Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Post-synthetic transamination at position N4 of cytosine in oligonucleotides assembled with routinely used phosphoramidites

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1. Structures of routinely used phosphoramidites

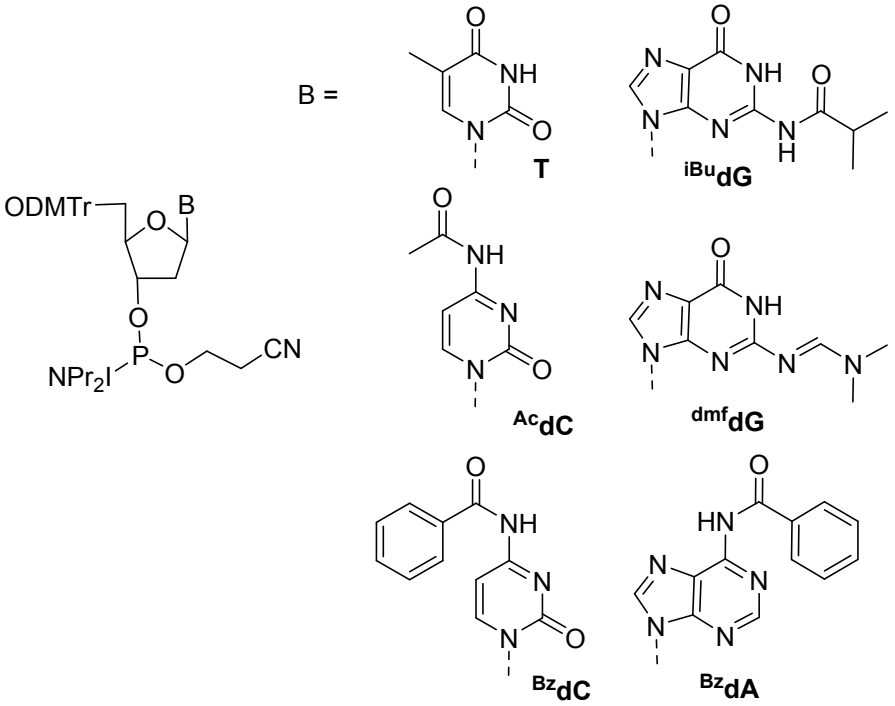


Figure S1. structure of the protected nucleobases used in the present study.

2. ESI-MS spectra of cyclopropylated ODNs 1b-7b

2.1 ODN **1b**

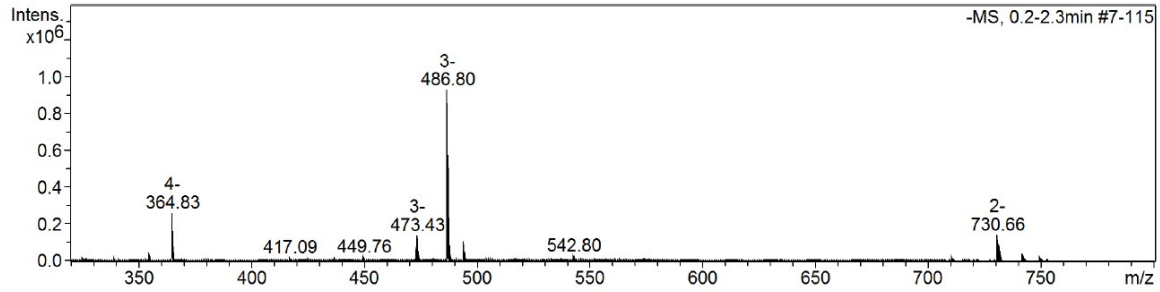
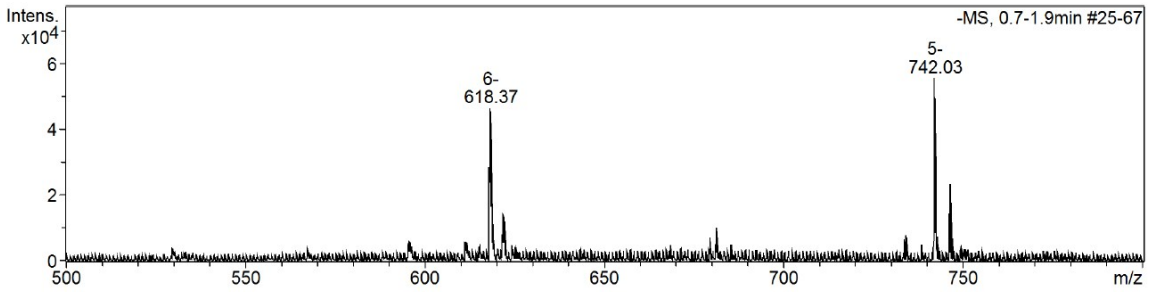


Figure S2. ESI-MS spectra of cyclopropylated ODN **1b.**

2.2 ODN **2b**

a



b

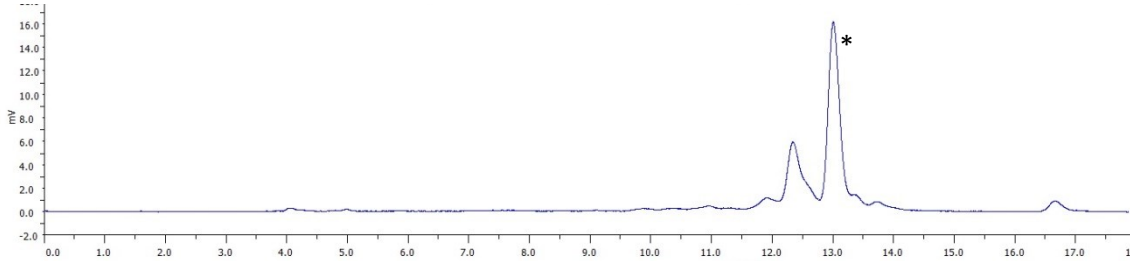
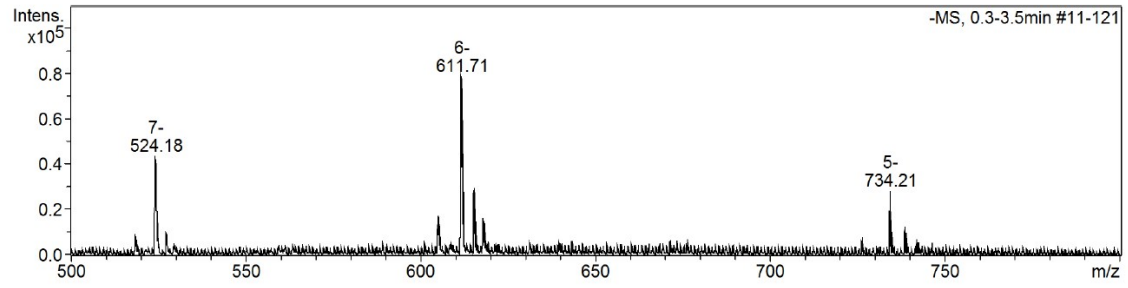


Figure S3. a) ESI-MS spectra of cyclopropylated ODN **2b** and b) Crude reaction mixture of ODN **2b** (peak of interest is indicated by a star).

