0662	99.9		256.0767	256.0769	0.79	0.79	99.7	99.95	99.98	279.0659	5
<input type="checkbox"/>	C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> S	C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> NaS	279.0675	99.41		256.0767	256.0783	6	6	99.75	99.67	99.08	279.0659	10
<input type="checkbox"/>	C <sub>16</sub> H <sub>8</sub> N <sub>4</sub>	C <sub>16</sub> H <sub>8</sub> N <sub>4</sub> Na	279.0641	96.91		256.0767	256.0749	-7.15	7.15	93.94	96.93	98.69	279.0659	15

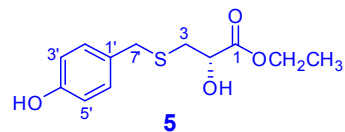
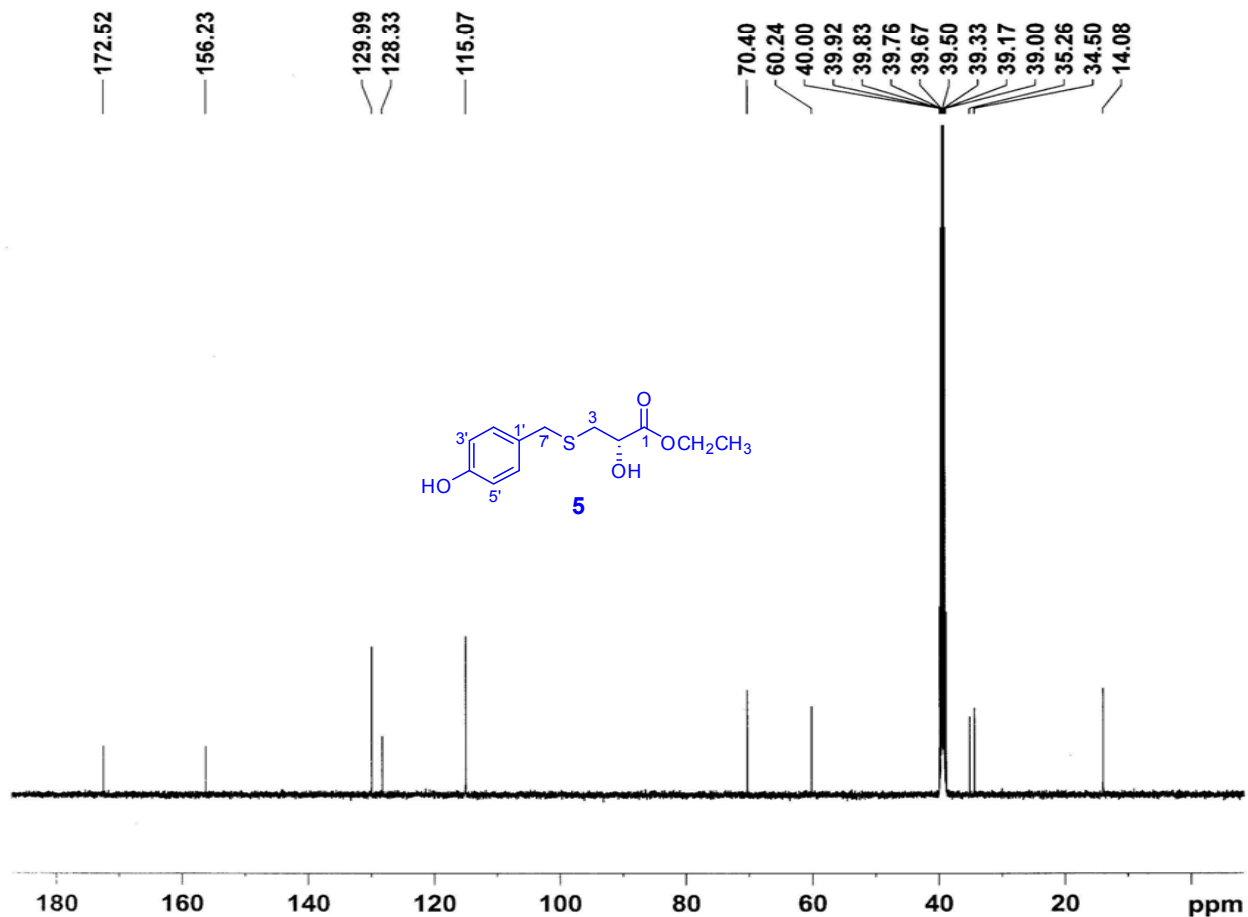


Figure S81. The (+)-HRESIMS Report of Compound 5, Page 3





BRUKER AV500-III 13C-NMR WYN-88B IN DMSO 2011.06.29  
 C13CPD DMSO D:\\ shijiangong 3



```

NAME      20110629-WYN-88B
EXPNO     2
PROCNO    1
Date_     20110704
Time_     8.11
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD        65536
SOLVENT   DMSO
NS        621
DS        4
SWH       29761.904 Hz
FIDRES    0.454131 Hz
AQ        1.1010548 sec
RG        203
DW        16.800 usec
DE        6.50 usec
TE        298.9 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0       500

===== CHANNEL f1 =====
NUC1      13C
P1        10.00 usec
PL1       0.90 dB
PL1W      73.29839325 W
SFO1      125.7527610 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       2.00 dB
PL12      16.77 dB
PL13      16.77 dB
PL2W      12.39386463 W
PL12W     0.41324416 W
PL13W     0.41324416 W
SFO2      500.0620002 MHz
SI        32768
SF        125.7402475 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```

Figure S83. The  $^{13}\text{C}$  NMR Spectrum of Compound 5 in DMSO- $d_6$  (125 MHz)

BRUKER AV500-III DEPT-NMR WYN-88B IN DMSO 2011.06.29  
C13CPD DMSO D:\ shijiangong 3

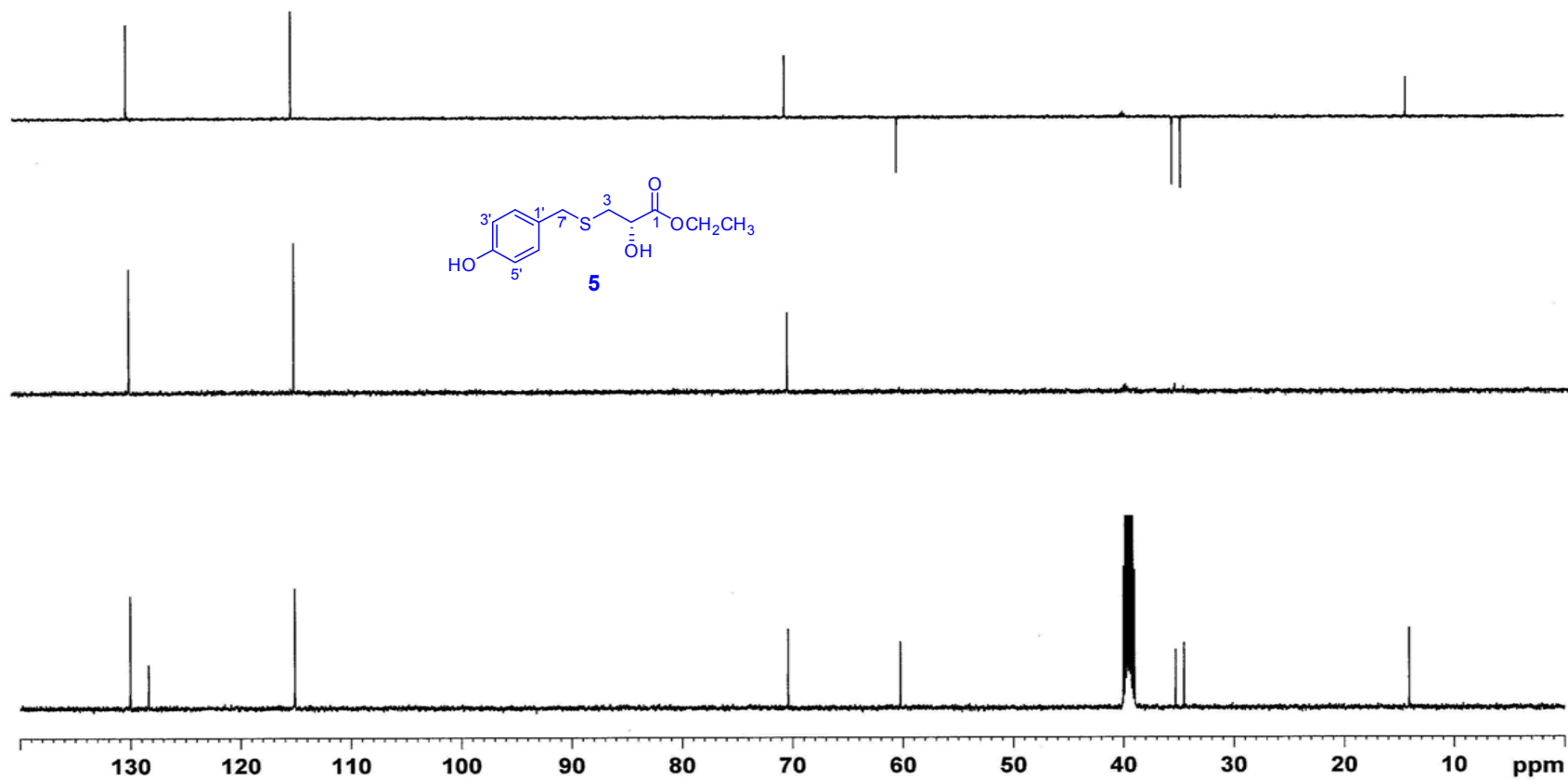


Figure S84. The DEPT Spectrum of Compound 5 in DMSO-*d*<sub>6</sub> (125 MHz)

BRUKER AV500-III COSY-NMR WYN-88B IN DMSO 2011.07.17  
 COSYGPMSW DMSO D:\ shijiangong 5

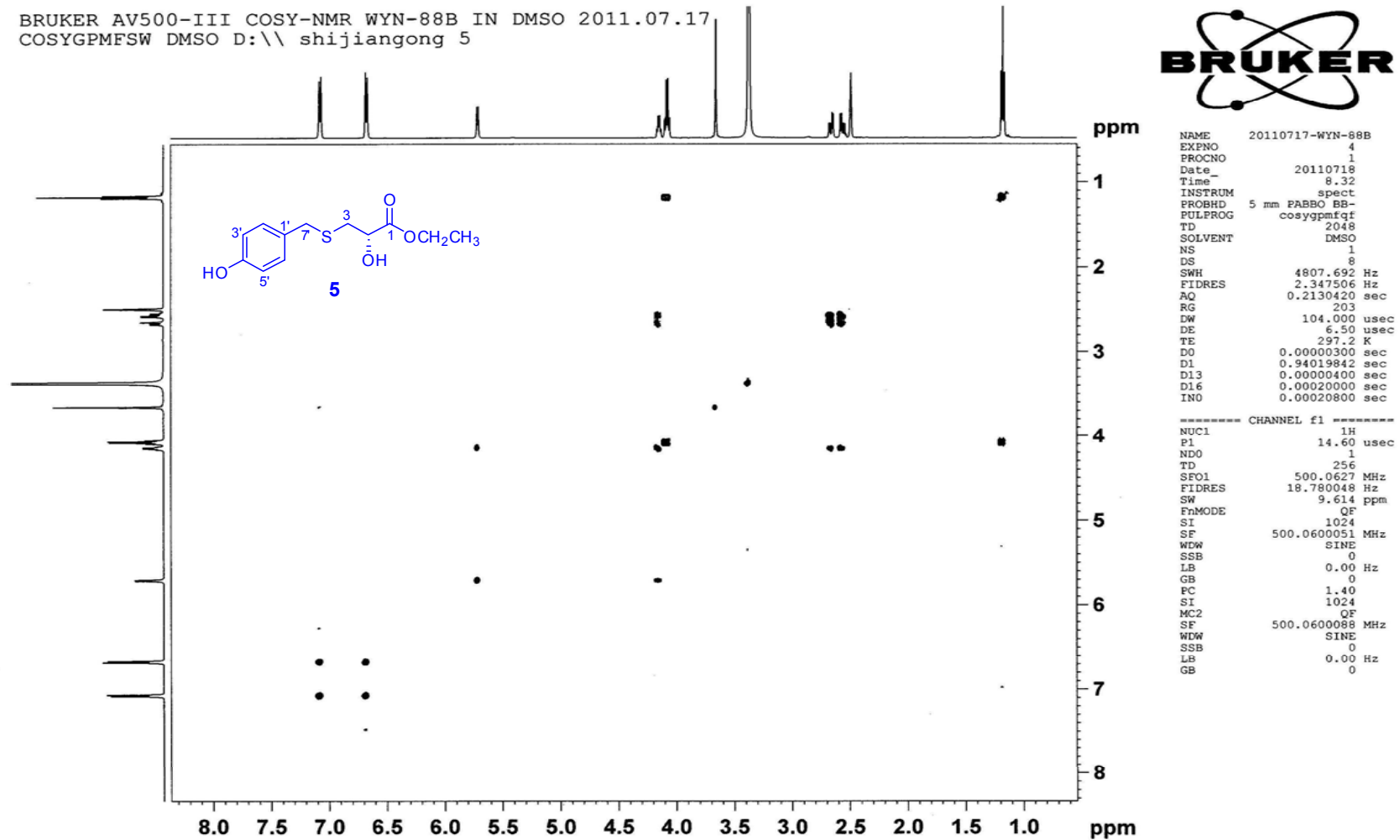


Figure S85. The  $^1\text{H}$ - $^1\text{H}$  COSY Spectrum of Compound 5 in DMSO- $d_6$  (500 MHz)

BRUKER AV500-III HSQC-NMR WYN-88B IN DMSO 2011.07.17  
