

# Supplementary Materials: Furostanol and Spirostanol Saponins from *Tribulus terrestris*

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Figures S1–S7 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 1

Figures S8–S13 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 2

Figures S14–S20 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 3

Figures S21–S26 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 4

Figures S27–S32 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 5

Figures S33–S38 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 6

Figures S39–S44 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 7

Figures S45–S50 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 8

Figures S51–S56 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 9

Figures S57–S62 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 10

Figures S63–S68 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 11

Figures S69–S75 1D and 2D NMR spectrum in C<sub>5</sub>D<sub>5</sub>N and HRESIMS spectrum in CH<sub>3</sub>CN of compound 12

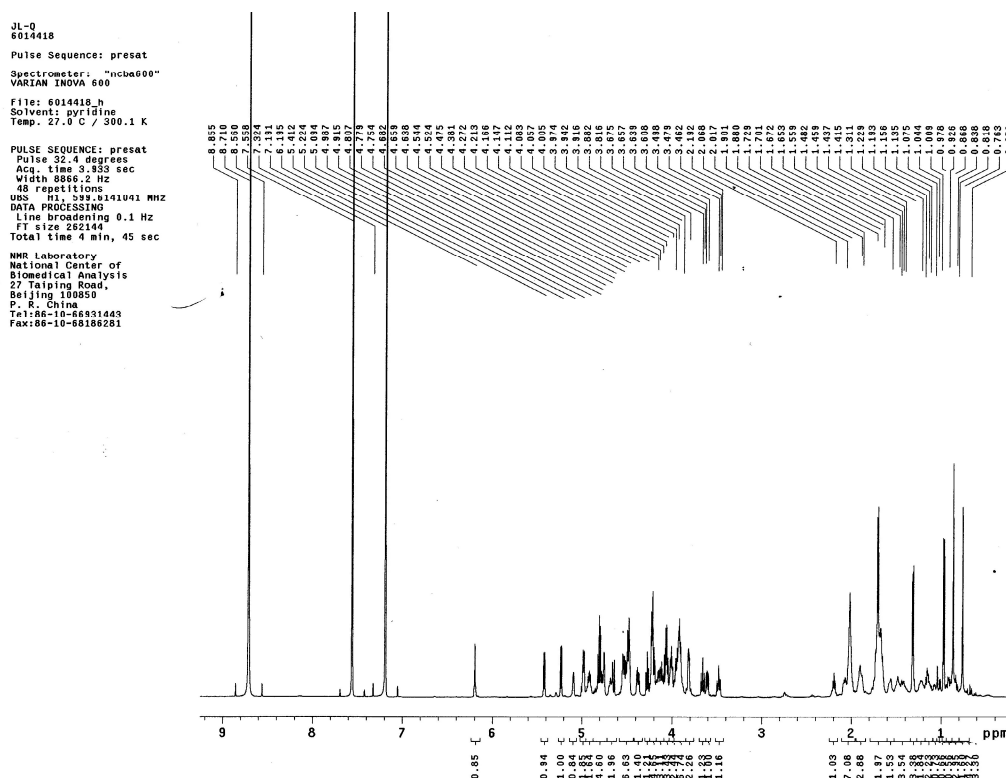
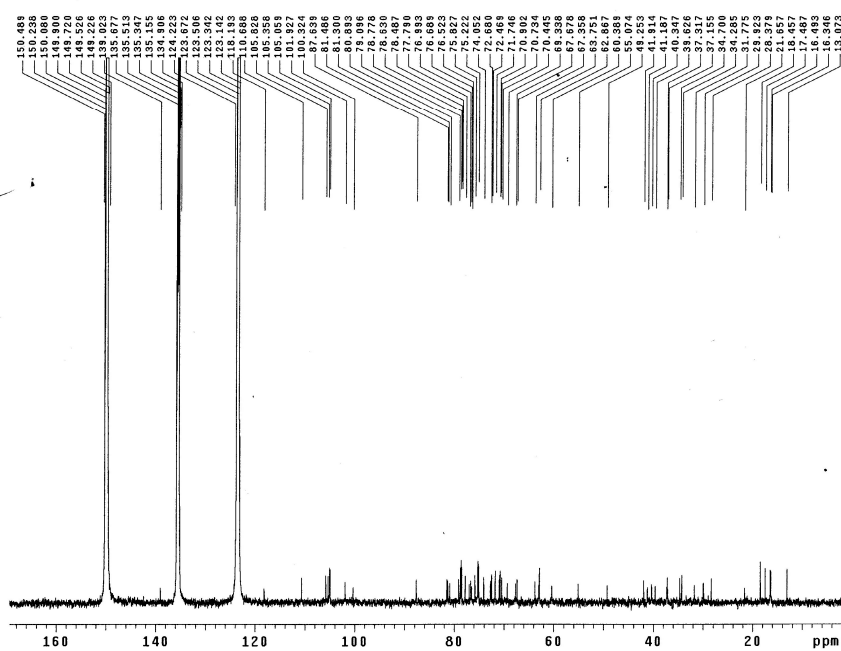
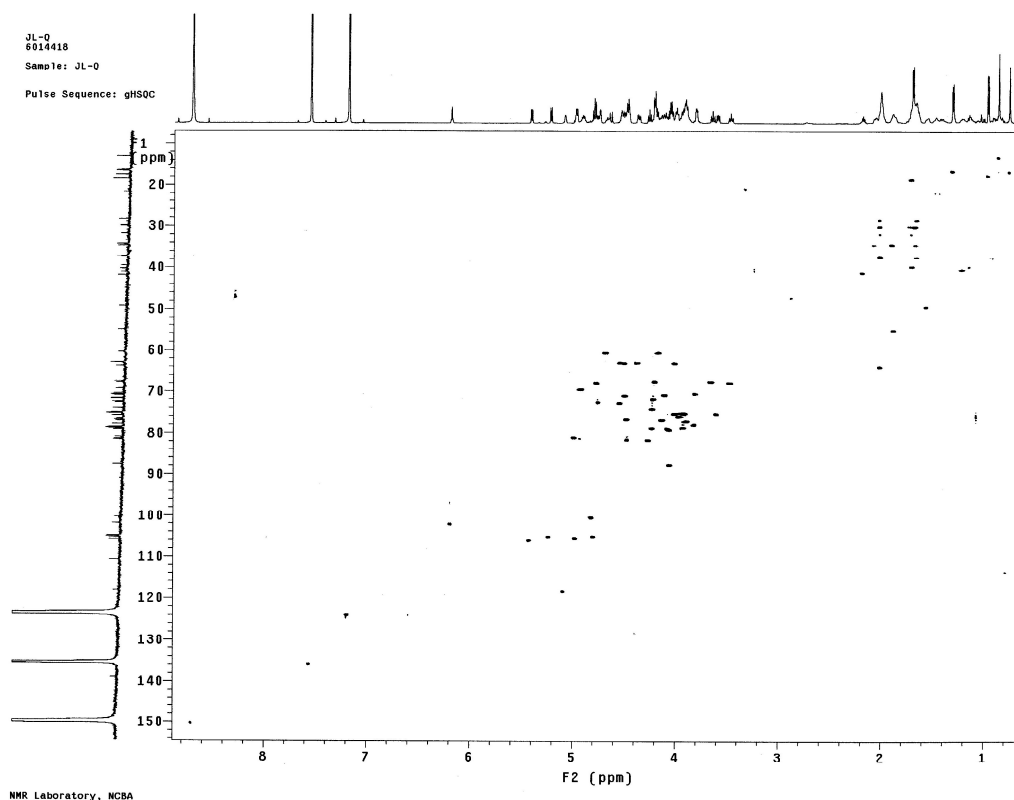
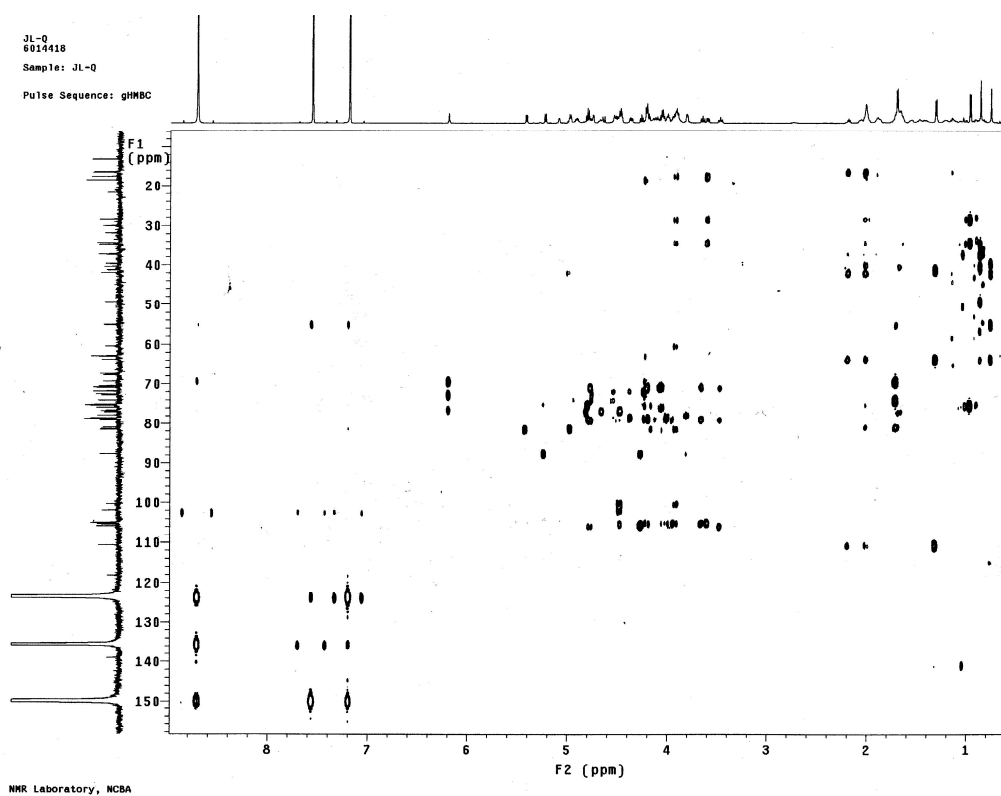
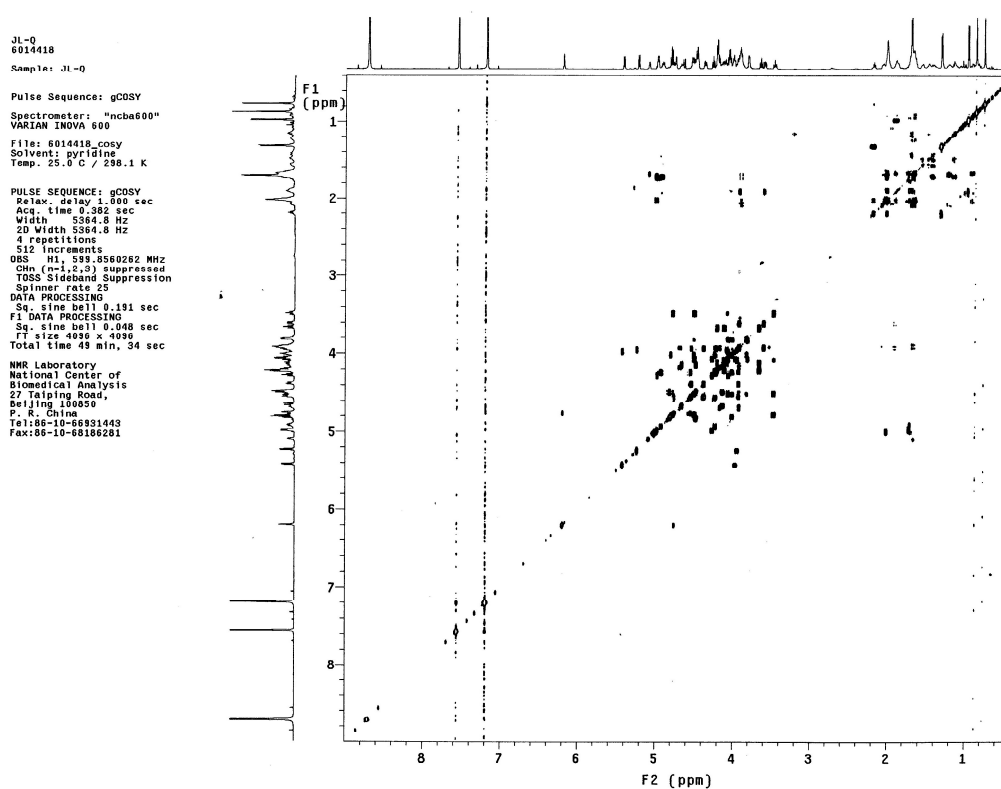


Figure S1. <sup>1</sup>H-NMR spectrum of compound 1 in C<sub>5</sub>D<sub>5</sub>N.

JL-0  
6014418  
Sample directory:  
Pulse Sequence: s2pul  
Spectrometer: "ncha600"  
VARIAN INOVA 600  
File: 6014418.c  
Solvent: pyridine  
Temp: 27.0 C / 300.1 K  
PULSE SEQUENCE  
Relax. delay 0.010 sec  
Pulse 21.1 degrees  
Acq. time 0.789 sec  
Width 40000.0 Hz  
15000 repetitions  
DSS C13, 150.7730500 MHz  
DEC H1, 598.6169152 MHz  
Power 44 dB  
on during acquisition  
off during delay  
GRP-1 modulated  
DATA PROCESSING  
Line broadening 3.0 Hz  
FT size 262144  
Total time 4 hr, 14 min  
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Figure S2.  $^{13}\text{C}$ -NMR spectrum of compound 1 in  $\text{C}_5\text{D}_5\text{N}$ .Figure S3. HSQC spectrum of compound 1 in  $\text{C}_5\text{D}_5\text{N}$ .

Figure S4. HMBC spectrum of compound 1 in C<sub>5</sub>D<sub>5</sub>N.Figure S5. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 1 in C<sub>5</sub>D<sub>5</sub>N.

JL-Q  
6014418  
Pulse Sequence: ROESY  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
File: 6014418\_roesy  
Solvent: pyridine  
Temp: 27.0 C / 300.1 K  
PULSE SEQUENCE: ROESY  
Relax. delay 1.000 sec  
Acq. time 0.342 sec  
Width 5990.7 Hz  
2D Width 5990.7 Hz  
16 repetitions  
2 x 256 increments  
OBS F1, 599.6116264 MHz  
DATA PROCESSING  
Sq. sine bell 0.342 sec  
Shifted by -0.342 sec  
F1 DATA PROCESSING  
Sq. sine bell 0.085 sec  
Shifted by -0.085 sec  
FT size 4096 x 4096  
Total time 3 hr, 52 min  
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Tel: 86-10-66931443  
Fax: 86-10-68186281

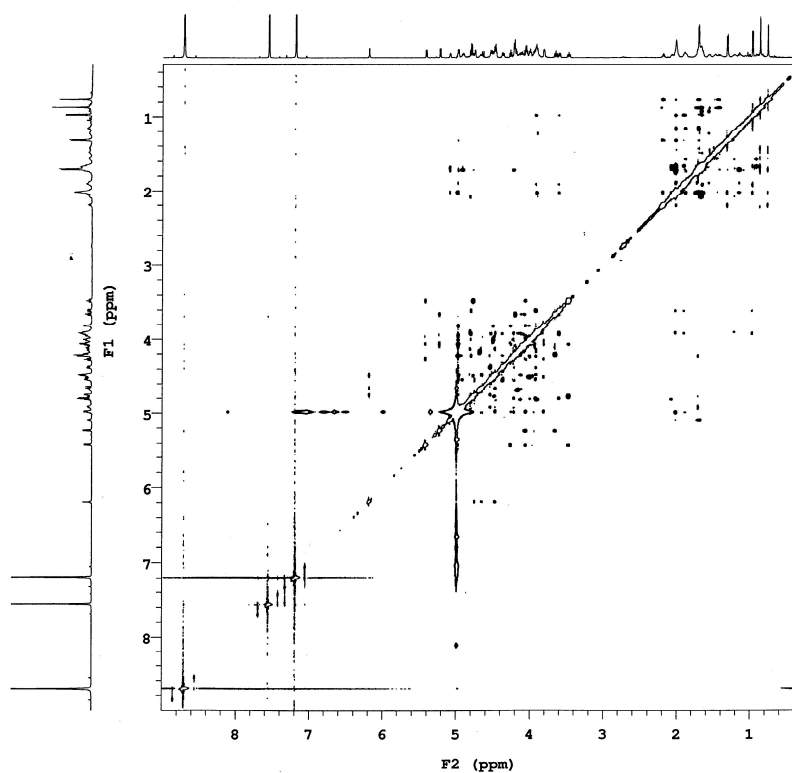


Figure S6. ROESY spectrum of compound 1 in C<sub>5</sub>D<sub>5</sub>N.

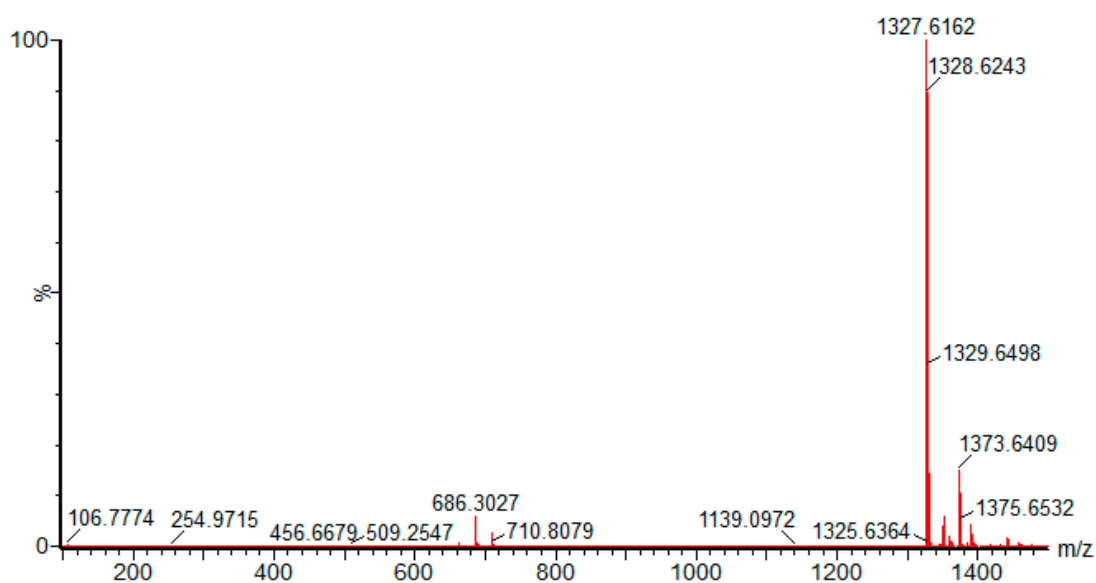


Figure S7. HRMSIMS of compound 1 in CH<sub>3</sub>CN.



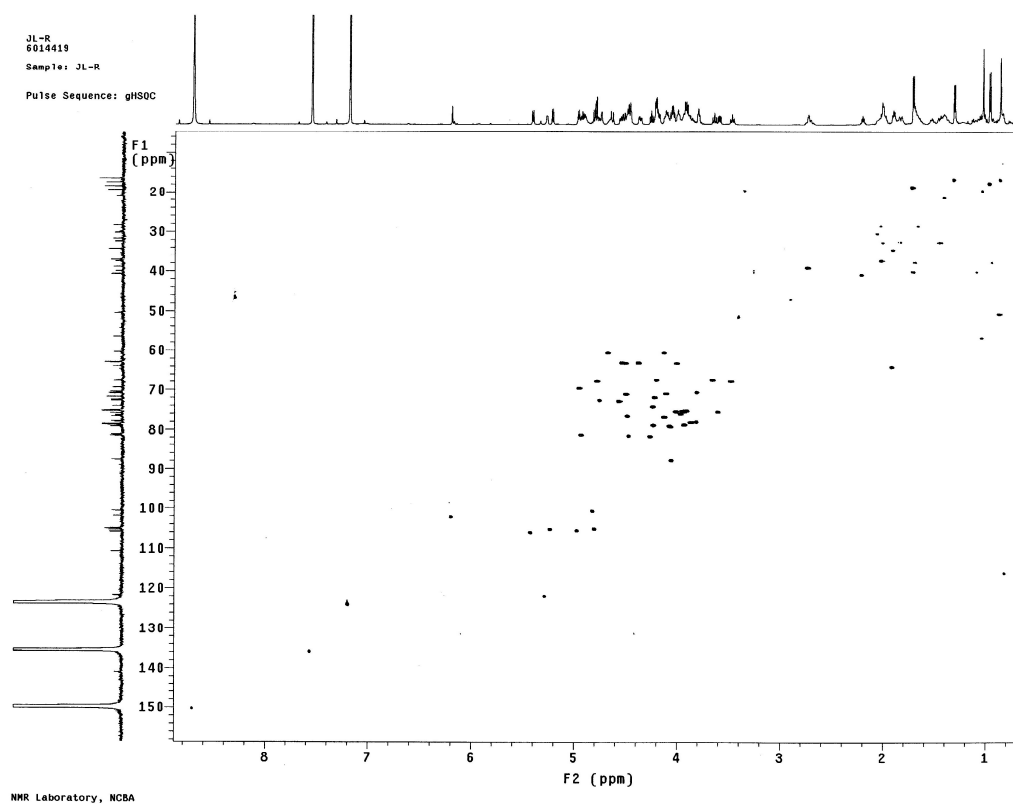


Figure S10. HSQC spectrum of compound 2 in  $C_5D_5N$ .

