Supplementary Information

Wavelength-selective light-triggered strand exchange reaction

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1. Synthesis of new compounds

General. Reagents and solvents were purchased from commercial suppliers and were used without purification unless otherwise specified. All experiments involving air- and/or moisture-sensitive compounds were carried out under an Ar atmosphere. All reactions were monitored with analytical TLC (Merck Kieselgel 60 F254; Merck, Darmstadt, Germany). Flash column chromatography was carried out using EPCLC-W-Prep 2XY (YAMAZEN, Osaka, Japan). Physical data were measured as follows: NMR spectra were recorded on a JNM-ECS-300 spectrometer (JEOL, Tokyo, Japan) using $CDCl_3$ or DMSO-d_6 as the solvent with tetramethylsilane as an internal standard. IR spectra were recorded on a FT/IR-4200 spectrometer (JASCO, Tokyo, Japan). Optical rotations were recorded on a JASCO P-2200 polarimeter. FAB mass spectra were measured on a JEOL JMS-700 mass spectrometer. Solid-phase ON synthesis was performed on an nS-8 Oligonucleotide Synthesizer (GeneDesign, Osaka, Japan). MALDI-TOF mass spectra were recorded on an ultrafleXtreme mass spectrometer (Bruker Daltonics, MA, US). Photo-irradiation experiments were conducted with a UV-LED lamp (ZUV-C30H; OMRON, Kyoto, Japan) for 365 nm and a Xenon lamp (MAX-303; Asahi Spectra, Tokyo, Japan) for 450 nm. UV-Vis absorption measurements and UV melting experiments were performed using a UV-1650PC UV-Vis spectrophotometer equipped with a TMSPC-8 T_m analysis accessory (SHIMADZU, Kyoto, Japan). Gel was imaged over a LED transilluminator (WAKO, Osaka, Japan)

Synthesis of 4-*tert*-butyldimethylsilyloxy-1-(2'-deoxy-3',5'-di-*O*-toluoyl-β-D-ribofuranosyl)-2-(2-nitrobenzylthio)-1*H*-benzimidazole (2). To a solution of **1** (700 mg, 2.50 mmol) in dry DMF (25 mL) was added 2-nitrobenzyl bromide (591 mg, 2.75 mmol) at room temperature. After being stirred for 3 h at room temperature, the resulting mixture was partitioned between Et_2O and H_2O. The separated organic layer was washed with saturated aqueous $NaHCO_3$, followed by brine. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The resulting residue was purified by a flash silica gel column, eluted with hexane/AcOEt (19:1 to 3:1). The resulting product was dissolved in dry MeCN (22 mL), and 60% sodium hydride (96 mg, 2.41 mmol) was added to the solution at 0 ˚C. After being stirred for 30 min at 0 ˚C, to the reaction mixture was added 1-chloro-2-deoxy-3,5-di-*O*-toluoyl-β-D-ribofuranose (850 mg, 2.19 mmol). The whole was stirred at room temperature for 30 min, and the reaction was quenched by addition of ice. The resultant mixture was partitioned between AcOEt and H_2O. The separated organic layer was washed with saturated aqueous $NaHCO_3$, followed by brine. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by a flash silica gel column, eluted with hexane to hexane/AcOEt (9:1), to give **2** (1.10 g, 57% over two steps) as a yellow foam; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (1H, dd, *J* = 8.5 and 1.5 Hz), 8.05-7.91 (5H, m), 7.50 (1H, dt, *J* = 7.0 and 1.0 Hz), 7.41 (1H, dt, *J* = 8.0 and 1.5 Hz), 7.30-7.23 (4H, m), 7.12 (1H, dd, *J* = 7.0 and 1.5 Hz), 6.69-6.61 (2H, m), 6.26 (1H, dd, *J* = 9.0 and 5.5 Hz, H-1'), 5.73-5.70 (1H, m, H-3'), 5.02 (1H, d, *J* = 14.0 Hz), 4.94 (1H, d, *J* = 14.0 Hz), 4.79 (1H, dd, *J* = 12.5 and 3.0 Hz, H-5'a), 4.71 (1H, dd, *J* = 12.0 and 4.0 Hz, H-5'b), 4.46 (1H, dd, *J* = 7.0 and 3.5 Hz, H-4'), 3.02-2.97 (1H, m, H-2'a), 2.45 (3H, s), 2.43 (3H, s), 2.40-2.34 (1H, m, H-2'b), 1.08 (9H, s), 0.27 (3H, s), 0.26 (3H, s); ^{13}C NMR (100

MHz, $CDCl_3$) δ 166.3, 166.0, 148.9, 147.8, 146.5, 144.5, 144.0, 136.4, 136.0, 133.9, 133.7, 132.8, 129.7(8), 129.7(5), 129.3, 129.2, 128.7, 126.8, 126.3, 125.2, 122.8, 113.0, 104.9, 85.0, 81.6, 73.7, 63.7, 36.1, 34.0, 25.8, 21.7(2), 21.7(0), 18.5, -4.2(3), -4.2(5); IR (KBr) 1720 (C=O), 1525 (NO_2 as), 1272 (NO_2 sy) cm^{-1}; $[\alpha]_D^{25}$ -65.0 (c 1.00, $CHCl_3$); FAB-LRMS m/z = 768 (MH^+); FAB-HRMS calcd for $C_{41}H_{45}N_3O_8SSi$ 768.2775, found 768.2780.

Synthesis of 1-(2'-deoxy-β-D-ribofuranosyl)-4-hydroxy-2-(2-nitrobenzylthio)-1*H*-benzimidazole (3). A suspension of **2** (1.00 mg, 1.30 mmol) in saturated methanolic ammonia (130 mL) was stirred at room temperature for 36 h. The solvent was removed in vacuo, and the residue was purified by a flash silica gel column, eluted with hexane/AcOEt (7:3) to AcOEt, to give **3** (280 mg, 52%) as a green powder; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.79 (1H, s), 8.16 (1H, dd, *J* = 8.0 and 1.0 Hz), 7.94 (1H, dd, *J* = 7.5 and 1.0 Hz), 7.75 (1H, dt, *J* = 7.0 and 1.0 Hz), 7.63 (1H, dt, *J* = 8.5 and 1.5 Hz), 7.19 (1H, d, *J* = 7.5 Hz), 7.00 (1H, t, *J* = 8.0 Hz), 6.65 (1H, d, *J* = 7.0 Hz), 6.18 (1H, dd, *J* = 8.5 and 6.0 Hz, H-1'), 5.42 (1H, d, *J* = 4.5 Hz), 5.04 (1H, t, *J* = 5.0 Hz), 4.99 (1H, d, *J* = 13.5 Hz), 4.93 (1H, d, *J* = 13.5 Hz), 4.38-4.36 (1H, m, H-3'), 3.83 (1H, dd, *J* = 8.5 and 5.0 Hz, H-4'), 3.69-3.65 (2H, m, H-5'), 2.53-2.46 (1H, m, H-2'a), 2.07-2.00 (1H, m, H-2'b); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.0, 147.9, 147.5, 136.0, 134.1, 133.2, 132.9, 132.6, 129.3, 125.1, 123.0, 107.4, 103.2, 87.1, 84.5, 70.3, 61.4, 38.0, 33.3, 30.4; IR (KBr) 3310 (OH), 1523 (NO_2 as), 1348 (NO_2 sy) cm^{-1}; $[\alpha]_D^{26}$ -1.30 (c 1.00, DMSO); FAB-LRMS m/z = 418 (MH^+); FAB-HRMS calcd for $C_{19}H_{20}N_3O_6S$ 418.1073, found 418.1073.

