Supporting Information

# A Program for Ligation at Threonine Sites: Application to the Controlled Total Synthesis of Glycopeptides

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**Content**



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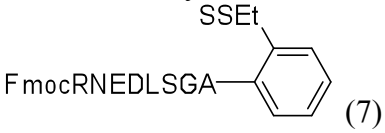
**LC-MS and MS characterization of peptides 7-46**

x-axis indicates time, y-axis indicates Diode Array intensity or ES+TIC intensity.

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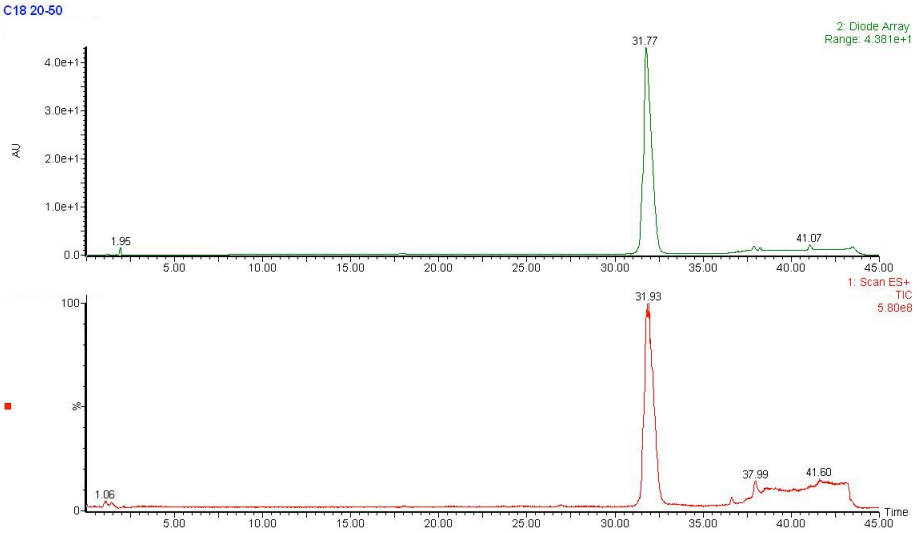


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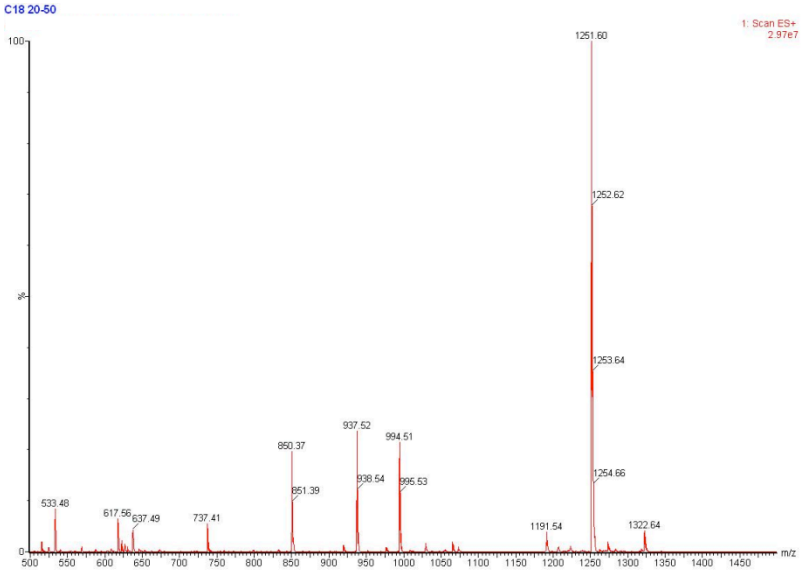
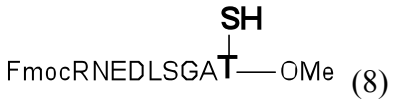



**Figure 1.** (a) UV and MS traces from LC-MS analysis of compound **7**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **7.** ESI-MS calcd for $C_{56}H_{74}N_{12}O_{17}S_2$ $[M+H]^+$ *m/z* = 1251.48, found: 1251.60.

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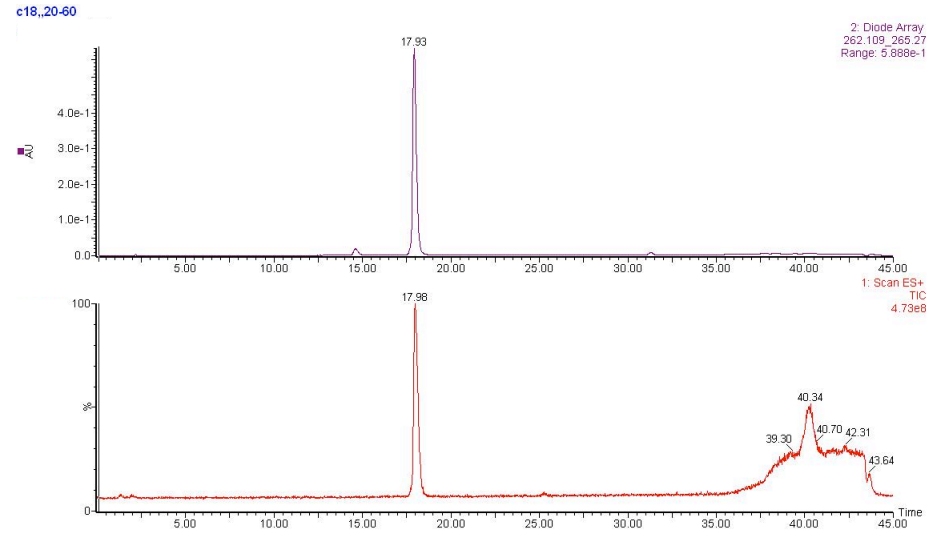


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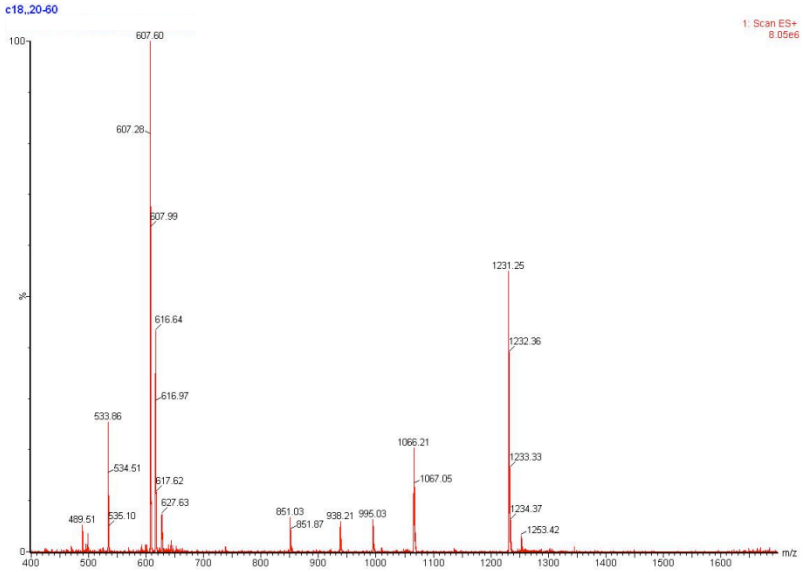


**Figure 2.** (a) UV and MS traces from LC-MS analysis of compound **8**: gradient 20-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **8.** ESI-MS calcd for $C_{53}H_{75}N_{13}O_{19}S$ $[M+H]^+$ *m/z* = 1230.51, found: 1231.12.

FmocRNEDLSGA**T**—OMe (9)

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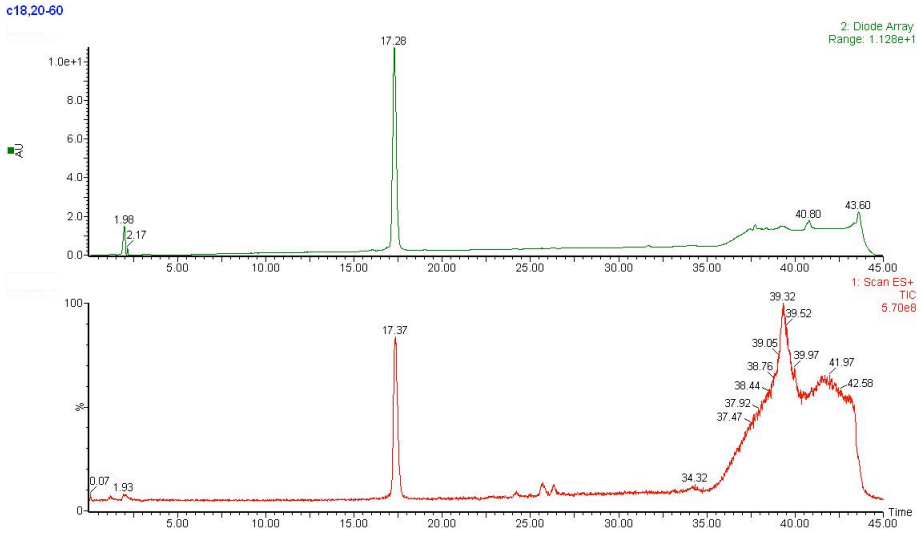


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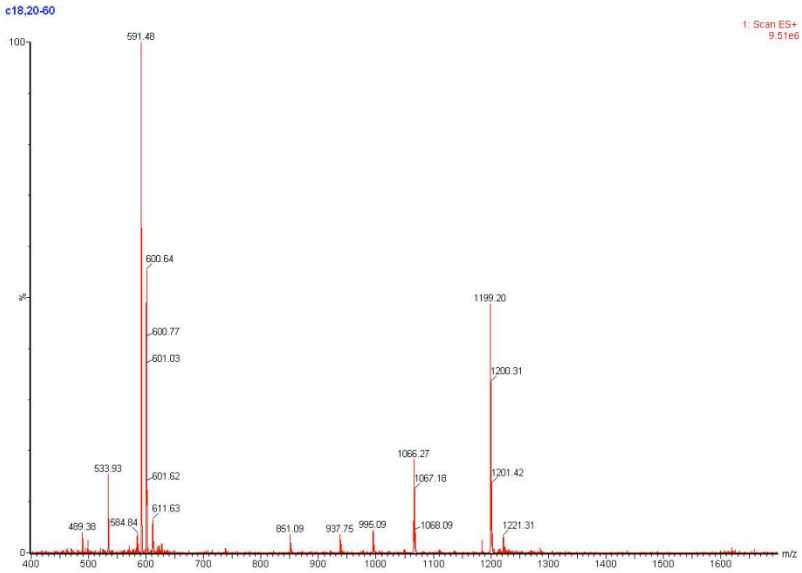
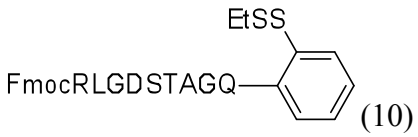



**Figure 3.** (a) UV and MS traces from LC-MS analysis of compound **9**: gradient 20-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **9.** ESI-MS calcd for $C_{53}H_{75}N_{13}O_{19}$ $[M+H]^+$ *m/z* = 1198.54, found: 1198.88.

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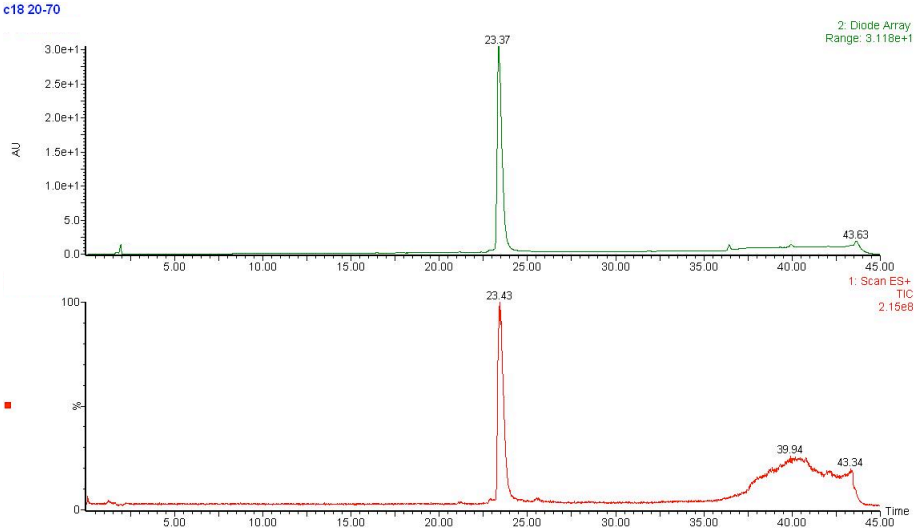


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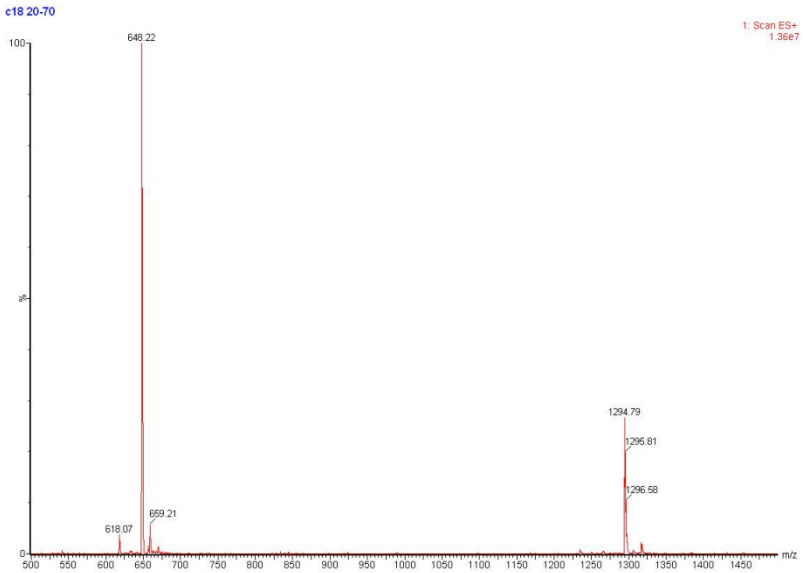
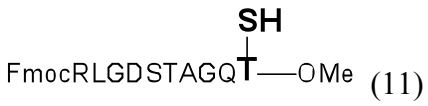



**Figure 4.** (a) UV and MS traces from LC-MS analysis of compound **10**: gradient 20-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **10.** ESI-MS calcd for $C_{58}H_{79}N_{13}O_{17}S_2$ $[M+H]^+$ *m/z* = 1294.53, found: 1294.79.

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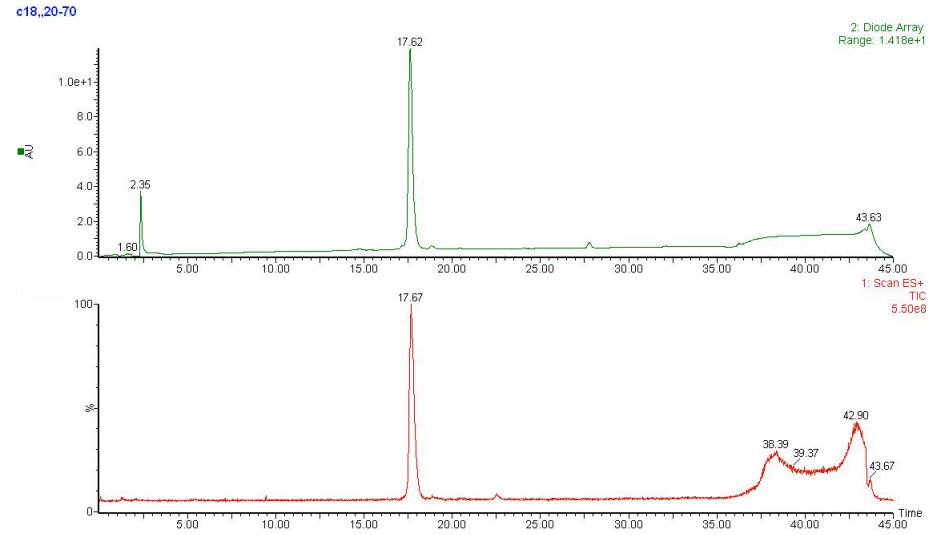


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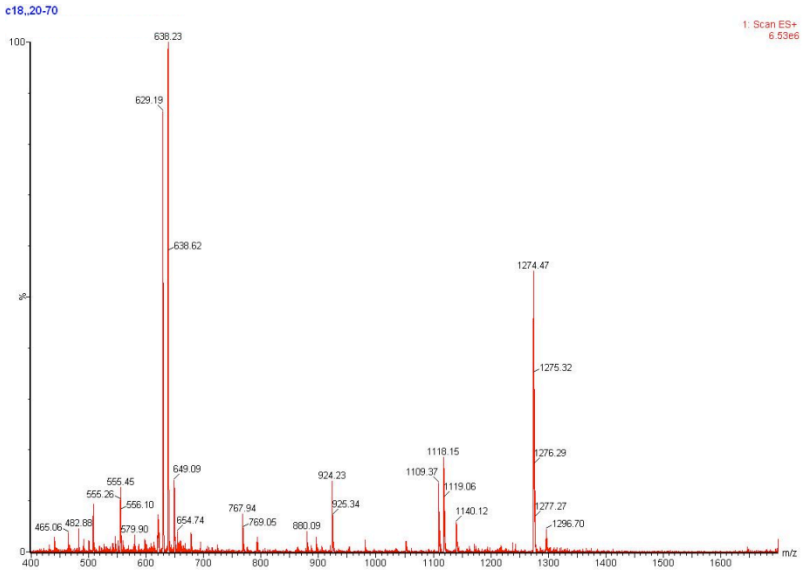
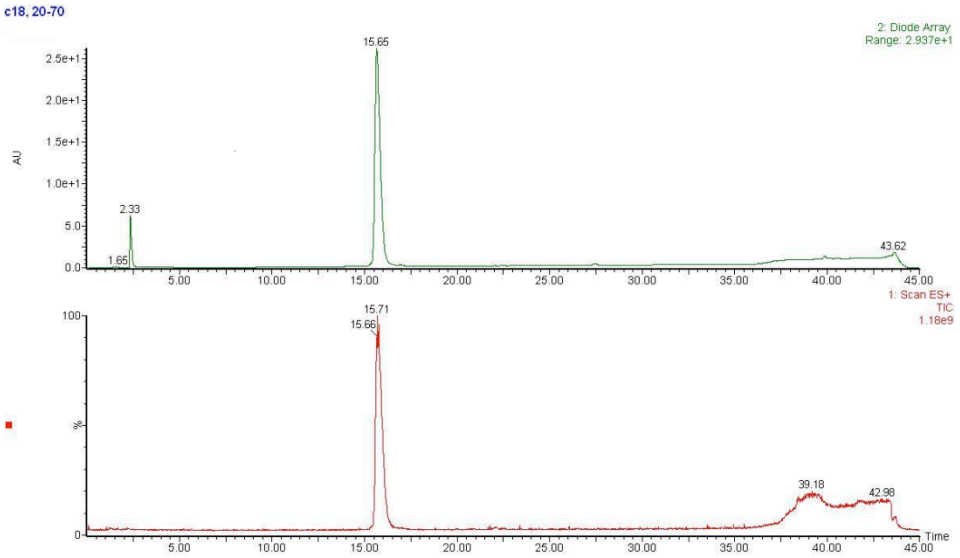



**Figure 5.** (a) UV and MS traces from LC-MS analysis of compound **11**: gradient 20-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **11.** ESI-MS calcd for $C_{55}H_{79}N_{14}O_{19}S$ $[M+H]^+$ *m/z* = 1273.55, found: 1274.08.

FmocRLGDSTAGQ**T**—OMe (12)

a

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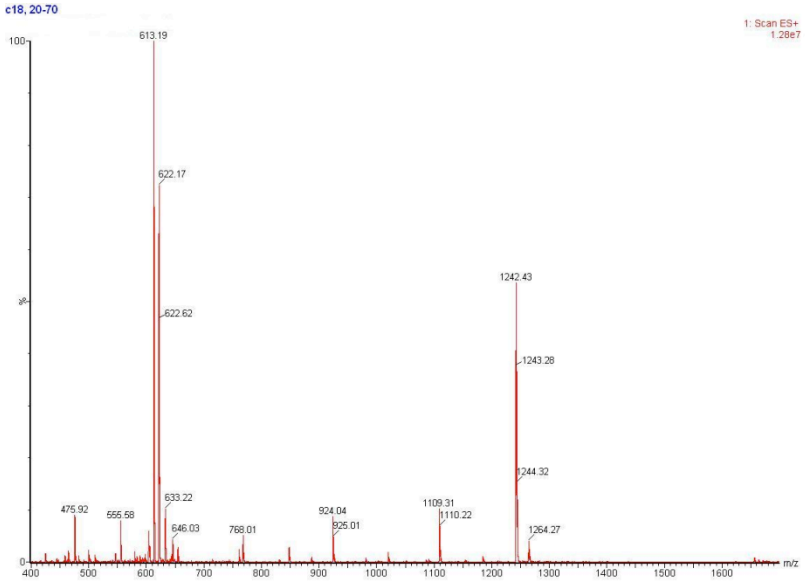
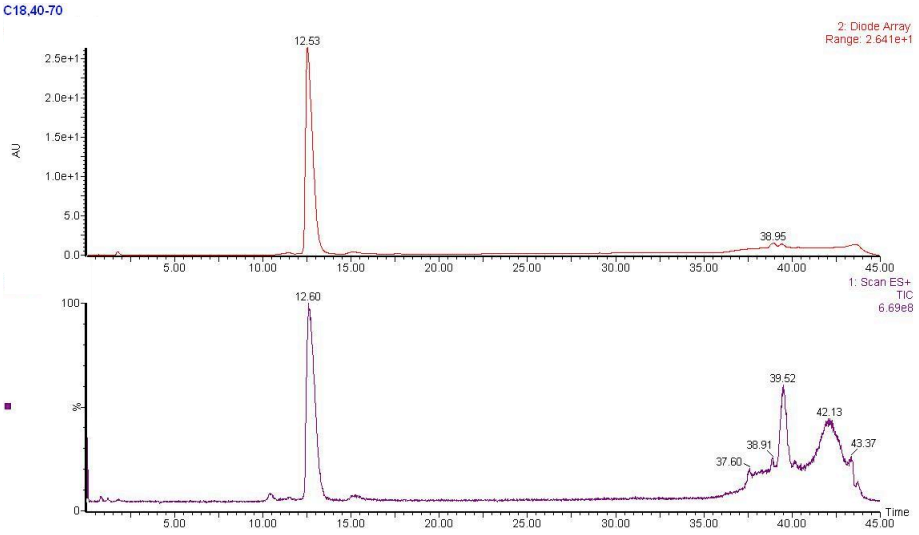



**Figure 6.** (a) UV and MS traces from LC-MS analysis of compound **12**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **12.** ESI-MS calcd for $C_{55}H_{80}N_{14}O_{19}$ $[M+H]^+$ *m/z* = 1241.58, found: 1241.91.

FmocRLGDSTAGY—SPh (13)

a

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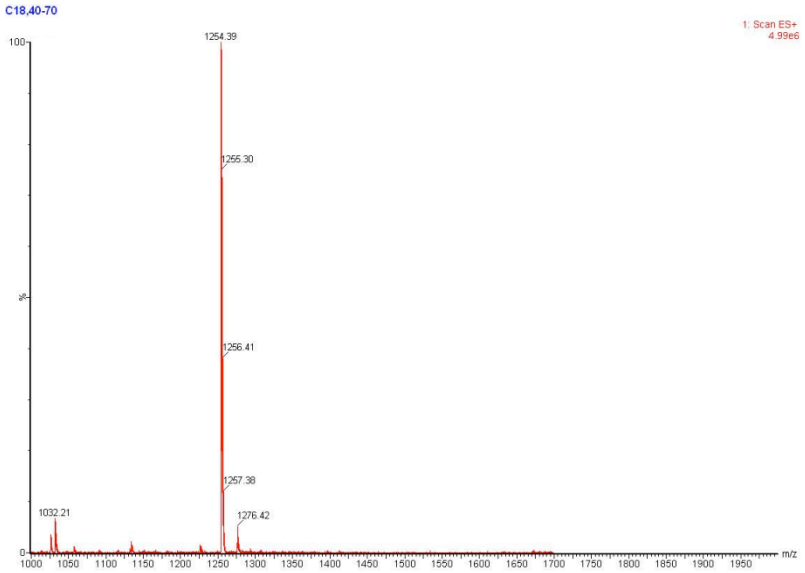
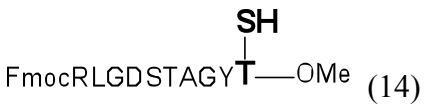
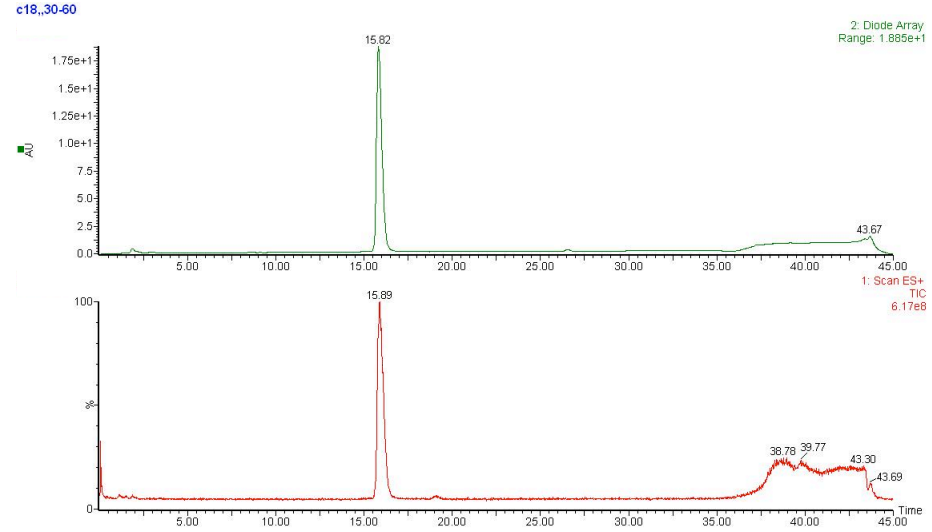



**Figure 7.** (a) UV and MS traces from LC-MS analysis of compound **13**: gradient 40-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **13.** ESI-MS calcd for $C_{60}H_{76}N_{12}O_{16}S$ $[M+H]^+$ *m/z* = 1253.53, found: 1254.20.