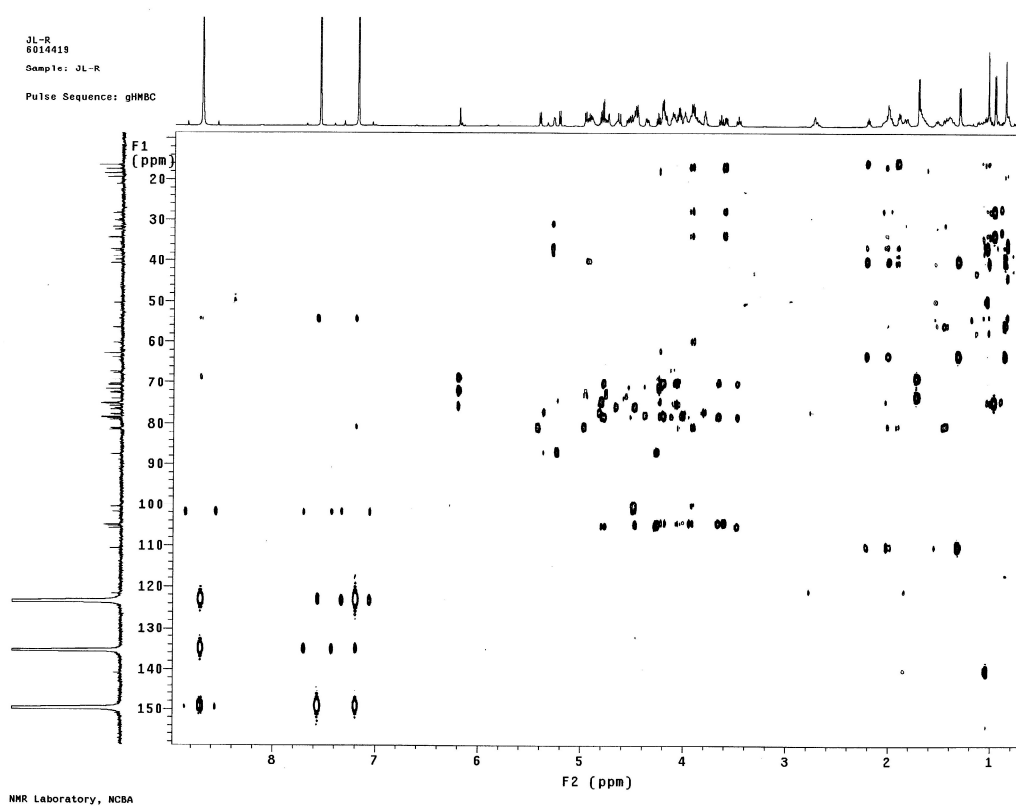
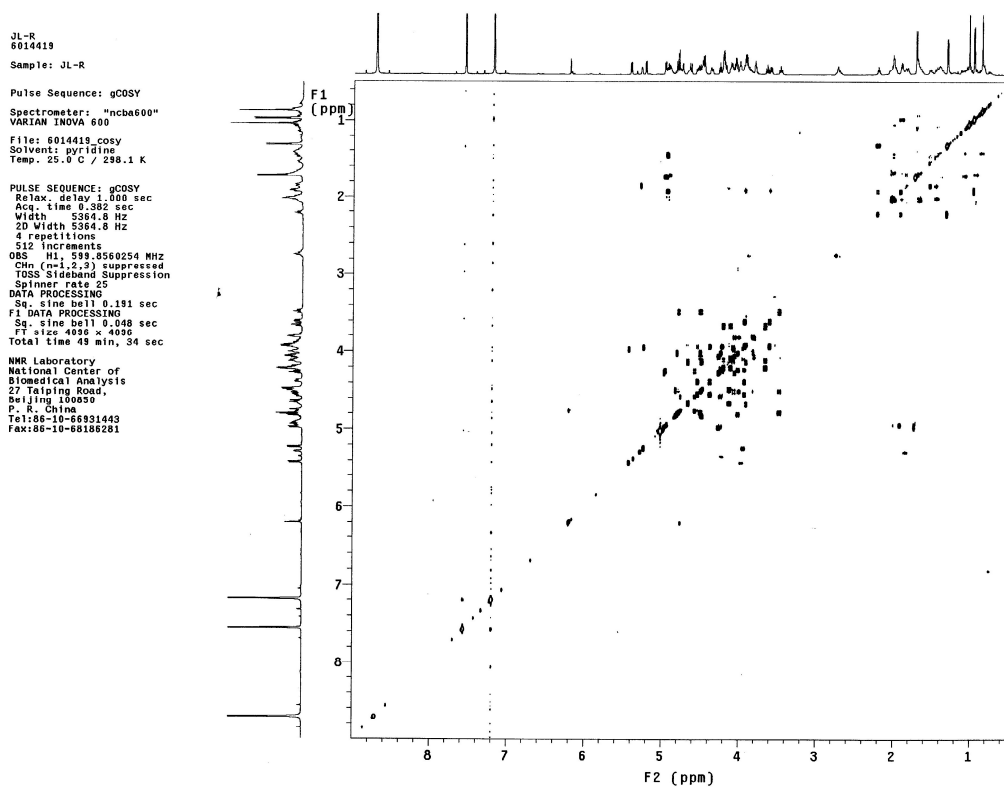
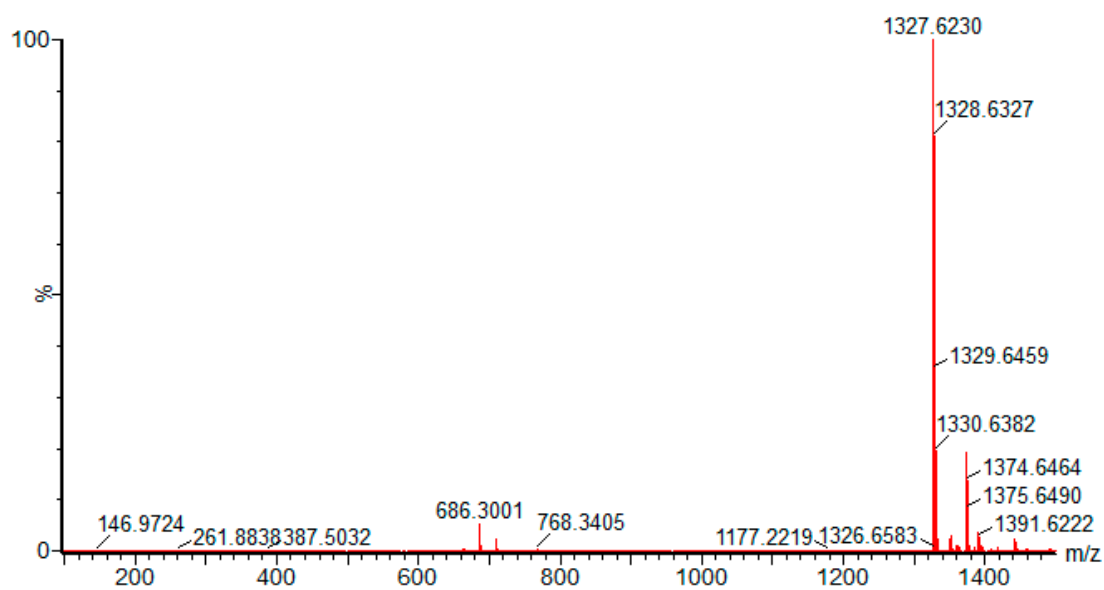
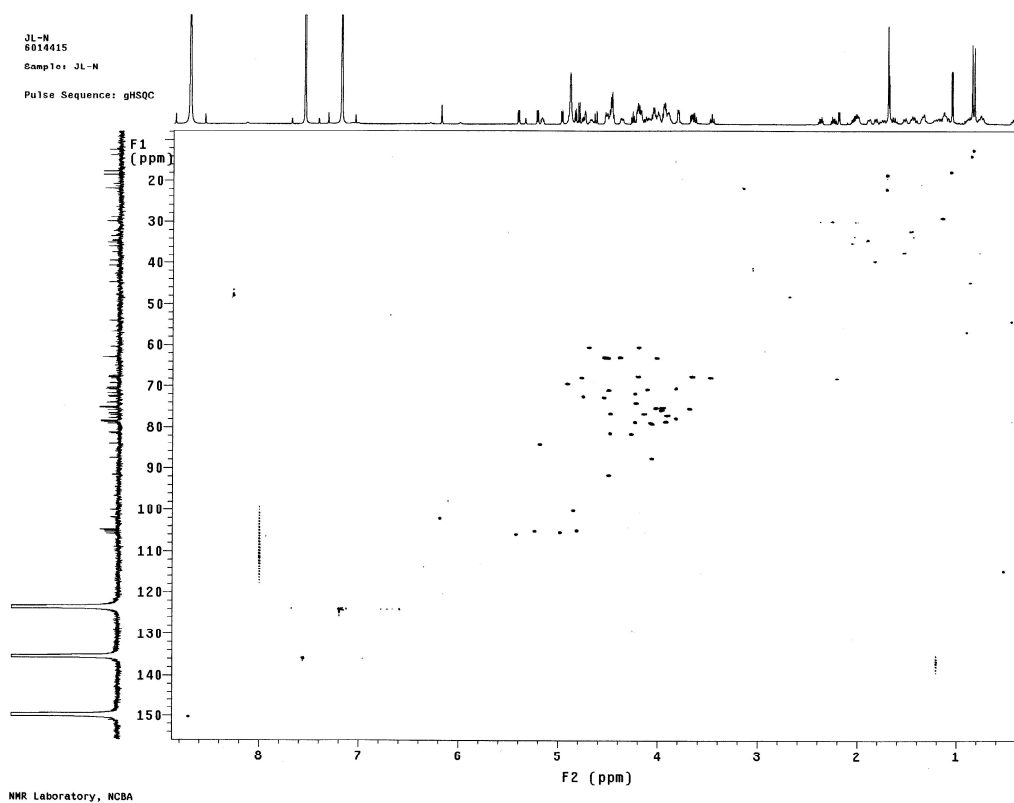
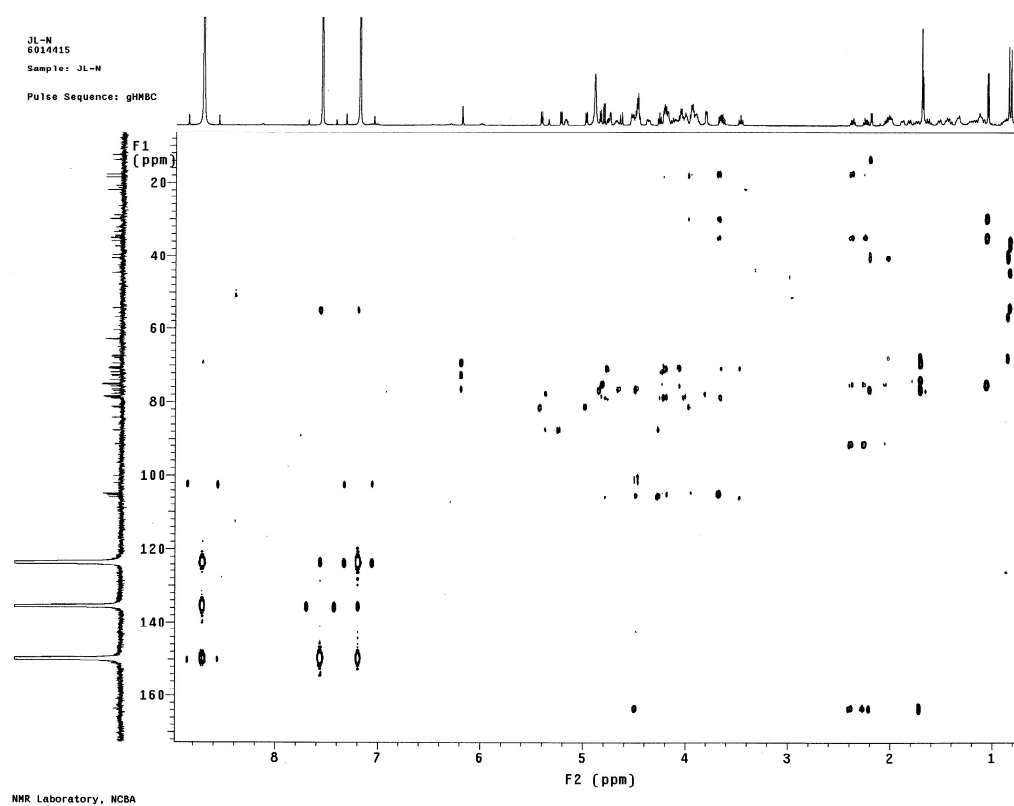


Figure S11. HMBC spectrum of compound 2 in  $C_5D_5N$ .

Figure S12.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 2 in  $\text{C}_5\text{D}_5\text{N}$ .Figure S13. HRESIMS of compound 2 in  $\text{CH}_3\text{CN}$ .





Figure S16. HSQC spectrum of compound 3 in C<sub>5</sub>D<sub>5</sub>N.Figure S17. HMBC spectrum of compound 3 in C<sub>5</sub>D<sub>5</sub>N.

JL-N  
6014415  
Sample: JL-N  
Pulse Sequence: gCOSY  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
File: 6014415\_cosy  
Solvent: pyridine  
Temp. 25.0 C / 298.1 K  
PULSE SEQUENCE: gCOSY  
Relax. delay 1.000 sec  
Acq. time 0.362 sec  
Width 5364.8 Hz  
2D Width 5364.8 Hz  
4 repetitions  
512 increments  
OBS H1, 599.8560272 MHz  
Chn (ns1,2,3) suppressed  
Spinner rate 25  
DATA PROCESSING  
Sq. sine bell 0.191 sec  
F1 DATA PROCESSING  
Sq. sine bell 0.024 sec  
F1 size 4096 x 4096  
Total time 48 min, 34 sec  
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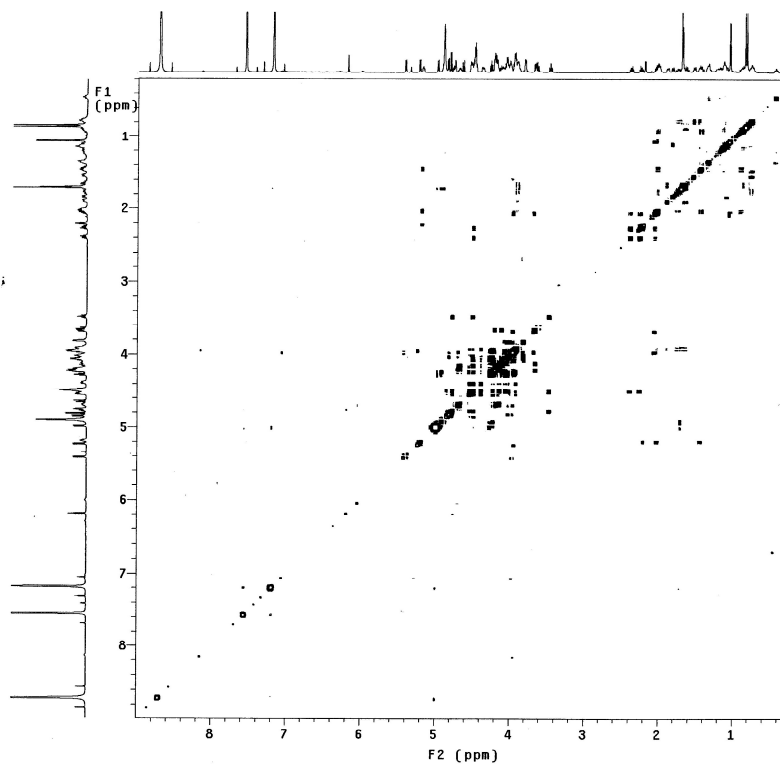


Figure S18.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 3 in  $\text{C}_5\text{D}_5\text{N}$ .

JL-N  
6014415  
Pulse Sequence: ROESY  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
File: 6014415\_rossy  
Solvent: pyridine  
Temp. 27.0 C / 300.1 K  
PULSE SEQUENCE: ROESY  
Relax. delay 1.000 sec  
Acq. time 0.154 sec  
Width 6630.8 Hz  
2D Width 6630.8 Hz  
32 repetitions  
2 x 200 increments  
OBS H1, 599.6116277 MHz  
DATA PROCESSING  
Sq. sine bell 0.154 sec  
Shifted by -0.154 sec  
F1 DATA PROCESSING  
Sq. sine bell 0.060 sec  
Shifted by -0.060 sec  
F1 size 2048 x 2048  
Total time 5 hr, 22 min  
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Biomedical Analysis  
27 Taiping Road,  
Beijing 100850  
P. R. China  
Tel:86-10-66931443  
Fax:86-10-68186281

