Return of the lysergamides. Part VII: Analytical and behavioural characterization of 1-valeroyl-*d*-lysergic acid diethylamide (1V-LSD)

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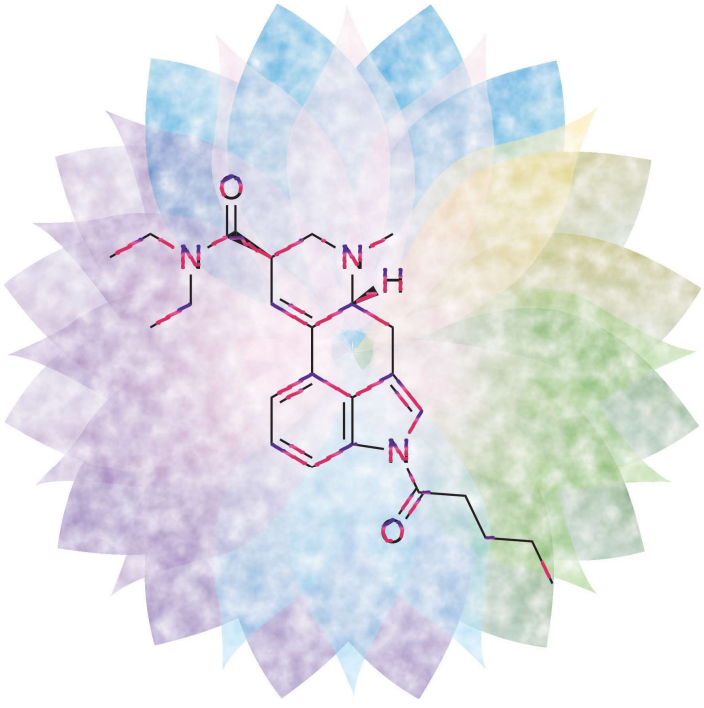
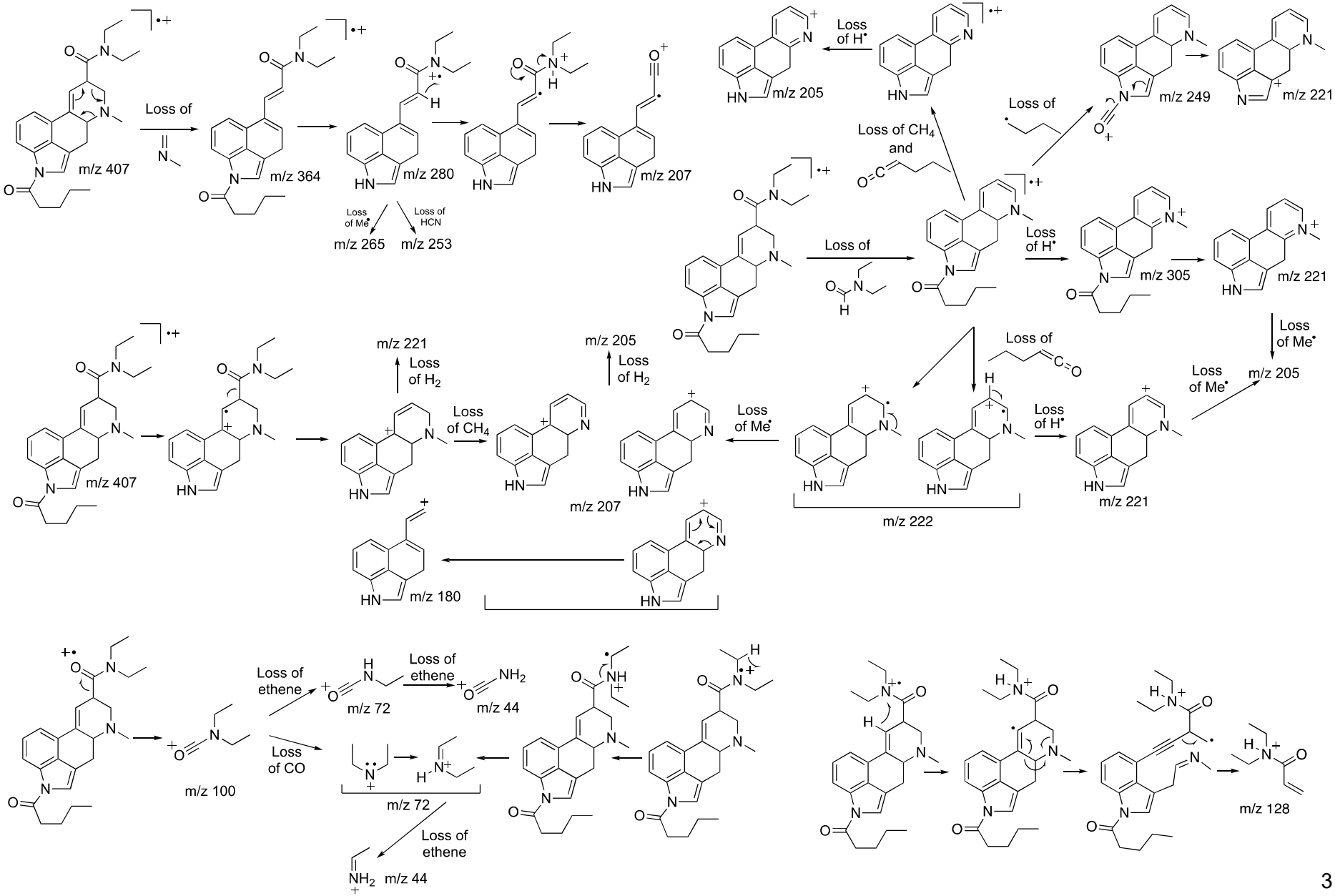
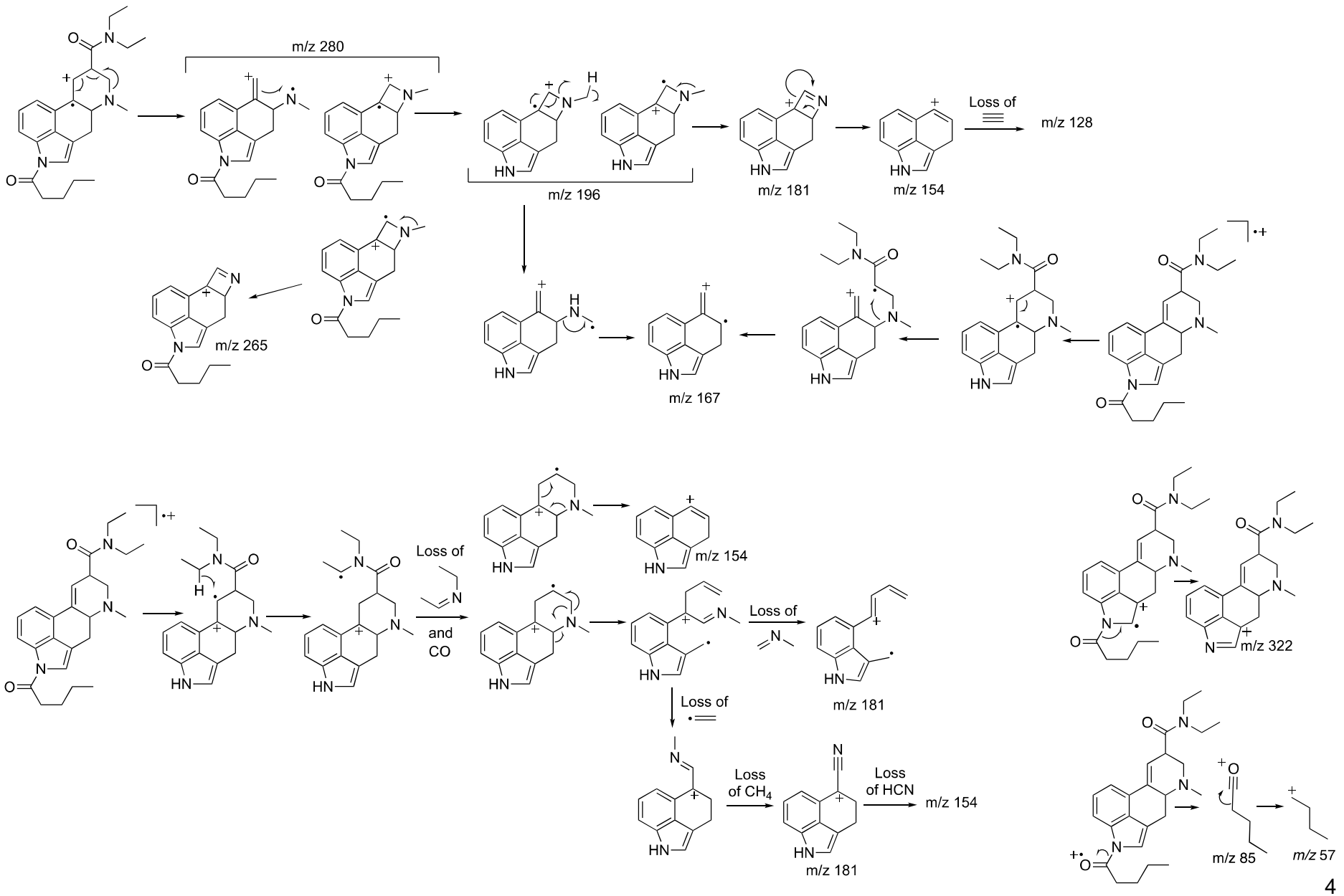
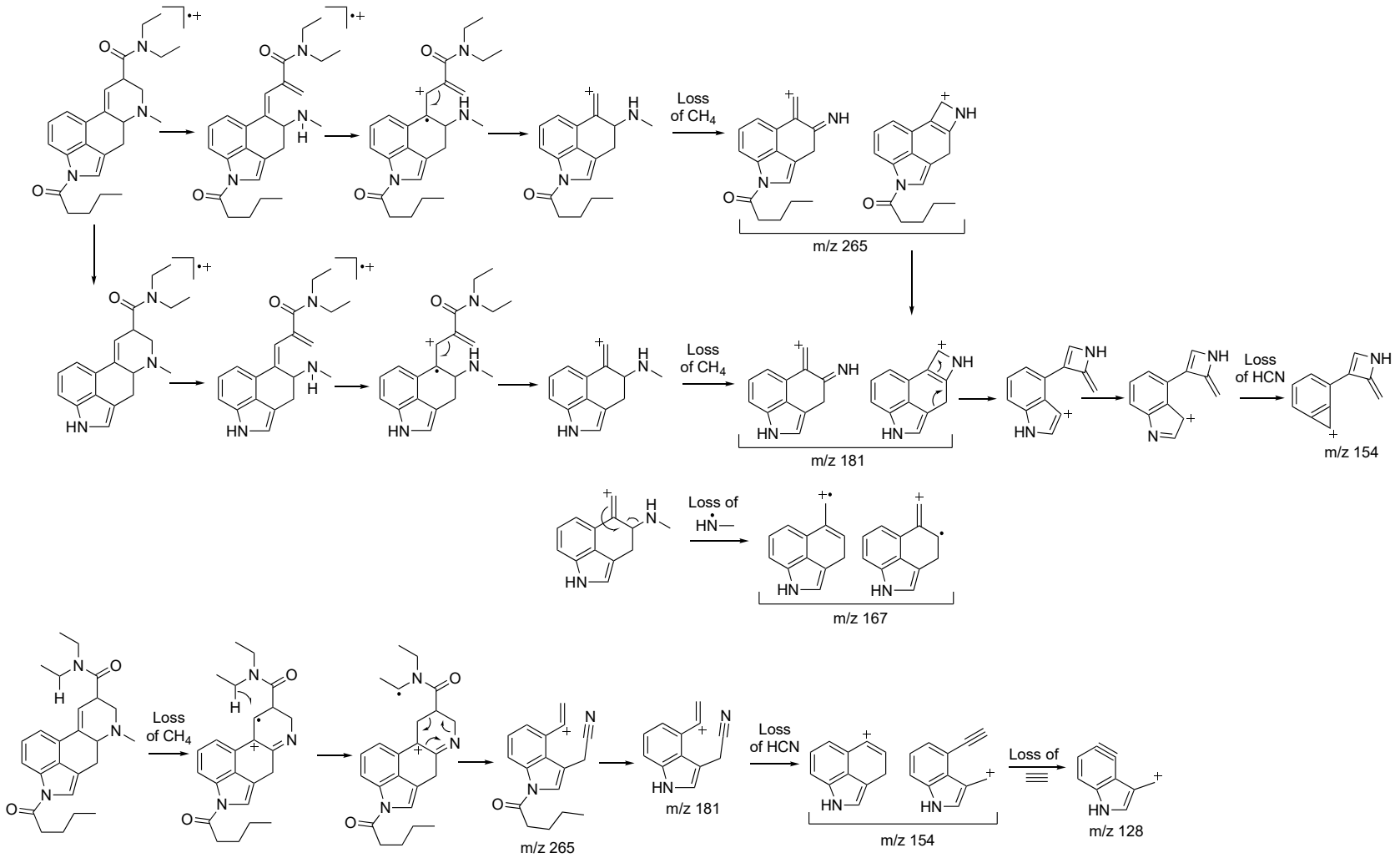
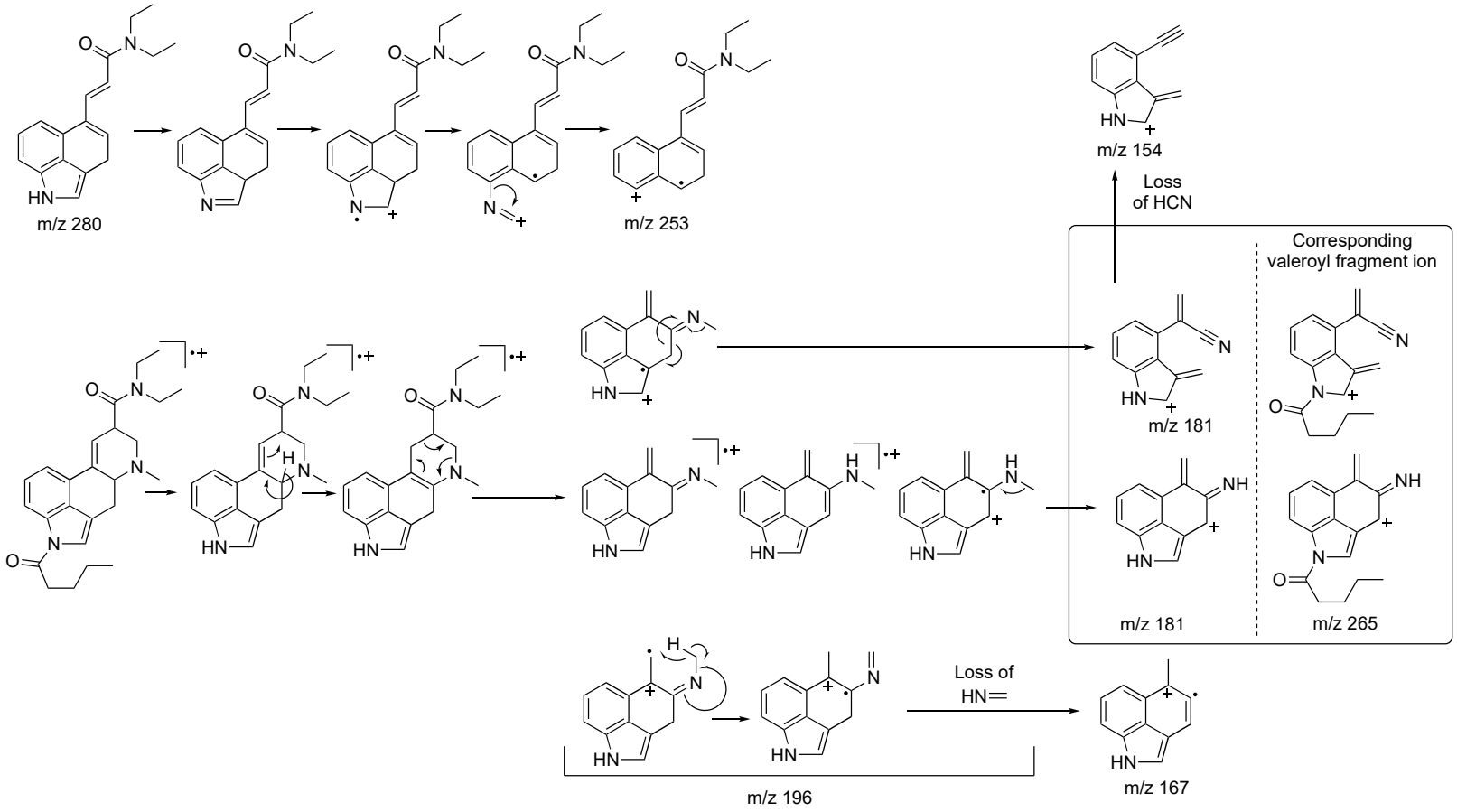



m/z 407
Loss of
m/z 364
m/z 280
Loss of Me
Loss of HCN
m/z 265
m/z 253
m/z 207
Loss of H•
m/z 205
Loss of CH4 and
Loss of
m/z 249
m/z 221
Loss of
Loss of H•
m/z 305
m/z 221
Loss of Me•
m/z 205
Loss of
Loss of Me•
m/z 221
Loss of H2
m/z 221
Loss of H2
m/z 205
Loss of CH4
Loss of Me•
m/z 207
m/z 222
m/z 180
Loss of ethene
m/z 72
Loss of ethene
m/z 44
Loss of CO
m/z 100
m/z 72
Loss of ethene
m/z 44
m/z 128

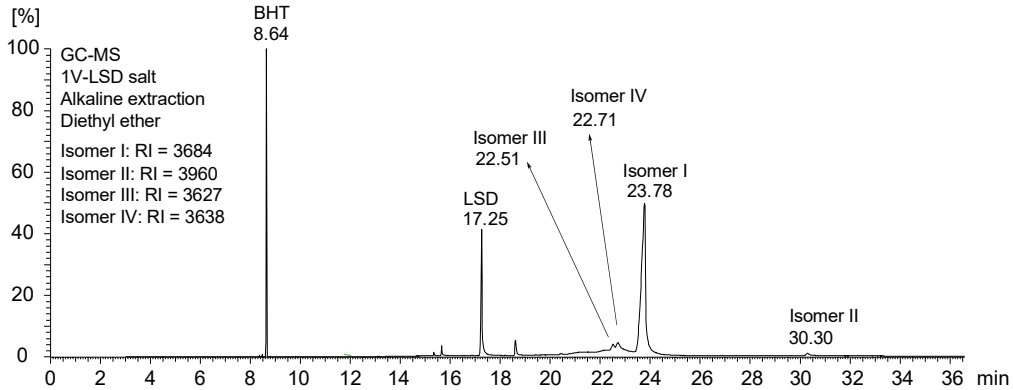

m/z 280
m/z 196
m/z 181
m/z 154
Loss of
m/z 128
m/z 265
m/z 167
Loss of
and
CO
m/z 154
Loss of
m/z 181
Loss of
Loss
of CH_4
Loss
of HCN
m/z 154
m/z 181
m/z 322
m/z 85
m/z 57


Loss of CH_4
m/z 265
Loss of CH_4
Loss of HCN
m/z 181
m/z 154
Loss of HN—
m/z 167
Loss of CH_4
m/z 265
m/z 181
Loss of HCN
m/z 154
Loss of
m/z 128


m/z 280
m/z 253
m/z 154
Loss
of HCN
Corresponding
valeroyl fragment ion
m/z 181
m/z 181
m/z 265
Loss of
HN═
m/z 196
m/z 167

(A) GC-MS analysis of 1V-LSD hemitartrate (2:1) followed by alkaline extraction and GC-induced formation of three minor 1V-LSD isomers. The alkaline extraction procedure led to formation of LSD. BHT: butylated hydroxytoluene additive in diethyl ether. (B) GC-MS analysis of 1V-LSD salt dissolved in methanol. (C) LC-ESI-ion trap-MS analysis of 1V-LSD salt in methanol (extracted ion chromatogram) without detection of other isomers.

