Supporting Information for

Palladacyclic conjugate group promotes hybridization of short oligonucleotides

Madhuri Ashok Hande, Sajal Kumar Maity and Tuomas Lönnberg*

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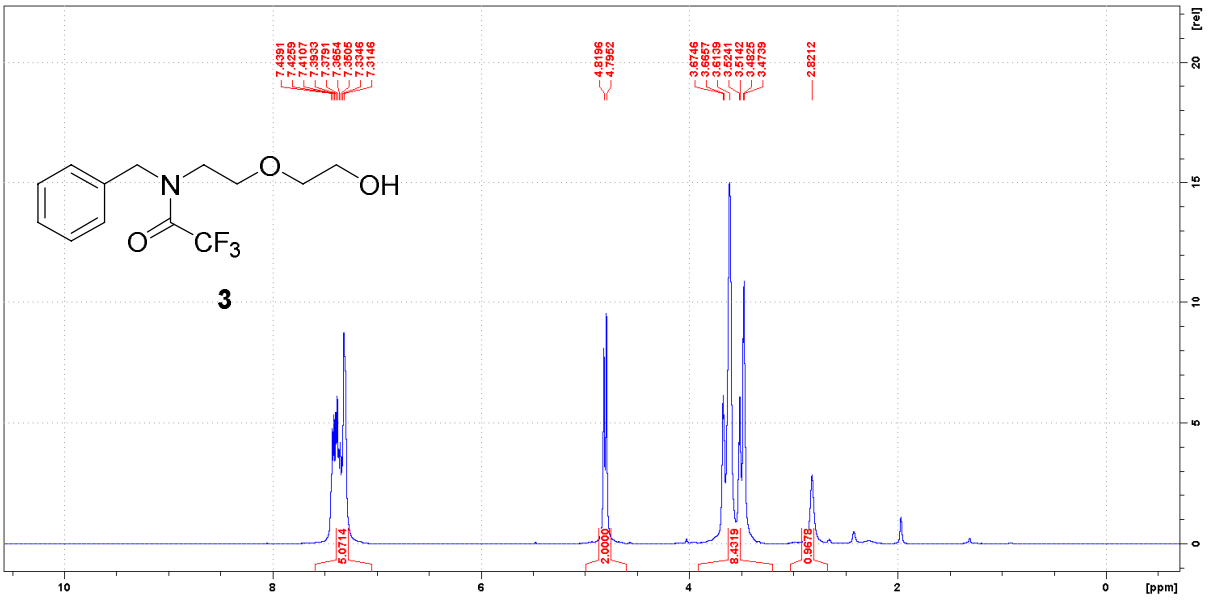
Contents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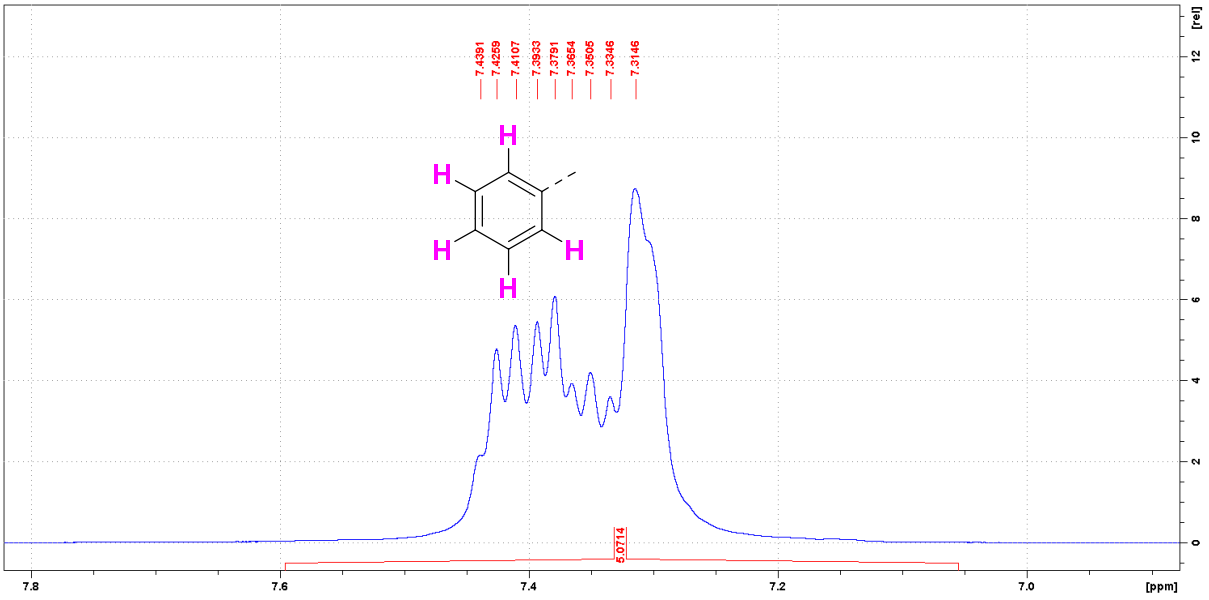
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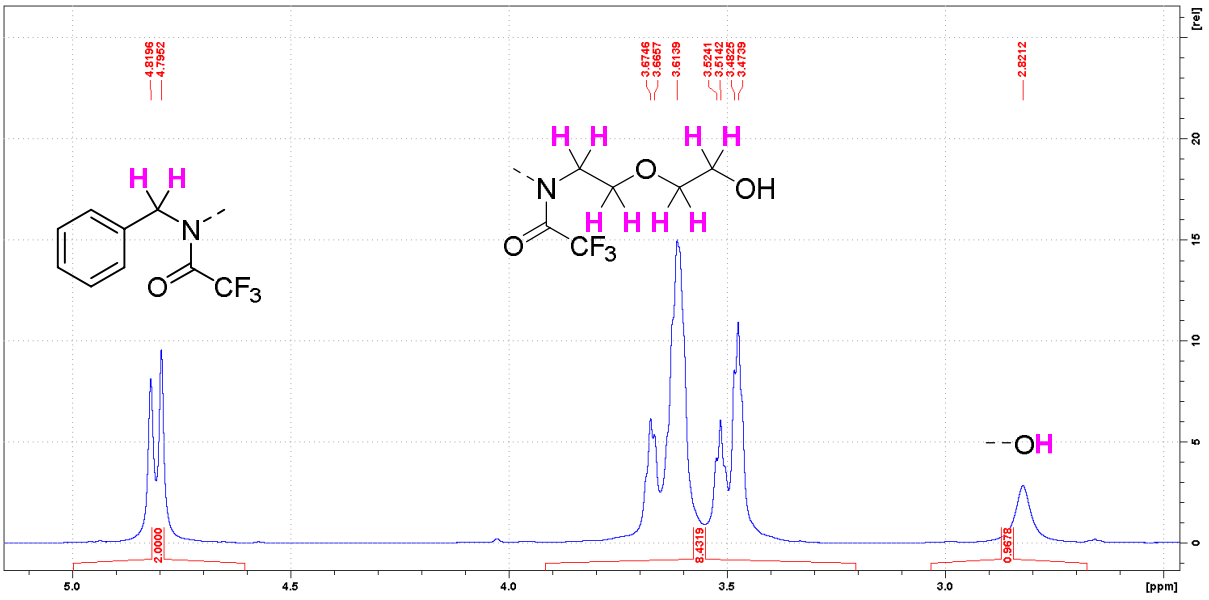
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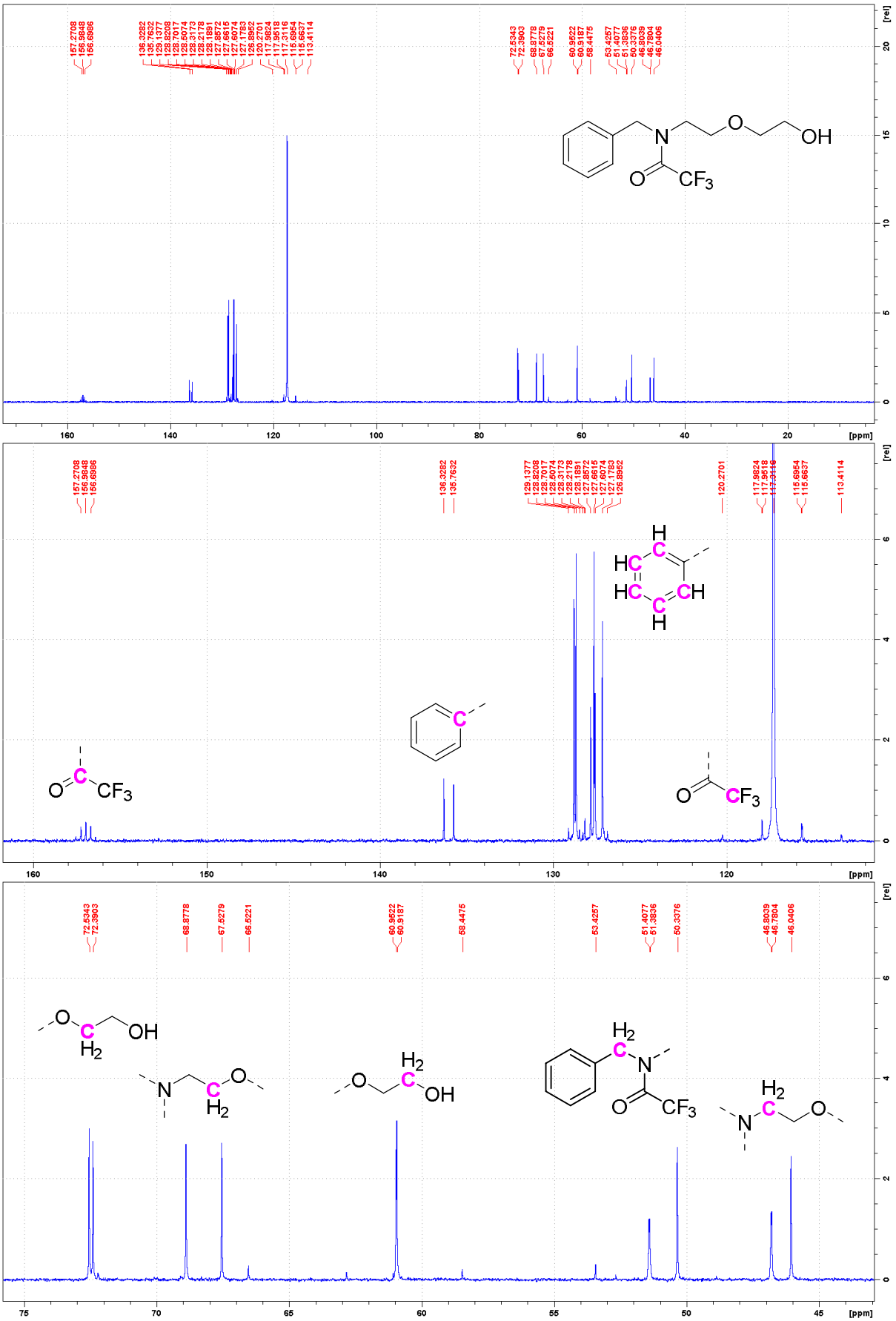

