

Supplementary Data

New methyl threonolactones and pyroglutamates of *Spilanthes acmella* Murr. and their bone formation activities

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Figure S29: ^{13}C NMR of compound **4** in 150 MHz, CD_3OD

Figure S30: COSY of compound **4** in 600 MHz, CD_3OD

Figure S31: HSQC of compound **4** in 150 and 600 MHz, CD_3OD

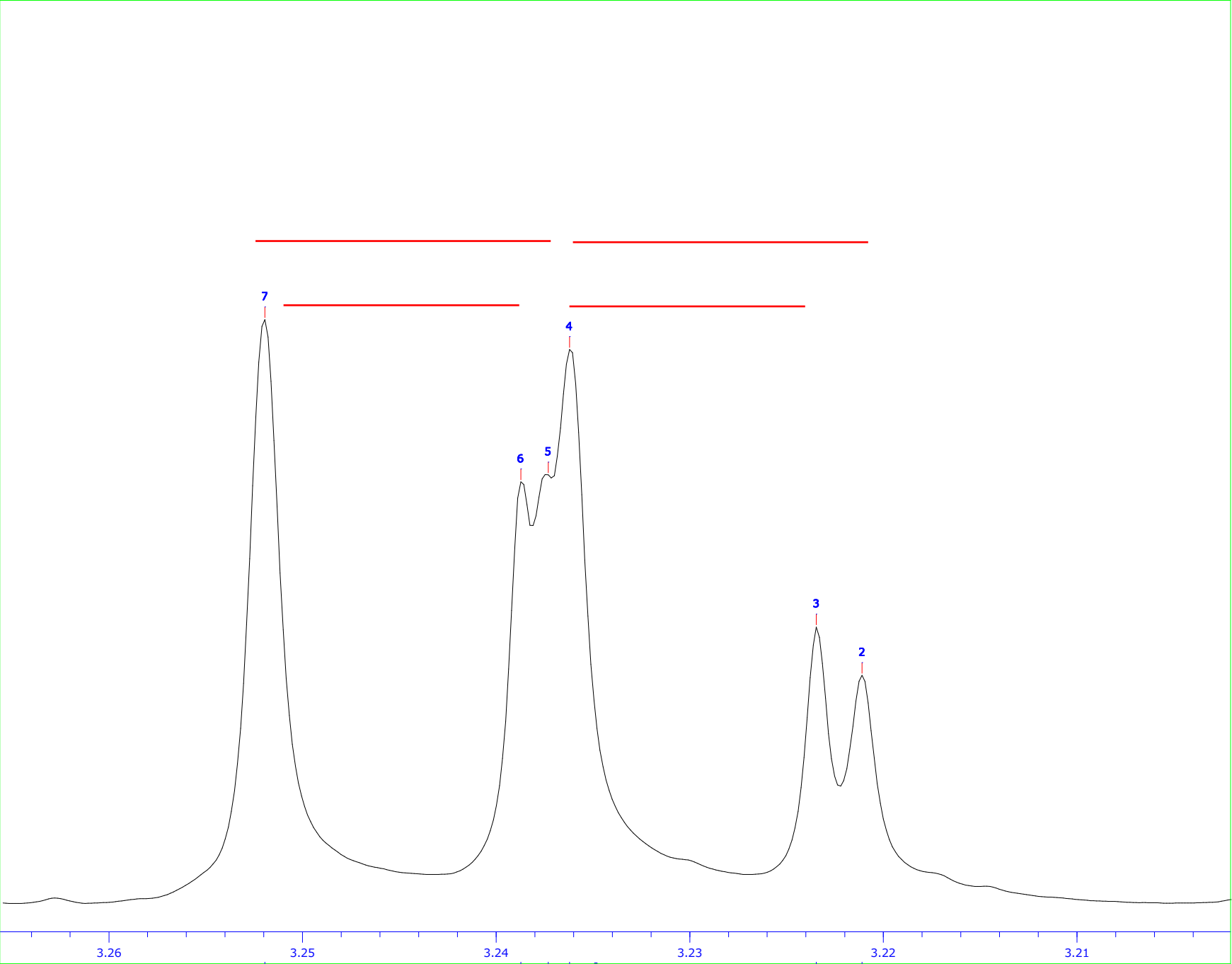
Figure S32: HMBC of compound **4** in 150 and 600 MHz, CD_3OD

Chemical Shift (ppm)	Integration
4.5383	1.0
4.5273	1.06
4.5224	1.09
4.5116	1.0
4.4400	1.03
4.4293	1.08
4.4186	1.0
4.3717	1.64
4.3588	1.97
4.1102	0.9957
4.0995	1.0317
4.0943	1.0847
4.0838	1.0
3.9219	2.7504
3.9178	1.642
3.9025	1.9744
3.8984	1.0
3.6200	1.0
3.6077	1.06
3.6008	1.09
3.5885	1.0
3.3755	1.0
3.3605	1.06
3.3490	1.09
3.3454	1.0
3.3371	1.03
3.3155	1.08
3.3128	1.0
3.3100	1.64
3.3073	1.97
3.3047	1.0
3.2519	1.0
3.2387	1.06
3.2362	1.09
3.2235	1.0
3.2211	1.03
1.311	1.08

OBNUC	¹ H
EXMOD	ZG30
OBFRQ	600.13 MHz
OBSET	0.0 kHz
OBFIN	9987.786 Hz
POINT	65536
FREQU	12376.24 Hz
SCANS	8
ACQTM	5.2953 s
PD	1.0 s
PW1	10.0 μs
IRNUC	??
PROBHD	5 MM TXI 1H-13C/15N-D XYZ-GRD Z
	8
PULSPRG	ZG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	MEOD
EXREF	3.31 ppm
BF	0.0944 Hz
WINDOW	Exponential

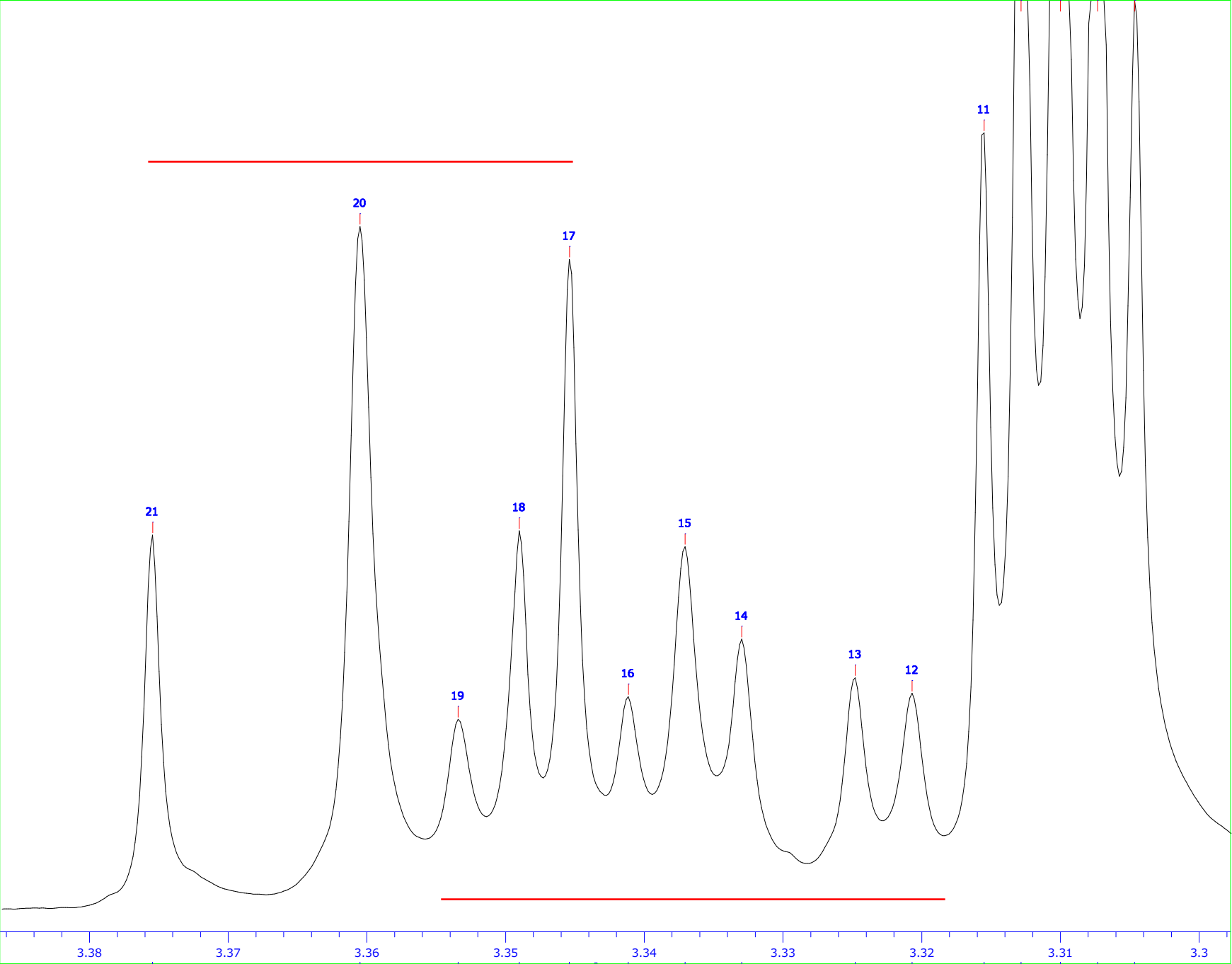
1.4086

Figure S2 1H NMR (3.237 & 3.238 ppm) of compound 1 in 600MHz, CD₃OD



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1-6 (CPD G)	¥1R.RM1
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COMNT	Sab 11-1-6 MeOD 10.1 mg H
OBNUC	¹ H
EXMOD	ZG30
OBFRQ	600.13 MHz
OBSET	0.0 kHz
OBFIN	9987.786 Hz
POINT	65536
FREQU	12376.24 Hz
SCANS	8
ACQTM	5.2953 s
PD	1.0 s
PW1	10.0 µs
IRNUC	??
PROBHD	5 MM TXI 1H-13C/15N-D XYZ-GRD Z
8	
PULSPRG	ZG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	MEOD
EXREF	3.31 ppm
BF	0.0944 Hz
WINDOW	Exponential

Figure S3 1H NMR (3.34 & 3.36 ppm) of compound 1 in 600MHz, CD₃OD



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1-6 (CPD G)¥1R.RM1
DATIM 23/Nov/2014 12:04:11
COMNT
Sab 11-1-6 MeOD 10.1 mg H

OBNUC ¹H
EXMOD ZG30
OBFRQ 600.13 MHz
OBSET 0.0 kHz
OBFIN 9987.786 Hz
POINT 65536
FREQU 12376.24 Hz
SCANS 8
ACQTM 5.2953 s
PD 1.0 s
PW1 10.0 µs
IRNUC ??
PROBHD 5 MM TXI 1H-13C/15N-D XYZ-GRD Z
8
PULSPRG ZG30
GRDPRG
CTEMP 26.85 °C
SLVNT MEOD