(A)



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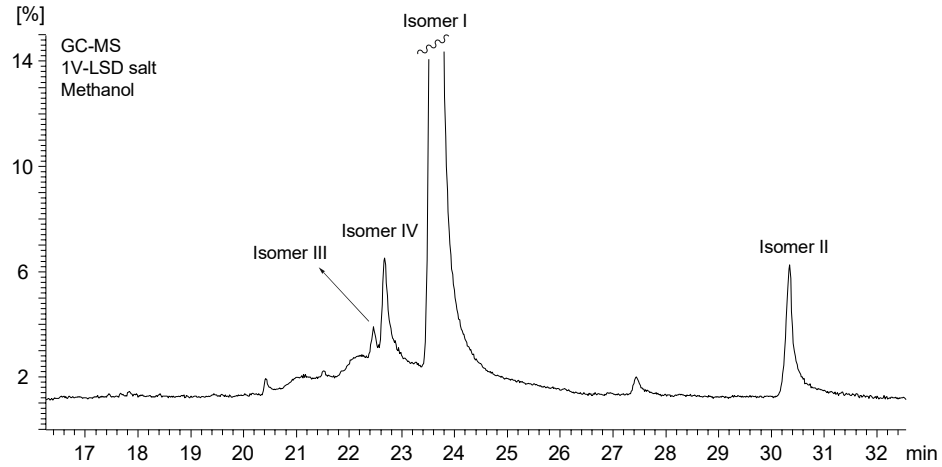
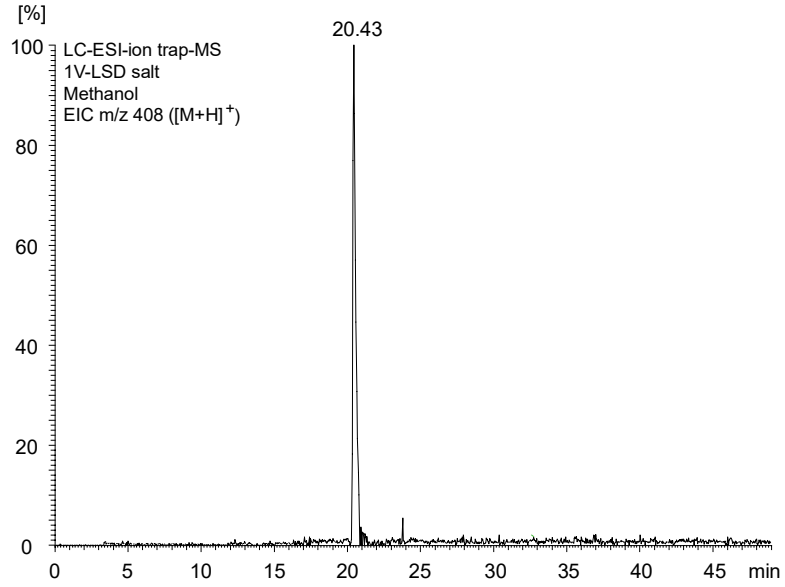
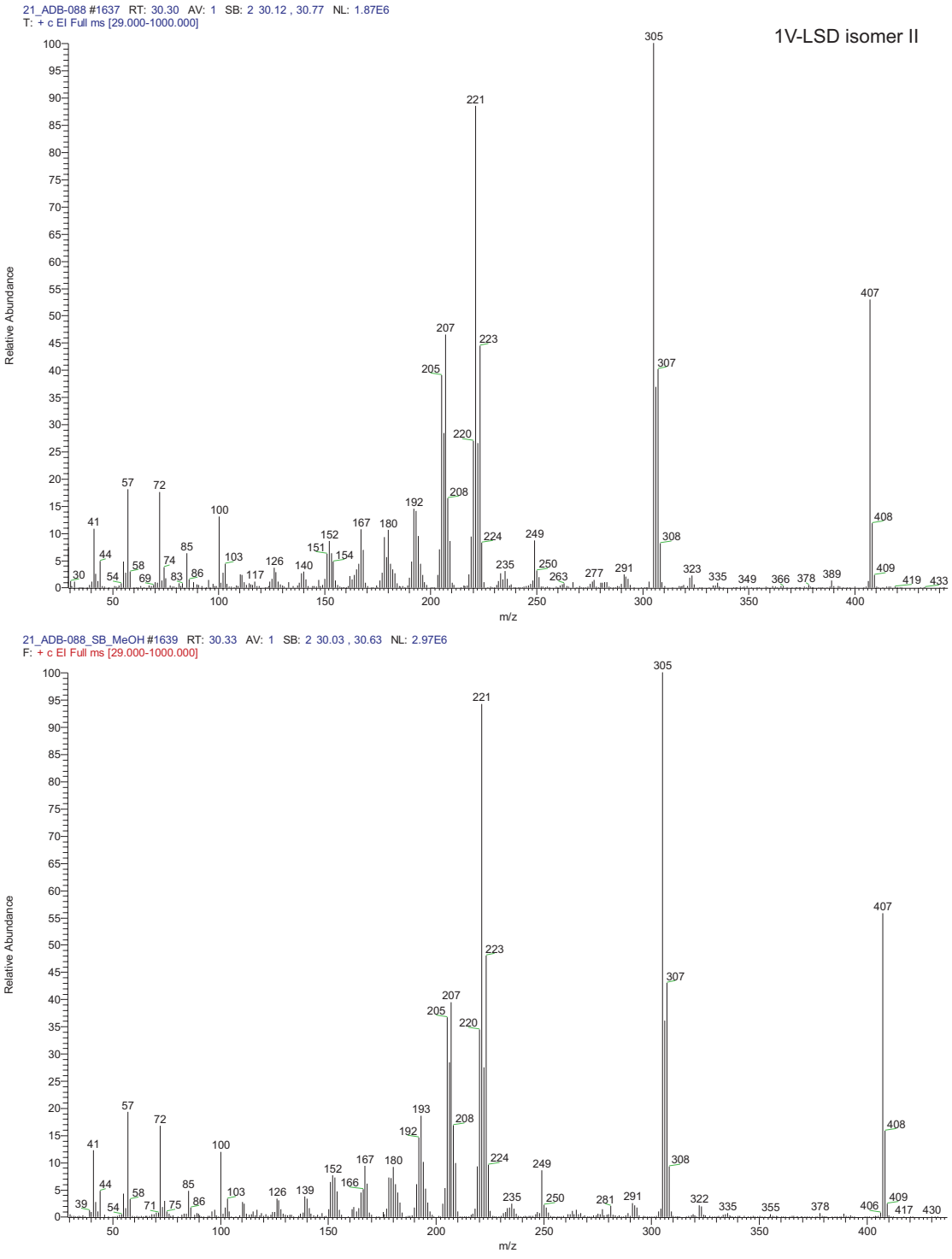


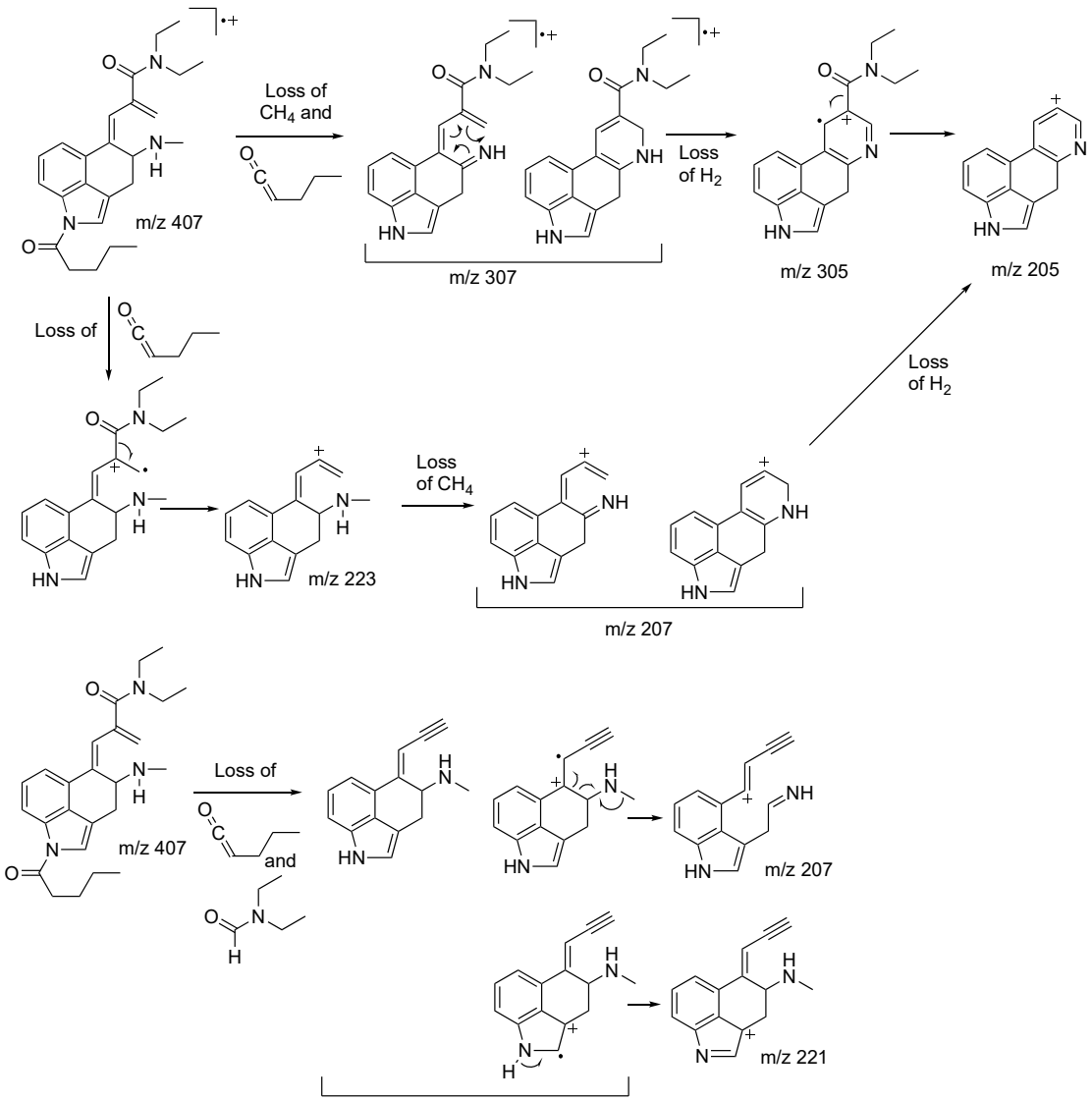
(C)

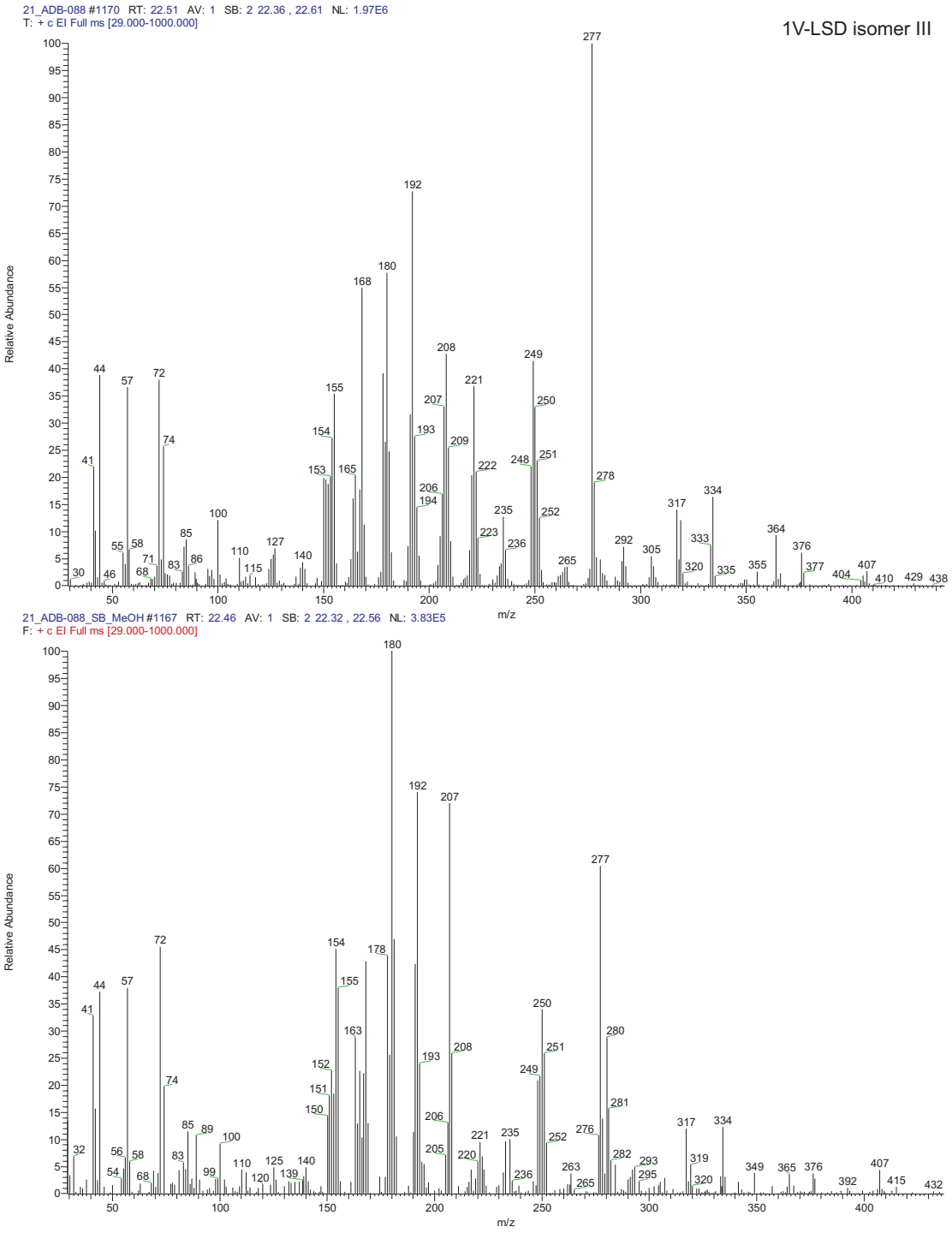




See also page 7. Top: GC-MS TIC trace following alkaline extraction into diethyl ether. Bottom: GC-MS TIC trace following analysis of 1V-LSD hemitartrate salt dissolved in methanol.