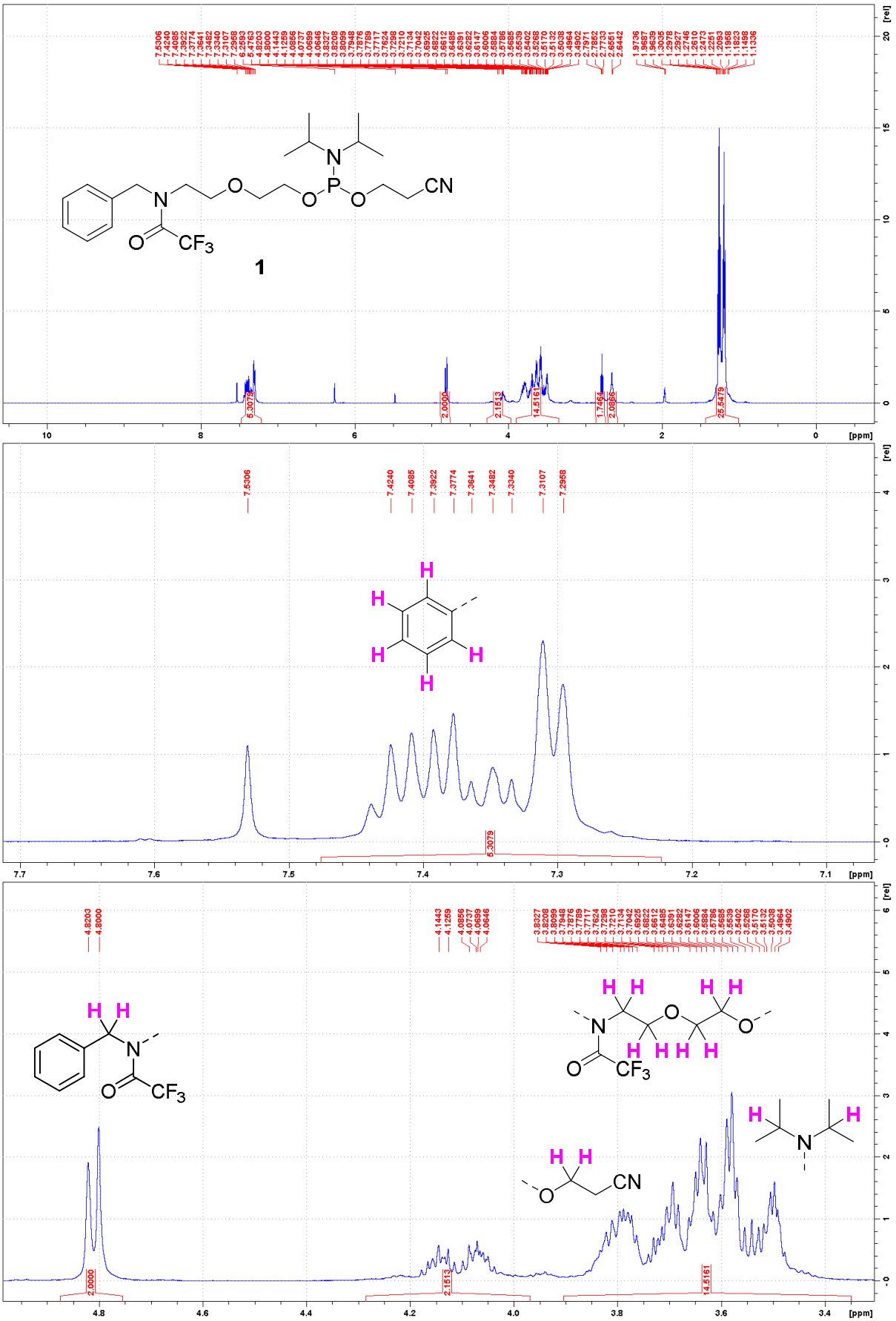
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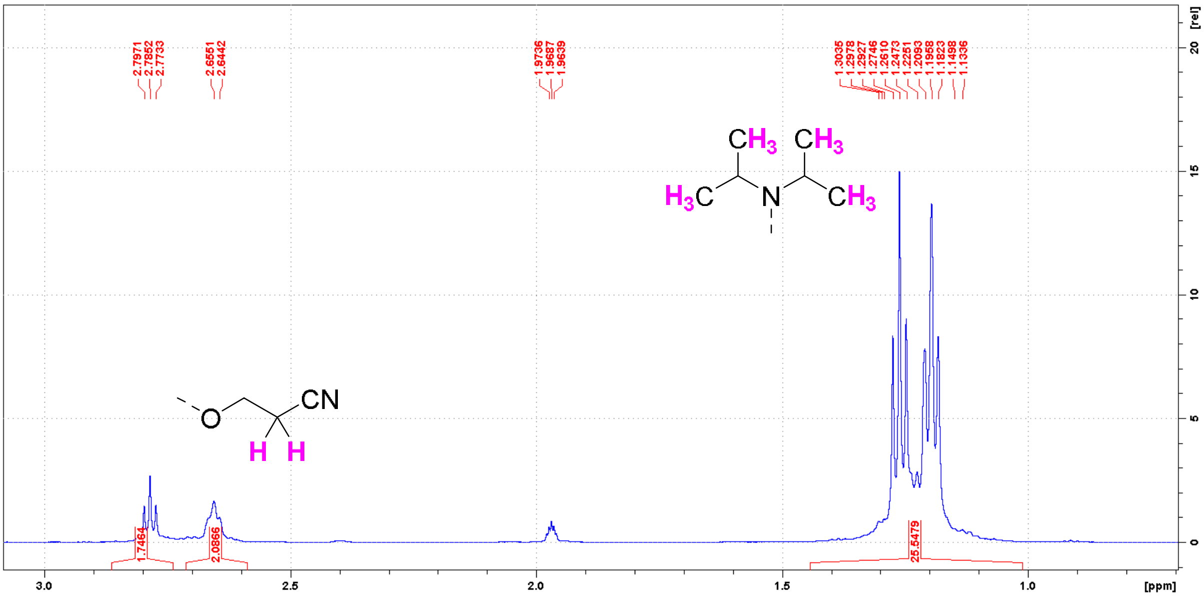
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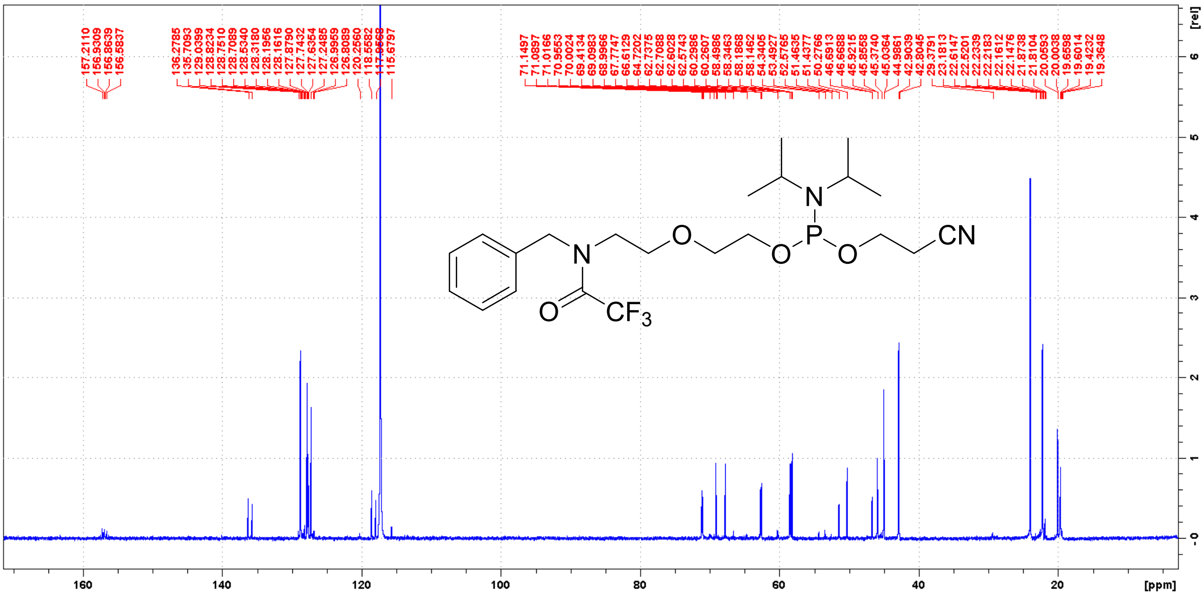
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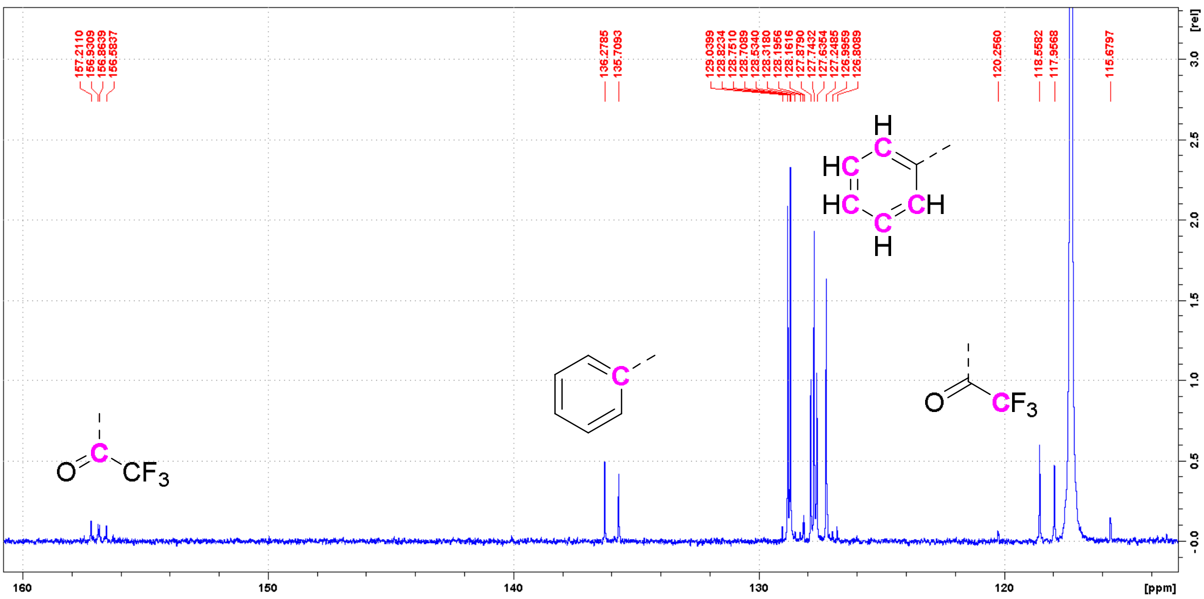
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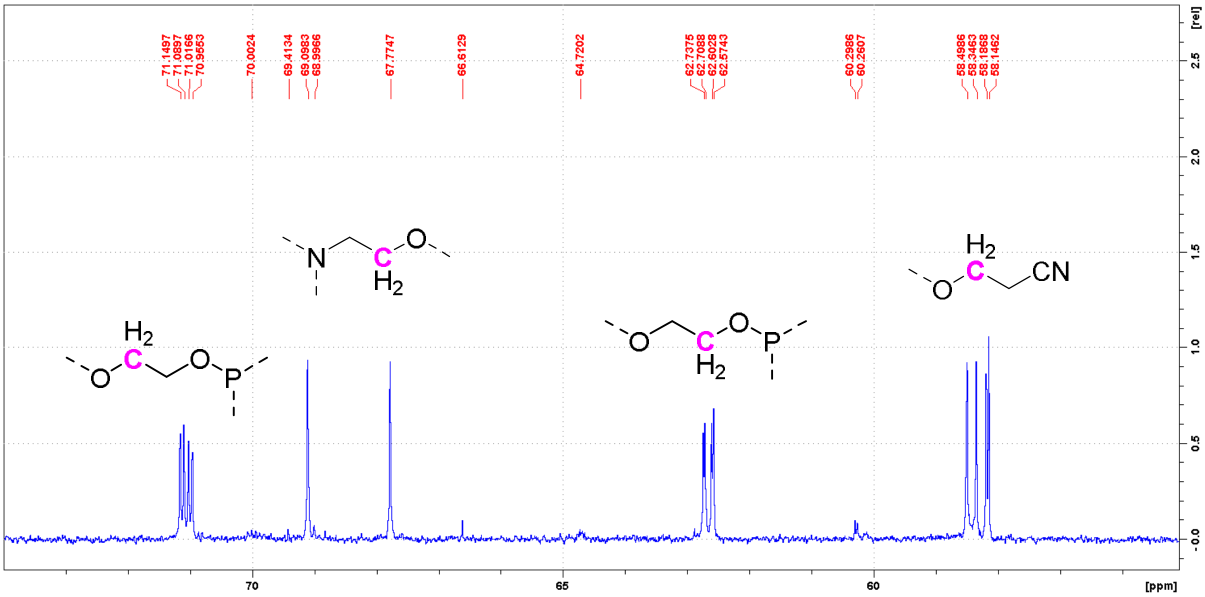
