

Methyl 3 α ,12 α -dihydroxy-5 β -cholan-24-oate (11)

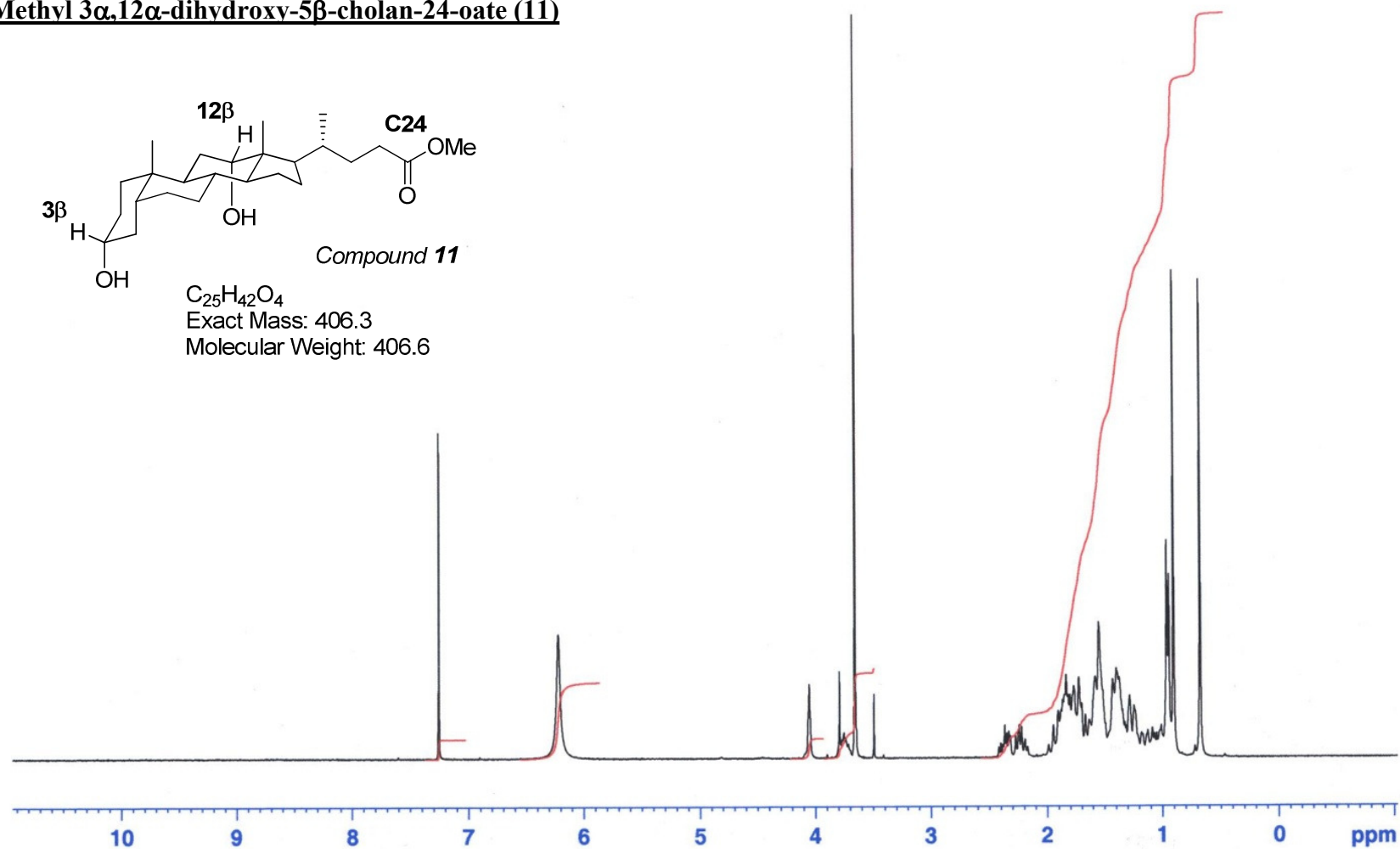


Figure S1. ¹H-NMR of compound 11.

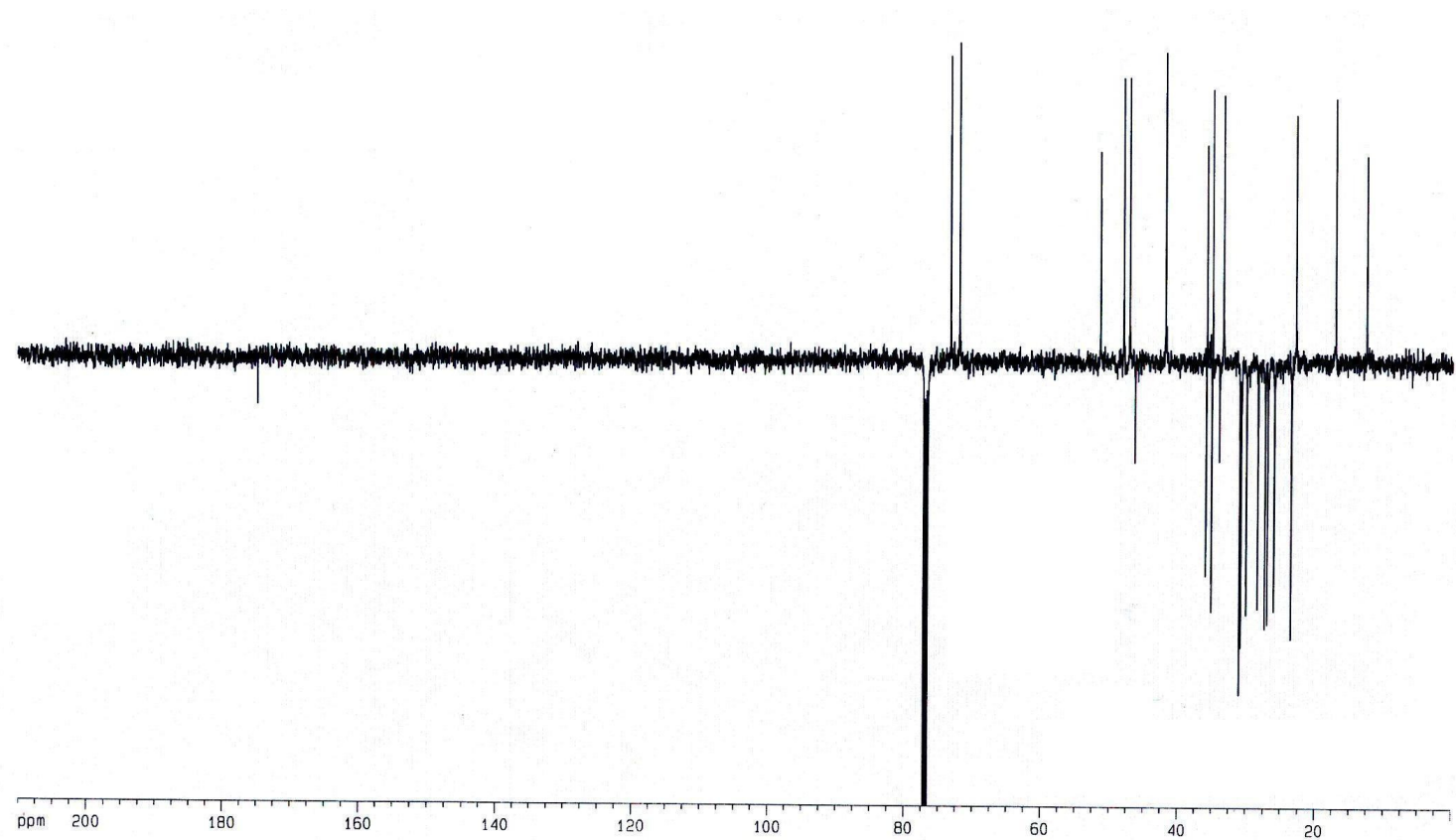


Figure S2. ^{13}C -NMR (APT) of compound **11**.

S#: 40 RT: 1.09 AV: 1 NL: 5.28E7
F: + c Full ms [150.00 - 2000.00]

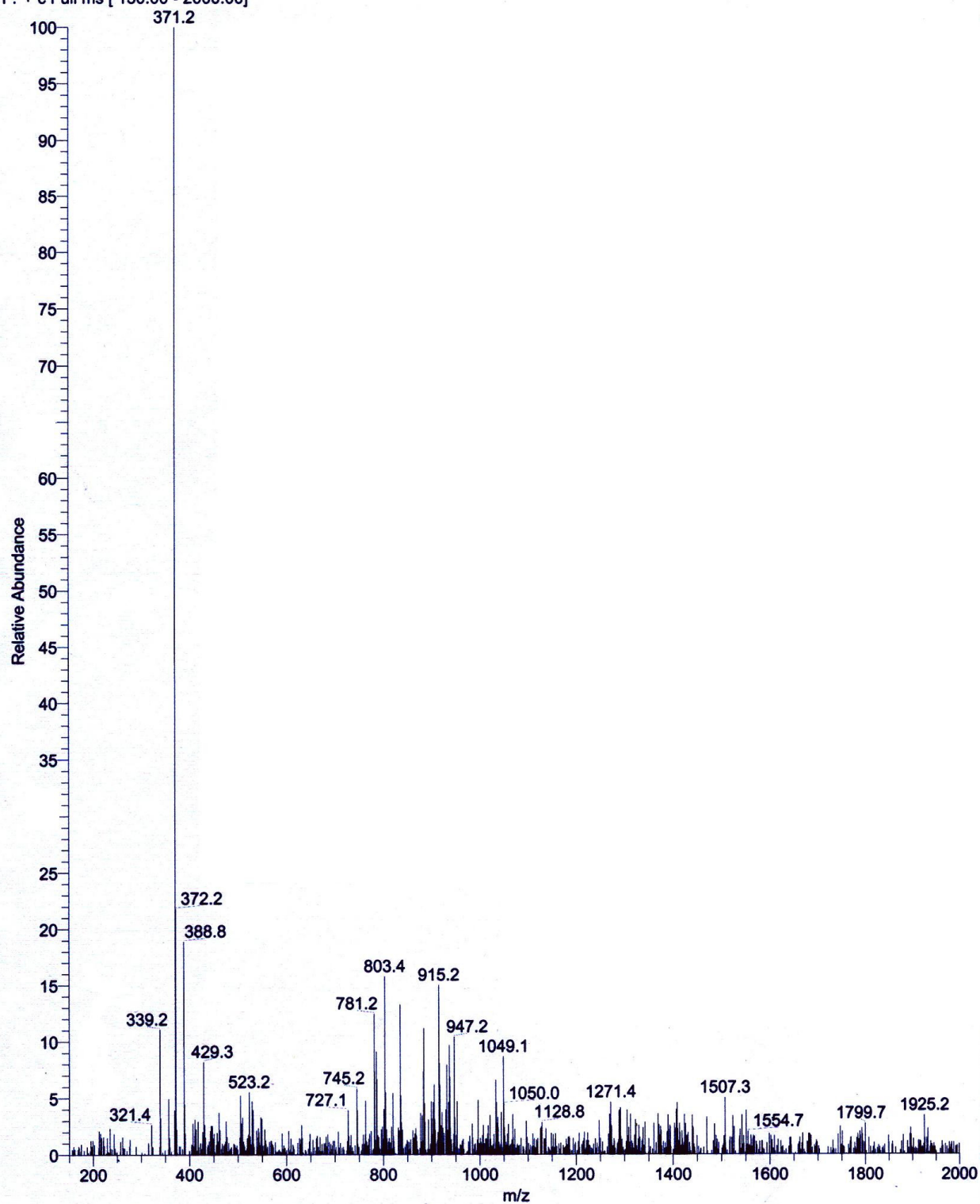


Figure S3. ESI-MS of compound 11.

