Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Direct and Selective Metal-Free N^6-Arylation of Adenosine Residues for Simple Fluorescence Labeling of DNA and RNA

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1. 1. General Information

All reagents were used from commercial sources without further purification. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV-400 spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane as the internal standard. UV–Vis spectra were recorded at room temperature using a Cary Series UV–Vis spectrophotometer (Agilent Technologies) and a 1-cm path-length quartz cuvette; absorbance changes were measured immediately after UV irradiation of the sample solution in the cuvette. Fluorescence emission spectra were recorded at room temperature using a PF–65000 spectrofluorometer. The confocal Microscopy images were recorded with All-natural oligonucleotides were purchased from Bioneer (Seoul, Republic of Korea). Deoxyribonucleotide triphosphates mixture 2 mM each (dNTPs), nfu special enzyme and buffer were purchased from Enzynomics (Bioneer, Republic of Korea).

Gel Electrophoresis

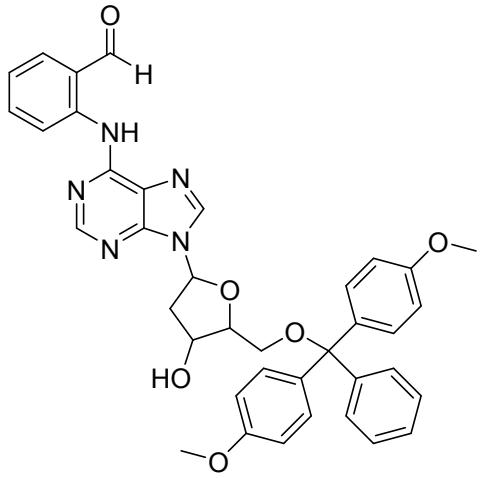
Native polyacrylamide gel electrophoresis (nPAGE, 18%) was adopted to characterize the DNA products. The reaction mixture (10 mL) was mixed with 2.5 mL of 6x loading buffer and loaded into the well. Gel electrophoresis was performed in 1x TBE buffer (89 mM Tris, 89 mM borate, 2 mM EDTA, pH 8.3) at a constant potential of 95/80 V for 90-180 min and a current of 3 mA, followed by scanning on a gel image system. Similarly, RCA products (15 µL) were mixed with the loading buffer (6×, 2.5 µL) and run with 2% agarose gel for 40/60 min (100/50 V) in 1x TBE buffer. The gel was stained with ethidium bromide (EB) and then photographed using a ChemiDoc MP imaging system (Bio-Rad).

2. General Procedure for Fluoroarylation of Deoxyadenosine Nucleoside

Dimethoxytrityl-protected deoxyadenosine (0.3 mmol) and K_3PO_4 (0.6 mmol) were suspended in DMSO (1 mL) in a screw-capped glass vial and then a fluoroaryl compound (0.36 mmol) was added. The resultant mixture was stirred at 100 °C for 16 h. The reaction was monitored using TLC (CH_2Cl_2/MeOH, 95:5). Upon completion of the reaction, the mixture was diluted with EtOAc (20 mL) and washed with H_2O (2 $\times$ 15 mL). The organic phase was separated, dried (anhydrous Na_2SO_4), and evaporated to dryness. The residue was purified through column chromatography to yield the corresponding arylated product.

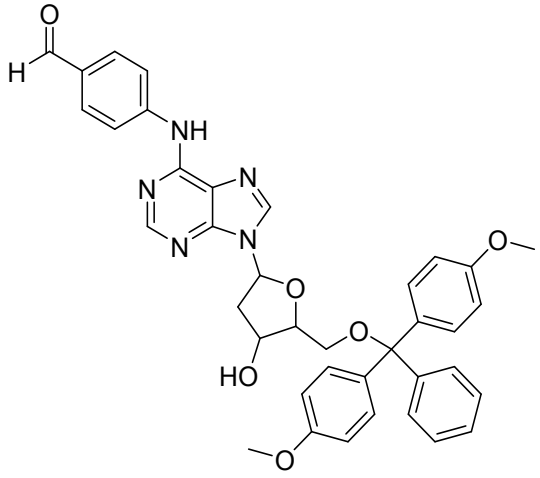
^{1}H and ^{13}C NMR Spectroscopic Data of All DMTdA Fluoroarylation Products

2-((9-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-9*H*-purin-6-yl)amino)benzaldehyde (2a):



White solid, Weight – 109 mg (92%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.48 (s, 1H), 7.97 (s, 1H), 7.87 (q, 1H, J_1 = 6.11 Hz, J_2 = 3.08 Hz), 7.48–7.40 (m, 3H), 7.32–7.19 (m, 8H), 7.13 (d, J = 8.38 Hz, 1H), 7.07 (d, J = 7.49 Hz, 1H), 6.80 (dd, J_1 = 5.94 Hz, J_2 = 2.97 Hz, 4H), 6.47–6.43 (m, 1H), 6.02 (br s, 2H), 5.26–5.24 (m, 1H), 4.47–4.44 (m, 1H), 3.77 (s, 6H), 3.64–3.60 (m, 1H), 3.51–3.47 (m, 1H), 3.29–3.22 (m, 1H), 2.77–2.69 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 189.13, 159.17, 158.56, 155.56, 152.91, 149.49, 144.35, 139.31, 135.79, 135.44, 135.42, 129.96, 129.93, 128.84, 127.99, 127.87, 126.96, 125.24, 121.42, 120.28, 113.43, 113.16, 86.95, 85.05, 83.35, 78.48, 63.22, 55.16, 36.56. **MS (HRMS, FAB$^+$):** Calculated for $C_{38}H_{35}N_5O_6$ ([M + H]): *m*/*z* 657.2666; found: 658.2669.

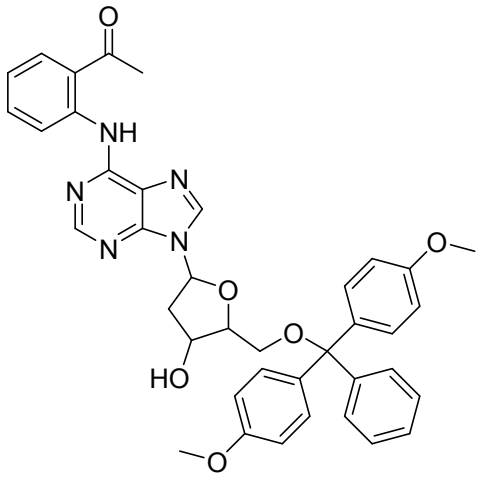
4-((9-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-9*H*-purin-6-yl)amino)benzaldehyde (2b):



White solid, Weight – 102 mg (86%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.90 (s, 1H), 8.27 (s, 1H), 7.96 (s, 1H), 7.80 (d, J = 8 Hz, 2H), 7.43–7.41 (m, 2H), 7.32–7.22 (m, 8H), 7.06 (d, J = 8 Hz, 1H), 7.07 (d, J = 7.49 Hz, 1H), 6.82–6.79 (m, 4H), 6.46 (dd, J_1 = 2.46 Hz, J_2 = 5.85 Hz, 1H), 5.62 (br s, 1H), 5.19–5.15 (m, 1H), 4.42–4.39 (m, 1H), 3.78 (s, 6H), 3.61–3.57 (m, 1H), 3.50–3.46 (m, 1H), 3.18–3.11 (m, 1H), 2.72–

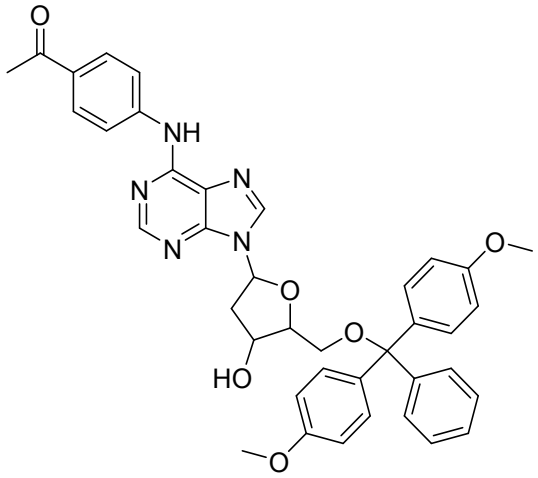
2.67 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 190.68, 161.91, 158.65, 155.39, 153.03, 149.65, 144.38, 139.23, 135.45, 132.05, 130.43, 130.02, 130.01, 128.06, 127.96, 127.07, 120.31, 119.35, 115.59, 113.24, 87.06, 84.94, 83.44, 78.28, 63.37, 55.23, 36.78. **MS (HRMS, FAB$^+$):** Calculated for $C_{38}H_{35}N_5O_6$ ([M + H]): *m*/*z* 657.2666; found: 658.2663.

1-(2-((9-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-9*H*-purin-6-yl)amino)phenyl)ethan-1-one (2c):



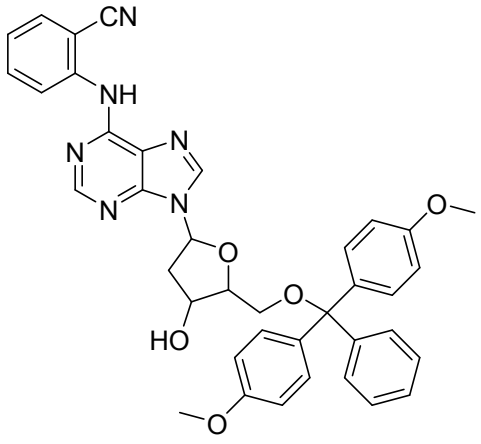
Light yellow solid, Weight – 78 mg (65%); **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.34 (s, 1H), 8.09 (s, 1H), 7.63 (dd, J_1 = 5.91 Hz, J_2 = 1.78 Hz, 1H), 7.51–7.47 (m, 1H), 7.36–7.31 (m, 5H), 7.22–7.17 (m, 6H), 7.07 (t, *J* = 7.74 Hz, 1H), 6.79 (t, *J* = 9.29 Hz, 4H), 6.44 (t, *J* = 6.72 Hz, 1H), 5.51–5.47 (m, 1H), 4.32 (q, *J* = 4.53 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.48–3.41 (m, 2H), 3.31–3.26 (m, 1H), 2.69–2.63 (m, 2H), 2.54 (s, 3H). **^{13}C NMR (DMSO-d_6, 100 MHz):** δ (ppm) 199.66, 159.00, 158.98, 157.09, 157.03, 153.44, 149.90, 145.66, 141.25, 136.32, 136.3, 134.69, 130.82, 130.61, 130.55, 129.39, 128.72, 128.54, 127.61, 121.93, 120.41, 114.91, 114.06, 114.04, 86.81, 84.91, 78.73, 64.05, 55.94, 46.60, 35.74, 32.85. **MS (HRMS, FAB$^+$):** Calculated for $C_{39}H_{37}N_5O_6$ ([M + H]): *m*/*z* 671.2822; found: 672.2824.

1-(4-((9-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-9*H*-purin-6-yl)amino)phenyl)ethan-1-one (2d):



White solid, Weight – 65 mg (54%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.28 (s, 1H), 7.98 (s, 1H), 7.89 (d, *J* = 8.89 Hz, 2H), 7.41 (d, *J* = 7.02 Hz, 2H), 7.32–7.22 (m, 8H), 6.98 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 1.77 Hz, 2H), 6.80 (d, *J* = 1.77 Hz, 2H), 6.44 (q, *J* = 4.67 Hz, 1H), 5.67 (br s, 2H), 5.17–5.15 (m, 1H) 4.41–4.39 (m, 1H), 3.78 (s, 6H), 3.59–3.55 (m, 1H), 3.49–3.45 (m, 1H), 3.15–3.08 (m, 1H) 2.71–2.67 (m, 1H), 2.56 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 196.64, 160.79, 158.64, 155.41, 153.01, 149.66, 144.39, 139.19, 135.48, 135.46, 130.87, 130.68, 130.03, 128.07, 127.95, 127.04, 115.0, 113.23, 87.03, 84.91, 83.51, 78.10, 63.42, 55.22, 36.89, 26.34. **MS (HRMS, FAB$^+$):** Calculated for $C_{39}H_{37}N_5O_6$ ([M + H]): *m*/*z* 671.2822; found: 672.2825.

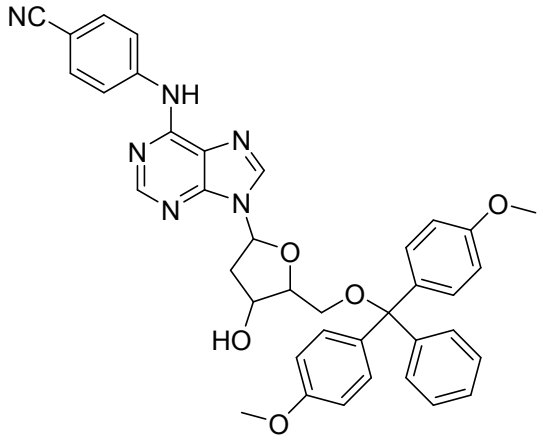
2-((9-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-9*H*-purin-6-yl)amino)benzonitrile (2e):



White solid, Weight – 110 mg (93%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.14 (s, 1H), 7.87 (s, 1H), 7.56–7.52 (m, 1H), 7.38–7.32 (m, 2H), 7.24–7.12 (m, 9H), 6.98 (t, *J* = 7.56 Hz, 1H), 6.75–6.71 (m, 4H), 6.37 (q, *J* = 4.66 Hz, 1H), 5.66 (br s, 2H), 5.15–5.13 (m, 1H), 4.38–4.35 (m, 1H), 3.71 (s, 6H), 3.61–3.57 (m, 1H), 3.43–3.38 (m, 1H), 3.34–3.27 (m, 1H), 2.66–2.60 (m, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 158.71,

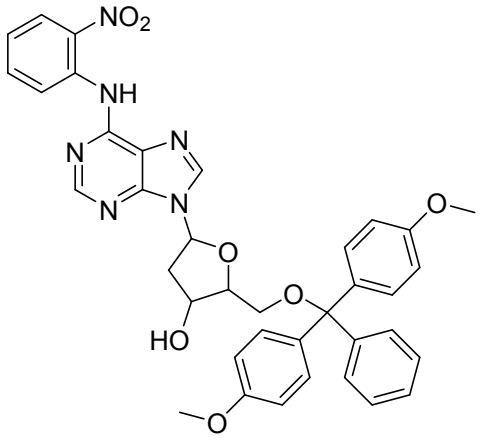
158.58, 155.42, 152.81, 149.57, 144.42, 139.97, 135.50, 134.28, 134.11, 133.54, 130.01, 129.99, 128.05, 127.90, 126.99, 121.48, 120.56, 116.57, 116.38, 113.39, 113.18, 102.69, 87.01, 85.49, 83.07, 79.12, 63.16, 55.21, 35.73. **MS (HRMS, FAB$^+$):** Calculated for $C_{38}H_{34}N_6O_5$ ([M + H]): *m*/*z* 654.2669; found: 655.2671.

4-((9-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-9*H*-purin-6-yl)amino)benzonitrile (2f):



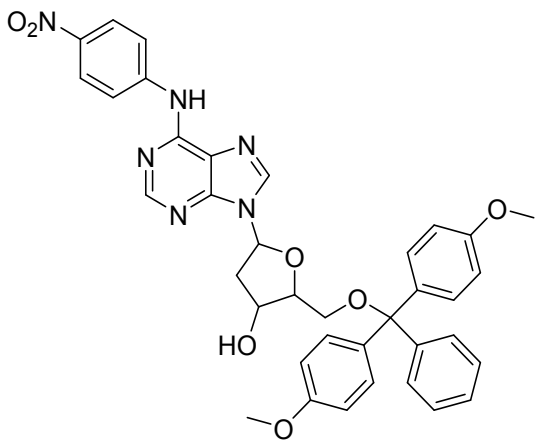
White solid, Weight – 113 mg (96%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.19 (s, 1H), 7.87 (s, 1H), 7.48–7.46 (m, 2H), 7.34–7.32 (m, 2H), 7.24–7.18 (m, 8H), 6.97–6.95 (m, 2H), 6.75–6.72 (m, 4H), 6.80 (q, *J* = 4.69 Hz, 1H), 5.57 (br s, 2H), 5.06–5.05 (m, 1H), 4.30–4.28 (m, 1H), 3.71 (s, 6H), 3.54–3.50 (m, 1H), 3.42–3.38 (m, 1H), 3.10–3.04 (m, 1H), 2.62–2.5 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 160.27, 158.70, 155.45, 153.05, 149.66, 144.38, 139.27, 135.41, 134.17 130.04, 130.03, 128.07, 128.01, 127.14, 120.37, 118.99, 116.05, 113.28, 104.77, 87.17, 84.98, 83.29, 78.38, 63.33, 55.28, 36.57. **MS (HRMS, FAB$^+$):** Calculated for $C_{38}H_{34}N_6O_5$ ([M + H]): *m*/*z* 654.2669; found: 655.2653.

2-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-5-(6-((2-nitrophenyl)amino)-9*H*-purin-9-yl)tetrahydrofuran-3-ol (2g):



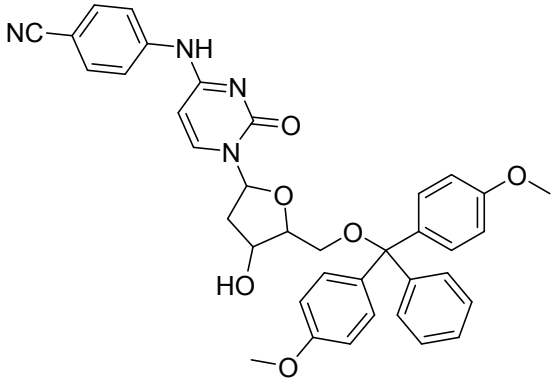
Yellow solid, Weight – 114 mg (94%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.14 (s, 1H), 7.86 (s, 1H), 7.80–7.78 (m, 1H), 7.37–7.32 (m, 3H), 7.25–7.14 (m, 9H), 7.02–6.98 (m, 1H), 6.74–6.71 (m, 4H), 6.34 (q, *J* = 4.67 Hz, 1H), 5.60 (br s, 2H), 5.17– 5.15 (m, 1H), 4.38–4.35 (m, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.60–3.56 (m, 1H), 3.41–3.37 (m, 1H), 3.32–3.25 (m, 1H), 2.65–2.59 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 158.64, 155.46, 152.87, 150.40, 149.64, 144.47, 140.46, 140.0, 135.55, 134.04, 130.05, 130.03, 128.10, 127.95, 127.04, 125.94, 121.14, 120.61, 115.72, 113.23, 87.06, 85.54, 83.03, 79.75, 63.15, 55.26, 35.80. **MS (HRMS, FAB$^+$):** Calculated for $C_{37}H_{34}N_6O_7$ ([M + H]): *m*/*z* 674.2567; found: 675.2571.

2-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-5-(6-((4-nitrophenyl)amino)-9*H*-purin-9-yl)tetrahydrofuran-3-ol (2h):



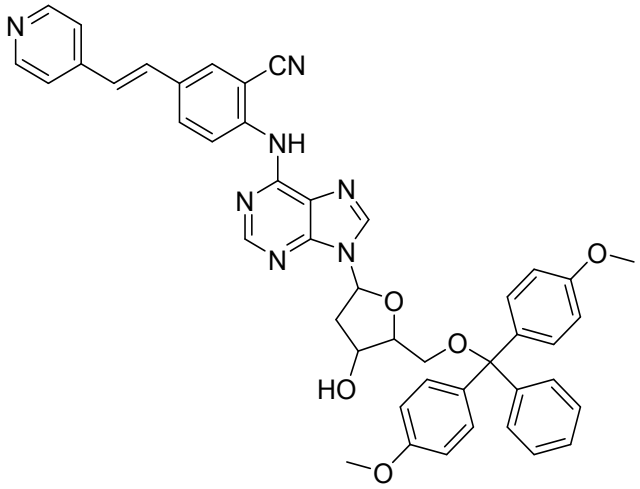
Yellow solid, Weight – 108 mg (89%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.27 (s, 1H), 8.16–8.14 (m, 2H), 7.94 (s, 1H), 7.42–7.40 (m, 2H), 7.31–7.23 (m, 8H), 7.05–7.23 (m, 2H), 6.83–6.80 (m, 4H), 6.45 (q, 1H, *J* = 4.68 Hz), 5.66 (br s, 2H), 5.18–5.16 (m, 1H), 4.39–4.37 (m, 1H), 3.79 (s, 6H), 3.63–3.58 (m, 1H), 3.50–3.47 (m, 1H), 3.21–3.14 (m, 1H), 2.71–2.66 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 161.94, 158.69, 155.44, 153.02, 149.61, 144.28, 141.96, 139.24, 135.38, 135.36, 130.02, 130.0, 128.04, 127.99, 127.13, 126.02, 120.33, 115.31, 113.26, 87.17, 84.95, 83.3, 78.78, 63.25, 55.24, 36.52. **MS (HRMS, FAB$^+$):** Calculated for $C_{37}H_{34}N_6O_7$ ([M + H]): *m*/*z* 674.2567; found: 675.2569.

4-((1-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-2-oxo-1,2-dihydropyrimidin-4-yl)amino)benzonitrile (3f):



White solid, Weight – 109 mg (92%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, 1H, *J* = 7.84 Hz), 7.49 (d, 2H, *J* = 8.91 Hz), 7.40–7.31 (m, 2H), 7.29–7.26 (m, 9H), 6.84–6.81 (m, 5H), 6.35–6.32 (m, 1H), 5.57 (d, 1H, *J* = 7.41 Hz), 4.85–4.84 (m, 1H), 4.26–4.27 (m, 1H), 3.79–3.78 (m, 6H), 3.58–3.54 (m, 1H), 3.47–3.44 (m, 1H), 2.81–2.75 (m, 1H). **MS (HRMS, FAB$^+$):** Calculated for $C_{37}H_{34}N_4O_6$ ([M + H]): *m*/*z* 630.2557; found: 631.2564.

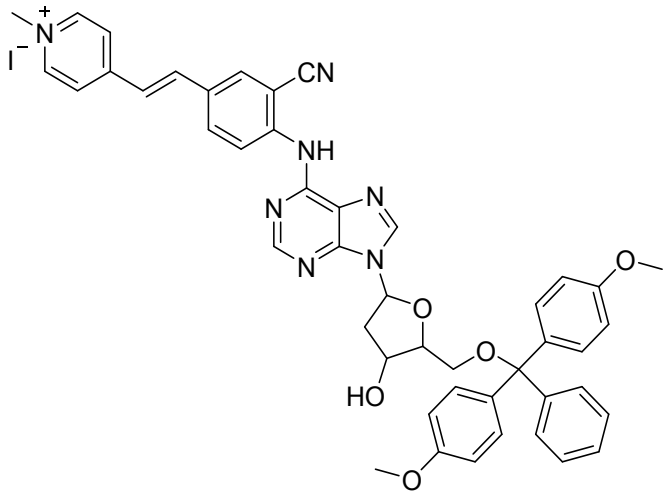
(*E*)-2-((9-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-9*H*-purin-6-yl)amino)-5-(2-(pyrid-4-yl)vinyl)benzonitrile (2h):



Pale yellow solid, Weight – 89 mg (65%); **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.58 (d, *J* = 5.96 Hz, 2H), 8.36 (d, *J* = 4.93 Hz, 1H), 8.26–8.23 (m, 2H), 8.08–8.03 (m, 2H), 7.58–7.56 (m, 1H), 7.54–7.53 (m, 2H), 7.4–7.32 (m, 3H), 7.25–7.18 (m, 8H), 6.82–6.78 (m, 4H), 6.36 (t, *J* = 6.38 Hz, 1H), 5.36 (br s, 1H), 4.49–4.48 (m, 1H), 4.00–3.97 (q, 1H, *J* = 5.8 Hz, 1H), 3.72 (s, 6H), 3.17 (d, *J* = 4.64 Hz, 2H), 2.91–2.85 (m, 2H), 2.36–2.30 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 158.46, 156.52, 152.96, 150.63, 149.81, 149.58, 145.36, 144.12, 139.90, 136.09, 136.02, 134.91, 134.82, 134.53, 134.5, 132.33, 130.27, 130.15, 130.27, 130.15, 130.09, 128.85, 128.83, 128.17, 128.14, 127.04124.88, 121.43, 119.73, 117.68, 117.48, 114.34,

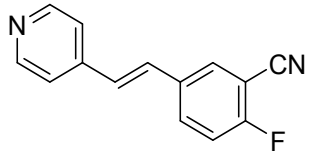
113.54, 104.17, 86.22, 85.88, 83.79, 71.15, 64.52, 55.46, 46.14. **MS (HRMS, FAB$^+$):** Calculated for $C_{45}H_{39}N_7O_5$ ([M + H]): *m*/*z* 758.3013; found: 758.3019.

(*E*)-4-(4-((9-(5-((Bis(4-methoxyphenyl)(phenyl)methoxy)methyl)-4-hydroxytetrahydrofur-2-yl)-9*H*-purin-6-yl)amino)-3-cyanostyryl)-1-methylpyridin-1-ium Iodide (3f):



Orange red solid, Weight – 47 mg (943%); **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.91 (d, *J* = 6.11 Hz, 2H), 8.34 (d, *J* = 5.64 Hz, 1H), 8.23–8.19 (m, 3H), 8.14–8.08 (m, 2H), 7.99 (d, *J* = 16.44 Hz, 1H), 7.70–7.61 (m, 2H), 7.34–7.32 (m, 2H), 7.24–7.19 (m, 8H), 6.82–6.77 (m, 4H), 6.35 (t, *J* = 6.38 Hz, 1H), 5.36–5.35 (m, 1H), 4.48 (s, 1H), 4.29 (s, 3H), 3.98–3.97 (m, 1H), 3.72 (s, 6H), 3.17 (d, *J* = 4.64 Hz), 2.9–2.85 (m, 2H), 2.35–2.28 (m, 1H). **^{13}C NMR (400 MHz, DMSO-d_6):** δ (ppm) 158. 96, 152.21, 149.57, 14, 2H 5.89, 145.35, 139.91, 137.45, 136.08, 136.02, 135.93, 133.39, 132.7, 103.14, 130.09, 128.17, 128.14, 127.05, 126.91, 126.0, 125.98, 124.33, 119.72, 118.09, 117.89, 114.13, 113.54, 113.53, 101.73, 87.96, 86.21, 85.87, 83.79, 71.14, 64.51, 55.48, 47.64, 46.25, 21.00. **MS (HRMS, FAB$^+$):** Calculated for $C_{46}H_{42}N_7O_5I$ ([M + H]): *m*/*z* 772.3242; found: 772.3239.

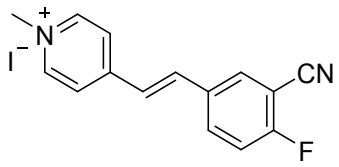
(*E*)-2-Fluoro-5-(2-(pyrid-4-yl)vinyl)benzonitrile (Y):



White solid, Weight – 556 mg (64%); **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.58–8.57 (m, 2H), 7.76–7.70 (m, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.26–7.19 (m, 2H), 6.98 (d, *J* = 18.0 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 162.08 (*J* = 260.8 Hz), 150.35, 149.94, 143.50, 133.59 (*J* = 3.77 Hz), 133.13 (*J* = 8.79 Hz), 131.58,

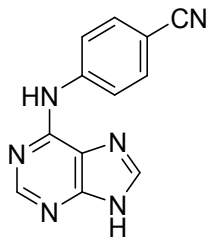
129.50, 128.52 (*J* = 8.79 Hz), 124.20, 120.96, 117.08 (*J* = 22.38 Hz), 113.61, 102.08 (*J* = 22.38 Hz); **MS (HRMS, FAB$^+$):** Calculated for $C_{15}H_{12}N_2FI$ ([M + H]): *m*/*z* 224.0750; found: 224.0753.

((*E*)-4-(3-Cyano-4-fluorostyryl)-1-methylpyridin-1-ium Iodide (Z):



Yellow solid, Weight – 798 mg (95%); **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.92 (d, *J* = 7.48 Hz, 2H), 8.35 (dd, J_1= 3.97 Hz, J_2= 2.15 Hz, 1H), 8.20 (d, J_1= 6.61 Hz, 2H), 8.16–8.12 (m, 1H), 8.01 (d, *J* = 17.84 Hz, 1H), 7.72–7.63 (m, 2H), 4.30 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 163.27 (*J* = 248.4 Hz), 152.18, 145.91, 137.44, 136.05 (*J* = 9.66 Hz), 133.38, 128.24, 126.90, 120.0, 117.08 (*J* = 2.07 Hz), 124.31, 118.01 (*J* = 20.31 Hz), 114.15, 101.65 (*J* = 20.31 Hz), 47.63; **MS (HRMS, FAB$^+$):** Calculated for $C_{15}H_{12}N_2FI$ ([M + H]): *m*/*z* 239.0979; found: 239.0983.

^{6}N-(4CyanoPhenyl)Adeneine:



White solid, Weight – 77 mg (65%); **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.47 (s, 1H), 8.25 (s, 1H), 8.20 (d, J_1= 6.61 Hz, 2H), 7.83–7.81(m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) 160.77, 155.31, 151.26, 149.23, 140.98, 134.85, 119.71, 119.48, 116.86, 103.92; **MS (HRMS, FAB$^+$):** Calculated for $C_{15}H_{12}N_2FI$ ([M + H]): *m*/*z* 237.0810; found: 237.0816.

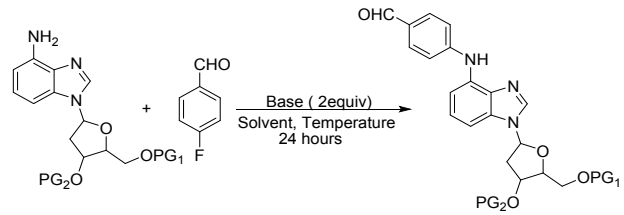
3. Discussion of procedure for Fluoroarylation of Deoxyadenosine Nucleosides

When using K_2CO_3 as the base and DMF as the solvent and heating at 90 °C for 24 h, no product was obtained (Table S1, entry 1). Suspecting that the free OH groups were the reason behind the failed reaction, we protected them with *tert*-butyldimethylsilyl groups and repeated the reaction, but again observed no product (Table S1, entry 2). Next, we changed the base to NaH (60% in mineral oil) to ensure more effective deprotonation of the amino group of the deoxyadenosine moiety, but found only that complete degradation of the starting material had occurred (Table S1, entry 3). Changing the solvent to DMSO also led to no reaction (Table S1, entry 4). Gratifyingly, when we changed the base to K_3PO_4 (which resembles the phosphate backbone of a nucleic acid) in DMSO at 90 °C, the arylation did

proceed, but the ^{1}H NMR spectrum of the product **2a1** (Supporting Information, Fig. S41) suggested that multiple arylation had occurred, on both the OH groups at the 5′ and 3′ ends (Table S1, entry 5). When we applied a reported procedure for the arylation of unprotected deoxyadenosine using *p*-bromobenzaldehyde,[31] we observed very slow conversion and a low yield (ca. 10%, by TLC; Table S1, entry 6). To our delight, protecting the 5′ end with a DMT group and reacting with *p*-fluorobenzaldehyde in DMSO using K_3PO_4 as the base provided the product in 84% yield after 24 h (Table S1, entry 7). Increasing the temperature and shortening the reaction time to 16 h resulted in a slightly improved yield (86%; Table S1, entry 8).