2.3 ODN **3b**

a



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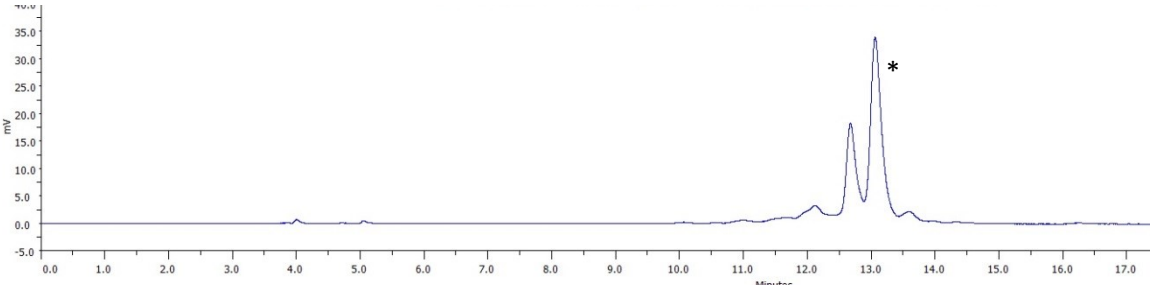
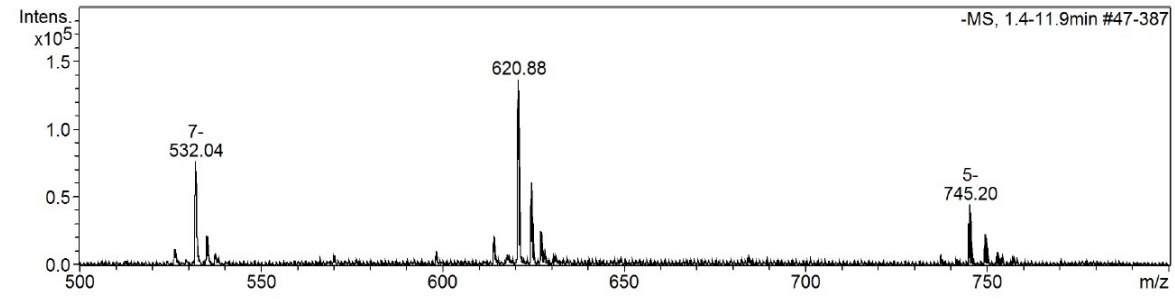


Figure S4. a) ESI-MS spectra of cyclopropylated ODN **3b** and b) Crude reaction mixture of ODN **3b** (peak of interest is indicated by a star).

2.4 ODN **4b**

a



b

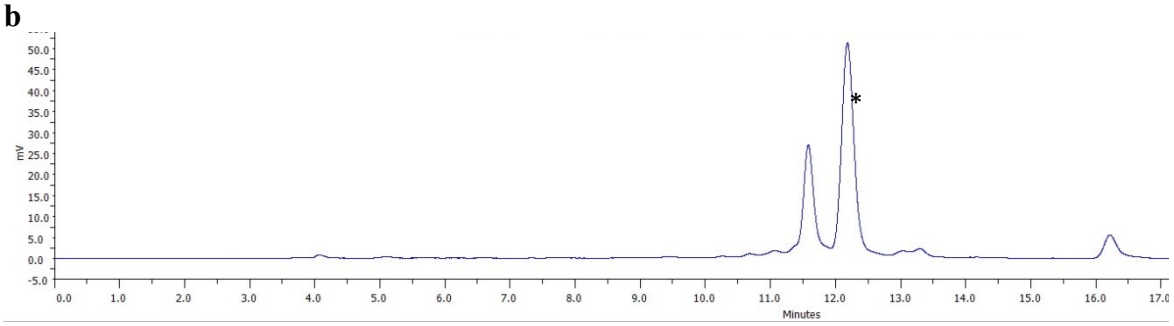
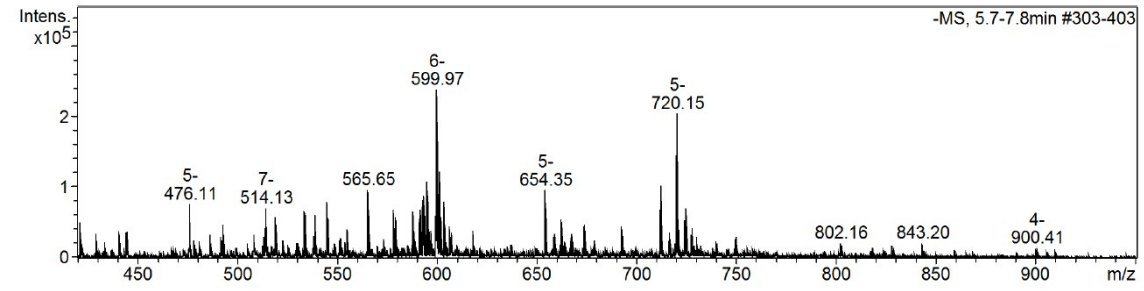


Figure S5. a) ESI-MS spectra of cyclopropylated ODN **4b** and b) Crude reaction mixture of ODN **4b** (peak of interest is indicated by a star).

2.5 ODN **5b**

a



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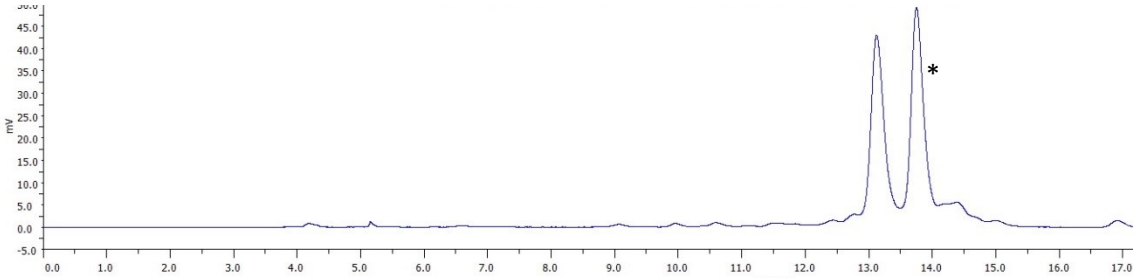
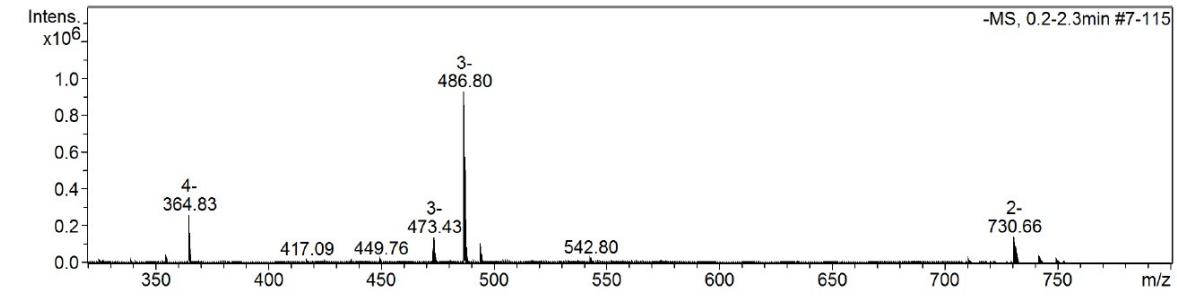


Figure S6. a) ESI-MS spectra of cyclopropylated ODN **5b** and b) Crude reaction mixture of ODN **5b** (peak of interest is indicated by a star).

