

# Flavonoids in the Poisonous Plant, *Oxytropis falcata*

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## Supporting information available

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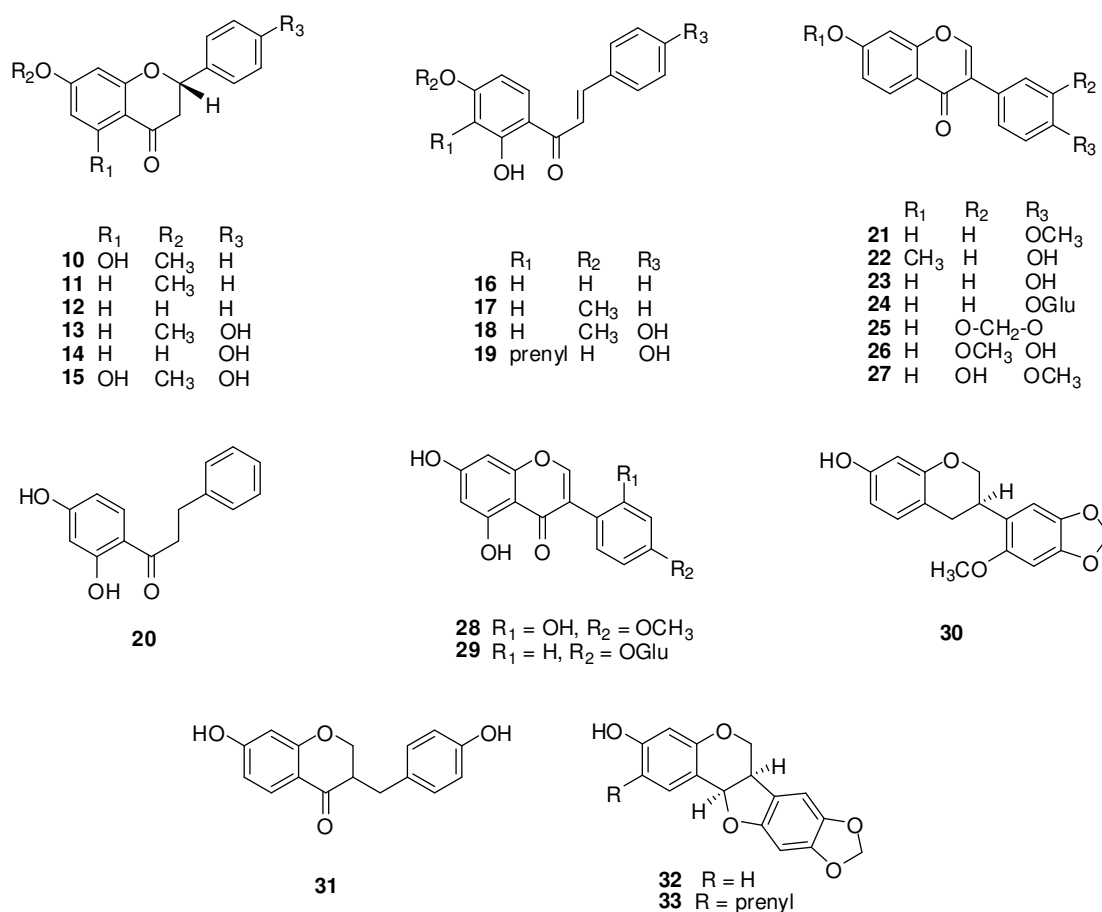
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**Figure S1.** Structures of flavonoids (**10–33**): (–)-pinostrobin (**10**),<sup>1</sup> (2*S*)-7-methoxyflavanone (**11**),<sup>2</sup> (2*S*)-7-hydroxyflavanone (**12**),<sup>3</sup> (2*S*)-4'-hydroxy-7-methoxyflavanone (**13**),<sup>4</sup> (–)-liquiritigenin (**14**),<sup>4</sup> (*S*)-(–)-sakuranetin (**15**),<sup>5</sup> 2',4'-dihydroxychalcone (**16**),<sup>6</sup> 2'-hydroxy-4'-methoxychalcone (**17**),<sup>6</sup> 4,2'-dihydroxy-4'-methoxychalcone (**18**),<sup>7</sup> isobacachalcone (**19**),<sup>8</sup> 2',4'-dihydroxydihydrochalcone (**20**),<sup>6</sup> formononetin (**21**),<sup>9</sup> 4'-hydroxy-7-methoxyisoflavone (**22**),<sup>10</sup> daidzein (**23**),<sup>10</sup> daidzein, 4'-β-D-glucopyranoside (**24**),<sup>11</sup> pseudobaptigenin (**25**),<sup>12</sup> 7,4'-dihydroxy-3'-methoxyisoflavone (**26**),<sup>13</sup> calycosin (**27**),<sup>9</sup> 2'-hydroxybiochanin A (**28**),<sup>14</sup> genistein, 4'-β-D-glucopyranoside (**29**),<sup>15</sup> astraciceran (**30**),<sup>16</sup> 7,4'-dihydroxyhomoisoflavanone (**31**),<sup>17</sup> (–)-maackiain (**32**),<sup>18</sup> and (–)-edunol (**33**),<sup>19</sup>

## References and Notes

- (1) Mongkolsuk, S.; Dean, F. M. *J. Chem. Soc.* **1964**, 4654–4655.
- (2) Bohlmann, F.; Jakupovic, J. *Phytochemistry* **1979**, *18*, 1189–1194.

- (3) Braga de Oliveira, A.; Fonseca e Silva, L. G.; Gottlieb, O. R. *Phytochemistry* **1972**, *11*, 3515–3519.
- (4) Yu, D. Q.; Yang, J. S. *Analytical Chemistry Handbook, Nuclear Magnetic Resonance spectra*, Beijing, Chemical industry press, 1999; pp 821–822.
- (5) Jerz, G.; Waibel, R.; Achenbach, H. Cyclohexanoid protoflavanones from the stem-bark and roots of *Ongokea gore*. *Phytochemistry* **2005**, *66*, 1698–1706.
- (6) Lu, F.; Xu, X. J. *Zhongguo zhongyao zazhi* **2007**, *32*, 318–320.
- (7) Yu, D. Q.; Yang, J. S. *Analytical Chemistry Handbook, Nuclear Magnetic Resonance spectra*, Beijing, Chemical industry press, 1999; pp 829–830.
- (8) Nakata, K.; Taniguchi, M.; Baba, K. *Nat. Med.* **1999**, *53*, 329–332.
- (9) Zhao, S. H.; Zhang, L. P.; Gao, P.; Shao, Z. Y. *Food Chemistry* **2009**, *114*, 869–873
- (10) Yu, D. Q.; Yang, J. S. *Analytical Chemistry Handbook, Nuclear Magnetic Resonance spectra*, Beijing, Chemical industry press, 1999; p 826.
- (11) Sang, Y. S.; Shi, H. M.; Min, Z. D. *Zhongcaoyao* **2002**, *33*, 776–778.
- (12) Biggs, D. R.; Lane, G. A. *Phytochemistry* **1978**, *17*, 1683–1684.
- (13) Takai, M.; Yamaguchi, H.; Saitoh, T.; Shibata, S. *Chem. Pharm. Bull.* **1972**, *20*, 2488–2490.
- (14) Lops, N. P.; Chicaro, P.; Kato, M. J.; Albuquerque, S.; Yoshida, M. *Planta. Med.* **1998**, *64*, 667–669.
- (15) Wang, J. H.; Wang, Y. L.; Luo, F. C. *Zhongguo Yaoke Daxue Xuebao* **2001**, *32*, 471–473.
- (16) Martin, S. S.; Townsend, C. E.; Lenssen, A. W. *Biochem. Syst. Ecol.* **1994**, *22*, 657–661.
- (17) Camarda, L.; Merlini, L.; Nasini, G. *Heterocycles* **1983**, *20*, 39–43.
- (18) (a) Kinoshita, T.; Ichinose, K.; Takahashi, C.; Ho, F. C.; Wu, J. B.; Sankawa, U. *Chem. Pharm. Bull.* **1990**, *38*, 2756–2759. (b) Mizuno, M.; Tanaka, T.; Katsuragawa, M.; Saito, H.; Iinuma, M. *J. Nat. Prod.* **1990**, *53*, 498–499.
- (19) Reyes-Chilpa, R.; Gómez-Garibay, F.; Quijano, L.; Magos-Guerrero, G. A.; Ríos, T. *J Ethnopharmacol.* **1994**, *42*, 199–203.