 HSQCETGPSI DMSO D:\\ shijiangong 5

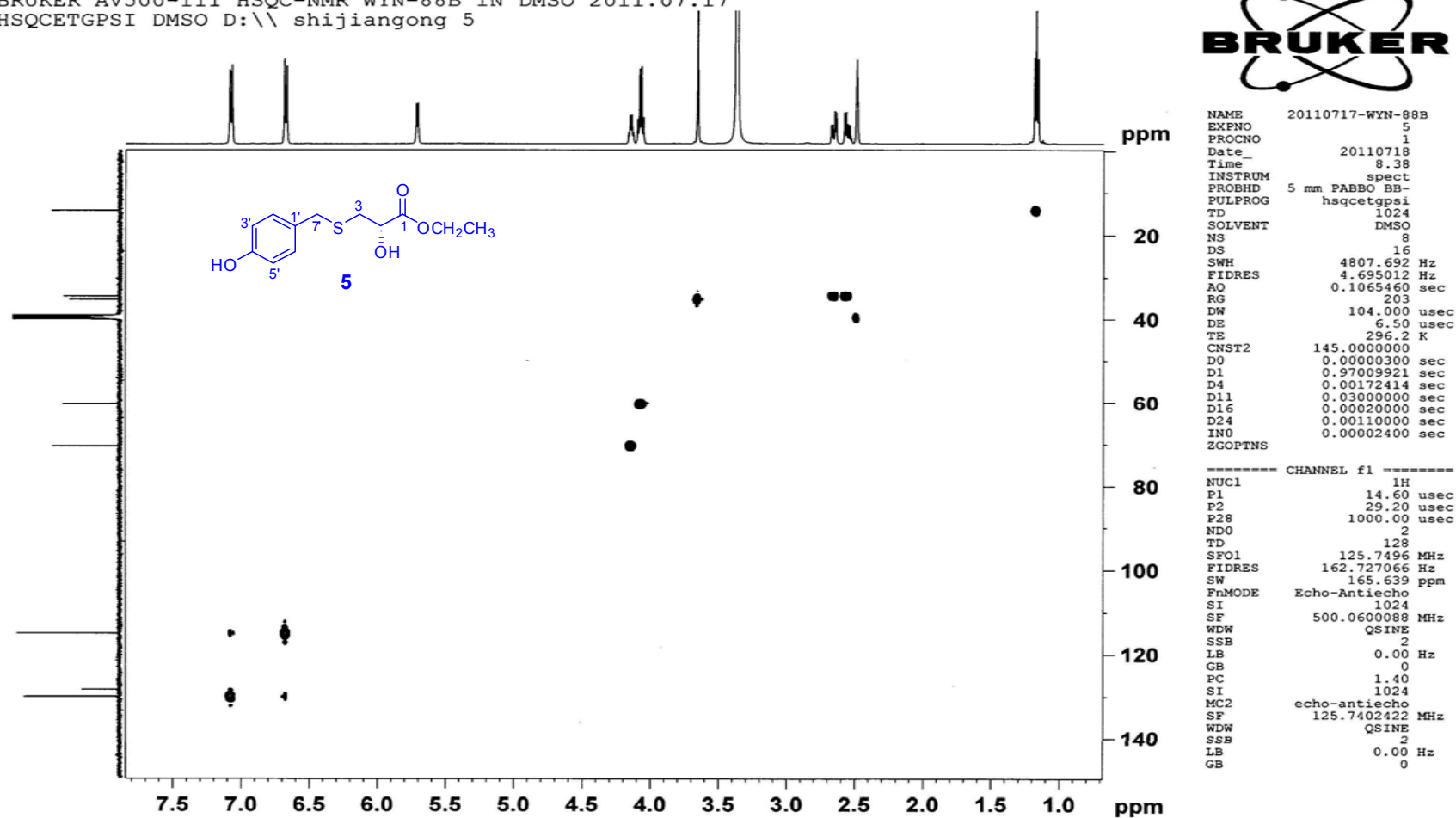


Figure S86. The HSQC Spectrum of Compound 5 in DMSO-*d*<sub>6</sub> (500 MHz)

BRUKER AV500-III HMBC-NMR WYN-88B IN DMSO 2011.07.17  
 HMBCGPND DMSO D:\\ shijiangong 5

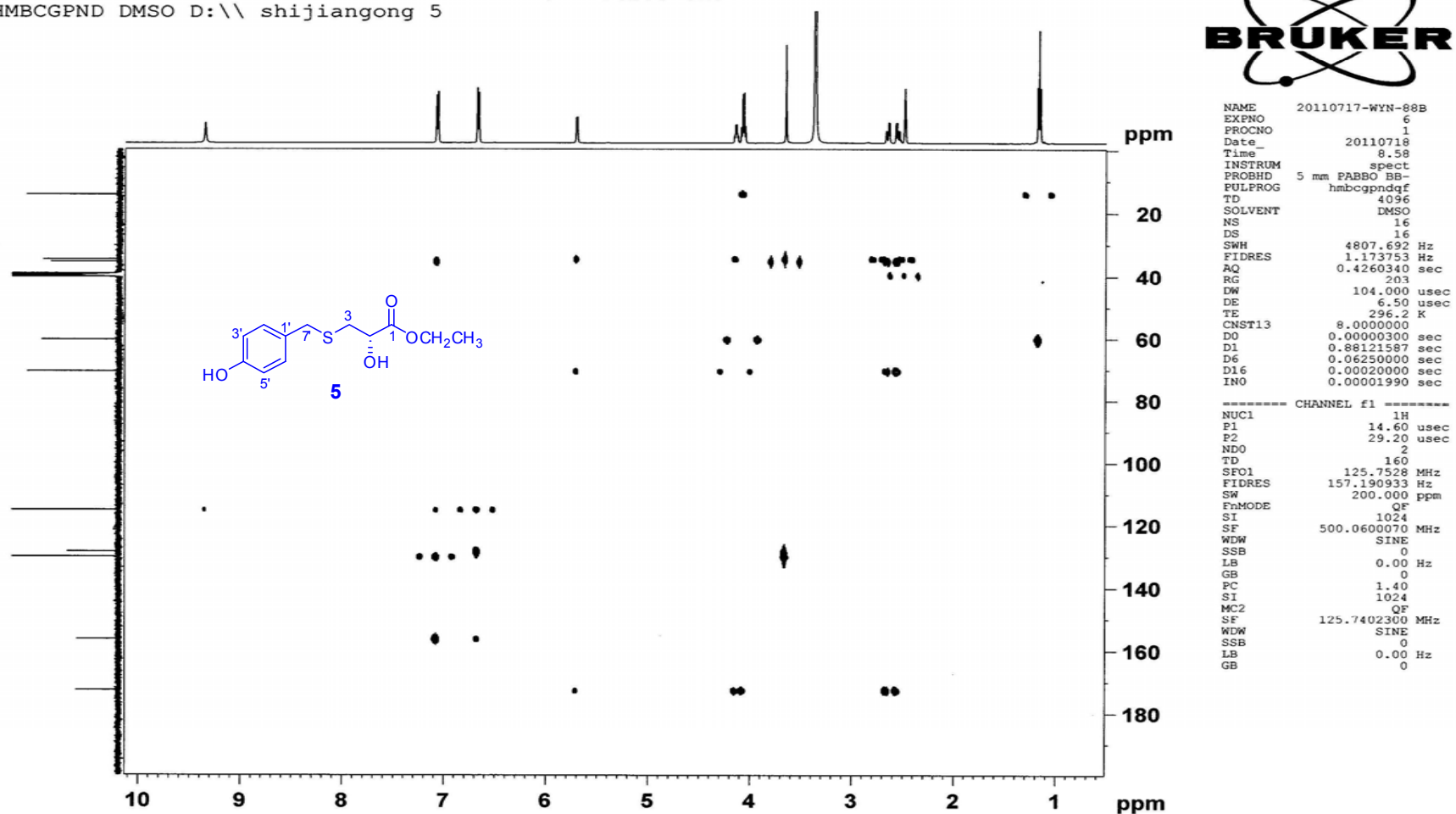
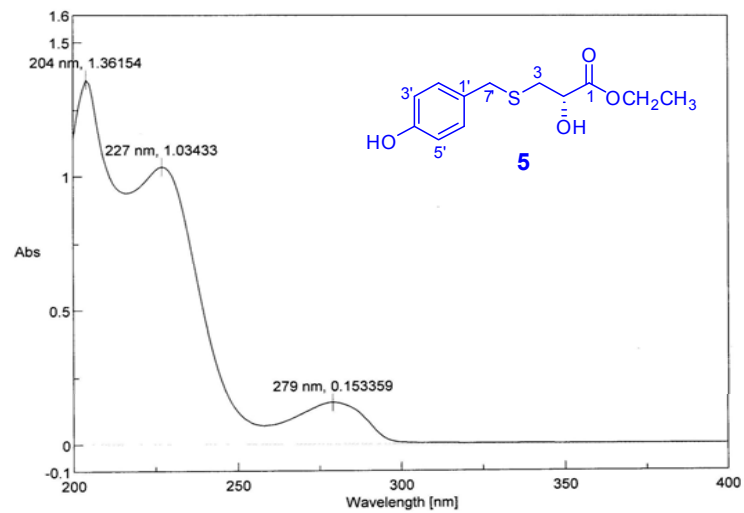
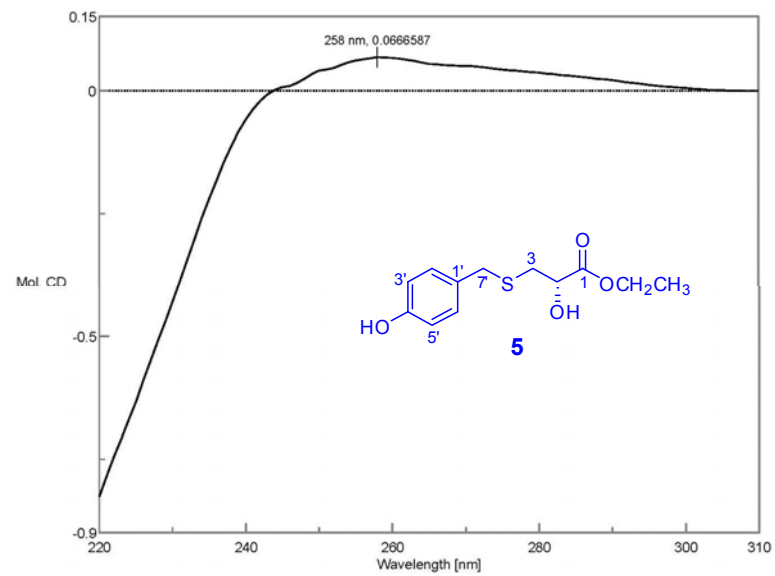


Figure S87. The HMBC Spectrum of Compound 5 in DMSO-*d*<sub>6</sub> (500 MHz)



**Figure S88.** The UV Spectrum of Compound **5** in MeOH



**Figure S89.** The CD Spectrum of Compound **5** in CH<sub>2</sub>Cl<sub>2</sub>

BRUKER Bruker AVANCEIII400 1H-NMR, in CDCL3, WYN-88B 2013/01/20

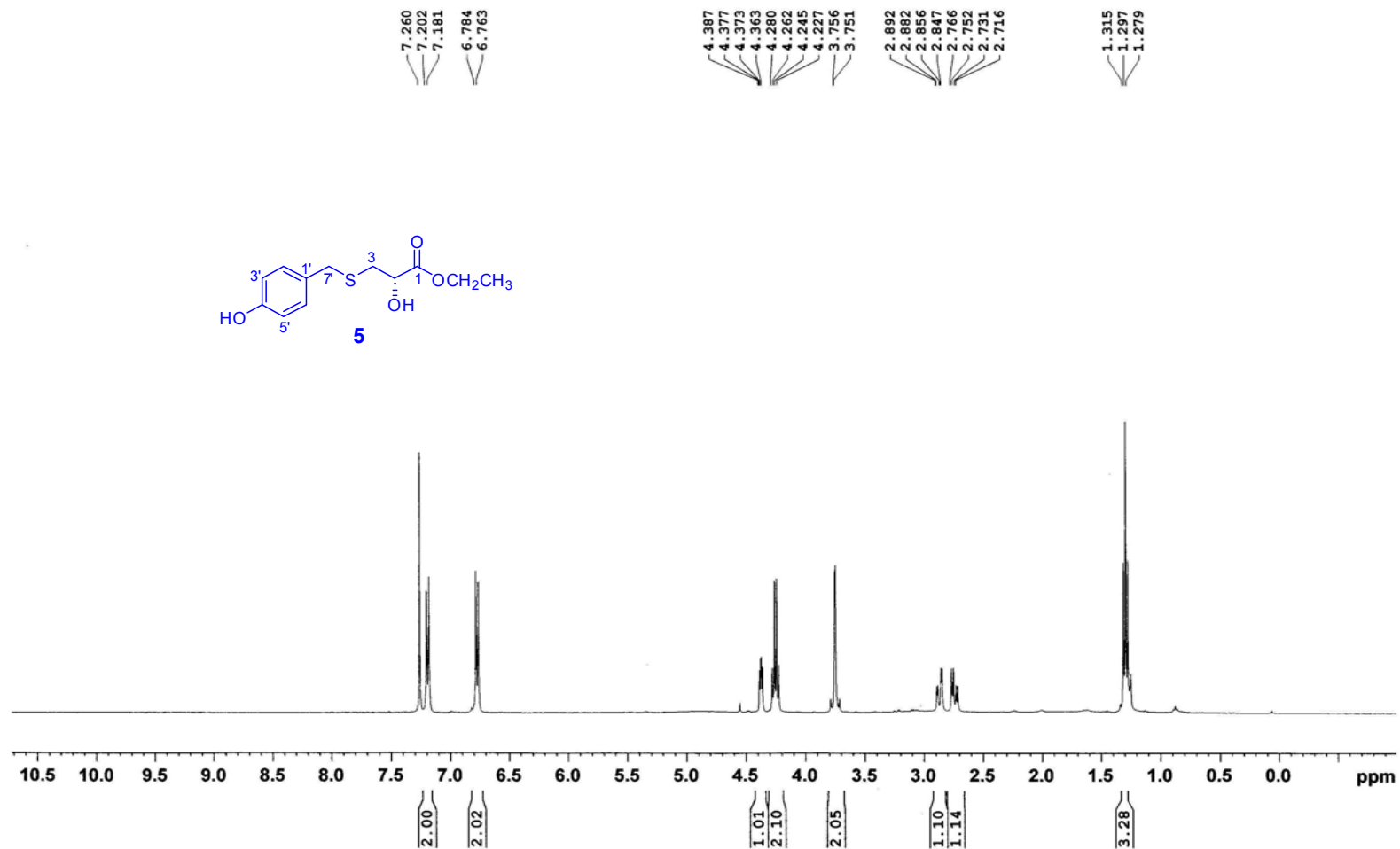


Figure S90. The <sup>1</sup>H NMR Spectrum of Compound 5 in CD<sub>3</sub>Cl (400 MHz)

BRUKER Bruker AVANCEIII400 1H-NMR, in CDCl3, WYN-88B (R)-MPA 2013/01/29

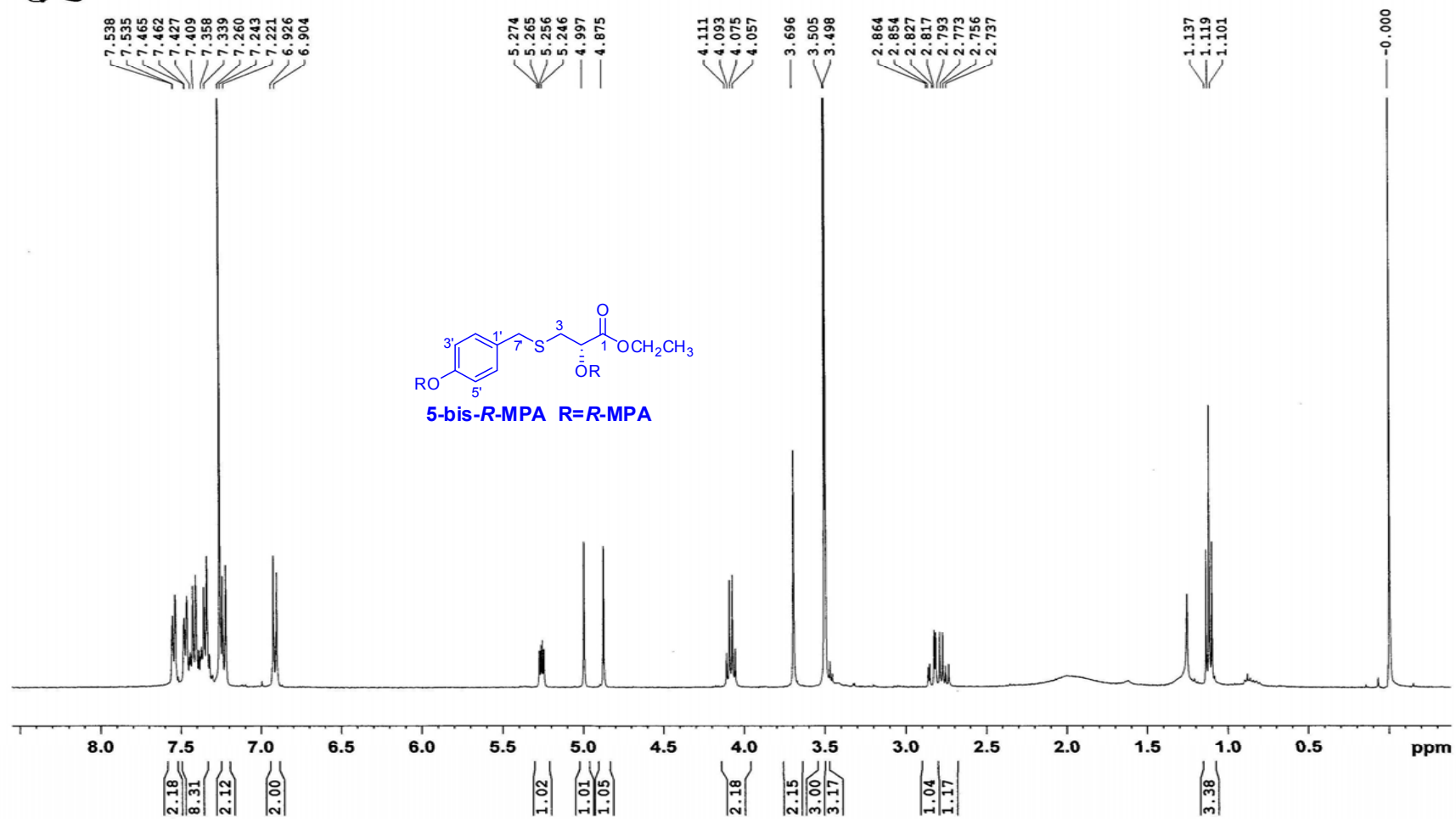


Figure S91. The <sup>1</sup>H NMR Spectrum of Compound 5-bis-(R)-MPA in CD<sub>3</sub>Cl (400 MHz)



BRUKER Bruker AVANCEIII400 1H-NMR, in CDCl3, WYN-88B (S)-MPA 2013/01/29

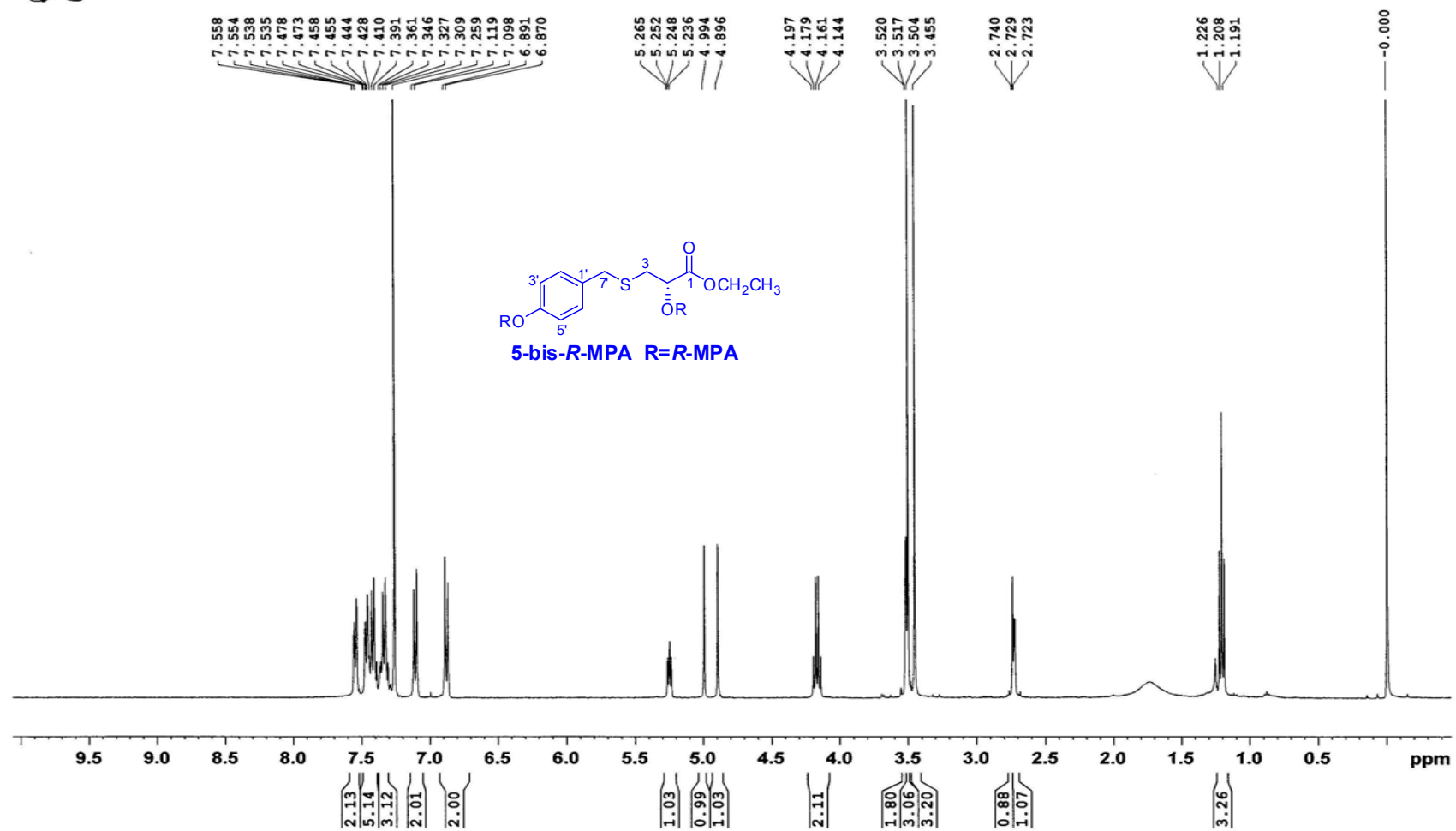
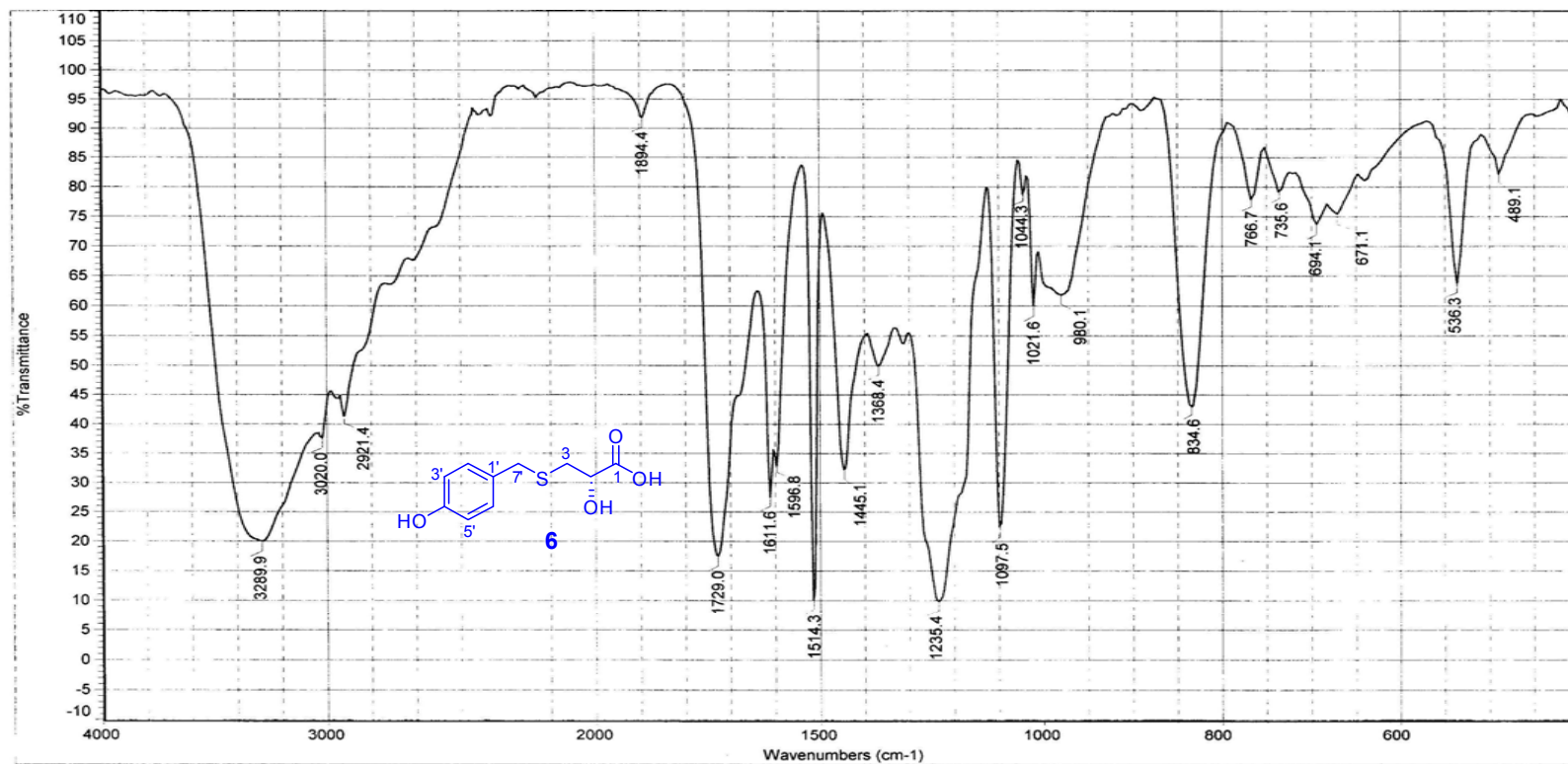


Figure S92. The  $^1\text{H}$  NMR Spectrum of Compound 5-bis-(S)-MPA in  $\text{CD}_3\text{Cl}$  (400 MHz)



日期: 星期五 12月 14 10:11:09 2012 (GMT+08: Sample Name : TMG - 50B

(显微镜透射法 FT- IR Microscope Transmission)

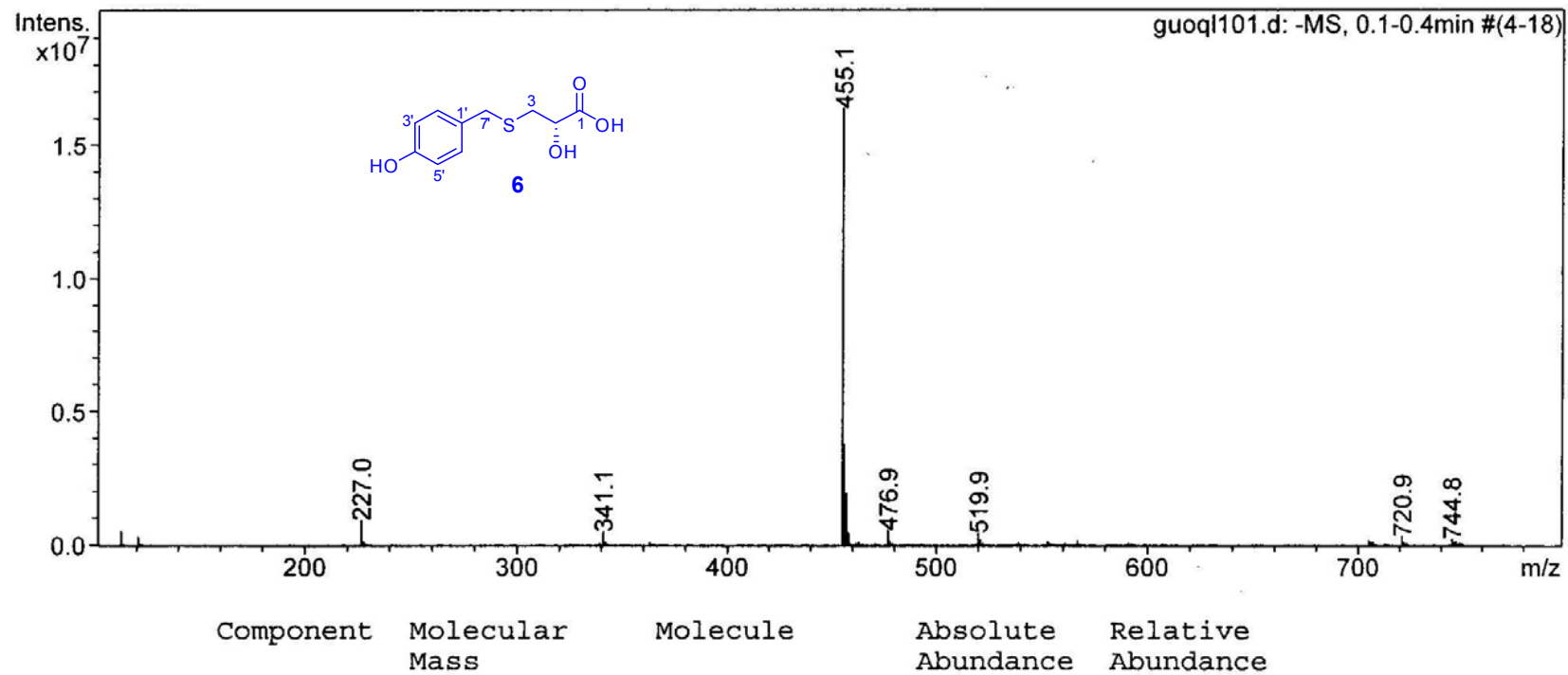
扫描次数: 100

傅里叶变换显微镜红外(FT-IR Microscope): Centaurus

分辨率: 8.000

美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S93. The IR Spectrum of Compound 6



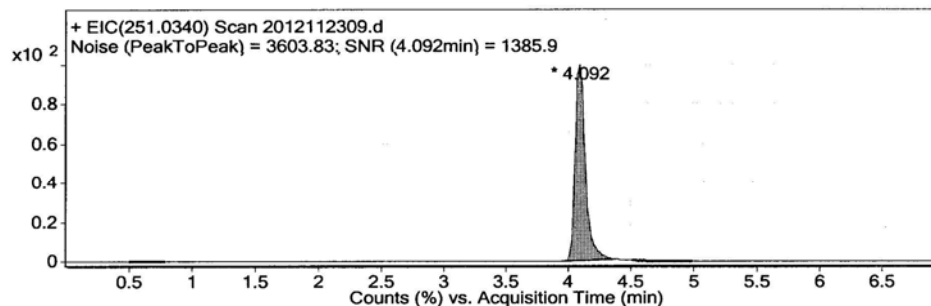
**Figure S94.** The (-)-ESIMS Spectrum of Compound 6

## Qualitative Analysis Report

Data Filename	2012112309.d	Sample Name	TMG-50B
Sample Type	Sample	Position	P1-E2
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	XXXXXXXXXX
DA Method	TEST LCMS.m	Comment	

### User Chromatograms

Fragmentor Voltage 135    Collision Energy 0    Ionization Mode ESI



#### Integration Peak List

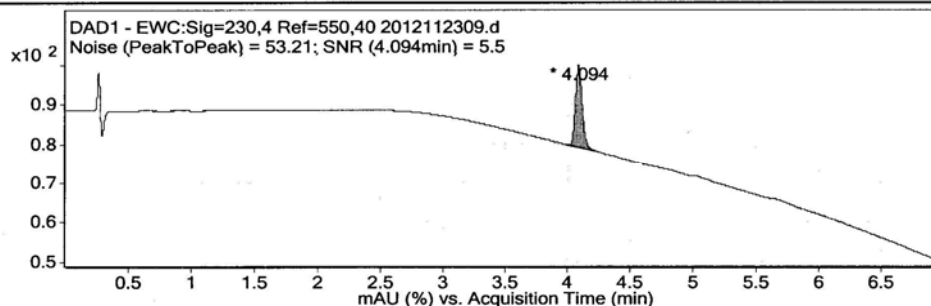