Synthesis of 4-acetoxy-1-(2'-deoxy-β-D-ribofuranosyl)-2-(2-nitrobenzylthio)-1*H*-benzimidazole (4). To a solution of **3** (250 mg, 0.599 mmol) in 2-propanol (6 mL) were added 2 M aqueous NaOH (0.3 mL, 0.599 mmol) and acetic anhydride (85 μL, 0.899 mmol) at 0 ˚C. After being stirred for 1.5 h at room temperature, the reaction was quenched by addition of saturated aqueous $NaHCO_3$. The resultant mixture was partitioned between AcOEt and H_2O. The separated organic layer was washed with saturated aqueous $NaHCO_3$, followed by brine. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by a flash silica gel column, eluted with hexane/AcOEt (2:3 to1:4), to give **4** (190 mg, 69%) as a white foam; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (1H, dd, *J* = 8.0 and 1.5 Hz), 7.81 (1H, dd, *J* = 8.0 and 1.0 Hz), 7.52 (1H, dt, *J* = 8.0 and 1.5 Hz), 7.40 (1H, dt, *J* = 8.5 and 1.5 Hz), 7.29 (1H, d, *J* = 8.0 Hz), 7.14 (1H, t, *J* = 8.0 Hz), 6.95 (1H, d, *J* = 8.0 Hz), 6.19 (1H, dd, *J* = 8.0 and 7.0 Hz, H-1'), 4.97 (1H, d, *J* = 13.5 Hz), 4.92 (1H, d, *J* = 13.5 Hz), 4.62-4.57 (1H, m, H-3'), 3.92-3.81 (3H, m, H-4' and H-5'x2), 2.68-2.58 (1H, m, H-2'a), 2.44 (3H, s), 2.19-2.11 (1H, m, H-2'b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 151.0, 147.7, 140.5, 136.3, 136.1, 133.7, 133.4, 133.1, 128.8, 125.2, 122.5, 115.0, 109.0, 86.0, 84.6, 70.8, 62.0, 38.7, 34.0, 21.0; IR (KBr) 3423 (OH), 1762 (C=O), 1524 (NO_2 as), 1348 (NO_2 sy) cm^{-1}; $[\alpha]_D^{25}$ -20.6 (c 1.00, $CHCl_3$); FAB-LRMS m/z = 460 (MH^+); FAB-HRMS calcd for $C_{21}H_{22}N_3O_7S$ 460.1178, found 460.1193.

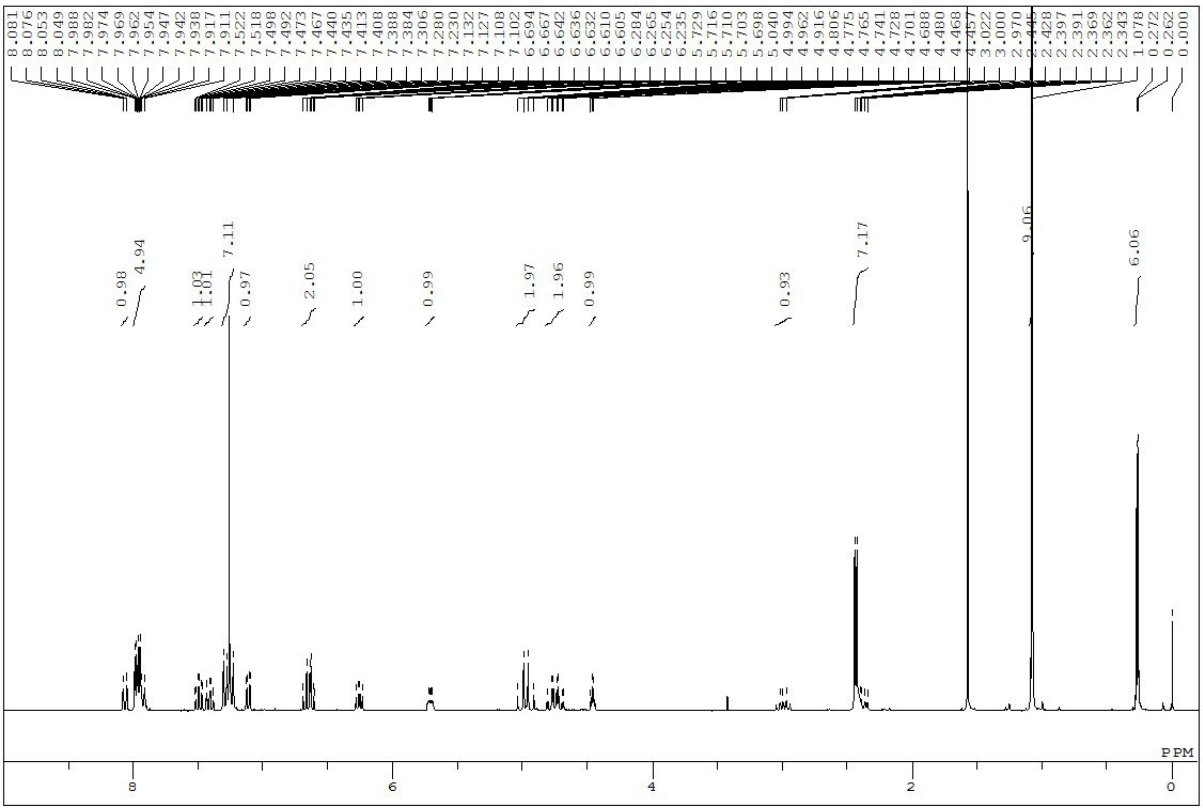
Synthesis of 4-acetoxy-1-[2'-deoxy-5'-*O*-(4,4'-dimethoxytrityl)-β-D-ribofuranosyl]-2-(2-nitrobenzylthio)-1*H*-benzimidazole (5). To a solution of **4** (150 mg,

0.327 mmol) in dry pyridine (3.3 mL) was added 4,4'-dimethoxytrityl chloride (166 mg, 0.491 mmol) at room temperature. After being stirred for 1 h, the reaction was quenched by addition of MeOH (1.0 mL) with 5 min stirring. The resultant mixture was partitioned between AcOEt and H_2O. The separated organic layer was washed with saturated aqueous $NaHCO_3$, followed by brine. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by a flash silica gel column, eluted with hexane/AcOEt (7:3 to 2:3 with 0.5% Et_3N) to give **5** (207 mg, 83%) as a yellow foam; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (1H, dd, *J* = 8.0 and 1.0 Hz), 7.81 (1H, dd, *J* = 8.0 and 1.0 Hz), 7.51 (1H, dt, *J* = 7.5 and 1.0 Hz), 7.45-7.24 (xxH, m), 6.88-6.71 (6H, m), 6.16 (1H, dd, *J* = 8.5 and 6.5 Hz, H-1'), 4.95 (1H, d, *J* = 14.0 Hz), 4.89 (1H, d, *J* = 13.5 Hz), 4.67-4.63 (1H, m, H-3'), 3.96 (1H, dd, *J* = 8.5 and 4.0 Hz, H-4'), 3.78 (6H, s), 3.50 (1H, dd, *J* = 10.5 and 4.0 Hz, H-5'a), 3.45 (1H, dd, *J* = 11.0 and 4.5 Hz, H-5'b), 2.69-2.59 (1H, m, H-2'a), 2.49 (3H, s), 2.16-2.09 (1H, m, H-2'b), 1.91 (1H, d, *J* = 3.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 158.5, 150.9, 147.7, 144.4, 140.5, 136.2, 136.0, 135.6, 135.4, 133.6, 133.2, 130.1, 128.7, 128.2, 127.9, 126.9, 125.1, 122.3, 114.8, 113.2, 110.2, 86.7, 85.0, 84.7, 71.7, 63.0, 55.2, 38.9, 33.9, 21.0; IR (KBr) 3524 (OH), 1765 (C=O), 1516 (NO_2 as), 1250 (NO_2 sy) cm^{-1}; $[\alpha]_D^{24}$ -28.0 (c 1.00, $CHCl_3$); FAB-LRMS m/z = 762 (MH^+); FAB-HRMS calcd for $C_{42}H_{40}N_3O_9S$ 762.2485, found 762.2483.

