

SUPPLEMENTARY MATERIAL

Secondary metabolites from the fermented rice of the fungus *Monascus purpureus* and their bioactivities

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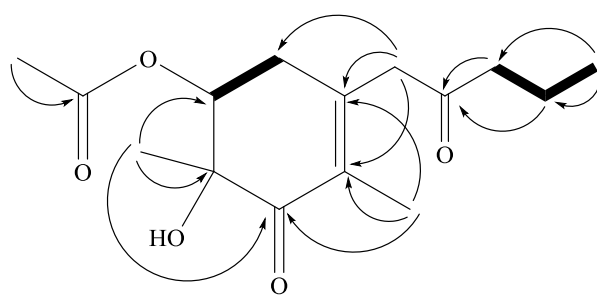
Phytochemical investigation of the EtOAc-soluble fraction of the ethanolic extract of a yellow mutant of the fungus *Monascus purpureus* BCRC 38110 (Eurotiaceae) grown on rice resulted in the isolation of one new azaphilone derivative, monapurpureusone (**1**), one acetophenone metabolite isolated for the first time from natural source, monapurpureusin (**2**), along with four known compounds, TW94a (**3**), ergosterol (**4**), monascin (**5**), and ankaflavin (**6**). The structures and relative configurations of these compounds were elucidated by spectroscopic analyses, including 1D- and 2D-NMR spectroscopy and mass spectrometry, and by the comparison of their NMR data with those of related compounds. Some phytochemicals were evaluated for both anti-inflammatory activity through the measurement of nitric oxide (NO) production levels in lipopolysaccharide (LPS)-stimulated murine-derived macrophages RAW264.7 cell lines and antioxidant activities.

Contents

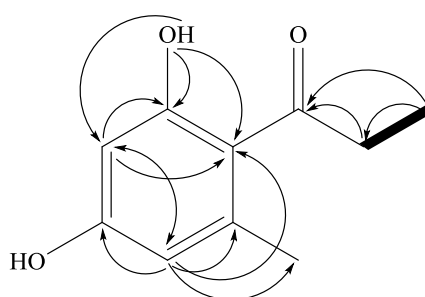
Table S1. ^1H - and ^{13}C -NMR Data (CDCl_3 , 600 and 150 MHz, resp.) of compounds 1 and 2 . δ in ppm, J in Hz.	3
Figure S1. COSY (—) and HMBC ($\rightarrow$) correlations of 1 and 2	4
Figure S2. NOESY correlations of 1 and 2	4
Figure S3. ^1H NMR spectrum of 1	5
Figure S4. ^{13}C NMR spectrum of 1	5
Figure S5. DEPT spectrum of 1	6
Figure S6. ^1H - ^1H COSY spectrum of 1	6
Figure S7. NOESY spectrum of 1	7
Figure S8. HSQC spectrum of 1	7
Figure S9. HMBC spectrum of 1	8
Figure S10. ^1H NMR spectrum of 2	8
Figure S11. ^{13}C NMR spectrum of 2	9
Figure S12. DEPT spectrum of 2	9
Figure S13. ^1H - ^1H COSY spectrum of 2	10
Figure S14. NOESY spectrum of 2	10
Figure S15. HSQC spectrum of 2	11
Figure S16. HMBC spectrum of 2	11

Table S1. ^1H - and ^{13}C -NMR Data (CDCl_3 , 600 and 150 MHz, resp.) of compounds **1** and **2**. δ in ppm, J in Hz.

	1		2	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	11.7	1.76 (<i>q</i> , $J = 1.2$)	166.3	
2			101.8	6.26 (<i>dd</i> , $J = 2.7, 0.6$)
3	205.6		160.5	
4	48.8	3.33 (<i>d</i> , $J = 16.8$), 3.50 (<i>d</i> , $J = 16.8$)	111.8	6.23 (<i>dq</i> , $J = 2.7, 1.2$)
4a	146.2			
5	37.9	2.49 (<i>ddd</i> , $J = 18.0, 10.5, 1.2$, H_{ax}), 2.53 (<i>ddd</i> , $J = 18.0, 6.2, 1.2$, H_{eq})	142.2	
6	67.9	4.84 (<i>dd</i> , $J = 10.5, 6.2$)	115.6	11.49 (<i>s</i>)
7	85.1		207.4	
8	195.1		37.3	2.92 (<i>q</i> , $J = 7.2$)
8a	132.1			
9	45.0	2.45 (<i>t</i> , $J = 7.8$)	8.9	1.21 (<i>t</i> , $J = 7.2$)
10	17.2	1.61 (<i>sextet</i> , $J = 7.8$)	25.1	2.56 (<i>s</i>)
11	13.6	0.92 (<i>t</i> , $J = 7.8$)		
Me-12	15.8	1.39 (<i>s</i>)		
14	170.2			
15	21.5	2.10 (<i>s</i>)		
OH-1				13.2 (<i>br s</i>)
OH-3				5.60 (<i>br s</i>)
OH-7		2.50 (<i>br s</i>)		

