

Bioactive Iridoid Glycosides from the Whole Plants of *Rehmannia chingii*

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and De-Quan Yu*

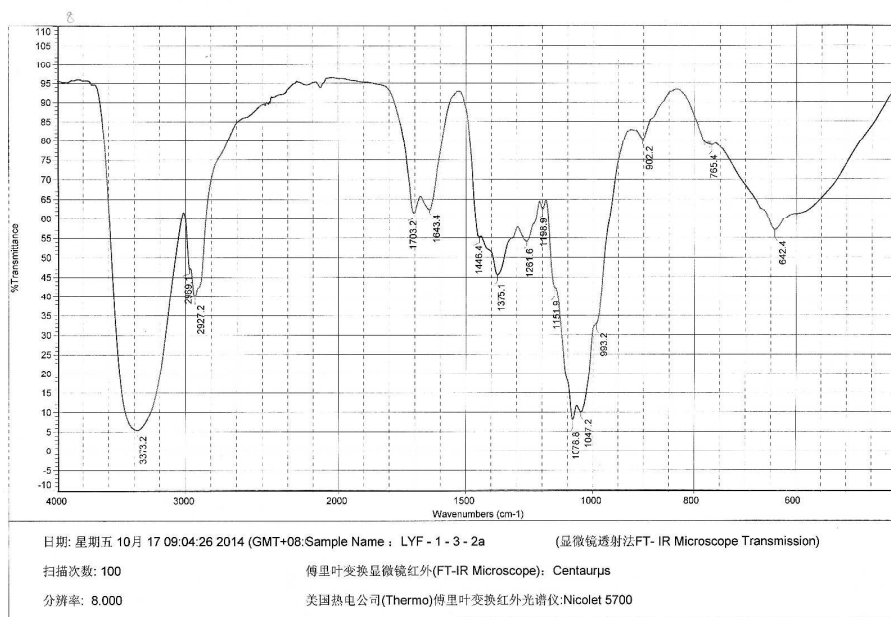
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Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union
Medical College, Beijing 100050, People's Republic of China*

Supporting Information

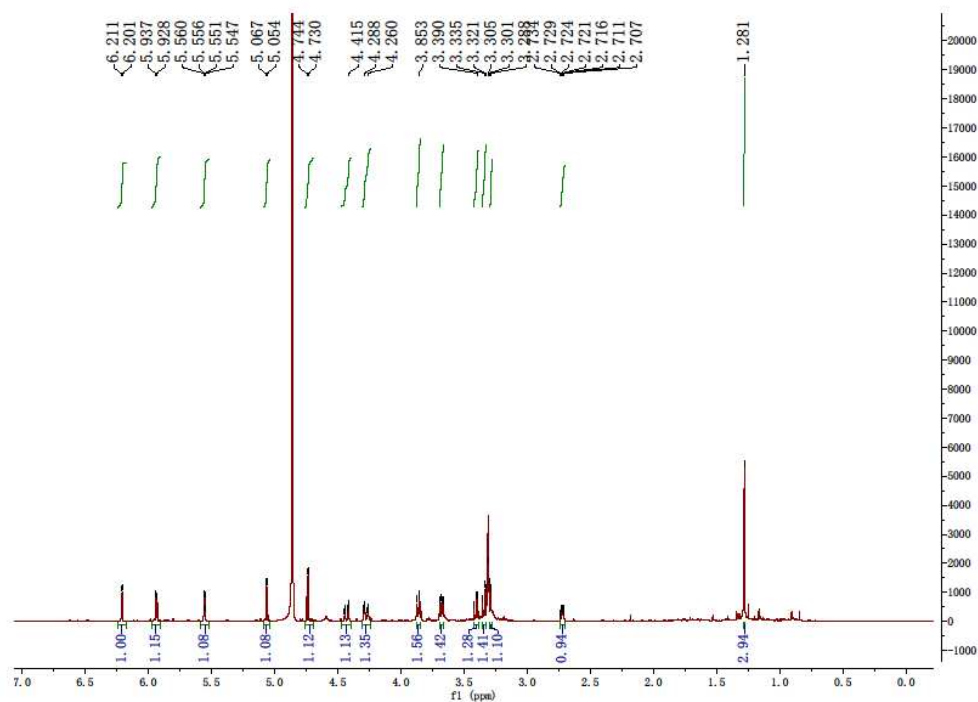
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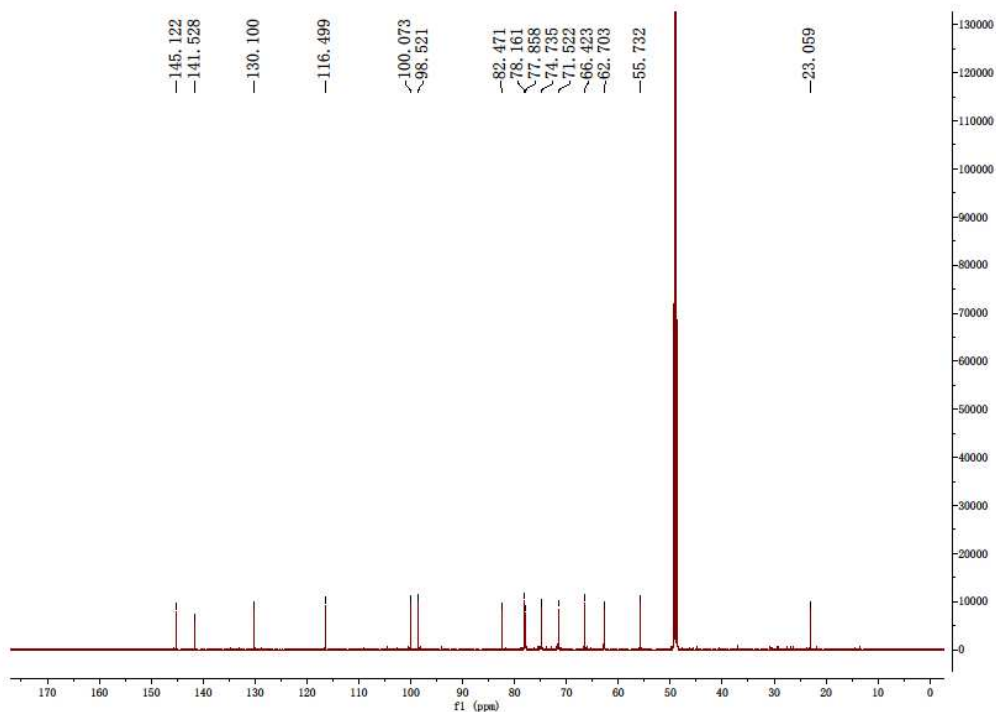
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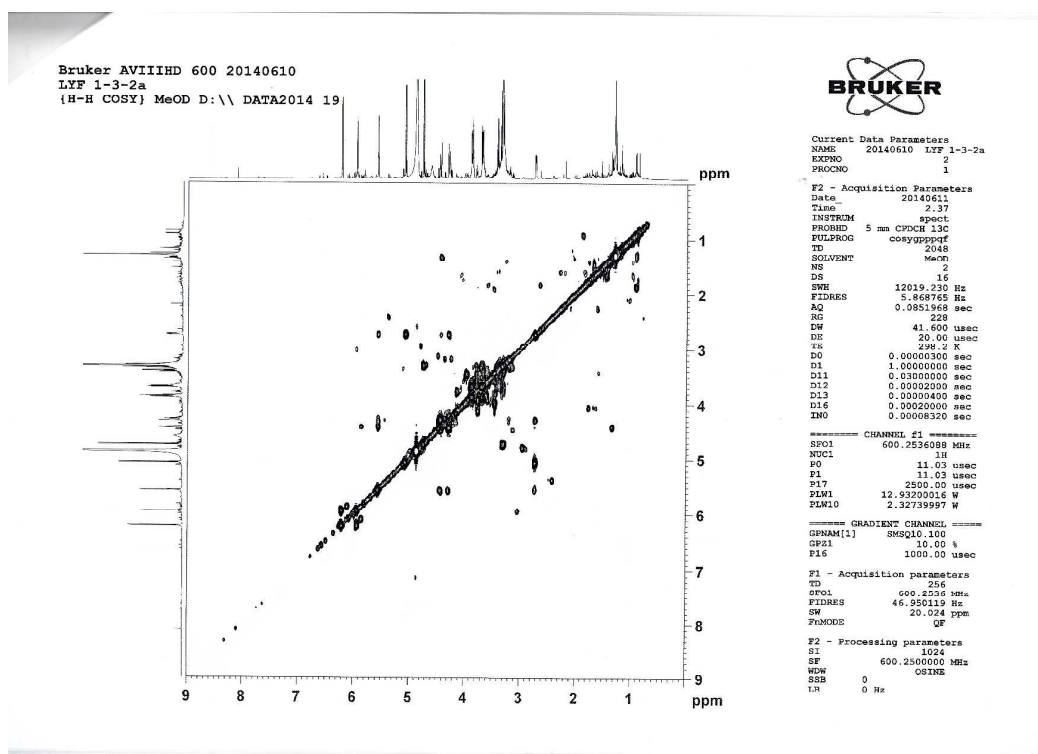
S1. IR Spectrum of compound 1



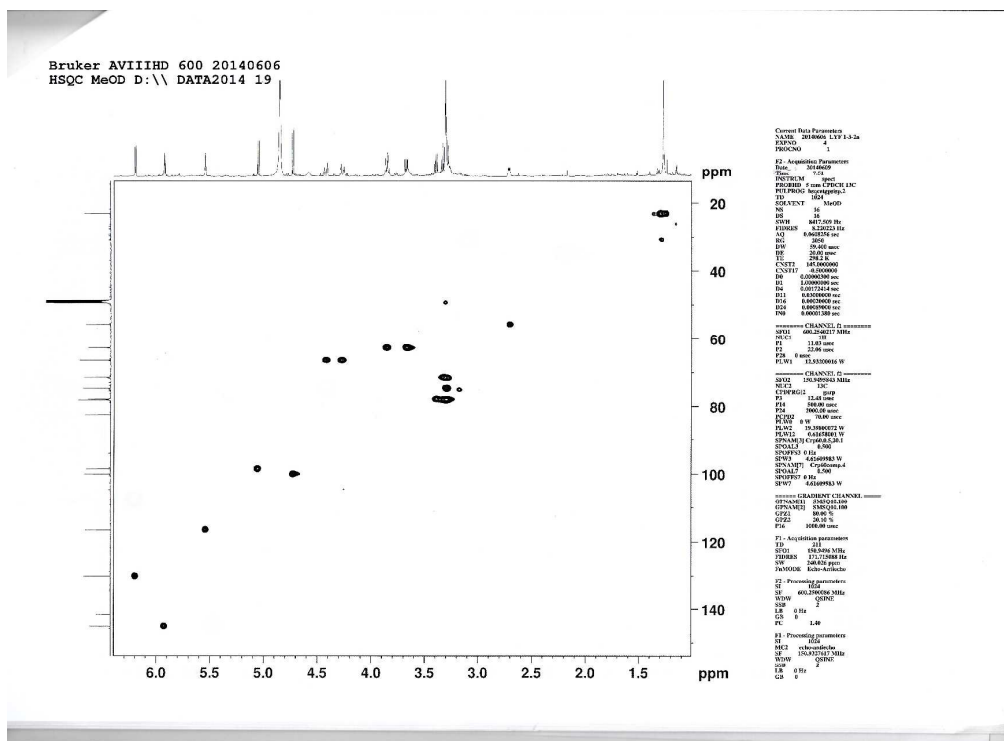
S2. ¹H NMR Spectrum of compound 1 (600MHz, Methanol-d₄)



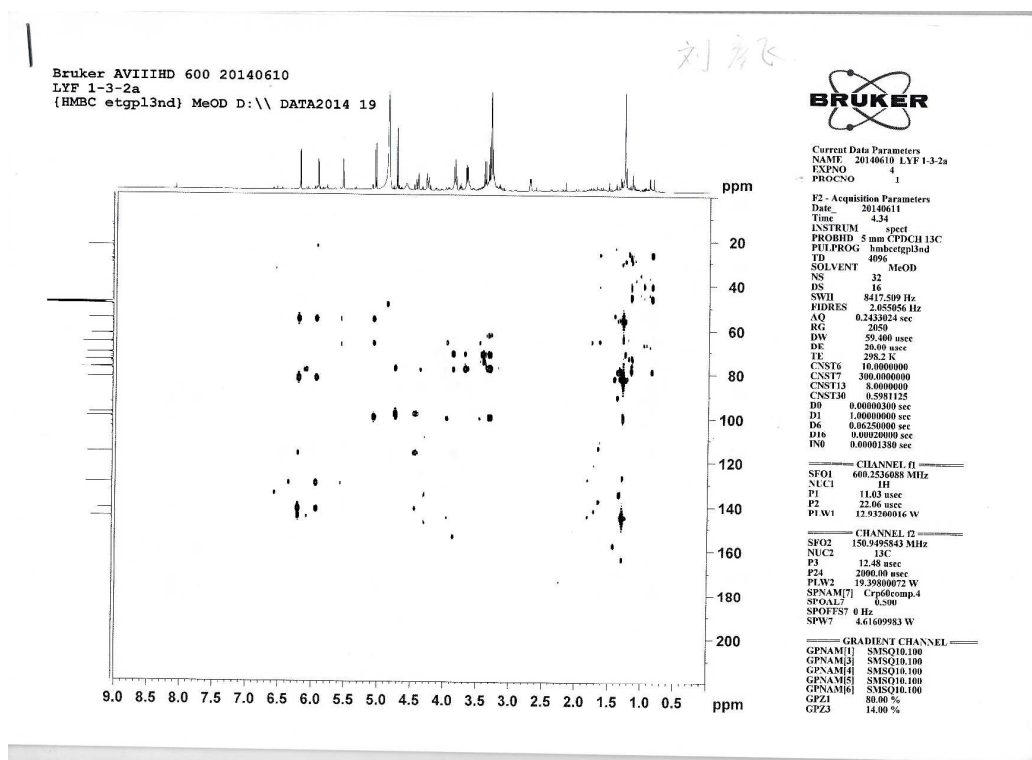
S3. ^{13}C NMR Spectrum of compound **1** (150 MHz, Methanol- d_4)



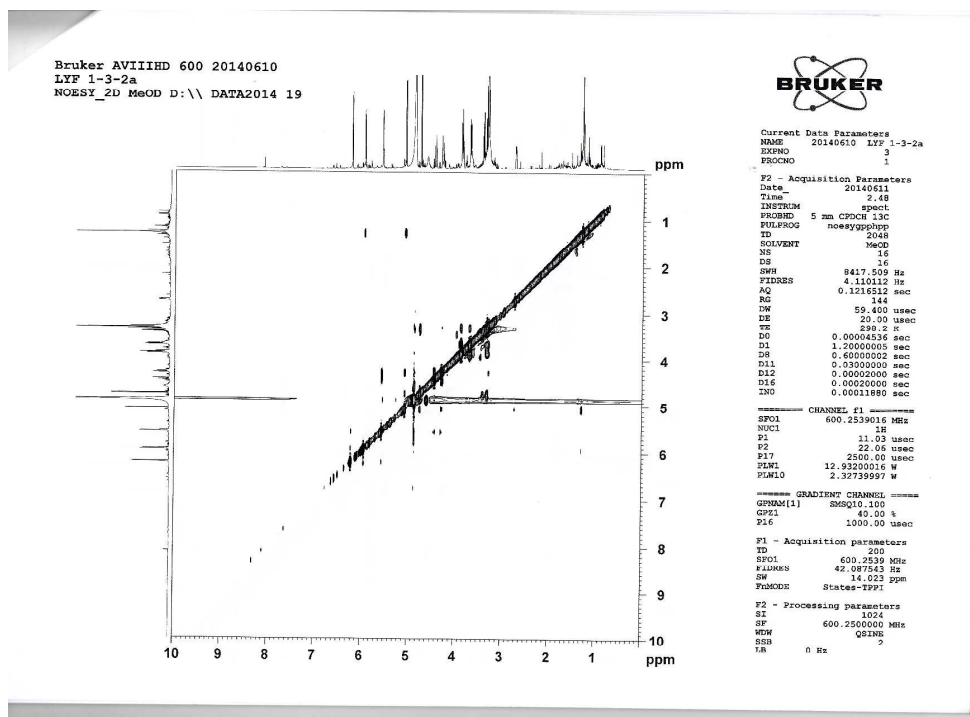
S4. ^1H - ^1H COSY Spectrum of compound **1**



S5. HSQC Spectrum of compound 1



S6. HMBC Spectrum of compound 1



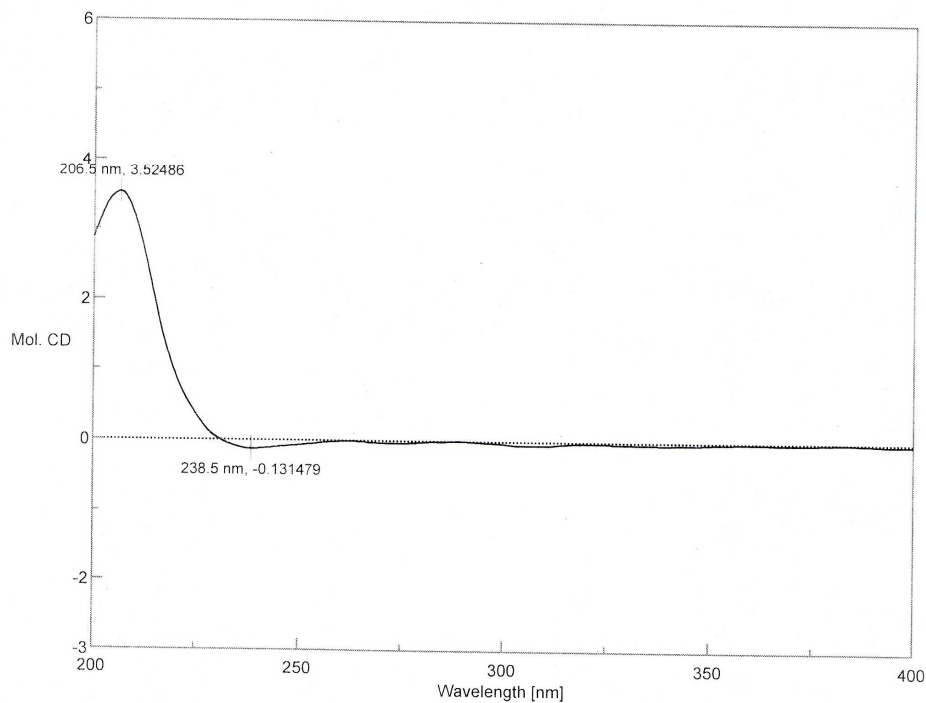
S7. NOESY Spectrum of compound 1

MS Formula Results: + Scan (4.170 min) Sub (2014090903.d)