Methyl 3 α -azido,12 α -hydroxy-5 β -cholan-24-oate (12)

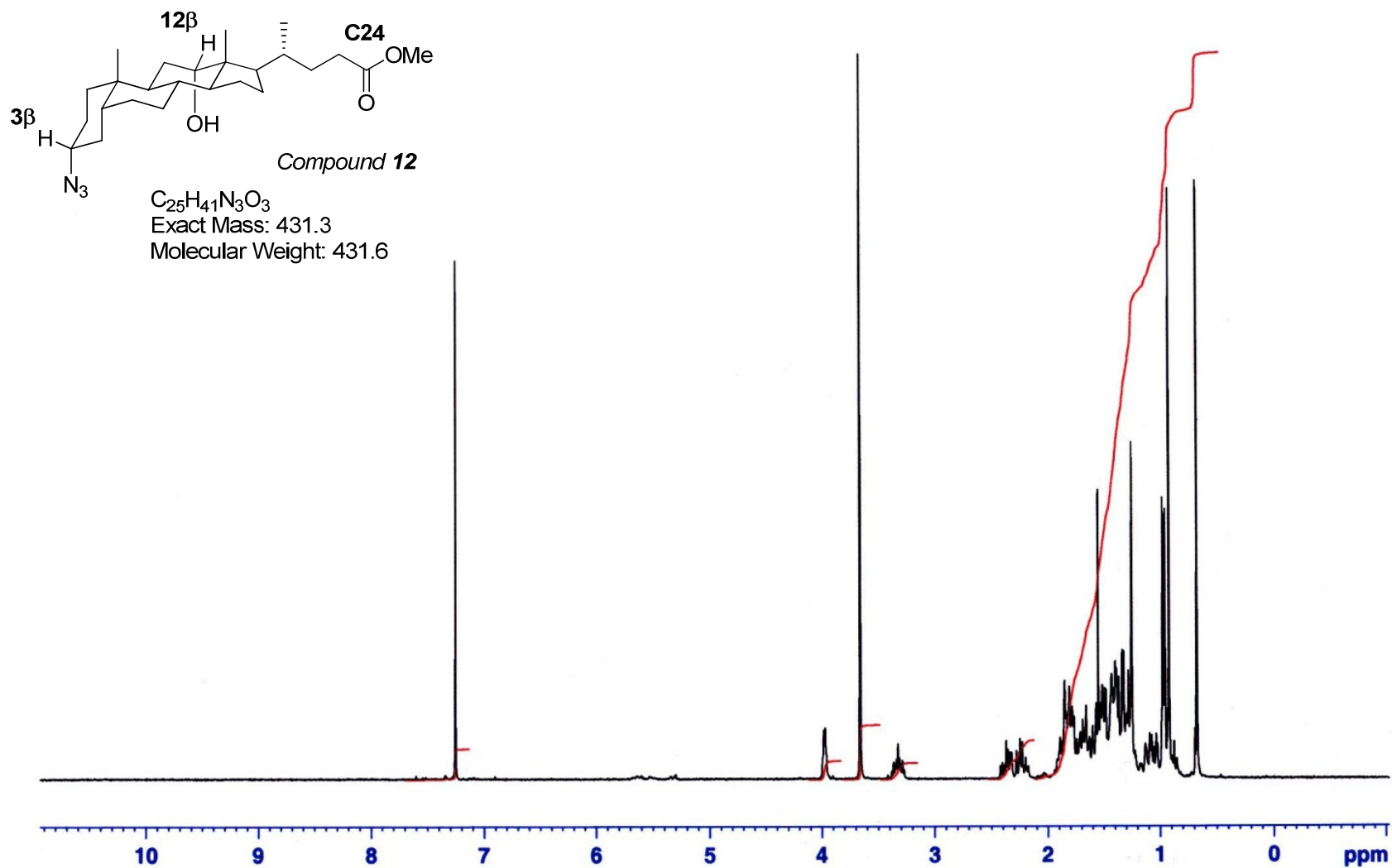


Figure S4. ¹H-NMR of compound 12.

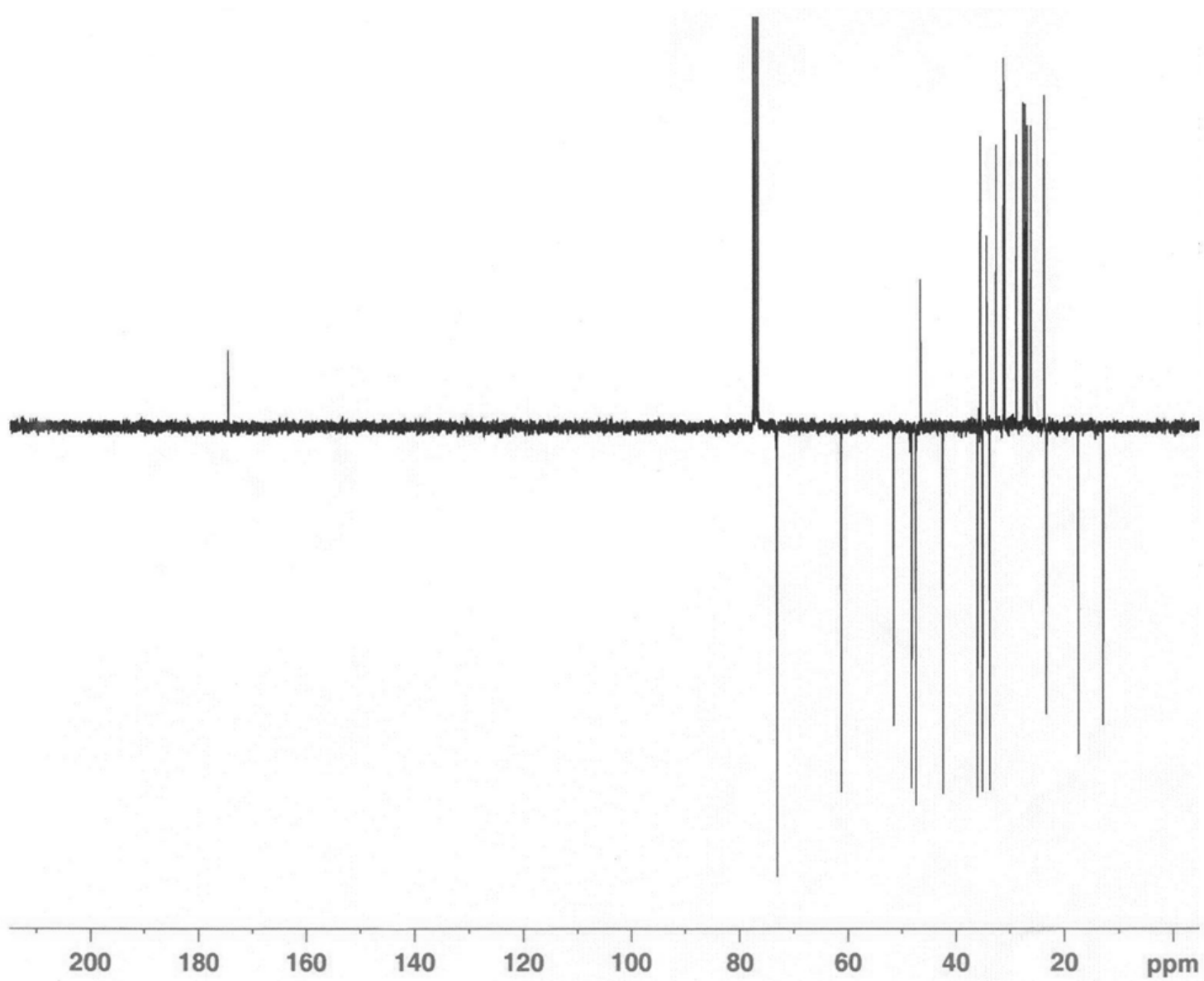


Figure S5. ^{13}C -NMR (APT) of compound **12**.

