New monoterpene phenyl ethers from *Illicium micranthum*

Zheng-Ye Guan, a,b Chuan-Fu Dong, a Li Gao, a,b Jia-Ping Wang, a Shi-De Luo, a and Yi-Fen Wang a,*

^aState Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, China

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Structures of compounds 1-7, 1a and 2a

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

^{*}To whom correspondence should be addressed. E-mail: wangyifen@mail.kib.ac.cn

Figure 1S-7S. NMR and MS spectra of compound 1

Figure 8S-14S. NMR and MS spectra of compound 2

Figure 15S-17S. NMR spectra of compound 1a

Figure 18S-20S. NMR spectra of compound 2a

Figure 21S-27S. NMR and MS spectra of compound 3

Figure 28S-34S. NMR and MS spectra of compound 4

Figure 35S-41S. NMR and MS spectra of compound 5

Figure 42S-48S. NMR and MS spectra of compound 6

Figure 49S-55S. NMR and MS spectra of compound 7

Figure 1S. ¹H NMR of compound 1.

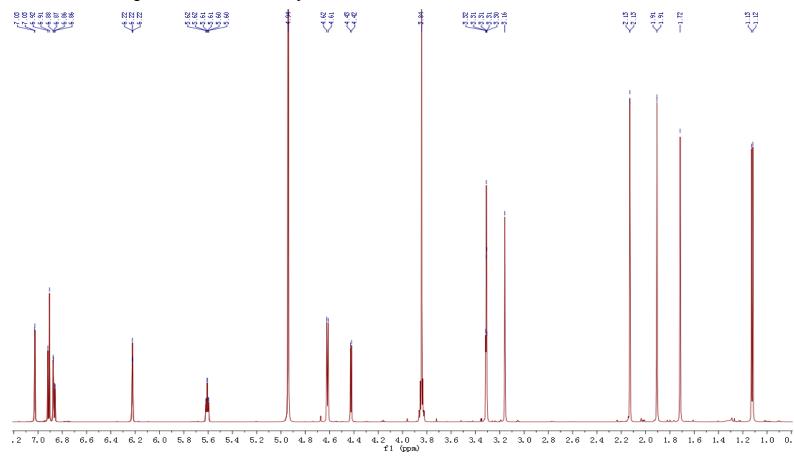
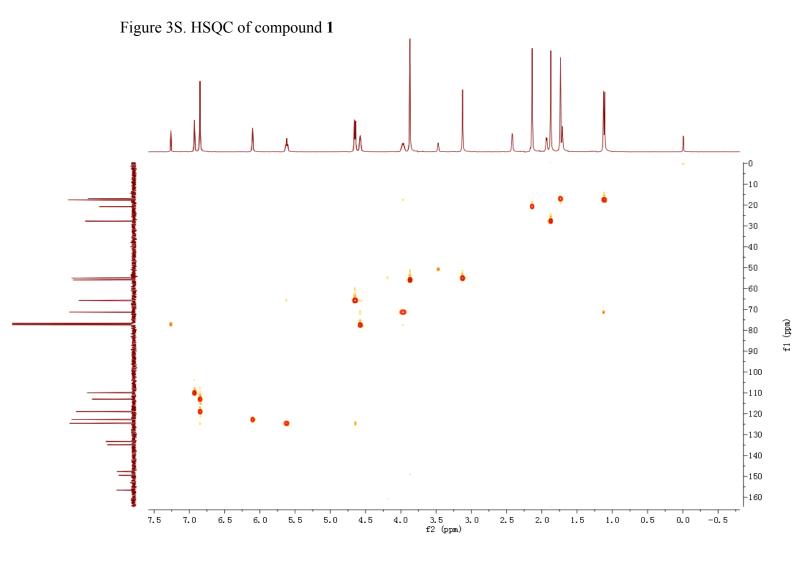
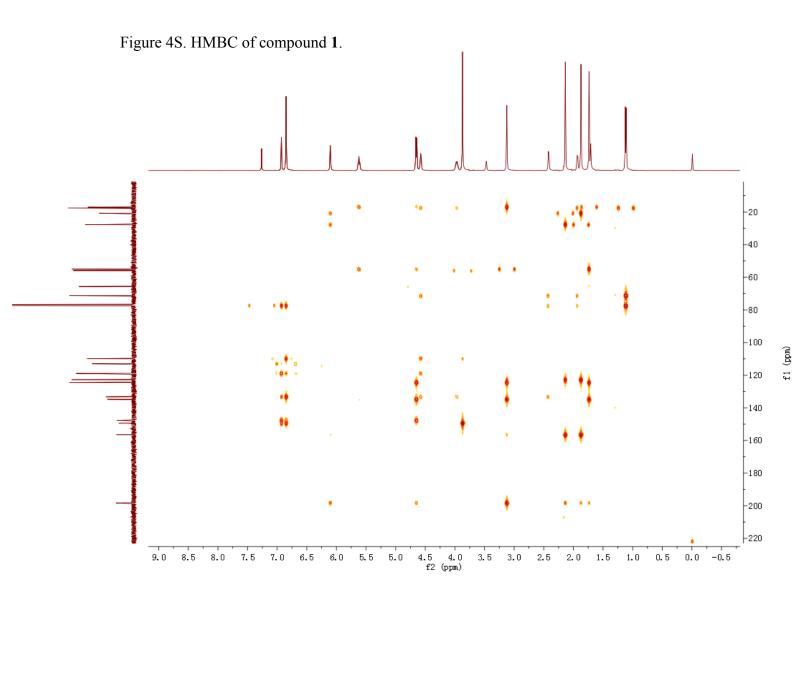


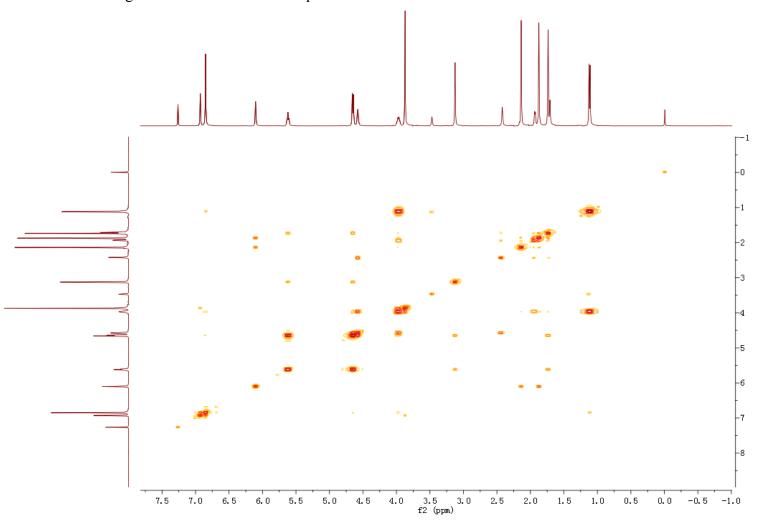
Figure 2S. ¹³C NMR and DEPT of compound 1. -198.28 -156.54 -149.45 134.79 ₹124.54 ₹122.77 ₹118.92 --112.95 --109.93 fl (ppm)





f1 (nnm)

Figure 5S. H-H COSY of compound 1.