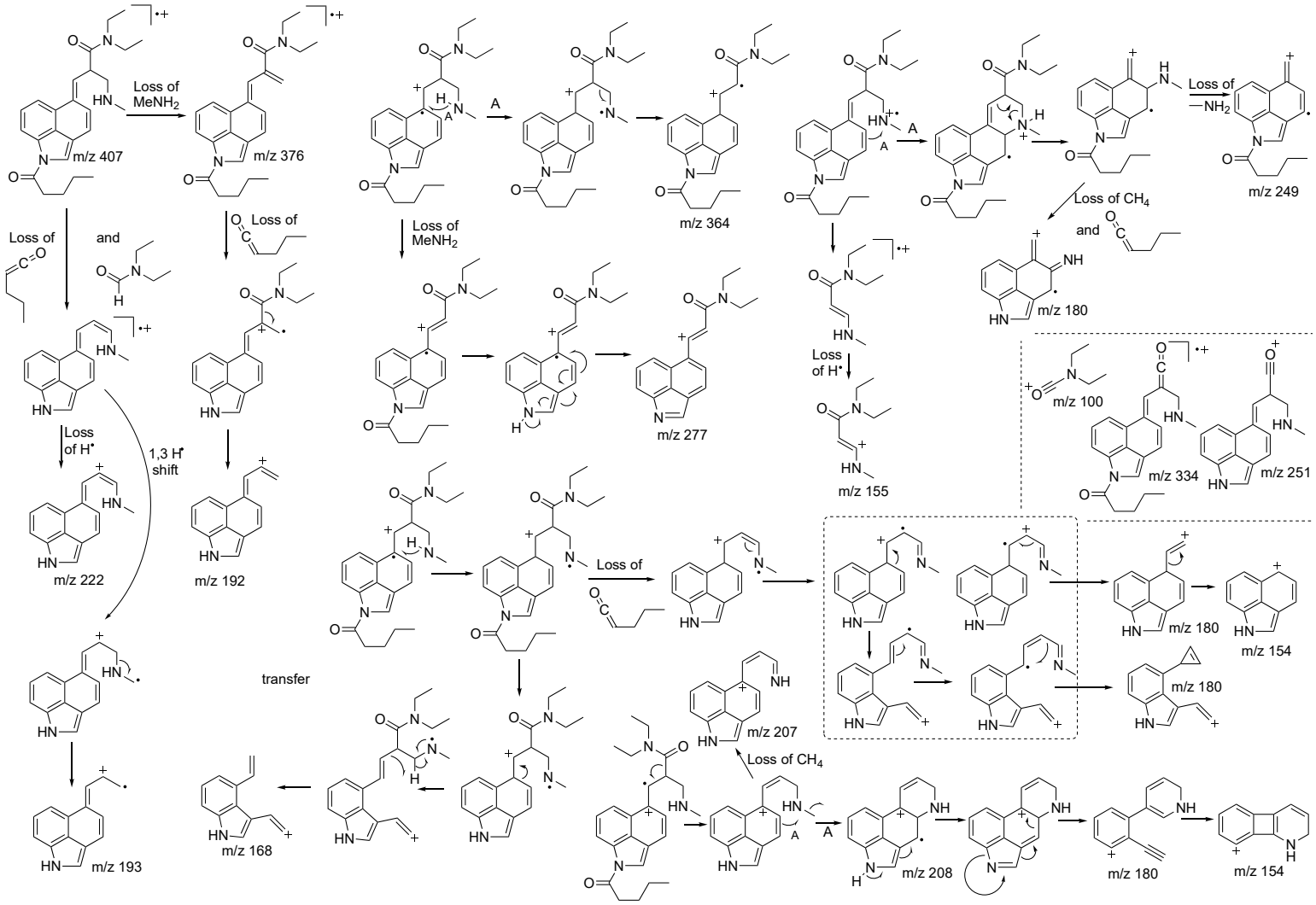
Tentative identification of isomer II

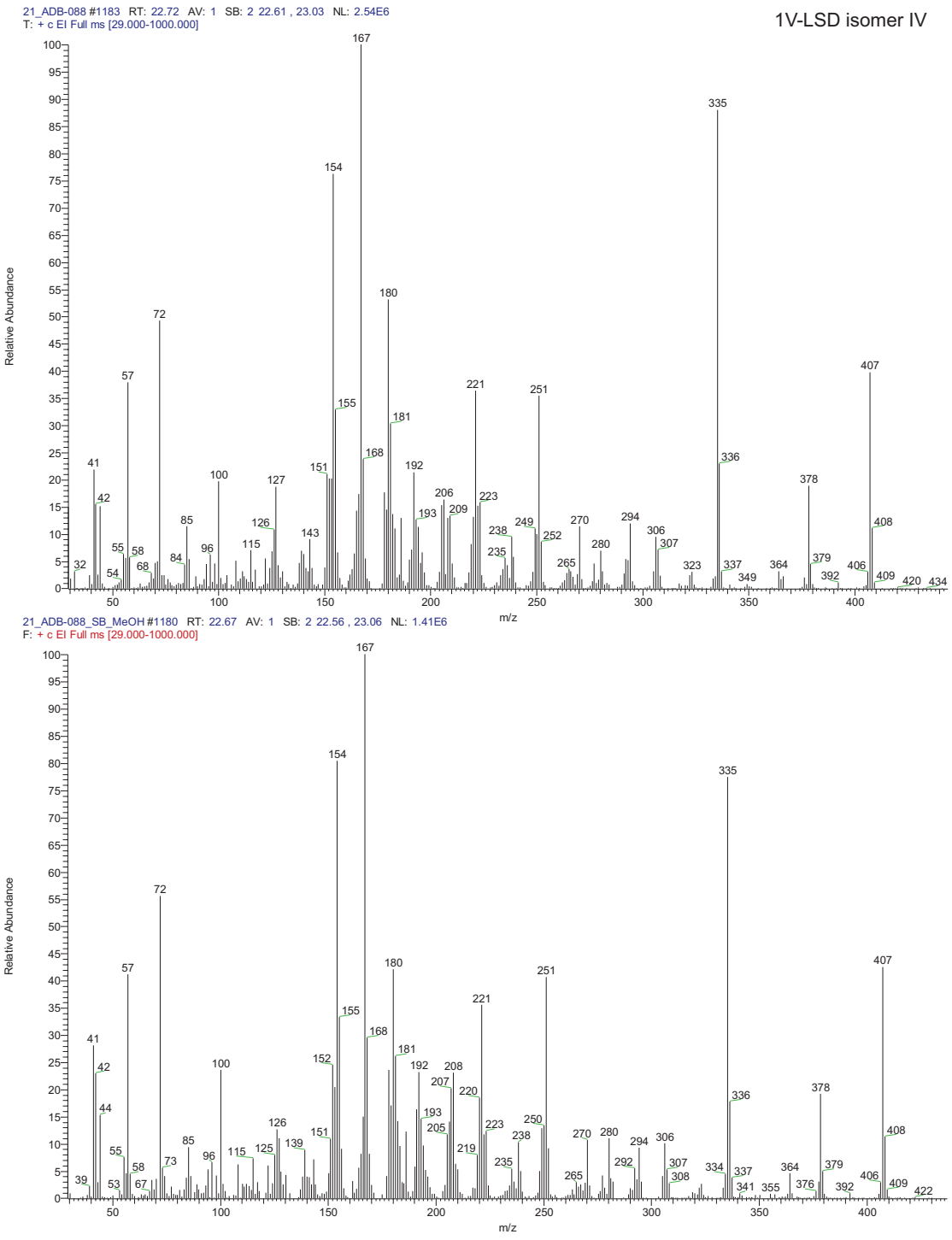




See also page 7. Top: GC-MS TIC trace following alkaline extraction into diethyl ether. Bottom: GC-MS TIC trace following analysis of 1V-LSD hemitartrate salt dissolved in methanol.

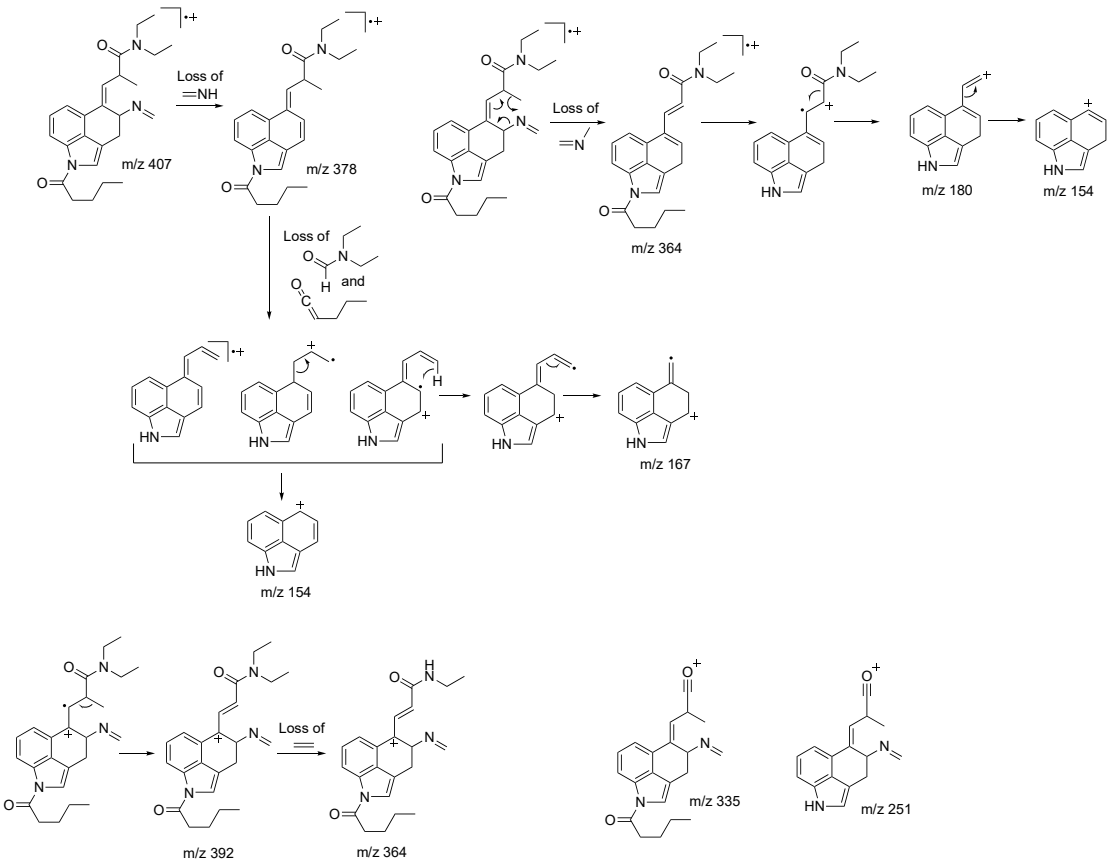
Tentative identification of isomer III





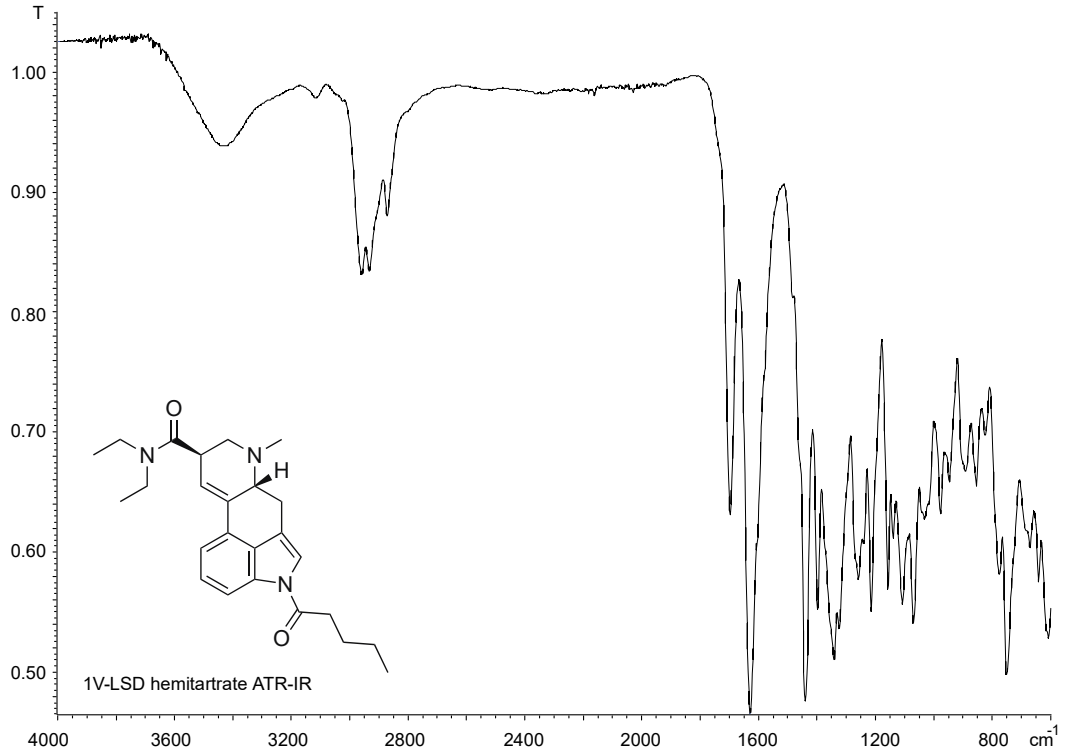
See also page 7. Top: GC-MS TIC trace following alkaline extraction into diethyl ether. Bottom: GC-MS TIC trace following analysis of 1V-LSD hemitartrate salt dissolved in methanol.

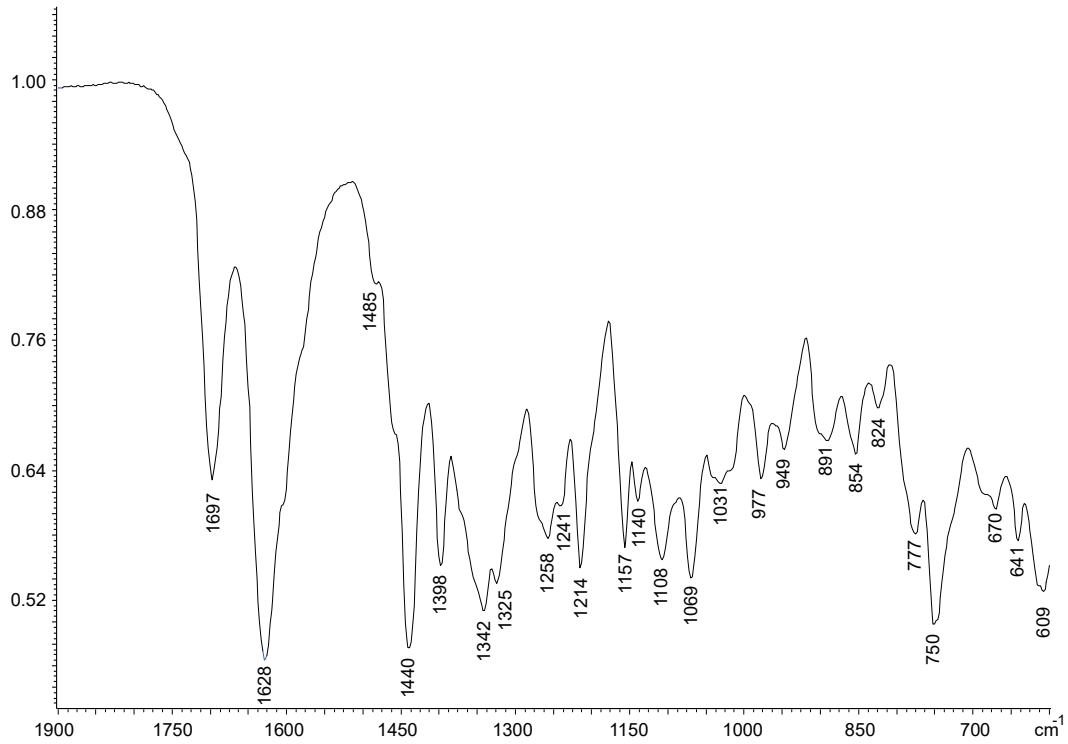
Tentative identification of isomer IV

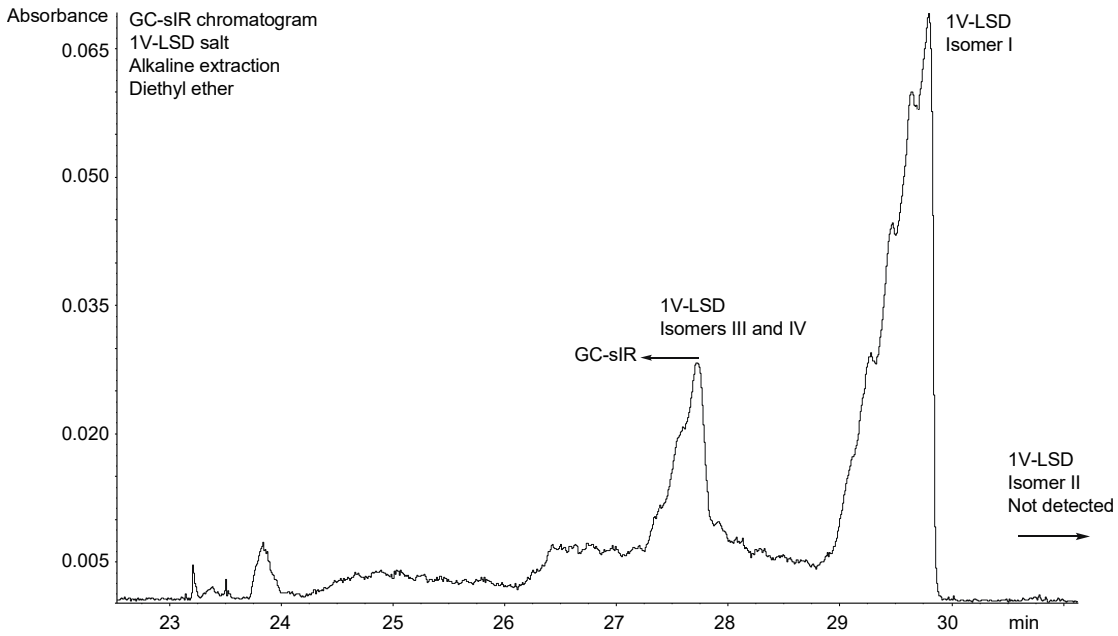


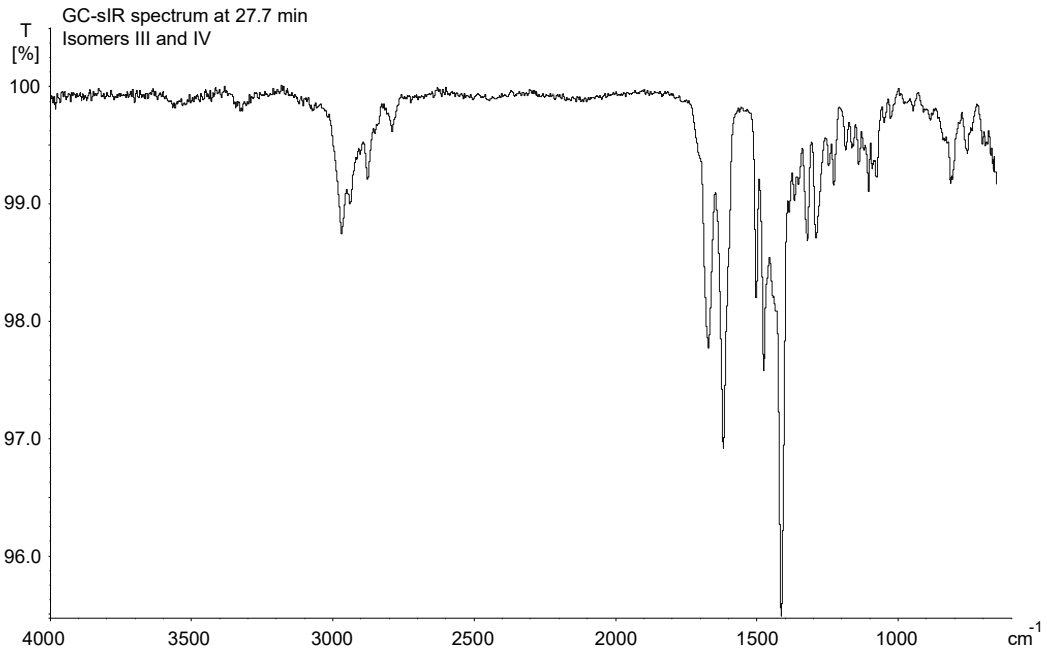
Attenuated total reflection-infrared spectroscopy (ATR-IR)

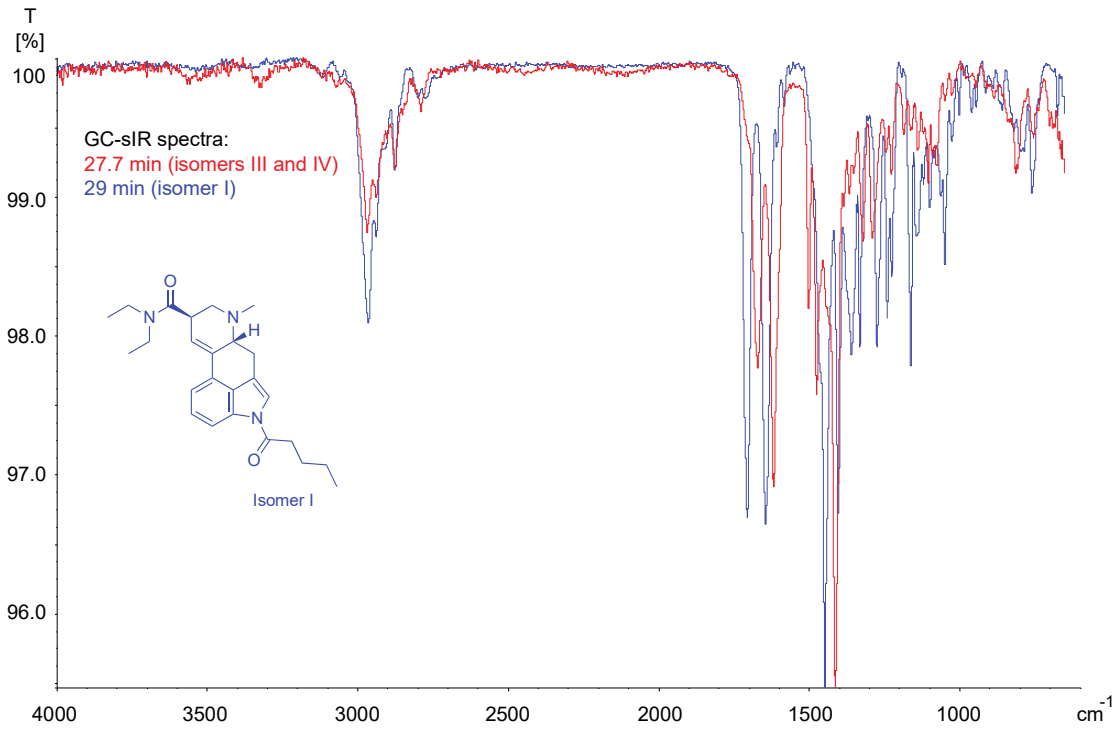
A Nicolet 380 FT-IR spectrometer with Smart Golden Gate Diamond ATR and the software OMNIC, Ver. 7.4.127 (Thermo Electron Corporation, Dreieich, DE) were used for data acquisition and data analysis, respectively. Wavelength resolution was 4 cm^{-1}, scan range 650–4000 cm^{-1}, and 32 scans/spectrum were acquired. IR spectra were recorded from the solid.