2.6 ODN **6b**

a



b

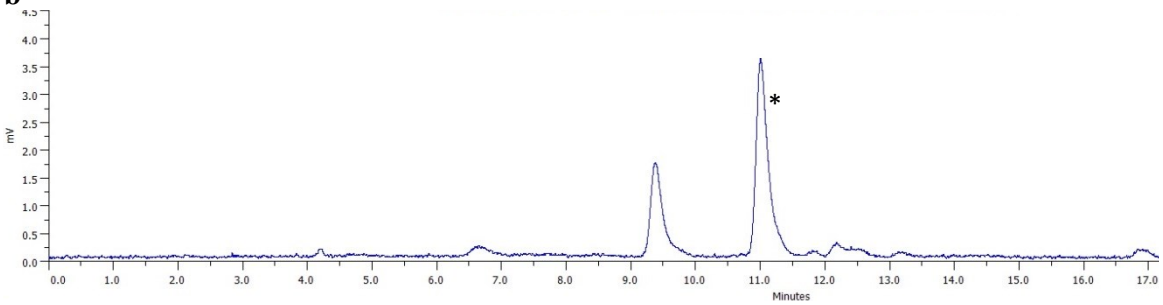
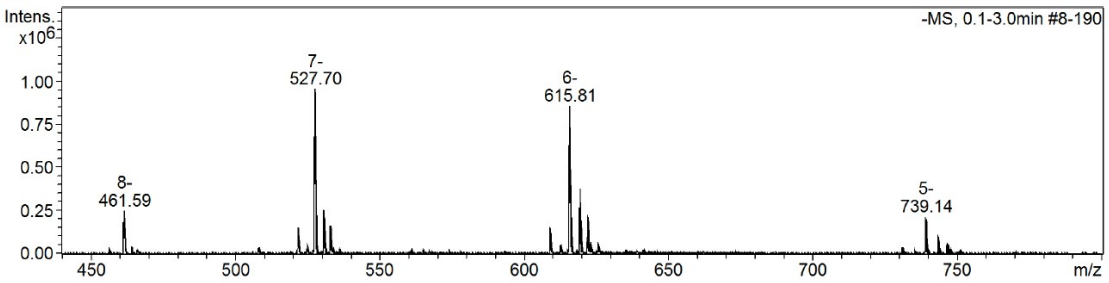


Figure S7. a) ESI-MS spectra of cyclopropylated ODN **6b** and b) Crude reaction mixture of ODN **6b** (peak of interest is indicated by a star).
Main peaks refer to $[M+K]^{n-}$ adducts (1463.3 amu), $[M+K+Na]^{n-}$ adducts were also detected (1485.3 amu).

2.7 ODN **7b**

a



b

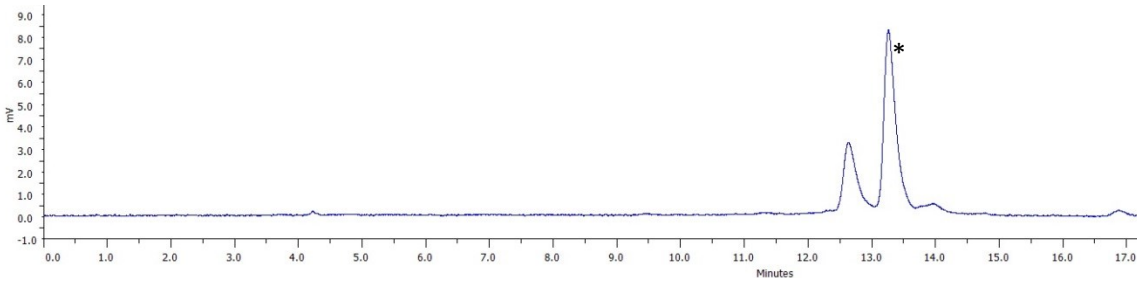


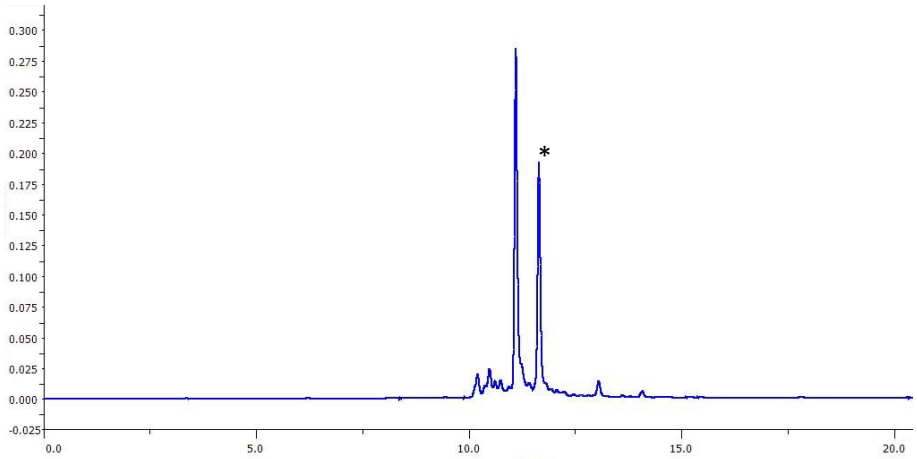
Figure S8. a) ESI-MS spectra of cyclopropylated ODN **7b** and b) Crude reaction mixture of ODN **7b** (peak of interest is indicated by a star).

3. RP-HPLC traces of the crude reaction mixture and ESI-MS spectra of functionalized ODNs 3c-10j

CPG-linked ODN **3a-10a** were treated as previously described excepted that neat corresponding amine (230 µL) was used instead of cyclopropylamine. Synthesis of ODNs functionalized by pyrene (**5h, 9h**) was performed using a warm (60°C) saturated solution of pyrenylmethylamine in isopropanol.