(14)

a

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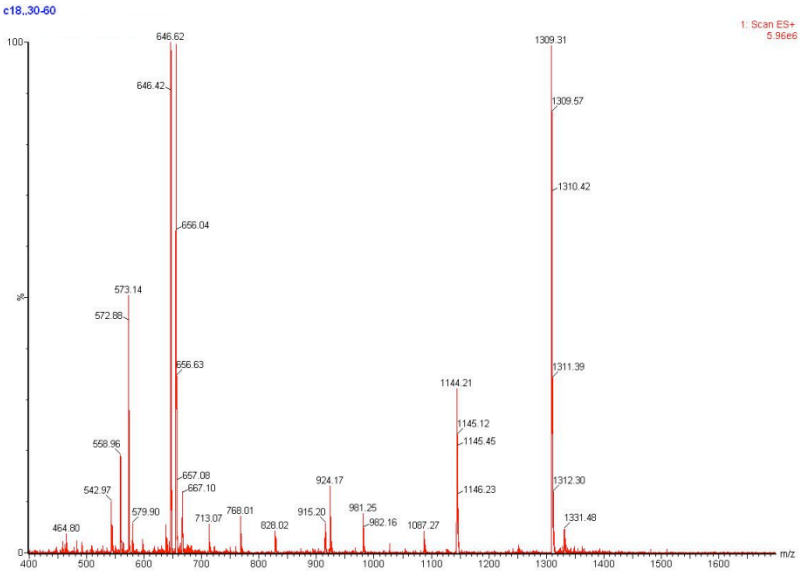
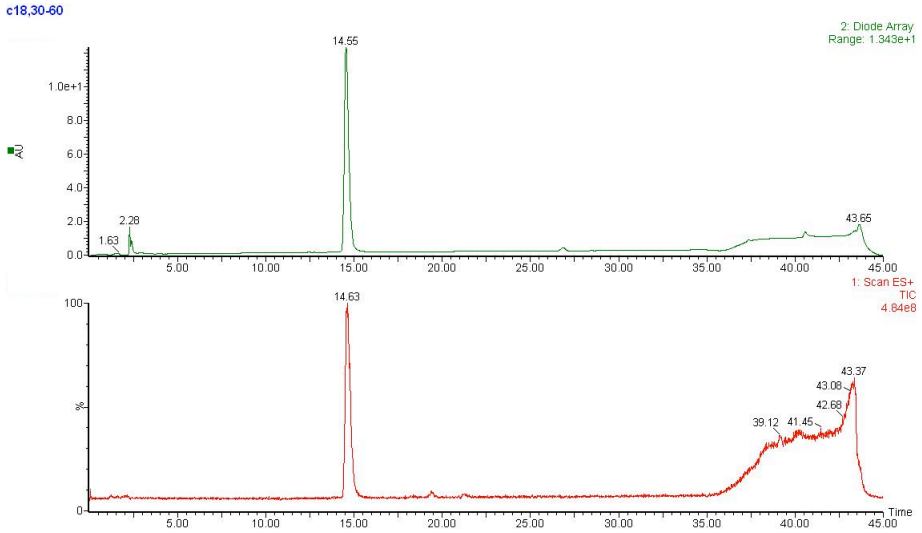



**Figure 8.** (a) UV and MS traces from LC-MS analysis of compound **14**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **14.** ESI-MS calcd for $C_{59}H_{81}N_{13}O_{19}S$ $[M+H]^+$ *m/z* = 1308.56, found: 1308.92.

FmocRLGDSTAGY**T**—OMe (15)

a

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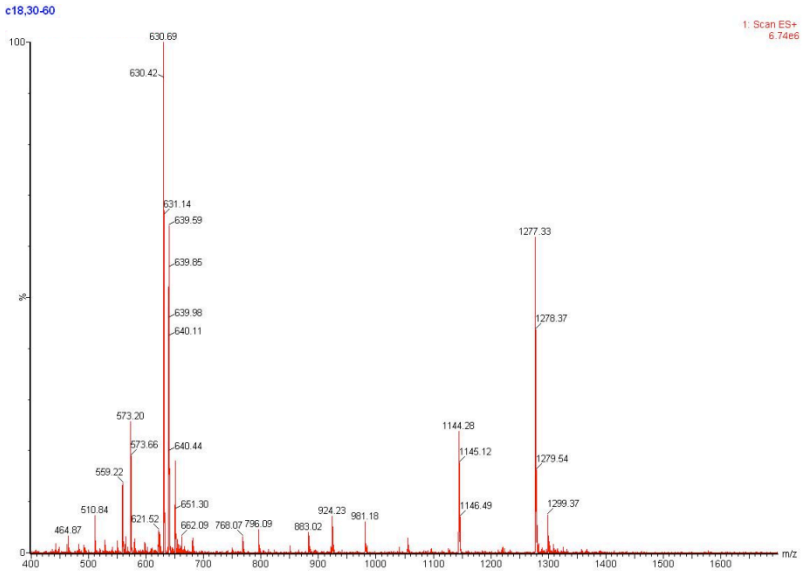
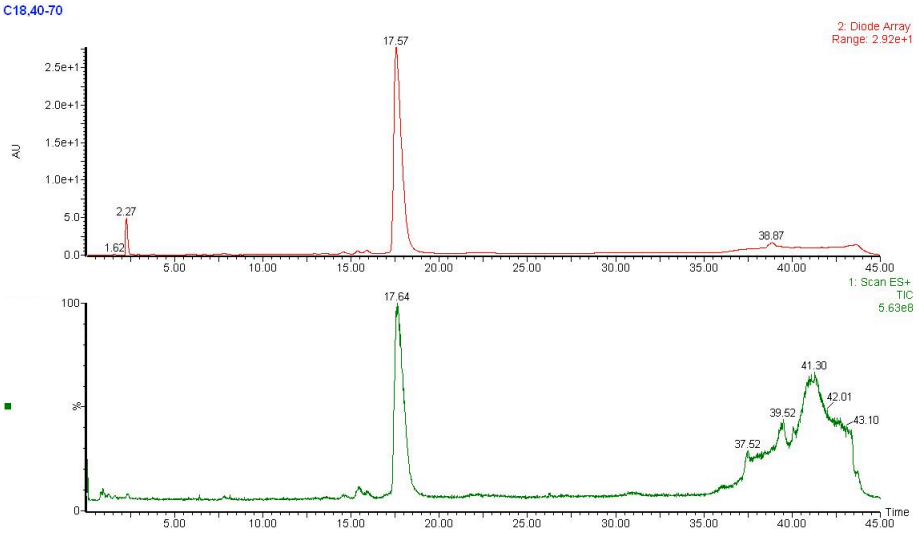



**Figure 9.** (a) UV and MS traces from LC-MS analysis of compound **15**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **15.** ESI-MS calcd for $C_{59}H_{81}N_{13}O_{19}$ $[M+H]^+$ *m/z* = 1276.59, found: 1277.07.

FmocRLGDSTAGW—SPh (16)

a

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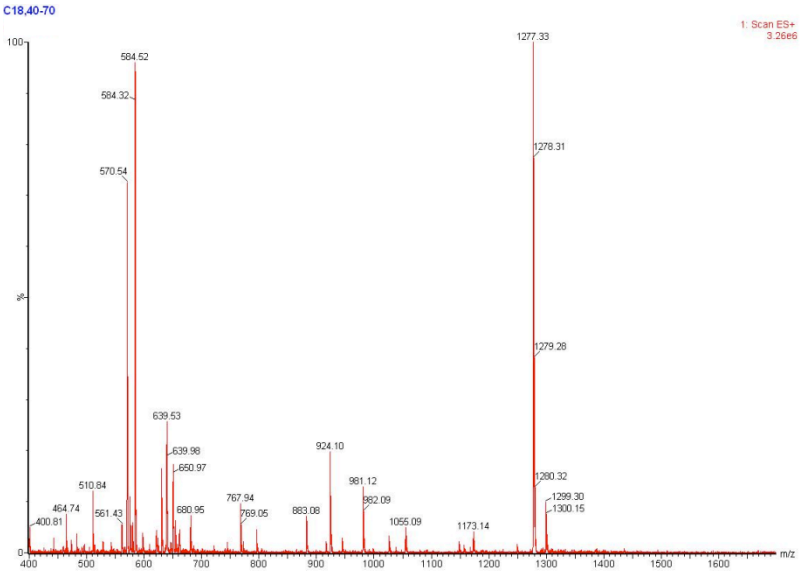
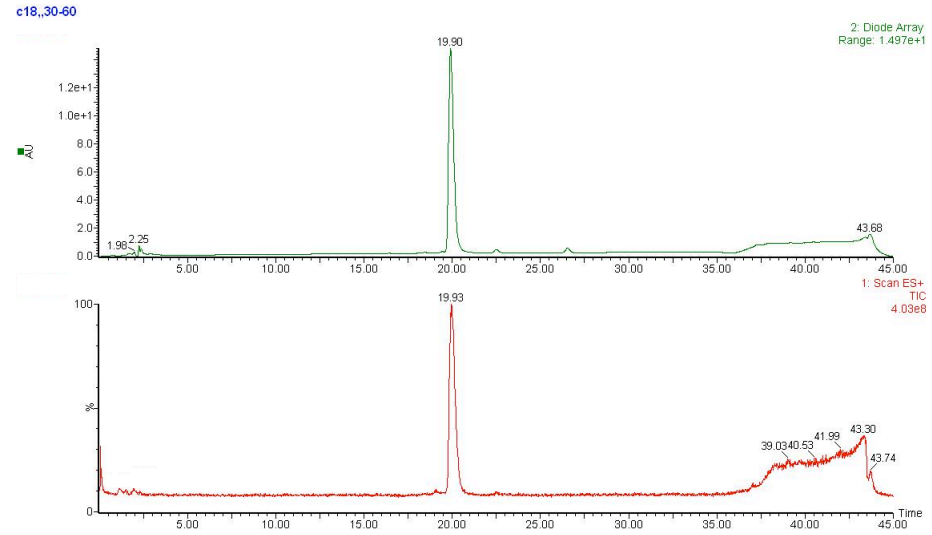



**Figure 10.** (a) UV and MS traces from LC-MS analysis of compound **16**: gradient 40-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **16.** ESI-MS calcd for $C_{62}H_{77}N_{13}O_{15}S$ $[M+H]^+$ *m/z* = 1276.55, found: 1276.81.


a

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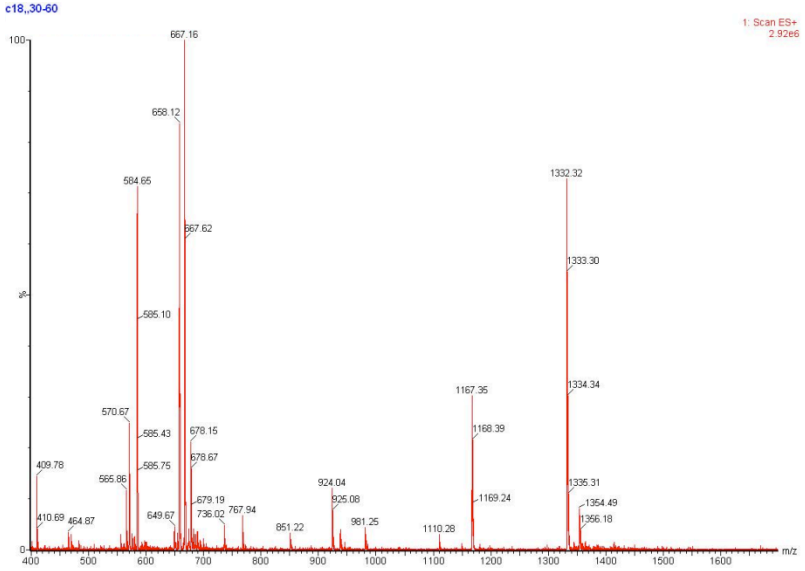
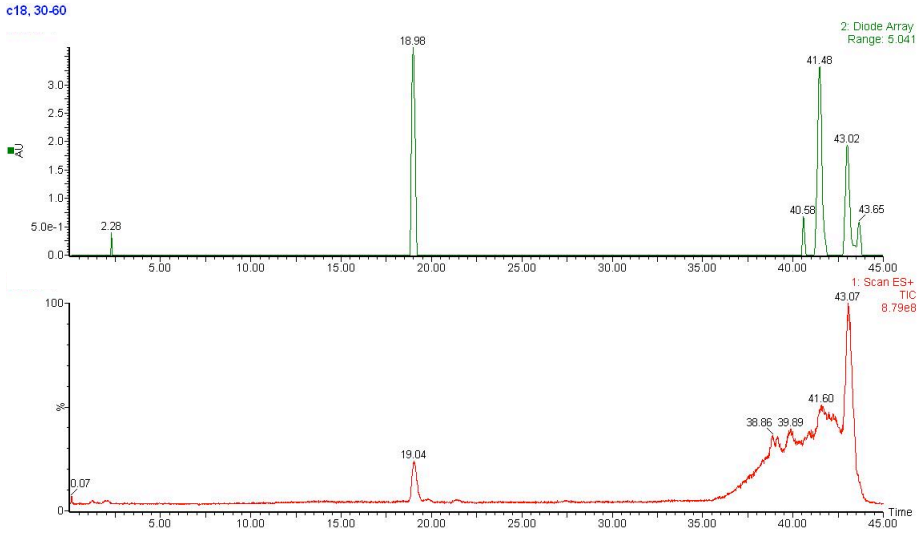



**Figure 11.** (a) UV and MS traces from LC-MS analysis of compound **17**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **17.** ESI-MS calcd for $C_{61}H_{82}N_{14}O_{18}S$ $[M+H]^+$ *m/z* = 1331.58, found: 1331.93.

FmocRLGDSTAGW**T**—OMe (18)

a

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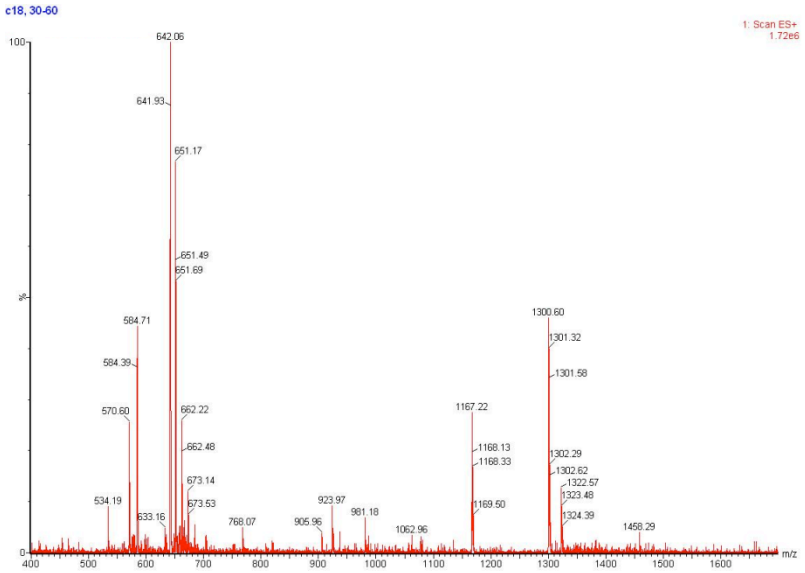
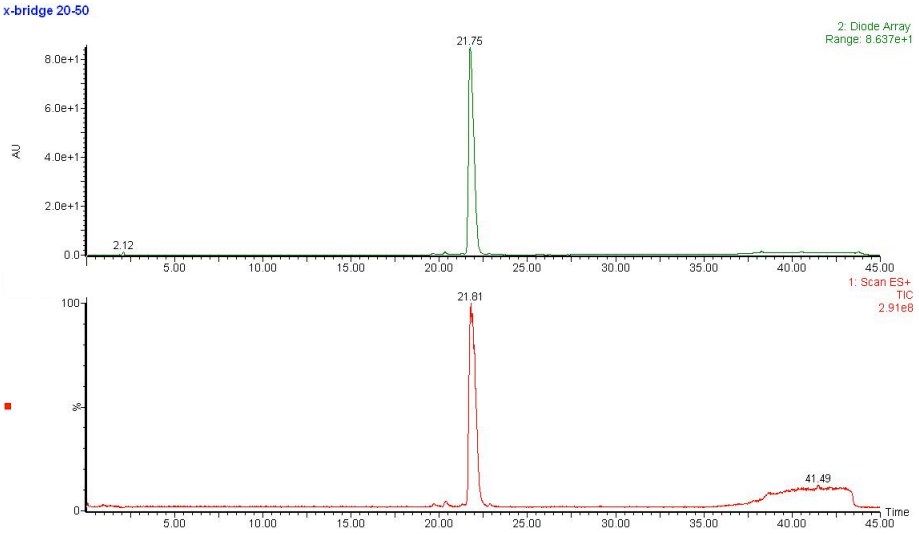



**Figure 12.** (a) UV and MS traces from LC-MS analysis of compound **18**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **18.** ESI-MS calcd for $C_{61}H_{82}N_{14}O_{18}$ $[M+H]^+$ *m/z* = 1299.60, found: 1300.02.

FmocRTGDSAGT——SPh (19)

a

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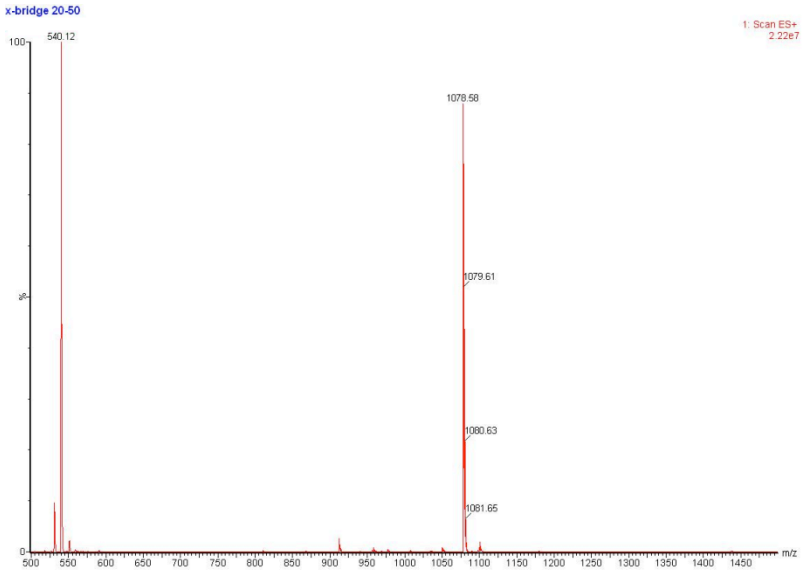
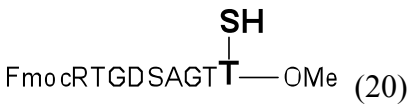



**Figure 13.** (a) UV and MS traces from LC-MS analysis of compound **19**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, x-bridge column. (b) ESI-MS of compound **19.** ESI-MS calcd for $C_{49}H_{63}N_{11}O_{15}S$ $[M+H]^+$ *m/z* = 1078.43 $[M+2H]^{2+}$ *m/z* = 539.72, found: 1078.58, 540.12.




(20)

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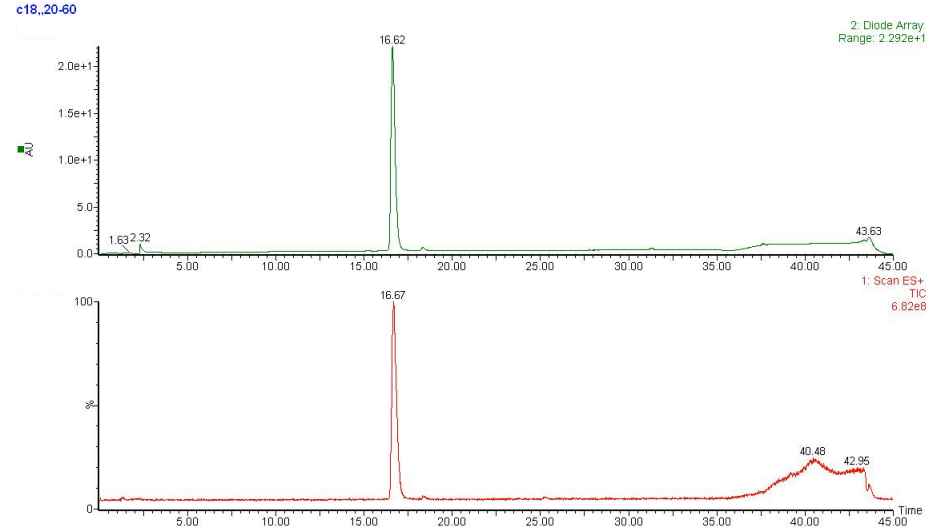


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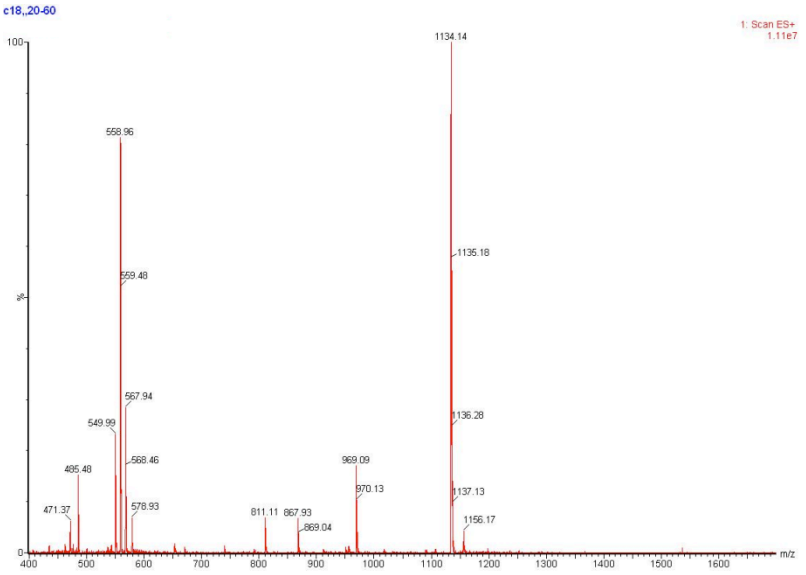
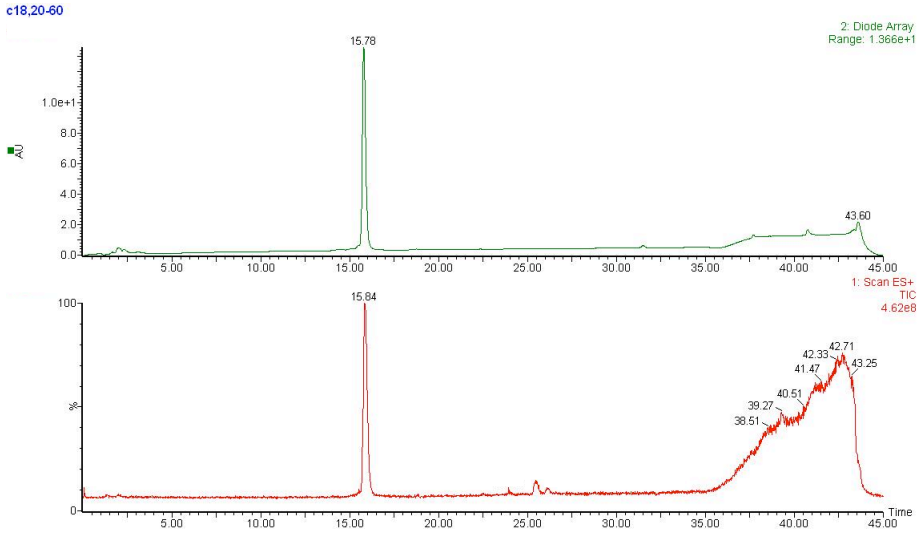



**Figure 14.** (a) UV and MS traces from LC-MS analysis of compound **20**: gradient 20-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **20.** ESI-MS calcd for $C_{48}H_{68}N_{12}O_{18}S$ $[M+H]^+$ $m/z$ = 1133.46, found: 1134.01.

FmocRTGDSAGT**T**—OMe (21)

a

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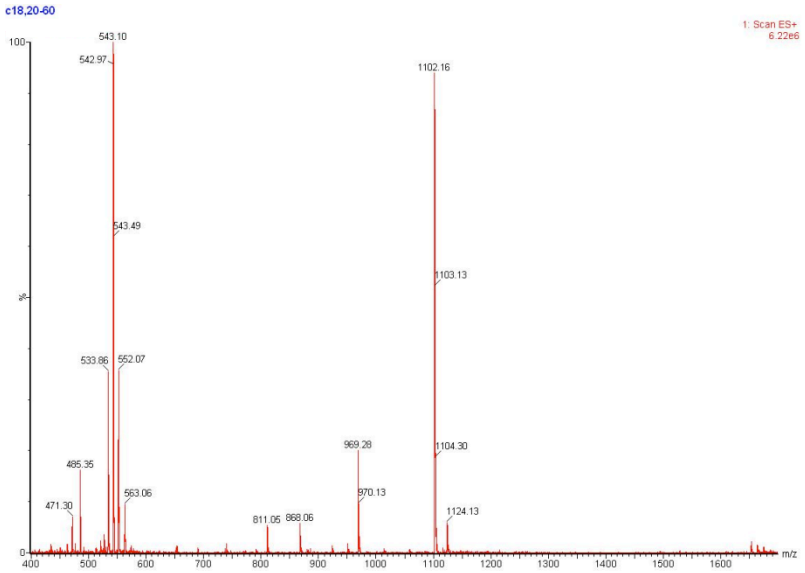
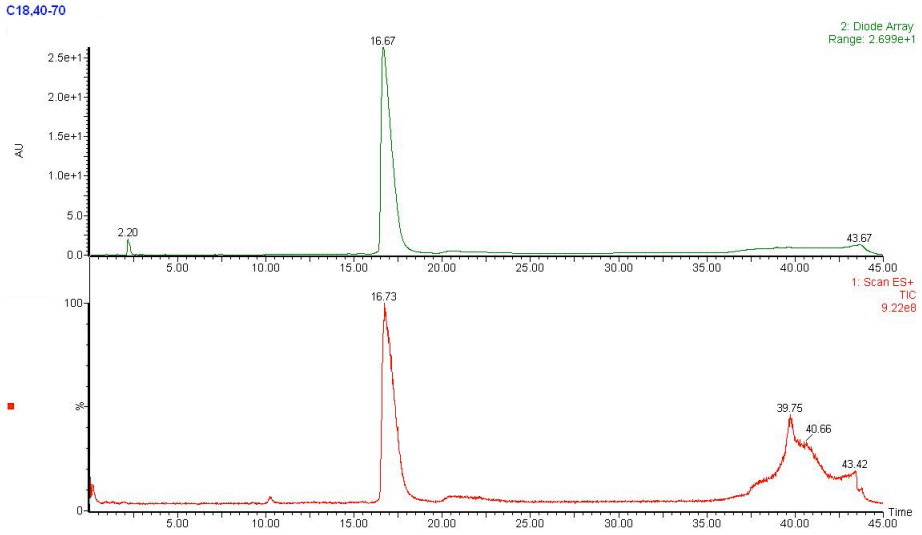



**Figure 15.** (a) UV and MS traces from LC-MS analysis of compound **21**: gradient 20-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **21.** ESI-MS calcd for $C_{48}H_{68}N_{12}O_{18}$ $[M+H]^+$ *m/z* = 1101.49, found: 1101.83.