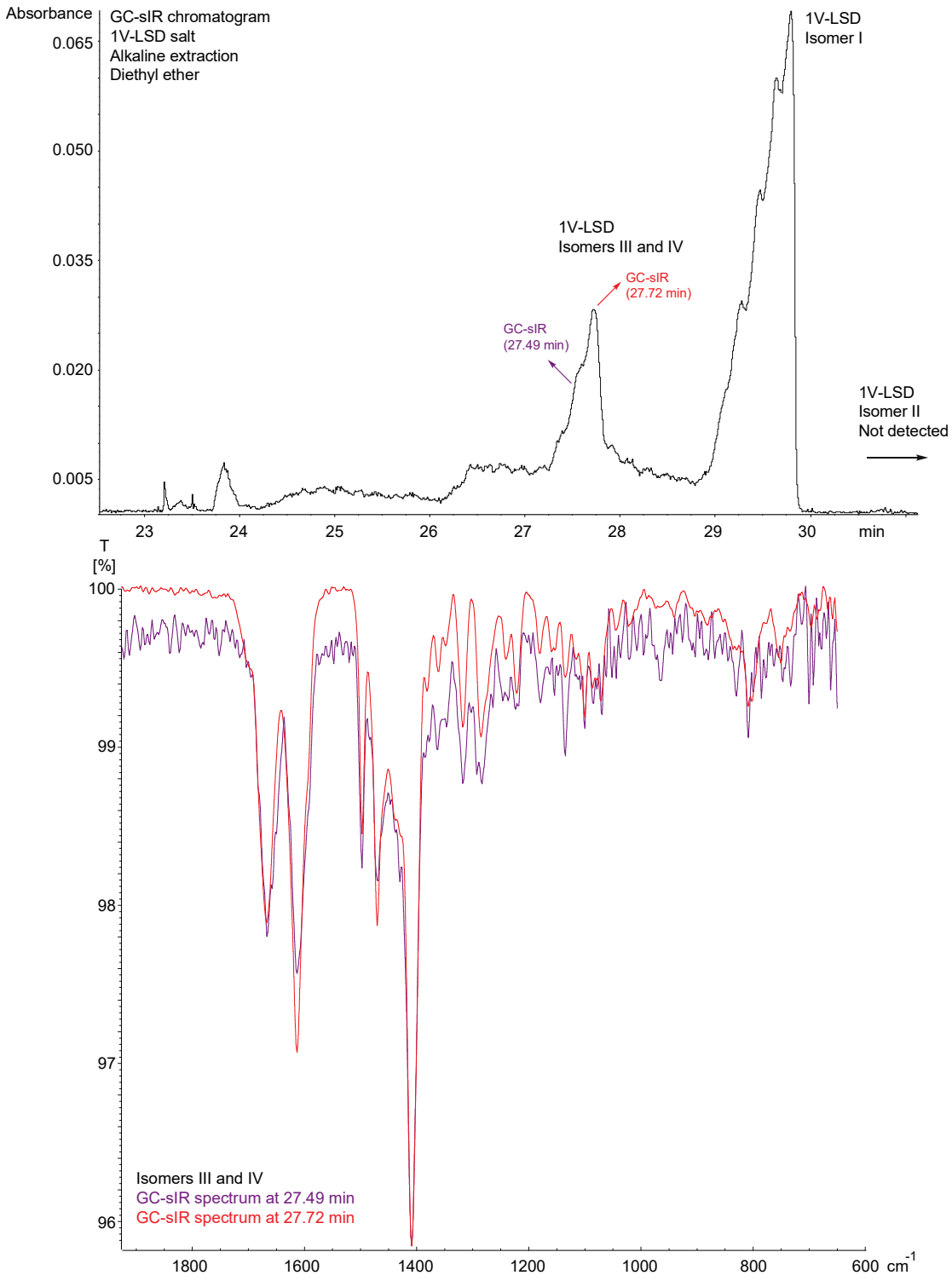





Absorbance
GC-sIR chromatogram
1V-LSD salt
Alkaline extraction
Diethyl ether
1V-LSD
Isomer I
1V-LSD
Isomers III and IV
GC-sIR
1V-LSD
Isomer II
Not detected
0.065
0.050
0.035
0.020
0.005
23
24
25
26
27
28
29
30
min

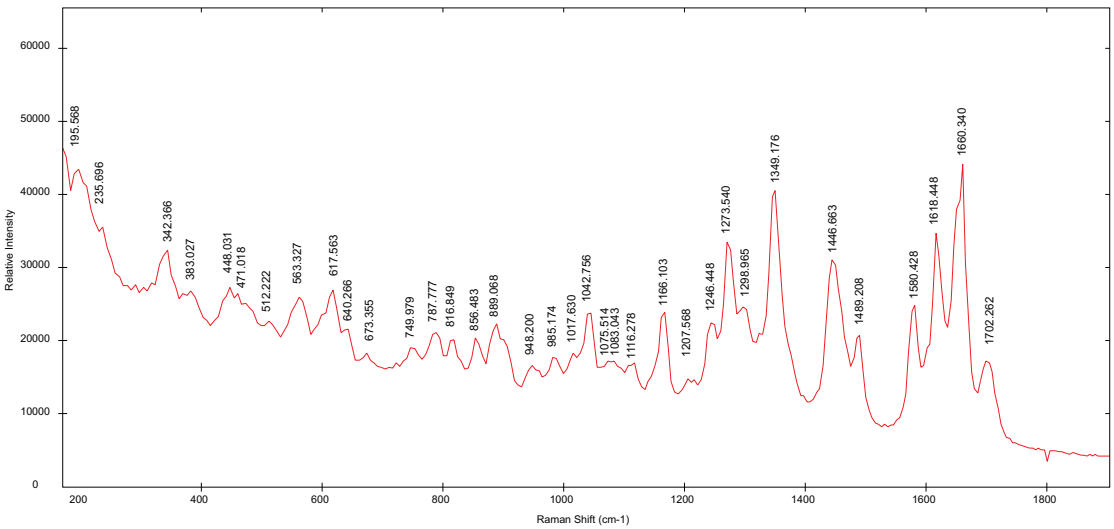

GC-sIR spectrum at 27.7 min
Isomers III and IV
T
[%]
100
99.0
98.0
97.0
96.0
4000
3500
3000
2500
2000
1500
1000
cm-1

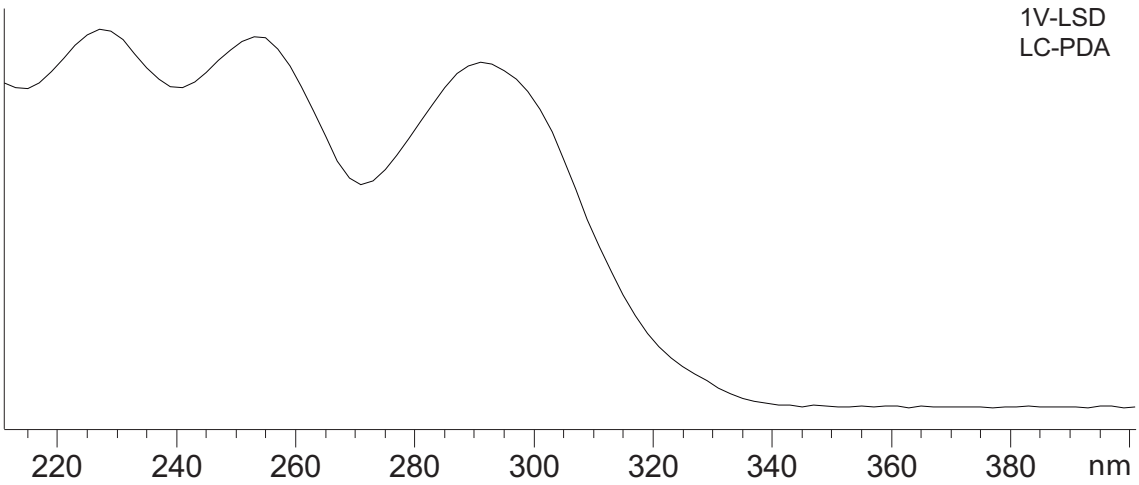

T
[%]
100
99.0
98.0
97.0
96.0
GC-sIR spectra:
27.7 min (isomers III and IV)
29 min (isomer I)
Isomer I
4000
3500
3000
2500
2000
1500
1000
cm-1


Absorbance
GC-sIR chromatogram
1V-LSD salt
Alkaline extraction
Diethyl ether
0.065
0.050
0.035
0.020
0.005
1V-LSD
Isomer I
1V-LSD
Isomers III and IV
GC-sIR
(27.72 min)
GC-sIR
(27.49 min)
1V-LSD
Isomer II
Not detected
23
24
25
26
27
28
29
30
min
T
[%]
100
99
98
97
96
Isomers III and IV
GC-sIR spectrum at 27.49 min
GC-sIR spectrum at 27.72 min
1800
1600
1400
1200
1000
800
600
cm-1

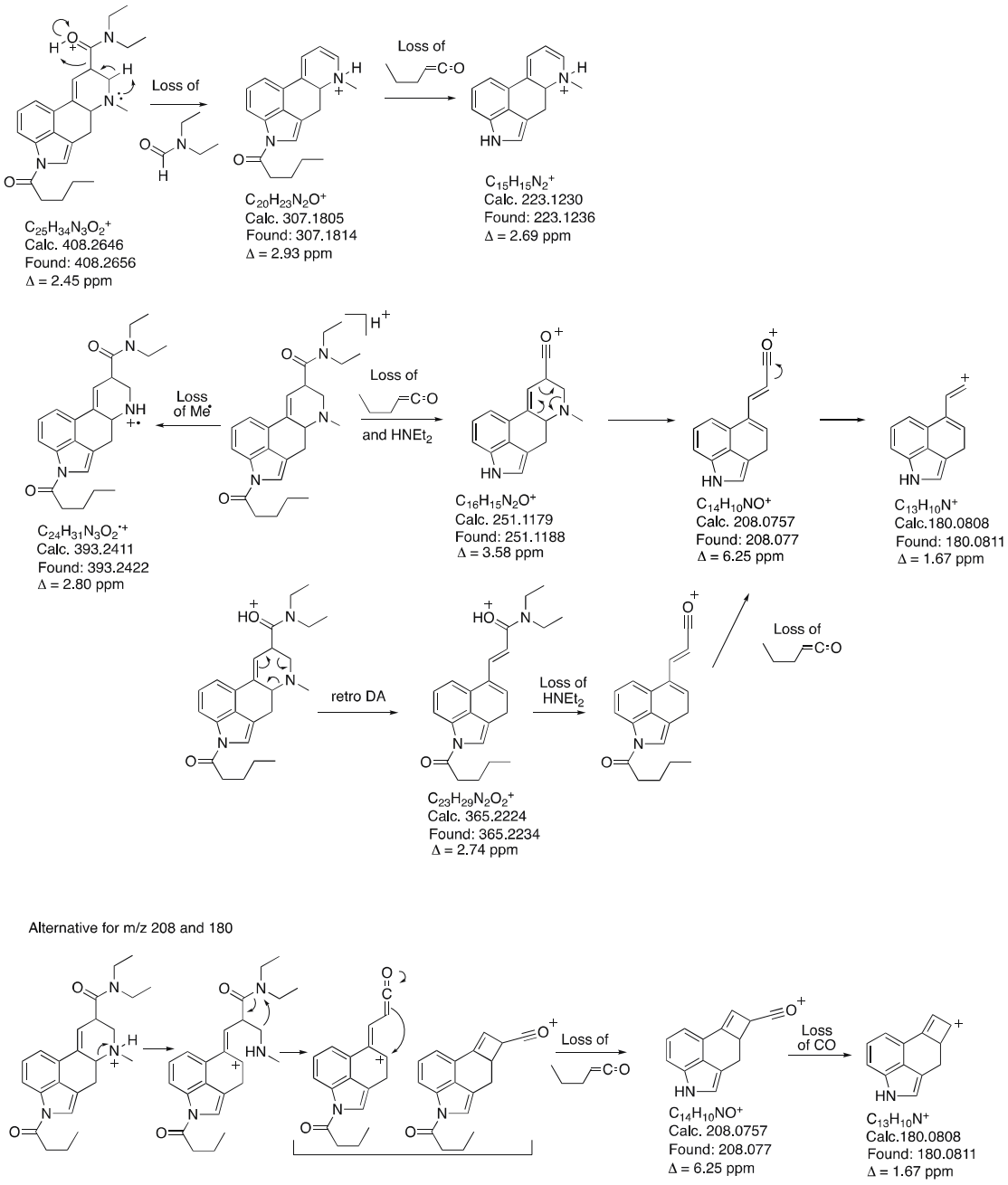
Raman spectroscopy

Raman spectroscopic data was acquired using laser irradiation at 1064 nm using an i-Raman® EX system and a BWS485-1064S-05 spectrometer using a scan range of 170 – 2502 cm^{-1}; the resolution was ~9.5 cm^{-1} at 1296 nm. A BAC151B Raman Video Microsampling System was applied with an objective lens magnification of 20x (camera: active pixels 1280 x 1024). The applied software was BWSpec® 4.10_4 (B&W TEK). Integration time was chosen to reach a relative intensity above 45,000 arbitrary units for the most intensive peak.



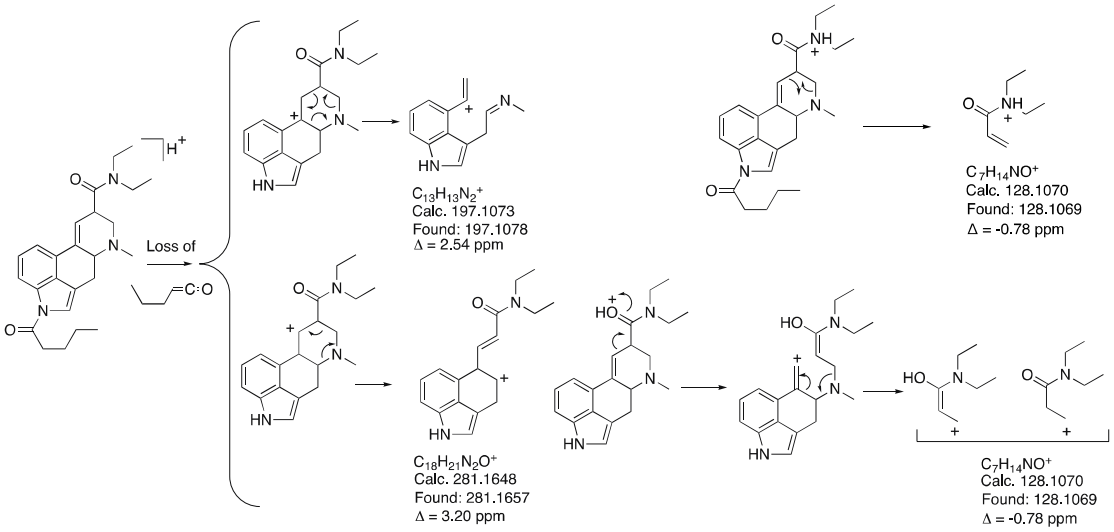


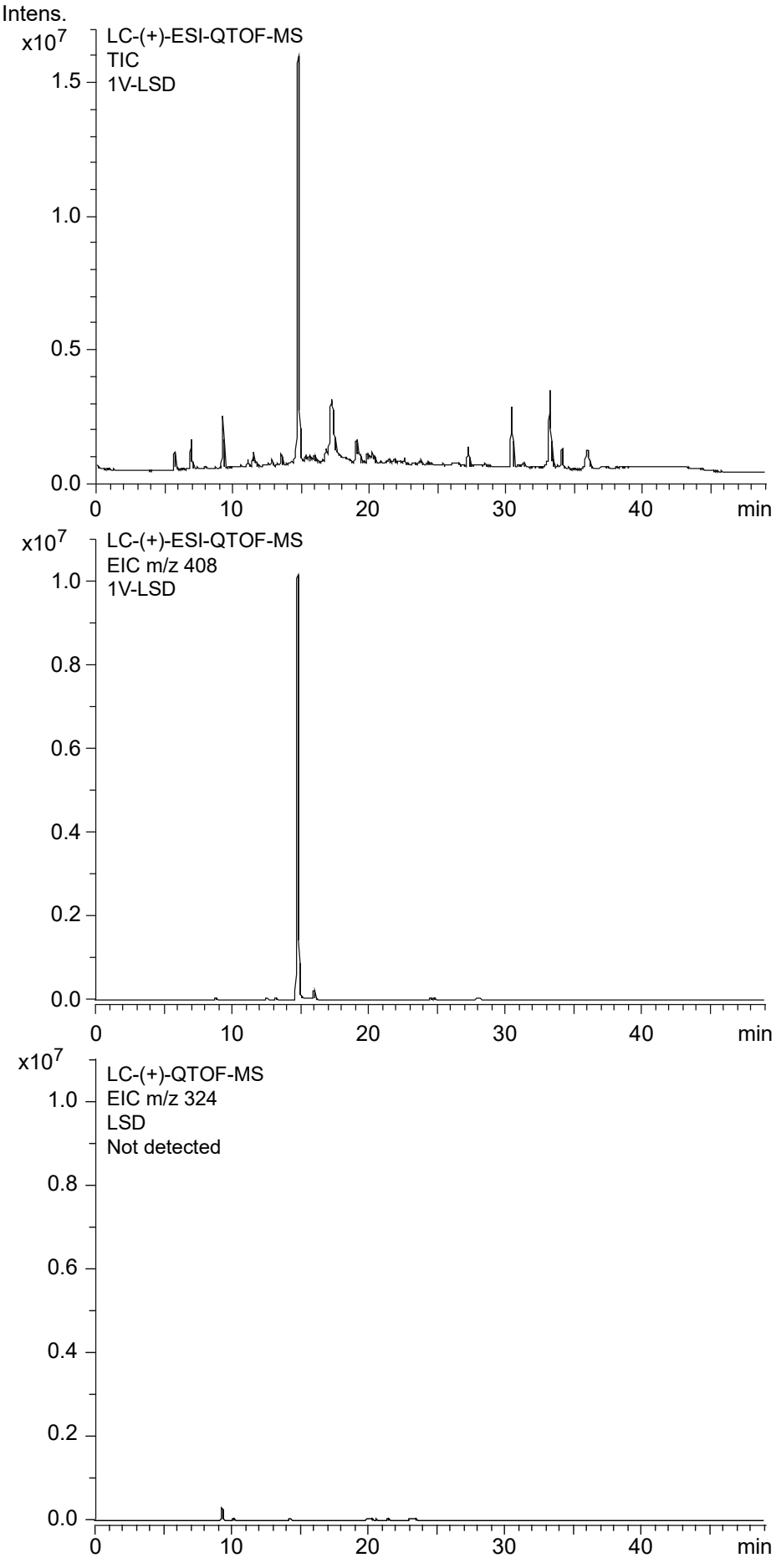
Proposed formation of product ions following collision-induced dissociation of 1V-LSD under QTOF-MS/MS conditions