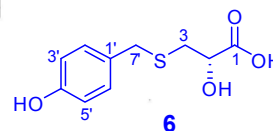
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	3.947	4.092	4.382	867130	4994421	100	1385.9

#### Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	3603.830811

#### Noise Regions

Start	End
0.5	0.8
4.5	5
8.6	9.4
9.8	11



#### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	3.98	4.094	4.224	76.98	292.021	100	5.5

#### Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Area	1	53.21118164

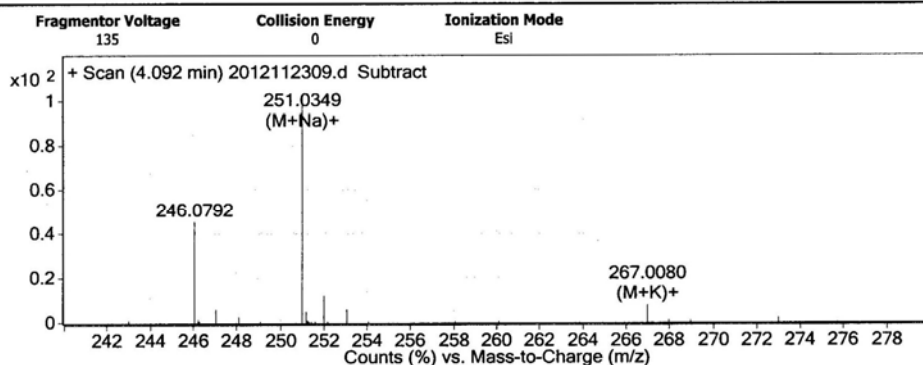
#### Noise Regions

Start	End
0.5	0.8
4.5	5
8.6	9.4
9.8	11

Figure S95. The (+)-HRESIMS Report of Compound 6, Page 1

# Qualitative Analysis Report

## User Spectra



### Peak List

m/z	z	Abund	Formula	Ion
107.0492		499117		
246.0792	1	395457		
247.0823	1	51766		
251.0349	1	869821	C <sub>10</sub> H <sub>12</sub> NaO <sub>4</sub> S	(M+Na) <sup>+</sup>
251.1709		44696		
252.0375	1	104046	C <sub>10</sub> H <sub>12</sub> NaO <sub>4</sub> S	(M+Na) <sup>+</sup>
253.0324	1	49455	C <sub>10</sub> H <sub>12</sub> NaO <sub>4</sub> S	(M+Na) <sup>+</sup>
267.008		63868	C <sub>10</sub> H <sub>12</sub> KO <sub>4</sub> S	(M+K) <sup>+</sup>
335.0937		87329		
476.0714		47936		

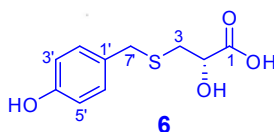
### Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	500
O	0	90
N	0	4
S	0	2
Cl	0	0
Br	0	1

### Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> S	TRUE	228.0457	228.0456	-0.3	C <sub>10</sub> H <sub>12</sub> NaO <sub>4</sub> S	99.96
C <sub>11</sub> H <sub>8</sub> N <sub>4</sub> S		228.0457	228.047	5.56	C <sub>11</sub> H <sub>8</sub> N <sub>4</sub> NaS	99.42
C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> S	TRUE	228.0448	228.0456	3.52	C <sub>10</sub> H <sub>12</sub> KO <sub>4</sub> S	99.72
C <sub>11</sub> H <sub>8</sub> N <sub>4</sub> S		228.0448	228.047	9.38	C <sub>11</sub> H <sub>8</sub> KN <sub>4</sub> S	98.64

--- End Of Report ---



**Figure S96.** The (+)-HRESIMS Report of Compound 6, Page 2

MS Formula Results: + Scan (4.092 min) Sub (2012112309.d)

m/z	Ion	Formula	Abundance
251.0349	(M+Na) <sup>+</sup>	C <sub>10</sub> H <sub>12</sub> NaO <sub>4</sub> S	869820.9