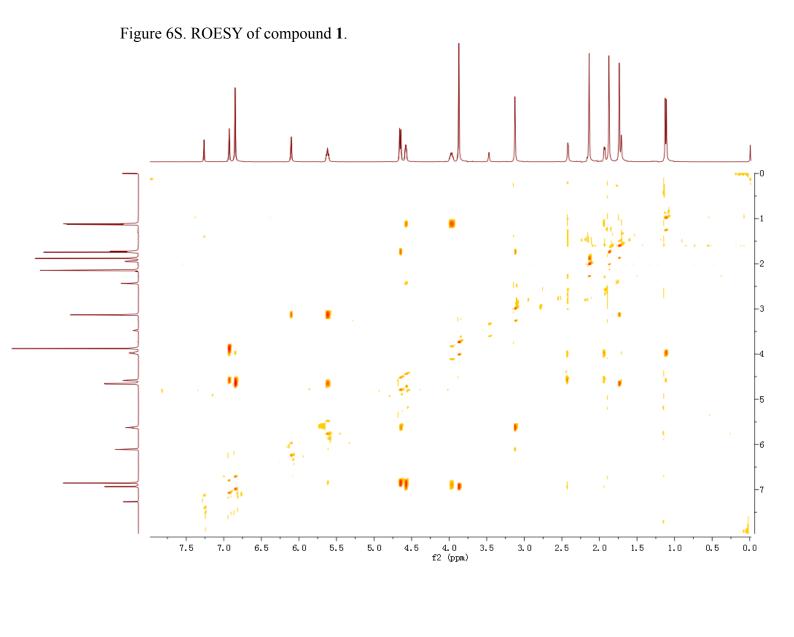


Figure 7S. HRESIMS of compound 1.

Page 1 **Elemental Composition Report** Single Mass Analysis (displaying only valid results) Tolerance = 10.0 PPM / DBE: min = 0.5, max = 60.0 Selected filters: None Autospec Premier KIB M120409EA-05AFAMM 9 (0.826) 348.1931 Dgzy-22a 11:17:05 09-Apr-2012 Voltage EI+ P776 15.1 % m/z 348.500 348.400 348.100 348.200 348.300 348.000 347.900 0.5 60.0 Minimum: 73.0 10.0 i-FIT Formula Calc. Mass \mathtt{PPM} DBE Mass 5546027.0 C20 H28 O5 -1.7 7.0 -0.6 348.1937 348.1931

Figure 8S. ¹H NMR of compound **2**.

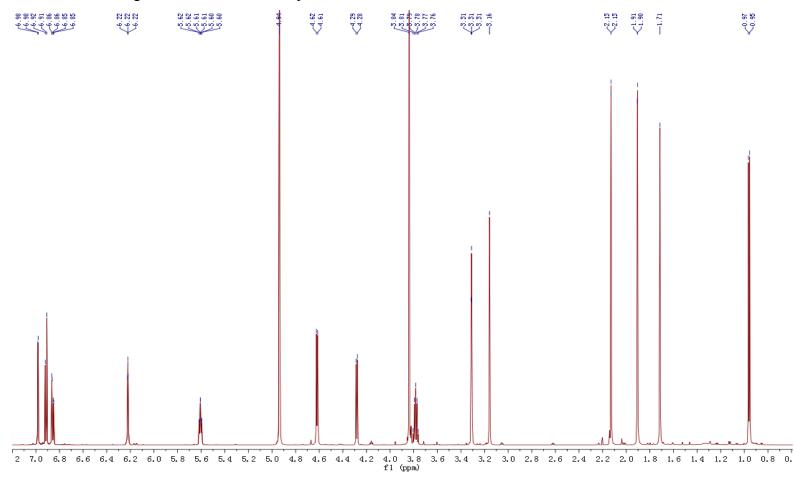


Figure 9S. ¹³C NMR and DEPT of compound **2**.

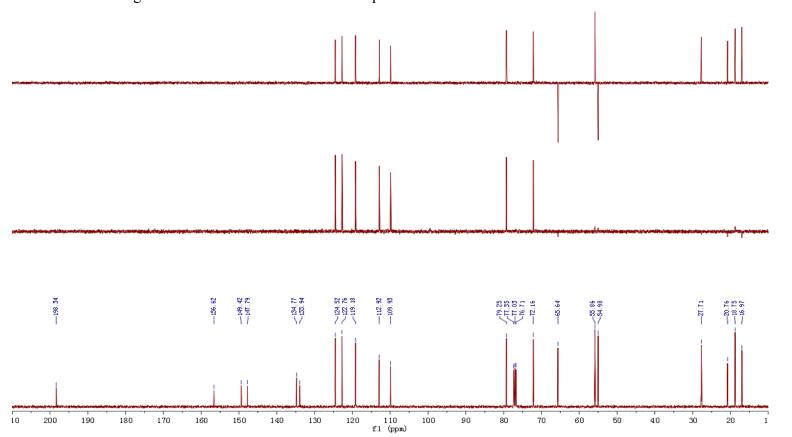


Figure 10S. HSQC of compound **2**.

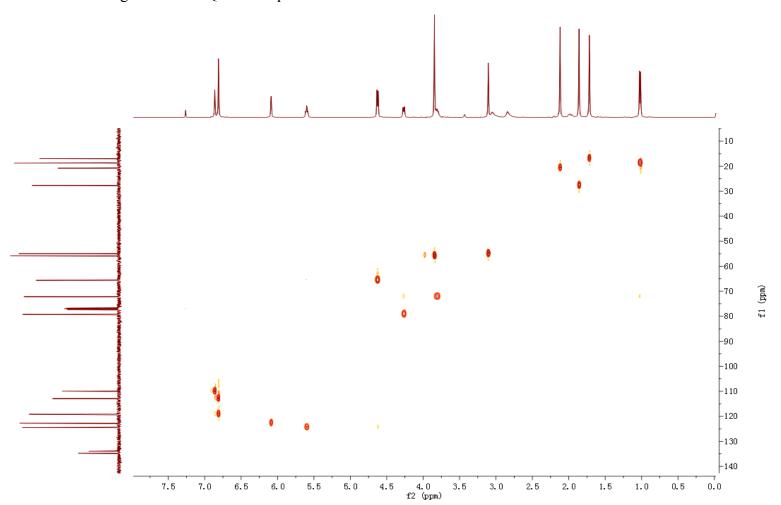


Figure 11S. HMBC of compound **2**.

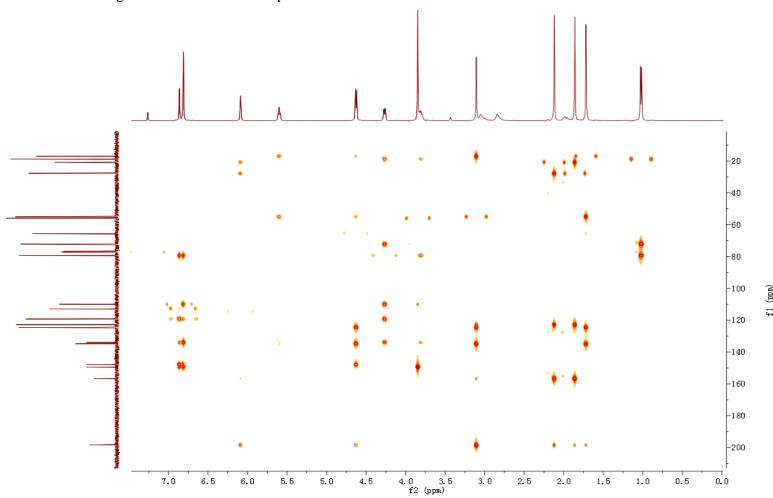


Figure 12S. ¹H-¹H COSY of compound **2**.

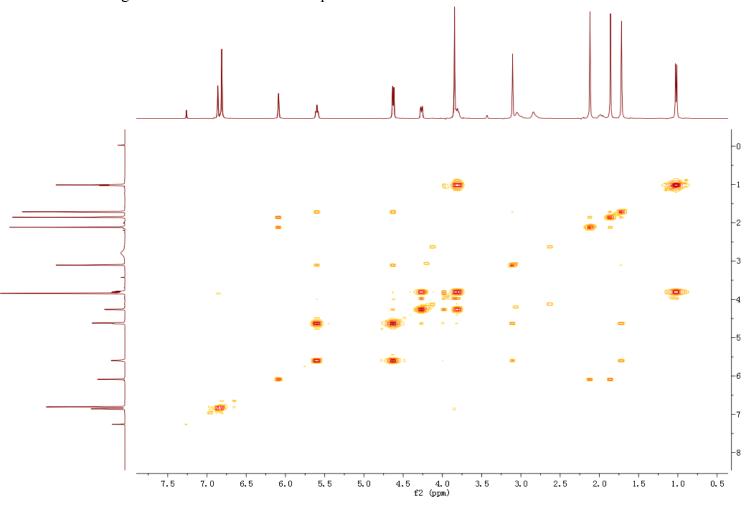


Figure 13S. ROESY of compound **2**.