S#: 7-17 RT: 0.13-0.33 AV: 11 SB: 5 0.02-0.10 NL: 1.97E7
T: + c sid Full ms [150.00 - 2000.00]

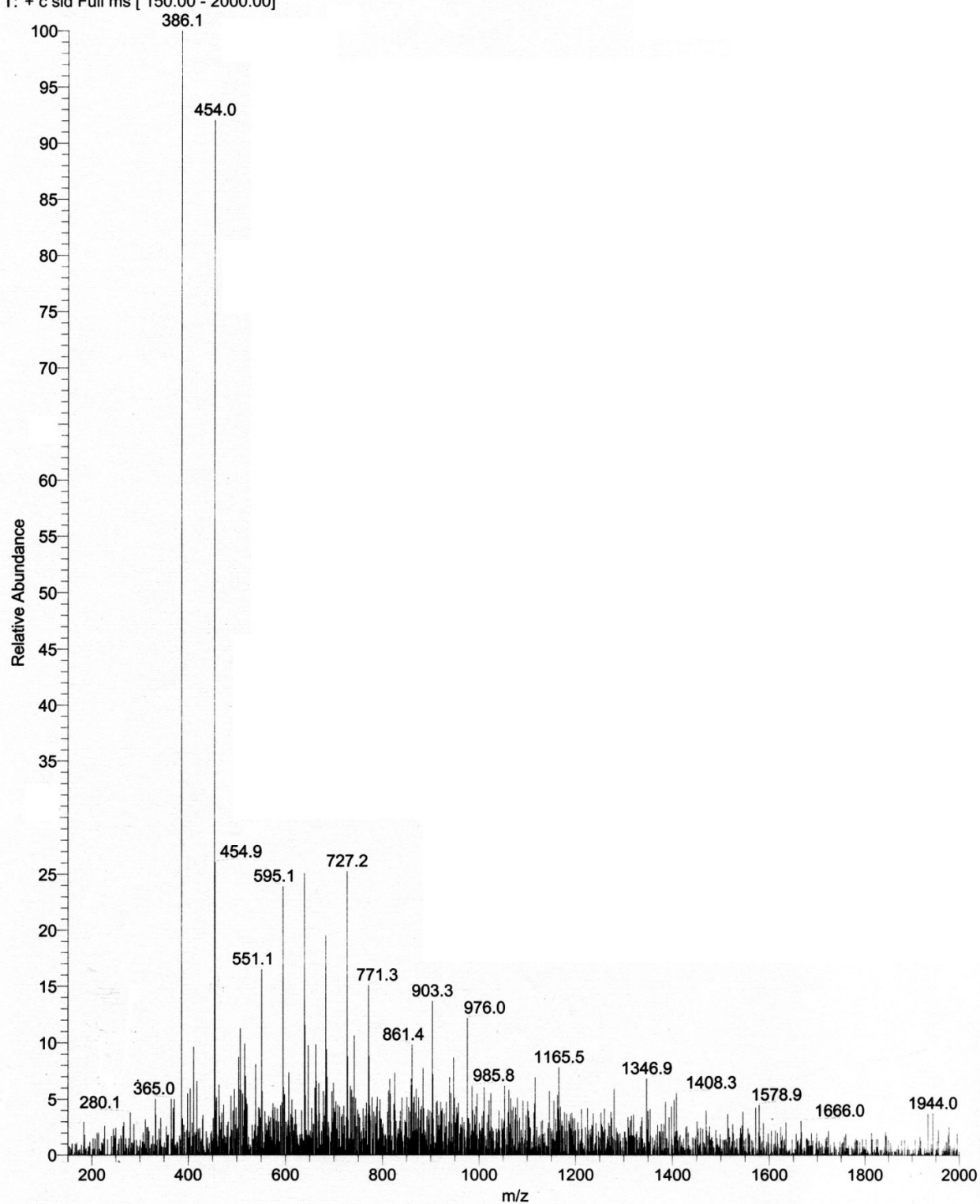


Figure S6. ESI-MS of compound 12.

3 α -Azido,12 α -hydroxy-5 β -cholan-24-oic acid (13)

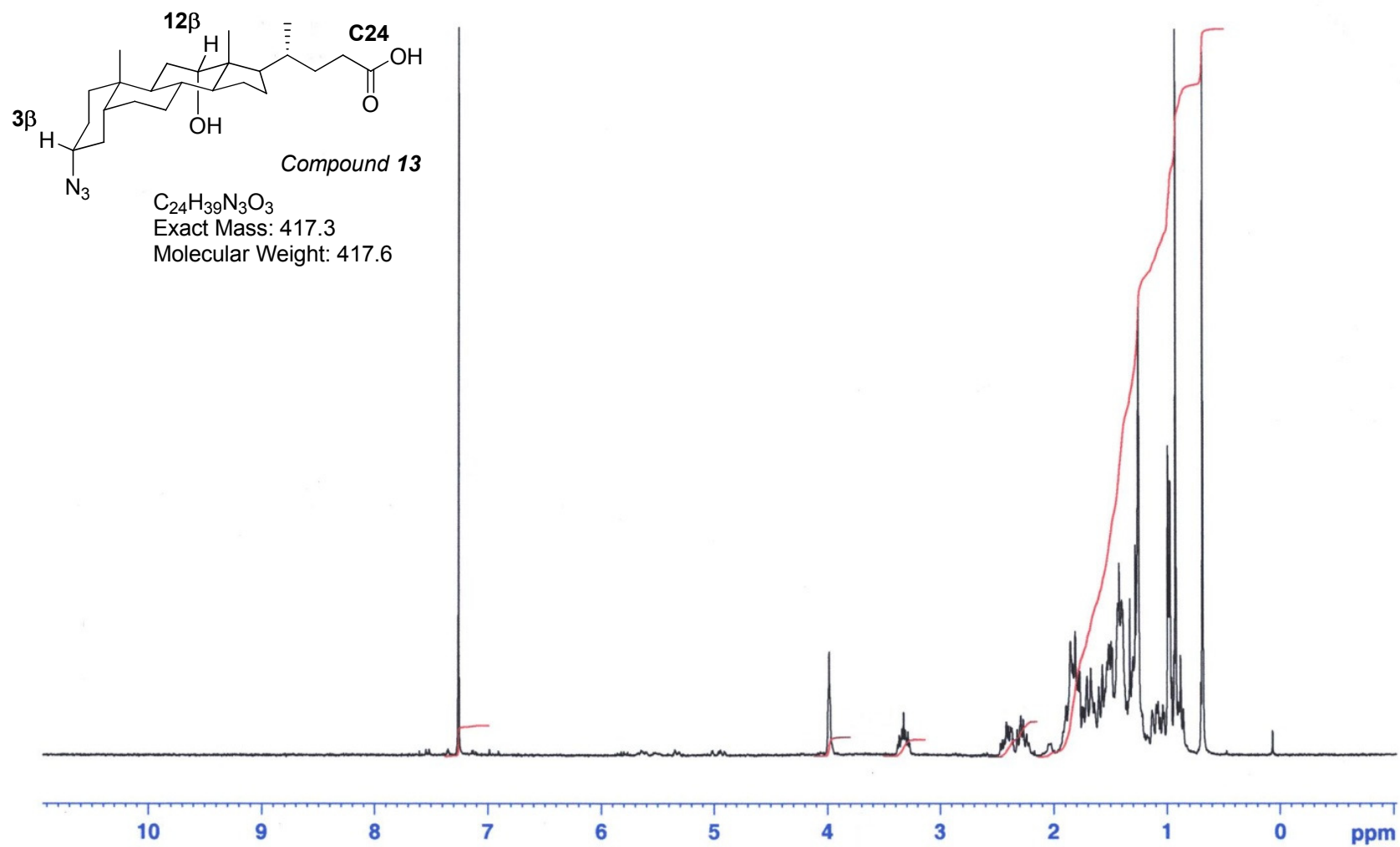


Figure S7. ¹H-NMR of compound 13.

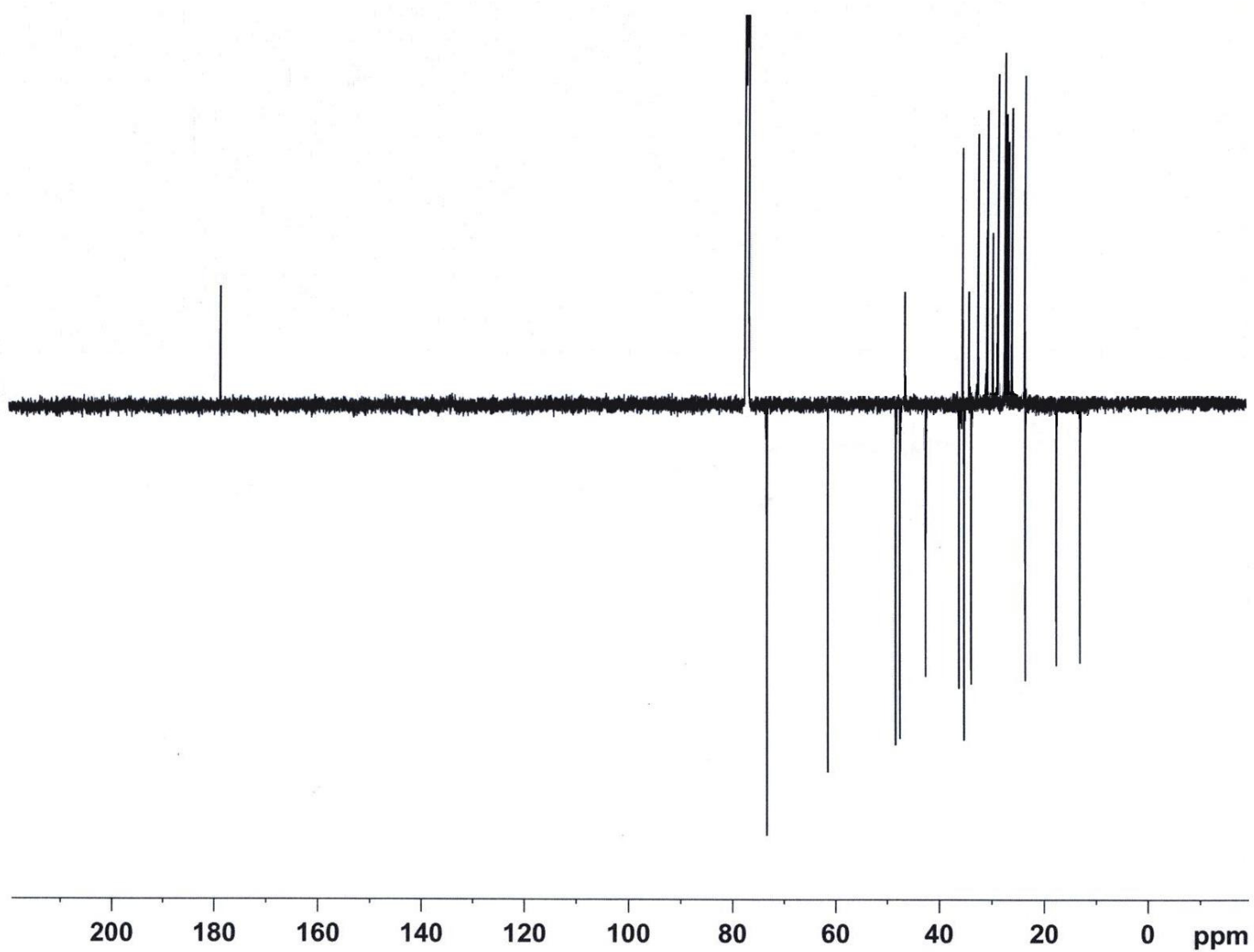


Figure S8. ^{13}C -NMR (APT) of compound **13**.