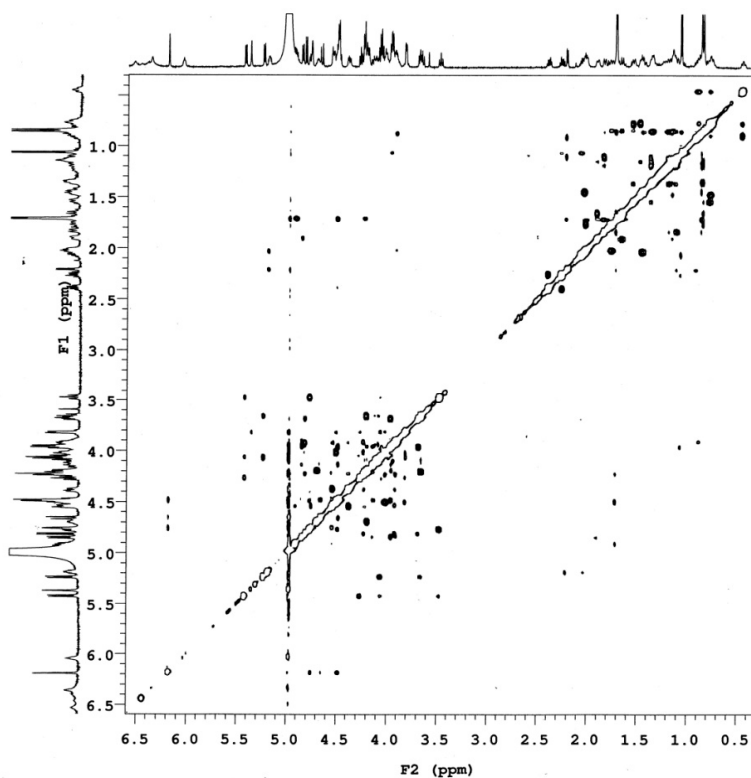
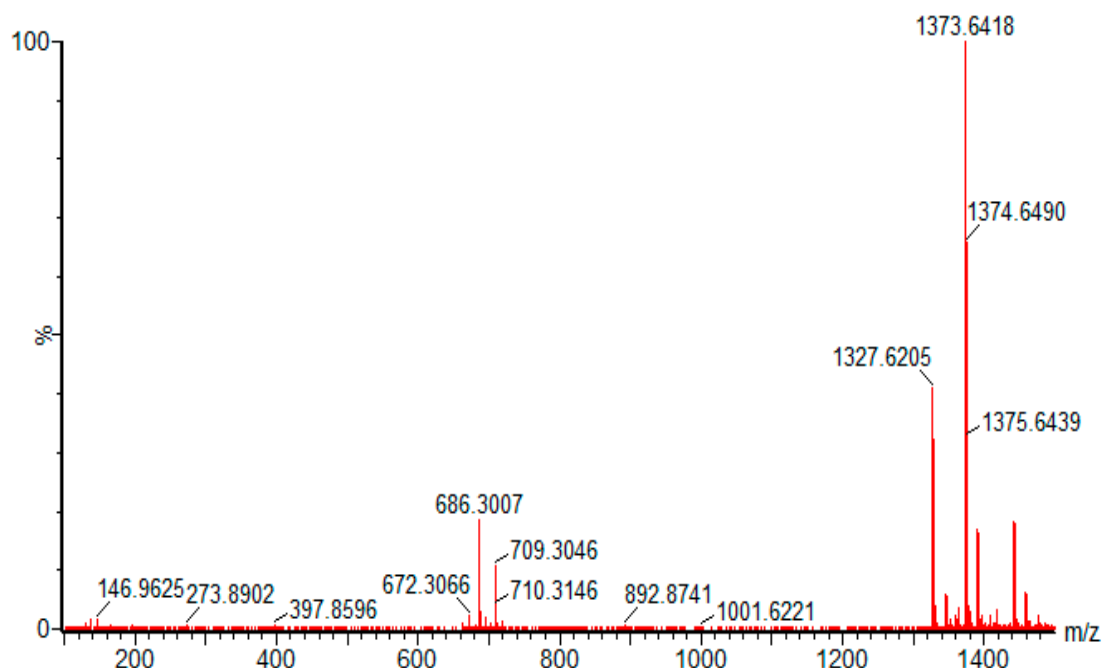
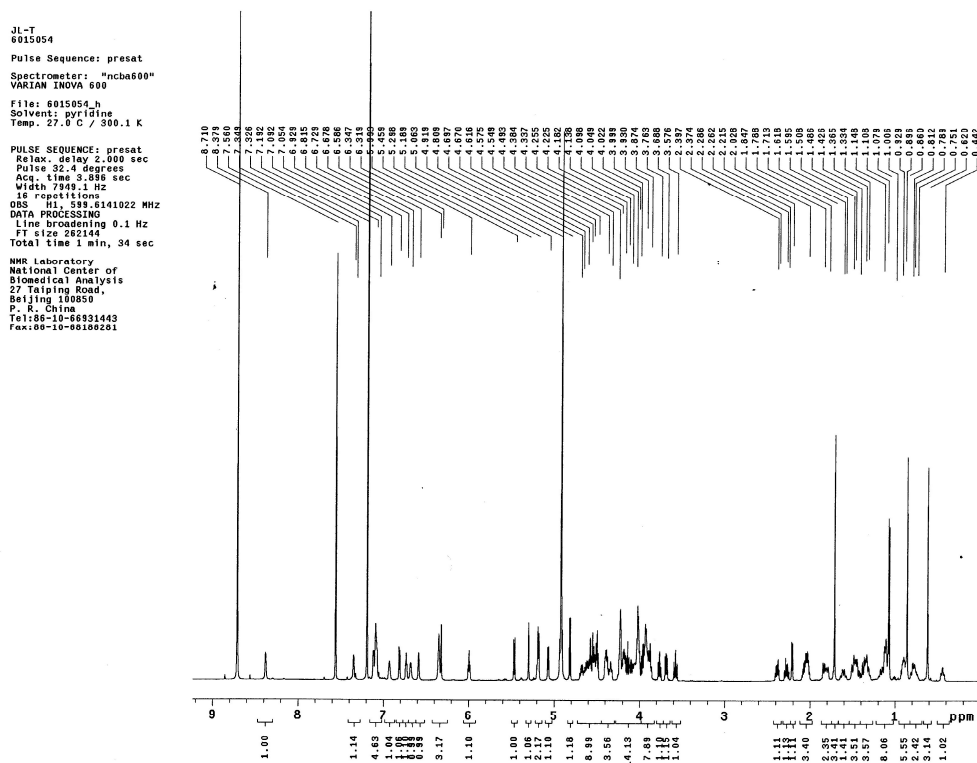
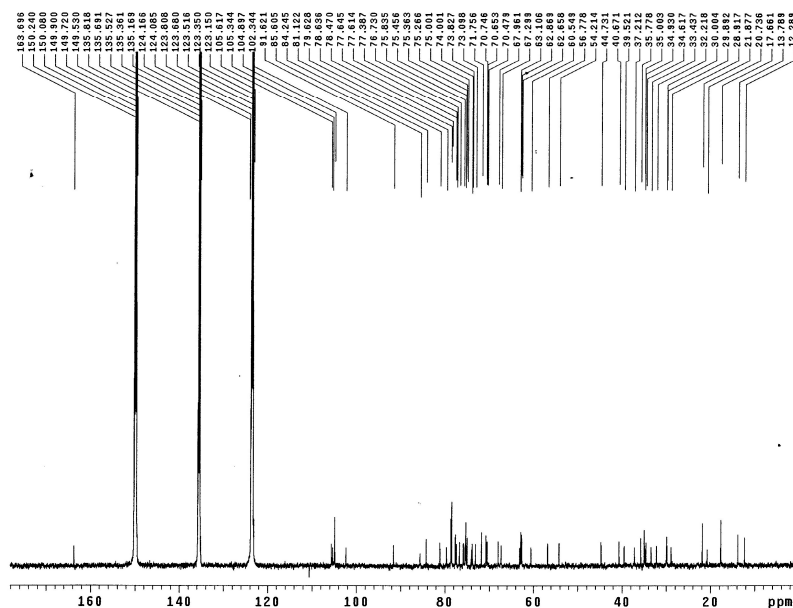
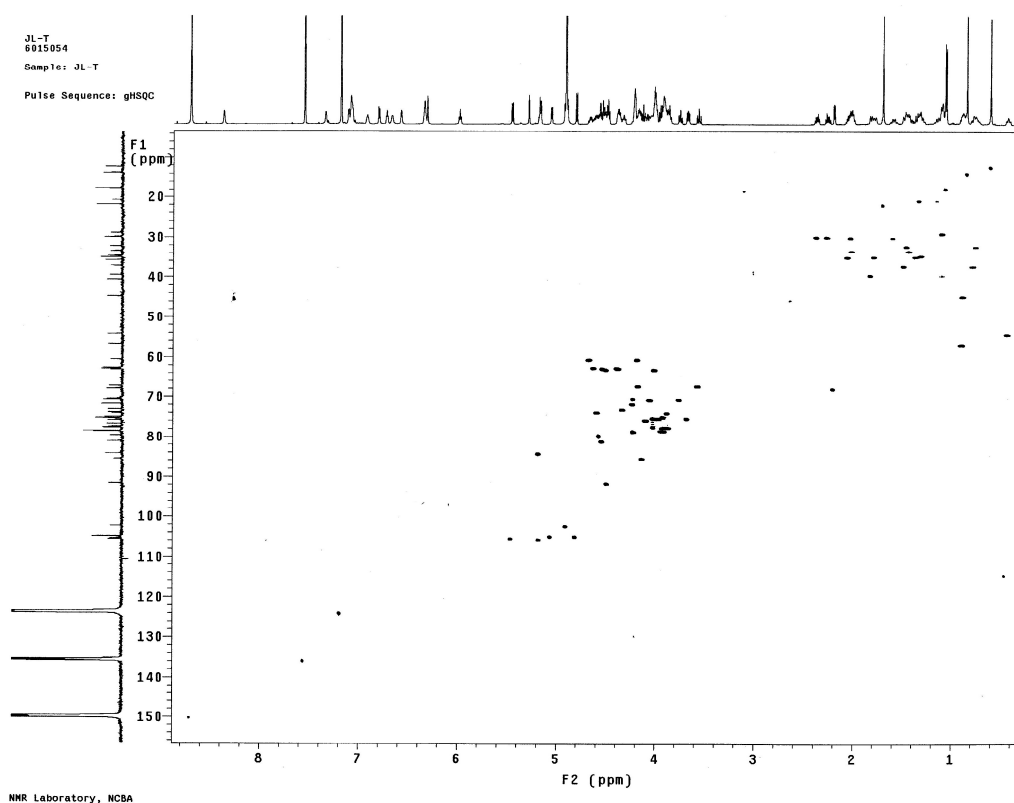


Figure S19. ROESY spectrum of compound 3 in  $\text{C}_5\text{D}_5\text{N}$ .

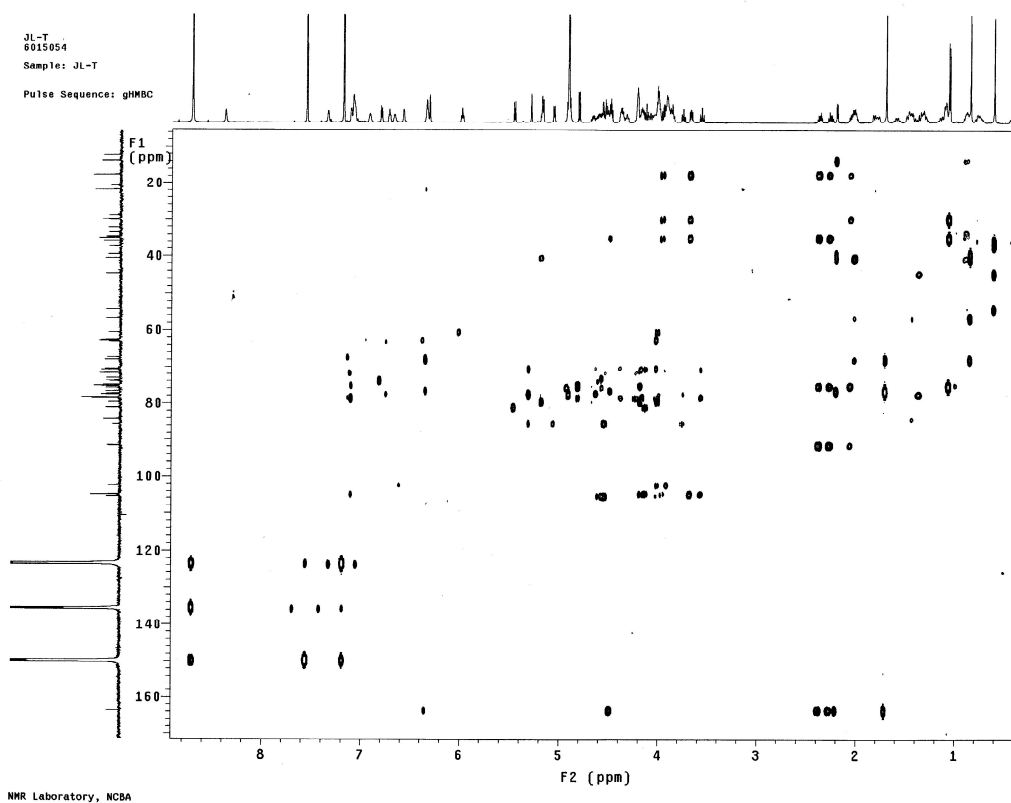
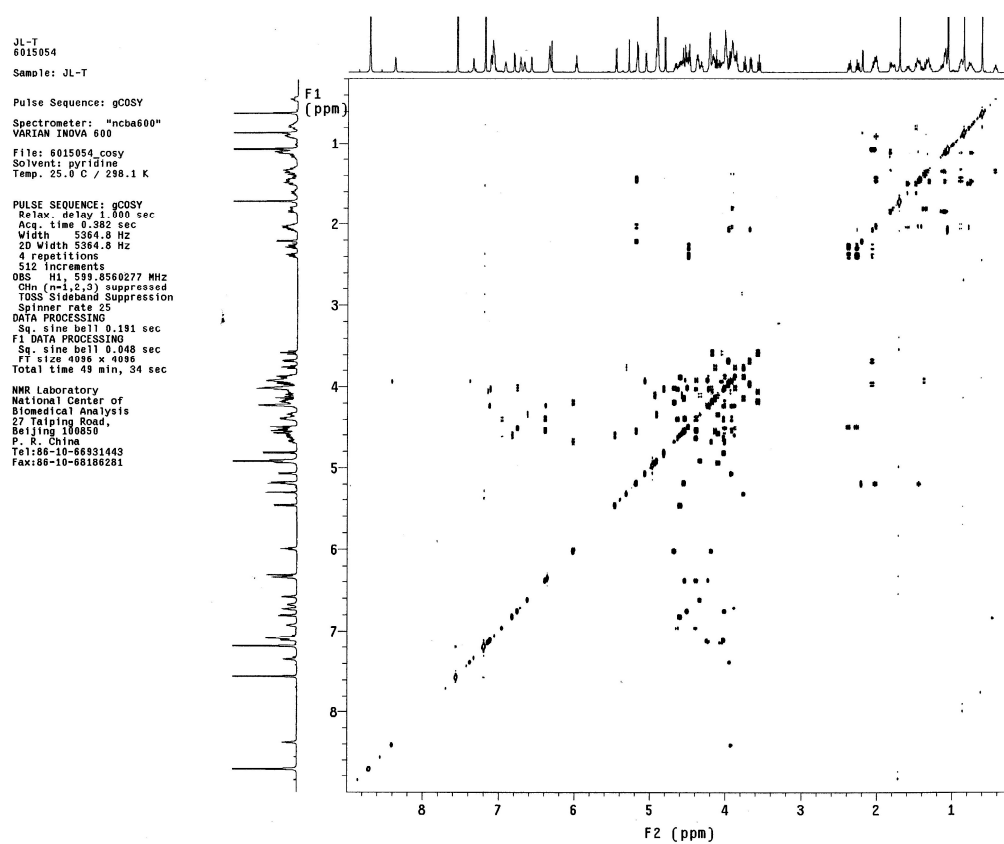
Figure S20. HRESIMS of compound 3 in CH<sub>3</sub>CN.Figure S21. <sup>1</sup>H-NMR spectrum of compound 4 in C<sub>5</sub>D<sub>5</sub>N.

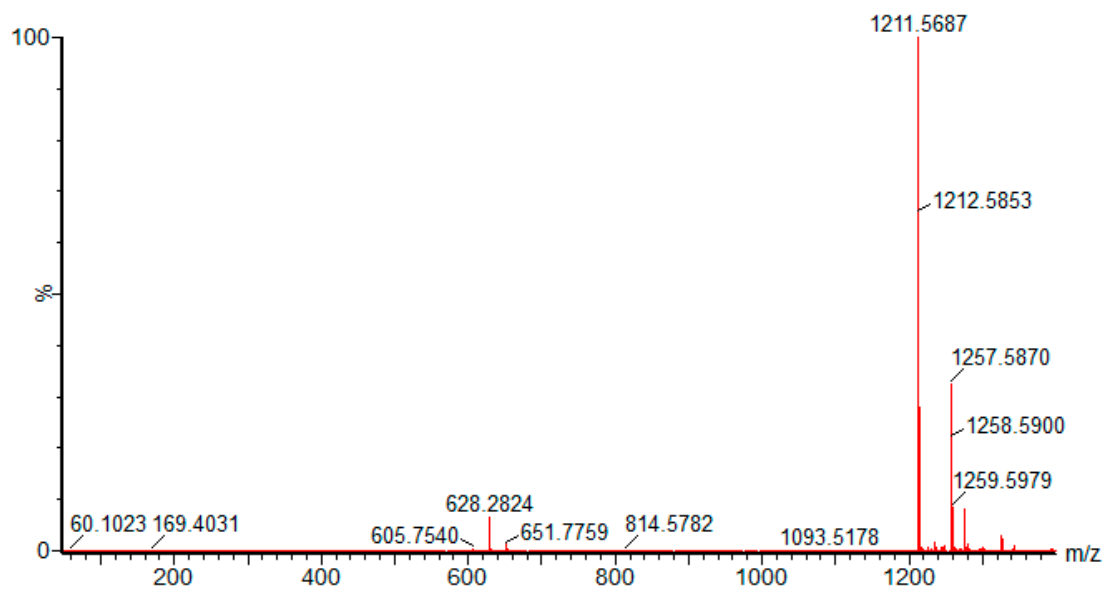
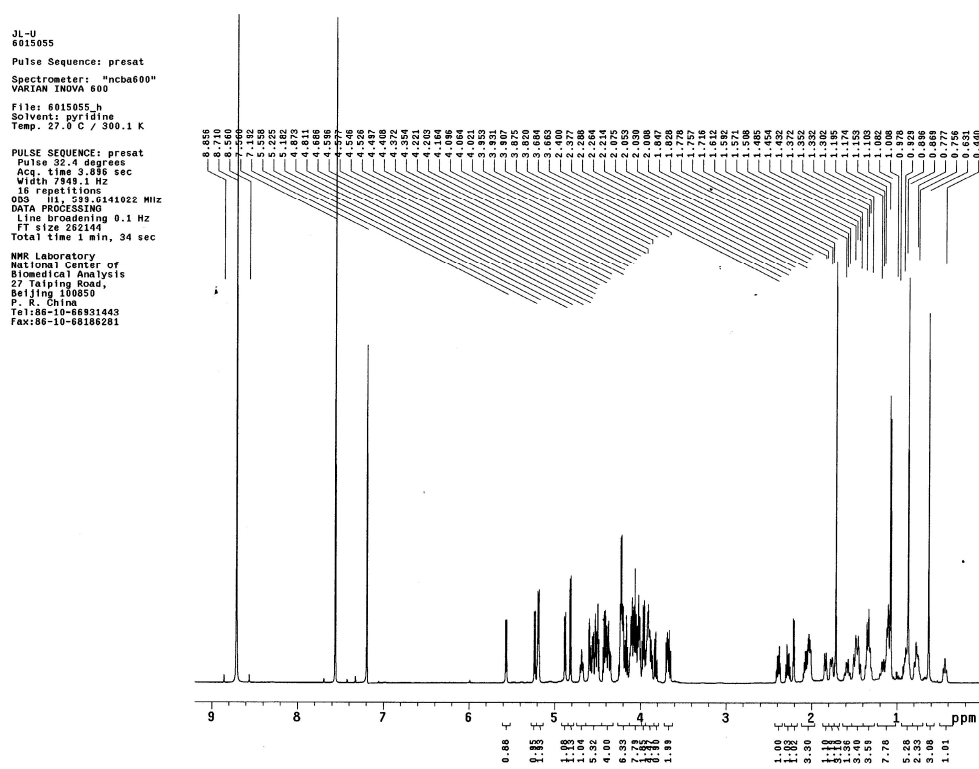
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6015054  
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Pulse Sequence: s2pul  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
Solvent: pyridine  
Temp. 27.0 C / 300.1 K  
PULSE SEQUENCE  
Relax. delay 0.010 sec  
Pulse 21.1 degrees  
Acq. time 0.739 sec  
Width 40000.0 Hz  
3256 repetitions  
OBS C13, 150.7728205 MHz  
DEC H1, 599.6169152 MHz  
Power 44 dB  
on during acquisition  
off during delay  
GARP-1 modulated  
DATA PROCESSING  
Line broadening 3.0 Hz  
FT size 262144  
Total time 2 hr, 48 min  
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Figure S22.  $^{13}\text{C}$ -NMR spectrum of compound 4 in  $\text{C}_5\text{D}_5\text{N}$ .

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Figure S23. HSQC spectrum of compound 4 in  $\text{C}_5\text{D}_5\text{N}$ .

Figure S24. HMBC spectrum of compound 4 in C<sub>5</sub>D<sub>5</sub>N.Figure S25. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 4 in C<sub>5</sub>D<sub>5</sub>N.

Figure S26. HRESIMS of compound 4 in CH<sub>3</sub>CN.Figure S27. <sup>1</sup>H-NMR spectrum of compound 5 in C<sub>5</sub>D<sub>5</sub>N.

JL-U  
6015055  
Sample directory:  
File: PROTON  
Pulse Sequence: s2pul  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
Solvent: pyridine  
Temp. 27.0 C / 300.1 K

PULSE SEQUENCE  
Relax. delay 0.010 sec  
Pulse 21.3 degrees  
Acq. time 0.739 sec  
Width 40000.0 Hz  
3200 repetitions  
OBS C13, 150.7728205 MHz  
DEC H1, 599.6189152 MHz  
Power 44 dB  
on during acquisition  
off during delay  
GARP-1 modulated  
DATA PROCESSING  
Line broadening 3.0 Hz  
FT size 262144  
Total time 2 hr, 49 min

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Fax:86-10-66186281

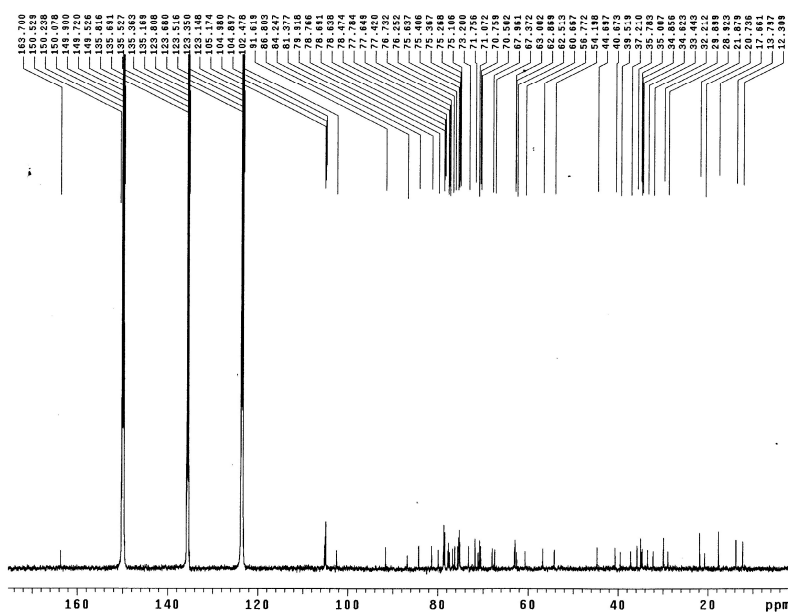


Figure S28.  $^{13}\text{C}$ -NMR spectrum of compound 5 in  $\text{C}_5\text{D}_5\text{N}$ .