When adenine alone was subjected to standard reaction condition, the ^{6}N-arylated product was obtained solely.

4. Table S1: Control Table for N-Arylation of Deoxyadenosine Derivatives



Entry	Protecting Group (PG)	Base	Solvent	Temp. (°C)	Yield[a] (%)
1	PG1-H, PG2-H	K_2CO_3	DMF	90	0
2	PG1-TBS, PG2-TBS	K_2CO_3	DMF	90	0
3	PG1-TBS, PG2-TBS	NaH (60%)	DMF	RT-90	0
4	PG1-H, PG2-H	K_2CO_3	DMSO	90	0
5	PG1-H, PG2-H	K_3PO_4	DMSO	90	0[d]
6[b]	PG1-H, PG2-H	K_3PO_4	DMSO	90	ca. 10
7	PG1-DMT, PG2-H	K_3PO_4	DMSO	90	84
8[c]	PG1-DMT, PG2-H	K_3PO_4	DMSO	110	86

[a]Isolated yield. [b]*p*-Bromobenzaldehyde (1.2 equiv), DMEDA (1 equiv), and CuI (1 equiv) were used. [c]Reaction time was 16 h. [d]Diarylated side product obtained as the major product (62%; ^{1}H NMR, Fig. S51).

5. Photophysical properties of the Arylated DMT nucleosides

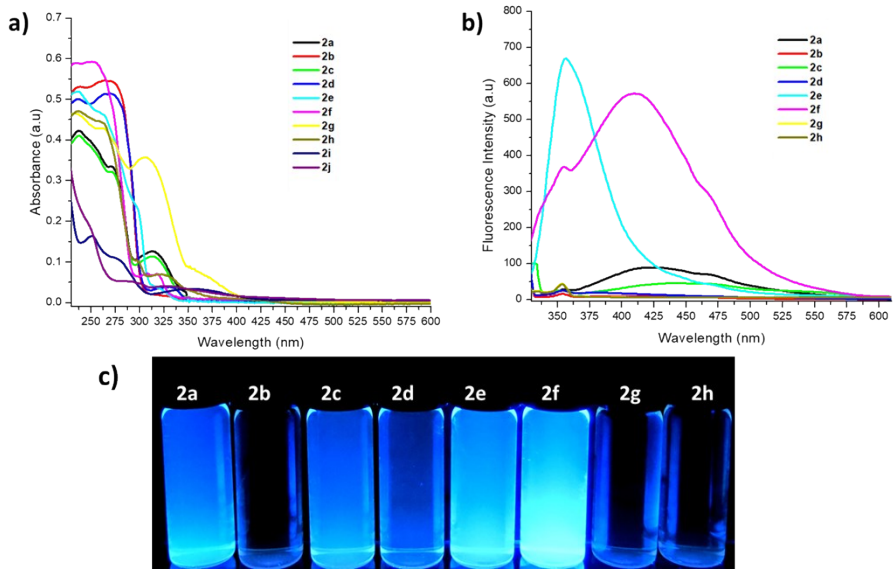
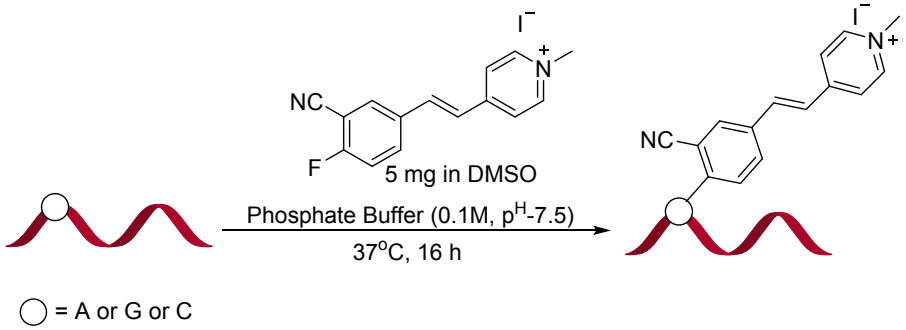


Figure S1: (a) UV–Vis absorption and (b) fluorescence spectra of the arylated DMTdA derivatives **2a**–**h** (16 mM) in DMSO. (c) Photograph of solutions of the arylated DMT deoxyadenosine derivatives **2a**–**h** (16 mM) in DMSO under long-range UV light (365 nm).

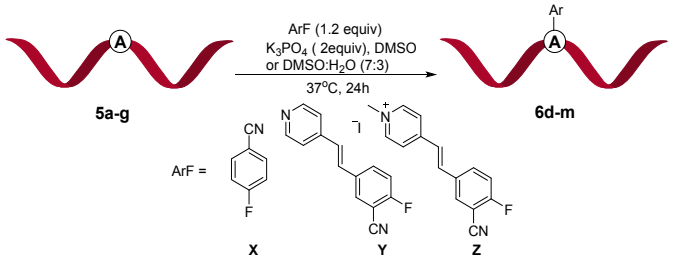
6. Table S2: Arylation of Deoxyadenosine-, Deoxycytosine-, and Deoxyguanosine-Containing Polythymine Oligonucleotides with Z in Phosphate Buffer

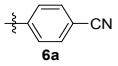
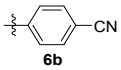
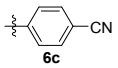
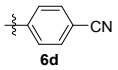
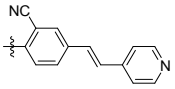
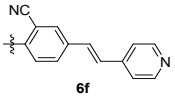
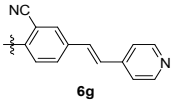
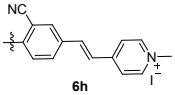
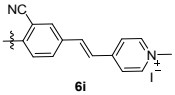
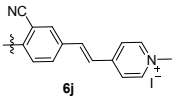


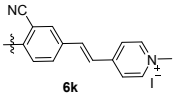
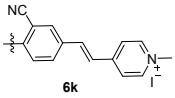
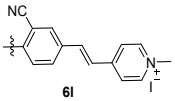
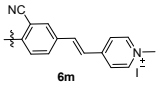
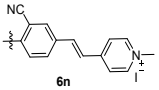
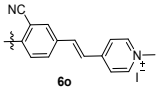
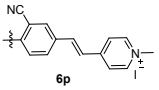
Entry	Oligonucleotide	Yield (%)[a]	SM (%)[b]
1	5′-PO_4^{3-}-**A**TTTTTTTTTTTTTT (**5a**)	64	36
2	5′-PO_4^{3-}-**C**TTTTTTTTTTTTTT (**7a**)	2	98
3	5′-PO_4^{3-}-**G**TTTTTTTTTTTTTT (**7b**)	5	95

[a]Product yield determined by relative integration of peaks in HPLC trace at 260 nm (Figs. S26–S28). [b]SM = Recovered starting material (oligonucleotide). Conditions: Oligonucleotide (100 pmol/μL, 50 μL) and **Z** (5 mg) in phosphate buffer (0.1M, pH 7.5, 200 μL) at 37 °C for 16 h.

7. Table S3: Fluoroarylation of Oligonucleotides with probes X , Y and Z.



Entry	Oligonucleotide	Group	Yield of 6a-k (%)[a]	SM (%)	Calculated MALDI	Observed MALDI[b]
1	5′-PO_4^{3-}ATTTTTTTTTTTTTT (5a)	 6a	75	25	4692.84	4692.71
2	5′-PO_4^{3-}ATTTTTTTATTTTTT (5b)	 6b	73	27	4804.85	4802.17
3	5′-PO_4^{3-}ATTTTTTATTTTTTA (5c)	 6c	70	30	4916.86	4908.71
4	5′-PO_4^{3-} TTTTTTTTTTTTTTATTTTTATTTTTATTT (5d)	 6d	72	28	9480.39	9425.04
5	5′-PO_4^{3-}ATTTTTTTTTTTTTT (5a)	 6e	77	16	4796.08	4801.00
6	5′-PO_4^{3-}ATTTTTTTATTTTTT (5b)	 6f	73	15	5010.48	5009.32
7	5′-PO_4^{3-}ATTTTTTATTTTTTA (5c)	 6g	59	13	5226.58	5223.11
8	5′-PO_4^{3-}ATTTTTTTTTTTTTT (5a)	 6h	99	0	4810.83	4806.33
9	5′-PO_4^{3-}ATTTTTTTATTTTTT (5b)	 6i	99	0	5041.41	5046.72
10	5′-PO_4^{3-}ATTTTTTATTTTTTA (5c)	 6j	99	0	5271.70	5272.98

11[c]	5′-PO_4^{3-}- GCGTTACGTGTGCTC - 3’ (5e)	 6k	89	11	4874.44	4875.31
12[c]	5′-PO_4^{3-}- GCGTTACGTGTGCTC - 3’ (5e) (ds DNA with complementary sequence)	 6k	0	99	-	-
13[c]	5′-PO_4^{3-}- GGG CGC GGC AGC TTT CGT TTG GCG CCC- 3’(5f) (Hairpin 1)	 6l	99	0	8595.56	8601.16
14[c]	5′-PO_4^{3-}- GGG CAC GGC GGC TTT CGT TTG GTG CCC - 3’(5f) (Hairpin 2)	 6m	0	99	-	-
15[c]	5′-PO_4^{3-}- TG TGG GTG GGT AGG GTG GGT TT- 3’ (5g) (G-Quadraplex)	 6n	89	0	7264.3	7266.67
16[d]	5′-PO_4^{3-}- GCG GCG AGC GCG GCG -3’ (5h) (ssRNA)	 6o	39	0	5199.67	5205.07
17[d]	5′-PO_4^{3-}- GCG GCG AGC GCG GCG -3’ (5h) (ds RNA with complementary sequence)	 6p	0	99	-	-

SM = Recovered Starting Oligonucleotide, [a]Yield = Product yield determined by relative integration in HPLC at 260 nm (Fig. S8-S25). [b]Fig. S29-S41. Condition: 5 mM of Oligonucleotide (in DMSO), 5mM of K_3PO_4, 10mM of p-fluoroarylonitrile in DMSO or DMSO: H_2O (7:3) at 37°C 24h. [c]Oligonucleotide (100 pmol/μL, 50 μL) and **Z** (5 mg) in phosphate buffer (0.1M, pH 7.5, 200 μL) at 37 °C for 24 h. [d]Oligonucleotide (100 pmol/μL, 50 μL) and **Z** (5 mg) in phosphate buffer (0.1M, pH 7.5, 200 μL) and DPEC water 100 μL at 37 °C for 8 h

8. UV-Vis Spectroscopy of the Arylated Oligonucleotides

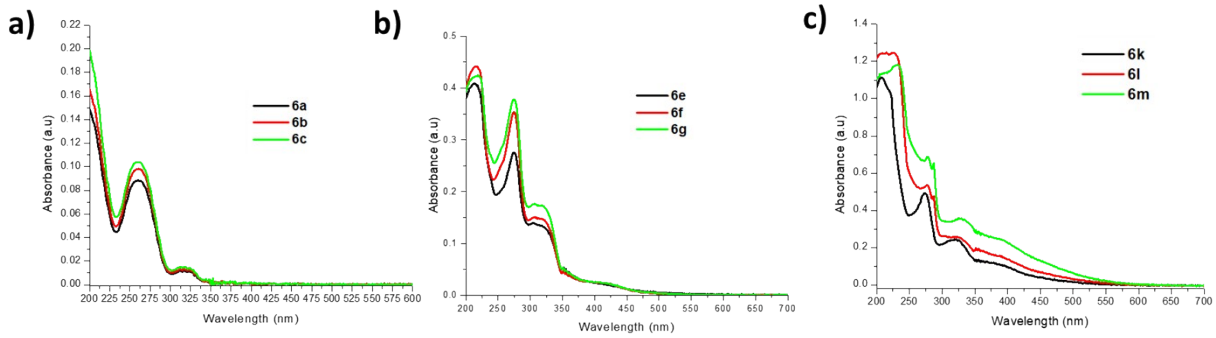


Figure S2: (a) UV–Vis absorption spectra of **6a**–**j** (1 μM each).

9. Excitation dependent emission of 6h

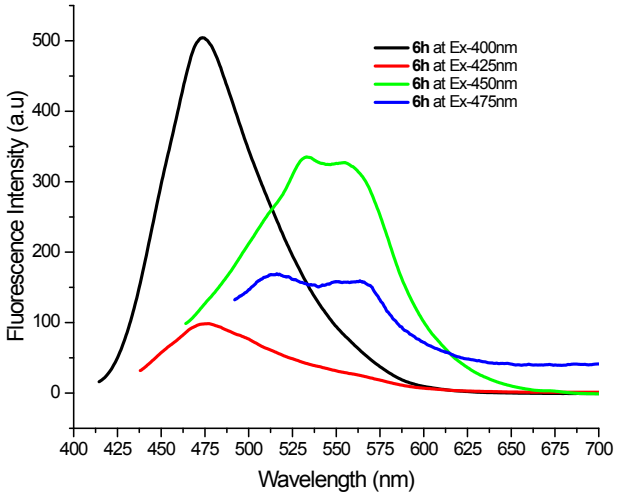


Figure S3: Excitation dependent fluorescence emission of oligonucleotide **6h**.

10. PAGE of 6a-c

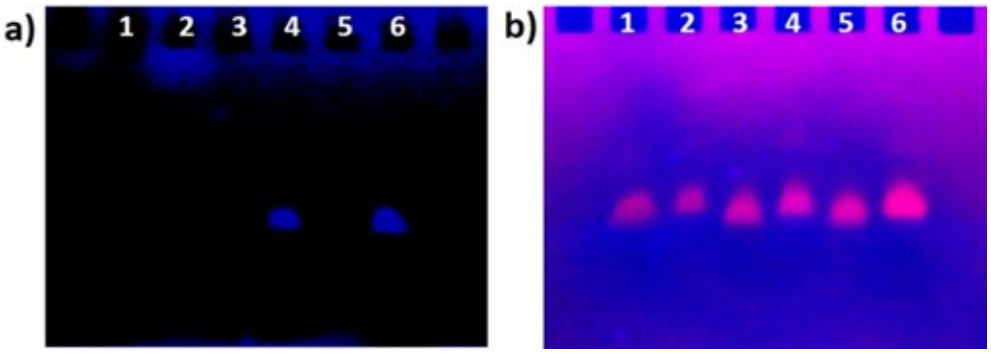


Figure S4: PAGE analysis of arylated oligonucleotides (a) before and (b) after staining with EtBr. Lane 1: 5a; lane 2: 6a; lane 3: 5b; lane 4: 6b; lane 5: 5c; lane 6: 6c. Note: PAGE gel analysis was performed using a 0.1 mM concentration of the oligonucleotides.

11. Time dependent fluorescence to know the optimum reaction time

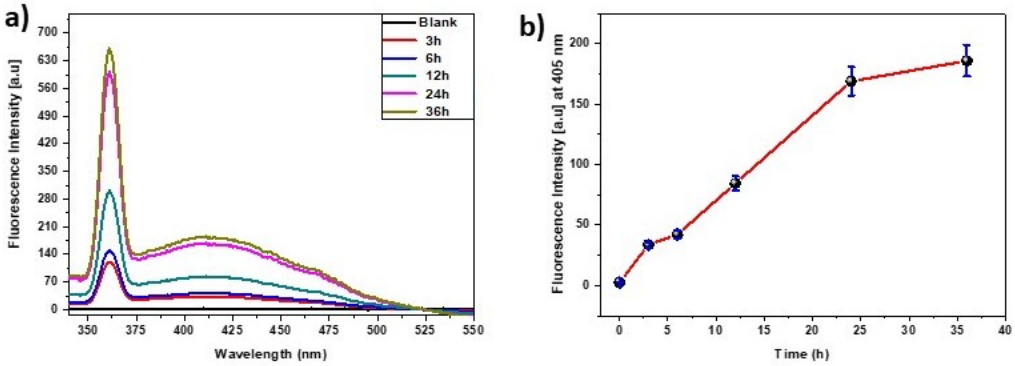


Figure S5: (a) Time-dependent fluorescence spectra of **6a** (0.1 mM) at 320 nm (I_{ex}). (b) Fluorescence intensity at 405 nm (I_{em}) plotted with respect to time (error bound: <±5%).

12. Primer Extension of Arylated Oligonucleotide 6d and Corresponding Melting Point Data

Figure S6. ^{32}P labeling experiment characterization for primer extension on arylated oligonucleotide 6d using A_{14} as primer. Lane 1: ^{32}P-A_{14} (see the supporting information for detailed ^{32}P labeling and duplex formation with 5d and 6d); Lane 2: ^{32}P-A_{14}:5d duplex primer extension using *nfu-special* DNA polymerase (2U) at 37°C for 24h; Lane 3: ^{32}P-A_{14}:6d duplex primer extension using *nfu*-special DNA polymerase (2U) at 37°C for 24h. All polymerase extensions were stopped by adding twice the amount of stop buffer (10 mM EDTA, 10 mM NaOH, 0.1% xylene cyanol, and 0.1% bromophenol blue in formamide). All product solutions were loaded onto a 20% denaturing polyacrylamide gel.

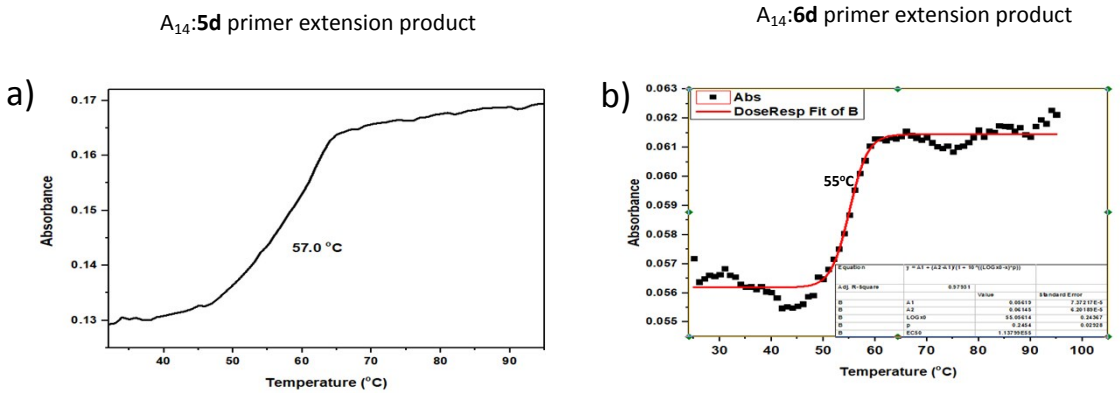
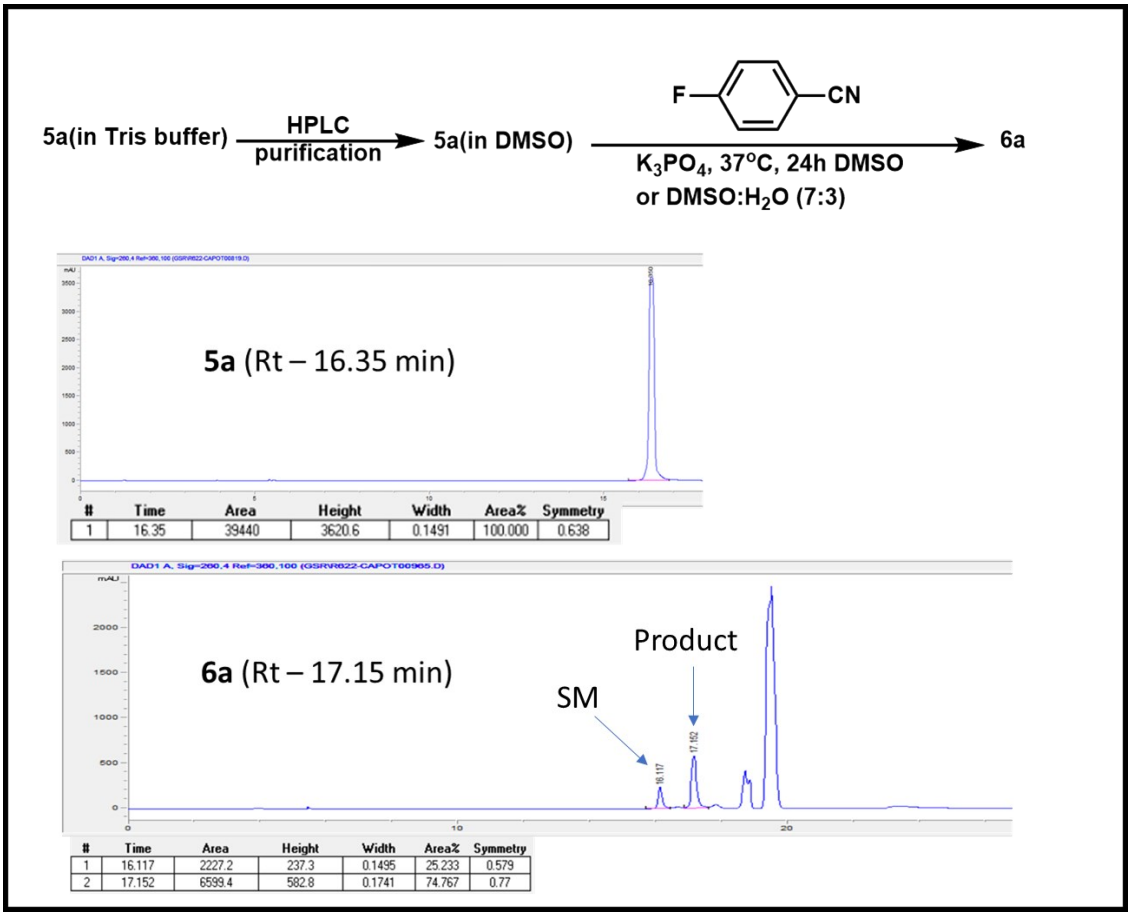


Figure S7: Melting temperatures of primer extension products using (a) A_{14} primer:**5d** duplex and (b) A_{14} primer:**6d** duplex. Duplexes were prepared by annealing 0.1 mM solutions of each at 95 °C and primer extensions were executed using dNTPs (2 mM) and *nfu-special* DNA polymerase (2U) at 37 °C for 24 h and purified using a QIAquick nucleotide removal kit. Melting temperatures were measured at 260 nm over the temperature range from 25 to 95 °C at a heating rate of 1 °C/min.

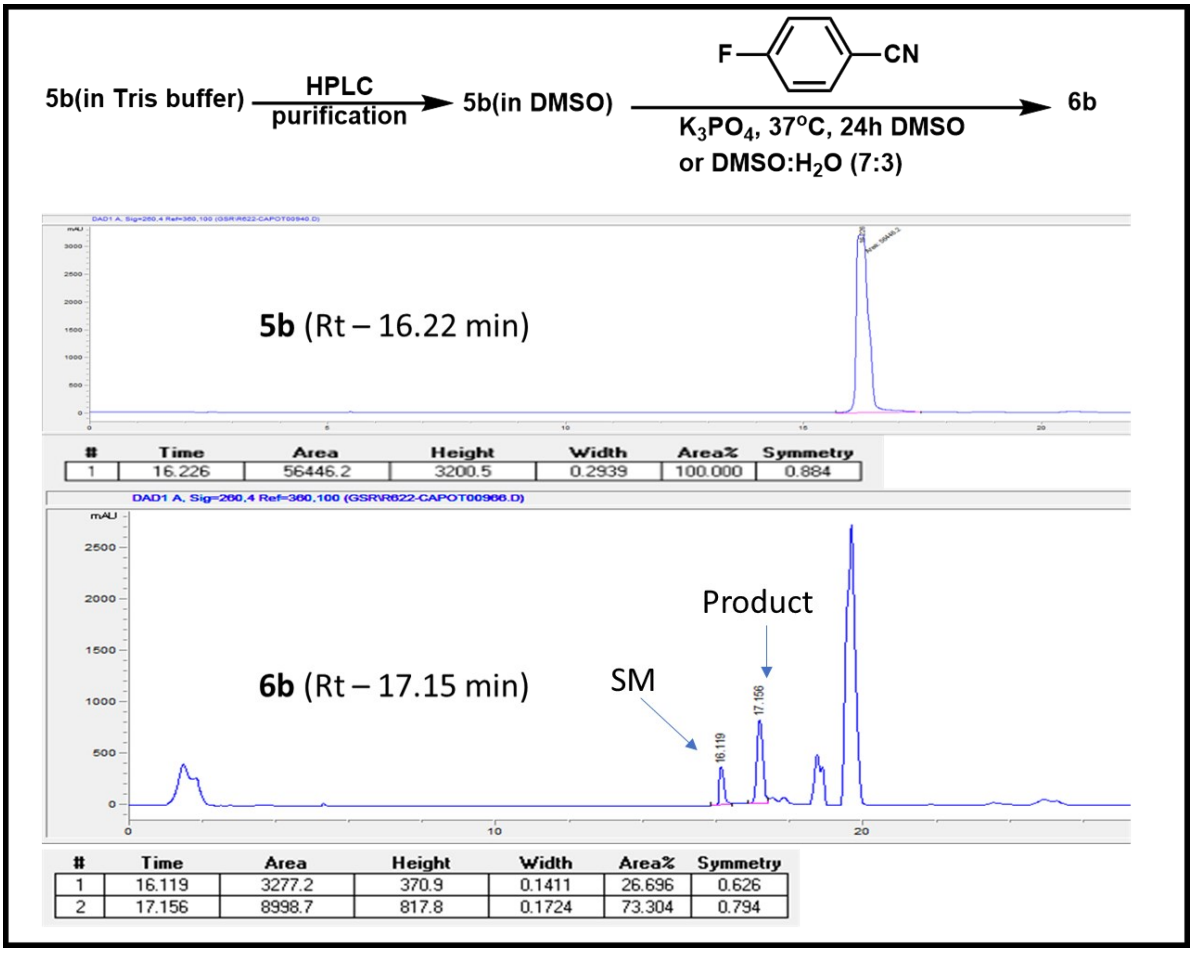
13. HPLC Data of Arylated Oligonucleotides



#	Time	Area	Height	Width	Area%	Symmetry
1	16.35	39440	3620.6	0.1491	100.000	0.638

#	Time	Area	Height	Width	Area%	Symmetry
1	16.117	2227.2	237.3	0.1495	25.233	0.579
2	17.152	6599.4	582.8	0.1741	74.767	0.77

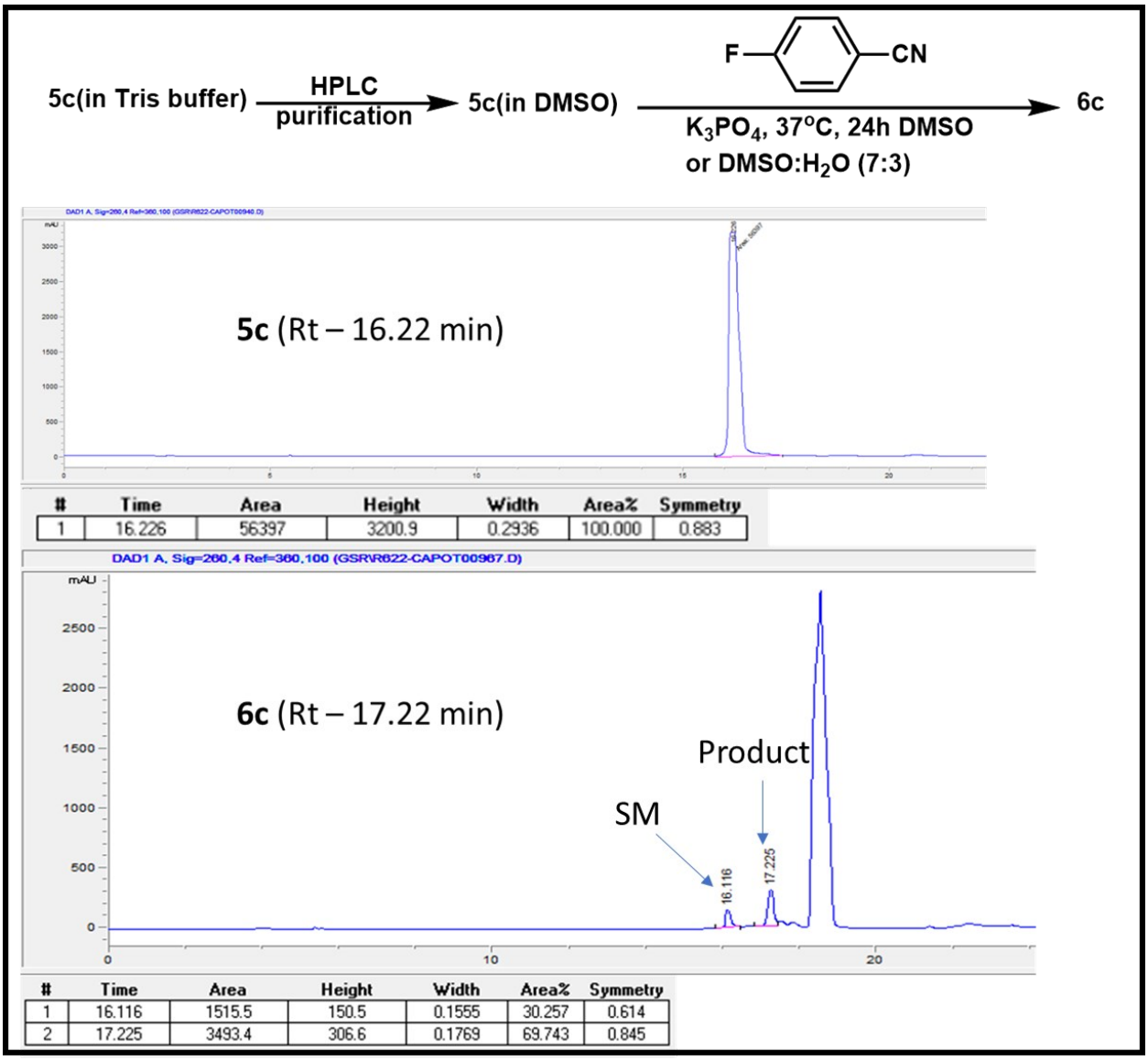
Figure S8: HPLC traces of **5a** and its corresponding product **6a**.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.226	56446.2	3200.5	0.2939	100.000	0.884