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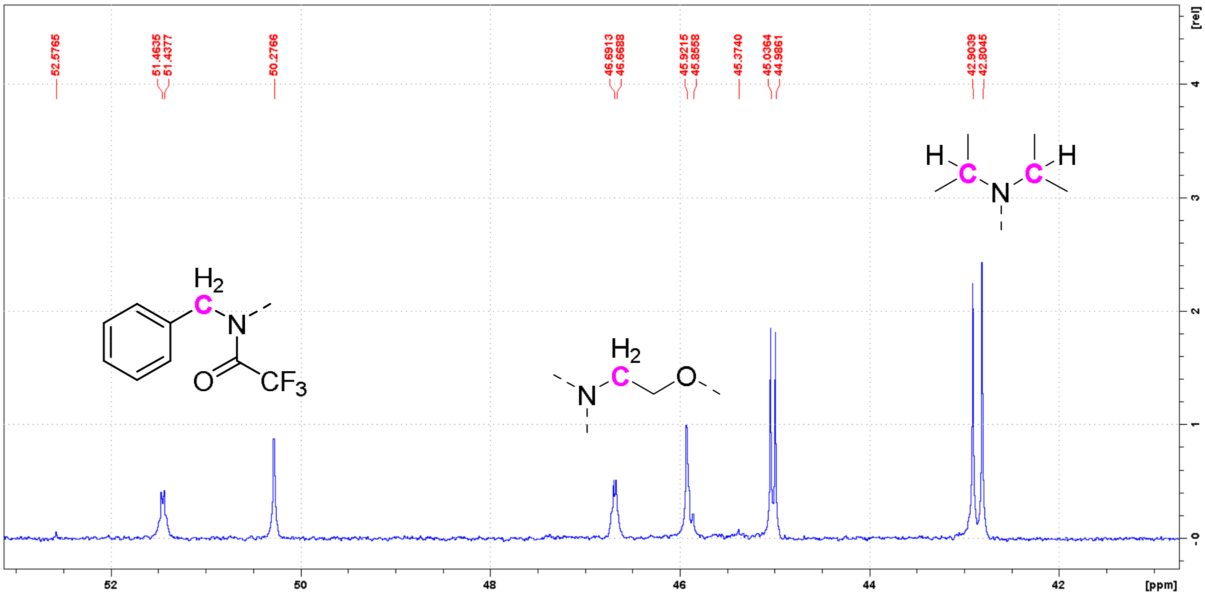
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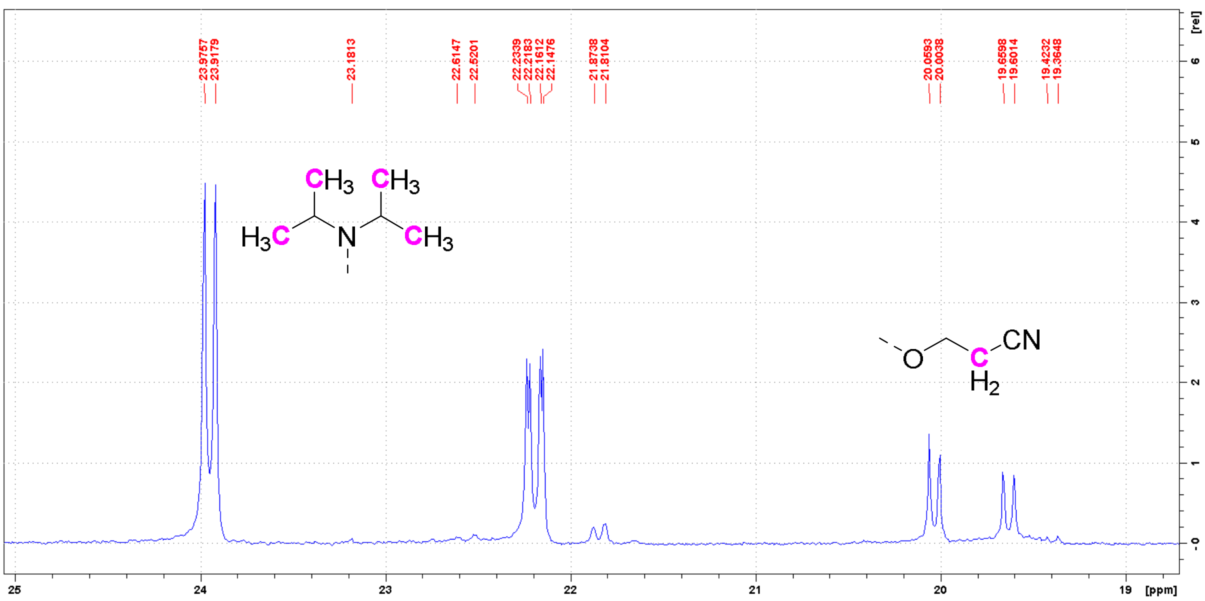
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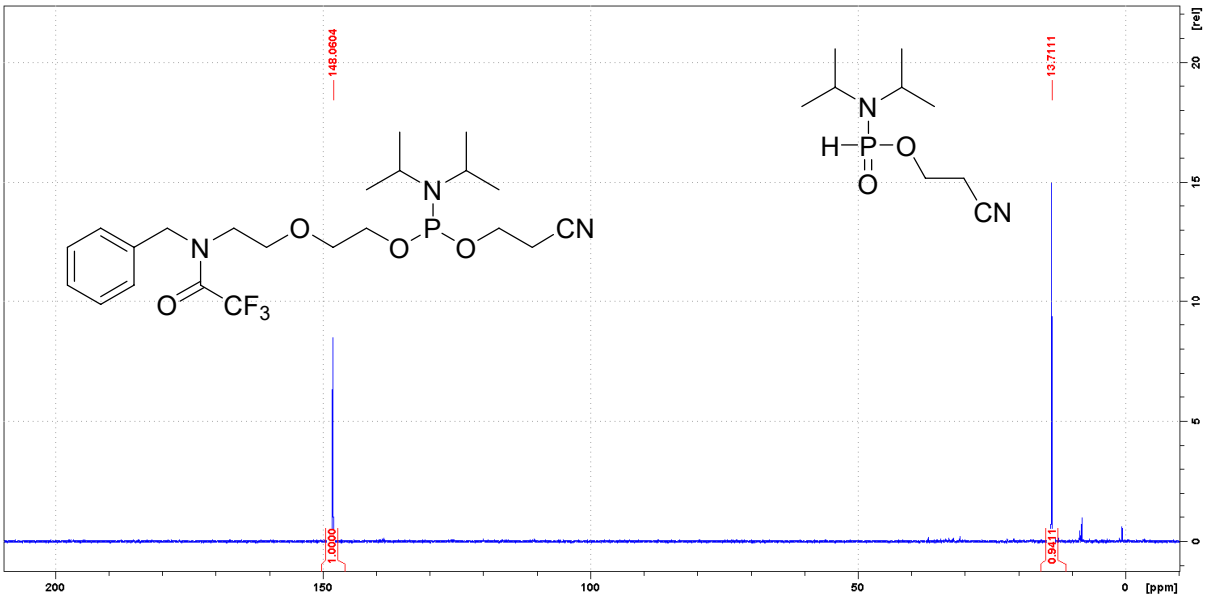
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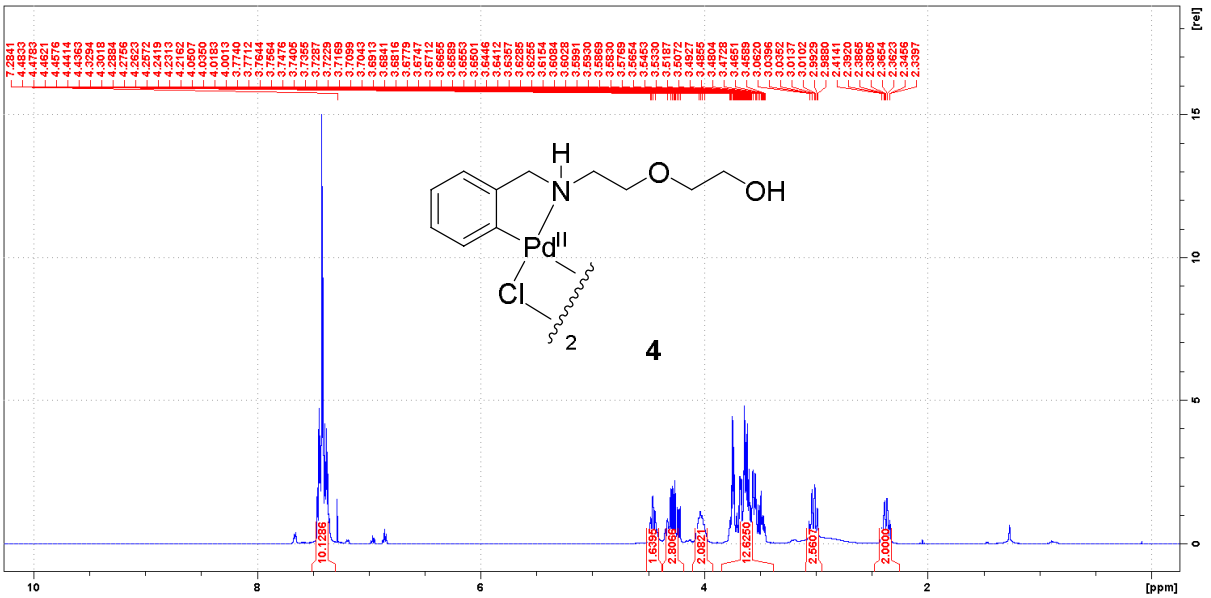
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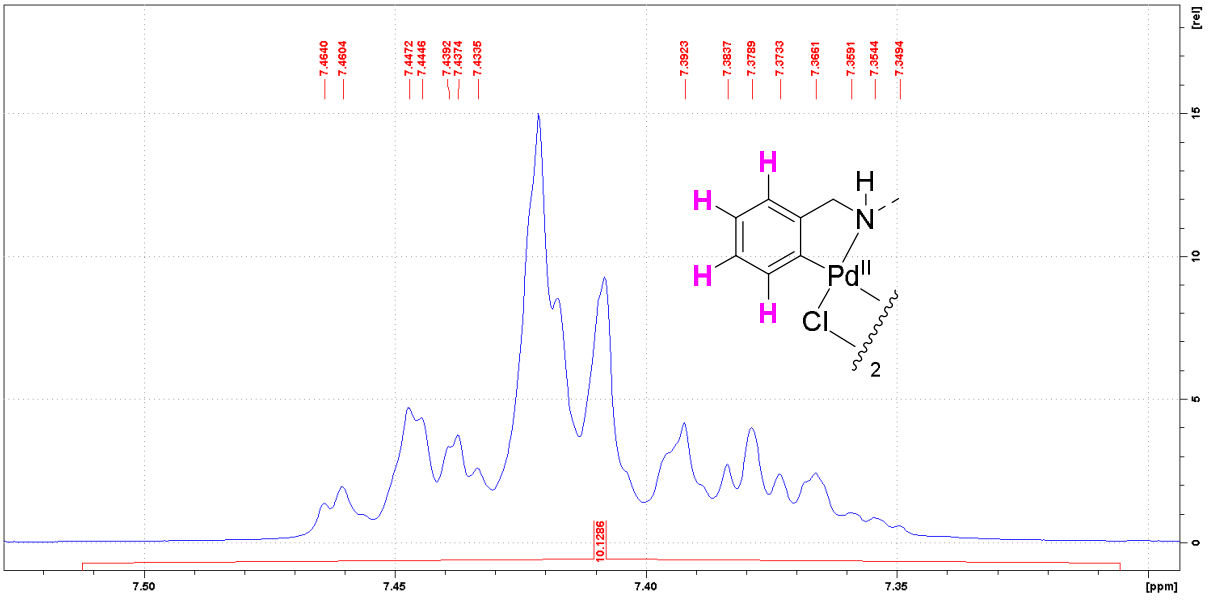

