

Supporting Information

for

**Aspergiloid I, an unprecedented spirolactone
norditerpenoid from the plant-derived endophytic
fungus *Aspergillus* sp. YXf3**

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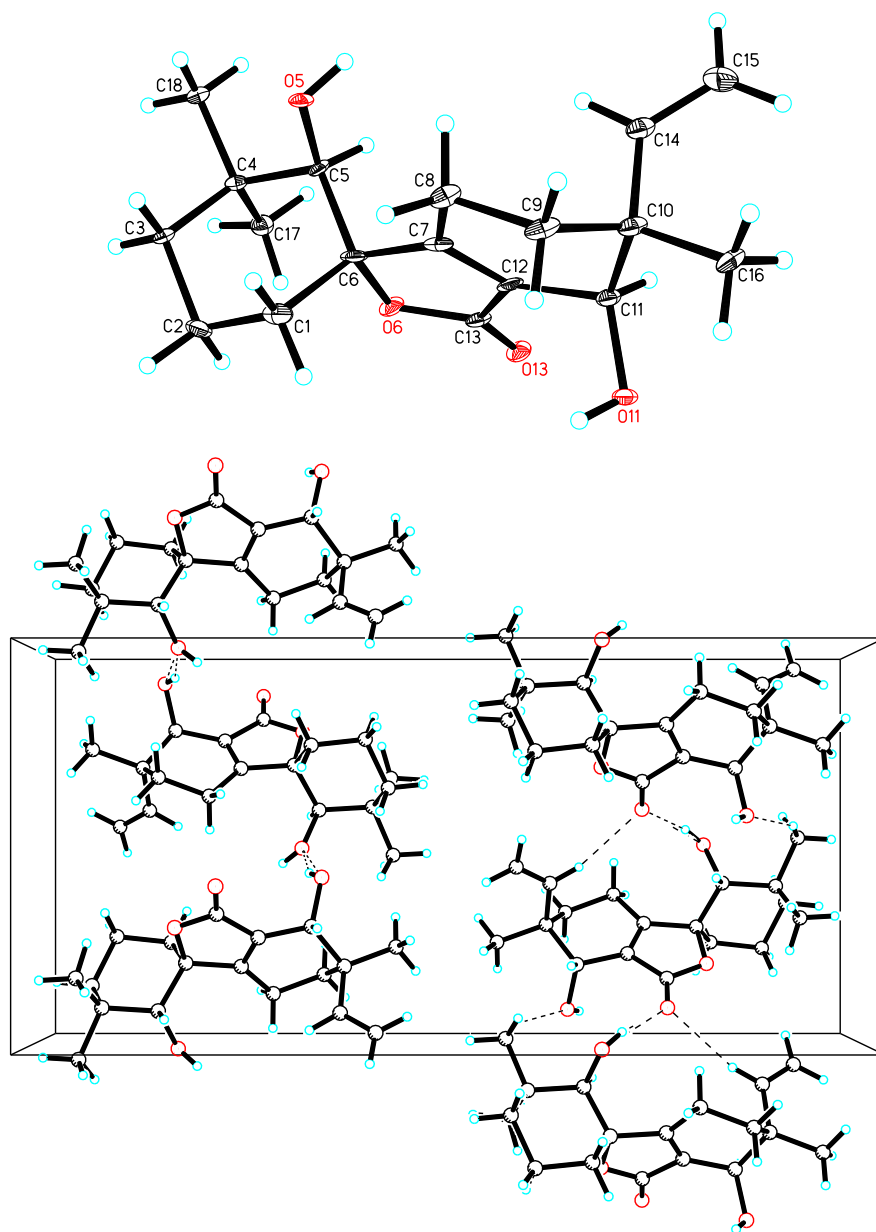
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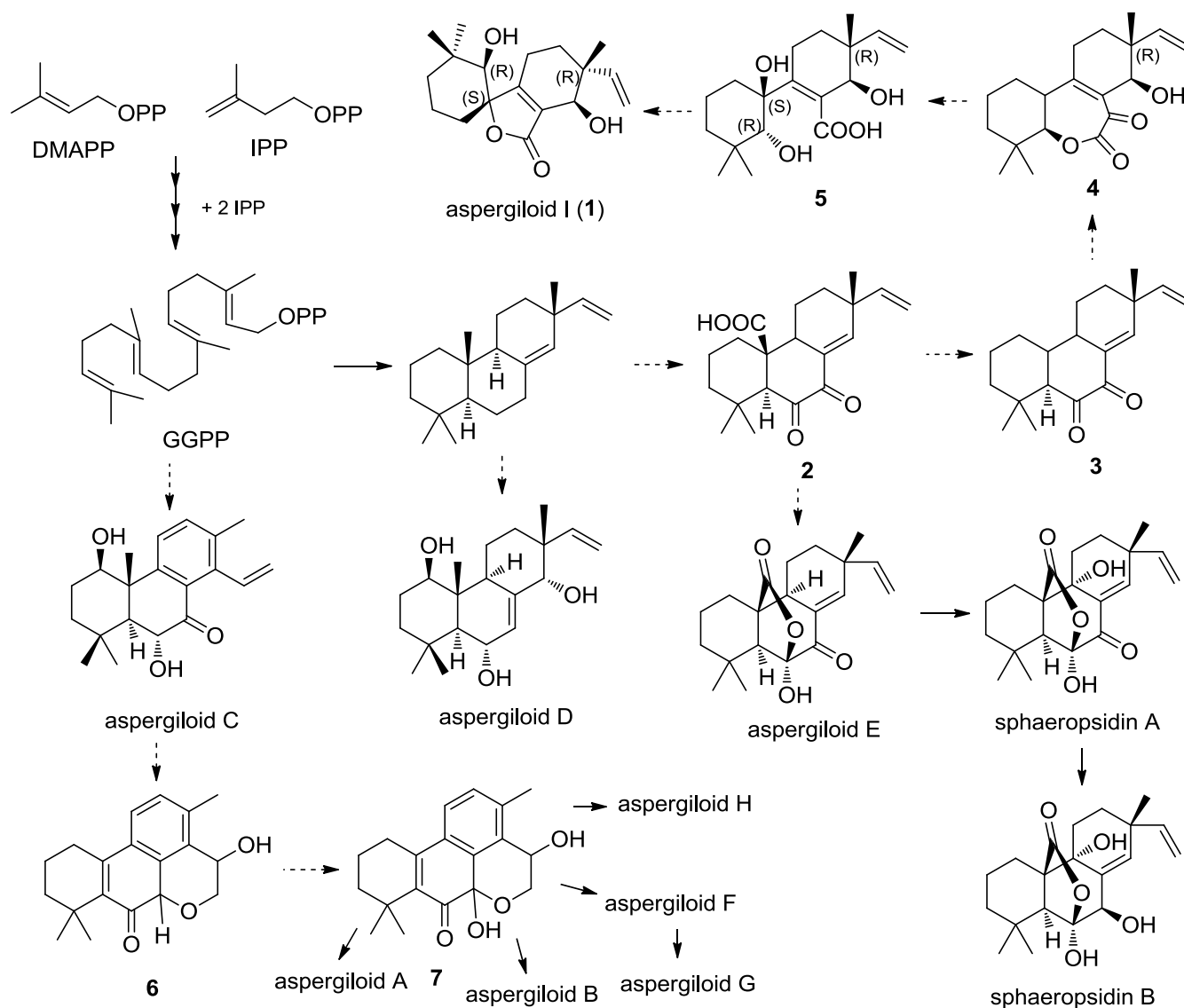
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Scheme S1. Plausible biosynthetic pathway of aspergiloid A-I and sphaeropsidin A-F



References:

- 1 Guo, Z. K.; Yan, T.; Guo, Y.; Song, Y. C.; Jiao, R. H.; Tan, R. X.; Ge, H. M. *J. Nat. Prod.* **2012**, 75, 15–21.
- 2 Yan, T.; Guo, Z. K.; Jiang, R.; Wei, W.; Wang, T.; Guo, Y.; Song, Y. C.; Jiao, R. H.; Tan, R. X.; Ge, H. M. *Planta Med.* **2013**, 79, 348–352.
- 3 Guo, Z. K.; Liu, S. B.; Ma S. *Nat. Prod. Res. Dev.* **2013**, 25, 778–781.
- 4 Ellestad, G. A. ; Kunstmann, M. P. ; Mirando, P.; Morton, G. O. *J. Am. Chem. Soc.* **1972**, 94, 6206–6208.
- 5 Evidente, A.; Sparapano, L.; Fierro, O.; Bruno, G.; Giordano, F.; Motta, A. *Phytochemistry*, **1997**, 45, 705–713.
- 6 Evidente, A.; Sparapano, L.; Bruno, G.; Motta, A. *Phytochemistry*, **2002**, 59, 817–823.
- 7 Dewick, P. M. *Nat. Prod. Rep.* **2002**, 19, 181–122.

