

Figure 1. ^1H -NMR characterization of starting material keto-ester.

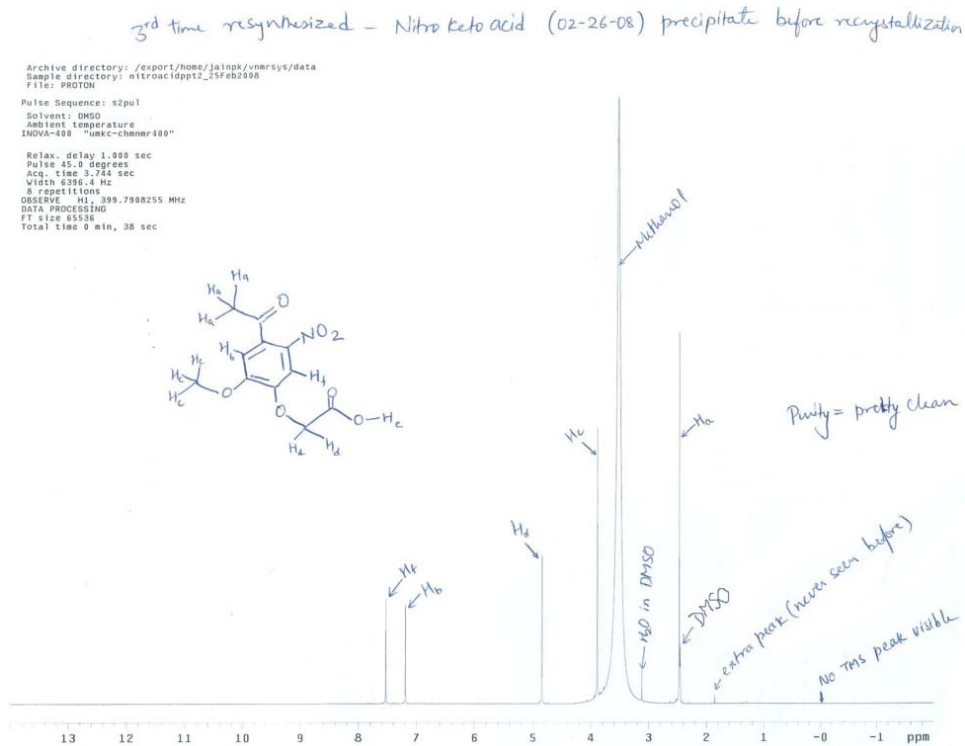


Figure 2. NMR of DMNPE-acid product shows high purity with out any non-nitro side-product