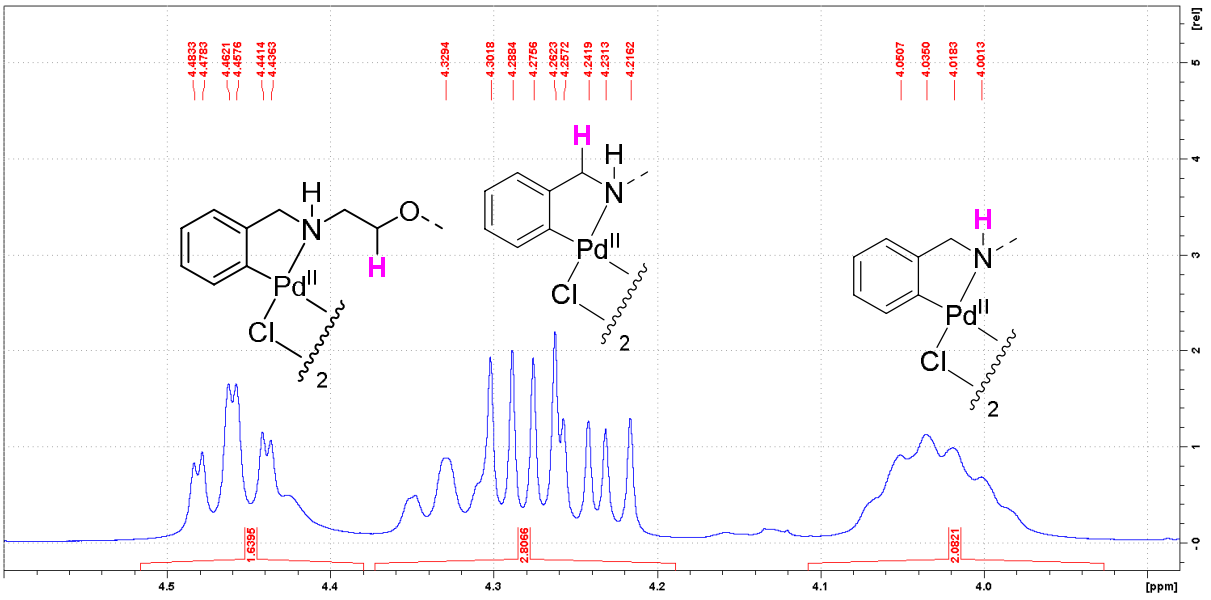

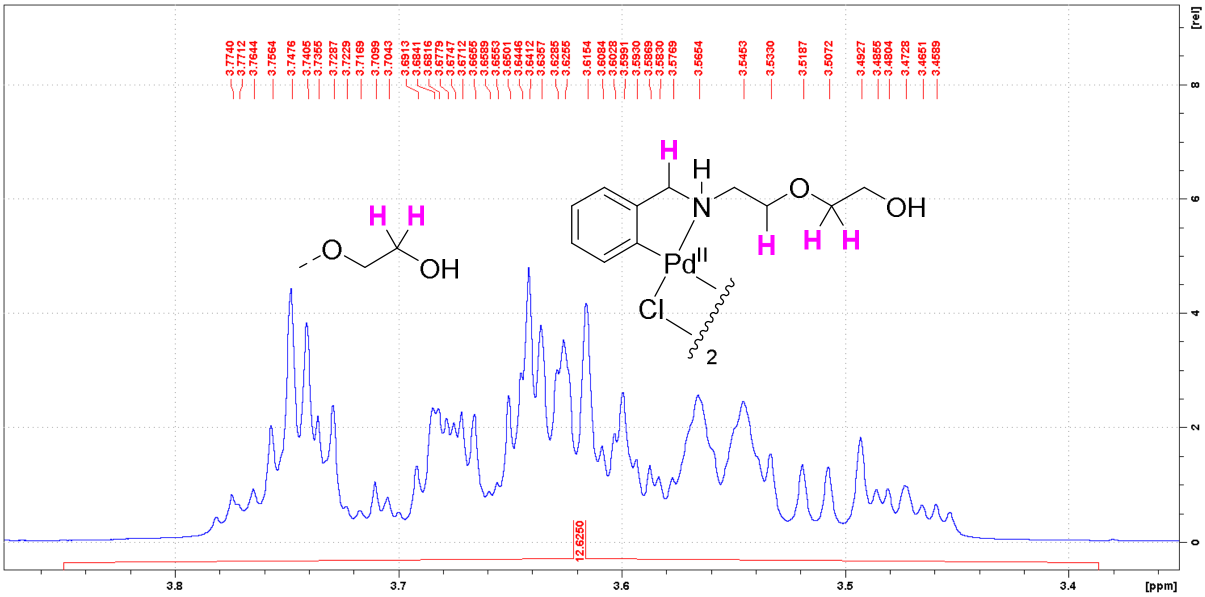
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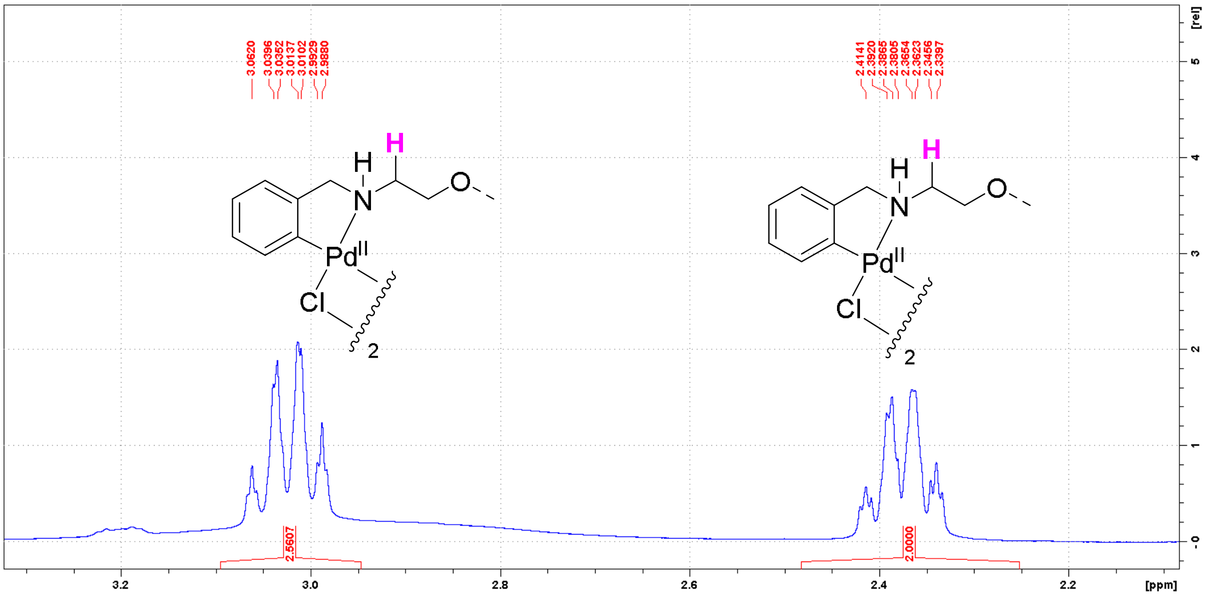
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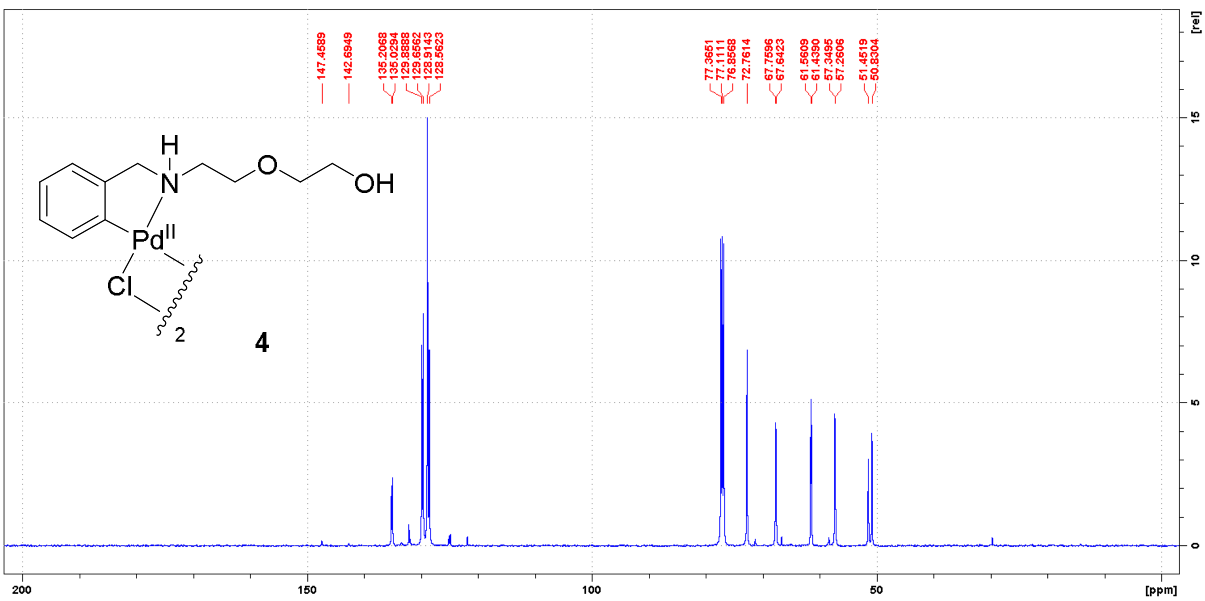
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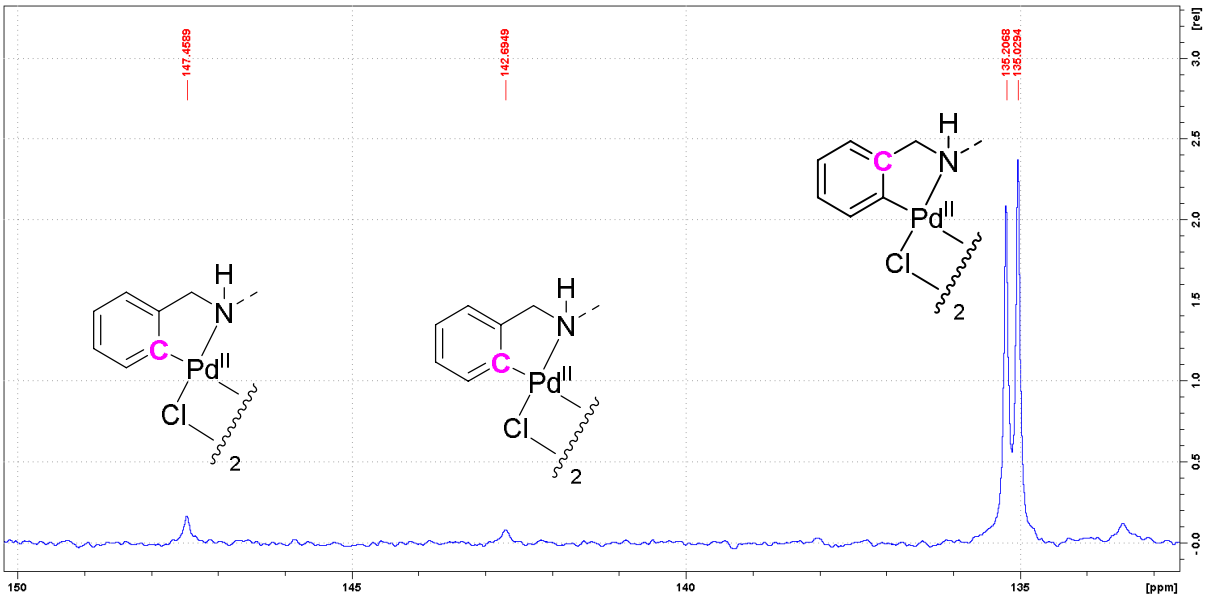
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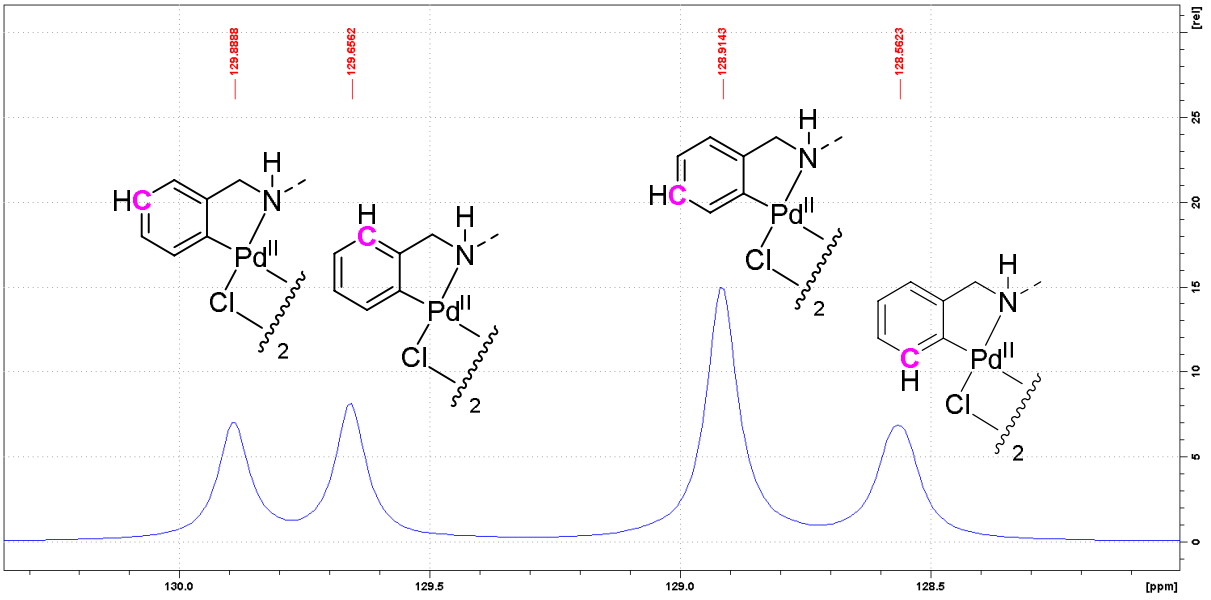
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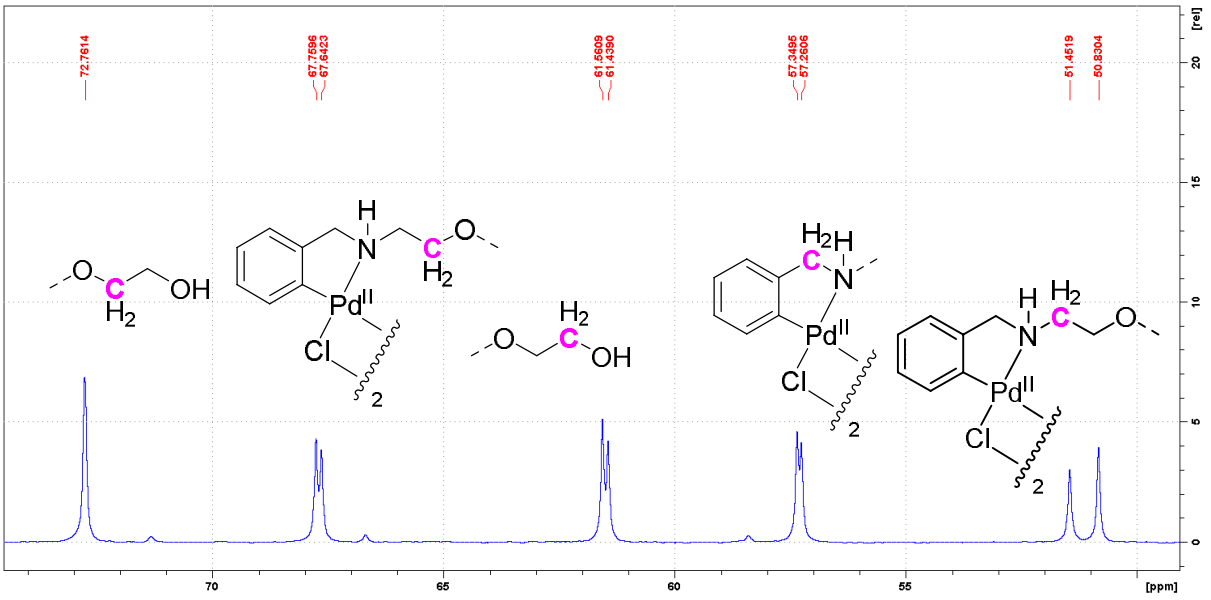
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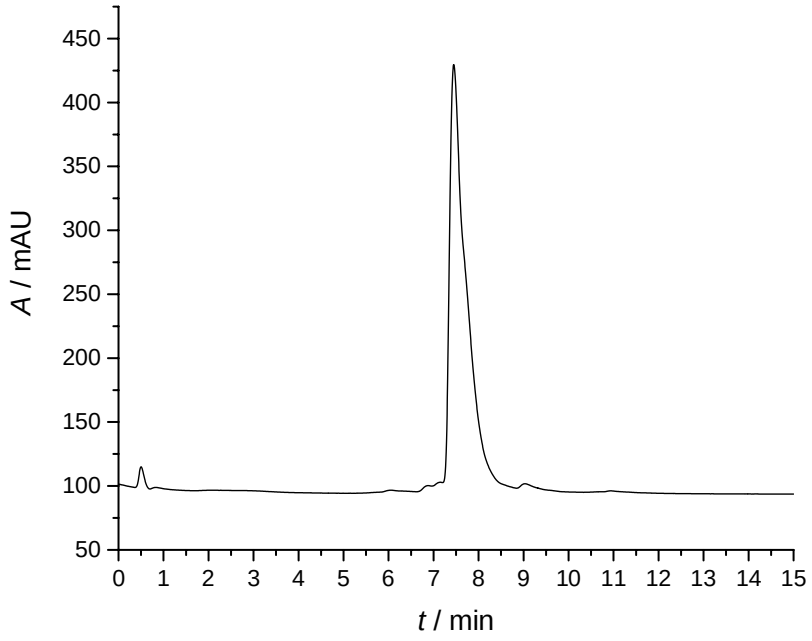


Figure S1. IE-HPLC trace of oligonucleotide ON1b; ProSwift™ SAX-1S column (50 × 1 mm, monolithic); flow rate = 0.20 mL min^{-1}; linear gradient (0.10 to 0.90 M over 15 min) of NaCl in 10 mM TRIS•HCl buffer (pH 7.6).

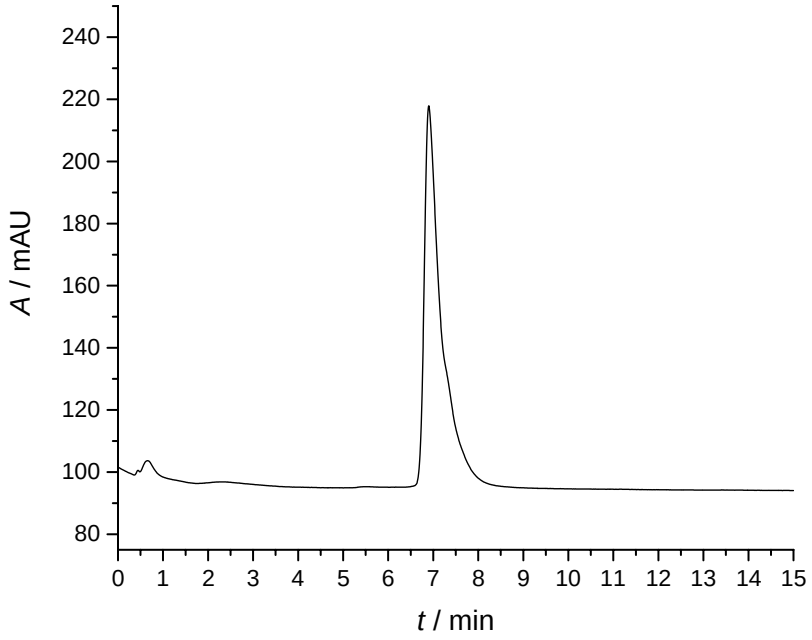


Figure S2. IE-HPLC trace of oligonucleotide ON2b; ProSwift™ SAX-1S column (50 × 1 mm, monolithic); flow rate = 0.20 mL min^{-1}; linear gradient (0.10 to 0.90 M over 15 min) of NaCl in 10 mM TRIS•HCl buffer (pH 7.6).

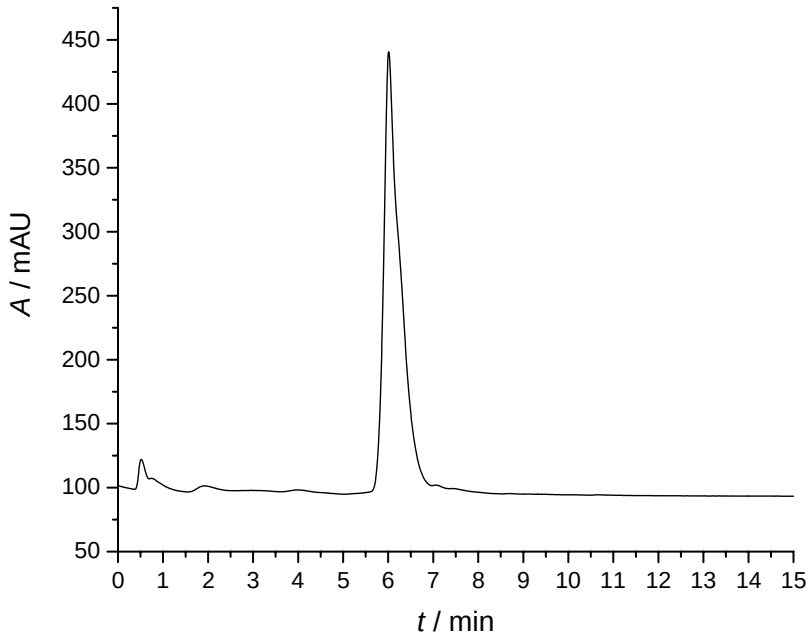


Figure S3. IE-HPLC trace of oligonucleotide ON3b; ProSwift™ SAX-1S column (50 × 1 mm, monolithic); flow rate = 0.20 mL min^{-1}; linear gradient (0.10 to 0.90 M over 15 min) of NaCl in 10 mM TRIS•HCl buffer (pH 7.6).