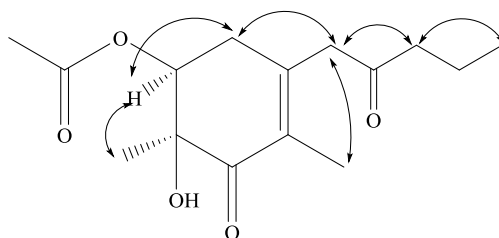


1

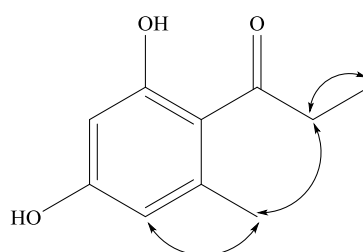


2

Figure S1. COSY (—) and HMBC (---) correlations of **1** and **2**.



1



2

Figure S2. NOESY correlations of **1** and **2**.

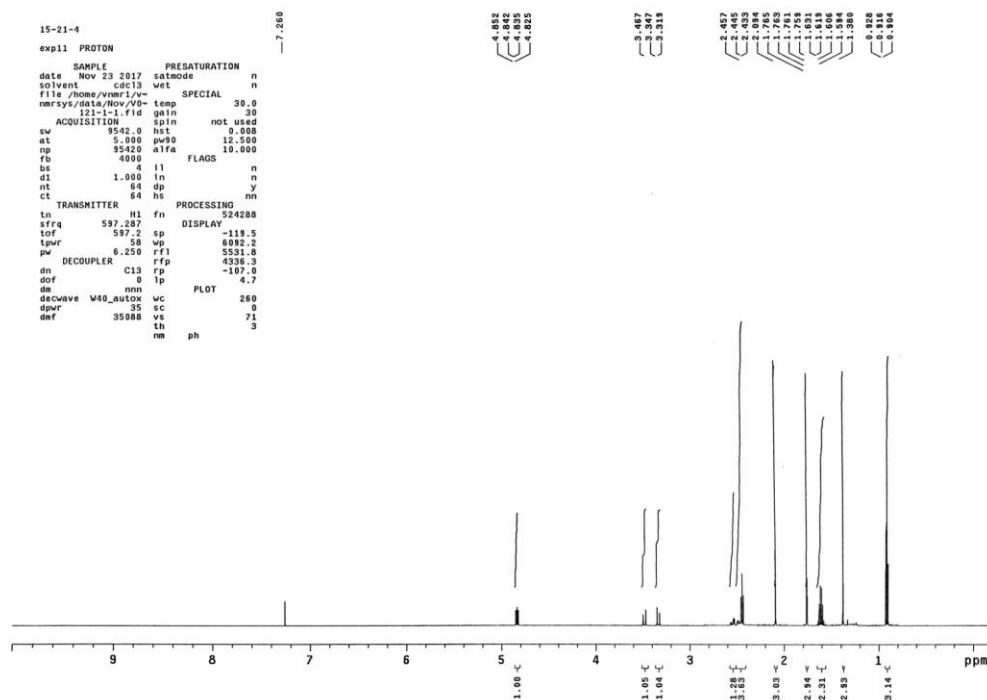


Figure S3. ^1H NMR spectrum of **1** (600 MHz in CDCl_3)

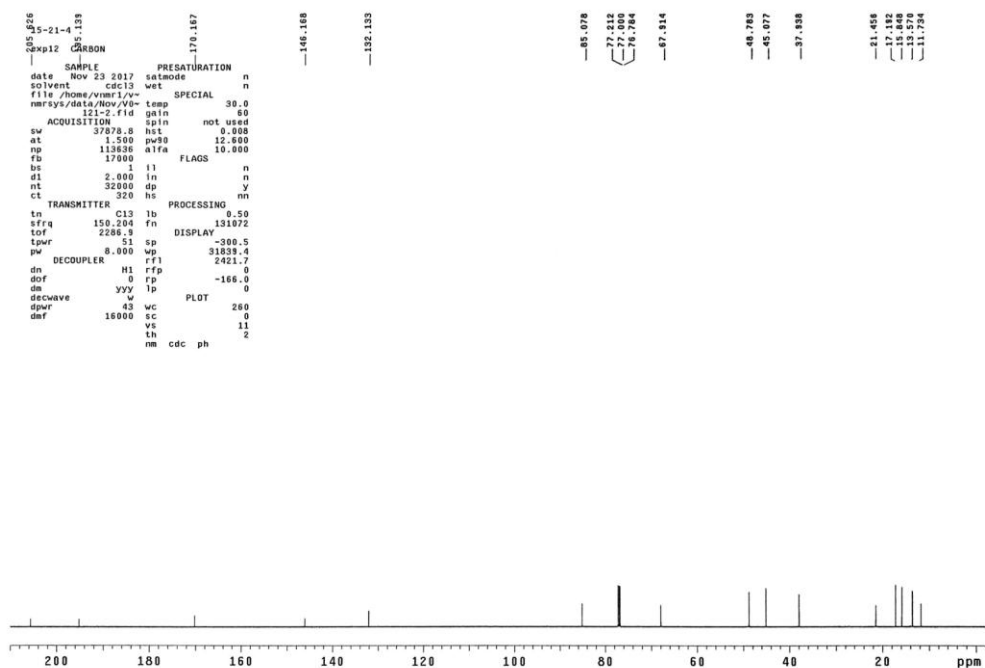


Figure S4. ^{13}C NMR spectrum of **1** (150 MHz in CDCl_3)

