Supplementary Materials: Functionalization of a Triazine Dendrimer Presenting Four Maleimides on the Periphery and a DOTA Group at the Core

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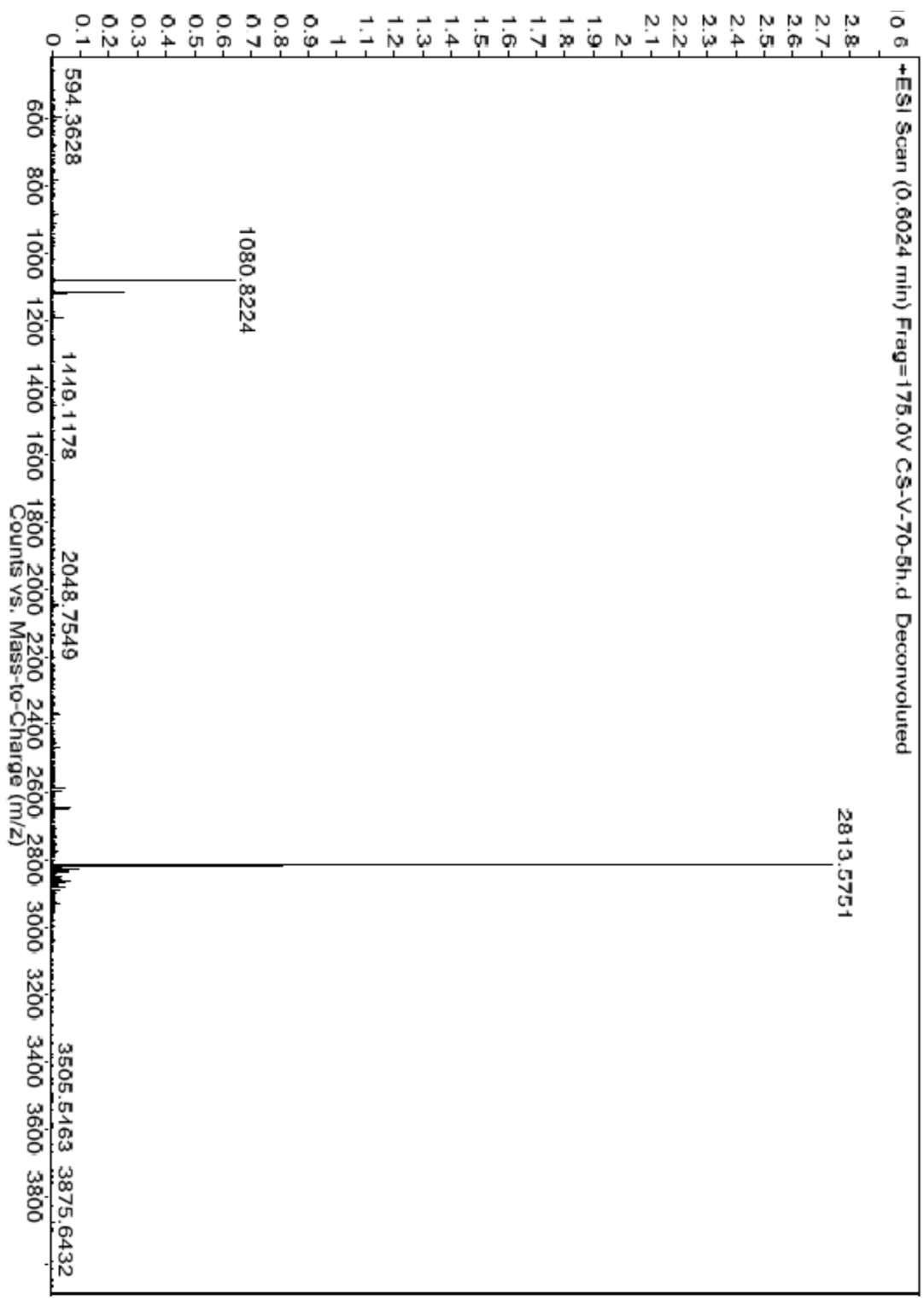


Figure S1. ESI-TOF MS of **1**. The line at *m*/*z* 1080 is not assigned.

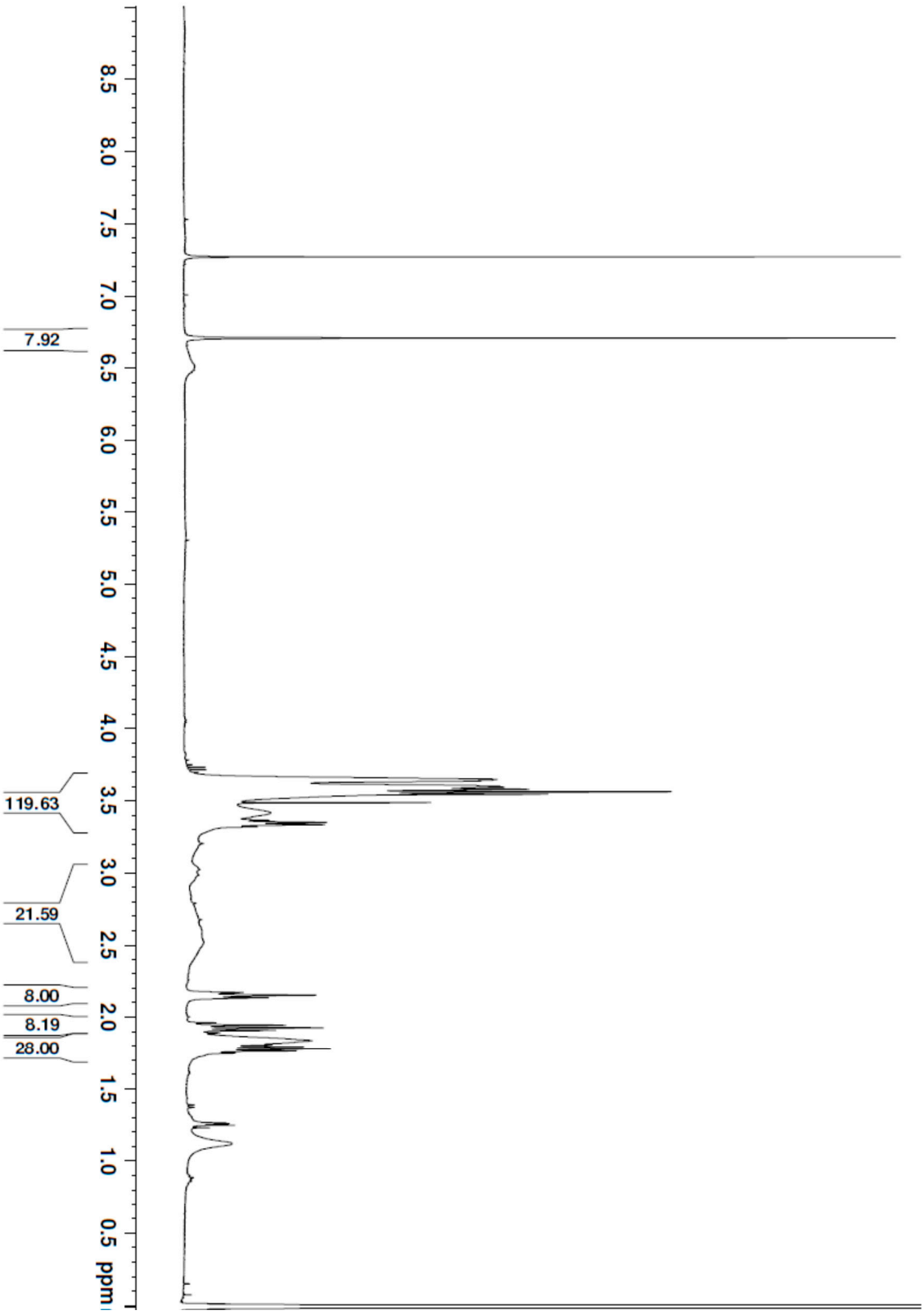


Figure S2. ^{1}H-NMR (400 MHz, $CDCl_3$) of **1**.

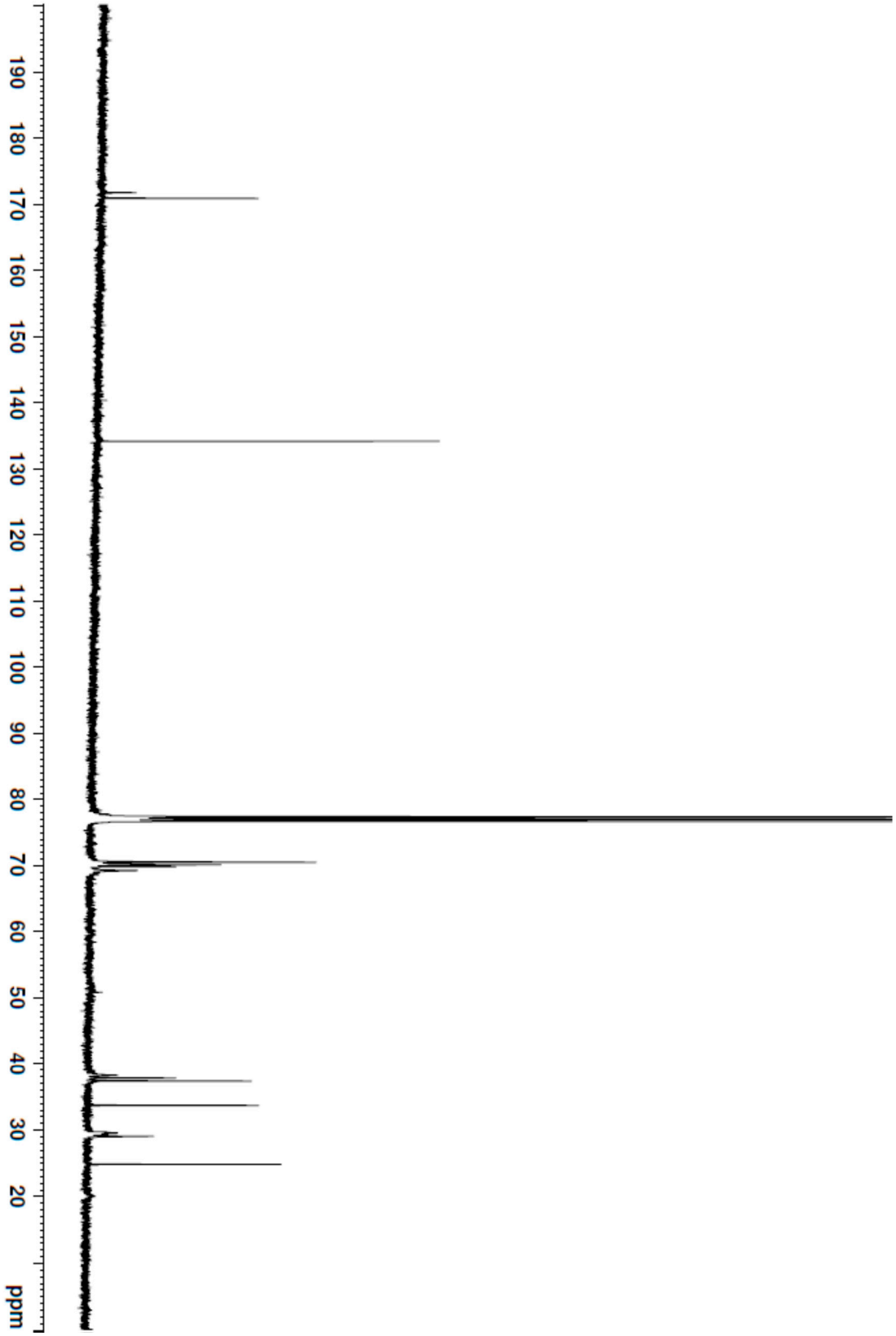


Figure S3. ^{13}C-NMR (400 MHz, $CDCl_3$) of **1**.

Panel 1: **1**

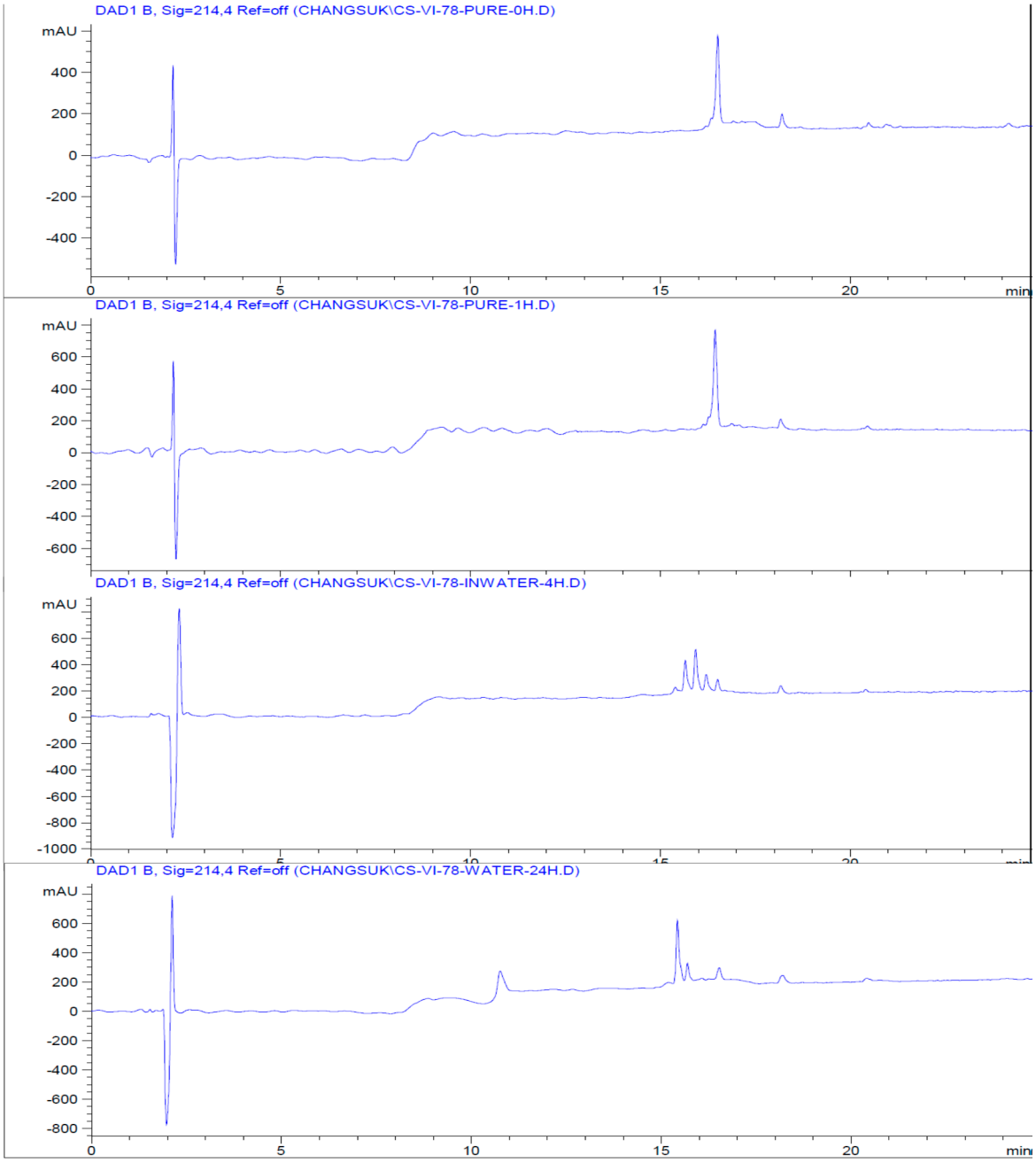
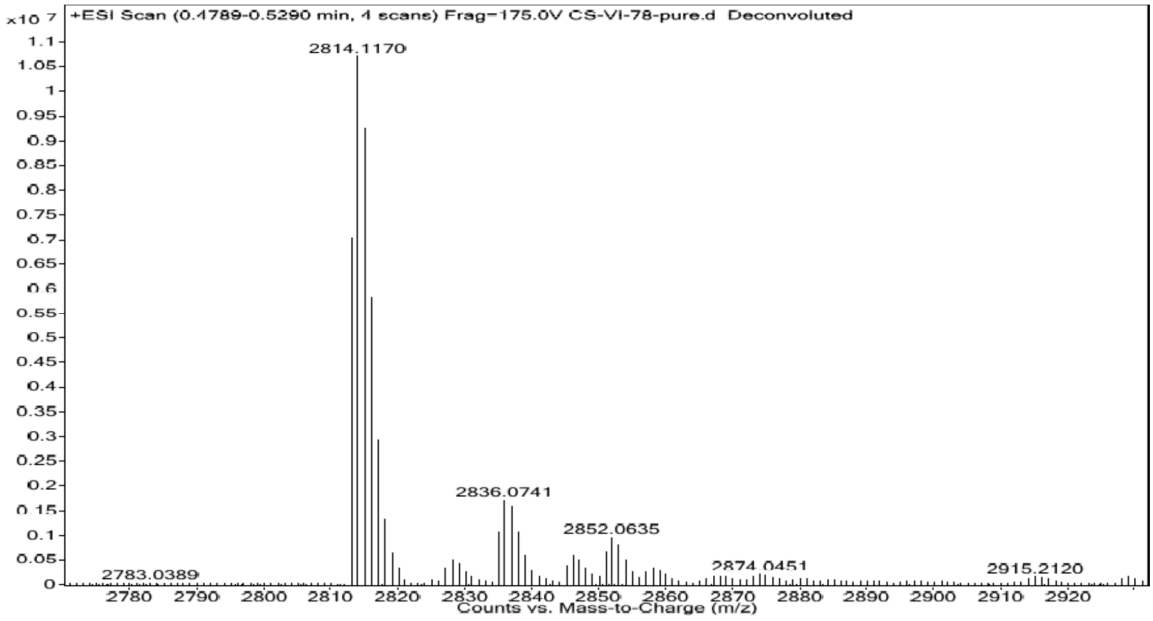
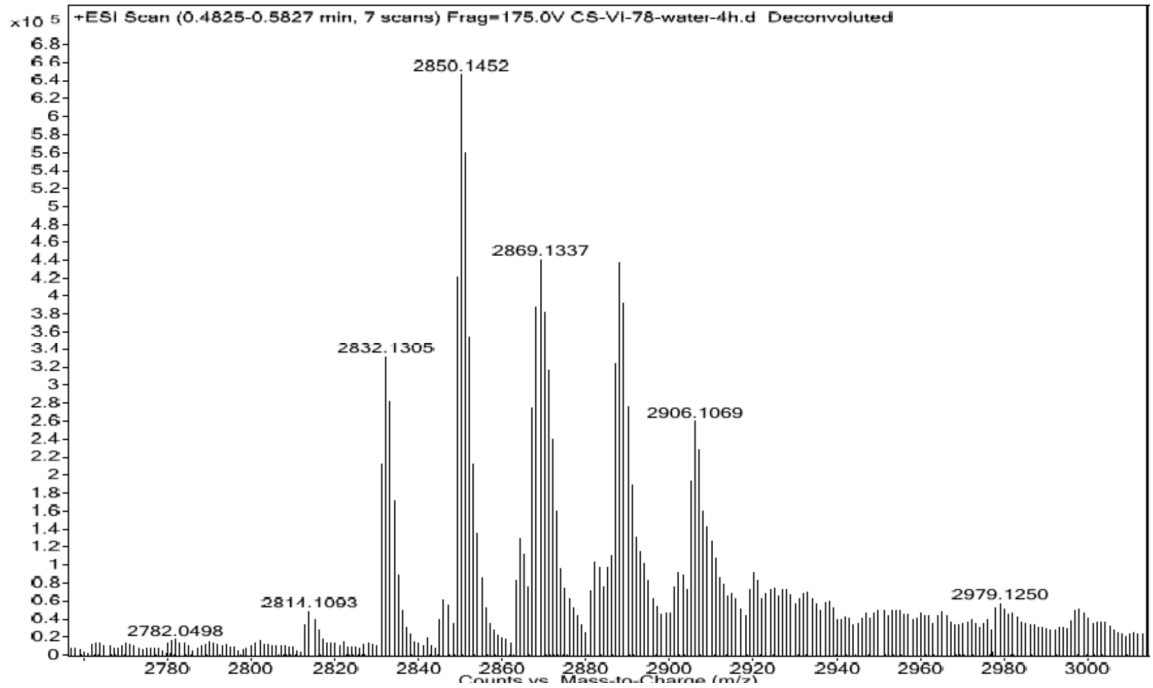


Figure S4. Stability test of **1** in water (pH 7.5) with monitoring by HPLC. Panels are **1**, **1** after 1h, **1** after 4h, **1** after 24h. The mobile phase consisted of water/acetonitrile (A/B, HPLC grade, 0.1% (*w*/*v*) trifluoroacetic acid) at a flow rate of 0.8 mL/min. The elution gradient was 10% MeCN for 5 min, ramp to 90% MeCN in 30 min, and ramp down to 10% MeCN in 15 min. The sample volume injected 5 µL at a concentration of 0.1 mg/mLwith HPLC-grade MeCN, and eluted sample was detected at 214 nm.

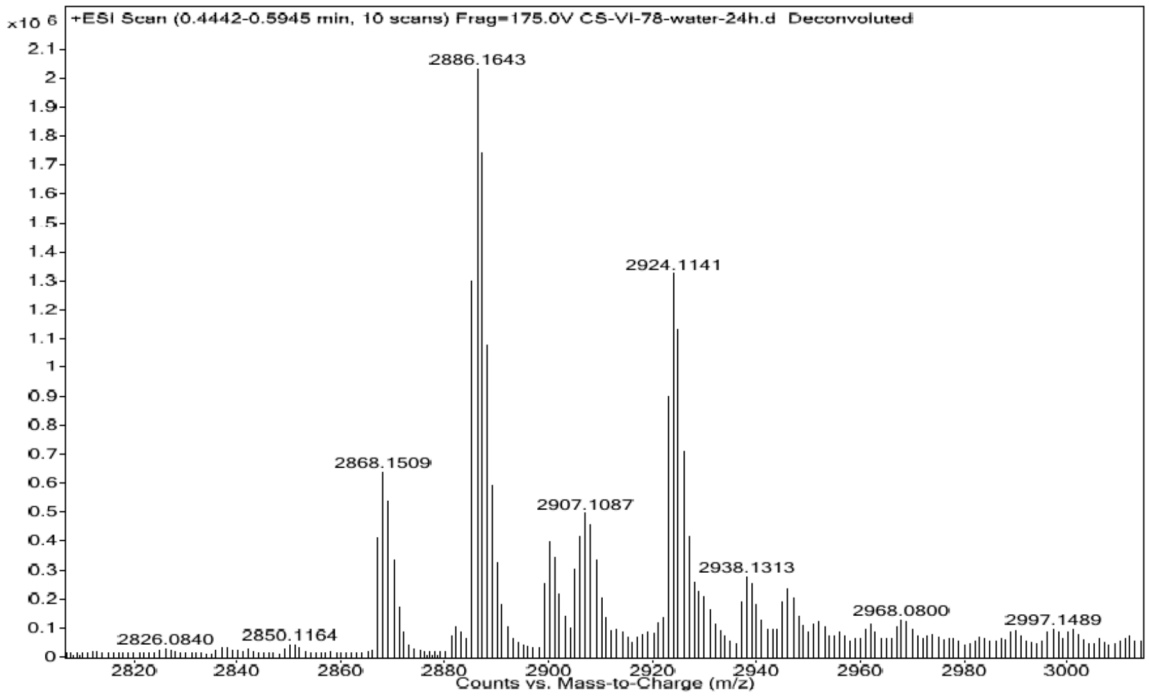


(**A**)



(**B**)

Figure S5. *Cont.*



(**C**)

Figure S5. Stability test of **1** in water (pH 7.5) with monitoring by ESI-TOF MS. (**A**) Panel 1: After 1 h; (**B**) Panel 2: After 4 h; (**C**) Panel 3: After 24 h

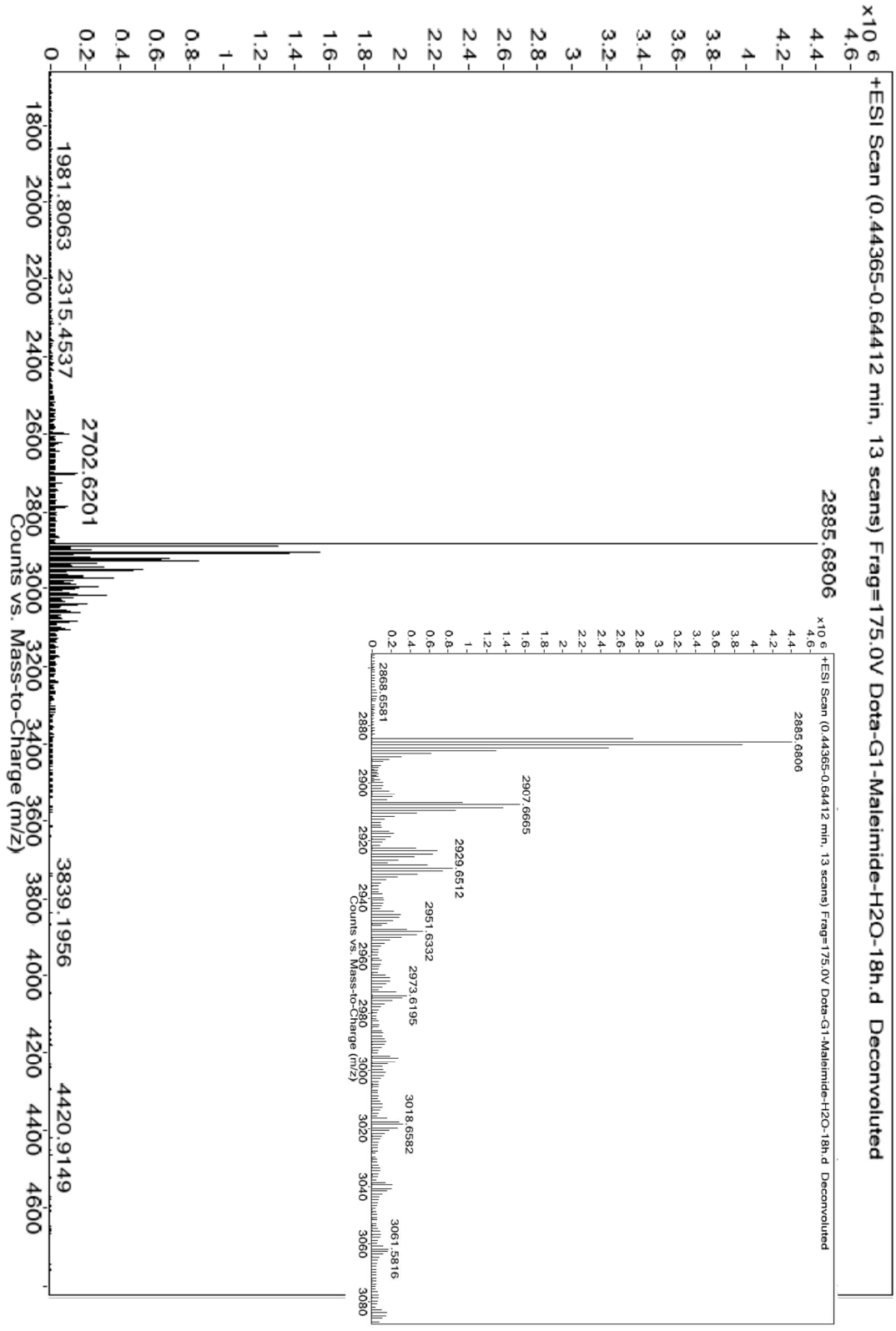


Figure S6. ESI-TOF MS of hydrolysis product of **1**. Inset shows the Na^+ adducts.

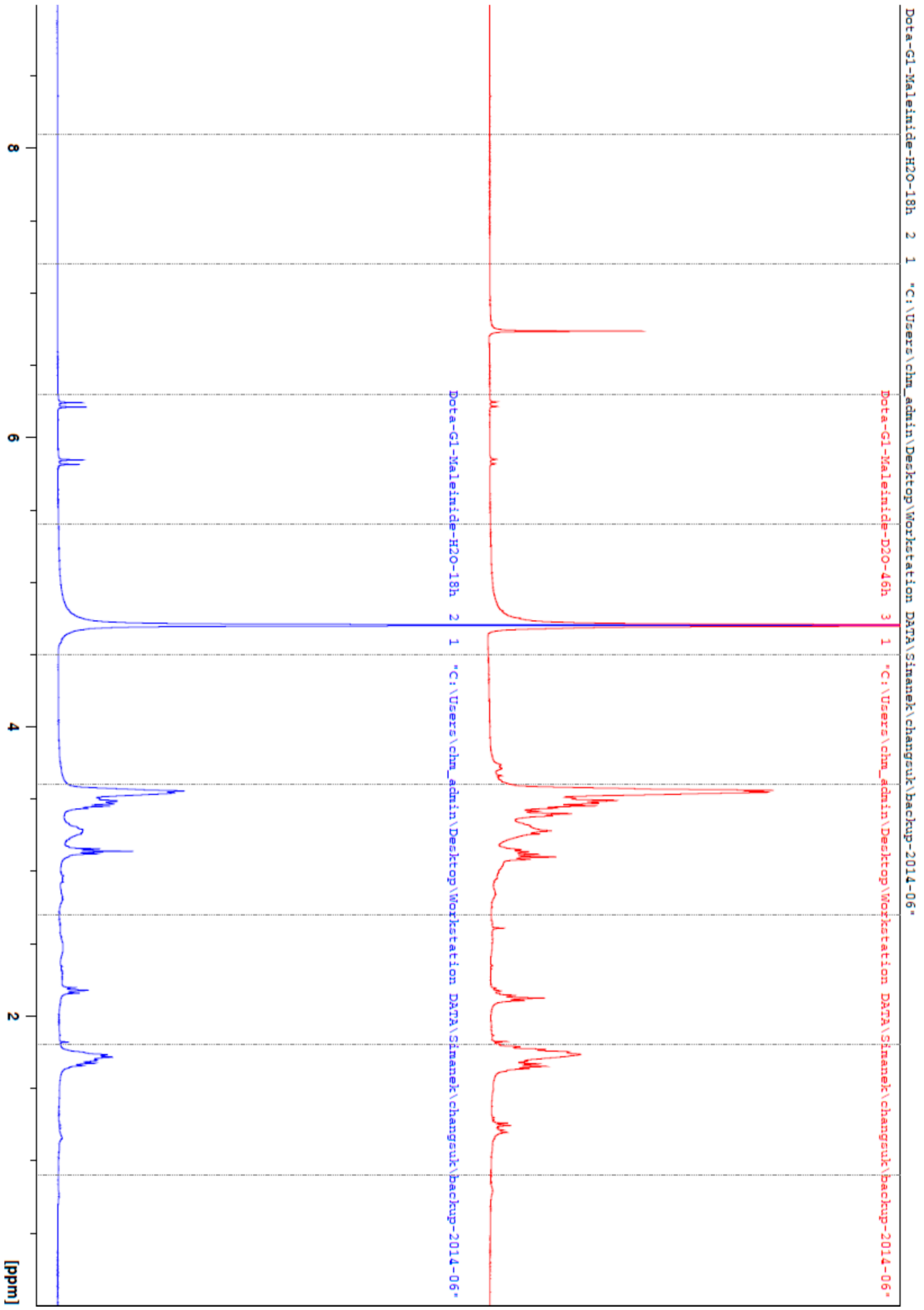


Figure S7. Comparative ^{1}H-NMR of the hydrolysis product. Panels are **1** after 48 h in D_2O, pH 7 (top red), and at pH 7–8, 18 h then lyophilized (bottom blue).