S#: 17-40 RT: 0.53-1.18 AV: 24 NL: 1.26E7
F: - c Full ms [150.00 - 2000.00]

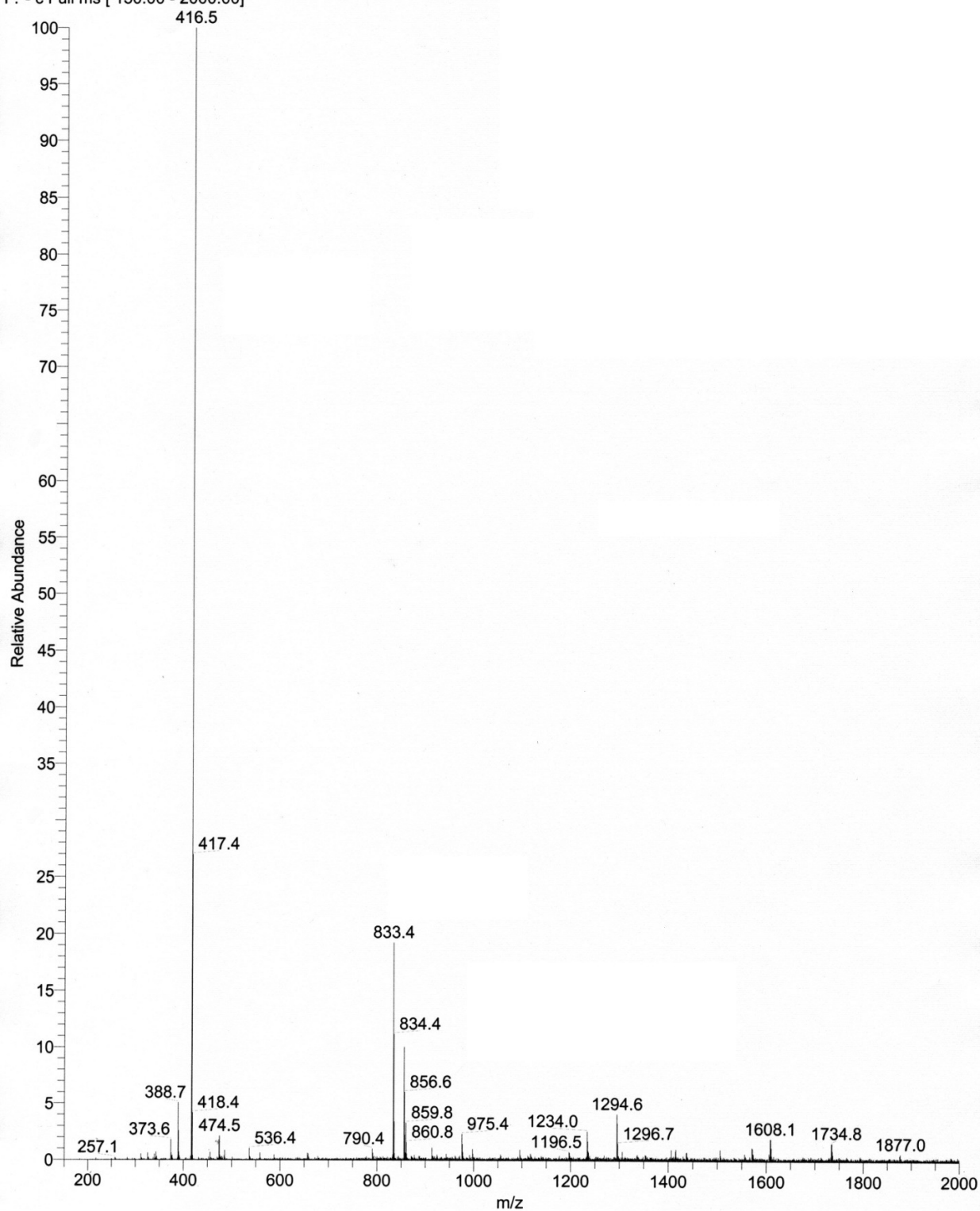


Figure S9. ESI-MS of compound **13**.

3 α -Azido,12 α -acetoxy-5 β -cholan-24-oic acid (10)

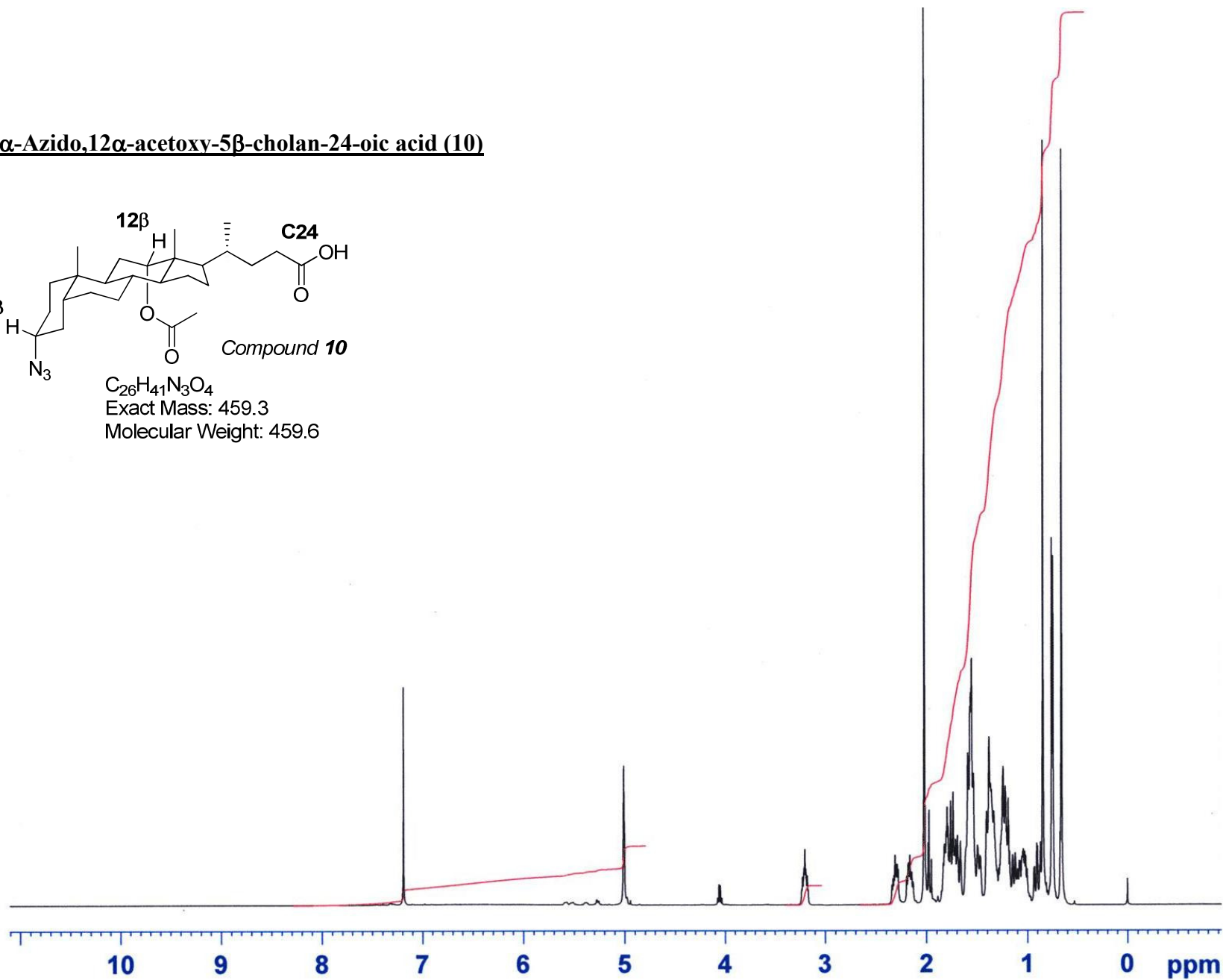
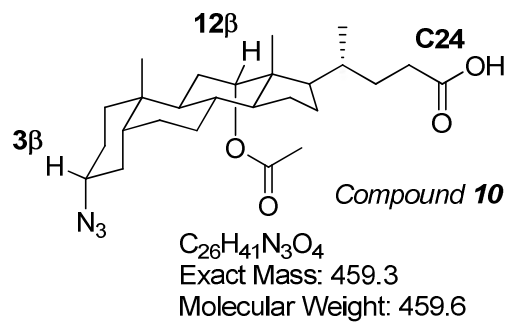


Figure S10. ^1H -NMR of compound 10.