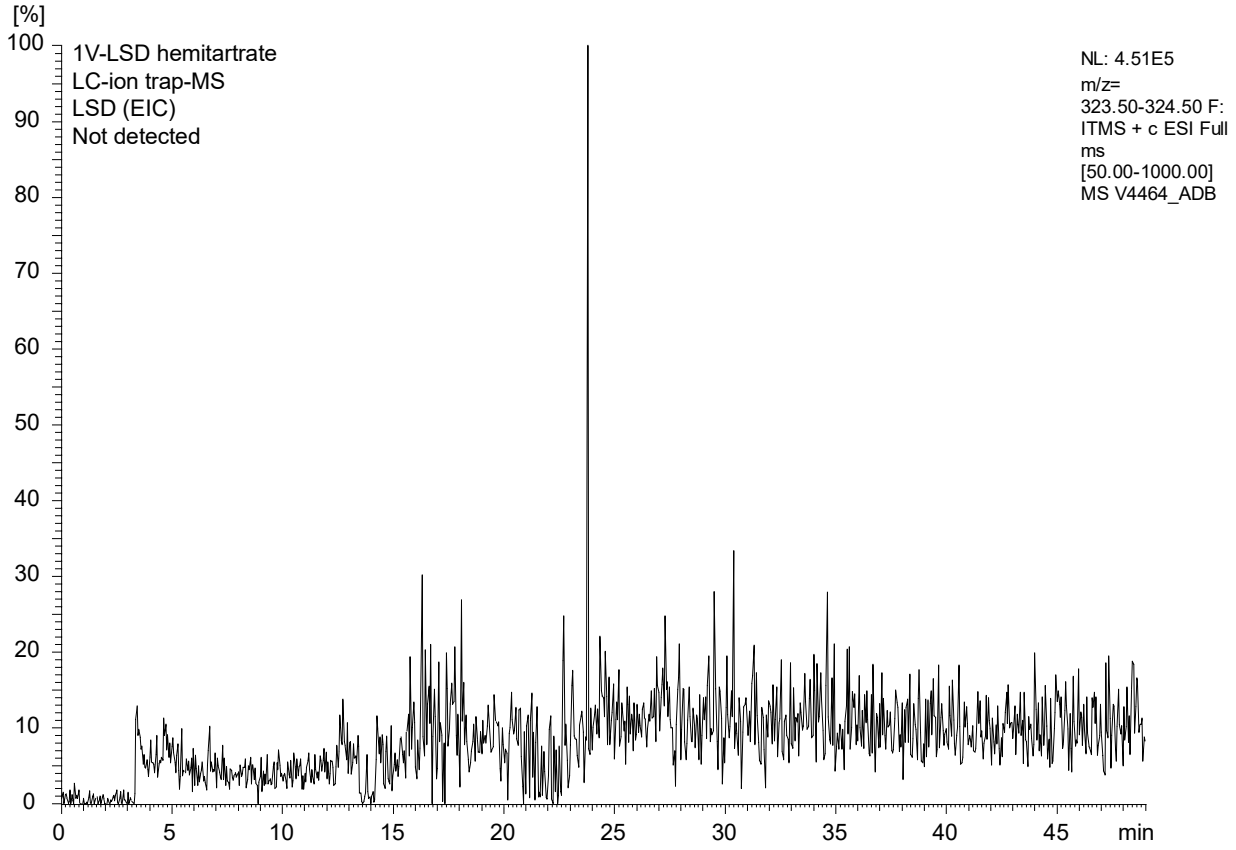


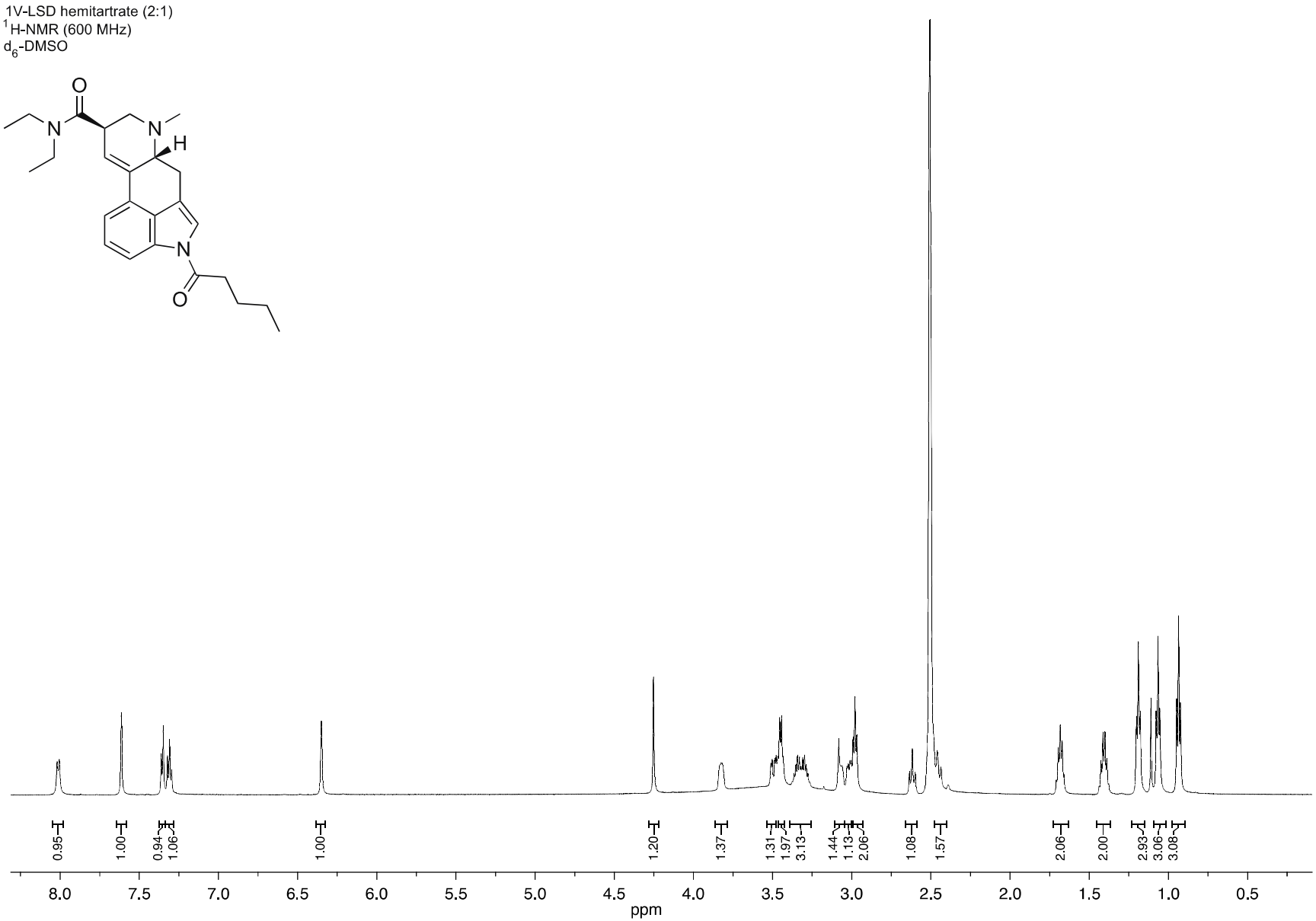
Alternative for m/z 208 and 180

Proposed formation of product ions following collision-induced dissociation of 1V-LSD under QTOF-MS/MS conditions (continued).

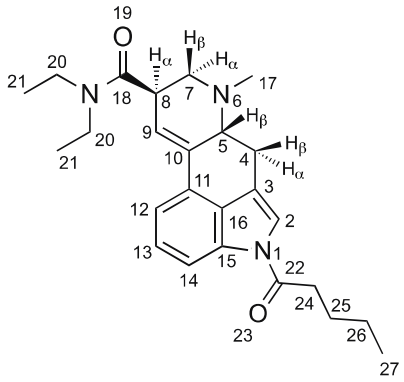


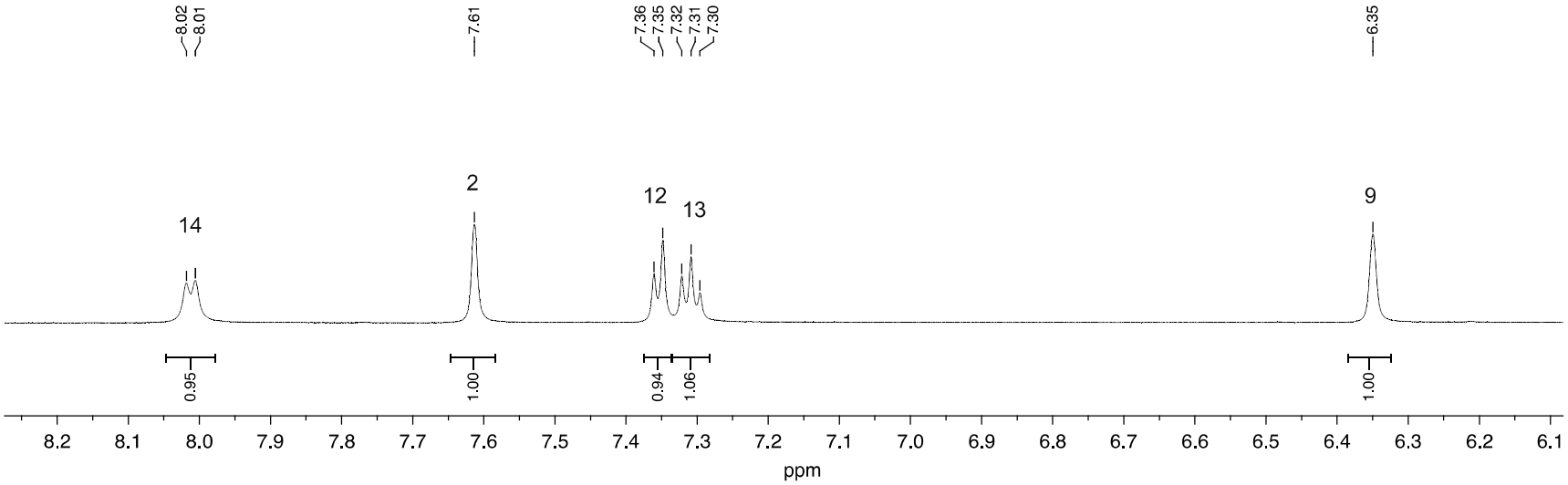

Intens.
x10^7
LC-(+)-ESI-QTOF-MS
TIC
1V-LSD
1.5
1.0
0.5
0.0
0
10
20
30
40
min
x10^7
LC-(+)-ESI-QTOF-MS
EIC m/z 408
1V-LSD
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
min
x10^7
LC-(+)-QTOF-MS
EIC m/z 324
LSD
Not detected
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
min


[%]
100
90
80
70
60
50
40
30
20
10
0
1V-LSD hemitartrate
LC-ion trap-MS
LSD (EIC)
Not detected
NL: 4.51E5
m/z=
323.50-324.50 F:
ITMS + c ESI Full
ms
[50.00-1000.00]
MS V4464_ADB
0
5
10
15
20
25
30
35
40
45
min

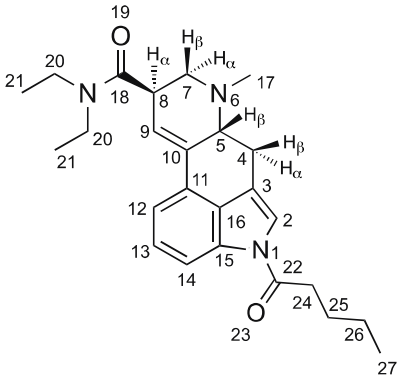

1V-LSD hemitartrate (2:1)
1H-NMR (600 MHz)
d6-DMSO
O
N
N
H
N
O
0.95
1.00
0.94
1.06
1.00
1.20
1.37
1.31
1.97
3.13
1.44
1.13
2.06
1.08
1.57
2.06
2.00
2.93
3.06
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

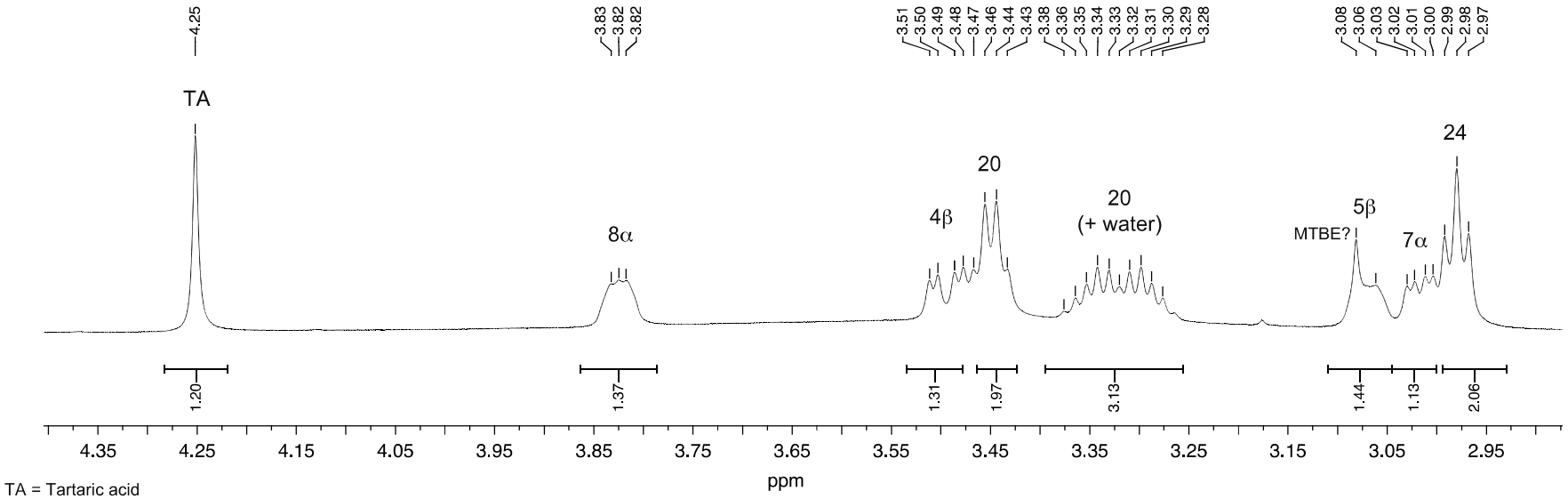
1V-LSD hemitartrate (2:1)
^{1}H-NMR (600 MHz)
d_6-DMSO



