

**CHEMBIOCHEM**

## Supporting Information

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# CHEMBIOCHEM

## Supporting Information

for

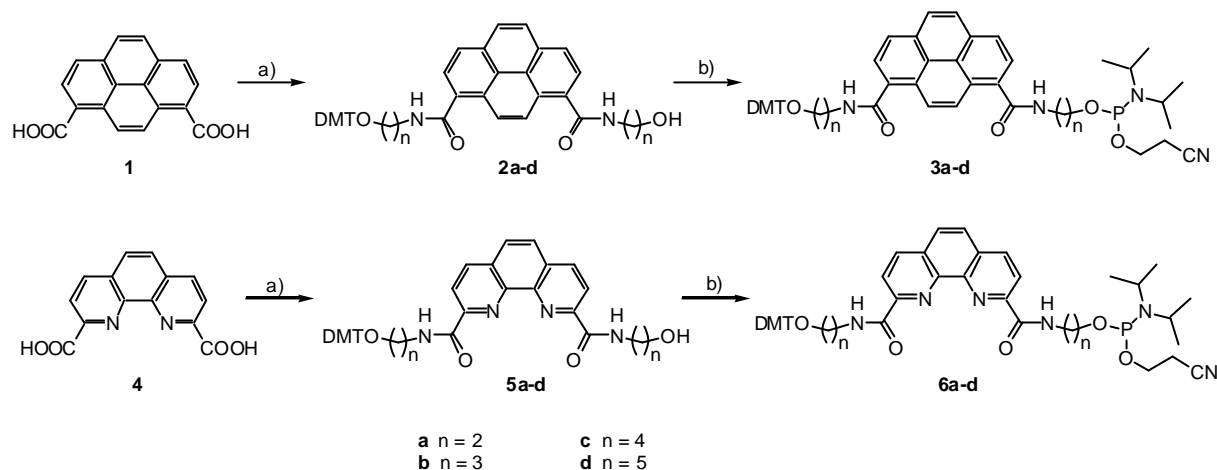
### Remarkable Stabilization of Duplex DNA Containing an Abasic Site by Non-Nucleosidic Phenanthroline and Pyrene Building Blocks

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#### Experimental Section

**General.** Chemicals, solvents, and reagents for reactions were from *Acros*, *Aldrich*, or *Fluka*, and were of the highest quality available. Solvents for extraction and chromatography were of technical grade and distilled prior to use. Thin layer chromatography (TLC): silica-gel 60  $F_{254}$  glass plates (*Merck*); visualisation by UV and/or A) by dipping in a soln. of anisaldehyde (10 mL), conc.  $H_2SO_4$  (10 mL), and AcOH (2 mL) in EtOH (180 mL) or B) cerium (IV) sulfate (3mM)/ammonium molybdate (250 mM in aq.  $H_2SO_4$  (10%)) followed by heating. Flash column chromatography (CC): silica gel 60 (40-63  $\mu m$ , 230-400 mesh, *Fluka*) at low pressure. The chromatography of acid sensitive compounds was carried out with eluent containing 2%  $NEt_3$ .  $^1H$  and  $^{13}C$  NMR: *Bruker AC-300*,  $\delta$  values in ppm (solvents signals as internal standards),  $J$  [Hz];  $^{31}P$  NMR: *Bruker AC-300*,  $\delta$  values in ppm (85%  $H_3PO_4$  as external standard). ESI-MS: *VG Platform* single quadrupole ESI mass spectrometer. DMT: 4,4'-dimethoxytrityl; BOP: (Benzotriazol-1-yloxy)-tris-(dimthylamino)-phosphonium-hexafluorophosphate; AcOEt: ethyl acetate; RT: room temperature; HR-ESI-MS: high resolution electrospray ionisation mass spectrometry.

## General Procedures



**Preparation of the intermediates 2a-d** : 1 eq. pyrene-1,8-dicarboxylic(1) acid and 5 eq. *Hünig's* base were solved in dry DMF (concentration of the acid 0.2M), then a solution of 1 eq. HO(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub> and 1 eq. DMTO(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub> in dry pyridine (concentration of the DMT protected linker 0.5M) was added at RT. After this 2.2 eq of BOP was added and stirred under N<sub>2</sub> atmosphere for 1h.

The mixture was diluted with AcOEt washed with 10% aq. citric acid and sat. aq NaHCO<sub>3</sub> soln. The org. layer was dried (K<sub>2</sub>CO<sub>3</sub>) and evaporated under reduced pressure. Purification of the resulting oil by CC (silica gel; CH<sub>2</sub>Cl<sub>2</sub> → CH<sub>2</sub>Cl<sub>2</sub>: MeOH (98: 2) (+2% Et<sub>3</sub>N)) furnished as yellow foam.

### Preparation of phosphoramidites 3a-d

1 eq. of the DMT protected pyrene was dissolved under a nitrogen atmosphere in dry CH<sub>2</sub>Cl<sub>2</sub> and 3 eq. *Hünig's* base. Then 1 eq. of 2-cyanoethyl diisopropylamido-chloridophosphite was added and the mixture was stirred for 1 h at RT. The reaction mixture was directly applied onto silica gel and purified by CC (silica gel; CH<sub>2</sub>Cl<sub>2</sub> → CH<sub>2</sub>Cl<sub>2</sub>: MeOH (98:2)(+ 2% Et<sub>3</sub>N)). Compounds **3a-d** were obtained as yellow foams.

Pyrene-1,8-dicarboxylic acid 1-({2-[(4,4'-dimethoxytrityl)-oxy]-ethyl}-amide) 8-[(2-hydroxy-ethyl)amide] (**2a**). Yield: 28%, yellow foam. TLC (AcOEt): *R<sub>f</sub>* 0.25; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 3.47 (*t*, *J* = 4.7, ROCH<sub>2</sub>); 3.7-3.85 (*m*, CH<sub>2</sub>N, CH<sub>2</sub>N'); 3.72 (*s*, 2MeO); 3.97 (*m*, CH<sub>2</sub>OH); 6.79 (*d*, 4 arom. H); 7.15-8.1 (*m*, 15 arom. H); 8.25 (*m*, 2H). ESI-MS (*pos. mode*): 701 [*M*+Na]<sup>+</sup>

Pyrene-1,8-dicarboxylic acid 1-({3-[(4,4'-dimethoxytrityl)-oxy]-propyl}-amide) 8-[(2-hydroxy-propyl)amide] (**2b**). Yield: 22%, yellow foam. TLC (AcOEt): *R<sub>f</sub>* 0.25; <sup>1</sup>H NMR