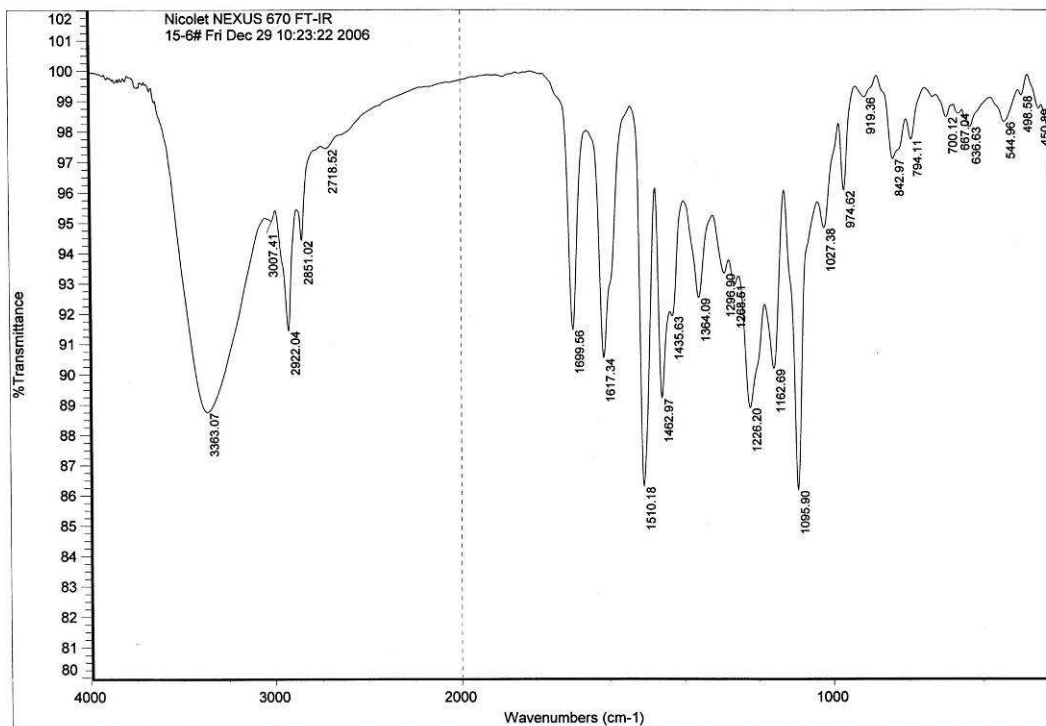


Figure S2. IR spectrum of oxytropisoflavan A (1).

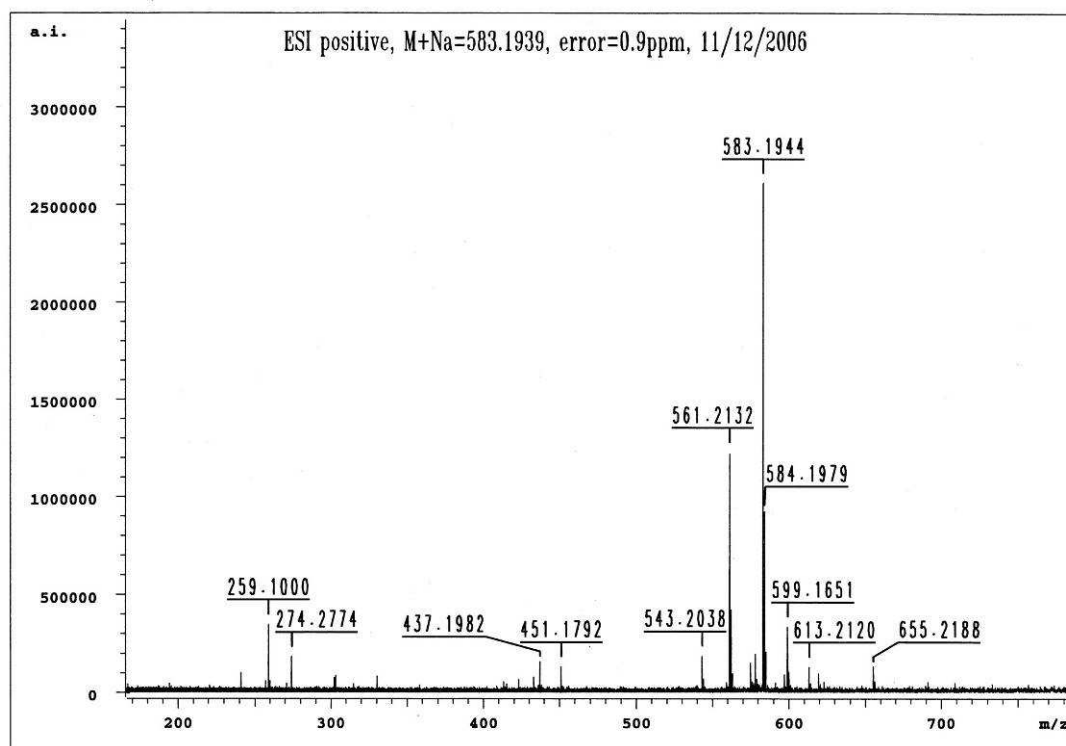
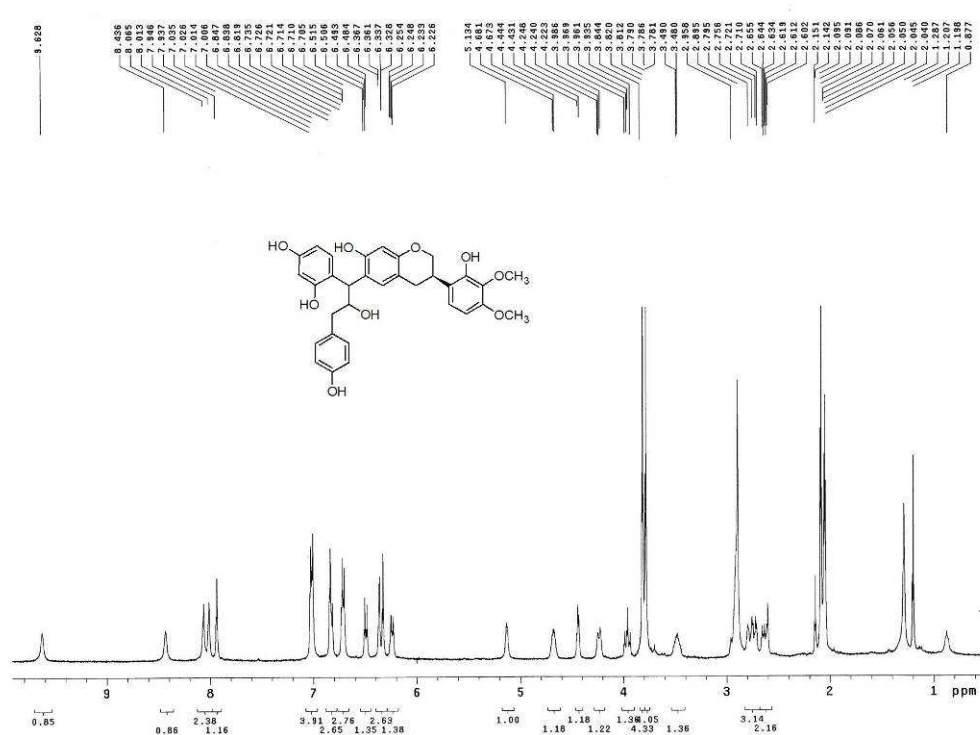
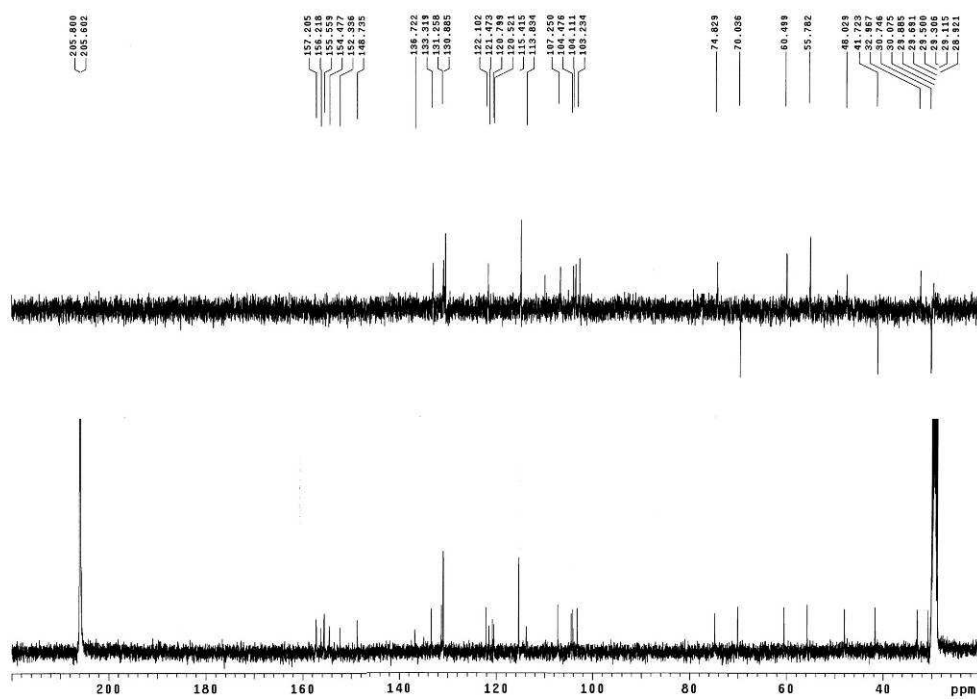


Figure S3. HRESIMS of oxytropisoflavan A (1).



