Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting information

Short-RNA selective binding of oligonucleotides modified using adenosine and guanosine derivatives that possess cyclohexyl phosphates as substituents

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General methods

The dry solvents were purchased and stored over molecular sieves 4A. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained at 500, 126, and 203 MHz, respectively. The chemical shifts were measured from $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.50 ppm) for ^{1}H NMR, $CDCl_3$ (77.0 ppm), DMSO-d_6 (39.5 ppm) for ^{13}C NMR and 85% phosphoric acid (0.0 ppm) for ^{31}P NMR. Oligonucleotides were purified on anion-exchange high performance liquid chromatography (HPLC) at 50 °C with a linear gradient (10–67%) of solvent I (1 M NaCl in 25 mM phosphate buffer (pH 6.0)) in solvent II (25 mM phosphate buffer (pH 6.0)) was used at a flow rate of 1.0 mL/min for 40 min. MALDI-TOF mass was performed using 3-hydoroxypicolinic acid (100 mg/mL) in H_2O-diammoniumhydrogen citrate (100 mg/mL) in H_2O (10 : 1, v/v) as a matrix.

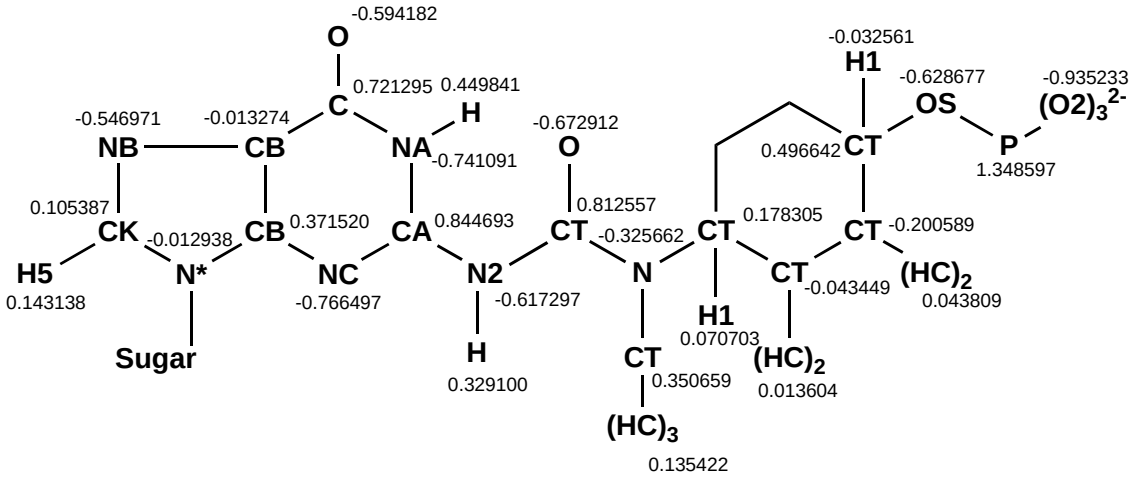
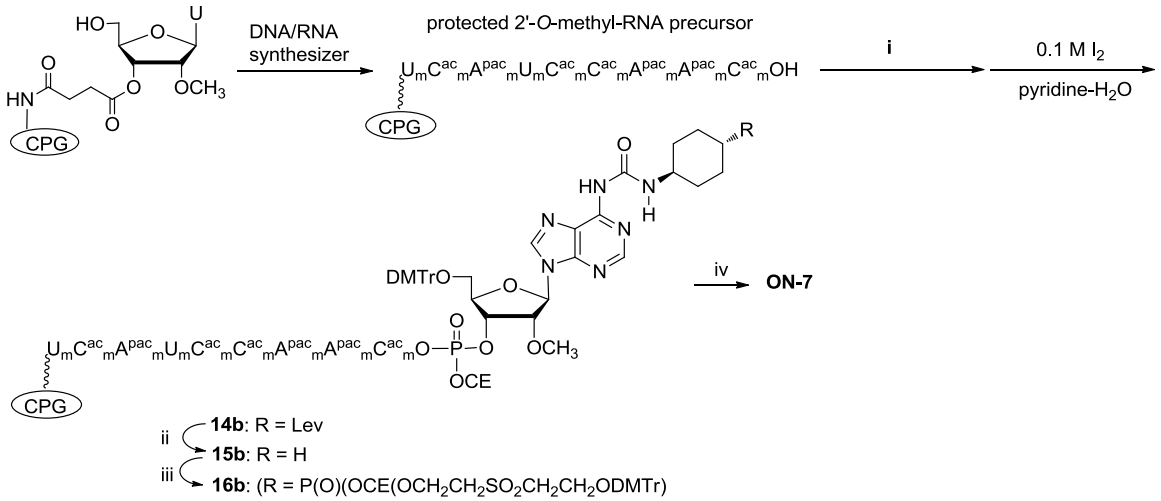
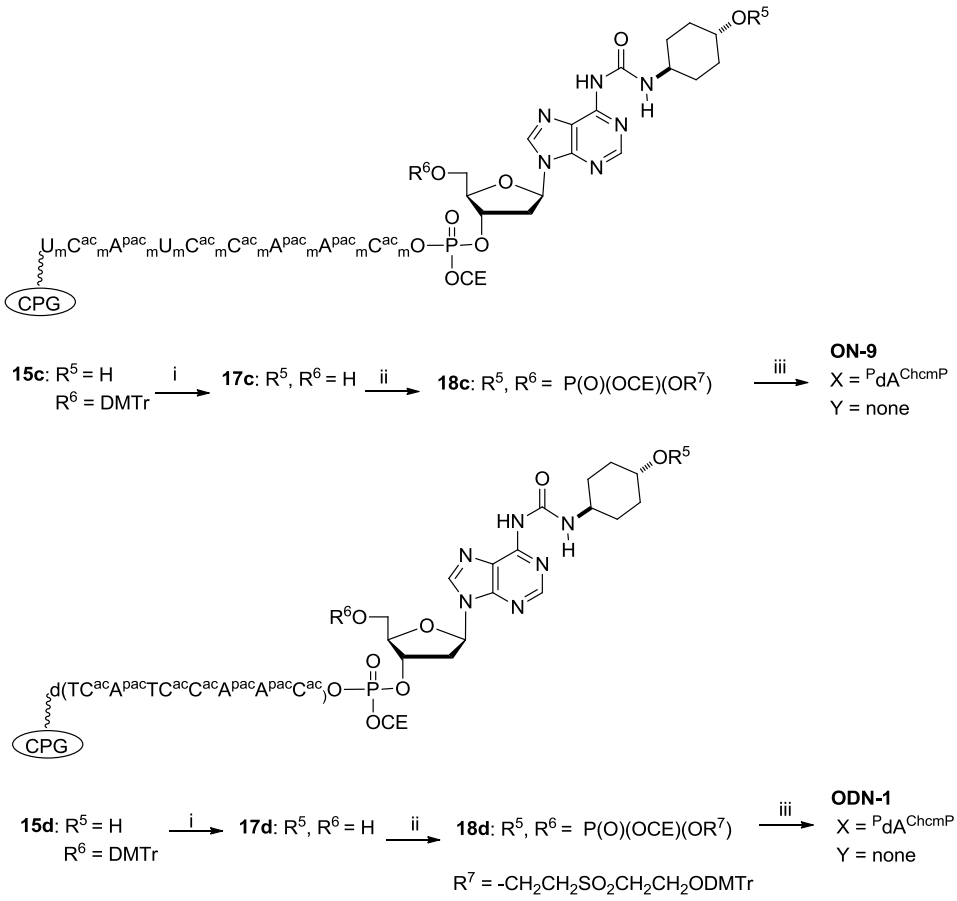