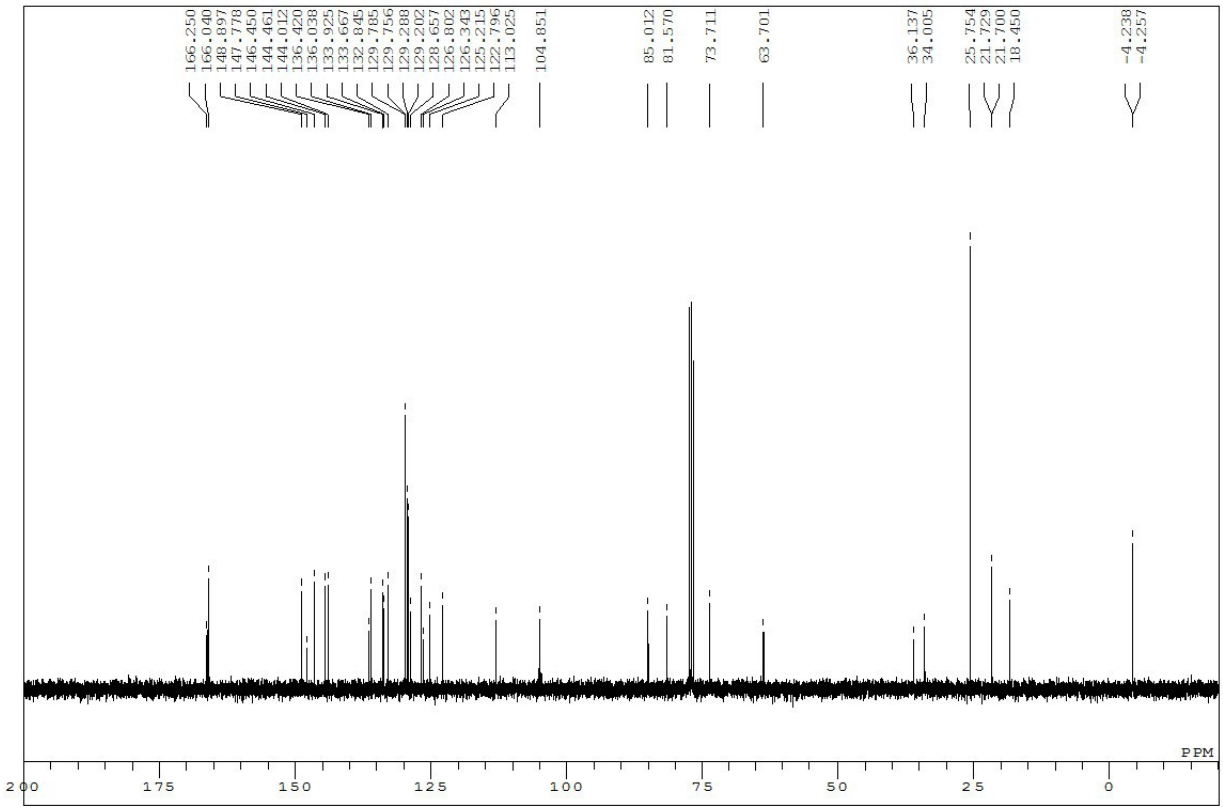
Synthesis of 4-acetoxy-1-[2'-deoxy-5'-*O*-(4,4'-dimethoxytrityl)-3'-*O*-(*N*,*N*-diisopropyl-β-cyanoethylphosphoramidyl)-β-D-ribofuranosyl]-2-(2-nitrobenzylthio)-1*H*-benzimidazole (6). To a solution of **5** (170 mg, 0.223 mmol) in dry MeCN (2.2 mL) were added *N*,*N*-diisopropylethylamine (117 μL, 0.669 mmol) and 2-cyanoethyl-*N*,*N*'-diisopropylchlorophosphoramidite (75 μL, 0.335 mmol) at room temperature. After being stirred for 30 min, the resultant mixture was partitioned between AcOEt and H_2O. The separated organic layer was washed with saturated aqueous $NaHCO_3$, followed by brine. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (4:1 to 1:1 with 0.5% Et_3N) to give a 10:9 diastereomeric mixture of **6** (156 mg, 73%) as a yellow foam; ^{31}P NMR δ 149.3, 148.5; IR (KBr) 2251 (CN), 1766 (C=O), 1516 (NO_2 as), 1250 (NO_2 sy) cm^{-1}; FAB-LRMS m/z = 962 (MH^+); FAB-HRMS calcd for $C_{51}H_{57}N_5O_{10}PS$ 962.3564, found 962.3566.