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> S	C <sub>10</sub> H <sub>12</sub> NaO <sub>4</sub> S	251.0349	99.96		228.0457	228.0456	-0.3	0.3	99.99	99.87	100	251.0349	5
<input type="checkbox"/>	C <sub>11</sub> H <sub>8</sub> N <sub>4</sub> S	C <sub>11</sub> H <sub>8</sub> N <sub>4</sub> NaS	251.0362	99.42		228.0457	228.047	5.56	5.56	99.23	100	99.24	251.0349	10

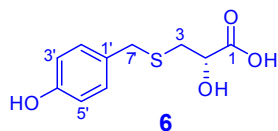
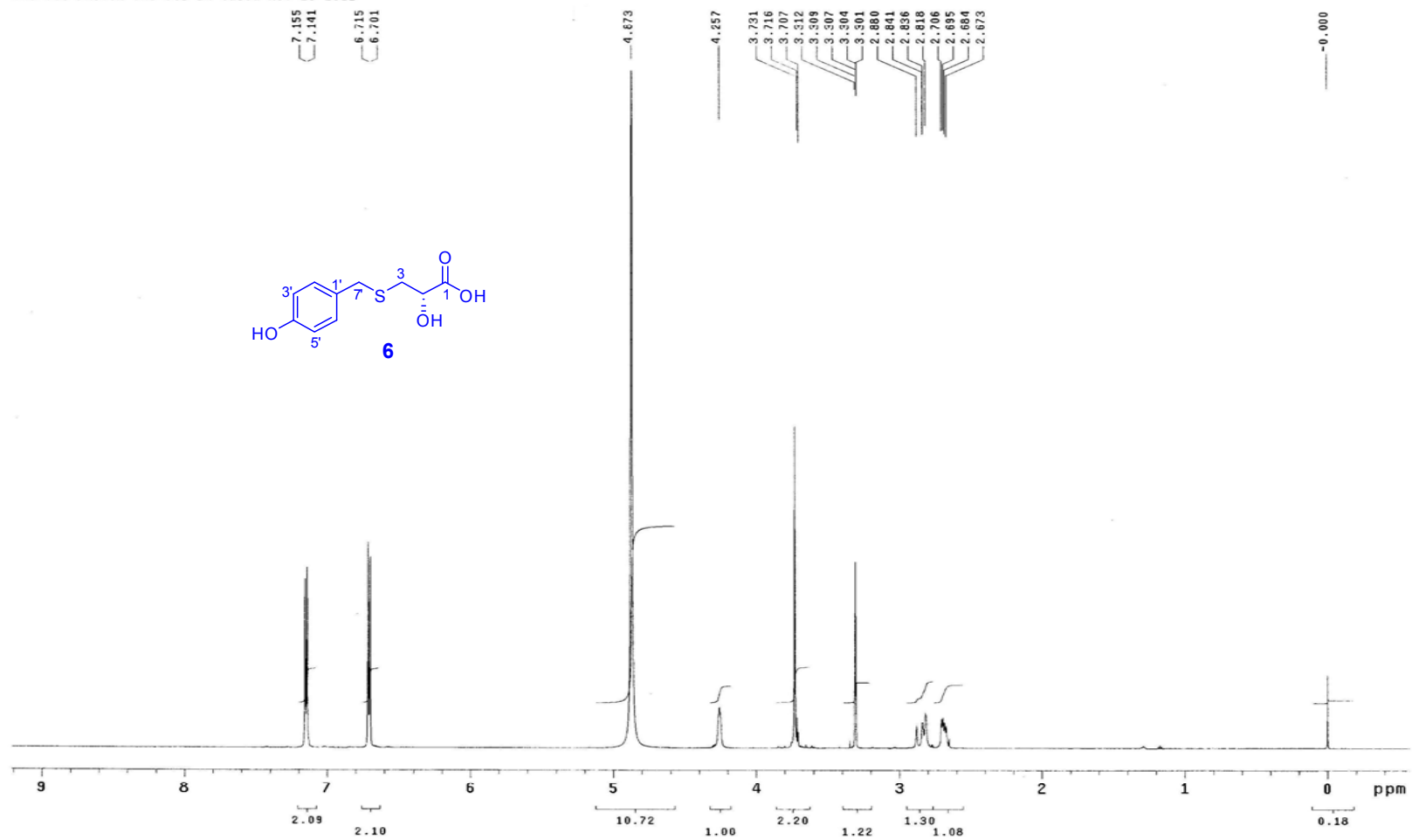


Figure S97. The (+)-HRESIMS Report of Compound 6, Page 3

VNS-600 PROTON TMG-50B IN cd3od Nov 28 2012



**Figure S98.** The  $^1\text{H}$  NMR Spectrum of Compound **6** in  $\text{MeOH-}d_4$  (600 MHz)

VNS-600 CARBON TMG-50B IN cd3od Nov 28 2012

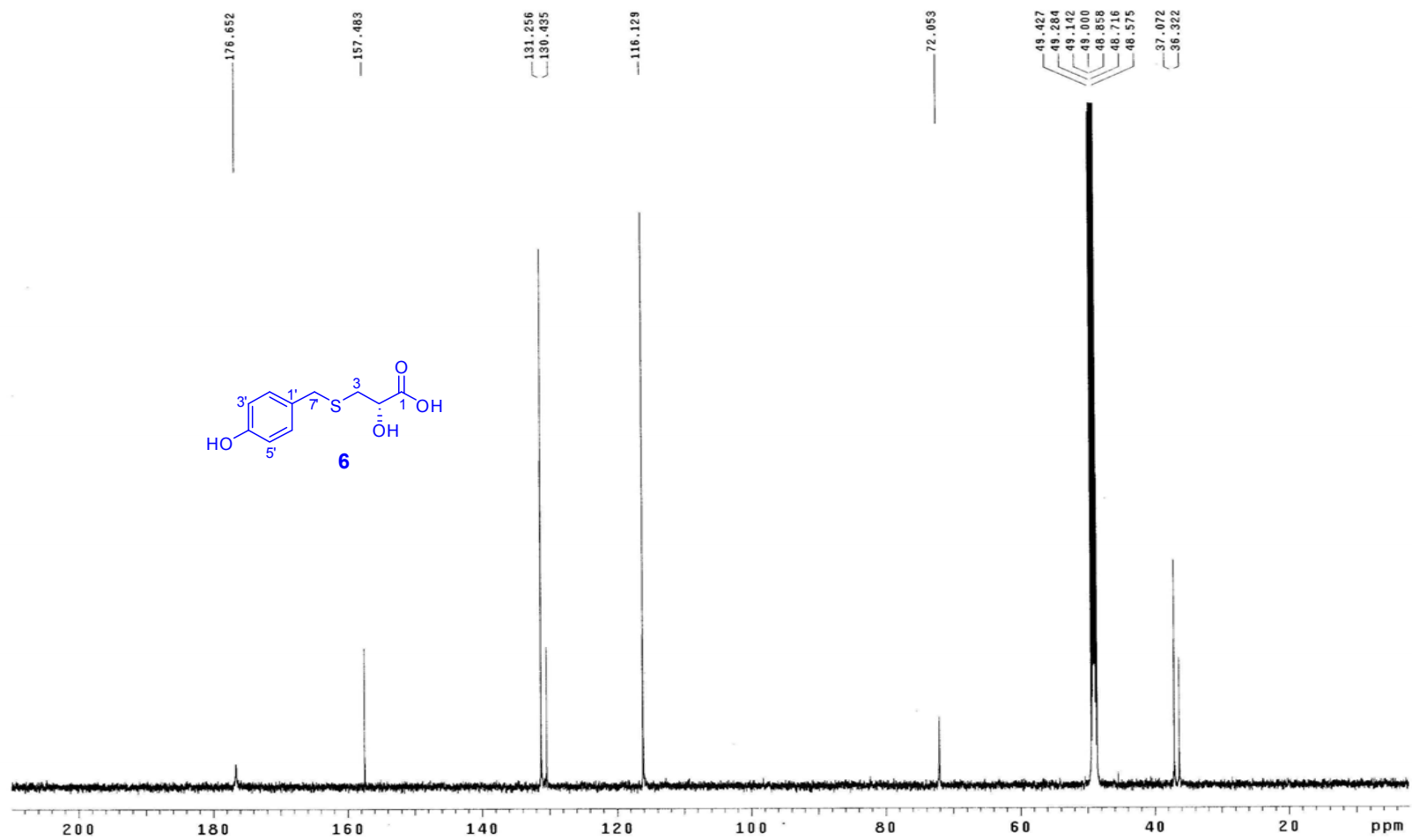


Figure S99. The  $^{13}\text{C}$  NMR Spectrum of Compound 6 in  $\text{MeOH-}d_4$  (150 MHz)



DD2-500 DEPT TMG-50B IN cd3od Nov 21 2012 coldprobe-Probe

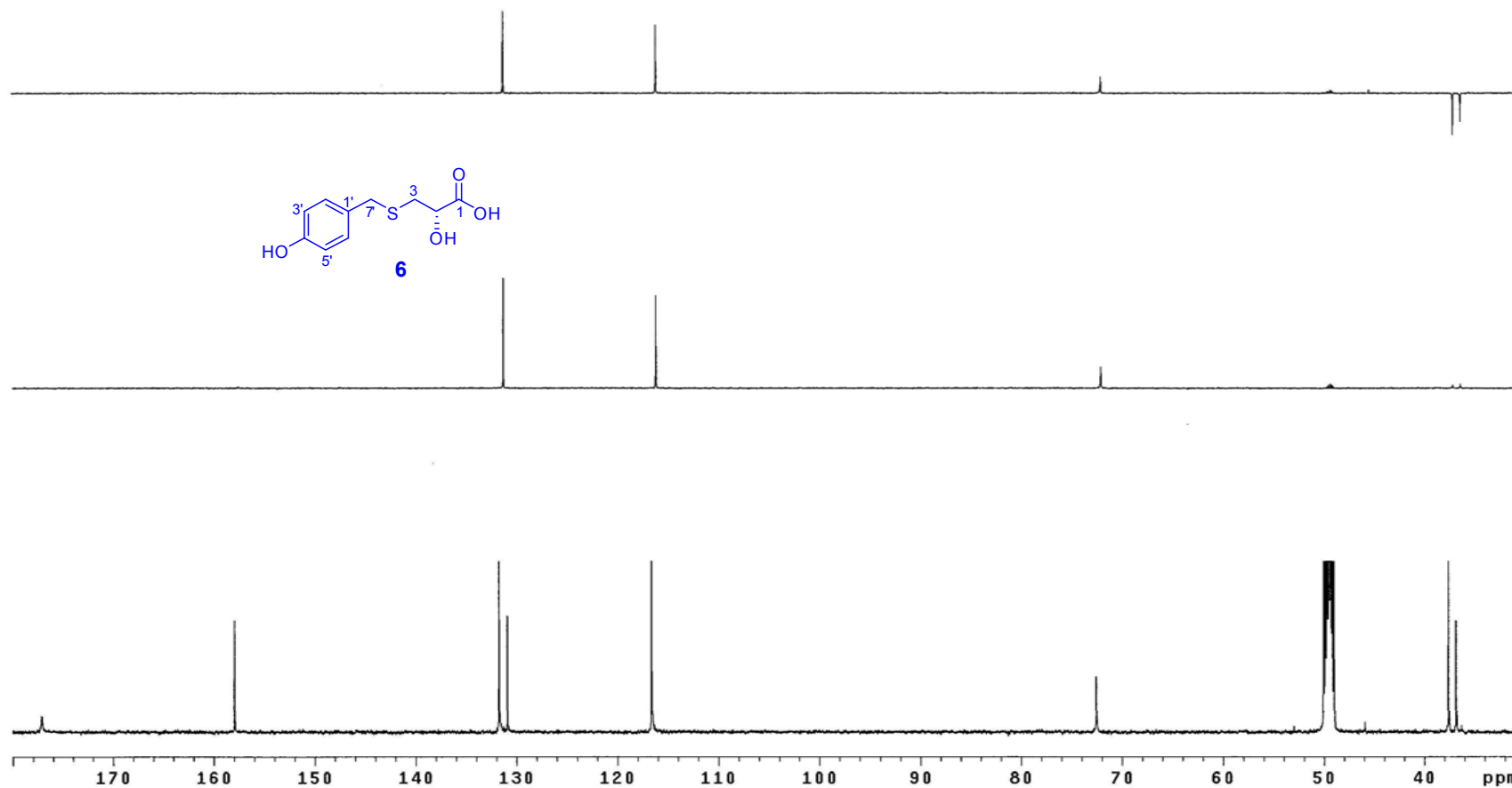


Figure S100. The DEPT Spectrum of Compound 6 in MeOH-*d*<sub>4</sub> (150 MHz)

VNS-600 gCOSY TMG-50B IN cd3od Nov 28 2012

Temp. 25.0 C / 298.1 K  
Sample #5, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.150 sec  
Width 6157.6 Hz  
2D Width 6157.6 Hz  
2 repetitions  
256 increments  
OBSERVE H1, 599.6921669 MHz  
DATA PROCESSING  
Sq. sine bell 0.075 sec  
F1 DATA PROCESSING  
Sq. sine bell 0.027 sec  
FT size 2048 x 2048  
Total time 10 min

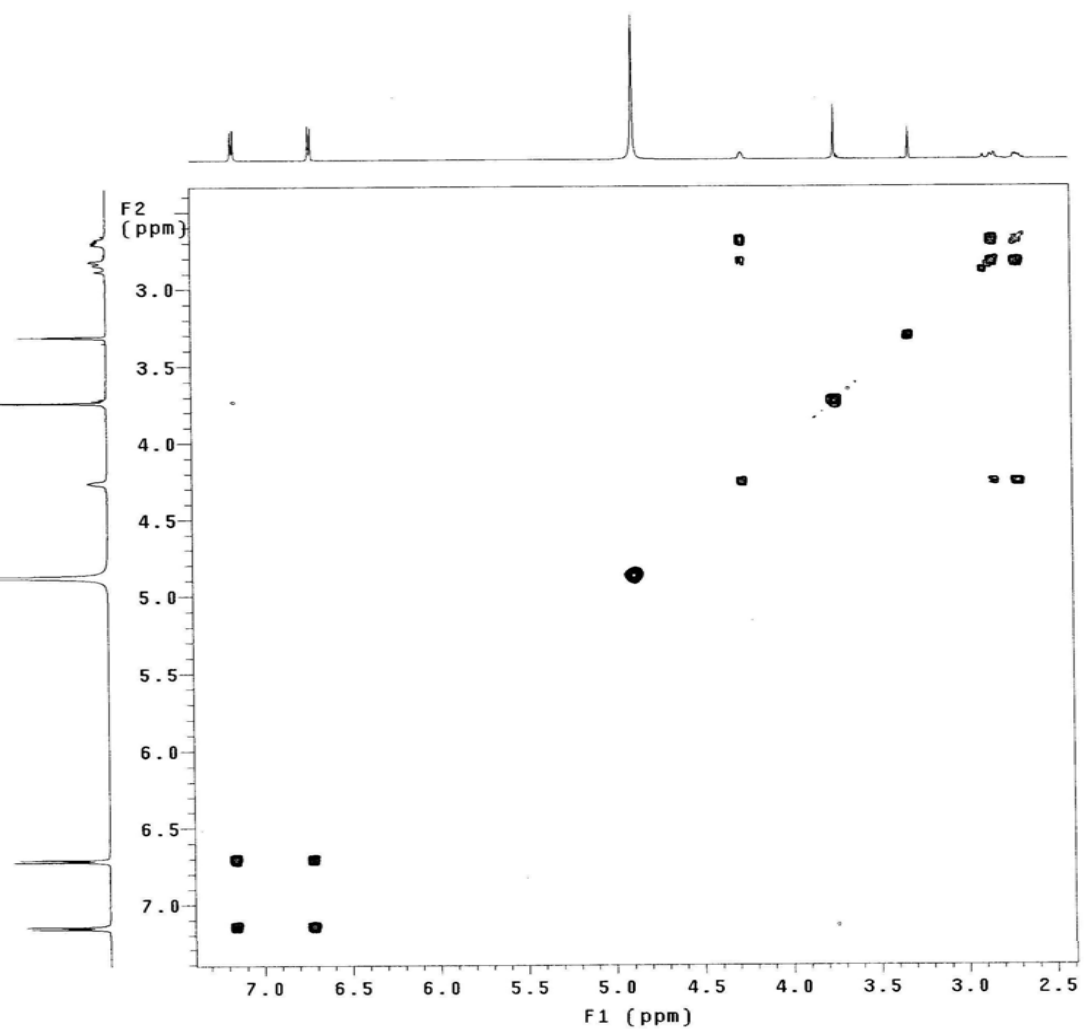
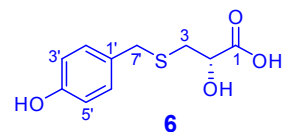


Figure S101. The  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum of 6 in  $\text{MeOH-}d_4$  (600 MHz)

VNS-600 gHSQCAD TMG-50B IN cd3od Nov 28 2012

Temp. 25.0 C / 298.1 K  
Sample #5, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.234 sec  
Width 6157.6 Hz  
2D Width 30154.5 Hz  
32 repetitions  
140 increments  
OBSERVE H1, 599.6921669 MHz  
DECOUPLE C13, 150.8062867 MHz  
Power 35 dB  
on during acquisition  
off during delay  
W40\_NEW-SW modulated  
DATA PROCESSING  
Sine bell 0.029 sec  
F1 DATA PROCESSING  
Sine bell 0.005 sec  
FT size 4096 x 2048  
Total time 1 hr, 29 min