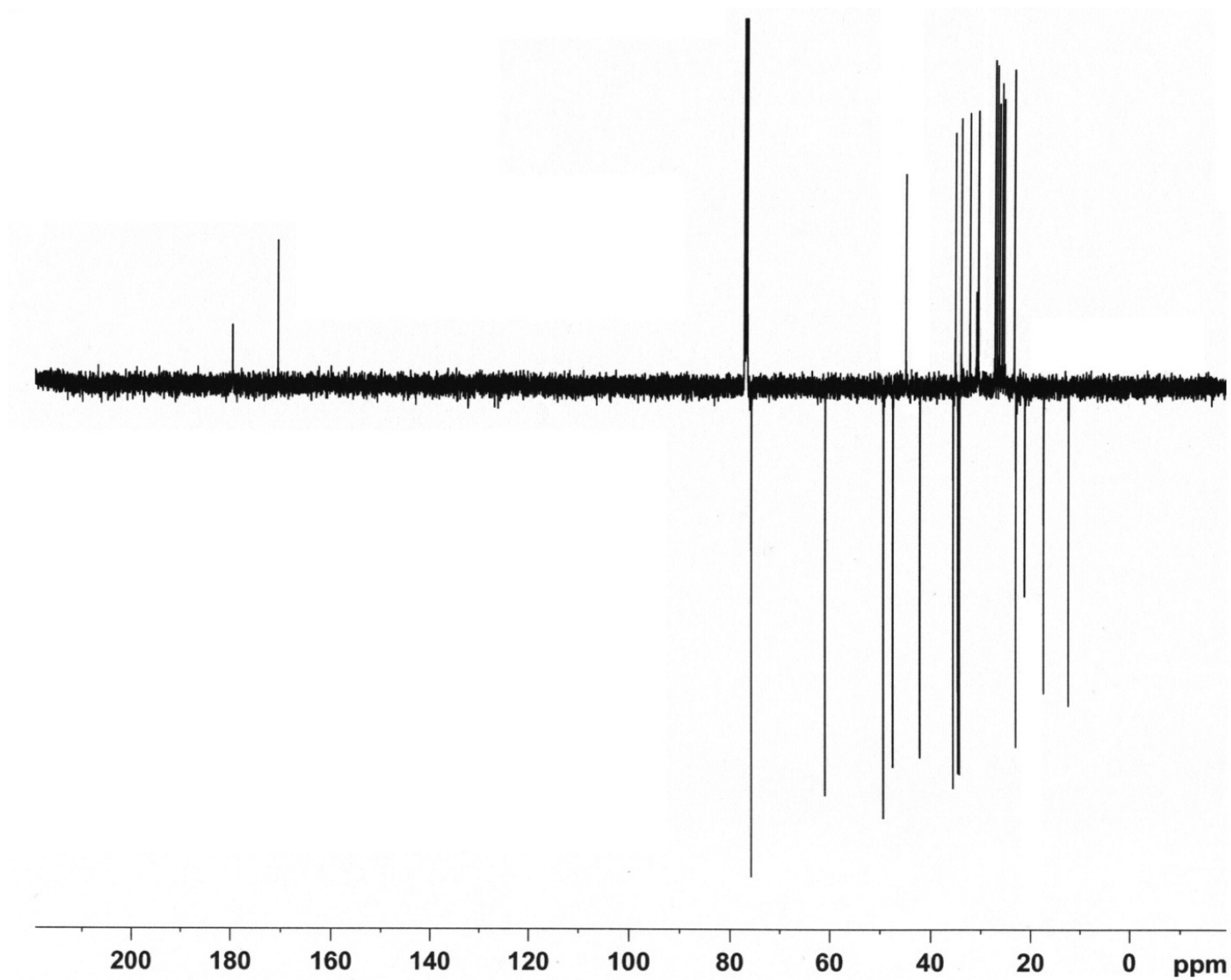


Figure S11. ^{13}C -NMR (APT) of compound **10**.

S#: 11-16 RT: 0.34-0.45 AV: 6 SB: 19 0.91-1.51 NL: 3.08E6
F: - c Full ms [150.00 - 2000.00]

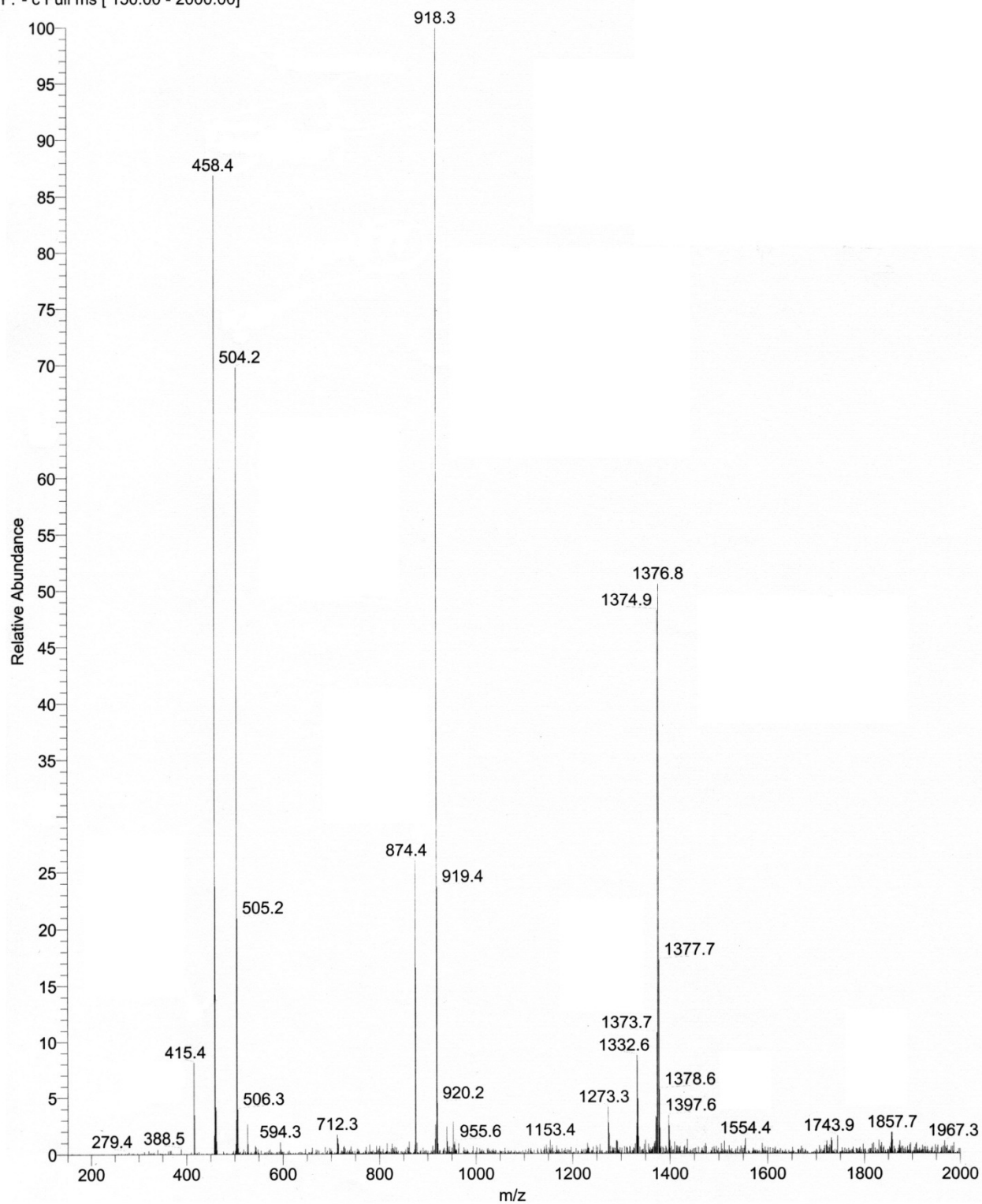


Figure S12. ESI-MS of compound 10.

N₃-C3 decorated scaffold cleaved from 14

S#: 13-21 RT: 0.34-0.53 AV: 9 SB: 12 0.01-0.31 NL: 8.85E5
T: + c Full ms [100.00 - 2000.00]

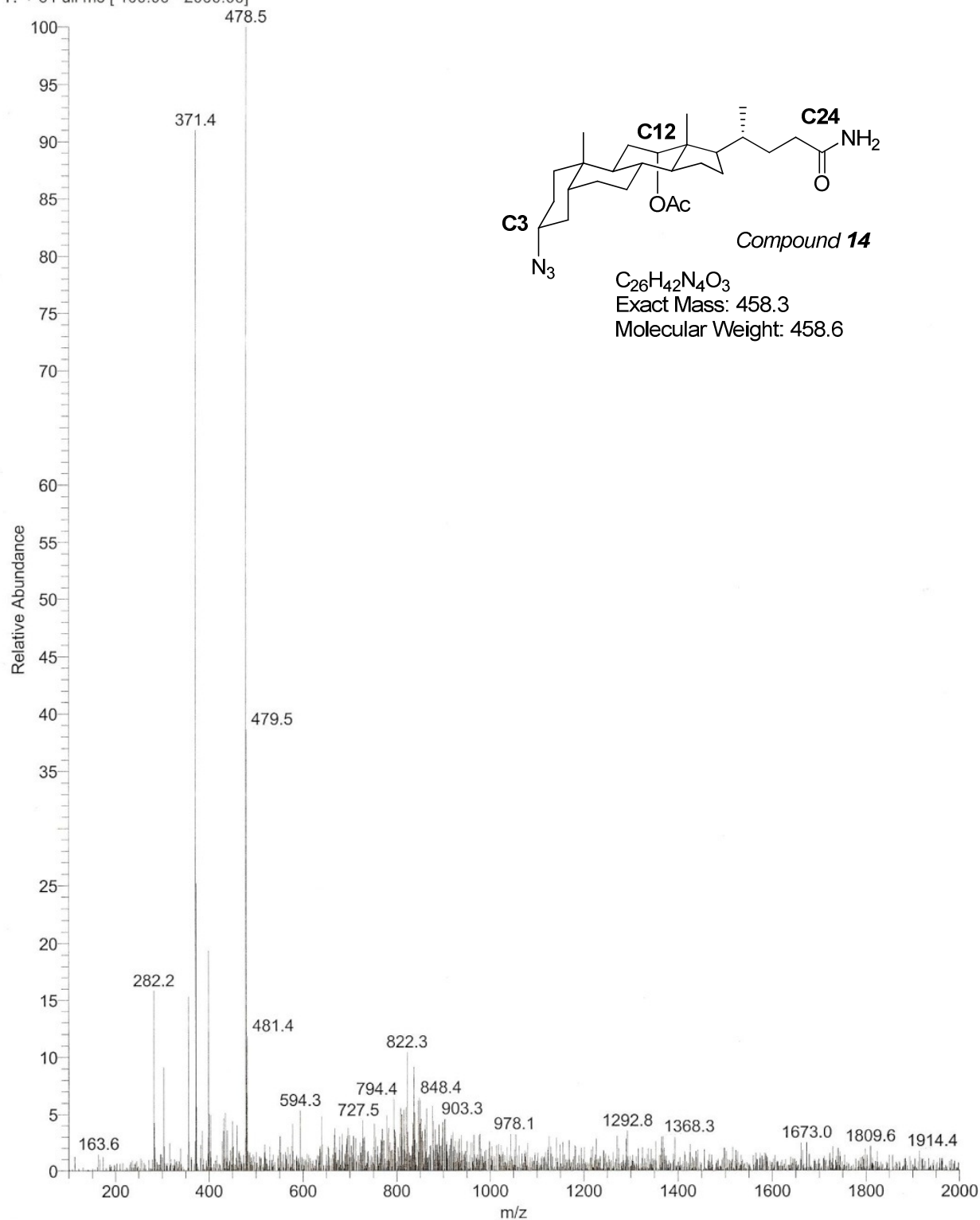


Figure S13. ESI-MS of compound 14.