2. ^{1}H, ^{13}C and ^{31}P spectra of new compounds

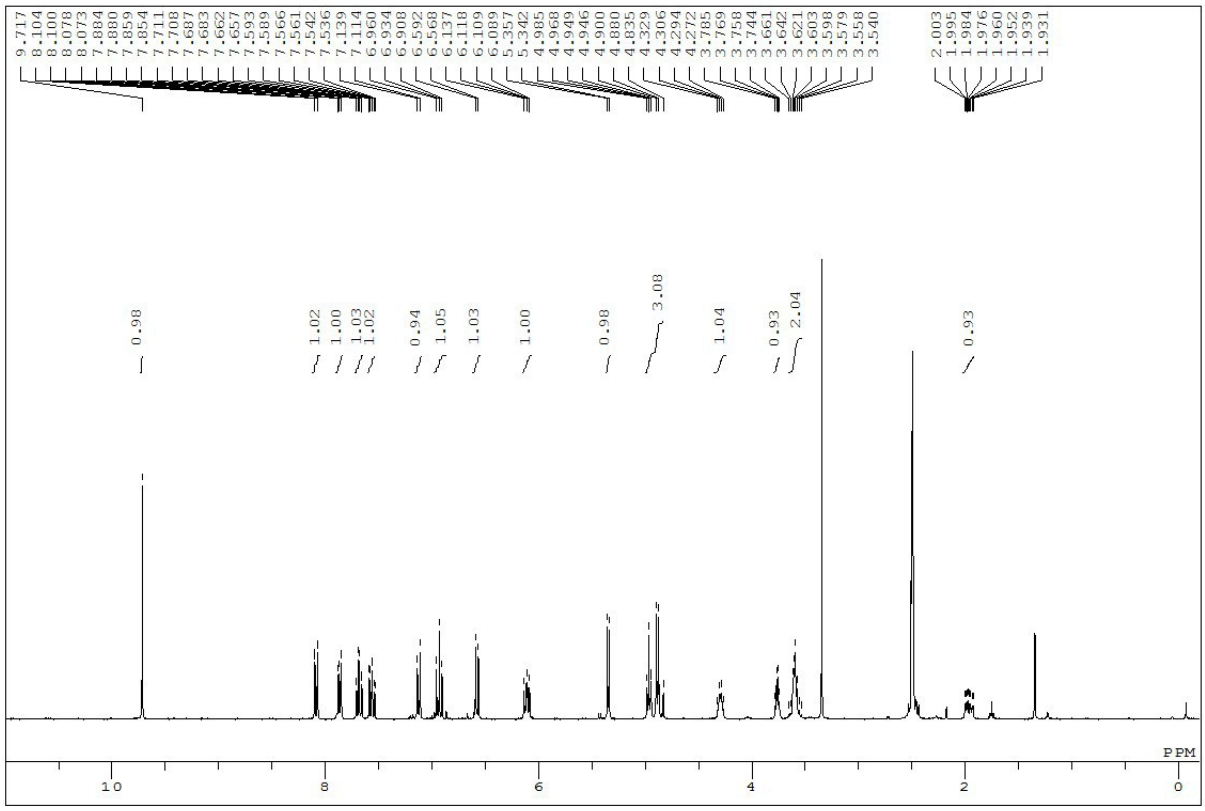
^{1}H spectrum of compound 2



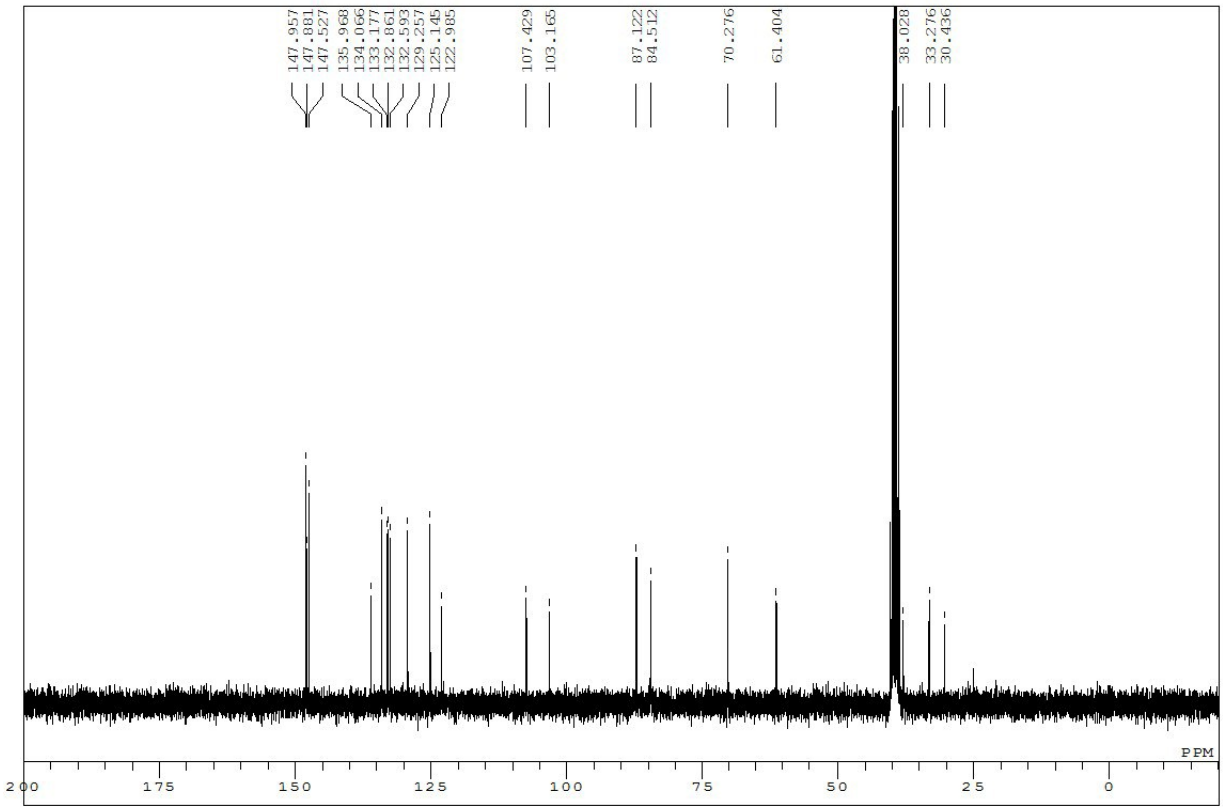
^{13}C spectrum of compound 2



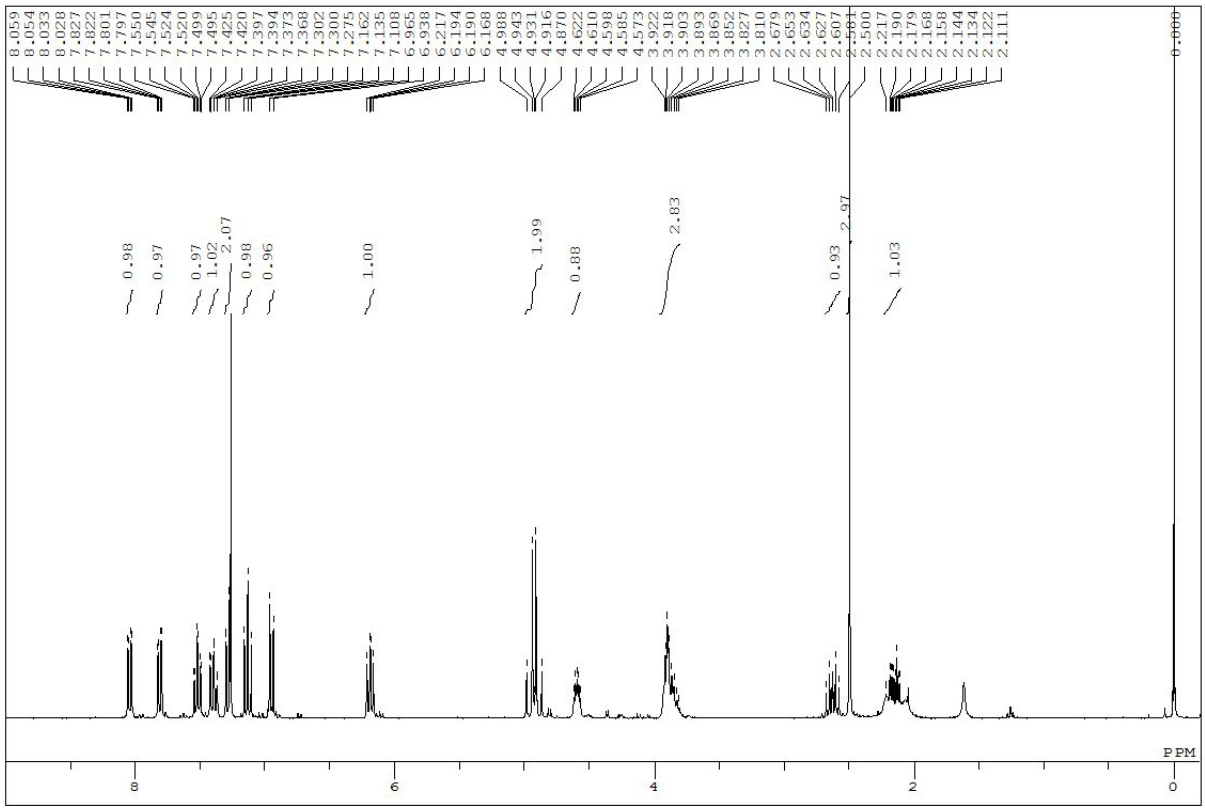
^{1}H spectrum of compound 3



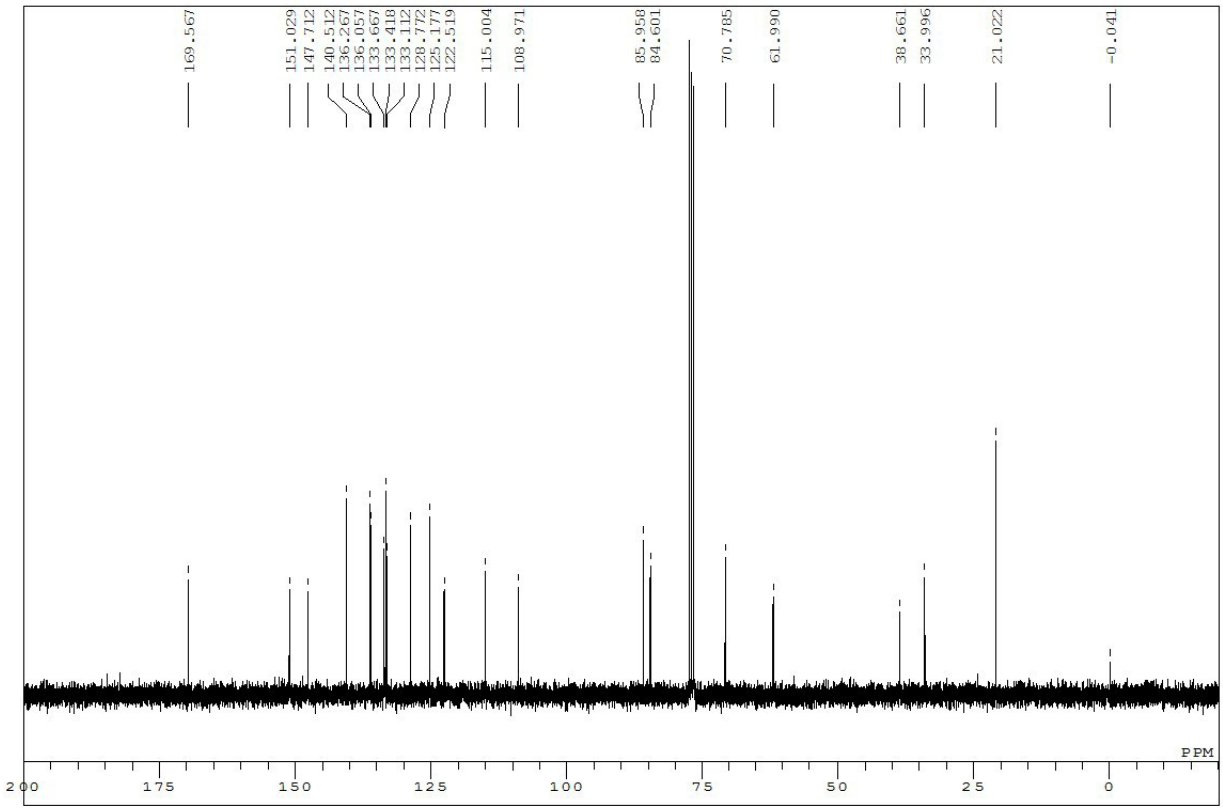