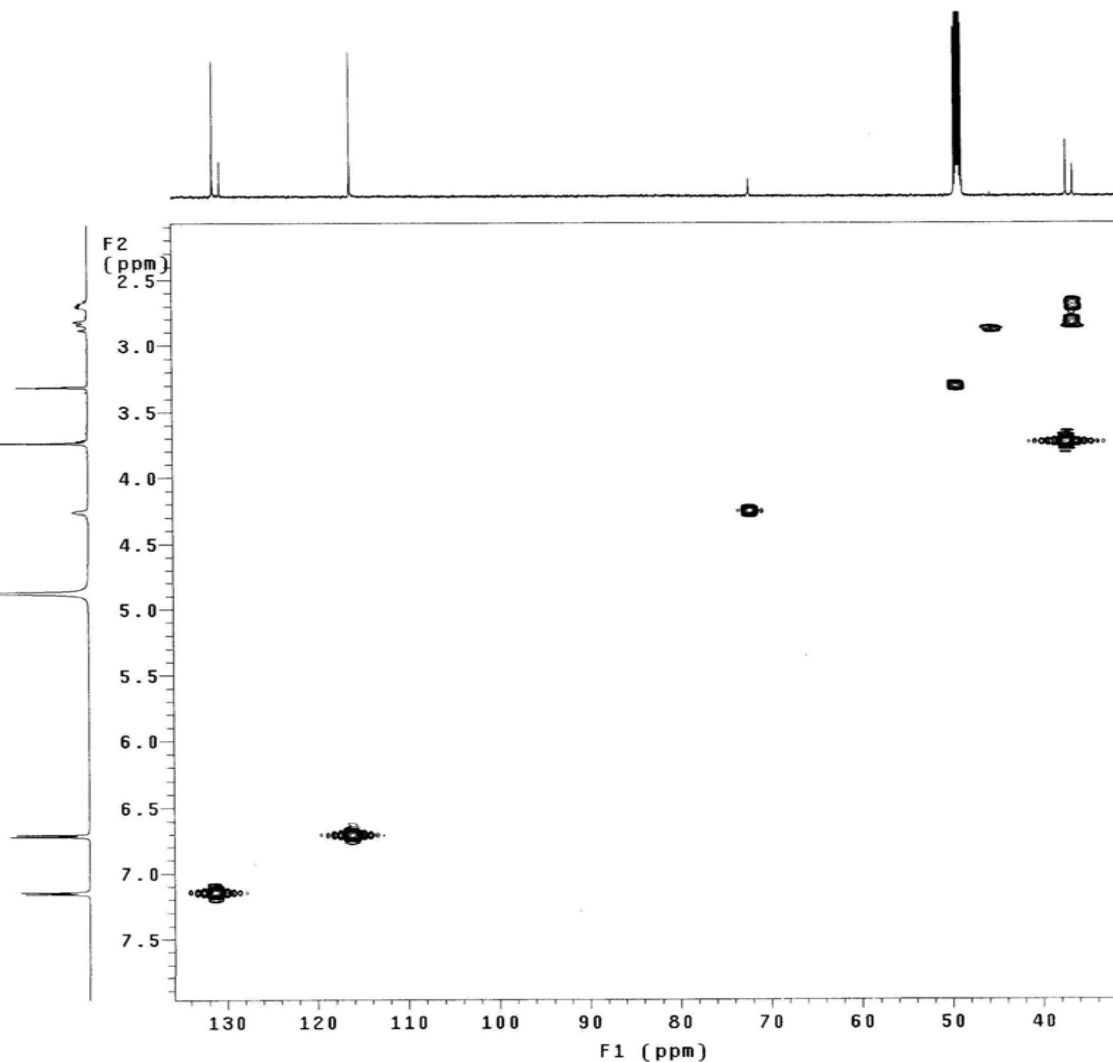
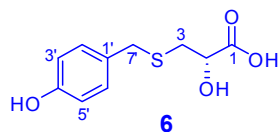


Figure S102. The gHSQC Spectrum of Compound 6 in MeOH-*d*<sub>4</sub> (600 MHz)

VNS-600 gHMBCAD TMG-50B IN cd3od Nov 28 2012

Temp. 25.0 C / 298.1 K  
Sample #5, Operator: vjwalk

Relax. delay 1.000 sec  
Acq. time 0.234 sec  
Width 6157.6 Hz  
2D Width 36182.7 Hz  
64 repetitions  
160 increments  
OBSERVE H1, 599.6921669 MHz  
DATA PROCESSING  
Sine bell 0.088 sec  
F1 DATA PROCESSING  
Sine bell 0.004 sec  
FT size 4096 x 2048  
Total time 3 hr, 31 min

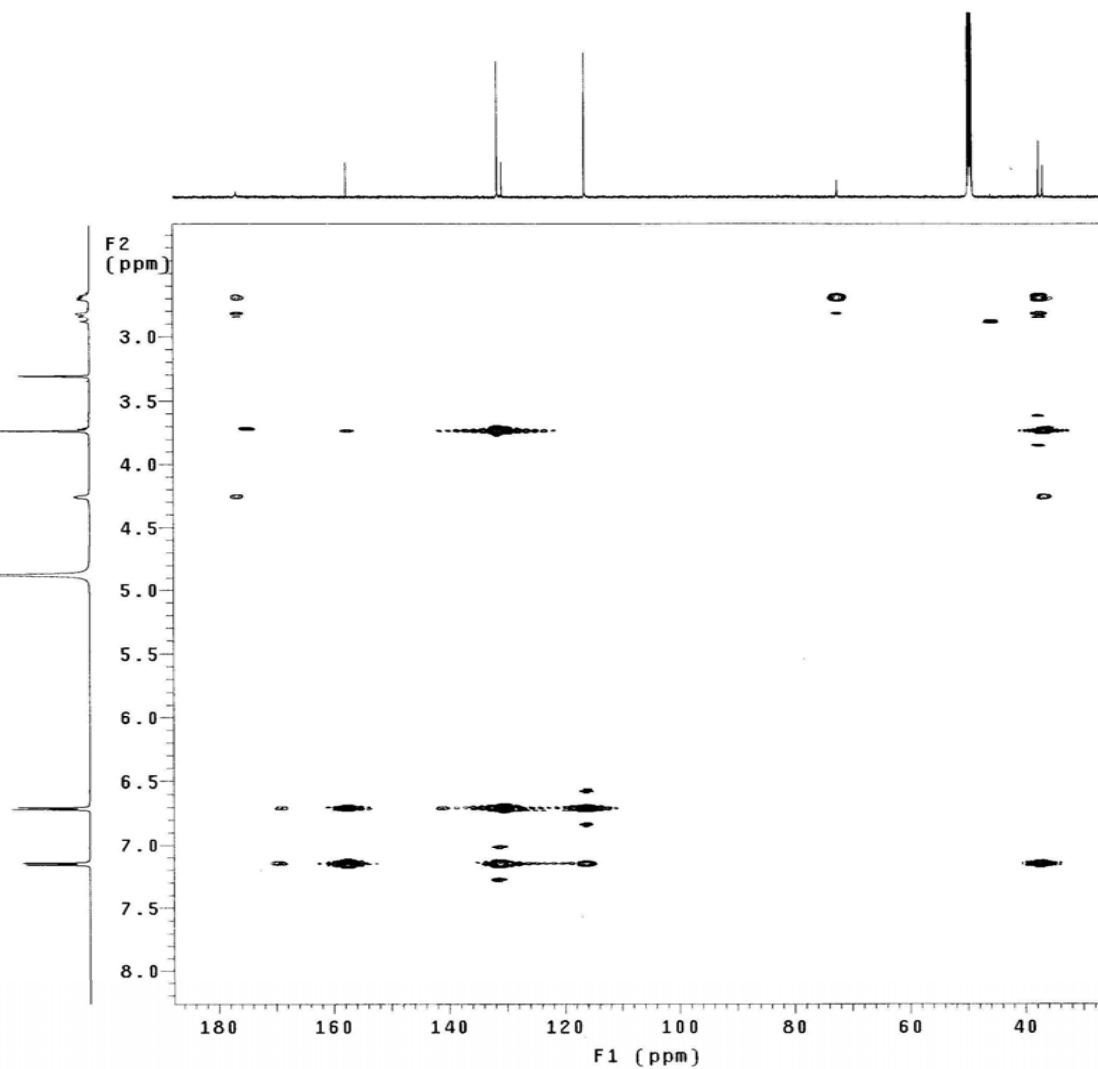
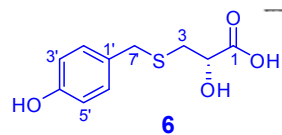
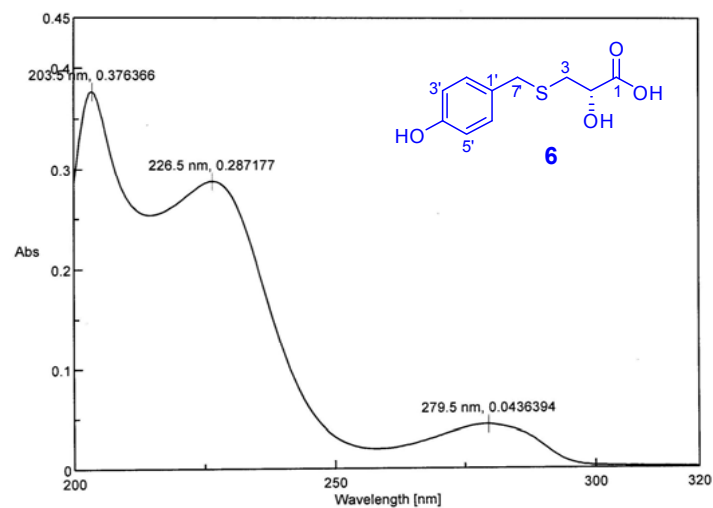
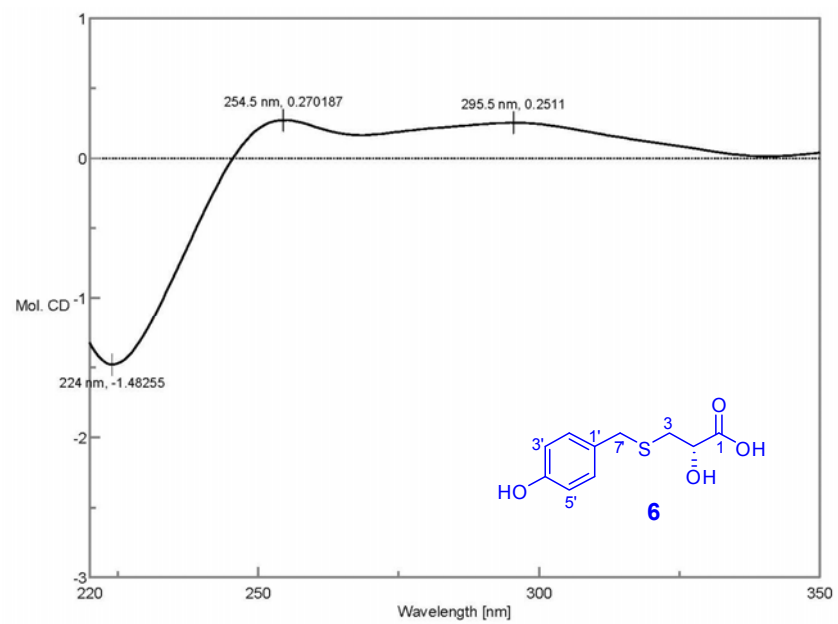


Figure S103. The gHMBC Spectrum of Compound 6 in MeOH-*d*<sub>4</sub> (600 MHz)



**Figure S104.** The UV Spectrum of Compound **6** in MeOH



**Figure S105.** The CD Spectrum of Compound **6** in MeOH

VNS-600 PROTON TMG-50BE IN dms0 Dec 25 2013

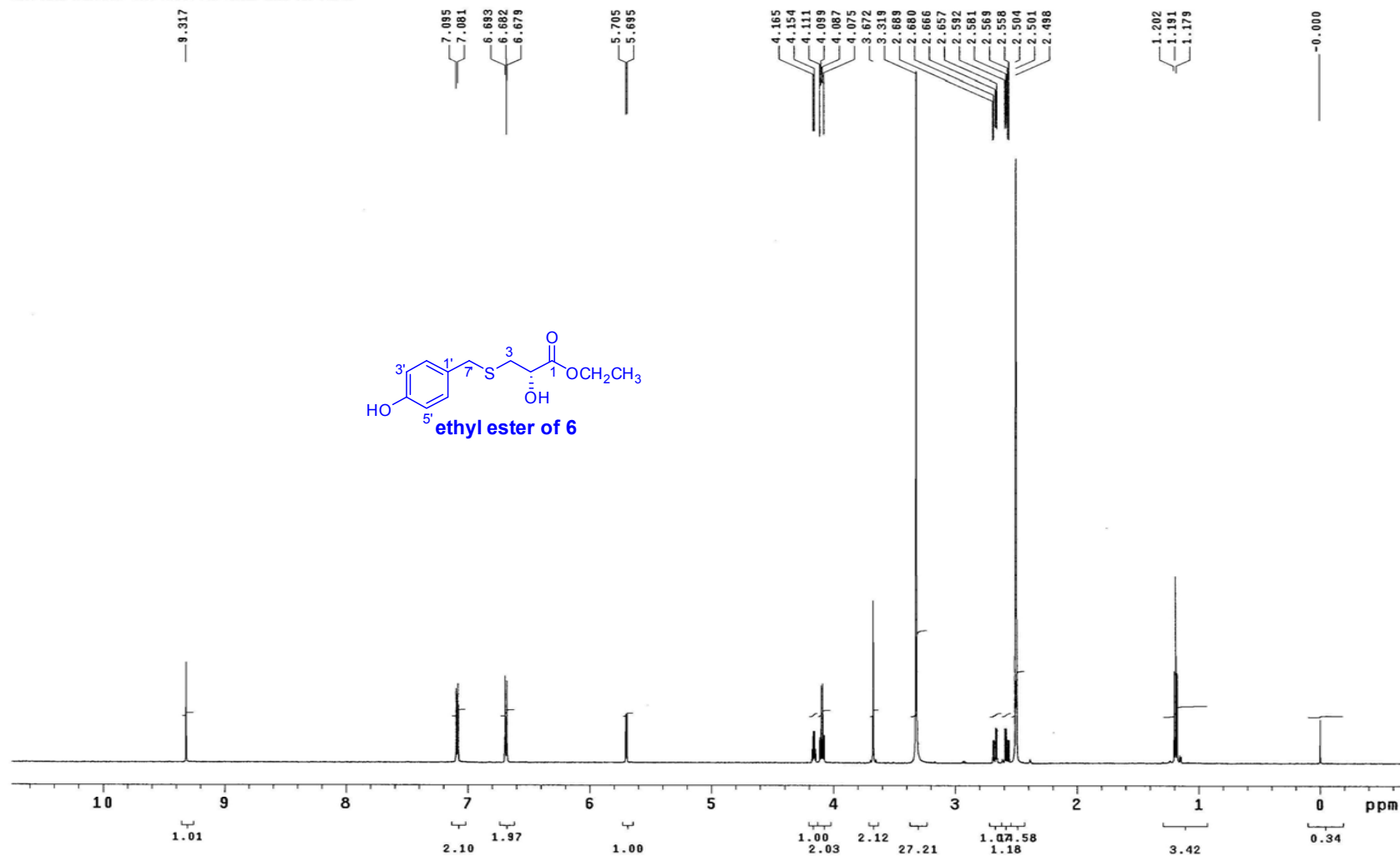


Figure S106. The <sup>1</sup>H NMR Spectrum of the Ethyl Ester of Compound 6 in DMSO-d<sub>6</sub> (600 MHz)

VNS-600 CARBON TMG-50BE IN dmsO Feb 15 2014

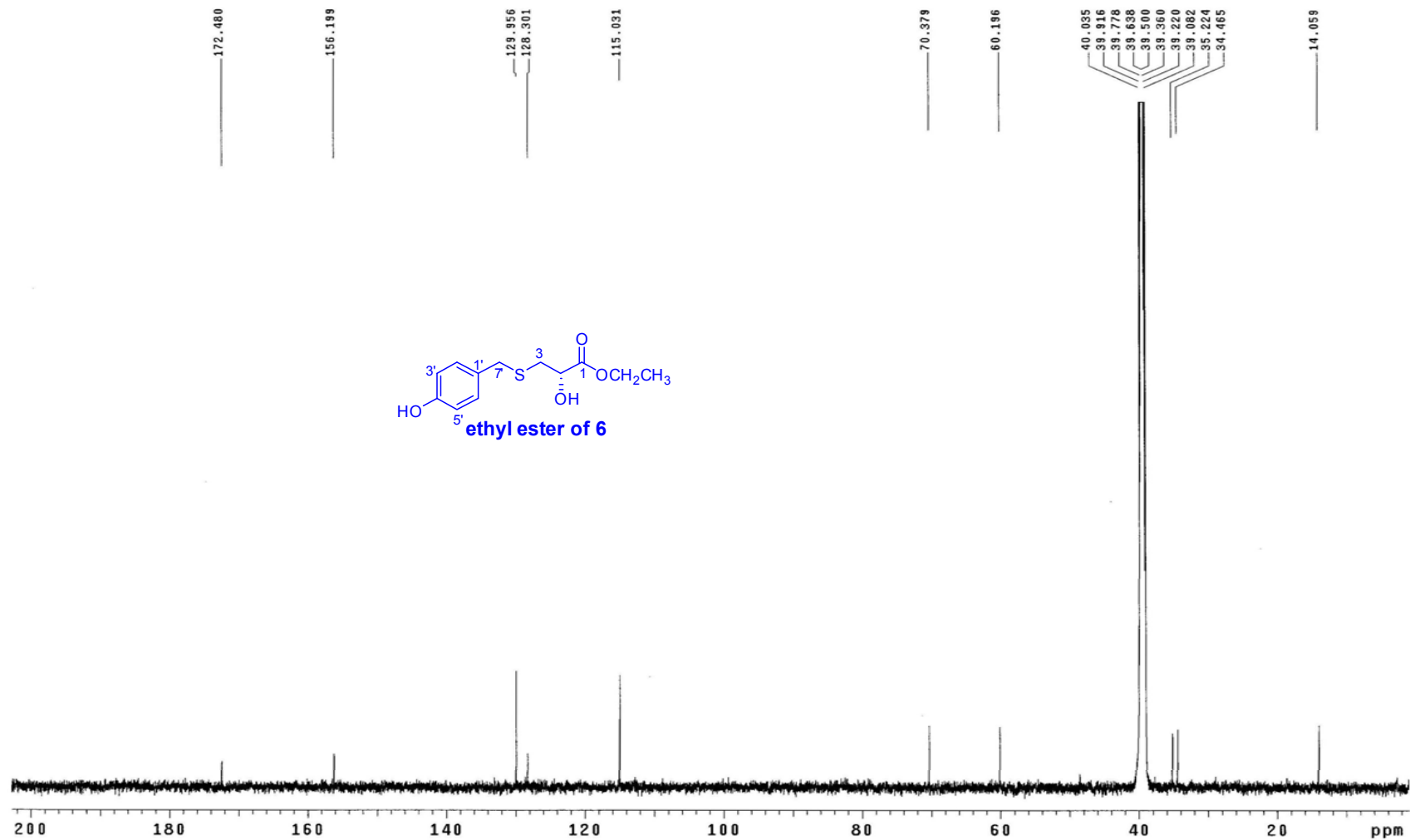


Figure S107. The <sup>13</sup>C NMR Spectrum of the Ethyl Ester of 6 in DMSO-*d*<sub>6</sub> (150 MHz)

VNS-600 PROTON TMG-508M IN dms0 Dec 25 2013

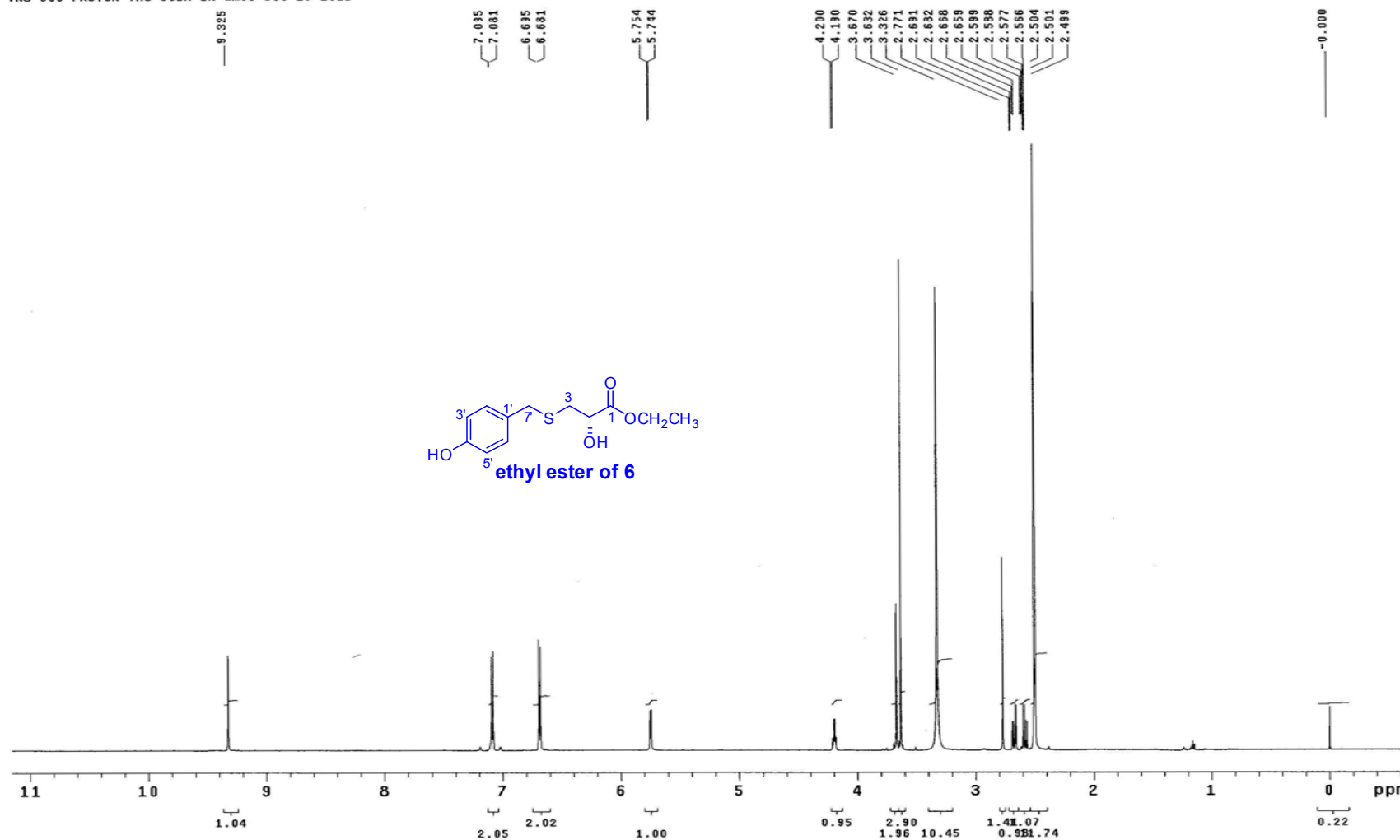


Figure S108. The  $^1\text{H}$  NMR Spectrum of the Methyl Ester of Compound 6 in  $\text{DMSO-}d_6$  (600 MHz)



VNS-600 CARBON TMG-50BM IN dms0 Feb 15 2014

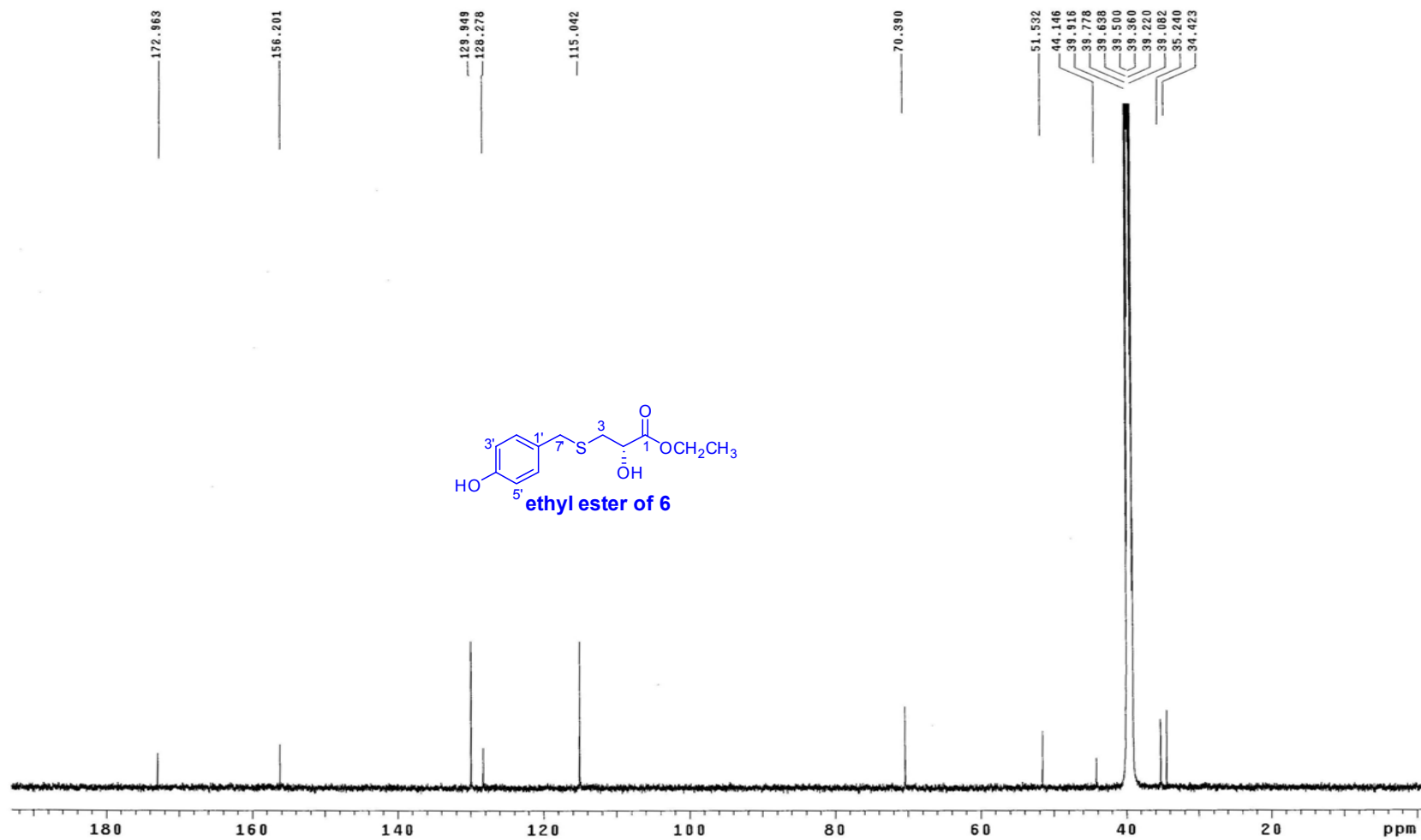
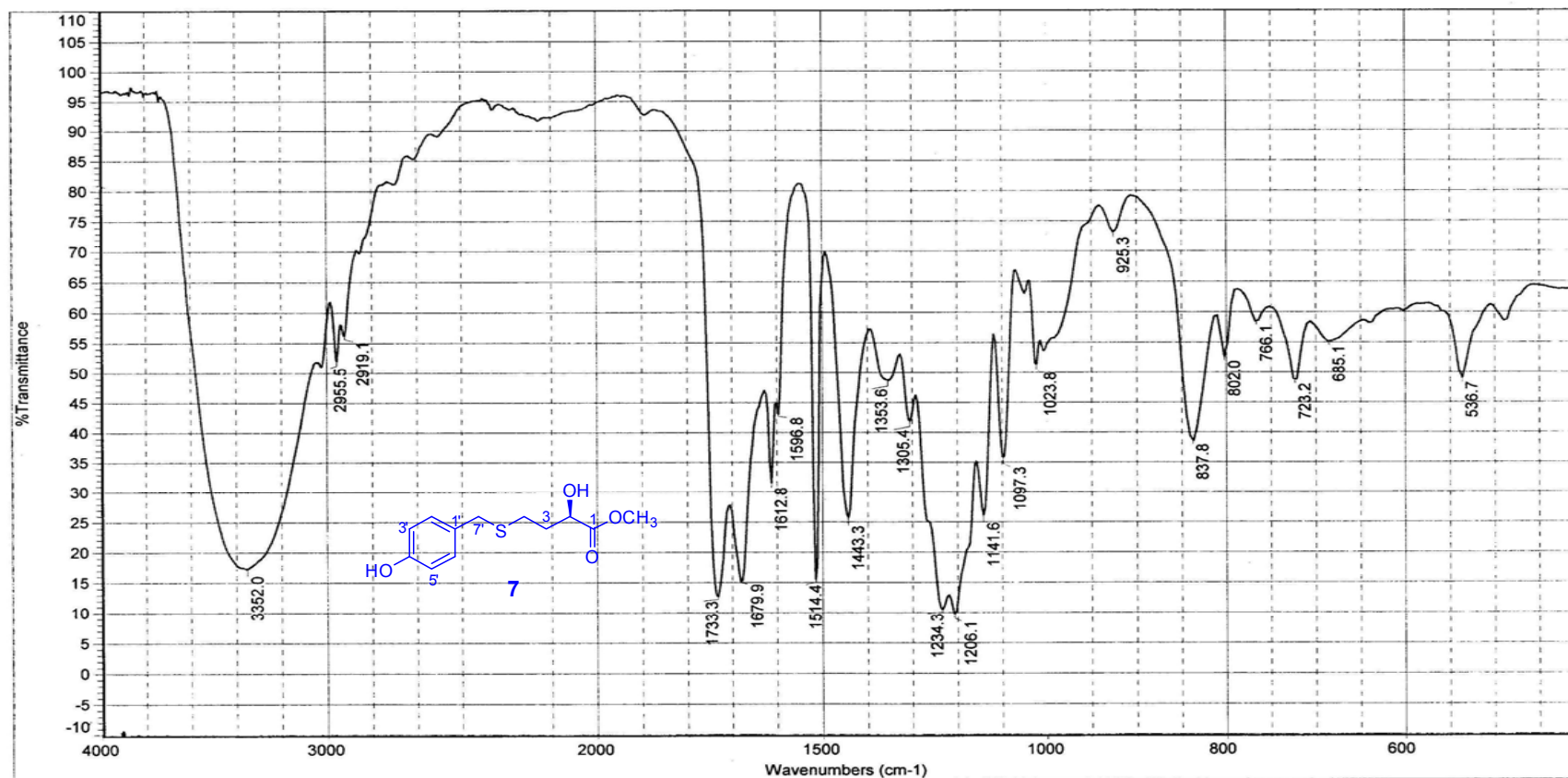


Figure S109. The <sup>13</sup>C NMR Spectrum of the Methyl Ester of Compound 6 in DMSO-*d*<sub>6</sub> (150 MHz)



日期: 星期四 4月 19 10:24:49 2012 (GMT+08:00) Sample Name : WYN - 89

(显微镜红外透射法FT- IR Microscope Transmission)

扫描次数: 100

傅里叶变换红外显微镜(FT-IR Microscope): Centaurus

分辨率: 8.000

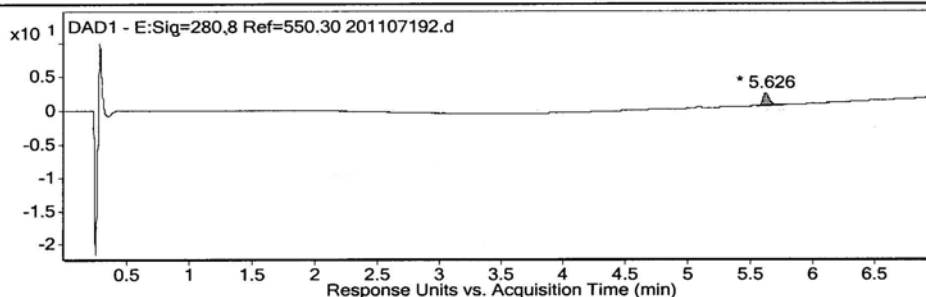
美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S110. The IR Spectrum of Compound 7

## Qualitative Analysis Report

<b>Data Filename</b>	201107192.d	<b>Sample Name</b>	WYN-89