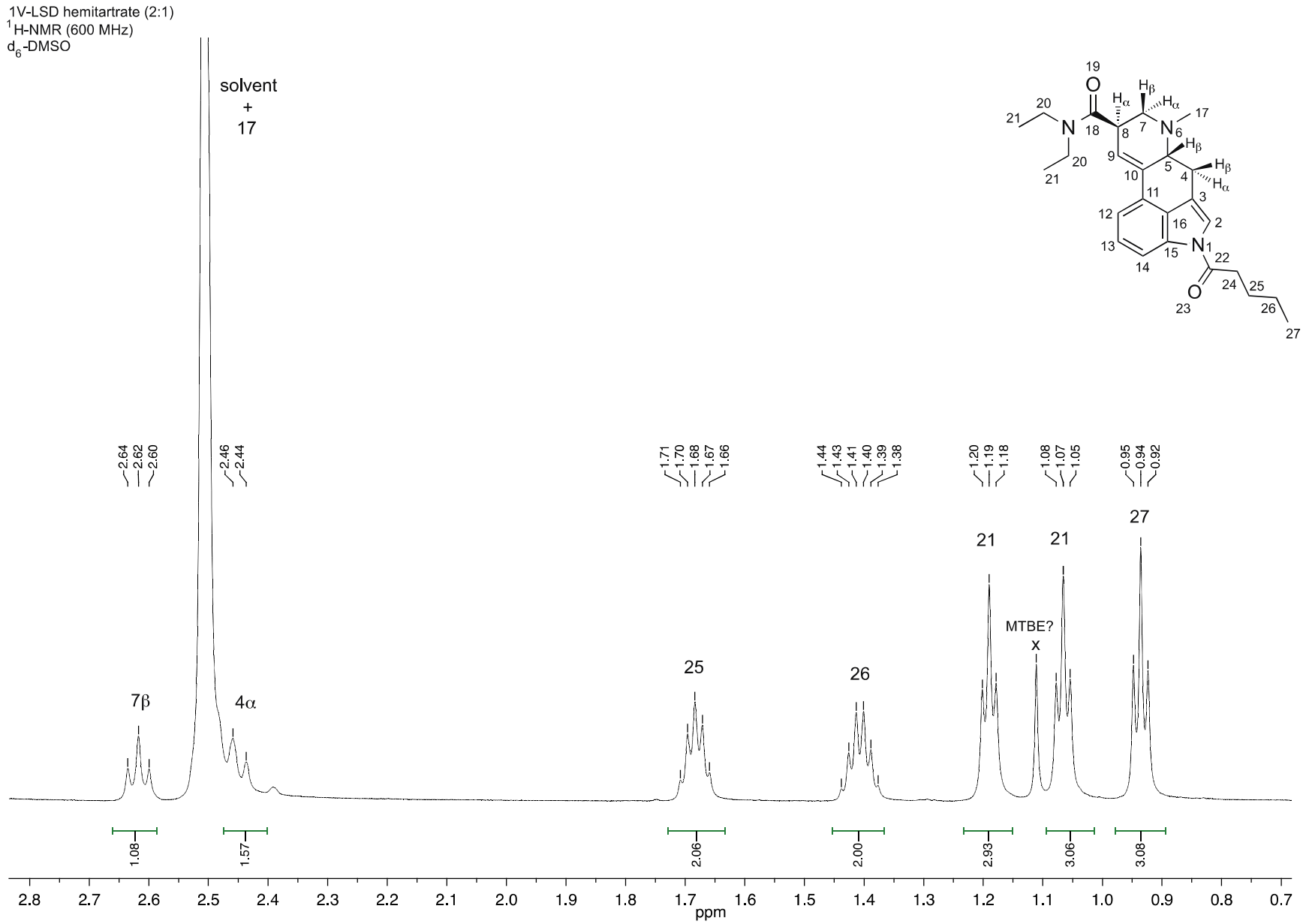


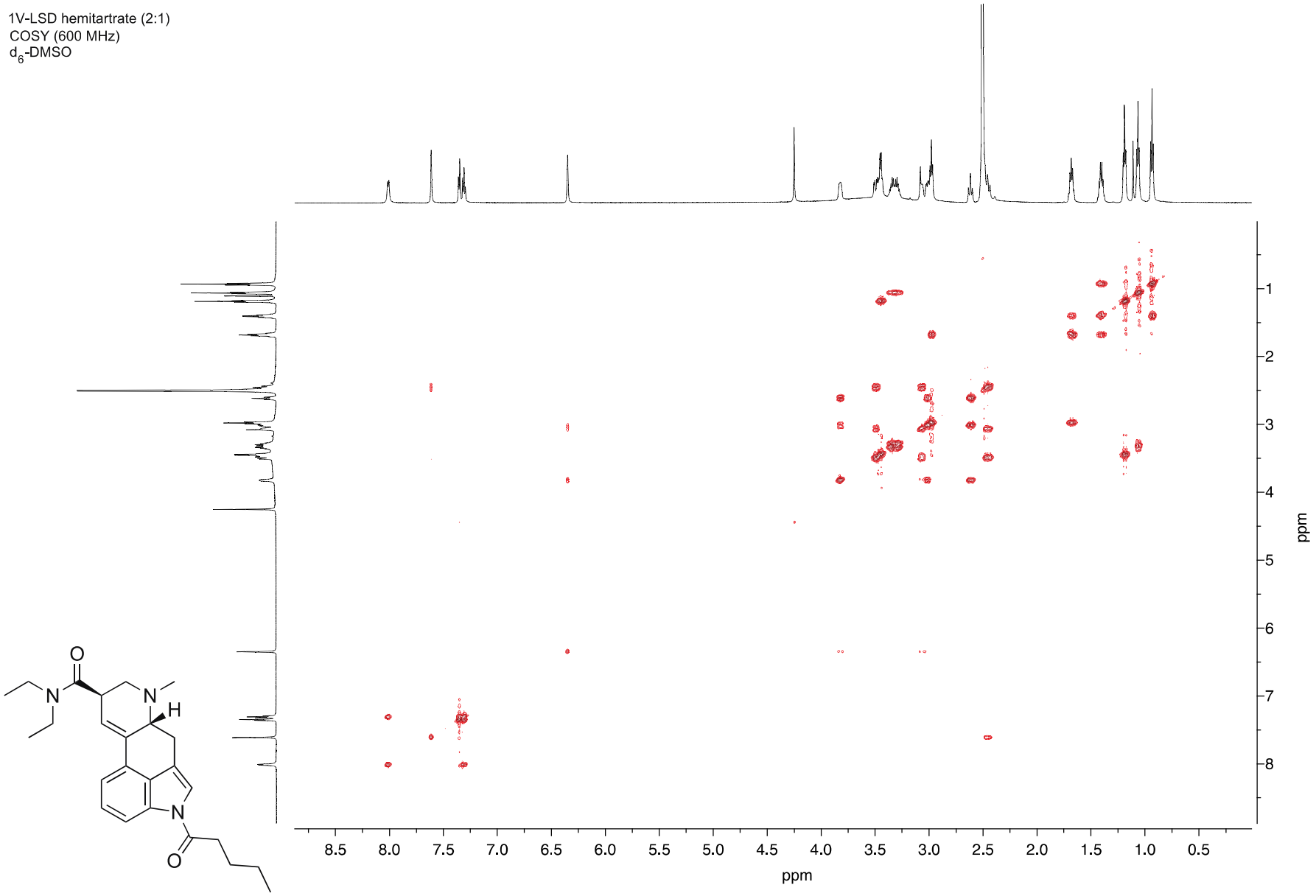
1V-LSD hemitartrate (2:1)
^{1}H-NMR (600 MHz)
d_6-DMSO



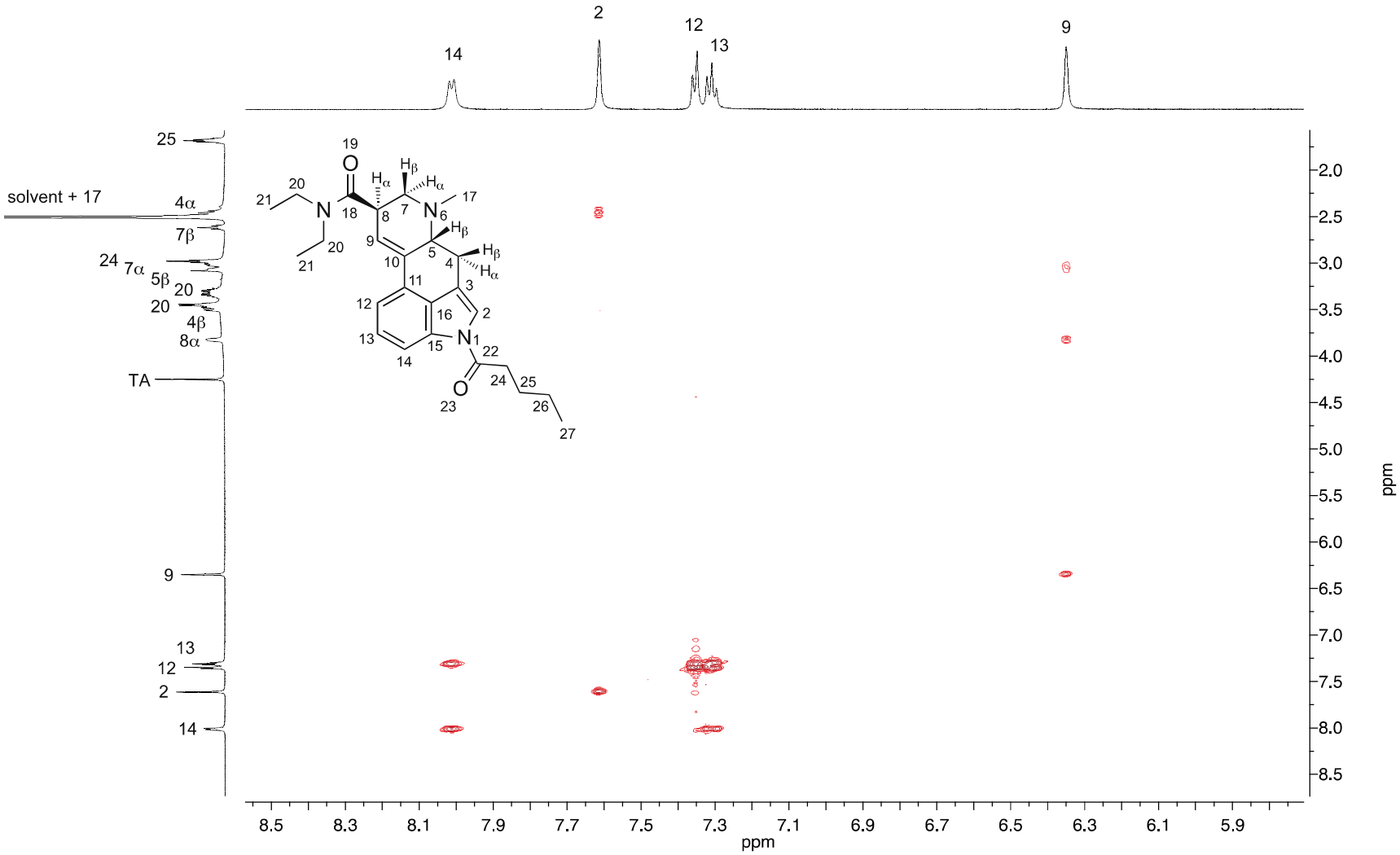


TA = Tartaric acid

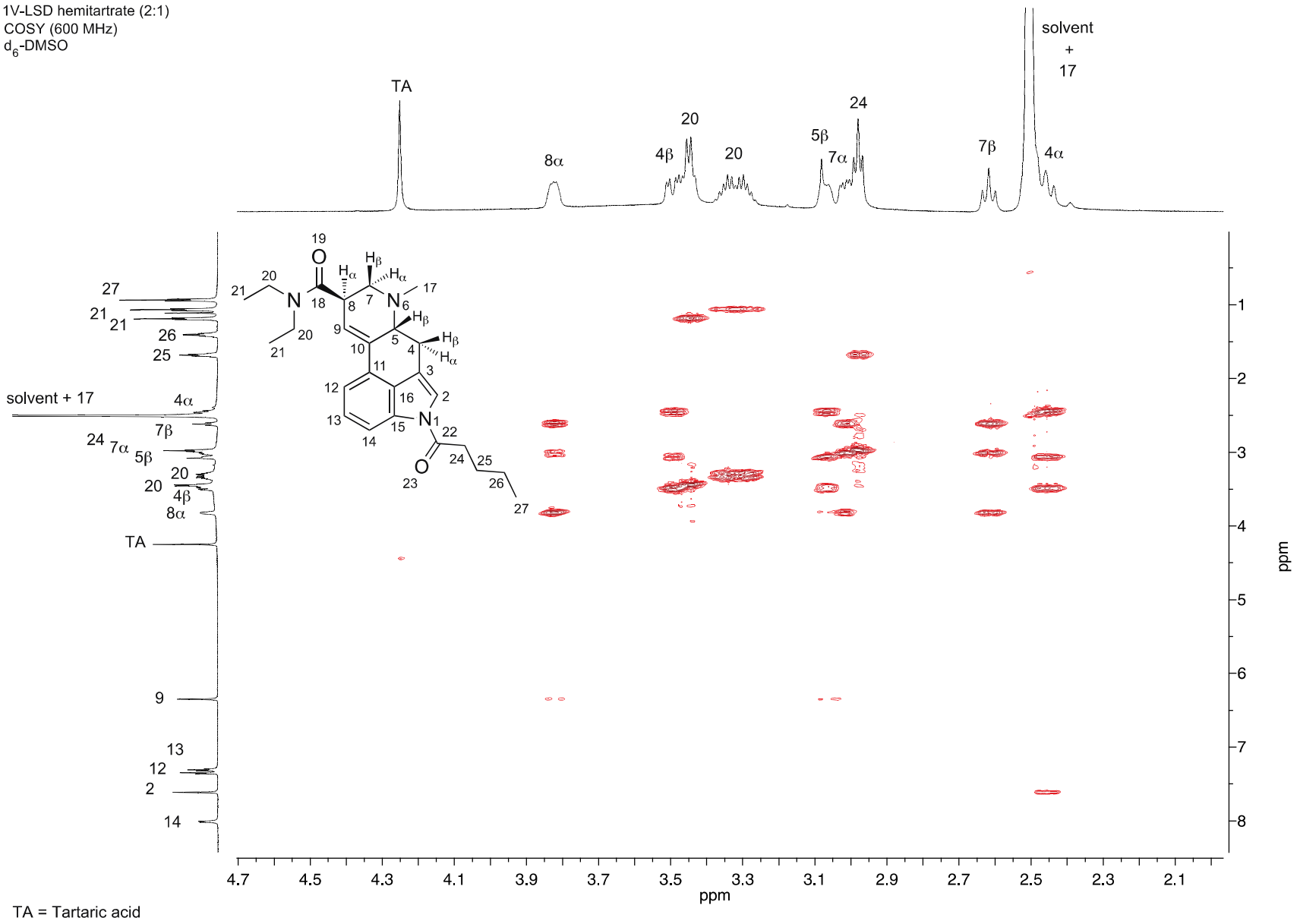

1V-LSD hemitartrate (2:1)
1H-NMR (600 MHz)
d6-DMSO
solvent
+
17
2.64
2.62
2.60
2.46
2.44
1.71
1.70
1.68
1.67
1.66
1.44
1.43
1.41
1.40
1.39
1.38
1.20
1.19
1.18
1.08
1.07
1.05
0.95
0.94
0.92
7β
4α
25
26
21
MTBE?
x
21
27
1.08
1.57
2.06
2.00
2.93
3.06
3.08
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
ppm

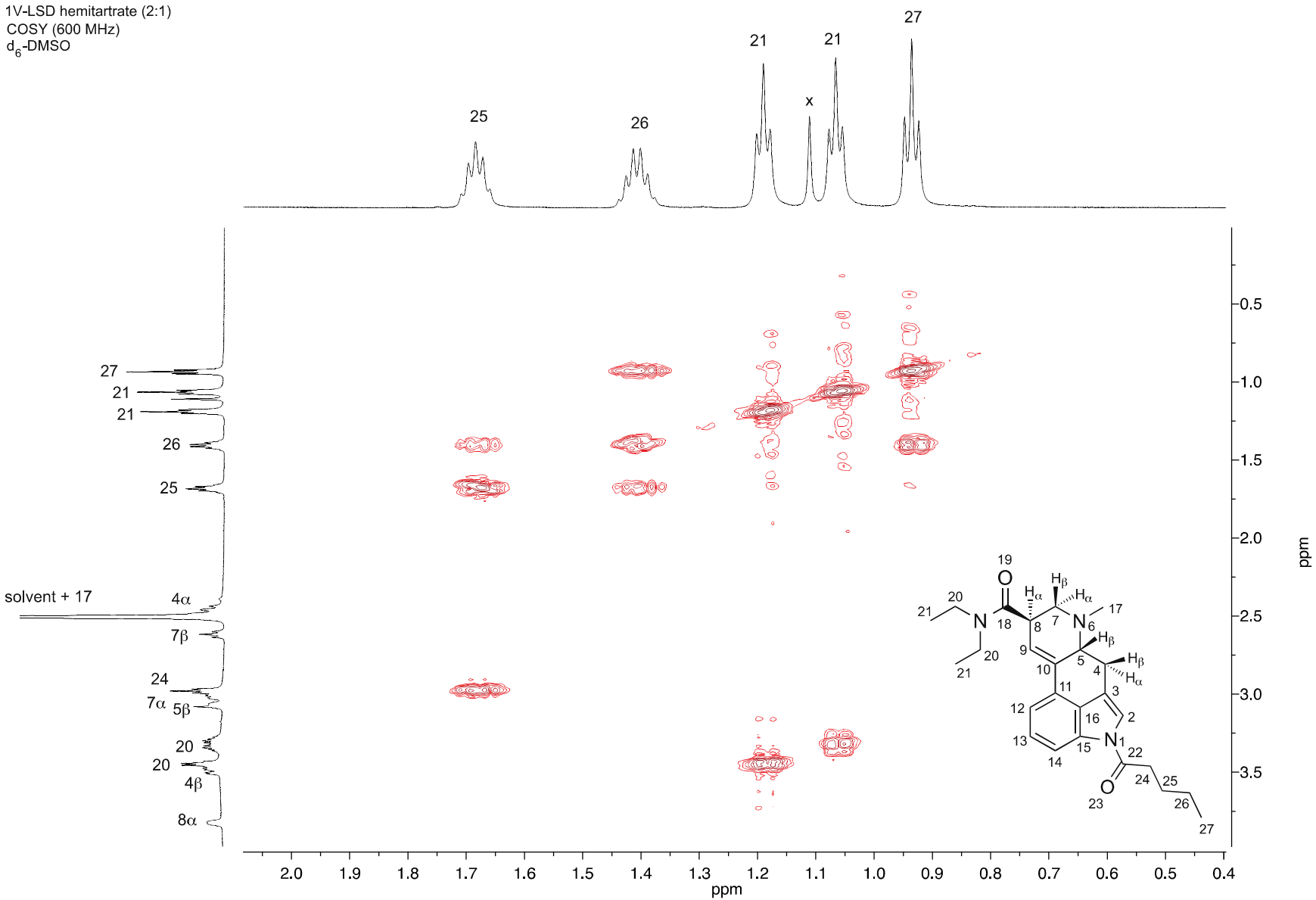

1V-LSD hemitartrate (2:1)
COSY (600 MHz)
d6-DMSO
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1
2
3
4
5
6
7
8
ppm
O
N
N
H
N
O