^{13}C spectrum of compound 3



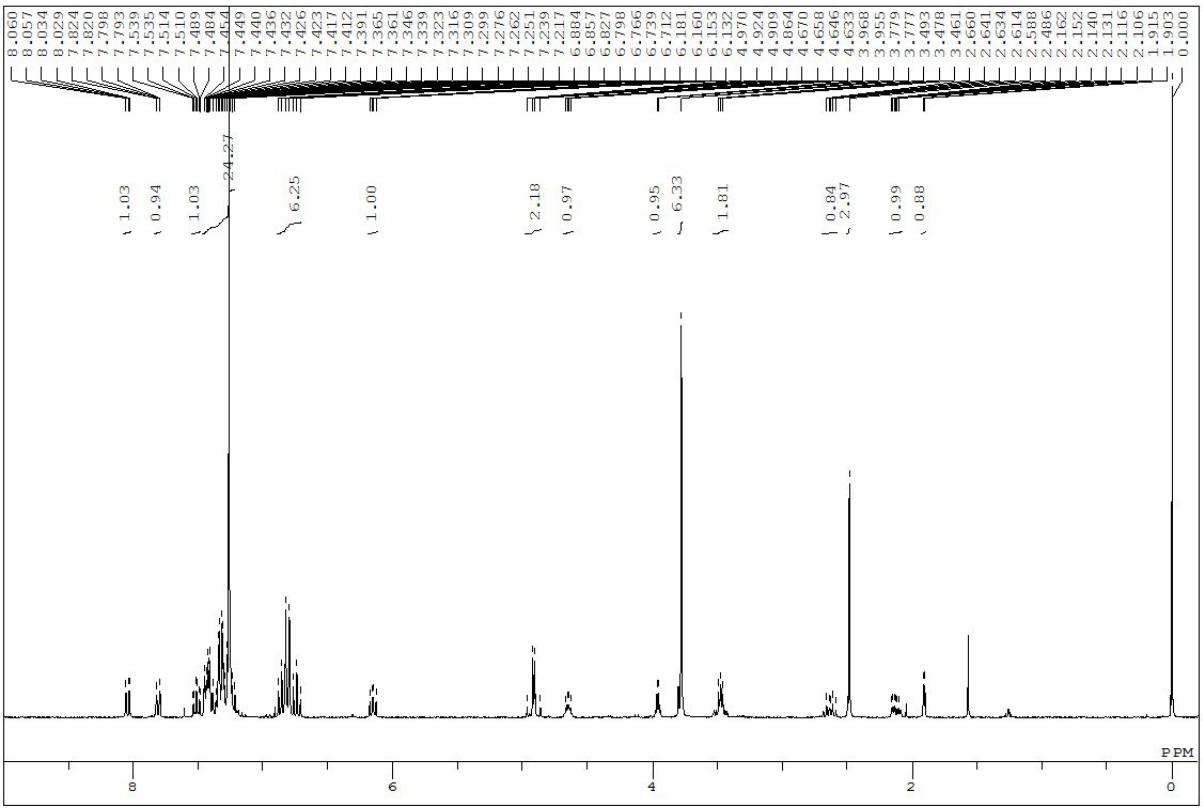
^{1}H spectrum of compound 4



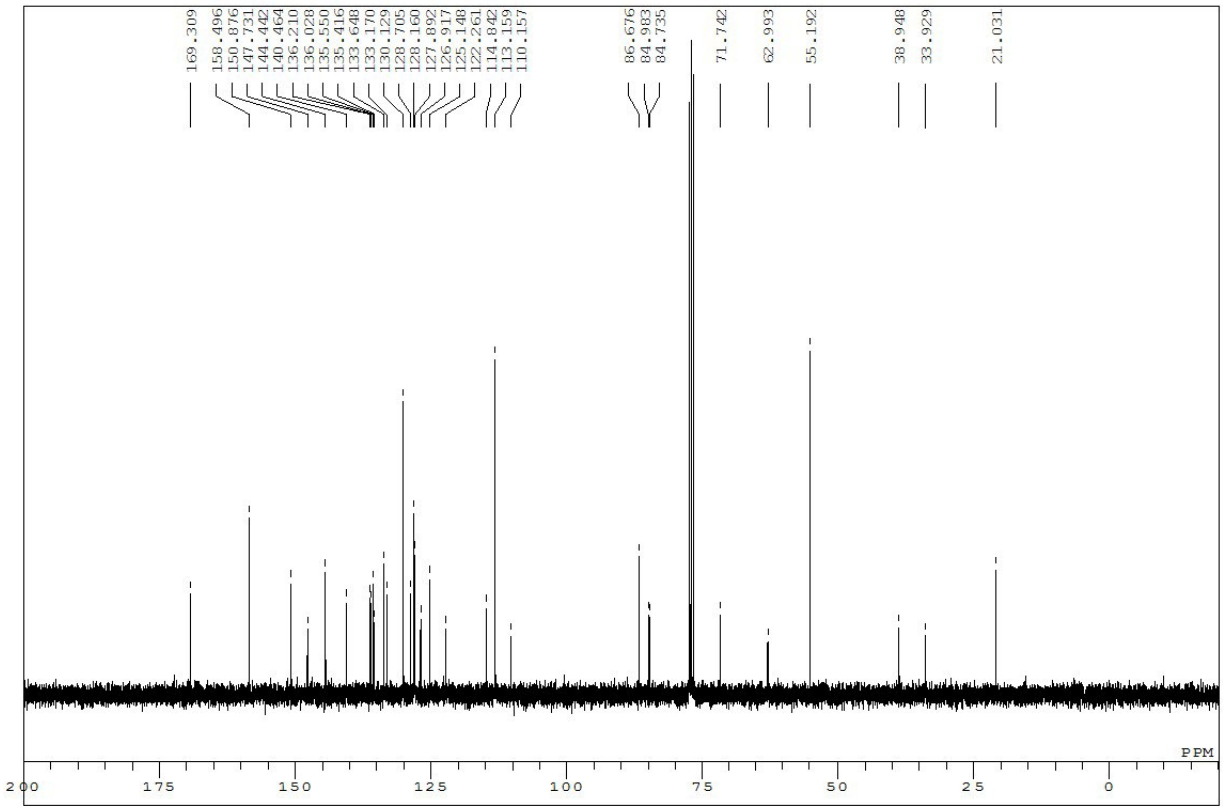
^{13}C spectrum of compound 4



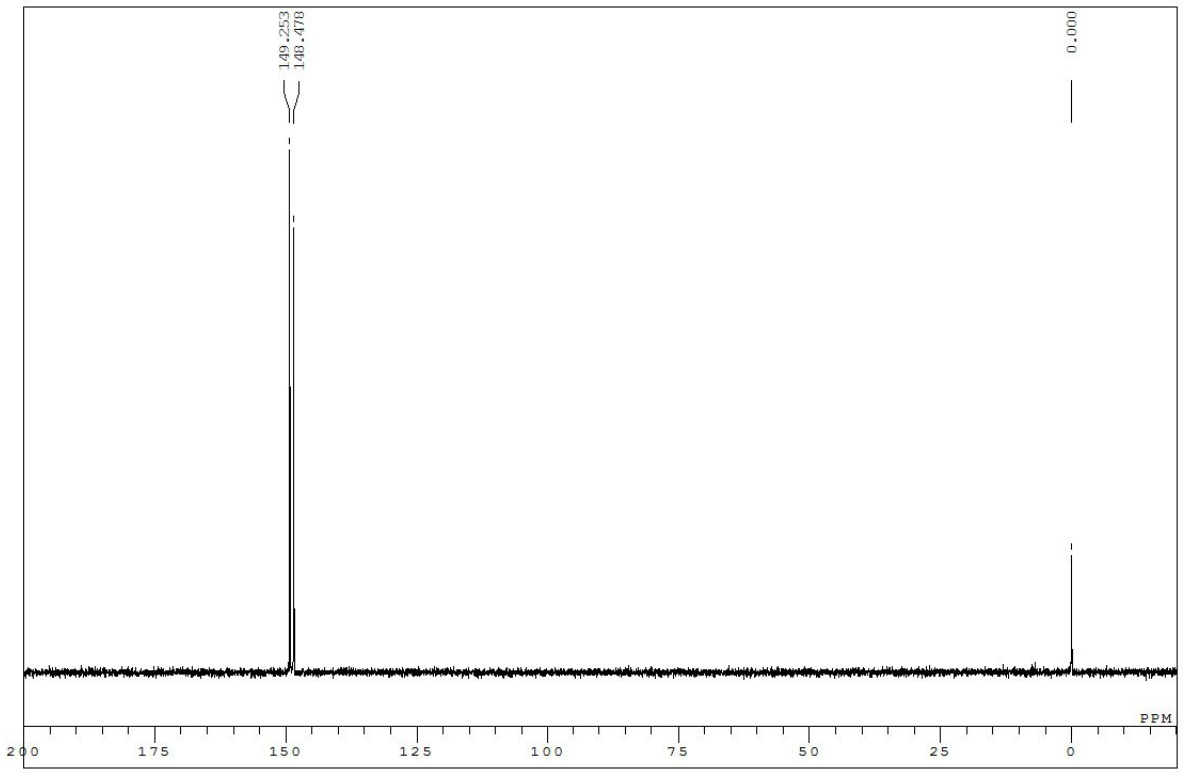
^{1}H spectrum of compound 5



^{13}H spectrum of compound 5