3.1 ODN **3c**

a



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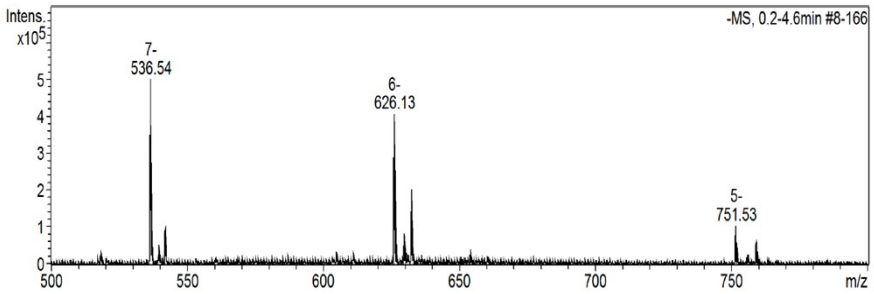


Figure S9. a) RP-HPLC analysis of crude reaction mixture of ODN **3a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **3c**.

3.2 ODN **4d**

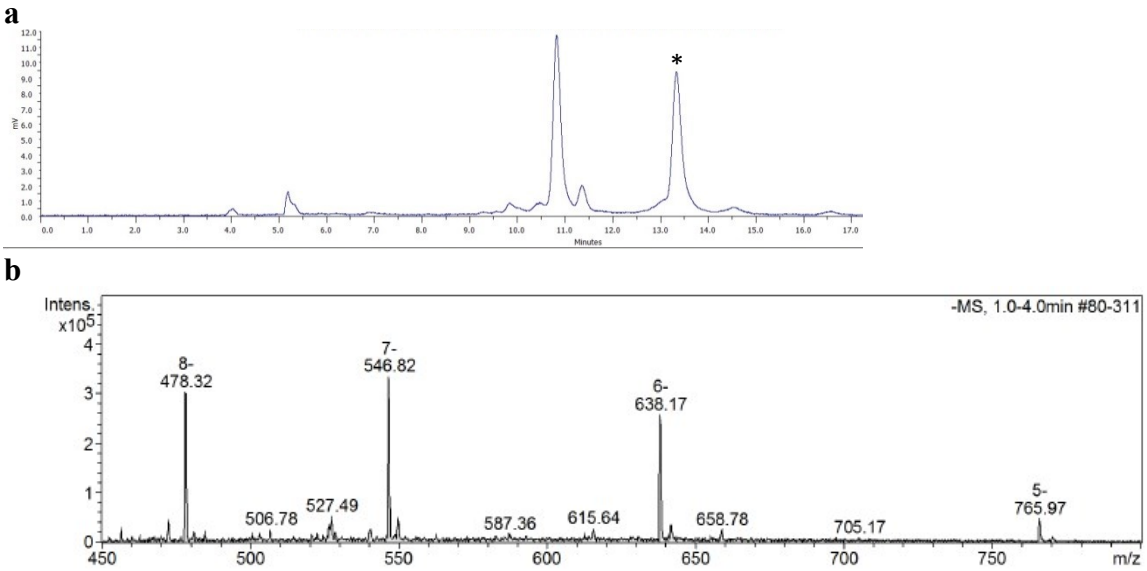


Figure S10. a) RP-HPLC analysis of crude reaction mixture of ODN **4a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **4d**.

3.3 ODN **4e**

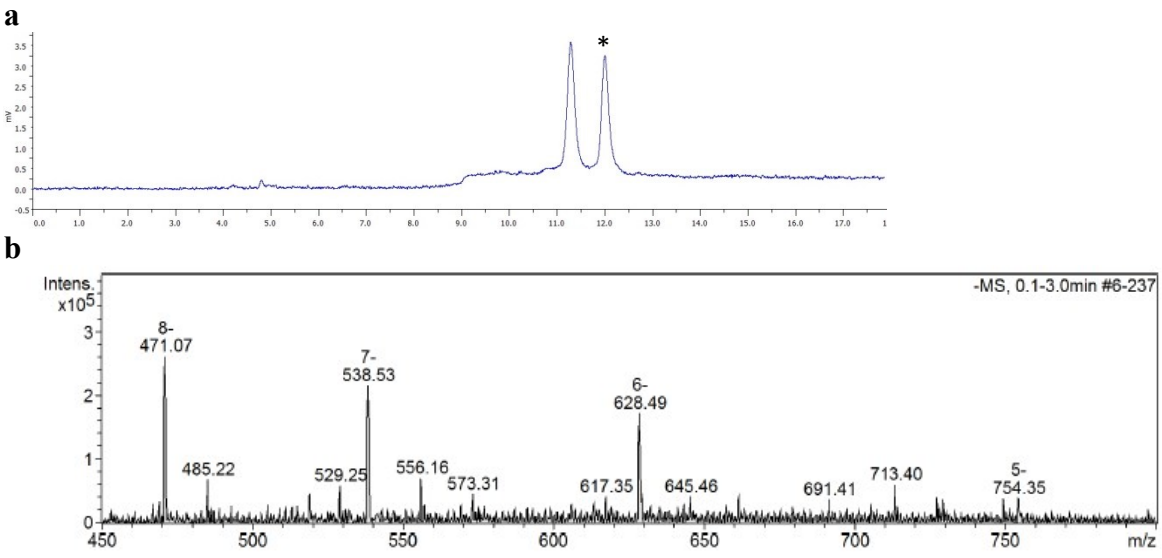
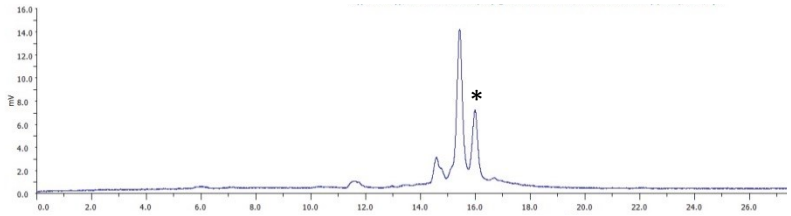


Figure S11. a) RP-HPLC analysis of crude reaction mixture of ODN **4a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **4e**.

3.4 ODN **4f**

a



b

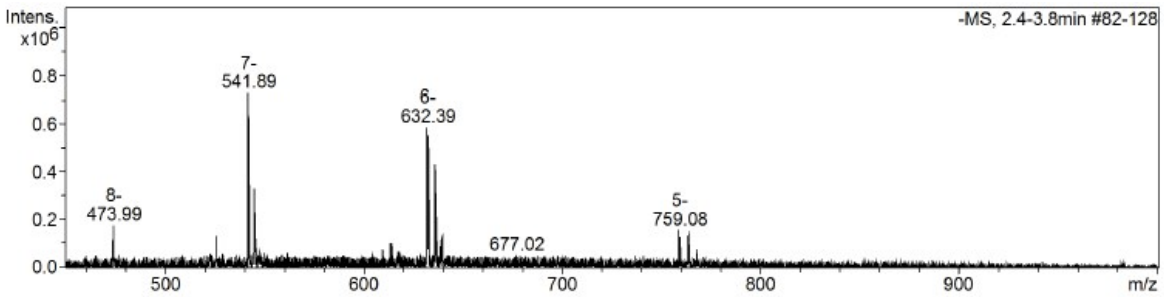
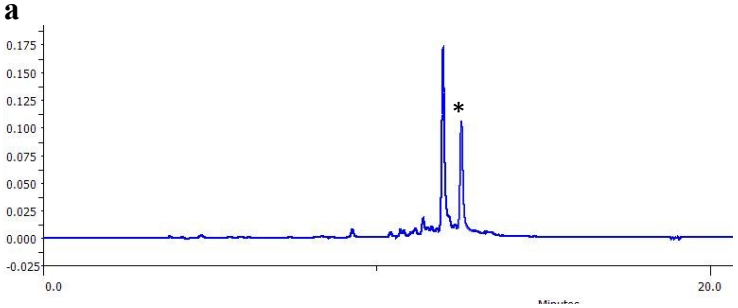


Figure S12. a) RP-HPLC analysis of crude reaction mixture of ODN **4a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **4f**.