3.3755

3.3605

3.3534

3.3490

3.3454

3.3412

3.3371

3.3330

3.3248

3.3207

3.3155

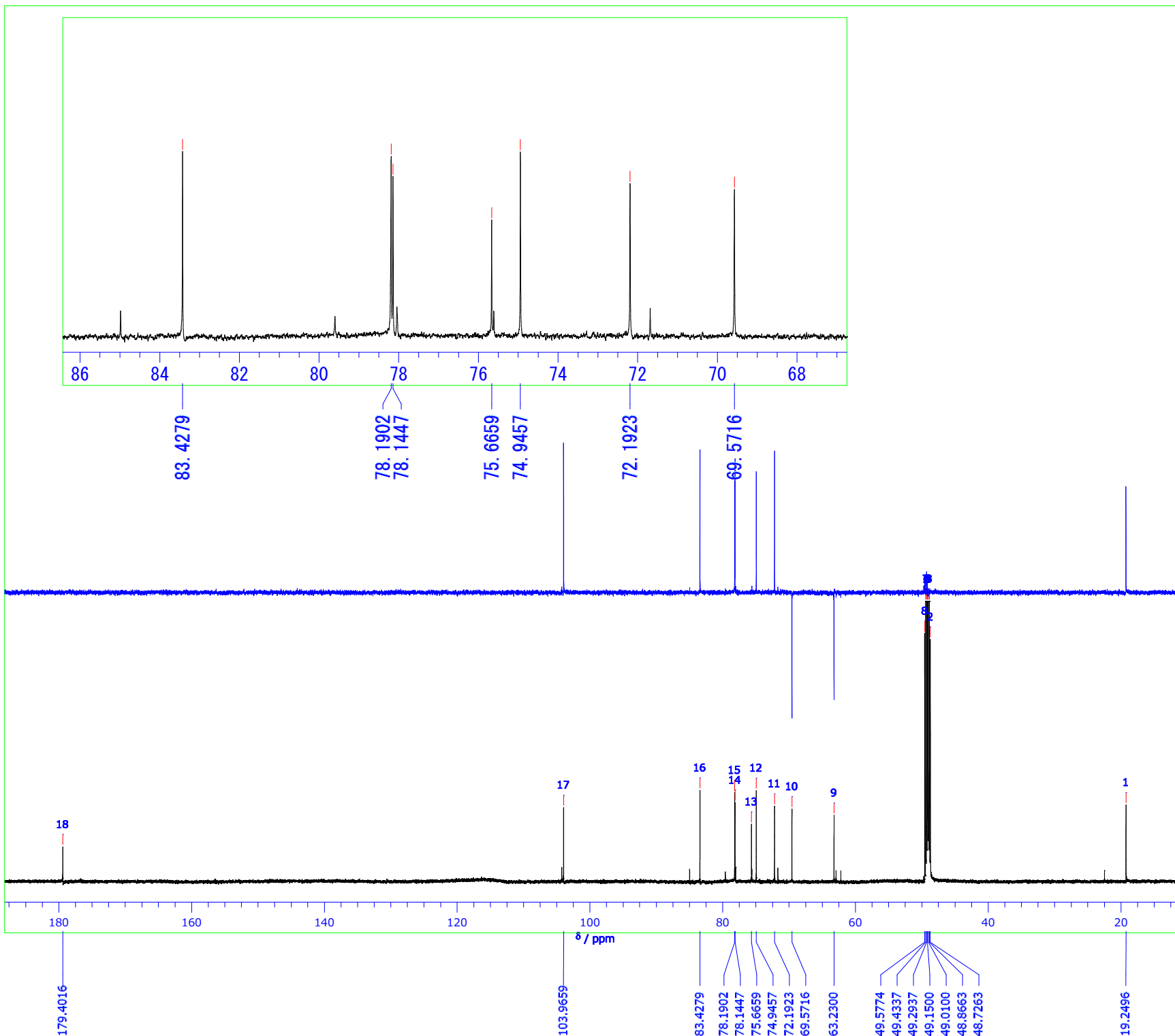
3.3128

3.3100

3.3073

3.3047

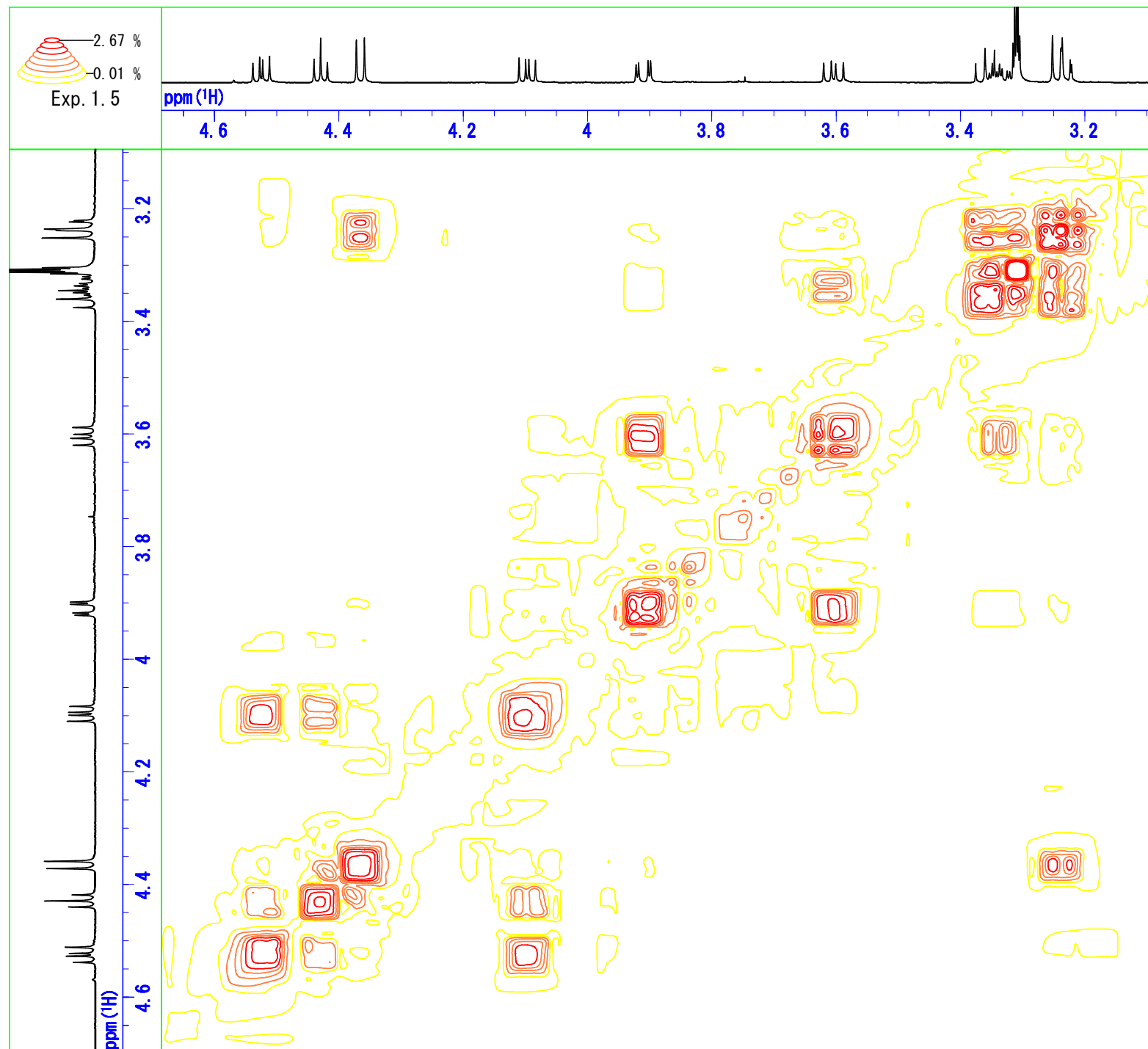
Figure S4 ^{13}C & DEPT135 NMR of compound 1 in 150 MHz, CD_3OD



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 DATIM 24/Nov/2014 05:25:23
 COMNT
 Sab 11-1-6 MeOD 10.1 mg c

OBNUC ^{13}C
 EXMOD ZGPG30
 OBFRQ 150.9 MHz
 OBSET 0.0 kHz
 OBFIN 10000.86 Hz
 POINT 32768
 FREQU 35971.22 Hz
 SCANS 10000
 ACQTM 0.911 s
 PD 2.0 s
 PW1 15.0 μs
 IRNUC ??
 PROBHD 5 MM TXI 1H-13C/15N-D XYZ-GRD Z
 8
 PULSPRG ZGPG30
 GRDPROG
 CTEMP 26.85 $^{\circ}\text{C}$
 SLVNT MEOD
 EXREF 49.15 ppm

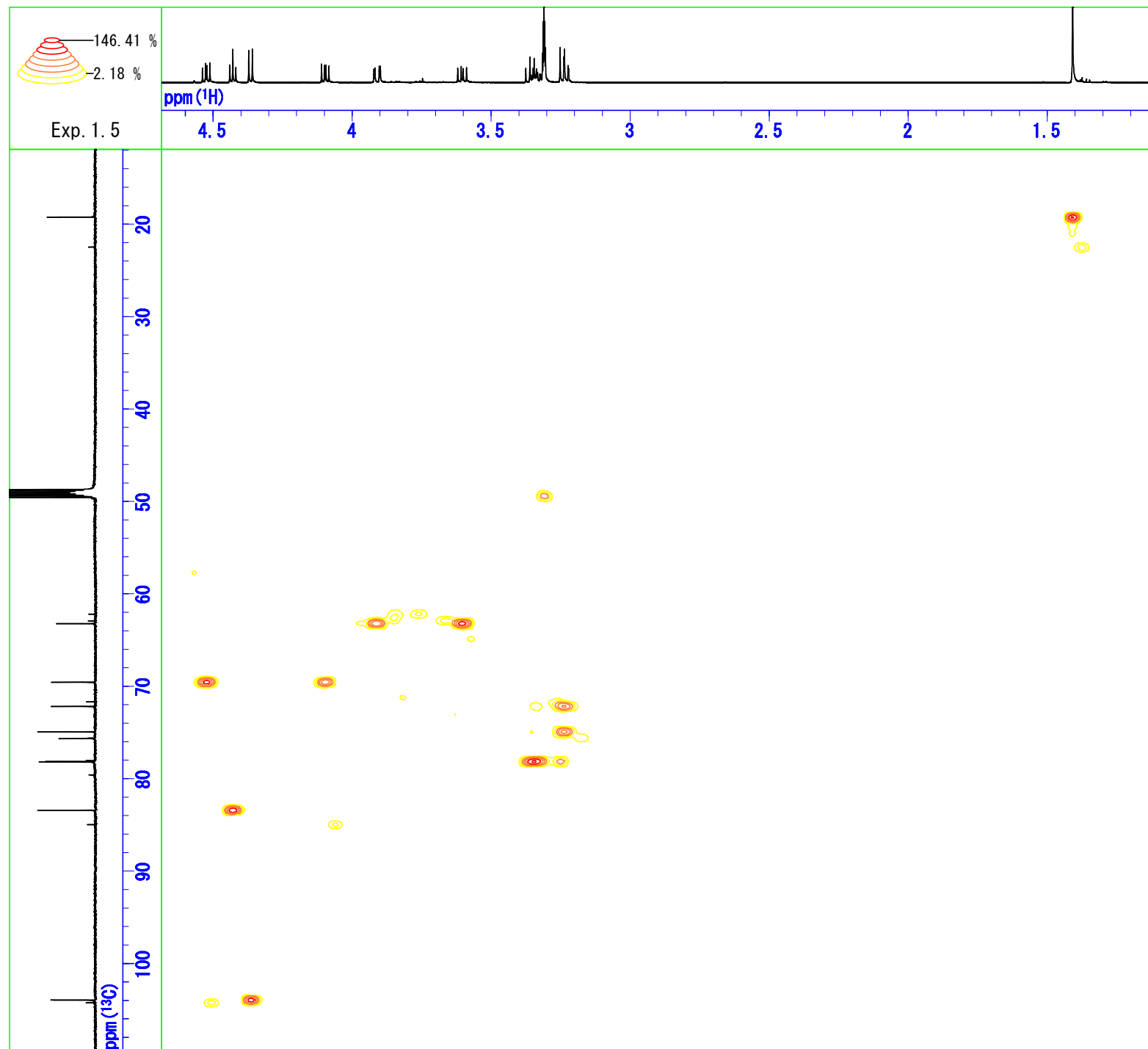
Figure S5 COSY of compound 1 in 600 MHz, CD₃OD



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CPD G)\COSY.RM2
ORGFIL C:\Users\PrimeVF17A\Desktop\RETNO
NMR\Sab 11-1-6 (Cpd G)\42\pdata\1\2rr
DATIM 23/Nov/2014 14:36:56
COMNT
Sab 11-1-6 MeOD 10.1 mg cosy

EXMOD V_HOMO(COSYGPQF)
OBNUC ¹H
OBFRQ 600.124 MHz
OBSET 0.0 kHz
OBFIN 10011.91 Hz
POINT 1024
FREQU 8012.82 Hz
CLPNT 1024
CLFRQ 8012.82 Hz
SCANS 15
ACQTM 0.1278 s
PD 1.4869 s
PW1 10.0 μs
PW2 10.0 μs
PW3 20.0 μs
PI1 1.4869 ms
PI2 0.0 ms
PI3 0.0 ms
IRNUC ¹H
CTEMP 26.85 °C
SLVNT MEOD
EXREF -0.6739 ppm
CLEXR -0.6739 ppm
RGAIN 64
1DSPC(F1/F2) G:\NOV23-2014RETNO\40\PDAT
A\1\11
PRNT_DATE 2020/Apr/29 16:48:09
OPERT

Figure S6 HSQC of compound 1 in 150 & 600 MHz, CD₃OD



DFILE D:\5 教室員研究\08 RETNO WIDYOWATI\
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 CPD G)\HSQC.RM2
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 DATIM 23/Nov/2014 19:26:58
 COMNT
 Sab 11-1-6 MeOD 10.1 mg hsqc

 EXMOD VPH_HETERO(HSQCETGP)
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 OBFRQ 600.124 MHz
 OBSET 0.0 kHz
 OBFIN 10011.91 Hz
 POINT 1024
 FREQU 8012.82 Hz
 CLPNT 1024
 CLFRQ 25000.0 Hz
 SCANS 15
 ACQTM 0.1278 s
 PD 1.5 s
 PW1 10.0 μs
 PW2 10.0 μs
 PW3 20.0 μs
 PI1 1.5 ms
 PI2 0.0035 ms
 PI3 0.0023 ms
 IRNUC ¹³C
 CTEMP 26.85 °C
 SLVNT MEOD
 EXREF -0.6739 ppm
 CLEXR -6.5465 ppm
 RGAIN 18390
 1DSPC(F1) G:\NOV23-2014RETNO\45\PDATA\1\
 1l
 1DSPC(F2) G:\NOV23-2014RETNO\40\PDATA\1\
 1l
 PRNT_DATE 2020/Apr/29 16:50:50
 OPERT

Figure S7 HMBC of compound 1 in 150 and 600 MHz, CD₃OD

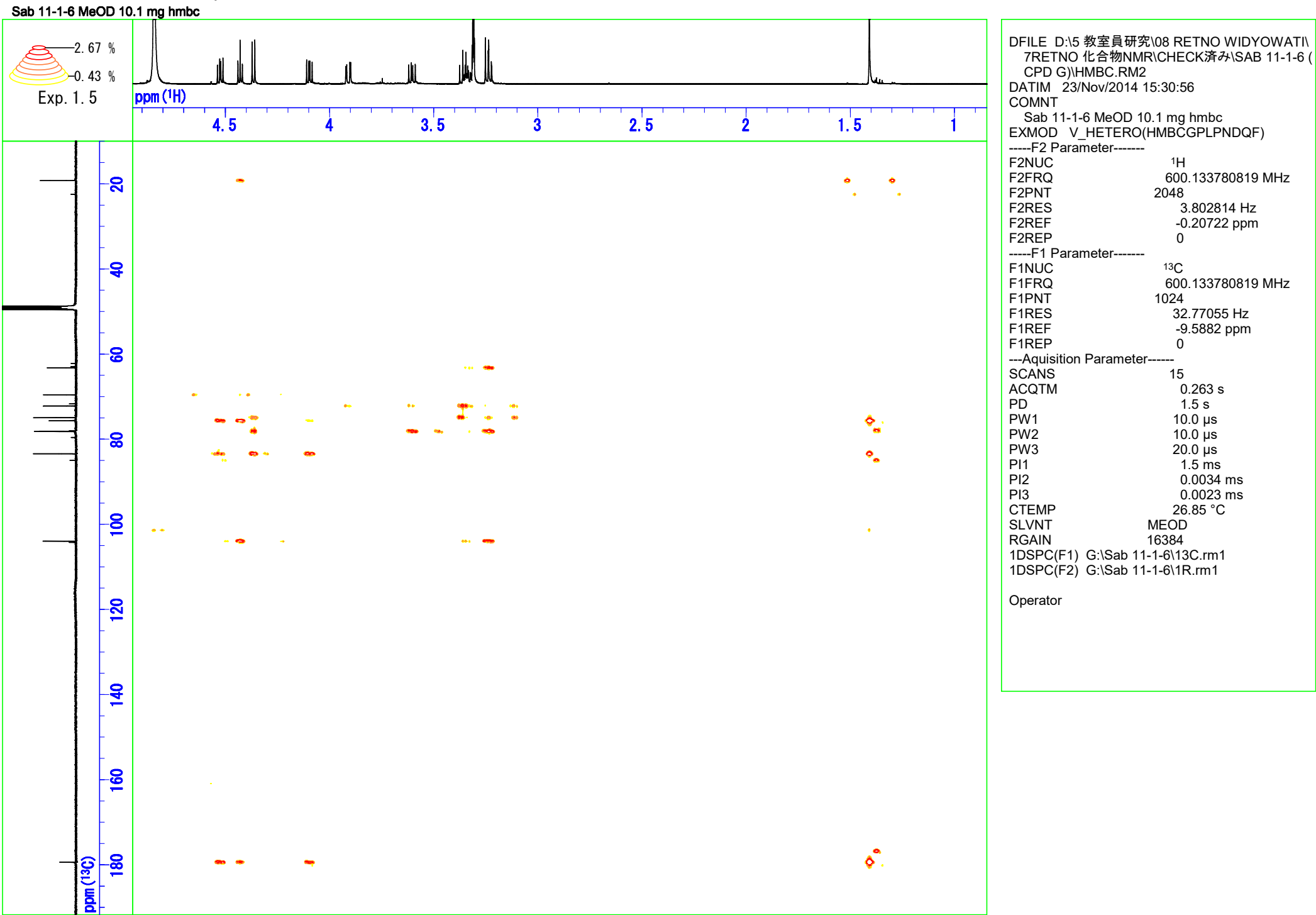
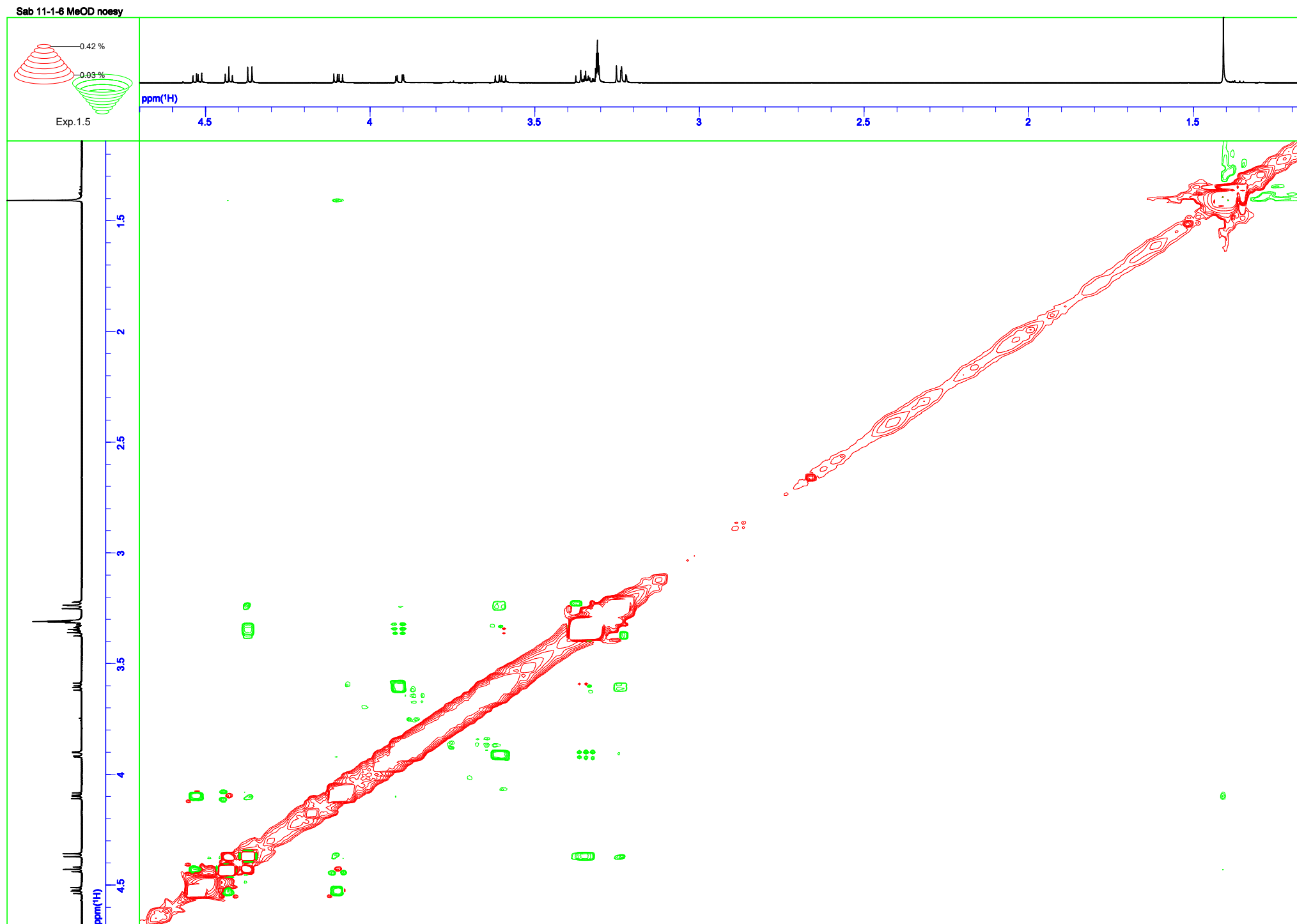
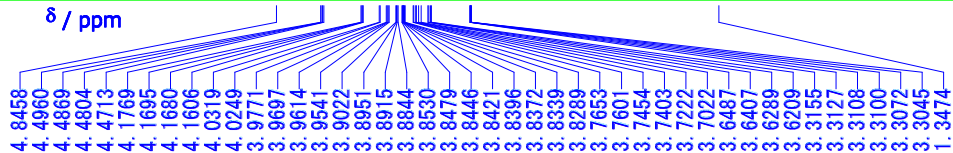