Figure S1. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) spectrum of compound **1**

YXf3-fj-B1-5-1 DMSO- d_6 1H-NMR AVANCEIII 500MHz

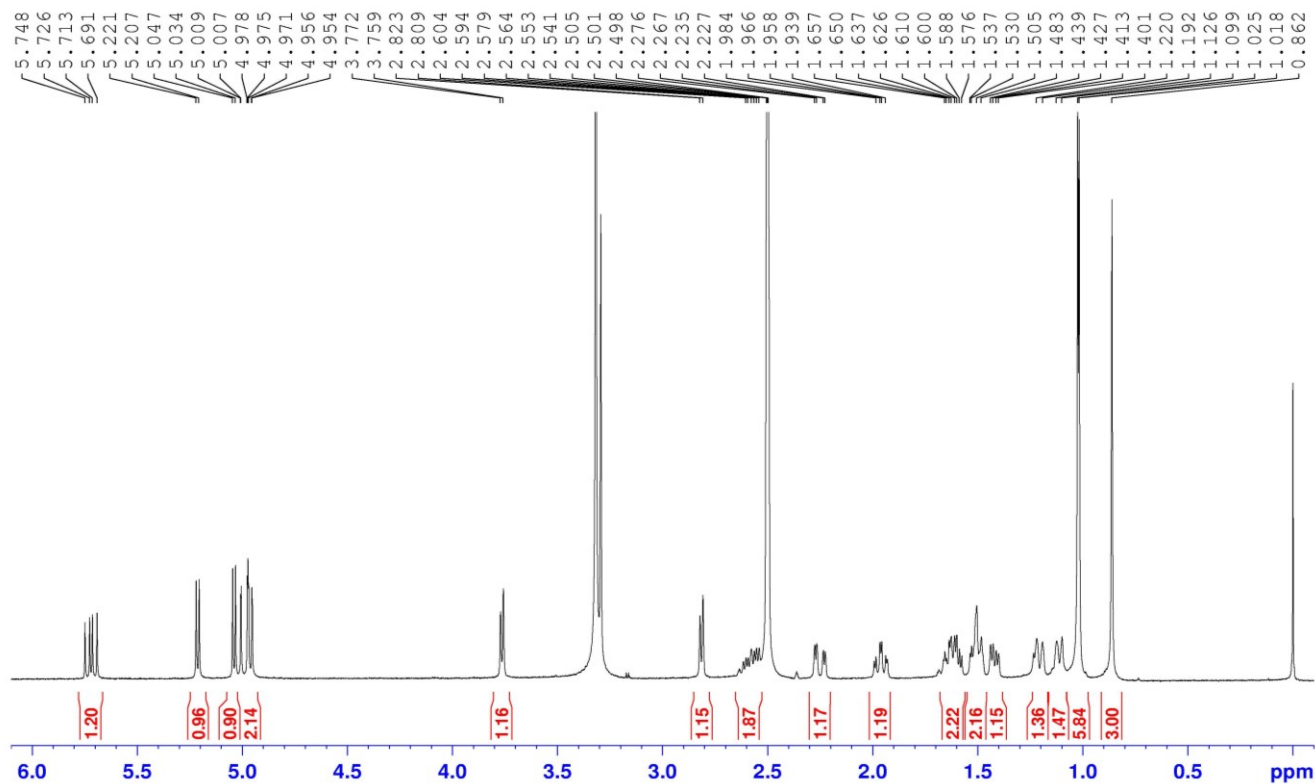
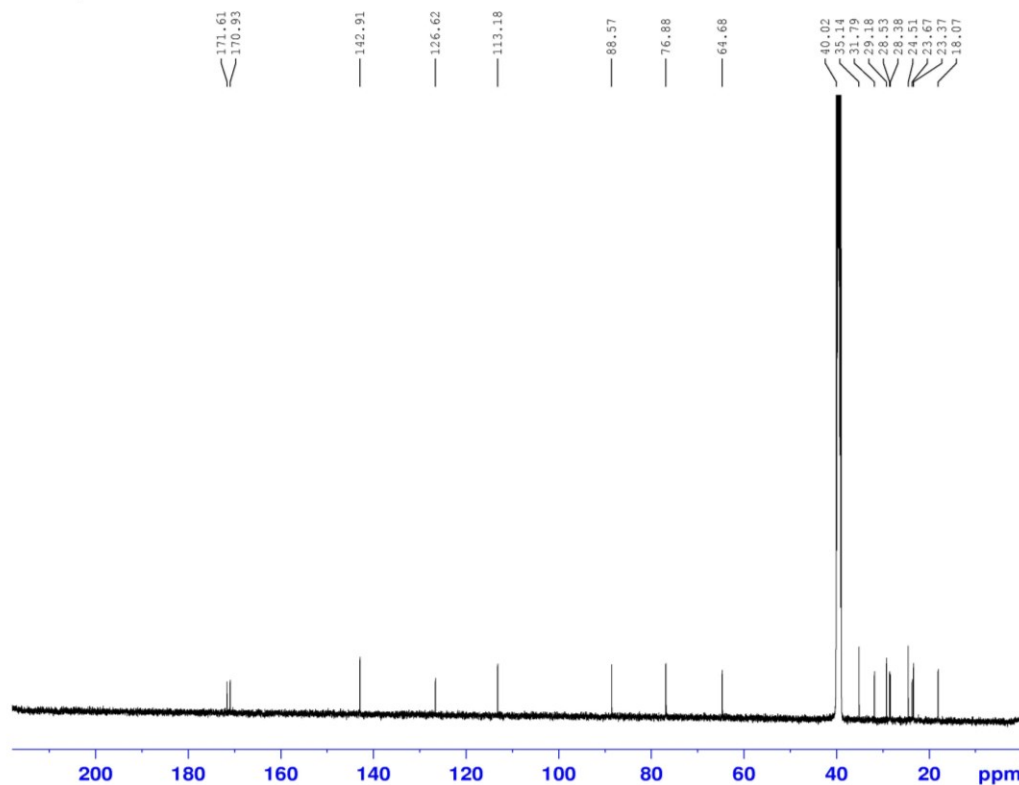


Figure S2. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) spectrum of compound **1**

YXf3-fj-B1-5-1 DMSO- d_6 13C-NMR AVANCEIII 500MHz



Current Data Parameters
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EXPNO 62
PROCNO 1

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SOLVENT DMSO
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SWH 27573.529 Hz
FIDRES 0.420739 Hz
AQ 1.1884362 sec
RG 184.66
DW 18.133 usec
DE 6.50 usec
TE 297.3 K
D1 2.00000000 sec
D11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 97.00000000 W
SFO1 125.7766519 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 14.00000000 W
PLW12 0.31500000 W
PLW13 0.20160000 W
SFO2 500.1520006 MHz

F2 - Processing parameters
SI 32768
SF 125.7628770 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S3. DEPT spectra of compound **1** in DMSO- d_6

