

Supporting Information

Direct Evidence of Superexchange Interaction of Energy Transfer in Zinc(II) Porphyrin -Free Base Porphyrin Dimers: Comparison of *m*- and *p*-di(phenylethynyl)-phenylene linked Dimers

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Identification data for porphyrin dimers

m-FbFb

- S1 Elemental analysis
- S2 ¹H-NMR spectrum
- S3 MASS Spectrum data
- S4 IR spectra

m-ZnFb (1)

- S5 ¹H-NMR spectrum
- S6 MASS Spectrum data

p-FbFb

- S7 Elemental analysis
- S8 ¹H-NMR spectrum MASS Spectrum data
- S9 MASS Spectrum data
- S10 IR spectrum

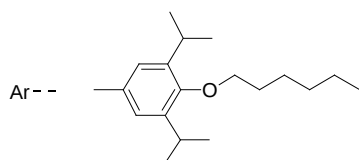
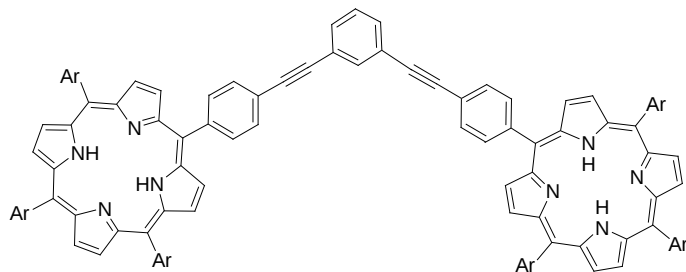
p-ZnFb (2)

- S11 ¹H-NMR spectrum
- S12 MASS spectrum

Geometrical parameters for averaging the orientation factor

- S13

1,3-bis((4-(10,15,20-tris(4-hexyloxy-3,5-diisopropylphenyl)porphyrin-5-yl)phenyl)ethynyl)benzene (*m*-FbFb)



- S1 Elemental analysis
- S2 ^1H -NMR spectrum data
- S3 MASS Spectrum data
- S4 IR spectra

S1: Data for elemental analysis of *m*-FbFb

Calcd. for $\text{C}_{170}\text{H}_{206}\text{N}_8\text{O}_6$ (mol wt 2457.50): C, 83.09; H, 8.45; N, 4.56.

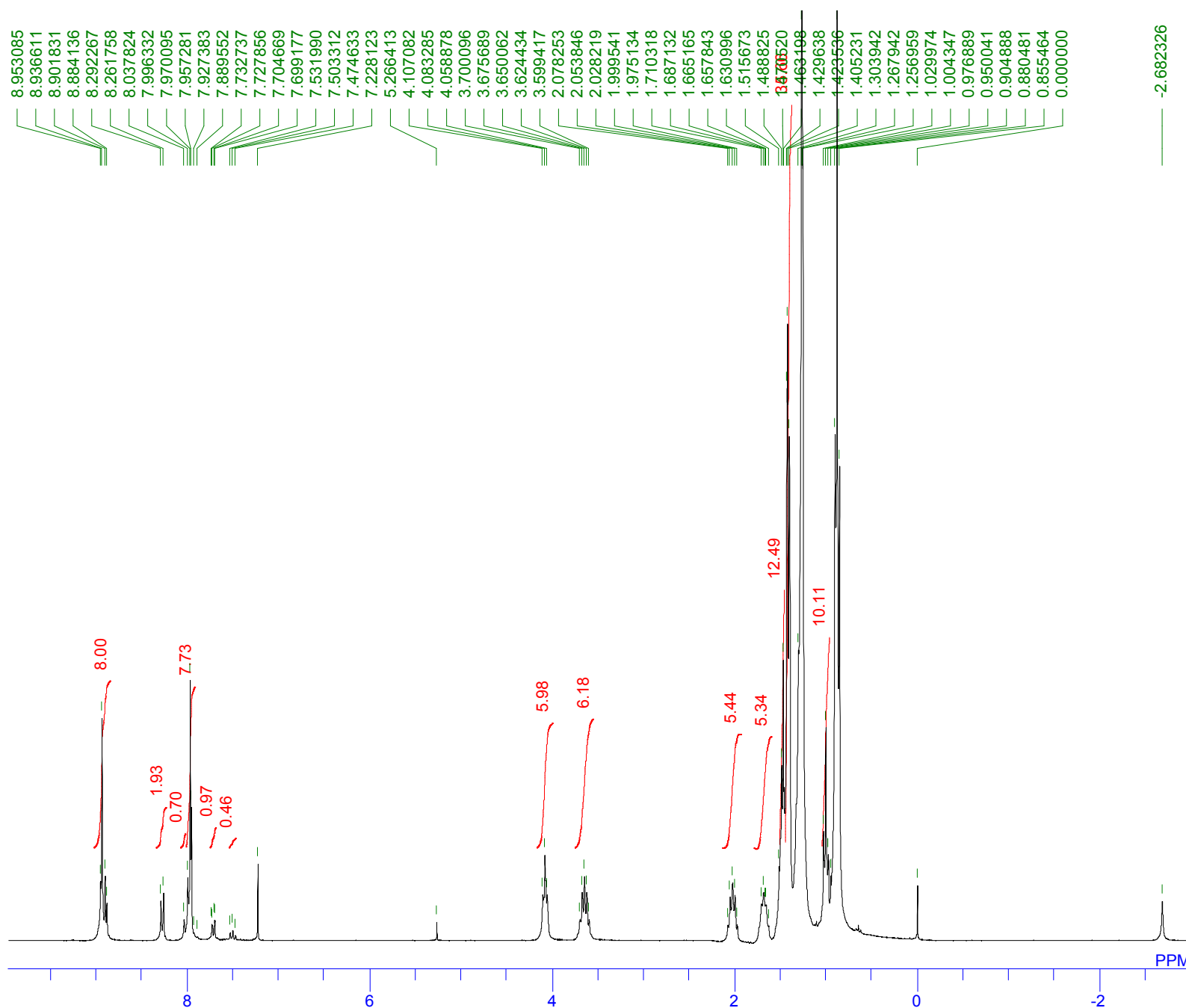
Found: C, 83.04; H, 8.61; N, 4.47.

S2 ^1H -NMR spectrum data of *m*-FbFb

S2-1 ^1H -NMR(270MHz, CDCl_3) JEOL Excalibur-270

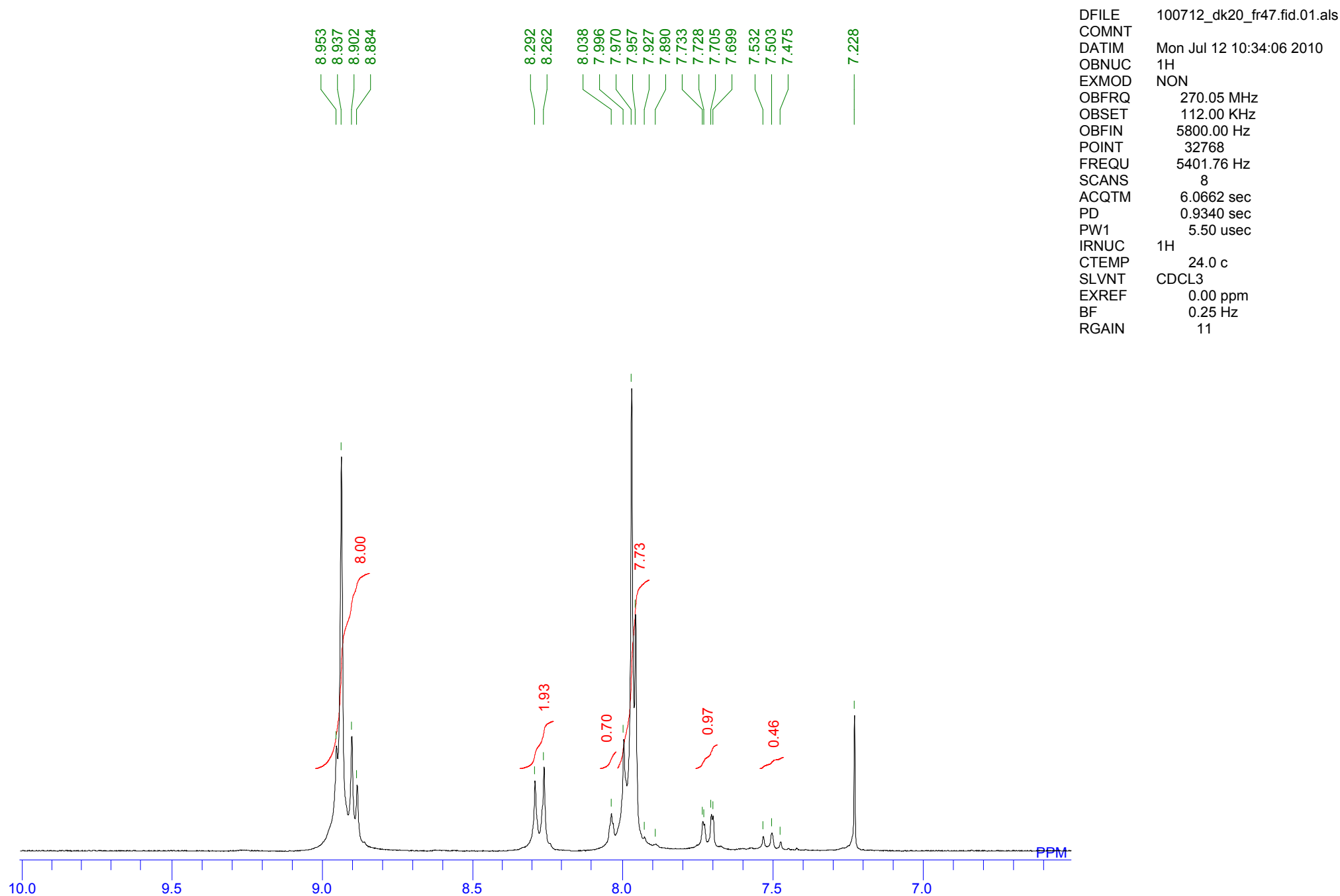
δ = 8.94 (4H, d, J = 4.8 Hz),
8.93₇ (8H, s),
8.87 (4H, d, J = 4.8 Hz),
8.28 (4H, d, J = 8.2 Hz),
8.04 (1H, bs),
8.00 - 7.93 (16H, m),
7.72 (2H, d, J = 7.7 Hz),
7.50 (1H, t, J = 7.7 Hz),
4.11 - 4.05 (12H, m),
3.65 (12H, quintet, , J = 6.9 Hz),
2.03 (12H, quintet, J = 6.9 Hz),
1.68 (12H, m),
1.50-1.38 (96H, m),
1.00 (18H, t, J = 6.9 Hz),
-2.68 (2H, bs) ppm.

S2-2 ¹H-NMR *mFbFb* □ □ □ □ □ □ □ □ □ □

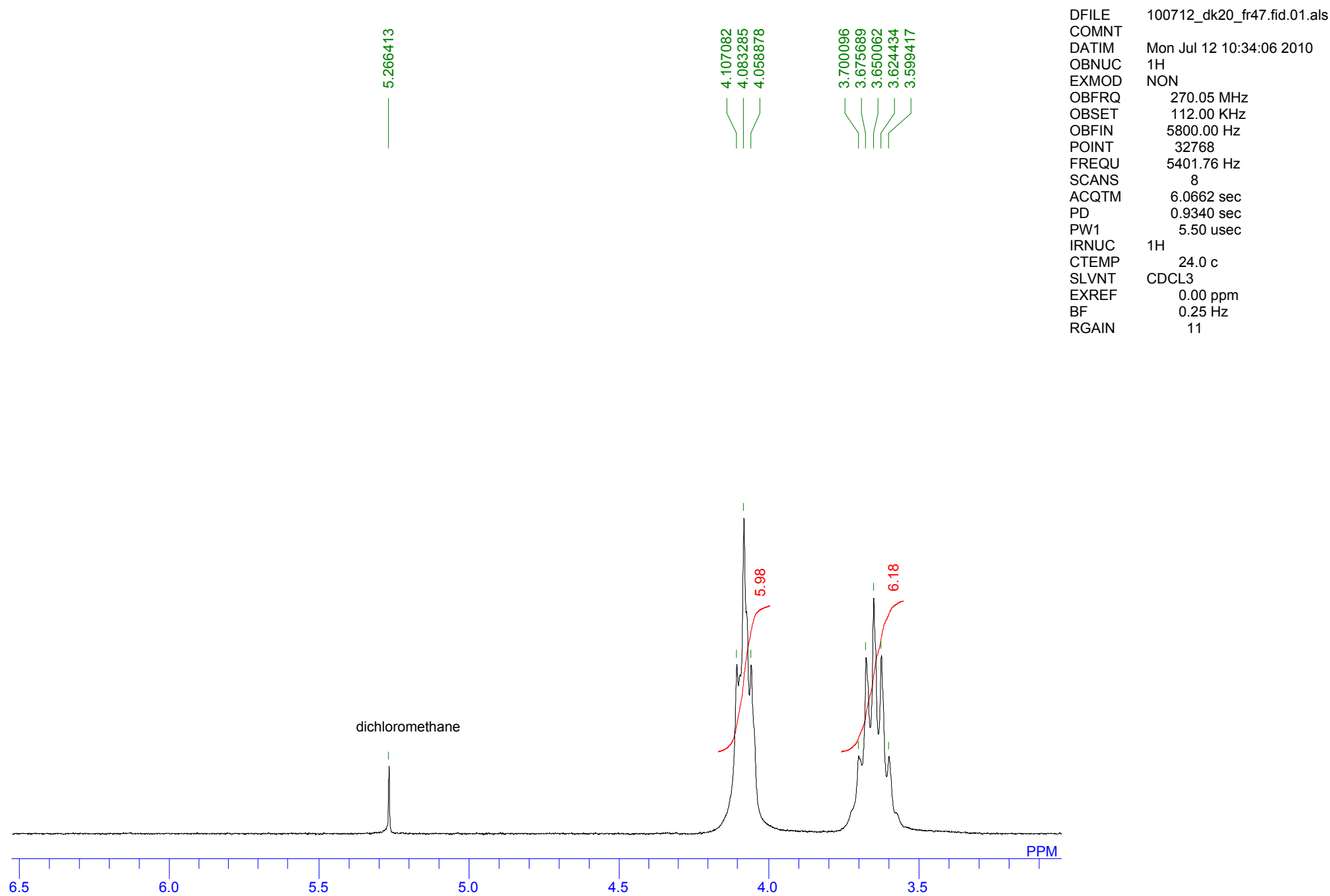


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 EXMOD NON
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 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 8
 ACQTM 6.0662 sec
 PD 0.9340 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 24.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.25 Hz
 RGAIN 11

