

Analytical profile of the lysergamide 1cP-AL-LAD and detection of impurities

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⁵ *Synex Synthetics BV, Karveelweg 20, 6222NH, Maastricht, The Netherlands*

⁶ *Isomer Design, 4103-210 Victoria Street, Toronto, ON, M5B 2R3, Canada*

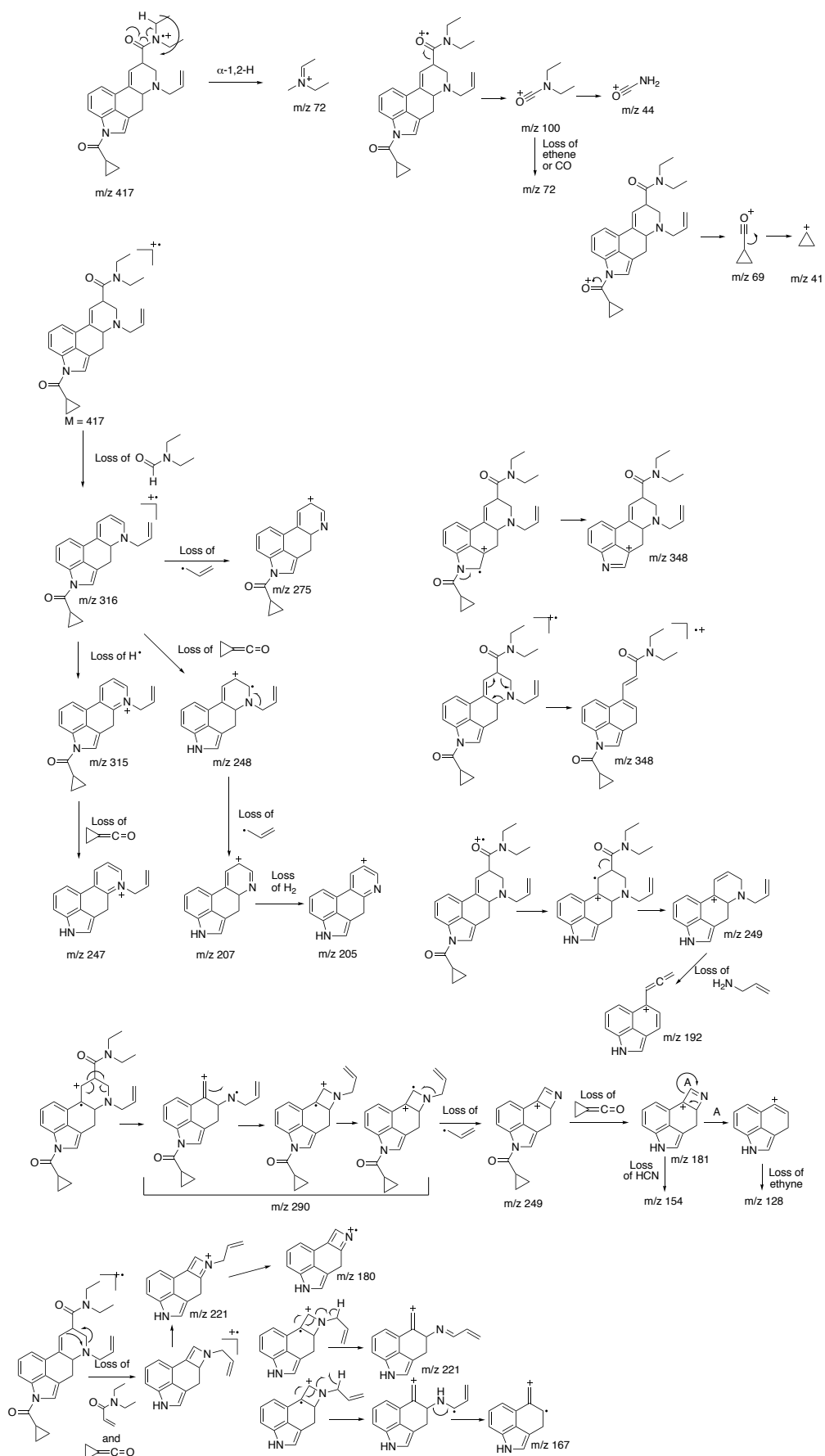
⁷ *Department of Psychiatry, University of California San Diego, La Jolla, CA 92093-0804, USA*

⁸ *Research Service, VA San Diego Healthcare System, San Diego, CA 92161, USA*

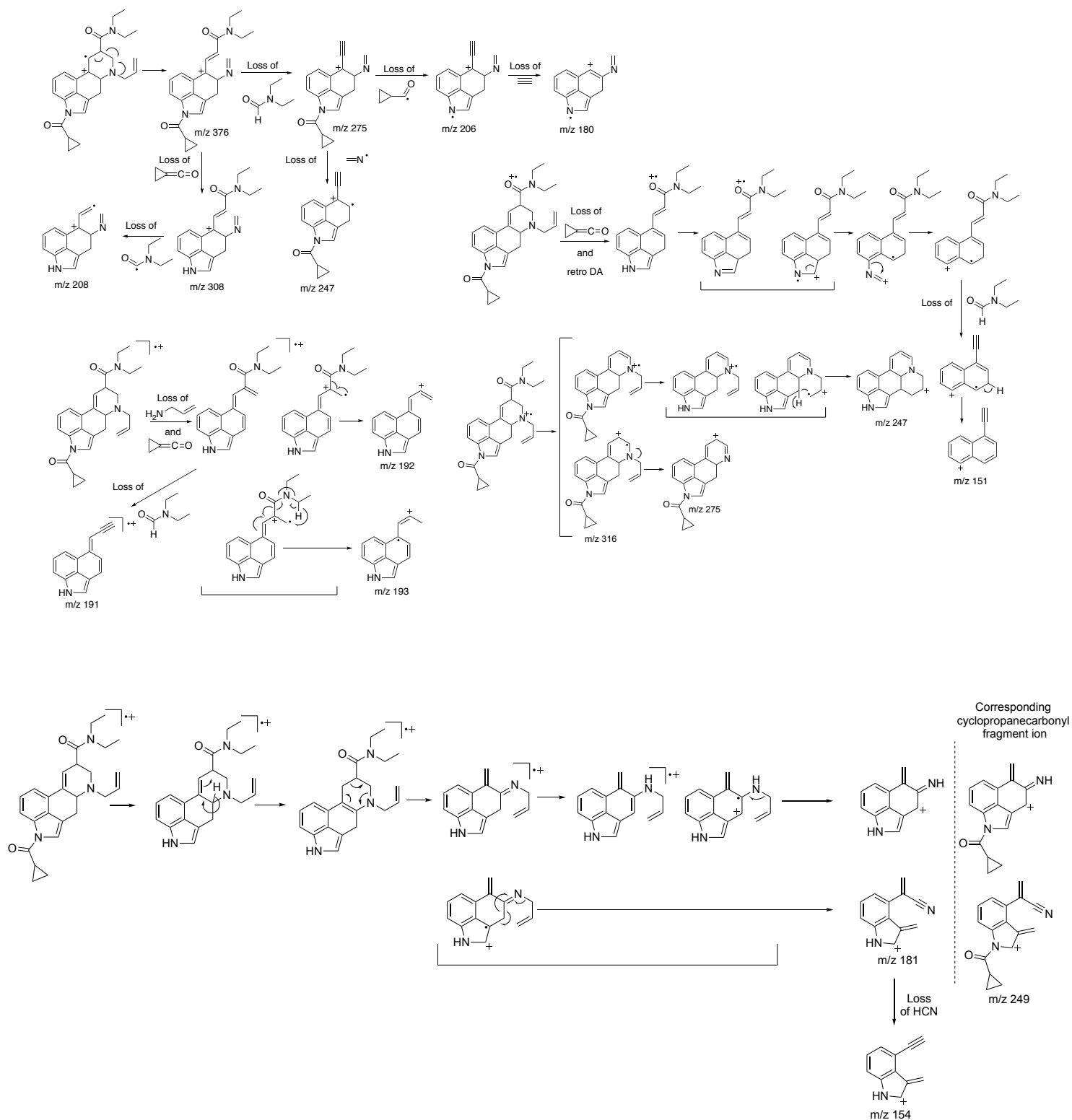
⁹ *School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University, Byrom Street, Liverpool L3 3AF, UK*

* Correspondence to: Simon D. Brandt, School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University, Byrom Street, Liverpool, L3 3AF, UK. E-Mail: s.brandt@ljmu.ac.uk

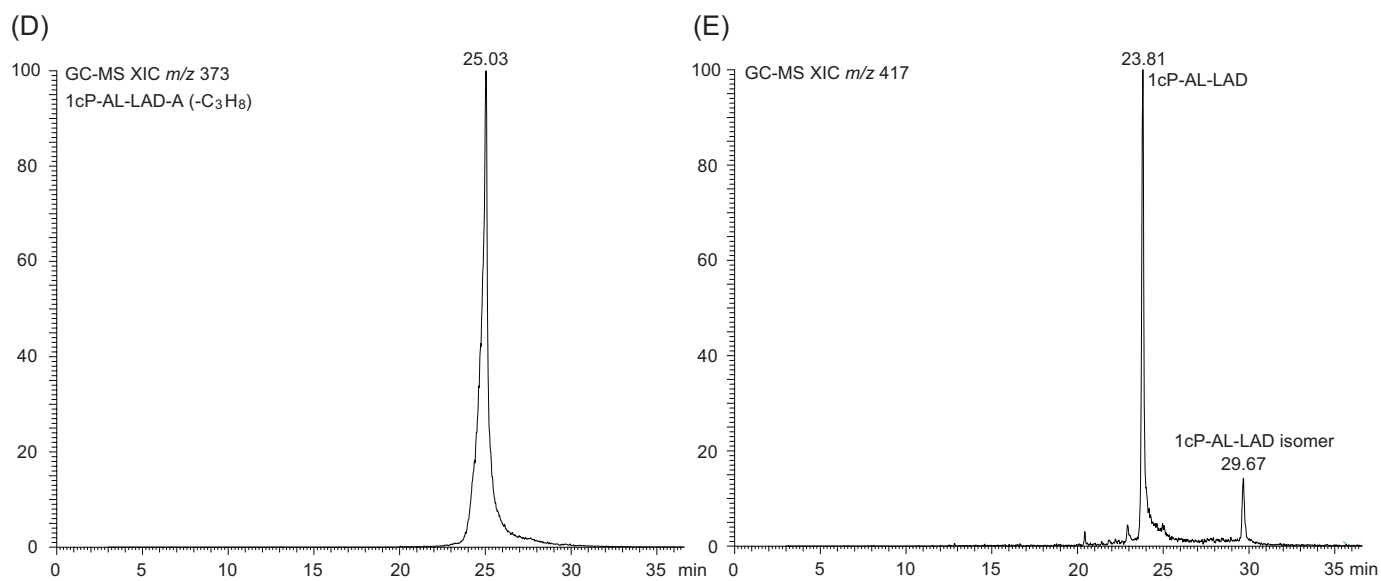
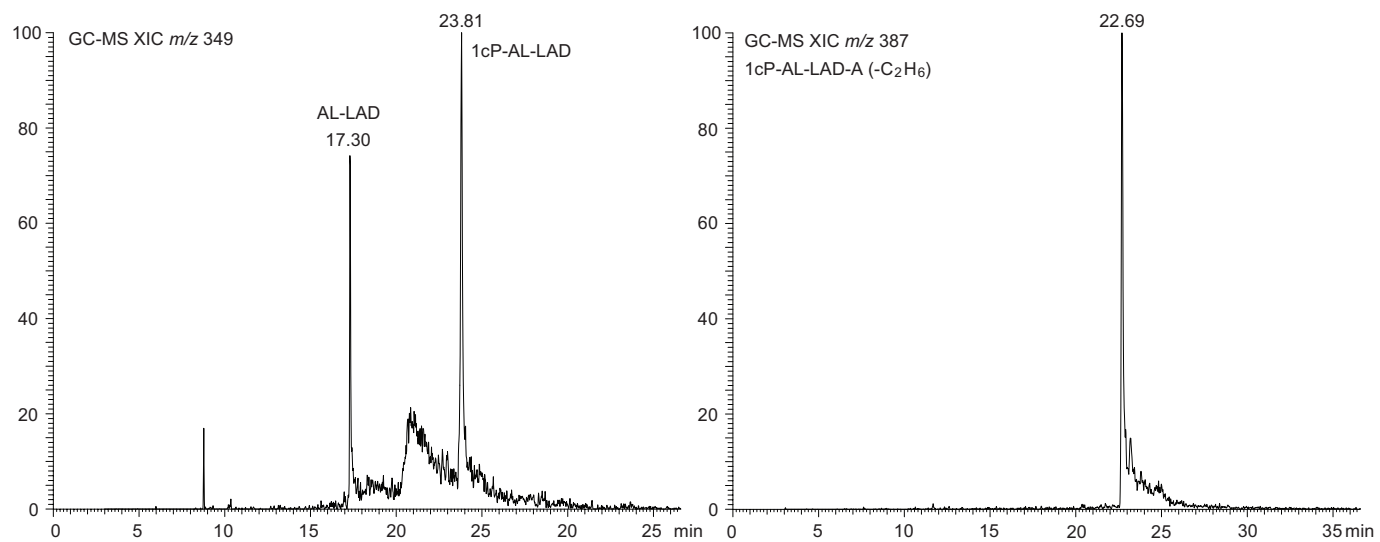
Proposed EI-MS fragmentation pathways (1cP-AL-LAD)

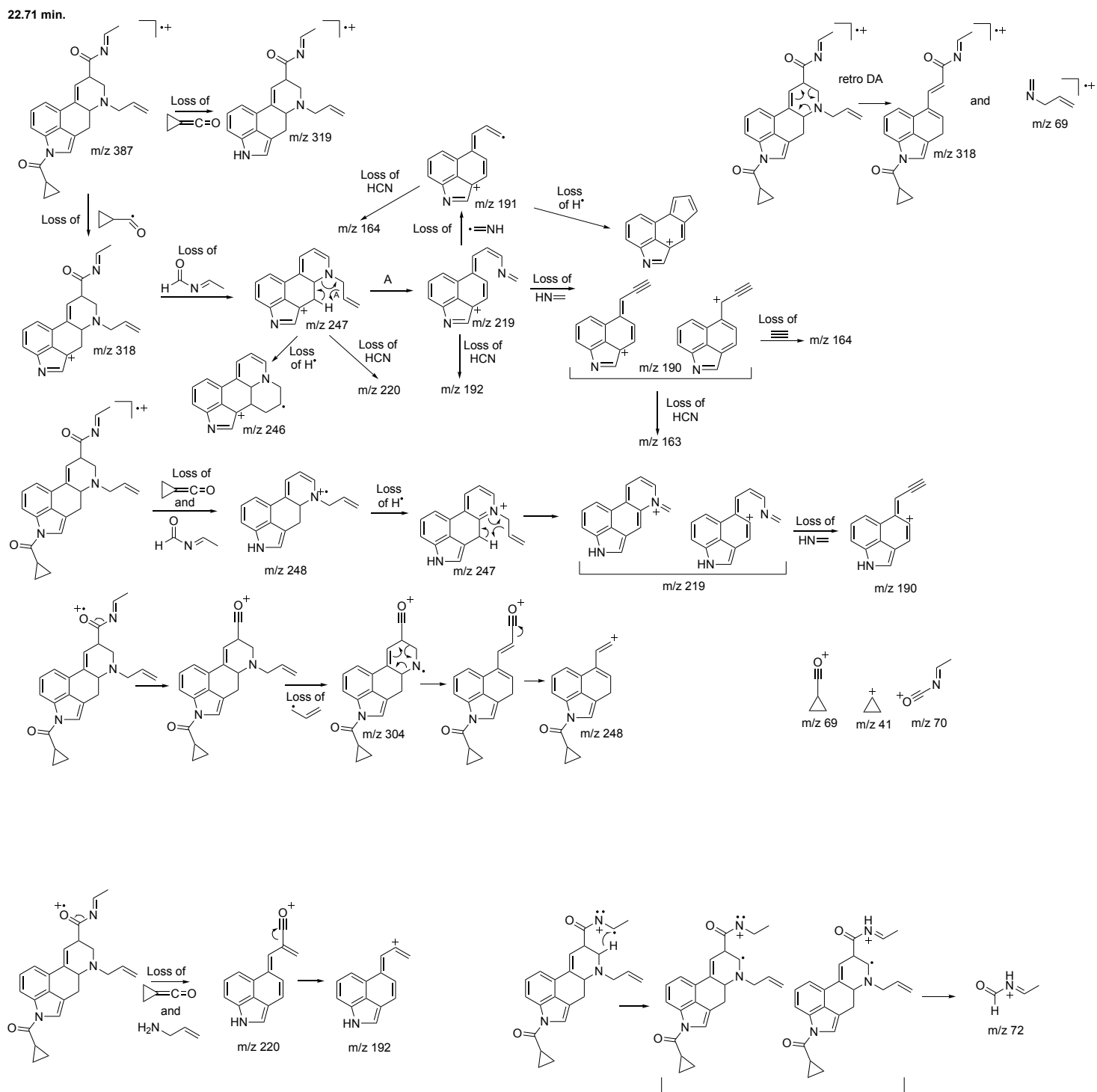


Proposed EI-MS fragmentation pathways (1cP-AL-LAD)