^{31}P spectrum of compound 6



3. HPLC and MALDI-TOF MS analysis of SB^{NB}-modified ODNs

ODN **8**

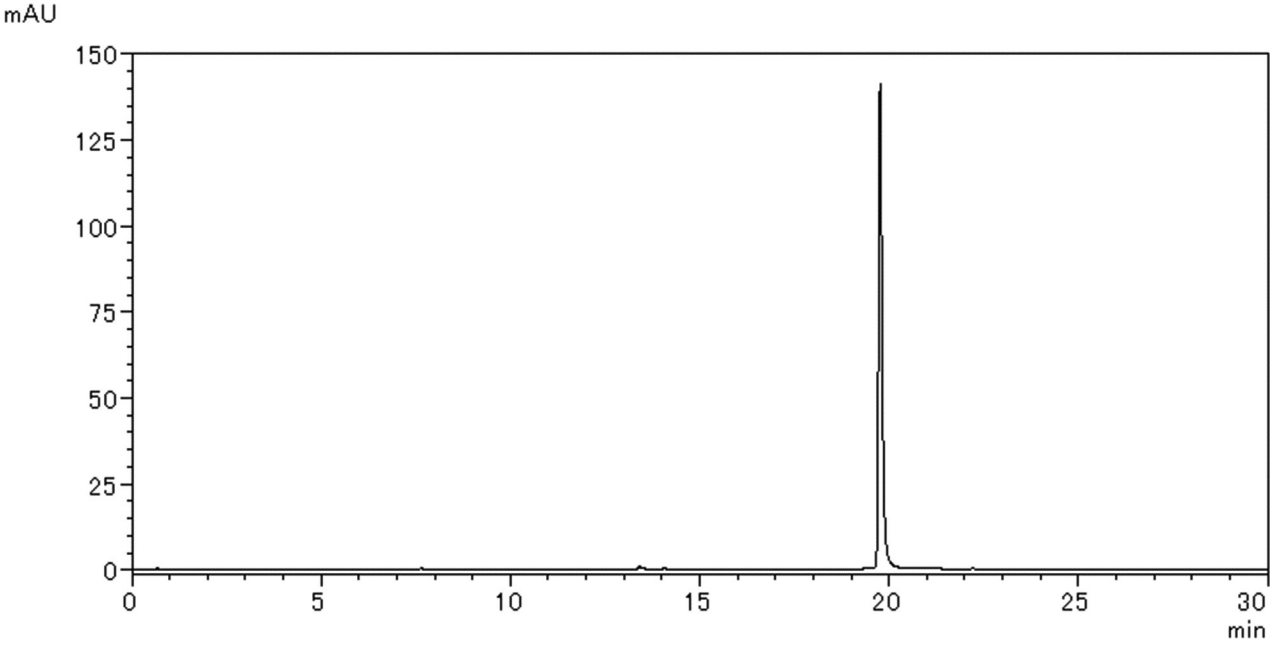
RP-HPLC

Column: Waters XBridge^{TM} OST C18 2.5 μm, 4.6 x 50 mm

Gradient: 5-20% MeCN (over 15 min) in triethylammonium acetate buffer (pH 7.0, 0.1 M)