3.5 ODN **4g**

a



b

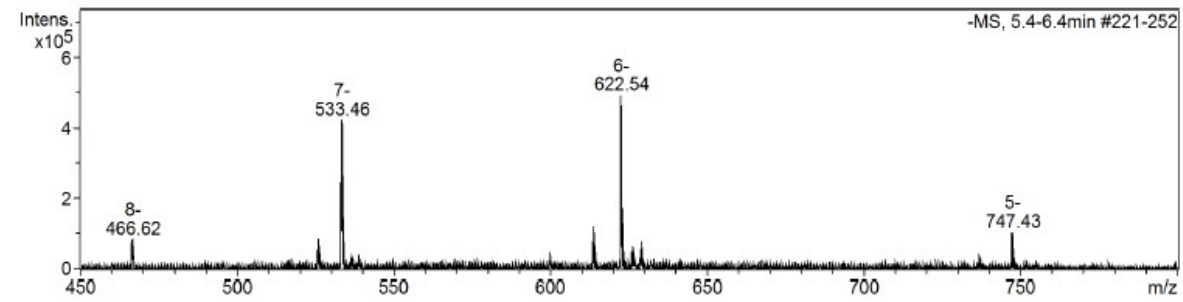


Figure S13. a) RP-HPLC analysis of crude reaction mixture of ODN **4a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **4g**.

3.6 ODN **5h**

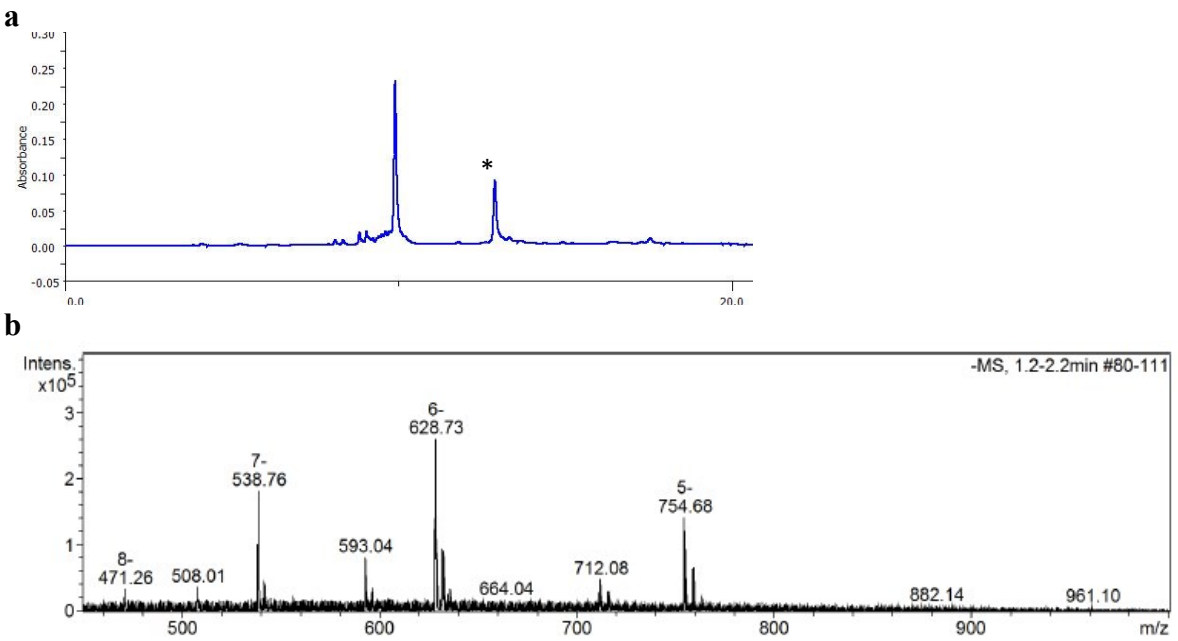


Figure S14. a) RP-HPLC analysis of crude reaction mixture of ODN **5a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **5h**.

3.7 ODN **7c**

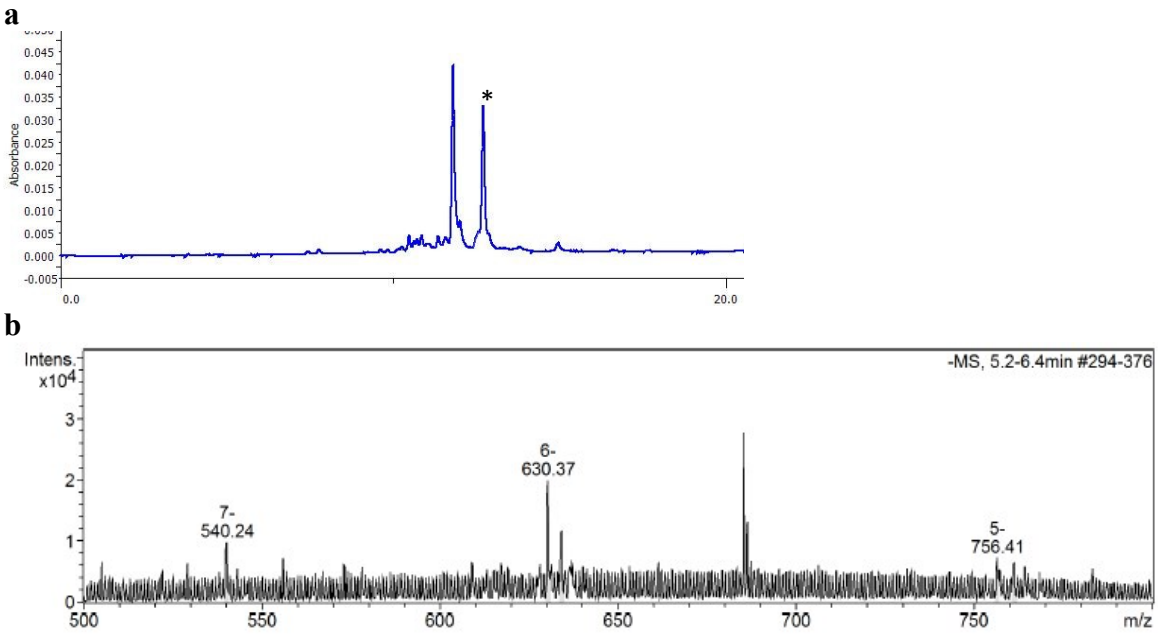
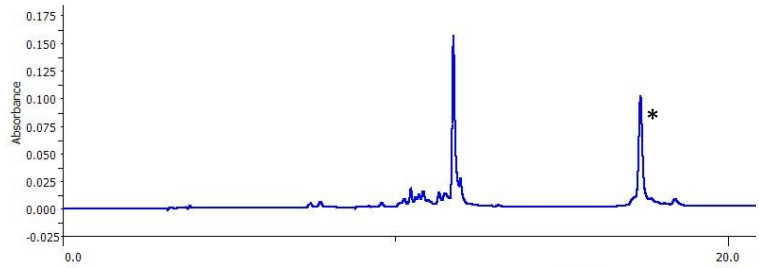