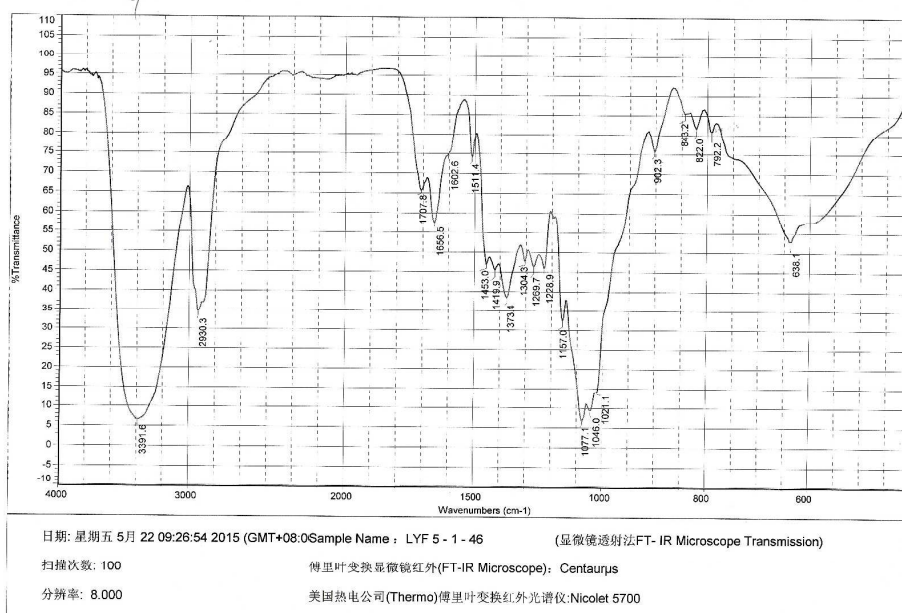
MS	Ion	Formula	Abundance
353.1211	[M+H] ⁺	C ₁₅ H ₂₂ N ₂ O	100.00

Best	Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc Mass	Calc mp	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spiking Match	DBE
✓	C ₁₅ H ₂₂ O	C ₁₅ H ₂₂ N ₂ O	99.93		330.1318	330.1315	353.1207	-1.34	1.34	99.96	99.99	99.99	5

S8. HRESIMS Spectrum of compound 1

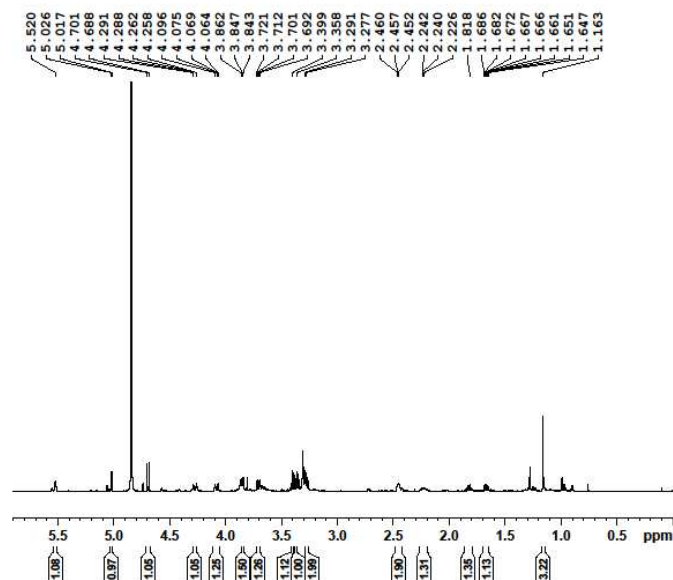


S9. CD Spectrum of compound 1 (CH₃OH)



S10. IR Spectrum of compound 2

Bruker AVIIHHD 600 20150109
PROTON CD3OD D:\DATA2015 44



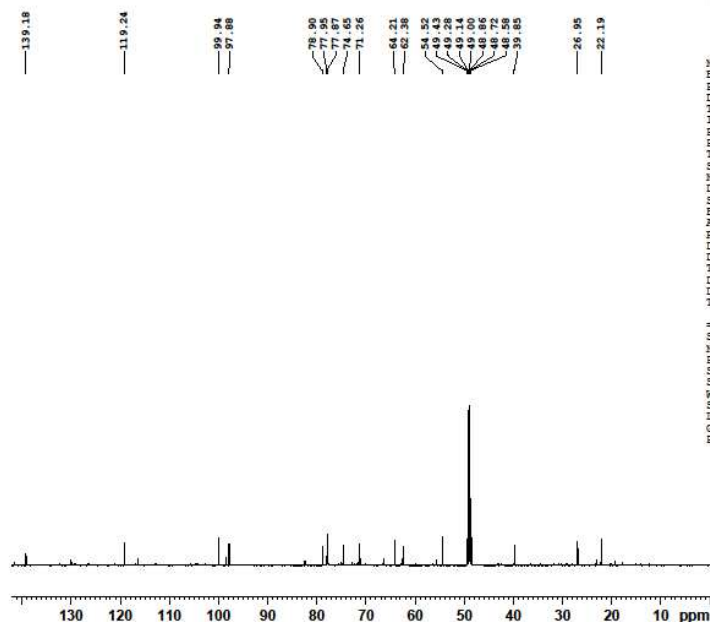
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PROCNO    1
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PULPROG    zg30
TD         65536
SOLVENT    CD3OD
NS         16
DS         2
SWH         12019.230 Hz
FIDRES     0.183399 Hz
AQ         2.7263477 sec
RG         32
DW         41.600 usec
DE         20.00 usec
TE         298.2 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1       600.2537068 MHz
NUC1        1H
P1         11.50 usec
SI         65536
SF         600.2499811 MHz
WDW         EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00
    
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S11. ¹H NMR Spectrum of compound 2 (600 MHz, Methanol-d₄)

Bruker AVIIIHD 600 20150105
C13 CD3OD D:\ DATA2015 10



```

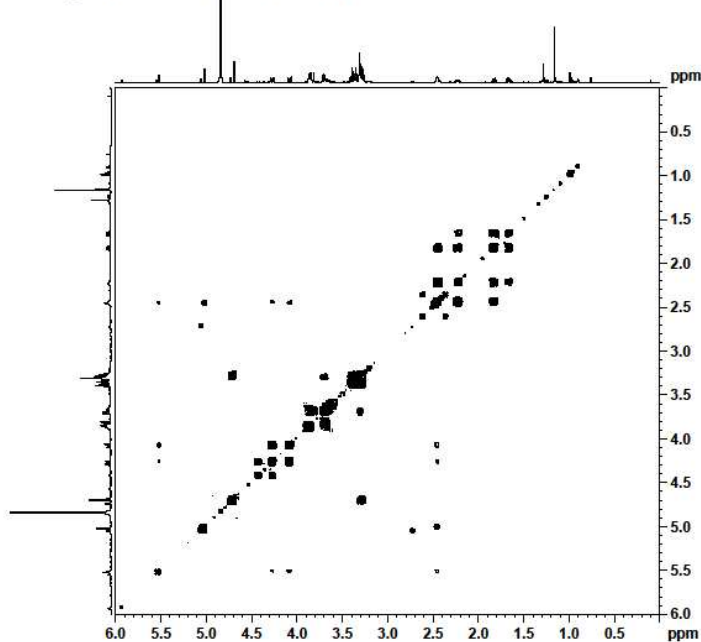
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EXPNO     1
PROCNO    1
Date_     20150106
Time      12.12
INSTRUM    spect
PROBHD     5 mm CPDCH 13C
PULPROG    zgpg30
TD         65536
SOLVENT    CD3OD
NS         555
DS         4
SWH        26087.691 Hz
FIDRES     0.580197 Hz
AQ         0.9088159 sec
RG         2050
DW         19.867 usec
DE         31.37 usec
TE         298.2 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0        250

===== CHANNEL f1 =====
SF01      150.9495842 MHz
NUC1       13C
P1         12.94 usec
SI         32768
SF         150.9327700 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```

S12. ^{13}C NMR Spectrum of compound **2** (150 MHz, Methanol- d_4)

Bruker AVIIIHD 600 20150109
COSY_MQF CD3OD D:\ DATA2015 44



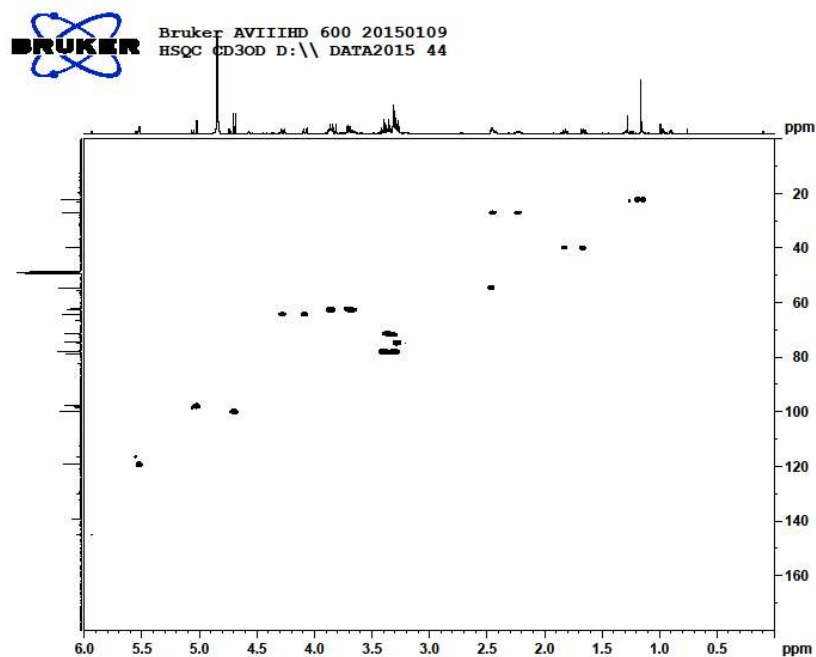
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PROCNO    1
Date_     20150111
Time      12.49
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PROBHD     5 mm CPDCH 13C
PULPROG    cosygmqf
TD         2048
SOLVENT    CD3OD
NS         16
DS         4
SWH        8417.509 Hz
FIDRES     4.110112 Hz
AQ         0.1217012 sec
RG         2050
DW         59.400 usec
DE         20.00 usec
TE         298.2 K
D0         0.00003000 sec
D1         2.00000000 sec
D13        0.00000400 sec
D16        0.00020000 sec
D19        0.00019000 sec
TD0        100

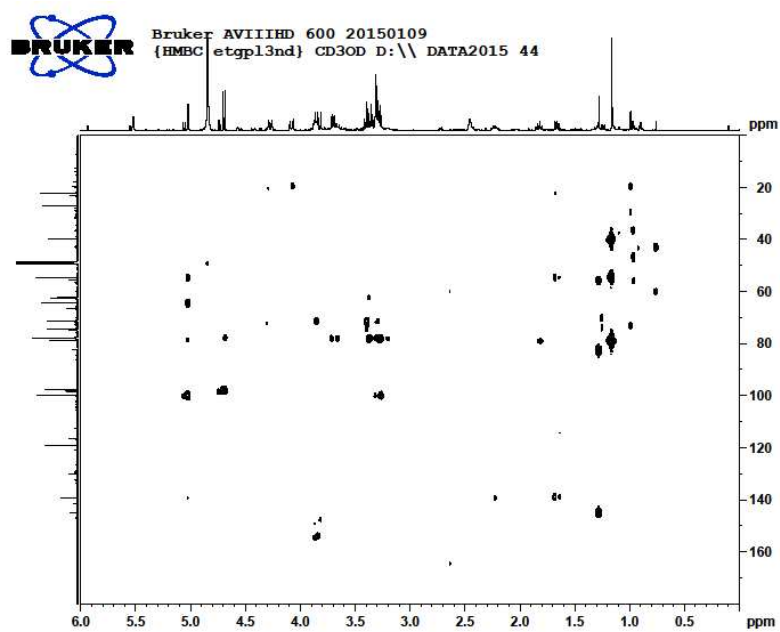
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SF01      600.2540217 MHz
NUC1       1H
P1         11.50 usec
WDW        1
SI         1024
SF         600.2499779 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
PC         1.40
SI         1024
SF         600.2499870 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0

```

S13. ^1H - ^1H COSY Spectrum of compound **2**

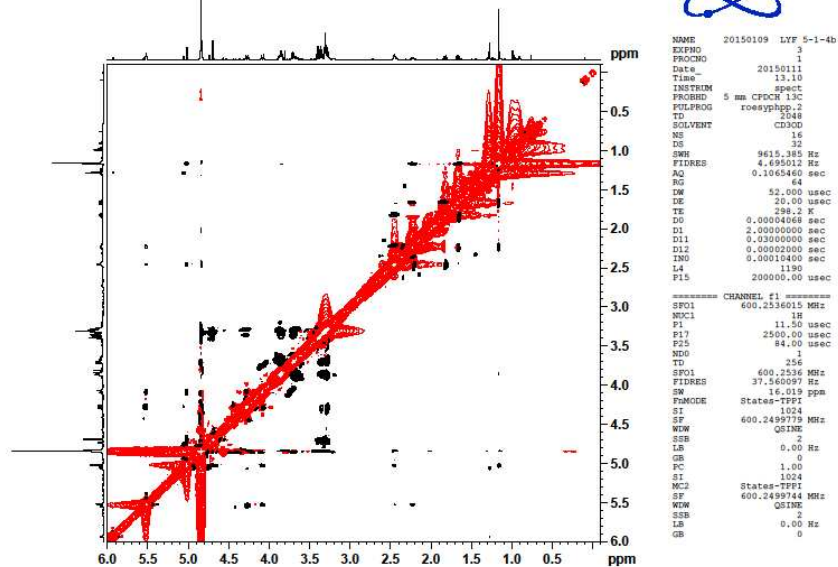


S14. HSQC Spectrum of compound 2



S15. HMBC Spectrum of compound 2

Bruker AVIIHD 600 20150109
ROESY CD3OD D:\DATA2015 44



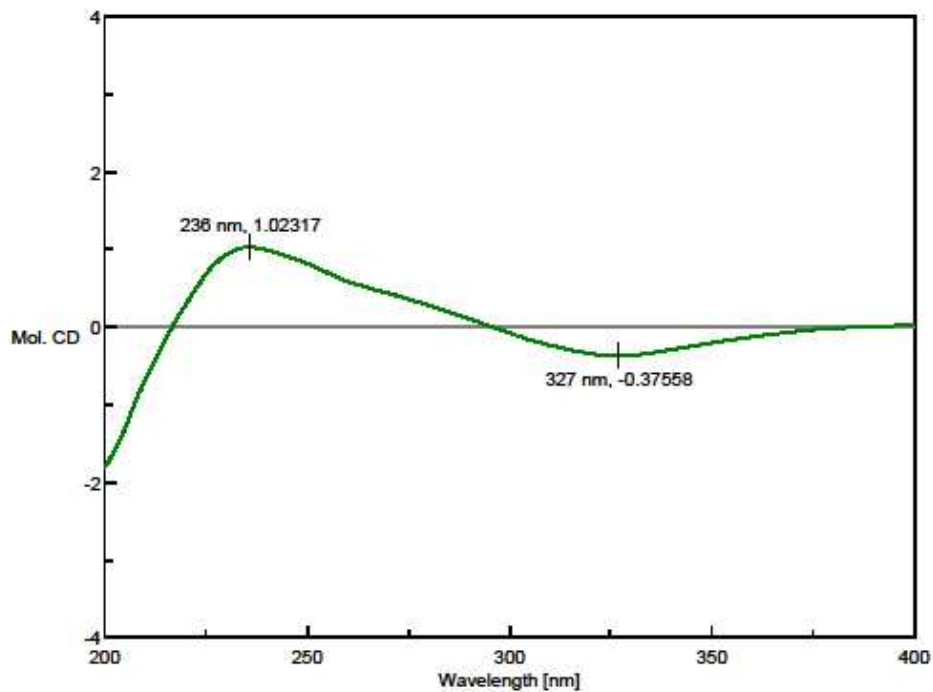
S16. ROESY Spectrum of compound 2

MS Formula Results: + Scan (4.457 min) Sub (2015012103.d)

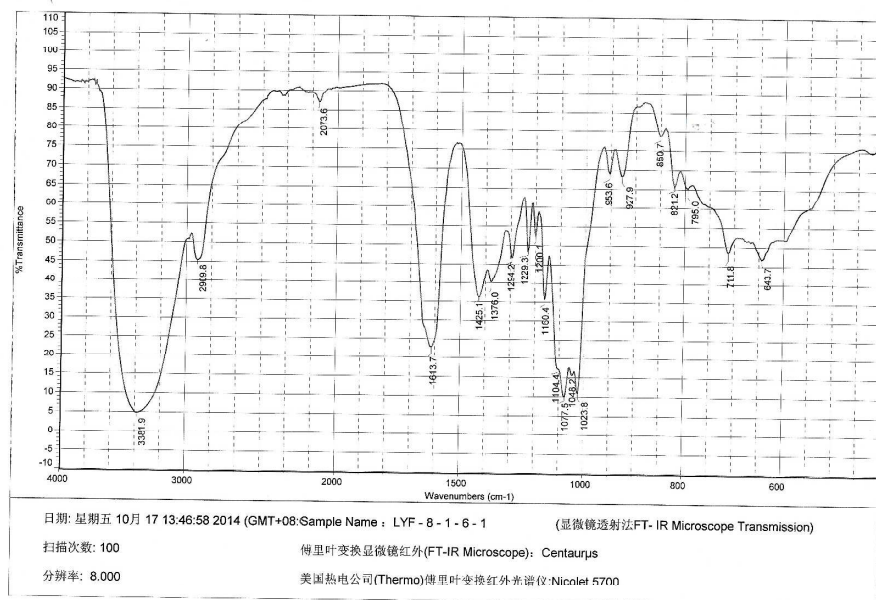
m/z	Ion	Formula	Abundance
355.136	(M+Na) ⁺	C15 H24 Na O8	2087076
Best	Formula (M)	Ion Formula	Score
+	C15 H24 O8	C16 H24 Na O8	99.96
-	C16 H28 O3 S2	C16 H28 Na O3 S2	97.24

Mass	Calc Mass	Calc m/z	Diff (ppm)	Abn Diff (ppm)	Mass Match	Abund Match	Spacing Match	DRE
332.1467	332.1481	335.1363	-1.12	1.12	99.96	99.99	99.93	4
332.1467	332.1481	355.1372	-3.73	3.73	98.61	91.61	99.27	3

S17. HRESIMS Spectrum of compound 2

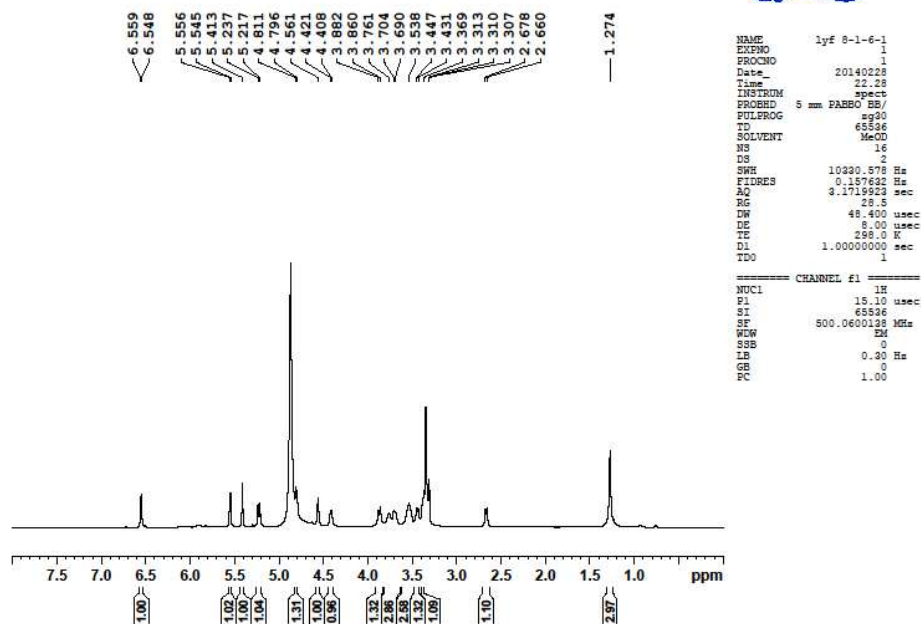


S18. CD Spectrum of compound 2 (CH₃OH)