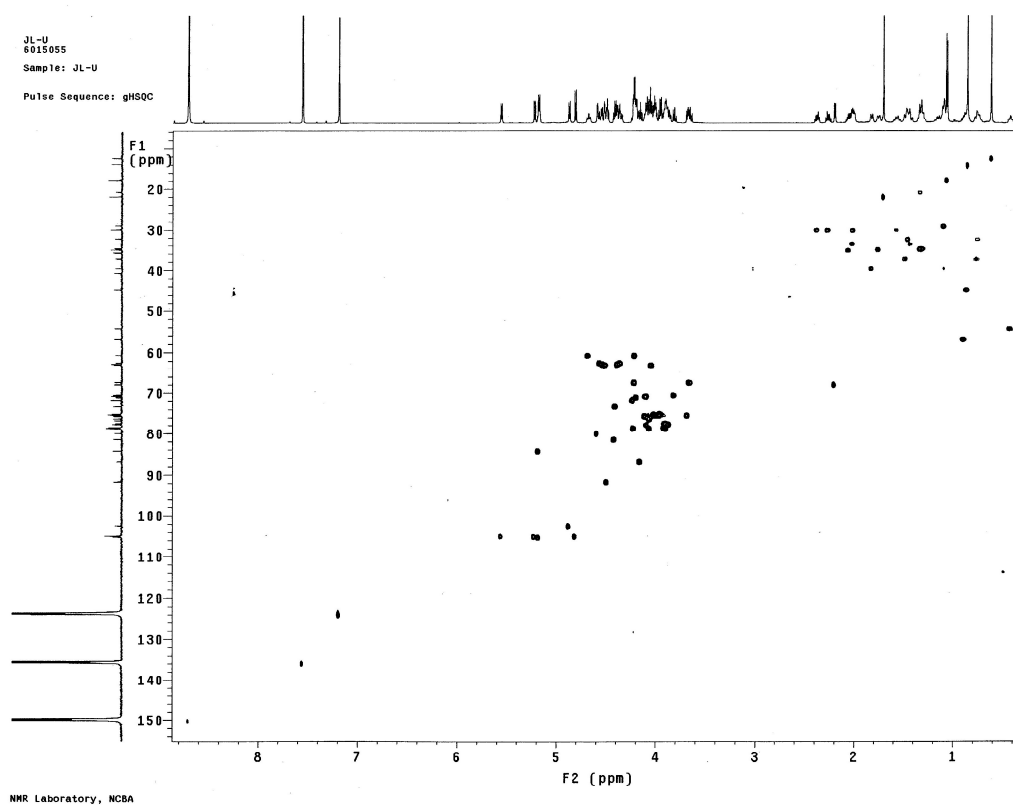
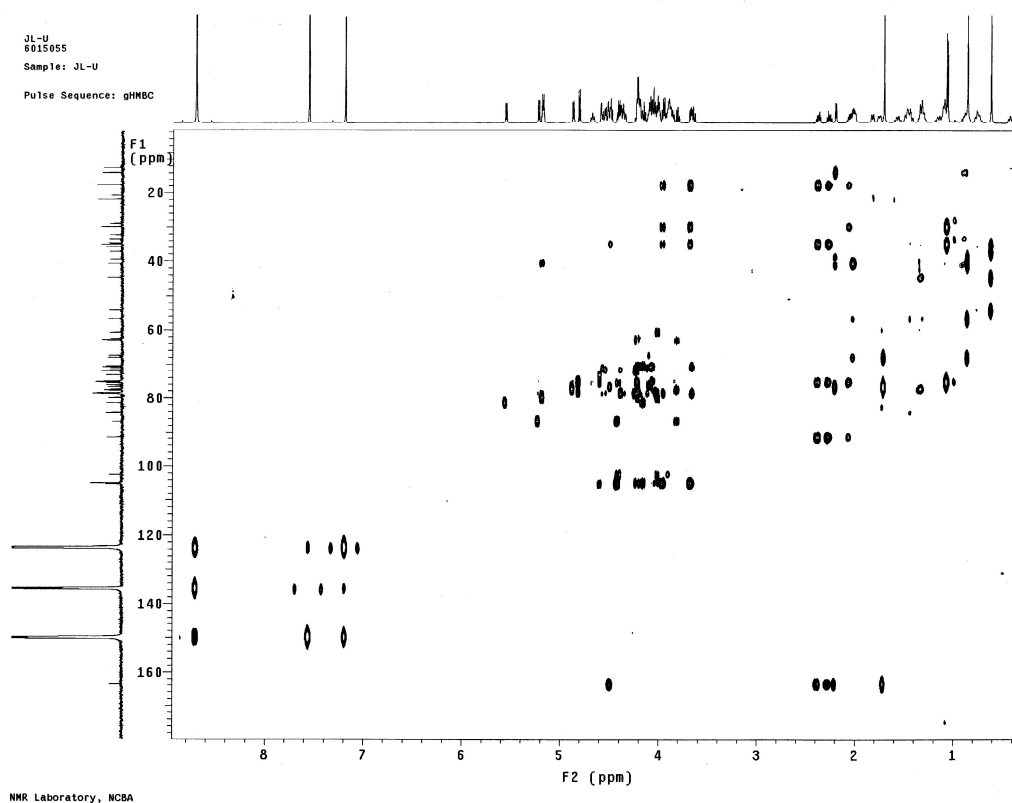
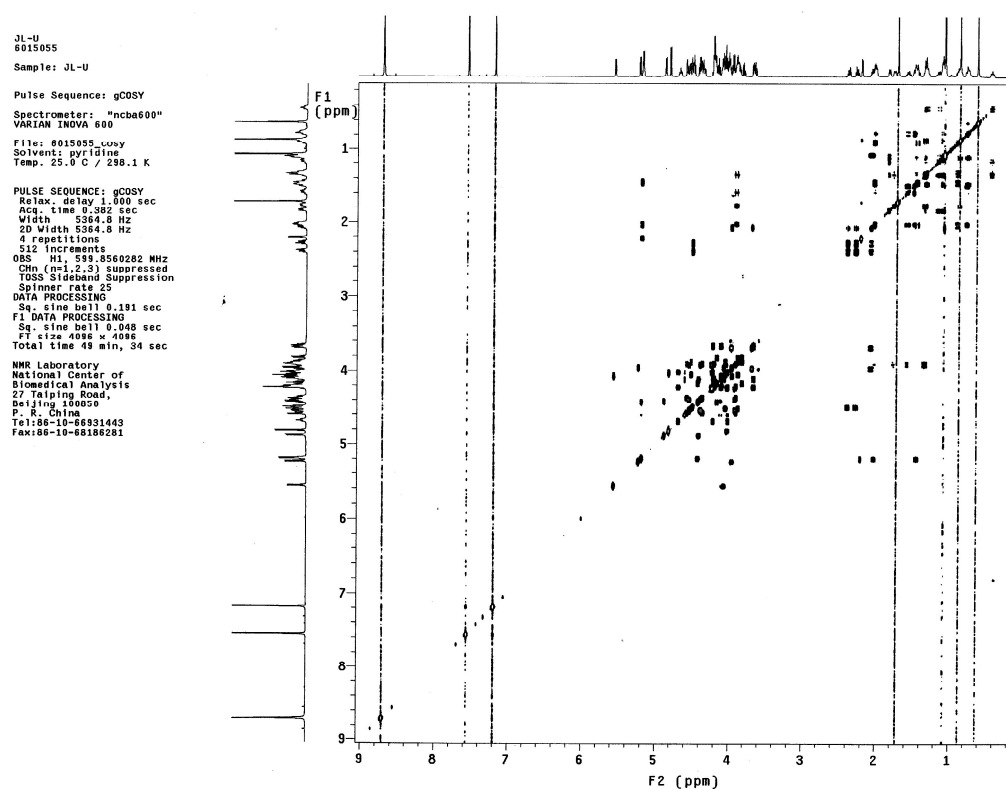
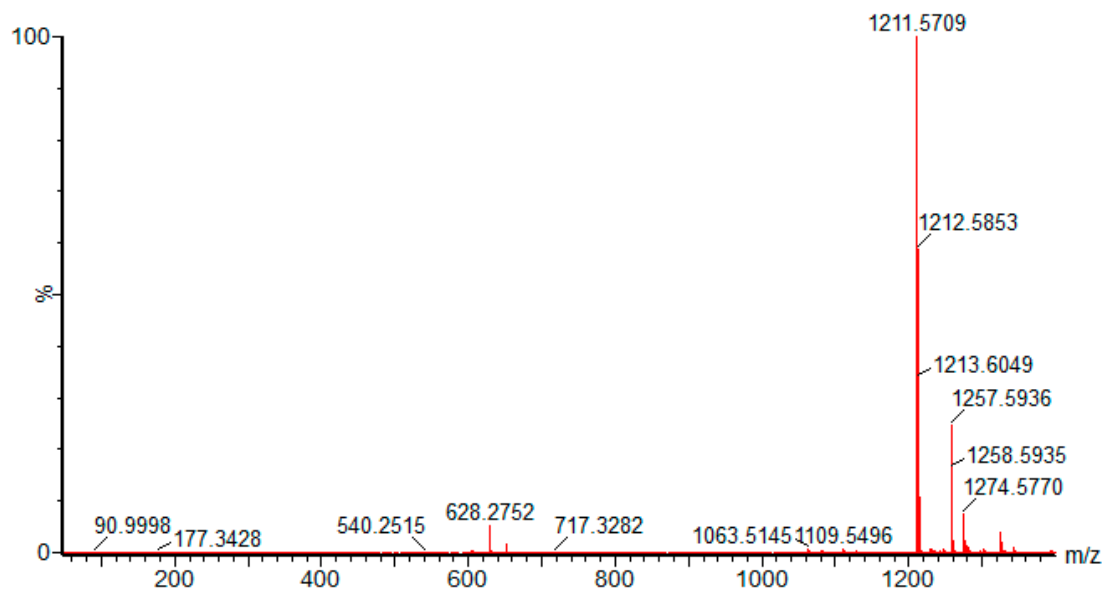


Figure S29. HSQC spectrum of compound 5 in  $\text{C}_5\text{D}_5\text{N}$ .

Figure S30. HMBC spectrum of compound 5 in C<sub>5</sub>D<sub>5</sub>N.Figure S31. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 5 in C<sub>5</sub>D<sub>5</sub>N.

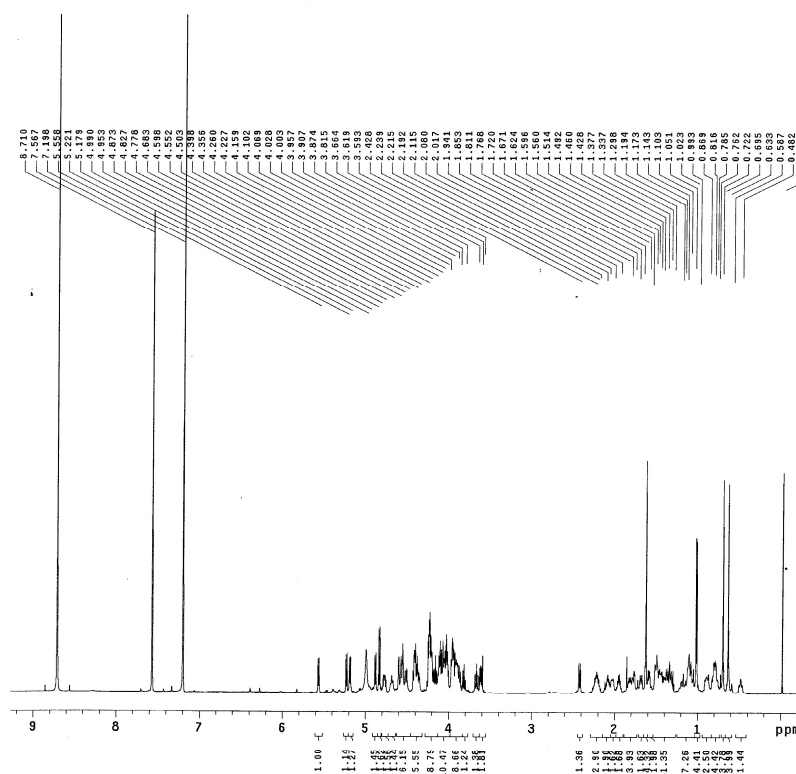


Figure S32. HRESIMS of compound 5 in CH<sub>3</sub>CN.

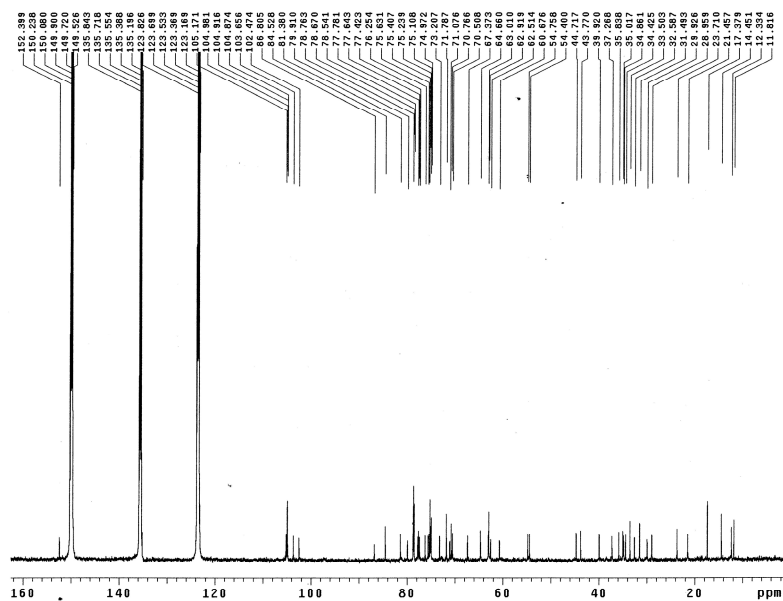
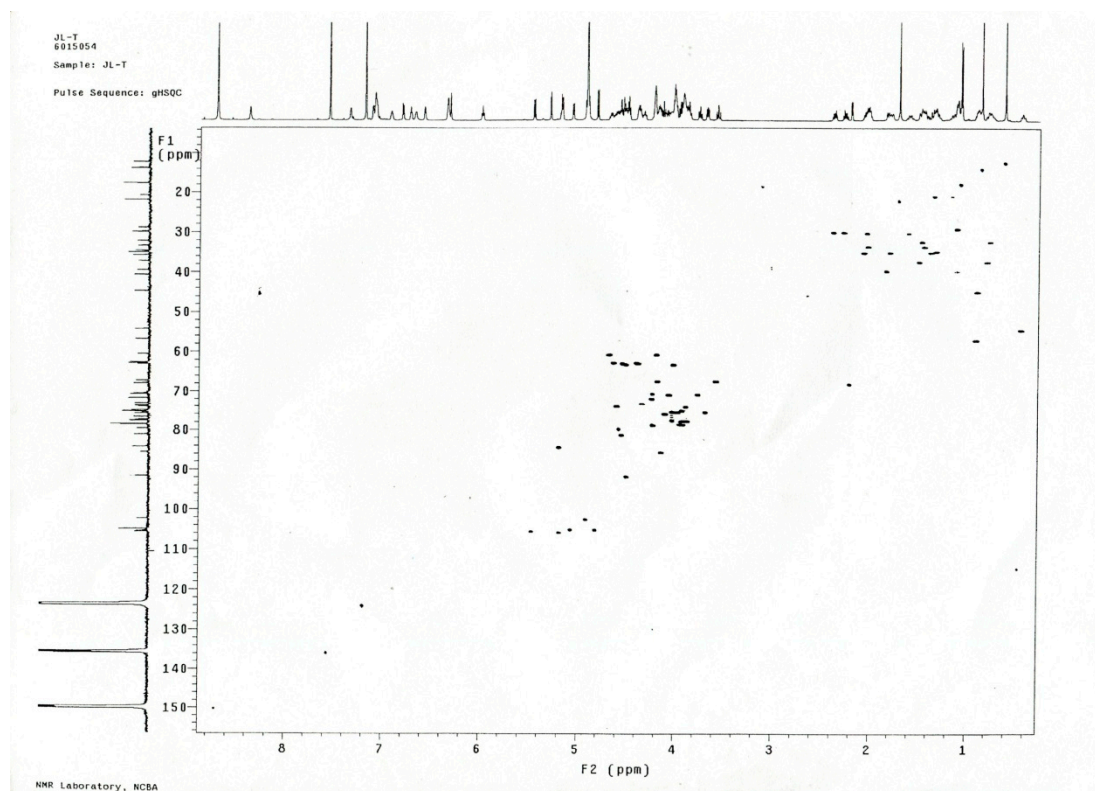
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6014324  
Pulse Sequence: presat  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
File: 6014324.h  
Solvent: pyridine  
Temp: 27.0 C / 300.1 K

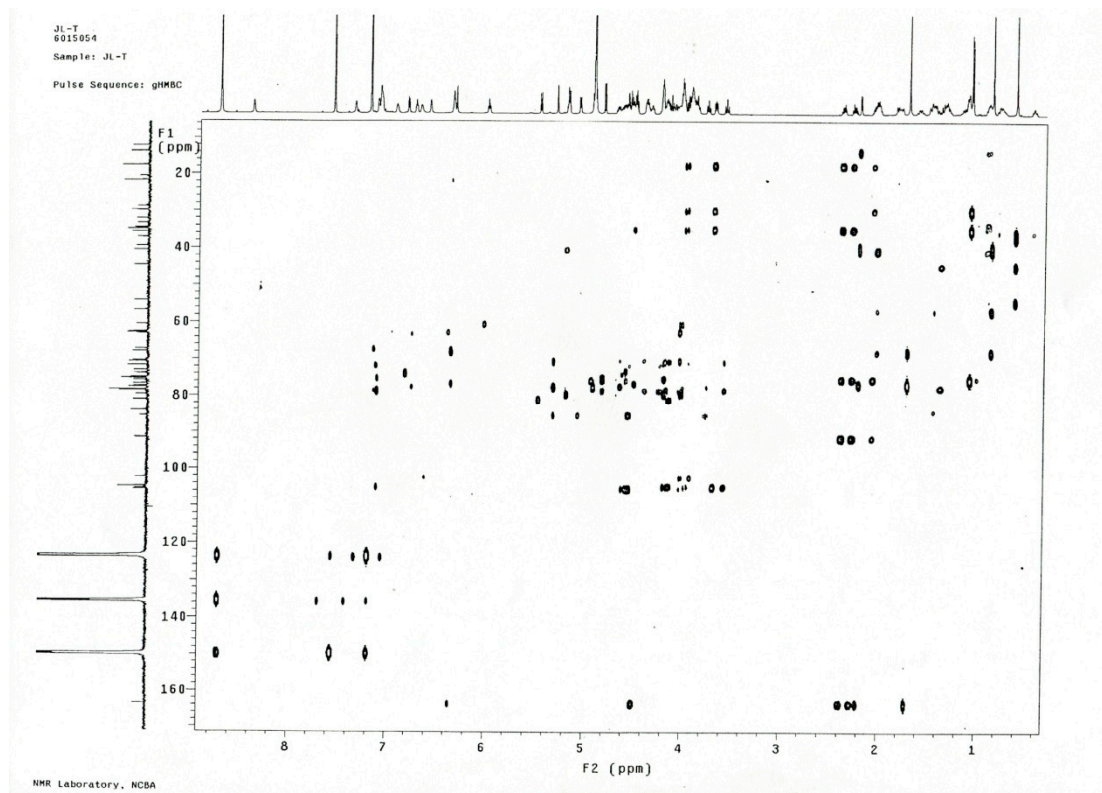
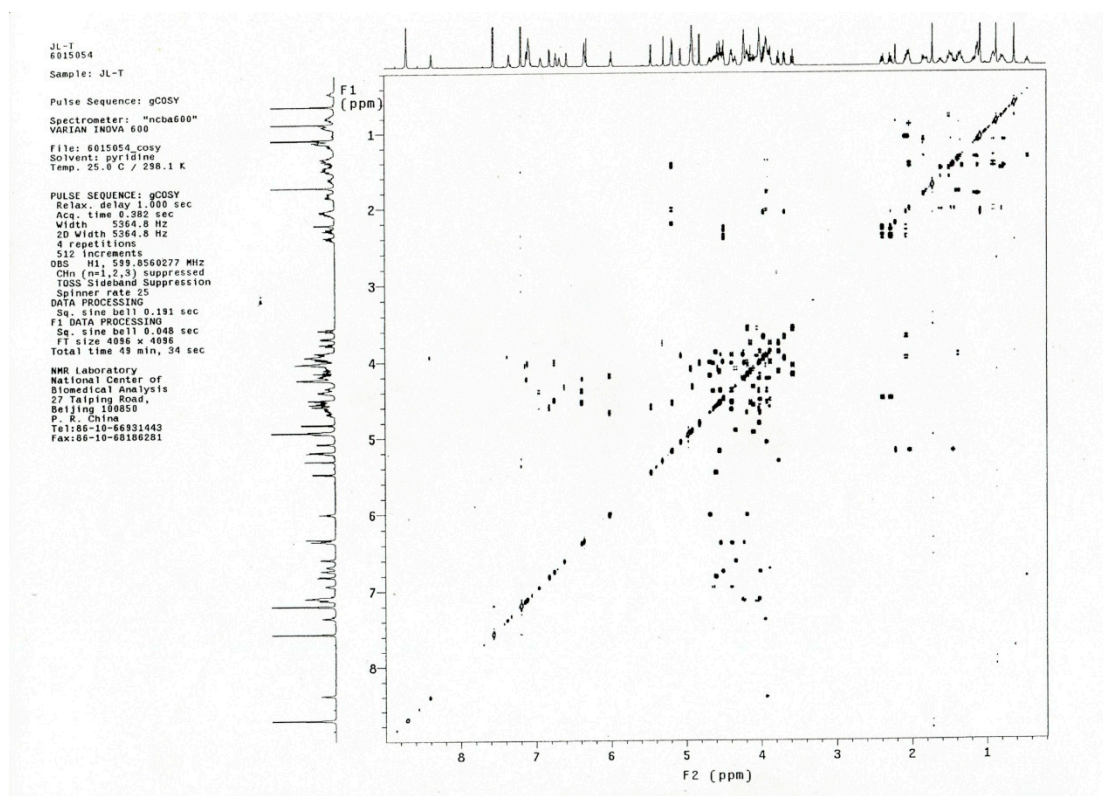
PULSE SEQUENCE: presat  
Pulse 32.4 degrees  
Acq. time 3.692 sec  
Width 8036.6 Hz  
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Obs F1: 599.6131982 MHz  
DATA PROCESSING  
Line broadening 0.1 Hz  
Total time 1 min, 34 sec