Figure S1. AMBER atom types and the partial charges of the base moiety of dG^{CmcmP}.



Reagents and conditions: i) **13b**, Activator42, CH_3CN, then 0.1 M DMAP, Ac_2O-pyridine (1:9, v/v); ii) 0.5 M NH_2NH_2/pyridine-AcOH (3:2, v/v); iii) {(*i*-Pr)$_2$N-P(OCE)($OCH_2CH_2SO_2CH_2CH_2ODMTr$), *1*H-tetrazole, CH_3CN, 1 min}x2, then 0.1 M I_2/pyridine-H_2O (9:1, v/v); iv) 28% aq. NH_3 8h, then 2% aq. TFA on C18-cartridge column.

SCHEME S1. Preparation of **ON-7** incorporating A_m^{ChcmP}.



Reagents and conditions: i) 3% dichloroacetic acid/CH_2Cl_2; ii) {(*i*-Pr)$_2$N-P(OCE)($OCH_2CH_2SO_2CH_2CH_2ODMTr$), 1*H*-tetrazole, CH_3CN, 1 min}x2, then 0.1 M I_2/pyridine-H_2O (9:1, v/v); iv) 28% aq. NH_3, then 2% aq. TFA on C18-cartridge column.

Scheme S2. Preparation of **ON-9** and **ODN-1**.