**Figure S4.** The <sup>1</sup>H NMR (400MHz, acetone-*d*<sub>6</sub>) of oxytropisoflavan A (1).



**Figure S5.** The <sup>13</sup>C NMR and DEPT135 (100MHz, acetone-*d*<sub>6</sub>) of oxytropisoflavan A (1).

STANDARD 1H OBSERVE

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Ambient temperature  
Mercury-400BB "ULAOC400"

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Acq. time 0.236 sec  
Width 4347.8 Hz  
2D Width 24154.6 Hz  
72 repetitions  
400 increments  
OBSERVE H1 400.1738853 MHz  
DATA PROCESSING  
Sine bell 0.118 sec  
F1 DATA PROCESSING  
Sine bell 0.008 sec  
FT size 2048 x 2048  
Total time 10 hr, 59 min, 43 sec

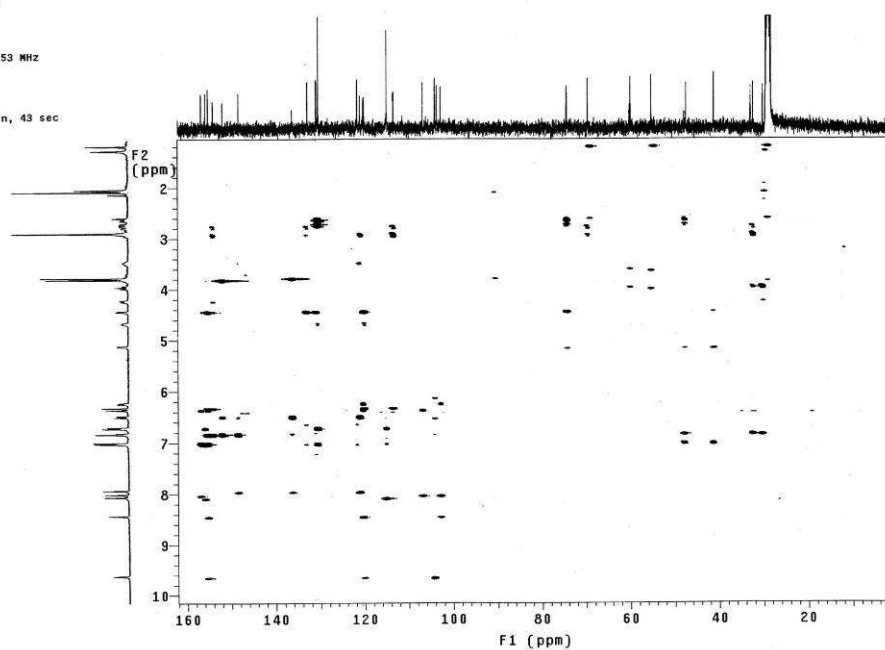


Figure S6. gHMBC spectrum of oxytropisoflavan A (1).

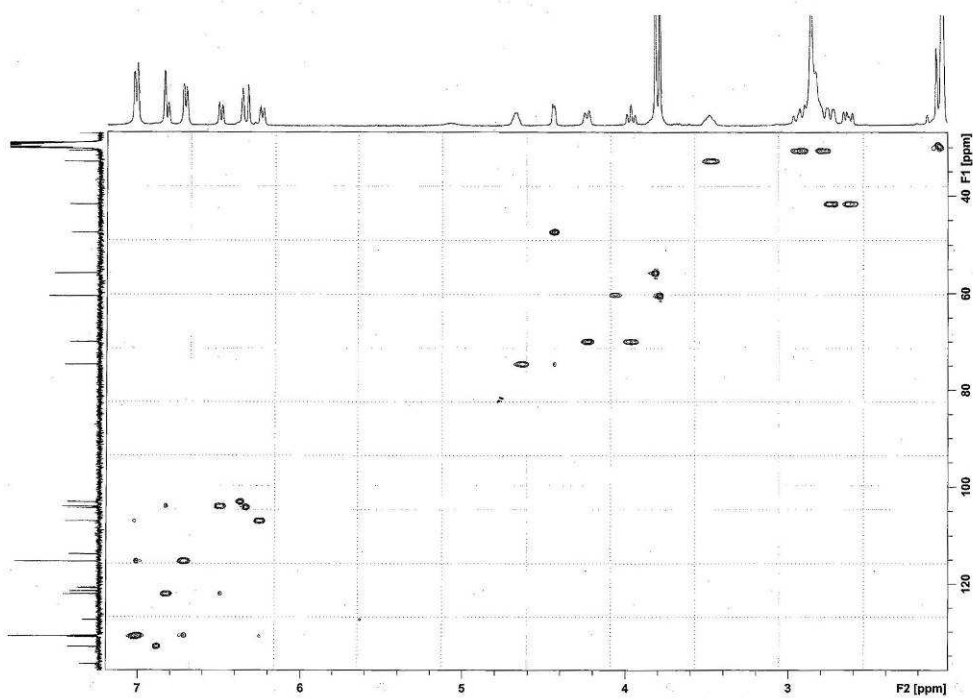


Figure S7. gHSQC spectrum of oxytropisoflavan A (1).

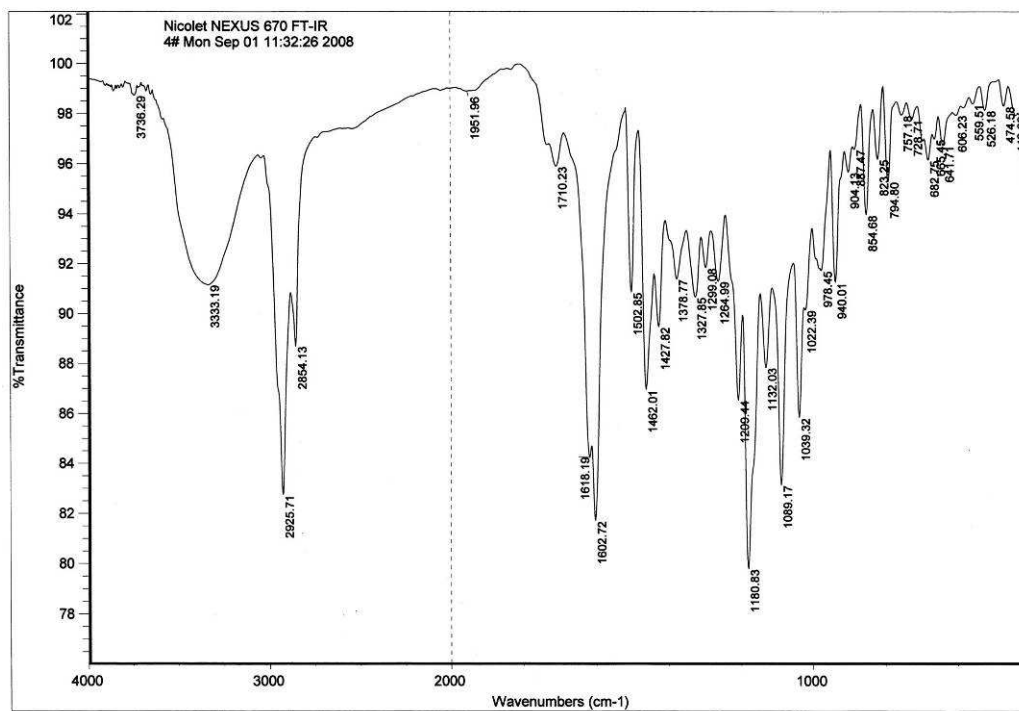


Figure S8. IR spectrum of oxytropisoflavan B (2).