YXf3-fj-B1-5-1 DMSO-d6 DEPT AVANCEIII 500MHz

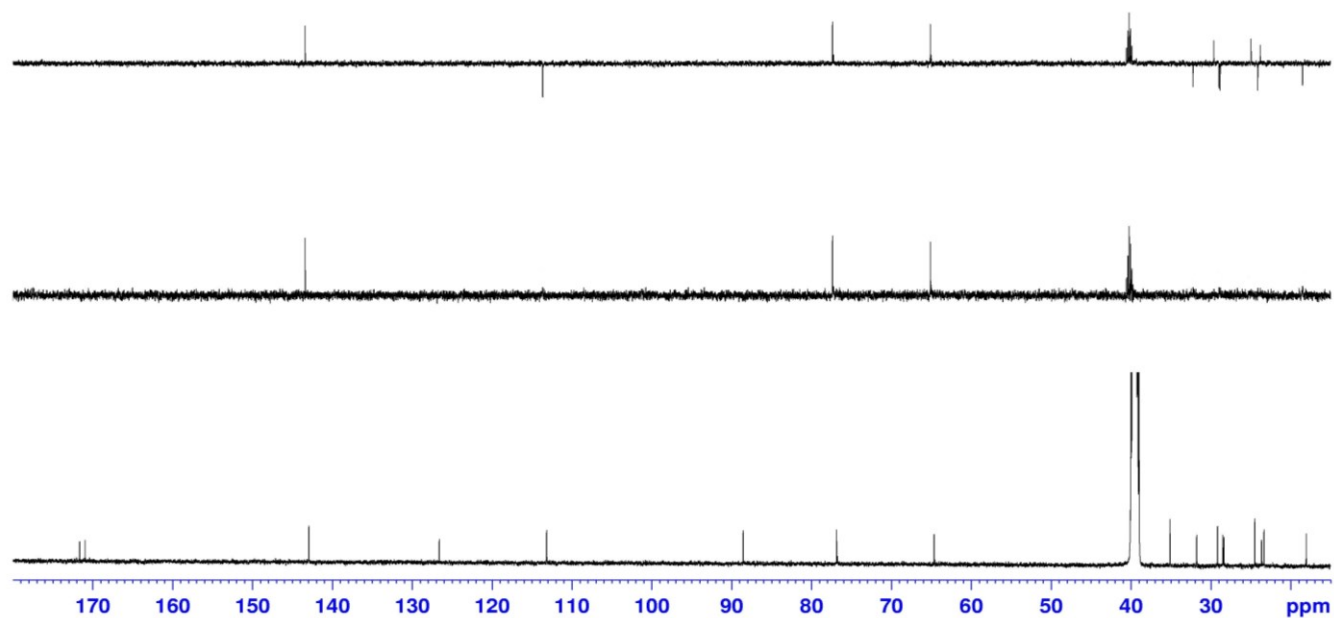


Figure S4. HSQC spectrum of compound **1** in DMSO- d_6

YXf3-fj-B1-5-1 DMSO-d6 HSQC AVANCEIII 500MHz

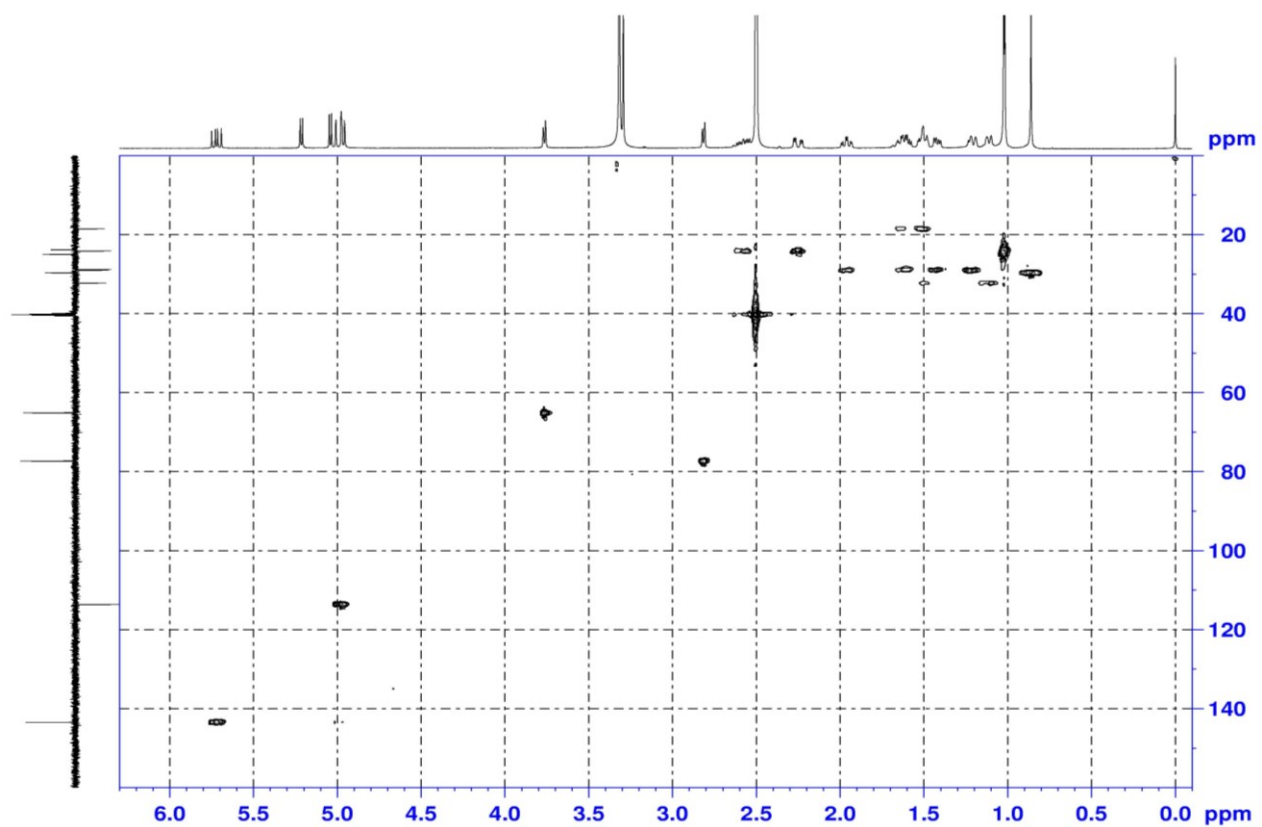


Figure S5. ^1H - ^1H COSY spectrum of compound **1** in $\text{DMSO-}d_6$