1V-LSD hemitartrate (2:1)
COSY (600 MHz)
d_6-DMSO

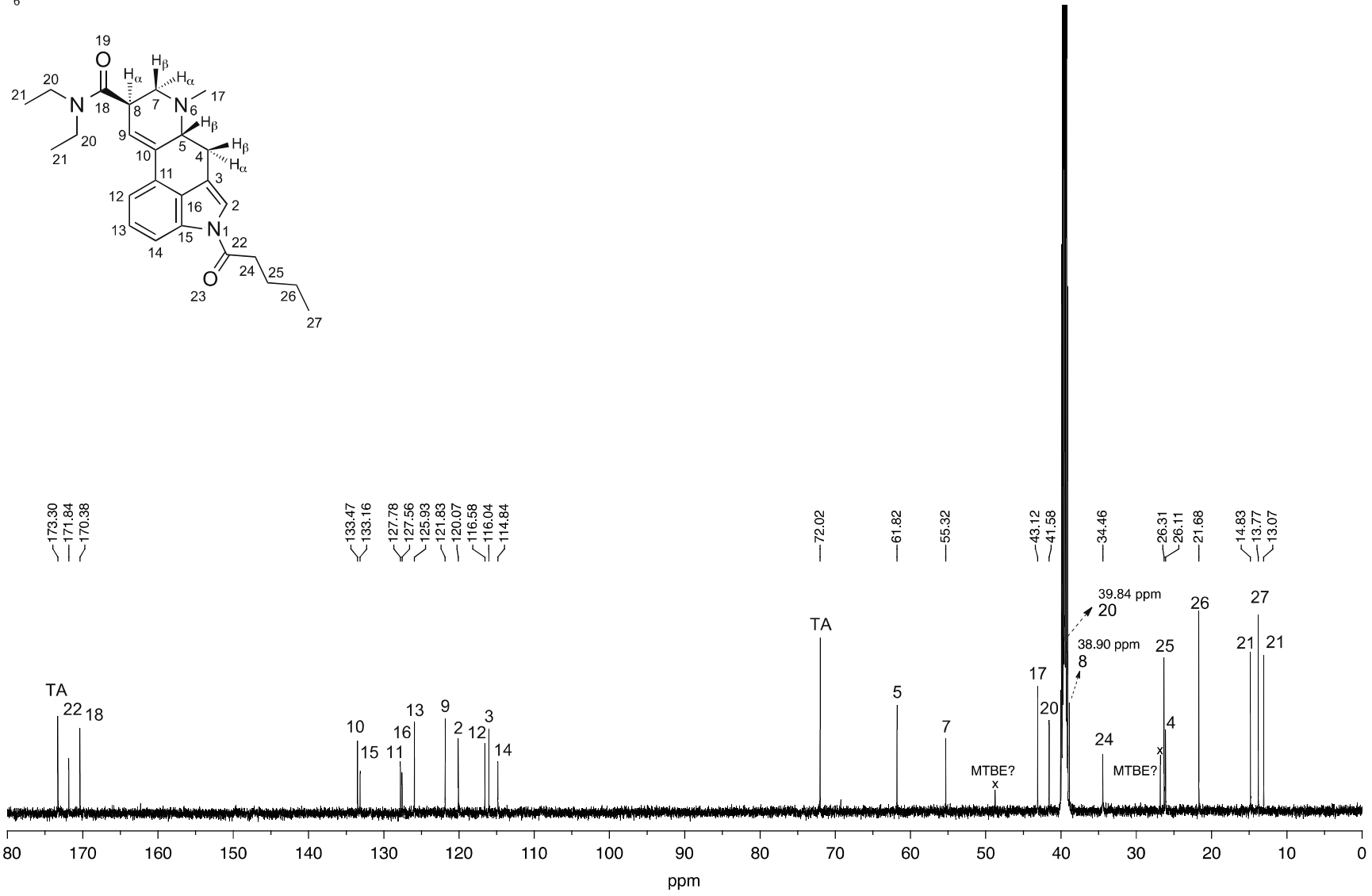


TA = Tartaric acid

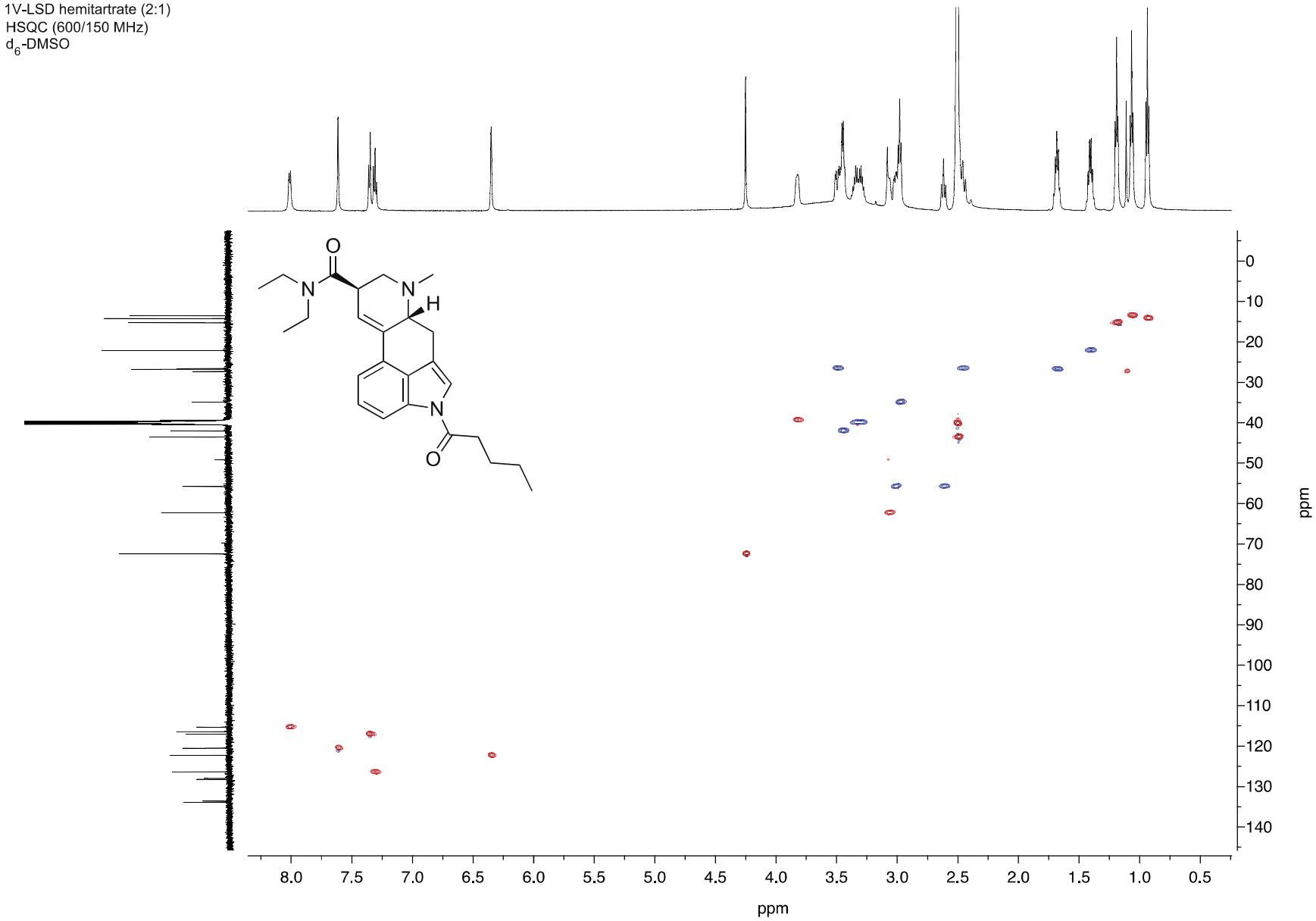

1V-LSD hemitartrate (2:1)
COSY (600 MHz)
d6-DMSO
TA
8α
4β
20
20
5β
7α
24
7β
4α
solvent
+
17
solvent + 17
TA = Tartaric acid
ppm


1V-LSD hemitartrate (2:1)
COSY (600 MHz)
d6-DMSO
25
26
21
x
21
27
27
21
21
26
25
solvent + 17
4α
7β
24
7α
5β
20
20
4β
8α
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4
ppm
0.5 1.0 1.5 2.0 2.5 3.0 3.5
ppm

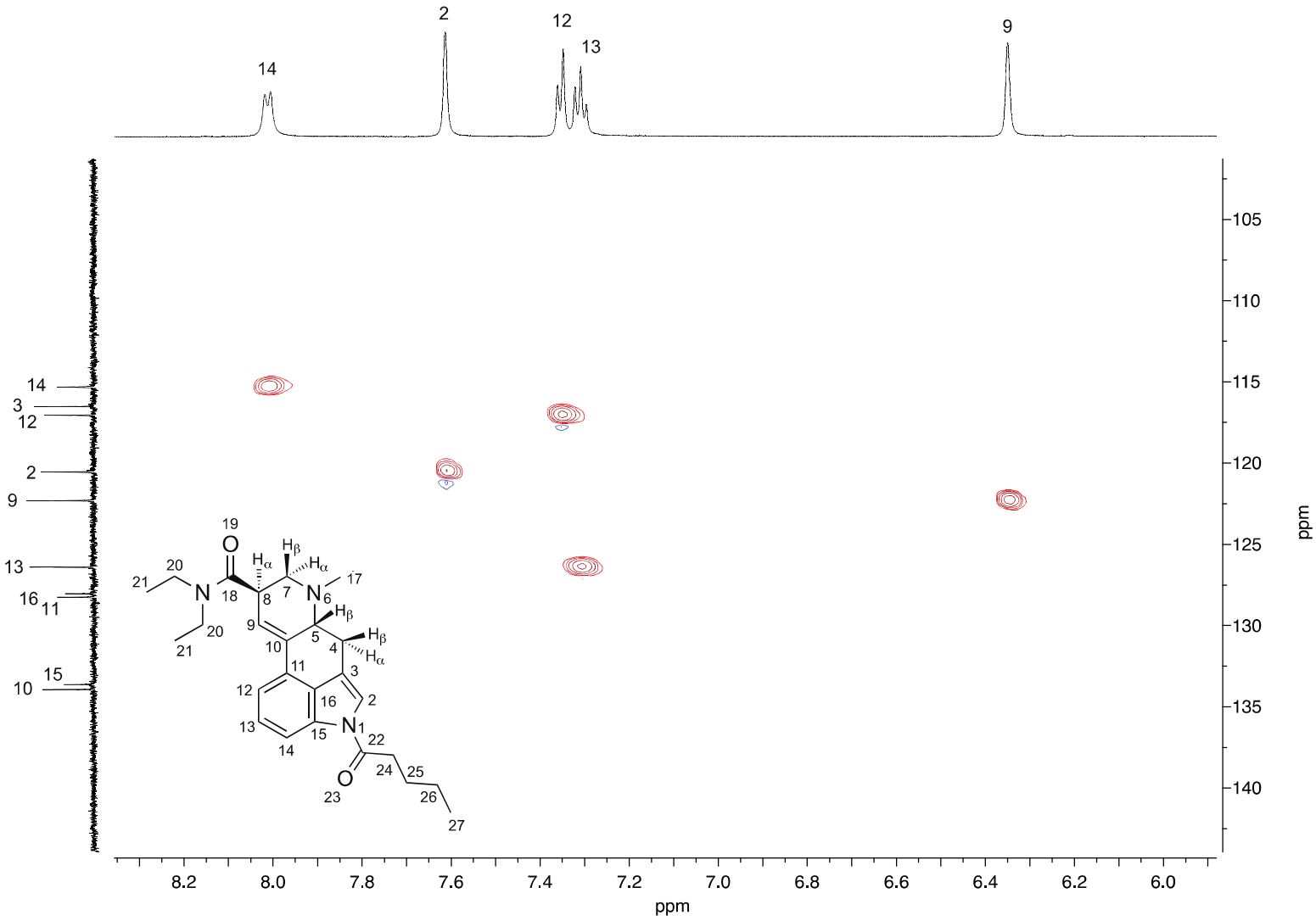
1V-LSD hemitartrate (2:1)
^{13}C-NMR (150 MHz)
d_6-DMSO

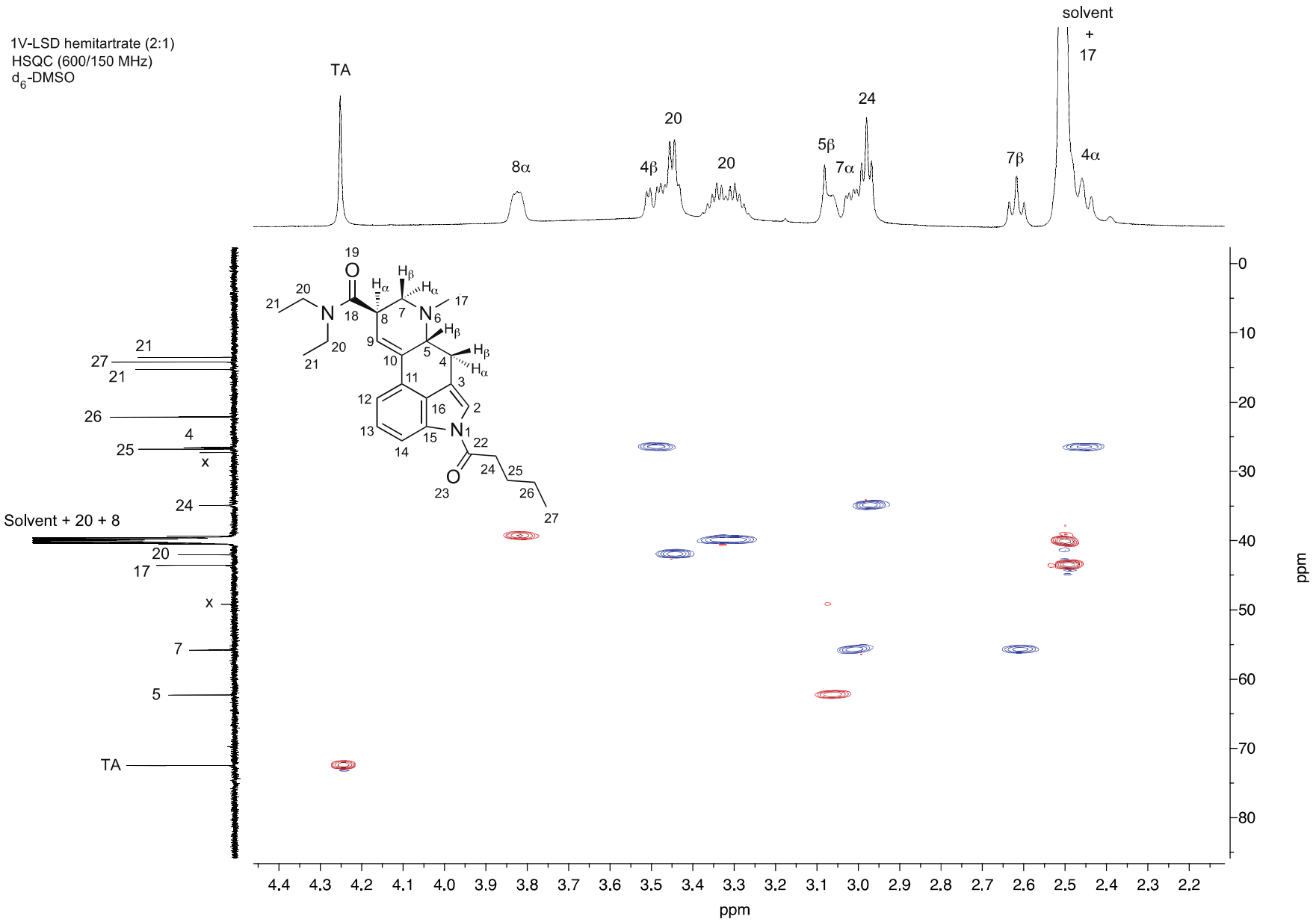


TA = Tartaric acid

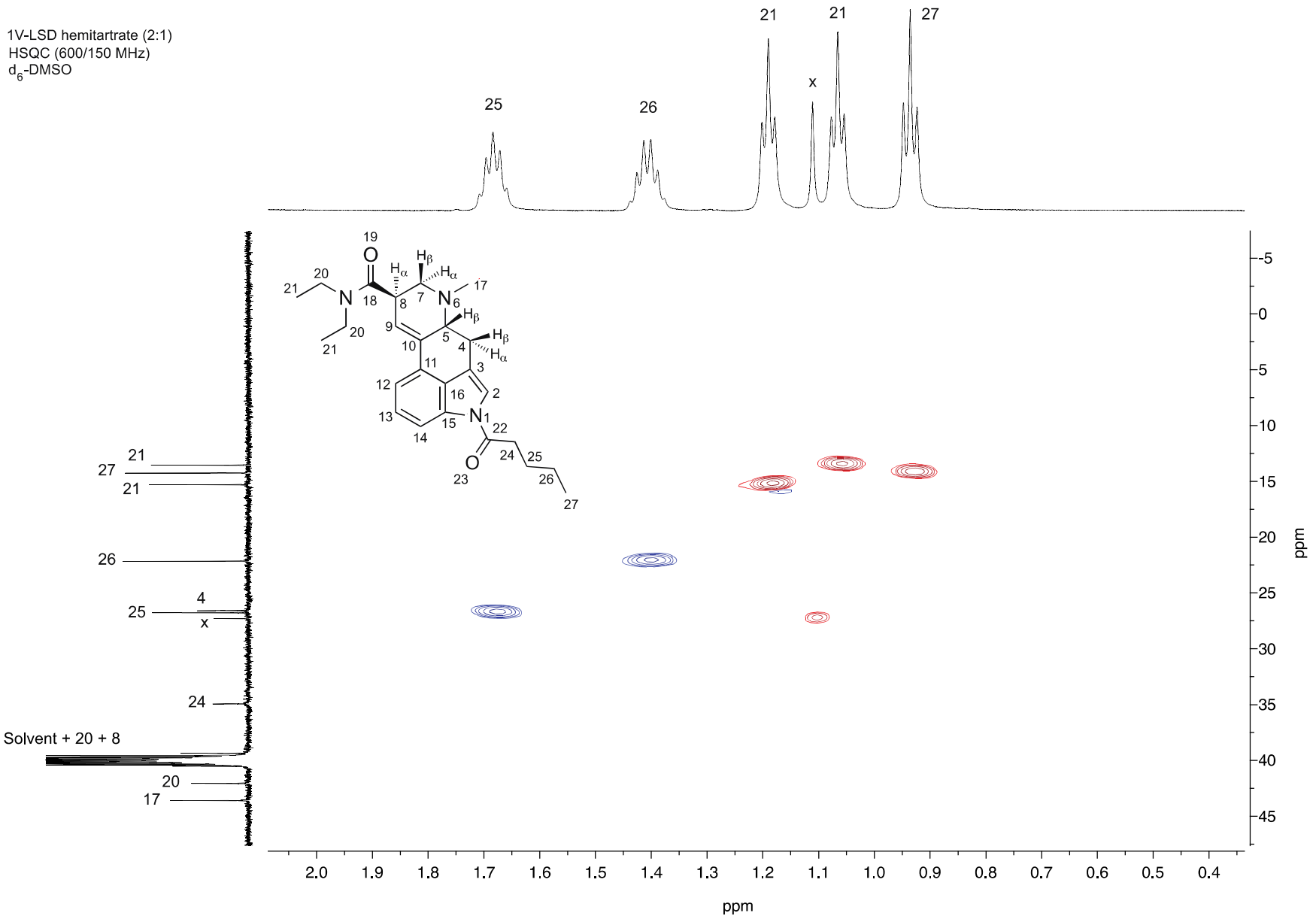

1V-LSD hemitartrate (2:1)
HSQC (600/150 MHz)
d6-DMSO
O
N
N
H
N
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
ppm

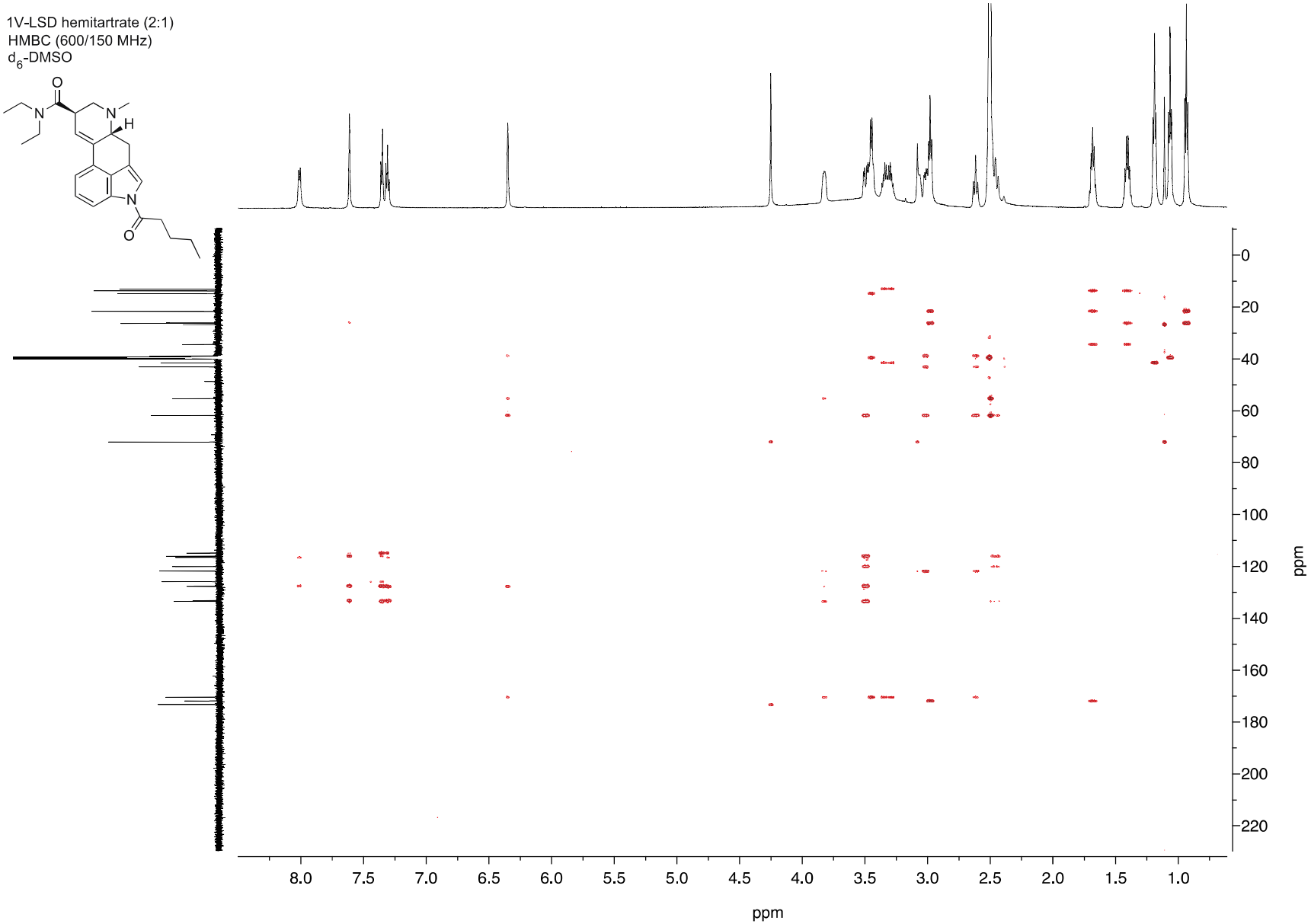
1V-LSD hemitartrate (2:1)
HSQC (600/150 MHz)
d_6-DMSO

