Supporting Information

**Selective chemical modification of DNA with alkoxy- and benzyloxyamines**

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**Table S1**. Optimization of the reaction of **oligo 1** with O-methoxylamine.[a]

| *Entry* | *pH* | *T (°C)* | *Time[b] (d)* | *Major Product[c]* |
|---|---|---|---|---|
| **1** | 5.5 | 37 | 1 | B |
| **2** | 5.5 | 25 | 2 | B |
| **3** | 4 | 37 | 1 | 1:1 |
| **4** | 4 | 50 | 1 | A |

[a]All experiments were carried out with in a presence of **oligo 1** [100μM], methoxylamine (**1)** [1.6 M]. [b]Determined by rp-HPLC. [b] Time after which full conversion was reached. [c] Determined by rp-HPLC.

Table S2. Optimization of the reaction of **2** with oligo 1.

| *Entry* | *2 (M)* | *Conversion[b] (%)* | *Time[c] (h)* | *Ratio[d] M2A/M2B* |
|---|---|---|---|---|
| **1** | 0.35 | 52 | 24 | 2:3 |
| **2** | 0.45 | 97 | 48 | 4:1 |
| **3** | 0.52 | 97 | 48 | 1:2 |
| **4** | 0.45 | 100 | 24 | 2:3 |

[a] All experiments were carried out in the presence of **oligo 1** [100 μM], alkoxyamine **2** (pH = 4 and rt) [b] Conversions were determined by RP-HPLC. [c] Time after which the reactions were sampled. [d] Determined by RP-HPLC.