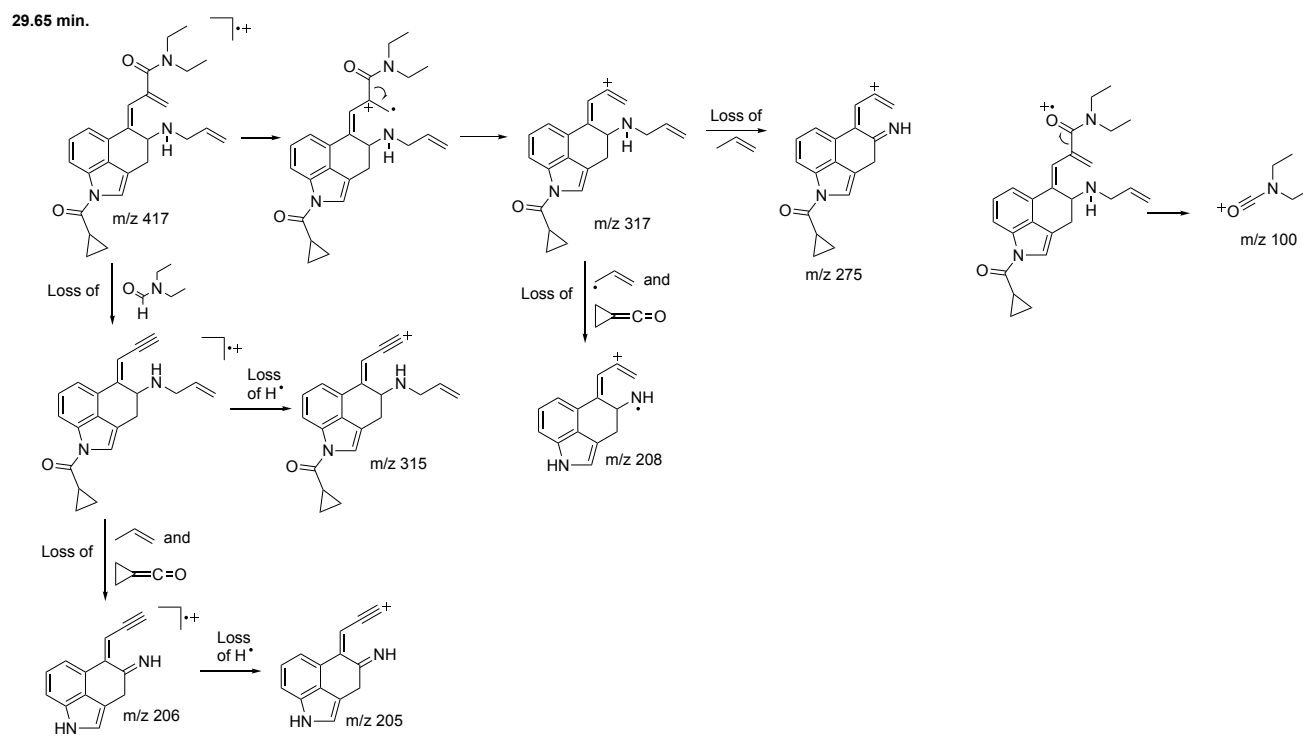


GC-MS XIC traces (powdered sample of 1cP-AL-LAD) including GC-induced artifacts

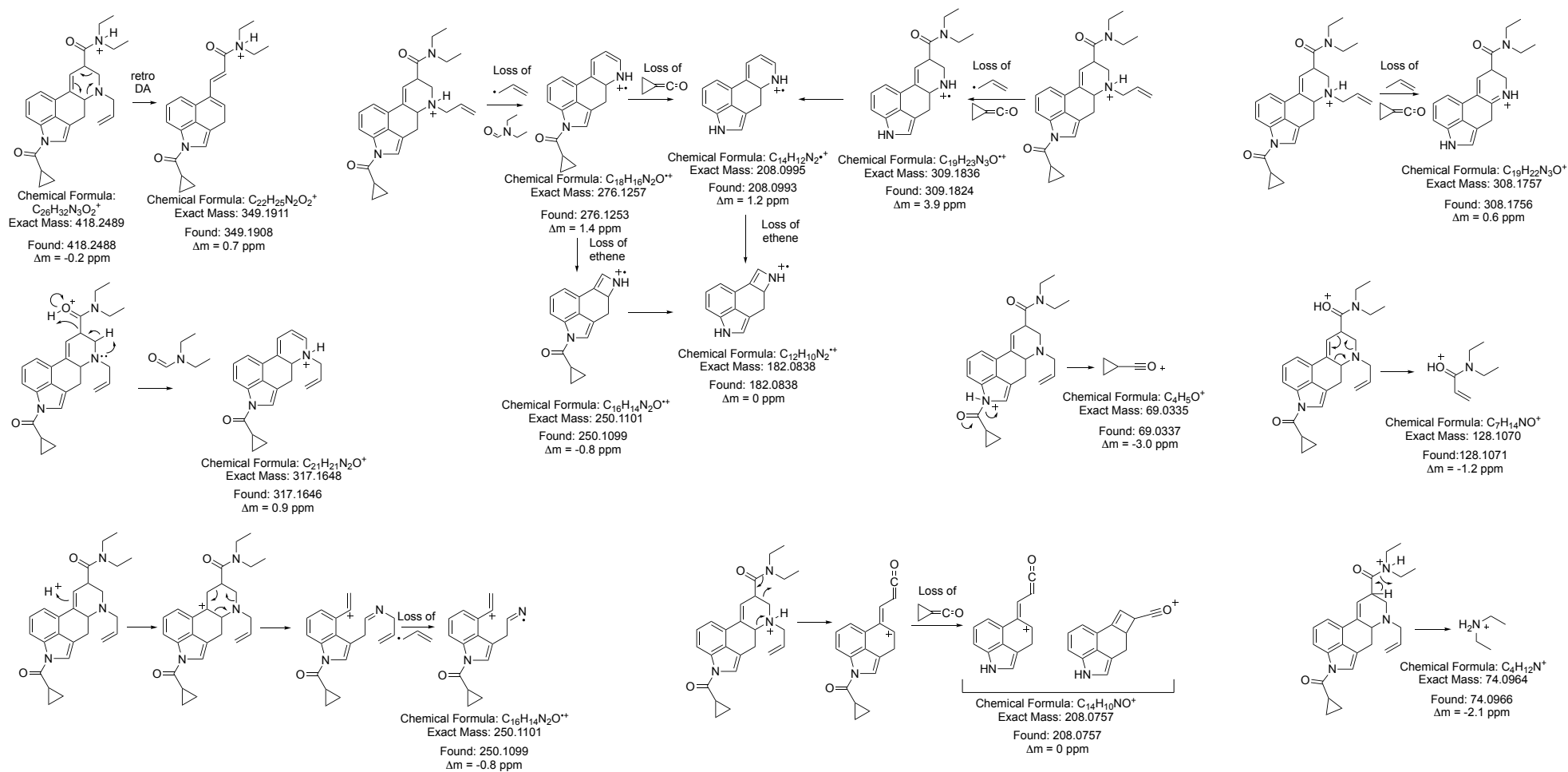


Proposed EI-MS fragmentation pathways for 1cP-AL-LAD-A (-C₂H₆)

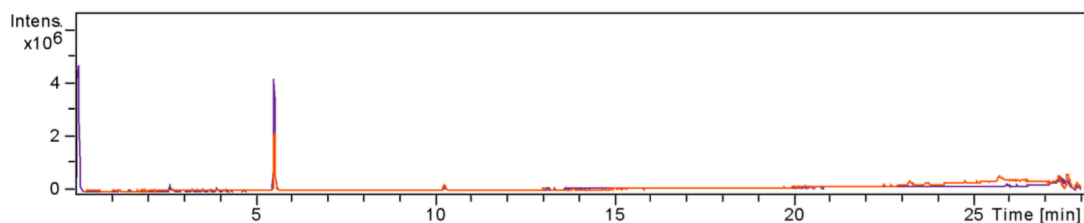
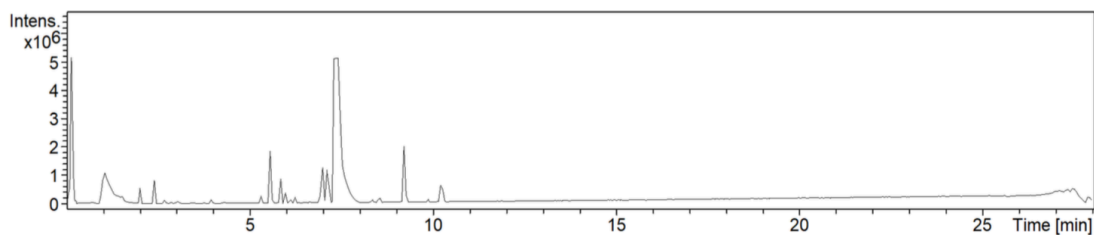
Proposed EI-MS fragmentation pathways (1cP-AL-LAD isomer)



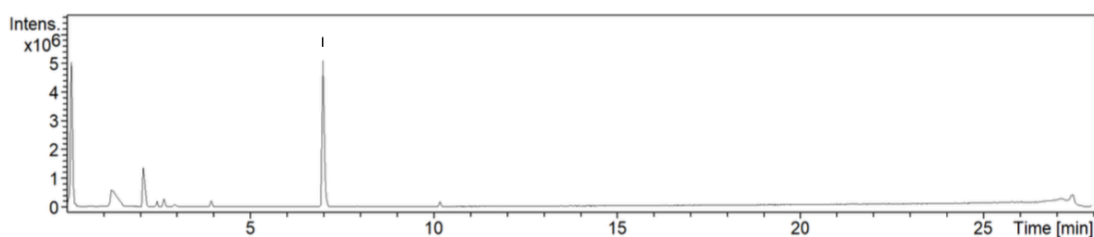
Proposed ESI-QTOF-MS/MS fragmentation pathways



LC-QTOF-MS/MS trace of 1cP-AL-AL-LAD (+bbCID MS/MS; 10 µg/mL 1cP-AL-LAD powder) and comparison with AL-LAD and 1P-AL-LAD standards

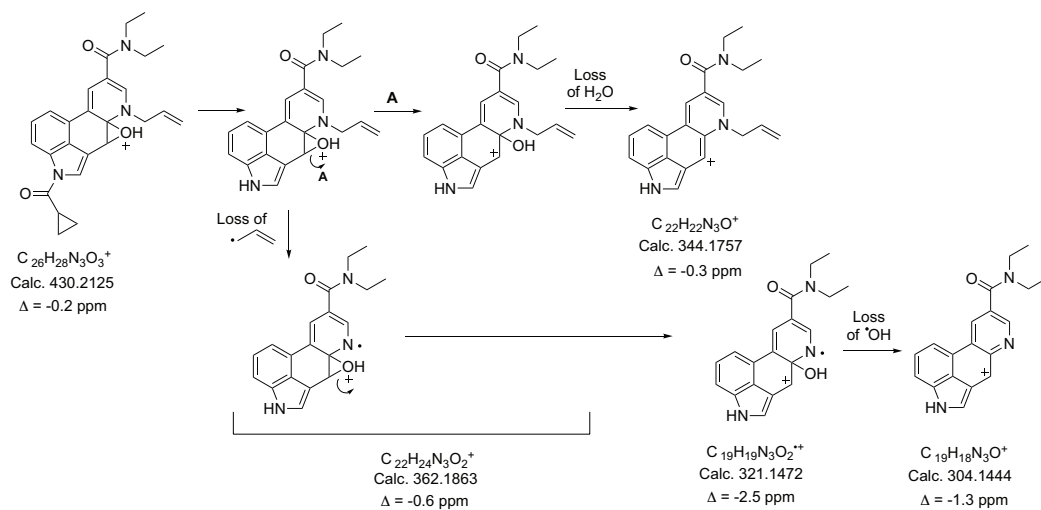
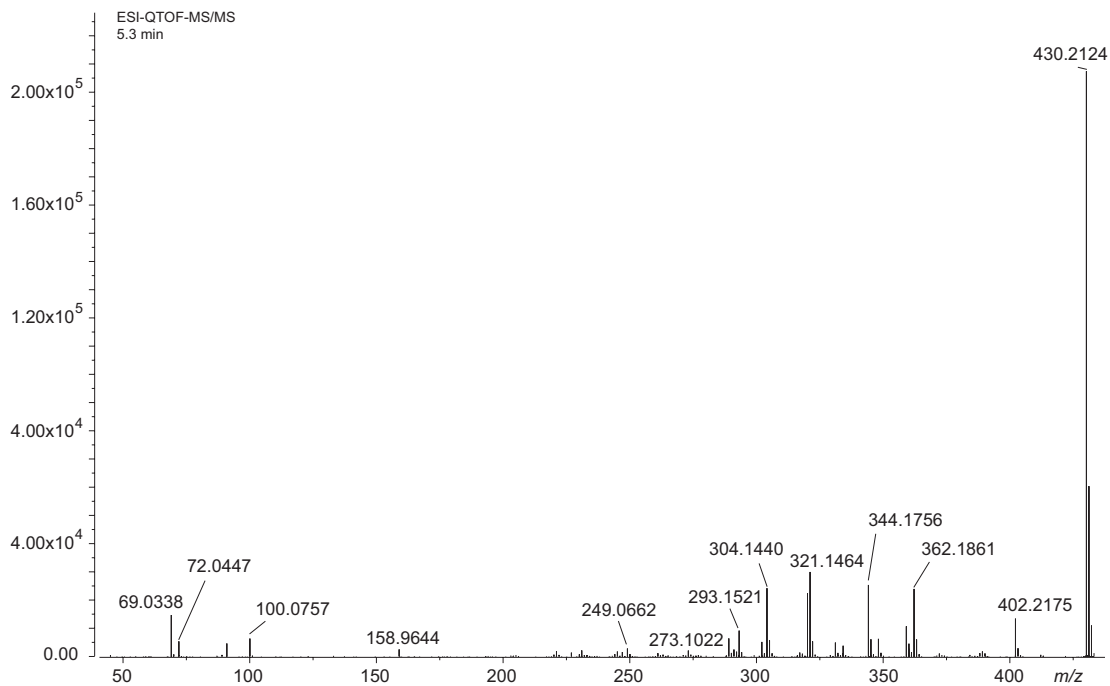


AL-LAD standard at 5.6 min (+bbCID MS; 1 µg/mL)

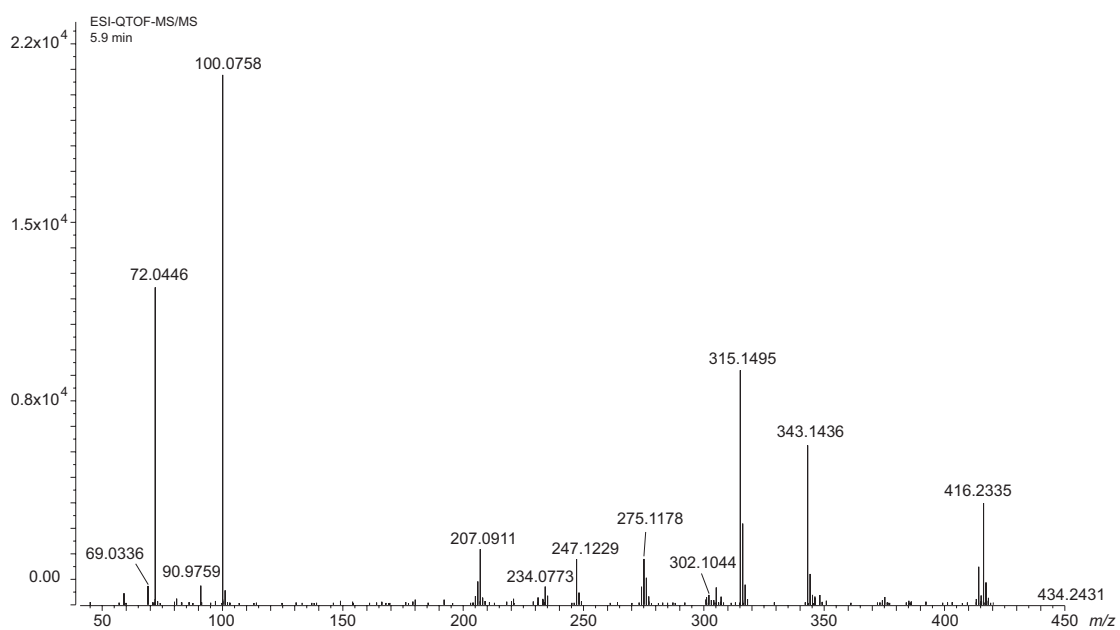
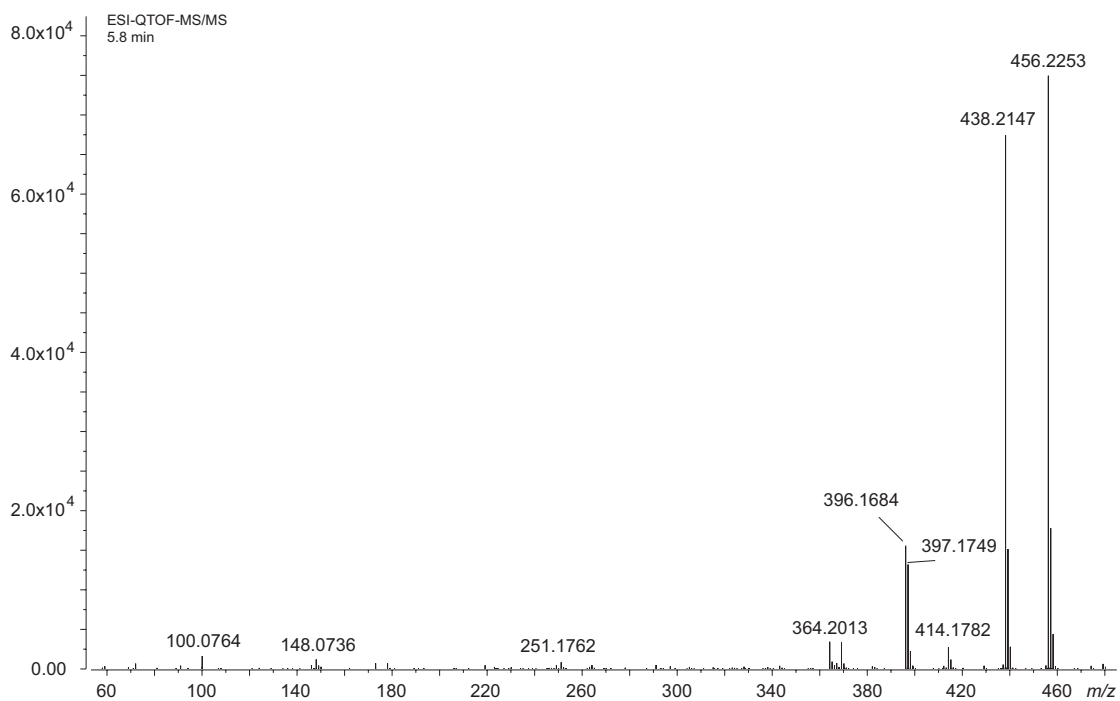


1P-AL-LAD standard at 7.0 min (+bbCID MS; 1 µg/mL)

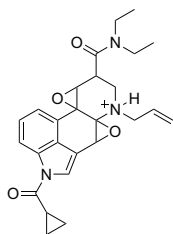
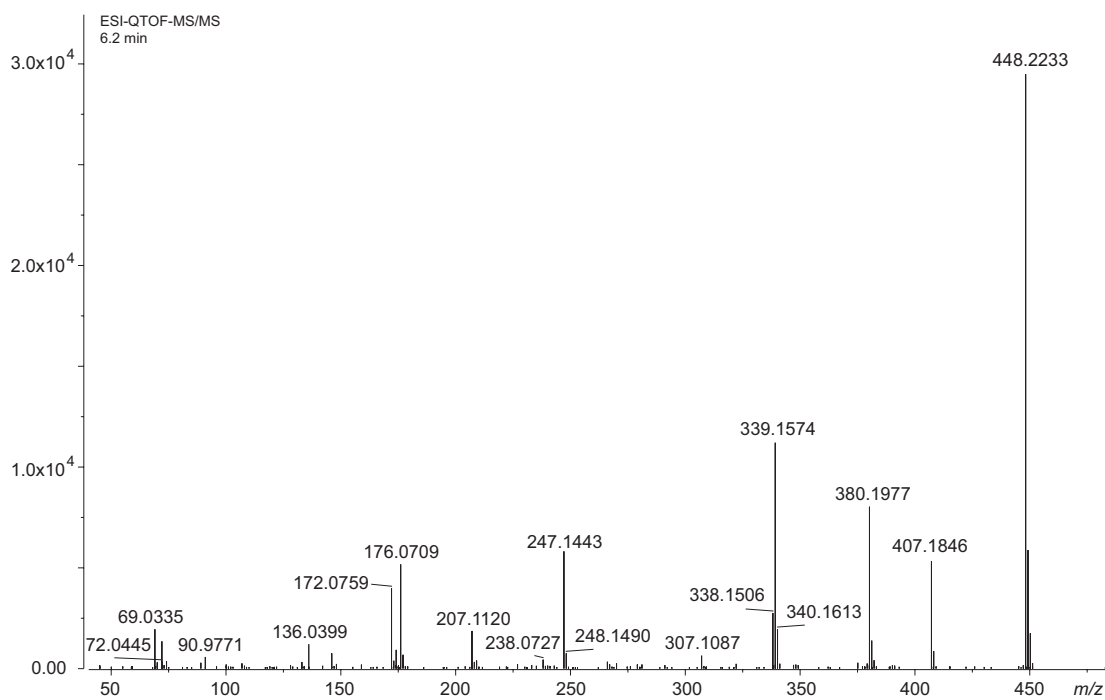
Additional tandem mass spectrum recorded in full scan/AutoMS/MS mode (powdered sample) and tentative identification



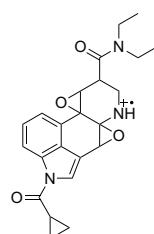
Additional tandem mass spectra recorded in full scan/AutoMS/MS mode (powdered sample)



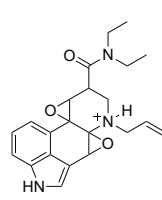
Additional tandem mass spectrum recorded in full scan/AutoMS/MS mode (powdered sample) and tentative identification



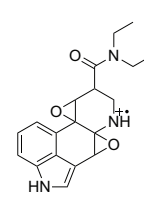
$C_{26}H_{30}N_3O_4^+$
Calc. 448.2231
 $\Delta = 0.4$ ppm