#	Time	Area	Height	Width	Area%	Symmetry
1	16.119	3277.2	370.9	0.1411	26.696	0.626
2	17.156	8998.7	817.8	0.1724	73.304	0.794

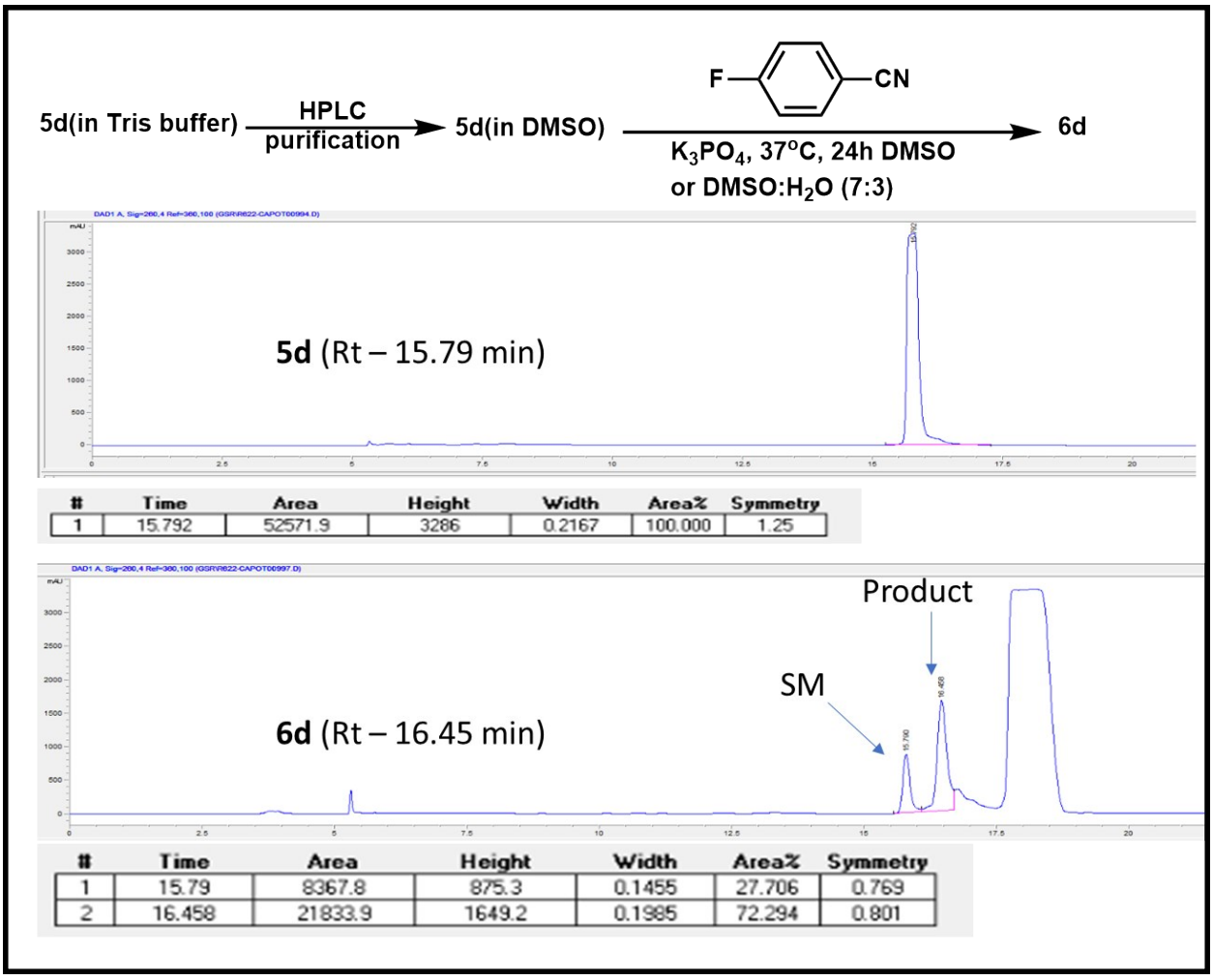
Figure S9: HPLC traces of **5b** and its corresponding product **6b**.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.226	56397	3200.9	0.2936	100.000	0.883

#	Time	Area	Height	Width	Area%	Symmetry
1	16.116	1515.5	150.5	0.1555	30.257	0.614
2	17.225	3493.4	306.6	0.1769	69.743	0.845

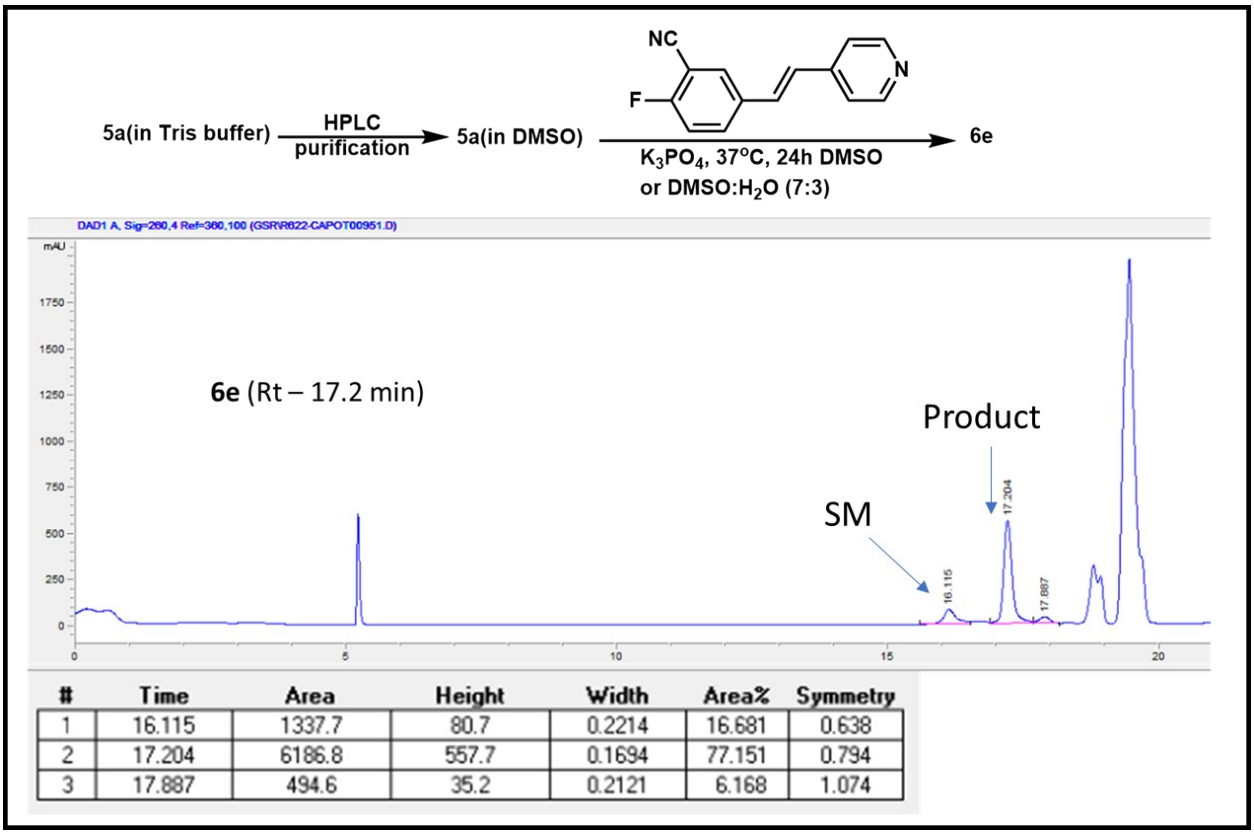
Figure S10: HPLC traces of **5c** and its corresponding product **6c**.



#	Time	Area	Height	Width	Area%	Symmetry
1	15.792	52571.9	3286	0.2167	100.000	1.25

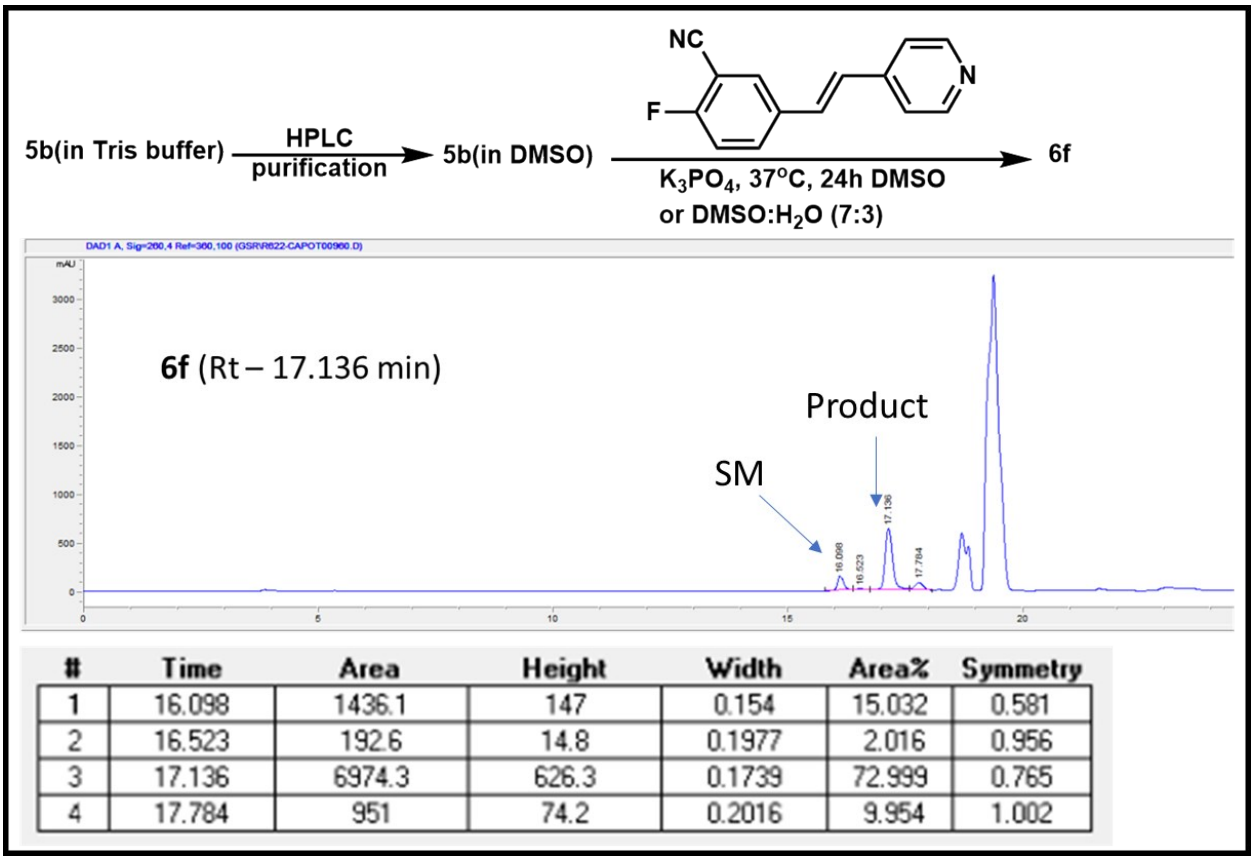
#	Time	Area	Height	Width	Area%	Symmetry
1	15.79	8367.8	875.3	0.1455	27.706	0.769
2	16.458	21833.9	1649.2	0.1985	72.294	0.801

Figure S11: HPLC traces of **5d** and its corresponding product **6d**.



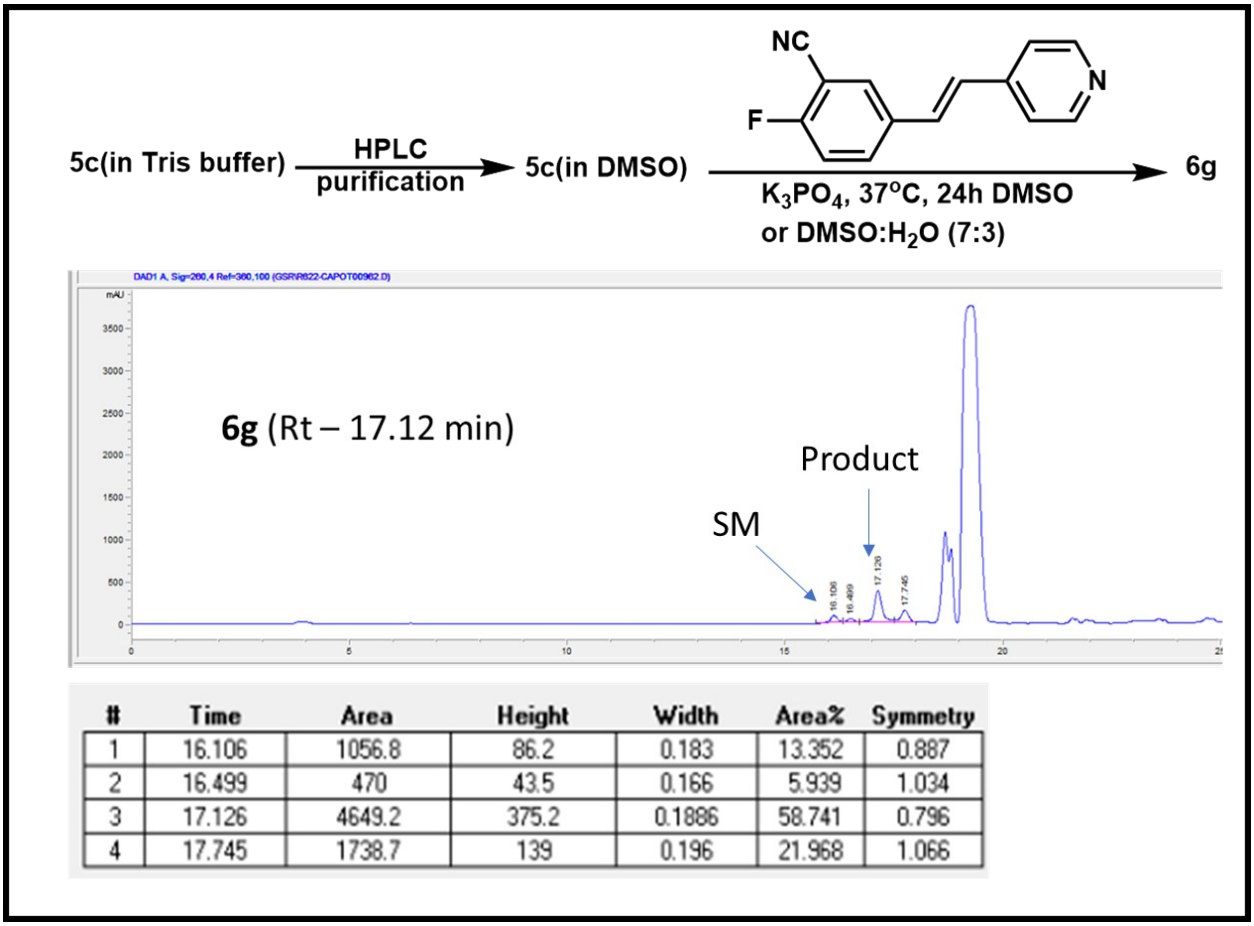
#	Time	Area	Height	Width	Area%	Symmetry
1	16.115	1337.7	80.7	0.2214	16.681	0.638
2	17.204	6186.8	557.7	0.1694	77.151	0.794
3	17.887	494.6	35.2	0.2121	6.168	1.074

Figure S12: HPLC trace of product **6e**.



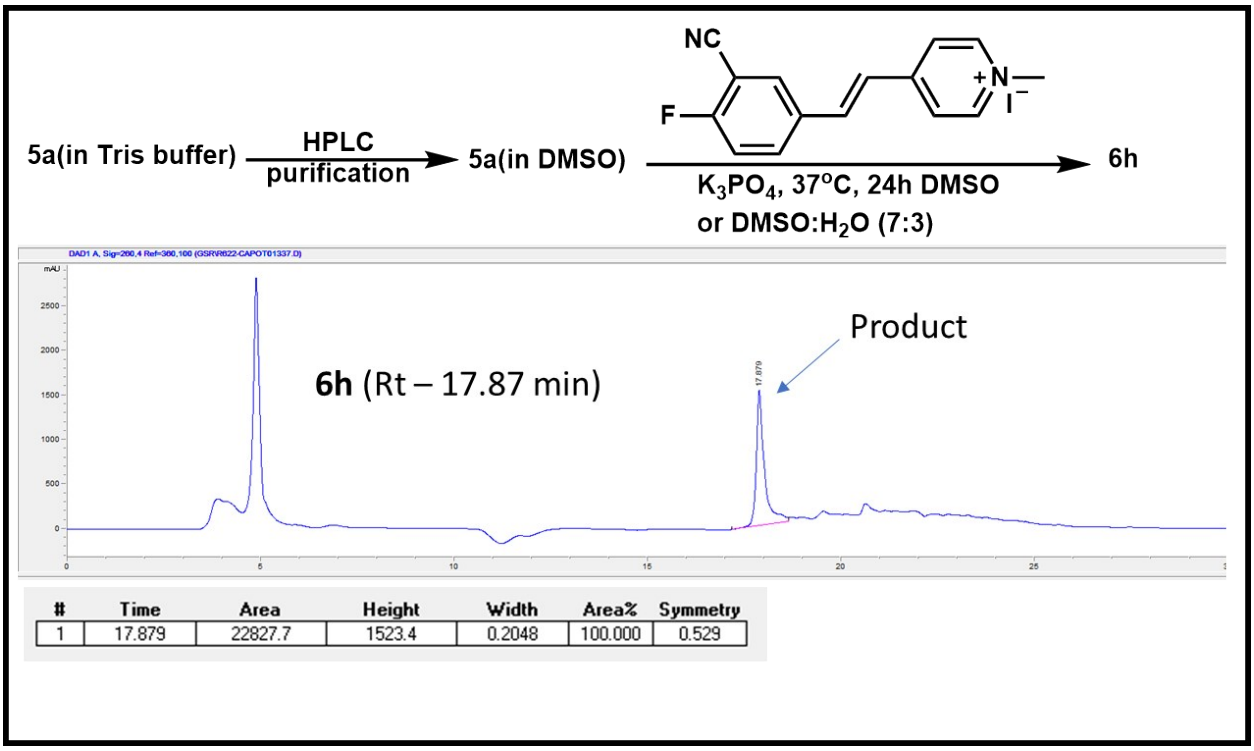
#	Time	Area	Height	Width	Area%	Symmetry
1	16.098	1436.1	147	0.154	15.032	0.581
2	16.523	192.6	14.8	0.1977	2.016	0.956
3	17.136	6974.3	626.3	0.1739	72.999	0.765
4	17.784	951	74.2	0.2016	9.954	1.002

Figure S13: HPLC trace of product **6f**.



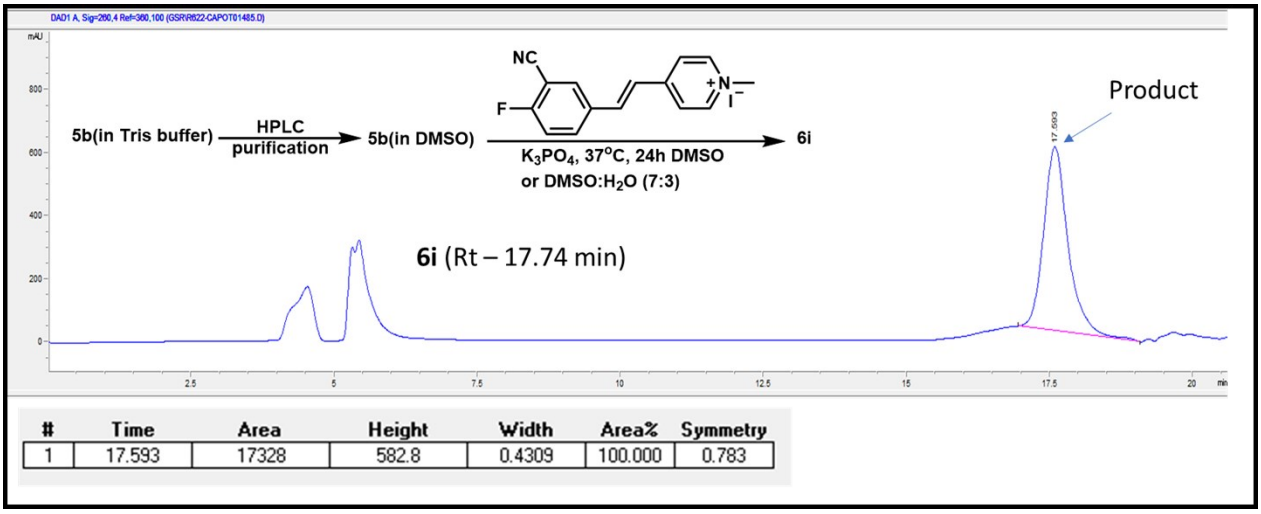
#	Time	Area	Height	Width	Area%	Symmetry
1	16.106	1056.8	86.2	0.183	13.352	0.887
2	16.499	470	43.5	0.166	5.939	1.034
3	17.126	4649.2	375.2	0.1886	58.741	0.796
4	17.745	1738.7	139	0.196	21.968	1.066

Figure S14: HPLC trace of product **6g**.



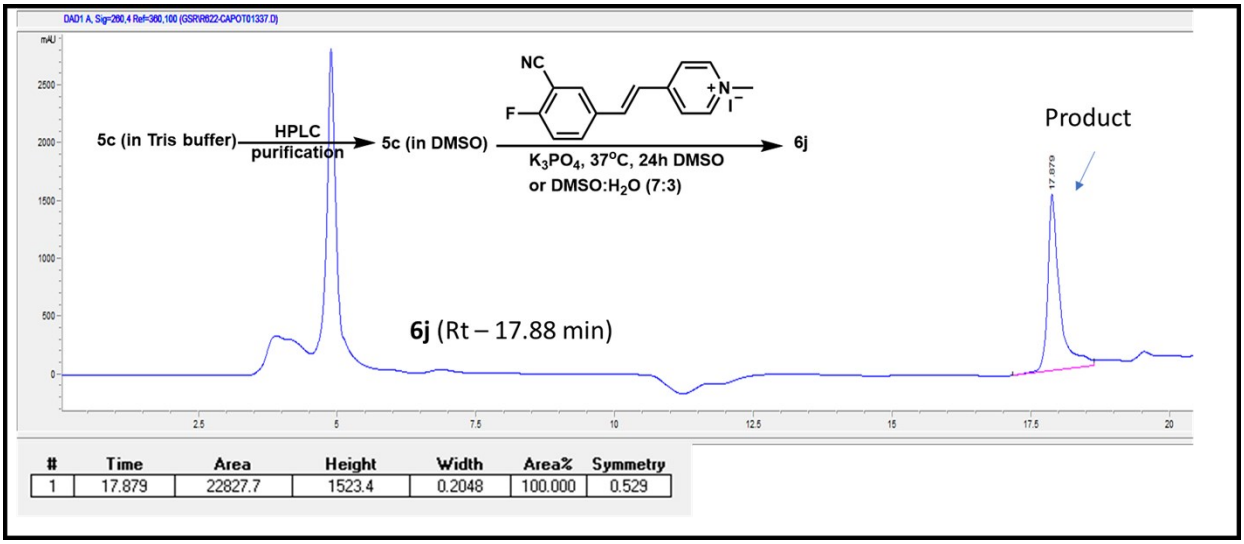
#	Time	Area	Height	Width	Area%	Symmetry
1	17.879	22827.7	1523.4	0.2048	100.000	0.529

Figure S15: HPLC trace of product **6h**.



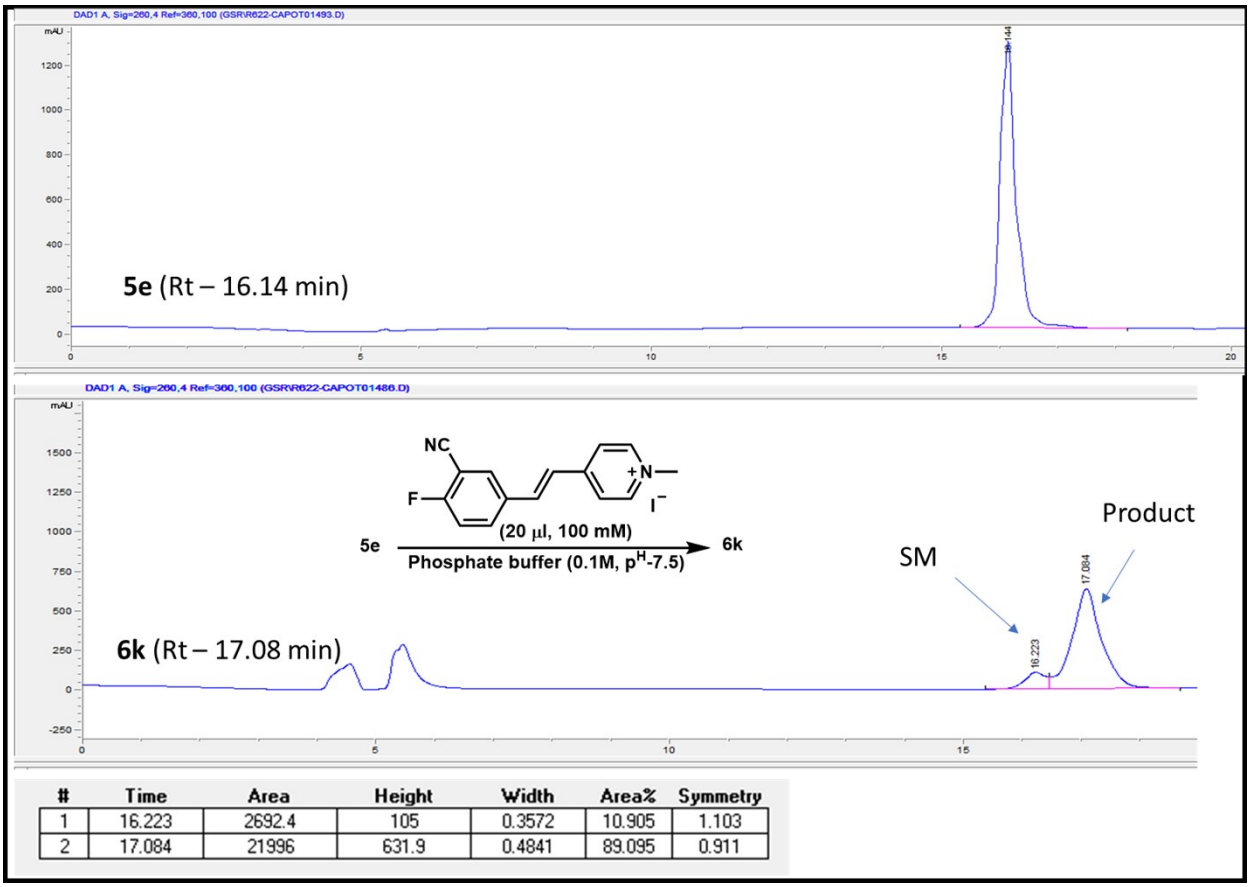
#	Time	Area	Height	Width	Area%	Symmetry
1	17.593	17328	582.8	0.4309	100.000	0.783

Figure S16: HPLC trace of product **6i**.



#	Time	Area	Height	Width	Area%	Symmetry
1	17.879	22827.7	1523.4	0.2048	100.000	0.529

Figure S17: HPLC trace of product **6j**.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.223	2692.4	105	0.3572	10.905	1.103
2	17.084	21996	631.9	0.4841	89.095	0.911

Figure S18: HPLC trace of single strand DNA **6k**.