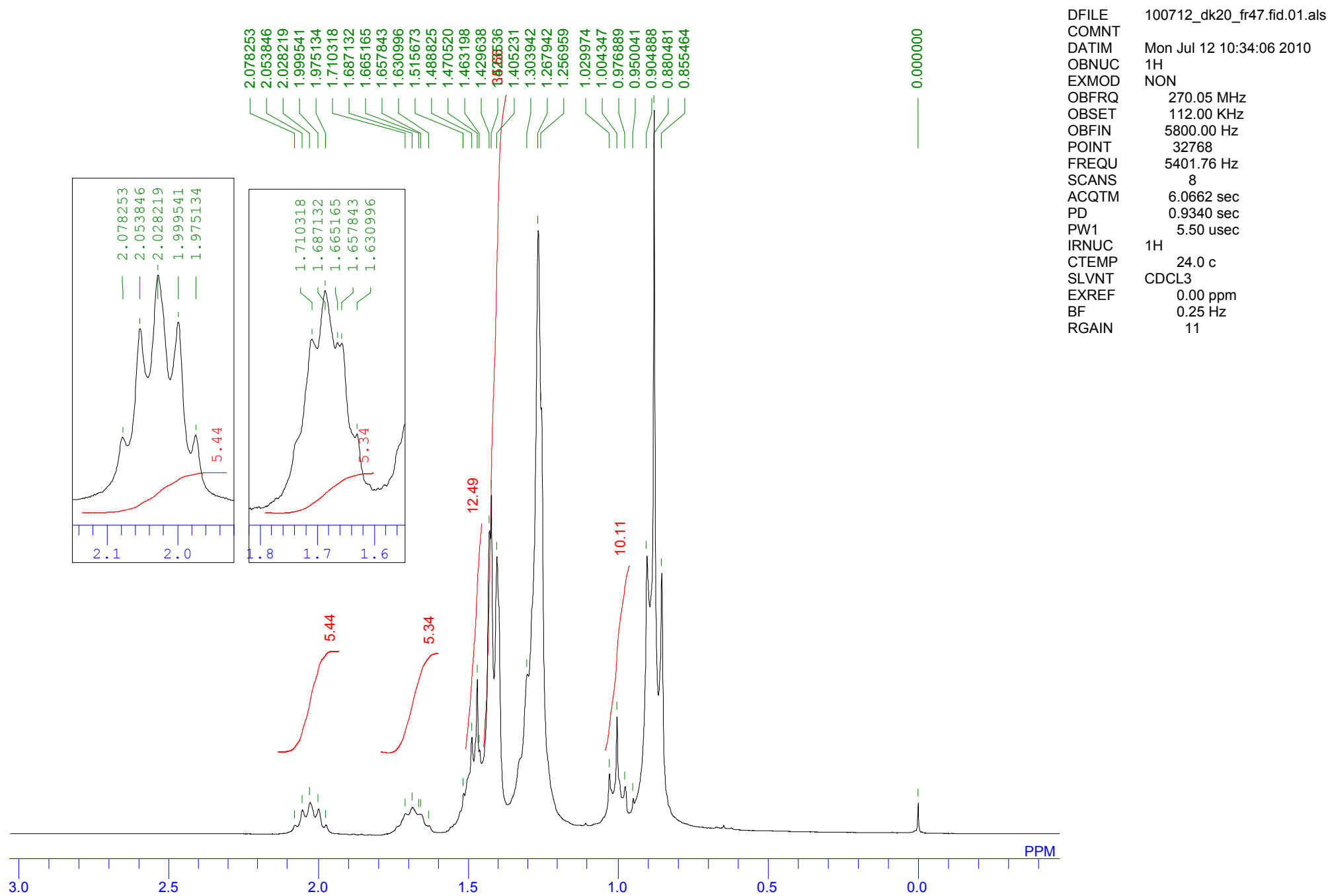
•S2-3 ^1H -NMR *m*FbFb



•S2-4 ^1H -NMR of *m*FbFb



•S2-5 ^1H -NMR of *m*-FbFb



S3 MASS Spectrum data of *m*-FbFb

Kratos Analytical KOMPACT PROBE spectrometer

Dithranol (1,8-dihydroxy-9(10H)-anthracenone, Sigma-Aldrich Co. Ltd.)

Exact mass for $C_{17}H_{12}O_6$ = 245.06

observed $[M^+]$ 245

dAcP&line2P_GPC@DT

Data: methaH2H2_DT75_high_best_0001.14 24 Mar 2010 20:43 Cal: tof 23 Mar 2010 5:12

Kratos PCKompact Probe V1.2.2: + Linear High, Power: 75, P.Ext. @ 2457 (bin 58)

• S3-1 MALDI TOF Mass Spectra of mFbFb

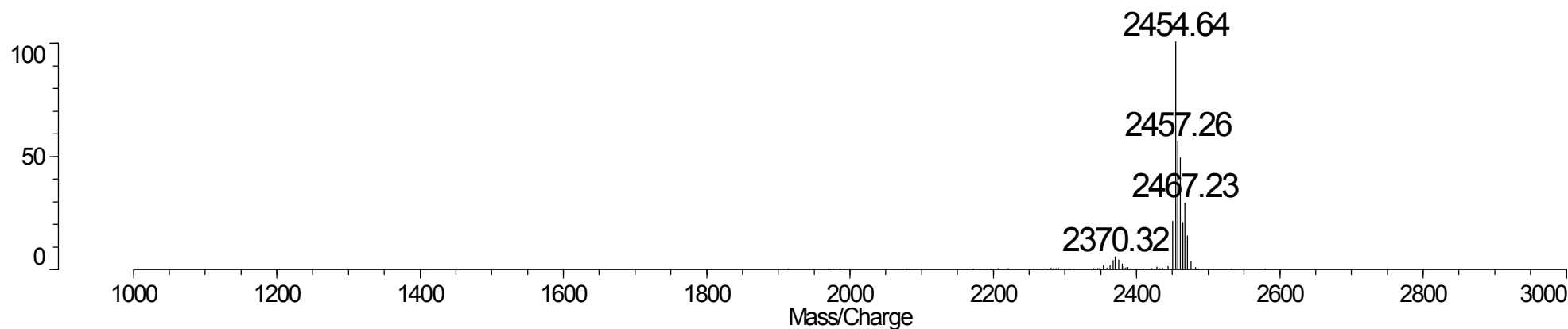
%Int. 100% = 45 mV Profile 100



%Int. 100% = 45 mV[sum= 4510 mV] Profiles 1-100 Unsmoothed



%Int. 100% = 15369 mV Profiles 1-100:



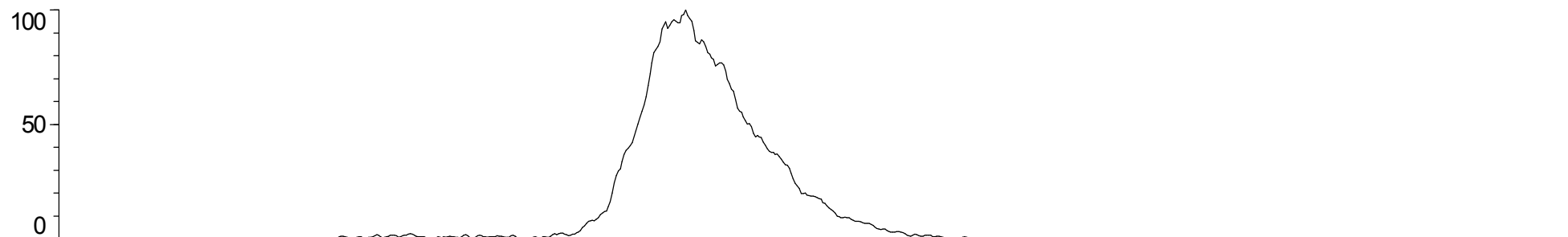
S3-2 MALDI TOF Mass Spectra of mFbFb

dAcP&line2P_GPC@DT

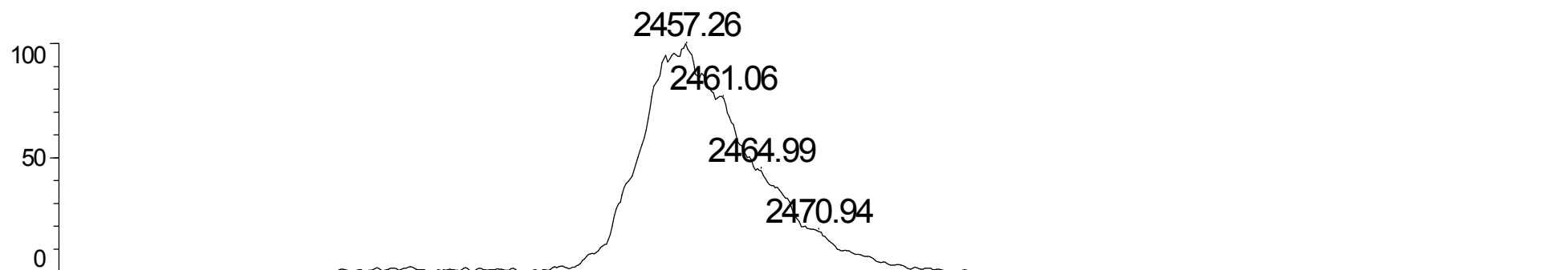
Data: methaH2H2_DT75_high_best_0001.14 24 Mar 2010 20:43 Cal: tof 23 Mar 2010 5:12

Kratos PCKompact Probe V1.2.2: + Linear High, Power: 75, P.Ext. @ 2457 (bin 58)

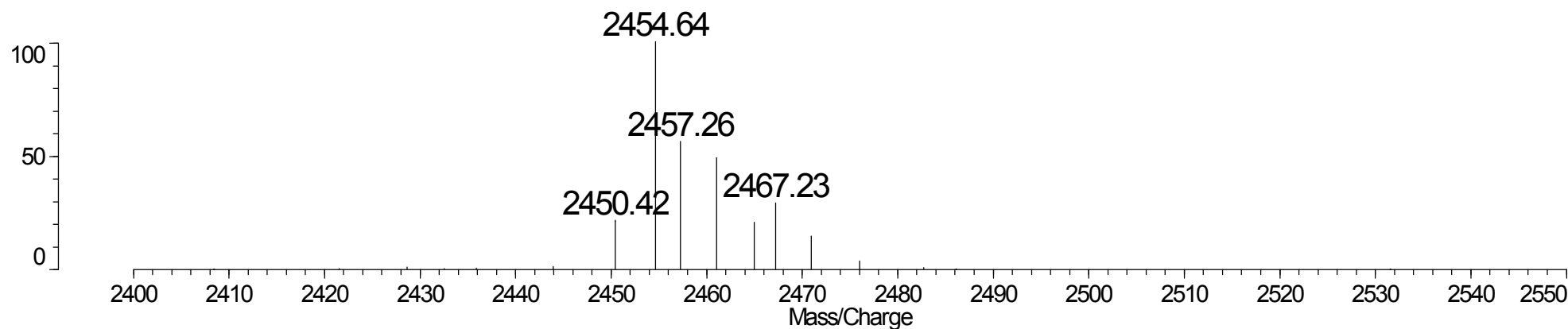
%Int. 100% = 45 mV Profile 100



%Int. 100% = 45 mV[sum= 4510 mV] Profiles 1-100 Unsmoothed



%Int. 100% = 15369 mV Profiles 1-100:



S4 IR spectra of *m*-FbFb

Shimadzu FTIR-8400 Infrared spectrometer

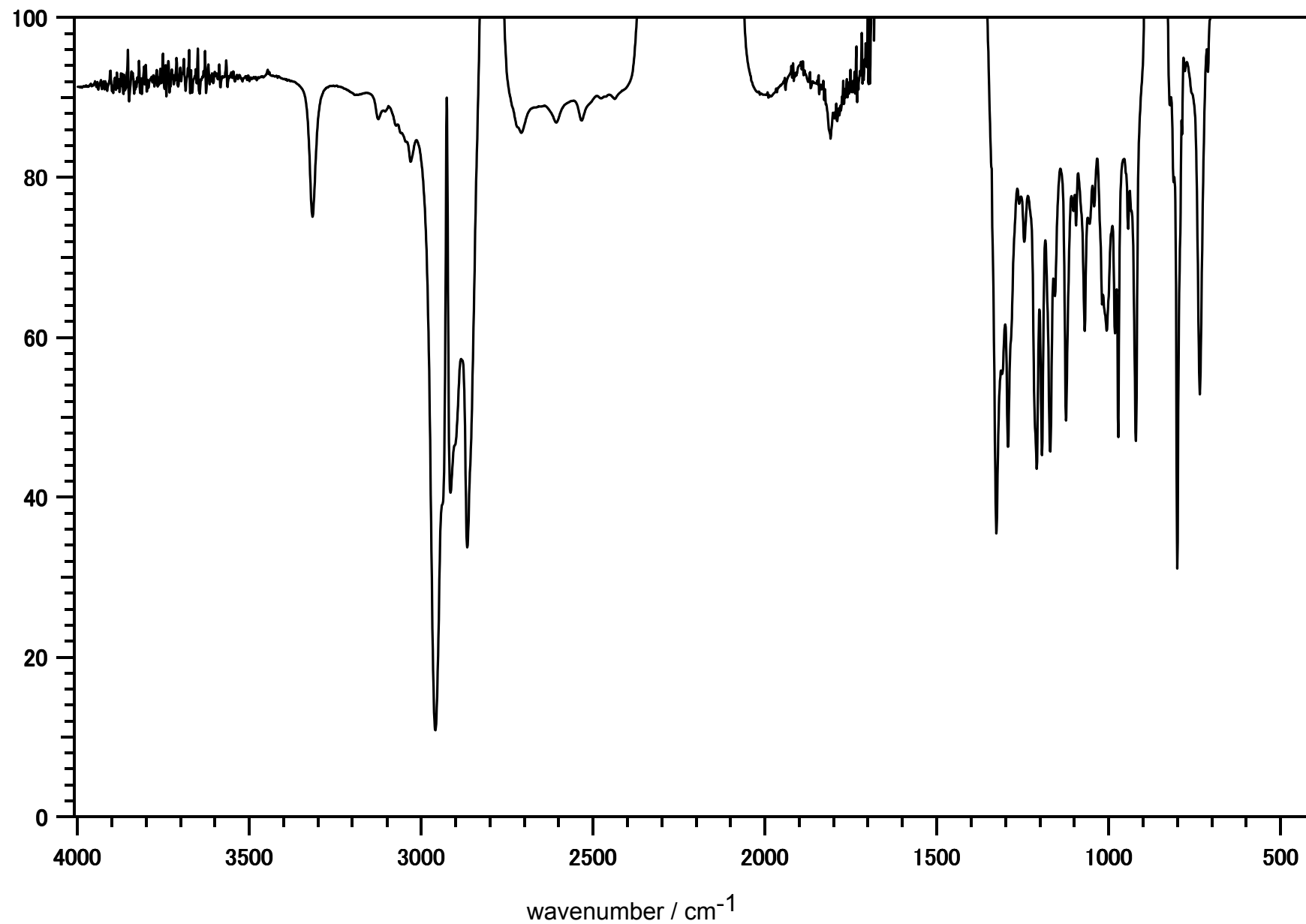
in CS₂

3316.4 (w), 2958.6 (s), 2915.2 (m), 2866.0 (m), 1326.9 (m),
1310.5 (m), 1293.2 (m), 800.4 (s), 734.8 (m) cm⁻¹