FmocRLGDSTAGL—SPh (22)

a

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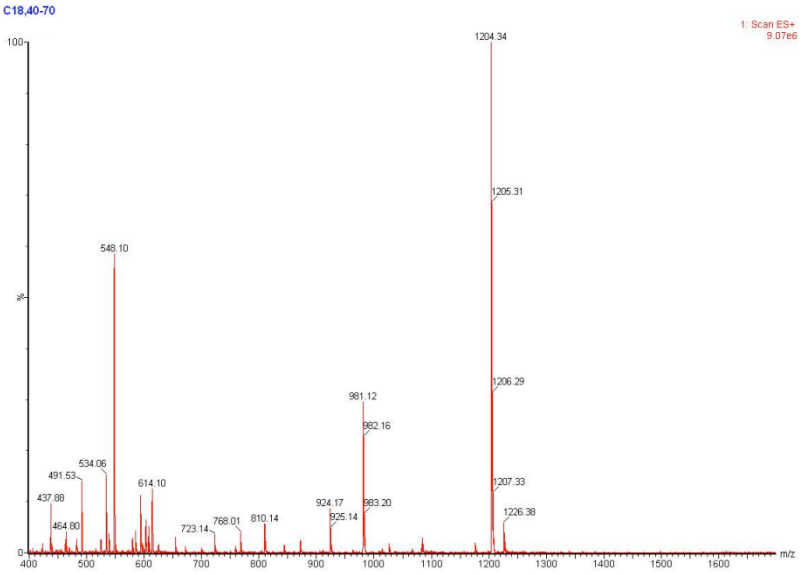
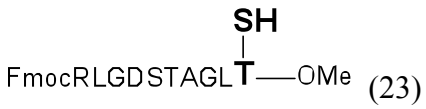
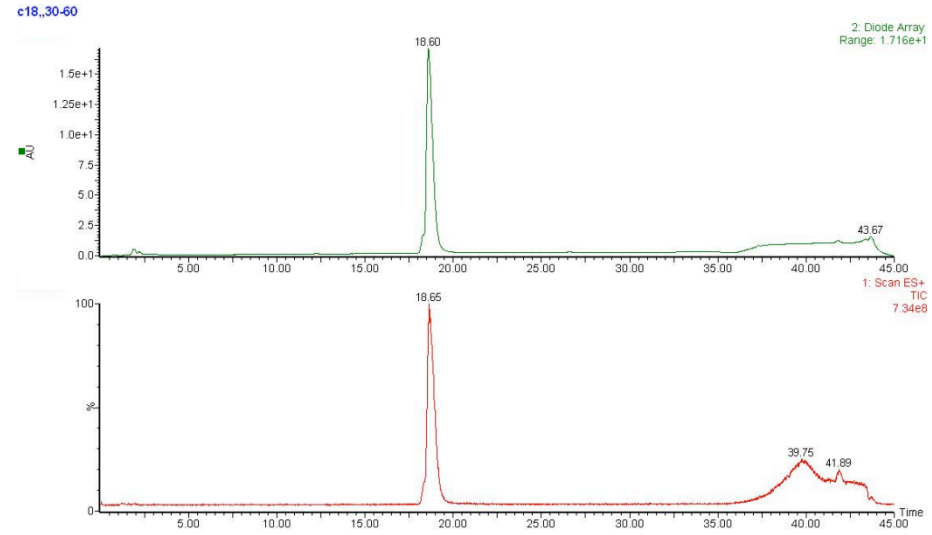



**Figure 16.** (a) UV and MS traces from LC-MS analysis of compound **22**: gradient 40-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **22.** ESI-MS calcd for $C_{57}H_{78}N_{12}O_{15}S$ $[M+H]^+$ *m/z* = 1203.55, found: 1204.02.




(23)

a

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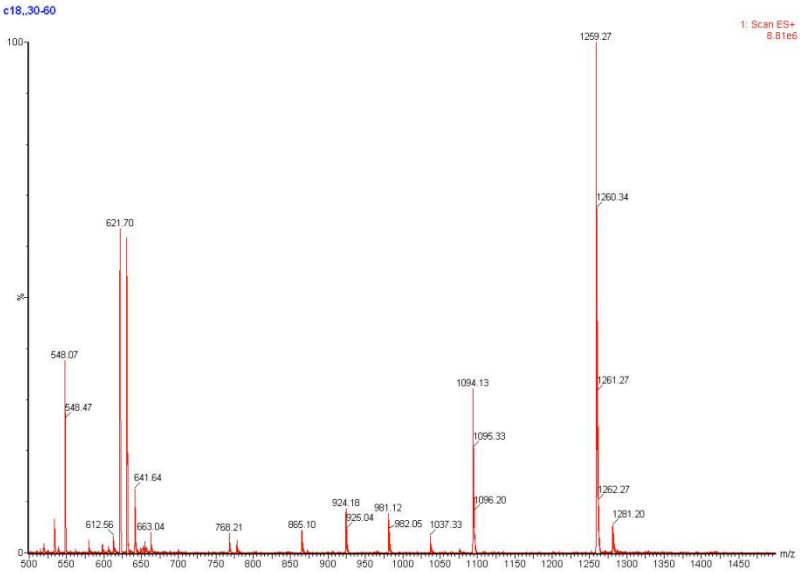
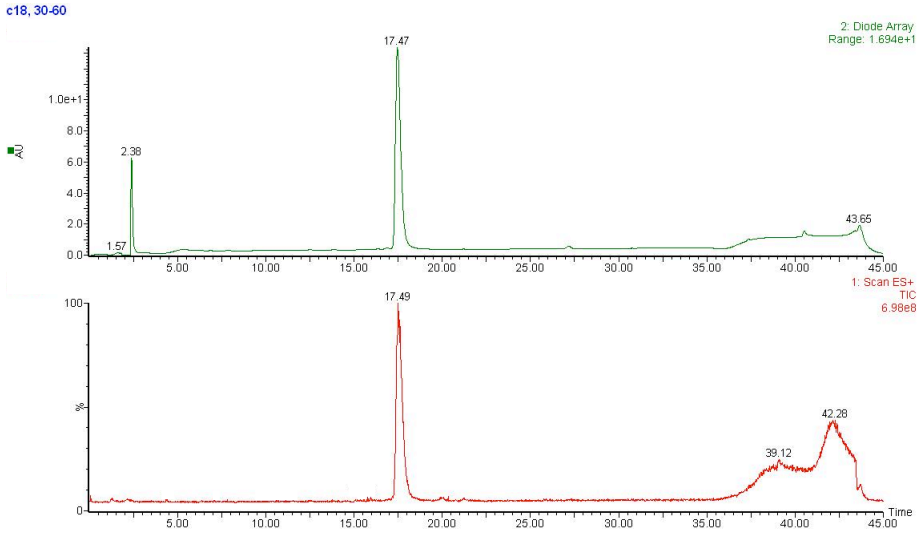



**Figure 17.** (a) UV and MS traces from LC-MS analysis of compound **23**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **23.** ESI-MS calcd for $C_{56}H_{83}N_{13}O_{18}S$ $[M+H]^+$ *m/z* = 1258.58, found: 1259.00.

FmocRLGDSTAGL**T**—OMe (24)

a




b

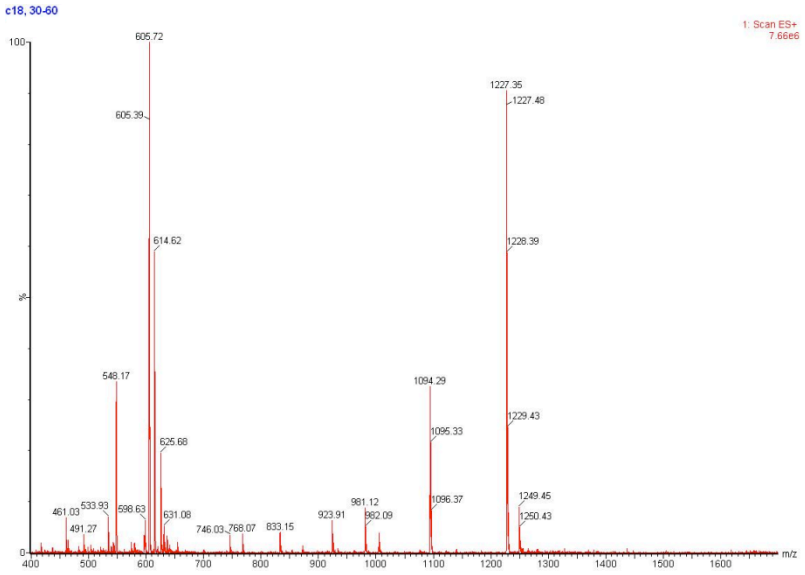
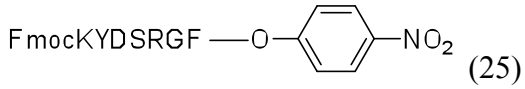
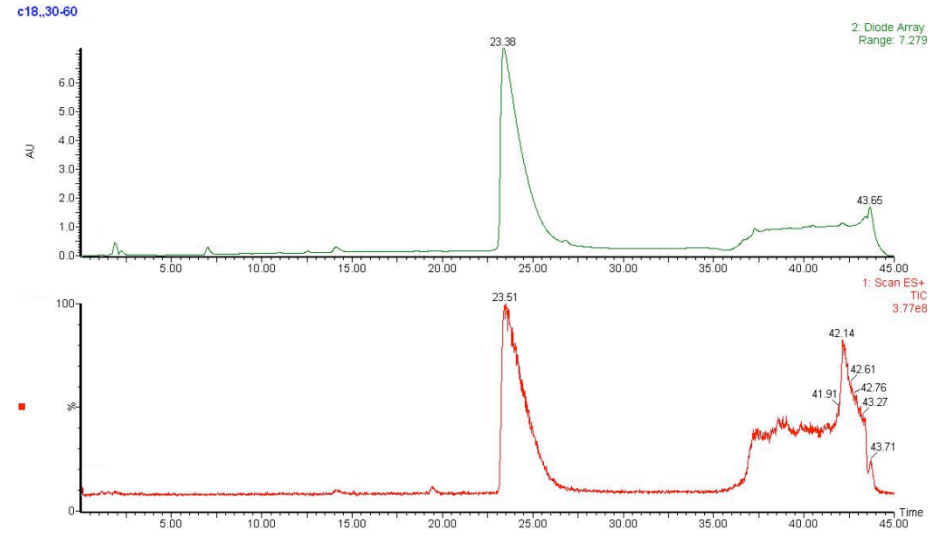



**Figure 18.** (a) UV and MS traces from LC-MS analysis of compound **24**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **24.** ESI-MS calcd for $C_{56}H_{83}N_{13}O_{18}$ $[M+H]^+$ *m/z* = 1226.61, found: 1227.09.




(25)

a




b

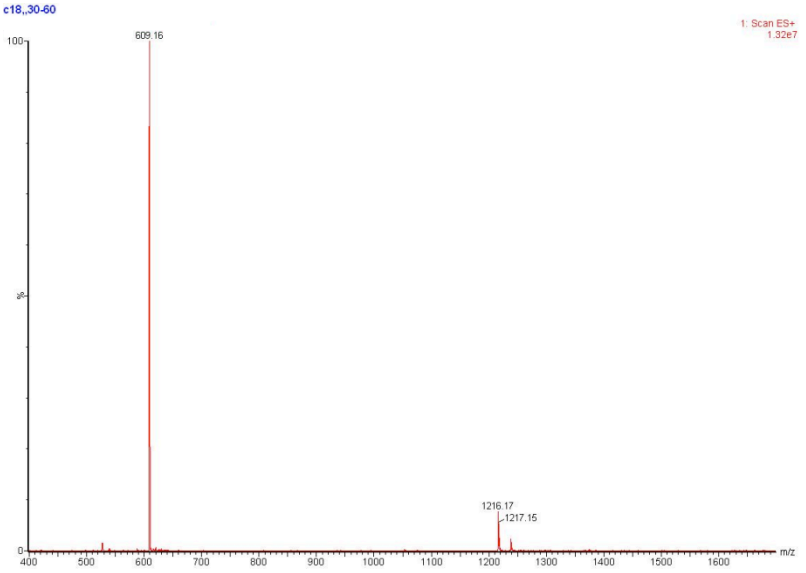
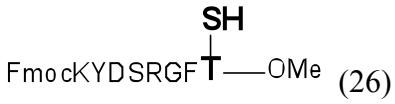
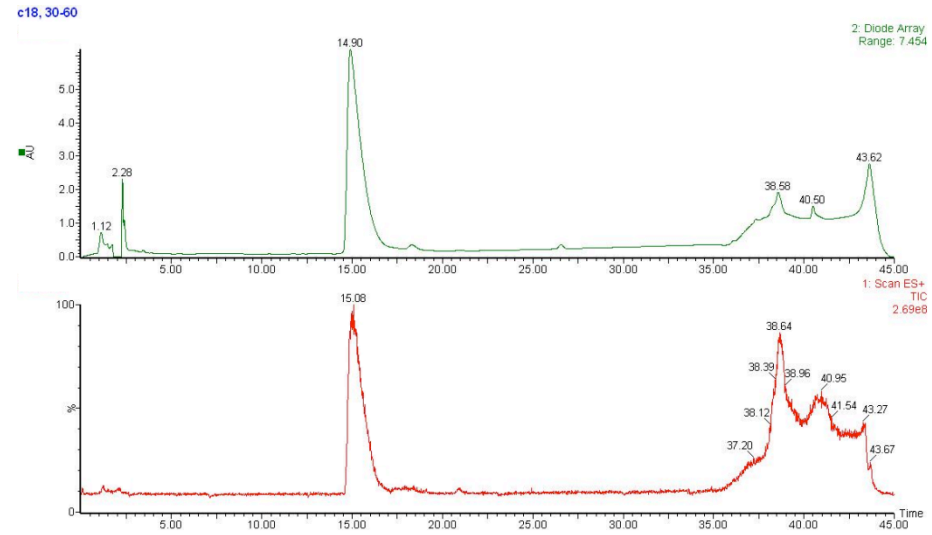



**Figure 19.** (a) UV and MS traces from LC-MS analysis of compound **25**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **25.** ESI-MS calcd for $C_{60}H_{70}N_{12}O_{16}$ $[M+H]^+$ *m/z* = 1215.51, $[M+2H]^{2+}$ *m/z* = 608.26; found: 1216.04, 608.71.




(26)

a




b

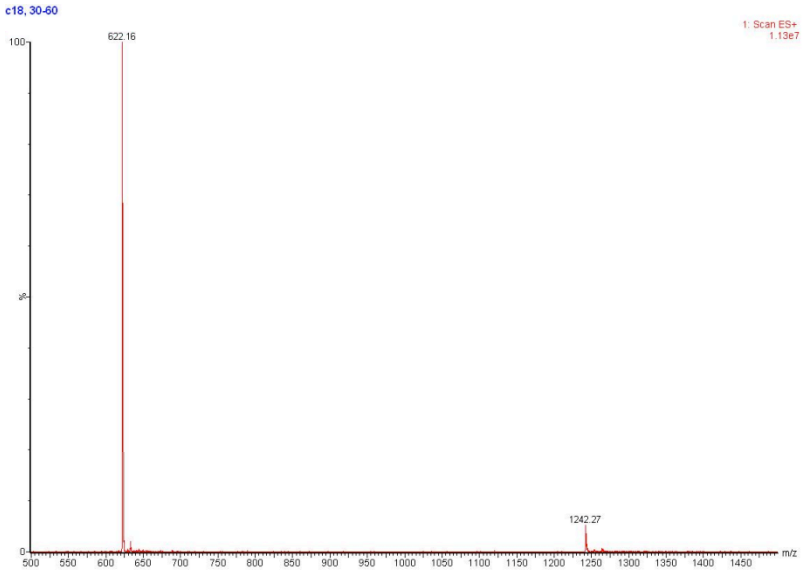
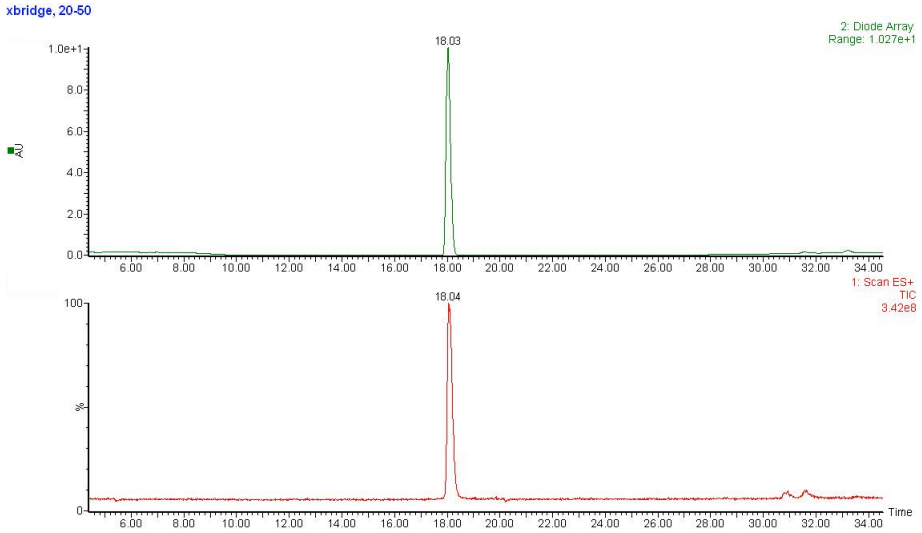



**Figure 20.** (a) UV and MS traces from LC-MS analysis of compound **26**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **26.** ESI-MS calcd for $C_{59}H_{76}N_{12}O_{16}S$ $[M+H]^+$ *m/z* = 1241.52, $[M+2H]^{2+}$ *m/z* = 621.27; found: 1241.94, 621.63.

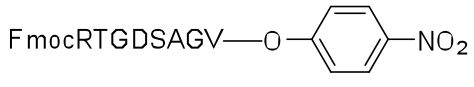
FmocKYDSRGF**T**—OMe (27)

a



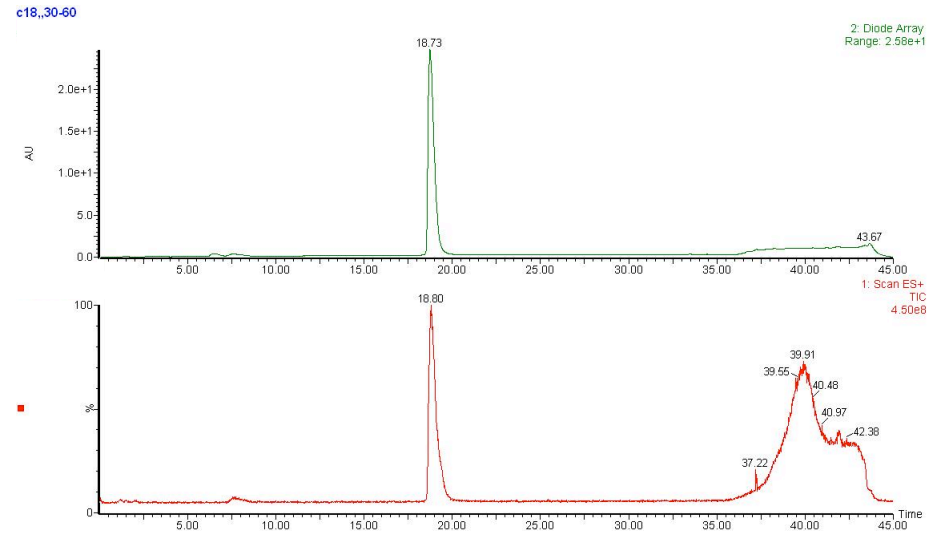

b


**Figure 21.** (a) UV and MS traces from LC-MS analysis of compound **27**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, x-bridge column. (b) ESI-MS of compound **27.** ESI-MS calcd for $C_{59}H_{76}N_{12}O_{16}$ $[M+H]^+$ *m/z* = 1209.56, $[M+2H]^{2+}$ *m/z* = 605.29; found: 1210.14, 605.69.




(28)

a




b

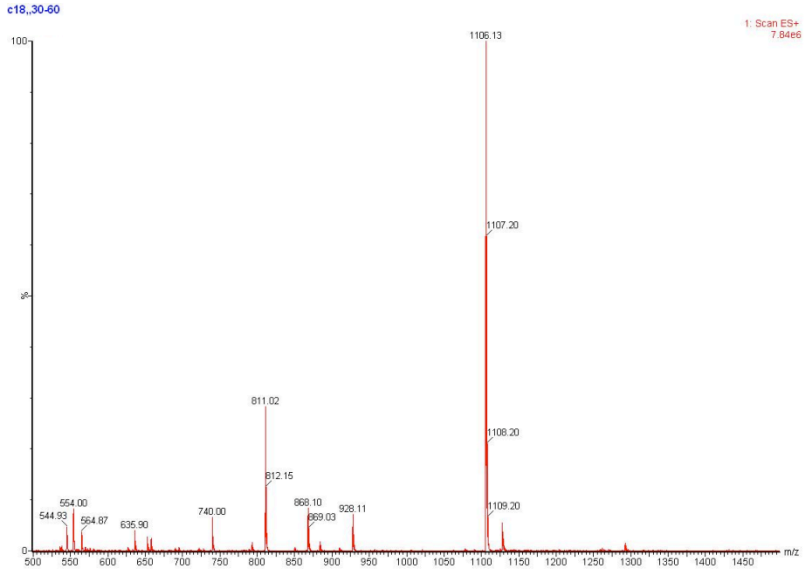
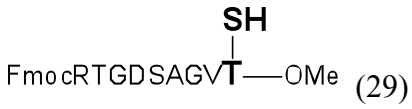
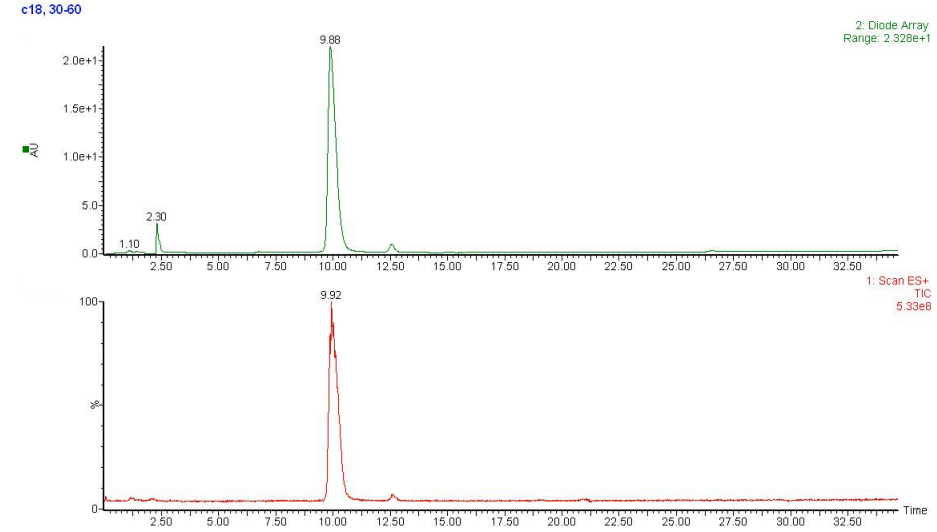



**Figure 22.** (a) UV and MS traces from LC-MS analysis of compound **28**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **28.** ESI-MS calcd for $C_{50}H_{64}N_{12}O_{17}$ $[M+H]^+$ *m/z* = 1105.46, found: 1105.80.




(29)

a




b

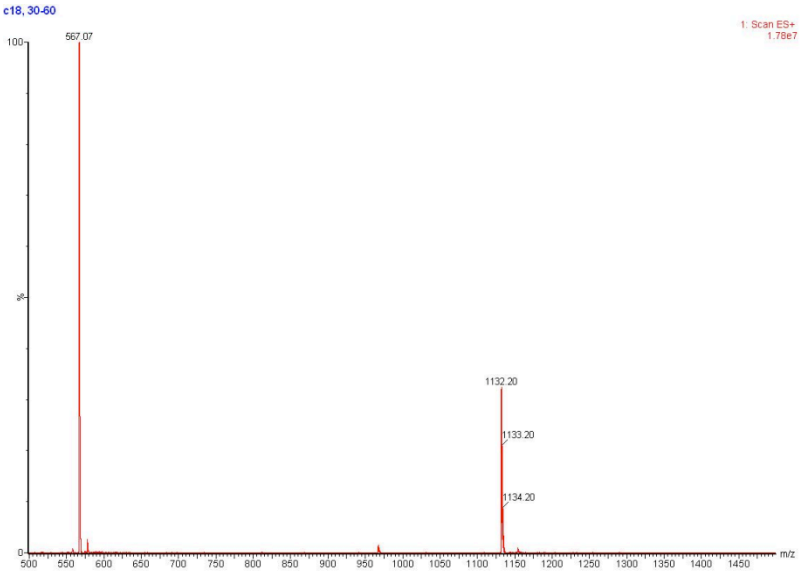
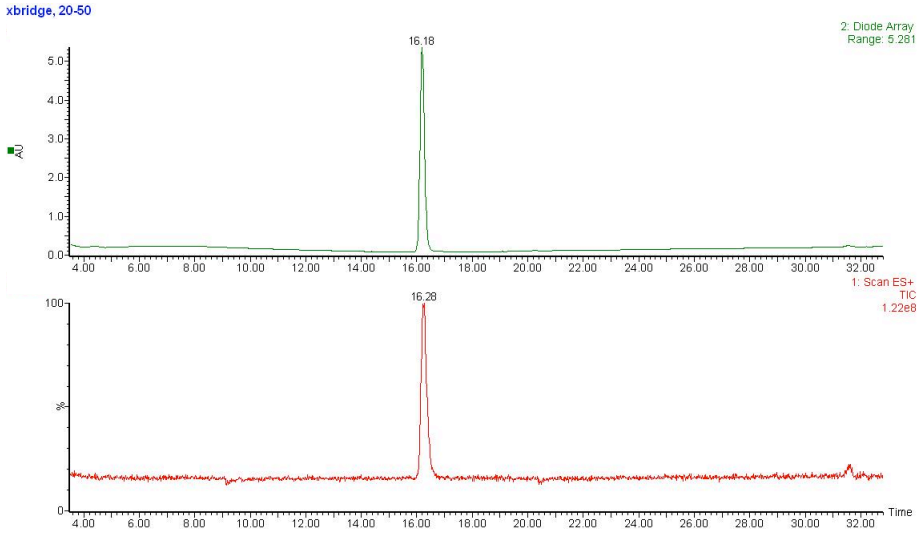



**Figure 23.** (a) UV and MS traces from LC-MS analysis of compound **29**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **29.** ESI-MS calcd for $C_{49}H_{70}N_{12}O_{17}S$ $[M+H]^+$ *m/z* = 1131.48, $[M+2H]^{2+}$ *m/z* = 566.25; found: 1131.87, 566.81.