Figure S8 PS-NOESY of compound 1 in 600 MHz, CD₃OD



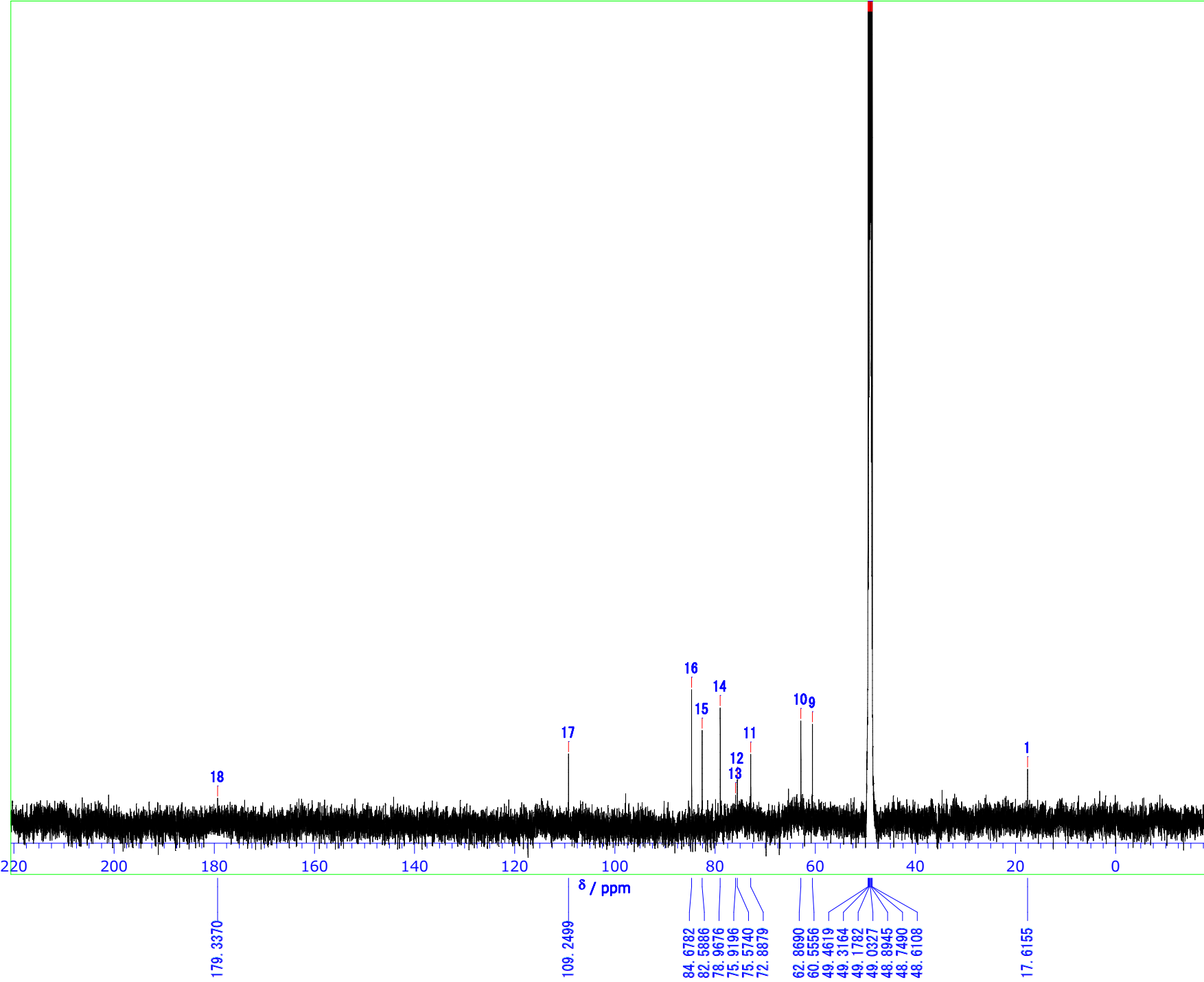
5



観測核種	¹ H
測定モード	ZG30
観測周波数(粗)	600.13 MHz
観測周波数offset	0.0 kHz
観測周波数Fine	9987.788 Hz
データ点数	65536
観測範囲	12376.24 Hz
実積算回数	8
FID取込時間	5.2953 s
待ち時間	0.0 s
パルス幅	10.0 μs
decouple核種	OFF
プログラム	5 MM TXI 1H-13C/15N-D XYZ-GRD Z8323/149 ATM Z8323/14
装置	DRX600
パルスプログラム	ZG30
Gradientプログラム	
試料温度	26.85 °C
測定溶媒	MEOD
Chemical shift参照値	3.31 ppm
Broadening係数	0.25 Hz

観測周波数offset	0.0 kHz
観測周波数Fine	9987.788 Hz
データ点数	65536
観測範囲	12376.24 Hz
実積算回数	8
FID取込時間	5.2953 s
待ち時間	0.0 s
パルス幅	10.0 μs
decouple核種	OFF
プロト 5 MM TXI 1H-13C/15N-D X-YZ-GRD Z8323/149 ATM Z8323/14	
装置	DRX600
パルスプログラム	ZG30
Gradientプログラム	
試料温度	26.85 °C
測定溶媒	MEOD
Chemical shift参照値	3.31 ppm
Broadening係数	0.25 Hz

Figure S10 13C NMR of compound 2 in 150 MHz, CD₃OD



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初期ファイル名 C:\¥USERS¥KMATS¥DESKT
OP¥DATA FOR CPD 2¥MAY17-201
5RETNO¥14 SAB 20-1-2 MEOD C
¥PDATA¥1¥1R
測定日時 18/May/2015 00:18:34
注釈
Sab 20-1-2 MeOD c

観測核種 ¹³C
測定モード ZGPG30
観測周波数(粗) 150.9 MHz
観測周波数offset 0.0 kHz
観測周波数Fine 10000.86 Hz
データ点数 32768
観測範囲 35971.22 Hz
実積算回数 5500
FID取込時間 0.911 s
待ち時間 0.0 s
パルス幅 15.0 μ s
decouple核種 ??
プログラム 5 MM TXI 1H-13C/15N-D XYZ-
GRD Z8

装置 DRX600
パルスプログラム ZGPG30
Gradientプログラム
試料温度 26.85 $^{\circ}$ C
測定溶媒 MEOD
Chemical shift参照値 220.6039 p
pm
Broadening係数 0.5489 H

Figure S11 COSY of compound 2 in 600 MHz, CD₃OD

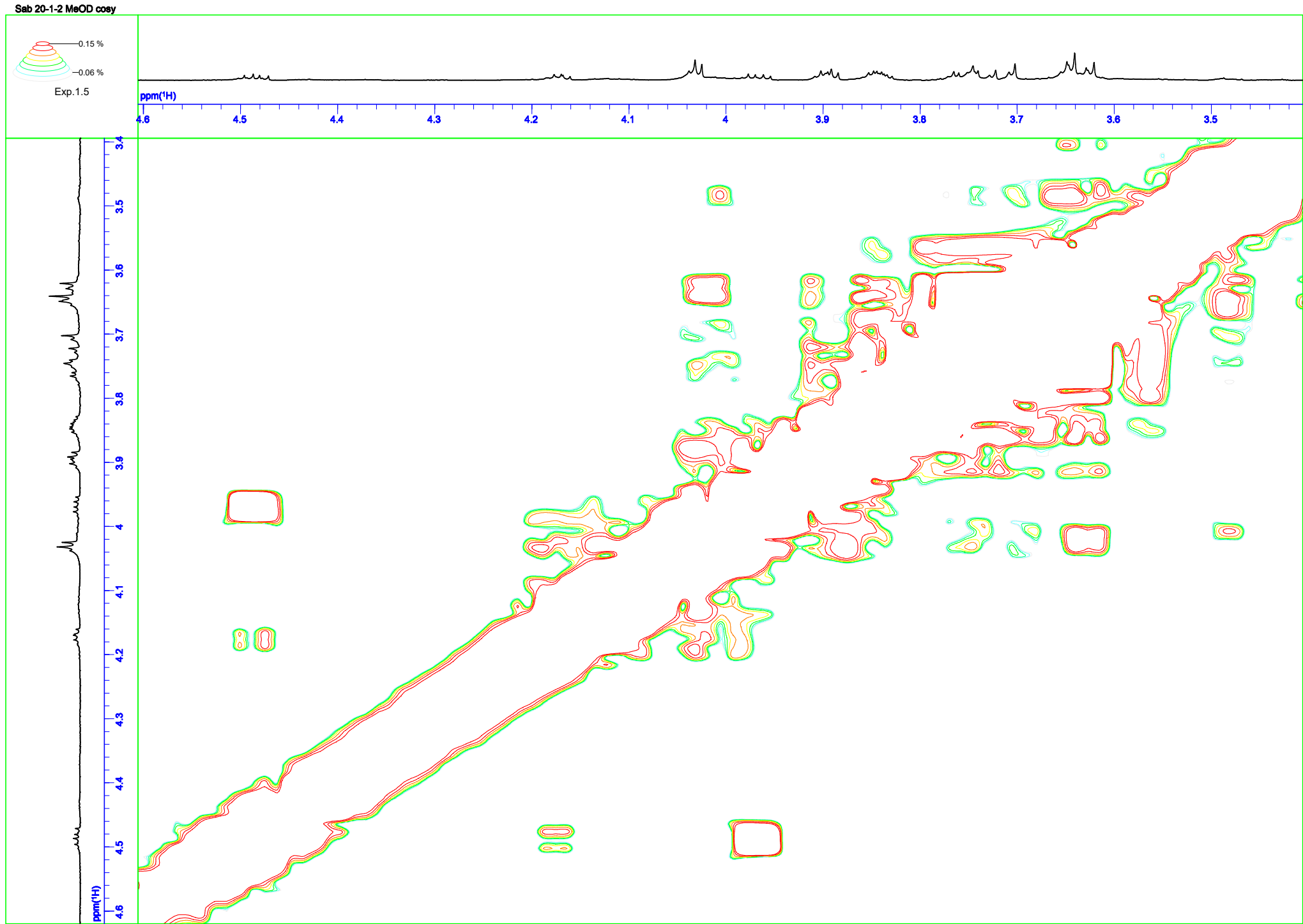


Figure S12 HSQC of compound 2 in 150 and 600 MHz, CD₃OD

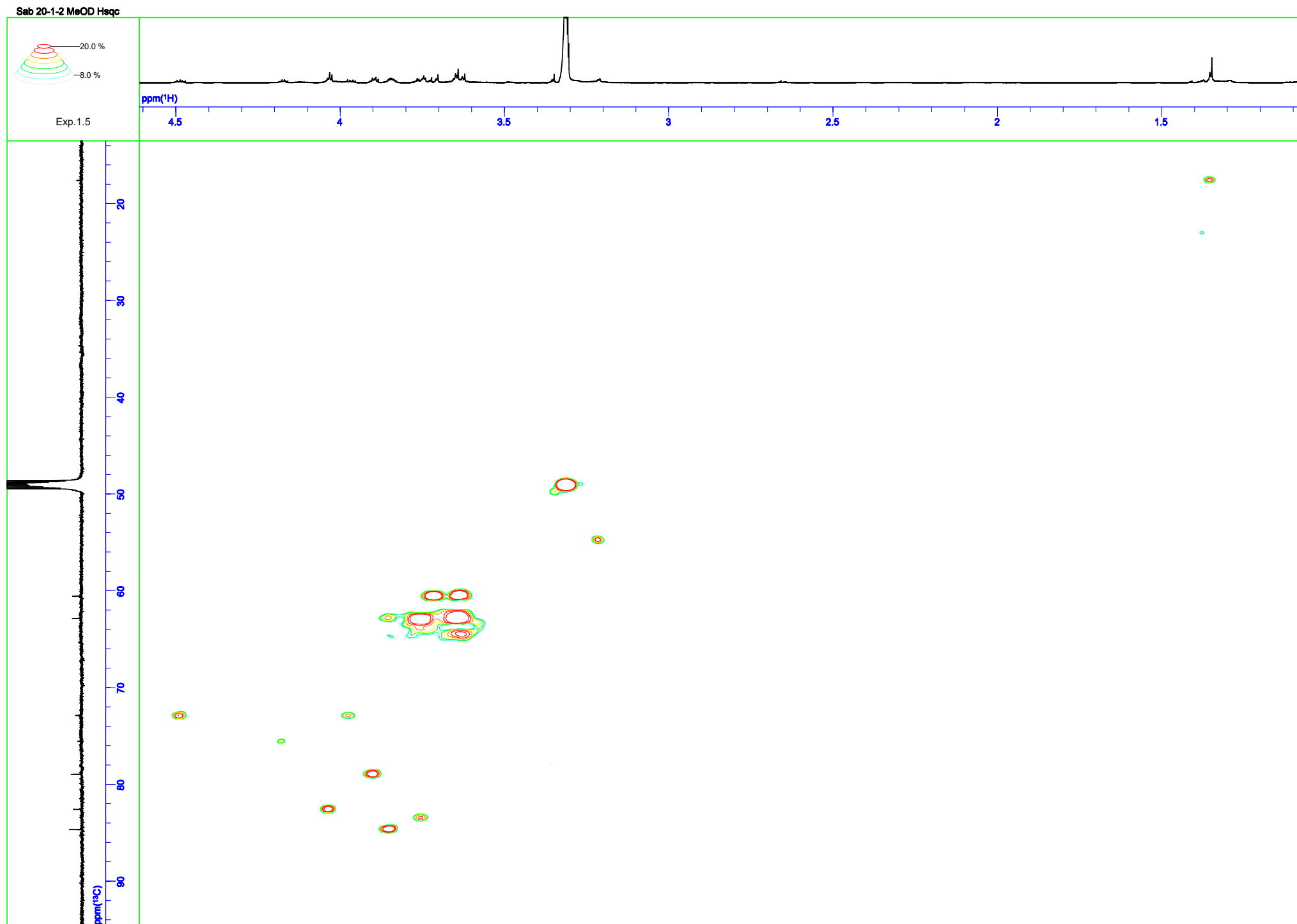
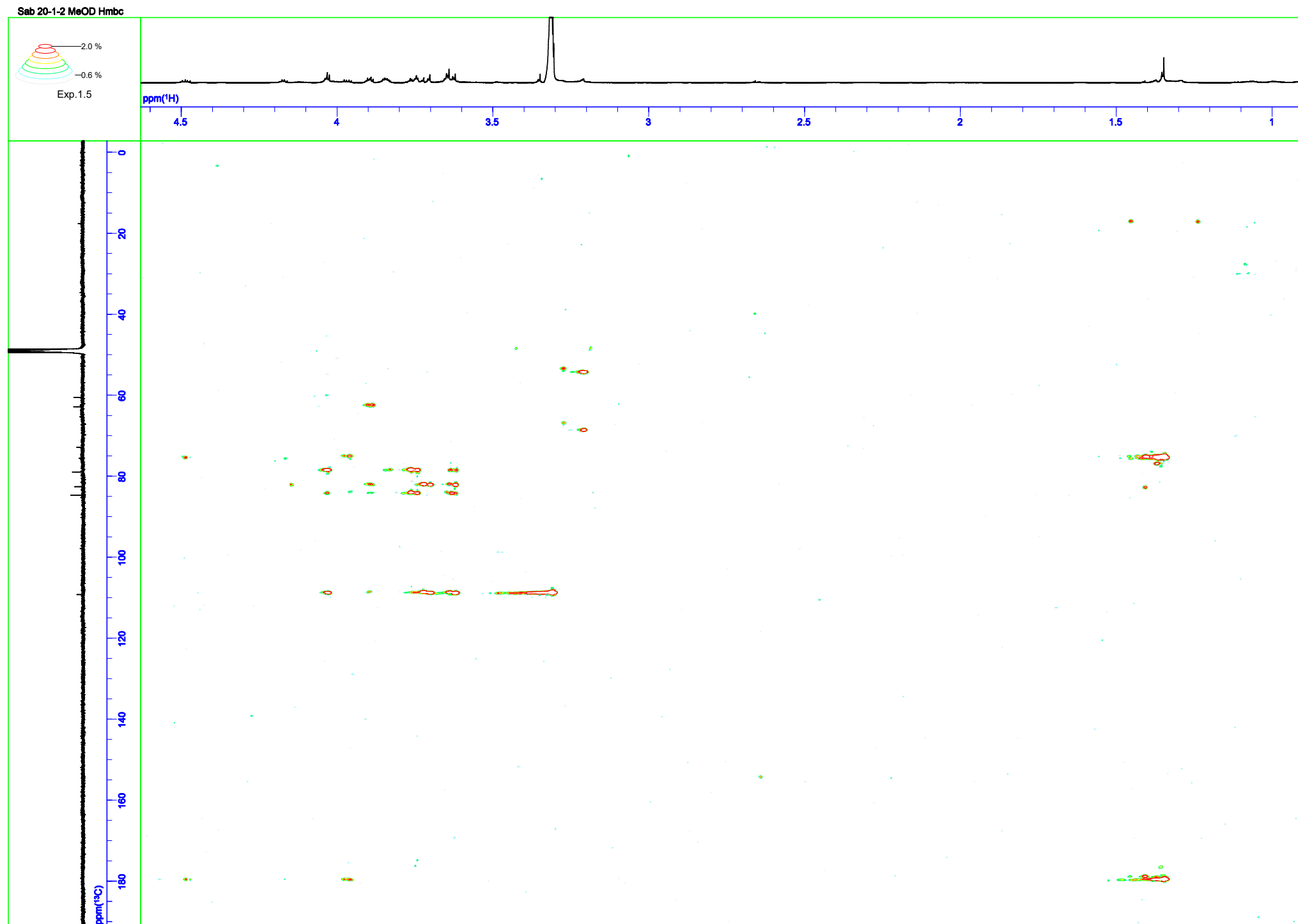