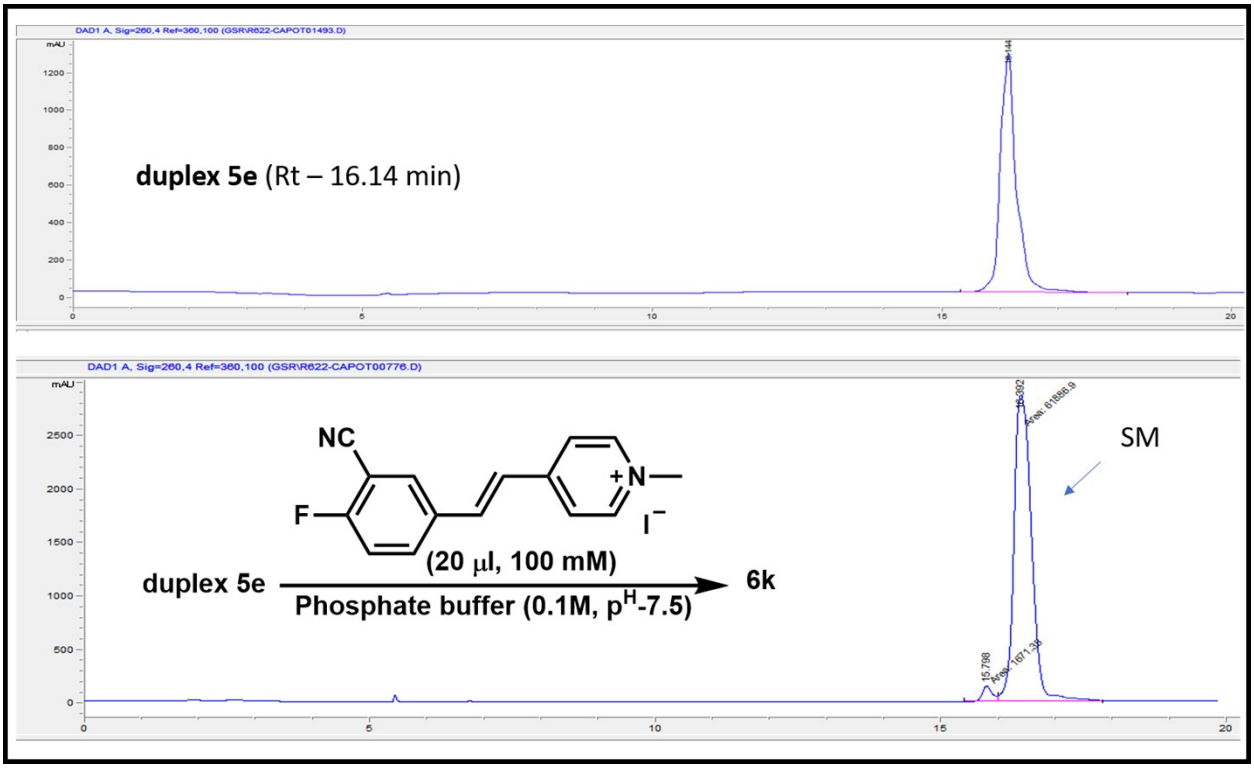
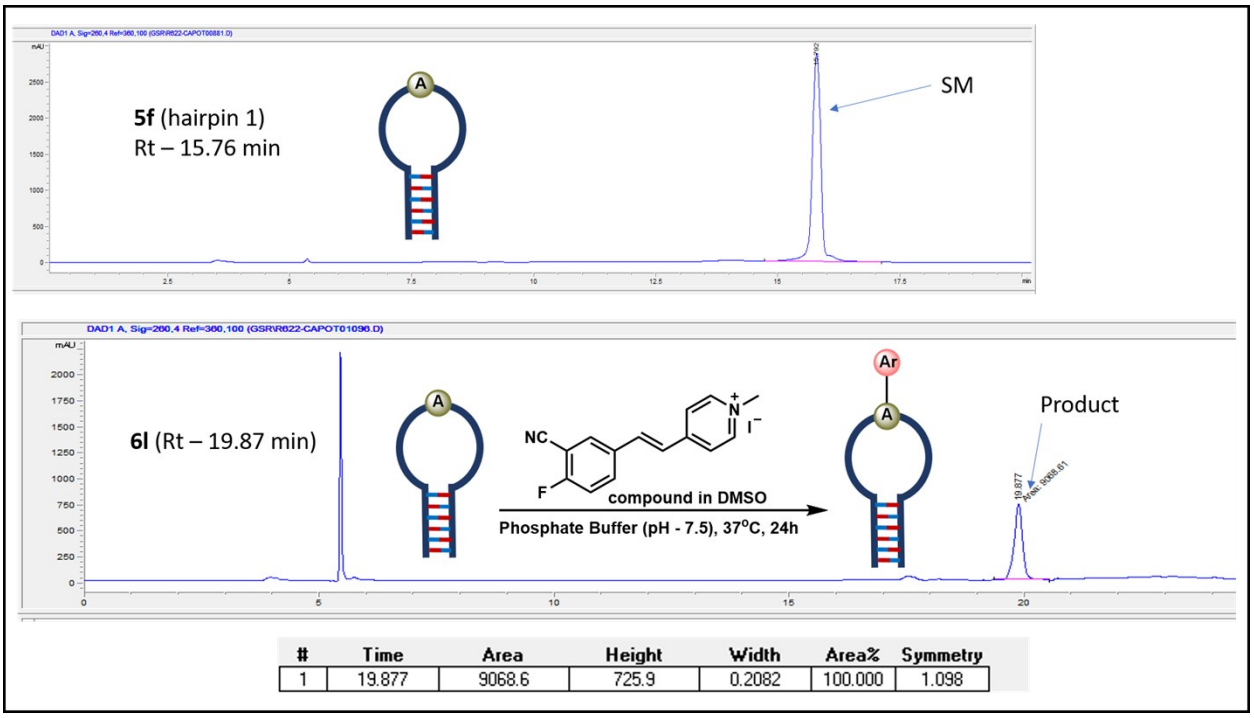
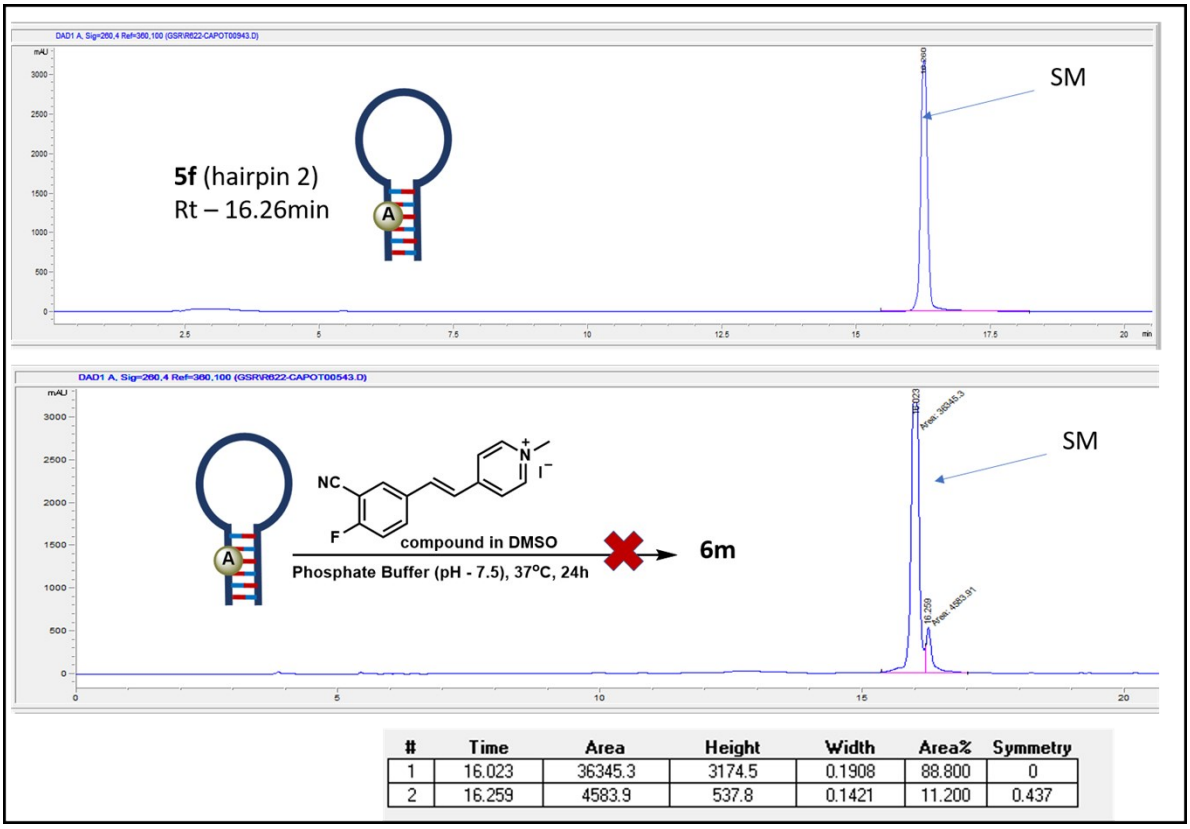


Figure S19: HPLC trace for duplex DNA **6k** (No reaction).



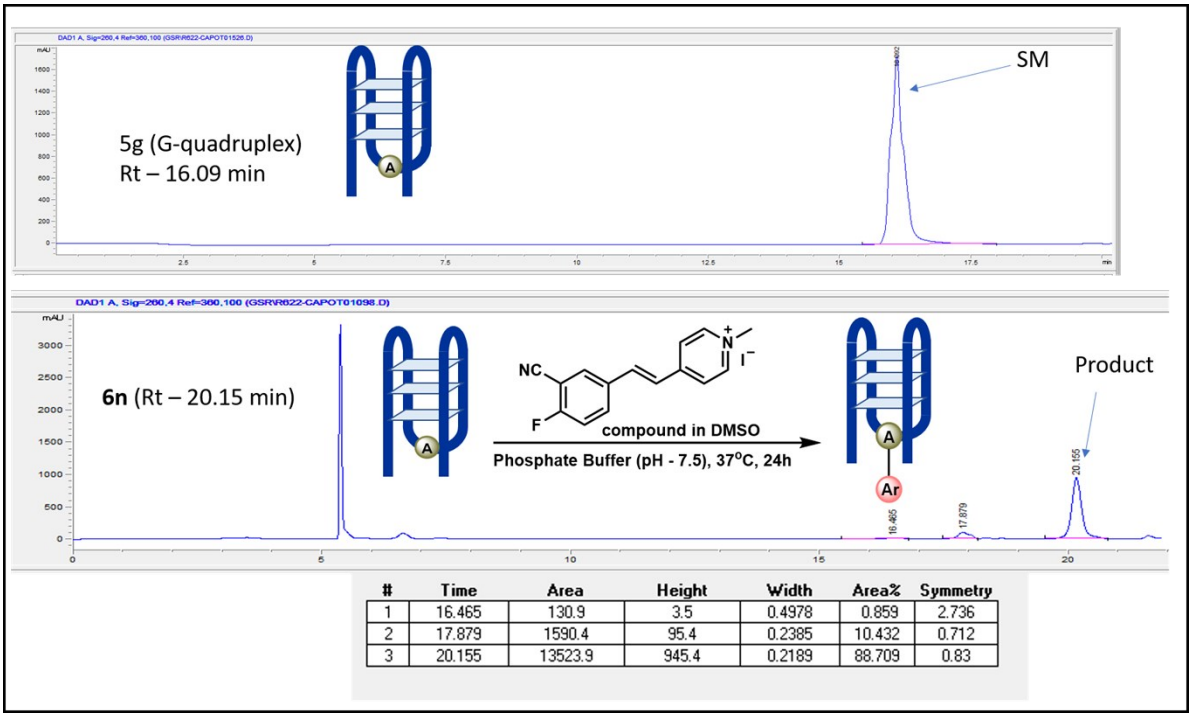
#	Time	Area	Height	Width	Area%	Symmetry
1	19.877	9068.6	725.9	0.2082	100.000	1.098

Figure S20: HPLC trace for hairpin loop **6l**.



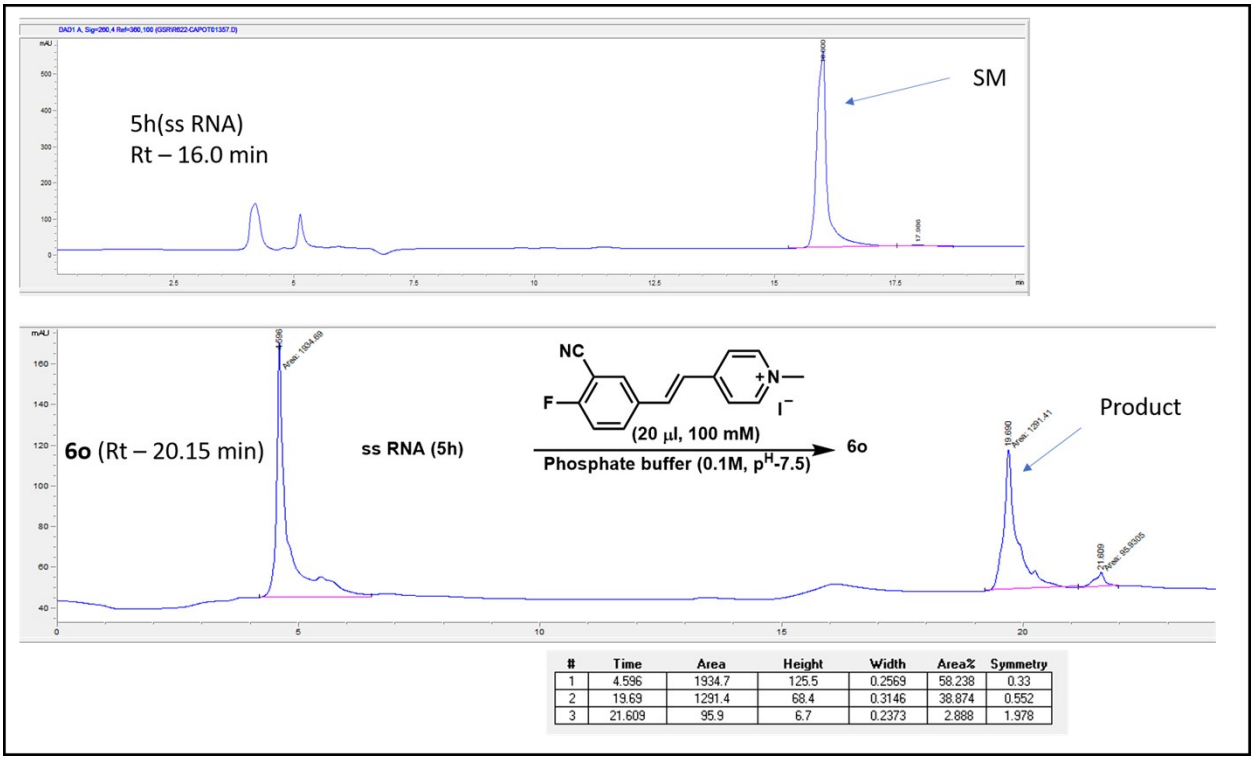
#	Time	Area	Height	Width	Area%	Symmetry
1	16.023	36345.3	3174.5	0.1908	88.800	0
2	16.259	4583.9	537.8	0.1421	11.200	0.437

Figure S21: HPLC trace for hairpin stem **6m** (No reaction).



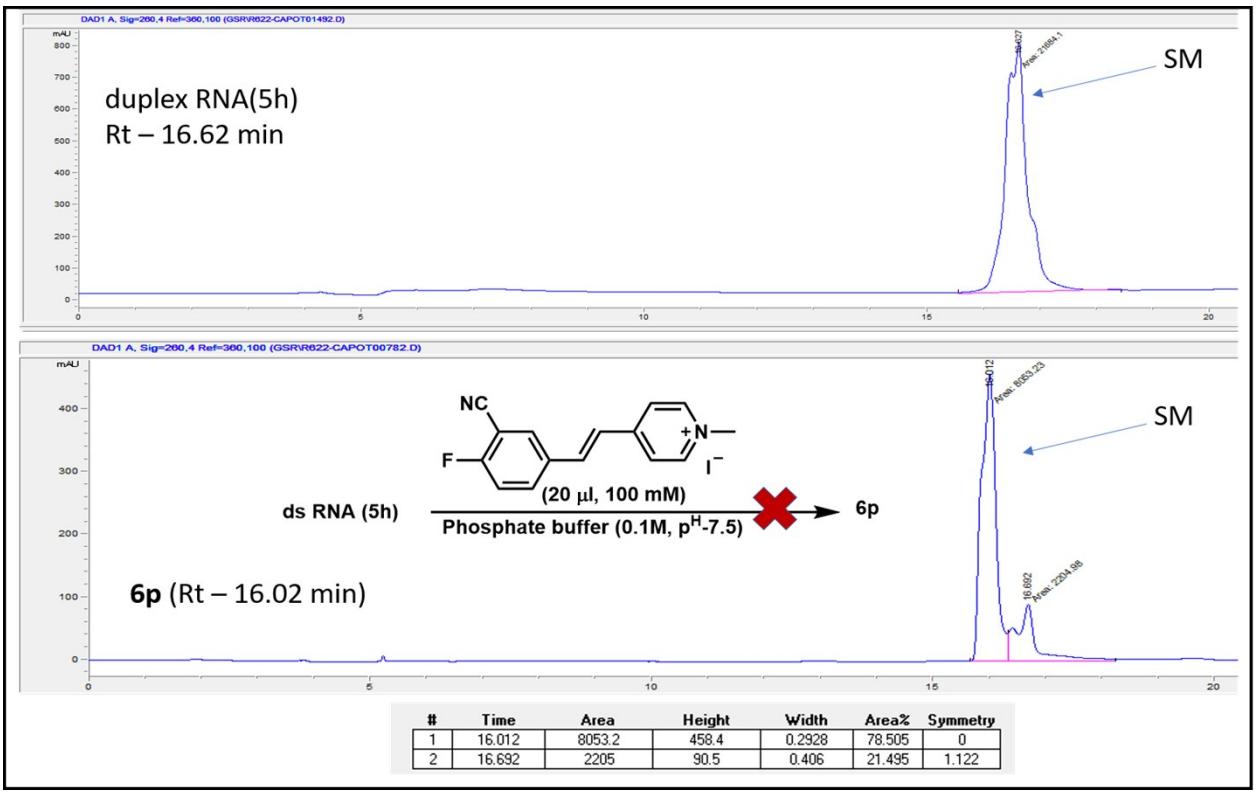
#	Time	Area	Height	Width	Area%	Symmetry
1	16.465	130.9	3.5	0.4978	0.859	2.736
2	17.879	1590.4	95.4	0.2385	10.432	0.712
3	20.155	13523.9	945.4	0.2189	88.709	0.83

Figure S22: HPLC trace for G-quadruplex Loop **6n**.



#	Time	Area	Height	Width	Area%	Symmetry
1	4.596	1934.7	125.5	0.2569	58.238	0.33
2	19.69	1291.4	68.4	0.3146	38.874	0.552
3	21.609	95.9	6.7	0.2373	2.888	1.978

Figure S23: HPLC trace for ssRNA **6o**.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.012	8053.2	458.4	0.2928	78.505	0
2	16.692	2205	90.5	0.406	21.495	1.122

Figure S24: HPLC trace for duplex RNA **6p**.

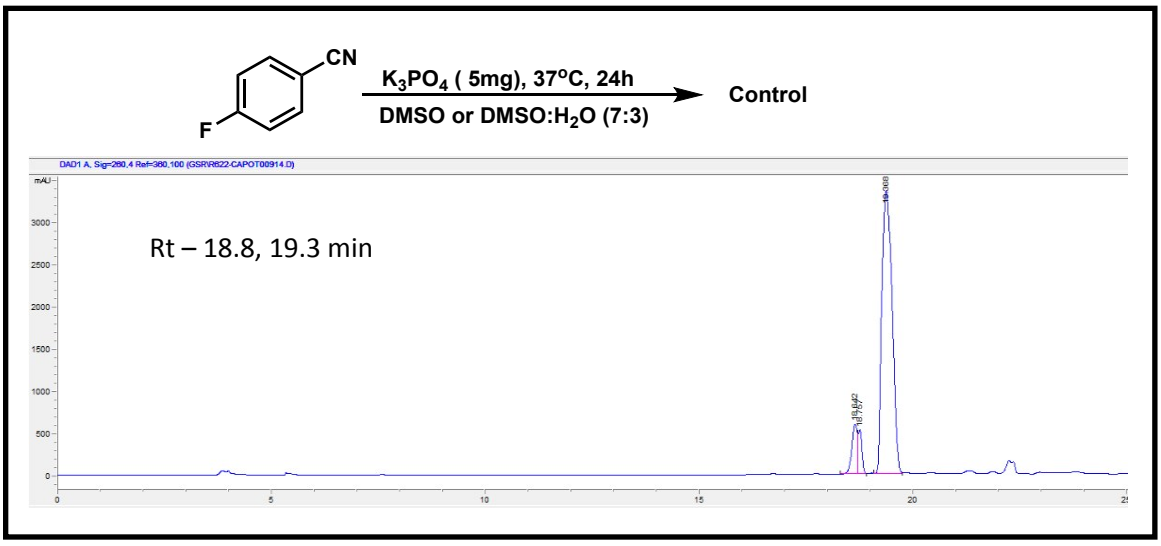
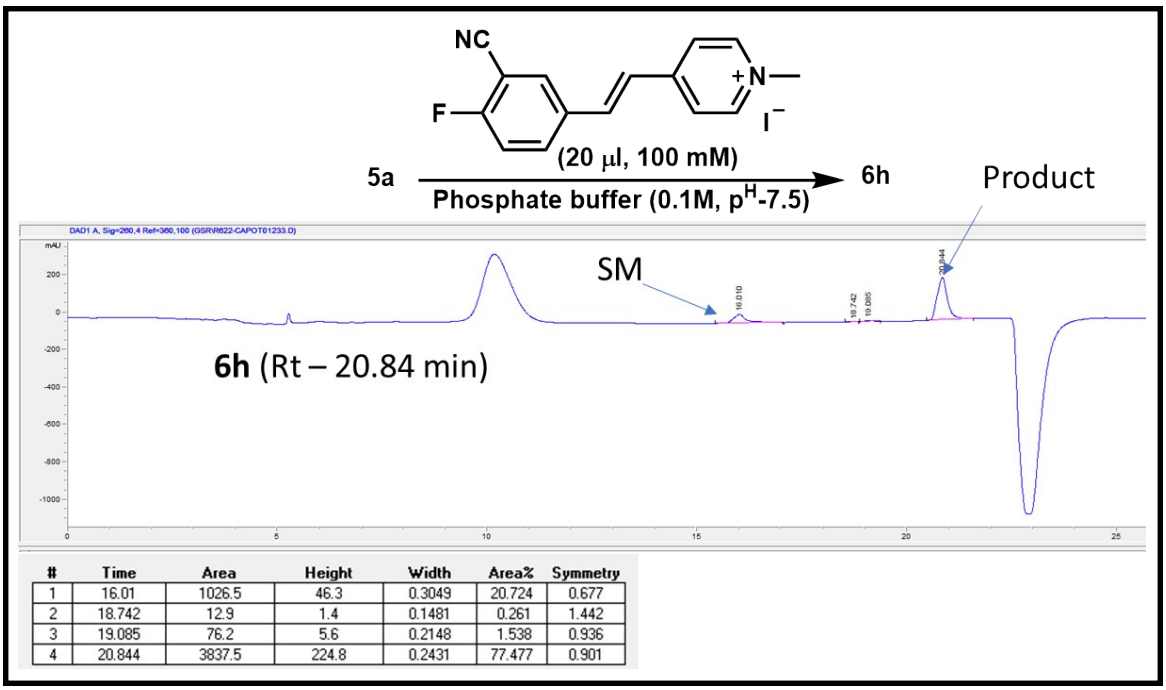
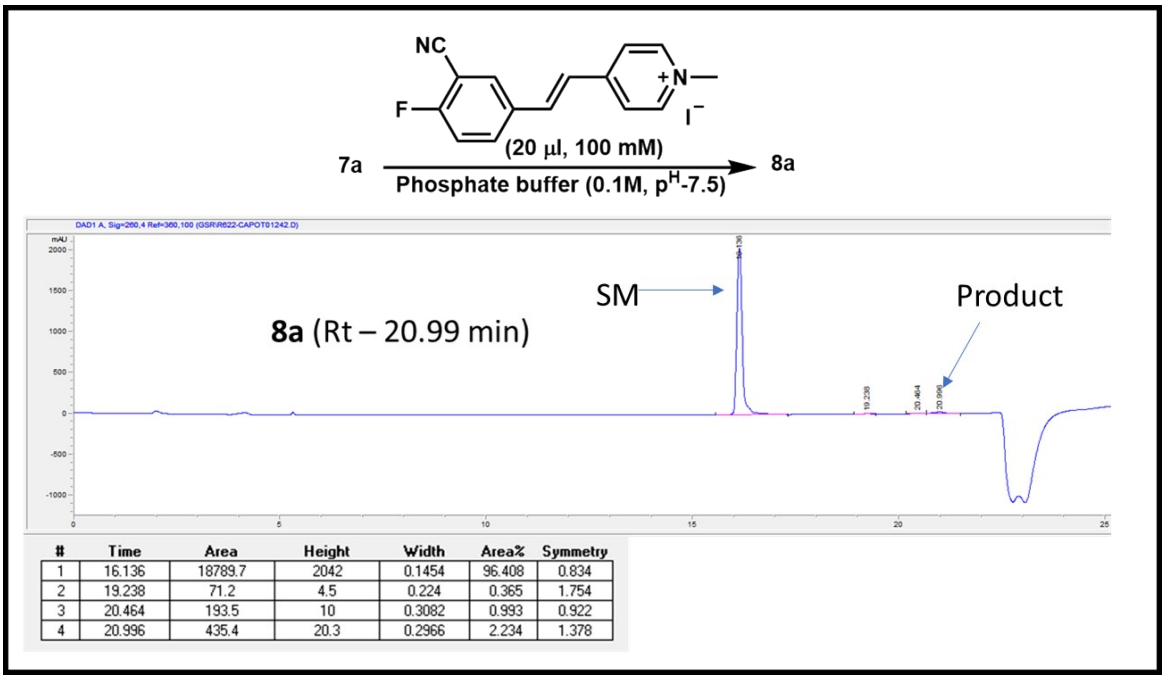


Figure S25: HPLC trace of control experiment to spot background signals.



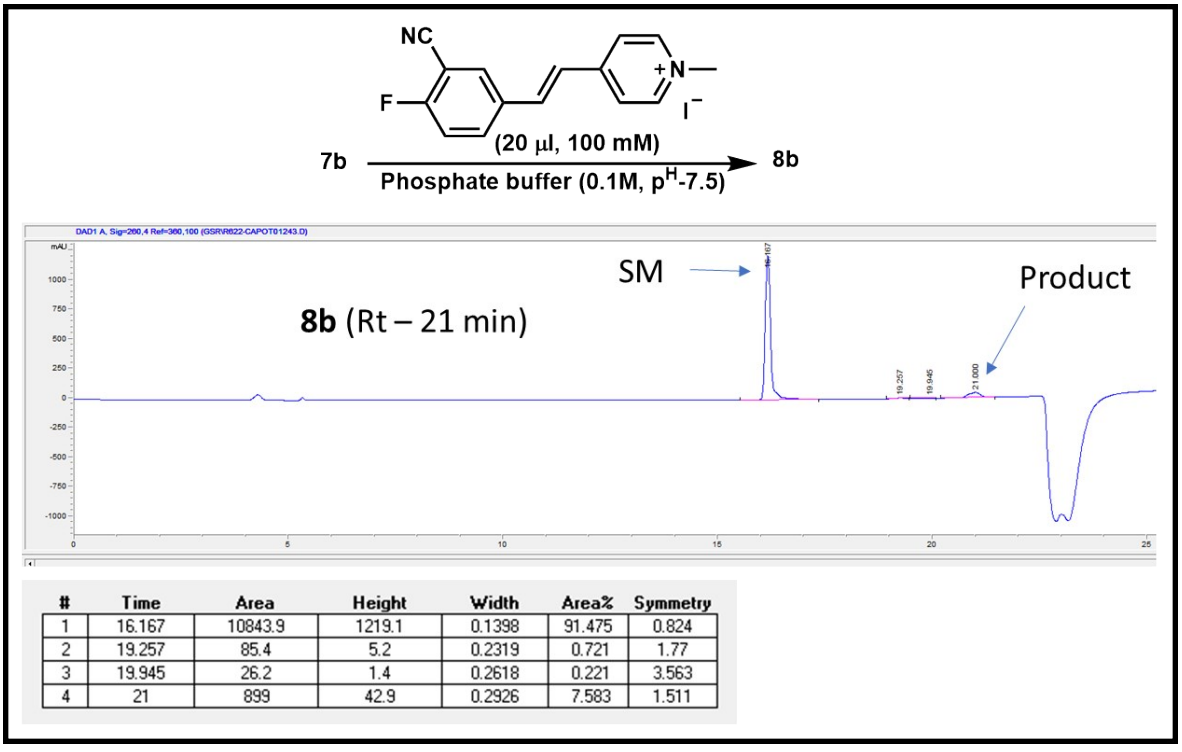
#	Time	Area	Height	Width	Area%	Symmetry
1	16.01	1026.5	46.3	0.3049	20.724	0.677
2	18.742	12.9	1.4	0.1481	0.261	1.442
3	19.085	76.2	5.6	0.2148	1.538	0.936
4	20.844	3837.5	224.8	0.2431	77.477	0.901

Figure S26: HPLC trace of the reaction of **5a** with **Z** (20 µL, 100 mM) in phosphate buffer (200 µL, 0.1 M, pH 7.5) to provide **6h** at 37 °C for 24 h.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.136	18789.7	2042	0.1454	96.408	0.834
2	19.238	71.2	4.5	0.224	0.365	1.754
3	20.464	193.5	10	0.3082	0.993	0.922
4	20.996	435.4	20.3	0.2966	2.234	1.378

Figure S27: HPLC trace of the reaction of **7a** with **Z** (20 µL, 100 mM) in phosphate buffer (200 µL, 0.1 M, pH 7.5) at 37 °C for 24 h.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.167	10843.9	1219.1	0.1398	91.475	0.824
2	19.257	85.4	5.2	0.2319	0.721	1.77
3	19.945	26.2	1.4	0.2618	0.221	3.563
4	21	899	42.9	0.2926	7.583	1.511

Figure S28: HPLC trace of the reaction of **7b** with **Z** (20 µL, 100 mM) in phosphate buffer (200 µL, 0.1 M, pH 7.5) at 37 °C for 24 h.

14. MALDI-TOF Mass Spectra of Arylated Oligonucleotides

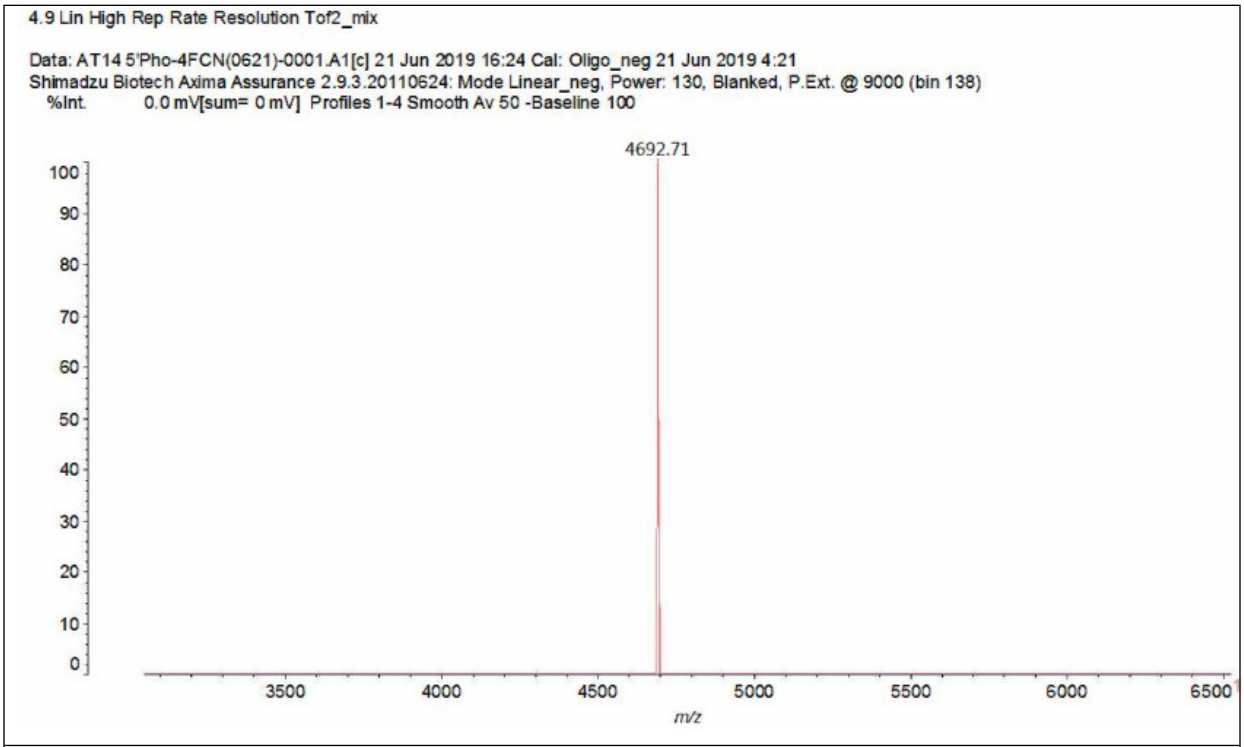


Figure S29: MALDI mass spectrum of the arylated oligonucleotide **6a** (calculated mass: *m*/*z* 4692.84; found: 4692.71).