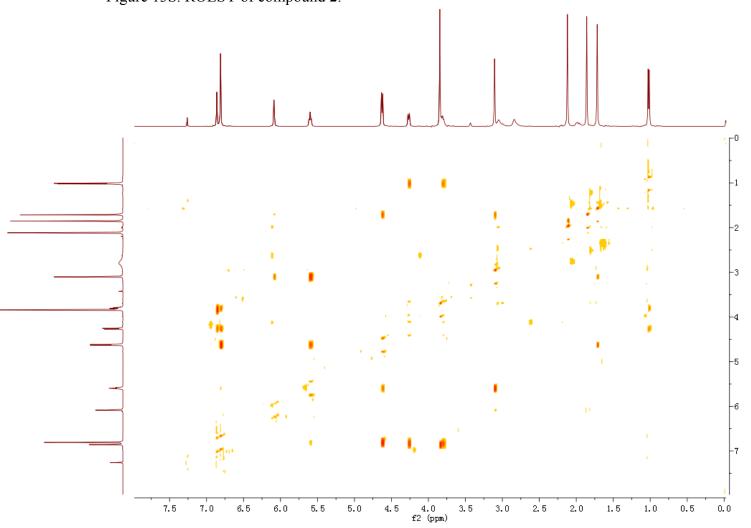


Figure 14S. HRESIMS of compound 2.

Page 1 **Elemental Composition Report** Single Mass Analysis (displaying only valid results) Tolerance = 10.0 PPM / DBE: min = 0.5, max = 60.0 Selected filters: None Monoisotopic Mass, Odd and Even Electron Ions 17 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass) Elements Used: C: 0-200 H: 0-400 O: 3-6 Dgzy-22b 11:20:53 09-Apr-2012 Voltage El+ 348.1921 KIB M120409EA-06AFAMM 12 (1.102) 348.1925 Autospec Premier P776 1.73e3 % 348.1375 348.500 348.400 348.300 347.900 348.000 348.100 348.200 347.800 Minimum: 0.5 73.0 10.0 Maximum: DBE i-FIT Mass Calc. Mass mDa PPM Formula 7.0 5546874.5 C20 H28 O5 348.1937 -1.2 -3.4 348.1925

Figure 15S. ¹H NMR of compound **1a**.

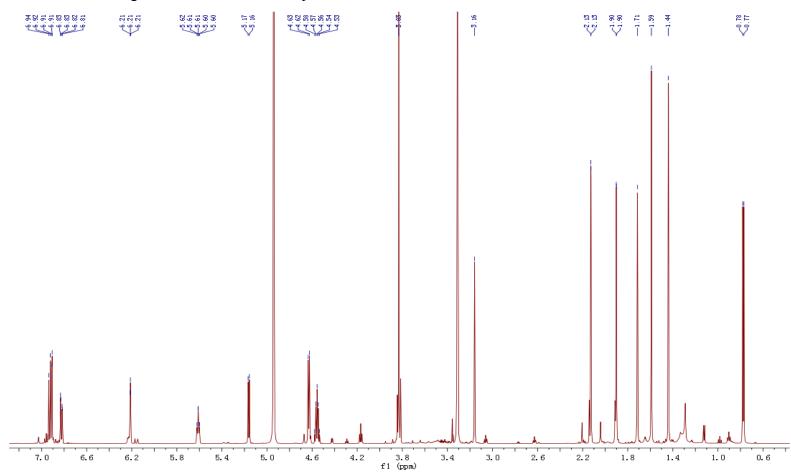
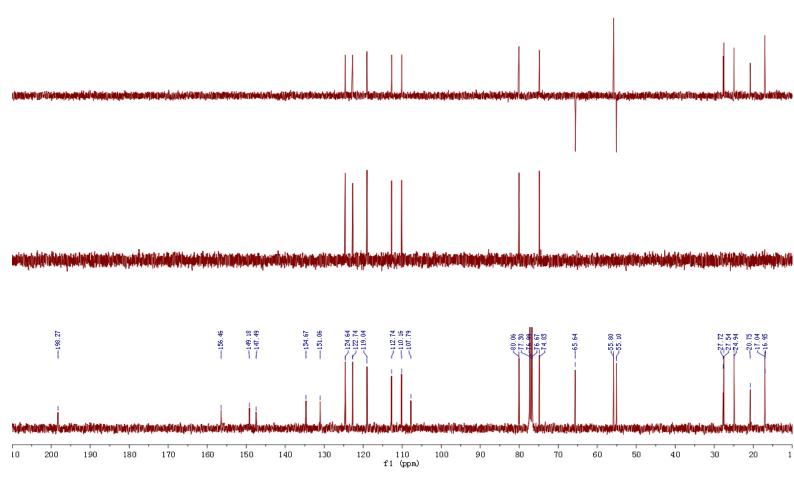


Figure 16S. ¹³C NMR and DEPT of compound **1a**.



f1 (mmm)

Figure 17S. ROESY of compound 1a.

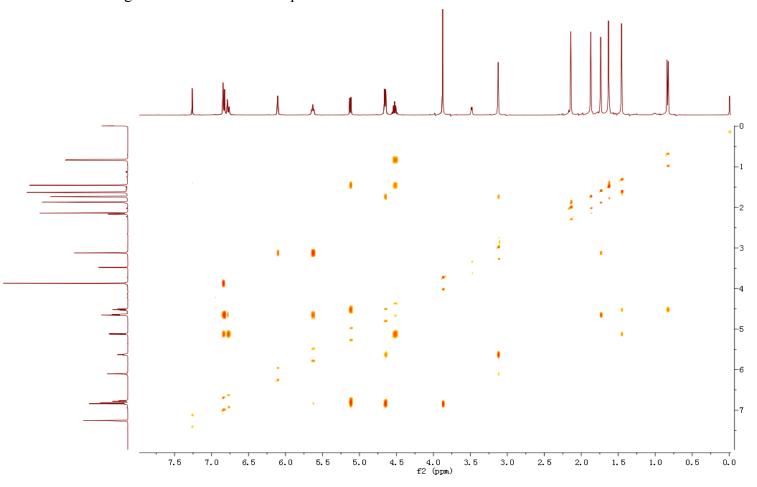


Figure 18S. ¹H NMR of compound **2a**.

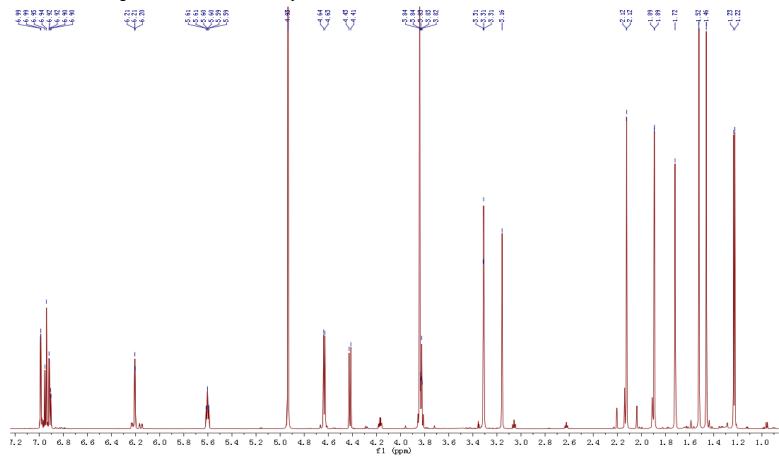


Figure 19S. ¹³C NMR and DEPT of compound **2a**.