FmocRTGDSAGV**T**—OMe (30)

a




b

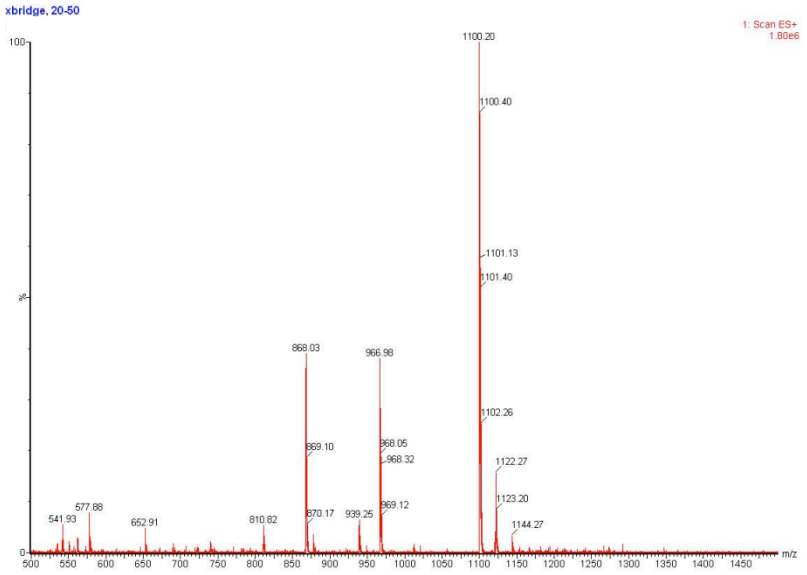
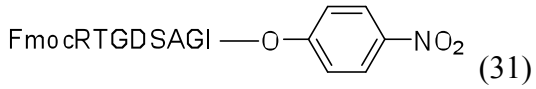
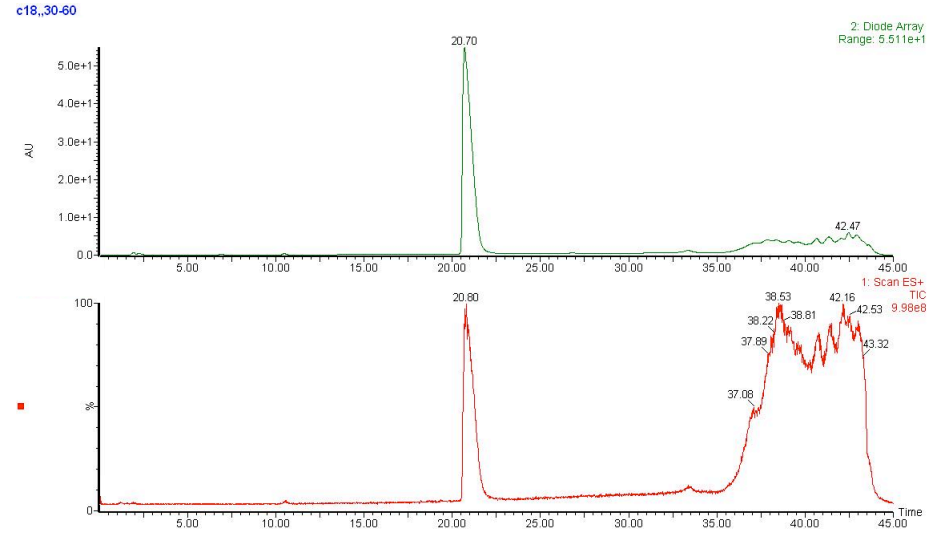



**Figure 24.** (a) UV and MS traces from LC-MS analysis of compound **30**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, x-bridge column. (b) ESI-MS of compound **30.** ESI-MS calcd for $C_{49}H_{70}N_{12}O_{17}$ $[M+H]^+$ *m/z* = 1099.51, found: 1099.86.




(31)

a




b

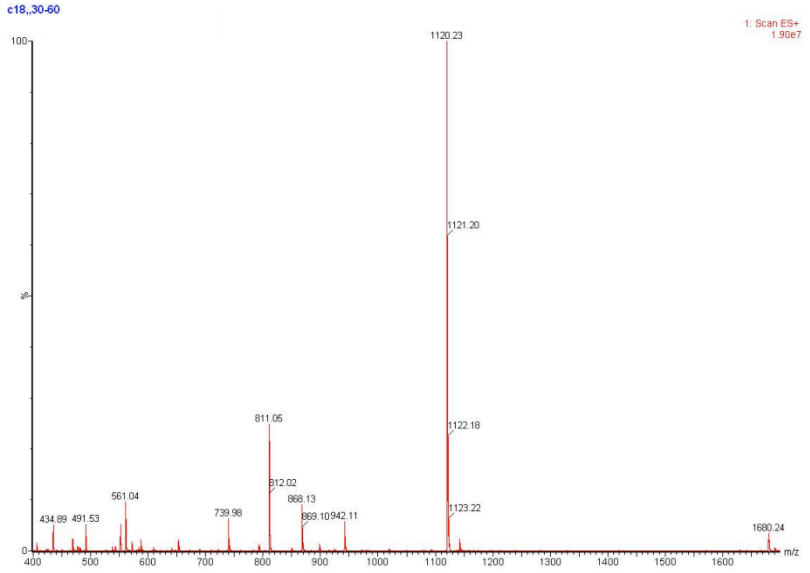
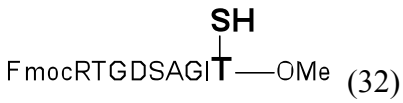
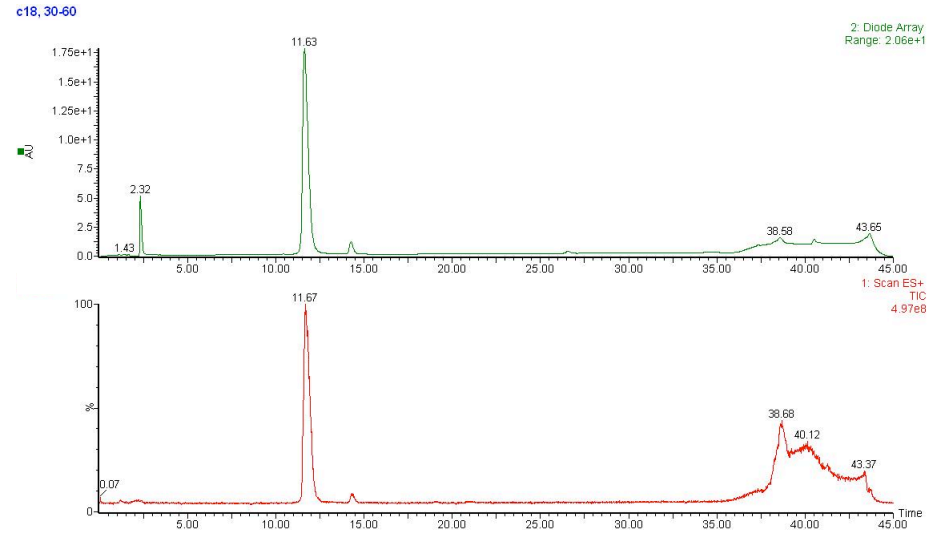



**Figure 25.** (a) UV and MS traces from LC-MS analysis of compound **31**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **31.** ESI-MS calcd for $C_{51}H_{66}N_{12}O_{17}$ $[M+H]^+$ *m/z* = 1119.48, found: 1120.10.




(32)

a

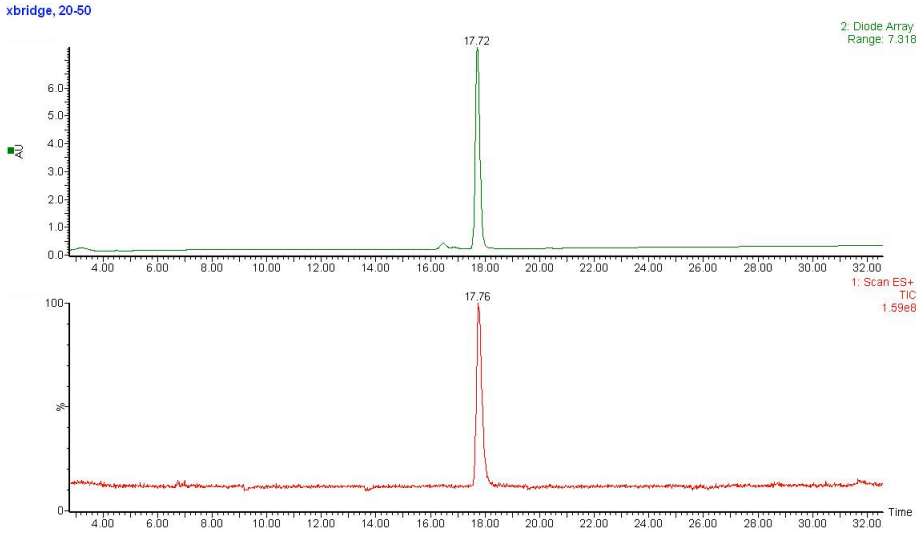



b


**Figure 26.** (a) UV and MS traces from LC-MS analysis of compound **32**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, x-bridge column. (b) ESI-MS of compound **32.** ESI-MS calcd for $C_{50}H_{72}N_{12}O_{17}S$ $[M+H]^+$ *m/z* = 1145.50, $[M+2H]^{2+}$ *m/z* = 573.26; found: 1145.93, 573.68.

FmocRTGDSAGI**T**—OMe (33)

a




b

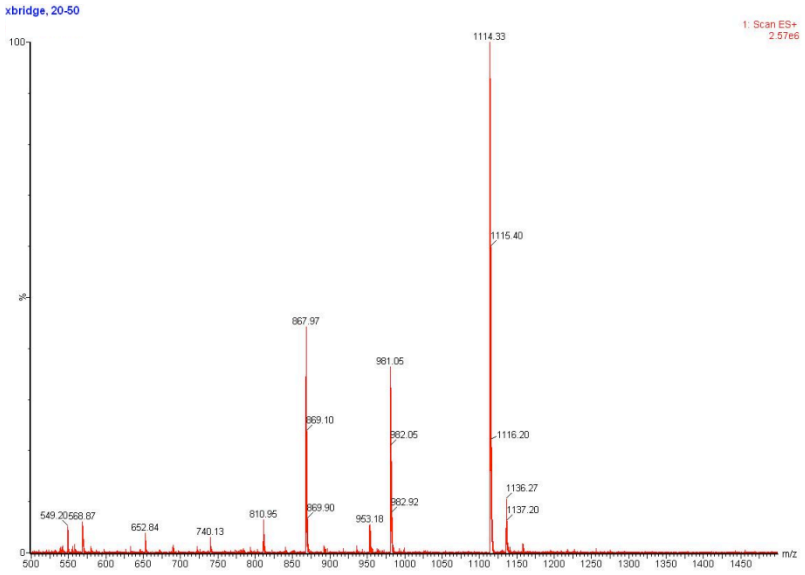
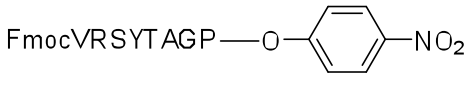
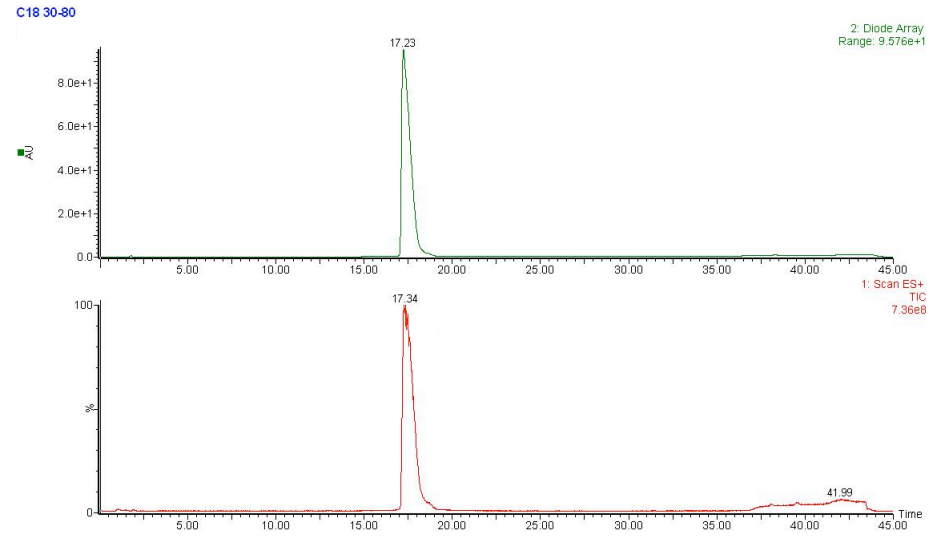



**Figure 27.** (a) UV and MS traces from LC-MS analysis of compound **33**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, x-bridge column. (b) ESI-MS of compound **33.** ESI-MS calcd for $C_{50}H_{72}N_{12}O_{17}$ $[M+H]^+$ *m/z* = 1113.52, found: 1113.87.




(34)

a




b

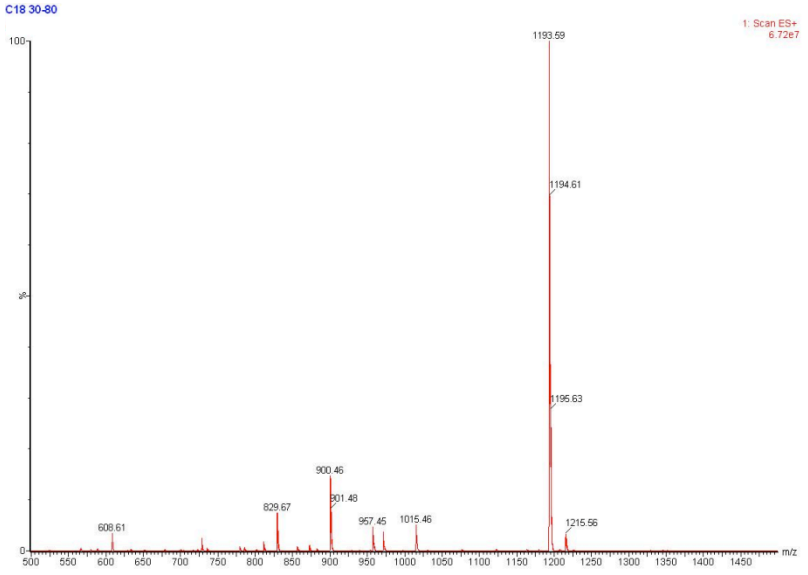
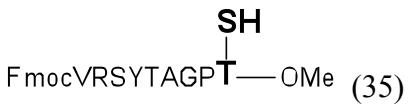
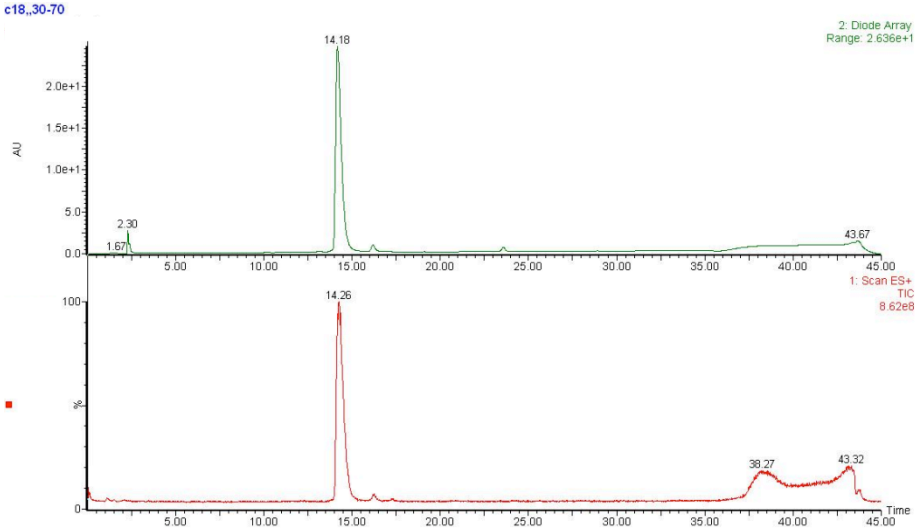



**Figure 28.** (a) UV and MS traces from LC-MS analysis of compound **34**: gradient 30-80% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **34.** ESI-MS calcd for $C_{58}H_{72}N_{12}O_{16}$ $[M+H]^+$ *m/z* = 1193.53, found: 1193.59.




(35)

a




b

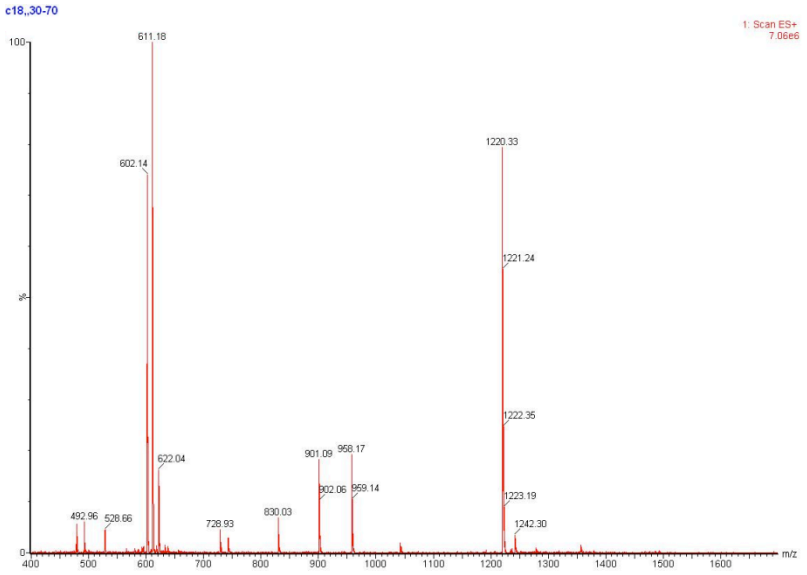
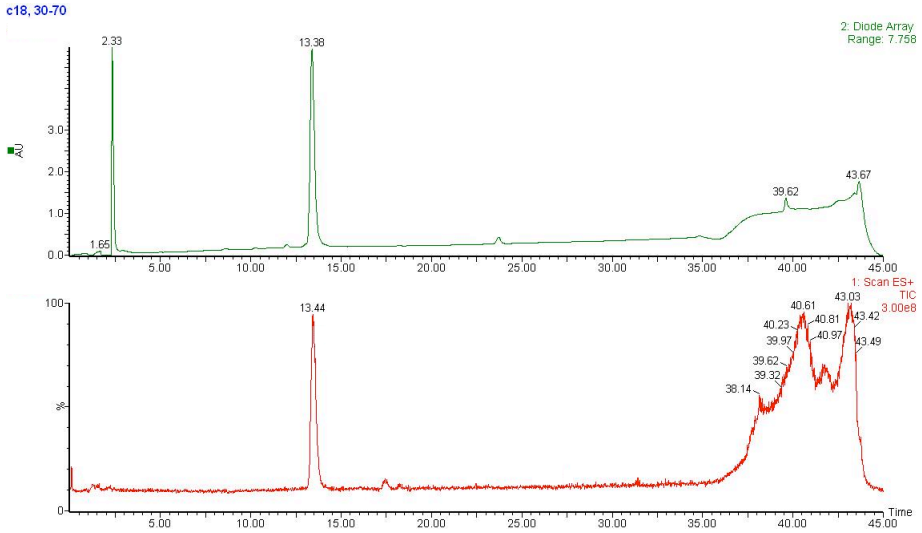



**Figure 29.** (a) UV and MS traces from LC-MS analysis of compound **35**: gradient 30-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **35.** ESI-MS calcd for $C_{57}H_{78}N_{12}O_{16}S$ $[M+H]^+$ *m/z* = 1219.55, found: 1220.01.

FmocVRSYTAGP**T**—OMe (36)

a




b

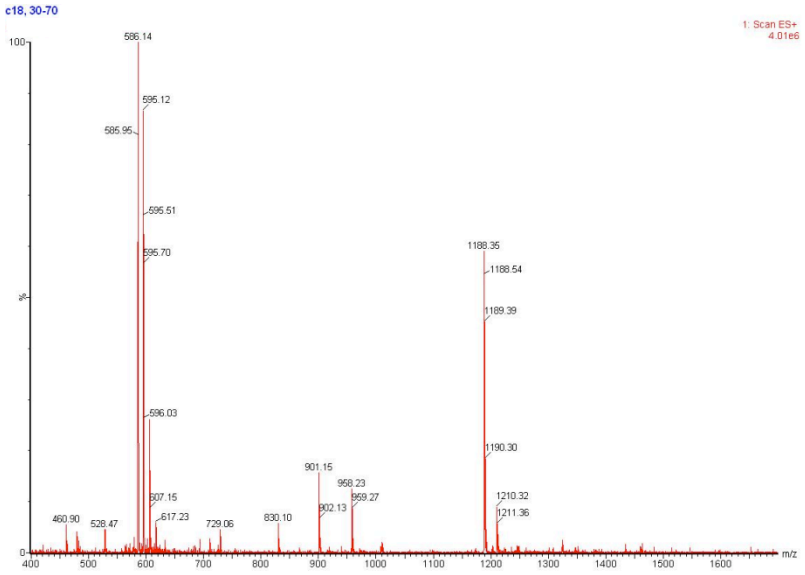
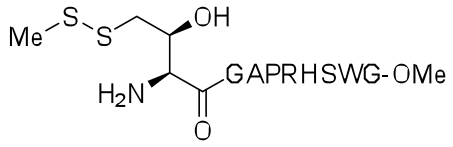
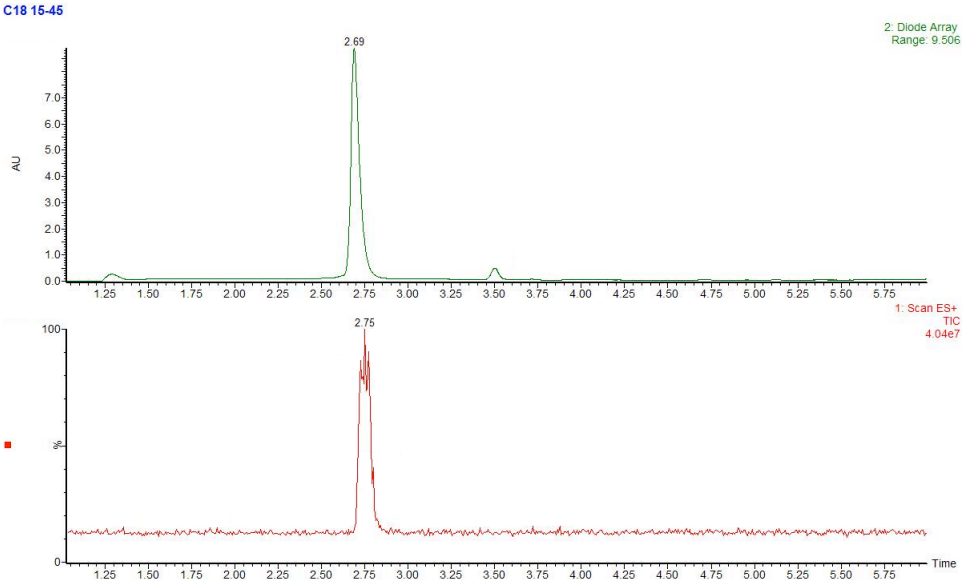



**Figure 30.** (a) UV and MS traces from LC-MS analysis of compound **36**: gradient 30-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **36.** ESI-MS calcd for $C_{57}H_{78}N_{12}O_{16}$ $[M+H]^+$ *m/z* = 1187.57, found: 1188.02.




(37)

a




b

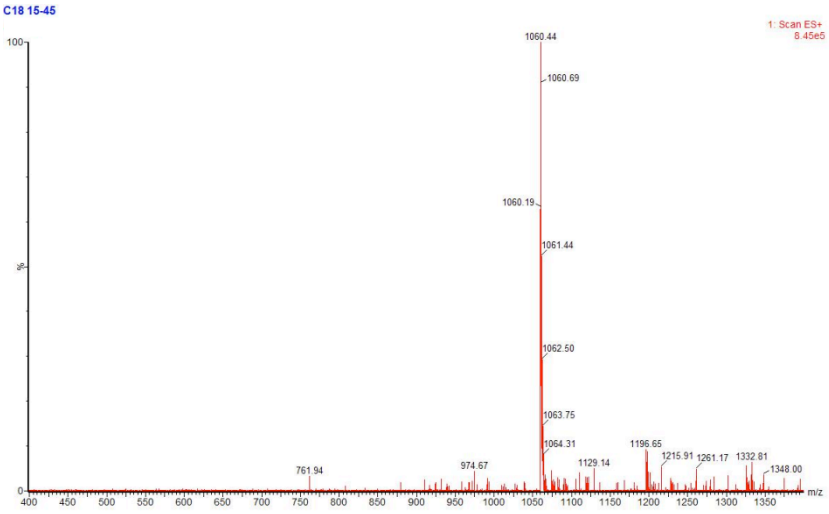
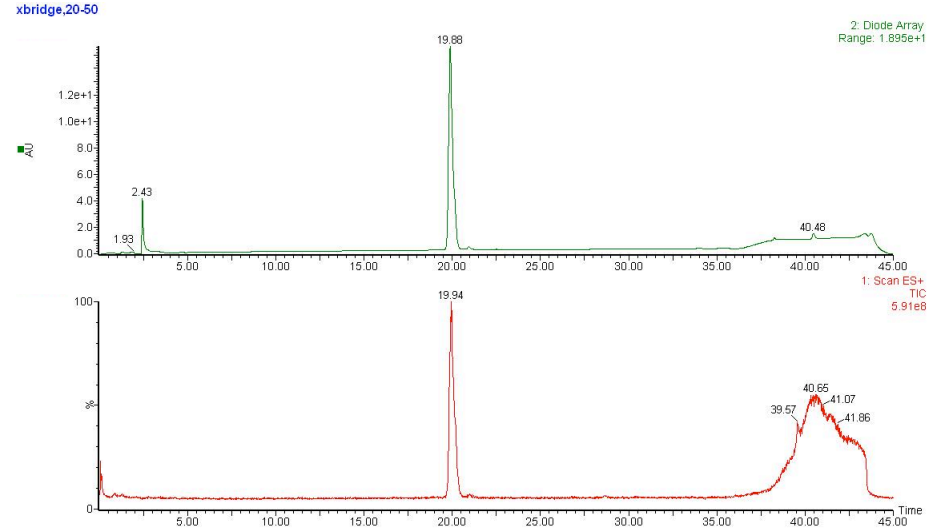



**Figure 31.** (a) UV and MS traces from LC-MS analysis of compound **37**: gradient 15-45% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **37.** ESI-MS calcd for $C_{44}H_{65}N_{15}O_{12}S_2$ $[M+H]^+$ *m/z* = 1060.45, found: 1060.44.