<b>Sample Type</b>	Sample	<b>Position</b>	P1-C9
<b>Instrument Name</b>	Instrument 1	<b>User Name</b>	
<b>Acq Method</b>		<b>IRM Calibration Status</b>	XXXXXXXXXX
<b>DA Method</b>	TEST LCMS.m	<b>Comment</b>	

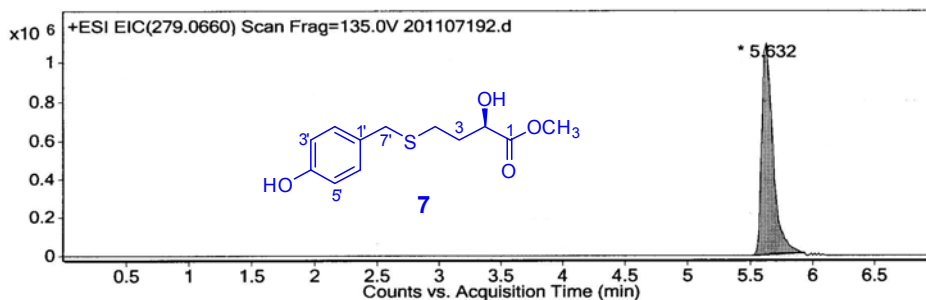
### User Chromatograms



### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	5.549	5.626	5.785	1.88	6.25	100

Fragmentor Voltage    135    Collision Energy    0    Ionization Mode    ESI



### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	5.52	5.632	5.937	1096521	6917023	100

### User Spectra

Fragmentor Voltage    Collision Energy    Ionization Mode  
135                            0                            ESI

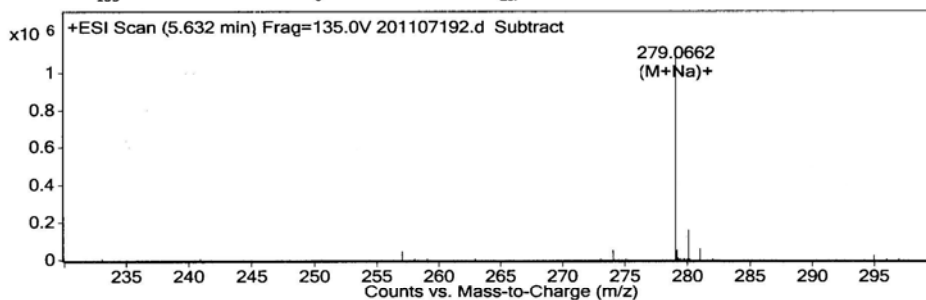


Figure S111. The (+)-HRESIMS Report of Compound 7, Page 1

## Qualitative Analysis Report

### Peak List

<i>m/z</i>	<i>z</i>	Abund	Formula	Ion
107.042		89810		
279.0662	1	1098965	C12 H16 Na O4 S	(M+Na)+
280.0694	1	160145	C12 H16 Na O4 S	(M+Na)+
281.0651	1	62389	C12 H16 Na O4 S	(M+Na)+

### Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	120
O	0	30
N	0	5
S	0	5
Cl	0	0

### Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C12 H16 O4 S	TRUE	256.077	256.0769	-0.22	C12 H16 Na O4 S	99.97
C13 H12 N4 S		256.077	256.0783	4.99	C13 H12 N4 Na S	99.54
C16 H8 N4		256.077	256.0749	-8.16	C16 H8 N4 Na	97.02
C8 H16 O9		256.077	256.0794	9.56	C8 H16 Na O9	96.99

--- End Of Report ---

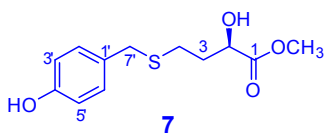


Figure S112. The (+)-HRESIMS Report of Compound 7, Page 2

MS Formula Results: + Scan (5.632 min) Sub (201107192.d)

m/z	Ion	Formula	Abundance
279.0662	(M+Na) <sup>+</sup>	C <sub>12</sub> H <sub>16</sub> NaO <sub>4</sub> S	1098964.5

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
<input checked="" type="checkbox"/>	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> S	C <sub>12</sub> H <sub>16</sub> NaO <sub>4</sub> S	279.0662	99.97		256.077	256.0769	-0.22	0.22	99.91	99.99	100	279.0662	5