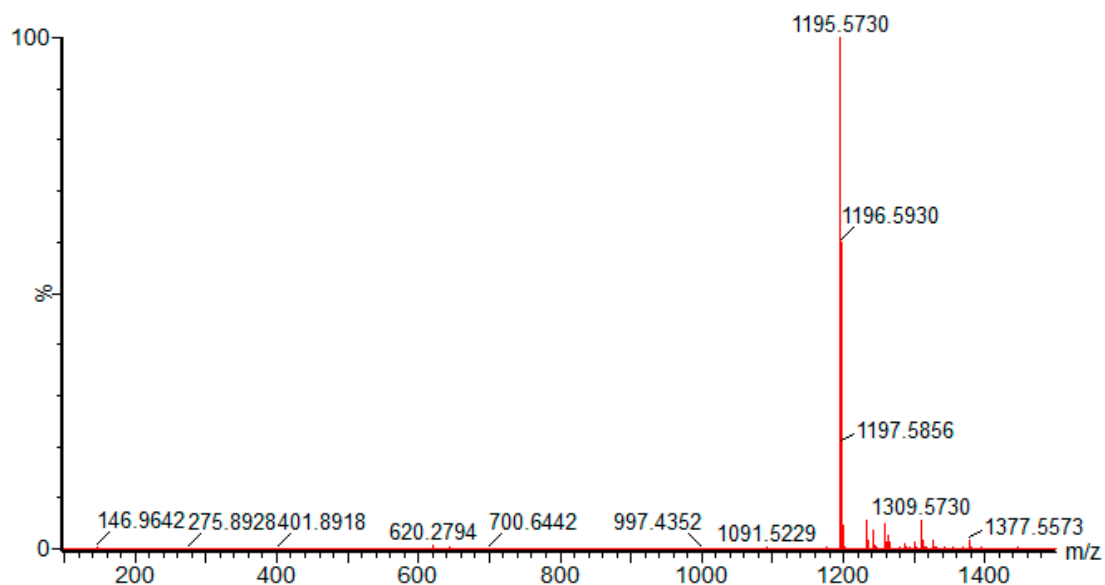
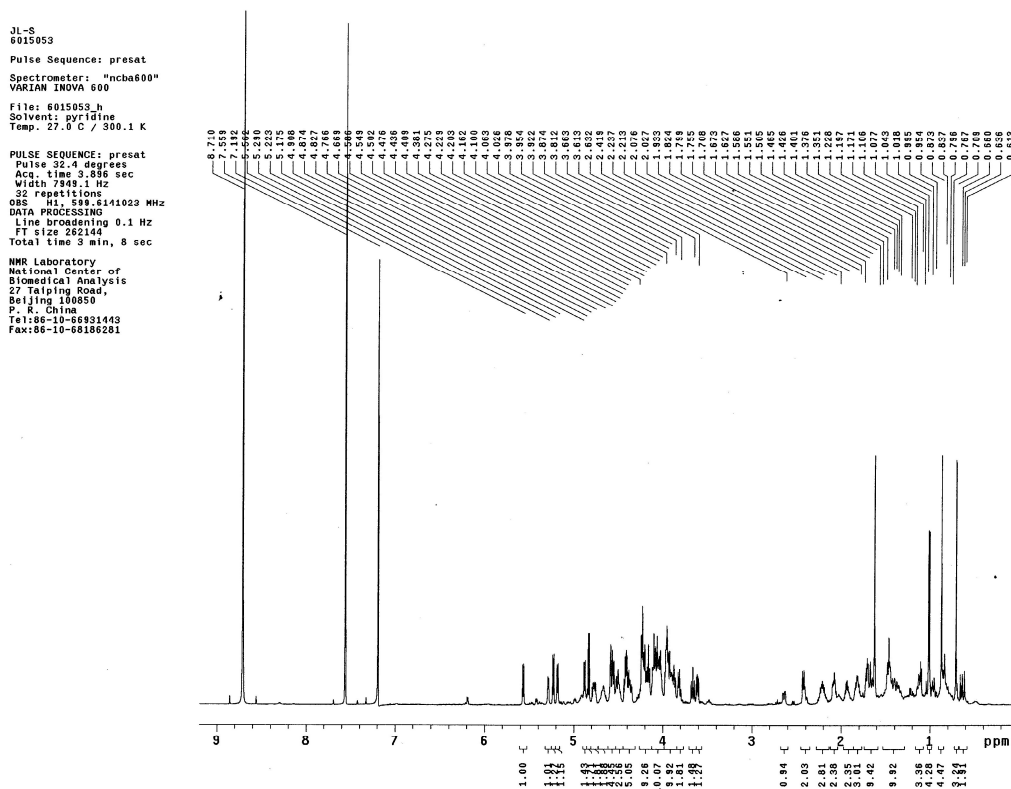
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Beijing 100850  
P. R. China  
Tel:86-10-66931443  
Fax:86-10-66186261

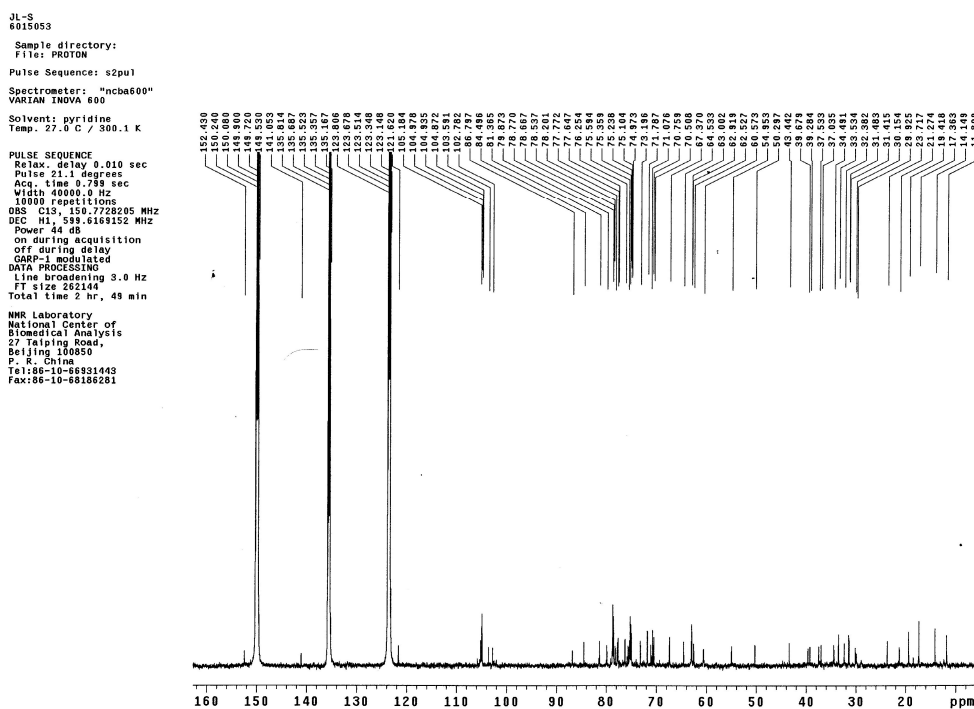
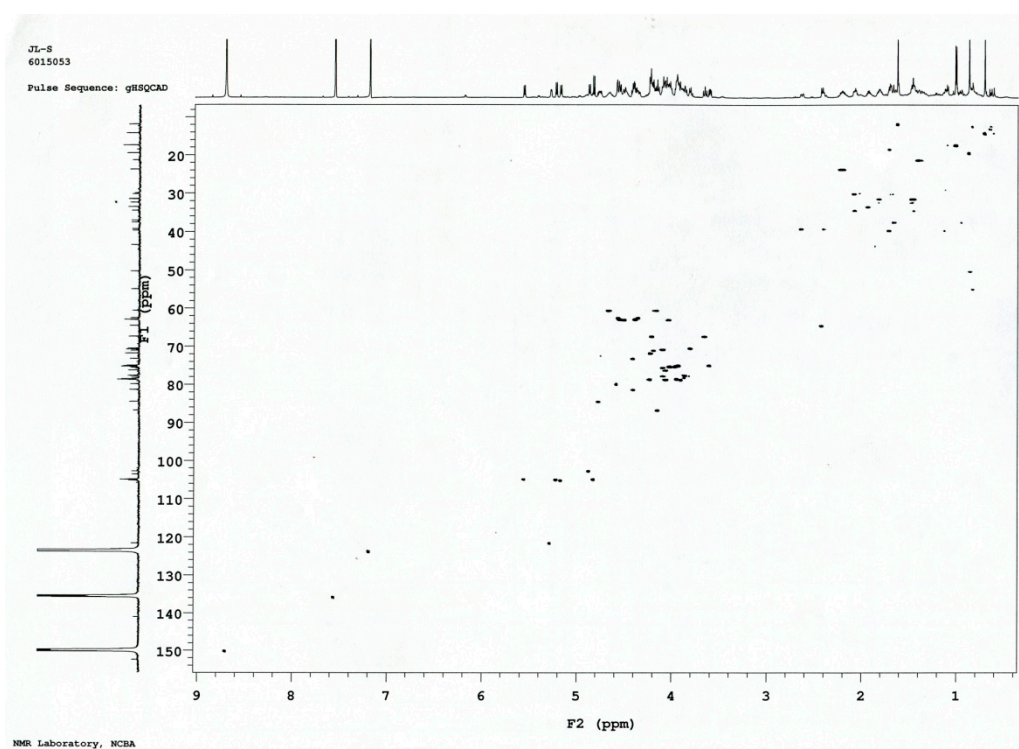
Figure S33. <sup>1</sup>H-NMR spectrum of compound 6 in C<sub>5</sub>D<sub>5</sub>N.

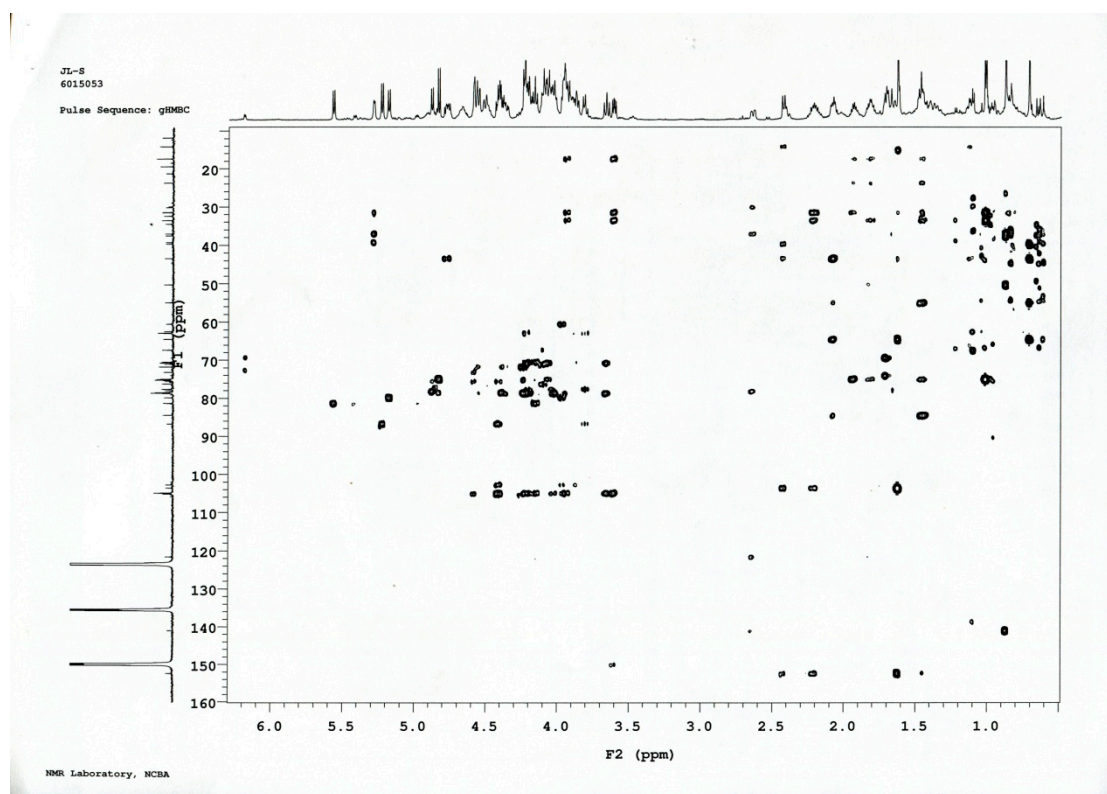
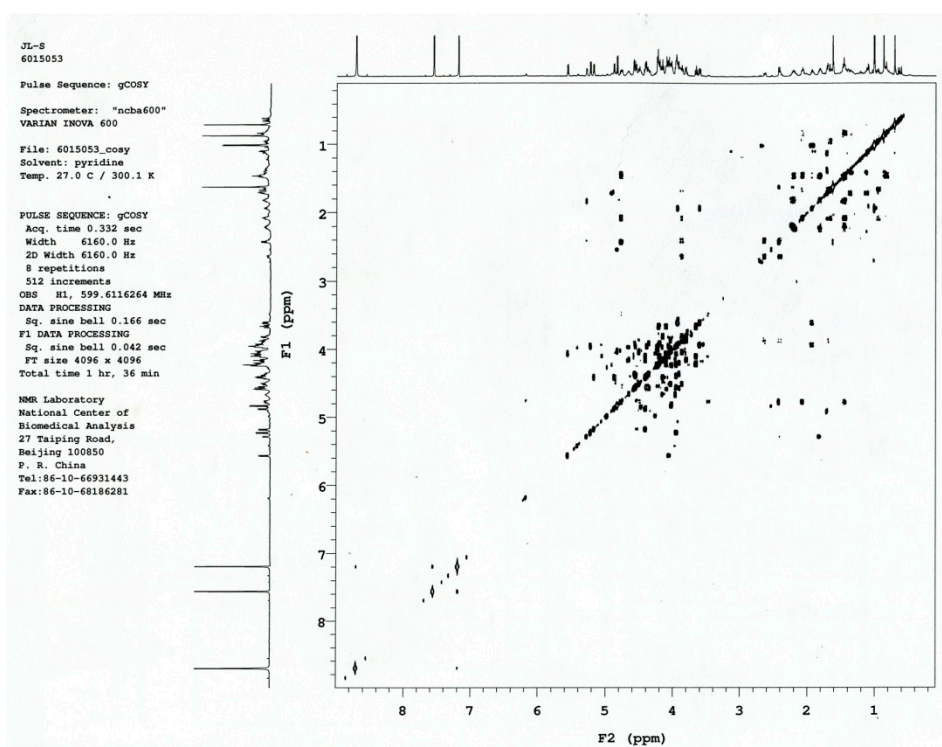
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6014324  
Sample directory:  
Pulse Sequence: s2pul  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
File: 6014324\_c  
Solvent: pyridine  
Temp: 27.0°C / 300.1 K  
PULSE SEQUENCE  
Relax: delay 0.010 sec  
Pulse 21.1 degrees  
ACS: time 0.600 sec  
Width 39960.0 Hz  
6258 repetitions  
OSS C15, 150.7756324 MHz  
DEC H1, 599.6268870 MHz  
Power 4d dB  
on during acquisition  
off during delay  
GARP-1 modulated  
DATA PROCESSING  
Line broadening 3.0 Hz  
FT size 262144  
Total time 2-hr, 50 min  
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Biomedical Analysis  
27 Taiping Road,  
Beijing 100850  
P. R. China  
Tel:86-10-66931443  
Fax:86-10-68186281

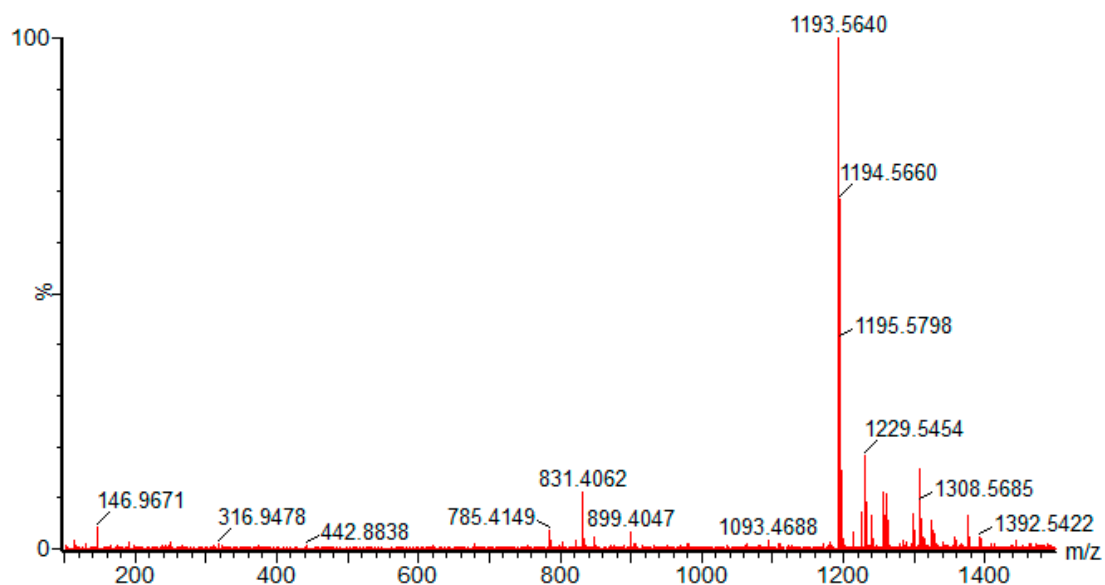
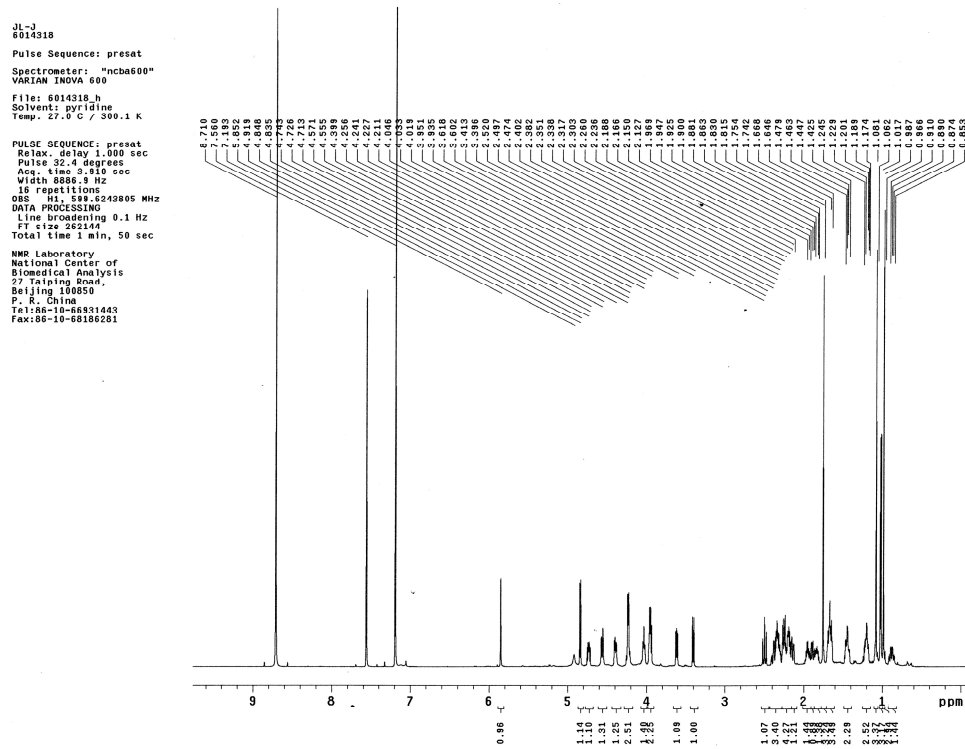
Figure S34.  $^{13}\text{C}$ -NMR spectrum of compound 6 in  $\text{C}_5\text{D}_5\text{N}$ .Figure S35. HSQC spectrum of compound 6 in  $\text{C}_5\text{D}_5\text{N}$ .

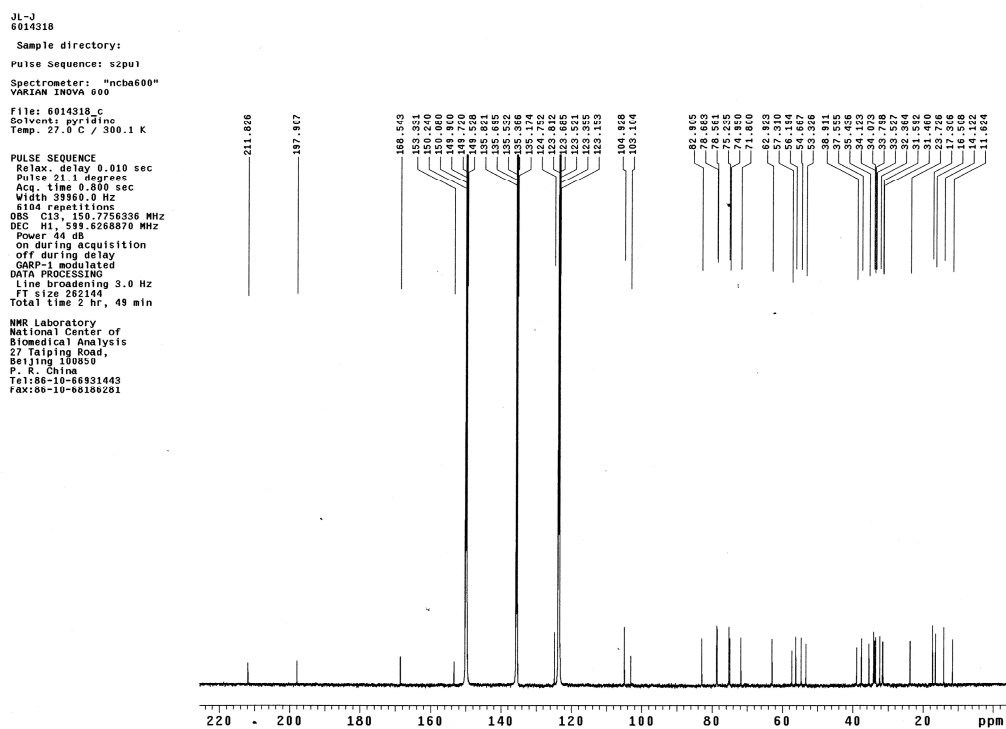
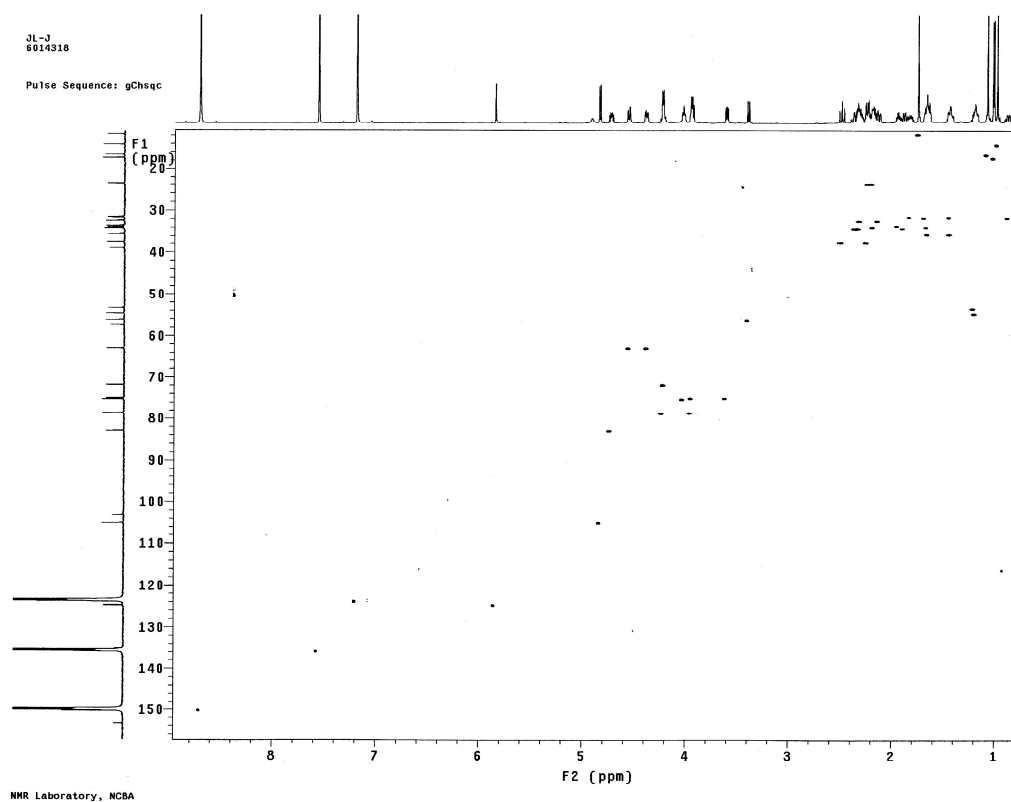
Figure S36. HMBC spectrum of compound 6 in C<sub>5</sub>D<sub>5</sub>N.Figure S37. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 6 in C<sub>5</sub>D<sub>5</sub>N.