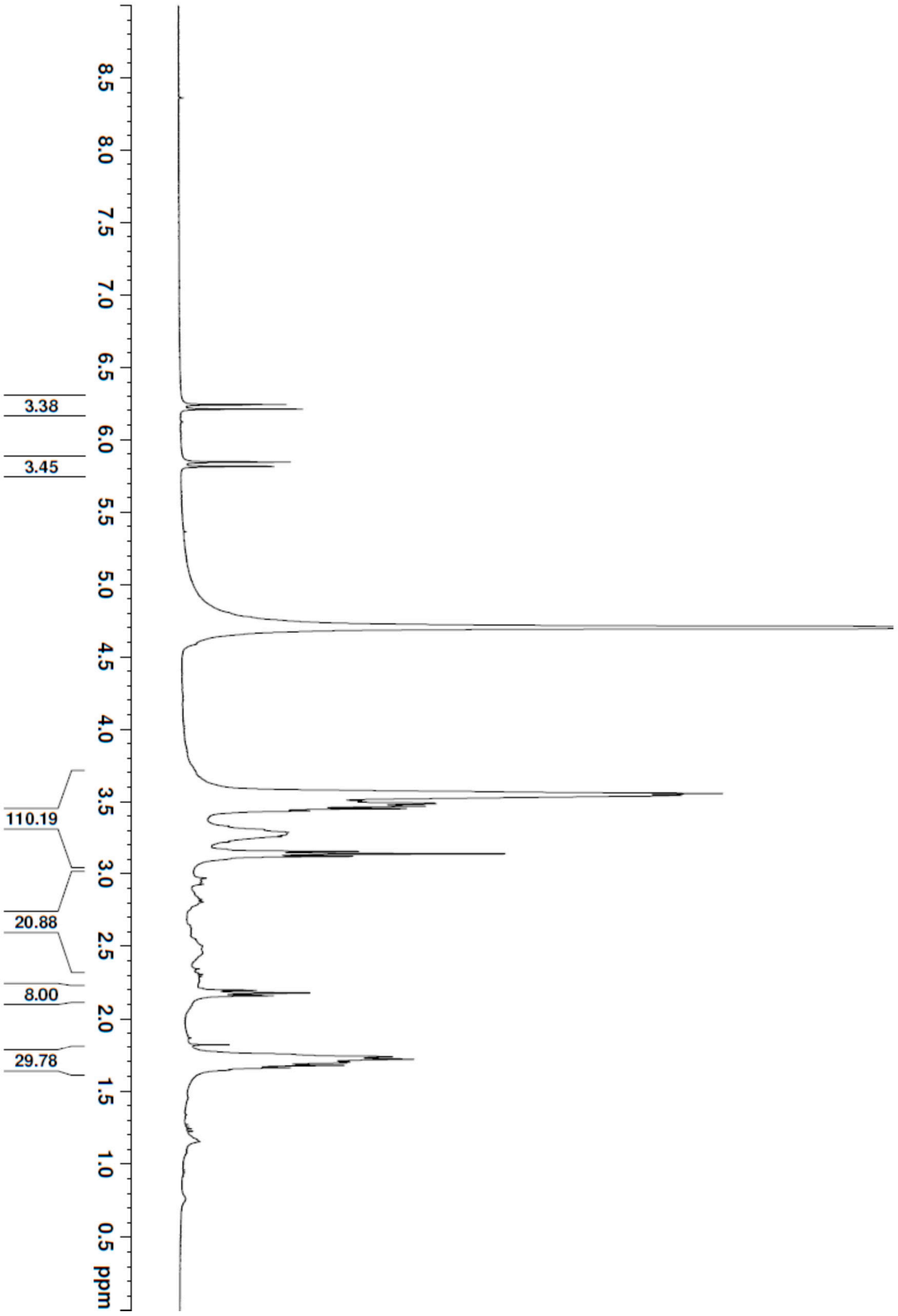


Figure S8. ^{1}H-NMR of the hydrolysis product (400 MHz, D_2O).

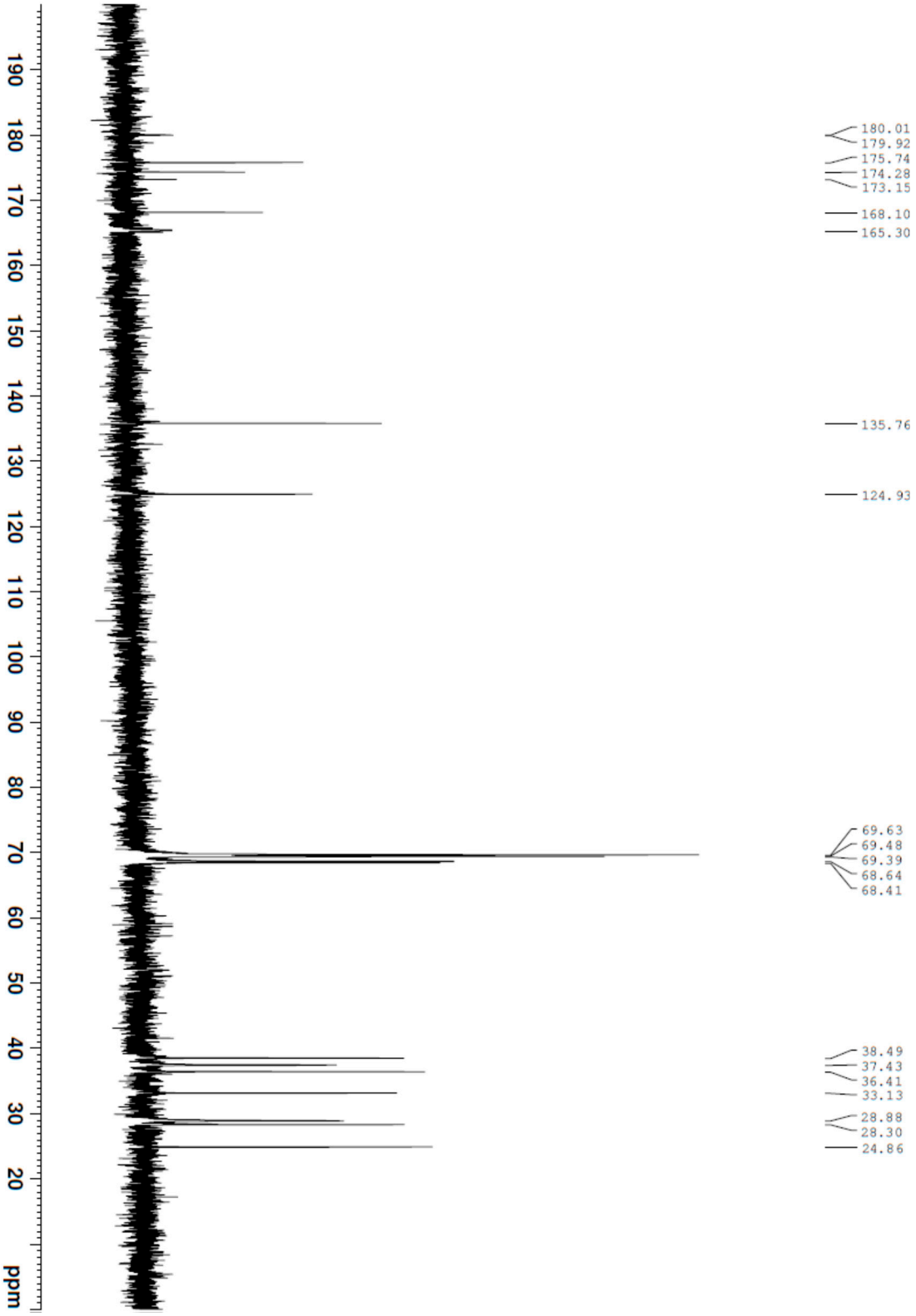


Figure S9. ^{13}C-NMR of the hydrolysis product (400 MHz, D_2O).

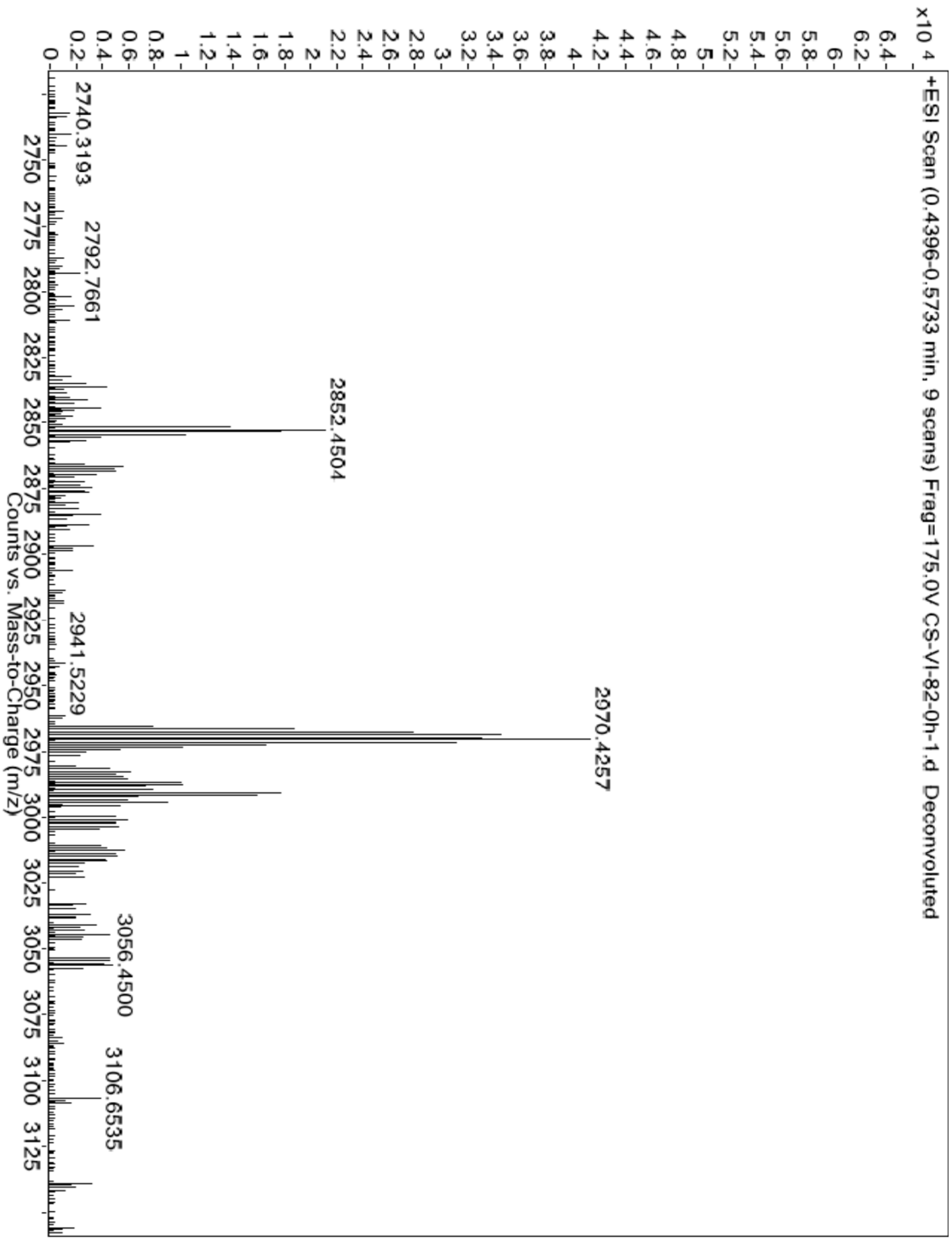


Figure S10. ESI-TOF MS analysis of formation of the Gd adduct of **1**. MS (ESI-TOF) calcd. for $C_{127}H_{213}GdN_{31}O_{40}$ 2970.4827, found 2970.4257 $[M + Gd]^+$.

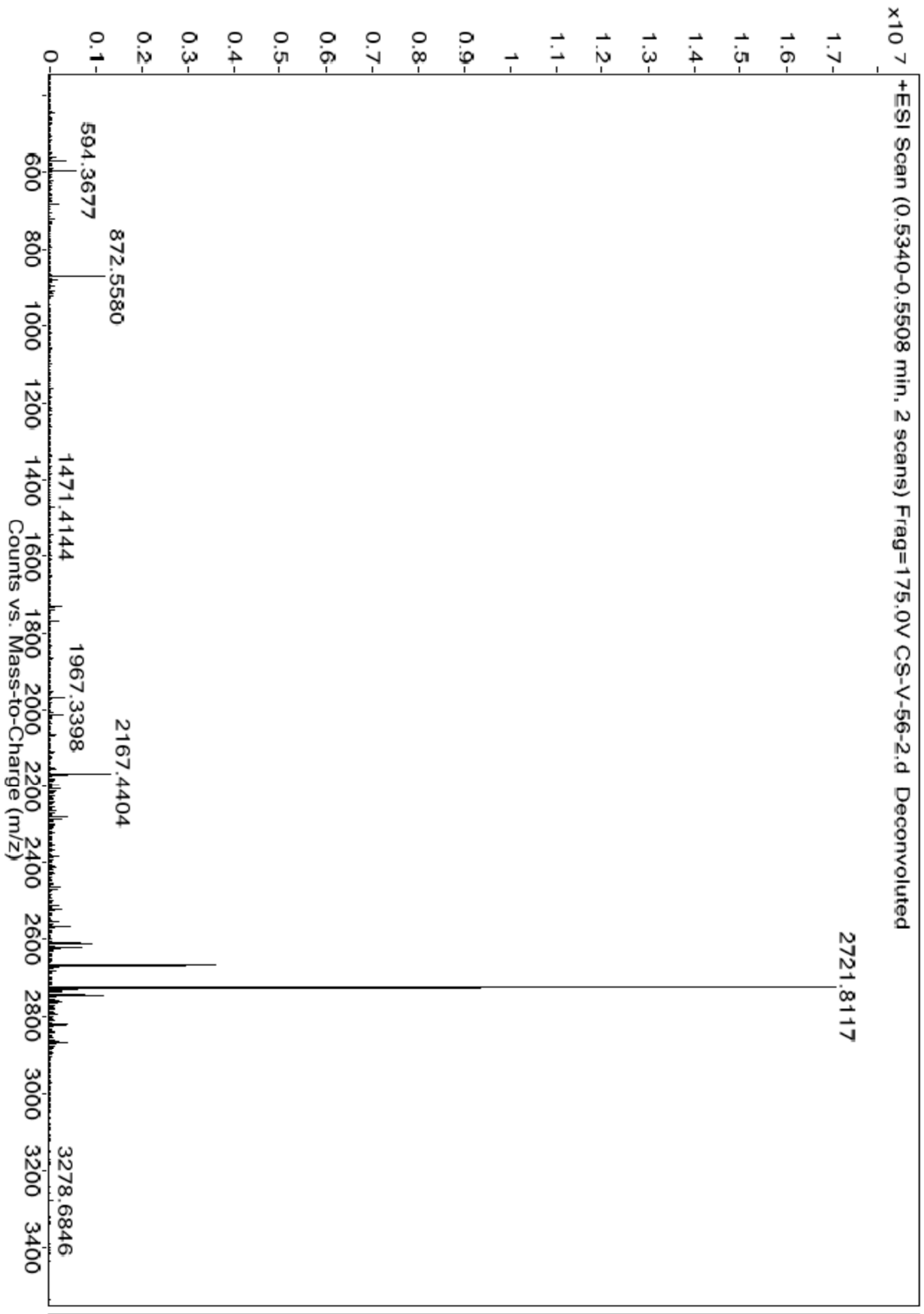


Figure S11. ESI-TOF MS of **4**. Loss of BOC groups are observed. The line at 2167 is not identified.

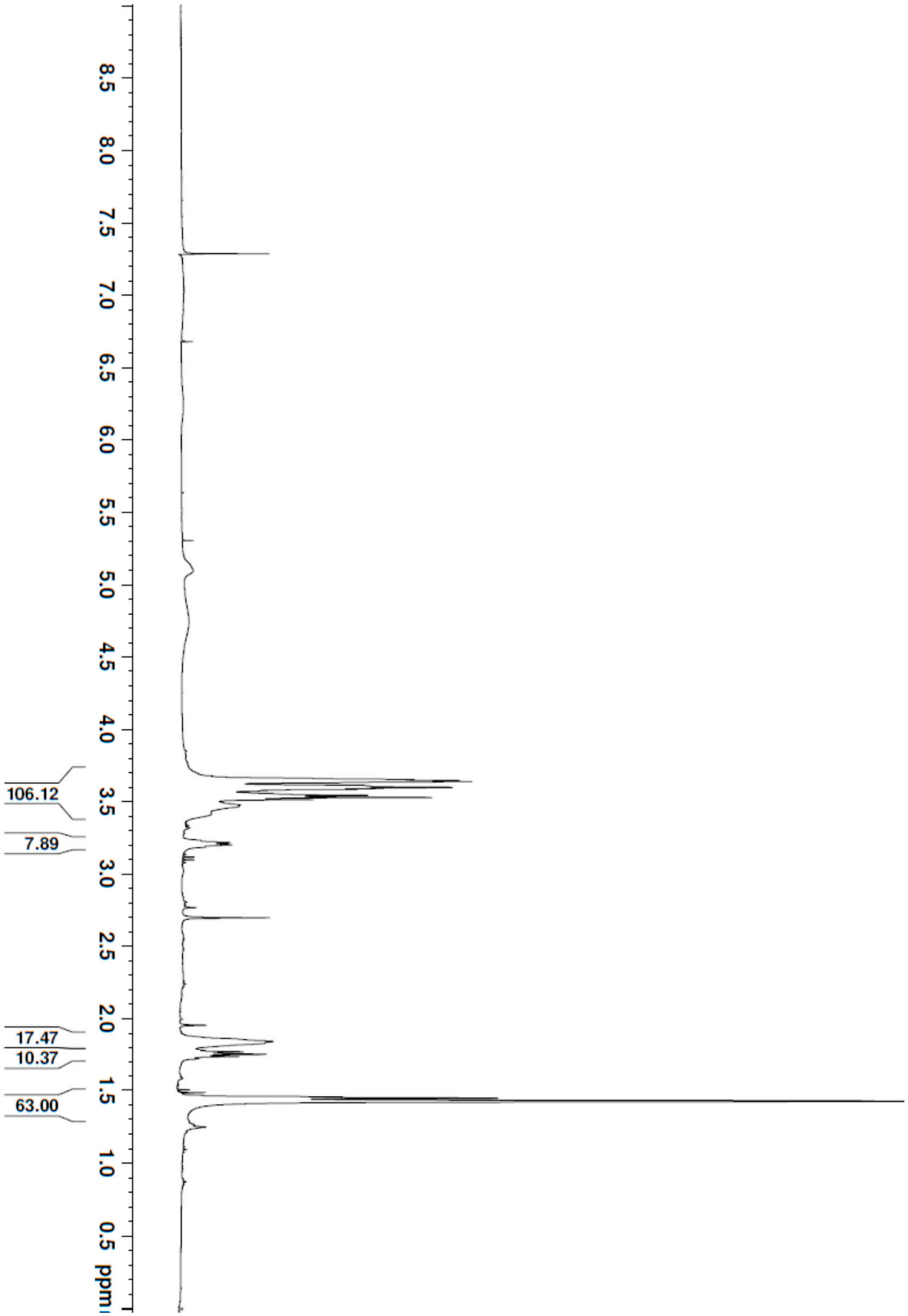


Figure S12. ^{1}H-NMR of **4** (400 MHz, $CDCl_3$).

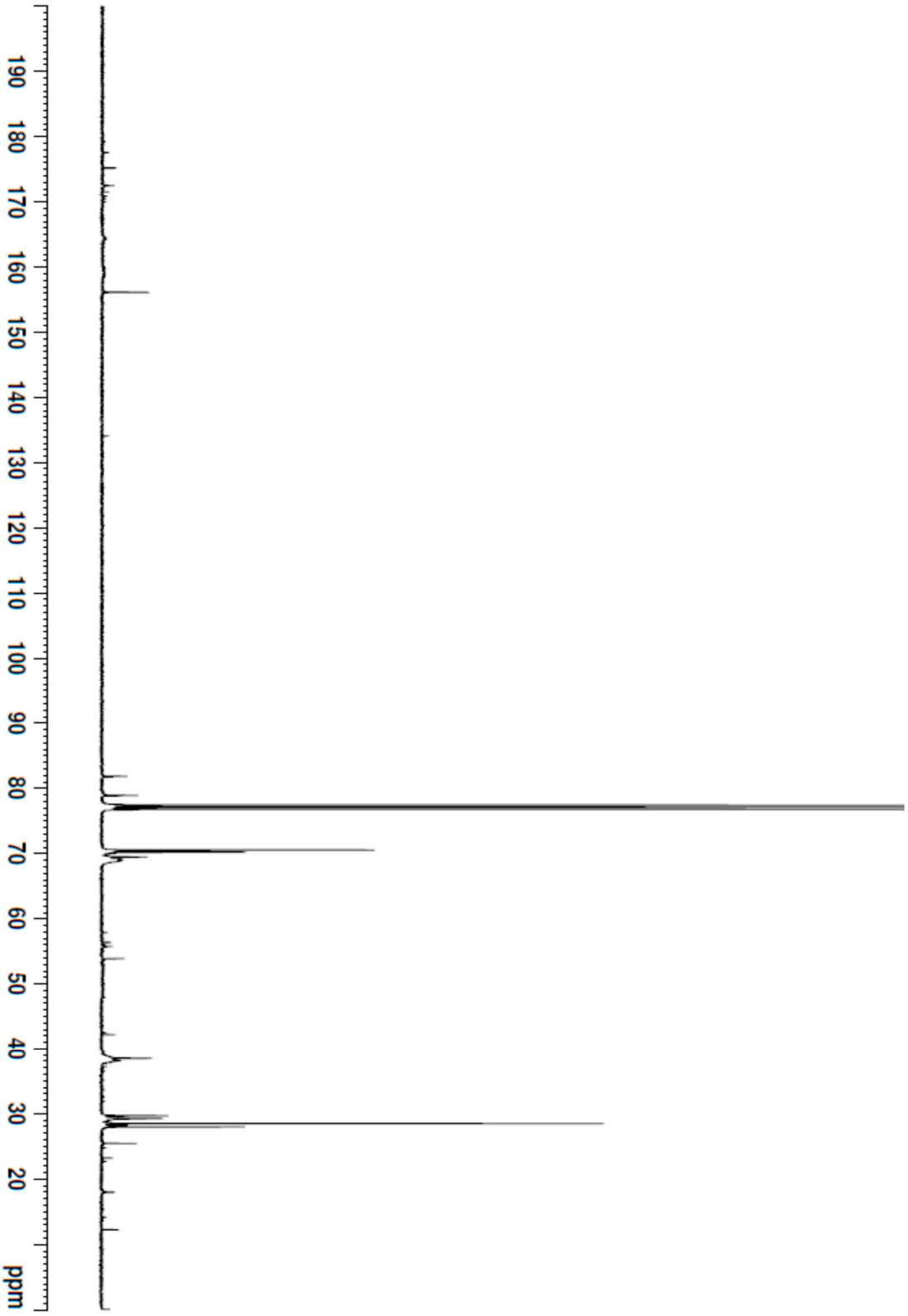


Figure S13. ^{13}C NMR of **4** (100 MHz, $CDCl_3$).

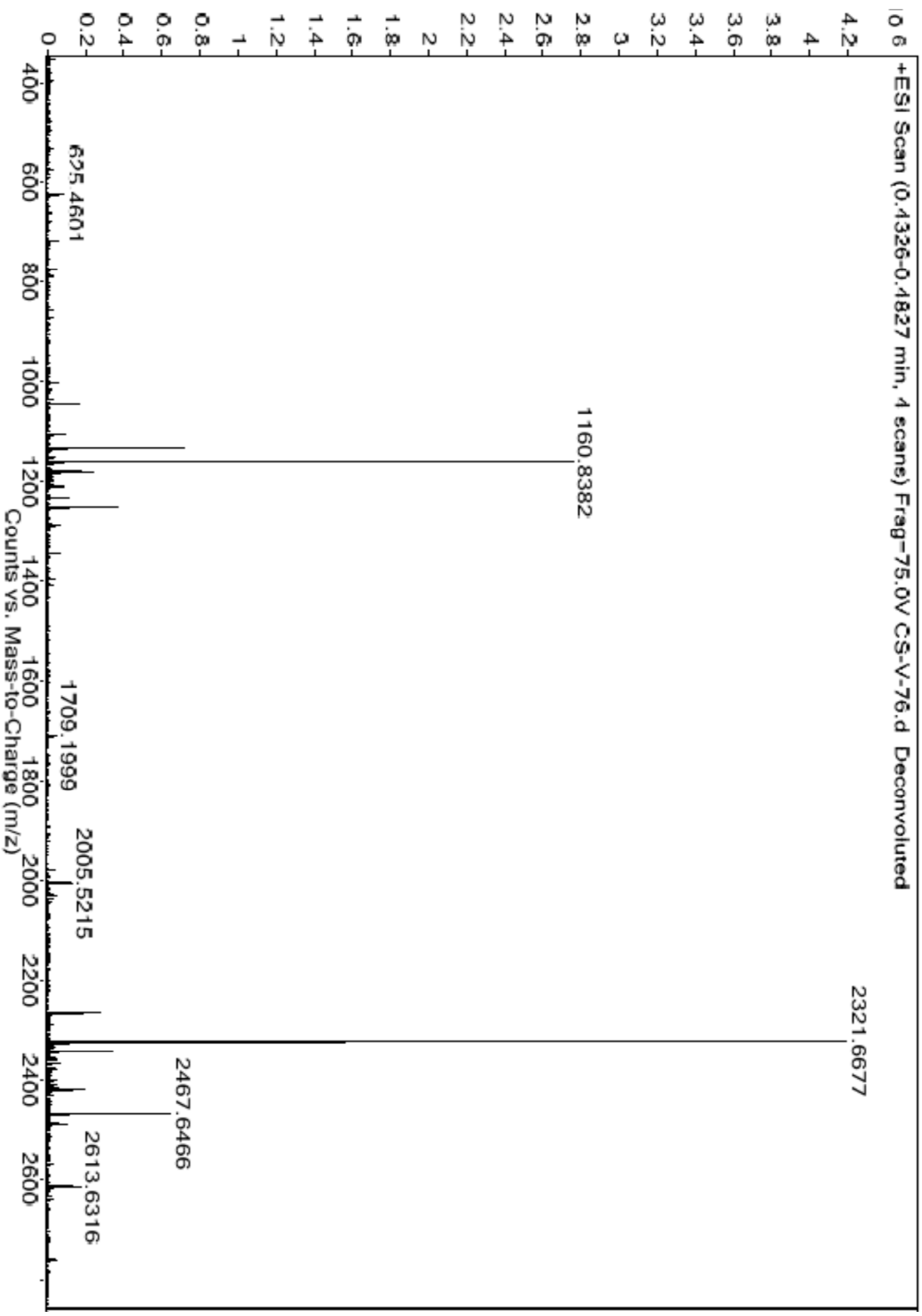


Figure S14. ESI-TOF MS of **5**. The line at *m*/*z* 1160 is the doubly charged species. The lines at *m*/*z* 2467 and 2613 are not identified.