(300 MHz, CDCl<sub>3</sub>): 1.95 (*m*, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 3.33 (*t*, *J* = 5.4, ROCH<sub>2</sub>); 3.55 (*s*, 2MeO); 3.7-3.9 (*m*, CH<sub>2</sub>N, CH<sub>2</sub>N', CH<sub>2</sub>OH); 6.59 (*d*, 4 arom. H); 7.0-7.8 (*m*, 15 arom. H); 8.25 (*m*, 2H). ESI-MS (*pos. mode*): 729 [*M*+Na]<sup>+</sup>

Pyrene-1,8-dicarboxylic acid 1-((4-[(4,4'-dimethoxytrityl)-oxy]-butyl)-amide) 8-[(2-hydroxy-butyl)-amide] (**2c**). Yield: 20%, yellow foam. TLC (AcOEt): *R<sub>f</sub>* 0.27; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.81 (*m*, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 3.14 (*m*, ROCH<sub>2</sub>); 3.70 (*s*, 2MeO); 3.5-3.8 (*m*, CH<sub>2</sub>N, CH<sub>2</sub>N', CH<sub>2</sub>OH); 6.70 (*d*, 4 arom. H); 7.1-8.0 (*m*, 15 arom. H); 8.29 (*m*, 2H). ESI-MS (*pos. mode*): 757 [*M*+Na]<sup>+</sup>

Pyrene-1,8-dicarboxylic acid 1-((5-[(4,4'-dimethoxytrityl)-oxy]-pentyl)-amide) 8-[(2-hydroxy-pentyl)amide] (**2d**). Yield: 17%, yellow foam. TLC (AcOEt): *R<sub>f</sub>* 0.36; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.69 (*m*, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 3.11 (*m*, ROCH<sub>2</sub>); 3.73 (*s*, 2MeO); 3.5-3.8 (*m*, CH<sub>2</sub>N, CH<sub>2</sub>N', CH<sub>2</sub>OH); 6.79 (*d*, 4 arom. H); 7.1-8.0 (*m*, 15 arom. H); 8.23 (*m*, 2H). ESI-MS (*pos. mode*): 785 [*M*+Na]<sup>+</sup>

**Preparation of phosphoramidites 3a-d:** 1 eq. of the DMT protected pyrene was dissolved under a nitrogen atmosphere in dry CH<sub>2</sub>Cl<sub>2</sub> and 3 eq. *Hünig's* base. Then 1 eq. of 2-cyanoethyl diisopropylamidochloridophosphite was added and the mixture was stirred for 1 h at RT. The reaction mixture was directly applied onto silica gel and purified by CC (silica gel; CH<sub>2</sub>Cl<sub>2</sub> → CH<sub>2</sub>Cl<sub>2</sub>: MeOH (98:2)(+ 2% Et<sub>3</sub>N)). Compounds **3a-d** were obtained as yellow foams.

Diisopropyl-phosphoramidous acid 2-[(8-{2-[bis-(4,4'-dimethoxytrityl)oxy]ethylcarbamoyl}pyrene-1-carbonyl)amino]ethyl ester 2-cyanoethyl ester (**3a**). Yield: 81%, yellow foam. TLC (AcOEt:hexane 6:4 + 2% Et<sub>3</sub>N): *R<sub>f</sub>* 0.22; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.17 (*d*, *J* = 6.9, 2 MeCHN); 2.46 (*t*, *J* = 6.2, CH<sub>2</sub>CN); 3.4-4.0 (*m*, CH<sub>2</sub>CH<sub>2</sub>N, CH<sub>2</sub>CH<sub>2</sub>N', OCH<sub>2</sub>CH<sub>2</sub>CN, 2 Me<sub>2</sub>CHN); 3.73 (*s*, 2MeO); 6.79 (*d*, 4 arom. H); 7.1-7.5 (*m*, 9 arom. H); 8.0-8.3(*m*, 6 arom. H); 8.64 (*m*, 2H). <sup>31</sup>P NMR(162MHz, CDCl<sub>3</sub>): 148.79. HR-ESI-MS (*pos. mode*): 901.3701 ([*M*+Na]<sup>+</sup>; calc. 901.3706)

Diisopropyl-phosphoramidous acid 2-[(8-{3-[bis-(4,4'-dimethoxytrityl)oxy]propylcarbamoyl}pyrene-1-carbonyl)amino]propyl ester 2-cyano-ethyl ester (**3b**). Yield: 43%, yellow foam. TLC (AcOEt:hexane 6:4 + 2% Et<sub>3</sub>N): *R<sub>f</sub>* 0.24; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.03, 1.04 (2d, *J* = 6.8, 2 MeCHN); 2.03 (*m*, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 2.35 (*m*, CH<sub>2</sub>CN); 3.3-3.9 (*m*, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N', OCH<sub>2</sub>CH<sub>2</sub>CN, 2 Me<sub>2</sub>CHN); 3.58 (*s*, 2MeO); 6.59 (*d*, 4 arom. H); 7.0-7.4 (*m*, 9 arom. H); 7.9-8.25 (*m*, 6 arom. H); 8.59

(*m*, 2H).  $^{31}\text{P}$  NMR(162MHz,  $\text{CDCl}_3$ ): 148.24. HR-ESI-MS (*pos. mode*): 925.4536 ( $[\text{M}+\text{Na}]^+$ ; calc. 925.4543)

Diisopropyl-phosphoramidous acid 2-[(8-{4-[bis-(4,4'-dimethoxytrityl)oxy]butylcarbamoyl}pyrene-1-carbonyl)amino]butyl ester 2-cyano-ethyl ester (**3c**). Yield: 61%, yellow foam. TLC (AcOEt:hexane 6:4 + 2%  $\text{Et}_3\text{N}$ ):  $R_f$  0.42;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.04, 1.05 (2d,  $J = 6.6$ , 2 MeCHN); 1.82 (*m*, 2  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ); 2.50 (*t*,  $J = 6.3$ ,  $\text{CH}_2\text{CN}$ ); 3.1-3.8 (*m*,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}'$ ,  $\text{OCH}_2\text{CH}_2\text{CN}$ , 2 Me $_2\text{CHN}$ ); 3.70 (*s*, 2MeO); 6.71 (*d*, 4 arom. H); 7.1-7.5 (*m*, 9 arom. H); 7.9-8.25(*m*, 6 arom. H); 8.57 (*m*, 2H).  $^{31}\text{P}$  NMR(162MHz,  $\text{CDCl}_3$ ): 147.71. ESI-MS (*pos. mode*): 952  $[\text{M}+\text{NH}_4]^+$