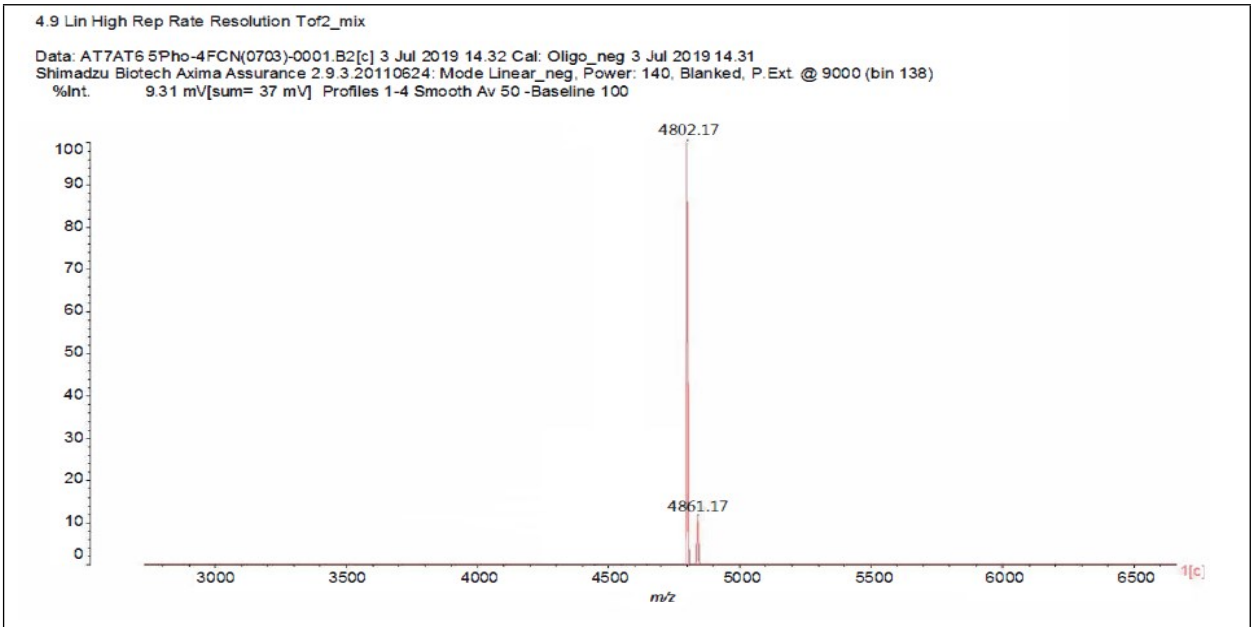


Figure S30: MALDI mass spectrum of the arylated oligonucleotide **6b** (calculated mass: *m*/*z* 4804.85;

found: 4802.17, doubly substituted).

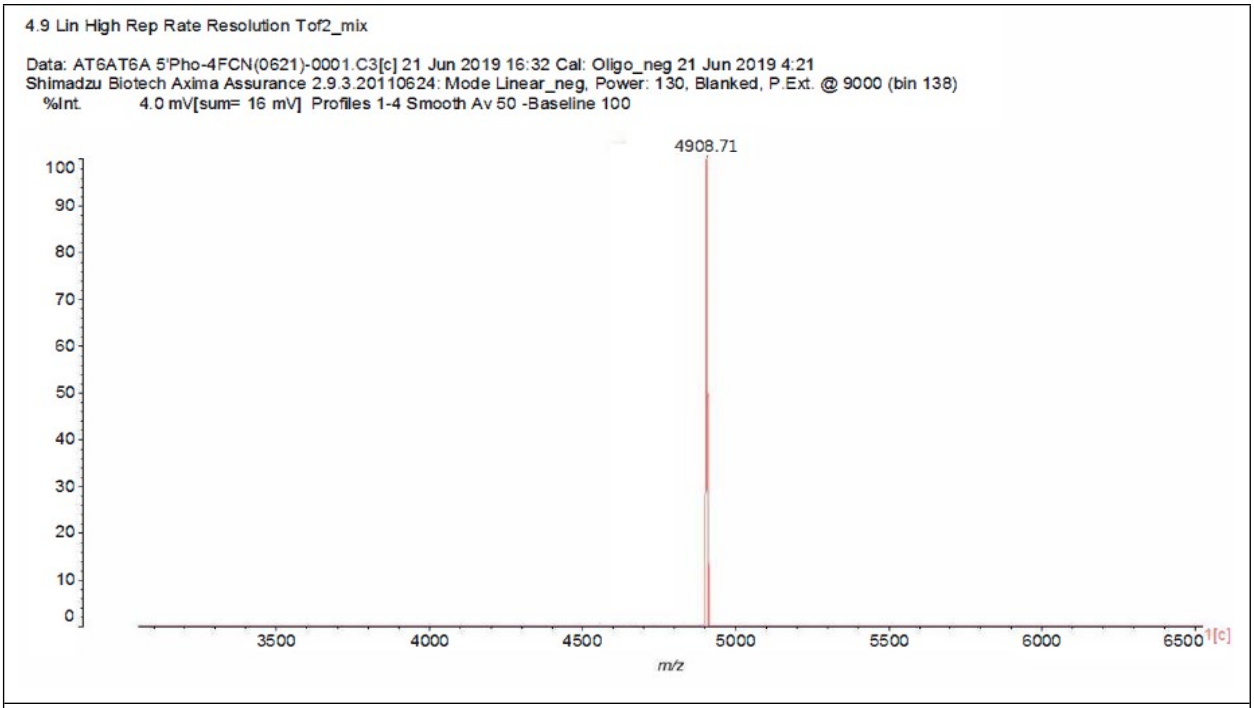


Figure S31: MALDI mass spectrum of the arylated oligonucleotide **6c** (calculated mass: *m*/*z* 4916.86; found: 4908.71, triply substituted).

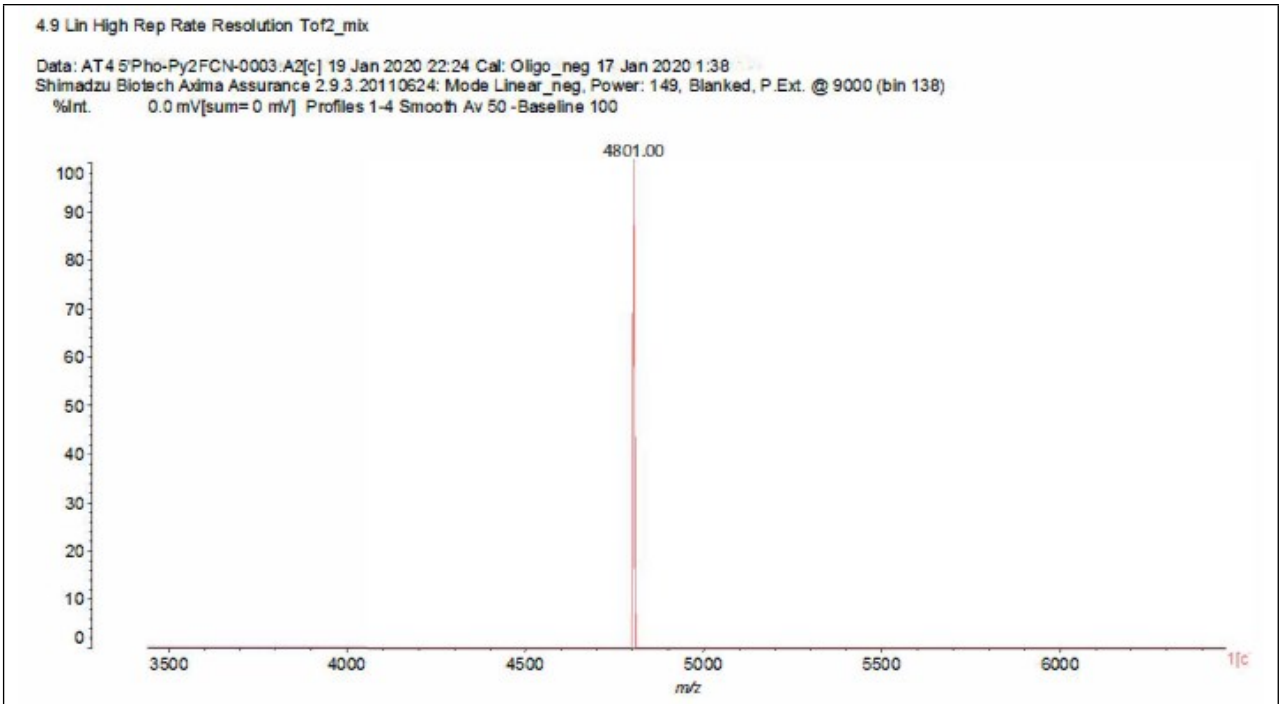


Figure S32*:* MALDI mass spectrum of the arylated oligonucleotide **6e** (calculated mass: m/z 4796.08; found: 4801.00).

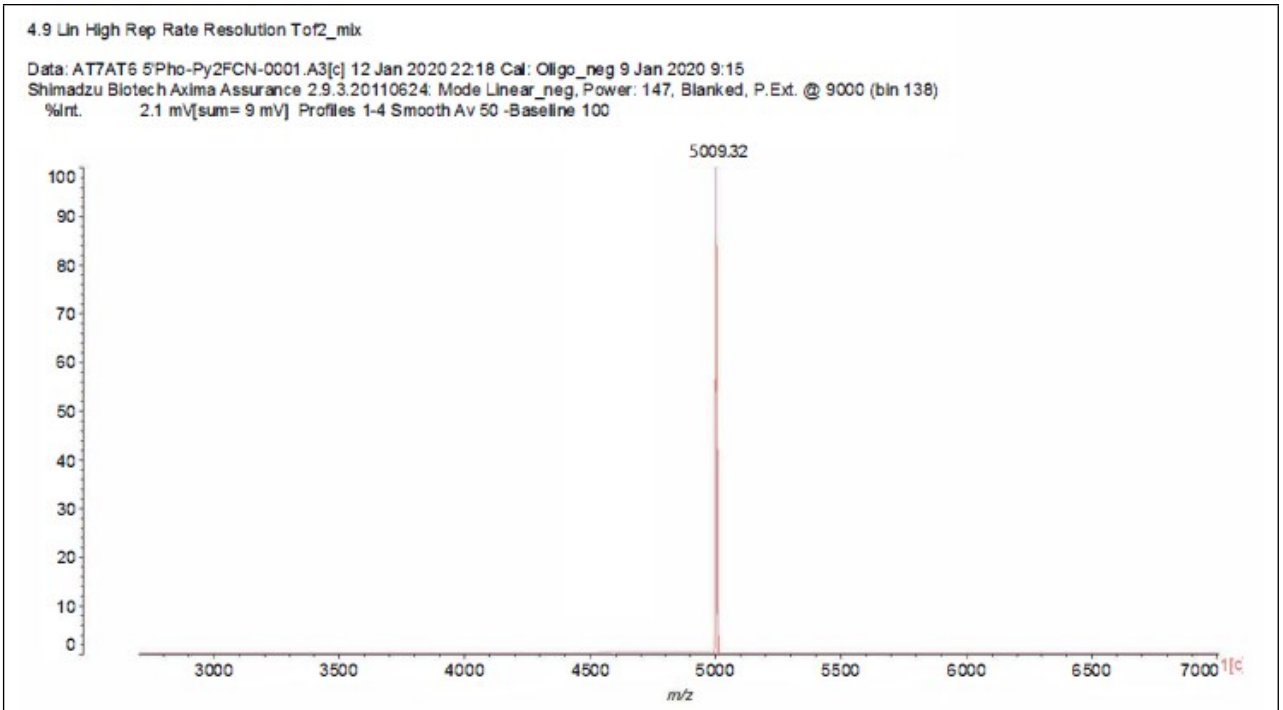


Figure S33*:* MALDI mass spectrum of the arylated oligonucleotide **6f** (calculated mass: m/z 5010.48; found: 5009.32).

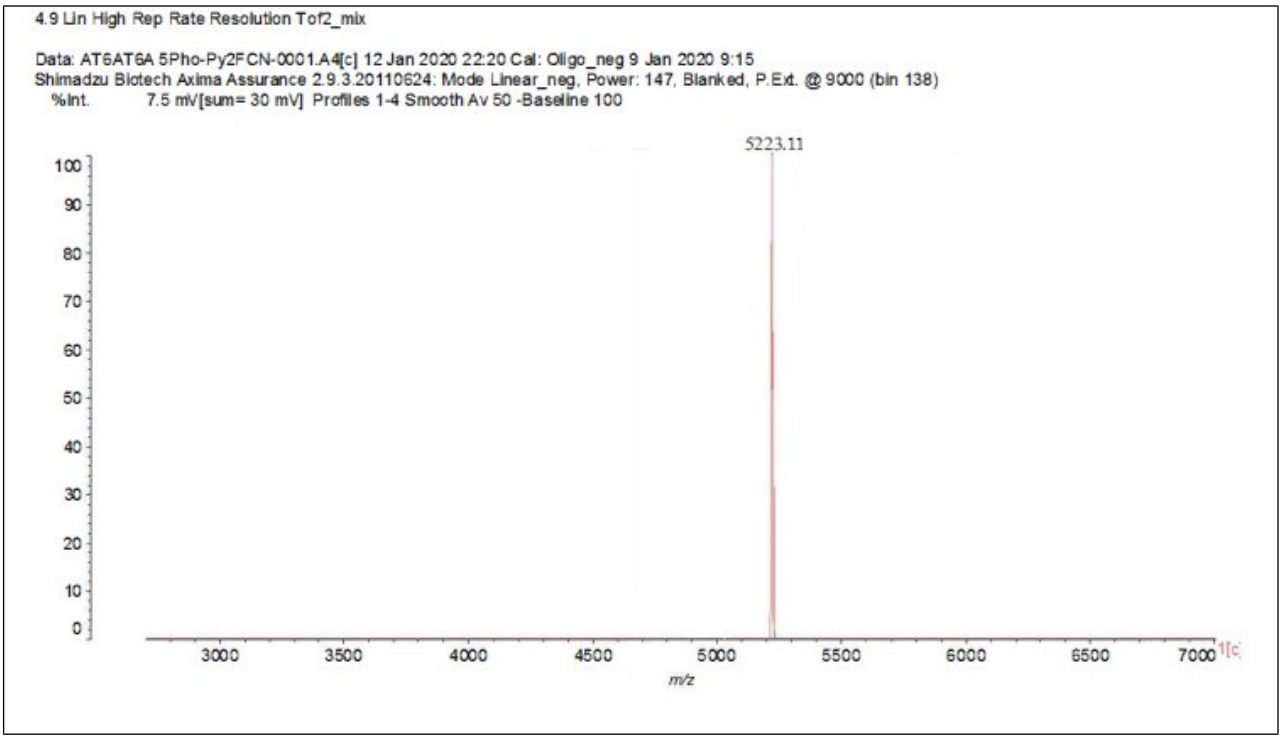


Figure S34*:* MALDI mass spectrum of the arylated oligonucleotide **6g** (calculated mass: m/z 5226.58; found: 5223.11).

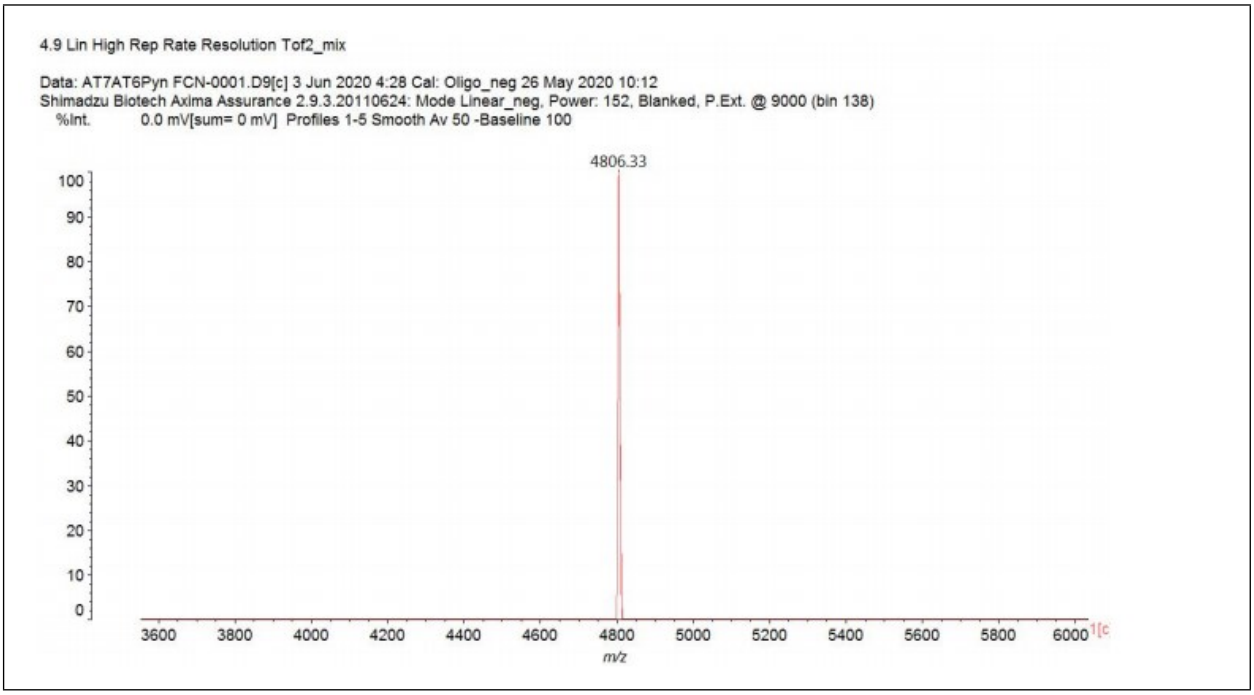


Figure S35: MALDI mass spectrum of the arylated oligonucleotide **6h** (calculated mass: *m*/*z* 4810.83; found: 4806.33).

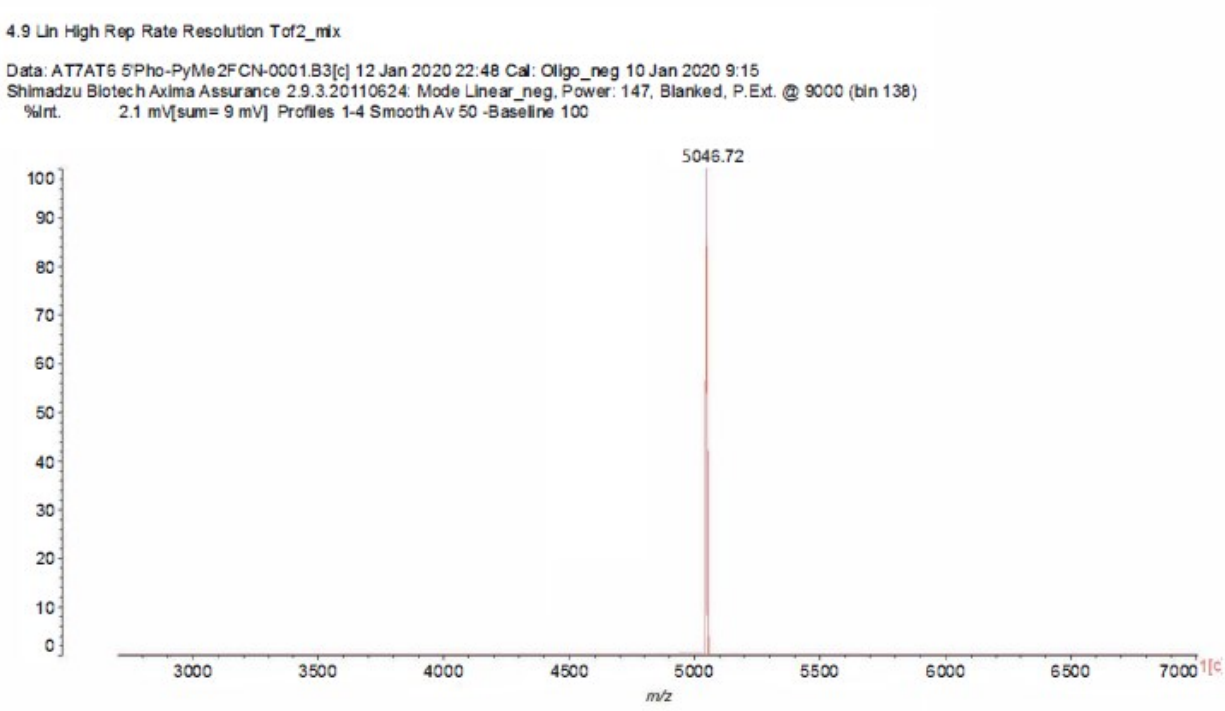


Figure S36: MALDI mass spectrum of the arylated oligonucleotide **6i** (calculated mass: *m*/*z* 5041.41; found: 5046.72).

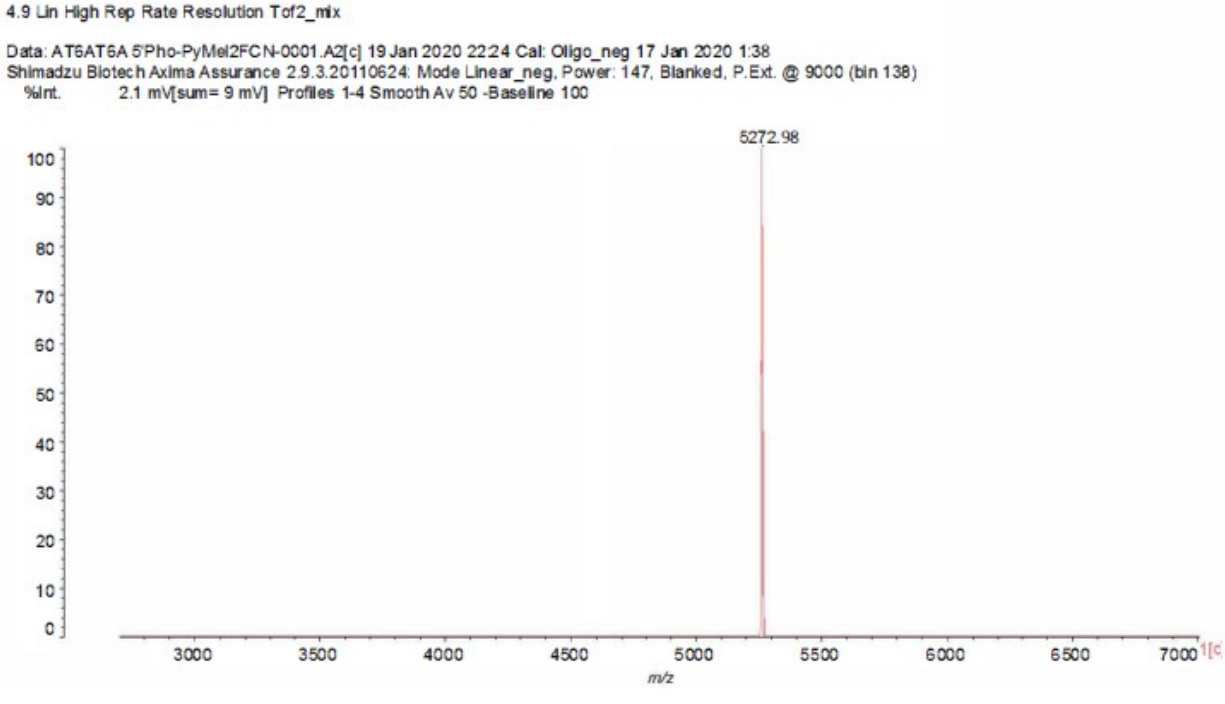


Figure S37: MALDI mass spectrum of the arylated oligonucleotide **6j** (calculated mass: *m*/*z* 5271.70; found: 5272.98).

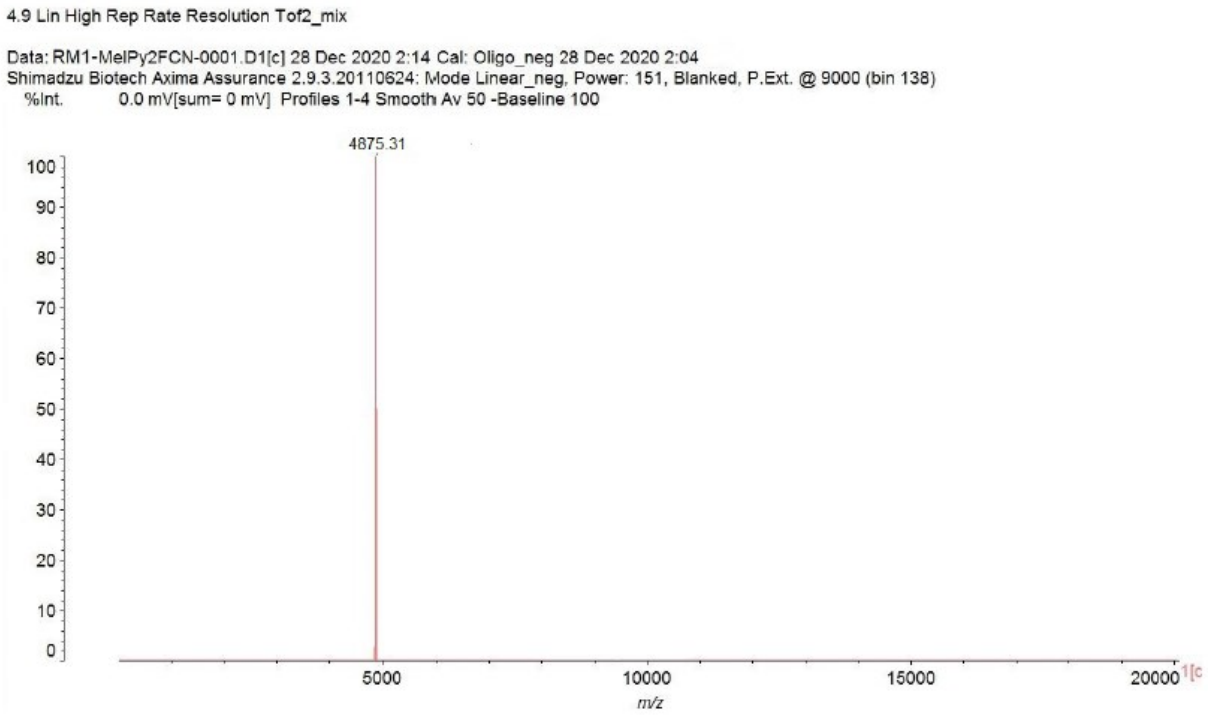


Figure S38: MALDI mass spectrum of the arylated oligonucleotide **6k** (calculated mass: *m*/*z* 4874.44; found: 4875.31).

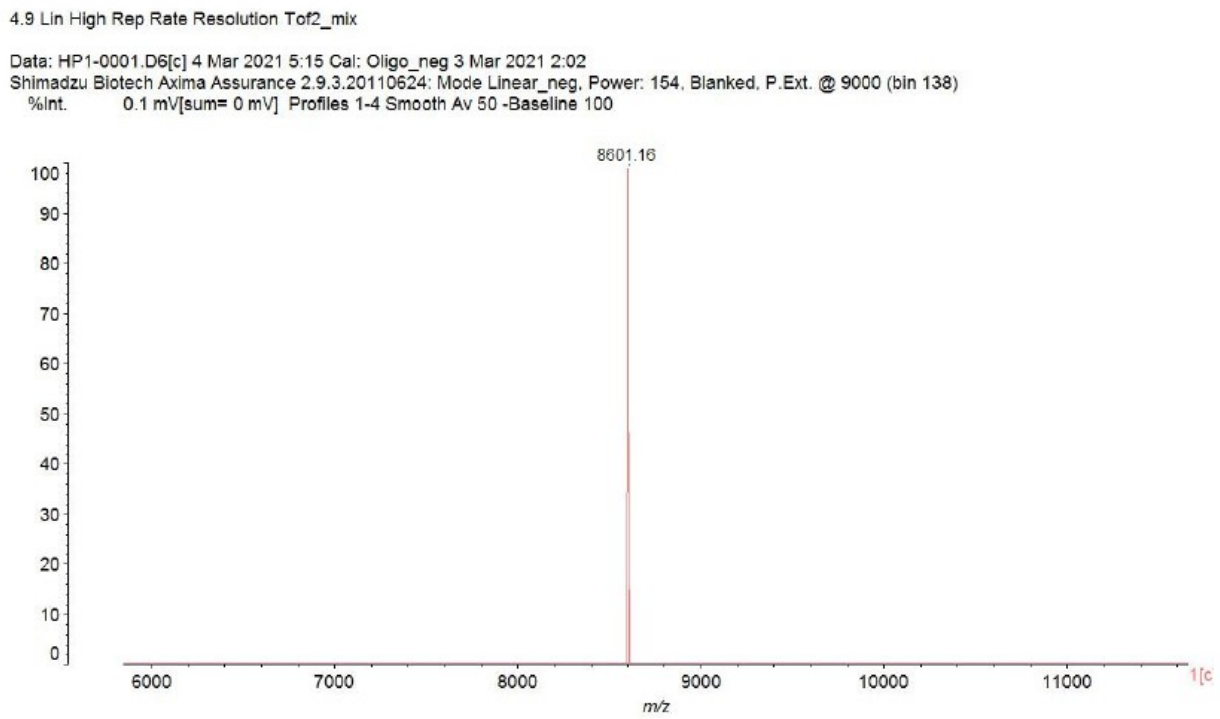


Figure S39: MALDI mass spectrum of the arylated oligonucleotide **6l** (calculated mass: *m*/*z* 8595.56; found: 8601.16).