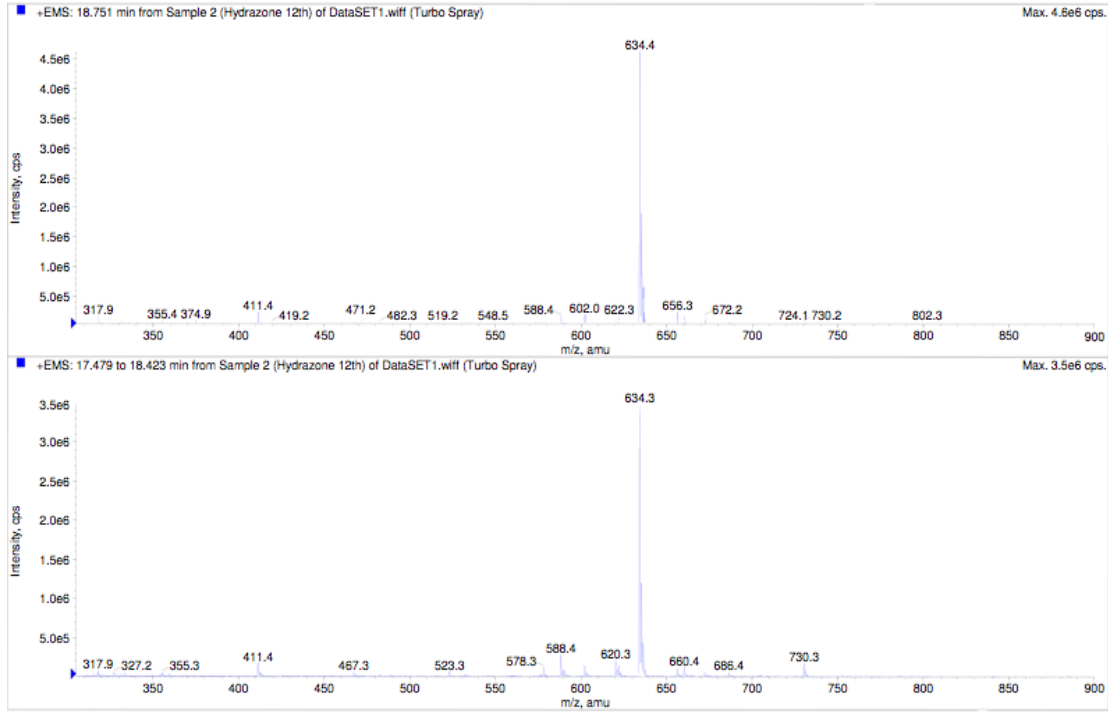


Figure 3. EMS from LC-MS infusion analysis of bis-DMNPE-hydrazone

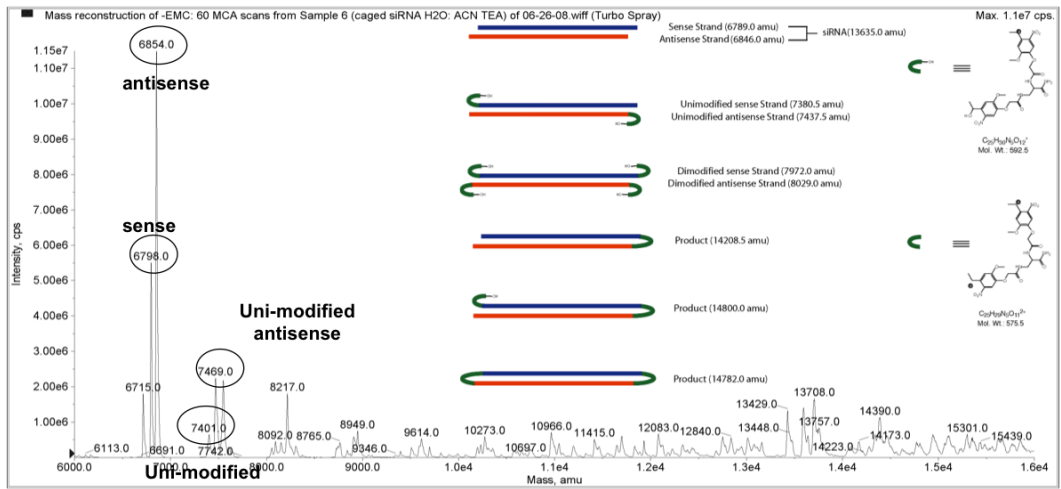


Figure 4. ESI-MS analysis of caged oligo.

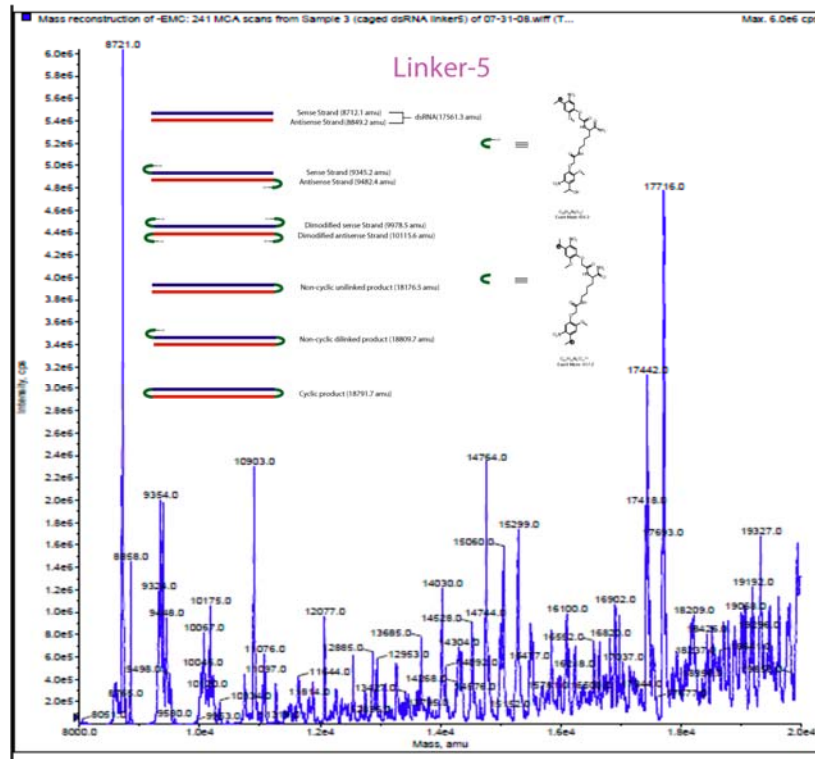


Figure 5. ESI-MS (negative mode) analysis of linker-5 caged dsRNA.