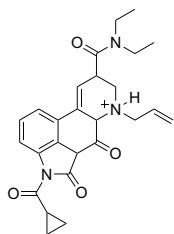
$C_{23}H_{25}N_3O_4^{++}$
Calc. 407.1840
 $\Delta = 1.5$ ppm



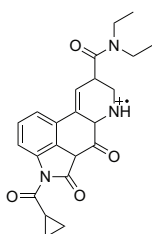
$C_{22}H_{26}N_3O_3^+$
Calc. 380.1969
 $\Delta = 2.1$ ppm



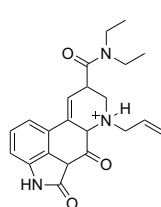
$C_{19}H_{21}N_3O_3^{++}$
Calc. 339.1577
 $\Delta = -0.9$ ppm



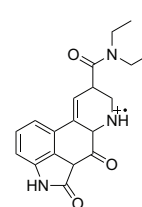
$C_{26}H_{30}N_3O_4^+$
Calc. 448.2231
 $\Delta = 0.4$ ppm



$C_{23}H_{25}N_3O_4^{++}$
Calc. 407.1840
 $\Delta = 1.5$ ppm

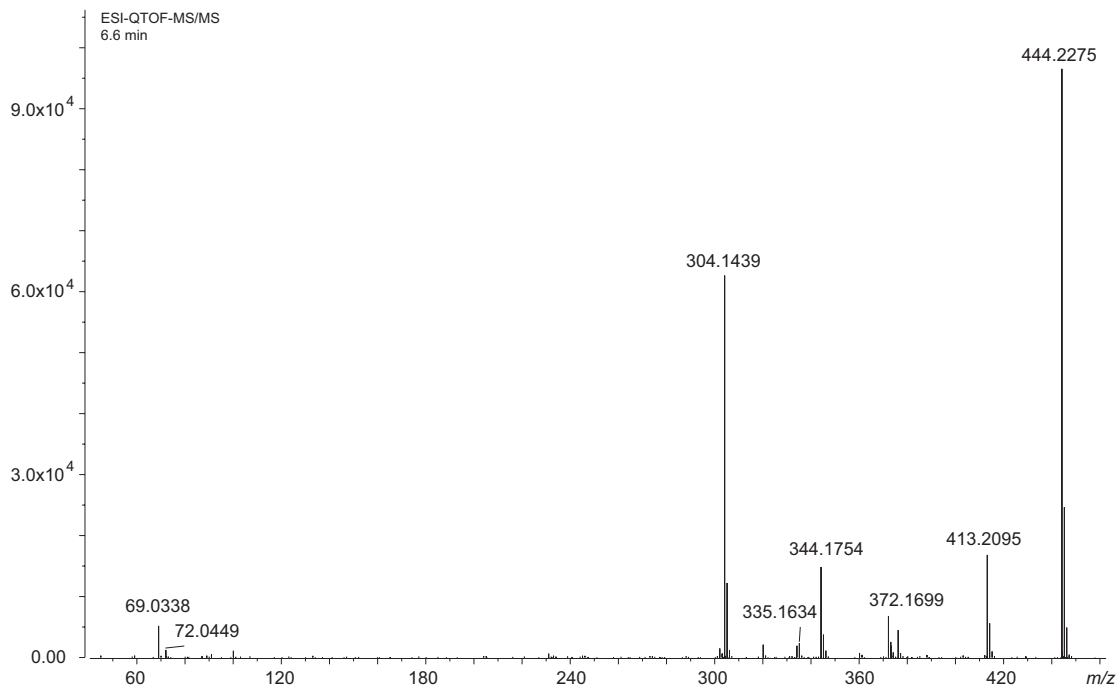


$C_{22}H_{26}N_3O_3^+$
Calc. 380.1969
 $\Delta = 2.1$ ppm

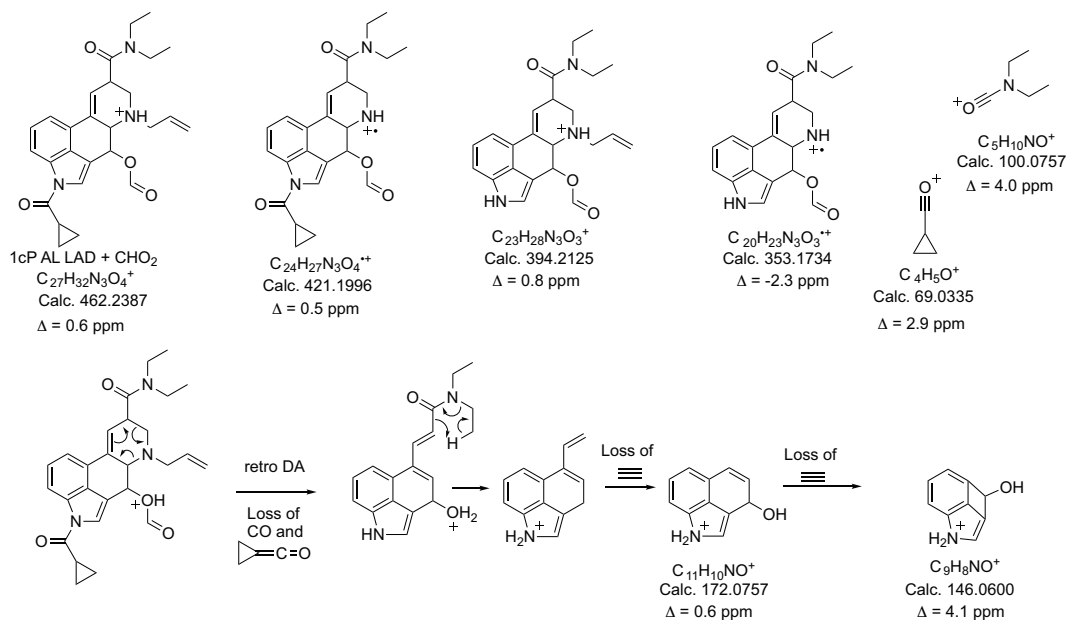
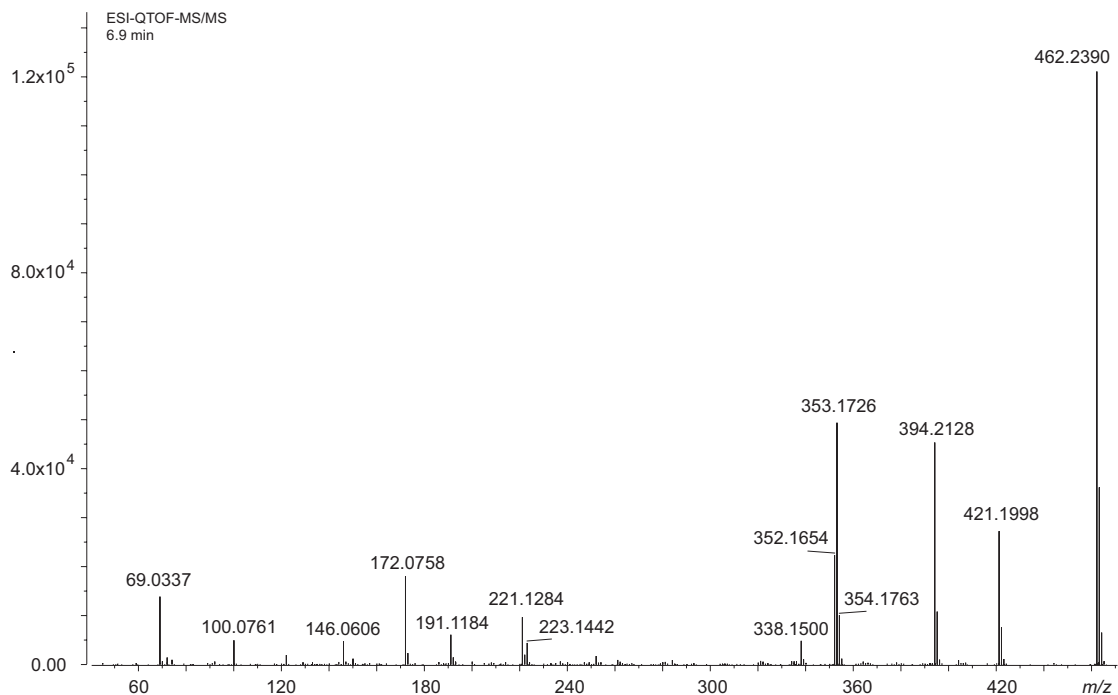


$C_{19}H_{21}N_3O_3^{++}$
Calc. 339.1577
 $\Delta = -0.9$ ppm

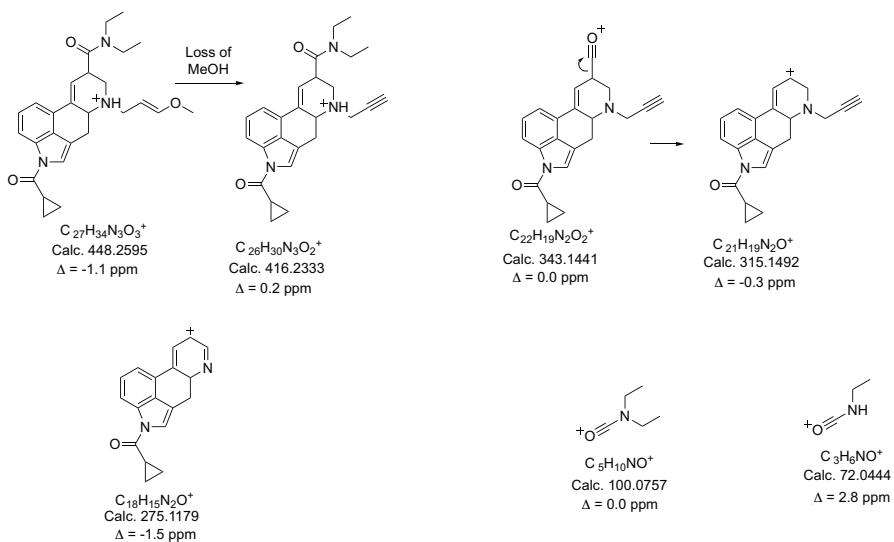
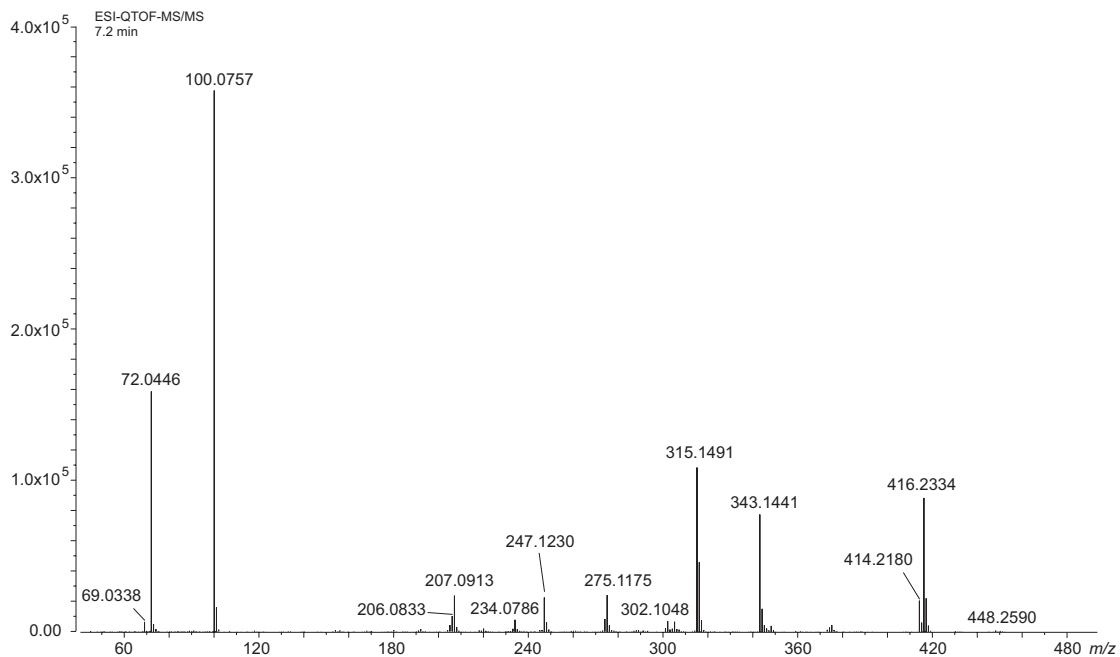
Additional tandem mass spectrum recorded in full scan/AutoMS/MS mode (powdered sample)



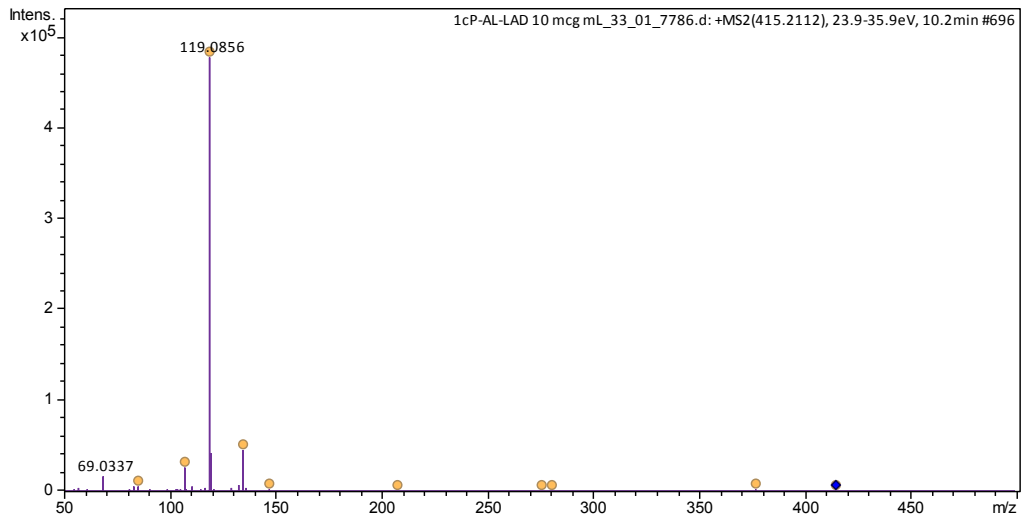
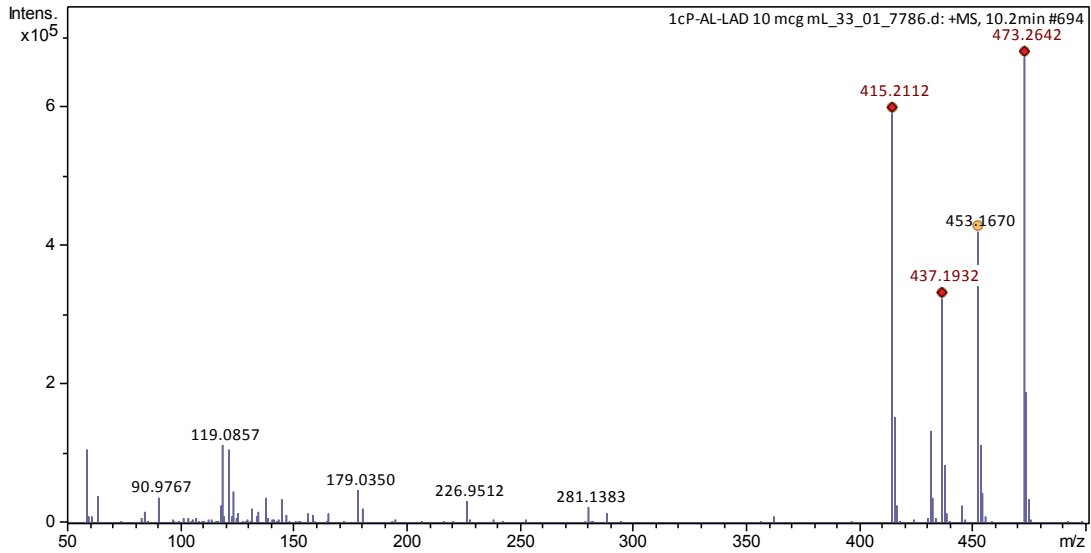
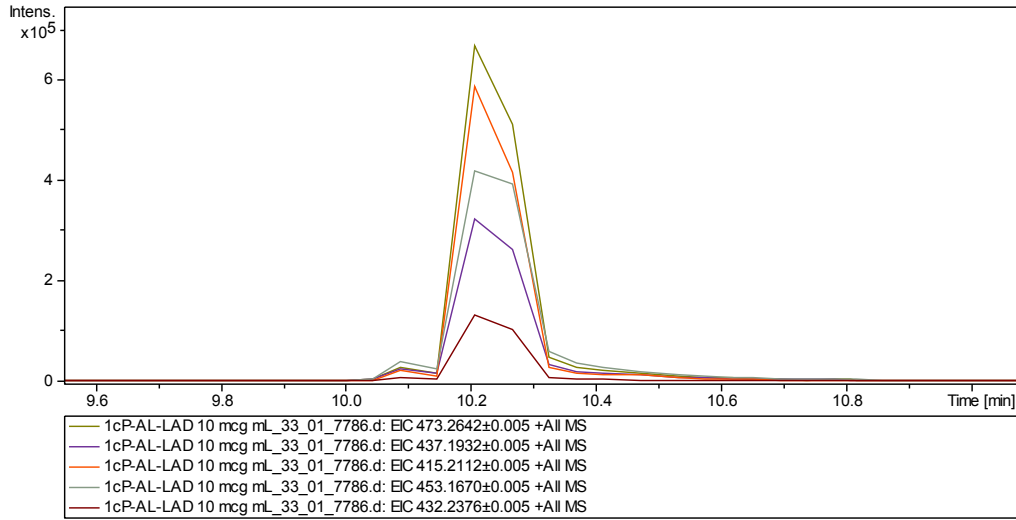
Additional tandem mass spectrum recorded in full scan/AutoMS/MS mode (powdered sample) and tentative identification



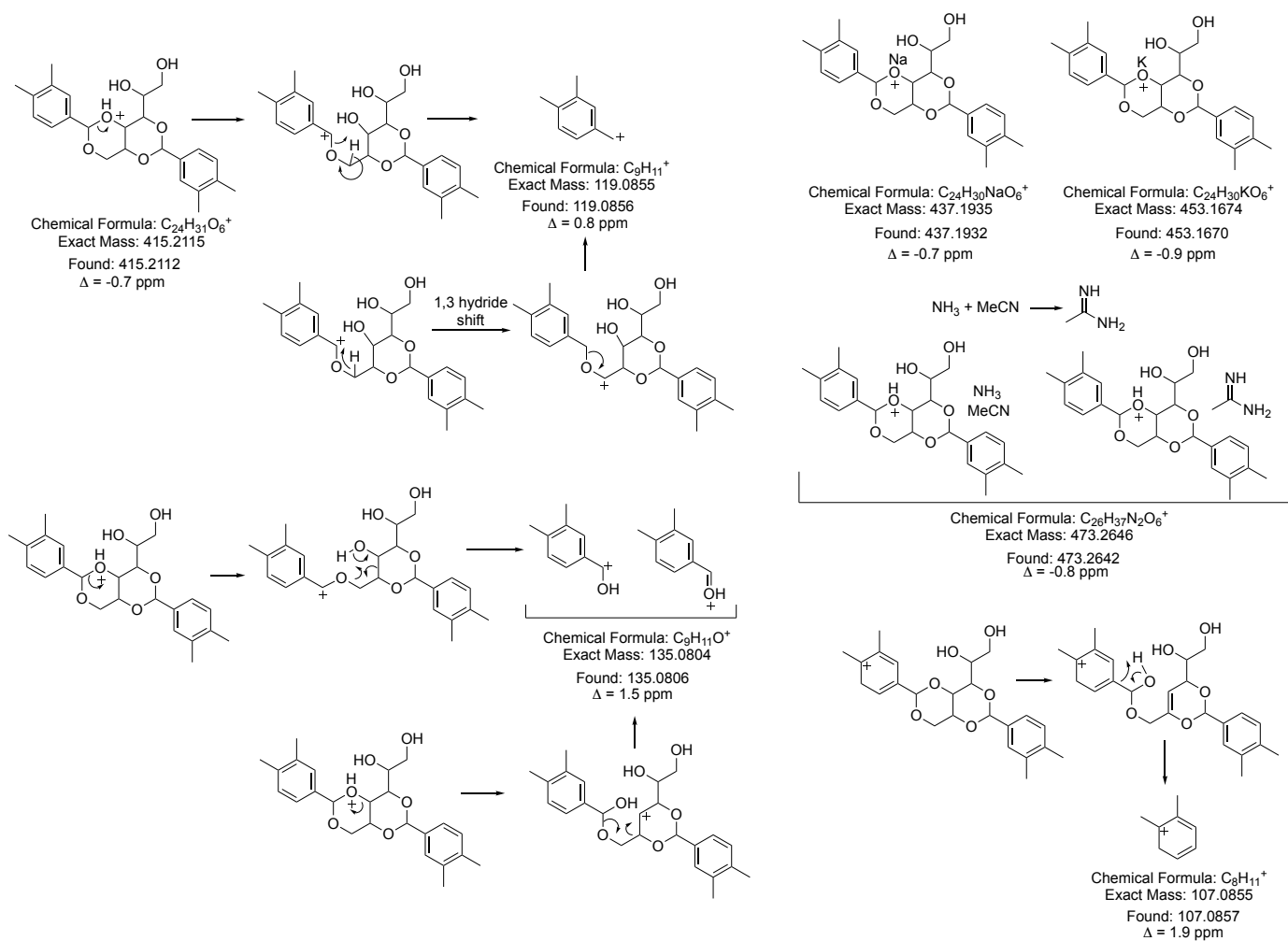
Additional tandem mass spectrum recorded in full scan/AutoMS/MS mode (powdered sample) and tentative identification



Peak at 10.2 min (1cP-AL-LAD powdered sample) following LC-QTOF-MS/MS analysis and tentative identification as dimethyldibenzylidene sorbitol (DBS), a plastics additive, presumably detected as part of the analytical procedure.