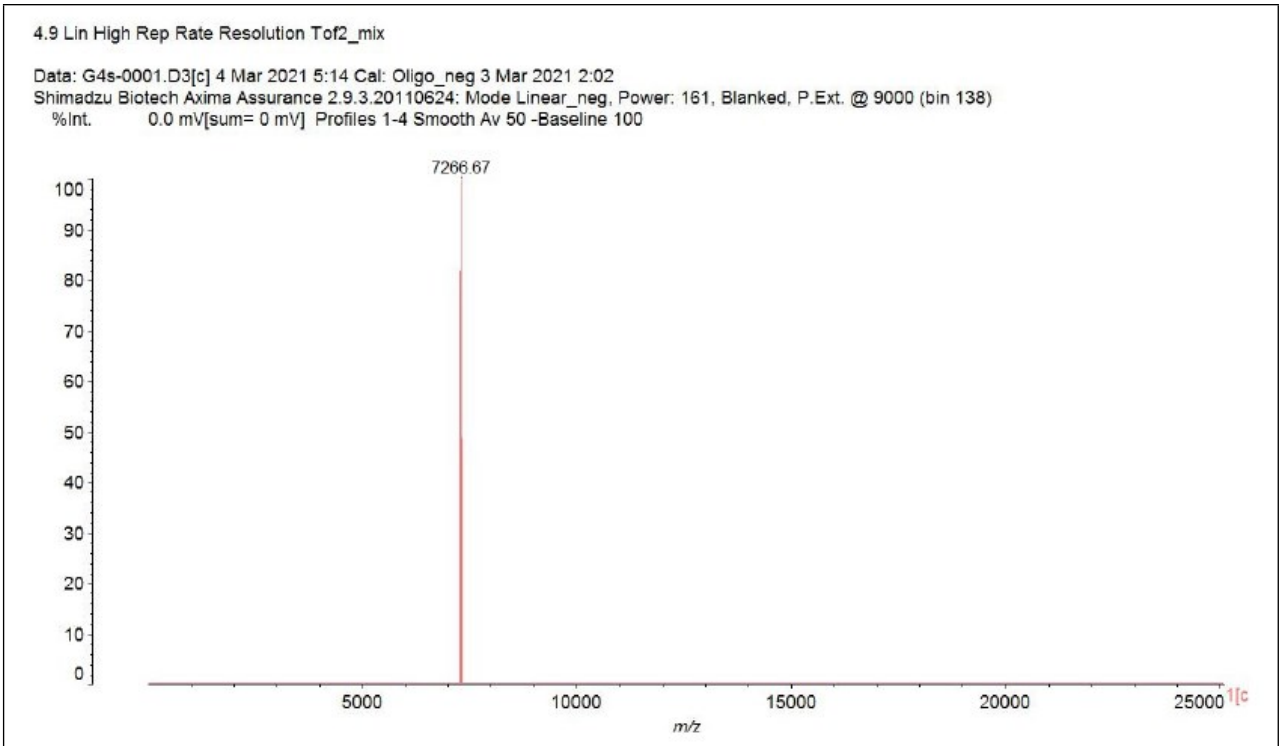


Figure S40: MALDI mass spectrum of the arylated oligonucleotide **6n** (calculated mass: *m*/*z* 7264.3; found: 7266.67).

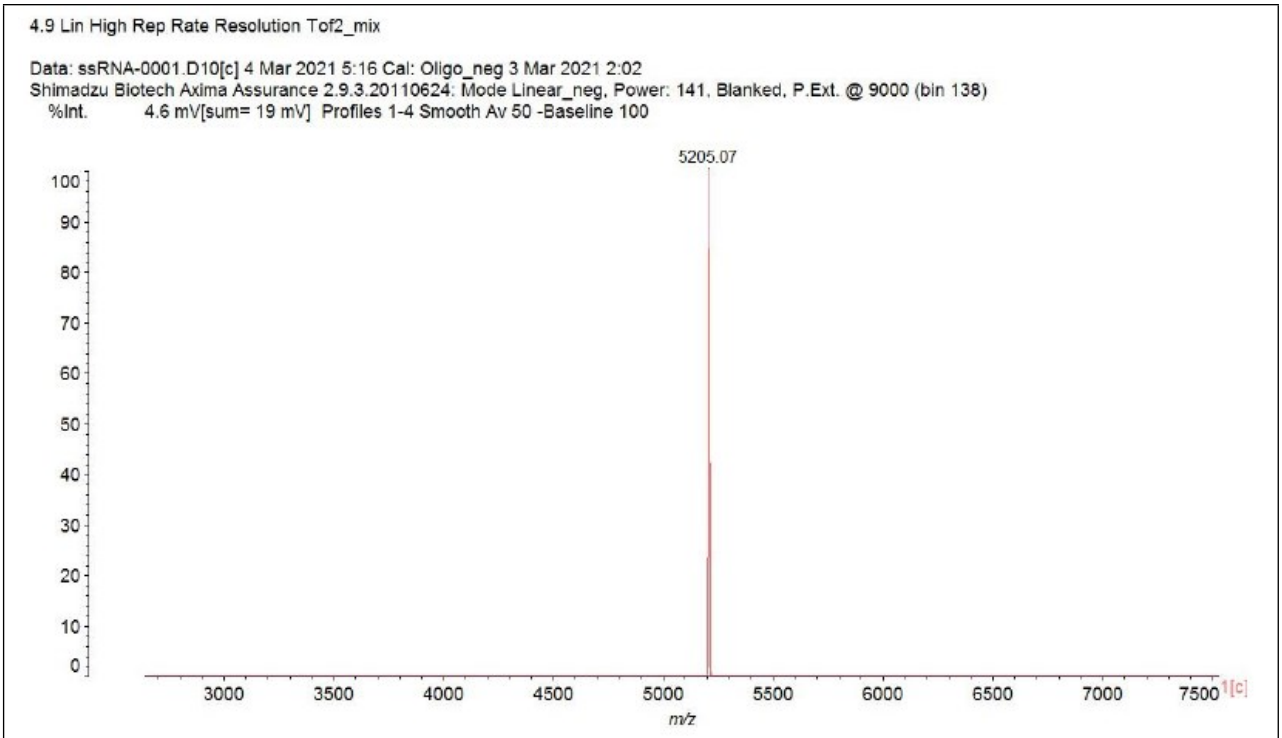


Figure S41: MALDI mass spectrum of the arylated oligonucleotide **6o** (calculated mass: *m*/*z* 5199.67; found: 5205.07).

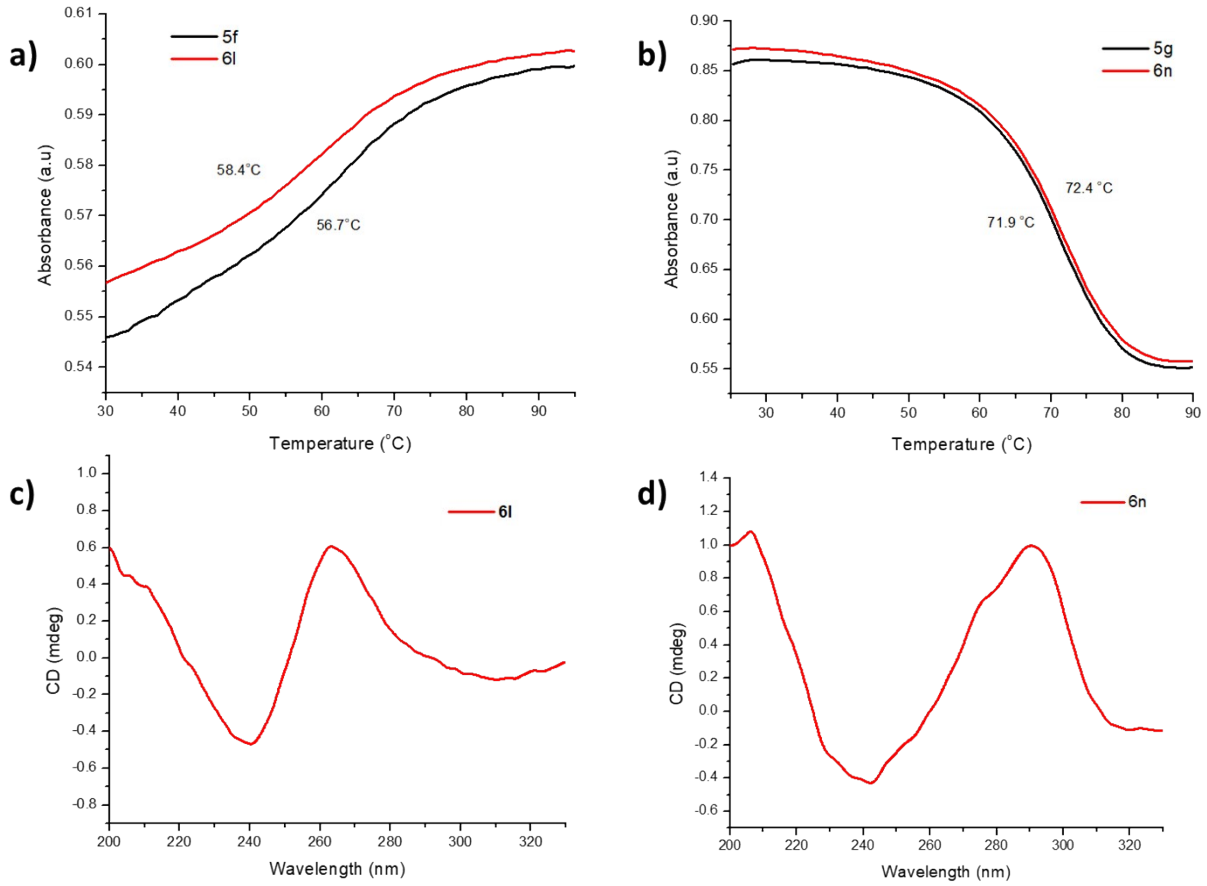


Figure S42: (a, b) Melting point of **6l** (after arylation) and **6n** (after arylation) in corresponds to their starting oligonucleotides 5f(before arylation) and 5g (before arylation) ; (c, d) CD spectra of arylated Haripin 1 **6l** and G-quadrauplex **6n** with range **of** 200–300 nm (2 μM each).

16. Photophysical Properties of Arylated Dimethoxytrityldeoxyadenosine Products

$$A = \varepsilon c l$$

- A is the absorbance of the compounds measured at the wavelength maximum (λ_{max}).

- ε is the extinction coefficient [M^{-1} cm^{-1}].

- c is the concentration [M].

- l is the path length of the cuvette [cm]

Compound	Absorbance at λ_{max}	Concentration (M)	Path length of cuvette (cm)	λ_{max} (nm)	Extinction coefficient (ε) (M^{-1} cm^{-1})
2a	0.0470	10×10^{-6}	1	320	4700
2c	0.0077	10×10^{-6}	1	321	770
2d	0.0048	10×10^{-6}	1	323	480
2e	0.0395	10×10^{-6}	1	300	3950
2f	0.0243	10×10^{-6}	1	284	2430
2i	0.04723	10×10^{-6}	1	353	4723
2j	0.04003	10×10^{-6}	1	450	4003

Calculated Quantum Yields of Fluorophore Compounds in DMSO

$$Q = Q_R \left(\frac{Grad}{Grad_R}\right)\left(\frac{n^2}{n_R^2}\right)$$

- Q is the fluorescence quantum yield of the compound.

- Q_R is the fluorescence quantum yield of the reference compound.

- *Grad* is the gradient obtained from the plot of the integrated fluorescence intensity and absorption.

- n the refractive index of the solvent (DMSO).

- the subscript R denotes the reference compound.

Using the literature value:

Q_R (acetone) = 0.99

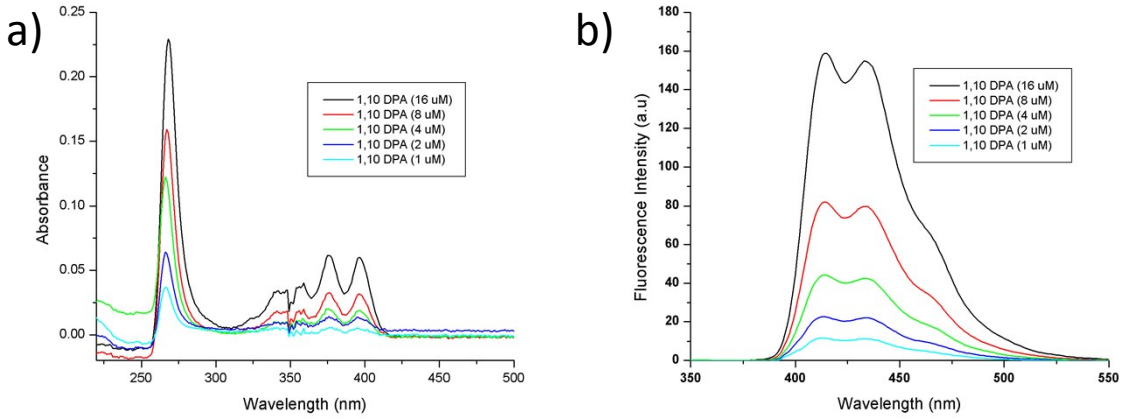


Figure S43: UV–Vis and fluorescence spectra of 1,10-diphenylanthracene.

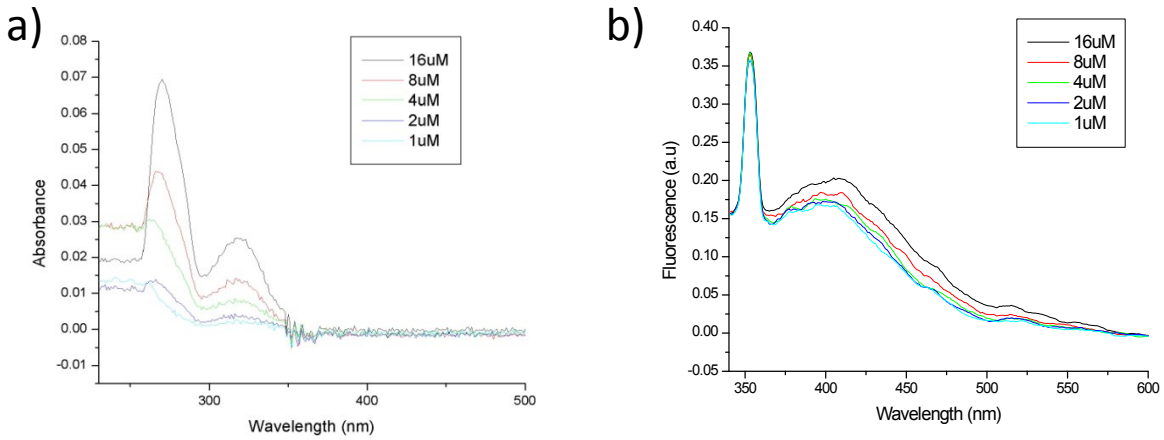


Figure S44: UV–Vis and fluorescence spectra of **2a**.

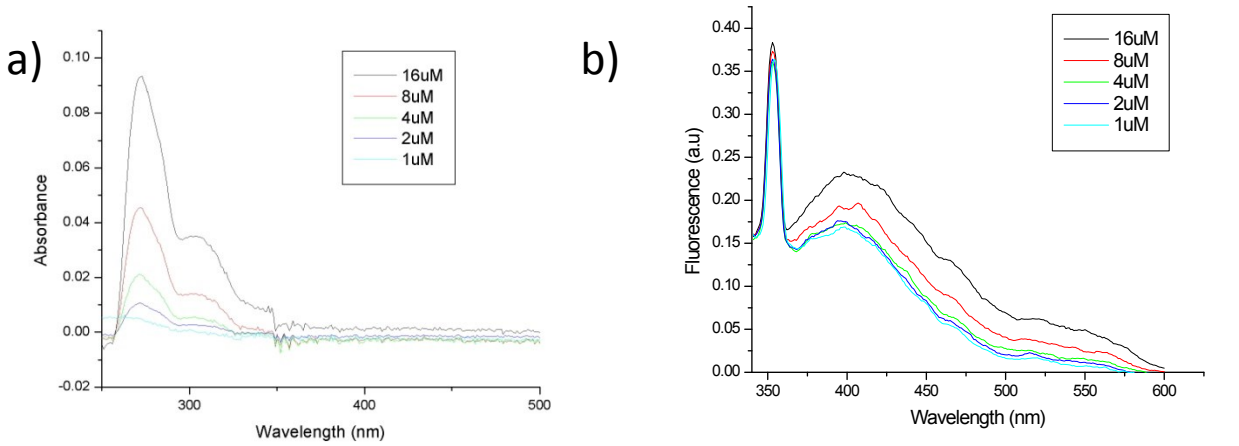


Figure S45: UV–Vis and fluorescence spectra of **2c**.

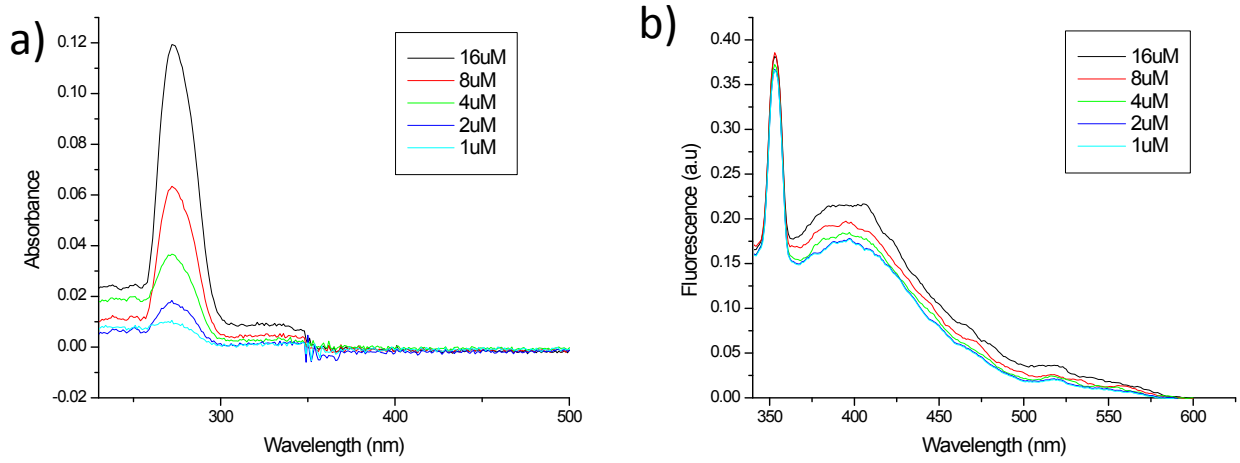


Figure S46: UV–Vis and fluorescence spectra of **2d**.

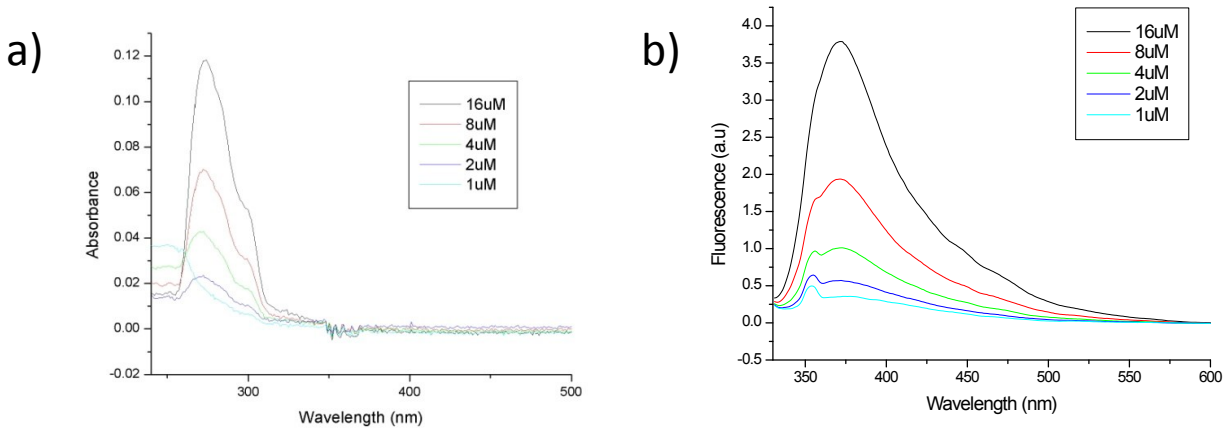


Figure S47: UV–Vis and fluorescence spectra of **2e**.

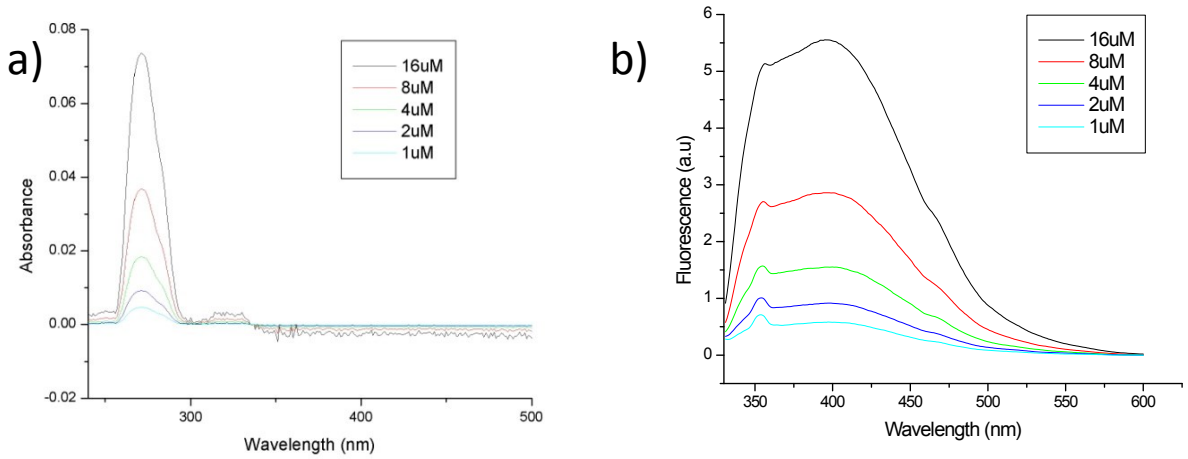


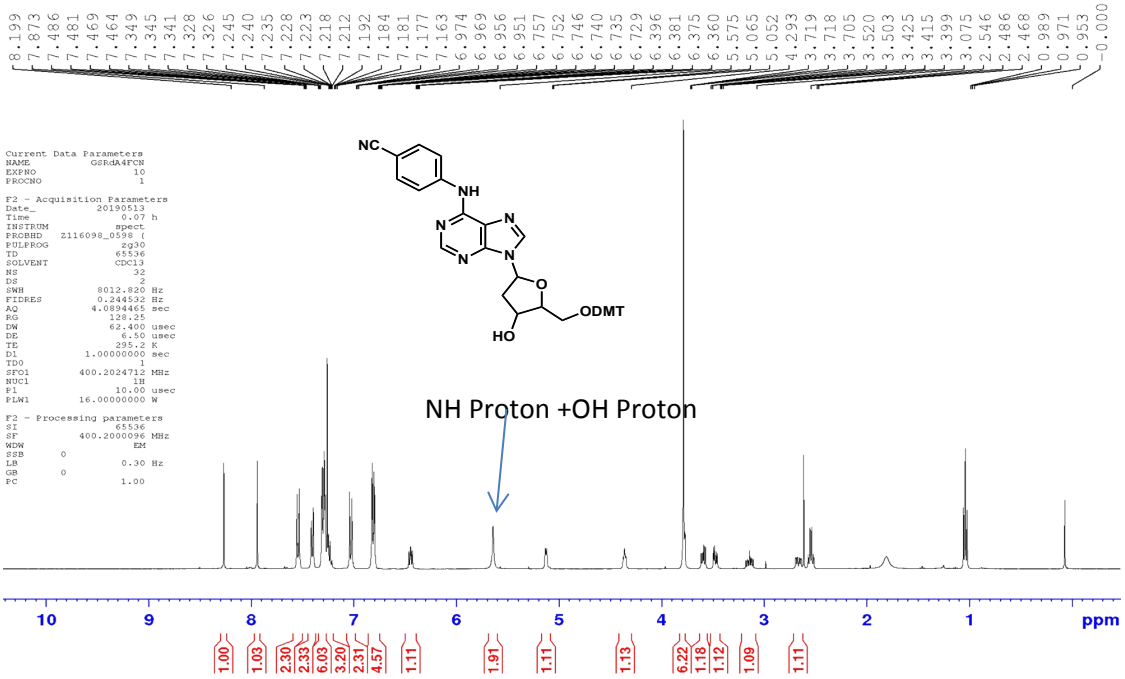
Figure S48: UV–Vis and fluorescence spectra of **2f**.

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Conc	9,10 DPA (UV)	Area of Flr	dADMT2FCHO(UV)	Area of Flr	dADMT2FCN(UV)	Area of Flr	dADMT2FCOCH3(UV)	Area of Flr	dADMT4FCOCH3(UV)	Area of Flr	dADMT4FCN(UV)	Area of Flr
2	1uM	0.003954114	0.0655703	0.001418769	0.0020101	0.006727388	0.0036177	0.000427943	0.0020317	0.000374628	0.0021815	0.002439748	0.00724
3	2uM	0.012541457	0.1319254	0.003403353	0.0020809	0.010366018	0.0051788	0.000831559	0.0021239	0.002198381	0.0022084	0.004879497	0.011329
4	4uM	0.018788697	0.2601691	0.007288649	0.0021401	0.017491985	0.0084667	0.001663118	0.0022055	0.002087015	0.0023	0.009758993	0.019218
5	8uM	0.030979982	0.4815824	0.013044128	0.0022834	0.029677397	0.0153337	0.006928054	0.002574	0.004611834	0.0024755	0.019517986	0.035124
6	16uM	0.05972271	0.9320033	0.025298245	0.0025968	0.052261405	0.0292328	0.021789201	0.0032866	0.009384462	0.0027429	0.039035972	0.068064
7													
8		Slope	16.098662		0.0241749		0.5667444		0.0564396		0.0651603		1.660292
9		Intercept	-0.0313942		0.0019783		-0.0008419		0.0020872		0.0021385		0.003081
10													
11		Y	16.06727		0.02615		0.5659		0.05852		0.06729		1.6633
12		Q.Y (ϕ)			0.0016		0.034		0.0036		0.004		0.102
13													

Figure S49: Quantum yield calculations.

17. ^{1}H and ^{13}C NMR Spectra of All DMTdA Fluoroarylation Products

a)



b)

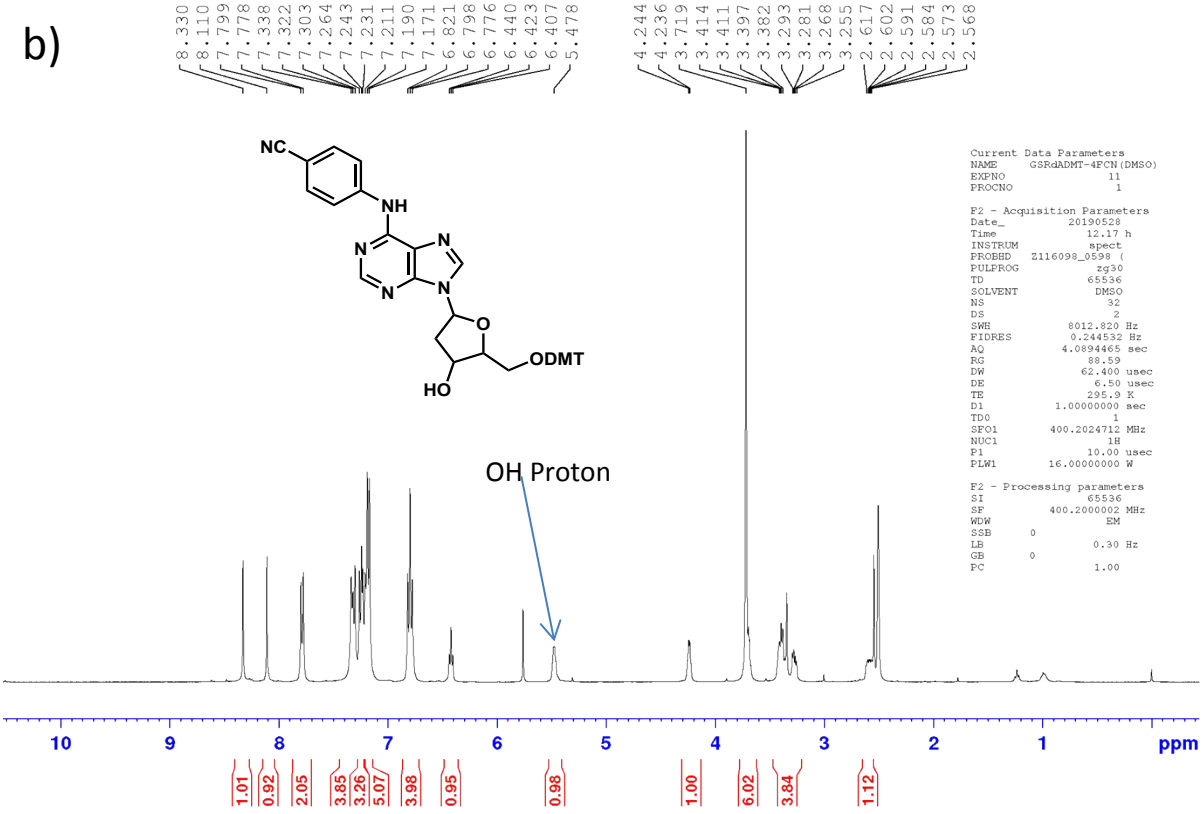
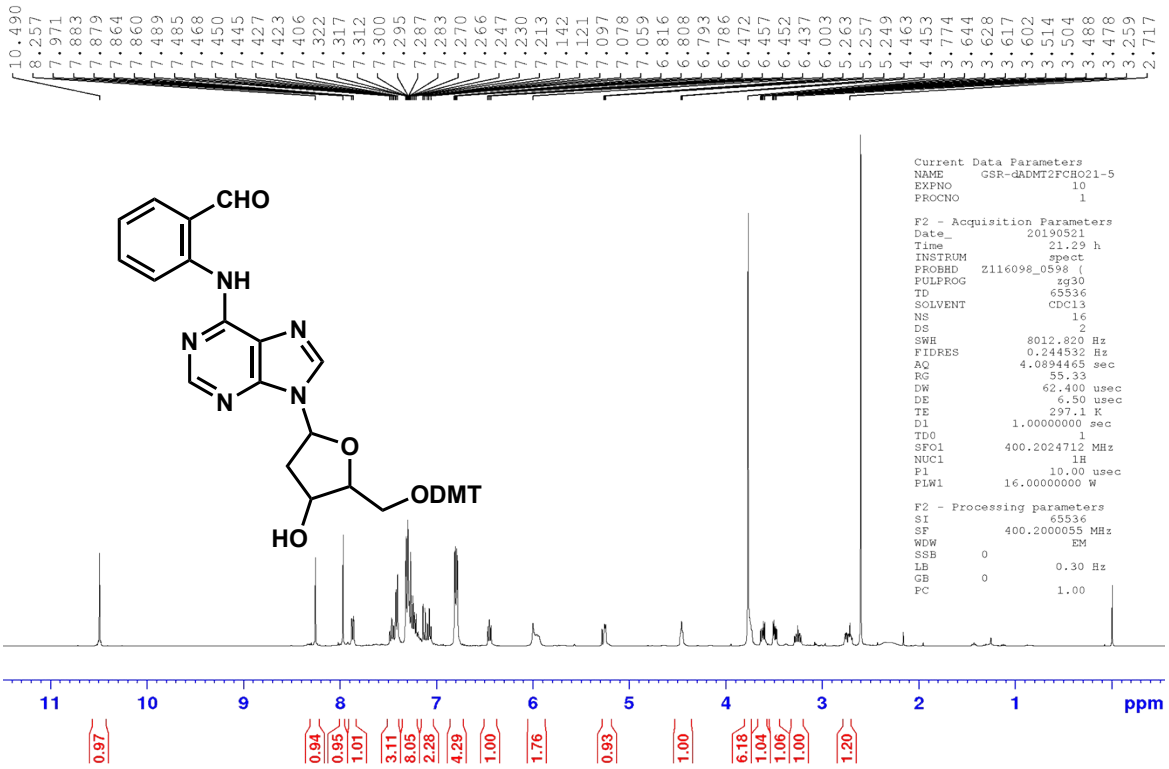


Figure S49: ^{1}H NMR spectra of **2f** in (a) $CDCl_3$ and (b) DMSO-d_6, recorded to determine whether the OH group of the sugar unit had been arylated or whether the arylation had occurred only at the N^6 position of dimethoxytrityldeoxyadenosine.