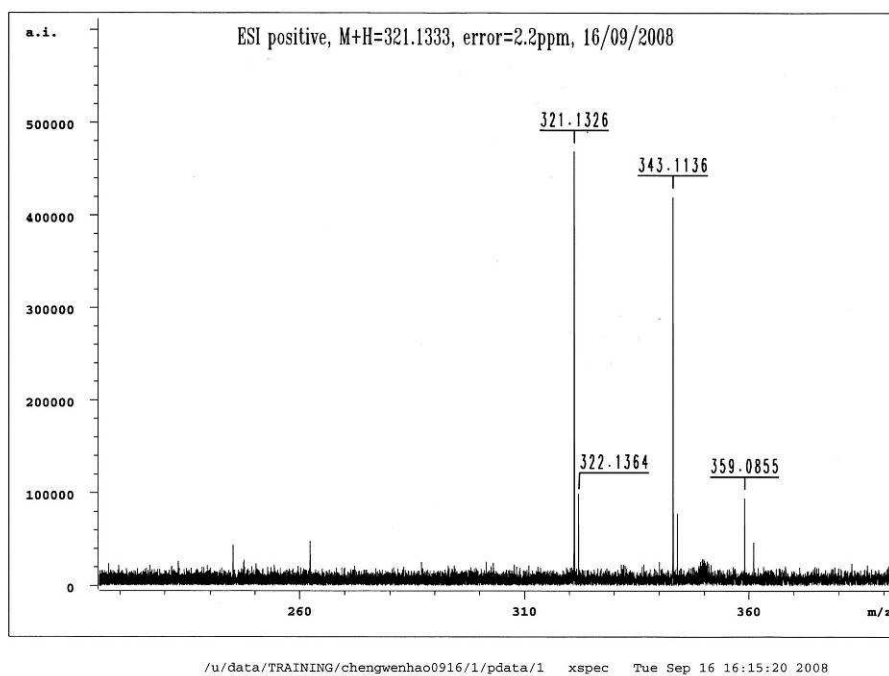
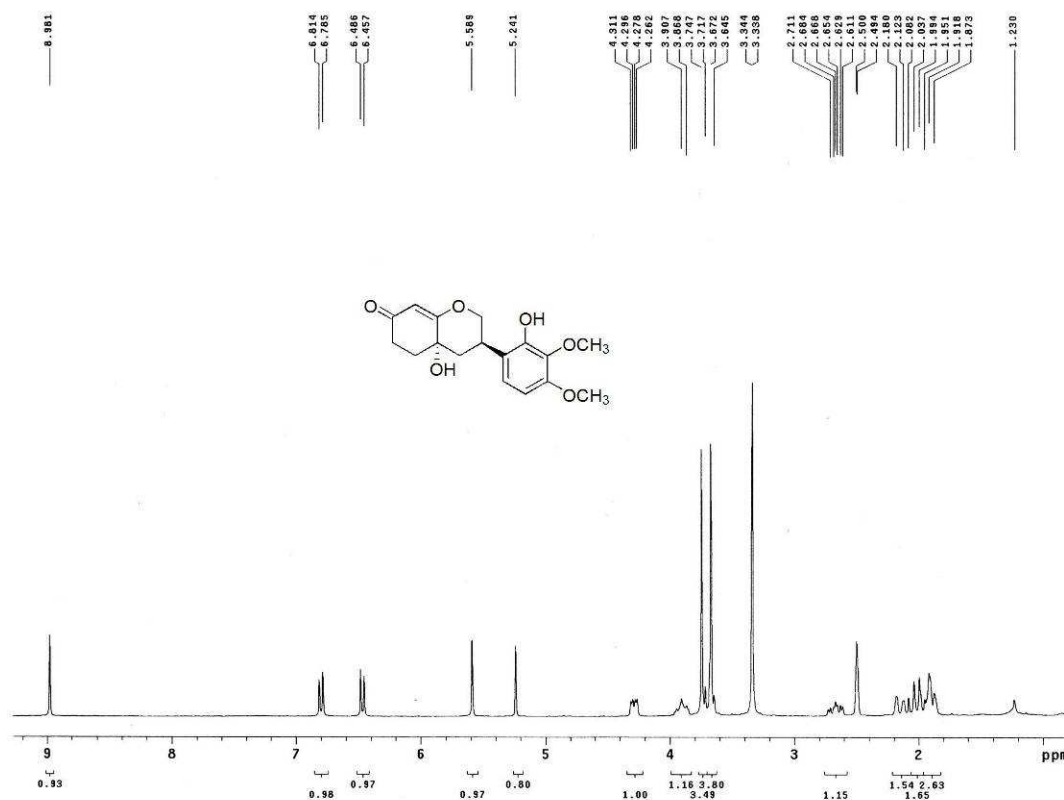
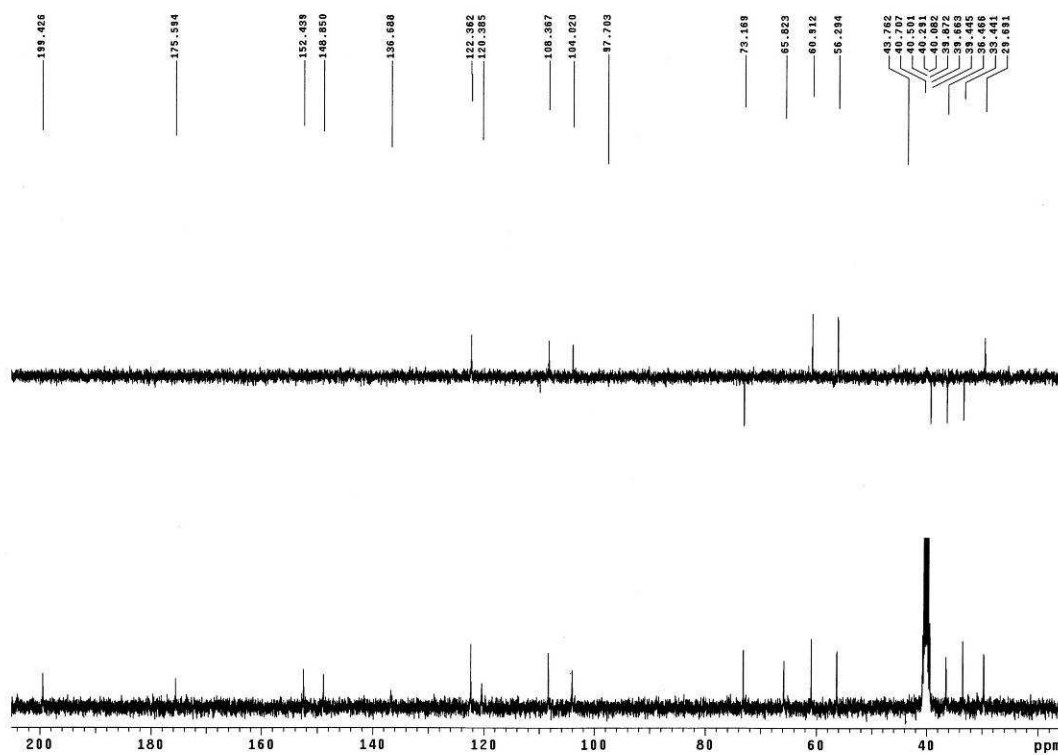


Figure S9. HRESIMS of oxytropisoflavan B (2).



**Figure S10.** The <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>) of oxytropisoflavan B (2).



**Figure S11.** The <sup>13</sup>C NMR and DEPT135 (100MHz, DMSO-*d*<sub>6</sub>) of oxytropisoflavan B (2).

STANDARD 1H OBSERVE

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Mercury-400SB "ULAGC400"

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Acq. time 0.160 sec  
Width 6410.3 Hz  
2D Width 24154.6 Hz  
32 repetitions  
400 increments  
OBSERVE H1, 400.1736908 MHz  
DATA PROCESSING  
Sine bell 0.080 sec  
F1 DATA PROCESSING  
Sine bell 0.008 sec  
FT size 2048 x 2048  
Total time 4 hr, 36 min, 58 sec

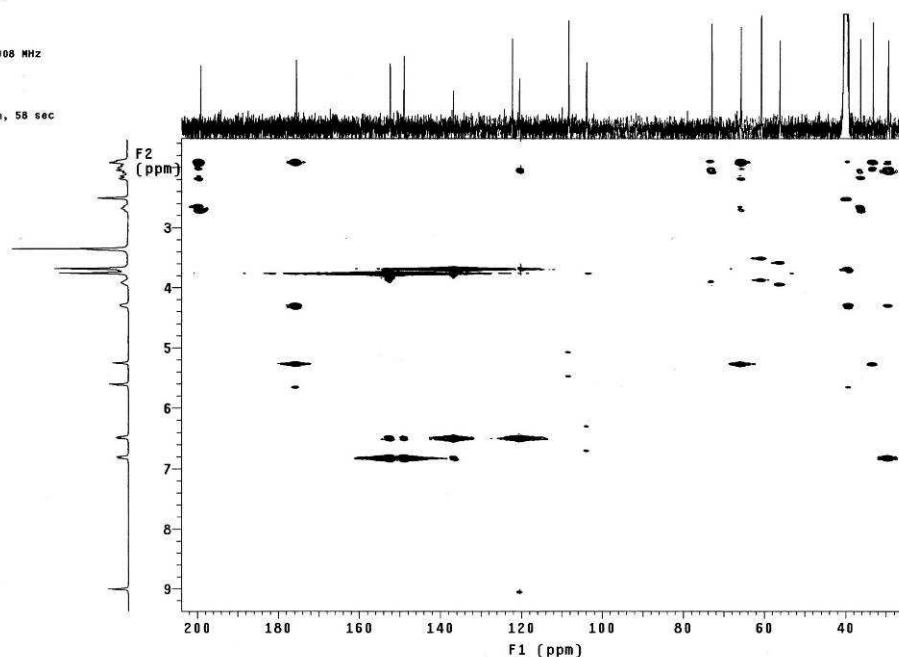


Figure S12. gHMBC spectrum of oxytropisoflavan B (2).

STANDARD 1H OBSERVE

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Solvent: DMSO  
Ambient temperature  
Mercury-300SB "LZU-NMR300"

Relax. delay 1.000 sec  
Acq. time 0.213 sec  
Width 4807.7 Hz  
2D Width 12820.5 Hz  
56 repetitions  
2 x 128 increments  
OBSERVE H1, 300.0746504 MHz  
DECOUPLE C13, 75.4594732 MHz  
Power 39 dB  
on during acquisition  
off during delay  
GASP-1 modulated  
DATA PROCESSING  
Gauss apodization 0.098 sec  
F1 DATA PROCESSING  
Gauss apodization 0.018 sec  
FT size 2048 x 2048  
Total time 5 hr, 19 min, 39 sec