Diisopropyl-phosphoramidous acid 2-[(8-{5-[bis-(4,4'-dimethoxytrityl)oxy]pentylcarbamoyl}pyrene-1-carbonyl)amino]pentyl ester 2-cyano-ethyl ester (**3d**). Yield: 68%, yellow foam. TLC (AcOEt:hexane 6:4 + 2%  $\text{Et}_3\text{N}$ ):  $R_f$  0.94.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.17, 1.18 (2d,  $J = 6.7$ , 2 MeCHN); 1.72 (*m*, 2  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ); 2.63 (*m*,  $\text{CH}_2\text{CN}$ ); 3.0-3.9 (*m*,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}'$ ,  $\text{OCH}_2\text{CH}_2\text{CN}$ , 2 Me $_2\text{CHN}$ ); 3.77 (*s*, 2MeO); 6.81 (*d*, 4 arom. H); 7.1-7.5 (*m*, 9 arom. H); 7.9-8.25(*m*, 6 arom. H); 8.55 (*m*, 2H).  $^{31}\text{P}$  NMR(162MHz,  $\text{CDCl}_3$ ): 147.35. HR-ESI-MS (*pos. mode*): 963.4828 ( $[\text{M}+\text{Na}]^+$ ; calc. 963.4825)

### Preparation of the intermediates 5a-d

1 eq. [1,10]Phenanthroline-2,9-dicarboxylic acid (**4**) and 5 eq. *Hünig's* base were dissolved in dry DMF (concentration of the acid was 0.2M); then a solution of 1 eq.  $\text{HO}(\text{CH}_2)_n\text{NH}_2$  and 1 eq.  $\text{DMTO}(\text{CH}_2)_n\text{NH}_2$  in dry pyridine(concentration of the DMT protected linker 0.5M) was added at RT. After this, 2.2 eq of BOP was added and the mixture was stirred under a nitrogen atmosphere for 1h.

The mixture was diluted with AcOEt, washed with 10% *aq.* citric acid and *sat. aq*  $\text{NaHCO}_3$  *soln.* The org. layer was dried ( $\text{K}_2\text{CO}_3$ ) and evaporated under reduced pressure. Purification of the resulting oil by CC (silica gel; AcOEt $\rightarrow$  AcOEt: MeOH (95: 5) (+2%  $\text{Et}_3\text{N}$ )) furnished **5a-d** as light yellow foams.

[1,10]Phenanthroline-2,9-dicarboxylic acid 2-({2-[bis-(4-methoxyphenyl)phenylmethoxy]ethyl}amide) 9-[(2-hydroxyethyl)amide] (**5a**). Yield: 28%. TLC (AcOEt):  $R_f$  0.2;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 3.29 (*m*,  $\text{ROCH}_2$ ); 3.45 (*m*,  $\text{CH}_2\text{N}$ ,  $\text{CH}_2\text{N}'$ ); 3.65 (*s*, 2MeO); 3.84 (*m*,  $\text{CH}_2\text{OH}$ ); 6.72 (*d*, 4 arom. H); 7.1-7.5 (*m*, 9 arom. H); 7.94 (*s*, 2 arom H);

8.46 (*m*, 2 arom. H); 8.56 (*m*, 2 arom. H); 9.09 (*t*, *J* = 6.6, NH); 9.30 (*t*, *J* = 5.4, N'H). ESI-MS (*pos. mode*): 679 [*M*+Na]<sup>+</sup>

[1,10]Phenanthroline-2,9-dicarboxylic acid 2-({3-[bis-(4-methoxyphenyl)phenylmethoxy]propyl}amide) 9-[(3-hydroxypropyl)amide] (**5b**). Yield: 27%. TLC (AcOEt): *R<sub>f</sub>* 0.2; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.81 (*m*, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OR); 2.07 (*m*, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH); 3.25 (*t*, *J* = 5.9, ROCH<sub>2</sub>); 3.34 (*m*, OH); 3.66 (*s*, 2MeO); 3.65-3.85 (*m*, CH<sub>2</sub>N, CH<sub>2</sub>N', CH<sub>2</sub>OH); 6.73 (*d*, 4 arom. H); 7.1-7.5 (*m*, 9 arom. H); 7.80 (*m*, 2 arom. H); 8.29 (*m*, 1 arom. H); 8.38 (*m*, 1 arom. H); 8.54 (*m*, 2 arom. H); 8.87 (*t*, *J* = 5.8, NH); 9.27 (*t*, *J* = 5.7, N'H). ESI-MS (*pos. mode*): 707 [*M*+Na]<sup>+</sup>

[1,10]Phenanthroline-2,9-dicarboxylic acid 2-({4-[bis-(4-methoxyphenyl)phenylmethoxy]butyl}amide) 9-[(4-hydroxybutyl)amide] (**5c**). Yield: 26%. TLC (AcOEt): *R<sub>f</sub>* 0.23; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.7 (*m*, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 3.14 (*m*, ROCH<sub>2</sub>); 3.61 (*m*, 3.70, CH<sub>2</sub>N, CH<sub>2</sub>N') 3.76 (*s*, 2MeO); 3.7-3.8 (*m*, , CH<sub>2</sub>OH); 6.79 (*d*, 4 arom. H); 7.15-7.45 (*m*, 9 arom. H); 7.90 (*s*, 2 arom. H); 8.45 (*m*, 2 arom. H); 8.58 (*m*, 1 arom. H); 8.65 (*m*, 1 arom. H); 9.19 (*t*, *J* = 5.7, NH); 9.34 (*t*, *J* = 5.7, N'H). ESI-MS (*pos. mode*): 735 [*M*+Na]<sup>+</sup>

[1,10]Phenanthroline-2,9-dicarboxylic acid 2-({5-[bis-(4-methoxyphenyl)phenylmethoxy]pentyl}amide) 9-[(5-hydroxypentyl)amide] (**5d**). Yield: 23%. TLC (AcOEt): *R<sub>f</sub>* 0.24; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.65 (*m*, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 3.08 (*m*, ROCH<sub>2</sub>); 3.5-3.7 (*m*, CH<sub>2</sub>N, CH<sub>2</sub>N', CH<sub>2</sub>OH); 3.75 (*s*, 2MeO); 6.79 (*d*, 4 arom. H); 7.1-7.45 (*m*, 9 arom. H); 7.93 (*s*, 2 arom. H); 8.44 (*m*, 2 arom. H); 8.62 (*m*, 2 arom. H); 8.99 (*t*, NH); 9.06 (*t*, N'H). ESI-MS (*pos. mode*): 763 [*M*+Na]<sup>+</sup>

### Preparation of phosphoramidites **6a-d**

1 eq. of the DMT protected phenanthroline was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> containing 3 eq. of *Hünig's* base. Then 1 eq. of 2-cyanoethyl diisopropylamidochloridophosphite was added under a nitrogen atmosphere and the mixture was stirred for 1 h at RT. The reaction mixture was directly applied onto silica gel and purified by CC (silica gel; AcOEt:hexane (3:7)→ AcOEt:hexane (7:3)(+ 2% Et<sub>3</sub>N)). Compounds **6a-d** were obtained as light yellow foams.