<input type="checkbox"/>	C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> S	C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> NaS	279.0675	99.54		256.077	256.0783	4.99	4.99	99.56	99.86	99.36	279.0662	10
<input type="checkbox"/>	C <sub>16</sub> H <sub>8</sub> N <sub>4</sub>	C <sub>16</sub> H <sub>8</sub> N <sub>4</sub> Na	279.0641	97.02		256.077	256.0749	-8.16	8.16	94.15	97.9	98.3	279.0662	15
<input type="checkbox"/>	C <sub>8</sub> H <sub>16</sub> O <sub>9</sub>	C <sub>8</sub> H <sub>16</sub> NaO <sub>9</sub>	279.0687	96.99		256.077	256.0794	9.56	9.56	94.63	98.46	97.67	279.0662	1

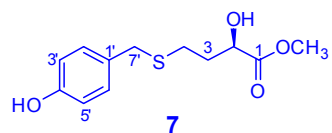
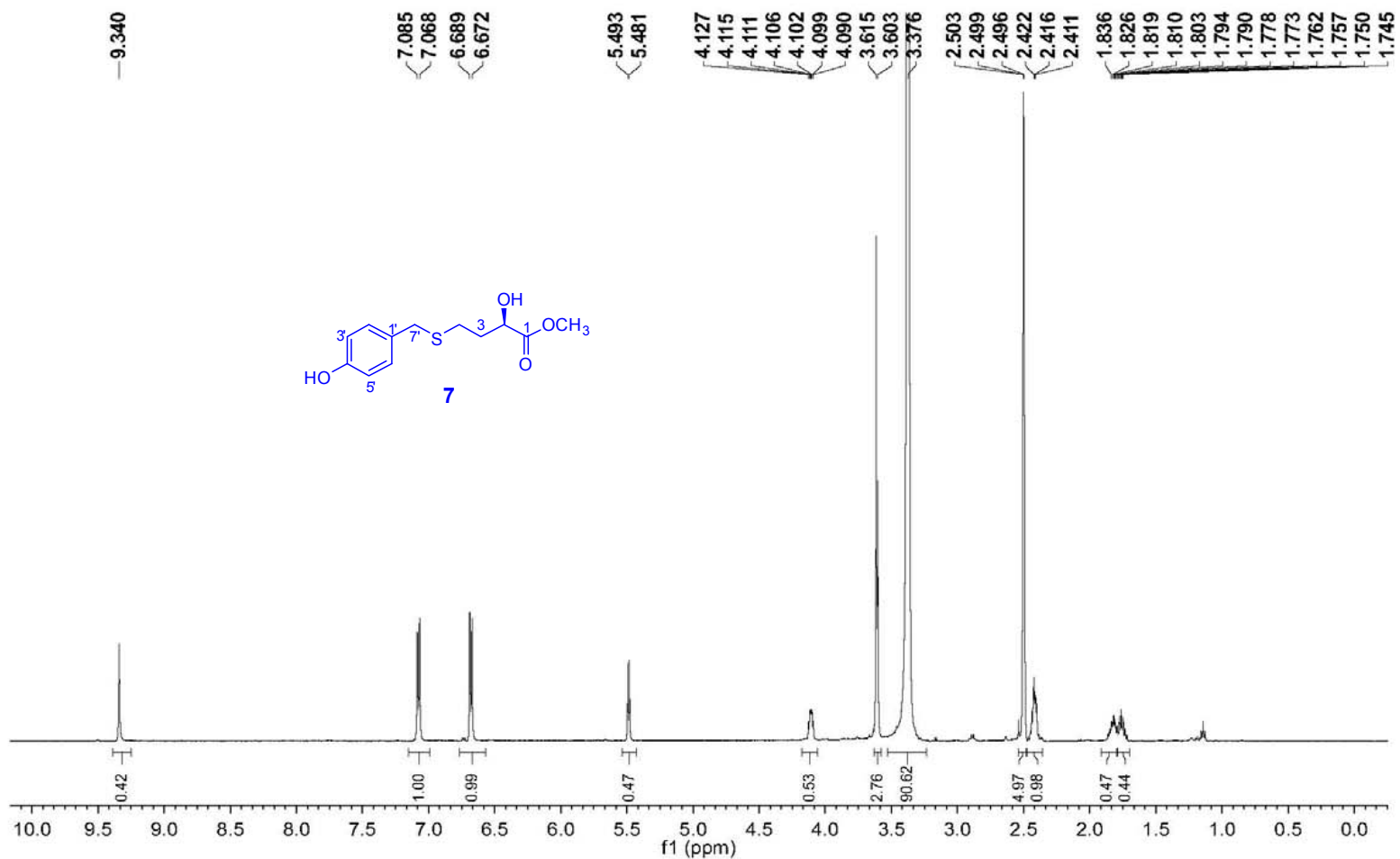


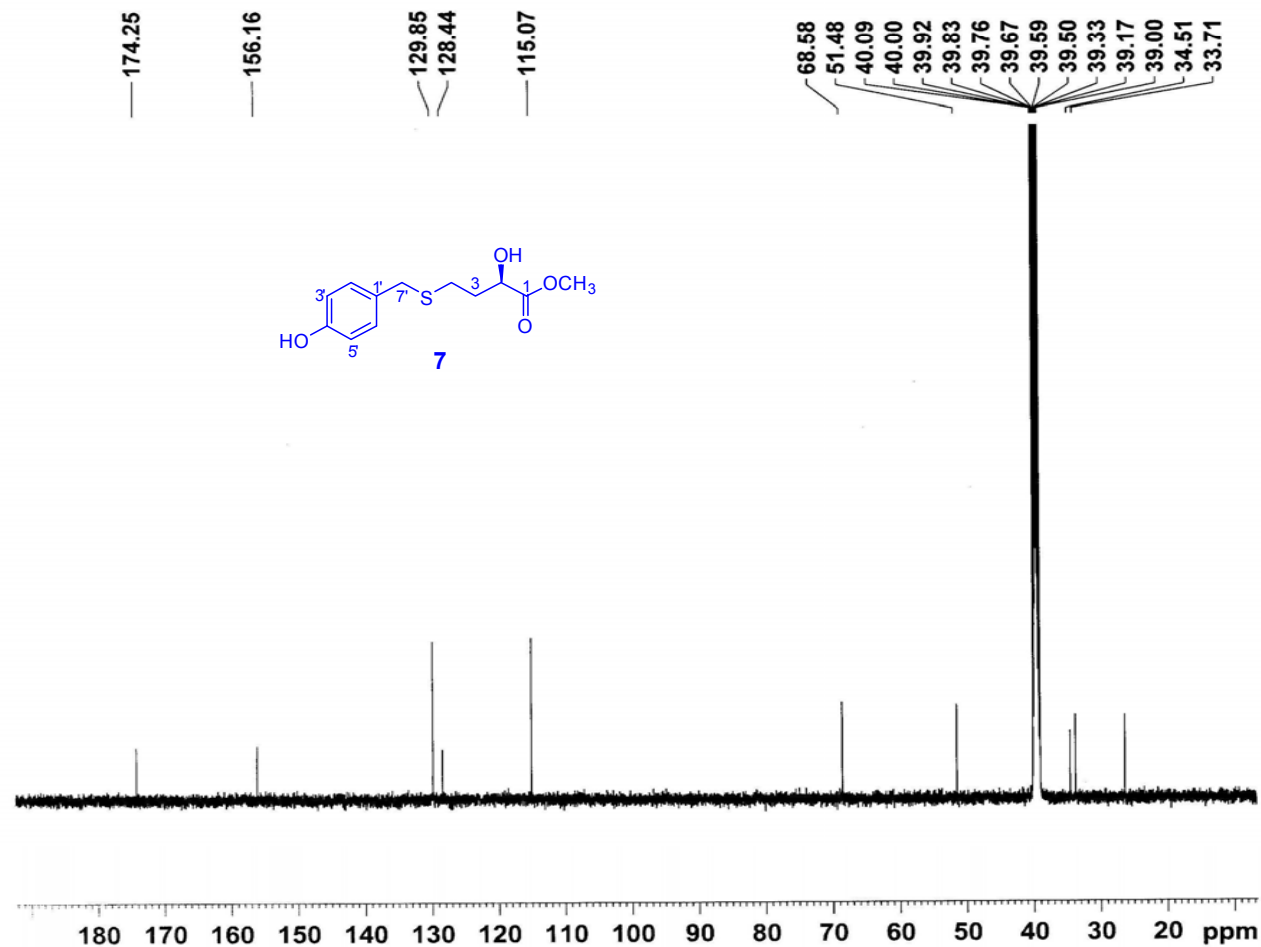
Figure S113. The (+)-HRESIMS Report of Compound 7, Page 3

BRUKER AV500-TIT 1H-NMR WYN-89 TN DMSO 2011.07.17  
PROTON DMSO D:\\ shijiangong 6



**Figure S114.** The <sup>1</sup>H NMR Spectrum of Compound 7 in DMSO-d<sub>6</sub> (500 MHz)

BRUKER AV500-III 13C-NMR WYN-89 IN DMSO 2011.06.29  
C:\3CPD DMSO D:\ shijiangong 4



```
NAME 20110629-WYN-89
EXPNO 2
PROCNO 1
Date_ 20110704
Time 8.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 4126
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 600

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.90 dB
PL1W 73.29839325 W
SFO1 125.7527610 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 16.77 dB
PL13 16.77 dB
PL12W 12.39386463 W
PL13W 0.41324416 W
SFO2 500.0620002 MHz
SI 32768
SF 125.7402476 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
```

Figure S115. The  $^{13}\text{C}$  NMR Spectrum of Compound 7 in DMSO- $d_6$  (125 MHz)

BRUKER AV500-III DEPT-NMR WYN-89 IN DMSO 2011.06.29  
C13CPD DMSO D:\ shijiangong 4

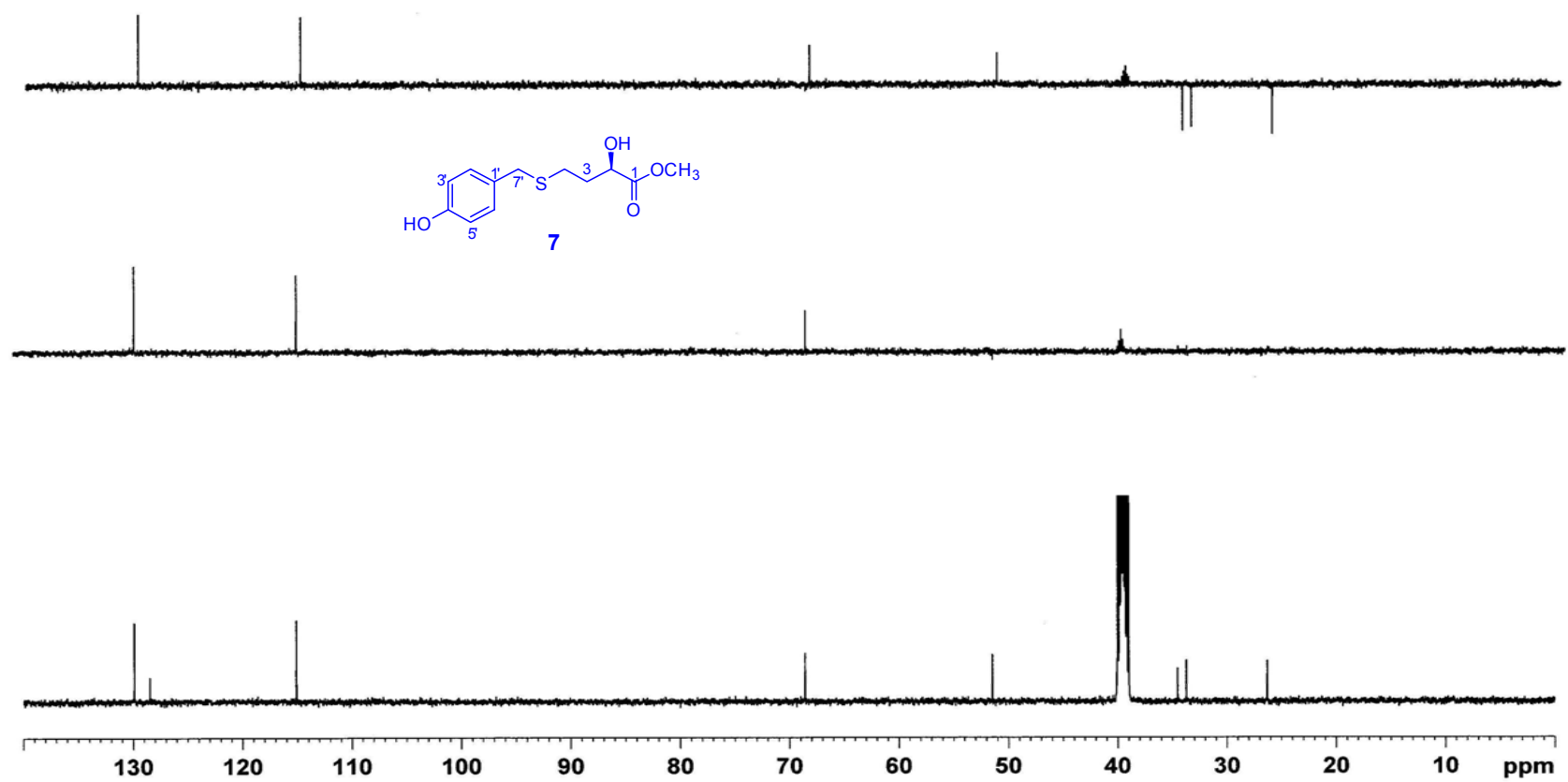


Figure S116. The DEPT Spectrum of Compound 7 in DMSO-*d*<sub>6</sub> (125 MHz)



BRUKER AV500-III COSY-NMR WYN-89 IN DMSO 2011.07.17  
COSYGPMFSW DMSO D:\\ shijiangong 6

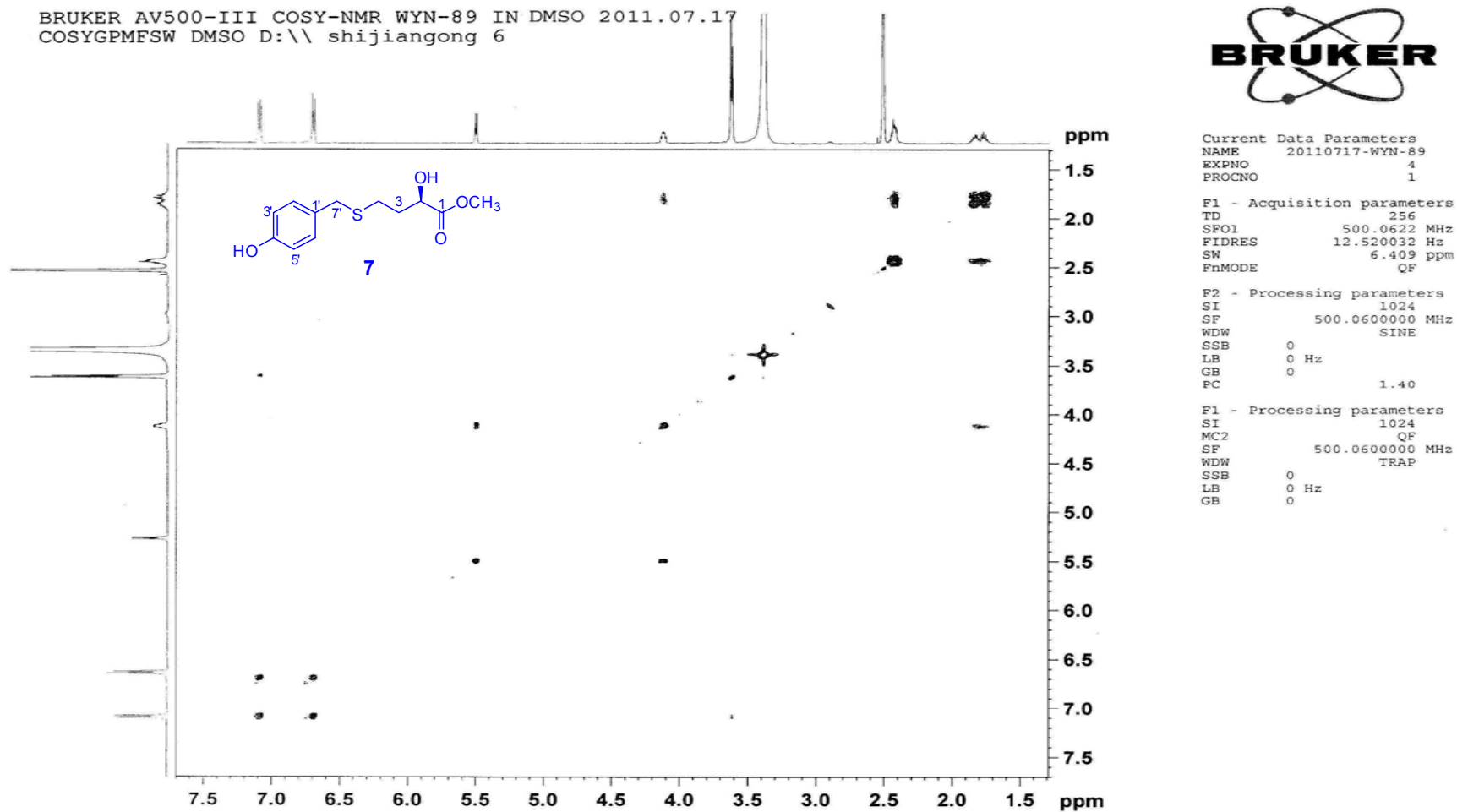


Figure S117. The  $^1\text{H}$ - $^1\text{H}$  COSY Spectrum of Compound 7 in DMSO- $d_6$  (500 MHz)

BRUKER AV500-III HSQC-NMR WYN-89 IN DMSO 2011.07.17  
 HSQCETGPSI DMSO D:\ shijiangong 6