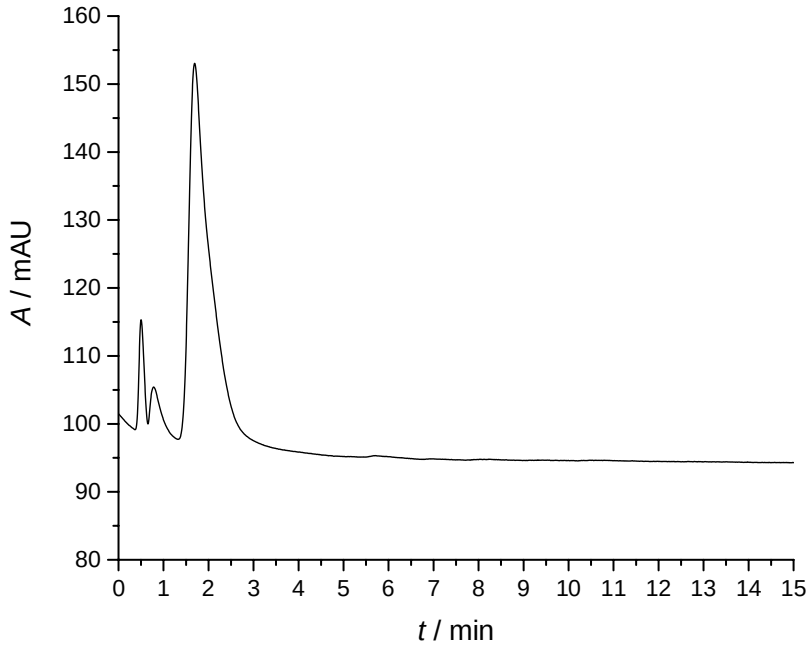


Figure S4. IE-HPLC trace of oligonucleotide ON4b; ProSwift™ SAX-1S column (50 × 1 mm, monolithic); flow rate = 0.20 mL min^{-1}; linear gradient (0.10 to 0.90 M over 15 min) of NaCl in 10 mM TRIS•HCl buffer (pH 7.6).

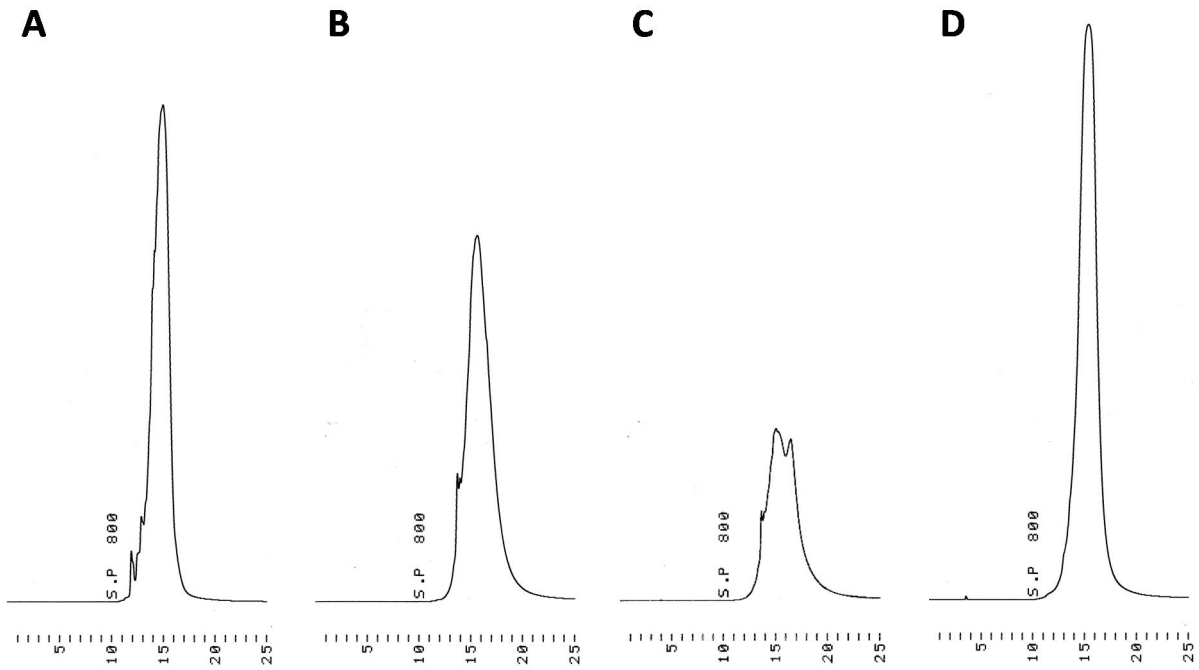


Figure S5. RP-HPLC traces of oligonucleotides A) ON1b-Pd, B) ON2b-Pd, C) ON3b-Pd and D) ON4b-Pd; Hypersil ODS C18 column (250 × 4.6 mm, 5 µm); flow rate = 1.0 mL min^{-1}; linear gradient (0 to 30% over 25 min) of MeCN in 50 mM aq. triethylammonium acetate.

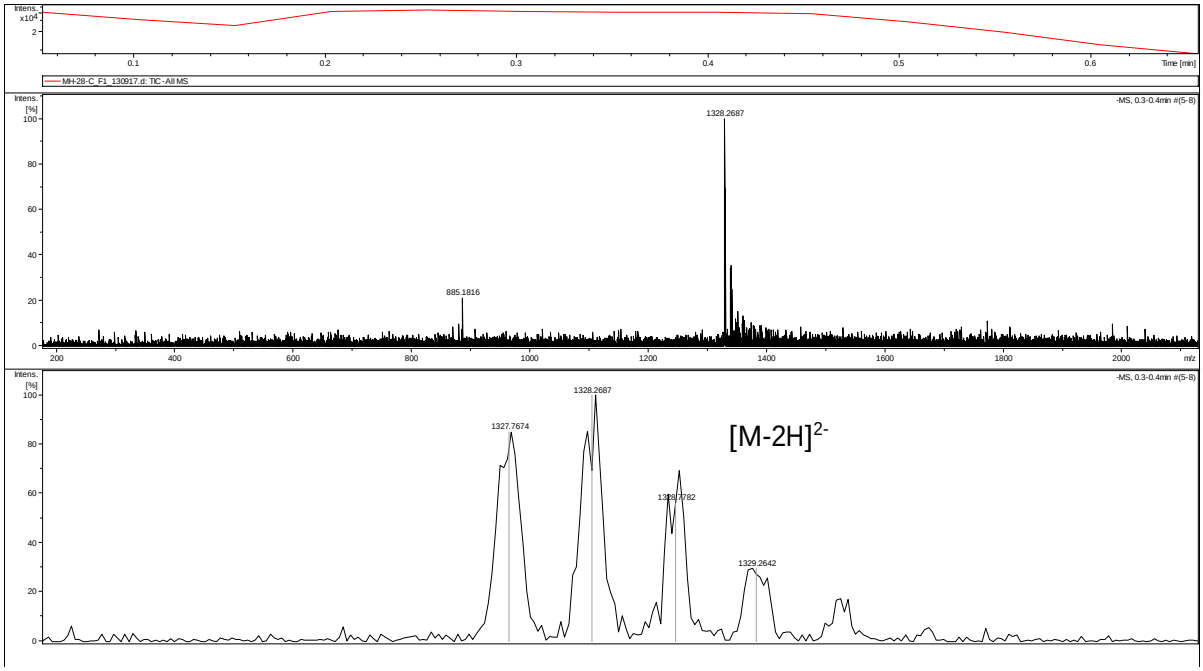
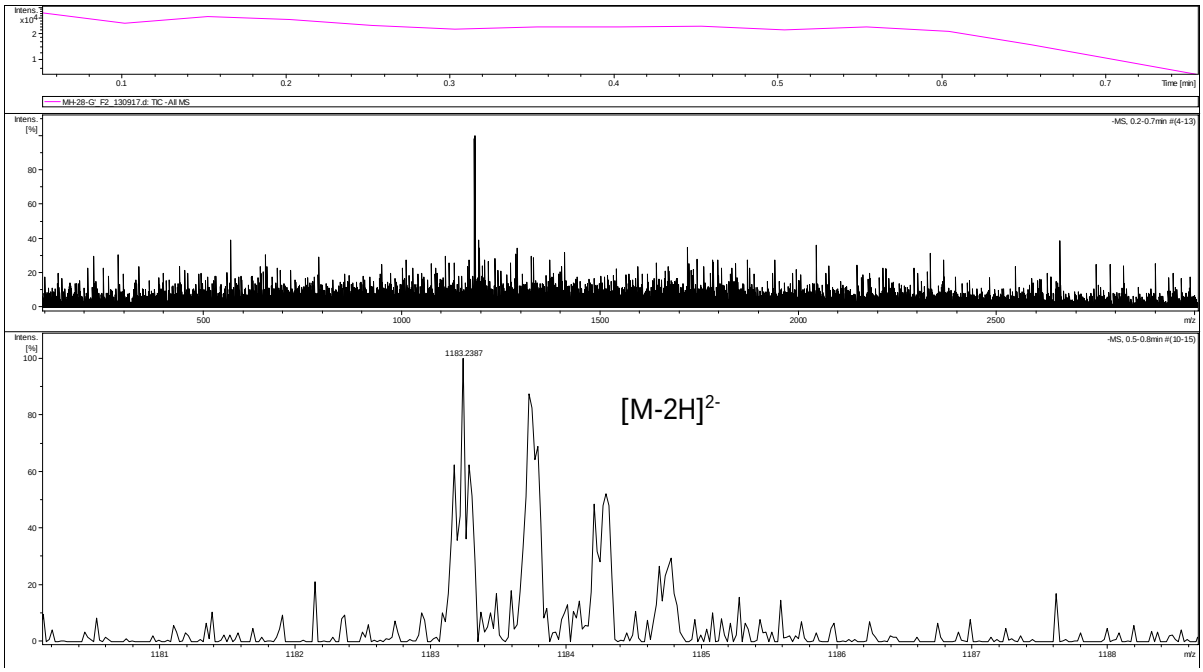


Figure S6. Mass spectrum of oligonucleotide ON1b.



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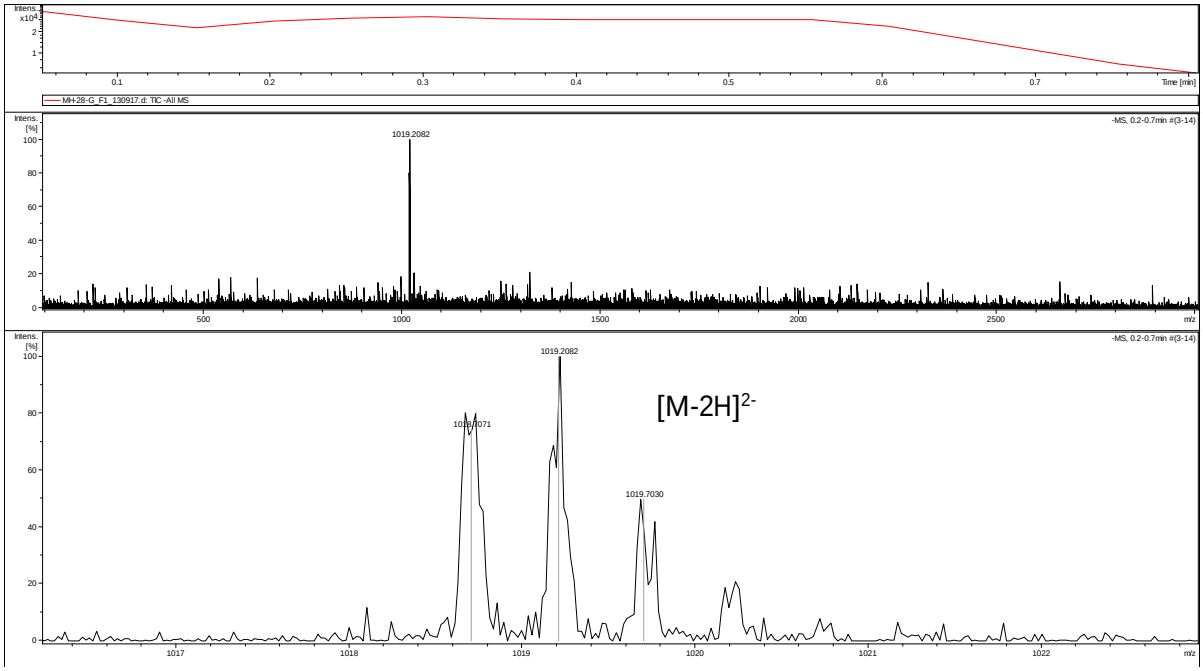

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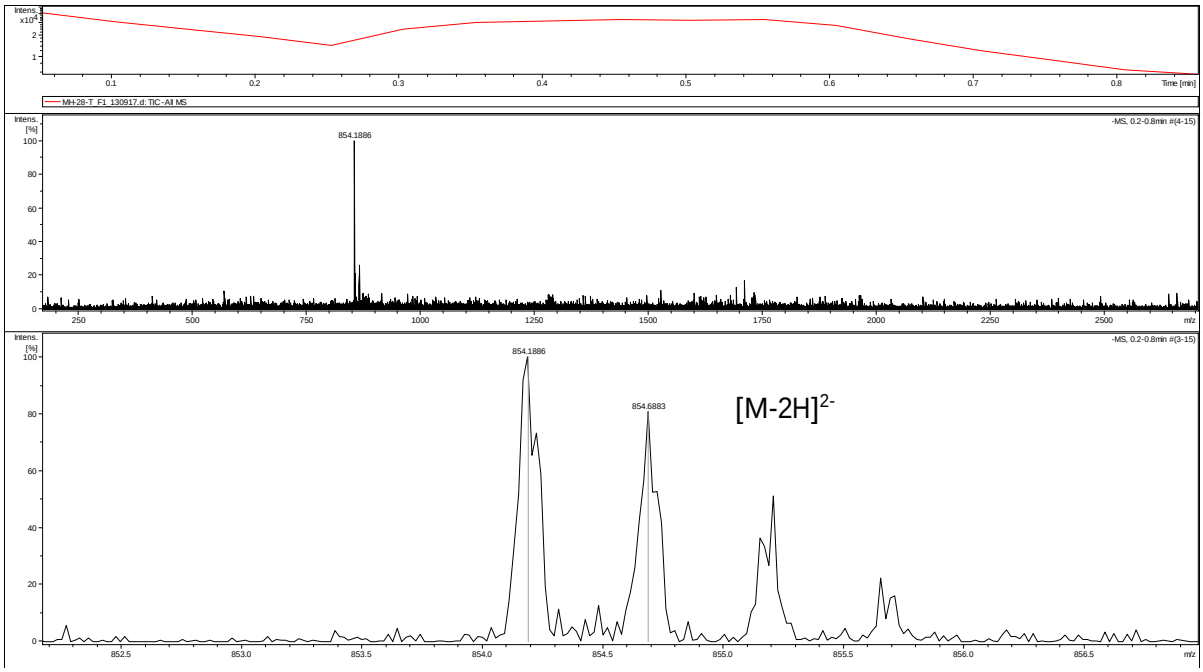