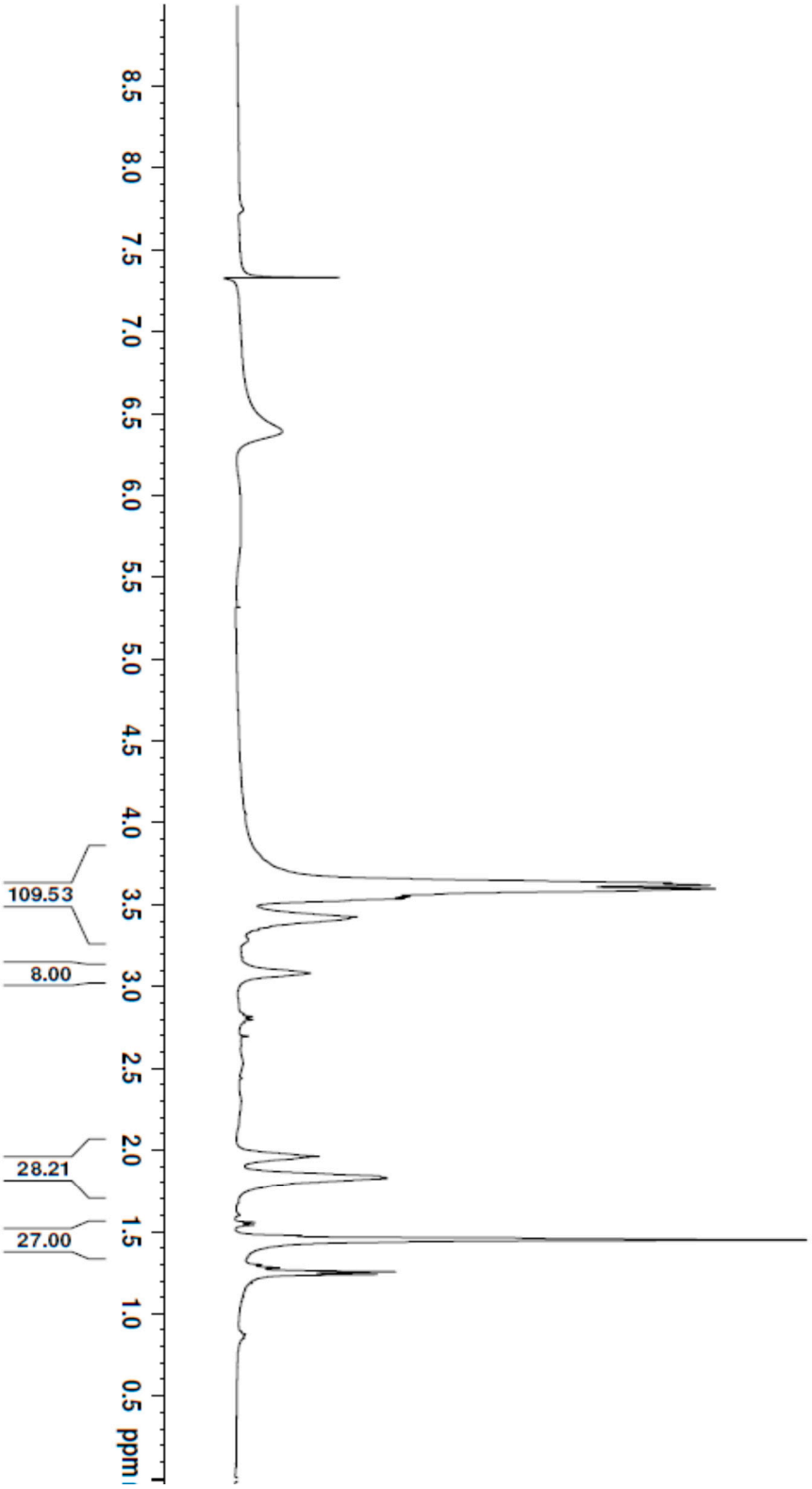


Figure S15. ^{1}H-NMR of **5** (400 MHz, $CDCl_3$).

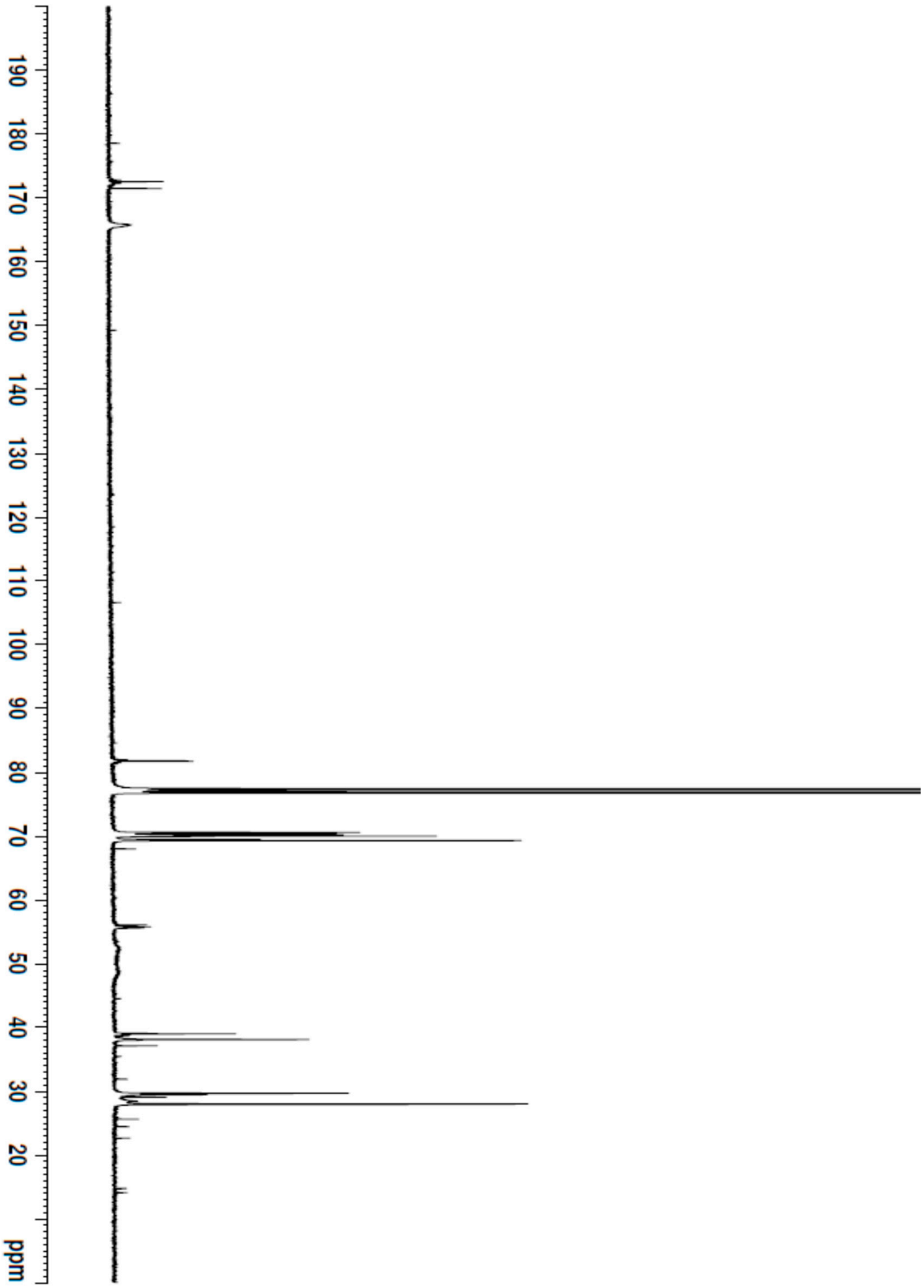


Figure S16. ^{13}C NMR of **5** (100 MHz, $CDCl_3$)

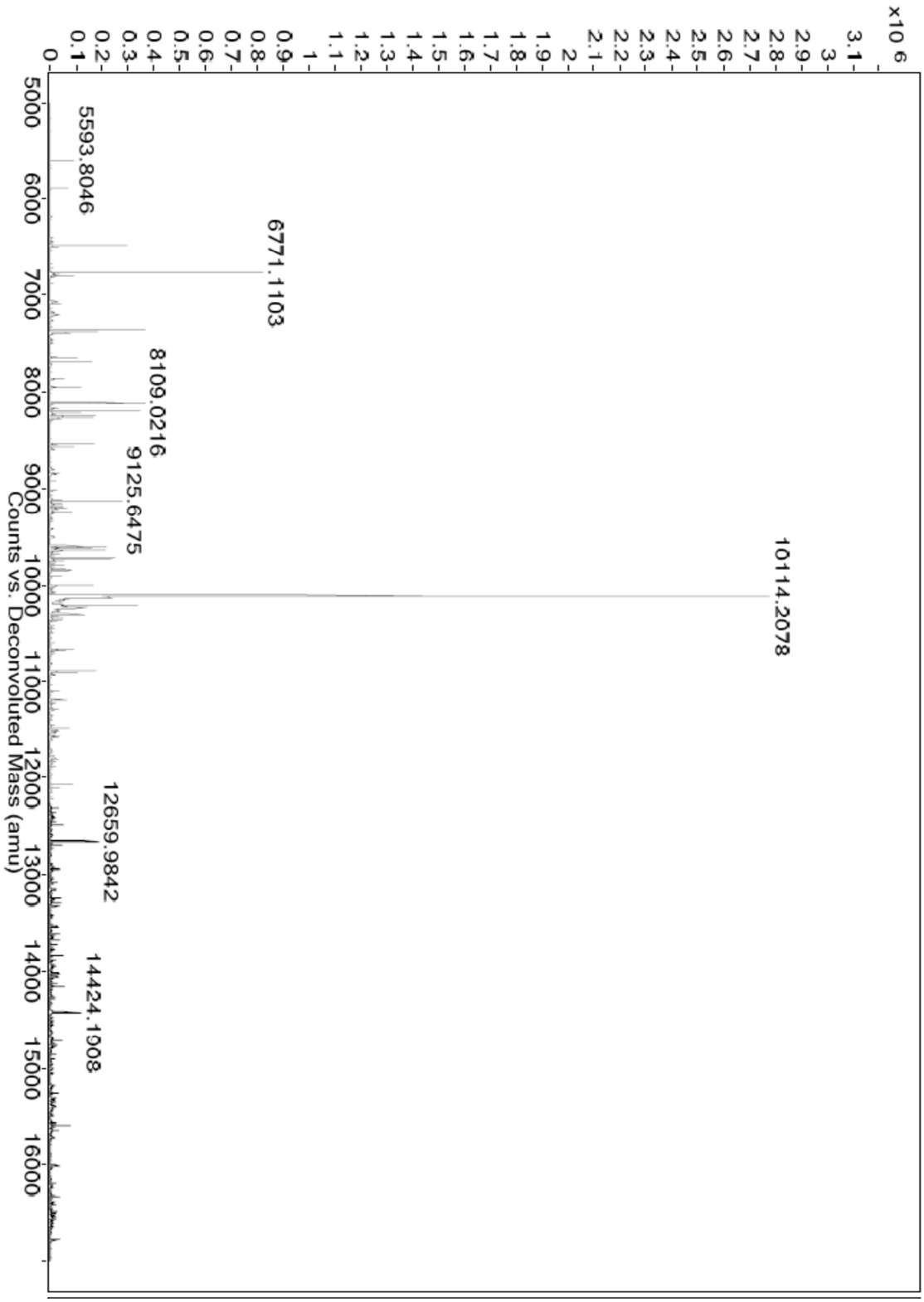


Figure S17. ESI-TOF MS of **G3.**

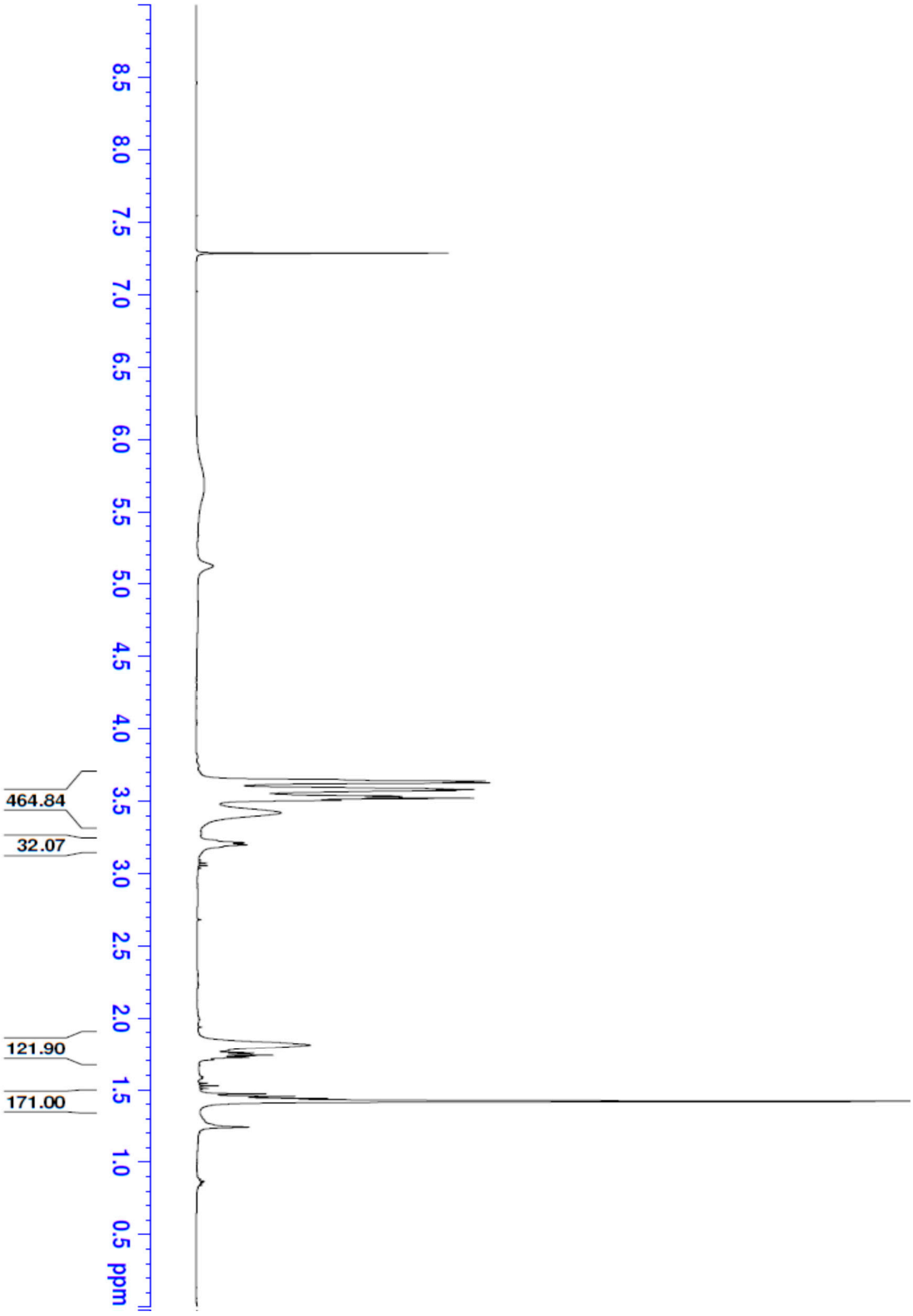


Figure S18. ^{1}H-NMR of **G3** (400 MHz, $CDCl_3$).

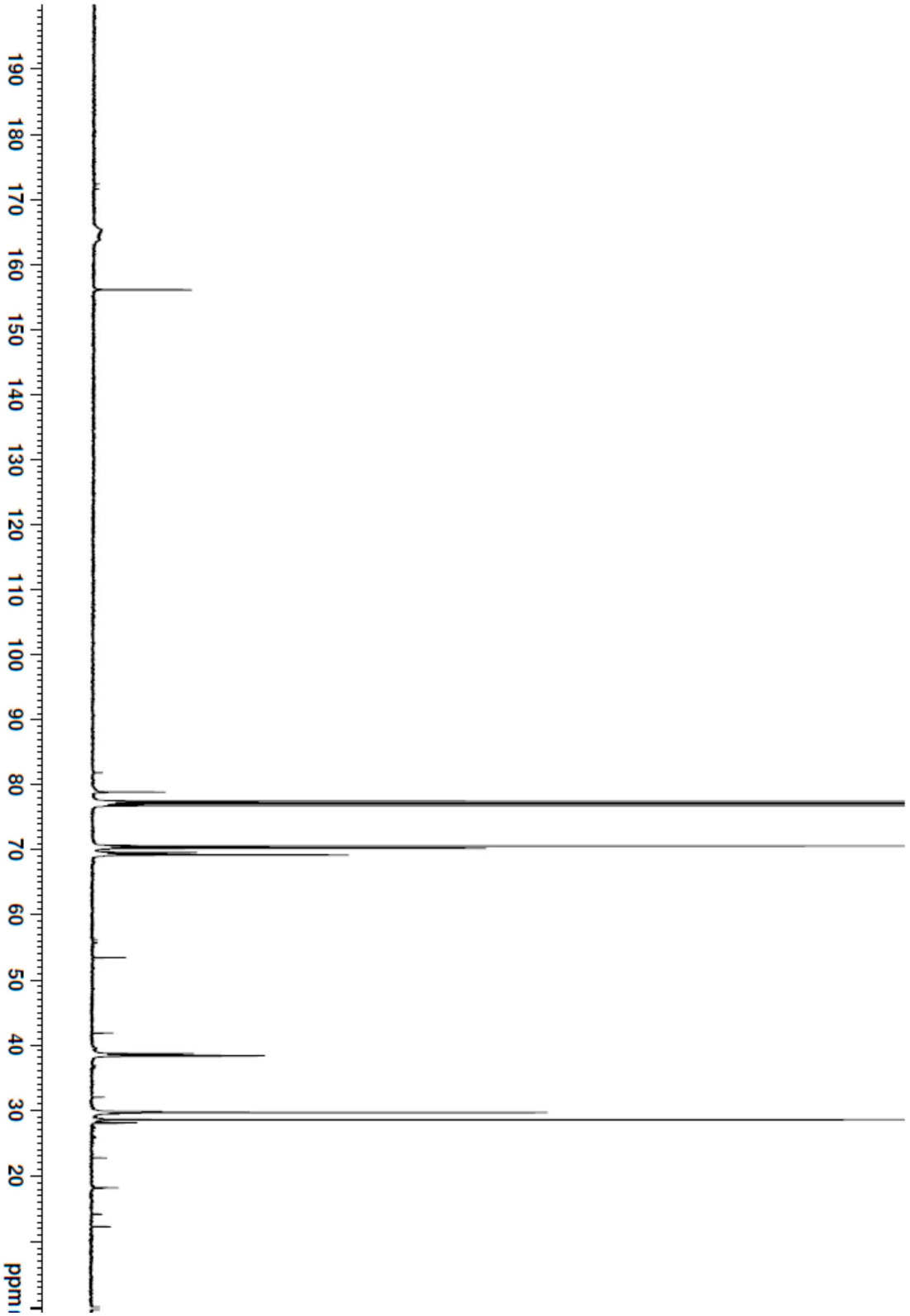


Figure S19. ^{13}C NMR of **G3** (100 MHz, $CDCl_3$).

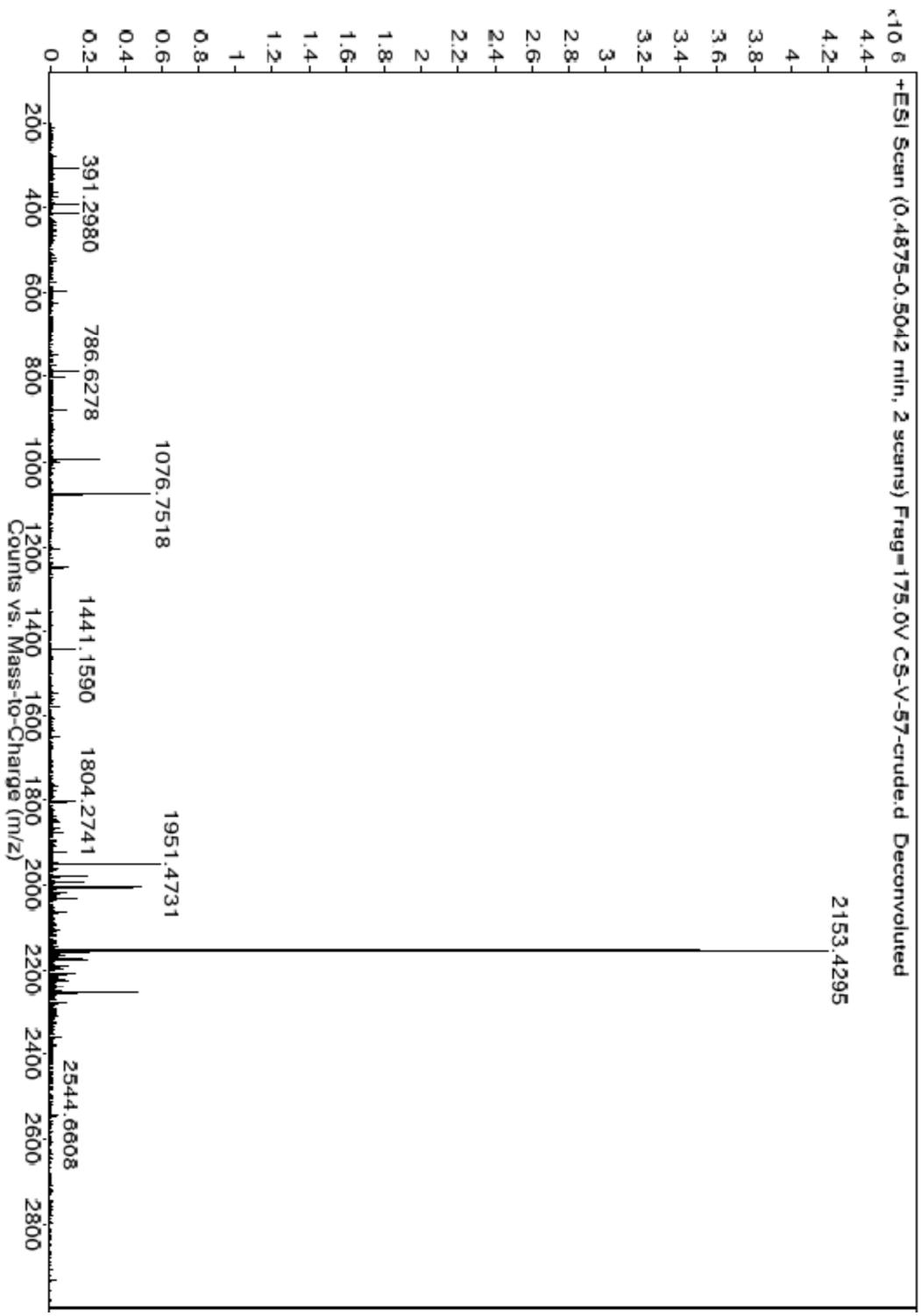


Figure S20. ESI-TOF MS of **6**. The line at *m*/*z* 1076 is the doubly charged species. The line at *m*/*z* 1951 is not identified.

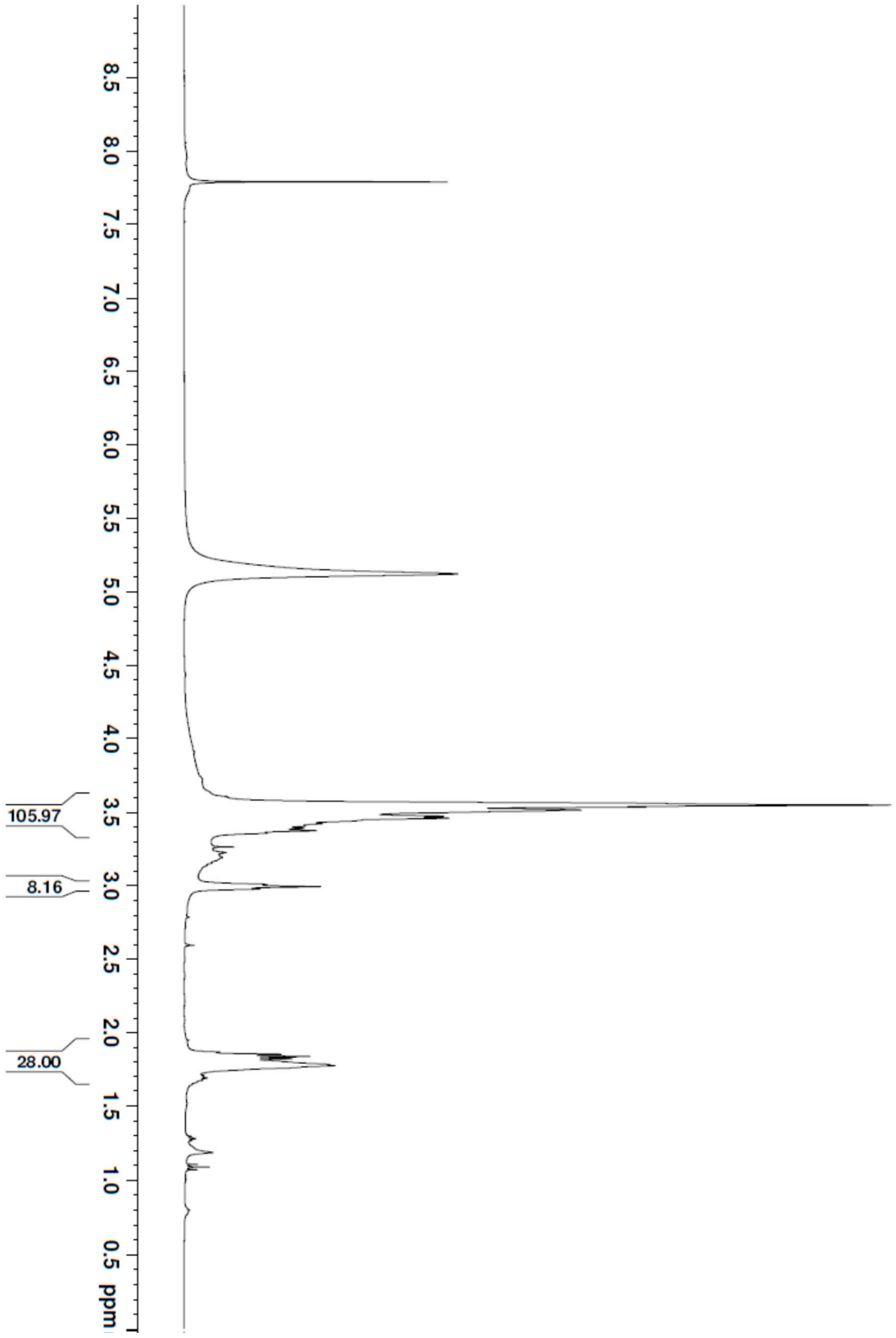


Figure S21. ^{1}H-NMR of **6** (400 MHz, CD_3OD).

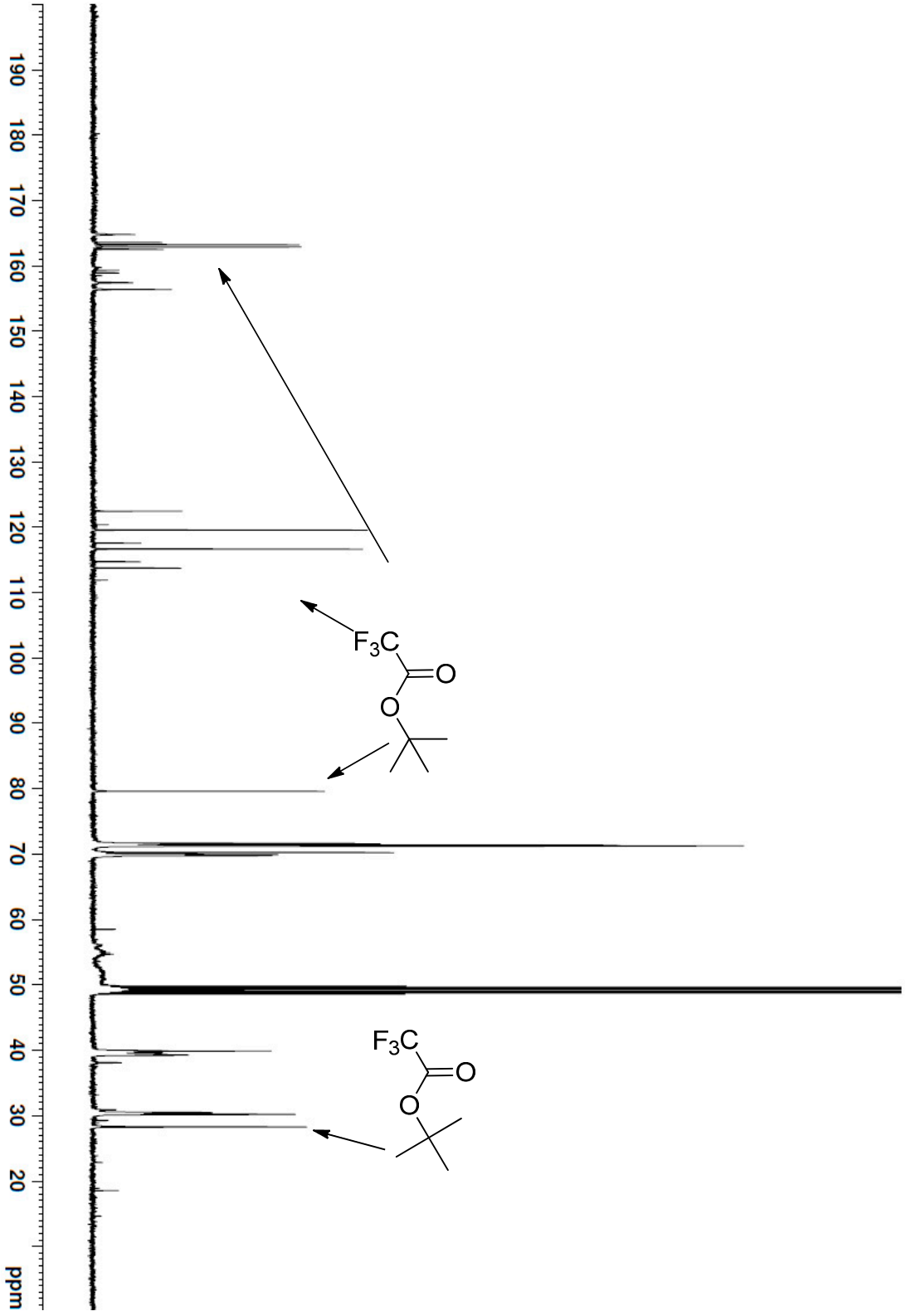


Figure S22. ^{13}C-NMR of **6** (100 MHz, CD_3OD). Lines assigned to t-butyl trifluoroacetate are identified.