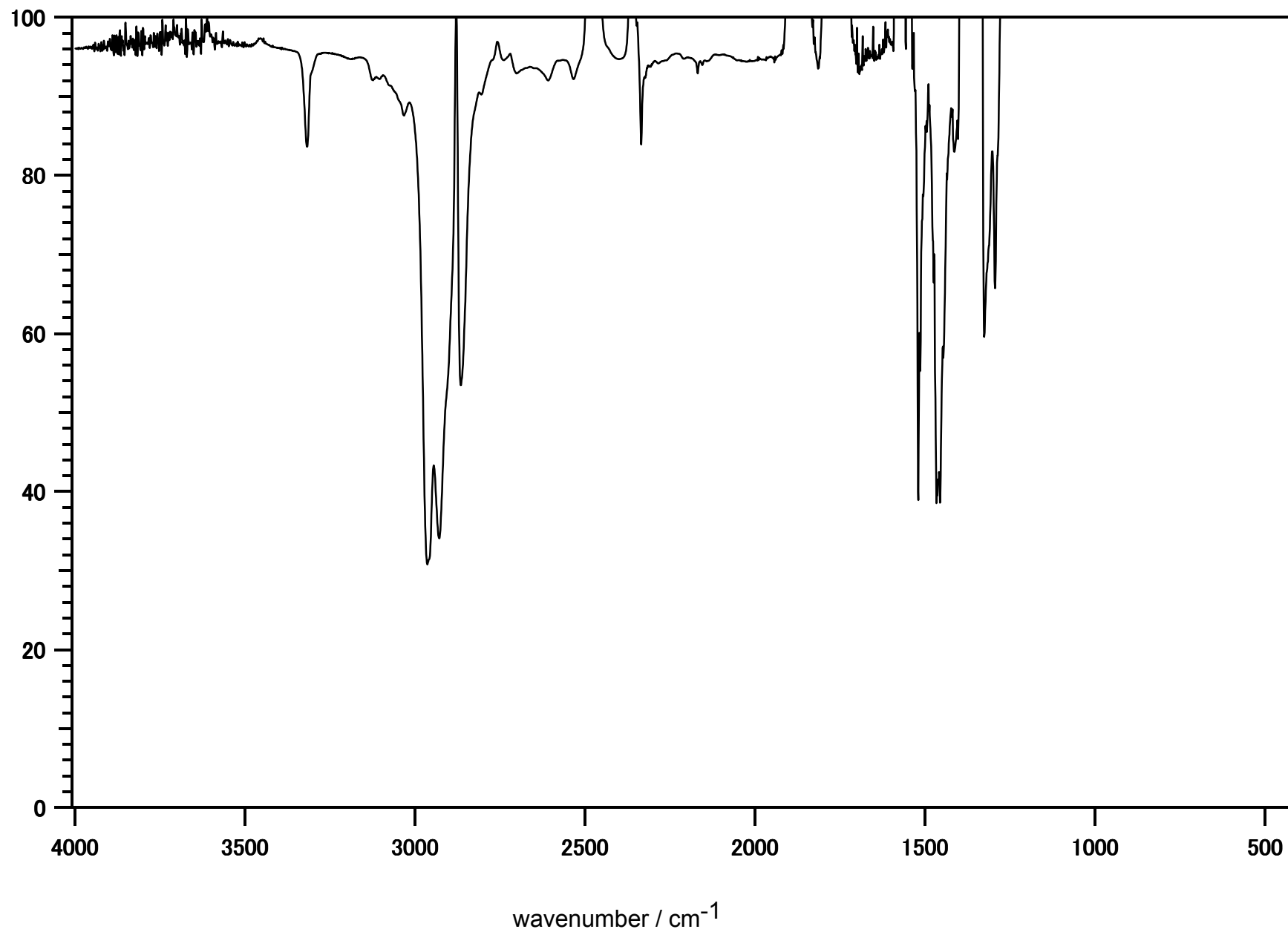
in CCl₂CCl₂

3317.3 (w), 2964.4 (s), 2928.7 (s), 1519.8 (m), 1466.8 (m), 1456.2 (m) cm⁻¹

•S4-1 IR of *m*FbFb□□in CS₂

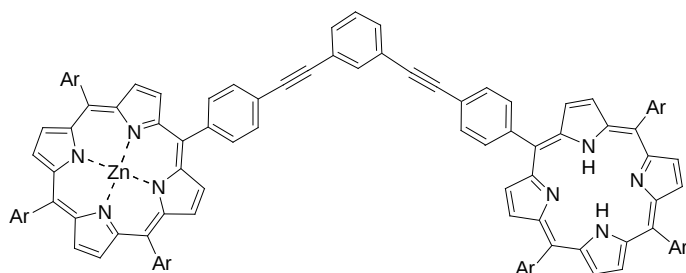


•S4-2 IR of *m*FbFb□□ in CCl₂CCl₂

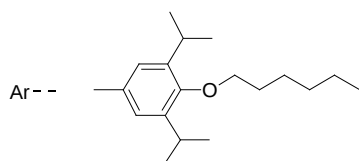


Compound 1 :

1-[4-(Zinc(II)10,15,20-tris(4-hexyloxy-3,5-diisopropylphenyl)
porphin-5-yl)-phenylethynyl]-3-[4'-(10,15,20-tris(4-hexyloxy-3,5-diisopropylphenyl)
porphin-5-yl)-phenylethynyl]benzene (***m*-ZnFb**)



1



S5 $^1\text{H-NMR}$ spectrum data

S6 MASS Spectrum data Exact mass for $\text{C}_{170}\text{H}_{204}\text{N}_8\text{O}_6\text{Zn}$ = 2517.52

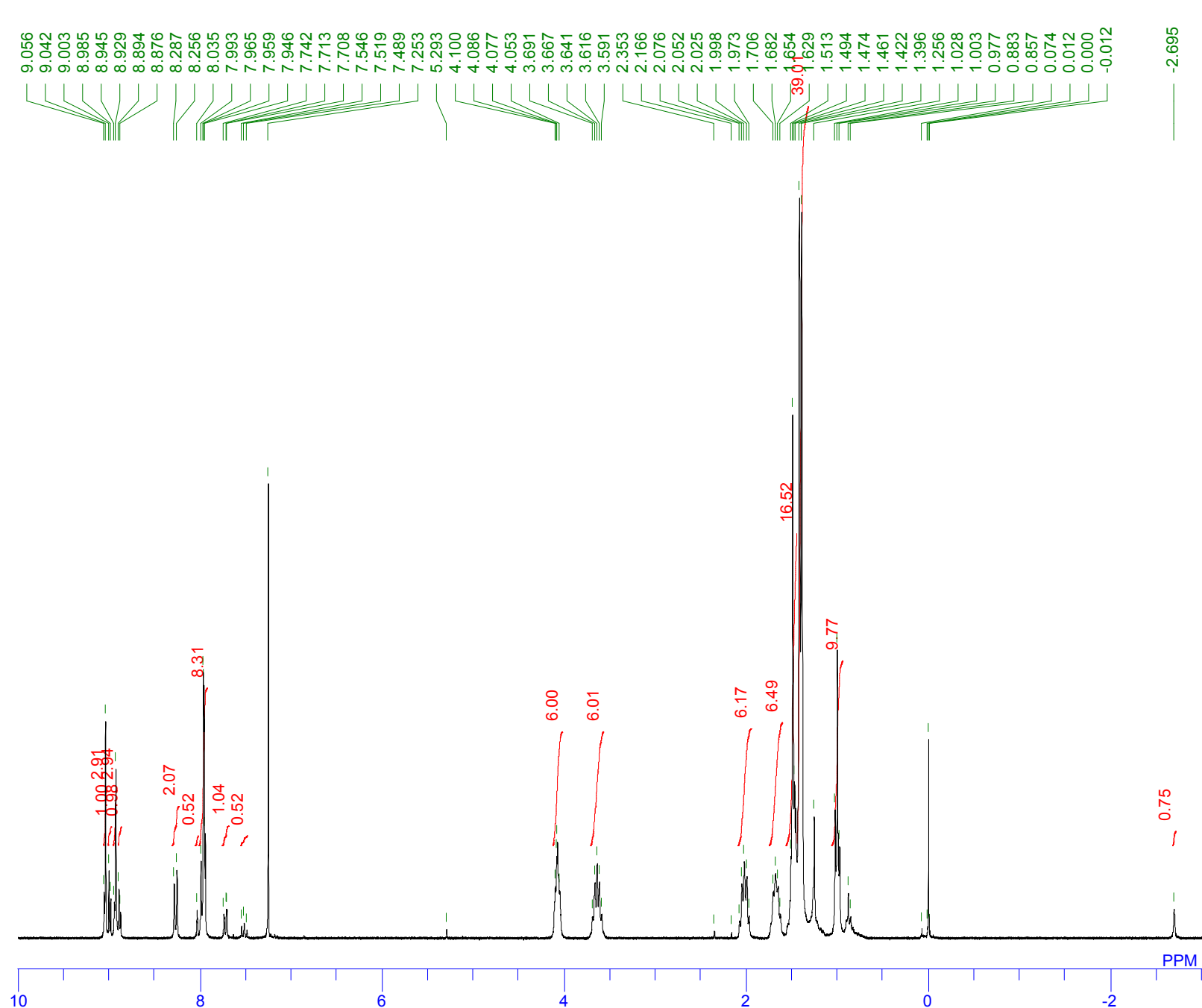
S5 ^1H -NMR spectrum data of *m*-ZnFb

S5-1 ^1H -NMR(270MHz, CDCl_3) JEOL Excalibur-270

$\delta = 9.05$ (2H, d, $J = 4.8$ Hz)
9.04 (4H, s),
9.00 (2H, d, $J = 4.8$ Hz),
8.94 (2H, d, $J = 4.9$ Hz),
8.93 (4H, s)
8.88 (2H, d, $J = 4.9$ Hz),
8.27 (4H, d, $J = 8.4$ Hz),
8.03 (1H, bs),
7.95-7.99 (16H, m),
7.73 (1H, d, $J = 7.7$ Hz),
7.72 (1H, d, $J = 7.7$ Hz),
7.52 (1H, t, $J = 7.7$ Hz),
4.05-4.12 (12H, m),
3.64 (12H, quintet, $J = 6.9$ Hz),
2.03 (12H, quintet, $J = 6.9$ Hz),
1.63-1.74 (12H, m),
1.39-1.47 (96H, m),
1.00 (18H, t, $J = 6.9$ Hz),
-2.70 (2H, bs) ppm.

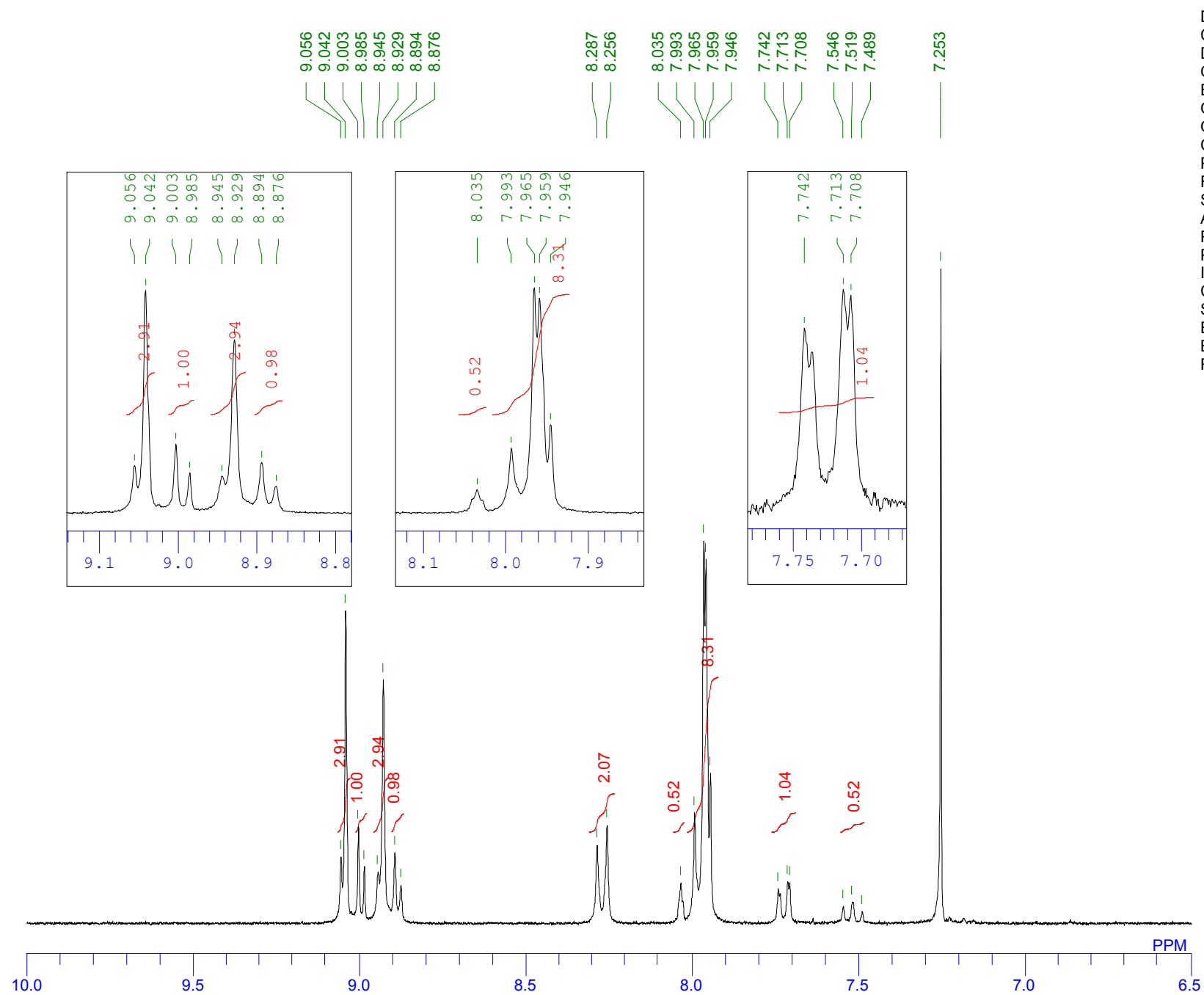
•S5-2 ¹H-NMR of *m*-ZnFb

□□□□□□□□



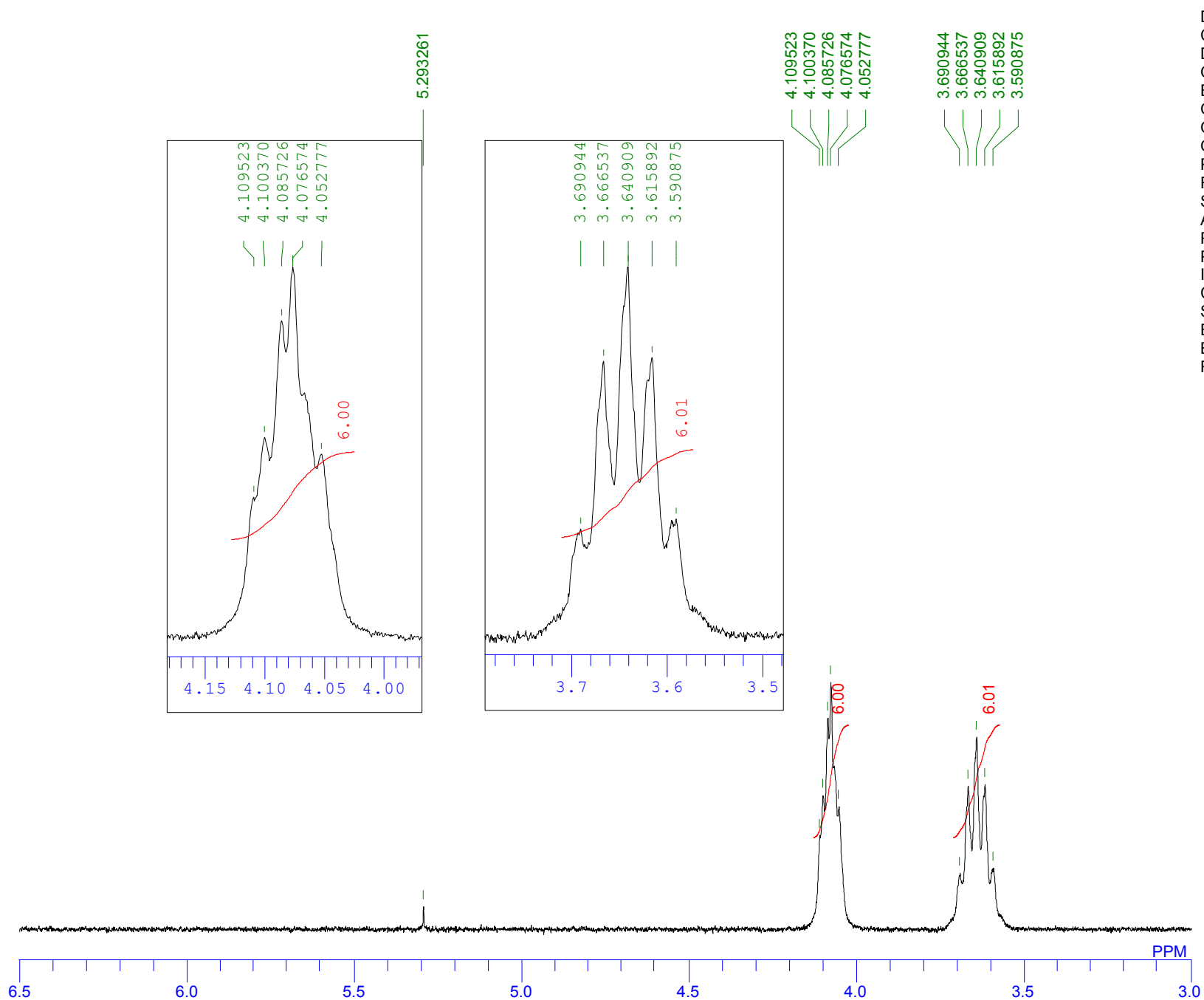
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EXMOD NON
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OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 32768
FREQU 5401.76 Hz
SCANS 8
ACQTM 6.0662 sec
PD 0.9340 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19

