Supporting Information Section

Additional data for the characterization of the peak J compound (21)

The MS analysis:

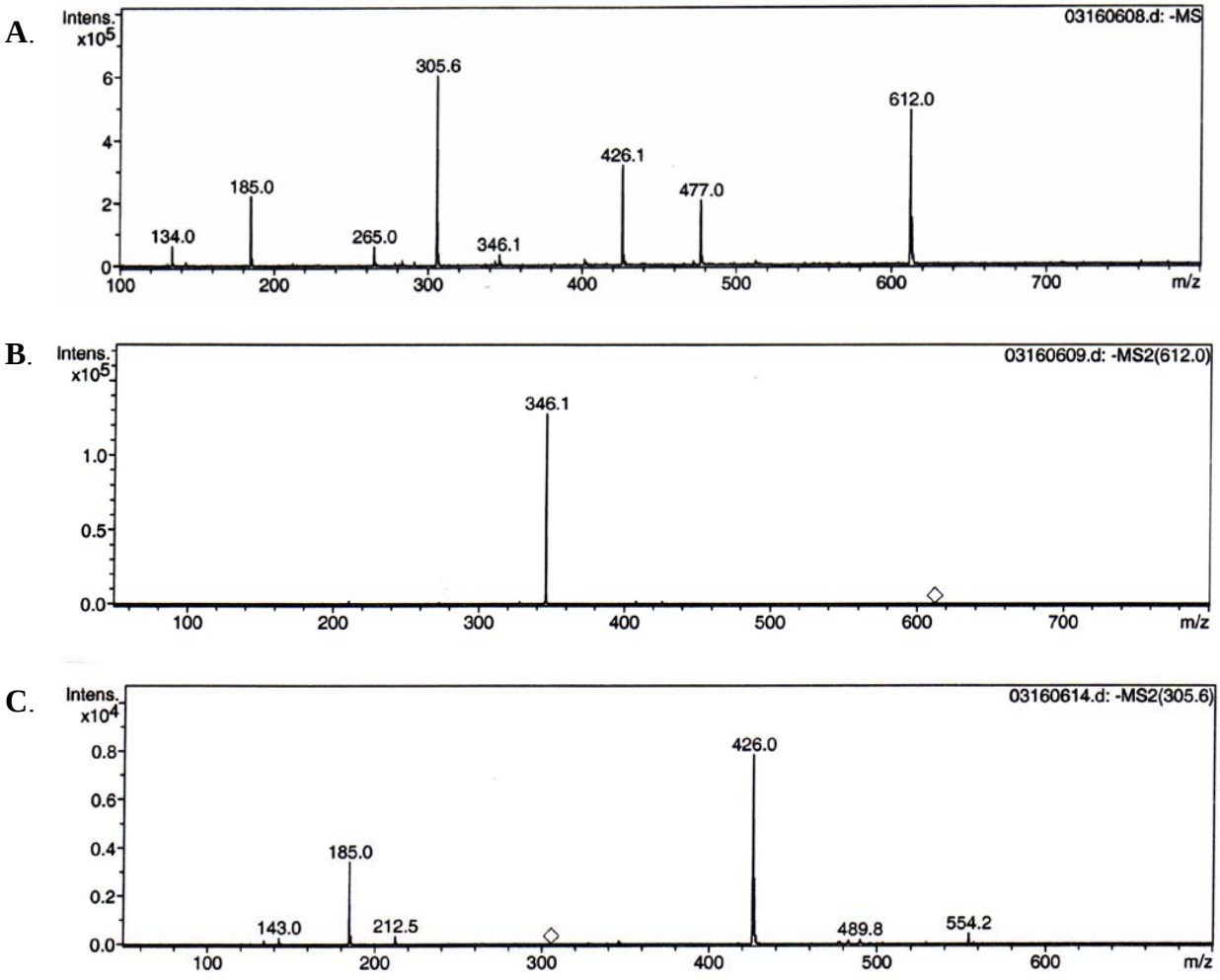


Figure S1: MS analysis of the compound **21**. A: Negative mode ESI-MS data of the compound **21**. B: Fragmentation analysis on the species with m/z = 612. C: Fragmentation analysis of the species with m/z = 305.6

Explanation of the fragmentation patterns:

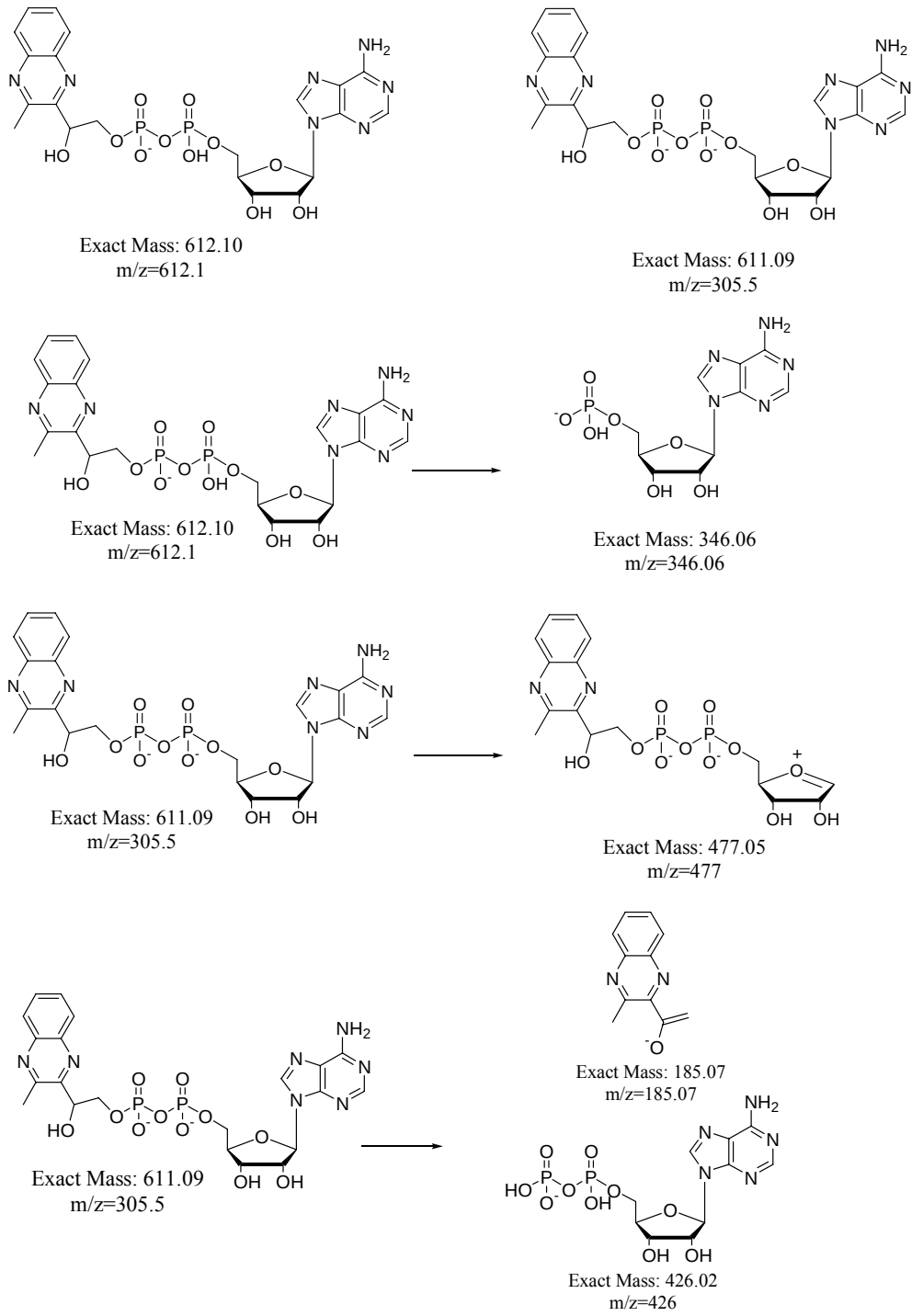


Figure S2: Explanation of the fragmentation patterns of the mono- and di-anionic compound **21**.

The major peak obtained is the one with m/z=305.6, corresponding to the dianionic compound **21**. The monoanionic species with m/z = 612 is also visible. Other than these peaks with m/z= 426, 477 and 185 are also observed, which are fragmentation products of the dianionic **21** (thermal degradation under spraying condition). The fragmentation patterns of both the mono- and the di-anionic species are explained in figure S2.

NMR analysis of the compound 21:

COSY:

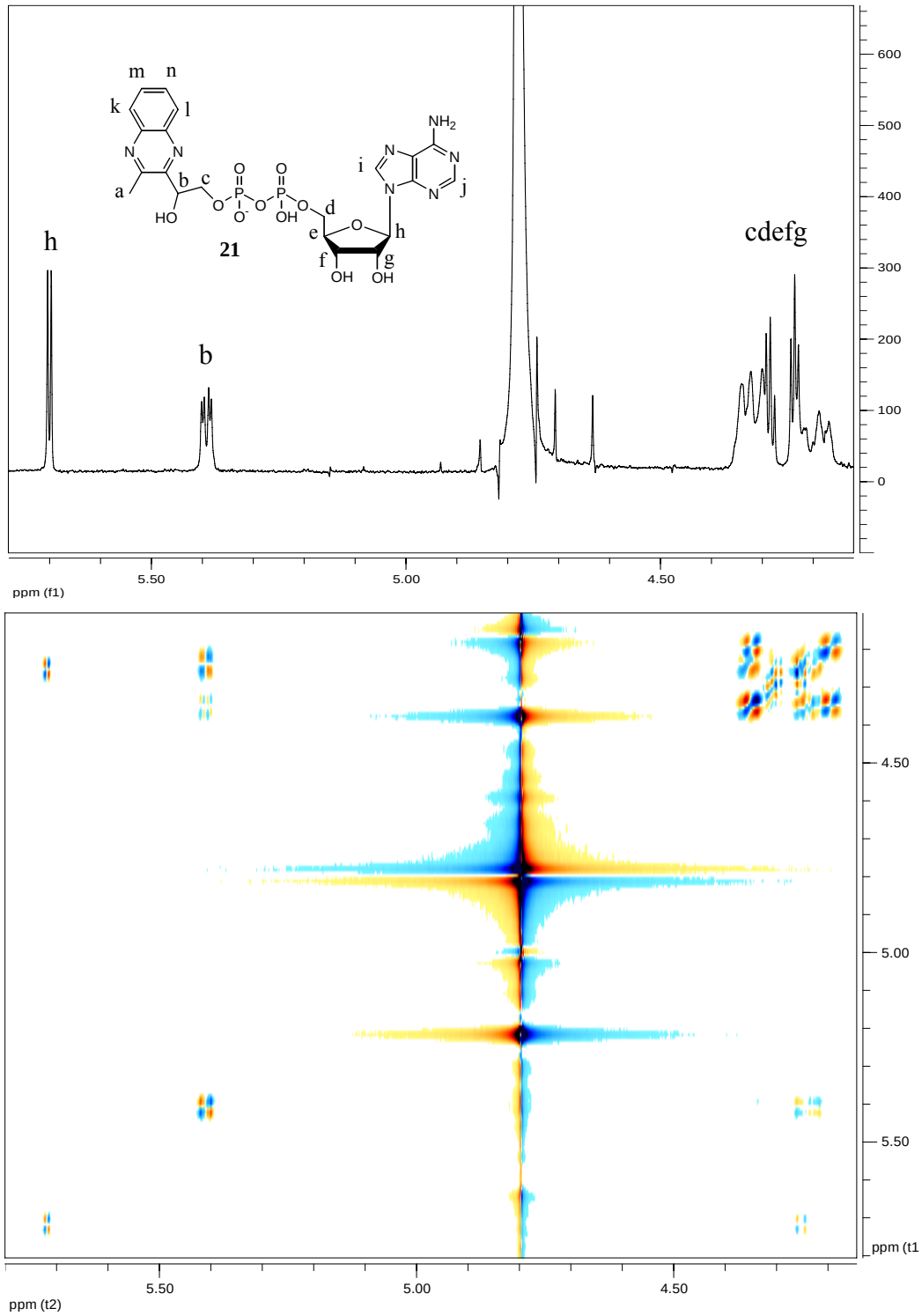


Figure S3: The COSY analysis of the compound **21**.

The COSY analysis showed the presence of two minor impurities: glycerol and lactic acid. It also identified that the protons c d e f g (figure S3) are clustered into a multiplet between 4.1 and 4.4 ppm.