Figure S38. HRESIMS of compound 6 in  $\text{CH}_3\text{CN}$ .Figure S39.  $^1\text{H}$ -NMR spectrum of compound 7 in  $\text{C}_5\text{D}_5\text{N}$ .

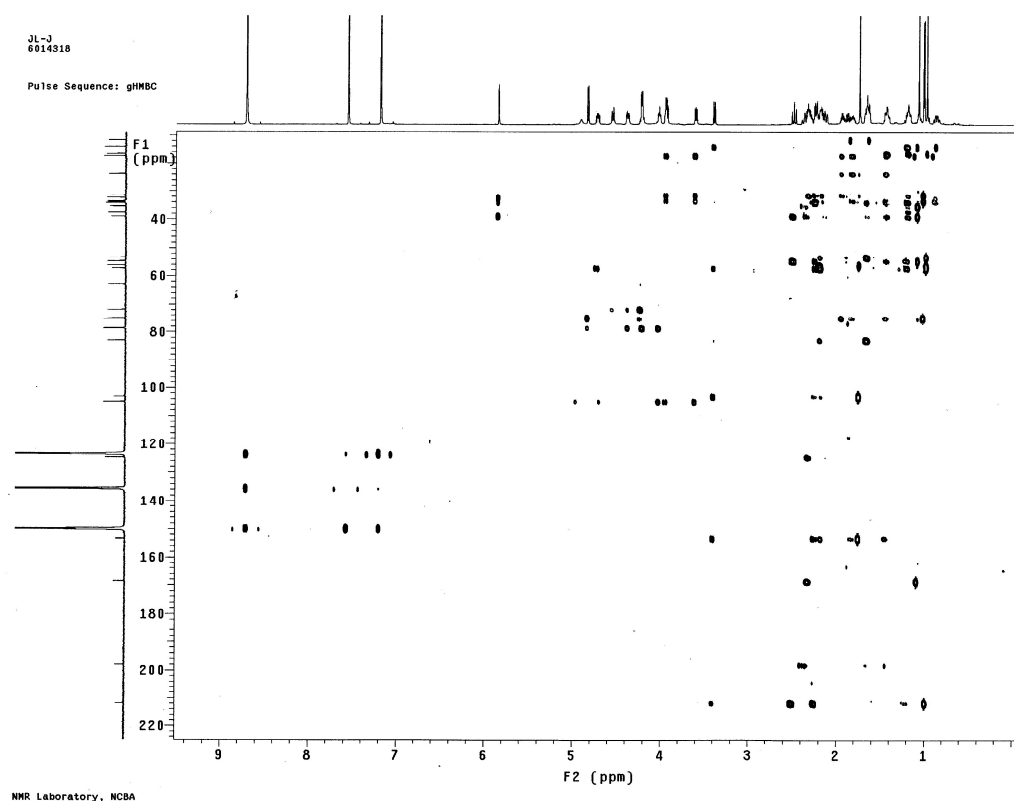
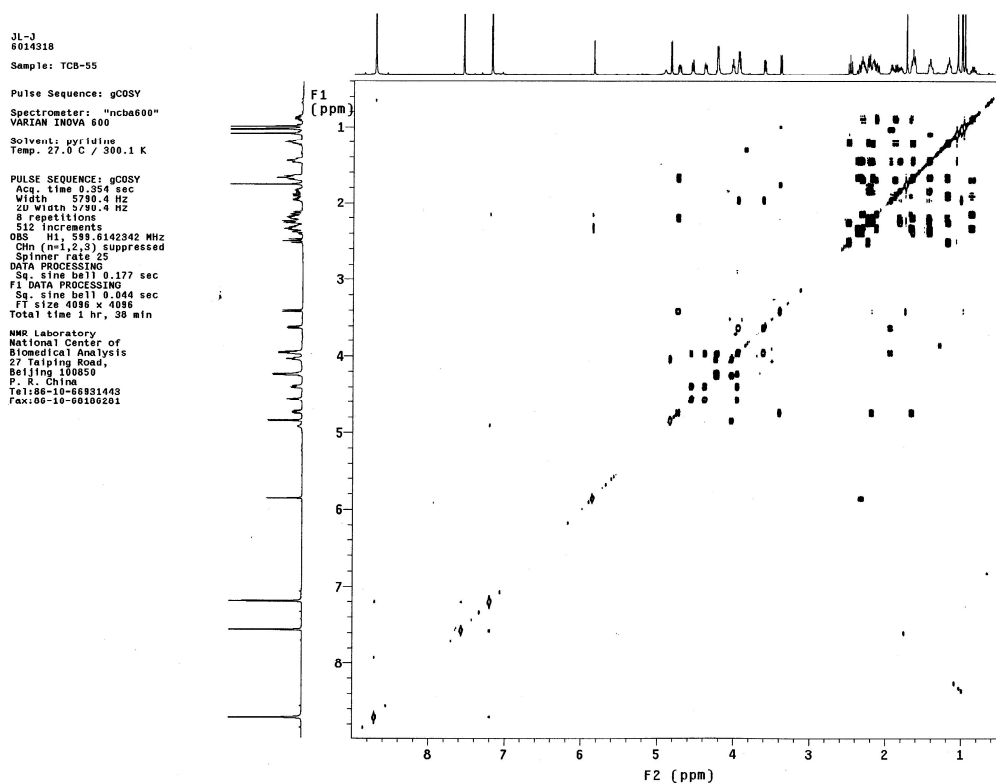
Figure S40.  $^{13}\text{C}$ -NMR spectrum of compound 7 in  $\text{C}_5\text{D}_5\text{N}$ .Figure S41. HSQC spectrum of compound 7 in  $\text{C}_5\text{D}_5\text{N}$ .

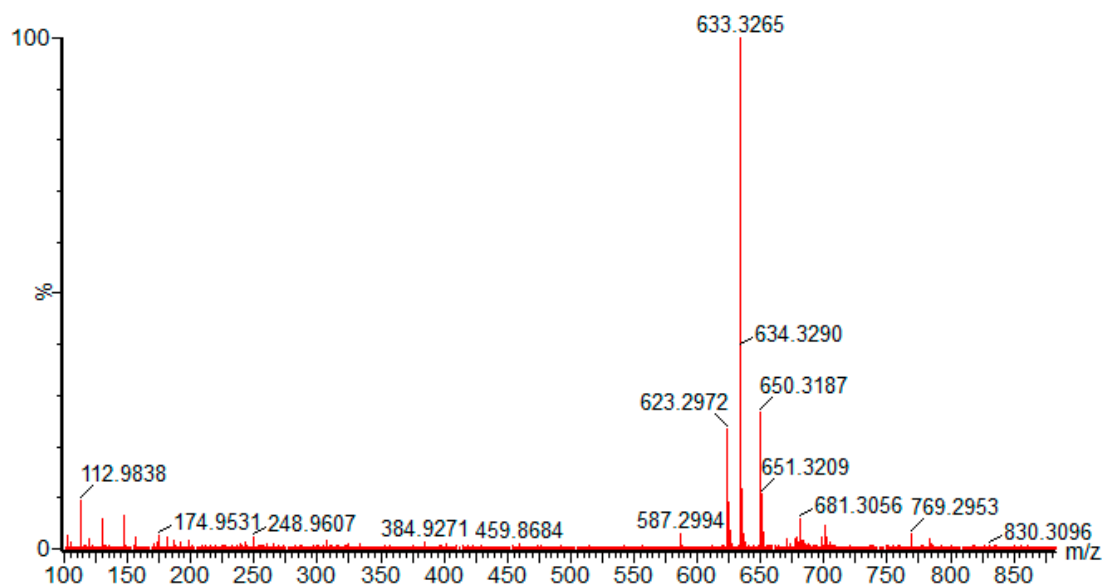
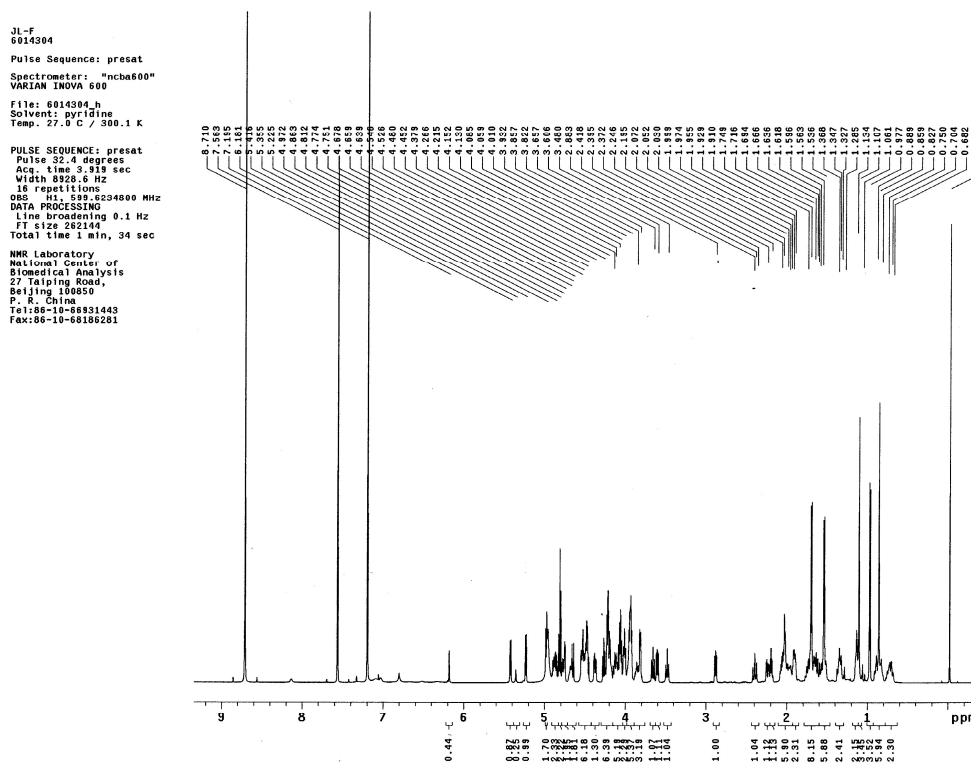
Figure S42. HMBC spectrum of compound 7 in C<sub>5</sub>D<sub>5</sub>N.Figure S43. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 7 in C<sub>5</sub>D<sub>5</sub>N.

Figure S44. HRESIMS of compound 7 in CH<sub>3</sub>CN.Figure S45. <sup>1</sup>H-NMR spectrum of compound 8 in C<sub>5</sub>D<sub>5</sub>N.

Figure S46.  $^{13}\text{C}$ -NMR spectrum of compound **8** in  $\text{C}_5\text{D}_5\text{N}$ .Figure S47. HSQC spectrum of compound **8** in  $\text{C}_5\text{D}_5\text{N}$ .



Figure S48. HMBC spectrum of compound 8 in C<sub>5</sub>D<sub>5</sub>N.Figure S49. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 8 in C<sub>5</sub>D<sub>5</sub>N.

Figure S50. HRESIMS of compound 8 in CH<sub>3</sub>CN.Figure S51. <sup>1</sup>H-NMR spectrum of compound 9 in C<sub>5</sub>D<sub>5</sub>N.

JL-F  
6014304  
Sample directory:  
Pulse Sequence: s2pul  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
File: 6014304.c  
Solvent: pyridine  
Temp: 27.0 C / 300.1 K  
PULSE SEQUENCE  
Relax. delay 0.010 sec  
Pulse 21.3 degrees  
Acq. time 0.800 sec  
Width 39860.0 Hz  
10000 Repetitions  
OBS C13, 150.7756318 MHz  
DEC H1, 598.8272020 MHz  
Power 44 dB  
on during acquisition  
off during delay  
GARP-1 modulated  
DATA PROCESSING  
Line broadening 3.0 Hz  
FT size 262144  
Total time 2 hr, 50 min  
NMR Laboratory  
National Center of  
Biomedical Analysis  
27 Taiping Road,  
Beijing 100850  
P. R. China  
Tel:86-10-68931443  
Fax:86-10-68185231

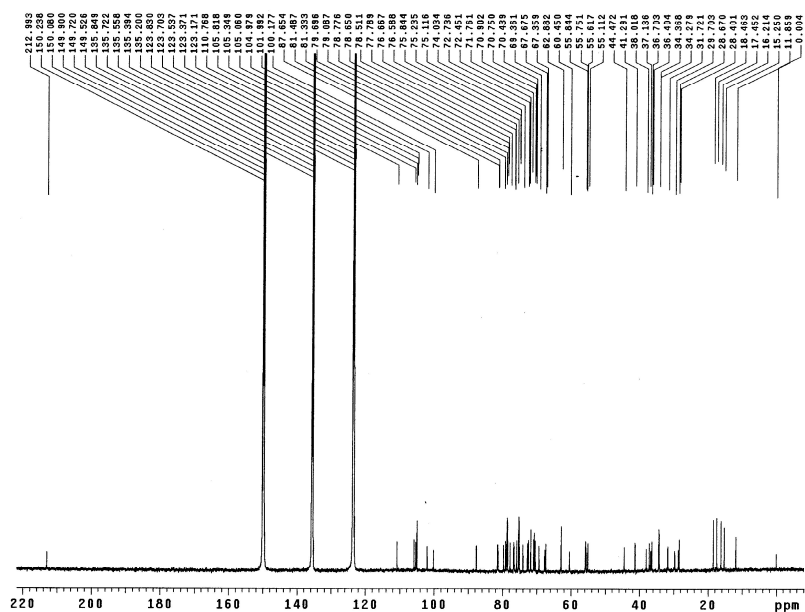
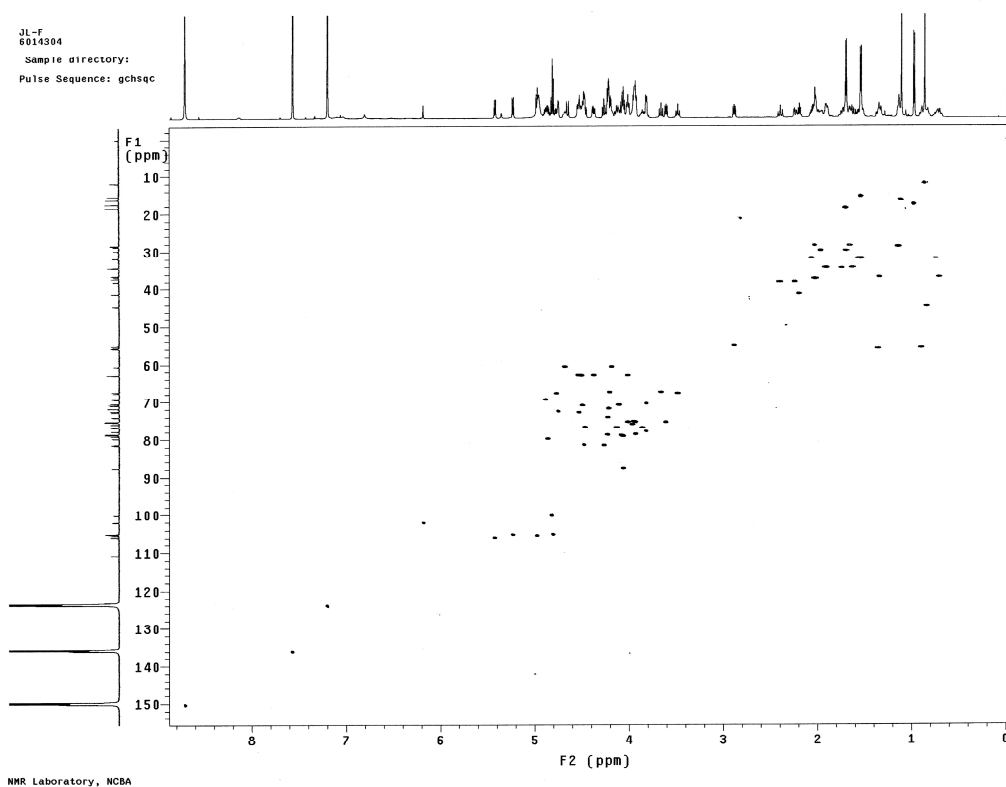
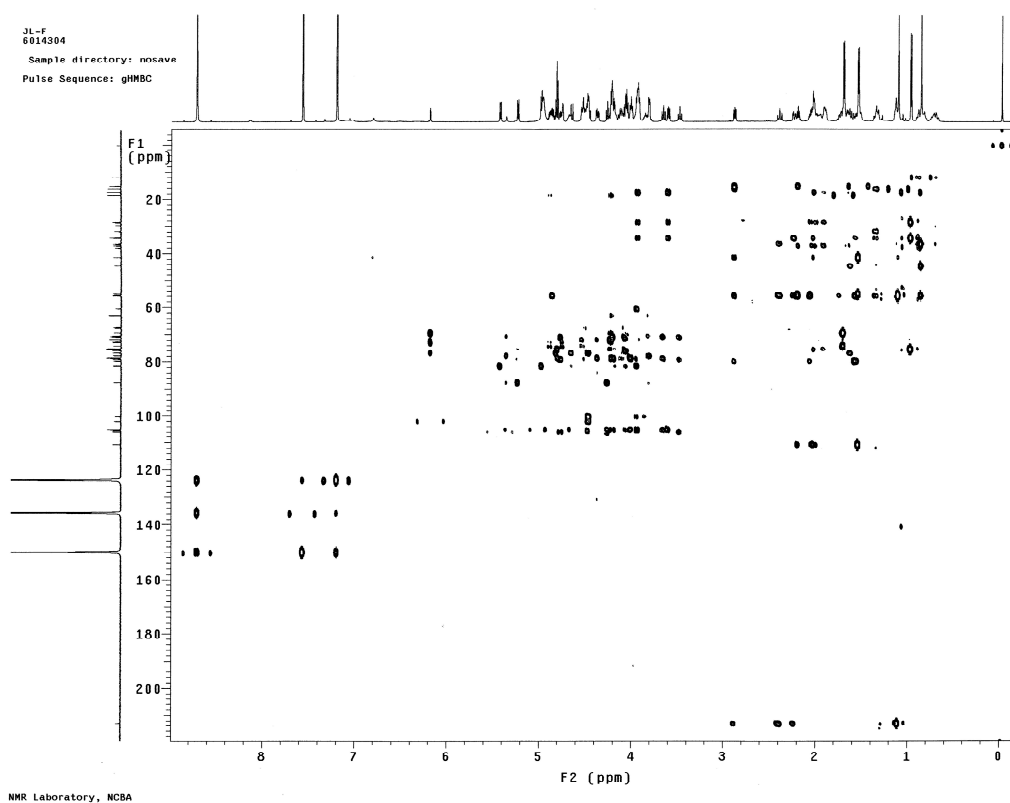
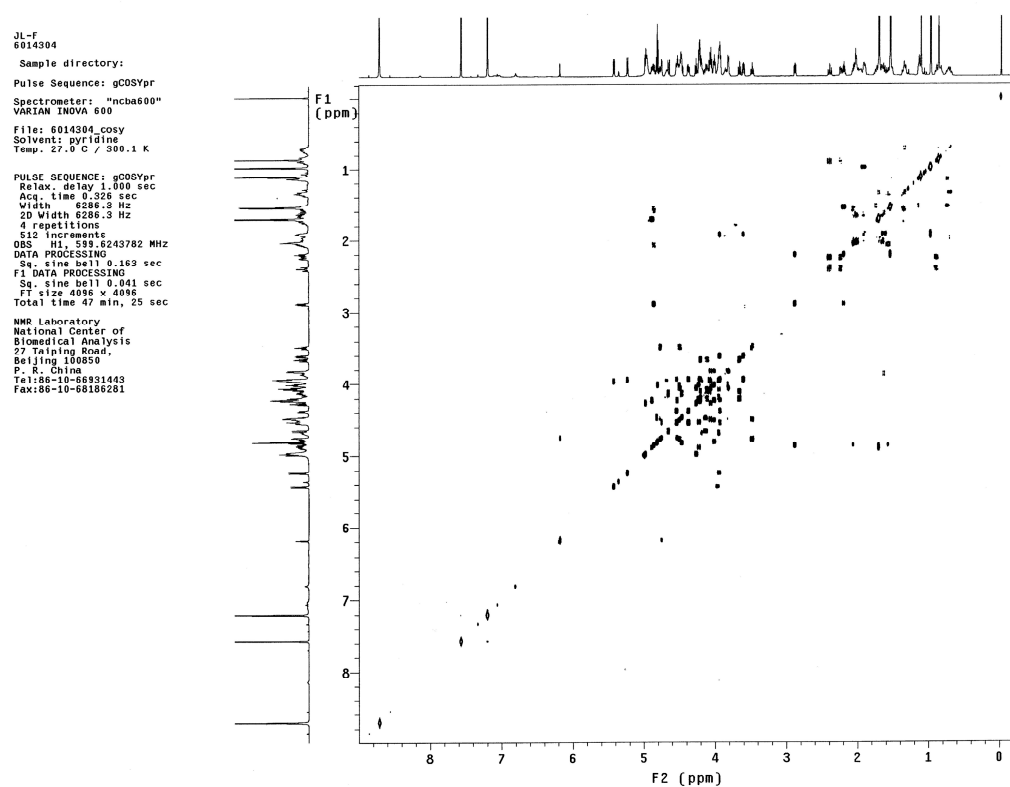


Figure S52.  $^{13}\text{C}$ -NMR spectrum of compound 9 in  $\text{C}_5\text{D}_5\text{N}$ .