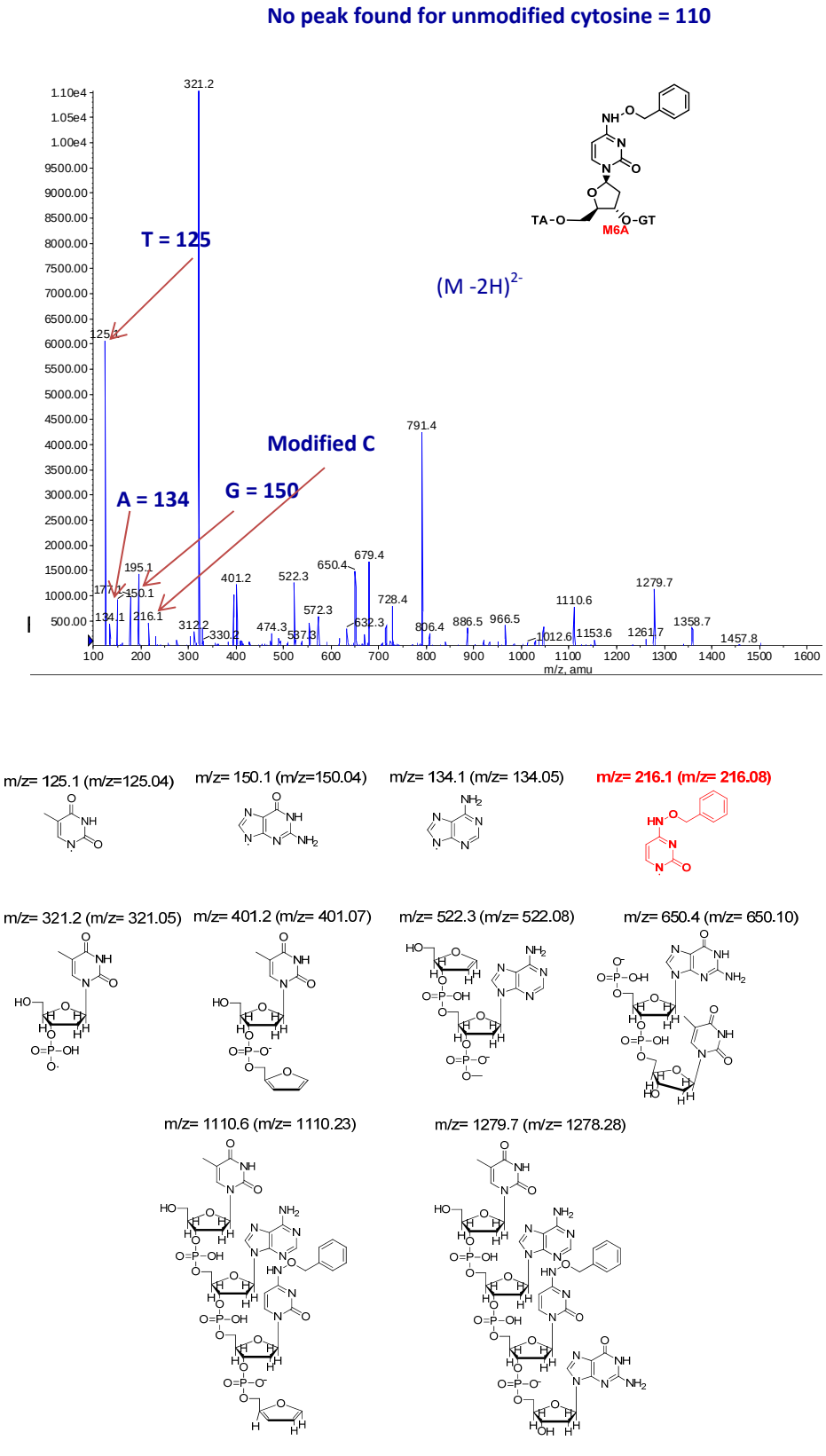



Figure S2. m/z and their structural assignment. In brackets are the calculated m/z

*HPLC and MALDI data*

Modification of DNA with methoxyamine **1**

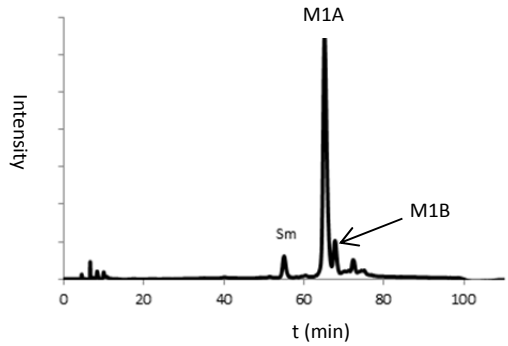



Figure S3. HPLC trace of table 1, entry 4 (Gradient B)

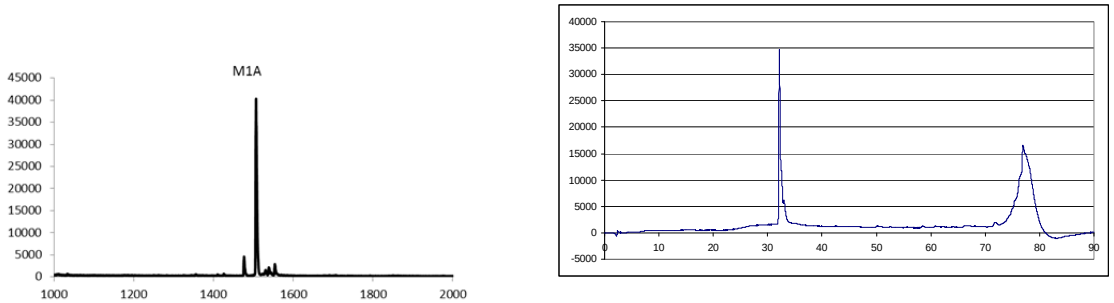



Figure S4. MALDI ( m/z= 1507) and HPLC trace of pure **M1A**

Modification of DNA with O-decylhydroxylamine hydrochloride **(2)**

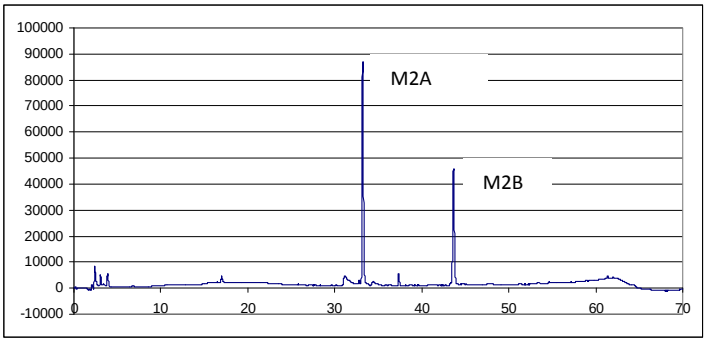



Figure S5. HPLC trace of the reaction of **oligo 1** with **2**; table 1 (supporting info) entry 2