Diisopropyl-phosphoramidous acid 2-[(9-{2-[bis-(4-methoxyphenyl)phenylmethoxy]ethylcarbamoyl}-[1,10]phenanthroline-2-carbonyl)amino]ethyl ester 2-cyanoethyl ester (**6a**). Yield: 70%. TLC (AcOEt:hexane 2:1 + 2% Et<sub>3</sub>N): *R<sub>f</sub>* 0.27; <sup>1</sup>H NMR (300

MHz, CDCl<sub>3</sub>): 1.10, 1.12 (2d, *J* = 6.8, 2 MeCHN); 2.47 (t, *J* = 6.2, CH<sub>2</sub>CN); 3.35-3.9 (m, CH<sub>2</sub>CH<sub>2</sub>N, CH<sub>2</sub>CH<sub>2</sub>N', OCH<sub>2</sub>CH<sub>2</sub>CN, 2 Me<sub>2</sub>CHN); 3.70 (s, 2MeO); 6.73 (d, 4 arom. H); 7.1-7.5 (m, 9 arom. H); 7.94 (s, 2 arom. H); 8.45 (m, 2 arom. H); 8.59 (m, 2 arom. H); 8.78 (t, *J* = 6.0, NH); 9.00 (t, *J* = 6.3, N'H). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): 148.23. HR-ESI-MS (*pos. mode*): 857.3813 ([*M*+H]<sup>+</sup>; calc. 857.3791)

Diisopropyl-phosphoramidous acid 3-[(9-{3-[bis-(4-methoxyphenyl)phenylmethoxy]-propylcarbamoyl}-[1,10]phenanthroline-2-carbonyl)amino]propyl ester 2-cyanoethyl ester (**6b**). Yield: 76%. TLC (AcOEt:hexane 7:3 + 2% Et<sub>3</sub>N): *R<sub>f</sub>* 0.28; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.11, 1.13 (2d, *J* = 6.7, 2 MeCHN); 2.03 (m, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 2.49 (t, *J* = 6.4, CH<sub>2</sub>CN); 3.25 (m, CH<sub>2</sub>ODMT) 3.3-3.9 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N', OCH<sub>2</sub>CH<sub>2</sub>CN, 2 Me<sub>2</sub>CHN); 3.65 (s, 2MeO); 6.74 (d, 4 arom. H); 7.1-7.5 (m, 9 arom. H); 7.93 (s, 2 arom. H); 8.44 (m, 2 arom. H); 8.59 (m, 2 arom. H, NH, N'H). <sup>31</sup>P NMR(162MHz, CDCl<sub>3</sub>): 147.78. HR-ESI-MS (*pos. mode*): 925.3943 ([*M*+Na]<sup>+</sup>; calc. 907.3924)

Diisopropyl-phosphoramidous acid 4-[(9-{4-[bis-(4-methoxyphenyl)phenylmethoxy]-butylcarbamoyl}-[1,10]phenanthroline-2-carbonyl)amino]butyl ester 2-cyanoethyl ester (**6c**). Yield: 63%. TLC (AcOEt:hexane 7:3 + 2% Et<sub>3</sub>N): *R<sub>f</sub>* 0.31; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.14, 1.15 (2d, *J* = 6.8, 2 MeCHN); 1.79 (m, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 2.56 (t, *J* = 6.4, CH<sub>2</sub>CN); 3.14 (m, CH<sub>2</sub>ODMT); 3.5-3.9 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N', OCH<sub>2</sub>CH<sub>2</sub>CN, 2 Me<sub>2</sub>CHN); 3.76 (s, 2MeO); 6.79 (d, 4 arom. H); 7.15-7.45 (m, 9 arom. H); 7.93 (s, 2 arom. H); 8.44 (m, 2 arom. H); 8.61 (m, 2 arom. H, NH, N'H). <sup>31</sup>P NMR(162MHz, CDCl<sub>3</sub>): 147.59. HR-ESI-MS (*pos. mode*): 913.4430 ([*M*+H]<sup>+</sup>; calc. 913.4417).

Diisopropyl-phosphoramidous acid 5-[(9-{5-[bis-(4-methoxyphenyl)phenylmethoxy]-pentylcarbamoyl}-[1,10]phenanthroline-2-carbonyl)amino]pentyl ester 2-cyanoethyl ester (**6d**). Yield: 67%. TLC (AcOEt:hexane 8:2 + 2% Et<sub>3</sub>N): *R<sub>f</sub>* 0.35. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.12, 1.13 (2d, *J* = 6.7, 2 MeCHN); 1.7 (m, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 2.54 (t, *J* = 6.4 CH<sub>2</sub>CN); 3.07 (t, *J* = 6.4, CH<sub>2</sub>DMT); 3.4-3.9 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N', OCH<sub>2</sub>CH<sub>2</sub>CN, 2 Me<sub>2</sub>CHN); 3.75 (s, 2MeO); 6.78 (d, 4 arom. H); 7.1-7.45 (m, 9 arom. H); 7.93(m, 2 arom. H); 8.44 (m, 2 arom. H); 8.59 (m, 2 arom. H, NH, N'H). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): 147.54. ESI-MS (*pos. mode*): 958 [*M*+NH<sub>4</sub>]<sup>+</sup>.