Figure S13 HMBC of compound 2 in 150 and 600 MHz, CD₃OD



3

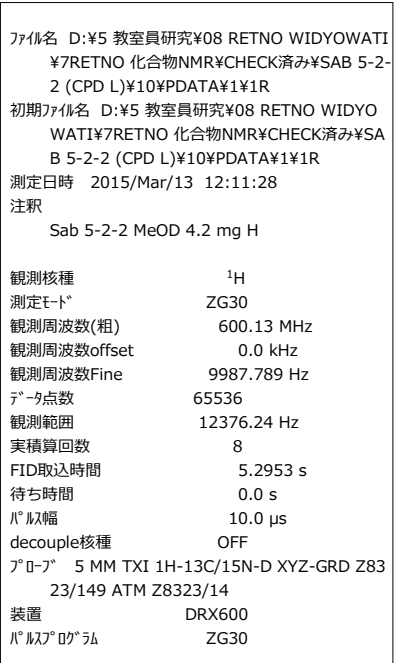
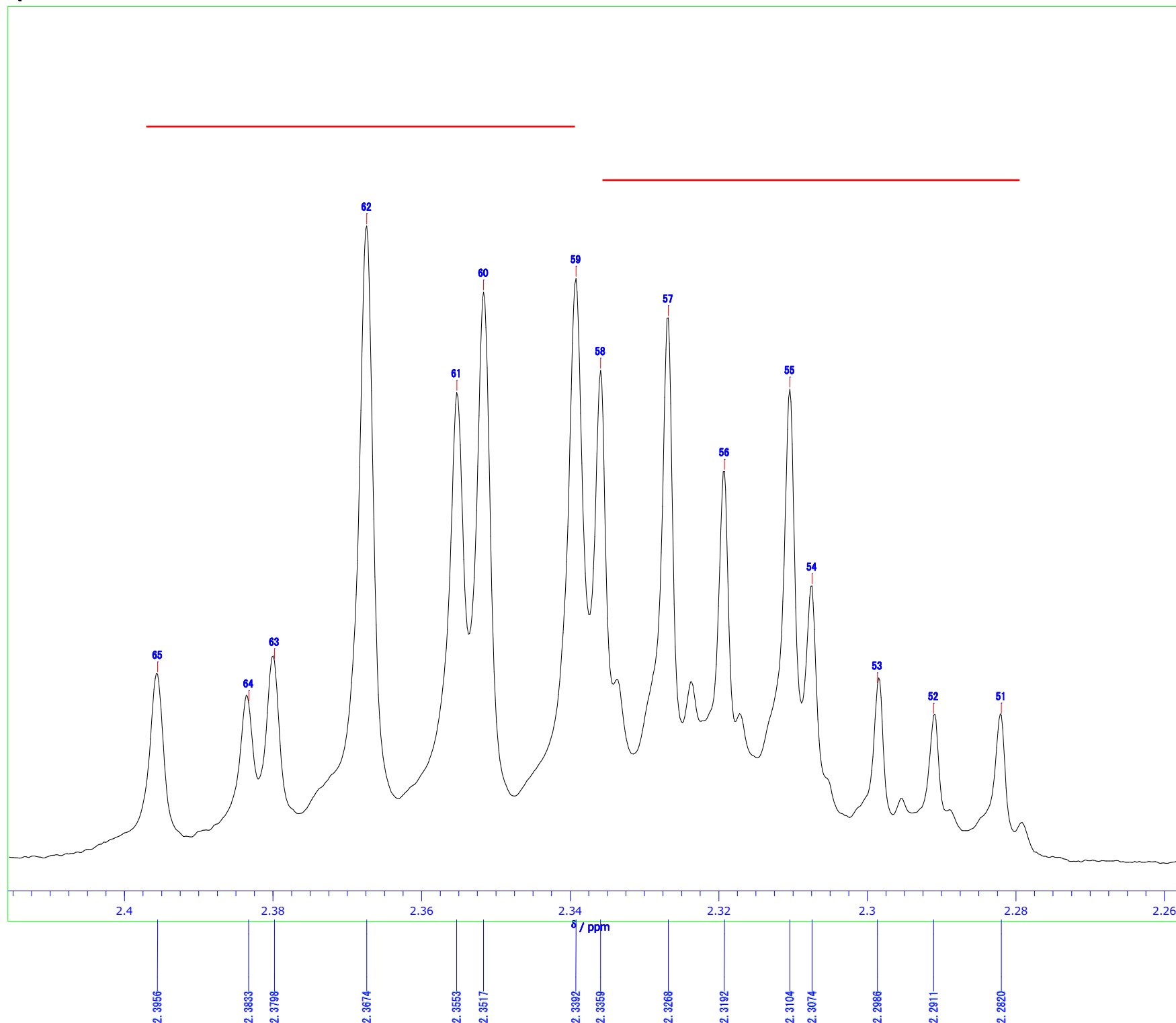


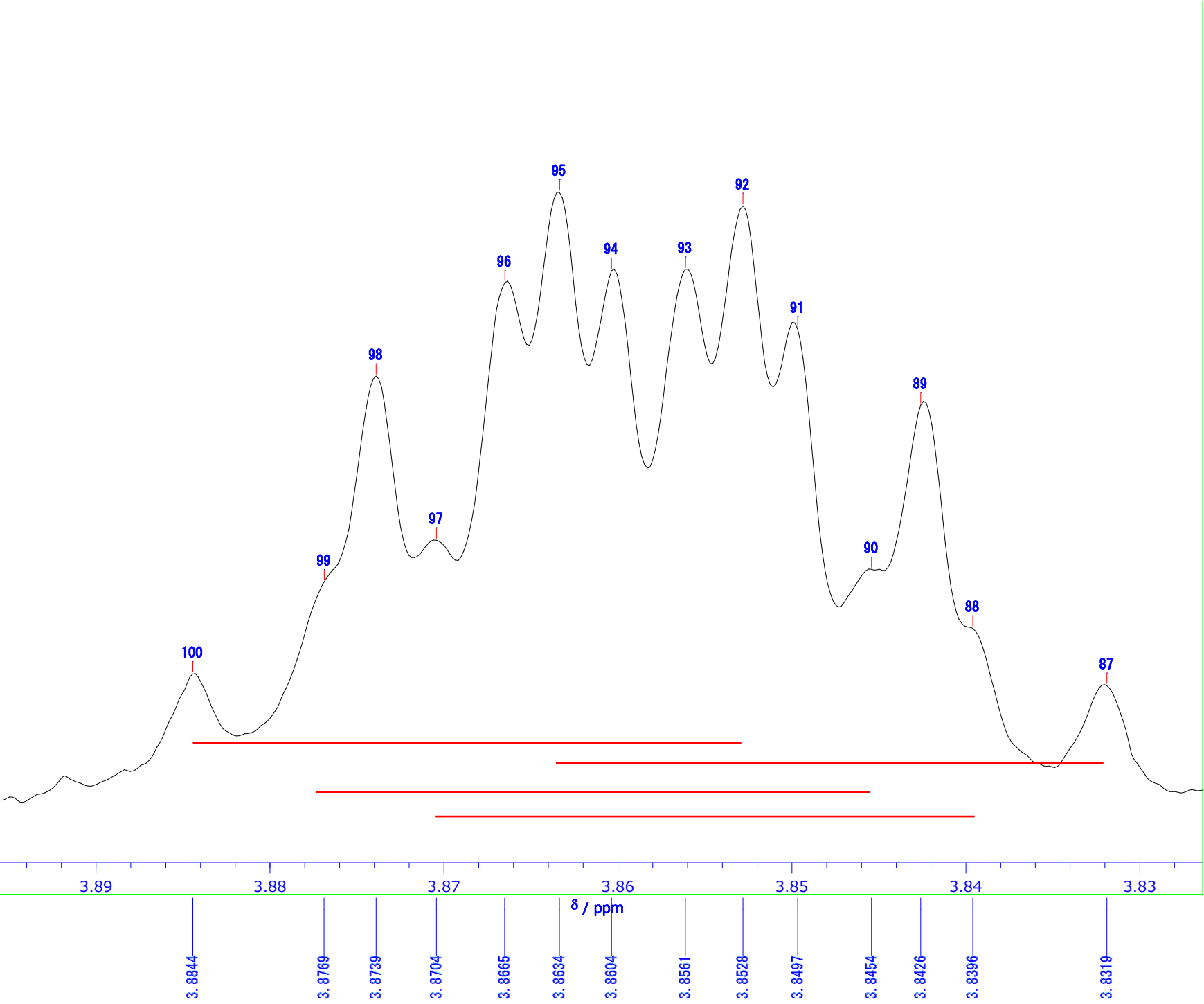
Figure S15 ^1H NMR (2.31 & 2.37 ppm) of compound 3 in 600 MHz, CD_3OD



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 2 (CPD L)¥10¥PDATA¥1¥1R
 初期ファイル名 D:\¥5 教室員研究¥08 RETNO WIDYO
 WATI¥7RETNO 化合物NMR¥CHECK済み¥SA
 B 5-2-2 (CPD L)¥10¥PDATA¥1¥1R
 測定日時 2015/Mar/13 12:11:28
 注釈
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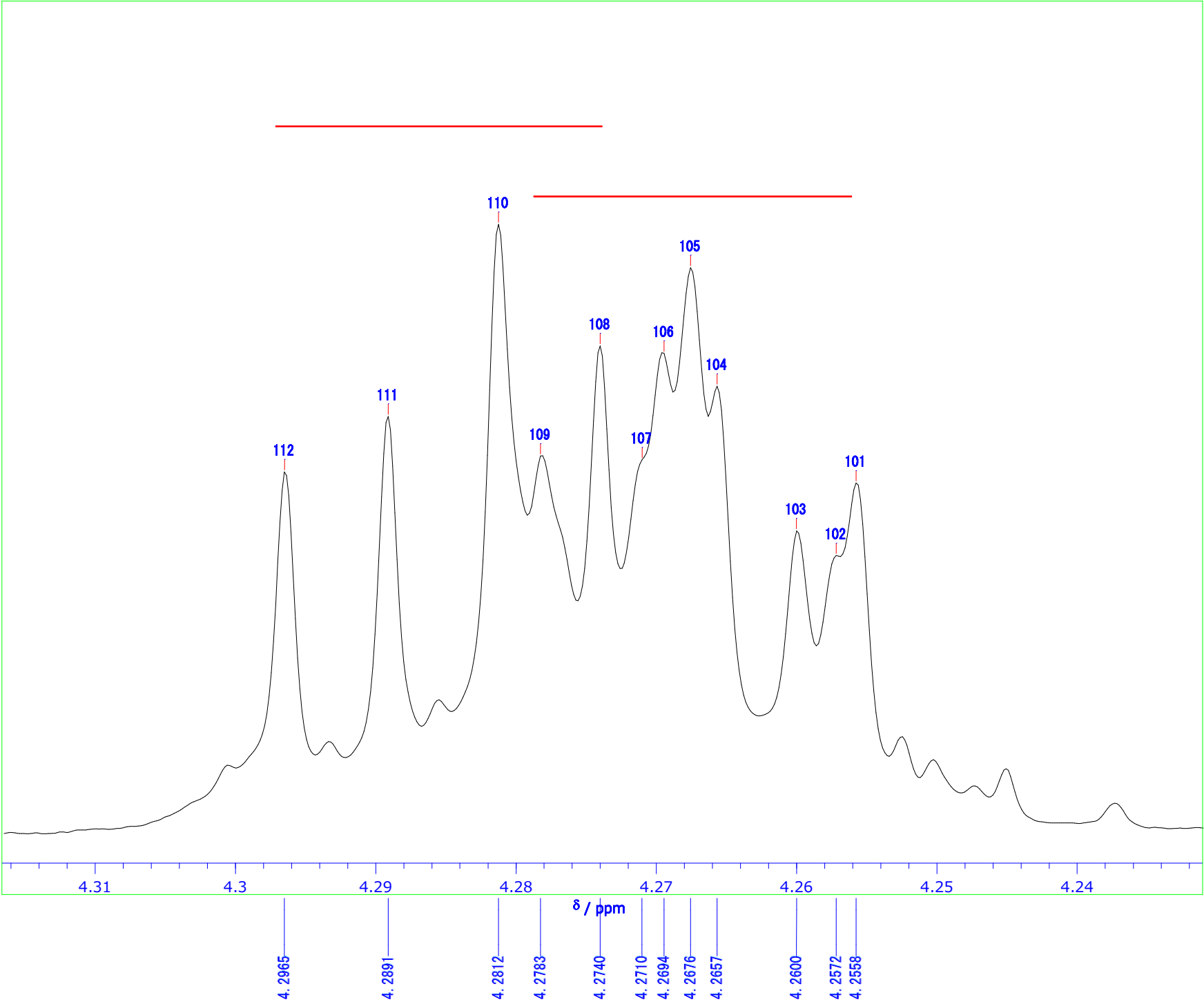
 観測核種 ^1H
 測定モード ZG30
 観測周波数(粗) 600.13 MHz
 観測周波数offset 0.0 kHz
 観測周波数Fine 9987.789 Hz
 データ点数 65536
 観測範囲 12376.24 Hz
 実積算回数 8
 FID取込時間 5.2953 s
 待ち時間 0.0 s
 パルス幅 10.0 μs
 decouple核種 OFF
 プログラム 5 MM TXI 1H-13C/15N-D XYZ-GRD Z83
 23/149 ATM Z8323/14
 装置 DRX600
 パルスプログラム ZG30