(38)

a




b

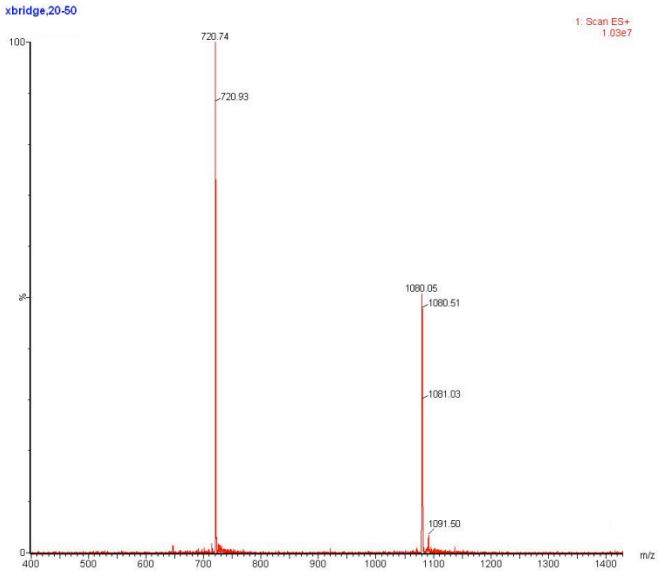
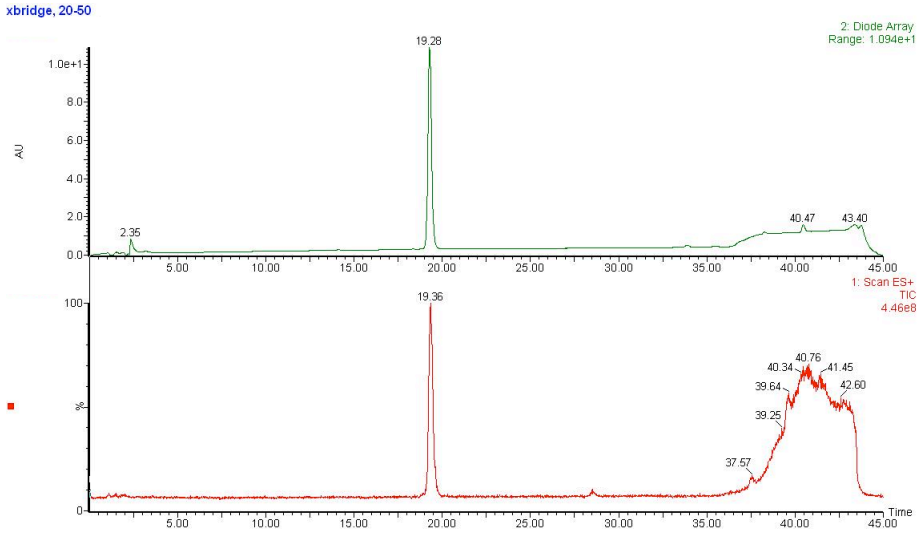



**Figure 32.** (a) UV and MS traces from LC-MS analysis of compound **38**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, xbridge column. (b) ESI-MS of compound **38.** ESI-MS calcd for $C_{97}H_{133}N_{27}O_{28}S$ $[M+2H]^{2+}$ *m/z* = 1078.99, $[M+3H]^{3+}$ *m/z* = 719.66, found: 1079.34, 719.96.

FmocRLGDSTAGYTGAPRHSWG——OMe (39)

a




b

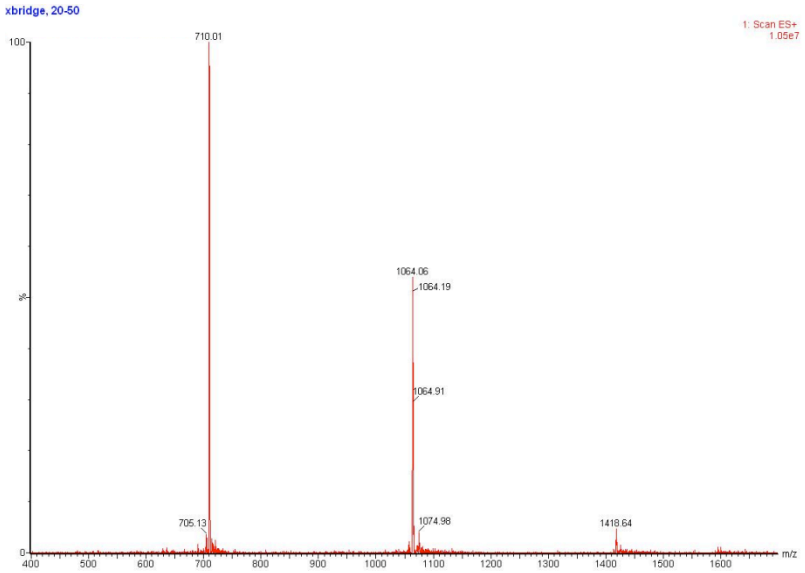



**Figure 33.** (a) UV and MS traces from LC-MS analysis of compound **39**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, xbridge column. (b) ESI-MS of compound **39.** ESI-MS calcd for $C_{97}H_{133}N_{27}O_{28}$ $[M+2H]^{2+}$ *m/z* = 1063.00, $[M+3H]^{3+}$ *m/z* = 709.00, found: 1063.35, 709.23.

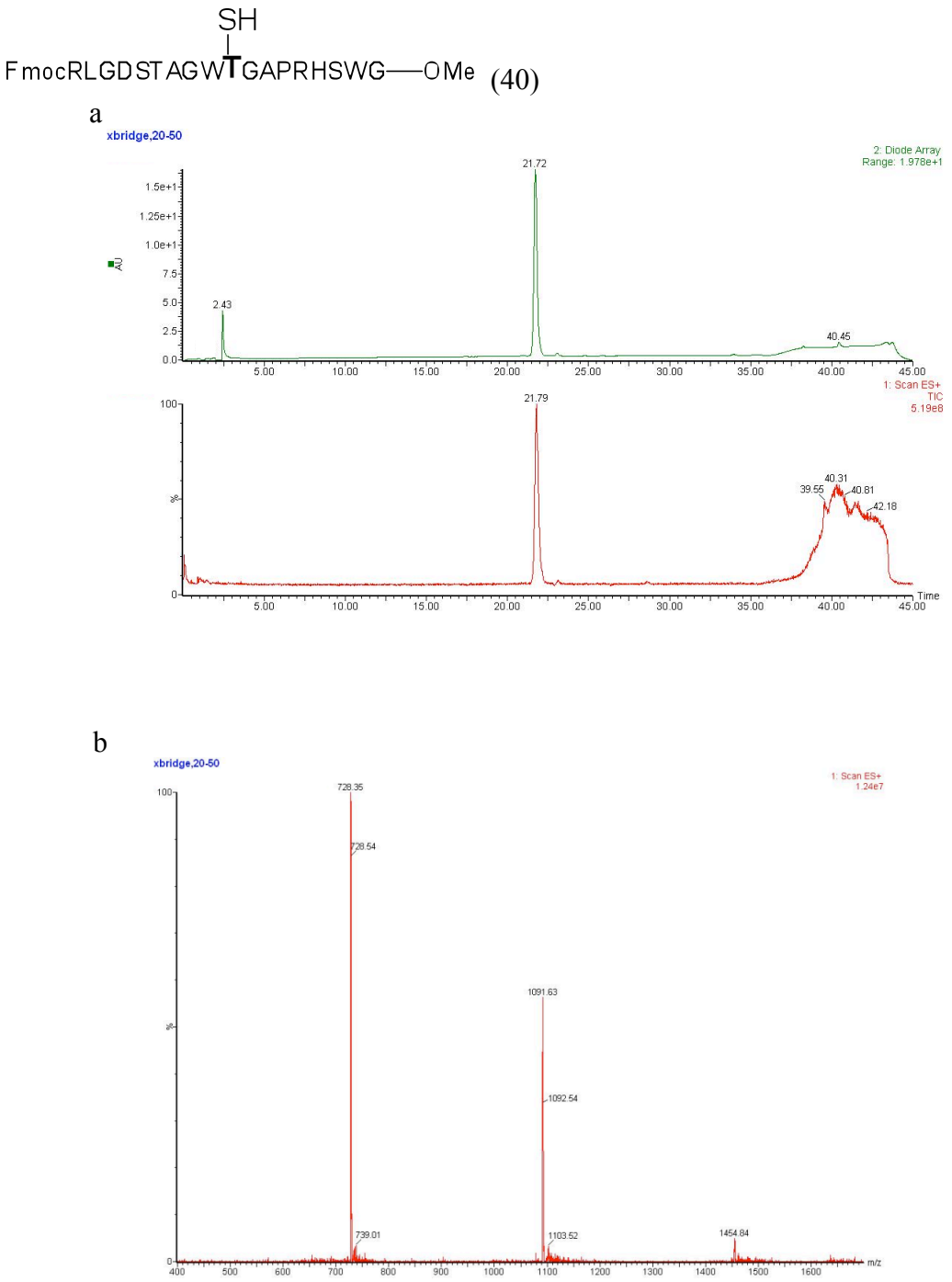
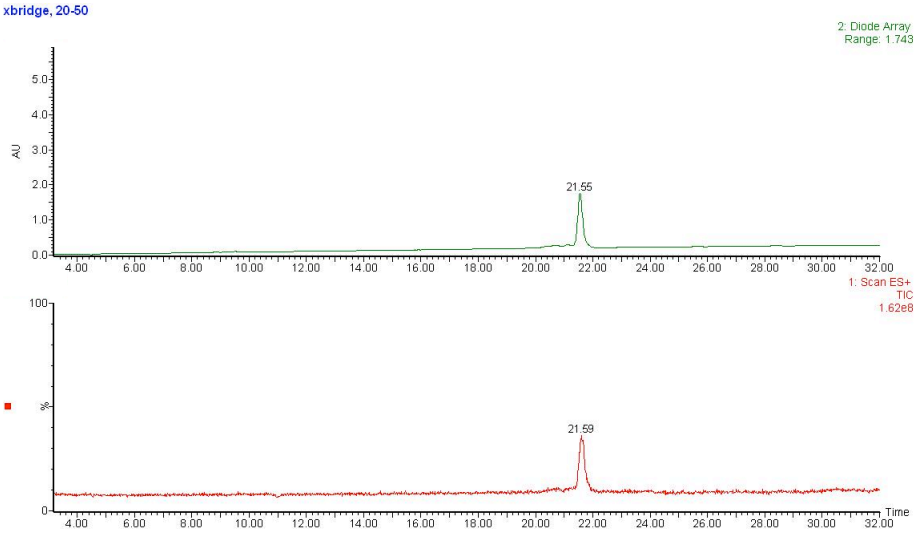



**Figure 34.** (a) UV and MS traces from LC-MS analysis of compound **40**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, xbridge column. (b) ESI-MS of compound **40.** ESI-MS calcd for $C_{99}H_{134}N_{28}O_{27}S$ $[M+2H]^{2+}$ *m/z* = 1090.50, $[M+3H]^{3+}$ *m/z* = 727.33, found: 1090.91, 727.57.

FmocRLGDSTAGW**T**GAPRHSWG—OMe (41)

a




b

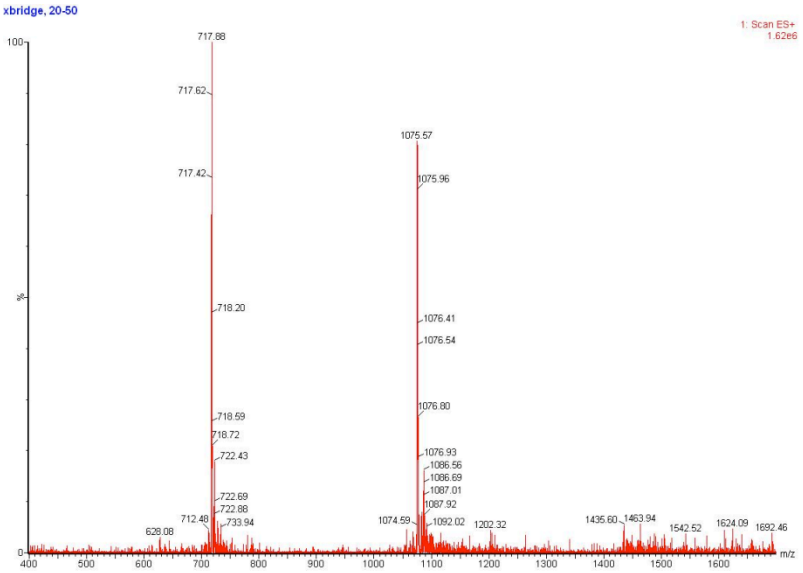
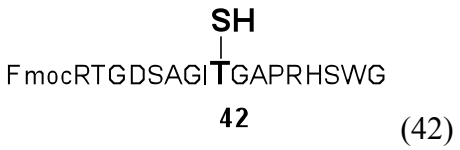
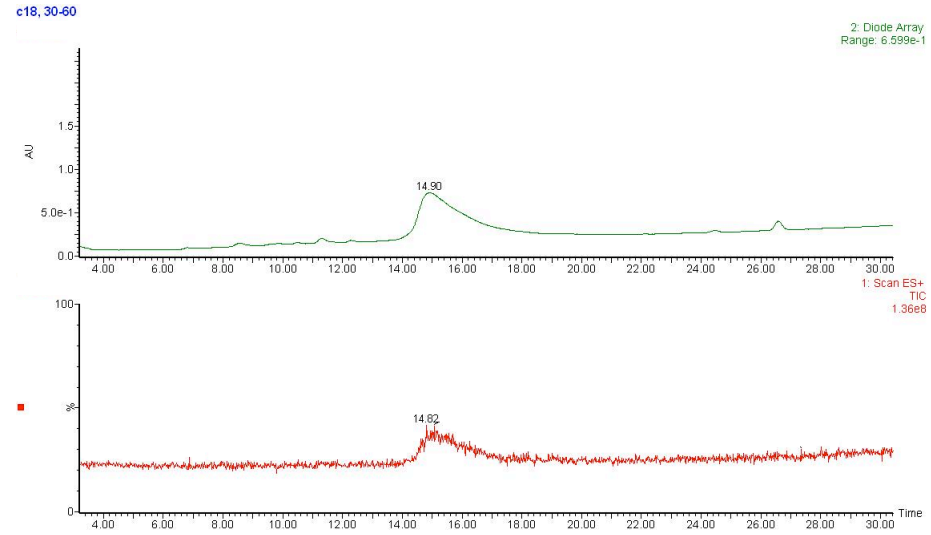



**Figure 35.** (a) UV and MS traces from LC-MS analysis of compound **41**: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, xbridge column. (b) ESI-MS of compound **41.** ESI-MS calcd for $C_{99}H_{134}N_{28}O_{27}$ $[M+2H]^{2+}$ *m/z* = 1074.50, $[M+3H]^{3+}$ *m/z* = 716.68, found: 1074.79, 716.97.




(42)

a




b

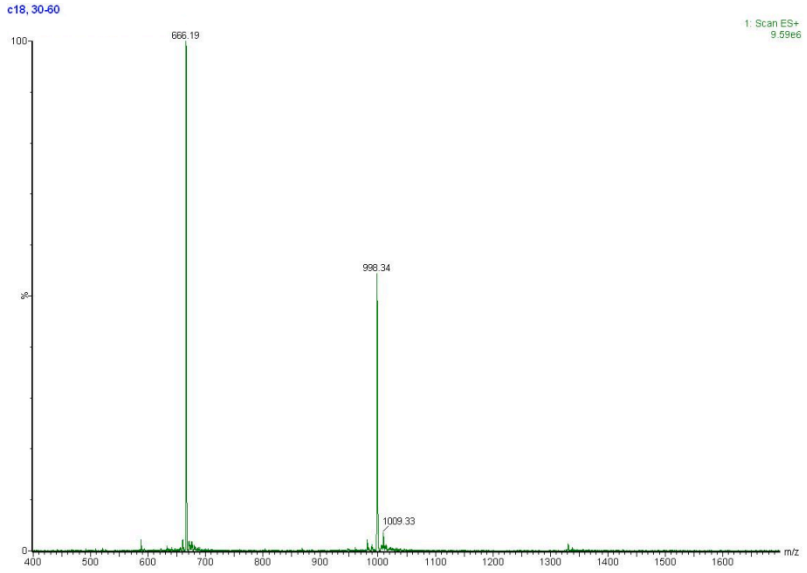
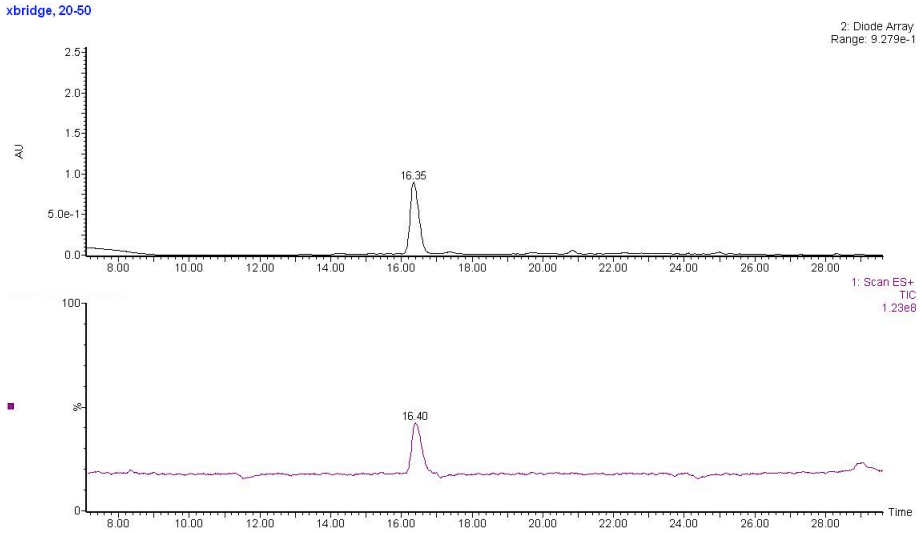



**Figure 36.** (a) UV and MS traces from LC-MS analysis of compound **42**: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **42.** ESI-MS calcd for $C_{88}H_{124}N_{26}O_{26}S$ $[M+2H]^{2+}$ *m/z* = 997.46, $[M+3H]^{3+}$ *m/z* = 665.31, found: 997.82, 665.60.

FmocRTGDSAGI**T**GAPRHSWG (43)

a




b

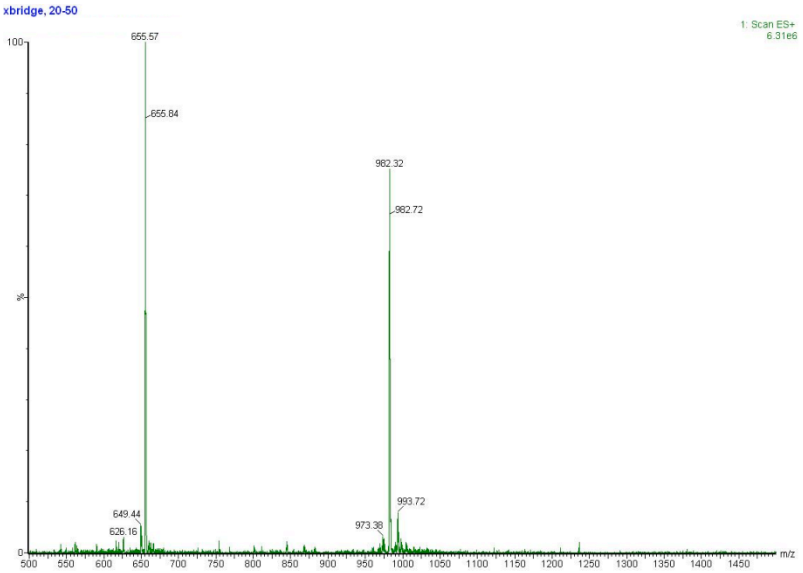
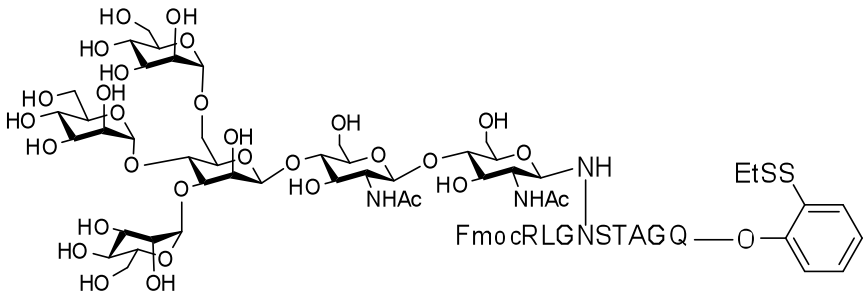
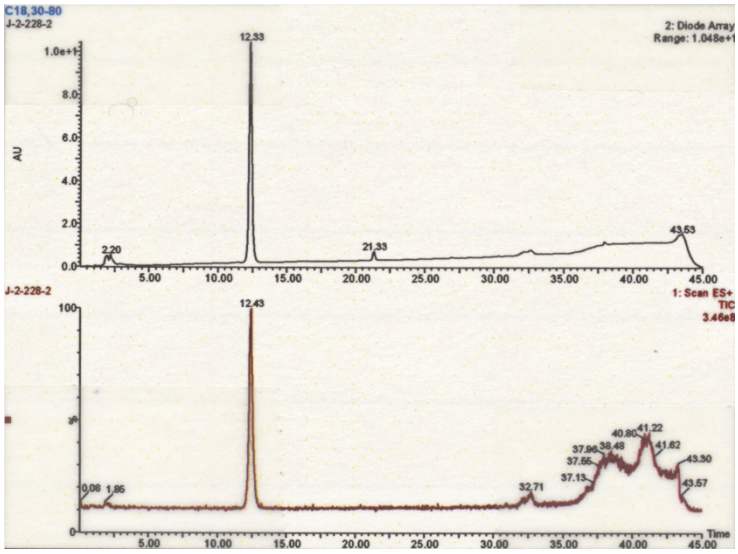



**Figure 37.** (a) UV and MS traces from LC-MS analysis of compound **43**: gradient 20-50%$CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, xbridge column. (b) ESI-MS of compound **43.** ESI-MS calcd for $C_{88}H_{124}N_{26}O_{26}$ $[M+2H]^{2+}$ *m/z* = 981.47, $[M+3H]^{3+}$ *m/z* = 654.65, found: 981.72, 654.97.




(44)

a




b

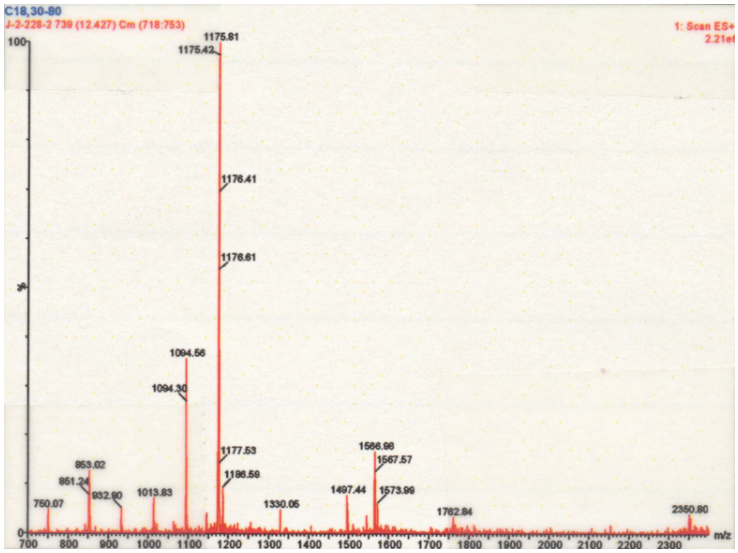
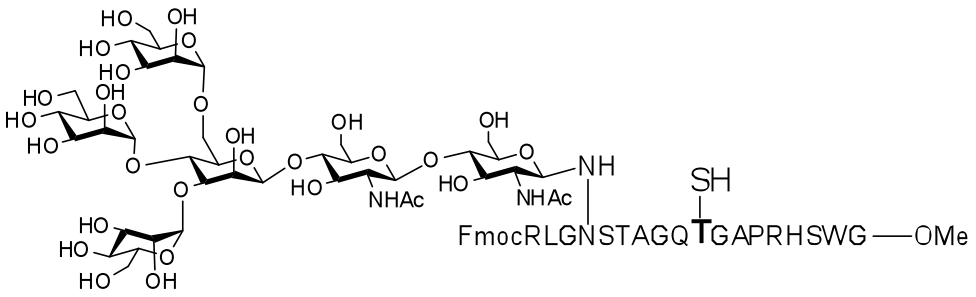
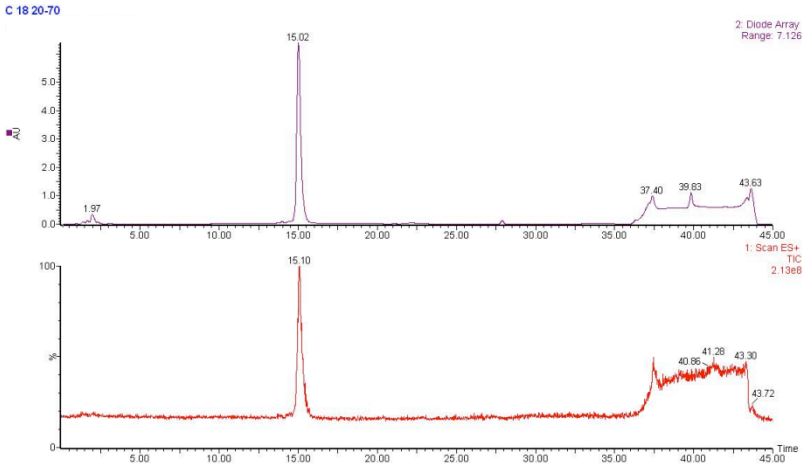



**Figure 38.** (a) UV and MS traces from LC-MS analysis of compound **44**: gradient 30-80% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **44.** ESI-MS calcd for $C_{98}H_{146}N_{16}O_{46}S_2$ $[M+2H]^{2+}$ *m/z* = 1174.46, found: 1175.42.