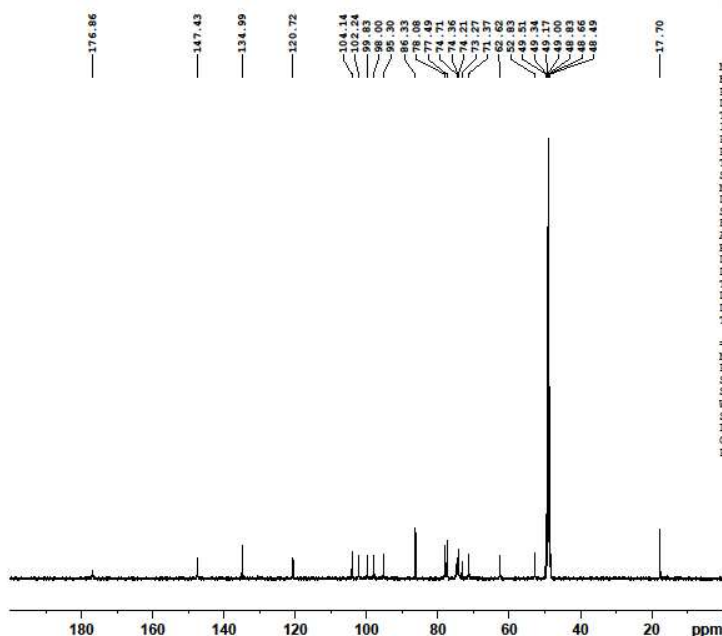
S19. IR Spectrum of compound 3

BRUKER AV-III-500 1H-NMR LYF 8-1-6-1 IN MeOD 2014.02.25



S20. ^1H NMR Spectrum of compound 3 (500MHz, Methanol- d_4)

BRUKER AV-III-500 13C-NMR LYF 8-1-6-1 IN MeOD 2014.02.13



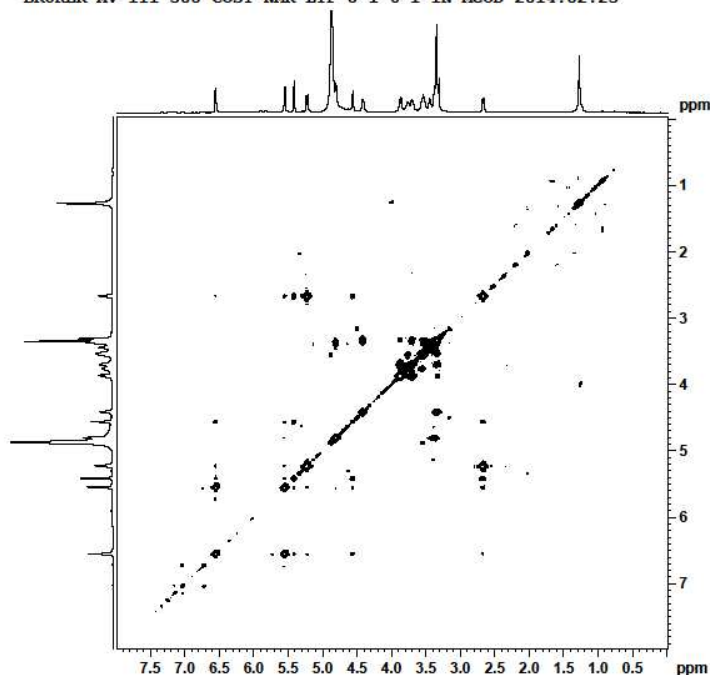
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PROCNO    1
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Time      13.58
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PULPROG    zgpg30
TD         65536
SOLVENT    MeOD
NS         1166
DS         4
SWH        29761.904 Hz
FIDRES     0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         298.5 K
D1         1.00000000 sec
D11        0.03000000 sec
TDO        800

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
SI         22768
SF         125.7400308 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

S21. ^{13}C NMR Spectrum of compound **3** (125 MHz, Methanol- d_4)

BRUKER AV-III-500 COSY-NMR LYF 8-1-6-1 IN MeOD 2014.02.25

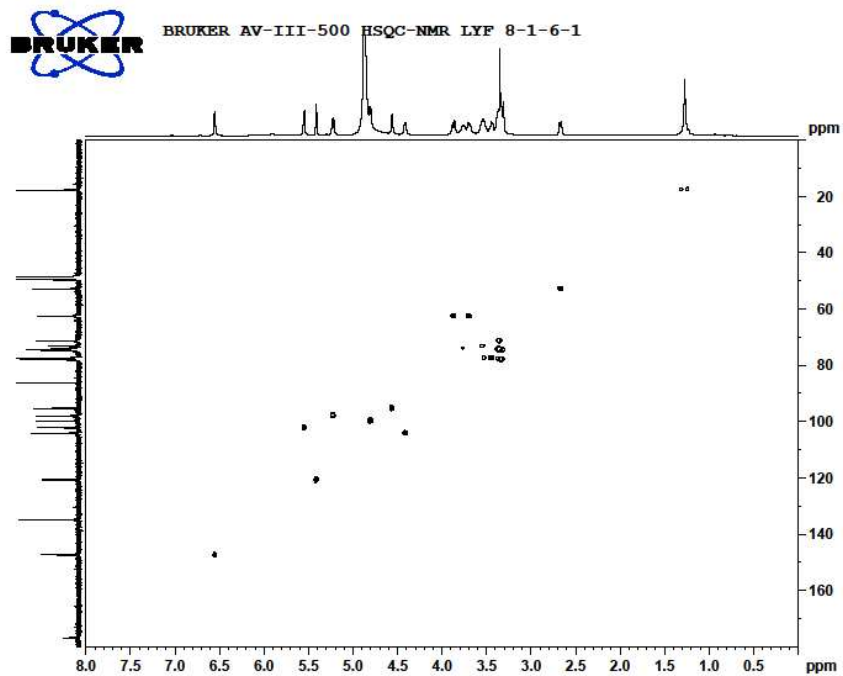


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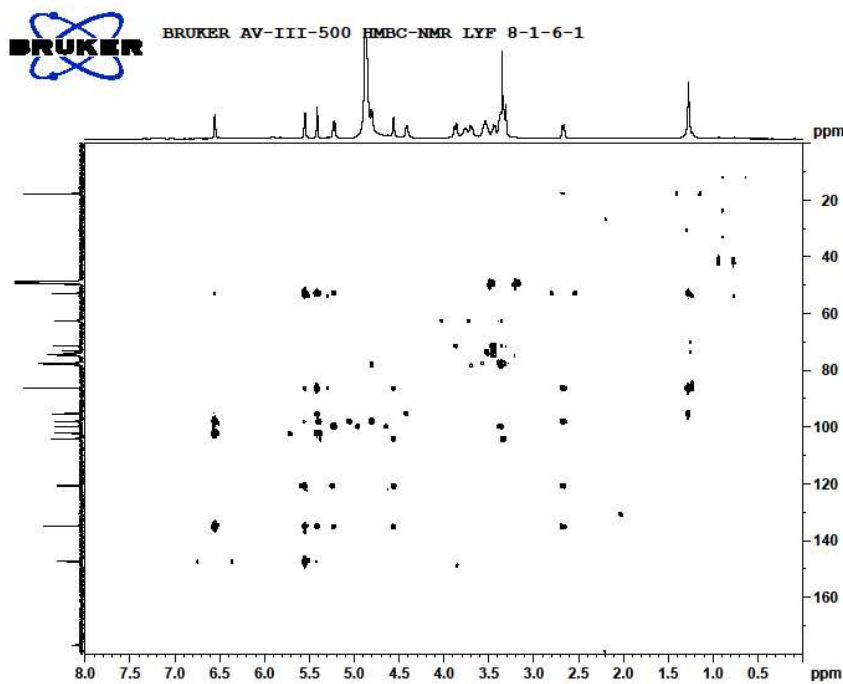
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EXPNO     2
PROCNO    1
Date_     20140228
Time      22.29
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PULPROG    cosyzgpg30
TD         2048
SOLVENT    MeOD
NS         2
DS         8
SWH        4000.000 Hz
FIDRES     1.953125 Hz
AQ         0.2560500 sec
RG         203
DW         125.000 usec
DE         8.00 usec
TE         297.9 K
D0         0.00003000 sec
D1         1.00000000 sec
D12        0.00004000 sec
D16        0.00020000 sec
TNO        0.00024995 sec

===== CHANNEL f1 =====
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P1         15.10 usec
WDW        1
SF         500.062 MHz
FIDRES     15.626941 Hz
SW         8.000 ppm
F2MODE     QF
SI         1024
SF         500.0600116 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
PC         1.40
SI         1024
MC2        500.0600121 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
  
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S22. ^1H - ^1H COSY Spectrum of compound **3**

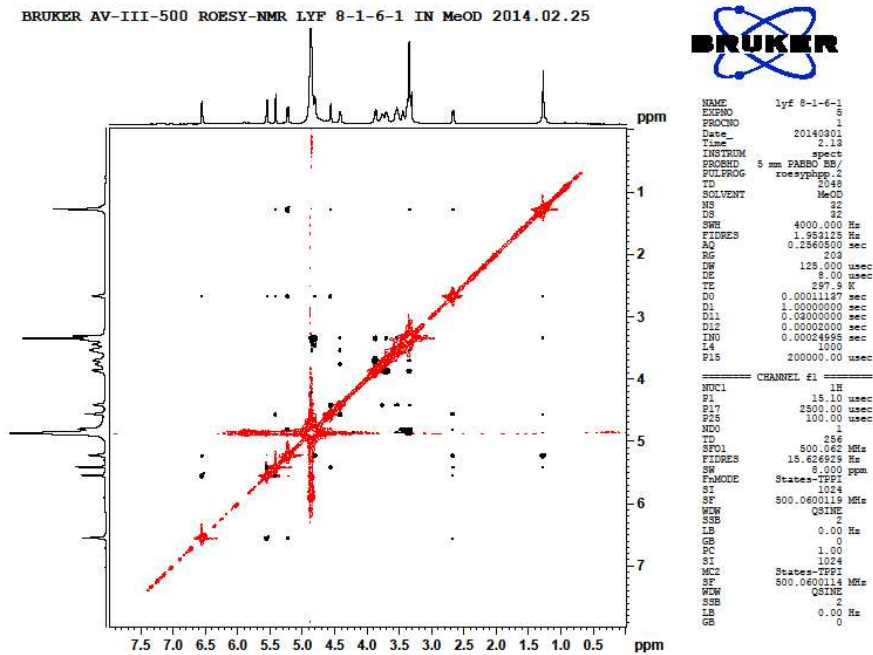


S23. HSQC Spectrum of compound **3**



S24. HMBC Spectrum of compound **3**

BRUKER AV-III-500 ROESY-NMR LYF 8-1-6-1 IN MeOD 2014.02.25



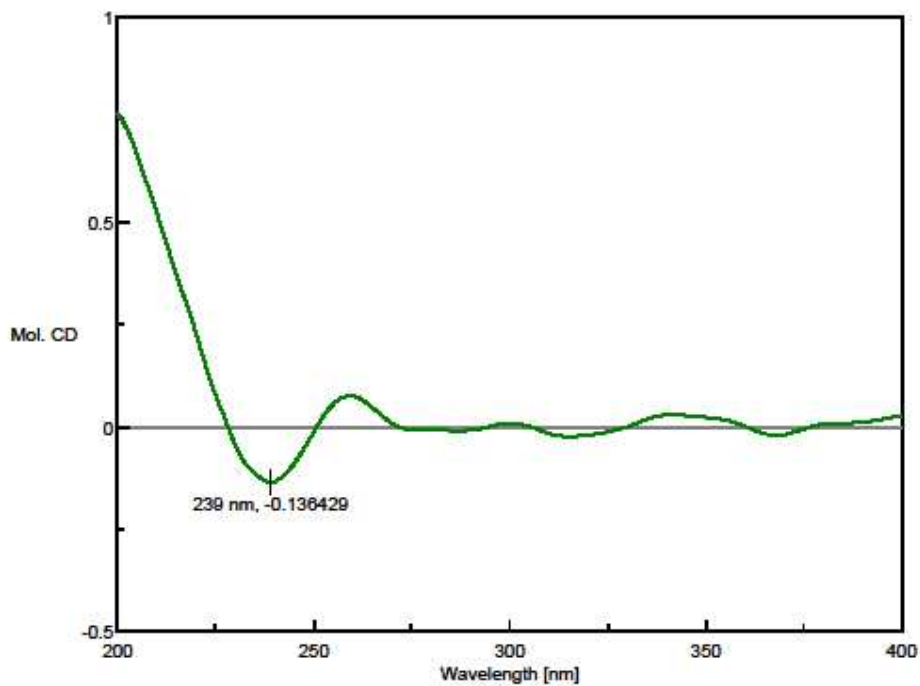
S25. ROESY Spectrum of compound 3

MS Formula Results: + Scan (2.783 min) Sub (2014090906.d)

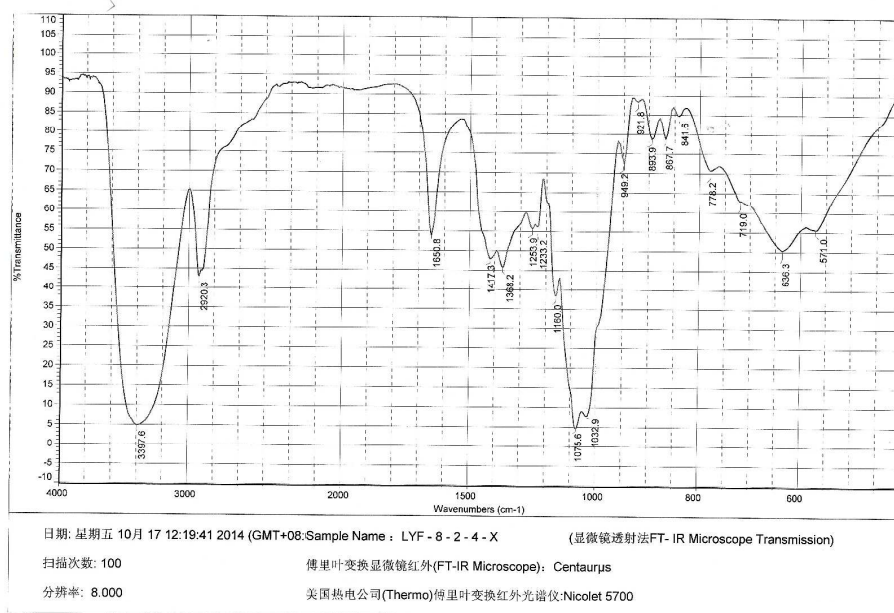
m/z	Ion	Formula	Abundance
255.140	(M+Na) ⁺	C21H30NaO16	48651.4
Best			
Formula (g)	Ion Formula	Score	Order Score
C21H30O16	C21H30NaO16	99.94	
C34H22N2O4	C34H22N2NaO4	95.95	

Mass	Calc Mass	Calc m/z	Diff (gsm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DSE
522.1588	522.1585	545.1477	-0.58	0.58	99.99	99.96		7
522.1588	522.158	545.1472	-1.56	1.56	99.92	99.78	99.77	25

S26. HRESIMS Spectrum of compound 3

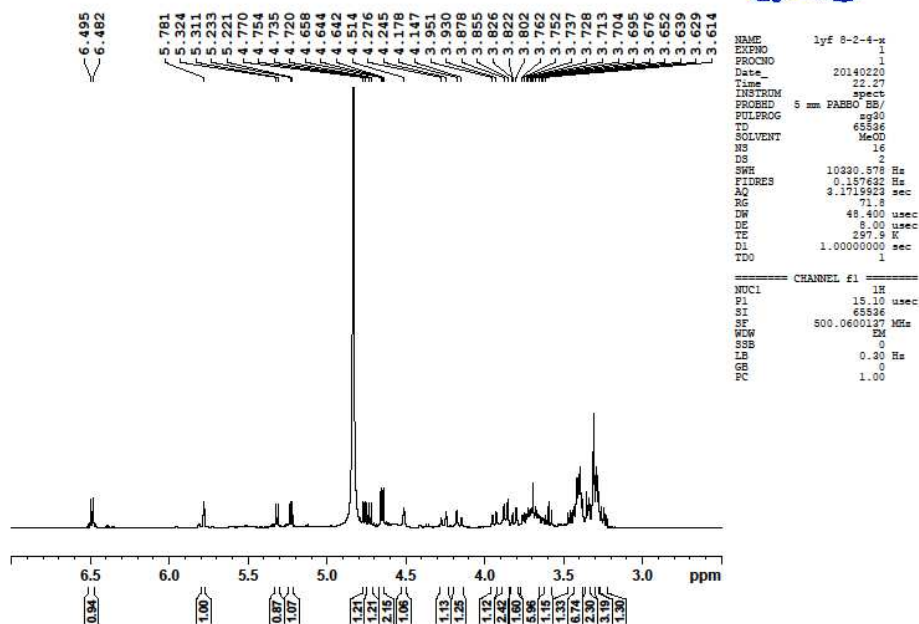


S27. CD Spectrum of compound 3 (CH₃OH)



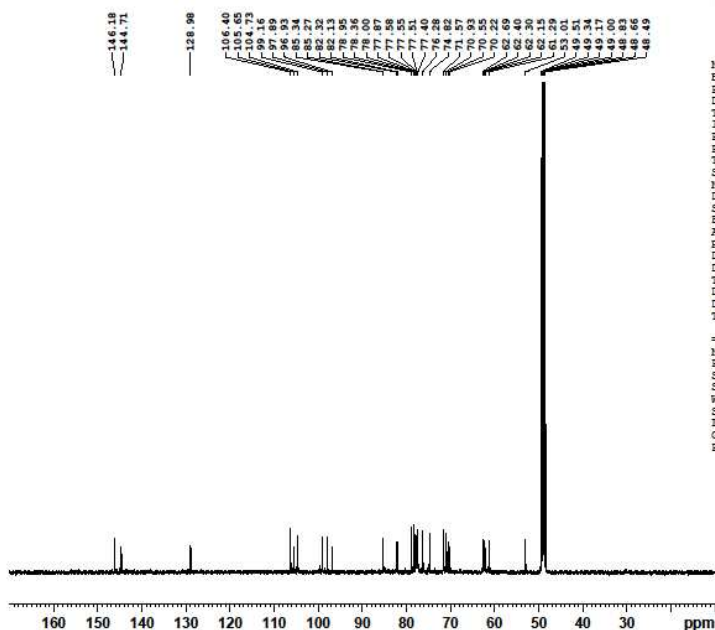
S28. IR Spectrum of compound 4

BRUKER AV-III-500 1H-NMR LYF 8-2-4-X IN MeOD 2014.02.20



S29. ^1H NMR Spectrum of compound 4 (500MHz, Methanol- d_4)

BRUKER AV-III-500 13C-NMR LYF 8-2-4-X IN MEOD 2014.02.13



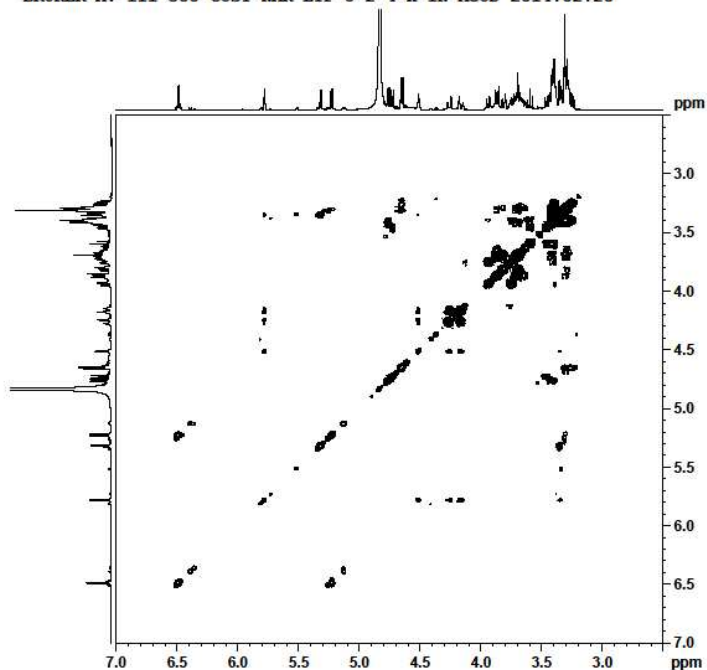
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PROCNO    1
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PULPROG   zgpg30
TD         65536
SOLVENT   MeOD
NS         1947
DS         4
SWH        29761.904 Hz
FIDRES     0.484131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         298.2 K
D1         1.00000000 sec
D11        0.03000000 sec
TDO        800