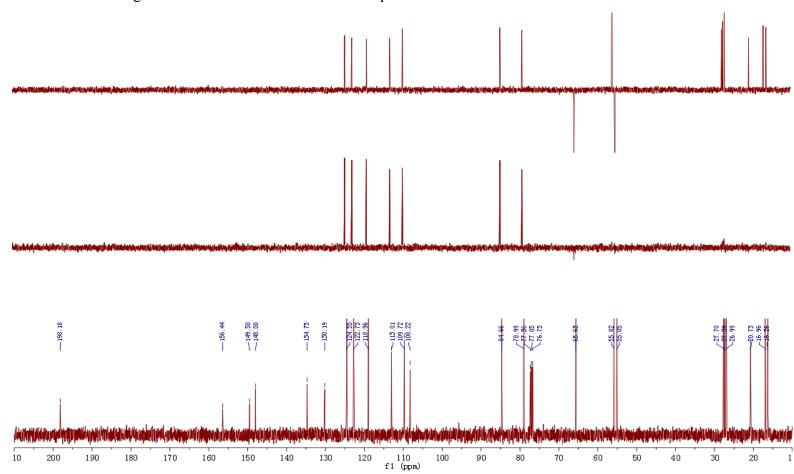


Figure 20S. ROESY of compound 2a.

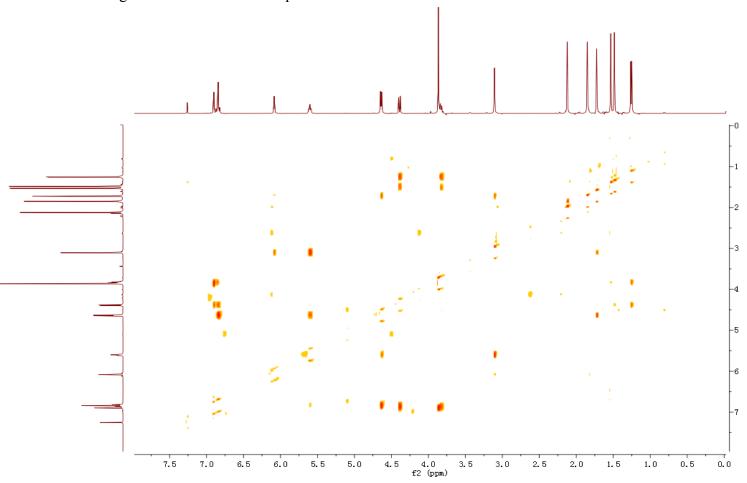


Figure 21S. ¹H NMR of compound **3**.

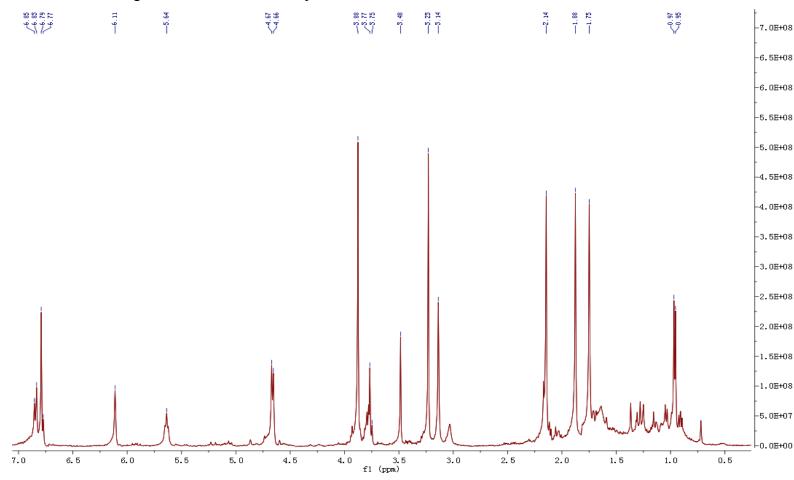


Figure 22S. ¹³C NMR and DEPT of compound **3**.

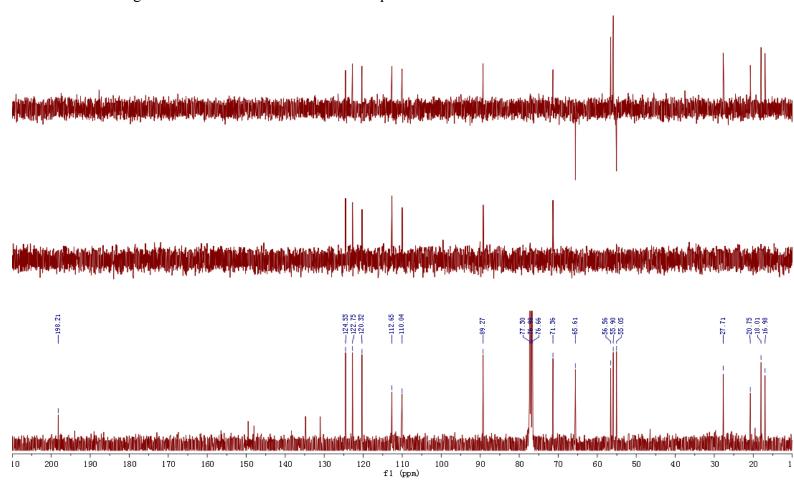
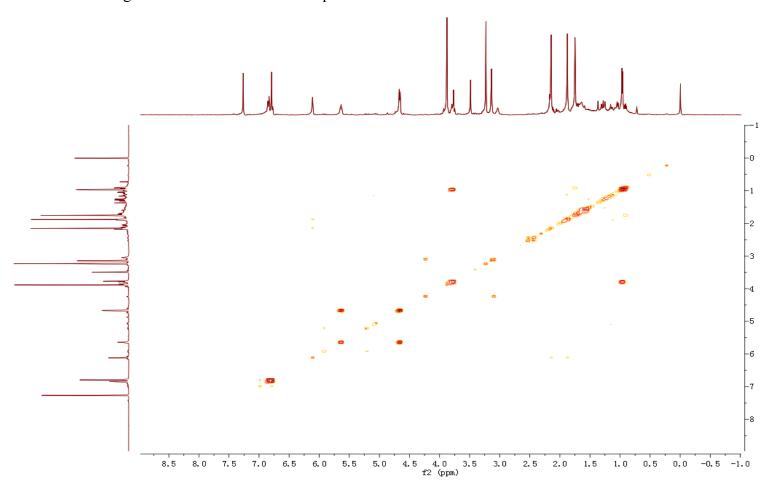


Figure 23S. HSQC of compound **3**. |10 -20 -30 -40 -50 -60 -80 -90 -100 -110 -120 -130 140 7.5 0.5 7.0 6.5 6.0 5.5 5.0 3.5 3.0 2.5 2.0 1.5 1.0

Figure 24S. HMBC of compound 3.

-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

Figure 25S. ¹H-¹H COSY of compound **3**.



f1 (nnm)

Figure 26S. ROESY of compound **3**.

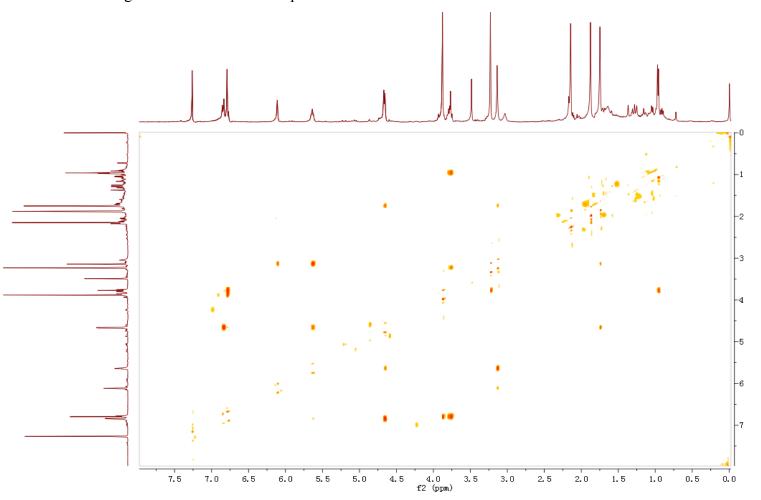


Figure 27S. HRESIMS of compound 3.