(45)

a




b

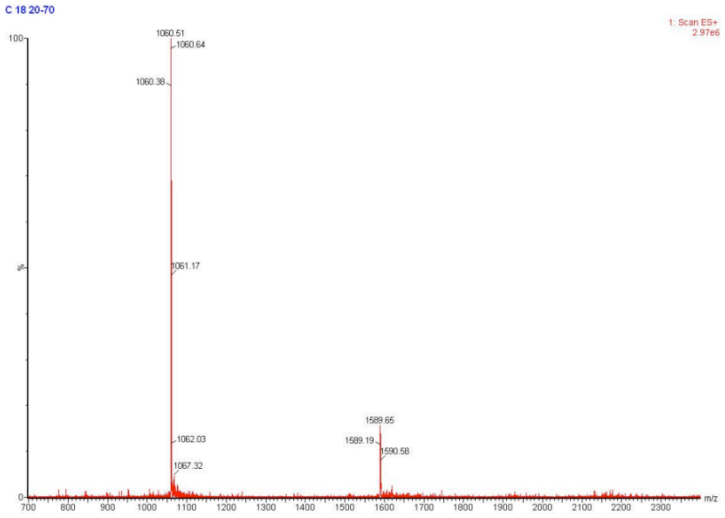
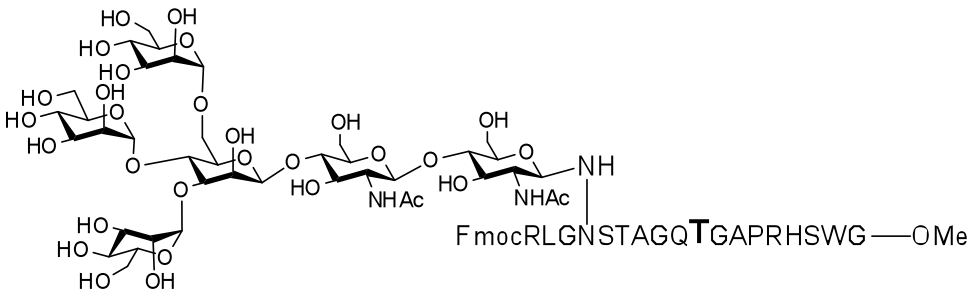
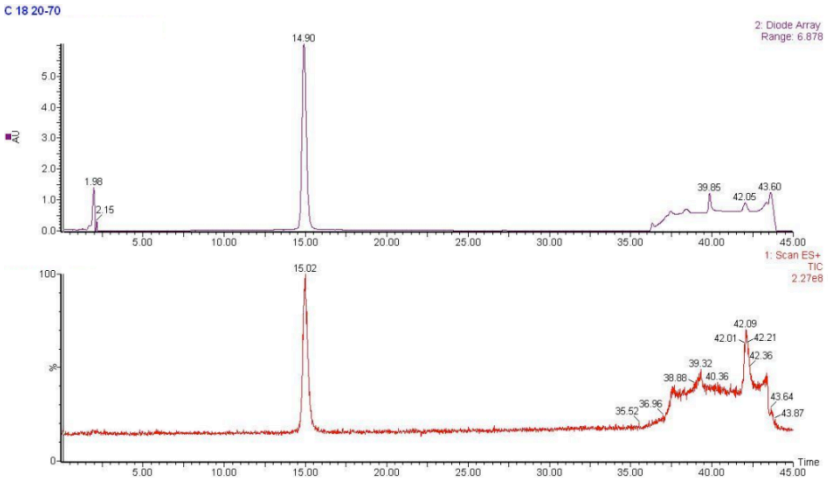



**Figure 39.** (a) UV and MS traces from LC-MS analysis of compound **45**: gradient 20-70%$CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **45.** ESI-MS calcd for $C_{133}H_{199}N_{31}O_{57}S$ $[M+2H]^{2+}$ *m/z* = 1588.18, $[M+3H]^{3+}$ *m/z* = 1059.12, found: 1588.27, 1059.25.




(46)

a




b


**Figure 40.** (a) UV and MS traces from LC-MS analysis of compound **46**: gradient 20-70%$CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound **46.** ESI-MS calcd for $C_{133}H_{199}N_{31}O_{57}$ $[M+2H]^{2+}$ *m/z* = 1572.19, $[M+3H]^{3+}$ *m/z* = 1048.46, found: 1572.66, 1048.74.

## LC-MS monitor of reactions in table 1 and table 2

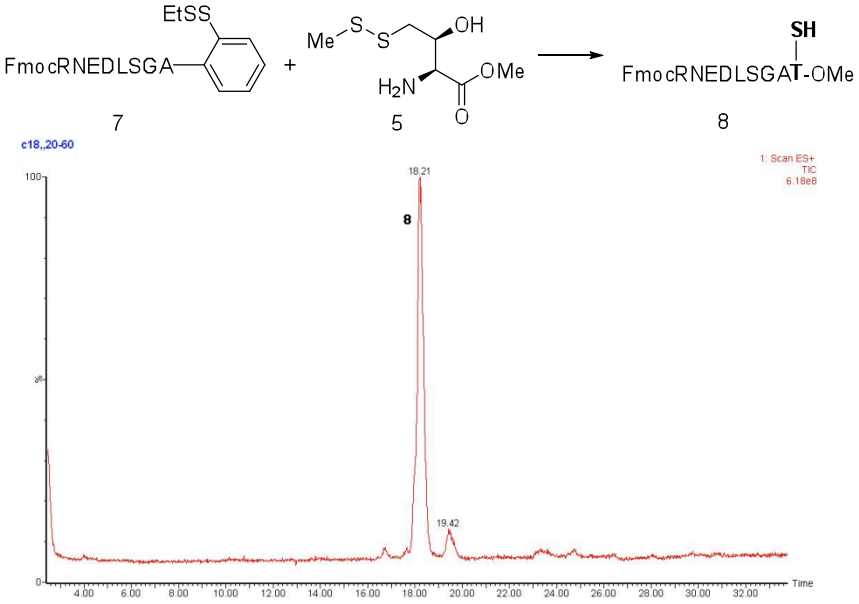



**Figure 41.** LC-MS trace of ligation between **7** and **5** at 1 h: gradient 20-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

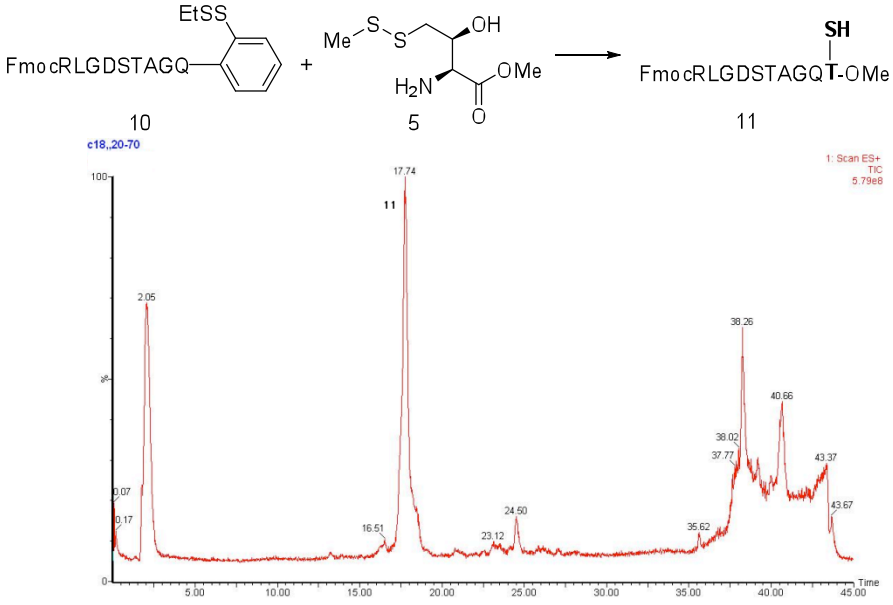



**Figure 42.** LC-MS trace of ligation between **10** and **5** at 30 min: gradient 20-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

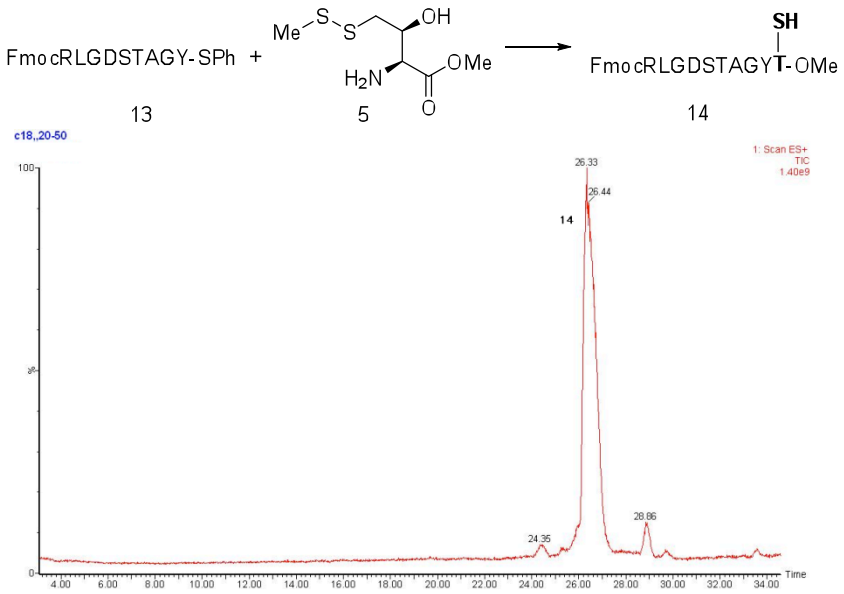



**Figure 43.** LC-MS trace of ligation between **13** and **5** at 30 min: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

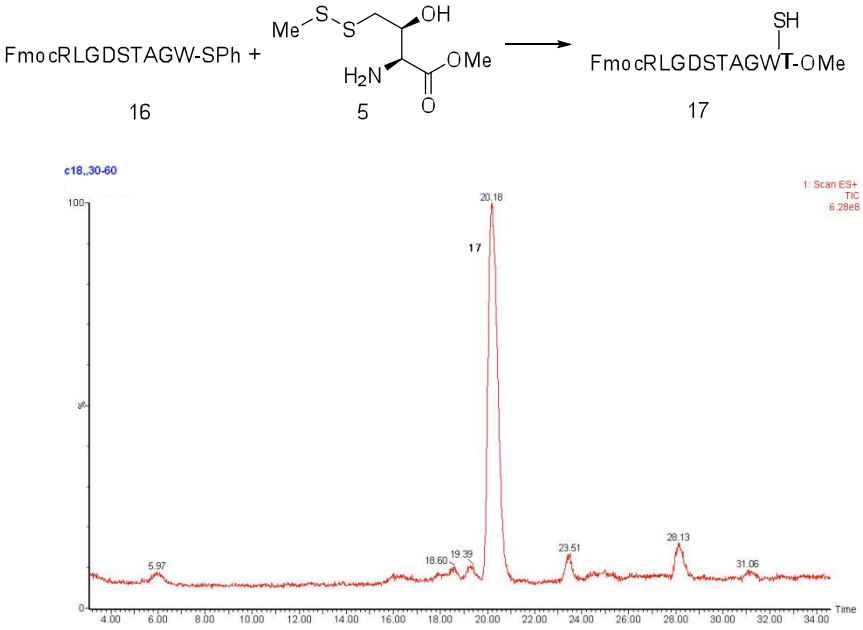



**Figure 44.** LC-MS trace of ligation between **16** and **5** at 30 min: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

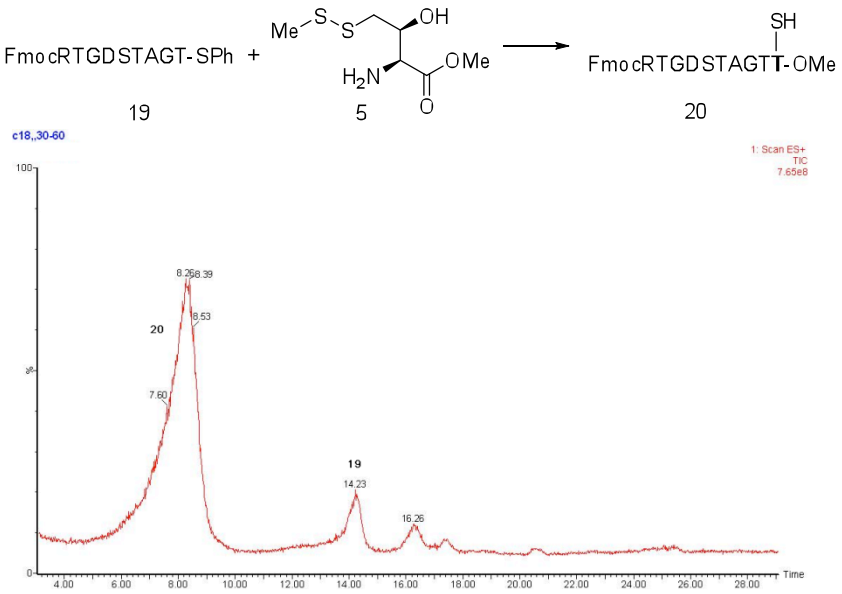



**Figure 45.** LC-MS trace of ligation between **19** and **5** at 30 min: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

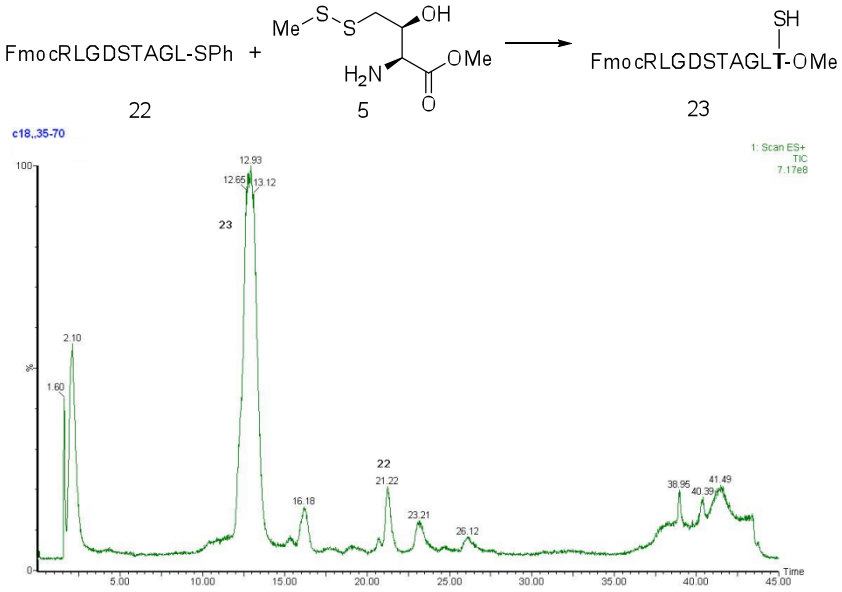



**Figure 46.** LC-MS trace of ligation between **22** and **5** at 30 min: gradient 35-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

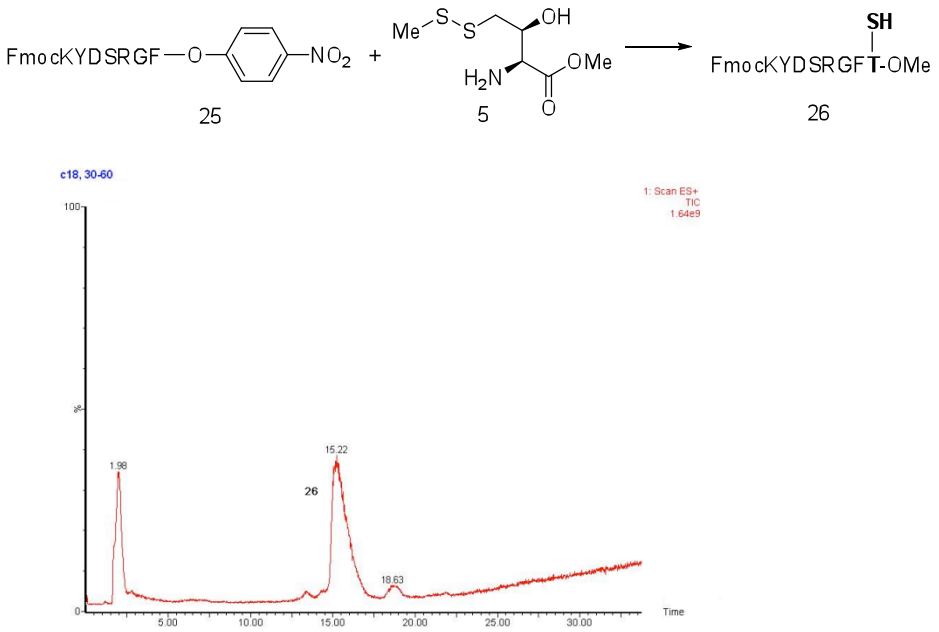



**Figure 47.** LC-MS trace of ligation between **25** and **5** at 30 min: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

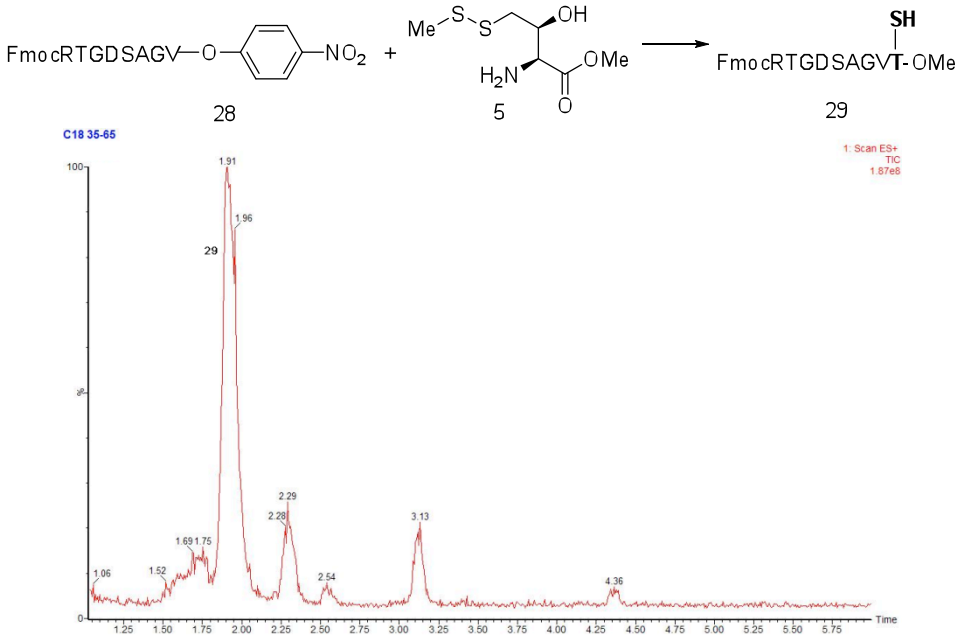



**Figure 48.** LC-MS trace of ligation between **28** and **5** at 3 h: gradient 35-65% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

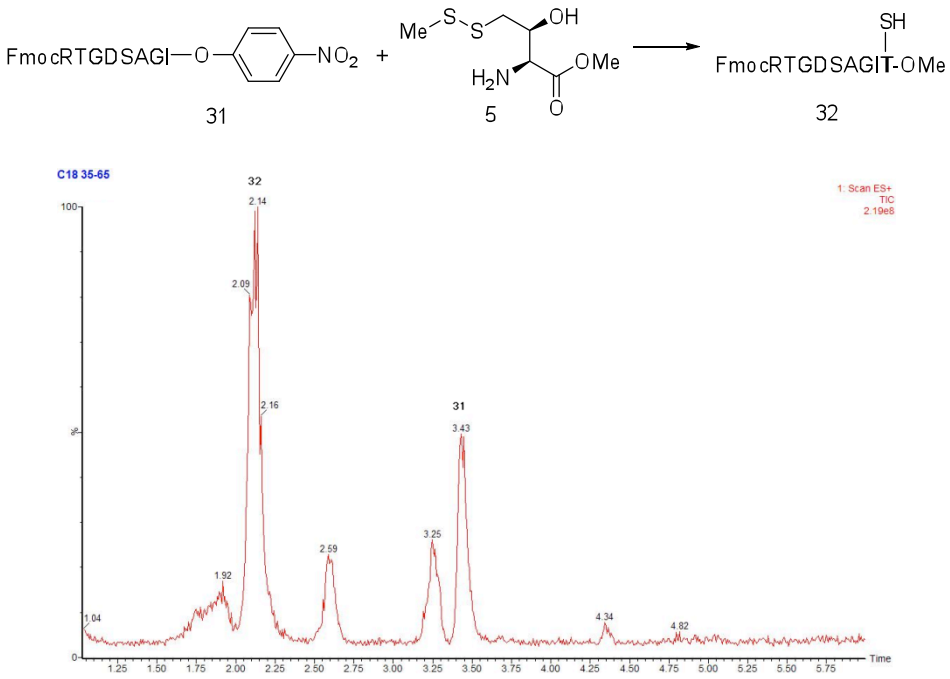



**Figure 49.** LC-MS trace of ligation between **31** and **5** at 4 h: gradient 35-65% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

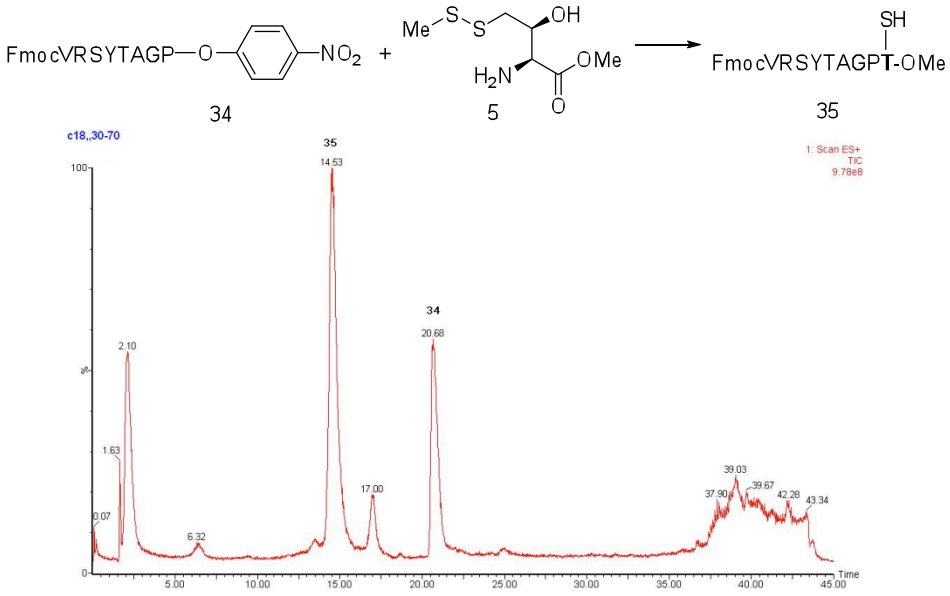



**Figure 50.** LC-MS trace of ligation between **34** and **5** at 1 h: gradient 30-70% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

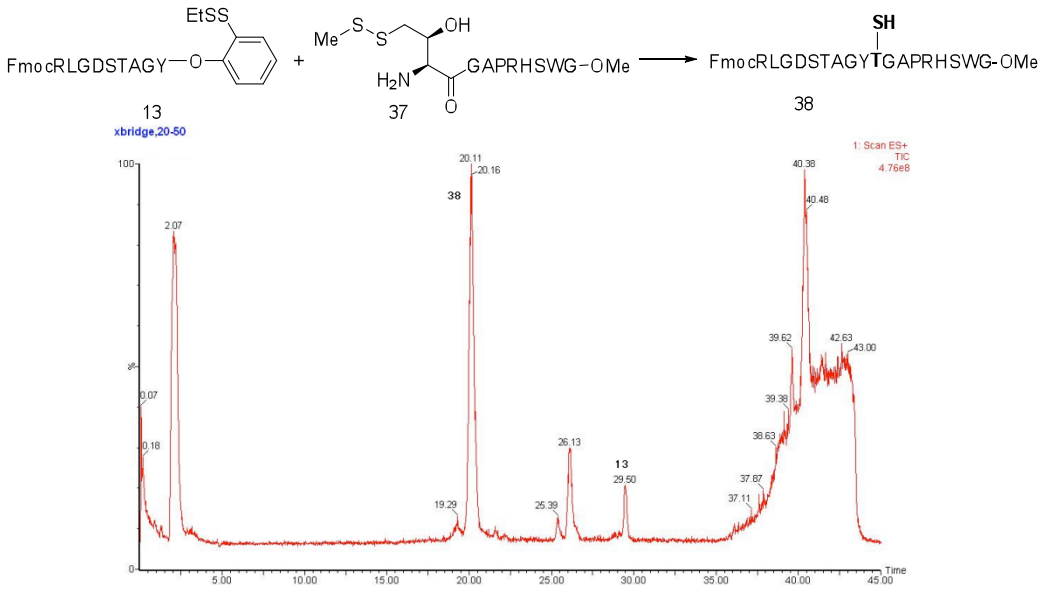



**Figure 51.** LC-MS trace of ligation between **13** and **37** at 1.5 h: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, xbridge column.

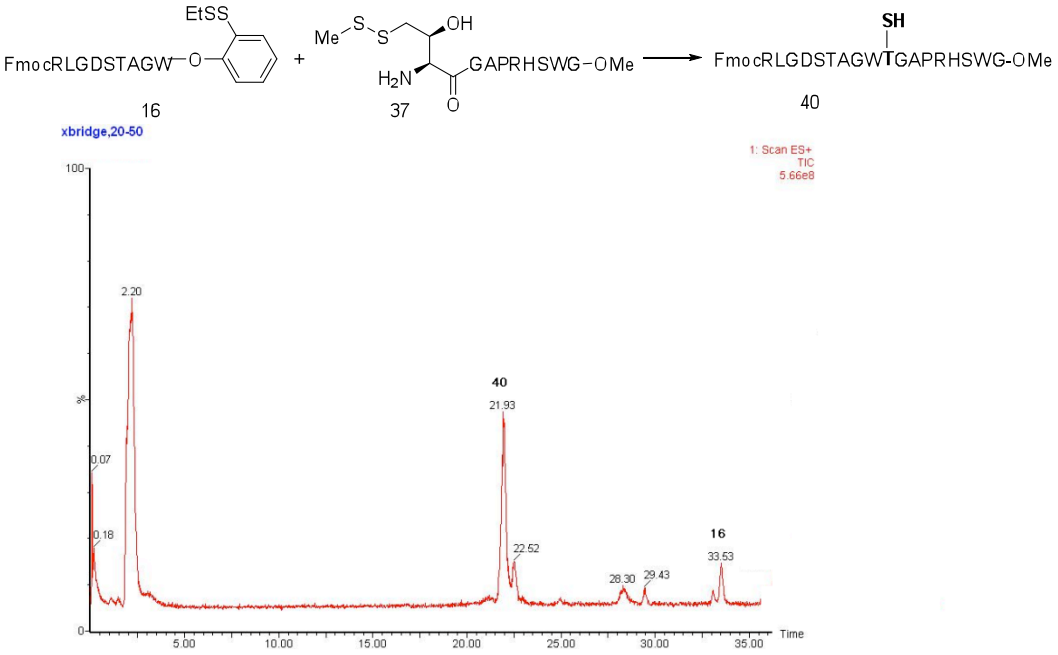



**Figure 52.** LC-MS trace of ligation between **16** and **37** at 1.5 h: gradient 20-50% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, xbridge column.