Figure S16 1H NMR (3.86 ppm) of compound 3 in 600 MHz, CD₃OD



ファイル名	D:\¥5 教室員研究¥08 RETNO WIDYOWATI¥7RETNO 化合物NMR¥CHECK済み¥SAB 5-2-2 (CPD L)¥1R 2.RM1
初期ファイル名	D:\¥5 教室員研究¥08 RETNO WIDYOWATI¥7RETNO 化合物NMR¥CHECK済み¥SAB 5-2-2 (CPD L) ¥10¥PDATA¥1¥1R
測定日時	13/Mar/2015 12:11:28
注釈	Sab 5-2-2 MeOD 4.2 mg H
観測核種	¹ H
測定モード	ZG30
観測周波数(粗)	600.13 MHz
観測周波数offset	0.0 kHz
観測周波数Fine	9987.789 Hz
データ点数	65536
観測範囲	12376.24 Hz
実積算回数	8
FID取込時間	5.2953 s
待ち時間	0.0 s
パルス幅	10.0 µs
decouple核種	NUL
プロセッサ	5 MM TXI 1H-13C/15N-D XYZ-GRD Z8
装置	DRX600
パルスプログラム	ZG30
Gradientプログラム	
試料温度	26.85 °C
測定溶媒	MEOD
Chemical shift参照値	3.31 ppm

Figure S17 1H NMR (4.27 & 4.29 ppm) of compound 3 in 600 MHz, CD₃OD



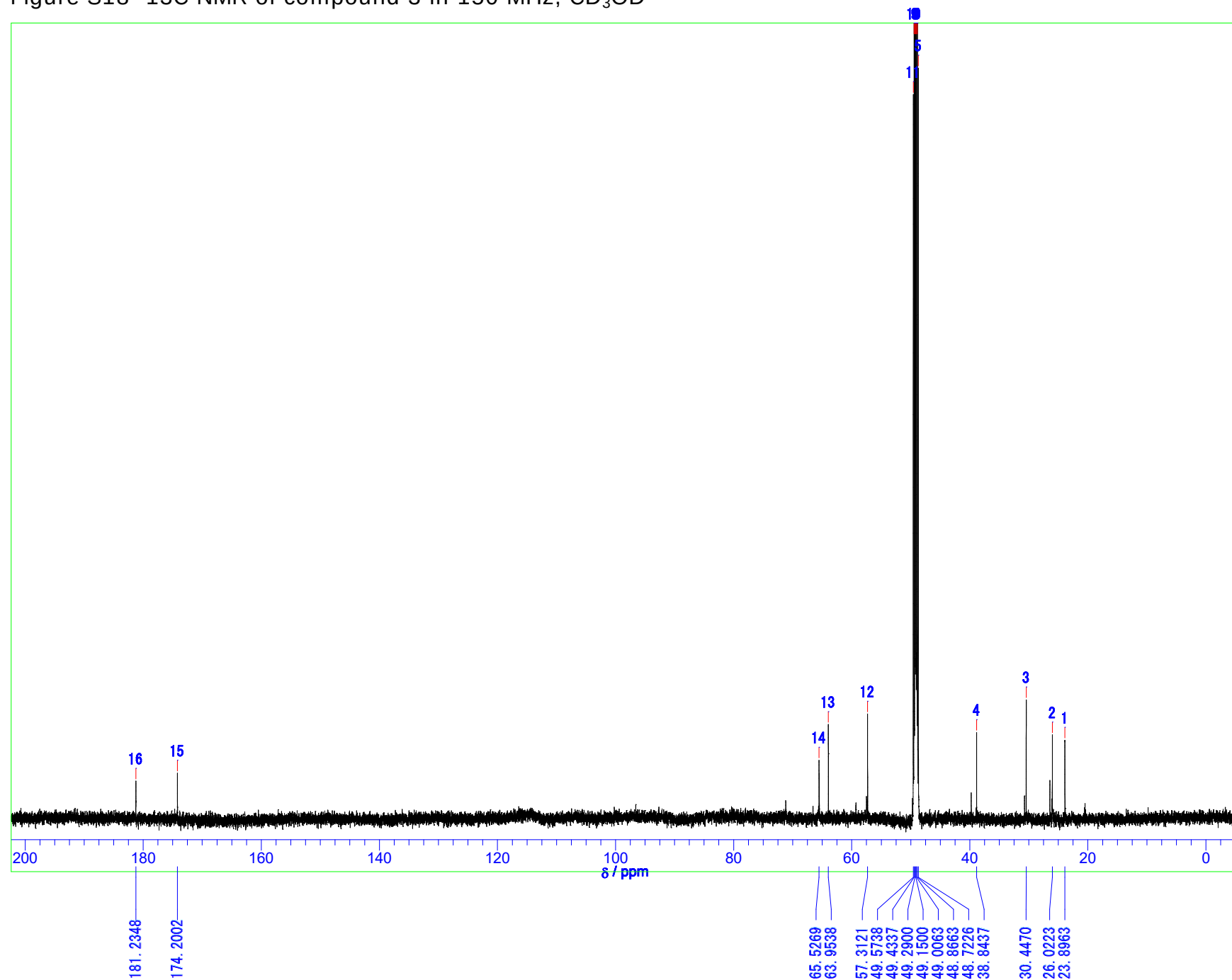
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測定日時 13/Mar/2015 12:11:28
注釈 Sab 5-2-2 MeOD 4.2 mg H

観測核種 ¹H
測定ポート ZG30
観測周波数(粗) 600.13 MHz

観測周波数offset 0.0 kHz
観測周波数Fine 9987.789 Hz
データ点数 65536
観測範囲 12376.24 Hz
実積算回数 8
FID取込時間 5.2953 s
待ち時間 0.0 s
パルス幅 10.0 µs
decouple核種 NUL
プログラム 5 MM TXI 1H-13C/15N-D XYZ-GRD Z8

装置 DRX600
パルスプログラム ZG30
Gradientプログラム
試料温度 26.85 °C
測定溶媒 MEOD
Chemical shift参照値 3.31 ppm

Figure S18 ¹³C NMR of compound 3 in 150 MHz, CD₃OD



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 13C2.RM1
 初期ファイル名 D:\5 教室員研究\08 RETNO WIDYOWATI\
 7RETNO 化合物NMR\CHECK済み\SAB 5-2-2 (CP
 D L)\13\PDATA\111R
 測定日時 14/Mar/2015 00:09:09
 注釈
 Sab 5-2-2 MeOD 4.2 mg C
 観測核種 ¹³C
 測定モード ZGPG30
 観測周波数(粗) 150.9 MHz
 観測周波数offset 0.0 kHz
 観測周波数Fine 10000.86 Hz
 データ点数 32768
 観測範囲 35971.22 Hz
 実積算回数 6300
 FID取込時間 0.911 s
 待ち時間 0.0 s
 パルス幅 15.0 μs
 decouple核種 ??
 プローブ 5 MM TXI 1H-13C/15N-D XYZ-GRD Z8
 装置 DRX600
 パルスプログラム ZGPG30
 Gradientプログラム
 試料温度 26.85 °C
 測定溶媒 MEOD
 Chemical shift参照値 49.15 ppm
 Broadening係数 0.5489 Hz
 窓関数 Exponential
 Receiver Gain 10321
 測定者
 印刷日時 2020/Apr/30 18:05:15