2. Synthesis of Scaffold 15

External FmocHN-(L)-Pra-GABA linker cleaved from 17

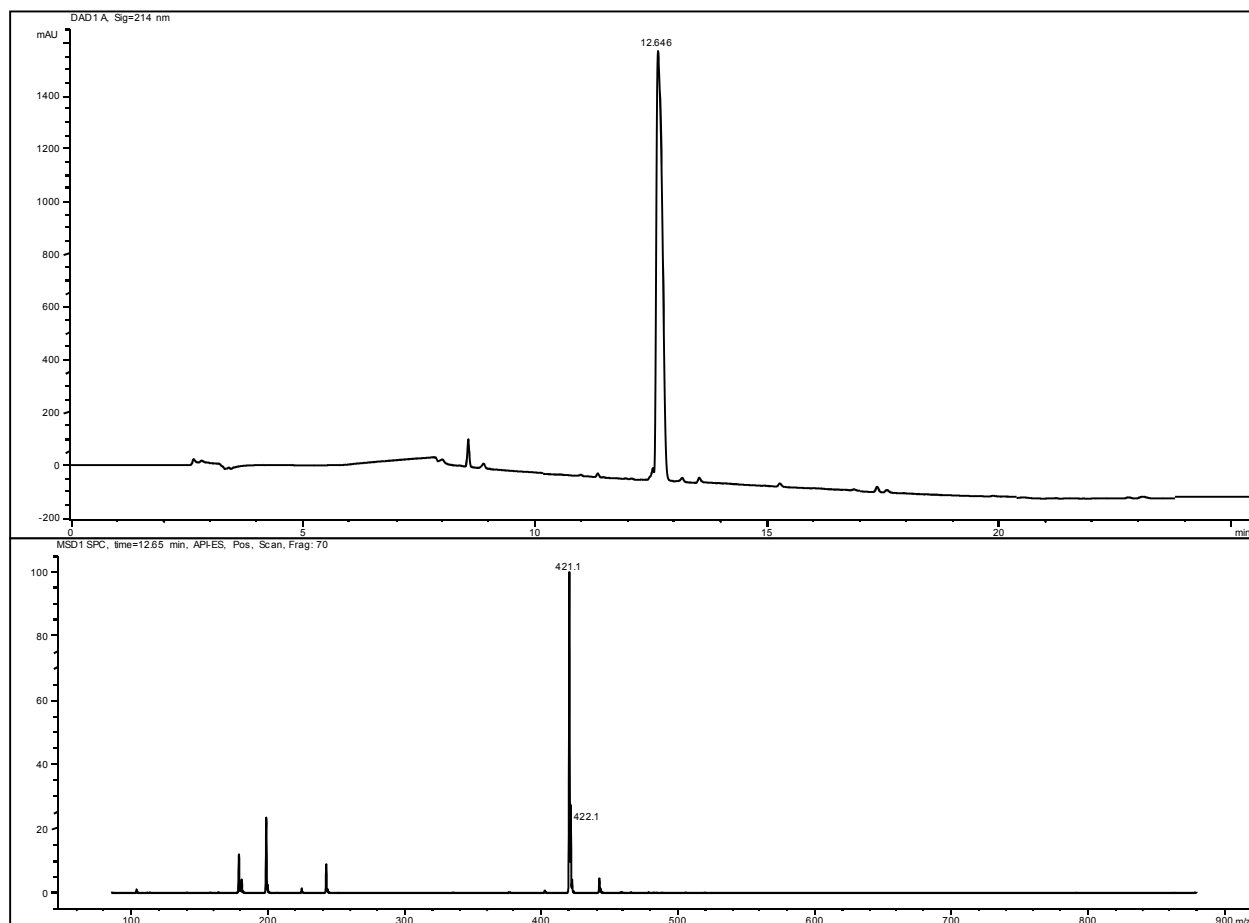
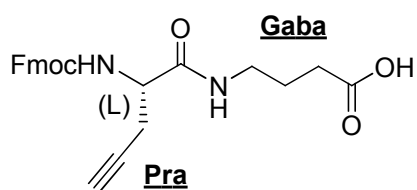


Figure S14. LC-MS of compound 17.



Compound 17

$C_{24}H_{24}N_2O_5$
Exact Mass: 420.2
Molecular Weight: 420.5

N₃-Gly-C3, C24-(L)-Pra-GABA decorated scaffold cleaved from 15

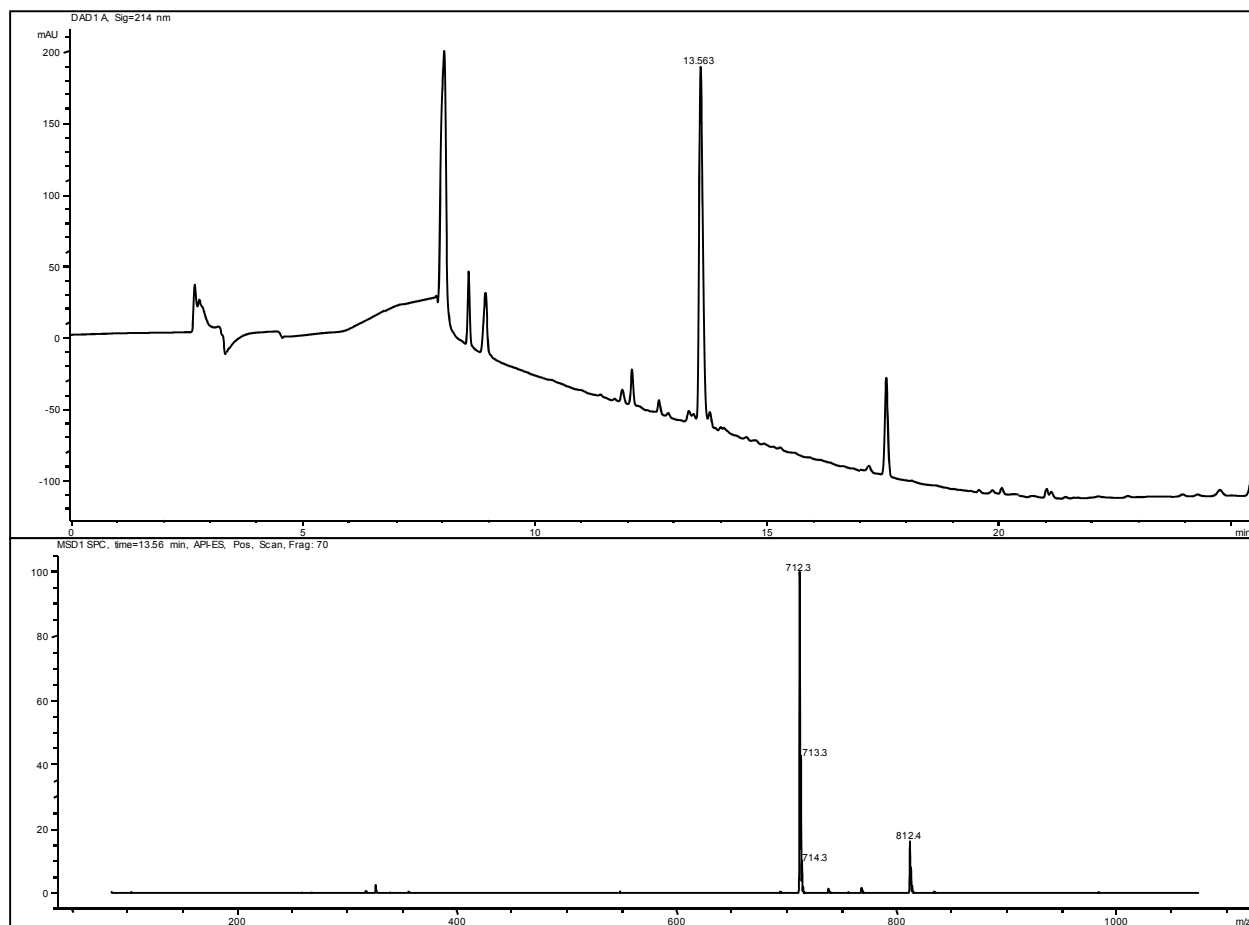
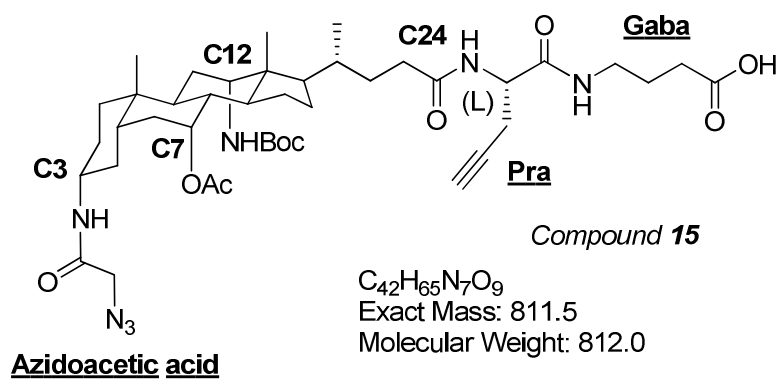


Figure S15. LC-MS of compound **15**.



