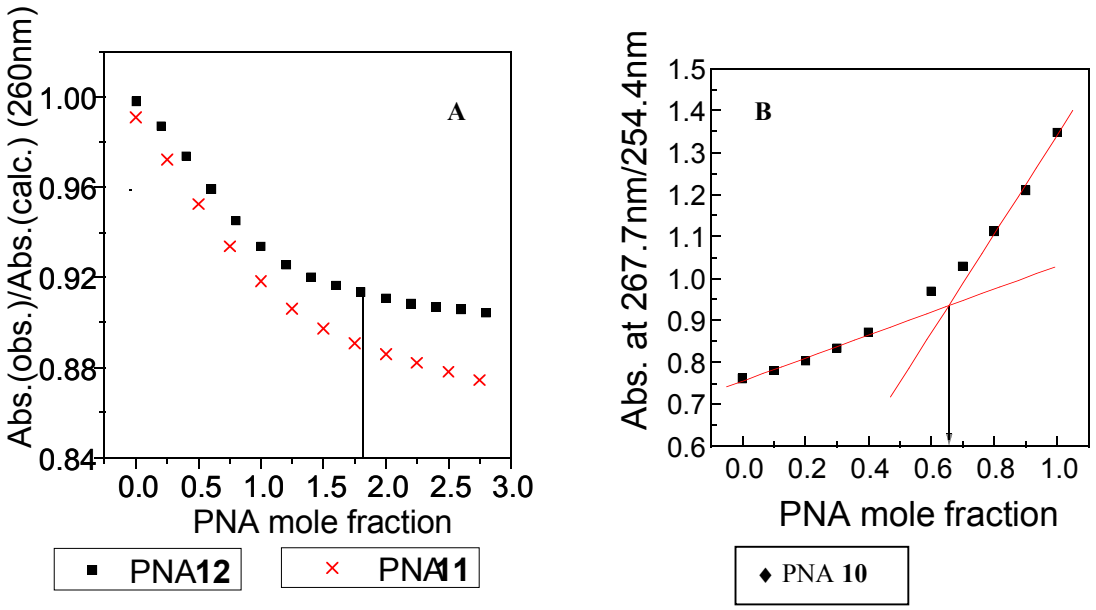


(**A**) UV titration curves of PNA**12** and PNA**11** and (**B**) UV-mixing curve of PNA**10,** with DNA**13** indicating 2:1 binding stoichiometry of PNA:DNA

## $^{1}$H NMR and $^{13}$C NMR data for selected compounds **3-7**

(2*S*, 4*R*)-1-(N-Boc-aminoethyl)-4-hydroxyproline methyl ester **3**: $^{1}$H NMR ($CDCl_3$) δ: 5.3 (br s, 1H, N*H*), 4.4 (m, 1H, *H*4), 3.7 (s, 3H, OC$H_3$), 3.5 (t, 1H, *H*5), 3.38 (dd, 1H, *H*5'), 3.1 (dd, 2H, Boc-NH-C$H_2$), 2.7 (br m, 4H, *H*2, Boc-NH-$CH_2$-C$H_2$, O*H*), 2.5 (dd, 1H, *H*3), 2.1 (m, 1H, *H*3'), 1.4 (s, 9H, C(C$H_3$)$_3$).

(2*R*, 4*R*)-1-(N-Boc-aminoethyl)-4-hydroxyproline methyl ester: $^{1}$H NMR ($CDCl_3$) δ: 5.3 (br s, 1H, N*H*), 4.25 (br s, 1H, *H*4), 3.72 (s, 3H, OC$H_3$), 3.37 (m, 1H, *H*5), 3.4-3.05 (m, 4H, *H*5', Boc-NH-C$H_2$, O*H*), 2.65 (m, 3H, *H*2, Boc-NH-$CH_2$-C$H_2$), 2.4 (m, 1H, *H*3), 1.92 (dd, 1H, *H*3'), 1.4 (s, 9H, C(C$H_3$)$_3$). $^{13}$C NMR ($CDCl_3$) δ: 174.9 (*C*OOMe), 156.1 (*C*OOC($CH_3$)$_3$), 78.6 (*C*($CH_3$)$_3$), 70.0 (O*C*$H_3$), 64.6 (*C*4), 61.6 (*C*5), 53.9 (*C*3), 51.9 (*C*2), 39.0 (*C*$H_2$-*C*$H_2$-NH-Boc), 28.3 ((*C*$H_3$)$_3$).

(2*S*, 4*S*)-1-(N-Boc-aminoethyl)-4-(N3-benzoylthymin-1-yl)proline methyl ester **4**: $^{1}$H NMR ($CDCl_3$) δ: 8.1 (1H, *T*-*H*6), 7.9 (d, 2H, Bz, *o*-C*H*), 7.65 (t, 1H, Bz, *p*-C*H*), 7.5 (t, 2H, Bz, *m*-C*H*), 5.25 (m, 2H, Boc-N*H*, *H*4), 3.8 (s, 3H, OC$H_3$), 3.25 (m, 4H, Boc-NH-C$H_2$, *H*5, *H*5'), 2.8 (m, 3H, Boc-NH-$CH_2$-C$H_2$, *H*2), 2.6 (m, 1H, *H*3), 2.0 (s, 3H, *T*-C$H_3$), 1.95 (m, 1H, *H*3'), 1.45 (s, 9H, C(C$H_3$)$_3$).