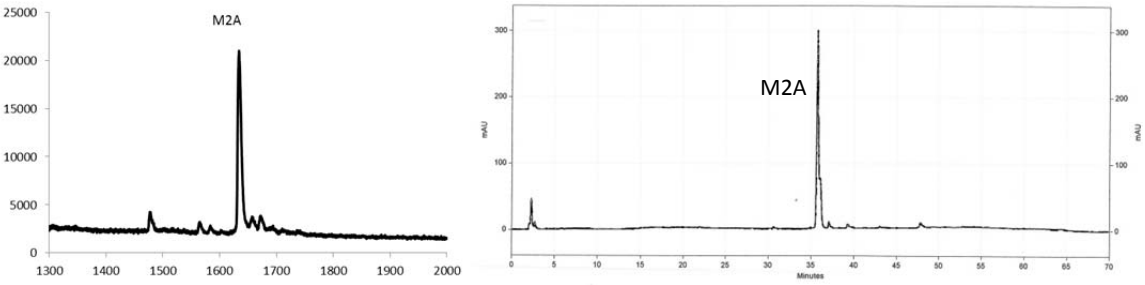



Figure S6. MALDI ( m/z= 1632) and HPLC trace of pure **M2A**.

Modification with O-benzylhydroxylamine hydrochloride **6**

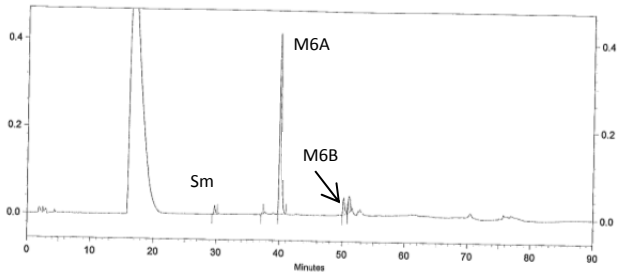



Figure S7. HPLC trace of the reaction of **oligo 1** with **6**; table 2,entry 2.

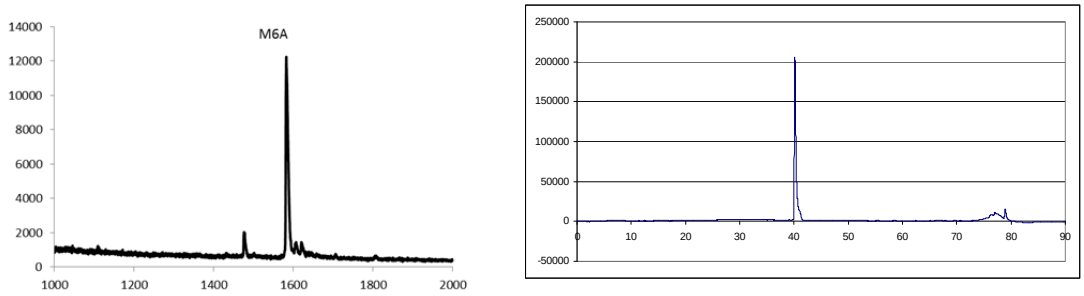



Figure S8. MALDI (m/z= 1585) and HPLC trace of pure **M6A**

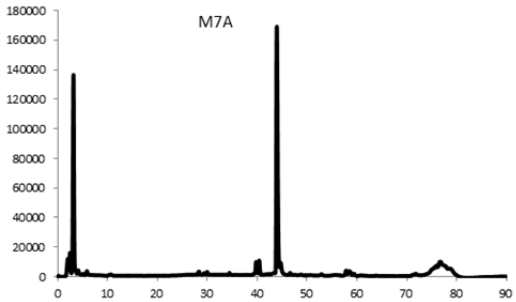



Figure S9. HPLC trace of **M7A** after size exclusion purification.