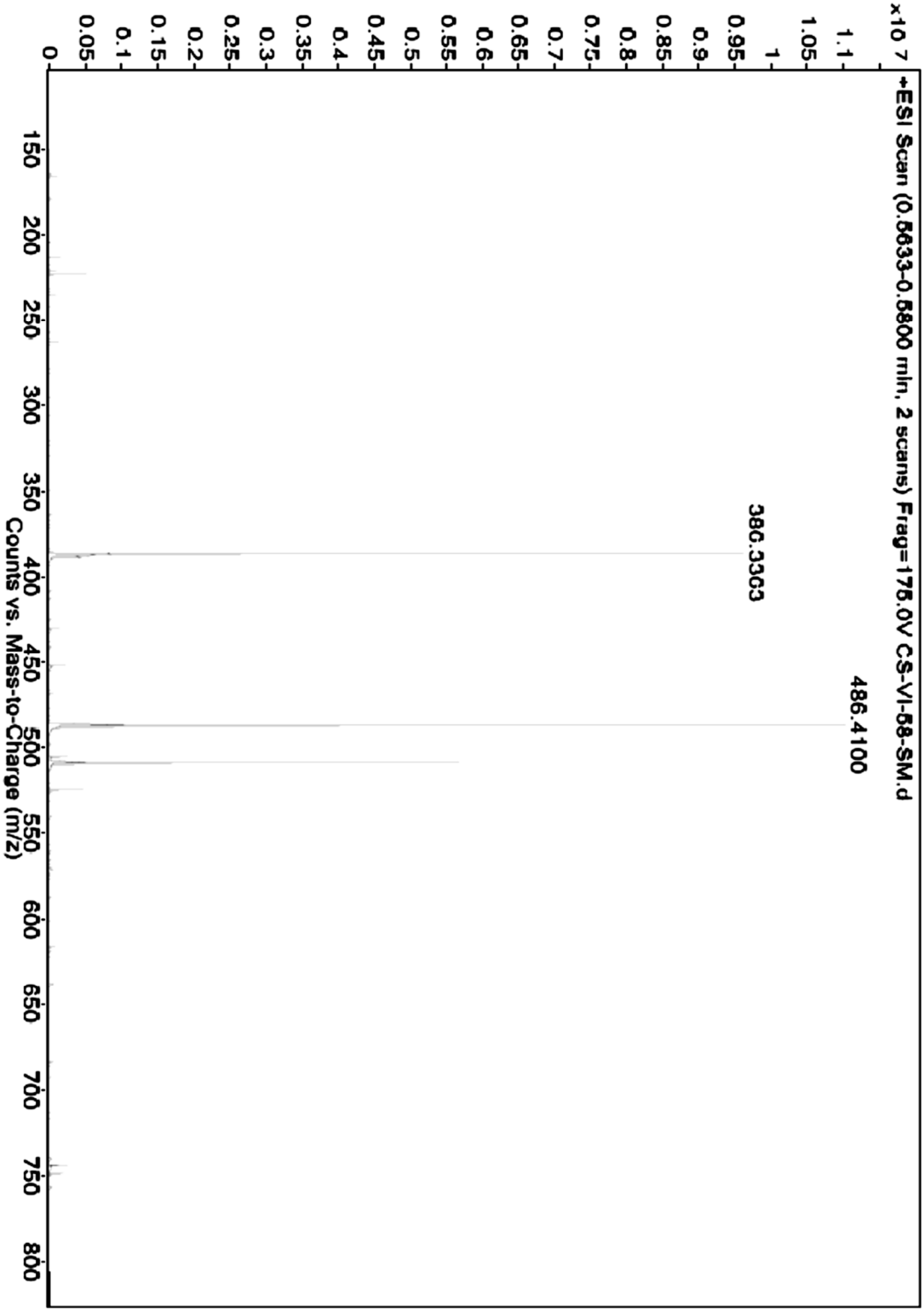


Figure S23. ESI-TOF MS of **7**. The line at *m*/*z* 386 is loss of BOC. Other lines correspond to sodium and potassium adducts.

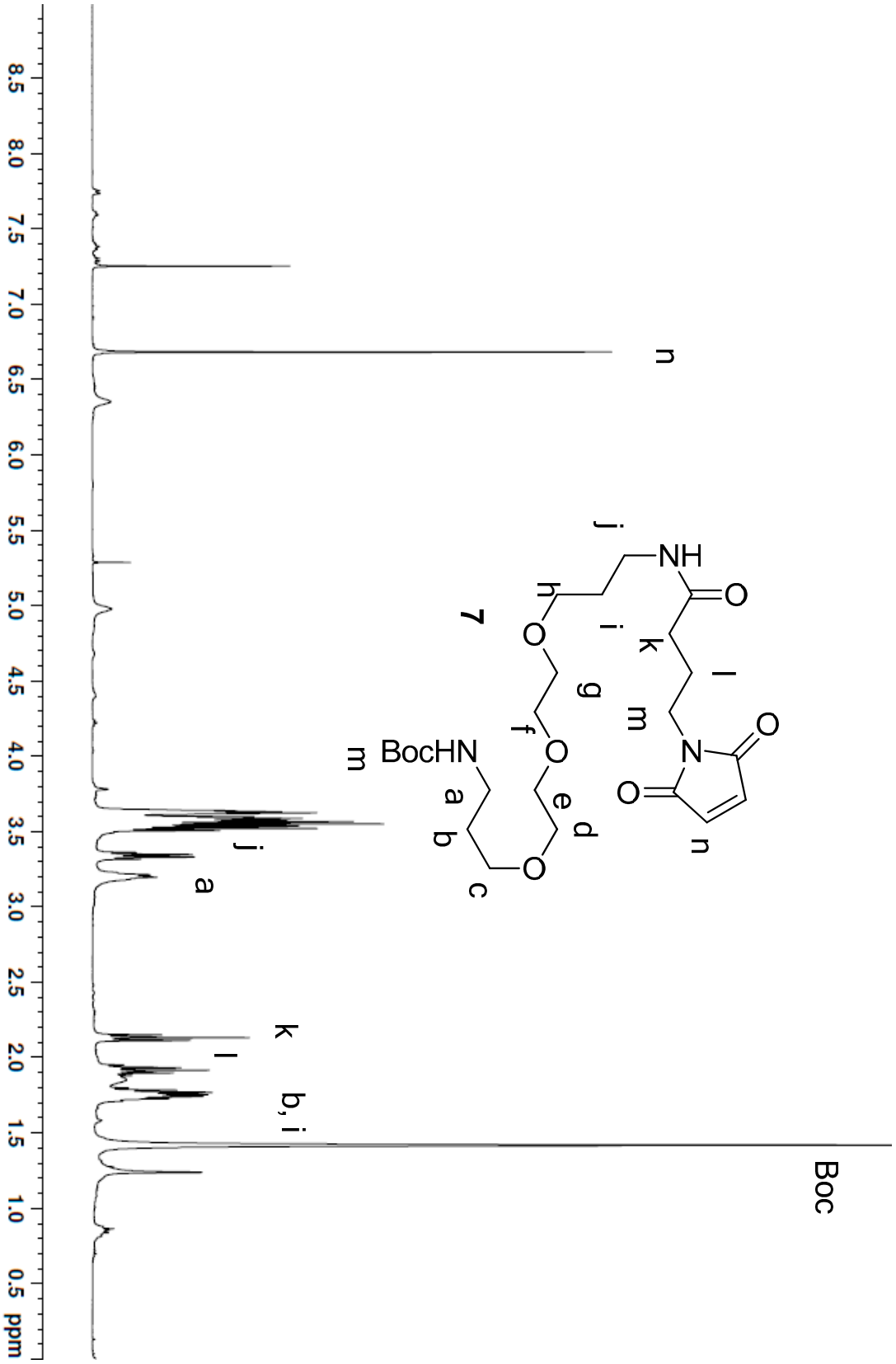


Figure S24. ^{1}H-NMR of **7** (400 MHz, $CDCl_3$).

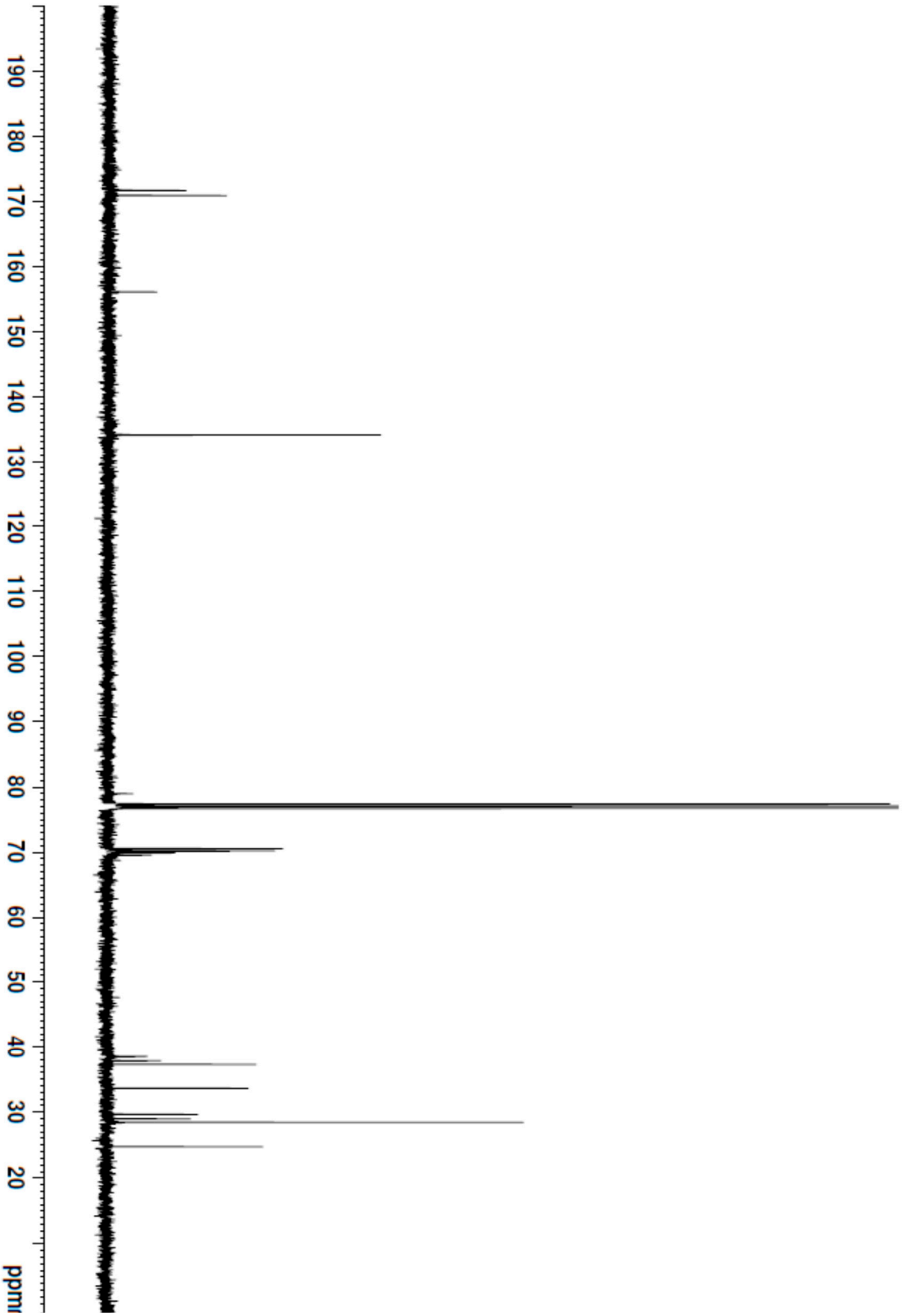


Figure S25 ^{13}C-NMR of **7** (100 MHz, $CDCl_3$).

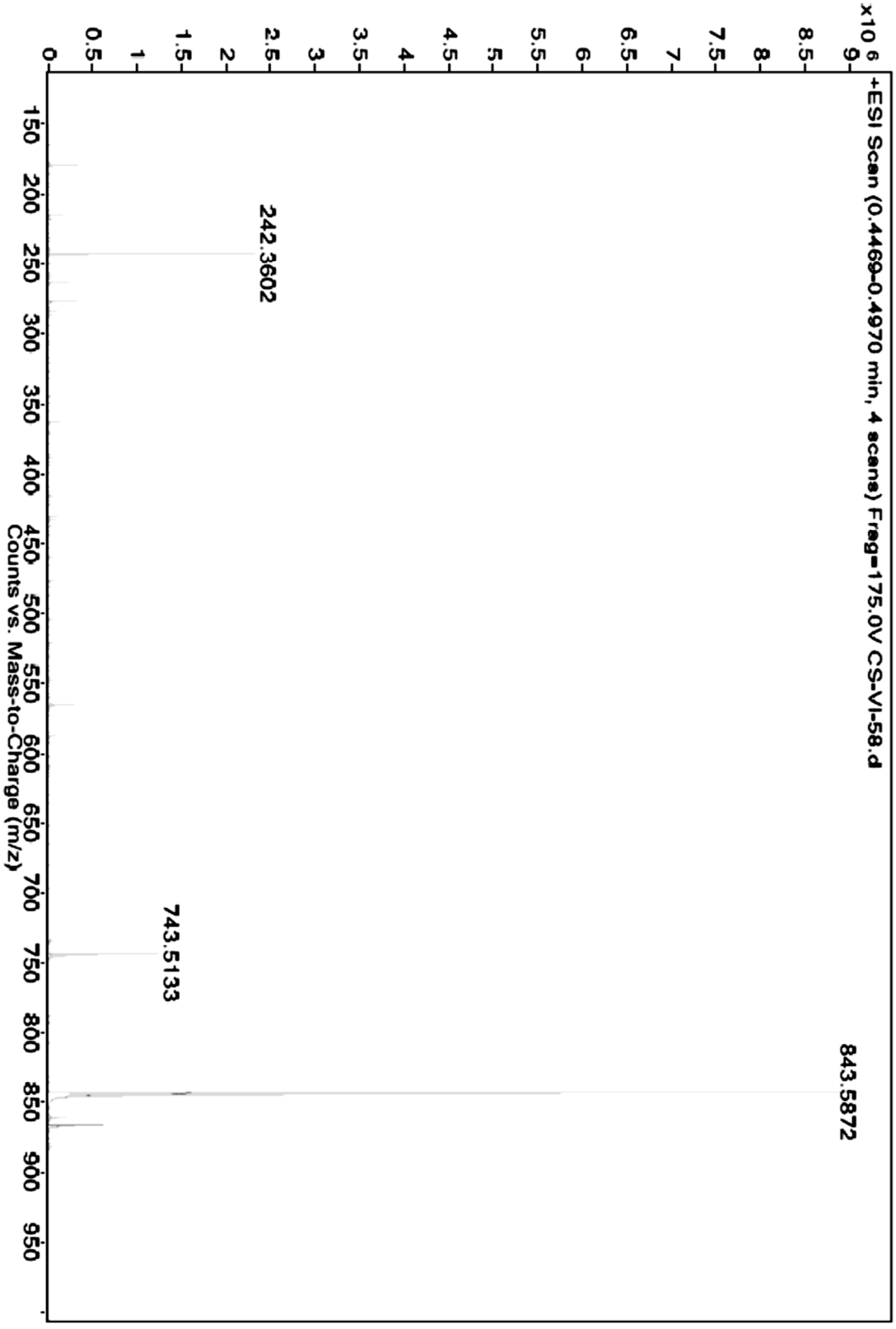


Figure S26. ESI-TOF MS of **7-A**. The spectrum also shows loss of BOC. The line at *m*/*z* 242 is not identified.

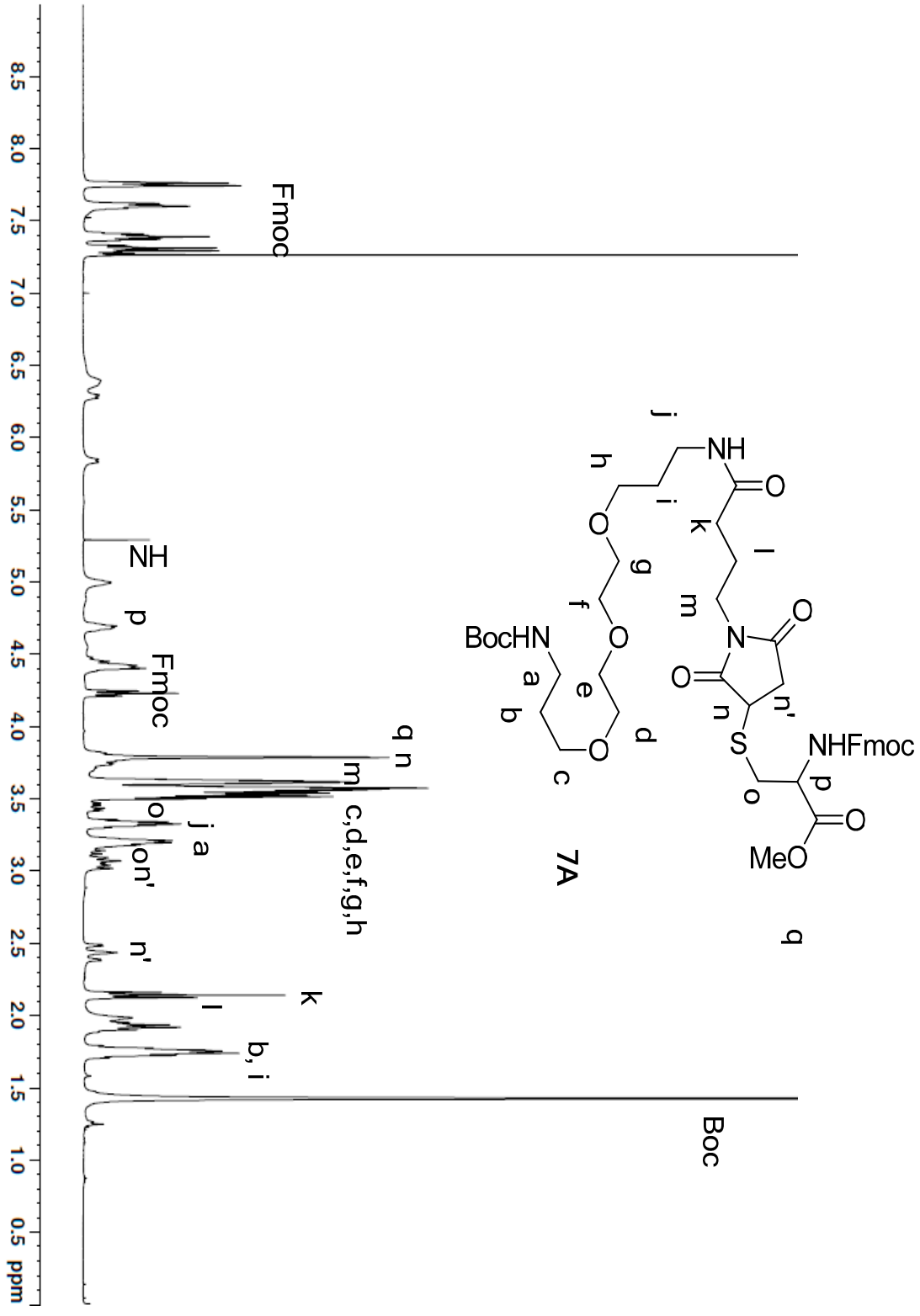


Figure S27. ^{1}H-NMR of **7-A** (400 MHz, $CDCl_3$).

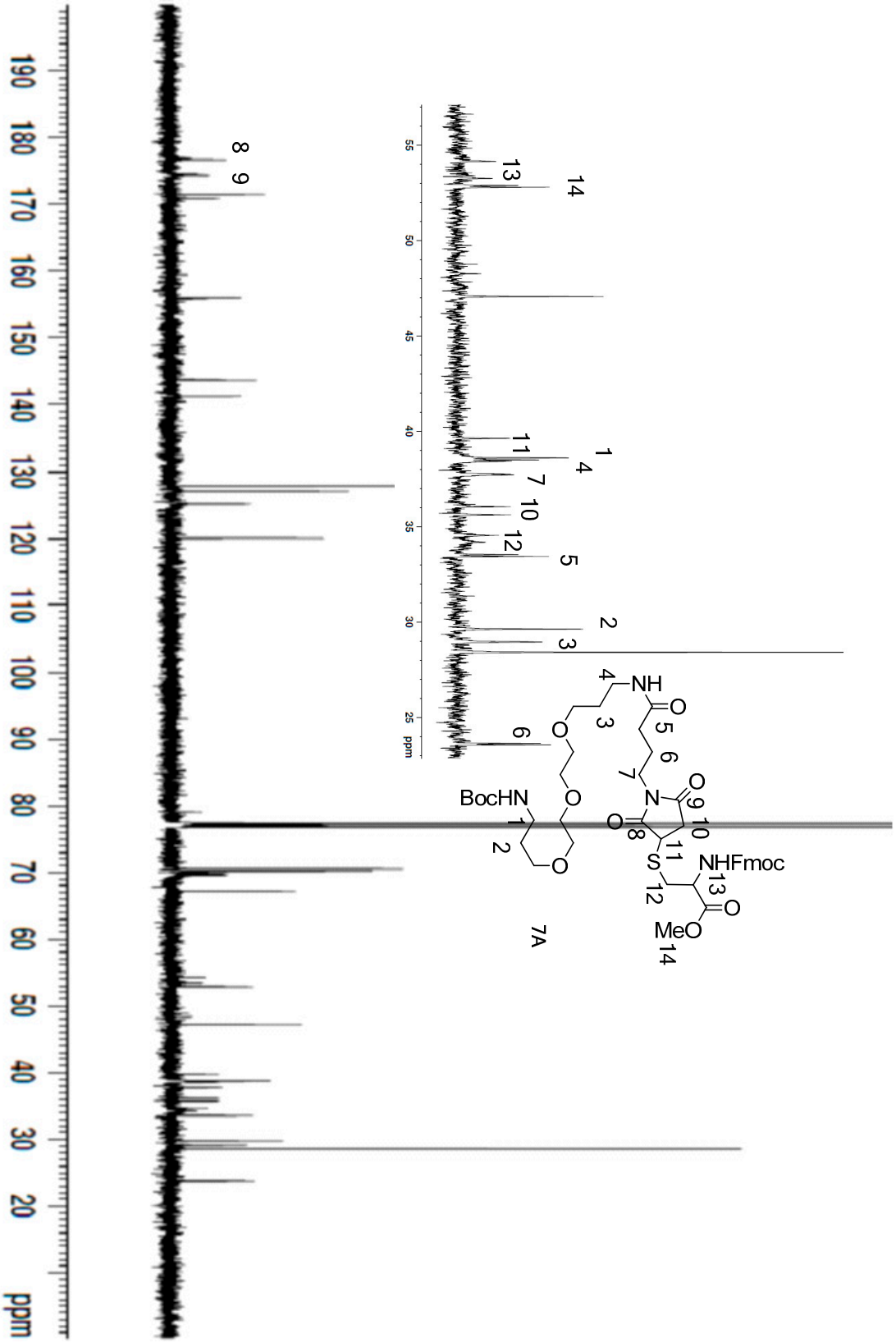


Figure S28. ^{13}C NMR of **7-A** (100 MHz, $CDCl_3$) with inset.

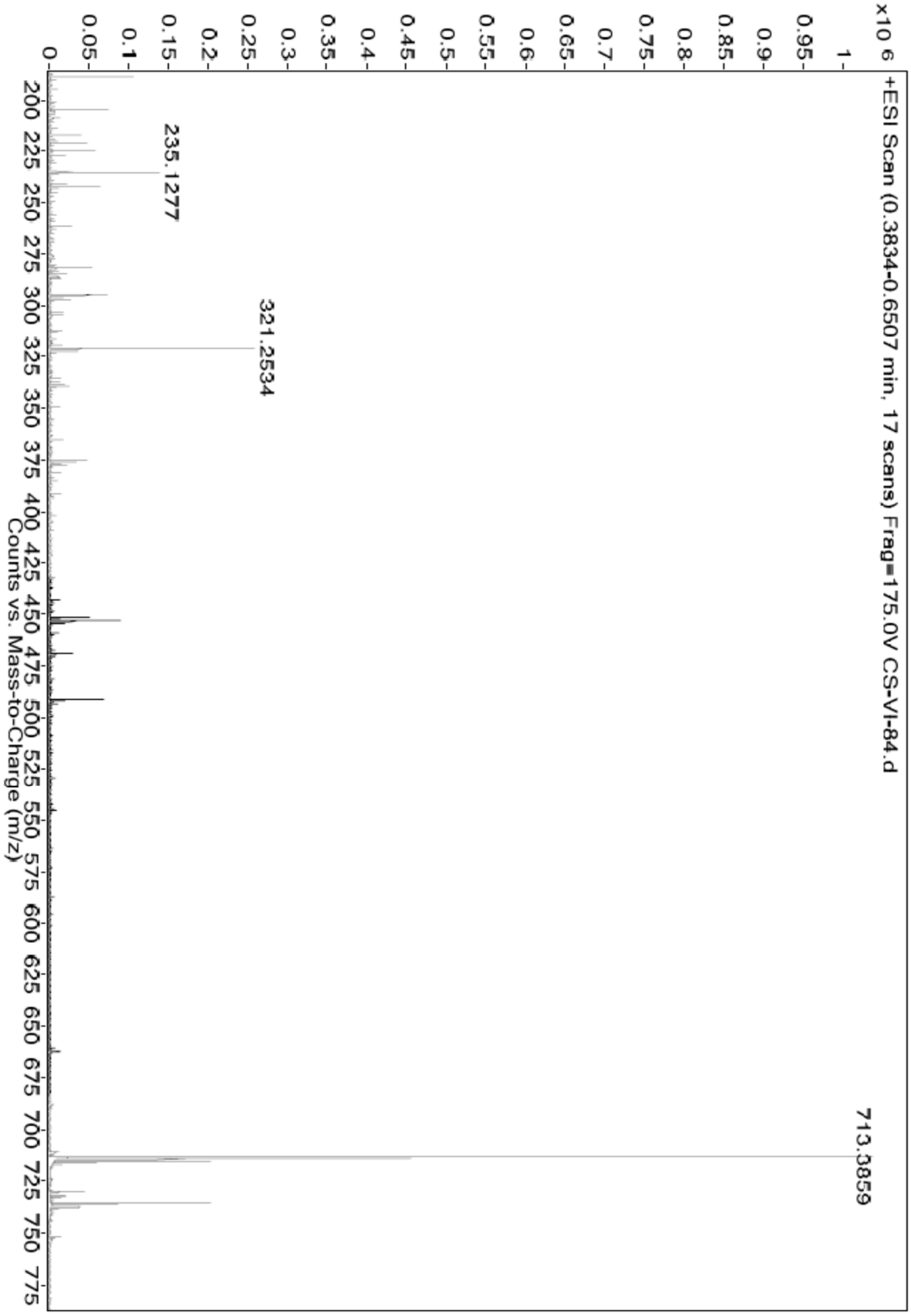


Figure S29. ESI-TOF MS of cysteine.

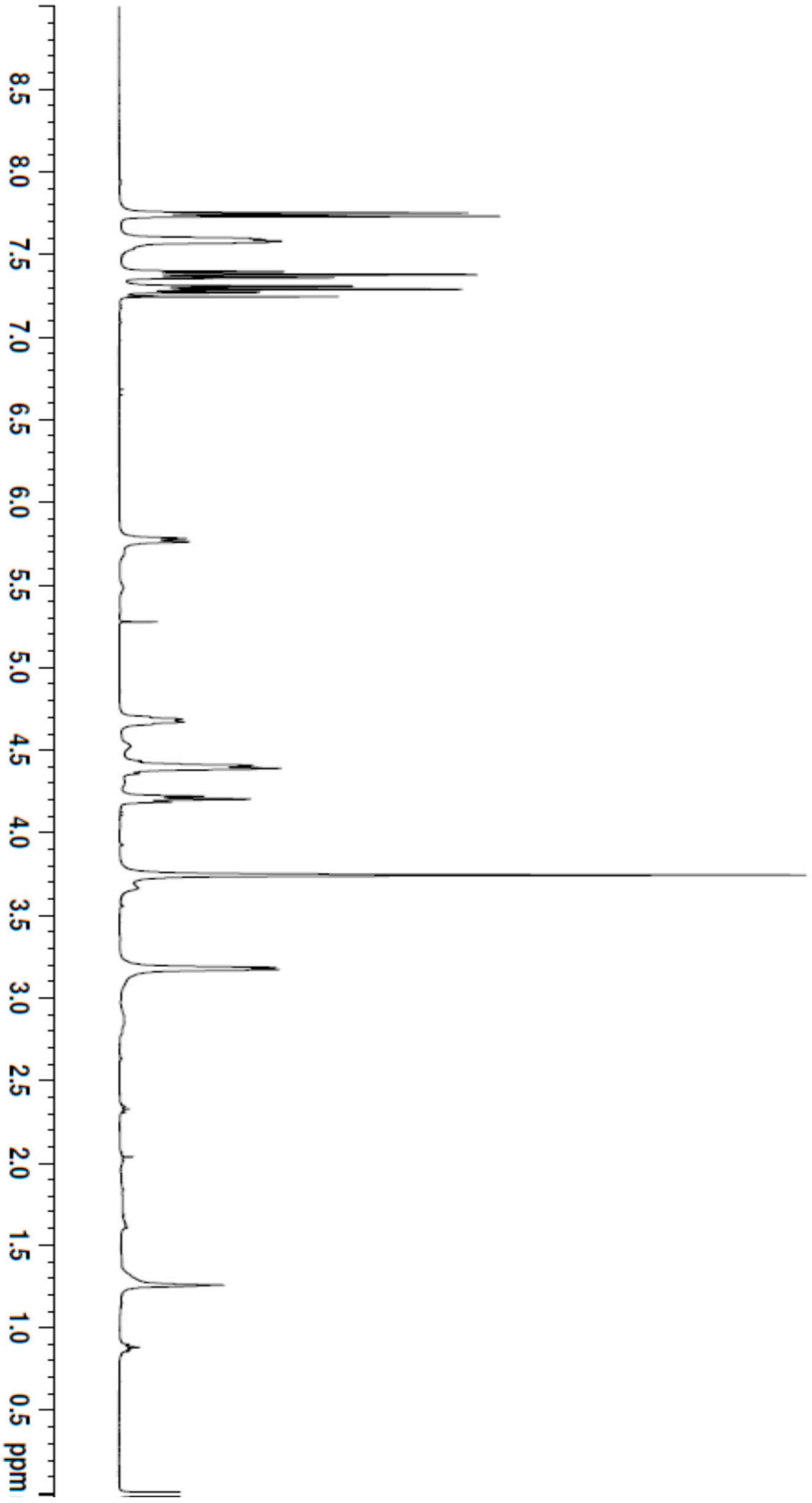


Figure S30. ^{1}H-NMR of cystine (400 MHz, $CDCl_3$).