Figure S15. a)RP-HPLC analysis of crude reaction mixture of ODN **7a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **7c**.

3.8 ODN **7j**

a



b

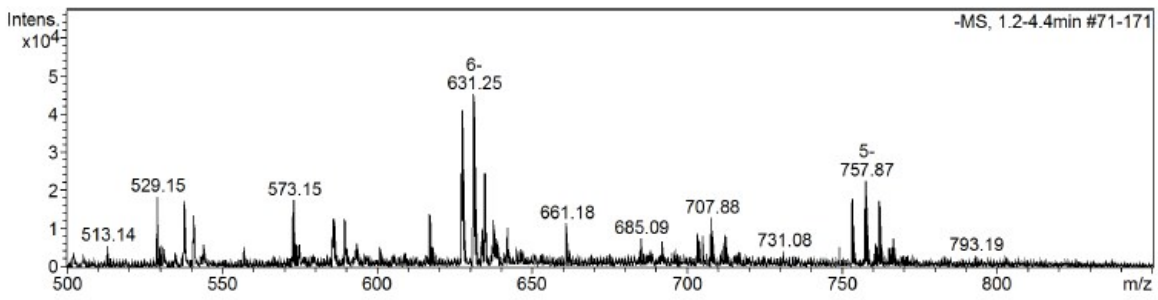
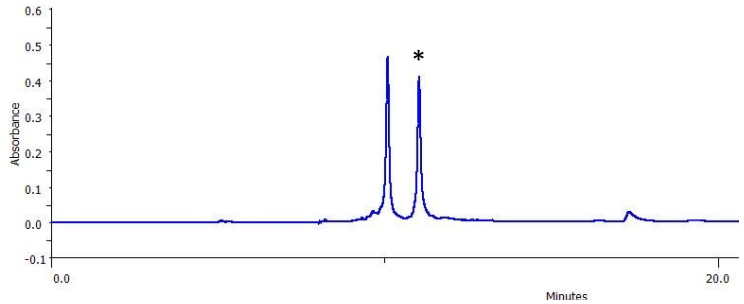


Figure S16. a) RP-HPLC analysis of crude reaction mixture of ODN **7a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **7j**; $[M+Na]^+$ and $[M+2Na]^{2+}$ ions are also observed.

3.9 ODN **8e**

a



b

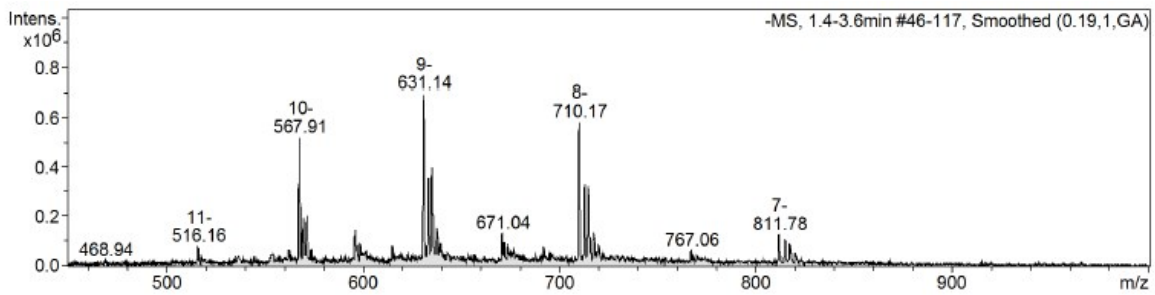


Figure S17. a) RP-HPLC analysis of crude reaction mixture of ODN **8a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **8e**.

3.10 ODN **8i**

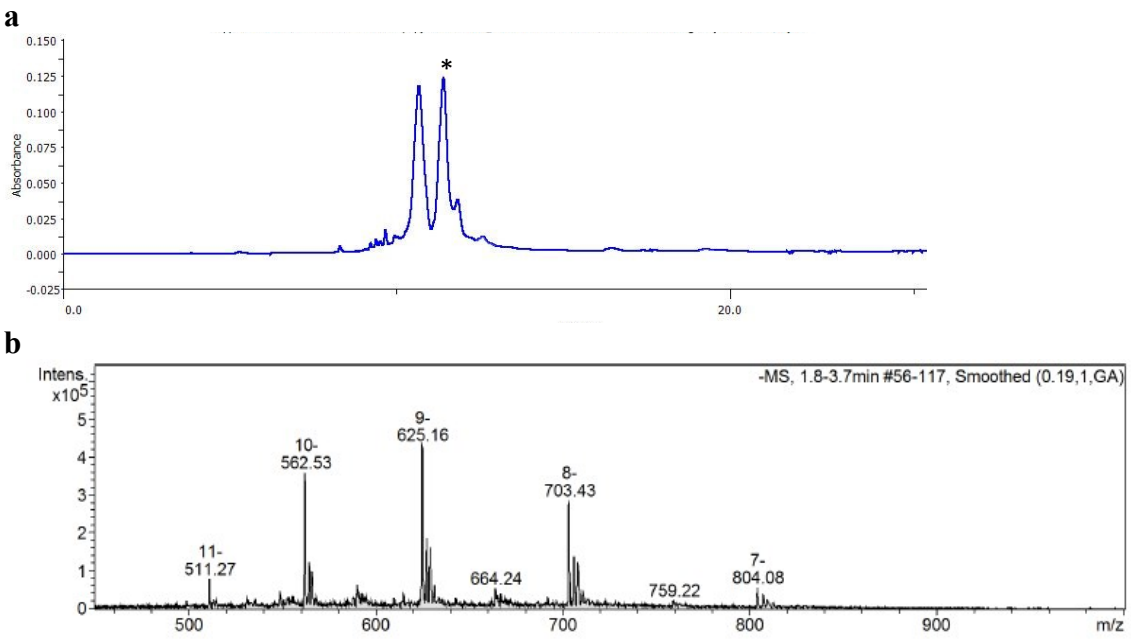


Figure S18. a) RP-HPLC analysis of crude reaction mixture of ODN **8a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **8i**.