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
SI         32768
SF         125.7400176 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

S30. ^{13}C NMR Spectrum of compound **4** (125 MHz, Methanol- d_4)

BRUKER AV-III-500 COSY-NMR LYF 8-2-4-X IN MeOD 2014.02.20

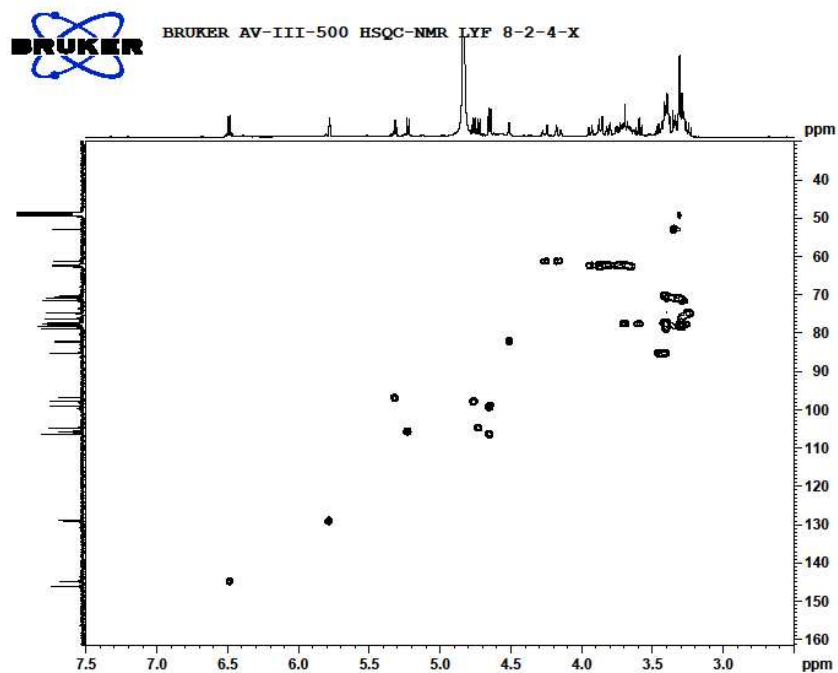


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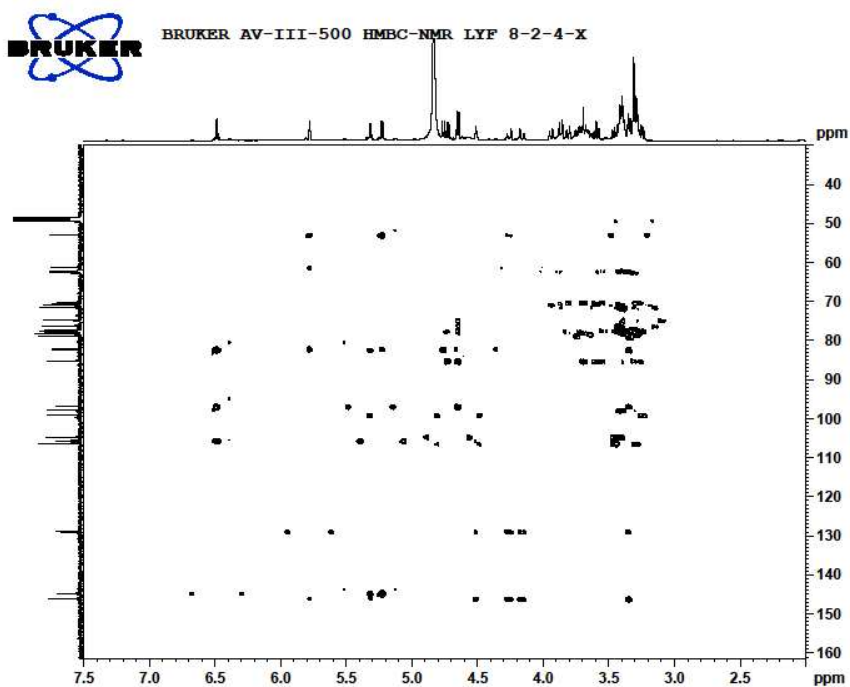
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EXPNO     2
PROCNO    1
Date_     20140220
Time      22.28
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PULPROG   cosygpcfgt
TD         2048
SOLVENT   MeOD
NS         8
DS         2
SWH        4000.000 Hz
FIDRES     1.958125 Hz
AQ         0.2860000 sec
RG         203
DW         125.000 usec
DE         8.00 usec
TE         298.0 K
D0         0.00000000 sec
D1         1.00000000 sec
D13        0.00000400 sec
D16        0.00020000 sec
INQ        0.00024995 sec

===== CHANNEL f1 =====
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P1         15.10 usec
ND0        1
TD         256
SF01       500.062 MHz
FIDRES     15.626941 Hz
SW         8.000 ppm
F2MODE     QF
SI         1024
SF         500.0600120 MHz
RGW        SINE
SSB        0
LB         0.00 Hz
GB         0
PC         1.40
SI         1024
MC2        QF
SF         500.0600119 MHz
RGW        SINE
SSB        0
LB         0.00 Hz
GB         0
  
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S31. ^1H - ^1H COSY Spectrum of compound **4**

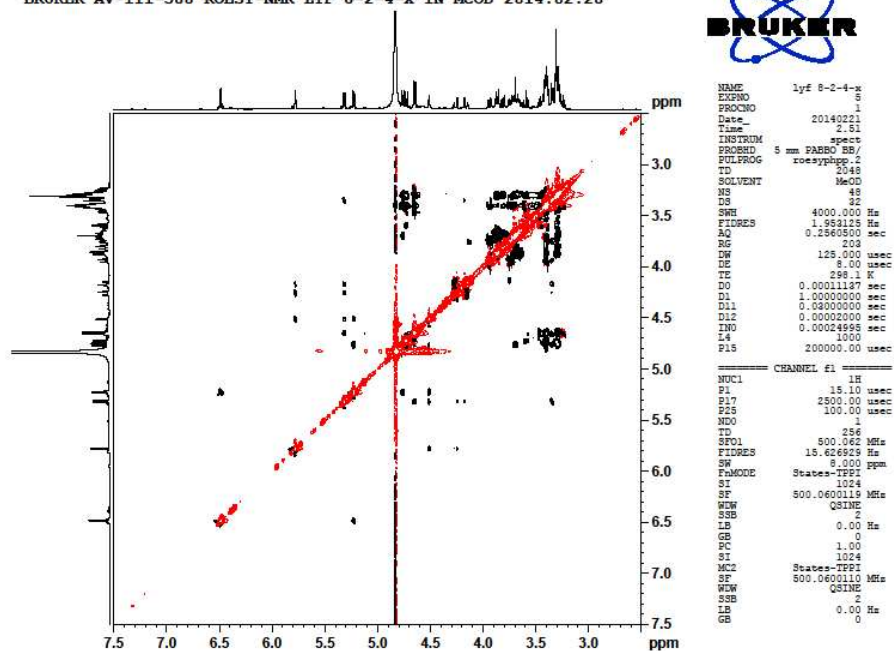


S32. HSQC Spectrum of compound 4



S33. HMBC Spectrum of compound 4

BRUKER AV-III-500 ROESY-NMR LYF 8-2-4-X IN MeOD 2014.02.20



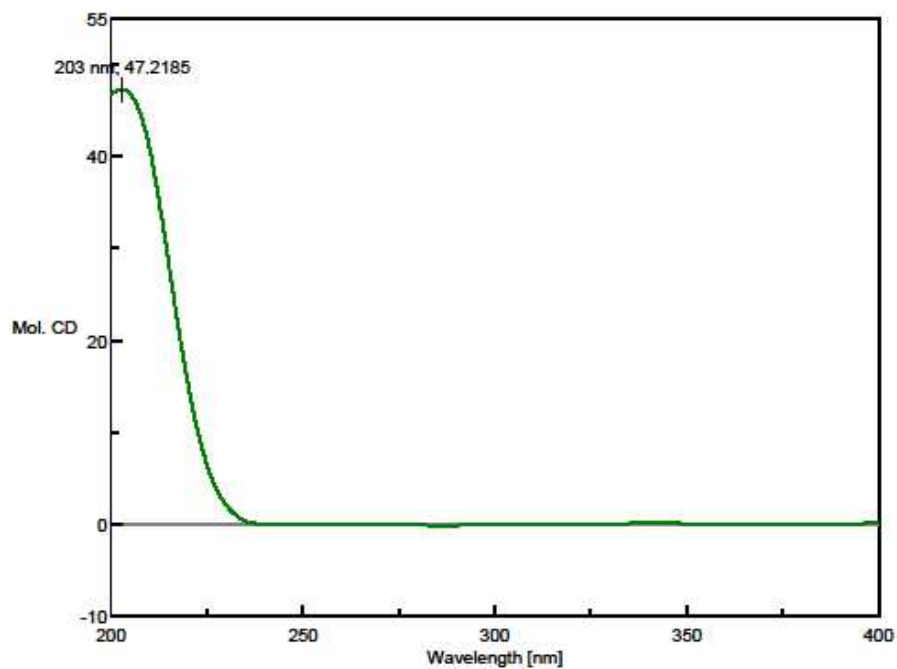
S34. ROESY Spectrum of compound 4

MS Formula Results: + Scan (2.850 min) Sub (2014090901.d)

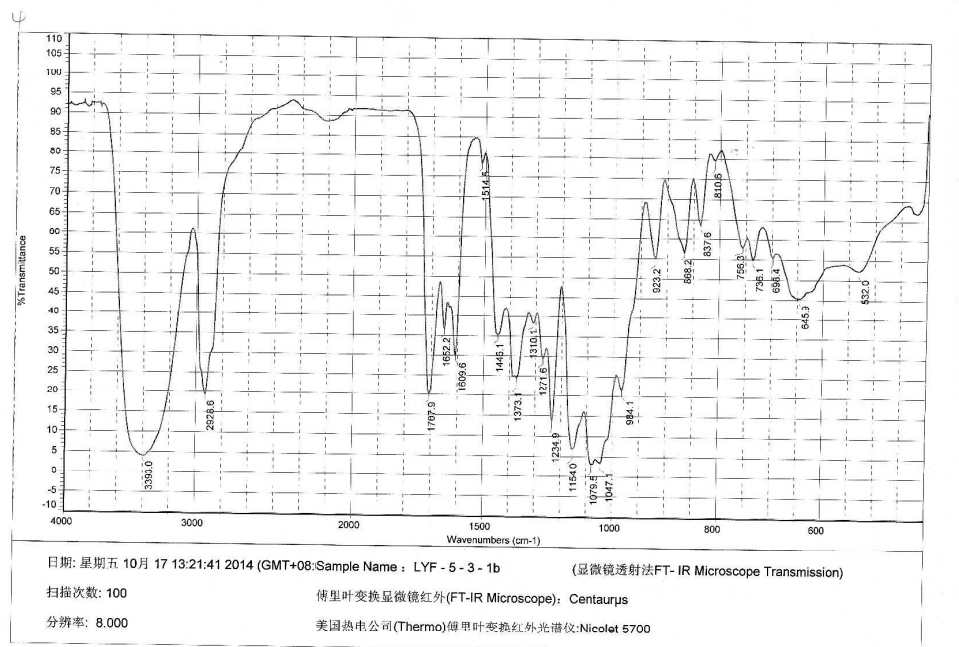
m/z	Ion	Formula	Abundance
871.2694	(M+H) ⁺	C33 H52 N2 O25	251423.3

Best	Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc Mass	Calc m/z	Diff (ppm)	Ass Diff (ppm)	Mass Match	Abund Match	Spacing Match	OBE
✓	C33 H52 N2 O25	C33 H52 N2 Na O25	99.97		848.2802	848.2799	871.265	-4.30	0.31	99.98	99.98		4
✓	C38 H52 N2 O27	C38 H52 N2 Na O27	99.13		848.2802	848.2757	871.265	-5.25	5.20	99.06	98.63	99.91	
✓	C39 H48 N2 O19	C39 H48 N2 Na O19	98.92		848.2802	848.2651	871.2743	5.8	5.8	98.84	97.93	99.86	17
✓	C46 H44 N2 O14	C46 H44 N2 Na O14	97.75		848.2802	848.2793	871.2685	-1.12	1.12	99.96	92.36	99.84	25

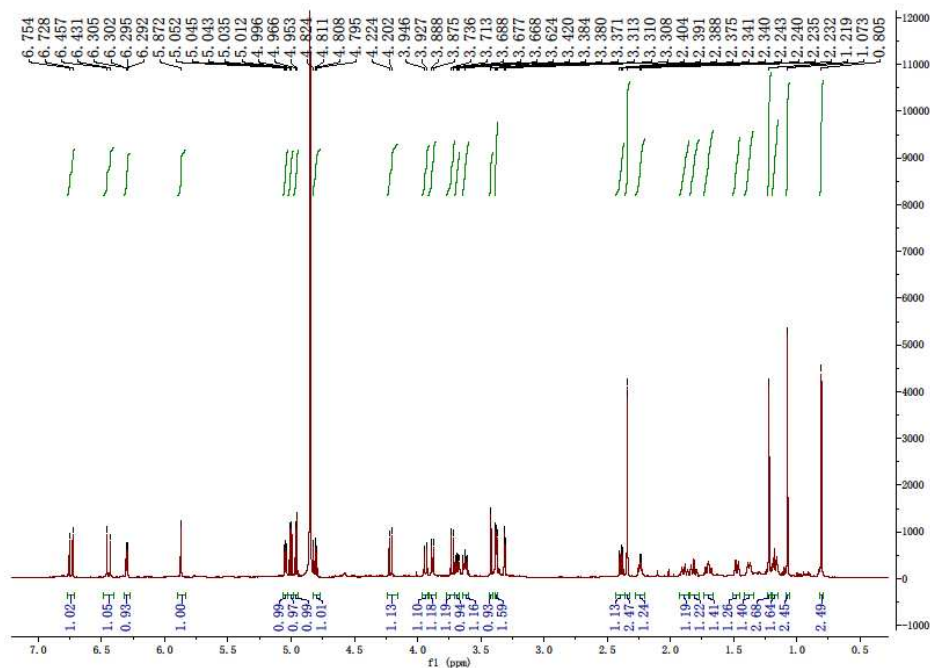
S35. HRESIMS Spectrum of compound 4



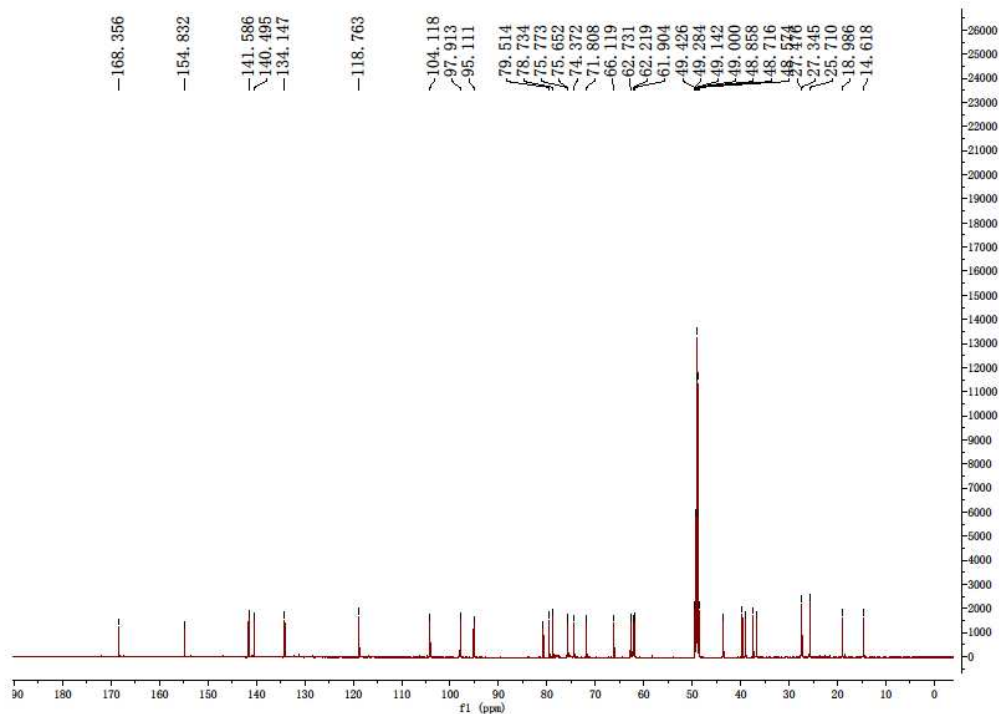
S36. CD Spectrum of compound 4 (CH₃OH)