Elemental Composition Report Page 1 Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = 0.5, max = 120.0 Selected filters: None Monoisotopic Mass, Odd and Even Electron Ions 17 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass) Elements Used: C: 0-200 H: 0-400 O: 3-6 Dgzy-28c 12:03:06 18-Apr-2012 Voltage EI+ KIB M120418EA-12AFAMM 11 (1.010) 362.2098 Autospec Premier P776 725 % 0-361.900 → m/z 362.000 362.100 362.200 362.300 362.400 362.500 Minimum: 0.5 120.0 40.0 10.0 Calc. Mass mDa PPM DBE i-FIT 362.2098 362.2093 0.5 1.4 7.0 5546375.0 C21 H30 O5

Figure 28S. ¹H NMR of compound **4**.

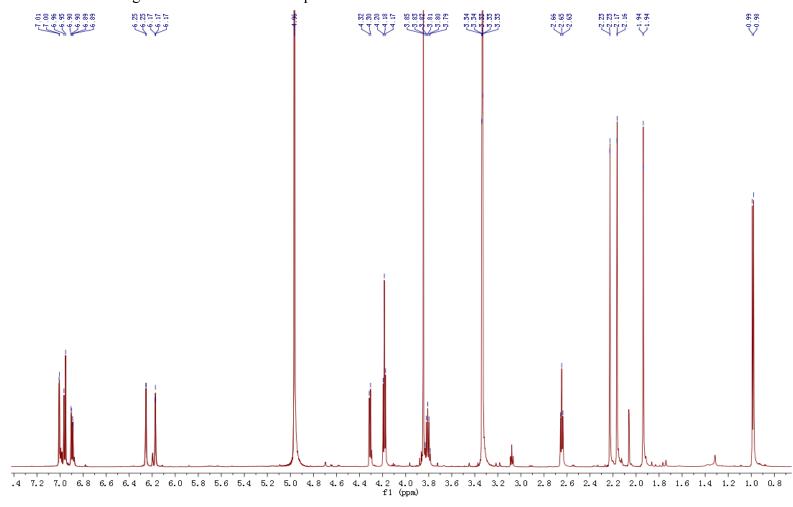


Figure 29S. ¹³C NMR and DEPT of compound **4**.

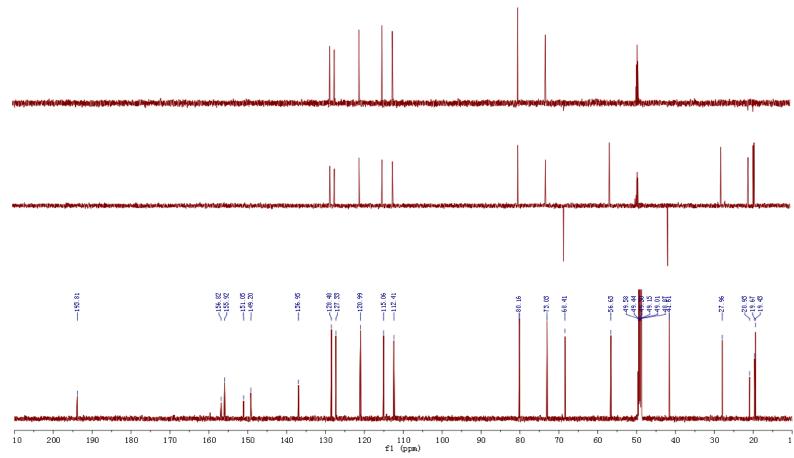


Figure 30S. HSQC of compound 4.

4.0 f2 (ppm) 3.0

2.5

7.0

6.5

6.0

5.5

5.0

4.5

-60

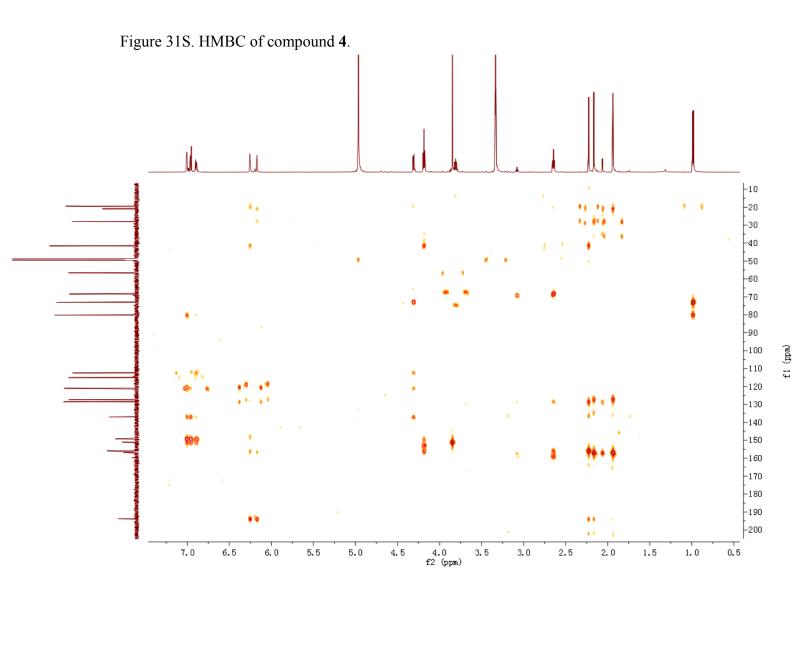
-80 -90 -100 -110 -120 -130

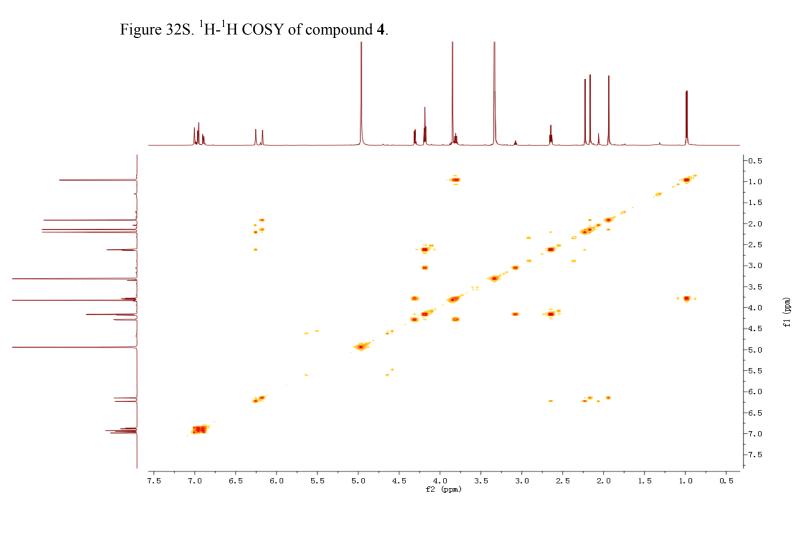
1.5

2.0

1.0

0.5





-1 -1 -2 -3 -4 -5

Figure 33S. ROESY of compound 4.

7.5

7.0

6.5

6.0

5.5

5.0

2.5

3.0

3.5

2.0

1.5

1.0

Figure 34S. HRESIMS of compound 4.