•S5-3 ^1H -NMR of *m*-ZnFb



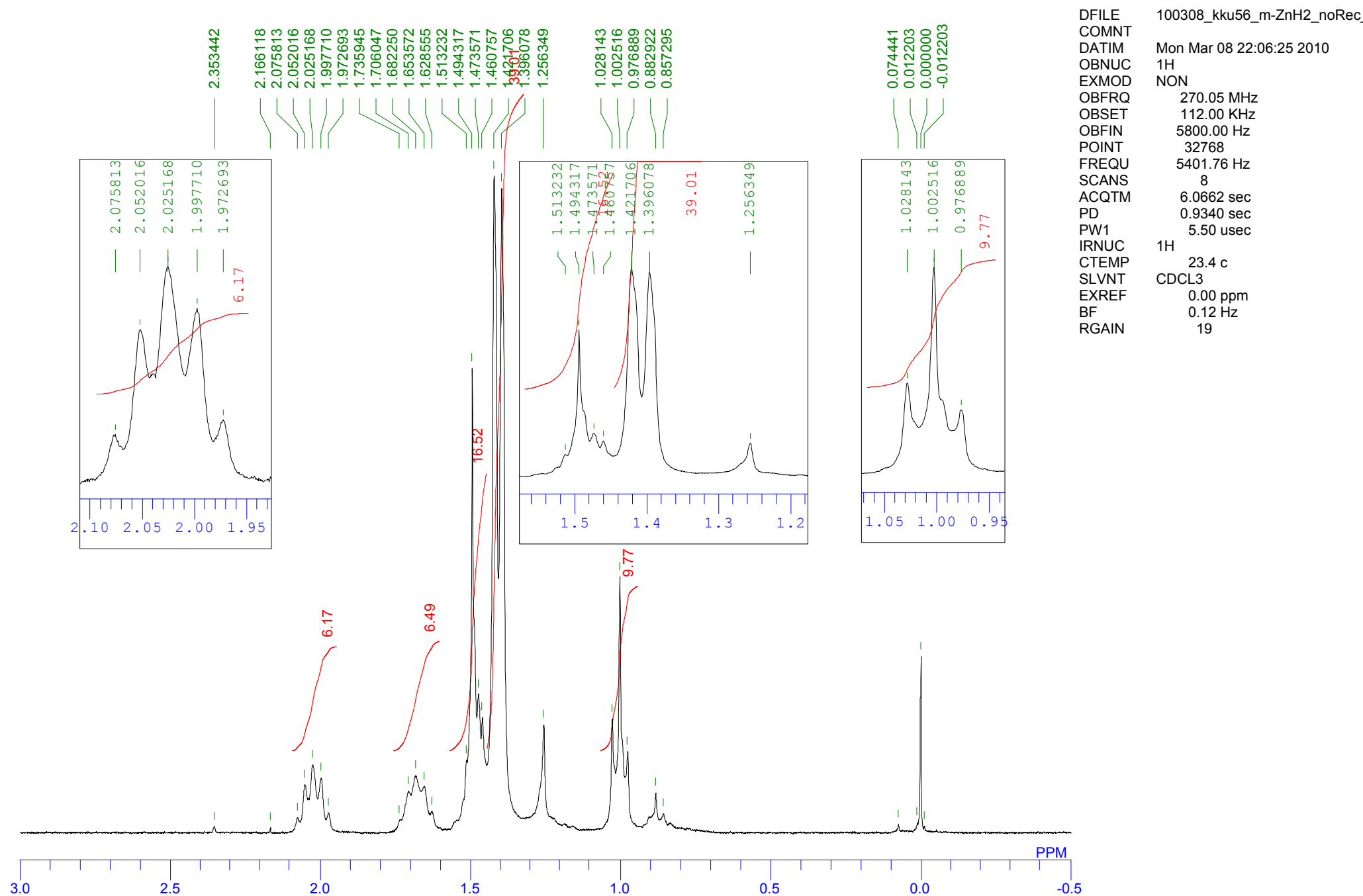
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 DATIM Mon Mar 08 22:06:25 2010
 OBNUC ^1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 8
 ACQTM 6.0662 sec
 PD 0.9340 sec
 PW1 5.50 usec
 IRNUC ^1H
 CTEMP 23.4 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 19

•S5-4 ^1H -NMR of *m*-ZnFb



DFILE	100308_kku56_m-ZnH2_noRec_
COMNT	
DATIM	Mon Mar 08 22:06:25 2010
OBNUC	^1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
POINT	32768
FREQU	5401.76 Hz
SCANS	8
ACQTM	6.0662 sec
PD	0.9340 sec
PW1	5.50 usec
IRNUC	^1H
CTEMP	23.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	19

•S5-5 ^1H -NMR of *m*-ZnFb



S6 MASS Spectrum data of *m*-ZnFb (1)

Kratos Analytical KOMPACT PROBE spectrometer

Dithranol (1,8-dihydroxy-9(10H)-anthracenone, Sigma-Aldrich Co. Ltd.)

Exact mass for $C_{170}H_{204}N_8O_6Zn = 2517.52$

observed $[M^+]$ 2518

S6-1 MALDI TOF Mass Spectra of *m*ZnFb

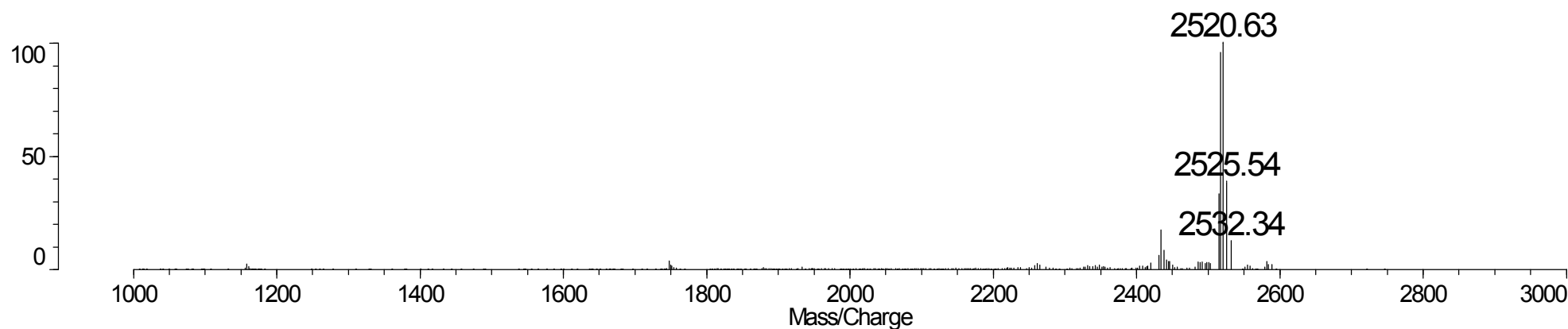
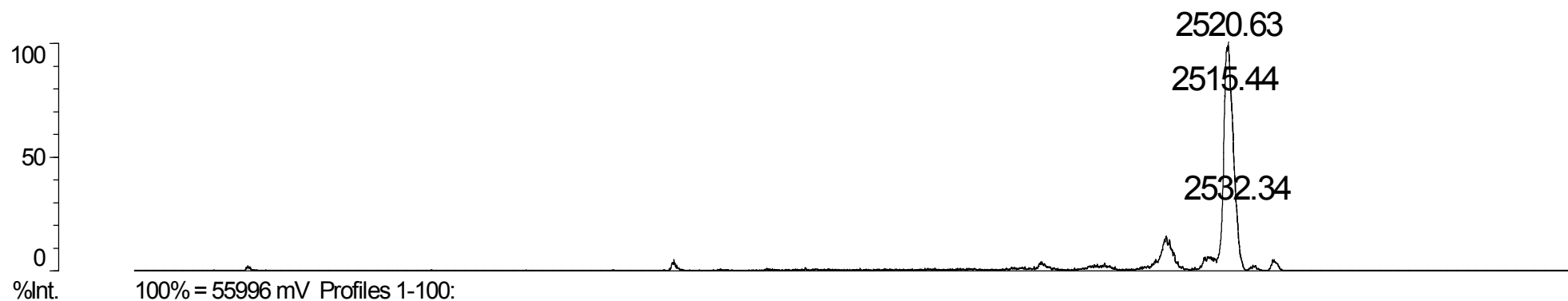
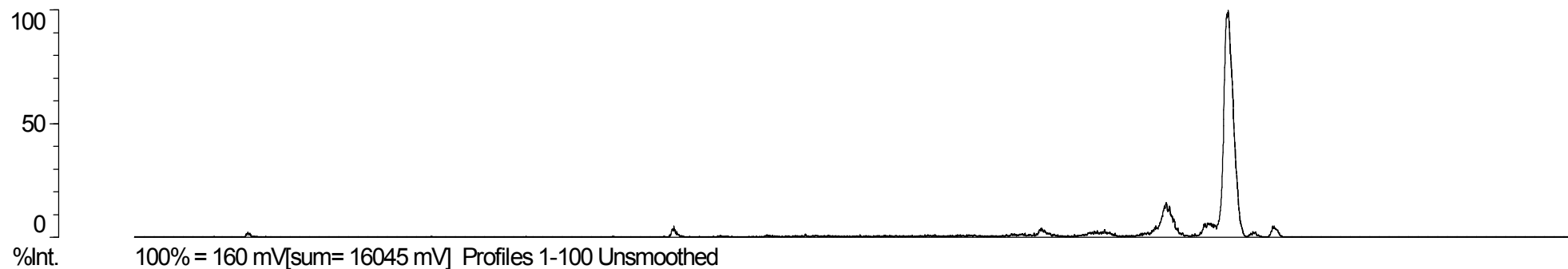
dAcP&line2P_GPC@DT

ZnPor+AnI2_GPC 2nd

Data: methaZnH2_DT80_high_best_0001.20 25 Mar 2010 9:46 Cal: tof 23 Mar 2010 5:12

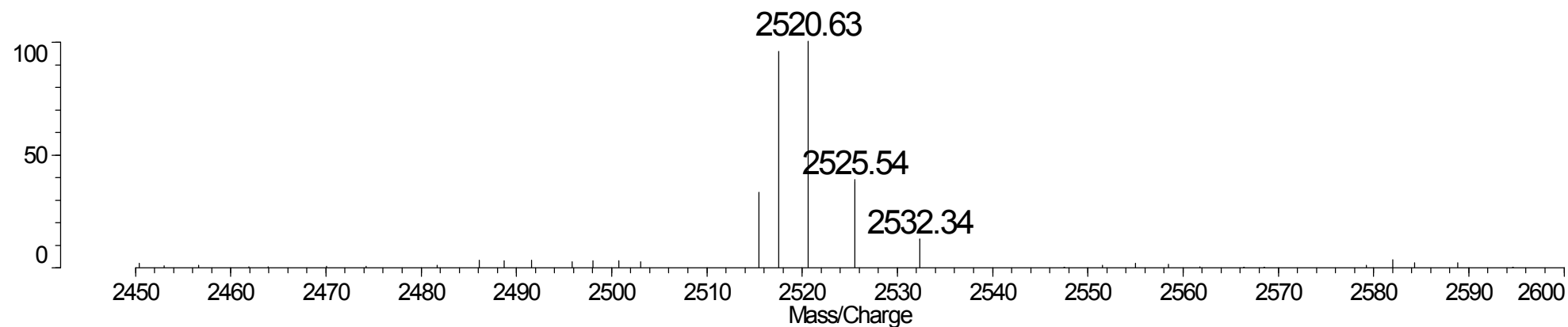
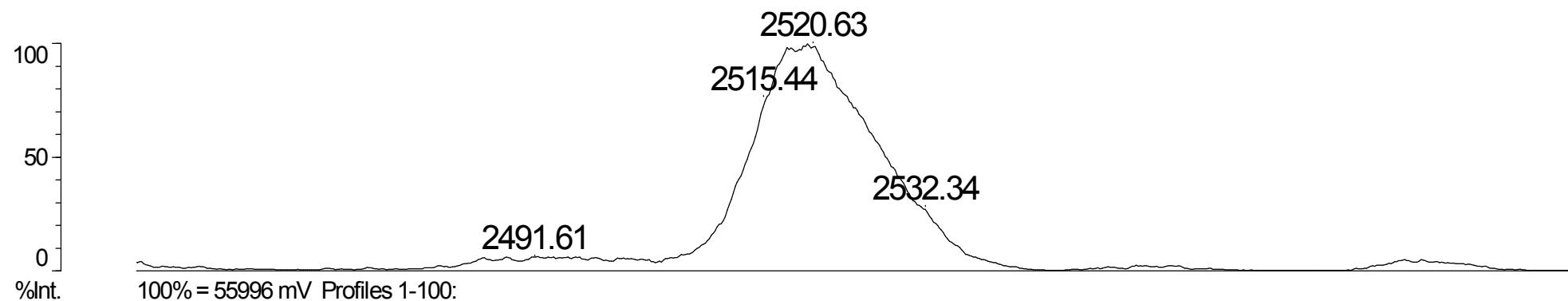
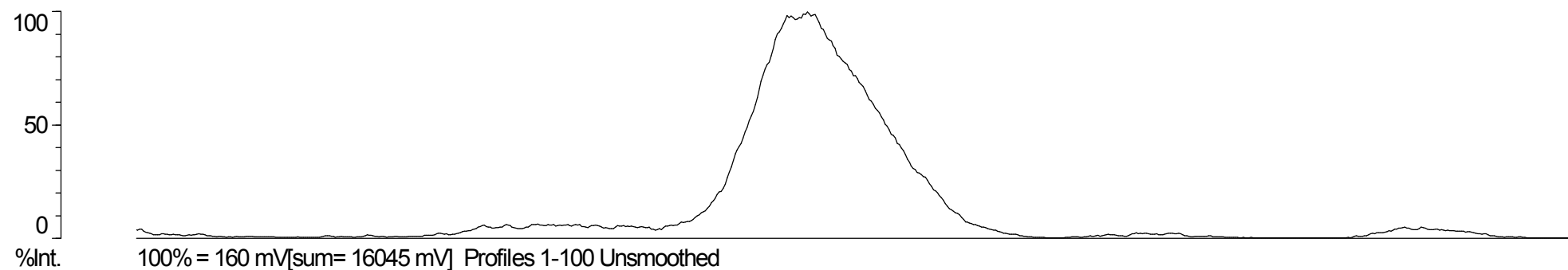
Kratos PCKompact Probe V1.2.2: + Linear High, Power: 80, P.Ext. @ 2520 (bin 59)

%Int. 100% = 160 mV Profile 100

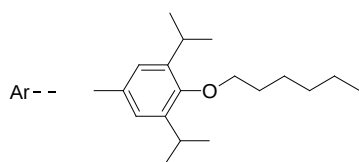
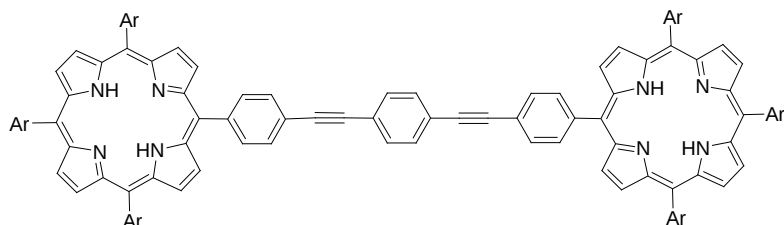


dAcP&line2P_GPC@DT
ZnPor+AnI2_GPC 2nd
Data: methaZnH2_DT80_high_best_0001.20 25 Mar 2010 9:46 Cal: tof 23 Mar 2010 5:12
Kratos PCKompact Probe V1.2.2: + Linear High, Power: 80, P.Ext. @ 2520 (bin 59)
%Int. 100% = 160 mV Profile 100

S6-2 MALDI TOF Mass Spectra of *m*ZnFb



1,4-bis((4-(10,15,20-tris(4-hexyloxy-3,5-diisopropylphenyl)porphyrin-5-yl)phenyl)ethynyl)benzene (***p*-FbFb**)



- S7 Elemental analysis
- S8 ^1H -NMR spectrum
- S9 MASS Spectrum data
- S10 IR spectrum

S7 Elemental analysis of *p*-FbFb

Calcd. for $\text{C}_{170}\text{H}_{206}\text{N}_8\text{O}_6$ (mol wt 2457.50): C, 83.09; H, 8.45; N, 4.56.