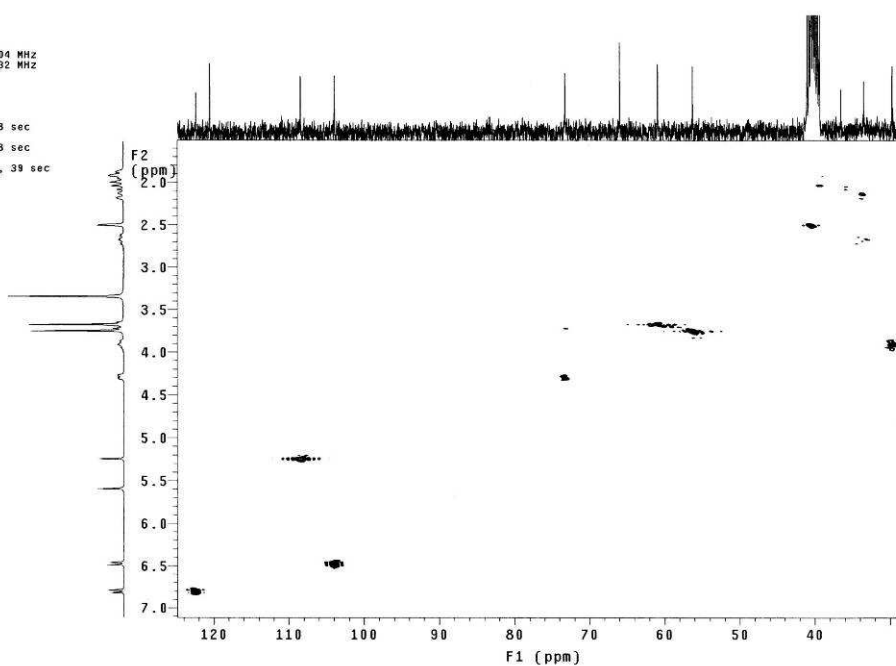
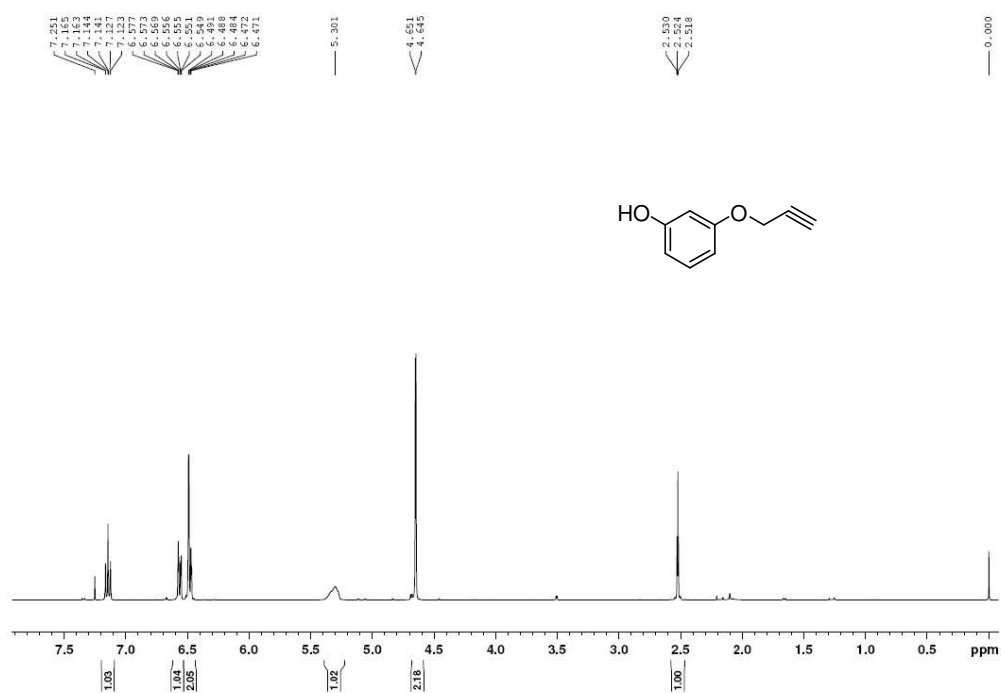
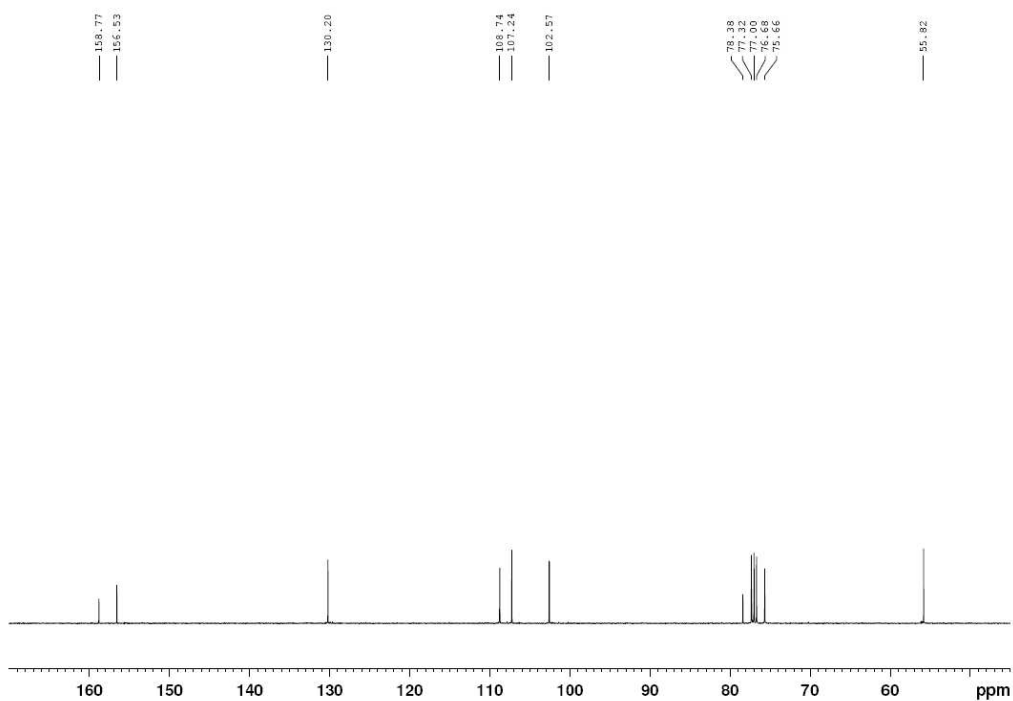


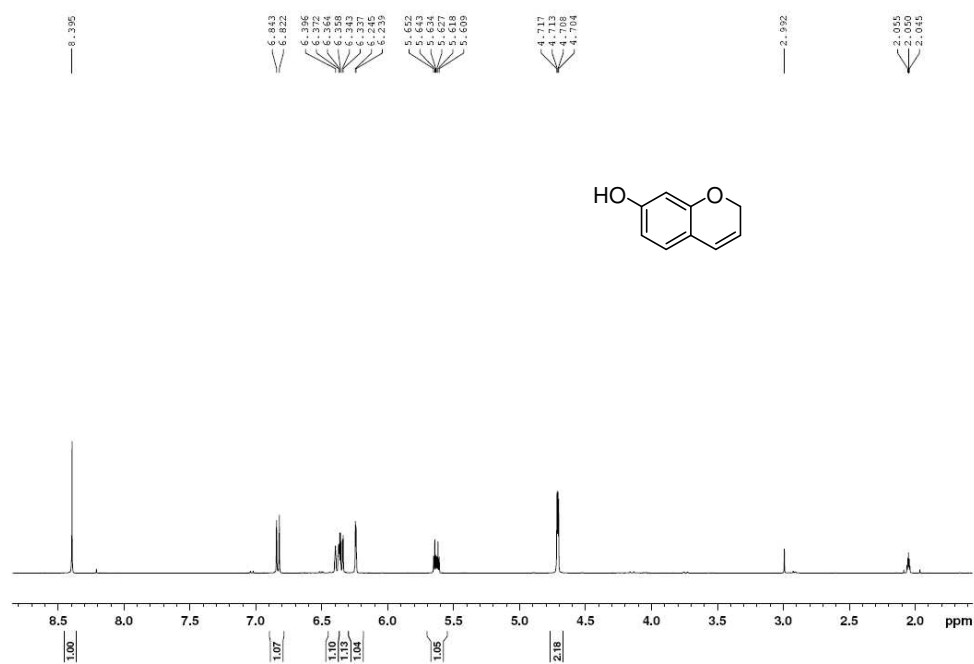
Figure S13. gHSQC spectrum of oxytropisoflavan B (2).



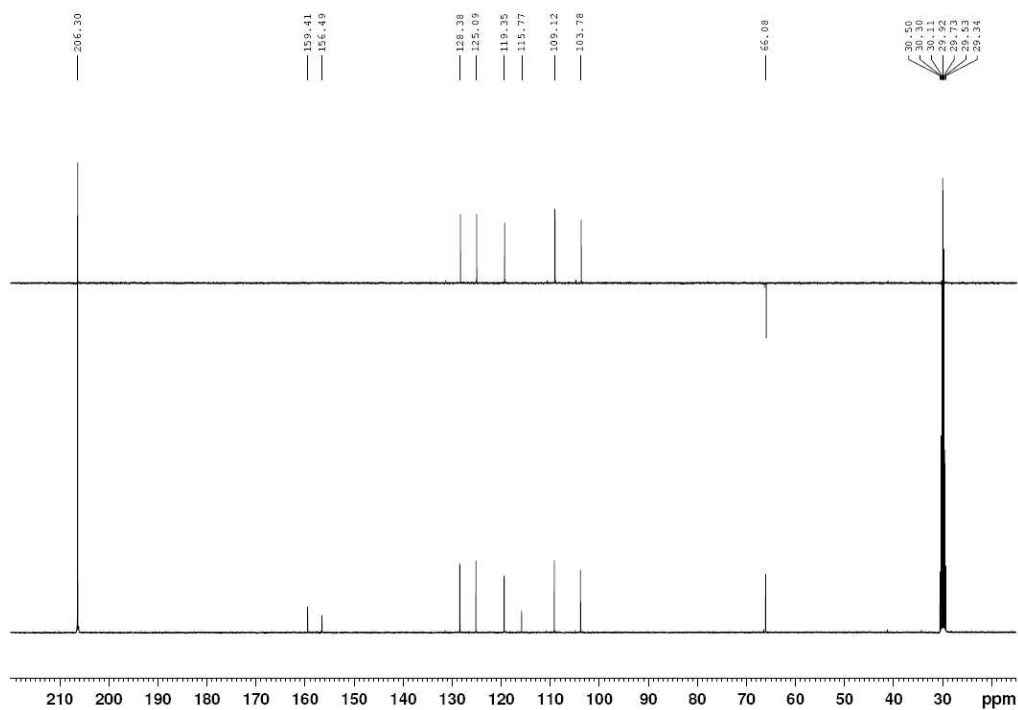
**Figure S14.** The <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) of compound **II**.