Elemental Composition Report Page 1 Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = 0.5, max = 120.0 Selected filters: None Monoisotopic Mass, Odd and Even Electron Ions To formula (e) evaluated with 1 results within limits (up to 51 closest results for each mass) Elements Used: C: 0-200 H: 0-400 O: 3-6 Dgzy-25c KIB 11:54:27 18-Apr-2012 Voltage EI+ 348. KIB M120418EA-10AFAMM 12 (1.102) 348_1937 Autospec Premier P776 1.98e3 % 348.1096348.1488 → m/z 347.800 347.900 348.000 348.100 348.200 348.300 348.400 348.500 Minimum: 0.5 120.0 Calc. Mass mDa DBE i-FIT Formula 348.1937 348.1937 7.0 5547000.5 C20 H28 O5

Figure 35S. ¹H NMR of compound **5**.

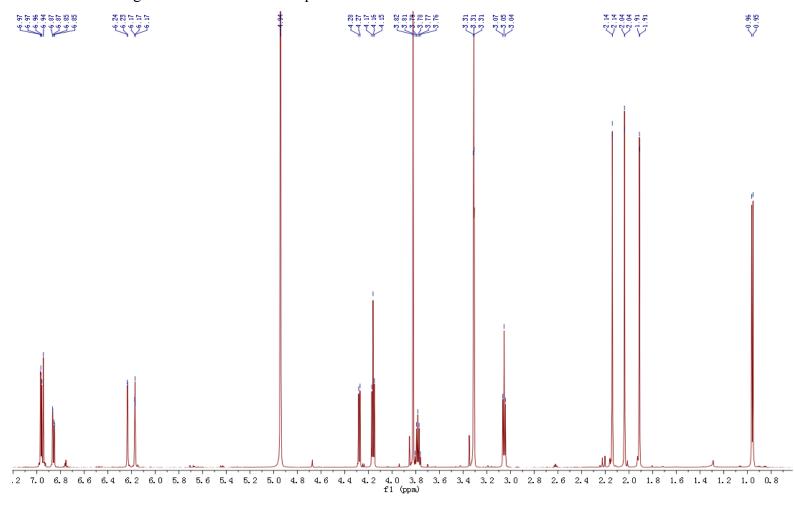


Figure 36S. ¹³C NMR and DEPT of compound **5**.

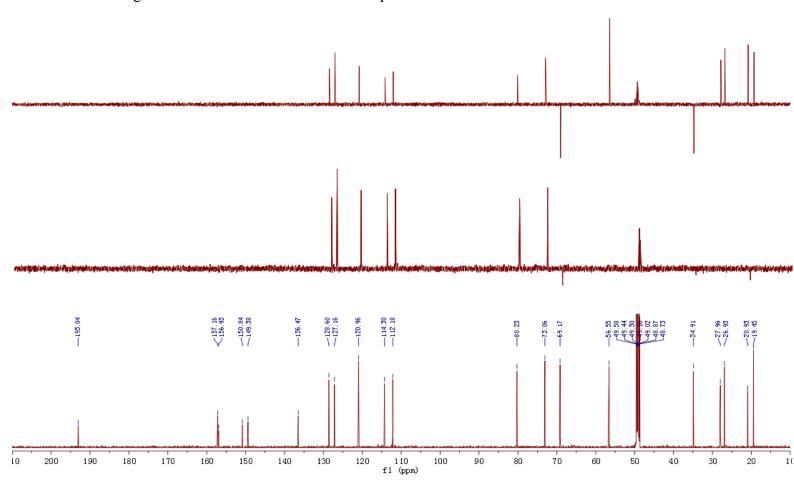


Figure 37S. HSQC of compound 5.

4.0 f2 (ppm)

7.5

7. 0

6.5

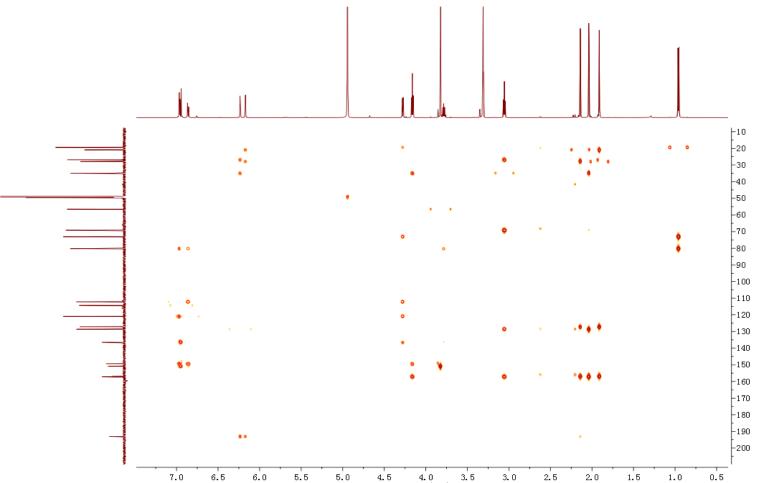
6.0

5.5

140

1.0

Figure 38S. HMBC of compound **5**.



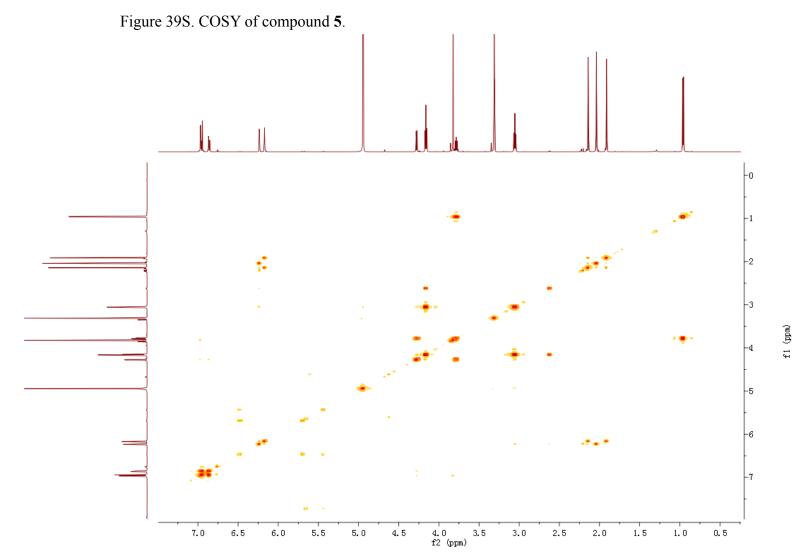


Figure 40S. ROESY of compound 5.

7.5

6.0

5.5

3.0

2.5

2.0

1.5

1.0

0.5

3.5

Figure 41S. HRESIMS of compound 5.

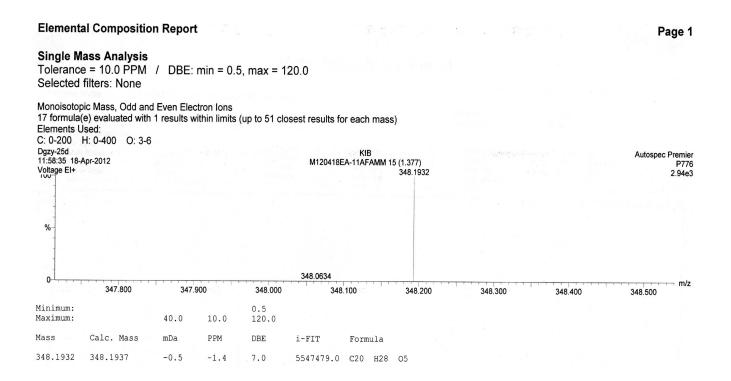


Figure 42S. ¹H NMR of compound **6**.