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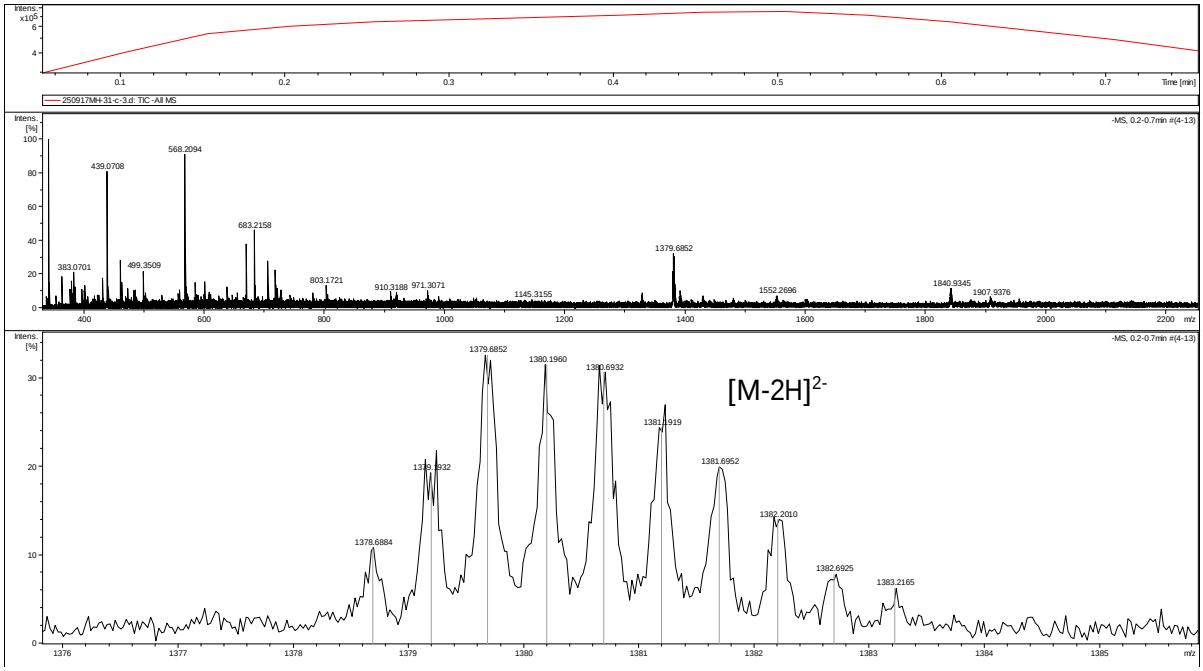

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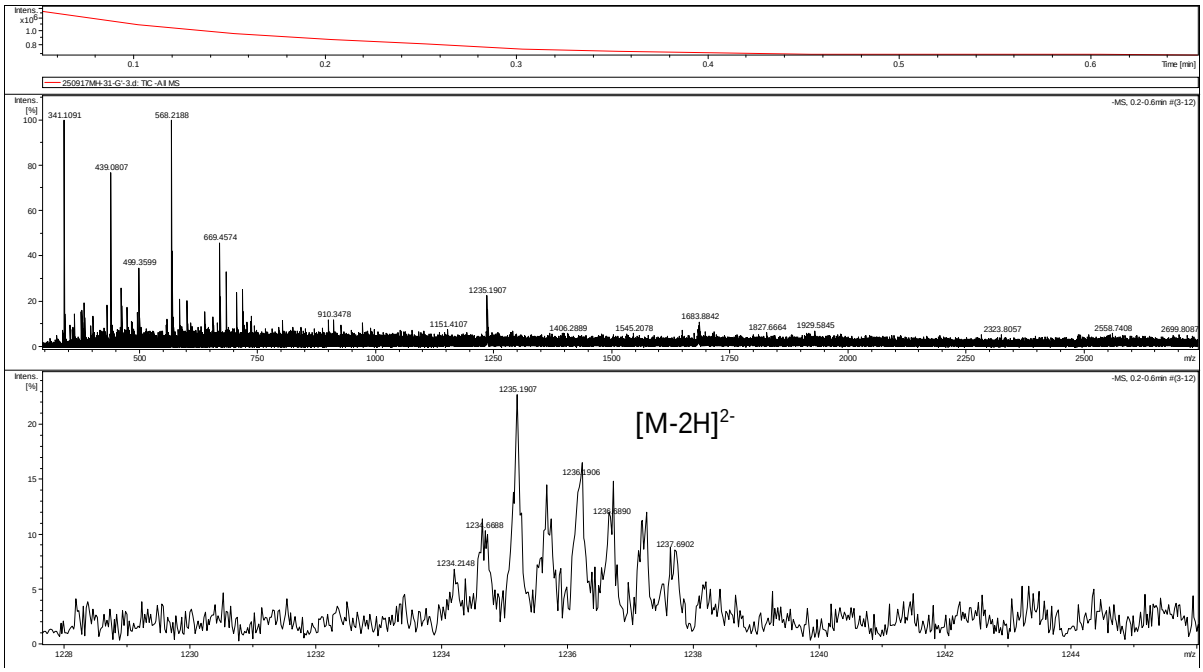

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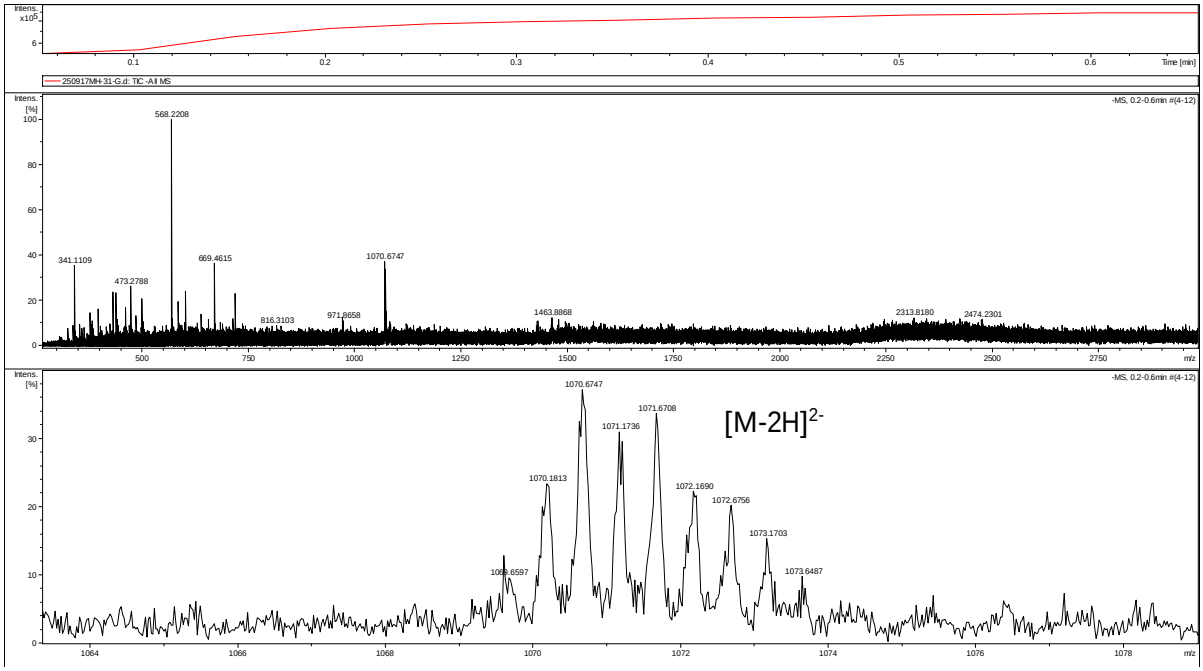

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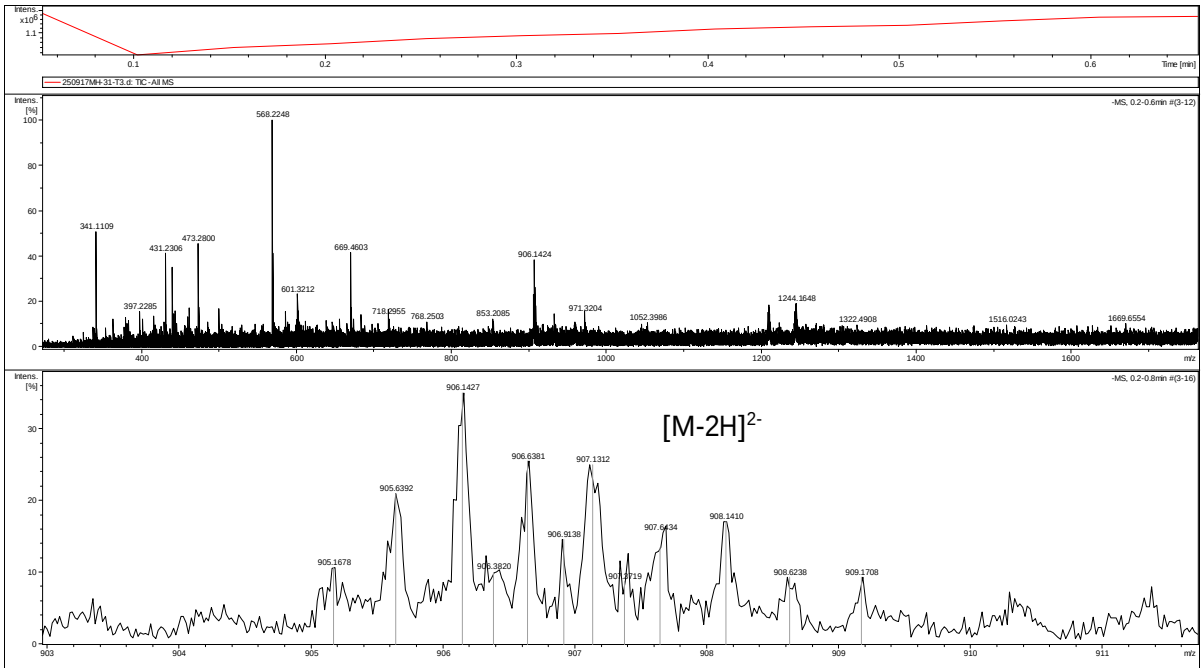

Figure S13. Mass spectrum of oligonucleotide ON4b-Pd.

Table S1. Melting temperatures of duplexes formed by ON1a, ON1b, ON1b-Pd, ON2a, ON2b, ON2b-Pd, ON3a, ON3b, ON3b-Pd, ON4a, ON4b and ON4b-Pd with ON5a, ON5c, ON5g and ON5t; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M.

	T_m / °C			
	ON5a	ON5c	ON5g	ON5t
ON1a	40.4 ± 0.7	n.a. [1]	17.6 ± 0.4	17.9 ± 0.3
ON1b	35.8 ± 0.6	n.a. [1]	16.0 ± 0.7	16.9 ± 0.4
ON1b-Pd	41.0 ± 0.1	n.a. [1]	22.6 ± 0.4	22.4 ± 0.7
ON2a	31.8 ± 1.3	n.a. [1]	n.a. [1]	n.a. [1]
ON2b	30.5 ± 1.3	n.a. [1]	n.a. [1]	n.a. [1]
ON2b-Pd	32.7 ± 1.0	n.a. [1]	n.a. [1]	n.a. [1]
ON3a	21.0 ± 0.9	n.a. [1]	n.a. [1]	n.a. [1]
ON3b	20.5 ± 0.8	n.a. [1]	n.a. [1]	n.a. [1]
ON3b-Pd	21.2 ± 1.2	n.a. [1]	n.a. [1]	n.a. [1]
ON4a	16.1 ± 0.4	n.a. [1]	n.a. [1]	n.a. [1]
ON4b	15.4 ± 0.8	n.a. [1]	n.a. [1]	n.a. [1]
ON4b-Pd	15.7 ± 0.8	n.a. [1]	n.a. [1]	n.a. [1]

[1] No sigmoidal melting curve was obtained.

Table S2. Melting temperatures of duplexes formed by ON1a, ON1b, ON1b-Pd, ON2a, ON2b, ON2b-Pd, ON3a, ON3b, ON3b-Pd, ON4a, ON4b and ON4b-Pd with ON5a, ON5c, ON5g and ON5t in the presence of 2-mercaptoethanol; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; [2-mercaptoethanol] = 100 μM; I($NaClO_4$) = 0.10 M.

	T_m / °C			
	ON5a	ON5c	ON5g	ON5t
ON1a	40.8 ± 0.6	n.a. [1]	16.2 ± 0.7	15.5 ± 0.3
ON1b	34.9 ± 1.1	n.a. [1]	16.8 ± 0.6	15.5 ± 1.1
ON1b-Pd	38.3 ± 0.9	n.a. [1]	17.3 ± 0.8	15.3 ± 0.7
ON2a	30.9 ± 1.2	n.a. [1]	n.a. [1]	n.a. [1]
ON2b	29.3 ± 0.8	n.a. [1]	n.a. [1]	n.a. [1]
ON2b-Pd	30.2 ± 0.1	n.a. [1]	n.a. [1]	n.a. [1]
ON3a	19.0 ± 0.5	n.a. [1]	n.a. [1]	n.a. [1]
ON3b	20.0 ± 0.9	n.a. [1]	n.a. [1]	n.a. [1]
ON3b-Pd	19.3 ± 0.3	n.a. [1]	n.a. [1]	n.a. [1]
ON4a	17.3 ± 1.0	n.a. [1]	n.a. [1]	n.a. [1]
ON4b	17.0 ± 0.8	n.a. [1]	n.a. [1]	n.a. [1]
ON4b-Pd	17.6 ± 0.9	n.a. [1]	n.a. [1]	n.a. [1]

[1] No sigmoidal melting curve was obtained.