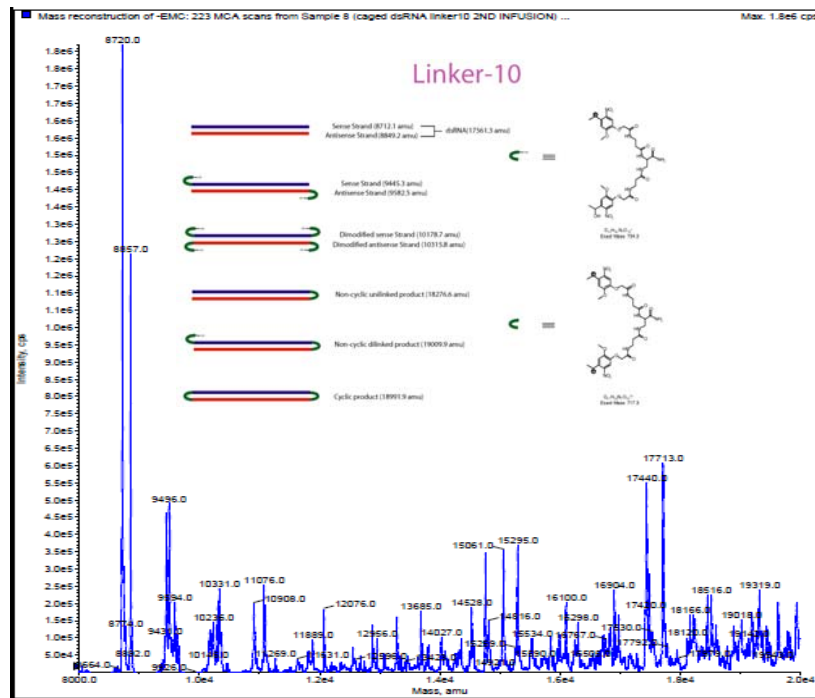


Figure 6. ESI-MS (negative mode) analysis of linker-10 caged dsRNA (bottom pane). Top pane represents expected masses.

Figure 7. ESI-MS (negative mode) analysis of linker-15 caged dsRNA (bottom pane). Top pane represents expected masses.

Figure 8. XIC of NLQ hydrazone. We observed two peaks in the XIC suggesting E/Z isomers.