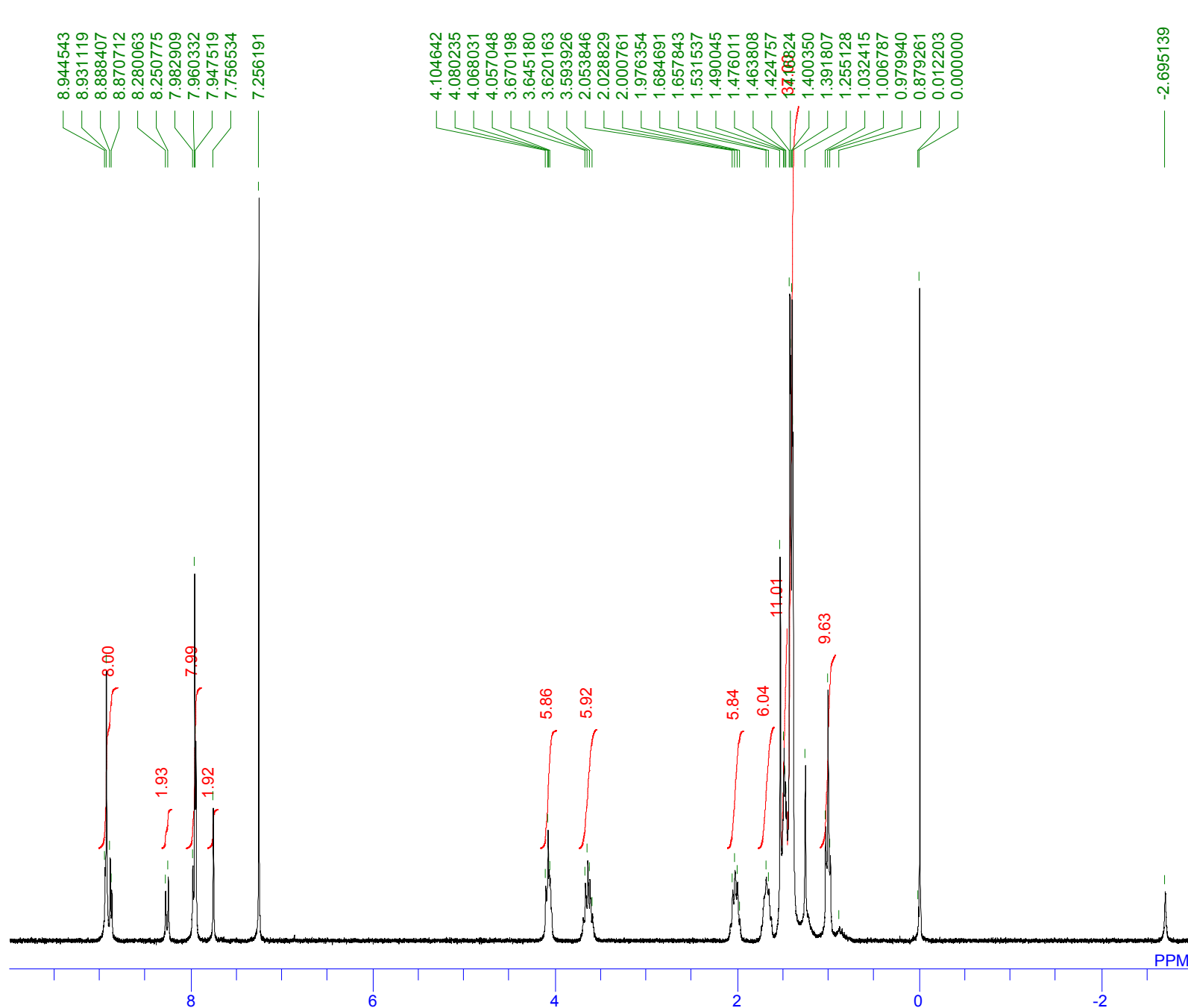
Found: C, 82.85; H, 8.54; N, 4.56.

S8 ^1H -NMR spectrum data of *p*-FbFb

S8-1 ^1H -NMR(270MHz, CDCl_3) JEOL Excalibur-270

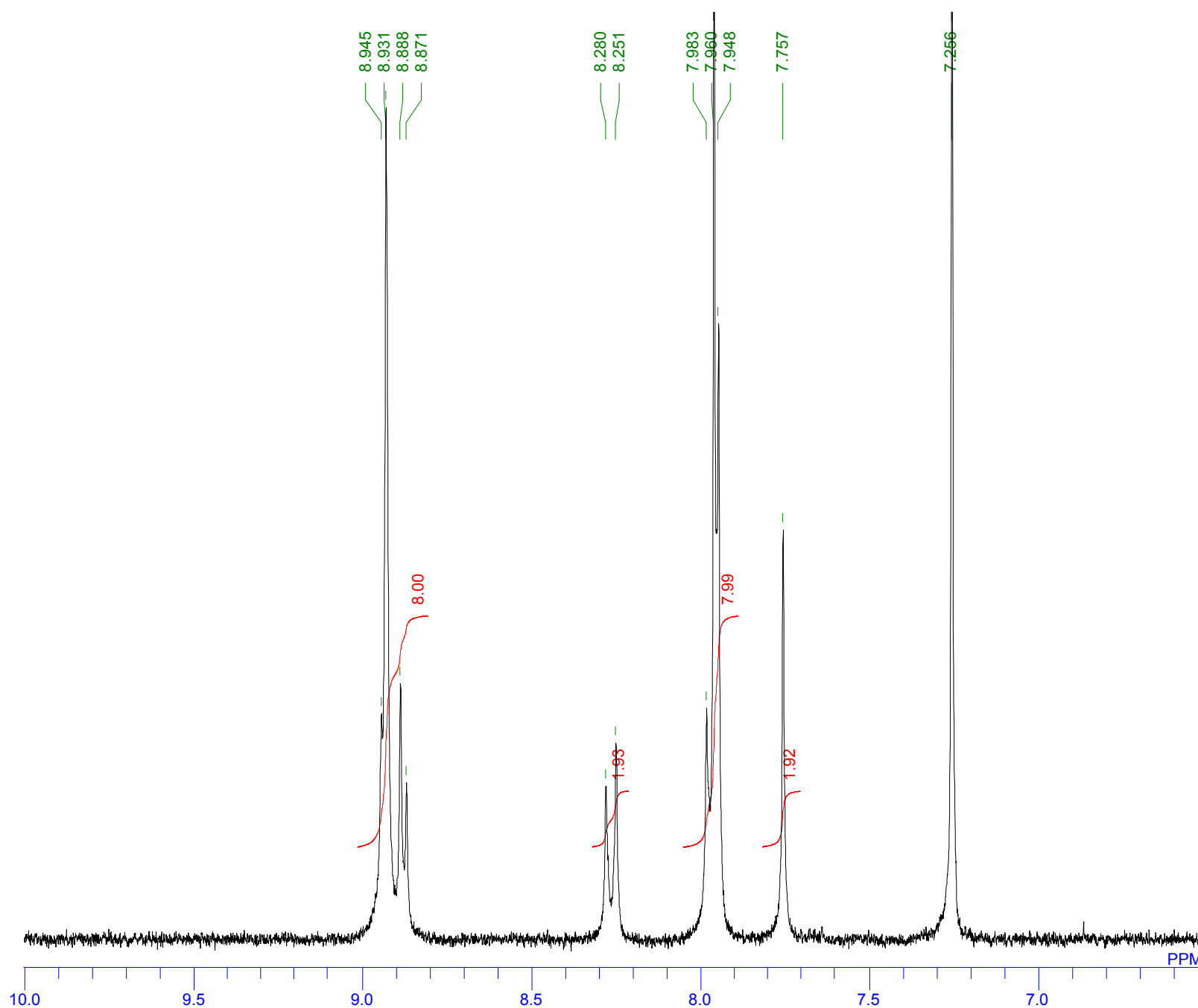
$\delta = 8.94$ (4H, d, $J = 4.8$ Hz),
8.93 (8H, s),
8.88 (4H, d, $J = 4.8$ Hz),
8.27 (4H, d, $J = 7.9$ Hz),
7.90 –7.97 (16H, m),
7.76 (4H, s),
4.05 - 4.1 (12H, m),
3.65 (12H, quintet, $J = 6.9$ Hz),
2.02 (12H, quintet, $J = 6.9$ Hz),
1.62-1.72 (12H, m),
1.38-1.51 (96H, m),
1.01 (18H, t, $J = 6.9$ Hz),
-2.70 (2H, bs) ppm.

S8-2 ^1H -NMR *p*FbFb □□□□□□□□□□



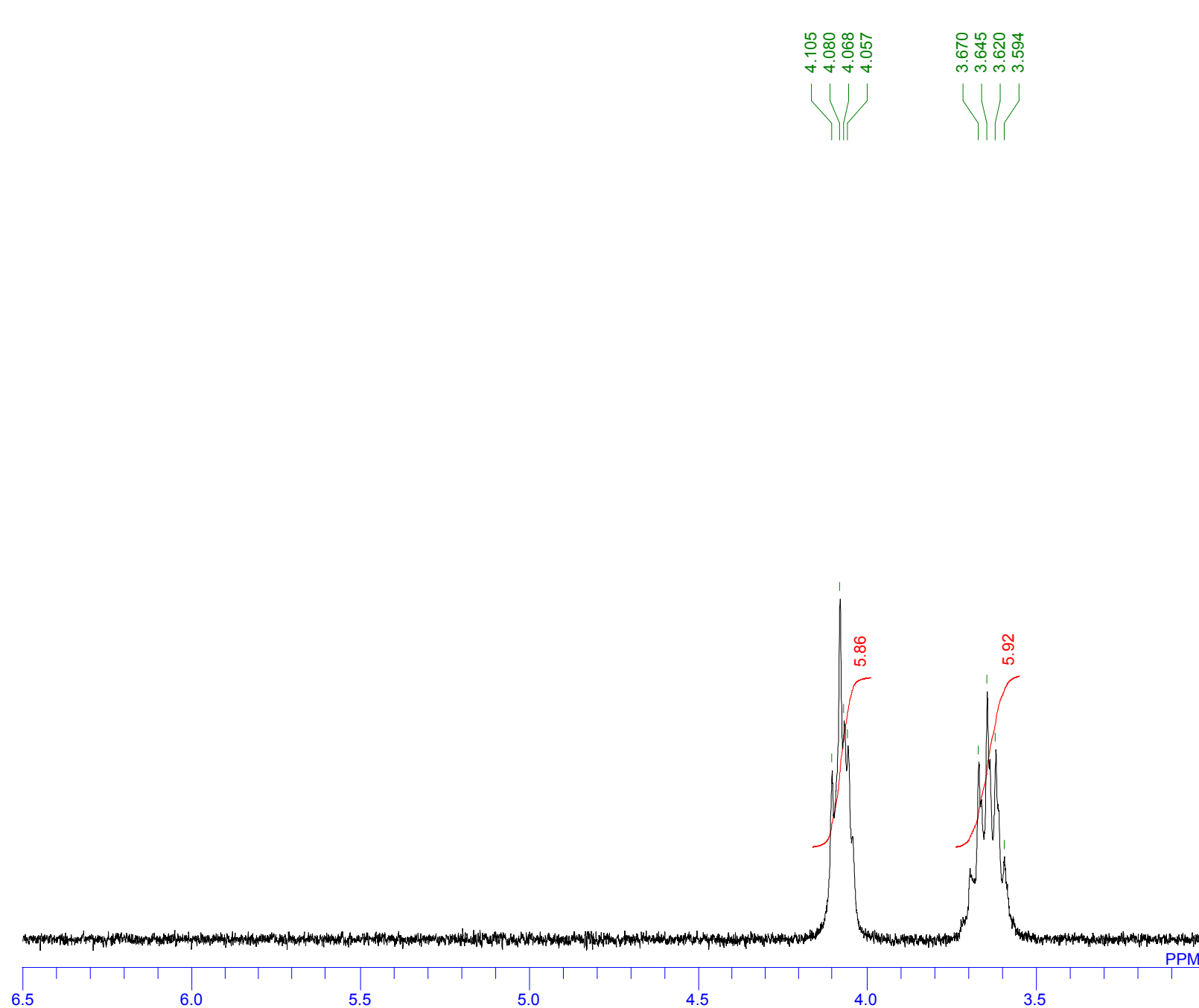
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OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 32768
FREQU 5401.76 Hz
SCANS 8
ACQTM 6.0662 sec
PD 0.9340 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21