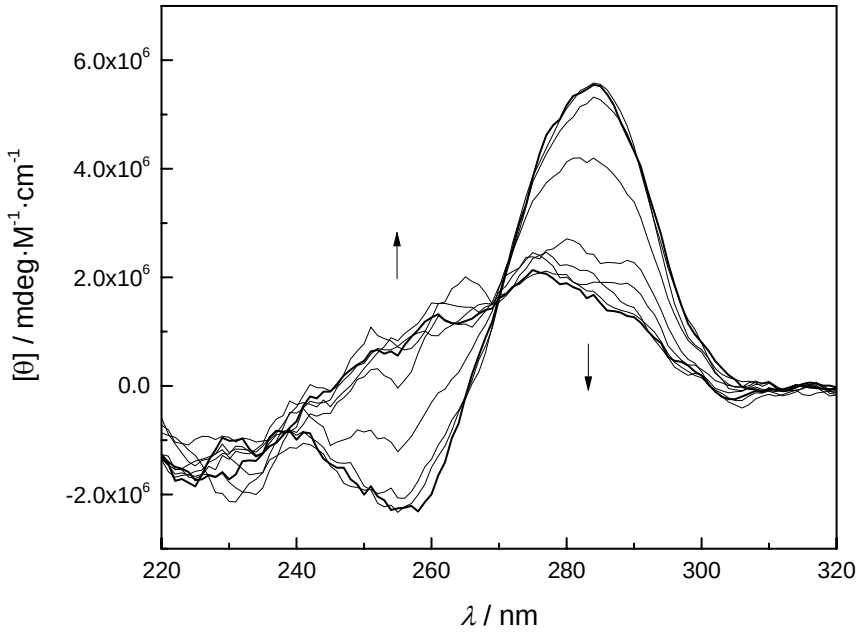

Figure S14. CD spectra of ON1b-Pd•ON5a, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

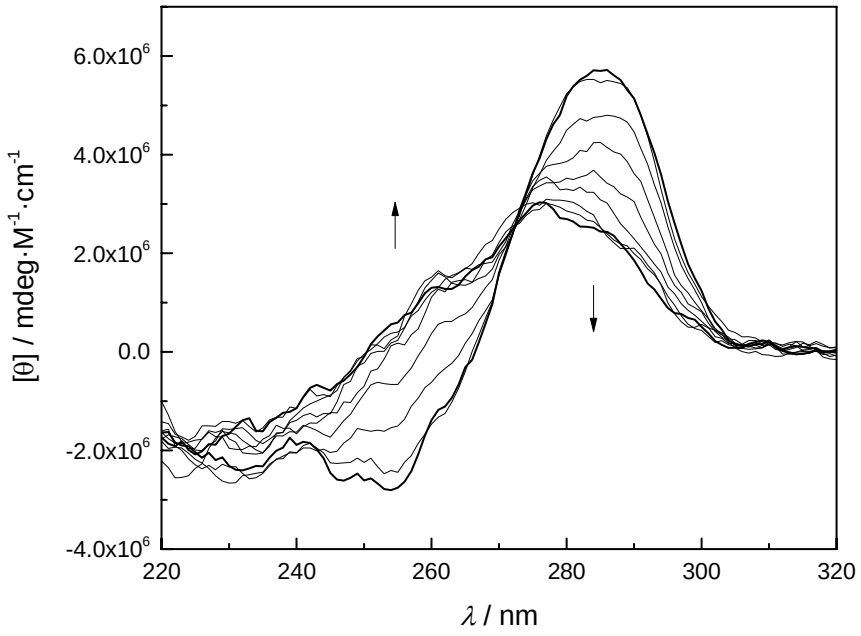

Figure S15. CD spectra of ON1b-Pd•ON5c, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

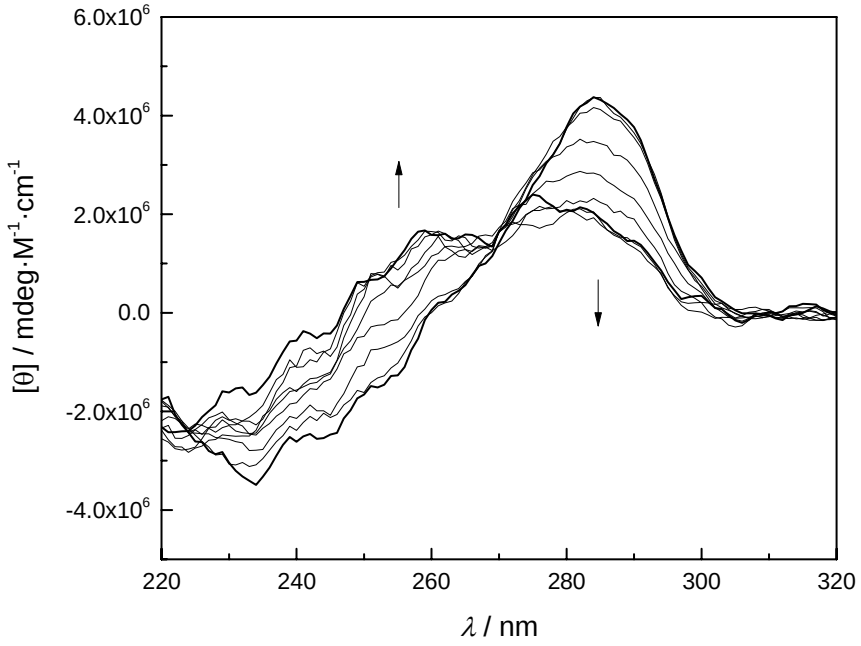

Figure S16. CD spectra of ON1b-Pd•ON5g, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

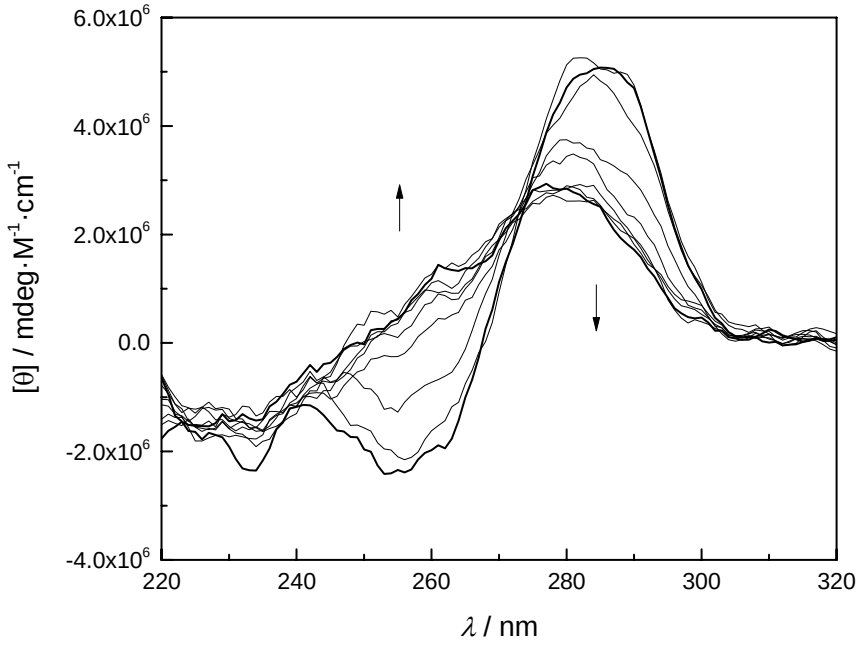

Figure S17. CD spectra of ON1b-Pd•ON5t, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

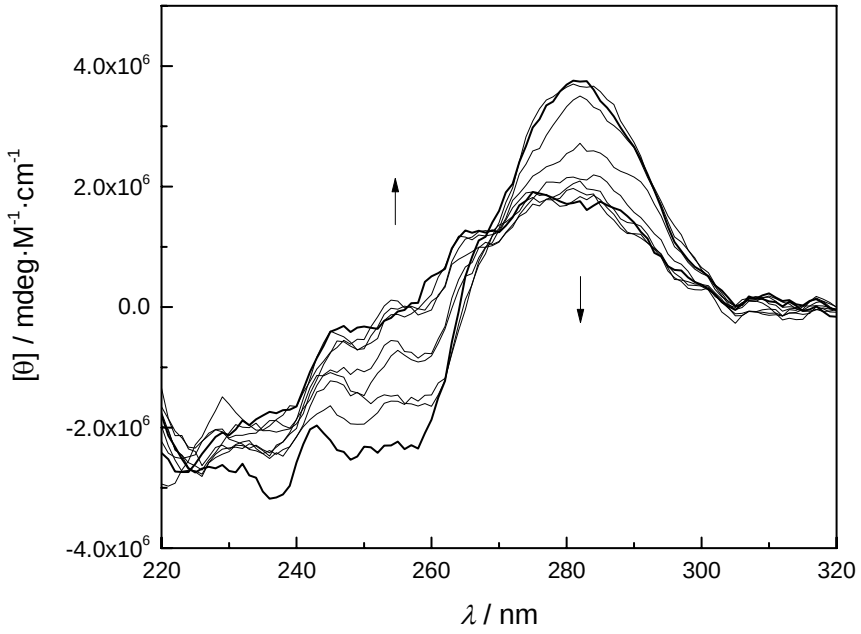

Figure S18. CD spectra of ON2b-Pd•ON5a, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

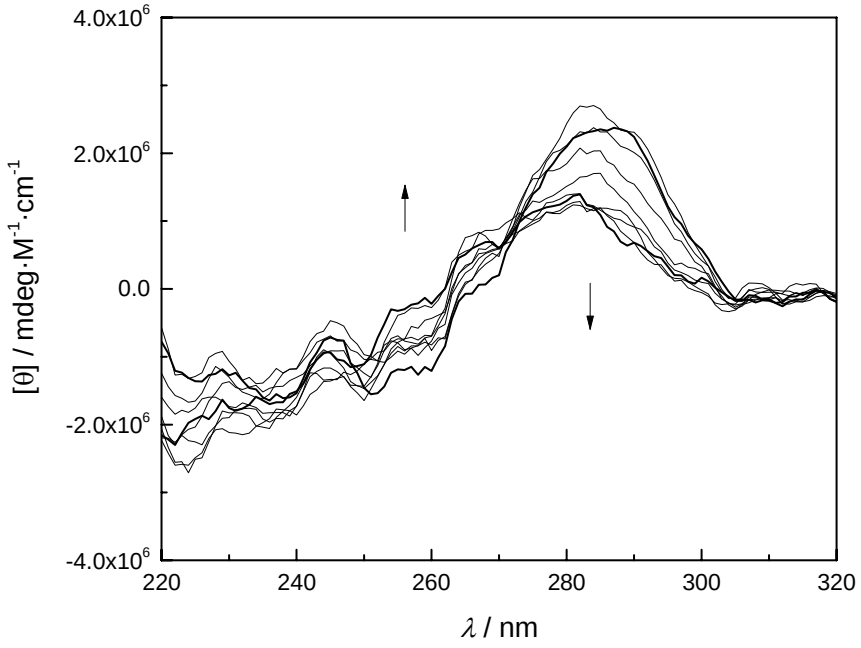

Figure S19. CD spectra of ON2b-Pd•ON5c, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

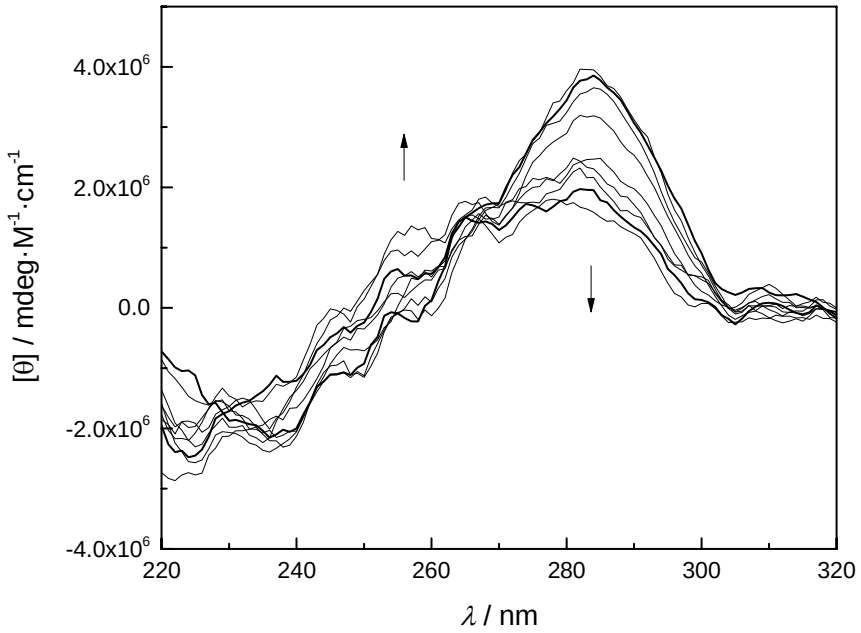

Figure S20. CD spectra of ON2b-Pd•ON5g, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

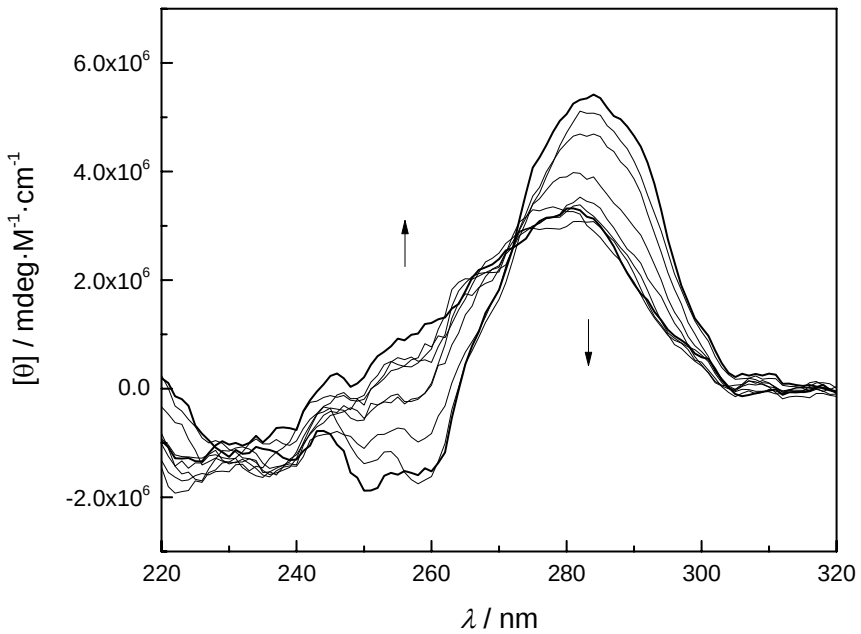

Figure S21. CD spectra of ON2b-Pd•ON5t, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