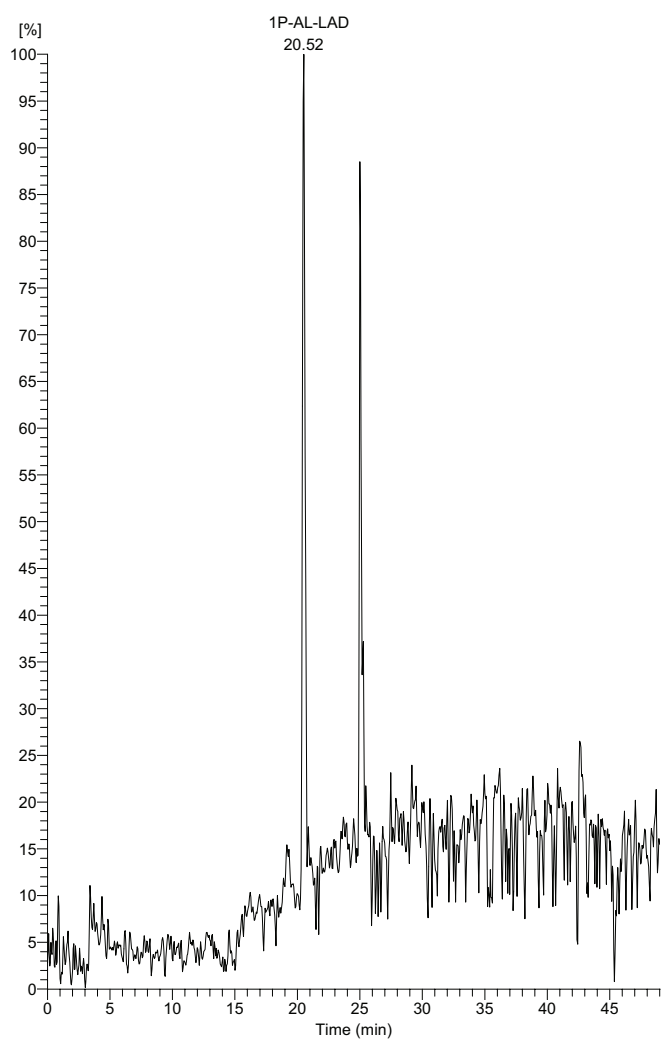


Proposed ESI-QTOF-MS/MS fragmentation pathways for DBS

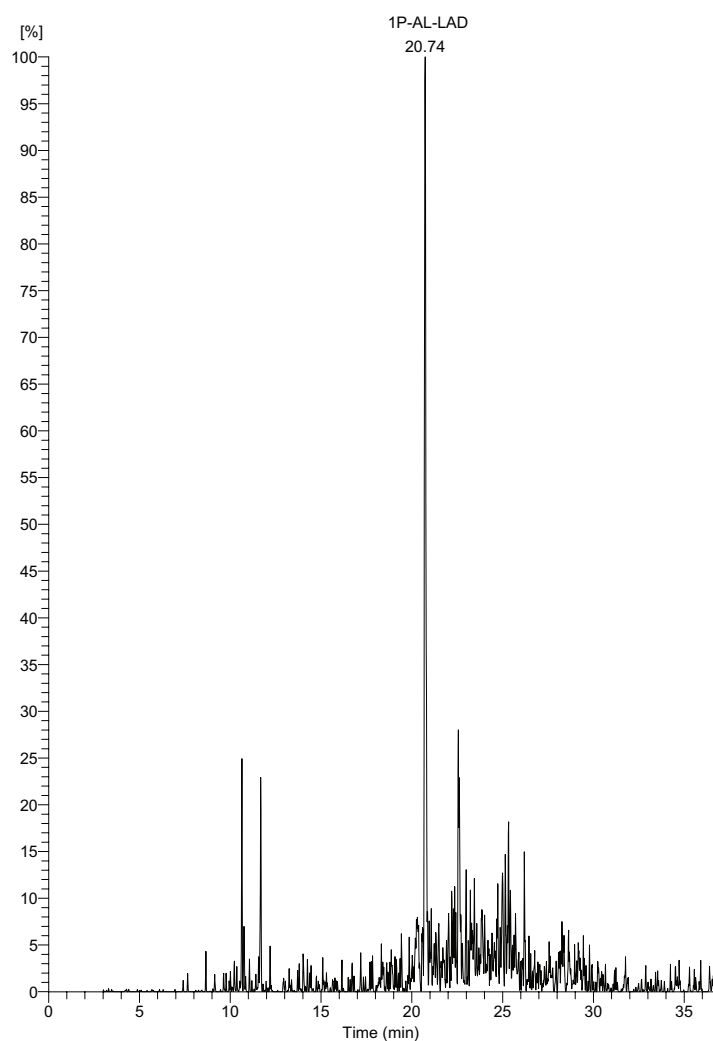


Detection of 1P-AL-LAD in methanolic blotter extract (10 blotters)

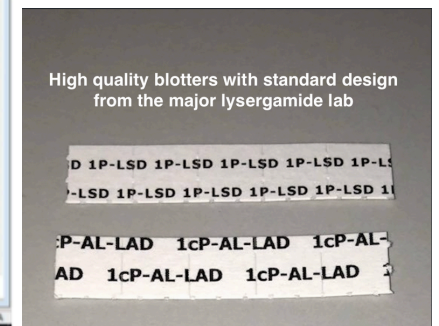
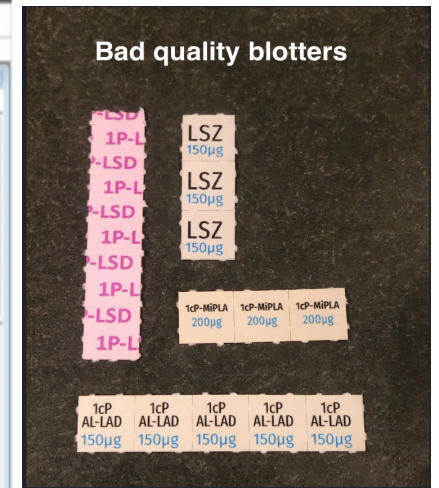
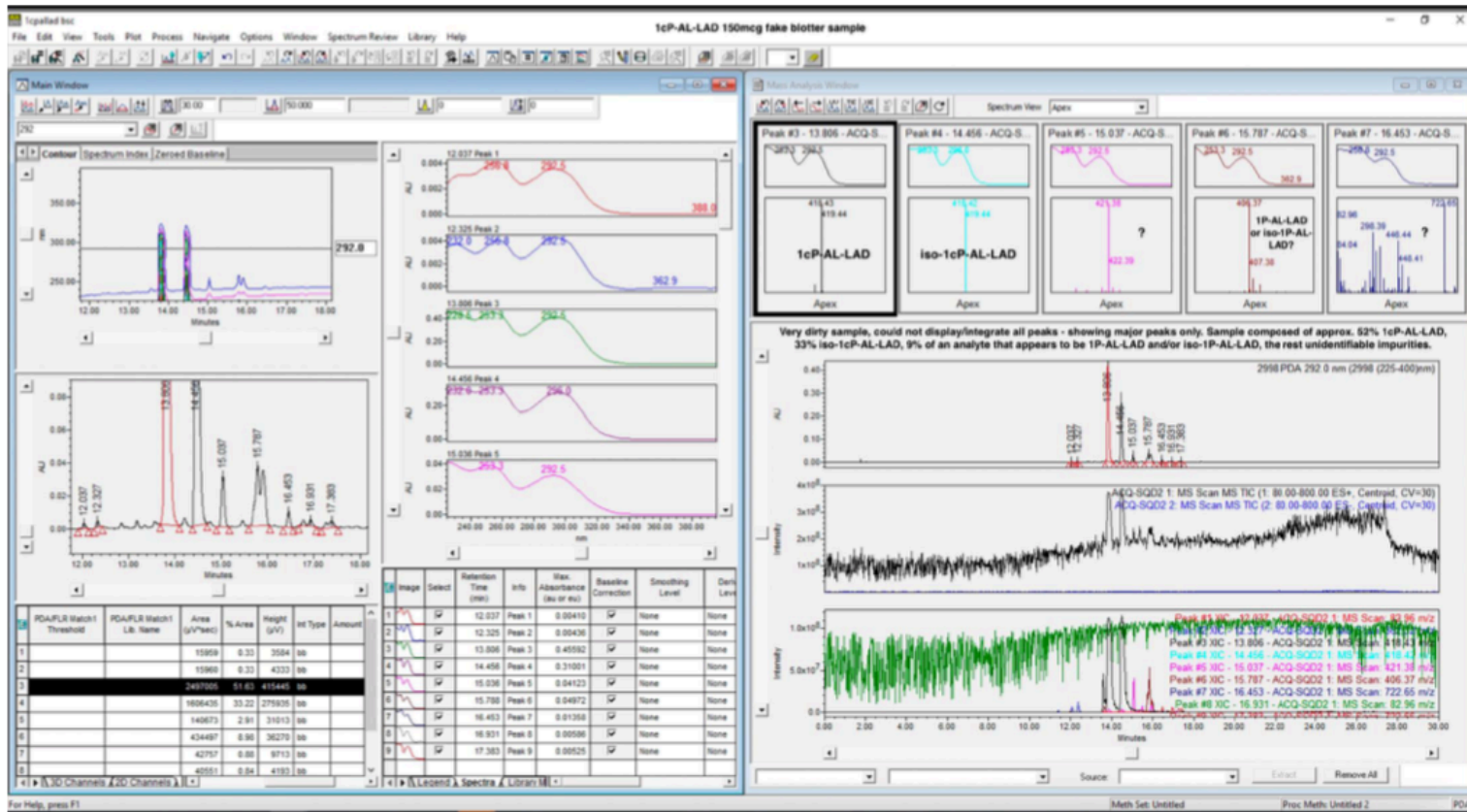
LC-ion trap-MS; XIC [M+H]⁺ at *m/z* 406



GC-MS; XIC [M⁺] at *m/z* 405

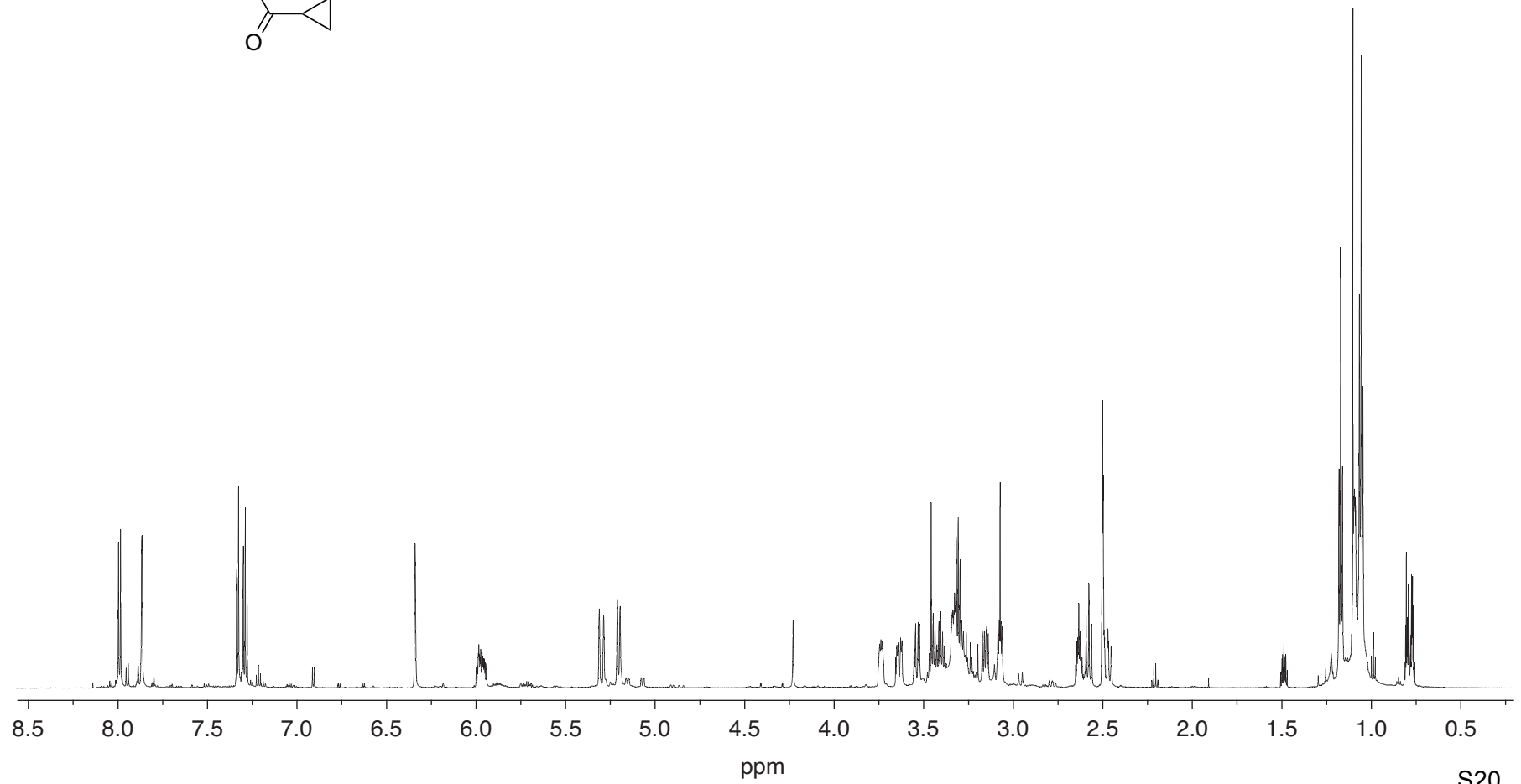
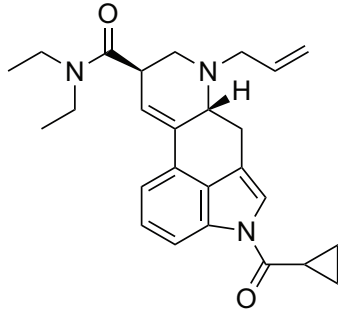


LC-MS analysis results involving contaminated 1cP-AL-LAD blotters posted anonymously on the Internet (https://pdfhost.io/v/qq9z.MDx6_Bad_blotter_reportpdf.pdf)



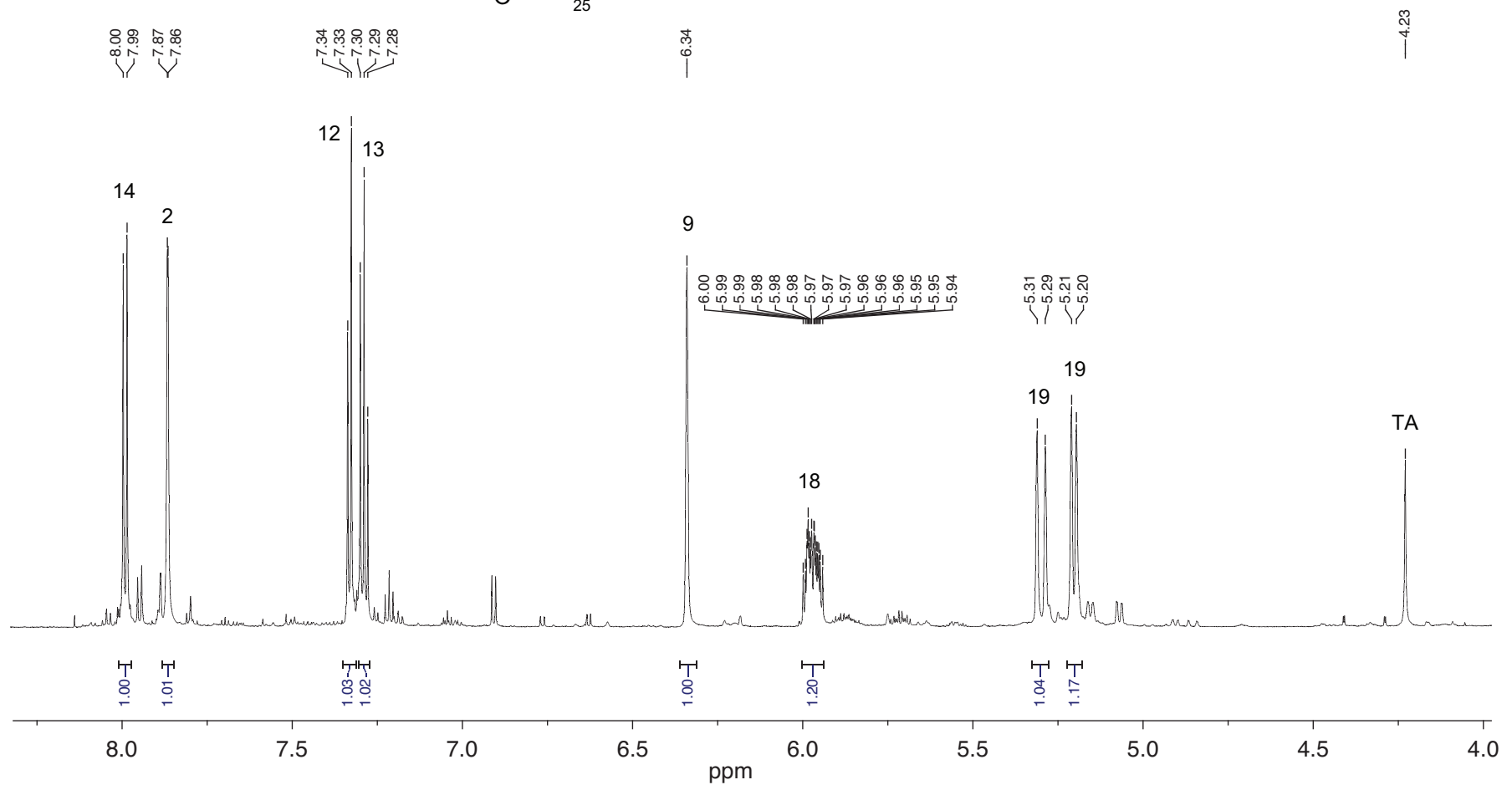
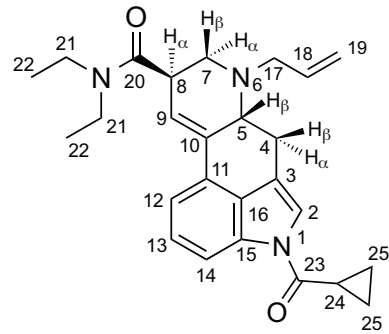
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
¹H-NMR (700 MHz)
d₆-DMSO