3.11 ODN **8j**

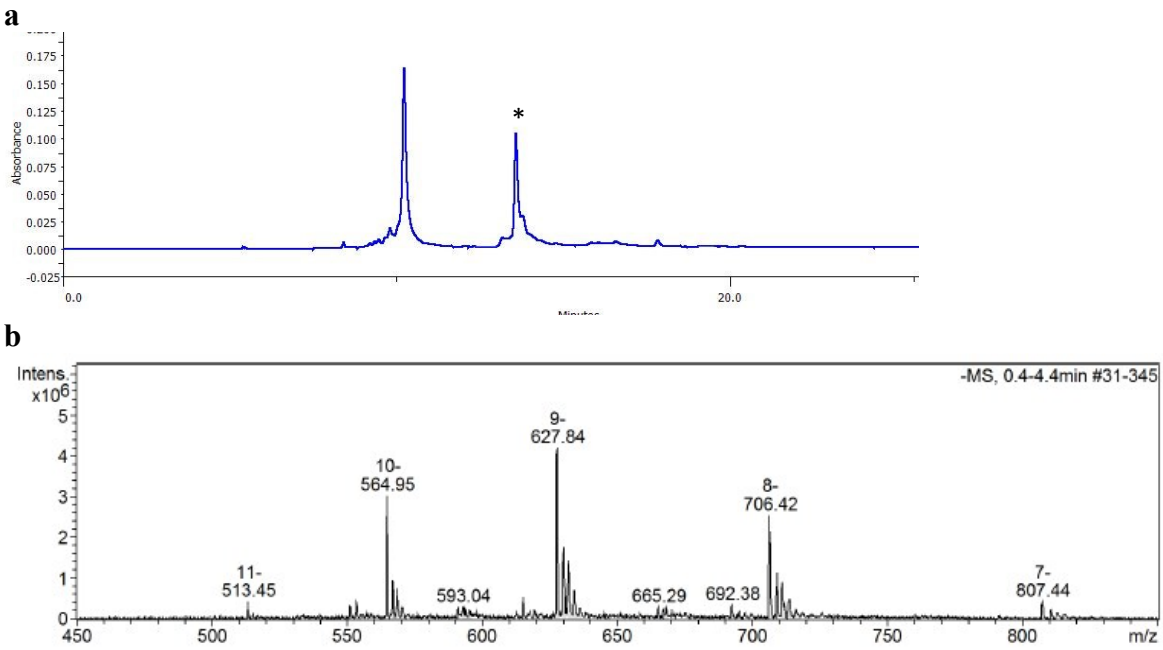


Figure S19. a) RP-HPLC analysis of crude reaction mixture of ODN **8a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **8j**.

3.12 ODN **9h**

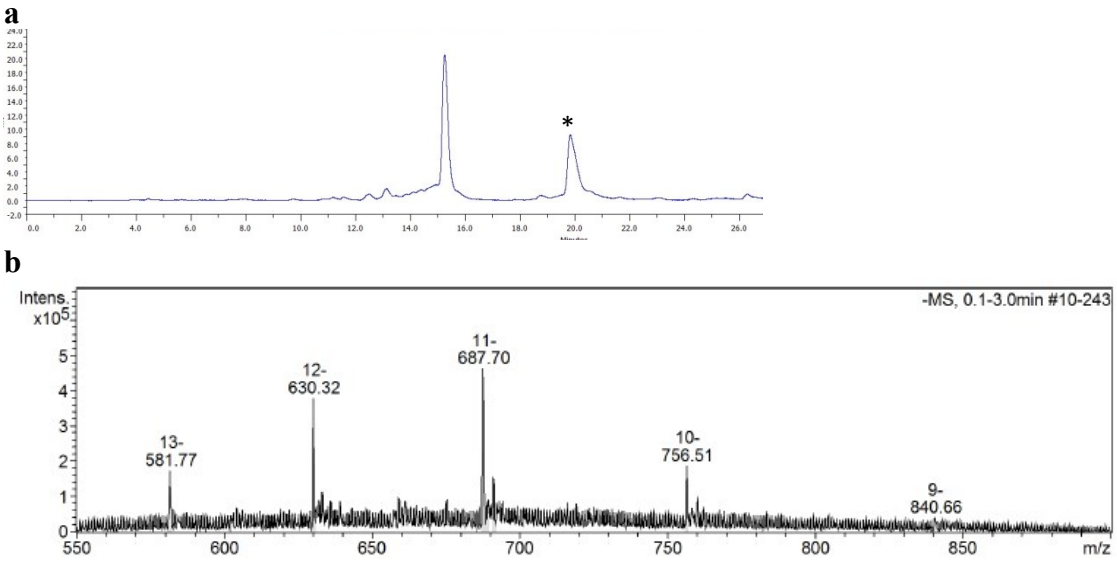


Figure S20. a) RP-HPLC analysis of crude reaction mixture of ODN **9a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **9h**.

3.13 ODN **10e**

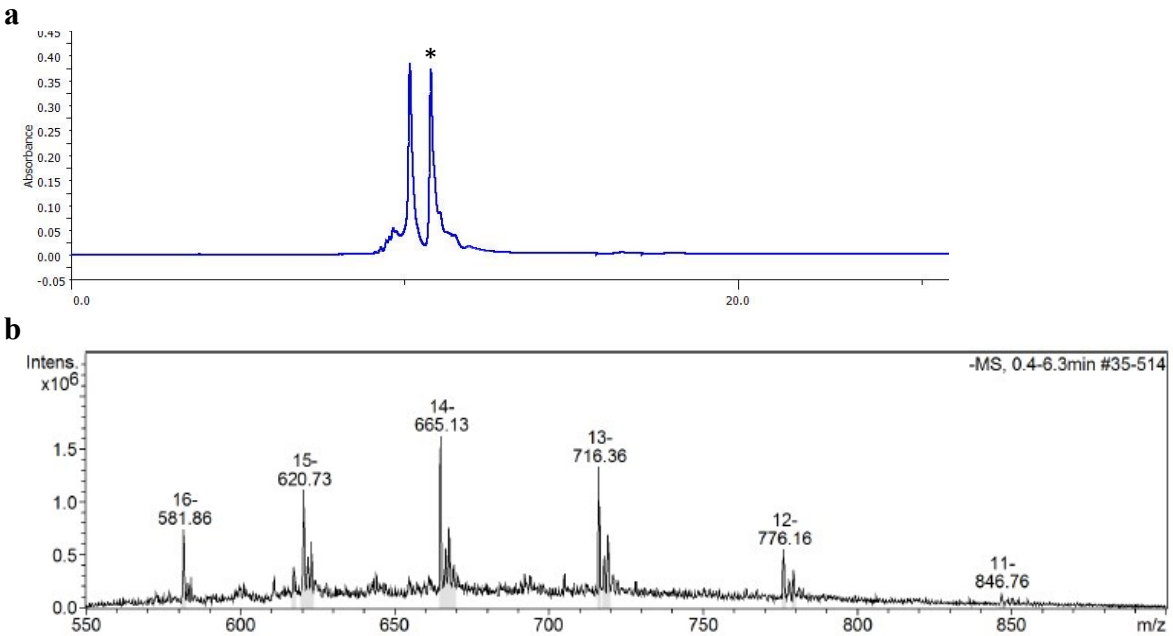


Figure S21. a)RP-HPLC analysis of crude reaction mixture of ODN **10a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **10e**.