Figure S19 COSY of compound 3 in 600 MHz, CD₃OD

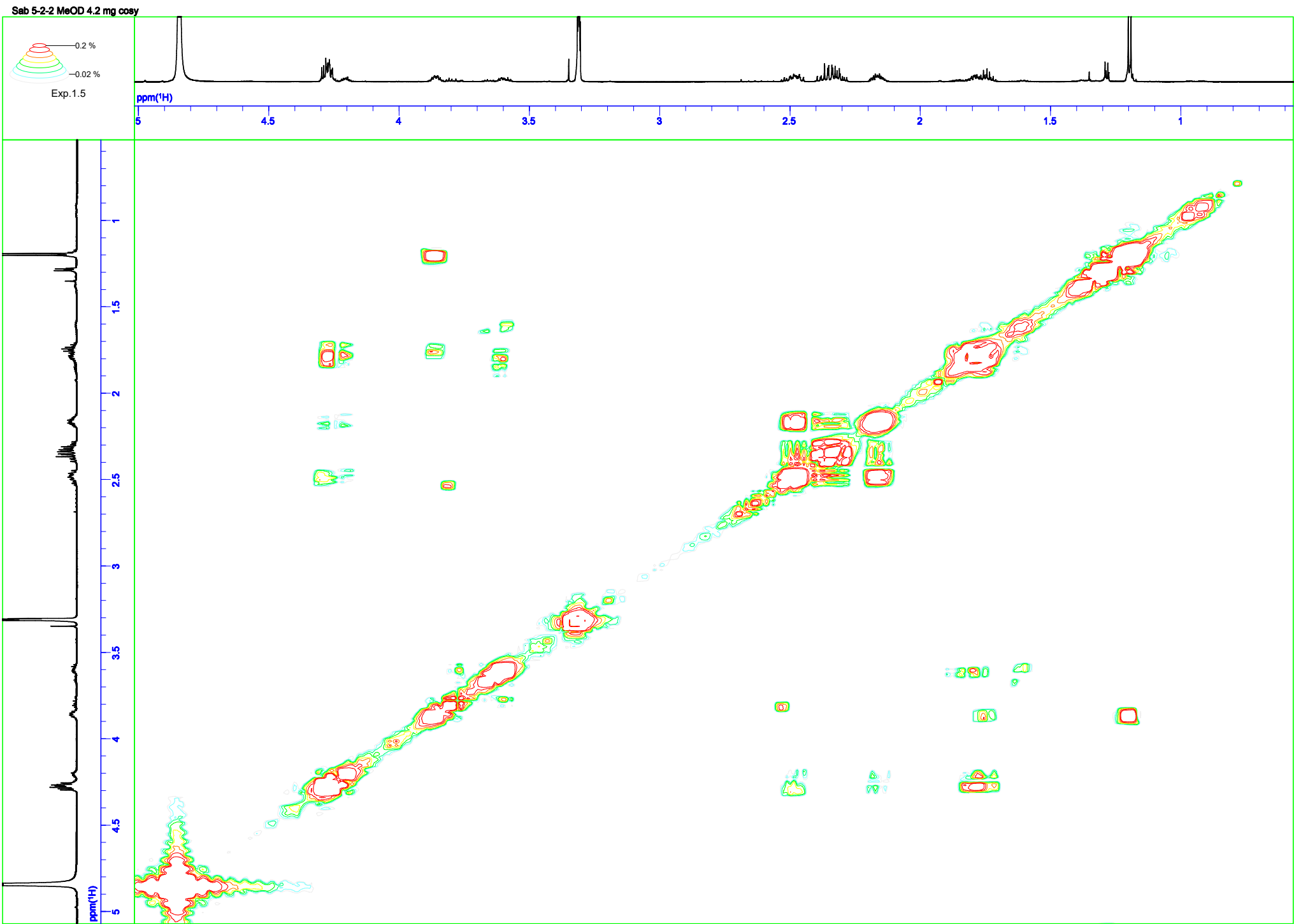


Figure S20 HSQC of compound 3 in 150 and 600 MHz, CD₃OD

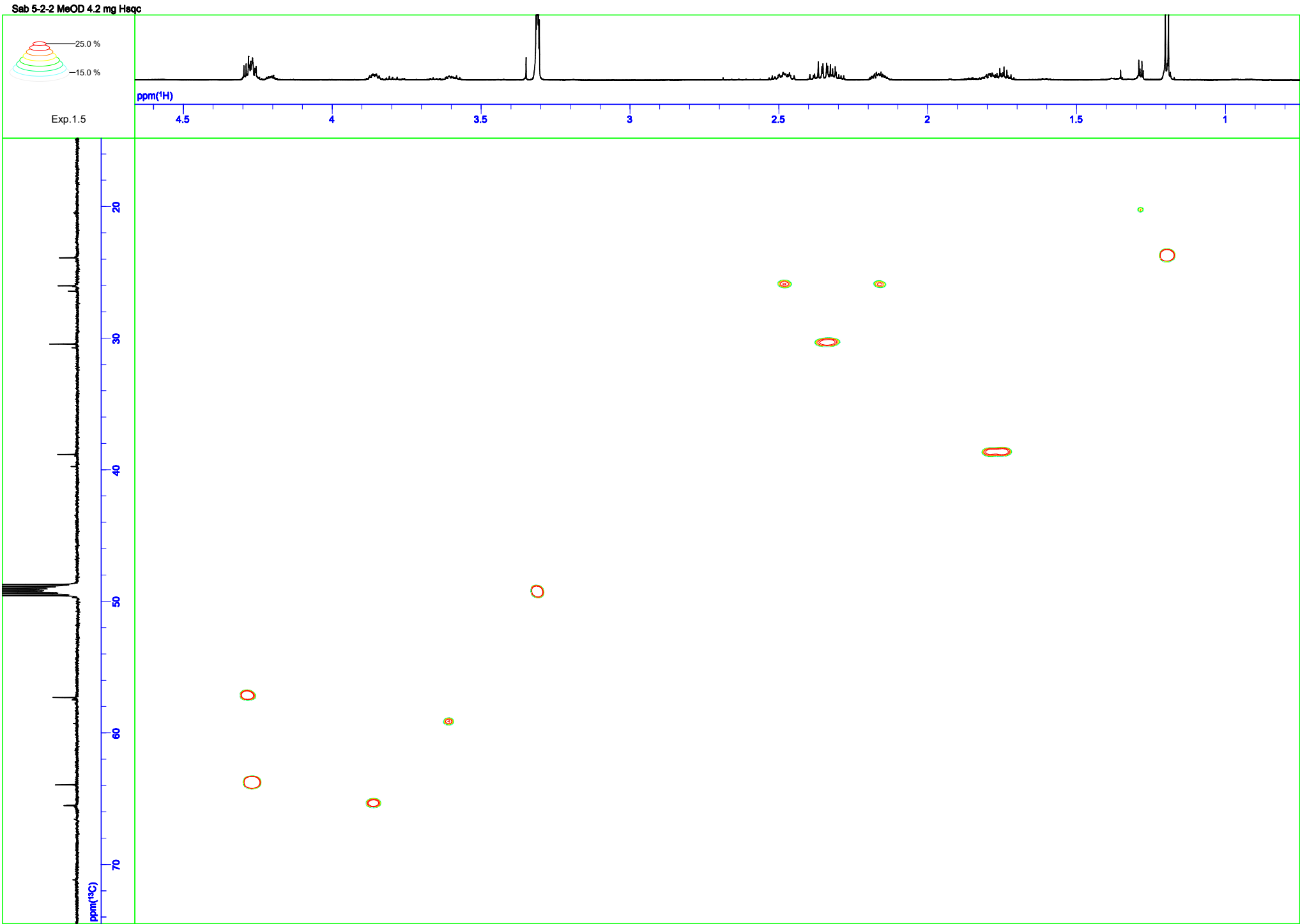


Figure S21 HMBC of compound 3 in 150 and 600 MHz, CD₃OD

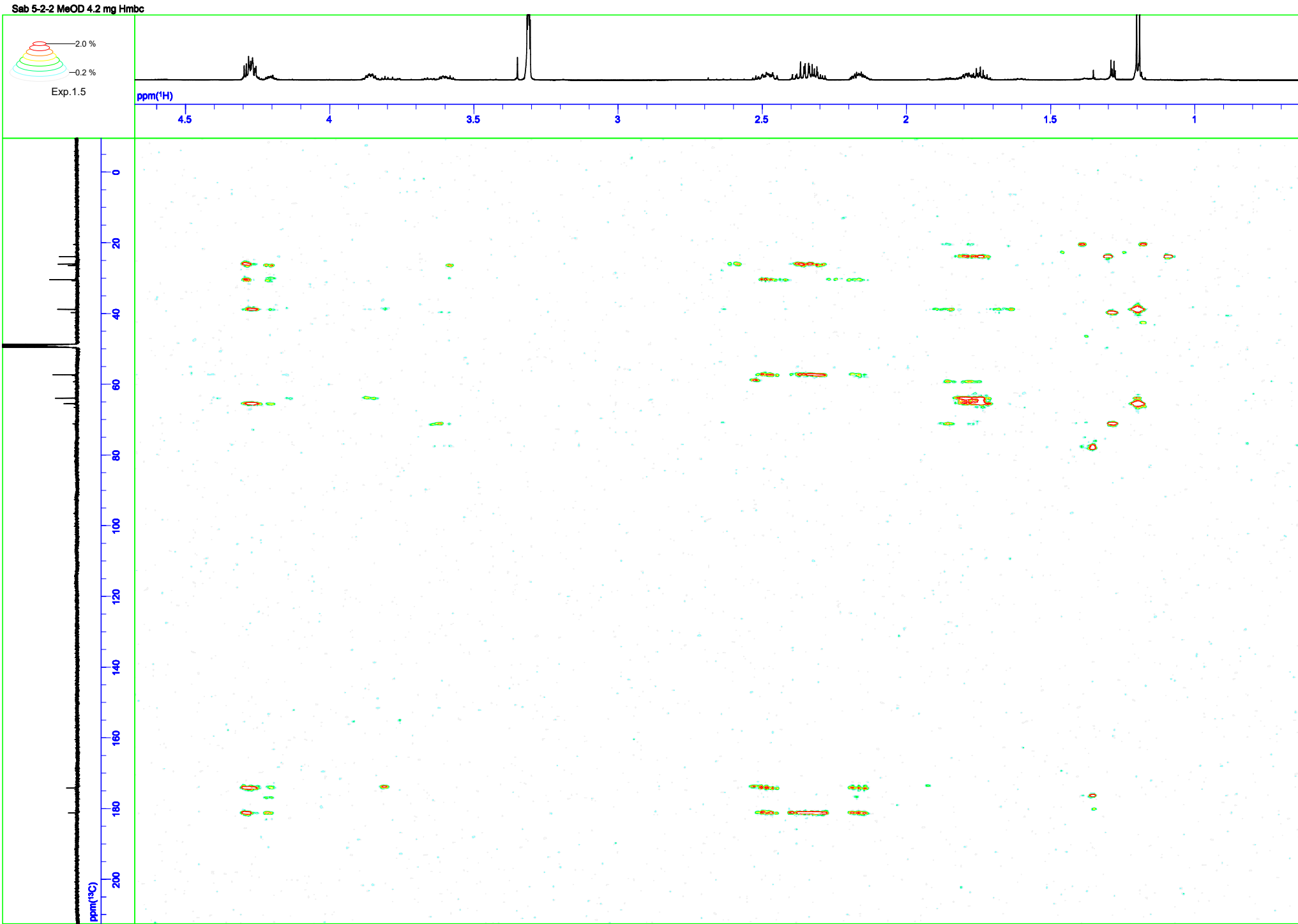


Figure S22 1H NMR of compound 4 in 600 MHz, CD₃OD

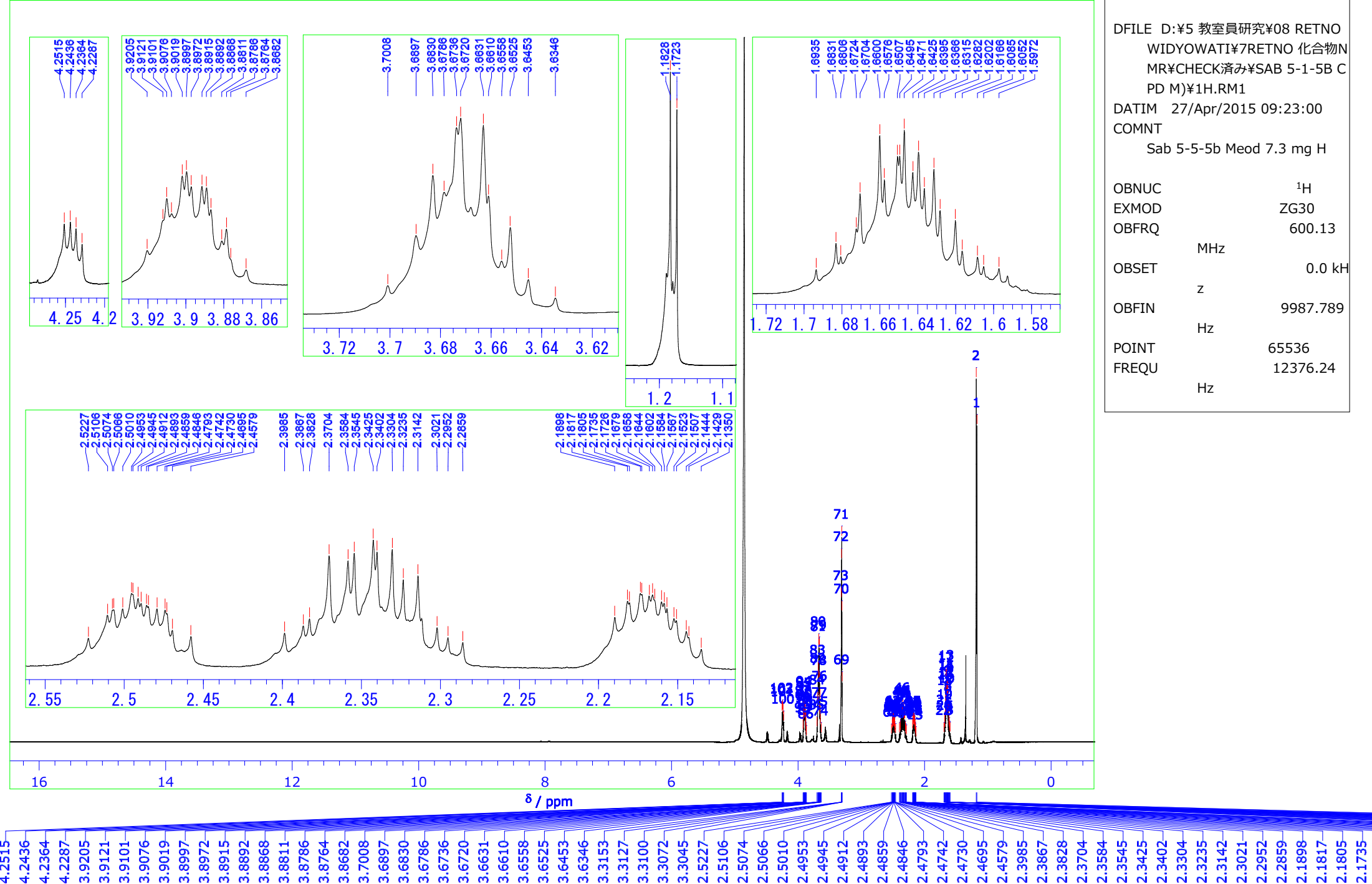
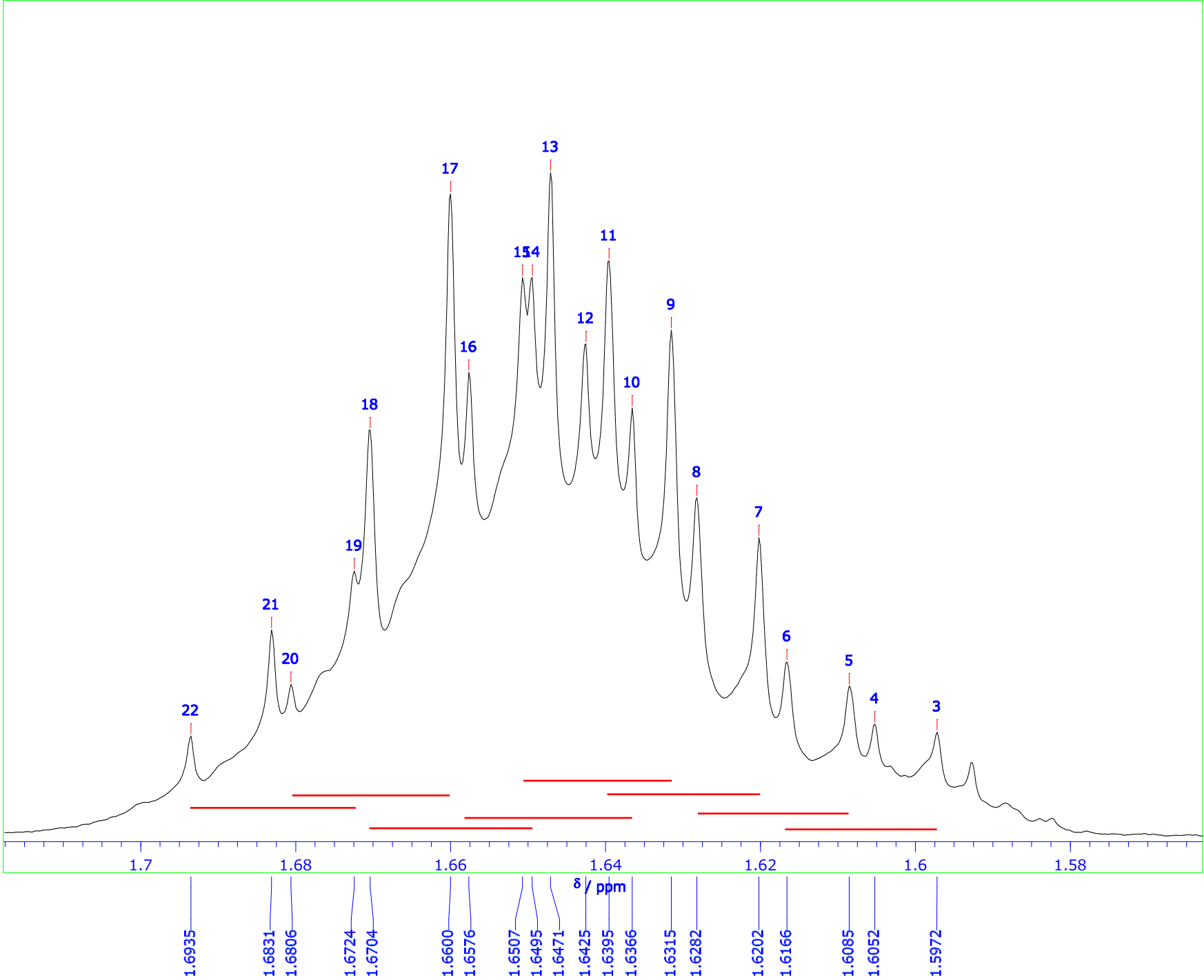
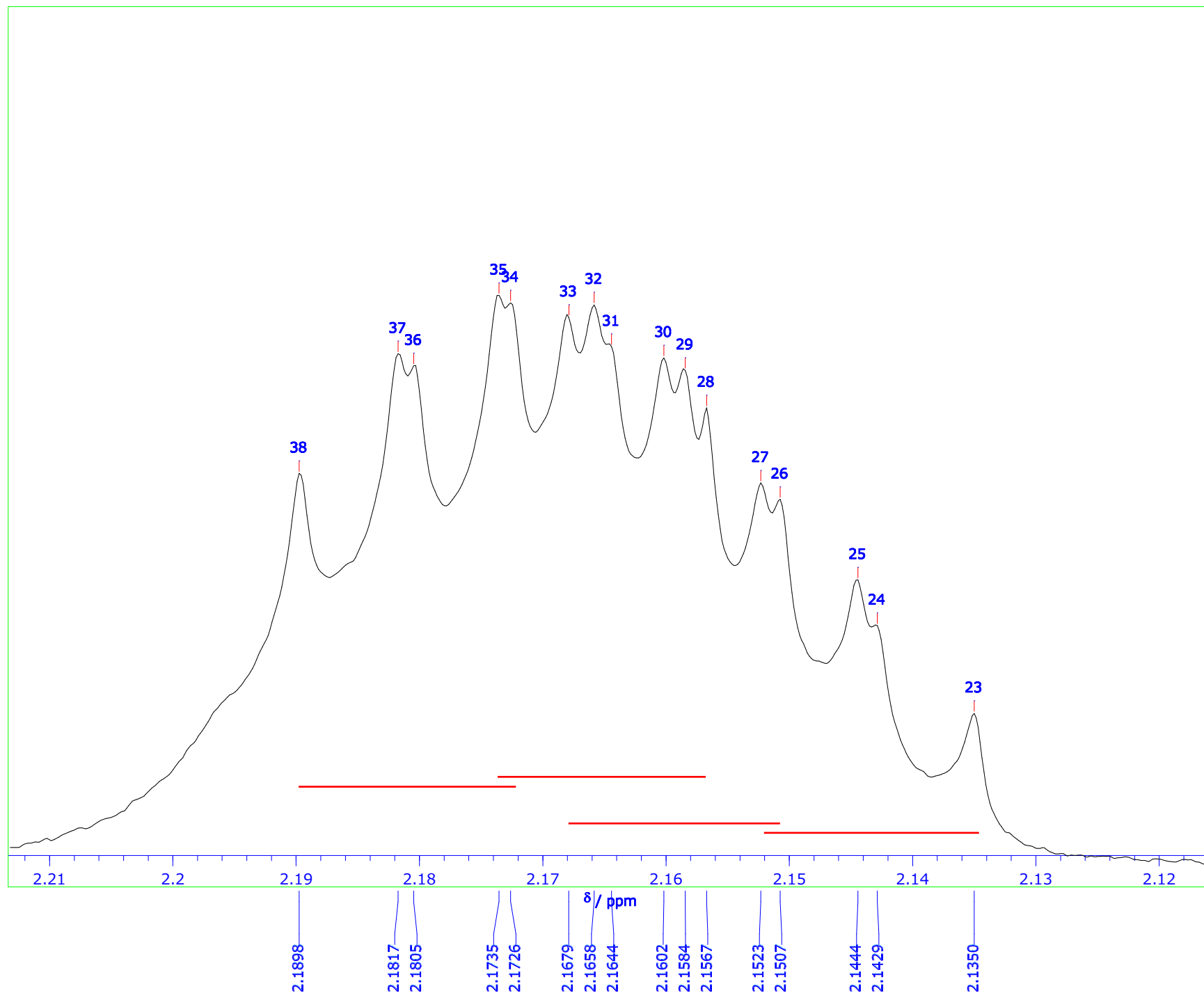


Figure S23 1H NMR (1.62 & 1.67 ppm) of compound 4 in 600 MHz, CD₃OD



DFILE	C:\¥USERS¥KMATS¥DESKTOP¥1
	H.RM1
DATIM	27/Apr/2015 09:23:00
COMNT	Sab 5-5-5b Meod 7.3 mg H
OBNUC	¹ H
EXMOD	ZG30
OBFRQ	600.13 MHz
OBSET	0.0 kHz
OBFIN	9987.789 Hz
POINT	65536
FREQU	12376.24 Hz
SCANS	8
ACQTM	5.2953 s
PD	1.0 s
PW1	10.0 µs
IRNUC	NUL
PROBHD	5 MM TXI 1H-13C/15N-D XY
	Z-GRD Z8
PULSPRG	ZG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	MEOD
EXREF	3.31 ppm
BF	0.0944 Hz
WINDOW	Exponential