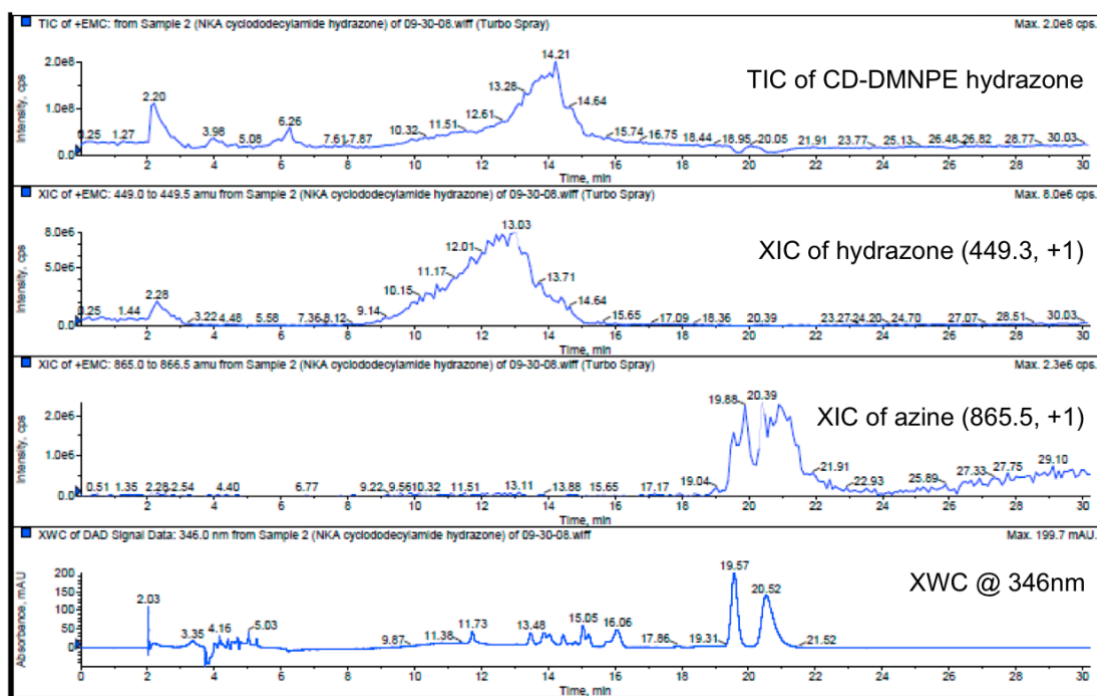


Figure 9. LC-MS analysis of CD-DMNPE Hydrazone product determined the problem of azine formation during synthesis. Analysis panes are labeled accordingly. Reaction conditions: CD-DMNPE ketone (11.5 μ moles) was dissolved in 1:1 mixture of NMP:95% ethanol/ H_2O (100 μ L) and refluxed for 3 h in a capped glass vial using heat block after addition of hydrazine hydrate (25.8 μ moles, 2.24 eq.), glacial acetic acid (11.5 μ moles, 1 eq.).

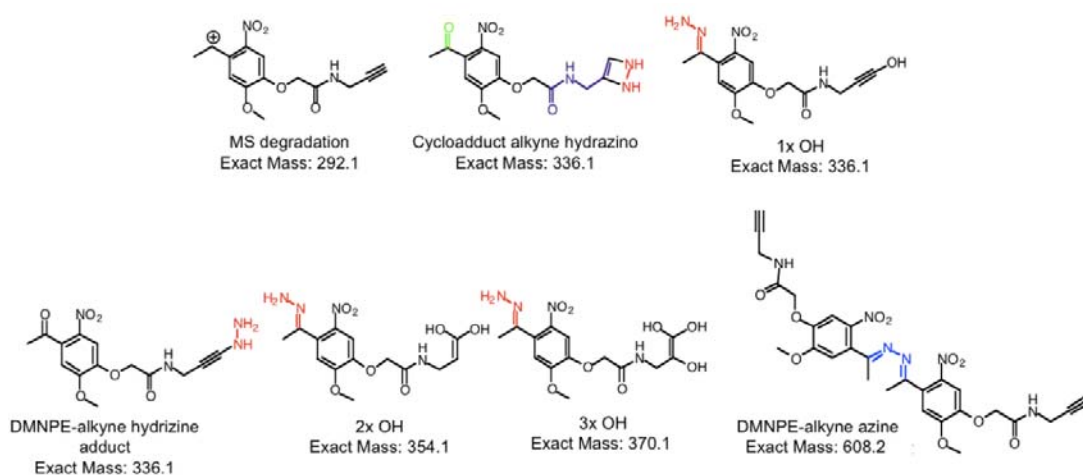


Figure 10. Putative structures formed during synthesis or characterization of DMNPE-alkyne hydrazone.