3. Synthesis of Scaffold 22

AllocHN-C3, BocHN-(L)-Cys(Trt)-C12 decorated scaffold cleaved from 20

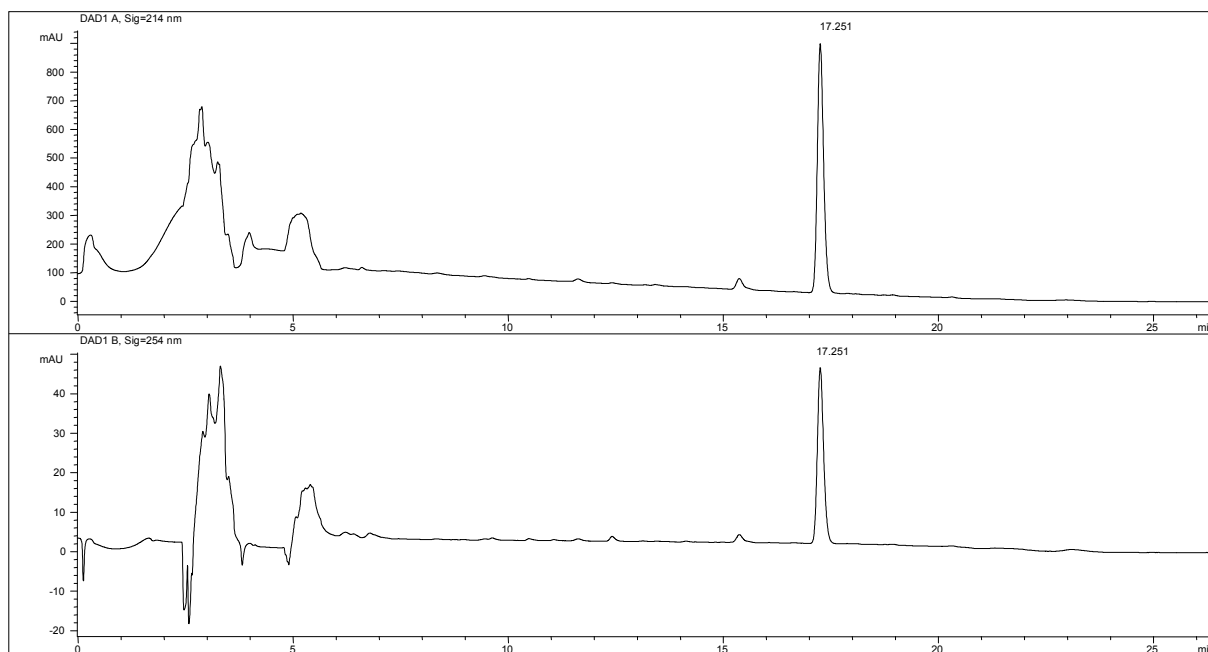
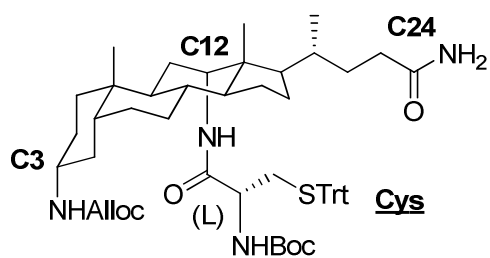


Figure S16. RP-HPLC of compound **20**.



Compound 20

$C_{55}H_{74}N_4O_6S$
Exact Mass: 918.5
Molecular Weight: 919.3

S#: 4-13 RT: 0.09-0.29 AV: 10 SB: 14 0.44-0.81 NL: 1.76E6
F: + c ms [100.00 - 2000.00]

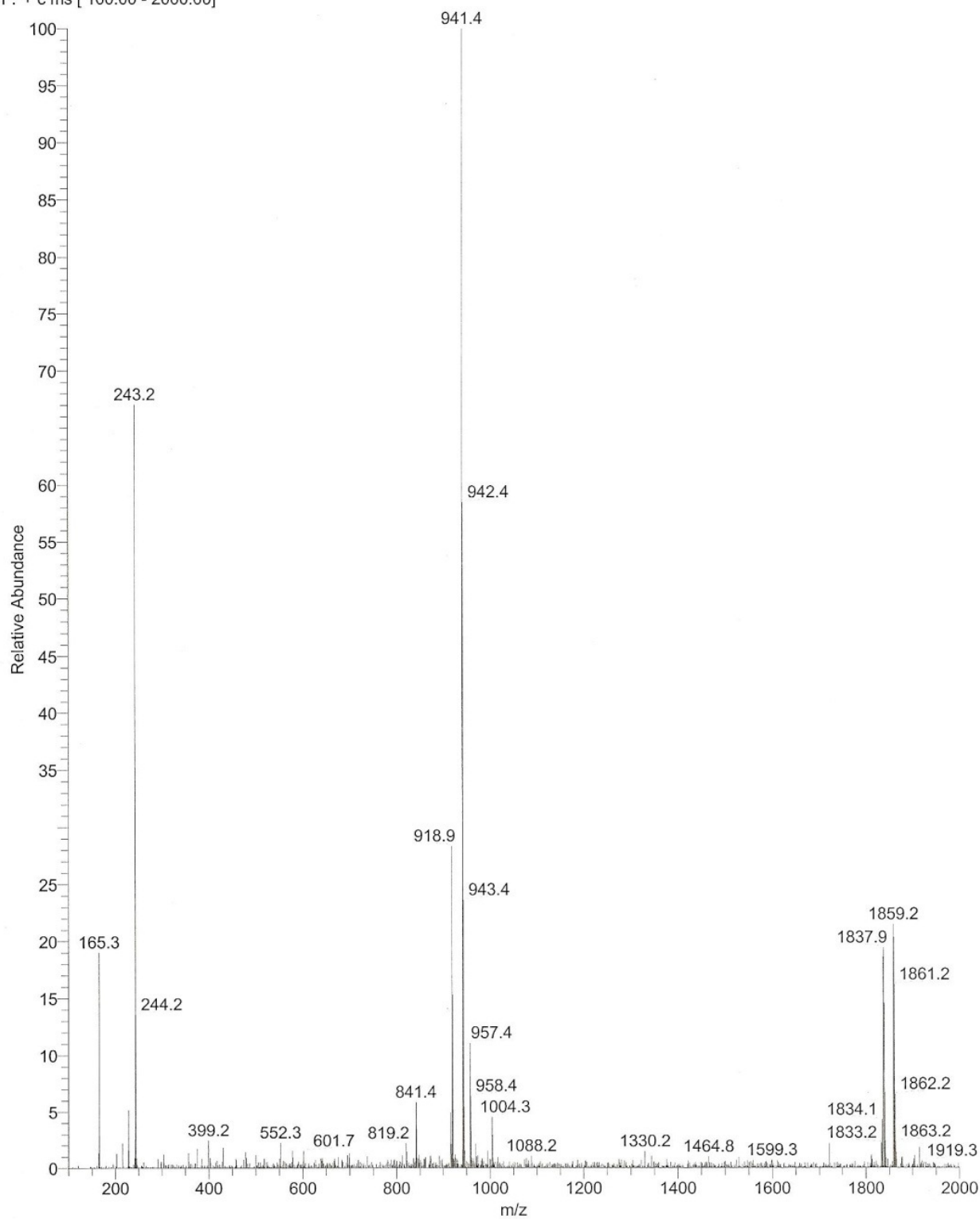


Figure S17. ESI-MS of compound **20**.

H₂N-C3, BocHN-(L)-Cys(Trt)-C12 decorated scaffold cleaved from 21

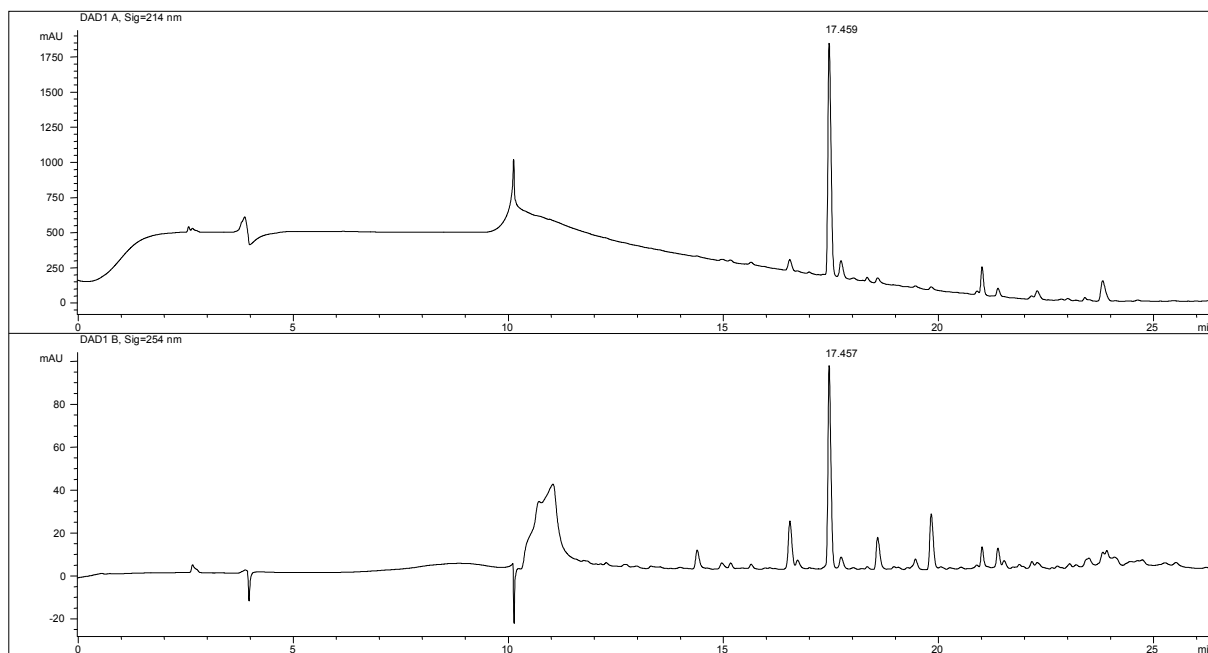
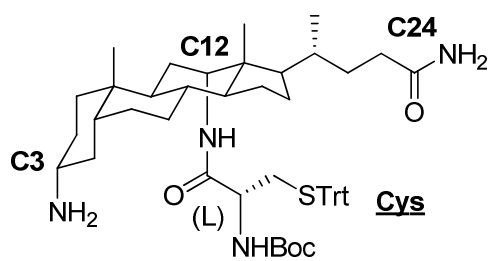


Figure S18. RP-HPLC of compound **21**.