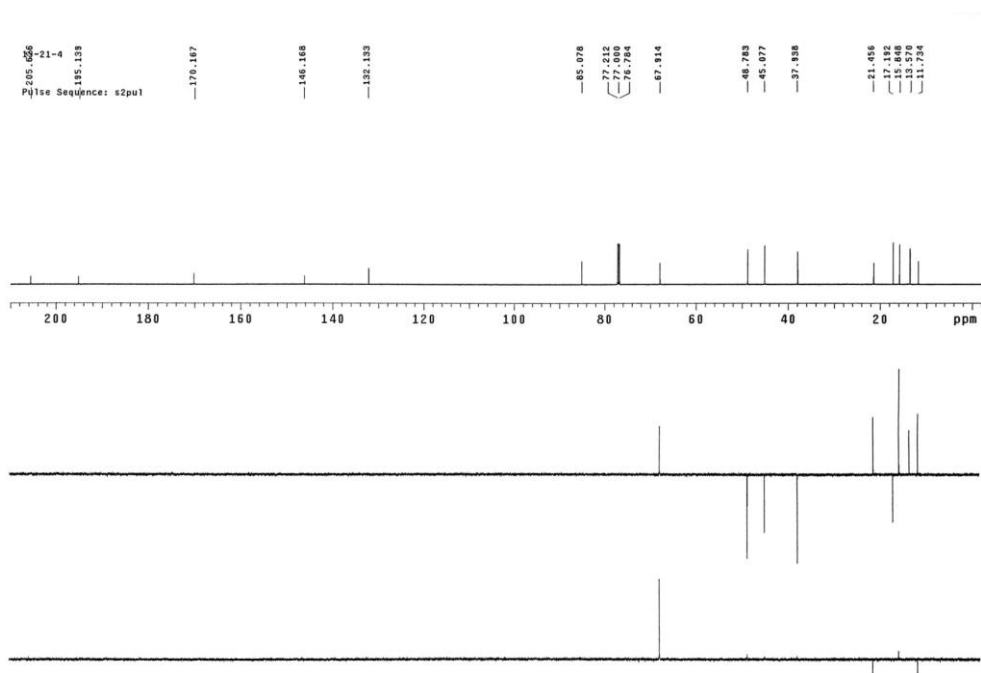


Figure S5. DEPT spectrum of **1** (150 MHz in CDCl₃)