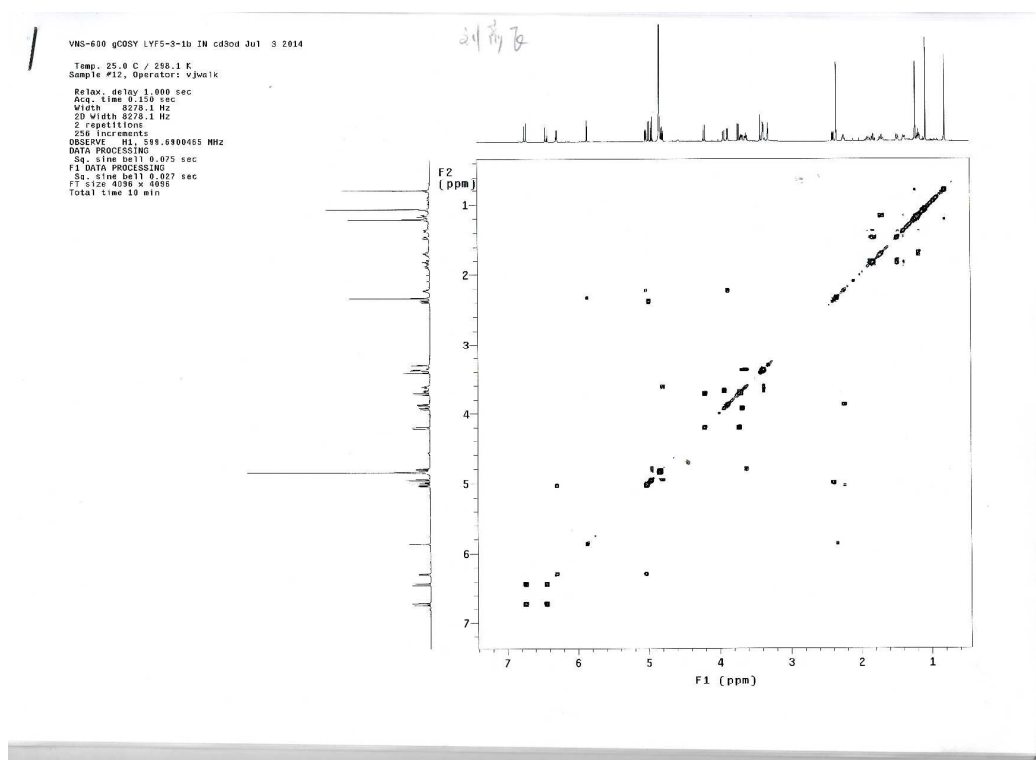
S37. IR Spectrum of compound **5**



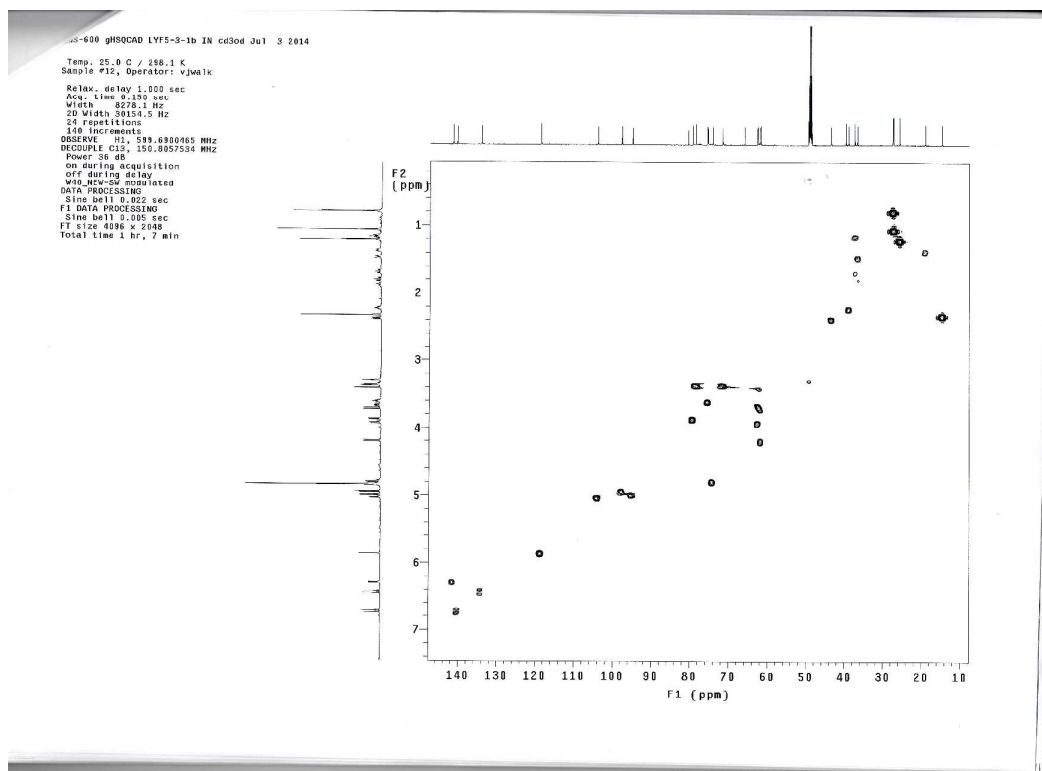
S38. ¹H NMR Spectrum of compound **5** (600 MHz, Methanol-d₄)



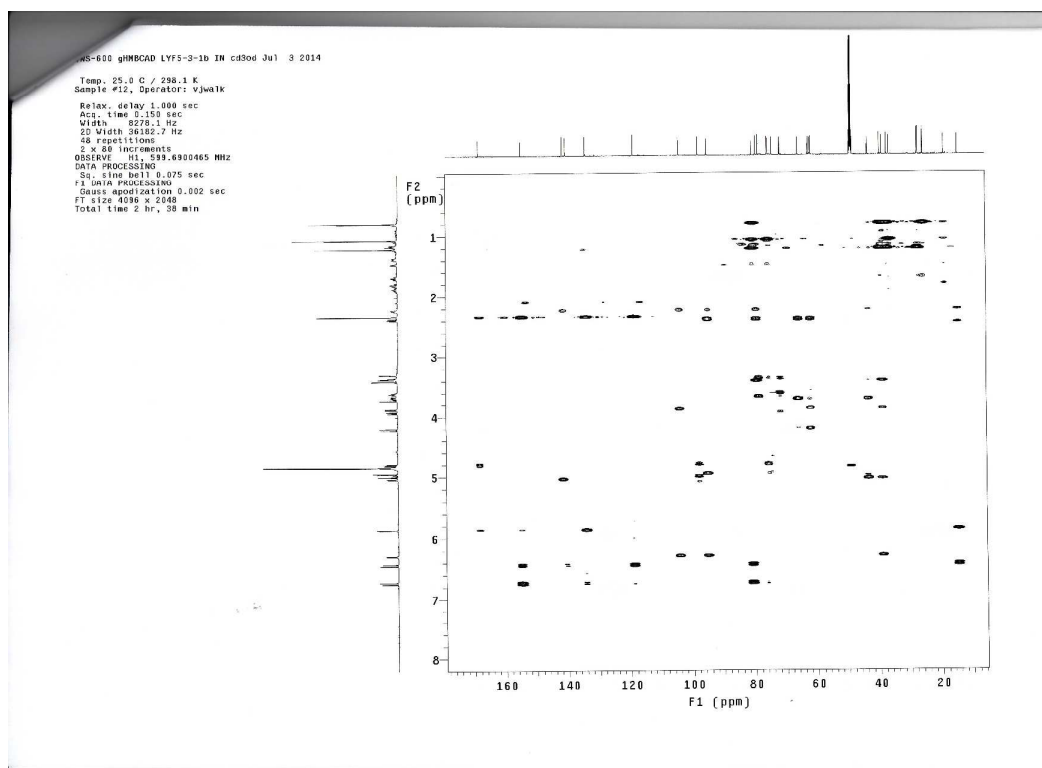
S39. ^{13}C NMR Spectrum of compound **5** (150 MHz, Methanol- d_4)



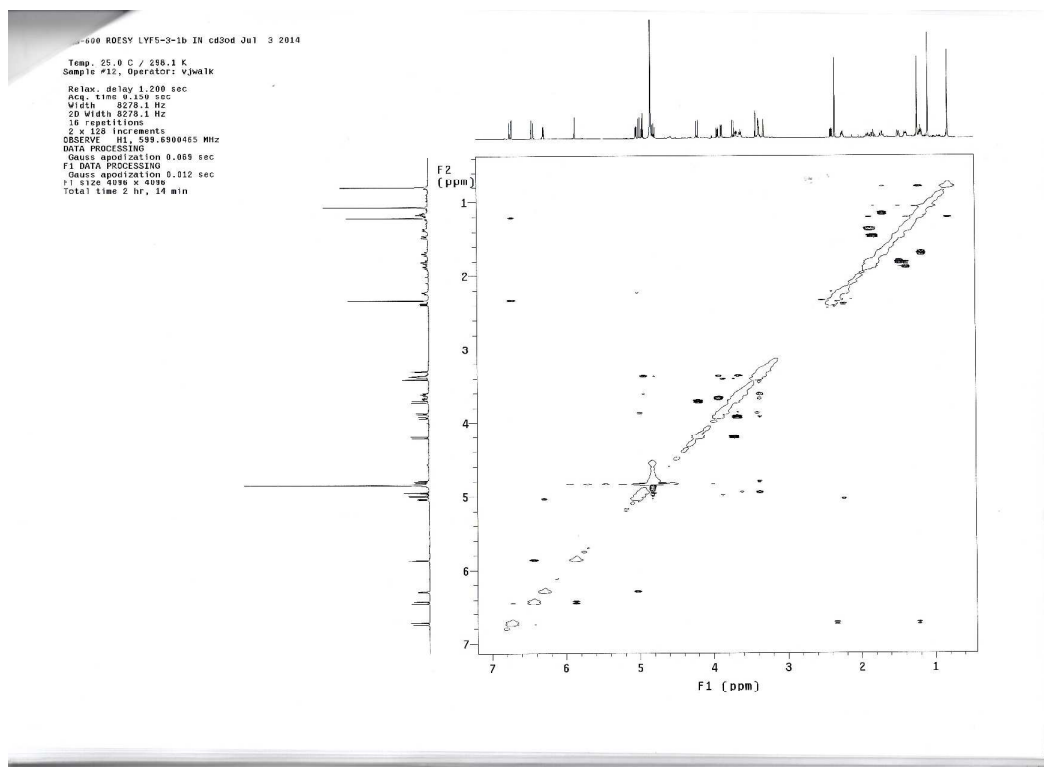
S40. ^1H - ^1H COSY Spectrum of compound **5**



S41. HSQC Spectrum of compound **5**



S42. HMBC Spectrum of compound **5**



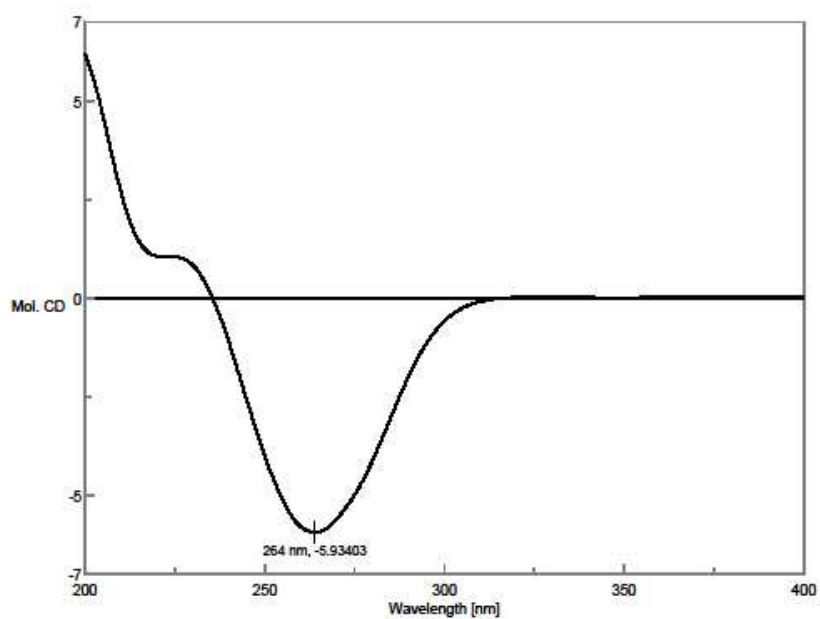
S43. ROESY Spectrum of compound **5**

MS Formula Results: + Scan (6.380 min) Sub (2014090902.d)

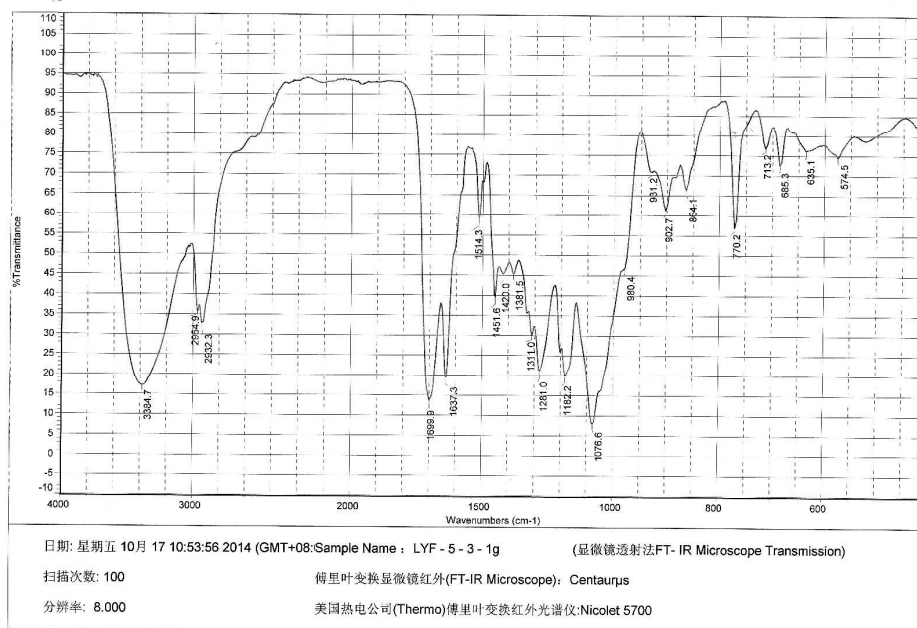
m/z	Ion	Formula	Abundance
635.268	HM-Na ⁺	C30 H44 Na O15	1876227.9

Ref	Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc. Mass	Calc. m/z	Diff (ppm)	Abs. OR (ppm)	Mass Match	Abund. Match	Spacing Match	DRE
✓	C30 H44 O15	C30 H44 Na O15	99.87		632.2768	632.2777	635.2674	-1.02	1.02	99.87	99.87	99.87	5
✓	C43 H56 N2 O2	C43 H56 N2 Na O2	97.87		612.2768	612.2777	635.2669	-1.68	1.68	99.88	93.18	99.9	27

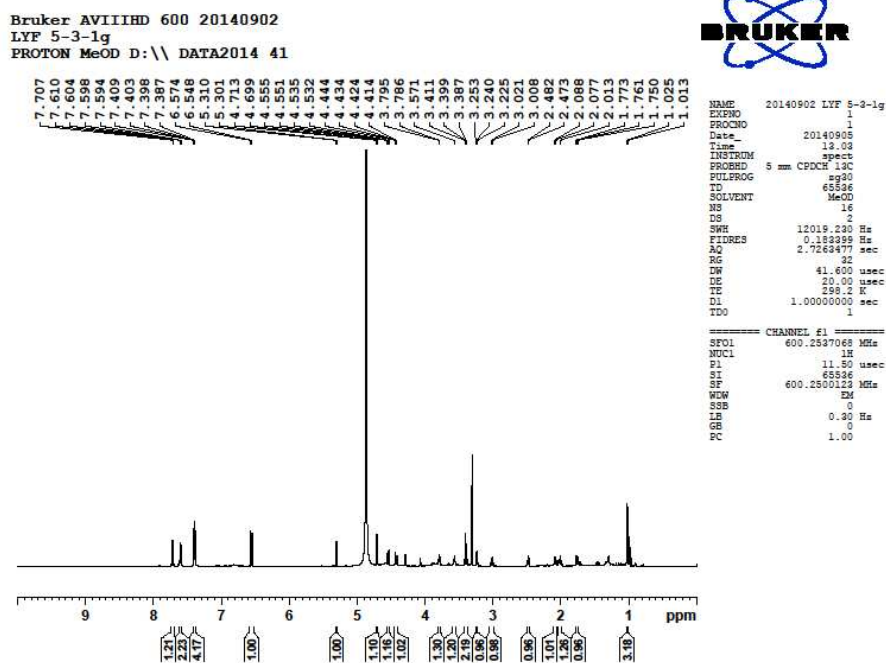
S44. HRESIMS Spectrum of compound **5**



S45. CD Spectrum of compound **5** (CH₃OH)

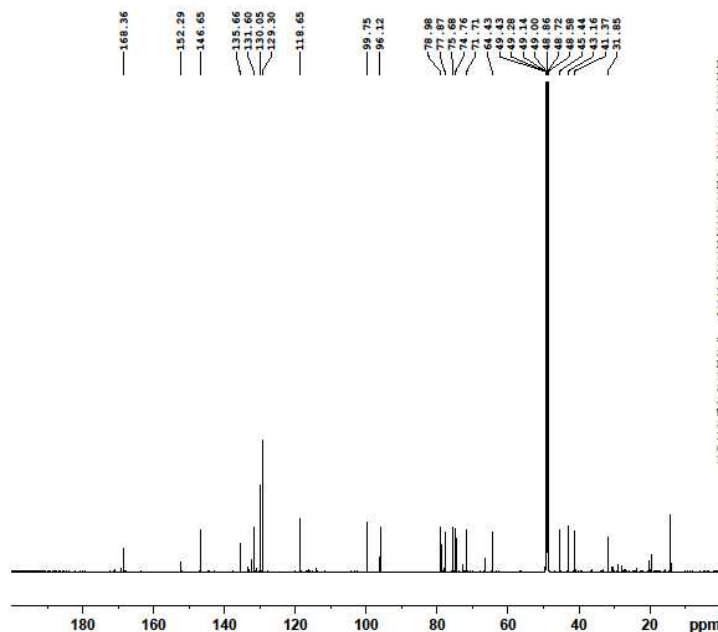


S46. IR Spectrum of compound 6



S47. ^1H NMR Spectrum of compound 6 (600MHz, Methanol- d_4)

Bruker AVIIIHD 600 20140701
C13 MeOD D:\ DATA2014 30

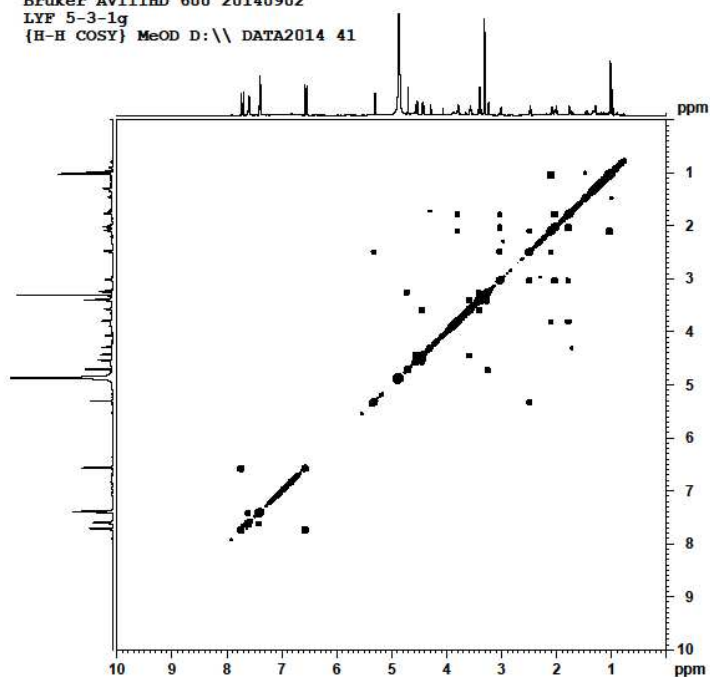


NAME 20140902 LYF 5-3-1g
EXPNO 1
PROCNO 1
Date 20140706
Time 16.33
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 2000
DS 4
SWH 36087.691 Hz
FIDRES 0.550197 Hz
AQ 0.9089159 sec
RG 2050
DW 13.867 usec
DE 31.37 usec
TE 298.2 K
D1 1.00000000 sec
D11 0.02000000 sec
TD0 250

===== CHANNEL f1 =====
SFO1 150.9495843 MHz
NUC1 13C
P1 12.84 usec
SI 32768
SF 150.9327723 MHz
WVW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

S48. ^{13}C NMR Spectrum of compound 6 (150 MHz, Methanol- d_4)