## Oligonucleotide Synthesis

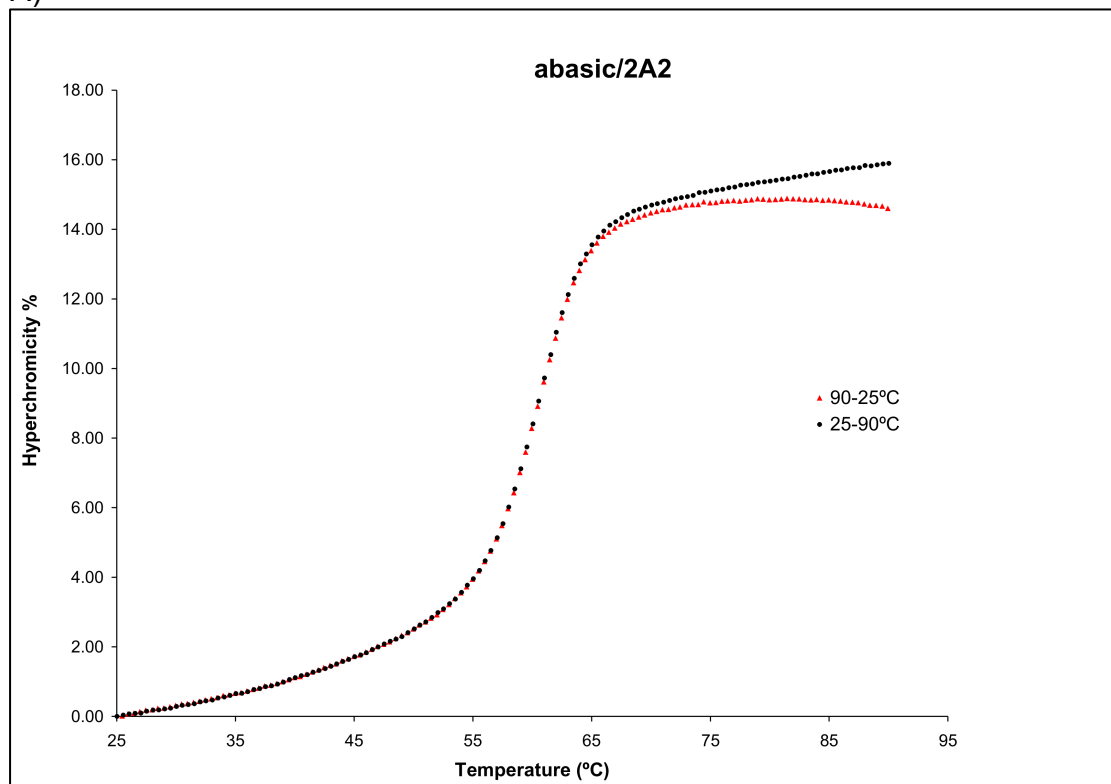
Phenanthroline- and pyrene-derived phosphoramidite building blocks **6a-d**, **3a-d** were incorporated into oligonucleotides *via* standard automated oligonucleotide synthesis using *l*/pyridine/water in the oxidation step. Coupling yields with **6a-d** and **3a-d** were equal to the ones obtained with standard phosphoramidite building blocks. All oligonucleotides were purified by reverse phase HPLC and characterised by MS (Table S1).

**Table S1.** Molecular weights of oligonucleotides used in this study (electrospray ionisation time-of-flight, ESI-TOF)

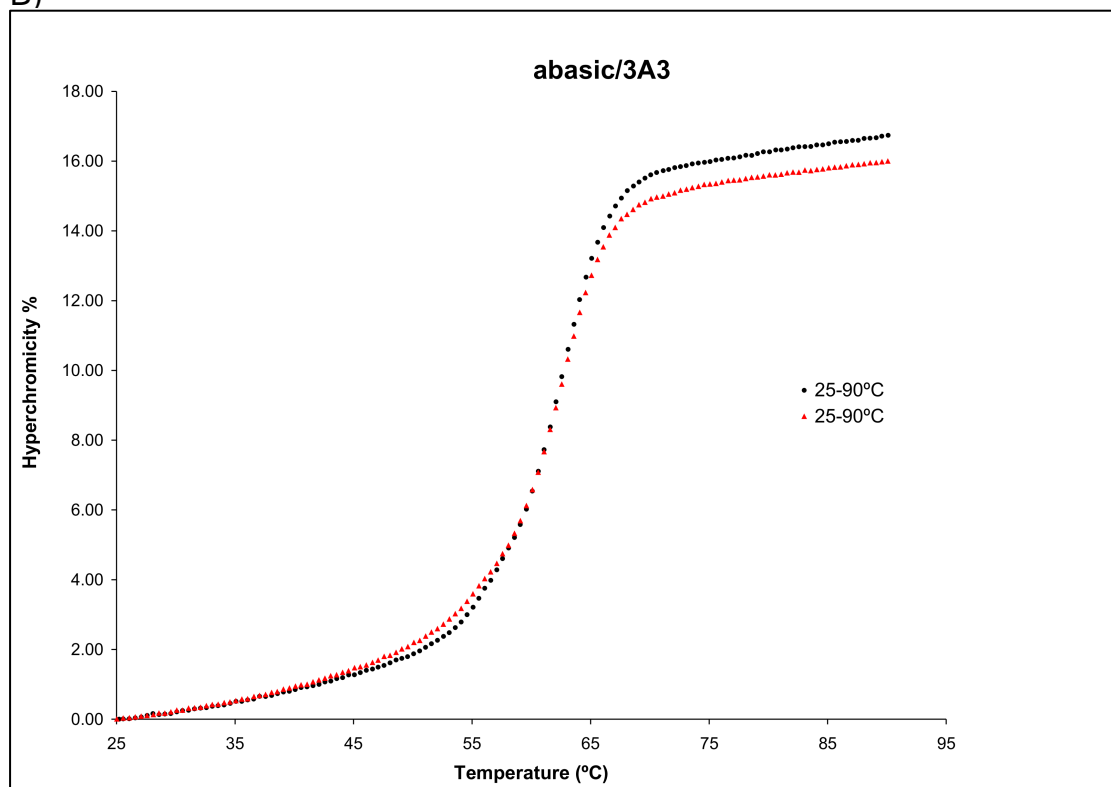
#	oligonucleotide	calculated for [M-H] <sup>-</sup>	found
I	5' AGC TCG GTC A <b>f</b> C GAG AGT GCA	6346.0	6346.2
II	3' TCG AGC CAG T <b>2A2</b> G CTC TCA CGT	6484.5	6484.5
III	3' TCG AGC CAG T <b>3A3</b> G CTC TCA CGT	6512.5	6512.5
IV	3' TCG AGC CAG T <b>4A4</b> G CTC TCA CGT	6540.5	6540.6
V	3' TCG AGC CAG T <b>5A5</b> G CTC TCA CGT	6568.5	6568.7
VI	3' TCG AGC CAG T <b>2B2</b> G CTC TCA CGT	6506.5	6506.5
VII	3' TCG AGC CAG T <b>3B3</b> G CTC TCA CGT	6534.5	6534.4
VIII	3' TCG AGC CAG T <b>4B4</b> G CTC TCA CGT	6562.5	6562.4
IX	3' TCG AGC CAG T <b>5B5</b> G CTC TCA CGT	6590.5	6590.3