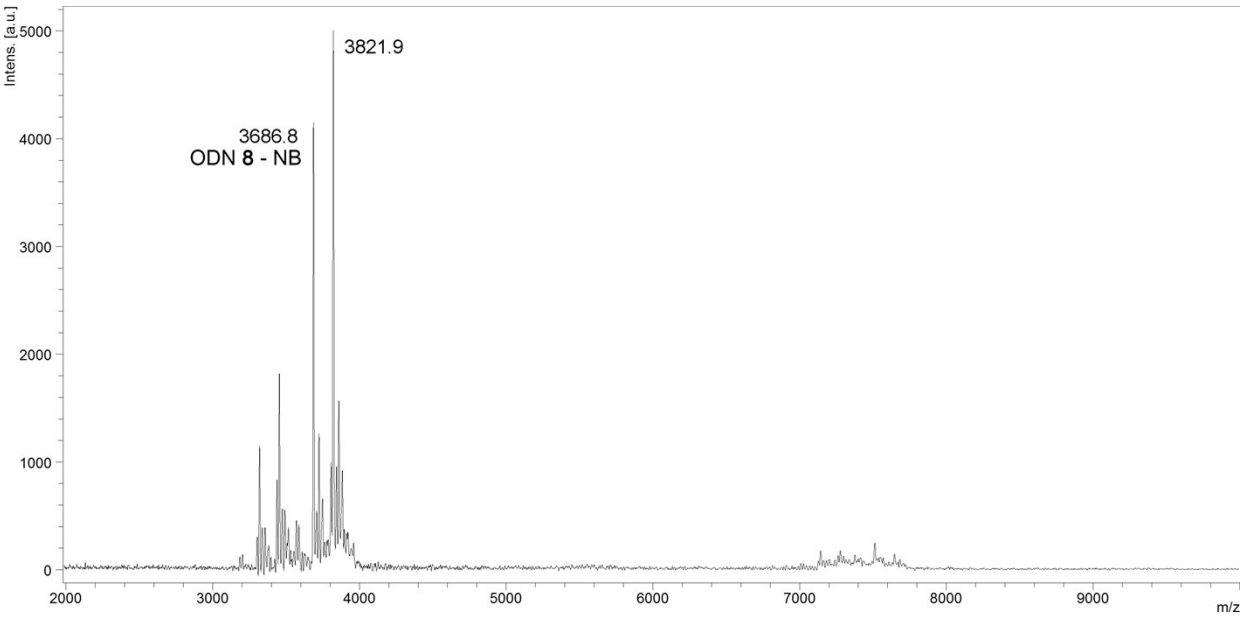
Flow rate: 1.0 mL/min

Column temperature: 50 ˚C

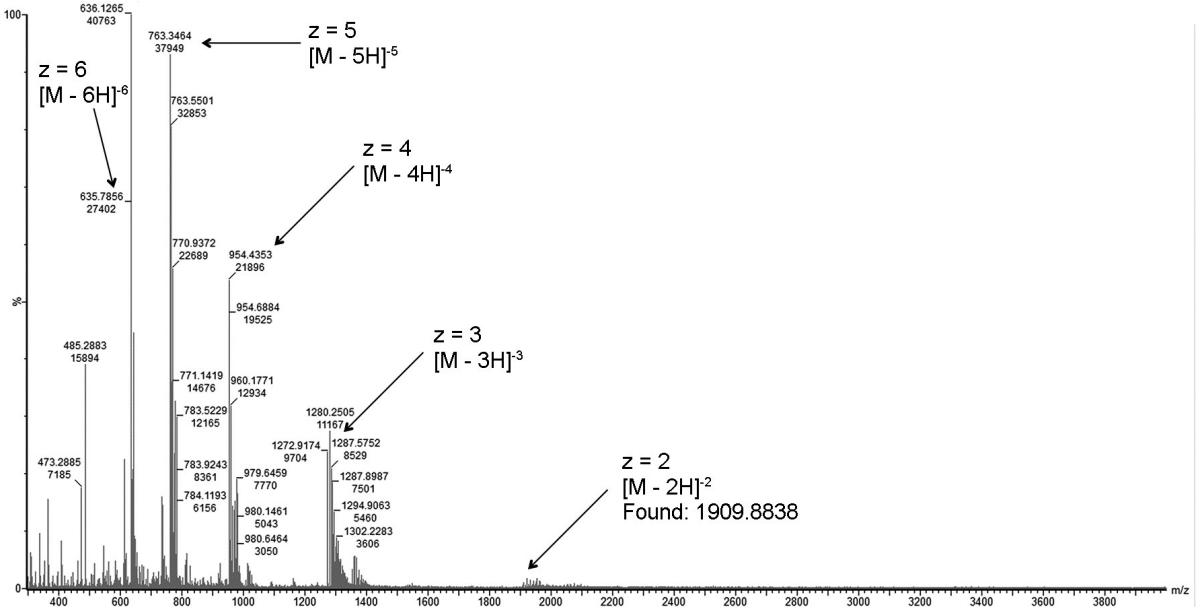


MALDI-TOF MS

Calcd. 3821.6 $[M-H]^-$



ESI MS



ODN **9**

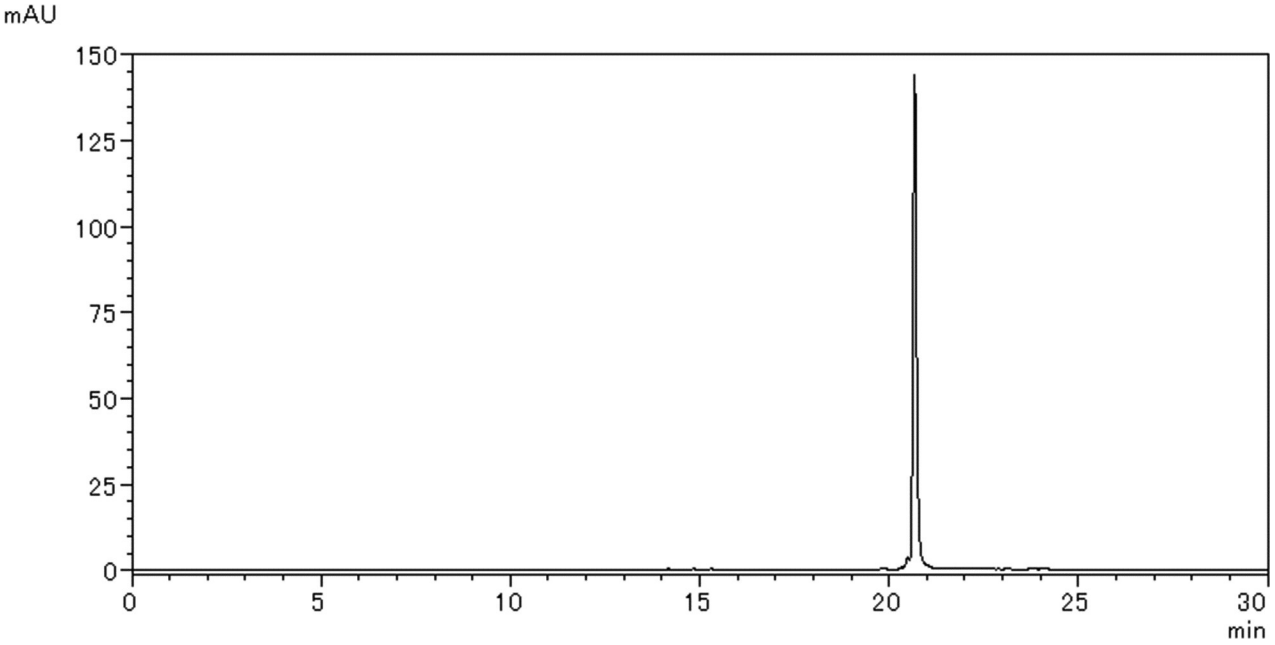
RP-HPLC

Column: Waters XBridge^{TM} OST C18 2.5 μm, 4.6 x 50 mm

Gradient: 5-20% MeCN (over 15 min) in triethylammonium acetate buffer (pH 7.0, 0.1 M)