YXf3-fj-B1-5-1 DMSO-d6 COSY AVANCEIII 500MHz

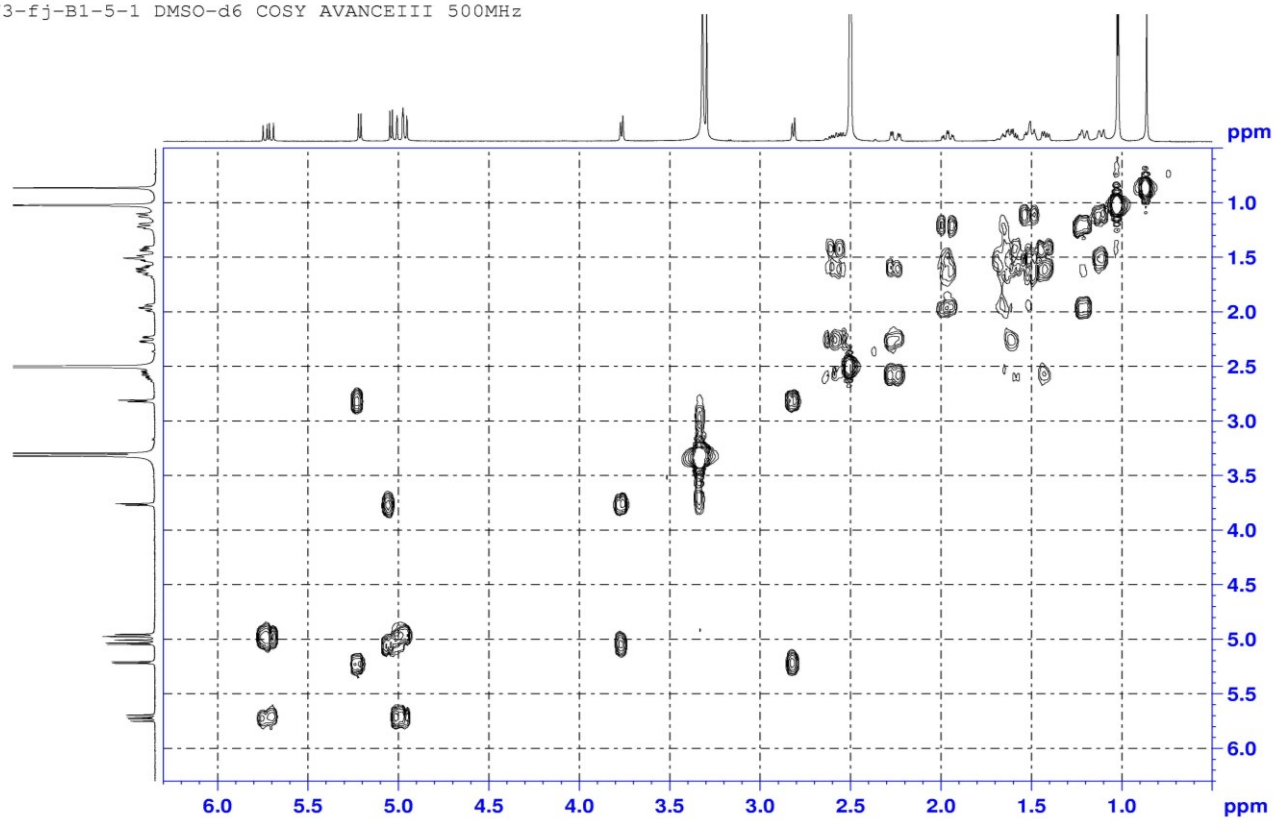


Figure S6. HMBC spectrum of compound **1** in $\text{DMSO-}d_6$

YXf3-fj-B1-5-1 DMSO-d6 HMBC AVANCEIII 500MHz

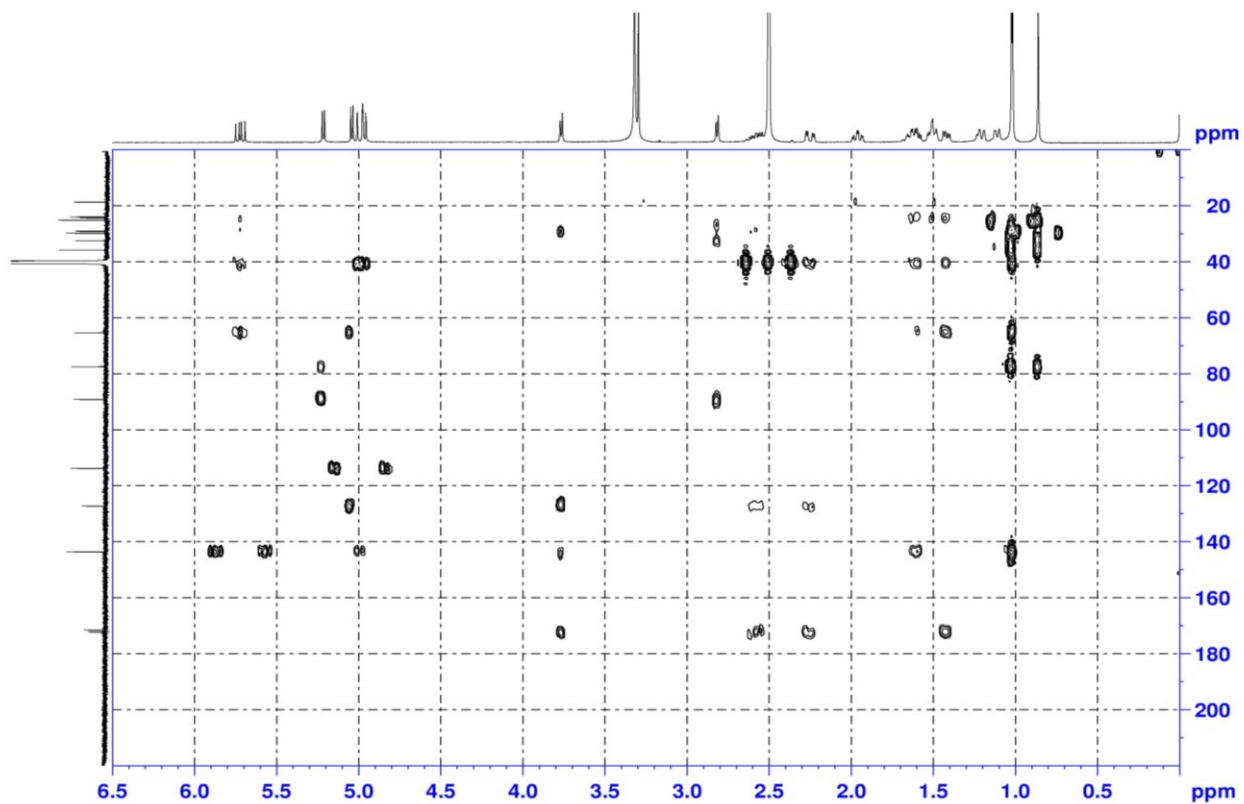


Figure S7. Enlarged HMBC spectrum (δ_C 180-160 ppm, δ_H 6.1-0.6 ppm) of compound **1** in DMSO- d_6