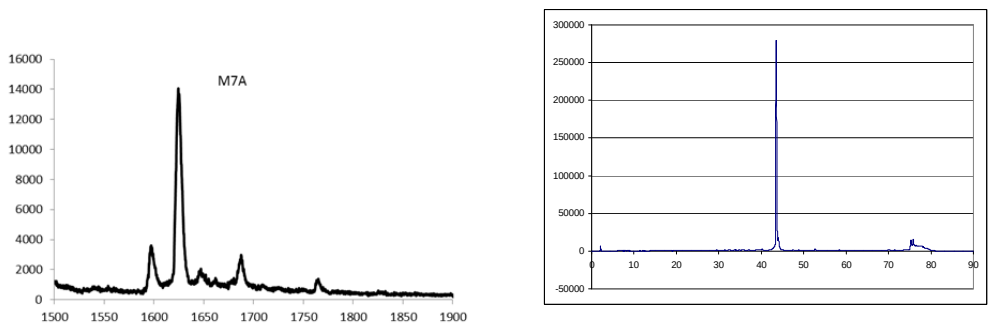



Figure S10. MALDI (m/z= 1624) and HPLC trace of purified **M7A**

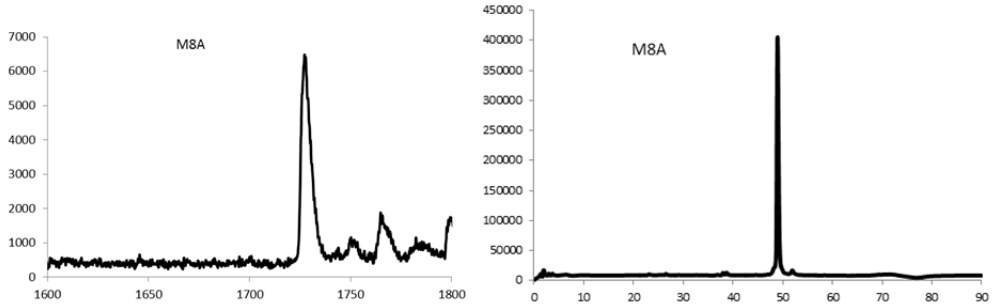



Figure S11. MALDI (m/z= 1726) and HPLC trace of M8A

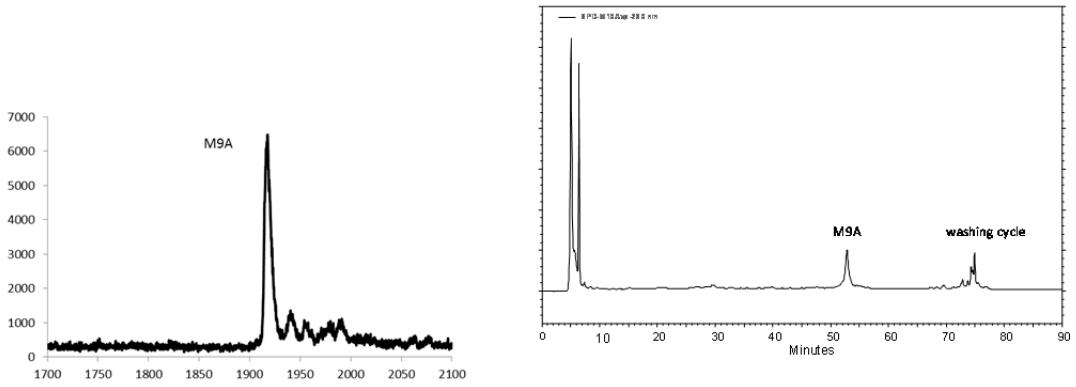



Figure S12 . MALDI (m/z= 1917 ) and HPLC trace of M9A

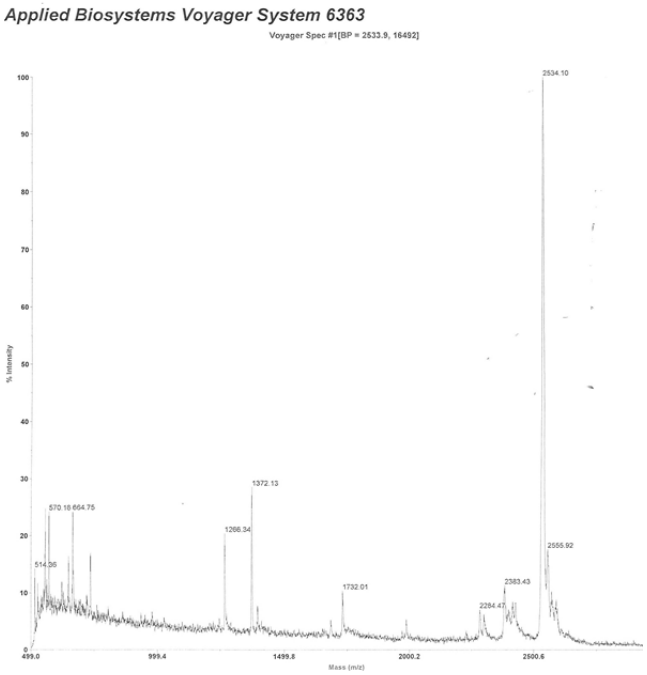