Supporting Information – Drug Testing and Analysis

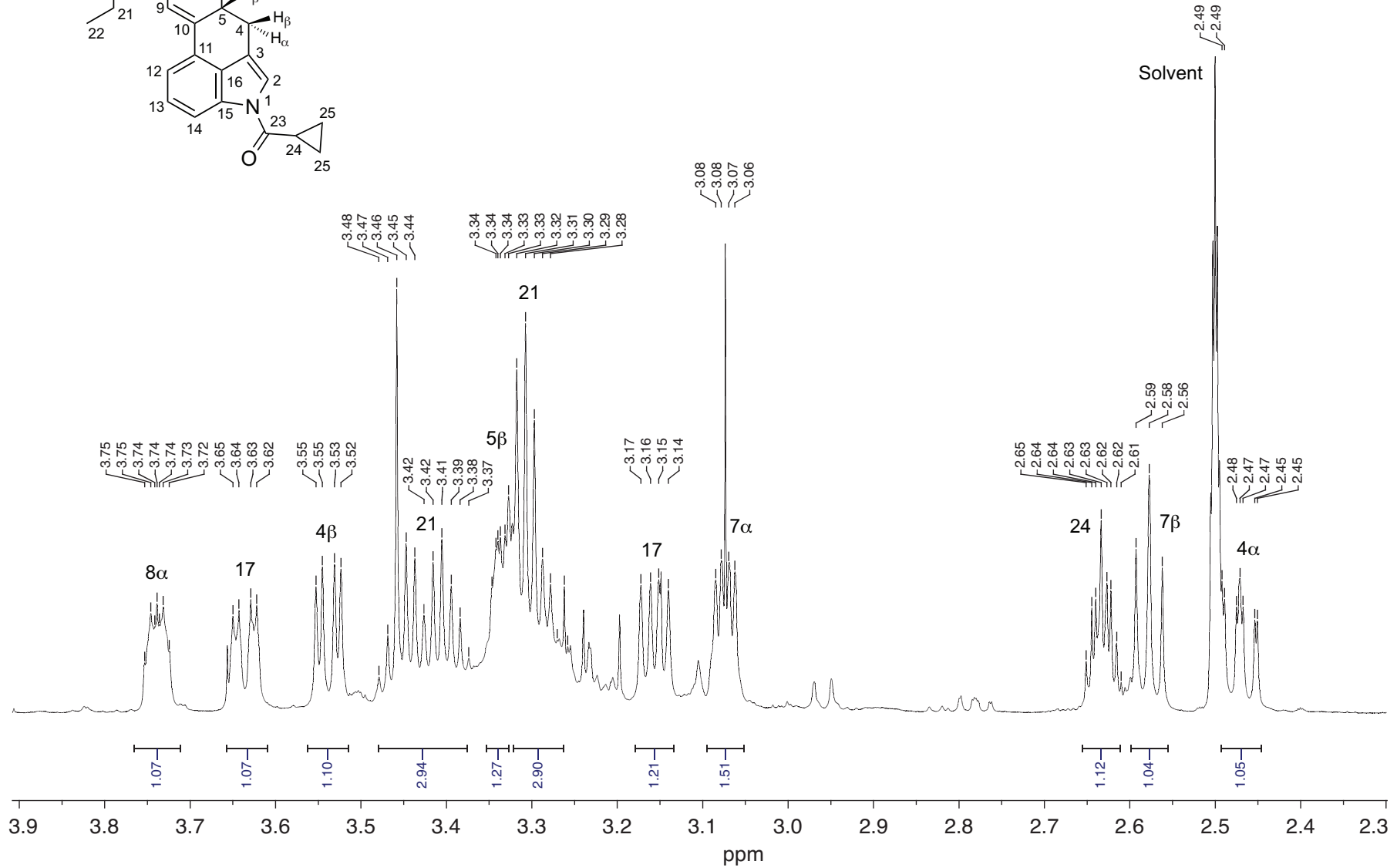
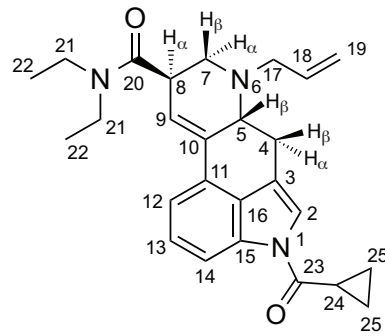
1cP-AL-LAD (including impurities)
¹H-NMR (700 MHz)
 d₆-DMSO



TA: tartaric acid

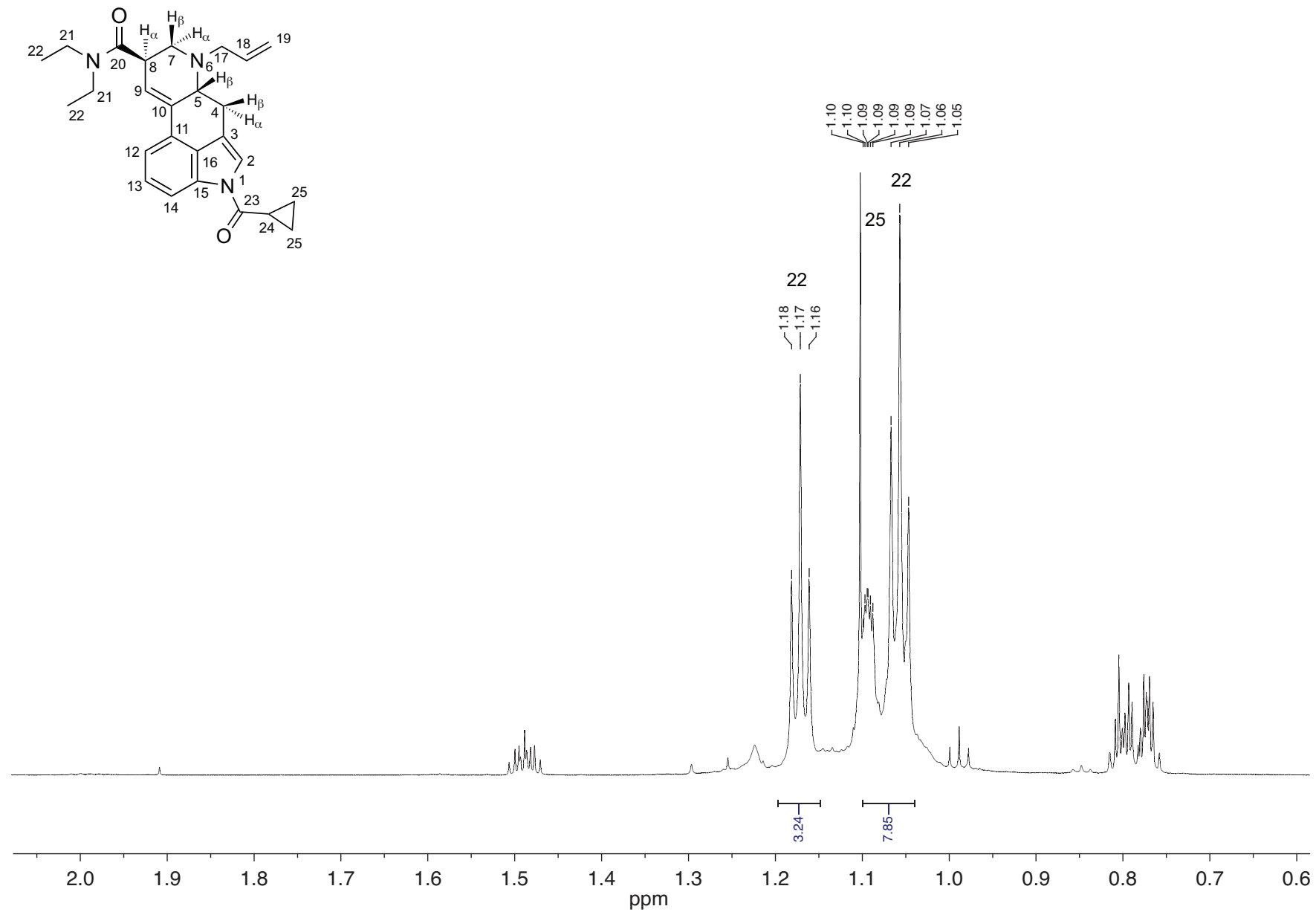
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
¹H-NMR (700 MHz)
d₆-DMSO



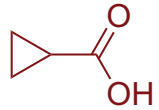
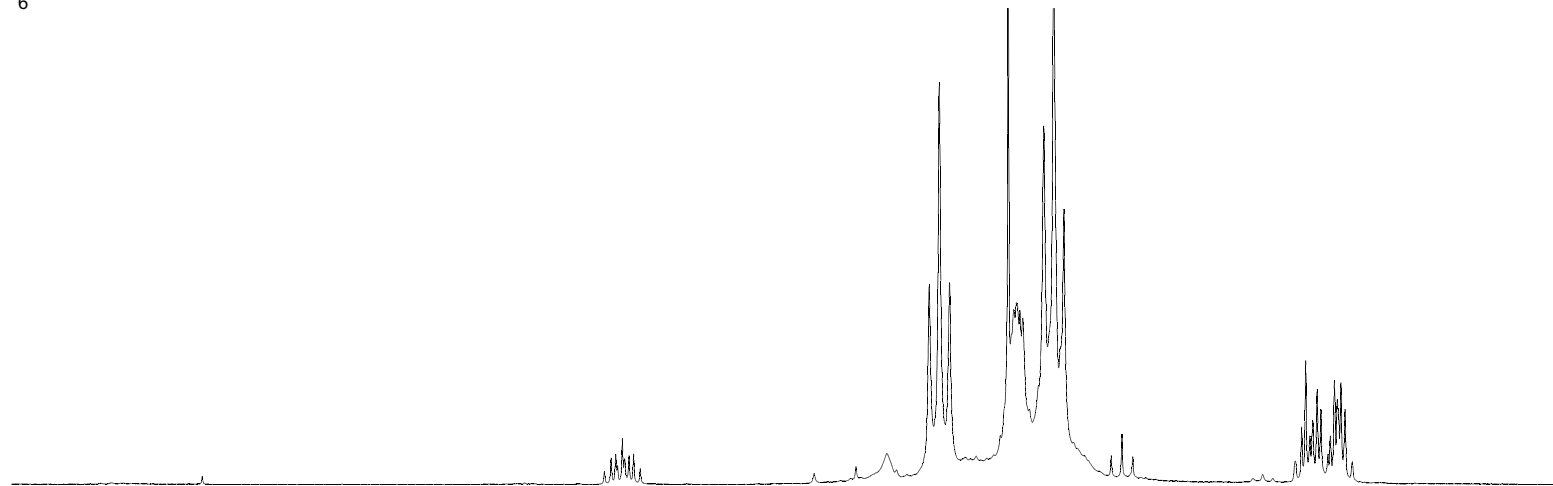
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
¹H-NMR (700 MHz)
d₆-DMSO

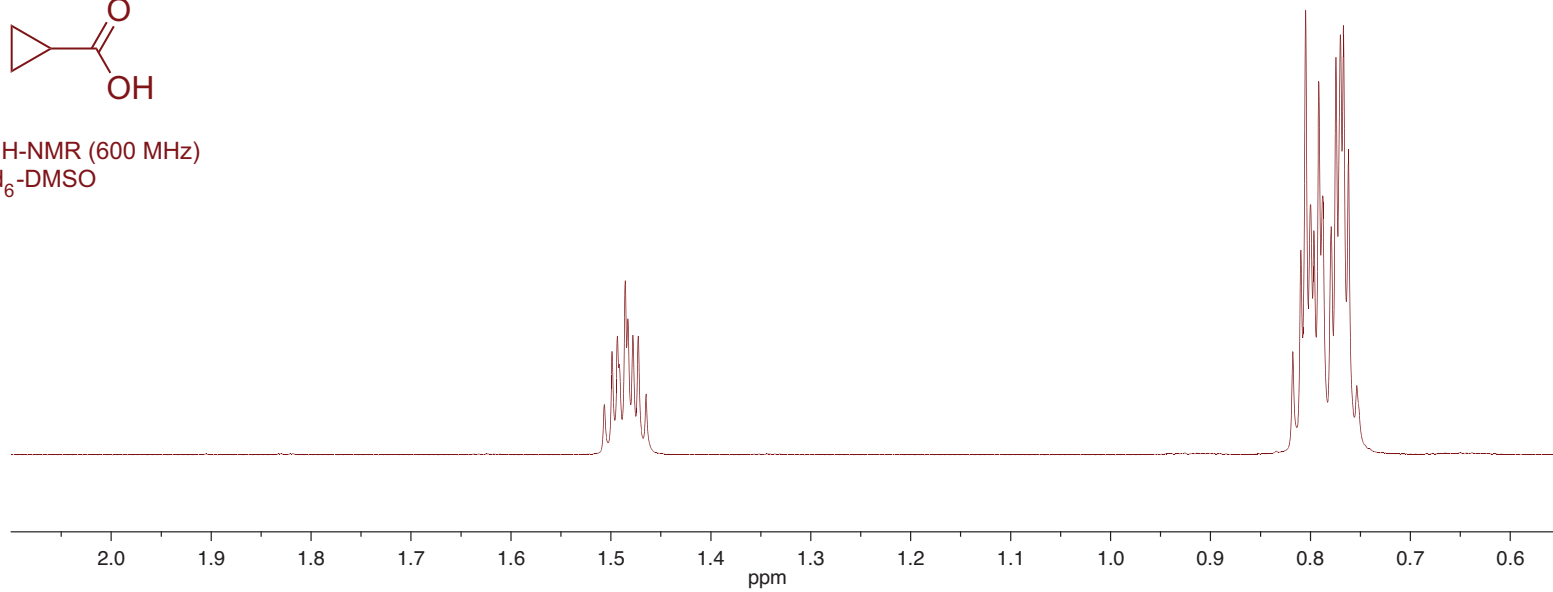


Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
¹H-NMR (700 MHz)
d₆-DMSO

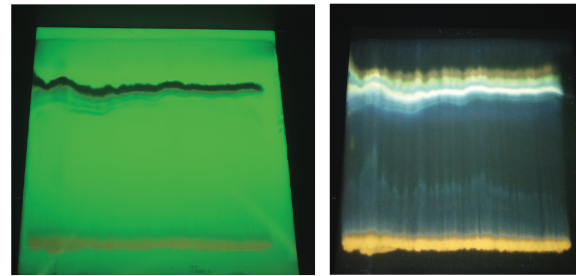


¹H-NMR (600 MHz)
d₆-DMSO

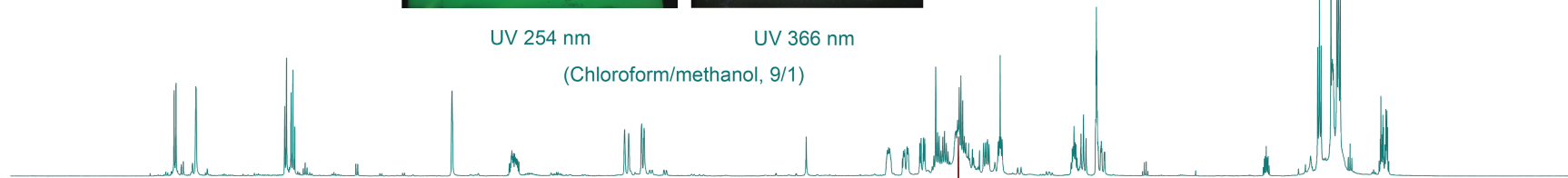


Supporting Information – Drug Testing and Analysis

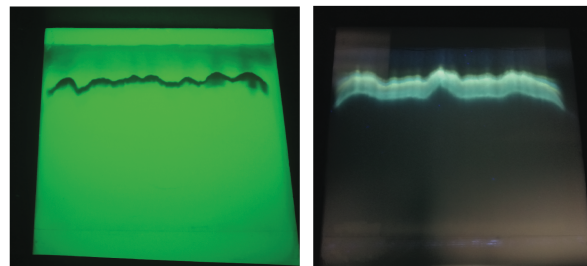
1cP-AL-LAD before prep TLC
¹H-NMR (700 MHz, DMSO-d₆)



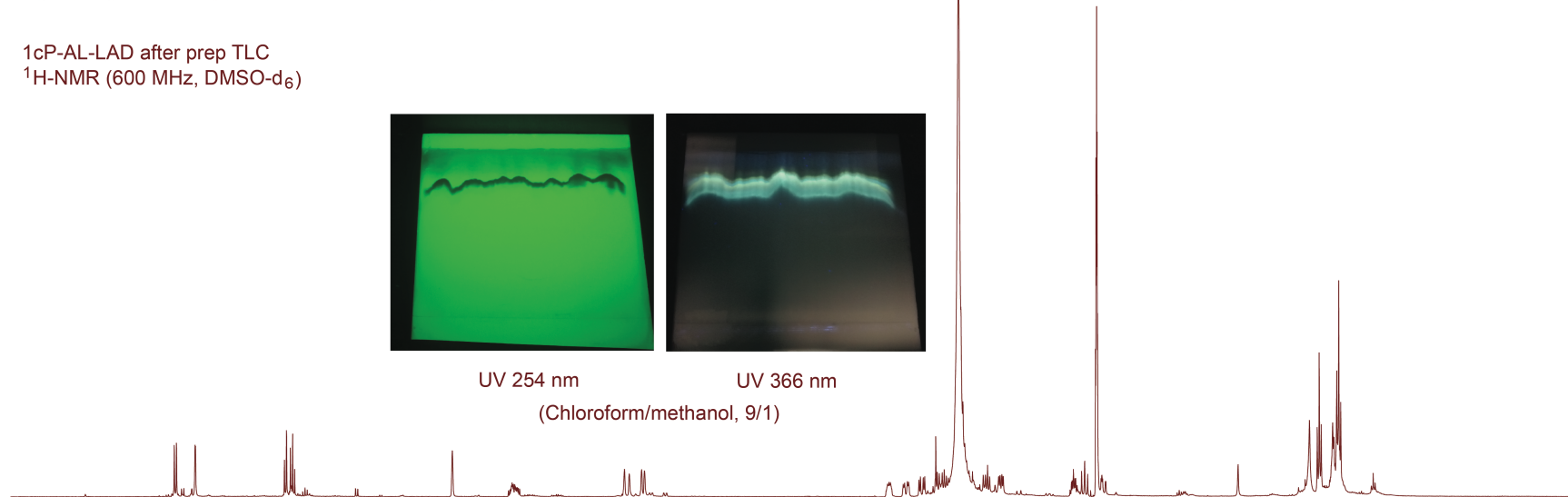
UV 254 nm UV 366 nm
(Chloroform/methanol, 9/1)



1cP-AL-LAD after prep TLC
¹H-NMR (600 MHz, DMSO-d₆)