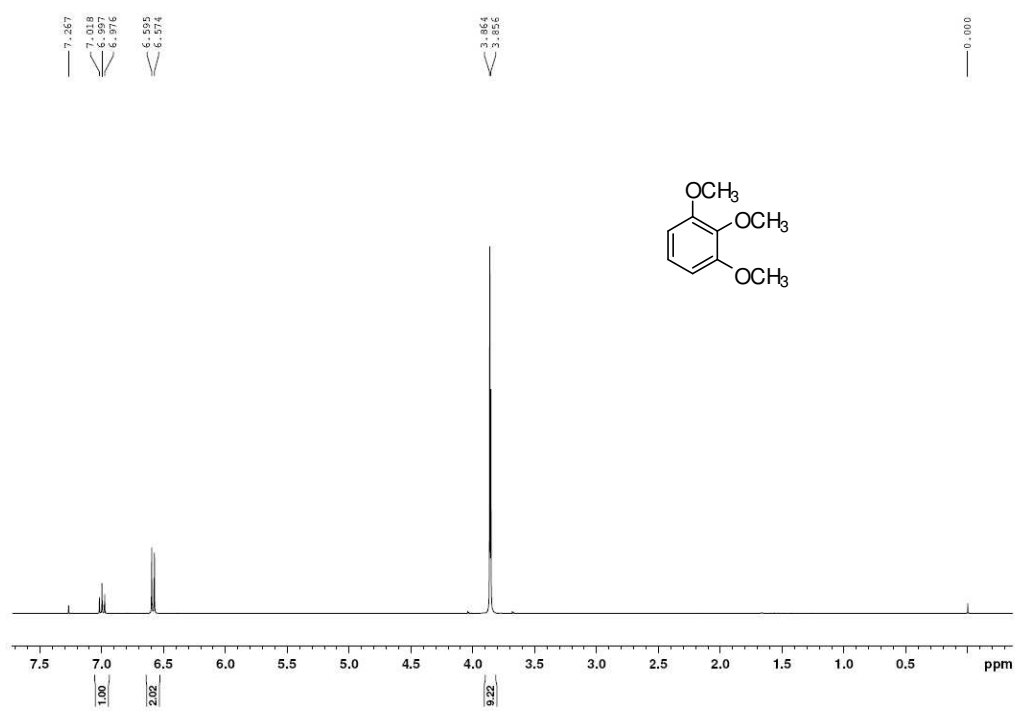
**Figure S15.** The <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) of compound **II**.



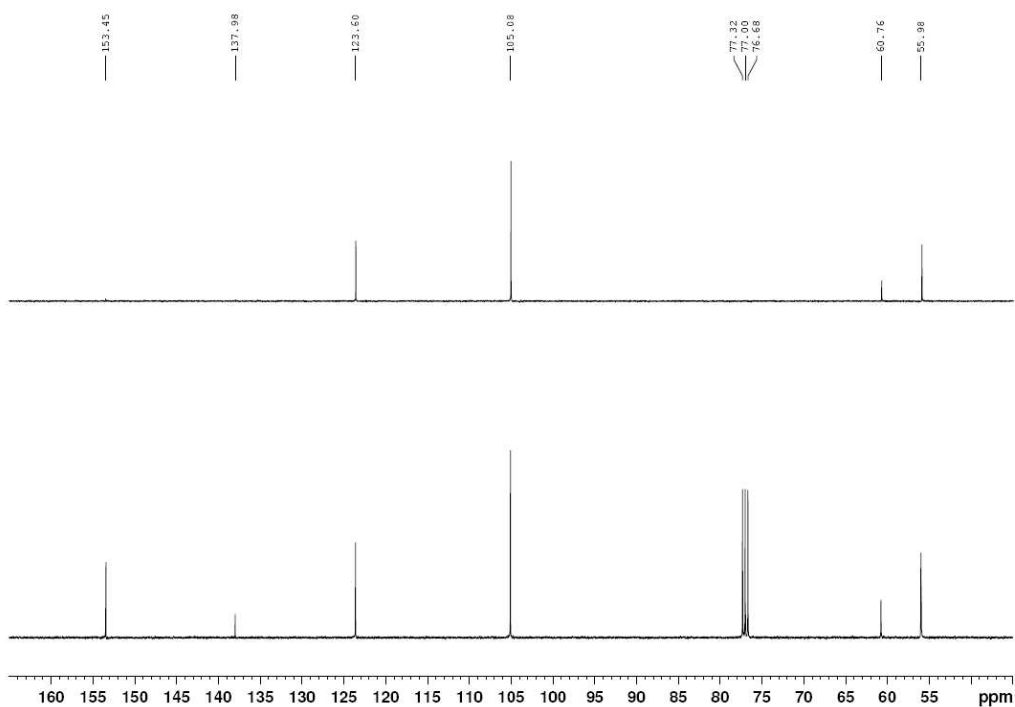
**Figure S16.** The <sup>1</sup>H NMR (400MHz, acetone-*d*<sub>6</sub>) of compound **III**.



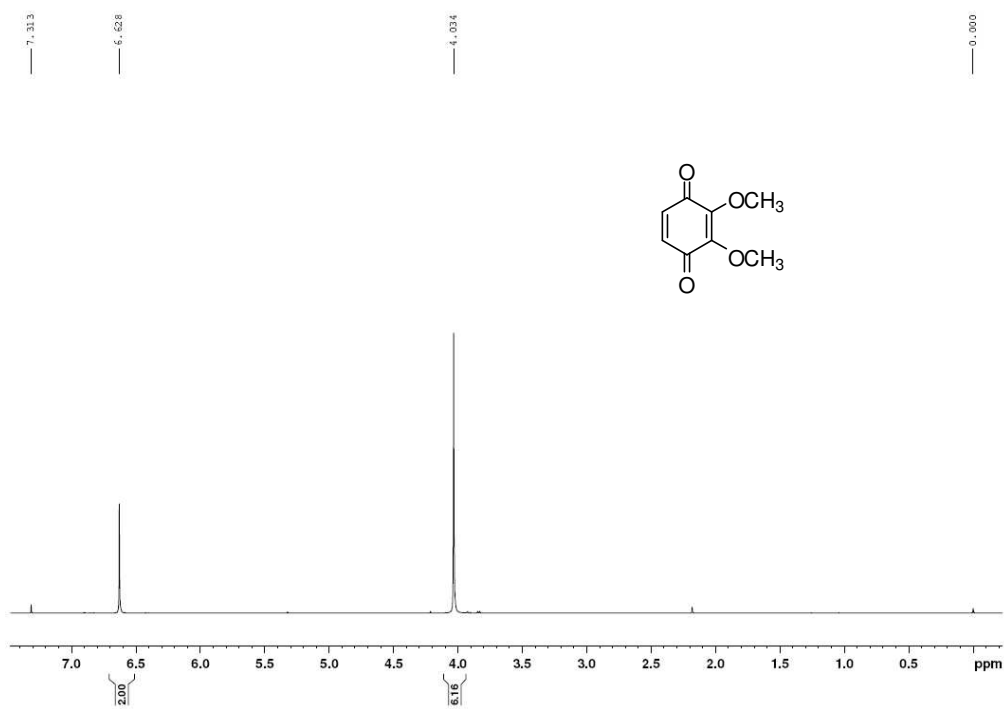
**Figure S17.** The <sup>13</sup>C NMR and DEPT135 (100MHz, acetone-*d*<sub>6</sub>) of compound **III**.



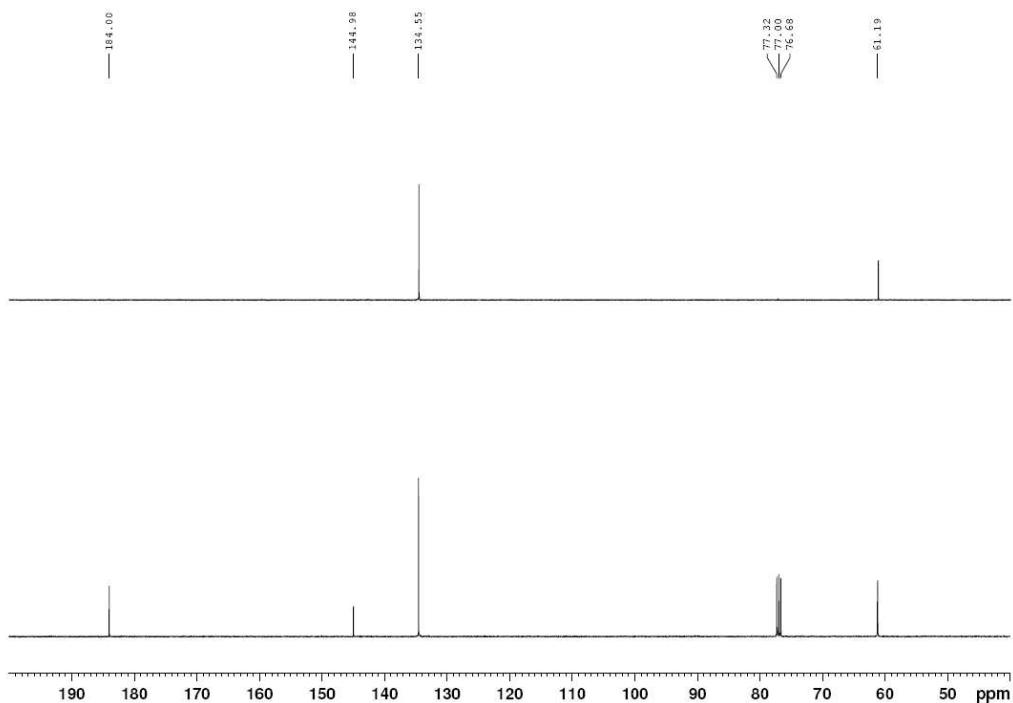
**Figure S18.** The <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) of compound V.