•S8-3 ^1H -NMR *p*FbFb



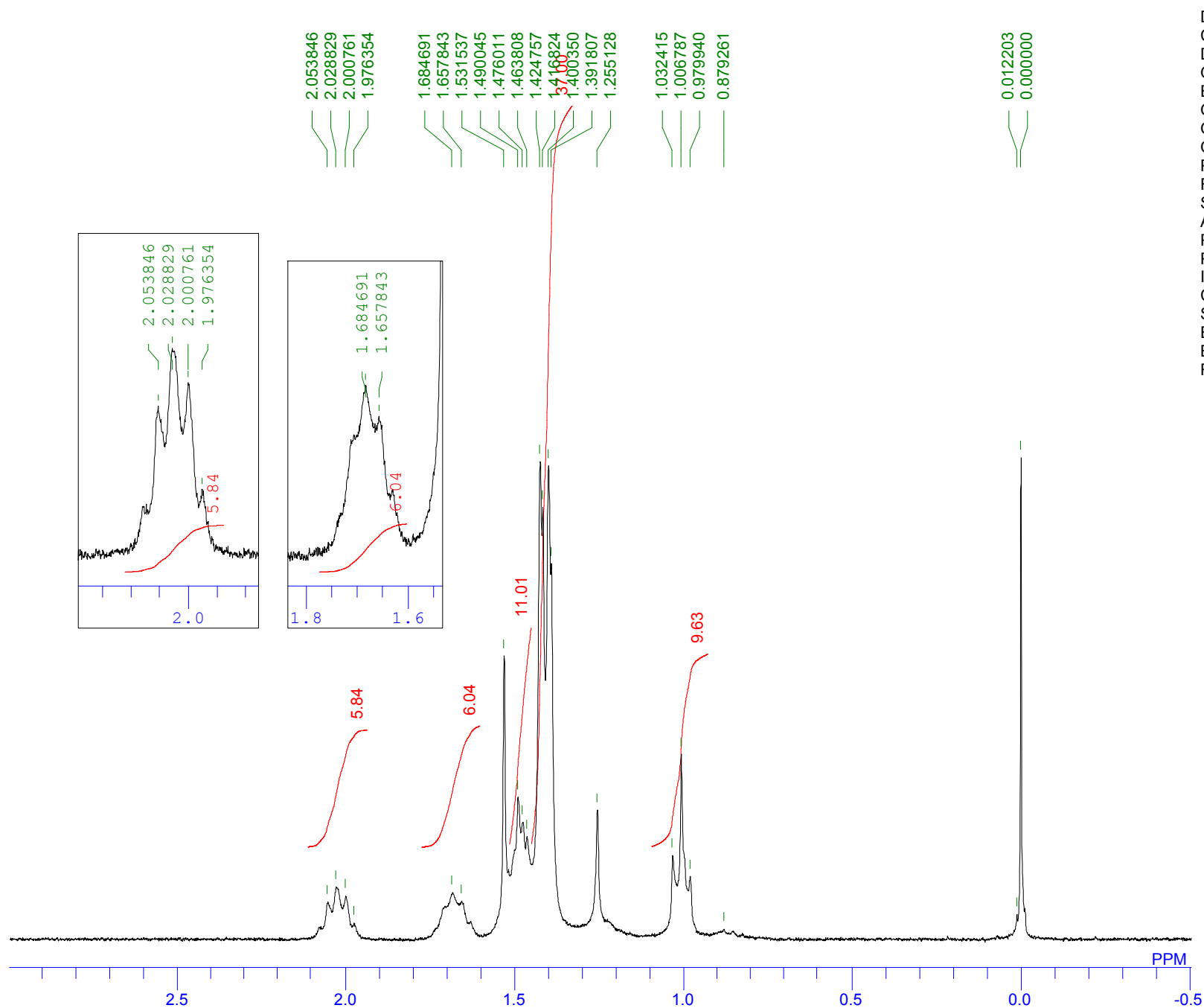
DFILE 100325_paraH2H2_epsilon_FID.
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 DATIM Thu Mar 25 10:33:16 2010
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 EXMOD NON
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 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 8
 ACQTM 6.0662 sec
 PD 0.9340 sec
 PW1 5.50 usec
 IRNUC ^1H
 CTEMP 22.3 c
 SLVNT CDCL₃
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 21

•S8-4 ^1H -NMR $p\text{FbFb}$



DFILE 100325_paraH2H2_epsilon_FID.
 COMNT
 DATIM Thu Mar 25 10:33:16 2010
 OBNUC ^1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 8
 ACQTM 6.0662 sec
 PD 0.9340 sec
 PW1 5.50 usec
 IRNUC ^1H
 CTEMP 22.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 21

•S8-5 ^1H -NMR $p\text{FbFb}$



DFILE 100325_paraH2H2_epsilon_FID.
 COMNT
 DATIM Thu Mar 25 10:33:16 2010
 OBNUC ^1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 8
 ACQTM 6.0662 sec
 PD 0.9340 sec
 PW1 5.50 usec
 IRNUC ^1H
 CTEMP 22.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 21

S9 MASS Spectrum data of *p*-FbFb

Kratos Analytical KOMPACT PROBE spectrometer

Dithranol (1,8-dihydroxy-9(10H)-anthracenone, Sigmna-Aldrich Co. Ltd.)

Exact mass for $\text{C}_{170}\text{H}_{206}\text{N}_8\text{O}_6$ = 2455.61

observed $[\text{M}^+ + \text{H}]$ 2457

S9-1 MALDI TOF Mass Spectra of pFbFb

dAcP&line2P_GPC@DT

Data: paraH2H2_DT70_high_0001.11 24 Mar 2010 20:36 Cal: tof 23 Mar 2010 5:12

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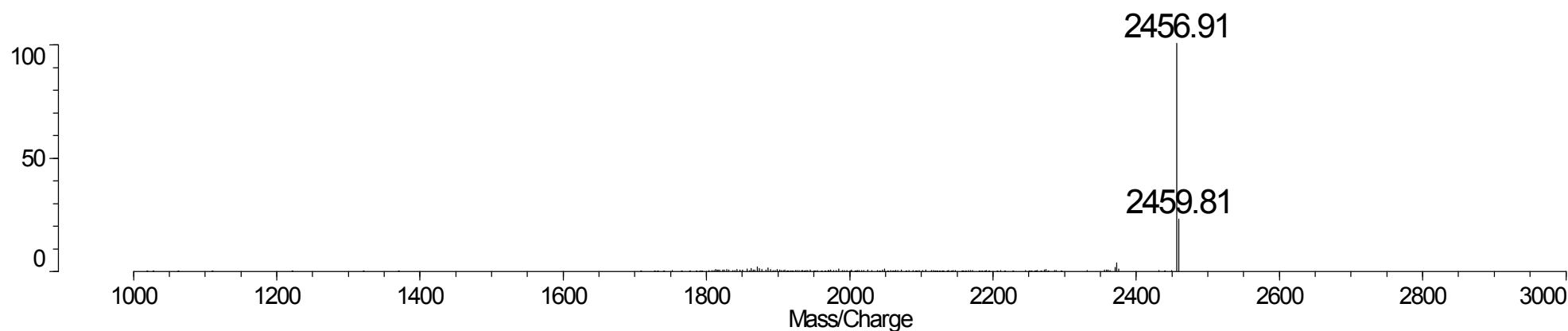
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%Int. 100% = 44 mV[sum= 4400 mV] Profiles 1-100 Unsmoothed



%Int. 100% = 17792 mV Profiles 1-100:



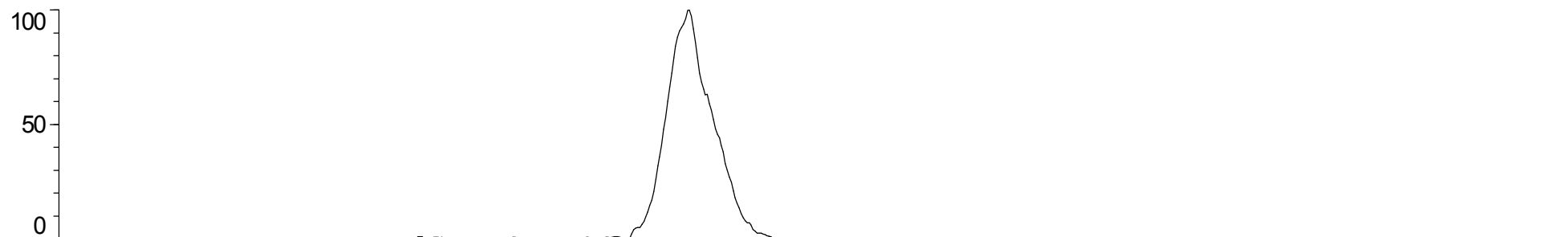
S9-2 MALDI TOF Mass Spectra of *p*FbFb

dAcP&line2P_GPC@DT

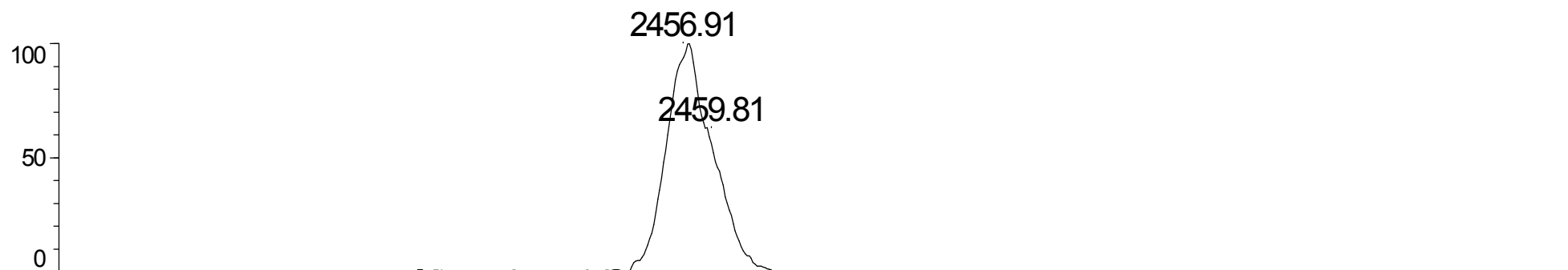
Data: paraH2H2_DT70_high_0001.11 24 Mar 2010 20:36 Cal: tof 23 Mar 2010 5:12

Kratos PCKompact Probe V1.2.2: + Linear High, Power: 70, P.Ext. @ 2457 (bin 109)

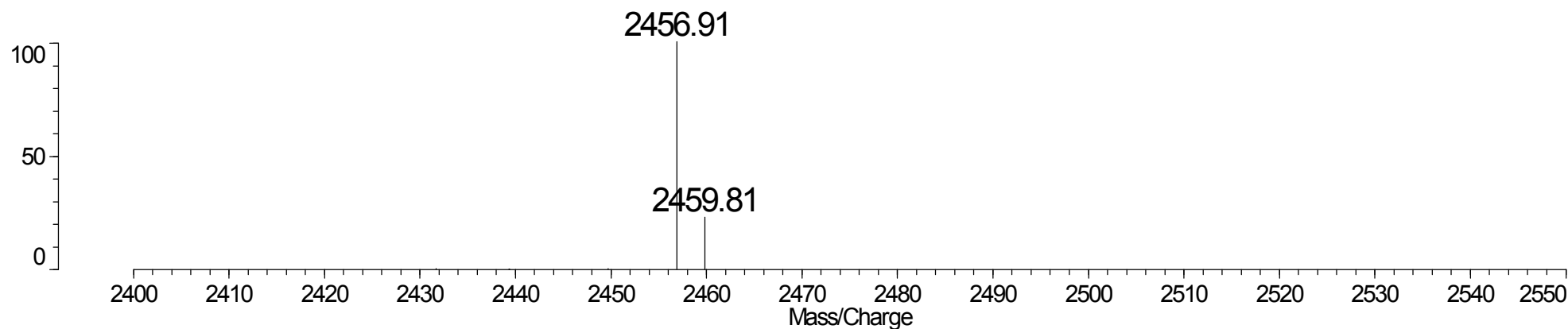
%Int. 100% = 44 mV Profile 100



%Int. 100% = 44 mV[sum= 4400 mV] Profiles 1-100 Unsmoothed



%Int. 100% = 17792 mV Profiles 1-100:

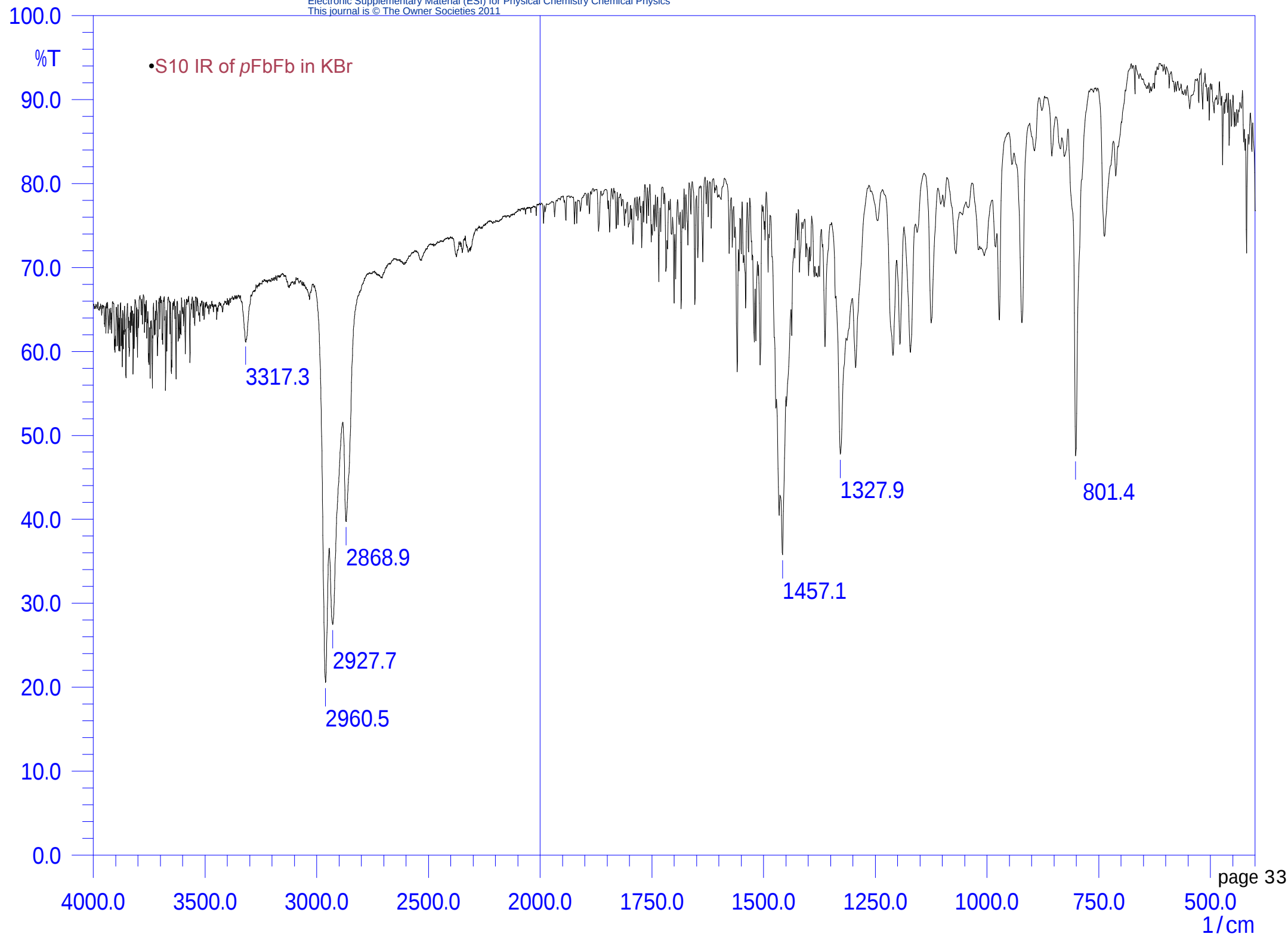


S10 IR spectra of *p*-FbFb

Shimazu FTIR-8400 Infrared spectrometer

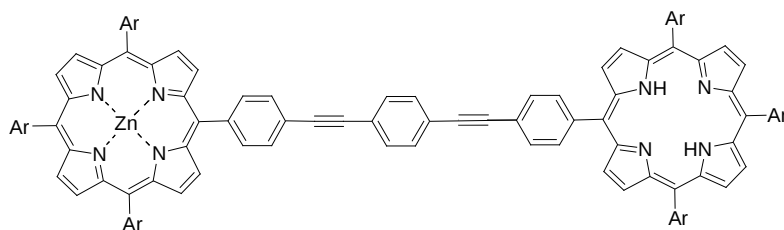
KBr pellet

3317.3 (w), 2960.5 (s), 2927.7 (s), 2868.9 (m), 1457.1 (m), 1327.9 (m)
801.4 (s)

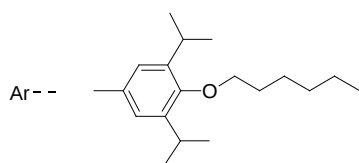


Compound 2 :