(2*R*, 4*S*)-1-(N-Boc-aminoethyl)-4-(N3-benzoylthymin-1-yl)proline methyl ester: $^{1}$H NMR ($CDCl_3$) δ: 7.92 (d, 2H, Bz, *o*-C*H*), 7.65 (t, 1H, Bz, *p*-C*H*), 7.5(t, 2H, Bz, *m*-C*H*), 7.4 (s, 1H, *T*-*H*6), 5.25 (m, 1H, *H*4), 4.9 (br t, 1H, Boc-N*H*), 3.9 (dd, 1H, *H*5), 3.72 (s, 3H, OC$H_3$), 3.3 (m, 3H, *H*5', Boc-NH-C$H_2$), 2.92 (dd, 1H, *H*2), 2.78 (t, 2H, Boc-NH-$CH_2$-C$H_2$), 2.55 m, 1H, *H*3), 2.20 (m, 1H, *H*3'), 2.0 (s, 3H, *T*-C$H_3$), 1.45 (s, 9H, C(C$H_3$)$_3$). $^{13}$C NMR ($CDCl_3$) δ: 172.5 (*C*OOMe), 169.0 (*C*OOC($CH_3$)$_3$), 162.5 (*T*-*C*2), 155.8 (Ph-*C*O), 149.5 (*T*-*C*4), 137.5 (*T*-*C*6), 134.8, 131.3, 130.0, 128.9 (arom), 111.1 (*T*-*C*5), 78.8 (*C*($CH_3$)$_3$), 63.1 (*C4*), 55.5 (Boc-NH-*C*$H_2$), 53.7 (C2), 51.4 ($OCH_3$), 50.6 (C5), 38.7 (Boc-NH-$CH_2$-*C*$H_2$), 35.1 (*C*3), 28.1 (C(*C*$H_3$)$_3$), 12.3 (T-*C*$H_3$) .

(2*S*,4*S*)-1-(N-Boc-aminoethyl)-4-(thymin-1-yl)proline **5**: $^{1}$H NMR ($D_2O$) δ: 7.4 (s, 1H, *T*-*H*6), 4.1 (br m, 2H, *H*4, *H*2), 3.6(br m, 4H, *H*5, *H*5', C$H_2$-NH-Boc), 3.4(br m,1H, C$H_2$-$CH_2$-NH-Boc), 3.1(br m, 1H, *H*3 & 1H, C$H_2$-$CH_2$-NH-Boc), 2.4(m, 1H, *H*3'), 1.8(s, 3H, *T*-C$H_3$), 1.4(s, 9H, C(C$H_3$)$_3$). $^{13}$C NMR ($D_2O$) δ: 172.1(C2-*C*O), 167.0(*T*-*C*2), 158.5(NH-*C*O-O), 152.6(*T*-*C*4), 143.4(*T*-*C*6), 111.5(*T*-*C*5), 82.2(*C*($CH_3$)$_3$), 70.4(*C*4), 59.6(*C*5), 55.1(*C*$H_2$-NH-Boc), 37.3(*C*$H_2$-$CH_2$-NH-Boc), 34.2(*C*3), 28.5(C(*C*$H_3$)$_3$), 12.2(*T*-C5-*C*$H_3$).

(2*R*,4*S*)-1-(N-Boc-aminoethyl)-4-(thymin-1-yl)proline **7** : $^{1}$H NMR ($D_2O$) δ: 7.4(s, 1H, *T*-*H*6), 4.4(t, 1H, *H*4), 4.2(m, 1H, *H*2), 3.7-3.3(br m, 6H, *H*5, *H*5', C$H_2$-C$H_2$-NH-Boc), 2.9(m, 1H, *H*3), 2.6(m, 1H, *H*3), 1.9(s, 3H, *T*-C$H_3$), 1.4(s, 9H, C(C$H_3$)$_3$). $^{13}$C NMR ($D_2O$) δ: 170.9(C2-*C*O), 164.8(*C*2), 156.5(NH-*C*O-O), 150.4(*C*4), 139.7(*T*-*C*6), 110.0(*T*-*C*5), 80.3(*C*($CH_3$)$_3$), 67.8(*C*4), 61.6(*C*$H_2$-NH-Boc), 55.1(*C*2), 53.9(*C*5), 35.7(*C*3), 31.2(*C*$H_2$-$CH_2$-NH-Boc), 26.6(C(*C*$H_3$)$_3$, 10.3(*T*-*C*$H_3$).

**MALDI-TOF mass spectrum of PNA 8**