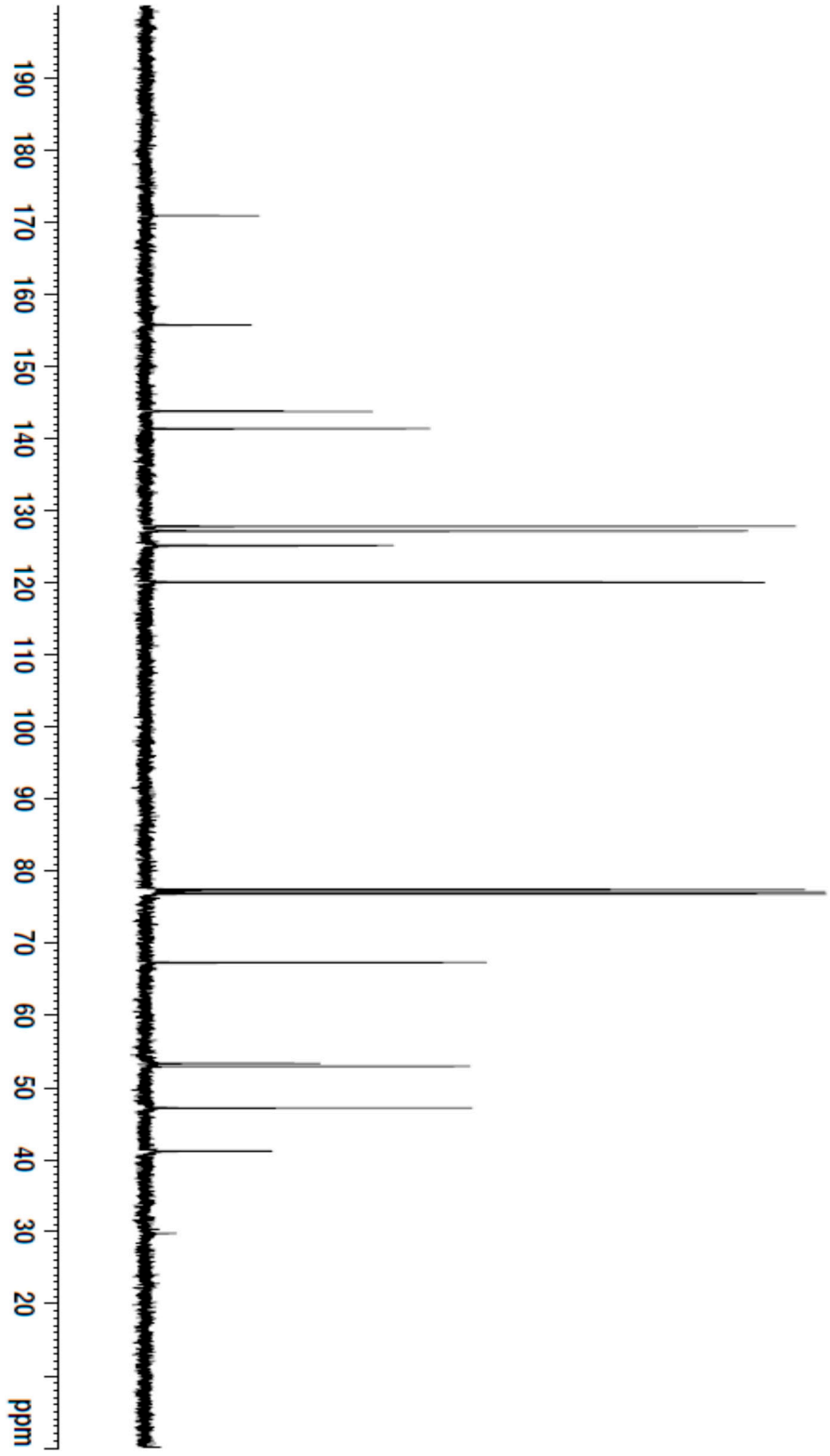


Figure S31. ^{13}C NMR of cystine (100 MHz, $CDCl_3$).

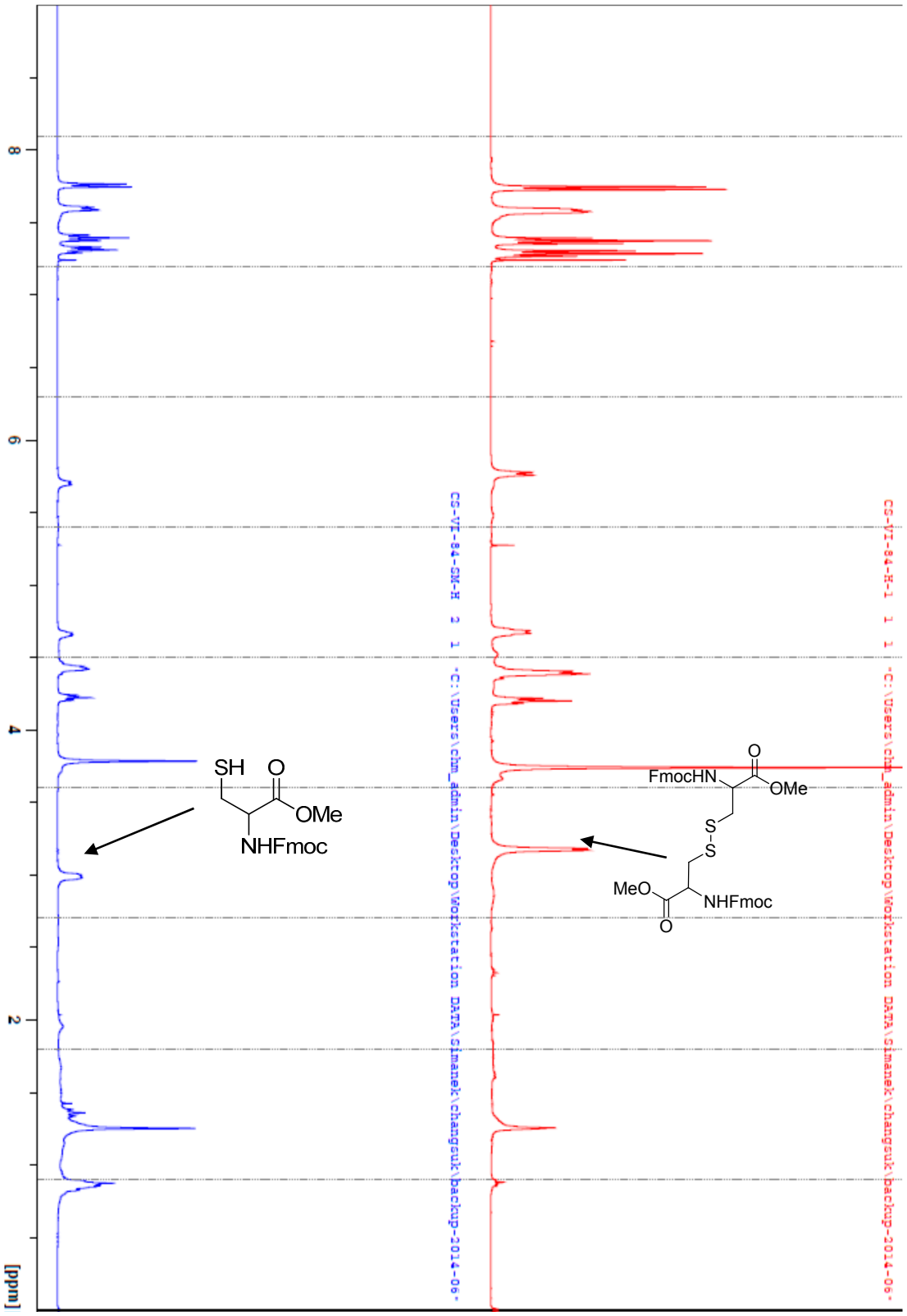


Figure S32. Comparison of **A** and cystine by ^{1}H-NMR (400 MHz, $CDCl_3$).

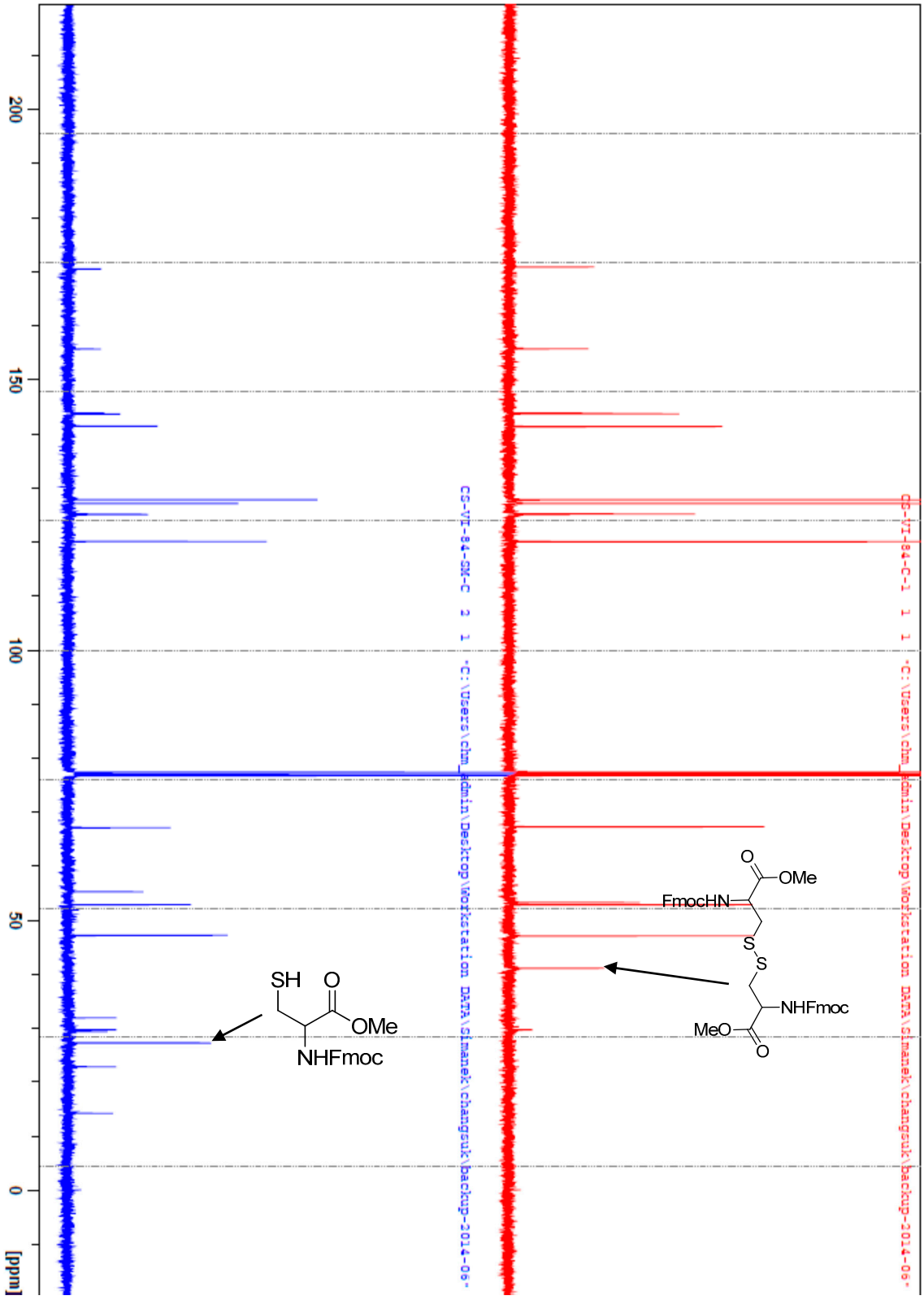


Figure S33. Comparison of **A** and cystine by ^{13}C-NMR

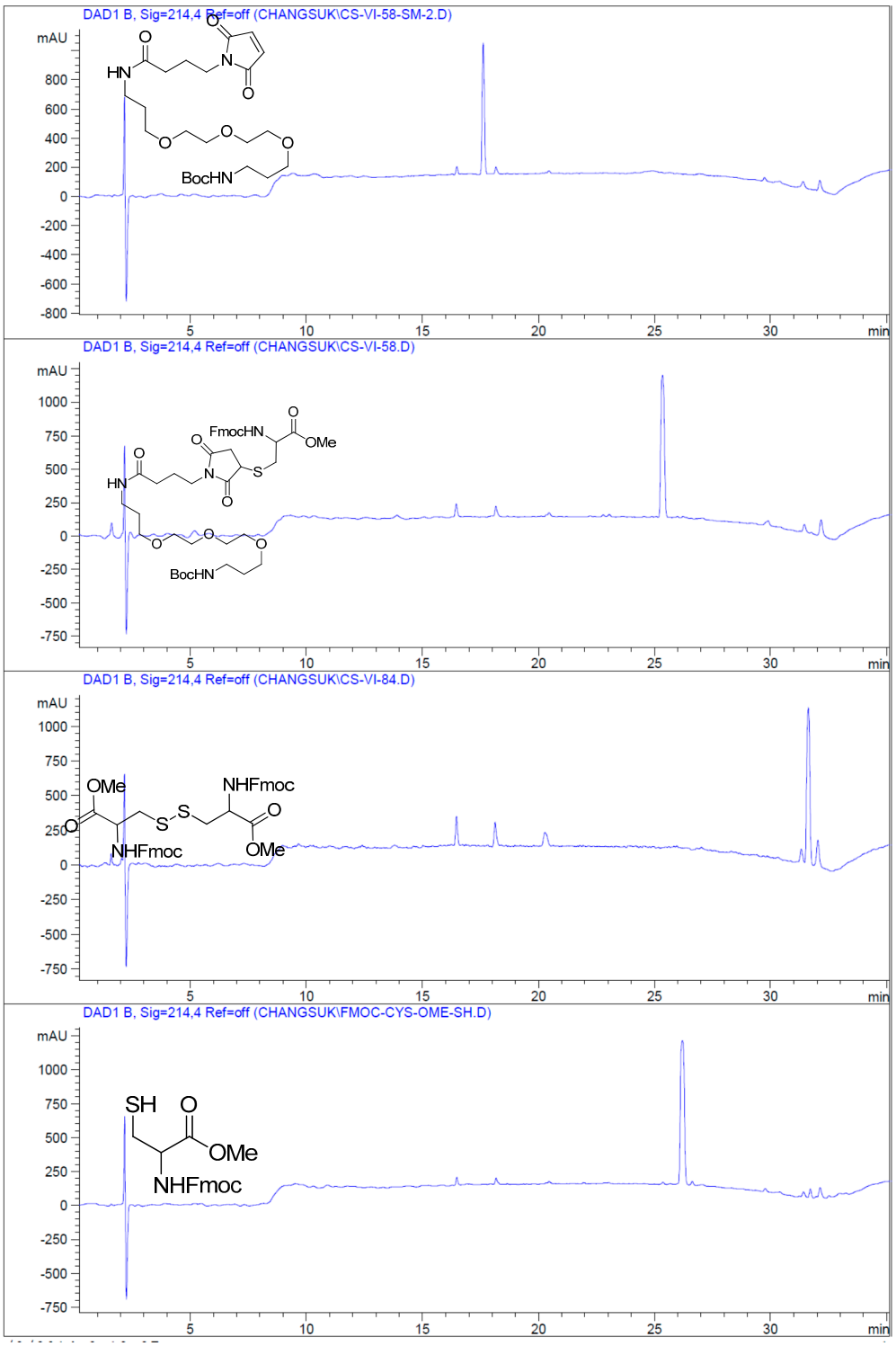


Figure S34. Comparison by HPLC of **7**, **7-A**, and cystine. The mobile phase consisted of water/acetonitrile (A/B, HPLC grade, 0.1% (*w*/*v*) trifluoroacetic acid) at a flow rate of 0.8 mL/min. The elution gradient was 10% MeCN for 5 min, ramp to 90% MeCN in 30 min, and ramp down to 10% MeCN in 15 min. The sample volume injected 5 μL at a concentration of 0.1 mg/mL (Acetonitrile) of each samples and eluted sample was detected at 214 nm.

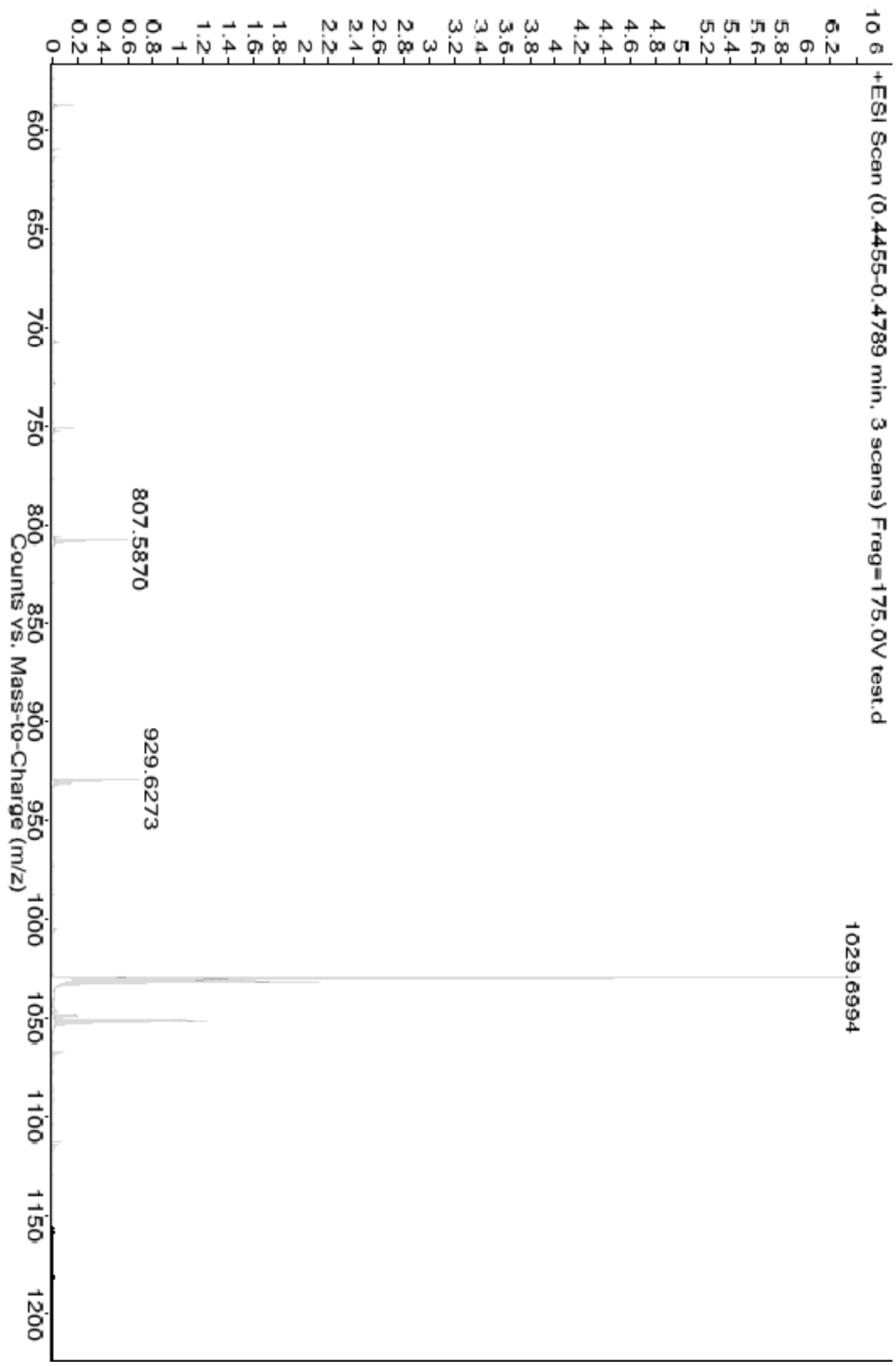


Figure S35. ESI-TOF MS of **7**-**B**. The trace shows loss of BOC. The line at *m*/*z* 807 is not identified.

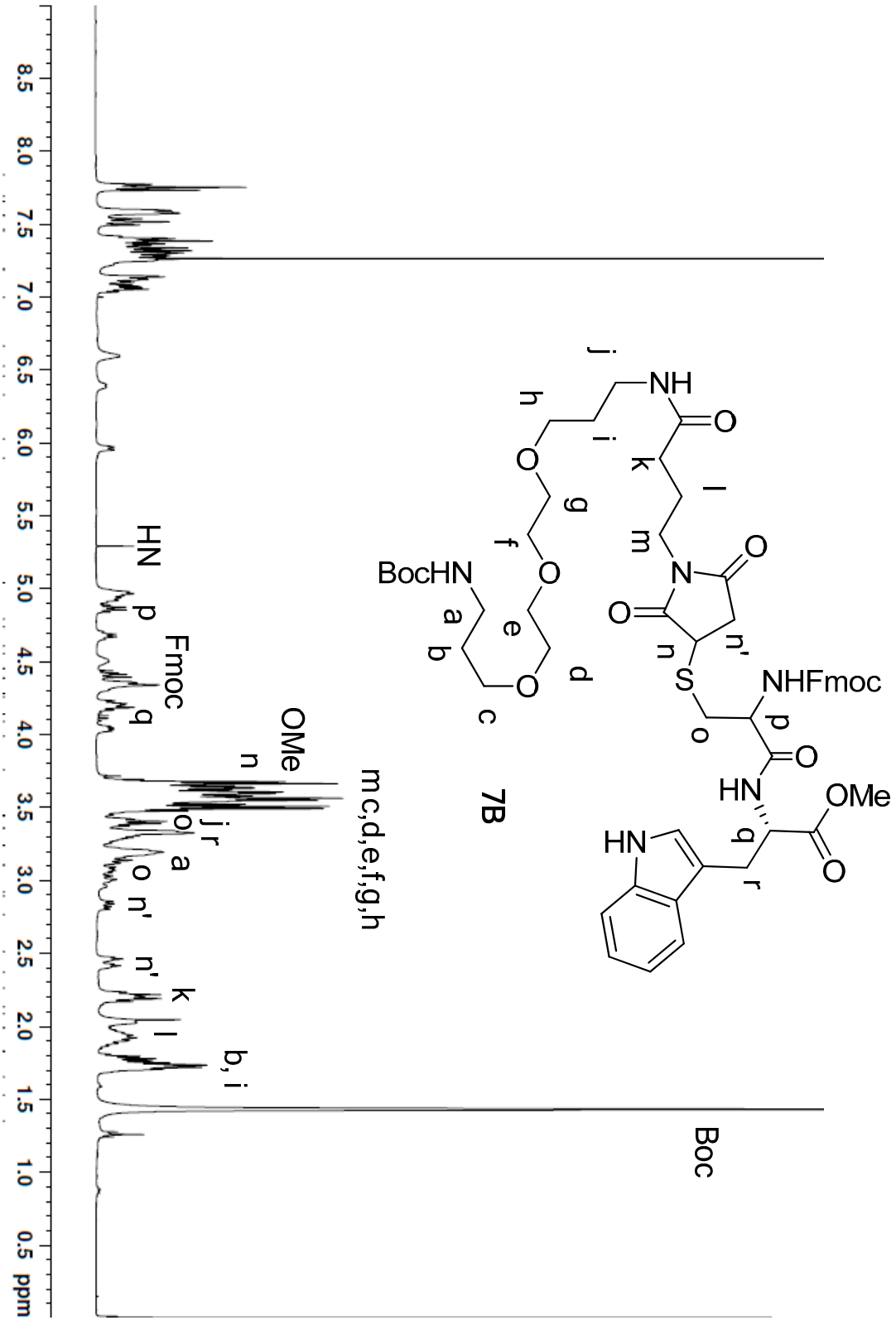


Figure S36. ^{1}H-NMR of **7-B** (400 MHz, $CDCl_3$).

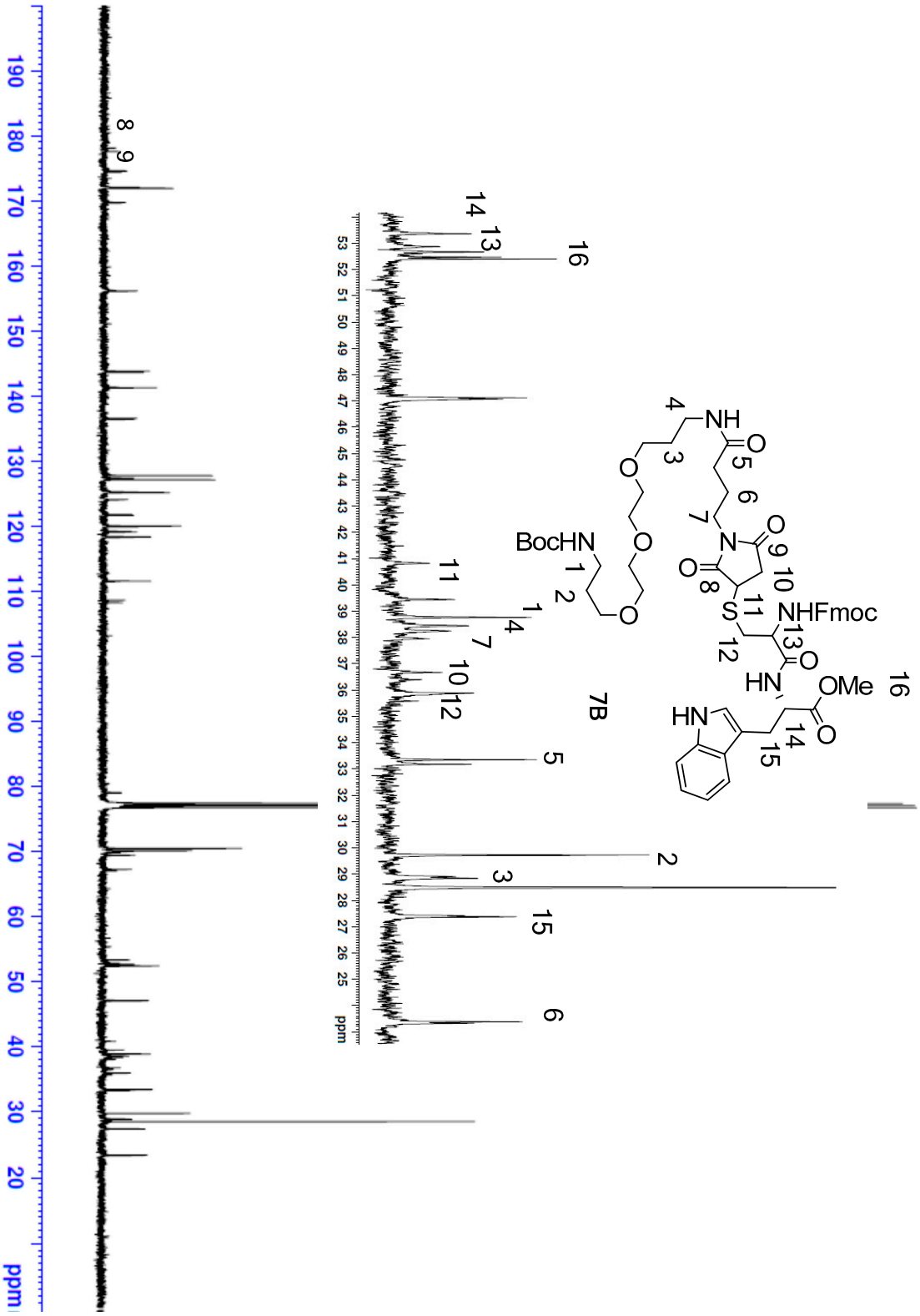


Figure S37. ^{13}C-NMR of **7-B** (100 MHz, $CDCl_3$).