Magnified image of the aromatic region in the COSY spectra:

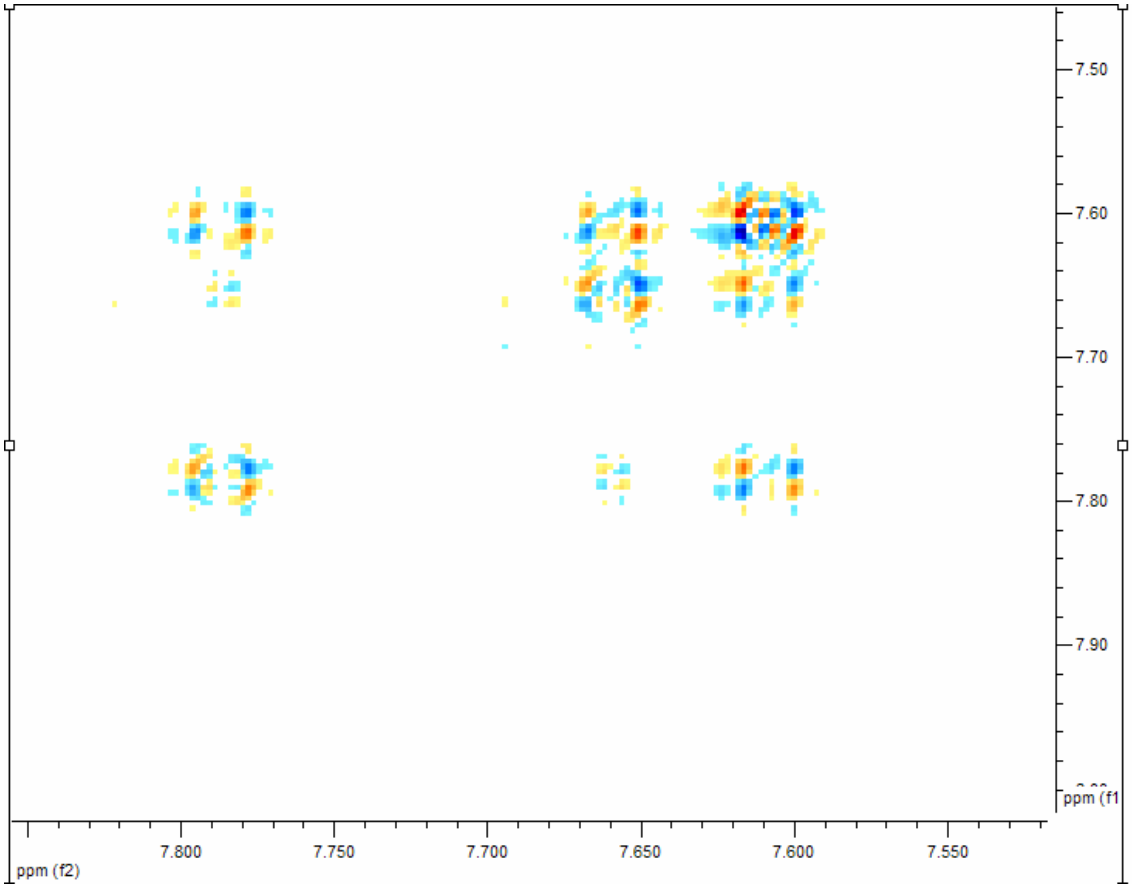


Figure S4: Magnified COSY correlation diagram

ROESY:

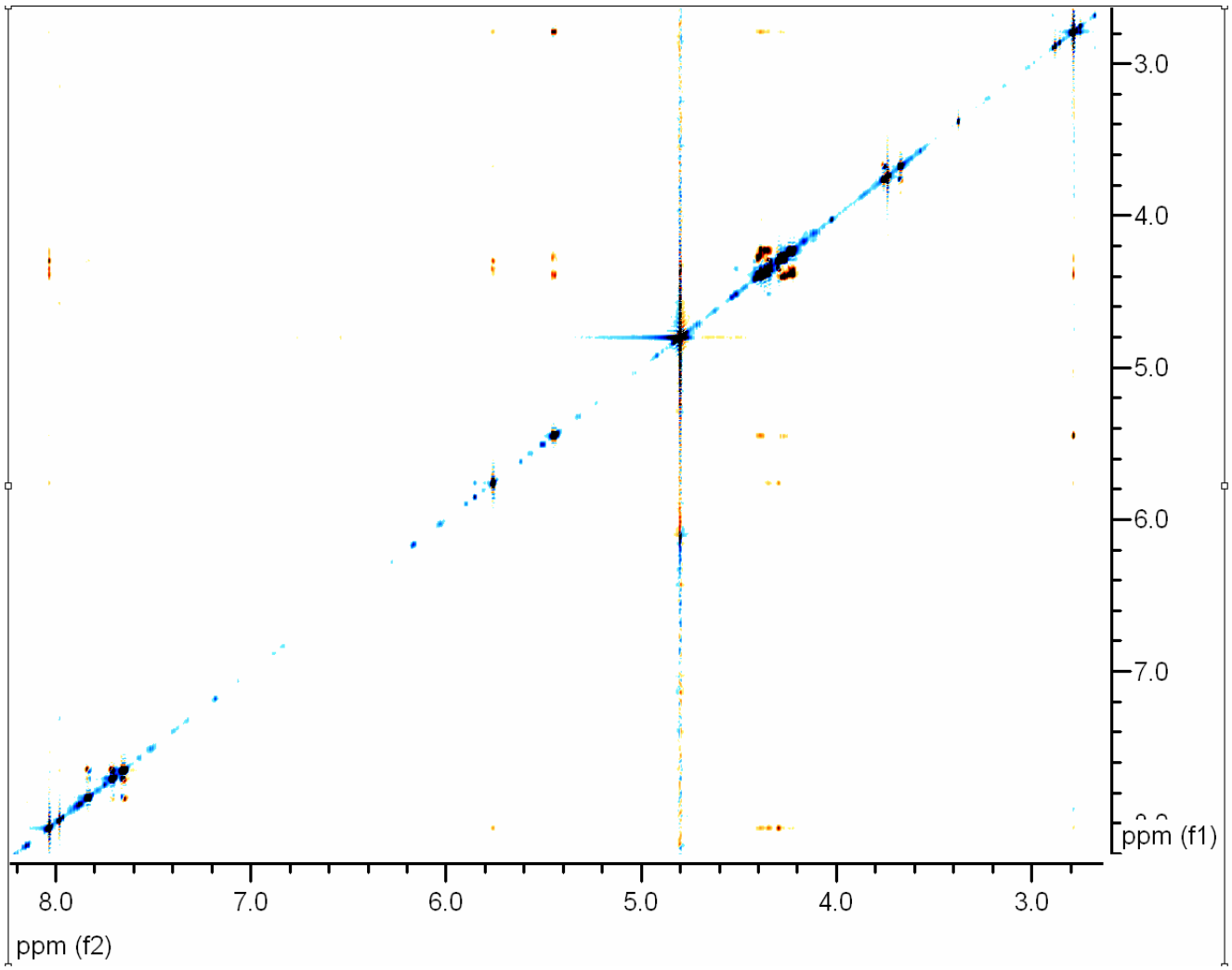


Figure S5: Phase-sensitive ROESY (mixing time 300 ms) of the compound **21**

HMQC:

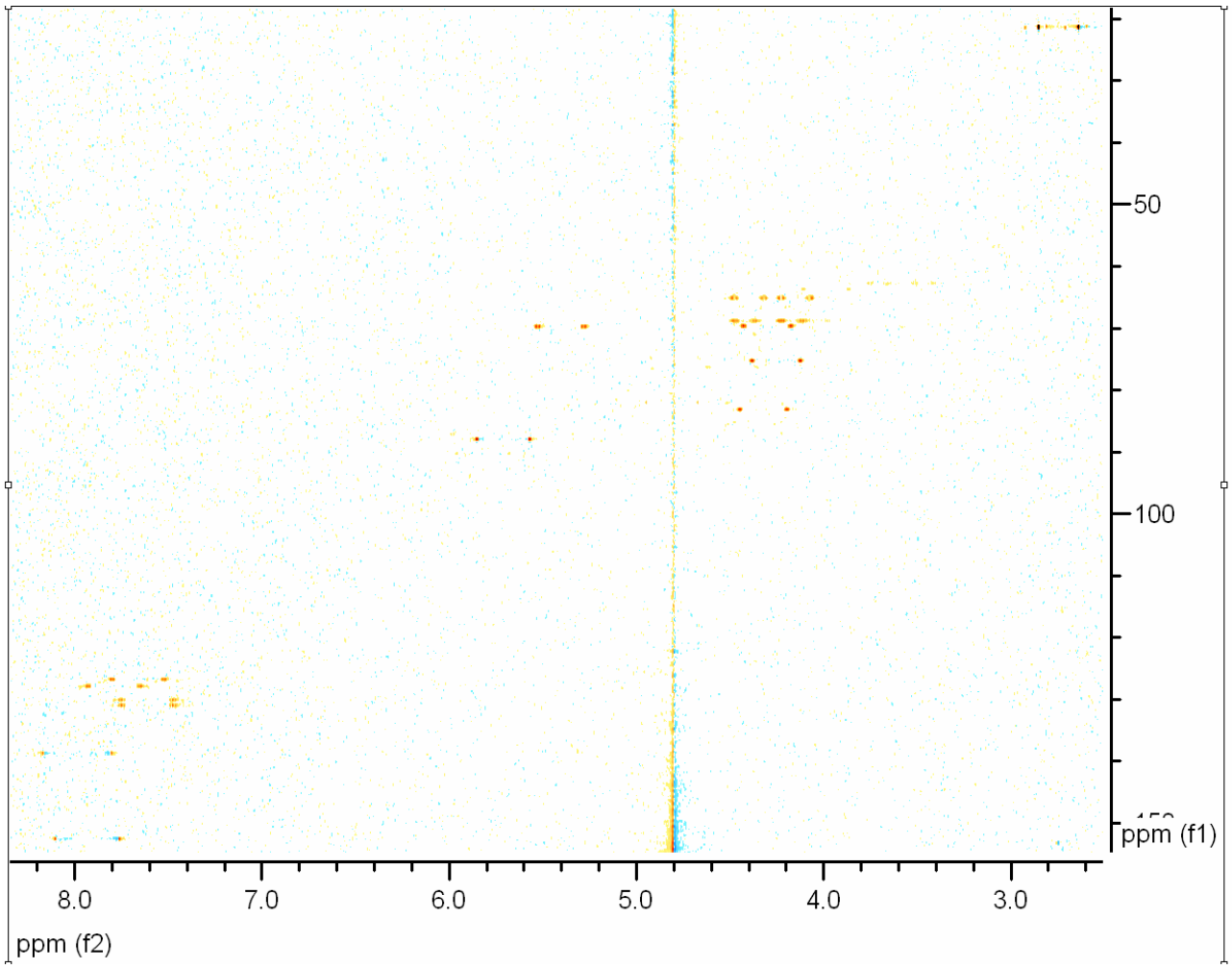


Figure S6: (^{1}H-^{13}C)-coupled phase-sensitive non-gradient HMQC analysis of the compound **21**

HMBC:

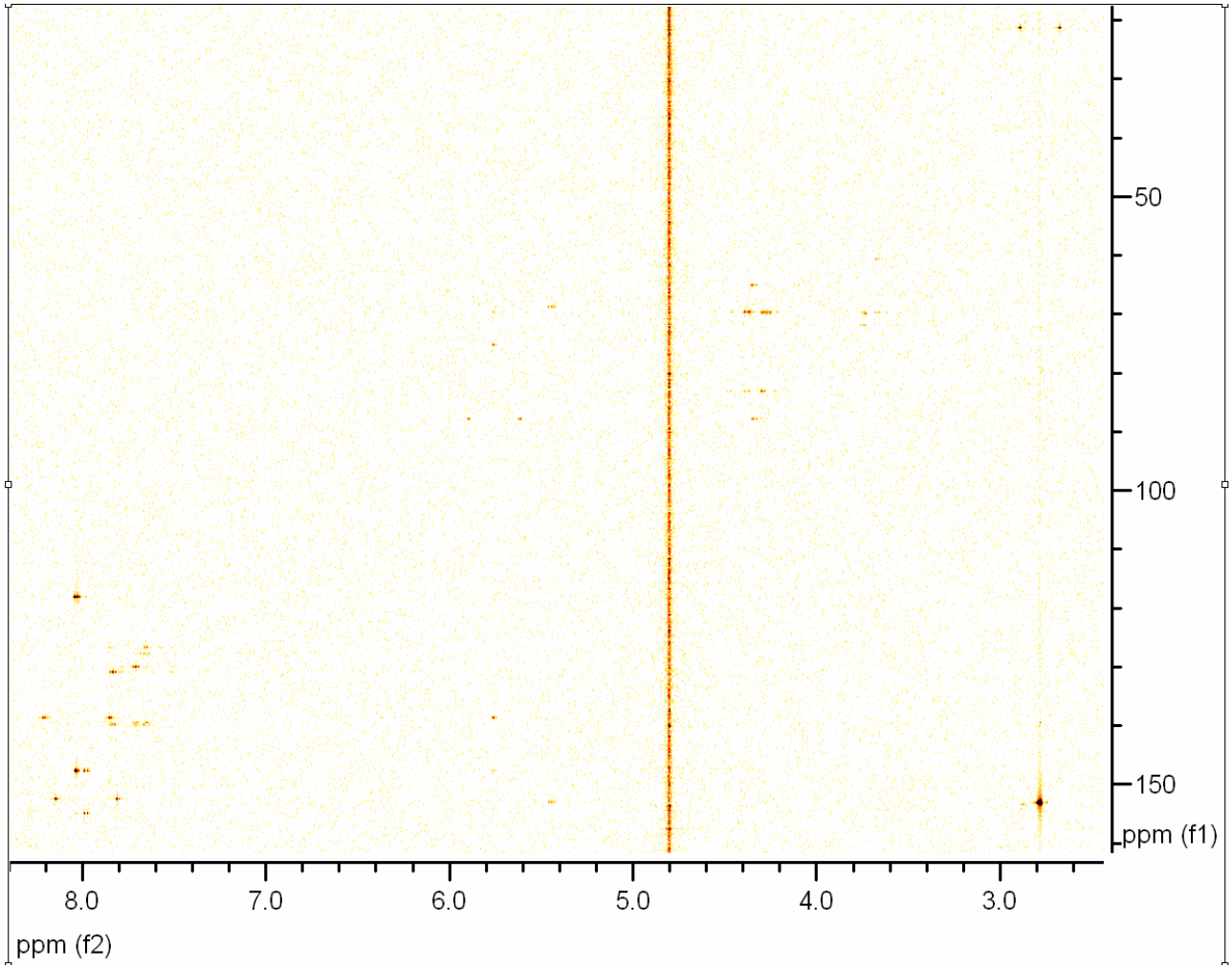


Figure S7: Non-gradient (^{1}H-^{13}C) HMBC analysis of the compound **21**

Magnified images of the different regions of the HMBC correlation diagram:

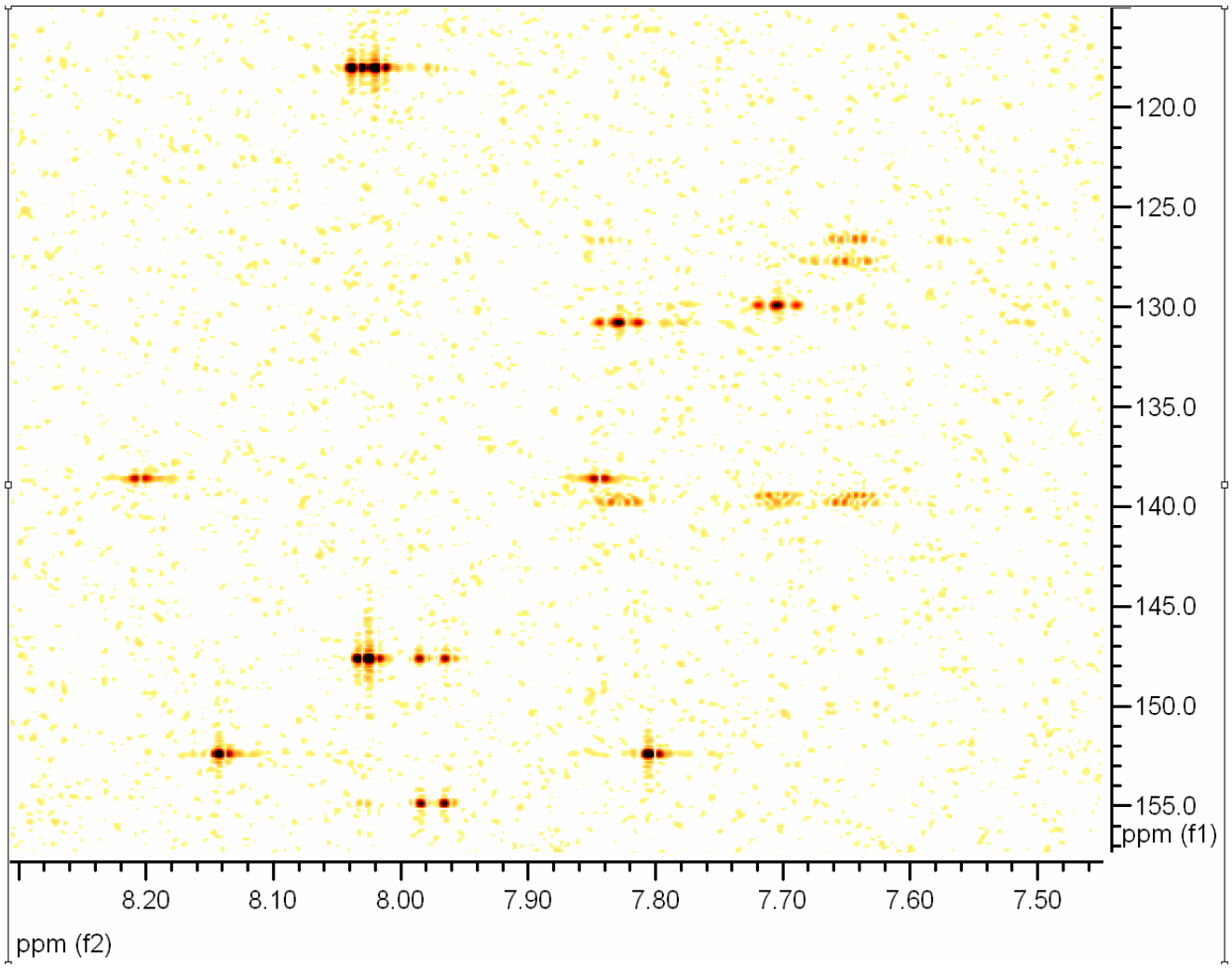


Figure S8: Magnified HMBC correlation diagram

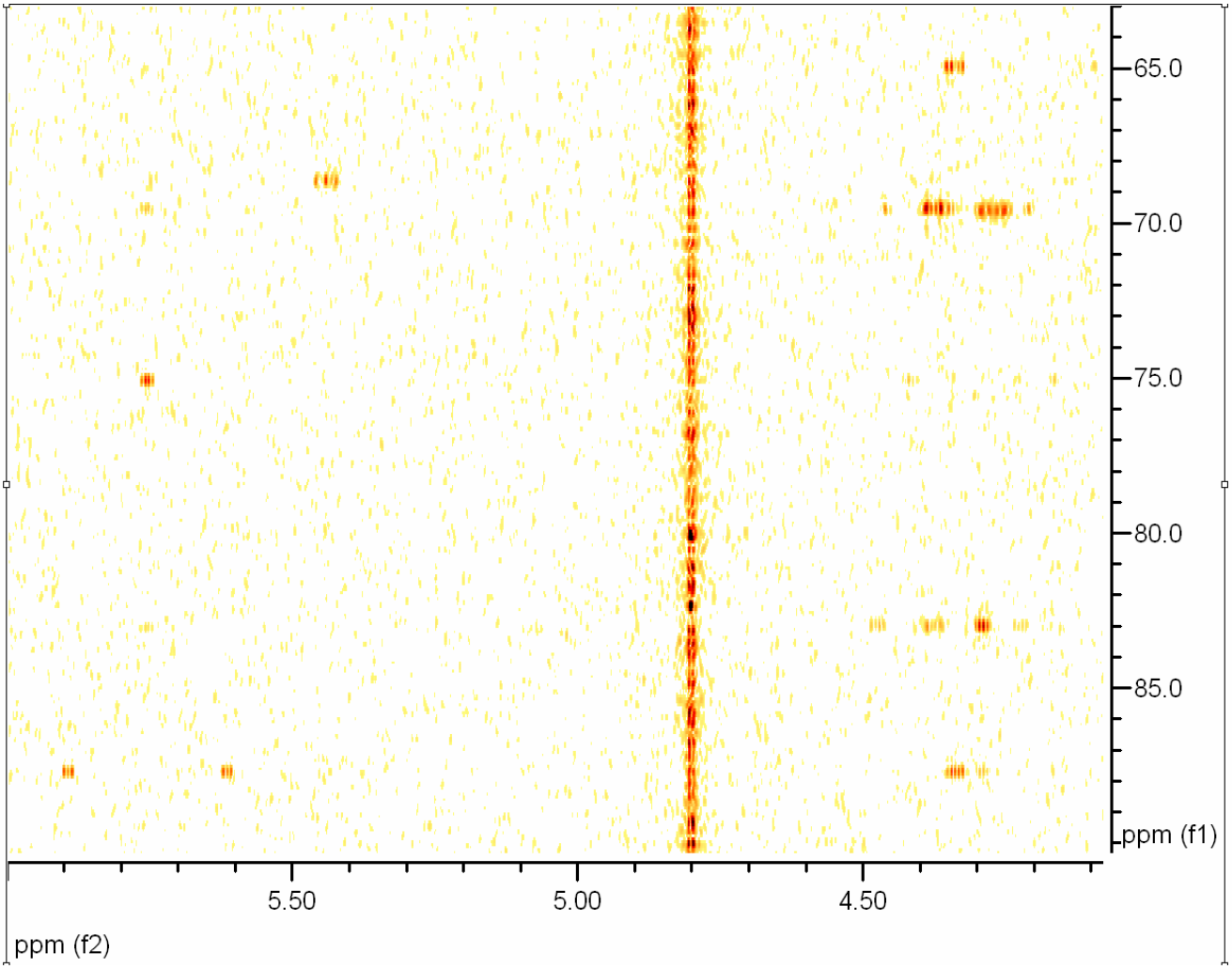


Figure S9: Magnified HMBC correlation diagram

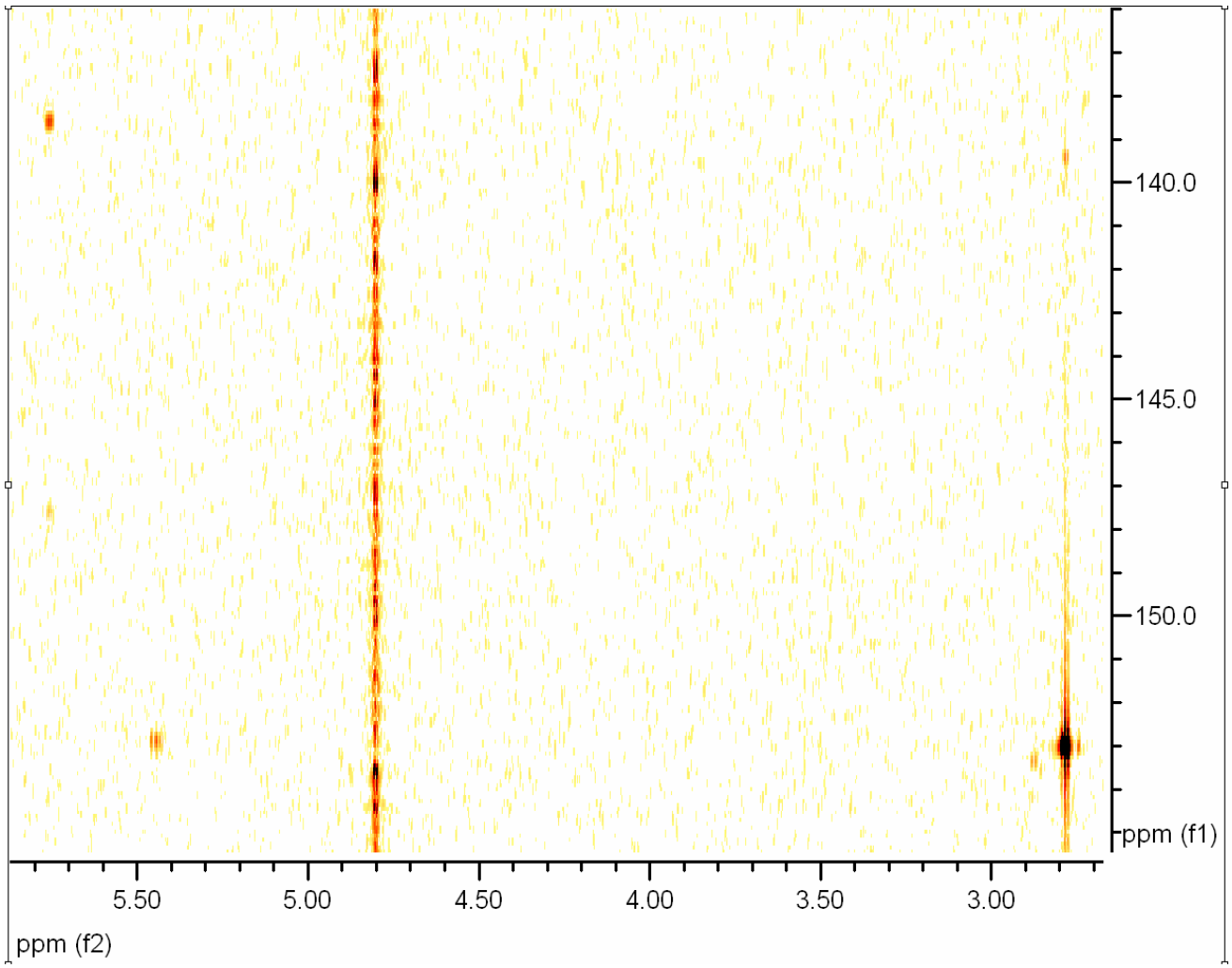
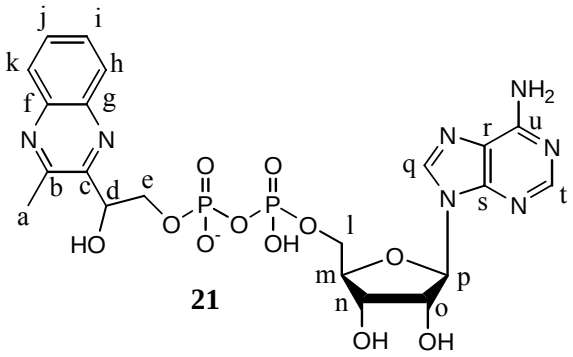