Figure S24 ^1H NMR (2.17 ppm) of compound 4 in 600 MHz, CD_3OD

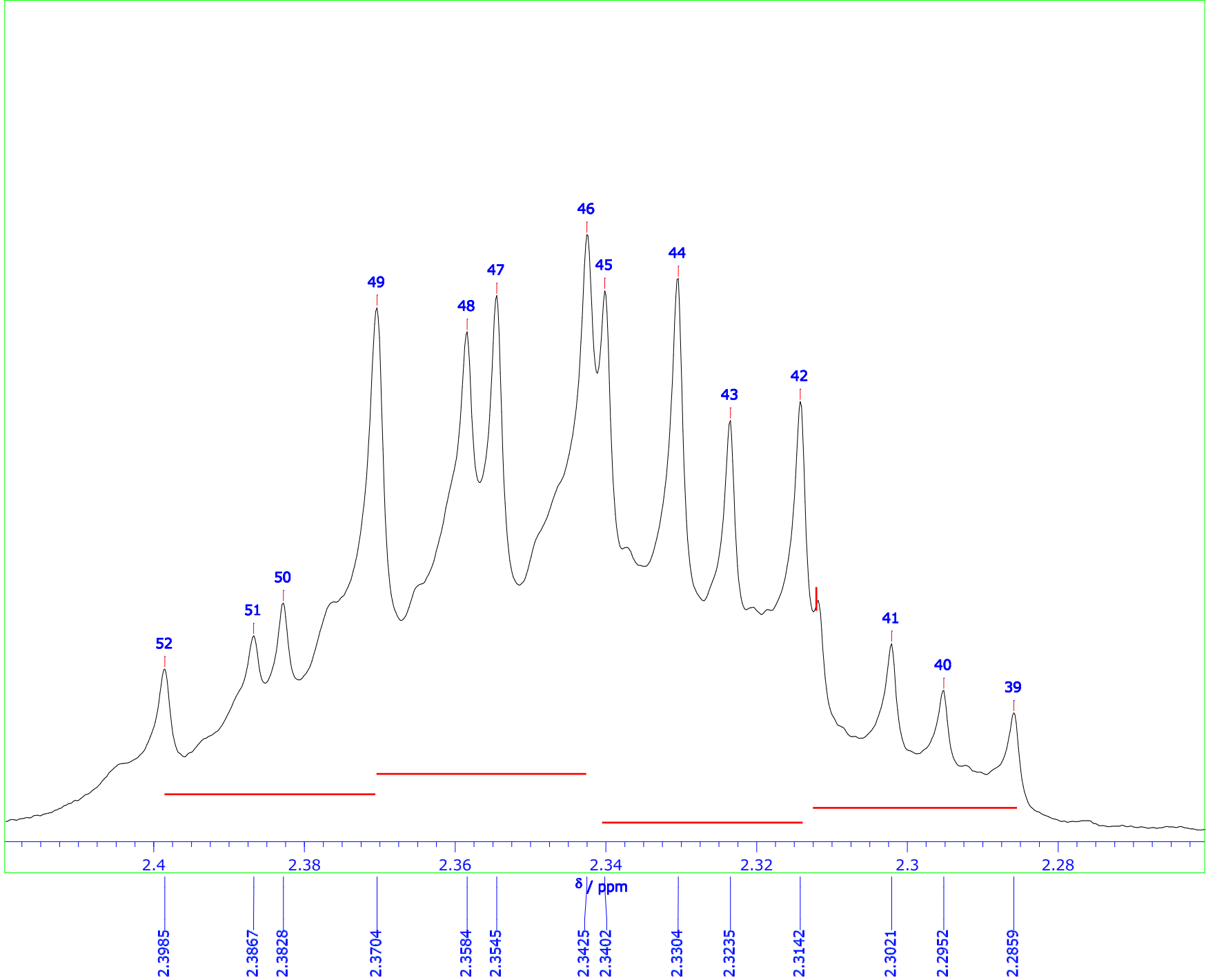


DFILE C:\¥USERS¥KMATS¥DESKTOP¥1
 H.RM1
 DATIM 27/Apr/2015 09:23:00
 COMNT
 Sab 5-5-5b Meod 7.3 mg H

OBNUC ^1H
 EXMOD ZG30
 OBFRQ 600.13 MHz
 OBSET 0.0 kHz
 OBFIN 9987.789 Hz
 POINT 65536
 FREQU 12376.24 Hz
 SCANS 8
 ACQTM 5.2953 s
 PD 1.0 s
 PW1 10.0 μs
 IRNUC NUL
 PROBHD 5 MM TXI ^1H - ^{13}C / ^{15}N -D XY
 Z-GRD Z8
 PULSPRG ZG30
 GRDPROG
 CTEMP 26.85 $^\circ\text{C}$
 SLVNT MEOD
 EXREF 3.31 ppm
 BF 0.0944 Hz

WINDOW Exponential

Figure S25 1H NMR (2.31 & 2.37 ppm) of compound 4 in 600 MHz, CD₃OD

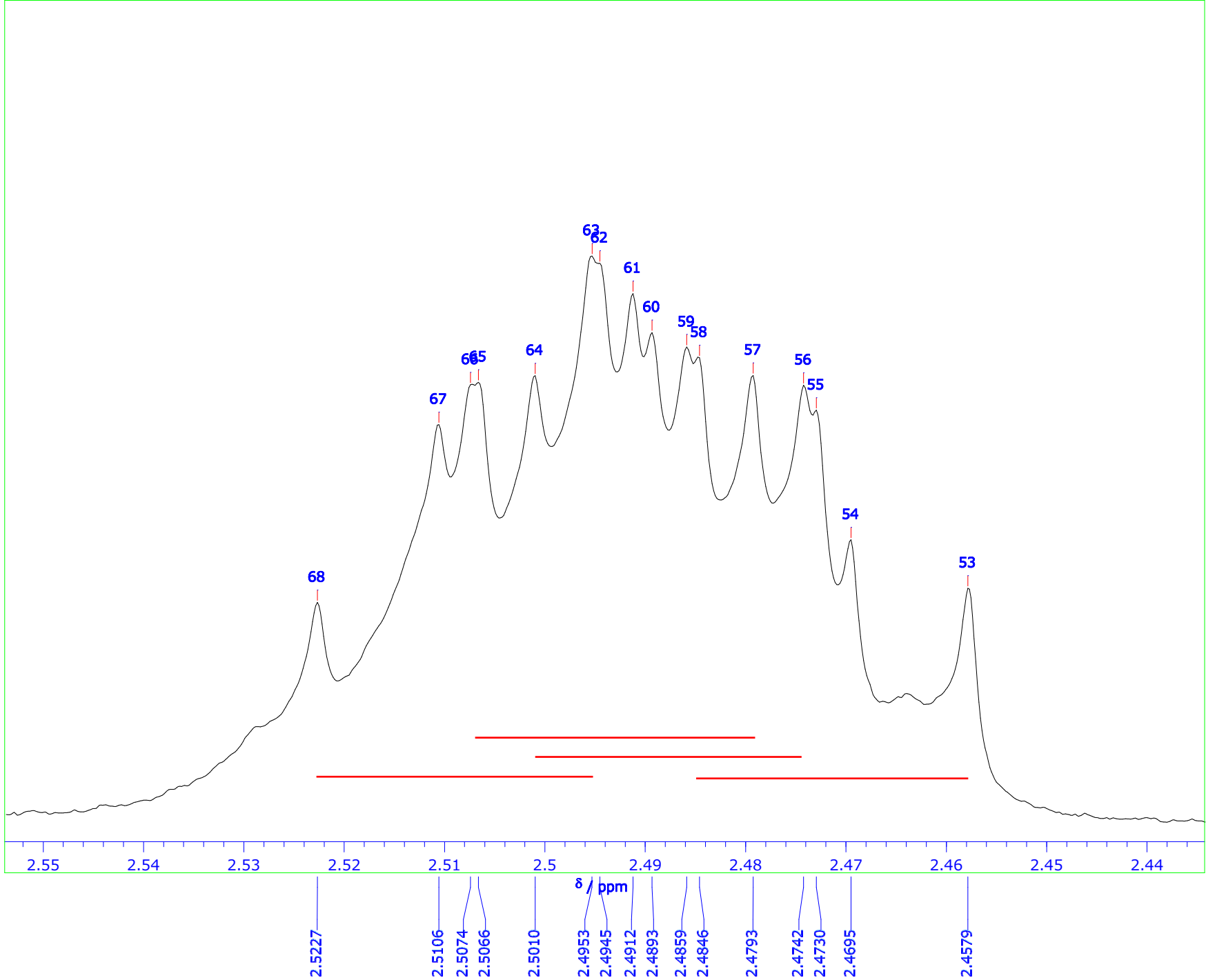


DFILE C:\¥USERS¥KMATS¥DESKTOP¥1
H.RM1
DATIM 27/Apr/2015 09:23:00
COMNT
Sab 5-5-5b Meod 7.3 mg H

OBNUC ¹H
EXMOD ZG30
OBFRQ 600.13 MHz
OBSET 0.0 kHz
OBFIN 9987.789 Hz
POINT 65536
FREQU 12376.24 Hz
SCANS 8
ACQTM 5.2953 s
PD 1.0 s
PW1 10.0 µs
IRNUC NUL
PROBHD 5 MM TXI 1H-13C/15N-D XY
Z-GRD Z8
PULSPRG ZG30
GRDPROG
CTEMP 26.85 °C
SLVNT MEOD
EXREF 3.31 ppm
BF 0.0944 Hz

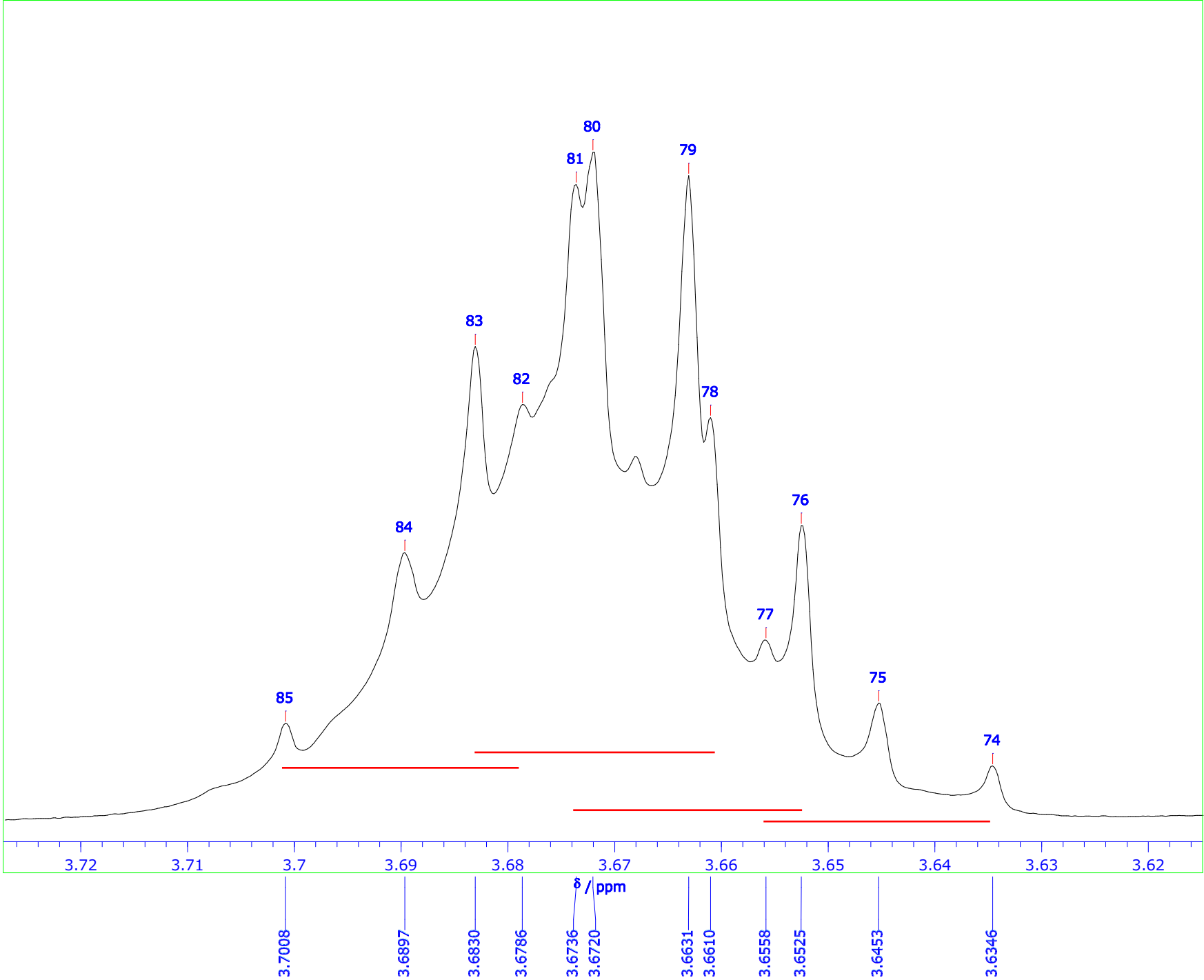
WINDOW Exponential

Figure S26 1H NMR (2.49 ppm) of compound 4 in 600 MHz, CD₃OD



DFILE	C:\USERS\KMATS\DESKTOP\1
	H.RM1
DATIM	27/Apr/2015 09:23:00
COMNT	Sab 5-5-5b Meod 7.3 mg H
OBNUC	¹ H
EXMOD	ZG30
OBFRQ	600.13 MHz
OBSET	0.0 kHz
OBFIN	9987.789 Hz
POINT	65536
FREQU	12376.24 Hz
SCANS	8
ACQTM	5.2953 s
PD	1.0 s
PW1	10.0 μs
IRNUC	NUL
PROBHD	5 MM TXI 1H-13C/15N-D XY
	Z-GRD Z8
PULSPRG	ZG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	MEOD
EXREF	3.31 ppm
BF	0.0944 Hz
WINDOW	Exponential

Figure S27 1H NMR (3.65 & 3.68 ppm) of compound 4 in 600 MHz, CD₃OD

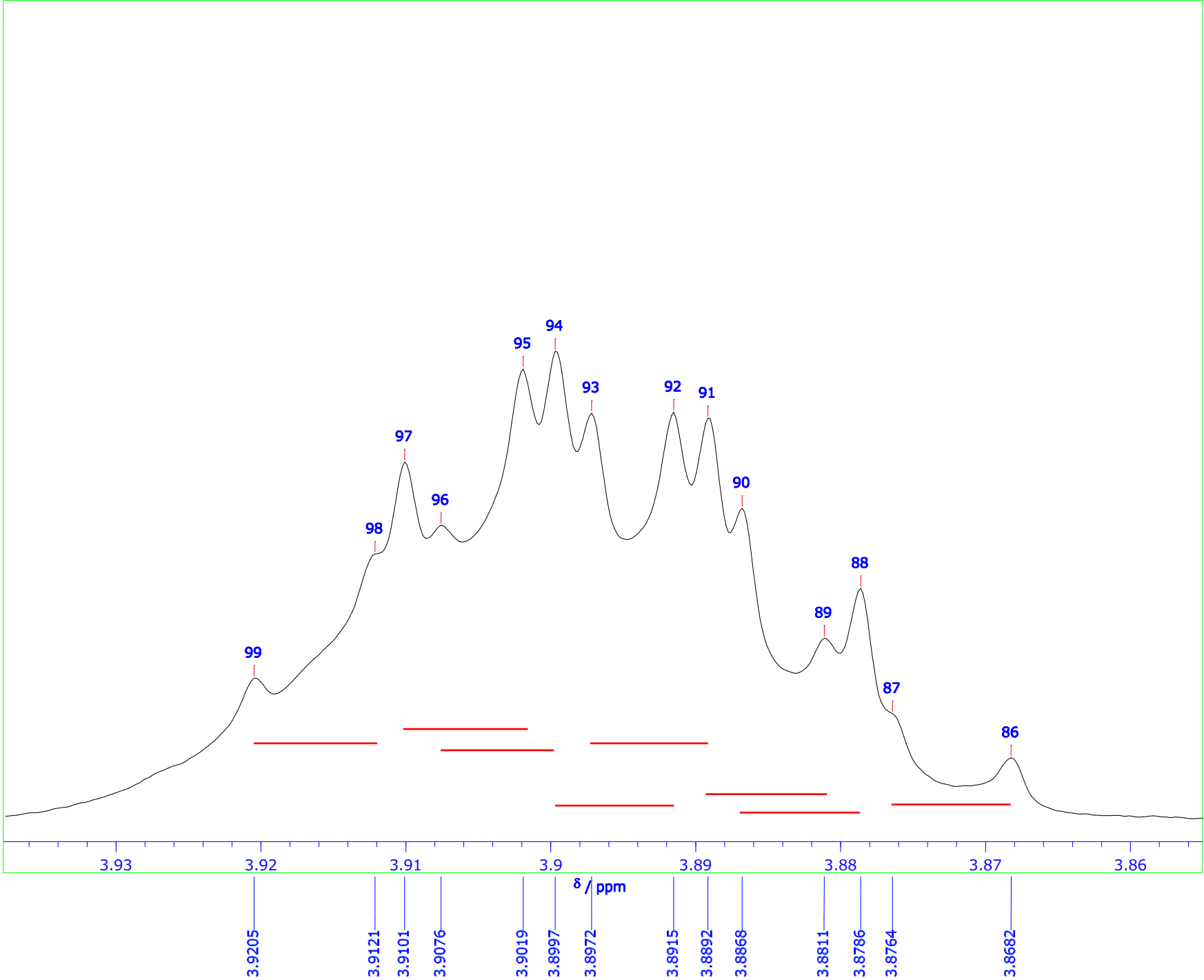


DFILE C:\¥USERS¥KMATS¥DESKTOP¥1
H.RM1
DATIM 27/Apr/2015 09:23:00
COMNT
Sab 5-5-5b Meod 7.3 mg H