Figure S13. MALDI (m/z=2534) of the product of the reaction of **oligo 2** with O-benzylhydroxylamine hydrochloride (**6**) (table 2, entry 3).

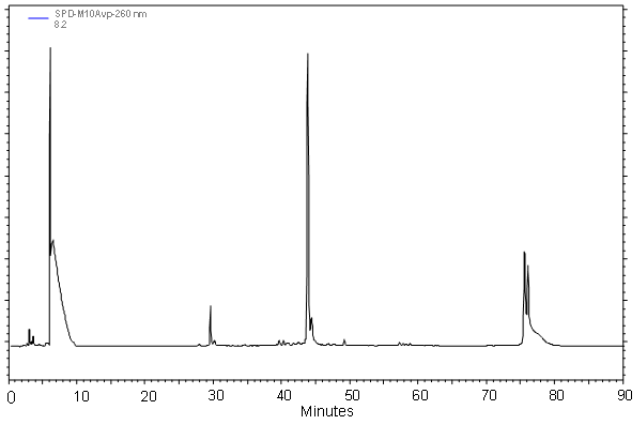



Figure 14. HPLC trace of the product of the reaction of **oligo 2** with O-benzylhydroxylamine hydrochloride (**6**) ( table 2 entry 3).

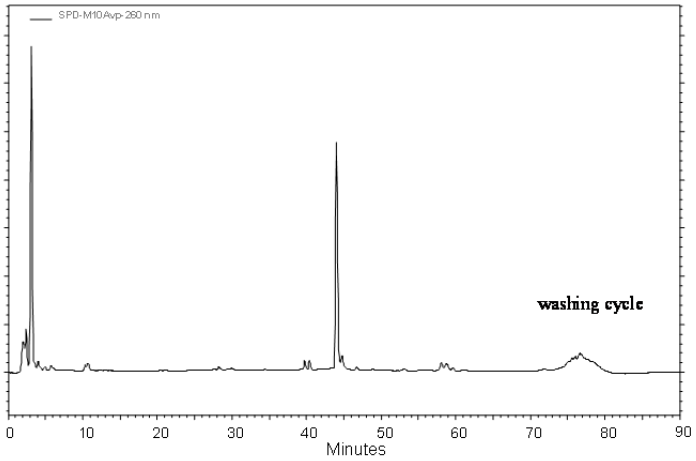
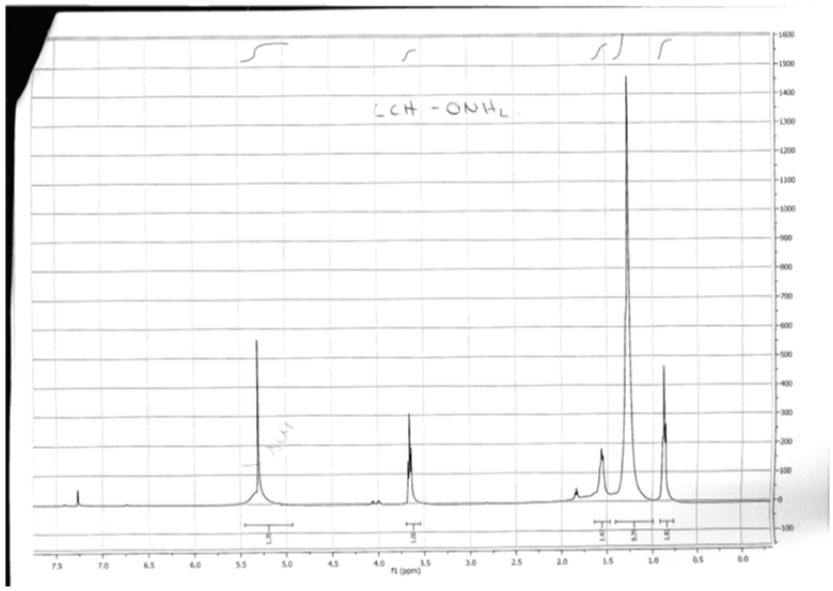