1-[4-(Zinc(II)10,15,20-tris(4-hexyloxy-3,5-diisopropylphenyl)-5-porphinyl)phenylethynyl]-4-[4'-(10,15,20-tris(4-hexyloxy-3,5-diisopropylphenyl)-porphin-5-yl)phenylethynyl]benzene
(*p*-ZnFb)



2



S11 ^1H -NMR spectrum

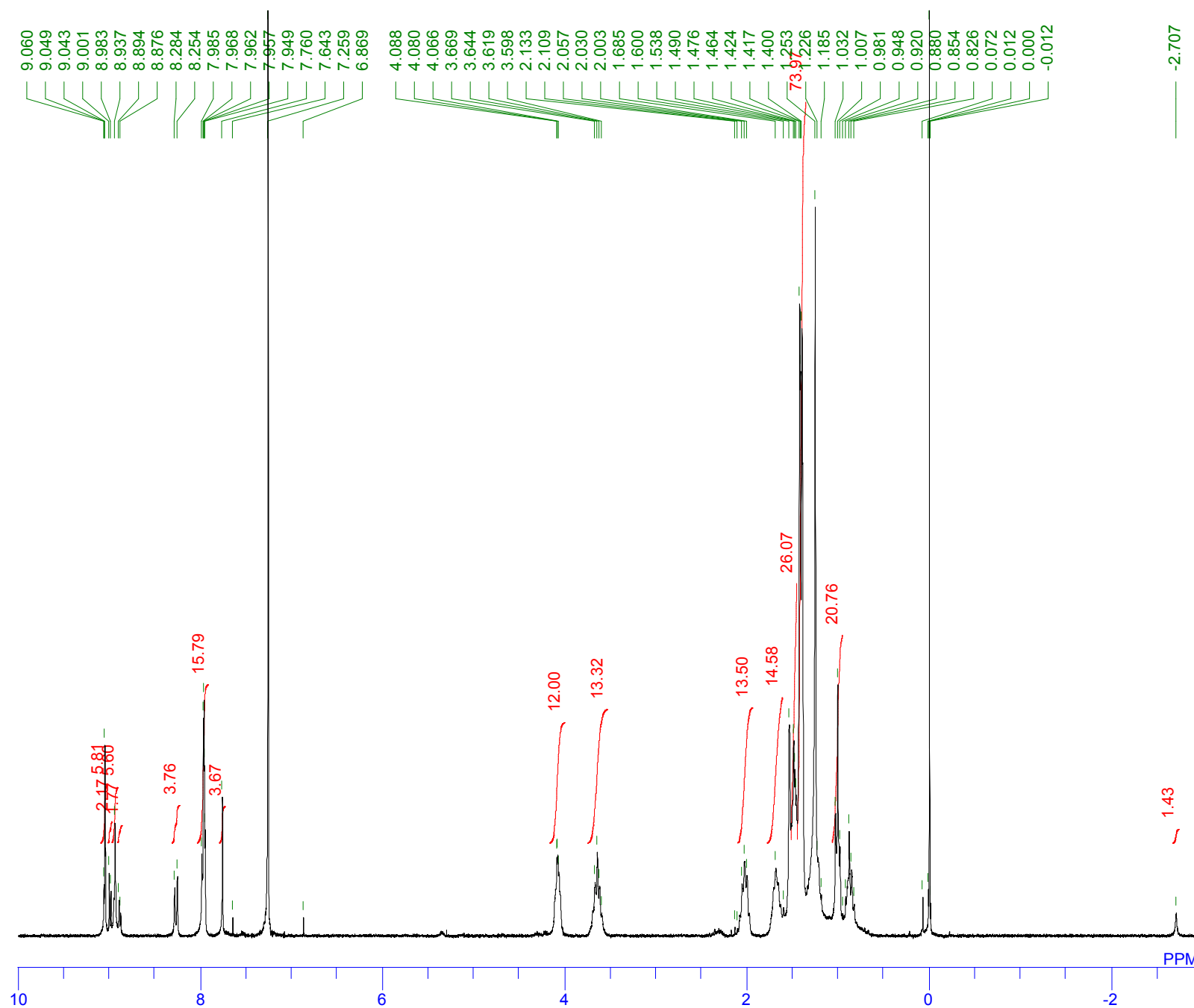
S12 MASS spectrum

S11 ¹H-NMR spectrum data of *p*-ZnFb(2)

S11-1 ¹H-NMR(270MHz, CDCl₃) JEOL Excalibur-270

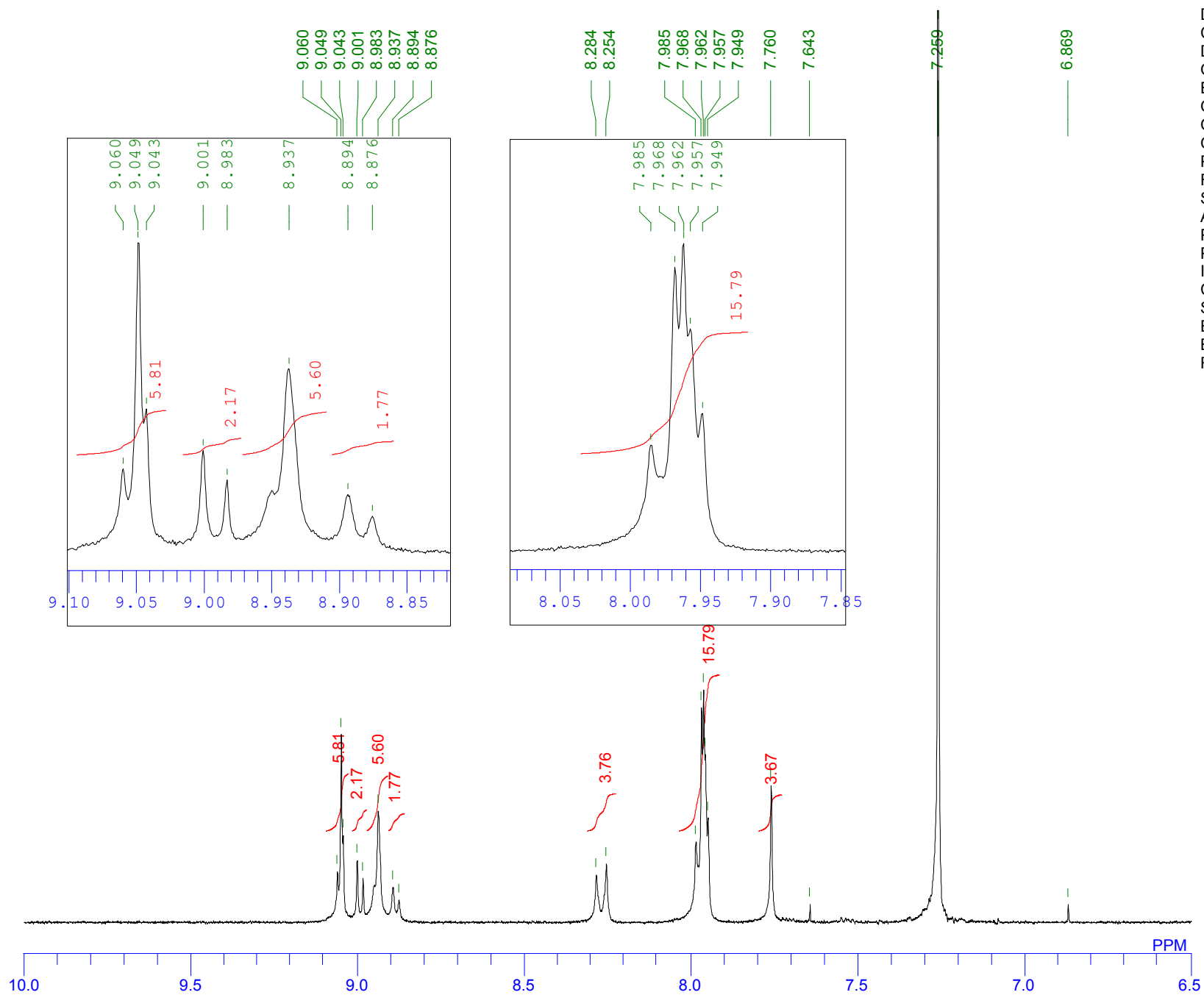
δ = 9.06 (2H, d, *J* = 4.9 Hz)
9.05 (4H, s),
8.99 (2H, d, *J* = 4.9 Hz),
8.88 (2H, d, *J* = 4.9 Hz),
8.95 (2H, d, *J* = 4.9 Hz),
8.94 (4H, s)
8.27 (4H, d, *J* = 8.1 Hz),
7.95 - 7.99 (16H, m),
7.76 (4H, s),
4.06 - 4.11 (12H, m),
3.65 (12H, quintet, *J* = 7.0 Hz),
2.03 (12H, quintet, *J* = 7.0 Hz),
1.63 - 1.73 (12H, m),
1.40 - 1.50 (96H, m),
1.01 (18H, t, *J* = 6.9 Hz),
-2.71 (2H, bs) ppm.

□S11-2¹H NMR of *p*-ZnFb□□□□□□□□□□



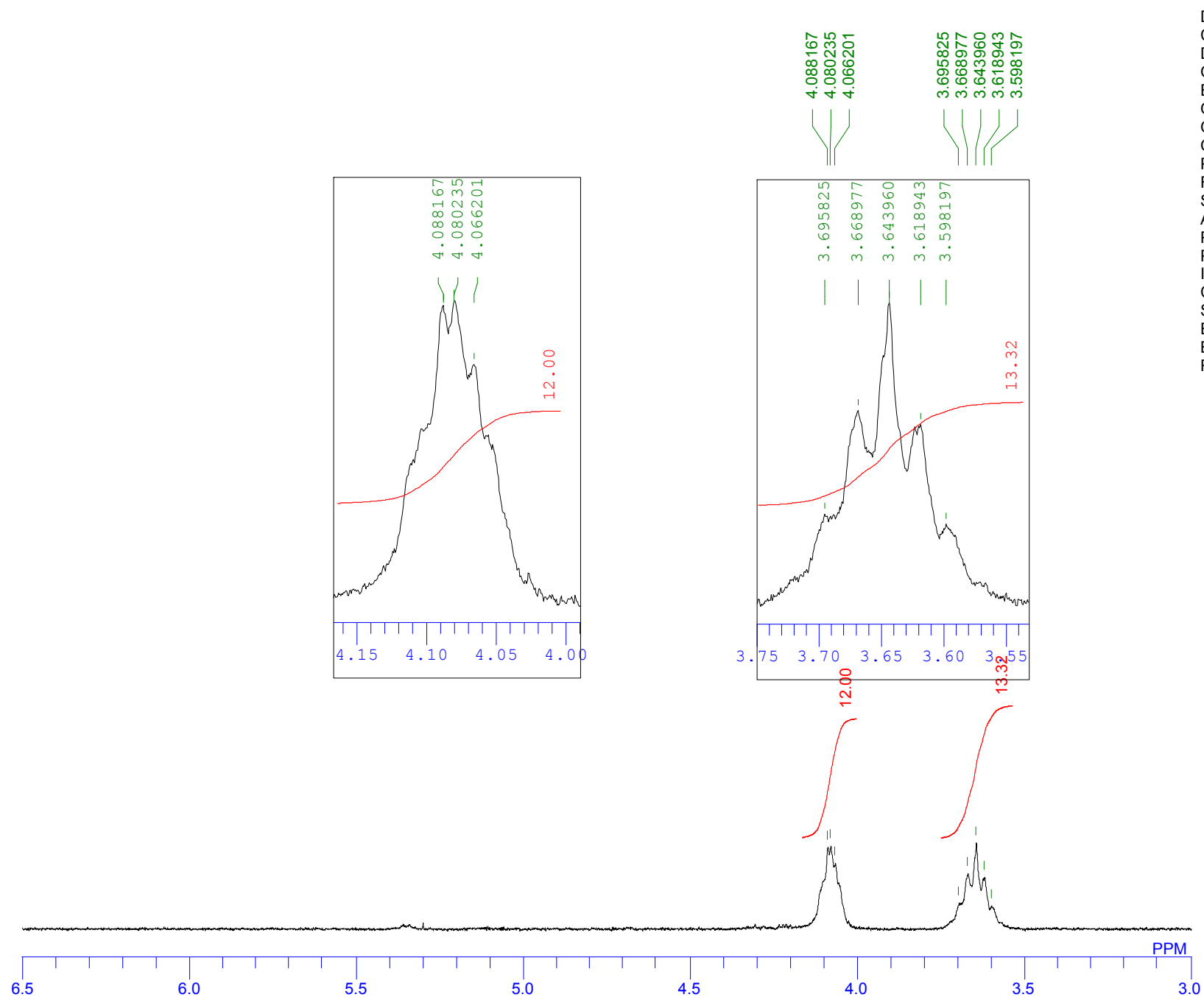
DFILE 100225_kku54_Zn_2H_para_fra
 COMNT
 DATIM Thu Feb 25 10:15:26 2010
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 16
 ACQTM 6.0662 sec
 PD 0.9340 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 17.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 19

•S11-3 ^1H -NMR of *p*-ZnFb



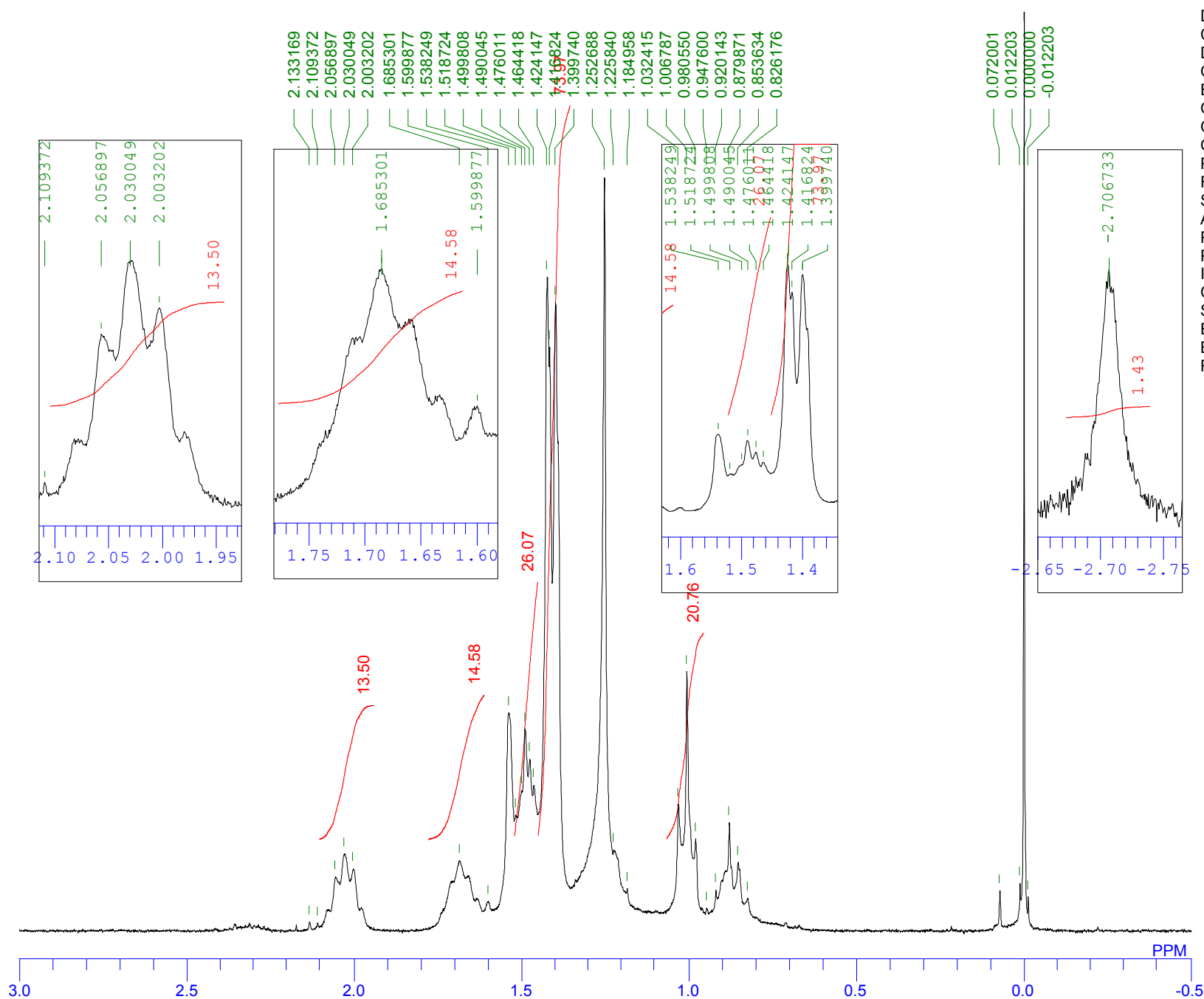
DFILE 100225_kku54_Zn_2H_para_fra
 COMNT
 DATIM Thu Feb 25 10:15:26 2010
 OBNUC ^1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 16
 ACQTM 6.0662 sec
 PD 0.9340 sec
 PW1 5.50 usec
 IRNUC ^1H
 CTEMP 17.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 19

•S11-4 ^1H -NMR of *p*-ZnFb



DFILE	100225_kku54_Zn_2H_para_fra
COMNT	
DATIM	Thu Feb 25 10:15:26 2010
OBNUC	^1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
POINT	32768
FREQU	5401.76 Hz
SCANS	16
ACQTM	6.0662 sec
PD	0.9340 sec
PW1	5.50 usec
IRNUC	^1H
CTEMP	17.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	19

•S11-5 ^1H -NMR of *p*-ZnFb



DFILE 100225_kku54_Zn_2H_para_fra
 COMNT
 DATIM Thu Feb 25 10:15:26 2010
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 16
 ACQTM 6.0662 sec
 PD 0.9340 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 17.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 19

S12 MASS Spectrum data of *p*-ZnFb (2)

Kratos Analytical KOMPACT PROBE spectrometer

Dithranol (1,8-dihydroxy-9(10H)-anthracenone, Sigma-Aldrich Co. Ltd.)