3.14 ODN **10j**

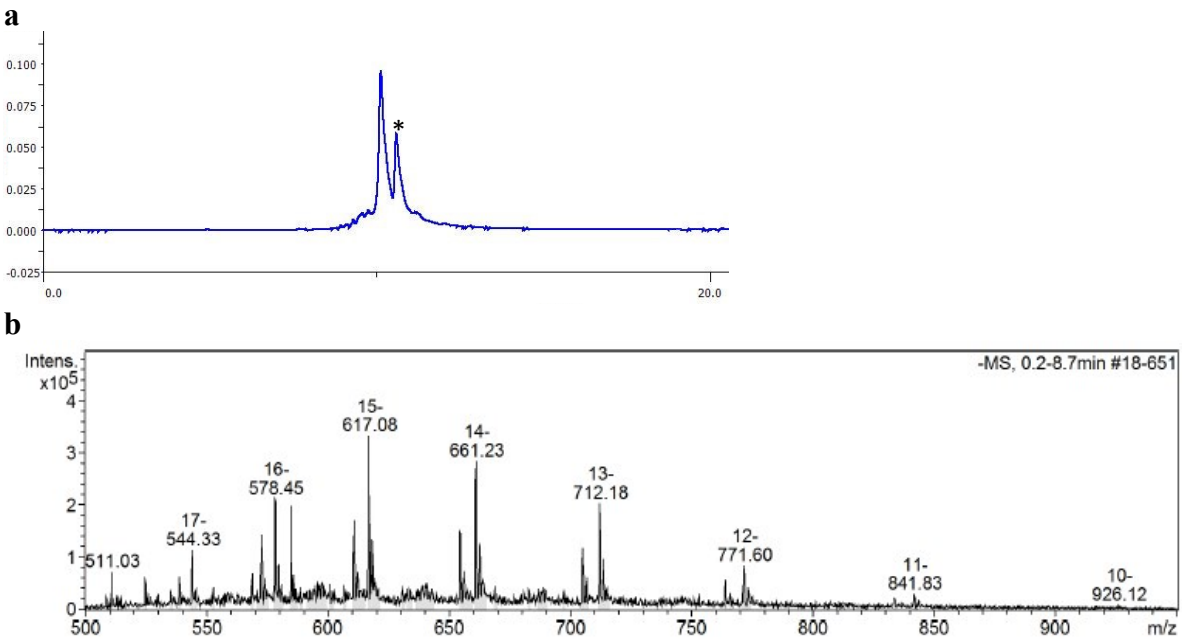


Figure S22. a) RP-HPLC analysis of crude reaction mixture of ODN **10a** submitted to our reaction conditions, b) ESI-MS analysis of the resulting purified product **10j**.

4. Assessment of the nucleobase chemoselectivity

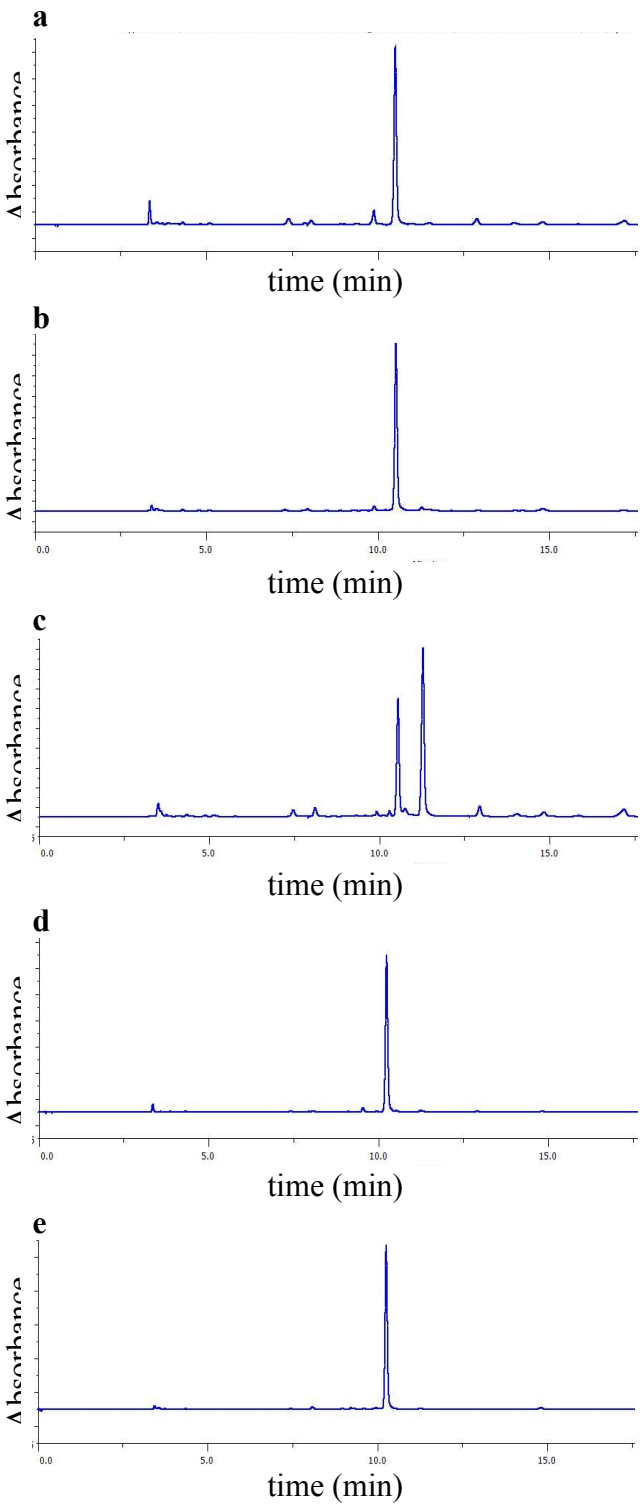


Figure S23. RP-HPLC analysis of a model CPG-linked ODN[a] 5'-TTNTT-3' subjected to our reaction conditions.[a] a) N = ^{Bz}dA, b) N = ^{Ac}dC , c) N = ^{Bz}dC, d) N = ^{dmf}dG, e) N = ^{iBu}dG