**Figure S1.** Melting curves of different hybrids. Conditions: oligomer concentration 1.0  $\mu\text{M}$ , 10 mM Tris-HCl, 100 mM NaCl, pH 7.4; temp. gradient: 0.5°C/min. Exptl. error:  $\pm 0.5^\circ\text{C}$ . Absorbance was measured at 260nm. **A)** duplex I\*II, **B)** duplex I\*III; **C)** duplex I\*IV; **D)** duplex I\*V; **E)** duplex I\*VI; **F)** duplex I\*VII; **G)** duplex I\*VIII; **H)** duplex I\*IX.

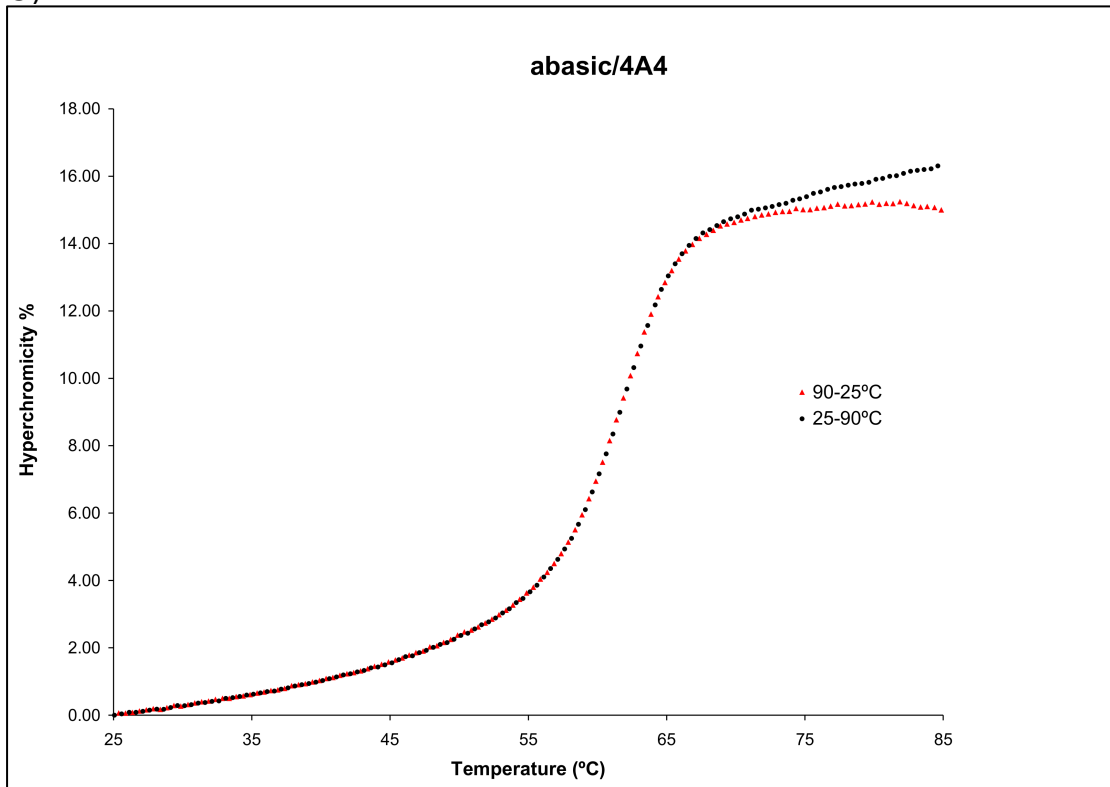
A)



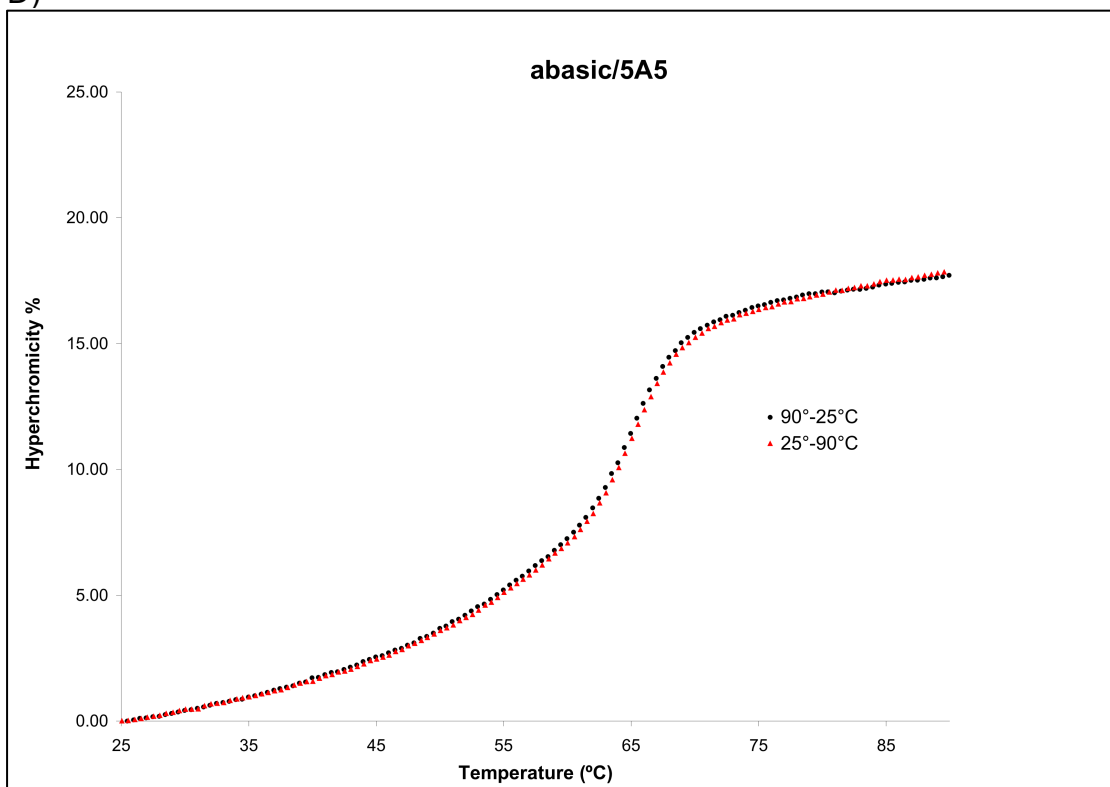
B)