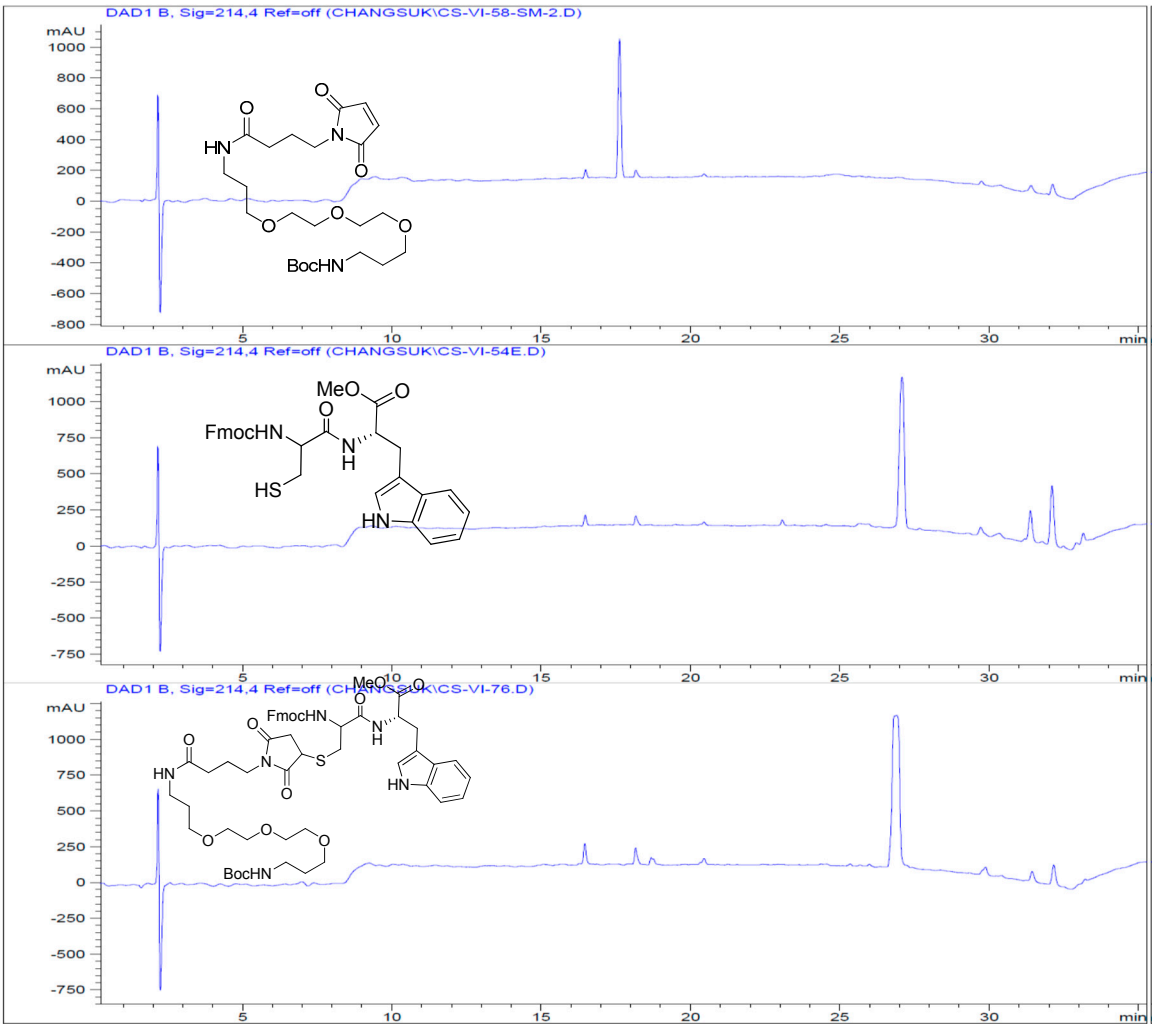


Figure S38. Comparison by HPLC of **7**, **7-B**, and cysteine. The mobile phase consisted of water/acetonitrile (A/B, HPLC grade, 0.1% (*w*/*v*) trifluoroacetic acid) at a flow rate of 0.8 mL/min. The elution gradient was 10% MeCN for 5 min, ramp to 90% MeCN in 30 min, and ramp down to 10% MeCN in 15 min. The sample volume injected 5 μL at a concentration of 0.1 mg/mL (Acetonitrile) of each samples and eluted sample was detected at 214 nm.

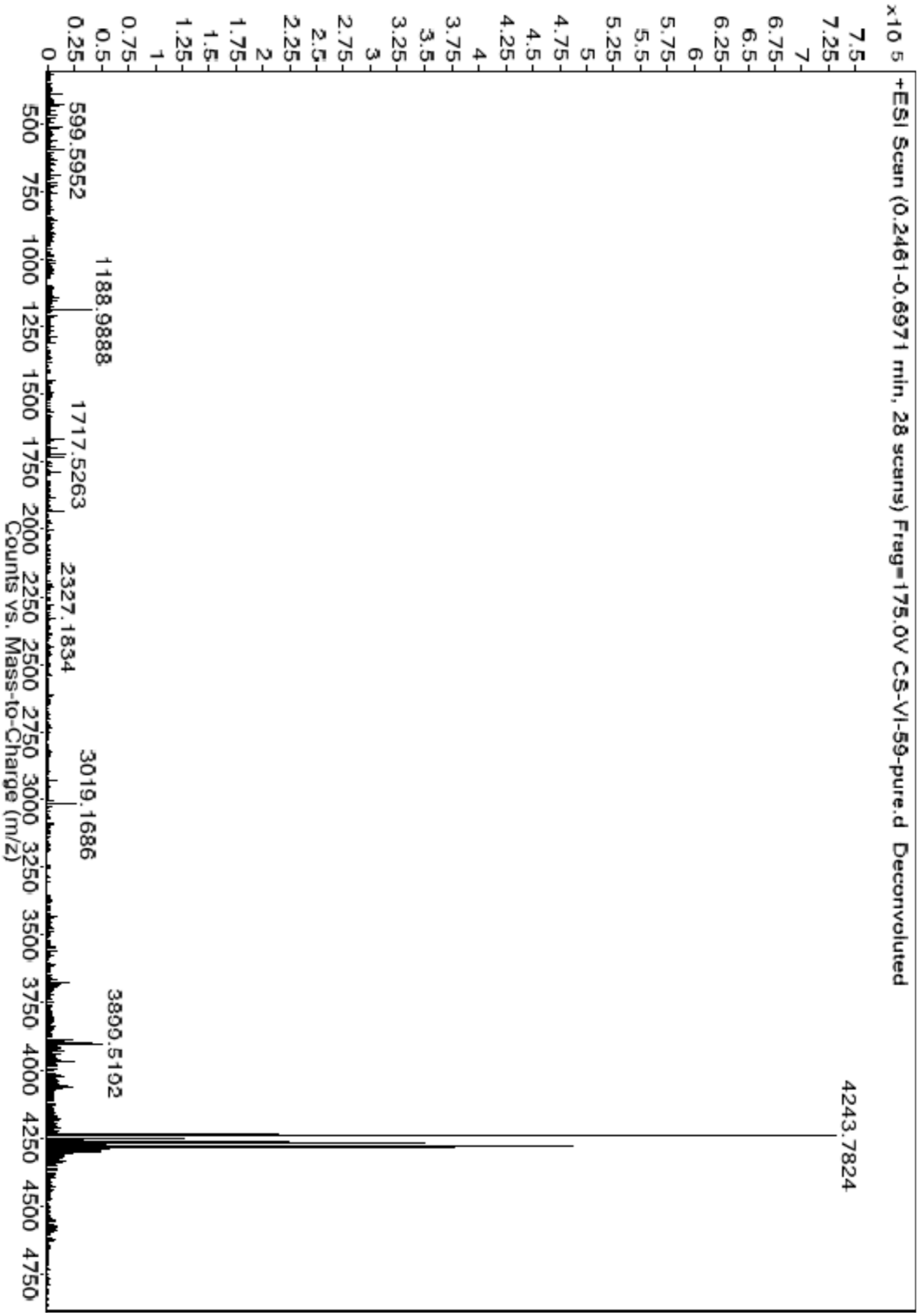


Figure S39. ESI-TOF MS of **1-A4**. The line at m/z 3899 corresponds to **1-A3**.

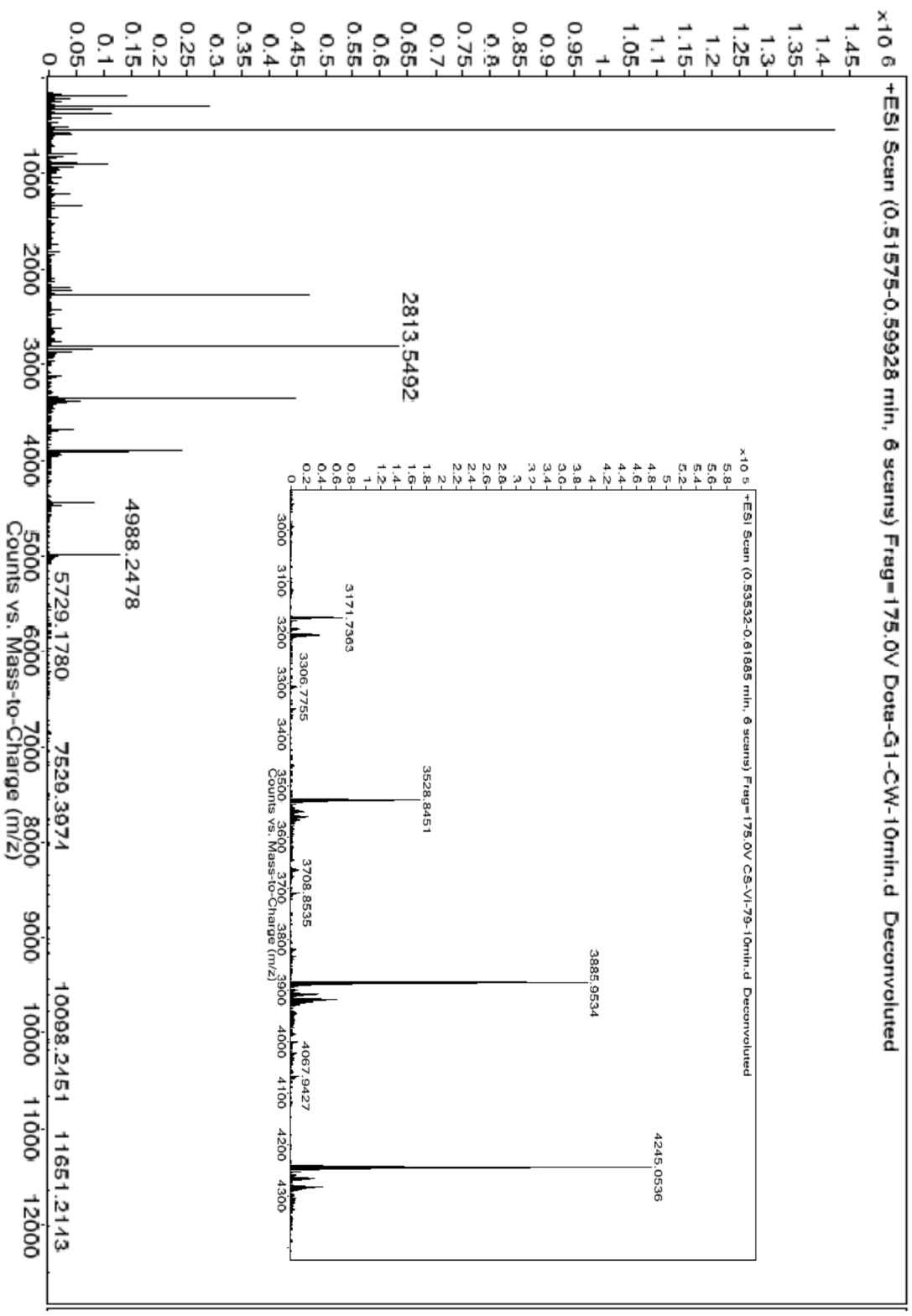


Figure S40. ESI-TOF MS of **1-A4** after 10 min. Lines corresponding to **1**, **1-A1**, **1-A2**, **1-A3,** and **1-A4** are clearly visible.

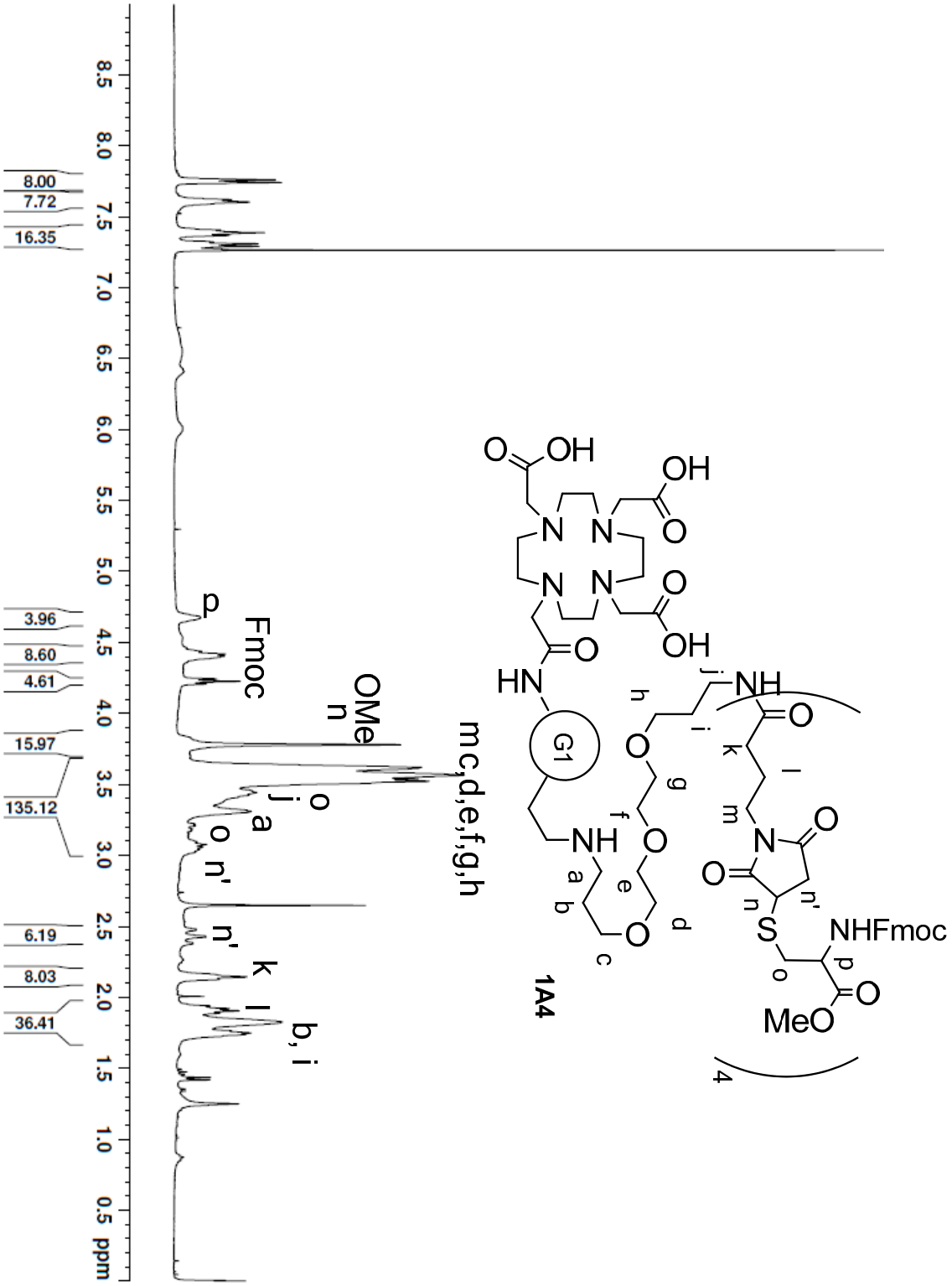


Figure S41. ^{1}H-NMR of **1-A$_4$** (400 MHz, CDCl$_3$).

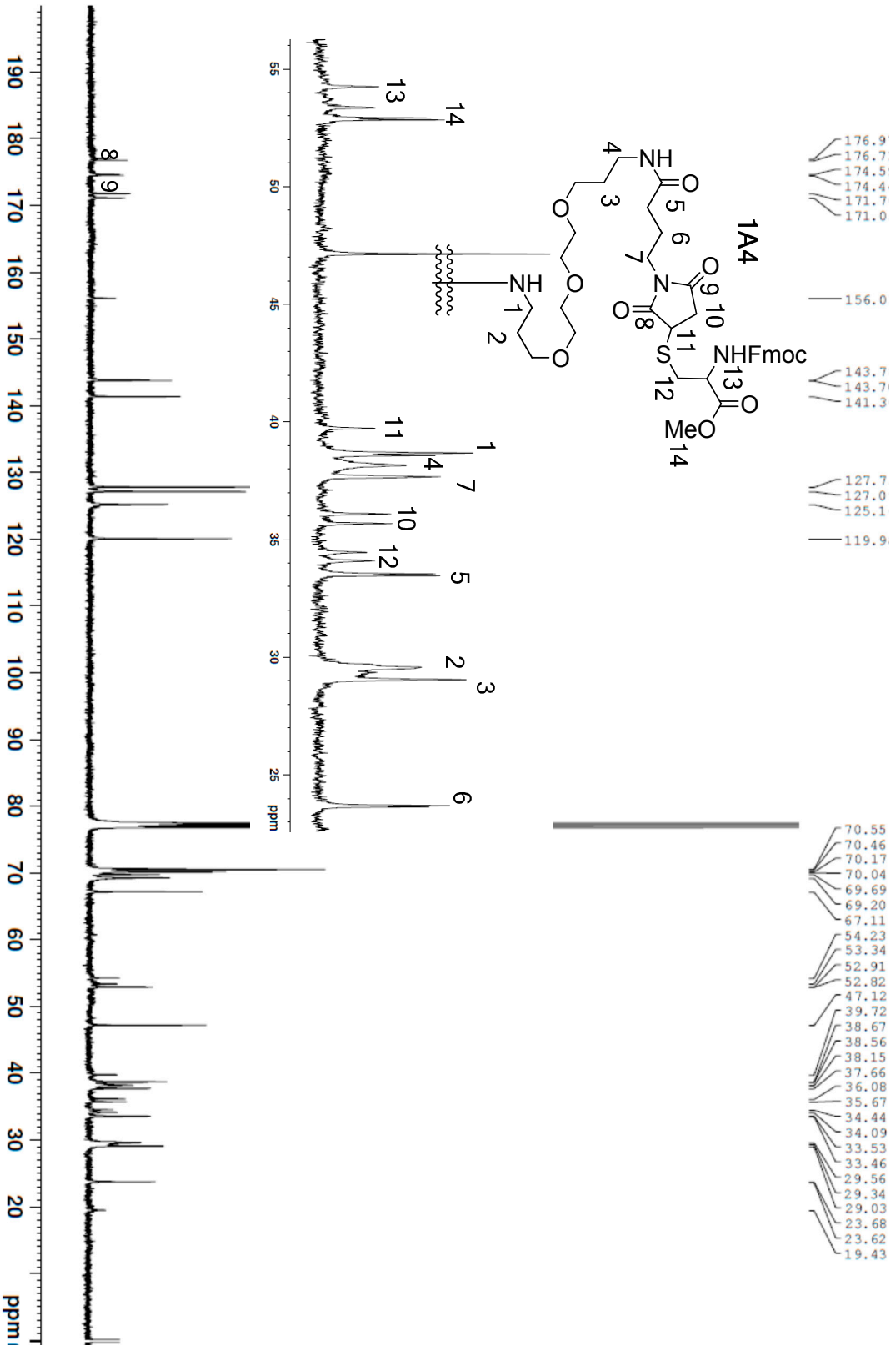


Figure S42. ^{13}C-NMR of **1-A$_4$** (100 MHz, $CDCl_3$).

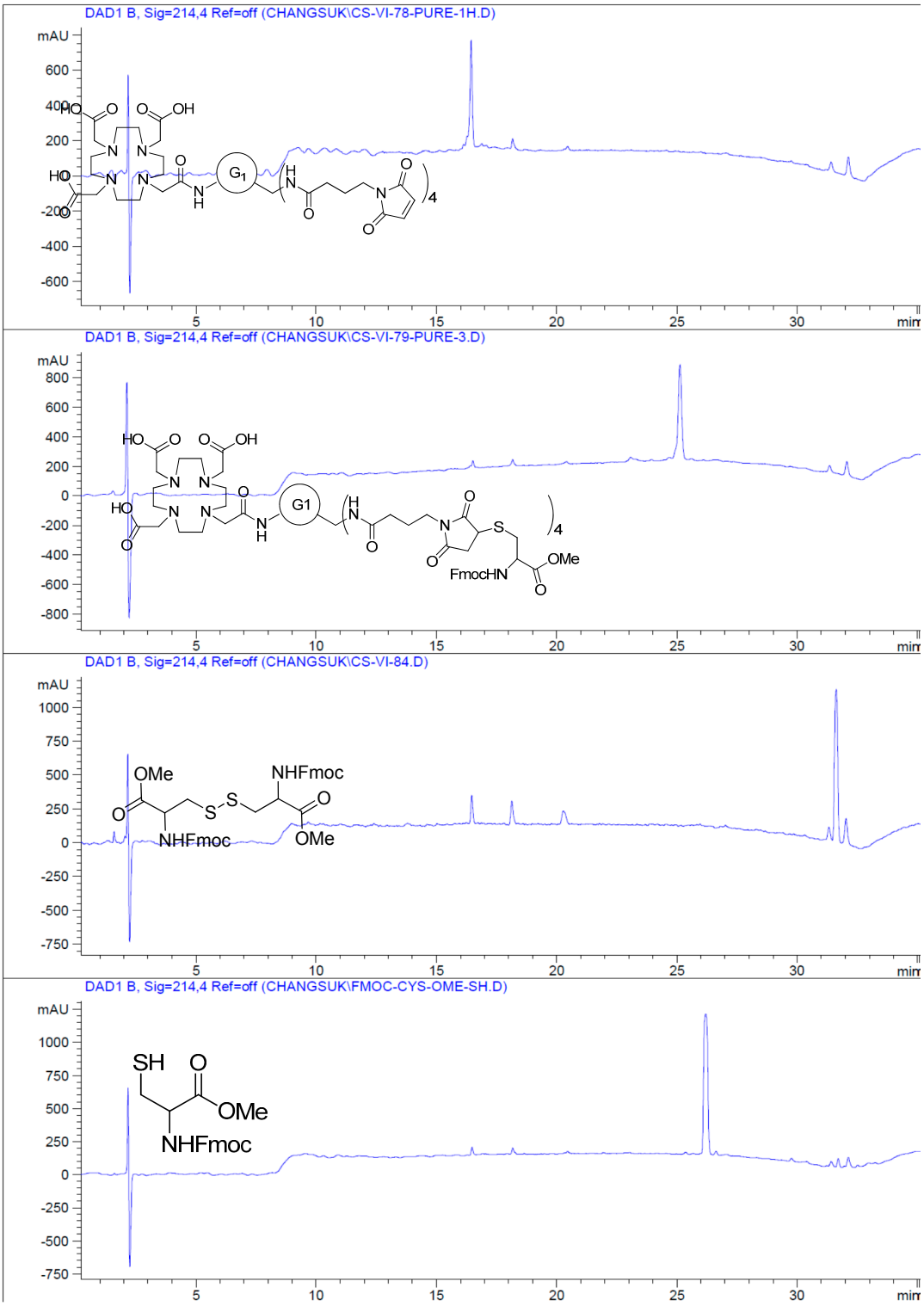


Figure S43. Comparison by HPLC of **1**, **1-A**$_4$, and cysteine. The mobile phase consisted of water/acetonitrile (A/B, HPLC grade, 0.1% (*w*/*v*) trifluoroacetic acid) at a flow rate of 0.8 mL/min. The elution gradient was 10% MeCN for 5 min, ramp to 90% MeCN in 30 min, and ramp down to 10% MeCN in 15 min. The sample volume injected 5 μL at a concentration of 0.1 mg/mL (Acetonitrile) of each samples and eluted sample was detected at 214 nm.

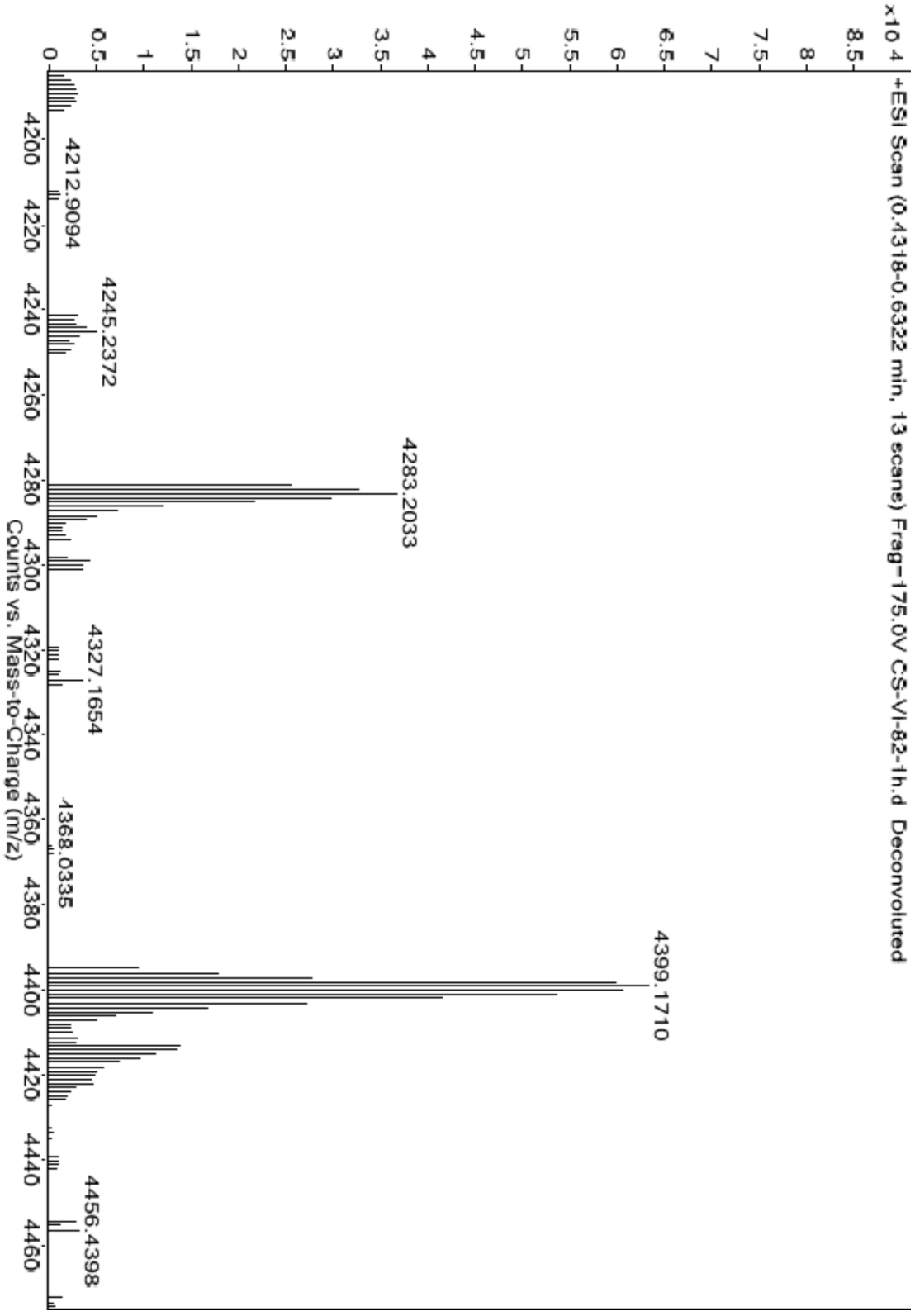


Figure S44. Gd-adduct of **1-A4** by ESI-TOF MS. Calcd. for $C_{203}H_{289}GdN_{35}O_{56}S_4$ 4398.8966, found 4399.1710 $(M + Gd)^+$. The line at *m*/*z* 4245 is **1-A4** while *m*/*z* 4283 is the K^+ adduct of **1-A4**.

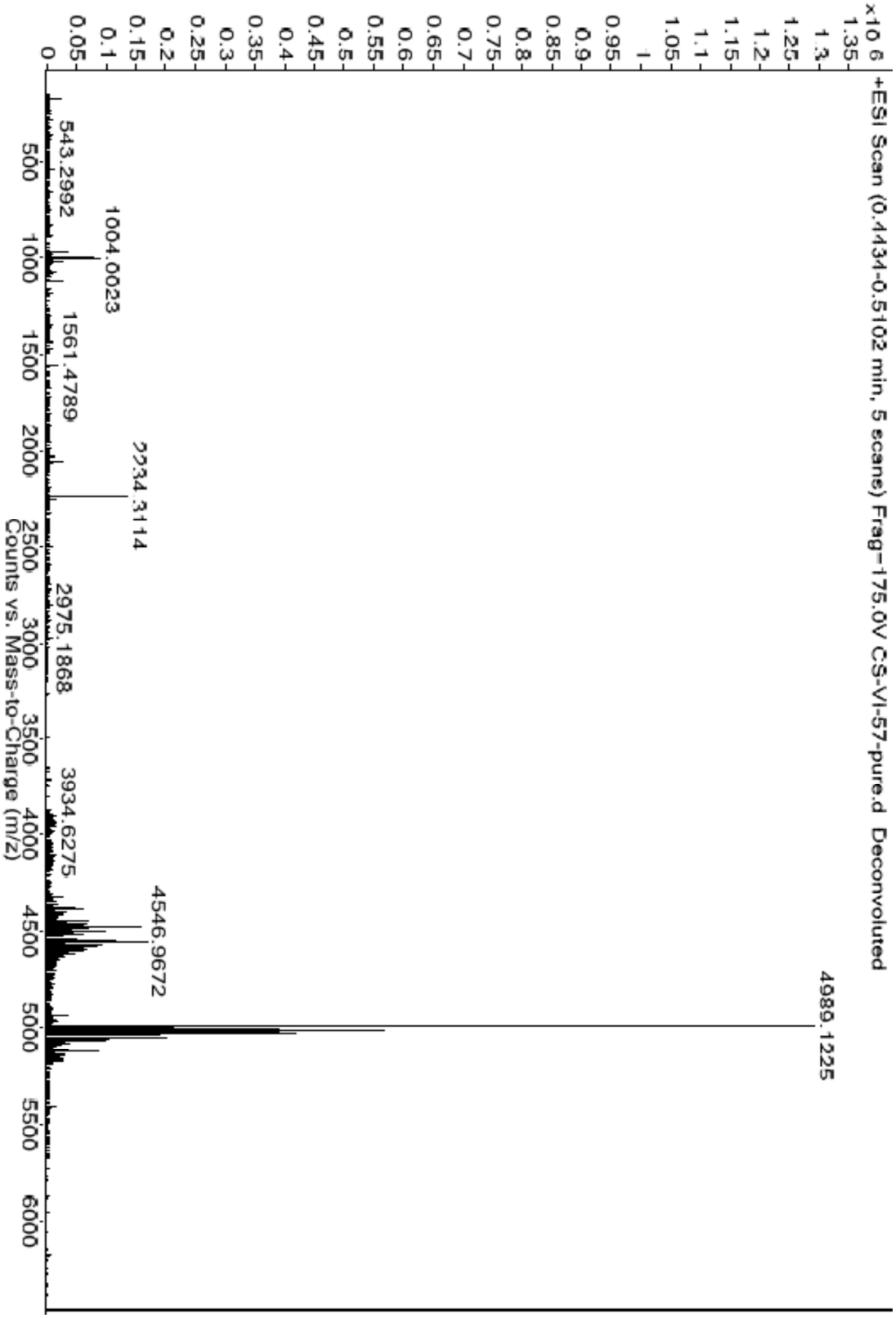


Figure S45. ESI-TOF MS of **1-B4**. The lines identified as *m*/*z* 4546 and 3934 likely correspond to **1-B3** and **1-B2**, respectively.