YXf3-fj-B1-5-1 DMSO-d6 HMBC AVANCEIII 500MHz

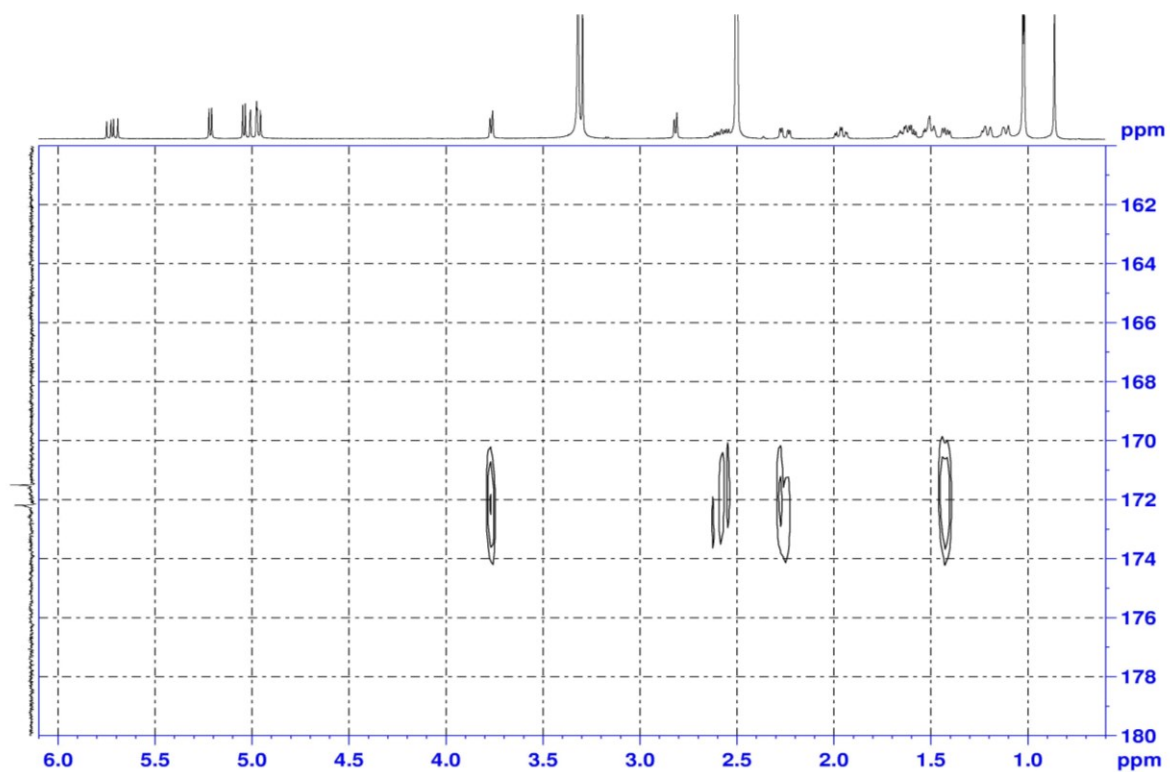


Figure S8. NOESY spectrum of compound **1** in DMSO- d_6

YXf3-fj-B1-5-1 DMSO-d6 NOESY AVANCEIII 500MHz

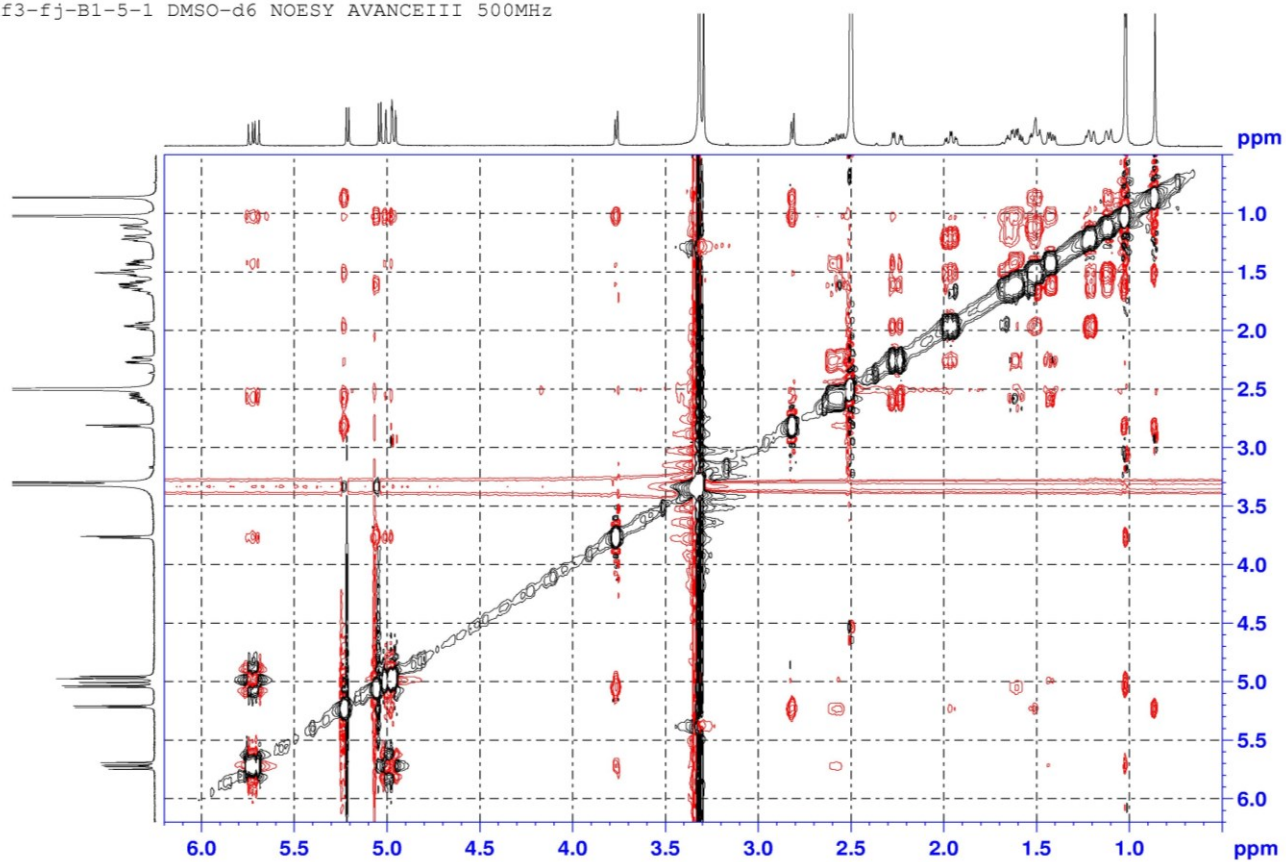


Figure S9. ^1H NMR (500 MHz, CDCl_3) spectrum of compound **1**

YXf3-fj-B1-5-1 CDCl_3 ^1H -NMR AVANCEIII 500MHz

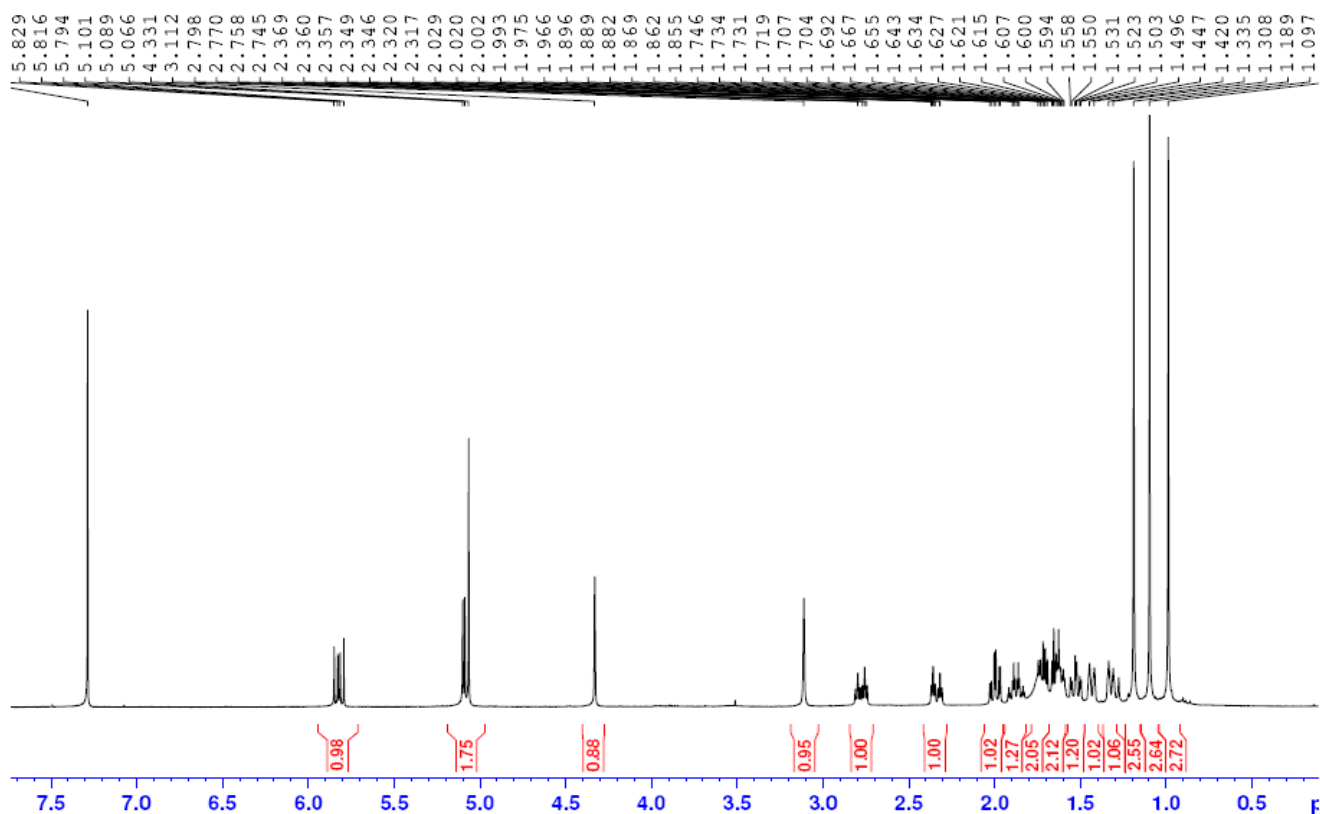
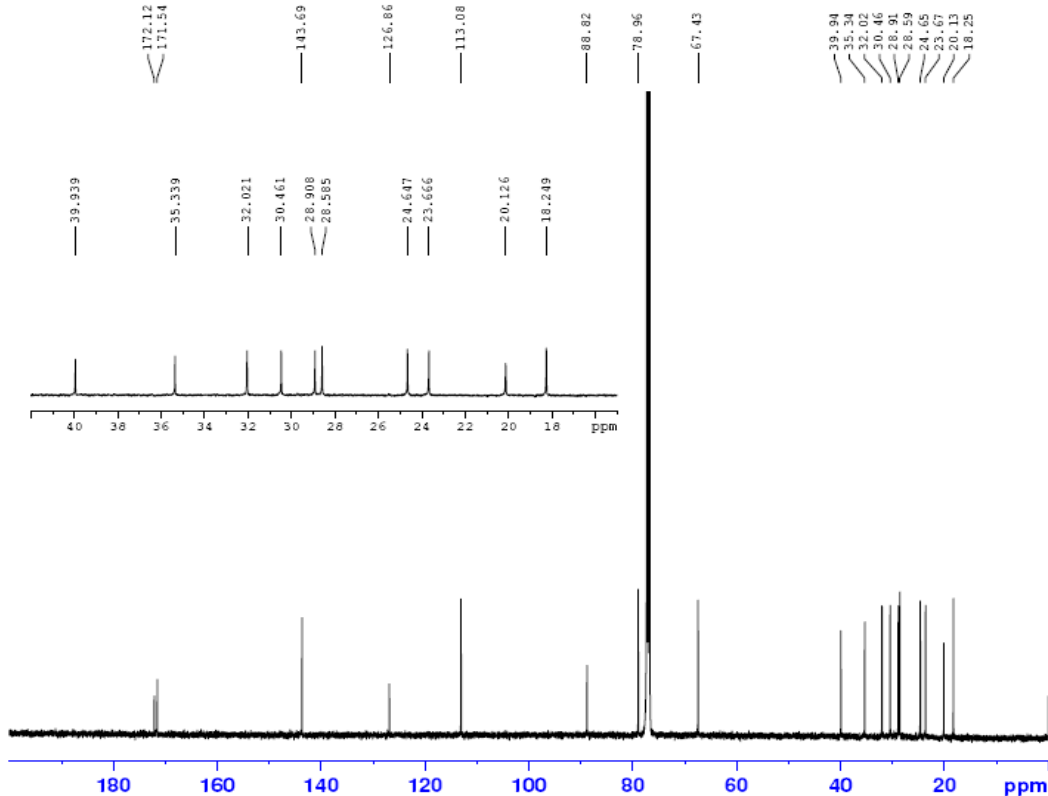