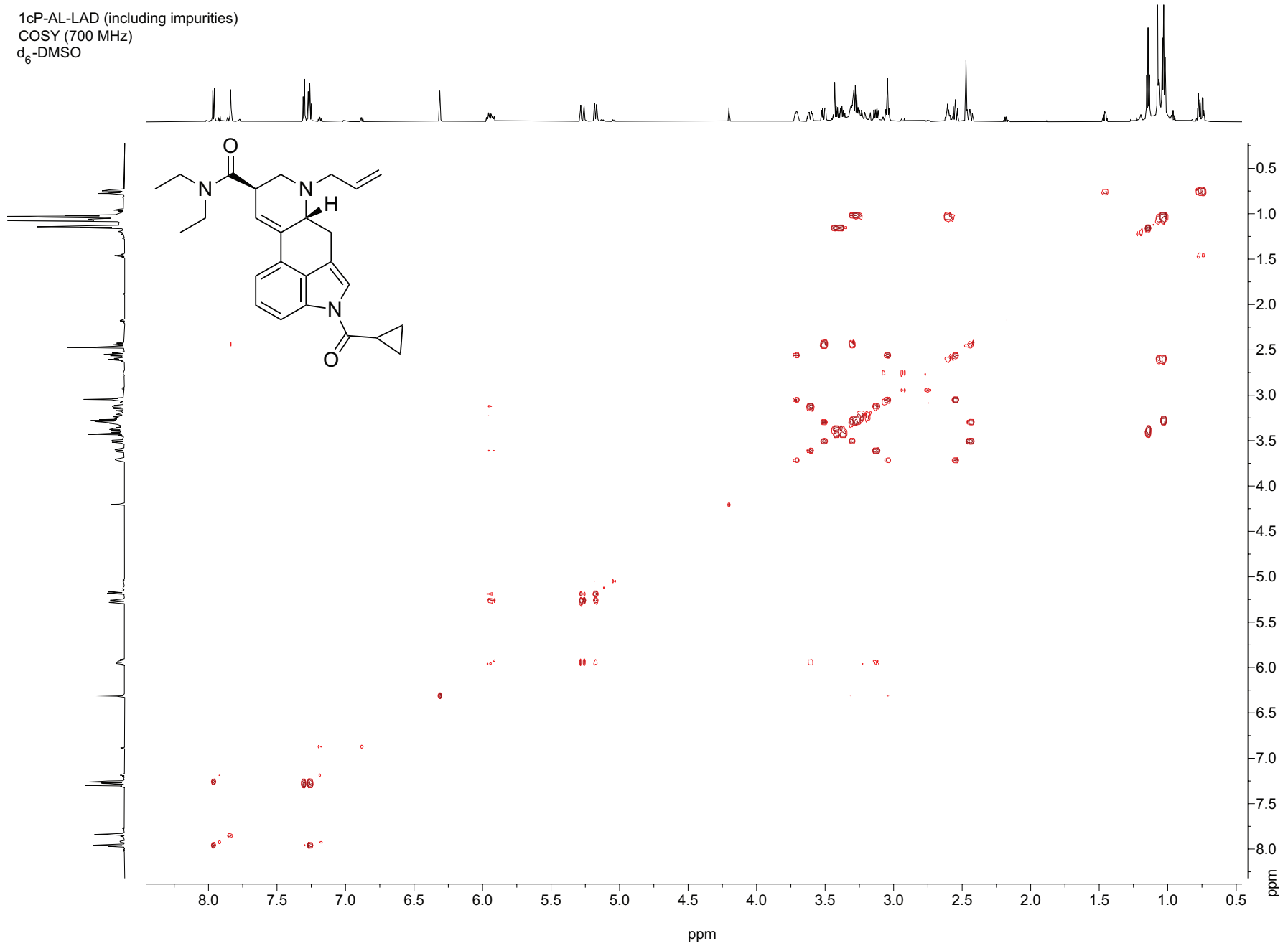
UV 254 nm UV 366 nm
(Chloroform/methanol, 9/1)



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 0.0
ppm

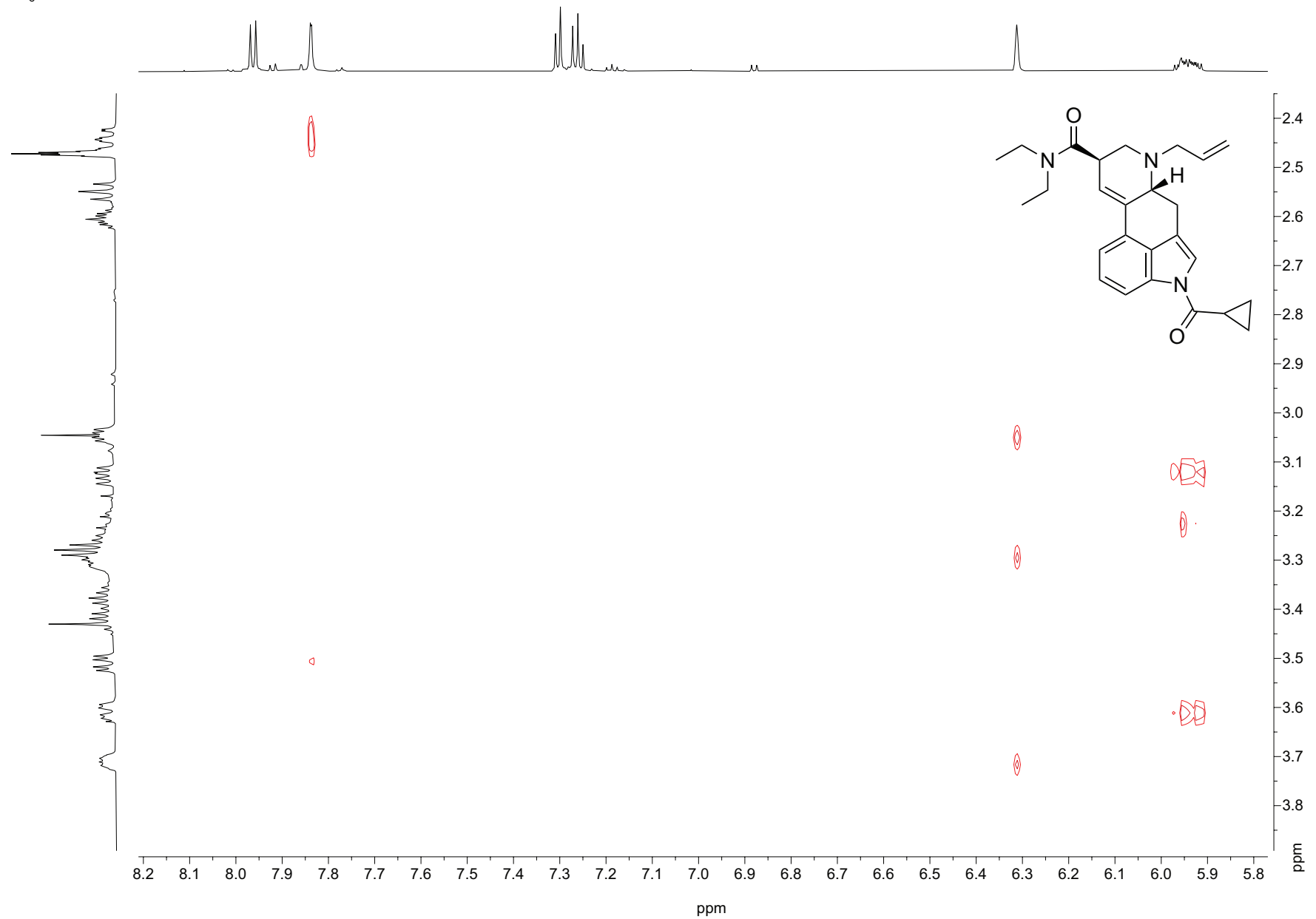
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
COSY (700 MHz)
d₆-DMSO



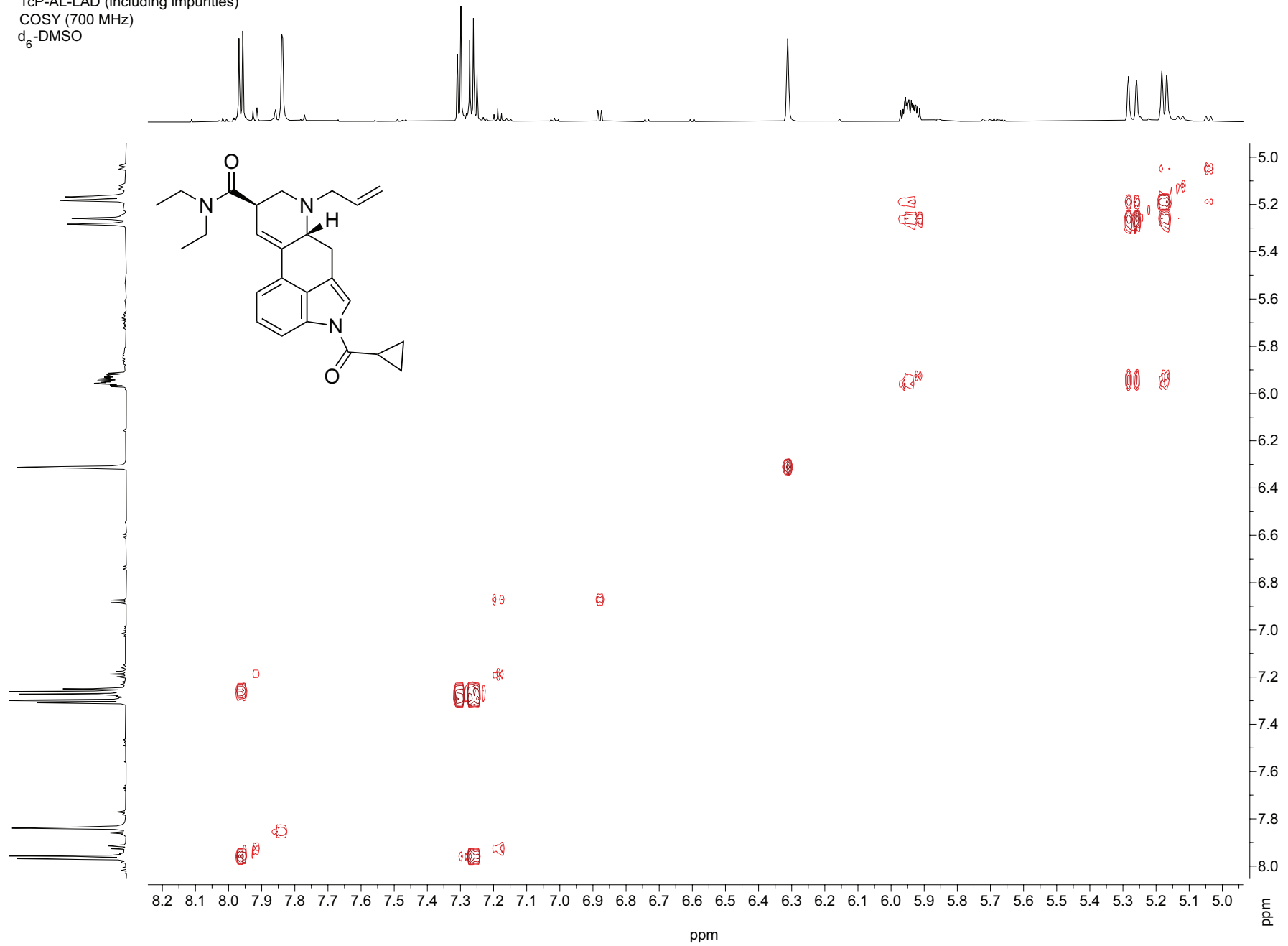
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
COSY (700 MHz)
d₆-DMSO



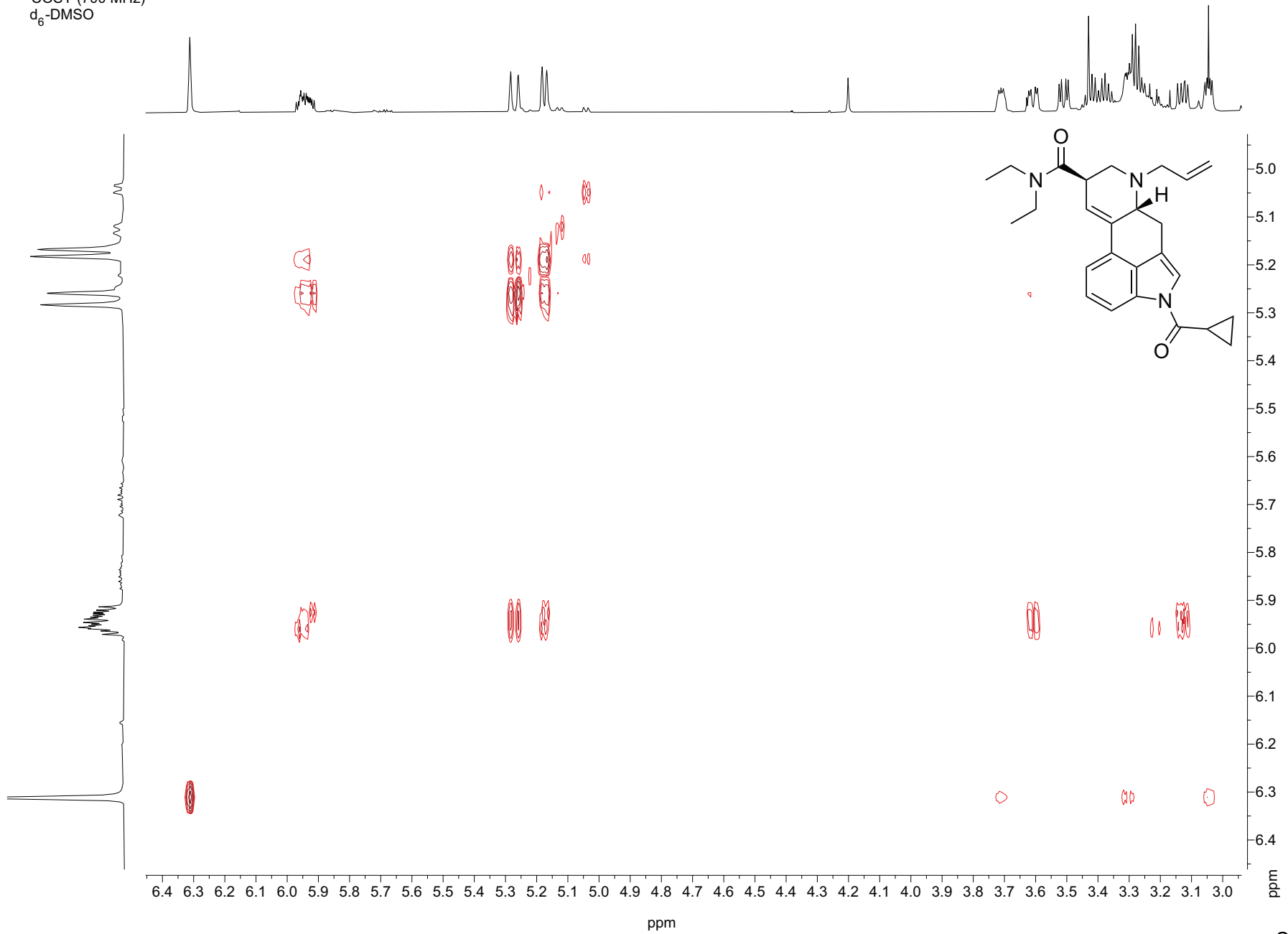
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
COSY (700 MHz)
d₆-DMSO



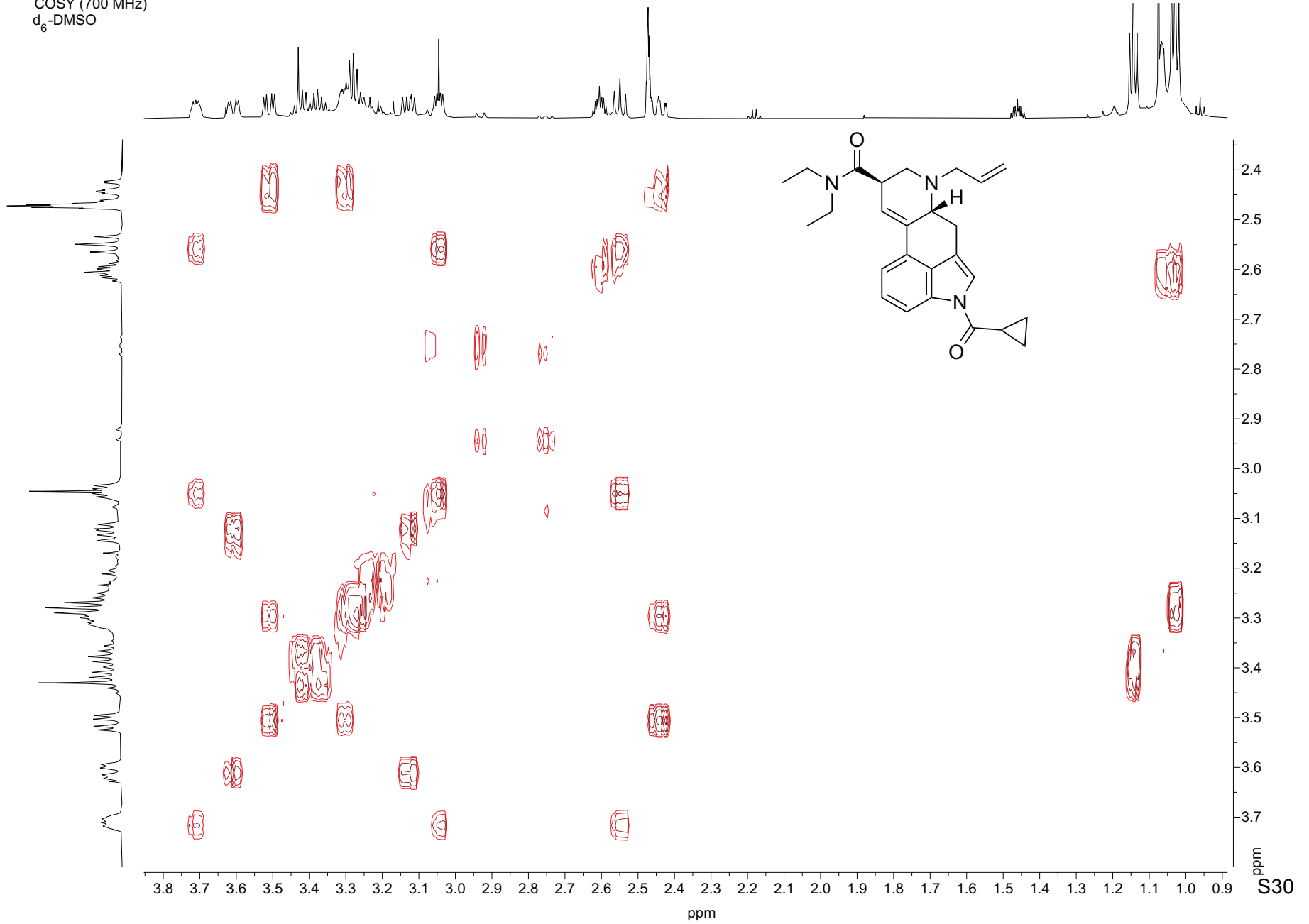
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
COSY (700 MHz)
d₆-DMSO