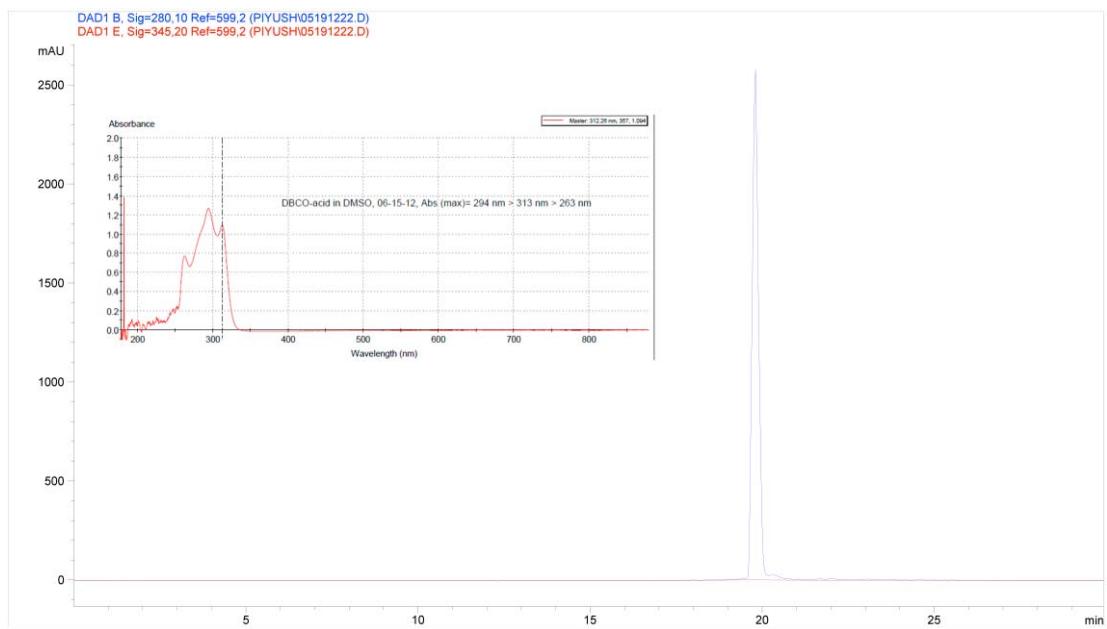


Figure 11. HPLC chromatogram and UV-visible absorbance of DBCO-acid. Represented an overlay of HPLC chromatogram monitored at 280 nm (blue) and 345 nm (red).

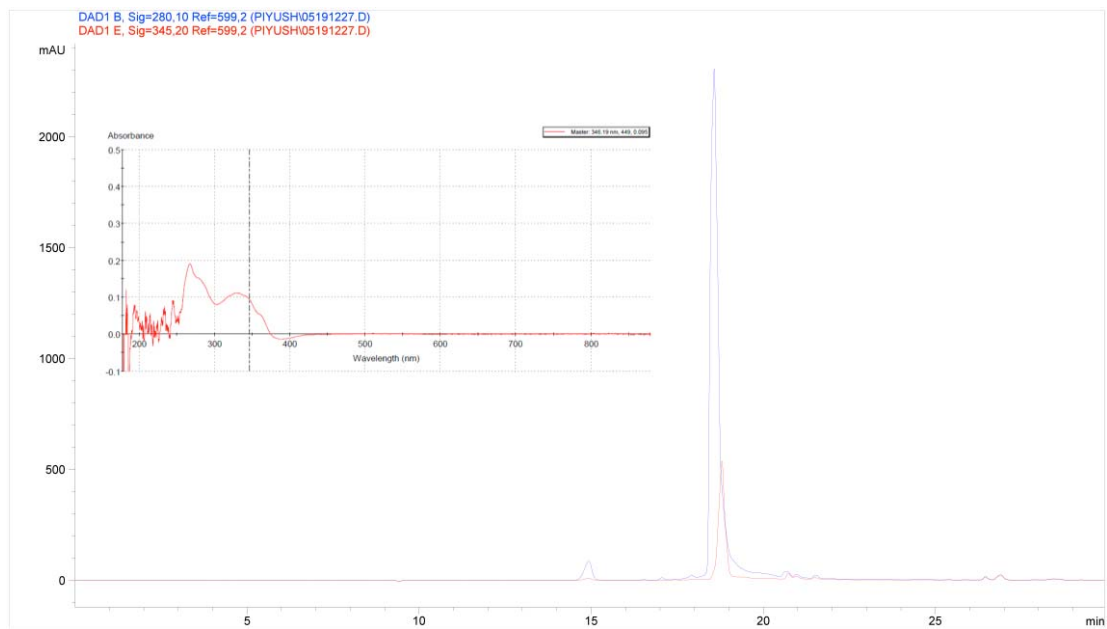


Figure 12. HPLC chromatogram and UV-visible absorbance of DBCO-amide cleaved from SpheriTide resin. Represented overlaid HPLC chromatogram monitored at 280 nm (blue) and 345 nm (red).