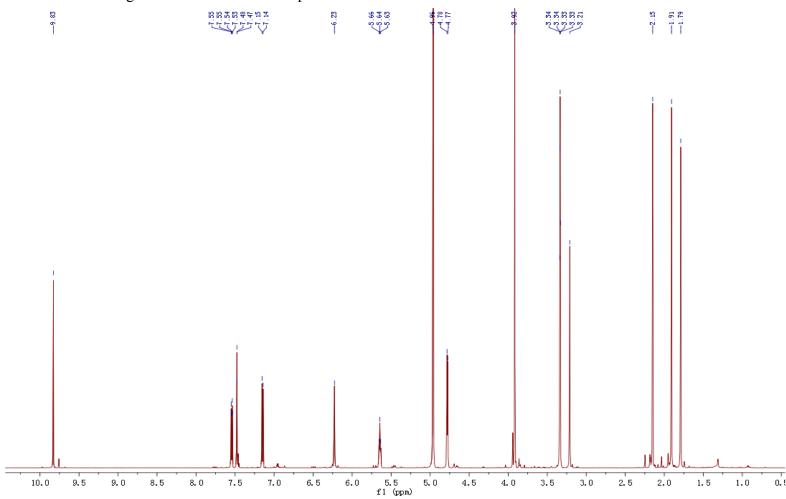


Figure 43S. ¹³C NMR and DEPT of compound **6**.

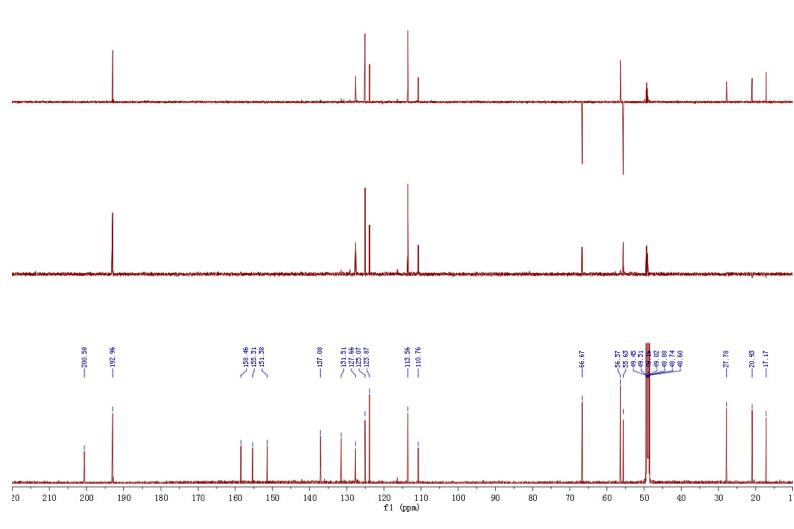


Figure 44S. HSQC of compound **6**.

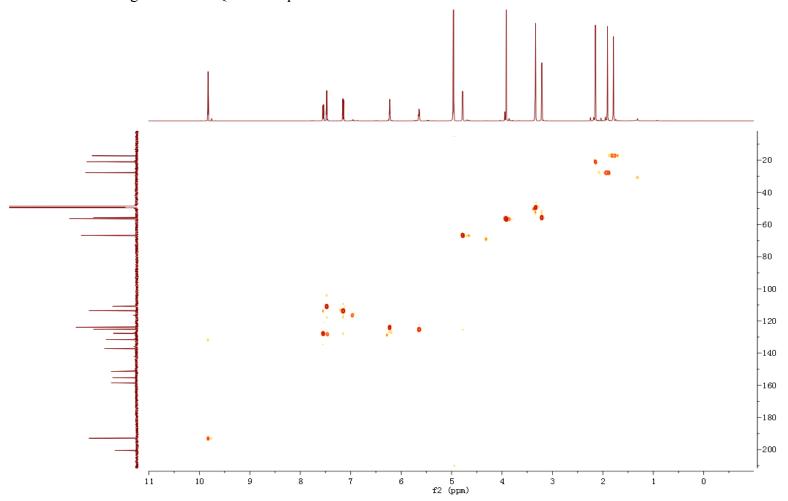


Figure 45S. HMBC of compound **6**.

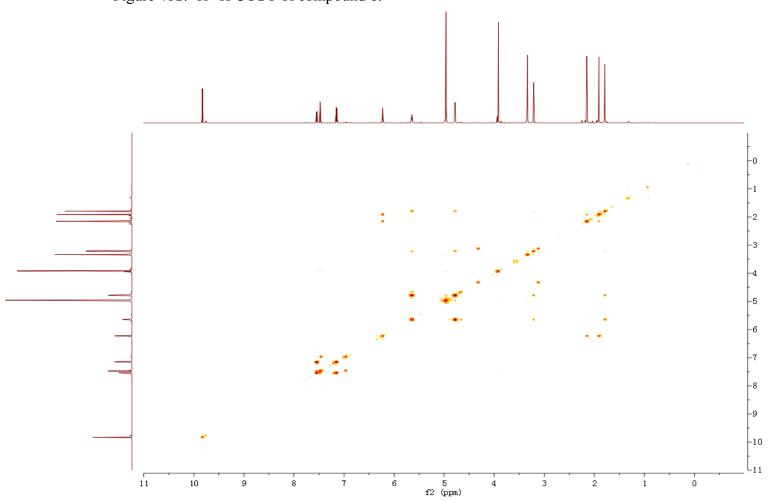
-20
-40
-80
-100
-140
-140

5 f2 (ppm) -180

-200

-220

Figure 46S. ¹H-¹H COSY of compound **6**.



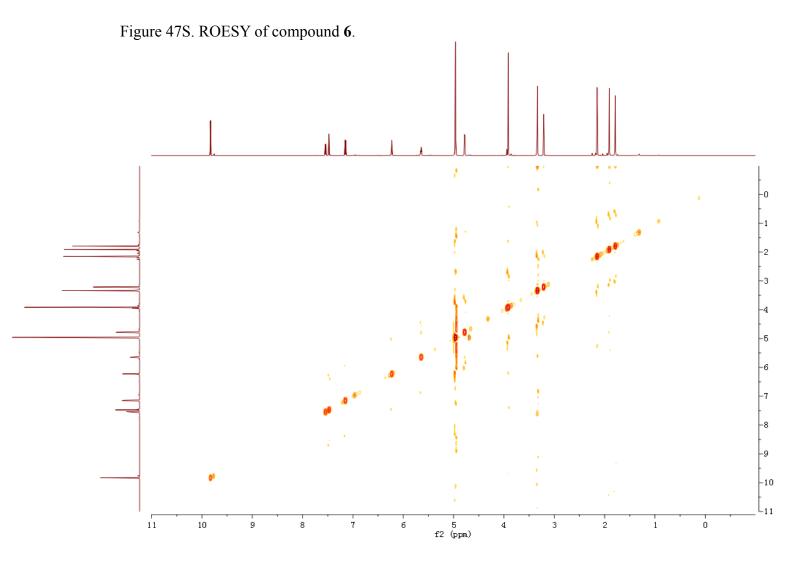


Figure 48S. HRESIMS of compound 6.