OBNUC ¹H
EXMOD ZG30
OBFRQ 600.13 MHz
OBSET 0.0 kHz
OBFIN 9987.789 Hz
POINT 65536
FREQU 12376.24 Hz
SCANS 8
ACQTM 5.2953 s
PD 1.0 s
PW1 10.0 µs
IRNUC NUL
PROBHD 5 MM TXI 1H-13C/15N-D XY
Z-GRD Z8
PULSPRG ZG30
GRDPROG
CTEMP 26.85 °C
SLVNT MEOD
EXREF 3.31 ppm
BF 0.0944 Hz

WINDOW Exponential

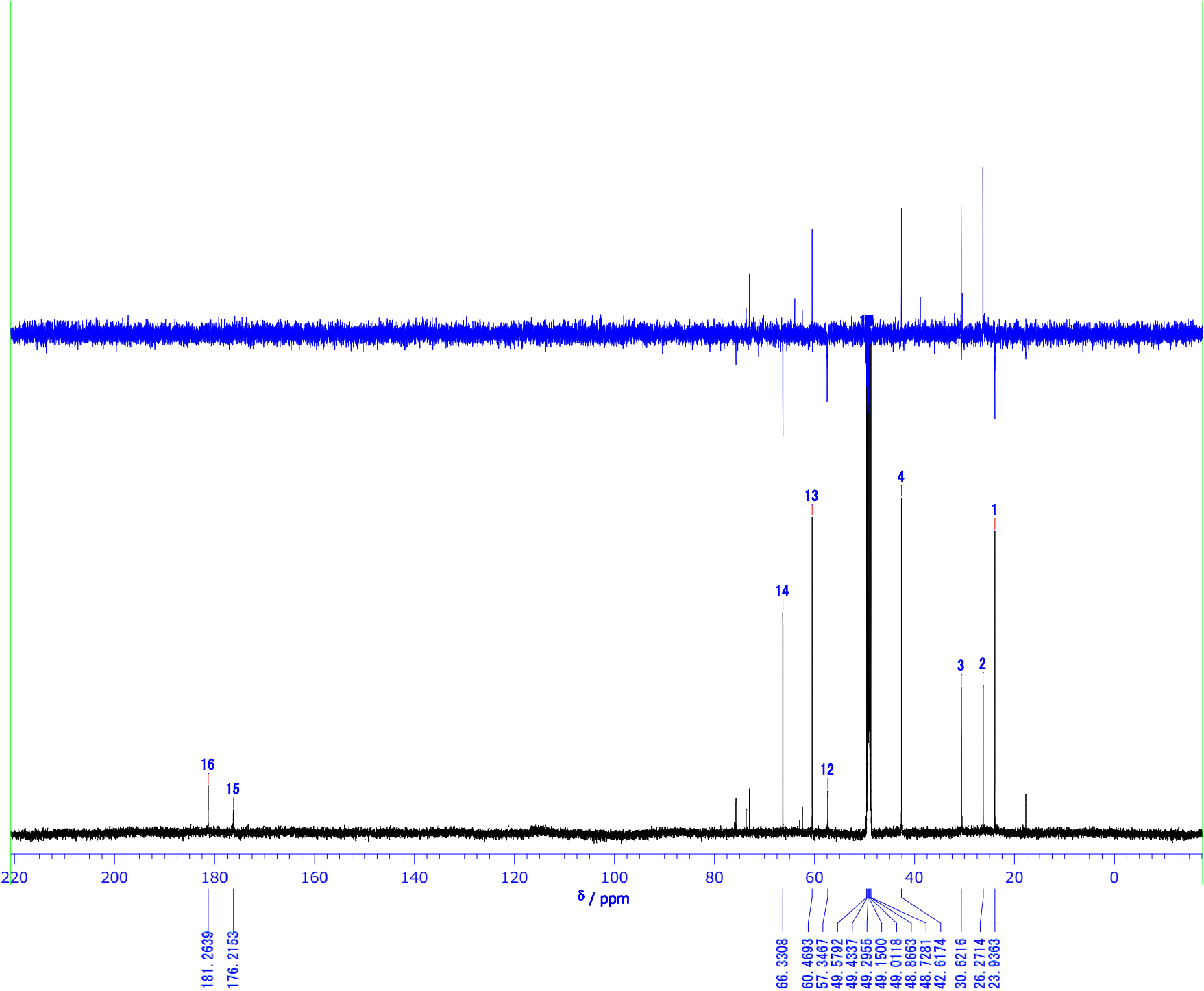
Figure S28 1H NMR (3.89 ppm) of compound 4 in 600 MHz, CD₃OD



DFILE D:\¥5 教室員研究¥08 RETNO WID
YOWATI¥7RETNO 化合物NMR¥CH
ECK済み¥SAB 5-1-5B CPD M)¥1H.
RM1
DATIM 27/Apr/2015 09:23:00
COMNT
Sab 5-5-5b Meod 7.3 mg H

OBNUC ¹H
EXMOD ZG30
OBFRQ 600.13 MHz
OBSET 0.0 kHz
OBFIN 9987.789 Hz
POINT 65536
FREQU 12376.24 Hz
SCANS 8
ACQTM 5.2953 s
PD 1.0 s
PW1 10.0 µs
IRNUC ??
PROBHD 5 MM TXI 1H-13C/15N-D XY
Z-GRD Z8
PULSPRG ZG30
GRDPROG
CTEMP 26.85 °C
SLVNT MEOD
EXREF 3.31 ppm
BF 0.0944 Hz

Figure S29 13C NMR of compound 4 in 150 MHz, CD₃OD



ファイル名 D:\¥5 教室員研究¥08 RETNO WI
DYOWATI¥7RETNO 化合物NMR¥C
HECK済み¥SAB 5-1-5B CPD M)¥1
3C&DEPT.RM1
初期ファイル名 D:\¥5 教室員研究¥08 RETNO
WIDYOWATI¥7RETNO 化合物NM
R¥CHECK済み¥SAB 5-1-5B CPD M
)¥23 13C¥PDATA¥1¥1R
測定日時 17/Apr/2015 00:05:05
注釈
Sab 5-1-5b MeOD 7.3 mg c

観測核種 ¹³C
測定モード ZPGPG30
観測周波数(粗) 150.9 MHz
観測周波数offset 0.0 kHz
観測周波数Fine 10000.86 Hz
データ点数 32768
観測範囲 35971.22 Hz
実積算回数 5759
FID取込時間 0.911 s
待ち時間 0.0 s
パルス幅 15.0 μ s
decouple核種 ??
プログラム 5 MM TXI 1H-13C/15N-D XYZ-
GRD Z8
装置 DRX600
パルスプログラム ZPGPG30
Gradientプログラム
試料温度 26.85 $^{\circ}$ C
測定溶媒 MEOD
Chemical shift参照値 49.15 ppm
Broadening係数 0.5489 H

Figure S30 COSY of compound 4 in 600 MHz, CD₃OD

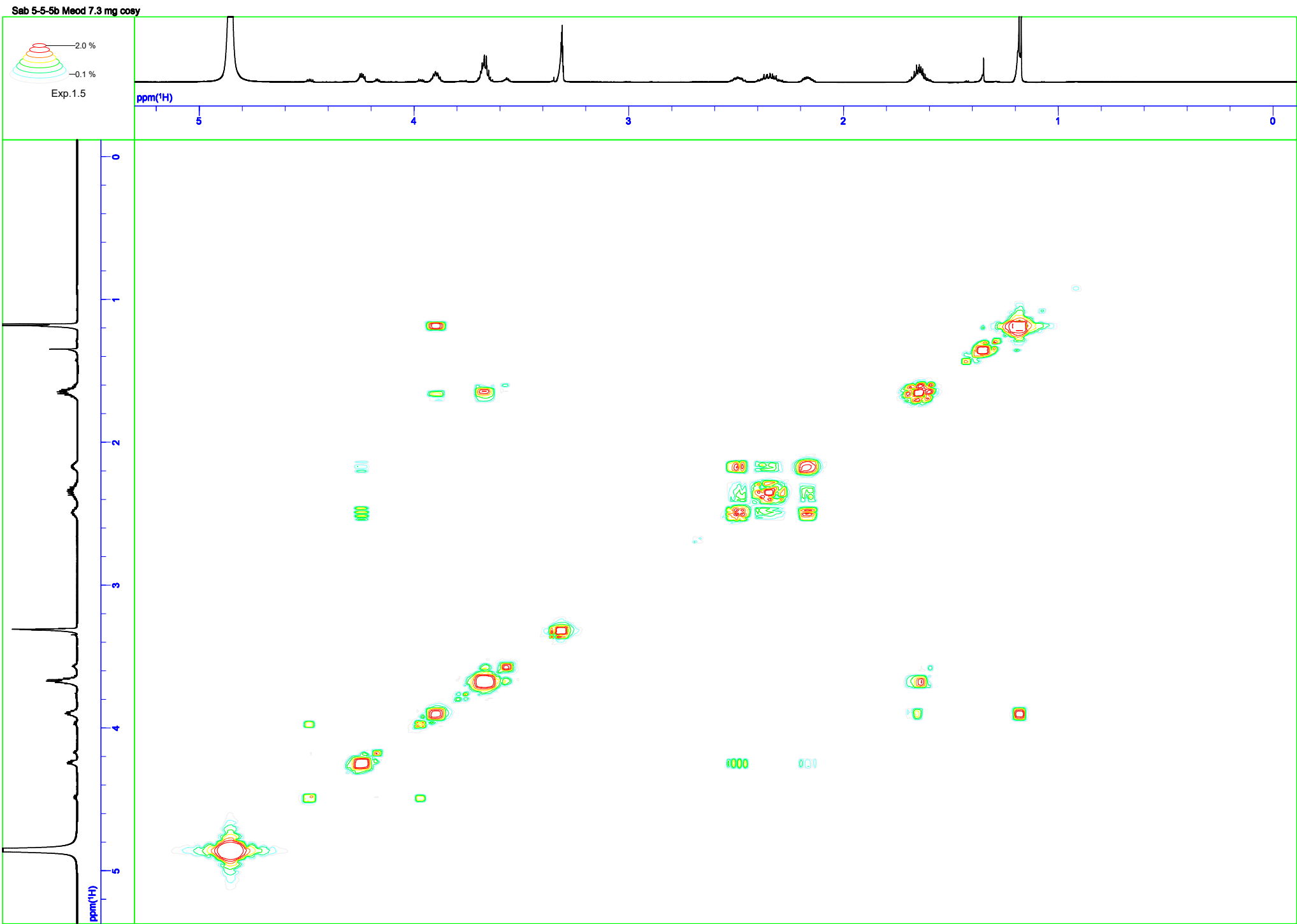


Figure S31 HSQC of compound 4 in 150 and 600 MHz, CD₃OD

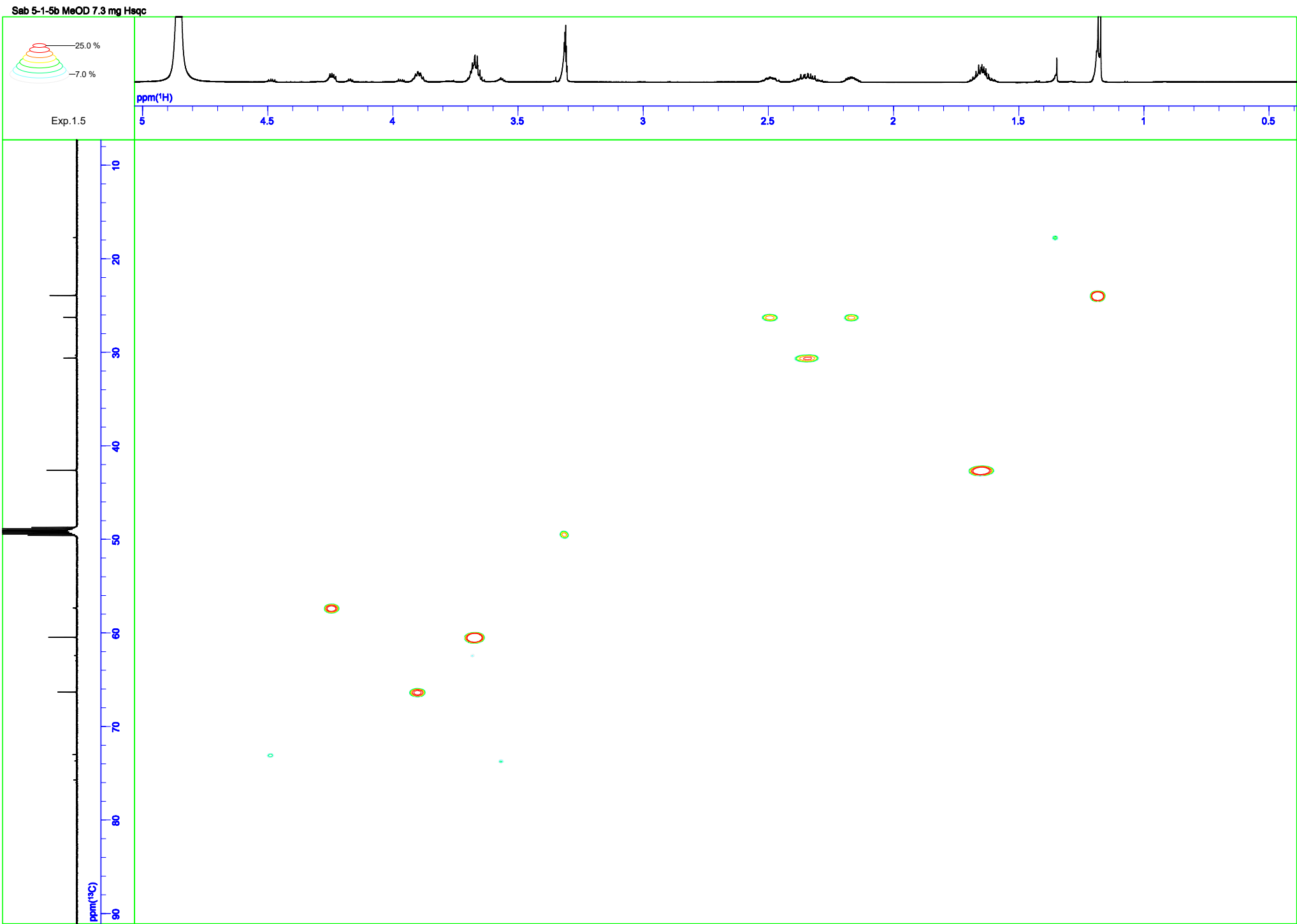


Figure S32 HMBC of compound 4 in 150 and 600 MHz, CD₃OD