Figure S10. ^{13}C NMR (125 MHz, CDCl_3) spectrum of compound **1**

YXf3-fj-B1-5-1 CDCl_3 ^{13}C -NMR AVANCEIII 500MHz



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PROCNO 1

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FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 184.66
DW 16.800 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec

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P1 10.00 usec
PLW1 97.00000000 W
SFO1 125.7703637 MHz

----- CHANNEL f2 -----
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NUC2 ^1H
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PLW2 14.00000000 W
PLW12 0.31500000 W
PLW13 0.20160000 W
SFO2 500.1320005 MHz

F2 - Processing parameters
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WDW EM
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LB 1.00 Hz
GB 0
PC 1.40

Figure S11. HMQC spectrum of compound **1** in CDCl₃

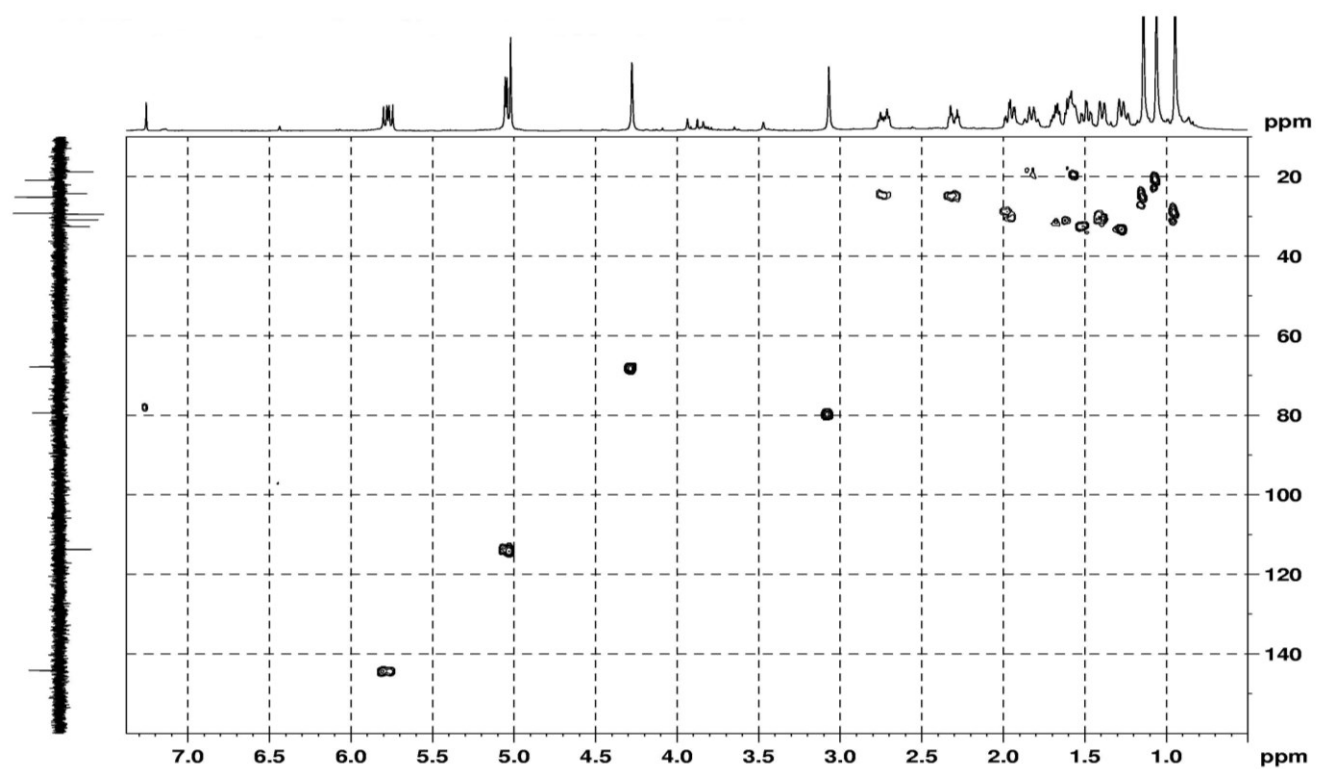


Figure S12. ¹H-¹H COSY spectrum of compound **1** in CDCl₃

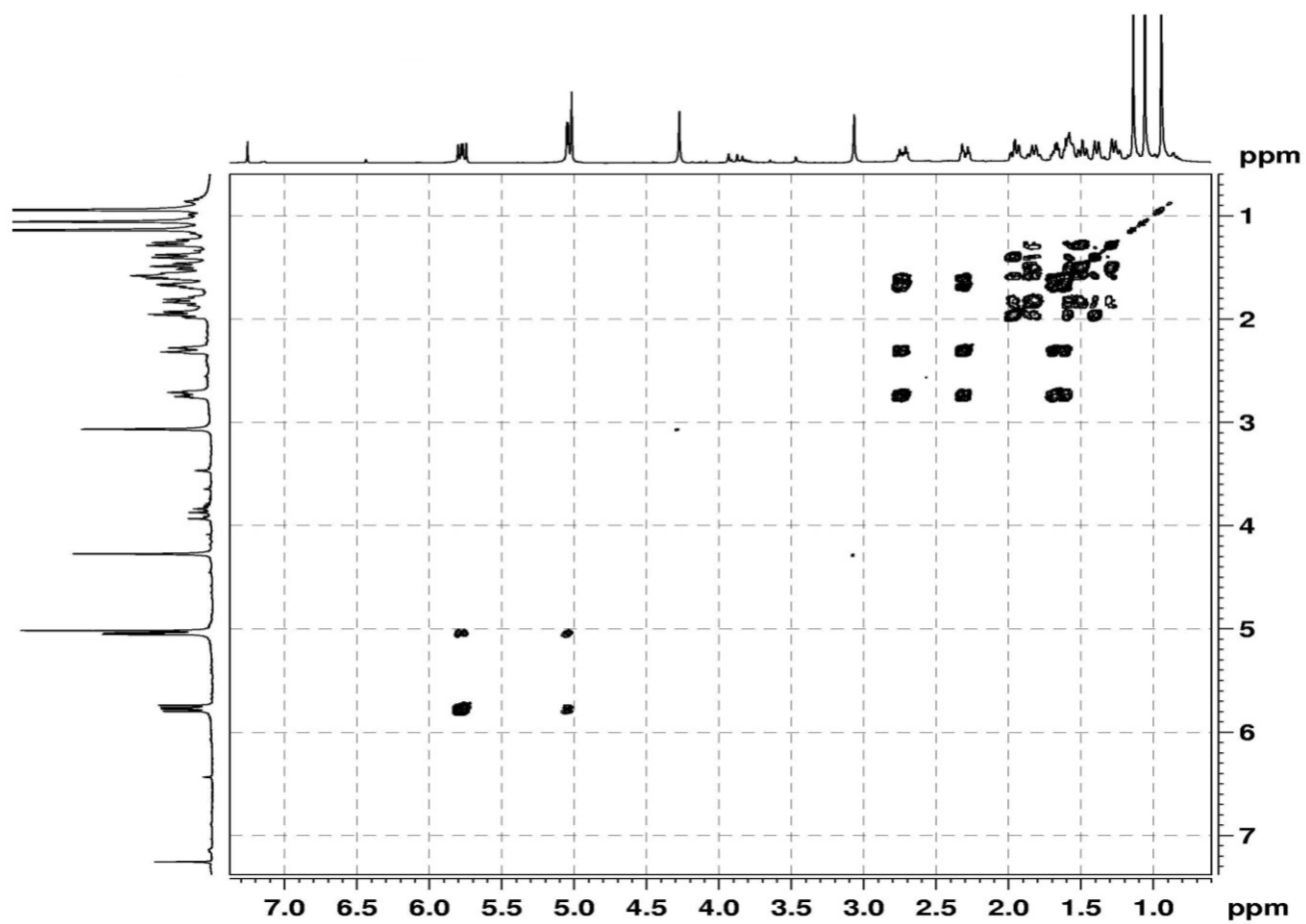


Figure S13. HMBC spectrum of compound **1** in CDCl₃

YXf3-fj-B1-5-1 CDCl₃ HMBC AVANCEIII 500MHz

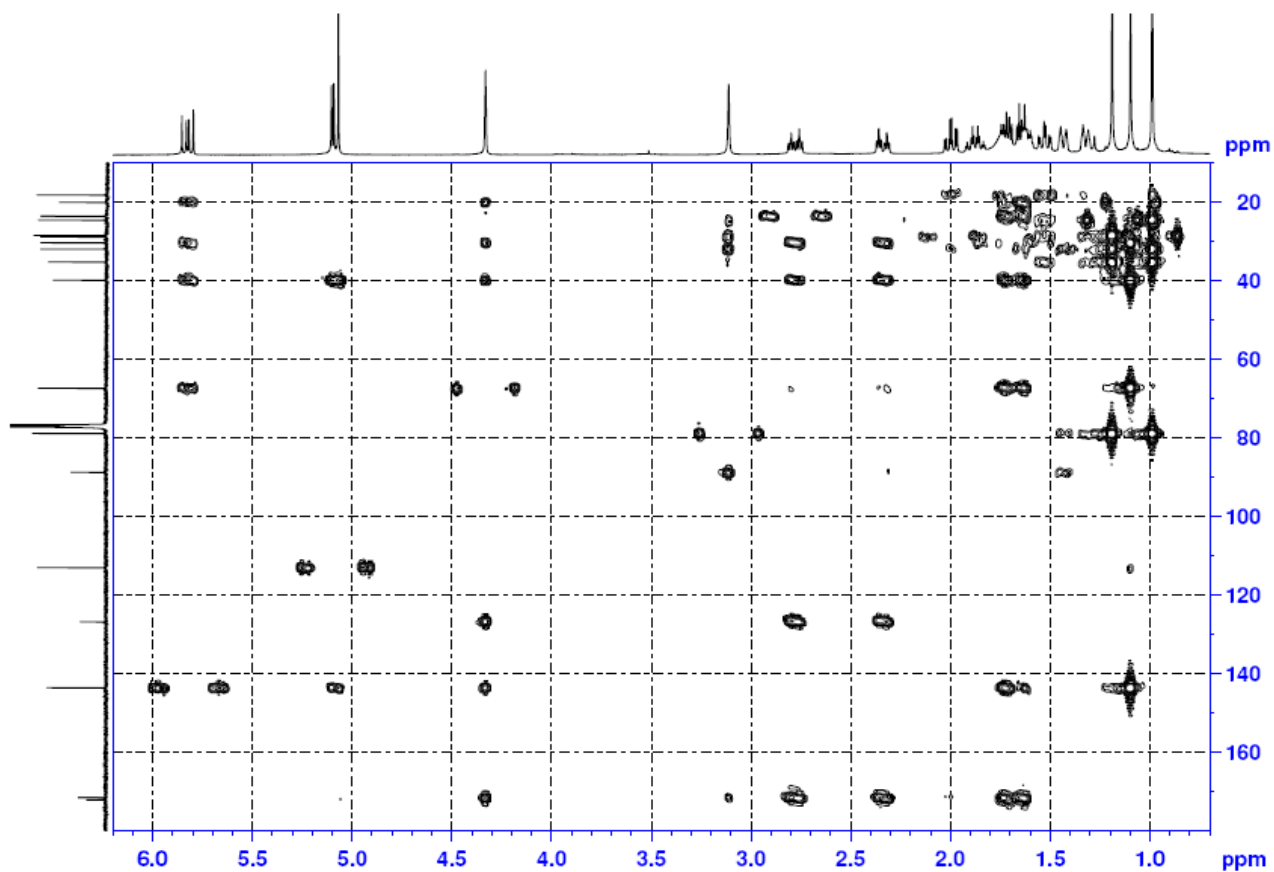


Figure S14. Enlarged HMBC spectrum (δ_C 177-167 ppm, δ_H 5.0-0.9 ppm) of compound **1** in CDCl₃

YXf3-fj-B1-5-1 CDCl₃ HMBC AVANCEIII 500MHz

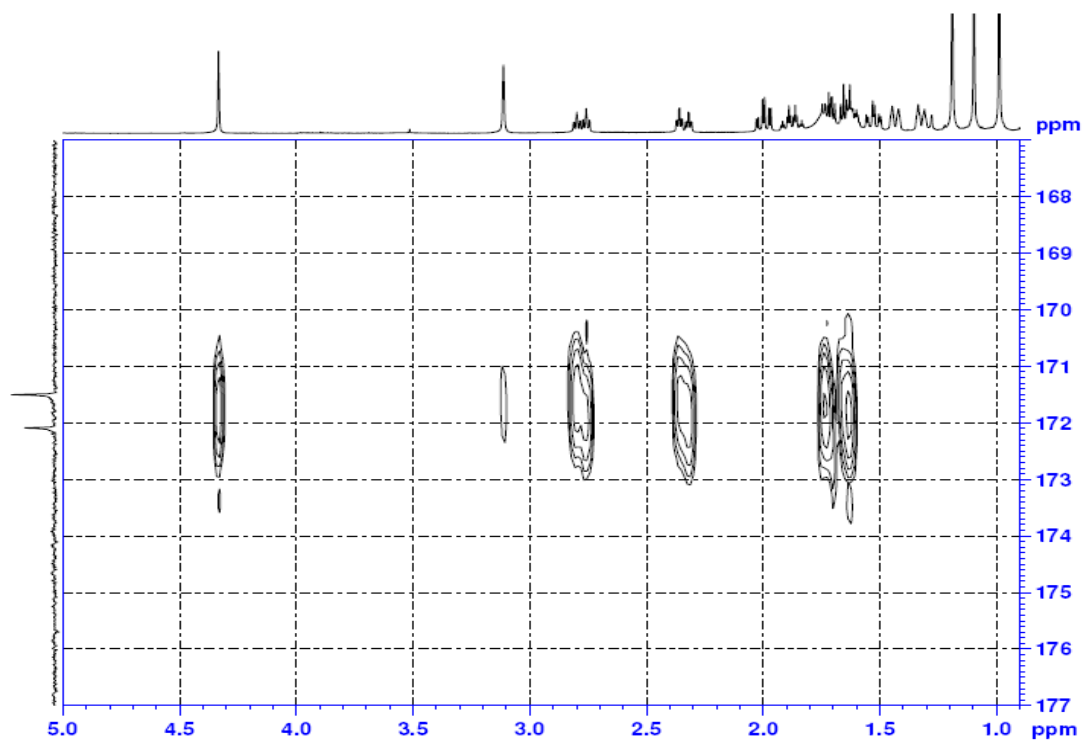
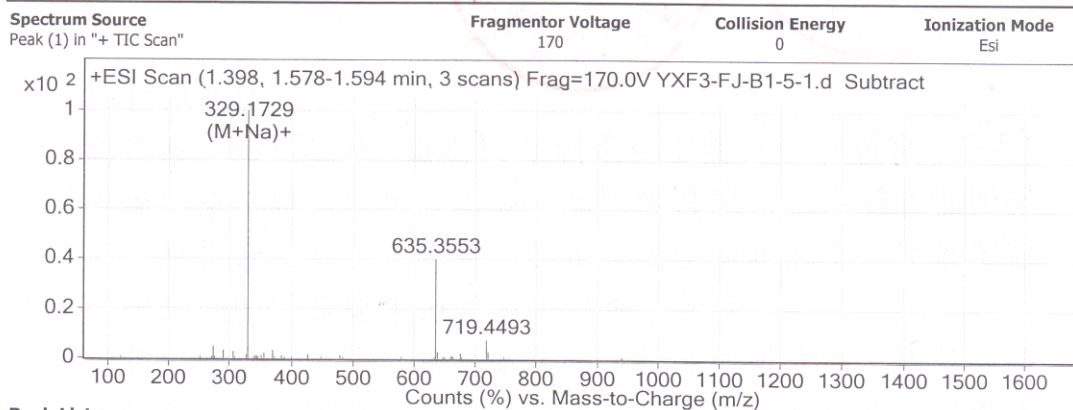


Figure S15. HRESI-MS spectrum of compound **1** in MeOH

Qualitative Analysis Report

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Instrument Name	Instrument 1	User Name	
Acq Method	TEMP2.m	Acquired Time	11/26/2010 3:40:55 PM
IRM Calibration Status	Some Ions Missed	DA Method	Default.m
Comment			