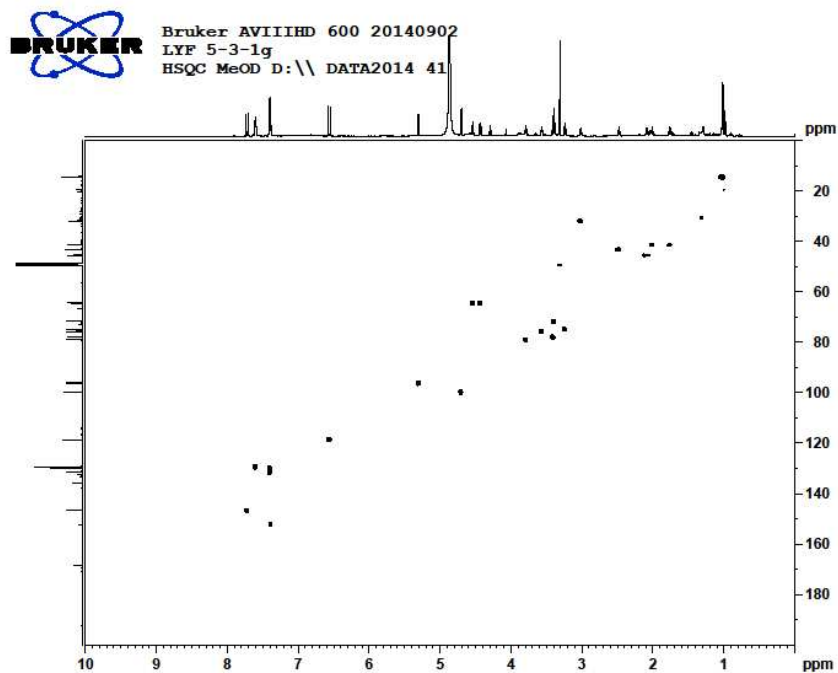
Bruker AVIIIHD 600 20140902
LYF 5-3-1g
[H-H COSY] MeOD D:\ DATA2014 41



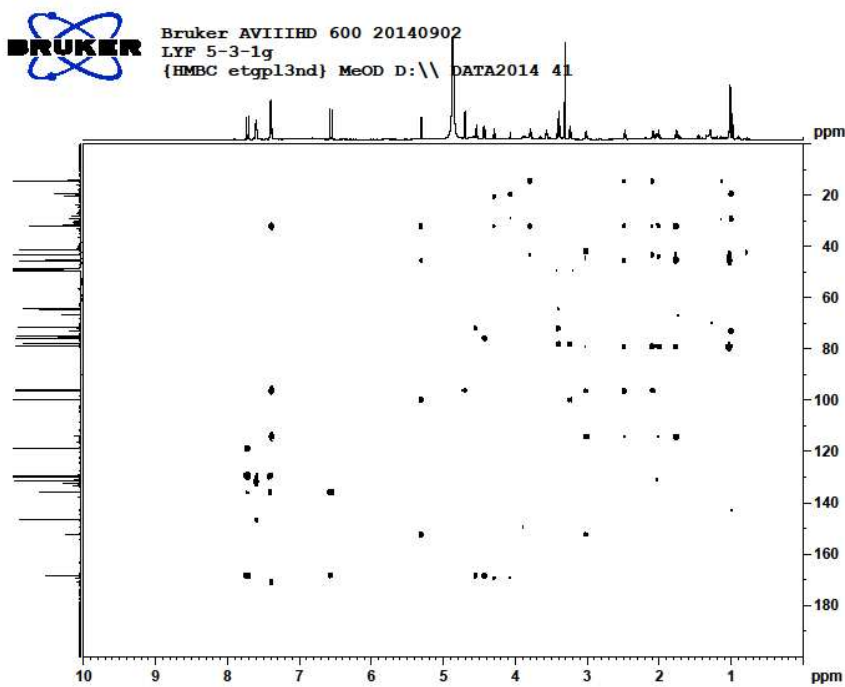
NAME 20140902 LYF 5-3-1g
EXPNO 2
PROCNO 1
Date 20140905
Time 12.04
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG cosygpgpgf
TD 2048
SOLVENT MeOD
NS 2
DS 16
SWH 12019.220 Hz
FIDRES 5.868768 Hz
AQ 0.0852468 sec
RG 161
DW 41.600 usec
DE 20.00 usec
TE 298.2 K
D0 0.00000000 sec
D1 1.00000000 sec
D11 0.02000000 sec
D12 0.00002000 sec
D16 0.00020000 sec
IN0 0.0000820 sec

===== CHANNEL f1 =====
SFO1 600.2536088 MHz
NUC1 1H
P0 11.50 usec
P1 11.50 usec
P17 2500.00 usec
NDO 1
TD 256
SFO1 600.13346 MHz
FIDRES 46.950119 Hz
SW 20.024 ppm
F2MODE QF
SI 1024
SF 600.2500000 MHz
WVW QSINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 QF
SF 600.2500000 MHz
WVW QSINE
SSB 0
LB 0.00 Hz
GB 0

S49. ^1H - ^1H COSY Spectrum of compound 6

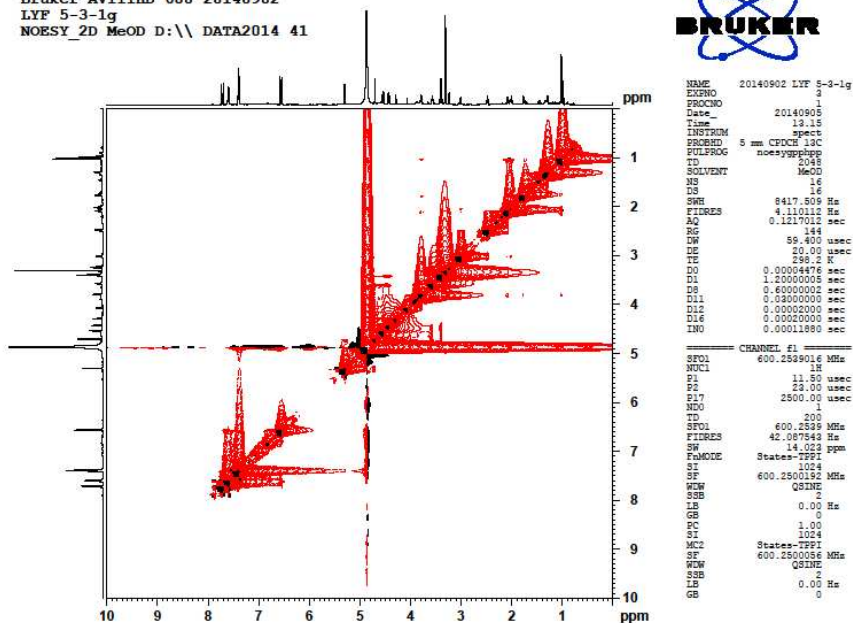


S450. HSQC Spectrum of compound **6**



S51. HMBC Spectrum of compound **6**

Bruker AVIIIHD 600 20140902
LYF 5-3-1g
NOESY_2D MeOD D:\ DATA2014 41

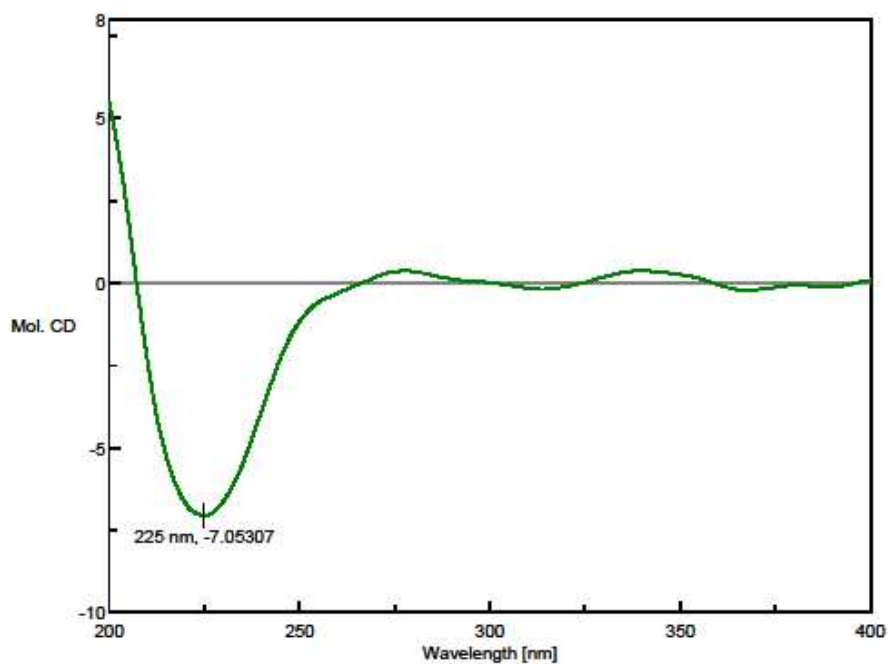


S52. NOESY Spectrum of compound 6

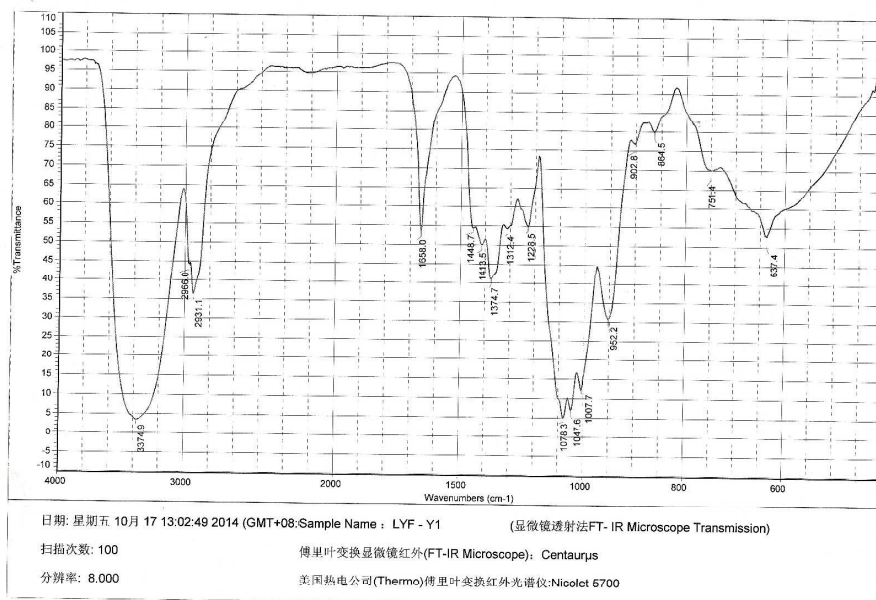
MS Formula Results: + Scan (6.422 min) Sub (2014090904.d)

m/z	Ion	Formula	Abundance										
507.1861	(M+H) ⁺	C25 H31 O11	72504.1										
Best	Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
✓	C25 H31 O11	C25 H31 O11	99.90		506.1700	506.1738	507.1861	0.01	0.01	100	99.90	99.90	11
m/z	Ion	Formula	Abundance										
529.1876	(M+Na) ⁺	C25 H30 Na O11	142177.9										
Best	Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
✓	C25 H30 O11	C25 H30 Na O11	99.94		506.1784	506.1788	529.1868	0.89	0.89	99.97	99.92	99.91	11

S53. HRESIMS Spectrum of compound 6

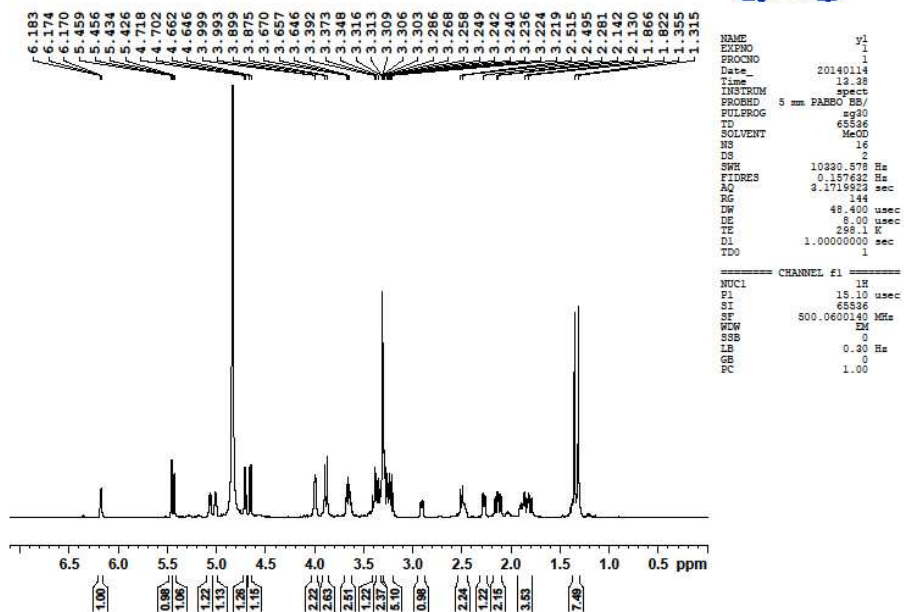


S54. CD Spectrum of compound 6 (CH₃OH)



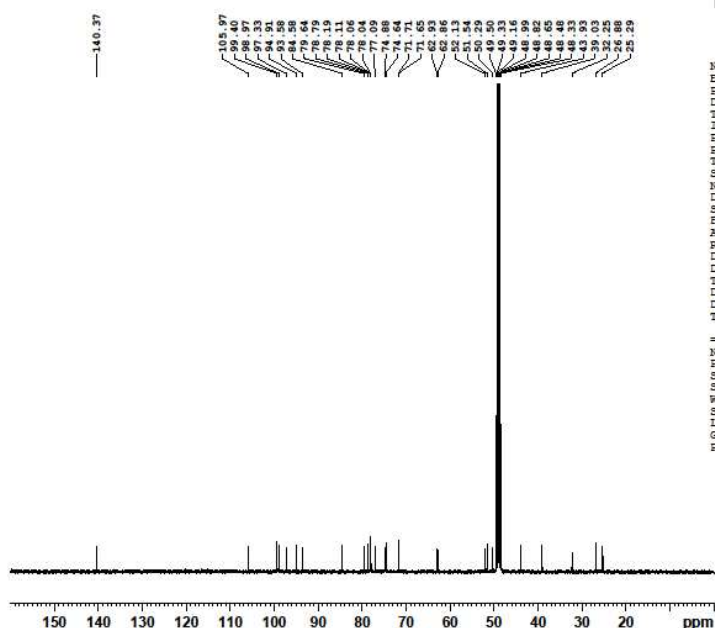
S55. IR Spectrum of compound 7

BRUKER AV-III-500 1H-NMR LYF Y-1 IN MeOD 2014.01.10



S56. ¹H NMR Spectrum of compound 7 (500MHz, Methanol-d₄)

BRUKER AV-III-500 ^{13}C -NMR LYF Y-1 IN MeOD 2014.01.10



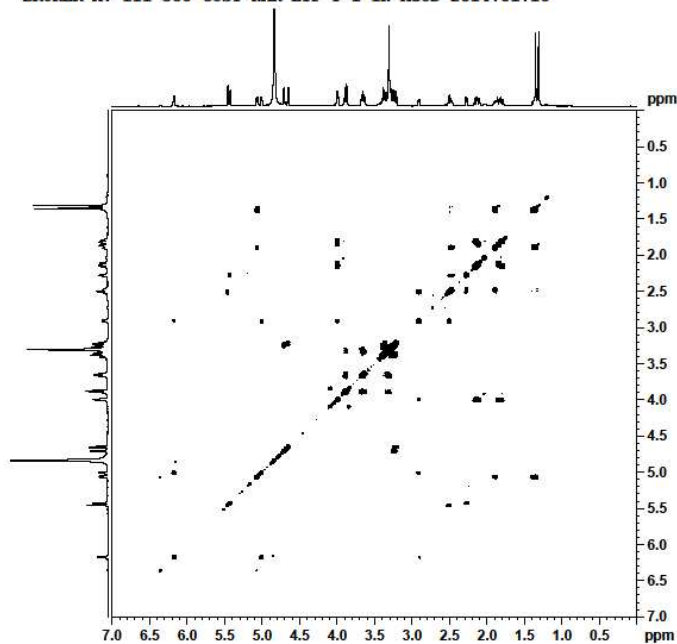
```

NAME          y1
EXPNO         2
PROCNO        1
Date_         20140114
Time          12.39
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            65536
SOLVENT       MeOD
NS            1912
DS            4
SWH           29761.904 Hz
FIDRES        0.484131 Hz
AQ            1.1010548 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            298.6 K
D1            1.00000000 sec
D11           0.03000000 sec
TDO           400

===== CHANNEL f1 =====
NUC1          13C
P1            10.00 usec
SI            29768
SF            125.7400148 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```

S57. ^{13}C NMR Spectrum of compound 7 (125 MHz, Methanol- d_4)

BRUKER AV-III-500 COSY-NMR LYF Y-1 IN MeOD 2014.01.10

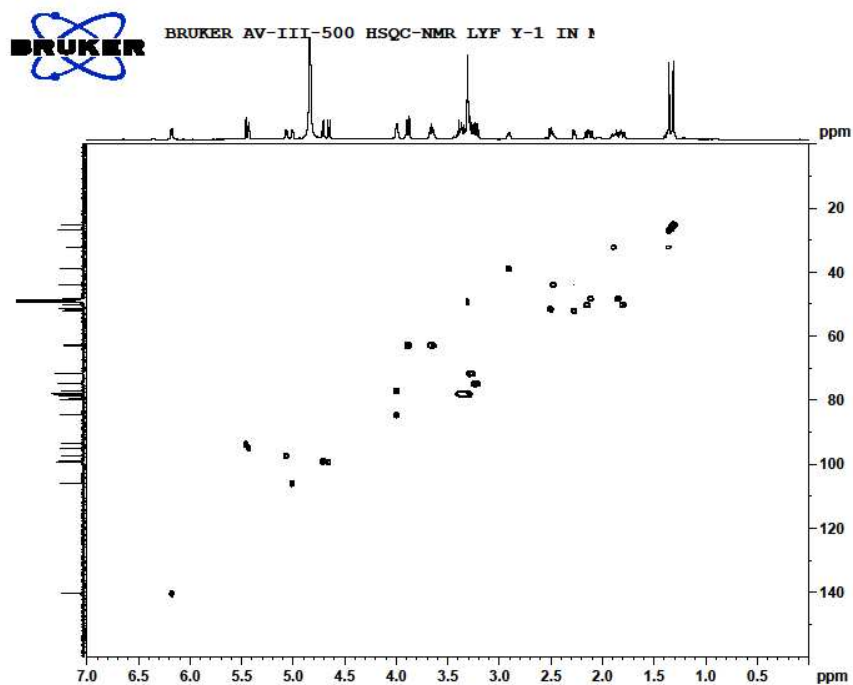


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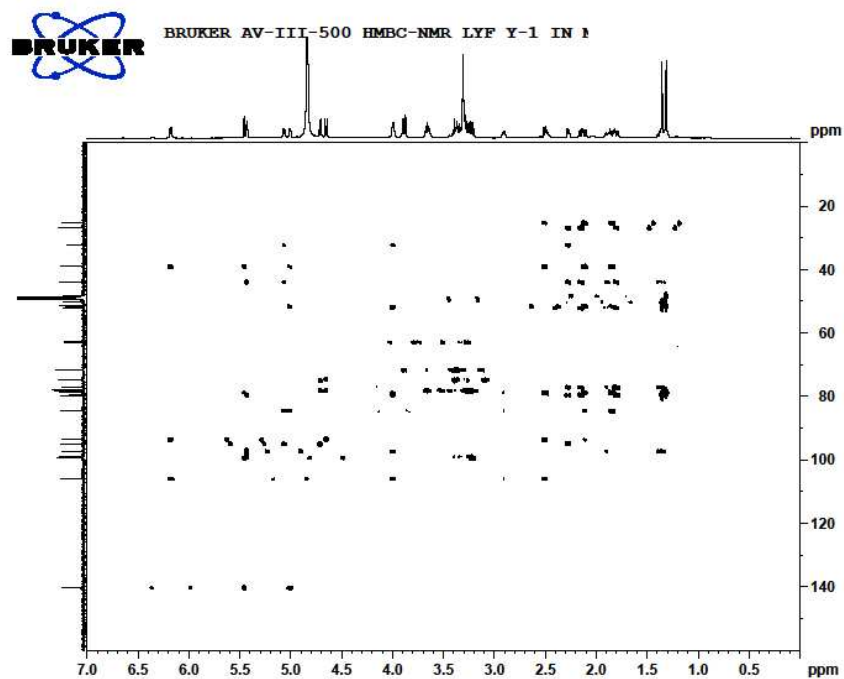
NAME          y1
EXPNO         3
PROCNO        1
Date_         20140115
Time          21.53
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       cosygpgf30
TD            2048
SOLVENT       MeOD
NS            1
DS            8
SWH           3501.401 Hz
FIDRES        1.709668 Hz
AQ            0.2925044 sec
RG            203
DW            142.800 usec
DE            8.00 usec
TE            297.7 K
D0            0.00000300 sec
D1            1.00000000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00028570 sec

===== CHANNEL f1 =====
NUC1          1H
P1            15.10 usec
ND0           1
TD            1
SF01          500.0618 MHz
FIDRES        13.678598 Hz
SW            7.000 ppm
P1MODE        QF
SI            1024
SF            500.0600129 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
PC            1.40
SI            1024
MC2           QF
SF            500.0600126 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
  