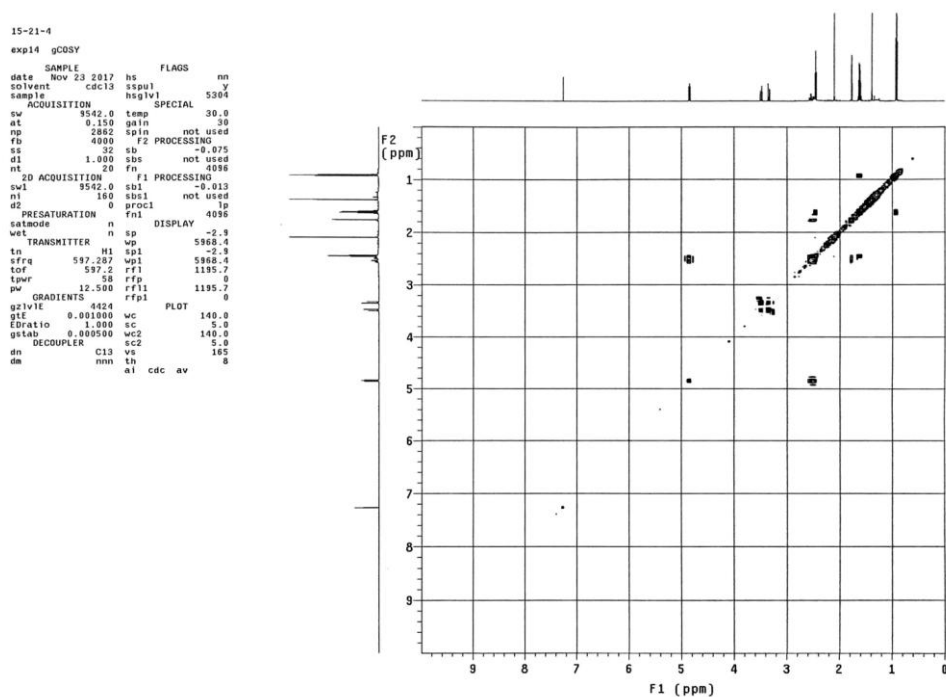


Figure S6. ¹H-¹H COSY spectrum of **1**

15-21-4

exp15 NOESY

```

SAMPLE          FLAGS
date Nov 23 2017 hs mn
solvent cdc13 sspul y
sample PFGf1g y
ACQUISITION     SPECIAL
sw 9542.0        SPECIAL 30.0
at 0.150 temp 26
np 2862 gain 20
fb 4000 spin not used
ss 32 F2 PROCESSING
dl 1.000 gfs not used
nt 20 gfs not used
2D ACQUISITION  fn 4096
sw1 9542.0 f1 PROCESSING
nl 160 g1 0.015
TRANSMITTER     gfs1 not used
t1 597.287 proc1 lp
sfrq 597.287 fml 4096
tof 597.2        DISPLAY
tpwr 50 sp -2.9
pw 12.500 sp 5968.4
NOESY            sp1 -2.9
mixN 0.600 wp1 5968.4
PRESATURATION    rf1 1195.7
satmode n rfp 0
wet n rf11 1195.7
DECOUPLER        rf1 0
dn C13 wc 140.0
dm nnn sc 0
          wc2 140.0
          sc2 5.0
          vs 1172
          th 2
          al cdc ph