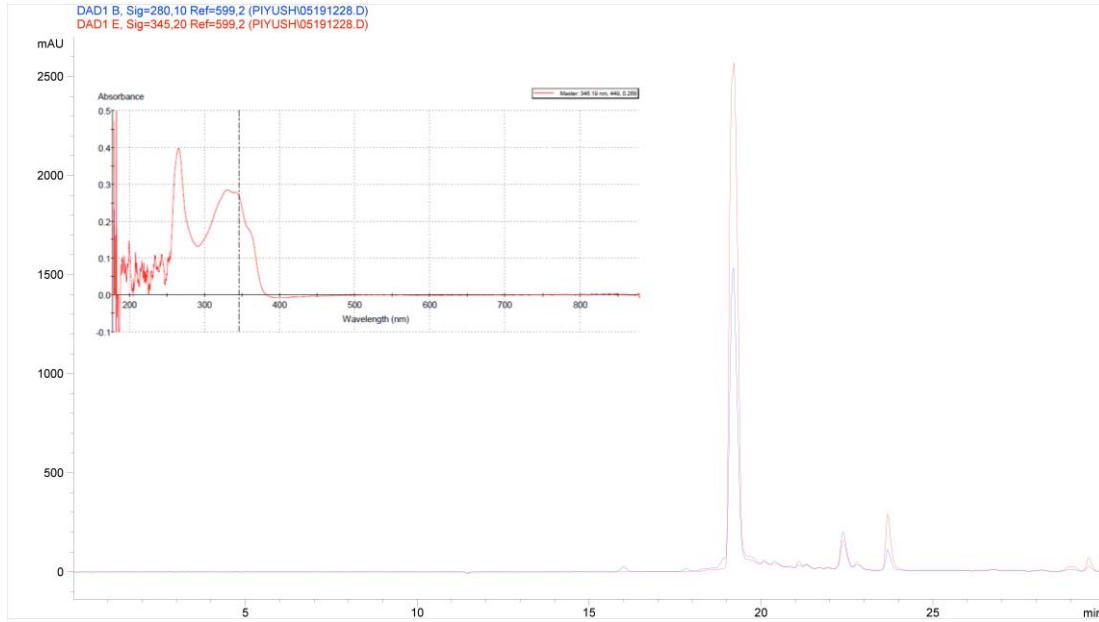


Figure 13. HPLC chromatogram and UV-visible absorbance of DBCO-amide cleaved from ChemMatrix resin. Represented overlaid HPLC chromatogram monitored at 280 nm (blue) and 345 nm (red).

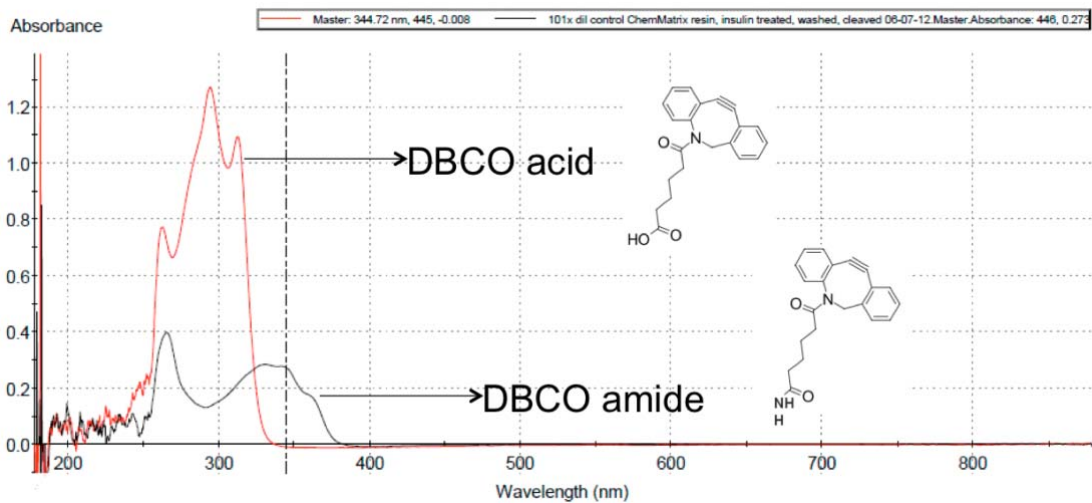
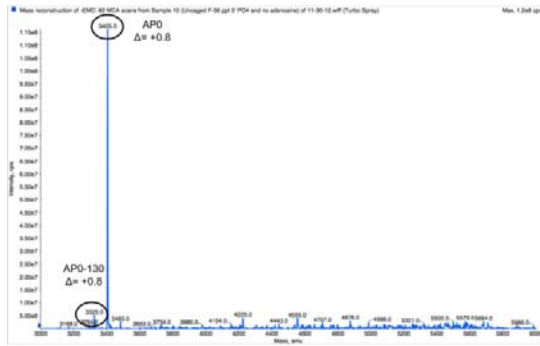
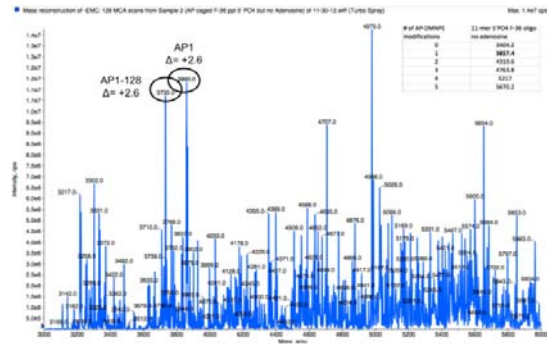