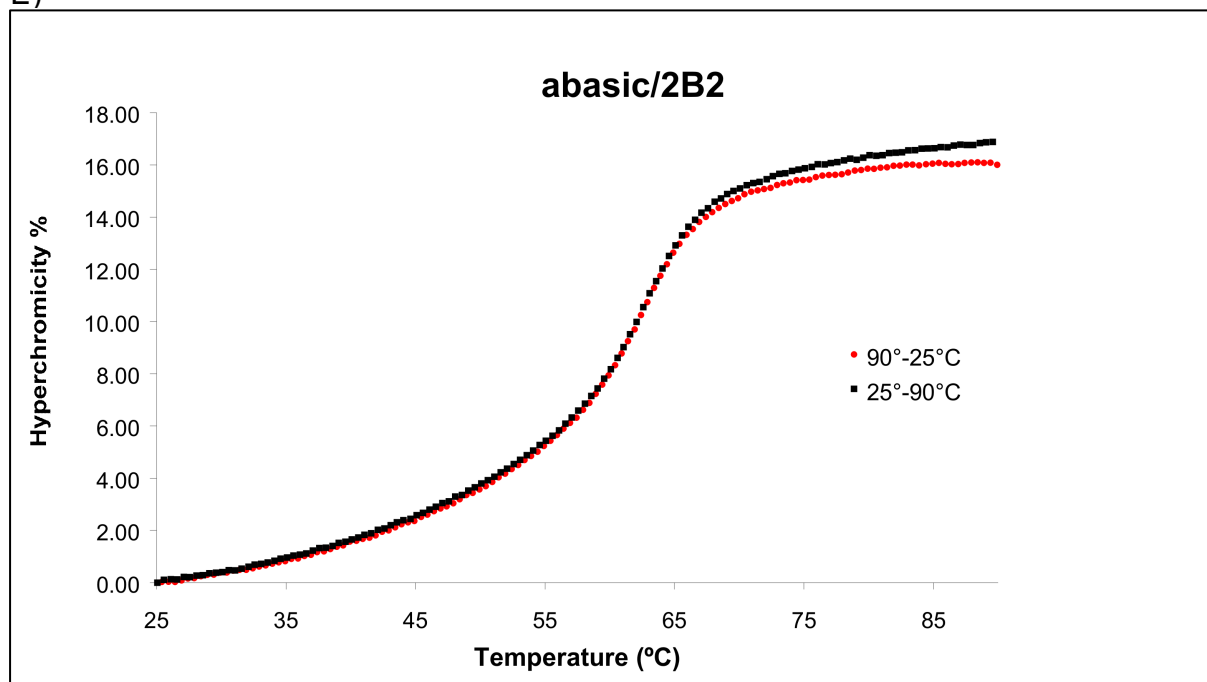
C)



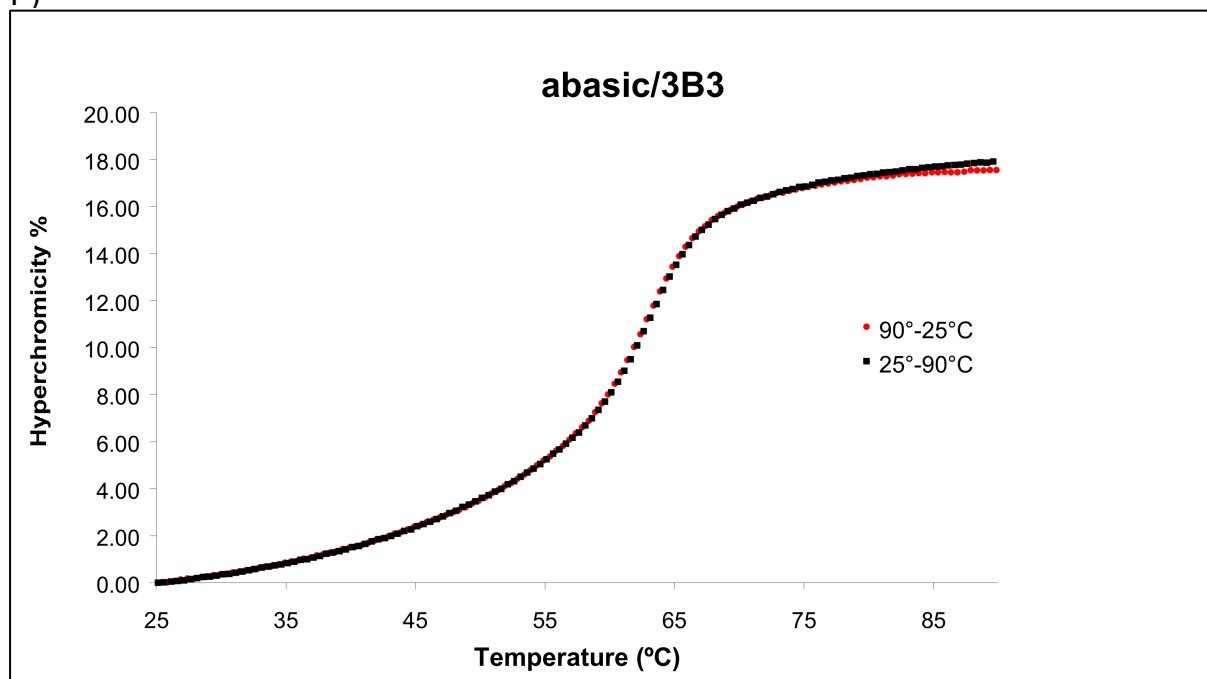
D)