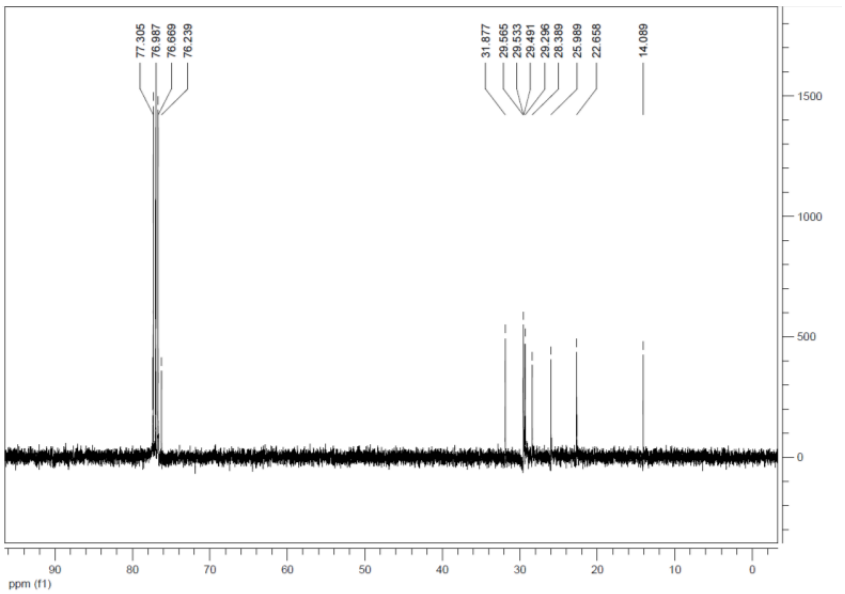

Figure 15. HPLC trace of the pure product of the reaction of **oligo 2** with O-benzylhydroxylamine hydrochloride (**6**)

***O*-decylhydroxylamine (10)**

$^{1}$H-NMR

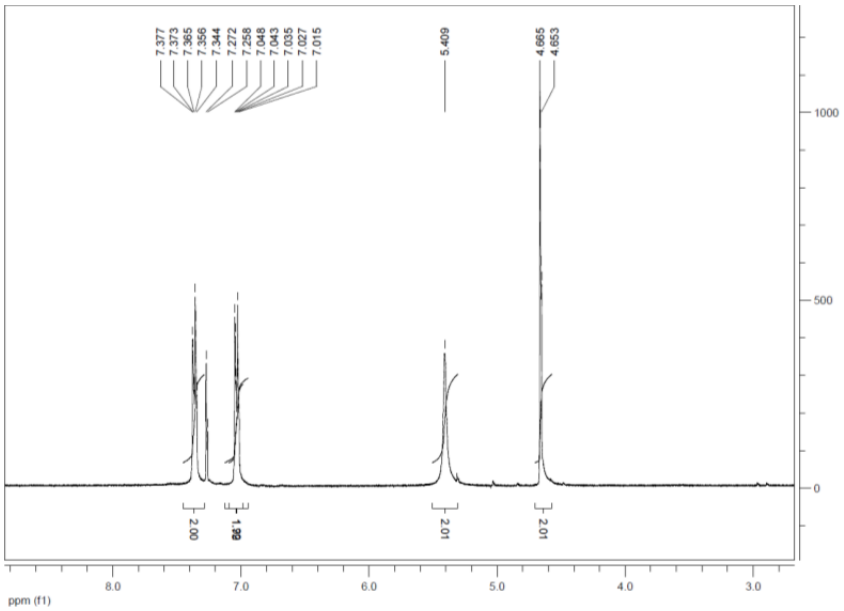



$^{13}$C-NMR



**O-(4-azidobenzyl) hydroxylamine (15)**

$^{1}$H-NMR




$^{13}$C-NMR