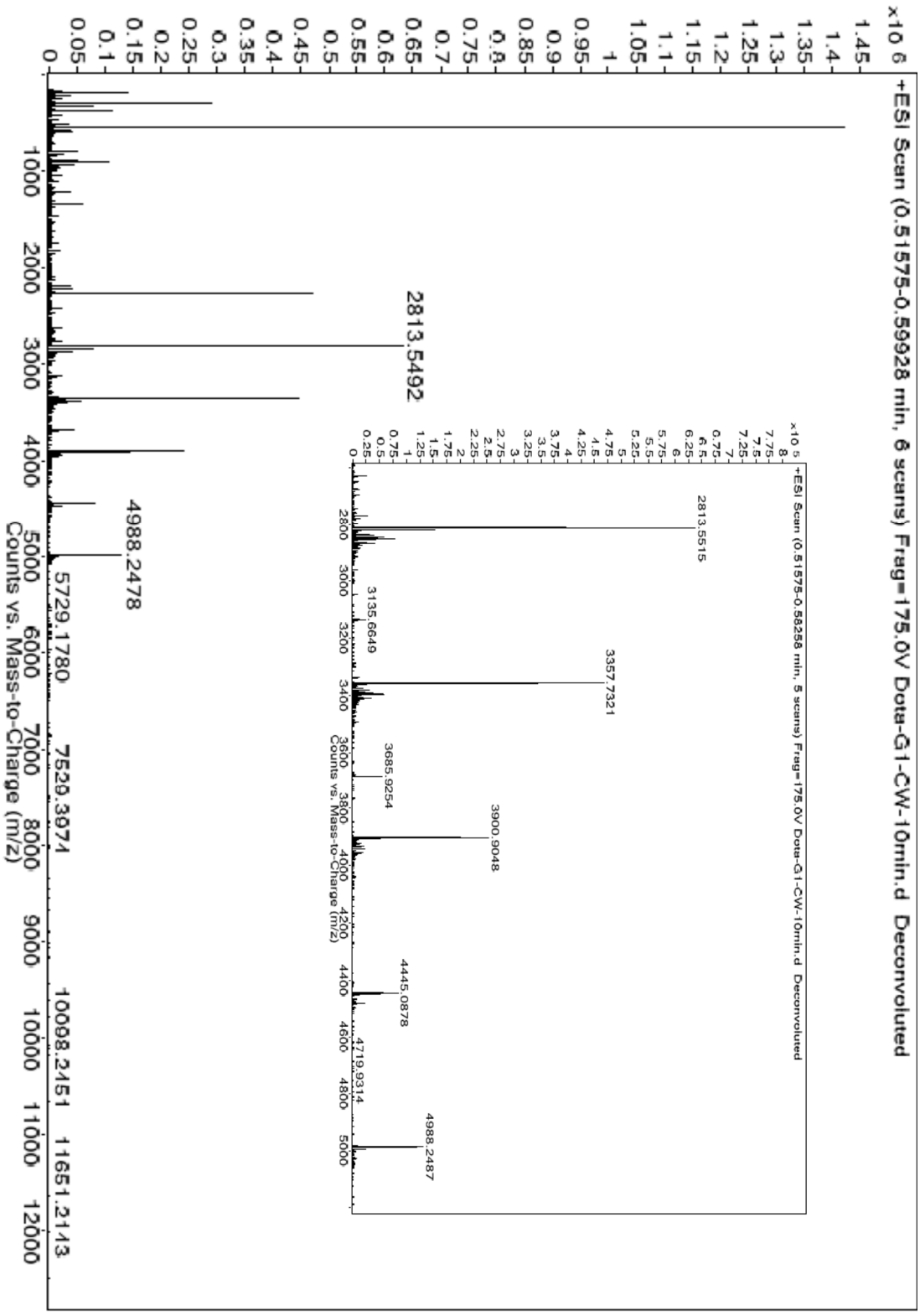


Figure S46. ESI-TOF MS of **1-B4** after 10 min. The lines identified as *m*/*z* 2813, 3357, 3900, and 4445 likely correspond to **1**, **1-B1**, **1-B2** and **1-B3**, respectively.

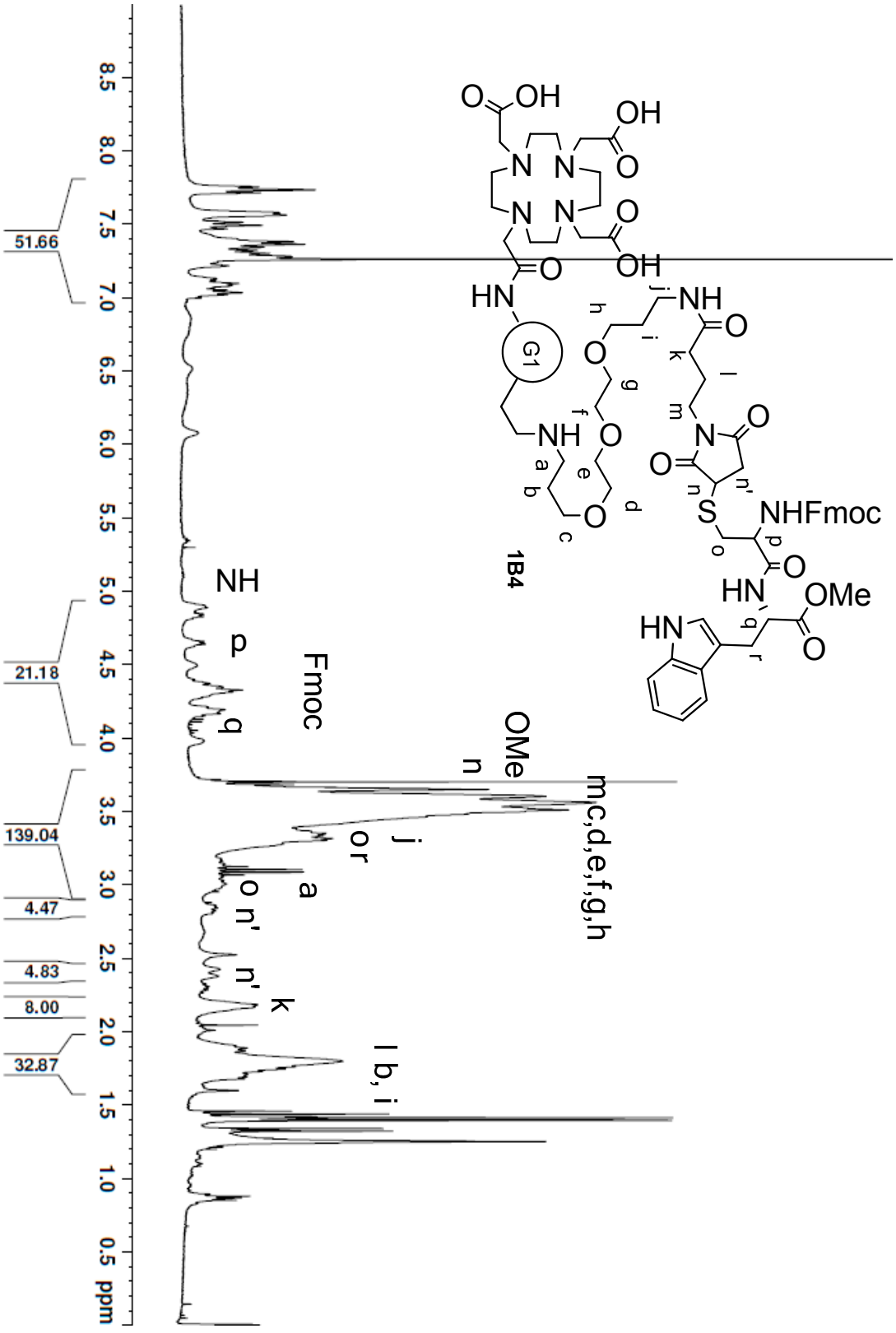


Figure S47. ^{1}H-NMR of **1-B$_4$** (400 MHz, $CDCl_3$).

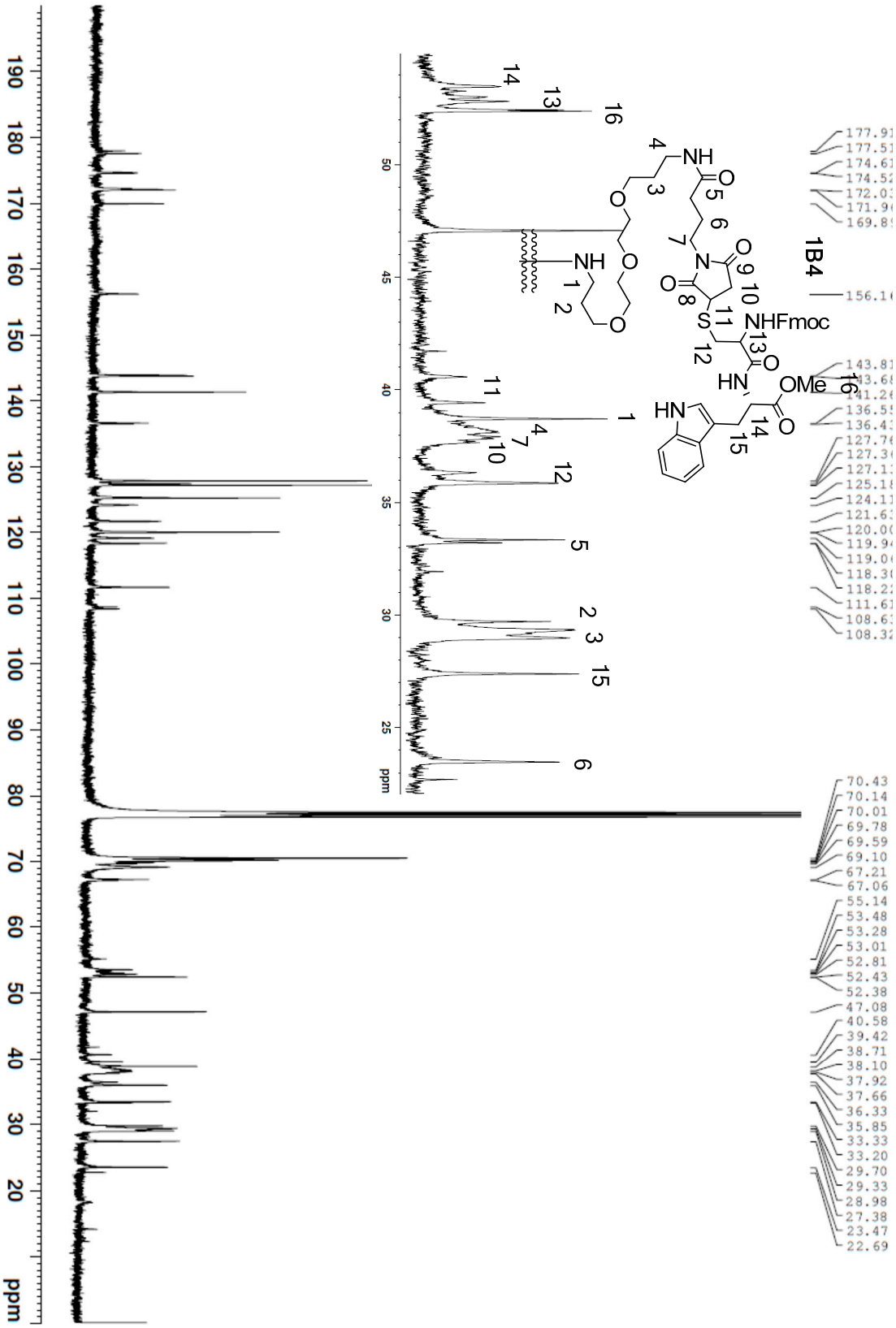


Figure S48. ^{13}C-NMR of **1-B4** (100 MHz, $CDCl_3$).

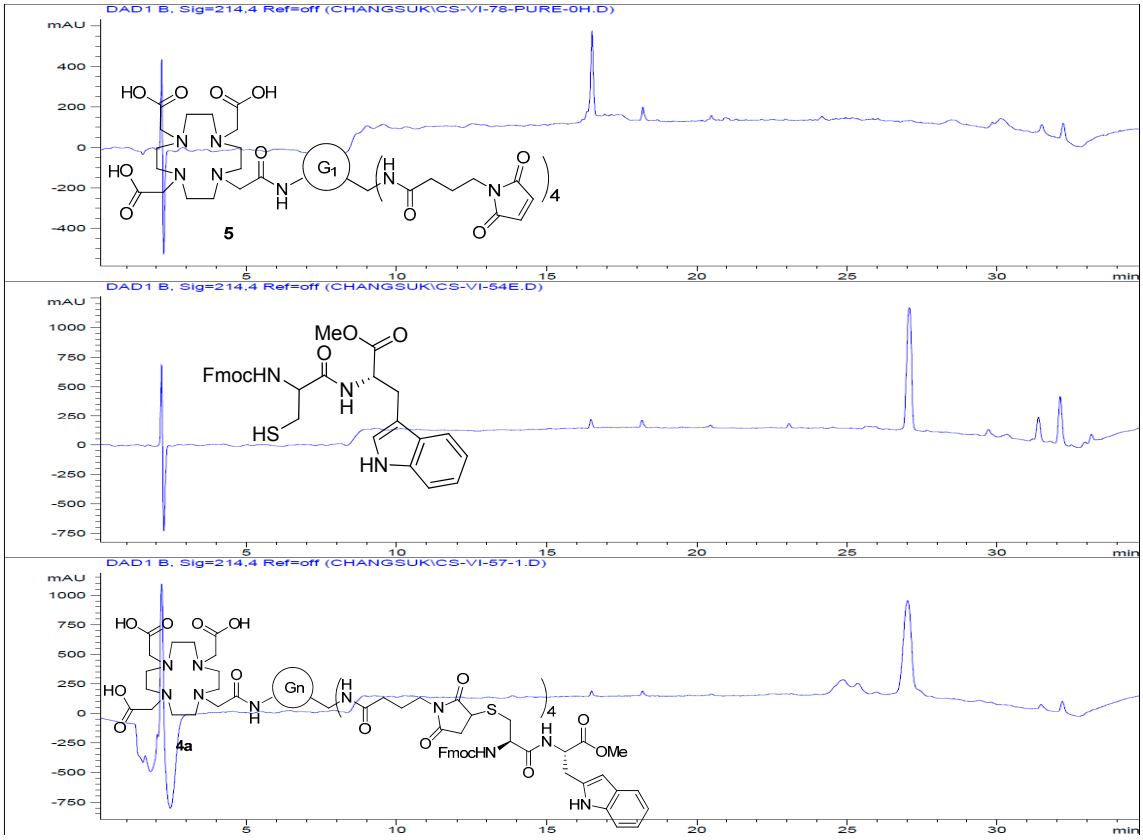


Figure S49. Comparison by HPLC of **1**, **B**, **1-B**$_4$. The mobile phase consisted of water/acetonitrile (A/B, HPLC grade, 0.1% (*w*/*v*) trifluoroacetic acid) at a flow rate of 0.8 mL/min. The elution gradient was 10% MeCN for 5 min, ramp to 90% MeCN in 30 min, and ramp down to 10% MeCN in 15 min. The sample volume injected 5 µL at a concentration of 0.1 mg/mL (Acetonitrile) of each samples and eluted sample was detected at 214 nm.

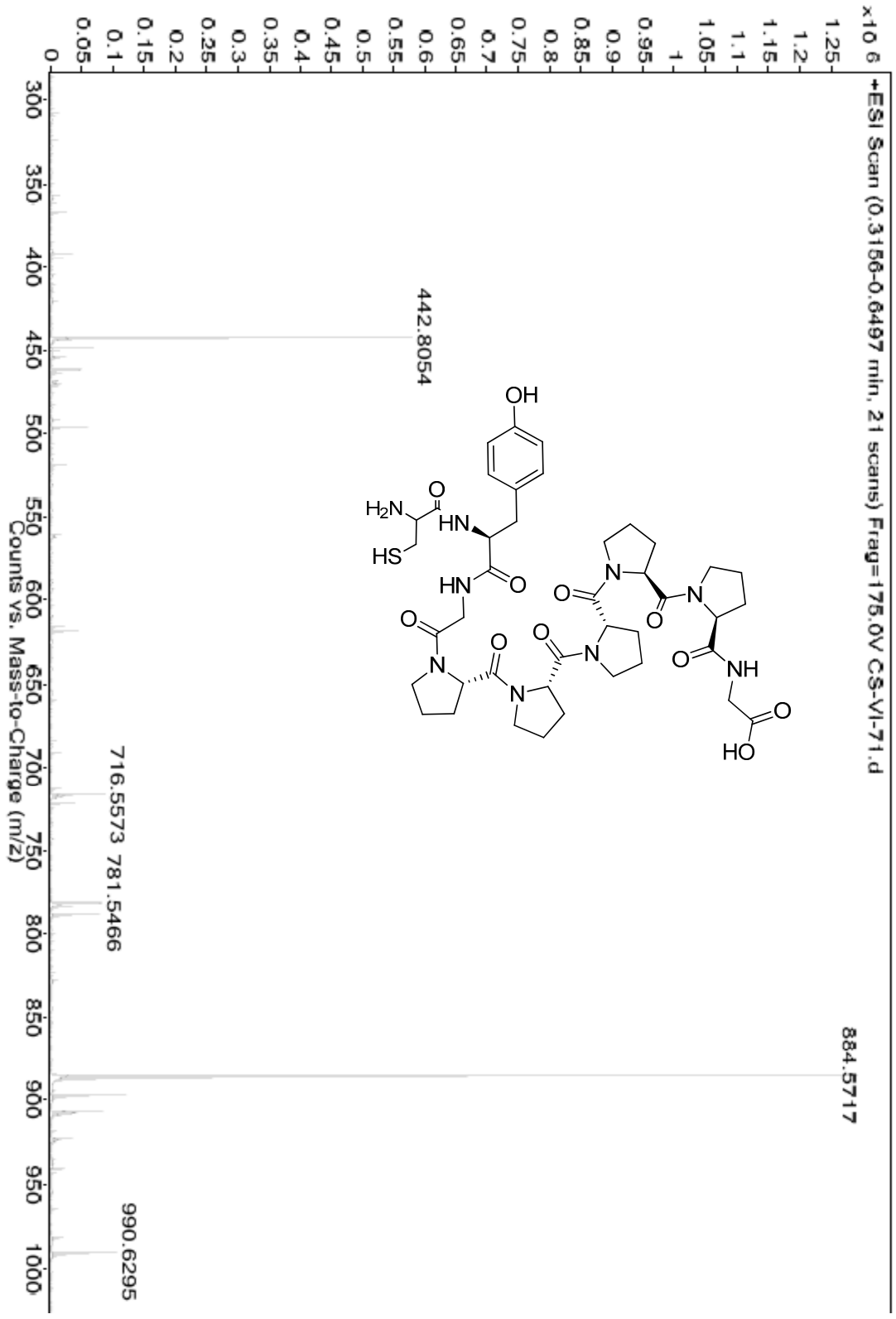


Figure S51. ESI-TOF MS of **1-C4**.

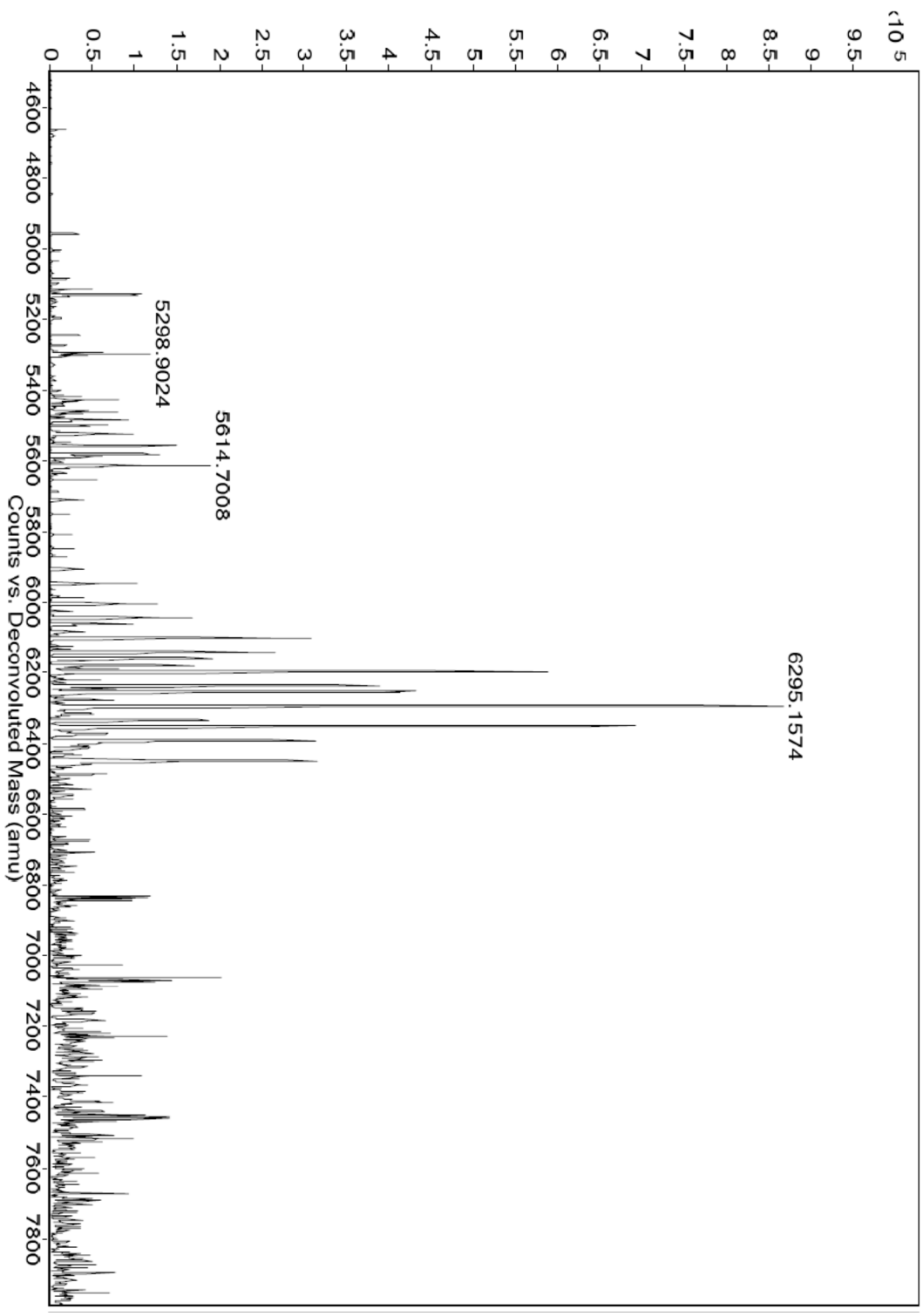


Figure S50. ESI-TOF MS of **C**. **C** is CYGPPPPPG. Calcd for $C_{41}H_{58}N_9O_{11}S$ 884.3977, found 884.5717 $[M + H]^+$ The line at *m*/*z* 442 is the doubly charged species. Lines at *m*/*z* 716 and 781 correspond to sequences missing amino acids.

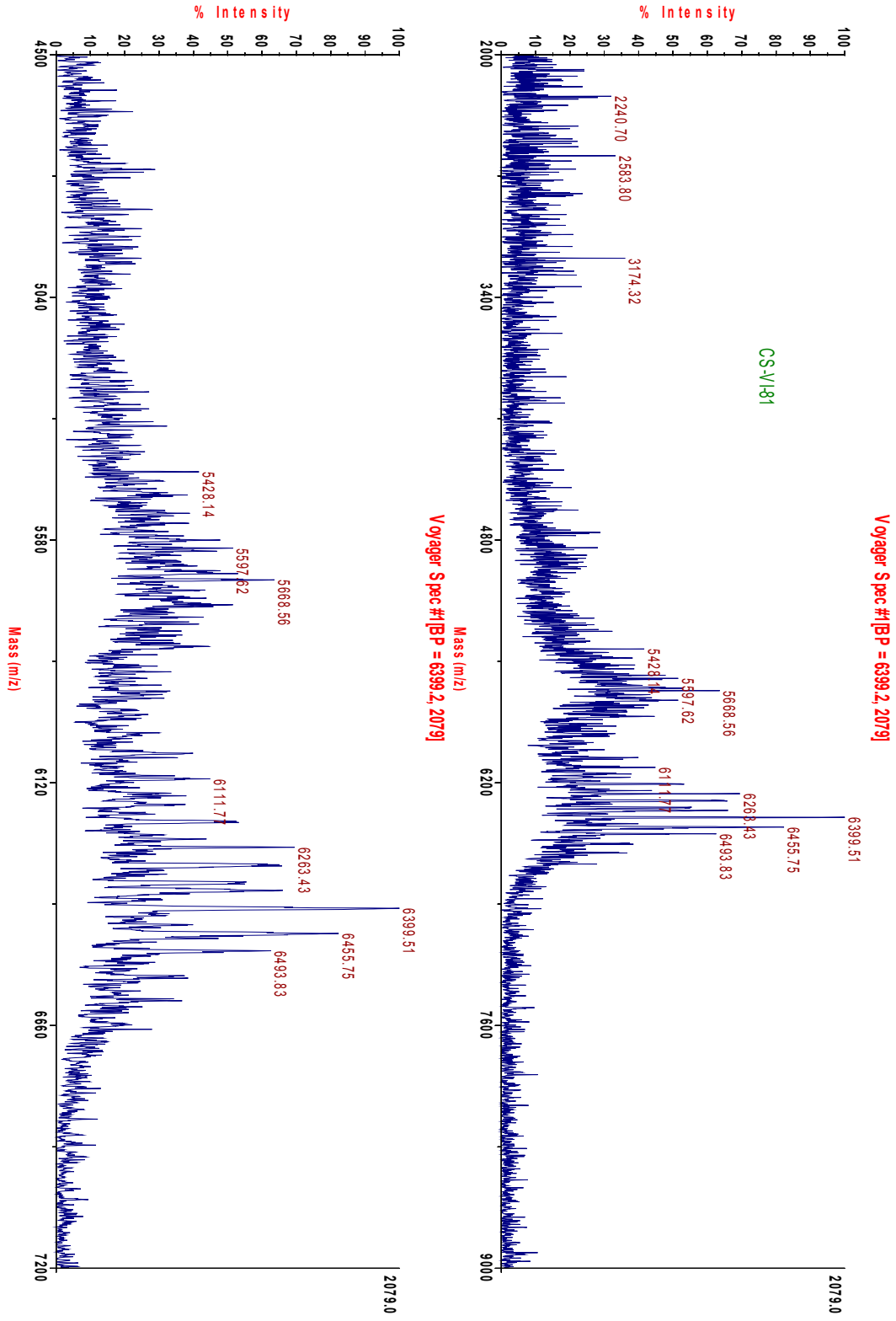


Figure S52. MALDI-TOF MS of **1-C4**.

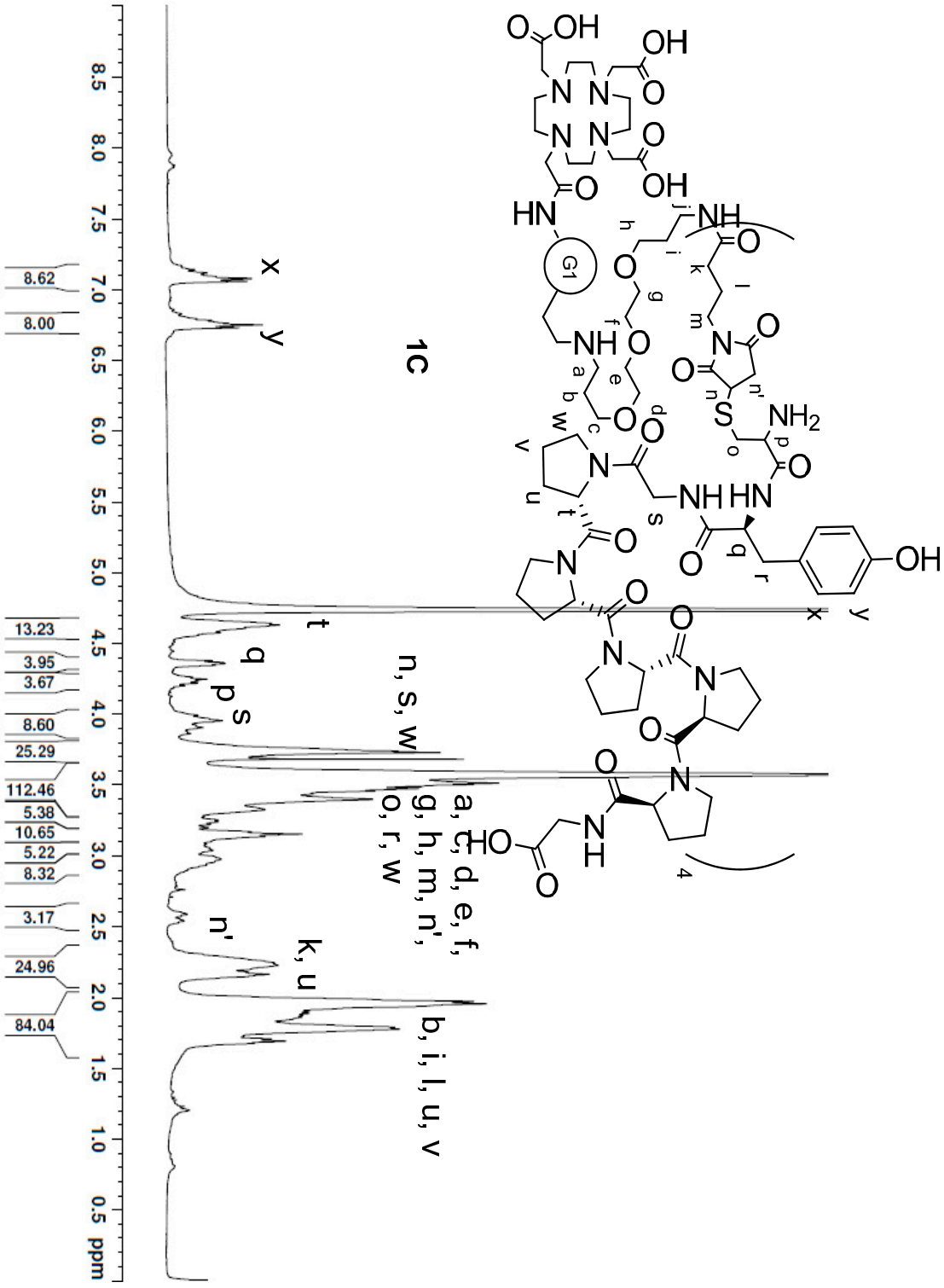


Figure S53. ^{1}H-NMR of **1-C$_4$** (400 MHz, D$_2$O).