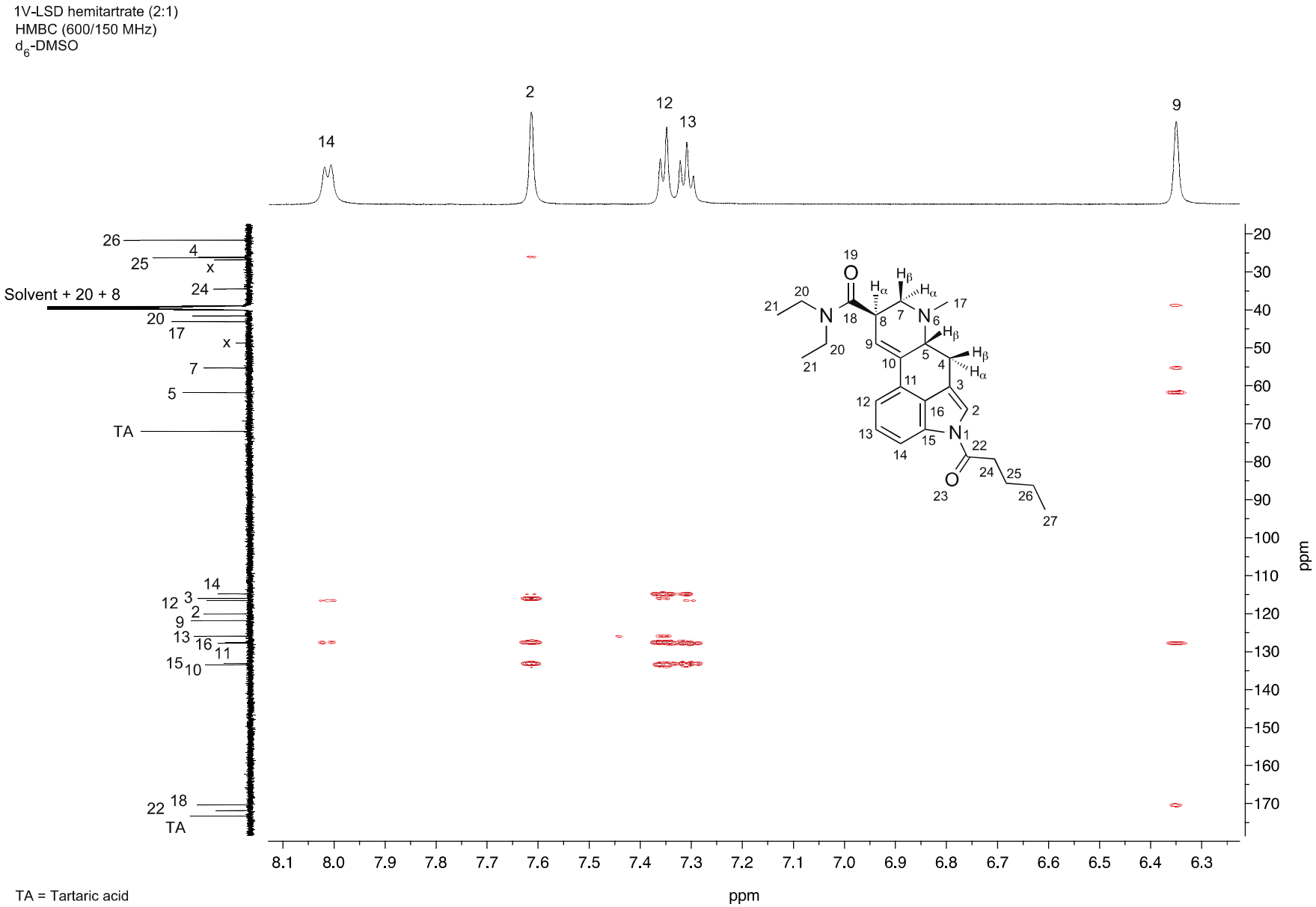


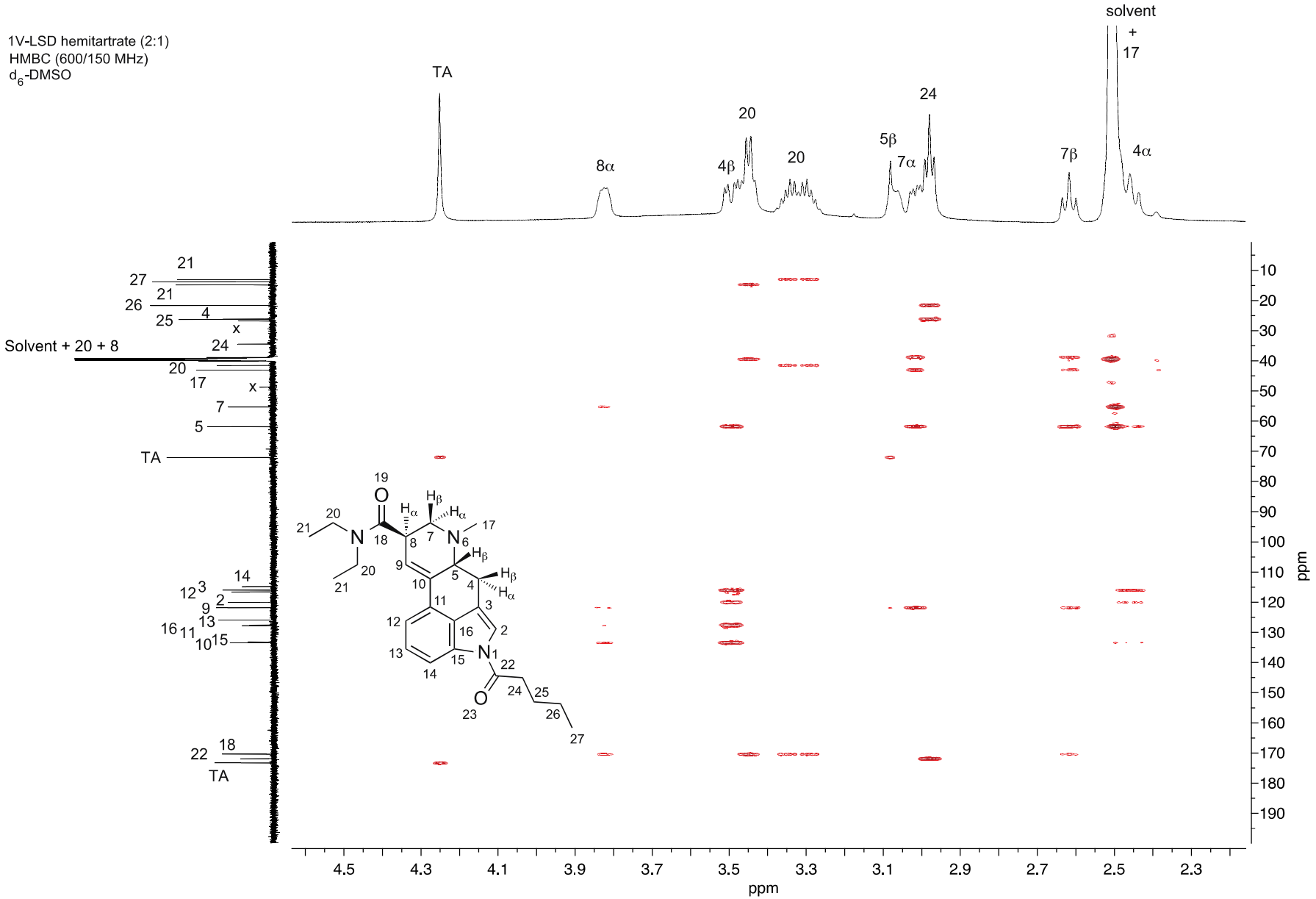


TA = Tartaric acid

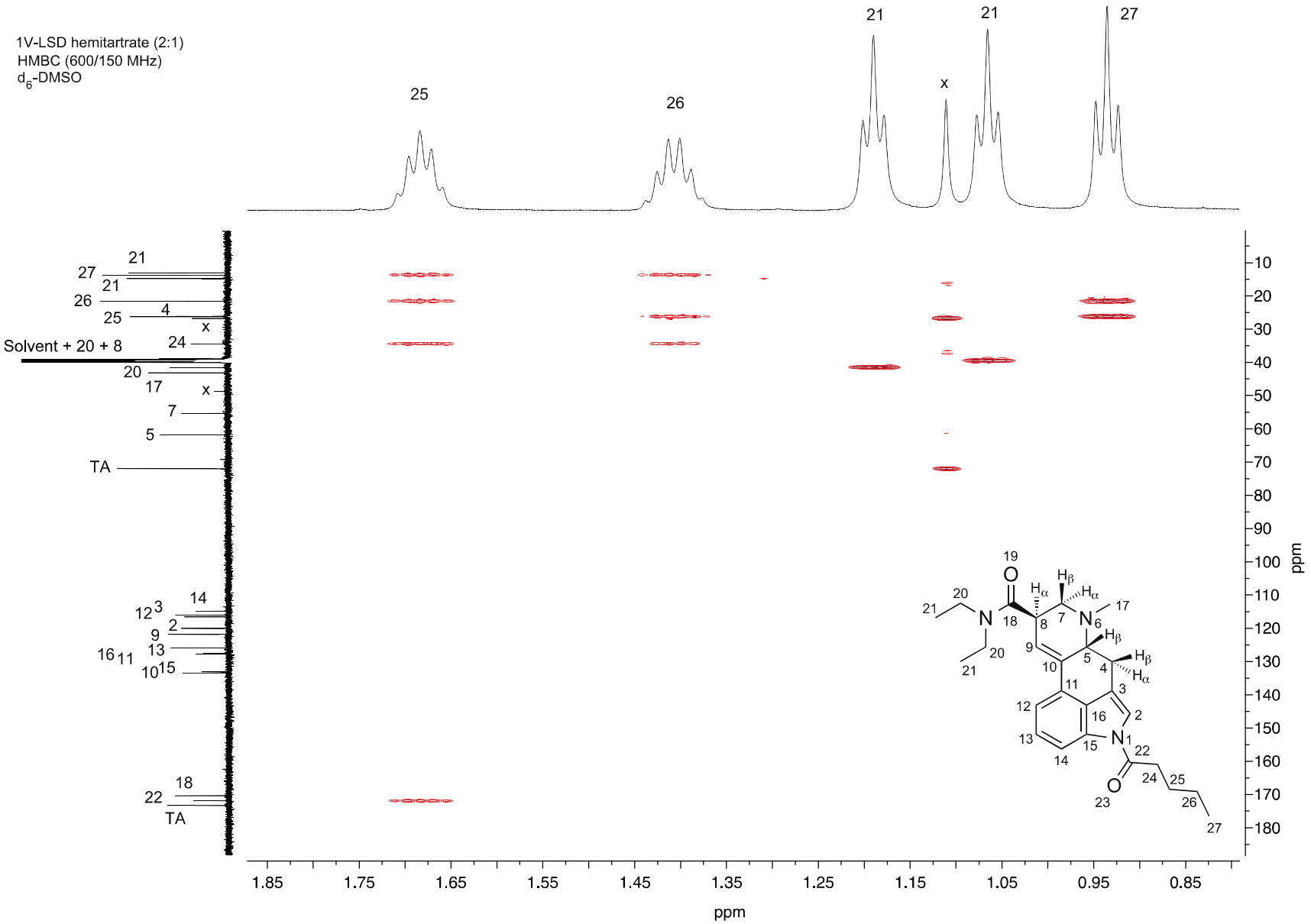

1V-LSD hemitartrate (2:1)
HSQC (600/150 MHz)
d_6-DMSO
25
26
21
x
21
27
Solvent + 20 + 8
ppm
ppm


1V-LSD hemitartrate (2:1)
HMBC (600/150 MHz)
d6-DMSO
O
N
N
H
N
O
0
20
40
60
80
100
120
140
160
180
200
220
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

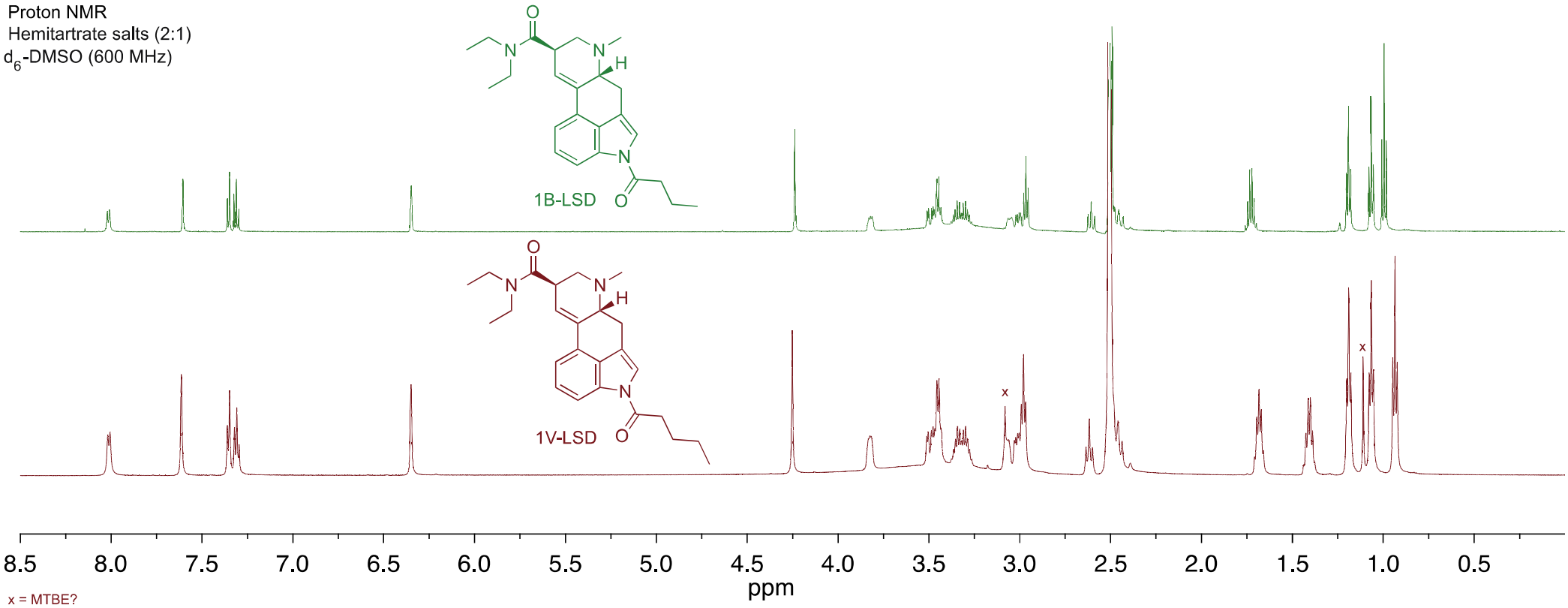

1V-LSD hemitartrate (2:1)
HMBC (600/150 MHz)
d6-DMSO
Solvent + 20 + 8
TA
TA = Tartaric acid
ppm
ppm



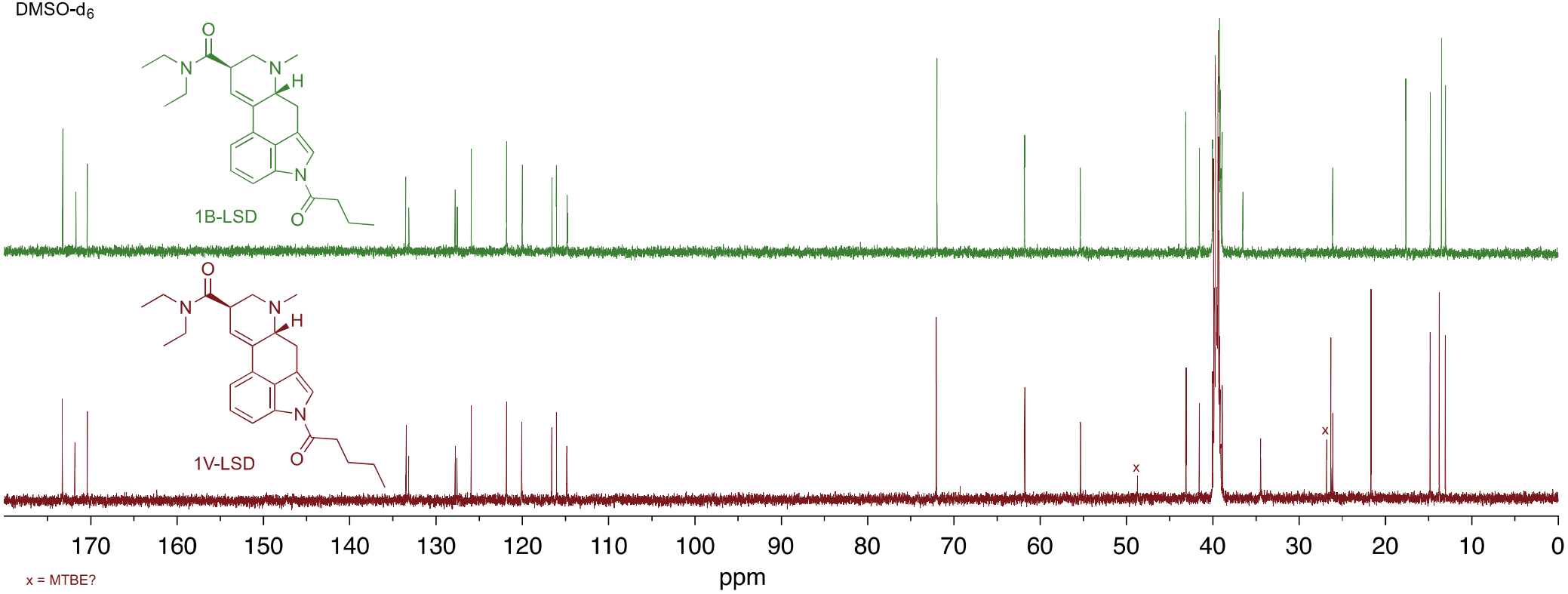
TA = Tartaric acid



TA = Tartaric acid


Proton NMR
Hemitartrate salts (2:1)
d6-DMSO (600 MHz)
1B-LSD
1V-LSD
x
x
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
x = MTBE?

Lysergamides - hemitartrate salts (2:1)
Carbon NMR (150 MHz)
DMSO-d_6



x = MTBE?