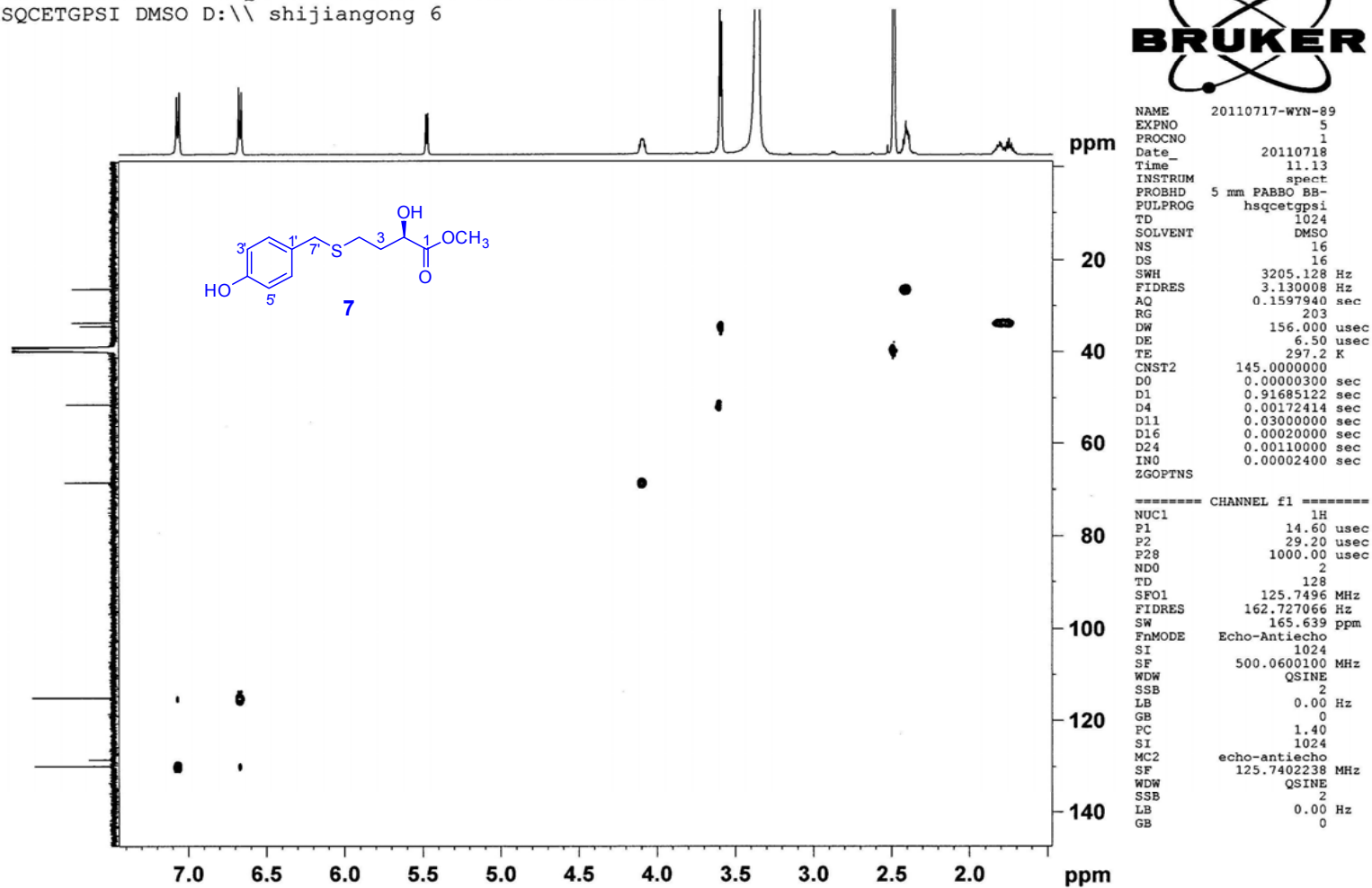


Figure S118. The HSQC Spectrum of Compound 7 in DMSO-*d*<sub>6</sub> (500 MHz)

BRUKER AV500-III HMBC-NMR WYN-89 IN DMSO 2011.07.17  
 HMBCGPND DMSO D:\shijiangong 6

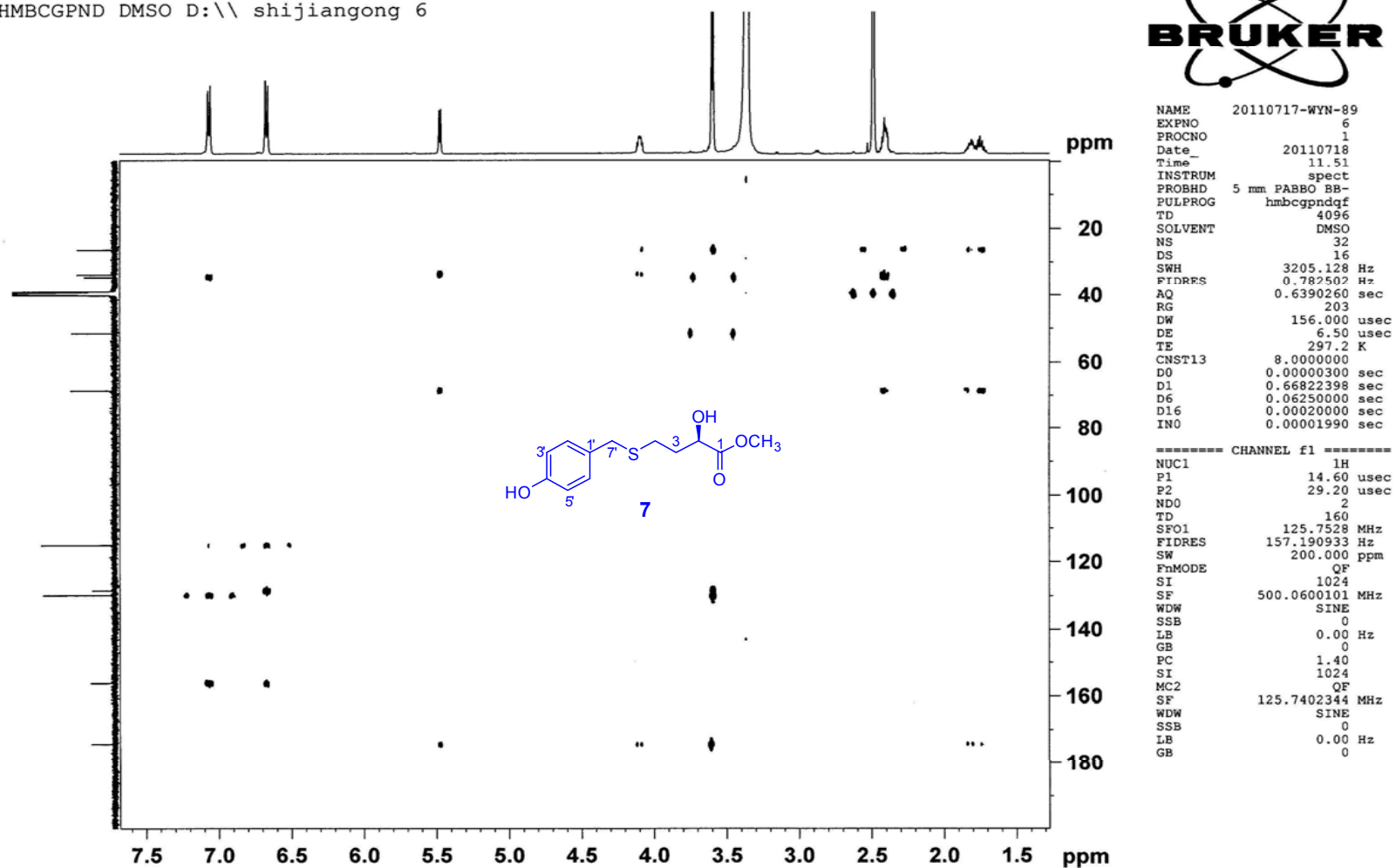
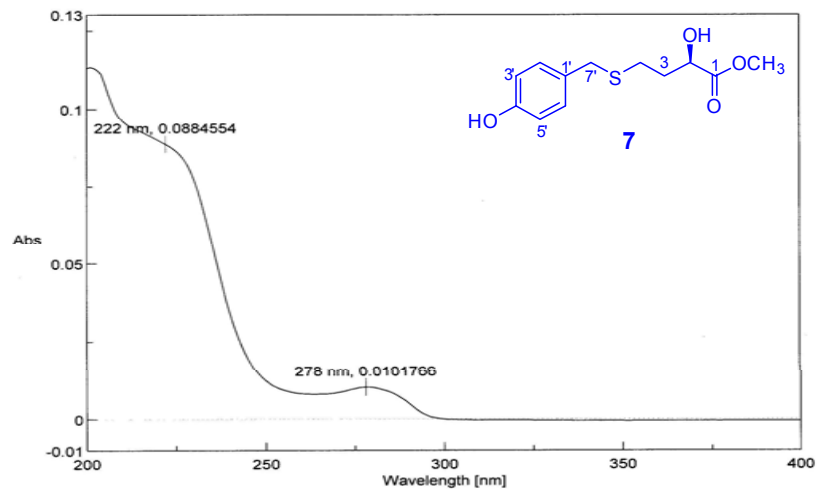
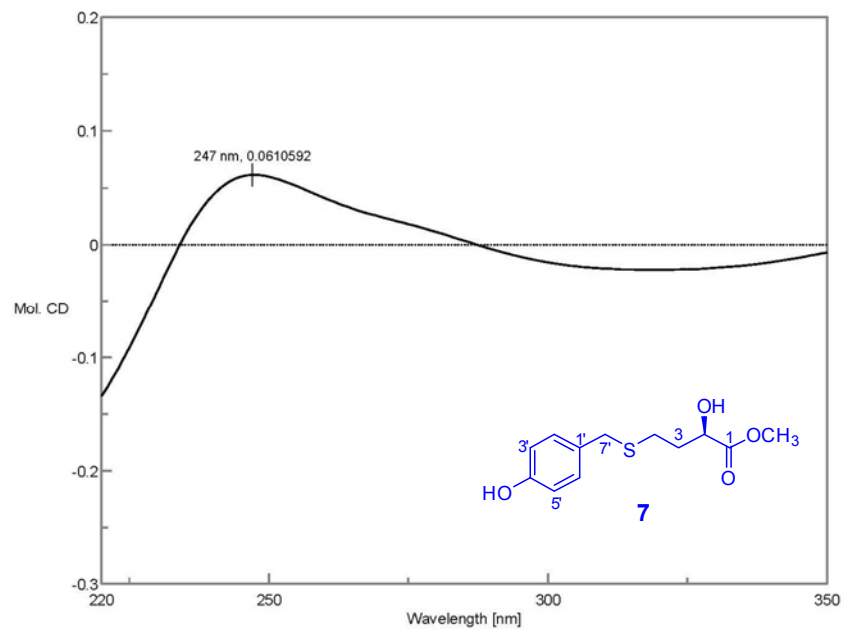


Figure S119. The HMBC Spectrum of Compound 7 in DMSO-*d*<sub>6</sub> (500 MHz)



**Figure S120.** The UV Spectrum of Compound **7** in MeOH



**Figure S121.** The CD Spectrum of Compound **7** in CH<sub>2</sub>Cl<sub>2</sub>

BRUKER Bruker AVANCEIII400 1H-NMR, in CDCl3, WYN-89 2013/01/14

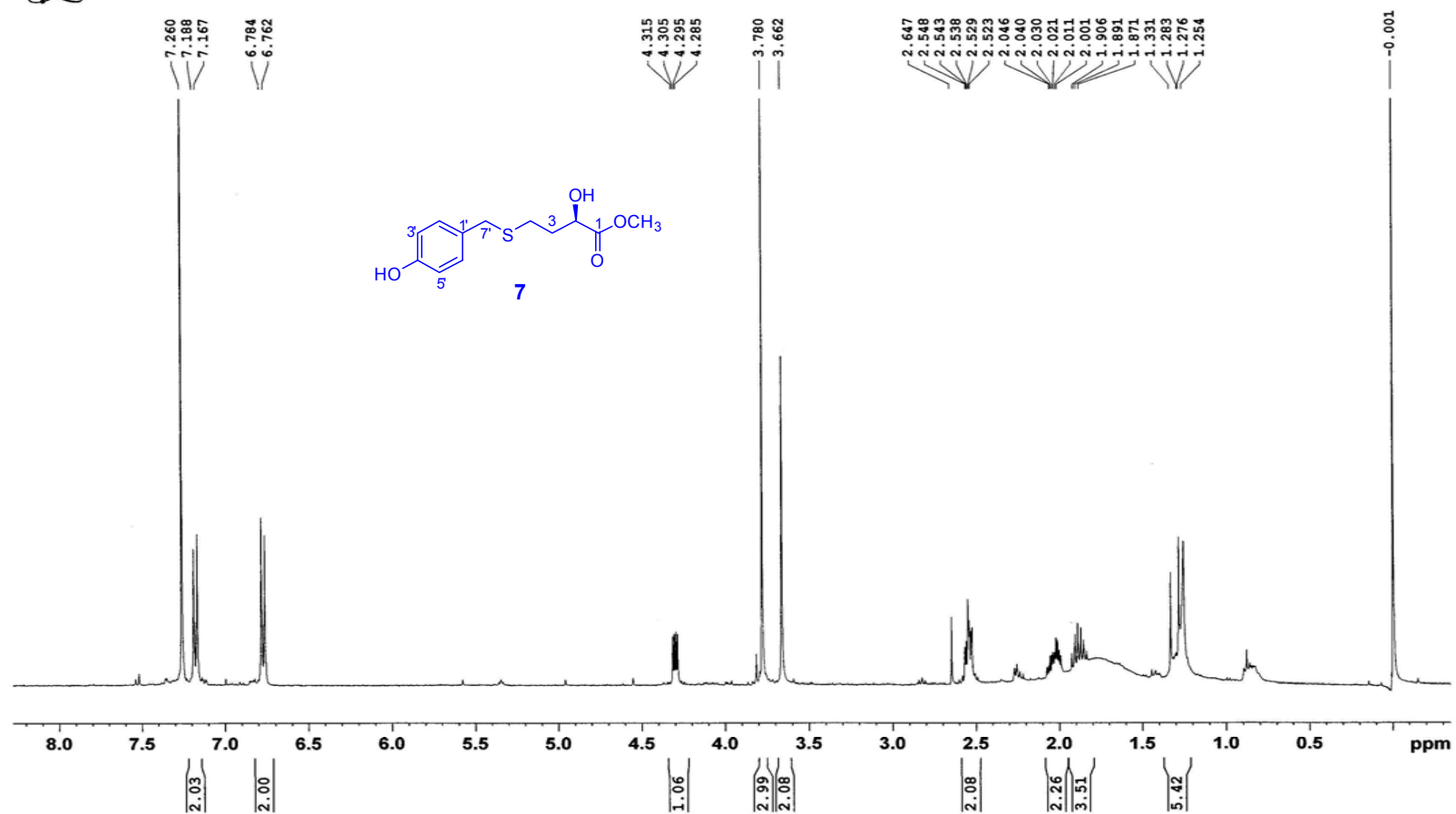


Figure S122. The  $^1\text{H}$  NMR Spectrum of Compound 7 in  $\text{CD}_3\text{Cl}$  (400 MHz)

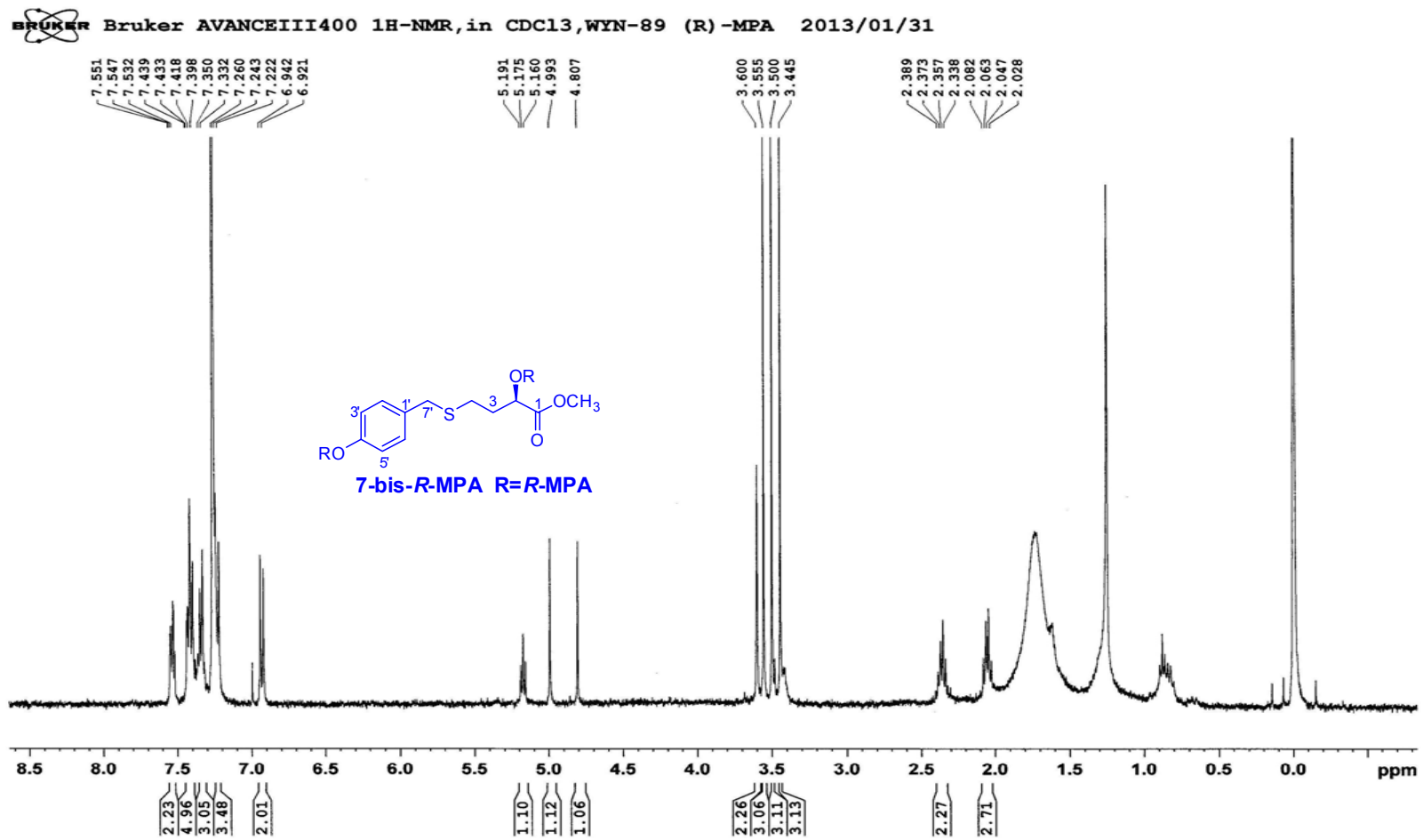


Figure S123. The  $^1\text{H}$  NMR Spectrum of Compound 7-bis-(*R*)-MPA in  $\text{CD}_3\text{Cl}$  (400 MHz)

BRUKER Bruker AVANCEIII400 1H-NMR, in CDCl<sub>3</sub>, WYN-89 (S)-MPA 2013/01/31

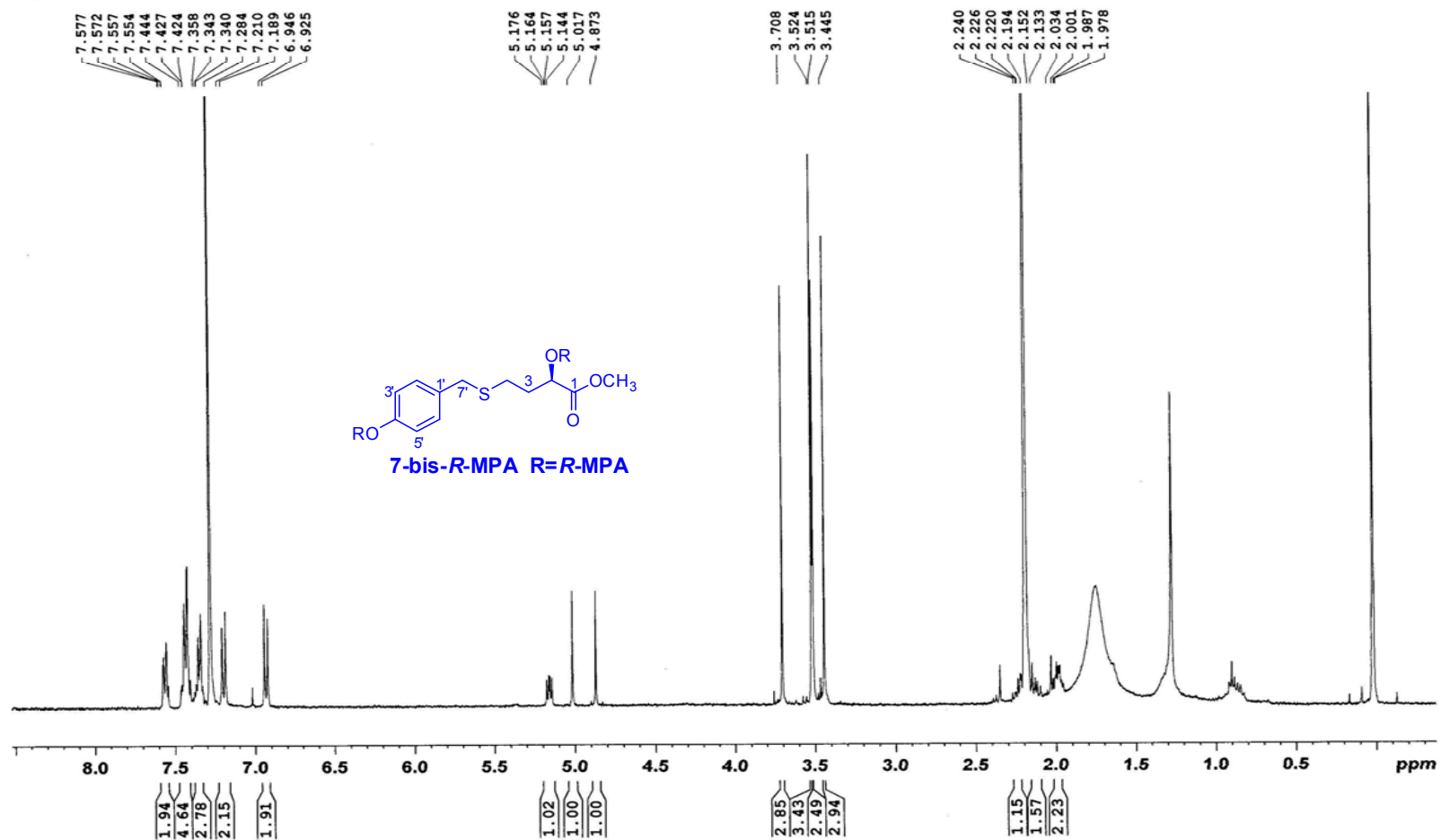
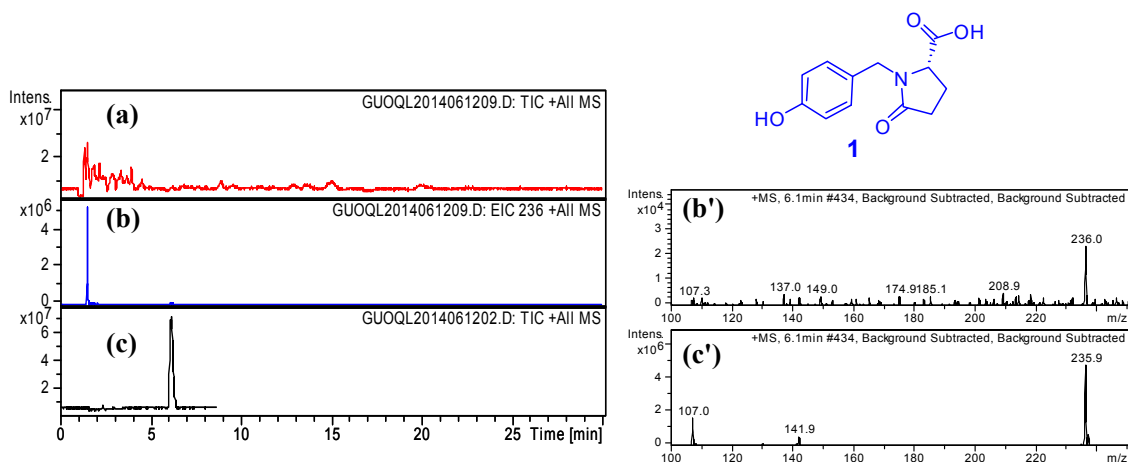
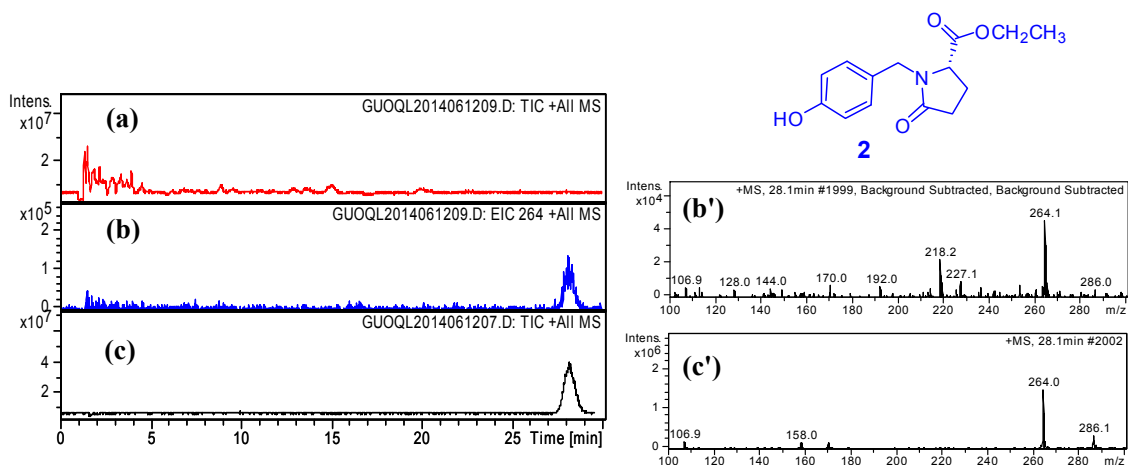


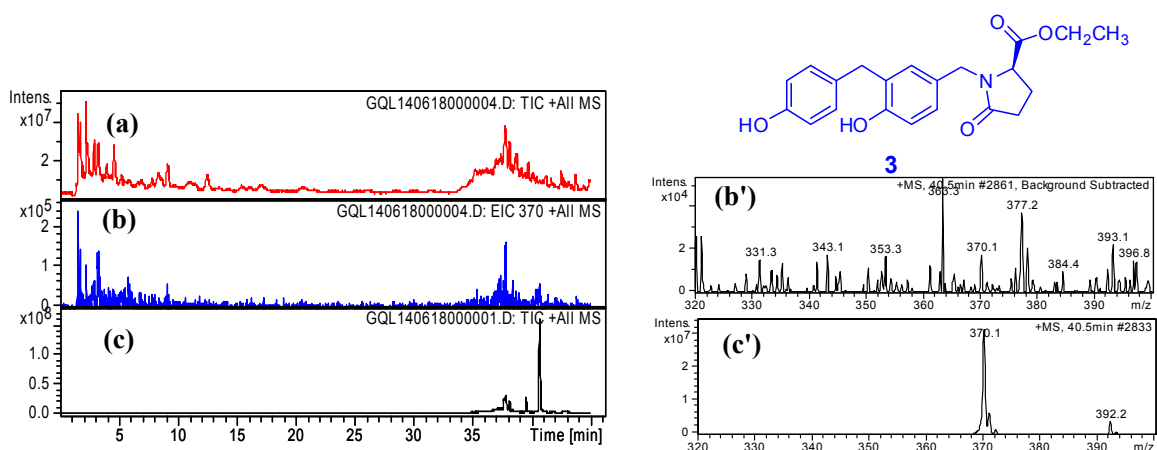
Figure S124. The <sup>1</sup>H NMR Spectrum of Compound 7-bis-(S)-MPA in CD<sub>3</sub>Cl (400 MHz)



**Figure S125.** (a) TIC of the aqueous extract of *Gastrodia elata* Blume rhizomes; (b) The extracted ion chromatogram of  $m/z$  236 from the aqueous extract TIC; (c) TIC of compound **1**; (b') The (+)-ESIMS of the extracted ion; (c') The (+)-ESIMS of compound **1**.



**Figure S340.** (a) TIC of the aqueous extract of *Gastrodia elata* Blume rhizomes; (b) The extracted ion chromatogram of  $m/z$  264 from the aqueous extract TIC; (c) TIC of compound **2**; (b') The (+)-ESIMS of the extracted ion; (c') The (+)-ESIMS of compound **2**.



**Figure S343.** (a) TIC of the  $\text{CH}_3\text{CN}$ -eluted fraction; (b) The extracted ion chromatogram of  $m/z$  370 from TIC of the  $\text{CH}_3\text{CN}$ -eluted fraction; (c) TIC of compound **3**; (b') The (+)-ESIMS of the extracted ion; (c') The (+)-ESIMS of compound **3**.