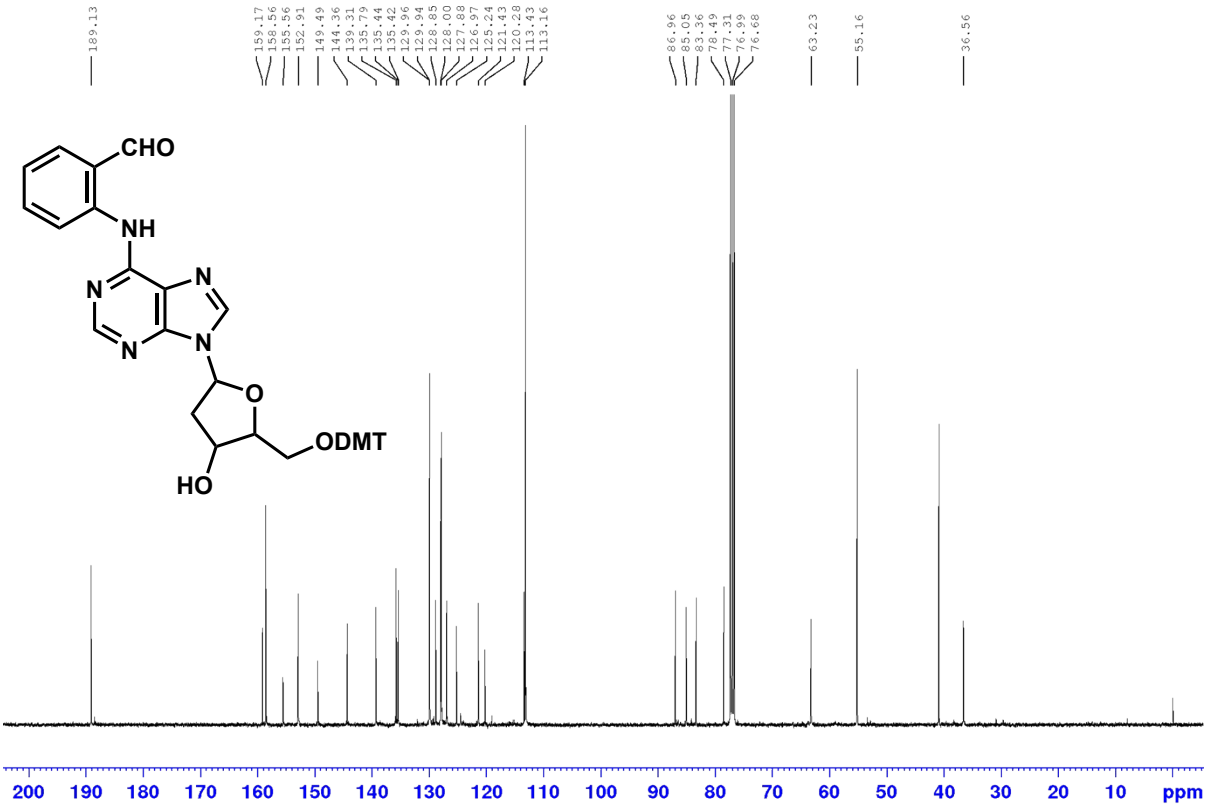
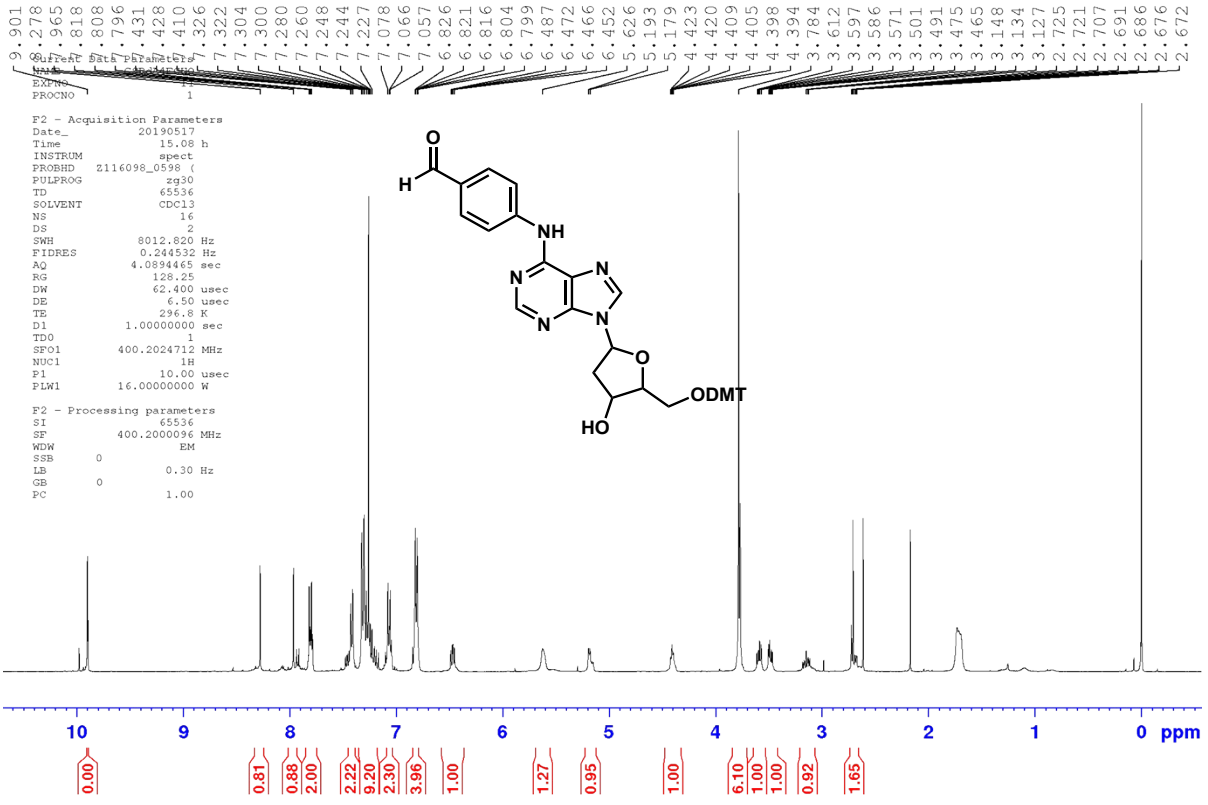


Figure S50: ^{1}H and ^{13}C NMR spectra of **2a** in $CHCl_3$.



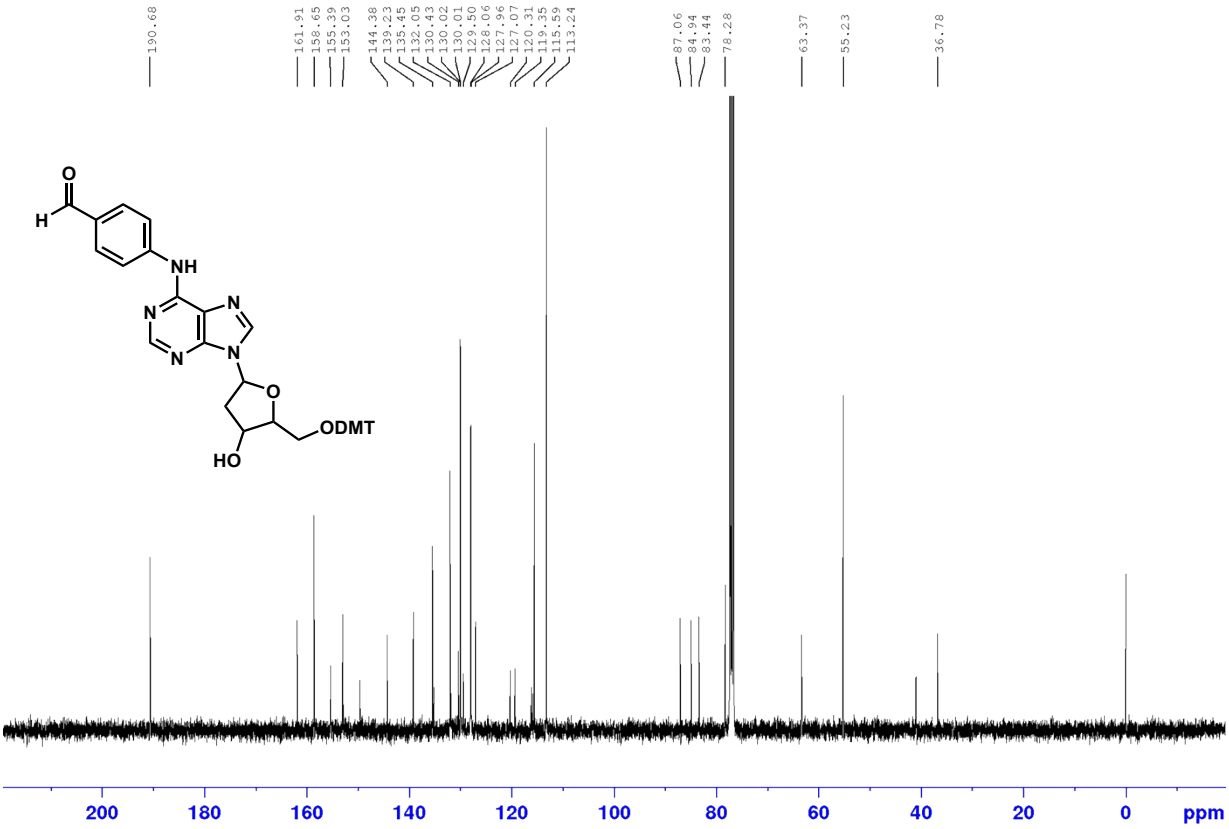


Figure S51: ^{1}H and ^{13}C NMR spectra of **2b** in $CHCl_3$.

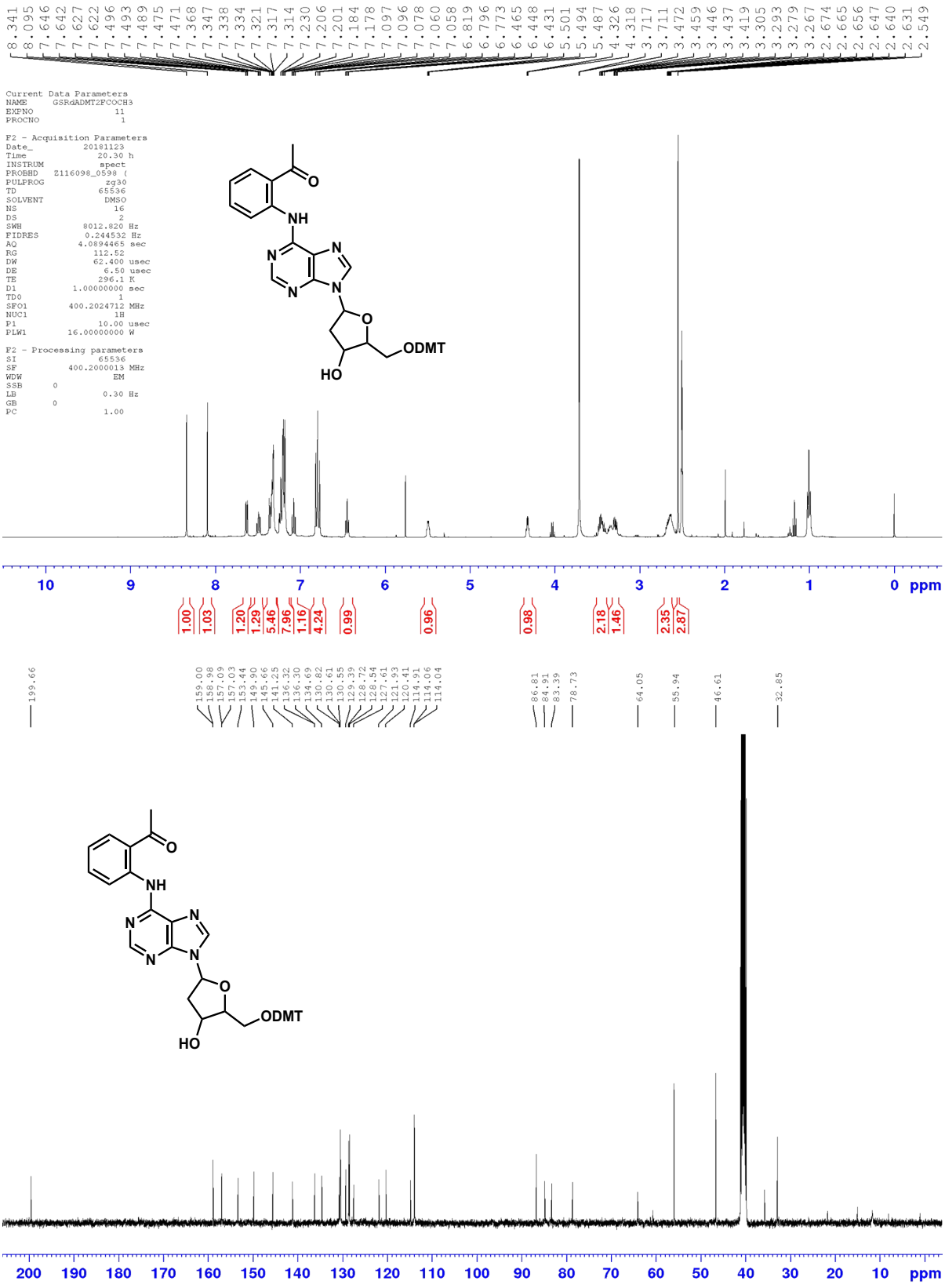


Figure S52: ^{1}H and ^{13}C NMR spectra of **2c** in DMSO-d_6.

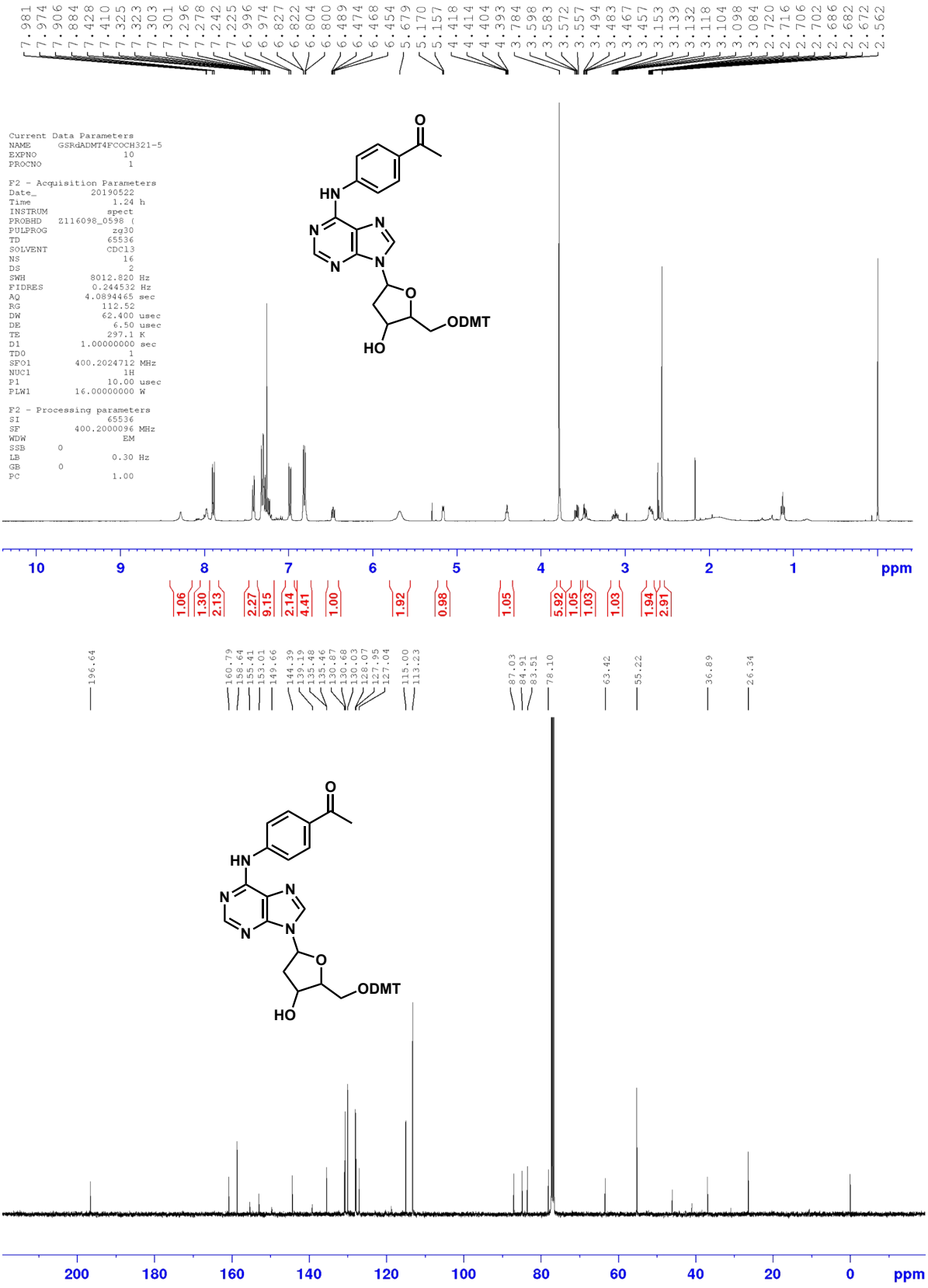


Figure S53: ^{1}H and ^{13}C NMR spectra of **2d** in $CDCl_3$.

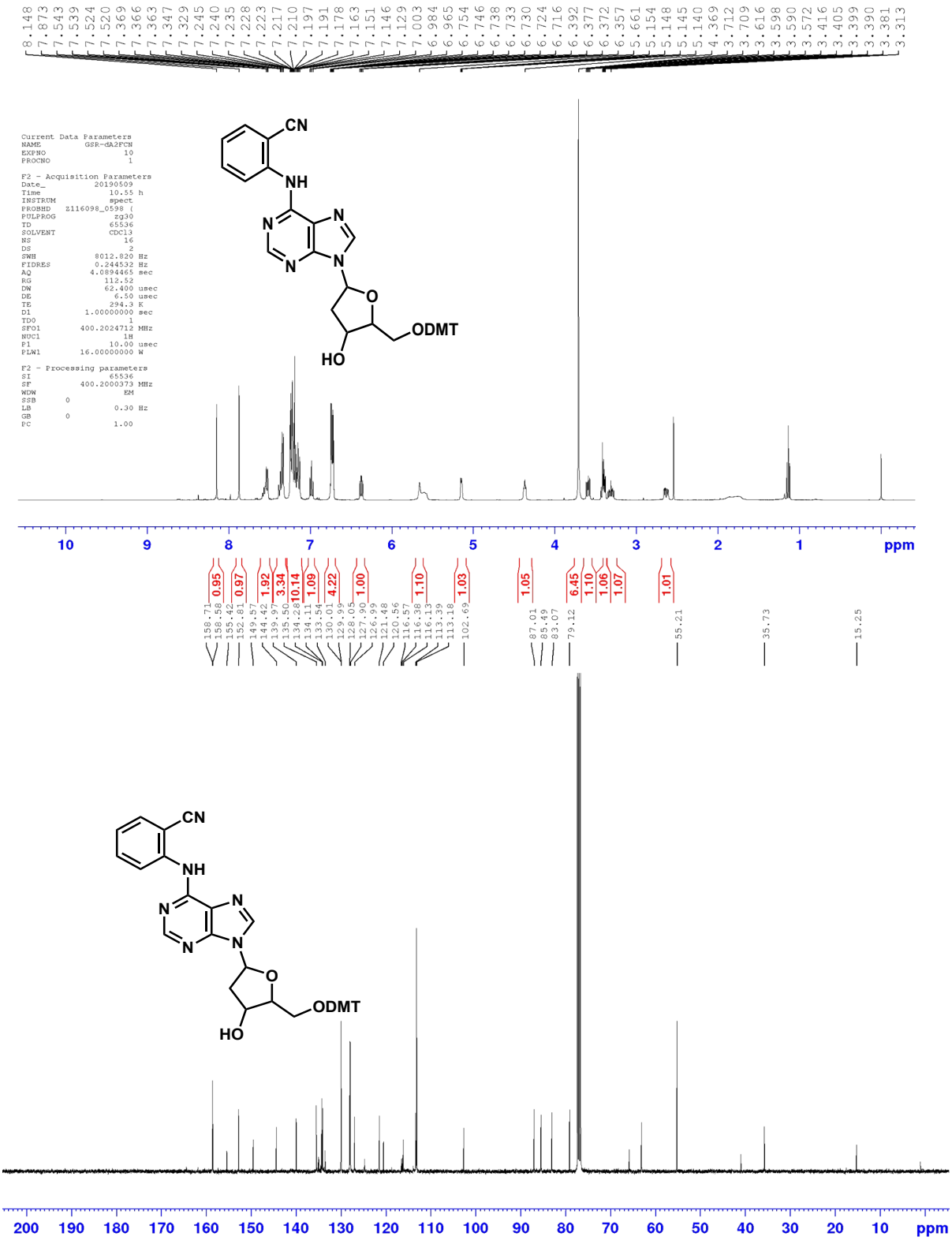


Figure S54: ^{1}H and ^{13}C NMR spectra of **2e** in $CDCl_3$.

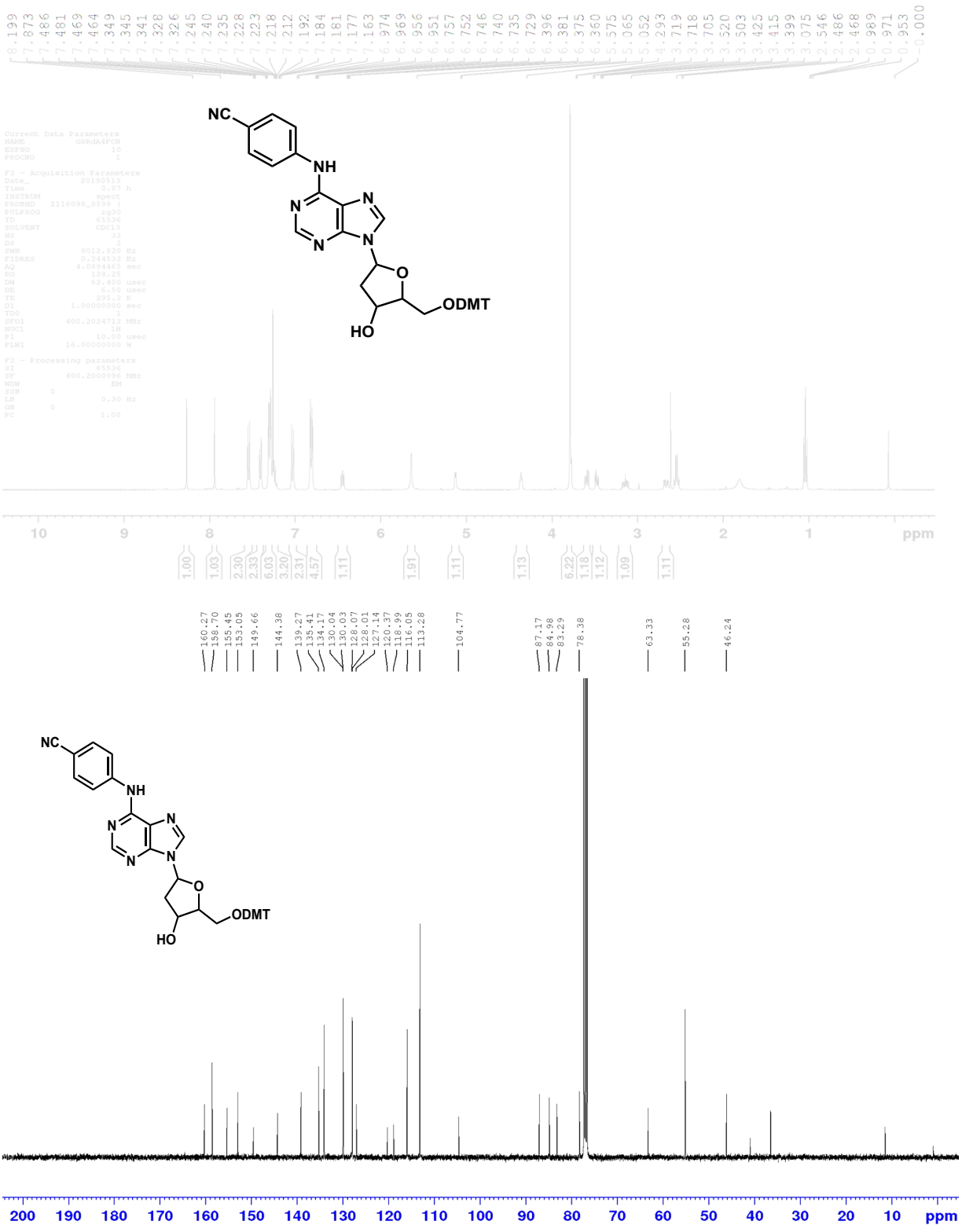


Figure S55: ^{1}H and ^{13}C NMR spectra of **2f** in $CDCl_3$.

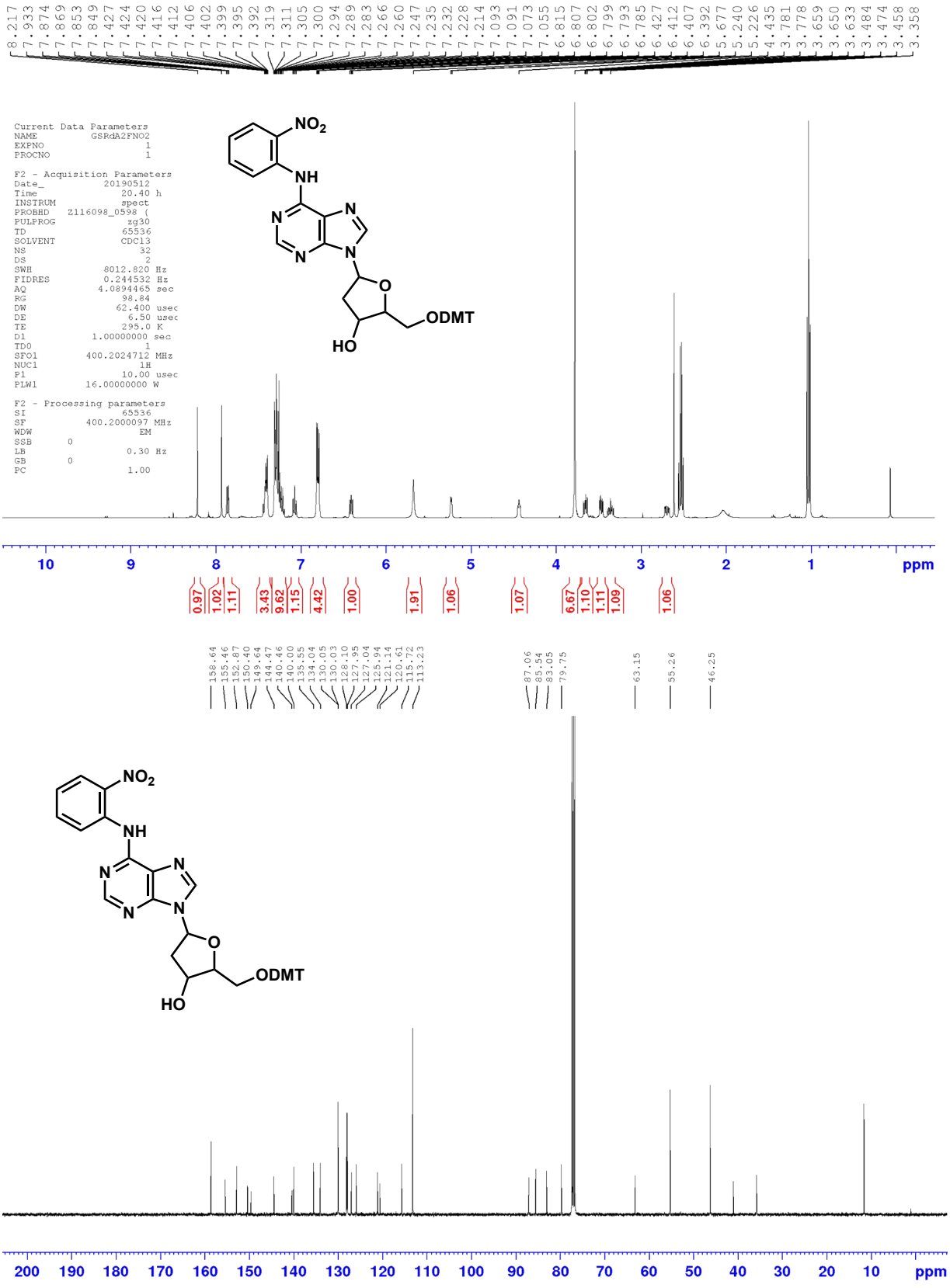


Figure S56: ^{1}H and ^{13}C NMR spectra of **2g** in $CDCl_3$.