Exact mass for $C_{170}H_{204}N_8O_6Zn = 2517.52$

observed $[M^+]$ 2518

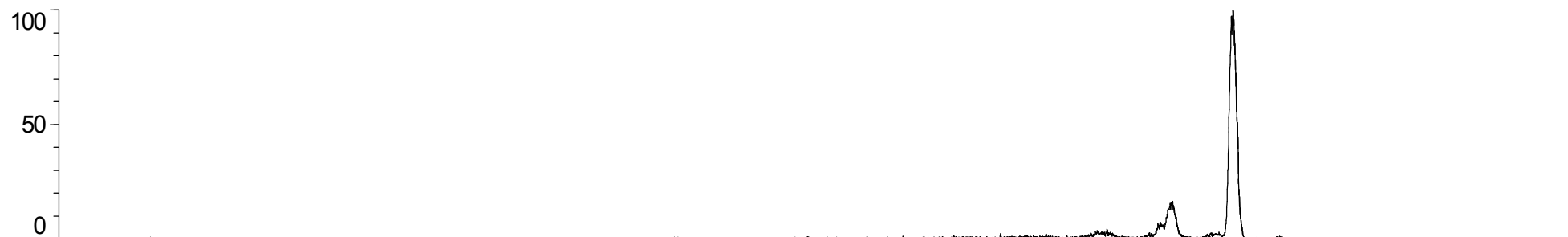
dAcP&line2P_GPC@DT

Data: paraZnH2_DT75_high_best_0001.15 25 Mar 2010 9:28 Cal: tof 23 Mar 2010 5:12

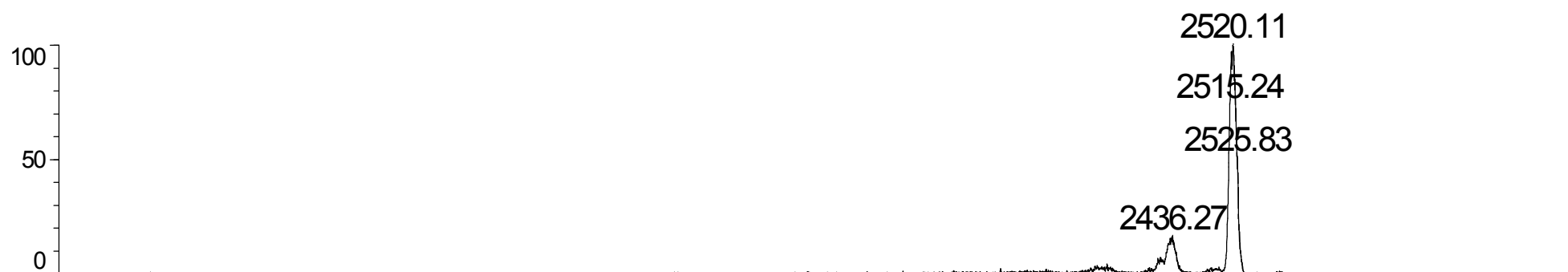
Kratos PCKompact Probe V1.2.2: + Linear High, Power: 75, P.Ext. @ 2457 (bin 58)

S12-1 MALDI TOF Mass Spectra of *p*ZnFb

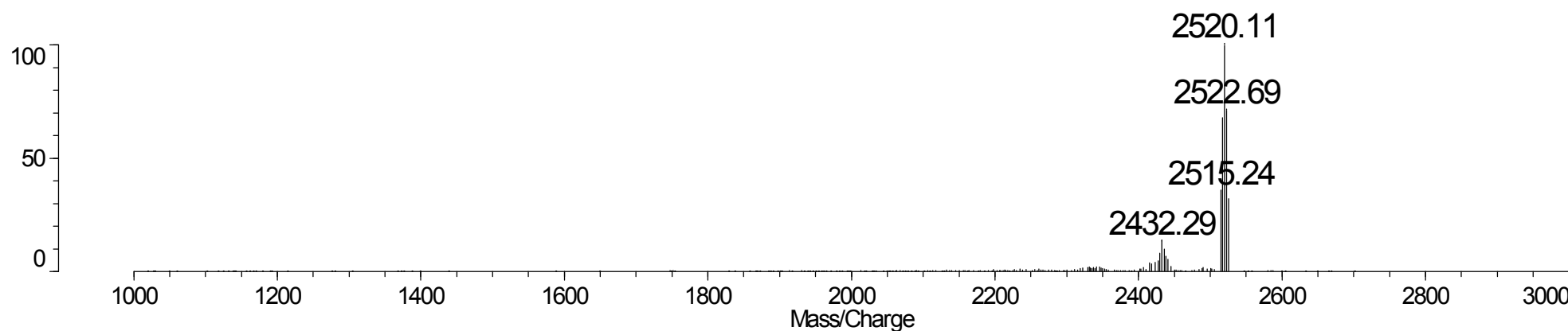
%Int. 100% = 86 mV Profile 100



%Int. 100% = 86 mV[sum= 8618 mV] Profiles 1-100 Unsmoothed



%Int. 100% = 27181 mV Profiles 1-100:



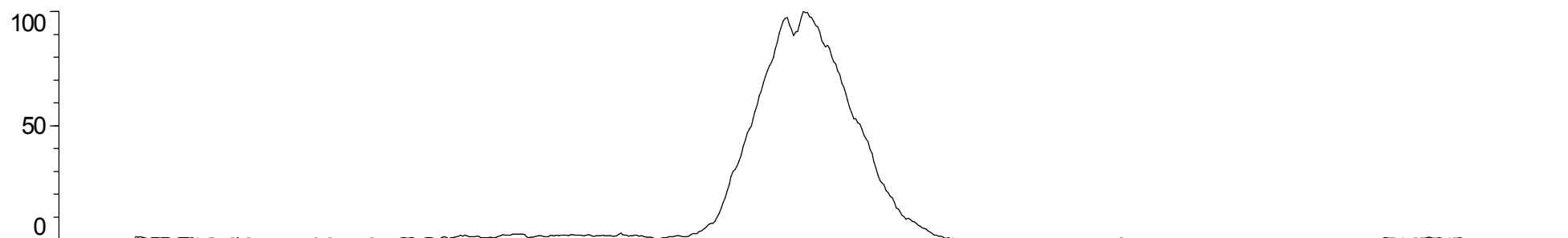
dAcP&line2P_GPC@DT

Data: paraZnH2_DT75_high_best_0001.15 25 Mar 2010 9:28 Cal: tof 23 Mar 2010 5:12

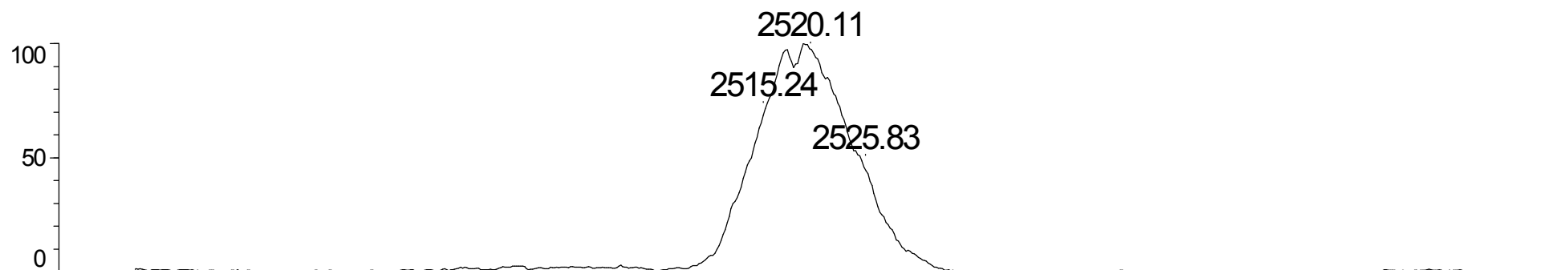
Kratos PCKompact Probe V1.2.2: + Linear High, Power: 75, P.Ext. @ 2457 (bin 58)

S12-2 MALDI TOF Mass Spectra of pZnFb

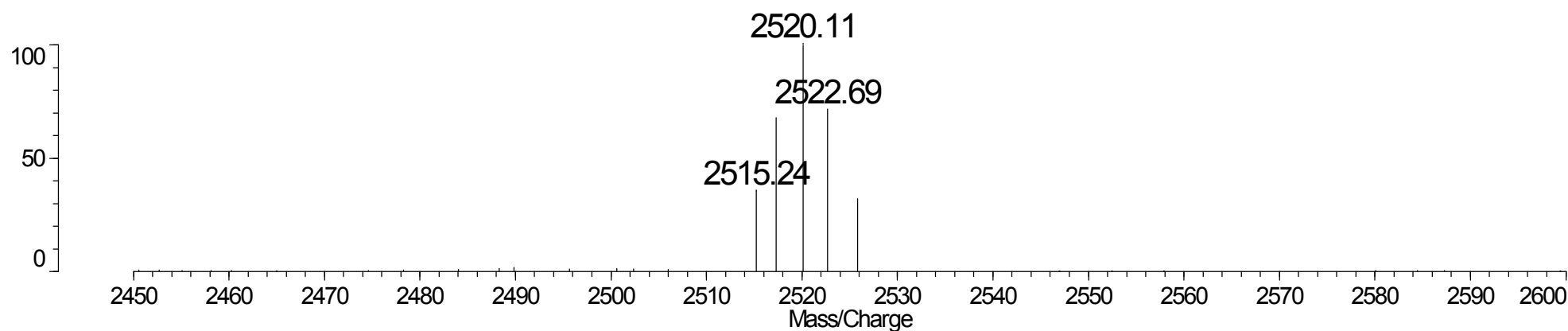
%Int. 100% = 86 mV Profile 100



%Int. 100% = 86 mV[sum= 8618 mV] Profiles 1-100 Unsmoothed

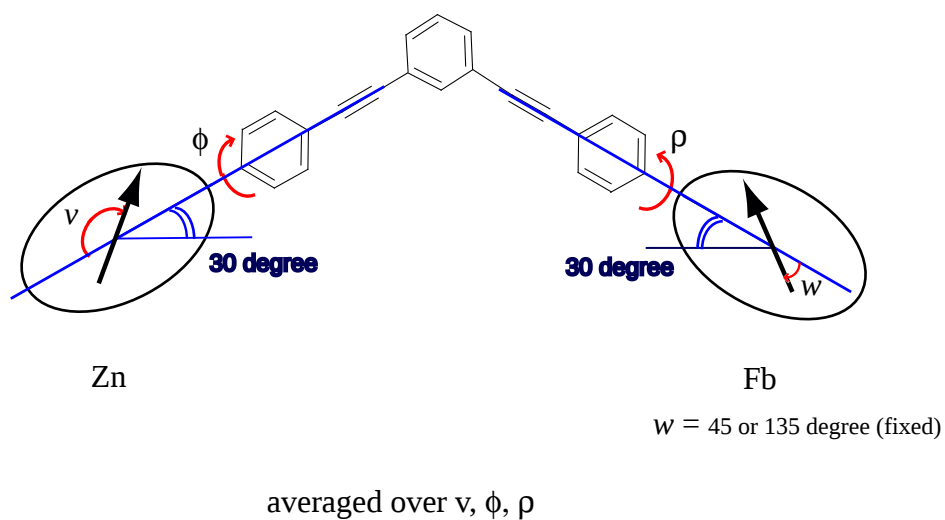


%Int. 100% = 27181 mV Profiles 1-100:

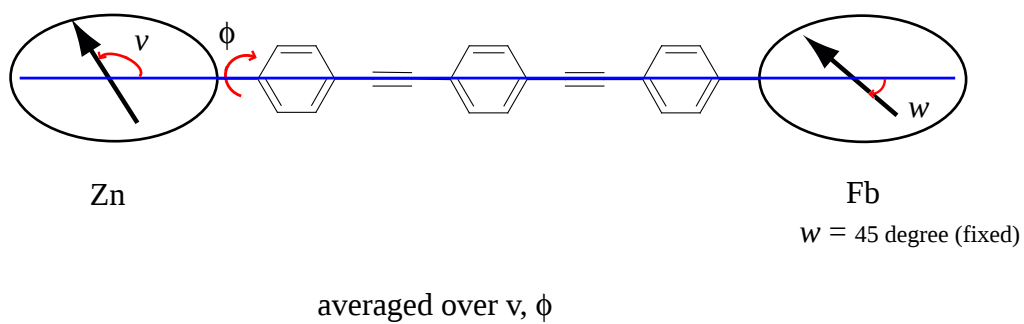


S13-1 Geometrical parameters for averaging the orientation factor, κ

1

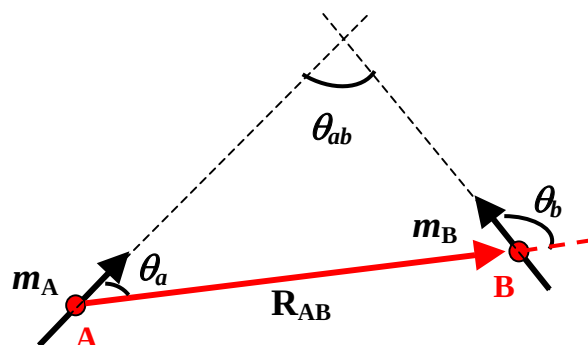


2



S13-2 definition of κ

$$\kappa = \cos \theta_{ab} - 3 \cos \theta_a \cdot \cos \theta_b$$



The above definition is equivalent to the following,

$$\kappa = \sin \theta_a \sin \theta_b \cos \varphi - 2 \cos \theta_a \cdot \cos \theta_b$$