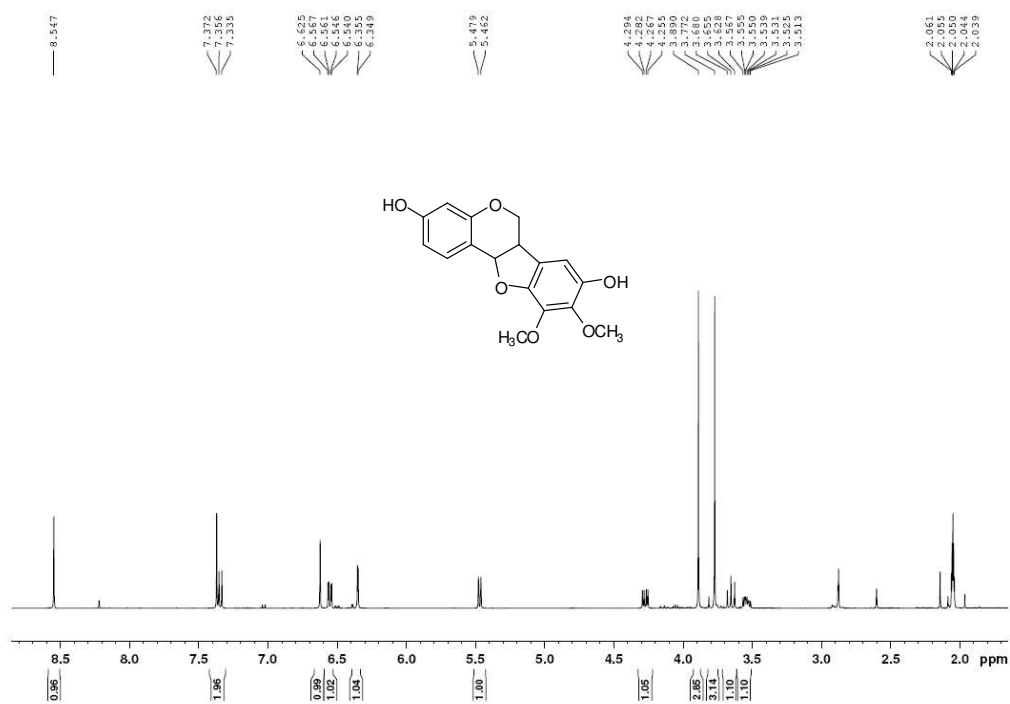
**Figure S19.** The <sup>13</sup>C NMR and DEPT135 (100MHz, CDCl<sub>3</sub>) of compound V.



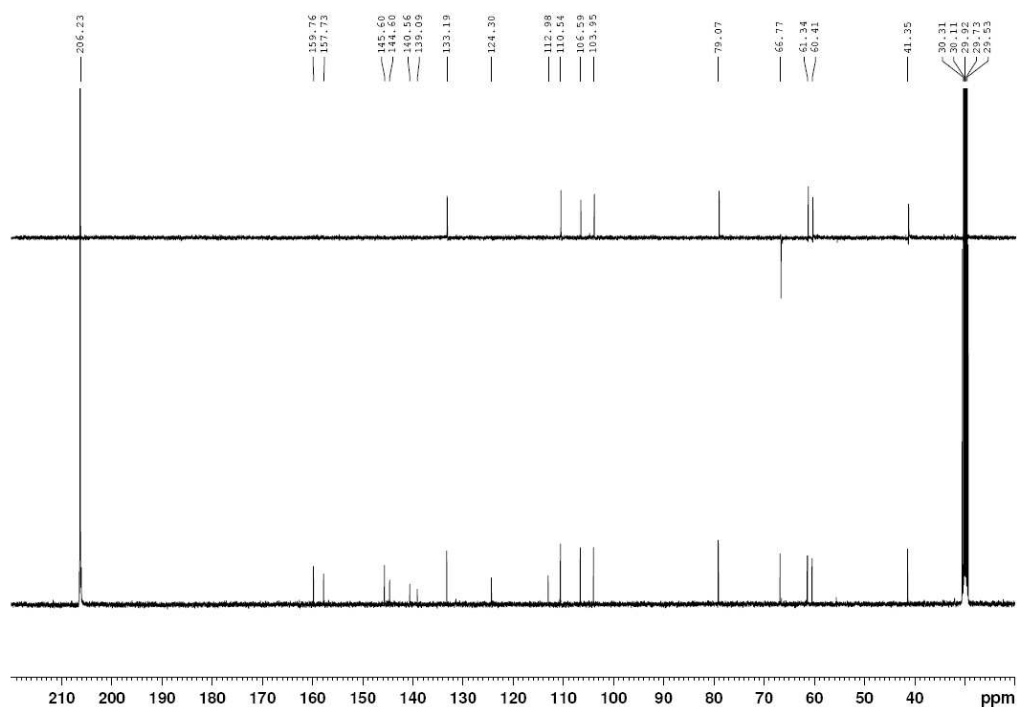
**Figure S20.** The  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) of compound VI.



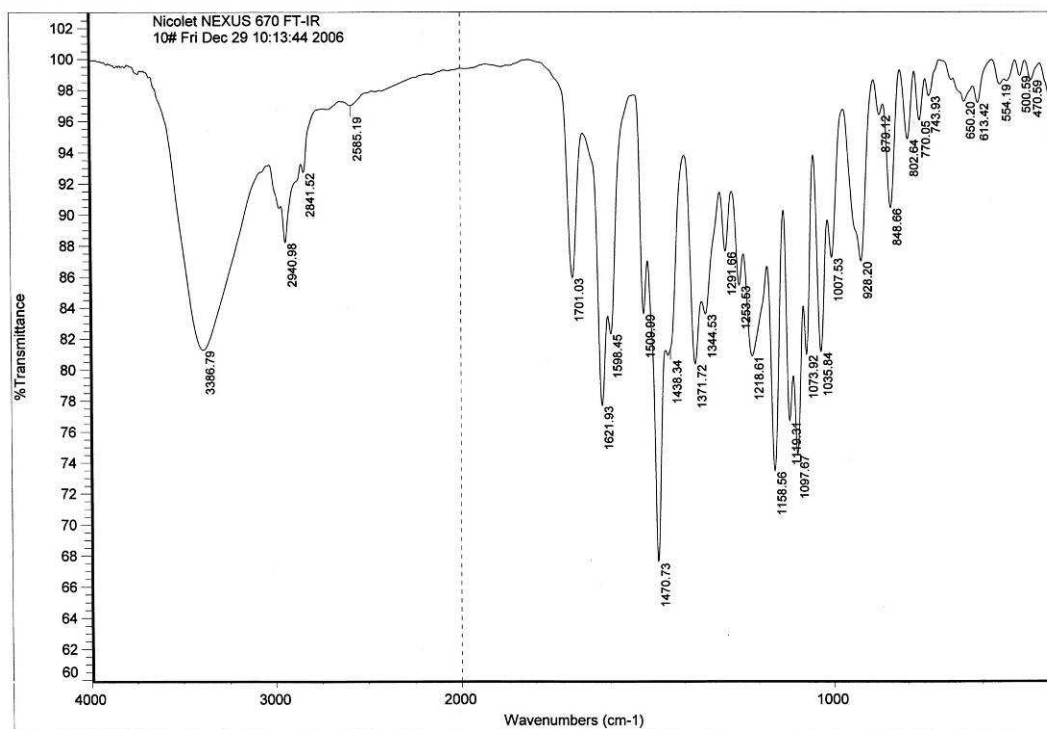
**Figure S21.** The  $^{13}\text{C}$  NMR and DEPT135 (100MHz,  $\text{CDCl}_3$ ) of compound VI.