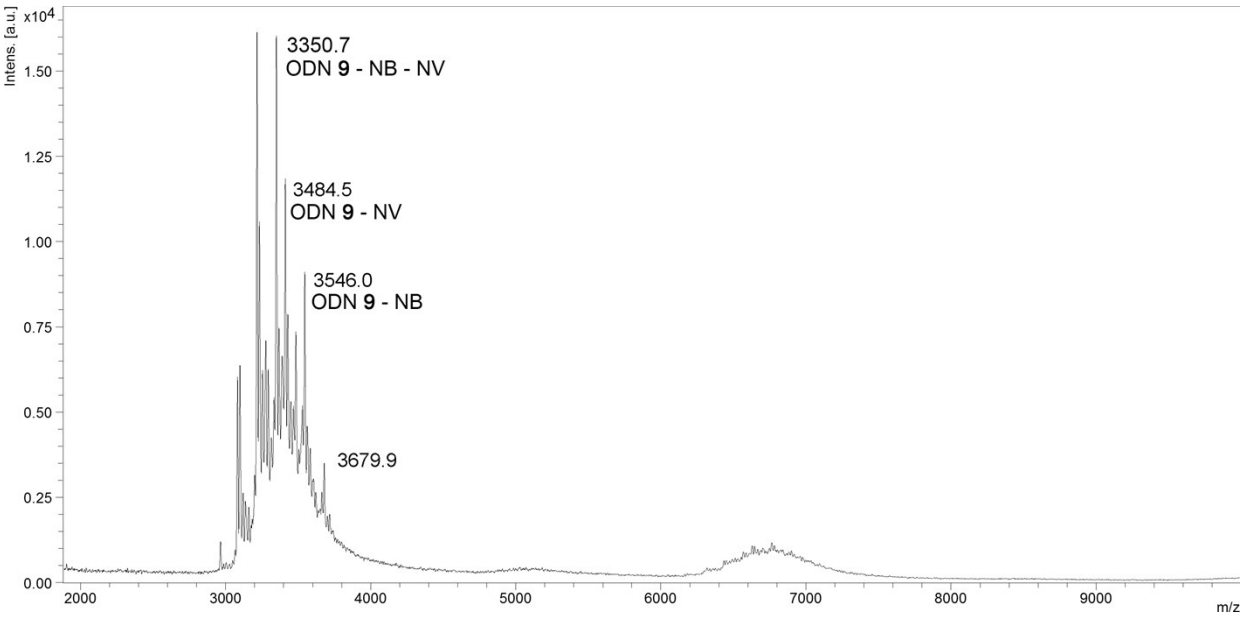
Flow rate: 1.0 mL/min

Column temperature: 50 ˚C

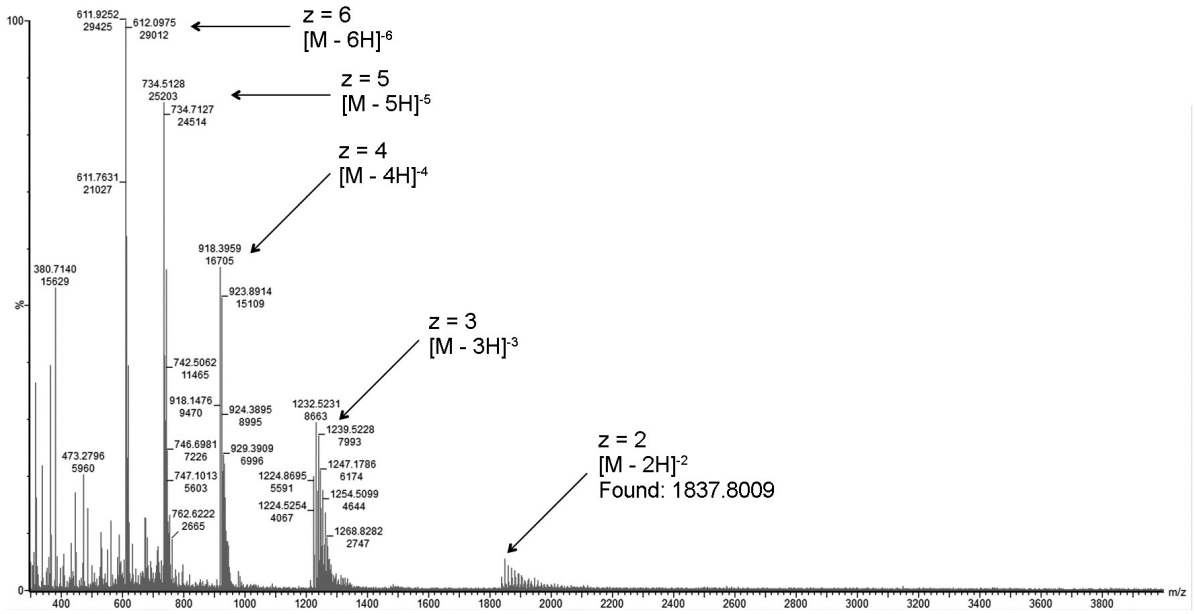


MALDI-TOF MS

Calcd. 3677.6 $[M-H]^-$



ESI MS



4. Photo-reaction of modified ODNs

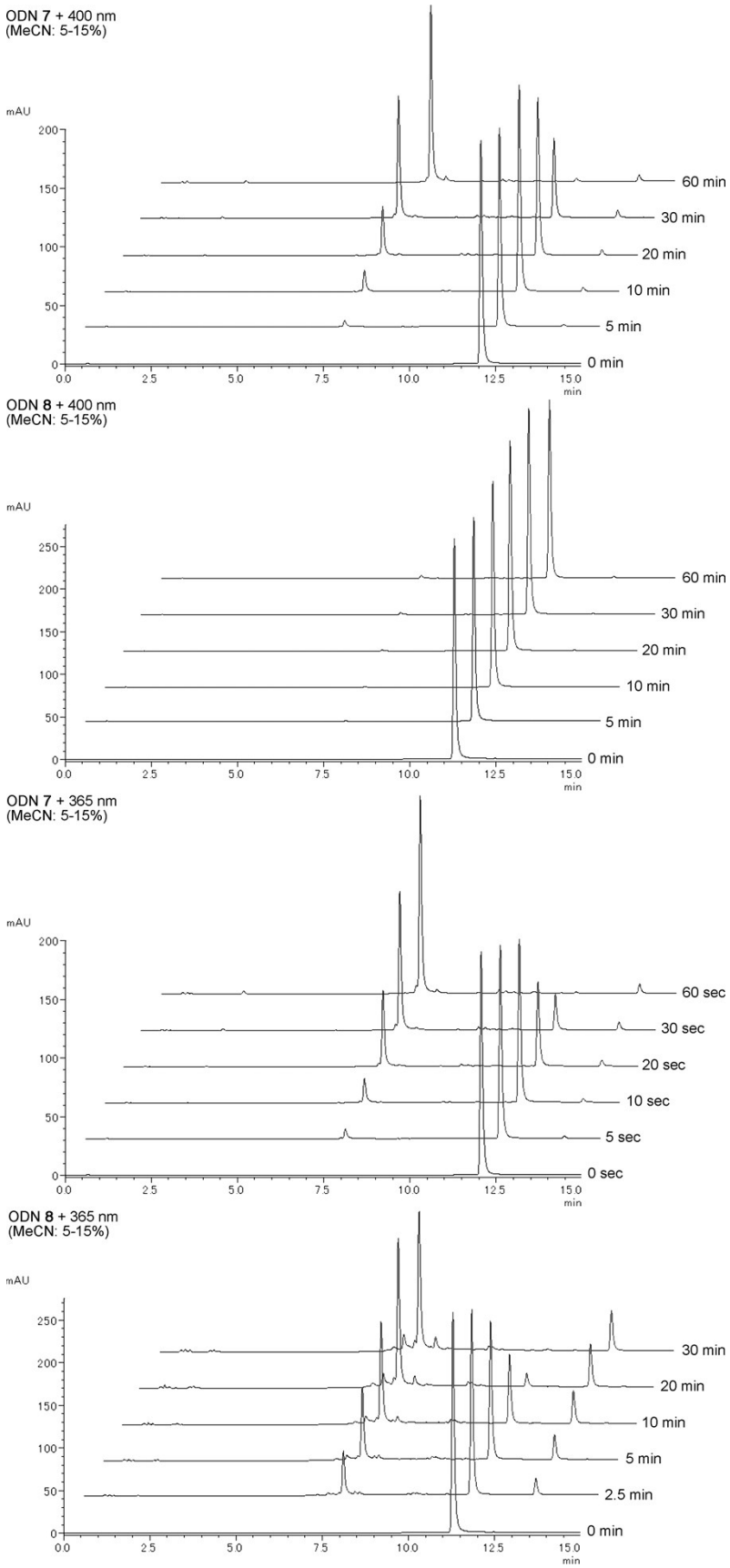


Fig. S1. HPLC analysis of photoreaction of ODN **7** and ODN **8**.