```

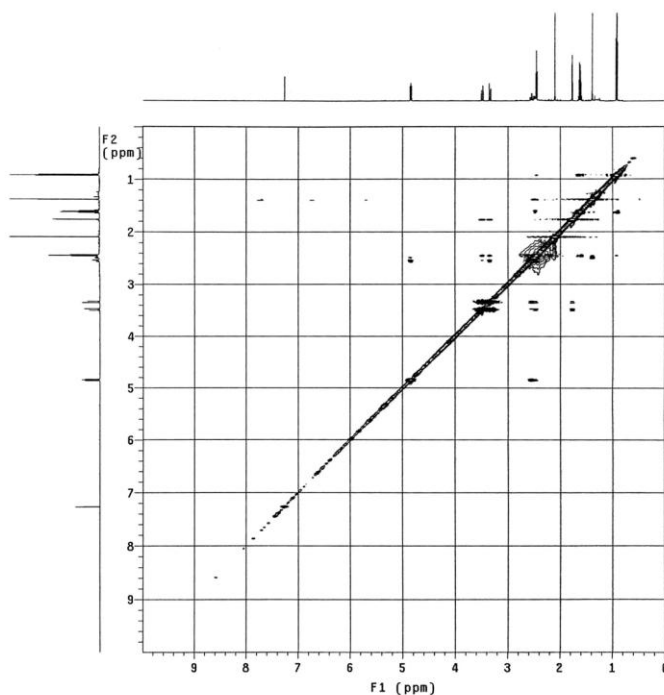


Figure S7. NOESY spectrum of 1

15-21-4

exp16 gHSQCAD

```

SAMPLE          FLAGS      ACQUISITION ARRAYS
date Nov 23 2017 hs mn      array phase
solvent cdc13 sspul y      arraydim 320
sample PFGf1g y
ACQUISITION     SPECIAL    1
sw 9542.0        SPECIAL 30.0 1
at 0.150 temp 26 1
np 2862 gain 20 1
fb 4000 spin not used 1
ss 32 GRADIENTS 4424 1
dl 1.000 g1 0.069 1
nt 20 g1 0.002000 1
2D ACQUISITION  Edratio 3.977 1
sw1 9542.0 g1 0.002000 1
nl 160 f2 PROCESSING 2
phase arrayed gfs not used
PRESATURATION    gfs not used
satmode n f1 PROCESSING
wet n rf1 4096
TRANSMITTER     gfs1 0.995
t1 597.287 proc1 not used
sfrq 597.287 fml lp
tof 597.2        DISPLAY 4096
tpwr 50 sp -2.9
pw 12.500 sp 5968.4
dn C13 sp1 -3.2
dm nny wp1 31827.4
          nny rf1 1195.7
decwave V40_autox rfp 0
dmf 35.000 rf11 2256.5