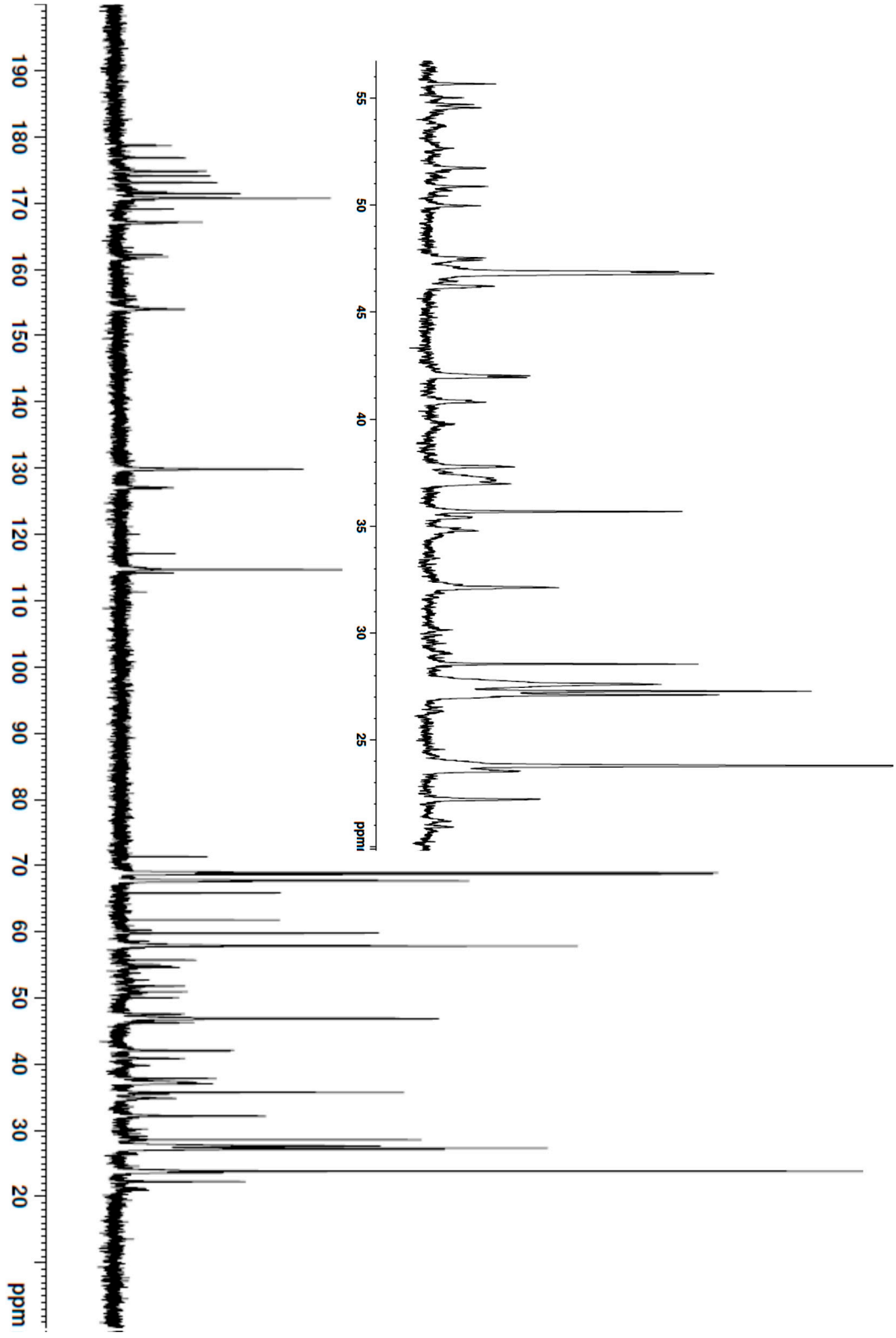


Figure S54. ^{13}C-NMR of **1-C$_4$** (100 MHz, D_2O).

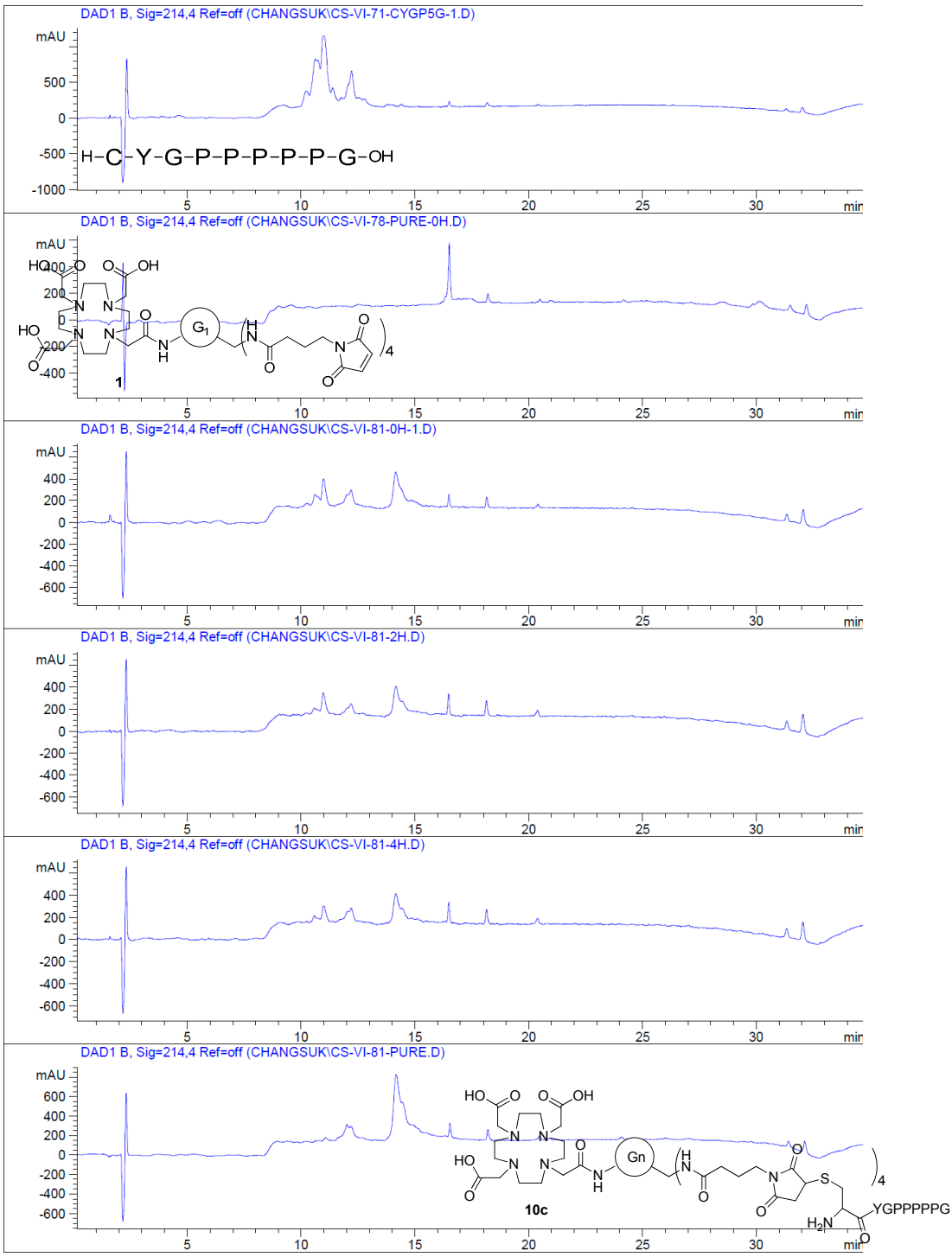


Figure S55. Comparison by HPLC of **1**, **C**, **1-C**$_4$. The mobile phase consisted of water/MeCN (A/B, HPLC grade, 0.1% (*w*/*v*) TFA) at a flow rate of 0.8 mL/min. The elution gradient was 10% MeCN for 5 min, ramp to 90% MeCN in 30 min, and ramp down to 10% MeCN in 15 min. The sample volume injected 5 μL at a concentration of 10 μL of reaction solution and mass up to 0.5 mL with HPLC-grade MeCN, and eluted sample was detected at 214 nm. Panels (from top to bottom) show the crude peptide **C**, **1**, the reaction at 1h, 2h, 4h, and product isolated by membrane filtration.

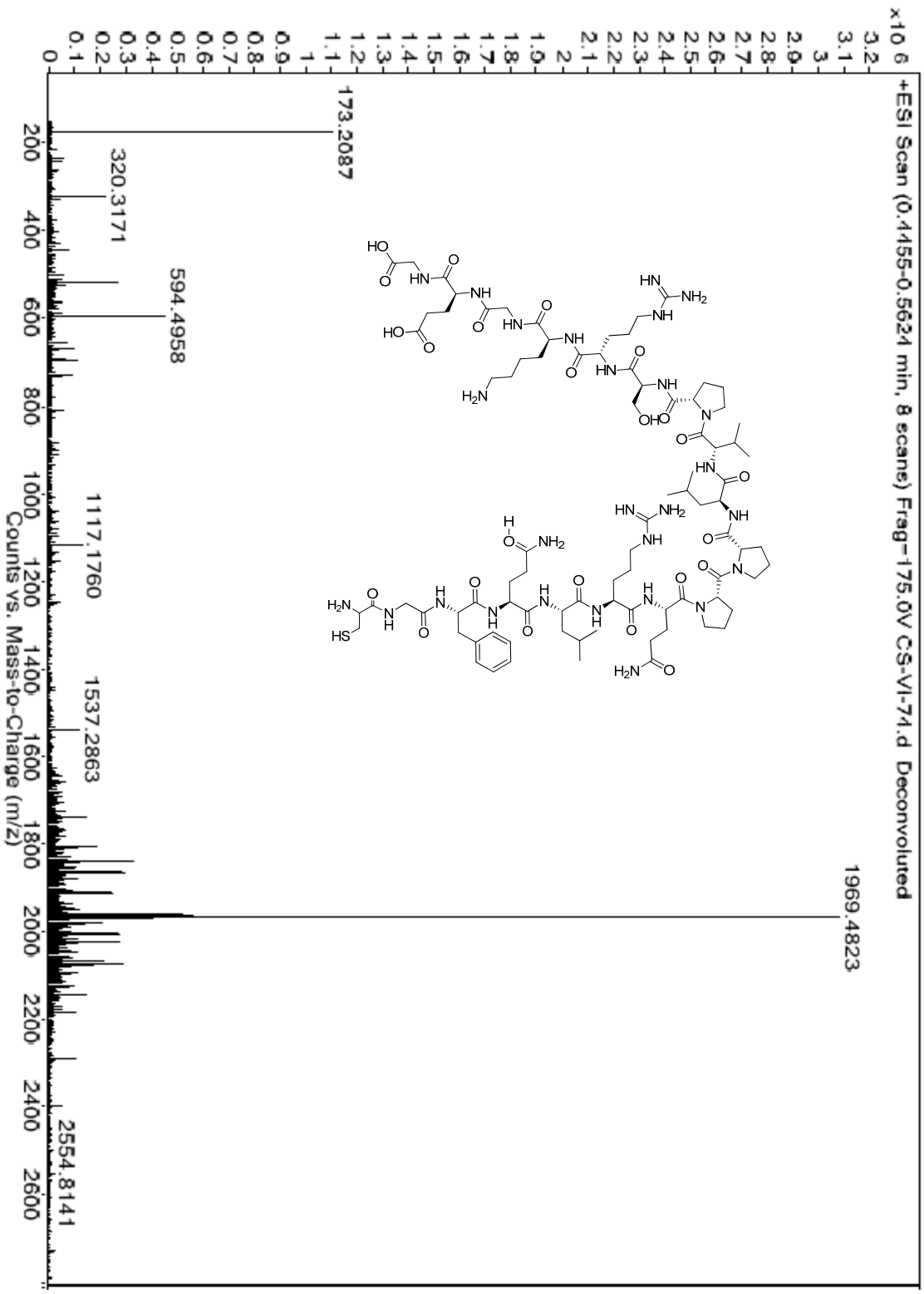


Figure S56. ESI-TOF MS of **D. D** is CGFQLRQPPLVPSRKGEG. Calcd. for $C_{86}H_{142}N_{27}O_{24}S$ 1969.0442, found 1969.4823 $[M + H]^+$.

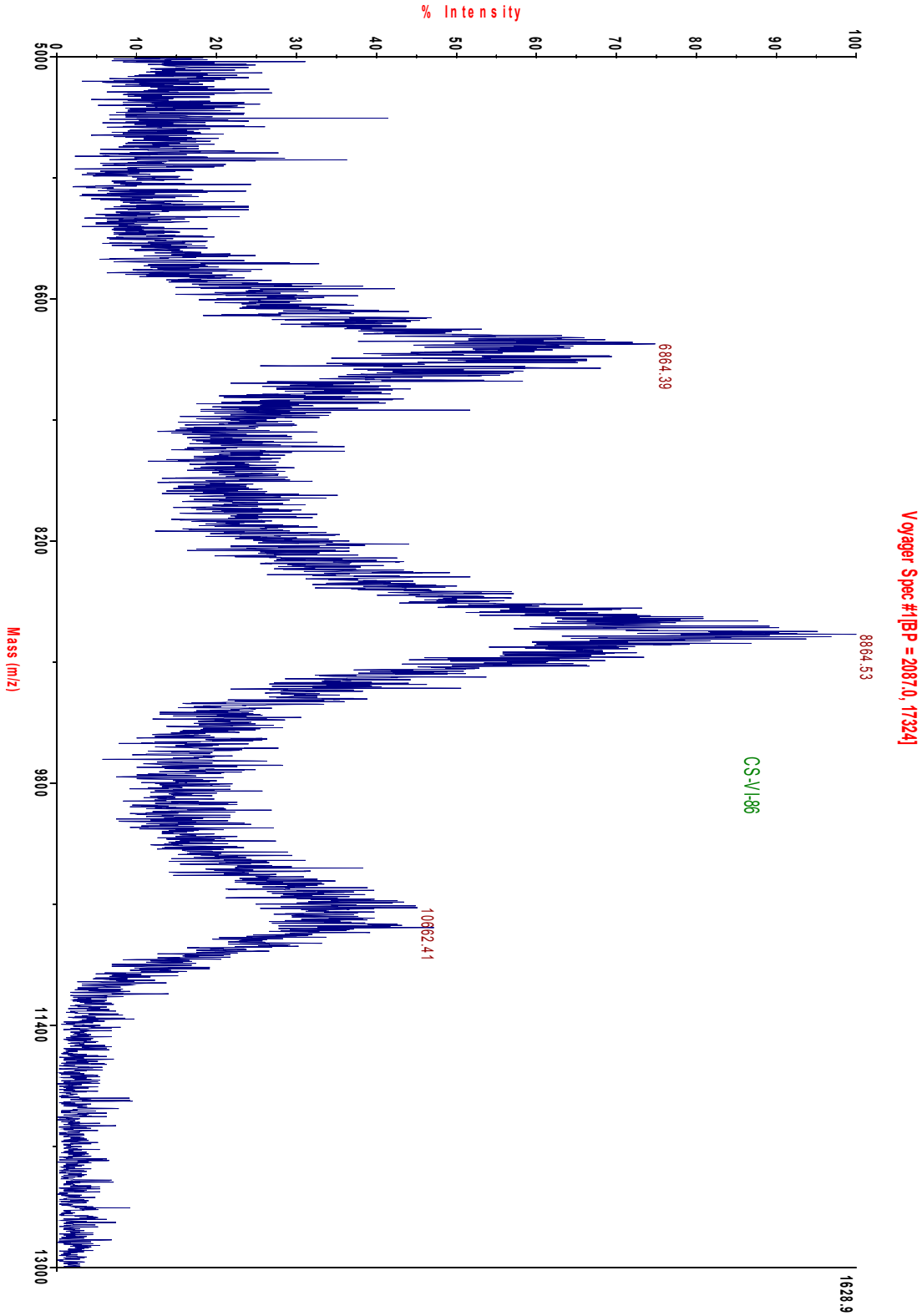


Figure S57. MALDI-TOF MS of **1-D4**. Calcd for $C_{471}H_{777}N_{139}O_{136}S_4$ 10684, found 10662. The other broad peaks likely correspond to **1-D2** and **1-D3**.

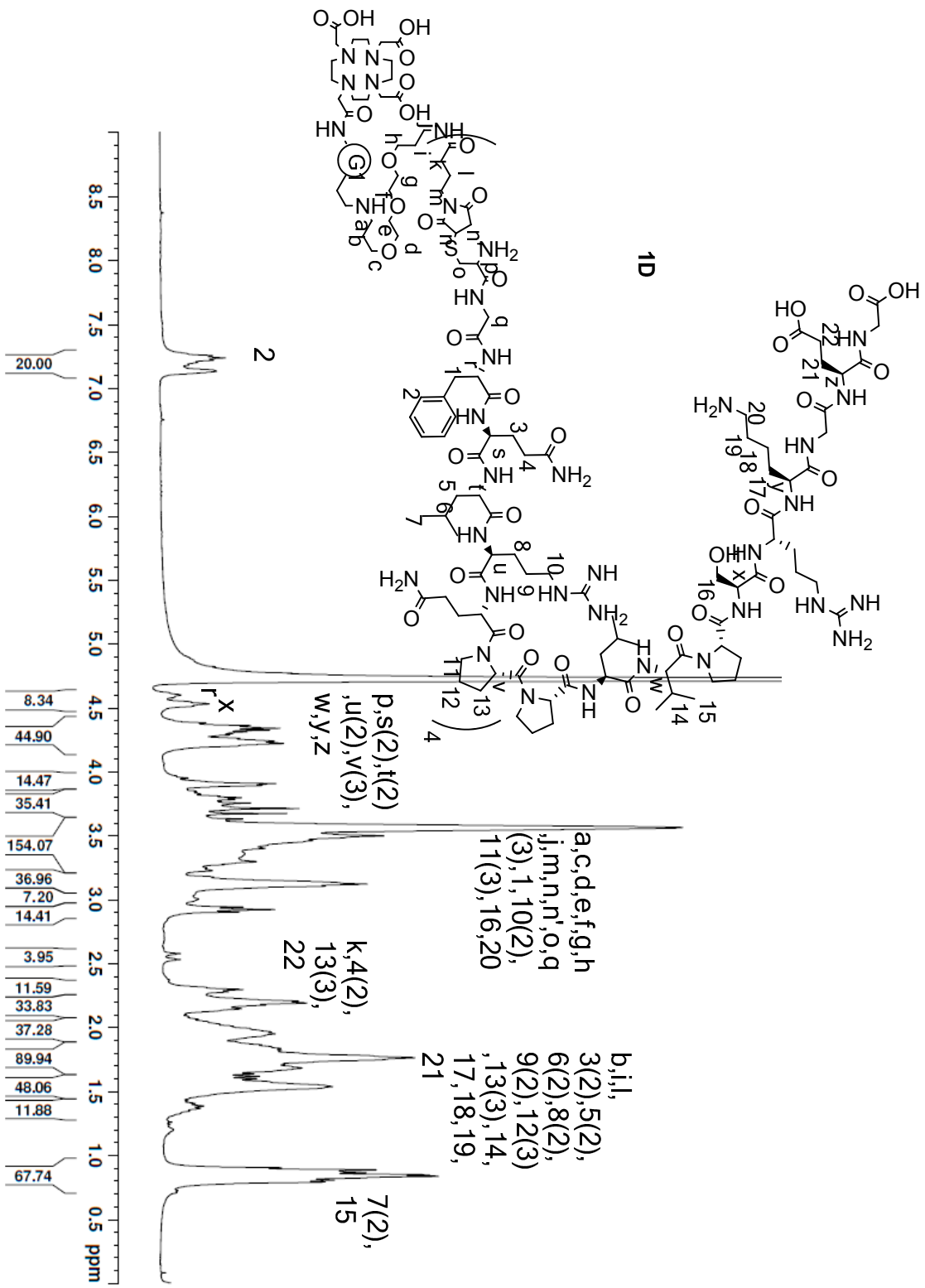


Figure S58. ^{1}H-NMR of **1-D$_4$** (400 MHz, D$_2$O).

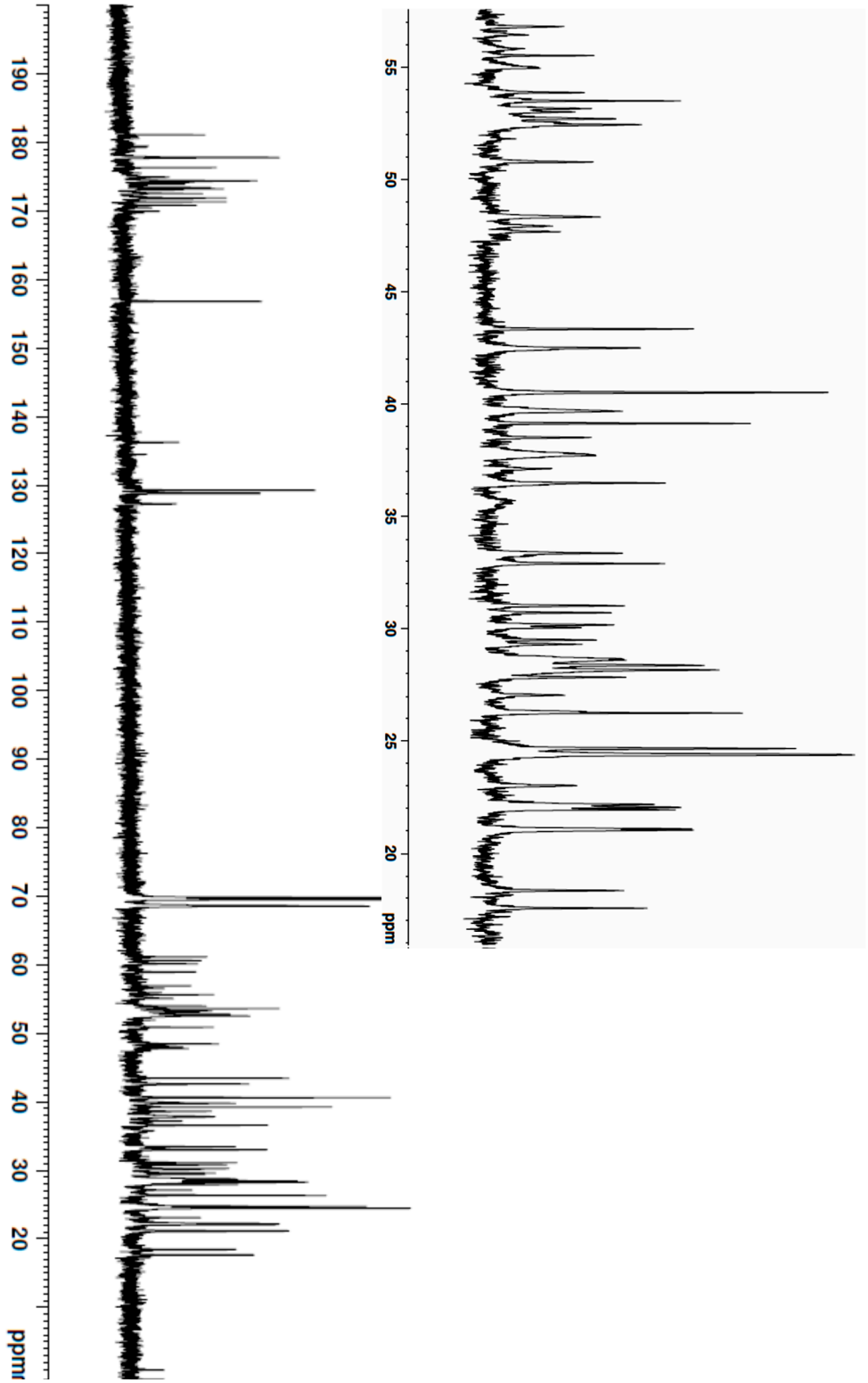


Figure S59. ^{13}C-NMR of **1-D$_4$** (100 MHz, D_2O).

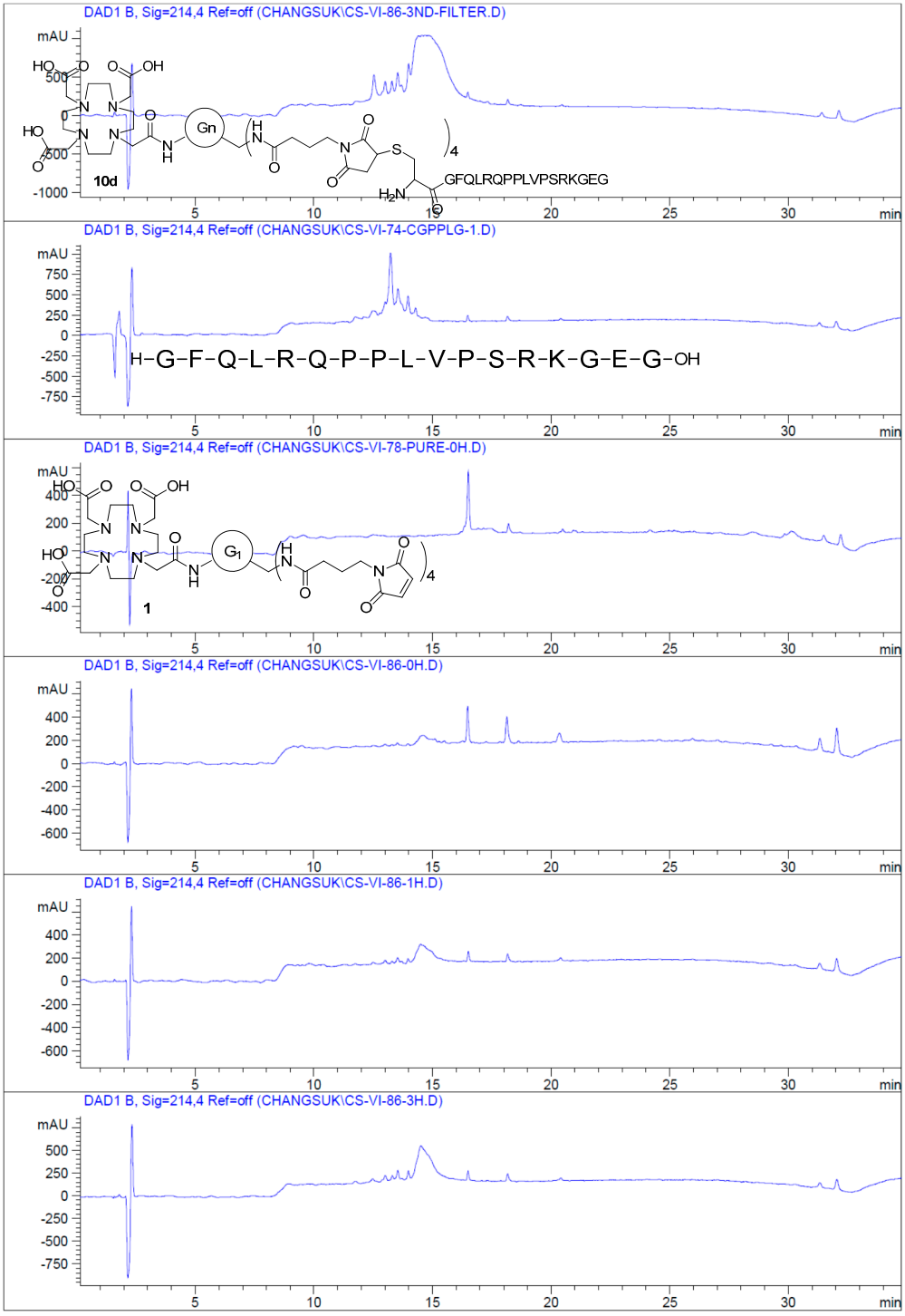


Figure S60. Comparison by HPLC of **1**, **D**, **1-D**$_4$. The mobile phase consisted of water/MeCN (A/B, HPLC grade, 0.1% (*w*/*v*) TFA) at a flow rate of 0.8 mL/min. The elution gradient was 10% MeCN for 5 min, ramp to 90% MeCN in 30 min, and ramp down to 10% MeCN in 15 min. The sample volume injected 5 μL at a concentration of 10 μL of reaction solution and mass up to 0.5 mL with HPLC-grade MeCN, and eluted sample was detected at 214 nm. Panels correspond to purified **1-D**$_4$**, D**, **1**, and the reaction at 0 h, 1 h, and 3 h.