```

S58. ^1H - ^1H COSY Spectrum of compound 7

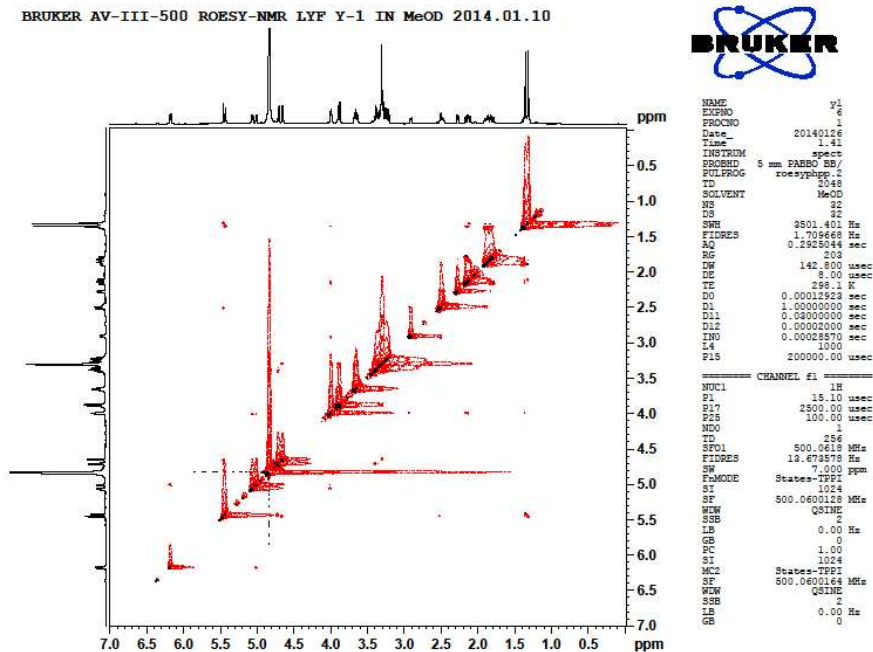


S59. HSQC Spectrum of compound 7



S60. HMBC Spectrum of compound 7

BRUKER AV-III-500 ROESY-NMR LYF Y-1 IN MeOD 2014.01.10



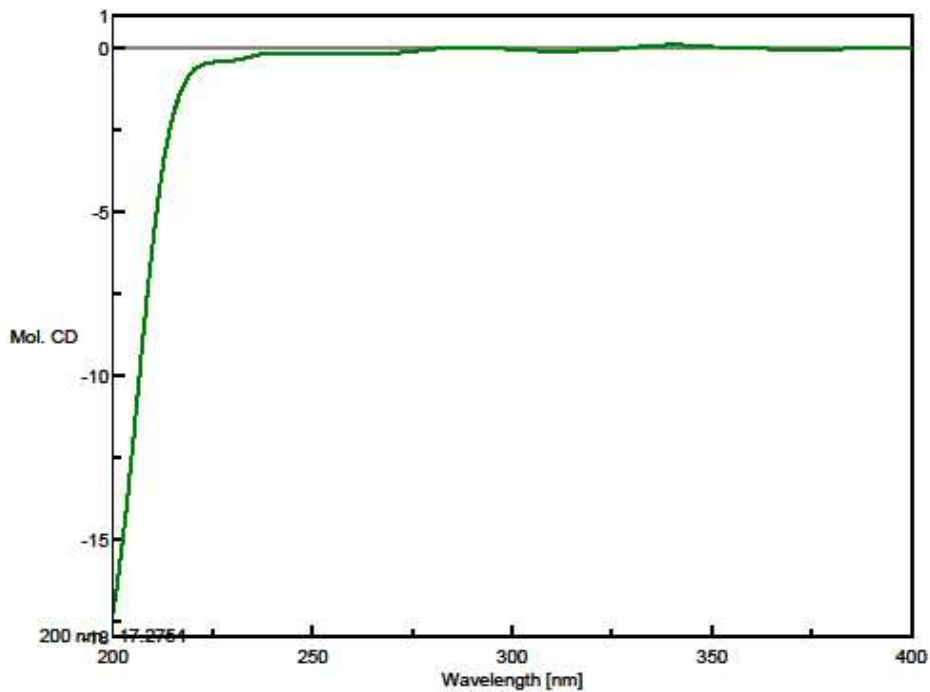
S61. ROESY Spectrum of compound 7

MS Formula Results: + Scan (3.520 min) Sub (2014090501.d)

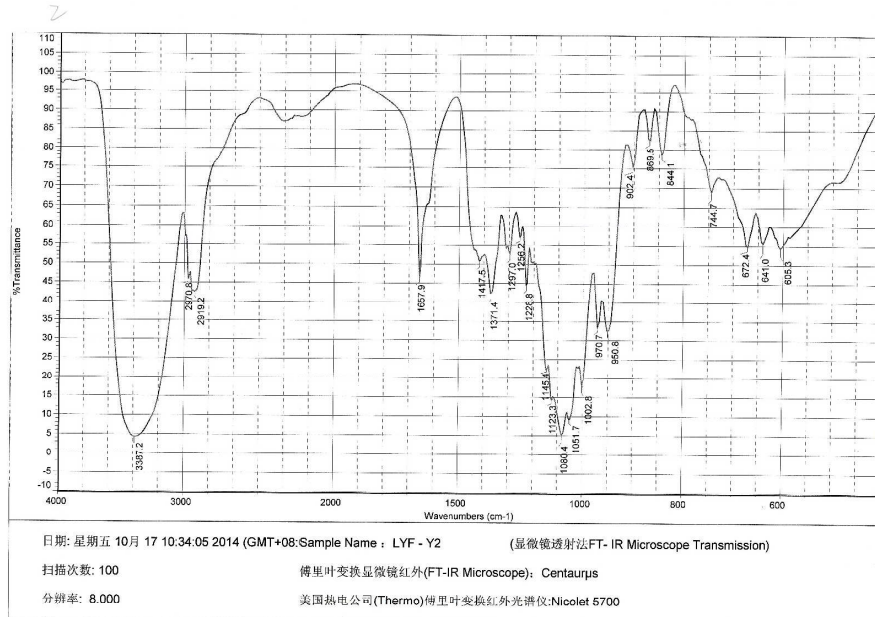
m/z	Ion	Formula	Abundance
719.2748	(M+Na) ⁺	C30 H48 Na O18	411252.3

Best	Formula (M)	Ion Formula	Score	Crash Score	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Isotop Match	DBE
✓	C30 H48 O18	C30 H48 Na O18	99.89		696.2854	696.2841	719.2733	-1.85	1.85	99.89	99.92	99.88	7
✓	C38 H64 N2 O12	C38 H64 N2 Na O12	98.5		696.2854	696.2854	719.2786	5.84	5.84	98.88	97.52	99.87	16
✓	C43 H80 N2 O7	C43 H80 N2 Na O7	97.42		696.2854	696.2836	719.2728	-2.59	2.59	99.77	91.48	99.84	25

S62. HRESIMS Spectrum of compound 7

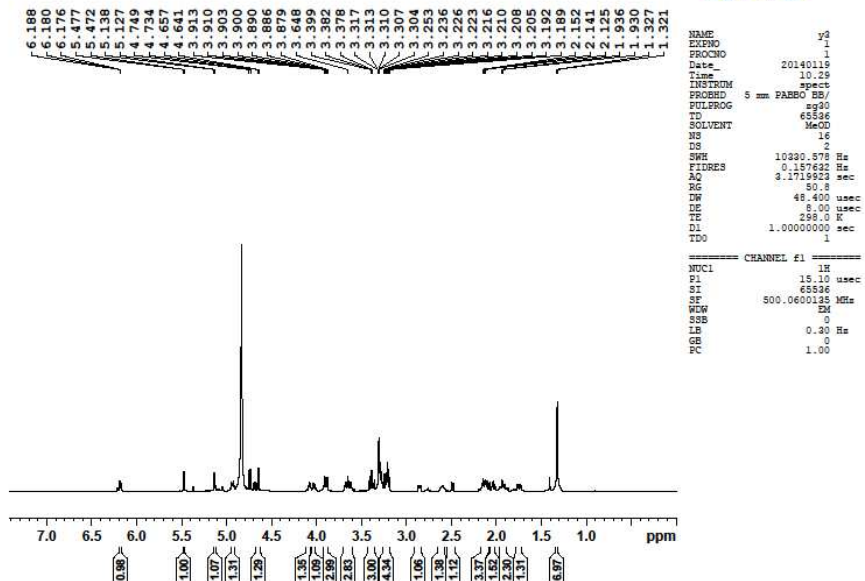


S63. CD Spectrum of compound 7 (CH₃OH)

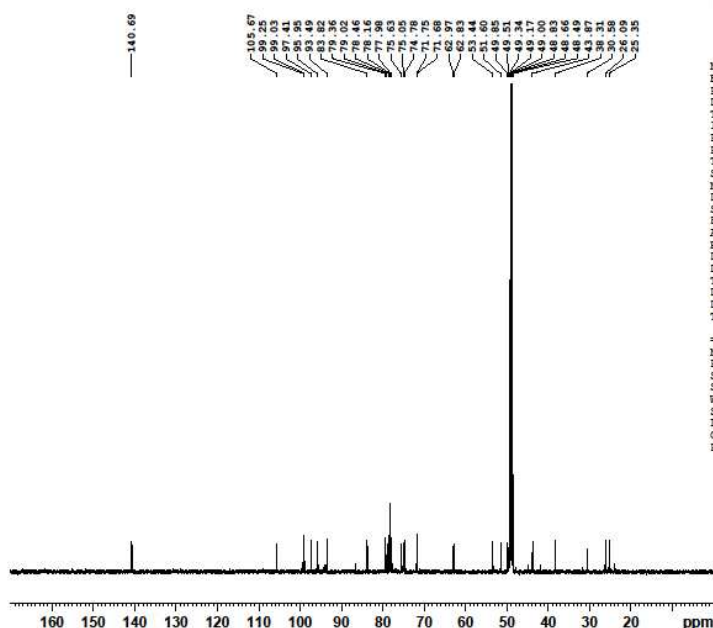


S64. IR Spectrum of compound 8

BRUKER AV-III-500 1H-NMR LYF Y-3 IN MeOD 2014.01.10

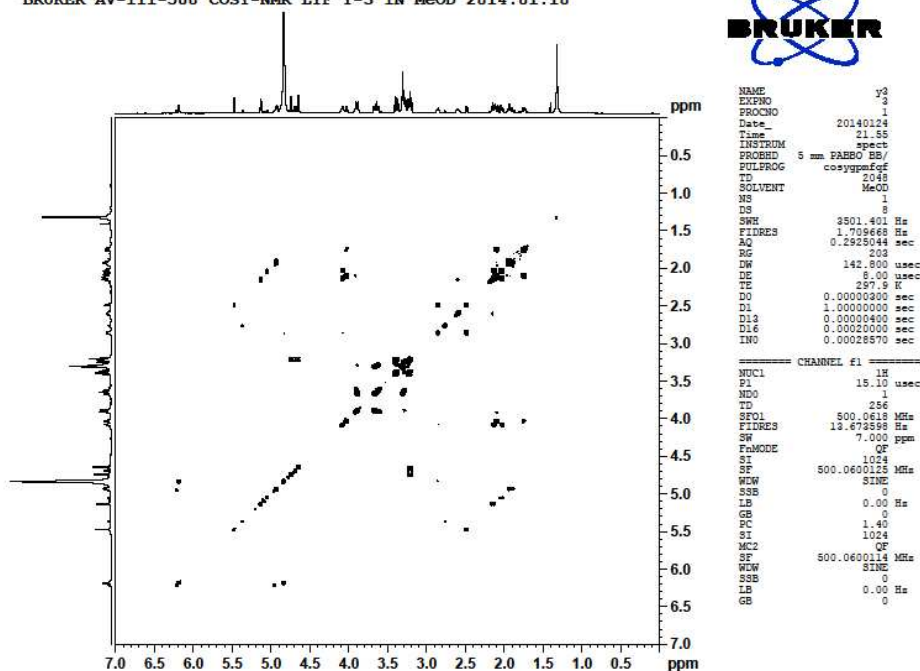


S65. ^1H NMR Spectrum of compound 8 (500MHz, Methanol- d_4)

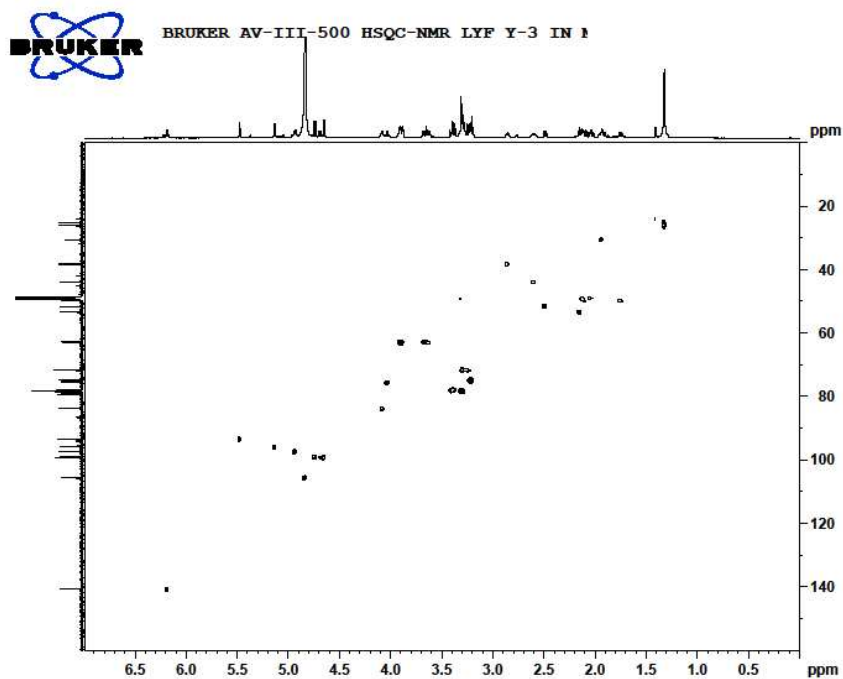


```
NAME                                     y2
EXPNO                                   2
PROCNO                                  1
Date_   _                               20140119
Time_    _                              10.31
INSTRUM                                    spect
PROBHD      5 mm PABBO BEP              spec
PULPROG          zgpg30                 prog
TD             65536                     size
SOLVENT                                MeOD
NS               32                       scans
DS                4                      DS
SWH            29761.904 Hz              freq
FIDRES         0.484141 Hz              fwhm
AQ             1.1010548 sec             time
RG              203                      pixels
DE             16.800                    um
TE           6.50                        degC
WE           298.6                        K
D1            1.000000000 sec            delay
D11           0.030000000 sec            d11
TD0            400                       points
===== CHANNEL 12 =====
NUC1              13C
P1              10.00 usec
SI              32768
SF       125.74000173 MHz
PC              EM
SSB
LB              1.00 Hz
GB
FC              1.40
```

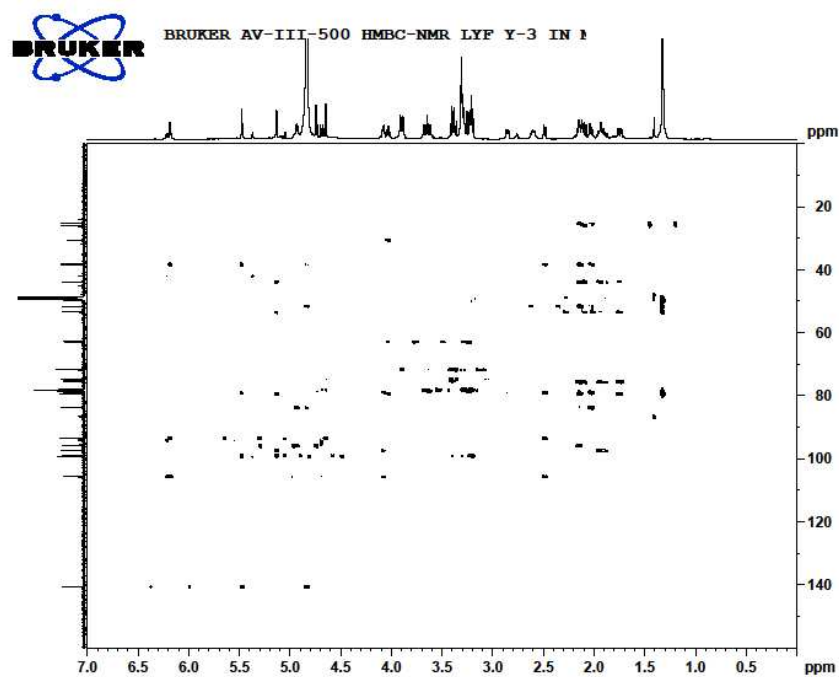
S66. ^{13}C NMR spectrum of compound **8** (125 MHz, Methanol- d_4)