Compound 21

C₅₁H₇₀N₄O₄S
Exact Mass: 834.5
Molecular Weight: 835.2

S#: 26-35 RT: 0.62-0.81 AV: 10 SB: 28 1.04-1.69 NL: 2.18E6
F: + c ms [100.00 - 2000.00]

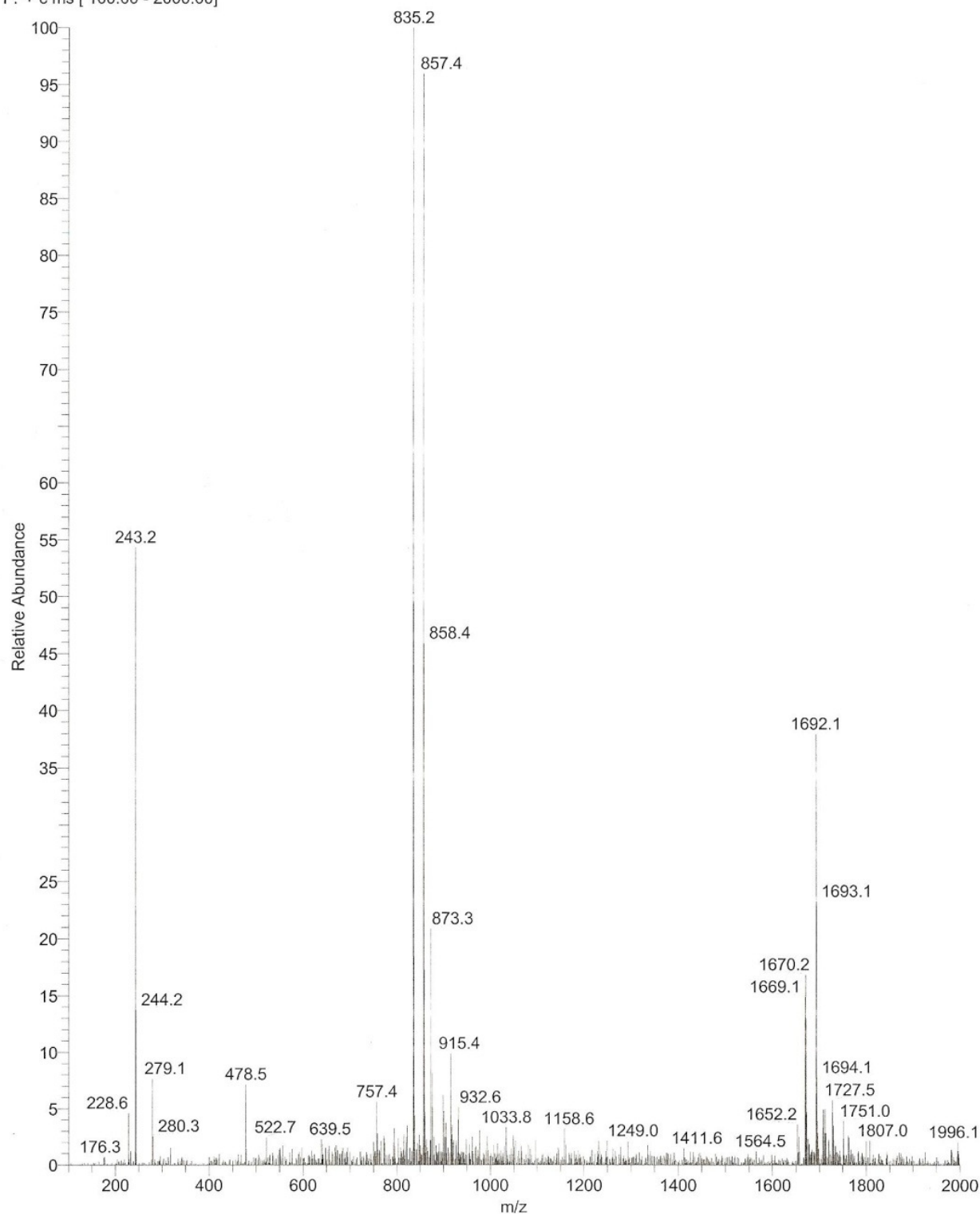


Figure S19. ESI-MS of compound **21**.

FmocHN-(L)-Cys(Trt)-C3, BocHN-(L)-Cys(Trt)-C12 decorated scaffold cleaved from 22

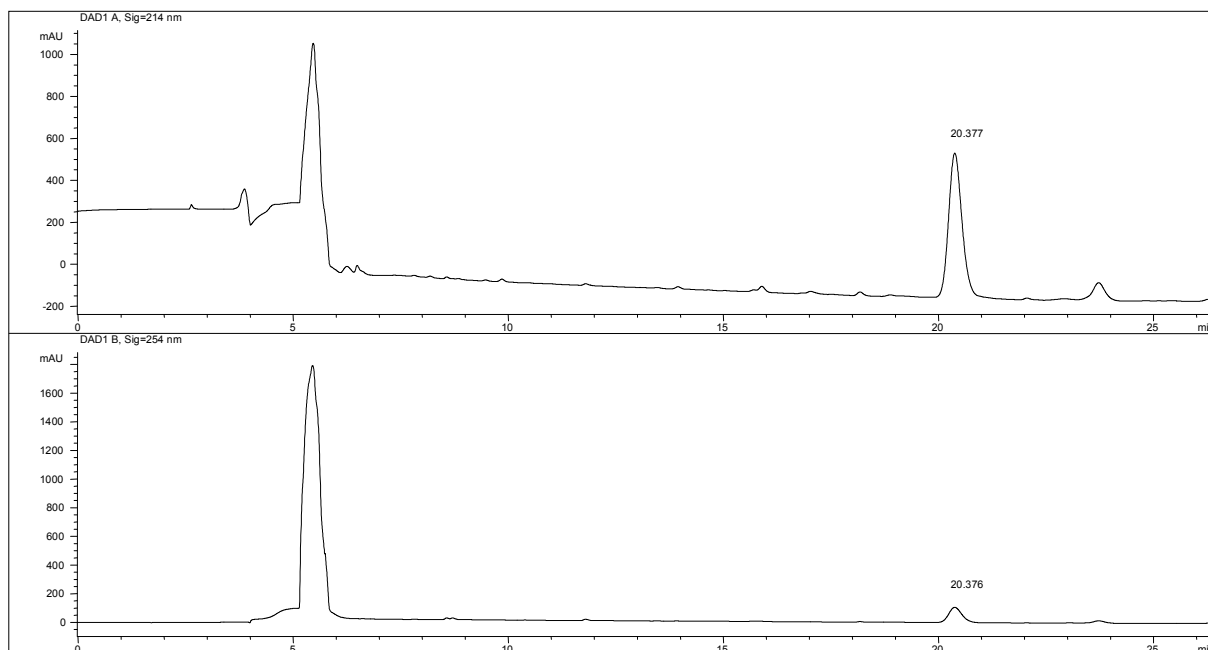
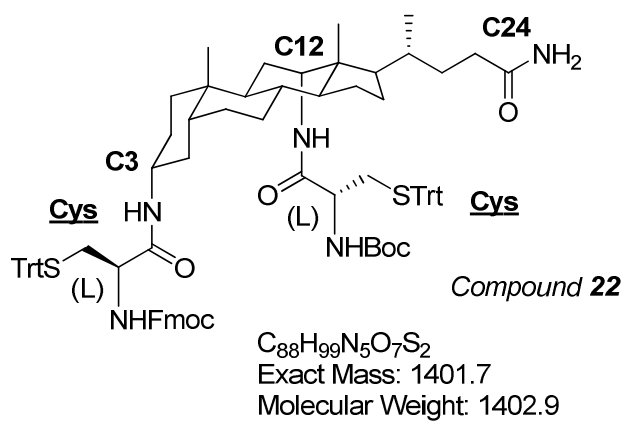


Figure S20. RP-HPLC of compound **22**.



S#: 5-12 RT: 0.16-0.36 AV: 8 SB: 28 0.94-1.80 NL: 2.79E5
F: + c ms [150.00 - 2000.00]

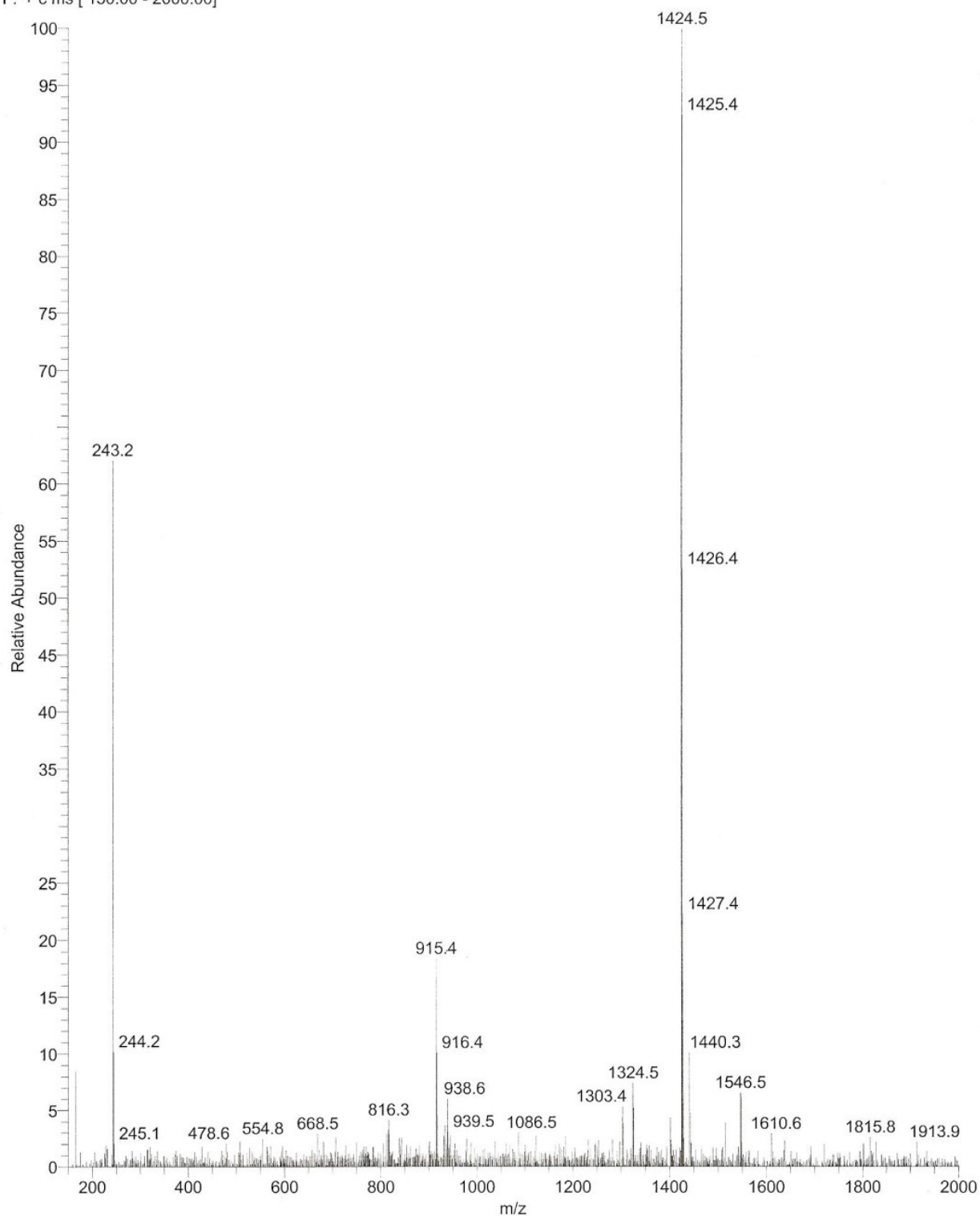


Figure S21. ESI-MS of compound 22.