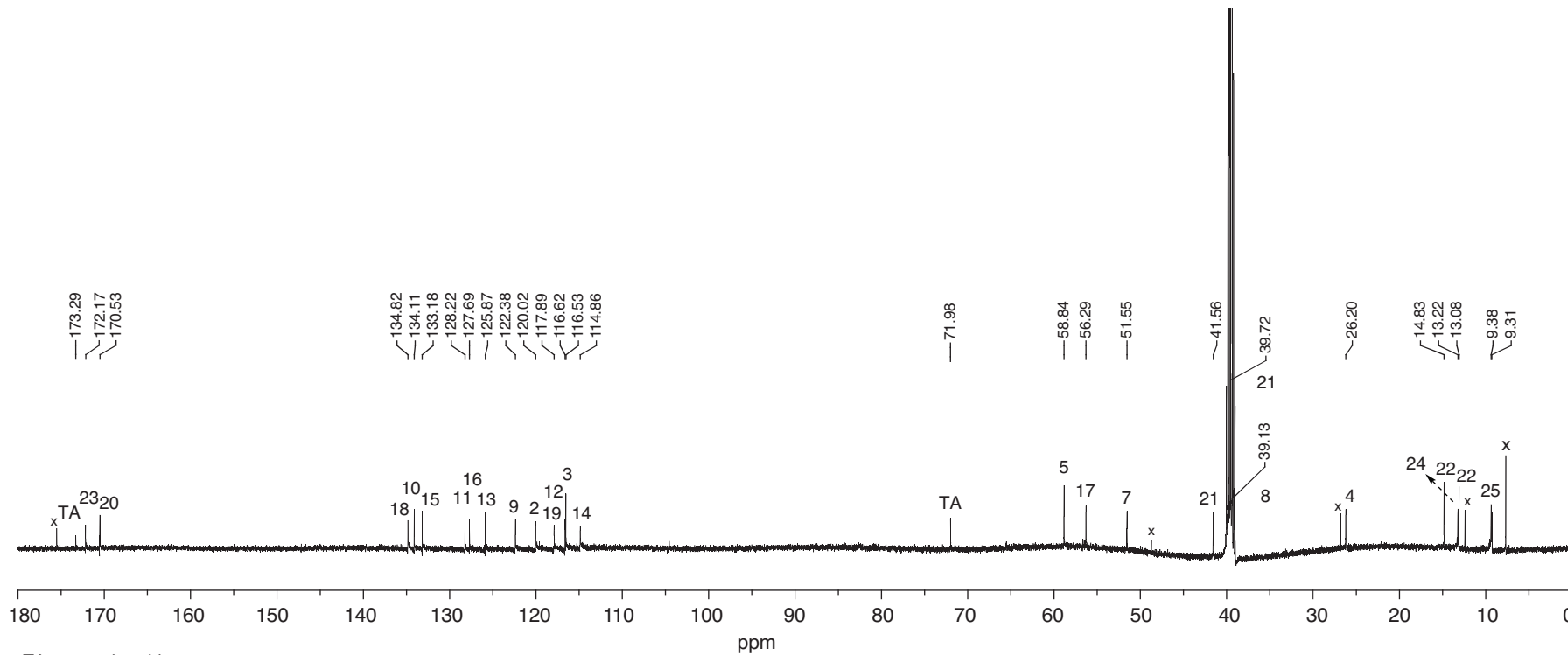
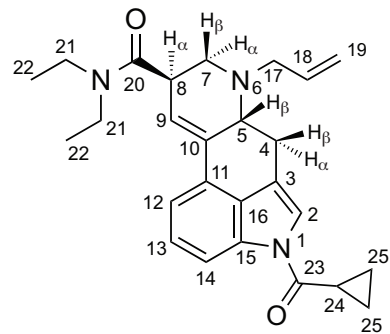
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
COSY (700 MHz)
d₆-DMSO



Supporting Information – Drug Testing and Analysis

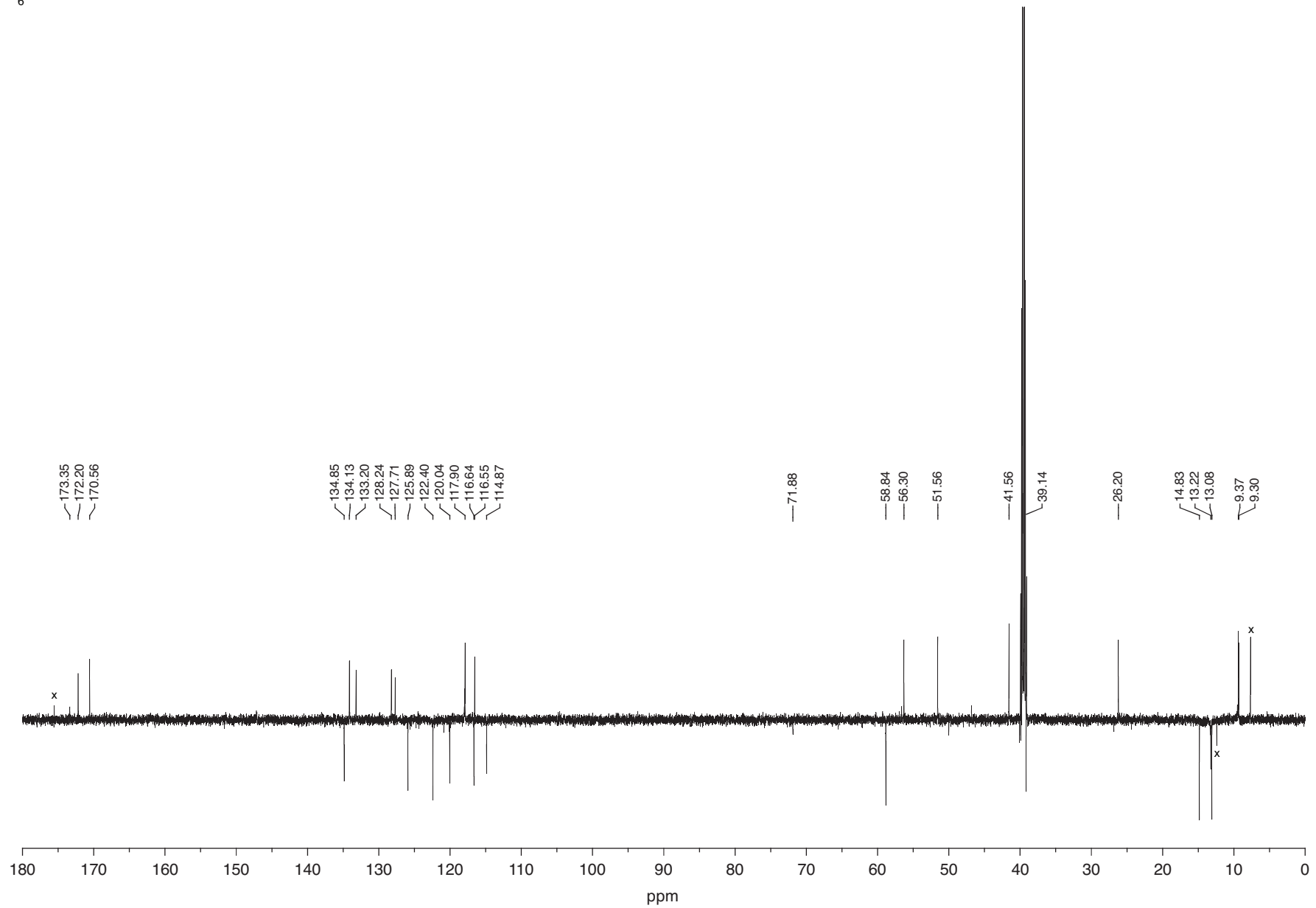
1cP-AL-LAD (including impurities)
¹³C-NMR (175 MHz)
d₆-DMSO



TA = tartaric acid

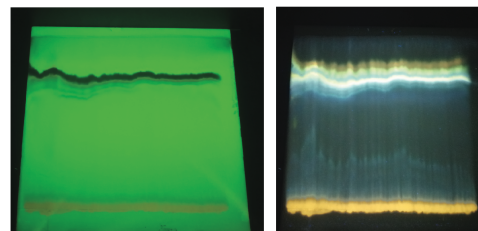
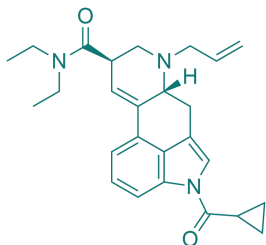
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
¹³C-NMR DEPTQ (150 MHz)
d₆-DMSO



Supporting Information – Drug Testing and Analysis

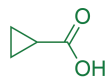
1cP-AL-LAD before prep TLC
¹³C-NMR (150 MHz, DMSO-d₆)



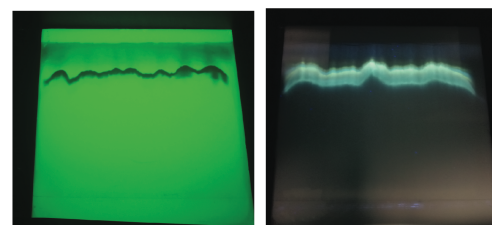
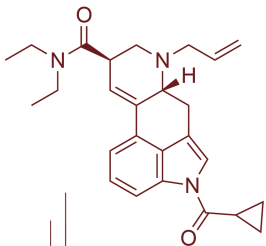
UV 254 nm UV 366 nm
 (Chloroform/methanol, 9/1)



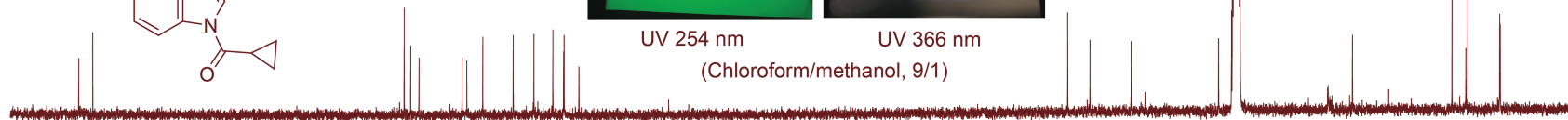
Cyclopropanecarboxylic acid
¹³C-NMR (150 MHz, DMSO-d₆)



1cP-AL-LAD after prep TLC
¹³C-NMR (150 MHz, DMSO-d₆)



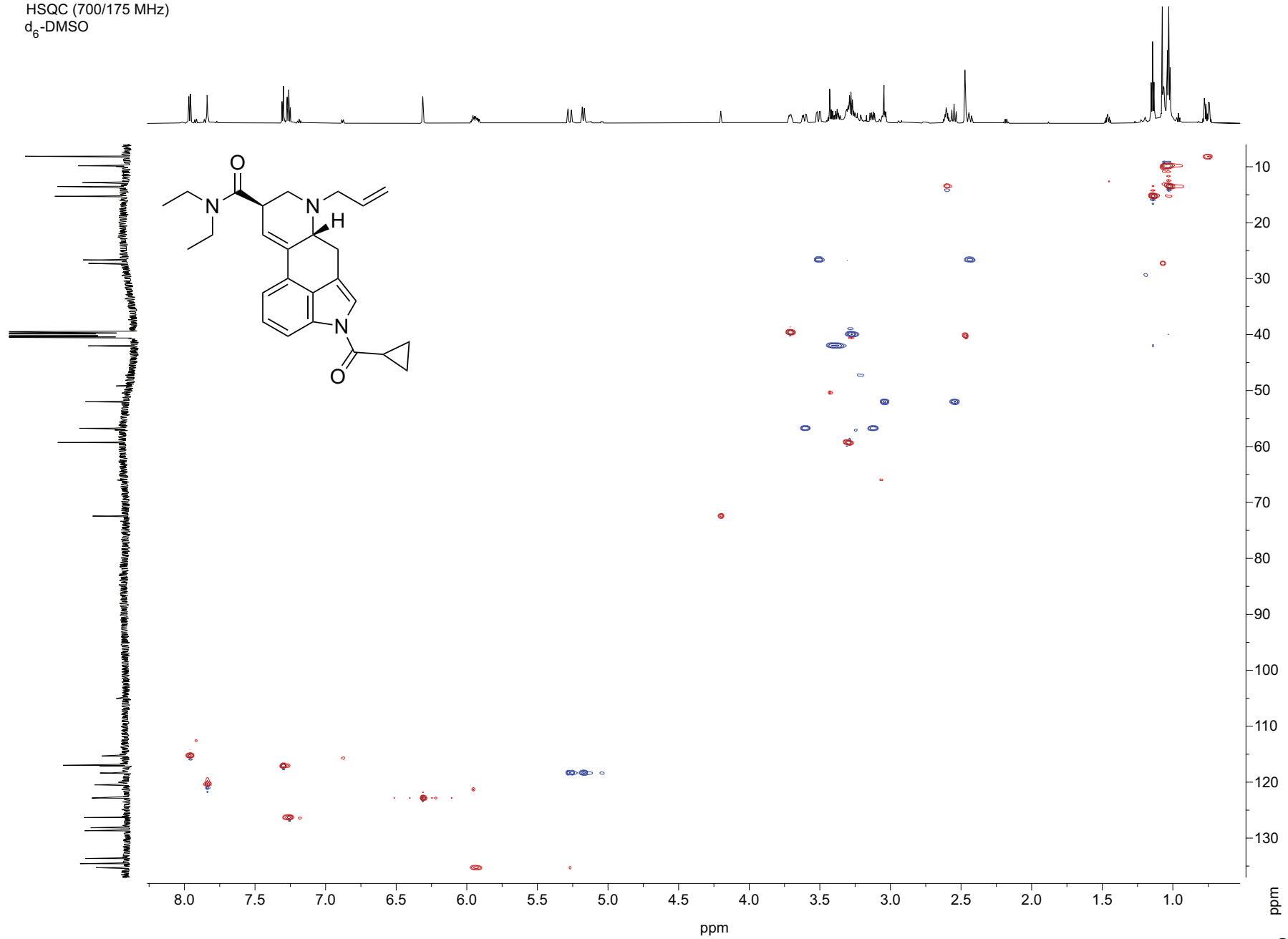
UV 254 nm UV 366 nm
 (Chloroform/methanol, 9/1)



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 ppm

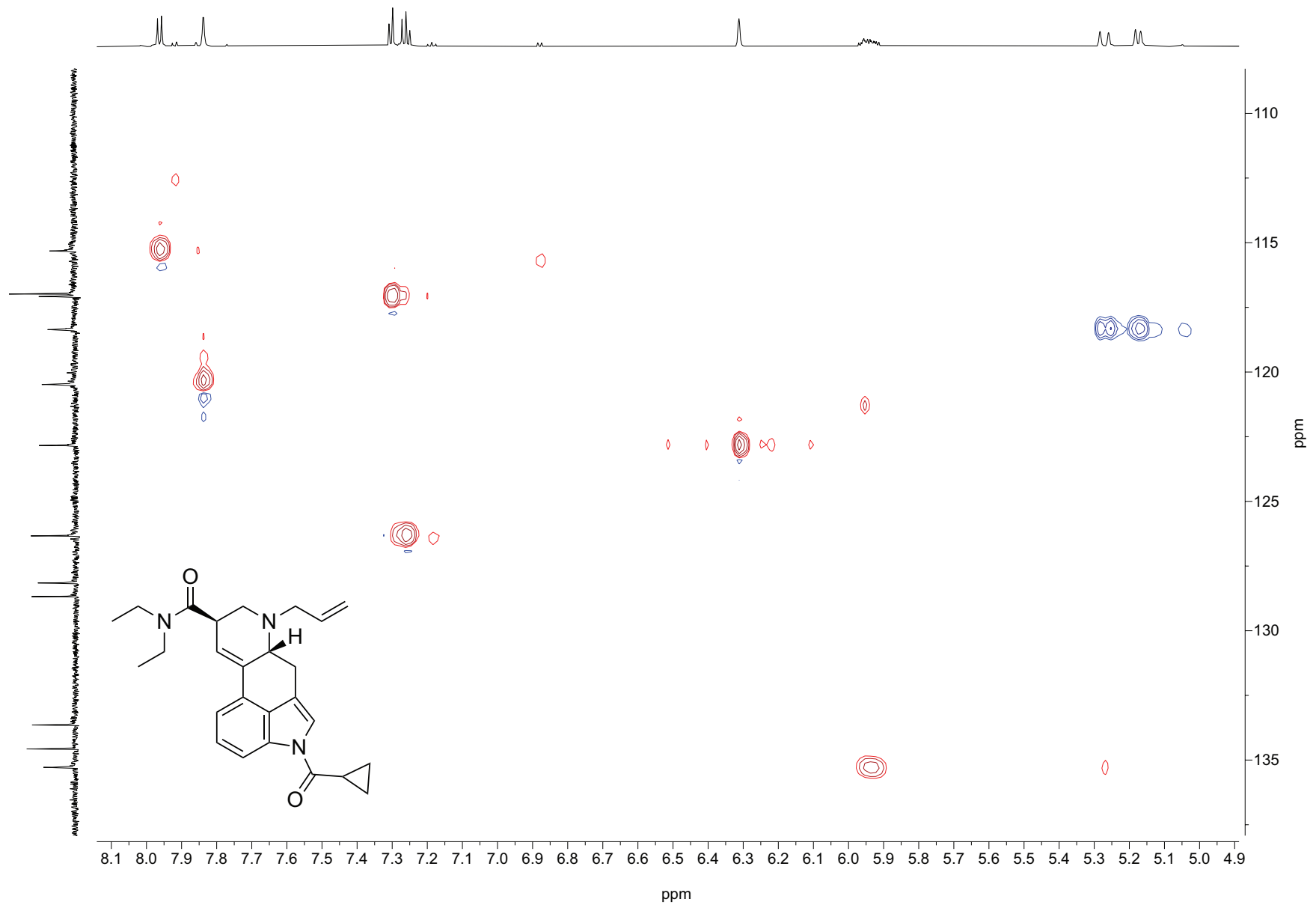
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
HSQC (700/175 MHz)
d₆-DMSO



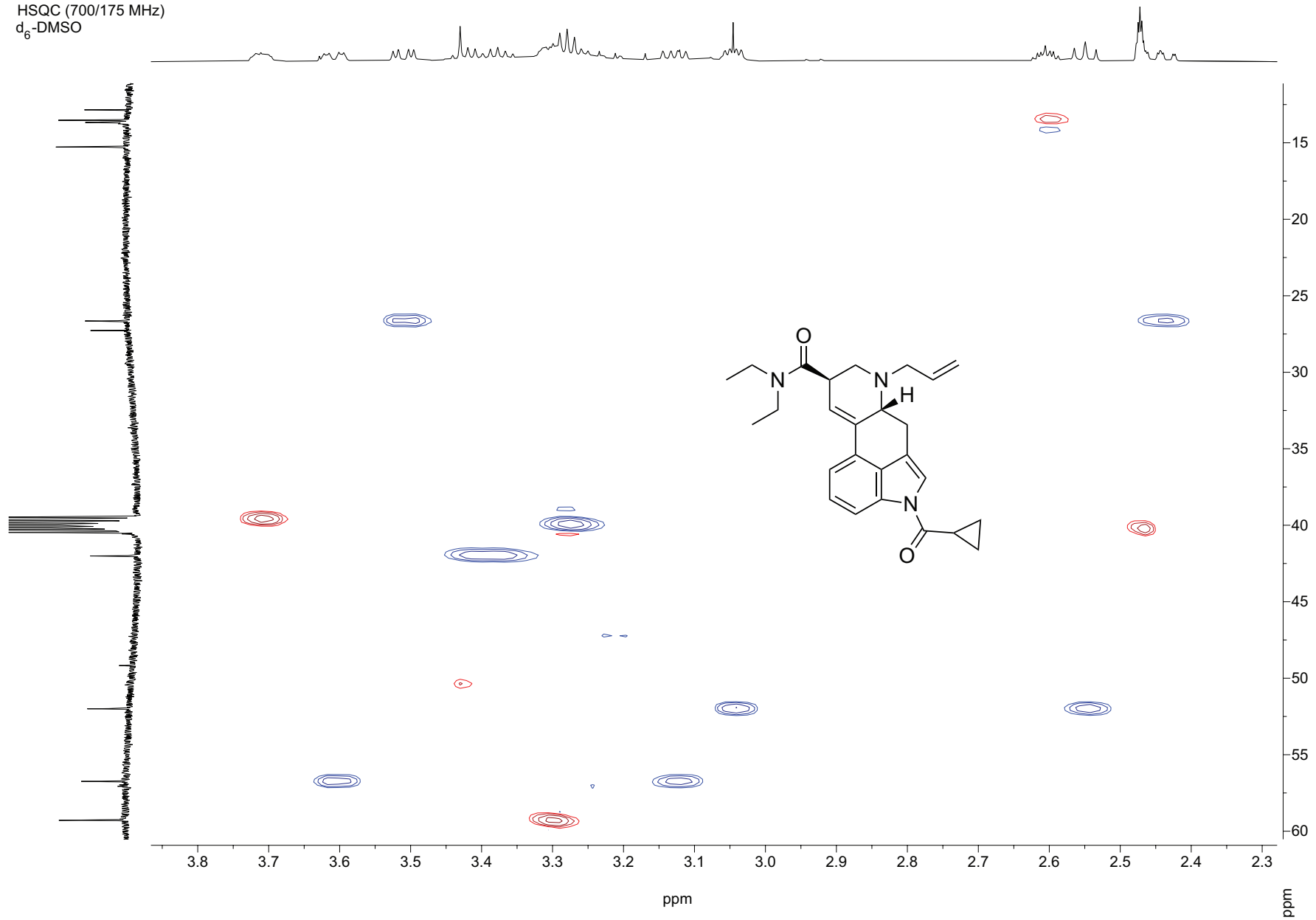
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
HSQC (700/175 MHz)
d₆-DMSO