dpwr 35 rfp1 0
          PLLOT
pwx1v1 54 wc 180.0
pwx 9.500 wc 0
          HSQC 140.0
          jlxh 140.0 wc2 140.0
          mult 0 y sc2 0
          mult 0 vs 47
          ADIABATIC th 4
pwx180ad autox_ad3= nm cdc ph
pwx180ad autox_ad= 00
pwx180 390R
pwx1v1180 400.0
pwx180ref autox_ref= F200
pwx180r 1998.8
pwx1v1180r 40

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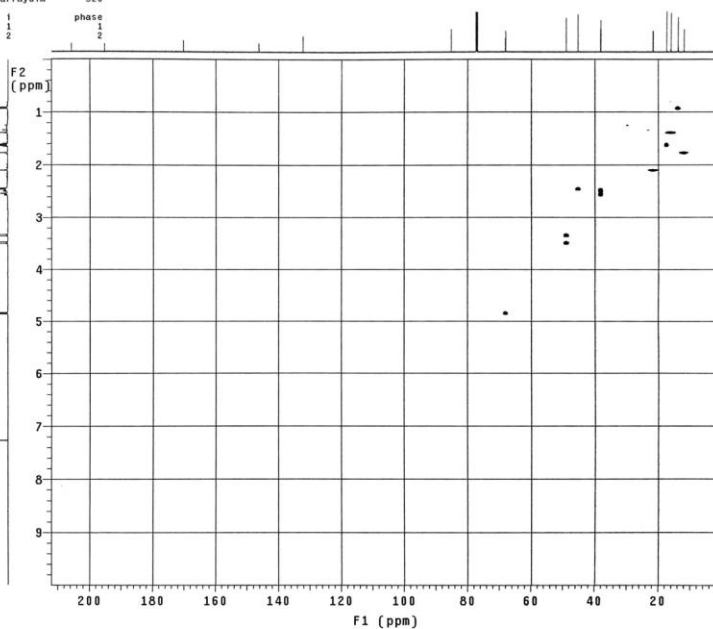


Figure S8. HSQC spectrum of 1

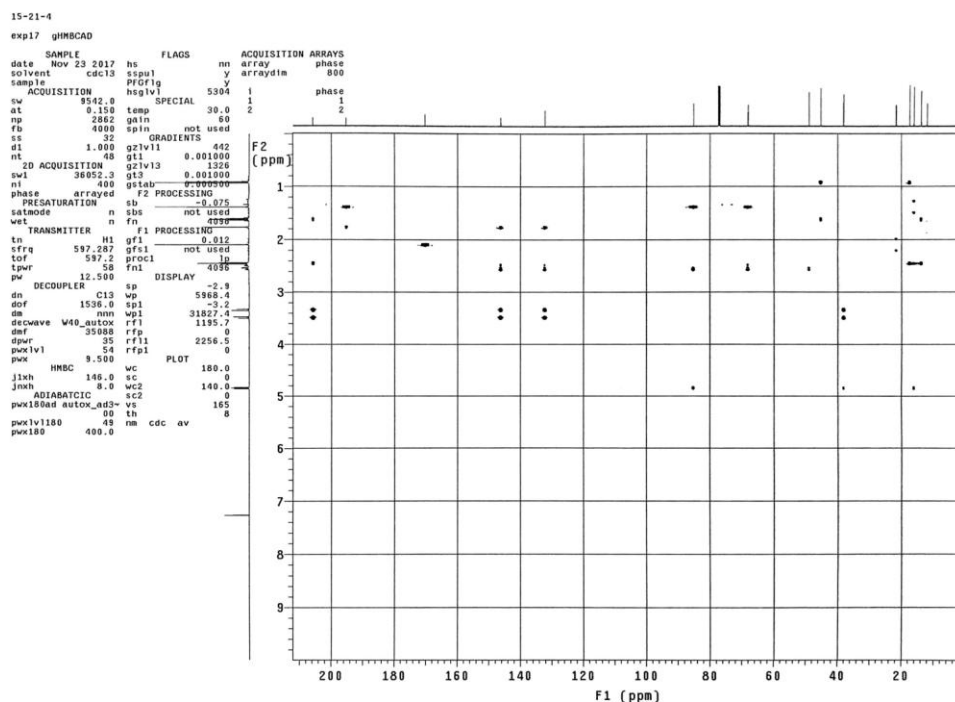


Figure S9. HMBC spectrum of **1**

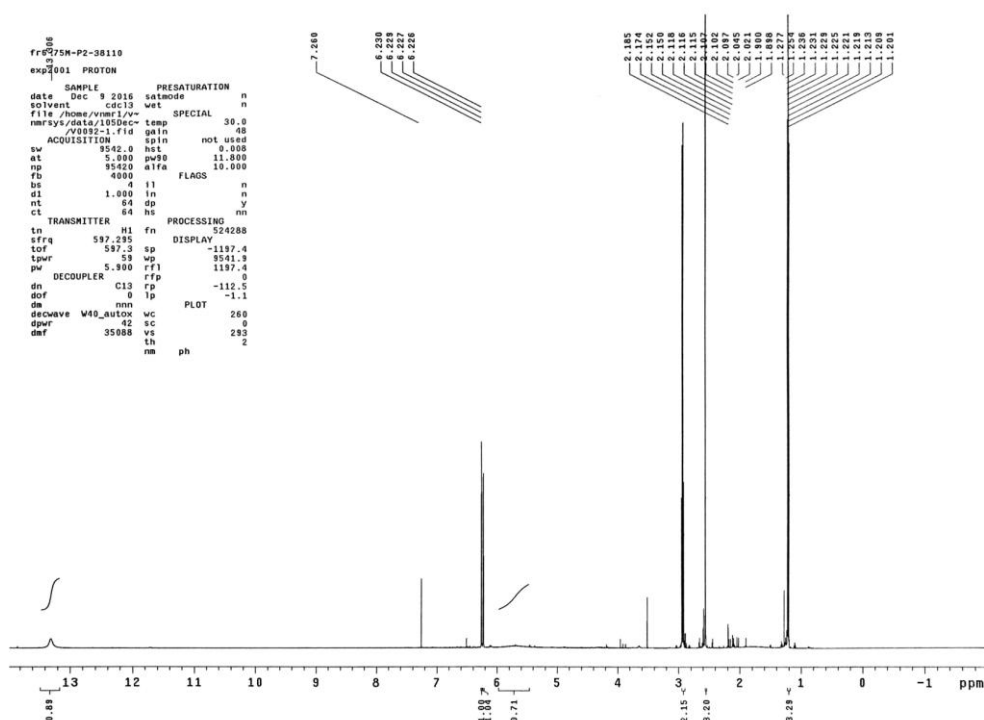


Figure S10. ^1H NMR spectrum of **2** (600 MHz in CDCl_3)

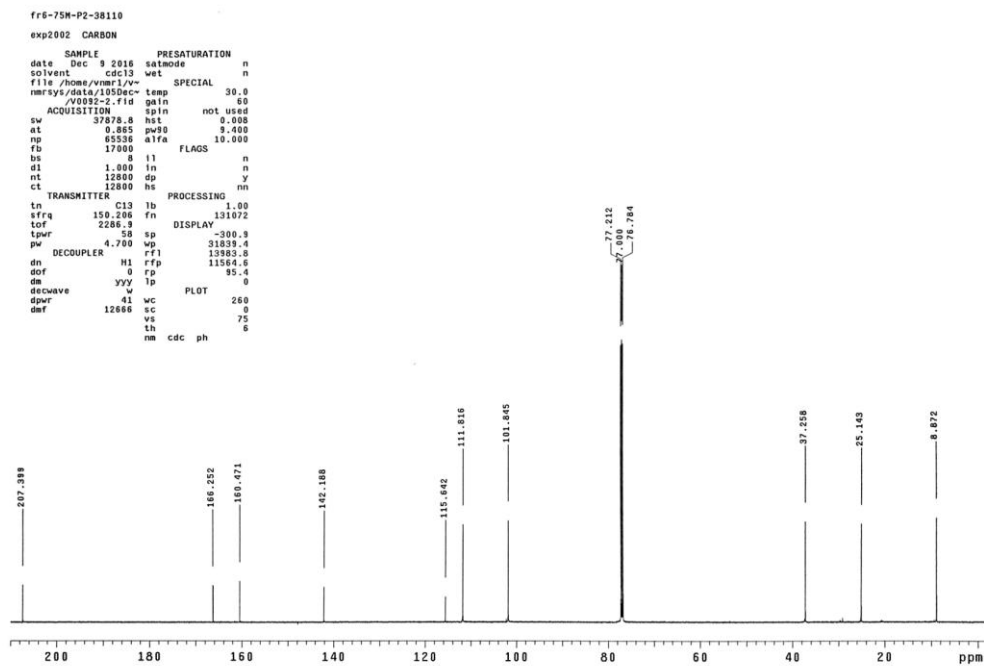


Figure S11. ^{13}C NMR spectrum of **2** (150 MHz in CDCl_3)

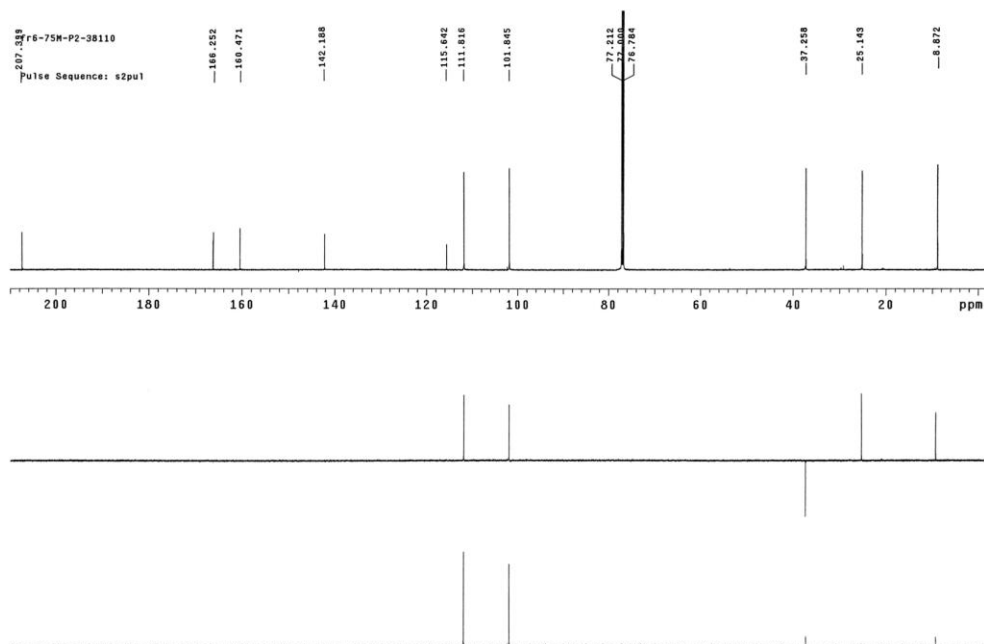


Figure S12. DEPT spectrum of **2** (150 MHz in CDCl_3)

fr8-75M-P2-38110
exp2004 gCOSY