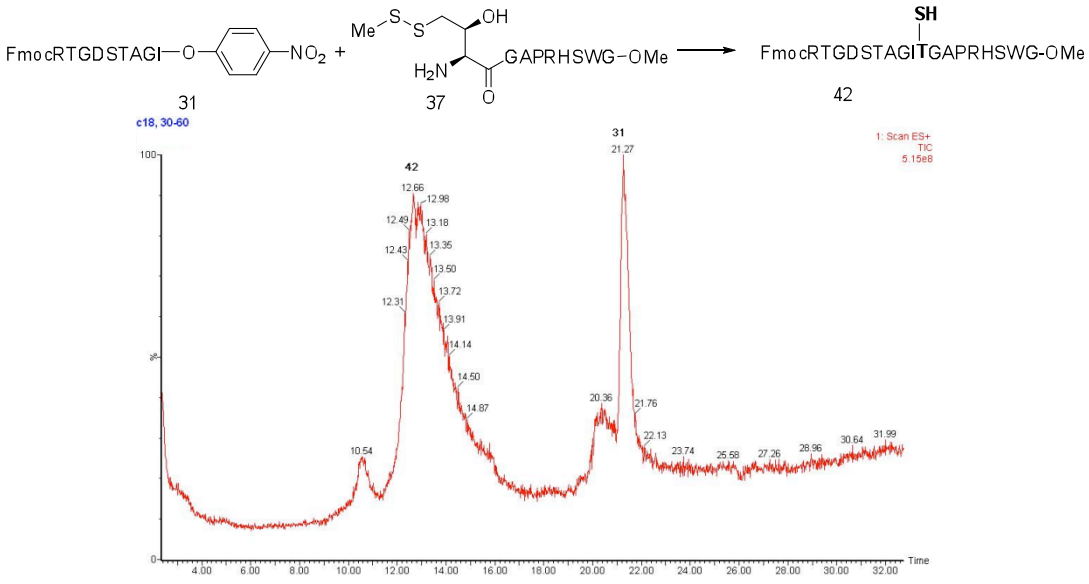



**Figure 53.** LC-MS trace of ligation between **31** and **37** at 3 h: gradient 30-60% $CH_3CN/H_2O$ over 30 min at a flow rate of 0.2 mL/min, C18 column.

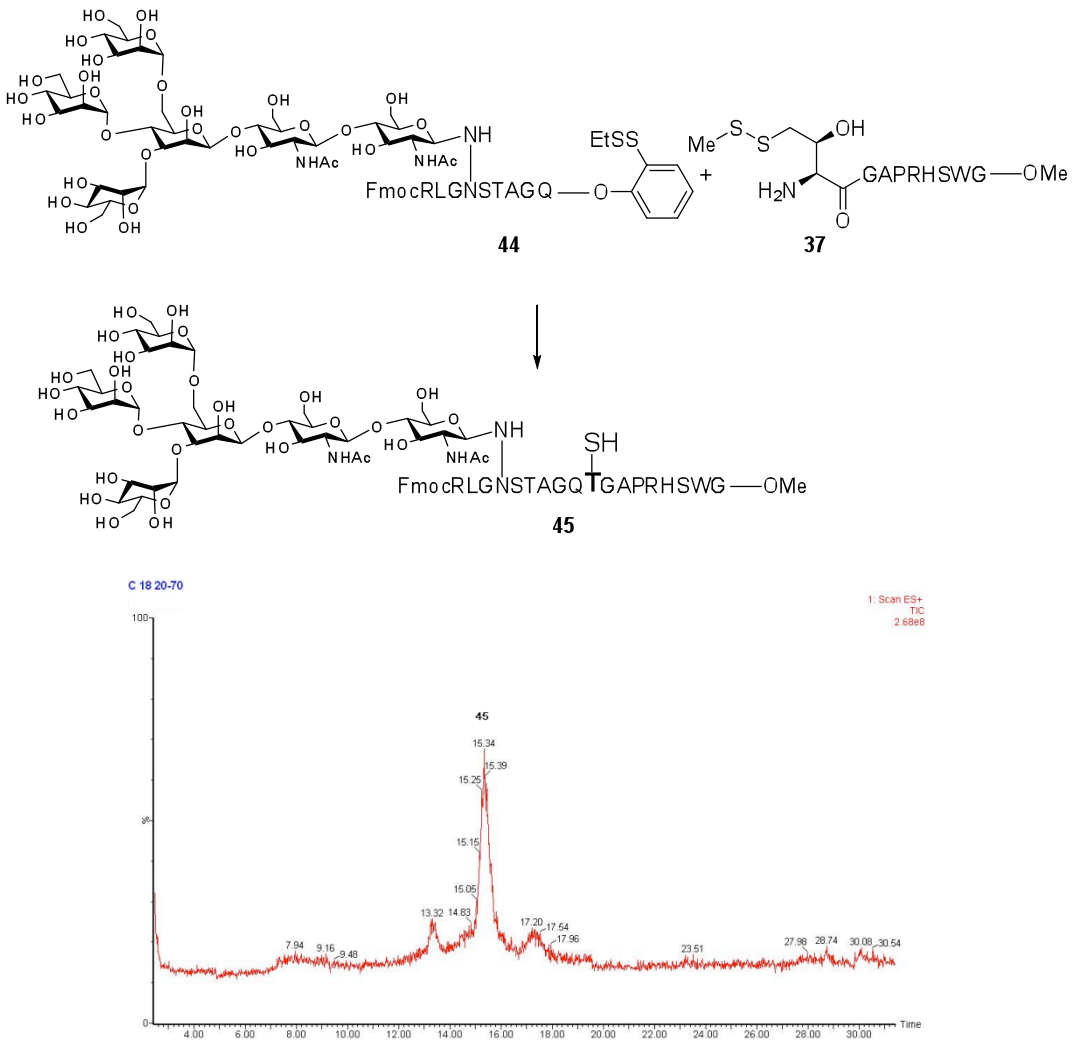
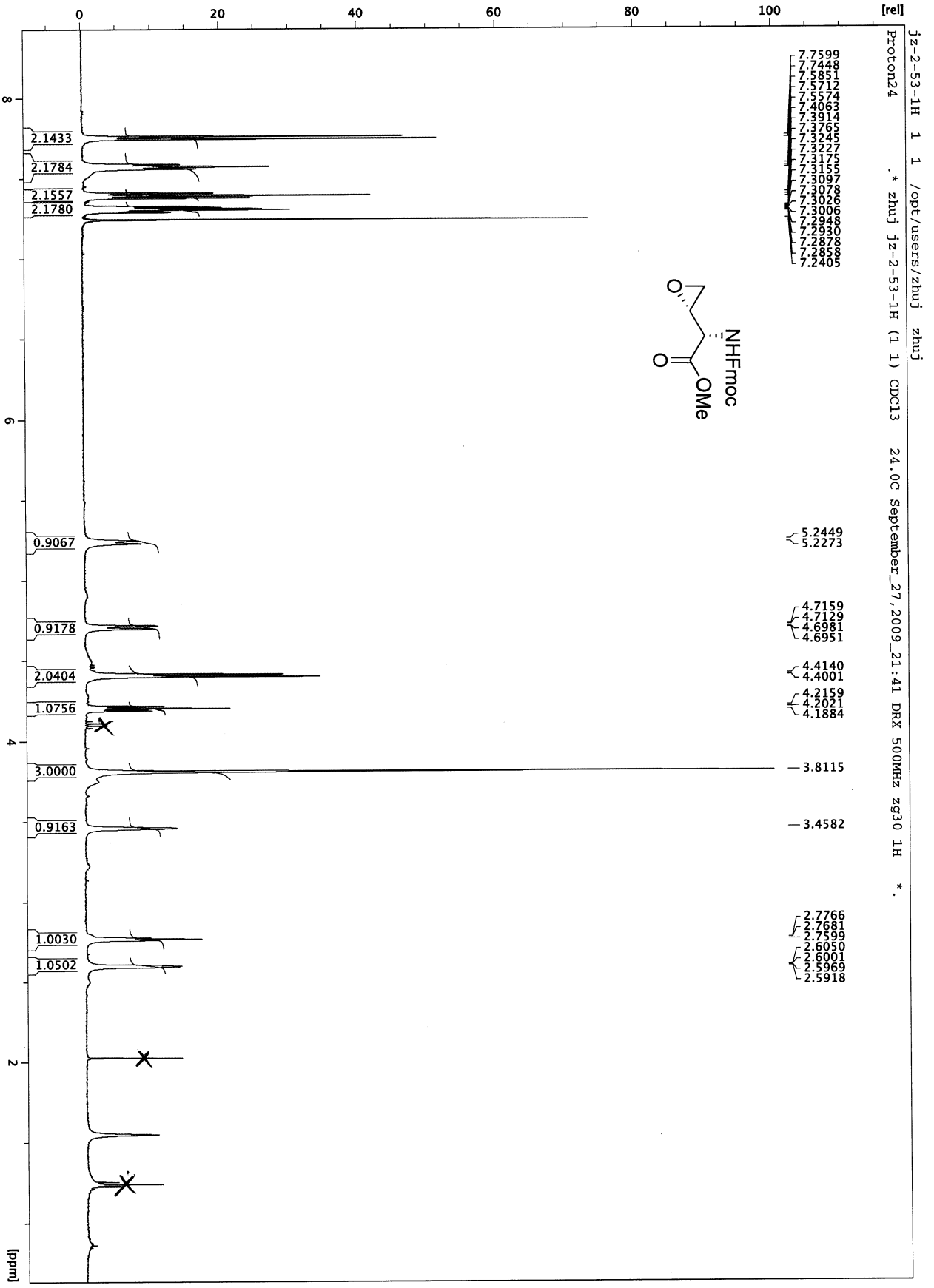