NMR Laboratory, NCBA

Figure S53. HSQC spectrum of compound 9 in  $\text{C}_5\text{D}_5\text{N}$ .

Figure S54. HMBC spectrum of compound 9 in C<sub>5</sub>D<sub>5</sub>N.Figure S55. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 9 in C<sub>5</sub>D<sub>5</sub>N.



JL-E  
6014303  
Sample directory:  
Pulse Sequence: s2pu1  
Spectrometer: "ncba800"  
VARIAN INOVA 600  
File: 6014303\_c  
Solvent: pyrDine  
Temp. 27.0 C / 300.1 K  
PULSE SEQUENCE  
Relax. delay 0.010 sec  
Pulse 21.1 degrees  
Acq. time 0.050 sec  
Width 39960.0 Hz  
9424 repetitions  
OBS C13, 150.7756315 MHz  
DEC H1, 508.6272029 MHz  
Power 44 dB  
On during acquisition  
Off during delay  
GRAP-1 modulated  
DATA PROCESSING  
Line broadening 3.0 Hz  
FT size 252144  
Total time 2 hr, 50 min  
NMR Laboratory  
National Center of  
Biomedical Analysis  
27 Taiping Road,  
Beijing 100850  
P. R. China  
Tel:86-10-68931683  
Fax:86-10-68186291

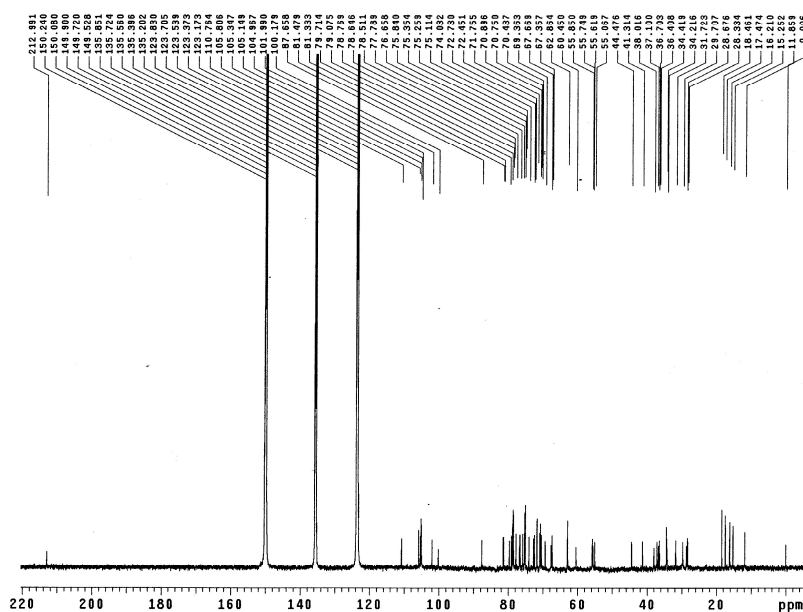


Figure S58.  $^{13}\text{C}$ -NMR spectrum of compound 10 in  $\text{C}_5\text{D}_5\text{N}$ .

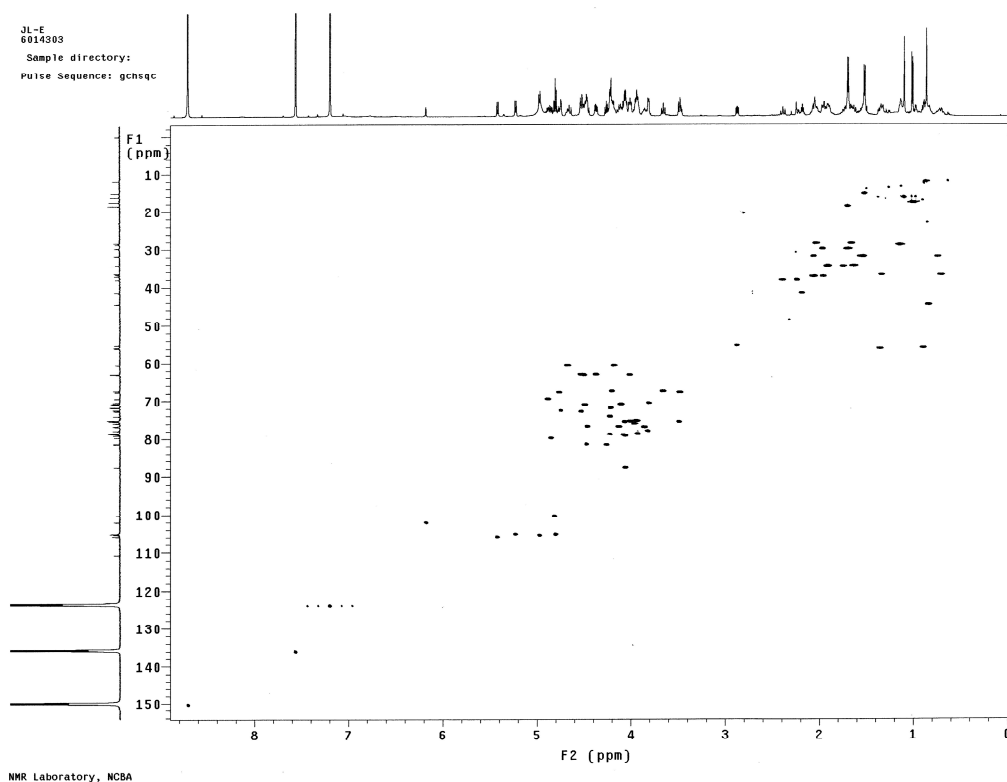
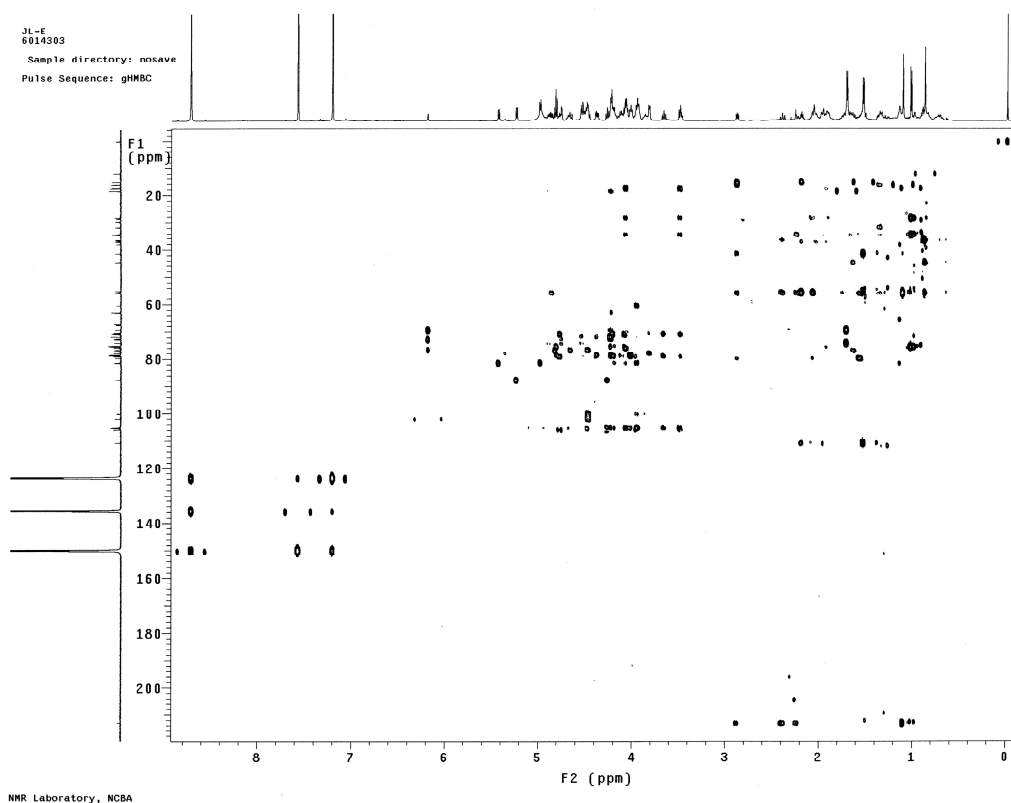
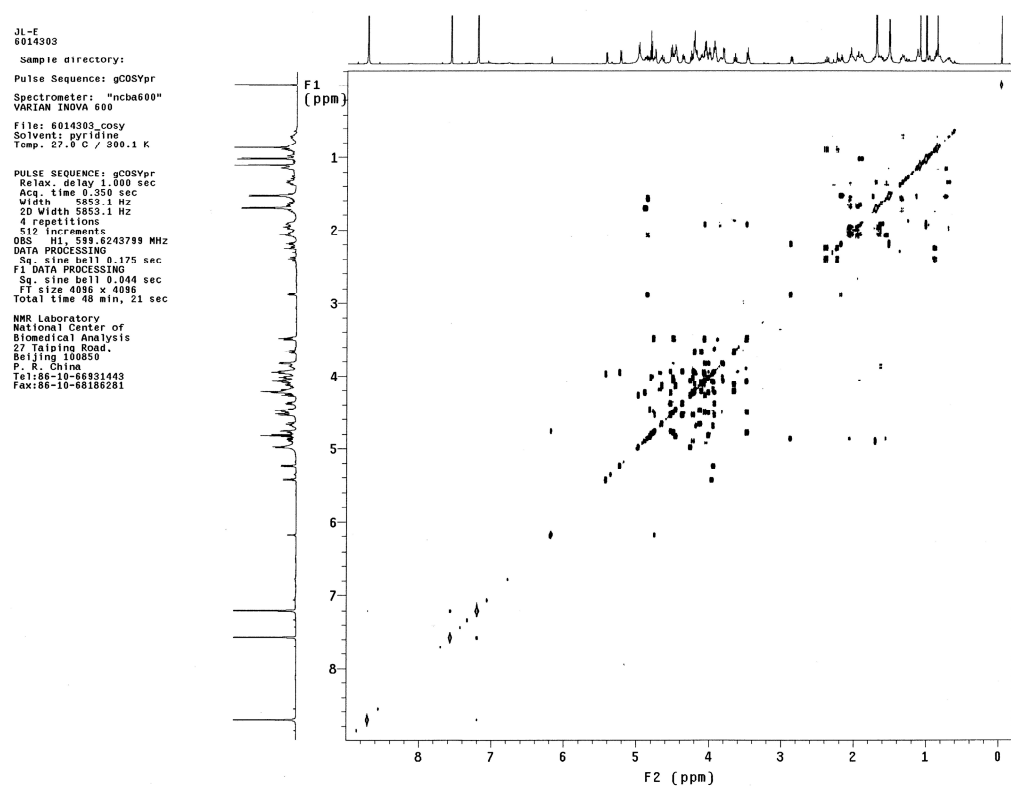


Figure S59. HSQC spectrum of compound 10 in  $\text{C}_5\text{D}_5\text{N}$ .

Figure S60. HMBC spectrum of compound 10 in C<sub>5</sub>D<sub>5</sub>N.Figure S61. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 10 in C<sub>5</sub>D<sub>5</sub>N.





JL-P  
6014417  
Sample directory:  
Pulse Sequence: s2pu1  
Spectrometer: "ncba600"  
VARIAN INOVA 600  
File: 6014417.c  
Solvent: pyridine  
Temp. 27.0 C / 300.1 K  
PULSE SEQUENCE  
Relax. delay 0.010 sec  
Pulse 21.1 degrees  
Acq. time 0.789 sec  
Width 40000.0 Hz  
3000 repetitions  
OBS. Ch1: 150.7730500 MHz  
DEC. H1: 599.6169152 MHz  
Power 44 dB  
on during acquisition  
off during delay  
GMP-1 modulated  
DATA PROCESSING  
Line broadening 3.0 Hz  
FT size 262104  
Total time 4 hr, 14 min  
NMR Laboratory  
National Center of  
Biomedical Analysis  
27 Taiping Road,  
Beijing 100850  
P. R. China  
Tel:86-10-66931443  
Fax:86-10-69162291

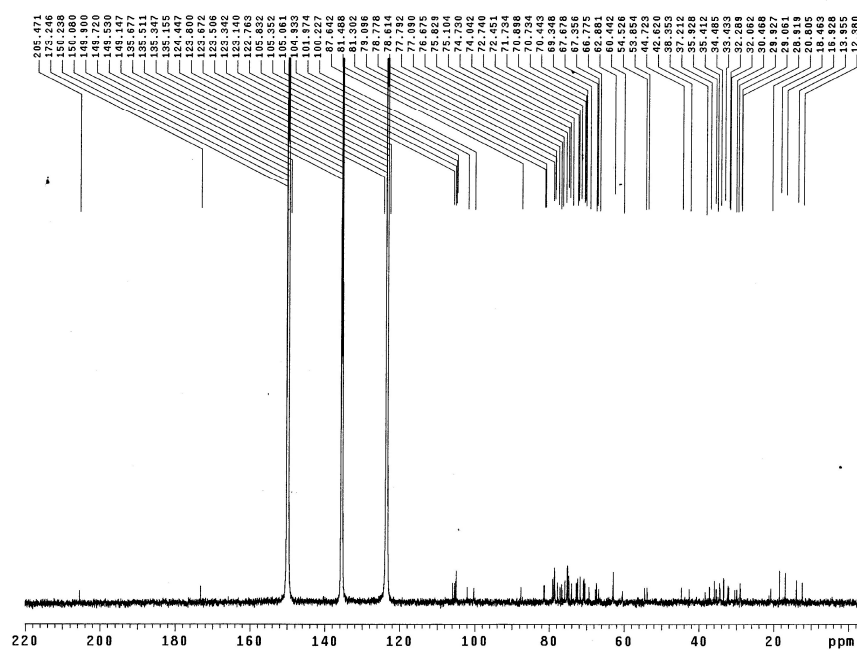


Figure S64.  $^{13}\text{C}$ -NMR spectrum of compound 11 in  $\text{C}_5\text{D}_5\text{N}$ .