```

SAMPLE          FLAGS      nn
date Dec 9 2016  hs          y
solvent cdc13  sspu1        y
sample         hsglv1      5352
ACQUISITION     SPECIAL
sw 9542.0 temp 30.0
at 0.150 gain not used
np 2882 spin not used
fb 4000 f2 PROCESSING
ss 32 sb -0.075
d1 1.000 sbs not used
nt 32 fn 4096
2D ACQUISITION  F1 PROCESSING
sw1 9542.0 sb1 -0.017
nl 160 sbs1 not used
d2 0 proc1 not used
lp 4096
PRESATURATION 0 fns
satmode n fns DISPLAY
wet n sp -0.0
TRANSMITTER    vp 8242.1
tn H1 sp1 -0.0
sfrq 597.295 wp1 8242.1
tor 597.3 rff1 1197.4
tpwr 59 rfp 0
pw 11.800 rff1 1197.4
rff1 0
gzlvie 1464 PLOT
glt 0.001000 wc 140.0
fdratio 1.000 sc 5.0
gstab 0.000500 wc2 140.0
DECOUPLER      sc2 5.0
dn C13 vs 17
de nnn th 2
al cdc av

```

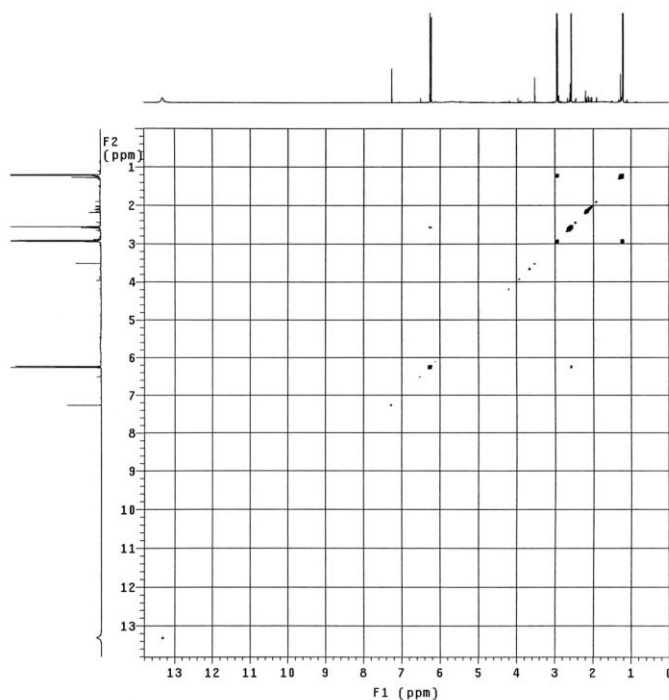


Figure S13. ^1H - ^1H COSY spectrum of 2

fr8-75M-P2-38110
exp2005 NOESY