S67. ^1H - ^1H COSY Spectrum of compound **8**

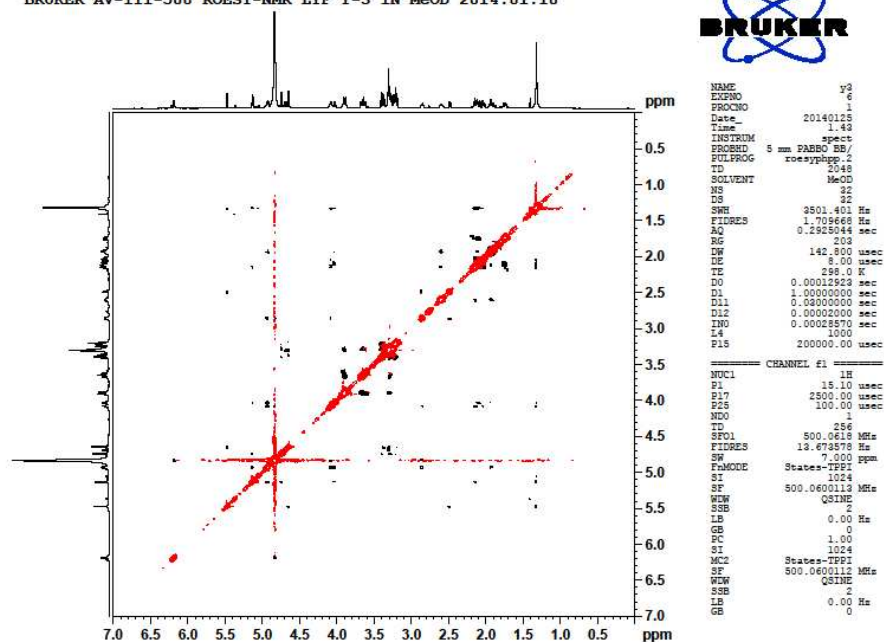


S68. HSQC Spectrum of compound **8**



S69. HMBC Spectrum of compound **8**

BRUKER AV-III-500 ROESY-NMR LYF Y-3 IN MeOD 2014.01.10



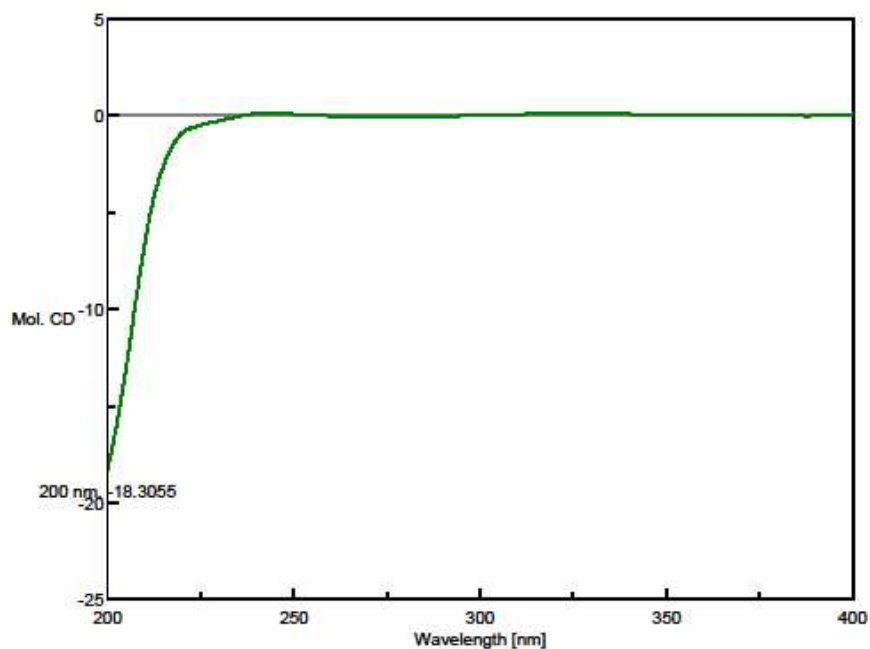
S6

70. ROESY Spectrum of compound 8

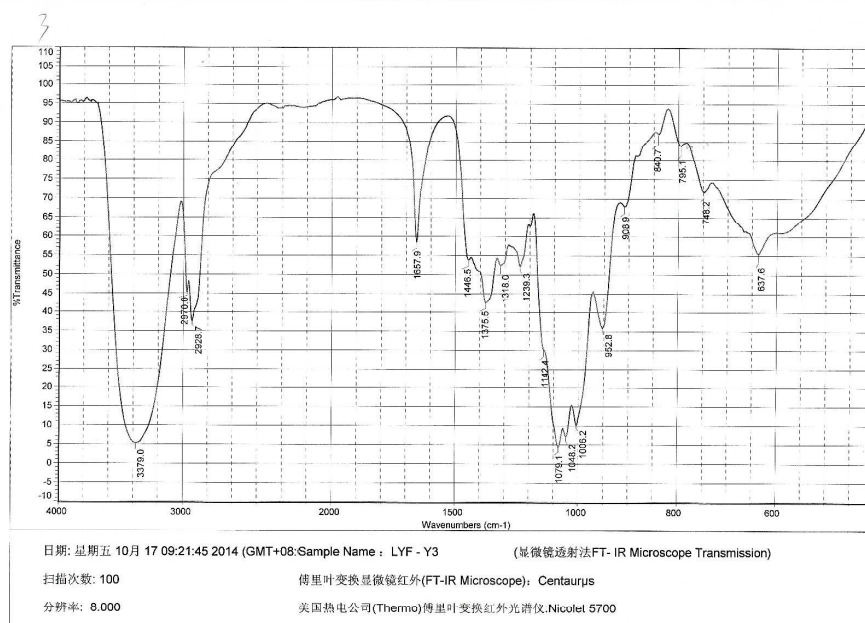
MS Formula Results: + Scan (4.061 min) Sub (2014090503.d)

m/z	Ion	Formula	Abundance											
718.275	[M+Na] ⁺	C36 H48 Na O18	902310.8											
1	Best	Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc. Mass	Calc. m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DGE
	✓	C36 H48 O18	C36 H48 Na O18	99.85		696.2858	696.2841	718.2733	-2.47	2.47	99.85	99.94	99.85	7
	□	C38 H44 Na O12	C38 H44 Na O12	98.50		696.2858	696.2894	718.2755	5.22	5.22	99.09	97.88	99.85	16
	□	C43 H49 Na O7	C43 H48 Na O7	97.4		696.2858	696.2838	718.2728	-3.21	3.21	99.65	91.84	99.82	25

S71. HRESIMS Spectrum of compound 8

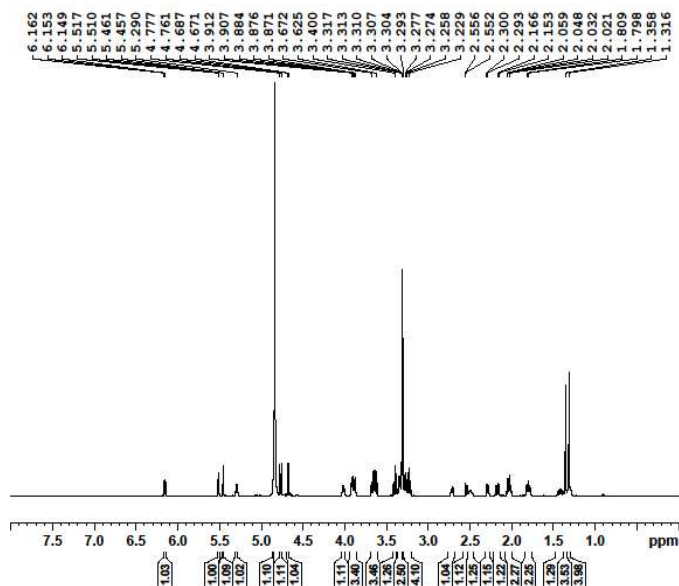


S72. CD Spectrum of compound 8 (CH₃OH)



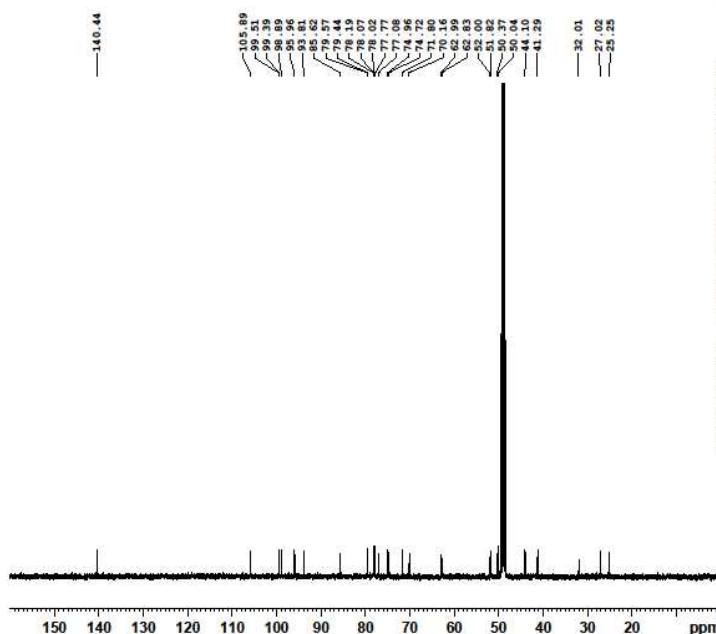
S73. IR Spectrum of compound 9

BRUKER AV-III-500 1H-NMR LYF Y-2 IN MeOD 2014.01.10



S74. ¹H NMR Spectrum of compound 9 (500MHz, Methanol-d₄)

BRUKER AV-III-500 13C-NMR LYF Y-2 IN MeOD 2014.01.10



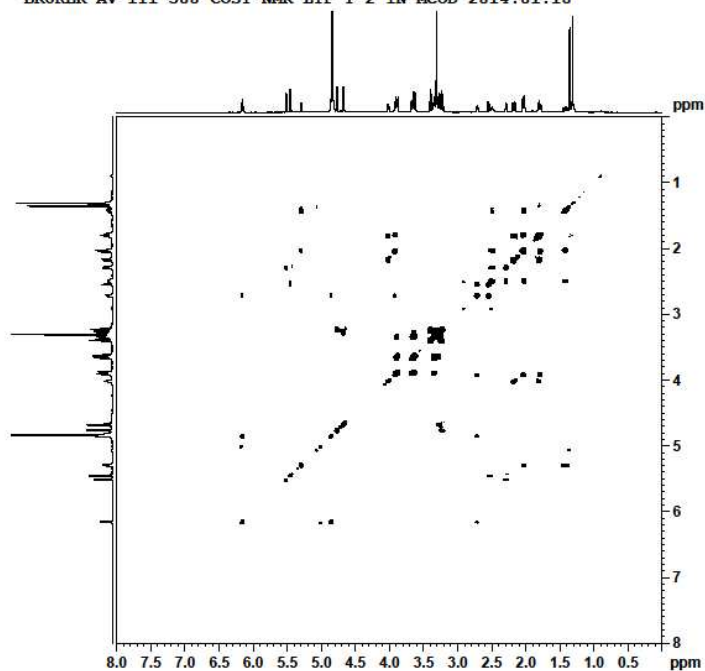
```

NAME          y2
EXPNO         2
PROCNO        1
Date_         20140119
Time          10.57
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            65536
SOLVENT       MeOD
NS            1088
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010345 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            298.2 K
D1            1.00000000 sec
D11           0.02000000 sec
TDO           400

===== CHANNEL f1 =====
NUC1          13C
P1            10.00 usec
SI            32768
SF            125.7400118 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```

S75. ^{13}C NMR Spectrum of compound **9** (125 MHz, Methanol- d_4)

BRUKER AV-III-500 COSY-NMR LYF Y-2 IN MeOD 2014.01.10

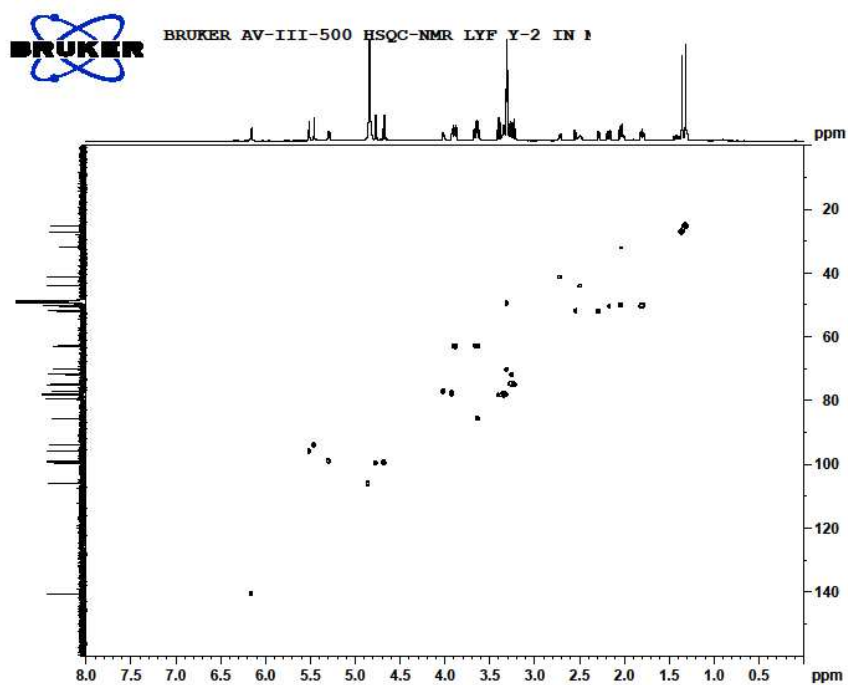


```

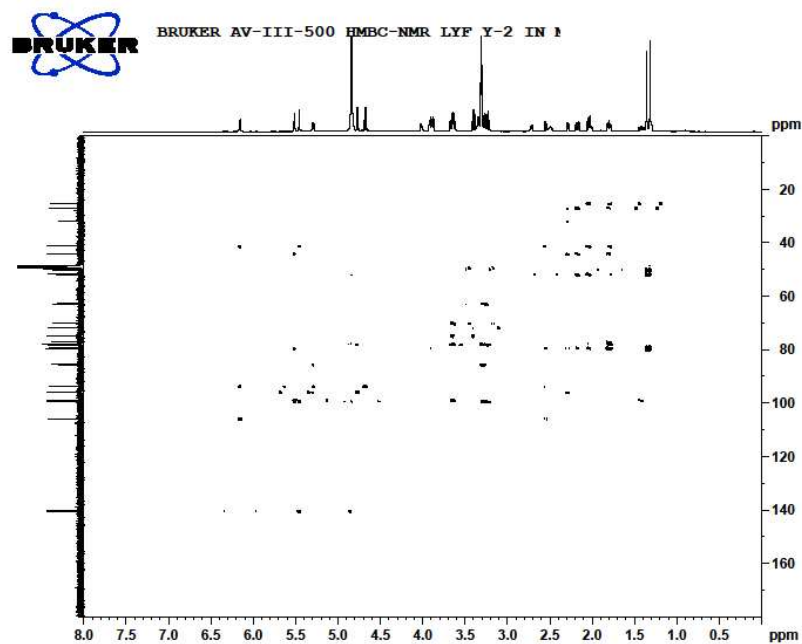
NAME          y2
EXPNO         3
PROCNO        1
Date_         20140123
Time          22.10
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       cosygpgf
TD            2048
SOLVENT       MeOD
NS            1
DS            8
SWH           3501.401 Hz
FIDRES        1.709668 Hz
AQ            0.2925044 sec
RG            203
DW            142.800 usec
DE            6.00 usec
TE            297.8 K
D0            0.00000305 sec
D1            1.00000000 sec
D12           0.00000480 sec
D16           0.00020000 sec
IN0           0.00028570 sec

===== CHANNEL f1 =====
NUC1          1H
P1            15.10 usec
WDW           1
SF01          500.0618 MHz
FIDRES        12.472356 Hz
SW            7.000 ppm
F0MODE        QF
SI            1024
SF            500.0600123 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
PC            1.40
SI            1024
MC2           QF
SF            500.0600115 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
  
```

S76. ^1H - ^1H COSY Spectrum of compound **9**

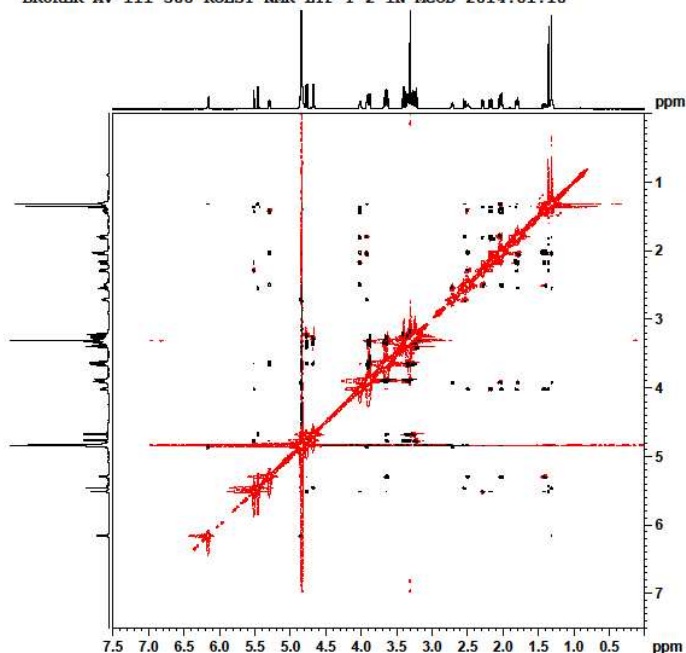


S77. HSQC Spectrum of compound **9**



S78. HMBC Spectrum of compound **9**

BRUKER AV-III-500 ROESY-NMR LYF Y-2 IN MeOD 2014.01.10



```

NAME      y2
EXPNO     6
PROCNO    1
Date_     20140114
Time      1.57
INSTRUM   spect
PROBHD    5 mm QNP1H/
PULPROG   roesyphpp.2
TD         2048
SOLVENT   MeOD
NS         32
DS         32
SWH        3501.401 Hz
FIDRES     1.709668 Hz
AQ         0.1925044 sec
RG         303
DW         142.800 usec
DE         8.00 usec
TE         298.0 K
D0         0.00012923 sec
D1         1.00000000 sec
D11        0.03000000 sec
D12        0.00002000 sec
JWD        0.00028570 sec
L4         1000
P15        200000.00 usec

===== CHANNEL f1 =====
NUC1       1H
P1         15.10 usec
P17        2500.00 usec
P18        100.00 usec
NUC2       1
TD         256
SF01       500.0618 MHz
FIDRES     13.478378 Hz
SW         7.000 ppm
PQMODE     States-TPPI
SI         1024
SF         500.0600130 MHz
WQW        QSIGN
SSB        2
LB         0.00 Hz
GB         0
PC         1.00
SI         1024
MC2        States-TPPI
SF         500.0600137 MHz
WQW        QSIGN
SSB        2
LB         0.00 Hz
GB         0
  
```

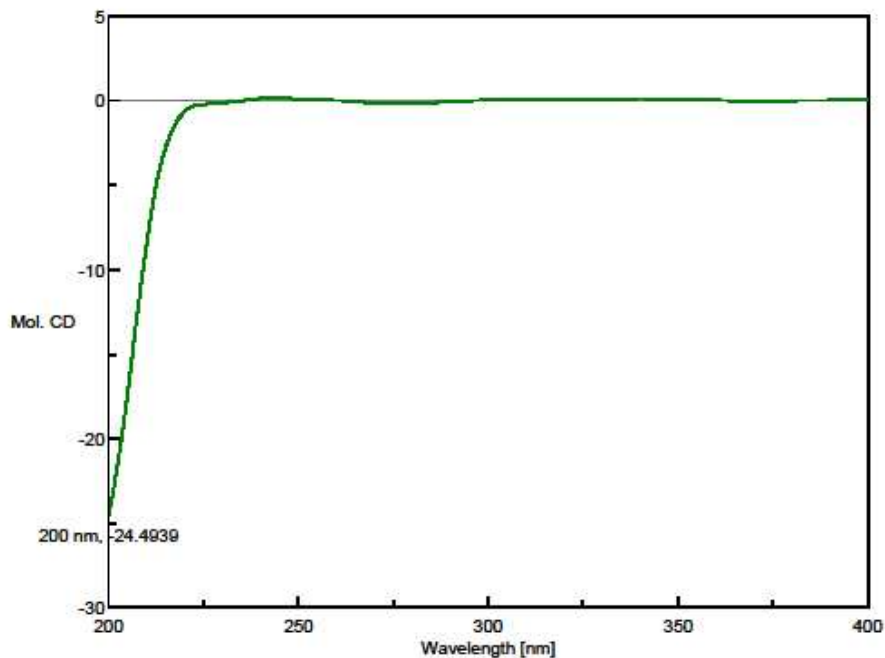
S79. ROESY Spectrum of compound **9**

MS Formula Results: + Scan (3.591 min) Sub (2014090502.d)

m/z	Ion	Formula	Abundance
719.2741	(M+Na) ⁺	C30 H48 Na O18	379871.4

Base	Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Off (ppm)	Mass Match	Abund Match	Spacing Match	DBE
✓	C30 H48 O18	C30 H48 Na O18	99.92		696.2645	696.2641	719.2733	-1.11	1.11	99.96	99.97	99.77	

S80. HRESIMS Spectrum of compound **9**



S81. CD Spectrum of compound **9** (CH₃OH)