User Spectra



Peak List

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329.399		51889		
330.1758	1	137615	C18 H26 Na O4	(M+Na)+
635.3553	1	309541		
636.3587	1	109646		
719.4493		57309		

--- End Of Report ---

Calc. (M+H)⁺ 307.1904
(M+Na)⁺ 329.1723

Figure S16. ^1H NMR (500 MHz, acetone- d_6) of compound **6**

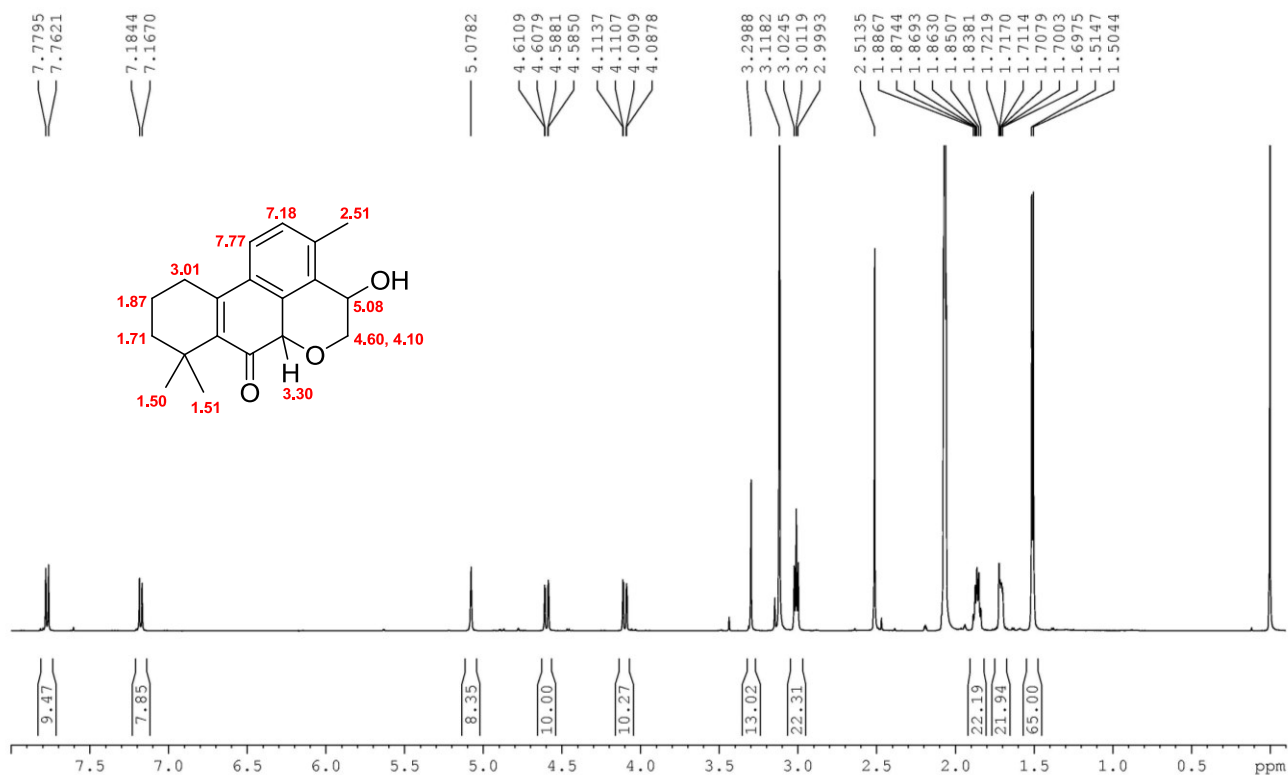
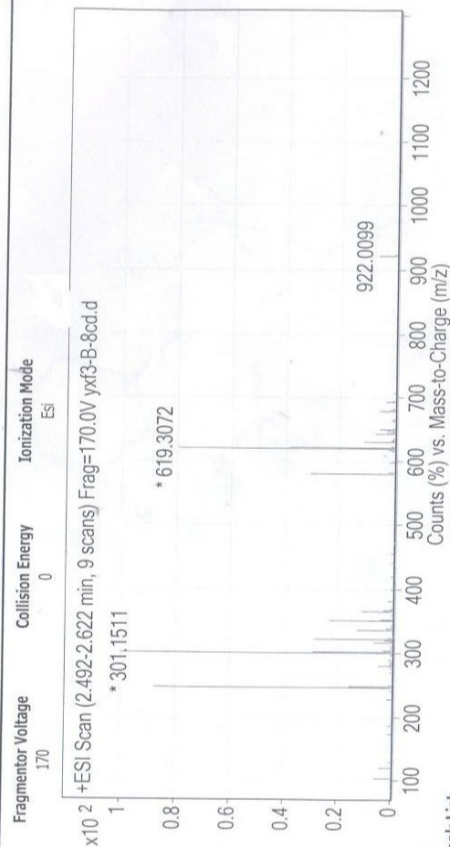


Figure S17. HRESIMS spectrum of compound **6**

Qualitative Analysis Report

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Comment			

User Spectra



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Figure S18. ¹H NMR (500 MHz, acetone-*d*₆) of compound 7

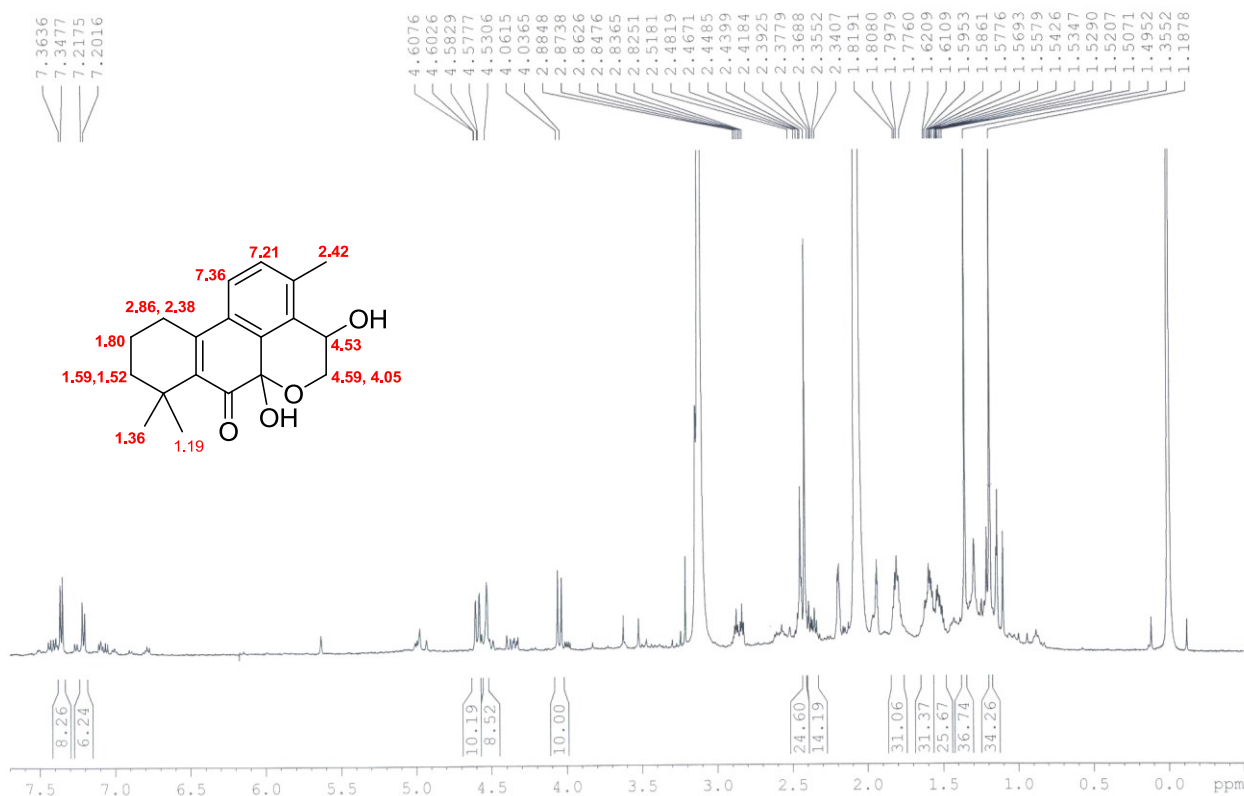


Figure S19. HRESIMS spectrum of compound 7