Figure S10: Magnified HMBC correlation diagram

Summary of all the chemical shifts and the correlations deduced from the NMR spectroscopic analysis of compound 21:



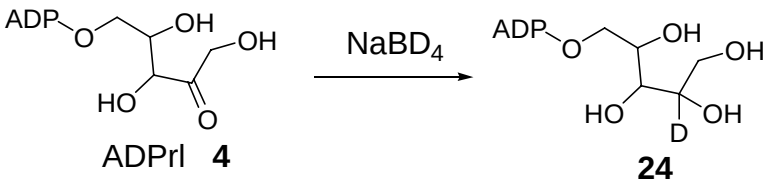
21

Position	δ ^{13}C [ppm]	δ ^{1}H [ppm]	Relevant HMBC Correlations	Relevant COSY Correlations	Relevant ROESY Correlations
a	**21.2**	**2.74**	**C-b, C-c, C-f**	**-**	**H-d, H-e**
b	**153.06**	**-**	**-**	**-**	**-**
c	**152.91**	**-**	**-**	**-**	**-**
d	**69.7**	**5.4**	**C-c, C-e**	**H-e**	**H-a, H-e**
e	**68.7**	**4.35** **4.24**	**C-d**	**H-d**	**H-d, H-a**
f	**139.4**	**-**	**-**	**-**	**-**
g	**139.8**	**-**	**-**	**-**	**-**
h	**127.7**	**7.78**	**C-g, C-i**	**H-i, H-j**	**-**
i	**130.8**	**7.57-7.62**	**C-f, C-g, C-h, C-k**	**H-h, H-j, H-k**	**-**
j	**129.9**	**7.57-7.62**	**C-f, C-g, C-h, C-k**	**H-h, H-i, H-k**	**-**
k	**126.6**	**7.66**	**C-j, C-f**	**H-i, Hj**	**-**
l	**65.1**	**4.35, 4.19**	**C-m**	**H-m**	**-**
m	**83.1**	**4.31**	**C-l, C-p**	**H-l, H-n**	**-**
n	**69.6**	**4.3**	**-**	**H-o, H-m**	**-**
o	**75.2**	**4.25**	**C-p**	**H-p, H-n**	**-**
p	**88.0**	**5.71**	**C-n, C-o, C-q, C-s**	**H-o**	**-**

q	**138.5**	**7.96**	**C-r, C-s**	**-**	**-**
r	**118.1**	**-**	**-**	**-**	**-**
s	**147.7**	**-**	**-**	**-**	**-**
t	**152.5**	**7.91**	**C-s, C-u**	**-**	**-**
u	**154.9**	**-**	**-**	**-**	**-**

Further charactarization of ADP-ribulose (ADPrl **4** peak **F**):

Purified ADPrl **4** was reduced with $NaBD_4$ and the corresponding product of reduction was purified by HPLC and was characterized by NMR (^1H and COSY).



ADPrl **4** **24**

Figure S11: Reduction of ADPrl **4** by $NaBD_4$ to stable deuterated reduction product **24**.

NMR analysis of compound 24:

1H NMR:

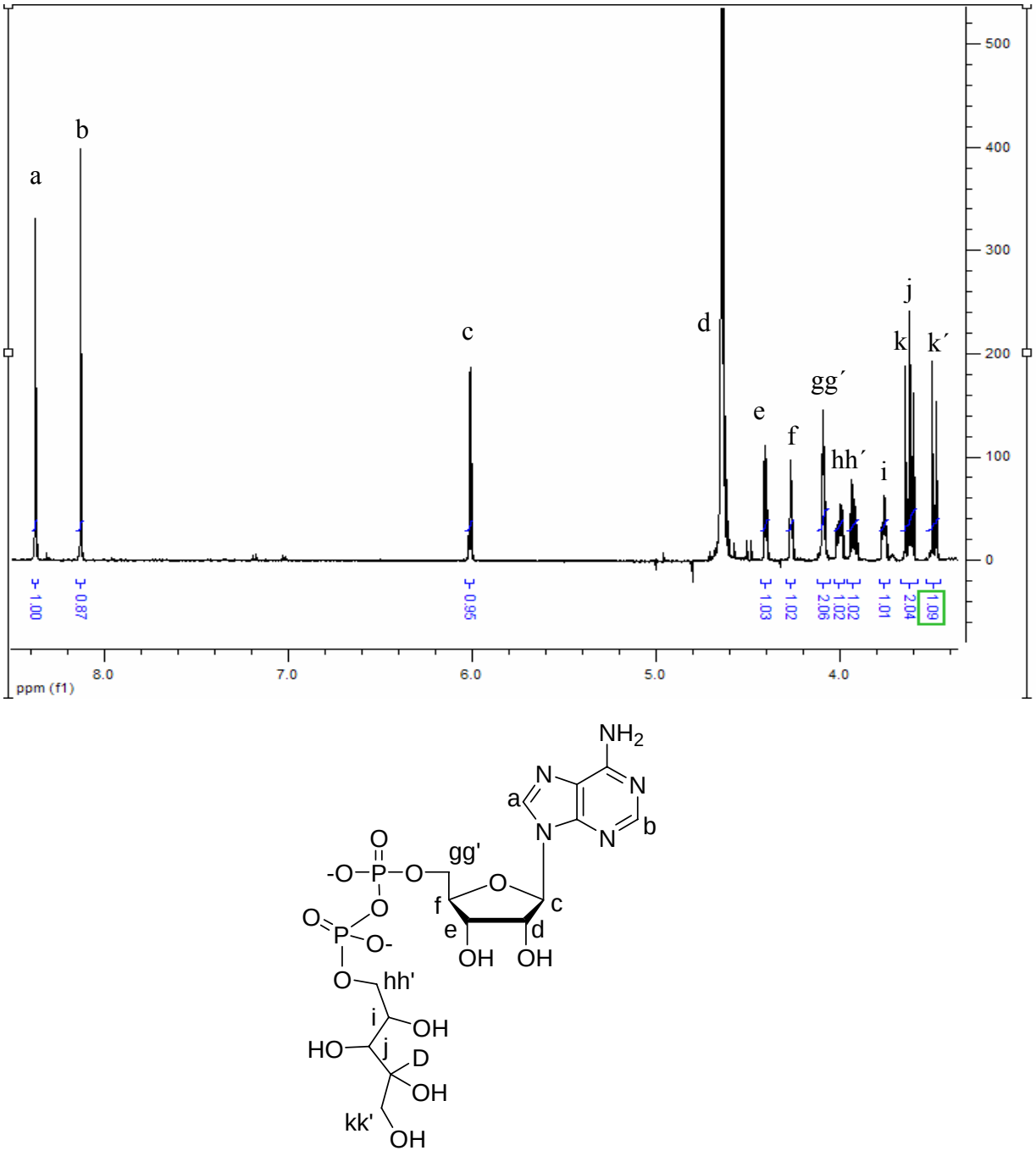


Figure S12: ^{1}H NMR of compound **24**. The assignments are based on the COSY experiment. The peak d is hidden under the water peak and is revealed from the COSY experiment.

COSY analysis:

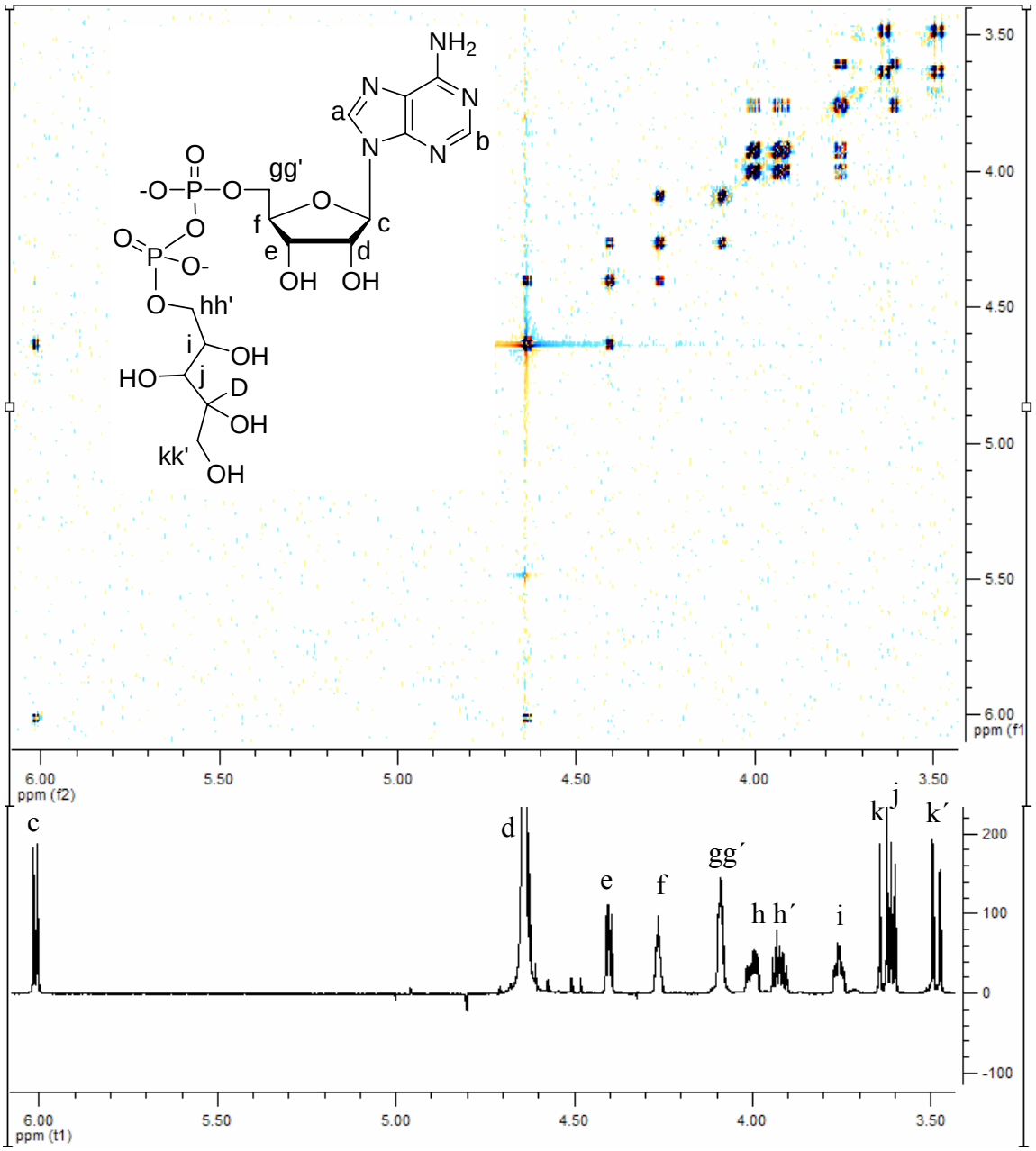


Figure S13: COSY analysis of the compound **24**.

Figure S14: Expanded region of the COSY spectrum of the compound **24**.