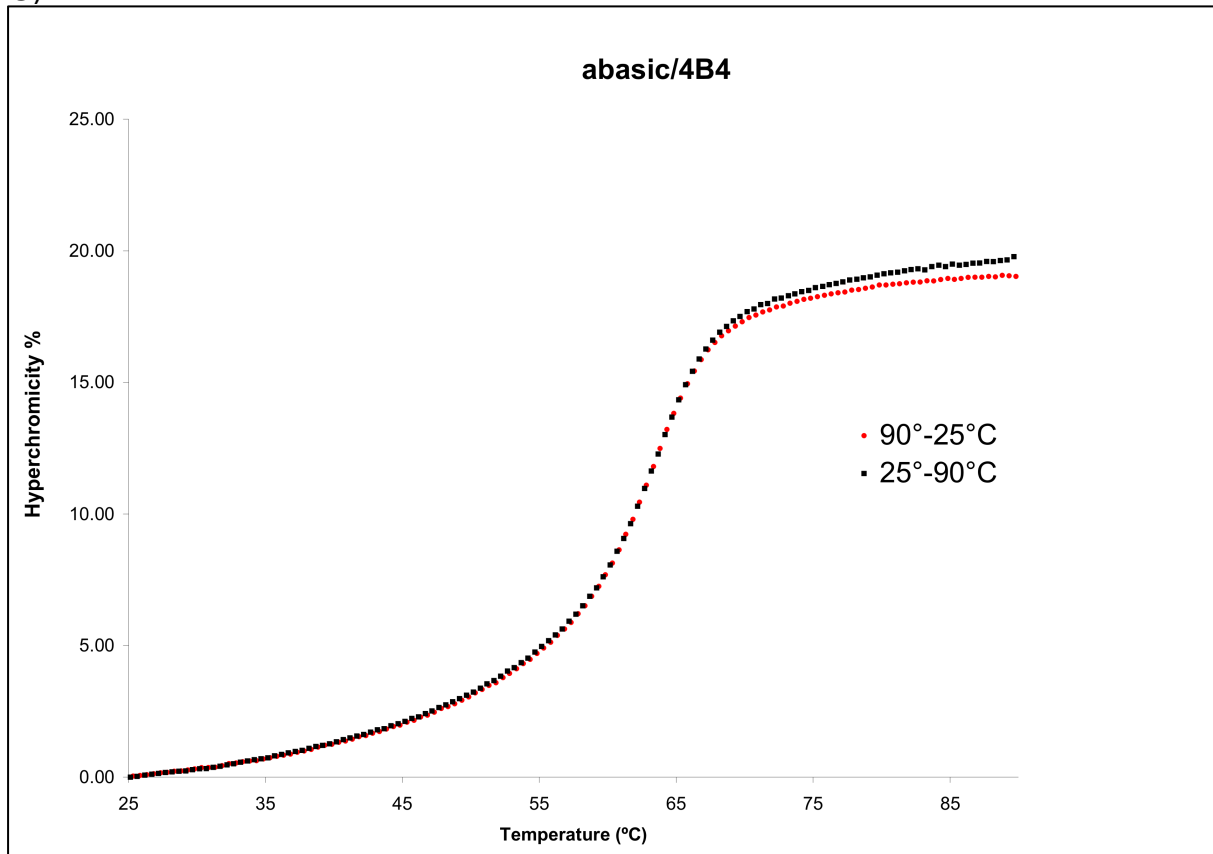
E)



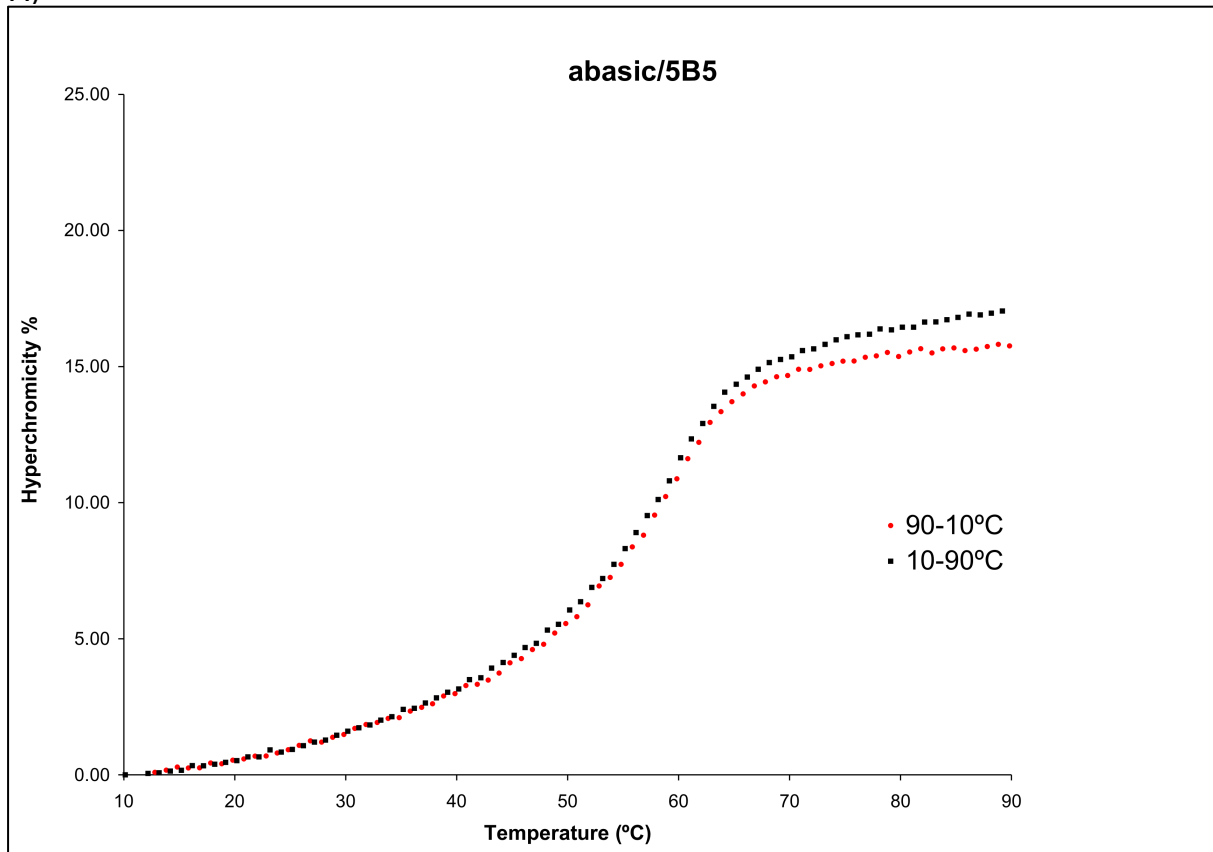
F)



G)



H)



**Figure S2.** Comparison of thermal denaturation curves of the duplex containing the phenanthroline building block with pentamethylene linkers (closed circles) or an adenosine (open circles) opposite to the abasic site. (Conditions: see Figure S1.)