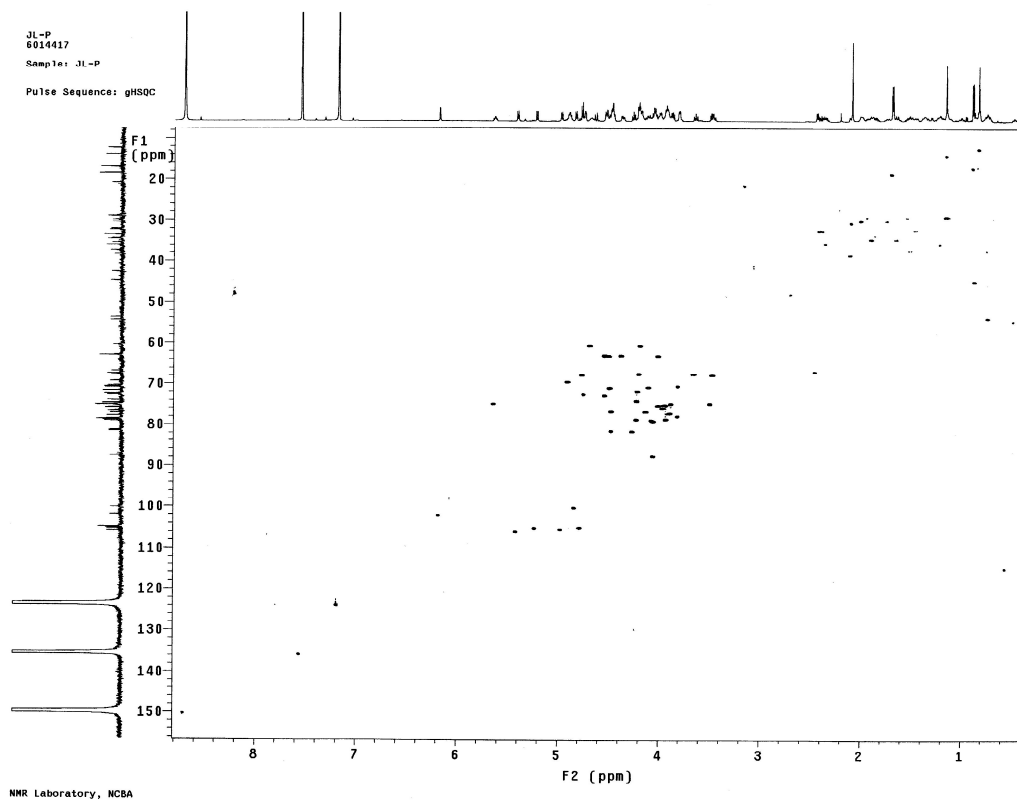
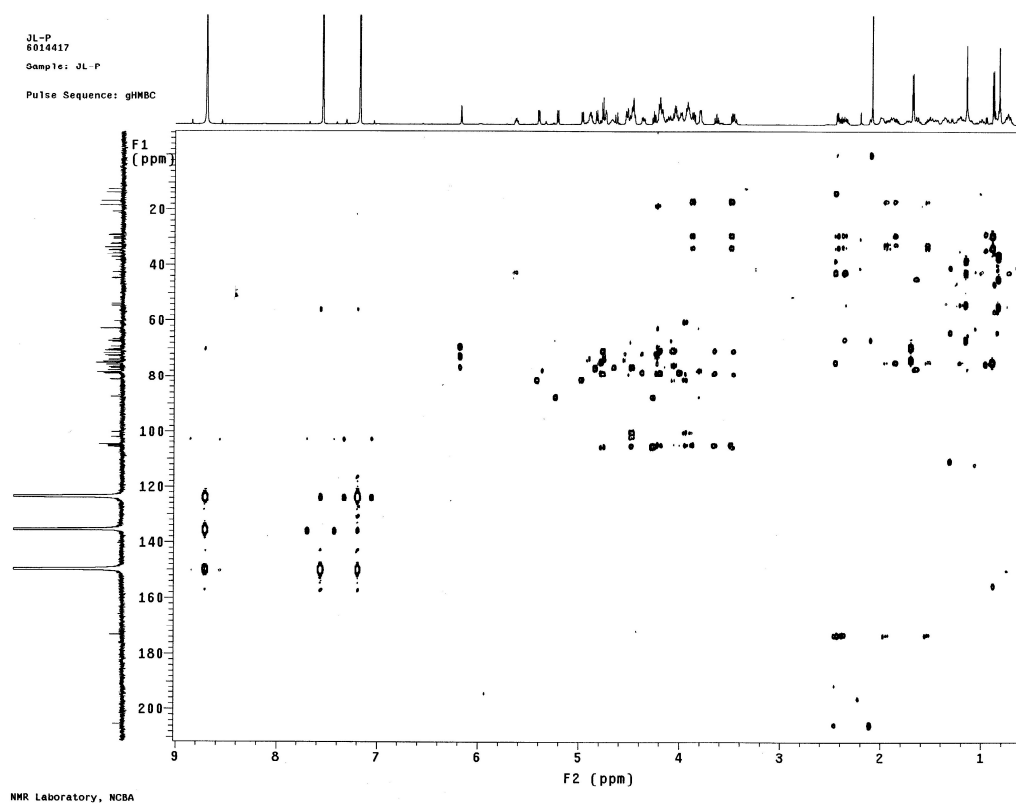
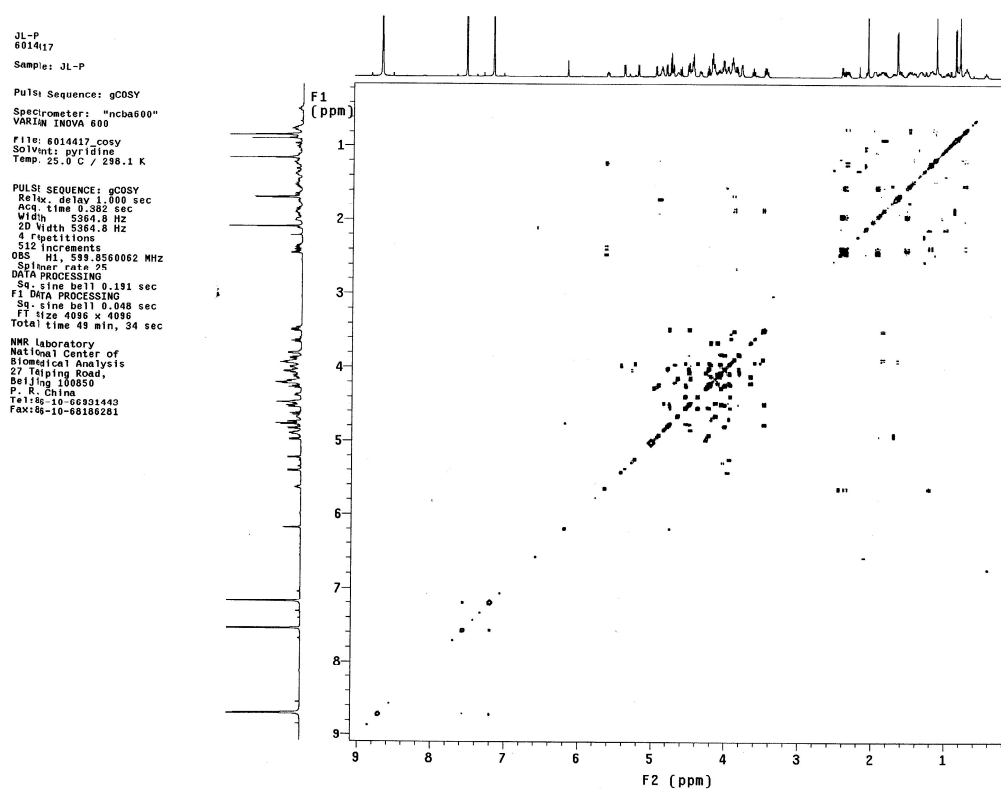
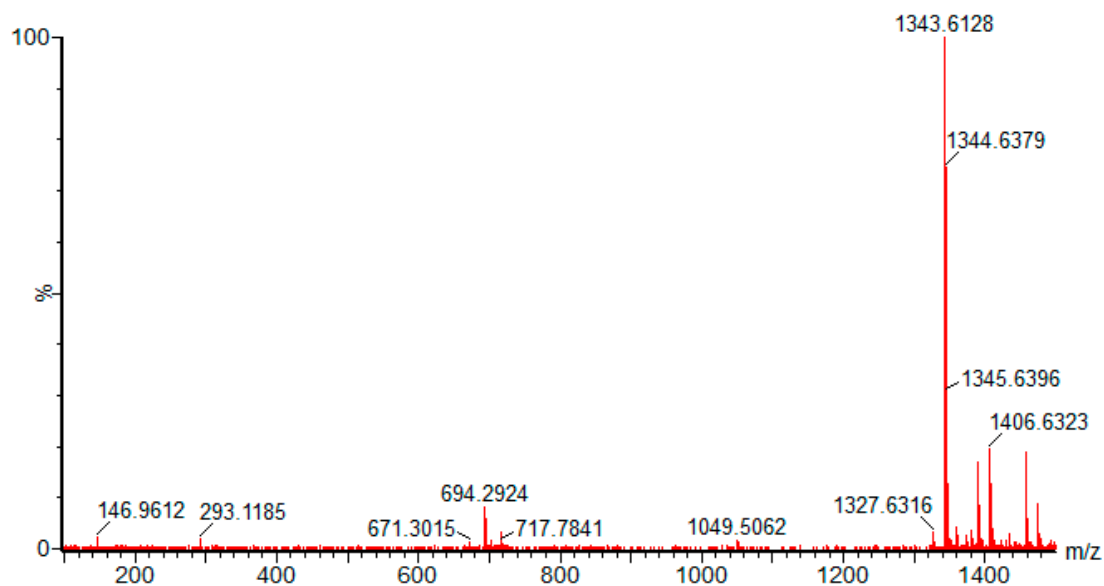
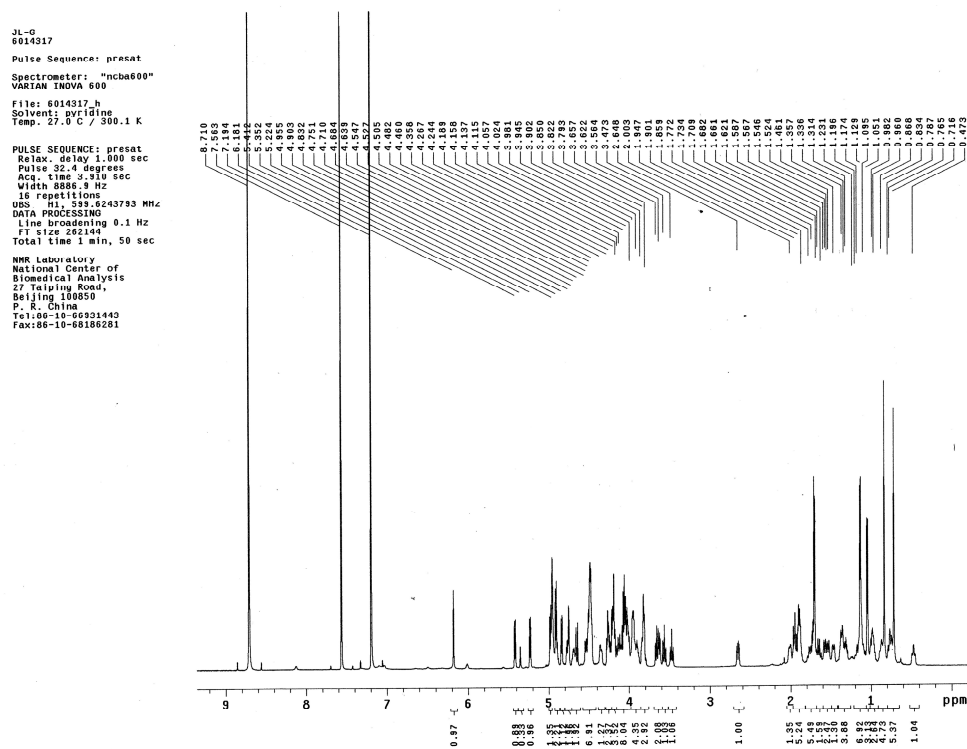
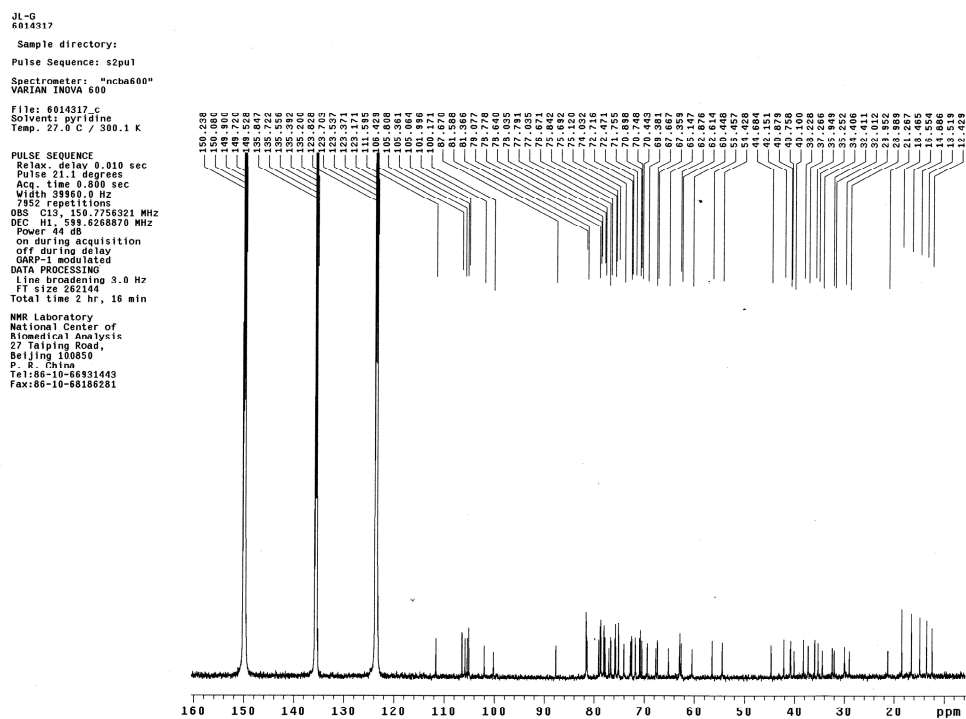
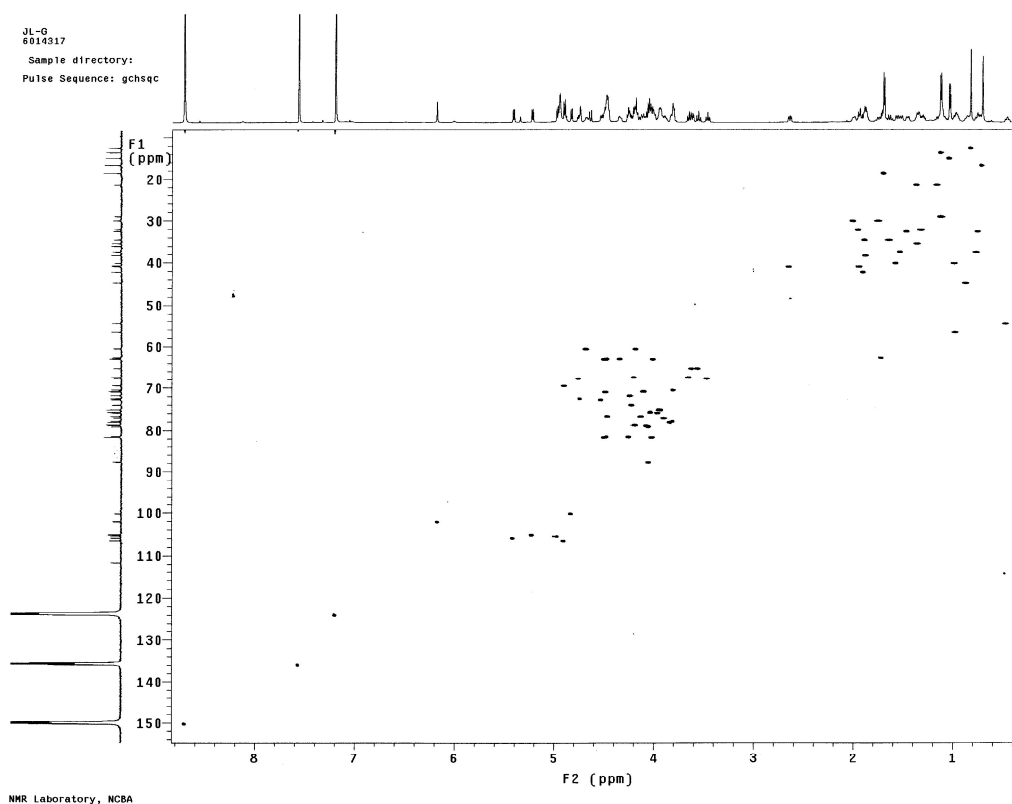
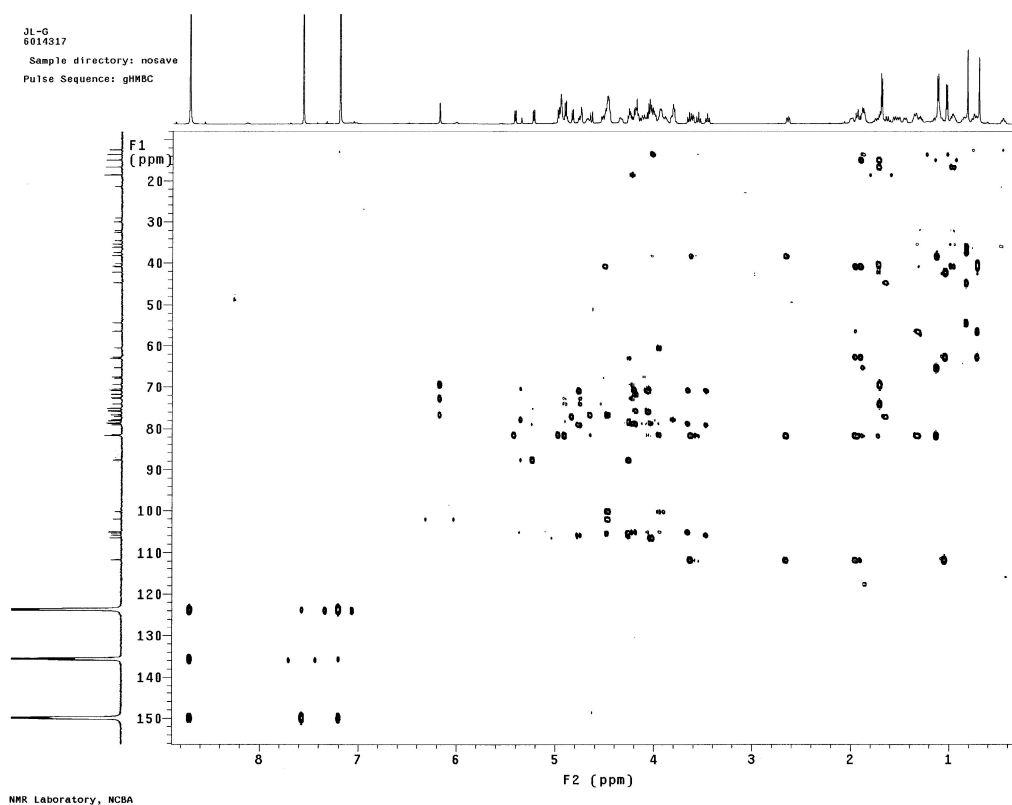
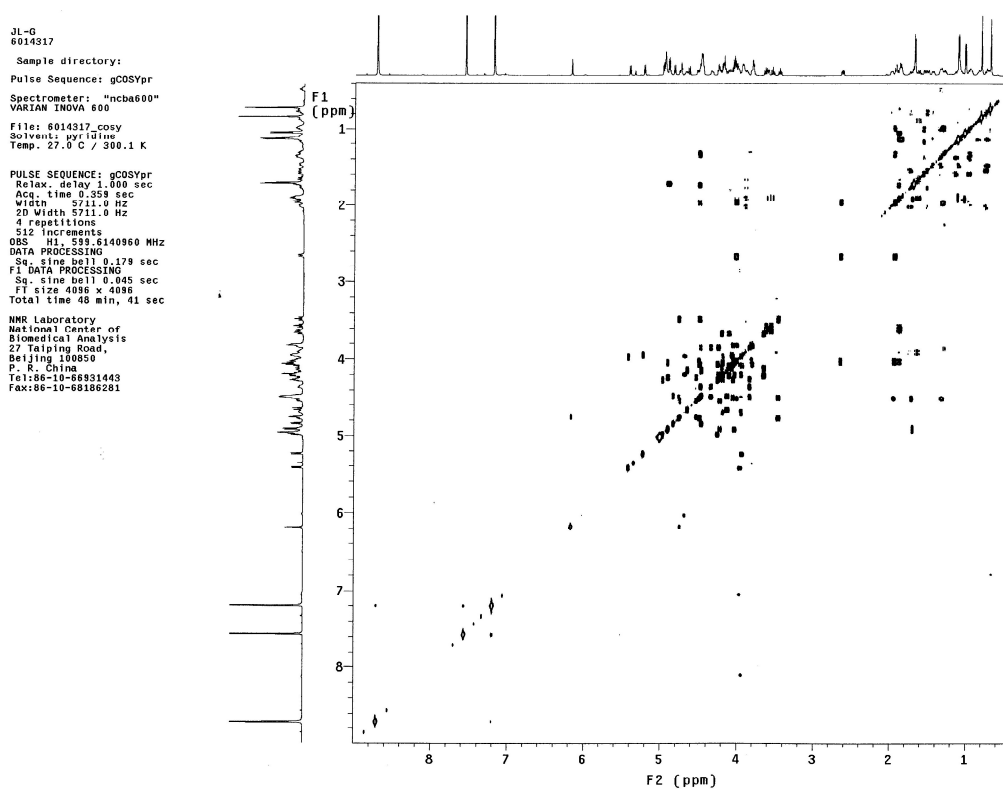


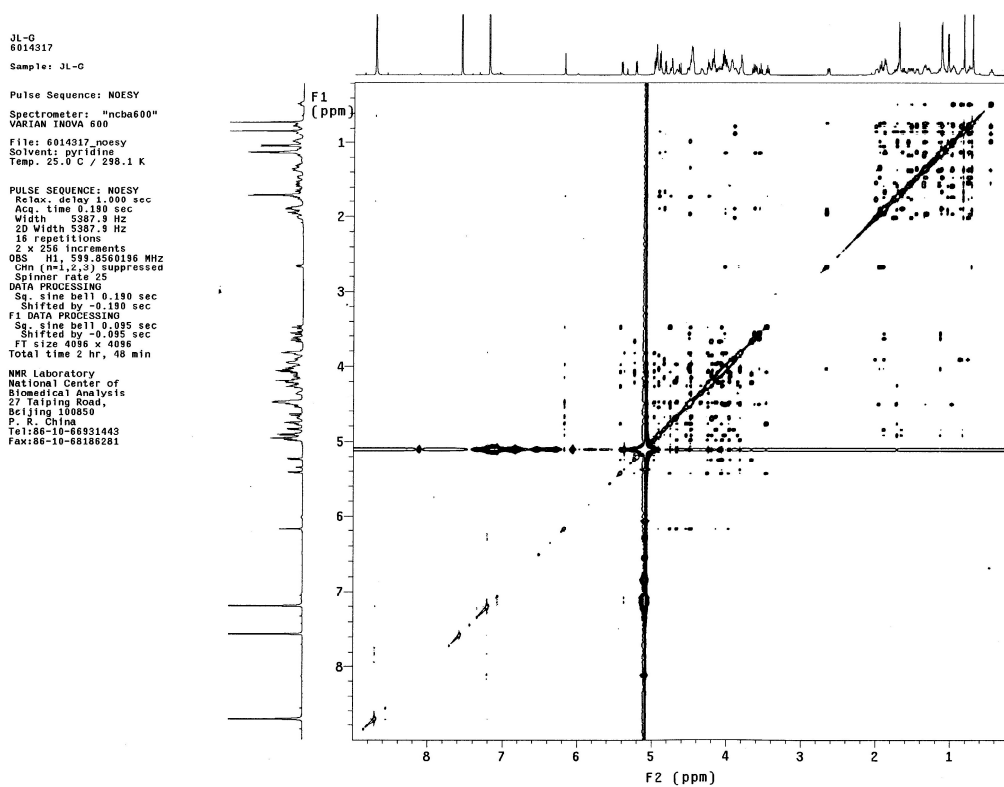
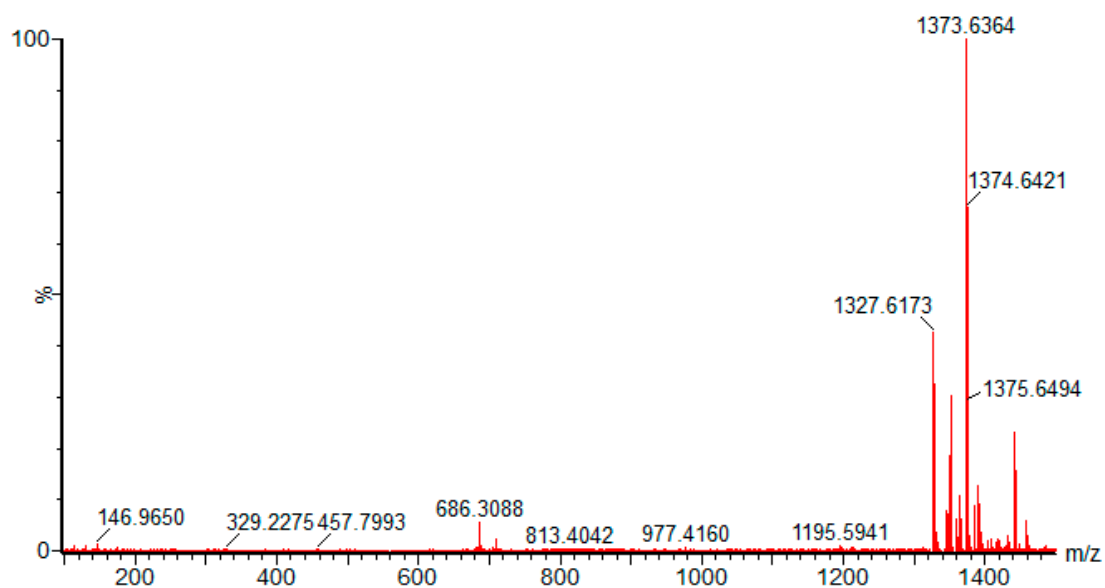
Figure S65. HSQC spectrum of compound 11 in  $\text{C}_5\text{D}_5\text{N}$ .

Figure S66. HMBC spectrum of compound 11 in C<sub>5</sub>D<sub>5</sub>N.Figure S67. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 11 in C<sub>5</sub>D<sub>5</sub>N.

Figure S68. HRESIMS of compound 11 in CH<sub>3</sub>CN.Figure S69. <sup>1</sup>H-NMR spectrum of compound 12 in C<sub>5</sub>D<sub>5</sub>N.

Figure S70.  $^{13}\text{C}$ -NMR spectrum of compound 12 in  $\text{C}_5\text{D}_5\text{N}$ .Figure S71. HSQC spectrum of compound 12 in  $\text{C}_5\text{D}_5\text{N}$ .

Figure S72. HMBC spectrum of compound 12 in C<sub>5</sub>D<sub>5</sub>N.Figure S73. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 12 in C<sub>5</sub>D<sub>5</sub>N.

Figure S74. ROESY of compound 12 in C<sub>5</sub>D<sub>5</sub>N.Figure S75. HRESIMS of compound 12 in CH<sub>3</sub>CN.