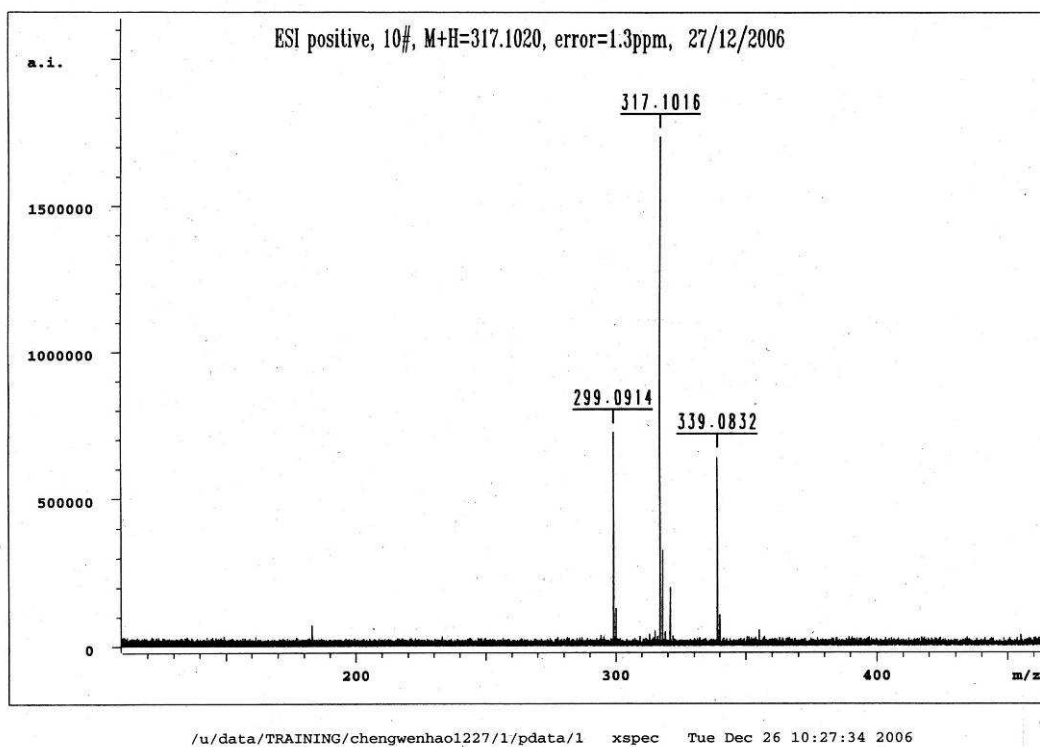
**Figure S22.** The <sup>1</sup>H NMR (400MHz, acetone-*d*<sub>6</sub>) of compound (±)-3.



**Figure S23.** The <sup>13</sup>C NMR and DEPT135 (100MHz, acetone-*d*<sub>6</sub>) of compound (±)-3.



**Figure S24.** IR spectrum of compound **3**



**Figure S25.** HRESIMS of compound **3**.

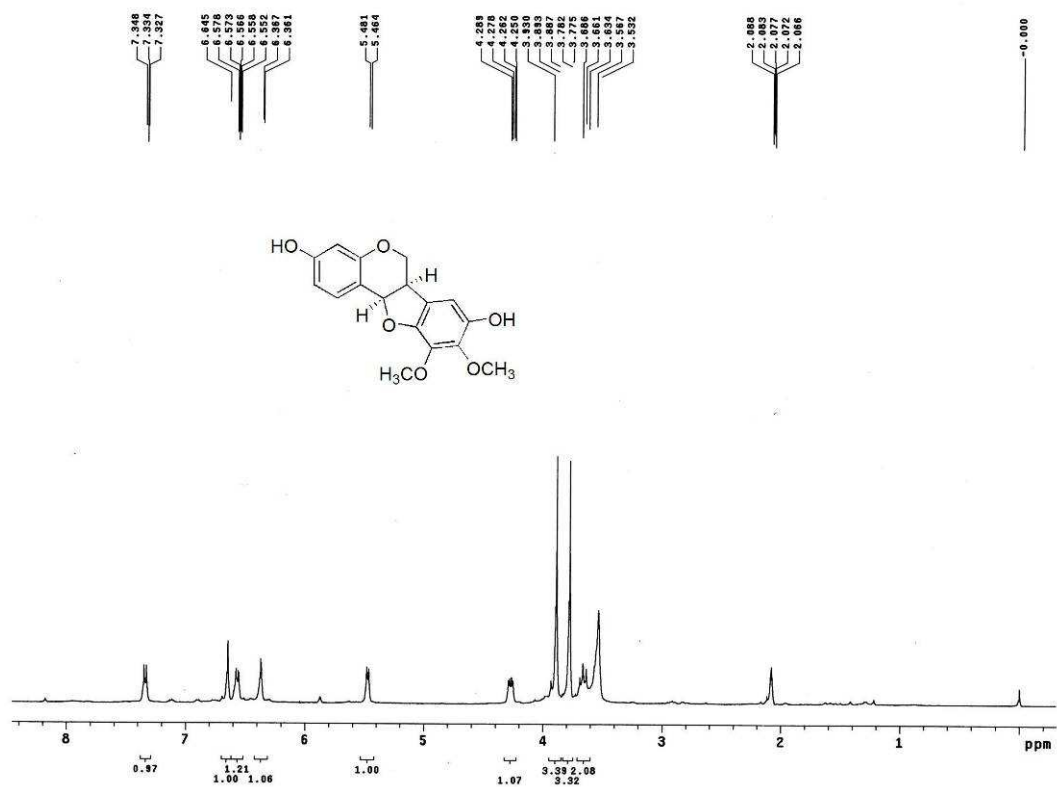


Figure S26. The <sup>1</sup>H NMR (400MHz, acetone-*d*<sub>6</sub>) of compound 3.

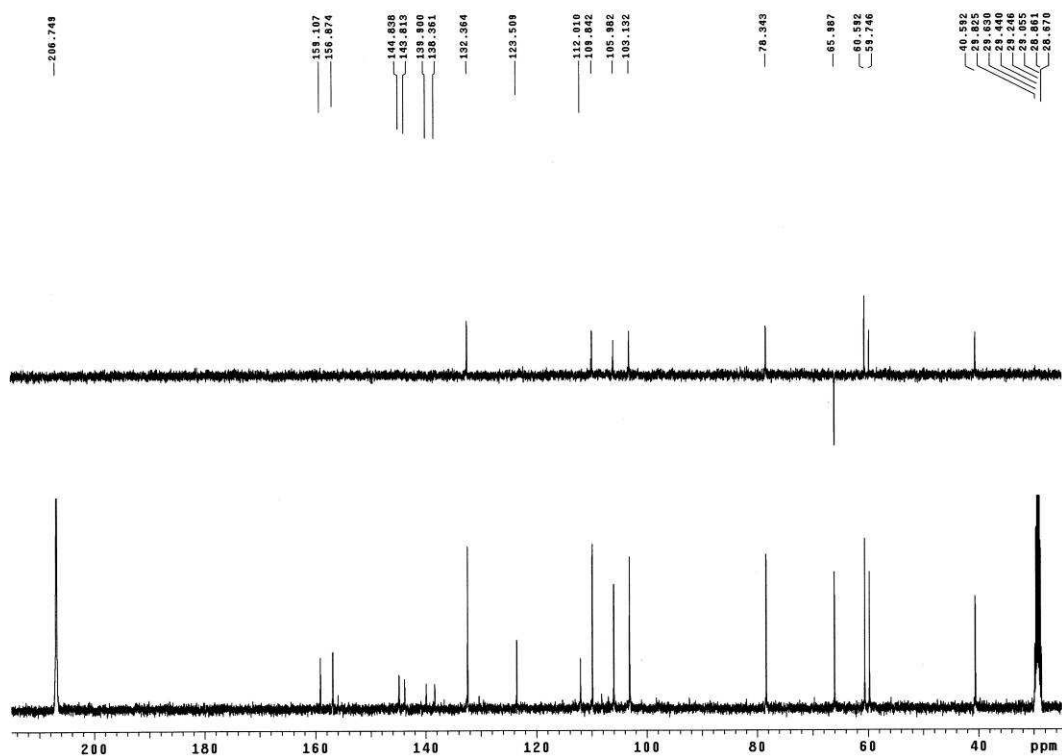


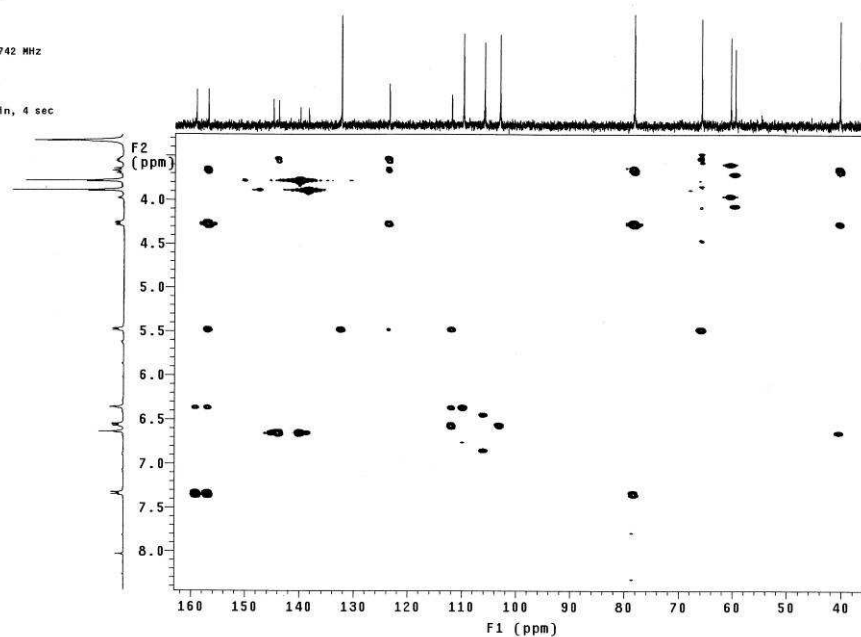
Figure S27. The <sup>13</sup>C NMR and DEPT135 (100MHz, acetone-*d*<sub>6</sub>) of compound 3.

STANDARD 1H OBSERVE

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Ambient temperature  
Mercury-400BB "ULAOC400"

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Width 3016.6 Hz  
2D Width 24154.6 Hz  
72 repetitions  
400 increments  
OBSERVE H1, 400.1738742 MHz  
DATA PROCESSING  
Sine bell 0.085 sec  
F1 DATA PROCESSING  
Sine bell 0.008 sec  
FT size 1024 x 2048  
Total time 10 hr, 26 min, 4 sec



**Figure S28.** gHMBC spectrum of compound **3**.