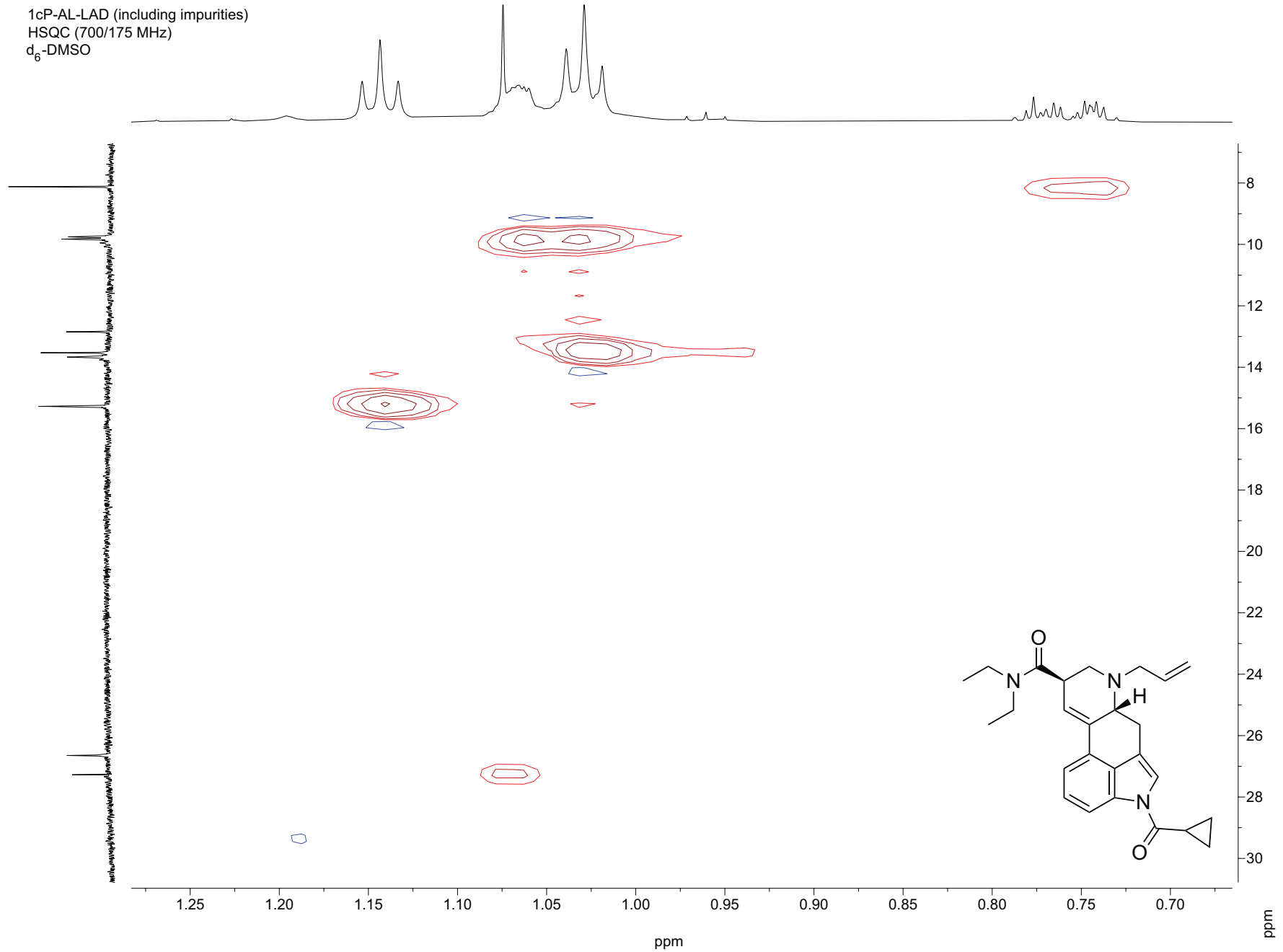
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
HSQC (700/175 MHz)
d₆-DMSO



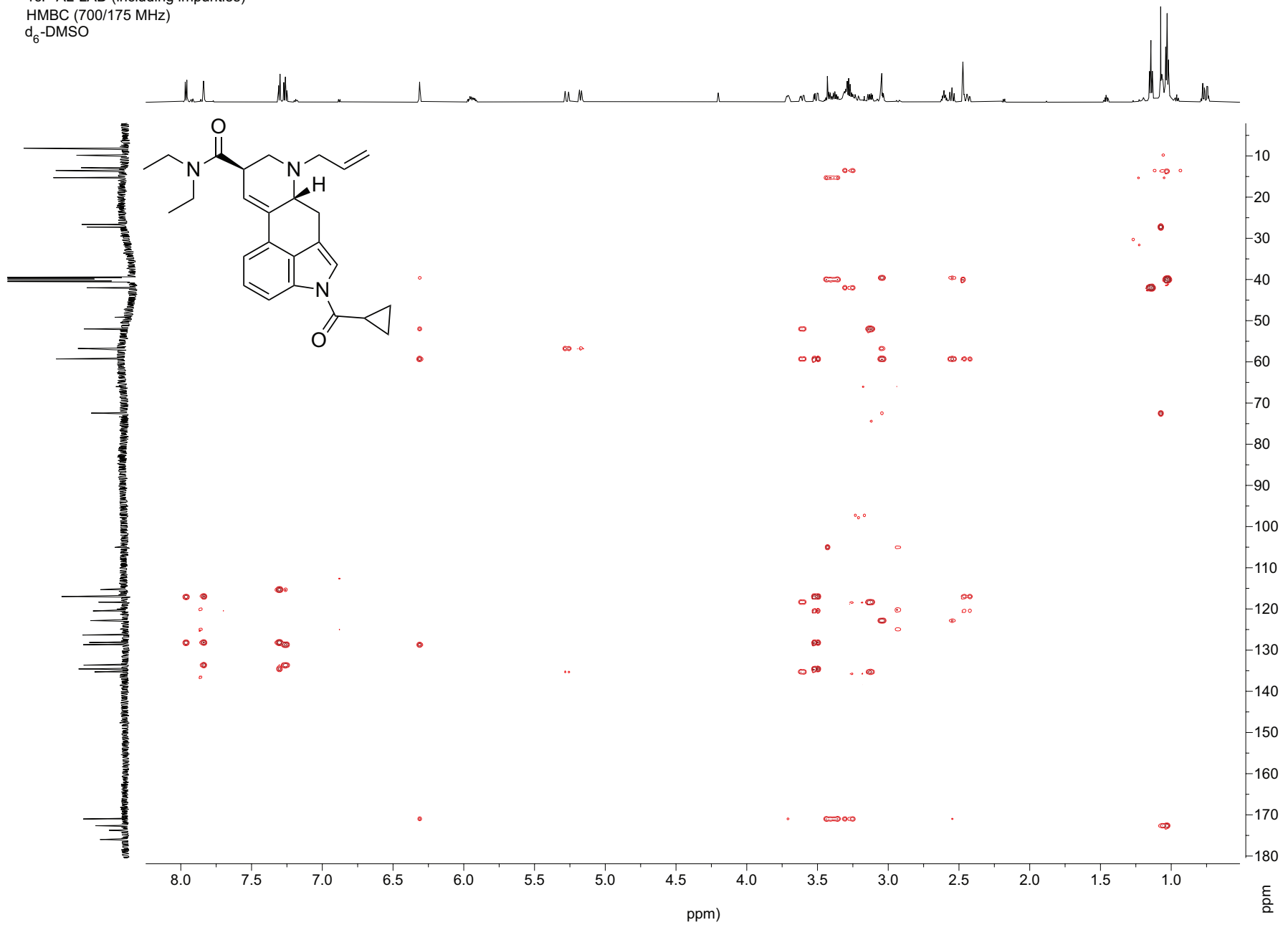
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
HSQC (700/175 MHz)
d₆-DMSO



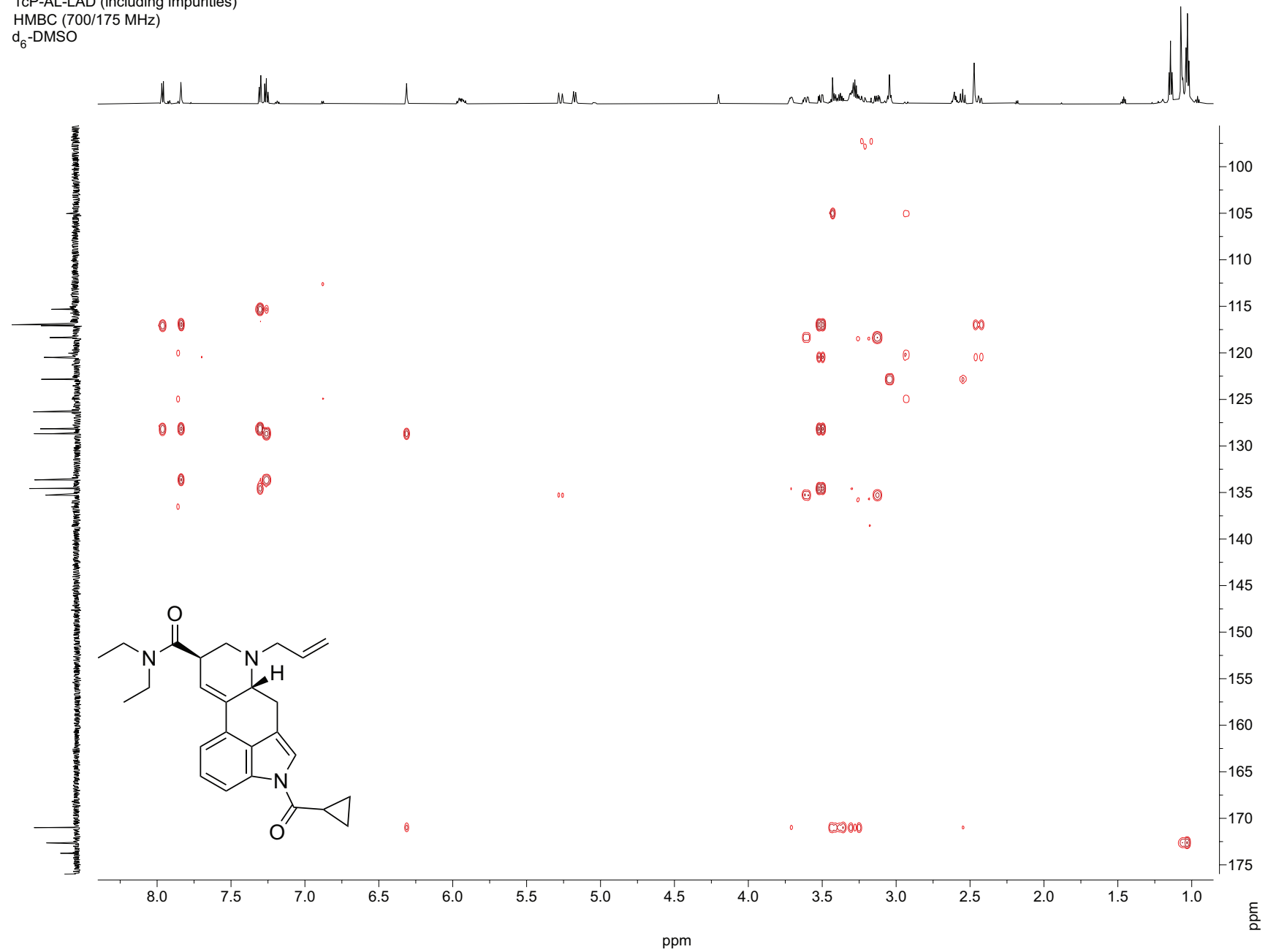
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
HMBC (700/175 MHz)
d₆-DMSO



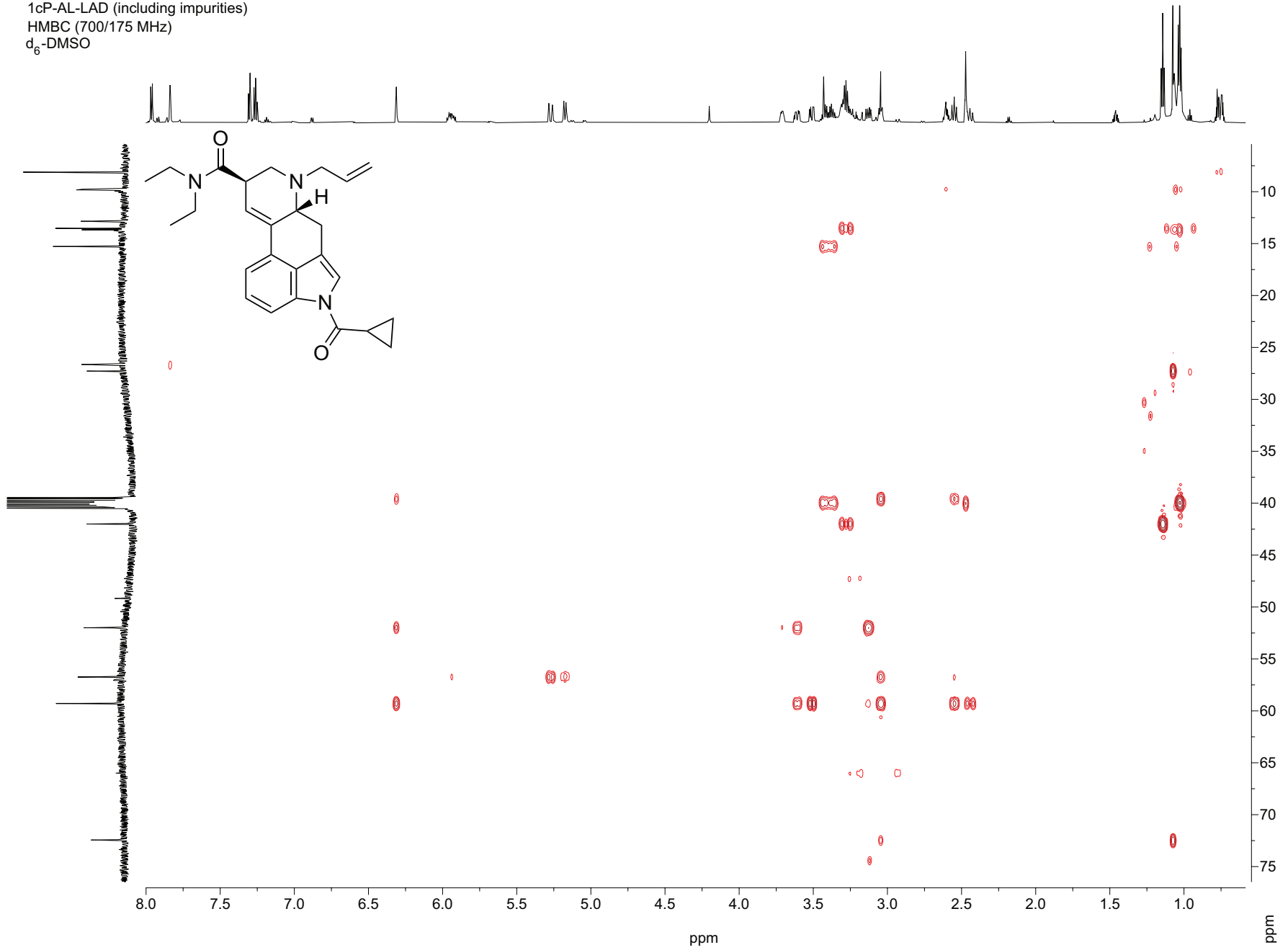
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
HMBC (700/175 MHz)
d₆-DMSO



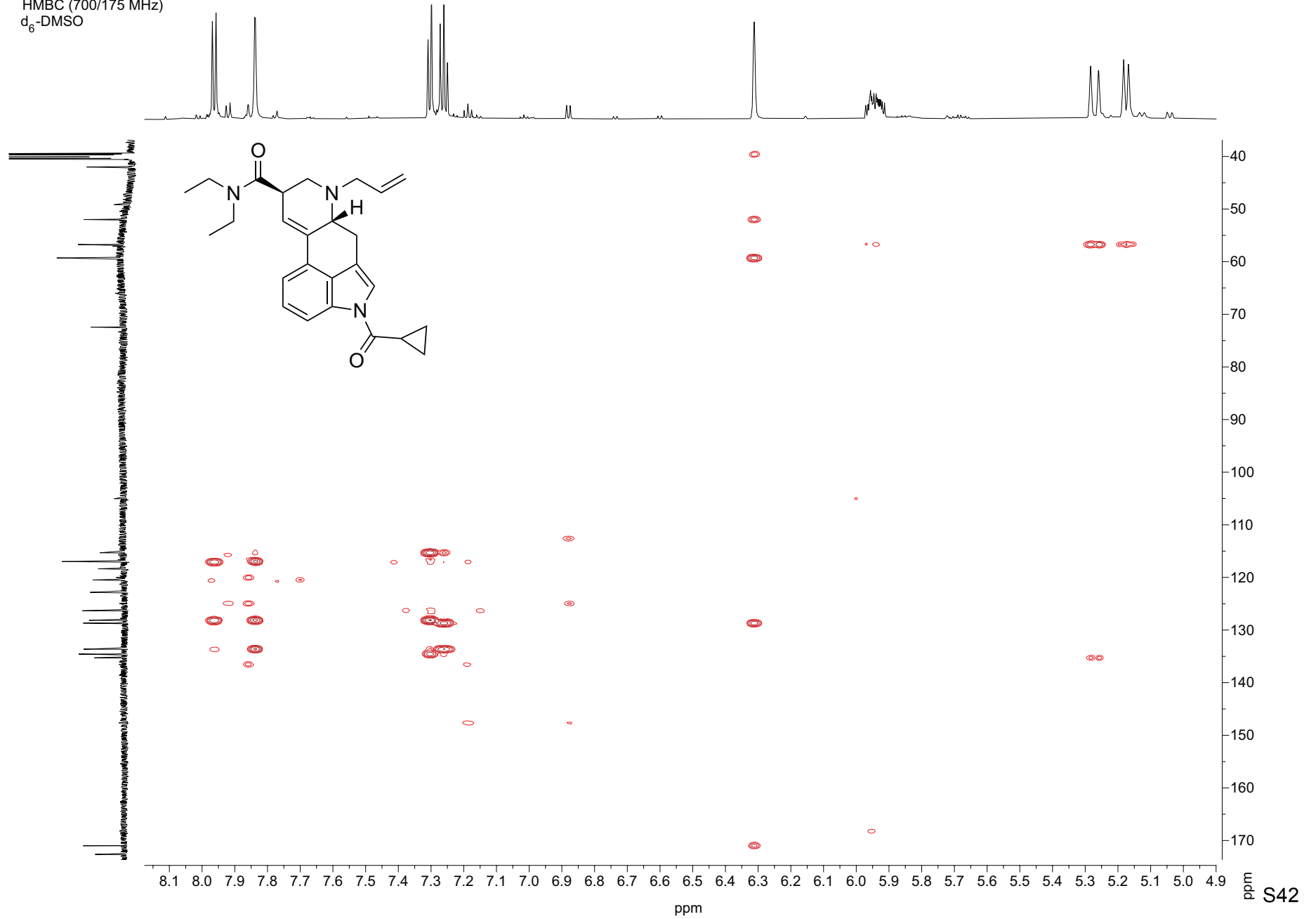
Supporting Information – Drug Testing and Analysis

1cP-AL-LAD (including impurities)
HMBC (700/175 MHz)
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