**Figure 54.** LC-MS trace of ligation between **44** and **37** at 2 h: gradient 20-70% CH3CN/H2O over 30 min at a flow rate of 0.2 mL/min, C18 column.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7.5574
7.4063
7.3914
7.3765
7.3245
7.3227
7.3175
7.3155
7.3097
7.3078
7.3026
7.3006
7.2948
7.2930
7.2878
7.2858
7.2405
5.2449
5.2273
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4.7129
4.6981
4.6951
4.4140
4.4001
4.2159
4.2021
4.1884
3.8115
3.4582
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2.7681
2.7599
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2.5969
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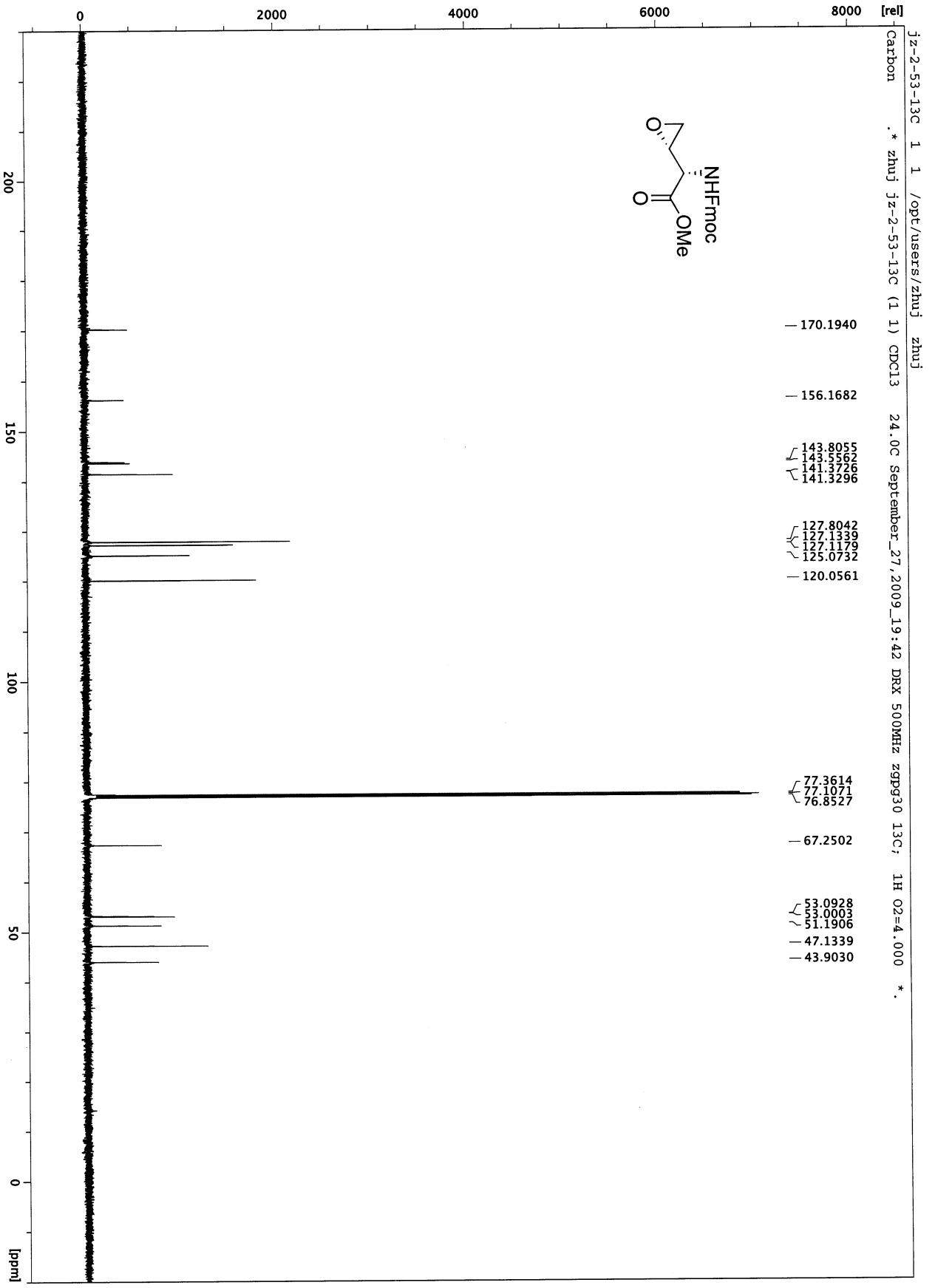
1.0502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8000
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150
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50
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OMe
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O
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125.0732
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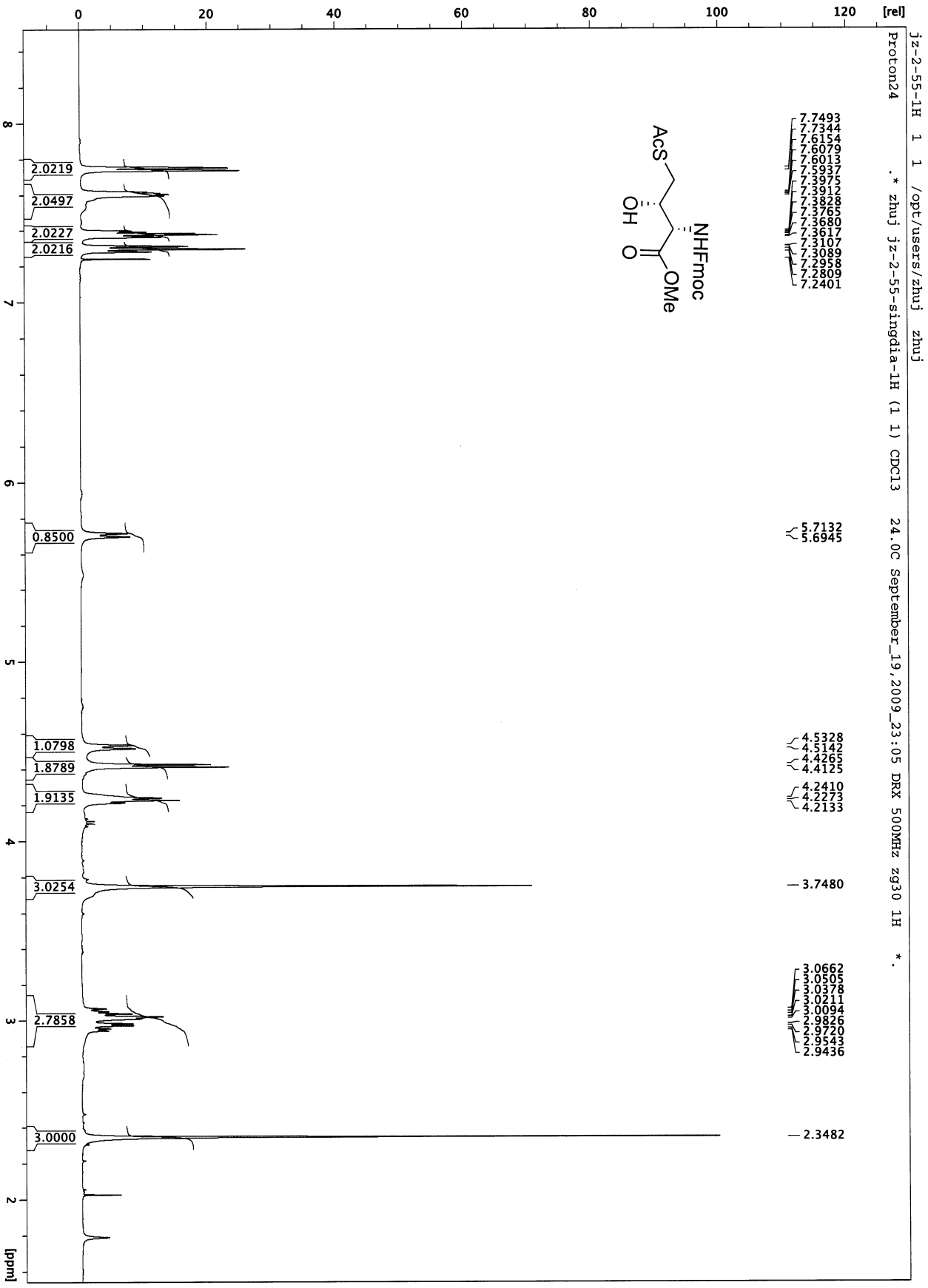
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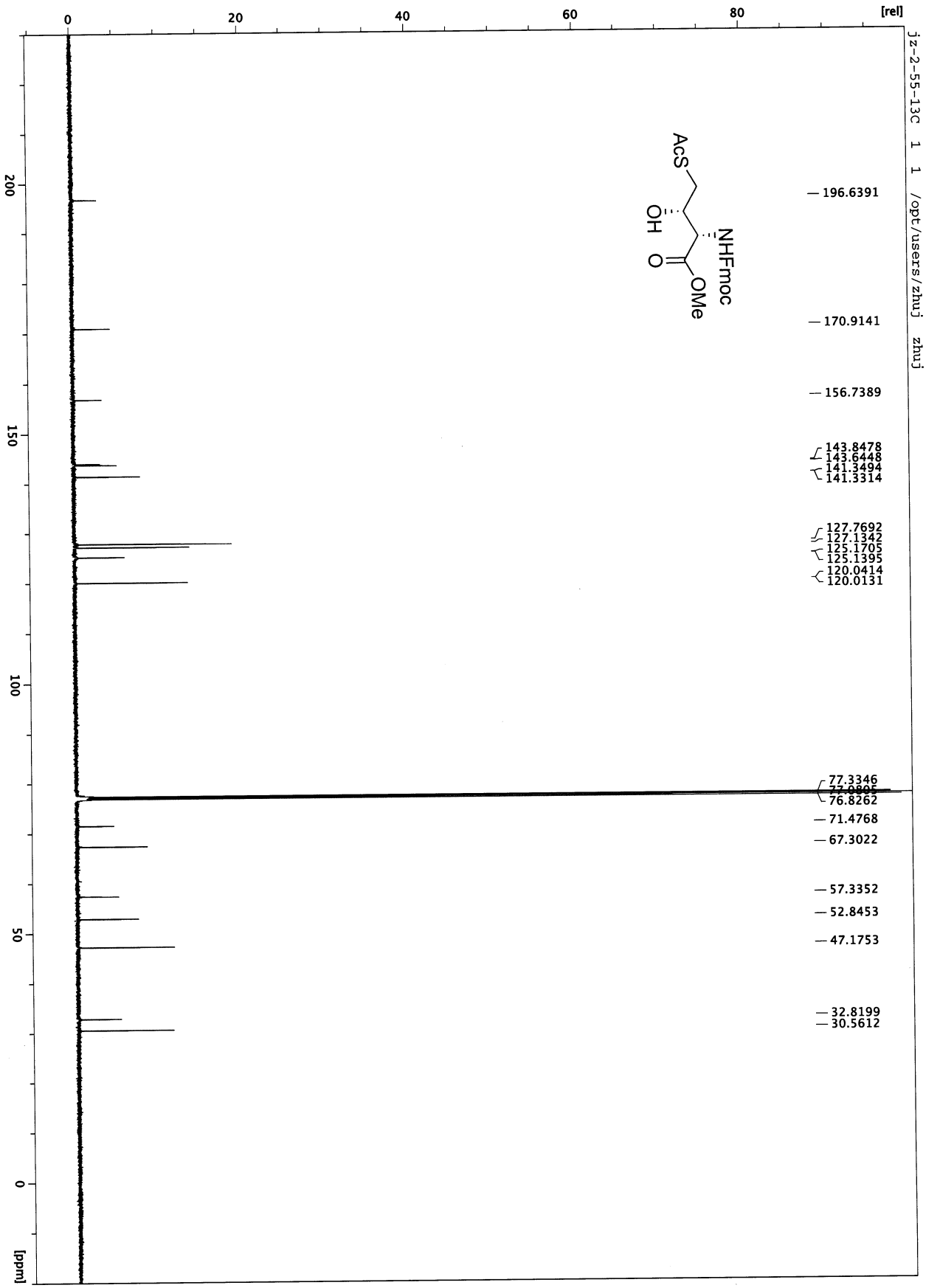
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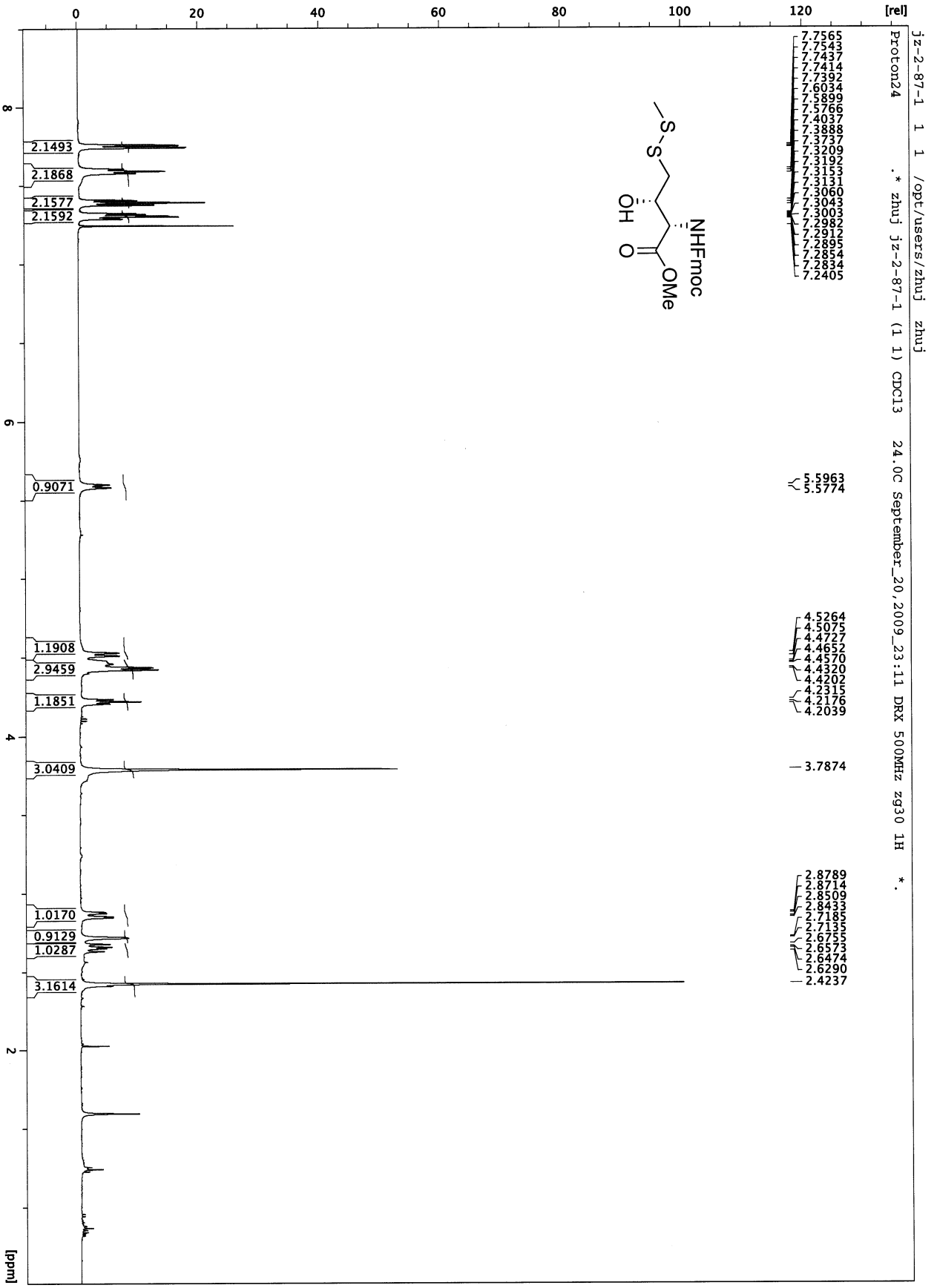
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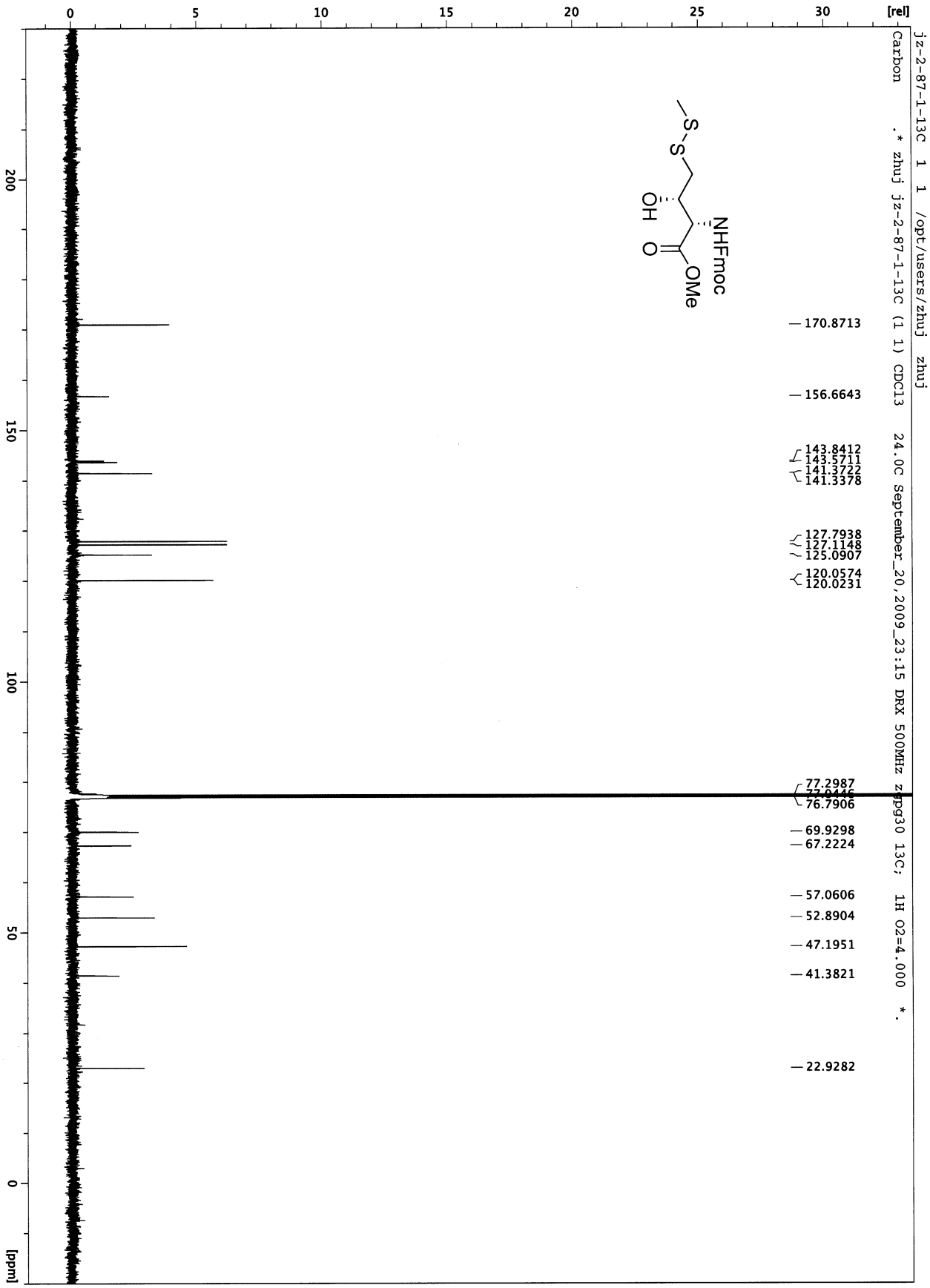
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41.3821
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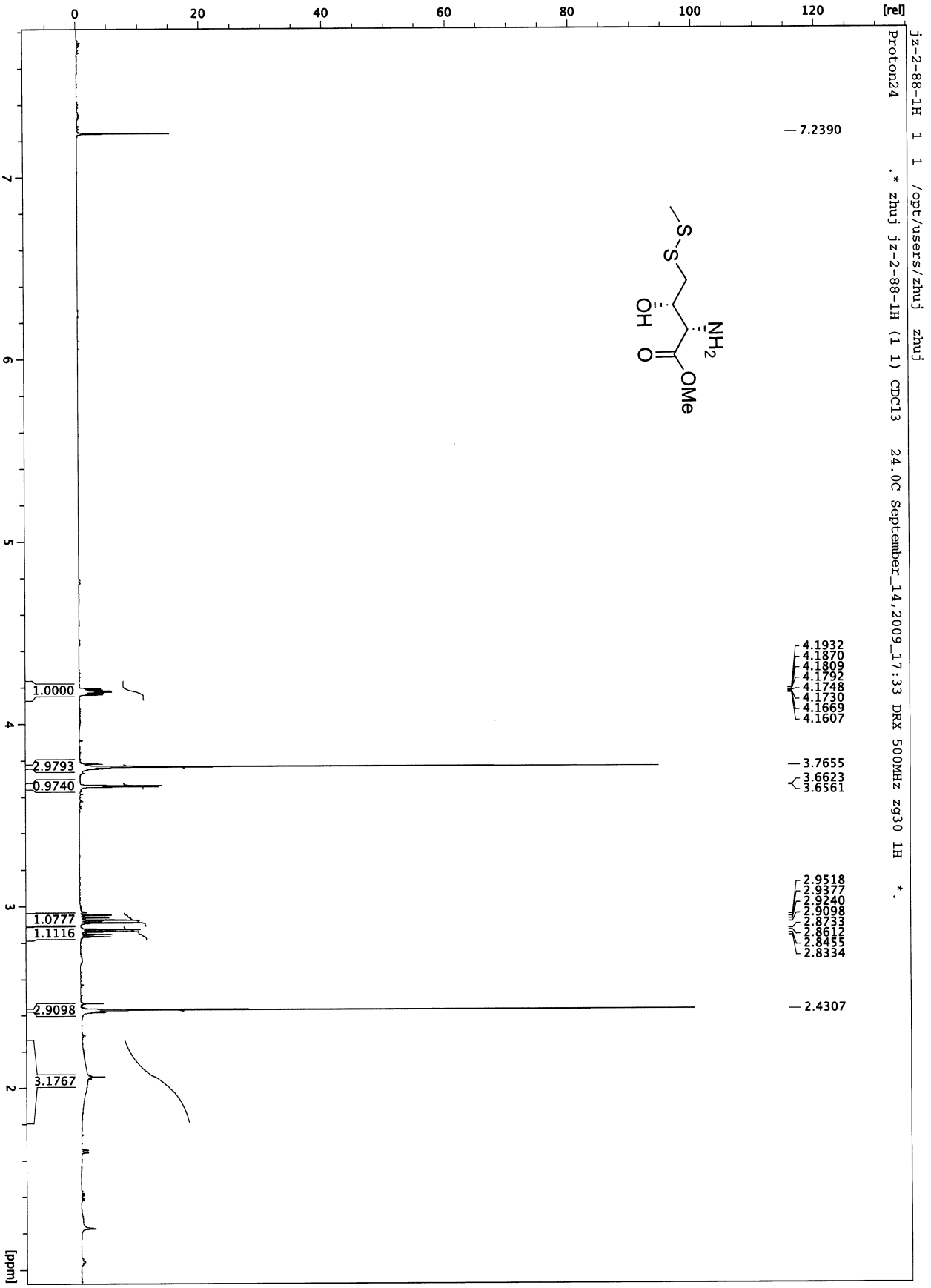
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2.9518
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2.9240
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2.8455
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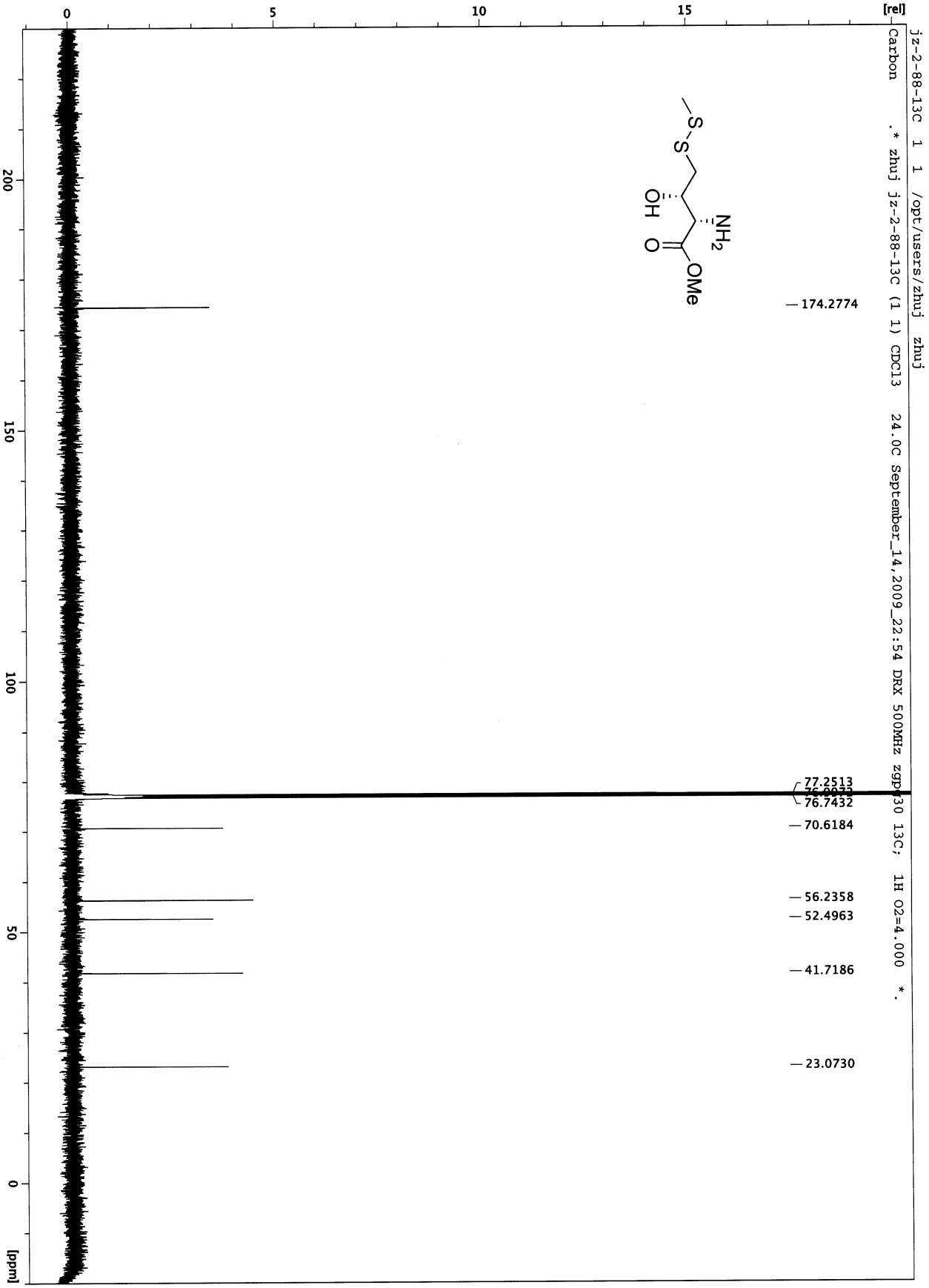
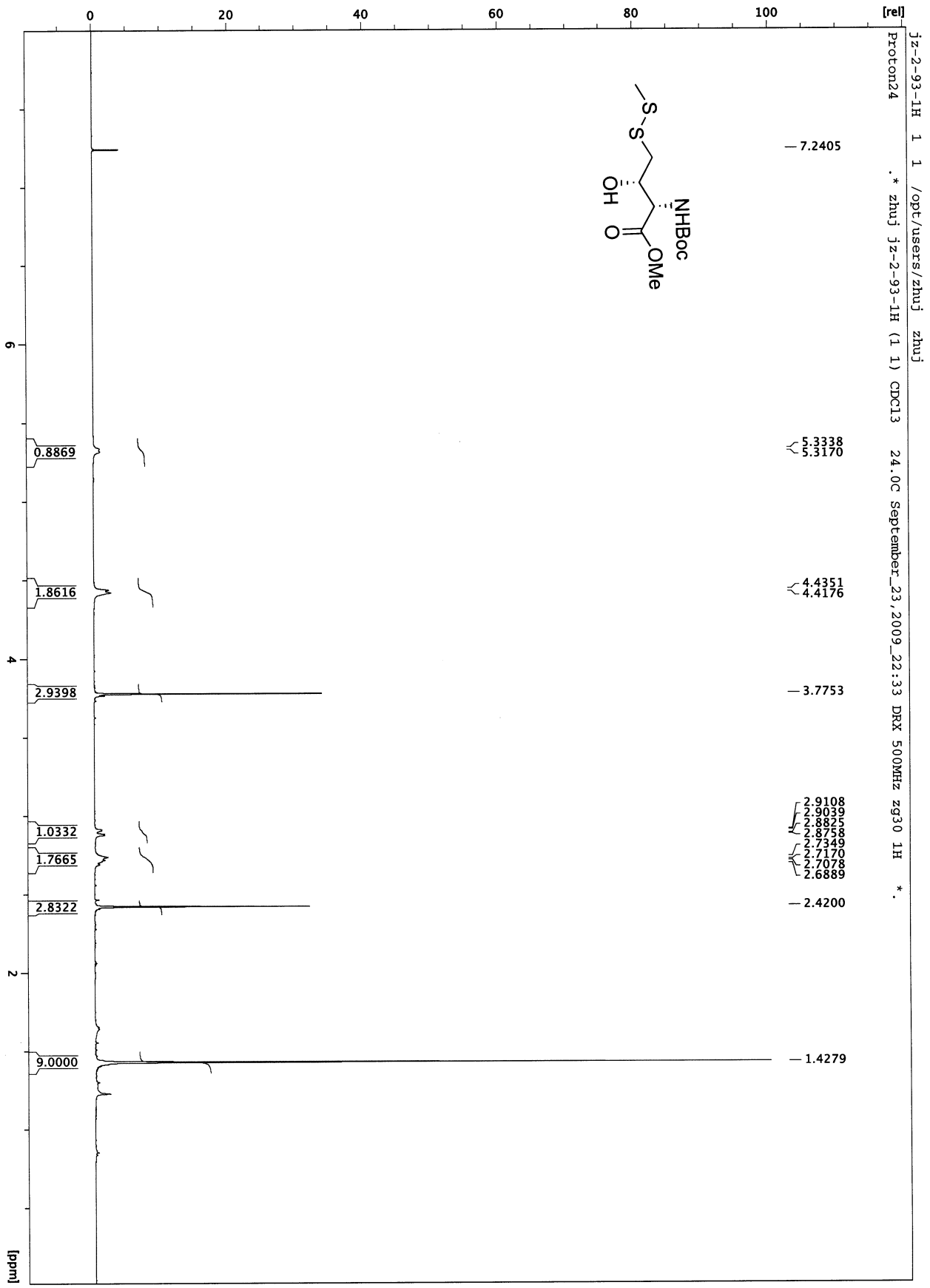
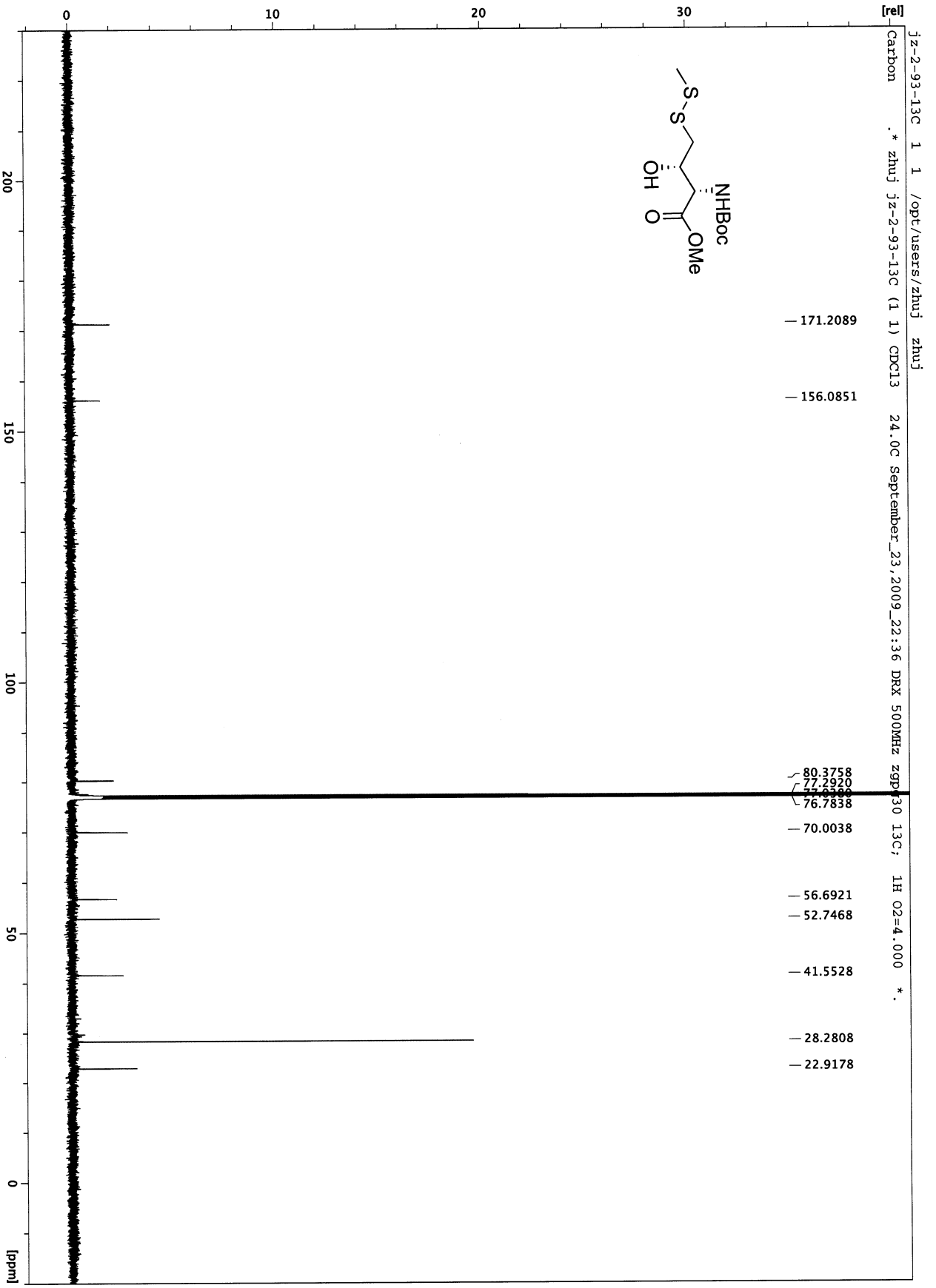
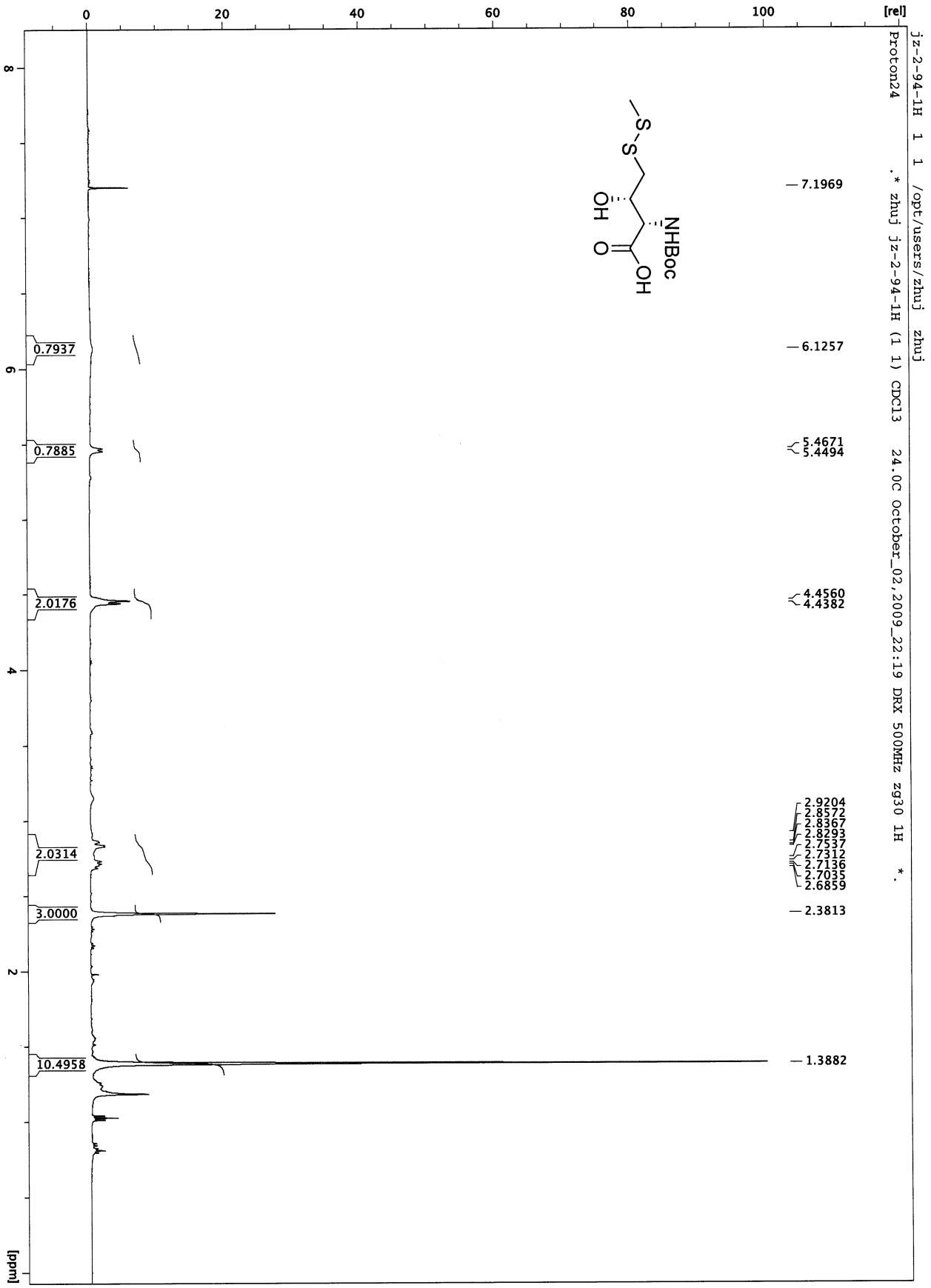
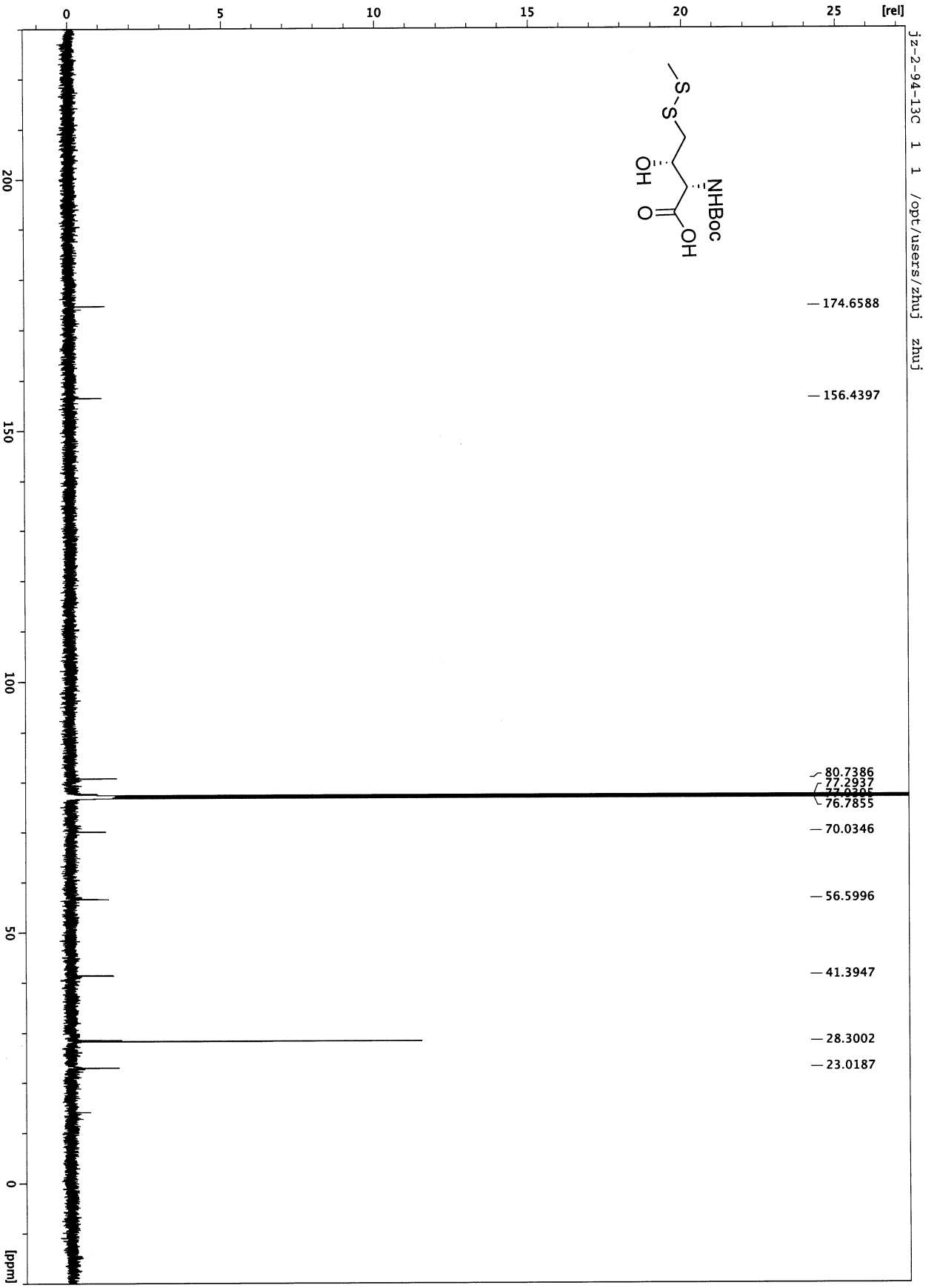
NH2
OMe


jz-2-88-13C 1 1 /opt/users/zhuj zhuj
Carbon .* zhuj jz-2-88-13C (1 1) CDCl3 24.0C September_14,2009_22:54 DRX 500MHz zgpg30 13C; 1H O2=4.000 *.
[rel]
0
5
10
15
200
150
100
50
0
[ppm]
NH2
OH
O
OMe
174.2774
77.2513
76.7432
70.6184
56.2358
52.4963
41.7186
23.0730


jz-2-93-1H 1 1 /opt/users/zhuj zhuj
Proton24 .* zhuj jz-2-93-1H (1 1) CDCl3 24.0C September_23,2009_22:33 DRX 500MHz zg30 1H *.
[rel]
0
20
40
60
80
100
[ppm]
6
4
2
NHBoc
OMe
OH
O
S
S
7.2405
5.3338
5.3170
4.4351
4.4176
3.7753
2.9108
2.9039
2.8825
2.8758
2.7349
2.7170
2.7078
2.6889
2.4200
1.4279
0.8869
1.8616
2.9398
1.0332
1.7665
2.8322
9.0000


jz-2-93-13C 1 1 /opt/users/zhuj zhuj
Carbon .* zhuj jz-2-93-13C (1 1) CDCl3 24.0C September_23,2009_22:36 DRX 500MHz zgpg30 13C; 1H O2=4.000 *.
[rel]
0
10
20
30
200
150
100
50
0
[ppm]
NHBoc
OMe
OH
O
171.2089
156.0851
80.3758
77.2920
76.7838
70.0038
56.6921
52.7468
41.5528
28.2808
22.9178


jz-2-94-1H 1 1 /opt/users/zhuj zhuj
Proton24 .* zhuj jz-2-94-1H (1 1) CDCl3 24.0C October_02,2009_22:19 DRX 500MHz zg30 1H *.
[rel]
0
20
40
60
80
100
[ppm]
8
6
4
2
NHBoc
OH
O
OH
S
S
7.1969
6.1257
5.4671
5.4494
4.4560
4.4382
2.9204
2.8572
2.8367
2.8293
2.7537
2.7312
2.7136
2.7035
2.6859
2.3813
1.3882
0.7937
0.7885
2.0176
2.0314
3.0000
10.4958


0
5
10
15
20
25
[rel]
200
150
100
50
0
[ppm]
jz-2-94-13C 1 1 /opt/users/zhuj zhuj
NHBoc
OH
O
OH
174.6588
156.4397
80.7386
77.2937
76.7855
70.0346
56.5996
41.3947
28.3002
23.0187