Page 1 **Elemental Composition Report** Single Mass Analysis (displaying only valid results) Tolerance = 10.0 PPM / DBE: min = 0.5, max = 60.0 Selected filters: None Monoisotopic Mass, Odd and Even Electron Ions 13 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass) Elements Used: C: 0-200 H: 0-400 O: 3-6 KIB M12040gEA-01AFAMM 13 (1.194) 302.1512 Autospec Premier P776 Dgzy-12 11:02:14 09-Apr-2012 Voltage EI+ 3.68e3 302.2315 302.1018 m/z 302.300 302.400 302.500 302.200 301.800 301.900 302.000 302.100 Minimum: Maximum: 73.0 Formula Calc. Mass PPM DBE 5547847.5 C18 H22 O4 302.1512 302.1518 8.0 -0.6 -2.0

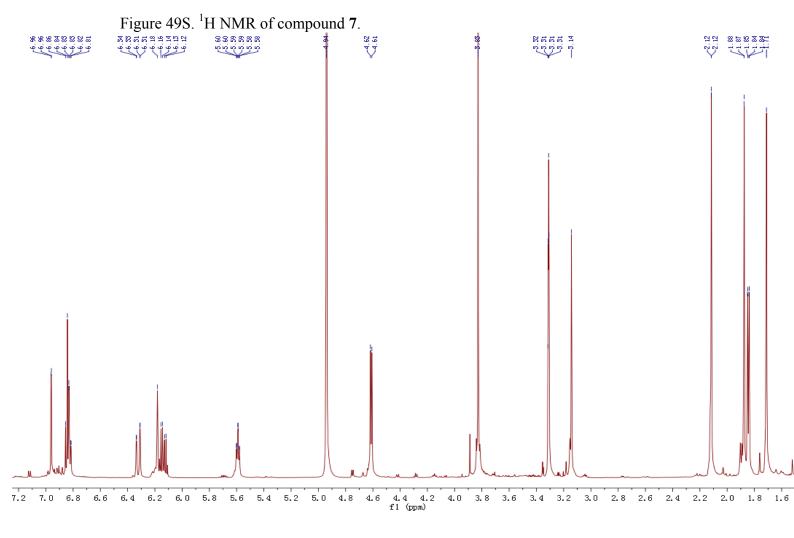
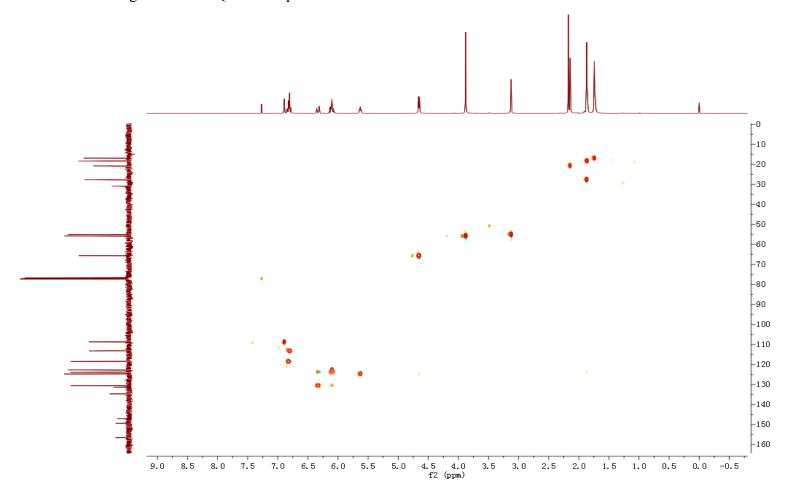


Figure 50S. ¹³C NMR and DEPT of compound 7. 110 100 fl (ppm)

Figure 51S. HSQC of compound 7.



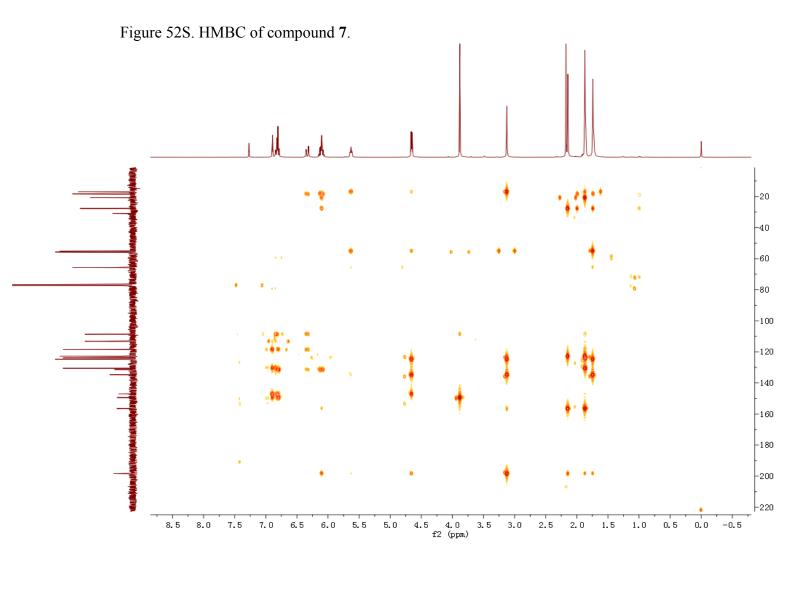


Figure 53S. ¹H-¹H COSY of compound **7**.

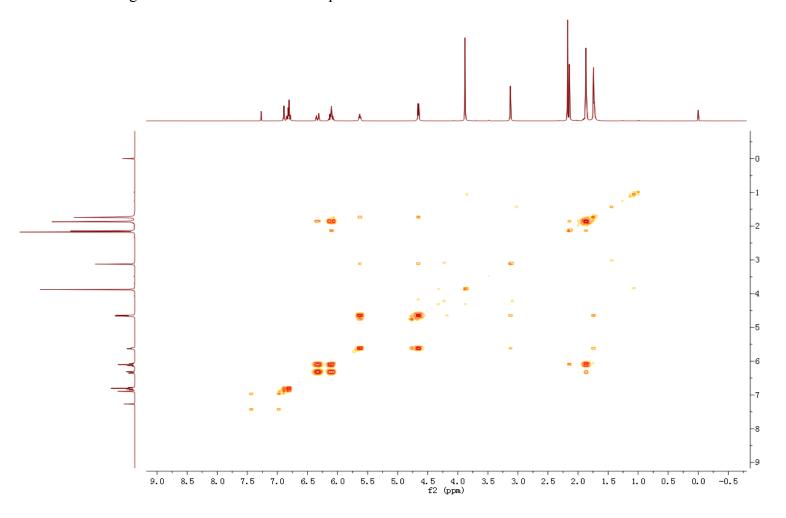


Figure 54S. ROESY of compound 7.

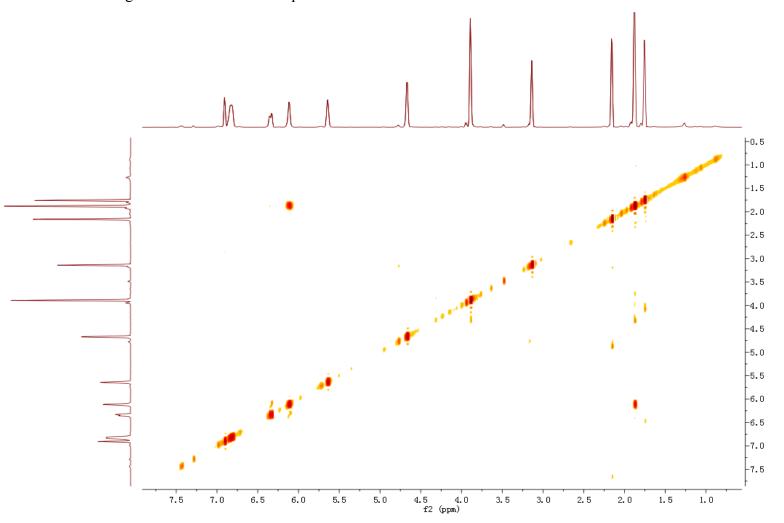


Figure 55S. HRESIMS of compound 7.

Page 1 **Elemental Composition Report** Single Mass Analysis (displaying only valid results) Tolerance = 10.0 PPM / DBE: min = 0.5, max = 60.0 Selected filters: None Monoisotopic Mass, Odd and Even Electron Ions 14 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass) Elements Used: KIB M120409EA-02AFAMM 9 (0.826) 314.1887 C: 0-200 H: 0-400 O: 3-6 Autospec Premier P776 2.26e4 Dgzy-3 11:06:26 09-Apr-2012 Voltage EI+ 314.2863 314.2525 314.0064 314.0695 314.1179 m/z 314.600 313.700 314.500 314.400 314.100 314.200 314.300 314.000 313.900 313.800 10.0 60.0 Maximum: Formula PPM DBE i-FIT Calc. Mass Mass 5557311.0 C20 H26 O3 8.0 314.1887 314.1882