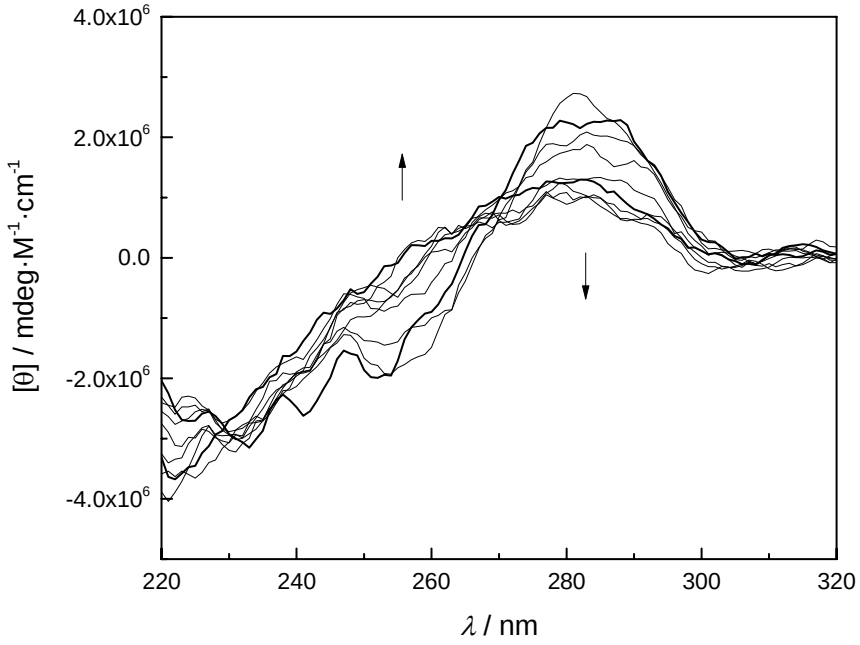

Figure S22. CD spectra of ON3b-Pd•ON5a, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

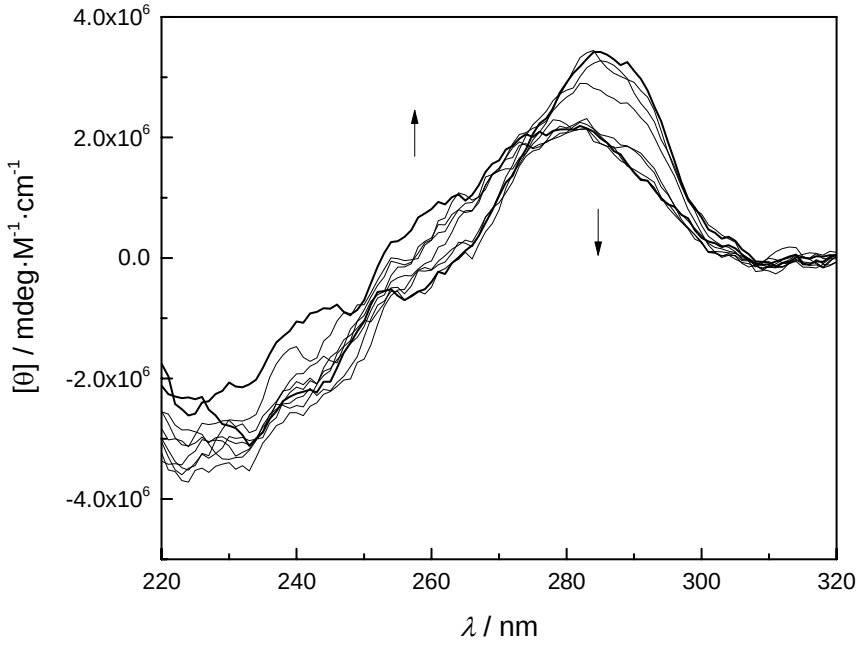

Figure S23. CD spectra of ON3b-Pd•ON5c, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

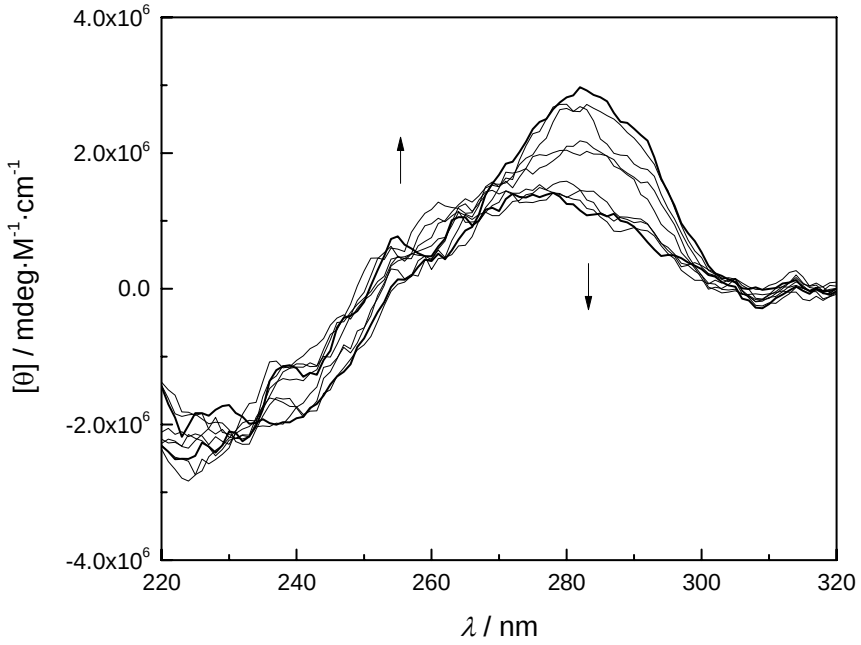

Figure S24. CD spectra of ON3b-Pd•ON5g, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

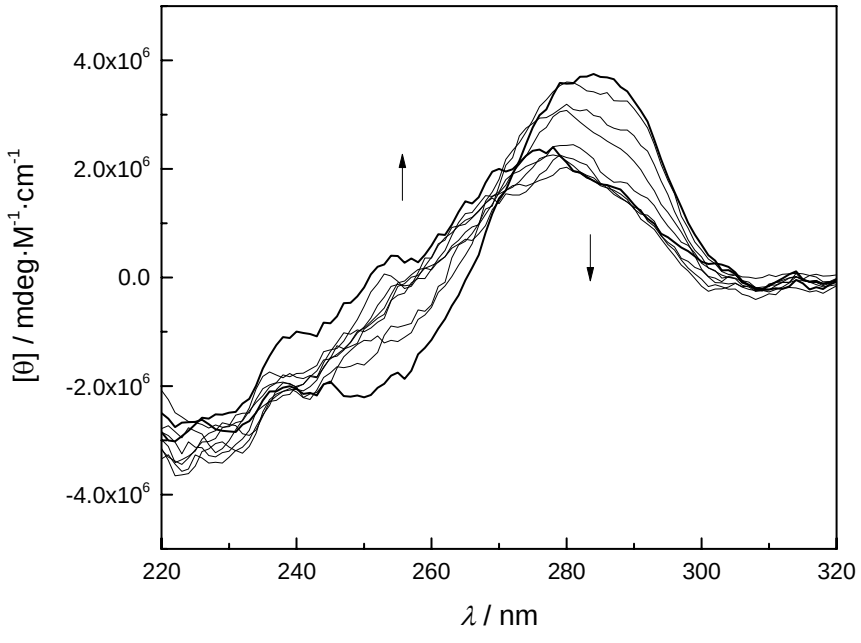

Figure S25. CD spectra of ON3b-Pd•ON5t, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

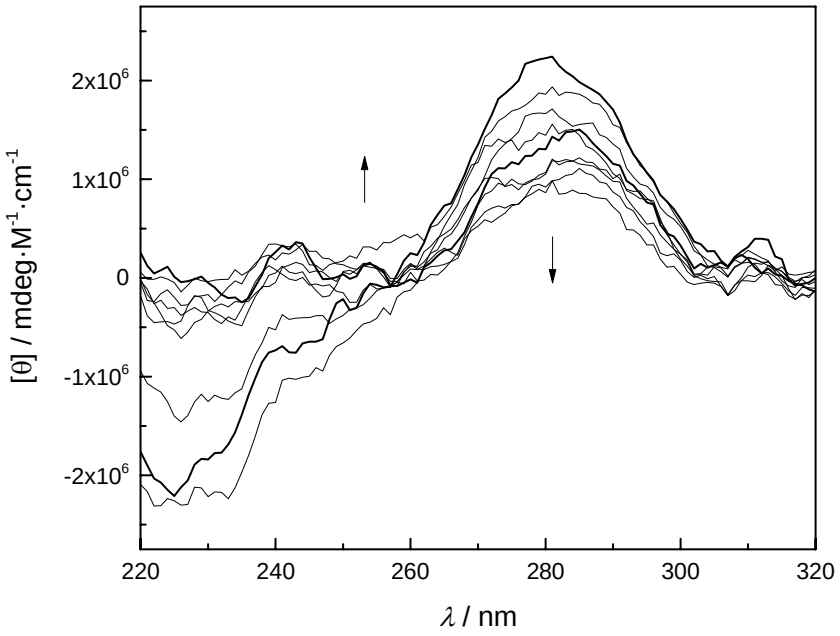

Figure S26. CD spectra of ON4b-Pd•ON5a, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

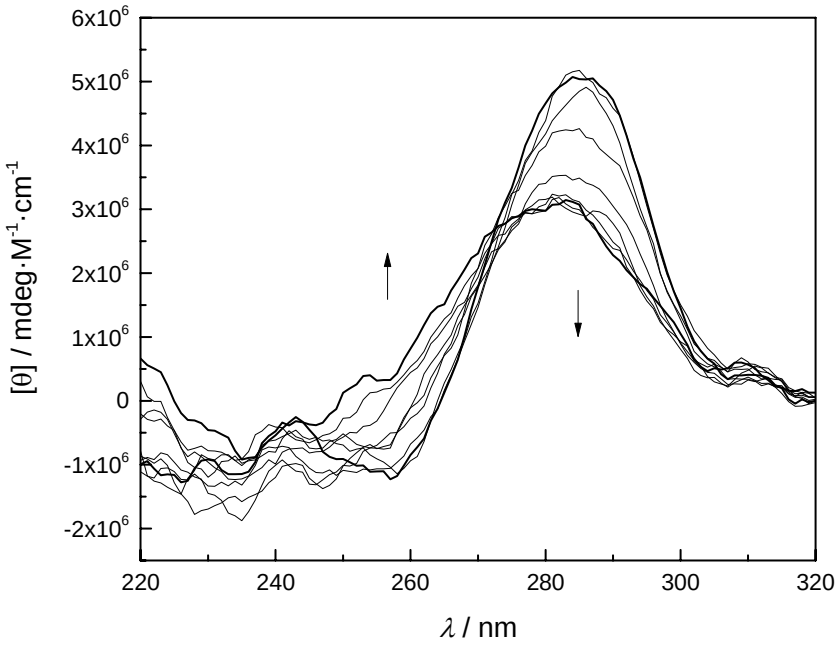

Figure S27. CD spectra of ON4b-Pd•ON5c, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

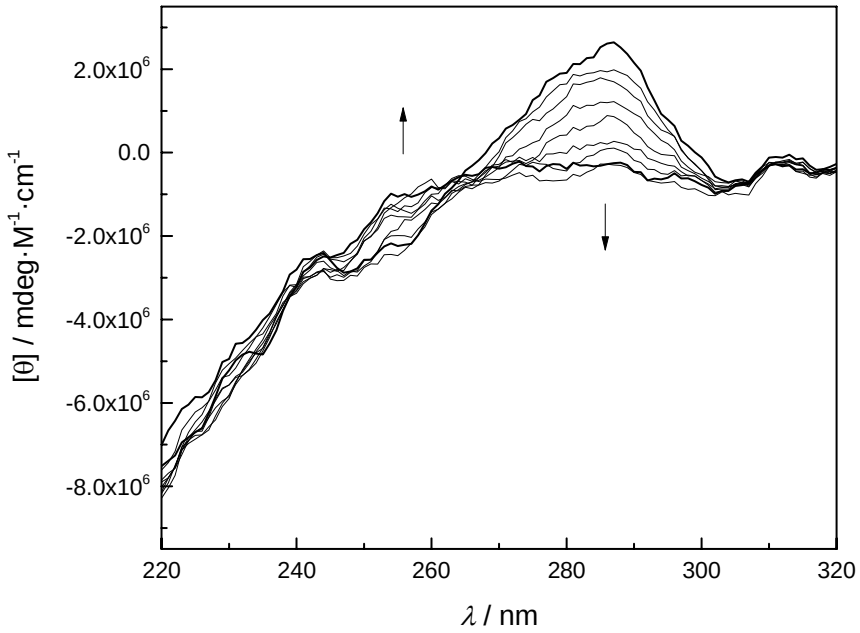

Figure S28. CD spectra of ON4b-Pd•ON5g, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.

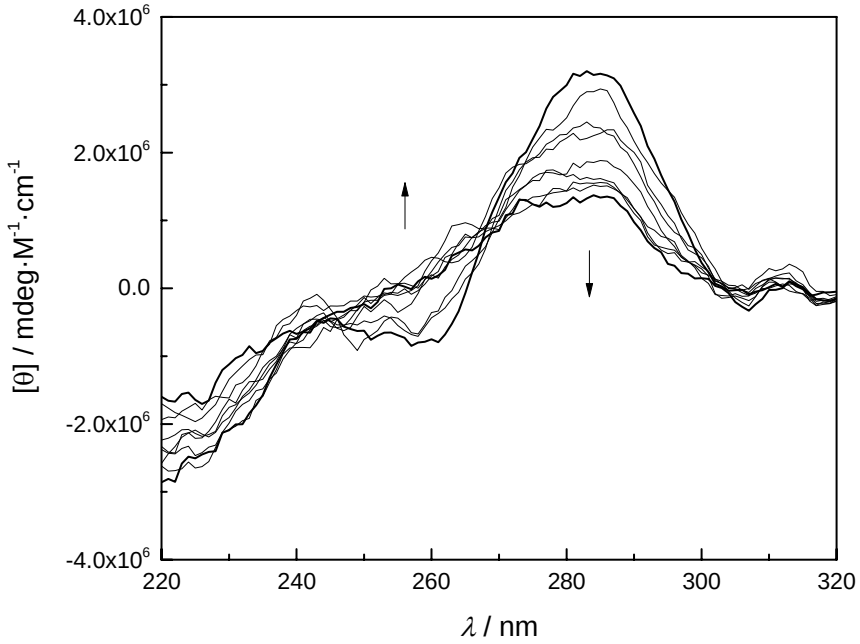

Figure S29. CD spectra of ON4b-Pd•ON5t, recorded at 10 °C intervals between 10 and 90 °C; pH = 7.4 (20 mM cacodylate buffer); [oligonucleotides] = 3.0 μM; I($NaClO_4$) = 0.10 M. Spectra acquired at extreme temperatures are indicated by thicker lines and thermal shifts of the minima and maxima by arrows.