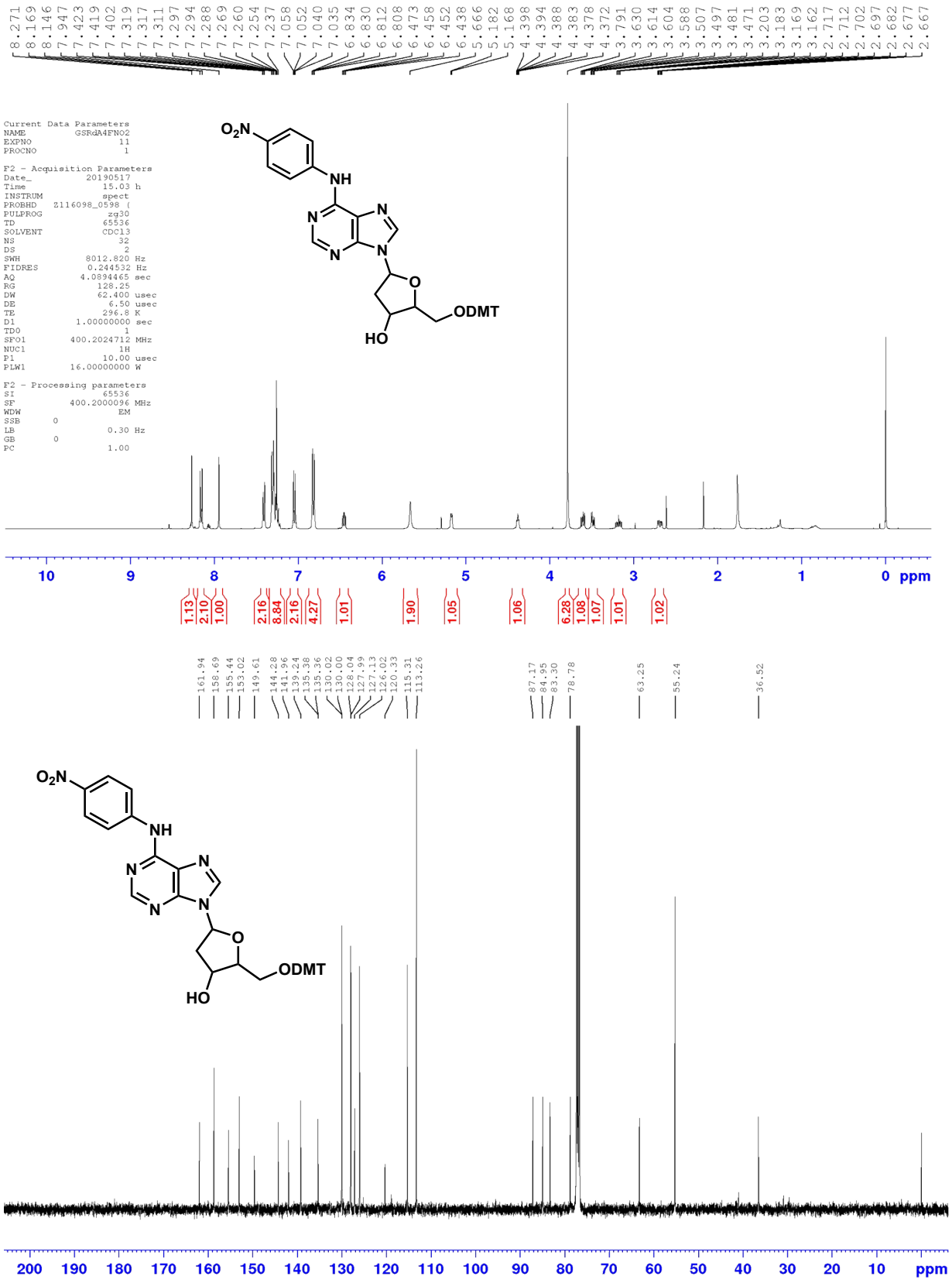
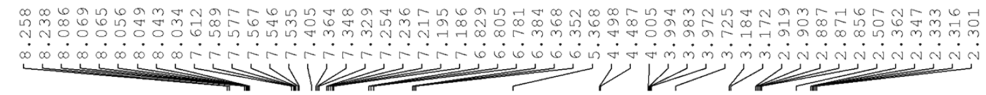
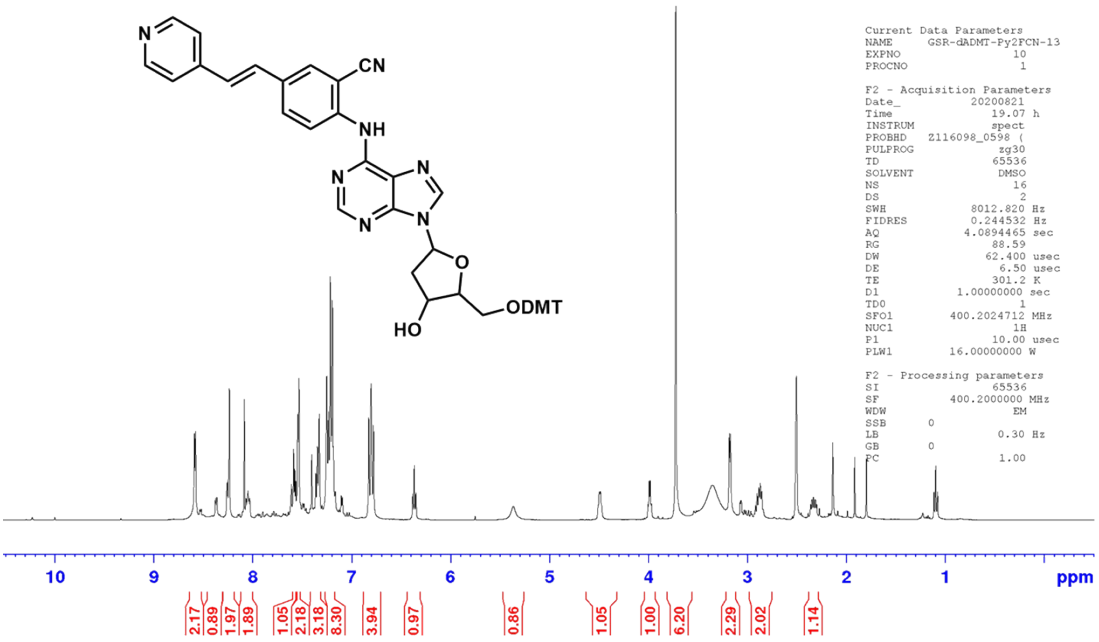


Figure S57: ^{1}H and ^{13}C NMR spectra of **2h** in $CDCl_3$.



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PROCNO                     1

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DS                        2
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AQ                4.0894465 sec
RG                     88.59
DW                   62.400 usec
DE                    6.50 usec
TE                   301.2 K
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NUC1                     1H
P1                   10.00 usec
PLW1          16.00000000 W

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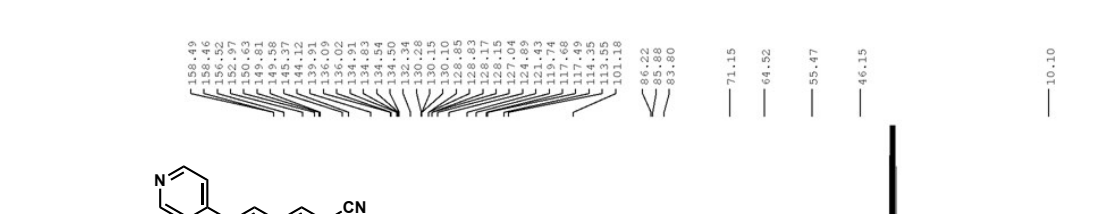


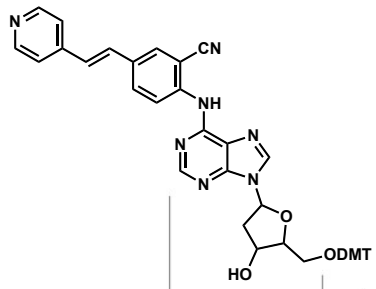


Figure S58: ^{1}H and ^{13}C NMR spectra of **2i** in DMSO-d_6.

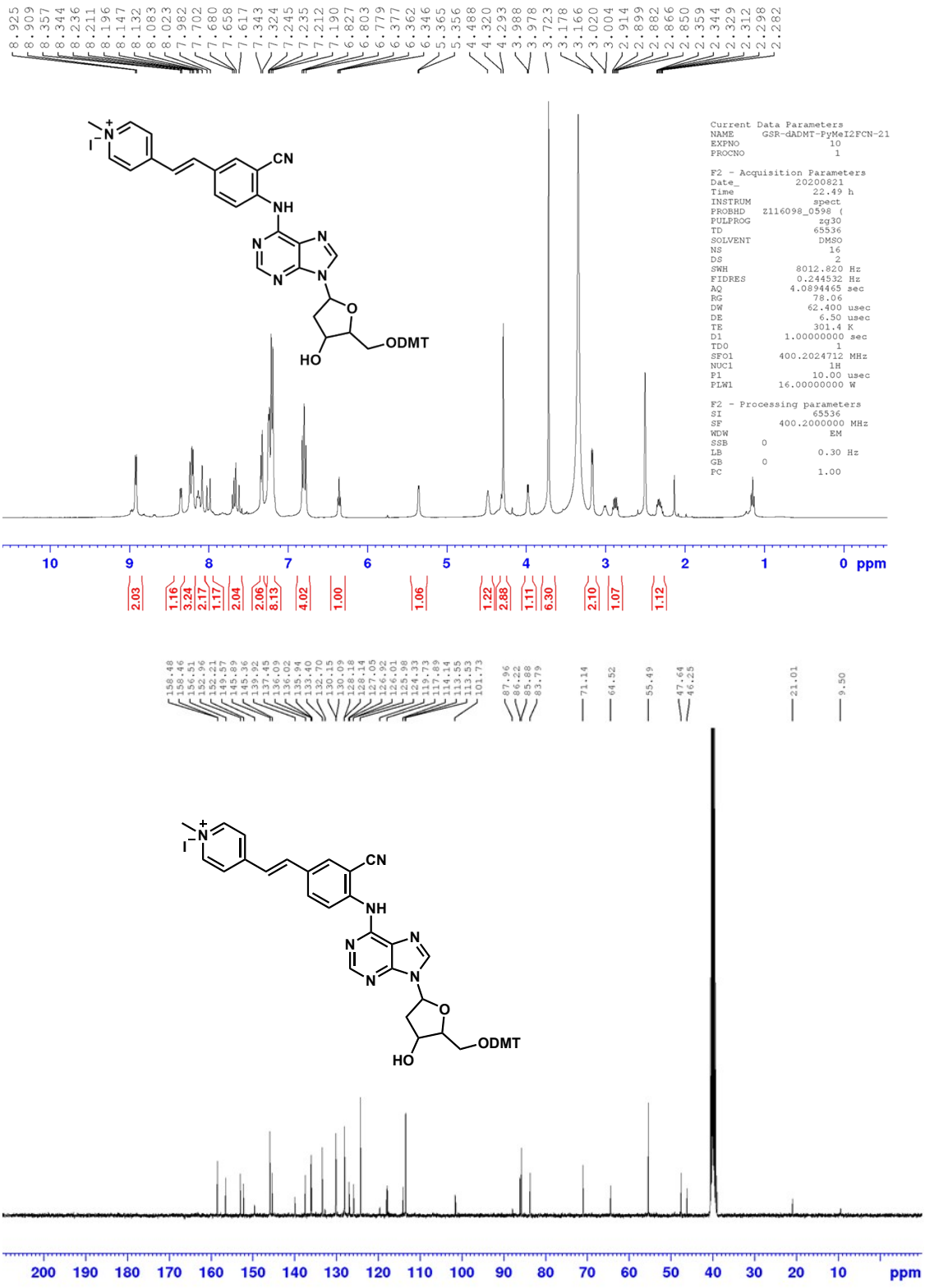


Figure S59: ^{1}H and ^{13}C NMR spectra of **2j** in DMSO-d_6.

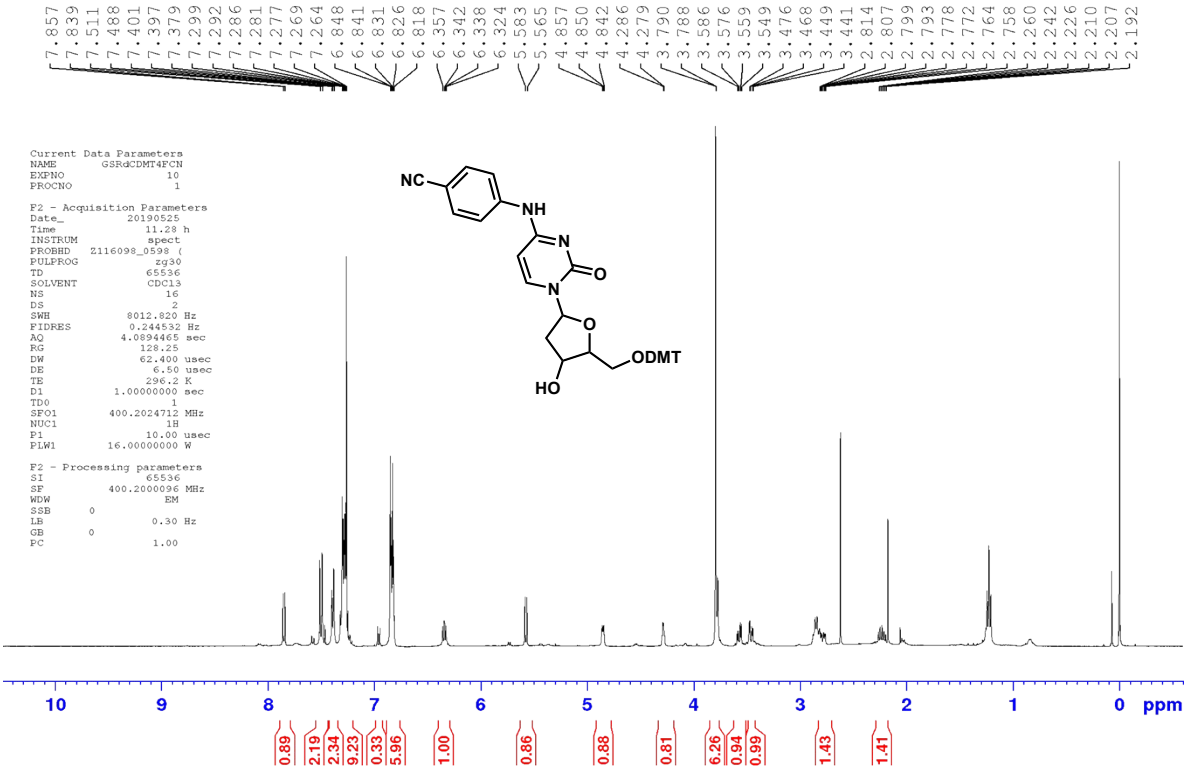
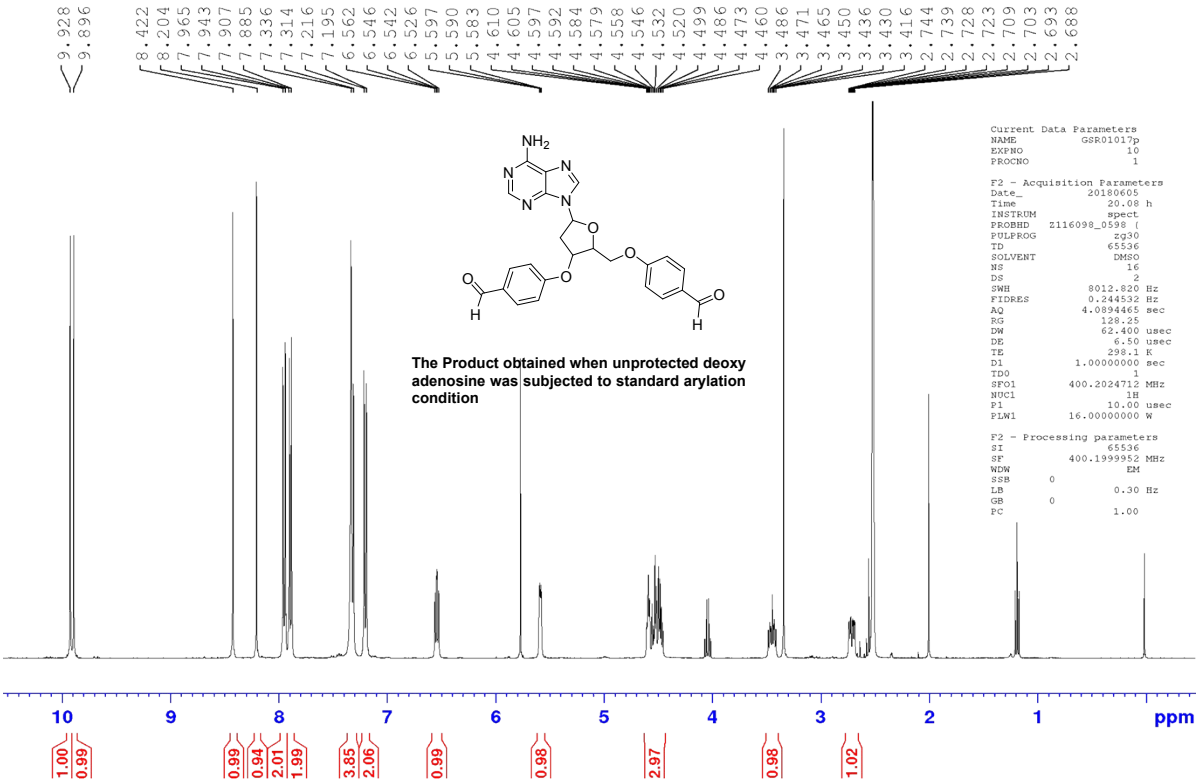


Figure S60: ^{1}H and ^{13}C NMR spectra of **3f** in $CDCl_3$.



The Product obtained when unprotected deoxy adenosine was subjected to standard arylation condition

Figure S61: ^{1}H and ^{13}C NMR spectra of **2a1** in $CDCl_3$.

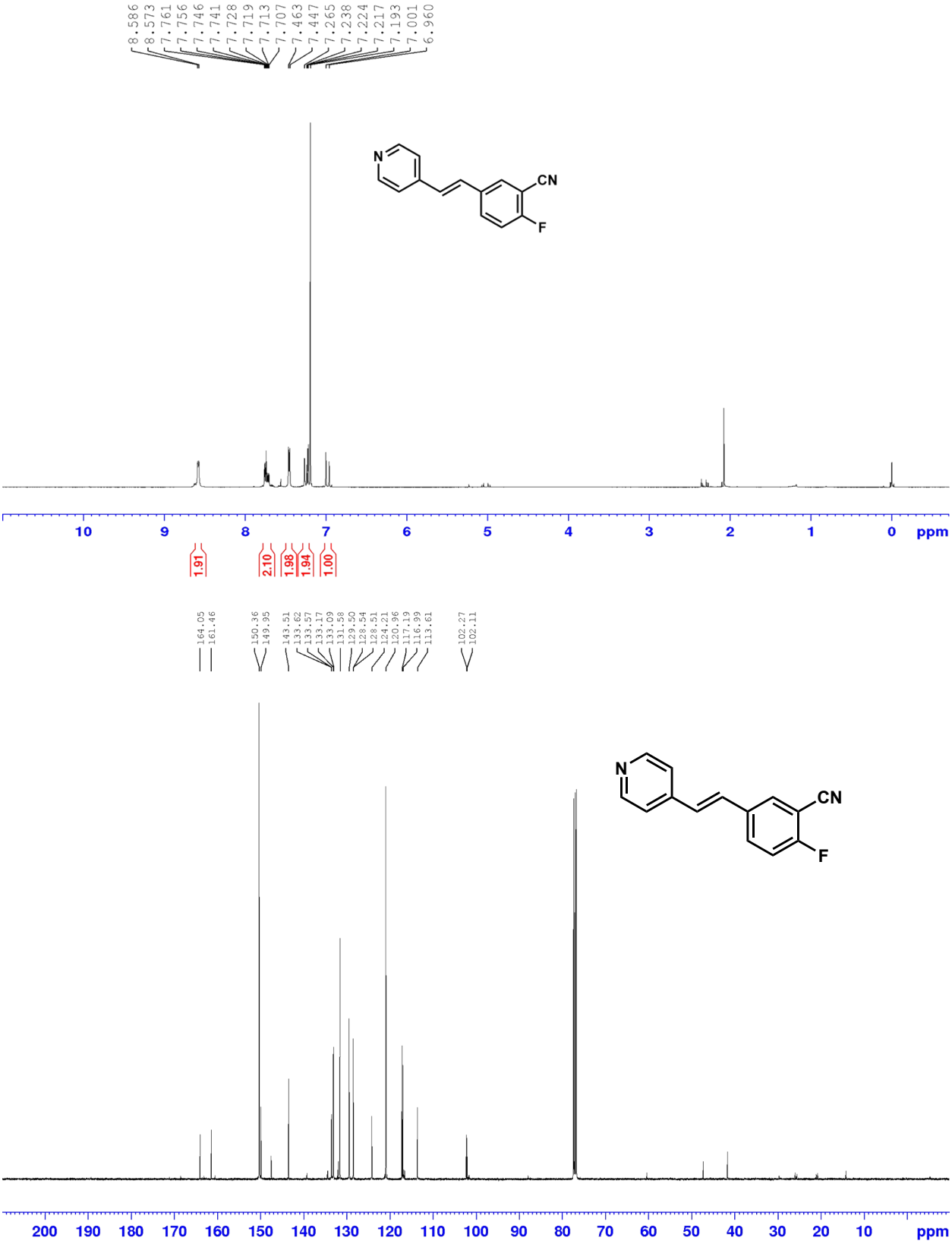


Figure S62: ^{1}H and ^{13}C NMR spectra of **Y** in DMSO-d_6.

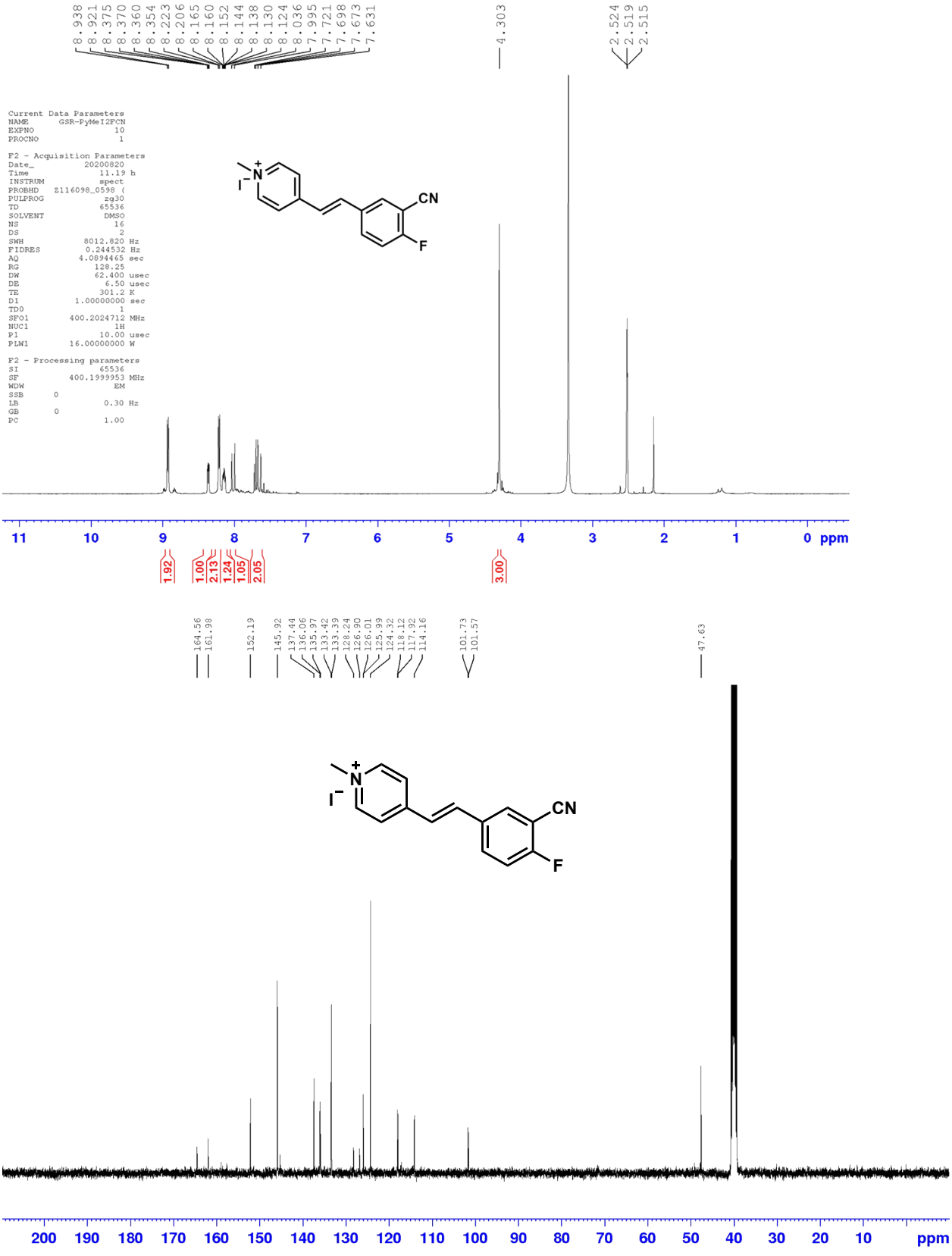


Figure S63: ^{1}H and ^{13}C NMR spectra of **Z** in DMSO-d_6.

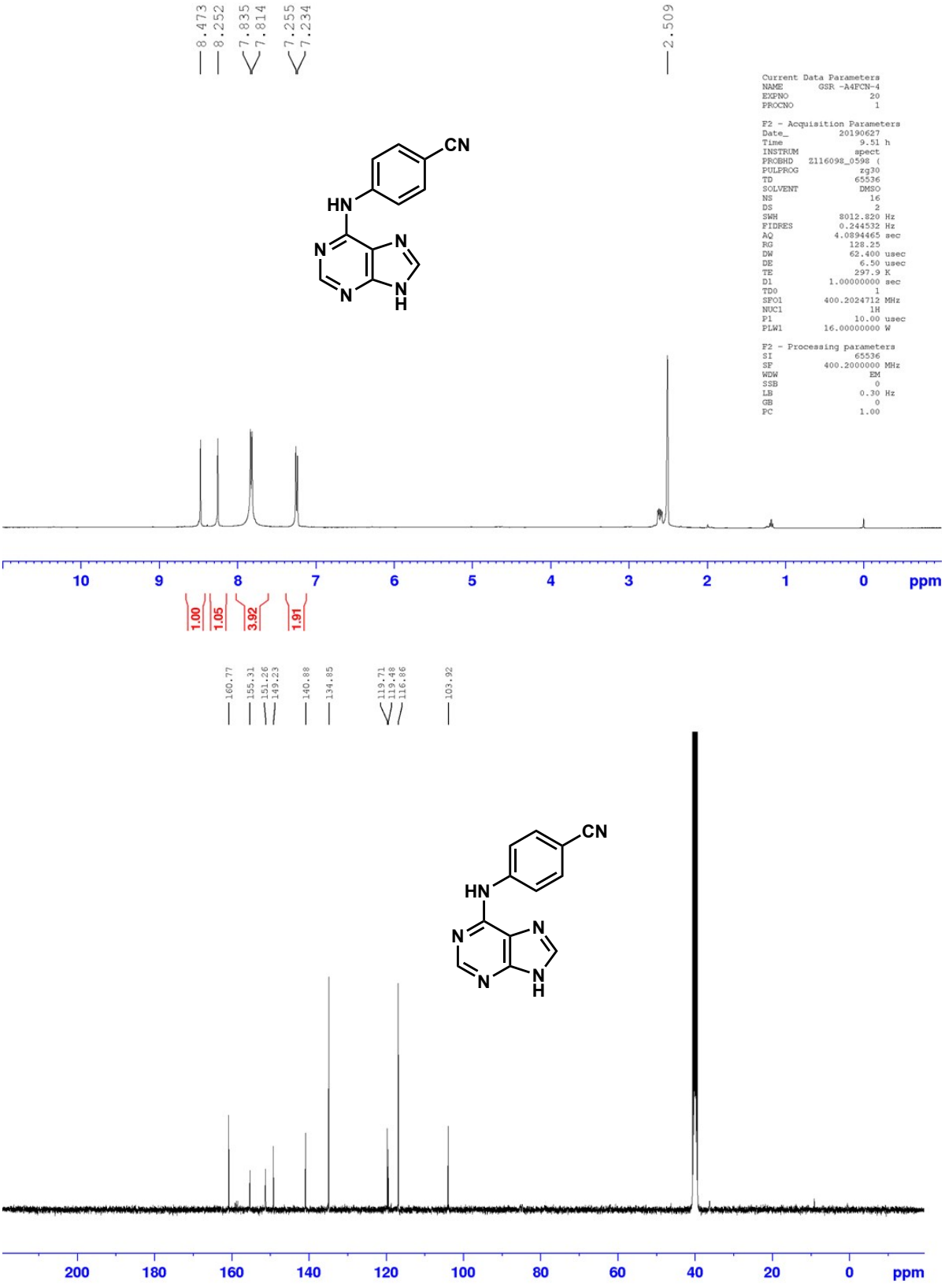


Figure S64: ^{1}H and ^{13}C NMR spectra of N-(4-Cyano Phenyl) Adenine in DMSO-d_6.