Figure 14. Overlay of spectra of DBCO-acid (red), obtained commercially, and DBCO-amide (black), cleaved from ChemMatrix resin, in DMSO. DBCO-containing ChemMatrix resin was also treated with insulin before cleavage.

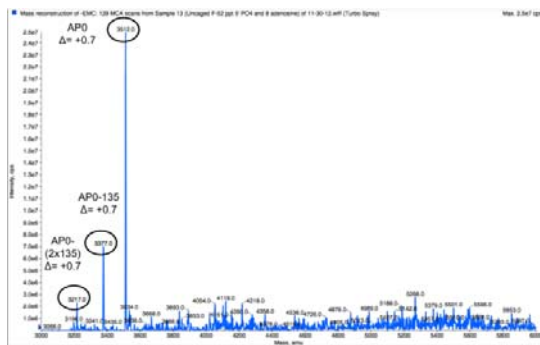
F-36



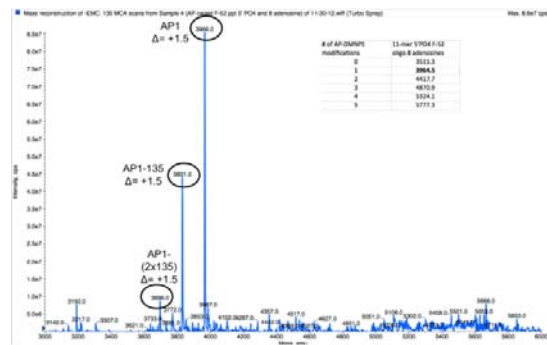
F-36 + DMNPE-azide diazo



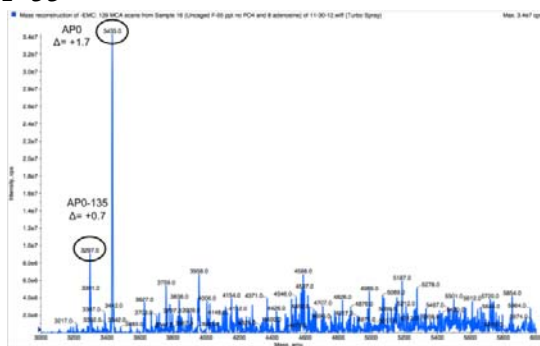
F-52



F-52 + DMNPE-azide diazo



F-55



F-55 + DMNPE-azide diazo

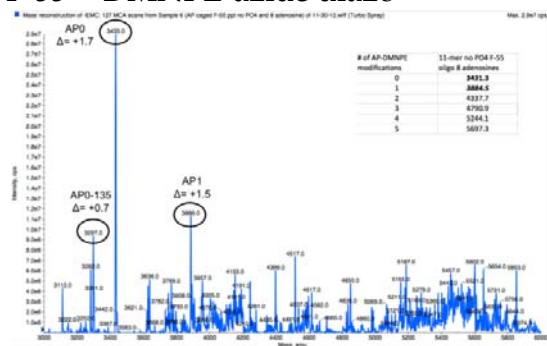


Figure 15. ESI-MS (negative mode) of F-36 (top), F-52 (middle), F-55 (bottom) oligos in presence (right) or absence (left) of reaction with DMNPE-azide diazo. APO suggests unmodified oligo, AP1 suggests one modification per strand. Delta symbol indicates the difference between observed and expected mass (amu).