```

SAMPLE          FLAGS      nn
date Dec 9 2016  hs          y
solvent cdc13  sspu1        y
sample         PFGf1g      5352
ACQUISITION     SPECIAL
sw 9542.0 temp 30.0
at 0.150 gain not used
np 2882 spin not used
fb 4000 f2 PROCESSING
ss 32 sb -0.075
d1 1.500 gf 0.069
nt 32 gfs not used
2D ACQUISITION  F1 PROCESSING
sw1 9542.0 sb1 -0.019
nl 160 sbs1 not used
d2 0 proc1 not used
lp 4096
PRESATURATION 0 fns
satmode n fns DISPLAY
wet n sp -0.0
TRANSMITTER    vp 8242.1
tn H1 sp1 -0.0
sfrq 597.295 wp1 8242.1
tor 597.3 rff1 1197.4
tpwr 59 rfp 0
pw 11.800 rff1 1197.4
rff1 0
NOESY 0.800
gzlvie 1464 PLOT
glt 0.001000 wc 140.0
fdratio 1.000 sc 5.0
gstab 0.000500 wc2 140.0
DECOUPLER      sc2 5.0
dn C13 vs 17
de nnn th 2
al cdc ph

```

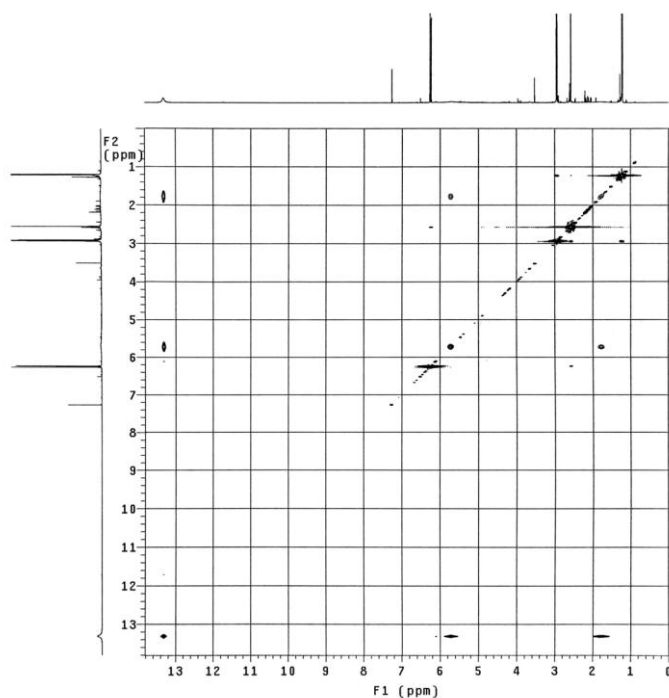


Figure S14. NOESY spectrum of 2

fr6-75M-P2-38110
Pulse Sequence: gHSQCAD

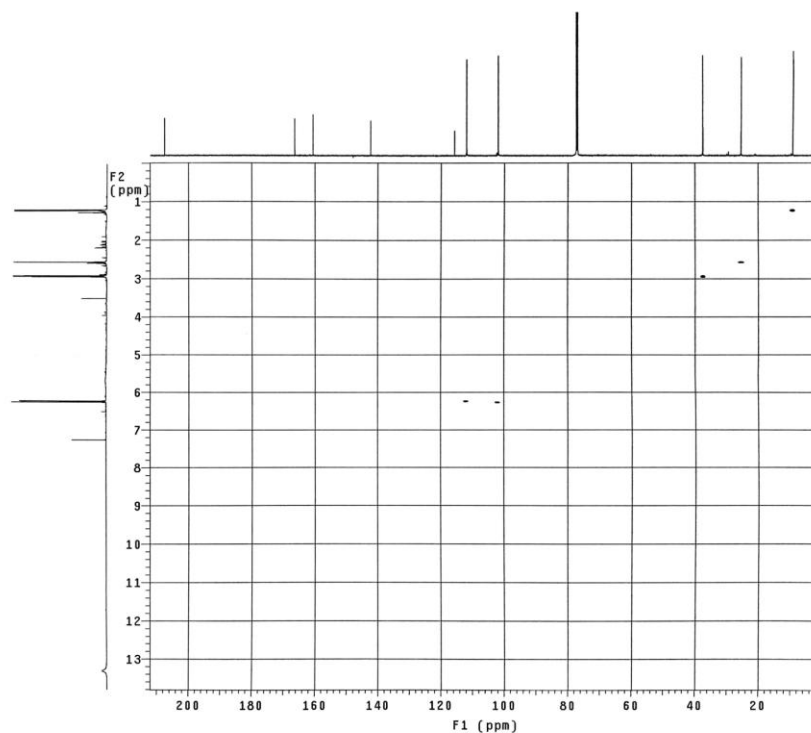


Figure S15. HSQC spectrum of **2**

fr6-75M-P2-38110
Pulse Sequence: gHMBCAD

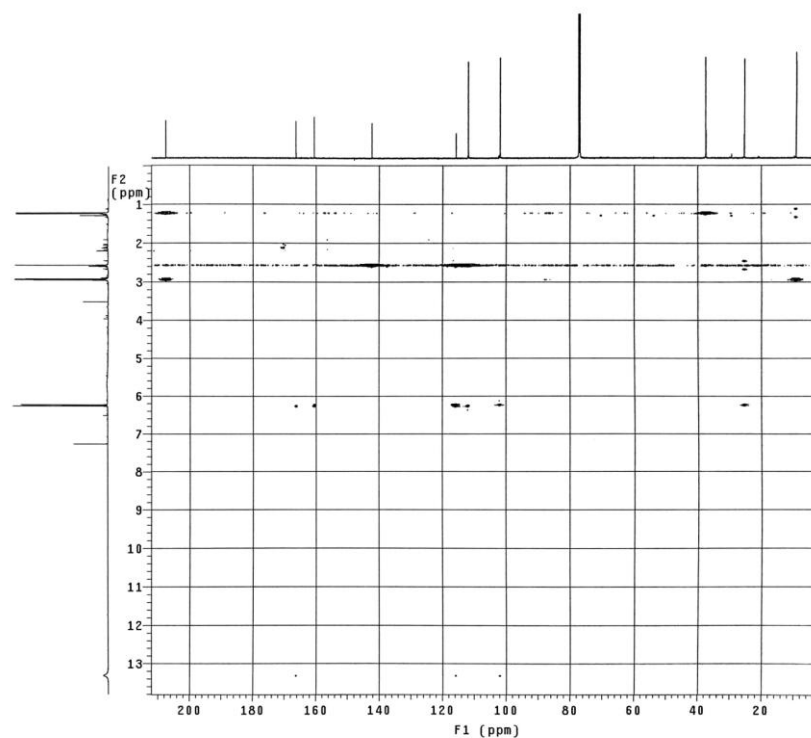


Figure S16. HMBC spectrum of **2**